The diabatic energy surface for H₃

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Abstract. The form of the diabatic energy surface for the H_3 system is considered. It does not have the full permutation symmetry of the nuclei. The diabatic crossing and the conical intersection are compared. A fit to the calculated points of Siegbahn and Liu using the exponential map is described and the results discussed.

Keywords. Diabatic potential energy surfaces; H_3 energy surface; fitting of potential energy surfaces.

1. Introduction

To investigate the dynamics of a molecular reaction it is first necessary to have a function representing the electronic energy of the molecule as a function of its nuclear configuration. The energy for selected configurations may be obtained from an *ab initio* calculation and some neighbourhoods may be known through analysis of vibration spectra; so, the problem is to fit these data into a formula which extrapolates the energy to any configuration. An extensive account of existing techniques for this purpose has been given by Murrell *et al* (1984).

In a previous publication (Hall and Okada 1985) the authors have proposed a new representation for the energy and illustrated it by fitting the H_3 data of Siegbahn and Liu (1978). The internuclear distances $R1$, $R2$, $R3$ are replaced by their exponential images:

$$X = \exp(-aR1); \ Y = \exp(-aR2); \ Z = \exp(-aR3), \tag{1}$$

and the energy represented as a power series

$$V(X, Y, Z) = \sum_{r,s,t}^{r+s+t \leqslant n} V_{rst} X^r Y^s Z^t. \tag{2}$$

The coefficients V_{rst} and the scale factor a are fitted by a least squares procedure. The diatomic limit, which has $Y = Z = 0$, is fitted first and the series then gives a natural generalization of the Morse potential

$$V(X,0,0) = \sum_{r=0}^{n} V_{r00} X^r. \tag{3}$$

The remaining coefficients are fitted to the triatomic *ab initio* calculated points. To maintain the symmetry of the energy surface the coefficients must satisfy full

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permutation symmetry:

$$V_{rst} = V_{srt} = V_{rts} \quad \ldots \ldots \tag{4}$$

This condition reduces the number of independent coefficients very considerably. An advantage of the form (2) is that it combines the diatomic data with the triatomic data smoothly and enables them to be determined independently. Since it does not appeal to any physical consideration to include terms of a special form it is more suited to general application, but it will require more terms to achieve a given accuracy of fit, than procedures that do take advantage of these considerations.

Most molecular calculations are based on the Born-Oppenheimer separation of the electronic motion from the nuclear motion and, in particular, restrict the electronic wavefunction to a representation of the space and spin symmetry of the Born-Oppenheimer Hamiltonian. When the energies of two different states become close these adiabatic surfaces may not be the most useful nor the most significant ones to find. It has been argued that the diabatic surfaces (Lichten 1963) have greater physical importance. For a review see O'Malley (1971). A diabatic surface for H_2O has been given by Murrell *et al* (1981) and one for O_3 by Carter *et al* (1982). In this paper the calculation of a diabatic surface using the exponential map will be demonstrated. It is convenient to use H_3 as an example again since this facilitates comparisons with previous work and since a diabatic surface for this system has many interesting aspects.

2. Symmetry breaking

It is not easy to give a rigorous definition of the diabatic energy since it is not the solution of an eigenvalue equation as the adiabatic energy is. As an energy, it is a smooth interpolation between an energy which is on the lower surface on one side of a crossing point and the upper surface on the other side. It is easier to define it as the mean energy of an approximate wavefunction which retains its character through the crossing. Near the crossing the adiabatic wavefunction will mix this wavefunction with the second diabatic one which crosses in the opposite direction.

One of the differences between diabatic and adiabatic wavefunctions is the treatment of symmetry. The adiabatic wavefunction must belong to an irreducible representation of the molecular symmetry group of the configuration and its energy surface must be fully symmetrical. The diabatic one need not. To have the correct relation to the adiabatic wavefunction the diabatic one, together with the second diabatic one which it crosses, should, as a pair, span one or two irreducible representations. This is a significant relaxation of the symmetry condition and implies that neither diabatic energy surface need be fully symmetrical though the two surfaces together must be. In a typical diabatic wavefunction some atoms are bonded and some are not. This bonding will be appropriate to the ground state for configurations in which these atoms are suitably placed but, for configurations which bring other atoms together, it may correspond to an upper state since there is another, more appropriate, choice of bonds. For H_3 it is readily shown that the equilateral configurations have spatially doubly-degenerate wavefunctions so that the two surfaces do cross there. This conical intersection has been discussed by Teller (1937) and by Herzberg and Longuet-Higgins (1963). The adiabatic surface has then a cusp at these equilateral points whereas the diabatic surface has a smooth crossing.

