

A Many-body Expansion of Polyatomic Potential Energy Surfaces: application to H_n Systems

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A method recently proposed to construct explicit functions for the potential energy hypersurfaces of triatomic molecules is extended to deal with larger polyatomic systems. This extension is based upon a many-body expansion of the total potential energy and has the objective of reproducing both the equilibrium properties of any stable molecule on the surface and the asymptotic dissociation limits. The surfaces for H_n clusters have been examined in order to test the convergence of the many-body expansion. Accurate *ab initio* calculations on H_3 and H_2 are used to construct a function for the H_3 surface, which is shown to be more accurate, when judged by its overall description of the surface, than previous functions. The 2 and 3-body terms obtained from this analysis are combined with *ab initio* calculations on H_4 to deduce a 4-body term and a complete 6-dimensional surface for H_4 . This surface is shown to have a trapezoidal transition state for the $H_2 - D_2$ exchange which is 6 kJ mol⁻¹ below the H_2 dissociation limit. A reaction path passing through this transition state is determined. The many-body expansion terminated at the 4-body term is used to predict energies for D_{5h} structures of H_5 and D_{6h} structures of H_6 . The optimum bond length for H_6 is $1.85a_0$, in good agreement with calculations. The potential well is, however, of lower energy than for $3H_2$, showing that a small repulsive 5-body term must be invoked to obtain an accurate energy for this structure.

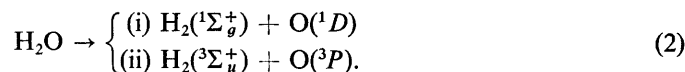
1. INTRODUCTION

In a previous paper (referred to as I)¹ we have shown how analytical functions can be constructed for the potential surfaces of stable triatomic molecules which have the correct asymptotic behaviour on dissociation and which reproduce the known spectroscopic force constants of the molecule.

The potential is written as a sum of three diatomic terms plus an interaction (3-body) term V_I which becomes zero at the diatomic dissociation limits

$$V_{ABC} = V_{AB}(R_1) + V_{BC}(R_2) + V_{CA}(R_3) + V_I(R_1, R_2, R_3). \quad (1)$$

The diatomic potentials are defined by the spin correlation rules for molecular dissociation.[†] For example, in the case of the ground state of H_2O , V_{HH} must allow for two possible dissociation channels for the removal of an oxygen atom



At the value $R_{HH} = 1.671 \text{ \AA}$ the separation of the singlet and triplet states of H_2 is equal to the $^1D - ^3P$ separation of the oxygen atom (1.958 eV); at shorter distances channel (i) has the lower energy and at larger distances channel (ii) has the lower

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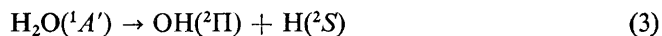
† The requirement that a polyatomic potential should reproduce equilibrium data and dissociation limits appears to have been first stated by Stearn and Eyring.²

energy. To satisfy the spin correlation rule V_{HH} must therefore have a cusp at $R_{HH} = 1.671 \text{ \AA}$.

The total potential of H_2O does not have any cusp except at infinite separation of the H_2 and O and a procedure was given in I for having a cancelling cusp in V_I . In practice it was possible to have continuity in all derivatives of the potential to fourth order at the cusp value of R_{HH} .

The potential for H_2O constructed according to the above principles has been tested by calculating the vibrational eigenvalues of the surface;^{1,3} good agreement with observed frequencies of spectroscopic bands has been obtained. There is also good agreement with the available quantum mechanical calculations of the H_2O surface except for regions corresponding to the linear configuration H-H-O. The method has also been used satisfactorily, with small modifications, for the O_3 and SO_2 surfaces.^{4,5}

Although expression (1) may appear at first sight to be sufficiently general to be able to reproduce exactly any triatomic potential, it is restricted by the fact that the diatomic dissociation fragments are independent of the shape of the three-atom triangle. Thus the potential does not always satisfy the spatial correlation rules: in the case of H_2O the correlation



which is used to define V_{OH} is not valid for linear configurations of the three atoms. However, this is not a fault that applies only to expression (1). One can show by examples that a potential function which satisfies spatial correlation rules cannot in general be single valued. A more flexible approach is at present under investigation for H_2O in which the potential is given by the eigenvalues of some $n \times n$ matrix.⁶

There is, however, the advantage of simplicity in having a single-valued potential, and for regions of a polyatomic surface which have no degeneracies this will probably be sufficient to interpret physical data. In this paper we therefore examine the extension of the method proposed in paper I to molecules with more than three atoms. Our ultimate objective is to establish general procedures for deriving the potentials needed in the molecular dynamics and conformational studies of large molecules.

An extension of expression (1) to larger molecules is straightforward and can be looked upon as a many-body expansion of the total potential. That such an expansion is convergent for some molecules for configurations close to equilibrium can be inferred from the body of chemical knowledge associated with bond transferable properties, or from the success already achieved in the field of molecular mechanics.^{7,8} There is, however, little evidence either from theory or experiment that such an expansion is generally convergent for molecular configurations of interest to chemists (*i.e.*, low energies on the potential hypersurface). In fact, apart from the near-equilibrium configurations of molecules that can be represented by perfect-pairing valence structures, chemists have shown no inclination for treating molecular energies by such an expansion.

The scarcity of reliable information on polyatomic potential surfaces over wide ranges of configuration makes it difficult to test convergence of the expansion away from equilibrium. However, systems for which such data are available are H_3 , and to a smaller extent, H_4 . In particular, the tetrahedral and square H_4 , for which no single valence structure can represent the molecular state, should provide a severe test of any many-body expansion. If such an expansion proves convergent then it may be applied to the species H_6 which has recently been invoked as the transition state in the $\text{H}_2 - \text{D}_2$ exchange reaction.⁹

Before describing our approach we comment on the possibility of extending functions of the LEPS type to many-atom surfaces. Such functions have been widely used for the surfaces of non-stable triatomic molecules, and H_3 has received particular attention. LEPS functions can either be treated as semi-empirical functions, for example the Porter–Karplus surface of H_3 ,¹⁰ or they may be used to fit *ab initio* data, for example the modified Porter–Karplus surface deduced by Yates and Lester.¹¹

London himself derived the valence bond eigenvalues for a tetra-atomic four-electron system¹² and this formalism has been used semi-empirically to discuss the H_2 – D_2 and H_2 – I_2 exchange reactions.^{13,14} The H_4 potential obtained by this method is not in good agreement with *ab initio* data. We have attempted to improve it by a least squares fitting to *ab initio* data for several geometries and we have not obtained satisfactory results. Our view, therefore is that functions of the LEPS type are not in general sufficiently flexible to fit many-atom surfaces.

