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An expansion of the intermolecular energy in a complete set of symmetry-adapted functions; convergence of the series for methane-methane and adamantane-adamantane interactions

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A general outline is given of the construction of a complete set of symmetry-adapted functions, which can be used as a basis for an expansion of the intermolecular energy. It is shown that other terms may be present in this expansion besides those generated by a multipole expansion of the atom-atom potentials generally used to describe the intermolecular energy. Expressions are derived for the multipole expansion of Buckingham-type potentials. Some partial sums are calculated for the purpose of studying the convergence of the infinite sum. The calculations are performed for several orientations of the interacting molecules. The examples studied are methane-methane and adamantane-adamantane interactions. It becomes clear that if only the first few terms in the expansion are used the results may be qualitatively wrong.

I. INTRODUCTION

Generally, a statistical mechanical theory starts with the description of the model whose thermal properties one intends to calculate. This description includes a definition of the model Hamiltonian, part of which is given by the interaction between the particles that make up the system. With nearly all statistical mechanical techniques it is of great advantage to have an expression for these interactions which is analytically manageable. This is partly reflected by the fact that the models studied most are ones with relatively simple interparticle interactions, e. g., Ising models and Heisenberg models.

In the case of molecular models the interparticle interaction is a function of the Euler angles describing the orientations of the two interacting molecules and of their intermolecular vector. The dependence on these variables shows up very nicely when the interaction is approximated as a pure electrostatic interaction between two charge distributions and the multipole expansion is used. One disadvantage of this method, however, is that dispersion, induction, and exchange contributions to the intermolecular energy cannot be taken into account. In recent years it has become customary to introduce these contributions by a fitting procedure that uses the atom-atom potential parameters.¹ According to this method the intermolecular energy consists of contributions from all atom pairs, the two atoms of which are situated in different molecules. The one-pair terms are given by a short-range repulsive part and a long-range attractive part. These terms contain some parameters which are fitted to as many experimental results as possible.

Disadvantages of the method described above are the very poor analytical properties of the expressions and the fact that the dependence on the natural variables such as Euler angles and the intermolecular vector is not very clear.

These problems have been overcome² by the construc-

tion of a bipolar expansion of the atom-atom potentials. When this expansion is used, the symmetry of the interacting molecules comes out very clearly just as it did in the electrostatic multipole expansion.

It is the purpose of this paper to show in a simple and systematic way how one can reduce a general expansion of the intermolecular energy in a complete set of functions by making use of the symmetry of the interacting molecules (Sec. II). Group-theoretical arguments have been given in the literature³ but it is the author's impression that there is still a need for a systematic account. For this reason we first discuss general group-theoretical arguments and then go on to give explicit expressions for the interaction between two molecules with tetrahedral symmetry.

Also in this paper we intend to study the convergence behavior of the resulting series. To this end we describe the "exact" intermolecular interaction by means of atom-atom potentials, because we feel that this will be a fairly realistic description. Buckingham potentials are used in this paper because these are the ones studied most in the literature. The interaction parameters figuring in the series derived in Sec. II can now be calculated from the atom-atom potential parameters. General expressions are given in Sec. III. To derive these expressions we need a bipolar expansion of $\exp(-Cr_{ij})$, which, as far as we know, does not appear anywhere in the literature. We have given a derivation of this expansion in an Appendix. In the same Appendix we derive from this expansion a bipolar expansion for $r_{ij}^n (n \geq 2)$, a derivation that is easier than the original one of Yasuda and Yamamoto.²

Finally, in Sec. IV some results of calculations for methane and adamantane are given.

II. REDUCTION OF THE MATHEMATICAL EXPRESSIONS BY SYMMETRY

The interaction between two molecules is a function of their relative orientations and the distance between

them. To describe the orientation of a molecule we attach a coordinate frame to it and give the Euler angles $\omega = \{\alpha, \beta, \gamma\}$ of the molecule-fixed frame relative to the laboratory frame. In this paper we will use the conventions for Euler angles as given by Edmonds.⁴ To fix the relative orientation and the intermolecular distance we need in addition to ω_1 and ω_2 the vector \mathbf{R} connecting the origins of the two molecular coordinate frames. This vector has polar angles $\Omega = \{\Theta_R, \Phi_R\}$ and length R .

We now expand the interaction in a complete set of orthogonal functions of ω_1 , ω_2 , and Ω . The coefficients in this expansion will then still depend on R . As a complete set we choose the products $D_{m_1 n_1}^{(l_1)}(\omega_1) \cdot D_{m_2 n_2}^{(l_2)}(\omega_2) \cdot C_n^{(l)}(\Omega)$. Here $D_{mn}^{(l)}(\omega)$ is an element of the matrix $D^{(l)}(\omega)$ that forms a representation of the three-dimensional rotation group. Again conventions will be those of Edmonds.⁴ $C_n^{(l)}(\Omega)$ is defined as $[4\pi/(2l+1)]^{1/2} \cdot Y_{lm}(\Omega)$, where $Y_{lm}(\Omega)$ is a spherical harmonic. We have chosen the above set of products as our expansion basis partly because the functions $D_{mn}^{(l)}(\omega)$, or linear combinations of these, when the asymmetric rotator is under investigation, appear as solutions of the rotational Schrödinger equation for rigid bodies. The quantum mechanical matrix elements of the intermolecular energy operator can then easily be calculated by using the Clebsch-Gordan techniques. Moreover, the transformation properties of $D_{mn}^{(l)}(\omega)$ and $C_n^{(l)}(\Omega)$ under rotations of the coordinate frames are well known; in fact, these properties will be used several times in this section.

A. Transformation properties of the $D_{mn}^{(l)}(\omega)$

At this point it is convenient to review the transformation properties of the spherical harmonics $C_n^{(l)}(\Omega)$ and the functions $D_{mn}^{(l)}(\omega)$, particularly because many different conventions have been used in the literature. In this paper we use the passive interpretation of rotation operators. The precise meaning of this phrase is that the scalar field, described in $f(\Omega)$ with respect to some reference frame, is described by $R_\Omega(n|\tilde{\alpha})f(\Omega)$ relative to a frame that can be constructed from the original one by a rotation $\tilde{\alpha}$ around n in the positive screw sense. Here $R_\Omega(n|\tilde{\alpha})$ is an operator acting in the space of functions f that map Ω to $f(\Omega)$. For a general rotation parametrized by the Euler angles $\tilde{\omega} = \{\tilde{\alpha}, \tilde{\beta}, \tilde{\gamma}\}$ it is well known that this operator is

$$R_\Omega(\tilde{\omega}) = \exp(i\tilde{\gamma}L_z) \exp(i\tilde{\beta}L_y) \exp(i\tilde{\alpha}L_x). \quad (2.1)$$

In this expression L_x and L_y are components of the angular momentum vector operator while here and in the sequel \hbar has been put equal to unity. Application of these operators to the spherical harmonics leads to

$$L_x C_n^{(l)}(\Omega) = n C_n^{(l)}(\Omega), \quad (2.2)$$

$$L_\pm C_n^{(l)}(\Omega) = [(l \mp n)(l \pm n + 1)]^{1/2} C_{n \pm 1}^{(l)}(\Omega),$$

where we have defined $L_\pm = L_x \pm iL_y$ as usual. From Eqs. (2.1) and (2.2) the transformation properties of the spherical harmonics can be shown⁴ to be

$$R_\Omega(\tilde{\omega}) C_n^{(l)}(\Omega) = \sum_m C_m^{(l)}(\Omega) D_{mn}^{(l)}(\tilde{\omega}). \quad (2.3)$$

In exactly the same way $f(\omega)$ transforms⁵ to $R_\omega(\tilde{\omega}) \times f(\tilde{\omega})$ under the above rotation where now

$$R_\omega(\tilde{\omega}) = \exp(i\tilde{\gamma}P_z) \exp(i\tilde{\beta}P_y) \exp(i\tilde{\alpha}P_x). \quad (2.4)$$

