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Representation of *ab initio* energy surfaces by analytic functions

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A method for the analytical representation of *ab initio* energy surface results is described. For a three-atom surface, the potential function is written as a sum of atomic, two-body, and three-body terms. This allows an easy fitting of the whole surface, including the dissociated and united atom limits. The theory is applied to an H_3 surface of limited accuracy calculated for these purposes. Comparisons are made, where possible, with more accurate calculations. Extensions to surfaces involving four or more atoms are also discussed.

I. INTRODUCTION

The determination from first principles of cross sections and rate constants for atomic and molecular processes requires a knowledge of the molecular potential energy surface over which the system moves, and a completely theoretical approach involves the use of surfaces obtained by *ab initio* methods. Recently, much progress has been made in developing methods for doing dynamics calculations given a surface,¹ but many studies have been made with surfaces defined semiempirically. A successful dynamics calculation requires rapid determination of the potential energy (or force) at nearly continuously distributed sets of molecular geometries. *Ab initio* methods do not lend themselves to giving such results, and interpolation or function fitting techniques must usually be used. Two general philosophies of fitting techniques are now developing. The *global* approach is exemplified by the least-square functions of Liu^{2b} and the analytical functions of Truhlar and Kuppermann.³

A *local* approach, used by McLaughlin and Thompson⁴ and Raff and co-workers,⁵⁻⁹ gives a fit of either *ab initio* or semiempirical potential surfaces with multidimensional cubic spline functions. These workers have found that multidimensional spline fitting of *ab initio* points can serve as a useful means of interpolation. Cubic splines have also found effective use in this laboratory for fitting H_2-H_2 potentials.¹⁰ In spite of these successes, the problem of obtaining analytic representations of *ab initio* surfaces for use in dynamics studies is still a major road block impeding their use in theoretical kinetics.

This article presents a general method of fitting *ab initio* surfaces to polynomial expressions. The discussion will concentrate on the reactive surface for three atoms, but we show how extensions to tetra-atomic systems can be made. The pivotal step of our method consists in isolating types of mathematical behavior of the surface in different terms so that they may be dealt with most simply. As shall be seen, the separation of terms providing the isolation also separates apart various physical and chemical phenomena for simpler qualitative understanding.

In many cases, the dynamics calculations require only a portion of the surface. Nevertheless, we examine the problem of fitting the whole range of variables by polynomial expressions.

II. THE GENERAL MATHEMATICAL PROPERTIES OF AN XYZ SURFACE

It is useful to examine the properties of a general triatomic surface. The internal geometric configuration is completely determined by the three interatomic distances r_{12} , r_{23} , and r_{13} , which we use for the variables of the potential functions, $V(r_{12}, r_{23}, r_{13})$. From the mathematical point of view, the most striking features of V are the three poles of order 1 when r_{12} , r_{23} , or r_{13} becomes zero. Most analytic fitting techniques for complicated functions involve either directly or indirectly the use of approximating polynomials, and it is well known that polynomials cannot represent poles well. Of course, the existence of poles can also have considerable influence at points distant from them, as is shown in the theory of convergence of power series in the complex plane.

These facts suggest that we can ease the polynomial fitting problems by eliminating the poles from V . This might be done by subtracting $Z_1 Z_2 / r_{12}$ and corresponding terms for the other pairs from V . These constitute the exact form of the poles from the nuclear term in the Hamiltonian for an adiabatic surface. The potential function V , modified in this way, still retains regions of reasonably rapid fluctuation. One may go farther and subtract other quantities from V . The procedure we use consists of writing V as a sum of three kinds of terms,¹¹

$$V(r_{12}, r_{23}, r_{13}) = A_1 + A_2 + A_3 + D_{12}(r_{12}) + D_{23}(r_{23}) + D_{13}(r_{13}) + T_{123}(r_{12}, r_{23}, r_{13}), \quad (1)$$

where A_i is the energy at infinity of the i th atom, D_{ij} is the diatomic molecule potential of the $i-j$ atom pair, and T_{123} is the remainder of the potential. The D_{ij} in (1) must be arranged to be asymptotic to zero for large values of r_{ij} . No approximations are involved in (1), of course.

