On the determination of potential energy surfaces of spectroscopic accuracy[☆]

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Abstract

The application of ab initio potential energy surfaces and surfaces fitted to spectroscopically determined rotation–vibration levels of triatomic molecules are considered with particular attention to H_3^+ and $H_2^{16}O$. Variational treatments of nuclear motion allow these surfaces to be determined with near spectroscopic accuracy and the breakdown of the Born–Oppenheimer (BO) approximation to be quantified. Methods for determining the BO adiabatic correction both ab initio and from spectroscopic data are described.

1. Introduction

Many elementary chemical processes such as reaction dynamics, molecular spectroscopy and heavy particle scattering as well as properties of the liquid and solid state are usually thought of as being governed by one or more potential energy surfaces. Deriving potential energy surfaces is thus a fundamental activity underpinning much of chemical physics and one to which Murrell and co-workers has made a major contribution [1–4].

Potentials can be derived using data from two sources. One can either solve the electronic structure problem at a grid of nuclear geometries and fit these to a functional form to yield an ab initio potential or one can fit potentials to measured properties of the system. The latter approach, which has been widely used for van der Waals molecules [5,6], cannot be done directly. Usually it is necessary to guess a potential, compute the observed properties of the system, refine the potential and continue the procedure until either a satisfactory representation of the observed data is achieved or ones patience and/or computer budget is exhausted. These approaches are summarized in Fig. 1.

There are problems associated with either of these two approaches. For ab initio surfaces the major difficulty is the accuracy of the underlying electronic structure calculations. This is true even for the simplest polyatomic molecule, H_3^+, which we discuss extensively below. For empirically determined surfaces the problem is often one of incomplete data: usually the available measurements are

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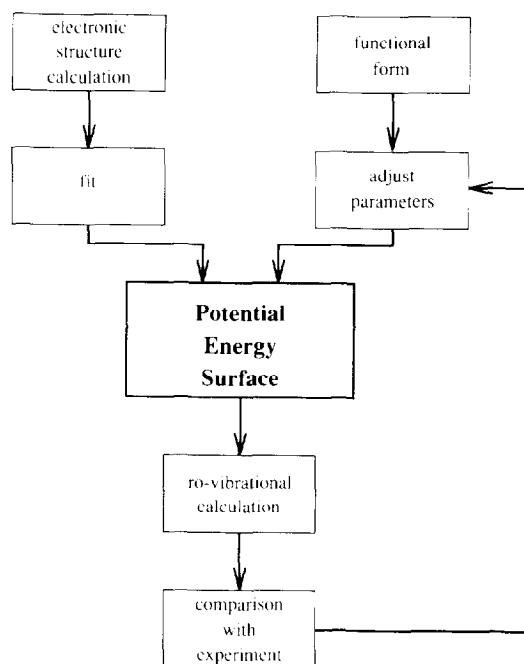
Fig. 1. Schematic diagram of how potentials are produced ab initio (left hand side) or by iterative fits to observed spectra (right hand side).

sensitive only to a particular portion of the whole surface. Murrell and co-workers have made extensive use of a hybrid between these two methods where experimental data is augmented by ab initio estimates of properties for which there are no reliable measurements [1].

Of course the concept of a potential energy surface is only valid within the Born–Oppenheimer (BO) approximation which separates the motions of the nuclei and electrons. This separation relies on the large ratio between the electron and nucleon mass. For molecules containing hydrogen this ratio is somewhat less than 2000; an error well inside the limits of many modern experiments, particularly in the field of high resolution spectroscopy.

Recently we have been concerned with deriving highly accurate potential energy surfaces for small molecules such as H_3^+ [7–9] and water [10–12] using spectroscopic data. Using methods described in the next section we have been able to develop surfaces which reproduce a variety of spectroscopic data with a typical accuracy of better than 0.05 cm^{-1}. This accuracy is considerably better than the BO

approximation for these molecules. Our experience is that surfaces derived for the major isotopomers, H_3^+ or $H_2^{16}O$ for example, perform relatively poorly for other isotopomers. This is particularly true for asymmetrically deuterated species such as H_2D^+ or $HD^{16}O$ [7,11].

