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PhD TUTORIAL

Theoretical methods for small-molecule ro-vibrational spectroscopy

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Abstract
The solution of the first principle equations of quantum mechanics provides an increasingly accurate and predictive approach for solving problems involving atoms and small molecules. A general introduction to the methods used for the *ab initio* calculation of rotational–vibrational spectra of small molecules is presented, with a strong focus on triatomic systems. The use of multi-reference electronic structure methods to compute molecular potential-energy and dipole-moment surfaces is discussed. Issues related to the construction of such surfaces and the inclusion of corrections due to relativistic and non-Born–Oppenheimer effects are reviewed. The derivation of exact, internal-coordinate nuclear-motion-effective Hamiltonians and their solution using a discrete-variable representation are discussed. Sample results for the water molecules are used throughout the tutorial to illustrate the theoretical and numerical issues in such calculations.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Rotational–vibrational (RV) molecular spectroscopy is one of the oldest and best-established areas of chemical physics. Infrared spectra of atmospheric gases were recorded by Ångström already at the end of the 19th century [15, 446], some 40 years before the development of the quantum mechanical formalism necessary to understand the observed spectra. The theory underlying molecular spectroscopy experienced considerable development in the period 1930–1950 and was expounded, for example, in the classic series of books by Herzberg [1–3].

Theoretical spectroscopy received new impetus with the development of computers and today is still an area of research of great importance for many scientific domains including atmospheric physics and astrophysics. 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 improvement of computer power and of methodology render theoretical approaches more and more accurate and useful.

In the usual Born–Oppenheimer framework, see section 2.1.1, computing molecular RV spectra requires two things: 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.

Even though the general strategy is straightforward, the technical details underlying the calculations are complicated and highly dependent on the size of the system under study. The purpose of this PhD tutorial is to guide a newcomer to the field of small-molecule theoretical RV spectroscopy through the relevant literature in a pedagogical and reasonably self-contained way. We will specialize in triatomic systems, using the water molecule to give indicative results.

Section 2 introduces the main theoretical framework of molecular spectroscopy. The Born–Oppenheimer approximation and relativistic effects are discussed in some detail. The Dirac–Coulomb–Breit many-electron relativistic Hamiltonian is discussed and its approximations are introduced. Some indicative values for the magnitude of relativistic effects in the water molecule are presented.

Section 3 consists in a rather detailed exposition of multi-reference electronic-structure methods, the most accurate quantum chemical treatment currently available for small molecules. Explicitly correlated methods of the R12/F12 family are also discussed. Illustrative data relative to the water molecule are presented.

Section 4 reviews some of the main features of molecular potential energy surfaces and introduces the problem of multi-dimensional surface building.

Section 5 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.

Finally, general considerations and an overview of possible future research directions are presented in section 7.

For an extended discussion of most of the topics treated in this PhD tutorial one may consult Lodi's original PhD thesis, which is available on-line [4].

2. Basic theoretical concepts

The theoretical framework on which most studies of atoms and molecules are couched is non-relativistic quantum mechanics [5]. In this section references treating necessary background concepts will be given and the general formalism will be outlined. In particular, the Born–Oppenheimer approximation and the treatment of relativistic effects will be reviewed in some detail.

2.1. *The molecular Hamiltonian*

The non-relativistic, quantum Hamiltonian for a system of n static, charged, point-like particles with masses m_i and charges q_i in the absence of external electric or magnetic fields can be written in atomic units [6, 7] as

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

This is the well-known *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 of the Coulomb Hamiltonian without making any further approximations is an incredibly difficult task which has been pursued only for small atoms and for diatomic molecules with less than about five particles [8–11]. The vast majority of calculations are instead based on an approximate decoupling of the electronic and nuclear motions, the Born–Oppenheimer approximation.

This approximate decoupling is perhaps the most important concept in molecular physics. It not only greatly simplifies practical computations but also introduces the fundamental concept of potential energy surface, which form the basis of modern understanding of molecules [12, 13]. The following subsections present an overview of this approximation.

2.1.1. *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 since the 1890s had to be ascribed to transitions between rotational and vibrational–rotational states of the atoms that make up molecules [14, 15]. When the Schrödinger equation was introduced it seemed to provide the long sought-after means to 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 treated the nuclei as static, fixed sources of the field in which the electrons moved [12, 13]. A theoretical justification of this procedure was first unsuccessfully sought by Bohr and Heisenberg [16] in the context of the old quantum theory and then famously by Born and Oppenheimer [17].[1] A detailed exposition of the Born–Oppenheimer approach can be found in [18]; in the following, we will only provide a general outline.

Indicating with m the electron mass and with M ‘some mean value of the (nuclear masses)’ [17], the Coulomb Hamiltonian (1) is partitioned as

$$\hat{H} = \hat{T}_N + \hat{T}_e + V = \hat{T}_N + \hat{H}_{\mathrm{cn}} = \left(\frac{m}{M}\right)\hat{H}_1 + \hat{H}_{\mathrm{cn}}, \qquad (2)$$

where $\hat{H}_1 = \hat{T}_N \times \left(\frac{M}{m}\right)$ is the rescaled kinetic energy of the nuclei and has a magnitude comparable to $\hat{T}_e$. $\hat{H}_{\mathrm{cn}}$ is the so-called clamped-nuclei Hamiltonian, which corresponds to a system where the nuclei are replaced by infinitely massive ones (see [19] for some qualifications). On the assumption that $\hat{H}_{\mathrm{cn}}$ has a deep energy minimum for some ‘equilibrium’ nuclear geometry, the term $\hat{H}_1$ is treated with perturbation theory, finally leading to an expansion of the exact energies and wavefunctions in series of $(m/M)^{1/4}$.

The practical procedure outlined by Born and Oppenheimer [17] consists of 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:

$$\hat{H}_{\mathrm{cn}}(\mathbf{r};\mathbf{R})\psi(\mathbf{r}|\mathbf{R}) = \varepsilon(\mathbf{R})\psi(\mathbf{r}|\mathbf{R}), \qquad (3)$$

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

$$(\hat{T}_N + \varepsilon(\mathbf{R}))\chi(\mathbf{R}) = E\chi(\mathbf{R}). \qquad (4)$$

We will discuss in more detail the electronic-motion problem, equation (3), in section 3 and the nuclear-motion problem, equation (4), in section 5. Following common usage, we will refer to a computed, approximate potential energy surface $\varepsilon(\mathbf{R})$ as ‘global’ if it correctly describes molecular configurations very far away from the equilibrium, possibly including one or more of the molecular dissociation channels.

The wavefunction of the system is approximately given in the Born–Oppenheimer approach by the product of the electronic and nuclear parts:

$$\Psi(\mathbf{r},\mathbf{R}) = \psi(\mathbf{r}|\mathbf{R})\chi(\mathbf{R}). \qquad (5)$$

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[1] An English translation can be found in [445].

The Born–Oppenheimer analysis soon became referenced to as a formal justification to the existing procedure of treating the nuclei as fixed [20]. However, several criticisms to the Born–Oppenheimer approach have been put forward over time [21–23]; the main ones are as follows.

(i) 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 not well defined. This difficulty has been fixed [24, 25] but the extension is not trivial.

(ii) The Born–Oppenheimer treatment is based on the assumption that the clamped-nuclei Hamiltonian has a deep potential minimum for a certain equilibrium configuration 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 criterion for the adequacy of the procedure is the energetic separation of other electronic states, but this is not apparent from the treatment; the Born–Oppenheimer treatment thus appears unnecessarily restrictive in the statement of its limits of validity [26].

(iii) The perturbation expansion around the minimum of the clamped-nuclei Hamiltonian is known to be divergent and this raises a series of issues if the aim is to improve on the approximation.

(iv) The Born–Oppenheimer paper [17] treats explicitly only diatomic molecules and the extension to a general polyatomic system using the same approach is not trivial.

2.1.2. *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 [22, 23]. This culminated in a different approach based on the variational principle which Born first proposed in [27] and was later reported as an appendix in the book by Born and Huang [28]. Incidentally, the same mathematical approach had been proposed much earlier by Slater [29], 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 elsewhere [30, 31]. The Hamiltonian is again partitioned in the clamped-nuclei Hamiltonian plus the nuclear kinetic energy

$$\hat{H} = \hat{T}_N + \hat{T}_e + V = \hat{T}_N(\mathbf{R}) + \hat{H}_{\mathrm{cn}}(\mathbf{R}, \mathbf{r}). \tag{6}$$

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 $\psi_j(\mathbf{r}|\mathbf{R})$:

$$\hat{H}_{\mathrm{cn}}\psi_j(\mathbf{r}|\mathbf{R}) = \varepsilon_j(\mathbf{R})\psi_j(\mathbf{r}|\mathbf{R}) \qquad j = 1, 2, \ldots, +\infty. \tag{7}$$

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

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_{j=1}^{+\infty} \chi_j(\mathbf{R})\psi_j(\mathbf{r}|\mathbf{R}), \tag{8}$$

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 (8) for the exact Ψ is inserted; making use of equation (7) and of the multi-dimensional chain rule, one obtains

$$\sum_{j=1}^{+\infty} \left\{ \varepsilon_j\psi_j + \psi_j\hat{T}_N + (\hat{T}_N\psi_j) - \frac{1}{M}\vec{\nabla}_{\mathbf{R}}\psi_j \cdot \vec{\nabla}_{\mathbf{R}} \right\}\chi_j = E\sum_{j=1}^{+\infty}\chi_j\psi_j \tag{9}$$

where, for simplicity, we have assumed that all nuclei have the same mass M. One proceeds by 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:

$$(\hat{T}_N + \varepsilon_i(\mathbf{R}))\chi_i(\mathbf{R}) + \sum_{j=1}^{+\infty} \hat{\Lambda}_{ij}(\mathbf{R})\chi_j(\mathbf{R}) = E\chi_i(\mathbf{R}), \tag{10}$$

where we have introduced the non-adiabatic matrix elements

$$\hat{\Lambda}_{ij}(\mathbf{R}) = \int \psi_i^*(\mathbf{r}|\mathbf{R})\hat{T}_N(\mathbf{R})\psi_j(\mathbf{r}|\mathbf{R})\,\mathrm{d}\mathbf{r} - \frac{1}{M}\left(\int \psi_i^*(\mathbf{r}|\mathbf{R})\vec{\nabla}_{\mathbf{R}}\psi_j(\mathbf{r}|\mathbf{R})\,\mathrm{d}\mathbf{r}\right)\cdot\vec{\nabla}_{\mathbf{R}}. \tag{11}$$

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 wavefunctions 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 for real wavefunctions (wavefunctions of the Coulomb Hamiltonian can always be chosen real) the second term of equation (11) does not contribute to $\hat{\Lambda}_{ii}$:

$$\int \psi_i(\mathbf{r}|\mathbf{R})\vec{\nabla}_{\mathbf{R}}\psi_i(\mathbf{r}|\mathbf{R})\,\mathrm{d}\mathbf{r} = \frac{1}{2}\int \vec{\nabla}_{\mathbf{R}}\psi_i(\mathbf{r}|\mathbf{R})^2\,\mathrm{d}\mathbf{r} = \frac{1}{2}\vec{\nabla}_{\mathbf{R}}\int \psi_i(\mathbf{r}|\mathbf{R})^2\,\mathrm{d}\mathbf{r} = 0. \tag{12}$$

The approximation in which only $\hat{\Lambda}_{ii}$ is retained is called the *adiabatic approximation*. If at least some of the off-diagonal elements $\hat{\Lambda}_{ij}$ are retained the calculation is generically called *non-adiabatic*.

Two observations can be made about $\hat{\Lambda}_{ij}$ for $i \neq j$. The first is that, contrary to the $i = j$ case, it is now the second term of equation (11) which is expected to be the larger one. This is so because, as a more detailed analysis can show [4], the matrix representation of the first term of equation (11) contains as a factor the square of the matrix representation of the second. As non-adiabatic terms are supposed to be small, the quadratic term will then be smaller than the linear one. Before making the second observation let us re-write the integral in the second term of equation (11) as

$$\langle \psi_i | \vec{\nabla}_{\mathbf{R}} | \psi_j \rangle = \frac{\langle \psi_i | [\vec{\nabla}_{\mathbf{R}}, \hat{H}_{\mathrm{cn}}] | \psi_j \rangle}{E_j(\mathbf{R}) - E_i(\mathbf{R})}, \tag{13}$$

where we have used the identity

$$\begin{aligned}\langle \psi_i | [\hat{A}, \hat{H}] | \psi_j \rangle &= \langle \psi_i | \hat{A}\hat{H} - \hat{H}\hat{A} | \psi_j \rangle \\ &= (E_j - E_i) \langle \psi_i | \hat{A} | \psi_j \rangle. \end{aligned} \tag{14}$$

Equation (13) hints at our second point: the non-adiabatic terms become large for configurations where two potential energy surfaces cross or come very close to one another. Special techniques are needed to deal with these cases (see section 4.1.2).

2.1.3. Criticisms and further developments. The Born–Huang treatment is much more satisfactory than the original one and is what is usually described in textbooks [32] under the denomination of the 'Born–Oppenheimer approximation' [33]. There are still, however, a number of undesirable features [23, 26, 34, 35].

(i) 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 $\hat{H}_{\mathrm{cn}}$ form a complete, discrete set of normalizable states, so expansion (8) is not completely justified.

(ii) 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.

One way of addressing point (i) is to separate out the centre-of-mass motion at the beginning of the treatment and then to study the Hamiltonian expressed in internal, translationally invariant (i.e. space-fixed, see section 5.3.1) coordinates [9, 23, 36–38]. However, this is technically cumbersome. A much simpler approach was introduced in practical calculations by Handy *et al* [39] and later formalized by Kutzelnigg [40]; 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 analysis 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.

The objections raised in point (ii) are discussed by Kutzelnigg [34] and Jaquet and Kutzelnigg [26]. 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 nuclear masses can give an approximation correct to $\mathcal{O}(M^{-2})$. A formalism with position-dependent masses was also notably developed by Herman and Asgharian [41], Bunker and Moss [42–44] and Pachucki and Komasa [45] from a different point of view; for a discussion and applications, see e.g. [46]. 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 [47].

2.1.4. The idea of molecular shape. As an aside we will mention that discussion has taken place in the scientific literature about the precise meaning of the classical, 'ball-and-sticks' concept of molecular shape in a quantum mechanical context; in particular, the conceptual implications of the Born–Oppenheimer scheme were discussed at length. The issue was raised and discussed particularly by Woolley [48–50] and several authors contributed [51–57], including a particularly thorough discussion by Claverie and Diner [58]. A related, less philosophically-inclined discussion treating the case of the water molecule was given by Császár *et al* [59, 60].

2.2. Relativistic effects

Already before the discovery of the Schrödinger equation in 1926, physicists had tried to unify quantum mechanics with special relativity [61, 62]. This line of research led to the Dirac equation [63] in 1928, while in the period from the 1930s to the 1950s a more complete formalism was developed under the name of quantum field theory [64]. Most textbooks on quantum-relativistic theories, e.g. [64–67], focus on particle physics and do not discuss applications to molecular systems; one exception is the book by Strange [68]. Relativistic effects in molecular systems are generally studied under the name of relativistic quantum chemistry, see e.g. the recent books by Dyall and Fægri [69] and by Reiher and Wolf [70] for some thorough and pedagogical expositions. Much shorter and more accessible introductions can be found in the book by Jensen [71] and by Piela [31] while other general reviews were given by Quiney *et al* [72, 73] and by Reiher [74]. A review focusing on the computation of relativistic effects in small, light molecules was given by Tarczay *et al* [75].

2.2.1. Quantum electrodynamics. The most complete theory describing interactions between matter and electromagnetic radiation is quantum electrodynamics (QED), see e.g. [64, 76, 77] for technical expositions and the reviews by Woolley [78, 79] and the book by Craig and Thirunamachandran [80] for expositions oriented towards molecular physics. Leaving aside some conceptual problems [81, 82], the application of the full QED formalism to molecular systems is numerically intractable and even the simplest cases such as the hydrogen atom have to be treated approximately [83]. 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 references [64, 76–80] for a detailed discussion of this complex subject.

2.2.2. The one-electron Dirac equation. Dirac [63, 64, 69] derived in 1928 a relativistic equation which describes a single particle with spin-1/2, such as an electron, in an external potential. The wavefunction of a Dirac particle is a four-component object

$$\psi(\mathbf{r}) = [\psi_1(\mathbf{r}), \psi_2(\mathbf{r}), \psi_3(\mathbf{r}), \psi_4(\mathbf{r})]. \tag{15}$$

Two distinct reasons [68, 69, 84] 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.

The time-independent Dirac equation for an electron in an external electric field V can be compactly written as the eigenvalue equation

$$\hat{h}_{\mathrm{D}}\psi = E\psi \qquad \text{where} \quad \hat{h}_{\mathrm{D}} = c\vec{\alpha}\cdot\hat{\mathbf{p}} + c^2\beta + V. \tag{16}$$

Despite its successes, the Dirac equation also has limitations; the external electric field is not quantized [84] and, as a consequence, the Dirac equation is not appropriate to describe the creation and annihilation of particles. This fact, however, does not constitutes a practical limitation in the low-energy context of molecular physics [68, 69].