The operators P_x and P_y are components along the axes of the laboratory frame of the total angular momentum vector operator of a rigid body. Explicit expressions in Euler angles have been given in Refs. 4 and 5. Defining $P_\pm = P_x \pm iP_y$, one can show using the methods of Shaffer⁵ that

$$P_x D_{mn}^{(l)}(\omega) = n D_{mn}^{(l)}(\omega),$$

$$P_\pm D_{mn}^{(l)}(\omega) = [(l \mp n)(l \pm n + 1)]^{1/2} D_{m \pm 1, n}^{(l)}(\omega). \quad (2.5)$$

Just as Eqs. (2.1) and (2.2) lead to Eq. (2.3), the transformation properties of the $D_{mn}^{(l)}(\omega)$ follow from Eqs. (2.4) and (2.5):

$$R_\omega(\tilde{\omega}) D_{mn}^{(l)}(\omega) = \sum_{m'} D_{m'n}^{(l)}(\omega) D_{mn'}^{(l)}(\tilde{\omega}). \quad (2.6)$$

In the following we will need the transformation properties of the $D_{mn}^{(l)}(\omega)$ under yet another rotation operation. The molecule-fixed coordinate frame could have been chosen to be one that has Euler angles $\tilde{\omega}$ relative to the original frame. Denoting this operation by $R'_\omega(\tilde{\omega})$, one can show⁵ that

$$R'_\omega(\tilde{\omega}) = \exp(-i\tilde{\gamma}P_c) \exp(-i\tilde{\beta}P_b) \exp(-i\tilde{\alpha}P_c). \quad (2.7)$$

In this expression P_c and P_b are components of the total angular momentum vector along the c and b axes, respectively, of the molecule-fixed frame. Again explicit expressions are given in Refs. 4 and 5. We now define $\bar{P}_\pm = P_a \mp iP_b$ and make use of

$$P_c D_{mn}^{(l)}(\omega) = m D_{mn}^{(l)}(\omega),$$

$$\bar{P}_\pm D_{mn}^{(l)}(\omega) = [(l \mp m)(l \pm m + 1)]^{1/2} D_{m \pm 1, n}^{(l)}(\omega). \quad (2.8)$$

Noticing that $2iP_b = -\bar{P}_+ + \bar{P}_-$ compared to $2iP_y = P_+ - P_-$, we conclude from Eqs. (2.7) and (2.8) that

$$R'_\omega(\tilde{\omega}) D_{mn}^{(l)}(\omega) = \sum_{m'} D_{m'n}^{(l)}(\omega) D_{mn'}^{(l)*}(\tilde{\omega}), \quad (2.9)$$

where as usual the star indicates a complex conjugate. Here we have made use of $D_{m'n}^{(l)*}(-\alpha, \beta, -\gamma) = D_{m'n}^{(l)*}(\alpha, \beta, \gamma)$.

Now that we have the above transformation properties at our disposal we can go on to simplify the general expansion formulas as far as possible. For the intermolecular interaction $\Phi(\omega_1, \omega_2, \Omega, R)$ between the molecules one and two we can generally write

$$\Phi(\omega_1, \omega_2, \Omega, R) = \sum \phi \left(R \begin{vmatrix} l_1 & m_1 & n_1 \\ l_2 & m_2 & n_2 \\ l_3 & n_3 \end{vmatrix} \right) \times D_{m_1 n_1}^{(l_1)}(\omega_1) D_{m_2 n_2}^{(l_2)}(\omega_2) C_{n_3}^{(l_3)}(\Omega), \quad (2.10)$$

where one has to sum over all subscripts and superscripts. This expression has to be invariant under a rotation of the laboratory frame and under rotations of the symmetry group of the molecules.

B. Rotations of the laboratory frame

One can formulate the invariance of an expression for the intermolecular energy under laboratory-frame rotations differently by saying that it has to transform like a scalar. Knowing that three angular momenta can be coupled to a zero resultant by the Wigner 3-*j* symbols,⁴ we can conclude at once that

$$\Phi(\omega_1, \omega_2, \Omega, R) = \sum \phi \left(R \begin{vmatrix} m_1 & m_2 & \\ l_1 & l_2 & l_3 \end{vmatrix} \right)$$

$$\times \sum_{n_1 n_2 n_3} \begin{pmatrix} l_1 & l_2 & l_3 \\ n_1 & n_2 & n_3 \end{pmatrix} D_{m_1 n_1}^{(l_1)}(\omega_1) D_{m_2 n_2}^{(l_2)}(\omega_2) C_{n_3}^{(l_3)}(\Omega). \quad (2.11)$$

The first summation is over l_1, l_2, l_3, m_1 , and m_2 . In the remainder of this section we will explicitly produce this formula. Because the expression has to be invariant under $R_\omega(\tilde{\omega})$ it also will be invariant under $(1/8\pi^2) \times \int d\tilde{\omega} R_\omega(\tilde{\omega})$, where $d\tilde{\omega} = d\tilde{\alpha} \sin\tilde{\beta} d\tilde{\beta} d\tilde{\gamma}$. The operator will act on all three factors in the angular dependent products, in the way given by Eqs. (2.3) and (2.6). The result will be

$$\begin{aligned} \frac{1}{8\pi^2} \int d\tilde{\omega} R_\omega(\tilde{\omega}) \Phi(\omega_1, \omega_2, \Omega, R) = & \sum \left[\sum_{m'_1 m'_2 m'_3} \phi \left(R \begin{vmatrix} l_1 & m_1 & m'_1 \\ l_2 & m_2 & m'_2 \\ l_3 & m_3 & m'_3 \end{vmatrix} \right) \frac{1}{8\pi^2} \int d\tilde{\omega} D_{n_1 m'_1}^{(l_1)}(\tilde{\omega}) \right. \\ & \left. \times D_{n_2 m'_2}^{(l_2)}(\tilde{\omega}) \cdot D_{n_3 m'_3}^{(l_3)}(\tilde{\omega}) \right] \cdot D_{m_1 n_1}^{(l_1)}(\omega_1) \cdot D_{m_2 n_2}^{(l_2)}(\omega_2) \cdot C_{n_3}^{(l_3)}(\Omega). \end{aligned} \quad (2.12)$$

The integral between the braces equals⁴ a product of two Wigner coefficients

$$\begin{aligned} \frac{1}{8\pi^2} \int d\tilde{\omega} D_{m_1 m'_1}^{(l_1)}(\tilde{\omega}) D_{m_2 m'_2}^{(l_2)}(\tilde{\omega}) D_{m_3 m'_3}^{(l_3)}(\tilde{\omega}) \\ = \begin{pmatrix} l_1 & l_2 & l_3 \\ m'_1 & m'_2 & m'_3 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}. \end{aligned} \quad (2.13)$$

When we introduce Eq. (2.13) into Eq. (2.12) we obtain the functional form of Eq. (2.11).

C. Rotations of the molecular symmetry groups

There is a second requirement that the expression for the intermolecular energy must satisfy. Operations as defined in Eq. (2.7) acting on one of the two molecules must leave the expressions unaltered when $\tilde{\omega}$ represents the Euler angles associated with a symmetry element of the molecule in question. Of course, the same is true for products of these operators. This brings us to the invariance of our expressions under the direct product group $G_1 \otimes G_2$, where G_i represents the symmetry group of molecule *i*. The requirement of invariance under the above group can be fulfilled if one uses in the expansion only those combinations of the $D_{mn}^{(l)}(\omega)$ that transform as the totally symmetric representation for this group. Because these functions can be constructed as products of totally symmetric representations for the two molecular symmetry groups, we can restrict ourselves to studying one molecular symmetry group at a time.

From Eq. (2.9) we see that the operations of the molecular symmetry groups will not affect the second subscript of the $D_{mn}^{(l)}(\omega)$, from which we conclude that totally symmetric combinations can be constructed as follows:

$$\Psi_n^{(l)}(\alpha A | \omega)_G = \sum_m \alpha A_{lm} D_{mn}^{(l)}(\omega). \quad (2.14)$$

In this expression the different combinations that can be

found in one level *l* are distinguished by α . For convenience we will suppress this index because its use will be clear. We conclude that the intermolecular energy can be written as

$$\begin{aligned} \Phi(\omega_1, \omega_2, \Omega, R) = & \sum_l \phi_l(R) \sum_m \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \\ & \times \Psi_{m_1}^{(l_1)}(A | \omega_1)_{G_1} \cdot \Psi_{m_2}^{(l_2)}(A | \omega_2)_{G_2} \cdot C_{m_3}^{(l_3)}(\Omega). \end{aligned} \quad (2.15)$$

We have used *l* to indicate the three indices $\{l_1, l_2, l_3\}$ and *m* to denote $\{m_1, m_2, m_3\}$.