In this paper we discuss the spectroscopic determination of potential energy surfaces and, for H_3^+, compare such surfaces with the best ab initio data. We show how a relatively simple ab initio procedure, due to Handy et al. [13], can give reliable estimates of the leading correction to the BO approximation in the case of molecules with well separated electronic states, the so-called adiabatic correction.

2. Fitting potential energy surfaces from spectra

Traditionally perturbation theory has been used to parameterize high resolution spectra. For strongly bound molecules, perturbation theory expansions are usually based on harmonic oscillators for the vibrational motion and rigid rotors for rotational motion. These methods have been highly successful in the sense that large quantities of data have been represented by relatively few parameters and, in many cases, the expansions have been found to have excellent predictive properties. Although these representations implicitly contain information about the underlying molecular potential, this is often difficult to extract as it is, for example, bound up with expansion of the kinetic energy operators and other properties of the expansions. The expansions may also be poorly behaved, particularly for hydrogen containing species, and may often have limited convergence properties [14]. Furthermore, it is difficult to transfer information, for instance on the potential, between vibrational and rotational parameters.

An alternative approach to the above procedure is to directly calculate the spectroscopic properties from the underlying potential energy surfaces and use this as a basis for refining the potential. This approach is potentially very powerful as it removes many of the problems with the perturbation theory based approaches. However care must be taken with its implementation as there is a danger that any shortcomings in the method used to calculate

the spectra will result in an artificial distortion of the resulting potential energy surface [15].

Vibration–rotation energy levels and wavefunctions can be calculated directly from potential energy surfaces of small molecules using procedures based on the Variational Principle. Kinetic energy operators can be derived for these variational methods which are exact within the BO approximation [16], and by using large basis set expansions, very accurate solutions can be obtained. Programs are available which solve these problems for chemically bound triatomics (see Refs. [17,18] and the computer code JGE0 described in Ref. [19]) and van der Waals complexes [20]. However, for chemically bound systems, the accuracy required to match large sets of high resolution data, which may typically have errors of less than 1 part in 10^7, can make repeating these computational calculations many times prohibitively expensive.

It is therefore necessary to find methods to speed up the repeated calculations required during a fit. One method, pioneered by Murrell and co-workers [3,4] and employed by us [7], is to perform most of the iterations using small, poorly converged basis sets with energy levels corrected accordingly. An alternative approach, also used by us [11,12], is to perform the bulk of the fitting with a much quicker approximate kinetic energy program, again with corrected energy levels. The approximate method we favour is the MORBID approach of Jensen [21], which we have found to be both rapid and reliable.

Finally we should note that we have found the use of the Hellmann–Feynman theorem very useful for greatly increasing the speed of fits [10]. If c_α is a constant in a potential energy surface, V, that is being optimized and $E_{J,n}$ is the energy of the nth level with rotational angular momentum J, then

$$\frac{\partial E_{J,n}}{\partial c_\alpha} = \left\langle J,n \left| \frac{\partial \mathscr{H}}{\partial c_\alpha} \right| J,n \right\rangle = \left\langle J,n \left| \frac{\partial V}{\partial c_\alpha} \right| J,n \right\rangle \quad (1)$$

The second equality, which reduces this procedure to a relatively simple one of evaluating a derivative free expectation value, is because the kinetic energy operator does not depend on the parameters of the potential.

The Hellmann–Feynman theorem is only strictly obeyed for exact wavefunctions. Experience with electronic structure calculations have shown that because of the approximate wavefunctions used, using this theorem in numerical calculations can give unreliable results. However, our variational procedures produce very accurate, or near exact wavefunctions, and tests against derivatives computed numerically by evaluating $V(c_\alpha + \delta c_\alpha) - V(c_\alpha)$ gives agreement with the Hellmann–Feynman results to about four digits. As for N potential parameters the numerical derivatives method requires the ro-vibrational problem to be solved $N + 1$ times and the Hellmann–Feynman method requires only one solution; the latter is clearly much quicker.

