

Effect of asymmetric isotopic substitution on atom-diatom potentials^{a)}

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A simple and accurate method is proposed for transforming the Legendre expansion of an atom-diatom potential about the diatom center of mass into a new Legendre expansion about a shifted (by isotope substitution) diatom center of mass. It is found that a simple quadrature procedure yields accurate results throughout the range of intermolecular separation of physical interest, while a previously proposed Taylor series expansion procedure gives comparable accuracy only for intermolecular separations greater than the equilibrium separation. Numerical tests of the method are performed for three model atom-plus-rigid diatom systems H₂(HD)-He, HCl(DCl)-Ar, and ³⁵ClF(³⁷ClF)-Kr. Extension of the quadrature procedure to the transformation of the potential for an atom plus nonrigid diatom is also discussed.

The interaction potential between an atom and a diatomic molecule is usually expressed as a Legendre expansion

$$V(r, R', \theta') = \sum_n V_n(r, R') P_n(\cos \theta'), \quad (1)$$

where the vector R' joins the position of the diatom center of mass (C') to the position of the atom, the diatom bond vector r points toward the lighter nucleus, and $\cos \theta' = \hat{R}' \cdot \hat{r}$ (see Fig. 1). Within the Born-Oppenheimer approximation, isotopic substitution does not change the intermolecular potential. However, it causes the center of mass (c. m.) of the diatom to shift a distance δ from C' to C , as shown in Fig. 1; here δ is defined to be positive if the c. m. shifts toward the lighter nucleus. Since bound state or scattering calculations for the substituted species are most conveniently carried out using the (R, θ) coordinates centered at C , the potential must be re-expressed in the new coordinates. To prevent errors in the performance of this coordinate transformation from affecting the calculation of isotope effects, it is essential that the procedure be as accurate as possible. Providing a simple and accurate means of performing this transformation is the purpose of this article.

I. COORDINATE TRANSFORMATION FOR ATOM PLUS RIGID DIATOM

For a rigid diatom the dependence of the potential on the bond length r of the diatom can be ignored. The change of coordinates caused by the shift of the diatom c. m. from C to C' is defined by¹

$$R' = R(1 + t^2 + 2t \cos \theta)^{1/2}, \quad (2)$$

$$\cos \theta' = (\cos \theta + t) / (1 + t^2 + 2t \cos \theta)^{1/2}, \quad (3)$$

where $t \equiv \delta/R$. The intermolecular potential may then be re-expressed in terms of the new coordinates (R, θ) as

$$U(R, \theta) \equiv V(R', \theta') = \sum_k U_k(R) P_k(\cos \theta). \quad (4)$$

Using the orthogonality properties of the Legendre polynomials, the functions $U_k(R)$ have been shown to be¹

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$$U_k(R) = (k + \frac{1}{2}) \int_{-1}^1 d(\cos \theta) P_k(\cos \theta) V(R', \theta') \quad (5a)$$

$$= (k + \frac{1}{2}) \sum_{n=0}^{\infty} \int_{-1}^1 P_k(x) V_n(R') P_n(x') dx, \quad (5b)$$

where $x = \cos \theta$, $x' = \cos \theta'$, and R' and θ' are given by Eqs. (2) and (3), respectively. Treating t as an expansion parameter and employing a Taylor series expansion of $V_n(R')$ about $t=0$, Kreek and Le Roy¹ obtained analytical expressions for the $U_k(R)$ functions of Eq. (5) in terms of the functions $V_n(R)$ and their derivatives. Such expressions have been used to compute the transformed potentials used in eigenvalue calculations for the van der Waals complexes HD-Ar^{1,2} and DCl-Ar.^{3,4}

Unfortunately, the explicit formulas for $U_k(R)$ presented in Ref. 1 only included terms up to $O(t^4)$ and were based on the assumption that the sum in Eq. (1) is truncated after $n=4$. Moreover, the convergence of the expansion in powers of t was not tested. Extending these results to include higher powers of t and more values of n would involve much complicated algebra. In addition, the higher derivatives of the $V_n(R)$ functions are often tedious to compute, particularly if the potential is only available in numerical form,⁵ or if it has discontinuities in its derivatives.^{6,7}

