

Accurate first principles calculations on the spectrum of water

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Water is arguably one of the most important molecules, and consequently is object of research in many scientific fields. Traditionally, the Born-Oppenheimer approximation and a purely non relativistic hamiltonian are the framework in which theoretical spectroscopists work. These approximations allow a full qualitative understanding of the physics underlying water spectrum. However, it has been shown that for practical purposes, a more detailed knowledge of water spectrum is required. Also, due to its simplicity, water is a benchmark for theoretical calculations.

Császár *et al.* have already demonstrated the importance of one-electron relativistic corrections. Following their works, two-electrons relativistic corrections have been studied. Those terms are shown to be significant. At the same level of accuracy, corrections to the Born-Oppenheimer approximation are investigated. Several models for including non-adiabatic effects are discussed. However, a systematic study of the water spectrum based on all the corrections so far investigated has still to be performed.

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Chapter 1

Introduction

The scientific importance of the water molecule is beyond doubt. Water is essential to all aspects of life, thus it is studied in every field of science, including medicine, biology, geology and physics. Also, spectra of water are extensively used in astronomy, and atmospheric science. Water is believed to be the third most abundant molecule in the universe, after hydrogen (H_2) and carbon monoxide (CO). Water has been observed in cool stars [1], as well as in sunspots [2, 3]. An accurate knowledge of the water spectrum is thus essential to astronomers, as it can be used to work out the temperature of stars. In atmospheric physics, detailed water spectra are a key part in modelling our atmosphere [4], as the sunlight is reflected and absorbed principally by water vapour. Data on water are also important for modelling processes in flames and exhausts, as hot water is a primary product of hydrocarbon combustion [5]. Similarly, the possibility to detect forest fires by tuning geostationary satellites to characteristic frequencies of hot water emissions has been suggested [6]. Furthermore, knowledge of the position and intensity of water vapour absorption lines is essential to extract and process data from the recently launched ERS-2 satellite [7], which measures backscattered sunlight from the Earth. Hence, there is an immense range of possible technological applications deriving from an accurate knowledge of the water spectrum.

Motivated by the reasons just mentioned, experimental spectroscopists have recorded an immense wealth of data on water. A compilation containing the available data is regularly published [8] (HITRAN, where the acronym stands for high resolution transmission molecular absorption database). This compilation also contains data on other molecules of atmospheric interest, such as CO_2 , methane, CO, etc. . The database is upgraded periodically, and the latest versions can be obtained from the website www.HITRAN.com. Recently, several groups have employed new experimental techniques to investigate the water spectrum with greater detail: long-path Fourier transform spectroscopy [4], cavity ring-down spectroscopy [9, 10], intra-cavity absorption spectroscopy [11] and frequency modulation spectroscopy [12] have been applied to detect weak water lines. Those lines are considered to play a major role in the absorption of sunlight in the Earth's atmosphere, where their weakness is compensated by very long path-lengths [4]. In addition to laboratory spectra, further information can be retrieved by analysing extraterrestrial emissions, such as light coming from our sun [13] or cool stars [14]. Those spectra are emitted at high temperatures ($T \approx 3000$ K), whereas for most wave-

lengths the hottest laboratory spectra reproducible are cooler ($T \approx 1850$ K, [15]). At the time of writing the group of Prof. P.F. Bernath has just been able to record a laboratory spectrum of approximately 3000 K [16], using emission spectroscopy combined with a Fourier transform spectrometer [17]. Because the number of vibrational-rotational levels involved increases with the temperature T , the higher the temperature the more congested the spectrum. As an example, the sunspot spectrum (at $T \approx 3200$ K) contains up to 50 water lines per wavenumber [3]. Fig. 1.1 presents a portion ($342\text{--}344\text{ cm}^{-1}$) of the water spectrum to show changes with temperatures. We have chosen three values for T , corresponding to room temperature (300 K), laboratory hot temperature (1500 K), and sunspot (3000 K). The spectrum has been simulated using the Miller-Tennyson (MT) line-list [18]. It is possible to see how the number of lines increases, as a consequence of higher vibrational-rotational levels becoming populated by thermal excitation.

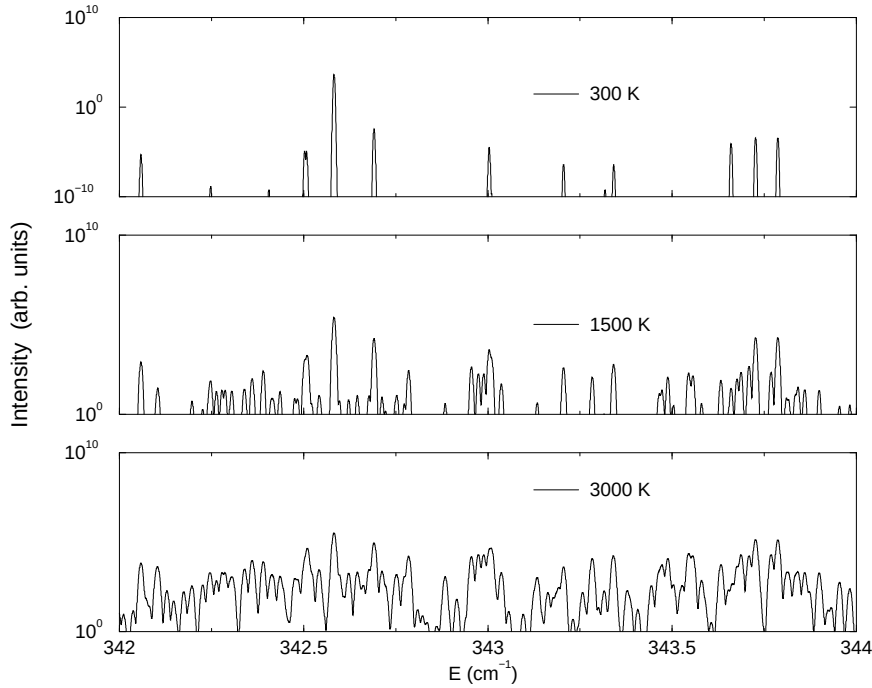


Figure 1.1: Simulation of water spectrum in the region $342\text{--}344\text{ cm}^{-1}$ at three different temperatures: room temperature (300 K), hot laboratory temperature (1500 K), and sunspot temperature (3000 K). The number of transitions involved increases rapidly with the increase of the temperature. The spectrum was simulated using the MT astronomical database [18]. We assumed a Doppler Gaussian profile [19] for the lines, and neglected nuclear degeneracy factors. Note the extended intensity scale at 300 K.

In order to analyse the recorded spectra, and thus to retrieve the most information possible from it, it is important to be able to assign the observed lines. The assignment of lines is a fundamental operation in spectroscopy, that consists of associating a particular line of the observed spectrum with a transition between two molecular vibrational-rotational levels. After a certain number of lines in the spectra has been identified, it is possible to extract the desired macroscopic information, such as the temperature of the emitting body, the density of water in the medium of interest, the opacity of the object, and other thermo-chemical properties.

Semi-empirical calculations have been very useful for assigning vibrational-rotational spectra of many molecules, including water [20]. These calculations combine *ab initio* methods with fits of selected parameters to experimental data. Alternatively, purely empirical surfaces, whose parameters are entirely determined by fitting them to experimental data, have also been published [21, 22]. The accuracy of both semi-empirical and empirical surfaces can be very high, making it possible to calculate energy levels to within the experimental error. However, their predictive power is poor outside the region of the fit. Conversely, purely *ab initio* calculations show better predictive power, although their accuracy is not comparable yet with empirical and semi-empirical methods [21].

The theory underlying the physics of molecules has been well known for several decades [23]. Nevertheless, it is impossible to obtain the exact solution of the system of differential equations involved. Starting from first principles, it is customary to employ simpler models which lead to a full qualitative understanding of molecular spectra. In this way it is usually possible to interpret the stronger lines in the spectrum. The water spectrum, however, is particularly complicated to analyse. It is both dense, due to the low symmetry of the molecule, and diffuse, as water absorbs radiation at many wavelength, ranging from the ultraviolet to the infrared region. Consequently, more sophisticated theoretical models need to be employed, in particular for the weaker lines to be assigned.

Traditionally, molecular systems containing light atoms are studied using a non-relativistic approach. A further very important simplification is given by the Born-Oppenheimer (BO) approximation [24, 25]. Taking advantage of the difference in mass between electrons and nuclei, the motions of the two sets of particles are studied separately. The uncoupling would be total in case of nuclei of infinite mass. Effects arising from the finite nature of the nuclear mass are then considered as small perturbations. A further source of error, and usually the most important one, arises from the impossibility of building exact electronic wavefunctions, which is largely due to the strong correlation among electrons. As a consequence of all those approximations, purely *ab initio* spectra are normally much less accurate than the ones determined with other approaches.

There has thus been considerable effort by theoretical spectroscopists aimed at producing *ab initio* spectra whose accuracy could ultimately be comparable with, or even replace, empirically determined surfaces. Water is considered as a benchmark system for testing theoretical and computational methods, due to the wealth of experimental data available.

The major factor determining the accuracy of an *ab initio* spectrum is the potential energy surface (PES) [26]. Within the BO approximation, the force acting among the nuclei is given by their mutual Coulomb repulsion plus their interaction with the electrons, averaged over all the possible positions in space for the electrons, as the latter are assumed to move infinitely faster than the former. The total field experienced by the nuclei is given the name of Potential Energy Surface. The PES normally also contains multi-body terms, due to, for example, electron-electron interactions. The precision with which a PES is calculated depends to the precision with which the quantum-mechanical wavefunction for the electrons can be obtained. Standard techniques normally used in molecular structure theory can predict vibrational band origins (VBOs) to within few wavenumbers [20]. How to improve such predictions of vibrational-rotational levels is the topic of this thesis.

As has already been mentioned, to obtain an accurate solution of the electronic Schrödinger

equation (see eq. (2.5)) is a very demanding task. Difficulties arise, for instance, from the number of electrons present (10 in a molecule as small as water), hence from the numbers of degrees of freedom of the problem (30 in water). Further complications are caused by the very different nuclear configurations at which the electronic Schrödinger equation (2.5) has to be solved. For example in water, typical nuclear geometries of interest include equilibrium, stretches and bends of the molecular bonds. In order to build an accurate potential energy surface, the inclusion of high energy configurations, to constrain the surface to the right dissociation channels, is essential [20]. The study of such different molecular configurations requires large and flexible basis sets. The analysis of basis set convergence is one of the fundamental problems in electronic structure calculations. In the literature several standard basis sets are available for most elements of the periodic table (also electronically [27]). In this work we have used the basis sets of Dunning and co-workers [28], see below.

A second major problem in electronic structure theory is related to the building of the wavefunction. Electrons have half integer spin, and, as a consequence of the Pauli principle, their wavefunction must be completely antisymmetric. To obtain a good description of the electronic wavefunction one should deal with all the degrees of freedom simultaneously, due to the strong electron correlation. This is clearly very difficult, if not impossible, because of the high dimensionality of the problem. Instead, the wavefunction is expressed as a product of one-particle functions, called orbitals. The orbitals are expanded in terms of the basis sets discussed below, and the coefficients of the expansion can be determined with an iterative procedure (the most commonly used methods are the self-consistent field (SCF), the Multi-Configuration Self Consistent Field (MCSCF) and the Complete Active Space Self-Consistent Field (CASSCF) [29]). The Hartree-Fock product represents the simplest way to write the wavefunction, as only the occupied orbitals are included. The accuracy of a Hartree-Fock calculation depends on the completeness of the one-particle basis set employed to describe the orbitals. The limit of an infinite basis set is called the Hartree-Fock limit. This limit represents the best single determinant wavefunction that can be obtained. The Hartree-Fock wavefunction is quite accurate in the proximity of the equilibrium configuration, and it is able to recover up to 95 % (or even more) of the electronic energy, but loses in accuracy as the geometry is distorted far from equilibrium. For example, a chronic illness of a Hartree-Fock wavefunction is that it does not dissociate properly.

The difference between the electronic energy calculated with a Hartree-Fock wavefunction, at the Hartree-Fock limit, and the exact solution of the non-relativistic Born-Oppenheimer electronic equation is called the electron correlation energy. This energy constitutes a small part of the total electronic energy, nonetheless it is very important for describing chemical phenomena. The techniques commonly employed to improve the wavefunction use the Hartree-Fock wavefunction as a starting point.

To go beyond the Hartree-Fock level of theory one also needs to consider unoccupied orbitals. The number of orbitals, however, depends on the dimension of the basis set employed. If one uses M basis functions, for a closed-shell molecule with N electrons, the Hartree-Fock restricted method will yield $N/2$ occupied and $M-N/2$ unoccupied orbitals. If one could include all the orbitals in the wavefunction it would be possible to obtain the exact solution of the electronic Schrödinger equation, in the limit of an infinite basis set. This level of theory is called the full configuration interaction (full CI) level. Thus, the accuracy of electronic structure calculations depends upon two factors: the level at which the correlation energy is taken

into account, and the number (and type) of functions that constitute the one-particle basis set.

There are two types of basis functions commonly used: Slater type orbitals, and Gaussian type orbitals. The former have the advantage of reproducing properly the behaviour of the orbital both near the nuclei and asymptotically, whereas the latter allow for easy evaluation of molecular integrals, and are therefore preferred. In this work we used the correlation consistent polarised valence basis sets of Dunning and co-workers [30], indicated by the acronyms cc-pVXZ (X=D,T,Q,5,6, where X indicates the number of contracted functions employed for each valence orbitals, and also is related to the number of polarisation functions included), or aug-cc-pVXZ (where diffuse functions have been added to the corresponding cc-pVXZ), and cc-pCVXZ (with the inclusion of tight functions for the study of core valence effects). The advantage of Dunning's sets is that they generate a sequence in X converging toward the CI basis set limit, while the HF problem is assumed to be solved. For example, test cases [29] show that the cc-pVDZ basis can provide $\approx 65\%$ of the total (valence) correlation energy, the cc-pVTZ $\approx 85\%$, the cc-pVQZ $\approx 93\%$, the cc-pV5Z $\approx 96\%$, and the cc-pV6Z $\approx 98\%$. Thus it is possible to try to recover the complete basis set (CBS) limit by extrapolation [31]. On the other hand, the main difficulty in using Dunning sets is that in each step the number of functions almost doubles.

Additionally, one needs to deal with the correlation energy. With the use of large basis sets the number of orbitals that can be included in a calculation is limited. There are physical arguments that allow one to include in a selective way only those configurations that are expected to contribute the most. Without entering into the details, it is possible to work at the level of single excitation CI, double, triple, etc. Alternatively, coupled-cluster (CC) theories have been introduced as they guarantee a faster convergence to the full CI. CC calculations also present the advantage of being size-consistent, that is the quality of the calculation does not depend on the dimensionality of the system, in contrast to the standard CI method. Thus, we can have single-excitation CC (or CCS), double (CCSD), and so on. In addition, the Møller-Plesset theory also aims at the calculation of the exact electronic energy, using a perturbational approach [32].

In order to reduce the dimensionality of the mathematical problem, it is also a good approximation to freeze the degrees of freedom of the core orbitals. The physical reason behind this approximation is that the core orbitals are not directly involved in the molecular bonding, so one expects them to be almost independent of the nuclear geometries. Moreover, the valence and core orbitals have a complete different form, as the former are extended and may polarise along the molecular bonds, whereas the latter are tight around the nuclei.

The development of computational methods for electronic structure calculations has been a major subject of research in the past decades. As a result, several codes have been published and made available, some of which are even available free of charge. Gaussian [33] is probably one of the most commonly used. GAMESS [34] is also quite widespread as it is a free software, and we used it for part of the calculations in chapter 4. In chapter 5, the computer code MOLPRO [35] has been employed to calculate water electronic energies at the MRCI level. We also need to cite DIRCC12 [36], an electronic structure code that employs explicitly correlated variants of the CC theory [37], and BERTHA [38, 39], a fully relativistic four component code. All these codes offer to choose at which level of theory and with which basis sets one desires to solve the electronic Schrödinger equation. The usual constraint is the available

computer resources.

It is common to calculate PESs with mE_h accuracy ($1 \text{ mE}_h = 219.474636 \text{ cm}^{-1}$). But if one aims for a spectroscopically accurate theoretical calculation of vibrational-rotational molecular levels (that is, to 1 cm^{-1} or better), the approximations normally introduced in electronic structure calculations need to be relaxed somehow. The inclusion of core-valence effects in electronic structure calculations, as well as the determination of the full CI and one-electron basis set limits [26, 40], aims toward the exact solution of the electronic Schrödinger equation. Those studies have also been given impetus by the continuous improvements in computational facilities.

Recently, Császár *et al.* [40, 41] investigated the conformational and spectroscopic importance of relativistic corrections to the electronic motion. Although a fully relativistic molecular theory has long been available, the non-relativistic approach has traditionally been preferred for simplicity and computational tractability. For heavy elements such as gold, mercury or lanthanides and actinides, the importance of relativistic corrections has been acknowledged for decades [42], whereas for light atoms, such as those in the first two rows of the periodic table, the spectroscopic consequences of the commonly neglected relativistic terms have only recently become a subject of research [43].

A further source of error is introduced by the procedure of fitting calculated data points to an analytical form. The electronic energies, and relativistic and adiabatic Born-Oppenheimer corrections (for the latter see below) are normally calculated on a finite number of nuclear configurations, of the order of one thousand or less. In a second stage those data points are fitted to an analytical form in order to be employed in the calculation of vibrational-rotational energy levels. The choice of the functional form employed is delicate, as its capability to reproduce the calculated data can represent a limit on the accuracy of the calculation. There are standard techniques to fit a set of data with satisfactory accuracy, like the least-squares algorithm [44], existing in the linear and non-linear form. On the other hand, the ability to choose a suitable functional form, as well as meaningful physical parameters to manipulate to improve the agreement with the data can only be given by the experience and physical intuition. The most commonly used functional form is a polynomial. This choice allows for a good interpolation of the data points, but normally extrapolates poorly outside the data region.

Once the PES has been determined, within the BO approximation, the remaining problem is to solve for the motion of three nuclei interacting through a known potential. There are several techniques which are normally applied to solve this kind of problem. The most popular approach follows the work of Watson [45]. Firstly, a zeroth order Hamiltonian can be built starting from rigid rotor and harmonic approximations [46]. Then, using perturbation theory, corrections to these approximations are considered, which may include, for instance, anharmonicity, Coriolis coupling, vibro-rotation coupling, centrifugal distortion, and so on. The expansion terms in the Hamiltonian can be directly related to experiment by fitting the observed data.

However, it is well known that the perturbation expansion diverges for a molecule as light as water [47]. This problem could be dealt with using some specific mathematical tools, such as Padé approximants.

Alternatively, for a three-body system it is possible to seek an exact solution of the quantum

mechanical problem. Choosing a suitable system of coordinates, and also a particular embedding of the molecular fixed Cartesian frame, an exact kinetic energy operator (KEO) can be derived [48]. Several numerical techniques have been developed and tested in the past years to solve the system of nine-dimensional second order differential equations connected with the physical problem of interest [49, 50, 51]. The most popular ones make use of the Rayleigh-Ritz variational theorem [52, 53]. In its most common implementations, the variational method is used to determine the coefficients of the expansion of the wavefunction for the three particles in terms of a selected basis set, whose choice is case dependent. This method is known as a finite basis representation (FBR). In some situations, the discrete variable representation (DVR, [54]) offers a more powerful tool. The DVR method has already been successfully employed in the determination of vibrational-rotational energy levels for water [55]. In particular, the DVR3D program suite [56] offers a well tested instrument for the study of triatomics.

The main object of this thesis is to investigate small effects neglected in *ab initio* spectroscopy, with the ultimate goal of improving our quantitative understanding of the water spectrum, eventually achieving a first-principle description of the water energy levels whose accuracy could be comparable with experiments. Using as a starting point the most accurate *ab initio* water PES available in the literature [20], together with well known computational techniques [55, 56], the importance of several terms, including the Breit and Gaunt term [43], and the breakdown of the BO approximation, is evaluated completely from first principles. Computationally, the terms considered can be divided into two categories: corrections to the PES, or corrections to the nuclear Kinetic Energy Operator (KEO). The former can be accounted for almost exactly. Conversely, the inclusion of the latter presents big difficulties, at both the theoretical and computational level. Consequently, simpler but realistic models are developed to treat couplings which go beyond the BO approximation.

The work is organised as follows. Chapter 2 introduces the theoretical background underlying this work. Almost all the material presented in this chapter is well known from the literature, so its main goal is to organise the notation in a clear fashion. The water Hamiltonian is presented in both the non-relativistic (Section 2.1) and relativistic forms (Section 2.7). The Born-Oppenheimer equations are shown in subsection 2.1. The method used to solve those equations is also outlined. Section 2.6 describes the water PES of Partridge and Schwenke, which, at the time of writing, is the most accurate totally *ab initio* PES for water in the literature.

In Chapter 3 several models which go beyond the BO approximation are presented. The simplest correction to the BO approximation is known as Born-Oppenheimer Diagonal Correction (BODC). It mainly arises from the mass polarisation term. In other words, it is a correction to the error made in considering the centre of mass of the system being coincident with the centre of mass of the nuclei. Section 3.1 presents BODC surfaces for water calculated at several levels of electronic structure theory. Beyond the BODC one has to consider the coupling between the nuclear and electronic motions. While the nuclei vibrate or rotate, coupling between the ground and excited electronic states can occur. Considering all possible excitations means dealing with an infinite number of coupled second order differential equations. If the solution of such a problem were possible, it would give the exact (non-relativistic) molecular vibrational-rotational levels. The difference between the results obtained at this level and those calculated with the electrons frozen in their ground state (considering also the BODC correction) is called the non-adiabatic approximation. In Section 3.2 several methods

to include non-adiabatic effects are presented. They are all related to a simple model elaborated for homonuclear diatomics by Bunker and Moss [57], and then extended by the same authors to triatomics [58]. Here, the g -factor provides an excellent link between theory and experiment. The g -factor which can be directly measured [59], is closely related to the rotational non-adiabaticity (see subsection 3.2.3). We will refer to all corrections beyond the BO approximations generally as non-BO corrections.

It is well known that the coupling between charged particles and the electro-magnetic field is weak, the coupling constant α being approximately $1/137.036$ (in atomic units, [23]). This allows for a perturbative expansion of the molecular Hamiltonian, in terms of α . The smallest order of the electromagnetic interaction is represented by the Coulomb potential. First order corrections have already been shown to be of great spectroscopic importance for water [60] and H_2S [61]. Namely, the Mass-Velocity (MV) and one-electron Darwin (D1) terms can modify VBOs predictions by up to 100 cm^{-1} . In Section 4.4 the contribution of the MVD1 correction is reviewed. In addition, the spectroscopic importance of higher order terms is investigated for both H_2O and H_2S . These terms are included for the first time in *ab initio* molecular calculations. In Section 4.3 the origin of the molecular relativistic effect is investigated. Following the work of Katriel *et al.* [62], the relativistic corrections are split into their respective orbital contributions.

The final chapter focuses on the agreement between theory and experiment. Starting from the most accurate *ab initio* PES available, and having added several corrections to it, one expects to be able to predict vibrational-rotational levels to within 1 cm^{-1} or less. However, this is not the case. In line with previous analyses [55], we find that the problem with a spectroscopically accurate *ab initio* prediction of water energy levels is due to a lack of convergence in Partridge and Schwenke's hypersurface, and notably in the angular coordinate. This introduces an error as high as 30 cm^{-1} in the predicted VBOs. As part of this project, Polyansky and Császár have begun to calculate a new PES, using a larger basis together with high quality extrapolation techniques to the CBS limit. This work is currently under way and only the main details along with some preliminary results are presented in the chapter. It is hoped that the combination of all the efforts described in this thesis could lead to a spectroscopically accurate fully *ab initio* prediction of vibrational-rotational levels for water. Finally, the possibility of extending this work to other molecules is discussed.

Theoretical background

2.1 The Born-Oppenheimer approximation

Let us consider a generic molecular system, composed of N electrons, of mass m , charge $-e$, and positions $\{\mathbf{r}_i\}$ ($i = 1, \dots, N$), related to any laboratory reference frame; and L nuclei of mass M_A , charge $Z_A e$ and positions $\{\mathbf{R}_A\}$ ($A = 1, \dots, L$). In the coordinate representation, the time independent Schroedinger, ie non-relativistic, equation for this system is written [63]:

$$\mathcal{H} \Psi(\{R\}, \{r\}) = \mathcal{E} \Psi(\{R\}, \{r\}). \quad (2.1)$$

$\mathcal{H}$ is the Hamiltonian operator :

$$\mathcal{H} = - \sum_{i=1}^N \frac{\hbar^2}{2m} \nabla_i^2 - \sum_{A=1}^L \frac{\hbar^2}{2M_A} \nabla_A^2 + V(\{\mathbf{R}_A\}, \{\mathbf{r}_i\}), \quad (2.2)$$

$\Psi(\{\mathbf{R}_A\}, \{\mathbf{r}_i\})$ is the molecular wave function. The potential $V(\{\mathbf{R}_A\}, \{\mathbf{r}_i\})$ is given by the sum of all Coulomb pair potentials:

$$V(\{\mathbf{R}_A\}, \{\mathbf{r}_i\}) = \sum_{A < B}^L \frac{Z_A Z_B e^2}{|\mathbf{R}_A - \mathbf{R}_B|} - \sum_{A=1}^L \sum_{i=1}^N \frac{Z_A e^2}{|\mathbf{R}_A - \mathbf{r}_i|} + \sum_{i < j}^N \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_i|}. \quad (2.3)$$

To find the stationary states of eq (2.1) represents a very difficult task. However, it is possible to simplify the original problem by taking advantage of the difference between the masses of the electrons and nuclei. This approximation is known as Born-Oppenheimer (BO) approximation [24, 25]. In fact, while the forces to which they are subject are of comparable magnitude, the nuclei's inertia is about $10^3 - 10^5$ times greater than the electrons'. Consequently, the electrons move much faster than the nuclei, and, to a very good approximation, the two sets of particles can be studied separately. Practically, it is possible to assume that the electrons are permanently in a single state (which in our case will be the ground state) regardless of the nuclei motion, which then is obtained by averaging their interaction with the electrons over several electron revolutions.

Mathematically, these ideas are implemented in the following way. We can express the total wavefunction of the system as:

$$\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_A\}) = \sum_{n=0}^{\infty} \phi_n(\{\mathbf{R}_A\}) \psi_n(\{\mathbf{r}_i\}; \{\mathbf{R}_A\}), \quad (2.4)$$

where the functions $\psi_n(\{\mathbf{r}_i\}; \{\mathbf{R}_A\})$ are chosen as eigenfunctions of the electronic part of the Hamiltonian, i.e.:

$$\left\{ - \sum_i \frac{\hbar^2}{2m} \nabla_i^2 + V(\{\mathbf{r}_i\}; \{\mathbf{R}_A\}) \right\} \psi_n(\{\mathbf{r}_i\}; \{\mathbf{R}_A\}) = E_n(\{\mathbf{R}_A\}) \psi_n(\{\mathbf{r}_i\}; \{\mathbf{R}_A\}). \quad (2.5)$$

In this differential equation the nuclear coordinates act only as parameters. This is equivalent to solving the Hamiltonian problem (2.1) with the nuclei clamped at positions $\{\mathbf{R}_A\}$. As a result, we obtain the electronic energies $E_n(\{\mathbf{R}_A\})$ and eigenfunctions $\psi_n(\{\mathbf{r}_i\}; \{\mathbf{R}_A\})$ depending on the nuclear coordinates. If we consider also the nuclear motion, we obtain a second equation for the functions $\phi_n(\{\mathbf{R}_A\})$:

$$\left(\sum_A \frac{\hbar^2}{2M_A} \nabla_A^2 + E_n(\{\mathbf{R}_A\}) - \mathcal{E} \right) \phi_n + \sum_{n'} C_{nn'} \phi_{n'} = 0, \quad (2.6)$$

where

$$C_{nn'} = \sum_A \frac{\hbar^2}{2M_A} (\mathbf{A}_{nn'}^{(A)} \nabla_A + B_{nn'}^{(A)}), \quad (2.7)$$

and

$$\mathbf{A}_{nn'}^{(A)} = \langle \psi_n | \nabla_A | \psi_{n'} \rangle, \quad (2.8)$$

$$B_{nn'}^{(A)} = \langle \psi_n | \nabla_A^2 | \psi_{n'} \rangle. \quad (2.9)$$

So far no approximation of any kind has been introduced, and solving the two coupled differential equations (2.5), (2.6) is perfectly equivalent to solving the original eq. (2.1). However, it is customary to consider in eq. (2.5) the electronic coordinates referring to the nuclei's center of mass, instead of the molecular center of mass. This is a first approximation which introduces in the hamiltonian a term normally described as *mass polarization* (see eq. (7) in [64]). Within the Born-Oppenheimer approximation we can neglect the derivatives of the ψ_n with respect to the nuclear coordinates, i.e. the terms $C_{nn'}$. This will uncouple eq. (2.6) and eq. (2.5), resulting in a sizable simplification of the original problem. As a result, the nuclei will be subject not only to their Coulomb interaction, which is strongly repulsive, but also to a potential given by their interaction with the electrons, which can lead to an overall attractive force $E_n(\{\mathbf{R}_A\})$. The curves $E_n(\{\mathbf{R}_A\})$ are usually referred to as Potential Energy (hyper)Surfaces (PES). The accuracy with which they are determined often represents the limit to which molecular energy levels and related transition intensities can be calculated.

The corrections to the BO approximation are therefore represented by considering the terms $C_{nn'}$. There are two corrections to the BO equation (2.6) arising from the terms $C_{nn'}$: the adiabatic (BODC) represents the case of $n' = n$, and the non-adiabatic contains the terms with $n' \neq n$. For the electronic ground state ($n = 0$), the BODC does not involve derivatives of the nuclear functions ϕ_0 , and it can be accounted for as an extra term in the effective nuclear

potential. The non-adiabatic corrections are more difficult to include, mainly because the electronic quantum number n ceases to be a good one, and coupling between different electronic states must be considered, including states lying in the continuum.

Finally, it is important to notice that the BO approach gives a good description of those molecular states lying deep in the potential well. In fact the BO approximation is useful when there is a large separation between electronic energy surfaces, and fails if the nuclei move in areas where two or more PESs come close together, or even cross [65]. This normally happens in highly energetic motions, such as dissociation or very highly excited vibrations. In water [65, 66, 67] the X and B states cross for linear HOH and HHO, giving rise to two conical intersections, at energies of approximately $40,000 \text{ cm}^{-1}$ or more¹. In these situations, the coupling between different electronic states becomes important. The canonical intersections are also closed to the first dissociation channel, that is $\text{H}_2\text{O} \rightarrow \text{OH} + \text{H}$, at an energy of 41200 cm^{-1} (more precisely, Ruscic *et al.* [68] recommend the value of $41128 \pm 24 \text{ cm}^{-1}$). In this work analysis of the water bound states will be limited in the range $0 - 25000 \text{ cm}^{-1}$; this is the range for which experimental data are available.

2.2 Water molecule

The equations (2.5) and (2.6) refer to any generic molecular system. In this section we will focus on eq. (2.6), i.e. on the nuclear part of the problem, and we will restrict our study to the water molecule. Given those premises, the Hamiltonian problem we are interested in is:

$$\mathcal{H}_{BO}^{nuc} \phi_n = \mathcal{E} \phi_n, \quad (2.10)$$

where

$$\mathcal{H}_{BO}^{nuc} = \frac{P_O^2}{2M_O} + \frac{P_{H_1}^2}{2M_H} + \frac{P_{H_2}^2}{2M_H} + V, \quad (2.11)$$

where V is the BO PES relative to the electronic ground state ($E_0(\{\mathbf{R}_A\})$ using the notation of eq. (2.6)). A detailed description of the water PES will be given in section 2.6. For our purposes it is important to notice that it depends only on the relative distances among the three nuclei. That will allow further simplifications in eq. (2.10). M_O and M_H are respectively the nuclear mass of oxygen ($M_O = 15.990726 \text{ a.m.u.}$) and hydrogen ($M_H = 1.007276 \text{ a.m.u.}$). However, as will be explained in detail in the next chapter, the values to be used for the masses M_O and M_H represent a subject for discussion. The three momenta ($\mathbf{P}_O, \mathbf{P}_{H_1}, \mathbf{P}_{H_2}$) refer to a laboratory Cartesian frame. In the coordinate representation, eq. (2.10) specifies a 9 dimensional coupled second order differential problem.

We can reduce the effective dimensions of this problem by exploiting the symmetries of Hamiltonian (2.11), namely its invariance under uniform translation and rotation. The former invariance allows us to eliminate the motion of the centre of mass of the nuclei, which is a phase in the total wave function, reducing the total number of degrees of freedom of the system to 6. The latter tells us that the Hamiltonian operator $\mathcal{H}_{BO}^{nuc}$ must commute with the operator of total nuclear angular momentum $\mathbf{J}$, i.e., $[\mathcal{H}_{BO}^{nuc}, \mathbf{J}] = 0$. We can then choose a basis set of

¹All the energies in this thesis are given using the vibrational-rotational-electronic water ground state as zero energy point

common eigenvectors of the operators $\mathcal{H}$, J^2 , J_z , the last two being, respectively, the square modulus of $\mathbf{J}$ and its projection on an arbitrary axis, that we fix to be the z -axis of the laboratory frame. This choice leads us to label the wave-function of the system with the quantum numbers n, J, M . We also need two additional quantum numbers (say v, τ) to label the solutions of eq. (2.10). The quantum number v will refer to the vibrational part of the motion. If the potential is harmonic, or if we assume an harmonic approximation for it, v will be the set of vibrational numbers (v_1, v_2, v_3). As for each value of J and v there are $2J + 1$ solutions of eq. (2.10), the quantum number τ will be used to label the rotational levels. Both v and τ will be discussed in Section 2.5.

We can then write the nuclear wavefunction as a product of functions of internal coordinates and symmetric top rotational eigenfunctions [48, 49, 69]:

$$\phi_{n,v,\tau}^{(J,M)} = \sum_{k=-J}^J \Phi_{v,\tau,n}^{J,k}(\text{internal}) \mathcal{D}_{M,k}^{J*}(\{\Omega\}), \quad (2.12)$$

here $\mathcal{D}_{M,k}^{J*}$ is a (conjugate) rotation matrix element [63] depending only on the three Euler angles ($\{\Omega\} = \{\alpha, \beta, \gamma\}$) of the transformation relating the lab frame with the one embedded on the molecule, and k is the projection of the total angular momentum $\mathbf{J}$ on the z -axis of the frame embedded on the molecule. For sake of simplicity in notation, we will omit the index n , as we will deal only with the electronic ground state. In addition to v, τ, J, M two more quantum numbers need to be considered to include the symmetry of the wavefunction with respect to rotational parity and exchange of the two identical hydrogen nuclei. They will be introduced in the next Section.

There are many different possibilities for the internal coordinates [70]. If we describe our system with two lengths (R_1, R_2) and an angle Θ , they can be generalised by mean of two geometric parameters g_1 and g_2 , defined as [69] (see figure 2.1) :

$$g_1 = \frac{A_3 - P}{A_3 - A_2}, \quad g_2 = \frac{A_3 - R}{A_3 - A_1}. \quad (2.13)$$

Among all possible choices we point up Jacobi coordinates ($g_1 = 0.5$ and $g_2 = 0$, if $A_3 = A_2$), and bond coordinates ($g_1 = g_2 = 0$). For the water molecule, previous works [71, 72] suggested that Radau coordinates are computationally more convenient than bond coordinates. Introduced by Radau [73], they have the particular advantage of being orthogonal, i.e. the kinetic energy operator does not have terms with mixed derivatives, and also, for light-heavy-light triatomics they are very close to the bond coordinates. The Radau coordinates are obtained from eq. (2.13) with the choice $g_1 = g_2 = \gamma$, where

$$g_1 = g_2 = \gamma = 1 + \frac{M_O}{M_H} - \sqrt{\left(1 + \frac{M_O}{M_H}\right)^2 - 1} \approx 0.03. \quad (2.14)$$

Hereafter, we will indicate with $\{R_1, R_2, \Theta\}$ the set of internal bond-length ($R_1 = \overline{OH_1}$, $R_2 = \overline{OH_2}$), bond-angle ($\Theta = \widehat{HOH}$) coordinates, and with $\{r_1, r_2, \theta\}$ the corresponding set of Radau coordinates, determined by eq. (2.13) when the prescription (2.14) is used. The definition of Radau coordinates given here follows Tennyson and Sutcliffe [49], which slightly differs from the one commonly used in literature, as for instance in [71, 72]. A detailed explanation of the differences, as well as useful formulae to switch between the two can be found

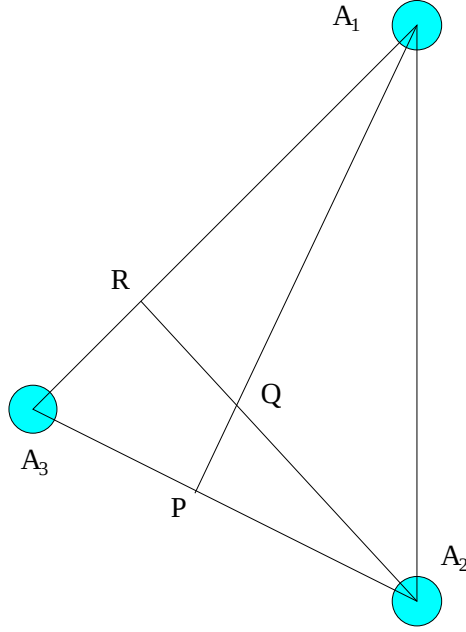


Figure 2.1: General coordinates system for a triatomic molecule, described by two lengths $(\overline{RA_2}, \overline{PA_1})$ and the included angle $\widehat{A_1QA_2}$. The position of both P and R is defined by the choice of the coordinate system and by the masses of the atoms [69].

in appendix A of ref. [74]. The difference in the coordinates also modifies the definition of reduced masses.

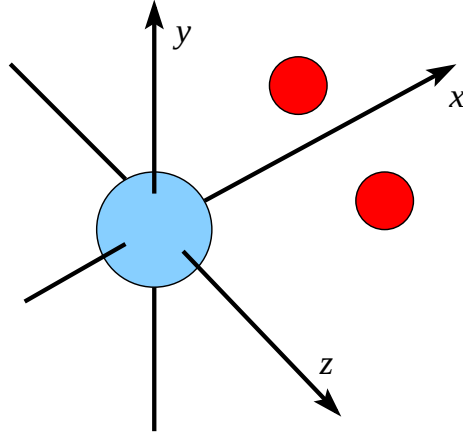


Figure 2.2: Orientation of the molecule embedded frame. The origin of the embedded Cartesian frame is in the CM of the system. Due to the high value of the ratio of the masses of oxygen and hydrogen ($M_O/M_H \approx 16$), the CM is very close to the oxygen nucleus.

The kinetic energy operator $\hat{K}$ in term of these coordinates has been derived by Sutcliffe

and Tennyson [48, 69]. Their derivation was general and allows for an almost entirely arbitrary choice of the embedding of the body reference frame. For water it is preferable to require the x -axis of the body embedded frame to bisect the angle θ , the z -axis to lie in the plane of the molecule perpendicular to x , and y to be such that (x, y, z) form a right handed frame (see figure 2.2). For the Radau bisector embedding, the kinetic operator reads:

$$\hat{K} = \hat{K}_V + \hat{K}_{VR}, \quad (2.15)$$

where $\hat{K}_V$ is a purely vibrational operator,

$$\hat{K}_V = -\frac{1}{2\mu} \left[\frac{\partial}{\partial r_1} r_1^2 \frac{\partial}{\partial r_1} + \frac{\partial}{\partial r_2} r_2^2 \frac{\partial}{\partial r_2} + \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right], \quad (2.16)$$

and $\hat{K}_{VR}$ is a mixed vibration-rotation operator:

$$\hat{K}_{VR} = \frac{1}{2} [M_{xx} \hat{J}_x^2 + M_{yy} \hat{J}_y^2 + M_{zz} \hat{J}_z^2 + M_{xz} (\hat{J}_x \hat{J}_z + \hat{J}_z \hat{J}_x)] + \frac{1}{i} \hat{K}_{cor}. \quad (2.17)$$

$\hat{K}_{cor}$ is the term that mixes vibrations and rotations

$$\hat{K}_{cor} = \left[\frac{1}{2\mu} \left(\frac{1}{r_1^2} - \frac{1}{r_2^2} \right) \left(\frac{\partial}{\partial \theta} + \frac{\cot \theta}{2} \right) \right] \hat{J}_y. \quad (2.18)$$

This term (usually referred to as Coriolis term) is zero at equilibrium. Finally, the inverse generalised inertia tensor $M_{\alpha\beta}$ are given by:

$$M_{xx} = \frac{1}{2\mu(1 - \cos \theta)} (r_1^{-2} + r_2^{-2}), \quad (2.19)$$

$$M_{yy} = \frac{1}{4\mu} (r_1^{-2} + r_2^{-2}), \quad (2.20)$$

$$M_{zz} = \frac{1}{2\mu(1 + \cos \theta)} (r_1^{-2} + r_2^{-2}), \quad (2.21)$$

$$M_{xz} = \frac{1}{2\mu \sin \theta} (r_2^{-2} - r_1^{-2}). \quad (2.22)$$

The reduced mass μ is given by

$$\mu^{-1} = (\gamma^2 + 1) M_H^{-1} + (1 + \gamma)^2 M_O^{-1}. \quad (2.23)$$

It is convenient to express eqs. (2.16) and (2.17) in a so-called manifestly Hermitian form, by eliminating the factor $r_1^2 r_2^2$ from the Jacobian. This is done by choosing an internal coordinates wave function $r_1^{-1} r_2^{-1} \Phi_{v,\tau,n}^{J,k}$ and obtaining an operator for the reduced part $\Phi_{v,\tau,n}^{J,k}$ alone. While $\hat{K}_{VR}$ is left unaltered by this transformation, $\hat{K}_V$ is replaced by:

$$\hat{K}_V = -\frac{1}{2\mu} \left[\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} + \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} \right]. \quad (2.24)$$

Following the work of Sutcliffe and Tennyson [48], it is possible to construct an effective radial Kinetic Energy Operator from eqs. (2.17), (2.24). This is done by integrating out the Euler angles and the included angle θ . As angular functions it is convenient to choose associated

Legendre Polynomials ($\Theta_{j,k}(\theta)$, *vide infra*, eq. (2.37)), where k is explicitly coupled to the Wigner function $\mathcal{D}_{k,M}^{J*}$.

