High Accuracy Rotation–Vibration Calculations on Small Molecules

Jonathan Tennyson

Department of Physics and Astronomy, University College London, London, UK

1 INTRODUCTION

High-resolution spectroscopy measures the transitions between energy levels with high accuracy; typically, uncertainties are in the region of 1 part in 10^8. Although it is possible, under favorable circumstances, to obtain this sort of accuracy by fitting effective Hamiltonians to observed spectra (*see* Bauder 2011: **Fundamentals of Rotational Spectroscopy**, this handbook), such ultrahigh accuracy is largely beyond the capabilities of purely ab initio procedures. Given this, it is appropriate to address the question of why it is useful to calculate the spectra of molecules ab initio (Tennyson 1992).

The concept of the potential energy surfaces, which in turn is based on the Born–Oppenheimer approximation, underpins nearly all of gas-phase chemical physics. The original motivation for calculating spectra was to provide stringent tests of potential energy surfaces. As discussed in Section 5, this procedure has now been turned round and spectra can be used to construct or more commonly refine potential energy surfaces. The fact that spectra can be recorded with high accuracy does not necessarily mean that they are easy to interpret. The second motivation for first-principles calculation of spectra is to make predictions before any experiment and to aid with the assignment process afterward.

A third reason is the analysis of spectra or, indeed, radiation transport models at high temperatures. The rotation–vibration spectra of even rather small molecules become very complicated at elevated temperatures. A comprehensive understanding requires the knowledge of many millions, perhaps even billions, of individual transitions (Tennyson *et al*. 2007). It is not practical to measure this much data in the laboratory and therefore a more realistic approach is the development of an accurate theoretical model, benchmarked against experiment.

The incompleteness of most experimental datasets means that calculations are useful for computing other properties that can be associated with spectra. The partition functions and the variety of thermodynamic properties that are linked to this (Martin *et al*. 1991) are notable among these. Again, calculations are particularly useful for estimating these quantities at high temperature (e.g., Neale and Tennyson 1995).

Other more fundamental reasons for calculating spectra include the search for unusual features, such as clustering of energy levels (Jensen 2000) or quantum monodromy (Child *et al*. 1999), or to link with semiclassical analysis. These reasons are not discussed here.

Many of the above reasons relate closely to working with measurements but the results from calculations can be important in their own right. For most practical applications of spectroscopy, such as those involved in remote sensing or radiative transfer modeling, information on transition intensities is as important as that on line positions. Accurate absolute intensity measurements are difficult; they can usually only be made in situations where it is possible to get a well thermalized, known column of the sample and even then certain experiments simply do not yield this information. For small molecules, ab initio theoretical techniques are advanced sufficiently that the intensities they produce may often be more trustworthy than laboratory ones, even when they are available.

Handbook of High-resolution Spectroscopy. Edited by Martin Quack and Frédéric Merkt.
ISBN: 978-0-470-74959-3.

2 SEPARATING ELECTRONIC, VIBRATIONAL, ROTATIONAL, AND TRANSLATIONAL MOTION

It is straightforward to write down the Schrödinger equation governing the motion of a molecule containing N atoms each with charge Z_I and mass M_I and n electrons, each with charge $-e$ and mass m_e. The associated nonrelativistic Hamiltonian is

$$\begin{aligned}\hat{H} &= -\sum_{I=1}^{N}\frac{\hbar^2}{2M_I}\nabla_I^2 - \frac{\hbar^2}{2m_e}\sum_{i=1}^{n}\nabla_i^2 - \left[\sum_{I=1}^{N}\sum_{i=1}^{n}\frac{eZ_I}{|\boldsymbol{R}_I - \boldsymbol{r}_i|}\right.\\ &\quad \left. -\sum_{I=1}^{N}\sum_{J<I}\frac{Z_I Z_J}{|\boldsymbol{R}_I - \boldsymbol{R}_J|} - \sum_{i=1}^{n}\sum_{j<i}\frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}\right] / (4\pi\varepsilon_0)\\ &= \hat{T}_N + \hat{T}_e + V_{Ne} + V_{NN} + V_{ee} \qquad (1)\end{aligned}$$

where the terms denote the nuclear motion kinetic energy operator, $\hat{T}_N$, the electronic motion kinetic energy operator, $\hat{T}_e$, the potential due to the coulombic attraction between the electrons and the nuclei, V_{Ne}, the potential due to the coulombic repulsion between the nuclei, V_{NN} and the potential due to the coulombic repulsion between the electrons, V_{ee}. The coordinates used to represent the Hamiltonian of equation (1), $\boldsymbol{R}_I$ for the nuclei and $\boldsymbol{r}_i$ for the electrons, are all defined relative to some arbitrary origin. This Hamiltonian has $3(N+n)$ degrees of freedom.

Though it may be straightforward to write down the Hamiltonian given by equation (1), there are a number of steps that need to be taken before tractable solutions can be found to the related Schrödinger Equation. These steps can be characterized as separating the nuclear and electronic motions, removing the translational motion of the whole system and, less crucially, distinguishing between the vibrational and rotational nuclear motion. Although there are different methods available for studying molecules that skip each of these steps, none of them have been generally used to study the rotation–vibration states of chemically bound molecules; these methods are not discussed here.

2.1 The Born–Oppenheimer Approximation

The first standard step, the separation of electronic and nuclear motion, is based upon what is known as the *Born–Oppenheimer approximation*. This approximation starts by characterizing the total wave function of the system as a product of electronic and nuclear wave functions:

$$\Psi = \psi^{\text{elec}}(\boldsymbol{r}_i; \boldsymbol{R}_I)\psi^{\text{nuc}}(\boldsymbol{R}_I) \qquad (2)$$

As the notation shows, the nuclear motion wave function, ψ^{nuc}, is a function only of the nuclear coordinates and the electronic motion wave function, ψ^{elec}, depends explicitly on the electronic coordinates and parametrically on the nuclear motion coordinates. That is, there is a different electronic wave function for each nuclear configuration. In practice, this wave function depends only on the internal or relative nuclear coordinates, which are defined below.

Within the Born–Oppenheimer approximation, the electronic wave function is obtained as the solution of the Schrödinger equation given by:

$$(\hat{T}_e + V_{Ne} + V_{ee})\psi^{\text{elec}} = E^{\text{elec}}\psi^{\text{elec}} \qquad (3)$$

The electronic energy, E^{elec}, obtained from this equation depends parametrically on the relative nuclear coordinates, $\boldsymbol{Q}$; it is used in the nuclear motion Schrödinger equation:

$$\left(\hat{T}_N + V(\boldsymbol{Q})\right)\psi^{\text{nuc}} = E\psi^{\text{nuc}} \qquad (4)$$

where E is the total energy for the state under consideration. A very important part of equation (4) is the potential energy surface V which is defined as:

$$V(\boldsymbol{Q}) = V^{\text{BO}}(\boldsymbol{Q}) = E^{\text{elec}}(\boldsymbol{Q}) + V_{NN}(\boldsymbol{Q}) \qquad (5)$$

This potential is independent of the mass of the nuclei and therefore is the same for all isotopologues of a particular molecule. This is an important result of the Born–Oppenheimer approximation and one which can be used to quantify its reliability.

The basis of the Born–Oppenheimer approximation is that the electrons move rapidly compared to the nuclei because m_e is very much less than M_I. This approximation is worst for the lightest nucleus, hydrogen, where M_H is still 1836 m_e. There are also serious problems with the Born–Oppenheimer approximation when two electronic potential energy surfaces come very close to each other or even cross, because under this circumstance, the separability of the electronic and nuclear wave functions, equation (2), can fail badly.

The Born–Oppenheimer approximation actually involves two approximations: the separation of the electronic and nuclear wave functions, equation (2), and neglect of the term where the nuclear kinetic energy operator, $\hat{T}_N$ acts on the electronic wave function, ψ^{elec}. It is reasonably straightforward to improve on the Born–Oppenheimer approximation by allowing for the case where $\hat{T}_N$ acts on ψ^{elec}. The simplest way of writing this correction, W^{ad}, is:

$$W^{\text{ad}}(\boldsymbol{Q}) = \left\langle\psi^{\text{elec}}|\hat{T}_N|\psi^{\text{elec}}\right\rangle \qquad (6)$$

where the integration implied by the Dirac notation is over all electronic coordinates. This is the Born–Oppenheimer diagonal correction (BODC) and adding it to the potential of equation (5) gives the adiabatic approximation. It is important to note that the BODC is mass dependent and therefore there is a new effective potential for each isotopologue in the adiabatic approximation.

For high-accuracy work, it is therefore often desirable to define a more general, effective, potential energy function which can be written as follows:

$$W^{\mathrm{eff}}(\boldsymbol{Q}) = V^{\mathrm{BO}}(\boldsymbol{Q}) + V^{\mathrm{rel}}(\boldsymbol{Q}) + W^{\mathrm{ad}}(\boldsymbol{Q}) \tag{7}$$

W^{eff} is the sum of the mass-independent Born–Oppenheimer potential plus relativistic correction, V^{rel}, which is discussed below, and the mass-dependent adiabatic correction. Note that the mass dependence of the adiabatic correction is implicitly included in the nuclear kinetic energy operator, $\hat{T}_N$, in equation (6).

If one writes $\hat{T}_N$ in Cartesian coordinates, the BODC has a fairly simple form which involves the second derivative of electronic wave function with respect to the coordinates of the nuclei (Handy *et al.* 1986). Integrals involving such terms are available in a number of quantum chemistry programs where they are used to compute harmonic vibrational frequencies. The use of $\hat{T}_N$ in Cartesian coordinates actually involves a very slight approximation because it does not allow for the separation of the translational motion, an issue which is discussed in the next section. This means that the electronic contribution to the translation motion of the whole molecule is neglected. Early treatments of the BODC used a rigorous, but generally rather complicated, formulation of the Hamiltonian. The more recent consensus is that this is not really necessary (Kutzelnigg 1997) as the error introduced by using the simple Cartesian form is so small that the simpler form is sufficient for practical purposes. Calculation of the contributions to the BODC separately for each nucleus allows the BODC to be calculated for every isotopologue in a single calculation, see Zobov *et al.* (1996) for an example.

Correcting for the remainder of the Born–Oppenheimer approximation by introducing the so-called nonadiabatic corrections is altogether a more difficult proposition. Within the spirit of the wave function separation of equation (2), one can write the exact wave function as

$$\Psi = \sum_{n=0}^{\infty} \psi_n^{\mathrm{elec}}(\boldsymbol{r}_i; \boldsymbol{R}_I)\psi_n^{\mathrm{nuc}}(\boldsymbol{R}_I) \tag{8}$$

where ψ_0^{elec} is the ground state electronic wave function that has been considered up until now. The sum in equation (8) runs over all electronic states of the molecule including those lying in the electronic continuum. Formally the nonadiabatic correction can therefore be written:

$$W^{\mathrm{nonad}}(\boldsymbol{Q}) = \sum_{n>0} \left\langle \psi_0^{\mathrm{elec}} | \hat{T}_N | \psi_n^{\mathrm{elec}} \right\rangle \tag{9}$$

The infinite sum over electronic states makes working with this form of the wave function very difficult, and full treatments of the nonadiabatic corrections are rare. In practice, the sum is often truncated after two or three terms in the important case of electronic states which lie near to each other. Schwenke (2001) has given a treatment based on performing the full sum over the finite set of states given by a restricted (Hartree–Fock) treatment of the electronic problem.

More pragmatic treatments of the nonadiabatic problem are usually employed. The starting point for these is the observation that the nonadiabatic corrections are usually best modeled by corrections to the nuclear kinetic energy operator, $\hat{T}_N$, rather than the potential. Furthermore, these corrections take a rather different form for the vibrational and the rotational motions. For diatomic molecules, nonadiabatic effects have been explicitly taken into account when modeling the vibration–rotation spectrum for a variety of even quite heavy diatomic species.