The benefits of writing the energy in this form arise because the large fluctuations in V derive mainly from the D_{ij} , which now are functions of only one variable and may be dealt with quite simply. The difficult term, T_{123} , is quite smooth, and is zero except in those regions where significant chemical interaction of all three atoms occurs. We return to this aspect of the three-body term for more discussion later.

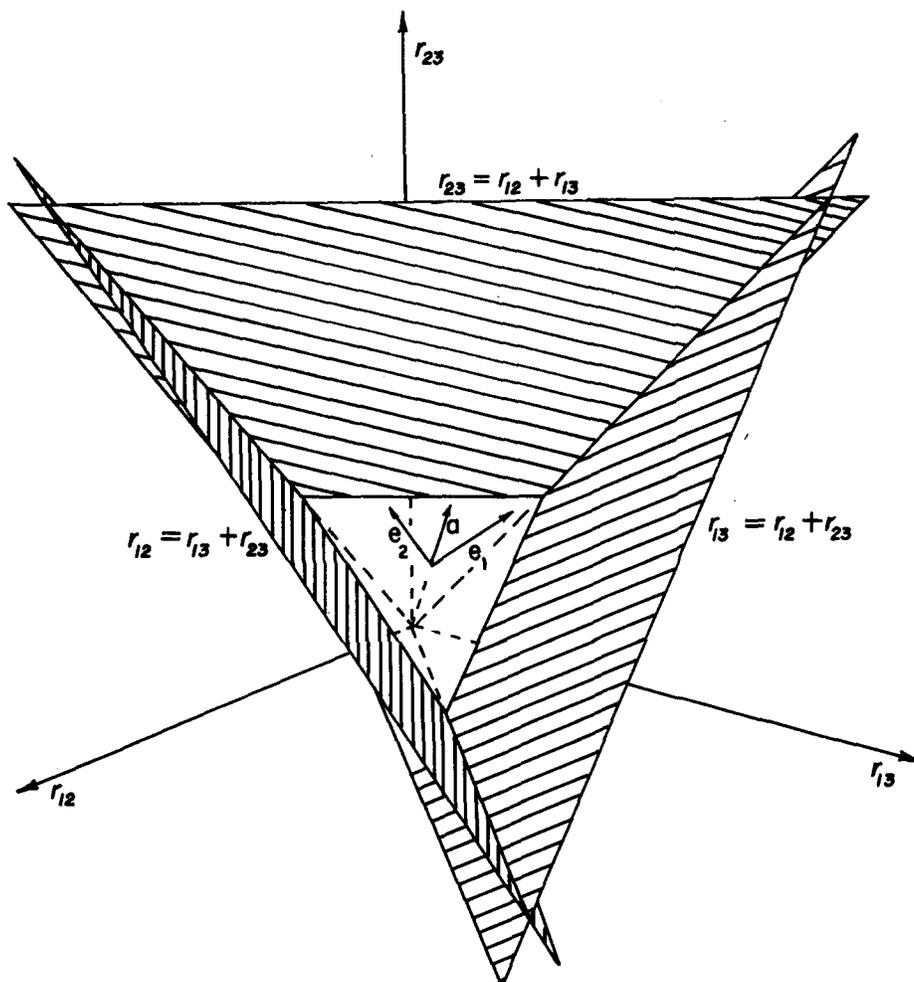


FIG. 1. The r_{12} , r_{13} , r_{23} coordinate system, constraining planes and relations to a , e_1 , and e_2 .

III. DESCRIPTION OF T_{123}

The use of cubic splines and piecewise-Hermite polynomials¹² for representing arbitrary functions has become popular in recent years.¹³ Multidimensional applications are possible and we use a combination of bi-cubic Hermite interpolation and cubic splines.