D. Expressions for tetrahedral molecules

We now construct the functions (2.14) for the tetrahedral group *T*. By inserting these functions into Eq. (2.15) one can find an expression for the intermolecular interaction between two tetrahedral molecules. For brevity and to fit in with the notation of Yasuda² we define $T_n^{(l)}(\omega) = \sum_m A_{lm} D_{mn}^{(l)}(\omega) = \Psi_n^{(l)}(A | \omega)_T$, where again the suffix α is suppressed. These functions are sometimes called the tetrahedral rotation functions.

The tetrahedral group *T* consists of 12 rotations which are listed in Table I together with the Euler angles $\tilde{\omega}$ associated with them. The way in which the standard body-fixed coordinate frame is attached to the molecule is clear from this table. We have seen in Eq. (2.9) that only the first subscript of the $D_{mn}^{(l)}(\omega)$ is affected by the rotations in *T*; so we can consider the second subscript as being merely a parameter. In that case we can construct linear combinations of all $D_{mn}^{(l)}(\omega)$ with *l* and *n* fixed which will form irreducible representations of the group. Conversely, these functions can be used as an expansion basis for $D_{mn}^{(l)}(\omega)$. The totally symmetric functions $T_m^{(l)}(\omega)$ can then be projected from those Wigner functions in which they are contained. This can be done by means of the group theoretical projection operator⁶ for the totally symmetric representation

TABLE I. Rotations of the tetrahedral point group and the associated Euler angles $\tilde{\omega} = \{\tilde{\alpha}, \tilde{\beta}, \tilde{\gamma}\}$.

Class	Rotation	$\tilde{\omega}$
1	Identity operation	(0, 0, 0)
2	Rotation through π about the x axis	(π , π , 0)
	Rotation through π about the y axis	(0, π , 0)
	Rotation through π about the z axis	(π , 0, 0)
3	Rotation through $(2/3)\pi$ about the $[1, 1, 1]$ axis	(0, $(1/2)\pi$, $(1/2)\pi$)
	Rotation through $(2/3)\pi$ about the $[\bar{1}, 1, 1]$ axis	($(1/2)\pi$, $(1/2)\pi$, 0)
	Rotation through $(2/3)\pi$ about the $[\bar{1}, \bar{1}, 1]$ axis	(0, $-(1/2)\pi$, $(1/2)\pi$)
	Rotation through $(2/3)\pi$ about the $[1, \bar{1}, 1]$ axis	($(1/2)\pi$, $-(1/2)\pi$, 0)
4	Rotation through $(4/3)\pi$ about the $[1, 1, 1]$ axis	($-(1/2)\pi$, $-(1/2)\pi$, 0)
	Rotation through $(4/3)\pi$ about the $[\bar{1}, 1, 1]$ axis	(0, $-(1/2)\pi$, $-(1/2)\pi$)
	Rotation through $(4/3)\pi$ about the $[\bar{1}, \bar{1}, 1]$ axis	($-(1/2)\pi$, $(1/2)\pi$, 0)
	Rotation through $(4/3)\pi$ about the $[1, \bar{1}, 1]$ axis	(0, $(1/2)\pi$, $-(1/2)\pi$)

$$P^{(A)} = \frac{1}{|T|} \sum_{\epsilon \in T} R'_{\omega}(\tilde{\omega}_{\epsilon}), \quad (2.16)$$

where $|T| = 12$ is the order of the group. When this operator acts on $D_{mn}^{(l)}(\omega)$ the result will be $k_n^{(l)} T_n^{(l)}(\omega)$, where $k_n^{(l)}$ is the expansion coefficient of $T_n^{(l)}(\omega)$ in $D_{mn}^{(l)}(\omega)$. Thus,

$$\begin{aligned} P^{(A)} D_{mn}^{(l)}(\omega) &= \sum_{m'} \left[\frac{1}{12} \sum_{\epsilon \in T} D_{m'm}^{(l)}(\tilde{\omega}_{\epsilon}) \right]^* D_{m'n}^{(l)}(\omega) \\ &= k_m^{(l)} \sum_{m'} A_{im'} D_{m'n}^{(l)}(\omega). \end{aligned} \quad (2.17)$$

From this we see that the matrix $A^{(l)} = [\sum_{\epsilon \in T} D_{m'm}^{(l)}(\tilde{\omega}_{\epsilon})]^*$ has as elements $A_{mn}^{(l)} = 12 k_n^{(l)} A_{im}$. This means that we can easily read off the tetrahedral rotation functions from the columns of $A^{(l)}$. Calculation of these matrices

is somewhat tedious but straightforward. In Table II the tetrahedral rotation functions are given up to $l = 10$. Normalization constants have been chosen such that $(1/8\pi^2) \int d\omega T_{m_1}^{(l_1)*}(\omega) T_{m_2}^{(l_2)}(\omega) = \delta_{l_1 l_2} \delta_{m_1 m_2} (2l_1 + 1)^{-1}$ and phases such that $T_0^{(l)}(\omega)$ are real.

Finally, we obtain as an expression for the interaction between two tetrahedral molecules

$$\begin{aligned} \Phi(\omega_1, \omega_2, \Omega, R) &= \sum_I \phi_I(R) \sum_{\mathbf{m}} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \\ &\quad \times T_{m_1}^{(l_1)}(\omega_1) T_{m_2}^{(l_2)}(\omega) C_{m_3}^{(l_3)}(\Omega) \\ &= \sum_I \phi_I(R) S_I(\omega_1, \omega_2, \Omega). \end{aligned} \quad (2.18)$$

TABLE II. Tetrahedral rotation functions.^a

l	
0	$T_0^{(0)} = D_{00}^{(0)}$
3	$T_m^{(3)} = -\frac{1}{2} i (2)^{1/2} \{D_{2m}^{(3)} - D_{-2m}^{(3)}\}$
4	$T_m^{(4)} = \frac{1}{2} \left(\frac{7}{3}\right)^{1/2} \left\{ D_{0m}^{(4)} + \left(\frac{5}{14}\right)^{1/2} (D_{4m}^{(4)} + D_{-4m}^{(4)}) \right\}$
6	$1T_m^{(6)} = \frac{1}{4} (2)^{1/2} \left\{ D_{0m}^{(6)} - \left(\frac{7}{2}\right)^{1/2} (D_{4m}^{(6)} + D_{-4m}^{(6)}) \right\}$ $2T_m^{(6)} = \frac{1}{4} \left(\frac{11}{2}\right)^{1/2} \left\{ (D_{2m}^{(6)} + D_{-2m}^{(6)}) - \left(\frac{5}{11}\right)^{1/2} (D_{6m}^{(6)} + D_{-6m}^{(6)}) \right\}$
7	$T_m^{(7)} = -\frac{1}{4} i \left(\frac{13}{3}\right)^{1/2} \left\{ (D_{2m}^{(7)} - D_{-2m}^{(7)}) + \left(\frac{11}{13}\right)^{1/2} (D_{6m}^{(7)} - D_{-6m}^{(7)}) \right\}$
8	$T_m^{(8)} = \frac{1}{8} (33)^{1/2} \left\{ D_{0m}^{(8)} + \left(\frac{14}{99}\right)^{1/2} (D_{4m}^{(8)} + D_{-4m}^{(8)}) + \left(\frac{65}{198}\right)^{1/2} (D_{8m}^{(8)} + D_{-8m}^{(8)}) \right\}$
9	$1T_m^{(9)} = -\frac{1}{4} i \left(\frac{3}{2}\right)^{1/4} \left\{ (D_{2m}^{(9)} - D_{-2m}^{(9)}) - \left(\frac{13}{3}\right)^{1/2} (D_{6m}^{(9)} - D_{-6m}^{(9)}) \right\}$ $2T_m^{(9)} = -\frac{1}{4} i \left(\frac{17}{3}\right)^{1/2} \left\{ (D_{4m}^{(9)} - D_{-4m}^{(9)}) - \left(\frac{7}{17}\right)^{1/2} (D_{8m}^{(9)} - D_{-8m}^{(9)}) \right\}$
10	$1T_m^{(10)} = \frac{1}{8} \left(\frac{65}{6}\right)^{1/4} \left\{ D_{0m}^{(10)} - \left(\frac{66}{65}\right)^{1/2} (D_{4m}^{(10)} + D_{-4m}^{(10)}) - \left(\frac{187}{130}\right)^{1/2} (D_{8m}^{(10)} + D_{-8m}^{(10)}) \right\}$ $2T_m^{(10)} = \frac{1}{16} \left(\frac{247}{3}\right)^{1/2} \left\{ (D_{2m}^{(10)} + D_{-2m}^{(10)}) + \left(\frac{1}{26}\right)^{1/2} (D_{6m}^{(10)} + D_{-6m}^{(10)}) - \left(\frac{255}{494}\right)^{1/2} (D_{10m}^{(10)} + D_{-10m}^{(10)}) \right\}$