The implication for the fitting process of this symmetry breaking is considerable. To fit a cusp using analytic functions means rather slow convergence and this is what was found in the previous fitting. By eliminating the cusp the fitting should be more rapid. Furthermore, the reduction in symmetry increases the number of independent coefficients available for fitting and hence improves the fitting which is possible using terms of up to a given degree.

3. The shape of the H_3 diabatic surface

The H_3 system has some special features which arise from its three-fold symmetry and the space and spin properties of its states. These must be reflected in the fitted surfaces.

Since two surfaces cross at equilateral configurations there must be two energy states at all configurations. In the diatomic limit these two states are the ground state and the lowest triplet state of H_2, the bonding and the anti-bonding states. Both of these are known from accurate calculation, so the fitting must now include both.

In collinear configurations the two neighbouring atom pairs should be treated in the same way since both are partly bonded, and become fully bonded when the third atom retreats far away. It is the interaction between the extreme atoms which is distinguished from these and becomes the anti-bonding interaction. As the third atom retreats, its bonding and anti-bonding interactions tend to cancel, so releasing it from the molecule. Thus, the diabatic surface will retain the permutation symmetry of the first pair of atoms but break their symmetry with the third atom.

In an equilateral configuration the diabatic wavefunction will have two pairs of atoms bonded and the third anti-bonded. This will obviously have the same energy as that of the wavefunction which has a different choice for the third pair and so their energy surfaces will cross in this configuration. The second wavefunction can be derived from the first by applying a permutation to it. This permutation is one of those missing from the wavefunction and ensures that the two functions together span a degenerate representation of the full permutation group. This means that only one energy form is required to specify both diabatic surfaces. This self-intersection is a special feature of the H_3 system.

4. The fitting procedure

The suggested form for the diabatic energy surface is

$$V = \sum_{r,s,t=0}^{r+s+t \leqslant n} V_{rst} X^r Y^s Z^t, \tag{5}$$

where, now, the variables are

$$X = \exp(-aR1), \quad Y = \exp(-aR2), \quad Z = \exp(-bR3) \tag{6}$$

and the symmetry is

$$V_{rst} = V_{srt}. \tag{7}$$

When $R2 \leqslant R3$ and $R1 \leqslant R3$ this is the energy of the lower surface and when $R3 \leqslant R2$ or $R3 \leqslant R1$ it is an upper surface.

As before, the diatomic limit is first fitted, and the scale factor a found, using

$$V(X,0,0) = \sum_{r=0}^{n} V_{r00} X^r \tag{8}$$

to fit to the energy of the ground state of H_2. The triplet state energy of H_2 is similarly fitted to the other diatomic limit

$$V(0,0,Z) = \sum_{t=0}^{n} V_{00t} Z^t \tag{9}$$

and the scale factor b found. Both surfaces then have their correct asymptotic form.

The triatomic points whose energies were calculated by Siegbahn and Liu (1978) already have $R1 \leqslant R2 \leqslant R3$ so they can be fitted to the lower surface form without any modification. The least squares procedure gives the coefficients V_{rst} as the solution of a set of linear equations. This assumes that the diabatic and adiabatic surfaces remain very close together at all points used in the fitting and differ only when extrapolated beyond the crossing.