T_{123} is a function of the three coordinates r_{12} , r_{13} , r_{23} . We consider them to be a Cartesian set, but the values for the physical system are subject to restrictions,

$$\begin{aligned} r_{12} &\geq 0, \\ r_{23} &\geq 0, \\ r_{13} &\geq 0, \\ r_{12} + r_{23} &\geq r_{13}, \\ r_{23} + r_{13} &\geq r_{12}, \\ r_{13} + r_{12} &\geq r_{23}. \end{aligned} \quad (2)$$

The last three inequalities of (2) define planes in the r_{12} , r_{13} , r_{23} space which collectively confine the system point to a portion of the first octant as shown in Fig. 1. r_{12} , r_{13} , and r_{23} are not themselves a convenient set of coordinates to use, and we transform to a new set,

$$a = (r_{12} + r_{13} + r_{23})/3,$$

$$e'_1 = 2(r_{13} + r_{23} - 2r_{12})/3\sqrt{3}, \quad (3)$$

$$e'_2 = 2(r_{23} - r_{13})/3.$$

The new coordinate a is subject to the restriction $a \geq 0$, only, and the e'_1 - e'_2 coordinates satisfy the inequalities

$$\begin{aligned} e'_1 &\geq -a/\sqrt{3}, \\ e'_2 &\geq e'_1/\sqrt{3} - 2a/3, \\ e'_2 &\geq e'_1/\sqrt{3} + 2a/3, \end{aligned} \quad (4)$$

which define an equilateral triangle in the e'_1 - e'_2 plane as shown in Fig. 2.

A simple rotation would yield new coordinates in which a is "stretched" by a factor $\sqrt{3}$ compared to (3). Our choice makes a the arithmetic mean of r_{12} , r_{13} , and r_{23} , and gives a "better feel" for the size of the system. The coordinates e'_1 and e'_2 are subjected to a further stretching so that $-1 \leq e'_2/a \leq 1$, which provides some later simplifications.

A triatomic system may have the form XYZ, X_2Y , or X_3 . In the latter two cases T_{123} possesses symmetry, and the coordinates a , e'_1 , and e'_2 lie parallel or perpendicular to the symmetry planes. The resultant simplifications constitute the main justification for their use.

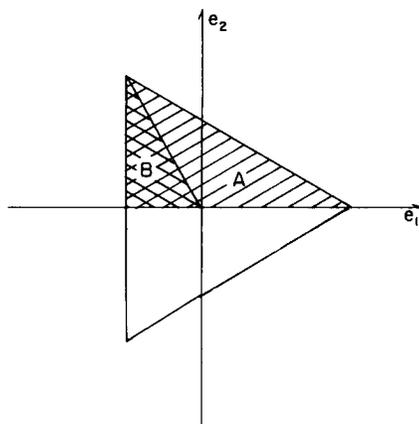


FIG. 2. The primary areas of calculation for X_2Y , $A+B$; and for X_3 , B .

A. X_2Y case

Let us take atoms 1 and 2 to be the same and atom 3 different. Under these circumstances, the potential V and also T_{123} are invariant to a permutation of the atom labels 1 and 2. This can be viewed as a reflection in the $a-e'_1$ plane, or the values of T_{123} in the upper-half triangle in Fig. 2 are reflected into the lower half. Therefore, when obtaining the original energies and representing them, we need only to know half of the triangle.

B. X_3 case

When all three atoms are the same, we need determine T_{123} in only one-sixth of the triangle. The functions V and T_{123} are invariant to all six permutations of the atom labels, or the symmetric group, S_3 . These operations on the labels generate the operations of the point group C_{3v} (which is isomorphic to S_3) in the a, e'_1, e'_2 space. The C_3 axis is along a , of course. Once we know the values of T_{123} in one of the small triangles in Fig. 2, we may rotate and reflect these values around to obtain the function everywhere.

When it is present, the symmetry provides other useful information for the fitting procedure. The gradient of T_{123} must be zero on and perpendicular to a symmetry plane. As we shall see, such symmetry conditions on the gradient help to determine the functions we use for representing T_{123} .

IV. REPRESENTATION OF T_{123} BY TRICUBIC POLYNOMIALS

The triangular pyramid region of Fig. 1 is still not completely suitable for tricubic polynomial fitting, and one more modification is necessary. We will actually use $e_1 = e'_1/a$ and $e_2 = e'_2/a$ in our expressions. The original set would require either of two unworkable alternatives, i.e., increasing the number of regions as a increases, or fitting regions bounded by surfaces none of which meet at right angles.

With this further transformation we will apply our theory to the X_3 case. Extensions to less symmetric systems are easily made.

