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Comment on fitting *ab initio* intermolecular potentials for scattering calculations^{a)}

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The angular dependence of the interaction between two rigid linear rotors is considered, and one of the two expansions in current use is shown to be inappropriate. Interpolation of tabulated radial interactions is also discussed, and numerical tests are presented which demonstrate the accuracy of Lagrange and spline algorithms as a function of the spacing between points.

The study of energy transfer in (nonreactive) molecular collisions has recently seen significant advances insofar as it has become possible to obtain an accurate theoretical description of collision dynamics for a number of systems.¹ Perhaps the most extensive calculations to date have been performed at NASA Goddard Institute for Space Studies on systems relevant to current radioastronomical observations.² In these studies the intermolecular potential energy surfaces were generally obtained from *ab initio* theoretical calculations, and it was therefore necessary to fit the computed points to analytic expressions for use in the scattering calculations.

The fitting of *ab initio* potential energy surfaces is not necessarily trivial, and has, in fact, received some attention in the recent literature.^{3,4} Although a moderate amount of experience in this area was gained in the studies cited in Ref. 2, other aspects of the problem were generally emphasized and few details of the potential fitting were reported. The present article will give further details on two aspects of potential fitting. Such fits are usually done in two steps: The angular dependence is expanded in some convenient set of functions, and the resulting intermolecular radial coefficients for each angular component are then fit. We will comment first on the angular expansion for the collision of two linear rigid rotors and, in particular, the inappropriateness of one of the expansions in current use.³ Our second point concerns methods for numerical interpolation of the radial functions.

For collisions of two linear rigid rotors two different expansions have been used in the past to describe the angular dependence of the interaction. These have come to be known, somewhat misleadingly, as a space-fixed and a body-fixed expansion, respectively. In the space-fixed method the rotor molecular axes are $\hat{\mathbf{R}}_1$ and $\hat{\mathbf{R}}_2$ and the collision coordinate from the center of mass of the target to the center of mass of the projectile is \mathbf{R} , with all vectors measured relative to space-fixed axes. The intermolecular potential can then be written as⁵⁻⁷

$$V(\hat{\mathbf{R}}_1, \hat{\mathbf{R}}_2, \mathbf{R}) = \sum_{i_1 i_2 i} A_{i_1 i_2 i}(R) I_{i_1 i_2 i}(\hat{\mathbf{R}}_1, \hat{\mathbf{R}}_2, \hat{\mathbf{R}}), \quad (1)$$

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where the angular expansion functions are

$$I_{i_1 i_2 i} = \sum_{m_1 m_2 m} \langle l_1 m_1 l_2 m_2 | l m \rangle Y_{l_1 m_1}(\hat{\mathbf{R}}_1) Y_{l_2 m_2}(\hat{\mathbf{R}}_2) Y_{l m}(\hat{\mathbf{R}})^*, \quad (2)$$

with $\langle abcd | ef \rangle$ a Clebsch-Gordan vector coupling coefficient and $Y_{lm}(\hat{\mathbf{R}})$ a normalized spherical harmonic. The $I_{i_1 i_2 i}$ form a complete, orthonormal set so that the radial coefficients may be obtained as

$$A_{i_1 i_2 i}(R) = \int d\hat{\mathbf{R}}_1 d\hat{\mathbf{R}}_2 d\hat{\mathbf{R}} I_{i_1 i_2 i}(\hat{\mathbf{R}}_1, \hat{\mathbf{R}}_2, \hat{\mathbf{R}}) V(\hat{\mathbf{R}}_1, \hat{\mathbf{R}}_2, \mathbf{R}). \quad (3)$$

In practice, it is often more convenient to obtain the radial coefficients by fitting a finite number of terms in Eq. (1), e.g., by a least-squares procedure, to *ab initio* points computed for a set of orientations.

In the body-fixed method the potential is written in terms of relative coordinates fixed in the collision system: θ_1 and θ_2 are the angles made by the rotors with the collision coordinate and ϕ is the dihedral angle between the rotors. These coordinates are related to the space-fixed $\hat{\mathbf{R}}_1$, $\hat{\mathbf{R}}_2$, and $\hat{\mathbf{R}}$ via

$$\hat{\mathbf{R}}_1 \cdot \hat{\mathbf{R}} = \cos \theta_1, \quad (4a)$$

$$\hat{\mathbf{R}}_2 \cdot \hat{\mathbf{R}} = \cos \theta_2, \quad (4b)$$

$$\hat{\mathbf{R}}_1 \cdot \hat{\mathbf{R}}_2 = \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos \phi. \quad (4c)$$