The form used for treating the rotation–vibration levels of $^1\Sigma$ electronic states of diatomic molecules originates with Bunker and Moss (1977), who wrote the Hamiltonian:

$$\begin{aligned}\hat{H} = &-\frac{\hbar^2}{2\mu^V R^2}\frac{\partial^2}{\partial R^2} + \frac{\hbar^2}{2\mu^R R^2}J(J+1)\\ &+ (1+\gamma)W^{\mathrm{eff}}(R)\end{aligned} \tag{10}$$

where R is the bond length and J the rotational quantum number. In equation (10), the effective potential W^{eff} is scaled by $(1+\gamma)$ to allow for nonadiabatic effects. This scaling is often small and even neglected; the main means by which nonadiabatic effects are accounted for is via the two effective reduced masses: μ^V which is the vibrational reduced mass and μ^R the rotational reduced mass. These reduced masses are in principle functions of the internal molecular geometry $\boldsymbol{Q}$, as discussed by Schwartz and Le Roy (1987).

On physical grounds, the effective masses must lie within a specific range. The upper limit is the atomic mass (i.e., nucleus plus electrons) for the species in question and the lower limit is the mass of the bare nucleus for the same species. Physically, this distinction depends on the degree to which the electrons travel within the nuclei. For many electron systems, it is therefore likely that inner shell electrons will contribute to the effective nuclear mass but less likely that the outer electrons will. In practice, there are a number of ways of choosing optimal masses, for example to give the correct behavior upon dissociation or to allow for the distribution of electrons within the system (Coxon and Hajigeorgiou 1999). It can also be argued on theoretical grounds that use of atomic masses in some part compensates for errors introduced by the Born–Oppenheimer approximation (Bunker *et al.* 1977).

3 NUCLEAR COORDINATES

It is usual to consider the motions of the nuclei in a molecule as falling into three categories:

1. Translation of the whole molecule through space;
2. rotation of the whole molecule; and
3. vibration or internal motion of the molecule.

However, so far no such distinction has been made in writing down the nuclear kinetic energy operator, $\hat{T}_N$. In its simplest form, used in equation (1), this operator can be written as the sum over terms representing the kinetic energy of N individual particles. These $3N$ coordinates carry all the above motions but do not distinguish between them.

The translational motion of the whole system gives a continuous spectrum, which is not interesting if one is dealing with spectroscopy. It is therefore necessary to separate off the three coordinates that represent the translational motion of the molecule; these are the laboratory coordinates of the molecular center of mass.

The remaining $3N - 3$ coordinates are a mixture of those representing vibration and rotation. These coordinates are often termed as *space-fixed*. They are useful for representing collision complexes, such as Van der Waals molecules, where a knowledge of the various angular momenta within the system is more important than separating between vibrational and rotational motions of the whole system (Hutson 1994). Space-fixed coordinates are also useful for solving problems in an external field, as the orientation in the laboratory frame is important in this case.

For high-accuracy treatments of chemically bound molecules, it is generally desirable to separate between the coordinates representing vibrational and rotational motions; these coordinates are termed as *body-fixed*. This distinction between vibrational and rotational coordinates is useful for a number of reasons and essential for the two-step treatment of rotational motion discussed in Section 3.7. However, only for diatomic systems, there is a unique and trouble-free way of achieving the separation, see equation (10) above. For polyatomic molecules, there are a number of considerations that need to be made and the choice of coordinates may, in the end, need to be a compromise between various possible demands.

To define body-fixed coordinates, one has to make two choices: the first is a set of internal coordinates to represent the vibrational motions and the second is a set of Cartesian axes defined in the frame of the molecule. The rotational motions are then represented by the Euler angles linking the space-fixed and body-fixed axis system. Usually, three Euler angles are required to make this transformation although only two are defined for linear systems; indeed there can be other reasons, such as preservation of symmetry, for only choosing two angles in this process (Brocks *et al.* 1983). It should be noted that the actual definition of body-fixed axes is only important for rotationally excited states because the Hamiltonian for $J = 0$ is independent of this choice.

Within the body-fixed frame there are $3N - 6$ internal or vibrational coordinates or $3N - 5$ if the system is linear. This is the number of coordinates sufficient to define the relative positions of the nuclei; these internal coordinates were denoted $\boldsymbol{Q}$ in the previous sections.

3.1 Internal Coordinates

There are many possible choices of internal coordinates, even for a three-particle system. Figure 1 illustrates some coordinates that are appropriate for triatomic systems. There are three issues that need to be considered when choosing an appropriate coordinate system. The first is that the process of body-fixing the coordinates inevitably leads to the introduction of singular points in the Hamiltonian. A well-known example of this is the behavior of bent molecules; when they become linear, one moment of inertia goes to zero. This almost always leads to problems with the Hamiltonian at such geometries as the rotational kinetic energy operator depends on the inverse of the moment of inertia. Such singularities can sometimes be handled by being

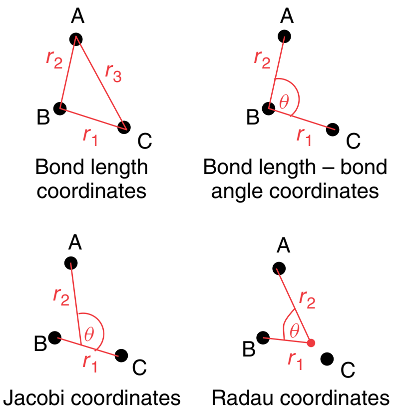


Figure 1 Four possible geometrically defined body-fixed coordinate systems for the triatomic molecule ABC.

careful with the structure of the calculation either by the choice of appropriate coupled basis functions (Tennyson and Sutcliffe 1982) or by avoiding singular regions if they lie at energies that are high enough not to be physically significant (Tennyson and Sutcliffe 1992).

The second issue is symmetry. Although molecules are often classified according to the point group of their equilibrium geometry, for nuclear motion problems, it can be more useful to deal the permutation-inversion group appropriate to the system (Bunker and Jensen 1998). If the molecule has a high-symmetry equilibrium geometry, the two groups are normally isomorphic. It is desirable to use symmetry coordinates not only because it is computationally much more efficient, but also perhaps even more importantly because it allows the automated inclusion of nuclear spin effects (*see* Section 6) into the final calculated spectrum.

The third issue governing the choice of coordinates is that some are simply more computationally efficient than others. For example, it may be natural to represent a triatomic system using the three atom–atom coordinates r_1, r_2, and r_3. However, these coordinates are unpleasant to work with because their integration ranges are coupled by triangle conditions of the form $|r_2 - r_3| \leq r_1 \leq r_2 + r_3$. In this case, a simple transformation of the coordinates into the so-called Pekeris coordinates

$$\tilde{r}_i = r_j + r_k - r_i \tag{11}$$

resolves the problem with integration ranges. However, these coordinates are still not widely used. Other issues of computational efficiency relating to choice of internal coordinates are discussed below.

Broadly speaking, the possible internal coordinate systems can be classified as follows:

1. **Normal coordinates** are the standard coordinates used to solve for the harmonic motions of molecules (Wilson *et al.* 1980) and are defined as displacements in the directions of the simple harmonic motions about a unique equilibrium structure. Normal coordinates are generally not suitable for giving high-accuracy results, particularly if the system undergoes large amplitude motion or has more than one minimum in its potential energy surface. However, they are widely used for semirigid systems and are the basis of a rather general treatment of the molecular vibration–rotation problem (Carter and Bowman 1998). It should be noted that even seemingly rigid systems will undergo large amplitude vibrational motion given enough vibrational energy, for example near any dissociation limit. Such states will almost inevitably lead to problems with normal coordinates.
2. **Physically motivated coordinates** are the ones which are used to define the chemical bonding schemes in a particular molecule; the bond length-bond angle coordinates shown in Figure 1 represents such coordinates for molecules such as water or H_2S. Potential energy surfaces are often written in these coordinates and there are good physical reasons for assuming that they often provide the most compact coordinate system for treating a molecule. The main disadvantage of these coordinates is that they lead to rather complicated kinetic operators that have to be explicitly rederived, and reprogrammed for each class of molecular bonding to be considered. The increasing use of discrete variable representation (DVR)-based methods, which thrive on having simple kinetic energy operators, and the move to study larger molecules have led to a decline in the use of such coordinates. There may also be more than $3N - 6$ physically motivated coordinates; the classic examples are XY_4 molecules such as methane, which are naturally represented by four radial and six angular coordinates. The extra, or redundant, coordinate in this problem is quite difficult to deal with elegantly (Manson and Law 2006).
3. **Orthogonal coordinates** are a special class of coordinates for which the kinetic energy operator contains no cross-derivative terms. These simple and rather general kinetic energy operators are particularly useful for DVR methods. Jacobi (or scattering) coordinates and Radau coordinates, which are illustrated in Figure 1, are the standard orthogonal coordinates for three atom problems. For larger molecules combinations of Jacobi and Radau coordinates, often known as *polyspherical coordinates*, also give orthogonal coordinate systems (Mladenovic 2000a, Schwenke 2003b, Iung and Gatti 2006). Of course orthogonal coordinates can also be physically motivated, such is the case of the H_2–Ar Van der Waals complex whose vibrations are naturally represented in Jacobi coordinates.
4. **Hyperspherical coordinates** define a single hyperradius, usually denoted ρ, related to the overall size of the molecule at each geometry and $3N - 7$ angular coordinates. Hyperspherical coordinates are particular well suited to highly symmetric X_N molecules as they treat all nuclei equally; they have therefore been quite extensively used for H_3^+ (Wolniewicz and Hinze 1994). However, they are quite difficult to use and basis set expansions in these coordinates quite often become very inefficient for large values of ρ.

Examples of calculations that use all the above coordinate systems can be found in the scientific literature. It should be noted that for polyatomic systems, the precise definition of the reduced mass is coordinate dependent.

3.2 Rotational Motion and Coordinates

The Wigner rotation matrices, $D^J_{Mk}(\alpha,\beta,\gamma)$, provide a complete basis for describing the rotational motion of molecule with total rotational angular momentum J. M is the projection of J onto the laboratory or space-fixed axis system. In the absence of any external field, the results are degenerate on M and this quantum number can be ignored. Quantum number k is the projection of J onto the body-fixed axes which are related to the space-fixed ones by the Euler angles (α,β,γ). As k runs from $-J$ to $+J$ it naturally takes $2J+1$ values. However, even for asymmetric systems, the rotational parity as given by $(-1)^{J+p}$, provides an extra conserved quantity; it is therefore more usual to rewrite the rotation basis as

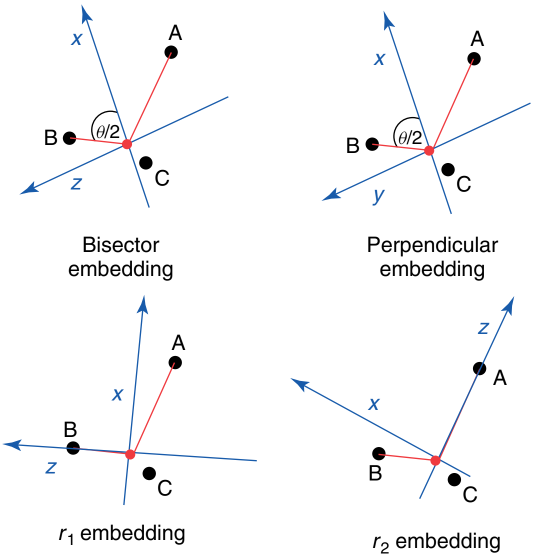
$$|Jkp\rangle = 2^{-\frac{1}{2}}(1+\delta_{k0})^{-\frac{1}{2}}\left(D^J_{Mk} + (-1)^p D^J_{M-k}\right) \qquad (12)$$

where p can take the values 0 (sometimes called 'e') and 1 (called 'f'). Note that the above definition of the rotational basis is not unique and others, which differ by various phase factors, are also in regular use (Szalay and Lane 1992).