Figure 3 shows the small triangle which we take as our primary fitting region. This may be divided into a number of rectangular and triangular regions. A tricubic polynomial is written

$$P^{(3)}(a, e_1, e_2) = \sum_{i=0}^3 \sum_{j=0}^3 \sum_{k=0}^3 C_{ijk} a^i e_1^j e_2^k, \quad (5)$$

and 64 coefficients are required to define the function in one right angled parallelepiped shaped volume. One set is needed for each of the regions we take in the a, e_1 , and e_2 directions. In addition to the full regions, we also have the ones shaped like triangular prisms. Again referring to Fig. 3, the symmetry requires the gradient of T_{123} to be zero across the lines \overline{AO} and \overline{BO} . Such requirements reduce the number of independent coefficients in (5) to 40. A reasonably simple calculation shows that this reduction arises from the 24 relations,

$$\begin{aligned} \sqrt{3}a_{i10} + a_{i01} &= 0, \\ \sqrt{3}a_{i20} - a_{i11} - \sqrt{3}a_{i02} &= 0, \\ 3\sqrt{3}a_{i30} - 5a_{i21} + \sqrt{3}a_{i12} + 9a_{i03} &= 0, \\ 2a_{i31} - \sqrt{3}a_{i22} &= 0, \\ 7\sqrt{3}a_{i32} - 9a_{i23} &= 0, \\ a_{i33} &= 0, \end{aligned} \quad (6)$$

in which i takes on the values 0, 1, 2, and 3. When these relations are used with the standard connections at the knots, or with known slopes at each knot, we have a set of tricubic polynomials to represent T_{123} in the primary triangle, and throughout the whole region.

V. APPLICATION AND DISCUSSION

It is not the purpose of this article to present an energy surface of high accuracy for the H_3 system. We have however, calculated the energies of H_3 with a $[2s]$ basis at a number of points in the primary triangle, and applied the theory of the previous sections to test these procedures. We have purposely used a very small number of geometries in our calculations. This will make the test severe. Unfortunately, earlier, more accurate calculations,² have not been done at a set of geometries appropriate to the present treatment.

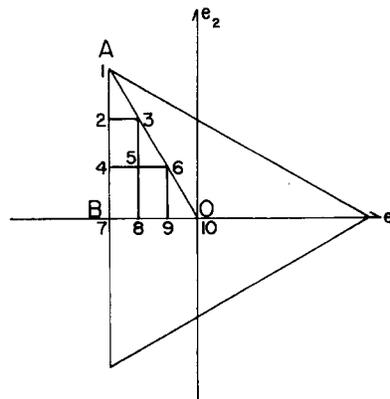


FIG. 3. The mesh of points for calculating 10 point energy surface for X_3 .

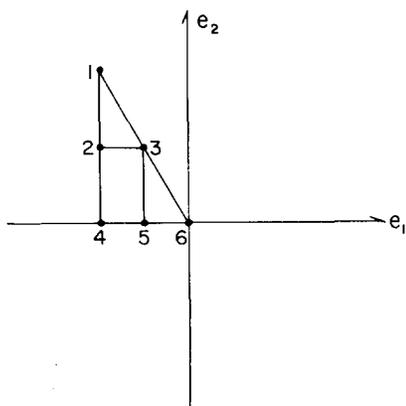


FIG. 4. Positions used in primary triangle for present H_3 calculation.

A full CI calculation based upon the six-function basis, with a $1s$ and a $1s'$ at each nuclear center, was done at 36 geometries. Figure 4 shows the positions calculated in the primary triangle, and Table I gives the actual values of r_{12} , r_{13} , and r_{23} used. An energy of H_2 with the same basis was also determined at each of the r_{ij} values present in the H_3 calculation. Our results give a dissociation energy for H_2 of 98 kcal, approximately 11 kcal too low. In spite of its deficiencies, the H_3 calculation reported here describes the important physical aspects of the real system. In several cases, additional CI calculations beyond the original 36 were done for comparisons.