2. THE GENERAL 4-ATOM POTENTIAL

We define the six interparticle distances for the molecule ABCD as R_{AB} , R_{AC} , R_{AD} , R_{CD} , R_{BD} , $R_{BC} = R_1$ to R_6 respectively. The 2-body terms are defined by diatomic dissociation limits such as

$$V_{AB+CD} = V_{AB}(R_1) + V_{CD}(R_4). \quad (4)$$

If the spin correlation rules do not allow for both diatomics to be in their lowest electronic states then these diatomic potentials will have cusps as in the triatomic case, but the position of the cusp will depend on the bond length of the other fragment. We imply this by writing our diatomic potentials in the form

$$V_{AB}(R_1|R_3) \quad (5)$$

this being a function of R_1 but having a parametric dependence on R_4 .

The many-body expansion we can now write as follows

$$\begin{aligned} V_{ABCD}(R_1 \dots R_6) = & V_{AB}(R_1|R_4) + V_{AC}(R_2|R_5) + V_{AD}(R_3|R_6) + V_{CD}(R_4|R_1) \\ & + V_{BD}(R_5|R_2) + V_{BC}(R_6|R_3) + V'_{ABC}(R_1, R_2, R_6) + V'_{BCD}(R_4, R_5, R_6) \\ & + V'_{CDA}(R_2, R_3, R_4) + V'_{DAB}(R_1, R_3, R_5) + V''(R_1 \dots R_6). \end{aligned} \quad (6)$$

The 3-body terms are defined by the triatomic dissociation fragments thus

$$V_{ABC} = V_{AB}(R_1|\infty) + V_{AC}(R_2|\infty) + V_{BC}(R_6|\infty) + V'_{ABC}(R_1, R_2, R_6). \quad (7)$$

In order to relate the potential of the tetra-atomic molecule to appropriate diatomic and triatomic potentials it is convenient to eliminate the 3-body terms from (6) by using expressions such as (7). The result is as follows

$$\begin{aligned} V_{ABCD} = & \sum_{WXY} V_{WXY}(R_{WX}, R_{XY}, R_{YW}) \\ & + \sum_{WX} V_{WX}(R_{WX}|R_{YZ}) - 2 \sum_{WX} V_{WX}(R_{WX}|\infty) + V''_{ABCD}(R_1 \dots R_6). \end{aligned} \quad (8)$$

In this expression the summations are over all pair or triple combinations of the four atoms as appropriate.

3. THE H₃ POTENTIAL

Functions representing the H₃ potential have already been obtained which reproduce experimental and theoretical features of the surface. The Porter-Karplus potential, which is a modified LEPS function, has been extensively studied.¹⁰ However, the properties of the saddle point of this surface (particularly the bond lengths and bending force constant) are not in very good agreement with the best *ab initio* calculations. A function has been proposed by Yates and Lester¹¹ which improves the saddle point properties but, as has been pointed out by Choi and Tang,¹⁵ this function has the wrong asymptotic behaviour at dissociation.

In order to obtain a reliable estimate of the 4-body term for the H₄ surface we must have H₄, H₃ and H₂ potentials calculated to a similar degree of accuracy. The best variational results for the singlet state of H₄ are those of Silver and Stevens¹⁶ for two points near the *D_{4h}* saddle point and by Bender and Schaeffer¹⁷ for some collinear configurations. These calculations are SCFMO with a basis of Slater orbitals (1*s*, 1*s*', 2*p*) with partially optimized exponents and configuration interaction with all singly and doubly-excited configurations. In order to make use of these points we therefore calculate the 3-body and 2-body energies from H₃ and H₂ potentials calculated at the same level of accuracy. The H₂ potential was given the form¹⁸

$$V_{\text{HH}} = -D_e(1 + a_1r + a_2r^2 + a_3r^3) \exp(-a_1r) \quad (9)$$

the parameters in this being determined from the dissociation energy and force constants of ref. (19). The data for this potential are given in table 1 and compared

TABLE 1.—COMPARISON OF THE *ab initio* AND SPECTROSCOPIC DATA ON H₂(¹Σ_g⁺). ALL VALUES ARE IN ATOMIC UNITS.

	<i>ab initio</i>	spectroscopic
<i>R_e</i>	1.401 8	1.401 4
<i>D_e</i>	0.169 59	0.174 55
<i>F₂</i>	0.368 5	0.369 7
<i>F₃</i>	−1.279 5	−1.271 3
<i>F₄</i>	4.257 5	4.263 1
<i>a₁</i>	2.082 2	2.132 0
<i>a₂</i>	1.081 2	1.214 8
<i>a₃</i>	0.499 6	0.566 9

with the spectroscopic data. The H₃ results are from the *ab initio* calculations of Shavitt *et al.*¹⁹ and Porter *et al.*,²⁰ which we refer to as the SSMK and PSK results respectively.

To obtain the H₃ potential we follow a procedure already used for O₃ and express the 3-body term in symmetry adapted displacement coordinates from a *D_{3h}* configuration of bond length *R*⁰

$$\begin{pmatrix} Q_1 \\ Q_2 \\ Q_3 \end{pmatrix} = \begin{pmatrix} \sqrt{\frac{1}{3}} & \sqrt{\frac{1}{3}} & \sqrt{\frac{1}{3}} \\ 0 & \sqrt{\frac{1}{2}} & -\sqrt{\frac{1}{2}} \\ \sqrt{\frac{2}{3}} - \sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{6}} \end{pmatrix} \begin{pmatrix} R_1 - R^0 \\ R_2 - R^0 \\ R_3 - R^0 \end{pmatrix} \quad (10)$$

The total potential must be symmetric to permutation amongst the three atoms, and a polynomial to quartic terms which is analytic in the symmetry coordinates is as follows

$$P = \alpha_0 + \alpha_1 Q_1 + \alpha_2 Q_1^2 + \alpha_3 q_r^2 + \alpha_4 Q_1^3 + \alpha_5 Q_1 q_r^2 + \alpha_6 q_s^3 + \alpha_7 Q_1^4 + \alpha_8 Q_1^2 q_r^2 + \alpha_9 Q_1 q_s^3 + \alpha_{10} q_r^4 \quad (11)$$

where

$$q_r^2 = Q_2^2 + Q_3^2 \text{ and } q_s^3 = Q_3^3 - 3Q_2^2 Q_3. \quad (12)$$

However, in the D_{3h} configurations the H_3 ground state is doubly degenerate and in the two dimensional space (Q_2, Q_3) has a conical intersection characteristic of a Jahn-Teller system.²¹

It has been shown by others²⁰ that the non-analytic part of the potential (the Jahn-Teller intersection) may be expressed by additional terms depending on q_r , and to quartic terms these are

$$P' = q_r \{\beta_1 + \beta_2 Q_1 + \beta_3 Q_1^2 + \beta_4 q_r^2 + \beta_5 Q_1^3 + \beta_6 Q_1 q_r^2 + \beta_7 q_s^3\} \quad (13)$$

q_r now being taken as the positive square root of q_r^2 to give us the lower sheet of the Jahn-Teller surface.