3. Potential energy surfaces for H_3^+

3.1. Ab initio potentials

H_3^+ is only a two electron system and is therefore amenable to accurate ab initio calculation. There is a long history of such calculations, see Ref. [22], which combined with variational calculations of the type described above have provided the main method of elucidating laboratory spectra of H_3^+ [23–25].

Particularly accurate ab initio potential energy surfaces have been calculated using wavefunctions which include terms explicitly in the electron–electron coordinate. These Hylleraas–CI calculations, which have been performed by Lie and Frye [26] and Röhse et al. [27], yield potentials for the H_3^+ system which are very close to being the true BO surface of the system. In particular, Röhse et al. estimate that their surface is within 1 cm^{-1} of the BO surface of the system.

Table 1 presents results of a number of H_3^+ rotation–vibration calculations performed with this and an empirically determined potential energy surface (see below). These calculations compared the ab initio predictions with the 243 "observed" H_3^+ energy levels used by Dinelli et al. [7] in their fit of the H_3^+ potential energy surface. All calculations were performed with the TRIATOM program suite [17] and basis sets developed previously [7]. The first column presents results of calculations which use Röhse et al.'s BO potential

Table 1

Comparison of rotation–vibration term values for H_3^+ in cm^{-1} for the Born–Oppenheimer (BO) potential of Röhse et al. [27], the ab initio adiabatic corrected potential of Dinelli et al. [28] and the spectroscopically determined effective potential of Dinelli et al. [7]. ν gives the calculated band origin for each band. $\langle \delta E \rangle = \langle E_{obs} - E_{calc} \rangle$ is the average error and σ the standard deviation, both in cm^{-1}, in reproducing the n observed term values in that band

(ν_1, ν_2^l)	n	V_{BO}			$V_{BO} + \frac{1}{\mu}\Delta V_{ad}$			V_{eff}		
		ν	$\langle \delta E \rangle$	σ	ν	$\langle \delta E \rangle$	σ	ν	$\langle \delta E \rangle$	σ
(0.0^0)	35	0.00	−0.112	0.130	0.00	0.015	0.018	0.0	−0.014	0.017
(0.1^1)	82	2521.17	0.081	0.160	2521.58	−0.148	0.149	2521.40	0.20	0.024
(1.0^0)	14	3178.82	−0.586	0.612	3178.35	−0.078	0.081	3178.16	−0.007	0.062
(0.2^0)	14	4777.66	0.620	0.644	4778.58	−0.227	0.227	4778.40	−0.094	0.100
(0.2^2)	62	4997.60	0.212	0.299	4998.41	−0.361	0.367	4998.04	−0.014	0.037
(1.1^1)	24	5554.59	−0.329	0.363	5554.62	−0.365	0.371	5554.31	0.002	0.036
(0.3^1)	12	7005.18	0.963	1.008	7006.63	−0.458	0.460	7006.09	0.066	0.096

and use a nuclear mass of 1.0076422 amu which is equivalent to that of a hydrogen atom minus one third of an electron. Calculations which use simply nuclear masses have been reported previously [27,28] but give significantly larger standard deviations, rising to 1.4 cm^{-1} for the (1, 1^1) band.

The use of (effective) atomic rather than nuclear masses is a crude method of allowing for some of the failure of the BO approximation. It is clear that Röhse et al.'s ab initio potential is good and that the BO approximation is the major source of error in using it to calculate ro-vibrational levels.

Interestingly, and in contrast to the H_3^+ results presented here, calculations on D_3^+ by Dinelli et al. [28] have found that using Röhse et al.'s ab initio potential and a nuclear mass of atomic D minus one third of an electron gives results as reliable as explicitly including the adiabatic correction to the BO potential (see below). This result suggests that explicit inclusion of a non-BO potential may only be necessary for species containing hydrogen.