In fact, the diabatic energy surface differs from the adiabatic one in one major respect. It gives a crossing of the diabatic energies for any isosceles configuration $R2 = R3$. This is not required by the symmetry of the system, so it is a diabatic crossing and not an adiabatic one. It is a two-dimensional crossing (any $R1$, $R2 = R3$) whereas the adiabatic crossing is one-dimensional $R1 = R2 = R3$). Such a difference in the crossing is exactly what is expected but it complicates the fitting process because, near such crossing, the adiabatic points should not be used to fit the diabatic surface. Since the equilateral configuration does have a crossing, the points that should be avoided are ones close to $R2 = R3$ and with $R1$ rather different. One such point was readily identified in the Siegbahn and Liu list (at 0·9, 2·64, 3·449). These points can be identified more quantitatively by finding the separation between upper and lower surfaces at each point and selecting those which are close. After these near-crossing points have been identified the fitting of the remaining points must be repeated. This should result in an improved fitting.

The near-crossing points can also be analysed. At these the adiabatic energies can be defined as the eigenvalues of a 2×2 matrix whose diagonal elements are the diabatic energies for upper and lower surfaces. The off-diagonal element is a new variable. Thus, with the upper and lower energies

$$V_u = \sqrt{\frac{1}{3}} (V(X, Z, Y) - V(Z, Y, X)), \quad V_l = V(X, Y, Z), \quad X \geqslant Y \geqslant Z, \tag{10}$$

and the interaction element U, the matrix

$$\begin{pmatrix} V_u & U \\ U & V_l \end{pmatrix} \tag{11}$$

has eigenvalues

$$E_t = \tfrac{1}{2}(V_u + V_l) \pm \tfrac{1}{2}\{(V_u - V_l)^2 + 4U^2\}^{\frac{1}{2}}. \tag{12}$$

The interaction U will also depend on configuration. Since it connects two wave-functions which permute either into themselves or into one-another it must be fully symmetric. Since the diatomic limits are already accurately fitted, U must vanish at these limits. It must also vanish for equilateral configurations. These conditions imply

that the first non-zero term in the expansion of U will be

$$U = u(X^2Y + Y^2Z + Z^2X + X^2Z + Y^2X + Z^2Y - 6XYZ), \tag{13}$$

where u is a constant. This constant can be fitted using the near-crossing points previously omitted from the diabatic fitting and the eigenvalue formula (12). This U is not a part of the diabatic fitting itself but it is relevant to it since it features in calculations that use the diabatic energy concept.

5. Results for H_3

The procedure described above was applied to H_3. The very accurate calculations of Kolos and Wolniewicz (1965) were used for the diatomic limits (8) and (9). Next, all points given by Siegbahn and Liu were fitted to the diabatic form (5). As suggested by Truhlar and Horowitz (1978), these energies were depressed by $0\cdot001167$ h to make the bottom of the channel join smoothly with the molecular minimum. This was repeated for terms of up to the nth degree for $n = 2, \ldots 8$. The root mean square (RMS) error of these fittings is shown in figure 1 with the label Dia(156). It may be compared with the corresponding RMS error for the adiabatic fitting given in the earlier paper and labelled Adi. With the exception of the fitting for $n = 3$, the improvement in fitting is evident.

Next, the point mentioned above as a near-crossing point was removed from the list and the fittings were repeated. The RMS errors for these are shown in figure 1 with the label Dia(155). For $n > 6$ the improvement in fitting is dramatic. As the fitting improves so these near-crossing points limit the accuracy obtainable and their removal allows the truly diabatic points to be fitted more closely. When the energies of both states were calculated this special point did indeed emerge as close to the crossing. Three other points were also identified as near-crossing points and removed from the list of fitting. When the fitting was repeated there was a further improvement in accuracy, but a very modest one.

As a fitting process this procedure is far from ideal. The upper surface contributes no points, apart from the diatomic limit, so the fitting can do anything there. Inspection of the results of this fit suggests that the results are quite unreliable for the upper surface away from the crossing points. The procedure for finding u also proved to be difficult because it was highly sensitive to the remaining errors in what was already a good fit. Furthermore, the fitting process ensures that the diabatic surface will overestimate some adiabatic points and underestimate others. However, the use of the eigenvalues (12) assumes that the diabatic surface is always above the adiabatic one for the lower surface and below it for the upper one. This contradiction indicates the need for some feed-back between the two calculations but a suitable one was not found. A least squares fit of u at the same time as the other coefficients would have led to much more complicated non-linear calculations and the risk of numerical instability.

The coefficients of the best fitting for $n = 8$ using 155 points are given in table 1.