The effective radial KEO reads:

$$\hat{K}(r_1, r_2) = \hat{K}_V^{(a)} + \hat{K}_V^{(b)} + \hat{K}_{VR}^{(1)} + \hat{K}_{VR}^{(2)} + \hat{K}_{VR}^{(3)}, \quad (2.25)$$

where

$$\hat{K}_V^{(a)} = -\delta_{k,k'}\delta_{j,j'}\frac{1}{2\mu}\left[\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} - j(j+1)(r_1^{-2} + r_2^{-2})\right], \quad (2.26)$$

$$\hat{K}_V^{(b)} = -\delta_{k,k'}\frac{k^2}{2\mu}(r_1^{-2} + r_2^{-2})\langle j', k' | \sin^{-2}\theta | j, k \rangle, \quad (2.27)$$

$$\begin{aligned} \hat{K}_{VR}^{(1)} &= \delta_{k',k}\frac{(r_1^{-2} + r_2^{-2})}{8\mu}\left(J(J+1)\langle j', k' | \frac{3 - \cos\theta}{1 - \cos\theta} | j, k \rangle - k^2\langle j', k' | \frac{1}{2} + \right. \\ &\quad \left. + \frac{3}{1 - \cos\theta} - \frac{4}{\sin^2\theta} | j, k \rangle\right), \end{aligned} \quad (2.28)$$

$$\hat{K}_{VR}^{(2)} = \delta_{k',k\pm 1}\frac{C_{jk}^\pm}{4\mu}(r_2^{-2} - r_1^{-2})(\delta_{j,j'}C_{jk}^\pm + \left(k \pm \frac{1}{2}\right)\langle j', k' | \frac{1 + \cos\theta}{\sin\theta} | j, k \rangle), \quad (2.29)$$

$$\hat{K}_{VR}^{(3)} = \delta_{k',k\pm 2}(r_1^{-2} + r_2^{-2})\frac{C_{jk\pm 1}^\pm C_{jk}^\pm}{8\mu}\langle j', k' | \frac{1 + \cos\theta}{1 - \cos\theta} | j, k \rangle, \quad (2.30)$$

where the angular factor is:

$$C_{jk}^\pm = \sqrt{j(j+1) - k(k \pm 1)}, \quad (2.31)$$

and the integrals are defined as follows:

$$\langle j', k' | f(\theta) | j, k \rangle = \int_0^\pi \Theta_{j',k'}(\theta) f(\theta) \Theta_{j,k}(\theta) \sin\theta d\theta. \quad (2.32)$$

2.3 Finite Basis Representation

Using a Finite Basis Representation (FBR), the wavefunction of eq. (2.12) can be expanded in a direct product of one dimensional basis sets:

$$\Phi = \sum c_{m_1 m_2 j} |m_1\rangle |m_2\rangle |j, k\rangle = \sum c_{m_1 m_2 j} |m_1, m_2, j, k\rangle, \quad (2.33)$$

where the expansion functions for the radial coordinates ($|m_1\rangle, |m_2\rangle$) can be chosen as Morse oscillator-like functions [75]:

$$|t\rangle = H_t(r) = \beta^{\frac{1}{2}} N_{t\alpha} \exp\left(-\frac{y}{2}\right) y^{(\alpha+1)/2} L_t^\alpha(y) \quad (t = 0, \dots, \infty), \quad (2.34)$$

with

$$y = A \exp(-\beta(r - r_e)), \quad (2.35)$$

where

$$A = \frac{4D_e}{\beta}, \quad \beta = \omega_e \sqrt{\frac{\mu}{2D_e}}, \quad \alpha = \text{Integer}(A). \quad (2.36)$$

The parameter μ, r_e, ω_e and D_e can be associated with the reduced mass, equilibrium separation, fundamental frequency and dissociation energy of the relevant coordinate respectively. In practice, with the exception of μ , they are treated as non linear variational parameters and optimised accordingly. $N_{t\alpha} L_t^\alpha$ is a normalised Laguerre polynomial [76].

The angular functions are chosen as normalised associated Legendre Polynomials with the phase convention of Condon and Shortley [77].

$$|j, k\rangle = \Theta_{j,k}(\theta) \quad (j = |k|, |k| + 1, \dots, \infty). \quad (2.37)$$

However, the wavefunction (2.33) does not possess the right symmetry properties under interchange of hydrogen atoms or parity. Starting from eq. (2.12), and considering also the expansion (2.33), a wave-function of defined symmetry is then built in the following fashion:

$$\begin{aligned} \phi_{q,p,v,\tau}^{(J,M)} = \sum_{k=p}^J \sum_{\substack{m_1 \geq m_2+q \\ j \geq k}} c_{m_1,m_2,j,k}^{p,q,J,M,v,\tau} \mathcal{A}(|m_1\rangle|m_2\rangle + (-1)^q|m_2\rangle|m_1\rangle) \times \\ \times \mathcal{B}|j, k\rangle (\mathcal{D}_{M,k}^{J*} + (-1)^p \mathcal{D}_{M,-k}^{J*}), \end{aligned} \quad (2.38)$$

where $c_{m_1,m_2,j,k}^{p,q,J,M,v,\tau}$ are the expansion coefficients, $q, p = 0, 1$, and $\mathcal{A}, \mathcal{B}$ are simply normalisation factors

$$\mathcal{A} = \frac{1}{\sqrt{2(1 + \delta_{m_1,m_2})}}, \quad \mathcal{B} = \frac{1}{\sqrt{2(1 + \delta_{k,0})}}. \quad (2.39)$$

It is useful to express eq. (2.38) in a more compact form:

$$\phi_{v,\tau}^\beta = \sum_{k=0}^J \sum_{m_1,m_2,j} c_{m_1,m_2,j,k}^{\beta,v,\tau} |m_1, m_2, j, k, \beta\rangle, \quad (2.40)$$

where the index β refers cumulatively to the 'good quantum numbers', $\beta = \{J, M, q, p\}$, and the vectors $\{|m_1, m_2, j, k, \beta\rangle\}$ are the expansion basis, therefore defined as:

$$|m_1, m_2, j, k, \beta\rangle = \mathcal{A}(|m_1\rangle|m_2\rangle + (-1)^q|m_2\rangle|m_1\rangle) \mathcal{B}|j, k\rangle (\mathcal{D}_{M,k}^{J*} + (-1)^p \mathcal{D}_{M,-k}^{J*}). \quad (2.41)$$

Finally, the wavefunction (2.40) possesses the right symmetry properties [69]. Under parity inversion, the wavefunction transforms as $(-1)^{J+p}$, whereas under permutation of the hydrogen nuclei, it transforms as $(-1)^{q+k}$. Due to the Pauli principle, the total molecular wavefunction must be anti-symmetric with respect to interchange of the two hydrogen nuclei. It is important then to include also the spin of the hydrogens. Therefore a singlet spinor is associated with even values of $q + k$, whereas a triplet spinor corresponds to odd values. As the potentials we consider are spin independent, we can safely neglect the spin part in the wavefunction (2.40). However, the spin dependency will need to be considered *a posteriori* in the spectrum, as ortho lines will be three times more intense than para lines.

The symmetry properties of the molecular wavefunction explored so far originate from the symmetry properties of eq. (2.11). The full symmetry group of the nuclear water Hamiltonian has four irreducible representations (see table 2.1). This group is isomorphic to the C_{2v} group, which is the group of symmetry of the nuclear equilibrium configuration [78]. Both the eigenfunctions and the observables we consider must then belong to any one but only one of these representations. As is well known, group theory is then a powerful tool for calculating matrix elements, allowing us to spot at a glance whether a matrix element may or not be zero. A matrix element is zero unless its corresponding integral contains the A_1 representation.

Table 2.1: Symmetry point group C_{2v} . In the first part the character table is given for the four elements of the group ($E, C_2, \sigma_{xz}, \sigma_{xy}$). Then the transformation properties of some observables and of the wavefunction are presented. The wavefunction is labelled as ortho (for triplet H_2 states, or $q + k$ odd) or para (for singlet, $q + k$ even). Moreover, the labels e (f) are used for $p = 0$ ($p = 1$). The total parity symmetry is given by $J + p$, being even if $J + p$ is even, and vice versa. Finally, the product table for the group C_{2v} is shown. (x, y, z) as in figure 2.2

C_{2v}	E	C_2	σ_{xz}	σ_{xy}		ϕ	A ₁	A ₂	B ₁	B ₂
A ₁	+1	+1	+1	+1	x, x^2, y^2, z^2	even-para	A ₁	A ₂	B ₁	B ₂
A ₂	+1	+1	-1	-1	R_x, yz	odd-para		A ₁	B ₂	B ₁
B ₁	+1	-1	+1	-1	y, R_z, xy	even-ortho			A ₁	A ₂
B ₂	+1	-1	-1	+1	z, R_y, xz	odd-ortho				A ₁

2.4 Variational Method in the Discrete Variable Representation

To work out the coefficients $c_{m_1 m_2 j k}^{\beta, v, \tau}$ in eq. (2.40) we make use of the Rayleigh-Ritz variational principle [53]. The implementation of this method with respect to the variation of the linear variational parameters $\{c_{m_1 m_2 j k}^{\beta, v, \tau}\}$ leads to the solution of an appropriate generalised eigenvalue problem:

$$\sum_{m'_1, m'_2, j', k'} c_{m'_1 m'_2 j' k'}^{\beta, v, \tau} < m'_1, m'_2, j', k', \beta | \mathcal{H} - \mathcal{E} | m_1, m_2, j, k, \beta > = 0. \quad (2.42)$$

The dimension of the matrices involved is related to three indexes: the number of angular functions $|j, k\rangle$, the number of Morse like oscillator functions $|m_1\rangle$ and $|m_2\rangle$, and the value of angular momentum J considered. Also the value of the parameters q and p influences the size of the calculation. According to the Hylleraas-Undheim-MacDonald's theorem [79, 80], there exists a one-to-one correspondence between the approximate energy levels $\mathcal{E}_i(N)$ and the exact levels $\epsilon_i \equiv \mathcal{E}_i(\infty)$, the i -th approximate level being an upper bound to the i -th exact level². N here is the size of the basis set used for expansion (2.40). Mathematically the following relations hold:

$$\mathcal{E}_{i+1}(N+1) \geq \mathcal{E}_i(N) \geq \mathcal{E}_i(N+1), \quad (2.43)$$

and

$$\lim_{N \rightarrow +\infty} \mathcal{E}_i(N) = \epsilon_i. \quad (2.44)$$

The implementation of this method then consists of employing bigger and bigger basis sets, until convergence in the eigenvalues up to the desired energy cut-off is obtained. Moreover, an optimum choice of the non-linear parameters r_e, ω_e and D_e can be used to improve the pattern of convergence. However usually in these calculations only a small proportion ($\approx 5\%$) of the solutions obtained are of any significance [81]. This implies that basis set calculations normally perform poorly when a large number of energy levels are required. To overcome this limit, a Discrete Variable Representation (DVR) has been preferred to the FBR. Although the DVR method is not strictly variational, it has strong formal and practical links with the basis

²The index i corresponds to the vibrational and rotational quantum numbers v, τ

set methods discussed above. This is because the formulation of the problem in DVR first requires, at least in principle, the construction of the secular matrix in terms of appropriate basis functions. This matrix is then transformed to a grid of points determined by the appropriate Gaussian quadrature scheme for each function. Superficially this transformation achieves nothing as the DVR and FBR matrices are isophormic. However, in the DVR it is easy to define a hierarchy in the diagonalisation process, such that only the lowest and more important solutions can be selected and retained for the next step. In this fashion final Hamiltonian matrices are constructed with very high information content, as much as half of the final eigenvectors may be physically significant.

The Discrete Variable Representation of the Hamiltonian is connected to a Finite Basis Representation by means of a linear transformation:

$$\mathcal{H}_{\eta,\eta',\xi,\xi',\chi,\chi',(k,k')}^{DVR} = \sum_{\substack{m_1,m_2,j \\ m'_1,m'_2,j'}} \mathcal{T}_{m_1,m_2,j}^{\eta,\xi,\chi} \mathcal{T}_{m'_1,m'_2,j'}^{\eta',\xi',\chi'} \mathcal{H}_{m_1,m'_1,m_2,m'_2,j,j',(k,k')}^{FBR}, \quad (2.45)$$

where

$$\mathcal{H}_{m_1,m'_1,m_2,m'_2,j,j',(k,k')}^{FBR} = \langle m'_1, m'_2, j', k' | \beta | \mathcal{H} | m_1, m_2, j, k, \beta \rangle. \quad (2.46)$$

The transformation operators $\mathcal{T}$ are defined by the choice of the FBR basis set. In our case the basis functions are expressed as a product of one-dimensional functions, consequently the operator separates into a product of one-dimensional operators:

$$\mathcal{T}_{m_1,m_2,j}^{\eta,\xi,\chi(k)} = T_{m_1}^{\eta} T_{m_2}^{\xi} T_j^{\chi(k)}, \quad (2.47)$$

each of which is associated with one coordinate. The one-dimensional operator T is a function of the points $\{o_i\}$ and weights $\{w_i\}$ characteristic of the Gaussian integration formula used³:

$$T_j^i = \sqrt{w_i} |f_j(o_i)\rangle. \quad (2.48)$$

The weights $\{w_i\}$ are defined in terms of the points [44]:

$$w_i = \frac{\langle f_{N-1} | f_{N-1} \rangle}{f_{N-1}(o_i) f'_N(o_i)}. \quad (2.49)$$

The DVR equations derived from the transformation (2.45) are described in great detail in [56]. It is worth noting that the potential energy operator becomes diagonal in the DVR representation:

$$\sum_{\substack{m_1,m_2,j \\ m'_1,m'_2,j'}} \mathcal{T}_{m_1,m_2,j}^{\eta,\xi,\chi} \mathcal{T}_{m'_1,m'_2,j'}^{\eta',\xi',\chi'} V_{m_1,m'_1,m_2,m'_2,j,j',(k,k')}^{FBR} = V_{\eta,\eta',\xi,\xi',\chi,\chi',(k,k')}^{DVR} \delta_{\eta,\eta'} \delta_{\xi,\xi'} \delta_{\chi,\chi'}. \quad (2.50)$$

The UCL group has developed [56] a full triatomic rotation-vibration spectroscopic package (DVR3D) based on a three dimensional DVR approach. In ref. [56] a complete description of the DVR program suite is given. A new version is presently being tested. This code has then been successfully applied to the study of many triatomics, including HCN [82, 83], H_3^+ [84], H_2S [61] and water [60, 85]. For the latter, the pattern of convergence of the energy levels as functions of the number of points employed has been studied in detail in previous works [55, 86].

³In our case we have used Gauss-Laguerre formulae for the r_1 and r_2 coordinates, and Gauss-Legendre for the angular coordinate (see ref. [76] for more details about numerical integration techniques).

2.5 Notation

Traditionally, energy levels in water are labelled by three vibrational quantum numbers, v_1 , v_2 and v_3 and three rotational, J , K_a and K_c .

In order to describe the nuclear motion, it is possible, for a big class of molecules, to employ very simple physical models which lead straightforwardly to satisfactory results. This is the case, for instance, of semi-empirical Hamiltonians based on the harmonic approximation and/or rigid rotor model.

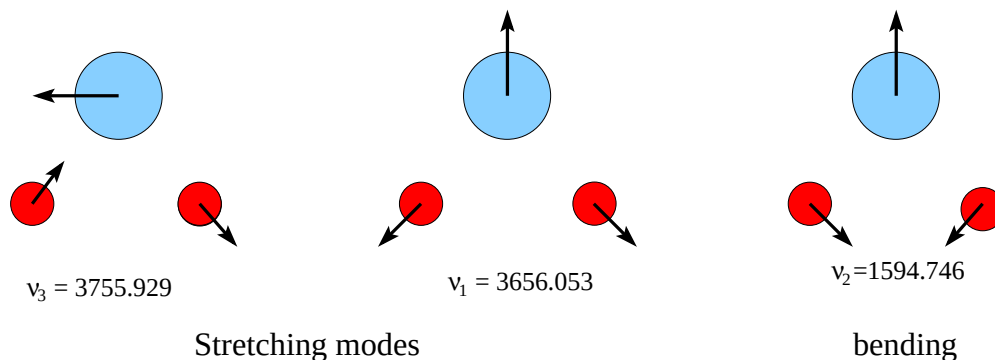


Figure 2.3: Harmonic vibrational modes in water. The values indicated for the frequencies (in cm^{-1}) are experimentally determined [87]. From left to right, the asymmetric stretch, the symmetric stretch, and the bending mode.

If we assume an harmonic approximation for the inter-nuclear potential energy surface, water has three vibrational modes (see figure 2.3). They are a symmetric stretch, a bending mode, and an asymmetric stretch. Energy levels are then described in “quanta” of excitation in each mode, by three numbers v_1 , v_2 , v_3 :

$$E(v_1, v_2, v_3) = v_1 \cdot \nu_1 + v_2 \cdot \nu_2 + v_3 \cdot \nu_3, \quad (2.51)$$

where the ground state energy has been chosen as zero. Of course this approximation limits itself to the lowest excited modes, because, as the vibrational energy increases, anharmonic effects become important.

In the literature it is also possible to find different vibrational notations. A polyad indicates a group of levels close in energy. For water, the notation in this case for the polyad v is $v\nu$ for an even number of bending quanta, $v\nu + \delta$ for an odd number of bending quanta. As examples, the polyad 1ν contains the states $(v_1, v_2, v_3) = (1, 0, 0)(0, 2, 0)(0, 0, 1)$, whereas $1\nu + \delta = (1, 1, 0)(0, 3, 0)(0, 1, 1)$. All these states are close in energy as $\nu_1 \approx \nu_3 \approx 2\nu_2$. Also local mode labels, instead of normal modes, can be used. The theory underlying the local modes definition is more difficult, and can be found in [88, 89]. The advantage of the local mode notation is that it allows a better representation of the high stretches. For high values of ν , the levels $(\nu, 0, 0)$ and $(\nu - 1, 0, 1)$ are quasi degenerate. However, recent papers often give energy levels in both normal and local mode notation.

The rigid rotor model provides a useful zeroth order description of the rotational motion in water. However, as water belongs to the class of asymmetric top molecules, in which no two principal moments of inertia are equal, even a rigid molecule approach presents some complexity. If we consider the nuclei clamped at their equilibrium positions, the resulting Hamiltonian is:

$$\mathcal{H}_{rigid} = \frac{\hat{J}_z^2}{2I_z} + \frac{\hat{J}_x^2}{2I_x} + \frac{\hat{J}_y^2}{2I_y} = A\hat{J}_z^2 + B\hat{J}_x^2 + C\hat{J}_y^2. \quad (2.52)$$

Experimentally determined values for the rotational constants for the electronic and vibrational ground state of water are $A = 27.880591 \text{ cm}^{-1}$, $B = 14.5216246 \text{ cm}^{-1}$, $C = 9.27774594 \text{ cm}^{-1}$ [90]. From eq. (2.52), it is possible to obtain the following estimate for the energy levels [91]:

$$E(J, K_a, K_c) = \frac{A+B}{2} J(J+1) + \left(C - \frac{A+B}{2} \right) K_c^2, \quad (2.53)$$

where K_c is the value of projection of the total angular momentum on the y -axis of the molecular embedded frame (see figure 2.2). This formula refers to the case of an oblate symmetric top, for which the levels are degenerate in pairs. In the water spectrum such levels split, due to asymmetry of the constants A and B . It is then customary to introduce a second quantum number, K_a , which represents the projection of the total angular momentum on the z -axis. At equilibrium, K_a coincides with the k previously defined (eq. (2.12)). K_a can assume the values $0, 1, \dots, J$, whereas $K_c = J - K_a, J - K_a + 1$. The states are then labelled as $J_{K_a K_c}$. Spectroscopically, the quantum number K_a is very important because the energy levels depend on K_a more strongly than J . Consequently, levels with low K_a are easier to assign. It is possible to find in literature also the rotational notation J_τ ($\tau = -J, -J+1, \dots, +J$). The two sets of rotational quantum numbers are related by $\tau = K_a - K_c$ [92].

The quantum numbers v_1, v_2, v_3 and K_a, K_c are not rigorous ones, as they originate from zeroth order approximations, yet they provide a clear physical picture for the lower energy levels. We have already seen that a more rigorous approach is based on group theory. To relate the two pictures, it can be shown that the $(-1)^{q+k} = (-1)^{v_3+K_a}$, and $(-1)^{J+p} = (-1)^{K_a+K_c+J+v_3}$.

In table 2.2 the lowest energy levels for $J = 0, 2$ have been calculated using equations (2.51),(2.53). As expected, the calculated levels can qualitatively explain the water spectrum, but are far from spectroscopic accuracy. The very basic model of harmonic oscillator and rigid rotor can be improved using a perturbative approach. It is possible to add third order terms or higher in eq. (2.51), or mixing of vibrations and rotations in eq. (2.53). However, a variational approach is preferable, as it leads to a better understanding of the physics of the various processes under study. Also, perturbation theory limits itself to low energy levels: particularly, for water, the rotational expansion is divergent already for $J > 7$ [47]. Furthermore, for water, the switch from perturbational approaches to variational calculations has led to an improvement of almost three orders of magnitude in the predictions of vibrational-rotational levels (see table 1.4 in [55]). In fact it has long been recognised that perturbation theory is inappropriate to treat molecules containing hydrogen. Among them, water is particularly floppy, undergoing large amplitude motions already at relatively low energies.

2.6 Partridge and Schwenke's *ab initio* and empirical Potential Energy Surfaces

In 1997 Partridge and Schwenke published their *ab initio* potential energy surface and dipole moment function for the ground electronic state of water [20]. This surface is presently the most accurate in the literature. They solved the equations for the electronic motion for 771 different nuclear configurations. They used the cc-pV5Z basis set [30] augmented with diffuse s, p and d functions on oxygen and s and p on hydrogen, at the multireference configuration-interaction (MRCI) level of theory. Their points spanned a range $30 \leq \Theta \leq 180$ degrees and $0.7 \leq R \leq 1.7$ Å. Their grid is “sufficiently dense to accurately define the PES to $35000 - 40000$ cm^{-1} (above the equilibrium geometry). There are 285 points above 40000 cm^{-1} , which are useful in helping define the high-energy portions of the surface, but the density of points is not sufficient to accurately specify the surface in this energy range” [20].

Within their publication they provided an analytic fit to their *ab initio* data points:

$$V^{ai} = V^{5Z} - \Delta V^{core}, \quad (2.54)$$

with

$$V^{5Z}(R_1, R_2, \Theta) = V^a(R_1) + V^a(R_2) + V^b(R_{HH}) + V^c(R_1, R_2, \Theta), \quad (2.55)$$

where R_{HH} is the HH distance and

$$V^a(r) = D \exp[-2a(r - r_0)] - 2D \exp[-a(r - r_0)], \quad (2.56)$$

$$V^b(r) = A \exp(-br), \quad (2.57)$$

$$V^c = c_{ooo} + \exp\{-\beta[(R_1 - R_e)^2 + (R_2 - R_e)^2]\} \times \sum_{ijk} c_{ijk} [(R_1 - R_e)/R_e]^i [(R_2 - R_e)/R_e]^j [\cos \Theta - \cos \Theta_e]^k. \quad (2.58)$$

Parameters D , a , r_0 , A , b and c_{ijk} were determined using a weighted least squares fit to the *ab initio* data, β was fixed to $2 a_o^{-2}$ to give fast enough damping and R_e and Θ_e remained fixed. Their final fit used $i + j \leq 8$ and $k \leq 14 - (i + j)$ for 245 different parameters $\{c_{ijk}\}$ in V^c . In eq. (2.55) the two terms V^a represent the OH interaction, V^b is needed to account for the HH repulsion at short distance, and V^c introduces three-body effects. It should be noticed that the two-body terms in eq. (2.55) are not meant to give a faithful representation of the O-H and H-H interactions, and are introduced mainly to facilitate the fit. Their coefficients are thus optimised accordingly. For instance, the H_2 molecule can form bound states, whereas the functional form used for the H-H potential in eq. (2.57) is strictly repulsive. The term ΔV^{core} represents core-valence correlation in the PES. It has the same form as V^c (eq. (2.58)), and is obtained by fitting 50 parameters c_{ijk} ($i + j + k \leq 6$) to a total of 371 points. The correlation between the oxygen 1s and the outer orbitals was calculated using cc-pVQZ basis functions modified and augmented by tight d and f functions, and diffuse s, p and d derived from the aug-cc-pVQZ set.

In addition to this fully *ab initio* surface, Partridge and Schwenke also calculated a semi-empirical PES. Starting from eq. (2.54), their second PES is written in the form

$$V^{emp} = e^{5Z} V^{5Z} + e^{core} \Delta V^{core} + e^{basis} \Delta V^{basis} + \Delta V^{rest}. \quad (2.59)$$

ΔV^{basis} estimates the effect of a further basis set enlargement, fitted the same way as ΔV^{core} . The free parameters in eq. (2.59) are then c^{5Z} , c^{core} , c^{basis} and c_{ijk} in ΔV^{rest} . They have been adjusted in order to match all lines from the database HITRAN92 with $J \leq 5$. Finally, Partridge and Schwenke also published in their paper results for water isotopomers, including $H_2^{17}O$, $H_2^{18}O$, HDO, HTO, $D_2^{16}O$ and $T_2^{16}O$, obtained with the potential energy surfaces (2.54) and (2.59).

In figure 2.4 graphical representations of the potential energy curves V^{ai} ((2.54), hereafter indicated as PS1) and V^{emp} ((2.59), PS2) are given. Due to the difficulties in plotting a three dimensional surface, we reported only the symmetric part of the curve, i.e. $V(R, R, \Theta)$ as a function of R and Θ . In figure 2.4 it is possible to visualise the barrier to linearity (BL). The BL is defined as the difference between the minimum of the surface at the linear configuration ($R = R_L, \Theta = \pi$) and the equilibrium position ($R = R_e, \Theta = \Theta_e$). The BL values for the fully *ab initio* PES and the semi-empirical are respectively 11155.42 cm^{-1} (calculated at $R_L = 1.7635 \text{ a}_0$) and 11127.35 cm^{-1} (at $R_L = 1.7641 \text{ a}_0$). The BL represents an interesting conformational quantity although it is not possible to measure it directly from experiments. It allows tests of the accuracy of *ab initio* electronic structure calculations, as it affects even the low-lying bending states [41, 93]. In figure 2.4 there is also plotted the difference between the fully *ab initio* and the “adjusted” surface. The resulting curve should contain information on the contributions neglected in the *ab initio* surface, such as relativistic and adiabatic non-BO effects. We note that the surface has a stronger dependence on the angular coordinate than the radial, and it is smooth in both coordinates.

Finally, in table 2.2 we report the lowest water energy levels for $J = 0, 2$, calculated using the totally *ab initio* potential eq. (2.54) denoted as PS1, and also calculated using their semi-empirical fit, eq. (2.59), denoted as PS2. The standard deviations⁴ σ are calculated over 30 levels for $J = 0$, and 10 for $J = 2$. They give the order of magnitude of the agreement between theory and experiment. For $J = 0$, we obtain 280 cm^{-1} using a purely harmonic approximation (2.51); this is improved by more than one order of magnitude if we solve the exact three body Hamiltonian (2.11) with the *ab initio* potential (2.54) ($\sigma=10 \text{ cm}^{-1}$), we gain two further orders of magnitude using the PS2 surface ($\sigma=0.08 \text{ cm}^{-1}$). For $J = 2$, the standard deviation follows a similar pattern: we obtain $\sigma = 10 \text{ cm}^{-1}$ using a rigid rotor approximation (2.53), $\sigma=0.01 \text{ cm}^{-1}$ with PS1, $\sigma=0.00 \text{ cm}^{-1}$ with PS2. The levels are obtained using the code DVR3D. A detailed description of the input parameters for the calculations reported is presented in table 3.2. The experimental energy levels used as reference are selected from [87]. All through this thesis energy levels quoted as “experimental” will come from ref [87]. Moreover, among the 12 226 levels assigned in ref. [87] (with J up to 35), only the levels with purely experimental errors have been used. For the vibrational band origins, this include only those levels for which a transition to the 0_{00} state has been observed.

⁴The standard deviation we use is defined in the following fashion (calculated over N levels): $\sigma^2 = \sum_{i=1}^N \frac{\Delta E_i^2}{N-1}$

Figure 2.4: Potential energy surfaces for water. In (a) the surface PS1 is plotted, contour lines range from 0 to 30,000 cm^{-1} , spaced by 5,000 cm^{-1} . (b) shows the two-body part of the potential, namely the OH curve and the HH repulsive potential. In (c) the three body part of PS1 is plotted (contour lines going from 0 to 200,000 cm^{-1} , at intervals of 5,000 cm^{-1}). The total water potential originates from big cancellations between the two-body and three-body part. In (d) the difference PS1-PS2 is shown (contour lines from -50, at the bottom left corner, to 100 cm^{-1} , at the top right corner, at intervals of 10 cm^{-1}).

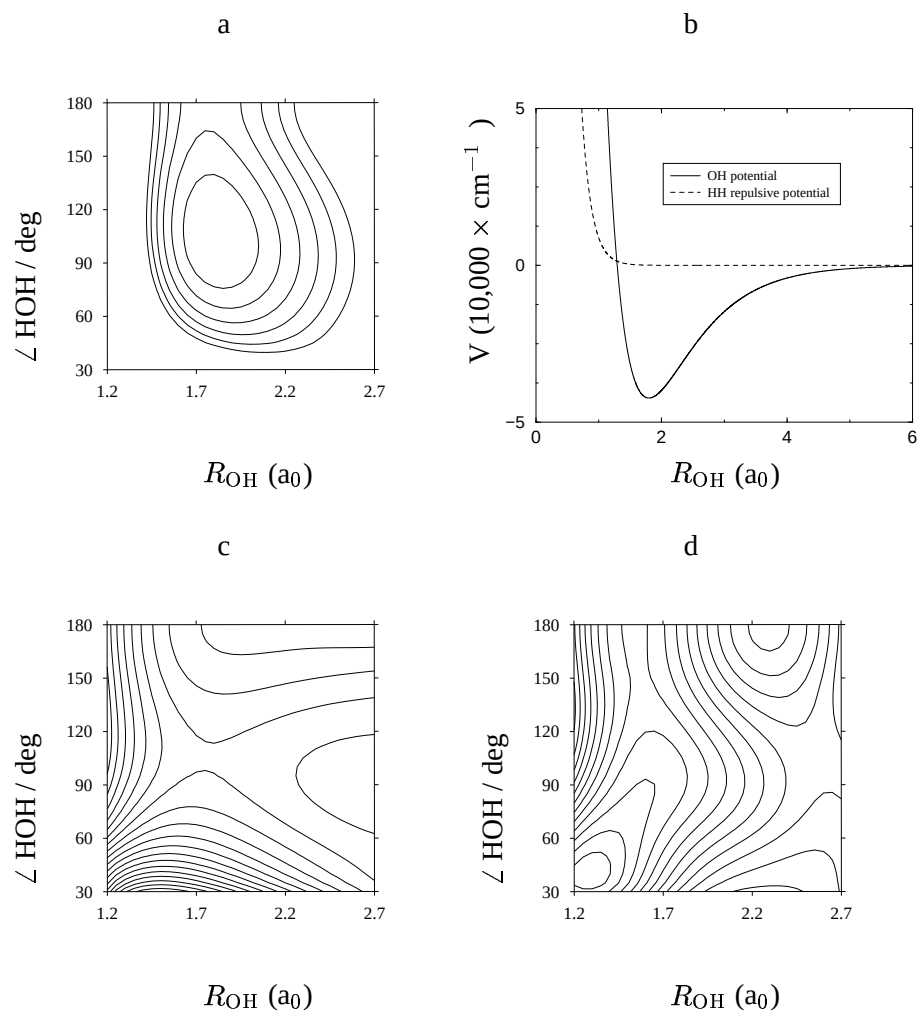


Table 2.2: Lowest water energy levels for J=0 and J=2. Levels are labelled by means of three vibrational numbers (v_1, v_2, v_3) , and three rotational J, K_a, K_c (details in Section 2.5). Experimental values (columns 2 and 7) from ref. [87]. Calculated levels (col.3-5,8-10) are given as obs.-calc. Columns 3,8 report levels calculated simply using formulae (2.51) and (2.53). Columns 4,5,9 and 10 report energy levels calculated using the DVR3D program suite, and PES from Partridge and Schwenke [20], employing both the totally *ab initio* surface PS1 (4,9) and the semi-empirical fit PS2 (5,10).

J=0									
(v_1, v_2, v_3)	obs.	calc.			(v_1, v_2, v_3)	obs.	calc.		
		eq. (2.51)	PS1	PS2			eq. (2.51)	PS1	PS2
(010)	1594.75	0.00	-2.86	-0.03	(001)	3755.93	0.00	-2.70	-0.02
(020)	3151.63	-37.86	-5.51	0.01	(011)	5331.27	-19.41	-5.47	0.06
(100)	3657.05	0.00	-3.94	0.01	(021)	6871.52	-73.90	-8.20	-0.03
(030)	4666.79	-117.45	-8.09	0.00	(101)	7249.82	-163.16	-6.18	-0.03
(110)	5234.98	-16.82	-6.85	-0.06	(031)	8373.85	-166.31	-10.86	-0.03
(040)	6134.01	-244.97	-10.62	-0.01	(111)	8807.00	-200.73	-9.00	-0.04
(120)	6775.09	-71.45	-9.47	-0.02	(041)	9833.58	-301.33	-13.39	-0.03
(200)	7201.54	-112.57	-7.26	-0.01	(121)	10328.73	-273.74	-11.52	0.06
(002)	7445.05	-66.81	-5.81	-0.06	(201)	10613.35	-456.68	-8.96	0.00
(050)	7542.44	-431.29	-13.19	-0.07	(003)	11032.41	-235.38	-8.32	-0.03
(130)	8273.98	-167.32	-12.06	-0.08	(131)	11813.21	-384.01	-14.10	-0.02
(210)	8761.58	-147.27	-10.13	-0.08	(211)	12151.25	-513.53	-11.72	-0.02
(012)	9000.14	-106.47	-8.58	0.04	(013)	12565.01	-297.53	-11.10	0.02
(220)	10284.37	-219.23	-12.63	0.01	(141)	13256.00	-535.97	-16.76	-0.26
(300)	10599.69	-371.47	-9.45	0.04	(221)	13652.66	-606.87	-13.91	0.24
J=2									
$(v_1, v_2, v_3)=(000)$					$(v_1, v_2, v_3)=(010)$				
(J_{K_a, K_c})	obs.	calc.			(J_{K_a, K_c})	obs.	calc.		
		eq. (2.53)	PS1	PS2			eq. (2.53)	PS1	PS2
2 ₀₂	70.09	-13.36	-0.04	0.00	2 _{0,2}	1664.96	0.00	0.00	0.00
2 ₁₂	79.50	-3.95	-0.01	0.00	2 _{1,2}	1677.06	-3.88	0.03	0.00
2 ₁₁	95.18	-24.04	-0.03	0.00	2 _{1,1}	1693.65	12.70	0.01	0.00
2 ₂₁	134.90	15.68	0.02	0.00	2 _{2,1}	1742.31	13.42	0.08	0.00
2 ₂₀	136.16	5.02	0.02	0.00	2 _{2,0}	1743.49	14.60	0.08	0.00

2.7 Relativistic Hamiltonian

The relativistic counterpart of the Born-Oppenheimer electronic Schrödinger equation (2.5) can be written [94]

$$\begin{aligned}\mathcal{H}_{DC} u_n(\{\mathbf{R}_A\}, \{\mathbf{r}_i\}) &= E_n(\{\mathbf{R}_A\}) u_n(\{\mathbf{R}_A\}, \{\mathbf{r}_i\}), \\ \mathcal{H}_{DC} &= \sum_i \mathcal{H}_D(i) + \sum_{i<j} \mathcal{H}_{ij},\end{aligned}\quad (2.60)$$

where $\mathcal{H}_D(i)$ is the relativistic Dirac Hamiltonian for electron i moving in the Coulomb potential $w(\mathbf{r}_i)$ generated by the L nuclei

$$\begin{aligned}\mathcal{H}_D(i) &= \beta mc^2 + \alpha \cdot (c\mathbf{p} + e\mathbf{A}) + ew(\mathbf{r}_i), \\ w(\mathbf{r}_i) &= -\sum_B \frac{Z_B e}{|\mathbf{R}_B - \mathbf{r}_i|},\end{aligned}\quad (2.61)$$

and $\mathcal{H}_{ij}$ contains the electron-electron repulsion. In a fully covariant approach, the derivation of the term $\mathcal{H}_{ij}$ requires quantum-electrodynamics [23]:

$$\mathcal{H}_{ij} = \frac{e^2}{r_{ij}} - \frac{e^2}{2r_{ij}} \left[\alpha_i \cdot \alpha_j + \frac{(\alpha_i \cdot \mathbf{r}_{ij})(\alpha_j \cdot \mathbf{r}_{ij})}{r_{ij}^2} \right] + o((Z\alpha)^2). \quad (2.62)$$

In the operator $\mathcal{H}_{ij}$, the leading term in α is the electron-electron Coulomb repulsion. The next term in the expansion is given by the emission of a single photon, which can be absorbed either by the same electron, or by a different one. The first case leads to the two-electron Lamb shift, whereas the second case, in the approximation of a weak external field ($Z_B \ll 137$), leads to the so-called Breit term. The two-electron Lamb shift is smaller than the Breit correction by a factor $(Z\alpha)$.

The vector α is a vector operator, whose components $(\alpha_1, \alpha_2, \alpha_3)$, together with the operator $\beta = \alpha_4$, satisfy the commutation relations

$$\alpha_k \alpha_i + \alpha_i \alpha_k = 2\delta_{ik}, \quad (i, k = 1, 2, 3, 4). \quad (2.63)$$

The electronic wavefunction ψ_n in eq. (2.5) is replaced by a four components spinor u_n in eq. (2.60). A complete explanation of the Dirac theory for atomic systems can be found in the book by Bethe and Salpeter [23], as well as in ref. [94, 95, 96]. It is possible to connect the non-relativistic electronic Hamiltonian, eq. (2.5) and (2.60), using the Pauli approximation [23]:

$$\begin{aligned}\mathcal{H}_{BPD} &= \{Nmc^2\} + \left\{ \sum_i \left(\frac{p_i^2}{2m} + ew(\mathbf{r}_i) \right) + \sum_{i<j} \frac{e^2}{r_{ij}} \right\} + \\ &+ \left\{ \sum_i \left[-\frac{1}{8m^3c^2} p_i^4 - \frac{e}{2m^2c^2} \mathbf{s}_i \cdot (\mathbf{p}_i \times \mathbf{E}_i) + \frac{ie\hbar}{(2mc)^2} \mathbf{p}_i \cdot \mathbf{E}_i \right] + \right. \\ &+ \sum_{i<j} \left[\frac{2e\mu}{mc} \frac{(\mathbf{r}_{ij} \times \mathbf{p}_j) \cdot \mathbf{s}_i}{r_{ij}^3} - \frac{e^2}{2m^2c^2} \left(\frac{\mathbf{p}_i \cdot \mathbf{p}_j}{r_{ij}} + \frac{(\mathbf{r}_{ij} \cdot \mathbf{p}_i)(\mathbf{r}_{ij} \cdot \mathbf{p}_j)}{r_{ij}^3} \right) - \right. \\ &- \left. \left. \frac{32\pi\mu^2}{3} (\mathbf{s}_i \cdot \mathbf{s}_j) \delta(\mathbf{r}_{ij}) + \frac{\mathbf{s}_i \cdot \mathbf{s}_j}{r_{ij}^3} - \frac{3(\mathbf{s}_i \cdot \mathbf{r}_{ij})(\mathbf{s}_j \cdot \mathbf{r}_{ij})}{r_{ij}^5} \right] \right\} \\ &= \{H_0\} + \{H_1\} + \{H_2\},\end{aligned}\quad (2.64)$$

where μ is the electron magnetic moment, $\mu = e\hbar/2m$. The operators $\{\mathbf{s}_i\}$ are defined in terms of the ordinary 2×2 Pauli spin matrices $\{\sigma_i\}$, by means of the relation $\mathbf{s}_i = 1/2\sigma_i$. $\mathbf{E}_i$ is the electric field experienced by the electron i , and possible interactions with external fields have been neglected.