^a $\alpha T_m^{(l)} \equiv \alpha T_m^{(l)}(\omega)$ and $D_{mn}^{(l)} \equiv D_{mn}^{(l)}(\omega)$.

The angular dependent sum $S_1(\omega_1, \omega_2, \Omega)$ is defined by the second equals sign in Eq. (2.18).

E. Remarks about $\phi_1(R)$

In this section we will consider some properties of the $\phi_1(R)$ for two interacting tetrahedral molecules. The corresponding results for molecules with different symmetry are easily derived in the same way.

(1) When the two interacting molecules are identical it is possible to derive a symmetry relation between the $\phi_1(R)$ from $\Phi(\omega_1, \omega_2, \mathbf{R}) = \Phi(\omega_2, \omega_1, -\mathbf{R})$. Define $\tilde{\Omega} = \{\pi - \theta_R, \phi_R + \pi\}$, from which it follows that $C_m^{(1)}(\tilde{\Omega}) = (-1)^m C_m^{(1)}(\Omega)$. Then one easily shows that $S_1(\omega_2, \omega_1, \tilde{\Omega}) = (-1)^{l_1+l_2} S_1(\omega_1, \omega_2, \Omega)$, where $\mathbf{l}_P = \{l_2, l_1, l_3\}$.

Using this one finds

$$\begin{aligned} \Phi(\omega_2, \omega_1, -\mathbf{R}) &= \sum_{\mathbf{l}} \phi_1(R) S_1(\omega_2, \omega_1, \tilde{\Omega}) \\ &= \sum_{\mathbf{l}} \phi_1(R) (-1)^{l_1+l_2} S_1(\omega_1, \omega_2, \Omega) \\ &= \sum_{\mathbf{l}_P} \phi_{\mathbf{l}_P}(R) (-1)^{l_1+l_2} S_1(\omega_1, \omega_2, \Omega). \end{aligned} \quad (2.19)$$

Equating this to $\Phi(\omega_1, \omega_2, \mathbf{R})$, one finds

$$\phi_{\mathbf{l}_P}(R) = (-1)^{l_1+l_2} \phi_1(R) \quad (\mathbf{l}_P = \{l_2, l_1, l_3\}). \quad (2.20)$$

(2) As a consequence of the choice of phases for the tetrahedral rotation functions we have $T_m^{(1)*}(\omega) = (-1)^m T_{-m}^{(1)}(\omega)$, from which $S_1^*(\omega_1, \omega_2, \Omega) = (-1)^{l_1+l_2+l_3} \times S_1(\omega_1, \omega_2, \Omega)$. So the angular-dependent sum is real when $l_1 + l_2 + l_3$ is even and imaginary when $l_1 + l_2 + l_3$ is odd. The same is true for $\phi_1(R)$, because the total expression (2.18) has to be real. It is noteworthy that by slightly altering the definitions $S_1(\omega_1, \omega_2, \Omega)$ and $\phi_1(R)$ can be made real. This will be achieved when $C_m^{(1)}(\Omega)$ is replaced by $C_m^{(1)}(\Omega) = (i)^l C_m^{(1)}(\Omega)$ and when we use real A_{lm} in the tetrahedral rotation functions, because then $C_m^{(1)*}(\Omega) = (-1)^{l+m} C_m^{(1)}(\Omega)$ and $T_m^{(1)*}(\omega) = (-1)^{l+m} T_m^{(1)}(\omega)$.

(3) To make Eq. (2.18) explicit one has to calculate the coefficients $\phi_1(R)$. When the interaction is known numerically this can be done by integrating

$$\begin{aligned} \phi_1(R) &= [1] \cdot \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}^{-1} \int \frac{d\omega_1}{8\pi^2} \int \frac{d\omega_2}{8\pi^2} \int \frac{d\Omega}{4\pi} \\ &\quad \times T_{m_1}^{(l_1)*}(\omega_1) T_{m_2}^{(l_2)*}(\omega_2) C_{m_3}^{(l_3)*}(\Omega) \Phi(\omega_1, \omega_2, \Omega, R), \end{aligned} \quad (2.21)$$

where m_1, m_2 , and m_3 may be chosen to make the integration as simple as possible, while $[1] \equiv (2l_1 + 1)$

$\times (2l_2 + 1)(2l_3 + 1)$ and $d\Omega = \sin\theta_R d\theta_R d\phi_R$. When the interaction is described by means of atom-atom potential parameters the $\phi_1(R)$ can be calculated directly from these parameters.

III. CALCULATION OF THE $\phi_1(R)$ FROM ATOM-ATOM POTENTIAL PARAMETERS

It has already been shown by Yasuda² how the $\phi_1(R)$ in Eq. (2.18) can be calculated from the atom-atom potential parameters¹ in the particular case of two interacting methane molecules. In this section we will briefly describe the general method and give some relevant formulas. One important difference between our approach and Yasuda's is that we calculate the $\phi_1(R)$ directly from the Buckingham potentials whereas Yasuda had to transform them first into Lennard-Jones potentials. To this end we have to find a two-center expansion for $\exp(-r_{\alpha\beta})$ figuring in the Buckingham potentials. A derivation of this expansion has been given in the Appendix.

Before starting to calculate $\phi_1(R)$ we give a brief survey of some two-center expansions.

A. Two-center expansions:

Suppose we are given two coordinate frames with their axes directed along the corresponding axes of the laboratory frame. The vector from the origin of frame one to that of frame two will be denoted by \mathbf{R} , with polar coordinates R and $\Omega = \{\theta_R, \phi_R\}$. We now attach a vector \mathbf{r}_α with polar coordinates r_α and $\Omega_\alpha = \{\theta_\alpha, \phi_\alpha\}$ to the origin of frame one and similarly a vector \mathbf{r}_β with coordinates r_β and $\Omega_\beta = \{\theta_\beta, \phi_\beta\}$ to the origin of frame two. The distance between the end points of these vectors will be denoted by $r_{\alpha\beta}$, which is the length of the vector $\mathbf{R} - \mathbf{r}_\alpha + \mathbf{r}_\beta$. When $R > r_\alpha + r_\beta$ we can derive (see the Appendix)

$$\begin{aligned} f(n|r_{\alpha\beta}) &= f(n|R) \sum_{\mathbf{l}} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} (-1)^{l_2} [1] g_1(n|r_\alpha, r_\beta, R) \\ &\quad \times \sum_{\mathbf{m}} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} C_{m_1}^{(l_1)}(\Omega_\alpha) C_{m_2}^{(l_2)}(\Omega_\beta) C_{m_3}^{(l_3)}(\Omega) \end{aligned} \quad (3.1)$$