The intermolecular potential is then written in the body-fixed method as

$$V(\hat{\mathbf{R}}_1, \hat{\mathbf{R}}_2, \mathbf{R}) = \sum_{i_1 i_2 i} \bar{A}_{i_1 i_2 i}(R) \bar{I}_{i_1 i_2 i}(\hat{\mathbf{R}}_1, \hat{\mathbf{R}}_2, \hat{\mathbf{R}}), \quad (5)$$

where

$$\bar{I}_{i_1 i_2 i} = P_{i_1}(\hat{\mathbf{R}}_1 \cdot \hat{\mathbf{R}}) P_{i_2}(\hat{\mathbf{R}}_2 \cdot \hat{\mathbf{R}}) P_i(\hat{\mathbf{R}}_1 \cdot \hat{\mathbf{R}}_2), \quad (6)$$

with $P_l(\cos \theta)$ being the usual Legendre polynomial. This expansion apparently originated with Davison's⁸ study of $\text{H}_2\text{-H}_2$ collisions where coupling matrix elements of the potential in this form were given. It has been used more recently in a similar study by Monchick, Brown, and Munn.⁹ Rabitz,¹⁰ who presented the first derivation of matrix elements for two rotors within the coupled states approximation,¹¹ which is a "body-fixed decoupling" approximation, also chose this as the natural expansion of the potential. Rabitz¹⁰ further noted the conversion from body-fixed radial coefficients $\bar{A}_{i_1 i_2 i}$ to space-fixed ones $A_{i_1 i_2 i}$. Coupled states matrix elements

have subsequently been given in terms of the space-fixed expansion of the potential.¹² Recently, Alexander and DePristo³ have fit an *ab initio* surface for the HF-HF system, using the body-fixed expansion and subsequently converting to the space-fixed expansion.

Despite its previous use, the *body-fixed expansion is a most unfortunate choice*, since the $\bar{I}_{1_1 1_2 l}$ do not form an orthonormal set. Therefore, it is not possible to obtain the body-fixed radial coefficients $\bar{A}_{1_1 1_2 l}$ in a manner analogous to Eq. (3). While it is possible to fit a set of *ab initio* points to a truncated body-fixed expansion, e. g., by a least-squares procedure,³ the nonorthogonality of the expansion functions implies that "convergence" of the $\bar{A}_{1_1 1_2 l}$ with an increasing number of terms cannot be expected; that is, as higher terms are added, lower terms which are not orthogonal will have to change to compensate, and this can cause apparently erratic behavior of the lower terms on increasing the size of the expansion. It is instructive to consider in this context the integral

$$K = \int d\hat{\mathbf{R}}_1 d\hat{\mathbf{R}}_2 d\hat{\mathbf{R}} \bar{I}_{111} \bar{I}_{000} . \quad (7)$$

From Eqs. (4) and (6) it is apparent that $\bar{I}_{000} = 1$ and that

$$K = \int_0^{2\pi} d\phi \int_0^\pi \sin\theta_1 d\theta_1 \int_0^\pi \sin\theta_2 d\theta_2 \cos\theta_1 \cos\theta_2 \\ \times (\cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos\phi) = 8\pi/9 . \quad (8)$$

It is therefore apparent that \bar{A}_{000} does not have the desirable property of being the spherical average of the potential, as is the case for the space-fixed A_{000} . (This last point is implicit in the work of Monchick.^{9(b)})

Thus, the only advantage of the body-fixed expansion might be its alleged closer connection to the body-fixed, or relative coordinates normally used in obtaining *ab initio* potentials. However, even this does not hold. As noted previously⁷ the space-fixed angular terms [Eq. (2)] are rotationally invariant and simply related to body-fixed coordinates as

$$I_{1_1 1_2 l} = [(2l+1)/(4\pi)]^{1/2} \sum_{m=0}^l (-1)^m \\ \times (2 - \delta_{m0}) \langle l_1 m l_2 - m | l 0 \rangle P_{l_1 m}(\theta_1) P_{l_2 m}(\theta_2) \cos(m\phi) . \quad (9)$$

The convention here for defining the associated Legendre polynomial P_{lm} is best given by noting its relationship to the usual normalized spherical harmonic¹³

$$Y_{lm}(\theta, \phi) = P_{lm}(\theta) e^{im\phi} . \quad (10)$$

Equation (9) has recently been used²⁽¹⁾ with no difficulty to directly fit space-fixed expansions to several *ab initio* surfaces which have been proposed for the H₂-H₂ system. In conclusion, it would appear that the *space-fixed angular expansion* [Eq. (1)], is to be preferred in all cases for describing the interaction of two linear molecules.