Figure 5 is a three-dimensional contour drawing which shows graphically how T_{123} behaves as a function of a , e_1 , and e_2 . The important property of smoothness is apparent. We also see that T_{123} is in general a monotonically decreasing function of a . We use this fact and will actually fit $e^{\alpha a} T_{123}$ with our tricubic polynomials. Each of the three regions shown in Fig 4 will be fit with a bicubic Hermite polynomial for the averages $a = 1, 2, 3, 4, 6$. We then consider the coefficients for the above polynomials to be functions of a and we fit the coefficients with cubic splines. The full tricubic polynomial is written

$$T_{123}^{lmn}(a, e_1, e_2) = e^{-\alpha a} \sum_{i=0}^3 \sum_{j=0}^3 \sum_{k=0}^3 C_{ijk}^{lmn}(e_1 - e_{1,m})(e_2 - e_{2,n})(a - a_i) \quad (7)$$

$$\text{for } \alpha = 0.5, e_{1,m} \leq e_1 \leq e_{1,m+1},$$

$$e_{2,n} \leq e_2 \leq e_{2,n+1}, \text{ and } a_i \leq a \leq a_{i+1}.$$

The quantities, a_i , $e_{1,m}$, and $e_{2,n}$ are the boundaries of the interpolation regions for the tricubic polynomials. The ground state electronic energy of the H_2 molecule, as a function of the internuclear distance R , is represented as a piecewise-cubic spline. The authors will be happy to provide anyone with actual coefficients for calculating the H_3 surface described here. The region from 0.0 to 6.0 has been divided into 11 regions and the coefficients for a cubic spline determined in each. The spline is written

$$E_{H_2}^i(R) = \sum_{j=0}^3 C_{j,i}(R - R_i)^j \quad (8)$$

TABLE I. Geometries and energies of three-body terms for H_3 calculation.

Point ^a	a	r_{12}	r_{13}	r_{23}	T_{123}
1	1	1.500 ^b	0.000	1.500	0.479480
	2	3.000	0.000	3.000	0.113526
	3	4.500	0.000	4.500	0.013572
	4	6.000	0.000	6.000	0.001162
	6	9.000	0.000	9.000	0.000006
	2	1	1.500	0.375	1.125
2		3.000	0.750	2.250	0.185144
3		4.500	1.125	3.375	0.042945
4		6.000	1.500	4.500	0.007592
6		9.000	2.250	6.750	0.000167
3		1	1.250	0.500	1.250
	2	2.500	1.000	2.500	0.209033
	3	3.750	1.500	3.750	0.046241
	4	5.000	2.000	5.000	0.007122
	6	7.500	3.000	7.500	0.000104
	4	1	1.500	0.750	0.750
2		3.000	1.500	1.500	0.247013
3		4.500	2.250	2.250	0.098955
4		6.000	3.000	3.000	0.040169
6		9.000	4.500	4.500	0.004885
5		1	1.250	0.875	0.875
	2	2.500	1.750	1.750	0.284748
	3	3.750	2.625	2.625	0.096254
	4	5.000	3.500	3.500	0.027131
	6	7.500	5.250	5.250	0.001594
	6	1	1.000	1.000	1.000
2		2.000	2.000	2.000	0.355576
3		3.000	3.000	3.000	0.129346
4		4.000	4.000	4.000	0.033873
6		6.000	6.000	6.000	0.001351

^aThis refers to the point numbering in Fig. 4.

^bAll distances and energies are in atomic units.

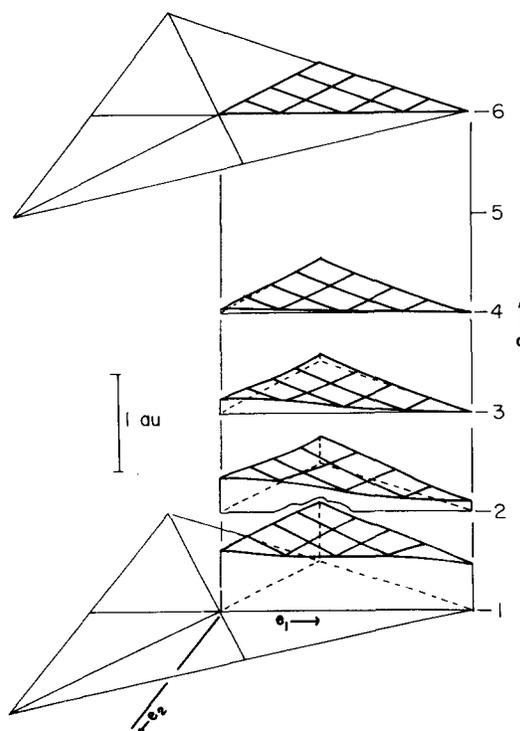


FIG. 5. Graphical representations of T_{123} for H_3 .