Following the procedure adopted in paper I we represent the interaction 3-body term by a sum of the polynomials P and P' multiplied by an exponentially decaying range factor. In our study of O_3 we considered two forms of this range factor, namely⁴

$$\prod_{i=1,2,3} [1 - \tanh \gamma(R_i - R^0)/2\sqrt{3}] \quad (14)$$

and

$$(1 - \tanh \gamma Q_1/2) \quad (15)$$

both of them behaving as $k \exp(-\gamma Q_1)$ for large positive values of Q_1 . We have found little difference in the overall potentials that result from using these two forms and since the second function is rather easier to handle analytically we have used it in this paper.

The parameters in the 3-body term were obtained by the following procedure:

- (i) R^0 was taken as the bond length of the minimum energy ($1.965a_0$) D_{3h} structure.*
- (ii) $\alpha_0, \alpha_1, \alpha_2, \alpha_4, \alpha_7$ and γ were obtained by fitting 5 points on the PSK *ab initio* potential curve for D_{3h} structures²⁰ ($q_r = 0, q_s = 0$) plus the condition of a minimum at R^0 . The resulting D_{3h} potential curve is shown together with the *ab initio* points in fig. 1.
- (iii) β_1 was constrained to give the slope of the Jahn-Teller intersection ($\partial V/\partial q_r$) at the D_{3h} minimum quoted by Porter *et al.*²⁰
- (iv) The remaining 12 parameters were fitted by a least squares procedure to calculated points on the SSMK surface at bond angles of $180^\circ, 150^\circ$ and 120° (61 points in all).

The standard deviation of this fit was 2×10^{-3} a.u. and the maximum error in the energy of H_3 relative to three hydrogen atoms was 2%, this maximum being in a high energy part of the surface: typical errors were 0.3% over most of the fitted points.

The complete parameters of the 3-body term are given in table 2. Fig. 2 shows contours for the Jahn-Teller displacement coordinate (symmetry E') from the D_{3h} configuration having $Q_1 = 0.696a_0$. This is qualitatively similar to the same plot of the Porter-Karplus surface.¹⁰ The parameters of the collinear transition state calculated from our potential are given in table 3 and compared with the results of others. Our parameters are in good agreement with the SSMK *ab initio* results,¹⁹ as anticipated from our fitting procedure, the largest error being in the bending force

* a_0 = a.u. of length $\approx 0.5292 \times 10^{-10}$ m. a.u. of energy ≈ 2625.5 kJ mol⁻¹.

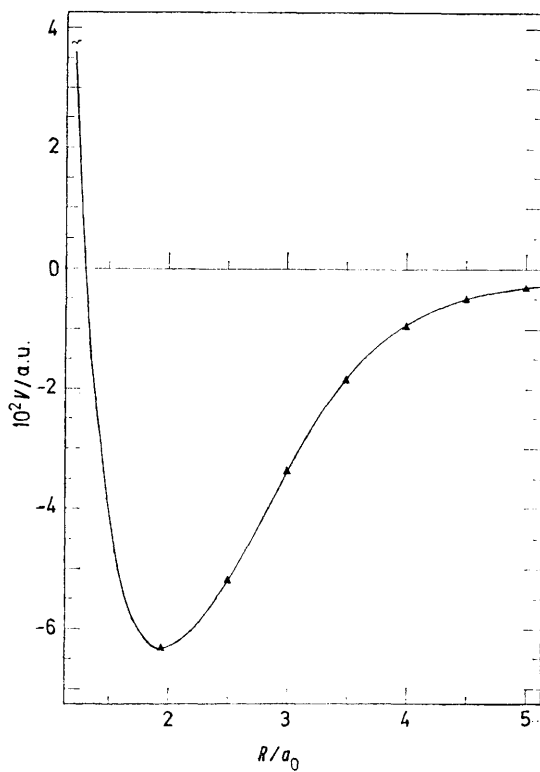


FIG. 1.—The D_{3h} potential for H_3 . The *ab initio* results of ref. (20) are shown as triangles.

TABLE 2.—COEFFICIENTS FOR THE 3-BODY INTERACTION TERM OF H_3 AS DEFINED IN (11), (13) AND (15). ATOMIC UNITS ARE USED WITH THE POWER OF 10 GIVEN IN PARENTHESIS.

coefficient	value
α_0	3.472 17 (−1)
α_1	1.379 61 (−2)
α_2	1.067 07 (−2)
α_3	9.373 56 (−3)
α_4	5.108 73 (−3)
α_5	−5.491 04 (−2)
α_6	3.499 75 (−2)
α_7	9.872 37 (−4)
α_8	−7.094 84 (−3)
α_9	9.741 61 (−3)
α_{10}	−2.960 11 (−2)
β_1	−1.395 97 (−1)
β_2	−3.972 36 (−3)
β_3	1.054 70 (−2)
β_4	6.560 09 (−2)
β_5	−1.001 22 (−3)
β_6	3.075 69 (−2)
β_7	−2.062 14 (−2)
γ	9.427 46 (−1)

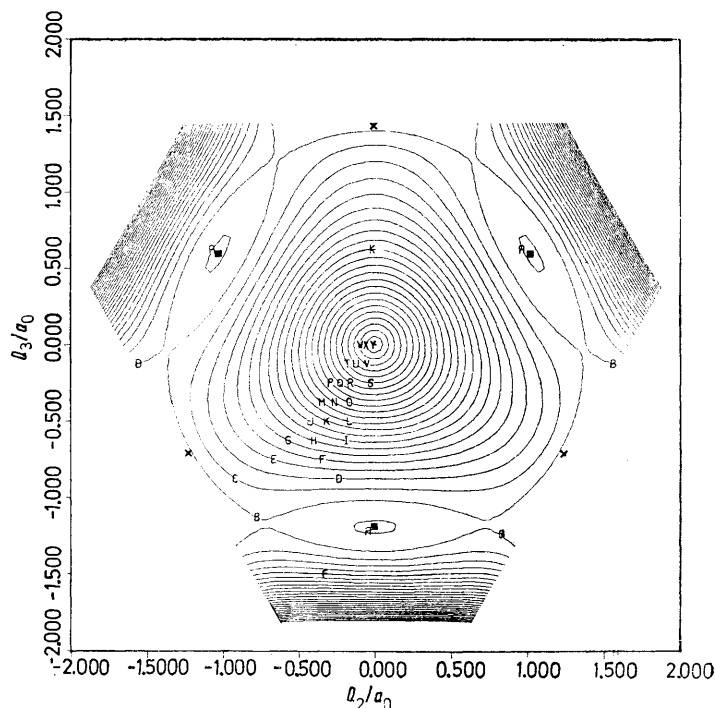


FIG. 2.—The H_3 surface for $Q_1 = 0.696a_0$ showing the Jahn-Teller cusp in the centre and the three collinear saddle points indicated by stars. The points marked ■ represent C_{2v} structures with one atom far away from the other two. Only the physical space of (Q_2, Q_3) is shown. Contour A is for an energy 0.016 a.u. and subsequent contours are at intervals of 0.004 a.u.