Here again $[1] = (2l_1 + 1)(2l_2 + 1)(2l_3 + 1)$. The functions are defined by $f(n|r_{\alpha\beta}) = r_{\alpha\beta}^{-n}$ when n is finite and by $f(\infty|r_{\alpha\beta}) = \exp(-r_{\alpha\beta})$ when n is infinite. It should be noticed that Ω represents the polar angles of \mathbf{R} as defined above. Were Ω to represent the angles of $-\mathbf{R}$, then $(-1)^{l_1}$ should be substituted for $(-1)^{l_2}$ in Eq. (3.1). The expressions for $g_1(n|r_\alpha, r_\beta, R)$ in this equation are

$$\begin{aligned} g_1(1|r_\alpha, r_\beta, R) &= \delta_{l_1+l_2, l_3} \frac{(2l_3)!}{(2l_1+1)!(2l_2+1)!} \frac{l_1!l_2!}{l_3!} \left(\frac{r_\alpha}{R}\right)^{l_1} \left(\frac{r_\beta}{R}\right)^{l_2}, \\ g_1(n|r_\alpha, r_\beta, R) &= \frac{1}{(n-2)!} \left(\frac{r_\alpha}{R}\right)^{l_1} \left(\frac{r_\beta}{R}\right)^{l_2} \sum_{m_1=0}^{\infty} \sum_{m_2=0}^{\infty} \left(\frac{r_\alpha}{R}\right)^{2m_1} \left(\frac{r_\beta}{R}\right)^{2m_2} \\ &\quad \times \frac{(n-2+l_1+l_2-l_3+2m_1+2m_2)!}{(2l_1+2m_1+1)!(2m_1)!(2l_2+2m_2+1)!(2m_2)!} \frac{(n-2+l_1+l_2+l_3+2m_1+2m_2)!}{(n-2+l_1+l_2-l_3+2m_1+2m_2)!}, \end{aligned}$$

$$g_1^{(\infty)}(r_\alpha, r_\beta, R) = (-1) \exp(R) [(1 + l_1 + l_2 + l_3) \mathfrak{J}_{l_1}(r_\alpha) \mathfrak{J}_{l_2}(r_\beta) \mathfrak{K}_{l_3}(R) + r_\alpha \mathfrak{J}_{l_1+1}(r_\alpha) \mathfrak{J}_{l_2}(r_\beta) \mathfrak{K}_{l_3}(R) + r_\beta \mathfrak{J}_{l_1}(r_\alpha) \mathfrak{J}_{l_2+1}(r_\beta) \mathfrak{K}_{l_3}(R) - R \mathfrak{J}_{l_1}(r_\alpha) \mathfrak{J}_{l_2}(r_\beta) \mathfrak{K}_{l_3+1}(R)] . \quad (3.2)$$

The second of these equations is valid for $n \geq 2$. The double factorials are defined as $(2m)!! = m! 2^m$ and $(2m+1)!! = (2m+1)/(2m)!!$. The functions $\mathfrak{J}_l(z)$ and $\mathfrak{K}_l(r)$ are related to the modified spherical Bessel functions⁷ of the first and third kind, respectively, by $\mathfrak{J}_l(z) = (\frac{1}{2}\pi/z)^{1/2} I_{l+1/2}(z)$ and $\frac{1}{2}\pi \mathfrak{K}_l(z) = (\frac{1}{2}\pi/z)^{1/2} K_{l+1/2}(z)$. Explicit expressions are

$$\mathfrak{J}_l(z) = z^l \left(\frac{1}{z} \frac{d}{dz} \right)^l \frac{\sinh z}{z} = -\frac{1}{2} [(-1)^l \mathfrak{K}_l(z) + \mathfrak{K}_l(-z)] , \quad (3.3)$$

$$\mathfrak{K}_l(z) = (-z)^l \left(\frac{1}{z} \frac{d}{dz} \right)^l \frac{e^{-z}}{z} = e^{-z} \sum_{m=0}^l \frac{(l+m)!}{(l-m)!} \frac{z^{-m-1}}{(2m)!!} .$$

When either r_α or r_β equals zero, expressions (3.1) and (3.2) reduce to somewhat simpler formulas, which can easily be derived. When $r_\alpha = r_\beta = 0$, Eq. (3.1) reduces to $f(n|r_{\alpha\beta}) = f(n|R)$, as can be seen if $g_1(n|0, 0, R) = \delta_{1,0}$ is inserted.

B. Calculation of $\phi_1(R)$

In the atom-atom potential method it is supposed that the interaction $\Phi(1, 2)$ between molecule 1 and molecule 2 can be written as

$$\Phi(1, 2) = \sum_{\alpha \in 1} \sum_{\beta \in 2} V^{X_\alpha X_\beta}(r_{\alpha\beta}) . \quad (3.4)$$

The summation index α runs over all atoms of molecule 1, and β over all atoms of molecule 2. The superscripts $X_\alpha X_\beta$ of the one-pair terms $V^{X_\alpha X_\beta}(r_{\alpha\beta})$ are meant to indicate the chemical nature of the two interacting atoms; $r_{\alpha\beta}$ is the distance between the atoms α and β . For the one-pair terms we will use Buckingham potentials augmented with a point-charge model

$$V^{X_\alpha X_\beta}(r_{\alpha\beta}) = B^{X_\alpha X_\beta} \exp(-C^{X_\alpha X_\beta} r_{\alpha\beta}) - A^{X_\alpha X_\beta} r_{\alpha\beta}^{-6} + q_\alpha q_\beta r_{\alpha\beta}^{-1} , \quad (3.5)$$

in which q_α and q_β are the charges on atom α and atom β , respectively.

We now introduce two-center expansions into these equations to get

$$\Phi(1, 2) = \sum_1 \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} (-1)^{l_2} [1] \cdot \sum_{\alpha \in 1} \sum_{\beta \in 2} \left[B^{X_\alpha X_\beta} \exp(-C^{X_\alpha X_\beta} R) g_1^{(\infty)}(C^{X_\alpha X_\beta} r_\alpha, C^{X_\alpha X_\beta} r_\beta, C^{X_\alpha X_\beta} R) \right. \\ \left. \times \frac{-A^{X_\alpha X_\beta}}{R^6} g_1(6|r_\alpha, r_\beta, R) + \frac{q_\alpha q_\beta}{R} g_1(1|r_\alpha, r_\beta, R) \right] \cdot \sum_{\mathbf{m}} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} C_{m_1}^{(l_1)}(\Omega_\alpha) C_{m_2}^{(l_2)}(\Omega_\beta) C_{m_3}^{(l_3)}(\Omega) . \quad (3.6)$$

The next step is to partition the set of atoms of molecule 1 into classes. These classes together constitute the set A_1 . The classes are chosen such that all atoms in a given class $a \in A_1$ have the same $r_\alpha = r_a$, $X_\alpha = X_a$, and $q_\alpha = q_a$. In the same way we construct the classes $b \in B_2$ of atoms of molecule 2. Equation (3.6) can then be written as

$$\Phi(1, 2) = \sum_1 \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} (-1)^{l_2} [1] \cdot \sum_{a \in A_1} \sum_{b \in B_2} \left[B^{X_a X_b} \exp(-C^{X_a X_b} R) g_1^{(\infty)}(C^{X_a X_b} r_a, C^{X_a X_b} r_b, C^{X_a X_b} R) \right. \\ \left. \times \frac{-A^{X_a X_b}}{R^6} g_1(6|r_a, r_b, R) + \frac{q_a q_b}{R} g_1(1|r_a, r_b, R) \right] \cdot \sum_{\mathbf{m}} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \left[\sum_{\alpha \in a} C_{m_1}^{(l_1)}(\Omega_\alpha) \right] \left[\sum_{\beta \in b} C_{m_2}^{(l_2)}(\Omega_\beta) \right] C_{m_3}^{(l_3)}(\Omega) . \quad (3.7)$$

Finally, we transform to the molecule-fixed coordinate frames that we introduce in the preceding section. Denoting for the moment the angular coordinates of atom α in the frame attached to molecule 1 by Ω_α^0 , we can write $\sum_{\alpha \in a} C_{m_1}^{(l_1)}(\Omega_\alpha) = \sum_n [\sum_{\alpha \in a} C_n^{(l_1)}(\Omega_\alpha^0)] D_{nm}^{(l_1)}(\omega_1)$, where we have made use of Eq. (2.3). Because the left-hand side of this equation is invariant under all operations of the molecular symmetry group G_1 , the right-hand side must be invariant too. From this we conclude that $\sum_{\alpha \in a} C_n^{(l_1)}(\Omega_\alpha) = k_a^{(l_1)} \Psi_n^{(l_1)}(A|\omega_1)_{G_1}$. When there is more than one totally symmetric combination in the level l the right-hand side of the equation will be a summation over all these totally symmetric combinations. The summation with running index β can be treated analogously.

