

Theoretical Rotational-Vibrational Spectroscopy of Water

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of
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by
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I, Lorenzo Lodi, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.

Abstract

High-resolution spectroscopy of water vapour is of the greatest importance in many scientific domains including atmospheric physics and astrophysics. Although water is a well-studied molecule its spectrum is still unsatisfactorily known in several respects, particularly for physical conditions difficult to experimentally investigate, e.g. for high-temperature spectra ($T \gtrsim 3,000$ K), and in regard to line intensities. This thesis deals with the calculation of the rotation-vibration (RV) spectrum of the water molecule.

Because of the complexity of the quantum many-body problem, the accurate calculation of high-resolution RV spectra of even small molecules remains a very difficult task. Fortunately, the continuous improvements of computer power and of methodology render theoretical approaches more and more accurate and useful. For the computation of molecular RV spectra one needs the molecular potential-energy surface (PES) and the dipole-moment surface (DMS). From these the Schrödinger equation for the nuclear motion can be solved and line positions and intensities computed. This thesis also describes in detail the computation of water PES's and DMS's and assesses their quality against available experimental data.

The thesis begins with a description of the theoretical tools used for the calculation of RV spectra and a review into the present spectroscopic knowledge of water. Various approaches for the construction of PES's and DMS's by fitting or interpolation are discussed and applications to water are presented. In the following chapters a new water DMS is presented and RV spectra calculated with it are analysed and compared with line lists and high-resolution experiments. A study is then presented where we discuss in detail the long-range behaviour of the water PES along the dissociation channel.

Finally, various considerations and an overview of possible future research directions are presented in the final chapter.

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Introduction

1.1 The importance of water

The rotation-vibration spectrum of water is arguably the single most important spectrum of any chemical species. The spectroscopy of water vapour is of fundamental importance in many scientific areas including astrophysics and atmospheric science [Ber02]. Water is the third most abundant molecular species in space after the H_2 and CO molecules and is present in a large variety of astrophysical environments [BTHT05, Ten03]. For example, it has been possible in recent years to detect water vapour on the Sun [PZV⁺97, TP98] and in the atmosphere of the 63 light-year distant extra-solar planet HD 189733 b [TVML⁺07].

Water vapour dominates both the incoming and the outgoing (“greenhouse”) absorption of radiation [Ark99, MT03, KMM⁺05] and thus plays a major role in atmospheric science in the modelling of the Earth’s atmosphere. Indeed, several satellite missions have been launched with the monitoring of water vapour columns as their major goal [KSA⁺96, Mel00, PPC⁺05].

Water vapour is also a major product of most combustion processes and it can be used to detect and monitor them [Ber02]. For example, spectroscopic observation of water vapour has been used for purposes as diverse as tracking the evolution of forest fires [FCPM76, WBR97] and studying rocket and jet engine exhaust plumes [Ber02].

Because of this wealth of practical applications water is one of the most studied molecules, both experimentally and theoretically. Along with other molecules of importance for atmospheric science, water vapour transition wavenumbers (“line positions”), transition intensities (“line intensities”) and other spectroscopic parameters are collected in several periodically-updated databases including HITRAN [Rot05, HIT], GEISA [JHSC⁺08], SISAM [Tot] and the JPL database [JPL].

In the remainder of this introduction we will briefly discuss why theoretical studies of water vapour are of great practical importance and then proceed to describe the general structure of this thesis.

1.2 Motivation of this study

Laboratory techniques to measure rotational-vibrational spectra of small molecules have reached a high level of sophistication. The present state of the art is best described discussing separately line positions and line intensities.

Also of considerable importance are line profiles, that is, information on the shape and width of each spectroscopic peak. For example, line profiles are important in line-by-line models for atmospheric radiative transfer modelling, see e.g. [TPR⁺03, MCKT04, KMM⁺05]. There are several factors that contribute to the overall profile of a spectroscopic line including inter-molecular interactions, the Doppler effect and the intrinsic line-width of the transition, see e.g. the books by Hartmann, Boulet and Robert [HBR08], Hollas [Hol04] and Bernath [Ber05] for more details. In actual practice — for example in the analysis of experimental spectra — peaks are fitted to a chosen line shape function. Widely-used line shape functions are the Lorentzian, Gaussian and Voigt profiles and generalisations thereof, see e.g. [BWB07, SNF07]. Because of this underlying complexity line profiles are not routinely computed *ab initio* and they will not be discussed further in this thesis.

Line positions

Line positions can be determined very accurately by several experimental techniques such as infrared Fourier-transform spectroscopy (FTIR) [GD07]. Uncertainties of the order of $5 \times 10^{-3} \text{ cm}^{-1}$ are routinely obtained [TZW⁺01, FCT07] and in precision experiments uncertainties down to about $2 \times 10^{-6} \text{ cm}^{-1}$ can be reached [FC08]. Experimental line positions can also be inverted to obtain energy levels [FCT07, FC08], from which the molecular partition function and other data can also be derived.

First-principle theoretical calculations, on the other hand, can currently provide energy levels and line positions with accuracies of the order of 1 cm^{-1} [Ten06, TBK⁺02]. Only if semi-empirical parameters fit to experimental data are introduced it is possible to obtain calculated line positions with accuracies of the order of 0.05 cm^{-1} on the average [PS97, SPZ⁺03, SPZ⁺06, YVT⁺08].

It is clear from what has just been said that, from the point of view of accuracy, experimental line positions (when available) are preferable to theoretically-calculated ones. There exist, however, several reasons why theoretical line positions are necessary. A very important motivation is the assignment of observed lines, which for water largely relies on theoretical line lists. Line assignment is the process by which observed lines are identified as originating from a specific molecule and are then assigned quantum numbers uniquely identifying the upper and lower energy levels involved. In a typical modern line-assignment work, see e.g. [PZVT98], some transitions can be predicted from known experimental energy levels (so-called “trivial” assignments); the assignment of the bulk of them, however, relies entirely on accurate theoretical line lists. Theoretical calculations are of particular importance for the analysis of spectra involving high-energy ($\gtrsim 30,000 \text{ cm}^{-1}$) energy levels which are poorly known experimentally, see e.g. [MRB06, MMZ⁺07].

Furthermore, there are many situations where experimental data are not available at all. One simple reason for this is merely due to the sheer number of lines which make up the whole water

spectrum. The rotation-vibration spectrum of water spans approximately between 10 cm^{-1} to $40,000\text{ cm}^{-1}$ and modern line lists include of the order of 500 million lines [BTHT05]. Experimental measurement of even only a significant fraction of them is unfeasible and theoretical line positions are then necessary to cover energy regions where experimental data are not available. Another situation where experiments are difficult or impossible is the case of spectra at very high temperatures ($T \gtrsim 3000\text{ K}$) [CBC⁺05], which are important in many astrophysical environments. Again, in this case one has to rely on theoretical calculations [PZV⁺97].

Line intensities

Absorption line intensities can be obtained by various forms of spectrometry, including various laser-based techniques [Wika] like cavity ring-down spectroscopy (CRDS) [BPM00].

Accurate measurement of water line intensities in the laboratory is technically demanding even at room temperature [Ten] and there appears to be no available data on absolute intensities for high temperature water, despite their importance in many applications [Ber96]. Water vapour tends to stick to the walls of the container and to form droplets in an unpredictable fashion, adding uncertainty to the concentration of the sample. Another difficulty is due to the fact that the spectrum is so dense than finding a baseline against which absorptions can be measured can become a problem. As a consequence of these difficulties there still exist much uncertainty on water transition intensities, see e.g. [BSS⁺00], and typical relative uncertainties are at best of the order of 1%.

This state of affairs places considerable emphasis on theory to produce reliable transition intensities, which in many cases constitutes the only available data. Theoretically calculated line intensities are also beginning to approach the same level of accuracy of the best experiments, see Chapters 8 and 9, which makes them even more valuable.

1.3 Thesis structure

During the last two decades substantial progress was made in the theoretical spectroscopy of triatomic molecules and of water in particular [Ten06]. This progress resulted from the availability of both efficient programs for the solution of the nuclear-motion problem and of higher quality potential-energy and dipole-moment surfaces, obtained either from first principles or by semi-empirical approaches. At the same time the effect of many small correction terms usually neglected (relativistic and non-adiabatic effects) has been evaluated and found important in the $\pm 1\text{ cm}^{-1}$ accuracy range.

However, despite these remarkable advances, the present situation is still in many respects unsatisfactory. While for medium-strong transitions not involving highly excited states a very high accuracy is ordinarily obtainable, this is not the case for very weak transitions and/or transitions that involve states approaching the dissociation threshold; for these transitions experimental data are few and predictions generally unreliable. In the light of the importance of the possible applications, a determined effort towards a better theoretical description of the water spectrum is well justified.

This thesis constitutes a detailed study of several aspects of the theoretical spectroscopy of water vapour. This work is organised as follows.

Chapter 2 introduces the main theoretical framework of molecular spectroscopy. The Born-Oppenheimer approximation and relativistic effects are discussed in detail. The Dirac-Coulomb-Breit many-electron relativistic Hamiltonian is discussed and approximation of it are introduced. Some indicative values for the magnitude of relativistic effects on the barrier to linearity of the water molecule are discussed.

Chapter 3 consists in a detailed exposition of the electronic-structure methods used for small molecules, with particular emphasis to multi-reference methods. Explicitly correlated methods of the R12/F12 family are also discussed. A benchmark study of the hydrogen molecule is presented illustrating the accuracy achievable with presently-available Gaussian basis-sets.

Chapter 4 discusses the methodology used for the solution of the nuclear-motion problem using variational methods. The separation of the internal degrees of freedom and the derivation of exact effective Hamiltonians for the nuclear motion is discussed. The discrete variable representation (DVR) technique is introduced and discussed.

In Chapter 5, after a review of the main features of molecular potential energy surfaces, various techniques for the construction of global surfaces from grids of values are discussed. Several one-dimensional model cases are examined. The problematic of multi-dimensional surface building is introduced and various approaches are discussed.

Chapter 6 consists in a study of the performance of electronic-structure methods for the computation of the ground electronic potential energy surface of the water molecule. A new reference space for multi-reference methods is introduced and results are presented which suggest it leads to more accurate energies than the ones previously used. The computations of relativistic corrections to the energy is also discussed.

Chapter 7 examines the ground-state dipole moment surface of water. A study of the sensitivity of rotation-vibration transition intensities to small changes in the molecular dipole-moment surface is presented. The conclusion is that transition intensities are extremely sensitive to small oscillations in the bond-angle coordinate. An examination of the water ground-state equilibrium dipole is presented and the theoretical value is compared with the experiment. The computation of relativistic corrections to the dipole is discussed. Finally, a many-body expansion of the dipole analogous to the one commonly employed for energies is introduced.

Chapter 8 presents the new CVR water dipole-moment surface. The problem of spurious oscillations arising in the fitting process is discussed.

Chapter 9 compares water line intensities computed using the CVR dipole-moment surface with various experimental sources, including the HITRAN2004 database. A new linelist of purely rotational line intensities is presented and calculated lines are compared with the available experimental data.

Chapter 10 studies the long-range intramolecular van der Waals interaction in water when one of the O-H bonds is broken. This is of relevance in the construction of global potential surfaces describing the dissociation channel. It is suggested that commonly-used expansions in inverse-powers of the bond length do not provide a good starting point as they only become reliable when the interaction energy is very small.

Finally, Chapter 11 presents some general conclusions and indications for future work.

Theoretical concepts

In this chapter we will review the general formalism and introduce the basic approximation of molecular physics, the Born-Oppenheimer approximation. We will then discuss how relativistic effects can be incorporated in a quantum-mechanical formalism. Specific methods used to solve the Schrödinger equation for the electronic and nuclear motion will be discussed respectively in Chapters 3 and 4.

2.1 Non-relativistic Quantum Mechanics

The basic theoretical framework on which the study of atoms and molecules is couched is given by non-relativistic quantum mechanics. The principles of non-relativistic quantum mechanics are discussed in depth in many monographs [Gri04, CTDL77] and we will not discuss them. Among the many references covering mathematical aspects of the formalisms we may mention [Pru06, Thi01, RS80, Tes05, von96, Mor07] for the functional analysis part and [Tin03, Vve01, Ham89, Sch65, Bon04] for the group theory one. For more discussion on the mathematical structure of quantum mechanics see e.g. [Gie00, dIM05, dIMM01]. Interpretational and philosophical problems are discussed e.g. in the books [Aul00, Cus94, Omn94, Per95, Bal98, Pri83] and in the articles [Omn92, Lal01, Sch05a]. The book by Primas [Pri83] is noteworthy as it is one of the few where the discussion is set in the context of quantum chemistry.

2.2 The molecular Hamiltonian

The Hamiltonian of a system of electrons and nuclei is obtained, according to the general rules of quantum mechanics [CTDL77, Per95], by taking the corresponding classical-mechanics Hamiltonian and substituting to the variables $\mathbf{x}_i, \mathbf{p}_i$ the quantum operators $\hat{\mathbf{x}}_i, \hat{\mathbf{p}}_i = -i\hbar\nabla$.

The classical, non-relativistic Hamiltonian for a system of n static, charged, point-like particles in the absence of external electric or magnetic fields can be written as (see Section 2.2.1 for some qualifications):

$$H(\vec{r}_1, \dots, \vec{r}_n; \vec{p}_1, \dots, \vec{p}_n) = T + V = \sum_{i=1}^n \frac{|\vec{p}_i|^2}{2m_i} + \frac{1}{4\pi\epsilon_0} \sum_{i=1}^n \sum_{j=i+1}^n \frac{q_i q_j}{|\vec{r}_i - \vec{r}_j|} \quad (2.1)$$

The corresponding quantum Hamiltonian is then, using atomic units [SO96, Lev00]

$$\hat{H} = \hat{T} + \hat{V} = \sum_{i=1}^n -\frac{1}{2m_i} \nabla_i^2 + \sum_{i=1}^n \sum_{j=i+1}^n \frac{q_i q_j}{|\vec{r}_i - \vec{r}_j|} \quad (2.2)$$

This is called the *Coulomb Hamiltonian* and one of the main tasks of theoretical molecular physics and quantum chemistry is to find its eigenvalues and eigenfunctions.

A direct attack on the Coulomb Hamiltonian without making any further approximation is an incredibly difficult task which has been pursued only for small atoms and diatomic molecules with less than about 5 particles [BCA05, SW05, CBA03, KA93]. The vast majority of calculations are instead based on an approximate decoupling of the electronic and nuclear motions, the Born-Oppenheimer approximation. We will describe this approach in the following Section 2.3.

2.2.1 Further notes on the Coulomb Hamiltonian

Strictly speaking, if the charges are not static the Hamiltonian (2.1) is not fully appropriate as it does not include so-called “radiation-reaction” effects: a moving charged particle loses kinetic energy as radiation, an effect which in the Newtonian formalism is expressed by the Abraham-Lorentz-Dirac equation¹ [Jac98]. In the Hamiltonian formalism the situation is even more complicated because it is not possible to express the radiation-reaction effects with a Hamiltonian with a finite number of degrees of freedom [Mar02, Mar].

It is common in textbooks, e.g. [Sch07], to invoke radiation-reaction as the main reason why orbits of electrons in atoms are unstable in classical mechanics, arguing that electrons would quickly lose kinetic energy and fall into the nucleus². It may therefore appear singular that in the quantum treatment one neglects precisely those effects which were deemed fatal in the classical one. However, a rigorous derivation of the Coulomb Hamiltonian (2.1) can be obtained using Quantum Electrodynamics [Wol03, Wol99, CT98, CTDRG97, CTDRG98] studying the interaction electron-field perturbatively. Radiation-reaction terms do carry over from classical to quantum electrodynamics but in the quantum treatment they can be dealt with by the use of renormalization. This deeper analysis is the justification of the standard practice of neglecting radiation-reaction terms from the very beginning of the discussion.

2.3 The decoupling of nuclear and electronic motions

The approximate decoupling of nuclear and electronic motions is perhaps the most important concept in molecular physics. Not only it greatly simplifies practical computations but it also introduces the fundamental concept of a potential energy surface which is at the basis of modern understanding of molecules [Sut06, Sut95]. In the following sections an overview of this approximation will be presented.

¹Note that considerable controversy exists about this equation [Her06, Jac07, Hni07, Her07, Med06, Car06, Lid05, O’C03, Roh00, JC87, Coo84].

²A detailed analysis [Mar03] shows that the situation is not so simple and the ultimate fate of an orbiting classical electron may not necessarily be that of falling into the nucleus [Mar03].

2.3.1 Classical mechanics analogy

In a classical system of electrostatically-interacting particles the forces acting between any two particles are equal in magnitude and thus impart accelerations proportional to the inverse of the mass of each particle. As time goes by particles exchange momentum through collisions and one may assume that the system will eventually reach an equilibrium state where the total momentum has been redistributed approximately equally between all particles; in this situation massive particles move slowly and light particles quickly.

In the case of molecules one then expects to observe two different timescales for the motions of light particles (electrons) and heavy particles (nuclei), so different that one may assume that, on the one hand, nuclei ‘see’ only the time-averaged distribution of the electrons while, on the other hand, that the electrons follow instantaneously any movement of the nuclei. This classical analogy is useful to give an intuitive idea of the approximation involved but was criticised as not qualitatively correct by Essén [Ess77, Mon87a].

2.3.2 The Born-Oppenheimer perturbational approach

When quantum mechanics was devised in the 1920s it had already been conjectured that the infrared and microwave absorption spectra observed in molecules had to be ascribed to transitions between different rotational and vibrational-rotational states of the atoms that make up molecules [Hou12, Ogi98]. When the Schrödinger equation was introduced it seemed to provide at last a way of calculating the forces which held atoms together. The solution of the full Schrödinger equation for electrons *and* nuclei was not initially considered and early studies of the time treated the nuclei as static, fixed sources of field in which the electrons moved [Sut06, Sut95]. A theoretical justification of this procedure was first unsuccessfully sought by Bohr and Heisenberg [BH24] in the context of the old quantum theory and then famously by Born and Oppenheimer [BO27]. A detailed exposition of the Born-Oppenheimer approach can be found in [BJ00]; in the following we will only provide a general outline of this approach.

Indicating with m the electron mass and with M ‘some mean value of the [nuclear masses]’ [BO27] the Coulomb Hamiltonian (2.2) is partitioned as

$$\hat{H} = \hat{T}_N + \hat{T}_e + V = \hat{T}_N + \hat{H}_{\text{cn}} = \left(\frac{m}{M}\right) \hat{H}_1 + \hat{H}_{\text{cn}} \quad (2.3)$$

where $\hat{H}_1 = \hat{T}_N \times (\frac{M}{m})$ is the rescaled kinetic energy of the nuclei and has a magnitude comparable to $\hat{T}_e$. $\hat{H}_{\text{cn}}$ is the so-called clamped-nuclei Hamiltonian, which corresponds to a system where the nuclei are replaced by infinitely massive ones. In the assumption that $\hat{H}_{\text{cn}}$ has a deep energy minimum for some nuclear geometry the term $\hat{H}_1$ is treated with perturbation theory, finally leading to an expansion for the exact energies and wave functions in series of $(m/M)^{1/4}$.

The practical procedure outlined in the paper [BO27] consists in two steps. In the first step the clamped-nuclei Hamiltonian, which depends parametrically on the nuclear geometry, is solved for one of its eigenfunctions or ‘electronic states’, typically the lowest-energy one

$$\hat{H}_{\text{cn}}(\mathbf{r}; \mathbf{R})\psi(\mathbf{r}|\mathbf{R}) = \varepsilon(\mathbf{R})\psi(\mathbf{r}|\mathbf{R}) \quad (2.4)$$

where we indicated with $\mathbf{r}$ and $\mathbf{R}$ respectively the set of electronic and nuclear coordinates. The eigenvalue $\varepsilon(\mathbf{R})$ as a function of the nuclear geometry plays the role of a potential energy for

the motion of the nuclei in a second, nuclear-motion Schrödinger equation

$$\left(\hat{T}_N + \varepsilon(\mathbf{R})\right) \chi(\mathbf{R}) = E\chi(\mathbf{R}) \quad (2.5)$$

The wave function of the system is approximately given by the product of the electronic and nuclear parts

$$\Psi(\mathbf{r}, \mathbf{R}) = \psi(\mathbf{r}|\mathbf{R})\chi(\mathbf{R}) \quad (2.6)$$

The Born-Oppenheimer analysis soon became referenced to as a formal justification of the existing procedure of treating the nuclei as fixed; however, it is interesting to quote a 1947 comment by Condon on it [Con47]:

But in 1926 it did not occur to anyone that there was anything basically wrong with talking about definite values of both electronic and nuclear position and momentum being carried over without alteration in an electronic transition. [...] Besides studying the current papers [on quantum mechanics] I tried to solve the basic problem in quantum mechanics that underlies all molecular dynamics – the basic justification for the method of first working out the electronic states for fixed positions of the nuclei, so that the electronic energy levels depend parametrically on the nuclear coordinates and serve as the potential-energy functions for determination of the nuclear motions. The justification is, of course, connected with the smallness of electronic mass relative to nuclear mass, but I never could see how to work it out. Later the problem was handled in a basic paper by Born and Oppenheimer which, however, I have never felt that I properly understood. But Born is such a great master at seeing all physics in terms of ‘Entwicklungen nach einem kleinen Parameter Kappa’³ that I suppose it must be all right. The paper of Born and Oppenheimer is among those difficult ones that are more often cited than read.

Several criticisms to the Born-Oppenheimer approach have been put forward over time [WS03, Sut03a, Sut93]; the main ones are:

1. In the Born-Oppenheimer treatment the continuous spectrum due to the centre-of-mass motion is not separated out and, as a consequence, all subsequent series expansions are divergent or otherwise not well-defined. This difficulty has been fixed [CS80, KMSW92] but the extension is not trivial.
2. The Born-Oppenheimer treatment is based on the assumption that the clamped-nuclei Hamiltonian has a deep potential minimum for a certain equilibrium configurations of the nuclei. However, the practice of first solving the clamped-nuclei Hamiltonian and then using the resulting potential surface for the nuclear motion can also be used very far from the potential minimum or, indeed, it can be used for purely repulsive states which have no such minimum at all. The real criterium for the adequacy of the procedure is the energetic separation of other electronic states, but this is not apparent in the treatment; the Born-Oppenheimer treatment thus appears unnecessarily restrictive in the statement of its limits of validity [JK08].

³German for: expansions in a small parameter kappa

3. The perturbation expansion around the minimum of the clamped-nuclei Hamiltonian is known to be divergent and this raises a series of issues if it is desired to improve on the approximation.
4. The Born-Oppenheimer paper [BO27] treats explicitly only diatomic molecules and the extension to general polyatomic system is not trivial.

2.3.3 The Born-Huang variational approach

It appears that Born himself was not satisfied with the Born-Oppenheimer approach and he continued working on the problem in the following years [Sut03a, Sut93]. This culminated in a different approach based on the variational principle which Born first proposed in [Bor51] and was later reported as an appendix in the book by Born and Huang [BH54]. Incidentally, the same mathematical approach had been proposed much earlier by Slater [Sla27] in a study of the electronic structure of the helium atom but was then forgotten.

A detailed exposition of the Born-Huang approach can be found e.g. in [BJ98] and we will describe it only briefly. The notation is the same as in the previous section. The Hamiltonian is again partitioned in the clamped-nuclei Hamiltonian plus the nuclear kinetic energy

$$\hat{H} = \hat{T}_N + \hat{T}_e + V = \hat{T}_N(\mathbf{R}) + \hat{H}_{\text{cn}}(\mathbf{R}, \mathbf{r}) \quad (2.7)$$

It is then supposed that the Schrödinger equation for the clamped-nuclei Hamiltonian has been solved for all possible values of the nuclear geometries $\mathbf{R}$ and that for each of these there exist an infinite, complete and discrete set of orthonormal eigenfunctions $\psi_j(\mathbf{r}|\mathbf{R})$

$$\hat{H}_{\text{cn}}\psi_j(\mathbf{r}|\mathbf{R}) = \varepsilon_j(\mathbf{R})\psi_j(\mathbf{r}|\mathbf{R}) \quad j = 1, 2, \dots, +\infty \quad (2.8)$$

Because the set of eigenfunctions of $\hat{H}_{\text{cn}}$ is complete it is possible to expand any of the exact wave functions $\Psi(\mathbf{r}, \mathbf{R})$ as

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_{j=1}^{+\infty} \chi_j(\mathbf{R}) \psi_j(\mathbf{r}|\mathbf{R}) \quad (2.9)$$

where the $\chi_j(\mathbf{R})$ are expansion coefficients which depend on the nuclear coordinates $\mathbf{R}$.

One then considers the full Schrödinger equation $\hat{H}\Psi = E\Psi$ and expansion (2.9) for the exact Ψ is inserted; making use of eq. (2.8) one obtains

$$\sum_{j=1}^{+\infty} \left\{ \varepsilon_j \psi_j + \psi_j \hat{T}_N + (\hat{T}_N \psi_j) - \frac{1}{M} \vec{\nabla}_{\mathbf{R}} \psi_j \cdot \vec{\nabla}_{\mathbf{R}} \right\} \chi_j = E \sum_{j=1}^{+\infty} \chi_j \psi_j \quad (2.10)$$

where for simplicity we have assumed that all nuclei have the same mass M , for compactness we have omitted writing the variable dependence of $\chi_j(\mathbf{R})$ and of $\psi_j(\mathbf{r}|\mathbf{R})$ and we used the multidimensional version of Leibniz's law, namely

$$\nabla^2(fg) = g\nabla^2 f + f\nabla^2 g + 2\vec{\nabla} f \cdot \vec{\nabla} g \quad (2.11)$$

One proceeds multiplying by $\psi_i^*(\mathbf{r}|\mathbf{R})$ and integrating over all electronic coordinates $\mathbf{r}$. A set of coupled equations for the coefficients $\chi_i(\mathbf{R})$ is obtained:

$$\left(\hat{T}_N + \varepsilon_i(\mathbf{R}) \right) \chi_i(\mathbf{R}) + \sum_{j=1}^{+\infty} \hat{A}_{ij}(\mathbf{R}) \chi_j(\mathbf{R}) = E \chi_i(\mathbf{R}) \quad (2.12)$$

where we have introduced the non-adiabatic matrix-elements

$$\hat{\Lambda}_{ij}(\mathbf{R}) = \int \psi_i^*(\mathbf{r}|\mathbf{R}) \hat{T}_N(\mathbf{R}) \psi_j(\mathbf{r}|\mathbf{R}) d\mathbf{r} - \frac{1}{M} \left(\int \psi_i^*(\mathbf{r}|\mathbf{R}) \vec{\nabla}_{\mathbf{R}} \psi_j(\mathbf{r}|\mathbf{R}) d\mathbf{r} \right) \cdot \vec{\nabla}_{\mathbf{R}} \quad (2.13)$$

What we have done so far is (arguably) exact, and the Born-Oppenheimer scheme is recovered by neglecting all the non-adiabatic terms $\hat{\Lambda}_{ij}$. The rationale for doing this is that the electronic wave functions ψ_n are supposed to depend on the nuclear coordinates only ‘weakly’, so that the nuclear kinetic energy operator $\hat{T}_N$ is expected to approximately commute with them.

It is straightforward to keep the diagonal term $\hat{\Lambda}_{ii}(\mathbf{R})$, usually called the Born-Oppenheimer diagonal correction (BODC), which acts as an additive, mass-dependent correction surface to the electronic surface $\varepsilon(\mathbf{R})$. Note that in this case the second term in eq. (2.13) is zero for real wave functions⁴ as

$$\int \psi_i(\mathbf{r}|\mathbf{R}) \vec{\nabla}_{\mathbf{R}} \psi_i(\mathbf{r}|\mathbf{R}) d\mathbf{r} = \frac{1}{2} \int \vec{\nabla}_{\mathbf{R}} \psi_i(\mathbf{r}|\mathbf{R})^2 d\mathbf{r} = \frac{1}{2} \vec{\nabla}_{\mathbf{R}} \int \psi_i(\mathbf{r}|\mathbf{R})^2 d\mathbf{r} = 0 \quad (2.14)$$

The approximation in which only $\hat{\Lambda}_{ii}$ is retained is called the *adiabatic approximation*; note that $\hat{\Lambda}_{ii}$ depends on the mass of the nuclei, so potential energy surfaces in the adiabatic approximation are mass dependent. Finally, if at least some of the off-diagonal elements $\hat{\Lambda}_{ij}$ are retained the calculation is generically called *non-adiabatic*.

Two important observations can be made about $\hat{\Lambda}_{ij}$ for $i \neq j$. The first is that, in reverse to the $i = j$ case, it is now the second term of eq. (2.13) which is expected to be the larger one. The reason for this is that the matrix representation of the first term of eq. (2.13) contains as a factor the square of the matrix representation of the second. We can show this fact explicitly in a few passages:

$$\begin{aligned} \langle \psi_i | \frac{\partial^2}{\partial R_\alpha^2} | \psi_j \rangle &= \langle \psi_i | \frac{\partial}{\partial R_\alpha} \frac{\partial}{\partial R_\alpha} | \psi_j \rangle = \langle \psi_i | \frac{\partial}{\partial R_\alpha} \left(\sum_{k=0}^{+\infty} |\psi_k\rangle \langle \psi_k| \right) \frac{\partial}{\partial R_\alpha} | \psi_j \rangle = \\ &= \sum_{k=0}^{+\infty} \langle \psi_i | \frac{\partial}{\partial R_\alpha} | \psi_k \rangle \langle \psi_k | \frac{\partial}{\partial R_\alpha} | \psi_j \rangle \end{aligned} \quad (2.15)$$

where we used the resolution of identity relation $\sum |\psi_k\rangle \langle \psi_k| = 1$.

Before stating the second remark let us first remember the following identity for the commutator of a generic operator $\hat{A}$ with the Hamiltonian

$$\langle \psi_i | [\hat{A}, \hat{H}] | \psi_j \rangle = \langle \psi_i | \hat{A} \hat{H} - \hat{H} \hat{A} | \psi_j \rangle = (E_j - E_i) \langle \psi_i | \hat{A} | \psi_j \rangle \quad (2.16)$$

We can use this relation to re-write the integral in the second term of eq. (2.13) as

$$\langle \psi_i | \vec{\nabla}_{\mathbf{R}} | \psi_j \rangle = \frac{\langle \psi_i | [\vec{\nabla}_{\mathbf{R}}, \hat{H}_{\text{cn}}] | \psi_j \rangle}{E_j(\mathbf{R}) - E_i(\mathbf{R})} \quad (2.17)$$

This form demonstrates our second point: the non-adiabatic terms will become large for configurations where potential energy surfaces $E(\mathbf{R})$ cross or come very close to one another. Special techniques are needed to deal with these cases (see also section 5.1.2).

⁴For a real Hamiltonian like the Coulomb one given by eq. (2.2) wave functions can always be chosen real.

Criticisms and further developments

The Born-Huang treatment is much more satisfactory than the original Born-Oppenheimer one and is what is usually described in textbooks [AF05] under the denomination of ‘Born-Oppenheimer approximation’ [CC03]. There are still, however, a number of undesirable features [JK08, Kut07b, Sut93, Sut82]:

1. The continuum spectrum due to the translational motion is still not handled properly, making series expansions problematic. Furthermore, it is not true that the eigenfunctions of the clamped-nuclei Hamiltonian $\hat{H}_{\text{cn}}$ form a complete, discrete set of normalisable states, so expansion (2.9) is not completely justified.
2. In the Born-Huang formulation three levels of approximation emerge: the original Born-Oppenheimer scheme, the adiabatic approximation and the non-adiabatic treatment. However, it is found that non-adiabatic corrections to molecular energies are comparable in magnitude to the adiabatic ones, and not much smaller as one would hope. At the same time, while computing the adiabatic approximation is relatively straightforward, the non-adiabatic formalism becomes extremely difficult. These considerations suggest that the adiabatic approximation is in some sense unbalanced and one wonders if a more balanced and practical approach might exist.

Point 1. One way of dealing with the objections raised in Point 1 is to separate out the centre-of-mass motion at the beginning of the treatment and then to study the Hamiltonian in internal, translationally-invariant (i.e., space-fixed, see section (4.2.1)) coordinates [SW05, WS03, Sut00, Sut97, Sut93, Wol91, Sut91]. This is however technically complicated because the Hamiltonian has to be re-written in terms of the translationally-invariant coordinates.

A second, much simpler way of justifying the Born-Oppenheimer and adiabatic schemes was proposed by Kutzelnigg [Kut97a]; in this treatment the centre-of-mass motion is treated rigorously in a very simple way and without changing the general Born-Huang formalism. Furthermore, Kutzelnigg’s approach also showed that it is rigorously exact to compute the adiabatic correction $\langle \psi | \hat{T}_N | \psi \rangle_{\mathbf{r}}$ expressing $\hat{T}_N$ in Cartesian coordinates while leaving $\psi(\mathbf{r}|\mathbf{R})$ expressed in molecule-fixed nuclear coordinates (see section (4.2.1)).

Point 2. The objections raised in Point 2 are discussed by Kutzelnigg [Kut07b] and Jaquet and Kutzelnigg [JK08]. These authors showed that, in an expansion of the exact energy in inverse powers of the nuclear mass M , the Born-Oppenheimer approximation is correct to $\mathcal{O}(M^{-1})$, while the adiabatic correction includes some, but not all, terms in $\mathcal{O}(M^{-2})$. It is further shown that introducing a formalism with position-dependent effective masses for the nuclei can give an approximation correct to $\mathcal{O}(M^{-2})$. A formalism with position-dependent masses had already been developed notably by Bunker and Moss [BM77, BMM77, BM80] from a different point of view; for a discussion and applications see e.g. [Bar02, PT99]. The idea of using masses which are intermediate between the nuclear and the atomic ones for the calculation of the rotation-vibration spectrum is also physically appealing as one would expect electrons to partially follow the nuclei as they move. A discussion of this point starting from rather different considerations was also given by Essén [Ess77].

2.3.4 Other approaches

Hunter [Hun75] showed by a simple argument that the Born-Oppenheimer *ansatz* for the wave function

$$\Psi(\mathbf{r}, \mathbf{R}) = \chi(\mathbf{R})\psi(\mathbf{r}|\mathbf{R}) \quad (2.18)$$

where $\psi(\mathbf{r}|\mathbf{R})$ is the solution of the clamped-nuclei Hamiltonian may be *exact* provided $\chi(\mathbf{R})$ is appropriately chosen. This idea is discussed e.g. in [EA08, Sut03c, Sut00, Sut97]. This consideration has led some authors to look for possible definitions of ‘non-adiabatic’ potential energy surfaces which would produce the ‘exact’ nuclear wave function $\chi(\mathbf{R})$ [CC06, CW78]. However, this interesting approach has not found practical applications so far.

2.3.5 The idea of molecular shape

Between the end of the 1970s and the first half of the 1980s a discussion took place in the scientific literature about the precise meaning in a quantum mechanical context of the classical, “ball-and-sticks” concept of molecular shape; in particular, the conceptual implications of the Born-Oppenheimer scheme were discussed at length. The issue was raised and discussed particularly by Woolley [Wol76, WS77, Wol77, Wol78, Wol80a, Wol85, Wol86, Wol88, Wol91, WS03, SW05] and several authors contributed [Wol80b, Tri80, CD80, GB81, Ber81, Sut82, CJ86, Mon87b, Löw91, Ram97, Mon99, CA04, Moh04], including a particularly thorough discussion by Claverie and Diner [CD80]. The interested reader is referred to the cited literature for details, while in what follows we will only make a brief comment.

In quantum chemistry by “equilibrium geometry” of a molecule one intends the set of nuclear coordinate $\mathbf{R}_e$ for which the clamped-nuclei energy is a minimum, see e.g. [CCF⁺05]. It should be remembered, however, that these values do not literally represent the equilibrium position of the nuclei in a naive ‘ball-and-sticks’ sense. Like electrons, nuclei are delocalised over the molecule and the nuclear density of a certain nuclear species can be calculated from the squared modulus of the nuclear wave function $|\chi(\mathbf{R})|^2$ integrating out the coordinates of all other nuclei.

These nuclear density distributions may be strongly peaked at the equilibrium values $\mathbf{R}_e$, in which case the idea of molecular shape is approximately recovered, but need not be in all situations, like for example in the case of highly-excited rotation-vibration states or in that of molecules with only a shallow minimum in the clamped-nuclei Hamiltonian. In all these situations nuclear densities will be very spread out and incompatible with any classical idea of nuclear geometry; see e.g. [MRTM06, TBMS06] for examples of this sort.

2.4 Relativistic effects

Already before the discovery of the Schrödinger equation in 1926, physicists had tried to unify quantum mechanics with special relativity [Kra00, Meh87]. This line of research led in 1928 to the Dirac equation [MR00], while in the period going from the 1930s to the 1950s a more complete formalism was developed under the name of quantum field theory [Wei05]. Most textbooks on quantum-relativistic theories, e.g. [Wei05, Zee03, PS95, IZ06], focus on particle physics and do not discuss applications to molecular systems; one exception is the book by Strange [Str98]. The topic of relativistic effects in molecular systems is generally studied under the name of relativistic

quantum chemistry, see e.g. the recent book by Dyall and Fægri [DF07] for a very thorough and pedagogical exposition. A much shorter introduction can also be found in the book by Jensen [Jen06] and other general reviews were given by Quiney *et al* [Qui03, QSG99] and by Reiher [RH00]. A review focusing on the computation of relativistic effects in small, light molecules was given by Tarczay *et al* [TCKQ01]. Finally, we point out that several PhD dissertations on relativistic quantum chemistry containing ample introductions can be downloaded from the web-site of the program DIRAC [Dir].

2.4.1 Quantum electrodynamics

The most complete theory describing interactions between matter and electromagnetic radiation is quantum electrodynamics (QED), see e.g. [CTDRG97, CTDRG98, Wei05] for technical expositions and the reviews by Woolley [Wol03, Wol99] and the book by Craig and Thirunamachandran [CT98] for applications to molecular physics. Leaving aside some conceptual problems [Nik07, Cao04], the application of the full formalism of QED to molecular systems is numerically intractable and even the simplest cases such as the hydrogen atom have to be treated approximately [LJM⁺03]. On this point it is interesting to mention a wry remark by the nuclear physicist Gerald E. Brown (as quoted by Mattuk, [Mat74], pag.1):

In 18th-century Newtonian mechanics, the three-body problem was insoluble. With the birth of general relativity around 1910 and quantum electrodynamics in 1930, the two- and one-body problems became insoluble. And within modern quantum field theory, the problem of zero bodies (vacuum) is insoluble. So, if we are out after exact solutions, no bodies at all is already too many!

The main use of QED in molecular physics is to provide a rigorous starting point from which more usable approximations can be derived, often via perturbation theory; the reader is referred to the mentioned references [Wol03, Wol99, CT98, CTDRG97, CTDRG98, Wei05] for a detailed discussion of this complex subject.

2.4.2 The one-electron Dirac equation

Dirac [Wei05, DF07, MR00] derived in 1928 a relativistic equation which describes a single particle with spin $\frac{1}{2}$, e.g. an electron, in an external potential. The wave function of a Dirac particle is a four-component object,

$$\psi(\mathbf{r}) = [\psi_1(\mathbf{r}), \psi_2(\mathbf{r}), \psi_3(\mathbf{r}), \psi_4(\mathbf{r})] \quad (2.19)$$

Two distinct reasons [DF07, Rei06, Str98] can be identified for this four-fold increase in the number of components with respect to the non-relativistic case; the first reason is that the spin degrees of freedom are automatically included in the Dirac formalism, and the second is that the Dirac equation describes in fact a coupled particle-antiparticle pair and not a single particle.

It is convenient to present a few definitions which are common in relativistic quantum mechanics [DF07]; the Pauli spin matrices σ_s , ($s = x, y, z$) are defined by

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad , \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad , \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (2.20)$$

The Pauli matrices can be collected into a 3-component object $\vec{\sigma}$ which can be formally manipulated as a vector

$$\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z) \quad (2.21)$$

From the Pauli matrices we define four 4×4 matrices $\alpha_x, \alpha_y, \alpha_z$ and β

$$\alpha_i = \begin{pmatrix} \mathbf{0}_2 & \sigma_i \\ \sigma_i & \mathbf{0}_2 \end{pmatrix}, \quad \beta = \begin{pmatrix} \mathbf{1}_2 & \mathbf{0}_2 \\ \mathbf{0}_2 & -\mathbf{1}_2 \end{pmatrix} \quad (2.22)$$

where $\mathbf{0}_2$ and $\mathbf{1}_2$ are respectively the 2×2 zero matrix and the 2×2 identity matrix. Finally, in analogy with $\vec{\sigma}$, we define a 3-component object

$$\vec{\alpha} = (\alpha_x, \alpha_y, \alpha_z) \quad (2.23)$$

With these definitions the time-independent Dirac equation for an electron in an external electric field V can be written as the eigenvalue equation⁵

$$\hat{h}_D \psi = E \psi \quad \text{where} \quad \hat{h}_D = c \vec{\alpha} \cdot \hat{\mathbf{p}} + c^2 \beta + V \quad (2.24)$$

Despite its successes the Dirac equation also has limitations; the external electric field is not quantised [Rei06] and, as a consequence, the Dirac equation is not appropriate to describe the creation and annihilation of particles, for which the more complete quantum field theory formalism had to be introduced [Wei05]. This fact, however, does not constitute a practical limitation in the low-energy context of molecular physics [DF07, Str98].

From the computational point of view the Dirac equation is considerably more difficult to solve than the Schrödinger equation, one reason being that variational treatments are difficult to apply because of the negative-energy part of spectrum [DF07, Kut97b].

2.4.3 The spin-free Dirac equation

Dyall showed [Dya94] that it is possible to re-write the Dirac equation in a way that renders spin-dependent and spin-independent effects more explicit [DF07]. A modified Dirac Hamiltonian $\hat{\hat{h}}_D$ which has the same spectrum as the original $\hat{h}_D$ is derived

$$\hat{\hat{h}}_D = \begin{pmatrix} V \mathbf{1}_2 & \hat{T} \mathbf{1}_2 \\ \hat{T} \mathbf{1}_2 & [(\hat{\mathbf{p}}V \cdot \hat{\mathbf{p}} - \hat{T})/4c^2] \mathbf{1}_2 \end{pmatrix} + \begin{pmatrix} \mathbf{0}_2 & \mathbf{0}_2 \\ \mathbf{0}_2 & i\vec{\sigma} \cdot \hat{\mathbf{p}}V \times \hat{\mathbf{p}}/4c^2 \end{pmatrix} \quad (2.25)$$

It can be shown [DF07] that the second, spin-dependent term is small, and the spin-independent approximation consists in dropping it. This is an important reference point for comparisons with other, more approximate, ‘spin-free’ (also called ‘scalar relativistic’) approaches.

2.4.4 The many-electron Dirac equation

At variance with the Schrödinger equation, the Dirac equation is not rigorously generalisable to systems of many particles [Pol02, Rei06] and, more generally, a universally-accepted quantum-relativistic many-particle theory does not exist [Pol02, Neu]. However, applications to atoms and

⁵We use atomic units throughout, so that $\hbar = 1$, $e_0 = 1$, $4\pi\epsilon_0 = 1$ and $m_e = 1$. In these units the value of the speed of light c , being linked to the fine-structure constant by the relation $\alpha = e_0^2/(4\pi\epsilon_0\hbar c)$, is numerically equal to $\alpha^{-1} = 137.03599907$ [GHK⁺06].

molecules based on generalisations of the Dirac equation have been very successful [TCKQ01] and the general consensus is that numerical results obtained from the Dirac equation are adequate for chemical purposes.

The Dirac equation is generalized to a many-electron system by defining an N -particle Hamiltonian as

$$\hat{H}_{\text{rel}} = \sum_{i=1}^N \hat{h}_{\text{D}}(i) + \sum_{i=1}^N \sum_{j=i+1}^N \hat{g}(i, j) \quad (2.26)$$

where $\hat{g}(i, j)$ represents the electron-electron interaction. In first approximation one can take the Coulomb term [DF07]

$$\hat{g}_{\text{C}}(i, j) = \frac{1}{r_{ij}} \quad (2.27)$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. This choice of $\hat{g}$ leads to the so-called Dirac-Coulomb Hamiltonian. An expression which treats the electron-electron interaction correctly to order $\mathcal{O}(c^{-2})$ can be derived in a purely classical context [DF07] and gives the so-called frequency-independent Coulomb-Breit interaction:

$$\hat{g}_{\text{CB}}(i, j) = \hat{g}_{\text{C}}(i, j) - \frac{1}{2} \left(\frac{\vec{\alpha}_i \cdot \vec{\alpha}_j}{r_{ij}} + \frac{(\vec{\alpha}_i \cdot \mathbf{r}_{ij})(\vec{\alpha}_j \cdot \mathbf{r}_{ij})}{r_{ij}^3} \right) \quad (2.28)$$

The Dirac-Coulomb-Breit Hamiltonian applied in a four-component formalism represents the theoretically most rigorous method available to treat relativistic effects in molecules; unfortunately, it is also very computationally intensive and calculation are feasible only on small systems. For example, one can estimate [DF07] that Dirac-Hartree-Fock calculations are about a factor of 64 more expensive than the same non-relativistic Hartree-Fock calculation with an equivalently-sized basis set.

2.4.5 The Pauli Hamiltonian

It is formally possible to perform an expansion in powers of $\hat{\mathbf{p}}/mc$ of the one-electron Dirac-Coulomb Hamiltonian. The correction terms up to order $\mathcal{O}(c^{-2})$ give the Pauli Hamiltonian⁶, which now acts on 2-component wave functions:

$$\hat{H}_{\text{Pauli}} = \underbrace{\hat{T} + V}_{\hat{H}_0} - \underbrace{\frac{\hat{\mathbf{p}}^4}{8c^2}}_{\hat{H}_{\text{MV}}} + \underbrace{\frac{1}{8c^2}(\nabla^2 V)}_{\hat{H}_{\text{D1}}} + \underbrace{\frac{1}{4c^2}\vec{\sigma} \cdot (\nabla V) \times \hat{\mathbf{p}}}_{\hat{H}_{\text{SO}}} \quad (2.29)$$

$\hat{H}_0$ is the non-relativistic Coulomb Hamiltonian, $\hat{H}_{\text{MV}}$ is called the mass-velocity operator, $\hat{H}_{\text{D1}}$ is the one-electron Darwin operator and $\hat{H}_{\text{SO}}$ is the spin-orbit term. If the external potential V is due to a nucleus so that $V = -Z/r$ then $\hat{H}_{\text{D1}}$ and $\hat{H}_{\text{SO}}$ can be written as

$$\hat{H}_{\text{D1}} = \frac{\pi Z}{2c^2} \delta(\mathbf{r}) \quad \text{and} \quad \hat{H}_{\text{SO}} = \frac{Z}{2c^2} \frac{\vec{\sigma} \cdot \hat{\mathbf{l}}}{r^3} \quad (2.30)$$

where $\hat{\mathbf{l}} = \mathbf{r} \times \hat{\mathbf{p}}$ is the angular momentum of the electron.

There are technical problems with an expansion in powers of $\hat{\mathbf{p}}/mc$: the Hamiltonians one obtains are not self-adjoint and are unbounded from below; for this reason the Pauli Hamiltonian can only be used in perturbation theory. Other, rigorous perturbative expansions of the Dirac

⁶Note that this is not the same as the similarly-named Pauli equation [DF07, Str98], which is an *ad hoc* non-relativistic generalisation of the Schrödinger equation which includes spin.

equations have been derived, and one of such approaches is the Direct Perturbation Theory of Rutkowski, Kutzelnigg *et al* [Kut99, OK97, CK96, Kut96, Kut89]. The Pauli Hamiltonian is recovered in this more rigorous approach but it is found that if one uses approximate, and not exact, solutions of $\hat{H}_0$ as basis for the perturbation treatment a further term Δ^{DPT} arises, namely

$$\Delta^{\text{DPT}} = \frac{1}{2c^2} \hat{T}(\hat{H}_0 - E_0) \quad (2.31)$$

Inclusion of Δ^{DPT} accelerate the convergence of relativistic properties with respect to the quality of the non-relativistic wave function [DF07, TCKQ01, CK96].

Many-electron Pauli Hamiltonian

If an expansion in powers of $\hat{\mathbf{p}}/mc$ is applied to the many-electron Dirac-Coulomb-Breit Hamiltonian the mass-velocity, Darwin and spin-orbit terms simply generalize to a sum over all electrons

$$\hat{H}_{\text{MV}} = -\frac{1}{8c^2} \sum_i \hat{\mathbf{p}}_i^4 \quad \hat{H}_{\text{D1}} = \frac{\pi}{2c^2} \sum_{\alpha} Z_{\alpha} \sum_i \delta(\mathbf{r}_{i\alpha}) \quad \hat{H}_{\text{SO}} = \frac{1}{2c^2} \sum_{\alpha} Z_{\alpha} \sum_i \frac{\vec{\sigma}_i \cdot \hat{\mathbf{l}}_{i\alpha}}{r_i^3} \quad (2.32)$$

where α sums over the nuclei, i over the electrons, $\mathbf{r}_{i\alpha} = |\mathbf{r}_i - \mathbf{R}_{\alpha}|$ where $\mathbf{R}_{\alpha}$ is the nuclear position vector. Note that for molecules which are spin singlets the spin-orbit term vanishes at first-order of perturbation theory. At the c^{-2} order several other terms arise, and they are reviewed by Tarczay *et al* [TCKQ01]; at first-order perturbation and for spin-singlet states only two of these terms are non-zero, namely the two-electron Darwin interaction and the spin-spin interaction; the two-electron Darwin operator is given by [TCKQ01]

$$\hat{H}_{\text{D2}} = -\frac{\pi}{2c^2} \sum_{i=1}^N \sum_{j=i+1}^N \delta(\mathbf{r}_{ij}) \quad (2.33)$$

while the spin-spin interaction can be written as [TCKQ01]

$$\hat{H}_{\text{SS}} = \underbrace{-\frac{8\pi}{6c^2} \sum_{i=1}^N \sum_{j=i+1}^N (\vec{\sigma}_i \cdot \vec{\sigma}_j) \delta(\mathbf{r}_{ij})}_{\hat{H}_{\text{FC}}} + \underbrace{\frac{1}{2c^2} \sum_{i=1}^N \sum_{j=i+1}^N \left(\frac{\vec{\sigma}_i \cdot \vec{\sigma}_j}{r_{ij}} + \frac{(\hat{\mathbf{p}}_i \cdot \mathbf{r}_{ij})(\hat{\mathbf{p}}_j \cdot \mathbf{r}_{ij})}{r_{ij}^3} \right)}_{\hat{H}_{\text{DP}}} \quad (2.34)$$

The term $\hat{H}_{\text{FC}}$ is called ‘Fermi-contact’ and $\hat{H}_{\text{DP}}$ ‘dipolar interaction’.

2.4.6 Quantum electrodynamics corrections

The most important $\mathcal{O}(c^{-3})$ term in spin-singlet, light systems is the Lamb-shift; this effect is not included in the Dirac-Coulomb-Breit Hamiltonian and its derivation explicitly requires QED [DF07]; recent reviews discussing QED corrections for hydrogen-like and helium-like ions were given respectively by Soff *et al* [SBG⁺98] and by Artmyev *et al* [ASY⁺05]. The Lamb-shift is made up by two contributions, namely vacuum polarization and electron self-energy, both of which are difficult to calculate. In many-electron systems one can further partition the full effect in a one-electron contribution and a smaller two-electron one.

Even though the derivation and the exact treatment of the Lamb shift are too complex to be applied to molecules, Pyykkö *et al* [PDC⁺01] suggested some very simple approximate expressions which may be sufficiently accurate for chemical purposes. In this approximation the

Table 2.1: Effects of various relativistic corrections on the barrier to linearity of water, taken from Tarczay *et al* [TCKQ01]. The exact geometries taken for equilibrium and linearity are not reported but it is said they were calculated using non-relativistic, all-electron CCSD(T) with the aug-cc-pVTZ basis set.

Effect	cm ⁻¹
Mass-Velocity ^a	210.63
One-electron Darwin ^a	-158.42
Total MVD1 contribution	52.51
Δ^{DPT} (eq. 2.31) ^a	-0.37
Two-electron Darwin ^a	2.51
Breit (eq. 2.34) ^b	3.77
One-electron Lamb shift ^c	-3.54
Two-electron Lamb shift ^c	0.13
Total of the smaller effects	2.50
Total of all relativistic contributions	55.01

^a Calculated with the cc-pV5Z basis set and CCSD(T).

^b Calculated with the uncontracted cc-pCVTZ basis set and CCSD(T).

^c Calculated from the one- and two-electron Darwin contributions using formulae 2.35.

effect of the Lamb shift on the energies is proportional to the one-electron Darwin term, and the coefficients of proportionality are tabulated for atoms. In the case of water, it is expected that the effect originate mainly from the oxygen atom, so values relative to oxygen are taken

$$\begin{aligned} E_{L1} &= 0.02380 \times E_{D1} \\ E_{L2} &= 0.053334 \times E_{D2} \end{aligned} \tag{2.35}$$

2.4.7 The Douglas-Kroll-Hess Hamiltonian

The Douglas-Kroll-Hess method [DF07, Rei06] belongs to a family of methods where one performs a unitary transformation of the Dirac Hamiltonian with the end of uncoupling the negative-energy degrees of freedom. If the transformation is exactly unitary the transformed operator will have exactly the same electronic spectrum of the original Dirac Hamiltonian, but will act on two-component wave functions. These methods are sometimes called *quasi*-relativistic even though they are potentially equivalent to the ‘fully’ relativistic Dirac Hamiltonian.

There have been significant progress in this approach in the last 10 years and methods are now available that perform this transformation in a formally exact and computationally efficient way. A recent proposal of a method of this kind and a review of the present situation has been recently given by Kutzelnigg and Liu [LK07, KL05].

The Douglas-Kroll-Hess is probably the most well-known of these approaches and gives the unitary transformation as an infinite series of contributions starting from second order, giving

a series of approximations dubbed $\text{DKH}n$, $n = 2, 3, \dots$ [Rei06, Rei07]. Having to deal with an infinite expansion is generally not a serious practical limitation because it has recently been possible to efficiently compute corrections to essentially arbitrary order, and furthermore the convergence in n is usually rapid; for example, in the highly-charged hydrogen-like Sc^{21+} ($Z = 20$) the DKH energy is converged with respect to the exact solution of the Dirac equation to $10^{-9} E_h$ at the DKH6 level of the expansion [Rei07].

These methods can – and usually are – combined with the neglect of spin-dependent terms; if this is done the methods operate on single-component wave functions as in the non-relativistic case and, as the time required to set up the transformation is essentially negligible, they have the same computational cost as the corresponding non-relativistic method.

It is apparent that the DKH and related schemes are highly attractive, however for light systems the simple perturbation treatment of the MVD1 term yields sufficient accuracy and also gives with the same calculation the non-relativistic energy, which is in some cases desirable.

Solving the electronic-motion problem

3.1 Introduction

Finding the eigenvalues and the eigenvectors of the clamped-nuclei Coulomb Hamiltonian given by equation (2.2) is a very difficult and much studied problem known as *the quantum many-body problem*. Even though many mathematical properties of the many-electron Coulomb Hamiltonian and of its eigenfunctions are known [Thi01, RS80, Löw90, Sim00, HS00b, Yse03, Yse07, Sut08], analytical or semi-analytical solutions have so far been impossible to determine. This is in fact a general situation: inter-particle potentials which lead to exactly-solvable quantum many-body problems are few and far between and mostly confined to one or two spatial dimensions [Sut04b, Cal01, Zac96, Mat92, Kar08, LUEL06, LUL06, KC04, Sel99, KS62]. In the case of three spatial dimensions the only non-trivial exactly soluble many-particle model is the important case of particles interacting through harmonic forces [MS96, NO98].

Because analytical solutions are not obtainable the eigenvalue problem must be solved numerically. This has so far proven to be a hugely difficult task. Generic grid-based or finite-element numerical methods developed for partial differential equations [LP99] scale exponentially with the number of dimensions and thus become essentially impossible to use in systems with more than one or two particles. As an exemplification of the situation we will now present a straightforward approach equivalent (but computationally much more inefficient) to the full configuration-interaction method.

3.1.1 The Full Configuration Interaction approach

There is no difficulty of principle in writing down a simple procedure to find approximate eigenvalues and eigenvectors of the Schrödinger equation. Given a system containing N electrons and with total spin S , one can proceed as follows:

1. Fix a single-particle basis of $K \geq N/2$ one-electron functions (orbitals). A basis of $2K$ spin-orbitals can then be formed multiplying each basis function by a spin function $\alpha(\omega)$ or $\beta(\omega)$.
2. Build all the possible Slater determinants that can be obtained from the spin-orbital basis. From these, form all possible N_e linear combinations having the desired spin S ; each of

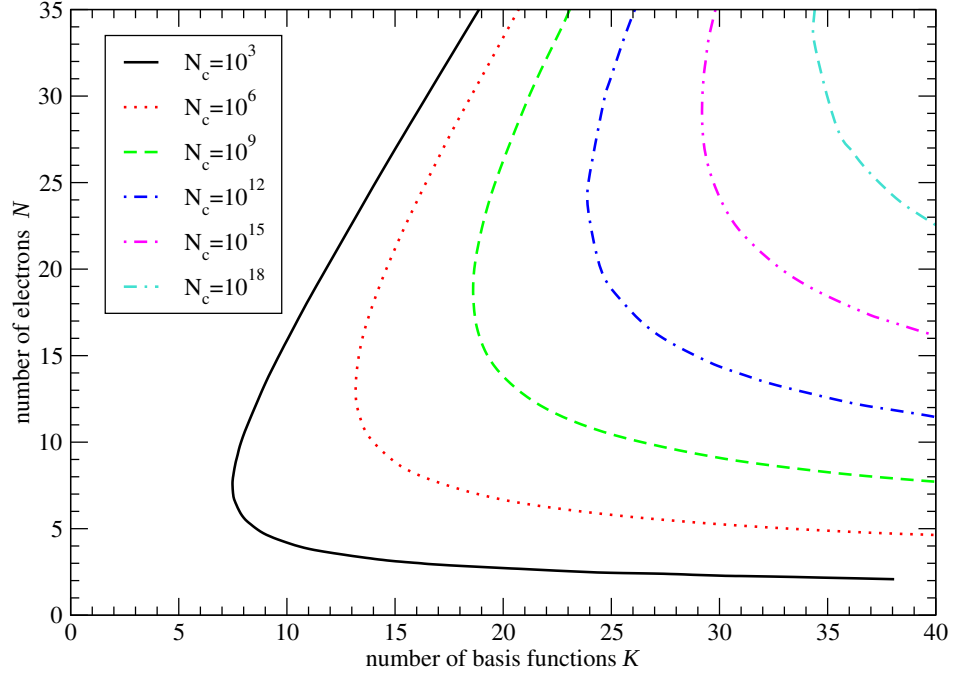


Figure 3.1: Size N_c of the Full-CI matrix according to eq. (3.1) for an $S = 0$ system (spin singlet). The limit of feasibility is presently of about $N_c = 10^9$. For a ten-electron system like water this corresponds to a basis of ≈ 25 orbitals, which should be considered very small.

these spin-adapted functions is called a configuration function (CF) or configuration state function (CSF).

3. Compute the matrix elements of the Hamiltonian in the basis of CFs, constructing the Hamiltonian matrix $\mathbf{H}$.
4. Calculate the desired eigenvalues and eigenvectors of $\mathbf{H}$. These are approximations of the first N_c electronic states with total spin S and in the limit of a complete basis set one recovers the exact eigenvalues and eigenvectors of the Hamiltonian.

This procedure is equivalent to the quantum-chemical method of *full configuration interaction* (FCI). The number of CFs arising from a system with N electrons and total spin S is given by the Weyl formula (also called Weyl-Robinson or Weyl-Paldus formula, see e.g. pag. 218 of [Pau95] and [Pal74]):

$$N_c = \frac{2S+1}{K+1} \binom{K+1}{\frac{N}{2}-S} \binom{K+1}{K-\frac{N}{2}-S} \quad (3.1)$$

A plot graphically illustrating the formula for a $S = 0$ system is given in Figure 3.1. The increase in the number of CFs is approximately exponential upon increases of K or N (see e.g. [Kar94] for a more detailed analysis) and this approach quickly becomes impracticable. This very steep increase of computational complexity with the dimensionality of a problem is sometimes referred to by the picturesque expression of *the curse of dimensionality* [GH07, Gri05].

Note that the procedure we have outlined would be in actual practice extremely inefficient, as it would require building and then diagonalising matrices of size $N_c \times N_c$. Very sophisticated

approaches to full-CI exist [RSS08, ABER00, ORJJ88, KH89, KH84] and at the time of writing computations with up to $\approx 10^9$ configurations have been performed [RSS08, ABER00]. For a recent review of full-CI implementations see Crawford and Schaefer III [CS00b]. What is clear is that, despite computational and algorithmic advances, full-CI computations are possible only for very small molecules with very small basis sets¹.

3.1.2 Further remarks and aim of this chapter

Because of the situation outlined in the previous section it is clear that to treat the quantum n -body problem very special methods had to be developed, all necessarily involving very drastic approximations. The development of such methods is one of the main goals of quantum chemistry and theoretical solid-state physics. This situation was already recognised at the very beginning of quantum mechanics, as for example vividly expressed by van Vleck in 1935 [vV35]:

The complexities of the n -body problem are, alas, so great that only for the very simplest molecule, namely H_2 , has it yet proved possible to integrate the Schrödinger wave equation with any real quantitative accuracy. Hence to date, anyone is doomed to disappointment who is looking Diogenes-like fashion² for honest, straightforward calculations of heats of dissociation from the basic postulates of quantum mechanics.

Another comment on the subject was famously given by Dirac [Dir29, Kut00] in 1929:

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It is therefore desirable that approximate methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex systems without too much computation.

Even though the notion that chemistry as a science consists only of applied physics can be criticised on the basis of its extremely reductionist character [Pri83, Sim02, Kut00, And72], Dirac's statement is rightfully considered prophetic [Kut00].

The aim of this chapter is to provide a broad overview to the quantum chemistry methods used in the following of this thesis, providing the relevant references and emphasising some lesser-known aspects.

3.2 The Hartree-Fock method

The Hartree-Fock method is of fundamental importance and is treated in most books on quantum chemistry and solid-state physics, among which we may mention, in approximately increasing order of sophistication, [Cra04, Jen06, Lev00, SO96, McW92, HMF92] for the quantum-chemistry

¹It has, however, been shown that quantum computers may be used to efficiently solve the full-CI problem. See, e.g. the recent analysis by Aspuru-Guzik *et al* [AGDLHG05]. From this reference one can extrapolate that a full-CI computation with a basis set with $K \approx 500$ would require a quantum computer with about 500 qubits of memory (present-day quantum computer have less than 7 qubits [BW08]).

²According to tradition, the cynic Greek philosopher Diogenes of Sinope used to walk about in full daylight with a lamp, and when asked what he was doing he would answer: "I am just looking for an honest man".

approach and [GRH91, NO98, FW03, Tho72] for the solid-state viewpoint. Some other excellent recent overviews covering more mathematical aspects of the methods are [EA08, LL05, Le 05, DL97]. Finally, some useful background mathematical topics are linear algebra [Lan00], calculus of variations [GF00], constrained minimization using Lagrange multipliers [Kar06, Jen] and the functional iteration method for the solution of non-linear equations [KC91].

3.2.1 General description

At the starting point one supposes that the exact N -electron wave function Ψ can be approximated by a single Slater determinant of N spin-orbitals (orbital ansatz):

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \approx \Psi_{\text{HF}} = \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix} \quad (3.2)$$

where $\mathbf{x} = (\mathbf{r}, \omega)$ and each χ_i is a one-electron spin-orbital which in the most general case is written as

$$\chi(\mathbf{x}) = \psi_\alpha(\mathbf{r})\alpha(\omega) + \psi_\beta(\mathbf{r})\beta(\omega) \quad (3.3)$$

As the Slater determinant is invariant with respect to similarity transformations one expects the optimal spin-orbitals not to be unique.

Application of the variational principle to the trial wave function Ψ_{HF} yields a set of n coupled equations which represent necessary conditions the energetically-optimal spin-orbitals have to obey and which are called the Hartree-Fock equations. Before writing down these equations it is useful to introduce some definitions. For more details see the cited literature, e.g. the book by Szabo and Ostlund [SO96], and the paper by Slater [Sla51].

Some useful definitions

We indicate the kinetic-energy operator by $\hat{t}$, the electrostatic potential due to the nuclei by $\hat{v}_n$ and we define the core operator $\hat{h}$ as the sum of the two:

$$\hat{t} = -\frac{1}{2}\nabla^2 \quad \hat{v}_n = -\sum_k \frac{Z_k}{r_k} \quad \hat{h} = \hat{t} + \hat{v}_n \quad (3.4)$$

where the sum is extended to all nuclei.

Then, for a given spin-orbital $\chi_a(\mathbf{x})$ we introduce two associated operators: a Coulomb operator $\hat{\mathcal{J}}_a$ and an exchange operator $\hat{\mathcal{K}}_a$, whose actions on a generic spin-orbital χ_i are defined by:

$$(\hat{\mathcal{J}}_a \chi_i)(\mathbf{x}) = \left(\int_{\mathbb{R}^3} \frac{|\chi_a(\mathbf{x}')|^2}{|\mathbf{x} - \mathbf{x}'|} d\mathbf{x}' \right) \chi_i(\mathbf{x}) \quad (3.5)$$

$$(\hat{\mathcal{K}}_a \chi_i)(\mathbf{x}) = \left(\int_{\mathbb{R}^3} \frac{\chi_i(\mathbf{x}')\chi_a(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d\mathbf{x}' \right) \chi_a(\mathbf{x})$$

It follows from the definitions that $\hat{\mathcal{J}}_a$ is a simple multiplicative operator corresponding to the electrostatic potential generated by a distribution of charge $|\chi_a(\mathbf{x}')|^2$; on the other hand $\hat{\mathcal{K}}_a$ is

an integral ('non-local') operator whose interpretation is less transparent. If we assume that the orbitals are real-valued³ we can re-write this term formally multiplying by $\chi_i(\mathbf{x})/\chi_i(\mathbf{x})$ and re-arranging some terms, obtaining

$$(\hat{\mathcal{K}}_a \chi_i)(\mathbf{x}) = \left(\int_{\mathbb{R}^3} \frac{\varrho_i^{(a)}(\mathbf{x}', \mathbf{x})}{|\mathbf{x} - \mathbf{x}'|} d\mathbf{x}' \right) \chi_i(\mathbf{x}) \quad \text{with} \quad \varrho_i^{(a)}(\mathbf{x}', \mathbf{x}) = \frac{\chi_i(\mathbf{x}')}{\chi_i(\mathbf{x})} \chi_a(\mathbf{x}') \chi_a(\mathbf{x}) \quad (3.6)$$

The effect of $\hat{\mathcal{K}}_a$ can then be interpreted as due to the electric potential generated by a distribution of charge $\varrho_i^{(a)}$ that changes shape as the particle moves around. If the spin-orbitals $\chi_a(\mathbf{x}')$ and $\chi_i(\mathbf{x}')$ are orthonormal, as it will be the case in what follows, it is easy to see that the integral of $\varrho_i^{(a)}(\mathbf{x}', \mathbf{x})$ in $d\mathbf{x}'$ adds up to zero if $i \neq a$ and adds up to one if $i = a$.

Next, given a set of N arbitrary spin-orbitals $\{\chi_a(\mathbf{x})\}_{a=1,\dots,N}$ we define the *total* Coulomb and *total* exchange one-particle operators associated with the set as

$$\hat{J}(\mathbf{x}) = \sum_{a=1}^N \hat{\mathcal{J}}_a(\mathbf{x}) \quad \hat{K}(\mathbf{x}) = \sum_{a=1}^N \hat{\mathcal{K}}_a(\mathbf{x}) \quad (3.7)$$

The meaning of the total Coulomb operator $\hat{J}$ is clear: it is the electric potential generated by the static distribution of charge $\varrho(\mathbf{x})$ formed by the sum of all the single-particle orbitals χ_a :

$$\varrho(\mathbf{x}) = \sum_{a=1}^N |\chi_a(\mathbf{x})|^2 \quad (3.8)$$

The effect of the total exchange operator $\hat{K}$ when acting on a spin-orbital χ_i can be interpreted as due to an electric potential generated by a distribution of charge which depends on χ_i and which varies in shape as the electron moves. The density $\varrho_i(\mathbf{x}', \mathbf{x})$ is called the exchange density and when acting on χ_i it is given the expression

$$\varrho_i(\mathbf{x}, \mathbf{x}') = \left(\sum_{a=1}^N \chi_a(\mathbf{x}') \chi_a(\mathbf{x}) \right) \frac{\chi_i(\mathbf{x}')}{\chi_i(\mathbf{x})} \quad (3.9)$$

Assuming again orthonormality of the spin-orbitals and integrating $\varrho_i(\mathbf{x}, \mathbf{x}')$ over $\mathbf{x}'$ it is easily seen that the total exchange charge always integrates exactly to +1 and thus represent a positive distribution of unit charge. A second important property is that at $\mathbf{x}' = \mathbf{x}$ the exchange charge density reduces to $\varrho(\mathbf{x})$.

We can now finally define the Fock operator associated with the set of N spin-orbitals by

$$\hat{f}(\mathbf{x}) = \hat{h}(\mathbf{x}) + \hat{J}(\mathbf{x}) - \hat{K}(\mathbf{x}) \quad (3.10)$$

3.2.2 The Hartree-Fock equations

With the definitions given in the previous section we can now write the (canonical) Hartree-Fock equations. These represent necessary conditions for the spin-orbitals $\chi_i(\mathbf{x})$ to make the energy of the Slater determinant formed from them a minimum:

$$\hat{f}(\mathbf{x}) \chi_i(\mathbf{x}) = \varepsilon_i \chi_i(\mathbf{x}) \quad i = 1, \dots, N \quad (3.11)$$

³The extension to complex spin-orbitals is straightforward but we do not discuss it here for simplicity.

or, more extensively,

$$-\frac{1}{2}\nabla^2\chi_i(\mathbf{x}) + v_n(\mathbf{x})\chi_i(\mathbf{x}) + \left(\int_{\mathbb{R}^3} \frac{\varrho(\mathbf{x})}{|\mathbf{x} - \mathbf{x}'|} d\mathbf{x}'\right)\chi_i(\mathbf{x}) - \left(\int_{\mathbb{R}^3} \frac{\varrho_i(\mathbf{x}, \mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d\mathbf{x}'\right)\chi_i(\mathbf{x}) = \varepsilon_i\chi_i(\mathbf{x}) \quad (3.12)$$

It can be noticed that the Fock operator is expressed in function of N of its eigenfunctions, so that equation (3.11) is not a proper eigenvalue equation and is sometimes called a pseudo-eigenvalue equation [SO96].

The corresponding Hartree-Fock energy is given by

$$E_{\text{HF}} = \sum_{a=1}^N \varepsilon_a - \sum_{i=1}^N \sum_{j=i+1}^N (J_{ij} - K_{ij}) \quad (3.13)$$

or, more extensively,

$$\begin{aligned} E_{\text{HF}} = & -\frac{1}{2} \sum_{i=1}^N \int_{\mathbb{R}^3} \nabla^2 \chi_i(\mathbf{x}) d\mathbf{x} + \int_{\mathbb{R}^3} \varrho(\mathbf{x}) v_n(\mathbf{x}) d\mathbf{x} \\ & + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\varrho(\mathbf{x})\varrho(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d\mathbf{x}d\mathbf{x}' - \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{|\varrho(\mathbf{x}, \mathbf{x}')|^2}{|\mathbf{x} - \mathbf{x}'|} d\mathbf{x}d\mathbf{x}' \end{aligned} \quad (3.14)$$

3.2.3 Varieties of Hartree-Fock schemes

In the previous section we did not impose any restriction on the form of the spin-orbitals, which were written in equation (3.3) as a sum of spin- α and spin- β components. The method which derives when this assumption is respected is the general (sometimes called generalised) Hartree-Fock method (GHF). Although sometimes advocated [HSA93] and extensively studied particularly by Fukutome in the 1970s (who, contrary to modern usage, calls it Unrestricted Hartree-Fock) [EA08, SP03, Pau03, McW92, Löw95, BLIS94, LM92, MP80, SP77, Fuk80, Ada62] the GHF method has historically been confined to rather niche applications [YSNY00, Jay98].

One of the reasons for this is linked to a problem which Löwdin [Löw66a, Löw63] dubbed the *symmetry dilemma*. The exact wave function Ψ is an eigenfunction of $\hat{S}$ and $\hat{S}_z$, while there is no guarantee that the solution of the GHF equations will be either ('spin contamination'). The dilemma consists in the balance between flexibility of the trial wave function – which allows for variationally-lower energies – and the respect of exact symmetry properties – which represent constraints that restrict variational freedom and hence increase the energy.

Symmetry properties are considered very important and several solutions to this 'dilemma' are possible, the simplest of which is to restrict from the beginning the trial wave function to a form which respects the required symmetry properties. Furthermore, it is an empirical fact that most stable molecules have an even number of electrons and are in their ground states spin singlets (i.e., eigenfunctions of $\hat{S}$ with eigenvalue zero); one can in this case easily impose that the trial eigenfunction be an eigenfunction of both $\hat{S}$ and $\hat{S}_z$ by constraining orbitals to be of the form $\chi = \psi(\mathbf{r})\alpha$ or $\chi = \psi(\mathbf{r})\beta$ and then coupling pairs of orbitals so that each pair has the same spatial part:

$$\chi_{2k}(\mathbf{x}) = \psi_{2k}(\mathbf{r})\alpha(\omega) \quad \chi_{2k+1}(\mathbf{x}) = \psi_{2k}(\mathbf{r})\beta(\omega) \quad k = 1, \dots, N/2$$

This choice defines the restricted-Hartree-Fock method (RHF), which is the older and most common implementation. Clearly, there are cases where the RHF method is by construction

inapplicable, for example if the state to be treated has an odd number of electrons; in these cases two possibilities are in common use: the restricted open-shell Hartree-Fock (ROHF) and the unrestricted Hartree-Fock method (UHF). We will briefly discuss only the UHF method. In this method the orbitals are taken of the kind $\chi = \psi(\mathbf{r})\alpha$ or $\chi = \psi(\mathbf{r})\beta$, but no restrictions on the spatial part of the orbitals are enforced. The Slater determinant formed by the UHF orbitals is still an eigenfunction of $\hat{S}_z$, but in general not of $\hat{S}$ ('spin contamination').

Another approach to the symmetry dilemma is to make use of spin-projection techniques like the ones developed by Löwdin [Kar86, May78, Löw66a, Löw59a, Löw59b]. One can construct a projection operator $\hat{P}(S, S_z)$ that acts upon an n -electron wave function and picks out the component with the specified spin quantum numbers. The projection operator can be applied in two ways, namely before or after the energy optimization. In the first case, which is the logically more consistent choice, one applies the variational principle to

$$E = \langle \hat{P}\psi | \hat{H} | \hat{P}\psi \rangle$$

where ψ is a UHF- or perhaps GHF-type wave function. It can be proven [May78, Löw66a, Löw60] that the projected wave function has a lower energy than the UHF or GHF solutions while at the same time possesses, by construction, the correct symmetry properties. This methodology is sometimes called extended Hartree-Fock (EHF) [PS87, MW90] but other authors use this term with completely unrelated meanings (e.g. [MI72]).

The projection can also be performed on a UHF or GHF wave function after a normal energy optimisation; this methodology, called projected Hartree-Fock (PHF), is easier to implement but introduces a cusp in the potential surface at the symmetry-breaking point [SP03, WS96, May78].

A plot of the potential surface of the BH molecule exemplifying the curves produced by some of these methods is reported as figure 3.2.

3.2.4 The Hartree-Fock-Roothaan equations

The Hartree-Fock equations for atoms are routinely solved with numerical grid-based methods [FBJ97, Joh07]. In the case of molecules the numerical route can still be pursued for very small molecules [KMW01, SH07b] (mainly diatomics) but in the general case the only viable way of solution consists in using a finite basis set. This methodology was introduced in parallel by Roothaan in the US and by Hall in the UK at the beginning of the 1950s [Roo91, Hal91]. Having chosen a basis set $\{\phi_\mu(\mathbf{r})\}_{\mu=1}^K$, it is possible to re-cast the Hartree-Fock equations in a form involving only $K \times K$ matrices and vectors, which can be managed efficiently with computers. For example, the finite basis-set version of the restricted Hartree-Fock equations gives the so-called Hartree-Fock-Roothaan equations [SO96]:

$$\mathbf{FC} = \mathbf{SC}\epsilon \tag{3.15}$$

where $\mathbf{C}$ is a matrix containing as n -th column-vector the expansion coefficients of the n -th orbital, $\mathbf{S}$ is the symmetric square matrix of the overlap integrals, $\mathbf{F}$ contains the matrix-elements of the Fock operator $\hat{f}$ (and thus depends on the coefficients matrix $\mathbf{C}$) and ϵ is a diagonal matrix containing the canonical orbital energies. Nowadays basis sets are almost universally constituted by atom-centred, fixed-exponent Gaussian basis function, see section 3.4.

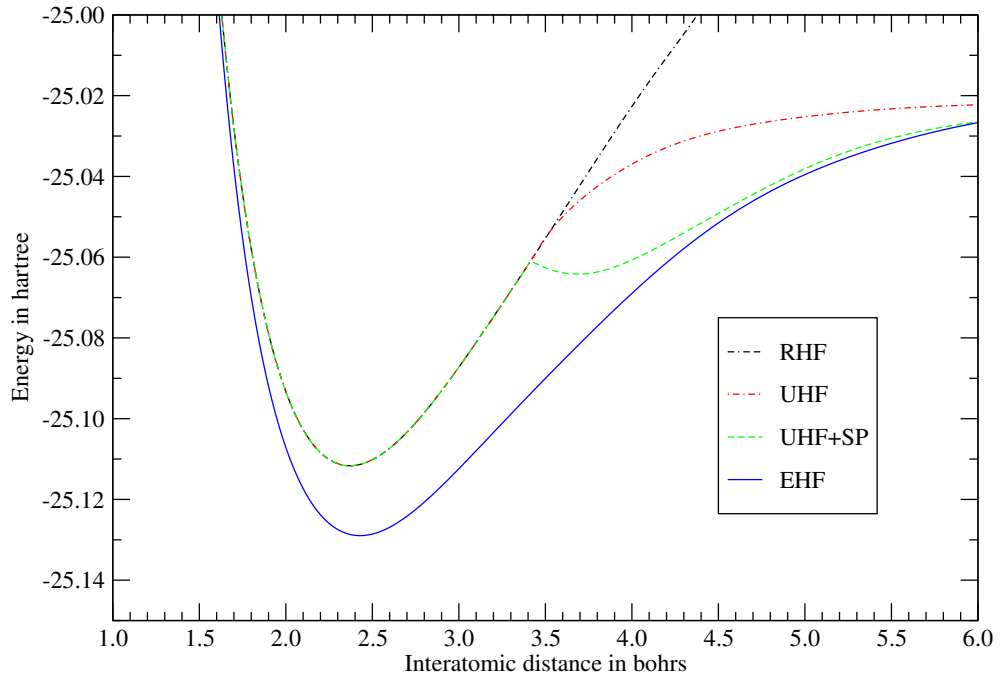


Figure 3.2: Potential energy curve of the BH molecule for different kinds of Hartree-Fock schemes. Reproduced from Figure 1 of ref. [May78]. The illustrated methods are: Restricted Hartree-Fock (RHF), Unrestricted Hartree-Fock (UHF), spin-projected Unrestricted Hartree-Fock (UHF+SP) and spin-projected Extended Hartree-Fock (EHF). In the UHF+SP method the spin-projection is performed on the UHF wave function after the energy optimization, while in the EHF method it is performed directly on a UHF-type trial wave function before optimizing the energy. The symmetry-breaking point for the UHF solution is at about $3.4 a_0$ and for smaller interatomic distances the UHF wave function reduces to the RHF one. See ref. [May78] for more details.

3.2.5 Method of solution

The Hartree-Fock equations are a system of non-linear equations and are typically solved by means of an iterative, functional iteration-type algorithm which explains the alternative name of “self-consistent field” method (SCF) given to the Hartree-Fock method. However, this solution scheme is not the only one possible [DMMV00, MV90] and is not an essential feature of the Hartree-Fock method, therefore “self-consistent field” could be considered a misnomer in that it overemphasizes the algorithm over the physical approximations used. Modern implementations use sophisticated numerical procedures to accelerate and render more robust the convergence properties of the numerical schemes employed, see e.g. [HOJ⁺08, Le 05, KSC02, KS07].

The Hartree-Fock equations only guarantee that the energy be stationary to variations of the orbitals, but is not necessarily a minimum. For example, it is well-known [Cou66] that the RHF solution for the helium atom is a saddle point and not a local minimum. Methods are available [SP03, YAGS90, SP77] to check the stability of the solution, but are seldom performed. However, experience has shown that if the starting guess is reasonable the solution found is usually a minimum.

3.2.6 The aufbau principle

When we introduced the Hartree-Fock equations (3.11) we did not say anything about the way the N spin-orbitals which enter in the definition of the Fock operator $\hat{f}$ should be chosen. In other words, before starting the calculation the occupation numbers of the molecular orbitals have to be decided and a prescription is hence needed. An in-depth discussion on this topic was given by Cook [Coo87] and the result is that for UHF or GHF wave functions a necessary condition for the Hartree-Fock energy to be stationary is that the molecular orbitals be filled following the order of their canonical energies; this prescription constitutes the famous aufbau principle. On the other hand, for RHF wave function the aufbau principle is not necessarily true [EA08] and there exist cases of non-aufbau occupation numbers [DMMV00, Coo87].

A possible ambiguity in the aufbau principle would occur if the highest-occupied molecular orbital were energetically degenerate with an unoccupied orbital. However, again only for UHF and GHF wave function, it has been proven that this cannot happen [BLLS94, Coo87].

3.2.7 Mathematical properties of the Hartree-Fock method

The rigorous mathematical study of the Hartree-Fock method, and indeed of all quantum chemical methods, is difficult and has received comparatively little attention as most research in the field is based more on numerical experimentation than on rigorous proofs [LL05, Le 05, BDL03, CDL99, DL99, MV99, DL97]. For example, the proof that the Hartree-Fock equations for a molecule admit a ground-state solution for neutral or positively-charged systems was given by Lieb and Simon only in 1977 [LL05, Le 05], some thirty years after such solutions were found numerically. The reader is referred to the cited literature for a discussion of these topics.

3.2.8 Virtual orbitals

The Fock operator $\hat{f}$ determined at the end of a Hartree-Fock calculation is a Hermitian operator and its eigenfunctions and eigenvalues are given by the canonical molecular orbitals and orbital

energies. The N molecular orbitals which enter in the definition of $\hat{f}$ constitute the occupied orbitals, while all the others are called unoccupied or virtual orbitals.

Virtual orbitals are discussed, often in connection with Koopmans' theorem, in many textbooks [SO96, McW92]. Incidentally, we would like to remark that Koopmans' theorem applies only to UHF or GHF wave functions, but not to RHF orbital energies [Coo87].

The usual interpretation of the virtual orbitals [SO96] is that they represent an extra 'ghost' electron which is invisible to the electrons in the occupied orbitals but that contrariwise perceives all the N 'real' electrons of the Hartree-Fock state. In this context it is said that the virtual orbital states approximately describes a negatively-charged state and that the virtual orbital energies represent electron affinities. There are, however, some *caveats* regarding this interpretation. The reason is explained for example by Davidson in his book [Dav76] (pag. 69)

If the virtual orbitals are generated from an exact (numerical) Hartree-Fock procedure, then all orbitals have a positive energy and lie in a continuum. If the virtual orbitals are leftovers from a Roothaan-Hartree-Fock calculation, they will span whatever space happened to be included in the basis set. Generally this will include some empty antibonding valence orbitals at positive orbital energies and no continuum.

This topic is also discussed by Cook [Coo87, Coo96]. These considerations imply that the spectrum of the *exact* Fock operator includes a discrete set of eigenvalues with generally negative energies (the occupied orbitals) plus a continuum spectrum starting from zero energy in which a number of discrete eigenvalues may be embedded. Hence, the energy of the virtual orbitals obtained by a finite-basis calculation is not a well-defined concept, and enlargement of the basis set – in particular, addition of diffuse function – will make all virtual orbital energies collapse to zero [Coo96].

These remarks also imply that considerations based on the virtual orbital energies should be taken with some circumspection. For example, in the context of Hartree-Fock-based perturbation theory or configuration-interaction calculations it is not effective to truncate the number of excitations on the basis of the virtual orbitals energies, and several other approaches for deriving 'improved' virtual orbitals for these purposes have been devised, the most famous of which is probably due to Huzinaga [HA70, HA71, MI72, Coo96, CFCM08].

3.2.9 Limits of the Hartree-Fock method

The Hartree-Fock equations are a considerable simplification of the electronic quantum n -body problem: the solution of a single eigenvalue equation in $3n$ dimensions is reduced to the solution of n coupled equations in 3 dimensions. A great deal of effort has been spent in practical implementations and optimisations of the Hartree-Fock method and it is taken as a starting point by the majority of quantum-chemical studies of atoms and molecules. Also, perhaps even more importantly, the single-particle picture of molecules which arises from the method is still deeply engrained in modern chemical thinking.

However, one should always bear in mind that the Hartree-Fock method, particularly in its RHF version, presents many deficiencies and is inadequate for accurate work. One of the main problems with the RHF method is that, by construction, it cannot properly describe bond-breaking reaction paths in the usual case where the fragments are open-shell species [SO96].

RHF calculations are thus inadequate for the calculations of global potential surfaces of strongly covalently-bound molecules. Also, it is well-known that there are many systems which are badly described by the Hartree–Fock method even around equilibrium, e.g. the electron-rich molecules O_3 [EAS07, Rag91], FOOF [Rag91] and SiNN [OUI97].

For our purposes, as we will expose in the following sections, it is best to think of the Hartree–Fock method as a first, preliminary step of the calculation whose main purpose is to provide a rough first guess for the exact wave function and, very importantly, a set of orthonormal molecular orbitals which can be later used as an expansion basis for the exact wave function.

The meaning of electronic energies and final remarks

The energy of a mechanical system, both in classical and quantum mechanics, is defined with respect to an arbitrary reference configuration which defines the zero-energy state. This simple fact implies that only *differences* of energies have an unambiguous meaning and that products, ratios or percentages of energies are somewhat ill-defined quantities as they depend on the arbitrary reference configuration.

The Coulomb Hamiltonian of eq. (2.2) takes as zero-energy configuration the state where all electrons and all nuclei are at infinite distance from each another. Because of this choice, total molecular energies will inevitably assume very large negative values and chemical processes will involve energy changes on a much smaller scale.

As a consequence, even relatively rough guesses will correspond to small relative errors, especially for systems with heavy atoms. In this light, the usual statement [McW92] that the Hartree–Fock method gives absolute energies “accurate to 99%” should not strike as indicating any particularly high accuracy.

As outlined in Section 2.3 about the decoupling of electronic and nuclear motions, we rely on electronic structure methods to obtain a PES from which rotation-vibration energy levels may be computed (see Chapter 4 for more details). We stress that it is indispensable to go beyond the Hartree–Fock method to obtain any quantitative agreement with experiment on the rotation-vibration energy levels. This is true even if we consider only low-energy ($E \lesssim 7000 \text{ cm}^{-1}$ for strongly-bound molecules like water) rotation-vibration states which are determined by the PES in correspondingly low-energy regions close to equilibrium.

3.3 The correlation energy

It is hard to avoid feeling that electron correlation problems are just like the biblical poor: they are always with us. Each new administration in Quantum Chemistry, just as each new administration in politics, hopes to have a solution to the problem.

B.T. Sutcliffe [Sut99]

The term “correlation energy” was introduced by Wigner and Seitz in 1934 in the context of solid-state studies [WS34, Wig34] and then made particularly popular in the context of quantum chemistry by a famous 1959 review paper by Löwdin [LÖw59a]. The correlation energy E_{corr} is defined as the difference between the true eigenvalue of the Schrödinger equation and the

Hartree–Fock energy:

$$E_{\text{corr}} = E - E_{\text{HF}} \quad (3.16)$$

In other words E_{corr} is the residual energy not accounted for by the Hartree–Fock solution, generally intended in its restricted Hartree–Fock variant. For systems where the RHF is not applicable, e.g. systems with an odd number of electrons, the ROHF or the UHF energy are usually taken as reference.

Correlation energy is discussed in all quantum chemistry and solid state physics textbooks mentioned in Section 3.2, in volume 2 of ref. [WMB03] and has periodically been the object of review papers, among which we may mention two recent ones by Kutzelnigg [Kut03, Kv00] among many others [TKH07, KSW00, Löw95, Rag91, MP80, Löw59a].

The meaning of correlation energy

The Hartree–Fock wave function can be seen as the exact solution of a model system of N independent electrons governed by the N -electron Fock Hamiltonian $\hat{F}$

$$\hat{F} = \sum_{i=1}^N \hat{f}(\mathbf{x}_i) \quad (3.17)$$

where the single-particle Fock operators $\hat{f}$ were defined in eq. (3.10). The exact eigenvalue of the Fock Hamiltonian $\hat{F}$ is given by the sum of the canonical orbital energies ε_i (note that this value is not the same as the Hartree–Fock energy E_{HF} [Lev00, SO96]).

Under the assumption that the Hartree–Fock wave function is a ‘good’ approximation⁴ to the exact wave function, see section 3.2.9, one can partition the Coulomb Hamiltonian as

$$\hat{H} = \hat{F} + \lambda \hat{H}'$$

where $\hat{H}' = \hat{H} - \hat{F}$ and $\lambda = 1$. The parameter λ switches between a system of non-interacting, ‘uncorrelated’ electrons for $\lambda = 0$ to the true ‘fully correlated’ system for $\lambda = 1$. With this partitioning the correlation energy E_{corr} can be interpreted as due to the $\hat{H}'$ part of the Hamiltonian, which is said to represent ‘correlation effects’.

Even though the definition of correlation energy is generally useful, one should bear in mind that, as the proposed partitioning of the Hamiltonian is essentially arbitrary, the correlation energy has little physical meaning in itself. This is all the more true when the Hartree–Fock solution happens to be a bad approximation and hence E_{corr} assumes large values.

Mathematical meaning of correlation

The term ‘correlation’ has a precise meaning in probability theory [Fel68] which is much more specific and not equivalent to the use of the word in quantum chemistry [Kut03, KDB68].