The present approach is to determine the functions $U_k(R)$ numerically from the exact $V(R', \theta')$ by applying a suitable quadrature formula to the integral in Eqs. (5). Since the parameter t is usually quite small, the variables R, R' and x, x' in Eqs. (5) are quite similar. Thus,

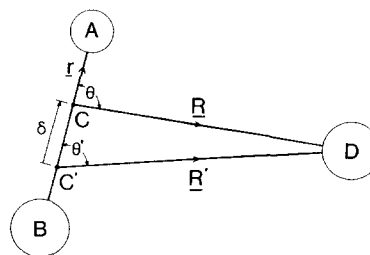


FIG. 1. The atom-diatom coordinates. A is the lighter nucleus of the diatom AB and D is the atom. C and C' indicate the positions of the center of mass of the isotopically substituted and unsubstituted diatom, respectively.

the integrand in Eq. (5b) is similar to a product of a slowly varying function of x with two polynomials in x of orders k and n . For this type of integral an N -point Gaussian quadrature, with $(k+n) \leq 2N-1$, should be highly accurate. Of course, Eq. (5a) is applicable even when $V(R', \theta')$ has not been resolved into a Legendre expansion.

II. TEST AND ANALYSIS OF THE METHOD FOR RIGID DIATOMS

To test this procedure a model potential of the form of Eq. (1) was chosen, except that the dependence of the potential upon r has been ignored. The radial potential strength functions are of the form

$$V_n(R') = \epsilon_n \{ m_n \exp[\alpha_n(1 - R'/R'_n)] - \alpha_n(R'_n/R')^{m_n} \} / (\alpha_n - m_n), \quad n = 0, 1, 2. \quad (6)$$

Values of the parameters m_n , ϵ_n , α_n , and R'_n appropriate to the systems H_2 -He,⁸ HCl -Ar,⁹ and ^{35}ClF -Ar⁹ are summarized in Table I. The $\text{H}_2(\text{HD})$ -He system has a weakly anisotropic potential with a large isotopic shift of the diatom c. m., while the ^{35}ClF (^{37}ClF)-Kr system corresponds to a strong anisotropy with a small isotopic shift, and the $\text{HCl}(\text{DCl})$ -Ar system is intermediate in both regards.

Values of the intermolecular potentials $U(R, \theta)$ for HD-He, DCl-Ar, and ^{37}ClF -Kr were generated for a range of R at a fixed value of θ , and the results are summarized in Table II. In each case, θ was chosen as the

TABLE I. Parameters of the model potentials used to test the various transformation procedures.

	H_2 -He ^a	HCl -Ar ^b	ClF -Kr ^c
α_0	13.782	14.9	29.
R'_0 (Å)	3.365	3.828	3.840
ϵ_0 (cm ⁻¹)	9.362	130.	7.0
m_0	6	6	6
α_1	...	10.2	8.9
R'_1 (Å)	...	4.128	2.416
ϵ_1 (cm ⁻¹)	...	56.5	-3.7
m_1	...	7	7
α_2	14.8344	12.9	8.9
R'_2 (Å)	3.614	4.281	4.068
ϵ_2 (cm ⁻¹)	0.9544	20.8	930.
m_2	6	6	6

^aFitted to the analytical form of Ref. 8 to reproduce ϵ_n , R'_n , and the inner repulsive wall from $0.4 R'_n < R < R'_n$; long range behavior does not reproduce that of Ref. 4.

^bReference 9.

^cReference 9; the sign of ϵ_1 has been reversed to conform with the definition of θ used in the present work.

angle which gives rise to the largest positive shift of the potential at small R , and it is equal to 0 or π depending on whether the isotopic substitution shifts the c. m. toward the heavier or the lighter nucleus of the diatom. The atom-diatom separation is expressed as R/R'_n where n was chosen so that ϵ_n is the "well depth" of largest magnitude. Column 2 of Table II gives the exact values of the potential obtained for given values of (R, θ) by substitution of Eqs. (2) and (3) directly into Eqs. (6) and (1). Column 3 shows the differences between these exact potentials and those obtained from Eqs. (4) and (5) for $k = 0-6$ employing a nine-point Gaussian quadrature formula to evaluate the integrals. Use of a higher-order (11- or 13-point) quadrature formula changes these results by less than 5 parts in 10^{10} . Thus, the nine-point quadrature results are essentially exact, in that the discrepancies shown in this table are due to neglect of $k > 6$ terms in Eq. (4).