The terms in eq. (2.64) can be interpreted as follows:

- H_0 : rest energy of N electrons. This term is spectroscopically irrelevant.
- H_1 : ordinary Schroedinger equation (2.5).
- H_2 : lower order relativistic corrections.

Among the first order corrections it is possible to recognise one- and two-electron contributions:

a) The Mass-Velocity (MV) term,

$$\Delta V_{MV} = - \sum_i \frac{1}{8m^3c^2} p_i^4. \quad (2.65)$$

This arises from the relativistic correction to the mass. Its contribution is always negative. Its energy correction can be estimated as [23] (for hydrogenic systems):

$$\Delta E_{MV} = - \frac{\alpha^2 Z^4}{2n^3} \left[\frac{1}{(l + \frac{1}{2})} - \frac{3}{4n} \right]. \quad (2.66)$$

b) The second term is the spin-orbit coupling:

$$\Delta V_{SO} = - \sum_i \frac{e}{2m^2c^2} \mathbf{s}_i \cdot (\mathbf{p}_i \times \mathbf{E}_i). \quad (2.67)$$

This term is negligible for the ground state of closed shell molecules: its contribution to the barrier to linearity of water is less than 0.01 cm^{-1} in absolute value [43].

c) The Darwin term,

$$\Delta V_D = \sum_i \frac{ie\hbar}{(2mc)^2} \mathbf{p}_i \cdot \mathbf{E}_i. \quad (2.68)$$

This term is caused by the presence of both positive and negative energy solutions in Dirac's theory, and is normally known as Darwin effect. It can be rewritten as:

$$\frac{ie\hbar}{(2mc)^2} \mathbf{p}_i \cdot \mathbf{E}_i = - \frac{e}{(2mc)^2} \nabla_i \cdot \mathbf{E}_i = \frac{\pi}{2c^2} \left[\sum_B Z_B \delta(\mathbf{r}_i - \mathbf{R}_B) - \sum_{j \neq i} \delta(\mathbf{r}_{ij}) \right]. \quad (2.69)$$

The first part is due to the electric field generated by the nuclei, whereas the second part to the electric field generated by the electrons. Consequently, the Darwin term can be split into a one-electron (D1) and two-electron Darwin (D2).

$$\Delta V_D = \Delta V_{D1} + \Delta V_{D2} \quad (2.70)$$

The D1 contribution is always positive, in contrast with the MV term. Conversely, D2 is always negative. For hydrogenic systems, the D1 energy correction can be calculated [23]:

$$\Delta E_{D1} = \frac{\alpha^2 Z^4}{2n^3} \frac{1}{(2l+1)} \begin{cases} (l+1)^{-1} & j = l + \frac{1}{2}, \\ l^{-1} & j = l - \frac{1}{2}. \end{cases} \quad (2.71)$$

The D2 contribution, although it cannot be evaluated within a hydrogenic approximation, is of the same order of perturbation theory as the D1. However, the two-electron Darwin term is about one order of magnitude smaller than D1 as a consequence of the Pauli principle [43].

- d) The first term in the last square bracket in eq. (2.64) represents the spin-own orbit interaction, which can be also safely disregarded for closed shell molecule [43].
- e) All the remaining two-electron contributions in the last square bracket in eq. (2.64) are derived from the Breit operator in (2.62). The term containing the momenta corresponds to the classical relativistic correction due to the retardation of the electro-magnetic interaction between the electrons. The spin part represents the interaction between the intrinsic magnetic moments of the electrons. It is made up by a Fermi-contact type term, whose contribute is proportional to the D2 (for an anti-symmetric wavefunction, $\langle \sum_{i<j} \delta(\mathbf{r}_{ij}) \mathbf{s}_i \cdot \mathbf{s}_j \rangle = -3/4 \langle \sum_{i<j} \delta(\mathbf{r}_{ij}) \rangle$, [97]), and a dipole-dipole term.

At this point, we can introduce the concepts of *energy corrections* and *spectroscopic corrections*. All mathematical terms presented so far have a clear physical interpretation related to the electronic motion. They all act as corrections ΔE to the electronic energy eigenvalues in eq. (2.5) (in this sense they are energy corrections). The order of magnitude of each can be estimated by simple physical models. However, for a spectroscopic analysis it is only important to consider the dependence of the corrections upon the nuclear geometries, as opposed to their absolute value. It can happen that smaller terms (in terms of “energy corrections”) can have a stronger geometry dependence than bigger terms. If a term is constant with geometry it does not influence at all the nuclear motion, resulting in no contribution whatsoever to the vibrational-rotational levels. Often the geometry dependence is smaller than the absolute value of the term. It is not easy to predict it or to suggest qualitatively models to make *a priori* estimates for these effects. In the literature, the spectroscopic consequences of the relativistic corrections are also given the name of *molecular relativistic effect* (see for example ref. [97]).

Non-Born-Oppenheimer Corrections

3.1 Born-Oppenheimer Diagonal Correction

In a recent publication [85], Zobov and coworkers investigated the importance of adiabatic corrections to vibrational-rotational levels of water. They used Self Consistent Field (SCF) wavefunctions obtained with a basis of (13s8p3d/8s6p3d) on O and (10s3p/6s3p) on each H, and repeated their calculations on a set of 325 geometries. The grid chosen covers OH bond-lengths in the interval $1.45 - 2.80$ a_0 and the bond-angle between 0.71 and 2.95 radians. The results were fitted to a surface:

$$\begin{aligned} \Delta V_{\text{XYO}}^{\text{BODC}} = & \frac{1}{m_{\text{O}}} f_{\text{O}}^S(S_1, S_2, S_3) + \left(\frac{1}{m_{\text{X}}} + \frac{1}{m_{\text{Y}}} \right) f_{\text{H}}^S(S_1, S_2, S_3) + \\ & + \left(\frac{1}{m_{\text{X}}} - \frac{1}{m_{\text{Y}}} \right) f_{\text{H}}^A(S_1, S_2, S_3), \end{aligned} \quad (3.1)$$

where it is allowed for different water isotopomers (X,Y=H,D,T), and consequently different symmetries. The asymmetric part f_{H}^A does not contribute for water (X=Y=H). The functions f are expressed as power series in the symmetrised displacement coordinates:

$$f(S_1, S_2, S_3) = \sum_{ijk} c_{ijk} S_1^i S_2^j S_3^k, \quad (3.2)$$

which are defined as:

$$\begin{aligned} S_1 &= \frac{R_1 + R_2}{2} - R_e, \\ S_2 &= \Theta - \Theta_e, \\ S_3 &= \frac{R_1 - R_2}{2}. \end{aligned} \quad (3.3)$$

In tables 3.4 and 3.5 the effect of the BODC correction is shown for the vibrational band origins up to 25000 cm^{-1} . The magnitude of this correction is less than 4 cm^{-1} , and its sign is predominantly negative. The effect is more pronounced in the bending states than in the stretches, by almost one order of magnitude.

Subsequently, Schwenke [64] analysed the convergence of the results in [85]. He repeated the SCF calculations using a more enlarged basis set (aug-cc-pVTZ) and showed that the results were well converged with respect to basis set size. He also computed the BODC at the Complete Active Space SCF (CASSCF) level using the cc-pVTZ basis set, with six a' and two a'' orbitals and 8 electrons active. He found a “sizable disagreement” with the SCF results, mostly in the stretching overtones, whereas the bending overtones were not significantly influenced by the change in the method. His analysis was limited to the range $0 - 10000 \text{ cm}^{-1}$.

We have unsuccessfully tried to reproduce his results using the fit to his points given in the article [64]. This problem was due to instability of his curve outside the region spanned by his data points (see fig. 3.1). To overcome this problem it was necessary to create a new fit to the CASSCF data, augmented with a few SCF points from the previous calculation of Zobov [85], at energies above 10000 cm^{-1} , weighted appropriately. The functional form used is similar to the one previously employed for the SCF surface, eqs. (3.1)-(3.2):

$$\Delta V^{\text{BODC}}(R_1, R_2, \theta) = \sum_{i,j,k} C_{i,j,k} \left[\frac{1}{2}(R_1 + R_2) - R_e \right]^i [\cos(\Theta) - \cos(\Theta_e)]^j \left[\frac{1}{2}(R_1 - R_2) \right]^k. \quad (3.4)$$

Equilibrium is given by $R_e = 1.80965034 \text{ a}_0$ and $\Theta_e = 1.82404493$ radians. The coefficients of this fit, which reproduces the original data with a standard deviation of 0.01 cm^{-1} , are given in table 3.1. This surface is no longer unstable but its behaviour for large values of the stretching coordinates is not well constrained by the *ab initio* data.

Table 3.1: Coefficients for the H_2O Born-Oppenheimer Diagonal Correction (BODC) surface, see eq. (3.4). The coefficients are in μE_h for bondlengths in a_0 and angles in radians.

i	j	k	C_{ijk}	i	j	k	C_{ijk}
0	0	0	2745.1055606459	3	1	0	-26.4139825271
1	0	0	-59.4634051943	1	3	0	6.0253244059
0	1	0	52.4468059982	2	2	0	96.0354596696
2	0	0	209.0157347415	2	0	2	400.8671847238
0	2	0	-30.9569390720	0	2	2	64.3311129088
0	0	2	222.8220666155	1	1	2	-159.3984157719
1	1	0	-32.0954739957	5	0	0	26.5108357242
3	0	0	-84.5603232875	0	5	0	27.9528744878
0	3	0	28.3636764469	4	1	0	3.3262475087
2	1	0	-82.9317097732	1	4	0	23.3582782463
1	2	0	74.5702444206	1	0	4	-62.8395365075
1	0	2	-301.3739913256	0	1	4	33.1944328259
0	1	2	0.4721526758	3	2	0	31.8104538207
4	0	0	17.0778691448	3	0	2	-11.0876529850
0	4	0	9.6100487312	2	3	0	-151.9675922959
0	0	4	118.9501245531	0	3	2	-33.6314521634

In figure 3.1 the symmetric cut $V(R, R, 100^\circ)$ is shown to illustrate the difference between the various BODC surfaces. The SCF and CASSCF curves show a marked different behaviour,

in line with the significant difference found by Schwenke for the stretching overtones. However, the behaviour of his fit outside the region covered by the data is clearly nonphysical, as the curve diverges rapidly.

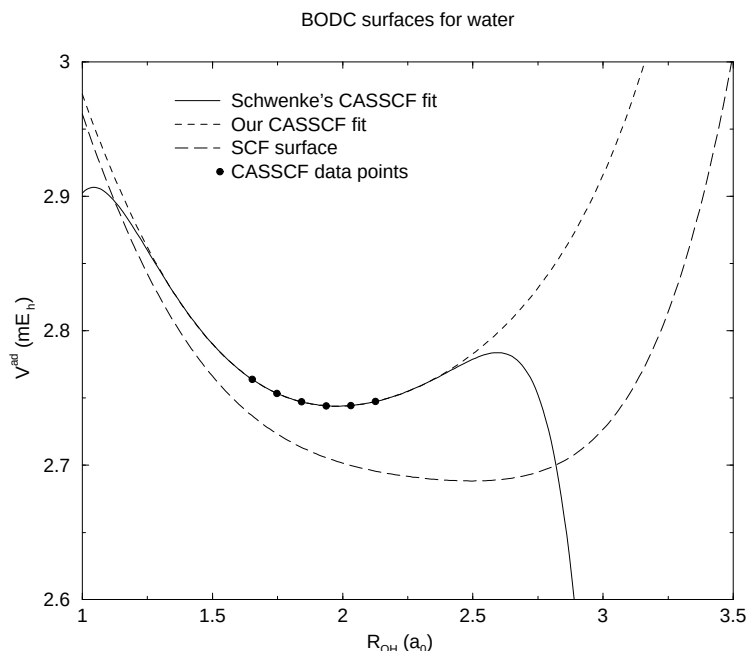


Figure 3.1: BODC surfaces for water. The symmetric cut $V(R, R, 100^\circ)$ is represented for the SCF surface from [85] (long dashed line), the CASSCF surface from [64] (solid line), and our fit of the CASSCF data points from [64] (dashed line), augmented with old SCF points at geometries with energy above 10000 cm^{-1} . Also some CASSCF data points are shown (circle).

Table 3.4 shows the effect of the CASSCF BODC correction on vibrational band origins (VBOs) up to 10000 cm^{-1} . The results presented are obtained with the new fit to the CASSCF data points. Results from [64] are also shown for sake of comparison. There is very good agreement in the bending overtones, whereas our new fit gives slightly different values for the stretching overtones. In table 3.5 the same analysis is extended to the range $10000\text{--}25000 \text{ cm}^{-1}$. Supporting Schwenke's finding, the CASSCF surface influences the stretching levels much more than the SCF surface does. Conversely, the two surfaces yield similar results for the bending overtones. The maximum magnitude of the correction becomes 9 cm^{-1} , and its sign is strictly positive for the stretches, negative for the bendings.

Values of adiabatic corrections for the rotational terms $J=10(000)$ and $J=20(000)$ are reported in tables 3.6 and 3.7, respectively. In table 3.6, the results obtained with our CASSCF surface have been compared to Schwenke's, and we found again a good agreement between the two. The choice of the surface (SCF or CASSCF) does not influence qualitatively the final result, although the CASSCF shifts are bigger for high K_a . For both rotational terms the magnitude of the corrections increases with K_a , being negative for low K_a , and changing sign for $K_a \approx J/2$.

3.2 Non-adiabatic corrections

It is well known that the inclusion of non-adiabatic effects in vibrational-rotational calculations is hard, for it involves a knowledge of all the electronic states, both in the bound and continuum part of the spectrum. Computationally, it necessitates the implementation of complicated differential operators, containing sums over all the electronic wavefunctions and eigenvalues.

A benchmark paper on the subject was written by Bunker and Moss [57]. They derived an effective Hamiltonian allowing for non-adiabatic corrections for the simple case of a homonuclear diatomic in a $^1\Sigma$ electronic state. Their most remarkable result was that non-adiabatic effects can be regarded as corrections to the inertia of the nuclei, and that they affect differently the rotational and vibrational part of the nuclear motion. In their effective vibrational-rotational Hamiltonian the vibrational reduced mass and the moment of inertia of the atom pair are, respectively:

$$\begin{aligned}\mu_{eff} &= \mu + 2 \sum_{n \neq 0} \frac{|\langle \psi_0 | -i \frac{\partial}{\partial R} | \psi_n \rangle|^2}{E_n(R) - E_0(R)}, \\ I_{eff} &= I + 2 \sum_{n \neq 0} \frac{|\langle \psi_0 | \hat{L}_R | \psi_n \rangle|^2}{E_n(R) - E_0(R)}.\end{aligned}\quad (3.5)$$

where both μ and I ($I = \mu R^2$) are calculated using the nuclear masses. R is the atom-atom distance, and $\hat{L}_R$ is the component of the electronic total angular momentum $\hat{L}$ along the molecular axis ($\hat{L} = \sum_i \hat{l}_i$). Bunker and co-workers applied the effective vibrational-rotation Hamiltonian derived in [57] to the study of H_2 and D_2 [58]. Instead of using directly eq. (3.5), they ignored the R -dependence in μ_{eff} and I_{eff} . They then manipulated the two vibrational and rotational effective masses (μ_v and μ_r) in order to fit at best the experimental data. The optimum choice for μ_r was very close to the nuclear mass, whereas the optimisation of vibrations led to a value for μ_v close to the atomic mass. Physically, since the electrons partially follow the nuclei in their movements, it is reasonable to expect that the vibrational effective mass would be close to the atomic value. For H_2 , they found:

$$\mu_v = 0.503892 \text{ a.m.u.}, \quad (3.6)$$

where the values for the atomic and nuclear masses are:

$$\begin{aligned}\mu_{nuc} &= 0.5036382 \text{ a.m.u.}, \\ \mu_{at} &= 0.5039125 \text{ a.m.u.}\end{aligned}\quad (3.7)$$

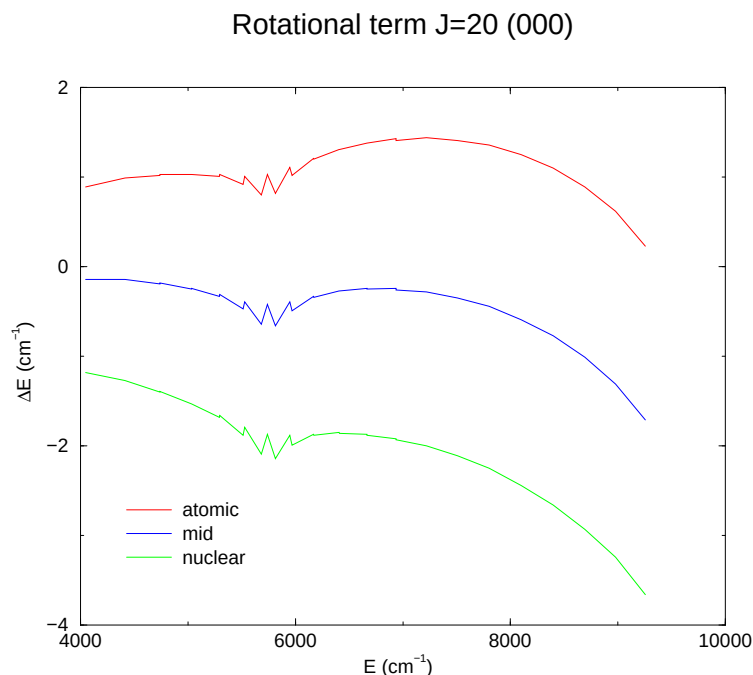
Bunker and Moss extended their method to the study of triatomics [98]. Although their physical conclusions are the same as for the diatomic case, the mathematics involved becomes more complex, and it is impossible to write down simple equations corresponding to (3.5). Very recently, Schwenke has utilised for the first time the rotation-vibration-electronic Hamiltonian from ref. [98]. His results will be discussed later, in Subsection 3.2.4.

3.2.1 Mass manipulation

The simplest way of accounting for non-adiabatic effects is to replace the nuclear reduced masses in the definition of the Kinetic Energy Operator (KEO, see eqs. (2.16),(2.17)) with an

effective mass. Zobov *et al.* [85] investigated the importance that mass-manipulation could have in predictions of vibrational-rotational levels in water. Although the reduced mass (eq. (2.23)) is a function of both the oxygen and hydrogen masses, they noted that their calculations are not particularly sensitive to the oxygen mass employed. This is because of the little weight that M_O holds in eq. (2.23). They finally found that the best results occurred with a value for M_H mid-way between its atomic ($M_H^{at} = 1.007825$ a.m.u.) and nuclear values ($M_H^{nuc} = 1.007276$ a.m.u.), i.e., $M_H^{mid} = 1.007551$ a.m.u.¹ Moreover, the rotational terms were strongly affected, so much that the prediction for the $J=20$ vibrational ground state term values improved by an order of magnitude. In figure 3.2 the effect of mass manipulation for the rotational term is shown. Three different values for the hydrogen mass are used, nuclear, atomic, and the middle mass. With the nuclear mass the levels are overestimated (obs-calc < 0), whereas with atomic they are underestimated (obs-calc > 0). From the picture, one could be tempted to conclude that the optimal choice for hydrogen mass is slightly above its middle value. However, relativistic effects are also important, as it will be shown in the next chapter, and the net effect of mass-manipulation could be estimated only after having included all such effects. Still, it is possible to envisage that mass-manipulation can be useful to model non-adiabatic effects.

Figure 3.2: Effect of mass manipulation on predictions for the rotational term $J=20$ (000). Three different values for the hydrogen mass have been used: nuclear, atomic, and middle mass. The data are plotted as obs.-calc. for 41 terms.



Following the work in [58], a slightly more complex model would allow for separate manipulation of the vibrational and rotational masses. However, if the two masses differ, the derivation of the KEO given in [48] and represented in Section 2.2 needs to be revised. In

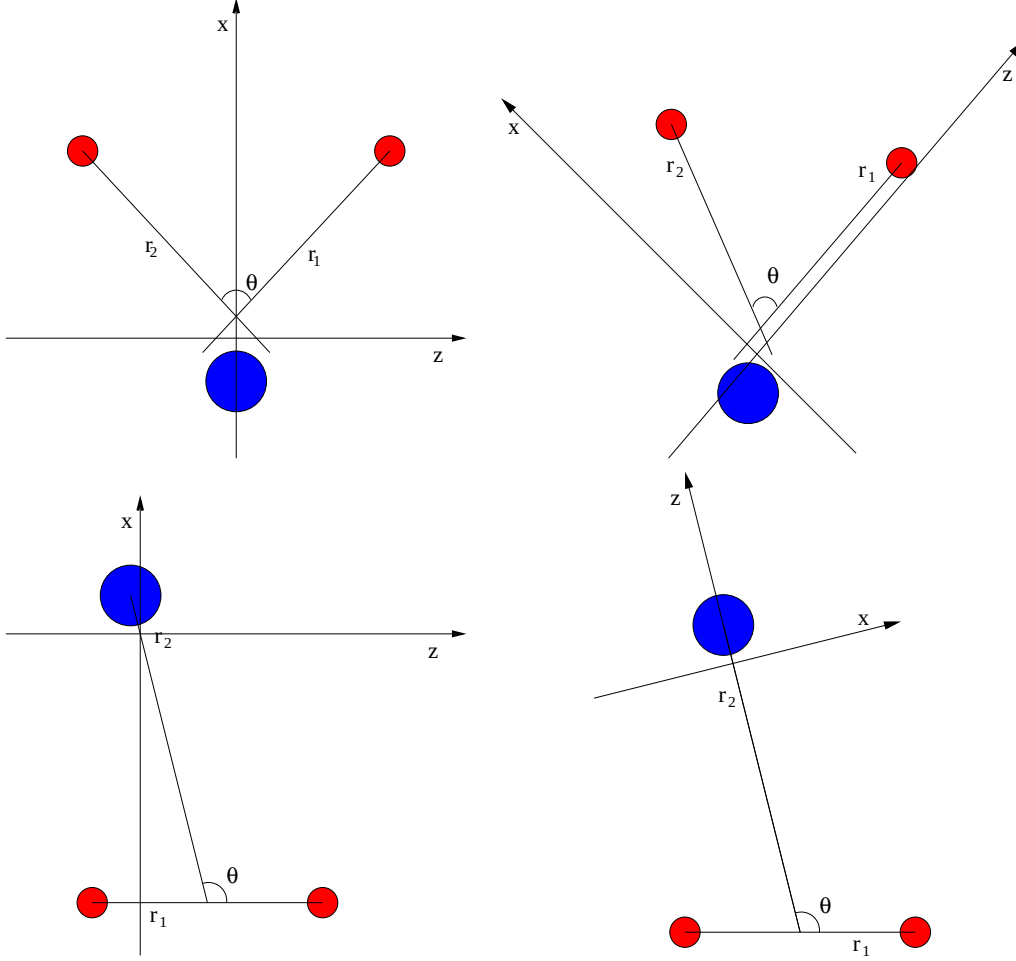
¹Consequently, we will adopt the notation μ_{at} , μ_{mid} and μ_{nuc} to indicate the nuclear reduced mass (eq. (2.23)) associated with M_H^{at} , M_H^{mid} and M_H^{nuc} , respectively.

particular, if the vibrational and rotational masses are set equal, the term $\hat{K}_V^{(b)}$ cancels out with the second term of $\hat{K}_{VR}^{(1)}$. On the other hand, if they differ, the cancellation is incomplete. Consequently an extra term must be considered in the KEO [84], which will be proportional to the difference between the vibrational and rotational reduced masses:

$$\hat{K}_{xt} = \delta_{k,k'} \frac{k^2}{2} (r_1^{-2} + r_2^{-2}) \left(\frac{1}{\mu_R} - \frac{1}{\mu_V} \right) \langle j', k' | \sin^{-2} \theta | j, k \rangle. \quad (3.8)$$

The extra term depends quadratically on k , and is also diagonal in k . As its origin is vibrational, its form is invariant under rotation of the molecular axes. Furthermore, because the purely vibrational part of the kinetic energy operator has the same expression in Jacobi and Radau coordinates, the form of $\hat{K}_{xt}$ must be identical in these coordinates. The angular integral over $\sin^{-2} \theta$ is divergent for $k = k' = 0$. However, the factor k^2 helps to avoid this problem.

Figure 3.3: Different possible embeddings and coordinate systems for water. The y -axis is out of plane, and it is always set to form a right-handed Cartesian frame. The origin of the molecule embedded frame is located at the nuclear CM. From top left to right, Radau bisector embedding (RB), Radau aligned embedding (RA), Jacobi r_1 -aligned embedding (J1), and Jacobi r_2 -aligned embedding (J2).



The effect of including $\hat{K}_{xt}$ in the Hamiltonian has been investigated by Polyansky and

Tennyson [84] for H_3^+ , where they used Jacobi coordinates as internal coordinates. They found the contribution of $\hat{K}_{xt}$ to vibrational-rotational energy levels to be of the order of 0.1 cm^{-1} or less for H_3^+ .

We have investigated the effect of including the term $\hat{K}_{xt}$ in the KEO for different choices of embeddings and coordinate systems for water. In particular, we have employed Radau coordinates with bisector and aligned embeddings, and Jacobi coordinates with the z -axis chosen parallel either to the r_1 vector or to the r_2 . These embeddings are illustrated in figure 3.3.

As a first step, we studied carefully the pattern of convergence of the vibrational band origins. The final values used for the basis sets and the variational parameters are reported in table 3.2. We found that calculations using the RA embedding, or Jacobi coordinates, are computationally much more expensive than the standard RB. Besides, we have experienced major problems for the convergence of some vibrational band in Jacobi coordinates. In fact, for those levels near or above the barrier to linearity the nuclei's wavefunction has a significant non-zero amplitude for $r_2 = 0$. Consequently, the choice of Morse-like oscillators (eq. (2.34)) is not appropriate anymore, and better radial basis functions are represented by the spherical oscillators [99]:

$$|t\rangle = H_t(r) = 2^{1/2} \beta^{1/4} N_{t\alpha+1/2} \exp\left(-\frac{y}{2}\right) y^{(\alpha+1)/2} L_t^{\alpha+1/2}(y), \quad (t = 0, \dots, \infty), \quad (3.9)$$

where

$$y = \beta r^2, \quad \beta = \sqrt{\mu \omega_e}, \quad (3.10)$$

and ω_e, α are treated as variational parameters and optimised accordingly. The spherical oscillator functions constitute a more appropriate basis for the problem associated with the boundary conditions given by the Jacobi r_2 coordinate [100]. The parameters used as input for the DVR3D program suite are presented in table 3.2. Our study of convergence is restricted only to vibrational band origins below $11,000 \text{ cm}^{-1}$. For the RB embedding a more detailed analysis of patterns of convergence and the variational parameters can be found in [55, 86]

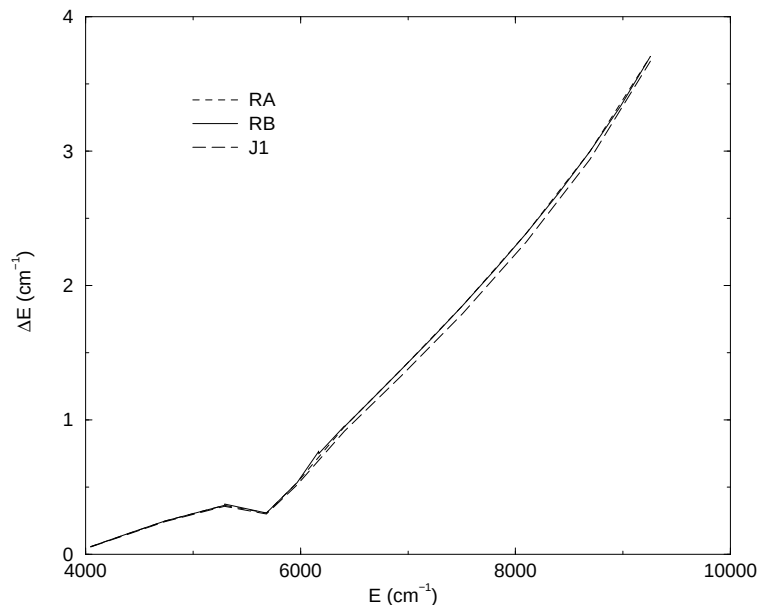
We have calculated the importance of the $\hat{K}_{xt}$ term using three (RA, RB and J2) of the four embeddings suggested in fig. 3.3. We have not been able to achieve full convergence for the fourth (J1): for this particular embedding, using the input described in table 3.2 for J2, we could only get convergence for the high K_a rotational levels. Several attempts to extend the convergence to the low K_a levels by modifying the variational parameters have not succeeded. For the three embeddings J2, RA and RB, the calculated values for the rotational terms are very close of each other (within fractions of wavenumber, the remaining difference can be attributed to the not fully achieved numerical convergence).

The effect of introducing the extra term (3.8) in the calculation of rotational states is shown in fig. 3.4. Following our choice of vibrational and rotational masses (μ_{at} for the former and μ_{mid} for the latter), the term is positive, and it monotonically increases in value due to the k^2 dependence. Furthermore, the effect of the extra-term is not influenced by the particular choice of coordinate system or embedding used.

Table 3.2: Values used as inputs for the DVR3D program suite. The square bracket indicates the default value of the variable. The code ROTLEV3 is used for the J1, J2 and RA embeddings, whereas ROTLEV3B for RB. The input for ROTLEV3 and ROTLEV3B are specific to the case $J = 20$ for water, and $J = 17$ for hydrogen sulphide.

DVR3D				
	H ₂ O			H ₂ S
Parameters	RB	RA	J2	RB
zmors1	[true]	[true]	false	[true]
zmors2	[true]	[true]	false	[true]
zquad2	[true]	[true]	false	[true]
zr2r1	[true]	[true]	false	[true]
NEVAL	200	200	200	250
NPNT1	-	24	40	-
NPNT2	21-28	24	40	28
NALF	40-48	48	50	49
MAX3D	1000-1500	1500	1500	2000
RE1,RE2 (r_e)	2.55	2.00	-	1.89
DISS1,DISS2 (D_e/α)	0.25	0.25	1.00,0.01	0.25
WE1,WE2 (ω_e)	0.007	0.007	0.008	0.007
EMAX1	-	100,000	85,000	-
M _H (a.m.u.)	1.007276-1.007851			
M _O (a.m.u.)	15.990726			
M _S (a.m.u.)	31.972071			
ROTELV3 or ROTLEV3B				
NVIB	130	200	200	250
NEVAL	200	200	200	200
IBASS	1000	4200	5000	1000

Figure 3.4: Corrections to the rotational term $J=20$ (000) when the extra term (3.8) is added to the KEO, for different choices of the molecular embeddings (see fig. 3.3). Atomic mass has been used for the vibrational reduced mass, and mid-mass for the rotational. The data are shown as with-without.



3.2.2 Eckart KEO in Radau coordinates

The distinction between rotational and vibrational motions in a molecule is not defined precisely. In particular, the so-called Coriolis term (2.18) in the KEO couples the two motions. Physical intuition suggests that a rotating non-rigid system stretches its bonds as a consequence of the centripetal force.

The importance of the Coriolis term within the KEO can be minimised by means of a suitable choice of the molecular embedded frame of reference. This problem was firstly solved by Carl Eckart [101], and the molecular embedded frame that minimises the Coriolis term is known as the Eckart frame. The Eckart conditions can be formulated as follows:

$$\sum_A M_A \mathbf{x}_{Ae} \times \mathbf{x}_A = 0, \quad (3.11)$$

where $\{\mathbf{x}_A\}$ are the nuclei's Cartesian coordinates, and $\{\mathbf{x}_{Ae}\}$ their equilibrium value. Notice that the Eckart embedding is undefined at equilibrium, as the conditions (3.11) vanish trivially for $\{\mathbf{x}_A\} = \{\mathbf{x}_{Ae}\}$: there are thus infinite ways to attach the Eckart frame to the molecule at equilibrium.

The major importance of the Eckart embedding is that it allows one to use normal coordinates, which have constituted the foundations of theoretical spectroscopy for decades [46]. In particular, the Eckart KEO presented by Watson has been widely employed for its simple form [102]. With the introduction of exact kinetic energy operator approaches, normal coordinates

have been abandoned in favour of other coordinates, such as Jacobi, Radau, hyperspherical, or bond-length bond-angle. At the same time, non-Eckart embeddings have been employed as they simplify the mathematical expression for the KEO. There are however two advantages that could possibly derive from the use of an Eckart embedded frame. Firstly, the minimisation of the Coriolis term could speed the convergence of the calculation, and secondly it could optimise the implementation of separate non-adiabatic corrections for vibrations and rotations by reducing the coupling among the different terms of the hamiltonian. The final goal is to improve the overall accuracy of the calculation.

Wei and Carrington [103] derived a procedure to obtain an Eckart KEO for several choices of internal coordinates. They also presented the explicit expression of the Eckart KEO in Radau coordinates [104]. They used the method of Handy [105], and their derivation was done by hand, and then checked with an algebraic manipulation program. Unfortunately, their definition of Radau coordinates differs from that of Tennyson and Sutcliffe [48].

We have repeated the derivation of the Eckart KEO in Radau coordinates following a different approach suggested by Lukka [106]. Details of the method used are reported in appendix A. The purposes of this work are two-fold. Firstly, to reproduce Carrington's results with a different approach allows to check the correctness of his procedure. Secondly, the difference in the definition of Radau coordinates needs to be accounted for if the Eckart Radau KEO has to be implemented computationally.

The Radau vectors, defined in fig. 2.13, can be expressed in terms of the Cartesian vectors of the three nuclei (compare the following equations to eqs. (28)-(29) in [103]):

$$\mathbf{r}_1 = \mathbf{x}_1 - \gamma \mathbf{x}_2 + (\gamma - 1) \mathbf{x}_3, \quad (3.12)$$

$$\mathbf{r}_2 = \mathbf{x}_2 - \gamma \mathbf{x}_1 + (\gamma - 1) \mathbf{x}_3, \quad (3.13)$$

where γ is defined in eq. (2.14), and $\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3$ indicate the Cartesian coordinates of the two hydrogen nuclei, and of the oxygen nucleus, respectively.

Combining eqs. (3.12)-(3.13) and (3.11), the Eckart conditions can be expressed in terms of the Radau vectors:

$$\mu_1 \mathbf{r}_{1e} \times \mathbf{r}_1 + \mu_2 \mathbf{r}_{2e} \times \mathbf{r}_2 = 0, \quad (3.14)$$

where μ_1 and μ_2 are the reduced masses associated with each Radau coordinate.

Finally, the Eckart embedding can be expressed by means of the angle η between one of the Cartesian axes and one of the Radau vectors:

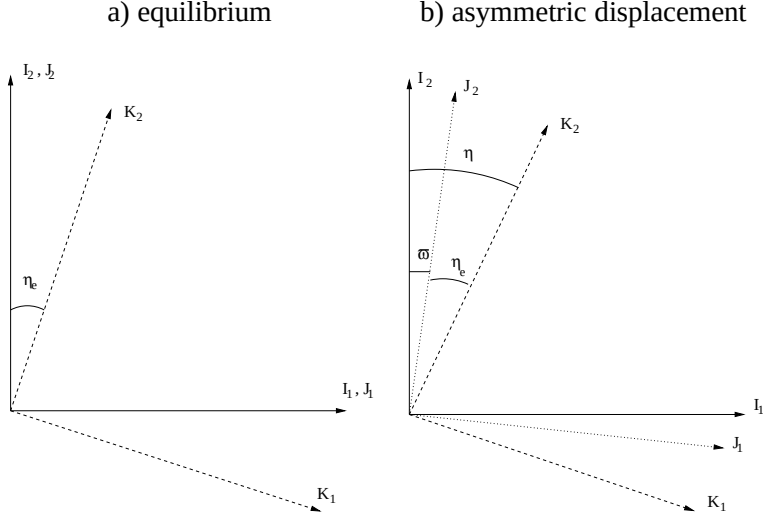
$$\tan \eta = \frac{r_2 \sin(\theta - \theta_e + \eta_e) + r_1 \sin \eta_e}{r_2 \cos(\theta - \theta_e + \eta_e) + r_1 \cos \eta_e}. \quad (3.15)$$

We have assumed that two of the three axes defining the molecular frame lie on the molecular plane, and which we will refer to as $\mathbf{K}_1$ and $\mathbf{K}_2$, whereas the third ($\mathbf{K}_3$) lies perpendicular to the molecular plane. $\mathbf{K}_1, \mathbf{K}_2$ and $\mathbf{K}_3$ form a right-handed Cartesian frame. The angle η_e defines the orientation of the Eckart frame at equilibrium (see fig. 3.5).

Carrington and Wei [103] found very interestingly that the Radau bisector frame and the Eckart Radau bisector (ie, with $\eta_e = \theta_e/2$) look very similar. If $\eta_e = \theta_e/2$, eq. (3.15) reduces to:

$$\eta = \frac{\theta}{2} + \tan^{-1} \left(\frac{r_2 - r_1}{r_1 + r_2} \tan \frac{\theta - \theta_e}{2} \right). \quad (3.16)$$

Figure 3.5: Eckart embeddings for water, at a) equilibrium, and b) nuclear asymmetric displacement. For clarity, the nuclei's positions and the Radau system of coordinates are not shown. Three different molecular embedded frames are presented: Radau aligned ($\mathbf{I}_1, \mathbf{I}_2$, solid line), corresponding to fig. 3.3-b, Eckart-Radau aligned ($\mathbf{J}_1, \mathbf{J}_2$, dotted line), and a generic Eckart-Radau parametrised by means of an angle η_e ($\mathbf{K}_1, \mathbf{K}_2$, dashed line). For each frame, the third axis is out of the molecular plane, and it is chosen to form a right handed frame. The axes origin is located at the nuclei's centre of mass. The angle ω between $\mathbf{I}_2$ and $\mathbf{J}_2$ can be expressed as $\eta - \eta_e$.



For pure bending ($r_1 = r_2 = r_e$) or pure stretching ($\theta = \theta_e$) motions the two embeddings are identical ($\eta = \theta/2$). They differ for simultaneous excitations of the bend and stretching coordinates.

The derivation of the Eckart KEO in Radau coordinates has been given in great detail in [104], where it is presented for a rather general choice of Radau coordinates, and a general choice of the parameter η_e . We report the main results from [104] trying to use the same notation where possible. We restrict ourselves to the homonuclear diatomic case ABA, and to $\eta_e = \theta_e/2$. Moreover, our embedded molecular frame (see fig. 2.2) is rotated compared to Wei and Carrington's, as the y -axis is chosen perpendicular to the molecular plane instead of the z -axis. Our derivation of the Eckart KEO using Lukka's method leads to exactly the same results as in [104].

The KEO can be generally expressed as:

$$\hat{K} = \hat{K}_V + \hat{K}_R + \hat{K}_{cor}, \quad (3.17)$$

where

$$\hat{K}_R = \frac{1}{2} \left[G_{xx} \hat{J}_x^2 + G_{yy} \hat{J}_y^2 + G_{zz} \hat{J}_z^2 + G_{xz} (\hat{J}_x \hat{J}_z + \hat{J}_z \hat{J}_x) \right], \quad (3.18)$$

$$\hat{K}_{cor} = -\frac{i}{2} \sum_{v=r_1, r_2, c} \left[G_{vy} \frac{\partial}{\partial v} + \frac{\partial}{\partial v} G_{vy} \right] \hat{J}_y, \quad (3.19)$$

where $c = \cos \theta$, and $\hat{K}_V$ is exactly the same as given in eq. (2.16).