3.2. Spectroscopically determined potentials

Dinelli et al. started from the ab initio surface of Lie and Frye [26] and used a dataset of 243 H_3^+ energy levels covering vibrational levels up to $3\nu_2$ and rotational levels up to $J = 9$ to determine an effective H_3^+ surface. The final columns in Table 1 present results obtained with this potential. The

spectroscopically determined potential gives excellent results which are significantly better than those obtained ab initio. Perhaps this is not surprising, but one should note that ab initio estimates of the vibration–rotation energy levels of molecular hydrogen, also a two electron system, by for example Schwartz and Le Roy [29], are significantly more accurate than those that can be obtained by inverting experimental data.

Test calculations on H_2D^+, D_2H^+ and D_3^+ have shown that the potential obtained by Dinelli et al. was not a true BO potential as it performed significantly worse for these deuterated isotopomers. In particular, the splitting between the ν_2 and ν_3 fundamentals in H_2D^+ and D_2H^+ was poorly reproduced. As these vibrational modes are degenerate in H_3^+ and D_3^+ and there is no term in the BO potential which can cause them to split: this was a clear indication that the effect was a consequence of the failure of the BO approximation.

Tennyson and Polyansky [8] showed that by using data for D_3^+ it was possible to obtain both a spectroscopically determined BO potential and a mass dependent non-BO function for these symmetric species. They identified this function with the adiabatic correction to the BO potential as, by analogy with H_2^+, this is likely to be the largest correction to the BO approximation.

The main difficulty with Tennyson and Polyansky's work was the lack of D_3^+ spectral data as only transitions in the bending fundamental were known. However very recently

Table 2

Comparison of fundamentals of H_2D^+ and D_2H^+ calculated using the ab initio BO potential of Röhse et al. (RKJK) [27], the spectroscopically determined effective H_3^+ potential of Dinelli et al. (DMT) [7] and the work of Polyansky et al. (PDLT) [33] who used the ab initio potential of RKJK and both symmetric and asymmetric adiabatic corrections. The calculated results are given as differences (Obs − Calc) from the observed fundamentals of Refs. [34–37]

	ν_1	ν_2	ν_3	$\frac{1}{2}(\nu_2 - \nu_3)$	$\nu_3 - \nu_2$
H_2D^+					
Obs	2992.50	2205.87	2335.45	2270.66	129.58
RKJK	−3.3	0.9	2.0	1.5	−0.9
DMT	−0.2	−0.3	0.6	0.0	−0.9
PDLT	−0.06	−0.22	−0.11	−0.16	0.10
D_2H^+					
Obs	2737.00	1968.17	2078.43	2023.30	110.26
RKJK	−2.5	0.9	0.7	0.8	−0.2
DMT	0.2	0.7	0.8	0.0	−1.4
PDLT	0.17	−0.09	−0.19	−0.14	−0.10

Amano et al. [30] have greatly extended the data available by making measurements not only on the fundamental band of D_3^+, but also on several other bands. Their observed transitions were assigned by using a spectroscopically determined potential due to Watson [31]. Recently we have been able to use these data to greatly improve our effective D_3^+ potential energy surface and hence get a reliable spectroscopic determination of both the BO and the symmetric adiabatic potential for the H_3^+ system [9].

3.3. Beyond the Born–Oppenheimer approximation

As it was clear that the BO approximation was the major stumbling block to accurate ab initio results for H_3^+, Dinelli et al. [28] calculated the BO diagonal correction (BODC) for H_3^+ as a function of geometry using a near-Hartree–Fock SCF wavefunction, Ψ, and the procedure due to Handy et al. [13].

This method yields, for internal coordinates $\underline{Q}$, an integral for the Ith nucleus:

$$f_I(\underline{Q}) = -\frac{1}{2}\langle\Psi|\nabla_I^2|\Psi\rangle \tag{2}$$

These were calculated using CADPAC [32]. The BODC can then be written in terms of nuclear

masses, m_I, as

$$\sum_{I=1}^{3}\frac{f_I(\underline{Q})}{m_I} \tag{3}$$

However direct fitting of this form of the adiabatic correction is unhelpful as, except in the symmetric case where all the m values are equal, it is not possible to separately identify the mass dependence of the function.