TABLE II. Potential-energy surface properties in saddle point region.

Surface	R_{sp}	E_{sp} ^a	A_{11}	A_{22}	A_{33}
1s, 1s'	1.791	-1.6248	0.276	0.029	-0.130
Analytical fit	1.786	-1.6270	0.351	0.030	-0.100
Shavitt <i>et al.</i> ^c	1.764	-1.6521	0.31	0.024	-0.061
Liu ^d	1.757	-1.6581	0.32	...	-0.058

^a E_{sp} is the total energy at the saddle point.

^bAll quantities are expressed in atomic units.

^cReference 2(a).

^dReference 2(b).

for $R_i \leq R \leq R_{i+1}$. The region 6.0 to ∞ is represented by a simple inverse power of R .

We may use our surface for the determination of the saddle point geometry and the force constants at the saddle point. The saddle point is defined as the minimum in the potential energy curve for linear symmetric H_3 . The separation at this point, R_{sp} , is defined by the following condition:

$$\frac{\partial}{\partial R} V_{H_3}(R_{AB}, R_{BC}) \Big|_{R_{AB}=R_{BC}=R_{sp}} = 0, \quad (9)$$

with R_{AB} and R_{BC} the interparticle distances. The force constants A_{ii} are defined in terms of the normal coordinates for the saddle point configuration of H_3 , where

$$\begin{aligned} g_1 &= 1/2(R_{AB} + R_{BC} - 2R_{sp}), \\ g_2 &= 1/2 R_{sp}(\pi - \theta), \\ g_3 &= 1/2(R_{AB} - R_{BC}), \end{aligned} \quad (10)$$

with θ being the angle $\angle ABC$. The force constants are then

$$\begin{aligned} A_{11} &= \frac{\partial^2 V}{\partial g_1^2} \Big|_{g_1=g_2=g_3=0}, \\ A_{22} &= \frac{\partial^2 V}{\partial g_2^2} \Big|_{g_1=g_2=g_3=0}, \\ A_{33} &= \frac{\partial^2 V}{\partial g_3^2} \Big|_{g_1=g_2=g_3=0}. \end{aligned} \quad (11)$$

Values for the force constant determined from V as well as values from previous calculations are given in Table II.

In a recent calculation Norbeck and Certain¹⁴ found the triangular arrangement of H_3 to be favored over the linear arrangement for values of $R \gtrsim 3.1 a_0$ (see Fig. 1, Ref. 14). Results from our polynomial surface and our *ab initio* surface are compared with those in Fig. 6.

It is evident that properties calculated with the polynomial surface do not agree completely with those calculated using the *ab initio* surface. However, the qualitative agreement is excellent. This is especially en-

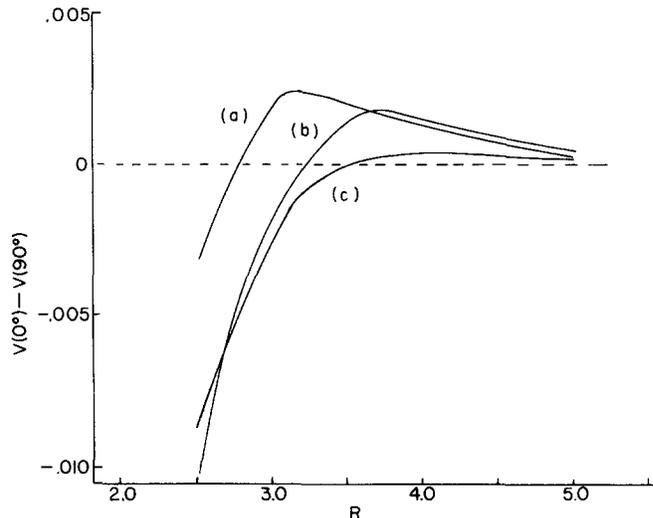


FIG. 6. Stability of the triangular arrangement of $H_2 + H$. Curve (a), 1s GTO (Table I, Ref. 14); Curve (b), Eq. (7), Table II; Curve (c), [2s] basis, this work. θ and R refer, respectively, to Fig. 1, Ref. 14.