The coefficients in eqs. (3.18)-(3.19) are:

$$G_{r_1 y} = -\Lambda r_2 \sin(\theta - \theta_e), \quad (3.20)$$

$$G_{r_2 y} = -\Lambda r_1 \sin(\theta - \theta_e), \quad (3.21)$$

$$G_{cx} = \Lambda \sin \theta [(r_1/r_2 - r_2/r_1) \cos(\theta - \theta_e)], \quad (3.22)$$

$$G_{xx} = \Lambda(1 - c^2)^{-1} [C_1^2 + C_2^2], \quad (3.23)$$

$$G_{yy} = 2\Lambda, \quad (3.24)$$

$$G_{zz} = \Lambda(1 - c^2)^{-1} [S_1^2 + S_2^2], \quad (3.25)$$

$$G_{xz} = \Lambda(1 - c^2)^{-1} [-C_1 S_1 + S_2 C_2], \quad (3.26)$$

where

$$\Lambda^{-1} = \mu [r_1^2 + r_2^2 + 2r_1 r_2 \cos(\theta - \theta_e)], \quad (3.27)$$

$$S_1 = \sin(\theta - \theta_e/2) + r_2/r_1 \sin(\theta_e/2), \quad (3.28)$$

$$C_1 = \cos(\theta - \theta_e/2) + r_2/r_1 \cos(\theta_e/2), \quad (3.29)$$

$$S_2 = \sin(\theta - \theta_e/2) + r_1/r_2 \sin(\theta_e/2), \quad (3.30)$$

$$C_2 = \cos(\theta - \theta_e/2) + r_1/r_2 \cos(\theta_e/2). \quad (3.31)$$

Following the same procedure outlined in [48], an effective radial operator can be derived for the Eckart KEO. The final expression is discussed in [104].

Finally, a few remarks on the advantages and disadvantages of using the Eckart-Radau KEO. One of the problems which affects most calculations with curvilinear KEO is the presence of singularities. In order to deal with this problem an appropriate choice of both internal coordinates and basis functions is needed. Sometimes the singularities happen to lie outside the molecular phase-space and can therefore be safely ignored. This is the case, for instance, of the singularity at $\theta = 0$ present in the Radau bisector KEO [69]. The Eckart-Radau bisector KEO present a singularity of the second order for $\theta = \pi$, ie, for linear configuration of the molecule. This is a major problem for studying a molecule such as water which becomes linear at relatively low energies. The problem can be partly avoided if the z -axis is chosen perpendicular to the plane. However, this choice is not the most appropriate for water [107]. Wei and Carrington discussed several basis functions that allow one to deal with the singularity at $\theta = \pi$. They recommend the use of Jacobi polynomials $P^{(a,b)}$ [76], where a and b will depend on both J and k . Those polynomials vanish for linear configurations fast enough to maintain finite matrix elements. However, this choice of functions slows down the convergence of the calculation.

3.2.3 The g -factor

The Zeeman effect is the shift in the vibrational-rotational energy levels caused by an applied external magnetic field H . Most stable molecules (and water among them) have A_1 singlet ground electronic state, hence the only permanent magnetic dipole moment is given by the

nuclear moments. However, additional magnetic moments are generated by the molecular rotations, or induced by external fields. The induced moment is normally much smaller than the one originating by the rotation. Neglecting the nuclear and the induced moments, the splitting in energy levels caused by the external field can be written as [108]:

$$E_H(J, \tau) = -\frac{\mu_N H \tau}{J(J+1)}(g_{xx}\langle J_x^2 \rangle + g_{yy}\langle J_y^2 \rangle + g_{zz}\langle J_z^2 \rangle), \quad (3.32)$$

where H is the magnitude of the applied field, μ_N is the nuclear magneton ($\mu_N = e\hbar/2M_p c \approx 3.15 \cdot 10^{-8} \text{ eV T}^{-1}$), J, τ are the rotational quantum numbers introduced in the previous Chapter, M_p is the proton mass ($M_p = M_H^{nuc}$). The quantities g_{xx} , g_{yy} and g_{zz} are the diagonal components of the rotational g -factor, and are defined as follows [108]:

$$\begin{aligned} g_{xx} &= \frac{M_p}{I_{xx}} \sum_{A=1}^L Z_A (y_A^2 + z_A^2) - \frac{2M_p}{mI_{xx}} \sum_{n>0} \frac{|\langle \psi_n | \hat{L}_x | \psi_0 \rangle|^2}{E_n - E_0}, \\ g_{yy} &= \frac{M_p}{I_{yy}} \sum_{A=1}^L Z_A (x_A^2 + z_A^2) - \frac{2M_p}{mI_{yy}} \sum_{n>0} \frac{|\langle \psi_n | \hat{L}_y | \psi_0 \rangle|^2}{E_n - E_0}, \\ g_{zz} &= \frac{M_p}{I_{zz}} \sum_{A=1}^L Z_A (y_A^2 + x_A^2) - \frac{2M_p}{mI_{zz}} \sum_{n>0} \frac{|\langle \psi_n | \hat{L}_z | \psi_0 \rangle|^2}{E_n - E_0}, \end{aligned} \quad (3.33)$$

where I_{xx} , I_{yy} and I_{zz} are the components of the moment of inertia tensor, (x_A, y_A, z_A) are the Cartesian coordinates for the nucleus A, $\hat{L}$ is the total electronic angular momentum. As a consequence of its definition, the g -factor is a dimensionless quantity. From the definition of the g -factor two different contributions can be identified: the first term in eq. (3.33) is given by the rotating nuclei, and is always positive, whereas the second represents the distortion of the ground electronic state due to the rotation. This term is always negative. By measuring the g -factor experimentally it is possible to obtain straightforward information on the rotational non-adiabaticity in a molecule. Flygare and Benson [59] provide a useful compilation of experimentally determined g -factors for several molecules, including water and H_2S .

On the other hand, the rotational g -factor is directly connected with the effective Hamiltonian derived by Bunker and Moss [57]. For a diatomic molecule lying along the z -axis, $g_{xx} = g_{yy} = g$:

$$g(R) = \frac{M_p}{\mu R^2} \sum_A Z_A z_A^2 - \frac{2M_p}{mI} \sum_{n>0} \frac{|\langle \psi_n | L_z | \psi_0 \rangle|^2}{E_n - E_0} = g^{nuc} + g^{elec}. \quad (3.34)$$

By substituting eq. (3.34) in eq. (3.5), we obtain:

$$I_{eff} = I - \frac{mI}{M_p} g(R) + \frac{Im}{M_p} g^{nuc}(R). \quad (3.35)$$

It can be shown [109] that the effect of g^{nuc} in eq. (3.35) is to shift the value of the moment of inertia I_{eff} toward an atomic value, whereas g has the opposite effect. For instance in H_2 [58], $g = 0.88291 \pm 0.00007$, whereas $g^{nuc} \approx 1$, as a result $I_{eff} \approx I$ ($I = \mu R^2$).

The values of $g_{\lambda\lambda}^{nuc}$ ($\lambda = xyz$) can be readily evaluated for water at equilibrium geometry: $g_{xx}^{nuc} \approx 0.986$, $g_{yy}^{nuc} \approx 0.643$ and $g_{zz}^{nuc} \approx 0.931$.

In order to derive a simple model of including rotational non-adiabaticity in a non-linear triatomic, one could try to generalise the expression for I_{eff} for a triatomic in which the moment of inertia is a tensor:

$$I_{eff,\lambda\lambda} \approx I_{\lambda\lambda} \left(1 - \frac{m}{M_p} g_{\lambda\lambda} + \frac{m}{M_p} g_{\lambda\lambda}^{nuc} \right) \quad (\lambda = x, y, z). \quad (3.36)$$

Despite its apparent simplicity, the g -factor is a complicated function of the nuclear coordinates: in fact, both the electronic wavefunctions and energies depend parametrically upon the nuclear coordinates R_A . As a first approximation this dependence can be neglected, and an effective value can be used for the functions $g_{\lambda\lambda}(R_A)$:

$$g_{\lambda\lambda}(R_A) \approx g_{\lambda\lambda}^{eff} \quad (\lambda = xyz). \quad (3.37)$$

This approximation is consistent with the results of Schwenke [64], which will be discussed in the next Subsection. In [64] Schwenke calculated purely *ab initio* the diagonal components of the g -factor, and at vibrationally averaged geometries, obtained the values 0.721, 0.683 and 0.658 for the xx , zz and yy components, respectively. These can be compared with the experimental values 0.718 ± 0.007 , 0.657 ± 0.001 and 0.645 ± 0.006 [59].

The presence of the g -factor in eq. (3.36) can be viewed as an effective rotational mass. If we treat the rotational non-adiabaticity as a small perturbation of the generalised inertia tensor $M_{\alpha\beta}$ (eqs. (2.19)-(2.22)), we can write:

$$M_{\lambda\lambda} \rightarrow M_{\lambda\lambda} \left(1 + \frac{m}{M_p} g_{\lambda\lambda} - \frac{m}{M_p} g_{\lambda\lambda}^{nuc} \right). \quad (3.38)$$

Since $M_{\lambda\lambda} \propto \mu^{-1}$, this is equivalent to setting

$$\mu_{R,\lambda\lambda}^{-1} = \mu^{-1} \left(1 + \frac{m}{M_p} g_{\lambda\lambda} - \frac{m}{M_p} g_{\lambda\lambda}^{nuc} \right), \quad (3.39)$$

i.e.

$$\mu_{R,\lambda\lambda} = \mu \left(1 - \frac{m}{M_p} g_{\lambda\lambda} + \frac{m}{M_p} g_{\lambda\lambda}^{nuc} \right). \quad (3.40)$$

As $\mu \approx M_p + o(M_p/M_O)$,

$$\mu_{R,\lambda\lambda} = M_p - m g_{\lambda\lambda} + m g_{\lambda\lambda}^{nuc}. \quad (3.41)$$

If one recalls the experimental values for the g -factor in water, together with the values for g^{nuc} calculated at the nuclear equilibrium position, one obtains the values $\mu_{R,xx} \approx M_p + 0.27m$, $\mu_{R,yy} \approx M_p$ and $\mu_{R,zz} \approx M_p + 0.29m$. The rotation with respect to the y -axis, which is out of plane, does not influence the rotational non-adiabaticity, as the two terms g and g^{nuc} cancel out almost completely.

Finally, we can write the contribution to the vibrational-rotational kinetic energy operator $\hat{K}_{VR}$ (eq. (2.25)). For simplicity, let us first rewrite eq. (3.38) as follows:

$$M_{\lambda\lambda} \left(1 + \frac{m}{M_p} g_{\lambda\lambda} - \frac{m}{M_p} g_{\lambda\lambda}^{nuc} \right) = M_{\lambda\lambda} + \epsilon_{\lambda\lambda}. \quad (3.42)$$

Inserting eq. (3.42) in eq. (2.17) introduces in the water Hamiltonian the term

$$\frac{1}{2}(\epsilon_{xx}\hat{J}_x^2 + \epsilon_{yy}\hat{J}_y^2 + \epsilon_{zz}\hat{J}_z^2). \quad (3.43)$$

The components of the tensor ϵ can have a very complicated dependence on the nuclear coordinates. If the terms in eq. (3.43) are then transformed to an effective KEO following the procedure outlined in subsection 2.2, the total contribution of the g -factor to the effective radial KEO (2.25) will be of the following form:

$$\begin{aligned} \hat{K}_{VR}^g = & \delta_{k',k} \left[J(J+1) \langle j', k' | \frac{\epsilon_{xx} + \epsilon_{yy}}{2} | j, k \rangle + k^2 \langle j', k' | \epsilon_{zz} - \frac{\epsilon_{xx} + \epsilon_{yy}}{2} | j, k \rangle \right] \\ & + \delta_{k',k\pm 2} C_{J,k\pm 1}^{\pm} C_{J,k}^{\pm} \langle j', k' | \frac{\epsilon_{xx} - \epsilon_{yy}}{4} | j, k \rangle. \end{aligned} \quad (3.44)$$

As already mentioned, it is a good approximation to neglect the dependence on the nuclear coordinates in the definition of the g -factor. If this choice is adopted, the components of the tensor ϵ become simple numbers, and the integrals in eq. (3.44) reduce to ordinary overlaps between Legendre polynomials, and can be calculated straightforwardly. We have implemented the rotational non-adiabatic corrections in our code DVR3D, using for the g -factor the experimental values from ref. [59]. Values for the J=20 (000) rotational term are reported in table 3.7. The shift to the levels caused by the term (3.44) is strictly negative, and its magnitude increase with K_a , up to a maximum of 3.46 cm^{-1} for the $20_{20,0}$ level. In order to compare the g -factor results with the more sophisticated model of Schwenke (see next Subsection), we have calculated also the corrections to the J=10 (000) rotational term. The results are shown in table 3.6. From both tables 3.6 and 3.7 one can see that the rotational non-adiabaticity calculated using expression (3.43) with the values for the g -matrix derived from the experiment is far from being accurate. The main reason for the disagreement between this model and the “exact” calculation of Schwenke is due to the erroneous assumption in eq. (3.36). In reality, the connection between rotational non-adiabaticity and the g -factor in a non-linear molecule is much more complex than in the linear case.

3.2.4 More sophisticated models

The models analysed so far try to allow for non-adiabaticity by empirically tuning some defined parameters in the *ab initio* nuclear Hamiltonian. In particular the value of the nuclear reduced masses can be adjusted. This is justified by a simple but realistic physical model.

A more accurate and detailed model needs to deal with complicated electronic structure calculations. The difficulties encountered in pursuing a fully *ab initio* approach to non-adiabaticity are two-fold. First, not only the ground state but also electronic excited states must be obtained to a reasonable level of accuracy, together with their respective wavefunctions, while the basis sets available in literature are normally optimised for the ground state only. Second, an infinite number of excited states must in principle be included in the calculation, comprising levels of very different nature, as the sum goes into the continuum.

About twenty years after the breakthrough paper of Bunker and Moss [98] in which they derived analytical expressions for the inclusion of non-adiabatic effects in the triatomic KEO,

Table 3.3: Values of non-adiabatic corrective terms at vibrationally averaged geometries, extracted from ref [64]. Difference in the definition of Radau coordinates and form of the Hamiltonian have been accounted for. Units are consistent with bondlength in a_0 , and energy in E_h .

$2.1787357 \times 10^{-7} \partial^2 / \partial r_1^2$
$1.4062589 \times 10^{-8} \partial^2 / \partial \theta^2$
$9.8205515 \times 10^{-9} \hat{J}_x^2$
$7.3757478 \times 10^{-9} \hat{J}_y^2$
$1.7082113 \times 10^{-8} \hat{J}_z^2$

Schwenke [64] carried out the first calculations of non-adiabatic effects in triatomics by evaluating fully *ab initio* the terms in [98]. He restricted his analysis to the molecules H_2 and H_2O . He checked the convergence of his calculations by comparing experimentally determined values for the g -factor with his own results. He concluded that he was able to recover 80 % of rotational non-adiabaticity in H_2 , and up to 90 % in water.

Schwenke also computed the corrections to vibrational-rotational energy levels given by non-adiabatic effects. For water he considered VBOs up to 10000 cm^{-1} , and the $J=10$ (000) rotational term. For the former he investigated three different ways of including vibrational non-adiabaticity. He considered full three-dimensional coupling surfaces, their vibrationally averaged values, and the diagonal components of the latter. A very interesting conclusion of his work was to notice that the simpler model gives similar results to the full calculation.

In table 3.3 the diagonal averaged values for the coupling surfaces are reported as given in Schwenke's paper. The values reported do not coincide exactly with those in table 4 of [64], because of the different definitions of both Radau coordinates and the angular momentum operators. Moreover, Schwenke calculated non-adiabatic vibrationally averaged corrections for all the terms in the KEO, whereas we have reported in table 3.3 only the terms referring to the diagonal terms in the KEO. As the neglected part includes, among others, the Coriolis term, it is possible to divide the terms considered into a purely vibrational correction and a purely rotational correction. The former is constituted by the terms $\partial^2 / \partial r_1^2$ and $\partial^2 / \partial \theta^2$ (by symmetry consideration, the two terms $\partial^2 / \partial r_1^2$ and $\partial^2 / \partial r_2^2$ have the same coefficients). The non-adiabatic corrections to the rotational part of the KEO affect the terms $\hat{J}_x^2$, $\hat{J}_y^2$ and $\hat{J}_z^2$.

We have introduced non-adiabatic corrections within our code DVR. Following Schwenke's analysis, we have implemented only the simplest form of non-adiabatic corrections, and namely the terms indicated in table 3.3. This allows for a great simplification of the computational effort without significant loss in final accuracy. The implementation of the three rotational terms follows closely the previous work done for the g -factor. The correction to the kinetic energy operator arising from those three terms has exactly the same expression as in eq. (3.44), where the functions ϵ_{xx} , ϵ_{yy} and ϵ_{zz} are replaced with the values given in table 3.3. The rotational non-adiabaticity can be switched on/off by means of the logical parameter *zs1*, which must be set within the input card PRT. The default value is *off*, which corresponds to ignoring the rotational non-adiabatic corrections.

The correction to the radial derivative can be interpreted as a correction to the relative reduced mass:

$$\frac{1}{\mu} \frac{\partial^2}{\partial r_1^2} \rightarrow \left(\frac{1}{\mu} - 1.0275213 \times 10^{-7} \right) \frac{\partial^2}{\partial r_1^2} \quad (3.45)$$

With a similar analysis to that given in the previous subsection, it is possible to show that the introduction of this term is equivalent to use a value for the hydrogen mass of 1.00769 *a.m.u.*. The implementation of the angular derivative requires some care. Using the properties of Associated Legendre polynomials, the correction to the effective kinetic operator reads:

$$\begin{aligned} \hat{K}_V^\theta &= \langle j', k' | 1.4062589 \times 10^{-8} \frac{\partial^2}{\partial \theta^2} | j, k \rangle = \\ &= 1.4062589 \times 10^{-8} \left(\delta_{k',k} \delta_{j',j} + \delta_{k',k} \langle j', k' | \frac{k^2}{\sin^2 \theta} | j, k \rangle \right) \end{aligned} \quad (3.46)$$

Again, the first term in the above expression can be interpreted as a mass correction to the vibrational angular reduced mass, whereas the second has the same significance as $\hat{K}_{xt}$ previously encountered (eq. (3.8)). The total vibrational non-adiabatic corrections (given by the first two terms in table 3.3) can be switched on/off in DVR3D by using the label *zs0*, to be set within the input card PRT. As for the rotational case, the default value is *off*. At the moment, the non-adiabatic corrections have only been implemented for the Radau bisector embedding.

In tables 3.4 and 3.5 values for non-adiabatic corrections to water VBOs are reported. The results obtained with our implementation of Schwenke's diagonal terms are very similar to its full calculation (see table 3.4). Thus, we have extended his analysis above 10000 cm^{-1} (table 3.5). The shift caused by the inclusion of non-adiabaticity is always negative, and it increases with the energy of the level. Its maximum value is about 3.5 cm^{-1} for the higher states. As a consequence, the total non-BO correction, given by the sum of BODC and non-adiabaticity, is enhanced for the bending modes, for which the two effects have the same sign, and reduced for the stretching modes, as they partially cancel. Furthermore, it is interesting to observe that the one-mass model shifts the VBOs in a similar pattern to the more sophisticated full coupling surfaces model. An optimum choice of the nuclei's reduced mass could in principle lead toward an even better agreement between the models.

The same analysis as above has been repeated for the rotational terms $J = 10(000)$, in order to compare our results with Schwenke [64] (table 3.6), and for $J = 20(000)$. We have calculated separately the shifts to the rotational levels caused by the purely vibrational and rotational non-adiabatic corrections. By comparing our results with table 6 in [64], we find a good agreement between our implementation of the diagonal vibrationally averaged non-adiabatic corrections, and the full coupling surfaces used in [64]. The shift is always negative, and the magnitude of the correction increases with k . In the total vibrational-rotational non-adiabaticity the rotational term is predominant. As for the VBO analysis, we found that the simple mass model gives a very good agreement with the more complex non-adiabatic calculations.

Table 3.4: Non-BO corrections in cm^{-1} to vibrational band origins in water, for levels up to 10000 cm^{-1} . Comparison with results of Schwenke [64]

(v_1, v_2, v_3)	BO ^a	Adiabatic correction ^b			Non-adiabatic correction ^c		
		SCF	CASSCF		$\mu_V \neq \mu^{nuc}$ ^d	diag ^e	accurate
			[64]	refit			[64]
(010)	1597.60	-0.50	-0.46	-0.46	-0.19	-0.06	-0.07
(020)	3157.14	-0.99	-0.94	-0.93	-0.38	-0.12	-0.15
(100)	3661.00	-0.06	-0.39	0.55	-0.46	-0.72	-0.70
(030)	4674.88	-1.48	-1.46	-1.43	-0.55	-0.18	-0.23
(110)	5241.83	-0.51	-0.01	0.16	-0.65	-0.77	-0.76
(040)	6144.64	-2.02	-2.03	-2.00	-0.71	-0.23	-0.30
(120)	6784.56	-0.94	-0.42	-0.23	-0.83	-0.83	-0.84
(200)	7208.80	-0.08	0.96	1.25	-0.88	-1.39	-1.37
(002)	7450.86	0.19	1.22	1.47	-0.90	-1.47	-1.57
(050)	7555.62	-2.65	-2.71	-2.71	-0.84	-0.28	-0.37
(130)	8286.03	-1.37	-0.87	-0.67	-1.00	-0.89	-0.91
(210)	8771.71	-0.47	-0.66	0.95	-1.07	-1.44	-1.43
(060)	8886.34	-3.51	-3.63	-3.67	-0.93	-0.31	-0.41
(012)	9008.72	-0.20	-0.90	1.17	-1.08	-1.52	-1.65
(001)	3758.63	0.12	0.75	0.62	-0.45	-0.75	-0.79
(011)	5336.74	-0.33	0.37	0.24	-0.64	-0.81	-0.87
(021)	6879.72	-0.74	-0.01	-0.16	-0.82	-0.88	-0.94
(101)	7256.00	0.06	1.43	1.19	-0.87	-1.40	-1.43
(031)	8384.71	-1.15	-0.41	-0.58	-0.99	-0.94	-1.02
(111)	8816.00	-0.33	1.14	0.88	-1.05	-1.46	-1.50
(041)	9846.97	-1.58	-0.86	-1.05	-1.15	-1.01	-1.05

^a BO: *ab initio* Born-Oppenheimer potential of Partridge and Schwenke [20].^b Adiabatic correction given relative to BO.^c Non-adiabatic correction given relative to the refitted CASSCF BODC.^d $M_H=1.007551$ a.m.u.^e Simplified diagonal correction, see text, multiplied by 1.1 as recommended by Schwenke [64].

Table 3.5: Non-BO corrections to vibrational band origins in cm^{-1} above 10000 cm^{-1} . Column headings are as given in Table 3.4. The values for the level (112) were uncorrectly reported in [110].

(v_1, v_2, v_3)	BO	Adiabatic correction		Non-adiabatic correction	
		SCF	CASSCF	$\mu_V \neq \mu^{nuc}$	diag
(220)	10297.00	-0.83	0.64	-1.24	-1.49
(300)	10609.14	-0.02	2.23	-1.30	-1.99
(102)	10879.00	0.01	2.01	-1.32	-2.10
(230)	11782.64	-1.19	0.30	-1.41	-1.55
(032)	12021.78	-0.88	0.57	-1.42	-1.64
(310)	12151.51	-0.34	2.03	-1.47	-2.03
(112)	12420.66	-0.35	1.75	-1.50	-2.13
(400)	13839.28	0.05	3.44	-1.73	-2.52
(122)	13926.37	-0.61	1.56	-1.67	-2.19
(202)	14234.86	-0.11	2.73	-1.74	-2.70
(004)	14548.39	0.37	3.22	-1.72	-2.79
(330)	15125.11	-0.88	1.63	-1.81	-2.15
(410)	15358.27	-0.22	3.27	-1.93	-2.54
(212)	15759.25	-0.36	2.60	-1.91	-2.73
(302)	17473.72	-0.06	3.86	-2.17	-3.23
(510)	18407.30	-0.03	4.77	-2.11	-2.94
(610)	21237.93	-0.17	6.12	-1.15	-3.34
(700)	22540.31	0.18	8.87	-3.35	-3.75
(620)	22646.30	-0.44	5.63	-1.91	-3.32
(121)	10340.25	-0.68	0.85	-1.23	-1.52
(201)	10622.32	0.04	2.33	-1.29	-2.00
(003)	11040.73	0.30	2.34	-1.31	-2.14
(131)	11827.31	-1.02	0.53	-1.40	-1.59
(211)	12162.98	-0.27	2.12	-1.47	-2.04
(013)	12576.10	-0.03	2.13	-1.49	-2.20
(221)	13666.57	-0.55	1.94	-1.64	-2.11
(301)	13841.87	0.06	3.45	-1.73	-2.52
(071)	13857.06	-3.60	-3.18	-1.46	-1.14
(023)	14079.96	-0.31	1.93	-1.66	-2.26
(103)	14330.58	0.17	3.10	-1.73	-2.72
(231)	15135.54	-0.81	1.72	-1.80	-2.17
(311)	15361.47	-0.17	3.36	-1.93	-2.55
(033)	15551.12	-0.56	1.73	-1.82	-2.32
(113)	15847.27	-0.09	2.97	-1.90	-2.75
(321)	16836.48	-0.33	3.49	-2.01	-2.68
(401)	16911.26	0.09	4.72	-1.79	-2.92
(123)	17329.30	-0.29	2.87	-2.06	-2.81
(203)	17509.84	0.11	4.11	-2.17	-3.23
(331)	18283.48	-0.58	3.29	-2.20	-2.73
(411)	18407.85	-0.03	4.74	-2.10	-2.95
(213)	19006.86	-0.06	4.09	-2.36	-3.25

Table 3.5: continued

(v_1, v_2, v_3)	BO	Adiabatic correction		Non-adiabatic correction	
		SCF	CASSCF	$\mu_V \neq \mu^{nuc}$	diag
(501)	19793.84	0.08	6.42	-0.67	-3.36
(303)	20559.11	0.10	5.33	-2.22	-3.64
(511)	21238.20	-0.16	6.13	-1.11	-3.35
(601)	22540.47	0.19	8.83	-3.31	-3.75
(521)	22647.89	-0.35	5.82	-1.68	-3.34
(701)	25127.96	0.33	11.85	-28.15	-4.03

Table 3.6: Non-BO corrections in cm^{-1} to the rotational term $J=10$ (000) for water. Comparison with results of Schwenke [64]. Part of column headings as in table 3.4. The shift to the levels caused by the non-adiabatic corrections has been split into the purely vibrational contribution (column V), and the purely rotational (R). Also the total shift is reported (column V+R).

(J_{K_a, K_c})	BO ^a	Adiabatic correction ^b			Non-adiabatic correction ^c					
		SCF	CASSCF		$\mu \neq \mu^{nuc\ d}$	V ^f	diag ^e R ^g	V+R ^h	accurate [64] ⁱ	g -factor ^j
			[64]	refit						
(10 _{0,10})	1114.95	-0.11	-0.08	-0.05	-0.29	0.00	-0.21	-0.21	-0.21	-0.06
(10 _{1,10})	1114.97	-0.11	-0.08	-0.05	-0.29	0.00	-0.21	-0.21	-0.21	-0.25
(10 _{2,8})	1438.58	-0.20	-0.15	-0.12	-0.38	-0.01	-0.25	-0.25	-0.25	-0.29
(10 _{3,8})	1446.67	-0.16	-0.11	-0.08	-0.38	-0.01	-0.25	-0.26	-0.25	-0.32
(10 _{4,6})	1617.18	-0.25	-0.20	-0.17	-0.42	-0.01	-0.27	-0.28	-0.27	-0.41
(10 _{5,6})	1719.18	-0.07	-0.02	0.03	-0.44	-0.03	-0.28	-0.31	-0.29	-0.43
(10 _{6,4})	1875.79	0.04	0.09	0.15	-0.47	-0.04	-0.30	-0.35	-0.32	-0.49
(10 _{7,4})	2054.53	0.17	0.22	0.30	-0.51	-0.06	-0.33	-0.39	-0.34	-0.56
(10 _{8,2})	2254.35	0.30	0.36	0.46	-0.55	-0.08	-0.36	-0.44	-0.37	-0.66
(10 _{9,2})	2471.21	0.44	0.50	0.62	-0.58	-0.10	-0.39	-0.49	-0.40	-0.76
(10 _{10,0})	2701.77	0.59	0.65	0.78	-0.62	-0.12	-0.43	-0.55	-0.42	-0.88

^a BO: *ab initio* Born-Oppenheimer potential of Partridge and Schwenke [20].

^b Adiabatic correction given relative to BO.

^c Non-adiabatic correction given relative to the refitted CASSCF BODC.

^d $\mu_V = \mu_R = \mu_{mid}$

^e Simplified diagonal correction, see text, multiplied by 1.1 as recommended by Schwenke [64]. ^f Vibrational non-adiabatic, corresponding to the first two terms in table 3.3.

^g Rotational non-adiabatic, given by the last three terms in table 3.3.

^h Total non-adiabatic corrections given by all the terms in table 3.3.

ⁱ Accurate rotational non-adiabatic, from table 6 in [64].

^j rotational g -factor, eq. (3.44)

Table 3.7: Non-BO corrections in cm^{-1} to the rotational term $J=20$ (000) for water. Column headings as in table 3.6.

(J_{K_a, K_c})	BO	Adiabatic correction		Non-adiabatic correction				
		SCF	CASSCF refit	$\mu \neq \mu^{nuc}$	diag			g -factor
					V	R	V+R	
(20 _{0,20})	4049.43	-0.39	-0.16	-1.04	0.01	-0.77	-0.76	-0.12
(20 _{1,19})	4413.59	-0.43	-0.18	-1.13	0.00	-0.82	-0.82	-0.24
(20 _{2,18})	4740.02	-0.48	-0.21	-1.21	-0.02	-0.86	-0.87	-0.59
(20 _{3,17})	5033.33	-0.55	-0.26	-1.28	-0.03	-0.90	-0.92	-0.59
(20 _{4,16})	5293.79	-0.64	-0.35	-1.35	-0.03	-0.93	-0.96	-1.00
(20 _{5,15})	5515.11	-0.80	-0.50	-1.40	-0.03	-0.96	-0.99	-0.87
(20 _{6,14})	5682.88	-1.03	-0.73	-1.45	-0.03	-0.98	-1.01	-1.41
(20 _{7,13})	5814.21	-1.04	-0.74	-1.48	-0.03	-1.00	-1.03	-1.29
(20 _{8,12})	5968.82	-0.78	-0.45	-1.51	-0.06	-1.02	-1.08	-1.51
(20 _{9,11})	6172.72	-0.52	-0.15	-1.54	-0.08	-1.05	-1.14	-1.54
(20 _{10,10})	6409.30	-0.32	0.07	-1.59	-0.11	-1.09	-1.20	-1.64
(20 _{11,9})	6666.05	-0.16	0.27	-1.63	-0.14	-1.13	-1.27	-1.75
(20 _{12,8})	6937.35	0.00	0.45	-1.68	-0.17	-1.17	-1.34	-1.89
(20 _{13,7})	7219.57	0.16	0.64	-1.72	-0.20	-1.22	-1.42	-2.04
(20 _{14,6})	7509.69	0.32	0.82	-1.77	-0.23	-1.28	-1.51	-2.20
(20 _{15,5})	7804.96	0.47	1.00	-1.81	-0.27	-1.33	-1.60	-2.38
(20 _{16,4})	8102.72	0.63	1.19	-1.85	-0.30	-1.40	-1.70	-2.57
(20 _{17,3})	8400.30	0.79	1.37	-1.88	-0.34	-1.46	-1.81	-2.78
(20 _{18,2})	8694.85	0.96	1.56	-1.91	-0.38	-1.53	-1.92	-2.99
(20 _{19,1})	8983.13	1.14	1.75	-1.93	-0.43	-1.61	-2.04	-3.22
(20 _{20,0})	9261.11	1.33	1.95	-1.95	-0.48	-1.69	-2.17	-3.46

3.3 Discussion

In this chapter several corrections to the BO approximation have been presented. Those corrections are customarily divided into adiabatic (sect. 3.1) and non-adiabatic (sect. 3.2).

The BODC term has recently been calculated at the CASSCF level of electronic correlation theory by Schwenke. We have extended his analysis above $10,000\text{ cm}^{-1}$. The difference between the SCF and CASSCF surfaces is marked (see fig. 3.1), and consequently calculated VBOs are shifted considerably differently by the two surfaces, in particular the pure stretching levels. When the same analysis is extended to the $J=10$ (000) and $J=20$ (000) rotational levels, we found a good agreement between the two surfaces. Moreover, the most striking feature of the BODC correction, that it affects significantly the high K_a levels, is present in both surfaces. The main conclusion of sect 3.1 is that the SCF level of theory is inadequate to calculate a BODC surface of spectroscopic accuracy. It is unclear how accurate the CASSCF surface itself is. To answer this question a study of the BODC correction at the multi-reference configuration interaction (MRCI) level of theory is currently under way. However, preliminary results seem to show good agreement between the CASSCF and MRCI calculations, within 10 % or less.

Beyond the BODC correction there are non-adiabatic terms. The spectroscopic consequences of these corrections are normally expected to be smaller than the BODC: this is the case, for instance, in H_3^+ [84]. However, some preliminary studies in water [85], and HF [111], suggested that non-adiabatic effects could be comparable with the BODC for those systems. In these studies the magnitude of non-adiabatic effects was estimated by varying the nuclei's reduced mass between its nuclear and atomic values.

In section 3.2 we have discussed and compared several methods to evaluate non-adiabatic effects. In the simplest model presented, the reduced mass in the KEO is considered a free parameter which can be used to maximise the agreement between observed and calculated energy levels. Fig. 3.2 shows that small variations of the nuclear reduced mass can have a strong influence on the calculated levels. This seems to confirm that non-adiabatic effects are much bigger in water than other molecules, such as H_3^+ . Previous studies [85] indicated that a hydrogen mass midway between the nuclear and atomic value represents the optimal choice for modelling non-adiabatic effects in water through mass scaling. However, this method systematically over-estimates non-adiabatic effects for the bending VBOs and under-estimates them for the stretches.

The next step consists of allowing separate manipulation of the vibrational and rotational reduced masses. We have not carried out, however, a systematic optimisation of the two parameters of this model. Instead, we have analysed in detail the extra term introduced in the KEO by using different vibrational and rotational reduced masses. The contribution of this term to rotational levels has been evaluated for different choices of the embedded molecular frame and internal coordinates. We can draw two conclusions from our analysis. Firstly, the Radau bisector embedding is by far the most appropriate for water. The other embeddings considered require much bigger basis sets to achieve numerical convergence. Moreover, as the water molecule becomes linear at relatively low energy, the use of Jacobi coordinates seems particularly inappropriate. Secondly, the contribution of the extra term is independent of the embedding chosen, and is considerably bigger than in H_3^+ . This finding is in line with the fact that non-adiabatic effects in water are generally larger than in H_3^+ [110].

In subsection 3.2.2 we have discussed the possibility and the advantages of implementing a Radau-Eckart embedding for water. Wei and Carrington [103, 104, 112] recently published a series of papers on the subject, and particularly, they presented a Radau-Eckart KEO. We have reproduced their main results following a different approach recently proposed by Lukka [106], which greatly simplifies the algebraic effort required to calculate a KEO. The Eckart-Radau embedding is much more complex than the simple Radau, and its implementation presents several computational difficulties. In particular, the KEO is singular at $\theta = 0$ and $\theta = \pi$. Whereas the first singularity lies in a region of the phase-space energetically prohibited, therefore can safely be neglected [69], to deal with the second point one needs to introduce *ad hoc* angular basis functions, and bigger basis sets. Furthermore, for pure bending and pure stretching motions the Radau bisector and Eckart-Radau bisector embeddings coincide.

We have implemented a simple model to account for rotational non-adiabaticity based on equations derived for diatomic molecules. This model involves three parameters, connected with the diagonal components of the nuclei's inertia tensor. As input parameters we used the experimental values provided by Flygare [59]. However, this model proved to be not very accurate. The main reason is that the rotational non-adiabatic term for non-linear molecules is much more complex than for simple diatomic molecules.

The last method considered is the full treatment by Schwenke [64]. Following his conclusions, we have implemented a reduced diagonal vibrationally averaged part of the coupling surfaces he calculated. This method gives significantly better results than all previous ones. However, it is very demanding to extend it to bigger molecules, due to computational and theoretical difficulties described in subsection 3.2.4. Interestingly, the main finding of the full treatment of non-adiabatic effects is that the surfaces can be approximated by five parameters described in table 3.3. Those parameters can be interpreted as corrections to the bending and stretching masses, and to the rotational inertia.

Finally, from our analysis of different methods of accounting for non-adiabatic effects we can conclude that simple models where few free parameters are manipulated to optimise the agreement between observed and calculated energy levels are capable of achieving spectroscopic accuracy. Those parameters can generally be considered as scaling factors to the nuclei's reduced masses, therefore their implementation is computationally inexpensive. Furthermore, the extension of this model to bigger molecules is relatively straightforward. However, it is unclear whether Hamiltonians so derived can have any predictive power outside the spectral region for which the parameters have been fitted, of whether it is possible to account for different isotopomers with the same set of parameters. Such analyses are currently under way.

3.3.1 Comments on the possible accuracy of isotopically invariant PESs

There are several isotopomers of water and hydrogen sulphide which are observed in high resolution spectra, including H_2^{16}O , D_2^{16}O , HD^{16}O , H_2^{32}S , D_2^{32}S , HD^{32}S , and so on. Those molecules differ for the presence of isotopic species, that is, nuclei with the same number of protons and different number of neutrons, thus with the same electrical charge, but different masses and spin. Consequently, the Schrödinger equation associated with each of them is similar but for the fact of different masses in the KEO (see eq. (2.2)), while the internal potential is the same. However, the adiabatic correction to the BODC PES introduces a term which is

explicitly dependent on the nuclei's masses. Thus, it is interesting to evaluate whether it is possible to build an accurate ($\leq 0.1 \text{ cm}^{-1}$) isotopically invariant PES, also considering the magnitude of the adiabatic BO correction, discussed in Section 3.1. A different approach would consist in firstly producing a PES relying only on the most common isotopomer (ie, H_2^{16}O or H_2^{32}S), for which normally a wealth of experimental data are available, and then trying to match the secondary isotopomers data by modelling an *ad hoc* explicitly mass-dependent correction.

We have considered the work of Partridge and Schwenke on water [20], and Tarczay *et al.* [61], and Tyuterev *et al.* [113] on hydrogen sulphide. Partridge and Schwenke followed the second approach. At first, they determined a highly accurate semi-empirical surface for H_2^{16}O (see eq. (2.59)). In a second step, they tried to reproduce the experimental data for the other water isotopomers with the H_2^{16}O surface. They found that they were able to calculate energy levels for the different oxygen isotopomers with satisfactory accuracy, with differences between observed and calculated levels being 0.03 cm^{-1} or less. Conversely, when they use their surface for the hydrogen isotopomers of water the discrepancy between obs. and calc. increased by almost one order of magnitude, with the maximum deviations for HD^{16}O . To improve on this, they introduced an explicitly mass-dependent correction, which allowed them to reduce the disagreement by one order of magnitude.

On the other hand, Tyuterev *et al.* [113] were able to produce an isotopically invariant PES which fits data for seven isotopomers of hydrogen sulphide with a root-mean-square deviation of 0.05 cm^{-1} . the maximum discrepancy occurs for the level (110) of HD^{32}S , and is 0.12 cm^{-1} . In line with the findings of Partridge and Schwenke, the agreement between observed and calculated levels is better for H_2^{32}S and its sulphur isotopomers than for its hydrogen isotopomers, particularly for HD^{32}S and HD^{34}S .

On the same molecule, Tarczay *et al.* [61] calculated a completely *ab initio* PES. Although their calculated levels are generally worse than the ones calculated with the empirical surface of Tyuterev *et al.*, it is possible to estimate the importance of non-BO effects and the accuracy of the global surface of Tyuterev *et al.* outside the fitting region, by comparing the works of the two groups. Fig. 3.6 shows asymmetric radial cuts $f(R)=V(R,R_e,\Theta_e)$ of the *ab initio* BODC term form [61] (indicated as ΔV^{BODC}), and the difference between the purely *ab initio* (ΔV^{ai}) and the empirical (ΔV^{emp}) surfaces. The greek letter Δ indicates that the surfaces are given relative to the point $r_{\text{HS}} = 1.337 \text{ \AA}$, $\Theta_{\text{HSH}} = 1.611$ radians. The BODC term is relative to the isotopomer HD^{32}S . The ΔV^{ai} term includes core-valence and relativistic corrections. By looking at the difference $\Delta V^{ai} - \Delta V^{emp}$ it is possible to note the little bump ($\approx 10 \text{ cm}^{-1}$) in the small r_{HS} part of the plot. This possibly unphysical behaviour is caused by the empirical surface.