In probability theory given two random variables r_1 and r_2 one defines their correlation coefficient τ by, indicating expectation values by $\langle \cdot \rangle$,

$$\tau = \frac{\langle r_1 r_2 \rangle - \langle r_1 \rangle \langle r_2 \rangle}{\sqrt{\langle r_1^2 \rangle - \langle r_1 \rangle^2} \sqrt{\langle r_2^2 \rangle - \langle r_2 \rangle^2}} \quad (3.18)$$

⁴There is no single criteria to define the quality of an approximate solution, but for our purposes we can consider Ψ_{HF} to be a good approximation to the exact wave function Ψ if $\langle \Psi_{\text{HF}} | \Psi \rangle$ is greater than about 0.95.

The two random variables are said to be correlated if $\tau \neq 0$. It can be showed that τ always lies between -1 and $+1$ and indicates strength and direction of a *linear* relationship between the two random variables.

Another relevant definition from probability theory is that of *independency* [Fel68]. Two random variables r_1 and r_2 are *independent* if their joint-distribution function $\varrho(r_1, r_2)$ is the product of their individual distribution functions:

$$\varrho(r_1, r_2) = \varrho(r_1)\varrho(r_2) \quad (3.19)$$

Independency is a stronger property than lack of correlation: independent variables are always uncorrelated but uncorrelated variables do not have to be independent. For example, consider the joint distribution probability of a random variable x uniformly distributed in $(-1, 1)$ and of $y = x^2$. The random variables x and y are uncorrelated, yet clearly not independent: in fact, the value of one determines the other with absolute certainty.

In quantum chemistry the probability distributions of electrons would be independent, and hence uncorrelated, if the many-electron wave function were written as a simple Hartree product of one-electron spin orbitals. On the other hand, when a Slater determinant is used electron distributions will not be independent and will in general be correlated. However, in quantum chemistry terminology, the Hartree–Fock solution is said to be ‘uncorrelated’. It is then apparent from this discussion that the use of the word ‘correlation’ in quantum chemistry has only a loose connection to the mathematical meaning given by eq. (3.18). See refs. [Kut03, KDB68] for a discussion on this matter.

Some general remarks on correlation effects in quantum systems

The concept of electron correlation gravitates around the concept of electrons mutually influencing each other’s motion, not only because they repel one another by Coulomb’s law but also because of the anti-symmetry requirement on the wave function of the system. We would like in this section to point out some, perhaps unexpected, consequences of the anti-symmetrisation postulate to the concept of electron correlation.

In chemical thinking one expects electron correlation effects to be relevant only for electrons which are spatially close – for example, in the same molecule. However, this expectation is not necessarily met in a strictly quantum mechanical setting [KDB68, Mar66].

On this matter Duch and Dierksen [DD94] pointed out by means of a simple example that quantum mechanics is a “holistic” theory, not well-suited towards the description of separated subsystems. These authors consider two systems with N_A and N_B electrons, each of which is described by its normalised, antisymmetric wave function Ψ_A and Ψ_B . It is then shown that the simple product function $\Psi_{AB} = \Psi_A \Psi_B$ is always “far” from the antisymmetrised product $\Psi = \mathcal{A}(\Psi_A \Psi_B)$. More precisely, the norm of the difference satisfies the inequality

$$\|\Psi_{AB} - \Psi\|^2 \geq 2 - \sqrt{2} \approx 0.58$$

The fact that identical particles can influence one another even when far away is well-known in the light of modern research on entangled systems and quantum non-locality [Per95, Bal98, Sch05a] but is generally assumed to be irrelevant to quantum chemistry. These issues have, however, been recently discussed notably by McWeeny [McW07, McW00, MA99, Krü97].

These and similar considerations have also led some authors to suggest alternative ways of indicating the quality of approximate wave functions other than the correlation energy [JM06, HK05, Gre81].

Static and dynamical correlation

Already in the early 1960s Sinanoğlu *et al* [TS64] suggested a partitioning of the correlation energy into two parts, a ‘dynamical’ and a ‘non-dynamical’ or ‘static’ one. More details can be found, e.g., in refs. [Tru07, CAYS00, MCH02, KSW00]. One of the reasons which led to this partitioning is that, in cases where the Hartree–Fock solution is not a good zero-order approximation, the correlation energy defined by eq. (3.16) stops being a useful concept. The correlation energy contribution due to blatant inadequacies of the Hartree–Fock method has been called non-dynamic or static correlation, while the remaining part constitutes the dynamical correlation. Siegbahn [Sie83] gave the following explanation of the difference between dynamical and nondynamical correlation energies:

In many situations it is further convenient to subdivide the correlation energy into two parts with different physical origins. For chemical reactions where bonds are broken and formed, and for most excited states, the major part of the correlation energy can be obtained by adding only a few extra configurations besides the Hartree–Fock configuration. This part of the correlation energy is due to near degeneracy between different configurations and has its origin quite often in artefacts of the Hartree–Fock approximation. The physical origin of the second part of the correlation energy is the dynamical correlation of the motion of the electrons and is therefore sometimes called the dynamical correlation energy. Since the Hamiltonian operator contains only one- and two-particle operators this part of the correlation energy can be very well described by single and double replacements from the leading, near degenerate, reference configurations.

Other ways of partitioning the correlation energy, such as ‘left-right’, have also been proposed [MCH02, HC01].

3.4 Gaussian basis-sets

3.4.1 General theory

The theory of Gaussian basis set expansion is treated in several excellent references [Wil03, Wil87, Wil83] and will not be discussed here in great detail. Other references treating general properties of basis sets are [Mor03, Kut94, Kla85b, Kla85a, Hil85, KM84].

3.4.2 Rate of convergence and correlation-consistent basis sets

An uncontracted Gaussian basis set is characterised for each angular momentum included $l = 0, 1, \dots, l_{\max}$ by N_l Gaussian exponents $\zeta_i^{(l)}$. In the case of even-tempered basis sets [Wil03] the exponents are taken in a geometric progression so that they are characterised by a minimum

exponent $\zeta_1^{(l)}$ and a maximum exponent $\zeta_{N_l}^{(l)}$, while the other exponents are given by

$$\zeta_i^{(l)} = \zeta_1^{(l)} \left(\frac{\zeta_{N_l}^{(l)}}{\zeta_1^{(l)}} \right)^{i/(N_l-1)} \quad i = 0, \dots, N_l - 1 \quad (3.20)$$

It can be proven [MW94, KW03, WM01] that in the limit of $l_{\max} \rightarrow +\infty$, $N_l \rightarrow +\infty$, $\zeta_1^{(l)} \rightarrow 0$ and $\zeta_{N_l}^{(l)} \rightarrow +\infty$ an even-tempered basis set becomes complete.

Many studies have been devoted to building hierarchies of increasingly-accurate basis sets where the various parameters $l_{\max}$, N_l (etc.) are increased in a balanced and systematic way [MW94, KW03, WM01]. Each of these increasingly-accurate basis sets can then be characterised by a single ‘cardinal number’ n .

In particular, Dunning and co-workers devised starting from 1989 [Dun89, KDH92, WD94, WD95, WvD96, van99], a family of basis sets called *correlation consistent* which have become very popular in correlated calculations [CAYS00]. These basis sets are called correlation consistent because each of them should contain all functions that lower the energy by a certain quantity. Dunning’s exponents do not follow exactly an even-tempered scheme, but they are very close to it. We will make large use of these basis sets in our calculations and the reader is referred to the mentioned references [Wil03] and [Dun89, KDH92, WD95, WvD96] for more information.

As an example, a plot graphically illustrating the uncontracted aug-cc-pCV5Z basis set for oxygen is presented as Fig. 3.3. Note that only s and p Gaussians are contracted and that the four most diffuse s and p functions of the cc-pV5Z set are not contracted. The superposition of the ‘core’ functions and of the tightest functions of the cc-pV5Z set does not create problems because the latter are contracted.

Speed of convergence

In the case of Hartree–Fock energies many studies [Wil03, Mor03, Kut94] showed that, for properly optimised atom-centred, fixed-exponent Gaussian basis sets, the error ε_{HF} scales with the size N of the basis set as $\varepsilon_{\text{HF}} = e^{-\alpha\sqrt{N}}$. Unfortunately, many studies proved [TKH07, KMTNV06, Wil03, Mor03, Klo00] that the rate of convergence for the correlation-energy portion is much, much slower, following a $\varepsilon_{\text{corr}} = \frac{A}{N}$ law. For correlation-consistent basis sets $N \propto n^3$ where n is the cardinal number, so this law can also be written as $\varepsilon_{\text{corr}} = \frac{A}{n^3}$. This excruciatingly slow convergence rate is one of the main hurdles in quantum-chemical calculations. The situation is exasperated by the fact that quantum chemical methods scale in time and computational resources as a rather large power of N , starting from N^4 for the Hartree–Fock method and *at least* N^5 for any electron correlation methods⁵ (see [Jen06], section 4.2.1).

These considerations lead to a very discouraging convergence rate of the energy with respect to the computational time spent [Klo00, KMTNV06]; for example, in the case of a N^5 -method like MP2 [Jen06] one expects a scaling of the error with respect to the computational time of the kind $\varepsilon_{\text{corr}} \propto t^{-1/5}$. This means that to obtain one more decimal figure of precision with respect to a given calculation one would have to perform a second calculation which takes 10^5

⁵For spatially-large systems it is possible to introduce simplifications so that the computational cost is asymptotically linear in N , see e.g. [WMK03]. However, our focus is on small systems where these techniques are not applicable.

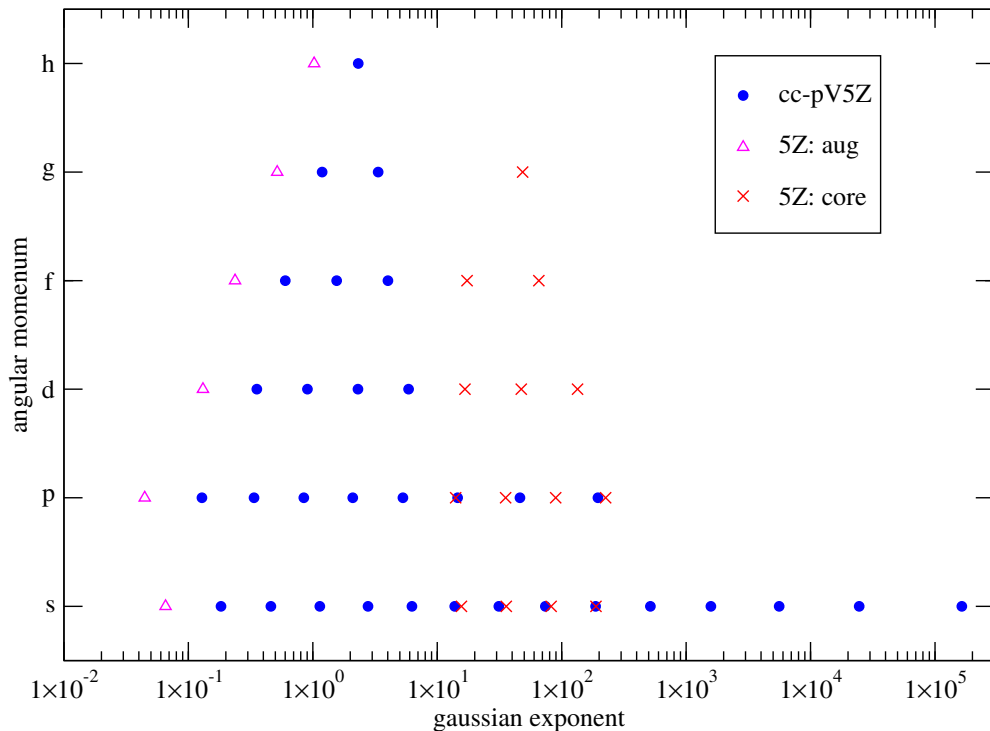


Figure 3.3: Gaussian exponents of the uncontracted aug-cc-pCV5Z basis set for oxygen (see text).

as much time and computational resources! We will discuss the reason for this slow convergence and some approaches aimed to rectify it in Section 3.11.

This very slow convergence of absolute energies also makes it very difficult to estimate the actual error of quantum chemical calculations. Methods which give rigorous bounds for the exact energy do exist, see e.g. [Mar07] for a recent proposal, but they are computationally expensive and the bounds given are much larger than the real error, so they are not in common use.

Extrapolation formulae for the energy

If one makes use of basis sets belonging to the Dunning family the regularity of the convergence pattern encourages the use of extrapolation formulae which might accelerate the convergence [BR06, Sch05b, Klo00, CAYS00, Var00, HKKN97] of the correlation energy. A simple but quite successful formula of this kind to be used for the extrapolation of the correlation energy is [Klo00, HKKN97]

$$E_{\infty} = E_n + \frac{A}{n^3} \quad (3.21)$$

This expression originated from studies of the convergence of the correlation energy in atoms, particularly Helium [KI92, Hil85]. It is used as follows: two energy calculations using the basis set n and $(n-1)$ are performed, obtaining E_{n-1} and E_n . These values are then fit to eq. (3.21) obtaining A and the extrapolated energy $E_{+\infty}$. Energies obtained by extrapolation procedures of this kind are often over-optimistically called *complete basis set* (CBS) energies.

Many kinds of extrapolation formulae have been proposed and investigated; examples of

three-parameter extrapolation formulae are [CAYS00]

$$E_{\infty} = E_n + \frac{A}{(n+d)^3} \quad (3.22)$$

and [Klo01]

$$E_{\infty} = E_n + \frac{A}{n^3} + \frac{B}{n^5} \quad (3.23)$$

where, as in the previous case, E_{∞} and the parameters A , d and B are obtained by a fit to two or three calculations using consecutive values of n .

The difference between the various extrapolation formulae is usually smaller than the difference between extrapolated and non-extrapolated values.

Especially if the basis sets used are small, i.e., less than about $3-\zeta$, it is advocated [Tru98] that the extrapolation formulae of the kind of eq. (3.21) be used only for the correlation part of the energy, while the Hartree–Fock energy be fit to a form of the kind [Jen05]

$$E_{+\infty} = E_n + Ae^{-\alpha n} \quad (3.24)$$

or also [KM06]

$$E_{+\infty} = E_n - A(L+1)e^{-\gamma\sqrt{L}} \quad (3.25)$$

where L is the maximum angular momentum included (for correlation-consistent basis sets, $L = n$ for second-row atoms).

As a rule of thumb [Var00] it is expected that $\{E_{n-1}, E_n\}$ extrapolated energies have errors of the same order or slightly better than the non-extrapolated E_{n+1} : see e.g. figure 3.7 for results of this kind for the hydrogen molecule. In other words, the extrapolation procedure is expected to give $(n+1)$ accuracy at an $n + (n-1)$ cost.

3.4.3 Basis set superposition error

The basis set superposition error (BSSE) is a particular aspect of basis set incompleteness. As an example, consider a model system composed by two non-interacting atoms A and B and suppose that two atom-centred basis sets are defined for the two atoms. A manifestation of the BSSE is that the energy of the composite non-interacting system $A-B$ is not constant as a function of the distance of the atoms. This happens because when the atoms are infinitely far away each of them can make use only of ‘its own’ basis functions, while when they approach atom A can also use the basis functions coming from atom B , and vice versa. This leads to an artificial lowering of the energy when the atoms approach.

BSSE is discussed e.g. in the textbook by Jensen [Jen06] and in several recent reviews by Wilson [Wil03], van Mourik *et al* [vWP⁺99] and Gutowski and Chałasiński [GC93]. A review more specifically concerned with intramolecular BSSE was provided by Senent and Wilson [SW01] while a study on the BSSE in the water molecule was performed by Jensen [Jen96].

3.4.4 Basis sets for relativistic calculations

In the case of relativistic 4-component calculations specific basis sets have to be employed. The general situation is somewhat more complicated with respect to the non-relativistic case because one needs two basis sets, one for the small and one for the large component, which have to obey

a relation known as *kinetic balance*. A detailed account is given in the book by Dyall and Fægri [DF07] and in the review by Wilson [Wil03] while a study of the rate of convergence was recently performed by Kutzelnigg [Kut07a].

3.5 Configuration interaction

Configuration interaction (CI) is discussed in all quantum chemistry textbooks, see e.g. [SO96, Jen06, Cra04] and the lecture notes by Sherrill [She95] for some good introductions. Some brief introductions at a more advanced level were given by Čársky [Čár98] and by Duch [Duc91] while for detailed expositions covering also algorithmic details see Karwowski and Shavitt [KS03], Sherrill and Shaefer III [SS99] and Siegbahn [Sie92]. An earlier, famous exposition was given by Shavitt [Sha77] while a recent perspective on the technique by the same author can be found in [Sha98].

The general idea behind CI is very simple. Assuming that the Hartree–Fock solution is a good approximation (see footnote 4 of this Chapter) one may presume that, in an expansion of the exact wave function in the basis of the eigenfunctions of the Fock operator, contributions coming from basis functions which differ from the Hartree–Fock ground state by multiple excitations should be smaller and smaller. This assumption leads to a hierarchy of methods where the Hamiltonian matrix is diagonalised in a basis which includes excited Hartree–Fock states only up to a certain level of excitation. Inclusion of excitation orders up to single, double, triple, quadruple, pentuple, hexuple, etc. gives origin to truncated-CI methods referred to by the acronyms CIS, CISD, CISDT, CISDTQ, CISDTQP, CISDTQPH etc.

Despite its logical simplicity, configuration interaction has several shortcomings. On the one hand, the scaling in computer time with respect to the number of excitations included rises very quickly; for a basis set containing N functions in the large- N limit CISD scales as N^6 , CISDT as N^8 and CISDTQ as N^{10} (see e.g. the book by Jensen [Jen06], section 4.2.3 or [SS99]). The consequence of this very steep scaling is that CISD is for most systems the only computationally-feasible CI level of treatment (see e.g. Table 6.4 for some benchmark timings for water). Unfortunately CISD energies, even when the reference Hartree–Fock wave function is a good approximation, are not particularly accurate [SS99] and higher-order excitations (in particular, quadruple excitations) give a significant contribution. On this matter it is interesting to quote this comment made by Shavitt in 1996 [HPS96]

By hindsight, our expectations at that time [in the early and mid 1950s] for the rate of convergence of the CI method were much too optimistic. Perhaps this was for the better, because had we known how many terms were needed for quantitative results for nontrivial problems, we might have been completely discouraged and chosen to devote our time to some other pursuit. As it were, perseverance and hard work, plus the development of new methods and the astounding advances in the speed and capacity of electronic computers, brought us to a stage today at which theoretical calculations of molecular structures and properties are a widely accepted major component of chemical research and make major contributions to our understanding of chemical phenomena.

Another very relevant deficiency in the CI approach is that when the Hartree–Fock solution is

not a good approximation (see section 3.2.9), e.g. as happens when covalent bonds are broken, the approximate ordering of energy contributions with respect to the level of excitation breaks down and CISD energies will in general be very poor [CAYS00, SS99]. This limitation, common to all methods which assume the Hartree–Fock solution to be a reasonably good starting point, essentially rules out truncated CI as a method to obtain reliable global potential energy surfaces.

Finally, there is another significant problem with truncated CI which indicates that the strategy of selecting configurations only on the basis of the level of excitation is intrinsically flawed. This problem is the lack of the properties of size-consistency and of size-extensivity of truncated CI, which we will discuss in the following section.

3.6 The properties of size extensivity and size consistency

The terms “size-extensive” and “size-consistent” are often used synonymously in the literature but they actually refer to different properties. For some comments see e.g. [CAYS00, CS00b, SS99, DD94, Bar81, BP80]. A precise definition of the concepts was given by Bartlett [Bar81]:

This term [size-extensivity] is borrowed from thermodynamics, where an extensive property is one that is proportional to the size of a homogeneous system. Pople *et al* [PBS76] proposed the term “size-consistency” for a closely related property. A method is considered size-consistent if the energy of a system made up of two subsystems A and B far apart is equal to the sum of the energies A and B computed separately by the same method. For closed-shell systems dissociating to closed-shell fragments, a RHF (restricted Hartree–Fock) reference function is size-consistent, and size-extensivity (or the absence of unlinked diagrams) is then a sufficient condition for size-consistency of a correlated model [of the perturbation-theory or coupled-cluster type] based upon that reference function.

On the other hand, for a single-determinant reference function to be size-consistent when considering open-shell fragments, A and B , a UHF (unrestricted Hartree–Fock) solution will usually be required. Since either a RHF or a UHF function can be used to generate a linked diagram, size-extensive expansion, the condition of size-consistency imposes another requirement on the reference function, in addition to the use of a linked diagram expansion. Hence, some confusion arose over the distinction between proper scaling with size in a homogeneous system (“extensivity”) and correct separation of a molecule into its fragments, which is a very different property. Adding to the confusion is the term “separability conditions”, which is also sometimes used [Kut77]. Hence, we prefer the term size-extensivity to suggest only correct scaling, and discuss correct separation as a second, equally desirable property, to avoid any possible confusion. Although there are fine differences [BSP79], the fundamental element suggested by all three terms is correct scaling with size. The idea of size-extension is implicit in the work of Brueckner, Goldstone, and co-workers, although Primas was one of the first to emphasize the concept [Pri65]. Meyer [Mey71, Mey73] used the idea as part of the justification of the CEPA models.

We will summarise and examine in some detail these properties in the following sections.

Size-extensive methods

- A method is *size extensive* if the energy becomes proportional to the number of electrons N in the limit $N \rightarrow +\infty$.

This definition strictly applies to applications to homogeneous systems, such as nuclear matter and solids, for which it makes sense to define a system size by the number of particles. In the case of atoms and molecules this concept does not strictly apply; for example, McWeeny [McW92] (section 9.6) says

the idea of increasing the size of a sodium atom, say, by adding electrons and keeping the density constant would obviously be nonsense, and the concept of extensivity does not apply [to atoms and molecules].

However, even though not strictly pertinent to molecular systems, a method which is not size extensive will probably not be suitable for large molecules [Bar81, BP80] as these can be approximately viewed as a collection of weakly-interacting electron-pair bonds.

The RHF method when applied to closed-shell systems is size extensive, as are RHF-based perturbation theory and coupled cluster methods [BM07, SS99, Bar81, BP80, PBS76, SO96]. On the other hand, all forms of truncated CI a part from full-CI are not size extensive [SS99, SO96]. In particular, it can be shown [SO96] that the CISD correlation energy is asymptotically proportional to the square root of the number of electrons, so that in an infinite system $\lim_{N \rightarrow +\infty} E_{\text{corr}}(\text{CISD})/N = 0$; this means that configuration interaction is generally unsuitable for studies of large molecules or solids.

Although exact size extensivity is certainly a desirable property, it is not in itself a guarantee of accuracy; for example, the very approximate Thomas–Fermi model is exactly size extensive [CCH01]. Also, as size extensivity concerns infinite or very large systems, it may be argued that its lack does not necessarily represent a major problem in the study of small molecules. On this matter Duch and Dierksen [DD94] commented that

making size extensivity the most important requirement of quantum chemical methods, although it does not guarantee correct physical description, seems to be based not that much on physical as on aesthetical criteria.

Size-consistent methods

- A method is *size consistent* if the energy calculated for an ensemble of isolated atoms or molecules (e.g., at infinite distance from one another) is equal to the sum of the energies of the individual atoms or molecules calculated with the same method one-by-one.

Exact size consistency guarantees that when a bond $M-A$ is stretched to infinity (M represents the fragment molecule and A the dissociating atom) the energy will asymptotically go to $E(M) + E(A)$ (where the energy of the fragments are computed by the same method). This clearly looks a very desirable property for any method to be used for calculating global potential energy surfaces.

RHF and RHF-based many-body perturbation theory and coupled cluster methods are exactly size consistent only in the case where the dissociating fragments are closed shell species [SS99, Bar81, BP80], e.g. in the case of the He–He dimer.

In the much more common case where fragments are open-shell species the RHF method cannot be applied to the fragments at all, the RHF energy of the dissociating bond will asymptotically go to a wrong value (see section 3.2.9) and truncated perturbation-theory or coupled-cluster calculations based on this reference will likewise be incorrect or incur in numerical difficulties and not converge at all, see e.g. [LP98, OJK⁺96]. RHF-based truncated CI is also not size-consistent.

On the other hand, UHF energies are size consistent and so are UHF-based MBPT and CC methods [Bar81].

Similarly to what we stated in the case of size-extensivity, the fact that a method such as UCCSD is exactly size-consistent is in itself no guarantee of accuracy in the description of bond-breaking reaction paths, as the intermediate-bond region may be poorly described; a recent review on the breaking of bonds with hydrogen in small molecule was given by Dutta and Sherrill [DS03] and the conclusion was that even the best-performing method, namely UHF-CCSD(T), has errors in the relative energies with respect to full-CI of the order of 1000–1400 cm^{−1} for medium bond lengths (≈ 3.5 – 7 a₀). Similar results for the single-bond stretching of water can be found in the review by Olsen *et al* [OJK⁺96].

On the other hand, lack of exact size consistency in a quantum chemical method may not be a severe drawback if the size-consistency violation is smaller than other sources of error present in the calculation such as basis set incompleteness, higher level electron correlation effects etc. We will discuss some approaches to partially correct the lack of size-extensivity and size-consistency of CI in Section 3.10.

3.7 Core–valence separation of correlation effects

It is an idea ingrained in chemical intuition [Lev00] that electrons can be partitioned into core and valence, and that core electrons are relatively insensitive to chemical changes undergone by the atoms. This intuitive idea is straightforward to implement in methods – like configuration interaction – that take the Hartree–Fock solution as a reference; in these methods one simply does not allow excitations from orbitals classified as ‘core’. This ‘frozen core’ approximation is generally accurate [CAYS00] and, especially for heavier atoms, considerably simplifies the calculation. However, we would like to point out that this procedure raises some conceptual issues related with electron indistinguishability which need some careful analysis; for a discussion of some of these issues see e.g. [McW99a, McW99b, Kar98, Sta98, LMBK84].

3.8 The CAS-SCF method

The complete active space self consistent field method (CAS-SCF) is a particular version of a class of methods called multi-configuration SCF and probably the most successful one. For a detailed description we refer to two reviews by Roos [Roo92a, Roo87] and to the original papers by Roos *et al* [Roo80, RTS80]. Other references discussing the basis of the method are those by Schmidt and Gordon [SG98] and Werner [Wer87]. For a more basic introduction see e.g. the book by Jensen [Jen06].

The main goal of the CAS-SCF method is to give a balanced description of the potential energy surface of a molecule even in regions far away from equilibrium, where the Hartree–Fock

solution is known to be very poor (see section 3.2.9).

At the starting point of the CAS-SCF method one considers the Hartree–Fock orbitals $\phi_i(\mathbf{x})$, both occupied and virtual. In the universally-adopted Hartree–Fock–Roothaan approach (see section 3.2.4) the orbitals are expressed as a sum of one-electron basis functions $\chi_\mu(\mathbf{x})$, $\mu = \{1, \dots, 2K\}$

$$\phi_i(\mathbf{x}) = \sum_{\mu=1}^{2K} C_{\mu}^{(i)} \chi_{\mu}(\mathbf{x}) \quad (3.26)$$

Any N -electron state Ψ_R specified by selecting a set of N indices $\{\alpha_i\}_{i=1}^N$ and forming the Slater determinant made up by the corresponding molecular orbitals is called a configuration function (CF)⁶.

$$\Phi_R(\mathbf{x}_1, \dots, \mathbf{x}_N) = \mathcal{A}(\Pi_{i=1}^N \phi_{\alpha_i}) = |\phi_{\alpha_1} \cdots \phi_{\alpha_N}\rangle \quad (3.27)$$

For example, if the N lowest-energy orbitals are selected one obtains the Hartree–Fock solution⁷, otherwise an excited Hartree–Fock state is selected instead.

One then writes a trial wave function as a linear superposition of N_c CFs

$$\Psi_{\text{CAS-SCF}} = \sum_{R=1}^{N_c} C_R \Phi_R \quad (3.28)$$

In the CI approach at this point one would limit the number of configurations N_c included in the expansion on the basis of the level of excitation with respect to the Hartree–Fock reference, and then obtain the linear C_R coefficients by diagonalisation of the Hamiltonian matrix.

In the CAS-SCF method the selection of the CFs included is different. A set of orbitals is selected on the basis of their Hartree–Fock canonical energies and of their spatial symmetry properties. These orbitals are called ‘active’ and the sub-space they define is called the Active Space. In the CAS-SCF method then a full-CI calculation *within the active space* is performed. Also, to partially account for excited configurations excluded from the expansion (3.28), the coefficients defining the active orbitals $C_{\mu}^{(i)}$ are permitted to change. This means that the optimised CAS-SCF active orbitals will differ from the original Hartree–Fock ones. Note that also orbitals not included in the active space (inactive orbitals) are modified in the CAS-SCF method; this happens because inactive orbitals are defined as the eigenfunctions of the Fock operator, and the Fock operator depends in turn on the occupied orbitals, see e.g. eq. (3.12). This fact also guarantees that all CAS-SCF orbitals, active and inactive, stay orthogonal between themselves.

If we disregard the change in the orbitals, a CAS-SCF calculation is equivalent to a regular full-CI calculation performed in the (generally small) basis set formed by the Hartree–Fock active orbitals. If the orbital space is big enough (see e.g. refs. [Roo92a, Roo87] for criteria for the selection of the active orbitals) CAS-SCF energies will thus be qualitatively correct over the whole set of possible molecular geometries. On the other hand, as the active space is necessarily small because of the computational cost of FCI, CAS-SCF energies will not in general be quantitatively very accurate. This is usually expressed saying that CAS-SCF recovers the static part of the correlation energy, but is very inefficient in treating the dynamical part (see section 3.3).

⁶A configuration function can also be a spin-adapted linear combination of Slater determinants, but for simplicity we will not consider this possibility in the following.

⁷Supposing the aufbau principle holds, see section 3.2.6.

As we showed a CAS-SCF calculation involves optimising both the CI coefficients C_R and the active orbital coefficients $C_\mu^{(i)}$. The energy depends linearly upon the C_R but highly non-linearly upon the $C_\mu^{(i)}$. Many non-trivial technical developments have been necessary to devise an optimal algorithm to solve the CAS-SCF equations. A review on the subject was given by Werner [Wer87]. A common strategy is to perform a first iteration where only the linear CI coefficients are optimised, usually using one of the standard methods used in CI calculations like Davidson diagonalisation [SS99]. Then, starting from the second iteration both orbitals and CI coefficients are optimised simultaneously using a non-linear minimisation algorithm. Some details on the performance of the minimisation algorithms implemented in MOLPRO [WKL⁺02] will be given in Section 6.9.2.

Finally, we would like to make a remark on the convergence pattern of the CAS-SCF correlation energy with respect to basis set size. As we have discussed above the CAS-SCF method is approximately equivalent to a full-CI calculation performed in a chosen active space. When the basis set is enlarged the Hartree–Fock orbitals defining the active space will change but the size of the active space will always stay the same regardless of the basis set size. As a consequence the CAS-SCF correlation energy is only very weakly dependent on basis set size and CAS-SCF total energies are best extrapolated using formulae like eq. (3.24) or (3.25) rather than of the kind (3.21) or (3.22).

3.9 Multi-reference configuration interaction (MRCI)

Multi-reference CI is considered an advanced topic and is not discussed in detail in introductory textbooks on electronic structure theory. The method is described in some detail by Sherrill and Schaefer III [SS99] who also cite older references; an older, more technical review was given by Werner [Wer87].

In the previous section 3.8 it was shown that the CAS-SCF method is able to recover the static part of the correlation energy, but is very inefficient in recovering the dynamical part. An interesting strategy to remedy this problem is to perform a CI computation on top of a CAS-SCF one counting the level of excitations from the CAS-SCF wave function. For example, we can perform a MR-CISD calculation including single and double excitations from *all* the N_c CAS-SCF references Φ_R of eq. (3.28). As each Φ_R will in general already be an excited configuration with respect to the Hartree–Fock wave function, MR-CISD includes configuration which from the point of view of single-reference CI are much more than two-time excited.

We will indicate with $\Phi(R)$ the reference functions of eq. (3.28) given by the CAS-SCF method, with $\Phi_i^x(R)$ a singly excited configuration and $\Phi_{ij}^{xy}(R)$ a doubly excited one. The indices i and j run over all occupied orbitals of a CF and x and y run over all unoccupied ones. A trial MR-CISD wave function can then be written as [SS99]

$$\Psi_{\text{MR-CISD}} = \sum_{R=1}^{N_c} c(R) \Phi_R + \sum_{R=1}^{N_c} \sum_{ix} c_i^x(R) \Phi_i^x(R) + \sum_{R=1}^{N_c} \sum_{ijxy} c_{ij}^{xy}(R) \Phi_{ij}^{xy}(R) \quad (3.29)$$

The various linear-expansion coefficients $c(R)$, $c_i^x(R)$ and $c_{ij}^{xy}(R)$ are then obtained, as in standard single-reference CI, by diagonalisation of the Hamiltonian matrix.

3.9.1 Internally contracted multi-reference CI

The computational effort of MRCI calculations is very large and various approximations have been proposed to reduce it. Many of these approaches are discussed in the reviews [SS99, Wer87]. We will only mention a scheme known as internal contraction, which is implemented in the software MOLPRO [WKL⁺02]. This approach is discussed briefly in the mentioned reviews [SS99, Wer87] while for more details the reader is referred to the original papers [DKH98, WK90, WK88, WR82, Sie80, Mey77]. In this scheme large classes of configurations are summed together with fixed coefficients (i.e. ‘contracted’, in the same way as basis functions in Gaussian basis sets are [Wil03]) and only the resulting sum is employed as a basis for the CI expansion. This reduces the number of free variational parameters and hence introduces a simplification. In the internal contraction scheme the contraction coefficients are determined from the expansion coefficients C_R of the reference wave function, eq. (3.28). In the implementation of Werner and Knowles [WK90, WK88] used in MOLPRO [WKL⁺02], only configurations involving two orbitals not belonging to the active space (so called doubly-external configurations) are contracted, while all the others are left uncontracted. Werner and Knowles showed [WK90] that the error introduced by the internal-contraction is only about 0.3 times the error of fully-uncontracted MR-CISD to FCI and is hence negligible.

3.10 Size-extensivity corrections to Configuration Interaction

Many approaches to modify CISD and MR-CISD so as to approximately correct their lack of size-extensivity have been proposed. Some of these approaches only correct the energy while others correct also the wave function.

In the first case a standard (MR-)CISD calculation is initially performed, then a correction to the energy is calculated from the CI expansion coefficients and added. The second class of methods involve a somewhat more radical change to the (MR-)CISD method right from the start of the calculation. We will briefly review some of these approaches in the following sections.

3.10.1 Corrections only to the energy

A broad review of this kind of corrections was given by Duch and Diercksen [DD94]. In what follows we will only discuss some of the most common ones, namely the Davidson, renormalised Davidson and Pople corrections.

We will begin writing the exact correlation energy E_{corr} as $E_{\text{corr}} = E_{\text{corr}}(\text{CISD}) + \Delta E$ where ΔE represents that part of the correlation due to excitations higher than two. What the various corrections try to do is to give an approximation to ΔE , in particular with a view to partially restoring size-extensivity.

In 1974 Langhoff and Davidson [LD74] proposed from a numerical study of the N_2 molecule an empirical formula for approximately estimating the effect of higher-order excitations in CISD energies

$$\Delta E_{\text{Davidson}} = (1 - c_0^2) \times E_{\text{corr}}(\text{CISD}) \quad (3.30)$$

where c_0 is the coefficient of the Hartree–Fock wave function in the normalised CISD wave function.

Shortly thereafter the correction was re-derived on more rigorous grounds from an analysis of a perturbative treatment of quadruple corrections [BS77].

In 1977 Davidson and Silver [DS77] pointed out that a more correct form for ΔE had already been derived in 1955 by Brueckner [Bru55] and had the form

$$\Delta E_{\text{Ren.}-\text{Davidson}} = \frac{1 - c_0^2}{c_0^2} \times E_{\text{corr}}(\text{CISD}) \quad (3.31)$$

Duch and Dierksen [DD94] call this correction ‘Renormalized Davidson correction’. We remark, however, that this formula is also sometimes confusingly called just ‘Davidson correction’; for example, it is this last formula (3.31), and not eq. 3.30, which is used by the software MOLPRO [WKL⁺02] under the name “Davidson correction”.

The Davidson and Renormalized Davidson corrections are manifestly incorrect for 2-electron systems, where $\Delta E = 0$ exactly. A more refined correction was devised by Pople, Seeger and Krishnan [PSK77]. If n is the number of correlated electrons and setting $\theta = \arccos(c_0)$ the Pople correction can be written in the equivalent forms

$$\begin{aligned} \Delta E_{\text{Pople}} &= \left(\frac{\sqrt{n^2 + 2n \tan(2\theta)^2} - n}{2(\sec(2\theta) - 1)} - 1 \right) \times E_{\text{corr}}(\text{CISD}) \\ &= \left[-\frac{n(2c_0^2 - 1)}{4(1 - c_0^2)} \left(1 - \sqrt{1 + \frac{8c_0^2(1 - c_0^2)}{n(2c_0^2 - 1)^2}} \right) - 1 \right] \times E_{\text{corr}}(\text{CISD}) \\ &= \left(1 - \frac{2}{n} \right) \Delta E_{\text{Davidson}} + \mathcal{O}\left((1 - c_0^2)^2\right) \end{aligned} \quad (3.32)$$

which also shows how $\Delta E_{\text{Davidson}}$ and ΔE_{Pople} are related. A plot of the three corrections is presented in Fig. 3.4. It is clear that, for systems with $N \approx 10$ electrons the three corrections give similar results. The Pople correction, despite its theoretical soundness, has received very limited attention in the literature; for some comments see [DD94, MRD92, MFG90, BS77] (note that formula (9) of ref. [MRD92] contains two mistakes). Duch and Dierksen [DD94] analysed in their review six forms for size-extensivity corrections to CISD energies, including the ones we mentioned. Their conclusion was that they all considerably improved the size-extensivity properties of configuration interaction, with the original Davidson correction consistently rating as the worse and the Pople correction among the best.

Finally, note that these corrections should be applied only when $c_0 \approx 1$ (e.g., $c_0 \gtrsim 0.9$) or will otherwise give unreliable or unphysical results (e.g., the Pople corrections diverges for $c_0 = 1/\sqrt{2} \approx 0.71$).

Multi-reference form of the corrections

It is formally easy to generalise Davidson-like corrections to multi-reference configuration interaction. One simply substitutes to the coefficient of the Hartree–Fock configuration c_0 the sum of the coefficients of all the reference configurations in the final MRCI wave function; for example, the Davidson correction (3.30) becomes

$$\Delta E_{\text{MR}-\text{Davidson}} = \left(1 - \sum_R C_R^2 \right) \times E_{\text{corr}}(\text{MR-CISD}) \quad (3.33)$$

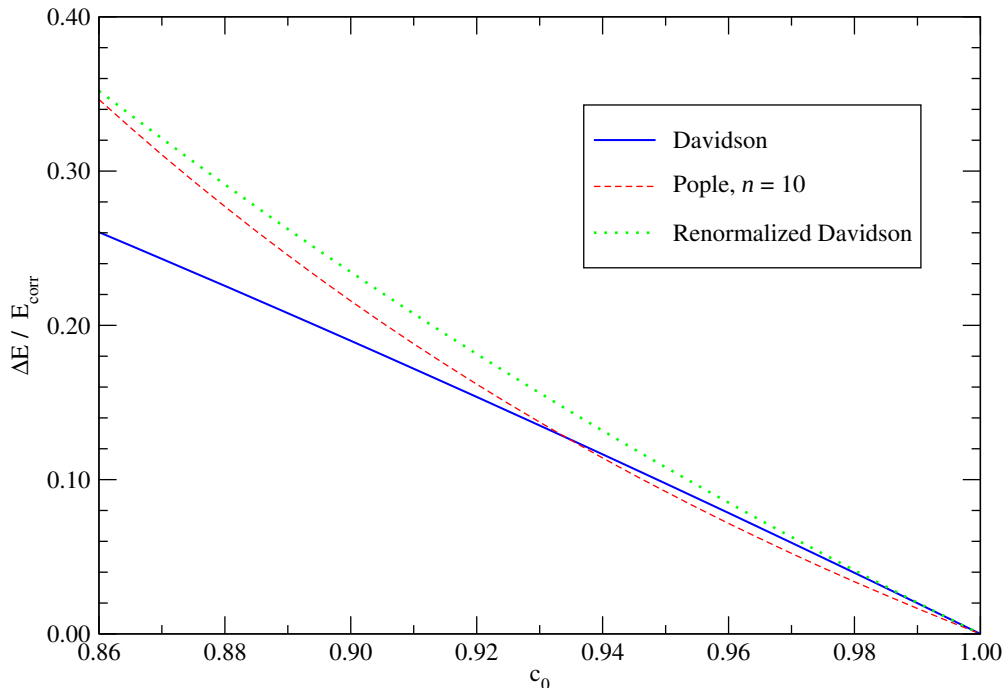


Figure 3.4: Davidson, renormalised Davidson and Pople correction factor for CISD energies.

This kind of generalisation was already employed in early applications of MRCI in the early 1980s [BPB80, BBBP83], even though no firm theoretical basis for these procedures has ever been given and their actual usefulness is somewhat dubious, especially if large reference spaces are employed [SS99]. A very brief analysis of the performance of some of these multi-reference corrections in the noble-gas system HArF is reported by Høst [Høs05]. In this study it is shown that the agreement with multi-reference coupled-cluster (MRCC) energies is better for Davidson-corrected MRCI values than uncorrected ones. As the sum of the squared reference coefficients is explicitly reported in this study, we could also calculate from these the renormalized Davidson and Pople corrections. The result is that the agreement with MRCC is even better using the renormalized Davidson correction and is best using the Pople form of the correction.

3.10.2 Corrections to energy and wave function

Another class of methods aim to modify CI or MRCI equations in such a way that the resulting method is (in general, approximately) size-extensive. The best-known of these methods is probably the Averaged Coupled Pair Functional (ACPF) of Gdanitz and Ahlrichs [GA88], while other proposals include the AQCC method of Szalay and Bartlett [SB95] and the ACPF-2 method of Gdanitz [Gda01]. The quadratic configuration interaction (QCISD) method of Pople, Head-Gordon and Raghavachari [PHR87] can also be considered as belonging to this class. Research in this field is still active and new methods are still being proposed and studied, see e.g. [AMMM08, Mei08, MMH03].

These methods are in general extremely attractive for potential-surface calculations. However, as the proposed modifications are usually based on some model system, it is not certain that they should always be better than regular MRCI or Davidson/Pople-corrected MRCI.

3.11 The R12 explicitly-correlated class of methods

We mentioned in Section 3.4.2 the problem of the very slow convergence of the correlation energy with respect to basis set size. As a consequence, basis set incompleteness is often the factor limiting the accuracy of quantum chemical calculations. The extrapolation techniques discussed in Section 3.4.2 help to assuage this problem but do not remove it.

This painfully slow convergence is a much-studied problem [TKH07, KMTNV06, Wil03, Mor03, Kut03, Kv00, Klo00] and the ultimate reason has been identified with the difficulty for orbital expansions of describing the electron-electron cusp present in the exact wave function. It has been known since the first days of quantum mechanics [RK03, Ryc03a, Ryc94] that trial wave functions which include as variables the inter-electronic distances r_{ij} lead to much faster convergence. However, these ‘explicitly correlated’ methods soon become unmanageable for systems with more than three or four electrons.

One approach which manages to introduce inter-electronic distances in the trial wave function while at the same time remaining computationally feasible for large systems is the R12 class of methods first pioneered in the late 1980s by Kutzelnigg and Klopper [Kut85, KK87]. These methods have since enjoyed growing attention as they potentially offer an improved speed of convergence with respect to the basis set size with only a modest increase of computation with respect to conventional methods.

In the development of working equations in the R12 approach various kinds of approximations have to be introduced and there exist many different acronyms referring to the particular technical choices adopted (e.g. Ansatz **1**, Ansatz **2**, standard approximation A, B or C); for recent reviews on the topic see e.g. [WAM07, KMTNV06, Klo00]. A particularly relevant technical development has been using as a correlation factor a function of the inter-electronic variable $f(r_{ij})$ instead of the inter-electronic distance r_{ij} itself as it was originally done. Methods of this kind are called F12 [KMTNV06], even though the older acronym R12 is sometimes used as an umbrella term for generically referring to any of these explicitly correlated methods.

R12 (or F12) methods may be used with ordinary correlation-consistent basis sets (see section 3.4) but best results are obtained with especially tailored basis sets, see e.g. [PAW08, KNV05, NV03].

We investigated the possible use of R12 explicitly correlated methods for the computation of a new water potential energy surface using the software AMICA. Unfortunately, this project eventually had to be abandoned. We will nonetheless report on our endeavours in this direction in Section 6.3.

3.12 Other Approaches

Many quantum chemical methods have been proposed over the years, none of them emerging as a clear all-round winner. In this respect Kutzelnigg [Kut03] mentions a kind of principle of ‘invariance of the difficulties’ for different approaches to the solution of the Schrödinger equation. In view of the extreme difficulty of the problem at hand it is to be expected that different methods will be needed for different applications.

The three correlated classes of methods that make up the bulk of computations performed today are probably Density Functional Theory [PY94, GDL03, van03, KBP96] (see also the

related approach of Bartlett *et al* [BLS05]), Coupled Cluster Theory [BM07, Pal03, CS00b, PL99, Bar97, Bar89] and Møller-Plesset perturbation theory [SO96]. Multi-reference extensions to coupled-cluster theory exist [ESA⁺08, BM07, LP08a, LP08b] but are still in a developmental stage. Several multi-reference perturbative schemes have been proposed, including CASPT [AMR92, Wer96] and NEVPT [APC07]. Another class of methods which has met with a resurgence in recent years is modern valence-bond theory [SH07a, Gal05, Coo02, ML03, SCR03, HS07a, Tru07, Shu06, McW99a, Kar98].

Among the many other methods proposed and applied to chemical problems we may mention: quantum Monte-Carlo method [Cep99]; explicitly correlated Gaussians [RK03, Ryc99] and other explicitly-correlated methods [Har04a, Ryc03a, RK03]; the contracted Schrödinger equation approach of Mazziotti [Maz06, Maz98]; the recently-developed quantum chemical version of the Density Matrix Renormalization Group method [FOZ98, DCDW00, MOM08, CKG04, MLPF03, MFO⁺01, MR07, HCC06, Cha04, CHG02]; the dimensional-scaling approach of Herschbach *et al* [SSH05, HAG92]; the recent Free Iterative Complement Interaction method of Nakatsuji [Nak05], which in the few-electron (up to 5) systems where it has been applied yielded extremely accurate energies [KNN05, NN07, NNN07].

3.13 Computational considerations

Quantum chemical methods are intimately linked to advances in computer technology: computational resources are always the ultimate limiting factor of any calculation. The TOP500 project (www.top500.org) has ranked every six months the 500 most powerful publicly-known computer systems in the world since 1993 and provides a good reference of the state of the art of supercomputers. A plot of the TOP500 speed data relative to the fastest and the slowest system (i.e., 500th) up to June 2008 is presented as Figure 3.5. At any given time first-rated computers are hugely expensive machines available only to the world's wealthiest institutions and with a cost of the order of £50-100 million or more. Systems close to the 500th place are systematically about 100 times slower than the fastest machine but are still, at any given time, very powerful and expensive systems with a cost of the order of perhaps £200-300,000. We can estimate that an off-the-shelf workstation costing $\approx$ £3,000 would be about 20 times slower than a 500th-position systems (economies of scale result in smaller systems with better value for money).

The data imply that supercomputer performance doubles every 14 months, which is even faster than the usual statement of Moore's law [Wikb] which predicts a doubling every 18-24 months. This means that a 12 year's wait is enough to fill the 2,000-fold speed factor between the fastest supercomputer and a regular workstation. It is to a large extent because of this exponential rise in computing power that accurate quantum chemical calculations are possible at all. We can also remark that computing molecular potential or dipole surfaces is a task particularly well suited to modern computers, because of its highly parallel character (the computation of every point of the surface can be performed completely independently from every other).

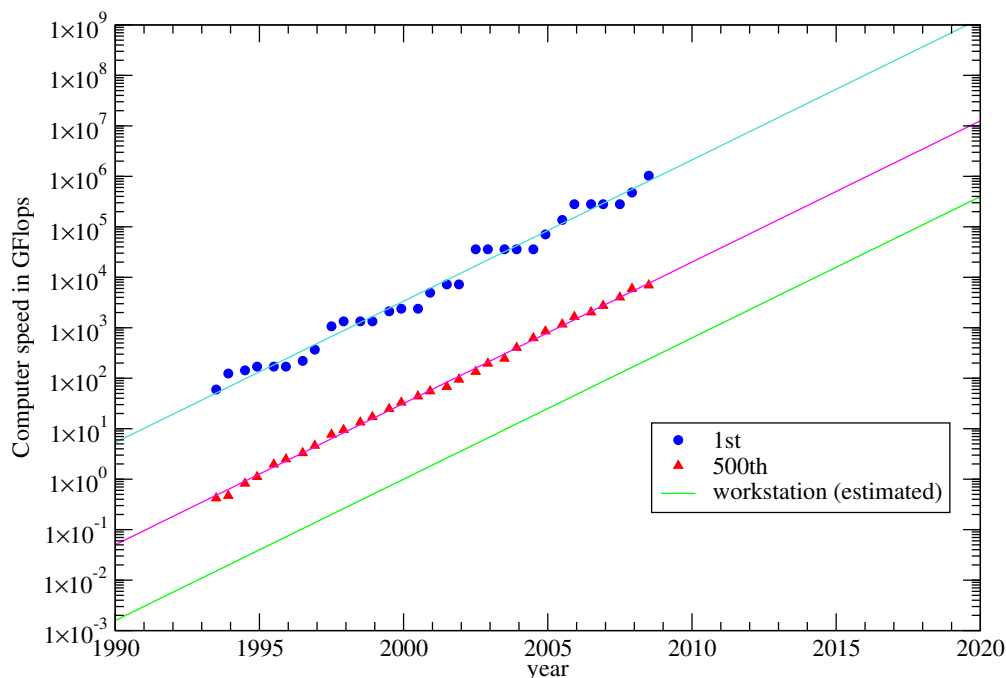


Figure 3.5: Computer speed in billion of floating-point operations per seconds (GFlops) of the 1st and the 500th fastest supercomputers up to June 2008, as reported on www.top500.org. The straight lines are exponential fits to the data, while the third line is the estimated speed of a $\approx$ £3,000 workstation.

3.14 A reference case: the hydrogen molecule

In this section we will treat in some detail the ground-state potential energy curve of the hydrogen molecule, both as an example of the state-of-the-art for the smallest molecular system and because we will make use these results in a study of long-range forces which will be presented in Chapter 10.

Energies obtained by explicitly correlated methods

Starting from the pioneering calculations by James and Coolidge [JC33] in 1933, there is a long history of accurate calculations of the electronic potential of the hydrogen molecule. A comprehensive review was recently given by Rychlewski [Ryc03a].

The hydrogen molecule has always received much attention and recent calculations have achieved a very high level of accuracy. Comparing the recent values from Sims and Hagstrom [SH06] with the ones from Rychlewski and Komasa [RK03] we estimate the energies by Sims and Hagstrom [SH06] to be accurate to at least 10^{-4} cm^{-1} or $5 \times 10^{-10} E_h$.

We report as Table 3.1 a comprehensive list of references from 1960 onwards that calculate energy values for the hydrogen molecule. The historical 1933 computation by James and Coolidge [JC33] is also included as reference. References that calculate only very few points close to equilibrium are not included.

A plot of the differences between the points taken from the various references and the values

by Sims and Hagstrom [SH06] is reported as figure 3.6. Points from Wolniewicz [Wol93] will be particularly useful for our long-range study presented in Chapter 10 as they extend up to 12 a_0 ; most other references stop at shorter bond lengths.

Points obtained by full-CI and Gaussian basis sets

We computed a series of full-CI energies using MOLPRO 2002.6 [WKL⁺02] or PSI3 [CSV⁺07] and various basis sets of the aug-cc-pVnZ family [Dun89]. Basis-Set Superposition Error was estimated calculating the counterpoise correction (Boys-Bernardi) correction [BB70] $\Delta E^{CP}(R) = 2[E_H - E_{HG}(R)]$, where E_H is the energy of the hydrogen atom with the given basis set, and $E_{HG}(R)$ is the energy of a hydrogen atom in the presence of the basis sets for the two hydrogens, for the aug-cc-pVQZ points. ΔE^{CP} is 0.311 cm^{-1} at 5 a_0 and decreases rapidly with R . Its effect is therefore small.

We present a plot of the errors for various full-CI calculations in Figure 3.7, and some technical data on the computations in Table 3.2. Note that PSI3 uses a different algorithm (by Olsen *et al* [ORJJ88]) for FCI than MOLPRO (by Knowles and Handy [KH89, KH84]) which is, at least when applied to the hydrogen molecule, much faster. Note, however, that FCI energies could be obtained with MOLPRO in a much more efficient way using the CCSD or the CISD programs, which are in this case equivalent to FCI.

As it can be seen comparing Figure 3.6 and Figure 3.7, absolute values of energies obtained by FCI are (unsurprisingly) much less accurate than the ones obtained by explicitly-correlated methods. For example, FCI aug-cc-pV6Z energies near equilibrium are about 25 cm^{-1} too high. However, as we shall discuss in full in Section 10.2.3, results are far more encouraging if one looks at relative energies, especially at long bond lengths.

Results for the long-range part of the energy curve are collected in Table 10.2 and will be discussed in Section 10.2.3.

Energies were extrapolated from the aug-cc-pVQZ, aug-cc-pV5Z and aug-cc-pV6Z using the form $E_n = E_\infty + A/(n + d)^3$. Other extrapolation formulae tried were the two-point formula $E_n = E_\infty + A/n^3$ and the three-point formulae $E_n = E_\infty + A/n^\alpha$ and $E_n = E_\infty + A/n^3 + B/n^5$ but they all gave worse extrapolated energies.

Table 3.1: References computing at least part of the energy curve of the hydrogen molecule. Hy-CI=Hylleraas CI; VMC=Variational Monte Carlo; KW=basis expansion of Kołos-Wolniewicz type (see the individual references for the exact form used). N_p is the total number of points computed, $R_{\max}$ is the largest bond distance calculated (in bohrs). We also report the RMS error and the standard deviation σ in cm^{-1} with respect to the data from Sims and Hangstrom [SH06], which are the most accurate available. See also Figure 3.6 for a plot of the estimated errors.

Technique	Author(s)	Reference	Year	$R_{\max}$	N_p	RMS	σ
Hy-CI	Sims and Hagstrom	[SH06]	2006	6.0	48	na	na
VMC	Alexander and Coldwell ^a	[AC04]	2004	10.0	24	0.25	0.11
ECG	Rychlewski and Komasa ^b	[RK03]	2003	40.0	11	0.00003	0.00001
KW	Wolniewicz	[Wol95]	1995	8.0	20	0.0008	0.0005
ECG	Rychlewski <i>et al</i>	[RCK94]	1994	3.4	15	0.008	0.0008
KW	Wolniewicz	[Wol93]	1993	12.0	55	0.009	0.005
KW	Kołos <i>et al.</i>	[KSM86]	1986	12.0	55	0.05	0.03
KW	Kołos and Wolniewicz	[KW75]	1975	8.0	30	0.3	0.11
KW	Kołos and Wolniewicz ^c	[KW74]	1974	12.0	17	0.02	0.01
KW	Kołos and Wolniewicz	[KW68]	1968	3.2	17	1.0	0.8
KW	Kołos and Wolniewicz	[KW65]	1965	10.0	87	3.3	1.9
JC	Kołos and Roothaan ^d	[KR60]	1960	4.2	25	349.1	291.4
JC	James and Coolidge	[JC33]	1933	1.7	6	588.8	32.2

^a The point at $R = 1.60 \text{ a}_0$ is non-variational and hence it is probably wrong. It was excluded from the computation of RMS and σ .

^b The point at $r = 6.00 \text{ a}_0$ differs considerably from the values reported by other references and is probably wrong. It was excluded from the computation of RMS and σ .

^c Data from [KW74] only have one point in common with [SH06], hence RMS and σ were computed with respect to [Wol93], the best available reference that covers the same range.

^d Points from [KW65] have a wrong behaviour at dissociation, hence the overall high values for RMS and σ . Also, the reported values for $R = 0.8$ and $R = 0.9 \text{ a}_0$ are non-variational and hence probably wrong. For R closer than $\approx 0.5 \text{ a}_0$ to equilibrium the RMS error is $\approx 10 \text{ cm}^{-1}$.

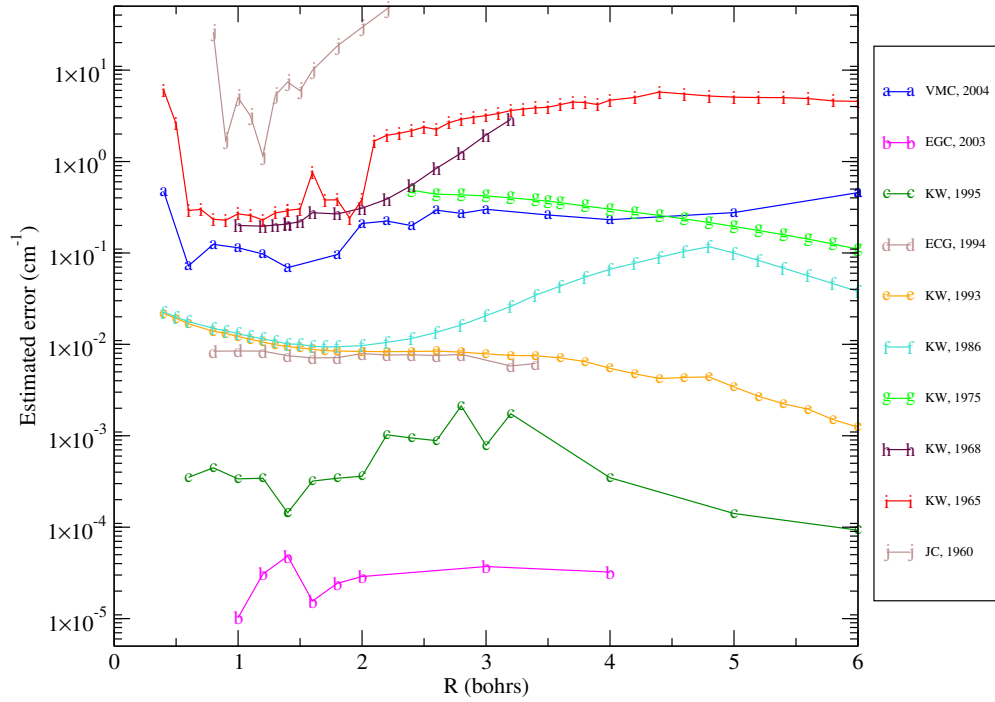


Figure 3.6: Estimated error in the energies of the hydrogen molecule for the references of Table 3.1. In the legend we indicated the year of calculation and the acronym of the technique used. The precise reference can be inferred by looking at Table 3.1.

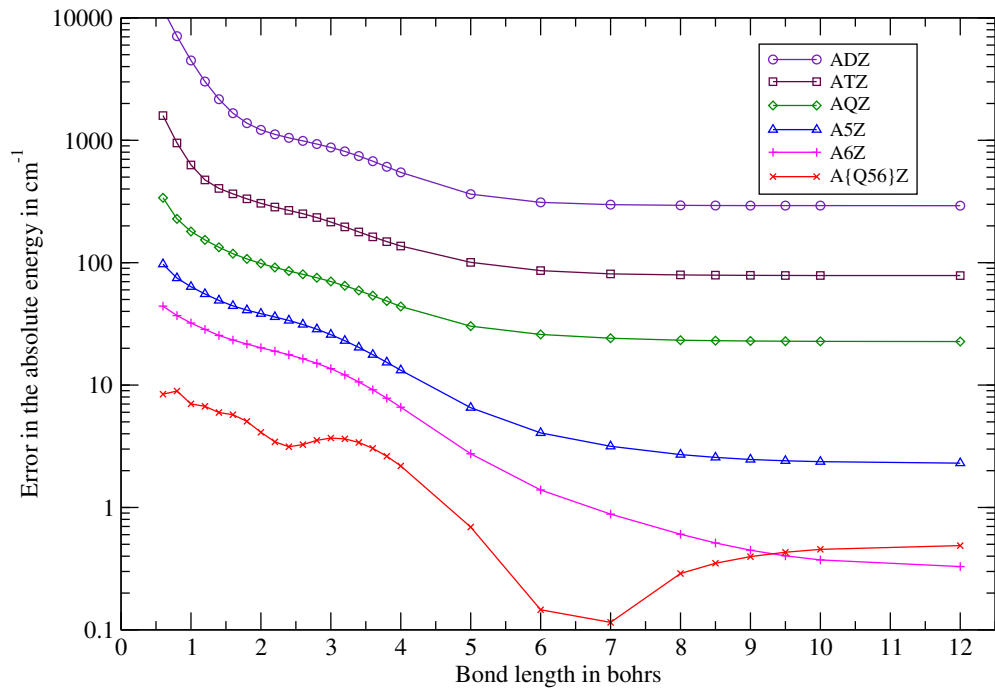


Figure 3.7: Errors of the total energies for the hydrogen molecule obtained by full-CI with various basis sets. The writing “ AnZ ” stands for aug-cc-pV nZ basis set. The series labelled “A{Q56}Z” was obtained by extrapolation of the AQZ, A5Z and A6Z values using the form $E_n = E_\infty + A/(n+d)^3$ (see text).

Table 3.2: Average running time in minutes for FCI computations on the hydrogen molecule using MOLPRO [WKL⁺02] and PSI3 [CSV⁺07]. Computations were done on a Pentium IV 3.4 GHz with 3 GiB of RAM in D_{2h} symmetry. The writing “ AnZ ” is shorthand for aug-cc-pVnZ. Disk space usage was about 1.5 GB for the largest A6Z runs.

		basis set			
		ATZ	AQZ	A5Z	A6Z
Contractions ^a =		46	92	160	254
MOLPRO	time:	0.02	0.23	5.38	121.00
PSI3	time:	0.00	0.00	0.02	3.44 ^b

^a Number of contracted basis functions in the respective basis set.

^b This computation could not be performed on the Pentium IV machine because the run required about 4 GiB of RAM; a 3 GHz Xeon 5160 system with 16 GiB of RAM running 64-bit Linux was used instead.

Solving the nuclear-motion problem in tri-atomic systems

4.1 Introduction to the problem

In the Born-Oppenheimer and related approaches (see section 2.3) once having obtained the electronic potential energy surface $V(\mathbf{x}_1, \dots, \mathbf{x}_N)$ one has to solve the Schrödinger equation for the nuclear motion. Similarly to the electronic-motion case the problem of finding eigenvalues and eigenfunctions of $\hat{H}$ quickly becomes a very difficult problem as the number of nuclei increases. The traditional way to treat this problem is discussed in many references, see e.g. the classic treatise by Wilson, Decius and Cross [WDC80], the books by Papoušek and Aliev [PA82] and Bunker and Jensen [BJ98] and the reviews by Wilson [Wil92a] and by Sutcliffe [Sut04a]. This approach is based on an approximate separation of vibrational and rotational degrees of freedom (Eckart conditions [Wil92a]) and on an harmonic expansion of the potential around the equilibrium positions of the nuclei. The approximations introduced are then partially corrected by some form of perturbation theory, often introducing semi-empirical parameters in the process; see e.g. the review by Sarka and Demaison [SD00] for more details on this class of methods.

While in large molecules approximations necessarily have to be introduced, for systems with less than four or five nuclei more specialised methods involving fewer approximations can be applied. In particular, starting from the late 1970s tri-atomic systems have received much attention and the formalism is now well established. It is in this case possible to solve the Schrödinger equation for the nuclear motion in an essentially exact way by numerical methods.

It is an approach of this kind which is implemented in the software suite DVR3D [TKB⁺04] which was used for all rotation-vibration calculation in this thesis. In the remainder of this chapter we will outline the main features of this approach. More detailed accounts can be found in the review articles by Tennyson [Ten00], Tennyson *et al* [TMH92], Bačić and Light [BL89] and Tennyson [Ten86], and in the original papers by Sutcliffe and Tennyson, particularly [ST91] and [TS92]. Also of interest is the review by Sutcliffe [Sut04a].

4.2 The internal degrees of freedom

The Hamiltonian in atomic units¹ for a triatomic system, for which $\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3$ indicate the Cartesian coordinates of the three nuclei, is

$$\hat{H} = \hat{K} + V = -\frac{\nabla_1^2}{2m_1} - \frac{\nabla_2^2}{2m_2} - \frac{\nabla_3^2}{2m_3} + V(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) \quad (4.1)$$

where m_i are the nuclear (or atomic) masses and V is the potential energy surface of the molecule.

It is possible to solve the eigenvalue problem directly in Cartesian coordinates, and this is in fact done in Monte Carlo calculations of vibrational spectra, see e.g. [NBMS96]. When this is done six zero eigenvalues result at the end of the calculation, corresponding to the three translational and three rotational degrees of symmetry of the Hamiltonian (see e.g. chapter 2 of [WDC80]).

It is however convenient to take full advantage of the symmetries of the Hamiltonian. The potential V , and hence also $\hat{H}$, is invariant with respect to translations and to rotations of the frame of reference. Following Wigner [Wig59] this can be formally expressed introducing two groups of operators $\hat{T}_{\mathbf{a}}$ and $\hat{R}_{\mathbf{w},\gamma}$ which acting on a function respectively rigidly translate it by the vector $\mathbf{a}$ or rigidly rotate it around an axis $\mathbf{w}$ by γ radians. The Hamiltonian (4.1) commutes with all $\hat{T}_{\mathbf{a}}$ and $\hat{R}_{\mathbf{w},\gamma}$ and these symmetries can be used to considerably simplify the problem of finding its eigenvalues and eigenfunctions. The details of this kind of analysis are non-trivial but have however been worked out long ago, see e.g. [CHA50] and the historical overview by Hirschfender [Hir83].

The final results are simple to state. The three translational degrees of freedom can be completely separated out by introducing the coordinates of the centre-of-mass of the system and are hence unproblematic. The treatment of the rotational symmetry of the Hamiltonian is more complicated [CHA50, Hir83] and will be outlined in the following sections of this chapter. In brief, the rotational degrees of freedom cannot be separated out but as the eigenfunctions of the rotation operator are known these degrees of freedom can be treated analytically and integrated over. This procedure results in a series of ‘effective Hamiltonians’ which depend only on three internal coordinates describing the internal degrees of freedom, thus reducing the dimensionality of the problem from nine in Cartesian coordinates to three in internal coordinates [PA82, Mak03]. As numerical methods scale exponentially with the dimensionality of the system this is a considerable simplification and it also provides physical insight.

A general formalism for this end has notably been developed by Sutcliffe and is described in [Sut03b, Sut92, Sut82]. Other recent treatments were given e.g. by Islamapour [IE05, Isl03], Schwenke [Sch03b], Lukka [Luk95], and Chapuisat and Iung [CI92].

The main inconvenience of abandoning the $3N$ Cartesian coordinates in favour of $(3N - 6)$ curvilinear internal coordinates is that the kinetic-energy term $\hat{K}$ of the Hamiltonian (4.1) has to be re-written in terms of the chosen internal coordinates. Even though this is in principle a purely mechanical process only involving multiple applications of the chain rule the required algebra is very involved, particularly in general formulations like the ones of e.g. refs. [CI92, Sut92].

¹Note that masses in atomic units (au) are *not* the same as in unified atomic mass units (u). In atomic units the reference mass is the electron mass, while in unified atomic mass units it is 1/12 of the mass of a ¹²C atom. The equivalence is given by, using the CODATA2006 data [MTN08], 1 u = 1822.88848(13) au

There is also another problem connected with the use of internal coordinates, namely that, no matter how the internal coordinates are chosen, there will be some points where these coordinate fail and introduce singularities in the Hamiltonian. This is a general result of topological origin [Sut04a, Sut03c] which in technical terms can be expressed by saying that the quotient space $\mathbb{R}^{3N-3}/O(3)$ is only a manifold with dimension $3N - 6$, but not a vector space. One possible solution to this problem is to choose the internal coordinates so that the singularities are at points where the potential energy surface is infinite or very large, see section 4.2.3 and e.g. [Sut04a, TS92].

4.2.1 Concepts from angular momentum theory

The treatment of the molecular vibration-rotation motion makes use of some theoretical tools developed in the theory of angular momentum. References treating these topic in detail are the books by Brink and Satchler [BS94], Rose [Ros95], Edmonds [Edm96], Zare [Zar88], Biedenharn and Louck [BL81], Thompson [Tho94] and the review by Van de Wiele [vdW01]. In what follows we will briefly introduce some concepts we will need in the rest of our discussion.

Reference frames

We will define three distinct Cartesian frames of reference:

1. *Laboratory-fixed frame.* It a reference frame fixed “in the laboratory”; in this frame the Hamiltonian assumes its simplest form given by eq. (4.1).
2. *Space-fixed frame.* It is a frame where the centre-of-mass motion has been removed. More precisely, this means that the space-fixed coordinates are invariant with respect to rigid translations of the laboratory-fixed ones. The axes are parallel to the laboratory-fixed frame and the origin is the centre-of-mass of the molecule.
3. *Body-fixed or molecule-fixed or embedded frame.* It is the frame where both the translational and rigid-rotation motions have been removed. More precisely this means that molecule-fixed coordinates are invariant with respect to global rotations of space-fixed ones. The origin of the molecule-fixed axes is the centre-of-mass of the molecule, so the molecule-fixed frame can be obtained by a rotation of the space-fixed one.

Euler angles

The orientation of a rigid body relative to a fixed frame of reference may conveniently be specified by fixing three parameters; one possible and commonly used way of doing this is by using the so-called Euler angles $(\alpha\beta\gamma)$, see e.g. [Tho94, WDC80]. Note that several conventions are in use for the definition of the Euler angles [Wikc]; we adopt the one used by Brink and Satchler [BS94], which is sometimes referred to as the *zyz* convention. Also note that other authors write (α, β, γ) for what in our notation is $(-\alpha, -\beta, -\gamma)$ [BS94].

The Euler angles are used to parametrise an orthogonal rotation matrix $\mathbf{C}$ which in our

convention reads ²

$$\mathbf{C}(\alpha\beta\gamma) = \begin{pmatrix} \cos\alpha \cos\beta \cos\gamma - \sin\alpha \sin\gamma & \sin\alpha \cos\beta \cos\gamma + \cos\alpha \sin\gamma & -\sin\beta \cos\gamma \\ -\cos\alpha \cos\beta \sin\gamma - \sin\alpha \cos\gamma & -\sin\alpha \cos\beta \sin\gamma + \cos\alpha \cos\gamma & \sin\beta \sin\gamma \\ \cos\alpha \sin\beta & \sin\alpha \sin\beta & \cos\beta \end{pmatrix} \quad (4.2)$$

We can use $\mathbf{C}$ to specify the orientation of the molecule-fixed frame with respect to the space-fixed frame; indicating with $\mathbf{t}$ and $\mathbf{z}$ respectively a space-fixed and a molecule-fixed vector we can write

$$\mathbf{t} = \mathbf{C} \cdot \mathbf{z} \quad (4.3)$$

Wigner rotation matrices

It is a well-known result [Tho94, BS94] that, in a given Cartesian frame defined by the axes xyz , the operators $\hat{J}^2$ and $\hat{J}_z$ have as simultaneous eigenfunctions the spherical harmonic functions $|j, m\rangle = Y_{jm}(\theta, \phi)$. Let us now consider a new frame of reference $x'y'z'$ with the same origin but rotated with respect to xyz and consider the operators $\hat{J}'^2$ and $\hat{J}'_z$ in the $x'y'z'$ frame. The general theory of angular momentum tells us that the eigenfunctions $|j, m'\rangle$ in the rotated frame can be written as a linear combination of the eigenfunctions in the original frame having the same value of j [BS94]

$$|j, m'\rangle = \sum_{k=-j}^j (-1)^k (\mathcal{D}_{m, -k}^j)^* |j, k\rangle \quad (4.4)$$

where the $(-1)^k (\mathcal{D}_{m, -k}^j)^*$ are linear expansion coefficients which also depend on the Euler angles; the somewhat convoluted way in which they are written follows from the convention we have adopted for $\mathcal{D}_{mk}^j$ [BS94]. This last represents the element mk of a $(2j+1) \times (2j+1)$ hermitian matrix called Wigner rotation matrix as defined in [BS94]. Also note that k is the quantum number corresponding to the projection along the molecule-fixed reference frame.

4.2.2 Exact quantum numbers for the rotation-vibration wave functions

The laboratory-fixed Hamiltonian (4.1) commutes with the laboratory-fixed total angular momentum operator $\hat{J}^2$ so each rotation-vibration wave function has as a good quantum number the total rotational angular momentum quantum number $J = 0, 1, 2, \dots$. Also, $\hat{J}^2$ is invariant with respect to translations and rotations of the coordinates, so wave functions are also eigenfunctions of the space-fixed and molecule-fixed total angular momentum operators. In the absence of external fields an eigenfunction belonging to the eigenvalue J is $(2J+1)$ -time degenerate and a possible, sensible choice is to take wave functions which are eigenfunctions of $\hat{J}_z$, the projection of the angular momentum along the laboratory-fixed (and hence also space-fixed) z axis; we introduce a quantum number $M = -J, \dots, +J$ to count over this degeneracy.

It was explained in the previous section how to relate eigenfunctions of the projection of the angular momentum along two different axes through the Wigner rotation matrices. These considerations imply that [Sut91, CHA50] wave functions in the laboratory-fixed frame can

²Note that this matrix is written assuming it acts from the left on column-vectors. Sometimes [Sut92] the convention of taking row-vectors is taken instead, and in that case the transpose $\mathbf{C}^\dagger$ should be used instead.

be written as, using $\mathbf{x}_i$ for laboratory-fixed Cartesian coordinates, $\mathbf{X}$ for the centre-of-mass coordinates, $(\alpha\beta\gamma)$ the Euler angles relating the space-fixed to the molecule-fixed Cartesian frames and with $\mathbf{q}$ a set of $(3N - 6)$ curvilinear internal coordinates

$$|J, M\rangle = \Psi^{J,M}(\mathbf{x}_1, \dots, \mathbf{x}_N) = \xi(\mathbf{X}) \times \sum_{k=-J}^J \Phi_k^J(\mathbf{q}) |J, M, k\rangle \quad (4.5)$$

where $|J, M, k\rangle$ is a function of the Euler angles only and is given by (with a change of normalisation with respect to eq. (4.4))

$$|J, M, k\rangle = \sqrt{\frac{2J+1}{8\pi^2}} (-1)^k \mathcal{D}_{M,-k}^J(\alpha\beta\gamma)^* \quad (4.6)$$

$|J, M, k\rangle$ are the (normalised) symmetric-top eigenfunctions. Finally, $\xi(\mathbf{X})$ represent the global translation motion of the system and can be taken for example as a plane wave.

Other symmetries

The Hamiltonian (4.1) is invariant to inversion of all the coordinates with respect to the origin ($\mathbf{x}_i \rightarrow -\mathbf{x}_i$), which implies wave functions have either odd or even parity. This introduces a further quantum number, the parity; to express this it is usual to use the so-called ‘Wang symmetry’ $p = 0, 1$, defined so that the symmetry to inversion is given by $(-1)^{J+p}$, with -1 indicating odd symmetry and $+1$ even symmetry.

We have not said anything so far about the spin degrees of freedom of the nuclei. As our Hamiltonian is spin-independent it is possible to write the total (i.e., spatial *and* spin) nuclear motion wave function as a product of a spatial part and a spin part.

If two or more nuclei are identical the total wave function must be symmetric or anti-symmetric with respect to exchange of the identical nuclei, depending on the nuclear spin of the nuclei in question. For example protons (hydrogen ^1H nuclei) are fermions with spin $1/2$. If there are two hydrogen nuclei four possible spin states are possible, namely one anti-symmetric ‘para’ state (spin singlet) and three degenerate symmetric ‘ortho’ states (spin triplets); the spatial part of the wave function must hence be symmetric by exchange of the identical ^1H nuclei if the spin state is para and anti-symmetric if the spin state is ortho. The spin state of the identical nuclei is specified by a further quantum number which is customarily taken as $q = 0, 1$.

4.2.3 The internal coordinates

The three internal coordinates needed for a tri-atomic system can be chosen in infinite ways and different molecules will benefit from different choices. In the Sutcliffe-Tennyson formalism [TMH92, ST91] internal coordinates are specified by two parameters g_1 and g_2 . This formalism does not include all conceivable possibilities but it nonetheless general enough to cover all cases of present interest. In what follows we will use the same notation as the review [TMH92].

We use $\mathbf{x}_1$, $\mathbf{x}_2$ and $\mathbf{x}_3$ for the Cartesian laboratory-fixed coordinates of atoms 1, 2 and 3. We then define two space-fixed, translationally invariant vectors $\mathbf{t}_1$ and $\mathbf{t}_2$ by

$$\begin{aligned} \mathbf{t}_1 &= (\mathbf{x}_2 - \mathbf{x}_3) + g_2(\mathbf{x}_3 - \mathbf{x}_1) \\ \mathbf{t}_2 &= (\mathbf{x}_1 - \mathbf{x}_3) + g_1(\mathbf{x}_3 - \mathbf{x}_2) \end{aligned} \quad (4.7)$$

where the two parameters g_1 and g_2 belong to the interval $0 \leq g_i \leq 1$. We take as internal coordinates (r_1, r_2, θ) the lengths of these vectors and the angle formed between them

$$r_1 = |\mathbf{t}_1| \quad r_2 = |\mathbf{t}_2| \quad \theta = \cos^{-1} \left(\frac{\mathbf{t}_1 \cdot \mathbf{t}_2}{t_1 t_2} \right) \quad (4.8)$$

Many commonly-used coordinate systems can be obtained by a suitable choice of g_1 and g_2 , see e.g. Table 1 of ref. [TMH92] for a summary. In particular, we will mention two choices which are particularly useful in calculations, namely Jacobi and Radau coordinates. These are also the only type of coordinates implemented in the software suite DVR3D [TKB⁺04]. More informations can be found e.g. in [Ten00, TMH92, BL89].

- In Jacobi (also known as scattering) coordinates r_2 and r_1 are given respectively by the bongh length between atoms 2 and 3 and the length between atom 1 and the baricentre of atoms (2, 3) and θ is the angle formed by these two vectors, chosen to be $0 < \theta < 90^\circ$. Jacobi coordinates are especially suited for a system formed by a strongly bound diatomic molecule (atoms 2 and 3) plus a weakly-bound atom.
- Radau coordinates were originally introduced by Radau in 1868 for describing the planets in the solar system. Their usefulness for molecular system was emphasised by Smith in 1980 [Smi80] and they have since enjoyed a rising popularity [BL89]. In the case where one atom is much heavier than the others Radau coordinates become very similar to bond-length bond-angle ones.

Which internal coordinates should be chosen?

One of the main criteria for the choice of the internal coordinates is dictated, as we mentioned in Section 4.2, by the singularity points which inevitably arise. For example, in Jacobi coordinates the angle θ becomes undefined in the linear configuration where atom 1 lies between atoms 2 and 3.

If we were treating the water molecule with oxygen as atom 1 this configuration would correspond to the linear configuration H–O–H, which is not at very high energies and thus could not be disregarded. On the other hand, if one the hydrogens is chosen as atom 1 the singular configuration becomes H–H–O, which is at much higher energies and generally inaccessible; however, this choice makes it harder to take advantage of the nuclear symmetry of the hydrogens. A better choice is given by Radau coordinates, where the singularity configurations correspond generally to very short O–H bond lengths and thus to very high energies.

Apart from the problem of singularities, an optimal choice of the internal coordinates will also speed up convergence. We refer to the reviews by Tennyson *et al* [Ten00, TMH92] and by Bačić and Light [BL89] for a discussion of this topic.

4.2.4 The orientation of the molecule-fixed frame

Before deriving the internal-coordinate Hamiltonian it is opportune to also specify the orientation of the molecule-fixed frame with respect to the space-fixed one, a process called ‘embedding’. The embedding has computational importance because one generally expands the internal-coordinate wave function in a basis of eigenfunctions of the operator $\hat{J}_z$, the projection of the total angular momentum on the molecule-fixed reference frame.

Only a few choices of embeddings have been used in actual calculations. In particular, the software suite DVR3D [TKB⁺04] allows four possible choices in combination with Jacobi or Radau internal coordinates (not all possibilities or coordinates/embeddings are presently implemented)

1. *r₁ embedding*. The molecule is the xz plane, z axis parallel to $\mathbf{t}_1$.
2. *r₂ embedding*. The molecule is the xz plane, z axis parallel to $\mathbf{t}_2$.
3. *Bisector embedding*. The molecule is the xz plane, x axis bisects the angle θ between $\mathbf{t}_1$ and $\mathbf{t}_2$.
4. *Perpendicular embedding*. The molecule is the xy plane, x axis bisects the angle θ between $\mathbf{t}_1$ and $\mathbf{t}_2$.

For more details on the choice of the embedding see [TKB⁺04, Ten00, TMH92].

4.2.5 The molecule-fixed Hamiltonian

Once both the internal coordinates (r_1, r_2, θ) and the embedding have been chosen it is possible to transform the laboratory-fixed Hamiltonian (4.1) into internal coordinates. As we remarked this only requires application of the chain-rule, but the algebra is cumbersome. We will only summarise the general process, while the reader is referred to refs. [Sut03b, Sut92, ST91] for more details.

By application of the chain-rule the kinetic energy operator $\hat{K}$ is re-written as the sum of three parts: a first depending only on the internal coordinates, a second depending also on the Euler angles and third one depending on the centre-of-mass coordinates

$$\hat{K} = \hat{K}_V(r_1, r_2, \theta) + \hat{K}_{VR}(r_1, r_2, \theta; \alpha, \beta, \gamma) + \hat{K}_{\text{trans}}(\mathbf{X}) \quad (4.9)$$

One then considers a matrix element of the Hamiltonian between two states $|J', M'\rangle$ and $|J, M\rangle$, inserts expansion (4.5) for the exact wave function and integrates over the Euler angles

$$\hat{H}_{\text{eff}}^J = \langle J', M' | \hat{H}(r_1, r_2, \theta; \alpha, \beta, \gamma) | J, M \rangle \quad (4.10)$$

This procedure yields an effective Hamiltonian $\hat{H}_{\text{eff}}^J$ that depends only on the internal coordinates and where the quantum numbers included in the expansion (4.5), namely J, J', k, k' and M, M' , appear as parameters. However, for symmetry reasons, the Hamiltonian results independent from M or M' [ST91].

The effective Hamiltonian $\hat{H}_{\text{eff}}^J$ thus obtained has a global factor $\delta_{JJ'}$ and is thus block-diagonal in J . This means that calculations for different J 's can be performed separately. The effective Hamiltonian is not diagonal in k but, depending on the axis embedding, it has some structure in k (i.e., it can be tridiagonal in k), a fact which can be taken advantage of in actual computations. For more details on the exact form of the effective Hamiltonian see [TMH92, ST91, Ten86].

Further symmetries

For simplicity in the previous presentation we did not mention the further symmetries present in the Hamiltonian discussed in Section 4.2.2, namely Wang parity p and nuclear symmetry q . The effective Hamiltonian, as the original one, is diagonal in p and q so calculations with different symmetries can be performed separately.

4.3 Basis functions for the internal-coordinate wave functions

As we discussed in the previous sections once the symmetries (J, p, q) of the states we are interested in have been assigned one needs to find eigenvalues and eigenfunctions of the effective Hamiltonian. A straightforward way of doing this is by means of the linear variational method [SO96, Lev00]: a set of basis functions is introduced and the Hamiltonian matrix $\mathbf{H}$ in this basis is build and then diagonalised.

A set of basis fuctions for the internal coordinates (r_1, r_2, θ) may be obtained as a product of basis functions for the individual coordinates. For more details see e.g. [TKB⁺04, Ten00, TMH92, BL89, Ten86]. Basis sets which are not obtained as products of one-dimensional basis sets are also possible, see e.g. Czakó *et al* [CFB⁺07] but we will not discuss them.

For the two ‘radial’ coordinates r_1 and r_2 typical choices are modified Morse-oscillator wave functions or spherical oscillator functions. For the angular coordinate θ it is convenient to use a special set of basis functions $|k, j\rangle$ $k = -j, \dots, j$, $j = 0, \dots, N_{\max}$, which are eigenfunctions of $\hat{J}_z$, the projection of the angular momentum along the molecule-fixed axis:

$$|k, j\rangle = |J, M, k\rangle \times P_j^{(k)}(\cos \theta) \quad \text{if } p = 0 \text{ and } k = 0$$

$$|k, j\rangle = \frac{1}{\sqrt{2}} \left(|J, M, -k\rangle + (-1)^p |J, M, k\rangle \right) \times P_j^{(k)}(\cos \theta) \quad \text{in all other cases}$$
(4.11)

where $P_j^{(k)}(\cos \theta)$ is a normalised associated Legendre polynomial with the Condon and Shortley phase convention and $|J, M, k\rangle$ is given by eq. (4.6) (j is simply an index and has no connection with the angular momentum J).

4.4 Method of solution: the DVR technique

Once the basis set has been decided the calculation can proceed in the way we outlined in the preceding section by building and diagonalising the Hamiltonian matrix $\mathbf{H}$. This way of proceeding is in this context called Variational Basis Representation (VBR) approach and was indeed employed in virtually all computations of this kind done before about the mid-1980s [Ten86]. However a new computational technique, the DVR or Discrete Variable Representation, has proved extremely effective and is also employed in the software suite DVR3D [TKB⁺04] we use. We will lay down the basis of this technique in this section.

4.4.1 Introduction

The first, *ante litteram*, application of the ‘Discrete Variable Representation’ (DVR) technique in quantum physics is usually traced back to a 1965 study by Harris *et al.* [HEG65]; shortly thereafter the connection between this approach and Gaussian integration rules was clarified by Dickinson and Certain [DC68]. After a gap of about fifteen years the technique was then independently developed in different area of physics by Light and co-workers [LPL82, LHL85], Shizgal and Blackmore [SB84, BS85] and Baye and Heenen [BH86]. In chemical-physics applications it is the notation and formalism of Light and co-workers [LHL85] that has become

the standard, and we will adopt it as well. Further to the cited references the technique was reviewed briefly by Bačić and Light [BL89] and, more recently and in more detail, by Light and Carrington [LC00].

The term ‘representation’ in the acronym DVR is used in the sense of matrix mechanics, where the numerical matrix $\mathbf{V}$ associated to an operator $\hat{V}$ depends upon the chosen ‘representation’, i.e. upon the chosen basis set. One may switch between one representation to an equivalent one by a similarity transform.

In a few words, a DVR basis set $\{\theta_n(x)\}_{n=1}^N$ is a set of N functions each of which is a strongly localised, bell-shaped function centered on a particular grid point x_n . The fundamental DVR approximation is to approximate matrix elements of a local operator $V(x)$ in this basis set by

$$\mathbf{V}_{\alpha\beta} = \int_a^b \theta_\alpha(x) V(x) \theta_\beta(x) dx \approx \delta_{\alpha\beta} V(x_\alpha) \quad (4.12)$$

It is in other words assumed that in the DVR basis all local operators are exactly diagonal; this assumption eliminates the need to calculate the $N(N+1)/2$ integrals that would be needed to compute the matrix representation of $V(x)$ in a generic, ‘diffuse’ basis set.

From an intuitive, non-rigorous point of view one may suppose that approximation (4.12) will become exact in the limit where the DVR basis functions become ‘similar’ to perfectly-localised Dirac delta functions, $\theta_\alpha(x) \rightarrow \delta(x - x_\alpha)$, and the corresponding set of grid points x_α become dense in $[a, b]$. Much of the machinery behind the general DVR theory is essentially a study of this approximation and of optimal ways of choosing the DVR grid points x_α and the DVR basis functions θ_α .

There are several ways of introducing the DVR technique, and the link between them is not always transparent. We will describe briefly the method in one dimension, while the reader is referred to the cited literature [LC00, BL89, BH86, BS85, SB84, DC68, HEG65] for more details.

4.4.2 Gaussian quadrature rules

Gaussian quadrature rules are a standard topic of numerical analysis, see e.g. [KC91, CdB80] or the books by Evans [Eva93] and Stroud and Secrest [SS66]. A Gaussian quadrature rule is a way of approximating integrals of the kind $I = \int_a^b \omega(x) f(x) dx$ where $\omega(x)$ is a known ‘weight’ function satisfying $\omega(x) > 0$ and f is an unknown function. In the Gaussian quadrature approach the integral I is approximated by

$$I = \int_a^b \omega(x) f(x) dx \approx \sum_{\alpha=0}^{N-1} W_\alpha f(x_\alpha) \quad (4.13)$$

where the N abscissae x_α and the N weights W_α are determined so that formula (4.13) is exact if $f(x)$ is a polynomial of degree up to $2N - 1$. In particular, the general theory tells us that the x_α are the N roots of the N -th degree orthogonal polynomial on $[a, b]$ with respect to the weight function $\omega(x)$, while the weights W_α can be equivalently expressed by several formulae one of which is [Eva93]

$$(W_\alpha)^{-1} = \sum_{j=0}^{N-1} p_j(x_\alpha)^2 \quad (4.14)$$

where $p_j(x)$ is the normalised j -th degree orthogonal polynomial on $[a, b]$ with respect to the weight $\omega(x)$ (N.B.: commonly tabulated orthogonal polynomials are usually unnormalised).

4.4.3 Gaussian quadrature DVR's in one dimension

Gaussian-quadrature DVR's are historically the first to be studied [HEG65, DC68, LC00] and arguably the most rigorous incarnation. For this class of methods it is possible to show that approximation (4.12) is equivalent to calculating the necessary integrals not exactly but by an N -point Gaussian quadrature rule.

The problem at hand is to find eigenvalues and eigenvectors of a Hamiltonian operator

$$\hat{H} = \hat{K} + V(x) \quad (4.15)$$

We will start defining a traditional, orthonormal, 'diffuse' basis function $\{f_n(x)\}_{n=0}^{N-1}$ having the form of a polynomial times the square root of a positive weight function $\omega(x)$:

$$f_n(x) = \sqrt{\omega(x)} p_n(x) \quad (4.16)$$

A typical example is given by the eigenfunctions of the harmonic oscillator, where in opportune units $\omega(x) = e^{-x^2/2}$ and $p_n(x) = N_n H_n(x)$ are the normalised Hermite polynomials.

The traditional way of obtaining eigenvalues and eigenvectors of $\hat{H}$ is to compute the matrix representation of the Hamiltonian in the chosen basis and then to diagonalise the resultant $N \times N$ Hamiltonian matrix $\mathbf{H}$. The eigenvalues of $\mathbf{H}$ are, by virtue of the famous Hylleraas-Undheim-MacDonald theorem (see e.g. [Lev00, SO96]), upper bounds to the true eigenvalues; it is also guaranteed that as the basis approaches completeness the eigenvalues will converge to their exact values.