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 the spectrum [69, 85, 86].

2.2.3. The spin-free Dirac equation. Dyall showed [87] that it is possible to re-write the Dirac equation in a way that renders spin-dependent and spin-independent effects more explicit [69]. A modified Dirac Hamiltonian $\hat{\tilde{h}}_D$ having the same spectrum as the original $\hat{h}_D$ was derived as the sum of a spin-independent term and a smaller spin-dependent one [69]. The spin-independent approximation consists in dropping the latter and constitutes an important reference point for comparisons with other, more approximate, 'spin-free' approaches.

2.2.4. The many-electron Dirac equation. In contrast to the Schrödinger equation, the Dirac equation is not rigorously generalizable to systems of many particles [84, 88] and, more generally, a universally accepted quantum-relativistic many-particle theory does not exist [88]. However, applications to atoms and molecules based on generalizations of the Dirac equation have been very successful [75] and the general consensus is that numerical results obtained from the Dirac equation are adequate for chemical purposes. The Dirac equation is generalized to many-electron systems by defining an N-particle Hamiltonian as

$$\hat{H}_{\mathrm{rel}} = \sum_{i=1}^{N} \hat{h}_{\mathrm{D}}(i) + \sum_{i=1}^{N}\sum_{j=i+1}^{N} \hat{g}(i,j), \tag{17}$$

where $\hat{g}(i,j)$ represents the electron–electron interaction. In the first approximation, one can take the Coulomb term [69]

$$\hat{g}_{\mathrm{C}}(i,j) = \frac{1}{r_{ij}}, \tag{18}$$

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 the context of classical electromagnetism [69] and gives the so-called frequency-independent Coulomb–Breit interaction:

$$\hat{g}_{\mathrm{CB}}(i,j) = \hat{g}_{\mathrm{C}}(i,j) - \frac{1}{2}\left(\frac{\vec{\alpha}_i\cdot\vec{\alpha}_j}{r_{ij}} + \frac{(\vec{\alpha}_i\cdot\mathbf{r}_{ij})(\vec{\alpha}_j\cdot\mathbf{r}_{ij})}{r_{ij}^3}\right). \tag{19}$$

The Dirac–Coulomb–Breit Hamiltonian applied in a four-component formalism represents the most rigorous method available to treat relativistic effects in molecules. Unfortunately, from a computational point of view, its solution is considerably more expensive than that for the corresponding non-relativistic Schrödinger Hamiltonian: see the book by Dyall and Fægri [69] for a quantitative discussion of this aspect.

2.2.5. The Pauli Hamiltonian. It is formally possible to perform an expansion in powers of $\hat{\mathbf{v}}/c \equiv \hat{\mathbf{p}}/mc$ of the one-electron Dirac–Coulomb Hamiltonian. The correction terms up to order $\mathcal{O}(c^{-2})$ give the Pauli Hamiltonian (note that this is not the same thing as the similarly named Pauli equation [68, 69], which is an *ad hoc* non-relativistic generalization of the Schrödinger equation which includes spin). The Pauli Hamiltonian acts on two-component wavefunctions:

$$\hat{H}_{\mathrm{Pauli}} = \underbrace{\hat{T} + V}_{\hat{H}_0} \underbrace{- \frac{\hat{\mathbf{p}}^4}{8c^2}}_{\hat{H}_{\mathrm{MV}}} \underbrace{+ \frac{1}{8c^2}(\nabla^2 V)}_{\hat{H}_{\mathrm{D1}}} \underbrace{+ \frac{1}{4c^2}\vec{\sigma}\cdot(\nabla V)\times\hat{\mathbf{p}}}_{\hat{H}_{\mathrm{SO}}} \tag{20}$$

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

$$\hat{H}_{\mathrm{D1}} = \frac{\pi Z}{2c^2}\delta(\mathbf{r}) \qquad \text{and} \qquad \hat{H}_{\mathrm{SO}} = \frac{Z}{2c^2}\frac{\vec{\sigma}\cdot\hat{\mathbf{l}}}{r^3}, \tag{21}$$

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 equations have been derived, such as the direct perturbation theory (DPT) of Rutkowski, Kutzelnigg *et al* [89–93]. The Pauli Hamiltonian is recovered in this more rigorous approach. It is also found that if approximate solutions of $\hat{H}_0$ as basis for the perturbation treatment, then a further term Δ^{DPT} arises, namely

$$\Delta^{\mathrm{DPT}} = \frac{1}{2c^2}\hat{T}(\hat{H}_0 - E_0). \tag{22}$$

Inclusion of Δ^{DPT} accelerates the convergence of relativistic properties with respect to the quality of the non-relativistic wavefunction [69, 75, 91].

2.2.6. The 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 [69]. We 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* [75]. At the first-order perturbation treatment and for spin-singlet states, only two of these terms are non-zero, namely the two-electron Darwin interaction and the spin–spin interaction [75].

2.2.7. The Douglas–Kroll–Hess Hamiltonian. A family of methods were developed where a unitary transformation of the Dirac Hamiltonian is performed with the aim of uncoupling the negative-energy degrees of freedom. If the transformation were exactly unitary, the transformed operator would have exactly the same electronic spectrum of the original Dirac Hamiltonian, but would act on two-component wavefunctions. In the last decade this approach has enjoyed significant success and methods are now available that perform this transformation in a formally exact and computationally efficient way. For a recent proposal and a review of the present situation, see Kutzelnigg and Liu [94, 95].

The Douglas–Kroll–Hess method [69, 84] 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 DHKn, $n = 2, 3, \ldots$ [84, 96].

These methods can be, and usually are, combined with the neglect of spin-dependent terms; when this is done the methods operate on single-component wavefunctions 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.

Special care is required when calculating molecular properties in the DKH framework. All the operators corresponding to the properties to be calculated need to be opportunely transformed, or otherwise an artefact called the picture-change effect is introduced [97, 98].

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.

2.2.8. 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 [69]; recent reviews discussing QED corrections for hydrogen-like and helium-like ions were given respectively by Soff *et al* [99] and by Artmyev *et al* [100]. The Lamb-shift is made up by two contributions, namely vacuum polarization and electron self-energy, both of which are difficult to calculate rigorously. In many-electron systems one can further partition the full effect in a one-electron contribution and a smaller two-electron one.

Because the exact treatment of the Lamb shift is far too complex to be applied to molecules, Pyykkö *et al* [101] suggested some very simple approximate expressions which may be sufficiently accurate for chemical purposes. In this approximation, the effect of the one- and two-electron Lamb shifts are assumed proportional to the one- or two-electron Darwin terms, and the coefficients of proportionality were tabulated for atoms. In the case of molecules containing only one heavy atom one may assume that the greatest contribution to the Lamb shift originates from it, and therefore it is reasonable to make use of the corresponding atomic coefficient of proportionality together with the molecular Darwin terms.

Table 1. Relativistic corrections to the barrier to linearity in water; values taken from Tarczay *et al* [75]. See the text for details.

Effect	cm^{-1}
Mass-velocity[a]	210.63
One-electron Darwin[a]	−158.42
Total MVD1 contribution	52.51
Δ^{DPT} (equation (22))[a]	−0.37
Two-electron Darwin[a]	2.51
Breit[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 as described in section 2.2.8 using $E_{\mathrm{L1}} = 0.023\,80 \times E_{\mathrm{D1}}$ and $E_{\mathrm{L2}} = 0.053\,334 \times E_{\mathrm{D2}}$ (values relative to the oxygen atom as tabulated by Pyykkö *et al* [101]).

2.3. Some indicative examples

Table 1, reproduced from Tarczay *et al* [75], illustrates the magnitude of various relativistic corrections to the barrier to linearity in the water molecule. The barrier to linearity is the energy difference between the equilibrium geometry and the lowest energy, linear geometry H–O–H; one of the best estimates of the non-relativistic value was calculated by Valeev *et al* [102] at 11 119 ± 15 cm^{-1}. The effect of the MVD1 correction is in this example about 20 times larger than that of further effects. This example suggests that, for small, light systems such as water, computing relativistic effects at the MVD1 level provides in most cases adequate accuracy.

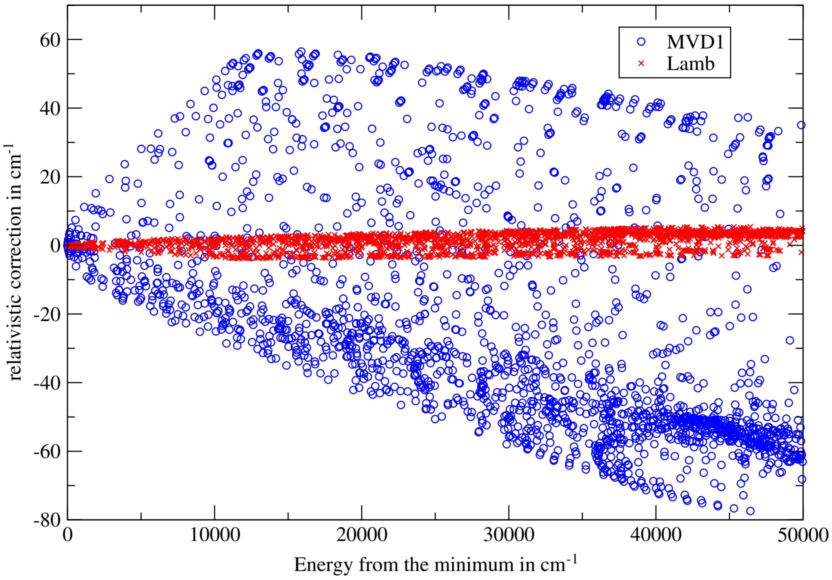

Figure 1. Relativistic MVD1 and one-electron Lamb shift for 2174 geometries of the water molecule. The corrections have been shifted so that they assume the value zero at the equilibrium. See the text for details.

Figure 1 illustrates the magnitude of relativistic corrections for a large set of geometries of the water molecule. Our group has performed a thorough study of the electronic structure of the water molecule, producing a new DMS [103] and PES [104, 105]. The data used for figure 1 were produced during these studies. The electronic-structure method used, which will be discussed in some detail in the next section, is IC-MRCI using an 8-electron 8-orbital reference space and the aug-cc-pCV6Z basis set; technical details can be found in [104, 106].

For water, the contribution to absolute energies of the MVD1 term is of about $-11\,400$ cm^{-1}. Its variation with molecular geometry, however, is much smaller. From figure 1 it is apparent that the MVD1 term in water can change the shape of the potential energy surface below 50 000 cm^{-1} by up to ± 70 cm^{-1}. This is a modest contribution, but important for accurate work. It can also be seen from the plot that the one-electron Lamb shift, calculated as proportional to the one-electron Darwin term as discussed in section 2.2.8, affects the potential energy only by about ± 4 cm^{-1}. This is a small shift, about ten times smaller than the estimated error in the non-relativistic IC-MRCI energies [106]. Nevertheless, past studies have shown that its inclusion slightly improves the agreement with the experiment [107]. Our studies also showed that basis-set incompleteness error of the MVD1 relativistic correction is small, being estimated at less than 1 cm^{-1} with the aug-cc-pCVQZ basis set and at less than 0.2 cm^{-1} with the aug-cc-pCV6Z one.

3. Solving the electronic-motion problem

3.1. Introduction

Finding the eigenvalues and the eigenvectors of the clamped-nuclei Coulomb Hamiltonian given by equation (1) is a 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 [108–114], no analytical or semi-analytical solutions are available. The intrinsic great complexity of the quantum many-body problem is also supported by computational complexity theory studies [115, 116].

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 [117] scale exponentially with the number of dimensions and thus become essentially impossible to apply to systems with more than one or two particles. It is clear that to treat the quantum *n*-body problem very special methods had to be developed, all necessarily involving significant approximations. The development of such methods is one of the main goals of quantum chemistry and theoretical solid-state physics. The aim of this section is to provide an overview to quantum chemistry methods used to compute global potential energy surfaces of small molecules, providing references and emphasizing 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, [6, 7, 31, 71, 118–121] for the quantum-chemistry approach and [122–125] for the solid-state viewpoint. Some other excellent, recent overviews covering mathematical aspects of the methods are [126–129]. Useful background topics are linear algebra [130], calculus of variations [131], constrained minimization using Lagrange multipliers [132] and the functional iteration method for the solution of nonlinear equations [133].

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

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n) \approx \Psi_{\mathrm{HF}} = \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \vdots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix}, \tag{23}$$

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

$$\chi(\mathbf{x}) = \psi_\alpha(\mathbf{r})\alpha(\omega) + \psi_\beta(\mathbf{r})\beta(\omega). \tag{24}$$

Application of the variational principle to the trial wavefunction 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. See the cited references for details.

3.2.2. Varieties of Hartree–Fock schemes. Equation (24) does not impose any restriction on the spin-orbitals, which are a sum of spin-α and spin-β components. The method which derives when this assumption is made is the general (sometimes called generalized) Hartree–Fock method (GHF). Although sometimes advocated [134] and extensively studied particularly by Fukutome in the 1970s (who, contrary to modern usage, calls it unrestricted Hartree–Fock) [31, 126, 135–138], the GHF method has been confined to rather niche applications [139–141]. Applying restrictions on the form of the spin-orbitals gives origin to the commonly-used restricted Hartree–Fock (RHF) and unrestricted Hartree–Fock (UHF) schemes. See the discussion in [4] for a longer discussion and more references.

3.2.3. 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 on numerical experimentation and not on rigorous proofs [127–129, 142–145]. 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 [127, 128], some 30 years after such solutions were found numerically. The interested reader is referred to the cited literature for a discussion of this aspect.

3.2.4. 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 [6, 119]. Incidentally, we note that Koopmans' theorem applies only to UHF or GHF wavefunctions, not to RHF orbital energies [146].

It is worth mentioning 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 [147]. 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 the energy of the lowest-unoccupied orbital collapse to zero [146, 148].

3.2.5. 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 three dimensions. Also, perhaps even more importantly, the single-particle picture of molecules which arises from the method is still deeply engrained in chemical thinking. However, one should always bear in mind that the Hartree–Fock method, particularly in its RHF version, has 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 [6]. RHF calculations are thus inadequate for the calculation of global potential surfaces of strongly covalently-bound molecules. It is also 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 [149, 150], FOOF [150] and SiNN [151]. For these reasons methods have been developed which take the Hartree–Fock solution as a starting point and then improve on it.

3.3. The correlation energy

The term 'correlation energy' was introduced by Wigner and Seitz in 1934 in the context of solid-state studies [152, 153] and then made particularly popular in the context of quantum chemistry by a famous 1959 review paper by Löwdin [154]. The correlation energy E_{corr} is defined as the difference between the true eigenvalue of the Schrödinger equation and the Hartree–Fock energy:

$$E_{\mathrm{corr}} = E - E_{\mathrm{HF}}. \tag{25}$$

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. Note that the term 'correlation' has a precise meaning in probability theory [155] which is much more specific and not equivalent to the use of the word in quantum chemistry [4, 156, 157].

Correlation energy is discussed in all quantum chemistry and solid-state physics textbooks mentioned in section 3.2, in volume 2 of [158], and has been the object of review papers,

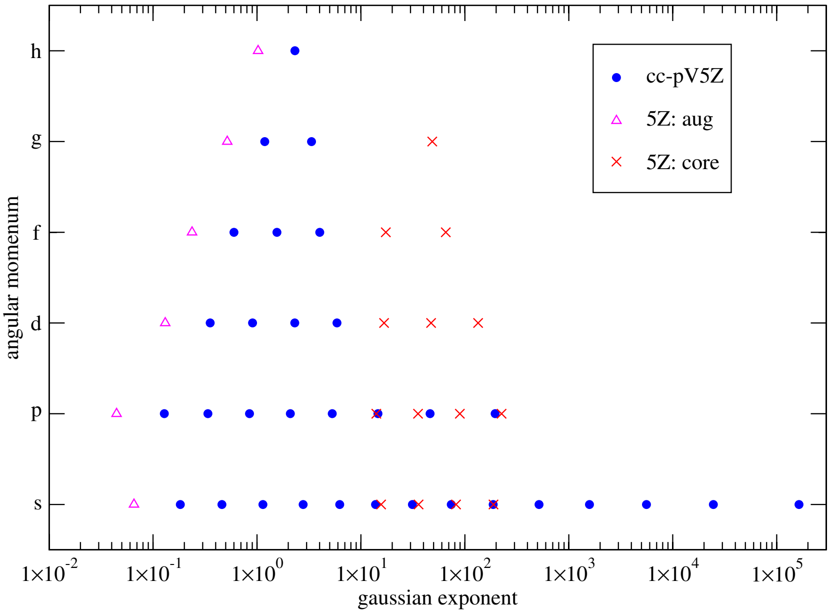

Figure 2. Gaussian exponents of the uncontracted aug-cc-pCV5Z basis set for oxygen. The fact that the exponents appear almost exactly equally spaced shows the quasi even-tempered nature of this family of basis sets (see the text).

among which we may mention two recent ones by Kutzelnigg [156, 159] among many others [135, 150, 154, 160–162].