In conclusion, an isotopically invariant PES for either water or hydrogen sulphide is expected to fit well all the levels for the main isotopomer and its oxygen (or sulphur) isotopes. On the other hand, to deal with the isotopes of hydrogen can require some extra care, particularly for the isotopomers containing HD. The results of Tyuterev *et al.* present their biggest discrepancies with the experimental data principally for the complexes HD^{32}S and HD^{34}S . Fitting of all the species into one surface can originate unwanted behaviours of the PES that are difficult to be kept under control, therefore resulting in a loss of predictive power, specially in those regions of the PES where the energy levels of the different isotopomers are densely

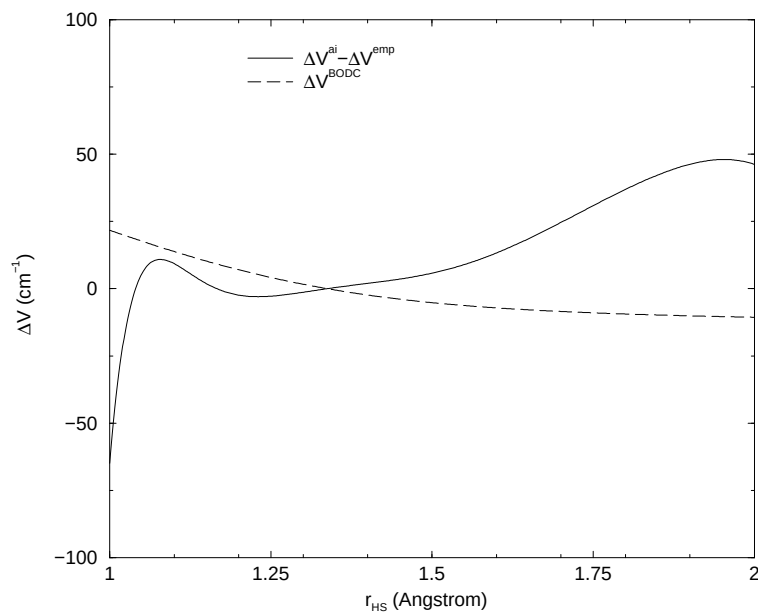


Figure 3.6: Comparison between the *ab initio* PES for hydrogen sulphide of Tarczay *et al.* [61], and the empirical isotopically invariant of Tyuterev *et al.* [113] (see text for details).

distributed. It is probably preferable to use very simple explicitly mass-dependent terms to improve the agreement between theory and experiment.

Two-electron Relativistic Corrections

4.1 State-of-the-art of Relativistic Corrections

In a first study concerning barrier heights in several light molecules, including water as well as ammonia, ethane, and others, Császár *et al.* [40] looked critically at various corrections to standard *ab initio* electronic structure calculations. In particular, the mass-velocity (MV) and one-electron Darwin (D1) corrections were found essential for water, raising in total the barrier height by 50 cm^{-1} , about 0.5%. In a follow-up study, the effect of the MVD1 term on the vibrational-rotational energy levels of water has been carefully investigated [55, 60]. In general, addition of the MVD1 relativistic correction lowers the band origins of the stretching states but raises the band origins of the bending modes, as expected from the increased barrier to linearity. In addition, these studies showed that MVD1 corrections are more important than the BODC. Furthermore, while the difference between observed and calculated vibrational band origins (VBOs) increases almost constantly with excitation energy without MVD1 corrections, with their inclusion in the *ab initio* potential the predictions for the stretching VBOs are greatly improved, at the expense of the bending bands. For water, it is believed that the geometry dependence of the MVD1 term is caused by the conformational changes which involve *sp* rehybridisation of lone pairs of electrons, due to the passage from the C_{2v} (or C_s) symmetry group at the bent configuration to the $D_{\infty h}$ at linearity, and consequently, by the requirement of orthogonality, between the valence and core orbitals in a small volume surrounding the O atom (see note 96 in [40]).

Due to the spectroscopic importance of the MVD1 term, and also to gain a better insight into the physics beyond it, a parallel study to [60] has been carried on H_2S [61]. The qualitative results for H_2S are the same as for water, although the correction to the barrier height is twice as big. In the next sections the work from ref. [60, 61] has been extended also to include two-electron relativistic terms. In particular, the spectroscopic importance of D2 and the Breit term has been studied in detail for the case of water and H_2S . Whereas the D2 term has been calculated using the Pauli-Coulomb Hamiltonian (2.64), the Breit term has been evaluated directly in a Dirac four-component formalism. However, the Breit (B) term (2.62) is normally

split into two parts:

$$B = \left(-\frac{e^2}{r_{ij}} \alpha_i \cdot \alpha_j \right) + \left(\frac{e^2}{2 r_{ij}} \alpha_i \cdot \alpha_j - \frac{(\alpha_i \cdot r_{ij})(\alpha_j \cdot r_{ij})}{r_{ij}^2} \right) \quad (4.1)$$

which are called respectively the Gaunt (G) and the retardation (ret) terms. The Gaunt term is often used as an approximation to the more complicated Breit term.

4.2 Computational Techniques

4.2.1 Water

For water, the energy correction due to the two-electron Darwin term, D2, has been computed at the first order of perturbation theory with cc-pVQZ CCSD(T) [114, 115] wave functions, at the same level of accuracy as the previous calculations of MVD1 correction energies [55, 60].

Relativistic energy corrections due to the Gaunt and Breit interactions were obtained with first order of perturbation theory using a four-component Dirac–Hartree–Fock (DHF) wave function [38], and the recommended exponent factors for the Gaussian nuclear charge distribution [116]. Three different basis sets have been employed for the large component in order to check the convergence of the fully relativistic calculations: basis A=[11s6p, 6s], B=[11s6p3d, 6s3p], and C=[11s6p3d2f, 6s3p2d]. The relativistic basis sets used can not be directly compared to the non-relativistic ones. The study of relativistic electrons requires tighter *s* and *p* functions, and more diffuse *d* and *f*, compared to their non-relativistic counterparts [117]. Furthermore, the development of relativistic basis sets is not as advanced as for the non-relativistic ones. We have employed different basis sets to ensure the convergence of our calculation with respect to the inclusion of angular functions. The restricted kinetic balance prescription [38] was used to generate the small-component basis functions from the large component set in a one-to-one mapping. The value for the exponents of the Gaussian functions are reported in table 4.1.

Table 4.2 shows the result of a study of convergence for the relativistic basis sets. The Breit and Gaunt corrections were calculated at three different C_{2v} geometries: equilibrium ($R_{OH} = 1.811 a_0$, $\Theta = 104$ degree), symmetric stretch ($R_{OH} = 2.5 a_0$, $\Theta = 104$ degree), and a linear configuration ($R_{OH} = 1.811 a_0$, $\Theta = 180$ degree). Table 4.2 shows both the absolute values of the corrections, and their relative values, with the equilibrium chosen as reference geometry. The Breit/Gaunt effect is very small in the angular coordinate, and much bigger for the symmetric stretch. The convergence obtained with the basis A is good for the bending, and poor for the stretch. On the other hand, basis sets B and C are consistent within 0.5 cm^{-1} .

The computer time required for these calculations was of the order of 15 min for the basis set A, 6 hours for B, and approximately 1 day for C on a local PC. We ultimately decided to employ the basis B in our final calculations, as it ensures a good convergence without being too expensive. The calculations have been repeated at 325 geometries, and were performed on local PCs, and partially on the Bentham supercomputer, located at the HiPerSPACE Computing Centre, UCL. The grid is the same used in previous relativistic calculations [60], for consistency, and is summarised in table 4.3.

Table 4.1: Exponents for relativistic basis functions.

H						
s	33.8700	5.09500	1.19000	0.32580	0.10270	0.02526
p	1.40700	0.38800	0.10200			
d	1.05700	0.24700				
O						
s	15330.0	2299.00	522.400	147.300	47.5500	16.7600
	6.20700	1.75200	0.68820	0.23840	0.07376	
p	34.4600	7.74900	2.28000	0.71560	0.21400	0.05974
d	2.31400	0.64500	0.21400			
f	1.42800	0.50000				
S						
s	1320000	990000	330000	110800	166100	378100
	107100	349.8000	126.300	49.2600	20.16	5.72
	2.1820	0.75	0.100			
p	108000	360000	120000	399.7	94.19	29.75
	10.77	4.119	1.625	0.75	0.09	
d	1.44	0.479	0.16			

The computer codes DIRCCR12 [36], MOLFDIR [118, 119] and BERTHA [38, 39] have been employed for the electronic structure calculations involving the D2, Gaunt and Breit terms, respectively.

In order to use the calculated relativistic corrections in nuclear motion calculations we have fitted them to an analytic functional form which is the same as the one used in Ref. [60], using the following symmetrised displacement coordinates:

$$\begin{aligned}
 S_1 &= \frac{R_1 + R_2}{2} - R_e \\
 S_2 &= \frac{R_1 - R_2}{2} \\
 S_3 &= \Theta - \Theta_e
 \end{aligned} \tag{4.2}$$

The surface was fitted as a simple power series in the displacement coordinates

$$\Delta V_{\text{rel}}(S_1, S_2, S_3) = \sum_{i,j,k} c_{i,j,k} S_1^i S_2^j S_3^k. \tag{4.3}$$

Terms up to seventh-order, $i + j + k \leq 7$, were retained in the expansion, although some terms, which were not well determined, were dropped. The only significant eighth order term $(ijk)=(008)$ was also retained. The equilibrium parameters for water are $R_e = 1.809645 \text{ a}_0$, and $\Theta_e = 1.8240445$ radians. The computer algebra package *Mathematica* [120, 121] was used for fitting and to automatically generate the subroutines in FORTRAN. Each fit gives an accurate representation of the data and has a standard deviation of 0.04 cm^{-1} or better. The coefficients for the analytical surfaces are reported in tables 4.4, 4.5 and 4.6 for the two-electron Darwin, Gaunt, and Breit terms, respectively.

Table 4.2: Study of convergence for relativistic basis sets in water. The calculations are repeated at three reference nuclear geometries (see text for details): equilibrium configuration (1), symmetric stretch (2), and linear geometry (3), for three different basis sets (A, B, C), respectively [6s/11s5p], [6s3p/11s5p3d] and [6s3p2d/11s5p3d2f] for [H/O]. For the coefficients of the Gaussian functions see table 4.1.

Breit					
	abs. energies (mE _h)			diff. (cm ⁻¹)	
	1	2	3	2-1	3-1
A	7.5777558	7.4998784	7.5841528	-17.09	1.40
B	7.5771268	7.4973377	7.5832150	-17.51	1.34
C	7.5771717	7.4971705	7.5834839	-17.56	1.39

Gaunt					
	abs. energies (mE _h)			diff. (cm ⁻¹)	
	1	2	3	2-1	3-1
A	7.8799902	7.7853422	7.8934998	-20.77	2.97
B	7.8795327	7.7827653	7.8924769	-21.24	2.84
C	7.8795869	7.7825747	7.8927948	-21.29	2.90

Table 4.3: Summary of the grids used for building the relativistic corrections to the PES for different energy intervals.

range (cm ⁻¹)	$\leq 1.0 \times 10^4$	$1.0 - 2.0 \times 10^4$	$2.0 - 2.5 \times 10^4$
H ₂ O	192	103	27
H ₂ S	73	62	44
range (cm ⁻¹)	$2.5 - 3.0 \times 10^4$	$\geq 3.0 \times 10^4$	total.
H ₂ O	2	1	325
H ₂ S	35	44	258

The nuclear calculations were performed with the DVR3D code, and details of the inputs used are described in table 3.2. Nuclear masses have been used.

4.2.2 Hydrogen sulphide

The procedure used to determine two-electron relativistic corrections to the vibrational-rotational energy levels for H₂S follows closely the work done for water.

The energy correction due to the two-electron Darwin term has been computed at the first order of perturbation theory with aug-cc-pCVTZ CCSD(T) [114, 115] wave functions, at the same level of accuracy as the previous calculations of MVD1 correction energies [61]. Relativistic energy corrections due to the Gaunt and Breit interactions were obtained with first-order perturbation theory using the four-component Dirac–Hartree–Fock (DHF) wave function [38] and the recommended exponent factors for the Gaussian nuclear charge distribution [116]. As

Table 4.4: Coefficients in eq. (4.3) for the two-electron Darwin correction surface for H_2O . Units are consistent with bondlengths in a_0 , bondangle in radian, for energies in μE_h .

C_{ijk}	i	j	k	C_{ijk}	i	j	k
-3263.067522028298	0	0	0	-9.17958228916955	0	2	0
-0.5165611032611932	0	4	0	-0.5157212949525876	0	6	0
18.31161578215203	2	0	0	30.14193751791963	1	2	0
-13.62543868575853	1	4	0	-43.37232019119388	2	0	0
-50.50353364079294	2	2	0	70.36441193443143	2	4	0
27.43935454999898	3	0	0	123.751990625258	3	2	0
-76.80240321256033	3	4	0	-9.50017804016001	4	0	0
-363.4487347625543	4	2	0	113.1940248029751	5	0	0
376.6560011408163	5	2	0	-164.6523756673548	6	0	0
9.16256842998227	0	0	1	-1.22230095639504	0	2	1
1.33032571356463	1	0	1	-0.94822119654751	1	2	1
0.7645470802285307	1	4	1	-11.77270680473595	2	0	1
-0.4065994514809928	2	4	1	-2.113651214829342	3	0	1
-3.653921741665064	4	2	1	26.53983199106825	6	0	1
3.099164302936567	0	0	2	-0.4668245990549825	0	2	2
0.05845413180128318	0	4	2	2.708722250876111	1	0	2
-0.1605392233404811	1	4	2	-10.57780429022803	2	0	2
-3.496293826717189	3	0	2	23.46280699747645	4	0	2
1.8547816858377	0	0	3	-0.4003662844685243	0	2	3
3.040229985315839	1	0	3	-4.955739113923876	2	0	3
14.05364889791468	3	0	3	-21.6926320924828	4	0	3
-1.321464834042384	0	0	4	2.298844571392118	0	2	4
-2.633405421645483	1	0	4	20.97178840867901	2	0	4
-32.18658937476802	3	0	4	-0.5992225949734171	0	0	5
2.059827452250273	1	0	5	0.6453850286056735	2	0	5
-0.4620689505336259	0	0	6	0.7465042626807512	1	0	6
-0.1254018119377959	0	0	7	0.01947721364782498	0	0	8
-2.578482367020144	1	2	2				

for water, the values of the exponents as well as the number of basis functions have been optimised in order to achieve a good convergence. The following basis set was ultimately used for the large component: [S,H]=[15s11p3d,6s3p]. The values for the exponents are reported in table 4.1. The calculations for H_2S are computationally more expensive than water, with an average duration of 12 hours per geometry. The restricted kinetic balance prescription [38] was used to generate the small-component basis functions from the large component set in a one-to-one mapping. The calculations have been repeated at over 250 structures in the coordinate range $1.1 \leq \text{distance} \leq 2.3 \text{ \AA}$ and $40 \text{ deg} \leq \text{angle} \leq 180 \text{ deg}$. Table 4.3 summarises the grid employed.

The 258 data points obtained were fitted to analytic surfaces as previously done for water.

Table 4.5: Coefficients in eq. (4.3) for the Gaunt correction surface for H_2O . Units are consistent with bondlengths in a_0 , bondangle in radian, for energies in μE_h .

C_{ijk}	i	j	k	C_{ijk}	i	j	k
7877.982883513934	0	0	0	63.10887595928893	0	2	0
8.03387896728612	0	4	0	-0.3041891495673817	0	6	0
-253.5191358749755	1	0	0	-136.5759956009869	1	2	0
-33.6570113816125	1	4	0	253.8929702610988	2	0	0
152.119066100767	2	2	0	91.5639250645856	2	4	0
-198.9425723076648	3	0	0	-42.9282903009852	3	2	0
-87.9454152216385	3	4	0	124.8351176801018	4	0	0
-268.9794777044373	4	2	0	38.55581427697435	5	0	0
352.2528696439553	5	2	0	-131.1529484382626	6	0	0
5.326890257310683	0	0	1	-0.4120148813337237	0	2	1
3.82422410547695	1	0	1	0.6206293336076872	1	2	1
0.02809410887592116	1	4	1	-0.901742150572343	2	0	1
-0.3728837427319114	2	4	1	-4.118183680630072	3	0	1
-0.4493270702547417	4	2	1	7.563785878558903	6	0	1
9.64804317964812	0	0	2	0.1812261160524592	0	2	2
0.01847954399593778	0	4	2	2.973939740794681	1	0	2
-3.777923390070938	1	2	2	0.4101354473300345	1	4	2
0.2592684136862402	2	0	2	1.376943387660969	3	0	2
0.4159893264447563	4	0	2	-1.745819723564219	0	0	3
2.024906172491523	0	2	3	-1.242519805262201	1	0	3
-4.734733153999302	2	0	3	1.431074125937998	3	0	3
-4.263321149401646	4	0	3	-0.4151227941709226	0	0	4
-1.104802675348885	0	2	4	8.31026860826823	1	0	4
0.0840222364277476	2	0	4	0.3567454621305059	3	0	4
-1.387991912514261	0	0	5	-6.319908690336135	1	0	5
7.690107916621922	2	0	5	-1.037440064866921	0	0	6
-0.1589663138643805	1	0	6	0.7066462981762655	0	0	7
0.07330160534466521	0	0	8				

The values for the equilibrium parameters are 1.3374 Å for the HS bondlength, and 88 degree for the bondangle. The final coefficients for the fits are reported in table 4.7 for the Breit surface, table 4.8 for the Gaunt, and table 4.9 for the D2 term. The standard deviation of the fits is 0.05 cm^{-1} for the Gaunt surface, 0.03 cm^{-1} for the Breit and the two-electron Darwin. Nuclear calculations were performed using the DVR3D program suite, with previously optimised basis sets ([61], also see table 3.2). Nuclear masses have been used.

Table 4.6: Coefficients in eq. (4.3) for the Breit correction surface for H_2O . Units are consistent with bondlengths in a_0 , bondangle in radian, for energies in μE_h .

C_{ijk}	i	j	k	C_{ijk}	i	j	k
7577.371974812879	0	0	0	54.16425693884002	0	2	0
6.774810680339735	0	4	0	-0.7125792752605449	0	6	0
-212.3502737780579	1	0	0	-119.8400228527018	1	2	0
-29.18501086262345	1	4	0	221.1271759652365	2	0	0
72.97844564936518	2	2	0	89.0829000401668	2	4	0
-180.6736318109525	3	0	0	321.1679099895901	3	2	0
-86.9772033725647	3	4	0	81.467133012329	4	0	0
-890.357807854604	4	2	0	-58.228375665496	6	0	0
57.52112099193129	5	0	0	676.0925261740228	5	2	0
1.323061103513093	0	0	1	-0.5270121336782832	0	2	1
0.01985434592556156	1	0	1	7.715533877300036	1	2	1
-6.229144779356836	1	4	1	-0.1710351457311522	2	0	1
9.92240371274571	2	4	1	10.47917821735698	3	0	1
-27.67291046310705	4	2	1	15.42094531691969	6	0	1
7.749223096520598	0	0	2	-0.2147443261198608	0	2	2
-1.164069372530965	0	4	2	10.24148015693046	1	0	2
-2.364801830233726	1	2	2	3.405435470980123	1	4	2
11.53659470986242	2	0	2	40.71096970108562	3	0	2
-65.49114275587444	4	0	2	0.5246601257334035	0	0	3
1.025008298074623	0	2	3	13.57824254391274	1	0	3
-7.469419914001589	2	0	3	-33.70757112970705	3	0	3
30.20514216972833	4	0	3	-10.53913543447923	0	0	4
-0.6159136295163627	0	2	4	-19.56431274355461	1	0	4
-20.81965238209867	2	0	4	5.998958874987758	3	0	4
-9.44711265431818	0	0	5	-22.55622148750276	1	0	5
16.30440168684215	2	0	5	19.20675957512514	0	0	6
19.78080962673524	1	0	6	8.08923849773384	0	0	7
-10.68490632273025	0	0	8				

4.3 Analysis of energy corrections

At the SCF level of the theory it is possible to calculate the contribution of each occupied orbital to the total relativistic correction. The non relativistic SCF electronic wavefunction must be totally antisymmetric with respect to the interchange of two electrons, thus it is normally written in a determinantal form:

$$\psi = \begin{vmatrix} \chi_1(\mathbf{r}_1) & \chi_2(\mathbf{r}_1) & \cdots & \chi_n(\mathbf{r}_1) \\ \chi_1(\mathbf{r}_2) & \chi_2(\mathbf{r}_2) & \cdots & \chi_n(\mathbf{r}_2) \\ \cdots & \cdots & \cdots & \cdots \\ \chi_1(\mathbf{r}_n) & \chi_2(\mathbf{r}_n) & \cdots & \chi_n(\mathbf{r}_n) \end{vmatrix} = |\chi_1, \chi_2, \dots, \chi_n\rangle \quad (4.4)$$

Table 4.7: Coefficients in eq. (4.3) for the Breit correction surface for H₂S. Units are consistent with bondlengths in a₀, bondangle in radian, for energies in E_h.

C_{ijk}	i	j	k	C_{ijk}	i	j	k
$+0.8765756926097 \times 10^{-1}$	0	0	0	$-0.7470466984977 \times 10^{-6}$	0	0	1
$-0.4591567724873 \times 10^{-3}$	1	0	0	$+0.2438277378851 \times 10^{-4}$	0	0	2
$+0.1059524622662 \times 10^{-2}$	0	2	0	$-0.3189553736298 \times 10^{-5}$	1	0	1
$+0.1089138001148 \times 10^{-2}$	2	0	0	$+0.7735193302669 \times 10^{-4}$	0	0	3
$+0.1406958041130 \times 10^{-4}$	0	2	1	$+0.1630810111481 \times 10^{-4}$	1	0	2
$-0.4542479540109 \times 10^{-2}$	1	2	0	$+0.1002856632993 \times 10^{-4}$	2	0	1
$-0.1520879954684 \times 10^{-2}$	3	0	0	$+0.1391996175182 \times 10^{-4}$	0	0	4
$-0.4717723013451 \times 10^{-5}$	0	2	2	$+0.1558678228909 \times 10^{-2}$	0	4	0
$+0.1437254575428 \times 10^{-4}$	1	0	3	$+0.4118703616626 \times 10^{-5}$	1	2	1
$-0.8390791525712 \times 10^{-4}$	2	0	2	$+0.9097378783447 \times 10^{-2}$	2	2	0
$+0.6306768748460 \times 10^{-4}$	3	0	1	$+0.1455020958607 \times 10^{-2}$	4	0	0
$-0.3661914850753 \times 10^{-3}$	0	0	5	$-0.9407748202265 \times 10^{-4}$	0	2	3
$-0.1601893683893 \times 10^{-4}$	1	0	4	$-0.1107885445634 \times 10^{-3}$	1	2	2
$-0.6333559444331 \times 10^{-2}$	1	4	0	$-0.2190907906757 \times 10^{-3}$	2	0	3
$-0.1851060535471 \times 10^{-3}$	3	0	2	$-0.1229283119564 \times 10^{-1}$	3	2	0
$-0.6863742081354 \times 10^{-3}$	5	0	0	$-0.2304221502848 \times 10^{-3}$	0	0	6
$-0.1158774739975 \times 10^{-3}$	0	2	4	$-0.4196870186460 \times 10^{-3}$	0	4	2
$+0.3119089521774 \times 10^{-3}$	0	6	0	$+0.8782036319681 \times 10^{-4}$	1	0	5
$-0.1283168422912 \times 10^{-3}$	1	4	1	$-0.2998997605629 \times 10^{-4}$	2	0	4
$+0.1394552871461 \times 10^{-1}$	2	4	0	$+0.2933772450811 \times 10^{-3}$	3	0	3
$+0.4098561367544 \times 10^{-3}$	4	0	2	$+0.1069104080091 \times 10^{-1}$	4	2	0
$-0.3326196046609 \times 10^{-3}$	6	0	0	$+0.4539164927449 \times 10^{-3}$	7	0	0
$+0.9544310398796 \times 10^{-4}$	1	0	6	$+0.2404606656808 \times 10^{-2}$	1	4	2
$+0.1954265488403 \times 10^{-3}$	2	0	5	$+0.1238735531947 \times 10^{-2}$	2	4	0
$+0.7499245400255 \times 10^{-3}$	3	0	4	$-0.1397979747135 \times 10^{-1}$	3	4	0
$+0.6977006962489 \times 10^{-4}$	4	0	3	$-0.2347201681002 \times 10^{-2}$	4	2	1
$-0.2837645063101 \times 10^{-2}$	5	2	0	$-0.9643600951545 \times 10^{-3}$	6	0	1
$+0.3831112710055 \times 10^{-3}$	0	0	8				

where $\{\chi_i\}$ are all the occupied orbitals. Because we are dealing only with closed shells systems such as water or H₂S, we can limit ourselves to a restricted closed-shell Hartree-Fock [122]. In this approach the spin-dependence in the orbitals $\{\chi_i\}$ is implicitly included by considering them doubly occupied. Thus the number of occupied orbitals n is equal to half the number of electrons ($n = N/2$). Each orbital is expanded on a set of Gaussian basis functions

$$\chi_i(\mathbf{r}, \{R_A\}) = \sum_a \mathcal{A}_a^i g_a(\mathbf{r}, \{R_A\}) \quad (4.5)$$

The mean value of the relativistic operators we are interested in can readily be obtained. Two cases need to be distinguished: one-electron and two-electron operator. For the former,

Table 4.8: Coefficients in eq. (4.3) for the Gaunt correction surface for H_2S . Units are consistent with bondlengths in a_0 , bondangle in radian, for energies in E_h .

C_{ijk}	i	j	k	C_{ijk}	i	j	k
$+0.9453750817097 \times 10^{-1}$	0	0	0	$-0.3527497454934 \times 10^{-5}$	0	0	1
$-0.5623398479453 \times 10^{-3}$	1	0	0	$+0.3184119943909 \times 10^{-4}$	0	0	2
$+0.1264983806594 \times 10^{-2}$	0	2	0	$-0.6433822892762 \times 10^{-6}$	1	0	1
$+0.1293621900960 \times 10^{-2}$	2	0	0	$+0.1153731226002 \times 10^{-3}$	0	0	3
$+0.1944371960638 \times 10^{-4}$	0	2	1	$+0.2062421277904 \times 10^{-4}$	1	0	2
$-0.5392912681481 \times 10^{-2}$	1	2	0	$+0.4215969663932 \times 10^{-4}$	2	0	1
$-0.1813768220418 \times 10^{-2}$	3	0	0	$+0.2231963765567 \times 10^{-4}$	0	0	4
$-0.1179435303219 \times 10^{-4}$	0	2	2	$+0.1829273468087 \times 10^{-2}$	0	4	0
$+0.1372457037480 \times 10^{-4}$	1	0	3	$+0.9512308901375 \times 10^{-5}$	1	2	1
$-0.9855111329499 \times 10^{-4}$	2	0	2	$+0.1075732737890 \times 10^{-1}$	2	2	0
$+0.5452750165331 \times 10^{-6}$	3	0	1	$+0.1720769005842 \times 10^{-2}$	4	0	0
$-0.5601955472518 \times 10^{-3}$	0	0	5	$-0.1114787862952 \times 10^{-3}$	0	2	3
$-0.5837076366327 \times 10^{-4}$	1	0	4	$-0.6509947703250 \times 10^{-4}$	1	2	2
$-0.7017410490921 \times 10^{-2}$	1	4	0	$-0.3784212684319 \times 10^{-3}$	2	0	3
$-0.2768081471488 \times 10^{-3}$	3	0	2	$-0.1342821012540 \times 10^{-1}$	3	2	0
$-0.4023255253942 \times 10^{-3}$	5	0	0	$-0.3576631673448 \times 10^{-3}$	0	0	6
$-0.1510735422018 \times 10^{-3}$	0	2	4	$-0.5715755491279 \times 10^{-3}$	0	4	2
$+0.3721121329871 \times 10^{-3}$	0	6	0	$+0.1125331380038 \times 10^{-3}$	1	0	5
$-0.5909045823656 \times 10^{-3}$	1	4	1	$-0.7479511751489 \times 10^{-4}$	2	0	4
$+0.1414703531371 \times 10^{-1}$	2	4	0	$+0.5764206029177 \times 10^{-3}$	3	0	3
$+0.4784970721672 \times 10^{-3}$	4	0	2	$+0.8571116522285 \times 10^{-2}$	4	2	0
$-0.1168581477947 \times 10^{-2}$	6	0	0	$+0.6891550629468 \times 10^{-3}$	0	0	7
$+0.1556515276934 \times 10^{-3}$	0	0	6	$+0.2905839729060 \times 10^{-2}$	1	4	2
$+0.3630809675061 \times 10^{-3}$	2	0	5	$+0.3296097239931 \times 10^{-2}$	2	4	1
$+0.1318009995887 \times 10^{-2}$	3	0	4	$-0.1360157387589 \times 10^{-1}$	3	4	0
$+0.1277729109407 \times 10^{-3}$	4	3	0	$-0.3918380101742 \times 10^{-2}$	4	2	1
$+0.1147719312132 \times 10^{-2}$	5	2	0	$-0.1036645894718 \times 10^{-2}$	6	0	1
$+0.5839982090765 \times 10^{-3}$	0	0	8				

we have

$$\begin{aligned}\hat{O}_1 &= \sum_{i=1}^n \hat{o}_i \\ \langle \psi | \hat{O}_1 | \psi \rangle &= 2 \sum_i \langle \chi_i | \hat{o}_i | \chi_i \rangle\end{aligned}\tag{4.6}$$

whereas for the latter

$$\begin{aligned}\hat{O}_2 &= \sum_{ij}^n \hat{q}_{ij} \\ \langle \psi | \hat{O}_2 | \psi \rangle &= \sum_{ij} 2 \langle \chi_i \chi_j | \hat{q}_{ij} | \chi_i \chi_j \rangle - \langle \chi_i \chi_j | \hat{q}_{ij} | \chi_j \chi_i \rangle\end{aligned}\tag{4.7}$$

Table 4.9: Coefficients in eq. (4.3) for the two-electron Darwin correction surface for H₂S. Units are consistent with bondlengths in a₀, bondangle in radian, for energies in E_h.

C_{ijk}	i	j	k	C_{ijk}	i	j	k
$+0.3288315669739 \times 10^{-1}$	0	0	0	$-0.7071887537443 \times 10^{-5}$	0	0	1
$+0.4746750997890 \times 10^{-4}$	1	0	0	$+0.1814642649677 \times 10^{-5}$	0	0	2
$-0.2069467427819 \times 10^{-3}$	0	2	0	$+0.7332242095409 \times 10^{-5}$	1	0	1
$-0.2186179022213 \times 10^{-3}$	2	0	0	$+0.2480861522819 \times 10^{-4}$	0	0	3
$+0.1737358816430 \times 10^{-4}$	0	2	0	$+0.6343875806066 \times 10^{-5}$	1	0	2
$+0.1214158968508 \times 10^{-2}$	1	2	0	$+0.7174021871713 \times 10^{-4}$	2	0	1
$+0.4123102067716 \times 10^{-3}$	3	0	0	$+0.9304285225731 \times 10^{-5}$	0	0	4
$+0.2645987433615 \times 10^{-4}$	0	2	2	$-0.4694606895261 \times 10^{-3}$	0	4	0
$-0.4614784740426 \times 10^{-5}$	1	0	3	$+0.6735986785697 \times 10^{-4}$	1	2	1
$-0.1031568297693 \times 10^{-4}$	2	0	2	$-0.3018352737328 \times 10^{-2}$	2	2	0
$-0.1687936203472 \times 10^{-3}$	3	0	1	$-0.5407081511795 \times 10^{-3}$	4	0	0
$-0.1486645300254 \times 10^{-3}$	0	0	5	$+0.2608702101747 \times 10^{-4}$	0	2	3
$-0.1054721356589 \times 10^{-3}$	1	0	4	$+0.4850358295734 \times 10^{-4}$	1	2	2
$+0.2354824772719 \times 10^{-2}$	1	4	0	$-0.1994232364960 \times 10^{-3}$	2	0	3
$-0.1698790405568 \times 10^{-3}$	3	0	2	$+0.5107201201947 \times 10^{-2}$	3	2	0
$+0.7453795906214 \times 10^{-3}$	5	0	0	$-0.1048145279829 \times 10^{-3}$	0	0	6
$-0.5027878777653 \times 10^{-4}$	0	2	4	$-0.6135483118135 \times 10^{-3}$	0	4	2
$-0.2786927682760 \times 10^{-3}$	0	6	0	$+0.2042132380410 \times 10^{-5}$	1	0	5
$-0.2260425245176 \times 10^{-2}$	1	4	1	$-0.4759906023180 \times 10^{-4}$	2	0	4
$-0.6101027027456 \times 10^{-2}$	2	4	0	$+0.4650204217126 \times 10^{-3}$	3	0	3
$+0.2376486217449 \times 10^{-3}$	4	0	2	$-0.7056553518283 \times 10^{-2}$	4	2	0
$-0.6813879534093 \times 10^{-3}$	6	0	0	$+0.1741840225940 \times 10^{-3}$	0	0	7
$+0.9478904115519 \times 10^{-4}$	1	0	6	$+0.1668130278001 \times 10^{-2}$	1	4	2
$+0.3089302549319 \times 10^{-3}$	1	0	5	$+0.7991472940019 \times 10^{-2}$	2	4	1
$+0.8269964331662 \times 10^{-3}$	3	0	4	$+0.7854115056298 \times 10^{-2}$	3	4	0
$-0.2205039469374 \times 10^{-3}$	4	3	0	$-0.4779484677740 \times 10^{-2}$	4	2	1
$+0.4917493052450 \times 10^{-2}$	5	2	0	$+0.9271691674515 \times 10^{-3}$	6	0	1
$+0.1574429558949 \times 10^{-3}$	0	0	8				

Inserting eq. (4.5) in (4.6) and (4.7), we obtain the expression for the mean value of the desired operators in terms of the Gaussian matrix elements and the SCF coefficients:

$$\langle \psi | \hat{O}_1 | \psi \rangle = \sum_i \sum_{ab} \mathcal{A}_a^i \mathcal{A}_b^i \mathcal{G}_{ab} \quad (4.8)$$

$$\langle \psi | \hat{O}_2 | \psi \rangle = \sum_{j>i} \sum_{abcd} 2\mathcal{A}_a^i \mathcal{A}_b^j \mathcal{A}_c^i \mathcal{A}_d^j \mathcal{G}_{abdc} - \mathcal{A}_a^i \mathcal{A}_b^j \mathcal{A}_c^j \mathcal{A}_d^i \mathcal{G}_{abcd} \quad (4.9)$$

where the Gaussian matrix elements are defined as follows:

$$\mathcal{G}_{ab} = \int g_a(\mathbf{r}, \{R_A\}) \hat{o}(\mathbf{r}) g_b(\mathbf{r}, \{R_A\}) d\mathbf{r} \quad (4.10)$$

$$\mathcal{G}_{abcd} = \int g_a(\mathbf{r}_1, \{R_A\}) g_b(\mathbf{r}_2, \{R_A\}) \hat{q}(\mathbf{r}_1, \mathbf{r}_2) g_c(\mathbf{r}_1, \{R_A\}) g_d(\mathbf{r}_2, \{R_A\}) d\mathbf{r}_1 d\mathbf{r}_2 \quad (4.11)$$

The coefficients $\{\mathcal{A}_a^i\}$ for each orbital have been calculated using the GAMESS package [34], with the cc-pVQZ basis set [27], which comprises 30 Gaussian functions for H, 55 for O and 58 for S. The basis employed is big enough to guarantee a good convergence of the wavefunction to the Hartree-Fock limit.

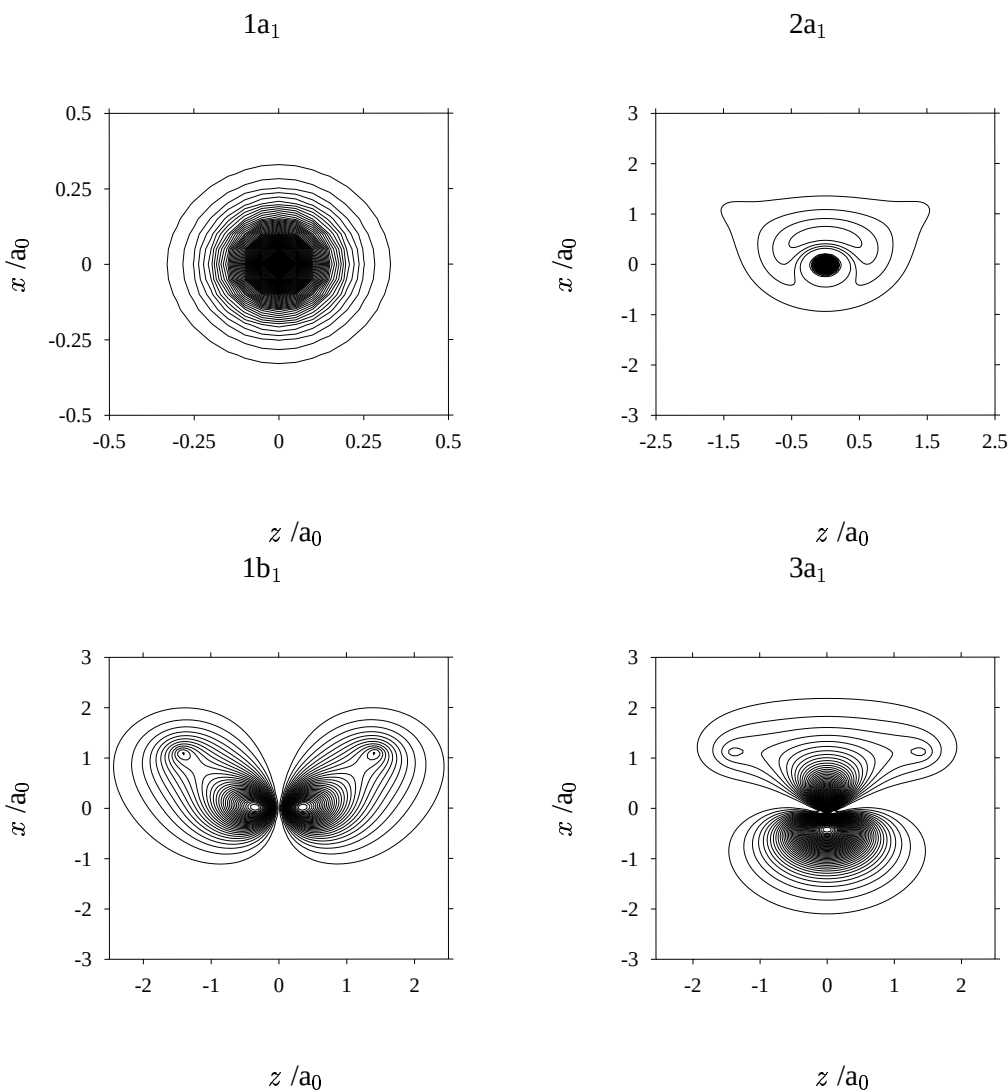
To study the origin of the molecular relativistic effect it is important to calculate the relativistic correction to a high accuracy. As will be discussed later, the core orbitals account for almost 99 % of the total MV or D1 shifts, and the molecular relativistic effects arise from very big cancellations. We compared the accuracy of our results with the ones from ref. [43], where an accurate analysis of the convergence of relativistic corrections with respect to the choice of basis set is reported for both the equilibrium and the saddle point geometries in H_2O and H_2S , as well as for other molecules. However, the results reported in [43] obtained with cc-pVQZ SCF wavefunctions slightly differ from the ones presented here. This is due to a slightly different definition of the cc-pVQZ basis set; more precisely, to the fact that the Gaussian functions can be defined as spherical functions, or Cartesian functions. The difference is that the spherical functions contain, for example in the case of angular momentum equal to 2, five basis functions (corresponding to $m = -2, -1, 0, +1, +2$), whereas the cartesian functions contain six (xx, yy, zz, xy, xz, yz). Moreover, as discussed in note (a) to table 2 in [43], further differences are caused by the number of significant digits in the contraction coefficients which define the Gaussian functions.

The second check was to compare our calculated Hartree-Fock values for the corrections with previously calculated [60] CCSD(T) results, obtained with a similar basis set. We found good agreement near the equilibrium geometry, and larger discrepancies for higher energy configurations, in particular those where the two OH bondlengths were contracted symmetrically. This behaviour was expected, as is well known that the Hartree-Fock wavefunction loses accuracy at large bondlengths. Nonetheless, we have included some results at higher energies as they appear qualitatively correct.

In figures 4.1 and 4.2 sections of the square modulus of water SCF orbitals on the molecular plane are plotted for two reference configurations, at equilibrium (figure 4.1) and at an almost linear ($\Theta = 170$ degrees) geometry (figure 4.2). Water has 5 occupied orbitals. One of them ($1b_2$), however, is antisymmetric with respect to the xz -plane, and therefore its projection onto the plane vanishes. As a consequence, this orbital is not involved in molecular bonds. The remaining four orbitals consist of a core orbital ($1a_1$), which is strongly localised in the proximity of the oxygen nucleus, and three valence orbitals ($2a_1$, $1b_1$ and $3a_1$). Of the latter, the $2a_1$ orbital is also well localised near the oxygen nucleus. The two other valence orbitals present different characteristics: in one ($1b_1$), the probability of finding the occupying electron is concentrated along the two bondlengths, and therefore this is the so-called bonding orbital, whereas the other ($3a_1$) extends in an area outside the bonding region. Both of them have nodes in proximity of the oxygen nucleus. By looking at the changes in the shape caused by the bending of the molecule, the differences in their character are easily highlighted: the $1b_1$ orbital follows closely the motion of the nuclei, without major distortions in its shape, whereas the orbital $3a_1$ becomes orthogonal to the molecule axis at linearity. This phenomenon is known as *sp*-rehybridisation [123].