One practical problem of this way of proceeding is that, while for a given choice of basis set one can compute the matrix elements of the kinetic energy operator $\hat{K}$ exactly once and for all, for each choice of $V(x)$ one has to compute its $N(N+1)/2$ matrix elements. We will call the matrix representation of $V(x)$ computed *exactly* in the 'diffuse' $\{f_n(x)\}$ basis set the 'Variational Basis Representation', $\mathbf{V}^{\text{VBR}}$:

$$\mathbf{V}_{ij}^{\text{VBR}} = \int_a^b f_i(x) V(x) f_j(x) dx \quad (4.17)$$

We stress that in the VBR representation the matrix elements of the potential are computed *exactly* and the only source of error in the results is due to basis set incompleteness.

As we will see, one of the main advantages of the DVR technique is that an *approximate* matrix representation of $V(x)$ can be obtained without computing any integral at all. The DVR approach can be introduced in (at least) two ways, which we will call the 'Gaussian quadrature viewpoint' and the 'product approximation viewpoint'. As shown by Dickinson and Certain [DC68, LC00] these two approaches are equivalent but they give different insight to the approximation introduced.

Gaussian quadrature viewpoint

In this approach one chooses to evaluate all the integrals necessary to build $\mathbf{V}_{ij}^{\text{VBR}}$ in an *approximate way* by using for each of them an N -point Gaussian quadrature formula. The number of quadrature point, N , is chosen equal to the number of basis functions employed. We will call the matrix representation of $V(x)$ built in this approximate way the 'Finite Basis Representation',

$\mathbf{V}^{\text{FBR}}$ (contrast the following with eq. 4.17)

$$\mathbf{V}_{ij}^{\text{FBR}} = \sum_{\alpha=0}^{N-1} W_{\alpha} f_i(x_{\alpha}) V(x_{\alpha}) f_j(x_{\alpha}) \quad (4.18)$$

We stress that, as in the FBR representation matrix elements are computed by approximate Gaussian quadrature rules, $\mathbf{V}^{\text{FBR}}$ is *not* (in general) equal to $\mathbf{V}^{\text{VBR}}$. However, by virtue of the properties of Gaussian quadrature, if we assume that $V(x)$ can be written as a polynomial expansion of the kind³

$$V(x) = \sum_{p=0}^{+\infty} c_p x^p \quad (4.19)$$

then formula (4.18) will be exact if $i + j + p \leq 2N - 1$; for example, the matrix element $\langle 0|V|0\rangle$ will be exact up and including the term with $p = 2N - 1$, while $\langle N - 1|V|N - 1\rangle$ will be exact only up to and including $p = 1$.

One can conveniently re-write relation (4.18) in matrix form introducing the $N \times N$ matrices⁴

$$\mathbf{T}_{\alpha j} = \sqrt{\frac{W_{\alpha}}{\omega(x_{\alpha})}} f_j(x_{\alpha}) = \sqrt{W_{\alpha}} p_j(x_{\alpha}) \quad (4.20)$$

and the diagonal matrix

$$\mathbf{V}^{\text{DVR}} = \text{diag}(x_0, \dots, x_{N-1}) \quad (4.21)$$

where the DVR superscript adopted will become clear presently. By virtue of our choice (4.16) of the basis set $\{f_n(x)\}$ and of the use of Gaussian rule it follows that $\mathbf{T}$ is a unitary matrix:

$$(\mathbf{T}^{\dagger} \mathbf{T})_{ij} = \sum_{\alpha=0}^{N-1} T_{i\alpha}^{\dagger} T_{\alpha j} = \sum_{\alpha=0}^{N-1} W_{\alpha} p_i(x_{\alpha}) p_j(x_{\alpha}) = \delta_{ij} \quad (4.22)$$

One can now re-write relation (4.18) in matrix form as

$$\mathbf{V}^{\text{FBR}} = \mathbf{T}^{\dagger} \mathbf{V}^{\text{DVR}} \mathbf{T} \quad (4.23)$$

The matrix $\mathbf{T}$ can then be interpreted as defining a change of basis from the original, ‘diffuse’ basis set $\{f_n(x)\}$ to a new basis set, the DVR one. The DVR basis set functions $\{\theta_{\alpha}(x)\}_{\alpha=0}^{N-1}$ are given by

$$\theta_{\alpha}(x) = \sum_{j=0}^{N-1} \mathbf{T}_{\alpha j} f_j(x) \quad (4.24)$$

As the transformation is unitary, the new basis set $\{\theta_{\alpha}(x)\}$ is orthonormal as we assumed that $\{f_n(x)\}$ was so. It can be shown that the DVR basis function $\theta_{\alpha}(x)$ is more and more localised around the grid point x_{α} as the size of the basis set increases; this property of ‘locality’ is perhaps best understood in the product approximation viewpoint discussed in the next paragraph, where it will be shown that $\theta_{\alpha}(x)$ tends to a Dirac delta function as $N \rightarrow +\infty$. Other analytical properties of the DVR functions can be proven, for example that $\theta_{\alpha}(x)$ is zero for all $x_{\beta} \neq x_{\alpha}$ [LC00].

³Note that this expansion does not necessarily have to be a Taylor expansion. The Weierstrass approximation theorem [Pin05, KC91, Pow81] guarantees that every continuous function on $[a, b]$ can be uniformly approximated by polynomials; this is a much larger class of functions with respect to those analytical on $[a, b]$.

⁴The theory of Gaussian quadrature guarantees that the weights W_i are all positive [Eva93] (see also eq. 4.14), so our definitions are well-posed.

Finally, we remark that if one computed the matrix elements exactly in the VBR and then moved to the DVR basis set transforming the matrix then no further approximations would be introduced and VBR and DVR would be equivalent. That is, the exact representation of $\mathbf{V}^{\text{VBR}}$ in the DVR representation would be

$$\mathbf{V}^{\text{DVR-VBR}} = \mathbf{T}^\dagger \mathbf{V}^{\text{VBR}} \mathbf{T} \neq \mathbf{V}^{\text{FBR}} \quad (4.25)$$

This matrix will not be diagonal, but as the basis set set functions are very localised off-diagonal elements are expected to be small. However, the whole point of using the DVR is to avoid computing the integrals so this is not ordinarily done in practice.

On the other hand a transformation from VBR to DVR is usually performed for the kinetic energy matrix $\mathbf{K}$, which is generally easy to calculate, sometimes even analytically, using the ‘diffuse’ basis functions.

Product approximation viewpoint

We will now discuss a different viewpoint to the DVR approach which has three advantages: first, is useful in practical applications, second, it provides further insight to the approximation introduced and, third, it suggests how other classes of DVR’s, not directly connected to Gaussian quadrature schemes, may be introduced.

We will start by the observation that, because an N -point Gaussian rule exactly integrates polynomials up to $2N - 1$, the matrix representation of the position operator x will be computed exactly in this case:

$$\mathbf{X}^{\text{VBR}} = \mathbf{T}^\dagger \mathbf{X}^{\text{DVR}} \mathbf{T} \quad (4.26)$$

where $\mathbf{X}^{\text{DVR}}$ is the diagonal matrix containing the abscissae points x_α . This relation means that the transformation $\mathbf{T}$ exactly diagonalises the exact (i.e., VBR) coordinate matrix and that therefore the DVR points and basis functions are nothing but the eigenvalues and eigenvectors of $\mathbf{X}^{\text{VBR}}$. This fact is well-known in numerical analysis where the matrix $\mathbf{X}^{\text{VBR}}$ is known as the terminal or Jacobi matrix, see e.g. [Eva93] pag. 46. This observation provides a very practical way of obtaining the Gaussian quadrature points x_α and the transformation matrix $\mathbf{T}$ by building and then diagonalising $\mathbf{X}^{\text{VBR}}$. In particular, because of the three-term recurrence relation all orthogonal polynomials obey, $\mathbf{X}^{\text{VBR}}$ is a tridiagonal matrix and its eigenvalues and eigenvectors can be found efficiently by various algorithms [BGT05, PTVF07].

This point of view shows explicitly that it is reasonable to conjecture that, in the limit of $N \rightarrow +\infty$, the DVR basis set functions should approach perfectly localised Dirac-delta functions, as these are the true (generalised) eigenfunctions of the position operator x . We may remark that a rigorous treatment of this point would be much more involved as we are trying to approximate an unbounded operator, x , with a succession of bounded operators, $\mathbf{X}$, and this would require a precise specification of the topology in which the convergence is evaluated. See e.g. the article of de la Madrid [dlM05] and appendix 4.7 of the book by Peres [Per95] for a flavour of how such a rigorous treatment might be formulated.

Viewing the DVR basis set as constituted by the eigenfunction of the position matrix $\mathbf{X}^{\text{VBR}}$ is the original procedure used by Harris *et al.* [HEG65] and provides an alternative and complementary way of looking at the DVR approximation introduced in the Gaussian-quadrature viewpoint by eqs. (4.18) and (4.23), namely computing all integrals using an N -point Gaussian

quadrature rule. More specifically, we will show that approximation (4.18) is equivalent to the assumption that the matrix $\mathbf{V}^{\text{VBR}}$ can be approximately given by

$$\mathbf{V}^{\text{VBR}} \approx V(\mathbf{X}^{\text{VBR}}) = \mathbf{V}^{\text{FBR}} \quad (4.27)$$

where $V(\mathbf{X}^{\text{VBR}})$ indicates we plug the matrix $\mathbf{X}^{\text{VBR}}$ as an argument of the function $V(x)$; if $V(x)$ is given by the polynomial expansion (4.19) then

$$V(\mathbf{X}^{\text{VBR}}) = \sum_{p=0}^{+\infty} c_p (\mathbf{X}^{\text{VBR}})^p \quad (4.28)$$

where the powers $(\mathbf{X}^{\text{VBR}})^p$ are given by p -times matrix products.

We showed that $\mathbf{X}^{\text{VBR}}$ is diagonal in the DVR basis, eq. (4.26), from which it follows that

$$(\mathbf{X}^{\text{VBR}})^p = (\mathbf{T}^\dagger \mathbf{X}^{\text{DVR}} \mathbf{T})^p = \mathbf{T}^\dagger (\mathbf{X}^{\text{DVR}})^p \mathbf{T} \quad (4.29)$$

As $\mathbf{X}^{\text{DVR}}$ is a diagonal matrix its p -th power is just the diagonal matrix containing the p -th powers of its elements. Putting together the results of eqs. (4.28) and (4.29) it follows

$$V(\mathbf{X}^{\text{VBR}}) = \mathbf{T}^\dagger \left(\sum_{p=0}^{+\infty} c_p (\mathbf{X}^{\text{DVR}})^p \right) \mathbf{T} = \mathbf{T}^\dagger \mathbf{V}^{\text{DVR}} \mathbf{T} \quad (4.30)$$

This shows that the approximation introduced by eq. (4.27) is exactly the same as the one introduced in the Gaussian quadrature viewpoint by eq. (4.18). However, in view of further developments, we will now show how the approximation introduced by eq. (4.27) can be analysed from a different viewpoint than quadrature rules. It follows from eq. (4.28) that the approximation must be ascribed to the fact that, if $p \geq 2$

$$(\mathbf{X}^{\text{VBR}})_{ij}^p \neq \langle f_i | x^p | f_j \rangle \quad (4.31)$$

This equivalence is approximate because $\mathbf{X}^{\text{VBR}}$ is a finite matrix; as the basis set increases, it becomes an exact relation. Let us illustrate this in the case $p = 2$.

The resolution of identity (RI) relation is

$$\sum_{\alpha=1}^{+\infty} |f_\alpha\rangle \langle f_\alpha| = \mathbf{I} \quad (4.32)$$

Inserting the RI between the products of x :

$$\begin{aligned} \langle f_i | x^2 | f_j \rangle &= \langle f_i | x \mathbf{I} x | f_j \rangle = \langle f_i | x \left(\sum_{\alpha=1}^{+\infty} |f_\alpha\rangle \langle f_\alpha| \right) x | f_j \rangle = \\ &= \sum_{\alpha=1}^{+\infty} \langle f_i | x | \alpha \rangle \langle \alpha | x | f_j \rangle \end{aligned} \quad (4.33)$$

On the other hand, if we compute the same matrix element by matrix products

$$(\mathbf{X}^{\text{VBR}})_{ij}^2 = (\mathbf{X}^{\text{VBR}} \mathbf{X}^{\text{VBR}})_{ij} = \sum_{\alpha=1}^N \langle f_i | x | f_\alpha \rangle \langle f_\alpha | x | f_j \rangle \quad (4.34)$$

so that expressions (4.33) and (4.34) differ; the reason can be viewed as due to the fact that in (4.34) we used a truncated form of the RI which includes only N basis set functions. The

two expressions, however, will become equal as $N \rightarrow +\infty$ if the basis set is complete. The same rationale holds for the p -th powers, where the DVR approximation can be seen as due to the $(p-1)$ -times insertion of a truncated RI. As the approximation is employed many times, it follows that the error for high powers of x will be larger. This point of view is called the ‘product approximation viewpoint’ because the error introduced in the DVR representation is ascribed as originating from eq. (4.31), that is from replacing the exact matrix representation for products of the coordinate operator, $\langle f_i | x^p | f_j \rangle$, with products of the matrix representation of the coordinate, $\mathbf{X}_{ij}^p$.

4.4.4 Other ways of defining DVR’s

The product-approximation viewpoint makes it easy to introduce DVR’s which are not directly linked to Gaussian quadrature. If the starting ‘diffuse’ basis set functions were of a form different from that specified by eq. (4.16), namely, of a polynomial times the square root of a weight function, then the product approximation scheme of taking as localised DVR basis the eigenfunctions of the position matrix $\mathbf{X}^{\text{VBR}}$ would not be equivalent to any Gaussian quadrature scheme. Still, in the limit of $N \rightarrow +\infty$, the DVR approximation still becomes exact if the ‘diffuse’ basis set approaches completeness. Furthermore, it is not even strictly necessary to take the eigenfunctions of $\mathbf{X}^{\text{VBR}}$ as the DVR basis; for example, also the (generalised) eigenfunctions of x^2 tends to delta functions, as in general the eigenfunctions of x^p ; diagonalising their respective matrices will result in other possible DVR’s.

It is also possible to introduce a set of DVR basis functions and of DVR points at the onset and then work out the transformation matrix $\mathbf{T}$; for example, a DVR of this kind is the ‘sinc’ DVR proposed by Colbert and Miller [CM92], where the DVR points x_α are chosen on a equispaced grid with grid spacing Δx and the respective DVR functions are given by

$$\theta_\alpha(x) = \frac{\sin(\pi t / \Delta x)}{\pi t} \quad \text{where} \quad t = (x - x_\alpha) \quad (4.35)$$

We refer to the review by Light and Carrington [LC00] and references therein for more details on these more general approaches.

4.4.5 An example: harmonic-oscillator wave functions

Consider the one-dimensional harmonic oscillator Hamiltonian [Gri04, CTDL77, Sha94]

$$\hat{H}_0 = \hat{K} + V = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega^2 x^2 \quad (4.36)$$

The normalised eigenfunctions of the harmonic oscillator Hamiltonian are the given by

$$\psi_n(x) = \sqrt{\frac{\alpha}{2^n n! \sqrt{\pi}}} e^{-\frac{\alpha^2 x^2}{2}} H_n(\alpha x) \quad \text{where} \quad \alpha = \sqrt{\frac{m\omega}{\hbar}} \quad (4.37)$$

and $H_n(t)$ are Hermite’s polynomials. The matrix elements of the position operator can be easily obtained either from the three-term recurrence relation the H_n obey or using the destruc-

tion/creation operators a and $a^\dagger$ [Gri04, CTDL77, Sha94]. The final result is

$$\mathbf{X} = \frac{1}{\alpha\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 & 0 & \cdots \\ 1 & 0 & \sqrt{2} & 0 & \cdots \\ 0 & \sqrt{2} & 0 & \sqrt{3} & \cdots \\ 0 & 0 & \sqrt{3} & 0 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \quad (4.38)$$

We report as Figure 4.4.5 some plots of the first nine wave functions ($n = 0, \dots, 8$) of the harmonic oscillator, representing the diffuse or VBR basis functions, and the corresponding DVR basis functions obtained by diagonalising the position matrix $\mathbf{X}$.

4.4.6 The DVR method and the variational principle

If the DVR approximation is done the variational character of the eigenvalues is lost and the eigenvalues obtained can be lower than their true value. However, in many practical situations the error due to basis set incompleteness dominates over the error due to the DVR approximation, so that DVR eigenvalues are often very close to being variational [LC00, Ten00, LHL85]. It is also possible [LBK04, BLK04] to use a wave function produced by a DVR calculation ψ_{DVR} as variational trial wavefunction calculating $\tilde{E} = \langle \psi_{\text{DVR}} | \hat{H} | \psi_{\text{DVR}} \rangle$. $\tilde{E}$ is, contrary to the DVR energy E_{DVR} , an upper bound to the true energy and may also enjoy an improved convergence behaviour.

4.4.7 DVR's in many dimensions

Even if it is not apparent from the previous discussion the real advantage of the DVR technique is manifested only in many dimensions. In one dimension simple grid-based approaches, see e.g. [ABC05], are ultimately more efficient. One of the main advantages of the DVR approach is that the resulting matrices are very sparse and so specialised, efficient algorithms can be applied [LC00]. Another advantage of the DVR approach is that it is very convenient for truncation/diagonalisation schemes such as those introduced by Tennyson *et al* [Ten86].

The simplest way of introducing multi-dimensional DVR's is as direct-products of one-dimensional DVR's for each coordinates. For example, in the case of three dimensions (r_1, r_2, θ) one can build the one-dimensional DVR localised basis functions in each dimension and then use as basis function all the possible products of one-dimensional basis functions. The three-dimensional DVR grid will similarly given by the Cartesian product of the three one-dimensional ones. For more detail see [LC00, LHL85].

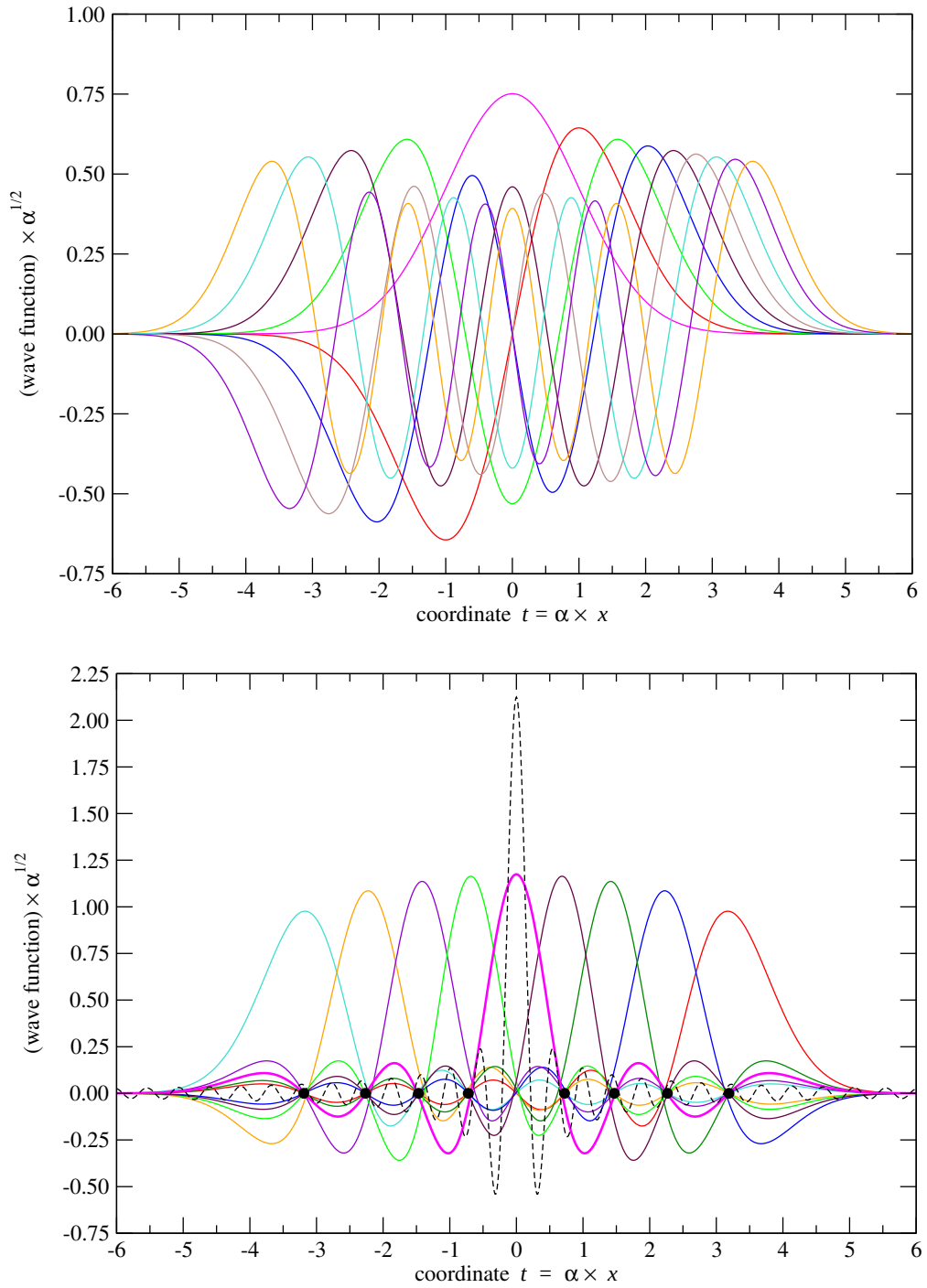


Figure 4.1: First figure: the first nine wave functions ($n = 0, \dots, 8$) of the harmonic oscillator. Second figure: the corresponding DVR basis; as an example, the basis functions corresponding to the DVR point $x = 0$ is in bold; the dashed line is the DVR basis function for the same point $x = 0$ but obtained from a much larger basis comprising the first 100 harmonic oscillator wave functions; it can be seen that it is much more strongly localised. The DVR grid points (i.e., Gauss-Hermite quadrature points) are reported along the abscissae axis.

Building molecular hypersurfaces

As expounded in the preceeding chapters the calculation of vibration-rotation line positions and intensities requires the knowledge of the molecular potential energy surface (PES) and dipole moment surface (DMS). It is possible in some applications to compute PES or DMS values on-the-fly as they are needed [ÖD01, WR02]. This is unfeasible in our case because the electronic structure methods we are interested in are far too slow to be used in this way. Another possibility [ST86] is to pre-compute the PES or DMS for all the geometries where its value will be needed, for example at all the quadrature points of a DVR grid. Again, this is highly unpractical because, first, the number of points to be calculated is too large and, second, any change in the grid would require the calculation of a whole new set of values.

The standard practice is to compute the surface for a set of geometries and then to build a full surface from these values. This approach falls into a well-know area of numerical analysis generally called *function approximation* or *function interpolation*, see e.g. the books by Conte and de Boor [CdB80], Kincaid and Cheney [KC91], Powell [Pow81] and Press *et al* [PTVF07] for some general introductions. We will generically call this process *surface building*. In one dimensional problems it is common to differentiate between ‘interpolation’ and ‘extrapolation’; this distinction cannot however be precisely defined in many dimensions and we will not use it.

Some basic questions to be answered are:

1. What accuracy is needed for the PES and DMS?

The next logical step is to set up a procedure to achieve the target accuracy in the most economical way. Two related questions to this end are:

2. How should an optimal set of geometries be chosen?
3. How should the surface be built from these discrete values?

We will discuss some possible strategies, along with a general introduction to the main features of molecular potential surfaces, in the remainder of this chapter.

5.1 Molecular potential surfaces

In this section some features specific to molecular potential energy surfaces will be reviewed. For more information see the book by Murrell *et al* [MCF⁺84] and the review by Sutcliffe [Sut03c].

5.1.1 The Wigner-Witmer correlation rules

Let us consider the water molecule H_2O . At the equilibrium geometry the electronic ground-state is a spin singlet. Now move away the oxygen atom until the two subsystems H_2 and O are very far apart from each other, letting the two hydrogens relax to their equilibrium distance as the oxygen is pulled away. Naively, one would expect the total energy to approach the sum of the ground state energies of the two fragments, namely one hydrogen molecule and one oxygen atom. However, this assumption raises an apparent paradox. The electronic ground state of the hydrogen molecule is a spin singlet with term $^1\Sigma_g^+$, while the electronic ground state of the oxygen atom is a spin triplet with term symbol ^3P and hence with spin one. By the rules of angular momentum addition [Tho94] it follows that the total angular momentum of the composite system $\text{H}_2(^1\Sigma_g^+)+\text{O}(^3\text{P})$ must have total spin $S = 1$ and hence be a spin triplet. But how can this be if the initial state had $S = 0$? Spin can only assume discrete values so the wave function of the system could not have gone from $S = 0$ to $S = 1$ with continuity: something must have happened in between. What happens in actual fact is that, as the oxygen atom is pulled away, at a certain point an electronically excited state with total spin one crosses the ground state curve and becomes lower in energy. It is *this* state which smoothly dissociates into $\text{H}_2(^1\Sigma_g^+)+\text{O}(^3\text{P})$, while the original curve leads instead to the state $\text{H}_2(^1\Sigma_g^+)+\text{O}(^1\text{D})$ where the oxygen atom is in an excited state. This situation is expressed by saying that the ground state electronic state of water does not correlate with $\text{H}_2(^1\Sigma_g^+)+\text{O}(^3\text{P})$.

This example is one instance of the application of the Wigner-Witmer correlation rules. For any electronic state of a molecule these rules predict the possible symmetries of the electronic states of the fragments into which said molecule may smoothly dissociate into. The rules are briefly discussed in the book by Murrell *et al* [MCF⁺84] and in more detail in the books by Zare [Zar88] and Landau and Lifshitz [LL81]. See also the articles by Pechukas and Zare [PZ72], Chiu [Chi73] and Bellary *et al* [BBS98].

5.1.2 Surface crossings

As we hinted in the previous section molecular potential energy surfaces may cross at some nuclear geometries. For states having the same symmetry, both spin and spatial, a special “non-crossing” rule holds. For an in-depth discussion of this rule see the reviews by Sutcliffe [Sut03c] and Yarkony [Yar99] and the article by Mead [Mea79]. For electronic states with different symmetry no special limitation on the possible crossings exist.

The non-crossing rule was initially derived for diatomic molecules, in which case it states that curves having the same symmetry cannot cross at all, whence its the name. For a molecule with $N \geq 3$ atoms the rule states that two potential surfaces with the same symmetry may cross only along a $(3N - 8)$ -dimensional manifold. For a triatomic molecule hence potential surfaces may cross along a one-dimensional curve or touch at a single point.

When a crossing does occur it generally indicates that the adiabatic separation of nuclear and electronic motions is not a good approximation. Various strategies for dealing with this situation are possible, for a discussion see the reviews by Yarkony [Yar00, Yar99] and Sutcliffe [Sut03a] and the book by Baer [Bae06].

The correlation rules and the non-crossing rule can be used to build a *correlation diagram*

which shows into which fragments an electronic state may smoothly dissociate. Such diagrams relative to water are reported e.g. by Shuler [Shu53], Tsurubuchi [Tsu75] and, in a simplified but more readable form, by Howard *et al* [HML79]. See also chap. 9 of the book by Murrell *et al* [MCF⁺84] for a discussion.

5.1.3 The many-body expansion

A many-body expansion representation of the PES [MCF⁺84, ATP98] can be conveniently applied to a triatomic molecule to incorporate the correct asymptotic dissociation limits. Consider a triatomic system with atoms A_1 , A_2 and A_3 with internuclear distances r_{12} , r_{23} and r_{13} . We define the *one-body* term $V^{(1)}$ as the sum of the atomic energies when the all atoms are infinitely distant from each other and in the appropriate electronic state:

$$V^{(1)} = V_1 + V_2 + V_3 \quad (5.1)$$

The one-body term $V^{(1)}$ can be taken as representing the energy of the system in the absence of mutual interactions. The *two-body* term is defined as the sum of all pair interactions, shifted so that they tend to zero at infinity:

$$V^{(2)} = [V_{12}(r_{12}) - V_1 - V_2] + [V_{23}(r_{23}) - V_2 - V_3] + [V_{13}(r_{13}) - V_1 - V_3] \quad (5.2)$$

where V_{ij} is the potential curve of the diatom A_iA_j . Finally, we define the *three-body* term as the difference between the total energy of the triatom $V(r_{12}, r_{23}, r_{13})$ and the one- and two-body terms

$$V^{(3)} = V(r_{12}, r_{23}, r_{13}) - V^{(2)} - V^{(1)} \quad (5.3)$$

The three-body term $V^{(3)}$ can be understood as that part of the total energy which is genuinely due to three-body interactions. Note that from this definition it follows that $V^{(3)} \rightarrow 0$ when any of the interparticle distances becomes sufficiently large.

With these definition we can then trivially re-write the exact potential surface of the triatom V as a sum of one, two and three body contributions:

$$V = V^{(1)} + V^{(2)} + V^{(3)} \quad (5.4)$$

We will now explain how this expansion is used in practice in the surface-building process. What is known at the beginning of the surface-building is the value of V corresponding to a set of geometries. One then calculates or estimates the one- and two-body contributions after which the value of the three-body term at the known geometries is calculated by eq. (5.3). The surface-building process is then applied not directly to V but to $V^{(3)}$, with the constraint that it should vanish when any of the internuclear distances r_{ij} goes to infinity. In this way the resulting PES is guaranteed by construction to incorporate the correct asymptotic limits upon dissociation of all the possible fragments.

For spectroscopic purposes it is generally convenient to use a potential $\tilde{V}$ shifted so that the zero-energy corresponds to the equilibrium configuration of the triatom $(r_{12}^{\text{eq}}, r_{23}^{\text{eq}}, r_{13}^{\text{eq}})$. This can

be achieved by a redefinition of the terms:

$$\begin{aligned}
 \tilde{V}^{(1)} &= -V(r_{12}^{\text{eq}}, r_{23}^{\text{eq}}, r_{13}^{\text{eq}}) \\
 \tilde{V}^{(2)} &= V^{(2)} \\
 \tilde{V}^{(3)} &= V(r_{12}, r_{23}, r_{13}) - V^{(2)} \\
 \tilde{V} &= \tilde{V}^{(1)} + \tilde{V}^{(2)} + \tilde{V}^{(3)}
 \end{aligned} \tag{5.5}$$

5.2 One dimensional curve-building

Function approximation, like many other numerical problems, disproportionately increases in complexity as the number of dimensions increases. Before dealing with the multi-dimensional case we will present some considerations and numerical experiments in one spatial dimension. One-dimensional function approximation is treated in most textbooks on numerical analysis, see e.g. [CdB80, KC91, Pow81, PTVF07]. A review focusing on applications of splines in physics was recently given by Bachau *et al* [BCD⁺01] and many details on practical implementation of interpolation and fitting schemes can be found in the manual of the NAG Fortran library [NAG].

5.2.1 Choice of the curve-building method

Most standard results in approximation theory [CdB80, KC91] concern interpolation with a single, high-order polynomial; this is however hardly ever done in practice because spurious oscillations between data points often arise (Runge's phenomenon [KC91, PTVF07]).

More workable choices are interpolation with piece-wise polynomials (including splines) or, especially if the data set of points is small ($N_{\text{points}} \lesssim 10$), least-square fits to an opportune functional form, usually involving polynomials.

5.2.2 Choice of the grid

The problem of defining an optimal grid is another classical problem of approximation theory; in the case of interpolation with a single polynomial the Chebyshev nodes represent the optimal choice [CdB80, Pow81, KC91] if no other information is known about the function to be approximated.

Optimal grid placement for piece-wise polynomial interpolation (including splines) has received some attention in the mathematical literature but there seem to be no general result of immediate practical use [Lin03, Mul92, MNSS89, Jup78, Bur77, PS75, Bra71]. A result of this kind is [Dod72, Dod]

Theorem 5.2.1 *For an appropriately smooth $f : [a, b] \rightarrow \mathbb{R}$, for error measured in the L^p norm, $1 \leq p \leq +\infty$, approximating f by polynomial spline functions of order n (degree $n - 1$) with $k - 1$ free knots, let $\sigma = 1/(n + 1/p)$, and let t_i , $i = 1, 2, \dots, k - 1$, be such that*

$$\int_a^{t_i} |f^{(n)}(x)|^\sigma dx = \frac{i}{k} \int_a^b |f^{(n)}(x)|^\sigma dx \tag{5.6}$$

where $f^{(n)}$ denotes the n -th derivative of f . Then as $k \rightarrow +\infty$, the order of approximation is optimal.

This result can also be stated by saying that, in the limit of $k \rightarrow +\infty$, the (unnormalised) optimal density of points is given by $|f^{(n)}(x)|^\sigma$. The main problem with this kind of estimates is that they require the knowledge of some high-order derivative of the function to be approximated, e.g. $f^{(4)}(x)$ for cubic splines, which in most practical cases is not available nor can be easily estimated.

More practical schemes for optimal grid placement adopt iterative schemes where the position of each grid point is considered as a non-linear parameters to be optimised. We will present a numerical experiment with a method of this kind in Section 5.2.4.

5.2.3 Choice of the interpolation variable

Most forms of interpolation or fitting are based on polynomials: given a data set (r_i, f_i) the interpolating or fitting function has the form of a (possibly piece-wise) polynomial in r . Polynomials are entire functions and have difficulties in approximating functions with singularities, even if these singularities do not lie on the real axis but in the complex plane; a famous example of this kind is given by the Runge function $1/(1 + 25x^2)$ [KC91] on the interval $[-5, 5]$. Polynomials also have difficulties with functions that grow faster or slower than polynomially, like respectively e^x and $\log(x)$.

If the form of the function f is such that polynomials are supposed to have difficulties in describing it, changing the interpolation basis from r^n to $g(r)^n$ can be of help. This can be easily attained by applying the function g to all abscissae and then interpolating the set $(g(r_i), f_i)$. The purpose of this transformation of variable is to try to eliminate singularities and other non-polynomial behaviours, so that the transformed data set can then be approximated more efficiently.

Potential energy curves of diatoms $V(r)$ are singular at $r = 0$ and go to a constant value for $r \rightarrow +\infty$ and both of these behaviours are unnatural for polynomials. On the other hand, the function $F(r) = V(1/r)$ is more well behaved: it goes to a constant for $r = 0$ and goes to infinity linearly at infinity. In might then be expected that interpolating $F(r)$ instead of $V(r)$ may lead to better results. Another strategy to eliminate the singularity is not to change the variable r but to interpolate $F(r) = r^2 V(r)$. Also in this case F is not singular at $r = 0$ and goes to infinity as r^2 for $r \rightarrow +\infty$.

These considerations are largely euristical and dictated by numerical experience. We have found no rigorous studies of this kind of stratagems in the mathematical literature. They are however commonly employed in the fit of diatomic energy curves, see e.g. Wilson [Wil92b].

Proposed interpolation variables and conclusions Over the years a large set of expansion variables have been proposed for diatomic molecules, see e.g. the review by Wilson [Wil92b] and chapter 3 of the thesis by Huang [Hua01] for more details. A selection of these is (r_e is the equilibrium distance)

1. Durnham [Wil92b, Hua01, Ogi98]: $\varrho = \frac{r - r_e}{r_e}$
2. Fougere and Nesbet¹ [Wil92b]: $\varrho = \frac{r - r_e}{r}$

¹Often attributed to Simons, Parr and Finlan

3. Beckel [Bec76, Wil92b]: $\varrho = \frac{r - r_e}{r + r_e}$
4. Šurkus [Hua01]: $\varrho = \frac{(r)^p - (r_e)^p}{(r)^p + (r_e)^p}$
5. Seto [Hua01, Set00]: $\varrho = \frac{(r)^p - (r_e)^p}{a_S(r)^p + b_S(r_e)^p}$
6. Morse [Var57]: $\varrho = 1 - e^{-\alpha(r-r_e)}$
7. Rydberg [Var57, ATP98]: $\varrho = r e^{-\alpha r}$

The original reason for introducing most of these variables was for use in approximate perturbative treatments of the vibration-rotation energies [Bec76] where the expansion variable is assumed to stay close to zero in the region of interest of the potential energy curve. If the transformed variables are merely used for fitting or interpolation of the whole surface their usefulness is reduced. If all terms ϱ^i up to a maximum ϱ^N are included in the fit or interpolation, as it is usually done, then Durnham's form 1 is equivalent to a plain expansion in powers of r , expansion 2 is equivalent to an expansion in powers of $1/r$ and expansion 6 is equivalent to an expansion in powers of $e^{-\alpha r}$.

5.2.4 Some experiments with one-dimensional interpolation

Morse potential We performed a first experiment approximating a Morse potential

$$V(r) = D_e(1 - e^{-\alpha(r-r_e)})^2 \quad (5.7)$$

the parameters of the potential were chosen to roughly approximate the O–H stretching in water [BSZ⁺06]: $r_e = 1.81 \text{ a}_0$, $\alpha = 1.25 \text{ a}_0^{-1}$, $D_e = 43,000 \text{ cm}^{-1}$.

For the fits we used the NAG routine E02BEF [NAG]. This routine takes as input a set of points (r_i, E_i) and a target root-mean-square error S . The routine then iteratively tries to find the smallest set of knots that gives the requested error S . Setting $S = 0$ performs traditional cubic spline interpolation. The knots are the points where the cubic polynomials that make up the spline join; for spline fits they do not generally coincide with any of the input points.

The input data set was a very dense grid of 1,000 points equispaced in $1 \leq r \leq 10 \text{ a}_0$. All points were given the same weight. We report two indicative plots of the errors in Figure 5.1. The first plot was obtained interpolating the original set (r_i, E_i) while the second $(1/r_i, E_i)$. The position of the knots can be inferred from the dips in the curves.

Looking at the plots one can see that the density of knots optimised by the routine is higher in regions where the potential varies very much and is smaller in the long-range region where the potential is nearly constant. This can be contrasted with the optimal grid point distribution as evaluated by Theorem 5.2.1, which in the case of a Morse potential can be computed analytically and is reported as Figure 5.2.

We also investigated the effect of a change of variable on the quality of the fit. Apart from fitting directly the dataset (r_i, E_i) we also used the same fitting procedure but applied to the sets $(1/r_i, E_i)$ and $(r_i, r_i^2 E_i)$. The numerical results for the RMS errors $\varepsilon_{\text{RMS}} = \sqrt{\sum \varepsilon_i^2 / N}$ are reported in Table 5.1 and some significant plots are presented as Figure 5.1.

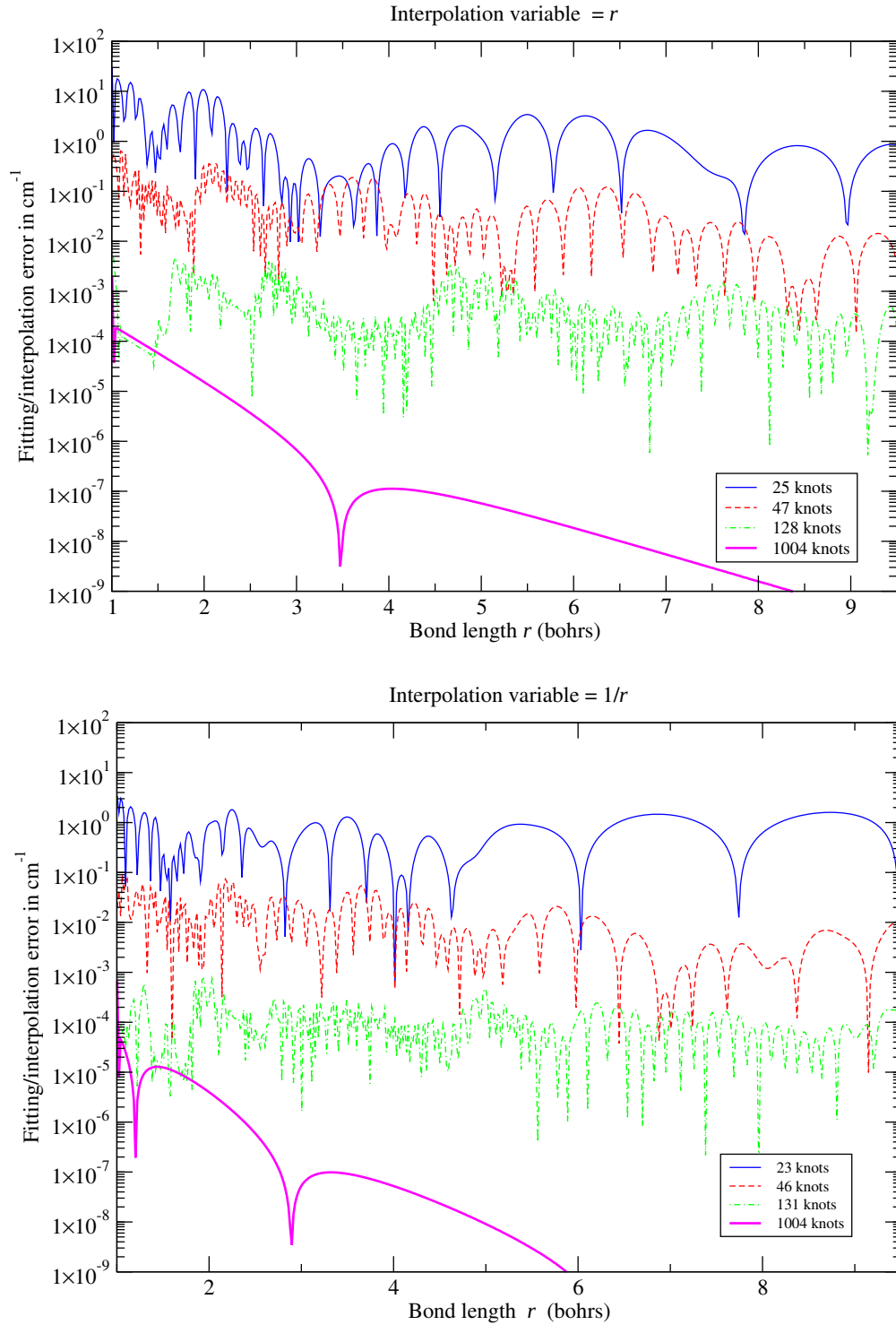


Figure 5.1: Plot of the errors of a fit of a Morse potential using cubic spline fits with various numbers of knots. The quantity plotted is the difference between the spline functions and the exact Morse function in between the points used for the fit. The first figure refers to a fit to (r_i, E_i) , the second to $(1/r_i, E_i)$ (see text).

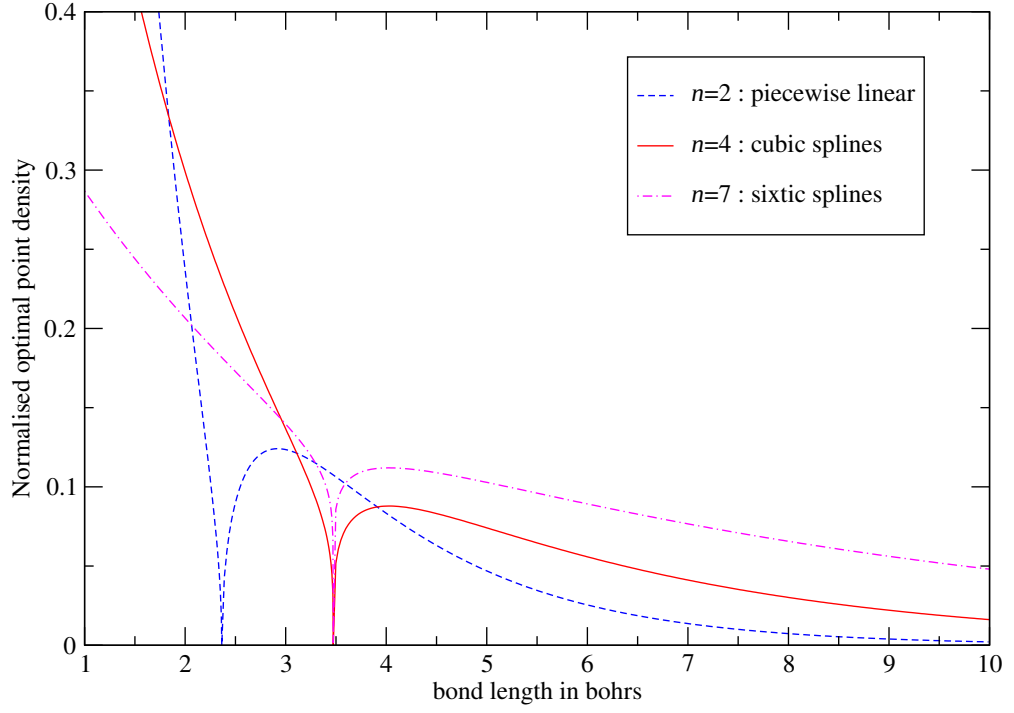


Figure 5.2: Optimal grid point density for an interpolation of the Morse potential (5.7) for $1 \leq r \leq 10$ with cubic splines (see text).

Fitted set	knots	RMS in cm^{-1}
$r, E(r)$	25	3.1
$r, E(r)$	47	9.6×10^{-2}
$r, E(r)$	128	9.8×10^{-4}
$r, E(r)$	1004	9.8×10^{-5}
$r^{-1}, E(r)$	23	9.9×10^{-1}
$r^{-1}, E(r)$	46	1.7×10^{-2}
$r^{-1}, E(r)$	131	1.7×10^{-4}
$r^{-1}, E(r)$	1004	3.0×10^{-5}
$r, r^2 E(r)$	23	4.6
$r, r^2 E(r)$	46	1.2×10^{-1}
$r, r^2 E(r)$	127	8.7×10^{-4}
$r, r^2 E(r)$	1004	3.9×10^{-5}

Table 5.1: Table of the RMS errors for the interpolation of a Morse potential $V(r)$ for $1 \leq r \leq 10$ using cubic splines with various numbers of knots (see text).

Looking at the data one can see that the $r^2E(r)$ set gave results only slightly better than the plain (r, E_i) one; on the other hand, the $1/r$ one gave a fit quality improved by a factor of 3 to 6. The conclusion of this small study is that, for interpolation with cubic splines, interpolating the transformed $(1/r_i, E_i)$ data sets improves the quality of the approximation.

Looking at Figure 5.1 and at Table 5.1 we can also conclude that, using cubic spline interpolation a grid of about 25 suitably placed points gives an accuracy of the order of 1 cm^{-1} , while 130 points should give an overall accuracy of about $2 \times 10^{-4} \text{ cm}^{-1}$.

O–H stretching curve A second numerical experiment was performed by interpolating the real O–H stretching curve in water to see if the conclusions of the previous study using the Morse oscillator carry over to a more realistic situation. We fixed the bond angle and one bond length r_1 to the equilibrium values $\theta = 104.5^\circ$ and $r_1 = 1.81 \text{ a}_0$ and then computed the curve relative to the stretching of the other bond. We used MOLPRO [WKL⁺02] to compute a total of 257 points equally spaced between $1.10 \leq r_2 \leq 7.5 \text{ a}_0$. The computation used the aug-cc-pVDZ basis set and the IC-MRCI method with the reference space labelled as [8, 8] in Table 6.2, using the frozen core approximation. Interpolation was performed using piece-wise polynomials [CdB80] of various orders $n = 2, \dots, 6$ using Mathematica [Mat07]. Four different interpolation variables were tried: r , $1/r$, $(r - r_e)/(r + r_e)$ and the Morse variable $(1 - e^{-\alpha(r-r_e)})$. The value of α in the Morse variable was fixed to $\alpha = 1.31 \text{ a}_0^{-1}$, the value obtained by a non-linear fit of a subset of data close to equilibrium with a single Morse potential. Two sets of interpolations were performed, a first using one point every six of the original grid (total of 43 points) and a second using one point every three of the original grid (total of 86 points). The quality of the interpolation was always assessed by looking at the error for points not included in the interpolation. Some indicative plots are reported as Figure 5.3.

The first conclusion is that, similar to the previous experiment, interpolating directly in the r variable always gives the worse results. The Morse variable gives better but less-than-optimal results. The other two variables tried, $1/r$ and $(r - r_e)/(r + r_e)$, gave generally comparable results, but $1/r$ performed better for short bond lengths, especially if low-order polynomials were used.

Our second conclusion is that the interpolation improves considerably with increasing order of the piece-wise polynomial, at least up to $n = 6$, the maximum order tried. This result implies that high-order interpolation increase the quality of the interpolation, as long as spurious oscillations do not arise. For the smaller set of 43 points we also considered a classical (i.e., not piece-wise) polynomial interpolation both in the r and $1/r$ variables. As expected, both interpolations show extreme oscillations between the data points of the order of 10^{17} cm^{-1} ; the polynomials in the $1/r$ variable was particularly unstable in this respect. There is, however, a small range approximately given by $3 \leq r \leq 6$ for the polynomial in the r variable where the interpolation was very good, with an RMS error of 10^{-3} cm^{-1} .

5.2.5 Sensitivity of energy levels and transition intensities to a small perturbation

It is straightforward to ascertain the quality of an approximate PES or DMS by some intrinsic test like computing the fitting error or the error for points not included in the interpolation

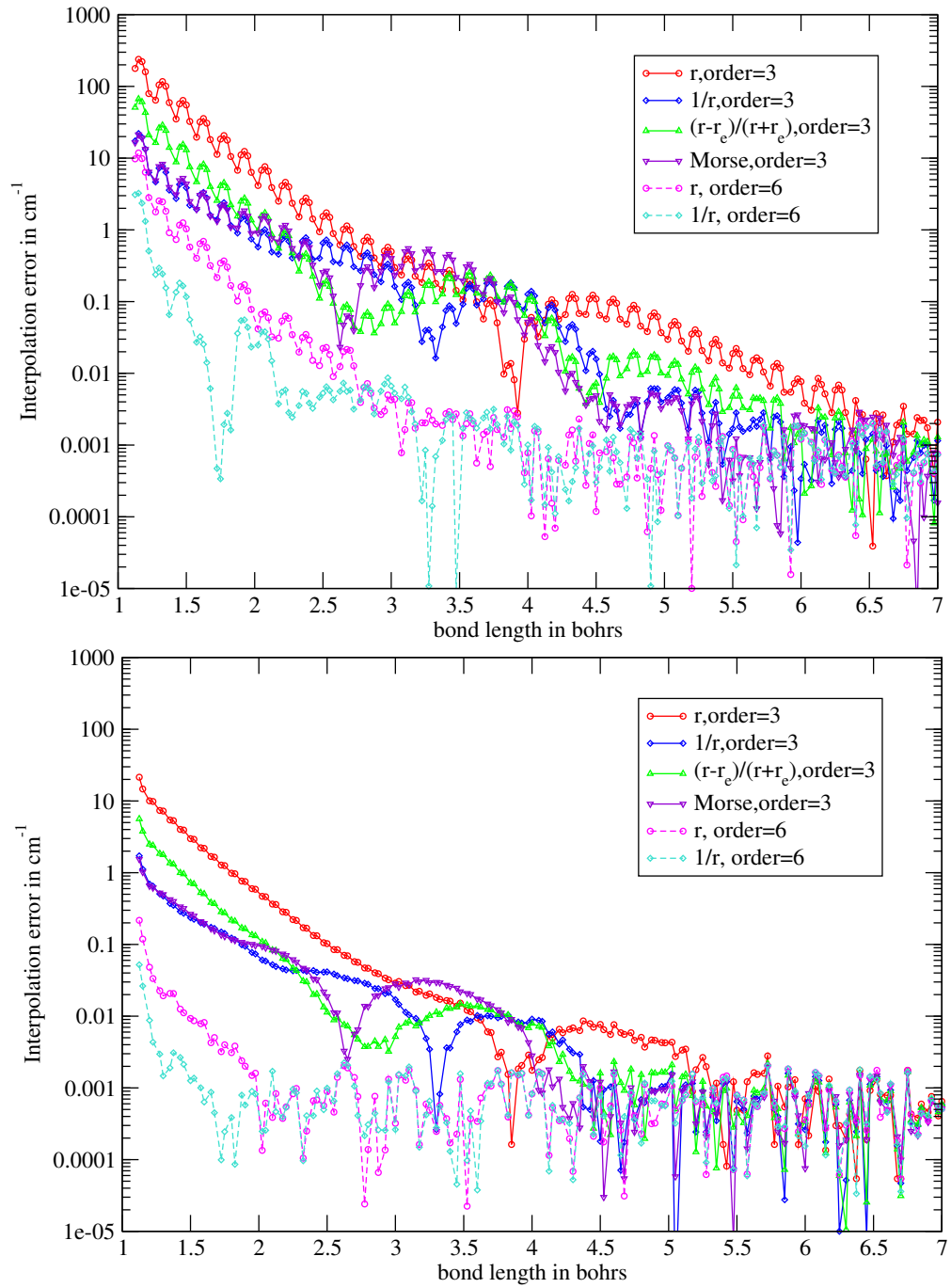


Figure 5.3: Plot of the errors in a fit of the O–H stretching curve in water using piece-wise polynomials of order three or six and various interpolation variables. The plot refers to equispaced grids in $1.1 \leq r \leq 7.5$, the first of 43 points and the second of 86 points (see text)

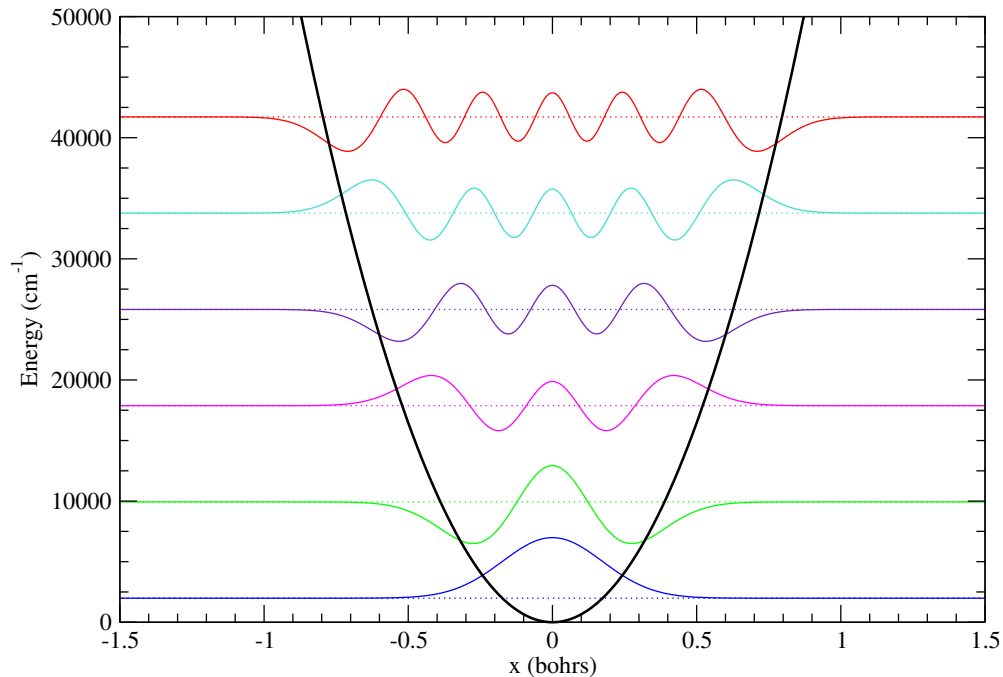


Figure 5.4: Plot of a harmonic potential $V(x) = \frac{1}{2}kx^2$ roughly modelling the O–H stretching in water ($k = 0.6 \text{ E}_h \text{ a}_0^{-2}$, $x = r - r_e$) and of some of its (unnormalised) even eigenfunctions ψ_n ($n = 0, 2, 4, 6, 8, 10$). The value of k was calculated from the potential surface by Barletta *et al* [BSZ⁺06]. Wave functions are translated upwards by their respective energy E_n . The purpose of the plot is to show that the wave functions are mostly concentrated in the classically-allowed region $V(x) < E_n$.

set (see e.g. section 6.4). However, the ultimate test of the quality of a surface should always be done comparing the convergence of properties calculated from it: in our case energy levels and transition intensities. We will use the simple harmonic oscillator as a model system to formulate some considerations on the sensitivity of energy levels and transition intensities to small perturbations in the PES and DMS.

Introduction

The quantum harmonic Hamiltonian and its normalised eigenfunctions were reported in Section 4.4.5. The energies of the system are given by [CTDL77]

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right) \quad n = 0, 1, \dots \quad (5.8)$$

where $\omega = \sqrt{\frac{k}{m}}$.

In classical mechanics the motion of a particle moving in an external potential is strictly confined to regions where $V < E$. In the quantum case wave function are not confined to the classically-allowed region where $V(x) < E_n$ but they are nonetheless mostly concentrated there. This can be quantitatively shown analytically for the case at hand but for our purposes it will suffice to look over Figure 5.4. As a wave function ψ is nearly zero outside the region

$V < E$ it follows that, if a perturbation potential W is introduced which is zero in this region, ψ will approximately be an eigenfunction also of the perturbed Hamiltonian $\hat{H}' = \hat{H} + W$. This consideration leads to a very simple but important guideline: a vibration-rotation wave function with energy E is mostly determined by the shape of the PES $V(x)$ in regions where $V(x) \lesssim E$. Naturally, there are situations (tunnelling, resonances) where this simple assumption is not true, but it certainly holds for rotation-vibration states of strongly bound molecules far away from dissociation.

Form of the perturbation

We will study the effect of an oscillating perturbation on the energy levels and transition intensities. We introduce a perturbation

$$W(x) = A \cos(\omega x) \quad (5.9)$$

which can be thought as being added to either the PES or DMS. We assume that the amplitude A is small with respect to the harmonic potential $V(x)$. In the following we show how matrix elements of the type $\langle \psi_n | W | \psi_m \rangle$ can be calculated analytically.

Mathematical preliminaries The Fourier transform operator $\mathcal{F}$ and its inverse $\mathcal{F}^{-1}$ are defined by [AW05]:

$$\begin{aligned} (\mathcal{F}f)(\omega) &= \hat{f}(\omega) = \int_{-\infty}^{+\infty} f(t) e^{-i\omega t} dt \\ (\mathcal{F}^{-1}\hat{f})(t) &= f(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \hat{f}(\omega) e^{i\omega t} d\omega \end{aligned} \quad (5.10)$$

Hermite functions are eigenfunctions of $\mathcal{F}$ with eigenvalue $(-i)^n$ [Wikd]:

$$(\mathcal{F}\psi_n)(\omega) = (-i)^n \psi_n(\omega) \quad (5.11)$$

The convolution of two function $f * g$ is defined by

$$(f * g)(t) = \int_{-\infty}^{+\infty} f(\tau) g(t - \tau) d\tau \quad (5.12)$$

and the convolution theorem is

$$[\mathcal{F}(fg)](\omega) = (\hat{f} * \hat{g})(\omega) \quad (5.13)$$

Matrix elements The matrix elements of $W(\omega)$ can be written, assuming $(n + m)$ even (the matrix element is otherwise zero by symmetry), as

$$\begin{aligned} \langle \psi_n | W | \psi_m \rangle / A &= \int_{-\infty}^{+\infty} \psi_n(\alpha x) W(\omega x) \psi_m(\alpha x) dx = \mathcal{F}(\psi_n \psi_m)(\omega) = \\ &= [\mathcal{F}(\psi_n) * \mathcal{F}(\psi_m)](\omega) = (-1)^{\frac{n+m}{2}} (\psi_n * \psi_m)(\omega) = \\ &= (-1)^{\frac{n+m}{2}} \int_{-\infty}^{+\infty} \psi_n(\alpha x) \psi_m\left(\frac{\omega}{\alpha} - \alpha x\right) dx \end{aligned} \quad (5.14)$$

where α is defined by eq. (4.37). The last integral is the overlap between two normalised functions, hence by the Cauchy-Schwarz inequality

$$|\langle \psi_n | W | \psi_m \rangle| \leq A \quad (5.15)$$

Also note that for $\omega = 0$ the right side of eq. (5.14) correctly reduces to δ_{nm} .

Introducing the variables $w = \omega/\alpha$, $t = \alpha x$ and writing down in full the normalisation factors eq. (5.14) can be written as

$$\langle \psi_n | W | \psi_m \rangle = A \frac{e^{-\frac{w^2}{4}} (-1)^{\frac{m+n}{2}}}{\sqrt{2^{n+m} n! m! \pi}} \int_{-\infty}^{+\infty} e^{-t^2} H_n\left(\frac{w}{2} - t\right) H_m\left(\frac{w}{2} + t\right) dt \quad (5.16)$$

An explicit expression for the last integral can be obtained using the generating-function representation of Hermite polynomials [AW05, Wikd]

$$F(s, t) = e^{2ts - s^2} = \sum_{n=0}^{+\infty} H_n(t) \frac{s^n}{n!} \quad (5.17)$$

To proceed one considers $e^{-t^2} F(p, \frac{w}{2} - t) F(q, \frac{w}{2} + t)$ and integrates both sides of the equation for t going from minus to plus infinity. This leads to

$$\begin{aligned} \int_{-\infty}^{+\infty} e^{-t^2} H_n\left(\frac{w}{2} - t\right) H_m\left(\frac{w}{2} + t\right) dt &= \sqrt{\pi} \left(\frac{\partial^{n+m} e^{-2pq + w(p+q)}}{\partial p^n \partial q^m} \right)_{p \rightarrow 0, q \rightarrow 0} = \\ &= \sqrt{\pi} \sum_{k=0}^{\min(n, m)} \binom{n}{k} \binom{m}{k} (-2)^k k! w^{(m+n-2k)} \end{aligned} \quad (5.18)$$

This expression is then a polynomial in w of degree $(n+m)$; it then follows that for $\omega \rightarrow +\infty$ the matrix element goes to zero as $w^{m+n} e^{-w^2/4}$, which is the expected behaviour for the Fourier of the product of a Gaussian and a polynomial of degree $(n+m)$.

The general behaviour of any of these matrix elements as functions of ω is then as follows: they start at A for $\omega = 0$ and tend to zero for $\omega \rightarrow +\infty$, always remaining in modulus less than A and having a maximum of $(n+m)$ local minima or maxima.

Energy levels We assume that the overall amplitude of the oscillation A is small, so W can be treated by perturbation theory. At first order [SO96, Lev00] the effect of the perturbation on the energy level E_n is given by substituting in Eqs. (5.16) and (5.18) $m = n$. After some simple manipulations we get

$$\Delta E_n = \langle \psi_n | W | \psi_n \rangle = A e^{-\frac{w^2}{4}} \sum_{k=0}^n \binom{n}{k} \frac{(-1)^k}{2^k k!} w^{2k} \quad (5.19)$$

We illustrate the effect on the energy levels E_0, E_1 and E_{10} in Figure 5.5.

The effect of the perturbation on the difference between two energy levels is zero for $\omega = 0$ and $\omega \rightarrow +\infty$ and is bounded by $2A$ by the triangle inequality. The conclusion is that a small perturbation of amplitude A will affect transition energies at most by $2A$ and that there is only a restricted range of frequencies where the transition energies are affected.

A numerical study up to $n = 120$ suggests that the last oscillation of equation (5.19) is approximately located at $w_{\max} = 2.838\sqrt{n} - 0.446$. This gives an estimate of the maximum frequency of oscillation which can have an effect on the energy levels.

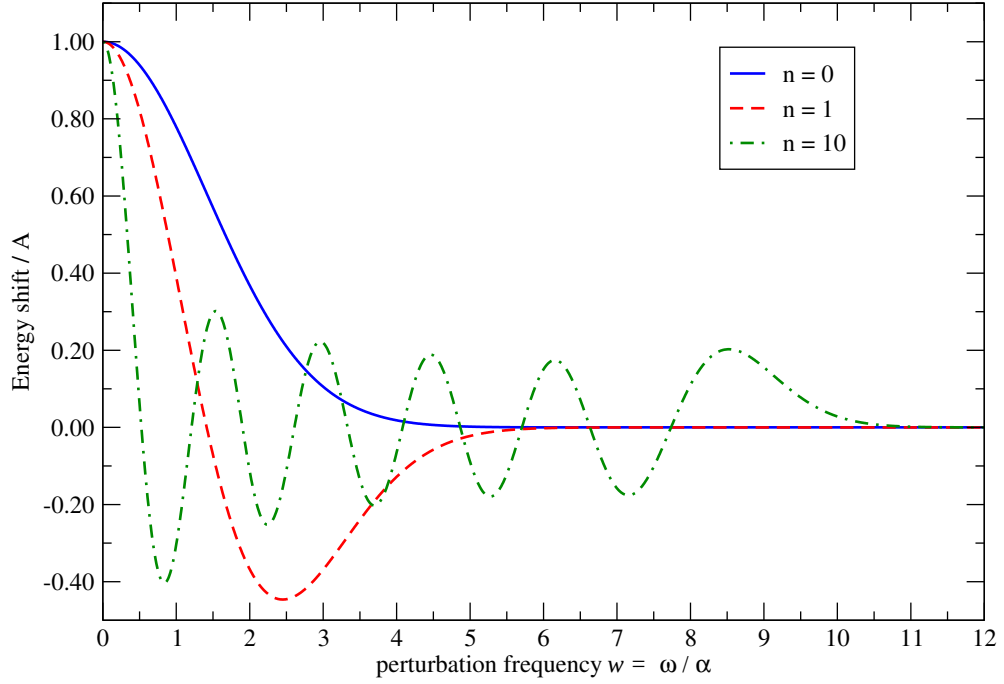


Figure 5.5: Plot of the matrix element $\langle \psi_n | \cos(\omega) | \psi_n \rangle$, representing the energy shift due to a small oscillating perturbation in the potential energy surface.

For the water O–H stretching $\alpha = 5.8 \text{ a}_0^{-1}$ from which follows that $\lambda_{\min} = 2\pi/(\alpha w_{\max})$ falls in the interval $0.5\text{--}0.1 \text{ a}_0$ for $n = 1\text{--}10$. This is about the order of magnitude of oscillations introduced by a fit or interpolation, as it is comparable with the typical point separation. For the bending motion the value of α is smaller, and hence the critical oscillations are at higher frequencies.

Transition intensities The effect of oscillations is potentially more dramatic in the case of transition intensities. Transition intensities $I_{m \rightarrow n}$ are proportional to the line strengths $S_{m \rightarrow n} = |\langle \psi_m | \mu | \psi_n \rangle|^2$, where $\mu(x)$ is the dipole moment function. In the usual treatment [AF05] $\mu(x)$ is approximated by a first-order polynomial, $\mu(x) \approx a + bx$, from which the selection rule $|m - n| = 1$ follows.

We now imagine to perturb the dipole moment function $\mu(x)$ with $W(x)$, so that $\tilde{\mu}(x) = \mu(x) + W(x)$. The perturbed lines $\tilde{S}_{nm}$ obey

$$\frac{\tilde{S}_{mn}}{S_{mn}} = 1 + 2 \frac{\langle \psi_n | W | \psi_m \rangle}{|\langle \psi_n | \mu | \psi_m \rangle|} + \left(\frac{\langle \psi_n | W | \psi_m \rangle}{\langle \psi_n | \mu | \psi_m \rangle} \right)^2 \quad (5.20)$$

The effect of the perturbation on the intensities can thus be potentially large when the unperturbed transition is very weak. We will now specialise to the case $m = 0$, i.e. transitions to the ground state and n even (the effect of the perturbation is otherwise zero by symmetry). Eqs. (5.16) and (5.18) give

$$\langle \psi_0 | W | \psi_n \rangle = A \frac{(-1)^{\frac{n}{2}}}{\sqrt{2^n n!}} e^{-\frac{w^2}{4}} w^n \quad (5.21)$$

This expression has a single maximum at the frequency $\bar{w} = \sqrt{2n}$. The origin of this resonant frequency $\bar{w}$ can also be given a clear graphical interpretation, see Figure 5.6. To give quantita-

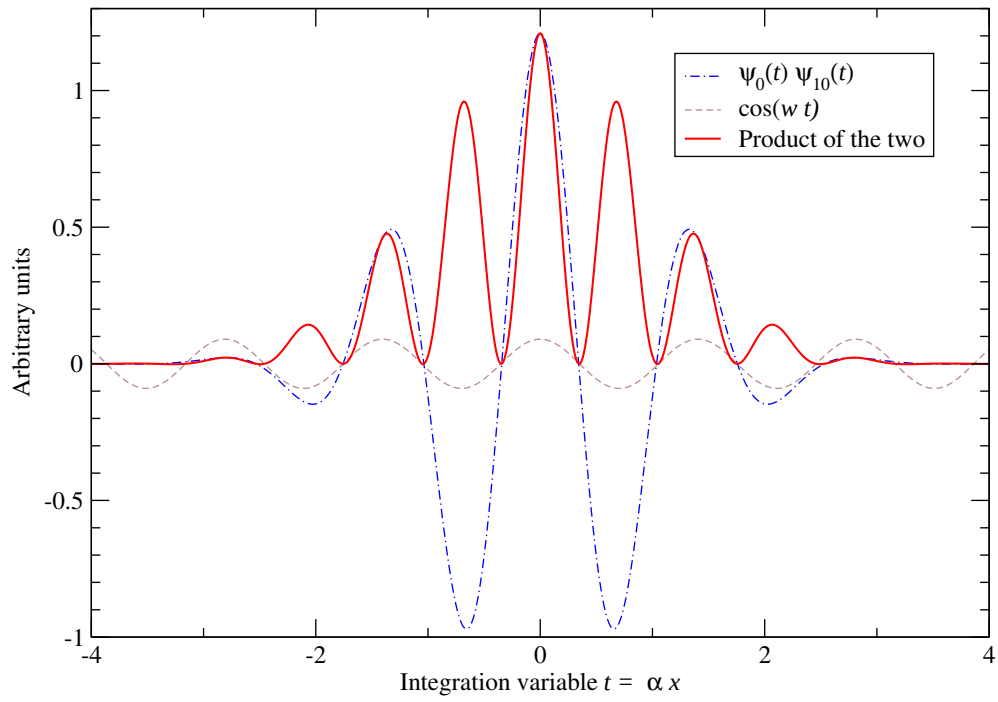


Figure 5.6: Plot of the perturbation $W(w) = \cos(wt)$ and of the product of the harmonic oscillator wave functions $\psi_0\psi_{10}$. When the frequency is $\bar{w}$ the perturbation has the same oscillations as the Hermite polynomial H_m their product has the same sign and its corresponding integral $\langle\psi_0|W(w)|\psi_{10}\rangle$ becomes larger.

tive results we should introduce in the model a dipole-moment curve $\mu(x)$ which goes beyond the linear approximation $\mu(x) = a + bx$ and/or abandon the harmonic potential in favour of a more realistic one. We chose not to do this but to study directly the real case of the water molecule in Section 7.2. We may however mention that, in the case of eigenfunctions of the Morse potential of eq. (5.7), one can show that the matrix elements of the kind $\langle \psi_0 | x | \psi_n \rangle$ contain a factor of $(x_e)^n$, where x_e is the anharmonicity coefficient $x_e \ll 1$ [Gal80, VC83]. We expect that also for more realistic forms of the potential and/or of the dipole moment function the transition intensities decrease exponentially with n . On the other hand, if we choose the perturbation to have the resonant frequency $w = \bar{w}$ it follows

$$\langle \psi_0 | W(\bar{w}) | \psi_n \rangle = A(-1)^{\frac{n}{2}} \sqrt{\frac{n^n e^{-n}}{n!}} \approx A \frac{(-1)^{\frac{n}{2}}}{(2\pi n)^{\frac{1}{4}}} \propto n^{-\frac{1}{4}} \quad (5.22)$$

where we have used Stirling's approximation [AW05] for the factorial. Because, as discussed above, unperturbed transition intensities decrease exponentially with n it follows that there is be a certain n^* after which the effect of the small perturbation given by eq. (5.22) dominates, provided the potential under exam supports that many bound states.

5.3 Multi-dimensional surface-building

5.3.1 Introduction

Interpolation of data in many-dimensions is much more difficult than in one-dimension. Some introductions to the problem can be found in the books by Kincaid [KC91] and Press *et al* [PTVF07]. One-dimensional methods of interpolation can be straightforwardly extended to the multi-dimensional case if the points lie on a grid which is the Cartesian product of one-dimensional ones. However, as the number of points of a regular grid of this kind increases exponentially with the number of dimensions, this strategy quickly becomes impracticable because of the enormous mass of data required. In three dimensions the use of regular grids is still (barely) conceivable, see e.g. [SR75] for an early experiment using 3D-spline interpolation. In general, however, it is much more efficient to use a much smaller set of scattered points.

Interpolating scattered points in many dimensions is a difficult problem and an active subject of recent mathematical research, see e.g. the books by Wendland [Wen05], Lai and Schumaker [LS07] and Fasshauer [Fas07], the review by Fasshauer [Fas06], the lecture notes by Fasshauer [Fas03] and the overview by de Boor *et al* [DBGKR07].

5.3.2 Practical approaches

Many approaches to the surface-building of small molecules containing up to ≈ 10 atoms have been proposed; most of these techniques originated in the mathematical literature but have then been tailored for the specific task at hand. The methods proposed in the recent literature include Reproducing Kernel Hilbert Space (RKHS) [HR96, HR00, HHR01, HHR99, HR03], Neural Networks [MC06, MWDC06], Interpolating Moving Least Squares (IMLS) [DTWM08, GTT⁺07], Modified Shepard Interpolation (MSI) [EM08, Col02], Distributed Approximating Functionals (DAF) [Sza99] and invariant polynomials theory [HBB05b].

Especially for molecules containing only three or four atoms the most common approach consists of fitting the data to an assigned functional form, very often based on multivariate polynomials in some of the variables mentioned in Section 5.2.3. There are at least two significant benefits in this strategy. First, by appropriately choosing the form of the fitting function, one can incorporate known characteristics of the surface. Second, in many cases the accuracy of a surface produced by a fit is higher than that obtained by more generic numerical interpolation schemes [SR75]. This is particularly true if the data set of points to be fitted is not very dense (i.e., if the points are scattered far away from each other).

Several problems may arise with polynomial-based fits, especially if the accuracy required for the fit is very high and/or if a large portion of the PES – possibly extending to the dissociation region – needs to be represented. A general problem with polynomial fits is their lack of “locality”: adding more points in a certain region of multi-dimensional space will affect the fit in regions far-away from it; conversely, adding more points in a specific region may not significantly improve the approximation in that region if the fit is somehow constrained by other points in other regions.

Another problem is that, like the one-dimensional case, polynomials are unconstrained in regions where there are no or few points and they are likely to assume very large, unphysical values there. This behaviour is usually mitigated by multiplying the polynomials with “damping” or “switching” functions but artifacts are likely to appear in the region where the damping is “switched on”.

Another problem that may arise is “overfitting”, that is including in the fit a high number of parameters when compared to the available data; in this situation spurious oscillations between the data points are likely to appear. On this respect multi-dimensional fits with polynomials are more problematic than one dimensional ones. In one-dimension it is well-known [KC91] that for any set of points it is possible to find a polynomial which goes through all of them. The situation is radically different in many dimensions. A theorem by Mairhuber and Curtis [Wen05, Fas03] states that not all sets of points in multi-dimensional space can be exactly interpolated by polynomials. This means that, in general, in many-dimensions we will not be able to make the fitted function go exactly through all the data points, no matter how many terms are included in the expansion. This result does not however preclude the possibility of approximating a function with polynomials: the Weierstrass approximation theorem can be extended to the many-dimensional case [Pin05] and states that any many-dimensional continuous function can be uniformly approximated by multivariate polynomials.

The ground electronic state of water

We will review in this chapter some studies on the calculation of the energy of the electronic ground state of the water molecule. We will comment on the performance of various quantum chemistry methods and estimate the magnitude of the residual errors in the calculations.

6.1 Point-group symmetries and axes convention

For non-linear geometries the point-group symmetry of the water molecule is C_{2v} if the two bond lengths r_1 and r_2 are equal or C_s if they are different. For linear configurations of the H–O–H kind the complete point group is $C_{\infty v}$ if $r_1 \neq r_2$ and $D_{\infty h}$ if $r_1 = r_2$; note however that electronic structure programs generally can only make use of abelian group symmetry, which means that these two last geometries will be treated respectively using the C_{2v} and D_{2h} point groups.

There exist a standard convention suggested by Mulliken [Mul55] which prescribes how a molecule should be oriented with respect to a Cartesian set of axes. In the case of water the Mulliken convention specifies that for C_s geometries the molecule should lie on the xy plane, but no restrictions are given on how the molecule should be oriented on this plane. However, for compatibility with the the program DIPOLE3B of the DVR3D suite [TKB⁺04], it is convenient to orient the molecule as shown in Figure 6.1, namely with the oxygen at the origin and the first/second hydrogen atom in the first/fourth quadrant and the x axis the bisecting the bond-angle. Fixing a specific orientation is important when one deals with the molecular dipole moment vector, and the program DIPOLE3B requires the two components of the dipole to be specified according to Figure 6.1.

For C_{2v} geometries the Mulliken convention states that the molecule should lie on the yz plane, with the z axis coinciding with the two-fold rotational axis C_2 ; unfortunately another convention is also in use for C_{2v} geometries where the xz plane is chosen instead as molecular plane, the rotational axis lying along the z axis. The labels of the C_{2v} irreducible representation b_1 and b_2 are swapped going from the yz to the xz convention or vice versa, so it is essential for the correct specification of the reference space in CASSCF and MRCI computations to know what convention should be adopted. For example, the software MOLPRO [WKL⁺02] uses by default the standard yz convention but COLUMBUS [LSS⁺] uses the xz one.

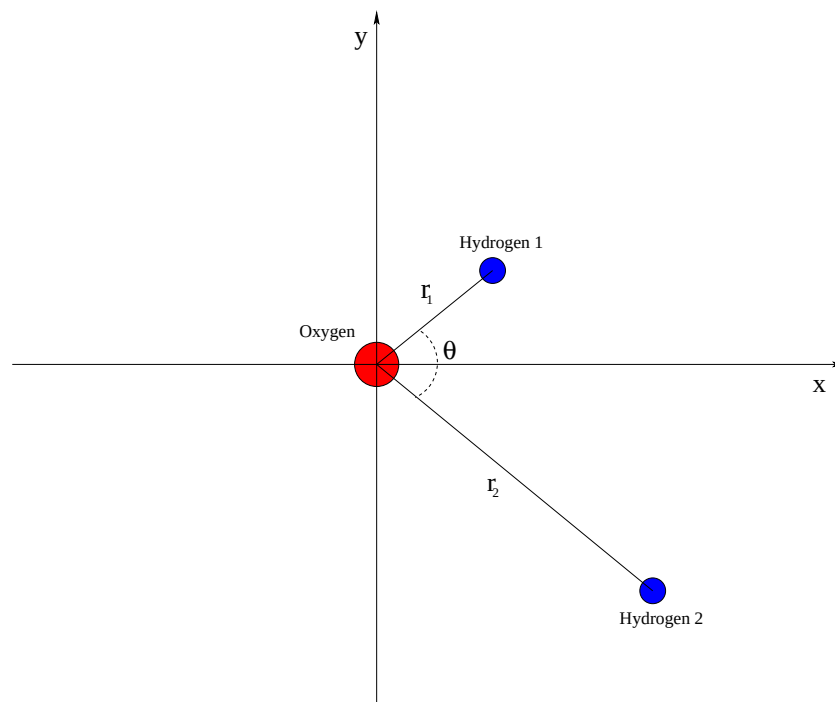


Figure 6.1: The water molecule positioned according to our standard convention (see text).

Finally, for linear H–O–H configuration the standard convention dictates that the atoms should lie along the z axis.

In our runs with MOLPRO we found it convenient to use the C_s orientation of the axes displayed in Figure 6.1 for all geometries; see section 6.9 for the technical details on how this was done in practice. Our way of proceeding avoids the need to manually re-orient molecular dipoles obtained for geometries with different point-group symmetries to a common system of axes.

6.2 Computational details

6.2.1 Quantum chemistry software used

The main quantum chemistry program used was MOLPRO 2002.6 and 2006.1 [WKL⁺06]. As a complement and to perform cross-checks we used PSI3 [CSV⁺07]. We also investigated the possible use of explicitly correlated methods using the software AMICA by Gdanitz [GBL⁺05], which in turn is based on the software suite COLUMBUS [LSS⁺]. However, the use of AMICA was eventually abandoned and no results based on it will be presented in this thesis; we will nonetheless report on our endeavours in this direction in Section 6.3.

6.2.2 Basis sets for water

For our calculations we mainly made use of the correlation-consistent basis sets by Dunning *et al* [Dun89, KDH92, WD94, WD95, WvD96, van99] discussed in Section 3.4; the notations nZ , AnZ and $ACnZ$ will be used as shorthand for respectively cc-pVnZ, aug-cc-pVnZ and aug-cc-pCVnZ.

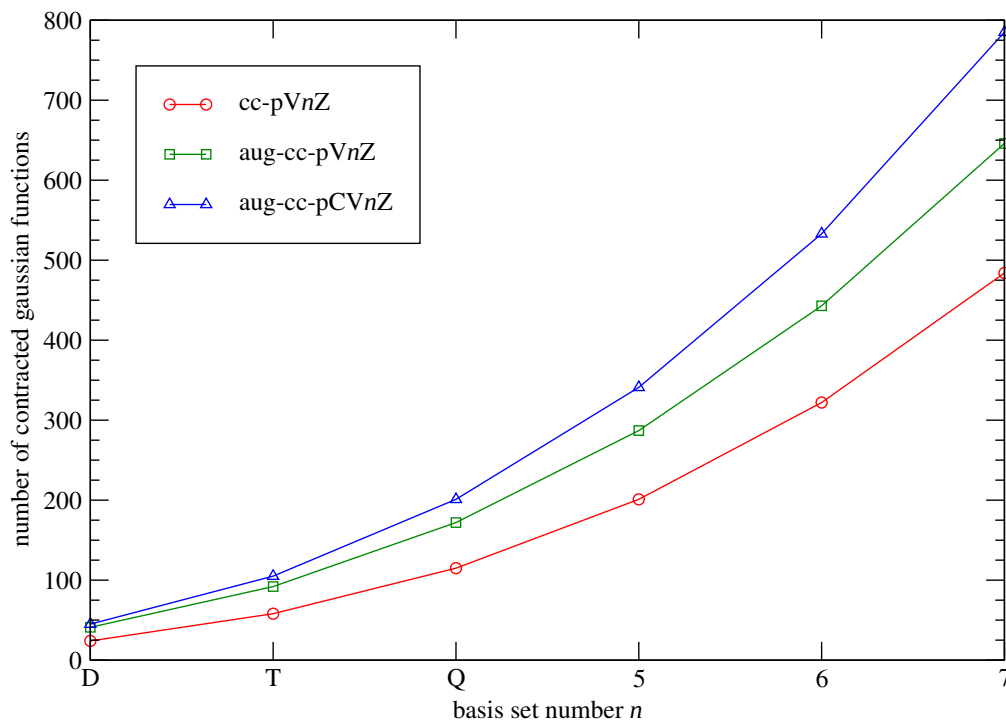


Figure 6.2: Number of contracted Gaussian functions for the correlation-consistent basis sets applied to for water.

Table 6.1 reports many details on the various correlation-consistent basis sets applied to water; some basis sets of the popular Pople family [Lev00, SO96] are also included for comparison. We also report as Figure 6.2 a plot of the number of contracted Gaussians in various basis sets applied to water, while a plot of the Gaussian exponents of the aug-cc-pCV5Z basis set for oxygen was reported as an example as Figure 3.3.

It was necessary in some cases to use non-standard basis sets; we will detail these in the following subsections.

The aug-pV7Z valence-only basis set

Correlation-consistent basis sets of the (aug-)cc-pVnZ family for hydrogen and oxygen have been published for $n = D, T, Q, 5$ and 6. For some tests we used an unpublished $n = 7$ basis set that is available from the EMSL database [EMS] under the name “aug-pV7Z”. The origin of this basis set are rather convoluted; its main ‘pV7Z’ part was introduced by Feller and Peterson [FP99], but two sets of k functions for oxygen which the correlation-consistent scheme prescribes could not be determined because of software limitations. The diffuse ‘aug’ functions were later introduced by Feller and Sordo [FS00] and, finally, the missing k functions were calculated by Valeev *et al* [WD03]. Unfortunately the present version of MOLPRO does not support k functions so when the aug-pV7Z basis set was used these had to be dropped.

NAME	OXYGEN										HYDROGEN										WATER	
	s	p	d	f	g	h	i	k	m	TOT	s	p	d	f	g	h	i	k	TOT	TOT		
STO-3G	2 ⁽⁶⁾	1 ⁽³⁾								5 ⁽¹⁵⁾	1 ⁽³⁾								1 ⁽³⁾	6 ⁽¹⁸⁾		
6-31G	3 ⁽¹⁰⁾	2 ⁽⁴⁾								9 ⁽²²⁾	2 ⁽⁴⁾								2 ⁽⁴⁾	11 ⁽²⁶⁾		
6-31G**	3 ⁽¹⁰⁾	2 ⁽⁴⁾	1							14 ⁽²⁷⁾	2 ⁽⁴⁾	1							5 ⁽⁷⁾	19 ⁽³⁴⁾		
6-31++G**	4 ⁽¹¹⁾	3 ⁽⁵⁾	1							18 ⁽³¹⁾	3 ⁽⁵⁾	1							6 ⁽⁸⁾	24 ⁽³⁹⁾		
cc-pVDZ	3 ⁽⁹⁾	2 ⁽⁴⁾	1							14 ⁽²⁶⁾	2 ⁽⁴⁾	1							5 ⁽⁷⁾	24 ⁽⁴⁰⁾		
cc-pVTZ	4 ⁽¹⁰⁾	3 ⁽⁵⁾	2	1						30 ⁽⁴²⁾	3 ⁽⁵⁾	2	1						14 ⁽¹⁶⁾	58 ⁽⁷⁴⁾		
cc-pVQZ	5 ⁽¹²⁾	4 ⁽⁶⁾	3	2	1					55 ⁽⁶⁸⁾	4 ⁽⁶⁾	3	2	1					30 ⁽³²⁾	115 ⁽¹³²⁾		
cc-pV5Z	6 ⁽¹⁴⁾	5 ⁽⁸⁾	4	3	2	1				91 ⁽¹⁰⁸⁾	5 ⁽⁸⁾	4	3	2	1				55 ⁽⁵⁸⁾	201 ⁽²²⁴⁾		
cc-pV6Z	7 ⁽¹⁶⁾	6 ⁽¹⁰⁾	5	4	3	2	1			140 ⁽¹⁶¹⁾	6 ⁽¹⁰⁾	5	4	3	2	1			91 ⁽⁹⁵⁾	322 ⁽³⁵¹⁾		
cc-pV7Z ^a	8 ⁽¹⁸⁾	7 ⁽¹²⁾	6	5	4	3	2	1		204 ⁽²²⁹⁾	7 ⁽¹⁴⁾	6	5	4	3	2	1		140 ⁽¹⁴⁷⁾	484 ⁽⁵²³⁾		
cc-pV8Z ^b	9 ⁽²⁰⁾	8 ⁽¹⁴⁾	7	6	5	4	3	2	1	285 ⁽³¹⁴⁾	8 ⁽¹⁶⁾	7	6	5	4	3	2	1	204 ⁽²¹²⁾	693 ⁽⁷³⁸⁾		
aug-cc-pVDZ	4 ⁽¹⁰⁾	3 ⁽⁵⁾	2							23 ⁽³⁵⁾	3 ⁽⁵⁾	2							11 ⁽⁹⁾	41 ⁽⁵⁷⁾		
aug-cc-pVTZ	5 ⁽¹¹⁾	4 ⁽⁶⁾	3	2						46 ⁽⁵⁸⁾	4 ⁽⁶⁾	3	2						25 ⁽²³⁾	92 ⁽¹⁰⁸⁾		
aug-cc-pVQZ	6 ⁽¹³⁾	5 ⁽⁷⁾	4	3	2					80 ⁽⁹³⁾	5 ⁽⁷⁾	4	3	2					48 ⁽⁴⁶⁾	172 ⁽¹⁸⁹⁾		
aug-cc-pV5Z	7 ⁽¹⁴⁾	6 ⁽⁹⁾	5	4	3	2				127 ⁽¹⁴⁴⁾	6 ⁽⁹⁾	5	4	3	2				83 ⁽⁸⁰⁾	287 ⁽³¹⁰⁾		
aug-cc-pV6Z	8 ⁽¹⁷⁾	7 ⁽¹¹⁾	6	5	4	3	2			189 ⁽²¹⁰⁾	7 ⁽¹¹⁾	6	5	4	3	2			131 ⁽¹²⁷⁾	443 ⁽⁴⁷²⁾		
aug-cc-pV7Z ^a	9 ⁽¹⁸⁾	8 ⁽¹³⁾	7	6	5	4	3	2		268 ⁽²⁹³⁾	8 ⁽¹⁵⁾	7	6	5	4	3	2		196 ⁽¹⁸⁹⁾	646 ⁽⁶⁸⁵⁾		
aug-cc-pV8Z ^b	10 ⁽²¹⁾	9 ⁽¹⁵⁾	8	7	6	5	4	3	2	366 ⁽³⁹⁵⁾	9 ⁽¹⁷⁾	8	7	6	5	4	3	2	276 ⁽²⁶⁸⁾	902 ⁽⁹⁴⁷⁾		
aug-cc-pCVDZ	5 ⁽¹¹⁾	4 ⁽⁶⁾	2							27 ⁽³⁹⁾	3 ⁽⁵⁾	2							11 ⁽⁹⁾	45 ⁽⁶¹⁾		
aug-cc-pCVTZ	7 ⁽¹³⁾	6 ⁽⁸⁾	4	2						59 ⁽⁷¹⁾	4 ⁽⁶⁾	3	2						25 ⁽²³⁾	105 ⁽¹²¹⁾		
aug-cc-pCVQZ	9 ⁽¹⁶⁾	8 ⁽¹⁰⁾	6	4	2					109 ⁽¹²²⁾	5 ⁽⁷⁾	4	3	2					48 ⁽⁴⁶⁾	201 ⁽²¹⁸⁾		
aug-cc-pCV5Z	11 ⁽¹⁹⁾	10 ⁽¹³⁾	8	6	4	2				181 ⁽¹⁹⁸⁾	6 ⁽⁹⁾	5	4	3	2				83 ⁽⁸⁰⁾	341 ⁽³⁶⁴⁾		
aug-cc-pCV6Z	13 ⁽²²⁾	12 ⁽¹⁶⁾	10	8	6	4	2			279 ⁽³⁰⁰⁾	7 ⁽¹¹⁾	6	5	4	3	2			131 ⁽¹²⁷⁾	533 ⁽⁵⁶²⁾		
aug-cc-pCV7Z ^b	15 ⁽²⁵⁾	14 ⁽¹⁹⁾	12	10	8	6	4	2		407 ⁽⁴³²⁾	8 ⁽¹⁵⁾	7	6	5	4	3	2		196 ⁽¹⁸⁹⁾	785 ⁽⁸²⁴⁾		
aug-cc-pCV8Z ^b	17 ⁽²⁸⁾	16 ⁽²²⁾	14	12	10	8	6	4	2	569 ⁽⁵⁹⁸⁾	9 ⁽¹⁷⁾	8	7	6	5	4	3	2	276 ⁽²⁶⁸⁾	1105 ⁽¹¹⁵⁰⁾		

^a Not yet published, but available through the EMSL database [EMS] (see text).^b Not yet available (estimate).