Any complete solution of the rotational problem is independent of the definition of k and hence the choice of body-fixed axes. However, the efficiency of any approximation is strongly dependent on making a good choice of these axes. The optimal choice rotational coordinates are ones that satisfy the Eckart conditions which go naturally with normal coordinates (Wilson *et al.* 1980). However, attempts to combine the use of Eckart conditions with other internal coordinate systems have led to ungainly Hamiltonians which have found little practical application because these conditions lead to body-fixed axes that are geometry dependent (Wei and Carrington 1997).

The more normal approach is to embed the axis system in the molecule by defining them geometrically (Tennyson and Sutcliffe 1982, 1992). Examples of different axes embeddings, all of which have been used in practical calculations, are given in Figure 2 for the single case of a triatomic molecule represented in Radau coordinates. It should be noted that while vibration-only, or $J=0$, Hamiltonian is the same for all three cases, the full rotation–vibration Hamiltonian is very different in each case as the pattern of the Coriolis coupling between the vibrational and rotational motion usually has a completely different structure.

Experience and physical intuition suggest that the best choice of axis embedding is the one in which k most closely resembles the dominant "K" in the molecule under consideration. In the examples of Figure 2, this suggests that the z-perpendicular embedding would be best for H_3^+ (Kostin *et al.* 2002) as in this case K, the projection of J onto an axis perpendicular to the plain of the molecule, is a good quantum number in the absence of vibrational motion. For water, the bisector embedding is best as, at least for symmetric structures, k is the same as the dominant K_a quantum number for this molecule (Tennyson and Sutcliffe 1992).



Bisector embedding

Perpendicular embedding

r_1 embedding

r_2 embedding

Figure 2 Four possible embeddings of a body-fixed axis system for the triatomic molecule ABC represented in Radau coordinates. In each case, the unspecified axis points out of the page giving a righthand set of axes.

The precise choice of the axes to embed follows similar considerations given above when discussing internal coordinates: singularities, symmetry, and computational efficiency. Singularities put a particularly strong constraint on the practical choice of axis embedding. Thus, for example, neither z-perpendicular nor bisector embeddings of Figure 2 have been formulated in a way that is usable for triatomic molecules with three unlike atoms. This means, for instance, that calculations on the HDO molecule have all been performed using the r_2-embedding.

3.3 Vibrational Motion

There are a number of ways of treating the vibrational motions of a system. The traditional method is to use perturbation theory often based on the use of harmonic oscillators as the zeroth-order basis functions (*see* Field *et al.* 2011: **Effective Hamiltonians for Electronic Fine Structure and Polyatomic Vibrations**, this handbook). This method is fairly easy to apply and can thus be used for relatively large systems. Indeed, the calculation of the parameters associated with this approach, known as *force constants*, is now a routine part of many ab initio electronic structure packages (*see* Breidung and Thiel 2011: **Prediction of Vibrational Spectra from Ab Initio Theory**, this handbook). However, accurate results can only be obtained in this way for the low-lying states of semirigid molecules. To go beyond this, it is necessary to find more complete solutions of the nuclear motion Schrödinger equation. These are considered in the following subsections.

3.4 Direct Integration

A straightforward and accurate method of solving for the vibrational motion is by direct numerical integration of the Schrödinger equation. At present, this is only done routinely for diatomic systems where it is the method of choice. There are a number of programs available for numerically solving the two atom nuclear motion Schrödinger equation; particularly recommended is the program LEVEL due to Le Roy (2007) which gives excellent results for both bound and quasibound states.

For triatomics direct integration can also be used for one coordinate if the others have already been solved for. This may be the atom–diatom Jacobi coordinate for Van der Waals complexes (Hutson 1994) or the hyperradius for hyperspherical coordinates. To date, multidimensional direct numerical integration has not made a significant impact on the polyatomic problem but this is likely to change as computer power increases.

3.5 Variational Methods

Variational methods use basis functions to represent the vibrational motions in a molecule. These are then used to obtain a direct solution for the nuclear motion problem for both the rotation–vibration wave function and the associated energy level. In this method, vibrational motions are often written as the product of one-dimensional basis functions. For concreteness, and to keep the expressions tractable, I explicitly consider a triatomic system with three vibrational degrees of freedom; generalization to larger systems is straightforward. For this case, the expansion can be written as

$$\begin{aligned}|nJp> &= \sum_{k=0}^{J} |Jkp\rangle \sum_{m_1m_2m_3} c^{nJp}_{km_1m_2m_3} \\ &\quad \times P^k_{m_1}(Q_1)P^k_{m_2}(Q_2)P^k_{m_3}(Q_3) \\ &= \sum_{km_1m_2m_3} c^{nJp}_{km_1m_2m_3}|Jkp\rangle|m_1m_2m_3\rangle \end{aligned} \tag{13}$$

where $|nJp\rangle$ is the wave function of the n^{th} vibration–rotation state with rotational symmetry, denoted (J, p). This state has energy E^{Jp}_n. The $|Jkp\rangle$ are the symmetrized rotational functions defined above, equation (12), and the $P^k_{m_i}$ are the vibrational basis functions, which may depend on k, and are each a function of a single internal coordinate denoted Q_i. The last line of Equation (13) simply represents the same thing in more compact Dirac notation.

The unknowns in equations (13) are the coefficients $c^{nJp}_{km_1m_2m_3}$. These are obtained using the variational principle by diagonalizing the secular Hamiltonian matrix implied by the basis functions $|Jkp\rangle|m_1m_2m_3\rangle$, *see* equation (14) below. This procedure relies on the more general formulation of the variational principle which also applies to excited states of the system. For a given rotational symmetry, (J, p), the lowest eigenvalue of the matrix gives an upper bound to the lowest energy with that symmetry, E^{Jp}_1; the second lowest eigenvalue gives an upper bound to the first excited energy with that symmetry, E^{Jp}_2, and so forth.

Equation (13) does not specify the number of basis functions used for each coordinate. In principle, and unlike the rotational basis functions discussed above, this number is infinite. It is therefore necessary to truncate each series at some finite number of functions N_i. This method has become known as the variational basis representation (VBR) (Light and Carrington 2000). A property of the variational principle and hence the VBR is that the energy levels obtained with $N_i + 1$ functions will always be lower than those obtained with only N_i functions. Convergence of the problem is obtained when increasing the size of the basis does not materially alter the energy levels of interest. Given that the computer time taken critically depends on the size of the secular matrix, usually as the cube of its total dimension, the choice of a compact basis is of great importance for obtaining efficient solutions. Therefore, the polynomial functions discussed below are often preconditioned or contracted to give more efficient basis sets.

To construct the secular matrix in terms of these basis functions, it is necessary to compute the individual matrix elements. For given (J, p) values, the matrix elements of a triatomic system can be written as

$$H^{Jp}_{SS'} = \langle Jkp|\langle m_1m_2m_3|\hat{H}^{\text{bf}}|m'_1m'_2m'_3\rangle|Jk'p\rangle \tag{14}$$

where the compound index S has been used to denote the quantum numbers k, m_1, m_2, m_3 and the Hamiltonian, $\hat{H}^{\text{bf}}$, is assumed to be one of the body-fixed ones discussed in Section 3. The Dirac notation in equation (14) implies integration over the three Euler angles representing the rotational motion and $3N - 6$ internal coordinates. The integration over the rotational coordinates can usually be achieved analytically but computing matrix elements for the vibrational coordinates is less straightforward.

As already discussed in Section 2.1, the potential energy surface upon which the nuclear motion occurs is a far from simple function. This means either the form of this potential must be approximated or numerical integration must be performed to obtain the potential energy contribution to the matrix element. For high accuracy results, the latter approach is preferable.

A variety of basis functions can be used in the expansion given by equation (13); indeed, for higher dimensional problems and for problems written in hyperspherical harmonics, it is usual to use multidimensional basis functions for the angular part of the motions. Coupled basis functions are also required when there is a symmetry operation linking two of the coordinates. The most common basis functions used are based on orthogonal polynomials. Such polynomials include Hermite, which are the solution of the harmonic oscillator problem, Laguerre, which are the solution of both the Morse oscillator and spherical oscillator problems, Legendre, which are the solution of the free rotor problem and Chebychev. Particularly for angular coordinates, a number of generalizations of these polynomials are in use; associated Legendre functions are widely used to allow for coupling between angular and rotational motion (Tennyson and Sutcliffe 1982), a further generalization to associated Jacobi functions was introduced by Mladenovic (2000b) and for polyatomic problems spherical harmonics or products of them (Brocks *et al.* 1983) are often used.

Orthogonal polynomials have a variety of useful properties not least of which is that numerical integration over matrix elements involving them can be performed particularly efficiently using Gaussian quadrature (Stroud and Secrest 1966). In Gaussian quadrature, the points, x_α, of an M-point quadrature based on polynomial P are given by the zeroes of P_M. The weight associated with each point, w_α, is also straightforwardly obtained from the properties of the same polynomials (Stroud and Secrest 1966). The solutions of the secular problem are only truly variational if the matrix elements are evaluated accurately and it can be shown that the $2N + 1$ Gaussian quadrature points, where N is the highest order polynomial used in the basis, are sufficient to evaluate the matrix elements exactly providing the operator under consideration, usually the potential, is itself polynomial. In practice, significantly fewer quadrature points, such as $N + 3$ (Tennyson and Sutcliffe 1982), are often found to be sufficient.

3.6 Grid-based Methods

It is possible to get excellent results for low-lying states using basis sets but they tend to become increasingly inefficient as more excited states are required. As a result, there has been a shift toward grid-based methods, which are generally more efficient under these circumstances.

The particular grid-based method of choice for solving the nuclear motion problem is the DVR. In a classical DVR approach, the grid points are obtained as the zeroes of an orthogonal polynomial, although there are variants of this approach which use other grids, such as ones adapted to the particular potential energy surface under consideration (Echave and Clary 1992). If the polynomials chosen as the basis of the DVR grid are the same ones that would have been used in a VBR calculation, there is a clear link between the DVR and VBR approaches. Indeed, they are numerically identical if polynomials up to order N_i are used with $N_i + 1$ quadrature points in the VBR and the DVR is performed using the same $N_i + 1$ quadrature points as its grid. In the DVR, these points provide both the functions and the quadrature scheme. The main disadvantage of the DVR is that $N_i + 1$ is suboptimal for evaluating the matrix elements meaning that in principle the method is not strictly variational and results are sometimes found to converge from below (Henderson *et al.* 1993). This means, in practice, that N_i needs to be somewhat larger for the DVR and than the VBR which makes the DVR a poor choice for problems where a very compact basis set is available or only very few solutions are required.

DVR-based methods have, however, a number of major advantages. Owing to the so-called quadrature approximation (Bačić and Light 1989) matrix elements over the potential, and indeed any other polynomial function, are simply diagonal. This can be used in one of the two ways. The most obvious is that if a simple kinetic energy operator is used the resulting secular matrix is very sparse, hence the advantage of orthogonal coordinates (*see* section 3.1). The eigenvalues of such matrices can be obtained very efficiently based on iterative procedures such as Lanczos diagonalization (*see* Carrington 2011: **Using Iterative Methods to Compute Vibrational Spectra**, this handbook). This has allowed vast problems to be solved using the DVR method (Light and Carrington 2000).

An alternative way of using the potential-diagonal property of a DVR is by intermediate diagonalization and truncation. It has been shown (Bačić and Light 1989) that the DVR provides an optimal coordinate separation scheme and if some coordinates are frozen at the appropriate DVR points and the resulting smaller secular problem diagonalized, the resulting solutions can be truncated to give a highly compact basis for the full problem. The aim of the diagonalization and truncation procedure is to give a final secular matrix with a very high information content. I have generally favored this method in my work because it is a good one for obtaining wave functions as well as energies. Wave functions are vital for calculating spectra, and, as discussed in the next section, vibrational wave functions can also be used to seed the full rotation–vibration problem.