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, 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.

3.3.1. Static and dynamical correlation. In the early 1960s, Tuan and Sinanoğlu [163] 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 [161, 164–166]. 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 equation (25) 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. See in particular [167] for a discussion. Other ways of partitioning the correlation energy, such as ‘left–right’, have also been proposed [166, 168].

3.4. Gaussian basis sets

Gaussian basis sets are treated in several excellent references [169–171] and will not be discussed here in great detail. Other references treating general properties of basis sets are [172–177].

3.4.1. Correlation-consistent basis sets. An uncontracted Gaussian basis set is characterized for each angular momentum included $l = 0, 1, \ldots, l_{\max}$ by N_l Gaussian exponents $\zeta_i^{(l)}$. In the case of even-tempered basis sets [169] the exponents are taken in a geometric progression so that they are characterized by a minimum exponent $\zeta_1^{(l)}$ and a maximum exponent $\zeta_{N_l}^{(l)}$, while the other exponents are given by

$$\zeta_i^{(l)} = \zeta_1^{(l)} \left(\frac{\zeta_N^{(l)}}{\zeta_1^{(l)}} \right)^{i/(N_l-1)} \qquad i = 0, \ldots, N_l - 1. \tag{26}$$

It can be proven [178–180] that in the limit of $l_{\max} \to +\infty$, $N_l \to +\infty$, $\zeta_1^{(l)} \to 0$ and $\zeta_{N_l}^{(l)} \to +\infty$, 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 [178–180]. Each of these increasingly accurate basis sets can then by characterized by a single ‘cardinal number’ n.

In particular, Dunning and co-workers devised [181–186], a family of basis sets called *correlation consistent* which have become very popular in correlated calculations [165]. These basis sets are called correlation consistent because each of them should contain all functions that lower the correlation energy by a certain quantity. Dunning’s exponents originated from an even-tempered basis set but they were then optimized to minimize the CISD energies for a set of reference molecules (see section 3.5 for a definition of CISD); because of this procedure, they do not follow exactly an even-tempered scheme, but they are very close to it. The reader is referred to the review by Wilson [169] and to references [181, 182, 184, 185] for more information. As an example, a plot illustrating the uncontracted aug-cc-pCV5Z basis set for oxygen is presented as figure 2. 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.

3.4.2. Speed of convergence. In the case of Hartree–Fock energies many studies [169, 172, 173] showed that, for properly optimized atom-centred, fixed-exponent Gaussian basis sets, the error $\varepsilon_{\mathrm{HF}}$ scales with the size N of the basis set as $\varepsilon_{\mathrm{HF}} = \mathrm{e}^{-\alpha\sqrt{N}}$. Unfortunately, many studies proved [160, 169, 172, 187, 188] that the rate of convergence for the correlation-energy portion is much, much slower, following a $\varepsilon_{\mathrm{corr}} = \frac{A}{N}$ law. For correlation-consistent basis sets $N \propto n^3$ where n is the cardinal number, so this law can also be written as $\varepsilon_{\mathrm{corr}} = \frac{A}{n^3}$. 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 method [71]. For spatially extended systems, the situation is somewhat better as techniques have been developed which, at the price of introducing adjustable, small errors, can cut the asymptotic computational cost down to linearity in N, see e.g. [189]. Our main concern here is in small systems where these techniques are not useful.

These considerations lead to a very discouraging convergence rate of the energy with respect to the computational time spent [187, 188]; for example, in the case of a N^5-method such as MP2 [71] one expects a scaling of the error with respect to the computational time of the kind $\varepsilon_{\mathrm{corr}} \propto t^{-1/5}$. 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. [190], but they are computationally expensive and the bounds given are much larger than the real error, so they are not in common use.

3.4.3. Extrapolation formulae for the energy. The regularity of the energy convergence pattern of basis sets belonging to the Dunning family encourages the use of extrapolation formulae which might accelerate the convergence of the correlation energy [165, 188, 191–194]. A simple but quite successful formula of this kind is [188, 194]

$$E_\infty = E_n + \frac{A}{n^3}. \tag{27}$$

This expression originated from studies of the convergence of the correlation energy of atoms, particularly helium [176, 195]. 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 fitted to equation (27) 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 extrapolation formulae have been investigated; examples of three-parameter extrapolation formulae are [165]

$$E_\infty = E_n + \frac{A}{(n+d)^3} \tag{28}$$

and [196]

$$E_\infty = E_n + \frac{A}{n^3} + \frac{B}{n^5}, \tag{29}$$

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–ζ, it is advocated [197] that extrapolation formulae of the kind of equation (27) be used only for the correlation part of the energy, while the Hartree–Fock energy be fit to a form of the kind [198]

$$E_{+\infty} = E_n + A\,\mathrm{e}^{-\alpha n} \tag{30}$$

or also [199]

$$E_{+\infty} = E_n - A(L+1)\,\mathrm{e}^{-\gamma\sqrt{L}}, \tag{31}$$

where L is the maximum angular momentum included (for correlation-consistent basis sets, $L = n$ for second-row atoms). As a guideline [193], one can expect $\{E_{n-1}, E_n\}$ extrapolated energies to have errors of the same order or slightly better than the non-extrapolated E_{n+1} (see also figure 5 for a specific example).

3.4.4. Basis sets for relativistic calculations. In the case of relativistic four-component calculations, special basis sets are needed. 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 [69] and in the review by Wilson [169] while a study of the rate of convergence was recently performed by Kutzelnigg [200].

3.5. Configuration interaction

Configuration interaction (CI) is discussed in all quantum chemistry textbooks, see [6, 71, 118, 121] for some good introductions. Some brief introductions at a more advanced level were given by Čársky [201] and by Duch [202] while for detailed expositions covering also algorithmic details, see Karwowski and Shavitt [203], Sherrill and Shaefer [204] and Siegbahn [205]. An earlier, well known exposition was given by Shavitt [206], who also gave a more recent perspective on the technique [207].

The general idea behind CI is very simple. Assuming that the Hartree–Fock solution is a 'good' approximation one may presume that, in an expansion of the exact wavefunction in the basis of the eigenfunctions of the Fock operator, contributions coming from determinants 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 diagonalized 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, etc gives origin to truncated-CI methods referred to by the acronyms CIS, CISD, CISDT, CISDTQ, CISDTQP (also written as CISDTQ5), 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 rises very quickly: for a basis set containing N functions CISD scales in the large-N limit as N^6, CISDT as N^8 and CISDTQ as N^{10} [71, 204]). The result of this very steep scaling is that for most systems CISD is the only computationally feasible CI level of treatment. Unfortunately CISD energies, even when the reference Hartree–Fock wavefunction is a good approximation, are not particularly accurate [204] as higher-order excitations (in particular, quadruple excitations) give a significant contribution [208].

Another very relevant deficiency in the CI approach is that when the Hartree–Fock solution is *not* a good approximation (see section 3.2.5), 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 [165, 204]. 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 flawed. This problem is the lack of the properties of size-consistency and of size-extensivity of truncated CI, which we will discuss in section 3.7.

3.6. Coupled cluster and other methods

Many electronic-structure methods have been proposed over the years, none of them emerging as an all-round winner. In view of the extreme difficulty of the problem, 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 arguably density functional theory (DFT) [209–212] coupled cluster (CC) theory [213–218] and Møller–Plesset perturbation theory (MP) [6, 219]. General introduction to these methods can be found in books such as those by Jensen [71], Cramer [118] and Piela [31].

The DFT acronym actually comprises a whole class of methods, each of which is characterized by a particular choice for a certain quantity called the exchange-correlation functional. Very many expressions for the exchange-correlation functional have been proposed in the literature, some of which include semi-empirical parameters fit to experimental data or to benchmark results obtained by other, higher-level methods. For molecular applications, a particularly successful and popular semi-empirical exchange-correlation functional is the B3LYP (Becke, three-parameter, Lee–Yang–Parr) introduced by Becke [220]. The DFT methodology is a considerable improvement over plain Hartree–Fock theory while, at the same time, requiring a similar computational cost; this makes DFT methods extremely attractive for applications to large systems where other correlated methods would be too expensive to employ. Unfortunately, DFT is not accurate enough for applications in high-resolution spectroscopy. Put another way, for small systems more accurate methods can be afforded and there is therefore no need to resort to DFT.

Coupled cluster is another extremely successful approach and is of particular relevance for accurate work. Similar to the configuration-interaction (CI) method discussed in section 3.5, coupled-cluster theory relies on the assumption that the Hartree–Fock solution is a reasonably good approximation to the exact wavefunction; an improved wavefunction is then obtained as an expansion of the eigenfunctions of the Fock operator. However, the form of the wavefunction expansion is different from CI and was introduced to enjoy certain desirable theoretical properties, most importantly the property of size consistency which will be discussed in section 3.7.

As in the CI approach, in coupled-cluster theory it is necessary to use truncated expansions; in this case the truncation corresponds to the maximum excitation order included in a certain expression called the cluster operator. Technical details can be found in the quoted literature.

The coupled-cluster (CC) strategy gives rise to a family of increasingly accurate—and increasingly computationally expensive—truncated-CC methods referred to by the acronyms CCS, CCSD, CCSDT, CCSDTQ, CCSDTQP (also written as CCSDTQ5), etc. To save computational effort, several schemes where the highest excitation order is treated in an approximate manner have also been developed. A recent overview on this topic was given by Kállay and Gauss [221]. A very successful approximation strategy gives origin to methods identified by acronyms using round brackets such as CCSD(T), CCSDT(Q), CCSDTQ(P), etc; these are approximations to CCSDT, CCSDTQ, CCSDTQP and so on. In particular, the CCSD(T) method achieves an excellent balance of accuracy and speed and is sometimes called ‘the gold standard of quantum chemistry’.

The problem with ordinary coupled-cluster theory is that, as also happens for configuration interaction, when the Hartree–Fock solution is not a good approximation to the exact wavefunction, higher excitations give significant contributions and truncated coupled-cluster methods such as CCSD(T) will not give even qualitatively accurate results. For example, when two single-bonds are stretched, the minimum level of theory required for quantitative accuracy is CCSDTQ, while to describe the breaking of a triple bond such as in the nitrogen molecule N_2 as high a level as CCSDTQPH is required [222]. Because of this situation, single-reference-based coupled-cluster theory is not adequate to describe molecular potential energy surfaces far away from equilibrium.

We will spend only a few words on Møller–Plesset perturbation theory (MP); a recent historical overview of this and related techniques was recently given by Kutzelnigg [219]. In its standard implementation, MP theory relies on the Hartree–Fock solution being a good approximation to the exact wavefunction and therefore fails, often very dramatically, at long bond lengths. Nowadays the use of Møller–Plesset perturbation theory is almost entirely limited to the second-order (MP2) version of the method, which is the fastest, non-DFT-based electron-correlation treatment available. It is mostly used for large systems where CCSD is too expensive to apply and where fast DFT-based methods do not perform well.

Some indicative results of DFT, CC and MP methods are presented in table 3.

3.7. 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 precise definitions, see Bartlett [223, 224], while further discussion can be found in [165, 204, 215, 225, 226]. We will summarize and examine in some detail these properties in the following sections.

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

This definition strictly applies 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 [119] (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].

A method which is not size extensive, however, will probably not be suitable for large molecules [223, 226] 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 [6, 204, 213, 223, 226, 227]. On the other hand, all forms of truncated CI apart from full-CI are not size extensive [6, 204]. In particular, it can be shown [6] that the CISD correlation energy is asymptotically proportional to the square root of the number of electrons, so that in an infinite system $\lim_{N\to+\infty} E_{\mathrm{corr}}(\mathrm{CISD})/N = 0$; this implies that configuration interaction is unsuitable for studies of large molecules or solids.

It may however be added that, although exact size extensivity is certainly a desirable property, it is not in itself a guarantee of accuracy; for example, the Thomas–Fermi model is exactly size extensive [228] but also inaccurate by our standards.

Size-consistency. 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 energies 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 when the dissociating fragments are closed shell species [204, 223, 226], as in the case of the He–He dimer.

In the much more common case of open–shell fragments, 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 3.2.5) 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. [229, 230]. 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 [223].

As 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.

On the other hand, lack of exact size consistency 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 3.10.2.

3.8. Core–valence separation of correlation effects

It is an idea ingrained in chemical intuition [7] 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 does not allow excitations from orbitals classified as 'core'. This 'frozen core' approximation is generally accurate [165] 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 [231–235].

3.9. 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 [236, 237] and to the original papers by Roos *et al* [238, 239]. Other references discussing the basis of the method are those by Schmidt and Gordon [240] and Werner [241]. For a more basic introduction, see the book by Jensen [71].

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.

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 [6], the orbitals are expressed as a sum of one-electron basis functions $\chi_\mu(\mathbf{x})$, $\mu = \{1, \dots, 2K\}$:

$$\phi_i(\mathbf{x}) = \sum_{\mu=1}^{2K} C_\mu^{(i)} \chi_\mu(\mathbf{x}). \qquad (32)$$

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) (a CF can also denote a spin-adapted linear combination of Slater determinants, but for simplicity we will not consider this possibility in the following):

$$\Phi_R(\mathbf{x}_1, \dots, \mathbf{x}_N) = \mathcal{A}\left(\Pi_{i=1}^N \phi_{\alpha_i}\right) = |\phi_{\alpha_1} \dots \phi_{\alpha_N}\rangle \qquad (33)$$

For example, if the N lowest-energy orbitals are selected and supposing the Aufbau principle holds the Hartree–Fock solution is obtained, otherwise an excited Hartree–Fock state is selected instead. The trial wavefunction is then written as a linear superposition of N_c CFs

$$\Psi_{\mathrm{CAS-SCF}} = \sum_{R=1}^{N_c} C_R \Phi_R. \qquad (34)$$

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 diagonalization of the Hamiltonian matrix. In the CAS-SCF method, the selection of the CFs 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. Orbitals not included in the active space are called 'inactive'. Then a full-CI calculation *within the active space* is performed. Also, to partially account for excited configurations excluded from expansion (34), the coefficients defining the active orbitals $C_\mu^{(i)}$ are permitted to change. This means that the optimized CAS-SCF active orbitals will differ from the original Hartree–Fock ones. Note that also inactive orbitals are modified, as they are defined as the eigenfunctions of the Fock operator, which in turn depends on the occupied orbitals. This fact guarantees that all CAS-SCF orbitals, active and inactive, remain orthogonal.

If we disregard the change in the orbitals, a CAS-SCF calculation is equivalent to a regular full-CI calculation performed in the basis set formed by the Hartree–Fock active orbitals. If the orbital space is big enough (see [236, 237] 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 by saying that CAS-SCF recovers the static part of the correlation energy, but is very inefficient in treating the dynamical part (see section 3.3.1).

Finally, we will make a remark on the convergence pattern of the CAS-SCF energy with respect to the basis set size. As 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 the basis set size and CAS-SCF total energies are best extrapolated using formulae such as equation (30) or (31) rather than of the kind (27) or (28).

3.10. 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 [204] who also cite older references; an older, more technical review was given by Werner [241].

In section 3.9 it was shown that the CAS-SCF method is able to recover the static part of the correlation energy, but is 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 wavefunction. 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 equation (34). As each Φ_R will in general already be an excited configuration with respect to the Hartree–Fock wavefunction, MR-CISD includes configuration which, from the point of view of single-reference CI, are much more than twice excited.

We will indicate with $\Phi(R)$ the reference functions of equation (34) 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 wavefunction can then be written as [204]

$$\Psi_{\mathrm{MR-CISD}} = \sum_{R=1}^{N_c} c(R)\Phi_R + \sum_{R=1}^{N_c}\sum_{ix} c_i^x(R)\Phi_i^x(R) + \sum_{R=1}^{N_c}\sum_{ijxy} c_{ij}^{xy}(R)\Phi_{ij}^{xy}(R). \qquad (35)$$

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 diagonalization of the Hamiltonian matrix.