Table 6.1: Number of contractions and primitives for some commonly used basis sets. The format used is $n_c^{(n_p)}$, where n_c is the number of contractions and n_p the number of primitives.

Basis sets for core-correlation

For core-correlated calculations it is necessary to supplement basis sets of the (aug-)cc-pVnZ family with tight (i.e., large-exponent) functions to allow for core-core and core-valence correlation; the resulting enlarged basis sets are labelled (aug-)cc-pCVnZ and were introduced by Woon and Dunning [WD95] for $n=D,T,Q,5$.

The (aug-)cc-pCV6Z basis set for oxygen has not yet been published but a preliminary version was made available in 2001 on the EMSL web site [EMS] under the name “cc-pCV6Z” with a reference to “D. Feller (to be published)”. In 2005 a slightly different basis set took the place of the previous one under the name “cc-pCV6Z” with a reference to “A.K. Wilson and T.H. Dunning (to be published)”, while the previous version was renamed to “cc-pCV6Z(old)”.

We were not aware of this switch-over and in all our calculations the older version now called “cc-pCV6Z(old)” was employed, supplemented with diffuse functions taken from the aug-cc-pV6Z basis set. However, the difference in relative energies between the “cc-pCV6Z(old)” and “cc-pCV6Z” basis sets is probably insignificant at the level of precision we are interested in.

Other all-electron basis sets considered Peterson and Dunning [PD02] introduced a new family of basis sets for core-correlation, the cc-pwCVnZ series, which should provide improved performance with respect to the older cc-pCVnZ one.

The cc-pwCVnZ basis sets were obtained by an optimisation strategy which puts more weight (whence the *w* in the acronym) on the convergence of core-valence correlation rather than on the sum of core-valence and core-core correlation as done in the original cc-pCVnZ series. The rationale behind this strategy is that the core-core correlation energy, while larger in absolute terms, has a smaller variation with molecular geometry and hence a smaller effect on relative energies.

Basis sets of the cc-pwCVnZ family are available for $n=D,T,Q,5$ but not for $n=6$, which is the level we are mainly interested in. We anyway estimated the expected difference in relative energies between the two families of basis sets; from the data reported in Table VII of ref. [PD02] we can calculate that the discrepancies between cc-pCVnZ and cc-pwCVnZ for the CCSD(T) dissociation energy of the CO molecule are for $n=D,T,Q,5$ respectively of 133, 150, 52 and 24 cm^{-1} . The cc-pwCV5Z dissociation energy itself is $D_e = 90,377 \text{ cm}^{-1}$. It is reasonable to expect that the difference between the aug-cc-pCV6Z basis set and a hypothetical aug-cc-pwCV6Z would be of about 10–15 cm^{-1} ; considering that in water core-correlation affects only one atom and not two as in the CO molecule, it may be expected that for water the difference between cc-pCV6Z and cc-pwCV6Z would be about 5–10 cm^{-1} , and hence small by our standards.

Basis sets for explicitly correlated calculation

The basis sets considered for explicitly correlated calculation with AMICA will be described in Section 6.3.1.

$[n_e, n_o]$	Orbitals		Name
	inactive	active	
[4, 4]	(2,0,0,0)	(2,0,2,0)	“minimal”
[8, 6]	(1,0,0,0)	(3,1,2,0)	FORS or “full valence”
[8, 8]	(1,0,0,0)	(4,2,2,0)	EIPM or “one-to-one”
[8, 10]	(1,0,0,0)	(6,2,2,0)	“extended”

Table 6.2: Reference spaces for water. The first column $[n_e, n_o]$ refers to the number of electrons and of orbitals included in the RS (see text for details).

6.2.3 Choice of the reference space

The choice of the reference space (RS) is an important and delicate step in CAS-SCF and MRCI calculations; the general principles are discussed in the reviews on the CAS-SCF method by Roos [Roo92a, Roo87], Schmidt and Gordon [SG98], and in the book by Jensen [Jen06]. See also Abrams and Sherrill [AS03] and Sears and Sherrill [SS05].

Details on the reference spaces we will be interested in are summarised in Table 6.2; the format used is (n_1, n_2, n_3, n_4) where the integers n_i refers to the number of orbitals belonging to a certain C_{2v} symmetry species to be taken, using the ordering (a_1, b_1, b_2, a_2) (the same as used by MOLPRO). The specification of the RS for C_s geometries can be easily obtained knowing that a_1 and b_1 correlate to a' while a_2 and b_2 correlate to a'' ; for example, the RS labelled “one-to-one” in C_s symmetry becomes [(1,0) (6,2)] for [(inactive) (active)] orbitals. Note that there are two conventions in use for the labelling of C_{2v} irreducible representation, see discussion in Section 6.1; the convention used here is the standard Mulliken one, also used by default by MOLPRO.

Two prescriptions for the selection of the RS are the “full valence” and the “one-to-one”. The “full valence reaction space”, also known as “fully optimised reaction space” (FORS), prescribes to include for each occupied or unoccupied valence orbital one extra orbital of the same symmetry. The “one-to-one”, also known as “extended independent-particle model” (EIPM), includes in the RS one extra orbital of the same symmetry for all orbitals (occupied or unoccupied) and core orbitals.

The case of the water molecule was discussed by Roos [Roo87, Roo80] and the conclusion was that the smaller “full valence” RS is unbalanced, particularly for quasi-linear geometries, while the “one-to-one” is a very good choice. It is in fact this last RS which was used in most recent accurate calculation on water, e.g. [PS97, BSZ⁺06]. However, probably because of computational limitations, many authors have also used smaller RS’s, sometimes resulting in instabilities, see e.g. [HHR96, KS97].

CAS-SCF and MRCI calculations based on the “full valence” and on the “one-to-one” RS’s were compared against FCI in a study of the double-stretching of water by Olsen *et al* [OJK⁺96] and the cc-pVDZ basis set. It emerged from this study that MRCI calculations based on the larger “one-to-one” RS (called CASB by Olsen *et al.*) were the most accurate. A similar study of the double-stretching curve of water against FCI was also performed by Sears and Sherrill [SS05] using the same basis set, confirming the quality of the “one-to-one” RS over the “full

basis set	RS ^a	Frozen core?	TOTAL TIME	Percentage of TOTAL TIME				Disk GB
				Integrals	RHF	CAS-SCF	IC-MRCI	
aug-cc-pVQZ	[8, 8]	yes	15.8m	5	1	2	92	1
aug-cc-pV5Z	[8, 8]	yes	49.6m	17	7	9	67	8
aug-cc-pV6Z	[8, 8]	yes	4.2h	31	11	7	51	41
aug-pV7Z ^b	[8, 8]	yes	18.7h	40	12	7	41	164
aug-cc-pCVQZ	[8, 8]	no	26.4m	5	3	5	87	2
aug-cc-pCV5Z	[8, 8]	no	2.9h	15	9	7	69	15
aug-cc-pCV6Z	[8, 8]	no	15.1h	24	9	13	54	91
aug-cc-pCVQZ	[8, 10]	no	2.5h	1	1	1	97	2
aug-cc-pCV5Z	[8, 10]	no	8.5h	5	4	3	88	15
aug-cc-pCV6Z	[8, 10]	no	26.4h	12	6	5	77	91

^a Reference space, using the notation of Table 6.2.

^b 30 primitives on oxygen with angular momentum k were dropped because not supported by MOLPRO.

Table 6.3: Timings for IC-MRCI with MOLPRO 2006.1. Timings are averages of many runs at different geometries, refer to a Pentium IV 3.4 GHz with 3 GiB or RAM and used C_s symmetry; computations in C_{2v} symmetry take approximately half of the time and use half of the disk space.

valence” one in MRCI calculations. Finally, yet another study of the double-stretching of water was presented most recently by Abrams and Sherrill [AS05] using the RS labelled as “minimal” in Table 6.2; however, the basis set used, 6-31G, is so small that its difficult to draw any definitive conclusion; for example, with this basis set the [8, 10] RS of Table 6.2 is equivalent to full-CI.

Using a larger RS will always produce lower CAS-SCF and MRCI total energies but will not necessarily produce better results for relative energies as a larger RS may spoil cancellation of errors which were present in a smaller one. Because these effects cannot be predicted, some numerical experimentation is in general necessary to assess the quality of a new RS.

We investigated some possible enlargement of the “one-to-one” [8, 8] RS and we finally focused on the RS labelled as [8, 10] in Table 6.2. In the following sections some results will be presented which seem to indicate that MRCI relative energies obtained with the [8, 10] RS are more accurate than those obtained with the [8, 8] one.

6.2.4 Indicative running times

Computer resources are the ultimate factor deciding the feasibility of a computation. We quote in Table 6.3 some indicative running times for IC-MRCI using MOLPRO and various basis sets and reference spaces. The final IC-MRCI calculation is in all cases the most expensive step, taking a fraction in the interval 41–97% of the total time. Particularly with the larger AV6Z and AV7Z basis sets the calculations of integrals is the second most expensive step, taking a fraction up to 40% of the total time.

6.3 Explicitly correlated calculations

Explicitly correlated methods of the R12 and F12 families were presented in Section 3.11. These methods promise faster convergence of the energy with respect to basis set size [KMTNV06] and are hence potentially very attractive for the computation of potential surfaces.

Most applications of R12/F12 methods has been based on single-reference methods, particularly MP2 and CCSD(T), typically accompanied with double- or triple-zeta basis sets, see e.g. [WMK03]. At the time of writing there is only one software which claims to apply the R12 methodology to multi-reference methods suitable for the calculation of extended potential surfaces, AMICA by R. Gdanitz [GBL⁺05]. AMICA is based on COLUMBUS [LSS⁺] and implements the R12 method for uncontracted MRCI, ACPF, AQCC and ACPF-2 calculations (see section 3.10 for an explanation of these acronyms).

AMICA has been used by Gdanitz and co-workers in several computations, e.g. [CG05], but mostly for atoms and diatomic systems. Unfortunately, a series of problems made us eventually decide to abandon the idea of using this software to compute a new water potential energy surface. The main reasons, which will be discussed in more detail later, are

1. AMICA, being based on COLUMBUS, uses uncontracted MRCI, which makes calculations much more expensive than internally-contracted MRCI.
2. AMICA does not make use of the most recent advances in explicitly correlated methods, which somewhat reduces its attractiveness.
3. We experienced many problems of lack of convergence and other instabilities.

Point 1. The lack of internal contraction in AMICA makes computations extremely expensive, especially with the larger basis sets. It is also not certain that much or indeed any accuracy is gained using uncontracted MRCI with respect to internally-contracted one, see e.g. the discussion in Section 6.5.

Furthermore, apart from the MRCI calculation, also all other steps of the computation (integral evaluation, Hartree–Fock, CAS-SCF) are consistently slower with AMICA than with MOLPRO, and this was sometimes an even greater factor limiting the speed of computation. For example, a MRCI calculation using the uncontracted cc-pVQZ basis set in C_s symmetry took about 5 hours, while the same computation with MOLPRO and IC-MRCI completed in only 2.5 minutes.

For larger basis sets the factor limiting the speed of AMICA was the conversion of integrals from the atomic-orbital basis to the molecular-orbital one, a step performed by a sub-program called ‘tran’. For example, a single-reference CISD calculation in C_s symmetry using a basis set with 306 uncontracted Gaussians (the “6z-r12-small” basis set described in the next subsection) took ≈ 32 hours, of which ≈ 25 hours were spent on the transformation of the integrals. The same calculation with MOLPRO took about 25 minutes. Two versions of ‘tran’ are available in AMICA, an old one used by default and a new one which can be accessed by editing the file ‘tranin’ and setting ‘newcod = .true.’. However, our tests revealed that the new version was in fact slower than the old one.

Even if the problems with ‘tran’ could be solved, it is clear that, on any given system, one would have to use with AMICA much smaller basis sets than it is possible with MOLPRO; it is

very uncertain that the advantage of using a R12 method could compensate this much reduced overall basis set size.

Point 2. There are at least two new developments in explicitly correlated methods which have taken place in the last ten years [KMTNV06, PAW08] and which are not implemented in AMICA. First, it was found that non-linear correlating factors like $e^{-\beta r_{12}}$ give much better results than the original linear r_{12} one; methods that use non-linear correlating factors are called F12 methods. Second, AMICA, like all early implementations [KMTNV06, PAW08], uses the basis of molecular orbitals not only for the CI expansion but also for the resolution of identity approximations needed in R12/F12 methods; this double role the basis set has to fulfil results in a constraint on its optimisation for the convergence of the correlation energy. Another consequence is that small basis sets cannot be used at all or numerical instabilities may occur. Besides these two major improvements other more technical developments have taken place [WAM07, KMTNV06] which are both simpler and more accurate than older approaches.

Point 3. We experienced various kinds of stability problems with AMICA. As described in more detail in the following section we ran some tests using the uncontracted cc-pVQZ basis set, but in some cases the R12-MRCI method did not converge; the reason is probably that the basis set is still too small to be used reliably in the resolution of identity approximation. We also experienced problems when using larger basis sets, like the “6z-r12-small” described in the following section. In this case for some geometries the program stopped at the R12-MRCI step complaining about linear dependencies among the basis functions; this happened for example at some bent geometries with $\theta = 160^\circ$.

Finally, we mention that the author of AMICA left academia and that the web sites [GBL⁺05] which in the past hosted the program are not working at the time of writing. The future of AMICA then appears very uncertain and further updates are probably unlikely.

6.3.1 Basis sets considered for explicitly correlated calculations

Explicitly correlated R12/F12 methods require for optimal results especially-designed basis sets. In particular, when the basis set is used also for the resolution of identity approximations it is necessary that it should be saturated in its s and p components. We considered three basis sets, all designed for valence-only calculations.

The first, conceived as a minimal basis set, in the uncontracted cc-pVQZ, which results in a $(12s, 6p, 3d, 2f, 1g)/(6s, 3p, 2f, 1g)$ for oxygen/hydrogen (total of 132 Gaussians); however, this basis set resulted too small and led to numerical problems in some cases.

A second basis set was purposely constructed by us for explicitly correlated calculations. For hydrogen we employed the same $(11s, 6p, 4d, 3f)$ basis set used by Gdanitz in a study of the HF molecule [GBL⁺05]. For oxygen we designed a $(18s, 13p, 8d, 6f, 4g, 3h, 2i)$ basis following the same recipe used in [GBL⁺05] to build a basis set for fluorine. The set of s and p exponents were taken from the $(18s, 13p)$ basis set by Partridge [Par89], which is available through the EMLS [EMS] under the name “Partridge Uncontr. 3”. We complemented these with the $(6d, 5f, 4g, 3h, 2i)$ functions from the aug-cc-pV6Z basis set; finally, we added two tight d and one tight f set of functions by logarithmic extrapolation (Formula 3.20). This procedure resulted in

a (18s, 13p, 8d, 6f, 4g, 3h, 2i) basis set for oxygen and in a basis set for water with a total of 374 Gaussians; our working name for it was “6z-r12”. Unfortunately this basis set proved too large to be employed in multi-reference calculations with the [8, 8] RS. In many tests we dropped the 2i functions on oxygen and the 3f functions on hydrogen, resulting in a more manageable (but still very large) basis set with 306 Gaussians; our working name for it was “6z-r12-small”.

We also considered the “Universal R12” basis set by Noga and co-workers [KNV05, NV03], which is a (19s, 14p, 8d, 6f, 4g, 3h)/(9s, 6p, 4d, 3f) for oxygen/hydrogen for a total of 348 Gaussians; unfortunately, as in the previous case, this basis set resulted so large that we were never able to use it for uncontracted MRCI with the [8, 8] RS.

Finally, we remark that the recently introduced valence-only basis sets by Peterson *et al* [PAW08] are designed for F12 methods which use an auxiliary basis set for the resolution of identity and are hence not suitable for AMICA.

6.4 Comparing energy calculations

It is often necessary to compare sets of energies calculated with different methods and/or with different basis sets; we will describe in this sections some ways of performing a comparison.

A straightforward option is to plot the differences of the energies, and this will be done in Section 6.7. As we are interested only in relative energies we are free to rigidly shift the computed differences by any amount and we always chose to set the difference to zero at equilibrium.

It is also desirable to define a single number which can compactly and quantitatively give an idea of how much the two sets differ. Again, as we are interested only in relative energies, it is desirable that this number be invariant to constant shifts in the values of either of the sets.

Calling the energies of the two sets $E_a(i)$ and $E_b(i)$ and $\Delta_i = E_a(i) - E_b(i)$ a possible measure of their similarity which satisfies our requirement of invariance to constant shifts is given by the standard deviation σ :

$$\sigma = \sqrt{\frac{1}{N} \sum_i (\Delta_i - \langle \Delta \rangle)^2} \quad \text{where} \quad \langle \Delta \rangle = \frac{1}{N} \sum_i \Delta_i \quad (6.1)$$

Another quantity we found useful is the nonparallelity error (NPE) introduced by Li and Paldus [LP95] and subsequently used by many authors [ESA⁺08, LIA07, DS03, AS03, SS05]. The NPE is defined as the difference between the maximum and minimum differences:

$$\text{NPE} = \max_i |E_a(i) - E_b(i)| - \min_i |E_a(i) - E_b(i)| \quad (6.2)$$

The NPE can be interpreted as the minimum energy width of a band within which the difference of the curves always lie. By contrast the standard deviation σ is the half-width of a band within which the differences mostly lie in an average sense.

6.5 FCI calculations on water

6.5.1 Introduction

Full-CI (FCI) energies are precious reference values; unfortunately, water with its ten electrons is already a difficult system to treat with FCI and only the smallest basis sets can be afforded.

basis set	program	excitation level ^a	TOTAL TIME	Disk space
cc-pVDZ	MOLPRO	8	7.4h	9 GB
cc-pVDZ	PSI3	8	2.5h	8 GB
cc-pVDZ	PSI3	6	47m	6 GB
cc-pVDZ	PSI3	4	2m	200 MB
cc-pVDZ	PSI3	2	15s	1 MB
aug-cc-pVDZ	PSI3	6	na ^b	
aug-cc-pVDZ	PSI3	4	59m	2 GB
aug-cc-pVDZ	PSI3	2	15s	6 MB

^a Maximum level CI excitations allowed; $n = 8$ corresponds to frozen-core FCI.

^b Not available: this computation requires ≈ 6 GB of RAM and could not be run.

Table 6.4: Timings for frozen-core truncated-CI and FCI calculations using MOLPRO and PSI3. Computations were done on a Pentium IV 3.4 GHz with 3 GiB of RAM and employed C_s symmetry.

As a consequence results will not be quantitatively accurate because of basis set incompleteness and, more importantly, the relative agreement of approximate quantum chemical methods with FCI may be somewhat different in the complete basis set limit.

The size N of the FCI matrix when Slater determinants are employed and spatial symmetry is not used is given for a spin-singlet system by $N = \binom{k}{n/2}^2$, where n and k are respectively the number of electrons and of basis functions; when point group symmetry is present N is reduced by a factor approximately given by the order of the symmetry group, namely two for C_s and four for C_{2v} . From this formula it follows that the asymptotic scaling with the number of basis function k is $N \approx k^{10}/14400$ for all-electron FCI and $N \approx k^8/576$ for frozen-core FCI; all-electron calculations are hence much more expensive than frozen-core ones. The RAM usage is for many FCI algorithms given by $N \times a \times s$, where a is a constant typically between two to three times and s is the storage space of a floating point number (very often eight bytes). Some indicative timings for various levels of frozen-core truncated CI including FCI are reported in table 6.4. Frozen-core FCI using the cc-pVDZ basis set and C_s symmetry are easily accessible using normal PCs, but after this point the computational cost increases very rapidly. All-electron FCI energies using the cc-pVDZ were presented by Olsen *et al* [OJK⁺96]; by today's standards these are still rather substantial calculations requiring according to our estimate ≈ 16 GiB of RAM in C_s symmetry.

6.5.2 Comparison with FCI values from Barletta *et al*

In ref. [BSZ⁺06], which presents the water CVRQD potential energy surface, frozen-core FCI values calculated with the cc-pVDZ basis set were presented for 10 geometries (a subset of the 14 geometries presented in Table 6.7). These values were contrasted against IC-MRCI, IC-MRCI+Q, uncontracted MRCI and uncontracted AQCC using the [8,8] RS of Table 6.2. The unexpected conclusion was that energies calculated with the IC-MRCI method were in better agreement with

FCI than those given by the other, more elaborate methods. In particular, we calculated from Table II of ref. [BSZ⁺06] the NPE with respect to FCI of IC-MRCI, IC-MRCI+Q, MRCI and AQCC and they are respectively of 41.8, 79.3, 77.0 and 128 cm⁻¹. However, too much importance should not be given to this result as the cc-pVDZ basis set is so small that the agreement of the various method with FCI may be very different in the complete basis set limit.

We can get an idea of the interaction of basis-set incompleteness with electron-correlation treatment contrasting the NPEs between two quantum chemistry methods using two different basis sets; if basis-set incompleteness were truly independent of the correlation treatment the NPEs would not change going from one basis set to another. From the values reported in [BSZ⁺06] we calculated the NPE between IC-MRCI and IC-MRCI+Q in the cc-pVDZ and aug-cc-pVQZ basis sets and they are respectively of 83.1 and 309.2 cm⁻¹. The difference between these values is larger than the cc-pVDZ NPEs with respect to FCI reported above, implying that a complete shuffling of the order of agreement with FCI in the complete basis set limit is likely. In fact, we will present in the next subsection the analysis of another set of FCI energies obtained with a slightly larger basis set where the order of agreement of the methods is practically reversed.

Finally, there is further support of the fact that size-extensivity-corrected energies like IC-MRCI+Q are preferable to plain IC-MRCI ones from the calculation of rotation-vibration energies computed with *ab initio* PES's.

6.5.3 FCI data from Chan and Head-Gordon

The largest FCI computations on water ever reported are those of Chan and Head-Gordon [CHG03]. These authors reported all-electron FCI energies for two molecular geometries using a basis set the same size as aug-cc-pVDZ (41 functions); it can be found on the EMSL database [EMS] under the name "Roos Augmented Double Zeta ANO". The method employed for the calculation was the Density-Matrix Renormalization Group approach (see references in section 3.12). Chan and Head-Gordon report that one iteration of their algorithm took 150 hours, 250 GB of RAM and 800 GB of disk space on a machine with 64 POWER3 CPUs at 375 MHz.

In their calculation all electrons were correlated, even though the basis set used does not include tight functions for core correlation; this means that core-correlation is not accounted for very well but it is probably not very relevant for our testing purposes. Also note that the reference geometry used by Chan and Head-Gordon corresponds to $\theta = 104.5^\circ$, $r_1 = r_2 = 1 \text{ \AA}$, while the correct value of the equilibrium bond length for the O-H bond is 0.959 Å; as a consequence the geometry chosen as reference is $\approx 600 \text{ cm}^{-1}$ away from the true equilibrium. Again, this is of no particular importance for our comparison purposes.

We compared the FCI data from Chan and Head-Gordon with various multi-reference methods using the [8, 8] and the [8, 10] RS's of Table 6.2; results are collected in Table 6.5 (a description of the methods used was presented in section 3.10). In Table 6.5 and in the following of this chapter we indicated with IC-MRCI+Q and IC-MRCI+P the IC-MRCI energy augmented respectively with the renormalised Davidson correction and with the Pople correction. RSPT2 and RSPT3 are multi-reference perturbative methods based on Rayleigh-Schrödinger perturbation theory, both of which are much faster than any of the variational IC-MRCI-like methods considered.

The agreement of the various methods with FCI is very different from what reported in the

Table 6.5: Comparison of all-electron FCI values from ref. [CHG03] with various methods using an augmented double-zeta basis set (see text). The bond angle is fixed at $\theta = 104.5^\circ$ and $r_e = 1 \text{ \AA}$. In the first geometry $r_1 = r_2 = r_e$, in the second $r_1 = r_2 = 1.5r_e$.

Method	RS	r_e E_h	$1.5r_e$ E_h	Δ cm^{-1}	error cm^{-1}
FCI ^a		-76.314715	-76.131050	40,310	0
RHF ^a		-76.057621	-75.817273	52,750	12,441
CISDTQ ^a		-76.314001	-76.128604	40,690	380
CCSDTQ ^a		-76.314696	-76.130885	40,342	32
CAS-SCF	[8,8]	-76.191791	-76.004382	41,131	822
RSPT2	[8,8]	-76.303558	-76.119108	40,482	172
RSPT3	[8,8]	-76.311169	-76.126194	40,597	287
IC-MRCI	[8,8]	-76.311535	-76.127234	40,449	140
IC-MRCI+Q	[8,8]	-76.314860	-76.131499	40,243	-67
IC-MRCI+P	[8,8]	-76.314239	-76.130718	40,278	-32
IC-ACPF	[8,8]	-76.314260	-76.130777	40,270	-40
IC-AQCC	[8,8]	-76.313629	-76.129943	40,314	5
CAS-SCF	[8,10]	-76.215231	-76.029141	40,842	532
RSPT2	[8,10]	-76.304080	-76.119609	40,487	177
RSPT3	[8,10]	-76.311380	-76.126425	40,593	-76
IC-MRCI	[8,10]	-76.312841	-76.128749	40,404	94
IC-MRCI+Q	[8,10]	-76.315030	-76.131539	40,271	-38
IC-MRCI+P	[8,10]	-76.314616	-76.131019	40,295	-15
IC-ACPF	[8,10]	-76.314625	-76.131047	40,291	-19
IC-AQCC	[8,10]	-76.314215	-76.130513	40,318	8

^a From ref. [CHG03].

Table 6.6: Frozen-core energies for the single-bond stretching in water. The bond angle is fixed to $\theta = 104.52^\circ$ while (r_1, r_2) for geometry 1 and 2 are respectively (0.9576, 0.9576) and (0.979, 8) Å.

	basis	RS	geom. 1	geom. 2	Δ	<i>error</i>
FCI	DZ	–	-76.241667	-76.059068	40,076	0
IC-MRCI	DZ	[8, 8]	-76.239969	-76.057486	40,050	-25
IC-MRCI+P	DZ	[8, 8]	-76.241835	-76.059621	39,991	-84
IC-MRCI+Q	DZ	[8, 8]	-76.241383	-76.059105	40,005	-70
IC-MRCI	DZ	[8, 10]	-76.240779	-76.058562	39,992	-84
IC-MRCI+P	DZ	[8, 10]	-76.242032	-76.059452	40,072	-4
IC-MRCI+Q	DZ	[8, 10]	-76.241727	-76.059234	40,053	-23

previous subsection using the smaller cc-pVDZ basis set. The conclusions are:

- The multi-reference perturbative methods RSPT2 and RSPT3, while improving on the CAS-SCF value, do not reach the same level of accuracy as the MRCI-type methods considered. Also, they seem to behave erratically on enlargement of the reference space.
- All MRCI-type methods which include size-extensivity corrections perform better than uncorrected IC-MRCI. In particular, IC-AQCC performs best, followed by IC-ACPF and IC-MRCI+P and finally by IC-MRCI+Q.
- Errors of MRCI-type methods are almost halved using the larger [8, 10] reference space, a part from the IC-AQCC value which was already very small with the smaller [8, 8] RS.

6.5.4 The dissociation energy

We performed a small study of the lowest-energy dissociation channel of water using frozen-core FCI in the cc-pVDZ basis set using the [8, 8] and the [8, 10] RS's of Table 6.2. Results are collected in Table 6.6. As in the case of the comparison with the FCI energies by Barletta *et al* discussed above the best agreement with FCI is obtained with uncorrected IC-MRCI using the [8, 8] RS, but as we discussed, this is probably an artifact due to the small basis set employed. Unfortunately it is not possible to draw more definitive conclusions on this matter but we remark that enlargement of the RS to [8, 10], while on the one hand spoils the good agreement of uncorrected IC-MRCI, on the other hand and makes IC-MRCI+P and IC-MRCI+Q energies quite accurate.

6.6 Study for selected geometries

A study was carried out using MOLPRO for 14 geometries to assess the behaviour of various electronic structure methods and basis sets. Unfortunately, no accurate reference values are available but some tentative conclusions can be drawn by analysing the scatter of the data. More information on the quantum-chemistry methods employed can be found in Section 3.10.

The reference geometries used in the study are a superset of those introduced by Barletta *et al* [BSZ⁺06] and are reported in Table 6.7. The *ab initio* results are presented in Table 6.8 and

nr	Symmetry	cm ⁻¹	r_1	r_2	θ
1	C _{2v}	0	1.81196	1.81196	104.343
2	C _{2v}	1,609	1.70075	1.70075	104.520
3	C _s	8,968	1.51178	1.70075	100.000
4	C _{2v}	10,741	1.79524	1.79524	170.000
5	C _{2v}	11,112	1.76521	1.76521	179.990
6	C _s	14,444	2.17318	2.36216	95.000
7	C _s	18,266	1.60627	2.55113	104.520
8	C _s	18,713	1.41729	1.60627	120.000
9	C _{2v}	19,299	2.36216	2.36216	104.520
10	C _s	24,614	1.79524	2.36216	179.900
11	C _{2v}	28,111	1.79524	1.79524	45.000
12	C _{2v}	31,560	1.41729	1.41729	100.000
13	C _s	32,359	1.79524	3.37795	104.520
14	C _{2v}	33,014	2.64562	2.64562	100.000

Table 6.7: Reference geometries for water; r_1 and r_2 are in bohrs, θ in degrees. The energies in the third column are the IC-MRCI+Q, AC6Z, [8, 8] ones relative to geometry 1.

relative energies in Table 6.9.

6.6.1 Analysis of the results

As an aid to the analysis of the large mass of data reported in Table 6.8 and 6.9 we calculated the non-parallelity error (NPE) defined by eq. (6.2) between several sets of energies; the NPEs are collected in table 6.10 and will be discussed in the following subsections. We point out that if sets of energies obtained with two different methods have a NPE of x cm⁻¹, it is then possible to rigidly shift the energy of one set so that they always differ from the energies in the other set by less than $\pm \frac{x}{2}$ cm⁻¹.

Relative energies We will analyse in this paragraph the first two sets of NPEs of table 6.10, namely those relative to {ACV6Z, [8, 8]}, and {ACV5Z, [8, 10]}.

MRCI-type methods including size-extensivity corrections, namely IC-MRCI+Q, IC-MRCI+P, IC-ACPF and IC-AQCC, lead to rather similar relative energies, as testified by NPEs between them in the range 22–118 cm⁻¹. More specifically, IC-ACPF energies lie between the IC-MRCI+Q and the IC-MRCI+P ones and agree well with either of them, with NPEs of 20–30 cm⁻¹. IC-AQCC energies agree best with the IC-MRCI+P ones, from which they differ by NPEs of about 50 cm⁻¹. It is not possible from these results alone to tell which of these methods is the most accurate with respect to FCI, but it is clear that they perform very similarly to one another.

Uncorrected IC-MRCI relative energies are well separated from the class of methods discussed above by NPEs in the range 210–370 cm⁻¹.

The multi-reference perturbative method RSPT2 is separated by NPEs of about 200 cm⁻¹ from *any* of the other methods considered when using the [8, 8] RS and by an even greater amount using the [8, 10] RS; also, RSPT2 energies agree better with uncorrected IC-MRCI rather than with any of the size-extensivity corrected MRCI-type methods. The situation is similar for

nr	IC-MRCI	IC-MRCI+Q	IC-MRCI+P	IC-ACPF	IC-AQCC	RSPT2	RSPT3
aug-cc-pCV6Z, all-electron RS=[8, 8]							
1	-76.427708	-76.434534	-76.433268	-76.433399	-76.432061	-76.423123	-76.430444
2	-76.420520	-76.427201	-76.425958	-76.426079	-76.424774	-76.415926	-76.423300
3	-76.387109	-76.393675	-76.392452	-76.392564	-76.391286	-76.382496	-76.389914
4	-76.378559	-76.385594	-76.384290	-76.384429	-76.383047	-76.374550	-76.381502
5	-76.376892	-76.383905	-76.382605	-76.382741	-76.381365	-76.372901	-76.379860
6	-76.361208	-76.368722	-76.367339	-76.367528	-76.366028	-76.356737	-76.363748
7	-76.344061	-76.351307	-76.349969	-76.350140	-76.348701	-76.339417	-76.346657
8	-76.342799	-76.349270	-76.348063	-76.348169	-76.346912	-76.338209	-76.345640
9	-76.338949	-76.346600	-76.345195	-76.345399	-76.343864	-76.334516	-76.341437
10	-76.314926	-76.322383	-76.321009	-76.321187	-76.319703	-76.310951	-76.317685
11	-76.299397	-76.306450	-76.305143	-76.305276	-76.303893	-76.294851	-76.302286
12	-76.284396	-76.290736	-76.289551	-76.289649	-76.288422	-76.279766	-76.287244
13	-76.279421	-76.287095	-76.285685	-76.285907	-76.284360	-76.275579	-76.281850
14	-76.276084	-76.284110	-76.282643	-76.282887	-76.281259	-76.272102	-76.278524
aug-cc-pCV5Z, all-electron RS=[8, 8]							
1	-76.425152	-76.431920	-76.430664	-76.430792	-76.429466	-76.419740	-76.427878
2	-76.417942	-76.424565	-76.423334	-76.423451	-76.422158	-76.412528	-76.420712
3	-76.384502	-76.391011	-76.389799	-76.389908	-76.388642	-76.379073	-76.387297
4	-76.375936	-76.382910	-76.381618	-76.381752	-76.380383	-76.371074	-76.378865
5	-76.374261	-76.381213	-76.379925	-76.380057	-76.378693	-76.369418	-76.377215
6	-76.358721	-76.366175	-76.364804	-76.364988	-76.363500	-76.353400	-76.361253
7	-76.341539	-76.348726	-76.347399	-76.347566	-76.346140	-76.336058	-76.344126
8	-76.340140	-76.346555	-76.345358	-76.345461	-76.344217	-76.334731	-76.342971
9	-76.336472	-76.344063	-76.342669	-76.342869	-76.341347	-76.331186	-76.338952
10	-76.312324	-76.319719	-76.318356	-76.318529	-76.317060	-76.307476	-76.315069
11	-76.296827	-76.303822	-76.302526	-76.302655	-76.301285	-76.291440	-76.299705
12	-76.281704	-76.287987	-76.286813	-76.286908	-76.285693	-76.276261	-76.284541
13	-76.277002	-76.284619	-76.283220	-76.283436	-76.281902	-76.272335	-76.279432
14	-76.273661	-76.281626	-76.280170	-76.280409	-76.278794	-76.268823	-76.276098
aug-cc-pCV5Z, all-electron RS=[8, 10]							
1	-76.427005	-76.432520	-76.431487	-76.431582	-76.430512	-76.419645	-76.428097
2	-76.419732	-76.425152	-76.424135	-76.424223	-76.423175	-76.412413	-76.420909
3	-76.386642	-76.391592	-76.390659	-76.390732	-76.389781	-76.379176	-76.387728
4	-76.377894	-76.383513	-76.382462	-76.382560	-76.381468	-76.371113	-76.379190
5	-76.376210	-76.381812	-76.380763	-76.380859	-76.379772	-76.369451	-76.377534
6	-76.361172	-76.366786	-76.365738	-76.365857	-76.364756	-76.353449	-76.361802
7	-76.343901	-76.349315	-76.348301	-76.348411	-76.347353	-76.336326	-76.344688
8	-76.342245	-76.347127	-76.346206	-76.346274	-76.345338	-76.334842	-76.343361
9	-76.338629	-76.344682	-76.343557	-76.343700	-76.342503	-76.331270	-76.339295
10	-76.314835	-76.320410	-76.319368	-76.319481	-76.318391	-76.307389	-76.315621
11	-76.298674	-76.304414	-76.303341	-76.303440	-76.302325	-76.291272	-76.299956
12	-76.283326	-76.288537	-76.287556	-76.287628	-76.286628	-76.276095	-76.284697
13	-76.279492	-76.284882	-76.283874	-76.284002	-76.282940	-76.273171	-76.280074
14	-76.275881	-76.282188	-76.281021	-76.281189	-76.279930	-76.268963	-76.276386
aug-cc-pV6Z, frozen-core RS=[8, 8]							
1	-76.367243	-76.372322	-76.371109	-76.371158	-76.369992	-76.368136	-76.361872
2	-76.359792	-76.364753	-76.363567	-76.363611	-76.362476	-76.360773	-76.354455
3	-76.326124	-76.330992	-76.329827	-76.329869	-76.328757	-76.326741	-76.320147
4	-76.317767	-76.323012	-76.321761	-76.321813	-76.320607	-76.318821	-76.312923
5	-76.316028	-76.321255	-76.320009	-76.320059	-76.318858	-76.317114	-76.311209
6	-76.301529	-76.307181	-76.305839	-76.305912	-76.304598	-76.301430	-76.295158
7	-76.283852	-76.289286	-76.287993	-76.288060	-76.286801	-76.283949	-76.277466
8	-76.281441	-76.286231	-76.285084	-76.285123	-76.284031	-76.282133	-76.275529
9	-76.279361	-76.285128	-76.283761	-76.283840	-76.282495	-76.279780	-76.273895
10	-76.254540	-76.260136	-76.258807	-76.258874	-76.257577	-76.254519	-76.248523
11	-76.239106	-76.244390	-76.243129	-76.243179	-76.241966	-76.240120	-76.233735
12	-76.222800	-76.227485	-76.226362	-76.226398	-76.225332	-76.223950	-76.217516
13	-76.219632	-76.225430	-76.224055	-76.224146	-76.222788	-76.219418	-76.213823
14	-76.216755	-76.222842	-76.221404	-76.221501	-76.220070	-76.217034	-76.211624

Table 6.8: Energies in Hartree for various quantum-chemistry methods, basis sets and reference spaces for the reference geometries of Table 6.7 (see text for details).

nr	IC-MRCI	IC-MRCI+Q	IC-MRCI+P	IC-ACPF	IC-AQCC	RSPT2	RSPT3
aug-cc-pCV6Z, all-electron RS=[8, 8]							
1	0	0	0	0	0	0	0
2	-32	1,609	-5	-3	-10	-30	-41
3	-57	8,968	-9	-5	-18	-51	-72
4	46	10,741	8	7	16	-81	0
5	41	11,112	7	6	15	-89	-10
6	151	14,444	26	13	49	126	194
7	92	18,266	16	7	29	105	123
8	-78	18,713	-13	-7	-25	-77	-101
9	181	19,299	31	14	58	148	235
10	138	24,614	24	13	45	5	133
11	50	28,111	9	9	18	41	16
12	-107	31,560	-18	-11	-35	-97	-131
13	186	32,359	32	12	58	23	253
14	263	33,014	44	19	83	131	328
aug-cc-pCV5Z, all-electron RS=[8, 8]							
1	0	0	0	0	0	0	0
2	-32	1,614	-5	-3	-10	-31	-41
3	-57	8,978	-10	-5	-19	-53	-72
4	45	10,756	8	7	16	-75	1
5	40	11,129	7	6	14	-84	-10
6	151	14,429	25	13	49	131	193
7	92	18,259	16	7	29	107	122
8	-77	18,735	-13	-7	-25	-78	-101
9	181	19,282	30	14	58	153	235
10	138	24,625	23	14	45	14	133
11	50	28,114	9	9	18	44	16
12	-106	31,590	-18	-11	-35	-100	-131
13	186	32,329	31	12	58	23	251
14	263	32,986	44	20	83	137	326
aug-cc-pCV5Z, all-electron RS=[8, 10]							
1	0	0	0	0	0	0	0
2	-21	1,617	-4	-2	-7	-30	-40
3	-124	8,983	-22	-17	-43	-101	-123
4	23	10,756	4	3	8	-104	-22
5	19	11,129	4	3	7	-113	-32
6	22	14,427	3	-2	5	101	123
7	-22	18,261	-4	-7	-10	25	45
8	-139	18,742	-25	-19	-48	-129	-144
9	118	19,278	20	10	38	118	212
10	13	24,605	2	-2	2	32	80
11	49	28,116	9	8	18	59	8
12	-67	31,601	-11	-6	-22	-95	-128
13	-27	32,403	-5	-13	-14	-255	84
14	174	32,994	29	13	55	77	303
aug-cc-pV6Z, frozen-core RS=[8, 8]							
1	0	0	0	0	0	0	0
2	-26	1,661	-6	-5	-12	-45	-33
3	-46	9,071	-11	-9	-21	14	87
4	36	10,822	8	8	16	1	-79
5	32	11,208	7	7	15	-10	-89
6	126	14,297	28	23	56	343	345
7	78	18,224	18	14	34	253	301
8	-63	18,895	-14	-12	-29	-19	55
9	151	19,137	34	27	67	255	172
10	113	24,622	25	22	50	314	255
11	45	28,078	11	10	21	18	45
12	-86	31,788	-20	-17	-39	-143	-106
13	158	32,239	36	26	68	401	254
14	221	32,807	49	39	97	356	169

Table 6.9: This table reports relative energies in cm^{-1} calculated from the *ab initio* values of table 6.8. In the column IC-MRCI+Q relative energies in cm^{-1} relative to geometry 1 are reported; what is reported in the other columns is the difference between the relative energy calculated with the method reported at the top of the column and the corresponding IC-MRCI+Q relative energy.

	IC-MRCI	IC-MRCI+Q	IC-MRCI+P	IC-ACPF	IC-AQCC	RSPT2
ACV6Z, all-electron, [8, 8]						
IC-MRCI+Q	370					
IC-MRCI+P	308	62				
IC-ACPF	340	30	32			
IC-AQCC	252	118	56	88		
RSPT2	176	224	214	229	194	
RSPT3	118	460	398	430	342	265
AC5Z, all-electron, [8, 10]						
IC-MRCI+Q	313					
IC-MRCI+P	259	54				
IC-ACPF	281	32	22			
IC-AQCC	210	103	49	71		
RSPT2	308	373	348	351	338	
RSPT3	190	447	393	415	354	391
all-electron, [8, 8], AC5Z→AC6Z^a						
IC-MRCI+Q	1.3					
IC-MRCI+P	1.1	0.4				
IC-ACPF	1.5	0.7	0.7			
IC-AQCC	1.3	0.7	0.7	0.7		
RSPT2	13.2	12.1	12.1	11.6	12.3	
RSPT3	3.3	2.6	2.6	3.3	3.1	12.5
AC5Z, all-electron, [8, 8] → [8, 10]^b						
IC-MRCI+Q	253					
IC-MRCI+P	210	43				
IC-ACPF	224	29	14			
IC-AQCC	169	85	42	56		
RSPT2	207	297	281	287	267	
RSPT3	108	170	130	143	99	183
A(C)6Z, [8, 8], frozen-core→all-electron^c						
IC-MRCI+Q	62					
IC-MRCI+P	70	7				
IC-ACPF	88	26	19			
IC-AQCC	80	18	11	8		
RSPT2	309	337	340	350	346	
RSPT3	473	424	418	404	410	482

^a NPEs between the net differences AC5Z→AC6Z.

^b NPEs between the net differences [8, 8] → [8, 10].

^c NPEs between the net differences frozen-core → all-electron.

Table 6.10: Non-parallelity errors (NPEs) between the energies reported in Table 6.8.

RSPT3, but the differences are even larger; typically RSPT3 energies differ by NPEs of $\approx 400 \text{ cm}^{-1}$ from any of the other methods. If one assumes that MRCI-type relative energies are the most accurate then clearly RSPT2 is not capable of providing the same accuracy and RSPT3 look even less accurate than RSPT2.

Effect of basis set enlargement Contrasting the NPEs relative to the AC5Z and AC6Z basis sets using the same RS=[8, 8] we can get an idea of the coupling between basis set incompleteness and electron correlation treatment. The change from AC5Z to AC6Z results for all methods in NPEs of about 60 cm^{-1} ; we can see from the third set of data in Table 6.10 that IC-MRCI+Q, IC-MRCI+P, IC-ACPF and IC-AQCC energies are shifted by the basis set enlargement by essentially the same amount within 1 cm^{-1} . The shift of uncorrected IC-MRCI is also very similar to those of the methods just mentioned.

The effect of the basis enlargement on RSPT2 energies differs from that of the other MRCI-type methods by a NPE of some 12 cm^{-1} . On the other hand RSPT3 is again in good agreement with the MRCI-type methods with NPEs of about 3 cm^{-1} .

These findings seem to show that, using the AC5Z basis set, the basis set incompleteness error is uncoupled from the correlation treatment by less than $\approx \pm 5 \text{ cm}^{-1}$. This result in turn led to some speculation about the possible use of the fast perturbative methods to compute a basis set incompleteness correction to supplement MRCI-type energies. For example, one could correct (IC-MRCI+Q, AC5Z) energies with the difference between (RSPT2, AC{56}Z) and (RSPT2, AC5Z). However, there are at least two considerations pointing against a procedure of this kind. Firstly, the very fast RSPT2 method does not seem to perform too well in modelling basis set incompleteness when compared with more advanced treatments; RSPT3 seems to be adequate and, while it is still considerably faster than IC-MRCI, the advantage in speed is not so great. Secondly, looking at the reference timings of Table 6.3, one can see that for basis sets larger than about AV6Z the step limiting the overall time is the integral calculation, and this again reduces the overall advantage in speed of perturbative over variational methods. These two considerations led to the conclusion that basis set extrapolation using perturbative method is not a very attractive option.

Effect of reference space enlargement Enlargement of the RS from [8, 8] to [8, 10] introduces a change corresponding of NPEs of 195, 94, 78, 85, 87, 220 and 107 cm^{-1} respectively for IC-MRCI, IC-MRCI+Q, IC-MRCI+P, IC-ACPF, IC-AQCC, RSPT2 and RSPT3. These values are hence larger than the effect of $\approx 60 \text{ cm}^{-1}$ due to basis set enlargement AC5Z to AC6Z discussed above.

Looking at the second, third and fourth sets of data of Table 6.10 we see that the NPEs between all the IC-MRCI-type methods are almost always slightly smaller going from the [8, 8] to the [8, 10] RS. This seems to indicate that these methods are very slowly converging to a common value, with any luck the exact energy. Also, by looking directly at the energies of Table 6.9 one can see that the effect of the RS enlargement on the relative energies is particularly small for IC-MRCI+Q, less than $\pm 6 \text{ cm}^{-1}$ for geometries with energies up to $20,000 \text{ cm}^{-1}$. As IC-MRCI+Q energies in the [8, 8] RS have been used to produce the most accurate water PES's available [PCS+03, BSZ+06] this finding shows that, even in a pessimistic scenario, the enlargement of the RS from [8, 8] to [8, 10] cannot significantly spoil the good results obtained with the former.

Table 6.11: Core-correlation effect on relative energies using the AC6Z basis set and the [8, 8] reference space.

nr	energy ^a	IC-MRCI	+Q	IC-ACPF	RSPT2	RSPT3	CC ^b
1	0	13.0	7.1	5.1	-8.3	15.2	
2	1,609	-44.7	-44.7	-44.7	-44.7	-44.7	-44.7
3	8,968	-101.1	-96.3	-94.5	-176.8	-247.1	
4	10,741	-58.7	-74.1	-77.2	-171.1	13.7	-81.8
5	11,112	-74.5	-89.0	-91.7	-183.8	-2.1	
6	14,444	185.5	154.4	142.3	-78.5	11.3	
7	18,266	69.2	49.0	40.5	-113.8	-120.6	30.8
8	18,713	-183.0	-174.4	-171.6	-247.3	-322.6	
9	19,299	205.5	169.5	154.8	46.8	241.3	134.5
10	24,614	30.4	-0.6	-10.7	-325.4	-114.3	-20.3
11	28,111	51.2	40.5	36.7	47.9	19.8	30.9
12	31,560	-235.2	-220.9	-216.5	-190.2	-238.5	-206.5
13	32,359	161.4	127.1	110.5	-265.9	134.8	
14	33,014	262.3	214.3	192.8	-26.0	382.2	166.4

^a Energies relative to equilibrium in cm^{-1} as reported in Table 6.7.

^b From ref. [BSZ⁺06] (see text for details).

On the other hand, similarly to what found in Sections 6.5.3 and 6.5.4, it is reasonable to expect that using the [8, 10] RS should actually *improve* MRCI-type relative energies with respect to those obtained with the [8, 8] one.

Effect of core correlation The effect of core-correlation using the A6Z and the AC6Z basis sets corresponds to a large overall change quantified by NPEs of 400–500 cm^{-1} (the effect on the absolute energies is $\approx 13,000 \text{ cm}^{-1}$). Looking at the fifth set of data of Table 6.10 one can see that the shift due to core correlation is described very similarly by all MRCI-type, approximately size-extensive methods considered, with NPEs among these methods in the range 10–20 cm^{-1} .

On the other hand, the effect of core-correlation on the relative energies obtained with RSPT2 and RSPT3 is *completely* different, as it can be seen from the large NPEs in the range 300–480 cm^{-1} reported. Note that RSPT2 and RSPT3, while not exactly size-extensive, are thought to be nearly so [Wer96]; size-extensivity is thought to be very important when the net core-correlation effect are calculated [BSZ⁺06] and we decided to investigate on this apparently bad behaviour of RSPT2 and RSPT3 a little further. Barletta *et al* [BSZ⁺06] computed core-correlation energies for water using various levels of single-reference Coupled Cluster theory (up to CCSDTQ) and various extrapolation techniques for 10 geometries, eight of which coincide with those used by us. We report some selected values for the core-correlation we calculated and the reference results by Barletta *et al* in Table 6.11. The reference equilibrium geometry used by us differs from the one used by Barletta *et al*, so we shifted the values so that they coincide for geometry 2. IC-AQCC energies agree with IC-ACPF ones within $\pm 4 \text{ cm}^{-1}$ and are not reported in the table; similarly, IC-MRCI+P corrections agree with the IC-MRCI+Q ones within $\pm 3.5 \text{ cm}^{-1}$ and are not reported.

If we believe the coupled cluster results by Barletta *et al* to be accurate, then the perturbative

RSPT2 and RSPT3 methods seems to be inadequate to accurately model core-correlation. On the other hand, all approximately size-extensive MRCI-type methods perform well, particularly IC-MRCI+P and IC-ACPF which differ from the coupled cluster values by less than $\pm 20 \text{ cm}^{-1}$. Incidentally, it is not at all certain that the coupled cluster results of by Barletta *et al* should be more accurate than the MRCI-type ones calculated by us, especially for high energies where the reference Hartree–Fock function is not a good approximation.

The conclusion of this analysis is that the RSPT2 and RSPT3 methods should not be used to compute accurate core-correlation corrections, while approximately size-extensive MRCI-type methods all seem capable of producing results accurate to within $\approx \pm 20 \text{ cm}^{-1}$.

The final conclusions of this analysis, complemented with the results described in the next section, will be presented in Section 6.8.

6.7 Ab initio energies for a new all-electron water PES

A new water potential energy surface has been developed by our group, with the main purpose of characterising the lowest-energy dissociation path. The grid of points used is a substantial extension of the one used for the CVRQD surface [PCS⁺03, BSZ⁺06] and comprises a total of 2174 points with geometries up to about $50,000 \text{ cm}^{-1}$. In particular, geometries where one of the O–H bonds is significantly stretched were added to the original set.

This new PES was computed with MOLPRO using the IC-MRCI method in the [8,8] RS (see Table 6.2) and correlating all electrons; the basis sets used are the correlation-consistent aug-cc-pCV n Z for $n=\text{Q},5,6$ (see section 6.2.2 for some qualifications about the $n=6$ basis set).

The $n=6$ and most of the $n=5$ points were computed by P. Maksyutenko from the Laboratory of Molecular Physical Chemistry of the École Polytechnique Fédérale de Lausanne, Switzerland and by S.V. Shirin from the Russianian Academy of Sciences in Nizhnii Novgorod, Russia. About 300 $n=5$ points and all the $n=4$ points were computed by the author, who also provided the input files. The author also collected, cleansed and analysed the resulting energy values. We will present in Section 6.7.1 the result of an analysis of the *ab initio* energies. This was performed mainly as a means of identifying unconverged or otherwise erroneous values but it is also an useful complement to the results presented in the previous sections. An analysis of the convergence of the MVD1 relativistic correction is also presented in Section 6.7.2.

6.7.1 Ab initio non-relativistic energies

Basis set extrapolation and observed convergence pattern

We extrapolated the aug-cc-pCV n Z energies in the same fashion as employed for the CVRQD surface [BSZ⁺06]. CAS-SCF energies for $n=\text{Q},5,6$ were extrapolated using the exponential formula (3.24)

$$E_{+\infty}^{\text{CAS-SCF}} = E_n + Ae^{-\alpha n}$$

More specifically, the extrapolated energy is calculated by

$$E_{+\infty}^{\text{CAS-SCF}} = \frac{E_4 E_6 - E_5^2}{E_4 - 2E_5 + E_6} \quad (6.3)$$

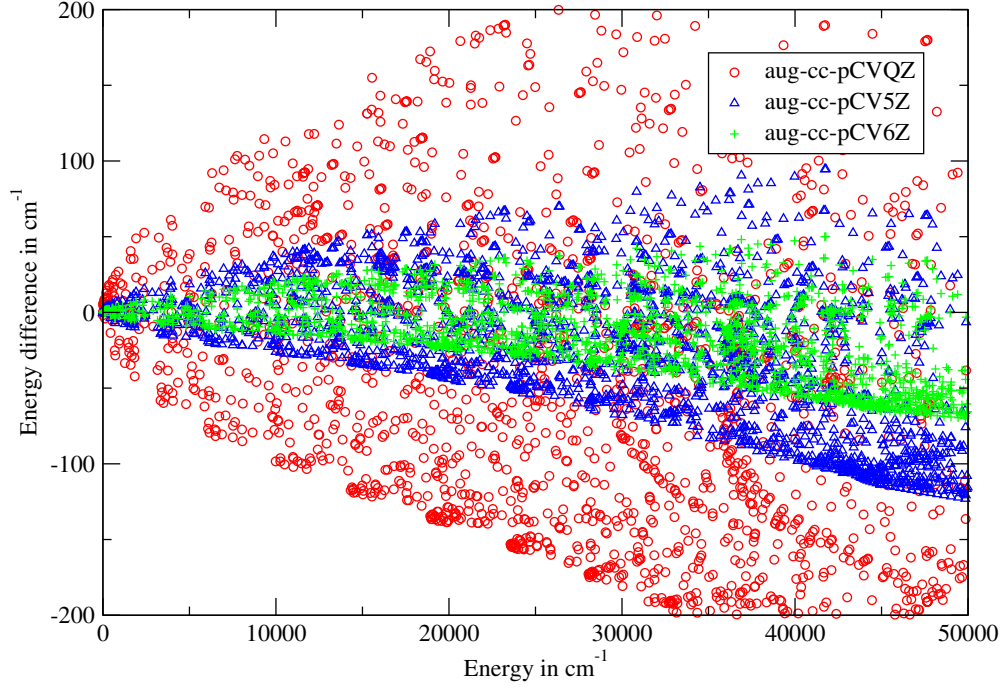


Figure 6.3: Differences of IC-MRCI energies calculated with the $ACnZ$ basis sets and the extrapolated $AC\{Q56\}Z$ ones. Energies have been shifted so that all surfaces coincide at the equilibrium geometry.

The dynamical-correlation part of the energy, that is the difference $E_{IC-MRCI} - E_{CAS-SCF}$, was extrapolated using the two-parameter inverse cubic formula (3.21)

$$E_{\infty} = E_n + \frac{A}{n^3}$$

The extrapolated correlation energy is then be obtained by

$$E_{+\infty}^{\text{corr}} = \frac{216E_6^{\text{corr}} - 125E_5^{\text{corr}}}{91} \quad (6.4)$$

A plot of the differences in the IC-MRCI energies with respected to the extrapolated $AC\{Q56\}$ ones is reported as Figure 6.3; the differences have been shifted so that all surfaces coincide at the equilibrium geometry. We also calculated the non-parallelity errors (NPEs, see Section 6.4 for the definition) for CAS-SCF and IC-MRCI energies for the $ACnZ$, $n=Q$, 5 and 6, basis sets with respect to the extrapolated energies; these are reported in Table 6.12.

It is very tempting to employ the difference between the extrapolated $ACV\{Q56\}Z$ and aug-cc-pCV6Z energies as an estimate of the basis set incompleteness error of the extrapolated energies; even though this might look a rather conservative estimate, it is probably not so. For example, in the case of the FCI calculations on hydrogen presented in section 3.14, the difference between the A6Z and the A{Q56} extrapolated energies is always greater than the error in the A{Q56} energies by a factor of 1.3 to 1.5. This factor further increases to 1.3 to 1.7 if the basis set extrapolation is performed with the inverse-cubic formula (3.21) instead of the three-parameter formula (3.22) which was found optimal for hydrogen. Similar remarks on the riskiness of using the difference between computed and extrapolated energies as an estimate of the error of the

basis set	maximum energy ^a					
	10,000 cm ⁻¹		25,000 cm ⁻¹		50,000 cm ⁻¹	
	CAS-SCF	IC-MRCI	CAS-SCF	IC-MRCI	CAS-SCF	IC-MRCI
aug-cc-pCVQZ	54	213	91	359	127	573
aug-cc-pCV5Z	7	63	11	121	16	218
aug-cc-pCV6Z	0.8	34	1.4	66	1.9	120

^a Maximum energy of the points included in the calculation of the NPEs.

Table 6.12: Non-parallelity errors with respect to extrapolated AC{Q56}Z energies (see text for details).

basis set	maximum energy ^a		
	10,000 cm ⁻¹	25,000 cm ⁻¹	50,000 cm ⁻¹
CAS-SCF	984	1679	2908
IC-MRCI	184	326	630
Pople	31	55	105

^a Maximum energy of the points included in the compute of the NPEs.

Table 6.13: Non-parallelity errors with respect to IC-MRCI+Q energies using the ACV6Z basis set.

extrapolated ones was also presented by Jeziorska *et al* [JCP⁺08] in a study of the helium dimer. In conclusion, it is reasonable to take the difference $E_{Q56Z} - E_{6Z}$ as a rather *optimistic* estimate of the basis set incompleteness error of the extrapolated energies.

Looking at the values of the NPEs of Table 6.12 it is clear that CAS-SCF energies converge to the complete basis set limit much faster than IC-MRCI ones; this is the expected behaviour as discussed in Section 3.4.2. For IC-MRCI AC6Z relative energies we found a NPEs with respect to extrapolated energies of 120 cm⁻¹ for points with energies up to 50,000 cm⁻¹; the basis set incompleteness error is then in the range ± 60 cm⁻¹ for these points.

Basis set errors for the absolute energies are much larger than those on relative ones. For example, the difference between IC-MRCI extrapolated AC{Q56}Z energies and the AC n Z ones for the equilibrium geometry are of 2909, 1293 and 732 cm⁻¹ respectively for $n=Q, 5$ and 6.

Differences in correlation energy treatment

We report in Figure 6.4 the differences in relative energies between CAS-SCF, IC-MRCI and IC-MRCI+P with respect to IC-MRCI+Q using the AC6Z basis set. The corresponding values of the NPEs are collected in Table 6.13.

The difference between CAS-SCF and IC-MRCI+Q energies gives an idea of the magnitude of dynamical correlation on relative energies; for energies up to 25,000 cm⁻¹ dynamical correlation changes the shape of the PES by $\approx \pm 800$ cm⁻¹, which is of course a very large value by our standards of accuracy.

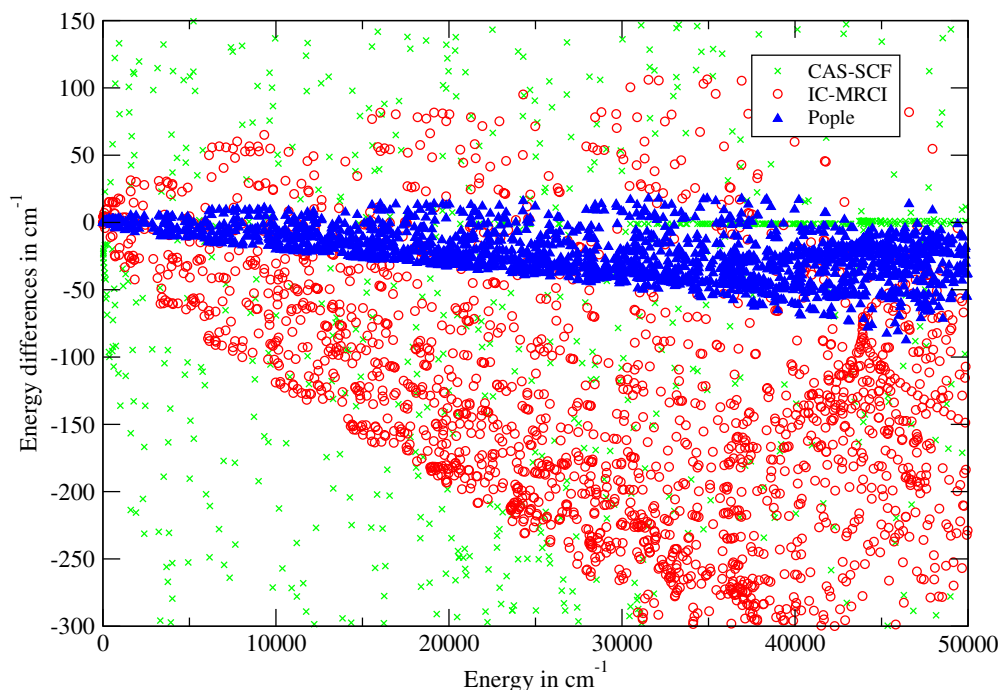


Figure 6.4: Differences of the AC6Z energies with respect to the IC-MRCI+Q ones. Energies have been shifted so that all surfaces coincide at the equilibrium geometry.

The NPE between IC-MRCI and IC-MRCI+Q energies could be taken as an estimate of the magnitude of further correlation effects not included in IC-MRCI; the (renormalised) Davidson energies differ from the uncorrected IC-MRCI ones by an NPE of 326 cm^{-1} for energies up to $25,000 \text{ cm}^{-1}$. This is a rather large value, and hopefully the real error of IC-MRCI+Q energies is smaller than this. The difference between Pople-corrected IC-MRCI+P and IC-MRCI+Q energies is much smaller, corresponding to a NPE of 55 cm^{-1} for energies up to $25,000 \text{ cm}^{-1}$.

Differences in the absolute energies are, as usual, much larger than the corresponding differences in relative energies discussed above. For example, for the equilibrium geometry and using the AC6Z basis set CAS-SCF, IC-MRCI and IC-MRCI+P absolute energies differ from the IC-MRCI+Q ones respectively by 51850 , 1498 and 278 cm^{-1} .

6.7.2 Convergence of the relativistic corrections

Relativistic corrections were computed as expectation values of the mass-velocity and one-electron Darwin terms (MVD1) described in Section 2.4. The absolute energy of the MVD1 correction in water is of about $-11,400 \text{ cm}^{-1}$, but its effect on the relative energies is much smaller. A plot showing the IC-MRCI AC6Z relativistic corrections is reported as Figure 6.5 and it can be seen from this plot that the corrections to relative energies lie in the range $\pm 70 \text{ cm}^{-1}$.

We studied the convergence of the MVD1 relativistic correction with respect to basis set size and of correlation treatment. The convergence with basis set size of the IC-MRCI relativistic energies is represented in Figure 6.6. We can see from the plot that already with the ACQZ basis set the MVD1 corrections differ by less than $\pm 1 \text{ cm}^{-1}$ from the AC6Z ones; the difference

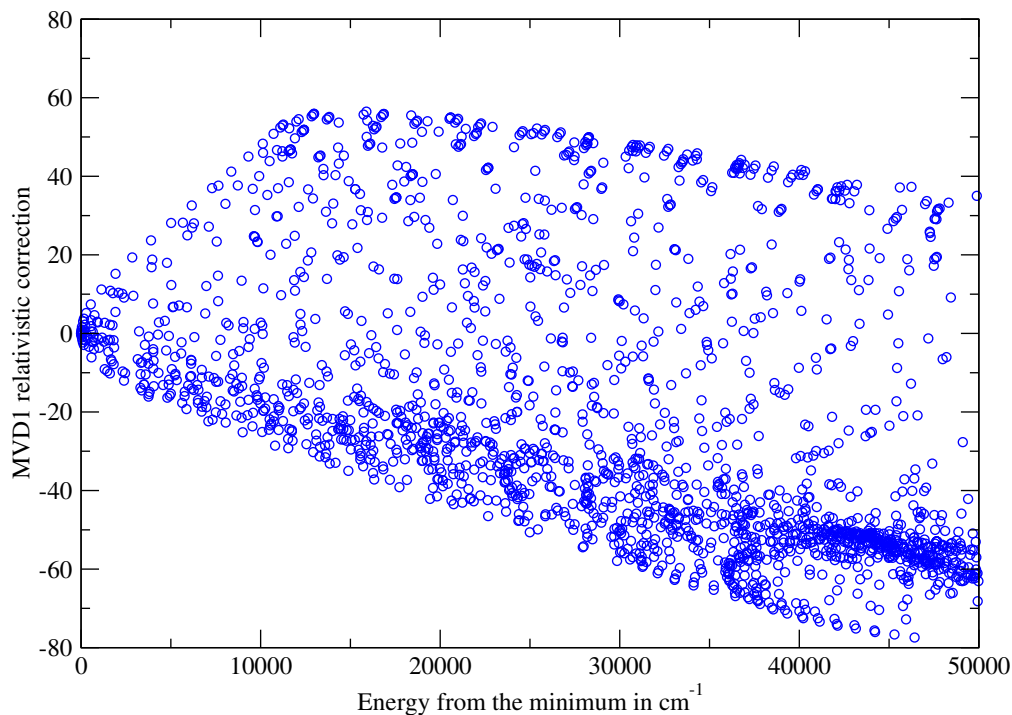


Figure 6.5: Relativistic MVD1 corrections computed in the AC6Z basis set as expectation value on the IC-MRCI wave function. The corrections have been shifted so that the correction at equilibrium is zero.

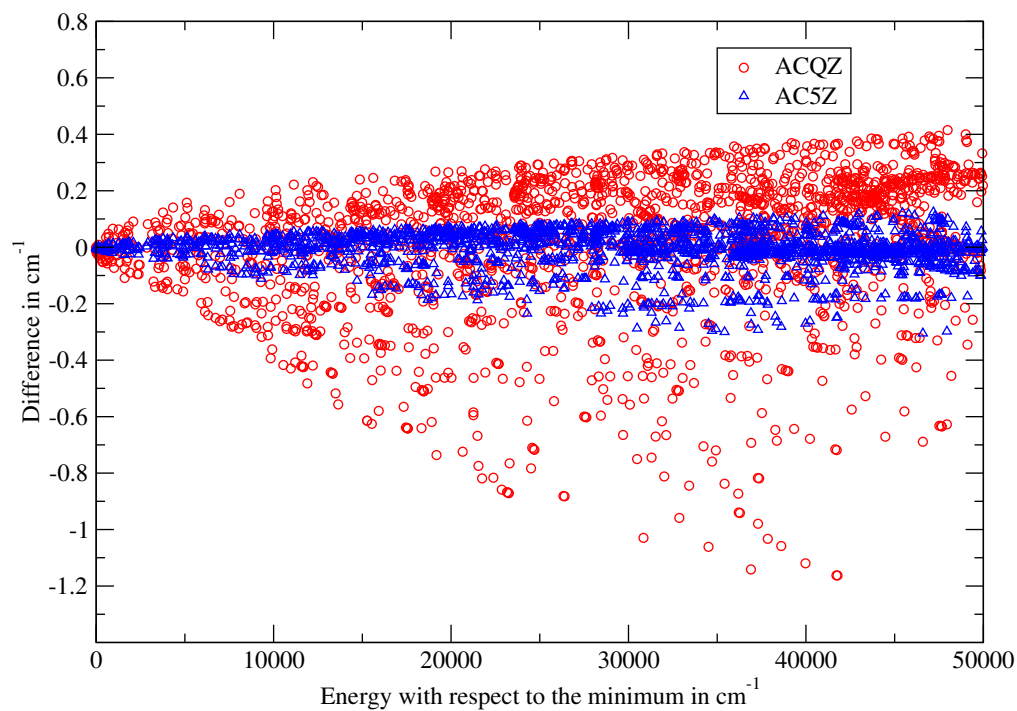


Figure 6.6: Differences of the MVD1 corrections for the ACQZ and AC5Z basis sets with respect to the ACV6Z ones.

from AC5Z to AC6Z is a minuscule $\pm 0.2 \text{ cm}^{-1}$. The convergence pattern with respect to basis set size of MVD1 corrections calculated with CAS-SCF and RHF wave functions is even faster.

These findings show that convergence of MVD1 relativistic corrections with respect to basis set size is fast and even small basis sets like ACQZ or even ACTZ provide a very good accuracy of a few cm^{-1} .

Finally, we investigated the effect of electron correlation on the MVD1 corrections using the AC6Z basis set.

Relative values of the MVD1 corrections calculated from the RHF wave function differ from the IC-MRCI ones by less than $\pm 5 \text{ cm}^{-1}$ for energies up to $20,000 \text{ cm}^{-1}$; this value grows to about $\pm 25 \text{ cm}^{-1}$ for energies up to $40,000 \text{ cm}^{-1}$. On the other hand the CAS-SCF MVD1 corrections differ from the IC-MRCI ones by about $\pm 5 \text{ cm}^{-1}$ for all energies up to $50,000 \text{ cm}^{-1}$. The net effect of dynamical correlation on the relativistic corrections is then estimated to be about $\pm 5 \text{ cm}^{-1}$.

The final conclusion of this study is that accurately computing the MVD1 relativistic correction is a comparatively simple task and even relatively low-levels of the theory like CAS-SCF combined with triple- or quadruple-zeta sized basis sets are enough to compute the correction surface with an error of only a few cm^{-1} .

Our conclusion that the convergence of MVD1 relative energies is “fast” is apparently at odds with some comments by Michauk and Gauss [MG07]; these authors performed a study of the MVD1 correction using the CCSD(T) method and described the basis set convergence as being “slow”. However, looking at the data published by these authors, there seem to be no contradiction with our findings; for example, it is reported in Table I and II of the cited reference that in a study of the HF molecule the MVD1 correction calculated with the cc-pCVTZ basis set gives an equilibrium bond-length converged to $\pm 10^{-6}$ nanometres and a harmonic vibrational frequency converged to $\pm 0.4 \text{ cm}^{-1}$. These are by our standards very good levels of convergence.

Finally, our studies also confirm the quality of previous calculations on the MVD1 correction for water [CKP⁺98a] using quadruple-zeta sized basis sets and the CCSD(T) method.

6.8 Conclusions about the calculations of *ab initio* energies

We summarise here the conclusions drawn in the previous sections 6.5, 6.6 and 6.7.

- The multi-reference perturbative methods RSPT2 and RSPT3 do not seem capable of the same accuracy as MRCI-type methods. Also, the slower RSPT3 method does not seem to improve on RSPT2.
- All approximately size-extensive MRCI-type methods perform similarly. In particular, ACPF is very close to IC-MRCI+P. As a single IC-MRCI calculation also gives at the same time the IC-MRCI+Q and IC-MRCI+P energies there does not seem to be any compelling reason for using IC-ACPF or IC-AQCC.
- Enlargement of the reference space from $[8, 8]$ to $[8, 10]$ seems to lead for MRCI-type methods to slightly more accurate results. Relative energies obtained with the $[8, 10]$ RS differ from those in the $[8, 8]$ one by up to about $\pm 50 \text{ cm}^{-1}$.

- Extrapolated AC{Q56}Z relative energies differ from AC6Z one by about $\pm 30 \text{ cm}^{-1}$ for energies up to $25,000 \text{ cm}^{-1}$ and by about $\pm 60 \text{ cm}^{-1}$ for energies up to $50,000 \text{ cm}^{-1}$. These values can be taken as an (optimistic) estimate of the residual basis set incompleteness error of AC{Q56}Z relative energies.
- Basis set incompleteness is uncoupled with respect to correlation treatment to within about $\pm 5 \text{ cm}^{-1}$ when using the AC5Z basis set. Unfortunately, the possibility of applying extrapolation techniques based on the fast RSPT2 or RSPT3 methods does not seem very attractive.
- Relativistic corrections computed as expectation value of the MVD1 operator converge rapidly with basis set size and are also not very sensitive to the level of electron correlation used. Relativistic MVD1 corrections calculated with IC-MRCI and the AC6Z basis set seem accurate to better than $\pm 1 \text{ cm}^{-1}$, which is less than the intrinsic accuracy of the MVD1 approximation [BSZ⁺06].

6.9 Practical notes

In this section we will report and explain in detail the format of the MOLPRO 2006.1 [WKL⁺06] input files we found optimal for our calculations on water. For more information see the manual of the program. We also point out that there exist a free graphical front-end called Gabedit [Gab] which can be used to create in a user-friendly way the input files for MOLPRO and many other quantum chemistry programs.

6.9.1 Minimal MOLPRO input file

A minimal input file that performs a frozen-core IC-MRCI calculation for water for a C_s geometry (i.e., $r_1 \neq r_2$) using the reference space labelled as [8, 8] in Table 6.2 is¹:

```
r1=1.7, r2=1.9, theta=104.5
geometry={0; H1,0,r1; H2,0,r2,H1,theta}
basis=cc-pVDZ
{RHF}
{MCSCF; OCC, 7, 2 ; CLOSED, 1,0 ; FROZEN, 0,0 }
{MRCI ; OCC, 7, 2 ; CLOSED, 1,0 ; CORE, 1,0 }
```

The first two lines specify the geometry of the molecule using the so-called Z-matrix format; bond lengths are assumed to be in bohrs and angles in degrees. The third line specifies the basis set. The fourth invokes a restricted Hartree–Fock calculation, using default choices for occupation numbers and convergence thresholds. The fifth line invokes the CAS-SCF program, again using default settings. The OCC, CLOSED and FROZEN keywords specify the reference space (RS) to be employed; remember that in the CAS-SCF method the RS is the orbital subspace within which FCI is performed. The couples of numbers n_1, n_2 represent the number of orbitals of a' and a'' symmetry to be included in a certain class of orbitals. More specifically:

- OCC is the sum of the active (=included in the RS) *and* inactive (=occupied, but not included in the RS) orbitals.

¹This example uses 6.5 MB of disk space, 30 MB of RAM and completes in 14 seconds on a 3.4 GHz Pentium IV.

- **CLOSED** specifies orbitals which should *not* be included in the RS but whose coefficients are permitted to be variationally optimised.
- **FROZEN** orbitals are *not* included in the RS and their coefficients are not permitted to be variationally optimised. However, note that also **FROZEN** orbitals will be indirectly changed by the CAS-SCF procedure because the Fock operator, from which all orbitals are derived, is modified (see section 3.8).

There is usually no reason to use **FROZEN** instead of **CLOSED** orbitals as in the latter case a little more electron correlation can be allowed for.

The final line specifies an IC-MRCI calculation; the specification of the RS – which in the MRCI method determines the subspace from which all single and double excitations to external orbitals are considered – follows a format similar to the one used in the CAS-SCF step. The **OCC** and the **CLOSED** keywords have the same meaning as in the CAS-SCF step and should be given the same values, so that the same RS is generated in CAS-SCF and IC-MRCI. The **CORE, 1,0** keyword indicates that single and double excitations from the energetically lowest a' orbitals should not be generated and thus specifies the frozen-core approximation. Also note that MOLPRO assumes that **CORE** orbitals are also **CLOSED**, so the last line could have been equivalently written as
`{MRCI ; OCC, 7, 2 ; CLOSED, 0,0 ; CORE, 1,0 }`

Finally, a word of notice. If $r_1 = r_2$ MOLPRO will by default use C_{2v} symmetry and expect the specification of the RS to be constituted by four numbers n_1, n_2, n_3, n_4 , representing orbitals belonging to the a_1, b_1, b_2 and a_2 symmetry species. If only two numbers are provided MOLPRO will assume the last two are zero, generating a wrong RS.

All-electron calculations

Only two small modifications are necessary to run an all-electron calculation. First, a basis set appropriate for core-correlation should be selected, e.g. modifying line three to

```
basis=cc-pCVDZ
```

Second, the IC-MRCI command should be changed to

```
MRCI ; OCC, 7, 2 ; CLOSED, 1,0 ; CORE, 0,0
```

thus allowing single and double excitations from the lowest-energy “core” orbital.

Note that the CAS-SCF step is unmodified, because even in an all-electron calculation core orbitals need not be included in the CAS-SCF RS.

6.9.2 Personalised MOLPRO input file

The minimal input described in the previous section is perfectly functional but it was found useful to customise some settings. These will be described in this section.

Output options and global threshold

We found it advisable to begin each input file with a header of this kind:

```
***, Calculation of H2O --- Input for MOLPRO 2006.1
```

```
MEMORY, 80.00, M
```

```
GEXPEC, DM, REL, DARWIN, MASSV
```

```
GTHRESH, ZERO=1.e-13, TWOINT=1.e-13, ENERGY=2.e-12, GRADIENT=1.e-3, ORBITAL=1.e-6,
CIVEC=1.e-5, COEFF=1.e-5
GPRINT, DISTANCE, ANGLES, VARIABLE
```

The first line is a title for the run and mentions the version of MOLPRO for which the input was written. The second line explicitly sets the maximum amount of RAM MOLPRO is allowed to use, in units of computer words²; in our example we specified 80×10^6 words, equivalent on our system to 640 MB of RAM. If MEMORY is omitted the default value will be used and MOLPRO will stop if more memory is required.

In the third line we ask to compute expectation values for the dipole moment (DM) and for the mass-velocity and Darwin relativistic correction terms; the extra computer time required is minimal so it is useful to always compute them. In the fourth line we specify some general convergence thresholds, using stricter values than the default ones (see the manual for more information). Finally, we explicitly require printing out of all bond lengths and bond angles, variables used internally by MOLPRO.

Geometry specification

By default MOLPRO automatically identifies the point-group symmetry of the molecule and then rotates and translates it according to the Mulliken conventions explained in Section 6.1. However, both the automatic identification of the symmetry and the rotation/translation may be undesirable. In particular, when dipole moments are calculated it is essential that they all refer to the same choice of the coordinate axes; this is complicated by the standard convention requirement that the molecule lie on the xy in C_s symmetry but on the xz plane in C_{2v} symmetry (see section 6.1). We preferred to use the axes convention explained in Section 6.1, with the oxygen atom at the origin and the two hydrogens in the first and fourth quadrants of the xy plane. For a C_s geometry ($r_1 \neq r_2$) the geometry input is as follows:

```
r1 = 1.7, r2 = 1.9, theta = 104.5
geomtyp = XYZ
geometry = {z, NOORIENT ;
3 ! number of atoms
Blank line
0, 0.d0 , 0.d0 , 0.d0
H, r1*cos(theta/2.d0)/ANG , r1*sin(theta/2.d0)/ANG , 0.d0
H, r2*cos(theta/2.d0)/ANG , -r2*sin(theta/2.d0)/ANG , 0.d0
}
```

where bond lengths are expressed in bohrs and the bond angle in degrees. For a C_{2v} geometry ($r_1 = r_2$) using the same convention for the axes only the third line should be changed to

```
geometry = {y, z, NOORIENT ;
```

Basis specification

If different basis sets need to be specified for different atoms a block of this kind can be used:

```
BASIS
```

²MOLPRO means as “computer word” the size of a floating point number; the usage in computer science of “word” is not the same.

```
default, cc-pVDZ, H=aug-cc-pVTZ, O=aug-cc-pCVTZ
```

```
END
```

Note that in MOLPRO v.2006.1 it is always necessary to specify a “default” basis set, even if specific basis sets are specified for all atoms.

Hartree–Fock step

The default settings for the Hartree–Fock step work well in most cases but some tweaking was found to be useful. By default MOLPRO will use as starting guess orbitals from a previous calculation, if these are available. For some high-energy geometries, e.g. at very long bond lengths, it was found that the Hartree–Fock solution found was sensitive to the starting guess; in this case the default behaviour made it difficult to exactly reproduce calculations as these depended on the previous history of calculations performed. Because of this, we preferred to generate a specific starting guess anew for each calculation, instead of using previous results. In these cases it was also found that the solution found using the specified starting guess and the default optimisation options converged to a solution which was slightly higher in energy than the one found by the programs PSI3 [CSV⁺07] or AMICA [GBL⁺05]. This convergence problem was found to have a very small and probably negligible effect in the subsequent CAS-SCF and IC-MRCI results, but it was also found the problem could be in many cases solved by specifying a shift in the DIIS optimisation step. Finally, we also selected stricter thresholds for the convergence of the energy (ENERGY) and of the sum of the square of the change of the density matrix elements (ACCURACY)³

```
{RHF, ENERGY=2.e-12, ACCURACY=5.e-11 ;
WF, NELEC=10, SYMMETRY=1, SPIN=0
OCC, 4, 1
START, TYPE=ATDEN
MAXIT, 60
ORBPRINT, 0
IPOL, DIIS , DIIS_START=3, DIIS_STEP=1, MAXDIIS=10
SHIFT, SHIFTC=-0.3
}
```

The second line specifies the total number of electrons, the symmetry species of the electronic state (‘1’ meaning a' , ‘2’ a'') and the total spin (but note that SPIN should equal $2S$ if S is the total spin); these values should be guessed correctly by MOLPRO in all cases but it does no harm to specify them. The third line specifies the occupation numbers of the Hartree–Fock wave function; again, these should always be automatically guessed correctly but we may specify them for extra clarity. If the geometry is of C_{2v} type the line should be changed to

```
OCC, 3, 1, 1, 0
```

The fourth line specifies to take as starting guess the natural orbitals of an approximate density matrix (see manual). This prevents the use of results of previous calculations as starting guess, as discussed above. The fifth line specifies that the maximum number of iterations is increased to 60. The sixth line specifies that the energies and expansion coefficients of the occupied

³Note that what is displayed in output as CONVERGENCE THRESHOLDS: x.xxE-xx (Density) is the square root of the value specified by ACCURACY.

orbitals should be printed, but not of the virtual orbitals. The seventh and eighth lines specify parameters for orbital optimisation which were found to give a better convergence pattern than the default ones in some situations.

CAS-SCF **step**

By default MOLPRO at the first CAS-SCF iteration will only find the linear CI coefficients by direct diagonalisation; starting from the second iterations both orbitals and CI coefficients are optimised simultaneously using a non-linear minimisation algorithm. Three different algorithms are available: Werner-Meyer-Knowles (WMK), Newton-Raphson (NR) and Augmented Hessian (AH).

The WMK algorithm was introduced by Knowles and Werner [Wer87, WK85, KW85] specifically for MC-SCF calculations, following an earlier, related method by Werner and Meyer [WM81, WM80]. It is a very sophisticated scheme, designed to be both robust and fast. In our experience this algorithm proved to be, by a significant extent, the fastest and most stable, normally converging the energy to $10^{-8} E_h$ in only 4 to 5 iterations, with each iteration taking less time than any of the other algorithms. However, in some cases mainly for geometries close to linearity we did encounter convergence problems.

The classical NR algorithm for the solution of a system of non-linear equations, see e.g. [PTVF07], was one of the first to be used in the CAS-SCF method [SRL80, Roo87], with generally good results. It is not as fast as WMK and it may take more iterations to converge; on the other hand, applied to the cases where WMK failed to converge, it sometimes did.

The AH method, discussed e.g. in [Roo87], is another method expressly created for MC-SCF with the goal of enlarging the radius of convergence of the NR scheme. In our tests, however, it proved to be both the slowest and the least robust of the three methods. We finally settled on a format that first runs CAS-SCF using the WMK algorithms and then, if convergence was not reached, tries again with the NR one:

```
{MCSCF
  ACCURACY, ENERGY=5.e-10;
  MAXITER, 15;
  {ITERATIONS;
    DO, DIAGCI, 1, TO, 2 ;
    DO, INTERNAL, 2, TO, 15 ;
    DO, WERNER, 1, TO, 15 ;
    DONT, AUGMENT, 1, TO, 15 ;
    DONT, NEWTON, 1, TO, 15 ;}
  OCC, 7, 2 ; CLOSED, 1,0 ; FROZEN, 0,0 ; }
  if(status.eq.1) goto EndOfCASSCF
{MCSCF
  ACCURACY, ENERGY=5.e-10;
  NOEXTRA;
  MAXITER, 25;
  {ITERATIONS;
    DO, UNCOUPLE, 1, TO, 25 ;
    DO, INTERNAL, 2, TO, 25 ;
```

```

DONT, WERNER, 1, T0, 25 ;
DONT, AUGMENT, 1, T0, 25 ;
DO, NEWTON, 1, T0, 25 ;}
OCC, 7, 2 ; CLOSED, 1,0 ; FROZEN, 0,0 ; }
if(status.ne.1) exit
EndOfCASSCF

```

This wordy format was found more effective than specifying performing the first, say, 15 iterations with WMK and then switching to NR, because sometime the WMK would stop before reaching the maximum number of iterations. In the second (eventual) CAS-SCF run we also specified the commands UNCOUPLE and NOEXTRA which may help the convergence (see the manual for more information).

IC-MRCI step

The IC-MRCI calculation was found to be the most unproblematic step. The input we used is:

```

{MRCI ;
THRESH, ENERGY=1.e-10
ORBITAL, IGNORE_ERROR
OCC, 7, 2 ; CLOSED, 1,0 ; FROZEN, 1,0 ;

```

Apart from the tighter convergence threshold we indicated to perform the calculation even if the previous CAS-SCF step reported lack of convergence (this condition never occurs if the last-but-one line of the previous CAS-SCF input is included).

6.9.3 Input for AMICA

A typical input file for a C_{2v} run with AMICA using the [8,8] reference space and r_{12} -MRCI is

```

&INT title 'H2O' group C2v atoms 2
TYPE H COORD 0.000000 1.344950 1.040996 basis ' cc-pVDZ '
TYPE O COORD 0.000000 0.000000 0.000000 basis ' cc-pVDZ '
&SCF title 'Ground state' occ 3 1 0 1
&PSI SPIN 1 ELEC 10 SYM 1 STATE 1 ASYM
DBL a1 ACT a1 a1 a1 a1 b1 b1 b2 b2
&MCSCF
&CI r12-ci

```

The same calculation in C_s symmetry is

```

&INT title 'H2O' group Cs atoms 3
TYPE H COORD -1.344950 1.040996 0.000000 basis ' cc-pVDZ '
TYPE H COORD 1.344950 1.040996 0.000000 basis ' cc-pVDZ '
TYPE O COORD 0.000000 0.000000 0.000000 basis ' cc-pVDZ '
&SCF title 'Ground state' occ 4 1
&PSI SPIN 1 ELEC 10 SYM 1 STATE 1 ASYM
DBL a' ACT a' a' a' a' a' a' a" a"
&MCSCF
&CI r12-ci

```

Note that in the symmetry convention used by AMICA/COLUMBUS b_1 and b_2 symmetry species

are swapped (see section 6.1). This is inconsequential for the [8, 8] RS because it is symmetric in b_1/b_2 , but may be of importance for other RS's.

If the keyword **ASYM** is not included the energy will depend slightly (within $1\text{--}5\text{ cm}^{-1}$) on the symmetry point group employed.

The ground-state electronic dipole moment of water

7.1 Introduction

The calculation of rotational-vibrational transition intensities relies on a knowledge of both the nuclear-motion wave functions of the upper and lower states involved, which in turn are obtained from the potential energy surface, and of the dipole moment surface (DMS).

Traditionally, considerable effort has been expended obtaining high-accuracy potential surfaces from which the corresponding rotation-vibration energies and wave functions can be calculated. Much less effort has been devoted to obtaining high-accuracy DMS's and transition intensities. This situation holds true both in general and for the specific case of the water molecule [FMT91, WR92, PS97, SPZ⁺03, PCS⁺03, SPZ⁺06, BSZ⁺06]. For example, in the case of the molecular ion H_3^+ the most accurate transition energies available come from experiment, while the best line intensities are theoretically-determined [NMT96].

If transition wavenumbers with an average accuracy of the order of 0.05 cm^{-1} are desired, it is necessary to tune *ab initio* potential energy surfaces by introducing semi-empirical parameters fit to experimental data [PS97, SPZ⁺03, SPZ⁺06, YVT⁺08]. Although it is in principle possible to tune DMS's to experimental data too [WR92], tests have shown that this gives poorer results than purely *ab initio* procedures [LMT95]. In part this is due to the fact that experimental uncertainties for transition intensities are much larger than for transition wavenumbers. This situation persists despite the recent advances in high precision experiments [CTT⁺02, TCRM05, LHC06, LH08]. There are several technical reasons that make laboratory experiments of water line intensity difficult, some of which were discussed in section 1.2. As a consequence of these difficulties, there still exists much uncertainty on water transition intensities, see e.g. [BSS⁺00].

On the other hand, monitoring water vapour is a major activity in many areas [Ber02] including astrophysics and atmospheric physics and several satellite missions have been launched with this as their major goal [KSA⁺96, Mel00, PPC⁺05]. The demand of modern remote sensing satellites require water line intensities to $\pm 1\%$ or better [Ten]. This demand is not primarily for monitoring water columns but because water absorption interferes with many other retrivals

that are being attempted. Failure to correctly model water absorption thus introduces a major source of error into these observations.

7.1.1 Molecular dipole moments

The molecular dipole-moment vector operator $\hat{\boldsymbol{\mu}}$ for a molecule containing N_n nuclei and N_e electrons is defined, in analogy with the classical definition [Jac98], by

$$\hat{\boldsymbol{\mu}} = \hat{\boldsymbol{\mu}}_N + \hat{\boldsymbol{\mu}}_e = \sum_{\alpha=1}^{N_n} e_0 Z_{\alpha} \hat{\mathbf{R}}_{\alpha} - \sum_{i=1}^{N_e} e_0 \hat{\mathbf{r}}_i \quad (7.1)$$

where e_0 is the proton charge and where we indicated with capital letters the coordinates of the nuclei and with lower-case letters those of the electrons. For electrically-neutral molecules the dipole moment is independent of the choice of the origin of the axes.

In the Born-Oppenheimer and related schemes (see Chapter 2) the clamped-nuclei dipole-moment function is given by

$$\boldsymbol{\mu} = \boldsymbol{\mu}_N + \boldsymbol{\mu}_e = e_0 \sum_{\alpha=1}^{N_n} Z_{\alpha} \mathbf{R}_{\alpha} - e_0 \int_{\mathbb{R}^3} \mathbf{r} \varrho(\mathbf{r}|\mathbf{R}_{\alpha}) d\mathbf{r} \quad (7.2)$$

where the nuclear vector coordinates $\mathbf{R}_{\alpha}$ specify a particular nuclear geometry and the electronic density $\varrho(\mathbf{r})$ can be obtained from the electronic wave function. The clamped-nuclei dipole moment, considered as a function of the nuclear coordinates, defines the molecular dipole-moment surface or DMS.