Columns 4-8 in Table II show the errors in calculated $U(R, \theta)$ values caused by truncation of the expansion formulas of Kreek and Le Roy¹ after terms of order $O(t^j)$, for $j = 0-4$, respectively. In general, the expansion of a given $U_k(R)$ to $O(t^j)$ takes account only of contributions from functions $V_n(R)$ for which $|n-k| \leq j$. Thus, truncation of this expansion introduces errors due both to inexact representation of the functions $U_k(R)$ which are generated, and to truncation of the Legendre expansion for $U(R, \theta)$ after the term corresponding to $k_{\text{max}} = n_{\text{max}} + j$, where n_{max} indicates the order of the highest Legendre function appearing in the unshifted potential.

The quantities $\Delta U(t^0)$ appearing in column 4 in fact correspond to the error which would be introduced by simply representing $U(R, \theta)$ by the unshifted potential $V(R, \theta)$, and effectively indicate the net effect of the isotopic substitution on the potential energy function. It is interesting to note that these effects depend at least as much on the potential strength as on the magnitude of the center-of-mass displacement [c.f. $\delta/r = 0.1665$ for $\text{H}_2(\text{HD})$ and 0.0126 for ^{35}ClF (^{37}ClF)].

It is clear from Table II that for $R \leq R'_n$, the results obtained using the lower order expansions in powers of t are poor, although they improve at large R . Thus, if interest is centered *only* on the long range behavior and an analytical expression for the shifted potential is desired, even the lower-order expressions of Kreek and Le Roy¹ are sufficiently accurate. However, while the higher-order expansions are superior to the lower-order ones, the quadrature calculations yield by far the best agreement with the exact results and often involve only a relatively modest increase in the *total* computing time in many applications. Moreover, the quadrature method is quite easy to apply, can be used to generate arbitrarily high order Legendre terms without reprogramming and, for the calculation including terms through $U_{k_{\text{max}}}(R)$ ($k_{\text{max}} = 2 + j$ in the present model), requires only about three times as much computer time as is required for the $O(t^j)$ calculation. Applications of the Gaussian quadrature procedure to scattering calculations¹⁰ and to the bound states of van der Waals molecules¹¹ are in progress.

TABLE II. Exact transformed potentials (column 2) and errors in various approximations to them (column 3–8) for the model potentials.^a