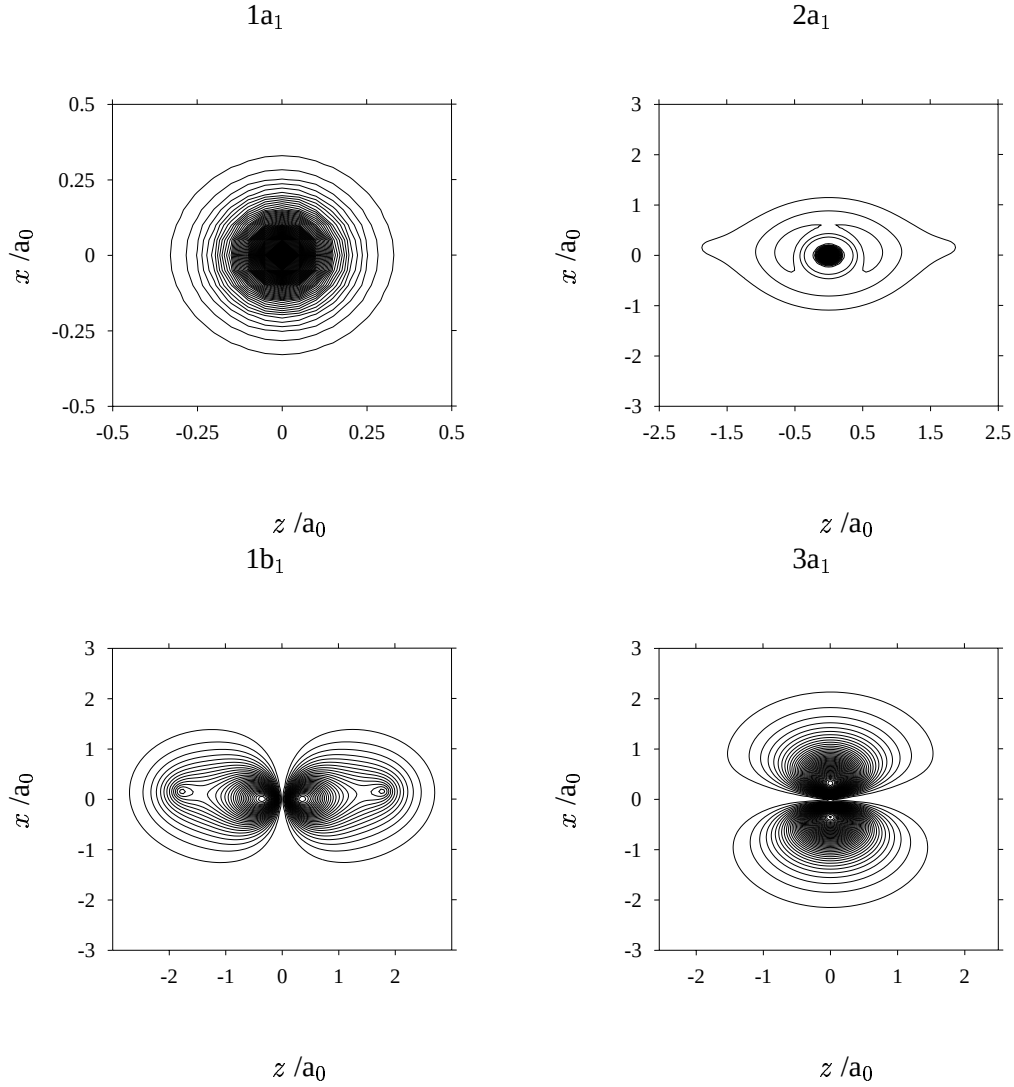
In tables 4.10 and 4.11 the contributions of each orbital to the one-electron Darwin and mass-velocity corrections, respectively, are shown at several nuclear C_{2v} geometries, including

Figure 4.1: Section through the square modulus of water orbitals at equilibrium nuclear geometry, on the $y=0$ plane. The oxygen nucleus is located at the point $(0,0,0)$, the two hydrogens are at $(-1.11,0,+1.43)$ and $(+1.11,0,+1.43)$. Note the different scale in the $1a_1$ plot.



pure bend and pure stretches of the molecule. Those corrections are strongly dominated by the $1a_1$ orbital, which alone accounts for 93.68 % of the total mass-velocity correction to the electronic ground state at nuclear equilibrium configuration, and 95.56 % of the one-electron Darwin. This correction is split into individual atomic contributions. As a consequence of the C_{2v} symmetry the two hydrogen contributions are exactly the same. The most important conclusions which can be drawn from tables 4.10 and 4.11 are that (a) the $1a_1$ orbital dominates both effects and (b) the effects seem to be localized near the oxygen nucleus, specially for the D1 term. In table 4.12 the two-electron Darwin term is shown for the same set of geometries previously discussed. As this is a two-electron term, its total contribution can not be split into

Figure 4.2: Section through the square modulus of water orbitals at an almost linear nuclear configuration, on the $y=0$ plane. The oxygen nucleus is located at the point $(0,0,0)$, the two hydrogens are at $(-1.80,0,+0.16)$ and $(+1.80,0,+0.16)$. The bond angle is 170 degree. Note the different scale in the $1a_1$ plots.



individual orbital contributions. However, inserting the definition of the two-electron Darwin (2.69) into eq. (4.11), and integrating over $\mathbf{r}_2$ (for instance), one obtains:

$$\mathcal{G}_{abcd} = -\frac{\pi}{2c^2} \int g_a(\mathbf{r}_1, \{R_A\}) g_b(\mathbf{r}_1, \{R_A\}) g_c(\mathbf{r}_1, \{R_A\}) g_d(\mathbf{r}_1, \{R_A\}) d\mathbf{r}_1 \quad (4.12)$$

and consequently the mean value of the two-electron Darwin operator reads:

$$\langle \psi | \hat{O}_2 | \psi \rangle = -\frac{\pi}{2c^2} \sum_{ij} \sum_{abcd} \mathcal{A}_a^i \mathcal{A}_b^j \mathcal{A}_c^i \mathcal{A}_d^j \mathcal{G}_{abdc} \quad (4.13)$$

$$= -\frac{\pi}{2c^2} \sum_{ij} \int (\sum_a \mathcal{A}_a^i g_a) (\sum_b \mathcal{A}_b^i g_b) (\sum_c \mathcal{A}_c^i g_c) (\sum_d \mathcal{A}_d^i g_d) d\mathbf{r}_1 \quad (4.14)$$

$$= -\frac{\pi}{2c^2} \sum_{ij} \int \psi_i^2 \psi_j^2 d\mathbf{r}_1 \quad (4.15)$$

The sum can be split into pure core, pure valence, and mixed core-valence contributions:

$$\langle \psi | \hat{O}_2 | \psi \rangle = -\frac{\pi}{2c^2} \left(\sum_{\substack{i=\text{core} \\ j=\text{core}}} \int \psi_i^2 \psi_j^2 d\mathbf{r}_1 + \sum_{\substack{i=\text{valence} \\ j=\text{valence}}} \int \psi_i^2 \psi_j^2 d\mathbf{r}_1 + 2 \sum_{\substack{i=\text{core} \\ j=\text{valence}}} \int \psi_i^2 \psi_j^2 d\mathbf{r}_1 \right) \quad (4.16)$$

In table 4.12 the total two-electron Darwin contribution is split as indicated in eq. (4.16), that is, into a pure core (c-c), mixed core-valence (c-v), and pure valence (v-v) contribution. As for the MV and D1 cases, the core contribution to the effect is by far the biggest, as the core-core part accounts for 86.87 % of the effect at the equilibrium nuclear geometry. The core-valence contribution is about 2.5 times bigger than pure valence.

Table 4.10: One-electron Darwin correction for the electronic ground state for water, calculated at different nuclear geometries. The total correction is decomposed into individual atomic contributions. Energies are in mE_h, bondlengths in a₀ and bondangle in degree.

symmetric stretch (R _{OH₁} =R _{OH₂} , Θ = Θ _e)							
		core		valence			total
R _{OH}		1a ₁	2a ₁	1b ₁	3a ₁	1b ₂	
1.811	O	194.692	8.102	0.000	0.867	0.000	203.661
	H	0.000	0.009	0.020	0.007	0.000	0.036
1.903	O	194.717	8.201	0.000	0.815	0.000	203.733
	H	0.000	0.007	0.018	0.007	0.000	0.033
1.997	O	194.739	8.314	0.000	0.762	0.000	203.814
	H	0.000	0.006	0.017	0.007	0.000	0.030
2.100	O	194.758	8.447	0.000	0.702	0.000	203.907
	H	0.000	0.005	0.015	0.007	0.000	0.027
2.218	O	194.776	8.603	0.000	0.635	0.000	204.014
	H	0.000	0.003	0.014	0.007	0.000	0.025
2.364	O	194.794	8.794	0.000	0.555	0.000	204.143
	H	0.000	0.002	0.013	0.007	0.000	0.023
1.781	O	194.683	8.074	0.000	0.883	0.000	203.639
	H	0.000	0.009	0.020	0.007	0.000	0.037
1.591	O	194.610	7.948	0.000	0.977	0.000	203.535
	H	0.000	0.014	0.025	0.007	0.000	0.047
1.471	O	194.548	7.936	0.000	1.027	0.000	203.512
	H	0.000	0.019	0.030	0.007	0.000	0.056
1.841	O	194.701	8.133	0.000	0.850	0.000	203.684
	H	0.000	0.008	0.019	0.007	0.000	0.035
bend (R _{OH₁} =R _{OH₂} =R _e)							
Θ _{HOH}		core		valence			total

Table 4.10: continued.

		1a ₁	2a ₁	1b ₁	3a ₁	1b ₂	
		1a ₁	2a ₁	1b ₁	3a ₁	1b ₂	
96.43	O	194.696	8.032	0.000	0.998	0.000	203.726
	H	0.000	0.009	0.019	0.008	0.000	0.036
88.34	O	194.699	7.944	0.000	1.142	0.000	203.785
	H	0.000	0.009	0.018	0.009	0.000	0.036
79.57	O	194.702	7.825	0.000	1.317	0.000	203.844
	H	0.000	0.010	0.017	0.010	0.000	0.036
68.78	O	194.705	7.633	1.575	0.000	0.000	203.913
	H	0.000	0.011	0.011	0.014	0.000	0.036
51.90	O	194.707	7.195	2.126	0.000	0.000	204.029
	H	0.000	0.014	0.015	0.009	0.000	0.038
112.77	O	194.687	8.161	0.000	0.737	0.000	203.586
	H	0.000	0.009	0.020	0.006	0.000	0.035
121.80	O	194.681	8.211	0.000	0.603	0.000	203.496
	H	0.000	0.008	0.021	0.005	0.000	0.035
132.77	O	194.673	8.256	0.000	0.445	0.000	203.375
	H	0.000	0.008	0.021	0.004	0.000	0.033
148.87	O	194.660	8.295	0.000	0.228	0.000	203.184
	H	0.000	0.008	0.022	0.002	0.000	0.032
100.02	O	194.694	8.066	0.000	0.938	0.000	203.697
	H	0.000	0.009	0.019	0.008	0.000	0.036
108.00	O	194.690	8.129	0.000	0.810	0.000	203.630
	H	0.000	0.009	0.020	0.007	0.000	0.036
170.00	O	194.647	8.313	0.000	0.027	0.000	202.988
	H	0.000	0.008	0.022	0.000	0.000	0.030

The origin of the relativistic molecular effect is analysed in table 4.13 for the D1 term, and table 4.14 for the MV. In those tables the values for the corrections are reported as relative to a reference geometry, which has been chosen at the nuclear equilibrium configuration. As expected, the $1b_2$ orbital has very little influence on the dependence of the MV correction upon the nuclear configurations, and no contribution at all to the D1. This is a direct consequence of its symmetry: as it lies perpendicular to the molecular plane, it is not significantly affected by changes in the relative position of the nuclei. The $1b_1$ orbital also has little influence on the relativistic molecular effect, compared to other valence orbitals. The big deviations present at small bondangles or small bondlengths have to be attributed to deficiencies of the Hartree-Fock wavefunction at these configurations, as previously discussed, and are not a feature of the relativistic molecular effect. On the other hand, the two other valence orbitals show a strong dependence upon the nuclear geometry. Their total contribution to the relativistic molecular effect for both the MV and D1 terms is strongly reduced as they always act in opposite directions. The only water core orbital, $1a_1$, gives a contribution to the total molecular relativistic effect

Table 4.11: Mass-velocity correction to the electronic ground state for water, at different nuclear geometries. Corrections are in mE_h , with bondlengths in a_0 and bondangle in degrees.

stretch ($R_{\text{OH}_1}=R_{\text{OH}_2}$, $\Theta = \Theta_e$)						
R_{OH}	core	valence				total
	$1a_1$	$2a_1$	$1b_1$	$3a_1$	$1b_2$	
1.471	-239.149	-11.996	-0.850	-2.454	-1.051	-255.501
1.591	-239.236	-12.000	-0.794	-2.358	-1.051	-255.440
1.781	-239.337	-12.178	-0.727	-2.184	-1.058	-255.484
1.811	-239.350	-12.220	-0.719	-2.154	-1.060	-255.503
1.841	-239.362	-12.265	-0.710	-2.124	-1.062	-255.523
1.903	-239.385	-12.365	-0.694	-2.061	-1.066	-255.572
1.997	-239.415	-12.535	-0.673	-1.963	-1.073	-255.659
2.100	-239.441	-12.735	-0.652	-1.855	-1.082	-255.766
2.218	-239.466	-12.972	-0.633	-1.732	-1.093	-255.896
2.364	-239.490	-13.262	-0.613	-1.586	-1.108	-256.059
bend ($R_{\text{OH}_1}=R_{\text{OH}_2}=R_e$)						
Θ_{HOH}	core	valence				total
	$1a_1$	$2a_1$	$1b_1$	$3a_1$	$1b_2$	
51.90	-239.369	-10.881	-3.821	-0.887	-1.067	-256.026
68.78	-239.366	-11.530	-3.087	-0.806	-1.066	-255.854
79.57	-239.363	-11.813	-0.769	-2.746	-1.065	-255.756
88.34	-239.360	-11.989	-0.746	-2.515	-1.064	-255.674
96.43	-239.355	-12.117	-0.731	-2.326	-1.063	-255.592
100.02	-239.353	-12.166	-0.725	-2.247	-1.062	-255.552
108.00	-239.348	-12.259	-0.714	-2.081	-1.059	-255.460
112.77	-239.344	-12.305	-0.709	-1.985	-1.057	-255.400
121.80	-239.336	-12.377	-0.701	-1.809	-1.053	-255.277
132.77	-239.326	-12.441	-0.694	-1.603	-1.047	-255.111
148.87	-239.309	-12.495	-0.687	-1.321	-1.038	-254.850
170.00	-239.292	-12.516	-0.682	-1.062	-1.028	-254.580

which is much less than the one from $2a_1$ or $3a_1$ at all the geometries considered, however it can become comparable to the total valence contribution due to the cancellations discussed above.

In table 4.15 the two-electron Darwin molecular effect is analysed. For the pure stretches, the dominant contribution is given by the pure valence orbitals. However, a small ($\approx 10\%$) correction to it is given by the pure core orbitals. Conversely, for the pure bends, the correction is dominated by the mixed core-valence part. This suggests that the effect along the bend is given by the modifications to the orbitals occurring near the oxygen nucleus to the sp -rehybridisation process, and the requirements of orthogonality between orbitals.

Table 4.12: Two-electron correction to the electronic ground state for water, at different nuclear geometries. Corrections are in mE_h, with bondlengths in a₀ and bondangle in degrees.

stretch ($R_{OH_1}=R_{OH_2}, \Theta = \Theta_e$)				
R_{OH}	c-c	c-v	v-v	total
1.4710	-2.96566	-0.324431	-0.161093	-3.45119
1.5910	-2.96776	-0.320762	-0.148227	-3.43675
1.7810	-2.96966	-0.318051	-0.132904	-3.42061
1.8110	-2.96987	-0.317861	-0.130997	-3.41872
1.8410	-2.97007	-0.317723	-0.129208	-3.41700
1.9030	-2.97043	-0.317581	-0.125857	-3.41387
1.9970	-2.97094	-0.317709	-0.121570	-3.41022
2.1000	-2.97139	-0.318236	-0.117771	-3.40740
2.2180	-2.97176	-0.319196	-0.114293	-3.40525
2.3640	-2.97204	-0.320701	-0.110916	-3.40366
bend ($R_{OH_1}=R_{OH_2}=R_e$)				
Θ_{HOH}	c-c	c-v	v-v	total
96.43	-2.97014	-0.318903	-0.131240	-3.42028
88.34	-2.97031	-0.319847	-0.131516	-3.42167
79.57	-2.97048	-0.320866	-0.131833	-3.42318
68.78	-2.97782	-0.322426	-0.128139	-3.42838
51.90	-2.97987	-0.329408	-0.138330	-3.44761
112.77	-2.96943	-0.316613	-0.130769	-3.41682
121.80	-2.96882	-0.315113	-0.130535	-3.41446
132.77	-2.96796	-0.313112	-0.130221	-3.41130
148.87	-2.96685	-0.309462	-0.129530	-3.40585
100.02	-2.97002	-0.318453	-0.131127	-3.41960
108.00	-2.96970	-0.317347	-0.130897	-3.41795
170.00	-2.96578	-0.304397	-0.128575	-3.39875

Table 4.13: Analysis of the one-electron Darwin molecular effect in water. The equilibrium configuration has been chosen as reference point. The total effect is decomposed into individual atomic contributions. Energies are in cm⁻¹, bondlengths in a₀ and bondangle in degrees.

stretch ($R_{OH_1}=R_{OH_2}, \Theta = \Theta_e$)								
R_{OH}		core	valence				total	total
		1a ₁	2a ₁	1b ₁	3a ₁	1b ₂		
1.471	O	-31.54	-36.42	0.00	35.28	0.00	-1.14	-32.68
	H	0.00	2.17	2.14	0.00	0.00	4.30	4.30
1.591	O	-17.97	-33.95	0.00	24.28	0.00	-9.67	-27.64
	H	0.00	1.21	1.21	-0.01	0.00	2.42	2.42
1.781	O	-2.04	-6.29	0.00	3.56	0.00	-2.74	-4.78
	H	0.00	0.13	0.14	0.00	0.00	0.27	0.27

Table 4.13: continued.

		core	valence					total
		1a ₁	2a ₁	1b ₁	3a ₁	1b ₂	total	
1.841	O	1.92	6.70	0.00	-3.61	0.00	3.09	5.01
	H	0.00	-0.12	-0.13	0.00	0.00	-0.25	-0.25
1.903	O	5.48	21.62	0.00	-11.22	0.00	10.39	15.87
	H	0.00	-0.36	-0.37	0.01	0.00	-0.73	-0.73
1.997	O	10.28	46.46	0.00	-23.04	0.00	23.43	33.70
	H	0.00	-0.66	-0.69	0.01	0.00	-1.34	-1.34
2.100	O	14.53	75.60	0.00	-36.11	0.00	39.49	54.02
	H	0.00	-0.92	-0.99	0.02	0.00	-1.89	-1.89
2.218	O	18.44	109.94	0.00	-50.92	0.00	59.02	77.46
	H	0.00	-1.16	-1.27	0.02	0.00	-2.40	-2.40
2.364	O	22.41	151.85	0.00	-68.48	0.00	83.38	105.78
	H	0.00	-1.38	-1.55	0.03	0.00	-2.90	-2.90
bend (R _{OH₁} =R _{OH₂} =R _e)								
		core	valence					total
Θ_{HOH}		1a ₁	2a ₁	1b ₁	3a ₁	1b ₂	total	
96.43	O	0.89	-15.40	0.00	28.73	0.00	13.33	14.22
	H	0.00	0.06	-0.17	0.18	0.00	0.07	0.07
88.34	O	1.64	-34.68	0.00	60.35	0.00	25.66	27.30
	H	0.00	0.14	-0.39	0.36	0.00	0.11	0.11
79.57	O	2.21	-60.86	0.00	98.88	0.00	38.02	40.23
	H	0.00	0.25	-0.70	0.57	0.00	0.12	0.12
68.78	O	2.79	-102.96	345.75	-190.20	0.00	52.59	55.38
	H	0.00	0.46	-1.87	1.52	0.00	0.11	0.11
51.90	O	3.38	-199.02	466.59	-190.20	0.00	77.37	80.76
	H	0.00	1.09	-1.14	0.43	0.00	0.38	0.38
112.77	O	-1.06	12.95	0.00	-28.35	0.00	-15.39	-16.46
	H	0.00	-0.05	0.13	-0.20	0.00	-0.12	-0.12
121.80	O	-2.31	23.97	0.00	-57.84	0.00	-33.88	-36.19
	H	0.00	-0.09	0.23	-0.42	0.00	-0.28	-0.28
132.77	O	-4.12	33.81	0.00	-92.52	0.00	-58.71	-62.83
	H	0.00	-0.14	0.31	-0.71	0.00	-0.53	-0.53
148.87	O	-6.95	42.40	0.00	-140.17	0.00	-97.77	-104.72
	H	0.00	-0.19	0.38	-1.14	0.00	-0.94	-0.94
100.02	O	0.44	-8.07	0.00	15.58	0.00	7.51	7.95
	H	0.00	0.03	-0.09	0.10	0.00	0.05	0.05
108.00	O	-0.43	5.92	0.00	-12.32	0.00	-6.40	-6.83
	H	0.00	-0.02	0.06	-0.08	0.00	-0.05	-0.05
170.00	O	-9.77	46.19	0.00	-184.19	0.00	-138.00	-147.78
	H	0.00	-0.23	0.41	-1.55	0.00	-1.37	-1.37

Table 4.14: Analysis of the Mass-velocity molecular effect in water. The equilibrium configuration is used as reference point. All energies are in cm^{-1} bondlengths are in a_0 bondangle in degree

stretch ($R_{\text{OH}_1}=R_{\text{OH}_2}, \Theta = \Theta_e$)							
	core	valence					total
R_{OH}	$1a_1$	$2a_1$	$1b_1$	$3a_1$	$1b_2$	total	
1.471	44.06	49.13	-28.80	-65.88	1.96	-43.59	0.47
1.591	25.10	48.22	-16.64	-44.80	1.91	-11.31	13.79
1.781	2.85	9.22	-1.93	-6.49	0.37	1.18	4.03
1.841	-2.67	-9.86	1.84	6.58	-0.40	-1.85	-4.53
1.903	-7.63	-32.00	5.37	20.42	-1.32	-7.53	-15.16
1.997	-14.23	-69.18	10.10	41.88	-2.91	-20.10	-34.33
2.100	-20.05	-113.09	14.56	65.63	-4.86	-37.76	-57.80
2.218	-25.33	-165.10	18.87	92.59	-7.29	-60.94	-86.27
2.364	-30.59	-228.82	23.23	124.67	-10.48	-91.40	-122.00
bend ($R_{\text{OH}_1}=R_{\text{OH}_2}=R_e$)							
	core	valence					total
Θ_{HOH}	$1a_1$	$2a_1$	$1b_1$	$3a_1$	$1b_2$	total	
51.90	-4.21	293.73	-680.81	278.04	-1.56	-110.61	-114.82
68.78	-3.56	151.43	-519.69	295.96	-1.30	-73.60	-77.16
79.57	-2.84	89.24	-11.01	-129.89	-1.16	-52.81	-55.66
88.34	-2.11	50.72	-6.10	-79.22	-0.89	-35.50	-37.61
96.43	-1.15	22.45	-2.63	-37.70	-0.51	-18.39	-19.54
100.02	-0.57	11.75	-1.36	-20.44	-0.30	-10.35	-10.91
108.00	0.56	-8.59	0.97	16.16	0.27	8.82	9.37
112.77	1.39	-18.76	2.11	37.16	0.67	21.18	22.56
121.80	3.02	-34.57	3.83	75.75	1.55	46.56	49.57
132.77	5.38	-48.51	5.36	120.98	2.80	80.62	86.00
148.87	9.05	-60.34	6.90	182.85	4.86	134.28	143.33
170.00	12.78	-65.11	8.07	239.72	7.05	189.73	202.51

From the analysis of the dependence of the relativistic corrections upon the nuclear geometry the following conclusions can be drawn. Firstly, the molecular relativistic effect seems to originate in a volume near the oxygen nucleus. This is suggested by the D1 results, which explicitly show that the hydrogen contribution is negligible, and also from the symmetry a_1 of the orbitals involved. The effect along the bending coordinate is dominated by the $3a_1$ orbital, which is reasonable as this orbital undergoes major distortions when the molecule bends, as it can be seen from comparing figure 4.1 and 4.2. Conversely, along the stretches the $2a_1$ orbital is predominant. Secondly, the effect seems to be caused by the distortions that the two a_1 valence orbitals experience as a consequence of the change of the relative nuclear positions. As a second order effect, the requirement of orthogonality between the different orbitals also generates a core relativistic effect, which can become comparable with the total valence relativistic effect due to cancellations between the contributions of the $2a_1$ and $3a_1$ orbitals.

Table 4.15: Analysis of the two-electron Darwin molecular effect in water. The equilibrium configuration is used as reference point. All energies are in cm^{-1} bondlengths are in a_0 bondangle in degree

stretch ($R_{\text{OH}_1}=R_{\text{OH}_2}, \Theta = \Theta_e$)				
R_{OH}	c-c	c-v	v-v	
1.4710	0.92268	-1.44180	-6.60529	-7.12441
1.5910	0.46263	-0.63649	-0.37816	-3.95543
1.7810	0.04607	-0.41652	-0.41868	-0.41426
1.8410	-0.04362	0.03036	0.39263	0.37938
1.9030	-0.12393	0.06147	1.12801	1.06555
1.9970	-0.23624	0.03342	2.06894	1.86613
2.1000	-0.33508	-0.08210	2.90275	2.48556
2.2180	-0.41622	-0.29294	3.66615	2.95699
2.3640	-0.47747	-0.62314	4.40714	3.30653
bend ($R_{\text{OH}_1}=R_{\text{OH}_2}=R_e$)				
Θ_{HOH}	c-c	c-v	v-v	total
51.90	-2.19506	-2.53409	-1.60946	-6.33860
68.78	-1.74541	-1.00169	0.62732	-2.11979
79.57	-0.13375	-0.65935	-0.18360	-0.97670
88.34	-0.09722	-0.43570	-0.11401	-0.64692
96.43	-0.05892	-0.22854	-0.05337	-0.34083
100.02	-0.03394	-0.12984	-0.02858	-0.19236
108.00	0.03612	0.11295	0.02195	0.17103
112.77	0.09500	0.27408	0.04994	0.41902
121.80	0.23072	0.60328	0.10140	0.93540
132.77	0.41762	1.04234	0.17024	1.63021
148.87	0.66125	1.84354	0.32188	2.82666
170.00	0.89770	2.95510	0.53143	4.38422

4.4 Spectroscopic analysis

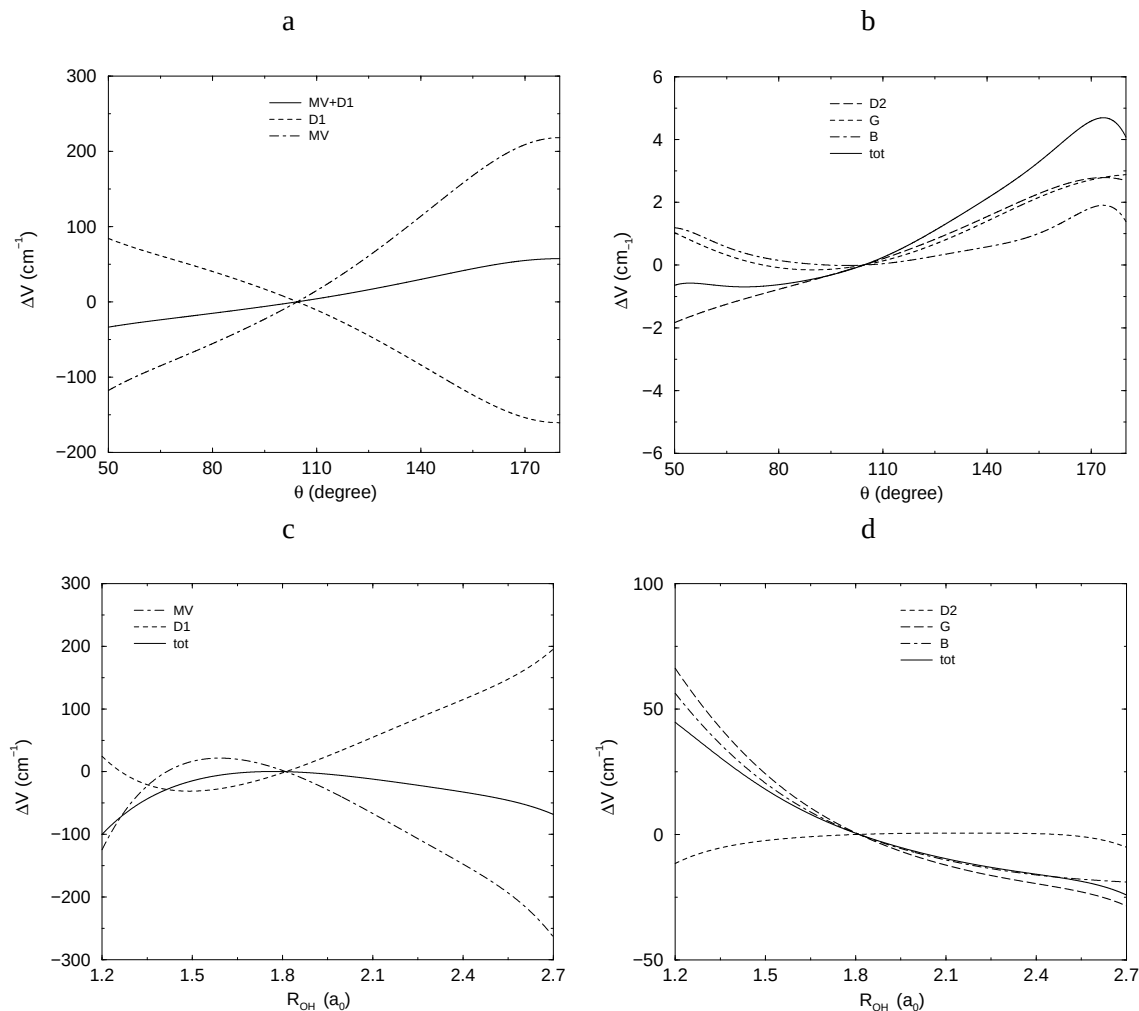
4.4.1 Water

The average absolute values of the relativistic energy corrections to the PES of water are (in mE_h) about -256 , 204 , 3.3 , 7.8 and 7.6 for the MV, D1, D2, G and B terms, respectively. The contribution of each term to the barrier to linearity is much smaller than their absolute values. The MVD1 effect raises it by about 55 cm^{-1} ($\text{MV}=+217 \text{ cm}^{-1}$, $\text{D1}=-162 \text{ cm}^{-1}$), as also reported in Ref. [60, 55]. The D2 term raises the barrier by 2.5 cm^{-1} . Beyond these scalar relativistic effects, the Gaunt correction raises the barrier by 6 cm^{-1} , the correction to it in the Breit operator compensates this effect by 2 cm^{-1} , and consequently the Breit correction raises the barrier by 4 cm^{-1} .

In figure 4.3 (plots a-d) two selected cuts along the relativistic surfaces are plotted, for both the one- (MV,D1) and two-electron corrections (D2,G,B). In particular, the cuts $V(R_e, R_e, \Theta)$ and $V(R, R, \Theta_e)$ are plotted as functions of Θ and R , respectively. The equilibrium point (R_e, R_e, Θ_e) has been chosen as reference energy. From the figure it is possible to notice some features of the corrections. For the one-electron case, the total (MVD1) surface results from a large cancellation between the individual MV and D1 surfaces, which are similar in magnitude but opposite in sign. The variations along the stretch and the bend are of the same order of magnitude. On the other hand, the two-electron surfaces show a qualitatively different behaviour. Firstly, the total correction is dominated by the Breit term. Secondly, the variation along the bend is one order of magnitude smaller than the radial one. Finally, the contribution of two-electron terms to the total molecular relativistic effect is much smaller than the one-electron terms.

Figure 4.4 presents two-dimensional plots of the relativistic surfaces for the MV, D1, MVD1, D2, B, and D2B corrections. The qualitative conclusions drawn from the analysis of figure 4.3 can be repeated in this case. The one-electron MV and D1 terms show a similar behaviour, and tend to cancel each other. This can be seen by comparing the number of lines in the single MV and D1 plots with the MV+D1 figure. The total one-electron surface (e) has an appreciable slope in both the stretching and bending coordinates. Conversely, the total two-electron surface (f) has almost no slope in the bend. The B (d) and D2 (c) surfaces display a different behaviour, and the total two-electron is dominated by the Breit term.

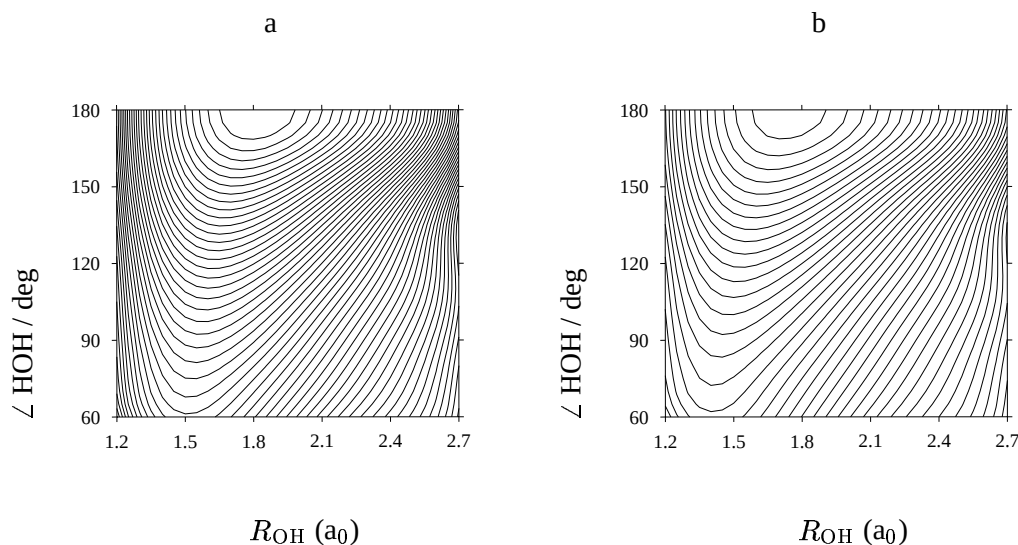
Figure 4.3: Sections through the relativistic correction surfaces for water. In fig a-b the surfaces are cut along the angular coordinate, at $R_1 = R_2 = R_e$. In fig c-d the angle is kept fixed $\Theta = \Theta_e$, and the inter-atomic distances are varied symmetrically.



Tables 4.16, 4.17 and 4.18 summarise calculations for selected vibrational and rotational term values of water, respectively. These calculations were all performed with PESs which are a sum of non-relativistic and relativistic correction surfaces, where the non-relativistic surface is the *ab initio* Born–Oppenheimer (BO) surface of Partridge and Schwenke (PS, section 2.6). As expected from the analysis of the surfaces, the MV and D1 cancel each other, and the total MVD1 contribution is much smaller than the individual ones. Also, because the shifts are calculated exactly, and not in a perturbative approach, the MVD1 shift is not given by the sum of MV and D1, but differs slightly. The total effect of MV is to raise the bending levels, and to lower the stretching ones. Conversely, D1 has the opposite behaviour. However, due to the slightly bigger absolute value of MV compared to D1, the total MVD1 effect is qualitatively the same as MV, i.e., the bends are raised, and the stretches lowered. The effect increases for higher

Figure 4.4: Contour plot of two-electron relativistic correction surfaces for water as a function of the bond angle (in degrees) and the symmetric stretching (in a_0) coordinates.

- (a) Mass-Velocity (MV) surface. The contour lines are separated by 10 cm^{-1} .
 (b) One-electron Darwin (D1) surface. The contour lines are separated by 10 cm^{-1} .
 (c) Two-electron Darwin (D2) surface. The contour lines are separated by 1 cm^{-1} .
 (d) Breit interaction (B) surface. The contour lines are separated by 2.5 cm^{-1} .
 (e) One-electron total (MV+D1) surface. The contour lines are separated by 10 cm^{-1} .
 (f) Two-electron total (D2+B) surface. The contour lines are separated by 2.5 cm^{-1} .



(continue)

band origins. The same happens to the rotational term $J=20(000)$ (table 4.18). The MV effect lowers each level, whereas D1 raises them. Their contribution increases with K_a , although not exactly monotonically. The net MVD1 effect is to lower the energies, but in absolute value is much smaller than the single MV or D1 terms. The PS and PS+MVD1 results reported in table 4.16, 4.17 and 4.18 are not the same as those reported by Kain and co-workers [60, 55] because nuclear instead of middle masses have been used.

The two-electron corrections have a substantial influence on the calculated VBOs. The main contribution is given by the Breit term, and the qualitative behaviour of the total two-electron shift is the same as for the Breit. The Gaunt has the same influence as the Breit, although is 20-30 % bigger in magnitude. Conversely, the D2 term has only a minor influence. As expected, the main deviation is for the stretching bands. The rotational results (see table 4.18) show a similar scenario. The B term is still the dominant two-electron effect, and the shift is negative for all the levels, increasing with K_a . Some important points can be learnt by the above analysis. First, in considering relativistic corrections all the terms at the same level of perturbation theory must be considered at the same time. Neglecting the D1 as opposed to the MV, or the D2 in favour of the Breit, etc., can lead to results which are also qualitatively wrong, as it seems that the various surfaces often act in opposite directions. Second, the two-electron

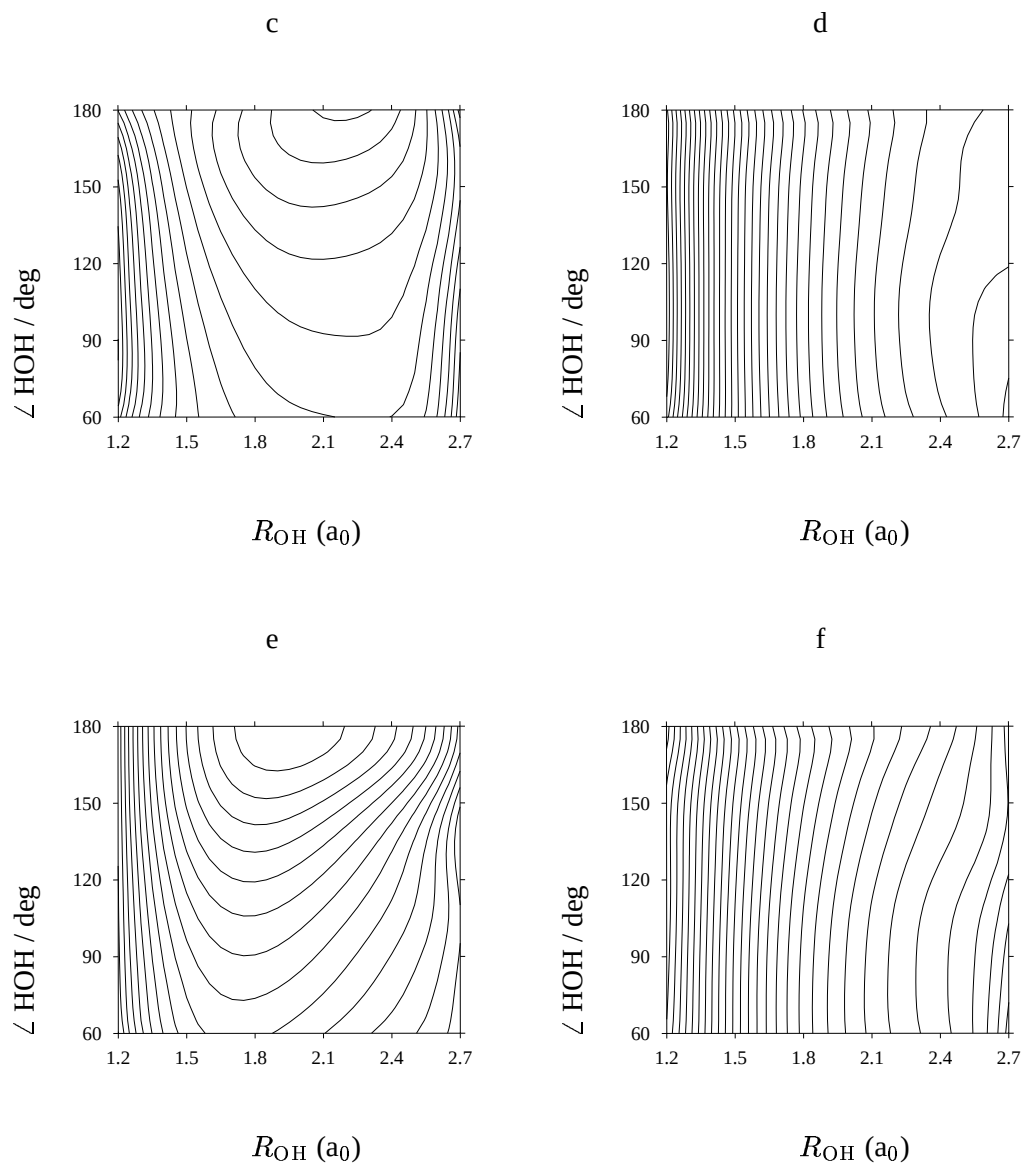


Figure 4.4: continued.

terms considered in this work have a consistent influence on VBOs and rotational levels, and therefore can not be neglected in calculations aiming to spectroscopic accuracy. Finally, these results are fairly insensitive to the level of sophistication of the calculation. The mean deviation between the changes in the Gaunt VBOs determined with basis A and basis B is only 0.05 cm^{-1} , or approximately 2%, with the larger basis B corrections giving slightly larger values. The results for the Breit correction are similar.