We therefore choose to represent the effective, explicitly mass dependent potential of the ith isotopomer as

$$V_i(\underline{Q}) = V_{BO}(\underline{Q}) + \frac{1}{\mu_i^S}\Delta V_{ad}^S(\underline{Q}) + \frac{1}{\mu_i^A}\Delta V_{ad}^A(\underline{Q}) \tag{4}$$

where the superscripts S and A denote symmetric and antisymmetric respectively. The adiabatic terms can be represented in terms of the BODC integrals by

$$\frac{1}{\mu^S}\Delta V_{ad}^S(\underline{Q}) = \left(\frac{1}{M} + \frac{2}{m}\right)\frac{1}{3}[f_1(\underline{Q}) + f_2(\underline{Q}) + f_3(\underline{Q})] \tag{5}$$

$$\frac{1}{\mu^A}\Delta V_{ad}^A(\underline{Q}) = \left(\frac{1}{M} - \frac{1}{m}\right)$$
$$\times \frac{1}{3}[2f_1(\underline{Q}) - f_2(\underline{Q}) - f_3(\underline{Q})] \tag{6}$$

where it has been assumed that the unique atom is 1 and has mass M and atoms 2 and 3 both have mass m. In the case that all atoms are the same, $M = m$ and the asymmetric term vanishes.

The symmetric term can be accurately represented [28] using an expansion in symmetry coordinates (see section 4.2 of Murrell et al. [1]), but the asymmetric term is rather more unusual. This term has the property that under the D_{3h} (or C_{3v}) point group appropriate to H_3^+ it is not totally symmetric, in fact it transforms as one component of a degenerate E representation, while under C_{2v}, the point group appropriate to the mixed isotopomers, it is totally symmetric. Furthermore, the reduced mass factor for the asymmetric term, μ^A, means that the contribution of this term to H_2D^+ is equal but of opposite sign to its contribution to D_2H^+.

Polyansky et al. [33] have fitted the ab initio BODC data of Dinelli et al. [28] for both the

Table 3
The differences between observed and calculated values of the fundamental band origins for isotopomers of water (in cm^{-1}) from Polyansky et al. [11]

$\nu_1\nu_2\nu_3$	$H_2^{16}O$	$D_2^{16}O$	$T_2^{16}O$	$HD^{16}O$	$HT^{16}O$
010	0.04	0.09	0.1	0.09	
100	−0.09	0.05	0.17	0.58	0.64
001	0.06	0.3	0.4	−0.25	−1.24

symmetric and asymmetric adiabatic corrections. With these they have recomputed the ab initio levels of H_2D^+ and D_2H^+, obtaining greatly improved agreement on the previous estimates (see Table 2).

It would seem logical, given the above discussion, to determine the asymmetric adiabatic correction from spectroscopic data as has been done for the symmetric adiabatic correction [8,9]. However, although there is a wealth of levels for all three fundamentals of both H_2D^+ and D_2H^+, most of these data are insensitive to the asymmetric adiabatic correction. In particular our test calculations have shown that while this term is important for the ν_2 and ν_3 band origins, and in particular the splitting between, it has little influence on the rotational term values associated with these vibrational modes. This means that there is essentially only two pieces of observed data, the $\nu_2 - \nu_3$ splittings in H_2D^+ and D_2H^+, which are sensitive to this term.

Our strategy will therefore be to use the ab initio asymmetric adiabatic correction, scaled if necessary, along with the spectroscopically determined BO potential and symmetric adiabatic correction. Work in this direction is currently in progress [9]: we are confident that it should yield the most accurate effective potential energy surfaces for H_3^+ and its isotopomers.

Such a high accuracy surface will of course not solve the full H_3^+ problem. Surfaces determined by experimental data are most reliable in the region to which the underlying experiment is sensitive. Although our potential energy surfaces show excellent extrapolation properties (see section 4), surfaces determined from standard infrared high resolution spectra cannot be expected to give a reliable representation of the dissociation without the inclusion of further information.