	R/R_n^b	U	$\Delta U(G)$	$\Delta U(t^0)$	$\Delta U(t^1)$	$\Delta U(t^2)$	$\Delta U(t^3)$	$\Delta U(t^4)$	
HD-He	0.40	51125.2	-2.50	-20458.4	-4635.4	-684.3	-64.5	-1.76	
	0.60	3175.4	-7.40(-2)	-1343.25	-326.52	-54.46	-6.84	-0.68	
	0.80	142.55	-2.83(-3)	-73.06	-19.40	-3.40	-0.44	-4.59(-2)	
	1.00	-8.799	-1.21(-4)	-1.22	-0.84	-0.18	-2.59(-2)	-1.50(-3)	
	$\delta/r = -0.1665$	1.20	-6.766	-4.44(-6)	0.96	5.20(-2)	-3.49(-3)	-1.13(-3)	-1.50(-4)
		1.40	-2.920	1.15(-7)	0.43	3.60(-2)	2.01(-3)	5.54(-5)	-3.16(-6)
		1.60	-1.306	9.33(-8)	0.17	1.39(-2)	8.31(-4)	3.94(-5)	1.42(-6)
	1.80	-0.636	3.01(-8)	7.62(-2)	5.50(-3)	3.04(-4)	1.40(-5)	5.57(-7)	
	2.00	-0.334	9.71(-9)	3.62(-2)	2.36(-3)	1.18(-4)	5.00(-6)	1.87(-7)	
DCl-Ar	0.40	897293.	-6.8(-3)	-117651.	-8274.6	-413.0	-16.9	-0.63	
	0.60	39537.5	-3.77(-4)	-5212.08	-351.3	-15.8	-0.54	-1.49(-2)	
	0.80	1264.6	-2.25(-5)	-211.84	-15.76	-0.74	-2.53(-2)	-6.85(-4)	
	1.00	-88.38	-1.47(-6)	-0.85	-0.44	-2.88(-2)	-1.13(-3)	-3.24(-5)	
	$\delta/r = 0.0264$	1.20	-42.73	-8.87(-8)	1.98	4.50(-2)	1.89(-4)	-2.62(-5)	-1.18(-6)
		1.40	-15.62	-1.49(-9)	0.61	1.59(-2)	3.14(-4)	4.33(-6)	2.67(-8)
		1.60	-7.15	1.39(-9)	0.21	4.30(-3)	7.74(-5)	1.24(-6)	1.66(-8)
	1.80	-3.87	5.73(-10)	9.57(-2)	1.48(-3)	2.01(-5)	2.71(-7)	3.56(-9)	
	2.00	-2.27	2.00(-10)	5.06(-2)	6.63(-4)	6.97(-6)	7.03(-8)	7.47(-10)	
³⁷ ClF-Kr	0.40	3.8232(7)	1.74(-2)	-5.48(7)	-413335.	-21032.	-806.4	-24.8	
	0.60	89020.5	1.27(-4)	-11764.1	-867.4	-44.25	-1.71	-5.28(-2)	
	0.80	778.98	-2.65(-7)	-126.95	-4.30	-0.12	-3.47(-3)	-1.04(-4)	
	1.00	-935.2	-2.89(-7)	-0.30	-0.42	-8.68(-3)	-9.97(-5)	-8.06(-7)	
	$\delta/r = -0.0126$	1.20	-642.9	-2.70(-8)	9.59	2.73(-2)	-9.18(-4)	-1.72(-5)	-1.75(-7)
		1.40	-330.9	2.40(-9)	5.78	4.83(-2)	1.67(-4)	-1.20(-6)	-2.49(-8)
		1.60	-164.1	2.35(-9)	2.83	2.63(-2)	1.59(-4)	5.52(-7)	-6.71(-10)
	1.80	-83.89	1.01(-9)	1.35	1.23(-2)	7.98(-5)	3.86(-7)	1.27(-9)	
	2.00	-45.10	3.86(-10)	0.67	5.70(-3)	3.60(-5)	1.82(-7)	7.39(-10)	

^aAll energies are in units of cm^{-1} ; the numbers in parentheses indicate appropriate powers of 10.

^b $n = 0$ for HD-He and DCl-Ar; $n = 2$ for ³⁷ClF-Kr.

Thus, if the calculations for which the transformation is required need a highly accurate potential for $R \lesssim R_n'$, then the Gaussian quadrature method is the only acceptable one. Also, should the transformation represent only a small fraction of the total computation time, the Gaussian quadrature method is again the best choice because of the higher accuracy attainable at a negligible increase in computing time. However, if the time needed for the transformation of potential represents a significant cost in computer time and high overall accuracy is not required, then the t -expansion formulas may prove sufficient.

III. EXTENSION TO ATOM PLUS NONRIGID DIATOM

When the diatom is allowed to vibrate, the intermolecular potential depends on the bond length r as well as on R' and θ' . Replacing r by a stretching coordinate $\xi = \xi(r)$ which is not affected by isotopic substitution, Eqs. (1) and (4) may be generalized to

$$V(\xi, R', \theta') = \sum_i \sum_n V_{ni}(R') T_i(\xi) P_n(\cos \theta'), \quad (7)$$

$$U(\xi, R, \theta) = \sum_i \sum_k U_{ki}(R) T_i(\xi) P_k(\cos \theta). \quad (8)$$

The $T_i(\xi)$ functions appearing here are members of any convenient set of orthonormal functions of ξ such that

$$\int d\xi w(\xi) T_i(\xi) T_j(\xi) = \delta_{ij}, \quad (9)$$

where $w(\xi)$ is an appropriate weight function. A particularly useful choice of ξ is given by¹²

$$\xi = (r - r_0)/(r + r_0), \quad (10)$$

where the reference length r_0 can be chosen to have any convenient value.¹³ Values of ξ defined by Eq. (10) range from -1 to +1 as the bond length r varies from 0 to ∞ , so that the $T_i(\xi)$ functions can be chosen to be the (normalized) Legendre polynomials.