6. Conclusion

The fitting of a diabatic energy formula to a calculated adiabatic energy surface involves some difficult problems and some major advantages. Since, by definition, the diabatic
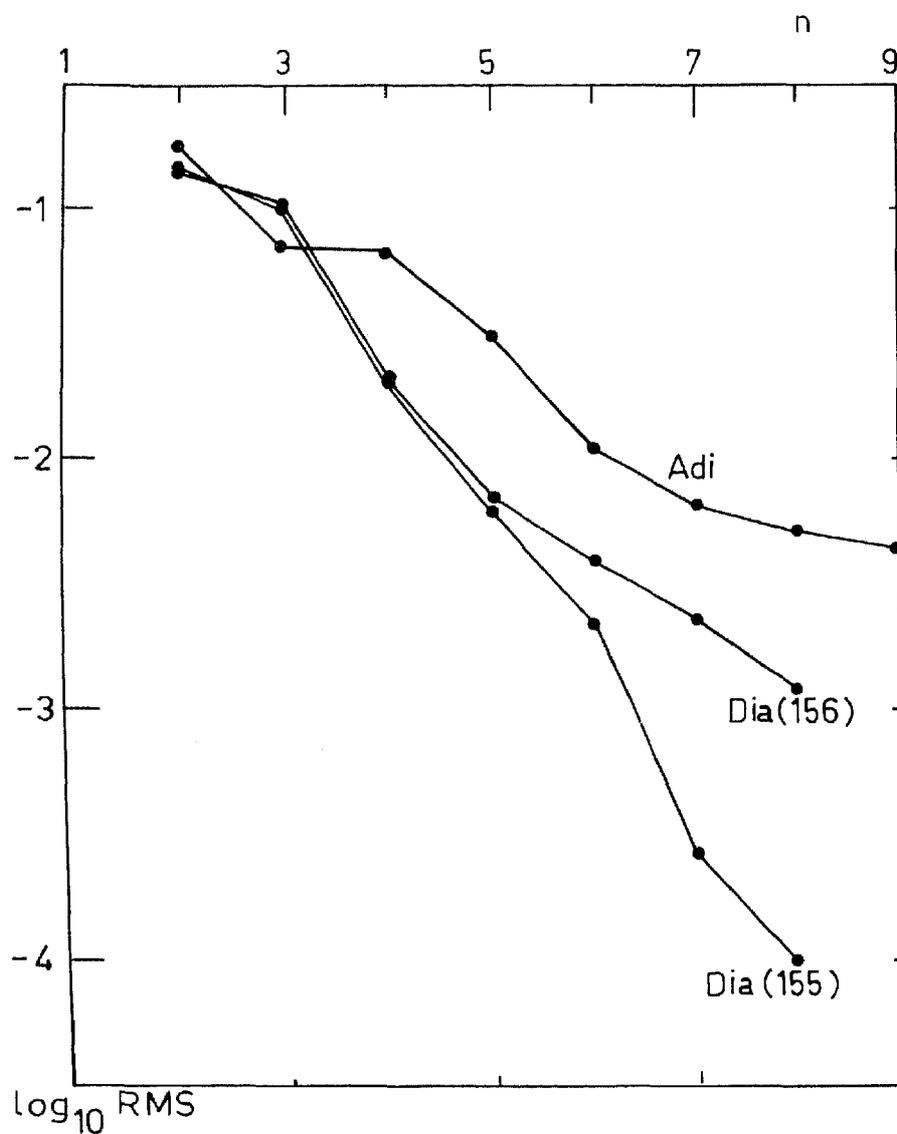
n

1   3   5   7   9

−1

−2   Adi

−3   Dia(156)

−4   Dia(155)

Log$_{10}$ RMS

Figure 1. The logarithm of the RMS error of fitting as a function of n, the highest degree terms included. Adi labels the adiabatic fitting and Dia the diabatic ones.

surface is a smooth interpolation between two adiabatic states it eliminates the cusps in the adiabatic surface which make the fitting of that energy so slow. On the other hand, there is no clear division between the points that belong to the diabatic surface and those that are in the crossing region and so should be excluded from the fitting. The procedure used above, of dividing the points according to the closeness of the surfaces, is clearly crude and does lead to difficulties.