3.10.1. 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 [204, 241]. We will mention here only a scheme known as internal contraction, which is implemented in the software MOLPRO [242]. This approach is discussed briefly in the mentioned reviews [204, 241] and more details can be found in

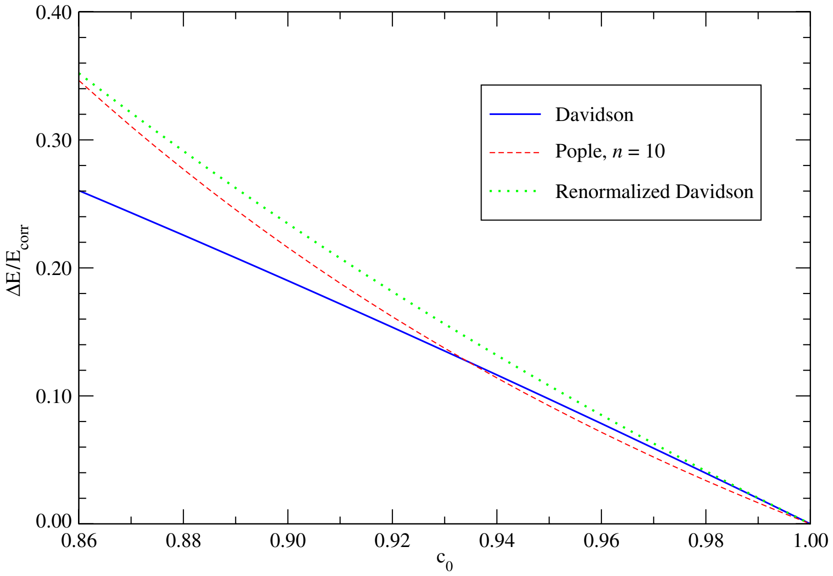

Figure 3. Davidson, renormalized Davidson and Pople correction factor for CISD energies.

the original papers [243–248]. 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 [169]) 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 wavefunction, equation (34).

3.10.2. 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 only correct the energy while others correct also the wavefunction.

In the first case, a standard (MR-)CISD calculation is initially performed, and 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 briefly review some of these approaches below.

Corrections only to the energy. Let us write the exact correlation energy E_{corr} as

$$E_{\text{corr}} = E_{\text{corr}}(\text{CISD}) + \Delta E, \tag{36}$$

where ΔE represents that part of the correlation due to excitation orders 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 [249] 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:

$$\Delta E_{\text{Davidson}} = \left(1 - c_0^2\right) \times E_{\text{corr}}(\text{CISD}), \tag{37}$$

where c_0 is the coefficient of the Hartree–Fock wavefunction in the normalized CISD wavefunction. Shortly thereafter this correction was justified on more rigorous grounds from a perturbative treatment of quadruple corrections [250].

In 1977 Davidson and Silver [251] pointed out that a more correct form for ΔE had already been derived in 1955 by Brueckner [252] and had the form

$$\Delta E_{\text{Ren.-Davidson}} = \frac{1 - c_0^2}{c_0^2} \times E_{\text{corr}}(\text{CISD}). \tag{38}$$

Duch and Diercksen [225] call this the ‘renormalized Davidson correction’. We remark, however, that this formula is also sometimes confusingly called just ‘Davidson correction’; for example, it is this last formula (38), and not equation (37), which is reported by MOLPRO [253] 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 [254]. If n is the number of correlated electrons and setting $\theta = \arccos(c_0)$ the Pople correction can be written as

$$\begin{aligned}\Delta E_{\text{Pople}} &= \left(\frac{\sqrt{n^2 + 2n\tan(2\theta)^2} - n}{2(\sec(2\theta) - 1)} - 1 \right) \times E_{\text{corr}}(\text{CISD}) \\ &= \left(1 - \frac{2}{n}\right) \Delta E_{\text{Davidson}} + \mathcal{O}\left(\left(1 - c_0^2\right)^2\right)\end{aligned} \tag{39}$$

which also shows how $\Delta E_{\text{Davidson}}$ and ΔE_{Pople} are related. A plot of the three corrections is presented in figure 3. 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 [225, 250, 255, 256] (note that formula (9) of [255] contains two mistakes). Duch and Diercksen [225] 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.

Multi-reference form of the corrections. It is formally easy to generalize Davidson-like corrections to multi-reference configuration interaction by substituting to the coefficient of the Hartree–Fock configuration c_0 the sum of the coefficients of all the reference configurations in the final MRCI wavefunction. This kind of generalization was already employed in early applications of MRCI in the early 1980s [257, 258], even though no firm theoretical basis for these procedures has ever been given and their actual usefulness is not generally proven, especially if large reference spaces are employed [204].

Corrections to energy and wavefunction. Another class of methods aims to modify CI or MRCI equations in such a way that the resulting method is approximately size-extensive. The best known of these methods is probably the averaged coupled pair functional (ACPF) of Gdanitz and Ahlrichs [259], while other proposals include the AQCC method of Szalay and Bartlett [260] and the ACPF-2 method of Gdanitz [261]. The quadratic configuration interaction (QCISD) method of Pople, Head-Gordon and Raghavachari [262] 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. [263–265].

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 by no means certain that they will always outperform regular MRCI or Davidson/Pople-corrected MRCI in real-world cases. We will give some indications of the performance of some of these methods when applied to the water molecule in section 3.14.

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 the 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 3.4.3 help to assuage this problem but do not remove it.

This painfully slow convergence is a much-studied problem [156, 159, 160, 169, 172, 187, 188] and the ultimate reason has been identified with the difficulty for orbital expansions of describing the electron–electron cusp present in the exact wavefunction. It has been known since the first days of quantum mechanics [266–268] that trial wavefunctions 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 wavefunction 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 [269, 270]. These methods have since enjoyed growing attention as they promise an improved speed of convergence with respect to the basis-set size with only a modest increase of computation with respect to conventional methods. They are most commonly employed in combination with the coupled-cluster method. For recent reviews on the topic, see [187, 188, 271]. 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 [187], 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 [272–274].

3.12. Computing molecular dipole moments

There is some discussion in the literature [275–279] concerning the most appropriate way of calculating first-order properties—in particular, dipole moments—from approximate solutions of the electronic Schrödinger equation. In what follows we will briefly summarize the situation while we refer to the mentioned literature and to chapter 10 of Jensen's book [71] for a more exhaustive discussion.

Dipole moments can be calculated in two ways:

(i) as the expectation value of the dipole operator $\hat{\mu}$ or
(ii) as the derivative of the electronic energy $E(\lambda)$, evaluated for $\lambda = 0$, of the perturbed Hamiltonian

$$\hat{H}' = \hat{H} + \lambda\hat{\mu}. \tag{40}$$

The perturbed Hamiltonian (40) 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 [71] that for exact wavefunctions these two ways of computation yield exactly the same values and are thus equivalent. In the practical case of approximate wavefunctions, the two methods do not, in general, give the same results and the question arises of which should be preferred.

It can be shown [71] that for some classes of approximate wavefunction (Hartree–Fock and CAS-SCF) the two methods give the same results, but not for all (truncated CI, MRCI or CC). Several theoretical arguments suggest that ED dipoles should be preferred over XP ones [277, 279–281]. Some of these reasons are as follows.

(i) An error in the wavefunction of the first order gives the energy accurate to second order, so quantities computed directly from the energies should be more accurate.

Table 2. 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 [284], which are the most accurate available. See also figure 4 for a plot of the estimated errors.

Technique	Author(s)	Reference	Year	$R_{\max}$	N_p	RMS	σ
Hy-CI	Sims and Hagstrom	[284]	2006	6.0	48	na	na
VMC	Alexander and Coldwell[a]	[285]	2004	10.0	24	0.25	0.11
ECG	Rychlewski and Komasa[b]	[266]	2003	40.0	11	0.000 03	0.000 01
KW	Wolniewicz	[286]	1995	8.0	20	0.0008	0.0005
ECG	Rychlewski *et al*	[287]	1994	3.4	15	0.008	0.0008
KW	Wolniewicz	[288]	1993	12.0	55	0.009	0.005
KW	Kołos *et al*	[289]	1986	12.0	55	0.05	0.03
KW	Kołos and Wolniewicz	[290]	1975	8.0	30	0.3	0.11
KW	Kołos and Wolniewicz[c]	[291]	1974	12.0	17	0.02	0.01
KW	Kołos and Wolniewicz	[292]	1968	3.2	17	1.0	0.8
KW	Kołos and Wolniewicz	[293]	1965	10.0	87	3.3	1.9
JC	Kołos and Roothaan[d]	[294]	1960	4.2	25	349.1	291.4
JC	James and Coolidge	[283]	1933	1.7	6	588.8	32.2

[a] The point at $R = 1.60\ a_0$ is non-variational and hence it is probably wrong. It was excluded from the computation of RMS and σ.

[b] The point at $r = 6.00\ a_0$ 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 [291] only have one point in common with [284]; hence, RMS and σ were computed with respect to [288], the best available reference that covers the same range.

[d] Points from [293] have a wrong behaviour at dissociation; hence, the overall high values for RMS and σ. Also, the reported values for $R = 0.8$ and $R = 0.9\ a_0$ are non-variational and hence probably wrong. For R closer than ≈0.5 a_0 to equilibrium, the RMS error is ≈10 cm^{-1}.

(ii) When higher-order properties like electric polarizability are computed as expectation values, the components may not obey the correct symmetry relations [279].

(iii) The ED approach allows dipoles to be computed also for quantum-chemical methods such as MP2, CCSD(T) and CISD+Q, for which the corresponding wavefunction 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 as corrections to the energy, such as relativistic corrections or the BODC [282].

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 components are to be determined, see e.g. section 4.1 of [278] for a related discussion.

3.13. A first reference case: the hydrogen molecule

In this section we will review in some detail ground-state potential energy curve calculations for the hydrogen molecule. The aim of this discussion is to give a general idea of the degree of accuracy obtainable for the smallest chemical neutral system both using specialized and more general quantum-chemical methods.

3.13.1. Energies obtained by explicitly correlated methods. Starting from the pioneering calculations by James and Coolidge [283] 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 [267].

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 [284] with the ones from Rychlewski and Komasa [266] we estimate the energies by Sims and Hagstrom [284] to be accurate to at least 10^{-4} cm^{-1} or 5×10^{-10} E$_h$. We report as table 2 a comprehensive list of references from 1960 onwards that calculate energy values for the hydrogen molecule. The historical 1933 computation by James and Coolidge [283] 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 [284] is reported as figure 4. It is clear from the data that, already from the mid-1960s, the hydrogen potential curve could be computed with errors of less than 1 cm^{-1}, a degree of accuracy generally unreachable for larger molecular systems.

3.13.2. Points obtained by FCI and atom-centred Gaussian basis sets. As hydrogen is a two-electron system, several quantum-chemical methods including CISD and CCSD are in this case equivalent to full CI (FCI). We used the CISD code in MOLPRO [242] to compute the hydrogen energies. The computation of one aug-cc-pV6Z energy point takes about 3 min on a 3.4 GHZ Pentium IV PC, uses 150 MB of RAM and 1.2 GB of disk space.

A plot of the errors is reported as figure 5; comparing it with figure 4 it is apparent that absolute values of energies

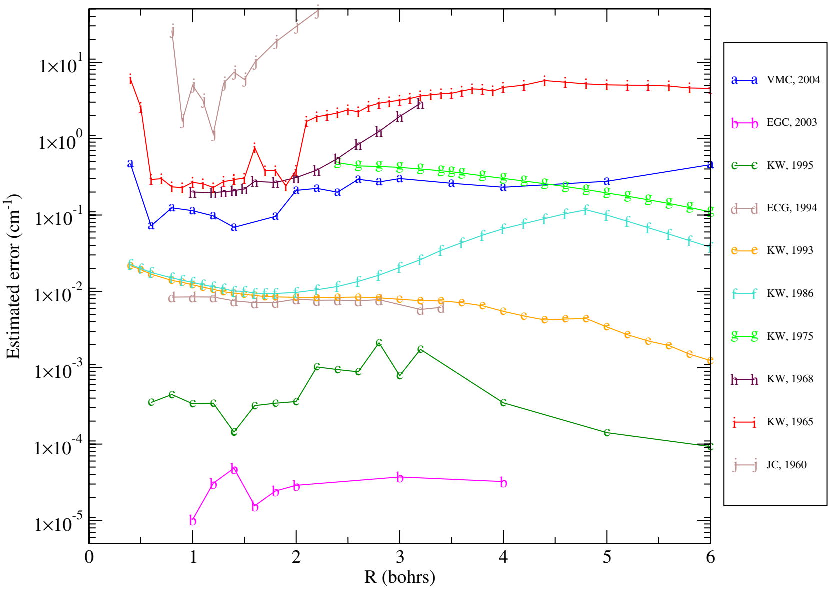

Figure 4. Estimated error in the energies of the hydrogen molecule for the references of table 2. In the legend we indicate the year of calculation and the acronym of the technique used. The precise reference can be inferred by looking at table 2.

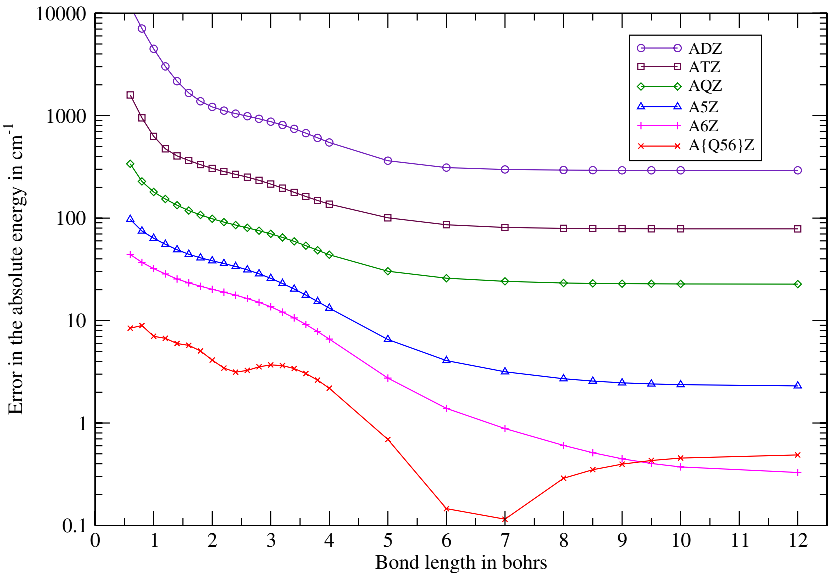

Figure 5. Errors in the total energies of the hydrogen molecule obtained using full-CI with various basis sets. The label ‘AnZ’ stands for aug-cc-pVnZ basis set. The series labelled ‘A{Q56}Z’ was obtained by extrapolation of the AQZ, A5Z and A6Z values using the form $E_n = E_\infty + A/(n+d)^3$.

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, results are far more encouraging if one looks at relative energies, especially at long bond lengths.

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. It is clear from figure 5 that the extrapolation reduced the error considerably, even though rather unsystematically along the potential curve. The fact that basis-set incompleteness errors become very small at long bond lengths is a feature specific to two electron systems: at $R = +\infty$ we are left with two one-electron systems for which the expected convergence pattern is of the $\exp(-\alpha\sqrt{n})$ kind rather than of the A/n^3 one found in dynamically correlated systems (see section 3.4.3). From these results we are led to expect a basis-set incompleteness error on relative energies of the order of ≈40 cm^{-1} for the aug-cc-pV6Z basis set and of ≈10 cm^{-1} for aug-cc-pV{Q56}Z extrapolated energies.

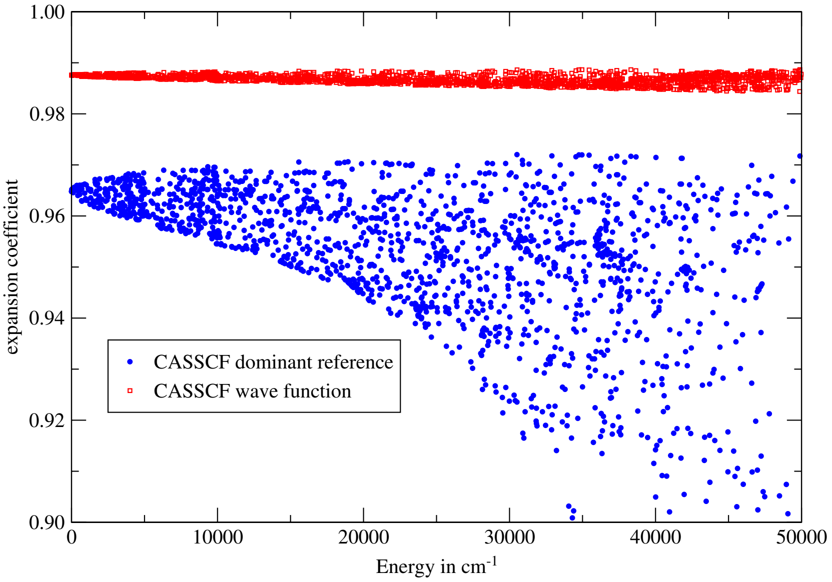

Figure 6. Expansion coefficients for the CASSCF wavefunction and for the CASSCF dominant configuration for a large set of points calculated with IC-MRCI in [8, 10] reference space and the aug-cc-pCV6Z basis set.