Introducing all this into Eq. (3.7), we find Eq. (2.15) in which

$$\phi_1(R) = \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} (-1)^{l_2} [1] \sum_{a \in A_1} \sum_{b \in B_2} k_a^{(l_1)} k_b^{(l_2)} \cdot \left[B^{X_a X_b} \exp(-C^{X_a X_b} R) g_1^{(\infty)}(C^{X_a X_b} r_a, C^{X_a X_b} r_b, C^{X_a X_b} R) \right. \\ \left. \times \frac{-A^{X_a X_b}}{R^6} g_1(6|r_a, r_b, R) + \frac{q_a q_b}{R} g_1(1|r_a, r_b, R) \right] . \quad (3.8)$$

We conclude this section with one final comment. From Eq. (3.8) we see that only those $\phi_1(R)$ are nonzero for which $l_1 + l_2 + l_3$ is even. As a consequence the atom-atom potential method will only generate terms with real $\phi_1(R)$. This gives us a criterion for testing the utility of the atom-atom potential method.

TABLE III. Atom-atom potential parameters.^a

XX	HH	CH	CC
A^{XX}	136	574	2414
B^{XX}	11 677	65 485	367 250
C^{XX}	3.74	3.67	3.60
q_H^b		0.153	

^aThe dimensions are kJ mol^{-1} for A^{XX} and B^{XX} , \AA for C^{XX} , and electrons for q_H . To obtain the electrostatic part in kJ mol^{-1} one has to multiply this term by 1389.3 when q is in electrons and r in \AA .

^bThe charges of the C atoms can be found by multiplying -0.153 by the number of H atoms having a bond to the C atom in question.

IV. CONVERGENCE OF THE SERIES

In this section we study the convergence of the series for the interaction between two tetrahedral molecules as constructed in Sec. II. To this end we calculate

$$\sum (l_{\max}) = \sum_{l_1=0}^{l_{\max}} \sum_{l_2=0}^{l_{\max}} \sum_{l_3=|l_1-l_2|}^{l_1+l_2} \phi_1(R) S_1(\omega_1, \omega_2, \Omega) \quad (4.1)$$

for several values of l_{\max} . The "exact" intermolecular interaction will be described by means of atom-atom potentials, in which case the $\phi_1(R)$ can be calculated as in the preceding section.

To keep the calculations as simple as possible we always choose the intermolecular vector along the Z axes, i. e., $\mathbf{R} = R \cdot \mathbf{k}$. The convergence will not be affected by this choice because the angular dependent sum is invariant under rotations of the laboratory frame.

We study two examples which we expect to be extreme in their convergence behavior. Firstly, we calculate the interaction between two methane molecules. The convergence is expected to be relatively fast. "Relatively" here has to be understood with reference to, for example, the convergence of the series for the interaction between two adamantane molecules; this in fact will be our second example. Although adamantane has

tetrahedral symmetry, it is almost spherically shaped, and to describe a sphere by means of tetrahedral functions is likely to be difficult.

As atom-atom potential parameters we choose set II of Starr and Williams.⁸ For convenience we have reproduced these parameters in Table III. These potentials were derived from microscopic properties (phonon frequencies) and can be expected to give a fairly realistic description of the intermolecular energy. They may be better for adamantane than for methane because the former was in the set of systems from which the potentials were derived. For calculations with these potentials the C-H bond distance has to be "foreshortened"⁸ to 1.04 \AA . The dimensions of the parameters are such that the intermolecular energy is given in kJ mol^{-1} . When we multiply the energy by $1000/R$, where R is the gas constant, we get the energy in units of 1 K . In this paper we use $R = 8.31441 \text{ J mol}^{-1} \text{ K}^{-1}$.

Finally, before we can calculate the intermolecular energy by means of Eqs. (4.1) and (3.8) we have to calculate the class constants $k_a^{(l)}$. These constants are dependent on the way in which we attach the molecule-fixed frame to the molecule. This of course has to be done in accordance with the choice we made in Sec. II. For the choices we made see Fig. 1.

A. Methane-methane interaction

The atoms constituting a methane molecule can be divided into two classes. The first class consists of the C atom. For this class we have $r_a = 0$ and $k_a^{(l)} = \delta_{l,0}$, consistent with the fact that $g_1(n|r_a, r_b, R)$ equals zero when either r_a or r_b is zero and the corresponding l index is not. The second class consists of the H atoms. For this class $r_a = 1.04 \text{ \AA}$, a foreshortened distance as was mentioned above. The class constants $k_a^{(l)}$ are equal to those in the first column of Table IV.

In Fig. 2 we have plotted $\sum (l_{\max})$ for several values of l_{\max} and for several orientations of the interacting molecules. In this figure γ_1 ranges from 0.75π to 1.75π while all the other Euler angles are kept fixed. The in-

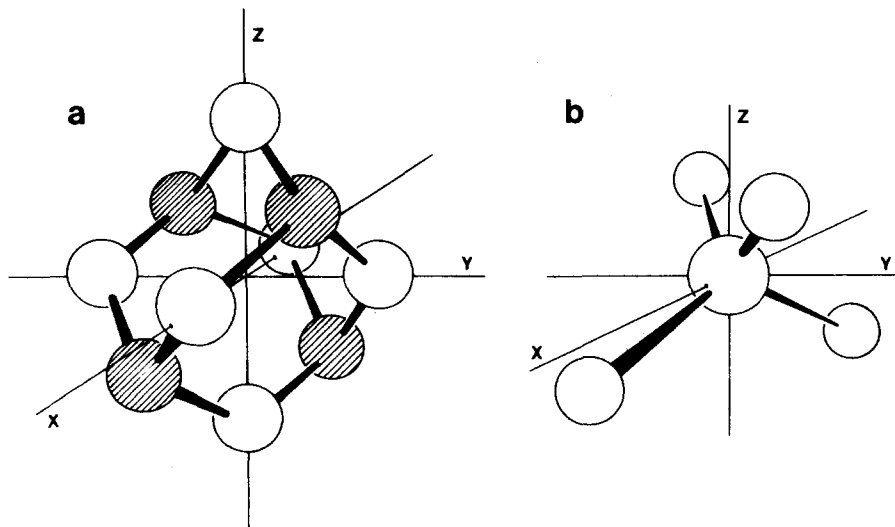


FIG. 1. Molecule-fixed coordinate frames for adamantane (a) and methane (b). In (a) the H atoms have been omitted and the tetrahedral C atoms are distinguished from the octahedral ones by shading.

TABLE IV. Class constants.

l	α	Class number			
		1	2	3	4
0		4	6	4	12
3		-2.981423	...	-2.981423	2.473772
4		-2.036700	4.582575	-2.036700	4.424409
6	1	2.514158	2.121318	2.514158	1.022411
	2
7		2.447810	...	2.447810	5.672731
8		0.851046	4.308422	0.851046	-2.704015
9	1	-2.071719	...	-2.071719	3.758669
	2
10	1	-2.600616	2.468551	-2.600616	0.108015
	2

termolecular vector \mathbf{R} , pointing from molecule 1 to molecule 2, has been directed along the laboratory frame z axis. Its length has been taken as 4.172 Å because this is the distance between two nearest neighbors in a methane crystal at low temperatures.⁹

The exact curve has not been drawn because it would fall within 0.2% of the curve with $l_{\max}=7$. The deviations from the exact values can even be lowered to 0.05% by truncating the series at $l_{\max}=10$. It is interesting to note that the results are qualitatively wrong when l_{\max} is less than 6. So we conclude that a good description of the interaction between two methane molecules with the above orientations can be found by truncating the series at l_{\max} equal to 6 or 7. The same convergence behavior has been found for several other orientations (and $R=4.72$ Å again).