TABLE 3.—COMPARISON OF THE COLLINEAR SADDLE POINT PROPERTIES OF THIS WORK POTENTIAL ENERGY SURFACE FOR H_3 WITH THOSE OF PREVIOUS WORKERS

	<i>ab initio</i> calculations ^a		<i>semi-empirical</i>	least-squares fitting	
	SSMK ¹⁹	Liu ²²	LEPS surface Porter-Karplus ⁽¹⁰⁾	YL ^b	this work
R_{sp}/a_0	1.765	1.757	1.701	1.742	1.775
$\Delta E_0^{class}/\text{kJ mol}^{-1}$	46.03	41.01	38.16	41.05	45.62
$A_{11}/\text{a.u.}$	0.32	0.320	0.364	0.324	0.322
$A_{22}/\text{a.u.}$	0.024	—	0.024	0.030	0.037
$A_{33}/\text{a.u.}$	−0.061	−0.058	−0.124	−0.071	−0.062

^a The parameters were obtained direct from *ab initio* calculations by making a Taylor expansion of the potential about the saddle point. The results of Liu are only for collinear configurations.

^b The least-squares fitting by Yates and Lester¹¹ is to the Liu results using a function similar to that of Porter and Karplus. However, this function does not have the correct asymptotic limits.¹⁵

constant. The curvature along the reaction coordinate, A_{33} , is in better agreement with either set of *ab initio* results, than is that obtained from the Porter-Karplus or Yates-Lester functions. We foresee no computational disadvantages that our function might have in dynamical studies on the H_3 surface and its greater accuracy over the PK and YL functions would commend it for future use.

4. THE H_4 POTENTIAL

The spin-conserved dissociation fragments for the lowest energy singlet state of H_4 are $H_3(^2A) + H(^2S)$ or $2H_2(^1\Sigma_g^+)$ for all configurations. Thus the 2-body and 3-body potentials appearing in the expansion (8) for the H_4 potential are the same as those used for the H_3 potential in the last section.

We start by examining the potential for H_4 that is obtained if the 4-body term is neglected. Contours of this for the D_{2h} structures are shown in fig. 3. Although the general shape of this potential is the same as has been deduced by *ab initio* calculations, we obtain a saddle-point that is too high in energy at too long a bond length. Further investigation shows that for all configurations for which *ab initio* data are available the sum of the 2 and 3-body energies is greater than the calculated energy and we, therefore, conclude that the 4-body term is attractive over the whole configuration space.

To obtain an expression for the 4-body term which is as flexible as the 3-body term already obtained would require accurate data at points on the surface over a wide range of configurations of the 4-atom system. We can adopt for the H_4 surface a similar procedure to that followed for the H_3 surface. We define normal modes of displacement from a tetrahedral H_4 structure which will transform as the irreducible representations A_1 , E and T_2 of the T_d group. From these one can set up analytic and non-analytic polynomials analogous to (11) and (13) and write the total 4-body potential as the sum of these multiplied by a range factor as (15). The very limited data we have on the H_4 surface at the required accuracy restricts the number of terms in these polynomials that we can at present determine.

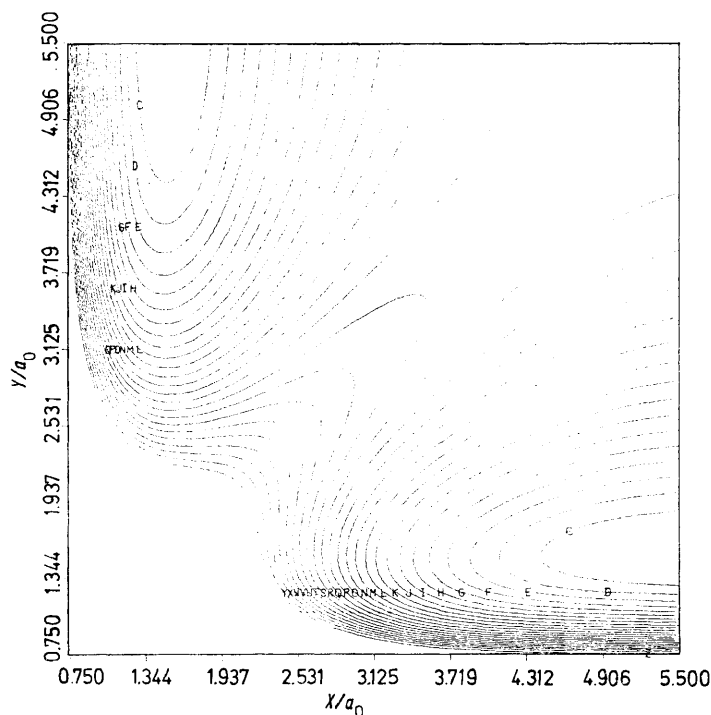


FIG. 3.—The D_{2h} surface for H_4 obtained from 2 and 3-body terms only. Contours are labelled from A = -0.35 a.u. in intervals of 0.02 a.u.

The totally symmetric displacement coordinate (A_1) of the tetrahedron is defined as

$$W_1 = \sqrt{\frac{1}{6}} \sum_{i=1,6} (R_i - R^0) \quad (16)$$

The simplest assumption we could make about the 4-body term would be that it is only a function of W_1 . However, we have not found that this gives an accurate representation of the D_{2h} surface. We note in passing that a function of the form (14), namely

$$V'' = -0.0105 \prod_{i=1,6} [1 - \tanh 0.4714 (R_i - 4.2355)] \text{ a.u.} \quad (17)$$

does give a good D_{2h} surface but it is poor for other configurations. We must therefore consider the inclusion of non totally symmetric displacement coordinates in the 4-body term.