Units of measure of the electric dipole moment

The atomic unit of electric dipole is given, using the CODATA2006 values [MTN08], by

$$1 \text{ au of dipole} = e_0 a_0 = 8.47835281(21) \times 10^{-30} \text{ C} \cdot \text{m} \quad (7.3)$$

Another unit in wide use in molecular physics is the debye, D. Using again the CODATA2006 values [MTN08] the debye is related to the atomic unit by the equivalence relation

$$1 \text{ au of dipole} \mapsto 2.54174623(6) \text{ D} \quad (7.4)$$

7.1.2 Transition intensities

Spectroscopy, and infrared spectroscopy in particular, is rife with a multitude of related quantities describing the amount of radiation absorbed by a transition; these include: line strengths, line intensities, absorption cross-sections, Einstein A coefficients, optical densities and oscillator strengths. Furthermore, the same quantities can be expressed in many different units of measure (SI units are practically never employed). A summary of this state of affairs can be found in the book by Bernath [Ber05] (pag. 272–278) and in the review by Hilborn [Hil82]. In the remainder of this section we will state the definitions of the quantities and units used by us; more details on the theory on light-matter interaction can be found e.g. in the books by Bunker and Jensen [BJ98] and by Cohen-Tannoudji *et al* [CTDRG97].

We define the line strength S relative to an electric-dipole-type transition from a state $|i\rangle$ to state $|f\rangle$ as

$$S(i \rightarrow f) = |\langle i | \boldsymbol{\mu} | f \rangle|^2 = \sum_{r=x,y,z} |\langle i | \mu_r | f \rangle|^2 \quad (7.5)$$

Assuming we are in a situation of thermal equilibrium at a temperature T , we define the integrated effective absorption cross-section S_σ , often just called “line intensity”, by the following formula in SI units [BJ98, Rot98]:

$$S_\sigma(i \rightarrow f) = \left[\frac{8\pi^3}{(4\pi\epsilon_0)3hc} \right] \frac{g_l \bar{\nu}}{Q(T)} \times e^{-\frac{hc\bar{\nu}_l}{k_B T}} \left(1 - e^{-\frac{hc\bar{\nu}}{k_B T}} \right) \times S(i \rightarrow f) \quad (7.6)$$

where $\bar{\nu}$ is the transition wavenumber, $\bar{\nu}_l$ is the wavenumber of the lower state, g_l is the nuclear spin weighting times the rotational degeneracy weighting, T is the temperature in kelvins, k_B is the Boltzmann constant and $Q(T)$ is the partition function of the molecule. In the common case where $\bar{\nu}$ is measured in cm^{-1} , the line strength $S(i \rightarrow f)$ in Debye squared and the line intensity S_σ in $\text{cm}/\text{molecule}$ (see below) the factor in square brackets of eq. (7.6) can be conveniently expressed as

$$\frac{4 \times 10^{-45} \pi^2}{3hc} \frac{\text{cm}/\text{molecule}}{\text{J}^{-1} \text{ s m}^{-1} \text{ cm D}^2} = 4.1623797121 \times 10^{-19} \frac{\text{cm}/\text{molecule}}{\text{cm D}^2}$$

where the CODATA2006 values [MTN08] for $\hbar$ and c were used.

Formula (7.6) specifies that S_σ , as a function of the transition wavenumber $\bar{\nu}$ and of the lower-state wavenumber $\bar{\nu}_l$, is proportional to

$$S_\sigma \propto e^{-\frac{hc\bar{\nu}_l}{k_B T}} \left(\bar{\nu} - \bar{\nu}_l e^{-\frac{hc\bar{\nu}}{k_B T}} \right) \quad (7.7)$$

At room temperature $T \approx 296 \text{ K}$ and $hc/(k_B T) \approx (1/200) \text{ cm}$. The first factor of eq. (7.7), will then be vanishingly small for $\bar{\nu}_l \gg 200$; this implies that observable room-temperature transitions originate from states with energies typically lower than about 800 to 1000 cm^{-1} and hence normally belong to the ground vibrational band. The second factor of eq. (7.7) depends on the transition wavenumber and its effect is much less dramatic. For $\bar{\nu} \ll 200 \text{ cm}^{-1}$ it goes to zero quadratically in $\bar{\nu}$ while for $\bar{\nu} \gg 200 \text{ cm}^{-1}$ it becomes asymptotic to $\bar{\nu}$.

Experimental measurement of S_σ

Experimentally S_σ can be measured by considering the Beer-Lambert law [Ber05]

$$I = I_0 \times e^{-\sigma(\bar{\nu}) [c] L} \quad (7.8)$$

where I and I_0 are the spectral irradiances of the incident and transmitted radiation beams, $\sigma(\bar{\nu})$ is the absorption cross-section, $[c]$ is the concentration of the sample and L the optical path length. S_σ is given by the integral over a spectral line of $\sigma(\bar{\nu})$:

$$S_\sigma = \int_{\text{Line}} \sigma(\bar{\nu}) d\bar{\nu} = \frac{1}{[c]L} \int_{\text{Line}} \ln \left(\frac{I_0(\bar{\nu})}{I(\bar{\nu})} \right) d\bar{\nu} \quad (7.9)$$

In a commonly-used system of units, employed e.g. by the HITRAN database [Rot05], $\bar{\nu}$ is measured in cm^{-1} , L in cm and $[c]$ in $\text{molecule}/\text{cm}^3$ so S_σ has units of $\text{cm}/\text{molecule}$.

Sometimes experimentalists, e.g. Kassi *et al* [KMNC05], instead of reporting S_σ report a quantity I , also referred to as “line intensity”, given by

$$I = \frac{1}{p L} \int_{\text{Line}} \ln \left(\frac{I_0(\nu)}{I(\nu)} \right) d\bar{\nu} \quad (7.10)$$

where p is the gaseous pressure of the sample. As laboratory experiments are usually done using very rarefied gases the pressure p can be related to the concentration $[c]$ by the perfect-gas relation $[c] = p/k_B T$, so that $S_\sigma = I \times k_B T$. The quantity I is usually expressed in $\text{cm}^{-2} \times \text{atm}^{-1}$; at the standard temperature $T = 296$ K the equivalence relation between S_σ and I is, using the CODATA2006 value for the Boltzmann constant,

$$1 \text{ cm}^{-2} \text{ atm}^{-1} \mapsto 4.033284 \times 10^{-20} \text{ cm/molecule} \quad (7.11)$$

7.2 Sensitivity of the line strengths S on the DMS

In Section 5.2.5 a model system was examined that suggested transition line strengths may be very sensitive to oscillating perturbations in the molecular dipole moment surface (DMS). In this section a numerical study on the water molecule is presented that provides a quantitative estimate of how errors in the DMS propagate into errors in the transition line strengths S . The experimentally-measured integrated absorption cross-sections S_σ are related to the line strengths by Formula (7.6). As a guideline line strengths smaller than about 10^{-11} D² will almost always result in line intensities S_σ smaller than 10^{-28} cm/molecule, which is the lower limit for lines included in the HITRAN database [Rot05]. As mentioned in the previous section our goal is to predict line intensities with an error of less than $\pm 1\%$, which translates in calculating line strengths S with the same relative error.

7.2.1 Results and analysis

We computed the ortho and para nuclear-motion wave function for $J = 0$ and 1 using the suite DVR3D [TKB⁺04] and the CVRQD potential energy surface by Barletta *et al* [BSZ⁺06]. Symmetric-Radau coordinates in the bisector embedding and the basis set parameters developed by Barber *et al* [BTHT05] were employed. These settings should remove virtually all issues to do with convergence of the nuclear-motion wave functions.

Reference line strengths were then computed using the CVR dipole moment surface by Lodi *et al* [LTT⁺08] for all four possible sets of transitions in H₂¹⁶O involving $J \leq 1$. Only transitions involving the first 100 lowest-energy rotation-vibration states of the ‘bra’ and ‘ket’ states were considered in the analysis. We generated with this recipe a total of $4 \times 100^2 = 40,000$ transition line strengths.

We then went on computing transition line strengths using a modified dipole moment surface where a small oscillatory “noise” function was added to the original CVR surface. In particular, the two components of the dipole surface were substituted by (see Figure 6.1 for the orientation of the axes)

$$\begin{aligned} \mu_x &\rightarrow \mu_x \times \left(1 + A \sin\left(\frac{2\pi}{\lambda_\theta} \theta\right) \sin\left(\frac{2\pi}{\lambda_r} r_1\right) \cos\left(\frac{2\pi}{\lambda_r} r_2\right) \right) \\ \mu_y &\rightarrow \mu_y \times \left(1 + A \cos\left(\frac{2\pi}{\lambda_\theta} \theta\right) \cos\left(\frac{2\pi}{\lambda_r} r_1\right) \sin\left(\frac{2\pi}{\lambda_r} r_2\right) \right) \end{aligned} \quad (7.12)$$

The wavelengths of oscillation λ_θ and λ_r were chosen to be comparable with half of the typical inter-point separations of the grid of *ab initio* points used to create the CVR dipole surface. The reason this form was chosen is that previous experience [LTT⁺08, SP00] has shown that spurious

oscillations in the DMS having this frequency — particularly, in the bond-angle coordinate — are likely to be introduced by the fitting process and cause devastating effects on the computed line intensities. See also Section 8.3.2 for more information on this issue. The initial values we chose for the oscillation frequencies are:

$$\lambda_\theta = 15^\circ \quad \text{and} \quad \lambda_r = 1.885 \text{ a}_0 \quad (7.13)$$

Finally, the amplitude of the oscillations A was chosen to be 10^{-2} , 10^{-3} , 10^{-4} and 10^{-5} . The absolute magnitude of the water dipole is about 0.7 au near equilibrium geometries so A approximately corresponds to the absolute value of the amplitude of the oscillations in au.

Once the ratios of the line strengths in presence of the oscillation were computed we took the ratios of these over the reference line strengths. Results are displayed in Figure 7.1. The first plot shows the line strength ratios; the second plot reports a quantity R which, as a function of line strength S , has the following meaning: line strength ratios near S mostly lie (in an average sense) in the interval $[R^{-1}, R]$. More specifically, R is given by e^σ , where σ is the standard deviation of the natural logarithm of the 101 ratios in the range $S_{i \pm 50}$. See Section 9.1 for more details on this way of analysing the intensity ratios.

It is apparent by looking at the plots that the sensitivity of very weak transitions to small oscillations is extreme. For $A = 10^{-2}$ lines show a sensitivity of up to a factor of 10 already for line strengths weaker than approximately 10^{-6} D^2 , and this factor grows to about 1,000 for lines weaker than 10^{-8} D^2 . For $A = 10^{-4}$ most, but not all, lines with S greater than about 10^{-7} D^2 differ from the unperturbed ones by less than $\pm 1\%$. Finally, setting A to 10^{-5} almost all lines down to about $S = 10^{-9} \text{ D}^2$ differ from the unperturbed ones by less than our target accuracy of $\pm 1\%$.

An amplitude of $A = 10^{-4}$ translates in an absolute error of $\pm 0.0001 \text{ au}$. As we will discuss in Section 7.4.2, it is very difficult but possible to compute water dipoles with this kind of accuracy so this value of A can be taken as indicative of what can be practically achieved at the time being.

As mentioned above, previous experience with the fit of dipole moment surfaces [LTT⁺08, SP00] indicated that transition intensities are mostly affected by oscillations in the bond-angle coordinate θ . To test this hypothesis we performed more tests using a perturbation only in the θ coordinate of the form

$$\begin{aligned} \mu_x &\rightarrow \mu_x \times (1 + A \sin(\omega_\theta \theta)) \\ \mu_y &\rightarrow \mu_y \times (1 + A \cos(\omega_\theta \theta)) \end{aligned} \quad (7.14)$$

These further tests fully confirm the above-mentioned hypothesis. Using the perturbation (7.14) with the same value of λ_θ given by (7.13) results in plots which are almost identical to those of Figure 7.1, where an oscillation in the bond-length coordinates r_1 and r_2 was present as well.

Finally, we kept the amplitude fixed to $A = 10^{-4}$ and we varied the wave length of the perturbation from 0.5 to 10 times the initial λ_θ given by (7.13). A plot of the R values introduced above for some indicative choices of the wave lengths is reported as Figure 7.2. The effect of the perturbation vanishes both for $\lambda_\theta \rightarrow 0$ and $\lambda_\theta \rightarrow \infty$, as predicted by the one-dimensional model system discussed in Section 5.2.5. We found that the effect of the perturbation is large if λ_θ is in the range $3\text{--}75^\circ$ and is maximum for $\lambda_\theta \approx 15^\circ$.

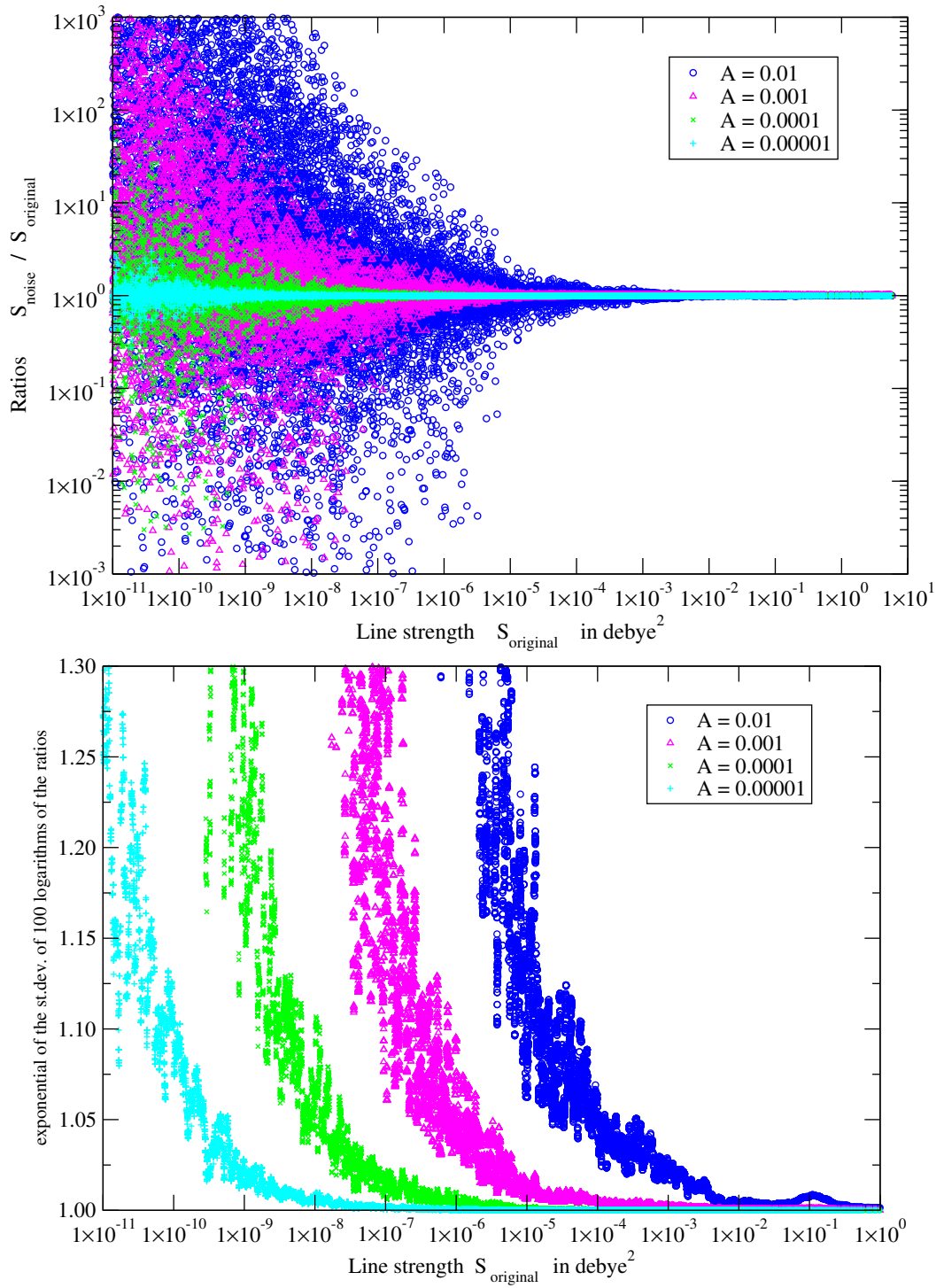


Figure 7.1: These pictures show the ratios between line strengths calculated using the CVR water dipole moment surface over those calculated adding an oscillatory noise with relative amplitude A both in the r and θ coordinates (see text for details).

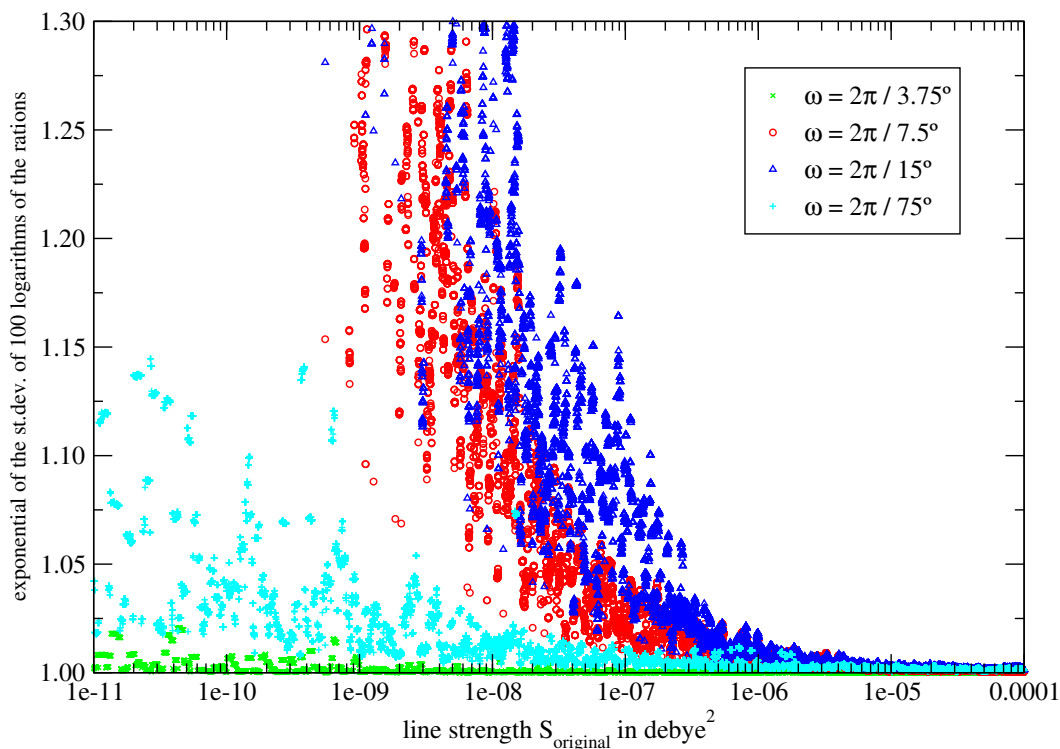


Figure 7.2: Effect of an oscillating perturbation with relative amplitude $A = 10^{-4}$ only in the θ coordinate (see text for details).

Oscillations of the kind specified by eq. (7.14) may be introduced during the fitting process [LTT⁺08, SP00]. If we assume that the wave length of these spurious oscillations is one half of the inter-point spacing of the grid points then the critical wave length of 15° would correspond to an inter-point spacing of about 7.5° . It follows from the previous analysis that for the oscillations introduced by the fit to have little effect grid points should have a spacing of less than about 1.5° . This is too small a value to be practical and a strategy to dampen the oscillations introduced by the fit will be discussed in Section 8.3.2.

7.3 Method of computation of the dipole

There is some discussion in the literature, see e.g. Refs. [NRS79, DRS81, EMP92, HJR99, Lip02], concerning the most appropriate way of calculating first-order properties — in particular, dipole moments — from approximate solutions of the electronic Schrödinger equation. The existence of an ambiguity in the definition of molecular properties is not always emphasised but proved to be an important issue at the level of precision we are interested in. In what follows we will briefly summarise the situation while we refer to the mentioned literature and to chapter 10 of Jensen’s book [Jen06] for a more exhaustive discussion.

Dipole moments can be calculated in two ways:

1. As the expectation value between the wave functions of the dipole operator $\hat{\mu}$

2. As the derivative of the electronic energy $E(\lambda)$ for $\lambda = 0$ of the perturbed Hamiltonian

$$\hat{H}' = \hat{H} + \lambda \hat{\mu} \quad (7.15)$$

The perturbed Hamiltonian (7.15) physically corresponds to a molecule in an external, uniform and static electric field of strength λ . We will use the acronyms XP and ED to refer respectively to the expectation-value or energy-derivative ways of computing dipoles. It can be shown using the Hellmann-Feynman theorem [Jen06] that for exact wave functions these two ways of computation yield exactly the same values and are thus equivalent. In the practical case of approximate wave functions the two methods do not, in general, give the same results and the question arises of which should be preferred.

It can be shown [Jen06] that an approximate wave function the two methods give the same results if the wave function is variationally optimised with respect to *all* its parameters; this includes wave functions obtained from the Hartree-Fock or CAS-SCF methods, but not from truncated CI, MRCI or CC.

Several theoretical arguments suggest that ED dipoles should be preferred over XP ones [WRR83, MUN97, EMP92, Lip02]. Some of these reasons are:

1. An error in the wave function of the first order gives the energy accurate to second order, so quantities computed directly from the energies should be more accurate.
2. When higher-order properties like electric polarizability are computed as expectation values the components may not obey the correct symmetry relations [Lip02].
3. The ED approach allows to compute dipoles also for quantum-chemical methods such as MP2, CCSD(T) and CISD+Q for which the corresponding wave function is not usually calculated or does not exist at all. In this approach it also becomes possible to compute the effect on the dipoles of terms in the Hamiltonian which are customarily treated by first-order perturbation theory for the energy, e.g. relativistic corrections.

The major inconvenience of the ED approach is that if analytical derivatives with respect to the perturbation strength are not implemented the derivatives have to be computed as finite differences and this involves at least $n + 1$ separate energy computations if n component are to be determined (i.e., at least three separate calculation to determine a C_s -geometry dipole for water). For a discussion of the advantages of using analytical derivatives over numerical differentiation see e.g. section IV A of ref. [HJR99].

7.3.1 Choice of the external field strength

In the energy-derivative (ED) approach one often has to resort to calculating the energy derivatives by finite differences. In this situation a further parameter, the external field strength λ , has to be introduced and the corresponding numerical error introduced has to be assessed. We will use the acronym FF to indicate dipoles obtained by computing approximate derivatives by

finite-differences. The formulae considered are [CdB80]:

$$\begin{aligned}
 E'(0) &= \frac{E(\lambda) - E(0)}{\lambda} + \mathcal{O}(\lambda) && \text{2-point forward difference} \\
 E'(0) &= \frac{E(\lambda) - E(-\lambda)}{2\lambda} + \mathcal{O}(\lambda^2) && \text{2-point central difference} \\
 E'(0) &= \frac{1}{3} \left(4 \frac{E(\lambda) - E(-\lambda)}{2\lambda} - \frac{E(2\lambda) - E(-2\lambda)}{4\lambda} \right) + \mathcal{O}(\lambda^4) && \text{4-point central difference}
 \end{aligned} \tag{7.16}$$

In principle any of these formulae can provide arbitrary high accuracy by taking λ small enough. However, in practice the change in energy should not be made too small to avoid the amplification of cancellation errors. Calling δ_E the numerical uncertainty with which the energies are known, this implies that each component of a dipole calculated from them using one of the Formulae (7.16) will have a corresponding uncertainty $\delta_\mu \approx \sqrt{2}\delta_E/\lambda$ au. For example, assuming $\delta_E \approx 5 \times 10^{-9}$ E_h and imposing $\delta_\mu < 10^{-5}$ it follows that $\lambda \gtrsim 7 \times 10^{-4}$ au. To give an idea of this quantity, this value for λ is approximately the magnitude of the electric field generated by an electron at 38 a₀ of distance.

Quite separate from the round-off error discussed above the finite-difference Formulae (7.16) are also affected by an intrinsic error due to the finiteness of λ . We investigated the magnitude of this error using the CAS-SCF method in the [8, 10] reference space of Table 6.2 and the aug-cc-pVTZ basis set. Dipoles were computed using the 2-point forward-difference and central-difference formulae with a field strength $\lambda = 7 \times 10^{-4}$ au for the large set of 2174 geometries covering energies up to about 50,000 cm⁻¹ discussed in Section 6.7. Expectation-value (XP) dipoles in the absence of external field were computed as well. In the CAS-SCF method XP and ED dipoles coincide so any difference between XP and FF dipoles is entirely due to the finiteness of λ . Of all the results 303 geometries showed convergence problems and were discarded. A plot of the differences between XP and FF dipoles is presented in Figure 7.3. The 2-point symmetric-difference formula resulted in an error of less than 10^{-5} au for energies up to 30,000 cm⁻¹ and almost always smaller than 10^{-4} for energies between 30,000 and 60,000 cm⁻¹. The 2-point forward-difference formula gave errors of between 5×10^{-3} and 10^{-2} au.

A further test was performed to verify that the residual discrepancies observed when using the 2-point symmetric formula were indeed due to the finite size of λ . Four points for which the difference $|\mu_{XP} - \mu_{FF}|$ was largest were selected and new FF dipoles were computed using the 4-point central-difference formula; this required four further calculations per point with a field strength of $\pm 2\lambda$. In all cases the discrepancies dropped from about 3×10^{-4} using the two-point formula to 4×10^{-6} using the 4-point formula. It is thus confirmed that the discrepancy can be put down to the size of the field strength.

These considerations indicate that the simpler 2-point forward-difference formula would require extremely tight convergence thresholds for the energies; to achieve an accuracy of 10^{-5} au with this formula one would need $\lambda \lesssim 5 \times 10^{-7}$, which in turns sets the maximum acceptable error on the energies to the very small value of $\delta_E \lesssim 5 \times 10^{-12}$ E_h.

It is probably safer to rely on the 2-point symmetric formula combined with a field strength $\lambda \approx 4 \times 10^{-4}$ au, which will guarantee FF dipoles accurate to 10^{-5} au for all geometries and requires energies to be accurate only to $\approx 2 \times 10^{-9}$ E_h.

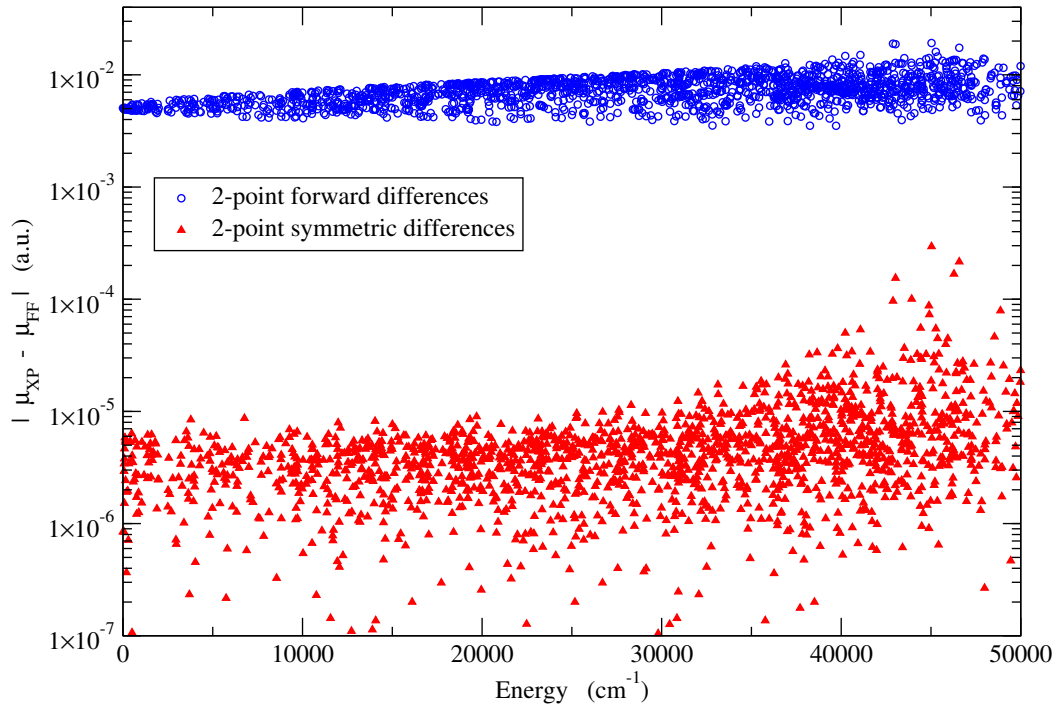


Figure 7.3: Numerical error of the finite-difference Formulae (7.16) using $\lambda = 7.5 \times 10^{-4}$ au. See text for details.

7.4 The equilibrium dipole of water

Studies on the computation of molecular dipoles, e.g. [BGH⁺00], generally focus on an accuracy of the order of ± 0.01 au, while, as discussed in Section 7.2, we would like to compute dipoles with a much better accuracy of the order of ± 0.001 au.

A highly accurate value of the dipole moment of the water molecule was computed as a test of the accuracy achievable with quantum-chemical methods. The theoretical value was then compared with the best available experimental data. It should be remembered that the quantity which relates most closely with what is measured by precision experiments is the expectation value of the total molecular dipole moment given by eq. (7.1), that is

$$\langle \boldsymbol{\mu} \rangle = \langle \Psi | \hat{\boldsymbol{\mu}}_N + \hat{\boldsymbol{\mu}}_e | \Psi \rangle \quad (7.17)$$

where Ψ is the full (=electronic and nuclear) molecular wave function, and not by the clamped-nuclei dipole given by eq. (7.2). However, in the Born-Oppenheimer approximation the total molecular dipole $\langle \boldsymbol{\mu} \rangle$ is given by the average of the dipole-moment surface over the ground-state rotational-vibrational nuclear-motion wave function; the effect of this vibrational averaging will be analysed in the following subsection.

7.4.1 Vibrational averaging

In the assumption that the shape of the presently-available water DMS's is essentially correct for geometries close to equilibrium and that the main effect with respect to a second DMS is a global shift, the value of the vibrationally-averaged dipole for a new surface can be estimated

Table 7.1: Effect of the vibrational averaging of dipole moments, in au, as function of (a) the potential energy surface used to provide the H_2^{16}O vibrational wave function and (b) the dipole moment surface used. The reference geometry used is $r_e = 1.81002 \text{ a}_0$ and $\theta_e = 104.485^\circ$.

PES	DMS		
	CVR(valence) ^b	CVR ^b	SP2000 ^c
Clamped-nuclei dipole at the ref. geometry	0.73448	0.73474	0.73362
CVRQD [PCS ⁺ 03, BSZ ⁺ 06]	0.73453	0.73478	0.73364
FIS3 [SPZ ⁺ 03]	0.73455	0.73480	0.73366
<i>net effect due to vibrational averaging</i>			
CVRQD [PCS ⁺ 03, BSZ ⁺ 06]	0.00005	0.00004	0.00002
FIS3 [SPZ ⁺ 03]	0.00007	0.00006	0.00004

^a Valence-only part of the CVR DMS by Lodi *et al* [LTT⁺08]

^b Complete CVR DMS by Lodi *et al* [LTT⁺08], (valence-core-relativistic).

^c Water DMS by Schwenke and Partridge [SP00]

by calculating a value for a single reference structure near equilibrium and then by adding the difference between the vibrationally-averaged value computed with the existing DMS and the value of the existing DMS for the reference geometry. We followed this recipe using the CVR DMS by Lodi *et al* [LTT⁺08] — which will be discussed in detail in Chapter 8 — and the SP2000 DMS surface by Schwenke and Partridge [SP00].

It should be noted that the value of this vibrational correction is sensitive to the choice of the reference structure and therefore has little meaning on its own. As reference structure for all our equilibrium dipole moment calculations we used the best estimate of the Born-Oppenheimer equilibrium geometry of H_2^{16}O , as given in [CCF⁺05], that is $r_e = 1.81002 \text{ a}_0$ and $\theta_e = 104.485^\circ$. Table 7.1 compares dipoles computed with different surfaces and averaged using vibrational wave functions generated using the CVRQD *ab initio* PES [PCS⁺03, BSZ⁺06] and the FIS3 semi-empirical PES of Shirin *et al.* [SPZ⁺03].

It can be seen that the net effect of the vibrational averaging is always in the range 2 to $7 \times 10^{-5} \text{ au}$; as we will see, this is a very small value with respect to the error of the clamped-nuclei dipole. Vibrationally-averaged dipoles computed with nuclear-motion wave functions produced using the *ab initio* CVRQD dipole surface are systematically larger by $2 \times 10^{-5} \text{ au}$ than those obtained from the semi-empirical FIS3 PES. We finally adopted for the contribution of vibrational averaging to the reference geometry a value of $0.0001 \pm 0.0001 \text{ au}$.

7.4.2 The equilibrium clamped-nuclei dipole

A thorough study of the equilibrium clamped-nuclei dipole was performed for a variety of quantum-chemical methods and basis sets. Calculations were done correlating all the electrons and with the aug-cc-pCVnZ (n=3-6) basis sets. MOLPRO was used for all calculations apart from one CCSDTQ calculation for which the codes ACES II [ACE] and MRCC [MRC] were used. Dipoles computed by finite-differences used $\lambda = \pm 7.5^{-4} \text{ au}$, which value should guarantee a numerical error smaller than 10^{-5} au (see Section 7.3).

Results are reported in Table 7.2 and are graphically illustrated in Figure 7.4.

Looking at the scatter of the data it is clear that computing dipoles with an accuracy of better than 10^{-3} au is not an easy task and achieving a precision of 10^{-4} au is extremely difficult. We will analyse and estimate the extent of the various sources of error in the next subsections.

Basis set dependence

The dependence of the dipole on the basis-set shows a rather regular pattern. The change increasing the cardinal number from $n = 2$ to $n = 3$ is the most irregular and corresponds to a reduction of about -2.5×10^{-3} au; starting from the $n = 3$ basis set the increase of the basis set cardinal number always corresponds to an expansion which is about 4×10^{-3} , 1.4×10^{-3} and 0.6×10^{-3} au going from $n = 3 \rightarrow 4$, $4 \rightarrow 5$ and $5 \rightarrow 6$ for all correlated methods considered. The regular convergence pattern observed for the larger basis sets suggests that a basis-set extrapolation scheme similar to the ones discussed in Section 3.4.2 can be attempted. For the extrapolation we used Mathematica [Mat07] to perform a fit of the $n = Q$, 5 and 6 dipoles to the three-parameter formula

$$\mu_n = \mu_\infty + \frac{A}{n^\alpha} \quad (7.18)$$

The extrapolated values are reported in the last column of Table 7.2. For all correlated methods the optimal exponent α lay in the range 3.5 to 3.8 and the extrapolated dipoles were always about 0.6×10^{-3} au larger than the 6Z ones. We also tried another extrapolation scheme using only the $n = 5$ and 6 data and the two-parameter formula

$$\mu_n = \mu_\infty + \frac{A}{n^3} \quad (7.19)$$

Dipoles obtained by this last formula were, with respect to those obtained by Formula (7.18), systematically larger by 0.2×10^{-3} au.

These results suggest that the uncertainty due to basis-set incompleteness of the $n = 6$ dipoles is about 0.7×10^{-3} au and that of the extrapolated dipoles is about 0.3×10^{-3} au.

Method of computation of the dipole

Changing the method of computation of the IC-MRCI dipoles from expectation value (XP) to finite-difference (FF) resulted in a reduction of about -5×10^{-3} au when using the $[8, 8]$ reference space of Table 6.2 and of -3×10^{-3} au when using the $[8, 10]$ reference space, quite independent of the basis set employed. This is a relatively large value at the level of accuracy we are interested in.

As discussed in Section 7.3, there are sound theoretical reasons to prefer FF over XP dipoles and our results support this assumption as well. FF IC-MRCI dipoles are much more stable with respect to an increase of the reference space than the XP ones; going from the $[8, 8]$ to the $[8, 10]$ reference space results (for all basis sets) in a change of about -0.7×10^{-3} au for the FF values but of about -5×10^{-3} au for the XP ones.

Furthermore, using FF dipoles allows one to use Davidson- or Pople-corrected calculations and this is very likely to further improve the quality of the results.

Table 7.2: All-electron dipole moments of water, in au, computed at the equilibrium geometry $r_e = 1.81002$ a₀ and $\theta_e = 104.485^\circ$.

Level ^a	RS ^b	XP/FF ^c	Basis set ^d					
			ACDZ	ACTZ	ACQZ	AC5Z	AC6Z	AC{Q56}Z ^e
HF		XP	0.78721	0.77996	0.77944	0.77951	0.77952	0.77952
CCSD		FF	0.73550	0.73408	0.73799	0.73939	0.73995	0.74058
CCSD(T)		FF	0.72761	0.72513	0.72894	0.73037	0.73091	0.73146
CCSDT		FF	0.72720	0.72502	...	...	...	...
CCSDTQ		FF	0.72664	...	...	...	...	...
CAS-SCF	[8, 8]	XP	0.75174	0.74800	0.74806	0.74862	0.74845 ^f	...
IC-MRCI	[8, 8]	FF	0.72897	0.72712	0.73095	0.73236	0.73290	0.73346
IC-MRCI+Q	[8, 8]	FF	0.72670	0.72430	0.72821	0.72963	0.73018	0.73077
IC-MRCI+P	[8, 8]	FF	0.72711	0.72479	0.72868	0.73011	0.73065	0.73120
RSPT2	[8, 8]	FF	...	...	...	...	0.73611	...
RSPT3	[8, 8]	FF	...	...	...	...	0.73346	...
IC-ACPF	[8, 8]	FF	...	...	...	...	0.73048	...
IC-AQCC	[8, 8]	FF	...	...	...	...	0.73108	...
CAS-SCF	[8, 10]	XP	0.73545	0.73001	0.73029	0.73065	0.73069	0.73070
IC-MRCI	[8, 10]	FF	0.72743	0.72487	0.72856	0.72995	0.73048	0.73103
IC-MRCI+Q	[8, 10]	FF	0.72665	0.72400	0.72783	0.72925	0.72980	0.73039
IC-MRCI+P	[8, 10]	FF	0.72679	0.72415	0.72796	0.72937	0.72992	0.73051
IC-MRCI	[8, 8]	XP	0.73363	0.73233	0.73611	0.73756	0.73811	0.73867
IC-MRCI	[8, 10]	XP	0.73041	0.72790	0.73135	0.73269	0.73320	0.73373

^a IC-MRCI+Q indicates IC-MRCI with the renormalised Davidson correction, IC-MRCI+P with the Pople correction.

^b For multi-reference methods it indicates the reference space, see Table 6.2.

^c Method of computation of the dipole, FF = finite-differences (field strength $\lambda = 7.5 \times 10^{-5}$ au) and XP = expectation value. For the HF and CAS-SCF methods XP and FF dipoles coincide.

^d The format ACnZ is shorthand for aug-cc-pCVnZ basis sets.

^e Dipoles extrapolated using the formula $\mu_n = \mu_\infty + A/n^\alpha$ (see text).

^f There was a convergence problem with the aug-cc-pCV6Z CAS-SCF run and the reported value may not be exact.

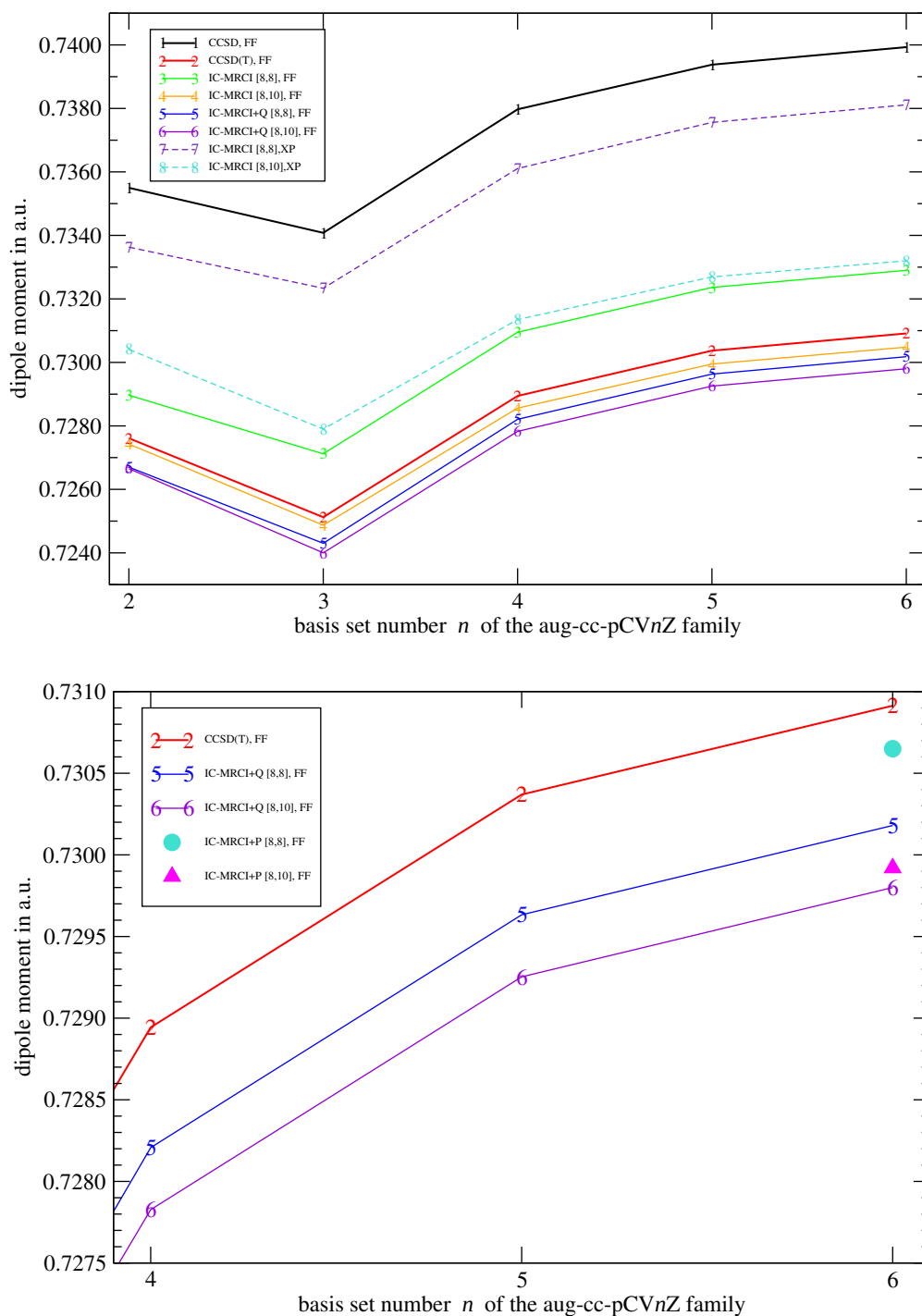


Figure 7.4: Value of the water equilibrium dipole computed with different methods and basis sets. The lower plot shows a zoomed-in area with respect to the upper (see text for details).

Electron correlation treatment

A very advanced treatment of electron correlation is essential to obtain an accurate value of the equilibrium dipole. The global effect of electron correlation corresponds, with respect to the Hartree-Fock value, to a large reduction of about -50×10^{-3} au.

Only for the smallest basis set, aug-cc-pCVDZ, could we afford a CCSDTQ calculation which should provide an accurate reference value. Comparing the values reported in Table 6.2 we see that Davidson-corrected IC-MRCI values agree extremely well with the CCSDTQ dipole, differing by only 0.06×10^{-3} au in the [8, 8] RS and by a minuscule 0.01×10^{-3} au in the [8, 10] RS. Pople-corrected values differ from the CCSDTQ dipole respectively by 0.5×10^{-3} and 0.2×10^{-3} in the [8, 8] and [8, 10] RS while uncorrected IC-MRCI FF dipoles differ by 2×10^{-3} and 0.8×10^{-3} for the two RS's.

On the other hand IC-MRCI XP dipoles differ from the CCSDTQ value by 7×10^{-3} and 4×10^{-3} for the two RS's. These observation strongly suggest that size-extensivity corrected, FF dipoles are much more accurate than XP, IC-MRCI ones. It also suggests that the expansion of the RS to [8, 10] discussed in Sections 6.5 improves results considerably. Finally, these results also seem to single out IC-MRCI+Q over IC-MRCI+P as the most accurate method but, as discussed in Section 6.5, this basis set may be too small to draw definitive conclusions.

The other conclusions we drew studying the values of Table 7.2 and of Figure 7.4 mirror those stated for the case of energies in Sections 6.5 and 6.6. Dipoles obtained with the multi-reference, perturbative RSPT2 and RSPT3 methods do not seem to reach the accuracy of the size-extensivity corrected MRCI-type methods, namely IC-MRCI+Q, IC-MRCI+P, IC-ACPF and IC-AQCC. Conversely, dipoles produced by methods belonging to this last class agree well with each other. IC-ACPF agrees particularly well with IC-MRCI+P and dipoles computed by these methods differ by less than 0.1×10^{-3} au in the [8, 8] RS. IC-AQCC dipoles differ slightly more from the other size-extensivity corrected MRCI-type methods but the differences are always smaller than 10^{-3} au using the [8, 8] RS.

Finally, we analyse briefly the coupled-cluster results. The change going from CCSD to CCSD(T) is about 20×10^{-3} au and is hence very large by our standards. The change from CCSD(T) to CCSDTQ in the aug-cc-pCVDZ basis set is about 10^{-3} au — which is a small but not negligible value — and it is 0.6×10^{-3} going from CCSDT to CCSDTQ; this finding is in line with the common assumption [Jen06] that CCSD(T) is a good approximation to the full CCSDT method. With the larger basis sets CCSD(T) dipoles always agree within 10^{-3} au with the ones produced by any of the size-extensivity corrected MRCI-type methods. A value of about 10^{-3} au is also the scatter between the size-extensivity corrected MRCI-type methods themselves. In conclusion it seems that, at equilibrium, CCSD(T) dipoles have an accuracy comparable with the various multi-reference methods using the [8, 8] RS.

Final value for the clamped-nuclei dipole

The dipoles we believe are the most accurate are the basis-set extrapolated IC-MRCI+Q and IC-MRCI+P [8, 10] ones, which are respectively 0.7304 and 0.7305 au if the three-parameter Formula (7.18) is used or 0.7306 and 0.7307 au if the two-parameter Formula (7.19) is used.

Another estimate can be obtained by taking the basis-set extrapolated CCSD(T) value and adding to this the aug-cc-pCVDZ CCSDTQ – CCSD(T) difference. This procedure leads to the

Table 7.3: Dipole, in au, at the reference structure $r_e = 1.81002 \text{ a}_0$ and $\theta = 104.485^\circ$.

	Value	Uncertainty
Non-relativistic, all electron	0.7306	0.0004
Relativistic correction	-0.0017	0.0001
Vibrational averaging	0.0001	0.0001
Final value for the ground-state dipole	0.7290	0.0004
Experimental value	0.7296	0.0002

value of 0.7305 au or 0.7307 using respectively Formula (7.18) or (7.18) for the extrapolation and are then compatible with the other estimates.

The uncertainty on our final value comes from the residual basis set incompleteness error — which we estimated in a previous section as 0.0003 au — and from the error in the correlation treatment. The good agreement between the extrapolated values suggests for this last an uncertainty of about 0.0001 but a more conservative value of 0.0002 if probably more judicious. Our final value is the average of the six mentioned extrapolated values, leading to a dipole of 0.7306 ± 0.0004 au.

7.4.3 Relativistic correction

Relativistic corrections to the dipole will be discussed in detail in Section 7.5. In this section we will just mention that, as in the case of relativistic correction to the energy presented in Section 6.7.2, relativistic corrections converge very quickly with respect to both basis-set size and correlation treatment and it is not difficult to compute them with an accuracy of 10^{-4} au or better.

For the equilibrium relativistic correction we adopted the value of -0.0017 ± 0.0001 au computed from the relativistic-correction part of the CVR water DMS [LTT⁺08].

7.4.4 Final value and comparison with experiment

There have been a number of reported experimental values for the dipole moment of the water molecule. The 1973 Stark measurement of Clough *et al* [CBKR73] gave 1.8546(6) D (= 0.7297 au). This study probably remains the most accurate performed to date. It is consistent with the more recent value of Gregory *et al* [GCL⁺97]. Table 7.3 gives 0.7296 ± 0.0002 au for the experimental dipole moment of water corresponding to the weighted average of these two measurements.

Our best theoretical estimate including vibrational averaging and relativistic corrections is 0.7290 ± 0.0004 au. This value is marginally consistent with the experimental value as the discrepancy between the values is 0.0006 ± 0.0004 au. It is not possible at this stage to tell if this discrepancy is due to an underestimation of the uncertainties in the calculated or experimental values or to further effects — for example, the diagonal Born-Oppenheimer correction or even non-adiabatic effects — which have not been included in the theoretical estimate.

Table 7.4: Structures used for tests of the relativistic contributions to the dipole moment of water.

Structure	θ deg.	r_1 Å	r_2 Å	Energy cm ⁻¹
equilibrium	104.52	0.9576	0.9576	0.2
near linear	170	0.80	1.00	18166.5
bond compressed	100	0.75	0.95	16022.0
bond stretched	100	0.95	1.00	417.6

^aThe reported energies are those given by the CVRQD surface of H₂¹⁶O [PCS+03, BSZ+06].

7.5 Relativistic effects

The relativistic effect is defined as the difference between the exact “fully-relativistic” value obtained by solution of the Dirac-Coulomb-Breit equation and the exact non-relativistic value. See Section 2.4 for more information on the theory used to treat relativistic effects.

7.5.1 Dirac-Coulomb calculations

A study of the water dipole using the 4-component Dirac equation was recently performed by van Stralen [van04] using the program program DIRAC [Dir]. Relativistic corrections performed by this author were used to compute the relativistic-correction part of the CVR dipole moment surface [LTT⁺08] which will be described in Chapter 8. A detailed description of these computations can be found in van Stralen’s thesis [van04]; in this subsection we will only give a summary of his main results.

Values of the dipole were tested at four structures each of which probe a different region of the DMS and which are presented in Table 7.4. The main conclusions of these tests were:

1. Spin-dependent terms — in particular, spin-orbit interaction — affect the dipoles by less than 2×10^{-6} au and are thus negligible. The spin-independent formalism of Dyall [Dya94] (see Section 2.4) can then be reliably used.
2. That fact that spin-orbit has a very small effect on dipoles implies that also the Gaunt and Breit interactions — corresponding to spin-other-orbit effects in a two-component picture — are small and can be neglected.
3. Neglect of the (SS|SS)-type two-electron integrals affects the dipoles by less than 10^{-7} au and can thus be safely neglected.
4. Relativistic corrections to the dipole converge quickly with basis set size. Going from the aug-cc-pVTZ to the aug-cc-pCVQZ basis set results in a change in the magnitude of the dipole of only about 2×10^{-5} au; this value is halved going from aug-cc-pCVTZ to aug-cc-pCVQZ.

Dirac-equation-based relativistic corrections for the four reference geometries using the CCSD(T) method are reported in the first four columns of Table 7.5. The values reported in the last two columns were computed by alternative methods and will be detailed in the next section.

Table 7.5: Test of different method of computation of the relativistic effects on the dipole moment. Basis set are from the aug-cc-p(C)VnZ family and were all uncontracted as described in the text. The usual shorthand notation is employed. Given in au is the net relativistic effect on the magnitude of the dipole, $|\vec{\mu}|_{\text{rel}} - |\vec{\mu}|_{\text{nonrel}}$.

geometry	SFDC ^a				MVD1 ^b	DKH2 ^c
	ATZ	ACTZ	AQZ	ACQZ	ACTZ	ACTZ
equilibrium	-0.001720	-0.001710	-0.001703	-0.001697	-0.001627	-0.001613
near linear	-0.000150	-0.000149	-0.000148	-0.000147	-0.000151	-0.000149
bond compressed	-0.001419	-0.001411	-0.001405	-0.001400	-0.001300	-0.001288
bond stretched	-0.001824	-0.001813	-0.001807	-0.001801	-0.001725	-0.001711

^aSFDC: spin-free Dirac-Coulomb with neglect of (SS|SS) integrals. The CCSD(T) method was used for electron correlation. Values taken from [van04].

^bMVD1: Perturbative treatment of the Mass-Velocity One-electron Darwin term. The IC-ACPF method in the [8, 8] reference space was used and dipoles were computed by energy derivatives.

^cDKH2: Second order scalar-relativistic Douglas-Kroll-Hess theory. The IC-ACPF method in the [8, 8] reference space was used and dipoles were computed as expectation values.

7.5.2 Alternative calculation of the relativistic corrections and conclusions

Relativistic effects were investigated with simpler levels of theory — namely, the perturbative MVD1 approach and the scalar-relativistic Douglas-Kroll-Hess (DKH2) theory — using MOLPRO; see Section 2.4 for more information about these methods.

We computed the MVD1 and DKH2 relativistic corrections for the four geometries listed in Table 7.4 using MOLPRO. The MVD1 correction was obtained by computing the derivative of the MVD1 energy using an external field strength of $\pm 7 \times 10^{-4}$ au. The DKH2 corrections were computed as the difference between the DKH2 and the non-relativistic expectation-value dipoles. The quantum-chemical methods investigated were CCSD, IC-MRCI, IC-ACPF, IC-AQCC and RSPT3; multi-reference methods used the [8, 8] reference space of Table 6.2. Some illustrative results are listed in Table 7.5. The main conclusions of this study are:

1. MVD1 and DKH2 relativistic corrections always agree within 5×10^{-5} au — and usually within 10^{-5} au — for all combinations of geometries, methods and basis sets considered. This small discrepancy could be due to a picture change error [KSH96] that is known to be small for valence properties of light elements and was not included. This difference is anyway at the level where numerical noise may become important.
2. With respect to spin-free Dirac-Coulomb calculations, the MVD1 and DKH2 corrections differ by up to about 10^{-4} au. As this value is smaller than the error of the non-relativistic part of the dipole both MVD1 and DKH2 corrections offer a simple and reliable way to obtain accurate relativistic corrections to the dipole.
3. Similarly to Dirac-Coulomb calculations the effect of basis-set size increase on MVD1 and DKH2 corrections is very small, only up to 10^{-5} au going from the aug-cc-pVTZ to the

aug-cc-pCVQZ basis sets. The effect of core-correlation is also less than 10^{-5} au and hence negligible.

- Both MVD1 and DKH2 relativistic corrections are rather insensitive to the level of electron-correlation employed. All correlated methods examined including CAS-SCF agree between themselves within 2×10^{-5} au. In fact, the effect of electron correlation on the dipole correction is only about 10^{-4} au for the four geometries considered so — at least close to equilibrium — even the RHF method would provide good accuracy.

The most economic way to compute the relativistic-correction to the dipole is probably to compute the difference between the DKH2 and the non-relativistic expectation-value dipoles. However, in the case where also the non-relativistic part of the dipole has to be computed with high accuracy, it will be in general necessary to compute dipoles as energy-derivatives (see discussion in Section 7.3) and in this case it would be simpler to use the MVD1 method.

7.5.3 Cancellation effects of core and relativistic effects

Relativistic effects typically have a magnitude of 1 to 2×10^{-3} au and almost always reduce the magnitude of the dipole moments, except for near-linear geometries where the magnitude of the nonrelativistic dipole is very small.

During the analysis of the data used for the CVR water dipole moment surface — which will be described in detail in Chapter 8 — it was found that the contribution to the dipole moment due to the correlation of the oxygen 1s core electrons has comparable magnitude but opposite sign. Figure 7.5 shows that these two corrections are strongly anti-correlated and their overall effect has a magnitude of less than about $\pm 5 \times 10^{-4}$ au. As yet we have not found any special theoretical explanation for this behaviour.

7.6 Representing the dipole moment of water

We adopt in this section the axes convention displayed in Figure 6.1. The dipole moment surface $\boldsymbol{\mu}$ of the water molecule should obey, as a function of the nuclear coordinates, the following symmetry relations:

- If all nuclear coordinates are globally translated $\boldsymbol{\mu}$ should not change.
- If all nuclear coordinates are globally rotated $\boldsymbol{\mu}$ should rotate with them.
- If the values of the two O–H bond lengths r_1 and r_2 are swapped the dipole should be reflected with respect to the bond-angle bisector.

All these properties can be automatically fulfilled by writing the dipole in the form

$$\boldsymbol{\mu}(\mathbf{x}_{\text{H}_1}, \mathbf{x}_{\text{H}_2}, \mathbf{x}_{\text{O}}) = q(r_1, r_2, \theta)(\mathbf{x}_{\text{H}_1} - \mathbf{x}_{\text{O}}) + q(r_2, r_1, \theta)(\mathbf{x}_{\text{H}_2} - \mathbf{x}_{\text{O}}) \quad (7.20)$$

where $\mathbf{x}_{\text{H}_1}, \mathbf{x}_{\text{H}_2}$ and $\mathbf{x}_{\text{O}}$ are vectors containing the Cartesian coordinates of the nuclei while (r_1, r_2, θ) are the internal coordinates represented by the two O–H bond lengths and the subtended angle. This form was introduced by Schwenke and Partridge [SP00] and has the further

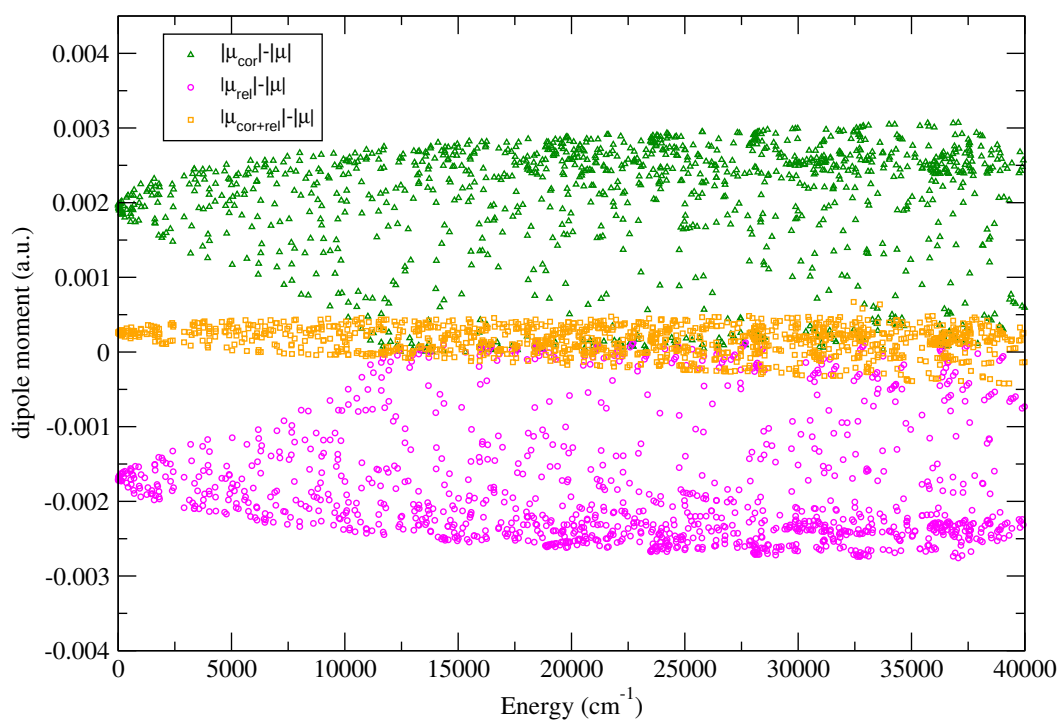


Figure 7.5: Comparison of the change in the dipole moment due to (a) the relativistic correction, (b) the core correction and (c) the sum of these two effects plotted as function of the potential energy. The corresponding 1491 geometries are those for which the valence-only dipole moments were calculated. Value for the core and relativistic correction for these geometries were obtained from the respective correction surfaces.

advantage that both components of the dipole can be described by the single scalar function q . In our coordinate system Formula (7.20) can also be written more explicitly as:

$$\begin{aligned}\mu_x &= \cos\left(\frac{\theta}{2}\right) \left(r_1 q(r_1, r_2, \theta) + r_2 q(r_2, r_1, \theta) \right) \\ \mu_y &= \sin\left(\frac{\theta}{2}\right) \left(r_1 q(r_1, r_2, \theta) - r_2 q(r_2, r_1, \theta) \right)\end{aligned}\quad (7.21)$$

The function q , which has the physical dimension of a charge, can be interpreted as representing fictitious point-charges concentrated on the H₁, H₂ and O atoms and of magnitude respectively $q(r_1, r_2, \theta)$, $q(r_2, r_1, \theta)$ and $[-q(r_1, r_2, \theta) - q(r_2, r_1, \theta)]$. Note that the function q itself has no special symmetry properties.

Schwenke and Partridge [SP00] proceeded writing q in the following fashion:

$$q(r_1, r_2, \theta) = e^{-\alpha x_1^2} \left\{ \sum_{i=0}^{n_r} c_i x_1^i + e^{-\alpha x_2^2} \sum_{i=0} \sum_{j=0} \sum_{k=0} c_{ijk} x_1^i x_2^j x_3^k \right\} \quad (7.22)$$

where r_e and θ_e are the equilibrium bond length and angle, $x_i = (r_i - r_e)/r_e$ ($i = 1, 2$), $x_3 = \cos \theta - \cos \theta_e$, and $i + j + k \leq n_\theta$, $j + k > 0$ and $i + j \leq n_r$. All the linear coefficients c_i and c_{ijk} were then determined by a least-square fit of the *ab initio* dipole data.

7.6.1 Imposing the correct asymptotics

A many-body decomposition similar to the one discussed in Section 5.1.3 can be applied to the dipole moment surface to insure the correct asymptotic behaviour upon dissociation into fragments. This can be done, instead of using the expression (7.21), by employing the modified relations

$$\begin{aligned}\mu_x &= \cos\left(\frac{\theta}{2}\right) \left[\mu_{\text{OH}}(r_1) + \mu_{\text{OH}}(r_2) + r_1 Q(r_1, r_2, \theta) + r_2 Q(r_2, r_1, \theta) \right] \\ \mu_y &= \sin\left(\frac{\theta}{2}\right) \left[\mu_{\text{OH}}(r_1) - \mu_{\text{OH}}(r_2) + r_1 Q(r_1, r_2, \theta) - r_2 Q(r_2, r_1, \theta) \right]\end{aligned}\quad (7.23)$$

where $\mu_{\text{OH}}(r)$ is the dipole moment of the O–H diatomic and the scalar function Q is required to go to zero if r_1 or r_2 go to infinity. Relations (7.23) can be easily solved for Q giving

$$\begin{aligned}Q(r_1, r_2, r_3) &= \frac{1}{2r_1} \left[\frac{\mu_x}{\cos(\frac{\theta}{2})} + \frac{\mu_y}{\sin(\frac{\theta}{2})} - 2\mu_{\text{OH}}(r_1) \right] \\ Q(r_2, r_1, r_3) &= \frac{1}{2r_2} \left[\frac{\mu_x}{\cos(\frac{\theta}{2})} - \frac{\mu_y}{\sin(\frac{\theta}{2})} - 2\mu_{\text{OH}}(r_2) \right]\end{aligned}\quad (7.24)$$

This last relations are useful to obtain Q from the two components of the dipole μ_x , μ_y and the O–H dipole curve.

Schwenke and Partidge's original form (7.22) can also be recast into this notation. Setting $x = (r - r_e)/r_e$ the original Formula 7.22 implies the choices:

$$\begin{aligned}\mu_{\text{OH}}(r) &= e^{-\alpha x^2} \sum_{i=1}^{n_r} c_i x^i \\ Q(r_1, r_2, \theta) &= e^{-\alpha (x_1^2 + x_2^2)} \sum_{i=0} \sum_{j=0} \sum_{k=0} c_{ijk} x_1^i x_2^j x_3^k\end{aligned}\quad (7.25)$$

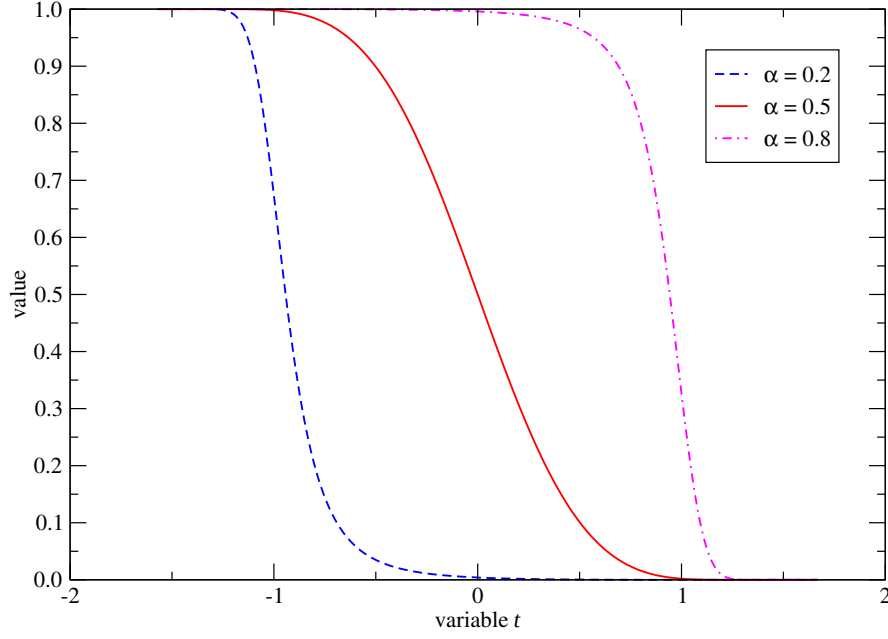


Figure 7.6: Plot of the suggested damping factor given by eq. 7.26 for various values of α .

Schwenke and Partridge in their surface [SP00] did not set the O–H dipole curve μ_{OH} at the onset but found the linear coefficients c_i by a fit of the water dipole data. Also note that the use of the reduced variable x_1, x_2 instead of r_1, r_2 is essentially immaterial as the effect of this change can be re-absorbed in a change of the linear coefficients.

Choice of the fitting function and the damping function

The condition that Q should go to zero as r_1 or r_2 go to infinity can be taken care of by introducing a damping factor ω and then writing $Q = \omega \times G$, where G is the function that will be determined by the least-square fit. The original choice made by Schwenke and Partridge consists in a Gaussian damping of the kind $\omega = e^{-\alpha(r_1^2 + r_2^2)}$.

The damping is also useful to mitigate the large, spurious oscillations polynomial fits of the kind expressed by expansion (7.22) will produce outside the region covered by the points included in the fit. For this purpose we found it is useful to use a sigmoid-shaped damping factor which can provide an arbitrarily strong damping in a certain region while staying constant outside this region. For this purpose we devised an infinitely smooth, sigmoid-shaped damping factor given by

$$\omega(r) = \begin{cases} 1 & r \leq a \\ [1 + \exp(4 \cot(\alpha\pi) + 4 \tan(t))]^{-1} & a < r < b \\ 0 & r \geq b \end{cases} \quad (7.26)$$

where

$$t = \pi \left(\frac{r - a}{b - a} - \frac{1}{2} \right) \quad (7.27)$$

The parameter $0 < \alpha < 1$ controls the asymmetry of the curve and if $\alpha = 1/2$ the curve is symmetric with respect to $(a + b)/2$, see Figure 7.6.

The CVR dipole-moment surface

8.1 Introduction

Despite the benchmark nature of the problem there are relatively few *ab initio* DMS's available for the water molecule. Notable examples are given in Refs. [PS97, GRR⁺93, JJ93, KS97, SP00]. In particular, the *ab initio* dipole surface by Partridge and Schwenke [SP00] was found to give very good transition intensities over a wide range of frequencies [DGZ⁺05, BTHT06] and provide a very valuable reference. We will denote this surface as SP2000. A new dipole moment surface for water was obtained and published [LTT⁺08] and will be described in this chapter.

Ab initio studies of the ground state PES of water [Sch01, PCS⁺03, BSZ⁺06], and indeed of other molecules [LTY⁺02, RKN⁺04, vHP⁺01, TCPT01], have shown the importance of including corrections [CAYS00, CTL⁺01, CAS98] to standard *ab initio* procedures in the form of core-core and core-valence corrections [PS97, PCS⁺03], first- [CKP⁺98b] and higher-order relativistic corrections [QBT⁺01], adjustments due to the limited precision of the Born-Oppenheimer approximation [ZPLT96, Sch01, Sch03a], and even quantum electrodynamic effects [PDC⁺01].

The CVR water DMS is the first surface which includes some of these corrections. The final surface is made up by the sum of three surfaces: a main, valence-only surface a core-correlation correction surface and finally a relativistic-correction surface. The complete surface was called CVR as an acronym of **C**ore-**V**alence-**R**elativistic, in analogy with its twin potential energy surface CVRQD [BSZ⁺06] which originated from the same set of calculations (the CVRQD PES also included **Q**ED and **D**iagonal Born-Oppenheimer corrections).

Building the CVR surface was a multi-stage process that required a combined effort by many researchers and, because of the problems encountered in obtaining a good-quality fit, it took as many as four years from the computation of the points to the final publication of the dipole surface.

The three surfaces whose sum gives the final CVR were obtained and fitted by different research groups. In order to identify the author's personal contributions to the project, for any specific stage the names of the people who worked on them will be explicitly stated.

We will discuss in the present chapter how the points for the three surfaces were computed and how the surfaces were obtained, while results of variational rotation-vibrational computation that use the CVR surface will be presented in Chapter 9.

8.2 Computation of the *ab initio* values

8.2.1 Valence-only dipoles

Dipole moments were computed mainly by S.V. Shirin and O.L. Polyansky using the IC-MRCI method as implemented in the software MOLPRO 2000.9 [WKL⁺00]. The reference space used is the 8-electrons–8-orbitals “one-to-one” of Table 6.2, dipole moments were calculated as expectation values and the basis set used is aug-cc-pV6Z [KDH92, EMS]. A total of 1497 geometries were computed, covering geometries with energies up to about 40,000 cm⁻¹. Most of these results are side-products of the extensive computations performed for computing the CVRQD energy surface [PCS⁺03, BSZ⁺06] but approximately 50 points were added to cover regions where graphical inspection of the fits suggested that the dipole moment components were particularly poorly determined. As will be discussed in Section 8.3, not all the dipole data computed were in the end used in our final fit.

It was our original intention to explore the idea of extrapolating the dipole calculations for different basis sets to give an estimate of the complete-basis-set-limit dipole at each geometry, as is routinely done for energies [BSZ⁺06, PCS⁺03]. This procedure however, as discussed in Section 7.4.2, is of dubious validity and, besides, also unnecessary in our case as dipoles are converged with respect to increases in the basis set size to better than 5×10^{-4} au while errors due to other causes (method of computation of the dipole, correlation treatment etc.) are larger than that amount by perhaps an order or magnitude or more (see discussion in Chapter 7 for a detailed analysis). For these reasons, the idea of extrapolation was not pursued.

8.2.2 Core-correlation dipole correction

The core-correlation correction surface computations were performed by A.G. Császár and utilized the coupled cluster CCSD(T) method [RTPHG89]. Coupled cluster theory was chosen over MRCI mainly because a size extensive method (see discussion in Section 3.6) is preferred when differences are taken between quantities computed for systems with a different number of electrons and coupled cluster is exactly size extensive in all of its truncated versions. The frozen-core and all-electron CCSD(T) dipole moment calculations utilized as the uncontracted aug-cc-pCVTZ and aug-cc-pVTZ basis sets [EMS, Dun89] and program package ACES II [ACE].

Core-corrections were calculated over a grid containing 364 points, which is the subset of the total points used to compute the energy surface presented by Polyansky *et al* in [PCS⁺03]. These geometries cover energies only up to about 25,000 cm⁻¹, so that the single-reference-based coupled cluster method should still perform well.

Since ACES II always reorients the molecular frame and performs the electronic structure calculations in the principal axes frame, special attention was paid to reorient the dipoles in order to make them consistent with the axes convention we have chosen to adopt (see section 6.1).

8.2.3 Relativistic dipole correction

Relativistic corrections to the dipole were computed in 2002 by J.N.P. van Stralen and L. Visscher using the Dirac-Coulomb equation (see section 7.5.1 for details on the underlying theory) as

implemented in the software DIRAC [Dir] for the same grid of 364 geometries used for the core-correlation corrections.

Dipoles were obtained as the sum of the Dirac–Hartree–Fock (DHF) dipole plus an electron-correlation contribution. The DHF main contribution was obtained using the uncontracted aug-cc-pCVQZ basis set (see [LTT⁺08, van04] for a minor point regarding the uncontraction of the basis sets) and the Dirac-Coulomb Hamiltonian. The correlation contribution was computed with the relativistic CCSD(T) method using the spin-independent Hamiltonian (again, see section 7.5.1 for more details) and the uncontracted aug-cc-pCVTZ basis set.

In the set of 364 geometries, three geometries were found which appeared particularly problematic for the CCSD(T) method. These are structures with one bond highly stretched, namely $\theta = 104.52^\circ$ and $r_1 = 0.95 \text{ \AA}$, while r_2 is 3.0, 5.0, and 7.0 $\text{\AA}$. These structures, for which the wave function is not well described by a single determinant, have been treated separately using the complete active space self-consistent-field (CAS-SCF) method. The CAS-SCF calculations were performed in C_s symmetry with the same frozen-core “one-to-one” active space used for the valence-only IC-MRCI computations and used the aug-cc-pCVQZ basis set. The DALTON electronic structure program [DAL] was used for the computations. Comparison of the non-relativistic CCSD(T) values with non-relativistic MRCI values for the other geometries of the set confirmed that CCSD(T) should be an adequate method to calculate the relativistic effect for the other 361 points.

8.3 Fitting the dipole surfaces

8.3.1 Fit of the core-correlation and of the relativistic correction points

Both the core-correlation correction and the relativistic correction points were fitted into two separate surfaces by A.E. Lynas-Gray. The functional form used for the fit is the same as used by Schwenke and Partridge [SP00] as described by formulae 7.20 and 7.22. In both fits the exponent β was fixed to 0.38 a_0^2 while $n_r = n_\theta = 6$, which applying the constraints on the indices indicated in the paragraph after Formula 7.22 leads to a total of 84 linear parameters.

The fit of the corrections was very straightforward, essentially for two reasons: *i*) as the order of magnitude of the corrections is about 10^{-3} au while the uncorrected dipole has magnitude unity, to achieve a comparable accuracy in the dipole surfaces the requirement on the corrections are about 1000 times less strict and, *ii*), the number of points to be fit and, more importantly, the extent of the portion of the dipole surface to be covered is smaller than for the valence-only surface. For these reasons the fit did not present any particular problem. The RMS of the fitting error for the core-correlation and relativistic correction surfaces is respectively of $1.3 \times 10^{-5} \text{ au}$ and $1.5 \times 10^{-5} \text{ au}$.

8.3.2 Fit of the valence-only points

As discussed extensively by Schwenke and Partridge [SP00] and by Kedziora and Shavitt [KS97], obtaining an analytical fit to *ab initio* dipole data for water with an accuracy of the order of 10^{-4} au or better is a challenging problem. In fact, fitting the valence-only points proved to be the major problem of the whole dipole-surface building process. The same functional form

introduced by Schwenke and Partridge [SP00] and also used for the correction surfaces was employed. A number of other methods was also tried by A.E. Lynas-Gray for over two years but did not give good results and were eventually abandoned.

The quality of the resulting surface was ascertained in two ways: first, by looking at the residual fitting error and at one dimensional cuts of the surface and, second, by using the resulting DMS to calculate ro-vibrational transition intensity that were then compared with those in the HITRAN2004 database [Rot05]. More specifically the set of 340 HITRAN transitions originating from $J=0$ to $J=1$ was used as a reference testing set.

The problem of spurious oscillations

The initial procedure to obtain the fit was to use the same weighting function and exponent $\beta = 0.4200428411 \text{ a}_0^{-2}$ as used by Schwenke and Partridge for their surface¹ [SP00] and then to increase the number of fitting basis functions increasing the indices n_r and n_θ .

The problem encountered with this straightforward procedure was that, as the number of parameters went beyond the range of 150-200 corresponding to an RMS fitting error of about 10^{-3} au, adding more basis functions made the residual errors decrease increasingly slowly and in the fit there appeared small, unphysical oscillations between the data points, see Figure 8.1. These appear particularly in the angular coordinate θ and in turn led to serious mispredictions of weak lines intensities, by factors of 100 (the effect of oscillations in the dipole surface was discussed in Section 7.2).

This kind of behaviour is not at all surprising as it is well-known in numerical analysis that high-order one-dimensional polynomial interpolants often give rise to irregular oscillations if the distribution of the points is not carefully chosen, see discussion in Section 5.2. In our case the situation appeared to be even worse because not only there were oscillations between the data points, but the fitting error also decreased very slowly on adding new basis functions, indicating problems of linear dependencies between the fitting basis functions.

Some well-known methods coming from numerical analysis and statistics were tried to reduce linear dependencies, such as singular value decomposition and analysis of the correlation matrix [BKW04], but were found insufficient to fully eliminate them. Also, many different weighting schemes were investigated, but they did not lead to significant improvements either.

In principle, two conceptually easy routes to follow would have been, *i*), to significantly increase the number of calculated points so as to better constrain the parameters, and/or *ii*) to use a different functional form or a different surface-building scheme which is immune from this problem. In practice, however, neither of those solutions could be pursued in the short run.

In the end, mirroring the approach taken by Schwenke and Partridge [SP00], we chose to supplement the data points with extra, “guide” points to ensure smoothness. These “guide” points were generated by plotting the function q to be fitted (see formulae 7.20 and 7.22) for fixed r_1 and r_2 against $x_3 = \cos(\theta) - \cos(\theta_e)$. This was possible because the points were computed in slices of constant θ on a grid having some regularity in r_1 and r_2 , so that many values for different θ had the same values for r_1 and r_2 . More specifically, 140 sets of points with common r_1 and r_2 with 7 or more x_3 values were obtained. Within each of these sets a one-dimensional

¹These authors state in their paper they used $\beta = 2\text{a}_0^{-2}$ but in fact in the surface they made available the value we report is used.

natural cubic spline was used to generate interpolated data on a grid of x_3 values in steps of 0.02. Some 12,000 extra points were generated in this fashion. These extra points were then merged with the original ones and used in the fit, although they were assigned a much smaller weight (see the following section for more details). As we mentioned most of the oscillations are present in the coordinate corresponding to bending motion and the aim of these guide-points is to smooth over the surface along this direction. As these extra points are generated from the original data without adding any new data, it may be argued that the *ab-initio* character of the approach be retained. In this way we were able to greatly assuage, even though not completely solve, the problem of oscillations and to finally obtain a satisfactory fit to the data.

Weighting function

Several weighting schemes were investigated. It is commonly held that one should give different weights to the computed points in relation to the energy of the corresponding geometry, with higher-energy points receiving lower weights. This prescription stems from two related considerations. First, and most importantly, the low-energy region of the DMS affects the intensity of *all* rotational-vibrational transitions, while higher-energy regions matter only for transitions involving ro-vibrational states which have correspondingly higher energies. Spectra recorded at ordinary temperatures do not generally sample transitions involving states with energies higher than about $28,000\text{ cm}^{-1}$, which are in turn determined by a similar range in energy of the PES (see discussion in Section 5.2.5); it is therefore sensible to favour points with energies lower than this. Second, because virtually all electronic structure methods gradually deteriorate as one moves away from the lowest-energy point, high-energy points are more likely to have larger errors. The exact form of the weighting function is generally dictated by convenience; the curves generally have a sigmoid shape (see Figure 8.2) which naturally divides the global energy range spanned into three parts:

1. A low-energy region where the points receive high weights;
2. A transition region where the weights rapidly decrease;
3. A final, high-energy region with essentially zero weight.

It may also be remarked that, if the weighting function is used as a means to achieve different accuracy goals for different energy regions, it should also take into account the density of points as function of the energy.

We tried several functions with different cut-off values, transition widths and fall-off speeds. In the end, we arrived to the somewhat unexpected conclusion that a simple step-function scheme gives better results than the more gradual ones. All *ab initio* data for geometries whose energy is $30,000\text{ cm}^{-1}$ or less above the potential minimum were given unit weight, while all higher-lying points were excluded from the fit. Similarly, only interpolation-generated points for geometries up to $30,000\text{ cm}^{-1}$ were included in the fit; these points received a weight of $1/850$.

The final dipole surface and conclusions

For our final fit we chose $n_r = 8$ and $n_\theta = 18$, giving 615 linear parameters. This fit reproduces the 878 *ab initio* dipole moments used in the fit with a RMS residual of 3×10^{-5} au. When the

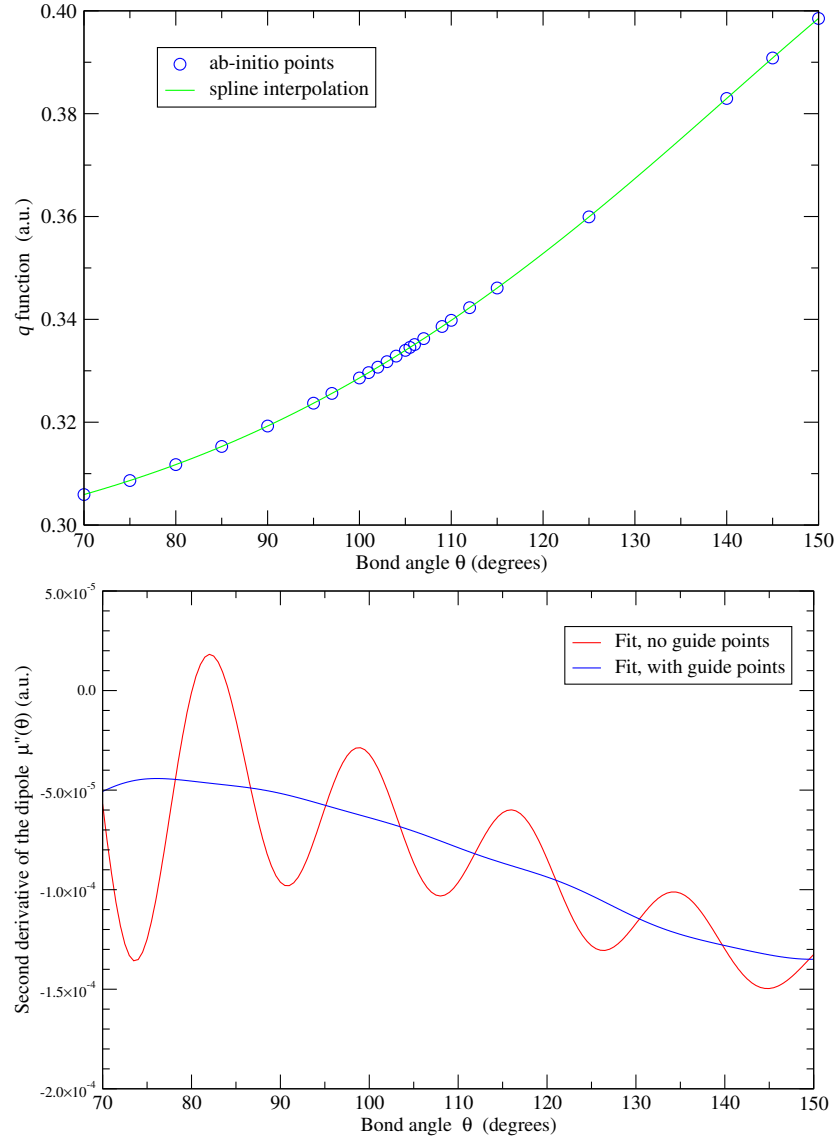


Figure 8.1: Plots illustrating the spurious oscillations arising in the polynomial fit and of the way the extra guide points were chosen. Both plots refer to one-dimensional cuts with r_1 and r_2 fixed to the value $r_1 = r_2 = 1.79524 \text{ a}_0$. The first plot shows the $q(r_1, r_2, \theta)$ values (see eq. 7.20) for the ab initio points and for a spline interpolation of these. The extra points were then obtained by sampling this spline curve. On this scale the spurious oscillations in the fit are not visible and the fit curve looks identical to the spline one. In the second plot we report the second derivative of the $\mu_{\parallel}$ component of the dipole for the fitted dipole ($n_r = 10$, $n_{\theta} = 18$) and for the one obtained including the guide points. It is evident that the guide points solved the problems of the spurious oscillations.

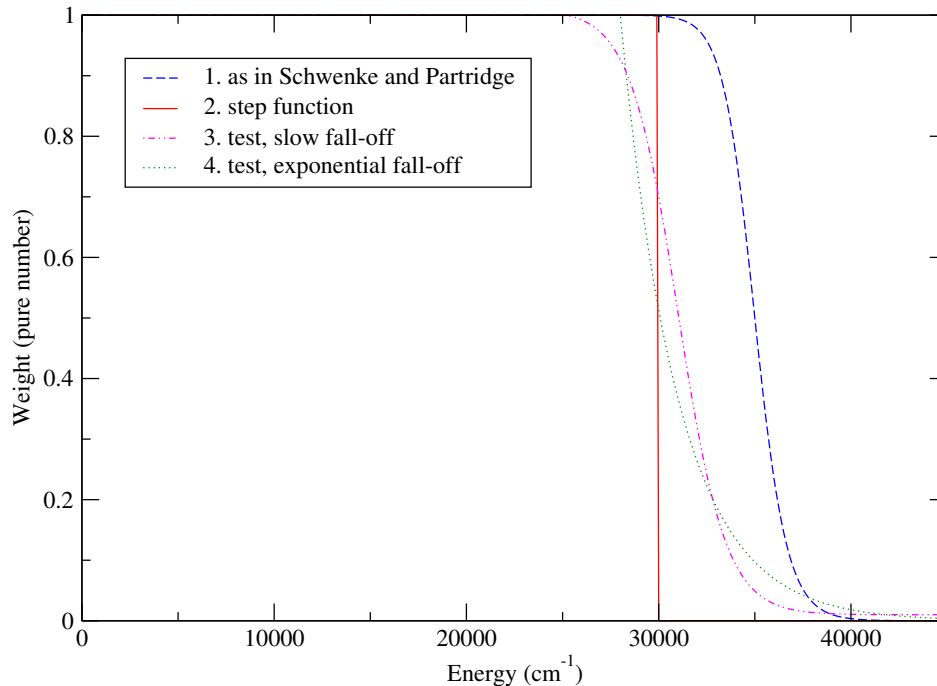


Figure 8.2: Some of the weighting functions considered. 1. is the weighting function used by Schwenke and Partridge in ref. [SP00]. 2. is the simple step-function eventually chosen for our final fit. 3. and 4. are examples of other functions tried but discarded, with different functional forms and cut-off energies.

fitted DMS is used to reproduce the 369 points lying in the energy range $30,000 - 40,000 \text{ cm}^{-1}$, the RMS is $8 \times 10^{-3} \text{ au}$ and it is $1.3 \times 10^{-2} \text{ au}$ for the points whose energy is between $40,000$ and $100,000 \text{ cm}^{-1}$. A plot of the fitting errors is presented as Figure 8.3. Table 8.1 compares calculated DMSS for our 14 key geometries presented in Table 6.7. This table is testament both to the quality of our fit and to the fact that our individual dipole values lie close to those of SP2000. The table also shows that the core and relativistic corrections to the dipoles appear to be of similar magnitude but of opposite sign not only at equilibrium but also along the surface, as already discussed in Section 7.5.3.

As it will be shown extensively in Chapter 9, test calculations over large datasets revealed that the CVR surface performs comparably to the best previous DMS of water by Schwenke and Partridge (SP2000) [SP00].

This lack of a major improvement can be readily understood by comparing how the SP2000 was obtained. With respect to Schwenke and Partridge’s DMS, the CVR surface used a larger basis set and made use of the core-correlation and relativistic correction surfaces. As shown in chapter 7, the basis set dependence of the dipoles after the aug-cc-pV5Z basis set is smaller than other sources of error while core and relativistic effects cancel out to a large extent over almost the whole configuration space considered. On the other hand both CVR and SP2000 used the same IC-MRCI electronic structure method, the same reference space and the same way of computing dipoles as expectation values.

Table 8.1: Calculated dipole moments, in au, for the reference structures presented in Table 6.7 as a function of the computational model. Note that geometry #5 was not included because both components of the dipole are zero in that case.

#	sym	r_1	r_2	θ	RE ^a	μ_{AGZ}		μ_{fit}		$\Delta\mu_{\text{rel}}$		$\Delta\mu_{\text{cor}}$		μ_{tot}		μ_{SP2000}	
		a_0	a_0	deg	cm ⁻¹	$\mu_{\parallel}$	$\mu_{\perp}$	$\mu_{\parallel}$	$\mu_{\perp}$	$\mu_{\parallel}$	$\mu_{\perp}$	$\mu_{\parallel}$	$\mu_{\perp}$	$\mu_{\parallel}$	$\mu_{\perp}$	$\mu_{\parallel}$	$\mu_{\perp}$
1	C _{2v}	1.81196	1.81196	104.343	0	n/a	n/a	0.73550	...	-0.00171	...	0.00197	...	0.73576	...	0.73463	...
2	C _{2v}	1.70075	1.70075	104.520	1,609	0.72226	...	0.72223	...	-0.00151	...	0.00178	...	0.72250	...	0.72150	...
3	C _s	1.51178	1.70075	100.000	8,968	0.73537	-0.02951	0.73536	-0.02951	-0.00139	0.00014	0.00169	-0.00018	0.73566	-0.02956	0.73461	-0.02940
4	C _{2v}	1.79524	1.79524	170.000	10,741	0.13209	...	0.13209	...	-0.00034	...	0.00031	...	0.13207	...	0.13212	...
6	C _s	2.17318	2.36218	95.000	14,444	0.81038	-0.00735	0.81037	-0.00734	-0.00250	0.00012	0.00269	-0.00013	0.81056	-0.00735	0.80865	-0.00712
7	C _s	1.60627	2.55113	104.520	18,266	0.74809	-0.10950	0.74806	-0.10949	-0.00211	0.00073	0.00231	-0.00079	0.74826	-0.10955	0.74692	-0.10858
8	C _s	1.41729	1.60627	120.000	18,713	0.60547	-0.04816	0.60547	-0.04814	-0.00104	0.00011	0.00116	-0.00017	0.60559	-0.04820	0.60511	-0.04806
9	C _{2v}	2.36216	2.36216	104.520	19,299	0.74573	...	0.74571	...	-0.00257	...	0.00265	...	0.74580	...	0.74428	...
10	C _s	1.79524	2.36216	179.900	24,614	0.00140	-0.33764	0.00138	-0.33761	-0.00001	0.00007	0.00001	-0.00012	0.00138	-0.33767	0.00138	-0.33718
11	C _{2v}	1.79524	1.79524	45.000	28,111	0.97419	...	0.97420	...	-0.00216	...	0.00248	...	0.97452	...	0.97260	...
12	C _{2v}	1.41729	1.41729	100.000	31,560	0.70660	...	0.70655	...	-0.00109	...	0.00135	...	0.70681	...	0.70599	...
13	C _s	1.79524	3.37795	104.520	32,359	0.55637	0.19903	0.55676	0.22845	-0.00201	0.00037	0.00227	-0.00040	0.55702	0.22841	0.41956	0.45973
14	C _{2v}	2.64562	2.64562	100.000	33,014	0.74675	...	0.74641	...	-0.00272	...	0.00284	...	0.74653	...	0.74471	...