Although I have introduced the VBR and DVR methods as distinct, competing Methods, this is in practice not entirely true. The ease of transformation between DVR and VBR means that it is common for calculations to use either hybrid methods or to transform between the two representations at intermediate steps during the calculation (*see* Gatti *et al*. 1999 for example).

3.7 Two-step Treatment of Rotation Motion

Equation (13) implies that rotational–vibrational motion is solved in a single step. This is indeed possible but it leads to a problem which scales as J^3 which means, for example, that doing a calculation for $J = 50$ would be over 100 000 times slower than solving the simple vibrational problem for $J = 0$. Under these circumstances, studying a high degree of rotational excitation, which occurs particularly for hot systems, is unlikely to be feasible.

An alternative approach is to find the solutions to equation (13) in two steps. In the first step, the initial summation over k is replaced by solving $J + 1$ effective "vibrational" problems which only depend parametrically on k. The lowest solutions of these problems are then used as a basis for solving the full problem. This second step is simpler because the diagonal elements of the secular matrix are simply the solutions of the first step and the off-diagonal elements are given by the Coriolis coupling terms appropriate for the particular embedding of the body-fixed axes that has been chosen. This leads to secular matrices, which get increasingly sparse as J increases because all matrix elements with $|k - k'| > 2$ are zero. These can often be diagonalized efficiently using iterative procedures.

The two-step procedure is still fully variational because it simply involves a further truncation of the basis. With an appropriate or fortunate choice of body-fixed axes which reduces the Coriolis coupling, it becomes particularly efficient. In the best case, which is often realized, the time taken is determined by the first "vibrational" step. Under these circumstances, the time required for treating rotationally excited states scales as J rather than the J^3 anticipated above; this represents a massive saving.

3.8 More Approximate Methods

The use of variational methods has been expanding rapidly. They are now the method of choice for triatomic systems, becoming increasingly common for tetratomics and are starting to be used for selected pentatomic problems. However, such methods scale exponentially with the number of degrees of freedom that are explicitly treated in any calculation. This makes the use of more approximate methods essential for larger systems. The most widely used of these is Multimode (Carter and Bowman 1998), which is based upon the use of normal vibrational models. Multimode is appropriate for systems undergoing small-amplitude motion about a single equilibrium geometry without too much coupling between the various normal modes.

4 ELECTRONIC MOTION

Figure 3 depicts the steps necessary to calculate the rotation–vibration spectrum of a molecule using entirely first-principles quantum mechanics. I note that this figure implicitly makes the Born–Oppenheimer approximation by separating the steps which solve for the electronic and nuclear motions. In practice, there are very few calculations that do not make this separation, even when corrections are introduced into the second, nuclear-motion step to compensate for deficiencies in the Born–Oppenheimer

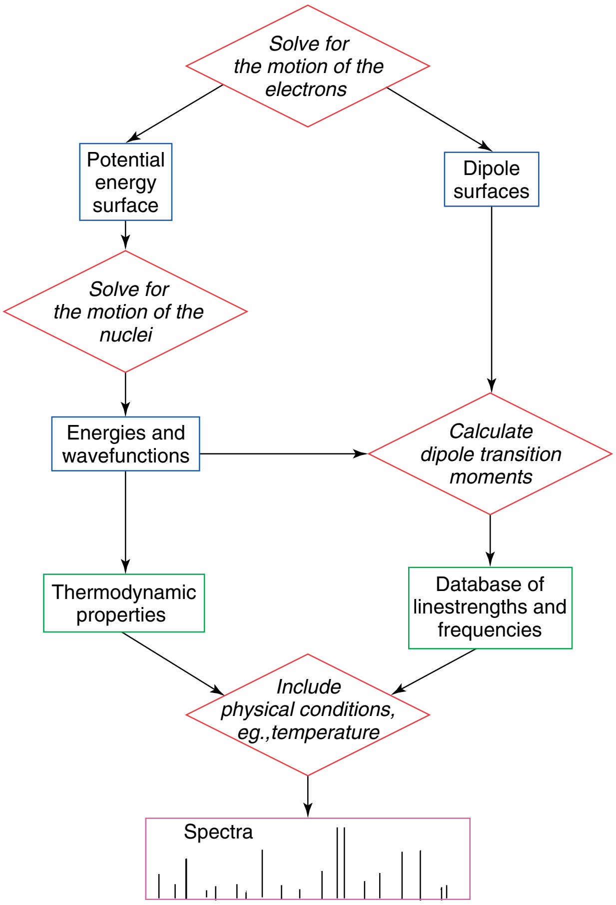


Figure 3 Schematic figure showing the steps in a first-principles calculation of the rotation–vibration spectrum of a molecule.

approximation. What is clear from Figure 3 is that calculating the instantaneous dipole moment of the system at the same time as one calculates its electronic energy allows for the treatment of the intensity problem. This issue will be dealt with in the following section, first the issues arising from the ab initio treatment of electronic motion are considered.

For many problems, particularly those involving diatomic and triatomic molecules, the accuracy of the results is essentially determined by the underlying potential energy surface as given by $V^{\mathrm{BO}}(\boldsymbol{Q})$ or more generally $W^{\mathrm{eff}}(\boldsymbol{Q})$. This can of course be calculated ab initio using a number of freely available or commercial quantum chemistry programs. It is not my purpose to review these but just to comment on their usefulness for high accuracy results; *see* Breidung and Thiel 2011: **Prediction of Vibrational Spectra from Ab Initio Theory**, this handbook, for a more general discussion.

4.1 Conventional Methods

Conventional calculations start by solving the Hartree–Fock problem for the molecule of interest. However, neither this approach, nor calculations based on the now widespread use of density functional theory (DFT), are capable of giving results which are more than semiquantitative in their agreement with observation. To obtain potential energy surfaces that are accurate, it is necessary to move beyond Hartree–Fock methods and treat the electron correlation problem using a high-level theory, and indeed also to use large basis sets.

There are two conventional high-level theories which are generally employed to get accurate results. These are coupled clusters (CC) and multi-reference configuration interaction (MR-CI). It is not my purpose to discuss these in detail and the reader is referred to standard quantum chemistry texts, such as the one by Jensen (2006), for details of these methods.

Configuration interaction (CI) involves representing the electron correlation using a linear combination of terms derived by promoting electrons from the ground state configuration of the molecule. A hierarchy is often written in terms of excitations, which can be denoted as single (S), double (D), triple (T), and so forth promotions from the reference configuration(s). For a given basis, the best possible (and variationally lowest) answer is given by a full-CI calculation in which all possible promotions are considered. However, full-CI are prohibitively expensive for many-electron systems for all but the smallest basis sets. They have therefore yet to have a significant impact on the calculation of potential energy surfaces.

CC and MR-CI methods differ in how they treat these excitation expansions. CC methods use an exponential form for the electron excitation operator, which has a number of theoretical benefits and has allowed the development of very efficient algorithms for building CC wave functions. The "gold standard" method is Coupled clusters with single and double excitation and perturbative triples (CCSD(T)); this is the usual way of denoting a CC calculation that explicitly treats single and double excitations but only approximately allows for triple excitations via perturbation theory. The main problem with CC approaches is that they use expansions based on excitation from a single configuration, usually the Hartree–Fock ground state. This is very efficient for states that are dominated by a single configuration but is not general. For example, it inevitably fails to correctly represent bond-breaking in most molecules. This means, as a rule of thumb, that CCSD(T) is good at mapping out the potential energy surface in the region about the equilibrium geometry of a molecule, but is not so reliable when one of the molecular bond lengths becomes significantly stretched.

MR–CI calculations avoid the problems caused by using a single reference configuration for the CI expansion by using a set of reference configuration, hence multireference, so that all the important configurations required for building up the wave function over all of the potential energy surface are in the starting expansion. Single and double excitations are then considered out of this enlarged reference space. Again, it is possible to approximately allow for the effect of triple and higher excitations using perturbation theory. The MR–CI ansatz is clearly very powerful and can be used to model surfaces involving a significant degree of stretching, or indeed other complications. However, MR–CI calculations are computationally very expensive, which limits their use with reasonable basis sets to relatively small molecules.

A good CCSD(T) or MR-CI calculation can recover a significant fraction of the correlation energy. How much correlation energy is recovered however is strongly dependent on the quality of the one-particle basis functions employed in the calculation. In practice, with these methods, it is the size of the basis set that can be practically used which usually determines their accuracy. One approach to mitigating the effects of the basis set truncation is to perform a series of calculations with systematically increasing basis sets and then extrapolate the results to what is known as the *complete basis set limit*.

4.2 Explicitly Correlated Methods

From the early days of quantum mechanics, it has been known that excellent wave functions can be obtained by including explicitly the interelectron distance, r_{12}, in the functional form of the wave function. For obvious reasons, methods that include this distance are generally known as *R12 methods*. However, the integrals involved in such calculations are formidably difficult and for many decades, the use of R12 methods was confined to two electron systems. Following work by Klopper and Kutzelnigg (1987), a method of calculating these integrals by the insertion of an extra (auxiliary) basis set and the use of the resolution of the identity have been developed. These have allowed the application of R12 methods to molecules with more than two electrons, albeit their use is still restricted to few electron systems. The general effect of R12 methods is to significantly accelerate the basis set convergence problem discussed in the previous section.

As two electrons approach each other, their combined wave function should show a cusp. This cusp can be well represented by the simple use of the electron–electron coordinate, r_{12}, but this can lead to problems with the wave function when the two electrons are well separated. These problems are solved using a function of the form $\exp(-r_{12})$ to represent the interaction. Very recently methods, known generically as *F12 methods*, have been developed which are based on the more appropriate use of functions of the electron–electron distance in the wave functions. These methods have been shown to have excellent basis set convergence properties. However, it is still early days for F12 procedures. To date, no MR-CI F12 calculations have been performed and CCSD(T)-F12 calculations have yet to be applied systematically to problems of spectroscopic importance.

4.3 Minor Corrections

The previous two subsections have discussed issues to do with obtaining the correct electronic energy for the system. However, as already discussed in Section 2.1, the effective potential energy surface $W^{\text{eff}}(\boldsymbol{Q})$, depends on more than the simple nonrelativistic electronic energy.

Quantum chemists often cite an error of $1\,\text{cm}^{-1}$ as spectroscopic accuracy. Reading other chapters in this book will quickly show that high-resolution spectroscopy routinely achieves much higher accuracy than this; for vibration–rotation spectra, line frequencies are generally measured with errors in the region of $0.001\,\text{cm}^{-1}$; errors as low as $10^{-6}\,\text{cm}^{-1}$ can be obtained in precision experiments. The $1\,\text{cm}^{-1}$ error limit is really a pragmatic limit as it represents the approximate accuracy that can be achieved with a high-quality treatment of the valence electrons of a molecule alone. To improve this accuracy involves considering a number of effects that are routinely neglected in nearly all treatments of the electronic structure problem. These effects are discussed here.

Before considering the effects in detail, it is worth noting that it is the shape, not the absolute energy of the potential energy surface that determines the vibration–rotation energies. Therefore, when including any corrections to the potential, it is important only to get the variation of these corrections as a function of molecular geometry rather than to get the absolute magnitude of the effect. Similar considerations apply to the CI calculations of the potential as one can rarely perform calculations that give the total energy of the system accurately.