3.14. A second reference case: the water molecule

The water molecule constitutes an interesting benchmark; while still being very small by chemical standards, having ten electrons it is a much more difficult system to treat than the hydrogen molecule. Our group has recently undertaken an extensive study of the electronic structure of water, assessing the performance of various methods including MRCI, ACPF, AQCC, RSPT2 and RSPT3, CI up to CISDTQPH, CC up to CCSDTQP and FCI. The ACPF (averaged coupled pair functional) [259] and the AQCC (averaged quadratic coupled cluster) [260] methods were introduced in section 3.10.2, while RSPT2 and RSPT3 are multi-reference methods based on Rayleigh–Schrödinger perturbation theory [295].

The software used were MOLPRO [242], MRCC [296][2] and PSI3 [297]. For multi-reference methods, two reference spaces were considered: an 8-electron 8-orbital ([8, 8]) and a larger 8-electron 10-orbital ([8, 10]) one. For details see [4].

Water is generally considered a prototypical closed-shell system which can be well described by single-reference methods. While this is true close to the equilibrium geometry, multi-reference methods are indispensable to describe the higher-energy regions of the potential energy surface. To illustrate this point we present as figure 6 a plot of some of the expansion coefficients for a large set of IC-MRCI points calculated using [8, 10] reference space and the aug-cc-pCV6Z basis set. The first coefficient reported is the weight of the CASSCF wavefunction in the IC-MRCI one $\langle \Psi_{\text{CASSCF}} | \Psi_{\text{IC-MRCI}} \rangle$, while the second is the coefficient of the dominant configuration in the IC-MRCI expansion, coefficient $c(1)$ of equation (35); this last coefficient would correspond to the weight of the RHF wavefunction if orbital optimization were not performed in the CASSCF step. It is apparent from the plot that the CASSCF wavefunction provides a high-quality reference throughout the whole energetic range considered; on the other hand for energies higher than about 15 000 cm^{-1}, $c(1)$ decreases quickly, indicating that single-reference methods will have difficulties in those regions.

To give a general idea of the computational expense of these calculation, we mention that an all-electron single-point IC-MRCI [8, 10] energy evaluation for a C_s geometry with MOLPRO using the aug-cc-pCV6Z basis set takes about 18 h and 100 GB of disk on a workstation with 4 GB of RAM and a 2.5 GHz Core 2 CPU. Of this total time about 14 h were spent on the IC-MRCI step of the calculation, 2 h on the calculation of molecular integrals and the remaining 2 h for the RHF and CASSCF steps. For comparison, the single-reference methods CCSD(T) and MP4 take overall about 5–6 h with the same basis set.

Comparison with FCI energies from Chan and Head-Gordon. For a given basis set, full configuration-interaction (FCI) energies constitute invaluable references against which the quality of all other electronic-structure methods can be assessed. The largest reported FCI computations on water are those of Chan and Head-Gordon [298]. These authors reported all-electron FCI energies for two molecular geometries using a basis set of the same size as aug-cc-pVDZ (41 functions). Chan and Head-Gordon report that one iteration of their algorithm took 150 h, 250 GB of RAM and 800 GB of disk space on a machine with 64 POWER3 CPUs at 375 MHz.

We compared the FCI data from Chan and Head-Gordon with coupled-cluster calculations and with various multi-reference methods using the [8, 8] and the [8, 10] reference spaces; results are collected in table 3, where we indicated with +Q and +P configuration-interaction energies augmented respectively with the renormalized Davidson correction and with the Pople correction. Calculations were performed using MOLPRO [242] and MRCC [296]; a single CCSDTQP calculation required about 200 GB of disk, 1 GB of RAM and

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[2] A string-based quantum chemical program suite written by Kállay. See also [296] as well as www.mrcc.hu.

Table 3. Comparison of all-electron FCI values from [298] with various methods using an augmented double-zeta basis set (see the text). The bond angle is fixed at $\theta = 104.5°$ and $r_e = 1$ Å. In the first geometry, $r_1 = r_2 = r_e$, and in the second $r_1 = r_2 = 1.5\,r_e$. The 'RS' column indentifies the reference space used in multi-reference methods. Δ is the difference between the two energies, $\Delta = E(1.5r_e) - E(r_e)$, expressed in cm^{-1}(1 E_h = 219 474.631 3705 cm^{-1}).

Method	RS	r_e (E$_h$)	$1.5r_e$ (E$_h$)	Δ (cm^{-1})	error (cm^{-1})
FCI[a]		−76.314 715	−76.131 050	40 309.8	0
RHF		−76.057 621	−75.817 273	52 750.3	12 440.5
DFT-B3LYP		−76.429 776	−76.237 795	42 134.8	1825.0
MP2		−76.302 020	−76.110 699	41 990.1	1680.3
MP3		−76.303 352	−76.099 395	44 763.2	4453.4
MP4		−76.307 551	−76.115 632	42 121.5	1811.7
CISD		−76.296 239	−76.092 256	44 769.2	4459.3
CISD+Q		−76.311 108	−76.125 640	40 705.5	395.7
CISD+P		−76.308 588	−76.120 983	41 174.5	864.7
CISDT		−76.302 586	−76.103 767	43 635.7	3325.9
CISDTQ[a]		−76.314 001	−76.128 604	40 689.9	380.1
CCSD		−76.307 118	−76.115 089	42 145.4	1835.6
CCSD(T)		−76.314 141	−76.129 442	40 536.8	227.0
CCSDT		−76.314 294	−76.129 387	40 582.3	272.5
CCSDT(Q)		−76.314 769	−76.131 335	40 259.2	−50.6
CCSDTQ[a]		−76.314 696	−76.130 885	40 341.9	32.0
CCSDTQ(P)		−76.314 701	−76.131 072	40 302.0	−7.8
CCSDTQP		−76.314 714	−76.131 047	40 310.2	0.4
CAS-SCF	[8, 8]	−76.191 791	−76.004 382	41 131.5	821.6
RSPT2	[8, 8]	−76.303 558	−76.119 108	40 482.1	172.3
RSPT3	[8, 8]	−76.311 169	−76.126 194	40 597.2	287.4
IC-MRCI	[8, 8]	−76.311 535	−76.127 234	40 449.4	139.6
IC-MRCI+Q	[8, 8]	−76.314 860	−76.131 499	40 243.0	−66.8
IC-MRCI+P	[8, 8]	−76.314 239	−76.130 718	40 278.3	−31.5
IC-ACPF	[8, 8]	−76.314 260	−76.130 777	40 270.0	−39.8
IC-AQCC	[8, 8]	−76.313 629	−76.129 943	40 314.4	4.6
CAS-SCF	[8, 10]	−76.215 231	−76.029 141	40 842.0	532.2
RSPT2	[8, 10]	−76.304 080	−76.119 609	40 486.6	176.8
RSPT3	[8, 10]	−76.311 380	−76.126 425	40 593.0	283.2
IC-MRCI	[8, 10]	−76.312 841	−76.128 749	40 403.5	93.7
IC-MRCI+Q	[8, 10]	−76.315 030	−76.131 539	40 271.4	−38.4
IC-MRCI+P	[8, 10]	−76.314 616	−76.131 019	40 294.7	−15.1
IC-ACPF	[8, 10]	−76.314 625	−76.131 047	40 290.5	−19.3
IC-AQCC	[8, 10]	−76.314 215	−76.130 513	40 317.9	8.1

[a] From [298].

about 15 days on a 3 GHz Xeon 5160 system, while on the same system an IC-MRCI calculation in the [8, 10] reference space took about 150 MB of disk and 10 min of time.

Some conclusions can be drawn from these data:

(i) 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 behave erratically on enlargement of the reference space.

(ii) 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. The Davidson or Pople corrections are also extremely beneficial to single-reference CISD.

(iii) 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.

(iv) The coupled-cluster hierarchy of methods quickly converges to the FCI limit. To match the accuracy of [8, 10], size-extensivity-corrected, IC-MRCI-type methods CCSDTQ or even CCSDTQ(P) are required. These latter methods have an extremely steep computational scaling with respect to the basis set size and are unfeasible with larger basis sets.

(v) Second-order Møller–Plesset perturbation theory (MP2) considerably improves over RHF. Unfortunately, higher levels (MP3 and MP4) of perturbation theory fail to improve over the MP2 result in this instance.

(vi) Density functional theory (DFT) using the B3LYP exchange-correlation functional is a considerable improvement over plain RHF and is about as accurate as MP2 or CCSD, but much less accurate than the other higher-level methods considered.

Further analyses [4] also confirm in a more general way these findings and size-extensivity-corrected, IC-MRCI-type methods based on the [8, 10] reference space provide the most

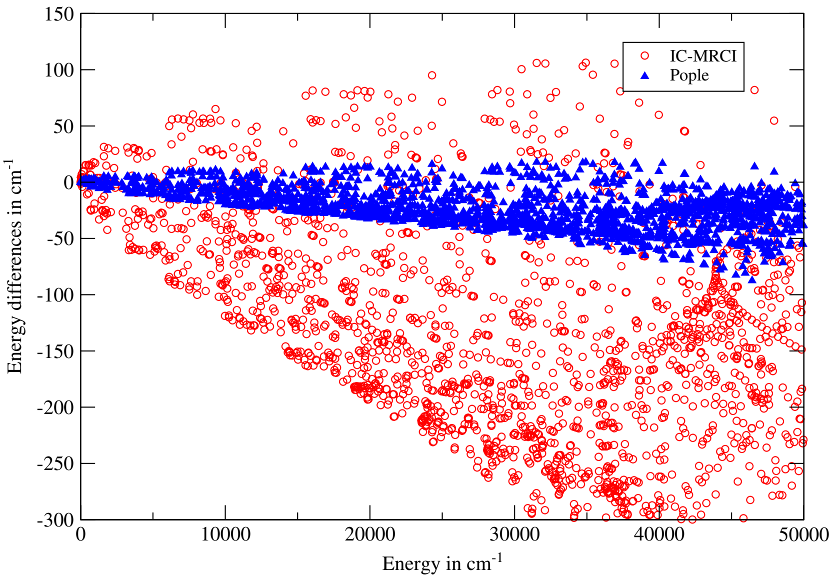

Figure 7. Size-extensivity corrections to IC-MRCI relative energies for water (see section 3.10.2). Triangles are (Davidson-corrected)−(Pople-corrected) energies, circles (Davidson-corrected)−(uncorrected IC-MRCI) ones. Corrections have been shifted so that they assume the value zero at equilibrium. The scatter of the Davidson−Pople points can be taken as an indication of the residual error due to electron correlation. The [8, 8] reference space (see the text) and the aug-cc-pCV6Z basis set were used.

accurate and yet affordable currently available methods to treat the electronic structure of water for energies at least up to about 50 000 cm^{-1}. IC-ACPF and IC-AQCC water energies are always extremely similar to Davidson- or Pople-corrected IC-MRCI ones, with no clear indication of being overall superior to them.

The residual electron-correlation error in IC-MRCI+Q energies was estimated at about 40 cm^{-1} for energies up to the water first dissociation channel at about 44 000 cm^{-1} [104], and about 50 cm^{-1} for energies up 50 000 cm^{-1}. The order of magnitude of these values is supported by the scatter of Davidson- and Pople- corrected IC-MRCI energies, see figure 7. It is also clear from figure 7 that the effect of size-extensivity corrections to MRCI is very relevant. Note that the IC-MRCI+Q-CASSCF differences, representing the effect of dynamical electron correlation, span a range from +500 to −1000 cm^{-1} and are thus off-scale to be plotted in figure 7.

The basis-set incompleteness error can be estimated in various ways, for example, by looking at the difference between extrapolated aug-cc-pCVQ56Z energies and aug-cc-pCV6Z ones as shown in figure 8. Basis-set incompleteness is estimated to affect relative energies up to about 50 000 cm^{-1} by up to 40–50 cm^{-1}.

These and other results [106, 121] suggest that at the present level of treatment a partial cancellation of errors takes place between the basis set and correlation error.

Dipole moments. Another test of the quality of electronic structure calculations comes from the calculation of molecular properties such as dipole moments. Dipole moments are necessary to compute vibrational–rotational line intensities, which is of great importance for many applications. It is outside the scope of this tutorial to discuss in any detail the calculation of dipole moments and the building of a dipole moment surface for water, for which the reader is referred to [4, 103, 299].

We report as table 4 the results of a highly accurate calculation of the water equilibrium dipole moment [103, 282]. It is worth remarking that to obtain agreement with experiment it is necessary to include small effects such as relativistic corrections and the DBOC.

Our final theoretical value for the dipole agrees with the experimental one within 0.000 05 au, while the theoretical uncertainty was estimated at 0.0004 au; the major source of uncertainty in the theoretical values comes from the non-relativistic value.

Table 4. Dipole, in au, at the reference structure $r_e = 1.810\,02\ a_0$ and $\theta = 104.485°$.

	Value	Uncertainty
Non-relativistic, all-electron[a]	0.7304	0.0004
Relativistic correction[b]	−0.0017	0.0001
DBOC contribution[c]	0.0008	0.0001
Vibrational averaging[d]	0.0001	0.0001
Final value for the ground-state dipole	0.7296	0.0004
Experimental value[e]	0.7296	0.0002

[a] IC-MRCI+Q, 8-electron 10-orbital reference space; dipole obtained as an energy-derivative; value extrapolated from the aug-cc-pCVnZ, n = Q,5,6 using $\mu_n = \mu_\infty + A/n^\alpha$.

[b] Obtained from the derivative of the MVD1 term using IC-MRCI+Q.

[c] Diagonal Born–Oppenheimer contribution, taken from [282].

[d] This is the estimated effect of averaging the dipole moment surface using the ground-state rotation-vibrational wavefunction. See [103] for details.

[e] Clough *et al* [300] and Gregory *et al* [301]. The reported value is the weighted average of these two measurements.

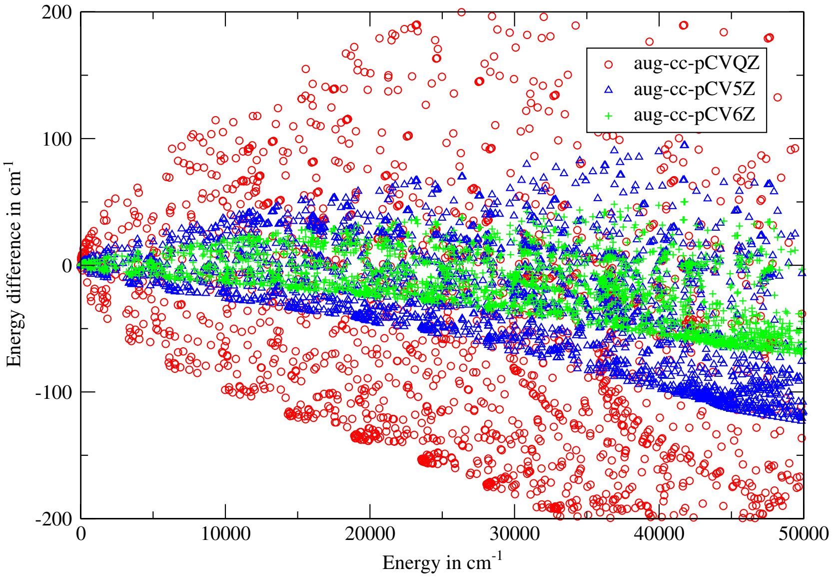

Figure 8. Basis-set errors to IC-MRCI relative energies for water. Shown in the plot are the differences between energies calculated with the aug-cc-pCVnZ basis sets (n = Q,5,6) and extrapolated aug-cc-pCV{Q56} energies. Corrections have been shifted so that they assume the value zero at equilibrium. The scatter of the aug-cc-pCV6Z energies can be taken as an indication of the residual error due to basis-set incompleteness. The [8, 8] reference space (see the text) was used.

4. Molecular hypersurfaces

As discussed in section 2 the calculation of vibration–rotation line positions and intensities requires the knowledge of the molecular potential energy surface (PES) and dipole moment surface (DMS). In some applications it is possible to compute PES or DMS values on-the-fly as they are needed [302, 303]. Unfortunately, the electronic structure methods appropriate for accurate spectroscopic work are far too slow to be used in this way. Another possibility [304] 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 numerical-integration grid. Again, this is highly impractical 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-known area of numerical analysis generally called *function approximation* or *function interpolation*, see e.g. the books by Conte and de Boor [305], Kincaid and Cheney [133], Powell [306] and Press *et al* [307] for some general introductions. We will generically call this process *surface building*. Three basic questions which arise are: (i) What accuracy is needed for the PES and DMS? (ii) How should an optimal set of geometries be chosen? (iii) 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 section.

4.1. 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* [308] and the review by Sutcliffe [309].

4.1.1. 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 ^{3}P and hence with spin equal to 1. By the rules of angular momentum addition [310] it follows that the total angular momentum of the composite system $H_2\left(^1\Sigma_g^+\right)$+O(^{3}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 wavefunction 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 equal to 1 crosses the ground-state curve and becomes lower in energy. It is *this* state which smoothly dissociates into $H_2\left(^1\Sigma_g^+\right)$+O(^{3}P), while the original curve leads instead to the state $H_2\left(^1\Sigma_g^+\right)$+O(^{1}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 $H_2\left(^1\Sigma_g^+\right)$+O(^{3}P).