^a Relative energies (RE) are with respect to structure #1, see Table 6.7.

^b $\mu_{\text{tot}} = \mu_{\text{fit}} + \Delta\mu_{\text{rel}} + \Delta\mu_{\text{cor}}$; $\mu_{\parallel}$ = component of $\vec{\mu}$ parallel to the bisector of the HOH angle; $\mu_{\perp}$ = component of $\vec{\mu}$ perpendicular to the bisector of the HOH angle.

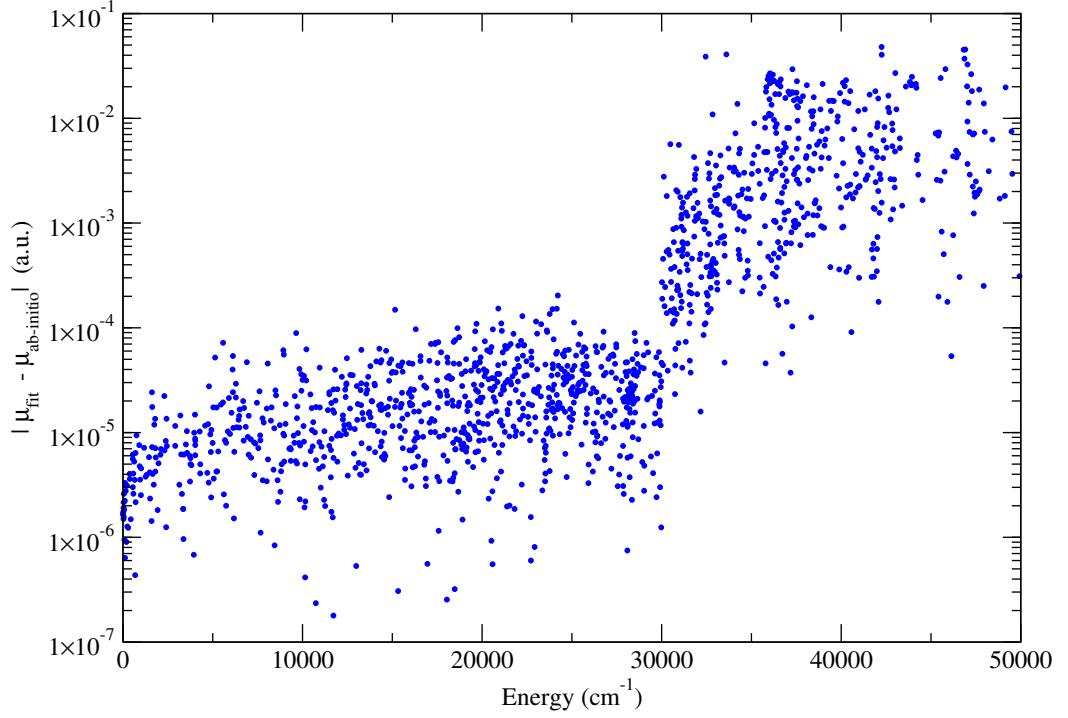


Figure 8.3: Residuals of the CVR dipole surface.

These considerations were not made before the dipole values were computed because, as we briefly mentioned in the section 8.1, the major focus of those computation was the production of the potential surface [BSZ⁺06] while dipoles were essentially a by-product. With hindsight, one may say that the computations were sub-optimal for the computations of dipoles. Also, the cancellation effect of core and relativistic corrections could not be foretold.

In conclusion, it was the desire to understand the reasons of the lack of improvements that spurred us to perform the extensive tests of the convergence of the dipole presented in Chapter 7.

Calculation of line intensities with the CVR dipole surface

9.1 Comparing line intensities: method of analysis

We would like to discuss in this section some practical issues which arise when one has to compare lists of line intensities. This may not be trivial because one may have to deal with data sets containing from a few hundreds to several tens or even hundreds of thousands of lines, so that some sort of statistical analysis is necessary.

Matching the lines

The first step to be taken when two line lists to be compared are given is to pair records referring to the same line. This is not difficult, but same care should be observed because of the volume of the data. Supposing each line in the two lists has been assigned transition quantum numbers, we found that an efficient procedure can proceed along these steps:

1. It is convenient to convert the 12 quantum numbers identifying the transition, e.g. (ν_1, ν_2, ν_3) and (J, K_a, K_c) for the upper and for the lower state, into a single object which we will call “sort-key”. An easy way to do this is to use a character variable containing the character code 0 to 255 corresponding to the quantum numbers. In Fortran this may be written as

```
character(len=12) :: sort_key
...
write(sort_key,"(12A1)") achar(i1),achar(i2), etc. ,achar(i12)
```

This will work as long as the quantum numbers are less than 255, which is always verified in our case. More sophisticated approaches using a hash function are also possible, but were not judged necessary.

2. Records from each list (transition intensity, wavenumber etc.) should be read from the files and stored in memory.

3. Both lists should be sorted with respect to the sort key using a fast sorting routine like quicksort or heapsort (in actual practice *ranking* rather than sorting may be preferred¹).
4. Both lists should be checked against repeated lines or other kind of errors. Having the lists sorted generally renders this step simpler.
5. Lines in the smaller list should be matched, one by one, with the ones in the larger list. This can be done using binary search or, even more efficiently, using a merge-sort-type scheme as the two sets are already sorted, see e.g. the book by Knuth [Knu98].
6. At the end of this process one should have produced three lists, one containing matched lines and two containing the unmatched lines from the two lists.
7. Further checks on the matched lines like comparing the transition wavenumber can be performed as a cross check.

If this is implemented correctly it will process lists with a few tens of thousands of lines in a matter of a few minutes. The RAM needed to match two sets each containing N lines and reading four double-precision numbers for each line (typically: transition wavenumber, and lower-state wavenumber, line intensity and line strength) is equal to $88N$ bytes so that, for example, for $N = 200,000$ the memory needed is 17.6 MB. Approaches which require much less memory are possible but they were not considered worthy the extra effort required given the typical size of linelists and the amount of memory normally available on today's machines. If the check for duplicate lines and errors in the data set is not necessary one may skip it (it is the most expensive step), sort only the smallest list and then look up the lines from the larger list one-by-one.

Statistical analysis

Once the lines in the two data sets A and B have been paired the actual comparison of the intensities I can take place. Some care is needed because, first, absolute values of intensity may cover more than ten orders of magnitude and, second, because for both calculations and experiments systematic errors may be present leading to a few cases where I_A and I_B differ greatly (so-called outliers). The presence of a few outliers can potentially render devoid of meaning quantities such as averages or standard deviations if they are taken in a naive way [Wat03]. Furthermore, both in theory and in experiment there can be systematic errors, for example in the form of multiplicative factors (e.g. due to improper calibration of the instruments), which one would like to easily identify.

In the light of these considerations we found that the most useful quantity to analyse is the logarithm of the ratio of the intensities, κ_i :

$$\kappa_i \stackrel{def}{=} \log \left(\frac{I_A(i)}{I_B(i)} \right) \stackrel{def}{=} \log(\varrho_i)$$

and that the most informative way to display the results is by producing a log-log plot with the absolute line intensities along the horizontal axis and the ϱ_i along the vertical axis. Many examples of such plots will be presented in following sections of this chapter. The basis used

¹Ranking consists in finding, for each element of a set, its rank in the sorted set, without effectively changing the initial order of the set.

for calculating the logarithms is not fundamental for the analysis but we found it useful to use natural logarithms, so that, if $\varrho = 1 + \epsilon$ with ϵ very small, then $\kappa = \ln \varrho \approx \epsilon$ is the relative discrepancy and 100κ is the percentage of discrepancy.

The main advantages of this kind of plot are:

- It can accommodate a very large range of variation along both axes, so that all data can be displayed together.
- The distribution of the points is simply mirrored with respect to the $\varrho = 1$ horizontal line by inversion of the ratio I_A/I_B to I_B/I_A , in contrast to a plot where the simple ratios I_A/I_B are plotted. This is a desirable property as the choice of I_A/I_B or I_B/I_A is arbitrary.
- Any multiplicative factor can be readily identified (see Figure 9.1 for such an example).

There is also a more theoretical consideration suggesting that the κ_i are indeed sensible quantities to look at. If we assume that each line intensity, both theoretical or experimental, differs from the exact value because of the action of many random, uncorrelated, multiplicative (as opposed to additive) factors it is then a consequence of the central-limit theorem [Fel68] that the probability distribution of the κ_i will tend to some stable probability distribution [Fel68]. For example, if the logarithms of the multiplicative random factors have finite variance then the ϱ_i will follow in the limit the log-normal probability distribution. On the basis of these considerations it appears well-advised to perform a quantitative statistical analysis of the distribution of the κ_i .

More specifically, one can compute the cumulative distribution function (CDF) of the κ_i , the derivative of which gives the probability density function (PDF), e.g. a Gaussian, Lorentzian etc. distribution. If there are a total of N κ_i their CDF can be easily calculated by sorting them in ascending order and then assigning to them the values $1/N, 2/N, \dots, (N-1)/N, 1$. The resulting curve can then be fitted to the CDF corresponding to, for example, a Gaussian or a Lorentzian distribution. Such a plot is shown e.g. in Figure 9.3.

From this kind of analysis is possible to identify any asymmetry with respect to the $\varrho = 1$ vertical line and, above all, to ascertain the behaviour of the tails of the distribution. If the tails are considerably longer (or, in statistical jargon, *fatter*) than those of a Gaussian distribution then some care should be taken when considering mean value or standard deviations of the κ_i , as these quantities are rigorously defined only for finite-variance PDF.

Final remarks In the case where the detailed statistical analysis has shown that the distribution of the κ_i can be roughly described as Gaussian, or in the case where the data set is too small to make a reliable statistical analysis, it is useful to calculate some quantitative number that give an idea of the margin of agreement between the two data sets. The two fundamental quantities we calculated are the geometric mean of the ϱ_i :

$$\langle \varrho \rangle_g = \left(\prod_i \varrho_i \right)^{\frac{1}{N}} = \exp \left(\frac{1}{N} \sum_i \kappa_i \right) \quad (9.1)$$

and the associated standard deviation of natural logarithm of the ratios

$$\sigma = \sqrt{\frac{1}{N} \sum_i [\ln(\varrho_i) - \ln(\langle \varrho \rangle_g)]^2} = \sqrt{\left(\frac{1}{N} \sum_i \ln(\varrho_i)^2 \right) - \ln(\langle \varrho \rangle_g)^2}, \quad (9.2)$$

The meaning of σ is that the statistical scattering of the ratios with respect to $\langle \varrho \rangle_g$ is given by a multiplicative factor $e^{\pm\sigma}$.

Another quantity often reported (for example in [Cou99]) is the root mean square (RMS) error given by

$$\sigma_{\text{RMS}} = \sqrt{\frac{1}{N} \sum_i \left(\frac{I_A(i) - I_B(i)}{I_B(i)} \right)^2} = \sqrt{\frac{1}{N} \sum_i (\varrho_i - 1)^2} \quad (9.3)$$

which reduces to the previously-defined σ if $\langle \varrho \rangle_g = 1$ (no systematic bias) and $\varrho_i \approx 1$ (small dispersion). However, in the case where even a few ratios differ significantly from 1, the analysis in terms of σ_{RMS} may give unreasonable results (in particular, this quantity is not symmetric with respect to inversion of the ratio I_A/I_B to I_B/I_A).

9.2 Calculation of the rovibrational nuclear wave functions

Nuclear-motion wave functions and transition intensities for J up to 15 were computed with the software suite DVR3D [TKB⁺04]. Intensities were generated at the HITRAN [Rot05] reference temperature of 296 K. Basis sets developed by Barber *et al* [BTHT05] in the course of their calculation of the comprehensive BT2 water line list were used for all calculations. These should be large enough to remove virtually all issues to do with convergence for the room temperature transitions considered here.

Two distinct sets of wave functions were used in the tests presented below; a first set was generated using the *ab initio* CVQD PES [BSZ⁺06, PCS⁺03] and a second using the spectroscopically determined FIS3 PES of Shirin *et al*. [SPZ⁺03]. Henceforth, the related wave functions are labeled CVRQD and FIS3, respectively. States with total rotational angular momentum J up to 15 were considered.

All computations were performed using a Pentium IV 3 GHz PC with 3 GB of RAM running 32-bit Linux and took altogether about two weeks of continuous computations.

9.3 Sensitivity of transition intensities with respect to the PES

Comparison with experiment is best made for dipole transition intensities rather than for the dipoles themselves.

Given that the nuclear motion calculations are highly converged, the accuracy of our approach depends only on the accuracy of the underlying PES used (and the associated corrections to the Born-Oppenheimer approximation [TBK⁺02] used) and the accuracy of the DMS.

To assess the importance of the PES used for the calculation of the nuclear-motion wave functions to be used for the intensity calculations we have analysed the change in intensity predicted for the 340 $J = 0 - 1$ transitions listed in HITRAN 2004 [Rot05] when using a dipole surface (either CVR or SP2000) and wave functions computed using the CVRQD surface or the FIS3 surface. For 334 of these lines, the effect of the wave function on the predicted transition intensity was only about 2 %, with transitions computed using the CVRQD PES being systematically about 2 % weaker. The remaining six lines, which are detailed in Table 9.1, show considerable sensitivity to the choice of the wave function. This behaviour is a reflection of

Table 9.1: Transition intensities involving states with $J = 0$ and/or 1 which are highly sensitive to the details of the rotational-vibrational wave function. The wave functions were generated from the purely *ab initio* CVRQD potential [BSZ⁺06, PCS⁺03] or the spectroscopically determined semi-theoretical FIS3 potential of Shirin *et al.* [SPZ⁺03]. All transitions are from the (0 0 0) vibrational ground state. Powers of ten are given in brackets.

Quantum numbers		Wavenumbers (cm ⁻¹)	Line Intensities (cm molecule ⁻¹)			
Upper	Lower		HiTran	CVR		SP2000
		HITRAN		CVRQD	FIS3	CVRQD FIS3
0 7 1 0 0 0	1 0 1	13811.5791	2.02(−25)	1.86(−26)	1.59(−25)	3.51(−26) 2.03(−25)
4 0 0 1 1 1	0 0 0	13861.6677	1.31(−25)	5.75(−27)	9.92(−26)	1.10(−26) 1.26(−25)
0 5 3 1 1 1	1 1 0	18374.5704	6.45(−27)	1.47(−26)	9.11(−27)	6.75(−27) 3.29(−27)
4 0 2 1 1 0	1 0 1	20546.5874	1.06(−26)	9.58(−30)	5.09(−30)	1.06(−26) 1.09(−26)
6 0 1 1 1 1	1 1 0	22517.8957	6.79(−26)	3.59(−29)	6.67(−26)	4.37(−28) 7.94(−26)
6 0 1 1 1 0	1 1 1	22527.8971	3.19(−26)	1.06(−30)	2.90(−26)	5.92(−29) 3.24(−26)

the effect of strong interaction between neighboring vibrational states (“resonances”) which, in particular, can lead to strong enhancement of weak transitions. This coupling is particularly sensitive to the details of the PES but would appear to affect only about 2 % of the transitions. Nevertheless, it reflects the difficulties one encounters in predicting intensities of exceedingly weak transitions which have become increasingly the subject of experimental investigations due to the advances in the relevant techniques. Below all calculations used the CVRQD PES unless otherwise stated.

An more specific analysis concerning purely rotational transitions, where the effect of the PES will be shown to be even smaller, will be presented in Section 9.6.2.

9.4 Comparison with the HITRAN2004 database

The 2004 edition of the HITRAN database [Rot05] provides a compilation of experimental results for H₂¹⁶O. Comparison between transition intensities calculated using our final DMS surface CVR and the HITRAN data is given in Fig. 9.1.

A comparison between transitions computed with the SP2000 dipole surface and HITRAN looks very similar to that of Fig. 9.1. Figure 9.2 therefore gives instead a direct comparison between our CVR surface and SP2000 for the transitions between levels with $J \leq 9$ listed in HITRAN. It can be seen that the agreement between the two sets of theoretical data is much closer than their agreement with HITRAN. Figure 9.3 presents the cumulative distribution function of the ratios of Fig. 9.1, as explained in Section 9.1. It can be seen that the distribution is better fitted by a Lorentzian function than a Gaussian although the Lorentzian fit still remains not entirely satisfactory.

Representing the distribution by a Lorentzian function then gives an average error (the peak of the Lorentzian function) and an approximate error given by the full width at half maximum of the Lorentzian, Γ . For the data given in Fig. 9.1 our intensities are 0.6 % too strong with a Γ approximately corresponding to a width of ± 17 %. These figures are almost identical to

the results obtained if the calculation is repeated using the SP2000 DMS, which gives 0.6 % and ± 16 % respectively. Indeed, there is a significantly higher correlation between results calculated with the two distinct DMSS than between the surfaces and HITRAN.

One interesting feature shown by the comparison of our results with HITRAN 2004, see Fig. 9.1, and the same comparison using SP2000, is the substructure at higher intensities suggesting some systematic disagreement. This substructure occurs for the recent mid-infrared measurements of Toth [Tot05]. No such systematic differences are found for data reported from any other source lying at either lower or higher frequency than this. The cause of this systematic discrepancy remains to be determined.

9.5 Comparison with accurate CW-CRDS measurements

A particularly stringent test of the DMS is given by a comparison with the work of Kassi *et al.* [KMNC05] on the absorption of water vapour near $13,320\text{ cm}^{-1}$. This spectrum, obtained by continuous-wave cavity ring-down spectroscopy (see e.g. [BPM00] for details on the technique), probes particularly weak transitions and it is such weak transitions which are particularly sensitive to the details of the fit, see the extensive discussion of this by Schwenke and Partridge [SP00].

Figure 9.4 compares the predicted CVR intensities for this spectrum with those of SP2000. We recomputed the SP2000 results but obtained results very similar to those quoted by Kassi *et al.* [KMNC05]. For the stronger portion of this spectrum, intensities above $10^{-27}\text{ cm molecule}^{-1}$, the CVR DMS clearly gives better agreement than SP2000: on average 3 % stronger with $\Gamma = 27$ % against 14 % stronger and $\Gamma = 39$ % for SP2000. Below $10^{-28}\text{ cm molecule}^{-1}$ both DMSS do less well, although ours again performs better, 16 % average error with $\Gamma = 52$ % against 31 % average error and $\Gamma = 68$ %. A direct comparison between the CVR and SP2000 DMSS for these lines suggests that our intensities are about 10 % less; even with this we are still overestimating the strength of weaker lines by about 15 %.

It should be noted that this comparison is not entirely straightforward since SP's intensities were used to assign the Kassi *et al.* spectrum which can lead to some systematic bias. Indeed, there are four lines, see Table 9.2, for which we obtain very significantly weaker intensities suggesting that the line may have been wrongly assigned because their predicted intensity was overestimated.

9.6 Comparison with purely rotational transition intensities

Pure rotational lines are important for monitoring water concentrations in many environments both in space and on earth. A list of line intensities of rotational transitions for H_2^{16}O was calculated and published [LT08] using variational nuclear motion wave functions and the CVR dipole moment surface. This methodology should be equally reliable for both allowed and forbidden rotational transitions. Extensive comparisons are made with available intensity data for these transitions including the HITRAN and JPL databases. Problems are identified with some of these data.

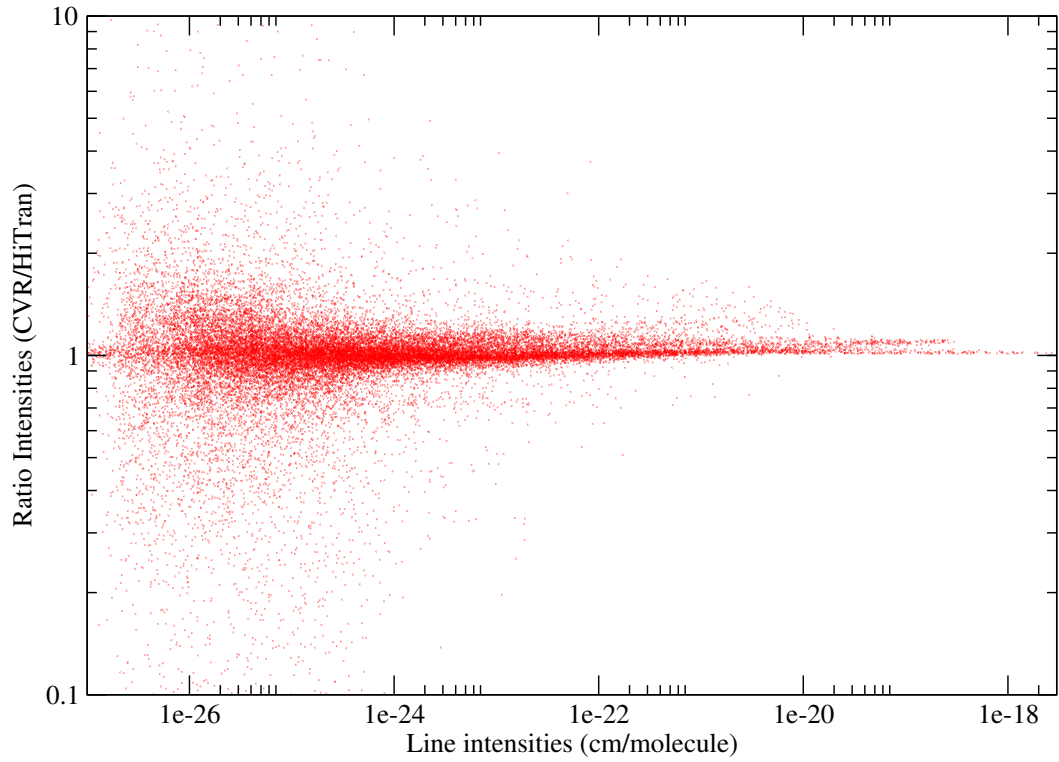


Figure 9.1: Ratio of dipole line intensities for H_2^{16}O predicted by the CVR dipole surface to those reported in the 2004 version of the HITRAN database [Rot05].

Table 9.2: Transitions from Kass *et al.* [KMNC05] for which we obtain significantly different intensities. All transitions are from the (0 0 0) vibrational ground state. Powers of ten are given in brackets.

$v'_1 v'_2 v'_3$	$J' K'_a K'_c$	$J'' K''_a K''_c$	Wavenumbers (cm^{-1})		Line Intensities ($\text{cm}/\text{molecule}$)		
			Obs[KMNC05]	calc.[SPZ ⁺ 03]	Obs[KMNC05]	This Work	SP2000
0 4 2	6 0 6	6 1 5	13351.5063	13351.6631	1.86(−28)	1.82(−29)	3.06(−28)
0 4 2	2 2 1	3 3 0	13361.8032	13362.0395	8.43(−28)	1.04(−28)	1.32(−27)
0 4 2	2 2 0	3 3 1	13362.9934	13363.2152	6.45(−28)	3.56(−29)	4.50(−28)
0 4 2	5 0 5	5 1 4	13376.2655	13376.4261	5.61(−28)	7.34(−29)	1.62(−27)

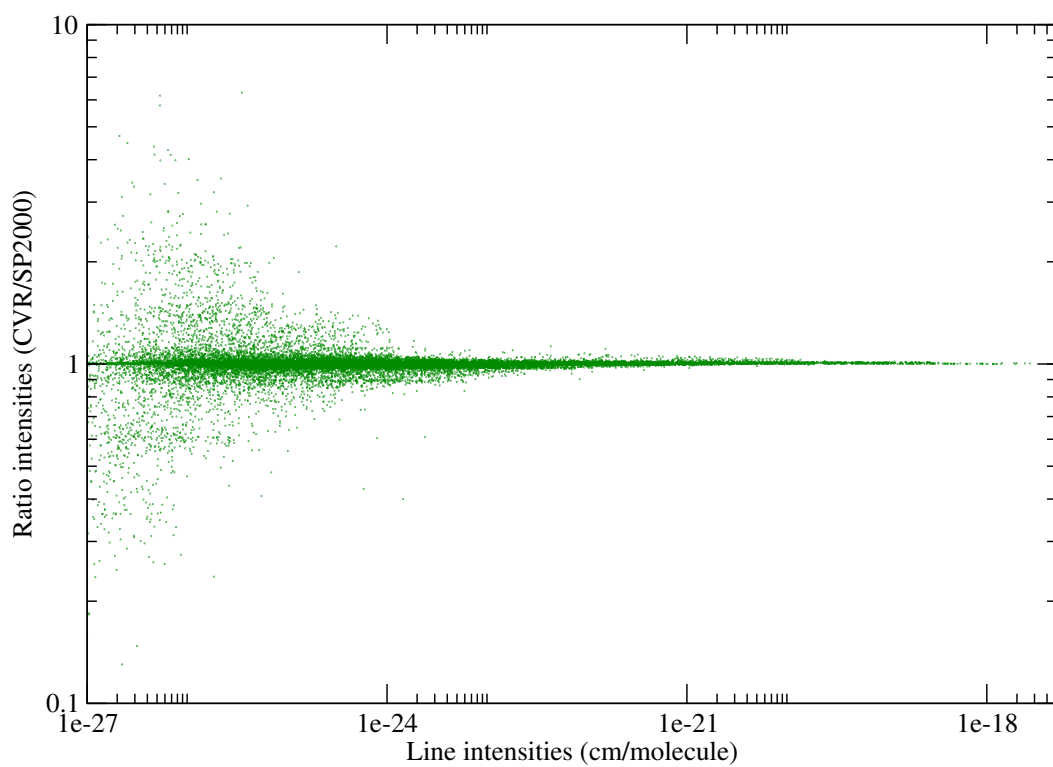


Figure 9.2: Ratio of dipole line intensities predicted by the CVR dipole surface and that of Schwenke and Partridge [SP00] for H_2^{16}O lines with $J \leq 9$ reported in the 2004 version of the HITRAN database [Rot05].

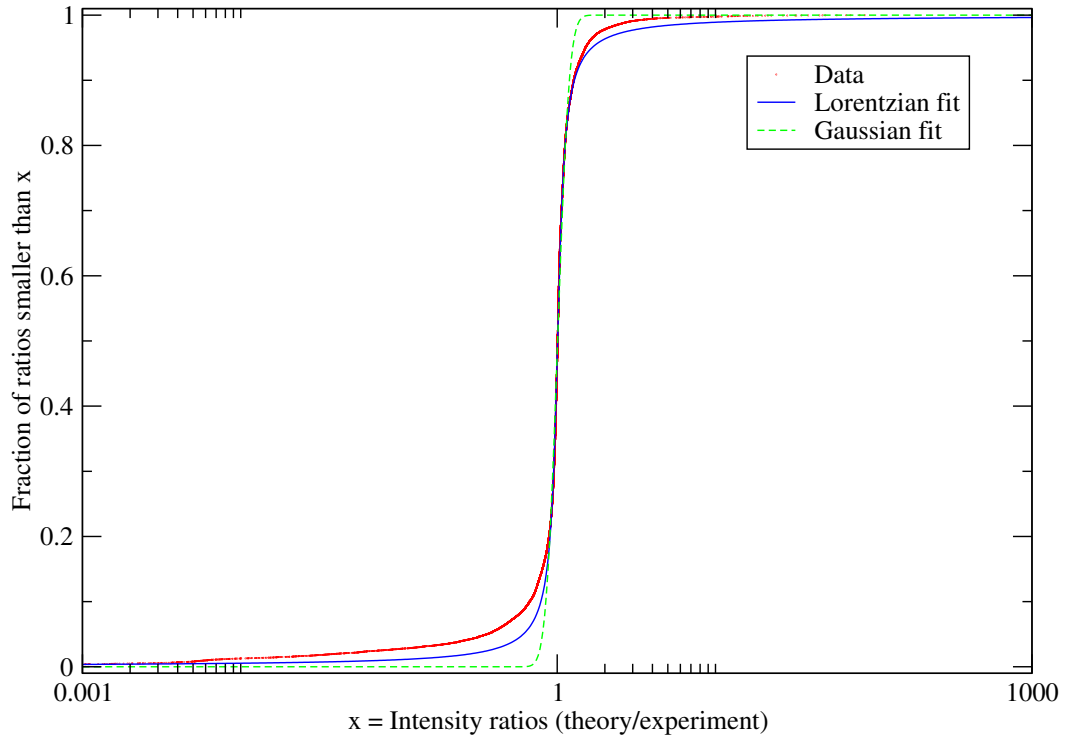


Figure 9.3: Cumulative distribution function of the ratios between the CVR dipole line intensities and those reported in the 2004 version of the HITRAN database [Rot05].

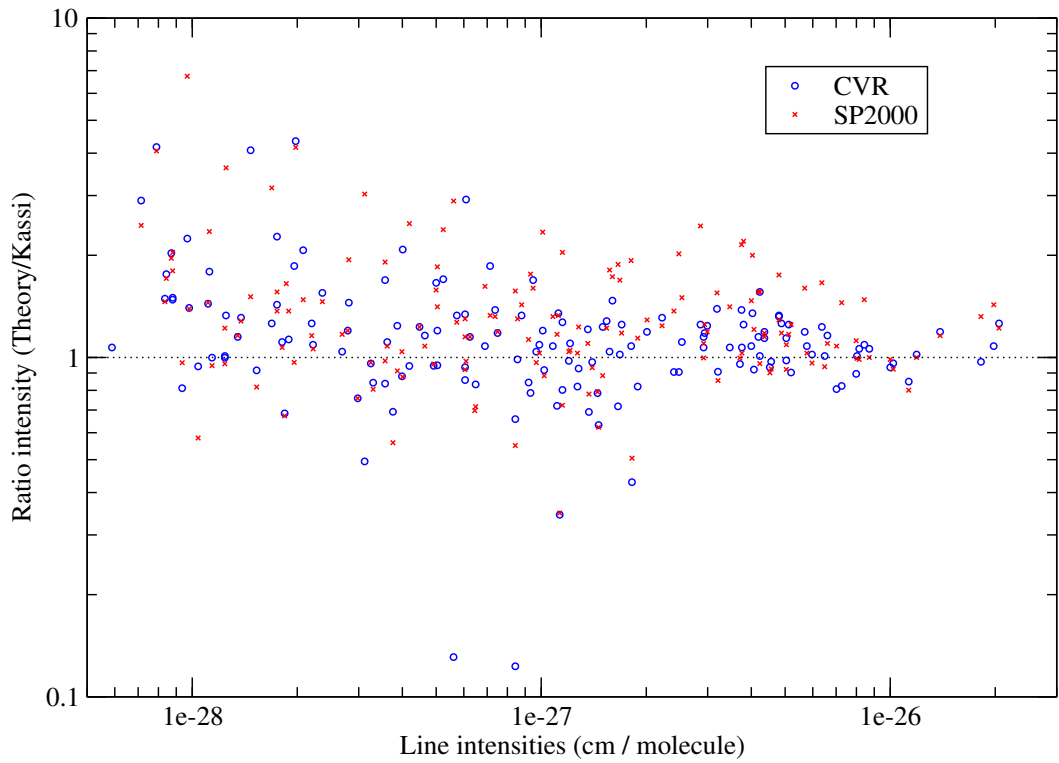


Figure 9.4: Comparison of intensity predictions of our DMS surface with that of Schwenke and Partridge [SP00] for the spectrum of Kassi *et al.* [KMNC05].

9.6.1 Introduction

Monitoring water vapour columns is a major activity in atmospheric physics, astrophysics and many other areas [Ber02]. Indeed, entire atmospheric and space satellite missions have been launched with this as their major goal [KSA⁺96, Mel00, PPC⁺05]. The reliability of the underlying spectroscopic data upon which this activity is based is therefore crucial to the success of these missions.

The rotational spectrum of H₂¹⁶O is experimentally well studied for transition energies but much less so for absolute intensities (eg. [HD67, RGSD91, BP96, Tot97, Tot00, Che00]). It is possible to classify lines of the water rotational spectrum into allowed and forbidden lines (see below for a precise definition of these terms); in atmospheric, and other, applications the allowed lines are generally saturated and are therefore not useful for monitoring purposes. The weaker forbidden lines, which generally lie at shorter wavelengths than the allowed ones, can therefore provide a useful tool with which to study water vapour.

Rotational spectra can be modelled usually very accurately using effective Hamiltonians based on perturbation theory [Cou97, Cou99, SD00]. In this work we use instead rotation-vibration wave functions defined from the variational principle rather than perturbation theory [Ten06]. These wave functions are calculated with the minimum number of approximations [PCS⁺03] and therefore should not bias one set of transitions over another. The original aim in undertaking this study was to check that the available perturbation theory based calculations, and indeed laboratory measurements, were of equal validity for the forbidden lines. In practise we found that data on pure rotational lines of water was in a less satisfactory state than we had anticipated. For this reason we decided to provide a complete listing of the pure rotational lines of water with intensities greater than 10⁻²⁸ cm/molecule at 296 K.

Neglecting weak nuclear spin coupling effects [MT04], the rotation-vibration energy levels of water have the following rigorous quantum numbers: rotational angular momentum, J , parity, p , and a further quantum number specifying whether the nuclear-spin state of the hydrogen nuclei is ortho or para. Electric-dipole transitions can in principle occur between any states within either of the ortho or para networks for which $\Delta J = \pm 1$ and $\Delta p = 0$ or $\Delta J = \pm 0$ and $\Delta p = 1$. Naturally not all these transitions are equally strong and it is usual to label the states in terms of approximate quantum numbers, from which it is easy to infer an approximate notion of the transition strength. For pure rotational states the approximate quantum numbers are the projection of the angular momentum on the A-axis, K_a , and on the C-axis, K_c . In terms of these the rigorous selection rules for pure rotational transitions correspond to transitions for which ΔK_a and ΔK_c are both odd. Analysis based on perturbation theory suggests that the strongest rotational transitions are those for which $\Delta K_a = \pm 1$ and $\Delta K_c = \pm 1$. Following the usual practise in atomic physics, see, for example, Chap. 5 of ref. [Ten05], we describe these transitions as allowed and the generally weaker transitions, for which ΔK_a and/or ΔK_c change by more than 1, as forbidden.

9.6.2 General overview

Details on how the calculations were done have already been given in section 9.2 and a general discussion of the sensitivity of the transition intensity with respect to the PES used was given in

Section 9.3 for general ro-vibrational transitions. However, a more specific analysis for the case at hand was performed and is presented hereafter.

In the case of room temperature transitions within the (000) band only rotational levels with low energies (up to about 5600 cm^{-1}) are involved which, in turn, are essentially determined by the corresponding low-energy portion of the potential energy surface used. Because of this, we expect the effect of the PES to be even smaller than for general ro-vibrational transitions, as all modern potential energy surfaces describe accurately the low-energy region. As a check we calculated a second set of nuclear-motion wave functions using a different PES, the recent CVRQD fully ab initio PES of Barletta *et al* [PCS⁺03, BSZ⁺06]. The result of the analysis is that, in consequence of the change of the nuclear-motion wave functions, line intensities generally change by less than 0.5 %.

The quality of the energy-surface can be partially evaluated by comparing computed transition wavenumbers with experimental ones. In most situations the measured wavenumbers are orders of magnitude more accurate than our computed ones. The reported wavenumbers from JPL and HITRAN always agree to better than 0.01 cm^{-1} and typically to about 0.0002 cm^{-1} . Our computed wavenumbers differ from experiment at worst by 0.10 cm^{-1} and typically to about 0.05 cm^{-1} . Such errors are 1 part in several thousand which is much higher accuracy than is aspired to for the line intensities. This analysis suggests that the major source of error in our calculations will be the DMS. The dependence of our results on the DMS will be discussed further below.

At 296 K we find 555 allowed and 846 forbidden rotational transitions within the ground, (000), vibrational band state that are stronger than $10^{-28}\text{ cm/molecule}$. There are then many other weaker forbidden lines. Fig. 9.5 gives a graphical representation of the distribution of the transitions by intensity and transition wavenumber. At 296 K the most intense lines lie around 250 cm^{-1} with intensities then falling exponentially with the transition wavenumber (this is due to a Boltzmann factor $e^{-E_{lower}/k_B T}$ in the intensity formula, as reported as equation 7.6 in Chapter 2). At higher temperatures there is significantly increased absorption due to rotational transitions at higher wavenumbers [SMT95].

Fig. 9.5 distinguishes between allowed and forbidden transitions. In general the allowed lines are the strongest. However below intensities of about $10^{-20}\text{ cm/molecule}$ there are many important forbidden lines.

9.6.3 Analysis

In order to understand our results and, in particular, to assess their reliability we made comprehensive comparisons with the available data on the intensities of pure rotational lines. We identified six key data sources which we compared against:

1. Lines from the HITRAN 2004 database [Rot05, HIT]
2. Lines from the JPL catalogue [PPC⁺98, Tot92, Pea, LCC01, FPC⁺03, JPL]
3. Experimental lines from Rinsland *et al* [RGSD91]
4. Experimental lines from Brown and Plymate [BP96]
5. Experimental lines from Toth [Tot00, Tot]

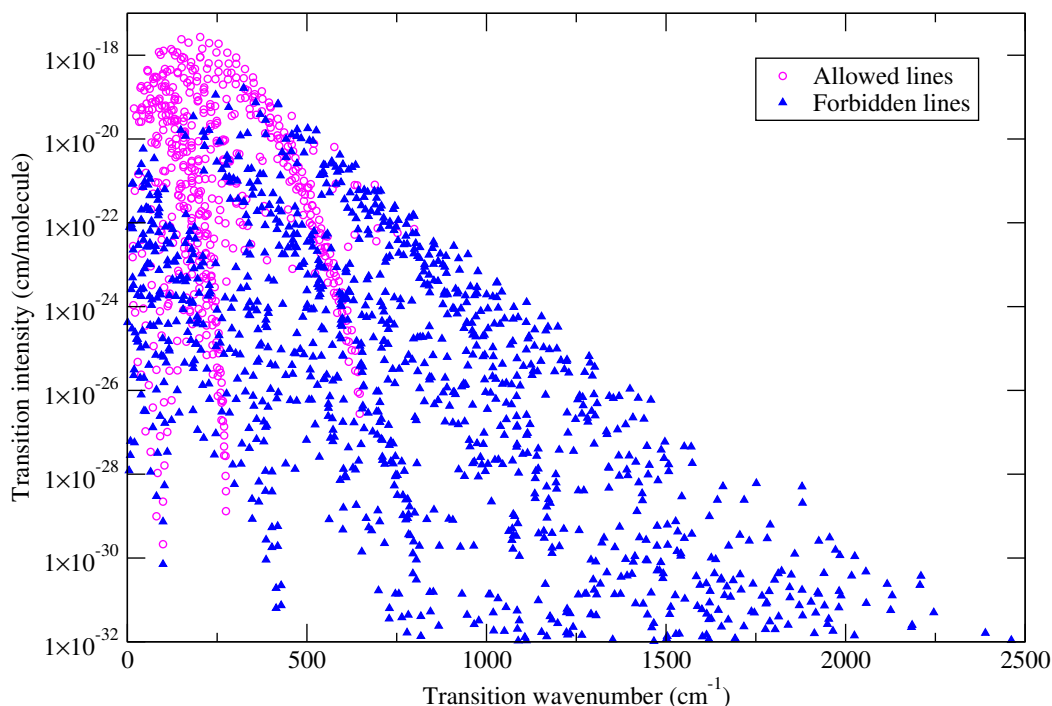


Figure 9.5: Plot of calculated transition intensity at 296 K against transition wavenumber for transitions within the (000) vibrational band.

6. Theoretical lines calculated from the BT2 [BTHT05] line list

We also compare our results with effective Hamiltonian calculations due to Coudert [Cou99].

Excluding the comprehensive BT2, there are for $J \leq 15$ a total of 1919 lines present in at least one of the data compilations above (555 allowed and 1364 forbidden), all of which could be matched with calculated lines. Table 9.3 presents a comparison of the published data with our calculations. For this purpose we have arbitrarily divided the transitions according to intensity (I in cm/molecule) into strong ($I > 10^{-20}$), medium ($10^{-24} < I \leq 10^{-20}$), weak ($10^{-28} < I \leq 10^{-24}$) and very weak ($I < 10^{-28}$). The very weak transitions are largely outside the scope of this study.

Our calculations give precisely 50 lines with intensity greater than 10^{-28} cm/molecule which do not appear in either the HITRAN or JPL databases. These lines are all forbidden and lie in the 996 – 1507 cm^{-1} region, usually not associated with pure rotational transitions of water. At 296 K the strongest omitted transition is $14_{8,7} - 13_{1,12}$ calculated to lie at 1422.61 cm^{-1} with an intensity of 6.6×10^{-28} cm/molecule.

To perform the analysis we used the same considerations and notation explained in section 9.1.

Comparisons with published data

Since the comparison with previous data highlighted a number of issues, the comparison below is given in an order designed to best illustrate these.

The BT2 water line list [BTHT05] was originally created using the DMS of Schwenke and Partridge [SP00] and the same FIS3 PES [SPZ⁺03] used in this work. As can be seen from Table

Table 9.3: Comparison of line intensities, I in cm/molecule, within the (000) vibrational band by intensity window. $\langle \varrho \rangle_g$ is the geometric mean of the ratios, σ the standard deviation of the natural logarithm of the ratios and n_p the number of lines falling in a specific intensity window. See text for precise definitions.

source	$I > 10^{-20}$						$10^{-24} < I \leq 10^{-20}$						$10^{-28} < I \leq 10^{-24}$						$I < 10^{-28}$					
	n_p	$\langle \varrho \rangle_g$	σ	n_p	$\langle \varrho \rangle_g$	σ	allowed	forbidden	n_p	$\langle \varrho \rangle_g$	σ	n_p	$\langle \varrho \rangle_g$	σ	allowed	forbidden	n_p	$\langle \varrho \rangle_g$	σ	allowed	forbidden	n_p	$\langle \varrho \rangle_g$	σ
BT2 [BTH05]	187	1.003	0.000	24	1.003	0.000	234	1.003	0.000	370	1.004	0.001	128	1.003	0.000	452	1.007	0.003	2	1.004	0.000	517	1.007	0.293
HITRAN [Rot05]	187	1.021	0.010	24	1.016	0.007	234	1.037	0.017	370	1.007	0.019	123	1.035	0.017	347	0.990	0.313	0	—	—	4	0.004	0.840
JPL [JPL]	187	1.007	0.009	24	0.999	0.010	234	0.997	0.021	363	0.999	0.035	128	0.974	0.038	318	1.008	0.102	6	0.939	0.011	102	0.975	0.798
Brown and Plymate [BP96]	62	0.978	0.023	2	0.954	0.031	0	—	—	0	—	—	0	—	—	0	—	—	0	—	—	0	—	—
Toth [Tot00, Tot]	0	—	—	0	—	—	9	1.034	0.021	138	1.021	0.036	6	1.012	0.075	98	0.932	0.328	0	—	—	0	—	—
Rinsland <i>et al</i> [RGSD91]	0	—	—	0	—	—	0	—	—	32	1.027	0.020	0	—	—	3	1.007	0.034	0	—	—	0	—	—

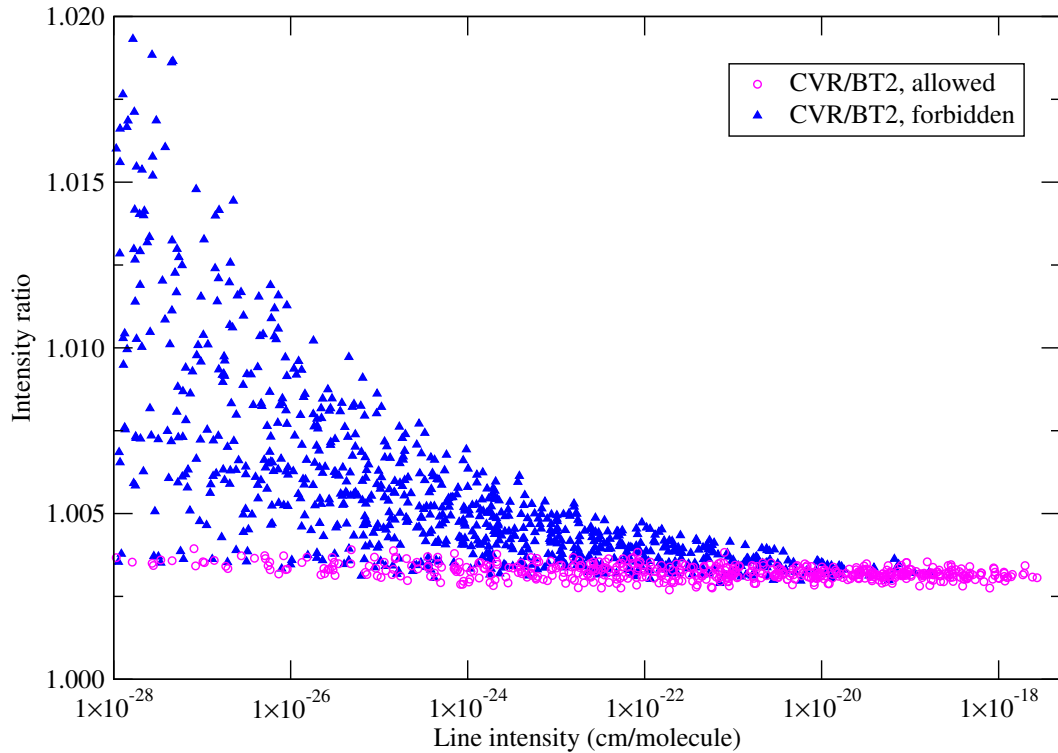


Figure 9.6: Comparison of differences in the line intensities computed in this work and as part of the BT2 line list [BTHT05].

9.3 and from Fig. 9.6, our line intensities agree closely with the BT2 ones. Our allowed lines are systematically 0.3% stronger than BT2 ones, independent of the absolute intensity of the line. On the other hand for forbidden lines our lines become increasingly stronger than the BT2 ones as the absolute intensity of the line decreases. The difference grows to about 2% for intensities of 10^{-28} cm/molecule (see Fig. 9.6). These differences are probably not significant when compared with other differences discussed below and are a consequence of the different underlying dipole surfaces used in the calculations. A more detailed comparison between the CVR and Schwenke and Partridge surfaces has been given elsewhere [LTT⁺08].

Next we consider the 2004 version of the HITRAN database [Rot05], which contains a mixture of experimentally measured and computed lines. Our lines are, globally, more intense than HITRAN's by about 2-3%. If we exclude this systematic difference from the analysis then our lines and HITRAN's show differences of about 1 – 2% for medium and strong lines ($I > 10^{-24}$ cm/molecule). The weak forbidden lines show a much greater scatter, about 30% with respect to ours (see Table 9.3 and Fig. 9.7). This large deviation for the weak lines is dominated by a small set of about 40 lines which deviate very significantly from the computed values. These lines all lie outside the range of Fig. 9.7. All these lines come from measurements by Toth [Tot] (Rothman LS, private communication). Table 9.4 lists all the outlying HITRAN lines whose ratio to ours is less than 0.80 or more than 1.20, i.e., all the lines not present in Fig. 9.7. A table of the outlying HITRAN lines whose ratio to ours is less than 0.80 or more than 1.20, i.e., all the lines not present in Figure 9.7, are reported in Table 9.4.

We note that in the cases where the intensity of these lines are also given by JPL, our results

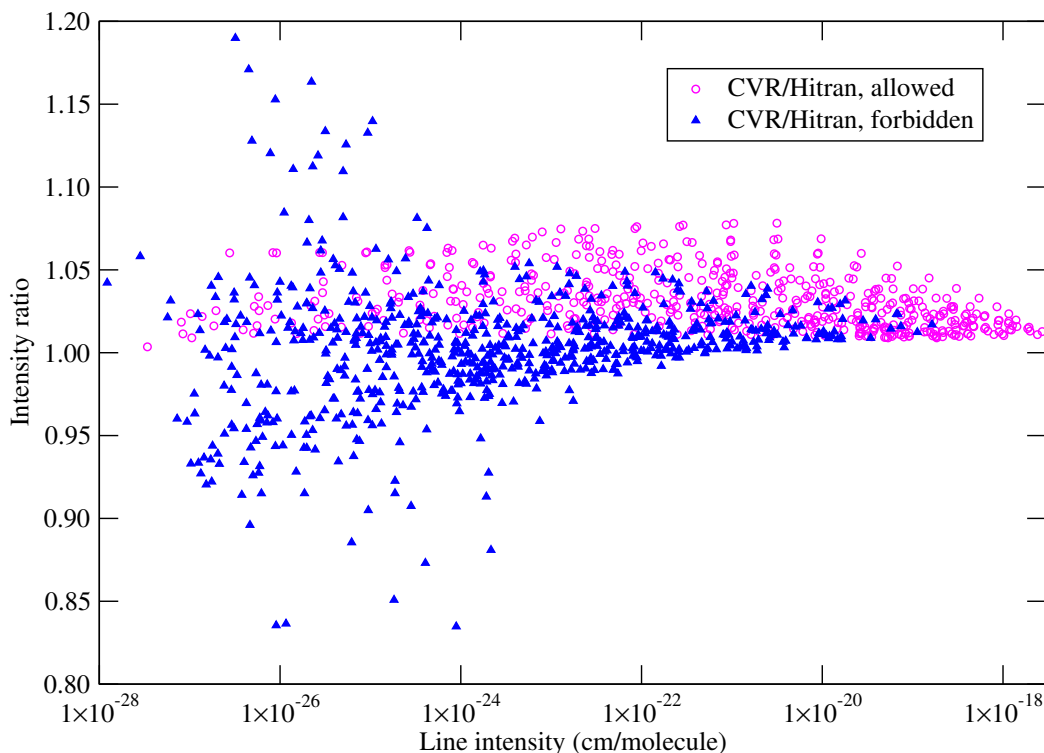


Figure 9.7: Comparison of differences in the line intensities computed in this work and given in the HITRAN database [Rot05]. The 37 outliers not displayed in the plot are listed in Table 9.4.

are all well within 10% of the JPL values. We regard the intensities given in HITRAN for these lines listed in Table 9.4 as likely to be wrong. In fact the next, 2008, version of HITRAN will use our own calculated values for these outliers [Rota].

The JPL database was obtained from its Internet website [JPL] on 26 February 2007. We note that the database is periodically updated and, in fact, the version available on-line at the time of writing is different from the one examined in the following analysis. Lines in the database are reported for a temperature of 300 K instead of 296 K and are expressed in different units. To convert them into the same format used for our computation the procedure outlined in HITRAN documentation [Rotb] was followed. In particular, we used formula (11) of the above mentioned reference to compute the temperature correction from 300 K to 296 K. The uncertainty of this formula depends on the molecule and, according to the quoted reference, should not exceed 2%. As an independent check we used the BT2 line list to calculate another set of lines at 300 K and then compared the intensity ratios $I_{\text{BT2}}(300\text{K})/I_{\text{BT2}}(296\text{K})$ with those predicted by the aforementioned formula. This comparison was done for the pure rotational lines in the (000) band up to 3500 cm^{-1} . The conclusion was that the formula reproduces the computed $I_{\text{BT2}}(300\text{K})/I_{\text{BT2}}(296\text{K})$ ratios extremely accurately (within a factor of $\pm 0.04\%$). We can thus very safely rely on the formula as any eventual error introduced by it would be about one hundred times smaller than the intrinsic uncertainty of the original data.

Fig. 9.8 compares our intensities with those given in the JPL catalogue. Besides the larger than expected differences, there also appear to be systematic structures in the comparison. Fig. 9.9 gives an alternative comparison of the same data, this time as a function of wavenumber.

Table 9.4: Outliers in the HITRAN database [Rot05]. The reported wavenumbers (in cm^{-1}) are computed ones. All intensities are in $\text{cm}/\text{molecule}$ and refer to 296 K and to 100% of H_2^{16}O (i.e. HITRAN intensities have been divided by the isotopic abundance of H_2^{16}O , 0.997317. JPL data [JPL], where available and converted to the same form as used by HITRAN, are reported for comparison. Ratios are given as $\text{Intensity}(\text{our})/\text{Intensity}(\text{other})$. Lines whose calculated intensities are weaker/stronger than JPL ones are listed in the upper/lower portion of the table.

Upper			Lower			Wavenumber		Intensities			Ratios	
J	K_a	K_c	J	K_a	K_c		CVR	HITRAN	JPL		HITRAN	JPL
10	9	2	9	0	9	1551.085	2.97E-30	2.07E-27	–		0.001	–
15	15	0	14	12	3	1182.460	3.91E-30	2.18E-27	–		0.002	–
10	10	1	9	3	6	1418.909	1.30E-29	2.07E-27	–		0.006	–
15	14	1	14	11	4	1167.519	5.01E-29	4.69E-27	–		0.011	–
8	8	0	7	1	7	1202.552	3.80E-28	1.04E-26	–		0.036	–
8	8	1	8	1	8	1044.879	1.73E-28	2.13E-27	–		0.081	–
10	8	3	10	1	10	1139.750	2.71E-28	3.32E-27	–		0.082	–
10	10	0	9	5	5	1226.874	9.70E-28	2.22E-27	–		0.437	–
8	7	1	8	0	8	846.631	2.03E-26	3.94E-26	1.87E-26		0.514	1.084
9	8	1	9	1	8	930.715	1.23E-26	2.35E-26	1.16E-26		0.523	1.060
9	9	1	9	4	6	884.553	1.79E-27	2.96E-27	1.83E-27		0.603	0.977
9	9	0	9	4	5	865.188	5.79E-27	9.47E-27	5.96E-27		0.612	0.972
9	7	3	8	0	8	1066.522	1.22E-25	1.59E-25	–		0.769	–
9	9	0	8	4	5	1102.727	3.79E-26	4.89E-26	–		0.773	–
14	7	8	14	2	13	936.485	1.45E-26	1.18E-26	1.37E-26		1.234	1.063
15	7	8	14	2	13	1301.254	3.63E-26	2.94E-26	–		1.236	–
8	8	1	7	3	4	946.645	4.00E-25	3.23E-25	4.15E-25		1.238	0.964
14	9	5	13	4	10	1259.199	7.49E-27	6.03E-27	–		1.243	–
14	8	7	14	3	12	913.426	8.06E-27	6.35E-27	8.30E-27		1.268	0.970
8	8	0	7	3	5	972.320	1.16E-25	8.74E-26	1.19E-25		1.327	0.970
15	8	7	14	3	12	1273.539	2.73E-26	2.05E-26	–		1.329	–
13	7	7	12	0	12	1369.283	7.23E-27	5.22E-27	–		1.386	–
14	6	9	14	1	14	1011.417	8.70E-27	6.19E-27	–		1.406	–
11	10	1	10	5	6	1254.071	6.05E-27	4.29E-27	–		1.411	–
13	8	6	12	1	11	1353.205	6.52E-27	4.53E-27	–		1.440	–
12	8	5	11	1	10	1288.670	4.55E-26	3.15E-26	–		1.445	–
11	7	4	11	0	11	994.832	1.81E-26	1.24E-26	–		1.458	–
15	9	6	14	4	11	1299.284	8.00E-27	5.38E-27	–		1.487	–
15	5	10	15	0	15	1002.470	3.57E-27	2.33E-27	–		1.531	–
7	7	0	7	0	7	808.567	2.83E-26	1.84E-26	2.65E-26		1.538	1.067
9	9	1	8	4	4	1093.653	1.29E-26	8.17E-27	–		1.579	–
12	9	4	11	2	9	1341.999	7.25E-27	3.69E-27	–		1.965	–
15	6	9	14	1	14	1399.500	1.09E-26	4.94E-27	–		2.205	–
14	7	8	13	0	13	1457.737	5.91E-27	2.43E-27	–		2.436	–
8	8	1	7	1	6	1084.803	2.21E-26	3.13E-27	–		7.052	–

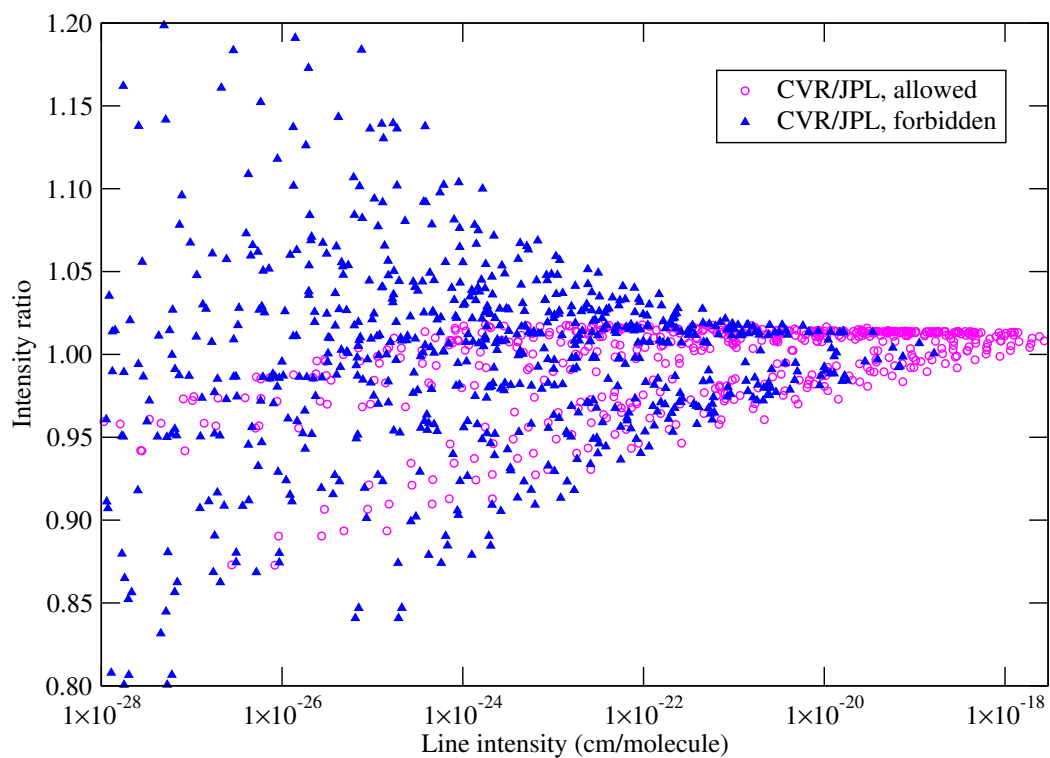


Figure 9.8: Comparison of differences in the line intensities computed in this work and given in the JPL database [JPL].

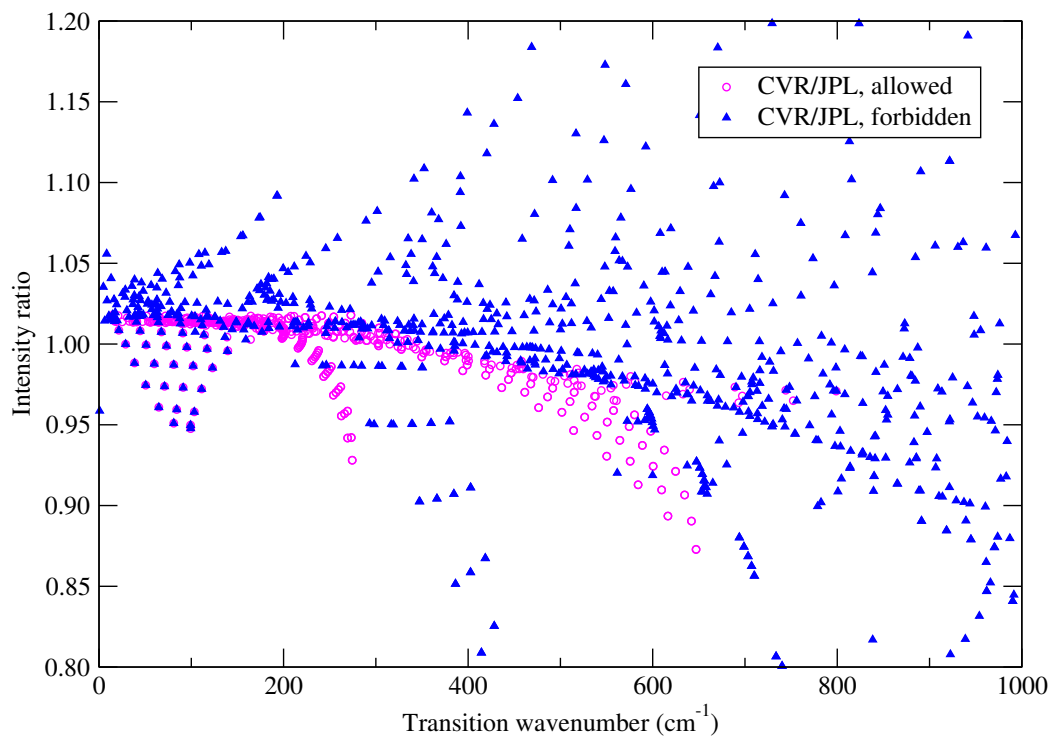


Figure 9.9: Comparison of line intensities with lines from the JPL database [JPL] as a function of the transition wavenumber.

This figure shows a series of remarkable systematic structures which cannot be explained by any likely error in our calculations. None of the other comparisons gave similar structures when plotted as a function of wavenumber. The discrepancies can also be studied in function of one of the rotational quantum numbers, for example J_{upper} ; analysis shows that, for the lines plotted in Figs. 9.8 and 9.9, the scatter in the ratios increases systematically with J_{upper} , with nearly all ratios lying within the range given by $1 \pm (\frac{J_{upper}}{30})^2$.

For strong lines JPL's are about 1% weaker than ours. As the lines get weaker, JPL's become comparatively stronger so that for weak lines the discrepancy can be up to about 20%. This seems to be due to a systematic error in the catalogue. In the case of forbidden lines weaker than about 10^{-28} cm/molecule there are several lines where the JPL values disagree strongly with the computed ones. Table 9.5 lists the 63 outliers whose intensity ratios do not lie in the range 1 ± 0.2 . In this case none of outlying allowed lines are reported in HITRAN (or indeed anywhere else that we found) and all except have an intensity below 10^{-28} cm/molecule in our calculations. All the lines involved are substantially stronger in JPL. Given that the linestrength of such allowed transitions is straightforward to compute accurately and the weakness arises only from Boltzmann effects at 296 K, we strongly suspect an extrapolation problem with the JPL data for the high K_a transitions. The outlying forbidden lines, conversely, are all systematically weaker in JPL than our calculations. Where there is data available for these line HITRAN, our results are within 10% of those given by HITRAN. It would appear that JPL has significantly underestimated the intensity of these transitions, all of which are weak or very weak.

Outliers whose JPL intensities are stronger than our calculated ones are all very weak lines not present in HITRAN (or indeed anywhere else that we found); in particular, JPL lines stronger by more than a factor of 2 with respect to calculated ones have absolute intensities of about 10^{-31} cm/molecule or less. Some of the outliers whose JPL intensities are weaker than calculated ones are present in HITRAN and for these our results are all within 10% of those given by HITRAN. Again, all lines that differ from the calculated ones by more of a factor of two are extremely weak lines with intensities less than 10^{-30} cm/molecule.

The systematic differences between our calculations and the JPL catalogue data are not confined to the outliers. Indeed they would appear to be shown by nearly all the higher J H_2^{16}O pure rotation data reported by JPL.

Brown and Plymate [BP96] published a list of 67 strong lines within the ground vibrational levels (65 allowed and 2 forbidden; see Fig. 9.10). 55 of these lines are compared by Coudert with his semi-empirical calculations. Brown and Plymate measured relative, not absolute, intensities which were normalised to the HITRAN 1992 values. Their reported lines are systematically 2% stronger than our calculated ones, a reflection of the HITRAN values used for the normalisation, with a scatter of 2%. The experimental lines become comparatively stronger as their absolute intensity decreases, with differences of up to about 7% for the weakest lines reported ($I \sim 3 \times 10^{-20}$ cm/molecule). If we disregard the constant multiplicative factor due to the normalisation, our calculated values almost always agree with the measurements within the reported experimental uncertainty. Brown and Plymate's lines are systematically stronger than Coudert's by 4% with a scatter of 2%. Our results are therefore essentially in agreement with the data presented by Coudert.

Table 9.5: Outliers in the JPL catalogue [JPL]. The reported wavenumbers (in cm^{-1}) are computed ones. All intensities are in $\text{cm}/\text{molecule}$ and refer to 296 K. HITRAN data [Rot05] are reported for comparison. Ratios are given as $\text{Intensity}(\text{our})/\text{Intensity}(\text{other})$. Lines whose calculated intensities are weaker/stronger than JPL ones are listed in the upper/lower portion of the table.

Upper			Lower			Wavenumber	Intensities			Ratios	
J	K_a	K_c	J	K_a	K_c		CVR	JPL	HITRAN	JPL	HITRAN
12	9	3	13	2	12	990.342	5.50E-34	3.10E-32	—	0.018	—
14	11	4	15	4	11	927.484	2.46E-34	1.04E-32	—	0.024	—
15	15	0	15	12	3	817.132	4.07E-32	1.34E-31	—	0.303	—
15	15	1	15	12	4	817.132	1.36E-32	4.48E-32	—	0.303	—
14	14	0	14	11	3	794.896	4.25E-31	8.37E-31	—	0.508	—
14	14	1	14	11	4	794.896	1.27E-30	2.51E-30	—	0.508	—
15	14	2	15	11	5	804.711	3.02E-31	5.85E-31	—	0.517	—
15	14	1	15	11	4	804.711	9.07E-31	1.76E-30	—	0.517	—
15	13	3	15	10	6	782.916	3.65E-30	5.33E-30	—	0.684	—
15	13	2	15	10	5	782.914	1.09E-29	1.60E-29	—	0.684	—
14	13	2	14	10	5	775.327	2.47E-29	3.60E-29	—	0.685	—
14	13	1	14	10	4	775.326	8.22E-30	1.20E-29	—	0.685	—
13	13	1	13	10	4	767.217	1.04E-29	1.51E-29	—	0.686	—
13	13	0	13	10	3	767.216	3.12E-29	4.54E-29	—	0.686	—
14	11	3	15	6	10	728.915	3.56E-32	5.04E-32	—	0.705	—
13	11	3	14	4	10	950.270	6.79E-33	9.54E-33	—	0.712	—
13	11	2	14	6	9	746.302	1.40E-31	1.93E-31	—	0.725	—
12	11	2	13	4	9	978.535	3.20E-32	4.35E-32	—	0.736	—
13	11	3	14	6	8	729.674	6.30E-32	8.35E-32	—	0.754	—
14	11	4	15	6	9	699.188	1.67E-31	2.16E-31	—	0.775	—
12	11	1	13	6	8	764.269	3.81E-32	4.91E-32	—	0.777	—
14	14	1	15	11	4	432.089	6.38E-33	8.17E-33	—	0.781	—
14	14	0	15	11	5	432.089	2.13E-33	2.72E-33	—	0.781	—
12	11	2	13	6	7	755.941	1.40E-31	1.77E-31	—	0.789	—
15	12	4	15	9	7	751.667	3.15E-29	4.00E-29	—	0.789	—
15	12	3	15	9	6	751.630	9.46E-29	1.20E-28	—	0.789	—
14	12	2	14	9	5	746.205	8.86E-29	1.12E-28	—	0.795	—
14	12	3	14	9	6	746.216	2.66E-28	3.34E-28	—	0.795	—
14	5	9	14	0	14	910.028	9.08E-27	7.56E-27	9.02E-27	1.201	1.006
13	4	9	14	1	14	460.415	2.45E-26	2.03E-26	2.60E-26	1.209	0.942
13	7	6	14	2	13	600.089	1.75E-27	1.45E-27	1.90E-27	1.212	0.922
11	6	5	12	1	12	586.262	1.98E-26	1.60E-26	2.10E-26	1.237	0.943
13	9	5	14	2	12	796.910	2.45E-30	1.98E-30	—	1.239	—
9	7	3	10	0	10	696.077	8.67E-28	6.96E-28	—	1.245	—
11	8	4	12	1	11	747.666	9.65E-29	7.69E-29	—	1.255	—
13	5	9	14	0	14	513.114	5.96E-27	4.75E-27	6.40E-27	1.256	0.932
14	7	7	15	2	14	635.313	1.28E-28	9.89E-29	—	1.291	—
14	4	10	15	1	15	522.683	1.52E-27	1.16E-27	1.65E-27	1.315	0.920
12	6	6	13	1	13	630.914	1.71E-27	1.28E-27	1.83E-27	1.338	0.936
10	7	4	11	0	11	727.273	1.48E-27	1.11E-27	1.48E-27	1.340	1.002
12	8	5	13	1	12	771.235	1.18E-28	8.80E-29	—	1.347	—
13	12	2	14	7	7	821.430	1.79E-33	1.31E-33	—	1.366	—
14	5	10	15	0	15	560.058	3.78E-27	2.76E-27	4.13E-27	1.368	0.914
11	10	2	12	3	9	866.912	2.39E-32	1.60E-32	—	1.494	—
11	7	5	12	0	12	764.020	1.99E-28	1.33E-28	—	1.499	—
13	8	6	14	1	13	799.968	1.20E-29	7.96E-30	—	1.505	—
13	6	7	14	1	14	683.008	1.03E-27	6.80E-28	1.10E-27	1.516	0.933
11	9	2	12	2	11	965.684	2.61E-32	1.70E-32	—	1.533	—
8	8	0	9	1	9	868.843	1.94E-30	1.23E-30	—	1.569	—
12	7	6	13	0	13	806.198	1.81E-28	1.01E-28	—	1.793	—
14	8	7	15	1	14	833.684	8.37E-30	4.61E-30	—	1.815	—
14	10	5	15	3	12	842.135	1.52E-31	8.37E-32	—	1.820	—
14	6	8	15	1	15	743.278	5.32E-29	2.85E-29	—	1.867	—
9	8	1	10	1	10	895.275	8.55E-30	4.52E-30	—	1.892	—
14	12	2	15	7	9	807.417	5.39E-34	2.30E-34	—	2.345	—
13	7	7	14	0	14	853.646	1.41E-29	5.76E-30	—	2.451	—
10	8	2	11	1	11	927.197	1.83E-30	6.62E-31	—	2.762	—
14	12	3	15	7	8	802.494	1.43E-33	4.27E-34	—	3.341	—
9	9	0	10	2	9	931.832	1.39E-31	3.24E-32	—	4.283	—
14	7	8	15	0	15	906.143	8.06E-30	1.76E-30	—	4.568	—
10	10	1	11	3	8	888.612	7.85E-33	1.15E-33	—	6.832	—
11	8	3	12	1	12	964.461	1.94E-30	2.39E-31	—	8.110	—
10	9	1	11	2	10	946.124	4.36E-32	2.31E-33	—	18.906	—

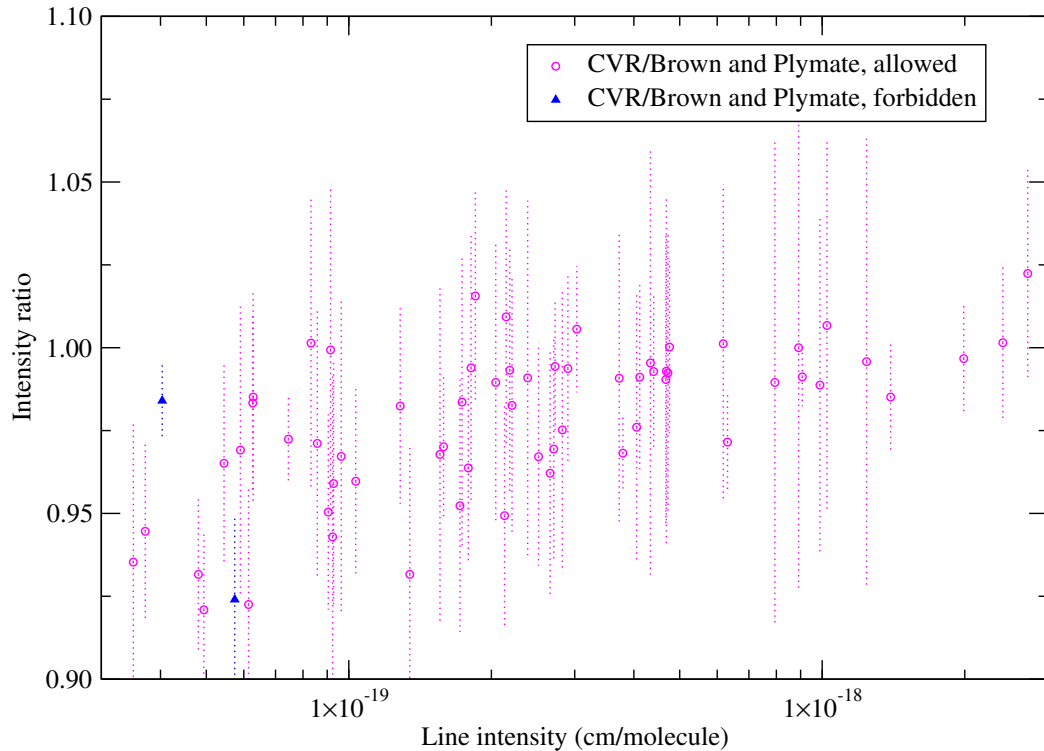


Figure 9.10: Comparison of differences in the line intensities computed in this work and measured by Brown and Plymate [BP96]. Lines frequencies lie between 55 and 328 cm^{-1} .

According to the JPL documentation their catalogue water intensity data are due to the semi-empirical calculations of Coudert [Cou99]. This reference actually reports lines that are only a sub-set of a larger list; the subset was chosen to include a selection of both strong and weak lines. Coudert's results are given with uncertainties which were derived from the overall standard deviation, corresponding to the σ_{RMS} of eq. (9.3), of 4.6% between computed and observed intensities. The allowed lines are about 2% stronger than our ones but agree in all case within the given error bars. Relatively few forbidden lines, all very weak, were report and these do not show any systematic differences. Indeed our overall agreement calculated in the same way as Coudert gives a value of σ_{RMS} equal to 3.8%, better than his assumed error. Our results can therefore be taken to be in agreement with the limited data presented by Coudert.

Toth measured the intensity of water transitions at wavenumbers above 500 cm^{-1} : some lines reported in [Tot00] and other lines available on-line from [Tot]. Fig. 9.11 compares our calculations with Toth's measurement. Our lines are, on average, about 3% stronger than Toth's. Outliers which differ by more than 20% are given in Table 9.6; for all of these lines our intensities are within 10% of those given in HITRAN. However for most lines our calculations agree within the stated experimental uncertainties. On the other hand, Coudert's [Cou99] calculated line intensities for a selection Toth's lines (22 lines, some of them with $J > 15$) are 2% stronger but with a scatter of 9%.

Table 9.6: Outliers in Toth’s database [Tot00, Tot]. The reported wavenumbers (in cm^{-1}) are computed ones. All intensities are in $\text{cm}/\text{molecule}$ and refer to 296 K. HITRAN 2004 data [Rot05] are reported for comparison. Ratios are given as $\text{Intensity}(\text{our})/\text{Intensity}(\text{other})$. Lines whose calculated intensities are weaker/stronger than JPL ones are listed in the upper/lower portion of the table.

Upper			Lower			Wavenumber	Intensities			Ratios	
J	K_a	K_c	J	K_a	K_c		CVR	Toth	HITRAN	Toth	HITRAN
12	10	3	11	5	6	1267.714	6.86E-27	8.31E-26	7.12E-27	0.083	0.964
12	12	1	11	9	2	1025.957	1.87E-26	4.68E-26	2.04E-26	0.399	0.915
12	10	3	12	7	6	653.942	8.18E-26	2.01E-25	8.08E-26	0.407	1.012
14	9	6	13	4	9	1151.542	4.99E-26	1.02E-25	4.61E-26	0.489	1.082
10	7	3	10	0	10	939.860	1.33E-26	2.57E-26	1.28E-26	0.518	1.040
12	9	4	11	4	7	1133.614	1.15E-25	2.19E-25	1.08E-25	0.526	1.063
11	7	5	10	0	10	1207.304	5.19E-26	7.26E-26	5.26E-26	0.714	0.986
9	8	2	8	3	5	959.600	4.06E-25	5.24E-25	4.65E-25	0.775	0.873
14	7	8	14	2	13	936.485	1.45E-26	1.87E-26	1.18E-26	0.777	1.234
15	5	11	15	2	14	638.337	1.50E-25	1.93E-25	1.52E-25	0.779	0.991
15	10	5	14	7	8	1018.937	6.46E-26	8.11E-26	6.23E-26	0.797	1.037
15	7	9	14	2	12	1073.334	1.48E-25	1.23E-25	1.46E-25	1.201	1.009
13	9	4	12	4	9	1222.801	4.98E-26	3.91E-26	4.49E-26	1.274	1.109
13	8	6	13	3	11	879.747	8.86E-27	6.74E-27	7.69E-27	1.315	1.153
10	8	3	9	1	8	1175.191	9.48E-26	6.66E-26	1.05E-25	1.424	0.905
11	9	2	10	4	7	1159.049	1.06E-25	6.78E-26	9.26E-26	1.557	1.140
15	6	10	14	1	13	1115.379	1.72E-25	1.06E-25	1.72E-25	1.618	1.000
10	9	2	9	4	5	1110.970	9.35E-26	5.28E-26	8.25E-26	1.770	1.133

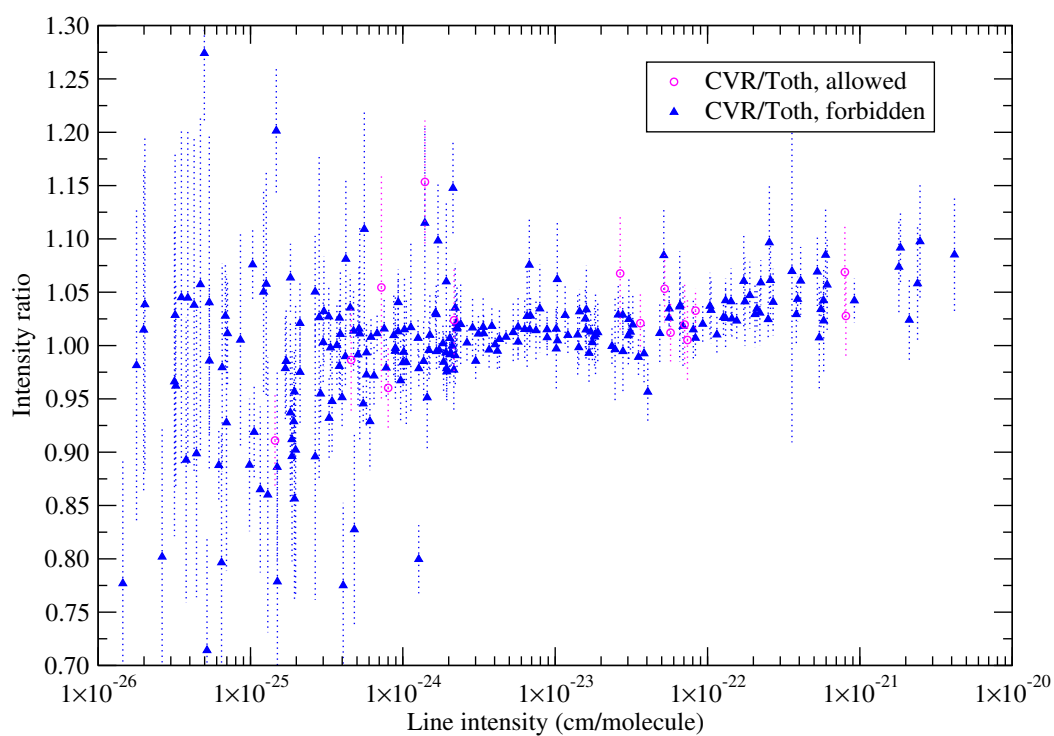


Figure 9.11: Comparison of differences in line intensities computed in this work and measured by Toth [Tot00, Tot]. The lines lie energetically between 590 and 1286 cm^{-1} , with most in the $600\text{--}800 \text{ cm}^{-1}$ region.

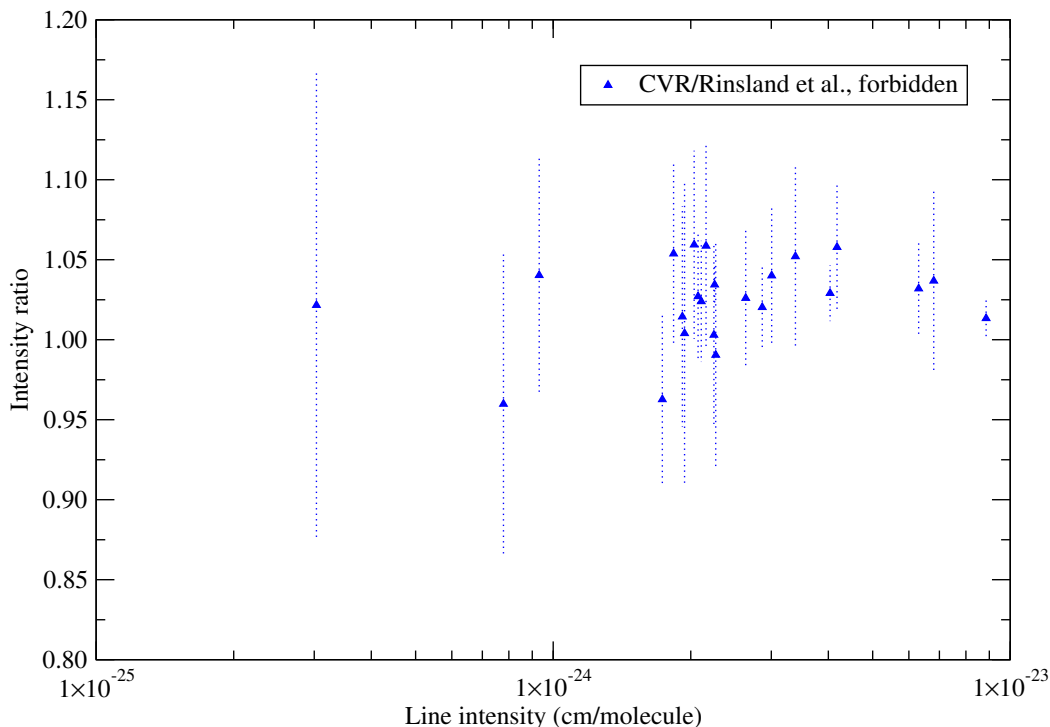


Figure 9.12: Comparison of differences in line intensities computed in this work and measured by Rinsland *et al* [RGSD91]. Line frequencies lie between 802 and 1042 cm^{-1} .

Rinsland *et al* [RGSD91] measured the intensity of water transitions at wavenumbers between 802 and 1043 cm^{-1} . Of these, 35 lines correspond to rotational transitions in the vibrational ground state with $J < 15$. Fig. 9.12 compares our calculations with the measurement. The trend is as the same as the one identified in the analysis of Toth’s data relative to medium-strength lines: our lines are about 3% stronger than the reported ones, with a scatter of about 2%. However the reported experimental uncertainties are in general larger (sometimes much larger) than the discrepancy with our calculation, so that we are fully consistent with the limited experimental data analysed.

9.6.4 Summary of the purely rotational lines comparison

We present a line list of pure rotational transitions for water, data which has been made available electronically. The aim of this list is not to present transition frequencies, as these can be measured to much higher accuracy than our calculations, but to present transition intensities. We believe these calculated intensities to be accurate over a large dynamic range. Our calculated intensities should be reliable within 5% of the true value in the worst case, and our line list therefore provides intensity data when reliable experimental values are not available.

We provide the line list as two separate files, one for allowed and one for forbidden lines. As an example of the format used we list the first record of the allowed-lines list:

J'	K'_a	K'_c	J''	K''_a	K''_c	$\bar{\nu}_{\text{th}}$	$\bar{\nu}_{\text{JPL}}$	I	A	$S(i \rightarrow f)$
7	5	2	6	6	1	14.782474	14.777500	1.511E-23	5.562E-06	3.315E-01

where J , K_a and K_c are the rotational quantum numbers for the upper and lower state respectively, $\bar{\nu}_{\text{th}}$ is the theoretical (computed) transition wavenumber in cm^{-1} , $\bar{\nu}_{\text{JPL}}$ is the tran-

sition wavenumber as reported by the JPL catalogue (when available), I is the line intensity in cm/molecule at 296 K, A is the Einstein coefficient for the transition in s^{-1} and finally $S(i \rightarrow f)$ is the ‘line strength’ in D^2 for all magnetic components of the line. As there are several definitions of ‘line strength’ we note that the reported $S(i \rightarrow f)$ is linked to the transition intensity I by equation 7.6.

Our line intensities have been compared with those available in the literature and found to be in good agreement with the semi-empirical results of Coudert [Cou99] and the forbidden-line measurements of Toth [Tot00]. Agreement with the latest version of the HITRAN database [Rot05] is also reasonable, although there are a small number of weaker lines for which we suggest there are significant errors in the intensities given by HITRAN. The situation regarding the JPL catalogue [JPL] is much less satisfactory; comparisons show a number of systematic differences even for lines which have been well characterised and cannot be a consequence of our calculations. We suggest that the water data in this catalogue should be systematically re-evaluated. This is particularly true because JPL is the major supplier of data for space missions several of which have observing pure rotational transitions of water as a major objective [KSA⁺96, MSA⁺00, HBB⁺05a, Har04b].

It is difficult to give error bars for calculated data such as those presented here as the errors are essentially all systematic. However it is possible to make some comments about the probable source and magnitude of the errors in our predicted transition intensities. As discussed above the major source of error for nearly all lines will be associated with imperfections in the CVR dipole moment surface used in this work. This surface overestimates the equilibrium dipole moment by 0.013 D or 0.7% [LTT⁺08]. In the rigid rotor approximation the intensity of allowed transitions depend on the square of this dipole so CVR should give transitions which are about 1.4% too strong. Comparisons given above with HITRAN, Toth and Coudert all suggest that our lines are indeed slightly too intense; it is possible that reducing their intensity by 1.4% would lead to more accurate predictions but we have not done this here because it is not clear this is the appropriate procedure in all cases and in any case 1.4% is less than the experimental error on any of the measured data we compare with.

Finally it should be noted that we have confined ourselves here to the study of pure rotational transitions involving $J \leq 15$ and within the vibrational ground state. These are the transitions of importance for studies at room temperature or below. Of course in hotter environments many more pure rotational transitions involving both higher J ’s and transitions within excited vibrational states become important [PZV⁺97, CBC⁺05]. Information on these transitions, and indeed other shorter wavelength vibration-rotation transitions, can be found in the BT2 line list [BTHT05].

Accurate modelling of long-range forces

10.1 Introduction

Apart from the case of the H_3^+ molecular ion [KJ06] potential surfaces of chemically bound systems with more than three atoms of sufficient accuracy for spectroscopic calculations cover only a limited region around equilibrium; for example in the case of water the recent CVRQD energy surface [BSZ⁺06] covers energies only up to about 25000 cm^{-1} . This state of affairs is due to the fact that, first, experimentally-observed transitions generally involve rotation-vibration states only up to about 25000 cm^{-1} , so that they are determined by a similar range in energy of the PES (see discussion in Section 5.2.5). Second, as discussed in Chapter 3, the farther one goes from equilibrium the more difficult it is to obtain accurate results.

There are, however, two recent developments that make it timely to reconsider the precise representation of these potentials at their dissociation limit. The first is the discovery that chemically bound polyatomic molecules support a series of long range bound states, so-called asymptotic vibrational states (AVS), in the region between their classical and quantal dissociation limits [MRT05, MRTM06]; analysis of these states suggests they should be ubiquitous and may only depend weakly on the form of the long-range potential [TBMS06]. The second is the development of a multiphoton technique capable of probing the vibration-rotation states of water just above and just below its dissociation limit with spectroscopic accuracy [MRB06]. A good representation of the potential energy surface in this region is essential for analysing these spectra and this was in fact our initial motivation for addressing the issues discussed in this work.

In view of the design of new water potential-energy surfaces covering the dissociation channel a detailed study of the relevance of intramolecular van der Waals interactions in the design of global potential energy surfaces was undertaken.

A dedicated study was necessary because, while long-range intermolecular interactions [CS00a, EÅK00] such as those found in weakly-bound van der Waals complexes [WvK00] have been well-studied, long-range *intramolecular* interactions in strongly bound systems (i.e., systems where breaking a bond takes more than about $10,000\text{ cm}^{-1}$) upon bond-breaking processes have received less attention. An exception is the model case of the hydrogen molecule which has been studied many times [OM06, MO05, MB05, MOF⁺98, Kog89, KUi87, Tha88, DL56, PB35,

KM69]. However, increasing efforts are being made to find global methods of representing potentials for chemically bound molecules [Var88]. Several methods either implicitly or explicitly assume that at long-range the interactions can be represented using potential forms developed for van der Waals systems [Var96, Var97, PPT97, PPKT00, BR03b, BR03a]. Indeed Ho *et al* [HHR96] developed a procedure for building potential energy surfaces for chemically bound systems which assumes that such surfaces go asymptotically as R^{-6} , where R is the length of the bond being stretched, as this is the expected leading term in the long-range form of the van der Waals interaction.

Asymptotic R^{-n} expansions have proved useful for representing global surfaces for systems with shallow wells, see for example the extensive work on the alkali metal complexes by Hutson *et al.* [CSH07, HS07b]. However it would appear that their usefulness is largely untested by either experiment or theory for the case of more strongly bound systems, such as the water molecule. For such strongly-bound molecules one is generally interested only in the region close to equilibrium as the high-energy, near-dissociation behaviour of the potential cannot be easily investigated by spectroscopic measurements.

At short and intermediate range the $R = 0$ divergence of expansions in R^{-n} hinders their practical implementation. A common remedy is to multiply each term by an empirical, sigmoid-type ‘damping’ function $f_n(R)$ defined to both suppress the singularity at $R = 0$ and to allow for exchange effects as the charge clouds of the separated functions overlap. Such functions are defined such that $\lim_{R \rightarrow +\infty} f_n(R) = 1$ so that the asymptotic limit is recovered.