Chemical understanding and intuition is entirely based on the behavior of valence electrons. It would therefore seem natural that one should be able to freeze core electrons when constructing a potential energy surface. The core electrons dominate the absolute energy of a molecule but, if they remain unperturbed while the molecule vibrates, it should not strongly influence the shape of the surface. For semiquantitative calculations, this is true, but for high-accuracy work, it is essential to consider the correlation between the core and valence electrons. Whether this core-valence (CV) correction is included in the original electronic structure calculation by means of an all-electron CI calculation or added as a correction afterwards depends on the details of the system under study and the methodology being employed.

The CV correction is probably the most important "minor correction," but there is a growing realization that the effect of relativity on the motion of the electrons should not be neglected. In principle, one can perform a complete relativistic treatment of the electronic structure problem using a Dirac formulation such as the Dirac–Coulomb Hamiltonian. However, the Dirac equation is significantly harder to solve than Schrödinger's necessitating, for example, the use of an extra set of basis functions for the relativistic small component. This inevitably leads to a compromise on the level of correlation that can be included in such calculations. A more practical strategy, at least for light nuclei, is to complete a comprehensive nonrelativistic (or Schrödinger) treatment of the problem and then to introduce relativistic effects using perturbation theory. Test calculations of water have shown that although the perturbation theory does not recover the absolute magnitude of the relativistic effects fully, it does a very good job of representing the shape of these corrections (Tarczay *et al*. 2001). As discussed previously, this is the key aspect required for modeling spectra.

Within a perturbation theory framework, there are a hierarchy of relativistic corrections that need to be considered. The largest contributions are generally taken to arise from operators that act on a single electron. These are the mass-velocity (MV) and the one-electron Darwin (D1) terms. Collectively, this one-electron correction is thus labeled mass-vecocity and one-electron Darwin (MVD1).

The mass-velocity term is the leading term in a standard (i.e., nonquantum mechanical) relativistic treatment of rapid motion, whereas the Darwin term, which normally acts to reduce the energy lowering of the mass-velocity correction, is a purely quantum mechanical effect with no classical analog. For light molecules, the MVD1 correction can be calculated using perturbation theory and nonrelativistic wave functions as a routine and computationally cheap addition to an electronic structure calculation performed with standard quantum chemistry packages.

In cases where the MVD1 correction is large, such as in water, it may be necessary to also consider two-electron corrections to the relativistic energy. The two-electron Darwin term (D2) has been calculated but has generally been found to be small. The other two-electron term of significance in the Breit correction, which arises from magnetic interactions that are not considered in the Dirac–Coulomb Hamiltonian. The Breit correction can be approximated by the simpler to calculate Gaunt correction although my experience is that the way these two terms contribute to a potential energy surface is sufficiently different that the saving engendered by using the Gaunt correction is not really worthwhile. The corrections can again be calculated using perturbation theory for light molecules (Tarczay *et al.* 2001).

Further corrections to the Schrödinger treatment of electronic motion are spin–orbit interaction and the Lamb shift. Experience has shown that while spin–orbit interaction may be important for open shell systems, its contribution to the spectroscopy of closed shell molecules can safely be ignored (Tarczay *et al.* 2001). Perhaps rather surprisingly, this is not true for the Lamb shift, which arises from a quantum electrodynamic (QED) treatment of electronic motion and is therefore an addition to the Dirac equation. A full QED treatment of a many-electron molecule would be a ferocious undertaking and to my knowledge has yet to be attempted. Fortunately, it is possible to approximate the effect of QED using integrals already calculated as part of a perturbative treatment of the one-electron Darwin (D1) term.

The above corrections are concerned with the electronic motion. As discussed in Section 2.1, accurate treatments must also consider corrections to the Born–Oppenheimer approximation. Table 1 summarizes the approximate magnitude of the various corrections to the vibrational band origins of a few well-studied light, triatomic systems. For comparison, the approximate error due to the incomplete treatment of the electronic motion of the valence electrons is also given. These numbers reflect what is available rather than, particularly for hydrogen sulfide, what is possible. While both water (Polyansky *et al.* 2003) and H_3^+ (Cencek *et al.* 1998) have been subjected to very systematic attempts to completely converge calculations of their potential energy surfaces, I am unaware of any recent attempt to do this for H_2S.

Table 1 shows a number of features which are worth discussing. Sulfur lies directly below oxygen in the periodic table and therefore has a very much larger absolute relativistic energy. However, the relativistic contribution to the potential energy surfaces of the two systems are either similar in magnitude, for MVD1 and D2, or much larger for water, for the Breit and QED corrections. There is a trade-off here; although the sulfur 1s electrons do indeed have a large relativistic contribution to their energy, they are effectively shielded from the valence interactions and therefore are only very weakly sensitive to the geometry of the H atoms in H_2S. Conversely for water, for which the MVD1 correction is about $10\,000\,\text{cm}^{-1}$ in magnitude, the rehybridization of the valence electrons from sp^3 at equilibrium to sp at linear geometries significantly perturbs the inner electrons. It should be noted that the barrier to linearity in water is only about $11\,000\,\text{cm}^{-1}$ and the relativistic contribution to this is about $50\,\text{cm}^{-1}$. This makes the bending vibrations particularly sensitive to the inclusion of relativistic effects. For H_3^+, Cencek *et al.* (1998) calculated a full relativistic surface. Their calculations show that the change in absolute energy due to the inclusion of relativistic effects is about $2\,\text{cm}^{-1}$, but this value is rather insensitive to the geometry of this systems so that relativistic effects make little contribution to the rotation–vibration energy levels. A study of the HF molecule, which is isoelectronic to water, by Müller *et al.* (1998) produced qualitatively similar results.

It is interesting to compare the two corrections to the Born–Oppenheimer approximation: the adiabatic or BODC and the nonadiabatic correction. It is known from calculations on H_2 and H_2^+ that for purely hydrogenic systems, the adiabatic correction is more important than the nonadiabatic one. The same is found to be true for the H_3^+ molecule. Conversely, diatomic studies show that for heavy systems with no H atoms, the nonadiabatic correction is dominant. For water and H_2S, the two are found to be similar in magnitude. The two effects tend to partially cancel although one must be careful with this as the effective potential energy surfaces of polyatomic systems are of course multidimensional and different effects do not behave in the same way as a function of the various coordinates.

Although Table 1 considers only vibrational energies, it should be noted that there are errors also associated with the rotational energy of each molecule which arise from any incomplete treatment of the electronic structure problem. In the case of water, the errors in the energy levels with $J = 20$ are of a similar magnitude to those tabulated for its vibrational band origins.

Table 1 Contribution of the various minor corrections to the observed vibrational band origins (VBOs) of the molecules H_2O, H_2S, and H_3^+.[(a)]

Effect	Contribution (cm^{-1})		
	H_2O	H_2S	H_3^+
One electron relativistic correction (MVD1)	−19	−20	±0.003
Two electron Darwin term (D2)	−0.8	−0.8	(b)
Gaunt correction	+5	+0.003	(b)
Breit correction	+6	+0.003	(b)
Lamb shift (QED correction)	+1.3	+1.5	(b)
Adiabatic correction (BODC)	+5	+2	±1.5
Nonadiabatic correction	−4	−3[(c)]	−0.5
Correlation convergence	3	+30	±0.003
Range of VBOs considered	25 000	14 000	8000

(a) The values given approximately represent the largest shift to an observed VBO for the specified molecule upon inclusion of the effect. Note that the Gaunt correction is an approximation to the Breit correction; these and the other corrections are discussed in the text. The "correlation convergence" is an estimate of the shift in the band origin expected due to an incomplete treatment of electron correlation problem. As experiments probe different numbers of VBOs for each system, the approximate frequency range spanned by the VBOs used to make the comparison is also given

(b) Unknown but assumed to be negligible

(c) Estimated as no high level calculation is available

4.4 Fitting the Potential Energy Surface

One of the least satisfactory parts of the first-principle calculation of a molecular rotation–vibration spectrum arises from the need to fit the electronic structure calculations to give a potential energy surface. This arises from the fact that the electronic structure calculations are performed at a discrete grid of geometries and, at least in principle, one usually needs to know the value of the electronic energy at all geometries within the energy range of interest. The usual means of bridging this gap is to fit the electronic energies with some suitable analytic function, which allows one to interpolate between those points for which the electronic energy has been explicitly calculated. In general terms, these fits take the form

$$V^{\text{fit}}(\boldsymbol{Q}) = \sum_i c_i f_i(\boldsymbol{Q}) \tag{15}$$

where the $f_i(\boldsymbol{Q})$ are some appropriate set of known function, often a product of one-dimensional polynomials in each of the coordinates. Fitting thus becomes the task of determining the coefficients, c_i. This is achieved using linear least-squares fitting, the theory and practice of which is very well developed.

The problem with fitting is that there is no universal function, which is entirely satisfactory for representing the potential energy surface of any given polyatomic molecule. In particular, to avoid losing accuracy in the fitted potential, it is often necessary to fit a very flexible function, which means a large number of parameters in this function must be determined. These parameters are often quite strongly correlated, which can lead to unstable behavior in the potential function. In the most extreme case, which is not uncommon, fitted potentials can display deep and unphysical minima, generally referred to as *holes*. In practice, it is usually possible, by a procedure that can be described as informed trial and error, to come up with a satisfactory fit to the electronic structure points that does not introduce a large additional error. It transpires, for reasons discussed below, that it is more difficult to obtain satisfactory fits to the dipole moments. I therefore return to the topic of fitting in Section 6.2.

In principle, there are at least two ways to avoid having to perform a fit to the electronic structure calculations. The first is simply to perform electronic structure calculations directly at the grid points that are required for the nuclear motion calculations. This procedure has been used a number of times going back even to the earliest variational treatments; however, it has disadvantages. First, it is inflexible; if one decides to alter the grid used in the nuclear motion step, a new set of electronic structure calculations have to be performed. The second, and in my opinion more serious problem, is that it is usually necessary to use many more grid points in the nuclear motion calculation than electronic structure points one would routinely compute as a precursor to fitting a potential: even for a triatomic molecule these may well differ by a factor of 50. The calculation of a very much larger number of electronic energies inevitably leads to compromises on the accuracy of these calculations. Because it is the electronic structure step of the calculation that usually determines its accuracy, this approach can seriously degrade the calculation.

There is a similar problem with the other obvious method of avoiding fitting: Lagrangian interpolation. There are very well-developed formulae for interpolating between grids of points, particularly in one dimension. Interpolation can be used instead of fitting but in practice requires many more electronic structure points to achieve a stable result. This is because one usually chooses fitting functions which include some physical insight in them such as the presence of the equilibrium structures. Indeed, many fits take the form of an expansion about equilibrium.

5 IMPROVING ON AB INITIO PROCEDURES

In nearly all cases, it not possible to achieve even close to experimental accuracy using purely ab initio procedures. Under these circumstances, it is sometimes useful to adjust the potential energy surface being used so that it reproduces more closely the measurements. A schematic procedure for doing this is given in Figure 4.

In principle, one can attempt a direct fit of the observed experimental data to a potential energy surface, and this has been done on a number of occasions. In practice, however, it is found that very much better results are obtained if the starting point is an ab initio surface. Indeed, experience has shown that the quality of the final fit systematically improves as the quality of the underlying ab initio surface is improved. It is generally found that with a good starting surface, it is only necessary to adjust a relatively few (typically about 10%) of the leading parameters in ab initio fit to improve it very significantly.