The spectroscopically determined surfaces for H_3^+ are reliable in a fairly large region about the equilateral triangle equilibrium geometry, probably extending as far as the lowest linear geometries of the system, but they give no information about the dissociation limit of this system which has been probed experimentally by Carrington et al. [38]. Surfaces which cover the dissociation region of H_3^+ are surprisingly hard to find. Perhaps the most reliable surface has been given by Murrell et al. (see chapter 11 of Ref. [1]), but to our knowledge this surface has never been used in any of the many theoretical studies of the spectrum of Carrington et al. Determination of an accurate surface in this region remains an important problem and one which may well be best tackled within the Sorbie–Murrell many body expansion approach [2].

4. Water

Water was the subject of the now classic Sorbie and Murrell paper [2] which introduced the concept of many body expansions for potentials of polyatomic molecules. This surface was improved by Murrell et al. (see Ref. [1], section 9.4), giving a potential which already reproduced the vibrational band origins of water more accurately than is still possible with state-of-the-art ab initio calculations. Of course water is a much more challenging system than H_3^+ for ab initio calculations.

Since Murrell et al., there have been a number of attempts to use spectroscopic data to give high accuracy potentials [10–12, 39–43]. Of the fits performed in the 1980s, the surface by Jensen [41] was the best but suffered from systematic errors introduced by his approximate MORBID Hamiltonian [15].

Recent studies have greatly improved the accuracy of these potentials, for example Polyansky et al. [11] used rotational data with $J \leq 14$ for 24 vibrational states of $H_2^{16}O$ together with a further 25 band origins. Their fit reproduced the 1600 terms values involved with a standard deviation of 0.36 cm^{-1}. For the 220 ground state energy levels the standard deviation was only 0.03 cm^{-1}, similar to that found in the H_3^+ calculations.

Furthermore the potential has excellent extrapolation properties reproducing the rotational levels as high as $J = 35$ (the highest observed) to high accuracy. This should be contrasted with standard effective Hamiltonian (perturbation) fits to high J water levels which suffer great difficulty with any extrapolation.

This illustrates an important property of these spectroscopically determined potentials. In principle either a complete set of rotational levels for one vibrational state or a complete set of rotationless vibrational band origins should be sufficient to fully determine the potential energy surface. In practice this property means that use of high lying vibrational levels can greatly improve the extrapolation properties of the surface for rotational excitation or vice versa.

Polyansky et al. [11] also showed that the small standard deviation they obtained for the ground state, and other low-lying vibrational states, meant that their $H_2^{16}O$ surface was more accurate than the BO approximation. In a similar fashion to the H_3^- problem discussed above, they found that their results for symmetrically substituted isotopomers such as $D_2^{16}O$ and $T_2^{16}O$ were less in error than the corresponding asymmetric isotopomers $HD^{16}O$ and $HT^{16}O$, see Table 3. This again strongly suggests the importance of an asymmetric non-BO term for these systems. Again it seems likely that an appeal to ab initio calculations will resolve this problem [44].

Finally it is interesting to note that a recent comparative study of dipole surfaces for water [45] concluded that for this property an ab initio pair of surfaces was more reliable than one determined from spectroscopic data. This was despite the fact that the level of theory used to compute ab initio dipole surfaces yielded band origins up to 30 cm^{-1} away from experiment [46]; this is some two orders of magnitude worse than our spectroscopically determined potential.

5. Conclusions

The use of high resolution spectroscopic data and variational calculations of corresponding accuracy has meant that the determination of potential energy surfaces for small molecules has entered a new era. This era has brought us potential energy surfaces of near spectroscopic accuracy; there are surfaces available for other systems not discussed here (e.g. Ref. [47]). This new accuracy has uncovered new phenomena and in particular highlighted the breakdown of the BO approximation. Somewhat unexpectedly, this effect has proved to be particularly strong for asymmetrically substituted species.

To address these new problems we have gone back to ab initio techniques to calculate the non-BO effects. We believe that this style of tackling problems, combining the best information from experiment with the best available ab initio data where experimental data is inadequate, is following in the footsteps of John Murrell. It is a pleasure for us to acknowledge his contribution to this field.

Acknowledgements

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