This example is one instance 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* [308] and in more detail in the books by Zare [311] and Landau and Lifshitz [312]. See also the articles by Pechukas and Zare [313], Chiu [314] and Bellary *et al* [315].

4.1.2. *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 [309] and Yarkony [316] and the article by Mead [317]. For electronic states with different symmetry, no special limitations 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 $N \geqslant 3$ 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 [316, 318] and Sutcliffe [22] and the book by Baer [319].

4.1.3. *The many-body expansion.*

A many-body expansion representation of the PES [308, 320] can be conveniently applied to any 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:

$$V^{(1)} = V_1 + V_2 + V_3. \tag{41}$$

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:

$$\begin{aligned} V^{(2)} = {} & [V_{12}(r_{12}) - V_1 - V_2] + [V_{23}(r_{23}) - V_2 - V_3] \\ & + [V_{12}(r_{13}) - V_1 - V_3], \end{aligned} \tag{42}$$

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

$$V^{(3)} = V(r_{12}, r_{23}, r_{13}) - V^{(2)} - V^{(1)}. \tag{43}$$

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 $V^{(3)} \to 0$ 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:

$$V = V^{(1)} + V^{(2)} + V^{(3)}. \tag{44}$$

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, so that the value of the three-body term at the known geometries is calculated by equation (43). 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 in 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 $\left(r_{12}^{\mathrm{eq}}, r_{23}^{\mathrm{eq}}, r_{13}^{\mathrm{eq}}\right)$. This can be achieved by a redefinition of the terms

$$\begin{aligned} \tilde{V}^{(1)} &= -V\left(r_{12}^{\mathrm{eq}}, r_{23}^{\mathrm{eq}}, r_{13}^{\mathrm{eq}}\right) \\ \tilde{V}^{(2)} &= V^{(2)} \\ \tilde{V}^{(3)} &= V(r_{12}, r_{23}, r_{13}) - V^{(2)} \\ \tilde{V} &= \tilde{V}^{(1)} + \tilde{V}^{(2)} + \tilde{V}^{(3)}. \end{aligned} \tag{45}$$

4.2. *One-dimensional curve building*

One-dimensional function approximation is a classical and well-understood chapter of numerical analysis, see e.g. [133, 305–307], but is not very representative of the difficulties encountered in the multi-dimensional case.

Most standard results in approximation theory [133, 305] 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 [133, 307]). More workable choices are interpolation with piecewise polynomials (including splines [306, 321]) or, especially if the data set of points is small ($N_{\text{points}} \lessapprox 10$), least-squares fit to an opportune functional form, usually involving polynomials.

4.2.1. *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 [133, 305, 306] if no other information is known about the function to be approximated.

Optimal grid placement for piecewise polynomial interpolation (including splines) has received some attention in the mathematical literature but there seem to be no general result of immediate practical use [322, 323]. A result of this kind for n-order natural spline functions [324] can be stated by saying that, in the limit of a great number of points, the (unnormalized) optimal point density is given by $|f^{(n)}(x)|^2$. The main problem with these kinds 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.

Interpolation variables. Over the years, a large set of expansion variables have been proposed for diatomic molecules, see e.g. the review by Wilson [325] and chapter 3 of the thesis by Huang [326] for more details. The purpose of this transformation of variable is to try to eliminate singularities and other non-polynomial behaviours in the function to be approximated, so that the transformed data set can then be approximated more efficiently. See the discussion in [4] for details.

4.3. Multi-dimensional surface building

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 [133] and Press *et al* [307]. 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 increases exponentially with the number of dimensions, this strategy quickly becomes impracticable because of the enormous quantity of data required. In three dimensions the use of regular grids is still (barely) conceivable, see e.g. [327] 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 [328], Lai and Schumaker [329] and Fasshauer [330], the review by Fasshauer [331] and the overview by de Boor *et al* [332].

4.3.1. Practical implementations. 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) [333–337], neural networks [338, 339], interpolating moving least squares (IMLS) [340, 341], modified Shepard interpolation (MSI) [342, 343], distributed approximating functionals (DAF) [344] and invariant polynomials theory [345].

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. 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 [327]. This is particularly true if the data set of points to be fitted is not very dense.

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 artefacts 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. In this respect multi-dimensional fits with polynomials are more problematic than one-dimensional ones. In one dimension it is well known [133] 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 [328, 346] 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 [347] and states that any many-dimensional continuous function can be uniformly approximated by multivariate polynomials.

4.4. Molecular dipole moment surfaces

Much of what has been said on the construction of energy surfaces can also be applied to molecular dipole moment surfaces. Dipole surfaces are vector functions, having two non-zero components for a triatomic system and three non-zero components for a generic molecule with four or more atoms. Each component can always be considered individually, but for triatomics of the AB_2 type it is also possible to combine the two components into a single, scalar function [299].

A more in-depth discussion of some of the problems specific to the construction of dipole moment surfaces can be found elsewhere [4, 103, 299]. We will only mention here that particular care must be employed in the construction of the surface as rotational–vibrational line intensities are extremely sensitive to the presence of spurious, small-amplitude oscillations in the dipole moment surface.

5. Solving the nuclear-motion problem in triatomic systems

5.1. Introduction to the problem

As explained in section 2, after obtaining the electronic potential energy surface $V(\mathbf{x}_1, \ldots, \mathbf{x}_N)$, the next step is to solve the Schrödinger equation for the nuclear motion. Similar to the electronic-motion case, as the number of nuclei increases finding the eigenvalues and eigenfunctions of $\hat{H}$ quickly becomes a very difficult problem. There exist some major qualitative differences between the electronic-motion and the nuclear-motion problems; most notably, in the electronic-motion case we are interested only in the ground state and possibly in a few (less than about ten) excited states, while in the nuclear-motion one we often want to compute many hundreds or even thousands of excited states. Another essential difference lies in the form of the interaction between particles; in the electronic-motion case particles interact through simple, two-body Coulomb attractions or repulsions, as shown by the Coulomb Hamiltonian given by equation (1). On the other hand, in the nuclear-motion problem, the interaction potential for the nuclei is given by the potential energy surface, which does not have a simple analytical expression and, more importantly, is a many-body operator (see the discussion in section 4.1.3).

The standard approach to the nuclear-motion problem and to explaining the main features of rotation–vibration spectra was developed in its main lines in the period 1930–1950 and is discussed in many references, among which we may recommend the books by Bernath [348], Papoušek and Aliev [349], Bunker and Jensen [30], Wilson, Decius and Cross [350], and the reviews by Wilson [351] and by Sutcliffe [352]. This now-traditional approach is based on an approximate separation of the vibrational and rotational degrees of freedom (Eckart conditions [351]) and on a harmonic expansion of the potential around the equilibrium positions of the nuclei. The approximations introduced can then be 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 [353] for more details on modern approaches particularly close to this framework.

This traditional approach is often implemented in quantum chemistry program such as GAUSSIAN [354], MOLPRO [242] and GAMESS [355], just to mention a few. Quantum chemistry programs can often compute second-order derivatives of the potential energy surface at the equilibrium geometry and, using these, are then able to perform a normal-mode analysis of the molecule and to compute the harmonic (and sometimes also anharmonic) vibrational frequencies. While this information is extremely useful for many purposes, e.g., for thermochemistry, it is insufficient for high-resolution rotation–vibration spectroscopy. More specifically, to compute high-resolution spectra we need many (typically, hundreds) vibrational–rotational energies, and not only the ground-state and vibrational fundamentals as is favoured in these implementations; furthermore, because of the inherent approximations made, the accuracy of the computed energies is too low for spectroscopic applications.

It should be clear from the above discussion that, to accommodate the needs of high-resolution rotational–vibrational spectroscopy, very specific theoretical approaches have been formulated. In the next subsection we will very briefly review some notable approaches, before specializing to a particular strategy based on a technique called the DVR approximation (see section 5.5 for details). For other general introductions see, e.g., the modern reviews by Tennyson [356] and Bowman *et al* [357].

5.2. Some high-accuracy approaches to rotational–vibrational spectroscopy

As discussed at the beginning of section 3, the computational complexity of the quantum many-body problem has an exponential scaling with respect to the number of particles included. Because of this, a fundamental discriminating factor in theoretical approaches to the nuclear-motion problem is the number of nuclei involved. While in molecules with more than about five or six nuclei very severe approximations necessarily have to be introduced, for smaller systems very specialized methods involving fewer approximations can be applied.

An approach appropriate for large molecules (in this context, 'large' means molecules with more than about five nuclei), or for clusters of small molecules, is the vibrational self-consistent field (VSCF) method [357–360]. This method applies the independent-particle approximation, also at the base of the electronic-structure Hartree–Fock method, to the nuclear-motion problem. Most notably, the VSCF approach has been implemented and applied, together with other ideas, by Carter, Bowman, Handy and co-workers in the program MULTIMODE [357, 361–363].

Some of the ideas at the base of electronic-structure methods (see section 3) such as configuration interaction (CI) or coupled cluster (CC) have also been implemented in the context of nuclear motion, giving origin to methods such as vibrational-CI (VCI) [357, 361] or vibrational-CC (VCC) [364].

With respect to large molecules, diatomic molecules are in many respect at the opposite end of the computational-complexity spectrum. In the case of diatomics, the nuclear-motion problem reduces to a one-dimensional problem which can be very easily dealt with using standard numerical techniques ordinarily used for differential equations; there are several program available for the two-atom nuclear-motion problem, among which we may mention the program LEVEL by Le Roy [365]. Many aspects on the spectroscopy of diatomics are described in detail in the treatise by Brown and Carrington [366].

Triatomic molecules and ions could be considered as a middle-ground, where extremely accurate results are possible but, at least in some applications, require great care and computational effort. In particular, starting from the mid-1970s, pioneering studies by Carter, Handy and co-workers [367–370], triatomic systems have received much attention and the formalism is now well established. Other notable methods specific for triatomics have been developed by Jensen and co-workers [371, 372] (MORBID method), Tennyson and co-workers [373] (DVR3D computer program suite), Schwenke [374] and Czakó *et al* [375, 376] (DOPI3 and D2FOPI computer programs). It is also worth remarking that studies on triatomics have led not only to very accurate predictions of line positions and intensities but also to the discovery of new, initially unexpected physical phenomena such as rotation–vibration energy cluster formation [371, 377–379] and quantum monodromy [380–382].

Several codes specific for tetra-atomic (four-atom) molecules exist, including WAVR4 by Kozin *et al* [383] and RVIB4 [384, 385] by Carter, Colwell and Handy.

Other recent, notable approaches oriented towards high-resolution spectroscopy of molecules with three to about five atoms are TROVE by Yurchenko, Thiel and Jensen [386], DEWE [387, 388] by Császár and co-workers, GENIUSH [389] also by Császár and co-workers and several methods developed by Carrington and co-workers [390–393].

In the remainder of section 5, we will outline some features relevant to many theoretical methods and particularly important for the approach developed by Tennyson and co-workers for triatomic systems. More detailed accounts of this approach can be found in the review articles by Tennyson [394], Tennyson *et al* [395], Bačić and Light [396] and Tennyson [397], and in the original papers by Sutcliffe and Tennyson, particularly [398] and [399].

5.3. The internal degrees of freedom

The Hamiltonian in atomic units and Cartesian coordinates for a triatomic system is

$$\hat{H} = \hat{K} + V = -\frac{\nabla_1^2}{2m_1} - \frac{\nabla_2^2}{2m_2} - \frac{\nabla_3^2}{2m_3} + V(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3), \quad (46)$$

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. [400]. 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 [350]).

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 [401] 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 (46) 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 non-trivial details of the analysis have been worked out long ago and are well established [402, 403]. 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 [402, 403] and will be outlined in the following sections. 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 on the rotational quantum numbers and on three internal coordinates describing the internal degrees of freedom. The number of dimensions of the problem is therefore reduced from nine in Cartesian coordinates to three in internal coordinates [349, 404]. 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 has notably been developed by Sutcliffe and is described in [35, 405, 406]. Other treatments were given, e.g., by Islamapour [407, 408], Schwenke [409], Lukka [410], and Chapuisat and Iung [411].

The main inconvenience of abandoning the $3N$ Cartesian coordinates in favour of $(3N - 6)$ curvilinear internal coordinates in that the kinetic-energy term $\hat{K}$ 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 [406, 411].

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 [309, 352] which in technical terms can be expressed by saying that the quotient space $\mathbb{R}^{3N-3}/O(3)$ is a manifold with dimension $3N - 6$, but not a vector space [398]. One simple 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 [352, 399]. Singularities can also be dealt with at later stages of the calculation, e.g. by a judicious choice of the basis set to be used to expand the wavefunctions [412] and/or by clever use of discretization schemes which avoid sampling the region of the singularity [399]; see also section 5.3.3.

5.3.1. 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 topics in detail are the books by Brink and Satchler [413], Rose [414], Edmonds [415], Zare [311], Biedenharn and Louck [416], Thompson [310] and the review by Van de Wiele [417]. In what follows, we will briefly introduce the concepts we will need in the rest of our discussion.

Reference frames. It is convenient to define three Cartesian frames of reference.

(i) *Laboratory-fixed frame.* It a reference frame fixed 'in the laboratory'; in this frame, the Hamiltonian assumes its simplest form given by equation (46).

(ii) *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.

(iii) *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 can be specified with continuity by three parameters; one possible and commonly used way of doing this is by means of the Euler angles $(\alpha\beta\gamma)$ [310, 350]. The Euler angles are used to parametrize an orthogonal rotation matrix $\mathbf{C}$ which, using the Brink and Satchler [413] or zyz convention, reads

$$\mathbf{C}(\alpha\beta\gamma) = \begin{pmatrix} c^\alpha c^\beta c^\gamma - s^\alpha s^\gamma & s^\alpha c^\beta c^\gamma + c^\alpha s^\gamma & -s^\beta c^\gamma \\ -c^\alpha c^\beta s^\gamma - s^\alpha c^\gamma & -s^\alpha c^\beta s^\gamma + c^\alpha c^\gamma & s^\beta s^\gamma \\ c^\alpha s^\beta & s^\alpha s^\beta & c^\beta \end{pmatrix}, \tag{47}$$

where we wrote for compactness $\cos\alpha = c^\alpha$, $\sin\alpha = s^\alpha$ and so on. 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

$$\mathbf{t} = \mathbf{C}\cdot\mathbf{z}. \tag{48}$$

Note that this matrix is written assuming it acts from the left on column-vectors. Sometimes, e.g. [406], the convention of taking row-vectors is taken instead, and in that case the transpose $\mathbf{C}^\dagger$ should be used instead.

Wigner rotation matrices. It is a well-known result [310, 413] 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 we written as a linear combination of the eigenfunctions in the original frame having the same value of j [413]

$$|j,m\rangle' = \sum_{k=-j}^{j} (-1)^k \left(\mathscr{D}^j_{m,-k}\right)^* |j,k\rangle, \tag{49}$$

where the $(-1)^k\left(\mathscr{D}^j_{m,-k}\right)^*$ are linear expansion coefficients which also depend on the Euler angles connecting the two frames; the somewhat convoluted way in which they are written follows from the convention we have adopted for $\mathscr{D}^j_{mk}$ [413]. This last represents the element mk of a $(2j+1)\times(2j+1)$ Hermitian matrix called the Wigner rotation matrix. Also note that k is the quantum number corresponding to the projection along the molecule-fixed reference frame.

5.3.2. Exact quantum numbers for the rotation–vibration wavefunctions. The Hamiltonian (46) commutes with the square of the total angular momentum operator $\hat{J}^2$; this implies that rotation–vibration wavefunctions have as a good quantum number the total rotational angular momentum quantum number $J = 0, 1, 2, \ldots$. 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 wavefunctions which are eigenfunctions of $\hat{J}_z$, the projection of the angular momentum along the laboratory-fixed (and hence also space-fixed) z-axis; a quantum number $M = -J, \ldots, +J$ can be introduced 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 [38, 402] wavefunctions in the laboratory-fixed frame can 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

$$|J,M\rangle = \Psi^{J,M}(\mathbf{x}_1,\ldots,\mathbf{x}_N) = \xi(\mathbf{X}) \times \sum_{k=-J}^{J} \Phi^J_k(\mathbf{q})|J,M,k\rangle, \tag{50}$$

where $|J,M,k\rangle$ is a function of the Euler angles only and is given by (with a change of normalization with respect to equation (49))

$$|J,M,k\rangle = \sqrt{\frac{2J+1}{8\pi^2}}(-1)^k \mathscr{D}^J_{M,-k}(\alpha\beta\gamma)^*, \tag{51}$$

where $|J,M,k\rangle$ are the (normalized) 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 (46) is invariant to inversion of all the coordinates with respect to the origin ($\mathbf{x}_i \to -\mathbf{x}_i$), which implies that wavefunctions 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 wavefunction as a product of a spatial part and a spin part.