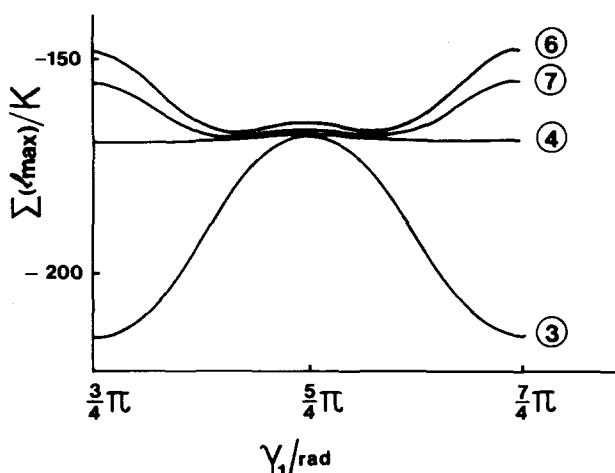


FIG. 2. Multipole expansion of the interaction between two methane molecules as a function of the angle of rotation of molecule one around its molecular z axis. The initial orientations are given by the Euler angles $\omega_1=\{(3/2)\pi, (1/4)\pi, (1/4)\pi\}$ and $\omega_2=\{(1/2)\pi, (1/4)\pi, (3/4)\pi\}$ while the vector from molecule one to molecule two points along the positive laboratory z axis and has length $R=4.172$ Å. The encircled numbers give the truncation limit l_{\max} .

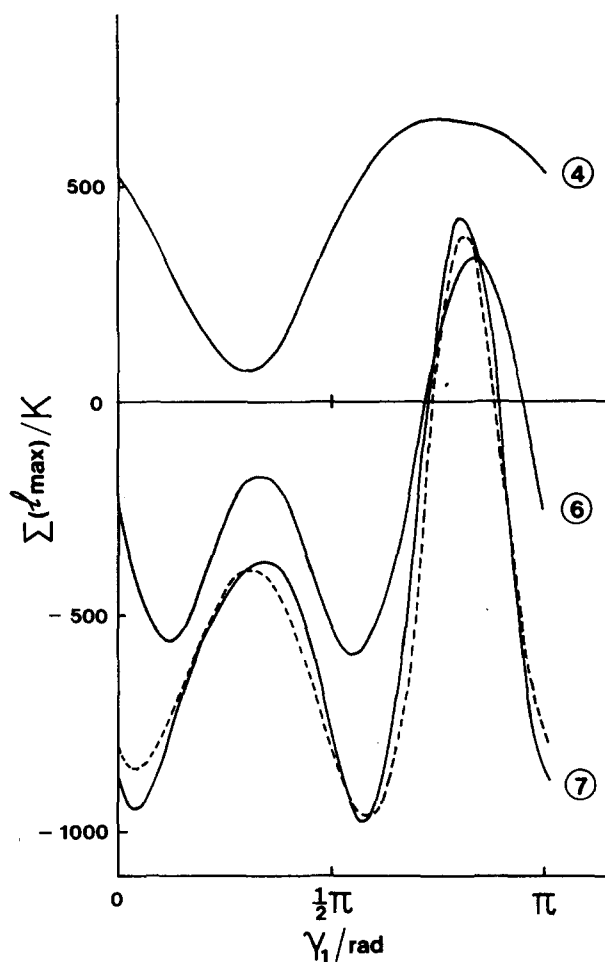


FIG. 3. Multipole expansion of the interaction between two adamantane molecules. The orientations of the two molecules are given by the Euler angles $\omega_1=\{(11/6)\pi, (1/6)\pi, \gamma_1\}$ and $\omega_2=\{(1/4)\pi, (1/6)\pi, 0\}$. The vector from molecule 1 to molecule 2 points along the positive laboratory z axis and has length $R=6.45$ Å. The encircled numbers give the truncation limit l_{\max} . The dashed line gives the exact values.

B. Adamantane-adamantane interaction

The adamantane molecule we use in our calculations has tetrahedral symmetry¹⁰; the C-C bond distances are 1.54 Å and C-H bond distances are 1.04 Å, the last distance again being a foreshortened distance. The set of atoms can be partitioned into four classes. The first class will be defined as consisting of the tetrahedral C atoms and the second class of the octahedral C atoms. The tetrahedral and octahedral H atoms will constitute classes three and four, respectively. The corresponding class constants $k_a^{(n)}$ are given in Table IV.

Calculations were performed for several orientations of the two molecules, which again were found by successive rotations of molecule one about its molecular z axis. The initial orientations were $\omega_1=\{(11/6)\pi, (1/6)\pi, 0\}$, $\omega_2=\{(1/4)\pi, (1/6)\pi, 0\}$, and $R=6.45$ Å. The results are shown in Figs. 3 and 4. This time we have incorporated the exact curve in Fig. 3. Again we see that for $l_{\max}=4$ the results are qualitatively wrong and that for $l_{\max}=7$ the approximation is fairly good. When we truncate the series at values higher than 7 there is lit-

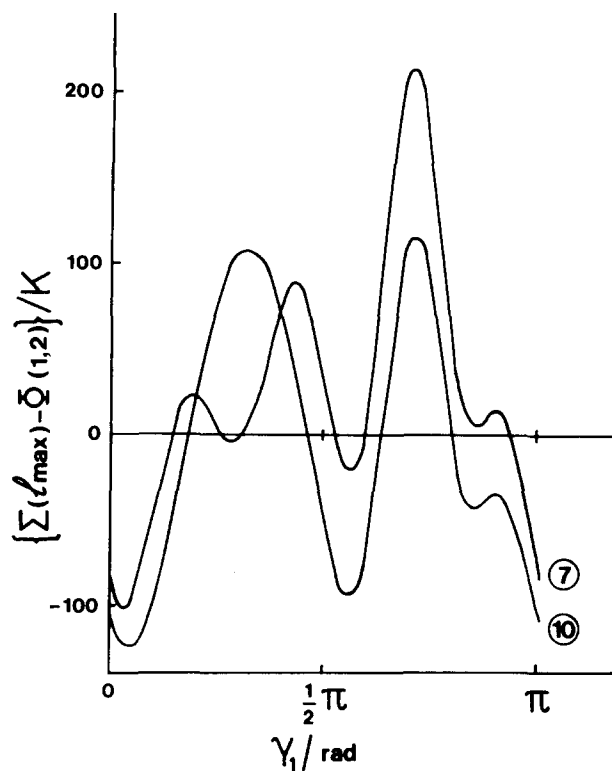


FIG. 4. Deviations from the exact values of the multipole expansions with upper summation limits l_{\max} encircled. The positions and orientations of the molecules are as in Fig. 3.

tle or no amelioration. The way in which the approximation with $l_{\max}=10$ differs from that with $l_{\max}=7$ can best be seen by comparing their deviations from the exact curve. This, in fact, we have plotted in Fig. 4. One sees that the main improvement consists of a better distribution of the deviations over the entire interval. Also, the extremities in the deviation vanish.

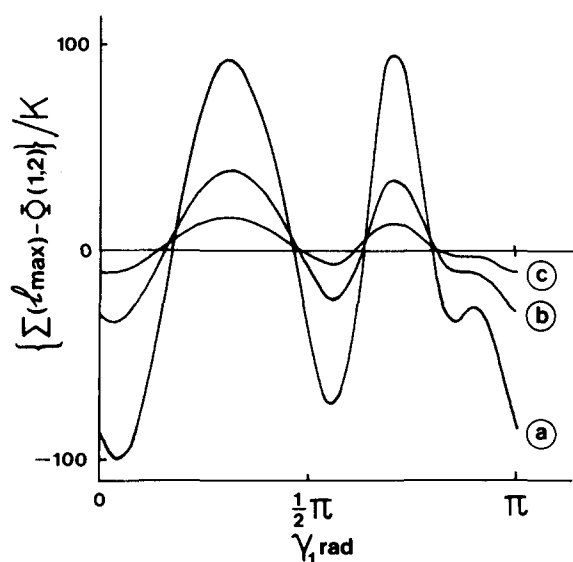


FIG. 5. Deviations from the exact values of multipole expansions with truncation limit $l_{\max}=10$ for several intermolecular distances. (a) $R=6.50$ Å, (b) $R=6.75$ Å, and (c) $R=7.00$ Å. Other position and orientation defining parameters are the same as in Fig. 3.