From *ab initio* calculations by Silver and Stevens¹⁶ on a square H_4 of side $2.4a_0$ we deduce a 4-body energy of -0.165 a.u. and from the results of Bender and Schaefer¹⁷ extrapolated to a linear structure with the same value of W_1 ($R_1 = R_4 = 1.4a_0$, $R_3 = R_6 = 1.997a_0$) we deduce a 4-body energy of -0.210 a.u. Such results give us some indication of the importance of non-symmetric displacements on the 4-body energy.

There are two totally symmetric quadratic functions of the displacement coordinates. One of these is W_1^2 and the other, being a combination of E and T_2 normal modes may be written

$$w_r^2 = \sum_{i=1,6} [\frac{5}{6}(R_i - R^0)^2 - \frac{1}{3} \sum_{j < i} (R_i - R^0)(R_j - R^0)]. \quad (18)$$

The non-analytic coordinate w_r is analogous to q_r of the H_3 system [expression (12)]. We shall proceed to an evaluation of the 4-body term by assuming that the analytic and non-analytic polynomials are functions only of W_1 and w_r . There will be other non-totally symmetric modes entering at the cubic level, which we shall ignore.

Only a few points on the H_4 surface have been calculated with the same accuracy as we have for points on the H_3 surface, although many points have been calculated at the $(1s, 1s')$ SCF CI level. To extend our data on which the coefficients in our 4-body term can be fitted we have, therefore, assumed that the difference in energy between the $(1s, 1s')$ and $(1s, 1s', 2p)$ levels is a linear function of W_1 , the parameters in this function being determined by the available data for D_{4h} geometries.¹⁶ Table 4 shows the values of the 4-body energies at different points on the surface that we have obtained by this assumption. There will be errors in these values that arise from the above assumption and these might be as large as ± 0.02 a.u. Such errors will clearly limit the accuracy of the 4-body function which we deduce by fitting these points.

Our fitting procedure for the 4-body term was as follows:

1. We assume that γ and R^0 are the same as in the 3-body term. This will ensure that the rate of decay of the 4-body term on dissociation is roughly comparable with the decay of the 2 and 3-body terms.
2. We have attempted an optimum fit of the D_{2h} and $D_{\infty h}$ surfaces, these containing points for which we have the accurate *ab initio* data, by fitting exactly the points indicated by an asterisk in table 4.
3. We required an approximate fit to the energies of the tetrahedral structures. Not only are these points for which we have no accurate data, but they are also

high in the potential energy surface and they are configurations in which Jahn-Teller non-analytic behaviour occurs.

Our potential surface will have non-analytic behaviour for T_d or C_{3v} symmetries due to the 3-body term. We also have the non-analytic terms w_r and w_r^3 in the 4-body term. However, we have made no attempt to reproduce the correct symmetry of the Jahn-Teller surface of the tetrahedron (an 1E state with a conical intersection along the E modes of vibration).

TABLE 4.—DATA USED TO CONSTRUCT THE H_4 4-BODY TERM. (ALL QUANTITIES IN a.u.)

geometry	W_1	w_r	H_4 <i>ab initio</i> energies ^a		I-II $\times 10^2$	2 + 3- body energy	4-body
			I (1s1s')	II (1s1s'2p)			
tetrahedral	−0.894	0	0.248 1 ^b	—	(3.97)	0.777 8	−0.569 4*
	1.065	0	0.044 0 ^b	—	(2.69)	0.371 3	−0.354 2*
	1.719	0	0.021 1 ^b	—	(2.26)	0.280 7	−0.282 2*
square	1.065	1.009	−0.065 3 ^{c,e}	−0.092 2 ^{c,e}	2.69	0.139 3	−0.231 0
	1.877	1.148	−0.077 2 ^c	−0.098 8 ^c	2.16	0.066 3	−0.165 1*
rectangular	1.065	1.765	−0.236 0 ^{c,e}	—	(2.69)	−0.027 6	−0.235 3
	1.877	2.323	−0.272 1 ^{c,e}	—	(2.16)	−0.171 5	−0.122 2*
linear	1.065	2.631	−0.215 0 ^c	−0.248 0 ^d	3.30	0.056 6	−0.304 6*
	1.877	3.039	−0.262 0 ^{c,e}	−0.291 9 ^{d,e}	2.99	−0.082 1	−0.209 8*
	2.862	3.596	−0.290 5 ^c	−0.319 2 ^d	2.87	−0.198 9	−0.120 3

^a Energy of H_4 minus energy of 4H. ^b From ref. (23). ^c From ref. (16). ^d From ref. (17).

^e Obtained by interpolation of the known *ab initio* data. * Points used to obtain the coefficients in eqn (20) and (21).

After examining several functions from the 4-body term we have selected the form

$$V'' = -a(1 + bW_1 + cW_1^2)(1 + dw'_r + ew'^2_r + fw'^3_r)(1 - \tanh \gamma W_1/2) \quad (20)$$

where

$$w'_r = w_r/(1 + gW_1). \quad (21)$$

The coefficients of these functions are defined in table 5.

TABLE 5.—THE COEFFICIENTS OF THE 4-BODY TERM DEFINED IN EXPRESSIONS (20) AND (21).

coefficient	value/a.u.
a	0.463 5
b	0.257 1
c	0.135 8
d	−0.336 5
e	−0.462 1
f	0.299 7
g	0.303 1

The function (20) might be said to have an *ad hoc* appearance, but in its defence we can say that we were unable to find a simpler function that behaved as well over the whole surface. The advantage of the scaling procedure defined by (21) is that the 4-body term is attractive over the whole surface for positive values of W_1 . The singularity at $W_1 = -g^{-1}$ is not in a physically accessible part of the surface.

Fig. 4 shows the D_{2h} surface we calculate from the complete potential. It has a very shallow minimum, in the entrance and exit valleys, which we believe has no physical significance and arises from a slight unbalance of the 3 and 4-body terms at large separations of the two molecules. The position and height of the D_{4h} saddle point ($R = 2.41a_0$, $\Delta E_0^{\text{class}} = 628 \text{ kJ mol}^{-1}$) are very close to those deduced from the Silver-Stevens calculations.¹⁶