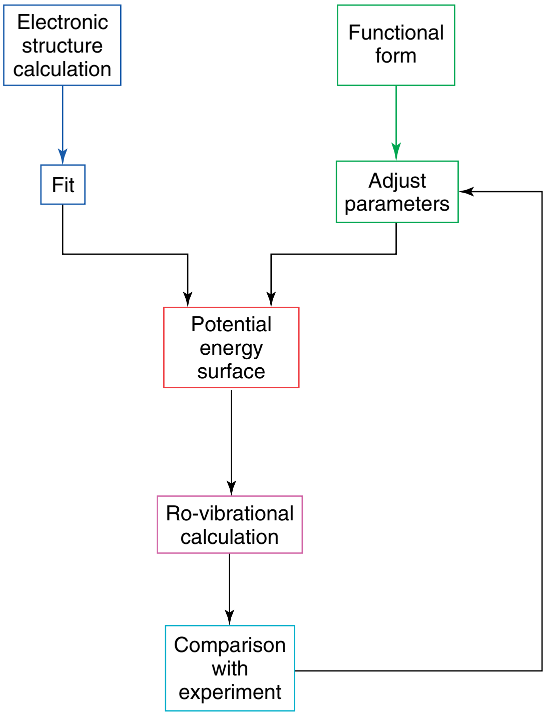


Figure 4 Schematic figure showing the steps in constructing a spectroscopically determined potential energy function.

There are now a number of cases where these fitted potentials, which are generally referred to as *spectroscopically determined potential energy surfaces*, give results that approach the accuracy of the experiment. One thing that greatly improves the computational efficiency of such fits is the use of the Hellmann–Feynman theorem that allows the expectation values of the derivatives of the potential with respect to changing one of the fit parameters to be calculated in very straightforward fashion using the expression

$$\begin{aligned}\frac{d\left\langle Jpn|V^{\mathrm{fit}}(\boldsymbol{Q})|Jpn\right\rangle}{dc_i} &= \left\langle Jpn\left|\frac{dV^{\mathrm{fit}}}{dc_i}\right|Jpn\right\rangle \\ &= \langle Jpn\,|f_i(\boldsymbol{Q})|\,Jpn\rangle \end{aligned} \tag{16}$$

where use has been made of the fact that the kinetic energy operator does not depend on c_i. Because this is cheap to evaluate, it can be used for all the coefficients in the expansion of equation (15) even if most of them are not actually varied in the final fit.

Starting from a good ab initio potential, one usually arrives at the spectroscopically determined potential within two or three iterations of the fitting procedure. However, the application of the actual procedure is not quite straightforward and usually requires many test iterations both to cleanse the spectroscopic data and to determine which is the optimal set of coefficients to vary.

6 TRANSITION INTENSITIES

The transition dipole for a pure rotation or vibration–rotation transition can be computed using the dipole moment surface, $\boldsymbol{\mu}(\boldsymbol{Q})$.

$$\boldsymbol{\mu}^{if} = \left\langle n_i J_i p_i \,|\mu(\boldsymbol{Q})|\, n_f J_f p_f \right\rangle \tag{17}$$

where i and f have been used to denote the initial and final states involved in a transition and wave functions are those defined (for a triatomic molecule) by equation (13). This integral encapsulates the rigorous selections rules:

$$\Delta J = \pm 1, \quad \Delta p = 0 \tag{18}$$

$$\Delta J = 0, \quad \Delta p = 1, \quad J \neq 0 \tag{19}$$

For molecules with identical atoms, further rigorous selection rules may arise from the symmetry; these can often be characterized using the rule that allowed transitions do not alter the nuclear spin state of the system. All other “selection rules”, such as those governing changes in vibrational quantum numbers or projections of the rotational angular momentum, which arise from less rigorous treatments, must be considered as only approximate. Such rules are best described as propensity rules.

It should be noted that for polyatomic systems, the dipole surface and the transition dipole given by equation (17) are vector quantities. It is therefore usual to work in terms of the sum over these, which gives a quantity known as the *linestrength* $S(i - f)$ which can be defined as:

$$S(i - f) = \sum \left(\sum_{l} \mu_l^{if} \right)^2 \tag{20}$$

where the inner summation in equation (20) runs over the components of the dipole, denoted by l. The outer summation over M_i and M_f, the projections of the rotational angular momenta on the space-fixed z-axis. A full derivation of this has been given by Miller *et al.* (1989) for the case of a triatomic molecule. As discussed in Section 3.2, the (field-free) energies do not depend on these quantum numbers. I note that different authors define the linestrength in different ways depending on such issues as the point at which sums over nuclear spin states or the M quantum numbers are introduced. There are also a number of ways for representing transition data (*see* Stohner and Quack 2011: **Conventions, Symbols, Quantities, Units and Constants for High-resolution Molecular Spectroscopy**, this handbook). The simplest is the Einstein A-coefficient, which can be defined in terms of the linestrength:

$$A_{if} = \frac{64\pi^4}{3c^3 h} \omega^3 \frac{S(f - i) g_i}{2J_f + 1} \tag{21}$$

where the lower state degeneracy factor, g_i, for a particular level is determined by nuclear spin statistics. A major advantage of the A_{if} is that there are no issues of units, they simply have dimensions of reciprocal time.

The intensity of a given transition as function of wavenumber, ν_{if}, and temperature, T, can be obtained using the formula for the integrated absorption coefficients:

$$I(\omega_{if}) = \frac{\frac{4.162034\times 10^{-19} \nu_{if} g_i}{[\exp(E''/kT) - \exp(E'/kT)]}}{Q(T)} S(i - f) \tag{22}$$

where $Q(T)$ is the partition function of the system, and E' and E'' are respectively the energies of the upper and lower state. The constant is appropriate for the intensity in cm/molecule if the transition wavenumber, ν_{if}, is given in cm^{-1}.

When trying to compute accurate transition intensities, two quantities have to considered: the wave functions of the states involved and the dipole moment surface. If accurate potentials are used to determine the wave functions, then experience shows that the calculated transition intensity is fairly insensitive to the details of the surface. For example, wave functions determined from high-quality ab initio potential energy surfaces and spectroscopically determined potentials give very similar results (Lodi *et al.* 2008). There is one exception to this situation: the intensity stealing that follows from the accidental interaction between nearby states. Such resonances are very sensitive to the precise details of the underlying potential and, as intensity stealing may result in a very weak transition becoming stronger by several orders of magnitude, this sensitivity is reflected in the computed transition dipoles. In other cases, it is the accuracy of the dipole moment surface which is crucial for calculating reliable transition dipoles.

6.1 Dipole Moment Calculations

Before discussing the procedures to calculate dipole moment surfaces, I would emphasize that, at least for light molecules, the most reliable dipole surfaces come from ab initio calculations rather than from fitting to experimental data (Lynas-Gray *et al.* 1995). This is in contrast with the situation with potential energy surfaces and, at least in part, arises from the much greater experimental uncertainty with which transition intensities and transition dipoles can be measured. Most experiments struggle to get accuracies significantly better than 10%, and, indeed, many experiments do not give reliable transition dipoles at all.

Many ab initio electronic structure calculations give the dipole moments at each geometry as a simple by-product of calculating the electronic wave function. This means that the dipole moment function can be determined at essentially no extra computational cost. However, such determinations usually make use of expectations values to compute the dipole moments. These are implicitly based upon the application of the Hellmann-Feynman theorem, which is only rigorously satisfied by exact wave functions. Experience has shown that for very high accuracy work, dipoles calculated using expectation values are inferior to ones computed by numerical calculation of the energy derivative as function of an external electric field. Unfortunately, the latter method is efficient only if the relevant derivatives can be calculated analytically but, particularly for high level calculations, this is often not possible; instead several electronic structure calculations are required to determine the dipole moments at each grid point.

The calculation of reliable dipole moments requires the inclusion of diffuse functions in the basis set. However, a recent detailed study on water (Lodi *et al.* 2008) showed that actually the dipole calculation converges much more quickly with basis set than the energy. The situation with the treatment of electron correlation was found to be less clear cut.

Given the importance of the so-called minor properties for determining reliable potential energy surfaces, it is interesting to ask whether they are also necessary to obtain high-accuracy dipoles. The recent study on water quoted above also investigated the contribution to the dipole moment due to the two leading energy correction terms, the CV correlation and the relativistic correction. Both corrections were found to be small, but not entirely negligible. However, it was found that the two corrections essentially canceled. This unexpected results suggests that an all-electron CI calculation, which does not allow for relativistic effects, will actually give worse results than a valence only study. Whether this is a general result remains to be determined.

6.2 Fitting a Dipole Moment Function

As for the potential energy surface, it is also necessary to fit or analytically continue the dipole moment surface between the points for which its value has been determined by the electronic structure calculations. Of course, as a vector, the dipole moment surface has several components; these can be fitted separately.

It turns out that if the aim of the study is to compute transition intensities for weak transitions, which have small transition dipoles, then fitting the dipole moment function is not at all straightforward. This problem can be simply understood by remembering how the dipole intensity of a vibrational transition is calculated within the harmonic oscillator approximation. Within this model, the intensity of a fundamental transition is approximated by the derivative of the dipole moment with respect to the coordinate that is being excited. The intensity of the first overtone is given by the second derivative, the second overtone by the third derivative and so forth. This means that higher overtones are very sensitive to the derivative of the dipole function, and in turn, to any artificial structure this surface may have.

Studies on water (*see* Lodi *et al.* (2008) for example) have shown that standard fits can lead to small oscillations in the resulting surface, which in turn lead to artificially strong transition moments for some weak overtone transitions. For water, which has been the benchmark molecule for these studies, the problem is particularly associated with the bending mode. In principle, the solution to this problem is to explicitly compute the dipole moments at a very large number of geometries. In practice, so far, artificially generated points have been used to keep the dipole moment surface smooth. This approach dampens down the strength of the artificially strong lines without totally eliminating the problem.

7 THE H_3^+ AS AN EXAMPLE

There are a number of chemically bound triatomic molecules, including water, ozone, HCN, and H_2S, and even some tetratomics such as ammonia, for which high-accuracy studies have been performed. Here the single system H_3^+ is considered as an example. This system has been the subject of the highest accuracy studies; indeed the ab initio calculation of its spectrum has been labeled a "solved problem" in molecular quantum mechanics, although in my opinion that is something of an exaggeration.

H_3^+ is a two-electron system with a highly symmetric, equilateral triangle equilibrium structure. Superficially, this should make it an easy system to work on theoretically and it is true that ultrahigh accuracy electronic structure calculations are available for this system (Cencek *et al.* 1998). However, as discussed below, nuclear motion calculations on H_3^+ are actually considerably more difficult than for the other triatomic systems listed above.

The electronic simplicity and high symmetry also make its spectrum rather simple. The symmetric isotopologues have no allowed rotational spectrum, the weak "forbidden" rotational transition predicted by theory (Miller and Tennyson 1988) have yet to be observed. H_3^+ also has no observed electronic spectrum and only a single allowed fundamental band, the degenerate ν_2 bending mode.

However, this seeming simplicity is also not the whole story. Unlike H_3^+, both H_2D^+ and D_2H^+ have an allowed pure rotational spectrum, which has been observed both in the laboratory and in space. H_3^+ itself has a much more complicated infrared spectrum than simple symmetry arguments would imply. This is mainly because transitions to the totally symmetric stretching mode are observed when these are allowed by rotation–vibration symmetry considerations, and also because transitions involving the bending overtone, $2\nu_2 - 0$ are unusually strong. The near-infrared therefore yields a variety of H_3^+ transitions involving several quanta of bending excitation.

H_3^+ is the dominant ion in cool hydrogen plasmas: it is formed rapidly following the ionization of H_2. This makes H_3^+ an very important astrophysical molecule; it has long been considered to be a major driver for interstellar chemistry and there has been an increasing realization of its importance in the atmospheres of gas giants (Miller *et al.* 2000).

Theory has played an important, perhaps vital, role in the spectroscopic detection of H_3^+. The calculations using ab initio potential energy surfaces and variational nuclear motion calculations predate the first successful characterization of its spectrum by Oka (1980). In fact, this spectrum was only successfully assigned by comparison with high-level theory. Similarly, the first astronomical detection of $H_3{}^+$, via an emission from its overtone from Jupiter's aurora, was also made by direct comparison with ab initio theory because at that time there was no assigned laboratory overtone spectrum (Drossart *et al.* 1989). To date, spectroscopic studies, which have reached progressively to higher levels (e.g., Asvany *et al.* 2007), continue to rely heavily on theory for both predictions and assignments.