Koide *et al.* [KMA81] proposed the use of a damping function of the form $f_n(R) = 1 - \exp(-a_n R - b_n R^2 - c_n R^3)^n$, while another well-known form is the one suggested by Tang and Toennies [TT77] and modifications thereof [TT84]. These damped expansions are widely used in potentials of weakly-bound systems where long-range interactions are fundamental for their description. However they require further parameters which can only be obtained from fitting rather than by theoretical asymptotic calculations. For strongly bound molecules, like water, a common practice is to incorporate in the potential an asymptotic behaviour of the simple C/R^6 type [Var96, HS00a]. As we demonstrate in this work, it is important that this form should not be enforced as soon as the region covered by the *ab initio* points ends if, as is often the case, points stop at $R \lesssim 5 a_0$.

The purpose of this chapter is to assess the relevance of intramolecular van der Waals interactions in the design of global potential energy surfaces to be used, for example, for the calculation of highly-excited rotational-vibrational states of small, strongly covalently bound molecules. We shall first consider the case of the hydrogen molecule as this is a well-analysed system; we will then use a similar analysis for the single-bond-breaking dissociation channel in the water molecule.

The main conclusion of this analysis is that such expansions do not provide a good starting point for this problem as they only become reliable when the interaction energy is very small.

All energies were converted from Hartrees to cm^{-1} using the CODATA 2006 [MTN08] value $1 E_h = 219,474.6313705 \text{ cm}^{-1}$.

10.2 The London interaction in molecular hydrogen

Hydrogen is the simplest molecule and, as mentioned above, its asymptotic properties have been well studied and the divergence problems of asymptotic expansions of the long-range energy are well understood. We use H_2 to underline some features which are present in larger systems as well.

10.2.1 Series expansion of the interaction energy

The analytic treatment of the long-range interaction between two ground-state hydrogen atoms is a paradigmatic example of the London dispersion interaction and has been studied in many papers [OM06, MO05, MB05, MOF⁺98, Kog89, KUi87, Tha88, DL56, PB35]. The standard treatment is based on Rayleigh-Schrödinger perturbation theory and is discussed in books [CTDL77, Kap06] and reviews [CS00a, EÅK00]. We will now very briefly sketch the general strategy. The Hamiltonian of the molecule is written as $H = H_A + H_B + W$ where H_A , H_B are the atomic Hamiltonians of atoms A and B and W is the electrostatic interaction of the particles of atom A with those of atom B . The procedure then consists of the following steps:

1. The interaction term W is expanded in series of $1/R^n$, where R is the internuclear distance of the atoms (multipole expansion).
2. Each of these terms is treated by some order of Rayleigh-Schrödinger perturbation theory; in the vast majority of studies, only the second-order contribution is considered.
3. Exchange terms are neglected, in the sense that the unperturbed, zero-order, wave functions are not antisymmetrized in the electronic coordinates. This is done mainly because the correct treatment of the exchange interaction makes the calculations much more difficult. More advanced perturbative treatments of intermolecular interactions which properly treat exchange have been developed and go generally under the name of symmetry-adapted perturbation theory (SAPT) [MWv00], but we will not discuss them. In any case it can be shown that exchange terms go to zero exponentially and hence give no contribution in a series of inverse powers of the intermolecular distance.

The final result is a series expansion in inverse powers of the interatomic distance R of the kind

$$E(R) = \sum_{n=6}^{+\infty} C_n R^{-n}, \quad (10.1)$$

where the C_n (dispersion coefficients) are in turn given by a sum of contributions from various orders of perturbation theory,

$$C_n = \sum_{p=2}^{\infty} C_n^{(p)}. \quad (10.2)$$

In particular, even/odd parity perturbation orders introduce corrections only to even/odd C_n 's (more specifically, the p -th order perturbation-theory introduces terms from $n = 3p$ when p is even and $n = 3p + 2$ when p is odd).

Although the procedure is conceptually simple calculations involving third and higher order of perturbation theory are rare and involve a great amount of both algebra and computation

[OM06]. This makes the computation of the higher-order C_n very inconvenient as high-order perturbation contributions grow more and more in importance as n increases and thus cannot be neglected for high n (e.g., the $p = 2$ term contributes by less than 50% to the full value of C_{30}).

A table of the recently-derived [OM06] all-order dispersion coefficients up to $n = 30$, along with other data which will be discussed in a later section, is presented as Table 10.1.

It was first conjectured [DL56] and later proven [You75] that the series expansion thus obtained is asymptotic in character and is in fact divergent as $n \rightarrow +\infty$ for all values of R . The convergence problems of expansion (10.1) have been extensively discussed in the literature. Kreek and Meath [KM69] derived a second-order perturbative expression for the long-range energies without performing the multipole expansion. This avoids the divergence problems but the resulting expressions are of little practical use in the fitting of potential surfaces based on the use of *ab initio* calculations. To our knowledge the explicit comparison of the asymptotic expansion with accurate *ab initio* data is restricted to a few cursory remarks by Kolos and Wolniewicz [KW74]. This matter will therefore be treated in detail in the following sections.

We remind the reader that a function $f(x)$ admits an asymptotic (as known as Poincaré or semiconvergent) expansion [Olv97, Jon97, JJ00, Spi64] in series of $1/x$ if there exist an infinite set of coefficients c_n such as these two conditions hold¹:

1. Given any integer $N \geq 0$ it is possible to write

$$f(x) = \sum_{n=0}^N \frac{c_n}{x^n} + \varepsilon(x) \quad (10.3)$$

and the error term $\varepsilon(x)$ goes to zero faster than $1/x^N$, i.e. $\lim_{x \rightarrow +\infty} x^N \varepsilon(x) = 0$

2. For any x no matter how large the limit

$$\lim_{N \rightarrow \infty} \sum_{n=0}^N \frac{c_n}{x^n}$$

is infinite or does not exist.

It can be shown that for an expansion of this kind each term c_n/x^n will, for x fixed and sufficiently large, decrease in magnitude up to a certain x -dependent value of $n = N_x$, and then start to increase as $n \rightarrow +\infty$. We shall discuss a criterion for truncating the sum in the following section.

Criteria for truncating the asymptotic expansion

As discussed in the previous section, in an asymptotic divergent power series like eq. (10.1), a criterion is needed for truncating the expansion at some R -dependent $n_{\max}(R)$ so that the truncated sum is in some sense optimal. The choice of such a criterion has been discussed in the mathematical literature [Olv97, Jon97, JJ00] and the general recommendation is to sum terms until they start to increase. Furthermore, if $C_n R^{-n} \ll C_{n-1} R^{-(n-1)}$ then $C_n R^{-n}$ may be used as a non-rigorous estimate of the residual error $\varepsilon(R)$ of the truncated expansion [Olv97]. This recipe was applied to the recent all-order C_n up to $n = 30$ by Ovsiannikov and Mitroy [OM06]

¹The following discussion is not rigorous but adequate for our purposes.

Table 10.1: Dispersion coefficients for the hydrogen molecule, with the uncertainties in the last figure given in brackets^a. R_{min} is the minimum value of R for which the relative term should be included according to the criterion described in Section 10.2.1 of the text. The next column gives the magnitude of the term at R_{min} , while the last column gives the exact interaction energy^b.

n	C_n (a ₀) ⁿ	R_{min} a ₀	$\frac{C_n}{(R_{min})^n}$ cm ⁻¹	$E(R_{min})$ cm ⁻¹
6	6.499026705406(1) × 10 ⁰	3.3	1074.971	-8778.443
8	1.243990835836(1) × 10 ²	4.4	187.461	-1973.357
10	3.285828414967(1) × 10 ³	5.5	27.215	-375.070
11	3.474898037882(1) × 10 ³	6.5	0.859	-86.787
12	1.227276087007(1) × 10 ⁵	6.6	3.735	-72.950
13	3.269869240441(1) × 10 ⁵	7.7	0.217	-17.617
14	6.361736045092(1) × 10 ⁶	7.7	0.509	-16.724
15	2.839558063300(1) × 10 ⁷	8.9	0.037	-4.879
16	4.412051922740(1) × 10 ⁸	8.8	0.070	-5.049
17	2.739281653140(1) × 10 ⁹	10.1	0.005	-1.842
18	3.935247733459(5) × 10 ¹⁰	9.9	0.010	-2.002
19	3.070824593893(1) × 10 ¹¹	11.2	0.0007	-0.842
20	4.36376277942(5) × 10 ¹²	11.0	0.001	-0.957
21	4.036038399661(5) × 10 ¹³	12.4	0.00009	-0.447
22	5.8603051640(5) × 10 ¹⁴	12.2	0.0002	-0.515
23	6.20021018266(5) × 10 ¹⁵	13.6	0.00001	-0.252
24	9.34336167(5) × 10 ¹⁶	13.3	0.00002	-0.297
25	1.10538854158(5) × 10 ¹⁸	14.8	0.000001	-0.150
26	1.74141131(5) × 10 ¹⁹	14.4	0.000003	-0.180
27	2.268395655(5) × 10 ²⁰	16.0	0.0000002	-0.093
28	3.7474032(5) × 10 ²¹	15.5	0.0000007	-0.114
29	5.31488551(5) × 10 ²²	17.2	0.00000002	-0.060
30	9.215791(5) × 10 ²³	16.6	0.00000005	-0.074

^a We derived the C_n 's and their uncertainties from Table 4 of ref. [OM06], considering an uncertainty of ± 1 on the last digit when no underline was present and of ± 5 for underlined digits and propagating the error of the sum in the usual way [Tay97] as $\varepsilon_n = \sqrt{\sum_p \varepsilon_p^2}$.

^b 'Exact' interaction energies as obtained from a fourth-order piecewise polynomial interpolation of the data of [Wol93] for $R < 12$ a₀ and as given by the asymptotic series truncated at $n = 12$ for $R > 14$ (the estimated accuracy for all values is 0.005 cm⁻¹ or better).

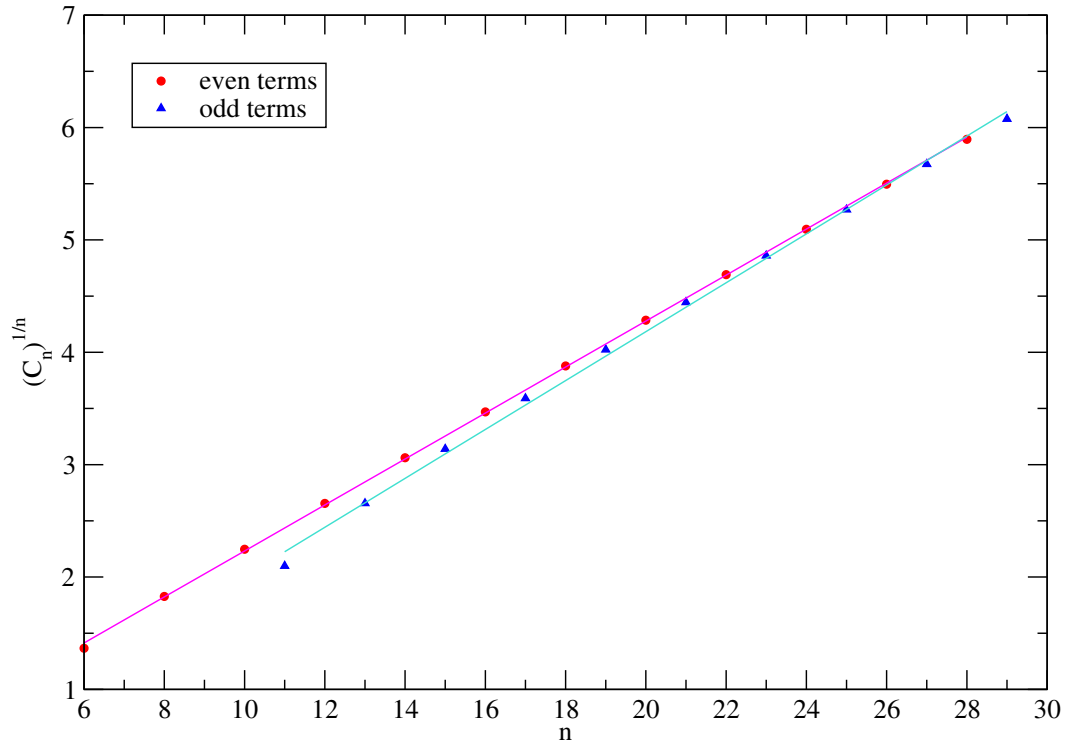


Figure 10.1: Plot of the $(C_n)^{1/n}$ against n and the respective linear fits.

and reported in Table 10.1. In virtue of their very high accuracy their numerical uncertainties are never a concern in the analysis.

To obtain $n_{\max}$ we proceeded as follows. A simple numerical examination shows that plotting $(C_n)^{1/n}$ against n yields approximately a straight line (see Figure 10.1), so that $(C_n)^{1/n} \approx An + B$. The fit with straight lines is even more precise if we use two different lines for the even- n and odd- n terms.

A and B were therefore obtained by a linear fit and then the integer $n_{\max}$ at which the series should be truncated was found by taking the derivative of $(An + B)^n R^{-n}$ with respect to n , setting it equal to zero and numerically solving for n . The final results for H_2 can be expressed as $n_{\max} = \lfloor 1.81R/a_0 \rfloor$ for n even and $n_{\max} = \lfloor 1.69R/a_0 \rfloor$ for n odd. This truncation criterion together with the non-rigorous estimate of the residual error mentioned above, leads to an expression for ε which can be well approximated for H_2 by an exponential function: $\varepsilon(R) \approx 10^{-0.72(R/a_0 - 5.34)} \text{ cm}^{-1}$.

10.2.2 Accurate reference points

There is a long history of accurate calculations of the electronic potential of the hydrogen molecule [RK03]; we reviewed what is available in the literature in Section 3.14.

Comparing the recent values from Sims and Hagstrom [SH06] with the ones from Rychlewski and Komasa [RK03] we estimate the energies by Sims and Hagstrom [SH06] to be accurate to at least 10^{-4} cm^{-1} ; we label these results “exact” below.

We computed a series of full-CI energies using MOLPRO 2002.6 [WKL⁺02] and various basis sets of the aug-cc-pVnZ family [Dun89], see section 3.14. Basis-Set Superposition Er-

ror was estimated calculating the counterpoise correction (Boys-Bernardi) correction [BB70] $\Delta E^{CP}(R) = 2[E_H - E_{HG}(R)]$, where E_H is the energy of the hydrogen atom with the given basis set, and $E_{HG}(R)$ is the energy of a hydrogen atom in the presence of the basis sets for the two hydrogens, for the aug-cc-pVQZ points. ΔE^{CP} is 0.311 cm^{-1} at $5 a_0$ and decreases rapidly with R . Its effect is therefore small. Unsurprisingly, absolute values of the energy obtained in this way are much less accurate (e.g. the full-CI aug-cc-pV6Z energies near equilibrium are about 25 cm^{-1} too high) but results for energy differences at long bond lengths are much more encouraging. Results are collected in Table 10.2 and are discussed in the following section.

10.2.3 Analysis

An overview of some of the truncated expansions of eq. 10.1 is presented in Fig. 10.2 while some quantitative values are reported in Table 10.2. It is apparent that all the expansions are essentially useless for bond lengths less than about $5 a_0$, as already suggested by the analysis of the expansion coefficients.

In the region $5 < R < 8 a_0$ asymptotic expansions are still not very accurate, and the improvement on adding terms of higher n (within the limit of the truncation criterion) is slow. Expansions with $n < 18$ underestimate the interaction energy while those with $n > 24$ overestimate it. In the range $8 < R < 10 a_0$ the $n = 6$ term still performs rather poorly, for example at $9 a_0$ the errors are about 1 cm^{-1} while the exact energy is only of -4.5 cm^{-1} . Adding terms with higher n only improves the values very slowly, with the $n = 24$ curve still lying relatively far from the exact one. Finally, it is only for $R > 10 a_0$ that the expansions give accurate values of the interaction energy. We note that terms with n higher than about 12 seem to only become useful for values of R greater than about $11 a_0$, when the residual interaction energy is a mere 1 cm^{-1} . The main conclusion of this analysis is that the high-order dispersion coefficients C_n computed by many authors [OM06, MO05, MB05, MOF⁺98, Kog89, KUi87, Tha88] have little practical usefulness as they are applicable only at very long-range, R greater than about $10 a_0$, when their effect is very small.

It can be seen from Table 10.2 that full-CI, aug-cc-pVnZ calculations describe the London interaction rather well. Already with an aug-cc-pVTZ basis set the interaction energy are, for $R < 10 a_0$, better than those obtained by asymptotic expansions of any order. The importance of diffuse basis functions was tested by removing the ‘aug’ function from the aug-cc-pVnZ basis sets and also by adding to these basis sets a further set of diffuse functions for every value of the angular momentum. The extra diffuse functions were obtained by logarithmic extrapolation (i.e., following an even-tempered scheme). The conclusion is that diffuse functions are essential in the description of the long-range interaction but double augmentation does not lead to a significant improvement.

10.3 Long-range interaction for O–H stretching in H₂O

The long-range interaction upon stretching of one O–H bond inside the water molecule was studied. More specifically, this corresponds to the reaction $\text{H}_2\text{O}(^1\text{A}_1) \rightarrow \text{H}(^2\text{S}) + \text{OH}(^2\Pi)$.

For simplicity, the bond angle θ and the unstretched bond length r_2 were fixed to the equilibrium values of 104.52° and r_2 to $1.8096 a_0$ respectively. This reaction path differs slightly

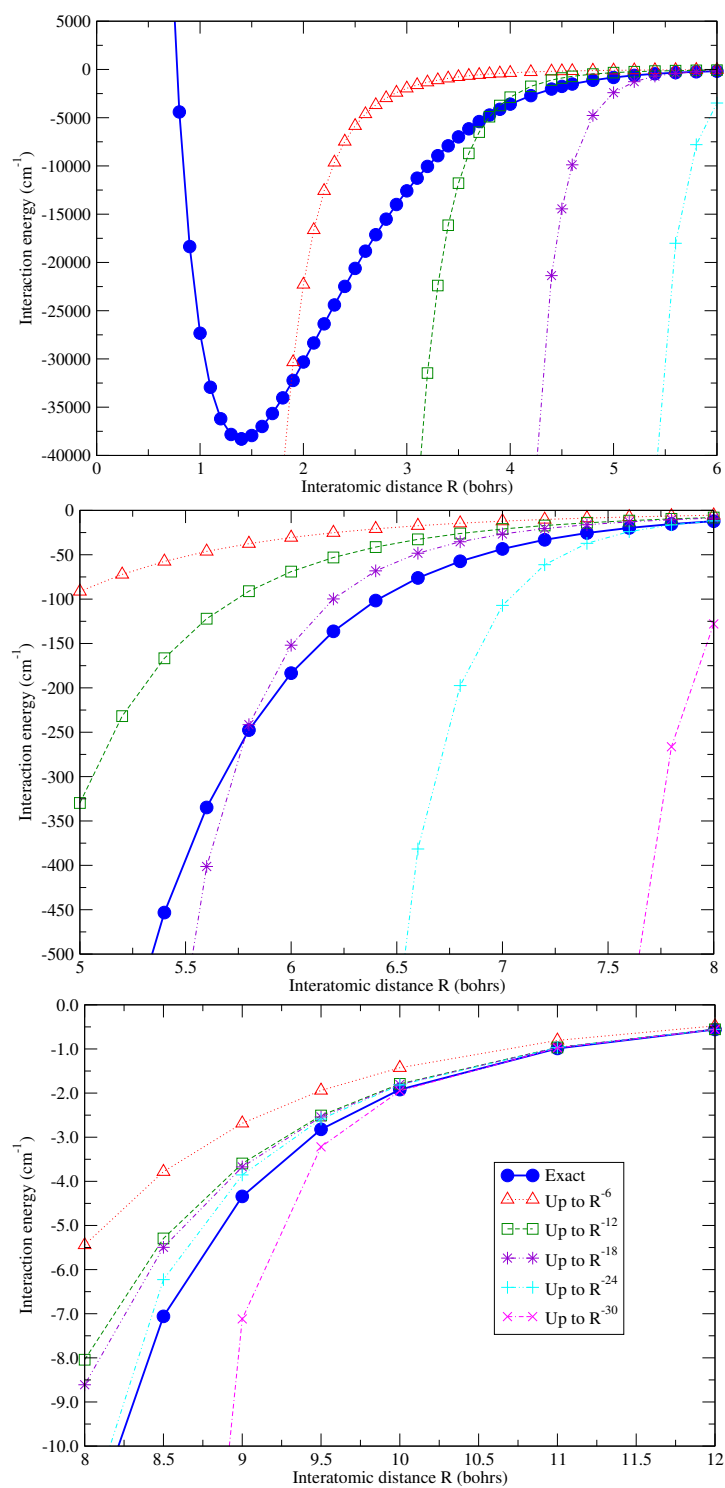


Figure 10.2: Comparison of potential energy curves for H₂ with several truncated asymptotic expansion of the long-range interaction energy and the exact curve.

Table 10.2: Long-range values for the interaction energy $E(+\infty) - E(R)$ of H₂, comparison of truncated asymptotic expressions with quantum chemistry calculations. R is in a_0 , all energies in cm^{-1} . Full-CI energies were obtained as $E(R) - E(70)$. The distance of 70 a_0 was chosen because of numerical limitations for longer R . The true $E(70)$ is 0.001 cm^{-1} . AnZ stands for aug-cc-p VnZ ; nZ stands for cc-p VnZ ; $AAAnZ$ stands for a double-augmented cc-p VnZ basis set obtained as described in the text.

R literature	series expansion up to n							full-CI						
	6	12	18	24	30	ATZ	AQZ	A5Z	A6Z	TZ	QZ	5Z	6Z	AAQZ
5.0 -830.856 ^a	-91.288	-329.7375	-2406.20	-3×10^5	-2×10^8	-808.712	-823.262	-826.605	-828.427	-716.607	-765.199	-794.252	-810.635	-811.654
8.0 -12.204 ^b	-5.441	-8.043	-8.610	-11.793	-127.950	-11.255	-11.649	-11.786	-11.917	-9.560	-6.565	-7.664	-8.633	-11.838
9.0 -4.341 ^c	-2.684	-3.596	-3.672	-3.855	-7.118	-4.048	-4.102	-4.163	-4.212	-3.145	-1.969	-2.434	-2.771	-4.432
10.0 -1.922 ^c	-1.426	-1.791	-1.804	-1.817	-1.950	-1.838	-1.842	-1.844	-1.866	-0.740	-1.028	-1.179	-1.354	-2.150
11.0 -0.989 ^c	-0.805	-0.966	-0.969	-0.970	-0.977	-0.943	-0.968	-0.954	-0.964	-0.327	-0.515	-0.609	-0.698	-1.213
12.0 -0.559 ^c	-0.478	-0.555	-0.555	-0.556	-0.556	-0.532	-0.548	-0.544	-0.547	-0.169	-0.284	-0.349	-0.400	-0.707
15.0 na	-0.125	-0.137	-0.137	-0.137	-0.137	-0.133	-0.135	-0.135	-0.136	-0.041	-0.070	-0.088	-1.101	-0.145
20.0 na	-0.022	-0.023	-0.023	-0.023	-0.023	-0.023	-0.023	-0.023	-0.023	-0.007	-0.012	-0.015	-0.018	-0.031
25.0 na	-0.006	-0.006	-0.006	-0.006	-0.006	-0.006	-0.006	-0.006	-0.006	-0.002	-0.003	-0.004	-0.005	-0.009

^a From [SH06], should be exact to the given precision.

^b From [Wol95], should be exact to the given precision.

^c From [Wol93], should be accurate to about 0.005 cm^{-1} .

from the real dissociation channel of water because in that case r_2 and θ relax as r_1 is stretched. However tests (not reported) showed that this small difference has no influence on our conclusions.

10.3.1 Calculations

All H₂O calculations are for the ground-state singlet $^1A'$ electronic state and make use of the standard, non-relativistic Hamiltonian. Spin-orbit and relativistic effects are not considered. Computations were performed with MOLPRO 2002.1 [WKL⁺02] and the IC-MRCI+Q method, i.e. internally-contracted multi-reference configuration interaction including the Davidson correction (see Section 3.9 for more details on the method). Two different active spaces were considered, corresponding the ones labelled [8, 8] and [8, 10] of Table 6.2, which we will now briefly describe again. The first is a (8 electrons, 8 orbitals) complete active space (CAS) constituted by $6a'$ orbitals and $2a''$ orbitals; the lowest-energy a' orbital, corresponding to the $1s$ atomic orbital of oxygen, was kept uncorrelated at the IC-MRCI step. This CAS is known to be a very good one for water [KS97, PS97, SS05, BSZ⁺06]. A second, larger (8 electrons, 10 orbitals) CAS which includes two further a' orbitals was also examined. The basis sets used are the ones from the aug-cc-pVnZ series for $n=T, Q, 5$ [Dun89]. A total of 32 values for $r_1 = 1.0$ to $r_1 = 25.0$ a_0 were computed and are reported in Table 10.3. All computations were done on a standard PC Pentium IV 3 GHz with 3 GiB of RAM and about 200 GB of hard disk space. Each of the aug-cc-pV5Z computations took about one hour and the other smaller computations between 5 and 30 minutes each.

10.3.2 Analysis

Looking at the data reported in Table 10.3 it can be seen that, as in the case of H₂, the calculated interaction energies for r_1 greater than about 5 a_0 are rather insensitive to the basis set used; already with the aug-cc-pVTZ basis set they are converged with respect to basis set increases to within 5 cm^{-1} or better. A similar level of convergence is observed with respect to increasing the CAS. Considering that the typical accuracy of potential energy surfaces for water near equilibrium is only in the region of 100 cm^{-1} [BSZ⁺06], the aug-cc-pVTZ values can already be considered as quite accurate.

It should be noted that the long-range energies given by the CAS-SCF step differ significantly with respect to the IC-MRCI+Q ones. While they show the same level of stability as IC-MRCI+Q energies with respect to basis set augmentation, they depend appreciably on the size of the CAS selected. These observations are consistent with the conventional view that an accurate description of long-range interactions requires an extensive treatment of dynamical electron correlation.

Once the accuracy of the computed values had been evaluated, the range where the asymptotic behaviour of the kind $Ar_1^{-\alpha}$ effectively begins was ascertained, $\alpha = 6$ being the expected value. To do this we plotted the quantity $-r_1 \frac{d}{dr_1} \log(|V(r_1)|)$ for the aug-cc-pV5Z energies, calculating the necessary derivative by finite differences, see Fig. 10.3. If $V(r_1)$ had a form of the kind $Ar_1^{-\alpha}$, the plot would yield a constant value equal to α , so that the curve can be interpreted as a ‘local exponent’ as a function of r_1 . This is also the value of α that would be obtained

Table 10.3: Interaction energies for the single bond stretching of water. Energies, in cm^{-1} , were obtained as $E(r_1) - E(25)$, where r_1 , in a_0 , is the length of the stretched OH bond.

		IC-MRCI+Q		
CAS =		(6a',2a'')	(8a',2a'')	
r_1	ATZ	AQZ	A5Z	ATZ
1.0	90626.95	89213.62	88751.50	90516.84
1.2	10539.00	9521.35	9223.82	10425.88
1.4	-25198.84	-25991.83	-26187.15	-25312.78
1.6	-39467.82	-40088.80	-40233.26	-39581.98
1.8	-43119.11	-43605.91	-43722.31	-43233.12
2.0	-41554.90	-41943.86	-42040.76	-41668.47
2.2	-37552.12	-37879.65	-37961.89	-37664.77
2.4	-32583.77	-32874.80	-32945.04	-32694.45
2.6	-27445.97	-27708.55	-27768.61	-27552.47
2.8	-22563.30	-22795.69	-22847.03	-22660.57
3.0	-18151.87	-18351.27	-18394.88	-18228.94
3.2	-14311.19	-14477.06	-14513.50	-14362.83
3.4	-11072.87	-11206.58	-11236.13	-11106.72
3.6	-8423.40	-8527.45	-8550.37	-8446.51
3.8	-6316.07	-6393.71	-6410.64	-6332.51
4.0	-4681.69	-4736.97	-4748.91	-4693.74
4.5	-2145.48	-2165.25	-2169.34	-2151.33
5.0	-967.34	-973.69	-974.41	-970.21
5.5	-440.68	-442.77	-442.40	-442.07
6.0	-206.70	-207.58	-206.98	-207.34
6.5	-101.47	-101.74	-101.27	-101.76
7.0	-52.94	-52.70	-52.41	-53.06
8.0	-17.63	-17.24	-16.94	-17.65
9.0	-7.45	-7.15	-6.92	-7.45
10.0	-3.68	-3.46	-3.36	-3.69
11.0	-2.01	-1.87	-1.82	-2.01
12.0	-1.16	-1.06	-1.03	-1.17
13.0	-0.70	-0.64	-0.62	-0.71
14.0	-0.43	-0.40	-0.39	-0.44
15.0	-0.27	-0.26	-0.25	-0.28
20.0	-0.03	-0.03	-0.03	-0.03
25.0	0.00	0.00	0.00	0.00

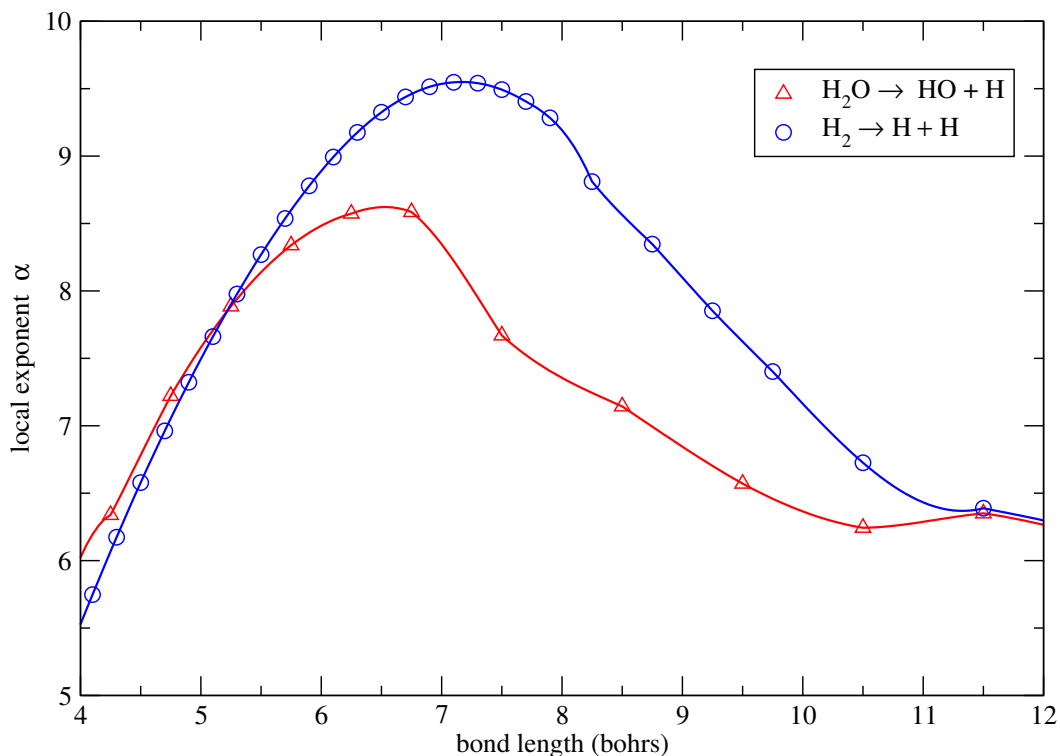


Figure 10.3: Plot of the quantity $-r \frac{d}{dr_1} \log(|V(r_1)|)$, corresponding to the local exponent α (see text). The plot shows that the asymptotic form A/R^6 is only reached for r_1 greater than about $10 a_0$.

if a small portion of $V(r_1)$ were fitted to the functional form A/r_1^α . It can be observed from Fig. 10.3 that the curve is not a constant, even at large r_1 , indicating that in the plotted range asymptotic behaviour is not yet reached; the figure shows that H_2 behaves similarly.

The plot suggests that the curve does indeed approach the expected value of 6, but it is still away from it at $r_1 = 10 a_0$ when the interaction energy is less than 4 cm^{-1} . This situation is thus quantitatively similar to the one found above for H_2 .

10.4 Conclusions

We showed that undamped high-order asymptotic expansions of the interatomic energy for the hydrogen molecule are only useful for R greater than about $10 a_0$. Furthermore we showed that these long-range interactions can be modelled accurately with standard quantum chemistry methods even with relatively small basis sets provided the model includes sufficient treatment of dynamical electron correlation. Conversely we showed that in the asymptotic van der Waals regime, taken as the region where the potential can be reliably represented by the functions AR^{-6} , starts only at $R \approx 10 a_0$ for both hydrogen and water. In both cases the interaction energy in this region is only $2\text{--}3 \text{ cm}^{-1}$ away from dissociation.

It is true that there are some important cases where the very long-range form of the interaction determines the physics of the systems, two notable examples being collisions of ultra-cold molecules and atoms [CKS⁺05] and near-dissociation rotation-vibration levels in diatomic

molecules [LB68]. However, in the case of strongly bound polyatomic molecules, such binding energies are less than the error encountered in standard least-squares fits to global *ab initio* potential energy surfaces.

Our conclusion is that for global potential surfaces of strongly chemically bound systems it will be in most cases unnecessary, and possibly harmful, to force the surface to have an asymptotic form of the kind AR^{-6} except when considerably larger values of R are used than is currently the case. In particular one should be cautious about the use of undamped expansions for these systems for values of R below about 10 a_0 .

Conclusions

In this thesis we presented a detailed study of various aspects of the vibration-rotation spectroscopy of water vapour.

In Chapters 2 to 5 a thorough review of the theoretical background and the methodology underlying the calculation of theoretical spectra was presented, along with the study of several one-dimensional model systems. Chapters 6 and 7 presented a very detailed study of the accuracy currently achievable with electronic-structure methods for the calculation of water energy and dipole moments. The performance of several multi-reference methods and reference spaces was investigated, as was the computation of relativistic corrections to the energy and to the dipole. The effect of spurious oscillations in the bond-angle coordinate was studied and shown to be crucial for the computation of weak line intensities. This result is important for the process of fitting of new water dipole moment surfaces and may be of use for other tri-atomic molecules.

In Chapter 8 the new CVR dipole moment surface was presented and in Chapter 9 line intensities calculated from it were compared with a very large set of experimental data. The new CVR-based line intensities were found to be slightly more accurate than the best previously available data. A new line list for purely rotational transitions was also presented which may help in the analysis of the experimental spectra observed for atmospheric water vapour.

Finally, in Chapter 10 we described the convergence behaviour of the power expansion of the intra-molecular van der Waals interaction. The late on-set of the R^{-6} asymptotic regime implies that such expansions only become reliable when the interaction energy is very small and hence have limited usefulness for the set-up of water potential energy surfaces for spectroscopy.

There are several directions in which the theoretical study of water can be continued. As discussed in Chapter 10, one recent experimental advance is the development of a multi-photon laser technique [MRB06] capable of studying very high-energy vibration-rotation states just above and just below its dissociation limit with spectroscopic accuracy. Presently-available line lists do not cover adequately such high-energy states as the potential energy surfaces used for their computation do not correctly describe such high-energy regions. To obviate this deficiency a new potential energy surface covering the dissociation channel is in preparation. This new surface will also provide an overall greater accuracy as it will be a fully all-electron calculation and will employ the larger 8-electron 10-orbital active space investigated in Chapters 6 and 7.

As discussed particularly in Chapters 7, 8 and 9 the major error in the CVR dipole moment

surface is due to the fact that dipoles were computed as expectation values instead of energy derivatives. A new dipole moment surface which employs the latter method of calculation is in preparation on UCL's new supercomputer Legion. This new surface too will be based on all-electron calculations in the larger 8-electron 10-orbital reference mentioned above. This new dipole moment surface should represent a major advance over the CVR one and line intensities calculated from it should finally have a sufficient accuracy to replace hundreds of person-years of measurements presently used in database compilations such as HITRAN. Considering the problems with spurious oscillations described in Chapter 8 we can foresee that the fit of the computed *ab initio* points will probably be a significant challenge.

Looking at the future of water vapour spectroscopy, advances in computational resources and in electronic structure methods will be beneficial in improving the quality of theoretical spectra. In particular, we can expect that in the near future multi-reference explicitly correlated F12-type methods will become available and will reduce the basis-set incompleteness error present in calculations. On a more long-term scale multi-reference coupled-cluster based methods are expected to become available, which should improve the treatment of high-order electron correlation effects.

Bibliography

- [ABC05] C. Angeli, S. Borini, and R. Cimiraglia. Kmonodim, a program for the numerical solution of the one-dimensional Schrödinger equation. *Journal of Chemical Education*, 82:795–800, 2005.
- [ABER00] R. Ansaloni, G. L. Bendazzoli, S. Evangelisti, and E. Rossi. A parallel full-CI algorithm. *Computer Physics Communications*, 128:496–515, 2000.
- [AC04] S. A. Alexander and R. L. Coldwell. A ground state potential energy surface for H-2 using Monte Carlo methods. *Journal of Chemical Physics*, 124:11557–11561, 2004.
- [ACE] ACESII Mainz-Austin-Budapest version, J. F. Stanton, J. Gauss, J. D. Watts, P. G. Szalay, R. J. Bartlett with contributions from A. A. Auer, D. B. Bernholdt, O. Christiansen, M. E. Harding, M. Heckert, O. Heun, C. Huber, D. Jonsson, J. Jusélius, W. J. Lauderdale, T. Metzroth, K. Ruud and the integral packages: MOLECULE (J. Almlöf and P. R. Taylor), PROPS (P. R. Taylor), and ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, and J. Olsen).
- [Ada62] W. H. Adams. Stability of Hartree-Fock States. *Physical Review*, 127:1650–1658, 1962.
- [AF05] P. W. Atkins and R. Friedman. *Molecular Quantum Mechanics*. Oxford University Press, 4th edition, 2005.
- [AGDLHG05] A. Aspuru-Guzik, A. D. Dutoi, P. J. Love, and M. Head-Gordon. Simulated quantum computation of molecular energies. *Science*, 309:1704–1707, 2005.
- [AMMM08] N. B. Armor, D. Maynau, J.-P. Malrieu, and A. Monari. Restoring the size consistency of multireference configuration interactions through class dressings: Applications to ground and excited states. *Journal of Chemical Physics*, 129:064112 (10 pages), 2008.
- [AMR92] K. Andersson, P.-Å. Malmqvist, and B. O. Roos. Second-order perturbation theory with a complete active space self-consistent field reference function. *Journal of Chemical Physics*, 96:1218–1226, 1992.

- [And72] P. W. Anderson. More is Different – Broken Symmetry and Nature of Hierarchical Structure of Science. *Science*, 177:393–396, 1972.
- [APC07] C. Angeli, M. Pastore, and R. Cimiraglia. New perspectives in multireference perturbation theory: the n-electron valence state approach. *Theoretical Chemistry Accounts*, 117:743–754, 2007.
- [Ark99] A. Arking. Bringing climate models into agreement with observations of atmospheric absorption. *Journal of Climate*, 76:1589–1600, 1999.
- [AS03] M. L. Abrams and C. D. Sherrill. An Assessment of the Accuracy of Multireference Configuration Interaction (MRCI) and Complete-Active-Space Second-Order Perturbation Theory (CASPT2) for Breaking Bonds to Hydrogen. *Journal of Physical Chemistry A*, 107:5611–5616, 2003.
- [AS05] M. L. Abrams and C. D. Sherrill. General-order single- and multi-reference configuration interaction and coupled cluster theory: Symmetric dissociation of water. *Chemical Physics Letters*, 404:284–288, 2005.
- [ASY⁺05] A. N. Artemyev, V. M. Shabaev, V. A. Yerokhin, G. Plunien, and G. Soff. QED calculation of the n=1 and n=2 energy levels in He-like ions. *Physical Review A*, 71:062104 (26 pages), 2005.
- [ATP98] A. Aguado, C. Tablero, and M. Paniagua. Global fit of ab initio potential energy surfaces I. Triatomic systems. *Computer Physics Communications*, 108:259–266, 1998.
- [Aul00] G. Auletta. *Foundations and Interpretation of Quantum Mechanics*. World Scientific, 2000.
- [AW05] G. B. Arfken and H. J. Weber. *Mathematical Methods For Physicists*. Academic Press, 6th edition, 2005.
- [Bae06] M. Baer. *Beyond Born-Oppenheimer: Electronic Nonadiabatic Coupling Terms and Conical Intersections*. Wiley-Interscience, 2006.
- [Bal98] L. E. Ballentine. *Quantum Mechanics: A Modern Development*. World Scientific Publishing Company, 1998.
- [Bar81] R. J. Bartlett. Many-body perturbation theory and coupled cluster theory for electron correlation in molecules. *Annual Review of Physical Chemistry*, 32:359–401, 1981.
- [Bar89] R. J. Bartlett. Coupled-Cluster approach to molecular-structure and spectra – A step toward predictive quantum chemistry. *Journal of Physical Chemistry*, 93:1697–1708, 1989.
- [Bar97] R. J. Bartlett (ed.). *Recent advances in Coupled-Cluster methods*. Word Scientific, 1997.

- [Bar02] P. Barletta. *Accurate first-principle calculations on the spectrum of water*. PhD thesis, University College London, London, UK, 2002.
- [BB70] S. F. Boys and F. Bernardi. Calculation of small molecular interactions by differences of separate total energies - Some procedures with reduced errors. *Molecular Physics*, 19:553–566, 1970.
- [BBBP83] P. G. Burton, R. J. Buenker, P. J. Bruna, and S. D. Peyerimhoff. Comparison of perturbatively corrected MRD CI results with a full CI treatment of the BH ground state. *Chemical Physics Letters*, 95:379–385, 1983.
- [BBS98] V. P. Bellary, T. K. Balasubramanian, and B. J. Shetty. On the Wigner-Witmer correlation rules for a homonuclear diatomic molecule with the like atoms in identical atomic states. *Pramana – Journal of Physics*, 51:445–452, 1998.
- [BCA05] S. Bubin, M. Cafiero, and L. Adamowicz. Non-Born-Oppenheimer variational calculations of atoms and molecules with explicitly correlated gaussian basis functions. *Advances in Chemical Physics*, 131:377–475, 2005.
- [BCD⁺01] H. Bachau, E. Cormier, P. Decleva, J. E. Hansen, and F. Martín. Applications of B-splines in atomic and molecular physics. *Reports on the Progress of Physics*, 64:1815–1942, 2001.
- [BDL03] G. Bertier, M. Defranceschi, and C. Le Bris. Shortcomings in computational chemistry. *International Journal of Quantum Chemistry*, 93:156–165, 2003.
- [Bec76] C. L. Beckel. Power-series expansions of vibrational potentials. V. radii of convergence for non-dunham series. *Journal of Chemical Physics*, 65:4319–4320, 1976.
- [Ber81] G. Berthier. Comments on the status of the chemical bond in quantum chemistry. *International Journal of Quantum Chemistry*, 19:985–989, 1981.
- [Ber96] P. F. Bernath. Infrared Fourier transform emission spectroscopy. *Chemical Society Reviews*, 25:111–115, 1996.
- [Ber02] P. F. Bernath. The spectroscopy of water vapour: Experiment, theory and applications. *Physical Chemistry Chemical Physics*, 4:1501–1509, 2002.
- [Ber05] P. Bernath. *Spectra of Atoms and Molecules*. Oxford University Press, 2nd edition, 2005.
- [BGH⁺00] K. L. Bak, J. Gauss, T. Helgaker, P. Jørgensen, and J. Olsen. The accuracy of molecular dipole moments in standard electronic structure calculations. *Chemical Physics Letters*, 319:563–568, 2000.
- [BGT05] D. A. Bini, L. Gemignani, and F. Tisseur. The Ehrlich-Aberth method for the nonsymmetric tridiagonal eigenvalue problem. *SIAM Journal on Matrix Analysis and Applications*, 27:153–175, 2005.
- [BH24] M. Born and W. Heisenberg. Zur Quantentheorie der Molekeln. *Annalen der Physik (Leipzig)*, 74:1–31, 1924.

- [BH54] M. Born and K. Huang. *Dynamical Theory of Crystal Lattices*. Oxford: Clarendon Press, 1954.
- [BH86] D. Baye and P. H. Heenen. Generalised meshes for quantum mechanical problems. *Journal of Physics A*, 19:2041–2059, 1986.
- [BJ98] P. R. Bunker and P. Jensen. *Molecular Symmetry and Spectroscopy*. NRC Research Press, 2th edition, 1998.
- [BJ00] P. R. Bunker and P. Jensen. The Born-Oppenheimer approximation. *Published in [JB00]*, pages 3–11, 2000.
- [BK03] E. J. Brändas and E. S. Kryachko (eds.). *Fundamental World of Quantum Chemistry (3 voll)*. Kluwer Academic, 2003.
- [BKW04] D. A. Belsley, E. Kuh, and R. E. Welsch. *Regression Diagnostics: Identifying Influential Data and Sources of Collinearity*. WileyBlackwell, 2004.
- [BL81] L. C. Biendeharn and J. D. Louck. *Angular momentum in quantum physics*. Longman Higher Education, 1981.
- [BL89] Z. Bačić and J. C. Light. Theoretical methods for rovibrational states of floppy molecules. *Annual Review of Physical Chemistry*, 40:469–498, 1989.
- [BLK04] P. Barletta, M. Lombardi, and A. Kievsky. Variational DVR calculations. *Few-body systems*, 34:11–14, 2004.
- [BLLS94] V. Bach, E. H. Lieb, M. Loss, and J. P. Solovej. There are no unfilled shells in unrestricted Hartree-Fock theory. *Physical Review Letters*, 72:2981–2983, 1994.
- [BLS05] R. J. Bartlett, V. F. Lotrich, and I. V. Schweigert. Ab initio density functional theory: The best of both worlds? *Journal of Chemical Physics*, 123:062205 (21 pages), 2005.
- [BM77] P. R. Bunker and R. E. Moss. The breakdown of the Born-Oppenheimer approximation: the effective vibration-rotation hamiltonian for a diatomic molecule. *Molecular Physics*, 33:417–424, 1977.
- [BM80] P. R. Bunker and R. E. Moss. Effect of the breakdown of the Born-Oppenheimer approximation on the rotation-vibration hamiltonian of a triatomic molecule. *Journal of Molecular Spectroscopy*, 80:217–228, 1980.
- [BM07] R. J. Bartlett and M. Musiał. Coupled-cluster theory in quantum chemistry. *Reviews of Modern Physics*, 79:291–352, 2007.
- [BMM77] P. R. Bunker, C. J. McLarnon, and R. E. Moss. Application of the effective vibration-rotation hamiltonian to H_2 and D_2 . *Molecular Physics*, 33:425–429, 1977.

- [BO27] M. Born and J. R. Oppenheimer. Zur Quantentheorie der Molekeln. *Annalen der Physik (Leipzig)*, 84:457–484, 1927. An English translation is freely available from B. T. Sutcliffe’s web page at <http://www.ulb.ac.be/cpm/people/scientists/bsutclif/bornop.pdf> and in [Het00], which is available as sample chapter at http://www.worldscibooks.com/chemistry/etextbook/3201/3201_chap1.pdf (accessed 26-Nov-2007).
- [Bon04] L. Bonolis. From the rise of the group concept to the stormy onset of group theory in the new Quantum Mechanics. A saga of the invariant characterization of physical objects, events and theories. *Rivista Del Nuovo Cimento*, 27:1–110, 2004.
- [Bor51] M. Born. Kopplung der Elektronen- und Kernbewegung in Molekeln und Kristallen. *Nachrichten der Akademie der Wissenschaften zu Göttingen. Ila. Mathematisch-Physikalische Klasse*, 6:1–3, 1951.
- [BP80] R. J. Bartlett and G. D. Purvis III. Molecular applications of coupled cluster and many-body perturbation methods. *Physica Scripta*, 21:255–265, 1980.
- [BP96] L. R. Brown and C. Plymate. H₂-broadened H₂¹⁶O in four infrared bands between 55 and 4045 cm⁻¹. *Journal of Quantitative Spectroscopy & Radiative Transfer*, 56:263–282, 1996.
- [BPB80] P. J. Bruna, S. D. Peyerimhoff, and R. J. Buenker. The ground state of the CN⁺ ion: a multi-reference CI study. *Chemical Physics Letters*, 72:379–385, 1980.
- [BPM00] G. Berden, R. Peeters, and G. Meijer. Cavity ring-down spectroscopy: Experimental schemes and applications. *International Reviews in Physical Chemistry*, 19:565–607, 2000.
- [BR03a] J. Brandão and C. M. A. Rio. Double-valued potential energy surface for H₂O derived from accurate ab initio data and including long-range interactions. *Journal of Chemical Physics*, 119:3148–3159, 2003.
- [BR03b] J. Brandão and C. M. A. Rio. Long-range interactions within the H₂O molecule. *Chemical Physics Letters*, 372:866–872, 2003.
- [BR06] L. Bytautas and K. Rudenberg. Correlation energy extrapolation by intrinsic scaling. V. Electronic energy, atomization energy, and enthalpy of formation of water. *Journal of Chemical Physics*, 124:174304 (13 pages), 2006.
- [Bra71] D. Braess. Chebyshev approximation by spline functions with free knots. *Numerical Mathematics*, 17:357–366, 1971.
- [Bru55] K. A. Bruencker. Many-body problem for strongly interacting particles. II. Linked cluster expansion. *Physical Review*, 100:36–45, 1955.

- [BS77] R. J. Bartlett and I. Shavitt. Determination of the size-consistency error in the single and double excitation configuration interaction model. *International Journal of Quantum Chemistry Symposium*, 11:165–173, 1977.
- [BS85] R. Blackmore and B. Shizgal. Discrete-ordinate method of solution of Fokker-Planck equations with nonlinear coefficients. *Physical Review A*, 31:1855–1868, 1985.
- [BS94] D. M. Brink and G. R. Satchler. *Angular momentum*. Oxford University Press, 3rd edition, 1994.
- [BSP79] R. J. Bartlett, R. J. Shavitt, and G. D. Purvis. The quartic force field of H₂O determined by many-body methods that include quadruple excitation effects. *Journal of Chemical Physics*, 71:281–291, 1979.
- [BSS⁺00] D. Belmiloud, R. Schermaul, K. Smith, N. F. Zobov, J. Brault, R. C. M. Learner, D. A. Newnham, and J. Tennyson. New studies of the visible and near-infrared absorption by water vapour and some problems with the HITRAN database. *Geophysical Research Letters*, 27:3703–3706, 2000.
- [BSZ⁺06] P. Barletta, S. V. Shirin, N. F. Zobov, O. L. Polyansky, J. Tennyson, E. F. Valeev, and A. G. Császár. CVRQD ab initio ground-state adiabatic potential energy surfaces for the water molecule. *Journal of Chemical Physics*, 125:204307 (18 pages), 2006.
- [BTHT05] R. J. Barber, J. Tennyson, G. J. Harris, and R. N. Tolchenov. A high accuracy computed water line list. *Monthly Notices of the Royal Astronomical Society*, 000:1–9, 2005.
- [BTHT06] R. J. Barber, J. Tennyson, G. J. Harris, and R. N. Tolchenov. A high-accuracy computed water line list. *Monthly Notices of The Royal Astronomical Society*, 368:1087–1094, 2006.
- [Bur77] H. G. Burchard. On the degree of convergence of piecewise polynomial approximation on optimal meshes. *Transactions of the American Mathematical Society*, 234:531–559, 1977.
- [BW08] R. Blatt and D. Wineland. Entangled states of trapped atomic ions. *Nature*, 453:1008–1015, 2008.
- [BWB07] C. D. Boone, K. A. Walker, and P. F. Bernath. Speed-dependent Voigt profile for water vapor in infrared remote sensing applications. *Journal of Quantitative Spectroscopy & Radiative Transfer*, 105:525–532, 2007.
- [CA04] M. Cafiero and L. Adamowicz. Molecular structure in non-Born-Oppenheimer quantum mechanics. *Chemical Physics Letters*, 387:136–141, 2004.
- [Cal01] F. Calogero. *Classical Many-Body Problems Amenable to Exact Treatments (Lecture Notes in Physics Monographs Vol. 66)*. Springer Verlag, 2001.

- [Cao04] T. Y. Cao (ed.). *Conceptual Foundations of Quantum Field Theory*. Cambridge University Press, new edition, 2004.
- [Car82] R. Carbó (ed.). *Current Aspects of Quantum Chemistry 1981*. Elsevier Scientific Publishing, 1982. Vol. 21 of the series Studies in Physical and Theoretical Quantum Chemistry.
- [Čár98] P. Čársky. Configuration interaction. *Published in [von98]*, pages 485–497, 1998.
- [Car06] A. Carati. On the existence of scattering solutions for the Abraham-Lorentz-Dirac equation. *Discrete and Continuous Systems B*, 6:471–480, 2006.
- [CAS98] A. G. Császár, W. D. Allen, and H. F. Schaefer III. In pursuit of the ab initio limit for conformational energy prototypes. *Journal of Chemical Physics*, 108:9751–9764, 1998.
- [CAYS00] A. G. Császár, W. D. Allen, Y. Yamaguchi, and H. F. Schaefer III. Ab initio determination of accurate ground electronic state potential energy hypersurfaces for small molecules. *Published in [JB00]*, pages 15–68, 2000.
- [CBA03] M. Cafiero, S. Bubin, and L. Adamowicz. Non-Born-Oppenheimer calculations of atoms and molecules. *Physical Chemistry Chemical Physics*, 5:1491–1501, 2003.
- [CBC⁺05] P. F. Coheur, P. F. Bernath, M. Carleer, R. Colin, O. L. Polyansky, N. F. Zobov, R. J. Barber, S. V. Shirin, and J. Tennyson. A 3000 K laboratory emission spectrum of water. *Journal of Chemical Physics*, 122:074307 (8 pages), 2005.
- [CBKR73] S. A. Clough, Y. Beers, G. P. Klein, and L. S. Rothman. Dipole-moment of water from stark measurements of h₂o, hdo, and d₂o. *Journal of Chemical Physics*, 59:2254–2259, 1973.
- [CC03] P. Cassam-Chenaï. Ab initio predictions for the Q-branch of the methane vibrational ground state. *Journal of Quantitative Spectroscopy & Radiative Transfer*, 82:251–277, 2003.
- [CC06] P. Cassam-Chenaï. On non-adiabatic potential energy surfaces. *Chemical Physics Letters*, 420:354–357, 2006.
- [CCF⁺05] A. G. Császár, G. Czakó, T. Furtenbacher, J. Tennyson, V. Szalay, S. V. Shirin, N. F. Zobov, and O. L. Polyansky. On equilibrium structures of the water molecule. *Journal of Chemical Physics*, 122:214305 (10 pages), 2005.
- [CCH01] G. K. L. Chan, A. J. Cohen, and N. C. Handy. Thomas-Fermi-Dirac-von Weizsäcker models in finite systems. *Journal of Chemical Physics*, 114:631–638, 2001.
- [CD80] P. Claverie and S. Diner. The concept of molecular structure in quantum theory: interpretation problems. *Israel Journal of Chemistry*, 19:53–81, 1980.

- [CdB80] S. D. Conte and C. de Boor. *Elementary Numerical Analysis*. McGraw-Hill, 3rd edition, 1980. Errata are available at Carl de Boor’s web site <http://pages.cs.wisc.edu/~deboor/> (accessed 29-Nov-2007).
- [CDL99] E. Cancès, M. Defranceschi, and C. Le Bris. Some recent mathematical contributions to quantum chemistry. *International Journal of Quantum Chemistry*, 74:553–557, 1999.
- [Cep99] D. M. Ceperley. Quantum Monte Carlo methods in chemistry. *Advances in Chemical Physics*, 93:1–38, 1999.
- [CFB⁺07] G. Czako, T. Furtenbacher, P. Barletta, A. G. Császár, V. Szalay, and B. T. Sutcliffe. Use of a nondirect-product basis for treating singularities in triatomic rotational-vibrational calculations. *Physical Chemistry Chemical Physics*, 9:3407–3415, 2007.
- [CFCM08] R. K. Chaudhuri, K. F. Freed, S. Chattopadhyay, and U. S. Mahapatra. Potential energy curve for isomerization of N_2H_2 and C_2H_4 using the improved virtual orbital multireference Møller–Plesset perturbation theory. *Journal of Chemical Physics*, 128:144304 (10 pages), 2008.
- [CG05] W. Cardoen and R. J. Gdanitz. Accurately solving the electronic schrödinger equation of atoms and molecules using explicitly correlated (r_{12} -) multireference configuration interaction. VII. the hydrogen fluorine molecule. *Journal of Chemical Physics*, 123:024304 (9 pages), 2005.
- [CHA50] C. F. Curtiss, J. O. Hirschfelder, and F. T. Adler. The separation of the rotational coordinates from the N-particle Schroedinger equation. *Journal of Chemical Physics*, 18:1638–1642, 1950.
- [Cha04] G. K. L. Chan. An algorithm for large scale density matrix renormalization group calculations. *Journal of Chemical Physics*, 120:3172–3178, 2004.
- [Che00] P. Chen *et al.* Submillimeter-wave measurement and analysis of the ground and $\nu_2 = 1$ states of water. *Astrophysical Journal Supplement Series*, 128:371–385, 2000.
- [CHG02] G. K. L. Chan and M. Head-Gordon. Highly correlated calculations with a polynomial cost algorithm: a study of the density matrix renormalization group. *Journal of Chemical Physics*, 116:4462–4476, 2002.
- [CHG03] G. K. L. Chan and M. Head-Gordon. Exact solution (within a triple-zeta, double polarization basis set) of the electronic schrodinger equation for water. *Journal of Chemical Physics*, 118:8551–8554, 2003.
- [Chi73] Y. N. Chiu. Reformulation and extension of Wigner-Witmer and Mulliken’s correlation rules for the spin and orbital states of diatomic molecules upon dissociation. *Journal of Chemical Physics*, 58:722–726, 1973.

- [CI92] X. Chapuisat and C. Iung. Vector parametrization of the N-body problem in quantum mechanics: Polyspherical coordinates. *Physical Review A*, 45:6217–6235, 1992.
- [CJ86] P. Claverie and G. Jona-Lasino. Instability of tunnelling and the concept of molecular structure in quantum mechanics: the case of pyramidal molecules and the enantiomer problem. *Physical Review A*, 33:2245–2253, 1986.
- [CK96] W. Cencek and W. Kutzelnigg. Accurate relativistic energies of one- and two-electron systems using Gaussian wave functions. *Journal of Chemical Physics*, 105:5878–5885, 1996.
- [CKG04] G. K. L. Chan, M. Kállay, and J. Gauss. State-of-the-art density matrix renormalization group and coupled cluster theory of the nitrogen binding curve. *Journal of Chemical Physics*, 121:6110–6116, 2004.
- [CKP⁺98a] A. G. Császár, J. S. Kain, O. L. Polyansky, N. F. Zobov, and J. Tennyson. Relativistic correction to the potential energy surface and vibration-rotation levels of water. *Chemical Physics Letters*, 293:317–323, 1998.
- [CKP⁺98b] A. G. Császár, J. S. Kain, O. L. Polyansky, N. F. Zobov, and J. Tennyson. Relativistic correction to the potential energy surface and vibration-rotation levels of water. *Chemical Physics Letters*, 293:317–323, 1998. erratum: 312, 613 (1999).
- [CKS⁺05] H. Cybulski, R. V. Krems, H. R. Sadeghpour, A. Dalgarno, J. Klos, G. C. Groenenboom, A. van der Avoir, D. Zgid, and G. Chałasiński. Interaction of NH($X^3\Sigma$) with He: Potential energy surface, bound states, and collisional Zeeman relaxation. *Journal of Chemical Physics*, 122:094307 (8 pages), 2005.
- [CM92] D. T. Colbert and W. H. Miller. A novel discrete variable representation for quantum mechanical reactive scattering via the S-matrix Kohn method. *Journal of Chemical Physics*, 96:1982–1991, 1992.
- [Col02] M. A. Collins. Molecular potential-energy surfaces for chemical reaction dynamics. *Theoretical Chemistry Accounts*, 108:313–324, 2002.
- [Con47] E. U. Condon. The Franck-Condon principle and related topics. *American Journal of Physics*, 15:365–374, 1947.
- [Coo84] R. J. Cook. Radiation reaction revised. *American Journal of Physics*, 52:894–895, 1984.
- [Coo87] D. B. Cook. Orbital energies: the aufbau principle and Koopman’s theorem in the UHF method. *International Journal of Quantum Chemistry*, 31:251–268, 1987.
- [Coo96] D. B. Cook. Virtual orbitals. *International Journal of Quantum Chemistry*, 60:793–801, 1996.
- [Coo02] D. L. Cooper (ed.). *Valence Bond Theory*. Elsevier Science B. V., 2002.

- [Cou66] C. A. Coulson. Note on the saddle-point character of Hartree and Hartree-Fock wave functions. *Published in [Löw66b]*, pages 97–103, 1966.
- [Cou97] L. H. Coudert. Analysis of the line positions and line intensities in the ν_2 band of the water molecule. *Journal of Molecular Spectroscopy*, 181:246–273, 1997.
- [Cou99] L. H. Coudert. Line frequency and line intensity analyses of water vapour. *Molecular Physics*, 96:941–954, 1999.
- [Cra04] C. J. Cramer. *Essentials of Computational Chemistry*. Wiley, 2nd edition, 2004.
- [CS80] J. M. Combes and R. Seiler. Spectral properties of atomic and molecular systems. *Appeared in [Wol80b]*, page 435, 1980.
- [CS00a] G. Chałasiński and M. M. Szczęśniak. State of the art and challenges of the ab initio theory of intermolecular interactions. *Chemical Review*, 100:4227–4252, 2000.
- [CS00b] T. D. Crawford and H. F. Schaefer III. An introduction to coupled cluster theory for computational chemists. *Reviews In Computational Chemistry*, 14:33–136, 2000. Also freely available on-line at http://zopyros.ccqc.uga.edu/lec_top/cc/cc.ps (accessed on 9-Mar-2008).
- [CSH07] M. T. Cvitaš, P. Soldán, and J. M. Hutson. Long range intermolecular forces in triatomic systems: connecting the atomdiatom and atomatomatom representations. *Molecular Physics*, 104:23–31, 2007.
- [CSV⁺07] T. D. Crawford, C. D. Sherrill, E. F. Valeev, J. T. Fermann, R. A. King, M. L. Leininger, S. T. Brown, C. L. Janssen, E. T. Seidl, J. P. Kenny, and W. D. Allen. PSI3: An open-source ab initio electronic structure package. *Journal of Computational Chemistry*, 28:1610–1616, 2007. see <http://www.psicode.org> (accessed on 21-08-2008).
- [CT98] D. P. Craig and T. Thirunamachandran. *Molecular Quantum Electrodynamics*. Dover Publications, 1998. Originally published in 1984.
- [CTDL77] C. Cohen-Tannoudji, B. Diu, and F. Laloë. *Quantum Mechanics (2 voll)*. Wiley-Interscience, 1977.
- [CTDRG97] C. Cohen-Tannoudji, J. Dupont-Roc, and G. Grynberg. *Photons and Atoms – Introduction to Quantum Electrodynamics*. Wiley-Interscience, 1997.
- [CTDRG98] C. Cohen-Tannoudji, J. Dupont-Roc, and G. Grynberg. *Atom-Photon Interactions: Basic Processes and Applications*. Wiley-Interscience, 1998.
- [CTL⁺01] A. G. Császár, G. Tarczay, M. L. Leininger, O. L. Polyansky, J. Tennyson, and W. D. Allen. Dream or reality: Complete basis set full configuration interaction potential energy hypersurfaces. *Published in [DSC01]*, pages 317–339, 2001.

- [CTT⁺02] A. Callegari, P. Theule, R. N. Tolchenov, N. F. Zobov, O. L. Polyansky, J. Tennyson, J. S. Muentner, and T. R. Rizzo. Dipole moments of highly vibrationally excited water. *Science*, 297:993–995, 2002.
- [Cus94] J. T. Cushing. *Quantum Mechanics: Historical Contingency and the Copenhagen Hegemony*. University of Chicago Press, 1994.
- [CW78] J. Czub and L. Wolniewicz. On the non-adiabatic potentials in diatomic molecules. *Molecular Physics*, 36:1301–1308, 1978.
- [DAL] DALTON, T. Helgaker, H. J. Aa Jensen, P. Jørgensen, J. Olsen, K. Ruud, H. Ågren, T. Andersen, K. L. Bak, V. Bakken, O. Christiansen, P. Dahle, E. K. Dalskov, T. Enevoldsen, B. Fernandez, H. Heiberg, H. Hettema, D. Jonsson, S. Kirpekar, R. Kobayashi, H. Koch, K. V. Mikkelsen, P. Norman, M. J. Packer, T. Saue, P. R. Taylor, and O. Vahtras, Oslo University, Norway, <http://www.kjemi.uio.no/software/dalton/dalton.html>.
- [Dav76] E. R. Davidson. *Reduced density matrices in quantum chemistry*. Academic Press, 1976.
- [DBGKR07] C. de Boor, C. Gout, A. Kunothe, and C. Rabut. Multivariate approximation: theory and applications. an overview. *Numerical Algorithms*, 48:1–9, 2007.
- [DC68] A. S. Dickinson and P. R. Certain. Calculation of matrix elements for the one-dimensional quantum mechanical problems. *Journal of Chemical Physics*, 49:4209–4211, 1968.
- [DCDW00] S. Daul, I. Ciofini, C. Daul, and S. R. White. Full-CI quantum chemistry using the density matrix renormalization group. *International Journal of Quantum Chemistry*, 79:331–342, 2000.
- [DD94] W. Duch and G. H. F. Diecksen. Size-extensivity corrections in configuration interaction methods. *Journal of Chemical Physics*, 101:3018–3030, 1994.
- [DF07] K. G. Dyall and K. Fægri Jr. . *Introduction to Relativistic Quantum Chemistry*. Oxford University Press, 2007.
- [DGZ⁺05] P. Dupre, T. Germain, N. Zobov, R. Tolchenov, and J. Tennyson. Continuous-wave cavity ringdown spectroscopy of the 8 nu polyad of water in the 25195–25340 cm⁻¹ range. *Journal of Chemical Physics*, 123:154307 (11 pages), 2005.
- [Dir] DIRAC, a relativistic ab initio electronic structure program, Release 3. 2 (2000), written by T. Saue, V. Bakken, T. Enevoldsen, T. Helgaker, H. J. Aa. Jensen, J. Laerdahl, K. Ruud, J. Thyssen and L. Visscher, <http://dirac.chem.sdu.dk>.
- [Dir29] P. A. M. Dirac. Quantum mechanics of many-electron systems. *Proceedings of the Royal Society of London Series A*, 123:714–733, 1929.
- [DKH98] A. J. Dobbyn, P. J. Knowles, and R. J. Harrison. Parallel internally contracted multireference configuration interaction. *Journal of Computational Chemistry*, 19:215–228, 1998.

- [DL56] A. Dalgarno and J. T. Lewis. The representation of long range forces by series expansions. I: The divergence of the series. II: The complete perturbation calculation of long range forces. *Proceedings of the Physical Society (London)*, A69:57–64, 1956.
- [DL97] M. Defranceschi and C. Le Bris. Computing a molecule: A mathematical viewpoint. *Journal of Mathematical Chemistry*, 21:1–30, 1997.
- [DL99] M. Defranceschi and C. Le Bris. Computing a molecule in its environment: A mathematical viewpoint. *International Journal of Quantum Chemistry*, 71:227–250, 1999.
- [dlM05] R. de la Madrid. The role of the Rigged Hilbert Space in Quantum Mechanics. *European Journal of Physics*, 26:287–312, 2005.
- [dlMM01] R. de la Madrid Modino. *Quantum Mechanics in Rigged Hilbert Space Language*. PhD thesis, Departamento de física teórica – Universidad de Valladolid, 2001. Available from <http://www.physics.ucsd.edu/~rafa/dissertation.html> (accessed on 4-Oct-2007).
- [DMMV00] L. E. Dardenne, N. Makiuchi, L. A. C. Malbouisson, and J. D. M. Vianna. Multiplicity, instability and SCF convergence problems in Hartree-Fock solutions. *International Journal of Quantum Chemistry*, 76:600–610, 2000.
- [Dod] D. S. Dodson, personal communication, 2007.
- [Dod72] D. S. Dodson. *Optimal-order approximation by polynomial spline functions*. PhD thesis, Purdue University, West Lafayette, IN, USA, 1972.
- [DRS81] G. H. F. Dierksen, B. Roos, and A. J. Sadlej. Legitimate calculation of 1st-order molecular-properties in the case of limited CI functions – Dipole-moments. *Chemical Physics*, 59:29–39, 1981.
- [DS77] E. R. Davidson and D. W. Silver. Size consistency in the dilute helium gas electronic structure. *Chemical Physics Letters*, 52:403–406, 1977.
- [DS03] A. Dutta and C. D. Sherrill. Full configuration interaction potential energy curves for breaking bonds to hydrogen: An assessment of single-reference correlation methods. *Journal of Chemical Physics*, 118:1610–1619, 2003.
- [DSC01] J. Demaison, K. Sarka, and E. A. Cohen (eds.). *Spectroscopy from Space*. NATO Science Series. II. Mathematics, Physics And Chemistry – Vol. 20, 2001.
- [DTWM08] R. Dawes, D. L. Thompson, A. F. Wagner, and M. Minkoff. Interpolating moving least-squares methods for fitting potential energy surfaces: A strategy for efficient automatic data point placement in high dimensions. *Journal of Chemical Physics*, 128:084107 (10 pages), 2008.
- [Duc91] W. Duch. Configuration interaction method: the past and future perspectives. *Journal of Molecular Structure: THEOCHEM*, 234:27–49, 1991.

- [Dun89] T. H. Dunning, Jr. Gaussian-basis sets for use in correlated molecular calculations. 1. the atoms Boron through Neon and Hydrogen. *Journal of Chemical Physics*, 90:1007–1023, 1989.
- [DW83] G. H. F. Diercksen and S. Wilson (eds.). *Methods in Computational Molecular Physics*. D. Reidel, Dordrecht, 1983.
- [Dya94] K. G. Dyall. An exact separation of the spin-free and spin-dependent terms of the Dirac-Coulomb-Breit hamiltonian. *Journal of Chemical Physics*, 100:2118–2127, 1994.
- [EA08] P. Echenique and J. L. Alonso. A mathematical and computational review of Hartree-Fock SCF methods in quantum chemistry. *Molecular Physics*, 105:3057–3098, 2008.
- [EÅK00] O. Engkvist, P. O. Åstrand, and G. Karlström. Accurate intermolecular potentials obtained from molecular wave functions: Bridging the gap between quantum chemistry and molecular simulations. *Chemical Review*, 100:4087–4108, 2000.
- [EAS07] F. A. Evangelista, W. D. Allen, and H. F. Schaefer III. Coupling term derivation and general implementation of state-specific multireference coupled cluster theories. *Journal of Chemical Physics*, 127:024102 (17 pages), 2007.
- [Edm96] A. R. Edmonds. *Angular momentum in quantum mechanics*. Princeton University Press, 1996. Reprint of the revised second edition from 1960.
- [EM08] C. R. Evenhuis and U. Manthe. Calculating vibrational spectra using modified Shepard interpolated potential energy surfaces. *Journal of Chemical Physics*, 129:024104 (10 pages), 2008.
- [EMP92] M. Ernzerhof, C. M. Marian, and S. D. Peyerimhoff. On the calculation of 1st-order properties - Expectation value versus energy derivative approach. *International Journal of Quantum Chemistry*, 43:659–668, 1992.
- [EMS] The Extensible Computational Chemistry Environment Basis Set Exchange v 1.2.1, see refs. [Fel96, SDE⁺07]. The web site of the database is <https://bse.pnl.gov/bse/portal> (accessed 24-Sep-2008).
- [ESA⁺08] F. A. Evangelista, A. C. Simmonett, W. D. Allen, H. F. Schaefer III, and J. Gauss. Triple excitations in state-specific multireference coupled cluster theory: Application of Mk-MRCCSDT and Mk-MRCCSDT-n methods to model systems. *Journal of Chemical Physics*, 128:124104 (13 pages), 2008.
- [Ess77] H. Essén. The physics of the Born-Oppenheimer approximation. *International Journal of Quantum Chemistry*, 12:721–735, 1977.
- [Eva93] G. Evans. *Practical Numerical Integration*. John Wiley & Sons, 1993.
- [Fas03] G. E. Fasshauer. *Multivariate Meshfree Approximation (lecture notes)*. 2003. Available from the author’s web site at <http://math.iit.edu/fass/603.html> (accessed 10-Sep-2008).

- [Fas06] G. E. Fasshauer. Meshfree methods. *Published in Ref. [RS06]*, pages 33–97, 2006. Also available at the author’s website at <http://math.iit.edu/fass/MeshfreeNano.pdf> (accessed 10-Sep-2008).
- [Fas07] G. E. Fasshauer. *Meshfree Approximation Methods With Matlab*. World Scientific, 2007.
- [FBJ97] C. Froese Fisher, T. Brage, and P. Jönsson. *Computational Atomic Structure: An MCHF Approach*. Taylor & Francis, 1997.
- [FC08] T. Furtenbacher and A. G. Császár. On employing H_2^{16}O , H_2^{17}O , H_2^{18}O , and D_2^{16}O lines as frequency standards in the 15–170 cm^{-1} window. *Journal of Quantitative Spectroscopy & Radiative Transfer*, 109:1234–1251, 2008.
- [FCPM76] J. M. Flaud, C. Camy-Peyret, and J. P. Maillard. Higher ro-vibrational levels of H_2O deduced from high-resolution oxygen-hydrogen flame spectra between 2800–6200 cm^{-1} . *Molecular Physics*, 32:499–521, 1976.
- [FCT07] T. Furtenbacher, A. Császár, and J. Tennyson. MARVEL: measured active rotational-vibrational energy levels. *Journal of Molecular Spectroscopy*, 245:115–125, 2007.
- [Fel68] W. Feller. *An Introduction to Probability Theory and Its Applications*, volume 1. John Wiley & Sons, 3rd edition, 1968.
- [Fel96] D. Feller. *Journal of Computational Chemistry*, 17:1571–1586, 1996.
- [FMT91] J. A. Fernley, S. Miller, and J. Tennyson. Band origins for water up to 22000 cm^{-1} - A comparison of spectroscopically determined potential-energy surfaces. *Journal of Molecular Spectroscopy*, 150:597–609, 1991.
- [FOZ98] G. Fano, F. Ortolani, and L. Ziosi. The density matrix renormalization group method: Application to the PPP model of a cyclic polyene chain. *Journal of Chemical Physics*, 108:9246–9252, 1998.
- [FP99] D. Feller and K. A. Peterson. Re-examination of atomization energies for the Gaussian-2 set of molecules. *Journal of Chemical Physics*, 110:8384–8396, 1999.
- [FPC⁺03] J. M. Flaud, C. Piccolo, B. Carli, A. Perrin, L. H. Coudert, J. L. Teffo, and L. R. Brown. Molecular line parameters for the MIPAS (Michelson interferometer for passive atmospheric sounding) experiment. *Atmospheric and Oceanic Optics*, 16:172–181, 2003.
- [FS00] D. Feller and J. A. Sordo. Performance of CCSDT for diatomic dissociation energies. *Journal of Chemical Physics*, 113:485–493, 2000.
- [Fuk80] H. Fukutome. Unrestricted Hartree-Fock Theory and Its Application to Molecular and Chemical Reactions. *International Journal of Quantum Chemistry*, 20:955–1065, 1980.

- [FW03] A. L. Fetter and J. D. Walecka. *Quantum Theory of Many-Particle Systems*. Dover Publishing, 2003. Originally published in 1969.
- [GA88] R. J. Gdanitz and R. Ahlrichs. The averaged coupled-pair functional (ACPF) – A size-extensive modification of MR CI(SD). *Chemical Physics Letters*, 143:413–420, 1988.
- [Gab] Gabedit is a graphical user interface to computational chemistry packages. It can be found at <http://gabedit.sourceforge.net/> (accessed 18-Oct-2008).
- [Gal80] J. A. Gallas. Some matrix elements for Morse oscillators. *Physical Review A*, 21:1829–1833, 1980.
- [Gal05] G. A. Gallup. *Valence Bond Methods: Theory and Applications*. Cambridge University Press, 2005.
- [GB81] M. García-Sucre and M. Bunge. Geometry of a quantal system. *International Journal of Quantum Chemistry*, 19:83–93, 1981.
- [GBL⁺05] R. J. Gdanitz, G. D. Black, C. S. Lansing, B. J. Palmer, and K. L. Schuchardt. Registering the AMICA electronic structure code in the extensible computational chemistry environment. *Journal of Computational Chemistry*, 26:214–225, 2005. The web sites which in the past hosted the software AMICA, <http://www.tu-bs.de/~gdanitz/amica/> and <http://gdanitz.hec.utah.edu/amica>, are not working at the time of writing (29-Sep-2008).
- [GC93] M. Gutowski and G. Chalaśiński. Critical evaluation of some computational approaches to the problem of basis set superposition error. *Journal of Chemical Physics*, 98:5540–5554, 1993.
- [GCL⁺97] J. K. Gregory, D. C. Clary, K. Liu, M. G. Brown, and R. J. Saykally. The water dipole moment in water clusters. *Science*, 275:814–817, 1997.
- [GD07] P. Griffiths and J. A. De Haseth. *Fourier Transform Infrared Spectrometry*. Wiley-Interscience, 2nd edition, 2007.
- [Gda01] R. J. Gdanitz. A new version of the Multireference Averaged Coupled-Pair Functional (MR-ACPF-2). *International Journal of Quantum Chemistry*, 85:281–300, 2001.
- [GDL03] P. Geerlings, F. De Proft, and W. Langenaeker. Conceptual density functional theory. *Chemical Reviews*, 103:1793–1873, 2003.
- [GF00] I. M. Gelfand and S. V. Fomin. *Calculus of Variations*. Dover Publishing, 2000. Originally published in 1963.
- [GH07] M. Griebel and J. Hamaekers. Sparse grids for the Schrödinger equation. *Mathematical Modelling and Numerical Analysis*, 41:215–247, 2007.

- [GHK⁺06] G. Gabrielse, D. Hanneke, T. Kinoshita, M. Nio, and B. Odom. New determination of the fine structure constant from the electron g value and QED. *Physical Review Letters*, 97:030802 (4 pages), 2006. Erratum: vol. 99, 039902(E) (2 pages) (2007).
- [Gie00] F. Gieres. Mathematical surprises and Dirac's formalism in quantum mechanics. *Reports on the Progress of Physics*, 63:1893–1931, 2000.
- [Gre81] H. H. Grelland. n -local energies as accuracy measures on approximate wave functions. *International Journal of Quantum Chemistry*, 125:847–857, 1981.
- [GRH91] E. K. U. Gross, E. Runge, and O. Heinonen. *Many Particle Theory*. Institute of Physics Publishing, 1991.
- [Gri04] D. J. Griffiths. *Introduction to Quantum Mechanics*. Addison Wesley, 2nd edition, 2004.
- [Gri05] M. Griebel. Sparse grids and related approximation schemes for higher dimensional problems. *Proceedings of the conference on Foundations of Computational Mathematics (FoCM05), Santander, Spain, 2005*. Accessible at <http://wissrech.ins.uni-bonn.de/research/pub.php4?list=griebel> (accessed 12-Dec-2007).
- [Gro00] J. Grotendorst (ed.). *Modern Methods and Algorithms of Quantum Chemistry*. John von Neumann Institute for Computing – NIC Series, 2nd edition, 2000. Freely available on-line at <http://www.fz-juelich.de/nic-series/NIC-Series-d.html> (accessed 21-03-2008).
- [GRR⁺93] W. Gabriel, E. A. Reinsch, P. Rosmus, S. Carter, and N. C. Handy. Theoretical integrated vibrational band intensities of water-vapor. *Journal of Chemical Physics*, 99:897–900, 1993.
- [GTT⁺07] Y. Guo, I. Tokmakov, D. L. Thompson, A. F. Wagner, and M. Minkoff. Interpolating moving least-squares methods for fitting potential energy surfaces: improving efficiency via local approximants. *Journal of Chemical Physics*, 127:214106 (8 pages), 2007.
- [HA70] S. Huzinaga and C. Arnau. Virtual orbitals in Hartree–Fock theory. *Physical Review A*, 1:1285–1288, 1970.
- [HA71] S. Huzinaga and C. Arnau. Virtual orbitals in Hartree–Fock theory. II. *Journal of Chemical Physics*, 54:1948–1951, 1971.
- [HAG92] D. R. Herschbach, J. S. Avery, and O. Goscinski (Eds.). *Dimensional Scaling in Chemical Physics*. Springer, 1992.
- [Hal91] G. G. Hall. Computational quantum chemistry - then and now. *Journal of Molecular Structure: THEOCHEM*, 234:13–18, 1991.
- [Ham89] M. Hamermesh. *Group Theory and its Application to Physical Problems*. Dover Publications, 1989. Originally published in 1962.

- [Har04a] F. E. Harris. Current methods for Coulomb few-body problems. *Advances in Quantum Chemistry*, 47:129–155, 2004.
- [Har04b] M. Harwit. The Herschel mission. *Advances in Space Research*, 34:568–572, 2004.
- [HBB⁺05a] A. Hjalmarson, P. Bergman, N. Biver, H. G. Floren, U. Frisk, and T. Hasegawa *et al.* Recent astronomy highlights from the Odin satellite. *Advances in Space Research*, 36:1031–1047, 2005.
- [HBB05b] X. Huang, B. J. Braams, and J. M. Bowman. Ab initio potential energy and dipole moment surfaces for H_5O_2^+ . *Journal of Chemical Physics*, 122:044308 (12 pages), 2005.
- [HBR08] J.-M. Hartmann, C. Boulet, and D. Robert. *Collisional Effects on Molecular Spectra*. Elsevier, 2008.
- [HC01] N. C. Handy and A. J. Cohen. Left-right correlation energy. *Molecular Physics*, 89:403–412, 2001.
- [HCC06] J. Hachmann, W. Cardoen, and G. K. L. Chan. Multireference correlation in long molecules with the quadratic scaling density matrix renormalization group. *Journal of Chemical Physics*, 125:144101 (12 pages), 2006.
- [HD67] R. T. Hall and J. M. Dowling. Pure rotational spectrum of water vapor. *Journal of Chemical Physics*, 47:2454–2461, 1967. Erratum: 54:4968 (1971).
- [HEG65] D. O. Harris, G. G. Egerholm, and W. D. Gwinn. Calculations of matrix elements for one-dimensional quantum-mechanical problems and the application to anharmonic oscillators. *Journal of Chemical Physics*, 43:1515–1517, 1965.
- [Her06] J. A. Heras. Preacceleration without radiation: The nonexistence of preradiation phenomenon. *American Journal of Physics*, 74:1025–1030, 2006.
- [Her07] J. A. Heras. Reply to refs. [Jac07] and [Hni07]. *American Journal of Physics*, 75:847–850, 2007.
- [Het00] H. Hettema. *Quantum Chemistry: Classic Scientific Papers*. World Scientific, 2000.
- [HHR96] T. S. Ho, T. Hollebeek, and H. Rabitz. A global H_2O potential energy surface for the reaction $\text{O}(^1\text{D}) + \text{H}_2 \rightarrow \text{OH} + \text{H}$. *Journal of Chemical Physics*, 105:10472–10486, 1996.
- [HHR99] T. Hollebeek, T.-S. Ho, and H. Rabitz. Constructing multidimensional molecular potential energy surfaces from an initio data. *Annual Review of Physical Chemistry*, 50:537–570, 1999.
- [HHR01] T. Hollebeek, T.-S. Ho, and H. Rabitz. Efficient potential energy surfaces from partially filled ab initio data over arbitrarily shaped regions. *Journal of Chemical Physics*, 114:3940–3944, 2001.

- [Hil82] R. C. Hilborn. Einstein coefficients, cross sections, f values, dipole moments, and all that. *American Journal of Physics*, 50:982–986, 1982. Erratum: 51, 471 (1983).
- [Hil85] R. N. Hill. Rates of convergence and error estimation formulas for the Rayleigh-Ritz variational method. *Journal of Chemical Physics*, 83:1173–1196, 1985.
- [Hin04] A. Hinchliffe (ed.). *Chemical Modelling: Applications and Theory*, volume 3. Royal Society of Chemistry Publishing, 2004.
- [Hir83] J. O. Hirschfelder. My adventures in theoretical chemistry. *Annual Review of Physical Chemistry*, 34:1–29, 1983.
- [HIT] The HITRAN 2004 database is available electronically from <http://www.cfa.harvard.edu/hitran/> (accessed on 12-Feb-2008).
- [HJR99] T. Helgaker, M. Jaszunski, and K. Ruud. Ab initio methods for the calculation of NMR shielding and indirect spin-spin coupling constants. *Chemical Review*, 99:293–352, 1999.
- [HK05] Z. Huang and S. Kais. Entanglement as measure of electronelectron correlation in quantum chemistry calculations. *Chemical Physics Letters*, 413:1–5, 2005.
- [HKKN97] T. Helgaker, W. Klopper, H. Koch, and J. Noga. Basis set convergence of correlated calculations on water. *Journal of Chemical Physics*, 106:9639–9646, 1997.
- [HMF92] F. E. Harris, H. J. Monkhorst, and D. L. Freeman. *Algebraic and Diagrammatic Methods in Many-Fermion Theory*. Oxford University Press, 1992.
- [HML79] R. E. Howard, A. D. McLean, and W. A. Lester Jr. Extended basis first-order CI study of the $^1a'$, $^3a''$, $^1a''$, and $\tilde{B}^1a'$ potential energy surfaces of the $\text{o}(^3\text{p}, ^1\text{d}) + \text{h}_2(^1\sigma_g^+)$ reaction. *Journal of Chemical Physics*, 71:2412–2420, 1979.
- [Hni07] V. Hnizdo. Comment on [Her06]. *American Journal of Physics*, 75:845–846, 2007.
- [HOJ⁺08] S. Høst, J. Olsen, B. Jansík, L. Thøgersen, P. Jørgensen, and T. Helgaker. The augmented Roothan-Hall method for optimizing Hartree-Fock and Kohn-Sham density matrices. *Journal of Chemical Physics*, 129:124106 (12 pages), 2008.
- [Hol04] J. M. Hollas. *Modern Spectroscopy*. Wiley, 4th edition, 2004.
- [Høs05] S. Høst. Properties of atoms and small molecules AND linear scaling methods. Progress report, Department of Chemistry – Theoretical Chemistry Group – University of Aarhus, Denmark, 2005. Available on-line at http://www.chem.au.dk/~teo/mainmenu/Staff/Stinne/progress_report.pdf (accessed 25-Sep-2008).
- [Hou12] R. A. Houston. The mechanics of the water molecule. *Proceedings of the Royal Society of London A*, 584:102–105, 1912.

- [HPS96] N. C. Handy, J. A. Pople, and I. Shavitt. Samuel Francis Boys. *Journal of Physical Chemistry*, 100:6007–6016, 1996.
- [HR96] T. S. Ho and H. Rabitz. A general method for constructing multidimensional molecular potential energy surfaces from ab initio calculations. *Journal of Chemical Physics*, 104:2584–2597, 1996.
- [HR00] T.-S. Ho and H. Rabitz. Proper construction of ab initio global potential surfaces with accurate long-range interactions. *Journal of Chemical Physics*, 113:3960–3968, 2000.
- [HR03] T.-S. Ho and H. Rabitz. Reproducing kernel hilbert space interpolation methods as a paradigm of high dimensional model representations: Application to multi-dimensional potential energy surface construction. *Journal of Chemical Physics*, 119:6433–6442, 2003.
- [HS00a] M. P. Hodges and A. J. Stone. A new representation of the dispersion interaction. *Molecular Physics*, 98:275–286, 2000.
- [HS00b] W. Hunziker and I. M. Sigal. The quantum n -body problem. *Journal of Mathematical Physics*, 41:3448–3510, 2000.
- [HS07a] P. C. Hiberty and S. Shaik. A survey of recent developments in ab initio valence bond theory. *Journal of Computational Chemistry*, 28:137–151, 2007.
- [HS07b] J. M. Hutson and P. Soldán. Molecular collisions in ultracold atomic gases. *International Reviews in Physical Chemistry*, 26:1–28, 2007.
- [HSA93] S. Hammes-Schiffer and H. S. Andersen. The advantages of the General Hartree-Fock method for future computer simulation of materials. *Journal of Chemical Physics*, 99:1901–1913, 1993.
- [Hua01] Y. Huang. *Determining Analytical Potential Energy Functions of Diatomic Molecules by Direct Fitting*. PhD thesis, University of Waterloo, Waterloo, Ontario, Canada, 2001.
- [Hun75] G. Hunter. Conditional probability amplitudes in wave mechanics. *International Journal of Quantum Chemistry*, 9:237–242, 1975.
- [IE05] R. Islampour and H. Ebrahimi. The molecular hamiltonian in internal coordinates. *Molecular Physics*, 103:1425–1430, 2005.
- [Isl03] R. Islampour. Generalized coordinates molecular hamiltonian. *Molecular Physics*, 101:2489–2496, 2003.
- [IZ06] C. Itzykson and J. B. Zuber. *Quantum Field Theory*. Dover Publications, 2006. Originally published in 1980.
- [Jac98] J. D. Jackson. *Classical Electrodynamics*. Wiley, 3rd edition, 1998.

- [Jac07] J. D. Jackson. Comment on [Her06]. *American Journal of Physics*, 75:844–845, 2007.
- [Jay98] D. Jayatilaka. Electron spin resonance g tensors from General Hartree-Fock calculations. *Journal of Chemical Physics*, 108:7587–7594, 1998.
- [JB00] P. Jensen and P. R. Bunker. *Computational Molecular Spectroscopy*. Wiley and Sons, 2000.
- [JC33] H. M James and A. S. Coolidge. The ground state of the hydrogen molecule. *Journal of Chemical Physics*, 1:825–835, 1933.
- [JC87] J. L Jiménez and I. Campos. A critical examination of the Abraham-Lorentz equation for a radiating charged particle. *American Journal of Physics*, 55:1017–1023, 1987.
- [JCP⁺08] M. Jeziorska, W. Cencek, K. Patkowski, B. Jeziorski, and K. Szalewicz. Complete basis set extrapolations of dispersion, exchange, and coupled-clusters contributions to the interaction energy: A helium dimer study. *International Journal of Quantum Chemistry*, 108:2053–2075, 2008.
- [Jen] A detailed pedagogical exposition of Lagrange multipliers is reported in Steuard Jensen’s Web site at <http://www.slimy.com/~steuard/teaching/tutorials/Lagrange.html> (accessed 10-Dec-2007).
- [Jen96] F. Jensen. The magnitude of intramolecular basis set superposition error. *Chemical Physics Letters*, 261:633–636, 1996.
- [Jen05] F. Jensen. Estimating the Hartree-Fock limit from finite basis set calculations. *Theoretical Chemistry Accounts*, 113:267–273, 2005.
- [Jen06] F. Jensen. *Introduction to Computational Chemistry*. Wiley, 2nd edition, 2006.
- [JHSC⁺08] N. Jacquinet-Husson, N. A. Scott, A. Chédin, L. Crépeau, R. Armante, V. Capelle, J. Orphal, A. Coustenis, C. Boone, N. Poulet-Crovisier, A. Barbe, M. Birk, L. R. Brown, C. Camy-Peyret, C. Claveau, K. Chance, N. Christidis, C. Clerbaux, P. F. Coheur, V. Dana, L. Daumont, M. R. De Backer-Barilly, G. Di Lonardo, J. M. Flaud, A. Goldman, A. Hamdouni, M. Hess, M. D. Hurley, D. Jacquemart, I. Kleiner, P. Köpke, J. Y. Mandin, S. Massie, S. Mikhailenko, N. Nemtchinov, A. Nikitin, D. Newnham, A. Perrin, V. I. Perevalov, S. Pinnock, L. Régalia-Jarlot, C. P. Rinsland, A. Rublev, F. Schreier, L. Schult, K. M. Smith, S. A. Tashkun, J. L. Teffo, R. A. Toth, V. G. Tyuterev, J. Vander Auwera, P. Varanasi, and G. Wagner. The GEISA spectroscopic database: Current and future archive for Earth and planetary atmosphere studies. *Journal of Quantitative Spectroscopy & Radiative Transfer*, 109:1043–1059, 2008.
- [JJ93] U. G. Jørgensen and P. Jensen. The dipole-moment surface and the vibrational transition moments of H₂O. *Journal of Molecular Spectroscopy*, 161:219–242, 1993.