Once the angular dependence of the potential has been fit there remain sets of radial coefficients $A_\lambda(R_i)$, where λ describes the angular symmetry appropriate to the

collision system and R_i are the intermolecular separations for which the potential is available. One can try to find a simple analytic fit for the $A_\lambda(R)$, such as was done, for example, by Alexander and DePristo.³ In most of our studies,² however, we have found it more convenient to employ polynomial interpolation of the tabulated points. At short range the A_λ are often found empirically to vary essentially exponentially, and, where necessary, extrapolation at small R has been done by fitting an exponential. At long range one expects on theoretical grounds (e. g., an electrostatic multipole expansion) that the A_λ behave asymptotically as inverse powers of R , and extrapolation at large R has been done accordingly. (Details of the extrapolation procedures are given by Green and Thaddeus.^{3(b)}) It should be emphasized that extrapolation is always somewhat dangerous, especially the short-range extrapolation here, and it is most desirable to obtain *ab initio* points for sufficiently small R .

In our quantum scattering calculations² interpolation of *ab initio* potentials has been done with a fifth-order Lagrange (local polynomial) algorithm.¹⁴ In order to demonstrate the reliability of this method and its sensitivity to the separation between R_i values, the following numerical tests were performed: Gordon¹⁵ has suggested a simple analytic model potential for the HCl-He system which appears to be reasonably realistic when compared with *ab initio* calculations for the same system.^{2(e)} This potential has three Legendre terms in the angular expansion, each of which is given by a Buckingham-type (exponential-inverse power) expression. Numerical values of this potential were generated for varying numbers of R_i between 2.49 and 13.72 bohr; the potential minimum in the spherical term occurs at 6.22 bohr for reference. (Results were insensitive to small changes in the minimum and maximum R_i values used.) Scattering calculations were then performed using the generated set of numerical potential points with interpolation and extrapolation as described above, and results were compared with values obtained with the analytic potential. In particular, scattering calculations were performed within the coupled states approximation,¹¹ at a total energy of 200 cm⁻¹, with a basis of HCl rotor levels $j=0$ through $j=5$; integral state-to-state cross sections were accumulated for partial waves $L=0$ through $L=15$. This does not give converged cross sections for this system, but it provides a convenient calculation which permits a meaningful comparison of different interpolations. Results are presented in Table I.

It is seen that calculations using fifth-order Lagrange interpolation with potential points separated by half a bohr or less gave cross sections virtually indistinguishable from those obtained with the analytic interaction. It is also seen that significant errors can arise when the potential points are more widely spaced. Although obtaining an adequate grid of *ab initio* potential points was generally not a severe problem in the studies cited in Ref. 2, it must be remembered that rigorous theoretical methods can be expensive, and prohibitively so for systems with many angular degrees of freedom. Several avenues of further research suggest themselves to alleviate this problem. First, the potential can be

TABLE I. Comparison of cross sections $\sigma(j \rightarrow j')$ in \AA^2 computed using fifth-order Lagrange (upper numbers) and cubic spline (lower numbers) interpolation of the interaction potential. The tabulated potential points were generated from an analytic function for varying numbers of equally spaced distances between 2.49 and 13.72 bohr. Further details of the calculation can be found in the text.

j	j'	Analytic	No. points/ ΔR , bohr				
			51	20	21	16	11
0	0	28.698	28.700	28.703	28.738	29.141	34.131
			28.698	28.676	28.874	26.781	32.204
0	1	5.0754	5.0757	5.0767	5.0769	5.0357	0.5782
			5.0753	5.0893	4.8885	6.3712	0.0932
0	2	0.33535	0.33538	0.33544	0.33507	0.32612	0.02699
			0.33539	0.33757	0.30910	0.54931	0.08386
0	3	0.01260	0.01261	0.01264	0.01260	0.01194	0.00068
			0.01261	0.01272	0.01138	0.02203	0.00106

adequately defined with fewer points if these are not constrained to be equidistant, as was done for convenience in the present study. One assumes that fewer points will be needed at short and long range than in the region of the minimum and the classical turning points, but this needs systematic testing. Second, fewer points should be necessary if the interpolating function is chosen to be more realistic than a simple polynomial. For example, the apparent success of Morse-spline-fitted-van der Waal potentials for rare gas interactions suggests using a local Morse fit (i. e., a sum of exponentials) at short range, a local sum of inverse powers at long range, and a local polynomial in the region of the well.