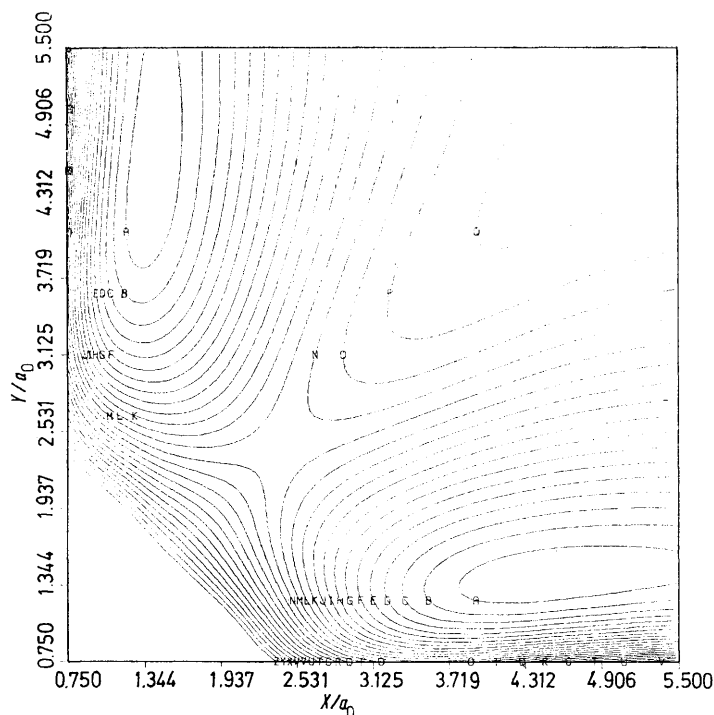


FIG. 4.—The D_{2h} surface with 2, 3 and 4-body terms. Contours as in fig. 3.

Comparison with *ab initio* points is seen most clearly through one-dimensional graphs; a series of these are shown in fig. 5, 6 and 7. The relative magnitude of the 2, 3 and 4-body terms for D_{4h} structures is shown in fig. 5. The 4-body term becomes important for squares with less than $3a_0$, and clearly has an important role in determining the saddle point.

Fig. 6 shows that we reproduce the repulsive energy for end-on approach of equilibrium hydrogen molecules but over-estimate the repulsion for side-on approach. Fig. 7 shows the worst feature of our potential, which is a failure to get the correct rate of decay of the 4-body energy for tetrahedral structures.

Other aspects of our surface which are of interest are shown in figs. 8 and 9. These structures have been examined in *ab initio* calculations. We reproduce the position and depth of the D_{3h} structure and the position of the cusp and the two minima in the rhombohedral structures. The cusp is due to the crossing of 1A_g and $^1B_{1g}$ surfaces²⁴ and in our potential arises from the non-analytic behaviour of the 3-body term at $\beta = 60^\circ$. There is no *a priori* reason for the 1A_g and $^1B_{1g}$ curves to cross at this angle, but the fact that they do is either fortuitous or a justification for our approach.

5. APPLICATION TO THE $\text{H}_2 - \text{D}_2$ EXCHANGE REACTION

Most of the calculations on H_4 have been stimulated by the problem of determining the configuration of the four-centre transition state for the exchange reaction. The most accurate calculations are in agreement that the activation energy for the concerted reaction is close to the H_2 dissociation limit and probably above it.¹⁶

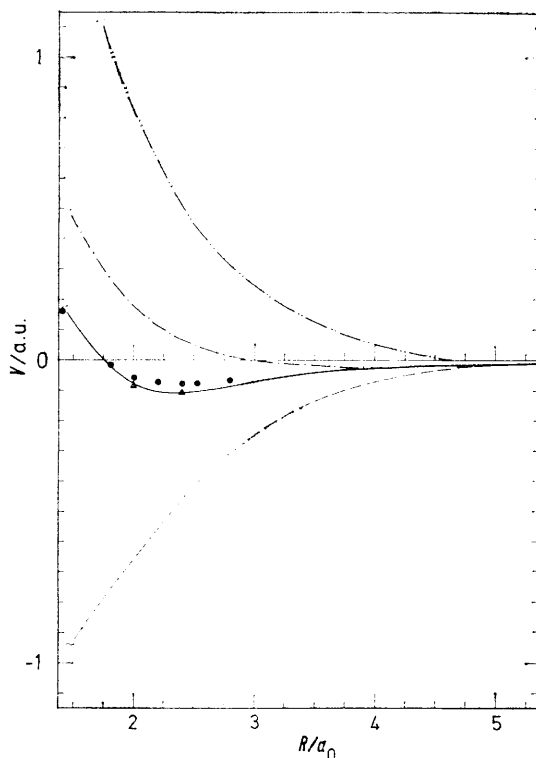


FIG. 5.—The D_{4h} potential for H_4 showing the 2-body (---), 3-body (— · — · —), 2 plus 3-body (— · · —) and full potential (—). *Ab initio* points¹⁶ at the $(1s, 1s')$ and $(1s, 1s', 2p)$ levels of calculation are shown by dots and triangles respectively.

It is a relatively easy task to scan the six dimensional space of our H_4 potential for possible reaction paths. We find, like Silver and Stevens,¹⁶ that a route through trapezoidal structures has the lowest activation energy. We have obtained a complete two-dimensional surface for trapezoidal structures with optimized ratio of the two unequal sides. A reaction path on this which is approximately that of steepest descent is shown in fig. 10.

On one side of the transition state the reaction path is asymptotic to a collinear structure. The approach to this is actually rather complicated as X first decreases and then increases. The transition state cannot by symmetry be collinear. The reason for this is that the reaction coordinate, being the one direction of negative curvature at a transition state, cannot be both along the internuclear axis and perpendicular to this, because these are orthogonal directions.

Our calculated activation energy is approximately 6 kJ mol^{-1} below the H_2 dissociation limit and 190 kJ mol^{-1} below the D_{4h} saddle point, but from the known accuracy

of our surface we would not put much weight on the fact that our activation energy is below the H_2 dissociation limit.

6. APPLICATION TO H_5 AND H_6

We have used our many-body terms, calculated from H_2 , H_3 and H_4 to predict potentials for the species H_5 and H_6 on the assumption that the expansion can be truncated at the 4-body term. An hexagonal H_6 structure (D_{6h}) has been proposed as an alternative transition state for the $\text{H}_2 - \text{D}_2$ exchange reaction.⁹

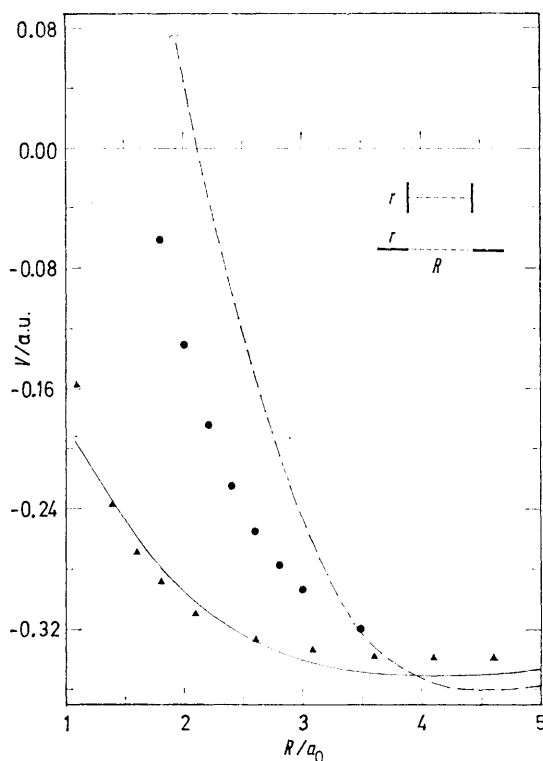


FIG. 6.—Potentials for side-on (---) and end-on (—) approach of two H_2 molecules at fixed (equilibrium) bond lengths. These curves are compared with *ab initio* points (dots) at the $(1s, 1s')$ level¹⁶ lowered by 0.036 a.u. to give the same asymptotic limit as our curve and at the $(1s, 1s', 2p)$ level¹⁷ (triangles), respectively. $r = 1.4a_0$.