Early ab initio studies on $H_3{}^+$ relied on traditional CI type treatments of the electronic structure problem, although, as $H_3{}^+$ is only a two-electron system, considering all single and double excitations from a single configuration is the equivalent to full-CI. These studies gave good, but not spectroscopically accurate, results. Thus, for example, the predictions that led to the assignment of the overtone emission spectrum on Jupiter were actually based on calculations that used a surface for which a single parameter had been adjusted to improve agreement for the observed bending fundamental (Meyer *et al.* 1986).

The use of explicitly correlated wave functions directly led to a major improvement in the accuracy of completely ab initio spectra. The best of these surfaces, by Cencek *et al.* (1998), has an estimated absolute error in the electronic energy of only $0.04\,\mathrm{cm}^{-1}$. The relative error, which affects the band origins, is an order of magnitude less than this.

Non-Born–Oppenheimer effects in $H_3{}^+$ manifest themselves in a very obvious way upon isotopic substitution. In the asymmetric isotopologues, the degenerate ν_2 bending mode splits. The majority of this splitting is recovered by using the correct mass factors in the body-fixed kinetic energy operator. However, analysis shows that the adiabatic or BODC correction contributes about $1\,\mathrm{cm}^{-1}$ to this splitting in a way that is antisymmetric between H_2D^+ and D_2H^+; that is, it increases the splitting in one and lowers it by the same amount in the other. The BODC was originally computed using a SCF wave function; calculations by Cencek *et al.* (1998) showed that this analysis underestimated the absolute magnitude of the BODC but did a good job at representing its shape. In this context, I note that calculations of the BODC for water have shown both its absolute and relative magnitude to be very sensitive to the level of correlation included in the treatment of the electronic wave function (Schwenke 2003a). Analysis of the small residual errors in ab initio transition frequencies suggest that they are due to incomplete treatment of corrections to the Born–Oppenheimer approximation, although whether they arise from adiabatic or nonadiabatic effects remains unclear.

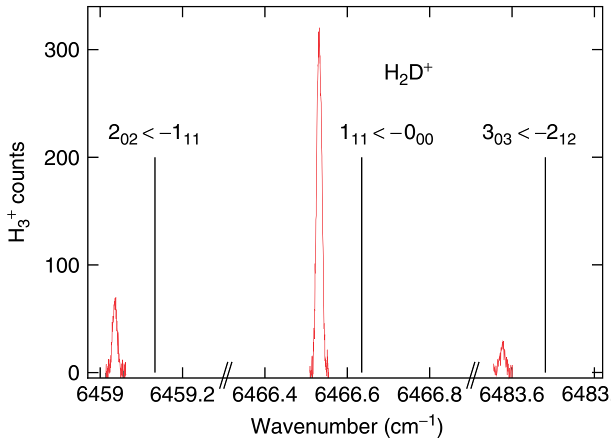


Figure 5 A part of the spectrum of the (0, 2, 1) combination band of H_2D^+ recorded with a highly sensitive laser induced reactions method (Asvany *et al.* 2007). With this method, trapped H_2D^+ ions at about 25 K undergo the endothermic reaction $H_2D^+ + H_2 \rightarrow H_3{}^+ + HD$. The resonant absorption of a photon is detected by counting the increase of the product $H_3{}^+$ ion. Within this band, the measured lines are found consistently about $0.1\,\mathrm{cm}^{-1}$ below the ab initio predictions. [I thank Dr Oskar Asvany for providing this unpublished figure.]

Figure 5 is taken from a recent, low-temperature spectroscopic study of the overtones of H_2D^+ and D_2H^+ (Asvany *et al.* 2007). The sample spectrum shows that the observed lines are systematically about $0.1\,\mathrm{cm}^{-1}$ below the ab initio predictions. This magnitude of error is typical for this and similar studies.

It should be noted that the nuclear motion calculations used to make these predictions and similar ones for the $H_3{}^+$ and $D_3{}^+$ isotopes were all performed in Jacobi coordinates. This is despite the fact that it is not possible to represent the full symmetry of the ions using these coordinates. There have been a series of studies using hyperspherical coordinates on these systems (for example Wolniewicz and Hinze 1994), but experience has shown that such calculations are actually computationally significantly more expensive.

An important aspect of the ab initio study of $H_3{}^+$ spectra is the calculation of transition intensities. This is because there is still no reliable experimental determination of the absolute intensity of any line for any isotopologue of $H_3{}^+$. Such transition intensity data is essential for all remote sensing applications which thus all rely on ab initio values. There is considerable indirect evidence that the calculated transition intensities are indeed reliable. Some of this evidence comes from the study of (Asvany *et al.* 2007) who, by measuring transitions in different bands starting from the same lower state, were able to get reliable relative intensities. All the results obtained were in perfect agreement with the ab initio predictions of these ratios.

Having developed a reliable theoretical model for $H_3{}^+$, one application has been to use it to calculate both a partition function (Neale and Tennyson 1995) which is reliable over an extended temperature range and a line list of all the rotation–vibration transitions which are required to reproduce hot spectra (Neale *et al.* 1996). This line list contains just over 3 million transitions, which is small by comparison with similar computations for other triatomic molecules. These data have found application for a variety of laboratory and astrophysical problems. For example, it has been discovered that emission from $H_3{}^+$ is a major coolant in the upper atmosphere of Jupiter. It is expected to play a similar role in many of the recently discovered extra solar planets (Koskinen *et al.* 2007). The line list also proved to be crucial in unraveling issues with population trapping in $H_3{}^+$ ions stored in storage rings (Kreckel *et al.* 2004).

Before leaving the topic of the high-resolution spectroscopy of $H_3{}^+$, mention must be made of its very rich near-dissociation spectrum which was extensively studied by Carrington and co-workers, for an account *see* Carrington and McNab (1989). In this work $H_3{}^+$ was prepared hot in discharge and then separated out using mass-spectroscopy techniques. A CO_2 laser (frequency 880–1022 cm^{-1}) was then used to dissociate the molecule:

$$H_3{}^+ + h\nu \longrightarrow H_2 + H^+ \qquad (23)$$

and the resulting protons were detected. These studies produced spectra with many lines, over 25 000 in the case of $H_3{}^+$, and other remarkable features. Despite significant attempts by theorists to interpret these spectra, they remain completely unassigned and thus show that even a seemingly simple system such as $H_3{}^+$ presents serious, unresolved problems.

8 CONCLUSION

The number of problems where first-principles calculation can actually predict line positions to the accuracy of high-resolution experiment is small (Leach and Moss 1995) and unlikely to grow significantly in the immediate future. However, this does not mean that striving to develop accurate ab initio procedures for computing spectra is unproductive. Predictive methods are of immense use in untangling complicated laboratory (or astrophysical) observations. Perhaps, even more importantly, first-principles calculation can give results in cases where laboratory measurements are not possible. There is increasing evidences that dipole transition intensities, which are essentially unobtainable for some systems in the laboratory, can be calculated with an accuracy competitive with the most precise measurements. Similarly, the huge datasets required for the analysis and modeling of hot spectra can readily be computed. These activities will ensure that the calculations of high-accuracy molecular spectra continue to be in demand.

ACKNOWLEDGMENT

I thank my coworkers whose work I have quoted freely above and, in particular, Bob Barber and Lorenzo Lodi for their helpful comments on my manuscript.

ABBREVIATIONS AND ACRONYMS

BODC	Born–Oppenheimer diagonal correction
CI	Configuration interaction
CV	Core-valence
CC	Coupled clusters
CCSD(T)	Coupled clusters with single and double excitation and perturbative Triples
D1	One-electron Darwin
D2	Two-electron Darwin
DFT	Density functional theory
DVR	Discrete variable representation
MR-CI	Multi-reference configuration interaction
MV	Mass-velocity
QED	Quantum electrodynamics
VBR	Variational basis representation

REFERENCES

Albert, S., Albert, K.K., Hollenstein, H., Tanner, C.M., and Quack, M. (2011) Fundamentals of rotation–vibration spectra, in *Handbook of High-resolution Spectroscopy*, Quack, M. and Merkt, F. (eds), John Wiley & Sons, Ltd., Chichester, UK.

Asvany, O., Hugo, E., Schlemmer, S., Müller, F., Kühnemann, F., Schiller, S., and Tennyson, J. (2007) Overtone spectroscopy of H_2D^+ and D_2H^+ using laser induced reactions. *Journal of Chemical Physics*, **127**, 154317.

Bačić, Z. and Light, J.C. (1989) Theoretical methods for rovibrational states of floppy molecules. *Annual Review of Physical Chemistry*, **40**, 469–498.

Bauder, A. (2011) Fundamentals of rotational spectroscopy, in *Handbook of High-resolution Spectroscopy*, Quack, M. and Merkt, F. (eds), John Wiley & Sons, Ltd., Chichester, UK.

Breidung, J. and Thiel, W. (2011) Prediction of vibrational spectra from ab initio theory, in *Handbook of High-resolution Spectroscopy*, Quack, M. and Merkt, F. (eds), John Wiley & Sons, Ltd., Chichester, UK.

Brocks, G., van der Avoird, A., Sutcliffe, B.T., and Tennyson, J. (1983) Quantum dynamics of non-rigid systems comprising two polyatomic molecules. *Molecular Physics*, **50**, 1025–1043.

Bunker, P.R. and Jensen, P. (1998) *Molecular Symmetry and Spectroscopy*, NRC, Canada.

Bunker, P.R., McLarnon, C.J., and Moss, R.E. (1977) Application of the effective vibration-rotation Hamiltonian to H_2 and D_2. *Molecular Physics*, **33**, 425–429.

Bunker, P.R. and Moss, R.E. (1977) The breakdown of the Born-Oppenheimer approximation: the effective vibration-rotation Hamiltonian for a diatomic molecule. *Molecular Physics*, **33**, 417–424.

Carrington Jr., T. (2011) Using iterative methods to compute vibrational spectra, in *Handbook of High-resolution Spectroscopy*, Quack, M. and Merkt, F. (eds), John Wiley & Sons, Ltd., Chichester, UK.

Carrington, A. and McNab, I.R. (1989) The infrared predissocation spectrum of $H_3{}^+$. *Accounts of Chemical Research*, **22**, 218.

Carter, S. and Bowman, J. (1998) The adiabatic rotation approximation for rovibrational energies of many-mode systems: description and tests of the method. *Journal of Chemical Physics*, **108**, 4397–4404.

Cencek, W., Rychlewski, J., Jaquet, R., and Kutzelnigg, W. (1998) Sub-microhartree accuracy potential energy surface for $H_3{}^+$ including adiabatic and relativistic effects. I. Calculation of the potential points. *Journal of Chemical Physics*, **108**, 2831.

Child, M.S., Weston, T., and Tennyson, J. (1999) Quantum monodromy in the spectrum of H_2O and other systems: new insight into the level structures of quasi-linear molecules. *Molecular Physics*, **96**, 371–379.

Coxon, J.A. and Hajigeorgiou, P.G. (1999) Experimental Born-Oppenheimer potential for the X $^1\Sigma^+$ ground state of HeH^+: comparison with the Ab Initio potential. *Journal of Molecular Spectroscopy*, **193**, 306–318.

Drossart, P., Maillard, J.P., Caldwell, J., Kim, S.J., Watson, J.K.G., Majewski, W.A., Tennyson, J, Miller, S., Atreya, S., Clarke, J. *et al.* (1989) Detection of $H_3{}^+$ on jupiter. *Nature*, **340**, 539–541.