If two or more nuclei are identical the total wavefunction must be symmetric or anti-symmetric with respect to exchange of the identical nuclei, depending on the nuclear spin of the nuclei in question [30]. For example, protons (hydrogen ^{1}H 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 wavefunction must hence be symmetric by exchange of the identical ^{1}H 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 $q = 0, 1$.

5.3.3. *The internal coordinates.*

The three internal coordinates needed for a triatomic system can be chosen in infinite ways and different molecules will benefit from different choices. In the Sutcliffe–Tennyson formalism [395, 398], internal coordinates are specified by two parameters g_1 and g_2. This formalism does not include all conceivable possibilities but it is nonetheless general enough to cover all cases of present interest.

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

$$\begin{aligned} \mathbf{t}_1 &= (\mathbf{x}_2 - \mathbf{x}_3) + g_2(\mathbf{x}_3 - \mathbf{x}_1) \\ \mathbf{t}_2 &= (\mathbf{x}_1 - \mathbf{x}_3) + g_1(\mathbf{x}_3 - \mathbf{x}_2), \end{aligned} \tag{52}$$

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

$$r_1 = |\mathbf{t}_1| \quad r_2 = |\mathbf{t}_2| \qquad \theta = \cos^{-1}\left(\frac{\mathbf{t}_1 \cdot \mathbf{t}_2}{t_1 t_2}\right). \tag{53}$$

Many commonly used coordinate systems can be obtained by a suitable choice of g_1 and g_2, see e.g. table 1 of [395] for a summary. In particular, we will mention two choices which are particularly useful in calculations, namely Jacobi and Radau coordinates. More information can be found in [394–396]. In Jacobi (also known as scattering) coordinates, r_2 and r_1 are given respectively by the bond 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 $0 < \theta < \pi$. 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 the molecular system was emphasized by Smith in 1980 [418] and they have since enjoyed a rising popularity [396]. In the case where one atom is much heavier than the others, Radau coordinates become very similar to bond-length bond-angle ones.

5.3.4. *The orientation of the molecule-fixed frame and the choice of the internal coordinates.*

In the process of deriving the internal-coordinate Hamiltonian, it is necessary 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 wavefunction in a basis of eigenfunctions of the operator $\hat{J}_z$, the projection of the total angular momentum on the molecule-fixed z-axis.

The choice of embedding is also important because, together with the choice of the internal coordinates, it determines the form of the singularities arising in the Hamiltonian, as discussed in section 5.3.

Apart from the problem of singularities, an optimal choice of the internal coordinates will also speed up convergence. We again refer to the reviews by Tennyson *et al* [394, 395] and by Bačić and Light [396] for a discussion of these topics.

5.3.5. *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 (46) into internal coordinates. As we remarked, this only requires application of the chain rule, but the algebra is cumbersome. We will only summarize the general process, while the reader is referred to [398, 405, 406] for 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:

$$\hat{K} = \hat{K}_{\mathrm{V}}(r_1, r_2, \theta) + \hat{K}_{\mathrm{VR}}(r_1, r_2, \theta; \alpha, \beta, \gamma) + \hat{K}_{\mathrm{trans}}(\mathbf{X}). \tag{54}$$

One then considers a matrix element of the Hamiltonian between two states $|J', M'\rangle$ and $|J, M\rangle$, inserts expansion (50) for the exact wavefunction and integrates over the Euler angles

$$\hat{H}^J_{\mathrm{eff}} = \langle J', M'|\hat{H}(r_1, r_2, \theta; \alpha, \beta, \gamma)|J, M\rangle. \tag{55}$$

This procedure yields an effective Hamiltonian $\hat{H}^J_{\mathrm{eff}}$ that depends only on the internal coordinates and on the quantum numbers included in expansion (50), namely J, J', k, k' and M, M' (in fact, for symmetry reasons, the Hamiltonian is independent of M or M' [398]).

The effective Hamiltonian $\hat{H}^J_{\mathrm{eff}}$ thus obtained has a global factor $\delta_{JJ'}$ and is thus block-diagonal in J. This means that calculations for different J 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 computations. For more details on the form of the effective Hamiltonian, see [395, 397, 398].

Further symmetries. For simplicity in the previous presentation, we did not mention the further symmetries present in the Hamiltonian discussed in section 5.3.2, 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.

5.4. *Basis functions for the internal-coordinate wavefunctions*

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 [6, 7]: a set of basis functions is introduced and the Hamiltonian matrix $\mathbf{H}$ in this basis is build and then diagonalized.

A set of basis functions 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.

[373, 394–397]. Basis sets which are not obtained as products of one-dimensional basis sets are also possible [419].

For the two 'radial' coordinates r_1 and r_2, typical choices are modified Morse-oscillator wavefunctions or spherical oscillator functions [412]. For the angular coordinate θ, it is convenient to use a special set of basis functions $|k, j\rangle$ $k = -j, \ldots, j$, $j = 0, \ldots, N_{\max}$, which are eigenfunctions of $\hat{J}_z$, the projection of the angular momentum along the molecule-fixed axis:

$$\begin{aligned}|k, j\rangle &= |J, M, k\rangle \times P_j^{(k)}(\cos\theta) \quad \text{if } p = 0 \quad \text{and} \quad k = 0\\ |k, j\rangle &= \tfrac{1}{\sqrt{2}}(|J, M, -k\rangle + (-1)^p|J, M, k\rangle) \times P_j^{(k)}(\cos\theta)\\ &\quad \text{in all other cases,}\end{aligned} \tag{56}$$

where $P_j^{(k)}(\cos\theta)$ is a normalized associated Legendre polynomial with the Condon and Shortley phase convention and $|J, M, k\rangle$ is given by equation (51) (j is simply an index and is not connected with the angular momentum J).

5.5. The DVR technique

Once the basis set has been decided, the calculation can proceed in the way outlined in the preceding section by building and diagonalizing the Hamiltonian matrix **H**. This way of proceeding is in this context called the variational basis representation (VBR) approach and was employed in virtually all computations of this kind done before about the mid-1980s [397]. However, a new computational technique, the DVR or discrete variable representation, has proved extremely effective. We will lay down the basis of this technique in this section.

5.5.1. 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* [420]; shortly thereafter the connection between this approach and Gaussian integration rules was clarified by Dickinson and Certain [421]. After a gap of about 15 years the technique was then independently developed in different areas of physics by Light and co-workers [422, 423], Shizgal and Blackmore [424, 425] and Baye and Heenen [426]. In chemical physics it is the notation and formalism of Light and co-workers [423] 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 [396] and, more recently and in more detail, by Light and Carrington [427].

The term 'representation' in the acronym DVR is used in the sense of matrix mechanics, where the numerical matrix **V** associated with an operator $\hat{V}$ depends upon the chosen 'representation', i.e. upon the chosen basis set. One may switch between one representation to another 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 localized function centred 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

$$\mathbf{V}_{\alpha\beta} = \int_a^b \theta_\alpha(x)V(x)\theta_\beta(x)\,\mathrm{d}x \approx \delta_{\alpha\beta}V(x_\alpha). \tag{57}$$

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 (57) should become exact in the limit where the set of grid points x_α become dense in $[a, b]$ and the corresponding DVR basis functions become 'similar' to Dirac delta functions $\theta_\alpha(x) \to \delta(x - x_\alpha)$. 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 [396, 420, 421, 424–427] for more details.

5.5.2. Gaussian quadrature rules. Gaussian quadrature rules are a standard topic of numerical analysis, see e.g. [133, 305] or the books by Evans [428] and Stroud and Secrest [429]. A Gaussian quadrature rule is a way of approximating integrals of the kind $I = \int_a^b \omega(x) f(x)\,\mathrm{d}x$ where $\omega(x)$ is a known 'weight' function satisfying $\omega(x) > 0$ and f is an unknown function. The integral I is approximated by

$$I = \int_a^b \omega(x) f(x)\,\mathrm{d}x \approx \sum_{\alpha=0}^{N-1} W_\alpha f(x_\alpha), \tag{58}$$

where the N abscissae x_α and weights W_α are determined so that formula (58) 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 Nth 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 [428]

$$(W_\alpha)^{-1} = \sum_{j=0}^{N-1} p_j(x_\alpha)^2, \tag{59}$$

where $p_j(x)$ is the *normalized* jth degree orthogonal polynomial on $[a, b]$ with respect to the weight $\omega(x)$ (note that commonly tabulated orthogonal polynomials are usually unnormalized).

5.5.3. Gaussian quadrature DVRs in one dimension. Gaussian quadrature DVRs were historically the first to be studied [420, 421, 427] and are arguably the most rigorous incarnation. For this class of methods it is possible to show that approximation (57) 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

$$\hat{H} = \hat{K} + V(x). \tag{60}$$

We will start by 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 $\omega(x)$:

$$f_n(x) = \sqrt{\omega(x)}p_n(x). \tag{61}$$

A typical example is given by the eigenfunctions of the harmonic oscillator, where in opportune units $\omega(x) = \mathrm{e}^{-x^2/2}$ and $p_n(x) = N_n H_n(x)$ are the normalized 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 diagonalize 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. [6, 7]), 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 $\hat{K}$ 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', $\mathbf{V}^{\mathrm{VBR}}$:

$$\mathbf{V}_{ij}^{\mathrm{VBR}} = \int_a^b f_i(x)V(x)f_j(x)\,\mathrm{d}x. \tag{62}$$

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 [421, 427], these two approaches are equivalent but they give a different insight to the approximation introduced.

Gaussian quadrature viewpoint. In this approach one chooses to evaluate all the integrals necessary to build $\mathbf{V}_{ij}^{\mathrm{VBR}}$ *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', $\mathbf{V}^{\mathrm{FBR}}$ (contrast the following with equation (62)):

$$\mathbf{V}_{ij}^{\mathrm{FBR}} = \sum_{\alpha=0}^{N-1} W_\alpha f_i(x_\alpha)V(x_\alpha)f_j(x_\alpha). \tag{63}$$

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

$$V(x) = \sum_{p=0}^{+\infty} c_p x^p, \tag{64}$$

then formula (63) will be exact if $i + j + p \leqslant 2N - 1$; for example, the matrix element $\langle 0|V|0\rangle$ will be exact up to 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 (63) in matrix form introducing the $N \times N$ matrices

$$\mathbf{T}_{\alpha j} = \sqrt{\frac{W_\alpha}{\omega(x_\alpha)}}f_j(x_\alpha) = \sqrt{W_\alpha}p_j(x_\alpha) \tag{65}$$

and the diagonal matrix

$$\mathbf{V}^{\mathrm{DVR}} = \mathrm{diag}(x_0, \ldots, x_{N-1}), \tag{66}$$

where the DVR superscript adopted will become clear presently. Also note that the theory of Gaussian quadrature guarantees that the weights W_α are all positive [428] (see also equation (59)), so our definitions are well posed.

By virtue of our choice (61) of the basis set $\{f_n(x)\}$ and of the use of Gaussian rule, it follows that $\mathbf{T}$ is a unitary matrix:

$$(\mathbf{T}^\dagger\mathbf{T})_{ij} = \sum_{\alpha=0}^{N-1} T_{i\alpha}^\dagger T_{\alpha j} = \sum_{\alpha=0}^{N-1} W_\alpha p_i(x_\alpha)p_j(x_\alpha) = \delta_{ij}. \tag{67}$$

One can now re-write relation (63) in matrix form as

$$\mathbf{V}^{\mathrm{FBR}} = \mathbf{T}^\dagger\mathbf{V}^{\mathrm{DVR}}\mathbf{T}. \tag{68}$$

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

$$\theta_\alpha(x) = \sum_{j=0}^{N-1} \mathbf{T}_{\alpha j} f_j(x). \tag{69}$$

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 localized 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 $\theta_\alpha(x)$ becomes similar to a Dirac delta function as $N \to +\infty$. Other analytical properties of the DVR functions can be proven, for example, that $\theta_\alpha(x)$ is zero for all $x_\beta \neq x_\alpha$ [427]. Finally, we remark that one could conceive an 'exact DVR' (EDVR) matrix representation by first computing exactly all the matrix elements of $\mathbf{V}^{\mathrm{VBR}}$ and then performing the similarity transformation inverse to the one given by equation (68):

$$\mathbf{V}^{\mathrm{EDVR}} = \mathbf{T}^\dagger\mathbf{V}^{\mathrm{VBR}}\mathbf{T} \neq \mathbf{V}^{\mathrm{FBR}}. \tag{70}$$

It follows that the EDVR representation would be exactly equivalent to the VBR, contrary to the DVR one. The $\mathbf{V}^{\mathrm{EDVR}}$ matrix would not be diagonal, but off-diagonal elements are expected to be small. However, the whole point of using the DVR is to avoid computing the integrals so $\mathbf{V}^{\mathrm{EDVR}}$ is never ordinarily calculated 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 easier 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, it is useful in practical applications; second, it provides further insight to the approximation introduced; and third, it suggests how other classes of DVRs, 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:

$$\mathbf{X}^{\mathrm{VBR}} = \mathbf{T}^{\dagger}\mathbf{X}^{\mathrm{DVR}}\mathbf{T}, \tag{71}$$

where $\mathbf{X}^{\mathrm{DVR}}$ is the diagonal matrix containing the abscissae points x_α. This relation means that the transformation $\mathbf{T}$ exactly diagonalizes the exact (i.e. VBR) coordinate matrix and that therefore the DVR points and basis functions are nothing but the eigenvalues and eigenvectors of $\mathbf{X}^{\mathrm{VBR}}$. This fact is well known in the numerical analysis where the matrix $\mathbf{X}^{\mathrm{VBR}}$ is known as the terminal or Jacobi matrix, see e.g. [428] p 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 diagonalizing $\mathbf{X}^{\mathrm{VBR}}$. In particular, because of the three-term recurrence relation all orthogonal polynomials obey, $\mathbf{X}^{\mathrm{VBR}}$ is a tridiagonal matrix and its eigenvalues and eigenvectors can be found efficiently by various algorithms [307, 430].

This point of view shows explicitly that it is reasonable to conjecture that, in the limit of $N \to +\infty$, the DVR basis set functions should approach perfectly localized Dirac-delta functions, as these are the true (generalized) 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 [431] and appendix 4.7 of the book by Peres [432] for a flavour of how such a rigorous treatment might be formulated.

Viewing the DVR basis set as constituted by the eigenfunctions of the position matrix $\mathbf{X}^{\mathrm{VBR}}$ is the original procedure used by Harris *et al* [420] and provides an alternative and complementary way of looking at the DVR approximation introduced in the Gaussian quadrature viewpoint by equations (63) and (68), namely computing all integrals using an N-point Gaussian quadrature rule. More specifically, we will show that approximation (63) is equivalent to the assumption that the matrix $\mathbf{V}^{\mathrm{VBR}}$ can be approximately given by

$$\mathbf{V}^{\mathrm{VBR}} \approx V(\mathbf{X}^{\mathrm{VBR}}) = \mathbf{V}^{\mathrm{FBR}}, \tag{72}$$

where $V(\mathbf{X}^{\mathrm{VBR}})$ indicates that we plug the matrix $\mathbf{X}^{\mathrm{VBR}}$ as an argument of the function $V(x)$; if $V(x)$ is given by the polynomial expansion (64) then

$$V(\mathbf{X}^{\mathrm{VBR}}) = \sum_{p=0}^{+\infty} c_p (\mathbf{X}^{\mathrm{VBR}})^p, \tag{73}$$

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

We showed that $\mathbf{X}^{\mathrm{VBR}}$ is diagonal in the DVR basis, equation (71), from which it follows that

$$(\mathbf{X}^{\mathrm{VBR}})^p = (\mathbf{T}^{\dagger}\mathbf{X}^{\mathrm{DVR}}\mathbf{T})^p = \mathbf{T}^{\dagger}(\mathbf{X}^{\mathrm{DVR}})^p\mathbf{T}. \tag{74}$$

As $\mathbf{X}^{\mathrm{DVR}}$ is a diagonal matrix its pth power is just the diagonal matrix containing the pth powers of its elements. Putting together the results of equations (73) and (74), it follows that

$$V(\mathbf{X}^{\mathrm{VBR}}) = \mathbf{T}^{\dagger}\left(\sum_{p=0}^{+\infty} c_p (\mathbf{X}^{\mathrm{DVR}})^p\right)\mathbf{T} = \mathbf{T}^{\dagger}\mathbf{V}^{\mathrm{DVR}}\mathbf{T}. \tag{75}$$

This shows that the approximation introduced by equation (72) is exactly the same as the one introduced in the Gaussian quadrature viewpoint by equation (63). However, in view of further developments, we will now show how the approximation introduced by equation (72) can be analysed from a different viewpoint than quadrature rules. It follows from equation (73) that the approximation must be ascribed to the fact that, if $p \geqslant 2$,

$$(\mathbf{X}^{\mathrm{VBR}})^p_{ij} \neq \langle f_i|x^p|f_j\rangle. \tag{76}$$

This equivalence is approximate because $\mathbf{X}^{\mathrm{VBR}}$ 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

$$\sum_{\alpha=1}^{+\infty} |f_\alpha\rangle\langle f_\alpha| = \mathbf{I}. \tag{77}$$

Inserting the RI between the products of x:

$$\langle f_i|x^2|f_j\rangle = \langle f_i|x\mathbf{I}x|f_j\rangle = \langle f_i|x\left(\sum_{\alpha=1}^{+\infty}|f_\alpha\rangle\langle f_\alpha|\right)x|f_j\rangle$$
$$= \sum_{\alpha=1}^{+\infty}\langle f_i|x|\alpha\rangle\langle\alpha|x|f_j\rangle. \tag{78}$$

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

$$(\mathbf{X}^{\mathrm{VBR}})^2_{ij} = (\mathbf{X}^{\mathrm{VBR}}\mathbf{X}^{\mathrm{VBR}})_{ij} = \sum_{\alpha=1}^{N}\langle f_i|x|f_\alpha\rangle\langle f_\alpha|x|f_j\rangle, \tag{79}$$

so that expressions (78) and (79) differ; the reason can be viewed as due to the fact that in (79) we used a truncated form of the RI which includes only N basis set functions. The two expressions, however, will become equal as $N \to +\infty$ if the basis set is complete. The same rationale holds for the pth 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, if 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 equation (76), 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, $(\mathbf{X}^p)_{ij}$.