Table 4.16: Vibrational band origins, in cm^{-1} , for H_2O , even parity states. Absolute values are given for the *ab initio* PES corresponding to the Born–Oppenheimer (BO) surface of Partridge and Schwenke (see eq. (2.54)), and increments are given for the relativistic one-electron mass-velocity (MV), Darwin (D1), the sum of them (MVD1), the two-electron Darwin (D2), the Gaunt (Gaunt), the full Breit (Breit), and the total two-electron (D2B) surface corrections. Increments are given as individual contributions. Nuclear masses have been used in these calculations.

(ν_1, ν_2, ν_3)	BO	+D1	+MV	+MVD1	+D2	+Gaunt	+Breit	+D2B
(010)	1597.60	−3.52	4.71	1.28	0.09	−0.10	−0.11	−0.02
(020)	3157.14	−7.48	9.98	2.72	0.18	−0.18	−0.21	−0.03
(100)	3661.00	7.77	−10.57	−2.80	−0.05	−0.78	−0.63	−0.68
(030)	4674.88	−12.11	16.10	4.37	0.28	−0.21	−0.29	0.00
(110)	5241.83	4.42	−6.06	−1.56	0.04	−0.89	−0.74	−0.70
(040)	6144.64	−17.78	23.53	6.36	0.40	−0.20	−0.32	0.08
(120)	6784.56	0.68	−1.10	−0.20	0.13	−0.96	−0.84	−0.71
(200)	7208.80	15.53	−21.11	−5.60	−0.09	−1.56	−1.26	−1.36
(002)	7450.86	16.33	−22.11	−5.79	−0.09	−1.65	−1.33	−1.42
(050)	7555.62	−25.25	33.19	8.94	0.54	−0.10	−0.29	0.25
(130)	8286.03	−3.73	4.71	1.37	0.23	−1.01	−0.92	−0.69
(210)	8771.71	12.36	−16.87	−4.42	−0.01	−1.66	−1.37	−1.38
(012)	9008.72	13.45	−18.26	−4.73	−0.01	−1.77	−1.45	−1.47
(220)	10297.00	8.96	−12.30	−3.17	0.07	−1.75	−1.47	−1.40
(300)	10609.14	23.24	−31.65	−8.42	−0.14	−2.32	−1.89	−2.03
(102)	10879.00	23.67	−32.15	−8.50	−0.14	−2.37	−1.92	−2.06
(230)	11782.64	4.95	−7.08	−1.74	0.16	−1.80	−1.56	−1.39
(032)	12021.78	6.61	−9.23	−2.25	0.15	−1.94	−1.66	−1.51
(310)	12151.51	20.38	−27.78	−7.34	−0.06	−2.44	−1.99	−2.05
(112)	12400.72	43.03	−8.59	10.04	0.67	−0.76	−0.78	−0.11
(400)	13839.28	30.62	−41.87	−11.21	−0.18	−3.06	−2.49	−2.67
(122)	13926.37	17.71	−24.70	−6.22	0.02	−2.57	−2.13	−2.11
(202)	14234.86	31.00	−42.24	−11.23	−0.18	−3.09	−2.51	−2.69
(004)	14548.39	32.46	−44.06	−11.60	−0.19	−3.25	−2.63	−2.83
(330)	15125.11	14.13	−19.63	−5.08	0.09	−2.62	−2.21	−2.11
(410)	15358.27	27.35	−36.99	−10.10	−0.10	−3.17	−2.58	−2.69
(212)	15759.25	28.21	−38.49	−10.16	−0.11	−3.20	−2.61	−2.71
(302)	17473.72	19.73	−34.36	−14.02	−0.23	−3.84	−3.10	−3.33
(510)	18407.30	31.72	−46.29	−12.18	−0.13	−3.84	−3.12	−3.25
(610)	21237.93	40.56	−53.68	−13.16	−0.16	−4.48	−3.65	−3.81

Table 4.17: Vibrational band origins, in cm^{-1} , for odd parity H_2O VBOs. Column headings as in 4.16

(ν_1, ν_2, ν_3)	BO	+D1	+MV	+MVD1	+D2	+Gaunt	+Breit	+D2B
(001)	3758.63	8.21	−11.10	−2.90	−0.05	−0.84	−0.67	−0.72
(011)	5336.74	5.05	−6.87	−1.74	0.04	−0.95	−0.79	−0.75

Table 4.17: continued

(ν_1, ν_2, ν_3)	BO	+D1	+MV	+MVD1	+D2	+Gaunt	+Breit	+D2B
(021)	6879.72	1.51	-2.18	-0.45	0.12	-1.04	-0.90	-0.77
(101)	7256.00	15.87	-21.54	-5.68	-0.09	-1.60	-1.29	-1.39
(031)	8384.71	-2.59	3.24	1.02	0.22	-1.09	-0.99	-0.77
(111)	8816.00	12.87	-17.50	-4.56	-0.02	-1.71	-1.41	-1.42
(041)	9846.97	-7.56	9.76	2.79	0.32	-1.10	-1.04	-0.72
(121)	10340.25	9.62	-13.20	-3.38	0.07	-1.80	-1.51	-1.45
(201)	10622.32	23.40	-31.88	-8.47	-0.14	-2.34	-1.90	-2.04
(003)	11040.73	24.47	-33.16	-8.71	-0.14	-2.46	-1.99	-2.13
(131)	11827.31	5.85	-8.23	-2.02	0.15	-1.87	-1.61	-1.45
(211)	12162.98	20.59	-28.07	-7.41	-0.06	-2.46	-2.01	-2.08
(013)	12576.10	21.98	-29.78	-7.76	-0.07	-2.59	-2.11	-2.18
(221)	13666.57	17.81	-24.49	-6.40	0.01	-2.56	-2.13	-2.12
(301)	13841.87	30.67	-41.89	-11.21	-0.18	-3.07	-2.49	-2.68
(071)	13857.06	-35.85	46.30	12.43	0.82	-0.52	-0.68	0.15
(023)	14079.96	19.21	-26.17	-6.76	0.00	-2.70	-2.23	-2.23
(103)	14330.58	31.69	-43.13	-11.43	-0.19	-3.17	-2.57	-2.75
(231)	15135.54	14.43	-19.59	-5.15	0.09	-2.64	-2.23	-2.13
(311)	15361.47	27.99	-38.33	-10.23	-0.11	-3.19	-2.60	-2.71
(033)	15551.12	16.04	-22.01	-5.61	0.08	-2.78	-2.34	-2.26
(113)	15847.27	29.21	-39.76	-10.48	-0.11	-3.29	-2.68	-2.79
(321)	16836.48	27.28	-38.47	-10.03	-0.08	-3.38	-2.78	-2.86
(401)	16911.26	36.67	-48.45	-12.90	-0.20	-3.71	-3.01	-3.21
(123)	17329.30	26.71	-35.23	-9.53	-0.04	-3.40	-2.80	-2.84
(203)	17509.84	38.74	-52.93	-14.12	-0.23	-3.87	-3.14	-3.37
(331)	18283.48	23.54	-33.86	-8.81	0.01	-3.45	-2.87	-2.87
(133)	18777.87	23.89	-32.90	-8.56	0.03	-3.50	-2.91	-2.89
(213)	19006.86	36.31	-49.66	-13.21	-0.16	-3.99	-3.24	-3.40
(501)	19793.84	45.34	-58.37	-14.36	-0.26	-4.43	-3.59	-3.84
(303)	20559.11	45.15	-61.81	-12.00	0.01	-3.50	-3.00	-3.00
(511)	21238.20	40.69	-53.69	-13.13	-0.16	-4.48	-3.65	-3.81
(601)	22540.47	50.76	-71.09	-19.53	-0.31	-5.07	-4.09	-4.40
(521)	22647.89	35.02	-47.73	-11.70	-0.06	-4.48	-3.69	-3.74

Table 4.18: Rotational term values $J=20$ (000), in cm^{-1} , for H_2O . For explanation of column headings see Table 4.16. The values relative to the Breit correction (+Breit), are reported uncorrectly in table 2 of ref. [124].

(J_{K_a, K_c})	BO	+MV	+D1	+MVD1	+D2	+Gaunt	+Breit	+D2B
(20 _{0,20})	4049.43	-4.07	3.60	-0.45	0.07	-1.06	-0.89	-0.82
(20 _{1,19})	4413.59	-4.38	3.88	-0.47	0.07	-1.16	-0.97	-0.89
(20 _{2,18})	4740.02	-4.34	3.88	-0.42	0.08	-1.23	-1.03	-0.94
(20 _{3,17})	5033.33	-4.00	3.64	-0.29	0.09	-1.29	-1.08	-0.98
(20 _{4,16})	5293.79	-3.15	3.00	-0.04	0.11	-1.32	-1.11	-1.00
(20 _{5,15})	5515.11	-1.08	1.38	0.53	0.14	-1.31	-1.11	-0.97
(20 _{6,14})	5682.88	2.26	-1.07	1.41	0.18	-1.25	-1.08	-0.89
(20 _{7,13})	5814.21	2.35	-0.84	1.41	0.19	-1.28	-1.10	-0.91
(20 _{8,12})	5968.82	-2.30	2.80	0.21	0.14	-1.45	-1.22	-1.08
(20 _{9,11})	6172.72	-7.23	6.44	-1.01	0.09	-1.63	-1.35	-1.26
(20 _{10,10})	6409.30	-11.05	9.29	-1.96	0.05	-1.79	-1.47	-1.42
(20 _{11,9})	6666.05	-14.48	11.88	-2.81	0.02	-1.93	-1.58	-1.56
(20 _{12,8})	6937.35	-17.81	14.40	-3.64	-0.01	-2.08	-1.69	-1.70
(20 _{13,7})	7219.57	-21.10	16.88	-4.46	-0.04	-2.23	-1.80	-1.84
(20 _{14,6})	7509.69	-24.36	19.35	-5.27	-0.07	-2.37	-1.91	-1.98
(20 _{15,5})	7804.96	-27.62	21.80	-6.08	-0.10	-2.52	-2.01	-2.11
(20 _{16,4})	8102.72	-30.87	24.25	-6.89	-0.13	-2.66	-2.12	-2.25
(20 _{17,3})	8400.30	77.75	26.71	-7.71	-0.16	-2.80	-2.23	-2.39
(20 _{18,2})	8694.85	-37.42	29.18	-8.53	-0.19	-2.94	-2.33	-2.52
(20 _{19,1})	8983.13	-40.77	31.70	-9.38	-0.22	-3.08	-2.43	-2.66
(20 _{20,0})	9261.11	-44.24	34.29	-10.25	-0.26	-3.21	-2.53	-2.79

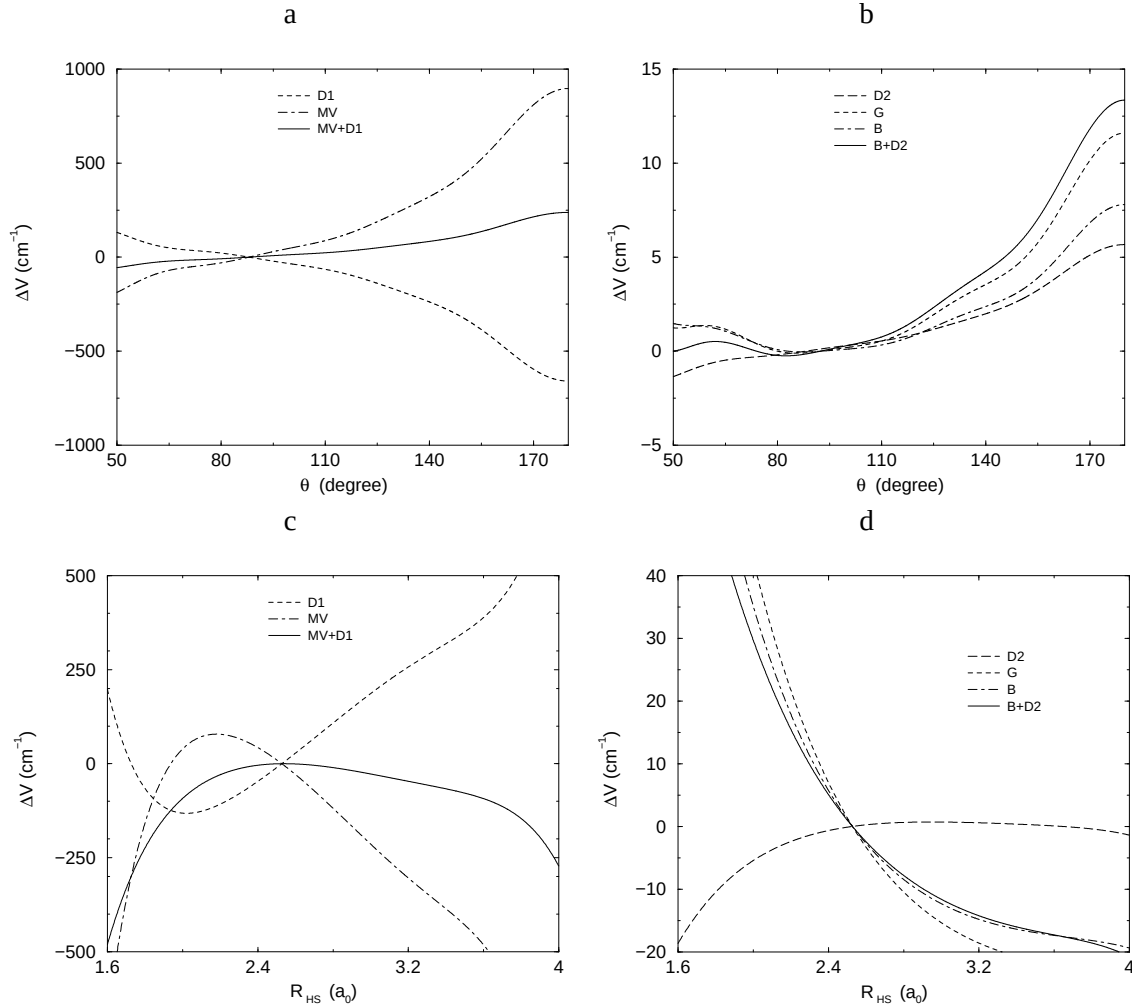
4.4.2 Hydrogen sulphide

The average absolute values of relativistic energy corrections to the PES for H_2S are much bigger than the corresponding for water, being, in mE_h , approximately -4600 , 3500 , -33 , 95 and 88 for the MV, D1, D2, G and B term respectively. The MV term lowers height of the barrier height by 892 cm^{-1} , whereas the D1 raises it by 661 cm^{-1} , so the total one-electron effect is -233 cm^{-1} [61]. The two-electron correction to the barrier height is minimal. The D2 lowers it, by 5.36 cm^{-1} , the B term adds to it further 9.50 cm^{-1} (of which 13.7 from the Gaunt operator, and $+4.2$ from the retardation part), so that the total two-electron effect is of -14.9 cm^{-1} , the same order of magnitude as in water, despite the big difference in the absolute values of the corrections.

Figure 4.5 (plots a-d) shows two cuts along the MV and D1 surfaces (plots a,c) and the B,G and D2 surfaces (plots b,d). The qualitative behaviour of the corrections is the same as in water: the MV and D1 have a similar slope, but with opposite signs, and the total MVD1 correction arises from a big cancellation. On the other hand, the Breit surface dominates the two-electron correction. Also, the MV and D1 surfaces present an appreciable slope in both cuts, whereas the variation of the two-electron surfaces along the radial coordinate is much smaller than along the angular coordinate.

In figure 4.6 contour plots of the surfaces are shown. Again, the total MVD1 term is the result of a big cancellations between the MV and D1, as can be seen by the larger number of lines in the MV and D1 plots as opposed in the MVD1 plot. The dominating two-electron effect is the Breit term. The two-electron surfaces are almost constant along the radial coordinate.

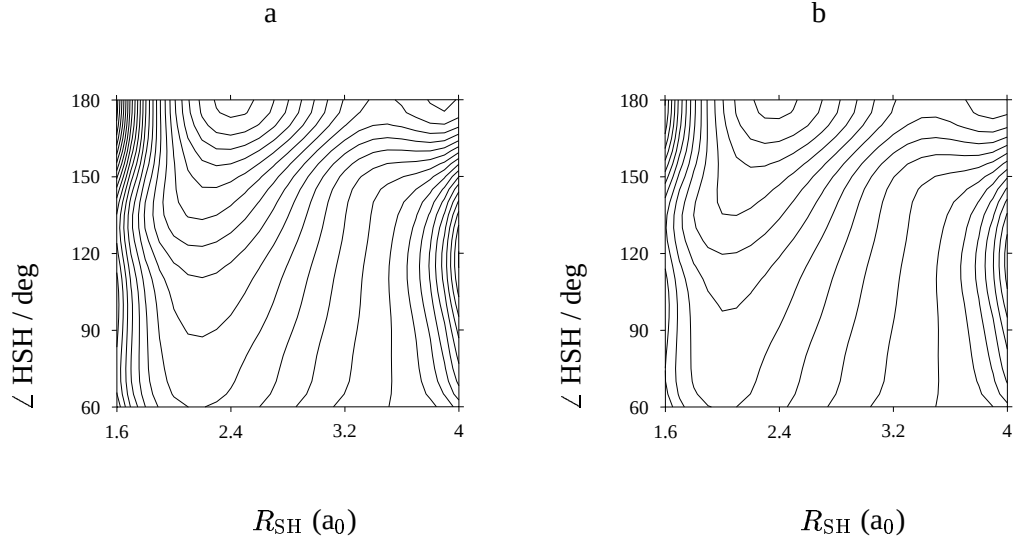
Figure 4.5: Sections through the relativistic correction surfaces for H_2S . In fig a-b the surface is cut along the angular coordinate, at $R_1 = R_2 = R_e$. In fig c-d the angle is kept fixed $\Theta = \Theta_e$, and the inter-atomic distances are varied symmetrically.



The influence of relativistic corrections on the vibrational band origins and on the $J=17$ (000) rotational term is presented in tables 4.19, for even parity VBOs, 4.20 for odd parity VBOs, and 4.21 for the rotational term. The effect of the MV term is to lower the stretching band origins, and it is almost completely negligible on the pure bending bands. As expected, the D1 partially compensates it, so that the net one-electron effect is much smaller than the individual D1 or MV. The maximum shift is about 20 cm^{-1} . On the other hand, the D2 correction is much smaller than the Breit. The total two-electron correction is negative for all the band origins, and increases with the energy of the levels, up to a maximum value of -2 cm^{-1} for the highest band considered. The effect of the relativistic corrections is as follows: the MV still dominates the one-electron correction, but not totally, so that the total MVD1 is not constant in sign. The absolute value of the shift increase with K_a although not monotonically,

Figure 4.6: Contour plot of two-electron relativistic correction surfaces for H_2S as a function of the bond angle (in degrees) and the symmetric stretching (in a_0) coordinates.

- (a) Mass-Velocity (MV) surface. The contour lines are separated by 100 cm^{-1} .
- (b) One-electron Darwin (D1) surface. The contour lines are separated by 100 cm^{-1} .
- (c) Two-electron Darwin (D2) surface. The contour lines are separated by 1 cm^{-1} .
- (d) Breit interaction (B) surface. The contour lines are separated by 0.2 cm^{-1} .
- (e) One-electron total (MV+D1) surface. The contour lines are separated by 100 cm^{-1} .
- (f) Two-electron total (D2+B) surface. The contour lines are separated by 1 cm^{-1} .



(continue)

and reaches a maximum of 4 cm^{-1} . The D1 correction is negligible. The Breit term lowers all the levels, with a maximum shift of -1.1 cm^{-1} .

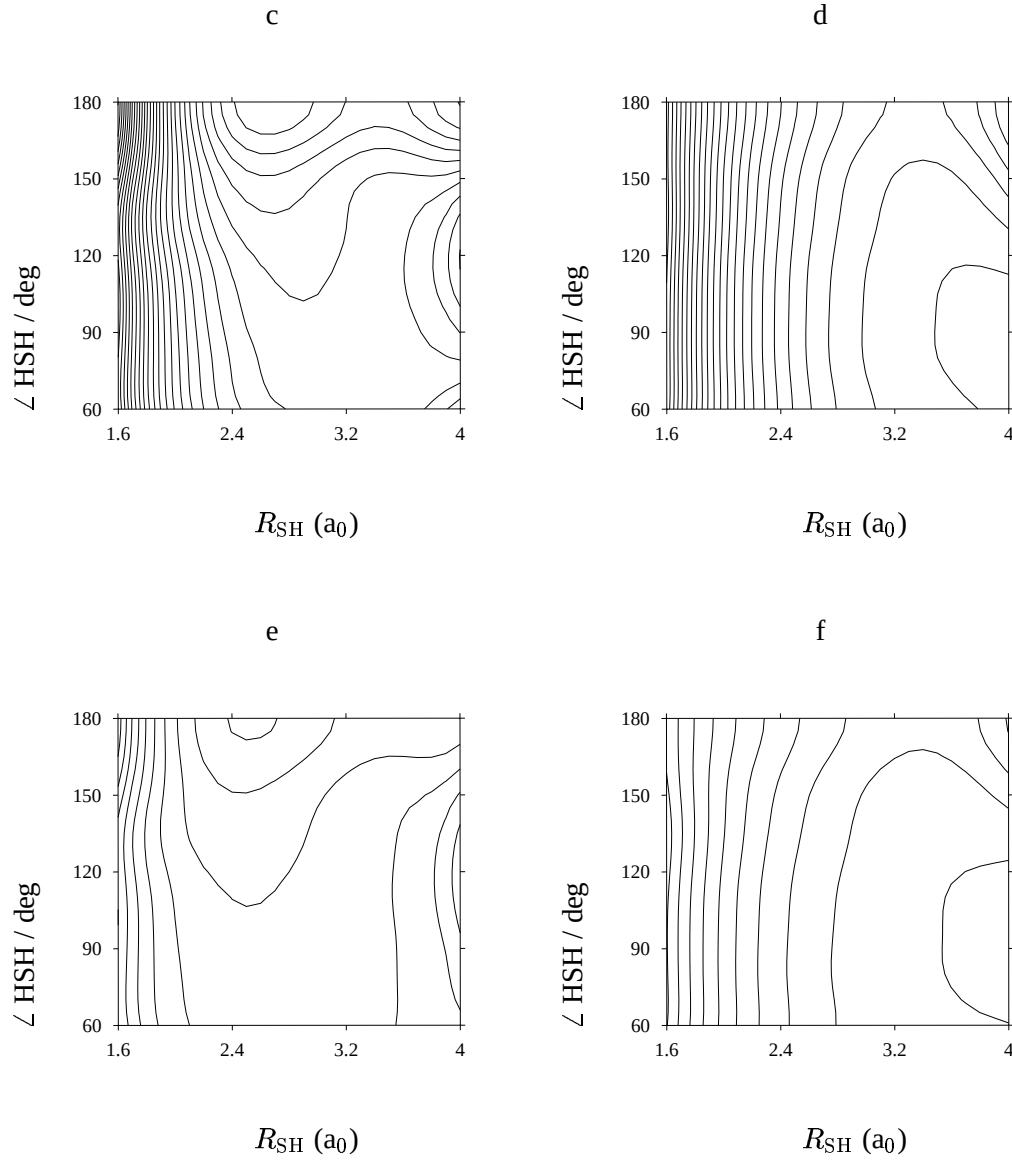


Figure 4.6: continued.

Table 4.19: Vibrational band origins, in cm^{-1} , for H_2S , even parity states. Column headings as in 4.16. The Born-Oppenheimer surface is the FCI-CBS from ref. [61], including also the core-valence correction.

(ν_1, ν_2, ν_3)	BO	+ MV	+D1	+MVD1	+D2	+Gaunt	+Breit	+D2B
(010)	1182.58	-0.27	0.66	0.68	0.03	-0.16	-0.13	-0.10
(020)	2359.24	0.73	0.13	1.49	0.08	-0.26	-0.22	-0.15
(100)	2621.92	-18.41	14.14	-4.34	-0.05	-0.53	-0.40	-0.45
(030)	3524.40	1.79	-0.59	2.18	0.12	-0.35	-0.31	-0.19
(110)	3787.24	-18.74	14.83	-3.76	-0.01	-0.68	-0.53	-0.54
(040)	4674.72	2.13	-0.89	2.60	0.15	-0.45	-0.39	-0.24
(120)	4947.13	-18.10	14.55	-3.09	0.03	-0.78	-0.62	-0.59
(200)	5161.40	-35.95	27.61	-8.42	-0.09	-1.05	-0.80	-0.89
(002)	5258.78	-35.87	27.60	-8.37	-0.09	-1.08	-0.83	-0.91
(050)	5808.66	1.40	-0.48	2.70	0.18	-0.57	-0.50	-0.31
(130)	6094.59	-17.75	14.31	-2.59	0.07	-0.87	-0.70	-0.64
(210)	6305.83	-36.22	28.26	-7.89	-0.05	-1.20	-0.93	-0.98
(012)	6402.09	-36.29	28.36	-7.85	-0.05	-1.22	-0.95	-1.00
(102)	7602.14	-53.14	40.79	-12.44	-0.13	-1.56	-1.19	-1.32
(300)	7776.98	-54.56	41.89	-12.80	-0.13	-1.57	-1.20	-1.33
(112)	8725.01	-53.48	41.50	-12.01	-0.10	-1.71	-1.31	-1.41
(202)	9946.60	-69.97	53.69	-16.42	-0.17	-2.06	-1.56	-1.74
(400)	10222.71	-43.29	55.06	-16.83	-0.18	-2.08	-1.58	-1.76
(212)	11047.27	-70.39	54.45	-16.09	-0.14	-2.20	-1.68	-1.82
(302)	12195.10	-86.22	66.16	-20.31	-0.21	-2.54	-1.93	-2.14
(024)	12526.25	-72.43	56.24	-16.04	-0.11	-2.35	-1.82	-1.93
(104)	12568.90	-88.29	67.73	-20.72	-0.22	-2.58	-1.96	-2.18
(520)	14340.97	-94.87	50.43	-20.37	-0.17	-2.77	-2.12	-2.29
(600)	14349.26	-94.77	55.88	-23.69	-0.23	-3.03	-2.31	-2.54

Table 4.20: Vibrational band origins, in cm^{-1} , for odd parity H_2S VBOs. Column headings as in 4.16 and 4.19

(ν_1, ν_2, ν_3)	BO	+ MV	+D1	+MVD1	+D2	+Gaunt	+Breit	+D2B
(001)	2636.12	-17.61	13.57	-4.08	-0.04	-0.55	-0.42	-0.47
(011)	3797.45	-17.88	14.24	-3.45	-0.01	-0.70	-0.55	-0.56
(021)	4953.05	-17.24	13.97	-2.77	0.03	-0.80	-0.64	-0.61
(101)	5163.41	-35.71	27.44	-8.34	-0.09	-1.06	-0.81	-0.90
(031)	6097.09	-16.79	13.68	-2.26	0.07	-0.90	-0.72	-0.65
(111)	6306.64	-36.05	28.15	-7.83	-0.05	-1.21	-0.93	-0.98
(121)	7444.26	-35.82	28.15	-7.29	-0.02	-1.31	-1.02	-1.04
(201)	7602.22	-53.10	40.77	-12.43	-0.13	-1.56	-1.19	-1.32
(003)	7803.96	-52.99	40.76	-12.33	-0.12	-1.62	-1.24	-1.37
(211)	8724.96	-53.47	41.49	-12.01	-0.10	-1.71	-1.31	-1.41
(301)	9946.60	-69.97	53.68	-16.42	-0.17	-2.06	-1.56	-1.74
(103)	10228.61	-71.13	54.62	-16.64	-0.17	-2.10	-1.60	-1.77
(311)	11047.27	-70.39	54.45	-16.09	-0.14	-2.20	-1.68	-1.82
(203)	12195.10	-86.22	66.16	-20.30	-0.21	-2.54	-1.93	-2.14
(401)	12569.39	-88.16	67.64	-20.68	-0.22	-2.58	-1.96	-2.18
(421)	14340.96	-94.85	56.54	-20.36	-0.17	-2.77	-2.12	-2.29
(501)	14349.27	-65.09	77.94	-13.85	0.01	-3.32	-2.79	-2.78

Table 4.21: Rotational term values $J=17$ (000), in cm^{-1} , for H_2S . For explanation of column headings see Table 4.16.

(J_{K_a, K_c})	BO	+MV	+D1	+MVD1	+D2	+Gaunt	+Breit	+D2B
(17 _{0,17})	1524.93	-4.03	3.96	-0.03	0.04	-0.49	-0.40	-0.36
(17 _{1,16})	1684.25	-4.44	4.37	-0.03	0.04	-0.54	-0.44	-0.40
(17 _{2,15})	1831.88	-4.80	4.73	-0.03	0.05	-0.59	-0.48	-0.43
(17 _{3,14})	1968.28	-5.09	5.03	-0.01	0.05	-0.63	-0.51	-0.46
(17 _{4,13})	2093.80	-5.32	5.27	0.01	0.06	-0.67	-0.54	-0.49
(17 _{5,12})	2208.69	-5.48	5.44	0.04	0.06	-0.70	-0.57	-0.51
(17 _{6,11})	2313.12	-5.54	5.53	0.10	0.06	-0.73	-0.60	-0.53
(17 _{7,10})	2407.13	-5.46	5.51	0.18	0.07	-0.76	-0.62	-0.55
(17 _{8,9})	2490.41	-5.13	5.25	0.32	0.07	-0.77	-0.63	-0.56
(17 _{9,8})	2561.54	-4.12	4.37	0.65	0.08	-0.78	-0.64	-0.56
(17 _{10,7})	2616.73	-1.86	2.64	1.27	0.09	-0.77	-0.64	-0.54
(17 _{11,6})	2657.46	-0.81	2.39	1.49	0.10	-0.77	-0.64	-0.54
(17 _{12,5})	2699.19	-3.72	5.03	0.71	0.09	-0.82	-0.67	-0.59
(17 _{13,4})	2752.86	-8.15	8.27	-0.37	0.06	-0.88	-0.72	-0.65
(17 _{14,3})	2814.34	-11.78	10.91	-1.23	0.05	-0.94	-0.76	-0.71
(17 _{15,2})	2877.88	-15.10	13.39	-2.03	0.03	-0.99	-0.80	-0.76
(17 _{16,1})	2939.50	-18.46	15.95	-2.85	0.02	-1.04	-0.83	-0.82
(17 _{17,0})	2992.01	-22.86	19.19	-3.91	-0.01	-1.09	-0.87	-0.87

Conclusions

5.1 Spectroscopic analysis

In the previous chapters we have analysed in detail several corrections to the standard Born-Oppenheimer non-relativistic molecular Hamiltonian, including adiabatic and non-adiabatic effects (chap. 3), and the mass-velocity, one- and two-electron Darwin, and the Breit and Gaunt terms (chap. 4). The main focus has been in showing how these corrections affect selected vibrational band origins and rotational terms. In this section we will look at how they affect the agreement between theory and experiment. Firstly, in subsection 5.1.1 their influence on the barrier to linearity is summarised, and compared with the most recent determinations of the barrier to linearity. Finally, in subsection 5.2.1 the effect of the various corrections on the agreement between theory and experiment is discussed.

5.1.1 Barrier to linearity

To date, the most accurate prediction of the inversion barrier for water has been determined by Kain *et al.* [93]. They showed that with the introduction of a simple angular correction to Partridge and Schwenke’s potential energy surface it is possible to account for much of the error in the prediction of vibrational band origins. As a result of their analysis they predicted the barrier to be $11105 \pm 5 \text{ cm}^{-1}$.

A summary of the state-of-the-art predictions for the height of the barrier to linearity of water is given in table 5.1, where we report the two semi-empirical values of Partridge and Schwenke [20] and Kain *et al.* [93], a series of high-quality purely *ab initio* investigations by Császár and co-workers [32, 40, 41], and the effect of all the small terms presented in the two previous chapters. All the corrections presented in this work have only a small influence on the barrier to linearity. In particular, they do not reduce the substantial disagreement ($+50 \text{ cm}^{-1}$) between the values of Kain *et al.*, and the purely *ab initio* of Partridge and Schwenke, but rather they increase the discrepancy. This behaviour suggests that the major source of error in the PS surface is connected to a poor convergence in the electronic correlation energy. This

Table 5.1: Comparison of predicted barrier to linearity (in cm^{-1}) for water. The equilibrium geometry is given by $R_{OH_1} = R_{OH_2} = 1.811 a_0$, $\Theta = 104.52^\circ$, and the linear geometry is $R_{OH_1} = R_{OH_2} = 1.764 a_0$, $\Theta = 180^\circ$.

^a mass-velocity and one-electron Darwin terms (MVD1)

^b several methods and basis sets, with the inclusion of MVD2 (mass-velocity, one- and two-electron Darwin) and BODC (SCF) effects

^c Quantum Monte Carlo

^d Second order Møller-Plesset complete basis set (CBS), with MVD2 and BODC (SCF) effects

^e MVD2+Breit

^f MVD2B+ BODC (CASSCF) + diagonal non-adiabatic (table 3.3)

<i>ab initio</i>	PS1 [20]	11155
<i>ab initio</i>	PS1+MVD1 ^a [60]	11192
semi-emp.	PS2 [20]	11128
semi-emp.	Kain <i>et al.</i> [93]	11105 ± 5
<i>ab initio</i>	Császár <i>et al.</i> ^b [40]	11046 ± 70
<i>ab initio</i>	Tarczay <i>et al.</i> ^b [41]	11127 ± 35
<i>ab initio</i>	Baer ^c [125]	11050 ± 80
<i>ab initio</i>	Valeev <i>et al.</i> ^d [32]	11119 ± 15
this work (<i>ab initio</i>)	PS1+MVD2B ^e	11214
this work (<i>ab initio</i>)	PS1+MVD2B ^d ^f	11197

hypothesis is also confirmed by the work of Császár and co-workers, whose series of results for the barrier height seem to converge toward the value of Kain *et al.*.

Finally, it is interesting to compare the work of Császár and co-workers [40] with that of Baer [125]. Császár and co-workers employed several high quality *ab initio* “conventional” methods to obtain the best possible *ab initio* value for the barrier height. Alternatively, the Quantum Monte Carlo method used by Baer offers a different route to a full CI complete basis set calculation. This method is expected to have a better scaling with system size than deterministic high-correlation methods, although it is not yet as accurate.

5.1.2 Rotational-vibrational levels

In tables 5.2 and 5.3 the difference between observed and calculated energy levels is reported for selected VBOs and the $J=20$ (000) rotational term, respectively. We collected all the corrections considered in the previous chapters in four groups: (i) one-electron first order relativistic corrections, comprising the MV and D1 terms (MVD1), (ii) two-electron corrections, including the D2 and Breit terms (D2B), (iii) adiabatic, calculated using the CASSCF surface, and (iv) non-adiabatic, represented by the diagonal averaged terms shown in table 3.3. For the vibrational band origins (VBOs) the agreement between observed and calculated levels is poor, with differences as high as 30 cm^{-1} . The standard deviation σ between obs. and calc., reported in the last row of table 5.2, is about 12 cm^{-1} when all the corrections are included.

The largest errors occur in the pure bending states, whereas the pure stretches are much more accurate. Furthermore, for the pure bending states, the difference obs.–calc. is generally negative, meaning that the levels are over-estimated. This is in line with the analysis of the previous subsection and other works [93], that is, that the current *ab initio* barrier to linearity is an over-estimate of its exact value. Similarly, the calculated rotational term differs significantly from the observed levels. The error increases rapidly with K_a . The high K_a rotational levels sample the small θ part of the PES, and thus give the opposite behaviour to the bending VBOs, that is, they are underestimated. Furthermore the inclusion of the non-adiabatic effects, although they are small, slightly worsens the agreement between observations and calculations.

On the other hand, the inclusion of relativistic corrections, despite leaving the average discrepancy between theory and experiment mostly unchanged, improves significantly the representation of the levels, making their error smoother. It is thus possible to improve the surface by combining the *ab initio* results with a fit to some experimental data, so as to produce a semi-empirical surface of 0.1 cm^{-1} accuracy for all known levels [126].

Table 5.2: Comparison between calculated and observed VBOs for water. The results are given as obs.-calc., in cm^{-1} .

^a PS1 potential

^b PS1 + MVD1 correction

^c PS1 + MVD1 + D2B

^d PS1 + MVD1 + D2B + (CASSCF) BODC

^e PS1 + MVD1 + D2B + full non-BO. (BODC + non-ad. from table 3.3)

(ν_1, ν_2, ν_3)	obs [87]	BO ^a	+MVD1 ^b	+D2B ^c	+ad ^d	+non-BO ^e
(010)	1594.75	−2.86	−4.14	−4.12	−3.71	−3.65
(020)	3151.63	−5.51	−8.22	−8.19	−7.31	−7.19
(100)	3657.05	−3.94	−1.14	−0.46	−0.98	−0.25
(030)	4666.79	−8.09	−12.46	−12.46	−11.02	−10.84
(110)	5234.98	−6.85	−5.29	−4.59	−4.74	−3.97
(040)	6134.01	−10.62	−16.99	−17.06	−15.01	−14.78
(120)	6775.09	−9.47	−9.27	−8.55	−8.28	−7.45
(200)	7201.54	−7.26	−1.66	−0.31	−1.50	−0.11
(002)	7445.05	−5.81	−0.02	1.40	0.06	1.53
(050)	7542.44	−13.19	−22.12	−22.37	−19.59	−19.31
(130)	8273.98	−12.06	−13.43	−12.73	−12.00	−11.11
(210)	8761.58	−10.13	−5.71	−4.33	−5.23	−3.80
(060)	8869.95	−16.38	−28.97	−29.57	−25.81	−25.50
(012)	9000.14	−8.58	−3.85	−2.38	−3.47	−1.96
(220)	10284.37	−12.63	−9.47	−8.07	−8.64	−7.15
(300)	10599.69	−9.45	−1.07	0.95	−1.20	0.79
(102)	10868.88	−10.13	−1.63	0.43	−1.44	0.66
(230)	11767.39	−15.25	−13.51	−12.12	−12.33	−10.78
(032)	12007.78	−14.00	−11.76	−10.25	−10.72	−9.09
(310)	12139.32	−12.20	−4.90	−2.85	−4.82	−2.79
(112)	12407.66	−13.00	−6.94	−6.06	−5.80	−3.94
(400)	13828.28	−11.01	0.06	2.73	−0.61	1.91
(122)	13910.90	−15.48	−9.26	−7.15	−8.56	−6.38

Table 5.2: continued

(ν_1, ν_2, ν_3)	obs [87]	BO ^a	+MVD1 ^b	+D2B ^c	+ad ^d	+non-BO ^e
(202)	14221.16	-13.70	-2.51	0.18	-2.39	0.30
(004)	14537.50	-10.89	0.70	3.53	0.50	3.29
(330)	15108.24	-16.87	-11.83	-9.71	-11.29	-9.14
(410)	15344.50	-13.77	-3.84	-1.15	-4.37	-1.84
(212)	15742.80	-16.46	-6.34	-3.62	-6.08	-3.36
(302)	17458.35	-15.36	-1.48	1.86	-1.82	1.41
(510)	18392.97	-14.33	-2.22	1.02	-3.61	-0.68
(610)	21221.57	-16.36	-2.00	1.82	-4.03	-0.68
(001)	3755.93	-2.70	0.19	0.91	0.24	0.99
(011)	5331.27	-5.47	-3.74	-2.98	-3.34	-2.53
(021)	6871.52	-8.20	-7.74	-6.97	-6.94	-6.06
(101)	7249.82	-6.18	-0.50	0.89	-0.46	0.94
(031)	8373.85	-10.86	-11.89	-11.12	-10.65	-9.71
(111)	8807.00	-9.00	-4.44	-3.01	-4.10	-2.65
(041)	9833.58	-13.39	-16.18	-15.45	-14.52	-13.51
(121)	10328.73	-11.52	-8.15	-6.70	-7.48	-5.96
(201)	10613.35	-8.96	-0.54	1.51	-0.73	1.27
(003)	11032.41	-8.32	0.38	2.51	0.34	2.48
(131)	11813.21	-14.10	-12.09	-10.63	-11.09	-9.51
(211)	12151.25	-11.72	-4.36	-2.28	-4.34	-2.30
(013)	12565.01	-11.10	-3.34	-1.15	-3.16	-0.97
(221)	13652.66	-13.91	-7.56	-5.44	-7.31	-5.21
(301)	13830.94	-10.94	0.13	2.80	-0.55	1.96
(071)	13835.37	-21.69	-34.12	-34.26	-31.08	-29.93
(023)	14066.19	-13.77	-7.01	-4.78	-6.60	-4.35
(103)	14318.81	-11.76	-0.39	2.37	-0.55	2.17
(231)	15119.03	-16.51	-11.41	-9.27	-10.94	-8.77
(311)	15347.96	-13.51	-3.45	-0.74	-4.03	-1.48
(033)	15534.71	-16.41	-10.80	-8.54	-10.16	-7.85
(113)	15832.76	-14.50	-4.07	-1.27	-4.11	-1.36
(321)	16821.64	-14.84	-4.90	-2.03	-5.47	-2.78
(401)	16898.84	-12.42	0.56	3.75	-0.78	2.13
(123)	17312.54	-16.76	-7.28	-4.44	-7.18	-4.37
(203)	17495.53	-14.31	-0.34	3.03	-0.87	2.35
(331)	18265.82	-17.66	-8.98	-6.10	-9.40	-6.66
(411)	18393.31	-14.54	-2.53	0.70	-3.88	-0.95
(213)	18989.96	-16.90	-3.86	-0.46	-4.40	-1.15
(501)	19781.10	-12.74	3.07	6.91	0.90	4.26
(303)	20543.14	-15.98	-4.04	-2.13	-3.52	-0.78
(511)	21221.83	-16.37	-2.02	1.79	-4.06	-0.71
(601)	22529.44	-11.03	7.61	12.08	4.28	8.02
(521)	22629.29	-18.60	-6.05	-2.30	-8.01	-4.66
σ (cm ⁻¹)		17.90	10.76	13.00	12.35	11.92

Table 5.3: Comparison between observed and calculated rotational term values $J=20$, in cm^{-1} , for the vibrational ground state of water. For explanation of column headings see Table 5.2.