- [JJ00] H. Jeffreys and B. Jeffreys. *Methods of Mathematical Physics*. Cambridge University Press, 3rd edition, 2000.
- [JK08] R. Jaquet and W. Kutzelnigg. Non-adiabatic theory in terms of a single potential energy surface. the vibration-rotation levels of h_2^+ and d_2^+ . *Chemical Physics*, 346:69–76, 2008.
- [JM06] T. Juhász and D. A. Mazziotti. The cumulant two-particle reduced density matrix as a measure of electron correlation and entanglement. *Journal of Chemical Physics*, 125:174105 (5 pages), 2006.
- [Joh07] W. R. Johnson. *Atomic Structure Theory: Lectures on Atomic Physics*. Springer, 2007.
- [Jon97] D. S. Jones. *Introduction to Asymptotics: A Treatment Using Nonstandard Analysis*. Word Scientific, 1997.
- [JPL] The JPL catalog for water is available electronically from: <http://spec.jpl.nasa.gov/ftp/pub/catalog/catdir.html> (accessed on 12-Feb-2008).
- [Jup78] D. L. B. Jupp. Approximation to data by splines with free knots. *SIAM Journal on Numerical Analysis*, 15:328–343, 1978.
- [KA93] P. M. Kozłowski and L. Adamowicz. Equivalent quantum approach to nuclei and electrons in molecules. *Chemical Reviews*, 93:2007–2022, 1993.
- [Kap06] I. G. Kaplan. *Intermolecular Interactions*. Wiley, 2006.
- [Kar86] P. Karadakov. The spin-projected Hartree-Fock method – Direct optimization schemes and stability conditions. *International Journal of Quantum Chemistry*, 30:239–264, 1986.
- [Kar94] J. Karkowski. Statistical theory of spectra. *International Journal of Quantum Chemistry*, 51:425–437, 1994.
- [Kar98] P. Karadakov. New trends in ab initio valence bond theory. *Annual Reports Section C: Physical Chemistry*, 94:3–48, 1998.
- [Kar06] H. Karabulut. The physical meaning of Lagrange multipliers. *European Journal of Physics*, 27:709–718, 2006.
- [Kar08] J. Karwowski. A separable model of n interacting particles. *International Journal of Quantum Chemistry*, 108:2253–2260, 2008.
- [KBP96] W. Kohn, A. D. Becke, and R. G. Parr. Density functional theory of electronic structure. *Journal of Chemical Physics*, 100:12974–12980, 1996.
- [KC91] D. Kincaid and W. Cheney. *Numerical Analysis*. Brooks/Cole Publishing Company, 1991.

- [KC04] J. Karwowski and L. Cyrnek. Harmonium. *Annalen der Physik*, 13:181–193, 2004.
- [KDB68] W. Kutzelnigg, G. Del Re, and G. Berthier. Correlation coefficients for electronic wave functions. *Physical Review*, 172:49–59, 1968.
- [KDH92] R. A. Kendall, T. H. Dunning Jr. , and R. J. Harrison. Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions. *Journal of Chemical Physics*, 96:6796–6806, 1992.
- [KH84] P. J. Knowles and N. C. Handy. A new determinant-based full configuration interaction method. *Chemical Physics Letters*, 111:315–, 1984.
- [KH89] P. J. Knowles and N. C. Handy. A determinant based full configuration interaction program. *Computer Physics Communications*, 54:75–83, 1989.
- [KI92] W. Kutzelnigg and J. D. Morgan III. Rates of convergence of the partial-wave expansions of atomic correlation energies. *Journal of Chemical Physics*, 86:4484, 1992.
- [KJ06] W. Kutzelnigg and R. Jaquet. Explicitly correlated potential energy surface of H-3(+), including relativistic and adiabatic corrections. *Journal of Chemical Physics*, 364:2855–2876, 2006.
- [KK87] W. Klopper and W. Kutzelnigg. Møller-Plesset calculations taking care of the correlation cusp. *Chemical Physics Letters*, 134:17–22, 1987.
- [KL05] W. Kutzelnigg and W. J. Liu. Quasirelativistic theory equivalent to fully relativistic theory. *Journal of Chemical Physics*, 123:211102 (4 pages), 2005.
- [Kla85a] B. Klahn. The convergence of CI calculations for atomic and molecular electronic bound states in a basis of floating Gauss orbitals. *Journal of Chemical Physics*, 83:5754–5759, 1985.
- [Kla85b] B. Klahn. A generalisation of the Müntz-Szász theorem to floating exponents with applications to Gauss- and Slater-type functions. *Journal of Chemical Physics*, 83:5749–5753, 1985.
- [Klo00] W. Klopper. R12 methods, gaussian geminals. *Published in [Gro00]*, pages 181–229, 2000.
- [Klo01] W. Klopper. Highly accurate coupled-cluster singlet and triplet pair energies from explicitly correlated calculations in comparison with extrapolation techniques. *Molecular Physics*, 99:481–507, 2001.
- [KM69] H. Kreek and W. J. Meath. Charge-overlap effects. Dispersion and induction forces. *Journal of Chemical Physics*, 50:2289–2302, 1969.
- [KM84] B. Klahn and J. D. Morgan III. Rates of convergence of variational calculations and of expectation values. *Journal of Chemical Physics*, 81:410–433, 1984.

- [KM06] A. Karton and J. M. L. Martin. Comment on ref. [Jen05]. *Theoretical Chemistry Accounts*, 115:330–333, 2006.
- [KMA81] A. Koide, W. J. Meath, and A. R. Allnatt. Second order charge overlap effects and damping functions for isotropic atomic and molecular interactions. *Chemical Physics*, 58:105–119, 1981.
- [KMM⁺05] D. P. Kratz, M. G. Mlynczaka, C. J. Mertensa, H. Brindley, L. L. Gordley, J. Martin-Torres, F. M. Miskolczy, and D. D. Turner. An inter-comparison of far-infrared line-by-line radiative transfer models. *Journal of Quantitative Spectroscopy & Radiative Transfer*, 90:323–341, 2005.
- [KMNC05] S. Kassı, P. Macko, O. Naumenko, and A. Campargue. The absorption spectrum of water near 750 nm by cw-crds: contribution to the search of water dimer absorption. *Physical Chemistry Chemical Physics*, 7:2460–2467, 2005.
- [KMSW92] M. Klein, A. Martinez, R. Seiler, and X. P. Wang. On the Born-Oppenheimer expansion for polyatomic-molecules. *Communications In Mathematical Physics*, 143:607–639, 1992.
- [KMTNV06] W. Klopper, F. R. Manby, S. Ten-No, and E. F. Valeev. R12 methods in explicitly correlated molecular electronic structure theory. *International Reviews in Physical Chemistry*, 25:427–468, 2006.
- [KMW01] J. Kobus, D. Moncrieff, and S. Wilson. Comparison of the polarizabilities and hyperpolarizabilities obtained from finite basis set and finite difference Hartree-Fock calculations for diatomic molecules. *Journal of Physics B – Atomic Molecular and Optical Physics*, 34:5127–5143, 2001.
- [KNN05] Y. Kurokawa, H. Nakashima, and H. Nakatsuji. Free iterative-complement-interaction calculations of the hydrogen molecule. *Physical Review A*, 72:062502, 2005.
- [Knu98] D. E. Knuth. *The Art of Computer Programming*, volume 3 – Sorting and Searching. Addison-Wesley Professional, 2nd edition, 1998.
- [KNV05] S. Kedzuch, J. Noga, and P. Valiron. Universal R12 suited basis sets for atoms from lithium to fluorine. *Molecular Physics*, 103:999–1005, 2005.
- [Kog89] T. Koga. Addendum to the van der Waals constants among ground-state hydrogen atoms. *Journal of Chemical Physics*, 90:605–606, 1989.
- [KR60] W. Kolos and C. C. Roothaan. Accurate electronic wave functions for the H-2 molecule. *Reviews of Modern Physics*, 32:219–232, 1960.
- [Kra00] H. Kragh. Relativity and quantum theory from Sommerfeld to Dirac. *Annalen der Physik*, 9:961–974, 2000.
- [Krü97] T. Krüger. EPR correlations in the molecular domain. *International Journal of Quantum Chemistry*, 64:679–687, 1997.

- [KS62] N. R. Kestner and O. Sinanoğlu. Study of electron correlation in helium-like systems using an exactly soluble model. *Physical Review*, 128:2687–2692, 1962.
- [KS97] G. S. Kedziora and I. Shavitt. Calculation and fitting of potential energy and dipole moment surfaces for the water molecule: Fully ab initio determination of vibrational transition energies and band intensities. *Journal of Chemical Physics*, 106:8733–8745, 1997.
- [KS03] J. A. Karwowski and I. Shavitt. A survey of recent developments in ab initio valence bond theory. *Published in [WMB03]*, 2:227–271, 2003.
- [KS07] K. N. Kudin and G. E. Scuseria. Converging self-consistent field equations in quantum chemistry – Recent achievements and remaining challenges. *ESAIM-Mathematical Modelling And Numerical Analysis – Modélisation Mathématique et Analyse Numérique*, 41:281–296, 2007.
- [KSA⁺96] M. F. Kessler, J. A. Steinz, M. E. Anderegg, J. Clavel, G. Drechsel, and P. Estaria *et al.* The infrared space observatory (iso) mission. *Astronomy and Astrophysics*, 315:L27–L31, 1996.
- [KSC02] K. N. Kudin, G. E. Scuseria, and E. Cancès. A black-box self-consistent field convergence algorithm: One step closer. *Journal of Chemical Physics*, 116:8255–8261, 2002.
- [KSH96] V. Kello, A. J. Sadlej, and B. A. Hess. Relativistic effects on electric properties of many-electron systems in spin-averaged Douglas-Kroll and Pauli approximations. *Journal of Chemical Physics*, 105:1995–2003, 1996.
- [KSM86] W. Kołos, K. Szalewicz, and H. J. Monkhorst. New Born-Oppenheimer potential-energy curve and vibrational energies for the electronic ground-state of the hydrogen molecule. *Journal of Chemical Physics*, 84:3278–3283, 1986.
- [KSW00] P. Knowles, M. Schütz, and H. J. Werner. Ab initio methods for electron correlation in molecules. *Published in [Gro00]*, pages 97–179, 2000.
- [KUi87] T. Koga and M. Uchiie. Accurate third order energy of the H(1s)-H(1s) van der Waals interaction. *Journal of Chemical Physics*, 87:1137–1141, 1987.
- [Kut77] W. Kutzelnigg. Pair correlated theories. *Published as Chapter 5 of [Sch77]*, pages 129–188, 1977.
- [Kut85] W. Kutzelnigg. R12-dependent terms in the wave-function as closed sums of partial-wave amplitudes for large-L. *Theoretica Chimica Acta*, 68:445–469, 1985.
- [Kut89] W. Kutzelnigg. Perturbation-theory of relativistic corrections. 1. The non-relativistic limit of the Dirac-equation and a Direct Perturbation Expansion. *Zeitschrift für Physik D – Atoms Molecules and Clusters*, 11:15–28, 1989.
- [Kut94] W. Kutzelnigg. Theory of the expansion of wave functions in a gaussian basis. *International Journal of Quantum Chemistry*, 51:447–463, 1994.

- [Kut96] W. Kutzelnigg. Stationary direct perturbation theory of relativistic corrections. *Physical Review A*, pages 1183–1198, 1996.
- [Kut97a] W. Kutzelnigg. The adiabatic approximation. 1. The physical background of the Born-Handy ansatz. *Molecular Physics*, 90:909–916, 1997.
- [Kut97b] W. Kutzelnigg. Relativistic one-electron Hamiltonians ‘for electrons only’ and the variational treatment of the Dirac equation. *Chemical Physics*, 225:203–222, 1997.
- [Kut99] W. Kutzelnigg. Effective hamiltonians for degenerate and quasidegenerate direct perturbation theory of relativistic effects. *Journal of Chemical Physics*, 110:8283–8294, 1999.
- [Kut00] W. Kutzelnigg. Perspective on [Dir29]. *Theoretical Chemistry Acta*, 103:182–186, 2000.
- [Kut03] W. Kutzelnigg. Theory of electron correlation. *Published in [Ryc03b]*, pages 3–89, 2003.
- [Kut07a] W. Kutzelnigg. Completeness of a kinetically balanced Gaussian basis. *Journal of Chemical Physics*, 126:201103 (5 pages), 2007.
- [Kut07b] W. Kutzelnigg. Which masses are vibrating or rotating in a molecule? *Molecular Physics*, 105:2627–2647, 2007.
- [Kv00] W. Kutzelnigg and P. von Herigonte. Electron correlation at the dawn of the 21(st) century. *Advances In Quantum Chemistry*, 36:185–229, 2000.
- [KW65] W. Kołos and L. Wolniewicz. Potential-energy curves for the $X\ ^1\Sigma_g^+$, $b\ ^3\Sigma_u^+$, and $C\ ^1\Pi_u$ states of the hydrogen molecule. *Journal of Chemical Physics*, 43:2429–2441, 1965.
- [KW68] W. Kołos and L. Wolniewicz. Improved theoretical ground-state energy of hydrogen molecule. *Journal of Chemical Physics*, 49:404–410, 1968.
- [KW74] W. Kołos and L. Wolniewicz. Variational calculation of the long-range interaction between two ground-state hydrogen atoms. *Chemical Physics Letters*, 24:457–460, 1974.
- [KW75] W. Kołos and L. Wolniewicz. Improved potential energy curve and vibrational energies for the electronic ground state of the hydrogen molecule. *Journal of Molecular Spectroscopy*, 54:303–311, 1975.
- [KW85] P. J. Knowles and H. J. Werner. An efficient second-order MC-SCF method for long configuration expansions. *Chemical Physics Letters*, 115:259–267, 1985.
- [KW03] E. S. Kryachko and S. Wilson. Generation of systematic sequences of even-tempered basis sets: empirical generating formulae. *International Journal of Quantum Chemistry*, 93:112–120, 2003.

- [Lal01] F. Laloë. Do we really understand quantum mechanics? Strange correlations, paradoxes, and theorems. *American Journal of Physics*, 69:655–701, 2001.
- [Lan00] S. Lang. *Linear Algebra*. Springer, 3rd edition, 2000.
- [LB68] R. J. LeRoy and R. B. Bernstein. Dissociation energy and vibrational terms of ground-state ($X^1\Sigma_g^+$) hydrogen. *Journal of Chemical Physics*, 49:4312–4321, 1968.
- [LBK04] M. Lombardi, P. Barletta, and A. Kievsky. Variational estimates using a discrete variable representation. *Physical Review A*, 70:032503, 2004.
- [LC00] J. C. Light and T. C. Carrington Jr. . Discrete-variable representations and their utilization. *Advances in Chemical Physics*, 113:263–310, 2000.
- [LCC01] R. Lanquetin, L. H. Coudert, and C. Camy-Peyret. High-lying rotational levels of water: an analysis of the energy levels of the five first vibrational states. *Journal of Molecular Spectroscopy*, 206:83–103, 2001.
- [LD74] S. R. Langhoff and E. R. Davidson. Configuration interaction calculations on the nitrogen molecule. *International Journal of Quantum Chemistry*, 8:61–72, 1974.
- [Le 05] C. Le Bris. Computational chemistry for the perspective of numerical analysis. *Acta Numerica*, 14:363–444, 2005.
- [Lev00] I. R. Levine. *Quantum Chemistry*. Prentice-Hall, 5th edition, 2000.
- [LH08] D. Lisak and J. T. Hodges. Low-uncertainty H₂O line intensities for the 930-nm region. *Journal of Molecular Spectroscopy*, 249:6–13, 2008.
- [LHC06] D. Lisak, J. T. Hodges, and R. Ciurylo. Comparison of semiclassical line-shape models to rovibrational H₂O spectra measured by frequency-stabilized cavity ring-down spectroscopy. *Physical Review A*, 73:012507 (13 pages), 2006.
- [LHL85] J. C. Light, I. P. Hamilton, and J. V. Lill. Generalized discrete variable approximation in quantum mechanics. *Journal of Chemical Physics*, 82:1400–1409, 1985.
- [LIA07] D. I. Lyakhy, V. V. Ivanov, and L. Adamowicz. State-specific multireference complete-active-space coupled-cluster approach versus other quantum chemical methods: dissociation of the n₂ molecule. *Molecular Physics*, 105:1335–1357, 2007.
- [Lid05] V. V. Lidski. Equation of motion for a radiating charged particle in classical electrodynamics. *Theoretical and Mathematical physics*, 143:583–598, 2005.
- [Lin03] M. J. Lindstrom. Penalised estimators of Free-Knot Splines. *Journal of Computational and Graphical Statistics*, 8:91–147, 2003.
- [Lip02] J. Lipiński. On the consequences of the violation of the Hellmann-Feynman theorem in calculations of electric properties of molecules. *Chemical Physics Letters*, 363:313–318, 2002.

- [LJM⁺03] E. O. Le Bigot, U. D. Jentschura, P. J. Mohr, P. Indelicato, and G. Soff. Perturbation approach to the self-energy of non-S hydrogenic states. *Physical Review A*, 68:042101 (17 pages), 2003.
- [LK07] W. J. Liu and W. Kutzelnigg. Quasirelativistic theory. II. Theory at matrix level. *Journal of Chemical Physics*, 126:114107 (14 pages), 2007.
- [LL81] L. D. Landau and L. M. Lifshitz. *Quantum Mechanics: Non-Relativistic Theory*. Butterworth–Heinemann, 3rd edition, 1981.
- [LL05] C. Le Bris and P. L. Lions. From atoms to crystals: A mathematical journey. *Bulletin of The American Mathematical Society*, 42:291–363, 2005.
- [LM92] P. O. Löwdin and I. Mayer. Some Studies of the General Hartree-Fock Method. *Advances in Quantum Chemistry*, 24:79–114, 1992.
- [LMBK84] S. C. Leasure, T. P. Martin, and G. G. Balint-Kurti. Ab initio valence-electron-only molecular electronic structure calculations: Theory and test applications. *Journal of Chemical Physics*, 80:1186–1200, 1984.
- [LMT95] A. E. Lynas-Gray, S. Miller, and J. Tennyson. Infrared transition intensities for water - A comparison of ab-initio and fitted dipole-moment surfaces. *Journal of Molecular Spectroscopy*, 169:458–467, 1995.
- [Löw59a] P. O. Löwdin. Correlation problem in many-electron quantum mechanics I. Review of different approaches and discussion of some current ideas. *Advances in Chemical Physics*, 2:207–322, 1959.
- [Löw59b] P. O. Löwdin. Quantum theory of many-particle systems. III. Extension of the Hartree-Fock scheme to include degenerate systems and correlation effects. *Advances in Chemical Physics*, 2:207–322, 1959.
- [Löw60] P.-O. Löwdin. Expansion theorems for the total wave function and extended Hartree-Fock schemes. *Reviews of Modern Physics*, 32:328–334, 1960.
- [Löw63] P. O. Löwdin. Discussion on the Hartree-Fock Approximation. *Reviews of Modern Physics*, 35:496–501, 1963.
- [Löw66a] P.-O. Löwdin. The Projected Hartree-Fock method : An extension of the independent particle scheme. *Published in [Löw66b]*, pages 601–623, 1966.
- [Löw66b] P.-O. Löwdin. *Quantum Theory of Atoms, Molecules, and the Solid State. A Tribute to John Slater*. Academic Press, 1966.
- [Löw90] P. O. Löwdin. On the long way from the Coulombic Hamiltonian to the intermolecular energy surfaces. *International Journal of Quantum Chemistry*, 38:741–758, 1990.
- [Löw91] P. O. Löwdin. On nuclear motion and the definition of molecular structure. *Journal of Molecular Structure (Theochem)*, 230:13–15, 1991.

- [Löw95] P. O. Löwdin. The historical development of the electron correlation problem. *International Journal of Quantum Chemistry*, 55:77–102, 1995.
- [LP95] X. Li and J. Paldus. Comparison of the open-shell state-universal and state-selective coupled-cluster theories: H4 and H8 models. *Journal of Chemical Physics*, 103:1024–1034, 1995.
- [LP98] X. Li and J. Paldus. Reduced multireference couple cluster method. II. application to potential energy surfaces of HF, F₂, and H₂O. *Journal of Chemical Physics*, 108:637–648, 1998.
- [LP99] L. Lapidus and G. F. Pinder. *Numerical Solution of Partial Differential Equations in Science and Engineering*. Wiley-Interscience, 1999.
- [LP08a] X. Li and J. Paldus. Partially linearized, fully size-extensive, and reduced multireference coupled-cluster methods. I. Formalism and mutual relationship. *Journal of Chemical Physics*, 128:144118 (11 pages), 2008.
- [LP08b] X. Li and J. Paldus. Partially linearized, fully size-extensive, and reduced multireference coupled-cluster methods. II. applications and performance. *Journal of Chemical Physics*, 128:144119 (13 pages), 2008.
- [LPL82] J. V. Lill, G. A. Parker, and J. C. Light. Discrete variable representations and sudden models in quantum scattering theory. *Chemical Physics Letters*, 89:483–489, 1982.
- [LS07] M. J. Lai and L. L. Schumaker. *Spline Functions on Triangulations*. Cambridge University Press – Vol. 110 of the series ‘Encyclopedia of Mathematics and its Applications’, 2007.
- [LSS⁺] H. Lischka, R. Shepard, I. Shavitt, R. M. Pitzer, Th. Müller, P. G. Szalay, S. R. Brozell, G. Kedziora, E. A. Stahlberg, R. J. Harrison, J. Nieplocha, M. Minkoff, M. Barbatti, M. Schuurmann, D. R. Yarkony, S. Matsika, E. V. Beck, and J.-P. Blaudeau. COLUMBUS is a collection of programs for high-level ab initio molecular electronic structure calculations. See <http://www.univie.ac.at/columbus/> (accessed 13-Sep-2008).
- [LT08] L. Lodi and J. Tennyson. A line list of allowed and forbidden rotational transition intensities for water. *Journal of Quantitative Spectroscopy & Radiative Transfer*, 109:1219–1233, 2008.
- [LTT⁺08] L. Lodi, R. N. Tolchenov, J. Tennyson, A. E. Lynas-Gray, S. V. Shirin, N. F. Zobov, O. L. Polyansky, A. G. Császár, J. N. P. van Stralen, and L. Visscher. A new ab initio ground-state dipole moment surface for the water molecule. *Journal of Chemical Physics*, 128:044304 (11 pages), 2008.
- [LTY⁺02] H. Lin, W. Thiel, S. N. Yurchenko, M. Carvajal, and P. Jensen. Vibrational energies for NH₃ based on high level ab initio potential energy surfaces. *Journal of Chemical Physics*, 117:11265–11276, 2002.

- [LUEL06] X. Lopez, J. M. Ugalde, L. Echevarría, and E. V. Ludeña. Exact non-Born-Oppenheimer wave functions for three-particle Hookean systems with arbitrary masses. *Physical Review A*, 74:042504 (14 pages), 2006.
- [Luk95] T. J. Lukka. A simple method for the derivation of exact quantum-mechanical vibration-rotation hamiltonians in terms of internal coordinates. *Journal of Chemical Physics*, 102:3945–3955, 1995.
- [LUL06] X. Lopez, J. M. Ugalde, and E. V. Ludeña. Exact non-Born-Oppenheimer wave functions for the Hooke-Calogero model of the H-2 molecule. *European Physical Journal D*, 37:351–359, 2006.
- [MA99] R. McWeeny and C. Amovilli. Locality and nonlocality in quantum mechanics: A two-proton EPR experiment. *International Journal of Quantum Chemistry*, 74:573–584, 1999.
- [Mak87] Z. B. Maksić (ed.). *Modelling of structure and properties of molecules*. Ellis Horwood Limited, 1987.
- [Mak91] Z. B. Maksić (ed.). *Theoretical Models of Chemical Bonding – Part 1*. Springer-Verlag, 1991.
- [Mak03] J. Makarewicz. The calculation of rotation-vibration energies for molecules with large amplitude vibrations. *Published in [JB00]*, pages 391–429, 2003.
- [Mar] M. Marino, personal communication, 2007.
- [Mar66] H. Margenau. Exclusion principle and measurement theory. *Published in [Löw66b]*, pages 81–91, 1966.
- [Mar02] M. Marino. Classical electrodynamics of point charges. *Annals of Physics*, 301:85–127, 2002.
- [Mar03] M. Marino. The unexpected flight of the electron in a classical hydrogen-like atom. *Journal of Physics A*, 36:11247–11255, 2003.
- [Mar07] M. G. Marmorino. New lower bound formula from the local energy. *International Journal of Quantum Chemistry*, 107:1543–1547, 2007.
- [Mat74] R. D. Mattuck. *A guide to Feynman diagrams in the Many-Body Problem*. McGraw-Hill International, 2th edition, 1974.
- [Mat92] D. C. Mattis. *The Many-Body Problem: An Encyclopedia of Exactly Solved Models in One Dimension*. Word Scientific, 1992.
- [Mat07] Mathematica 6 is a computer algebra and technical computing software by wolfram research, 2007. see <http://www.wolfram.com>.
- [May78] I. Mayer. Spin-Projected EHF method. IV. Comparison of potential curves given by different one-electron methods. *International Journal of Quantum Chemistry*, 14:29–38, 1978.

- [Maz98] D. A. Mazziotti. Contracted Schrödinger equation: Determining quantum energies and two-particle density matrices without wave functions. *Physical Review A*, 57:4219–4234, 1998.
- [Maz06] D. A. Mazziotti. Quantum chemistry without wave functions: Two-electron reduced density matrices. *Accounts of Chemical Research*, 39:207–215, 2006.
- [MB05] J. Mitroy and M. W. J. Bromley. Higher-order C_n dispersion coefficients for hydrogen. *Physical Review A*, 71:032709 (5 pages), 2005.
- [MC06] S. Manzhos and T. Carrington Jr. Using neural networks to represent potential surfaces as sums of products. *Journal of Chemical Physics*, 125:194105 (5 pages), 2006.
- [MCF⁺84] J. N. Murrell, S. Carter, S. C. Farantos, P. Huxley, and A. J. C. Varandas. *Molecular Potential Energy functions*. John Wiley & Sons, 1984.
- [MCH02] K. Molawi, A. J. Cohen, and N. C. Handy. Left-right and dynamic correlation. *International Journal of Quantum Chemistry*, 89:86–93, 2002.
- [MCKT04] M. Matricardi, F. Chevallier, G. Kelly, and J.-N. Thépaut. An improved general fast radiative transfer model for the assimilation of radiance observations. *Quarterly Journal of the Royal Meteorological Society*, 130:153–173, 2004.
- [McW92] R. McWeeny. *Methods of Molecular Quantum Mechanics*. Academic Press, 2nd edition, 1992.
- [McW99a] R. McWeeny. Classical Valence Bond Theory. *International Journal of Quantum Chemistry*, 74:87–96, 1999.
- [McW99b] R. McWeeny. Separability of quantum systems: A density matrix approach. *Advances In Quantum Chemistry*, 31:15–35, 1999.
- [McW00] R. McWeeny. On the Einstein-Podolsky-Rosen paradox. *Advances In Quantum Chemistry*, 36:365–384, 2000.
- [McW07] R. McWeeny. Quantum chemistry: The first seventy years. *Faraday Discussions*, 135:13–30, 2007.
- [Mea79] C. A. Mead. The “noncrossing” rule for electronic potential energy surfaces: The role of time-reversal invariance. *Journal of Chemical Physics*, 70:2276–2283, 1979.
- [Med06] R. Medina. Radiation reaction of a classical quasi-rigid extended particle. *Journal of Physics A*, 39:3801–3816, 2006.
- [Meh87] J. Mehra. Erwin schrödinger and the rise of wave mechanics. II. The creation of wave mechanics. *Foundations of Physics*, 17:1141–1188, 1987.
- [Mei08] L. Meissner. Coupled-cluster corrected MR-CISD method with noniterative evaluation of connected triples. *International Journal of Quantum Chemistry*, 108:2199–2210, 2008.

- [Mel00] G. J. Melnick *et al.* The submillimeter wave astronomy satellite: Science objectives and instrument description. *Astrophysical Journal*, 539:L77–L85, 2000.
- [Mey71] W. Meyer. *International Journal of Quantum Chemistry Symposium*, 5:341, 1971.
- [Mey73] W. Meyer. PNO–CI studies of electron correlation effects. I. Configuration expansion by means of nonorthogonal orbitals, and application to the ground state and ionized states of methane. *Journal of Chemical Physics*, 58:1017–1035, 1973.
- [Mey77] W. Meyer. Configuration expansion by means of pseudonatural orbitals. *Published in [Sch77]*, pages 413–446, 1977.
- [MFG90] J. M. L. Martin, J. P. Franco, and R. Gijbels. On size-consistency corrections for limited configuration-interaction calculations. *Chemical Physics Letters*, 172:346–353, 1990.
- [MFO⁺01] A. O. Mitrushenkov, G. Fano, F. Ortolani, R. Linguerri, and P. Palmieri. Quantum chemistry using the density matrix renormalization group. *Journal of Chemical Physics*, 115:6815–6821, 2001.
- [MG07] C. Michauk and J. Gauss. Relativistic correction to the potential energy surface and vibration-rotation levels of water. *Journal of Chemical Physics*, 127:044106 (8 pages), 2007.
- [MI72] K. Morokuma and S. Iwata. Extended Hartree–Fock theory for excited states. *Chemical Physics Letters*, 16:192–197, 1972.
- [ML03] R. McWeeny and J. Li. Valence bond theory using symmetric group methods. *Published in [WMB03]*, 2:122–139, 2003.
- [MLPF03] A. O. Mitrushenkov, R. Linguerri, P. Palmieri, and G. Fano. Quantum chemistry using the density matrix renormalization group. *Journal of Chemical Physics*, 119:4148–4158, 2003.
- [MMH03] J. Meller, J.-P. Malrieu, and J.-L. Heully. Size-consistent multireference configuration interaction method through the dressing of the norm of determinants. *Molecular Physics*, 101:2029–2041, 2003.
- [MMZ⁺07] P. Maksyutenko, J. S. Muentert, N. F. Zobov, S. V. Shirin, O. L. Polyansky, T. R. Rizzo, and O. V. Boyarkin. Approaching the full set of energy levels of water. *Journal of Chemical Physics*, 126:241101 (4 pages), 2007.
- [MNSS89] G. Meinardus, G. Nürnberger, M. Sommer, and H. Strauss. Algorithms for piecewise polynomials and splines with free knots. *Mathematics of Computation*, 53:235–247, 1989.
- [MO05] J. Mitroy and V. D. Ovsiannikov. Generating van der Waals coefficients to arbitrary orders of the atom-atom interaction. *Chemical Physics Letters*, 412:76–81, 2005.

- [MOF⁺98] V. Magnasco, M. Ottonelli, G. Figari, M. Rui, and C. Costa. Polarizability pseudospectra and dispersion coefficients for H(1s)-H(1s). *Molecular Physics*, 94:905–908, 1998.
- [Moh04] J. R. Mohallem. Evidences of molecular structure beyond the Born-Oppenheimer approximation: the model hamiltonian. *Journal of Molecular Structure (Theochem)*, 703:11–13, 2004.
- [MOM08] K. H. Marti, I. M. Ondik, and G. Moritz. Density matrix renormalization group calculations on relative energies of transition metal complexes and clusters. *Journal of Chemical Physics*, 128:014104 (13 pages), 2008.
- [Mon87a] H. J. Monkhorst. Chemical physics without the Born-Oppenheimer approximation: the molecular coupled-cluster method. *Physical Review A*, 36:1544–1560, 1987.
- [Mon87b] H. J. Monkhorst. On the theory of molecular structure – from concept to calculations. *Published in [Mak87]*, pages 41–50, 1987.
- [Mon99] H. J. Monkhorst. Views of a molecule by chemists and physicists. *International Journal of Quantum Chemistry*, 72:281–285, 1999.
- [Mor03] J. D. Morgan III. Analytical structure of exact atomic and molecular wave functions. *Published in [WMB03]*, 2:41–51, 2003. Chap. 5.
- [Mor07] V. Moretti. *Struttura matematica delle Teorie Quantistiche e Teoria Spettrale in Spazi di Hilbert. Lecture notes (in Italian)*. 2007. Available from V. Moretti’s web site at <http://www.science.unitn.it/~moretti/> (accessed 4-Dec-2007).
- [MP80] R. McWeeny and B. T. Pickup. Quantum theory of molecular electronic structure. *Reports on the Progress of Physics*, 43:1065–1144, 1980.
- [MR00] J. Mehra and H. Rechenberg. *The Historical Development of Quantum Theory*, volume 6 – The completion of Quantum Mechanics 1926–1941. Springer, 2000.
- [MR07] G. Moritz and M. Reiher. Decomposition of density matrix renormalization group states into a Slater determinant basis. *Journal of Chemical Physics*, 126:244109 (16 pages), 2007.
- [MRB06] P. Maksyutenko, T. R. Rizzo, and O. V. Boyarkin. A direct measurement of the dissociation energy of water. *Journal of Chemical Physics*, 125:181101 (3 pages), 2006.
- [MRC] MRCC, a string-based quantum chemical program suite written by M. Kállay. See also M. Kállay and P. R. Surján, *Journal of Chemical Physics* **115**, 2945 (2001), as well as: www.mrcc.hu.
- [MRD92] C. Murray, S. C. Racine, and E. R. Davidson. Calculation on model systems using quasi-degenerate variational perturbation theory with an average pair correction. *International Journal of Quantum Chemistry*, 42:273–285, 1992.

- [MRT05] J. J. Munro, J. Ramanlal, and J. Tennyson. Asymptotic vibrational states of the H-3(+) molecular ion. *New Journal of Physics*, 7:196 (8 pages), 2005.
- [MRTM06] J. J. Munro, J. Ramanlal, J. Tennyson, and H. Y. Mussa. Properties of high-lying vibrational states of the H-3(+) molecular ion. *Molecular Physics*, 104:115–125, 2006.
- [MS96] M. Moshinsky and Y. F. Smirnov. *Harmonic Oscillator in Modern Physics*. Harwood Academic, 1996.
- [MSA⁺00] G. J. Melnick, J. R. Stauffer, M. L. N. Ashby, E. A. Bergin, G. Chin, and N. R. Erickson *et al.* The *Submillimeter Wave Astronomy Satellite*: Science objectives and instrument description. *Astrophysical Journal Letters*, 539:L77–L86, 2000.
- [MT03] A. Maurellis and J. Tennyson. The climatic effects of water vapour. *Physics World*, 16:29–33, 2003.
- [MT04] A. Miani and J. Tennyson. Can ortho-para transitions for water be observed? *Journal of Chemical Physics*, 120:2732–2739, 2004.
- [MTN08] P. J. Mohr, B. N. Taylor, and D. B. Newell. CODATA recommended values of the fundamental physical constants: 2006. *Reviews of Modern Physics*, 80:633–730, 2008. Also available on-line at <http://physics.nist.gov/constants> (accessed on 25-07-2008).
- [Mul55] R. S. Mulliken. Report on notation for the spectra of polyatomic molecules. *Journal of Chemical Physics*, 23:1997–2011, 1955. Erratum: 24, 1118 (1956).
- [Mul92] B. Mulansky. Chebyshev approximation by spline functions with free knots. *IMA Journal of Numerical Analysis*, 12:95–105, 1992.
- [MUN97] M. Medved, M. Urban, and J. Noga. CCSD(T) expectation value calculations of first-order properties. *Theoretical Chemistry Accounts*, 98:75–84, 1997.
- [MV90] L. A. C. Malbouisson and J. D. M. Vianna. An algebraic method for solving Hartree-Fock-Roothan equations. *Journal de Chimie Physique et de Physico-Chimie Biologique*, 87:2017–2025, 1990.
- [MV99] G. E. Moyano and J. L. Villaveces. Approximation to wave functions, energies, and energy derivatives for molecular systems based on distribution theory. *International Journal of Quantum Chemistry*, 71:121–132, 1999.
- [MW90] M. M. Mestechkin and G. E. Whyman. Ground-state multiplicity by spin-extended Hartree-Fock method. *International Journal of Quantum Chemistry*, 38:279–282, 1990.
- [MW94] D. Moncrieff and S. Wilson. Computational linear dependence in molecular electronic structure calculations using Universal Basis Sets. *International Journal of Quantum Chemistry*, 51:447–463, 1994.

- [MWDC06] S. Manzhos, X. Wang, R. Dawes, and T. Carrington Jr. A nested molecule-independent neural network approach for high quality potential fits. *Journal of Physical Chemistry*, 110:5295–5304, 2006.
- [MWv00] R. Moszynski, P. E. S. Wormer, and A. van der Avoird. Symmetry adapted perturbation theory applied to the computation of intermolecular forces. *Published in [JB00]*, pages 69–108, 2000.
- [NAG] The NAG Fortran Library (Mark 21) is a collection of Fortran routines from the Numerical Algorithms Group. The documentation can be found at <http://www.nag.co.uk/numeric/FL/manual/html/FLlibrarymanual.asp> (accessed 5-Sep-2008).
- [Nak05] H. Nakatsuji. General method of solving the schrödinger equation of atoms and molecules. *Physical Review A*, 72:062110, 2005.
- [NBMS96] P. Niyaz, Z. Bačić, J. W. Moskowitz, and K. E. Schmidt. Ar_nHF ($n=1-4$) van der Waals clusters: a quantum Monte Carlo study of ground state energies, structures and HF vibrational frequency shifts. *Chemical Physics Letters*, 252:23–32, 1996.
- [Neu] A. Neumaier. A theoretical physics FAQ, question S2e: “Is there a multiparticle relativistic quantum mechanics?”. Available at <http://www.mat.univie.ac.at/~neum/physics-faq.txt> (accessed 27-03-2008).
- [Nik07] H. Nikolić. Quantum mechanics: Myths and facts. *Foundations of Physics*, 37:1563–1611, 2007.
- [NMT96] L. Neale, S. Miller, and J. Tennyson. Spectroscopic properties of the h_3^+ molecule: a new calculated line list. *The Astrophysical Journal*, 464:516–520, 1996.
- [NN07] H. Nakashima and H. Nakatsuji. Solving the schrödinger equation for helium atom and its isoelectronic ions with the free iterative complement interaction (ICI) method. *Journal of Chemical Physics*, 127:224104 (14 pages), 2007.
- [NNK07] H. Nakatsuji, H. Nakashima, and Y. Kurokawa. Solving the schrodinger equation of atoms and molecules without analytical integration based on the free iterative-complement-interaction wave function. *Physical Review A*, 99:240402, 2007.
- [NO98] J. W. Negele and H. Orland. *Quantum Many Particle Systems*. Westview Press, 1998.
- [NRS79] P. O. Nerbrant, B. Roos, and A. J. Sadlej. 1st-order properties and the Hellmann-Feynman theorem in the case of a limited CI wave-function. *International Journal of Quantum Chemistry*, 15:135–145, 1979.
- [NV03] J. Noga and P. Valiron. Towards universal R12 consistent basis sets. *Collection of Czechoslovak Chemical Communications*, 68:340–356, 2003.
- [O’C03] R. F. O’Connell. The equation of motion of an electron. *Physics Letters A*, 313:491–497, 2003.

- [ÖD01] Y. Öhrn and E. Deumens. Electron nuclear dynamics. *Advances in Chemical Physics*, 124:323–353, 2001.
- [Ogi98] J. F. Ogilvie. *The vibrational and rotational spectrometry of diatomic molecules*. Academic Press, 1998.
- [OJK⁺96] J. Olsen, P. Jørgensen, H. Koch, A. Balkova, and R. J. Bartlett. Full configuration interaction and state of the art correlation calculations on water in a valence double-zeta basis with polarization functions. *Journal of Chemical Physics*, 104:8007–8015, 1996.
- [OK97] E. Ottschowski and W. Kutzelnigg. Direct perturbation theory of relativistic effects for explicitly correlated wave functions: The He isoelectronic series. *Journal of Chemical Physics*, 106:6634–6646, 1997.
- [Olv97] F. W. J. Olver. *Asymptotics and special functions*. AKP Classics, 2nd edition, 1997.
- [OM06] V. D. Ovsiannikov and J. Mitroy. Regular approach for generating van der Waals C_s coefficients to arbitrary order. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 39:159–187, 2006.
- [Omn92] R. Omnès. Consistent interpretations of quantum mechanics. *Reviews of Modern Physics*, 64:339–382, 1992.
- [Omn94] R. Omnès. *The Interpretation of Quantum Mechanics*. Princeton University Press, 1994.
- [ORJJ88] J. Olsen, B. O. Roos, P. Jørgensen, and H. J. A. Jensen. Determinant based configuration-interaction algorithms for complete and restricted configuration-interaction spaces. *Journal of Chemical Physics*, 89:2185–2192, 1988.
- [OUI97] F. R. Ornellas, L. T. Ueno, and S. Iwata. Diazasiline (SiNN): Is there a conflict between experiment and theory? *Journal of Chemical Physics*, 106:151–157, 1997.
- [PA82] D. Papoušek and M. R. Aliev. *Molecular Vibrational–Rotational spectra*. Elsevier, 1982. Vol. 17 of the series ‘Studies in Physical and Theoretical Chemistry’.
- [Pal74] J. Paldus. Group theoretical approach to the configuration interaction and perturbation theory calculations for atomic and molecular systems. *Journal of Chemical Physics*, 61:5321–5330, 1974.
- [Pal03] J. Paldus. Coupled cluster methods. *Published in [WMB03]*, 2:272–313, 2003.
- [Par89] H. Partridge. Near Hartree-Fock quality GTO basis-sets for the 1st-row and 3rd-row atoms. *Journal of Chemical Physics*, 90:1043–1047, 1989.
- [Pau95] R. Pauncz. *The Symmetric Group in Quantum Chemistry*. CRC Press, 1995.

- [Pau03] R. Pauncz. Different orbitals for different spins, Löwdin's idea. *Published in [BK03]*, 1:155–182, 2003.
- [PAW08] K. A. Peterson, T. B. Adler, and H.-J. Werner. Systematically convergent basis sets for explicitly correlated wavefunctions: the atoms H, He, B–Ne, and Al–Ar. *Journal of Chemical Physics*, 128:084102 (12 pages), 2008.
- [PB35] L. Pauling and J. Y. Beach. The van der Waals interaction of hydrogen atoms. *Physical Review*, 47:686–692, 1935.
- [PBS76] J. A. Pople, J. S. Binkley, and R. Seeger. Theoretical models incorporating electron correlation. *International Journal of Quantum Chemistry Symposium*, 10:1–19, 1976.
- [PCS⁺03] O. L. Polyansky, A. G. Császár, S. V. Shirin, N. F. Zobov, P. Barletta, J. Tennyson, D. W. Schwenke, and P. J. Knowles. High-accuracy ab initio rotation-vibration transitions for water. *Science*, 299:539–542, 2003.
- [PD02] K. A. Peterson and T. H. Dunning Jr. . Accurate correlation consistent basis sets for molecular corevalence correlation effects: The second row atoms AlAr, and the first row atoms BNe revisited. *Journal of Chemical Physics*, 117:10548 (13 pages), 2002.
- [PDC⁺01] P. Pykkö, K. G. Dyall, A. G. Császár, G. Tarczay, O. L. Polyansky, and J. Tennyson. Estimation of Lamb-shift effects for molecules: Application to the rotation-vibration spectra of water. *Physical Review A*, 63:024502 (4 pages), 2001.
- [Pea] J. C. Pearson. Private communication (1999); Jet Propulsion Laboratory, Pasadena CA, USA.
- [Per95] A. Peres. *Quantum Theory: Concepts and Methods*. Springer, 1995.
- [PHR87] J. A. Pople, M. Head-Gordon, and K. Raghavachari. Quadratic configuration interaction. A general technique for determining electron correlation energies. *Journal of Chemical Physics*, 87:5968–5975, 1987.
- [Pin05] A. Pinkus. Density in approximation theory. *Surveys in Approximation Theory*, 1:1–45, 2005. Available on-line at <http://www.emis.de/journals/SAT/papers/1/> (accessed 11-Sep-2008).
- [PL99] J. Paldus and X. Z. Li. Critical assessment of coupled cluster method in quantum chemistry. *Advances in Chemical Physics*, 110:1–175, 1999.
- [Pol02] W. N. Polyzou. Cluster properties in relativistic quantum mechanics of N-particle systems. *Journal of Mathematical Physics*, 43:6024–6063, 2002.
- [Pow81] M. J. D. Powell. *Approximation theory and methods*. Cambridge University Press, 1981.

- [PPC⁺98] H. M. Pickett, R. L. Poynter, E. A. Cohen, M. L. Delitsky, J. C. Pearson, and H. S. P. Müller. Submillimeter, millimeter, and microwave spectral line catalog. *Journal of Quantitative Spectroscopy & Radiative Transfer*, 60:883–890, 1998.
- [PPC⁺05] A. Perrin, C. Puzzarini, J. M. Colmont, C. Verdes, G. Wlodarczak, and G. Cazoli *et al.* Molecular line parameters for the “MASTER” (millimeter wave acquisitions for stratosphere/troposphere exchange research) database. *Journal of Atmospheric Chemistry*, 51:161–205, 2005.
- [PPKT00] O. L. Polyansky, R. Prosmiti, W. Klopper, and J. Tennyson. An accurate, global, ab initio potential energy surface for the H-3(+) molecule. *Molecular Physics*, 98:261–273, 2000.
- [PPT97] R. Prosmiti, O. L. Polyansky, and J. Tennyson. A global potential energy surface for the H-3(+) molecule. *Chemical Physics Letters*, 127:107–114, 1997.
- [Pri65] H. Primas. *Published in [Sin65]*, pages 2–45, 1965.
- [Pri83] H. Primas. *Chemistry, Quantum Mechanics and Reductionism*. Springer-Verlag, 2nd edition, 1983.
- [Pru06] E. Prugovečki. *Quantum Mechanics in Hilbert Space*. Dover Publishing, 2nd edition, 2006. Originally published in 1981.
- [PS75] V. Pereyra and E. G. Sewell. Mesh selection for discrete solution of boundary problems in ordinary differential equations. *Numerical Mathematics*, 23:261–268, 1975.
- [PS87] P. Pavlides and K. D. Sales. Spin-projected EHF equations. *International Journal of Quantum Chemistry*, 32:711–722, 1987.
- [PS95] M. E. Peskin and D. V. Schroeder. *An Introduction To Quantum Field Theory*. Westview Press, 1995.
- [PS97] H. Partridge and D. W. Schwenke. The determination of an accurate isotope dependent potential energy surface for water from extensive ab initio calculations and experimental data. *Journal of Chemical Physics*, 106:4618–4639, 1997.
- [PSK77] J. A. Pople, R. Seeger, and R. Krishnan. Variational configuration interaction methods and comparison with perturbation theory. *International Journal of Quantum Chemistry Symposium*, 11:149–163, 1977.
- [PT99] O. L. Polyansky and J. Tennyson. Ab initio calculation of the rotation-vibration energy levels of H₃⁺ and its isotopomers to spectroscopic accuracy. *Journal of Chemical Physics*, 110:5056–5064, 1999.
- [PTVF07] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery. *Numerical Recipes – The Art of Scientific Computing*. Cambridge University Press, 3rd edition, 2007.

- [PY94] R. G. Parr and W. Yang. *Density-Functional Theory of Atoms and Molecules*. Oxford University Press, 1994.
- [PZ72] P. Pechukas and R. N. Zare. Elementary derivation of some of the wigner-witmer rules. *American Journal of Physics*, 40:1687–1688, 1972.
- [PZV⁺97] O. L. Polyansky, N. F. Zobov, S. Viti, J. Tennyson, P. F. Bernath, and L. Wallace. Water on the Sun: line assignments based on variational calculations. *Science*, 277:346–349, 1997.
- [PZVT98] O. L. Polyansky, N. F. Zobov, S. Viti, and J. Tennyson. Water vapour line assignments in the near infrared. *Journal of Molecular Spectroscopy*, 189:291–300, 1998.
- [QBT⁺01] H. M. Quiney, P. Barletta, G. Tarczay, A. G. Császár, O. L. Polyansky, and J. Tennyson. Two-electron relativistic corrections to the potential energy surface and vibration-rotation levels of water. *Chemical Physics Letters*, 344:413–420, 2001.
- [QSG99] H. M. Quiney, H. Skaane, and I. P. Grant. Ab initio relativistic quantum chemistry: four-components good, two-components bad! *Advances in Quantum Chemistry*, 32:1–49, 1999.
- [Qui03] H. M. Quiney. Relativistic molecular electronic structure. *Published as Part 4 of [WMB03]*, 2:375–484, 2003.
- [Rag91] K. Raghavachari. Electron correlation techniques in quantum chemistry: Recent advances. *Annual Reviews of Physical Chemistry*, 42:615–642, 1991.
- [Ram97] J. L. Ramsey. Molecular shape, reduction, explanation and approximate concepts. *Synthese*, 111:233–251, 1997.
- [RCK94] J. Rychlewski, W. Cencek, and J. Komasa. The equivalence of explicitly correlated Slater and Gaussian functions in variational quantum-chemistry computations – The ground-state of H-2. *Chemical Physics Letters*, 229:657–660, 1994.
- [Rei06] M. Reiher. Douglas-Kroll-Hess theory: a relativistic electrons-only theory for chemistry. *Theoretical Chemistry Accounts*, 116:241–252, 2006.
- [Rei07] M. Reiher. Regular no-pair Dirac operators: Numerical study of the convergence of high-order DouglasKrollHess transformations. *Physics Letters A*, 360:603–607, 2007.
- [RGSD91] C. P. Rinsland, A. Goldman, M. A. H. Smith, and V. M. Devi. Measurements of Lorentz air-broadening coefficients and relative intensities in the H₂¹⁶O pure rotational and ν_2 bands from long horizontal path atmospheric spectra. *Applied Optics*, 30:1427–1438, 1991.
- [RH00] M. Reiher and B. Heß. Relativistic electronic-structure calculations for atoms and molecules. *Published in [Gro00]*, pages 479–505, 2000.

- [RK03] J. Rychlewski and J. Komasa. Explicitly correlated functions in variational calculations. *Published in [Ryc03b]*, pages 91–147, 2003.
- [RKN⁺04] T. Rajamaki, M. Kállay, J. Noga, P. Valiron, and L. Halonen. High excitations in coupled-cluster series: vibrational energy levels of ammonia. *Molecular Physics*, 102:2297–2310, 2004.
- [Roh00] F. Rohrllich. The self-force and radiation reaction. *American Journal of Physics*, 68:1109–1112, 2000.
- [Roo80] B. Roos. The Complete Active Space SCF method in a Foc-matrix-based super-CI formulation. *International Journal of Quantum Chemistry Symposium*, 14:175–189, 1980.
- [Roo87] B. Roos. The CASSCF method. *Advances in Chemical Physics*, 69 – Ab initio Methods in Quantum Chemistry–II:399–445, 1987.
- [Roo91] C. C. J. Roothaan. My life as a physicist: memories and perspectives. *Journal of Molecular Structure: THEOCHEM*, 234:1–12, 1991.
- [Roo92a] B. O. Roos. The multiconfigurational (MC) self-consistent field (SCF) theory. *Published in [Roo92b]*, pages 177–254, 1992.
- [Roo92b] B. O. Roos (ed.). *Lecture Notes in Quantum Chemistry – European Summer School in Quantum Chemistry*. Springer, 1st edition, 1992. Vol. 58 of the series Lecture Notes in Quantum Chemistry.
- [Ros95] M. E. Rose. *Elementary Theory of Angular Momentum*. Dover Publications, 1995. Reprint of the original edition from 1957.
- [Rota] L. S. Rothman, personal communication, 2008.
- [Rotb] L. S. Rothman and I. Gordon. Steps for converting intensities from the JPL (or CDMS) catalog to HITRAN intensities. <http://www.cfa.harvard.edu/hitran/Download/Units-JPLtoHITRAN.pdf>.
- [Rot98] L. S. Rothman et al. The HITRAN molecular spectroscopic database and HAWKS (HITRAN atmospheric workstation): 1996 edition. *Journal of Quantitative Spectroscopy & Radiative Transfer*, 60:665–710, 1998.
- [Rot05] L. S. Rothman et al. The HITRAN 2004 molecular spectroscopic database. *Journal of Quantitative Spectroscopy & Radiative Transfer*, 96:139–204, 2005.
- [RS80] M. Reed and B. Simon. *Methods of Modern Mathematical Physics (4 voll)*. Academic Press, 1980.
- [RS06] M. Rieth and W. Schommers (Eds.). *Handbook of Theoretical and Computational Nanotechnology*. American Scientific Publishers, 2006.
- [RSS08] Z. Rolik, Á. Szabados, and P. R. Surján. A sparse matrix based full-configuration interaction algorithm. *Journal of Chemical Physics*, 128:144101 (11 pages), 2008.

- [RTPHG89] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon. A 5th-order perturbation comparison of electron correlation theories. *Chemical Physics Letters*, 157:479–483, 1989.
- [RTS80] B. Roos, P. R. Taylor, and P. E. M. Siegbahn. A Complete Active Space SCF method (CASSCF) using a density matrix formulated super-CI approach. *Chemical Physics*, 48:157–173, 1980.
- [Ryc94] J. Rychlewski. On the use of explicitly correlated functions in variational computations for small molecules. *International Journal of Quantum Chemistry*, 49:477–494, 1994.
- [Ryc99] J. Rychlewski. Explicitly correlated functions in molecular quantum chemistry. *Advances in Quantum Chemistry*, 31:179–199, 1999.
- [Ryc03a] J. Rychlewski. Electron correlation in few-electron systems. *Published in [WMB03]*, 2:199–218, 2003.
- [Ryc03b] J. Rychlewski (ed.). *Explicitly Correlated Wave Functions in Chemistry and Physics*. Springer, 2003.
- [SB84] B. Shizgal and R. Blackmore. A discrete ordinate method of solution of linear boundary value and eigenvalue problems. *Journal of Computational Physics*, 55:313–327, 1984.
- [SB95] P. G. Szalay and R. J. Bartlett. Approximately extensive modifications of the multireference configuration interaction method: A theoretical and practical analysis. *Journal of Chemical Physics*, 103:3600–3612, 1995.
- [SBG⁺98] G. Soff, T. Beier, M. Greiner, H. Persson, and G. Plunien. Quantum electrodynamics of strong fields: Status and perspectives. *Advances in Quantum Chemistry*, 30:125–161, 1998.
- [Sch65] D. S. Schonland. *Molecular Symmetry: an introduction to Group Theory and its uses in Chemistry*. Van Nostrand Company, 1965.
- [Sch77] H. F. Schaefer III (ed.). *Modern Theoretical Chemistry Vol. 3 – Methods of Electronic Structure Theory*. Plenum Press, 1977.
- [Sch01] D. W. Schwenke. Beyond the potential energy surface: Ab initio corrections to the Born-Oppenheimer approximation for H₂O. *Journal of Physical Chemistry A*, 105:2352–2360, 2001.
- [Sch03a] D. W. Schwenke. First principles prediction of isotopic shifts in h₂o. *Journal of Chemical Physics*, 118:6898–6904, 2003.
- [Sch03b] D. W. Schwenke. New rovibrational kinetic energy operators using polyspherical coordinates for polyatomic molecules. *Journal of Chemical Physics*, 118:10431–10438, 2003.

- [Sch05a] M. Schlosshauer. Decoherence, the measurement problem, and interpretations of quantum mechanics. *Reviews of Modern Physics*, 76:1267–1305, 2005.
- [Sch05b] D. W. Schwenke. The extrapolation of one-electron basis sets in electronic structure calculations: How it should work and how it can be made to work. *Journal of Chemical Physics*, 122:014107 (7 pages), 2005.
- [Sch07] F. Scheck. *Quantum Physics*. Springer, 2007.
- [SCR03] M. Sironi, D. L. Cooper, and M. Raimondi. Valence bond theory: Determinantal methods. *Published in [WMB03]*, 2:140–147, 2003.
- [SD00] K. Sarka and J. Demaison. Perturbation theory, effective Hamiltonians and force constants. *Published in [JB00]*, pages 255–303, 2000.
- [SDE⁺07] K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li, and T. L. Windus. Basis set exchange: A community database for computational sciences. *Journal of Chemical Information and Modeling*, 47:1045–1052, 2007.
- [Sel99] M. Selg. Exactly solvable modified Morse potentials for quantum-mechanical applications. *Physica Scripta*, 90:491–500, 1999.
- [Set00] J. Y. Seto. *Direct Fitting of Analytical Potential Functions to Diatomic Molecular Spectroscopic Data*. PhD thesis, University of Waterloo, Waterloo, Ontario, Canada, 2000.
- [SG98] M. W. Schmidt and M. S. Gordon. The construction and interpretation of MC-SCF wavefunctions. *Annual Review of Physical Chemistry*, 49:233–266, 1998.
- [SH06] J. S. Sims and S. A. Hagstrom. High precision variational calculations for the born-oppenheimer energies of the ground state of the hydrogen molecule. *Journal of Chemical Physics*, 124:094101 (7 pages), 2006.
- [SH07a] S. S. Shaik and P. C. Hiberty. *The Chemist’s Guide to Valence Bond Theory*. Wiley-Interscience, 2007.
- [SH07b] T. Shiozaki and S. Hirata. Grid-based numerical Hartree-Fock solutions of polyatomic molecules. *Physical Review A*, 76:040503(R) (4 pages), 2007.
- [Sha77] I. Shavitt. The method of configuration interaction. *Published as Chapter 6 of [Sch77]*, pages 189–275, 1977.
- [Sha94] R. Shankar. *The Principles of Quantum Mechanics*. Kluwer Academic, 2nd edition, 1994.
- [Sha98] I. Shavitt. The history and evolution of configuration interaction. *Molecular Physics*, 94:3–17, 1998.
- [She95] C. D. Sherrill. *An introduction to configuration interaction theory*. 1995. Available from Sherrill’s group web page at <http://vergil.chemistry.gatech.edu/notes/> (accessed 9-Mar-2008).

- [Shu53] K. E. Shuler. Adiabatic correlation rules for reactions involving polyatomic intermediate complexes and their application to the formation of $\text{oh}(^2\sigma^+)$ in the $\text{h}_2\text{-o}_2$ flame. *Journal of Chemical Physics*, 21:624–632, 1953.
- [Shu06] A. Shurki. Valence bond - rebirth of the phoenix or relix from the stone age. *Theoretical Chemistry Acta*, 116:253–261, 2006.
- [Sie80] P. Siegbahn. Direct configuration interaction with a reference state composed of many reference configurations. *International Journal of Quantum Chemistry*, 18:1229–1242, 1980.
- [Sie83] P. E. M. Siegbahn. The direct CI method. *Published in [DW83]*, pages 189–207, 1983.
- [Sie92] P. E. M. Siegbahn. The configuration interaction method. *Published in [Roo92b]*, pages 255—294, 1992.
- [Sim00] B. Simon. Schrödinger operators in the twentieth century. *Journal of Mathematical Physics*, 41:3523–3555, 2000.
- [Sim02] A. Simões. Dirac’s claim and the chemists. *Physics in Perspective*, 4:253–266, 2002.
- [Sin65] O. Sinanoğlu (ed.). *Modern Quantum Chemistry. Istanbul Lectures, Part II: Interactions*. Academic Press, 1965.
- [Sla27] J. C. Slater. The structure of the Helium atom. I. *Proceedings of the National Academy of Sciences*, 18:423–430, 1927.
- [Sla51] J. C. Slater. A simplification of the Hartree-Fock method. *Physical Review*, 81:385–390, 1951.
- [Smi80] F. T. Smith. Modified heliocentric coordinates for particle dynamics. *Physical Review Letters*, 45:1157–1160, 1980.
- [SMT95] J. H. Schryber, S. Miller, and J. Tennyson. Computed infrared-absorption properties of hot-water vapor. *Journal of Quantitative Spectroscopy & Radiative Transfer*, 53:373–380, 1995.
- [SNF07] M. Sampoorana, K. N. Nagendra, and H. Frisch. Generalized Voigt functions and their derivatives. *Journal of Quantitative Spectroscopy & Radiative Transfer*, 104:71–85, 2007.
- [SO96] A. Szabo and N. S. Ostlund. *Modern Quantum Chemistry*. Dover Publishing, 1996. Originally published in 1989.
- [SP77] R. Seeger and J. A. Pople. Self-consistent molecular orbital methods. XVIII. constraints and stability in Hartree-Fock theory. *Journal of Chemical Physics*, 66:3045–3050, 1977.

- [SP00] D. W. Schwenke and H. Partridge. Convergence testing of the analytic representation of an ab initio dipole moment function for water: Improved fitting yields improved intensities. *Journal of Chemical Physics*, 113:6592–6597, 2000.
- [SP03] J. L. Stuber and J. Paldus. Symmetry breaking in the independent particle model. *Published in [BK03]*, 1:67–140, 2003.
- [Spi64] M. R. Spiegel. *Complex Variables*. Shaum’s outline series, McGraw-Hill, 1964.
- [SPZ⁺03] S. V. Shirin, O. L. Polyansky, N. F. Zobov, P. Barletta, and J. Tennyson. Spectroscopically determined potential energy surface of (H₂O)-O-16 up to 25000 cm⁻¹. *Journal of Chemical Physics*, 118:2124–2129, 2003.
- [SPZ⁺06] S. V. Shirin, O. L. Polyansky, N. F. Zobov, A. G. Császár, and J. Tennyson. Spectroscopically determined potential energy surfaces of the (h₂o)-o-16, (h₂o)-o-17, and (h₂o)-o-18 isotopologues of water. *Journal of Molecular Spectroscopy*, 236:216–223, 2006.
- [SR75] N. Sathyamurthy and L. M. Raff. Quasiclassical trajectory studies using 3D spline interpolation of ab initio surfaces. *Journal of Chemical Physics*, 63:464–473, 1975.
- [SRL80] P. Siegbahn, B. Roos, and B. Levy. A comparison of the Super-CI and the Newton-Raphson scheme in the Complete Active Space SCF method. *Physica Scripta*, 21:323–327, 1980.
- [SS66] A. H. Stroud and D. Secrest. *Gaussian Quadrature Formulas*. Prentice-Hall, 1966.
- [SS99] C. D. Sherrill and H. F. Schaefer III. The configuration interaction method: Advances in highly correlated approaches. *Advances In Quantum Chemistry*, 34:143–269, 1999.
- [SS05] J. S. Sears and C. D. Sherrill. On the choice of reference in multi-reference electronic structure theory: minimal references for bond breaking. *Molecular Physics*, 103:803–814, 2005.
- [SSH05] A. A. Svidzinsky, M. O. Scully, and D. R. Herschbach. Simple and surprisingly accurate approach to the chemical bond obtained from dimensional scaling. *Physical Review Letters*, 95:080401, 2005.
- [ST86] B. T. Sutcliffe and J. Tennyson. The construction and fitting of molecular potential energy surfaces and their use in vibration-rotation calculations. *International Journal of Quantum Chemistry Symposium*, 20:507–520, 1986.
- [ST91] B. T. Sutcliffe and J. Tennyson. A general treatment of vibration-rotation coordinates for triatomic molecules. *International Journal of Quantum Chemistry*, 39:183–196, 1991.
- [Sta98] V. N. Staroverov. Monte Carlo study of core-valence separation schemes. *Journal of Chemical Physics*, 108:2873–2885, 1998.

- [Str98] P. Strange. *Relativistic Quantum Mechanics*. Cambridge University Press, 1998.
- [Sut82] B. T. Sutcliffe. Some problems in defining a nuclear motion Hamiltonian and their relation to the problem of molecular structure. *Published in [Car82]*, pages 99–125, 1982.
- [Sut91] B. T. Sutcliffe. The concept of molecular structure. *Appeared in [Mak91]*, pages 1–28, 1991.
- [Sut92] B. T. Sutcliffe. The mathematics of vibration–rotation calculations. *Published as chapter 2 of [Wil92b]*, pages 33–89, 1992.
- [Sut93] B. T. Sutcliffe. The coupling of nuclear and electronic motions in molecules. *Journal of the Chemical Society – Faraday Transactions*, 89:2321–2335, 1993.
- [Sut95] B. T. Sutcliffe. The idea of a potential energy surface. *Journal of Molecular Structure (Theochem)*, 341:217–235, 1995.
- [Sut97] B. T. Sutcliffe. The nuclear motion problem in molecular physics. *Advances in Quantum Chemistry*, 28:65–80, 1997.
- [Sut99] B. T. Sutcliffe. Quantum systems in chemistry and physics: Some hopes and fears. *Advances in Quantum Chemistry*, 31:1–13, 1999.
- [Sut00] B. Sutcliffe. The decoupling of electronic and nuclear motions in the isolated molecule Schrödinger hamiltonian. *Advances in Chemical Physics*, 114:1–121, 2000.
- [Sut03a] B. T. Sutcliffe. Breakdown of the Born-Oppenheimer approximation. *Published in [WMB03]*, 1:599–605, 2003.
- [Sut03b] B. T. Sutcliffe. Coordinate Systems and Transformations. *Published in [WMB03]*, 1:485–500, 2003. This chapter is freely available at Wiley’s web site <http://eu.wiley.com/WileyCDA/WileyTitle/productCd-0471623741,descCd-description.html> (accessed 10-Dec-2007).
- [Sut03c] B. T. Sutcliffe. Potential energy curves and surfaces. *Published in [WMB03]*, 1:574–587, 2003.
- [Sut04a] B. T. Sutcliffe. Calculations of the vibration-rotation spectra of small molecules. *Published as chapter 1 of [Hin04]*, pages 1–44, 2004.
- [Sut04b] B. Sutherland. *Beautiful Model – 70 Years of Exactly Solved Quantum Many-Body Problems*. Word Scientific, 2004.
- [Sut06] B. T. Sutcliffe. The idea of a potential energy surface. *Molecular Physics*, 104:715–722, 2006.
- [Sut08] B. T. Sutcliffe. What mathematicians know about the solutions of Schrodinger Coulomb hamiltonian. should chemists care? *Journal of Mathematical Chemistry*, 44:988–1008, 2008.

- [SW01] M. L. Senent and S. Wilson. Intramolecular basis set superposition errors. *International Journal of Quantum Chemistry*, 82:282–292, 2001.
- [SW05] B. T. Sutcliffe and R. G. Wolley. Molecular structure calculations without clamping the nuclei. *Physical Chemistry Chemical Physics*, 7:3664–3676, 2005.
- [Sza99] V. Szalay. Iterative and direct methods employing distributed approximating functionals for the reconstruction of a potential energy surface from its sampled values. *Journal of Chemical Physics*, 111:8804–8818, 1999.
- [Tay97] J. R. Taylor. *An Introduction to Error Analysis*. University Science Books, 2nd edition, 1997.
- [TBK⁺02] J. Tennyson, P. Barletta, M. A. Kostin, O. L. Polyansky, and N. F. Zobov. Ab initio rotation-vibration energy levels of triatomics to spectroscopic accuracy. *Spectrochimica Acta A*, 58:663–672, 2002.
- [TBMS06] J. Tennyson, P. Barletta, J. J. Munro, and B. C. Silva. The role of asymptotic vibrational states in H-3(+). *Philosophical Transactions of The Royal Society of London A*, 364:2903–2916, 2006.
- [TCKQ01] G. Tarczay, A. G. Császár, W. Klopper, and H. M. Quiney. Anatomy of relativistic energy corrections in light molecular systems. *Molecular Physics*, 99:1769–1794, 2001.
- [TCPT01] G. Tarczay, A. G. Császár, O. L. Polyansky, and J. Tennyson. Ab initio rovibrational spectroscopy of hydrogen sulfide. *Journal of Chemical Physics*, 115:1229–1242, 2001.
- [TCRM05] P. Theule, A. Callegari, T. R. Rizzo, and J. S. Muentert. Dipole moments of HDO in highly excited vibrational states measured by Stark induced photofragment quantum beat spectroscopy. *Journal of Chemical Physics*, 122:124312 (10 pages), 2005.
- [Ten] J. Tennyson, personal communication, 2008.
- [Ten86] J. Tennyson. The calculation of the vibration-rotation energies of triatomic molecules using scattering coordinates. *Computer Physics Reports*, 4:1–36, 1986.
- [Ten00] J. Tennyson. Variational calculations of rotation-vibration spectra. *Published in [JB00]*, pages 305–323, 2000.
- [Ten03] J. Tennyson. Molecules in space. *Published in [WMB03]*, 3:356–369, 2003.
- [Ten05] J. Tennyson. *Astronomical Spectroscopy*. Imperial College Press, 2005.
- [Ten06] J. Tennyson. Calculating the vibration-rotation spectrum of water. *Physica Scripta*, 76:C53–C56, 2006.
- [Tes05] G. Teschl. *Mathematical Methods in Quantum Mechanics*. 2005. Available from G. Teschl’s web site at <http://www.mat.univie.ac.at/~gerald/> (accessed 4-Dec-2007).

- [Tha88] A. J. Thakkar. Higher dispersion coefficients: accurate values for hydrogen atoms and simple estimates for other systems. *Journal of Chemical Physics*, 89:2092–2098, 1988.
- [Thi01] W. Thirring. *Quantum Mathematical Physics*. Springer, 2nd edition, 2001.
- [Tho72] D. J. Thouless. *The Quantum Mechanics of Many-Body Systems*. Academic Press, 2nd edition, 1972.
- [Tho94] W. J. Thompson. *Angular momentum*. John Wiley & Sons, 1994.
- [Tin03] M. Tinkham. *Group Theory and Quantum Mechanics*. Dover Publications, 2003. Originally published in 1964.
- [TKB⁺04] J. Tennyson, M. A. Kostin, P. Barletta, G. J. Harris, O. L. Polyansky, J. Ramanlal, and N. F. Zobov. DVR3D: a program suite for the calculation of rotation-vibration spectra of triatomic molecules. *Computer Physics Communications*, 163:85–116, 2004.
- [TKH07] D. P. Tew, W. Klopper, and T. Helgaker. Electron correlation: The many-body problem at the heart of chemistry. *Journal of Computational Chemistry*, 28:1307–1320, 2007.
- [TMH92] J. Tennyson, S. Miller, and J. R. Henderson. The calculation of highly excited vibration-rotation states of triatomic molecules. *Published as chapter 3 of [Wil92b]*, pages 91–139, 1992.
- [Tot] The SISAME-2007 compilation is available from the ‘MkIV Fourier Transform InfraRed (FTIR) Interferometer Atmospheric Chemistry Research Element’ website at <http://mark4sun.jpl.nasa.gov/>.
- [Tot92] R. A. Toth. Transition frequencies and absolute strengths of H₂¹⁷O and H₂¹⁸O in the 6. 2-mm region. *Journal of The Optical Society of America B*, 9:462–482, 1992.
- [Tot97] R. A. Toth. Water vapor measurements between 590 and 2582 cm⁻¹: line positions and strengths. *Journal of Molecular Spectroscopy*, 190:379–396, 1997.
- [Tot00] R. A. Toth. Air- and N₂-broadening parameters of water vapor: 604 to 2271 cm⁻¹. *Journal of Molecular Spectroscopy*, 201:218–243, 2000.
- [Tot05] R. A. Toth. Measurements of positions, strengths and self-broadened widths of H₂O from 2900 to 8000cm(-1): line strength analysis of the 2nd triad bands. *Journal of Quantitative Spectroscopy & Radiative Transfer*, 94:51–107, 2005.
- [TP98] J. Tennyson and O. L. Polyansky. Water on the Sun: line assignments based on variational calculations. *Contemporary Physics*, 39:283–294, 1998.
- [TPR⁺03] S. A. Tjemkes, T. Pattersona, R. Rizzi, M. W. Shephard, S. A. Clough, M. Matricardi, J. D. Haigh, M. Höpfner, S. Payan, A. Trotsenko, N. Scott, P. Rayer,

- J. P. Taylor, C. Clerbaux, L. L. Strow, S. DeSouza-Machado, D. Tobin, and R. Knuteson. The ISSWG line-by-line inter-comparison experiment. *Journal of Quantitative Spectroscopy & Radiative Transfer*, 77:433–453, 2003.
- [Tri80] C. Trindle. The quantum mechanical view of molecular structure and the shapes of molecules. *Israel Journal of Chemistry*, 19:47–53, 1980.
- [Tru98] D. G. Truhlar. Basis set extrapolation. *Chemical Physics Letters*, 294:45–48, 1998.
- [Tru07] D. G. Truhlar. Valence bond theory for chemical dynamics. *Journal of Computational Chemistry*, 28:73–86, 2007.
- [TS64] D. F. Tuan and O. Sinanoğlu. Many electron theory of atoms and molecules. IV. Be atom and its ions. *Journal of Chemical Physics*, 41:2677–2688, 1964.
- [TS92] J. Tennyson and B. T. Sutcliffe. Dcretization to avoid singularities in vibration-rotation hamiltonians: A bisector embedding for AB₂ triatomics. *International Journal of Quantum Chemistry*, 42:941–952, 1992.
- [Tsu75] S. Tsurubuchi. Correlation diagrams for electronic states of h₂o and fragment species. *Chemical Physics*, 10:335–344, 1975.
- [TT77] K. T. Tang and J. P. Toennies. A simple theoretical model for the van der Waals potential at intermediate distances. I. Spherically symmetric potentials. *Journal of Chemical Physics*, 66:1496–1506, 1977.
- [TT84] K. T. Tang and J. P. Toennies. An improved simple model for the van der Waals potential based on universal damping functions for the dispersion coefficients. *Journal of Chemical Physics*, 80:3726–3741, 1984.
- [TVML⁺07] G. Tinetti, A. Vidal-Madjar, M. C. Liang, J. P. Beaulieu, Y. Yung, S. Carey, R. J. Barber, J. Tennyson, I. Ribas, N. Allard, G. E. Ballester, D. K. Sing, and F. Selsis. Water vapour in the atmosphere of a transiting extrasolar planet. *Nature*, 448:169–171, 2007.
- [TZW⁺01] J. Tennyson, N. F. Zobov, R. Williamson, O. L. Polyansky, and P. F. Bernath. Experimental energy levels of the water molecule. *Journal of Physical And Chemical Reference Data*, 30:735–831, 2001.
- [van99] T. van Mourik. Benchmark calculations with correlated molecular wavefunctions. XIII. Potential energy curves for He₂, Ne₂ and Ar₂ using correlation consistent basis sets through augmented sextuple zeta. *Molecular Physics*, 96:529–547, 1999.
- [van03] R. van Leeuwen. Density functional approach to the many-body problem: Key concepts and exact functionals. *Advances In Quantum Chemistry*, 43:25–94, 2003.
- [van04] J. van Stralen. *Molecular Properties in Relativistic Electronic Structure Theory*. PhD thesis, Vrije Universiteit, Amsterdam, The Netherlands, 2004. The thesis is available on-line at <http://dirac.chem.sdu.dk/thesis/thesis-jvs2004.pdf> (accessed on 28-Feb-2008).

- [Var57] Y. P. Varshni. Comparative study of potential energy functions for diatomic molecules. *Reviews of Modern Physics*, 29:664–682, 1957.
- [Var88] A. J. C. Varandas. Intermolecular and intramolecular potentials - topographical aspects, calculation, and functional representation via a double many-body expansion method. *Advances in Chemical Physics*, 74:255–338, 1988.
- [Var96] A. J. C. Varandas. Energy switching approach to potential surfaces: An accurate single-valued function for the water molecule. *Journal of Chemical Physics*, 105:3524–3531, 1996. Erratum: 107, 5987 (1997).
- [Var97] A. J. C. Varandas. Energy switching approach to potential surfaces. 2. Two-valued function for the water molecule. *Journal of Chemical Physics*, 107:867–878, 1997.
- [Var00] A. J. C. Varandas. Basis set extrapolation of the correlation energy. *Journal of Chemical Physics*, 113:8880–8887, 2000.
- [VC83] V. S. Vasan and R. J. Cross. Matrix elements for Morse oscillators. *Journal of Chemical Physics*, 78:3869–3871, 1983.
- [vdW01] J. van de Wiele. Rotations et moments angulaires en mécanique quantique. *Annales de Physique*, 26:1–167, 2001. (In French).
- [vHP⁺01] T. van Mourik, G. J. Harris, O. L. Polyansky, J. Tennyson, A. G. Császár, and P. J. Knowles. Ab initio global potential, dipole, adiabatic, and relativistic correction surfaces for the HCN-HNC system. *Molecular Physics*, 115:3706–3718, 2001.
- [von96] J. von Neumann. *Mathematical Foundations of Quantum Mechanics*. Princeton University Press, 1996. Originally published in 1932.
- [von98] P. von Ragué Schleyer (Ed.). *Encyclopedia of Computational Chemistry*. John Wiley & Sons, 1998.
- [vV35] J. H. van Vleck. The quantum theory of valence. *Reviews of Modern Physics*, pages 167–228, 1935.
- [Vve01] D. Vvedensky. *Group Theory (lecture notes)*. 2001. Freely available from the author’s web site at <http://www.cmth.ph.ic.ac.uk/dimitri/courses.html> (accessed 9-Dec-2007).
- [vWP⁺99] T. van Mourik, A. K. Wilson, K. A. Peterson, D. E. Woon, and T. H. Dunning Jr. The effect of basis set superposition error (BSSE) on the convergence of molecular properties calculated with the correlation consistent basis sets. *Advances In Quantum Chemistry*, 31:105–135, 1999.
- [WAM07] H. J. Werner, T. B. Adler, and F. R. Manby. General orbital invariant MP2-F12 theory. *Journal of Chemical Physics*, 126:164102, 2007.

- [Wat03] J. K. G. Watson. Robust weighting in least-square fits. *Journal of Molecular Spectroscopy*, 219:326–328, 2003.
- [WBR97] H. Worden, R. Beer, and C. Rinsland. Airborne infrared spectroscopy of 1994 western wildfires. *Journal of geophysical research – Atmospheres*, 102:1287–1299, 1997.
- [WD94] D. E. Woon and T. H. Dunning Jr. . Gaussian basis sets for use in correlated molecular calculations. IV. Calculation of static electrical response properties. *Journal of Chemical Physics*, 100:2975–2988, 1994.
- [WD95] D. E. Woon and T. H. Dunning Jr. . Gaussian basis sets for use in correlated molecular calculations. V. Core-valence basis sets for boron through neon. *Journal of Chemical Physics*, 103:4572–4585, 1995.
- [WD03] D. E. Woon and T. H. Dunning Jr. . On the accuracy limits of orbital expansion methods: Explicit effects of k -functions on atomic and molecular energies. *Journal of Chemical Physics*, 118:8594–8610, 2003.
- [WDC80] E. B. Wilson Jr., J. C. Decius, and P. C. Cross. *Molecular Vibrations*. Dover Publications, 1980. Originally published in 1955.
- [Wei05] S. Weinberg. *The Quantum Theory of Fields*, volume 1 – Foundations. Cambridge University Press, 2005.
- [Wen05] H. Wendland. *Scattered Data Approximation*. Cambridge University Press, 2005.
- [Wer87] H. J. Werner. Matrix-formulated direct multiconfiguration self-consistent field and multiconfiguration reference configuration interaction methods. *Advances in Chemical Physics*, 69 – Ab initio methods in Quantum Chemistry-II:1–62, 1987.
- [Wer96] H.-J. Werner. Third-order multireference perturbation theory. The CASPT3 method. *Molecular Physics*, 89:645–661, 1996.
- [Wig34] E. Wigner. On the interaction of electrons in metals. *Physical Review*, pages 1002–1011, 1934.
- [Wig59] E. P. Wigner. *Group Theory: Its Application to the Quantum Mechanics of Atomic Spectra*. Academic Press, 1959.
- [Wika] Wikipedia has a comprehensive page on Laser Absorption Spectroscopy at http://en.wikipedia.org/wiki/Laser_absorption_spectrometry (accessed 13-Nov-2008).
- [Wikb] For a statement of Moore’s law see e.g. Wikipedia: http://en.wikipedia.org/wiki/Moore%27s_law (Accessed 21st August 2008).
- [Wike] A summary of the various conventions in use for Euler angles can be found on Wikipedia at http://en.wikipedia.org/wiki/Euler_angles (accessed 5-Sep-2008).

- [Wikd] Wikipedia has a very comprehensive page on Hermite polynomials at http://en.wikipedia.org/wiki/Hermite_polynomials (accessed 9-Sep-2008).
- [Wil83] S. Wilson. Basis sets. *Published in [DW83]*, pages 71–94, 1983.
- [Wil87] S. Wilson. Basis sets. *Advances in Chemical Physics*, 67 – Ab initio Methods in Quantum Chemistry-I:439–500, 1987.
- [Wil92a] S. Wilson. An introduction to molecular vibration theory. *Published as chapter 1 of [Wil92b]*, pages 1–31, 1992.
- [Wil92b] S. Wilson (ed.). *Methods in Computational Chemistry, Volume 4: Molecular Vibrations*. Plenum Press, 1992.
- [Wil03] S. Wilson. Finite basis set and the algebraic approximation. *Published in [WMB03]*, 2:585–640, 2003. Chap. 28.
- [WK85] H. J. Werner and P. J. Knowles. A second order multiconfiguration SCF procedure with optimum convergence. *Journal of Chemical Physics*, 82:5053–5063, 1985.
- [WK88] H.-J. Werner and P. J. Knowles. An efficient internally contracted multiconfiguration-reference configuration interaction method. *Journal of Chemical Physics*, 89:5803–5814, 1988.
- [WK90] H.-J. Werner and P. J. Knowles. A comparison of variational and non-variational internally contracted multiconfiguration-reference configuration interaction calculations. *Theoretical Chemistry Accounts*, 78:175–187, 1990.
- [WKL⁺00] H. J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, et al. MOLPRO, version 2000.9, a package of ab initio programs, 2000. see <http://www.molpro.net>.
- [WKL⁺02] H. J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, et al. MOLPRO version 2002.6 , a package of ab initio programs, 2002. see <http://www.molpro.net/>.
- [WKL⁺06] H. J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, et al. MOLPRO version 2006.1 , a package of ab initio programs, 2006. see <http://www.molpro.net/>.
- [WM80] H. J. Werner and W. Meyer. A quadratically convergent multiconfiguration-self-consistent field method with simultaneous optimization of orbitals and CI coefficients. *Journal of Chemical Physics*, 73:2342–2356, 1980.
- [WM81] H. J. Werner and W. Meyer. A quadratically convergent MCSCF method for the simultaneous optimization of several states. *Journal of Chemical Physics*, 74:5794–5801, 1981.
- [WM01] S. Wilson and D. Moncrieff. On ‘infinite basis set limits’ in molecular electronic structure calculations. *Computers and Chemistry*, 25:109–115, 2001.
- [WMB03] S. Wilson, R. McWeeny, and P. F. Bernath. *Handbook of Molecular Physics and Quantum Chemistry (3 voll)*. Wiley, 2003.

- [WMK03] H. J. Werner, F. R. Manby, and P. J. Knowles. Fast linear scaling second-order Moller-Plesset perturbation theory (MP2) using local and density fitting approximations. *Journal of Chemical Physics*, 118:8149–8160, 2003.
- [Wol76] R. G. Wolley. Quantum theory and molecular structure. *Advances in Physics*, 25:27–52, 1976.
- [Wol77] R. G. Wolley. The quantum interpretation of molecular structure. *International Journal of Quantum Chemistry*, 12 (Suppl. 1):307–313, 1977.
- [Wol78] R. G. Wolley. Further remarks on molecular structure in quantum theory. *Chemical Physics Letters*, 55:443–446, 1978.
- [Wol80a] R. G. Wolley. Quantum mechanics aspects of the molecular structure hypothesis. *Israel Journal of Chemistry*, 19:30–46, 1980.
- [Wol80b] R. G. Wolley (ed.). *Quantum Dynamics of Molecules: The new Experimental Challenge to Theorists*. Plenum Press, New York, 1980. NATO Advanced Study Institute B57.
- [Wol85] R. G. Wolley. The molecular structure conundrum. *Journal of Chemical Education*, 62:1082–1084, 1985.
- [Wol86] R. G. Wolley. Molecular shapes and molecular structure. *Chemical Physics Letters*, 125:200–204, 1986.
- [Wol88] R. G. Wolley. Must a molecule have shape? *New Scientist – 22 October 1988*, pages 53–57, 1988.
- [Wol91] R. G. Wolley. Quantum chemistry beyond the Born-Oppenheimer approximation. *Journal of Molecular Structure (Theochem)*, 230:17–46, 1991.
- [Wol93] L. Wolniewicz. Relativistic energies of the ground-state of the hydrogen molecule. *Journal of Chemical Physics*, 99:1851–1868, 1993.
- [Wol95] L. Wolniewicz. Nonadiabatic energies of the ground-state of the hydrogen molecule. *Journal of Chemical Physics*, 103:1792–1799, 1995.
- [Wol99] R. G. Wolley. Charged particles, gauge invariance, and molecular electrodynamics. *International Journal of Quantum Chemistry*, 74:531–545, 1999.
- [Wol03] R. G. Wolley. Quantum Electrodynamics of Atoms and Molecules. *Published as Part 7 of [WMB03]*, 1:621–704, 2003.
- [WR82] H.-J. Werner and E.-A. Reinsch. The self-consistent electron pairs method for multiconfiguration reference state functions. *Journal of Chemical Physics*, 76:3144–3156, 1982.
- [WR92] R. B. Wattson and L. S. Rothman. Direct numerical diagonalization - Wave of the future. *Journal of Quantitative Spectroscopy & Radiative Transfer*, 48:763–780, 1992.

- [WR02] G. A. Worth and M. A. Robb. Applying direct molecular dynamics to non-adiabatic systems. *Advances in Chemical Physics*, 124:355–431, 2002.
- [WRR83] H. J. Werner, P. Rosmus, and E. E. Reinsch. Molecular-properties from MCSCF-SCEP wave-functions. 1. Accurate dipole-moment functions of OH, OH-, and OH+. *Journal of Chemical Physics*, 79:905–916, 1983.
- [WS34] E. Wigner and F. Seitz. On the constitution of metallic sodium. II. *Physical Review*, pages 509–524, 1934.
- [WS77] R. G. Wolley and B. T. Sutcliffe. Molecular structure and the Born-Oppenheimer approximation. *Chemical Physics Letters*, 45:393–398, 1977.
- [WS96] J. M. Wittbrodt and H. B. Schlegel. Some reasons not to use spin projected density functional theory. *Journal of Chemical Physics*, 105:6574–6577, 1996.
- [WS03] R. G. Wolley and B. T. Sutcliffe. P.-O. Löwdin and the quantum mechanics of molecules. *Published in [BK03]*, 1–65:21–65, 2003.
- [WvD96] A. K. Wilson, T. van Mourik, and T. H. Dunning Jr. . Gaussian basis sets for use in correlated molecular calculations. VI. Sextuple zeta correlation consistent basis sets for boron through neon. *Journal of Molecular Structure (Theochem)*, 338:339–349, 1996.
- [WvK00] P. E. S. Wormer, A. van der Avoird, and G. Karlström. Intermolecular potentials, internal motions, and spectra of van der Waals and hydrogen-bonded complexes. *Chemical Review*, 100:4109–4143, 2000.
- [YAGS90] Y. Yamaguchi, I. L. Alberts, J. D. Goddard, and H. F. Schaefer III. Use of the molecular orbital hessian for self-consistent-field (SCF) wavefunctions. *Chemical Physics*, 147:309–326, 1990.
- [Yar99] D. R. Yarkony. Diabolical conical intersections. *Reviews of Modern Physics*, 68:985–1013, 1999.
- [Yar00] D. R. Yarkony. Vibronic energies and the breakdown of the Born-Oppenheimer approximation in diatomic molecules: adiabatic and diabatic representations. *Published in [JB00]*, pages 457–483, 2000.
- [You75] R. H. Young. Divergence of R-1 expansion for second-order H-H interaction. *International Journal of Quantum Chemistry*, 9:47–50, 1975.
- [Yse03] H. Yserentant. *On the electronic Schrödinger equation (Technical report)*. 2003. Available from H. Yserentant’s web site at <http://www.math.tu-berlin.de/~yserenta/index.en.html> (accessed 12-Dec-2007).
- [Yse07] H. Yserentant. *Regularity properties of wavefunctions and the complexity of the quantum-mechanical N-body problem*. 2007. Available from H. Yserentant’s web site at <http://www.math.tu-berlin.de/~yserenta/index.en.html> (accessed 12-Dec-2007).

- [YSNY00] D. Yamaki, Y. Shigeta, S. Yamanaka H. Nagao, and K. Yamaguchi. MP2, Tamm-Dancoff, and RPA methods based on the Generalized HF solution. *International Journal of Quantum Chemistry*, 80:707–707, 2000.
- [YVT⁺08] S. Yurchenko, B. A. Voronin, R. N. Tolchenov, N. Doss, O. V. Naumenko, W. Thiel, and J. Tennyson. Potential energy surface of HDO up to 25000 cm⁻¹. *Journal of Chemical Physics*, 128:044312 (12 pages), 2008.
- [Zac96] N.-C. H. Zachary. *Quantum Many-Body Systems in One Dimension*. Word Scientific, 1996.
- [Zar88] R. N. Zare. *Angular momentum*. Wiley-Interscience, 1988.
- [Zee03] A. Zee. *Quantum Field Theory in a Nutshell*. Princeton University Press, 2003.
- [ZPLT96] N. F. Zobov, O. L. Polyansky, C. R. Le Sueur, and J. Tennyson. Vibration-rotation levels of water beyond the Born-Oppenheimer approximation. *Chemical Physics Letters*, 260:381–387, 1996.