5.5.4. Other ways of defining DVRs. The product approximation viewpoint makes it easy to introduce DVRs which are not directly linked to Gaussian quadrature. If the starting 'diffuse' basis set functions were of a form different from that specified by equation (61), namely, of a polynomial times the square root of a weight function, then the product approximation scheme of taking as localized DVR basis the eigenfunctions of the position matrix $\mathbf{X}^{\mathrm{VBR}}$ would not be equivalent to any Gaussian quadrature scheme. Still, in the limit of $N \to +\infty$, 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 $\mathbf{X}^{\mathrm{VBR}}$ as the DVR basis; for example, also the (generalized) eigenfunctions of x^2 tends to delta functions, as in general the eigenfunctions of x^p; diagonalizing their respective matrices will result in other possible DVRs.

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 [433], where the DVR points x_α are chosen on a equispaced grid with grid spacing Δx and the respective DVR functions are given by

$$\theta_\alpha(x) = \frac{\sin(\pi t/\Delta x)}{\pi t}, \qquad \text{where} \quad t = (x - x_\alpha). \tag{80}$$

We refer to the review by Light and Carrington [427] and references therein for more details on these more general approaches.

5.5.5. An example: harmonic oscillator wavefunctions. Consider the one-dimensional harmonic oscillator Hamiltonian [5, 434, 435]

$$\hat{H}_0 = \hat{K} + V = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2 x^2. \tag{81}$$

The normalized eigenfunctions of the harmonic oscillator Hamiltonian are then given by

$$\psi_n(x) = \sqrt{\frac{\alpha}{2^n n!\sqrt{\pi}}}\,\mathrm{e}^{-\frac{\alpha^2 x^2}{2}} H_n(\alpha x), \qquad \text{where} \quad \alpha = \sqrt{\frac{m\omega}{\hbar}} \tag{82}$$

and where $H_n(t)$ are the Hermite 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 destruction/creation operators a and $a^\dagger$ [5, 434, 435]:

$$\mathbf{X} = \frac{1}{\alpha\sqrt{2}}\begin{pmatrix} 0 & 1 & 0 & 0 & \cdots \\ 1 & 0 & \sqrt{2} & 0 & \cdots \\ 0 & \sqrt{2} & 0 & \sqrt{3} & \cdots \\ 0 & 0 & \sqrt{3} & 0 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}. \tag{83}$$

We report as figure 9 some plots of the first nine wavefunctions ($n = 0, \ldots, 8$) of the harmonic oscillator, representing the diffuse or VBR basis functions, and the corresponding DVR basis functions obtained by diagonalizing the position matrix $\mathbf{X}$.

5.5.6. The DVR method and the variational principle. If the DVR approximation is applied, the variational character of the eigenvalues is lost and eigenvalues 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 [394, 423, 427]. It is also possible [436, 437] to use a wavefunction produced by a DVR calculation ψ_{DVR} as the variational trial wavefunction calculating $\tilde{E} = \langle\psi_{\mathrm{DVR}}|\hat{H}|\psi_{\mathrm{DVR}}\rangle$. $\tilde{E}$ is, contrary to the DVR energy E_{DVR}, an upper bound to the true energy and may also enjoy an improved convergence behaviour.

5.5.7. DVRs in many dimensions. What is not apparent from the previous discussion is that the real advantage of the DVR technique is manifested only in many dimensions. In one dimension simple grid-based approaches, see e.g. [438], are ultimately more efficient. One of the main advantages of the DVR approach is that the resulting matrices are very sparse and so specialized, efficient algorithms can be applied [427]. Another advantage of the DVR approach is that it is very convenient for truncation/diagonalization schemes such as those introduced by Tennyson *et al* [397].

The simplest way of introducing multi-dimensional DVRs is as direct-products of one-dimensional DVRs for each coordinates. For example, in the case of three dimensions (r_1, r_2, θ), one can build the one-dimensional DVR localized basis functions in each dimension and then use as the basis function all the possible products of one-dimensional basis functions. The three-dimensional DVR grid will similarly be given by the Cartesian product of the three one-dimensional ones. For more details see [423, 427].

6. Some indicative rotational–vibrational calculation results for the water molecule

Once the PES and DMS have been obtained, it is possible to use them to compute rotational–vibrational line positions and intensities. Their quality may be inferred by comparing them with known spectroscopic data such as those in the HITRAN database [439].

Our group has used the theory expounded in the previous sections, as implemented in the software suite DVR3D [373], to compute various sets of water rotational–vibrational line positions and intensities [104, 106, 440]. We will present here some illustrative results.

Some care is needed when comparing two data sets A and B of line intensities 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 [441]. 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.

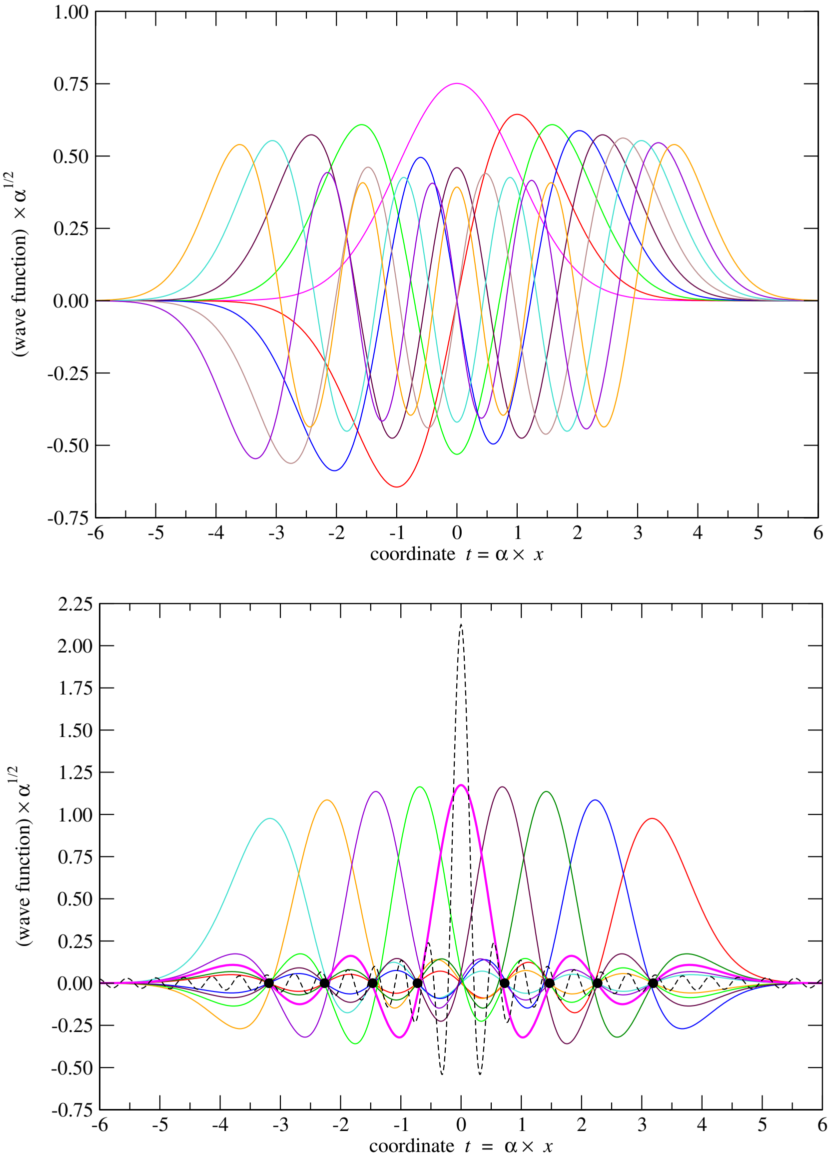

Figure 9. First figure: the first nine wavefunctions ($n = 0, \ldots, 8$) of the harmonic oscillator, given by normalized Hermite polynomials times the Gaussian weight $\mathrm{e}^{-\alpha^2 x^2/2}$. Second figure: the corresponding DVR basis; the basis functions corresponding to the DVR point $x = 0$ are 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 wavefunctions; it can be seen that it is much more strongly localized. The DVR grid points (i.e. Gauss–Hermite quadrature points) are reported along the abscissae axis.

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:

$$\kappa_i \overset{\text{def}}{=} \log\left(\frac{I_A(i)}{I_B(i)}\right) \overset{\text{def}}{=} \log(\varrho_i)$$

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. The basis used 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 as follows: (i) it can accommodate a very large range of variation along both axes, so that all data can be displayed together; (ii) 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; and (iii) any multiplicative factor can be readily identified. An example of such a plot is presented as figure 10. The plot shows the intensities ratios of about 30 000 theoretical line intensities, see [103] for details, with values taken from the HITRAN2004 database. Only lines with $J < 10$ were included in the comparison.

Here we only discuss a few features of figure 10, see [4, 103] for more details. The first, general observation is that the vast majority lines stronger than about 10^{-23} cm/molecule agree within the values from HITRAN2004 within roughly

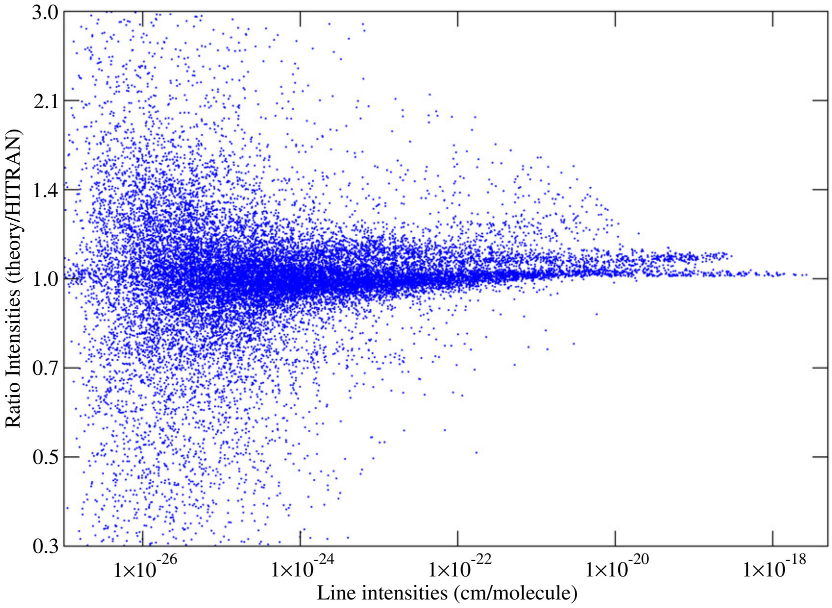

Figure 10. Ratio of dipole line intensities for $H_2{}^{16}O$ predicted by the CVR dipole surface to those reported in the 2004 version of the HITRAN database [439].

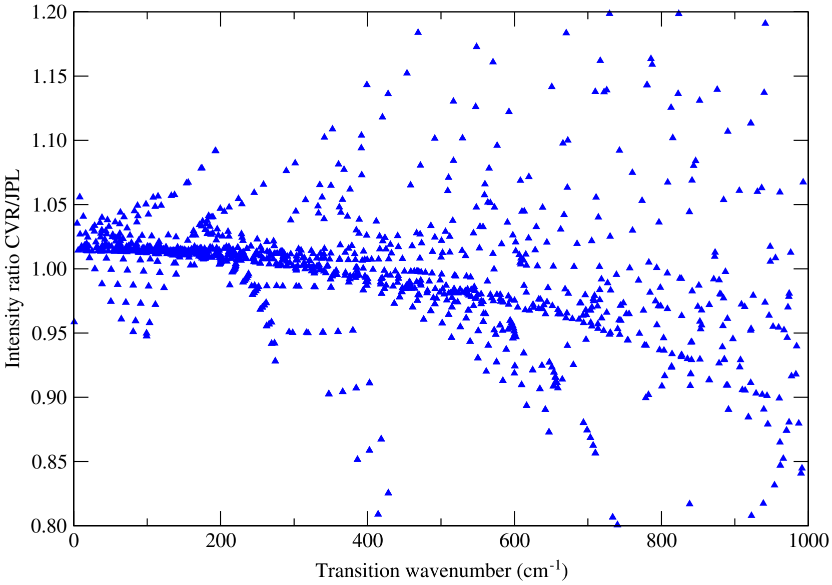

Figure 11. Comparison of line intensities with lines from the JPL database [442] as a function of the transition wavenumber.

±10% or better; this is a very good result, as both the calculation and the measurements of line intensities within a few % of error is a difficult enterprise. The substructure present at high intensities in the plot is due to problems in the HITRAN2004 database. We also note that there is a comparably small but still sizable number of weak lines for which theory and experiment disagree by one or even more orders of magnitude. In part this could be due to 'trivial' mistakes like mislabelled lines and/or errors of various kinds present in the database, but it is mainly due to the extreme sensitivity of many weak lines to the DMS and to the PES used in the calculations. In particular, the intensity of intrinsically weak transitions which become stronger as a result of intensity stealing arising from accidental mixing with a strong line is particularly sensitive to the details on the nuclear motion wavefunction and hence the PES.

A second plot, adapted from our earlier work [440], is presented as figure 11. The plot shows ratios for line intensities calculated by our group over intensities taken from a now-obsolete version of the JPL database[3]. The CVR acronym on the y-axis is the name of the DMS used [103]. The data are presented this time as a function of the transition wavenumber, and not of the transition intensities, because this makes the systematic structures of the ratios more apparent. Further analysis showed that the substructure was due to an incorrect procedure used in the compilation of the JPL database

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[3] The JPL catalogue for water is available electronically from http://spec.jpl.nasa.gov/ftp/pub/catalog/catdir.html.

which introduced small, systematic errors of up to about 5%. It is therefore remarkable that purely *ab initio* calculations can sometimes be useful to identify problems with existing, high-quality databases. If we disregard the substructures the agreement between theory and the JPL database for the lines considered is good, with most strong lines agreeing within about ±5%. Lines which differ by more than 10% are lines weaker than about 10^{-23} cm/molecule where, as discussed above, both theory and experiment become progressively inaccurate.

7. Conclusions

It is clear from our studies on the rotation–vibration spectroscopy of water, and indeed other triatomic systems, that it is possible to obtain essentially exact solutions to the nuclear motion problem. This means that further improvements to *ab initio* procedures will largely come from improved treatments of the electronic structure problem.

Looking to the future, 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 methods based on the explicitly correlated F12 technique discussed in section 3.11 should become widely available and will significantly reduce the basis-set incompleteness error present in calculations. At present the only publicly available program which is capable of multi-reference explicitly correlated calculations is AMICA [442],[4] which however is based on an old level of the R12 theory and, furthermore, is no longer maintained. Other approaches, such as the use of R12-based perturbation theory to correct for basis-set errors recently proposed by Torheyden and Valeev [443], are still in an experimental phase and not yet in widespread use.

Another significant advance in the area of electronic structure could come from multi-reference coupled-cluster methods (MRCC); these promising methods are unfortunately encumbered by many technical difficulties and at the moment even the most advanced versions such as [444] have not been demonstrated to be better than very well-tested approaches such as MRCI+Q or ACPF.

Although we concentrate here on triatomic systems, the electronic structure methodologies discussed are clearly applicable to larger molecules, with a corresponding scaling in computer costs for mapping out the relevant potential energy and dipole moment surfaces. For tetra-atomic and larger molecules, performing essentially exact nuclear motion calculations on a given potential energy surface is a more challenging task but one for which a variety of methods are becoming available. It is therefore to be expected that the techniques discussed in this review will be rapidly transferred to larger systems.

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