The full many-body expansions for the two systems involve the number of terms given in table 6. It is seen that a small error in the 4-body term may be unimportant for H_4 but it is magnified considerably for H_5 and H_6 . We must, therefore, recognize that our predictions are no more than qualitative even if the truncation of the expansion is valid.

Fig. 11 and 12 show one-dimensional potentials for the regular polygons. The limiting values for the dissociation limits with optimum fragment geometries are shown. We find that H_5 is unstable compared with both $2\text{H}_2 + \text{H}$ and $\text{H}_3 + \text{H}_2$. For H_6 we find an optimum hexagon of side $1.85a_0$ which is more stable by 560 kJ mol^{-1} than 3H_2 .

We carried out double zeta (0.9, 1.2) SCFMO (restricted Hartree-Fock) calculations on H_5 regular pentagonal structures and obtained an optimum structure with bond length $2.1a_0$ and energy -2.550 a.u. This bond length is close to that predicted in fig. 11. Calculations on H_6 regular hexagons^{9,25} have given optimum bond lengths of 1.8 and $1.86a_0$. Our predicted energy for H_6 is clearly too low. However, to bring this energy above the $3H_2$ limit would only require each 5-body energy to be

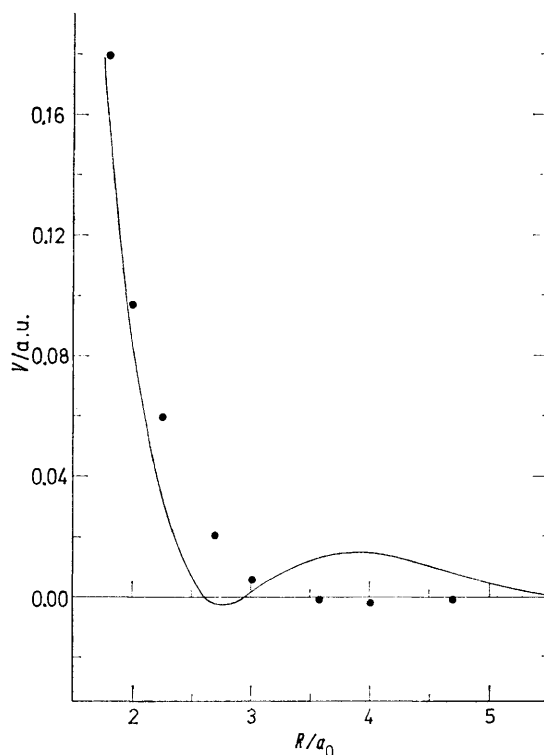


FIG. 7.—The potential for tetrahedral T_d configurations compared with $(1s,1s')$ calculations.²³

repulsive by 84 kJ mol^{-1} (0.032 a.u.). Thus even though our energy at this optimum geometry is not correct, the many-body expansion is converging as is shown from the results in table 6. We give as an estimate of the 5-body energy the energy required to bring the optimum H_6 energy to the $2H_2 + 2H$ limit, which is probably an upper bound. This energy is 20% of the 4-body energy.

We comment finally on the fact that for the H_n systems the n -body terms appear to oscillate in sign. We cannot be confident that this is true for all configurations. For square and tetrahedral configurations of four rare gas atoms or hydrogen atoms with maximum spin multiplicity the same has been found, although for three collinear atoms the 2 and 3-body terms have the same sign.²⁶⁻³⁰

7. CONCLUSIONS

The lack of accurate *ab initio* data for many points on the H_4 surface has prevented us from producing a very accurate six-dimensional potential energy function. The one we have obtained is reasonably satisfactory in most configurations and we have

used it to derive an optimum reaction path for the exchange reaction. Although the many-body expansion appears to be convergent for the low-energy regions of the surface, the 4-body term still has a dominant role in determining the position and height of the saddle points on the surface. Likewise, the optimum H_6 hexagon is

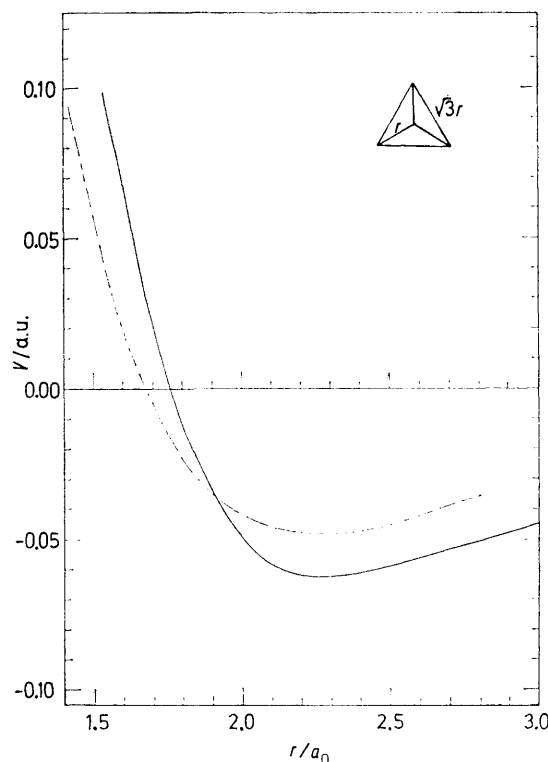


FIG. 8.—The potential for D_{3h} structures (—) compared with *ab initio* calculations at the $(1s, 1s')$ level¹⁶ (---).

found to be too low in energy. This may be due to the neglect of a small repulsive 5-body term or simply to the propagation of the errors inherent in our 4-body potentials. The accumulation of errors is a serious problem for any many-body expansion since the number of n -body components increases according to the combinatorial law.