(J_{K_a, K_c})	obs [87]	BO ^a	+MVD1 ^b	+D2B ^c	+ad ^d	+non-BO ^e
(20 _{0,20})	4048.25	-1.57	-1.12	-0.30	-0.14	-0.15
(20 _{1,19})	4412.32	-1.70	-1.23	-0.34	-0.16	-0.17
(20 _{2,18})	4738.62	-1.88	-1.46	-0.52	-0.30	-0.32
(20 _{3,17})	5031.80	-2.08	-1.79	-0.81	-0.54	-0.56
(20 _{4,16})	5292.11	-2.32	-2.28	-1.29	-0.94	-0.96
(20 _{5,15})	5513.23	-2.68	-3.21	-2.24	-1.74	-1.77
(20 _{6,14})	5680.79	-3.12	-4.53	-3.63	-2.90	-2.94
(20 _{7,13})	5812.07	-3.18	-4.59	-3.67	-2.94	-2.97
(20 _{8,12})	5966.83	-2.77	-2.99	-1.90	-1.46	-1.48
(20 _{9,11})	6170.84	-2.40	-1.38	-0.12	0.03	0.02
(20 _{10,10})	6407.45	-2.18	-0.22	1.20	1.13	1.13
(20 _{11,9})	6664.17	-2.03	0.78	2.34	2.07	2.08
(20 _{12,8})	6935.42	-1.93	1.71	3.41	2.96	2.97
(20 _{13,7})	7217.57	-1.84	2.62	4.46	3.82	3.84
(20 _{14,6})	7507.58	-1.80	3.47	5.45	4.63	4.65
(20 _{15,5})	7802.71	-1.78	4.30	6.42	5.41	5.44
(20 _{16,4})	8100.28	-1.81	5.08	7.33	6.14	6.18
(20 _{17,3})	8397.65	-1.86	5.84	8.23	6.86	6.89
(20 _{18,2})	8691.92	-1.97	6.56	9.09	7.53	7.57
(20 _{19,1})	8979.88	-2.11	7.27	9.92	8.18	8.21
(20 _{20,0})	9257.45	-2.33	7.92	10.71	8.76	8.80

5.2 Comments and future work

5.2.1 Toward a fully *ab initio* calculation of water vibrational-rotational levels of spectroscopic accuracy

The results presented in tables 5.2 and 5.3 highlight quite dramatically that the major problem in *ab initio* calculation of water vibrational-rotational levels originates from the poor convergence of Partridge and Schwenke's surface, principally along the angular coordinate. In this work several effects beyond the standard BO non-relativistic molecular Hamiltonian have been considered, and it is very unlikely that the remaining error in the predictions of vibrational-rotational levels could have a different origin.

As a part of this project, O.L. Polyansky and A.G. Császár investigated the convergence of Partridge and Schwenke's calculation [20]. They found that the partially augmented cc-pV5Z basis set employed by Partridge and Schwenke is not accurate enough for representing the water potential energy surface and a full augmentation of this basis was found to be particularly important. Consequently, Polyansky and Császár have begun to calculate a totally new potential energy surface. This work is currently under way, and only the main details along with few preliminary results will be reported here.

They performed over 300 calculations using Dunning's correlation consistent basis aug-cc-pVXZ (X=3 (T), 4 (Q), 5 or 6). The orbitals were determined at the Multi-Configuration SCF (MC-SCF) and multi-reference CI (MRCI) level of theory, keeping the oxygen $1s$ core orbitals frozen. The computer program MOLPRO [35] was used for the MRCI calculations. In particular, the aug-cc-pV6Z basis set required 64 processors on a parallel computer. The calculations were performed on a 512 processor Origin3000 machine Green run by the CSAR Service at the University of Manchester. The one-electron basis set was found to be not yet converged at the 6Z level, and the CBS limit was recovered by using an extrapolation technique [26].

The largest error left in the extrapolated surface was due to the neglected core-valence (CV) effects introduced by freezing the O($1s$) orbitals. This error was accounted for by using the same CV correction surface employed by Partridge and Schwenke in their *ab initio* potential, after its accuracy was proved by a variety of procedures and basis sets up to the 6Z level.

Once the electronic correlation energy has been calculated with satisfactory precision over a grid of nuclear geometries, the next step consists of providing an analytical fit to the data points, which is ultimately used to work out the vibrational-rotational levels. To make a fit of some set of data is not easy, and one must deal with two major sources of trouble: interpolation, and extrapolation, that is, respectively, the accuracy of the fit inside the data set, and its reliability outside.

The choice of the right analytical form is very important. The function used must be quite flexible inside the data set, and have the correct dissociation limits. In addition, the number of free parameters employed should be neither too small, to give the best possible representation of the initial data, nor too big, so that the fitted surface does not have any nonphysical behaviour. To fit the new *ab initio* PES for water, we used an analytical form similar to the one employed

by PS:

$$V^{\infty Z}(R_1, R_2, \Theta) = (1 - \mathcal{Y}(R_1))V^a(R_1) + (1 - \mathcal{Y}(R_2))V^a(R_2) + V^b(R_{\text{HH}}) + (1 - \mathcal{Y}(R_1))(1 - \mathcal{Y}(R_2))V^c(R_1, R_2, \Theta) + \mathcal{Y}(R_1)W^a(R_1) + \mathcal{Y}(R_2)W^a(R_2), \quad (5.1)$$

where R_{HH} is the HH distance and

$$V^a(r) = D(\exp[-2a(r - r_0)] - 2\exp[-a(r - r_0)] + 1), \quad (5.2)$$

$$W^a(r) = D_0(\exp[-2a(r - r_0)] - 2\exp[-a(r - r_0)] + 1), \quad (5.3)$$

$$\mathcal{Y}(r) = \frac{1}{1 + \exp(u_1(x_1 - r))}, \quad (5.4)$$

$$V^b(r) = A \exp(-br), \quad (5.5)$$

$$V^c(R_1, R_2, \Theta) = c_{000} + \exp\{-\beta[(R_1 - r_0)^2 + (R_2 - r_0)^2]\} \times \sum_{ijk} c_{ijk} S_1^i S_2^j S_3^k. \quad (5.6)$$

The polynomial term V^c is a function of the symmetrised coordinates S_1, S_2, S_3 , defined as follows:

$$S_1 = \frac{R_1 + R_2}{2} - R_e, \quad (5.7)$$

$$S_2 = \cos \Theta - \cos \Theta_e, \quad (5.8)$$

$$S_3 = \frac{R_1 - R_2}{2}. \quad (5.9)$$

The form chosen contains several linear ($\{c_{ijk}\}, D, A, D_0$), and non-linear ($r_0, R_e, \Theta_e, a, \beta, b, u_1, x_1$) parameters.

To fit the data points, we proceeded as follows. We tried to optimise all the linear parameters at once, while the non-linear ones were initially kept fixed to the same values as PS. At first we included a very high number of polynomials in the expansion (5.6). Most of the terms included were highly correlated, so we gradually excluded all the most correlated ones, together with those that showed a high fitting error ($\geq 10\%$). The values of the parameters along with their errors were determined using a linear least square algorithm [44]. We retained 113 parameters, that are able to reproduce the initial data with a standard deviation of 5.72 cm^{-1} . Then we tried to further improving the standard deviation of the fit by varying the non-linear parameters using the I-NoLLS program (an Iterative Non-Linear Least Square program, [127]). However, we did not achieve further improvement. Among the set of linear parameters, there is one (D) whose value is constrained by the dissociation limit of the surface, ie, by the OH+H channel. We found however that we were able to improve significantly the accuracy of the fit by varying D . We finally fixed it to the value indicated in table 5.5, and re-optimised all the other linear parameters accordingly, which has allowed us to obtain a standard deviation of 0.83 cm^{-1} for the fit. As a consequence, we added the functions W^a to impose the proper dissociation limit to $V^{\infty Z}$. The function $\mathcal{Y}$ is employed to switch between the inner region, where the fit is constrained by the data points, and the outer region, where it is constrained by the asymptotic behaviour. We choose the parameters of the switching functions in order to make the process as smooth as possible, and in a way that the switch between the two forms could happen in a region not constrained by the *ab initio* data. Furthermore, we checked that the

computed energy levels were not sensitive to the particular value of the switching parameters. The final value for the parameters used in eq. (5.1) are shown in tables 5.4 and 5.5.

In table 5.6 we present predictions for pure stretches and pure bending vibrational band origins obtained using the new surface $V^{\infty Z}$. The levels are shown as obs.–calc., for (i) the V^{5z} surface from [20] (see also eq. (2.55)), which does not include core-valence corrections, for (ii) a surface similar to V^{5z} , but calculated using the aug-cc-pV6Z basis set instead of cc-pV5Z (which will be referred to as v^{6z}), for (iii) the new surface $V^{\infty Z}$ alone, for (iv) the new surface corrected with core-valence effects, and finally (v) when all the corrections (MVD1, D2B, and non-BO) are included. From comparison of columns (i), (ii) and (iii) it can be seen that the cc-pV5Z basis set is not sufficient to fully converge the calculation. The levels most affected by the lack of convergence in the one-particle basis set are the pure bending bands. By extrapolating to the CBS limit the agreement between theory and experiment improves by almost one order of magnitude. On the other hand, the predictions for the stretches are not significantly modified by the use of bigger basis sets. If all the corrections considered in this thesis are included (column (v)), the discrepancy between theory and experiment is still as high as few wavenumbers for the higher energy states.

There are several factors which can be the cause of the residual errors in the prediction of VBOs. Firstly, it is possible that other neglected relativistic terms may contribute to the calculated VBOs: in column (vi) the effect of the one-electron Lamb-shift is shown (results from ref. [128]). Other neglected relativistic corrections are believed to be safely negligible [43]. Secondly, the error introduced in the PES by the fitting procedure described above represents a limit for the accuracy of the surface. The fitting error could in principle be reduced by computing more data points, but the grant supporting this work expired. It should also be mentioned that preliminary fits were carried out while computing the data points in order to optimise the choice of the geometries [129]. Finally, and more importantly, despite the use of extrapolation techniques for recovering the one-particle complete basis set limit, and sophisticated (MRCI) wavefunctions for recovering the correlation energy, neither of these problems can be considered completely solved. The lack of convergence of the one-particle basis set is believed to affect mostly the bending bands, whereas the missing part of the correlation energy is expected to modify the stretches. For the former it would be interesting to use an aug-cc-pV7Z basis set, in order to improve the extrapolated data. For the latter, there are full-CI calculations underway that employ small basis sets (aug-cc-pVDZ and aug-cc-pVTZ), to evaluate the effect of the full-CI limit. Hopefully, these will give us some insight on the importance of a full-CI calculation.

Table 5.4: Linear coefficients c_{ijk} of the term V^c , eq. (5.6). The units are consistent with bondlengths in a_0 , and energy in cm^{-1} .

C_{ijk}	i	j	k	C_{ijk}	i	j	k
$-0.5710475632463 \times 10^2$	0	0	0	$-0.9552657956071 \times 10^2$	0	0	1
$-0.6067577421565 \times 10^4$	1	0	0	$+0.1857072188807 \times 10^5$	0	0	2
$-0.3804871940410 \times 10^5$	0	2	0	$-0.2545869851885 \times 10^5$	1	0	1
$-0.5068038862818 \times 10^5$	2	0	0	$+0.1054898401242 \times 10^4$	0	0	3
$-0.2014577744857 \times 10^5$	0	2	1	$-0.9931435344154 \times 10^4$	1	0	2
$+0.7065816455505 \times 10^6$	1	2	0	$+0.2461185087692 \times 10^5$	2	0	1
$+0.2211920749729 \times 10^6$	3	0	0	$+0.3435869631455 \times 10^4$	0	0	4

Table 5.4: continued

C_{ijk}	i	j	k	C_{ijk}	i	j	k
$+0.5677448867330 \times 10^5$	0	2	2	$-0.4729349488906 \times 10^6$	0	2	0
$-0.1062810010743 \times 10^5$	1	0	3	$-0.1711113900137 \times 10^5$	1	2	1
$+0.6846686263643 \times 10^5$	2	0	2	$-0.2370095499969 \times 10^7$	2	2	0
$-0.7435062393867 \times 10^5$	3	0	1	$-0.5533282463806 \times 10^6$	4	0	0
$-0.2653776328915 \times 10^3$	0	0	5	$-0.8787425252359 \times 10^4$	0	2	3
$-0.4792685061143 \times 10^5$	0	4	1	$+0.7338375214709 \times 10^4$	1	0	4
$-0.2696329025096 \times 10^5$	1	2	2	$+0.3151302526351 \times 10^7$	1	4	0
$-0.2680019540619 \times 10^5$	2	0	3	$-0.3411155916783 \times 10^5$	2	2	1
$-0.2361101699812 \times 10^5$	3	0	2	$+0.4252318274899 \times 10^7$	3	2	0
$+0.1909629119429 \times 10^5$	4	0	1	$+0.1049781901349 \times 10^7$	5	0	0
$+0.1007604315157 \times 10^4$	0	0	6	$+0.3955134247500 \times 10^5$	0	2	4
$-0.1254283199622 \times 10^7$	0	6	0	$-0.4742047112461 \times 10^4$	1	0	5
$-0.1237633931215 \times 10^6$	1	2	3	$+0.1989124023766 \times 10^5$	2	0	4
$+0.3708558366230 \times 10^6$	2	2	2	$+0.6018342068259 \times 10^5$	4	0	2
$-0.1239376779228 \times 10^7$	6	0	0	$+0.8543568929153 \times 10^4$	0	2	5
$-0.8470361074768 \times 10^5$	0	6	1	$-0.4323120218548 \times 10^4$	1	0	6
$-0.7691197466131 \times 10^5$	1	2	4	$-0.4892966870779 \times 10^7$	1	6	0
$+0.4364087781854 \times 10^5$	2	0	5	$-0.3909155940947 \times 10^8$	3	4	0
$-0.1712950976860 \times 10^7$	4	2	1	$+0.2087371244764 \times 10^6$	5	0	2
$-0.2006710729271 \times 10^8$	5	2	0	$+0.8789956427347 \times 10^6$	7	0	0
$-0.4317629382959 \times 10^5$	0	2	6	$+0.1618789634550 \times 10^6$	0	4	4
$+0.1587687527646 \times 10^7$	0	6	2	$+0.3990003280266 \times 10^7$	0	8	0
$+0.2817080082968 \times 10^6$	1	2	5	$+0.4482768991684 \times 10^6$	1	4	3
$-0.4070569279958 \times 10^5$	2	0	6	$-0.8864550152825 \times 10^6$	2	2	4
$+0.6290955366349 \times 10^8$	2	6	0	$+0.8993645659488 \times 10^5$	3	0	5
$+0.9210094589981 \times 10^6$	3	2	3	$-0.1753794544813 \times 10^6$	4	0	4
$+0.1311789234505 \times 10^9$	4	4	0	$+0.1060664061203 \times 10^6$	5	0	3
$+0.5340569244466 \times 10^7$	5	2	1	$-0.3105624184638 \times 10^6$	6	0	2
$+0.4571723553398 \times 10^8$	6	2	0	$+0.7470215166875 \times 10^6$	7	0	1
$-0.2218921351107 \times 10^6$	0	4	5	$+0.1316232741184 \times 10^5$	1	0	8
$+0.2023964877189 \times 10^6$	1	2	6	$-0.7539991140488 \times 10^7$	1	6	2
$-0.3438106580968 \times 10^8$	1	8	0	$-0.1065626654616 \times 10^6$	2	0	7
$-0.2295235891775 \times 10^6$	2	2	5	$+0.1796585516193 \times 10^6$	3	0	6
$-0.2005145616345 \times 10^7$	3	4	2	$-0.1375861482407 \times 10^9$	3	6	0
$-0.3423607622386 \times 10^6$	4	0	5	$+0.6119673444298 \times 10^7$	4	2	3
$-0.1085580079570 \times 10^8$	5	2	2	$-0.1807866589974 \times 10^9$	5	4	0
$-0.4710714407573 \times 10^7$	6	2	1	$-0.3555338273642 \times 10^8$	7	2	0
$-0.4225310291748 \times 10^7$	8	0	1	$+0.6802694583683 \times 10^5$	0	2	8
$-0.3612806511976 \times 10^6$	0	6	4	$-0.1984202384497 \times 10^7$	0	8	2
$-0.5762585608683 \times 10^4$	1	0	9	$-0.4190242262127 \times 10^6$	1	2	7
$-0.6862320609996 \times 10^6$	1	4	5	$+0.6897610937412 \times 10^5$	2	0	8
$+0.1979393850517 \times 10^7$	2	2	6	$+0.1886232859991 \times 10^7$	2	4	4
$+0.1704308445329 \times 10^8$	2	6	2	$+0.5734113225539 \times 10^8$	2	8	0
$-0.1909984371034 \times 10^6$	3	0	7	$-0.4274427341543 \times 10^7$	3	2	5

Table 5.4: continued

C_{ijk}	i	j	k	C_{ijk}	i	j	k
$-0.3010333878947 \times 10^7$	3	4	3	$+0.2957770502057 \times 10^6$	4	0	6
$+0.4275754424910 \times 10^7$	4	2	4	$+0.7954251656913 \times 10^8$	4	6	0
$-0.1018371344211 \times 10^8$	5	2	3	$+0.2825744251920 \times 10^6$	6	0	4
$+0.1682459960715 \times 10^8$	6	2	2	$+0.1012584539651 \times 10^9$	6	4	0
$+0.5160076143117 \times 10^7$	9	0	1	$-0.4748852759269 \times 10^3$	11	0	0
$-0.1946436003678 \times 10^5$	0	2	9				

Table 5.5: Coefficients for the remaining terms in expression (5.1).

linear parameters					
A	(cm^{-1})	$0.895714083584240987 \times 10^6$	D	(cm^{-1})	$0.368181683997432046 \times 10^5$
D_0	(cm^{-1})	42395.535333			
non-linear parameters					
r_0	(a_0)	1.79894558	R_e	(a_0)	1.81158407
Θ_e	(degree)	104.3475	a	(a_0^{-1})	1.369484
β	(a_0^{-2})	0.5449204	b	(a_0^{-1})	3.546357
u_1	(a_0^{-1})	10.583544	x_1	(a_0)	4.724315

5.2.2 Possible extensions of this work

The major source of error in a fully *ab initio* determination of molecular vibrational-rotational levels is the potential energy surface. Due to the strong correlation between electrons, it is very difficult to determine a PES of spectroscopic accuracy, even for a system as small as water. We have also limited our analysis to states below $25,000 \text{ cm}^{-1}$, that is, to strongly bound levels, as the first dissociation channel is at an energy of 41128 cm^{-1} [68] above the ground state. Using different PESs, Mussa and Tennyson [130] have already presented calculations of rotational vibrational levels of water up to dissociation. In order to bypass the computational difficulties of such a calculation, they implemented a parallel version [131] of the DVR3D code. In this way they were able to obtain numerical convergence not only for the VBOs, but also for the rotationally excited states. It would thus be possible to extend this work above the current limit of $25,000 \text{ cm}^{-1}$, following the approach of Mussa and Tennyson.

It is also interesting to evaluate the possibility to calculate vibrational-rotational levels with high accuracy for molecules bigger than water. When considering larger molecules, two classes can be identified: triatomics with more electrons, or isoelectronic molecules with more nuclei (eg, NH_3 , CH_4). In both cases the extension of this work presents some difficulties, particularly due to the high sensitivity that this kind of calculation shows to the increase of degrees of freedom of the problem.

Table 5.6: Predictions for pure bending and pure stretches VBOs, obtained with the PES of eq. (5.1). Results are given as obs.–calc., in cm^{-1} .

^a Partridge and Schwenke’s *ab initio* PES V^{5z} (with the exclusion of core-valence corrections, eq. (2.55))

^b with the surface of eq. (2.55), using the aug-cc-pV6Z basis set, V^{6z}

^c with the surface of eq. (5.1), in the limit of complete basis set $V^{\infty Z}$

^d $V^{\infty Z}$ + core-valence (CV) corrections from [20].

^e $V^{\infty Z}$ + CV + MVD1, D2B, CASSCF adiabatic and diagonal non-adiabatic corrections

^f as above (e), with the inclusion of one-electron Lamb-shift [128]

		(i)	(ii)	(iii)	(iv)	(v)	(vi)
(ν_1, ν_2, ν_3)	obs [87]	BO ^a	BO ^b	BO ^c	+CV ^d	+corr ^e	+QED ^f
(100)	3657.05	3.31	4.55	4.20	−3.05	0.60	0.47
(200)	7201.54	7.11	9.38	8.72	−5.64	1.45	1.18
(300)	10599.69	11.90	15.61	13.72	−7.59	2.58	2.18
(400)	13828.28	17.02	22.71	18.86	−9.03	3.79	3.26
(010)	1594.75	−3.65	−2.30	−0.32	0.48	−0.27	−0.21
(020)	3151.63	−7.43	−2.38	−0.79	1.16	−0.50	−0.37
(030)	4666.79	−11.62	−3.24	−1.53	2.06	−0.74	−0.53
(040)	6134.01	−16.48	−5.54	−2.74	3.21	−1.06	−0.75
(050)	7542.44	−22.58	−9.19	−4.72	4.83	−1.47	−1.04
(060)	8869.95	−31.57	−14.88	−8.43	7.03	−2.36	−1.74

For triatomics, Császár *et al.* [61] carried out a similar study to this one on H_2S , which has almost twice as many electrons as water, although the number of valence electrons is the same. They were able to predict VBOs for H_2S up to $12,500 \text{ cm}^{-1}$ with a root-mean-square accuracy of 2.0 cm^{-1} . However, a study on HCN [132] presented more difficulties, due to the high number of valence electrons. Furthermore, for atoms beyond the second row in the periodic table of elements, the standard non-relativistic approach fails, and one must use the Dirac equation as a starting point for electronic structure calculations.

Alternatively, other techniques such as diffusion (Quantum) Monte Carlo or Density Functional Theory (DFT) have already been applied to the study of molecular systems. The first has been used by several groups [133, 134] to study van der Waals complexes: for these molecules, however, the PES is made of a sum of two-body interactions, so the problem highlighted above is easily circumvented. On the other hand, DFT [135] is routinely employed in organic and organometallic chemistry. DFT exploits the concept of “electron density” [136], which is a quantity depending on only 3 coordinates, independent of the number of electrons present. Density functional results are not yet of spectroscopic accuracy, and normally the method is applied to the study of molecules with a large number of electrons.

The study of molecules with more vibrational degrees of freedom is also extremely demanding. In this work, we have implicitly made use of our capability for a) solving the nuclei’s equations of motion with an arbitrary precision, and b) calculating all the corrections to the PES (and the PES itself) on a grid of about 10 points per degree of freedom. One major problem is then that the number of points needed to calculate a PES, and eventually relativistic or

adiabatic corrections to it, increases exponentially with the number of vibrational degrees of freedom. For a molecule with L nuclei that is 10^{3L-6} , although symmetry considerations may allow one to reduce the size of the grid. On the other hand, there is the problem of solving accurately a four- or five-body Hamiltonian. As we have seen, the three-body problem can be solved using several techniques in a almost exact fashion, only limited by numerical accuracy. In principle, any of those techniques can easily be extended to bigger systems, but in practice such extensions present several computational difficulties. For instance, the increase in the dimension of the basis set is again exponential with the number of vibrational degrees of freedom. The search and development of methods for solving four- and five-body quantum mechanical problems is an active field of research [137, 138, 139].

In summary, in this thesis we have analysed the spectroscopic relevance of corrections to the standard molecular Born-Oppenheimer non-relativistic Hamiltonian. We have found that the major limit in *ab initio* calculations for water is represented by the accuracy of the underlying PES. Concerning possible extensions of this work to other molecules, all the methods used for water (and H_2S) can in principle be extended to bigger molecules, although they become rapidly computationally very expensive as the number of degrees of freedom increase.

The derivation of kinetic energy operators in internal coordinates: Lukka's approach

The problem of the derivation of Kinetic Energy Operators (KEOs) for different choices of internal coordinate systems was in principle solved a long time ago [78, 105]. Given L nuclei, let us introduce the cartesian coordinates $\{\mathbf{x}_i\}$ ($i = 1, L$). A standard way of approaching the problem consists in choosing a set of internal coordinates $\{q_i\}$, together with a convenient molecule embedded frame of reference, defined by means of three unit vectors $\mathbf{I}_1, \mathbf{I}_2, \mathbf{I}_3$. Associated with the three unit vectors there are three Euler angles (α, β, γ) defining the spatial orientation of the molecular frame with respect to the laboratory fixed axes (see app. C in [63]).

It is then customary to introduce the collective variables $\{t_i\}$:

$$\begin{aligned} t_i &= q_i \quad (i = 1, 3L - 6), \\ t_{3L-5} &= \alpha, \quad t_{3L-4} = \beta, \quad t_{3L-3} = \gamma. \end{aligned} \quad (\text{A.1})$$

Finally, it is necessary to define the $\{t_i\}$ as functions of the cartesian coordinates $\{\mathbf{x}_i\}$

$$t_i = t_i(x_{\lambda,i}) \quad (\lambda = \{xyz\}, i = 1, L). \quad (\text{A.2})$$

By applying the chain rule, the KEO can finally be expressed in terms of the new coordinates [105]:

$$\hat{K} = -\frac{1}{2} \sum_{i=1}^L \sum_{\lambda} \frac{1}{m_i} \frac{\partial^2}{\partial x_{\lambda,i}^2} = -\frac{1}{2} \left[\sum_{jk}^{3L-3} g^{jk} \frac{\partial^2}{\partial t_j \partial t_k} + \sum_j^{3L-3} h^j \frac{\partial}{\partial t_j} \right], \quad (\text{A.3})$$

where the contravariant metric tensor g^{jk} reads

$$g^{jk} = \sum_{i=1}^L \sum_{\lambda} \frac{1}{m_i} \frac{\partial t_j}{\partial x_{\lambda,i}} \frac{\partial t_k}{\partial x_{\lambda,i}} = \mathbf{s}_j \cdot \mathbf{s}_k, \quad (\text{A.4})$$

and

$$h^j = \sum_{i=1}^L \sum_{\lambda} \frac{1}{m_i} \frac{\partial t_j^2}{\partial x_{\lambda,i}^2} = \nabla \cdot \mathbf{s}_j. \quad (\text{A.5})$$

The dots indicate mass weighted scalar products. The vectors $\{\mathbf{s}\}$ are defined as follows:

$$\mathbf{s}_j = \left(\frac{\partial t_j}{\partial x_{x,1}}, \frac{\partial t_j}{\partial x_{y,1}}, \dots, \frac{\partial t_j}{\partial x_{z,L}} \right). \quad (\text{A.6})$$

Following this procedure, Sutcliffe and Tennyson [48, 69] obtained a rather general expression for KEOs of triatomics when two bond-lengths and the included bond-angle were chosen as internal coordinates. Also KEOs for tetra-atomics had been derived [105]. However, this approach, although straightforward in principle, presents enormous algebraic difficulties when applied to bigger molecules (ie, containing more than four atoms). The main complication arises in calculating the derivatives of the Euler angle with respect to the cartesian coordinates, and also in referring the derivatives with respect to the Euler angles to the angular momentum operators.

A brilliant enhancement to the standard approach has been proposed by Lukka [106]. He pointed out that the KEO expressed in the coordinates $\{t_i\}$ does not depend on the Euler angles. This is equivalent to saying that the choice of the orientation of the initial frame of reference is arbitrary and does not influence the final result. Thus, a suitable choice of the orientation can be exploited to reduce the algebraic difficulties of the problem. The main finding of Lukka was that the orientation specified by the set of Euler angles $(0, \pi/2, 0)$ indeed allows for a great simplification of the algebraic problem, dispensing with any algebra involving Euler angles, and their derivatives.

When this choice is adopted, infinitesimal variations of the Euler angles around the point $(0, \pi/2, 0)$ correspond to infinitesimal rotations around the molecular embedded axes. Therefore the following relations hold:

$$\begin{aligned} i \frac{\partial}{\partial \alpha} &= \hat{J}_x, \\ i \frac{\partial}{\partial \beta} &= \hat{J}_y, \\ i \frac{\partial}{\partial \gamma} &= \hat{J}_z. \end{aligned} \quad (\text{A.7})$$

The derivatives of the Euler angles are readily obtained:

$$\begin{aligned} \frac{\partial \alpha}{\partial x} &= -\mathbf{I}_2 \cdot \frac{\partial \mathbf{I}_3}{\partial x} = \mathbf{I}_3 \cdot \frac{\partial \mathbf{I}_2}{\partial x}, \\ \frac{\partial \beta}{\partial x} &= -\mathbf{I}_3 \cdot \frac{\partial \mathbf{I}_1}{\partial x} = \mathbf{I}_1 \cdot \frac{\partial \mathbf{I}_3}{\partial x}, \\ \frac{\partial \gamma}{\partial x} &= -\mathbf{I}_1 \cdot \frac{\partial \mathbf{I}_2}{\partial x} = \mathbf{I}_2 \cdot \frac{\partial \mathbf{I}_1}{\partial x}, \end{aligned} \quad (\text{A.8})$$

where x indicates a generic variable. It must be stressed that equations (A.7) and (A.8) are valid only at the $(0, \pi/2, 0)$ point.

A.1 Implementation of Lukka's method to water hamiltonians

The kinetic energy operator for triatomic has been derived in quite a general form by Sutcliffe and Tennyson [48, 69], and the derivation has been repeated by other authors for testing purposes (Handy [105, 140], Lukka [106]). Wei and Carrington [104] have also derived an exact expression for the KEO using an Eckart embedding for the molecular fixed axes.

In order to familiarise ourselves with Lukka's approach, we have reproduced the results of Sutcliffe and Tennyson [48]. As a second step, we have reproduced Wei and Carrington's results [103]. We have calculated the s-vectors and their divergence using the same general embedding of ref. [103], for water in Radau coordinates. We will refer to the molecule embedded axes as $\mathbf{I}_1$, $\mathbf{I}_2$ and $\mathbf{I}_3$, which constitute a right handed cartesian frame of reference. The molecule lies in the $\mathbf{I}_1 - \mathbf{I}_2$ plane, and the angle between the $\mathbf{I}_2$ -axis and the coordinate r_1 can be adjusted by means of the parameter f . We will first derive the expression for the KEO for the f constant case, then we will deal with the more general case in which f is a complicated function of the Radau coordinates. With this choice, the molecular embedded cartesian vectors can be expressed:

$$\begin{aligned}\mathbf{I}_1 &= \frac{(a\hat{r}_1 + \hat{r}_2)}{\sqrt{a^2 + 1 + 2a \cos \theta}} = C_-(a\hat{r}_1 + \hat{r}_2), \\ \mathbf{I}_2 &= \frac{(f\hat{r}_1 + \hat{r}_2)}{\sqrt{1 + f^2 + 2f \cos \theta}} = C_+(f\hat{r}_1 + \hat{r}_2), \\ \mathbf{I}_3 &= \frac{\hat{r}_1 \times \hat{r}_2}{\sin \theta}.\end{aligned}\tag{A.9}$$

where

$$a = -\frac{f \cos \theta + 1}{f + \cos \theta},\tag{A.10}$$

and $\hat{r}_1, \hat{r}_2$ indicate the unit vectors along the Radau coordinates r_1 and r_2 . Using formulae (3.12)-(3.13), the gradients of the Radau coordinates with respect to the nuclear coordinates can easily be obtained:

$$\nabla_1 r_1 = \hat{r}_1\tag{A.11}$$

$$\nabla_1 r_2 = -\gamma \hat{r}_2\tag{A.12}$$

$$\nabla_1 \cos \theta = -\hat{r}_1 \left(\frac{\gamma}{r_2} + \frac{\cos \theta}{r_1} \right) + \hat{r}_2 \left(\frac{1}{r_1} + \frac{\gamma \cos \theta}{r_2} \right)\tag{A.13}$$

$$\nabla_2 r_1 = -\gamma \hat{r}_1\tag{A.14}$$

$$\nabla_2 r_2 = \hat{r}_2\tag{A.15}$$

$$\nabla_2 \cos \theta = \hat{r}_1 \left(\frac{1}{r_2} + \frac{\gamma \cos \theta}{r_1} \right) - \hat{r}_2 \left(\frac{\gamma}{r_1} + \frac{\cos \theta}{r_2} \right)\tag{A.16}$$

$$\nabla_3 r_1 = (\gamma - 1) \hat{r}_1\tag{A.17}$$

$$\nabla_3 r_2 = (\gamma - 1) \hat{r}_2\tag{A.18}$$

$$\nabla_3 \cos \theta = -\hat{r}_1 (\gamma - 1) \left(\frac{1}{r_2} + \frac{\cos \theta}{r_1} \right)\tag{A.19}$$

where γ is defined in eq. (2.14).

A little more algebra is necessary to work out the gradients of the Euler angles, ie of the unit vectors $\mathbf{I}_1$, $\mathbf{I}_2$ and $\mathbf{I}_3$ (see eq. (A.8)). We use the following notation:

$$(\mathbf{I}_a \nabla_b \mathbf{I}_c) = (\mathbf{I}_a \cdot \frac{\partial \mathbf{I}_c}{\partial x_b}, \mathbf{I}_a \cdot \frac{\partial \mathbf{I}_c}{\partial y_b}, \mathbf{I}_a \cdot \frac{\partial \mathbf{I}_c}{\partial z_b}). \quad (\text{A.20})$$

The expressions for the gradients of the Euler angles then are:

$$\begin{aligned} (\mathbf{I}_1 \nabla_1 \mathbf{I}_2) &= C_+ \left(\frac{f}{r_1} - \frac{\gamma}{r_2} \right) \mathbf{I}_1 - C_+ \left((\mathbf{I}_1 \cdot \hat{r}_1) \frac{\hat{r}_1}{r_1} f - \gamma (\mathbf{I}_1 \cdot \hat{r}_2) \frac{\hat{r}_2}{r_2} \right) + \\ &+ C_+ (\hat{r}_1 \cdot \mathbf{I}_1) \nabla_1 f, \end{aligned} \quad (\text{A.21})$$

$$\begin{aligned} (\mathbf{I}_1 \nabla_2 \mathbf{I}_2) &= C_+ \left(\frac{-f\gamma}{r_1} + \frac{1}{r_2} \right) \mathbf{I}_1 - C_+ \left(-f\gamma (\mathbf{I}_1 \cdot \hat{r}_1) \frac{\hat{r}_1}{r_1} + (\mathbf{I}_1 \cdot \hat{r}_2) \frac{\hat{r}_2}{r_2} \right) + \\ &+ C_+ (\hat{r}_1 \cdot \mathbf{I}_1) \nabla_2 f, \end{aligned} \quad (\text{A.22})$$

$$\begin{aligned} (\mathbf{I}_1 \nabla_3 \mathbf{I}_2) &= C_+ (1 - \gamma) \left(\frac{f}{r_1} + \frac{1}{r_2} \right) \mathbf{I}_1 - C_+ (1 - \gamma) \left((\mathbf{I}_1 \cdot \hat{r}_1) \frac{\hat{r}_1}{r_1} f + (\mathbf{I}_1 \cdot \hat{r}_2) \frac{\hat{r}_2}{r_2} \right) + \\ &+ C_+ (1 - \gamma) (\hat{r}_1 \cdot \mathbf{I}_1) \nabla_3 f, \end{aligned} \quad (\text{A.23})$$

$$(\mathbf{I}_3 \nabla_1 \mathbf{I}_2) = C_+ \left(\frac{f}{r_1} - \frac{\gamma}{r_2} \right) \mathbf{I}_3, \quad (\text{A.24})$$

$$(\mathbf{I}_3 \nabla_2 \mathbf{I}_2) = C_+ \left(\frac{f\gamma}{r_1} + \frac{1}{r_2} \right) \mathbf{I}_3, \quad (\text{A.25})$$

$$(\mathbf{I}_3 \nabla_3 \mathbf{I}_2) = C_+ (\gamma - 1) \left(\frac{f}{r_1} + \frac{1}{r_2} \right) \mathbf{I}_3, \quad (\text{A.26})$$

$$(\mathbf{I}_3 \nabla_1 \mathbf{I}_1) = C_- \left(\frac{a}{r_1} - \frac{\gamma}{r_2} \right) \mathbf{I}_3, \quad (\text{A.27})$$

$$(\mathbf{I}_3 \nabla_2 \mathbf{I}_1) = C_- \left(-\frac{\gamma a}{r_1} + \frac{1}{r_2} \right) \mathbf{I}_3, \quad (\text{A.28})$$

$$(\mathbf{I}_3 \nabla_3 \mathbf{I}_1) = -C_- (\gamma - 1) \left(\frac{a}{r_1} + \frac{1}{r_2} \right) \mathbf{I}_3. \quad (\text{A.29})$$

By inserting the above expressions into eqs. (A.3) it is possible to obtain the final expression for the KEO. It is helpful to recall the following relations (eq. (2.23)):

$$\mu^{-1} = \frac{1}{M_H} + \frac{\gamma^2}{M_H} + \frac{(\gamma - 1)^2}{M_O}, \quad (\text{A.30})$$

$$- \frac{2\gamma}{M_H} + \frac{(\gamma - 1)^2}{M_O} = 0. \quad (\text{A.31})$$

If f is considered to be a constant, the last term in eqs. (A.21)-(A.23) vanishes. On the other hand, if one wants to implement the Eckart embedding, the expression for f is rather complicated [103]:

$$f = \frac{\sin(\theta - \eta)}{\sin \eta}, \quad (\text{A.32})$$

where η is given in eq. (3.15). In this case one needs to calculate the derivative of f with respect to the Radau coordinates:

$$\frac{\partial f}{\partial r_1} = \frac{-r_2 \sin(\theta - \theta_e)}{(r_2 \cos(\theta - \theta_e/2) + r_1 \cos(\theta_2))^2}, \quad (\text{A.33})$$

$$\frac{\partial f}{\partial r_2} = \frac{r_1 \sin(\theta - \theta_e)}{(r_2 \cos(\theta - \theta_e/2) + r_1 \cos(\theta_2))^2}, \quad (\text{A.34})$$

$$\frac{\partial f}{\partial \cos \theta} = \frac{r_2^2 - r_1^2}{(r_2 \sin(\theta - \theta_e/2) + r_1 \sin(\theta_e/2))^2} \frac{\sin(\theta_e/2)}{\sin \theta} \cos(\theta - \theta_e/2). \quad (\text{A.35})$$

The final expressions for the KEO, obtained by inserting eqs. (A.11)-(A.19), and (A.21)-(A.29) into eq. (A.3), are shown in subsection 3.2.2.

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