The result of the fitting is a surface which fits the calculated points remarkably

Table 1. Coefficients of the diabatic energy for H_3. The index is equated to the value in hartrees. The exponent is in parenthesis.

a = 0·583788900	b = 0·536200000	
100 = −0·712085069 (−3)	001 = −0·856672657 (−3)	
200 = −0·132995913 (−1)	002 = −0·146339662 (0)	110 = 0·401040427 (1)
101 = −0·394985046 (1)		
300 = −0·333406637 (2)	003 = 0·829644260 (1)	210 = −0·417463883 (2)
201 = 0·154860307 (3)	102 = −0·189891297 (2)	111 = −0·886436238 (2)
400 = 0·210403701 (3)	004 = −0·329153955 (2)	310 = 0·223632902 (3)
301 = −0·157813687 (4)	103 = −0·809781429 (3)	220 = 0·724597086 (3)
202 = 0·200875280 (4)	211 = −0·462795459 (3)	112 = 0·239991159 (2)
500 = −0·611635040 (3)	005 = 0·887681408 (2)	410 = −0·162302758 (3)
401 = 0·597013137 (4)	104 = −0·226013080 (5)	320 = −0·488308306 (4)
302 = −0·102837946 (5)	203 = 0·200888630 (5)	311 = 0·731273207 (4)
113 = 0·882282274 (5)	221 = 0·316201689 (5)	212 = −0·543631675 (5)
600 = 0·975465474 (3)	006 = −0·155141866 (3)	510 = −0·689010998 (3)
501 = −0·108764381 (5)	105 = −0·208392950 (6)	420 = 0·310058104 (4)
402 = 0·519856651 (4)	204 = 0·233024233 (6)	411 = −0·368729470 (4)
114 = 0·106039695 (7)	330 = 0·433921190 (5)	303 = −0·513385250 (5)
321 = −0·195230475 (6)	312 = 0·278278426 (6)	213 = −0·101258881 (7)
222 = 0·817930862 (6)		
700 = −0·818267260 (3)	007 = 0·149210364 (3)	610 = −0·786701725 (3)
601 = 0·122602001 (5)	106 = −0·603599450 (6)	520 = 0·161238338 (5)
502 = −0·782001816 (3)	205 = 0·131715362 (7)	511 = −0·960138027 (4)
115 = 0·313676085 (7)	430 = −0·592397704 (5)	403 = 0·139585866 (6)
304 = −0·846477798 (6)	421 = 0·255141582 (6)	412 = −0·462108545 (6)
214 = −0·460963505 (7)	331 = 0·617444450 (6)	313 = 0·256186586 (7)
322 = −0·203336853 (7)	223 = 0·489785900 (7)	
800 = 0·287217386 (3)	008 = −0·538825542 (2)	710 = 0·268464941 (4)
701 = −0·753144931 (4)	107 = −0·267023381 (6)	620 = −0·132386778 (5)
602 = 0·253282624 (5)	206 = 0·126345705 (7)	611 = −0·141847397 (5)
116 = 0·128913578 (7)	530 = −0·382608799 (4)	503 = −0·256779051 (6)
305 = −0·189733379 (7)	521 = −0·766267203 (5)	512 = 0·384248761 (6)
215 = −0·326312916 (7)	440 = 0·144150579 (5)	404 = 0·113307128 (7)
431 = −0·125577742 (6)	413 = −0·202936209 (7)	314 = 0·388730910 (7)
422 = 0·940706903 (6)	224 = 0·386141761 (7)	332 = 0·808547638 (6)
323 = −0·267002284 (7)		

closely. The RMS error of the fitting in table 1 is 0·06 kcal/mol and the maximum deviation from the Siegbahn and Liu points is 0·31 kcal/mol. These are significantly smaller than those of the Truhlar and Horowitz (1978) fitting. As a representation of the calculated points, this fitting can have its uses. The upper surface, which is simply derived from the first by a permutation of variables, is not fitted to any calculated point and is not significant. An *ab initio* calculation of some points on this surface would be essential for a fitting of the full diabatic surface.

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