Field, R.W., Baraban, J.H., Lipoff, S.H., and Beck, A.R. (2011) Effective hamiltonians for electronic fine structure and polyatomic vibrations, in *Handbook of High-resolution Spectroscopy*, Quack, M. and Merkt, F. (eds), John Wiley & Sons, Ltd., Chichester, UK.

Echave, J. and Clary, D. (1992) Potential optimized discrete variable representation. *Chemical Physics Letters*, **190**, 225–230.

Gatti, F., Iung, C., Leforestier, C., and Chapuisat, X. (1999) Fully coupled 6D calculations of the ammonia vibration-inversion-tunneling states with a split Hamiltonian pseudospectral approach. *Journal of Chemical Physics*, **111**(16), 7236–7243.

Handy, N.C., Yamaguchi, Y., and Schaefer, H.F. (1986) The diagonal correction to the Born-Oppenheimer approximation—its effect on the singlet-tripet splitting of CH_2 and other molecular effects. *Journal of Chemical Physics*, **84**, 4481–4484.

Henderson, J.R., Tennyson, J., and Sutcliffe, B.T. (1993) All the bound vibrational states of $H_3{}^+$: a reappraisal. *Journal of Chemical Physics*, **98**, 7191–7203.

Hutson, J.M. (1994) Coupled channel methods for solving the bound-state schrödinger equation. *Computer Physics Communications*, **84**, 1–18.

Iung, C. and Gatti, F. (2006) Polyspherical parametrization of an N-atom system: principles applications. *International Journal of Quantum Chemistry*, **106**, 130–151.

Jensen, P. (2000) An introduction to the theory of local mode vibrations. *Molecular Physics*, **98**, 1253–1285.

Jensen, P. (2006) *Introduction to Computational Chemistry*, Wiley-Blackwell, London.

Klopper, W. and Kutzelnigg, W. (1987) Moller-Plesset calculations taking care of the correlation cusp. *Chemical Physics Letters*, **134**, 17–22.

Koskinen, T.T., Aylward, A.D., and Miller, S. (2007) A stability limit for the atmospheres of giant extrasolar planets. *Nature*, **450**, 845–848.

Kostin, M.A., Polyansky, O.L., and Tennyson, J. (2002) Calculations of rotation-vibration states with the z-axis perpendicular to the plane: high accuracy results for $H_3{}^+$. *Journal of Chemical Physics*, **116**, 7564–7573.

Kreckel, H., Schwalm, D., Tennyson, J., Wolf, A., and Zajfman, D. (2004) Rovibrational relaxation model for $H_3{}^+$. *New Journal of Physics*, **6**, 151-1–151-16.

Kutzelnigg, W. (1997) The adiabatic approximation 1. The physical background of the Born-Handy ansatz. *Molecular Physics*, **90**, 909–916.

Le Roy, R.J., (2007) LEVEL 8.0-A computer program for solving the radial Schrödinger equation for bound and Quasibound levels, University of Waterloo Chemical Physics Research Report CP-663. http://leroy.uwaterloo.ca/programs/.

Leach, C.A. and Moss, R.E. (1995) Spectroscopy and quantum-mechanics of the hydrogen molecular cation—a test of molecular quantum-mechanics. *Annual Review of Physical Chemistry*, **46**, 55–82.

Light, J.C. and Carrington Jr, T. (2000) Discrete-variable representations and their utilization. *Advances in Physical Chemistry*, **114**, 263–310.

Lodi, L., Tolchenov, R.N., Lynas-Gray, A.E., Shirin, S.V., Tennyson, J., Zobov, N.F., Polyansky, O.L., Császár, A.G., van Stralen, J., and Visscher, L. (2008) A high accuracy dipole surface for water. *Journal of Chemical Physics*, **128**, 044304.

Lynas-Gray, A.E., Miller, S., and Tennyson, J. (1995) Infra red transition intensities for water: a comparison of ab initio and fitted dipole moment surfaces. *Journal of Molecular Spectroscopy*, **169**, 458–467.

Manson, S.A. and Law, M.M. (2006) General internal coordinate gradient vectors and the vibrational kinetic energy operator of centrally-connected penta-atomic systems. Part I. *Physical Chemistry Chemical Physics*, **8**, 2848–2854.

Marquardt, R. and Quack, M. (2011) Global analytical potential energy surfaces for high-resolution molecular spectroscopy and reaction dynamics, in *Handbook of High-resolution Spectroscopy*, Quack, M. and Merkt, F. (eds), John Wiley & Sons, Ltd., Chichester, UK.

Martin, J.M.L., François, J.P., and Gijbels, R. (1991) On the effect of centrifugal stretching on the rotational partition-function of an asymmetric top. *Journal of Chemical Physics*, **95**, 8374–8389.

Meyer, W., Botschwina, P., and Burton, P.G. (1986) Ab initio calculations of near-equilibrium potential and multipole moment surfaces and vibration frequencies of H_3^+ and its isomers. *Journal of Chemical Physics*, **82**, 891–900.

Miller, S., Achilleos, N., Ballester, G.E., Geballe, T.R., Joseph, R.D., Prange, R., Rego, D., Stallard, T., Tennyson, J., Trafton, L.M. *et al*. (2000) The role of H_3^+ in planetary atmospheres. *Philosophical Transactions of the Royal Society of London, Series A*, **358**, 2485–2502.

Miller, S. and Tennyson, J. (1988) Calculated rotational and rovibrational transitions in the spectrum of H_3^+. *The Astrophysical Journal*, **335**, 486–490.

Miller, S., Tennyson, J., and Sutcliffe, B.T. (1989) First principles calculation of rotational and ro-vibrational line strengths: spectra for H_2D^+ and D_2H^+. *Molecular Physics*, **66**, 429–456.

Mladenovic, M. (2000a) Rovibrational Hamiltonians for general polyatomic molecules in spherical polar parametrization. I. Orthogonal representations. *Journal of Chemical Physics*, **112**, 1070–1081.

Mladenovic, M. (2000b) Rovibrational Hamiltonians for general polyatomic molecules in spherical polar parametrization. III. Global vs local axis system and angular coordinates. *Journal of Chemical Physics*, **113**, 10524–10534.

Müller, H., Franke, B., Vogtner, S., Jacquet, R., and Kutzelnigg, W. (1998) Toward spectroscopic accuracy of ab initio calculations of vibrational frequencies and related quantities: a case study of the hf molecule. *Theoretical Chemistry Accounts*, **105**, 2627–2647.

Neale, L., Miller, S., and Tennyson, J. (1996) Spectroscopic properties of the H_3^+ molecule: a new calculated linelist. *The Astrophysical Journal*, **464**, 516–520.

Neale, L. and Tennyson, J. (1995) A high temperature partition function for H_3^+. *The Astrophysical Journal*, **454**, L169–L173.

Oka, T. (1980) Observation of the infrared spectrum of H_3^+. *Physical Review Letters*, **45**, 531–534.

Polyansky, O.L., Császár, A.G., Shirin, S.V., Zobov, N.F., Barletta, P., Tennyson, J., Schwenke, D.W., and Knowles, P.J., (2003) High accuracy ab initio rotation-vibration transitions of water. *Science*, **299**, 539–542.

Schwartz, C. and Le Roy, R.J. (1987) Nonadiabtic eigenvalues and adiabatic matrix-elements for all isotopes of diatomic hydrogen. *Journal of Molecular Spectroscopy*, **121**, 420–439.

Schwenke, D.W. (2001) Beyond the potential energy surface: Ab initio corrections to the Born-Oppenheimer approximation for H_2O. *Journal of Physical Chemistry A*, **105**, 2352–2360.

Schwenke, D.W. (2003a) First principles prediction of isotopic shifts in H_2O. *Journal of Chemical Physics*, **118**, 6898–6904.

Schwenke, D.W. (2003b) New rovibrational kinetic energy operators using polyspherical coordinates for polyatomic molecules. *Journal of Chemical Physics*, **118**, 10431–10438.

Stohner, J. and Quack, M. (2011) Conventions, symbols, quantities, units and constants for high-resolution molecular spectroscopy, in *Handbook of High-resolution Spectroscopy*, Quack, M. and Merkt, F. (eds), John Wiley & Sons, Ltd., Chichester, UK.

Stroud, A.H. and Secrest, D. (1966) *Gaussian quadrature formulas*, Prentice-Hall, London.

Szalay, V. and Lane, S. (1992) Derivation of rotational-vibrational Hamiltonian matrices of real elements. *Molecular Physics*, **75**, 781–787.

Tarczay, G., Császár, A.G., Klopper, W., and Quiney, H.M. (2001) Anatomy of relativistic energy corrections in light molecular systems. *Molecular Physics*, **99**, 1769–1794.

Tennyson, J. (1992) Why calculate the spectra of small molecules? *Journal of the Chemical Society, Faraday Transactions*, **88**, 3271–3279 (Faraday Research Article).

Tennyson, J., Harris, G.J., Barber, R.J., La Delfa, S., Voronin, B., and Pavlenko, Y.V. (2007) Molecular linelists for modelling the opacity of cool stars. *Molecular Physics*, **105**, 701–714.

Tennyson, J. and Sutcliffe, B.T. (1982) The ab initio calculation of the vibration-rotation spectrum of triatomic systems in the close-coupling approach with KCN and H_2Ne as examples. *Journal of Chemical Physics*, **77**, 4061–4072.

Tennyson, J. and Sutcliffe, B.T. (1992) Discretisation to avoid singularities in vibration-rotation hamiltonians: a bisector embedding for ab_2 triatomics. *International Journal of Quantum Chemistry*, **42**, 941–952.

Weber, A. (2011) High-resolution Raman spectroscopy of gases, in *Handbook of High-resolution Spectroscopy*, Quack, M. and Merkt, F. (eds), John Wiley & Sons, Ltd., Chichester, UK.

Wei, H. and Carrington, T. (1997) Explicit expressions for triatomic Eckart frames in Jacobi, Radau, and bond coordinates. *Journal of Chemical Physics*, **107**, 2813–2818.

Wilson, E.B., Decius, J.C., and Cross, P.C. (1980) *Molecular Vibrations: The Theory of Infrared and Raman vibrational spectra*, Dover Publications.

Wolniewicz, L. and Hinze, J. (1994) Rotation-vibrational states of H_3^+ computed using hyperspherical coordinates and harmonics. *Journal of Chemical Physics*, **101**, 9817–9829.

Wörner, H.J. and Merkt, F. (2011) Fundamentals of electronic spectroscopy, in *Handbook of High-resolution Spectroscopy*, Quack, M. and Merkt, F. (eds), John Wiley & Sons, Ltd., Chichester, UK.

Zobov, N.F., Polyansky, O.L., Le Sueur, C.R., and Tennyson, J. (1996) Vibration-rotation levels of water beyond the born-oppenheimer approximation. *Chemical Physics Letters*, **260**, 381–387.

FURTHER READING

Bunker, P.R. and Jensen, P. (1998) *Molecular Symmetry and Spectroscopy*, 2nd edition, NRC.

Kutzelnigg, W. (2007) Which masses are vibrating or rotating in a molecule? *Molecular Physics*, **105**, 2627–2647.

Tennyson, J. (2005) *Astronomical Spectoscopy, An Introduction to the Atomic and Molecular Physics of Astronomical Spectra*, World Scientific.

RELATED ARTICLES

Albert *et al*. 2011: **Fundamentals of Rotation–Vibration Spectra**

Carrington 2011: **Using Iterative Methods to Compute Vibrational Spectra**

Marquardt and Quack 2011: **Global Analytical Potential Energy Surfaces for High-resolution Molecular Spectroscopy and Reaction Dynamics**

Stohner and Quack 2011: **Conventions, Symbols, Quantities, Units and Constants for High-resolution Molecular Spectroscopy**

Weber 2011: **High-resolution Raman Spectroscopy of Gases**

Wörner and Merkt 2011: **Fundamentals of Electronic Spectroscopy**