While Lagrange interpolation proved to be an efficient and accurate method for quantum scattering calculations, some difficulty was encountered in applying it to classical trajectory calculations.¹⁶ Classical trajectories require the first derivative of the potential. The local polynomials used in Lagrange interpolation provide a continuous function, but there are discontinuities at the tabulated points in the first derivative. To alleviate this problem cubic spline interpolation was used.¹⁷ Although this is also a local polynomial fit, it is constrained to give a continuous first derivative as well as a continuous potential. We have modified the usual spline algorithm in one respect. The second derivatives at the end nodes are generally set to zero (natural spline); however, we use extrapolation at short and long range as discussed above, and second derivatives at the terminal nodes were set to values given by the extrapolating functions.

Table I compares cross sections obtained by the cubic spline algorithm with those obtained by Lagrange interpolation for the same sets of tabulated points. It is seen that cubic spline interpolation is acceptably accurate (better than 1% agreement) for potential points separated by half a bohr or less. In general, however, Lagrange interpolation appears to give somewhat better accuracy for a given grid size.

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- ¹J. P. Toennies, *Ann. Rev. Phys. Chem.* **27**, 225 (1976); D. Secrest, *Ann. Rev. Phys. Chem.* **24**, 379 (1973).
- ²(a) HCN-He: S. Green and P. Thaddeus, *Astrophys. J.* **191**, 653 (1974); (b) HD-He: S. Green, *Physica (Utrecht)* **76**, 609 (1974); (c) H₂CO-He: B. J. Garrison, W. A. Lester, and W. H. Miller, *J. Chem. Phys.* **65**, 2193 (1976); B. J. Garrison, W. A. Lester, W. H. Miller, and S. Green, *Astrophys. J. Lett.* **200**, L175 (1975); (d) N₂H⁺-He: S. Green, *Astrophys. J.* **201**, 366 (1975); (e) HCl-He: S. Green and L. Monchick, *J. Chem. Phys.* **63**, 4198 (1975); (f) HCl-H₂: S. Green, *Chem. Phys. Lett.* **47**, 119 (1977). (g) NH₃-He: S. Green, *J. Chem. Phys.* **64**, 3463 (1966); (n) CO-He and CO-H: S. Green and P. Thaddeus, *Astrophys. J.* **205**, 766 (1976); (i) H₂-H₂: R. Ramaswamy, H. Rabitz, and S. Green, *J. Chem. Phys.* **66**, 3021 (1977); (j) CS-H₂, OCS-H₂, and H₂O-He: S. Green (unpublished results).
- ³M. H. Alexander and A. E. DePristo, *J. Chem. Phys.* **65**, 5009 (1976).
- ⁴M. H. Alexander and E. V. Berard, *J. Chem. Phys.* **60**, 3950 (1974); D. Secrest, *J. Chem. Phys.* **61**, 3867 (1974); M. H. Alexander, *J. Chem. Phys.* **61**, 3868 (1974); G. D. Billing and A. Hunding, *Chem. Phys. Lett.* **44**, 30 (1976).
- ⁵H. Klar, *Z. Phys.* **228**, 59 (1969).
- ⁶G. Englot and H. Rabitz, *Phys. Rev. A* **10**, 2187 (1974).
- ⁷S. Green, *J. Chem. Phys.* **62**, 2271 (1975).
- ⁸W. D. Davison, *Discuss. Faraday Soc.* **33**, 71 (1962).
- ⁹(a) L. Monchick, N. J. Brown, and R. J. Munn, *Mol. Phys.* **25**, 249 (1973); (b) L. Monchick, *Chem. Phys. Lett.* **24**, 91 (1974).
- ¹⁰H. Rabitz, in *Modern Theoretical Chemistry*, edited by W. H. Miller (Plenum, New York, 1976), Vol. 1, p. 33.
- ¹¹P. McGuire and D. J. Kouri, *J. Chem. Phys.* **60**, 2488 (1974).
- ¹²T. G. Heil and D. J. Kouri, *Chem. Phys. Lett.* **40**, 375 (1976).
- ¹³M. E. Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1957).
- ¹⁴Z. Kopal, *Numerical Analysis* (Wiley, New York, 1961).
- ¹⁵R. G. Gordon, *J. Chem. Phys.* **44**, 3083 (1966).
- ¹⁶S. Chapman and S. Green, *J. Chem. Phys.* (in press).
- ¹⁷A. Ralston and H. S. Wilf, *Mathematical Methods for Digital Computers* (Wiley, New York, 1960).