couraging in light of the low number of energy points used in determining the polynomials. We feel that the arrangement of geometries described here gives the greatest efficiency of utilization of *ab initio* energies for polynomial fitting. Of course, our technique does not need to be applied to the entire surface, but may be restricted if only some regions are of interest.

The tricubic polynomial representation of a surface requires a large number of coefficients. This can be looked upon as the result of precalculating and storing intermediate results in the interpolation problem. When the tricubic polynomial representation of a surface is used in a computer, an efficient algorithm for finding one polynomial is needed. With equal spacing on the regions as we have used, this algorithm can be designed so that the time required is independent of the total number of regions. Then a very important property of the tricubic polynomial representation becomes evident: The time required on the computer to retrieve a value of V is independent of the accuracy of the calculation, which affects only the storage required. No global method of function fitting will have this property.

VI. EXTENSIONS TO SURFACES INVOLVING MORE THAN THREE ATOMS

A. Four-atom surfaces

The geometric representation for three-atom surfaces described in Sec. II may be extended to the case of four atoms. Here again, we have written the general potential in terms of two-, three-, and four-body functions,

$$\begin{aligned} V(r_{12}, r_{13}, r_{14}, r_{23}, r_{24}, r_{34}) &= A_1 + A_2 + A_3 + A_4 + D_{12}(r_{12}) + D_{13}(r_{13}) + D_{14}(r_{14}) + D_{23}(r_{23}) + D_{24}(r_{24}) + D_{34}(r_{34}) \\ &+ T_{123}(r_{12}, r_{23}, r_{13}) + T_{124}(r_{12}, r_{14}, r_{24}) + T_{134}(r_{13}, r_{14}, r_{34}) + T_{234}(r_{23}, r_{24}, r_{34}) \\ &+ Q_{1234}(r_{12}, r_{13}, r_{14}, r_{23}, r_{24}, r_{34}). \end{aligned} \quad (12)$$

As in (1), the poles are all contained in the two-body terms.

The two- and three-body terms in (12) may be handled the way we have shown before. The four-body term presents a new problem. In this case, it is again convenient to make a transformation of variables,

$$\begin{aligned} a &= (r_{12} + r_{13} + r_{14} + r_{23} + r_{24} + r_{34})/\sqrt{6}, \\ e_1 &= (2r_{12} + 2r_{34} - r_{13} - r_{14} - r_{23} - r_{24})/\sqrt{12}, \\ e_2 &= (r_{13} + r_{24} - r_{14} - r_{23})/2, \\ t_1 &= (r_{12} - r_{34})/\sqrt{2}, \\ t_2 &= (r_{13} - r_{24})/\sqrt{2}, \\ t_3 &= (r_{14} - r_{23})/\sqrt{2}, \end{aligned} \quad (13)$$

which form bases for the [4], [3, 1], and [2, 2] representations of the symmetric group, S_4 . There are 12 inequalities of the type $r_{ij} + r_{jh} \geq r_{ik}$, plus the four tetrahedral inequalities involving the areas of the four faces, $A_i + A_j + A_k - A_l \geq 0$, etc., which must be satisfied. These constrain e_1 and e_2 to a triangular shaped region as before, and t_1 , t_2 , and t_3 to a tetrahedrally shaped volume.

A hexacubic polynomial to represent Q_{1234} in a six-dimensional volume requires $4^6 = 4096$ coefficients. This number, although large, is probably not out of the question for the computer technology on the horizon. The results of the three-atom suggest that Q_{1234} might be smoother than even the T_{123} -type terms. Concrete *ab initio* results to test this do not now exist.

B. Many-atom surfaces

The previous results appear to allow generalization, but the representation of spline functions for five or more centers will require prodigious numbers of coefficients. We shall not consider these cases further.

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