Although it is far from clear that a many-body expansion of the potential is the

TABLE 6.—THE NUMBER OF n -BODY TERMS CONTRIBUTING TO THE MANY-BODY EXPANSION AND THEIR CONTRIBUTION TO THE TOTAL ENERGY AT R_{MIN}

$n =$	2	3	4	5	6
H_5 number of n -body terms	10	10	5	1	0
energy/a.u.	-0.749 5	1.072 4	-0.592 9	—	—
H_6 number of n -body terms	15	20	15	6	1
energy/a.u.	-1.220 1	2.287 7	-1.768 6	(0.361 8)	—

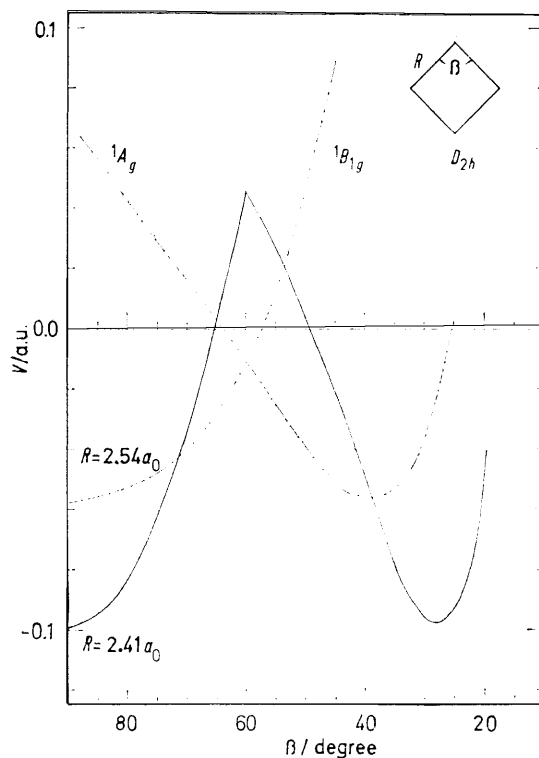


FIG. 9.—The potential for rhombohedral structures compared with *ab initio* CI calculations at the minimal basis (1*a*) level.²⁴

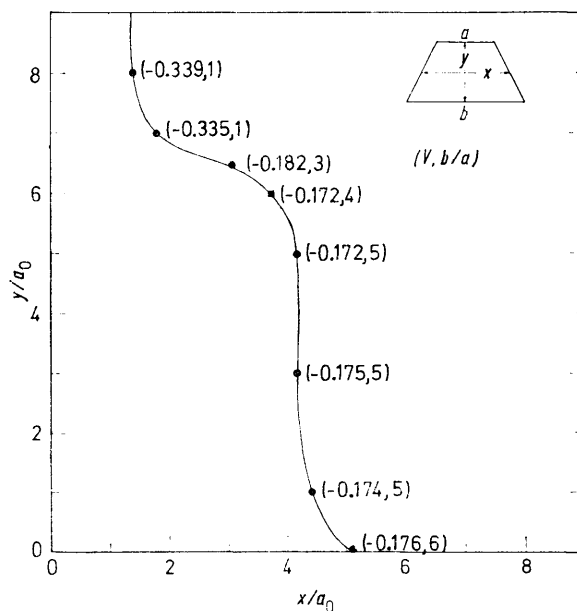


FIG. 10.—Reaction path for the $H_2 - D_2$ exchange reaction through regular trapezoidal structures with optimum ratio of $a:b$.

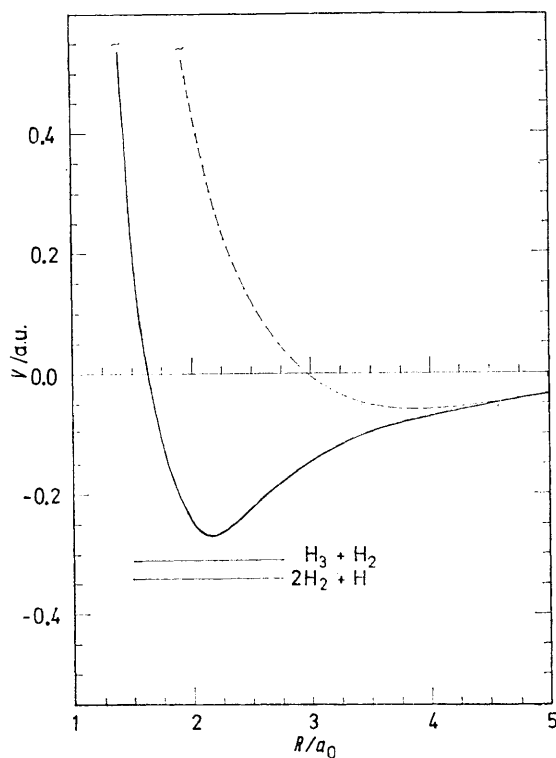


FIG. 11.—Predicted potential curve for $H_5(D_{5h})$ regular pentagons based upon the 2, 3 and 4-body potentials. The 2 plus 3-body potential is also shown as a dashed curve.

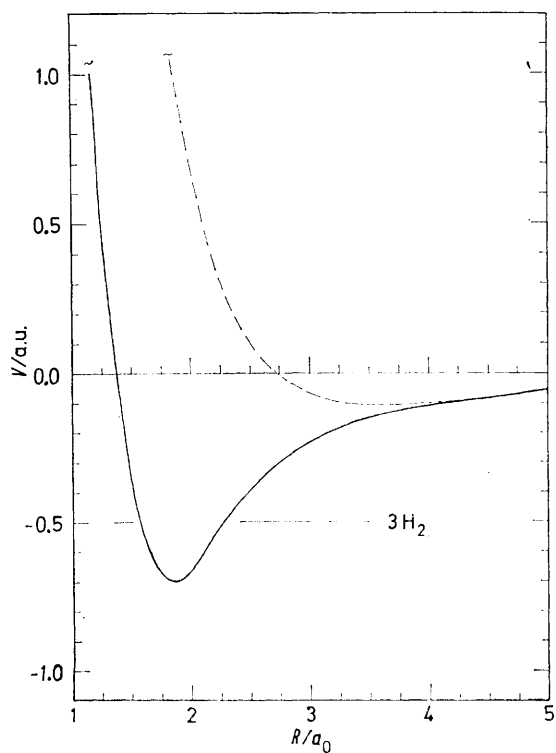


FIG. 12.—Predicted potential curve for $H_6(D_{6h})$ regular hexagons. Curves labelled as in fig. 11.

best approach for these regions of the surface in which the atoms are all in close proximity, the fact that it contains explicitly the correct asymptotic limits makes it appropriate for surfaces which are to be used for dynamical calculations.

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