The transformation between (R, θ) and (R', θ') coordinates is again given by Eqs. (2) and (3), except that the parameter t becomes ξ dependent; for the ξ 's defined by Eq. (10), t is given by

$$t = \delta/R = (\delta/r)(r_0/R)(1 + \xi)/(1 - \xi). \quad (11)$$

In Eq. (11) the factor (δ/r) is a constant, since a displacement δ due to isotopic substitution is a fixed fraction of the diatom bond length r . Thus, R' and θ' are now functions of R , θ , and ξ . Invoking orthogonality of both the T_i 's and P_k 's, expressions for the $U_{ki}(R)$ functions of Eq. (8) are obtained as

$$U_{ki}(R) = (k + \frac{1}{2}) \int_{-1}^1 d\xi w(\xi) T_i(\xi) \times \int_{-1}^1 d(\cos \theta) P_k(\cos \theta) V(\xi, R', \theta'), \quad (12)$$

which reduces to Eq. (5) in the absence of ξ dependence in the potential. In this case, evaluation of $U_{ki}(R)$ at a

given R requires a double instead of a single quadrature, but the procedure is no more complicated in principle than that for the rigid diatom case. While this approach yields $U(\xi, R, \theta)$ in the Legendre and $T_i(\xi)$ expansion form of Eq. (7), the initial potential $V(\xi, R', \theta')$ need not be expanded as Eq. (7), but could be any function which involves dependence on the three coordinates (ξ, R', θ') .

¹H. Kreek and R. J. Le Roy, *J. Chem. Phys.* **63**, 338 (1975).

Note that the sign convention for δ in the present work is the opposite to that of Kreek and Le Roy.

²R. J. Le Roy, J. S. Carley, and J. E. Grabenstetter, *Faraday Discuss. Chem. Soc.* **62**, 169 (1977).

³A. M. Dunker and R. G. Gordon, *J. Chem. Phys.* **64**, 354 (1976).

⁴S. L. Holmgren, M. Waldman, and W. Klemperer, "Internal Dynamics of van der Waals Complexes. II. Determination of a Potential Energy Surface for ArHCl," *J. Chem. Phys.* (in press).

⁵If the derivative of the model potential form has discontinuities,^{6,7} the higher order derivatives do not exist at those points, and the formulas of Kreek and Le Roy¹ are inapplicable there. On the other hand, the Gaussian quadrature procedure is still applicable, except that the integrals of Eqs. (5) must be divided into segments. Thus, for example,

if $V(R', \theta')$ has a discontinuous derivative at R'_d , Eq. (5b) becomes

$$U_k(R) = (k + \frac{1}{2}) \sum_n \left(\int_{-1}^{x_d} dx P_k V_n P_n + \int_{x_d}^1 dx P_k V_n P_n \right),$$

where x_d is the value of $\cos\theta$ such that $R'(R, x_d) = R'_d$. Note that x_d depends on R .

⁶P. E. Siska, J. M. Parsons, T. P. Shafer, and Y. T. Lee, *J. Chem. Phys.* **55**, 5762 (1971).

⁷J. Hepburn, G. Scoles, and R. Penco, *Chem. Phys. Lett.* **36**, 451 (1975).

⁸A. van der Avoird (private communication, 1977); P. J. M. Geurts, P. E. S. Wormer, and A. van der Avoird, *Chem. Phys. Lett.* **35**, 444 (1975).

⁹W. Klemperer, *Faraday Discuss. Chem. Soc.* **62**, 197 (1977).

¹⁰W.-K. Liu and F. R. McCourt, "DWBA calculations of relaxation and kinetic cross sections. III. Application to HD-He" (in preparation).

¹¹J. E. Grabenstetter and R. J. Le Roy, "Secular equation method calculations for strongly anisotropic van der Waals complexes" (in preparation).

¹²C. L. Beckel, *J. Chem. Phys.* **65**, 4319 (1976).

¹³A particularly convenient choice of r_0 would be the value for which the expectation value of ξ is zero for the ground state of the reference isotope of the diatom.