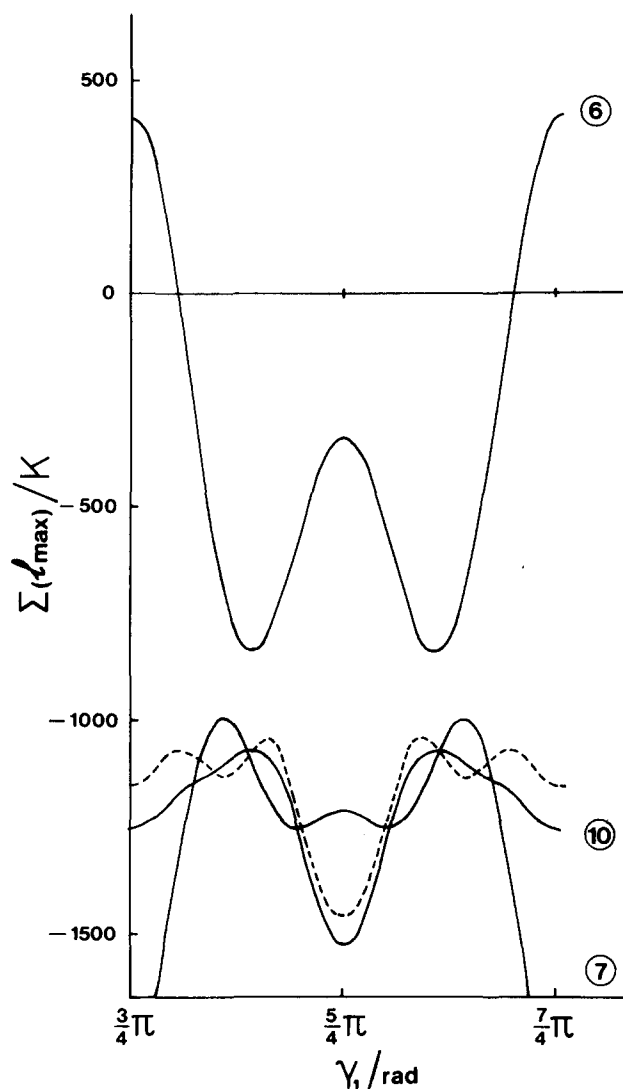


FIG. 6. Multipole expansion of the interaction between two adamantane molecules. The encircled numbers give l_{\max} . The vector from molecule 1 to molecule 2 points along the positive laboratory z axis and has length $R=6.45$ Å. The orientations are given by the Euler angles $\omega_1=\{\pi, \arccos(1/\sqrt{3}), \gamma_1\}$ and $\omega_2=\{\pi, \arccos(1/\sqrt{3}), (3/4)\pi\}$. The dashed line gives the exact values.

In Fig. 5 we have plotted $[\Sigma(10) - \Phi]$ for several values of R . It is seen that the approximation becomes rapidly better when the intermolecular distance increases. This makes us conclude that the series is better suited for calculations in the liquid phase than for calculations in the solid phase where in fact one finds distances of the order of 6.45 Å.

Finally, in Fig. 6 we present the results for yet another sequence of rotations of molecule one about its z axis. The initial orientations are $\omega_1=\omega_2=\{\pi, \arccos(1/\sqrt{3}), \frac{3}{4}\pi\}$ and $R=6.45$ Å. This time the convergence behavior is very striking. When l_{\max} equals four, one finds a curve with an absolute minimum at $\gamma_1 = \frac{5}{4}\pi$ and two maxima at $\gamma_1 = \pi$ and $\gamma_1 = \frac{3}{2}\pi$. The deviations from the exact curve are some 10%. For clarity this curve is not included in the figure. When one tries to improve the approximation by going to higher values

of l_{\max} the results get worse for l_{\max} equal to 6 or 7. Only when the upper summation limit is as high as 10 does one find a curve that is substantially better than the one for $l_{\max}=4$.

V. SUMMARY AND CONCLUSIONS

In this paper we have given a fairly comprehensive construction of a general expression for the interaction energy between two molecules. The resulting expression [Eq. (2.15)] is in the form of an infinite sum and shows the symmetry of the interacting molecules in a very direct way. Explicit formulas for the interaction between two tetrahedral molecules have been given in Sec. IID.

One way of describing the intermolecular interaction is by means of atom-atom potentials. In Sec. III we have shown how an expression of this kind can be translated into the one we constructed in Sec. II. From the resulting formula [Eq. (3.8)] it is seen that in this case terms with indices satisfying $l_1 + l_2 + l_3 = \text{odd}$ are missing. It is also clear from the derivation in Sec. IIIB that, when there are more $\alpha T_m^{(l)}$ for a certain l , only one (or one linear combination) of these will be generated by a two-center expansion of the atom-atom potentials. This aspect may possibly have some value as a criterion for the applicability of atom-atom potentials to the description of intermolecular interactions.

Finally, in Sec. IV we have studied the convergence of the series derived in Sec. II. To this end we calculated the intermolecular energy of two methane molecules by means of the expression of Sec. II (and Sec. III) for several upper summation limits and for several orientations of the interacting molecules. The results are compared with the corresponding exact values. As a set of exact values we have chosen one that could be described exactly by means of atom-atom potentials. The same procedure was adapted for two interacting adamantane molecules.

With regard to convergence three aspects should be mentioned. First, the convergence becomes worse with decreasing intermolecular distances. Secondly, it is a general feature of the interactions studied in the present paper that truncation of the series after the first

few terms gives results that are even qualitatively wrong. In view of this it is astonishing that, in the study of the phase transitions of methane, good results have been found¹⁴ by means of a model that includes only the octopole-octopole interaction. One should notice, however, that many terms will cancel when the molecules surround each other in a very symmetrical way as in the methane crystals. It is easy to take this effect into account for terms that depend on the orientation of only one molecule.¹⁴

Finally, it is not always certain that one obtains better results by increasing the upper summation limits by one unit (Fig. 6). A temporary worsening however will finally be compensated for by higher terms.

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APPENDIX A. TWO-CENTER EXPANSION FOR $\exp(-r_{\alpha\beta})$

In order to arrive at a two-center expansion for a general function f we write¹¹

$$f(r_{\alpha\beta}) = \frac{1}{(2\pi)^{3/2}} \int d\mathbf{k} \phi(k) \exp[i\mathbf{k} \cdot (\mathbf{R} - \mathbf{r}_\alpha + \mathbf{r}_\beta)], \quad (\text{A1})$$

where $\phi(k)$ is the three-dimensional Fourier transform of $f(r)$, and where $d\mathbf{k} = k^2 dk d\Omega_k$, with $\Omega_k = \{\theta_k, \phi_k\}$ the angular polar coordinates of \mathbf{k} . In the above equation we have made use of $\mathbf{r}_{\alpha\beta} = \mathbf{R} - \mathbf{r}_\alpha + \mathbf{r}_\beta$, as follows from the definitions in Sec. III. For the three exponential factors in the integrand we introduce the Rayleigh expansion

$$\exp(i\mathbf{k} \cdot \mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^l (i)^l (2l+1) j_l(kr) C_m^{(l)}(\Omega_r) C_m^{(l)*}(\Omega_k). \quad (\text{A2})$$

In this equation $j_l(z)$ is the spherical Bessel function of the first kind

$$j_l(z) = (-z)^l \left(\frac{1}{z} \frac{d}{dz} \right)^l \frac{\sin z}{z} = \sum_{m=0}^{\infty} \frac{(-1)^m z^{l+2m}}{(2m)! (2l+2m+1)!}. \quad (\text{A3})$$

The double factorials have been defined in Sec. III. Formula (A1) now reads

$$f(r_{\alpha\beta}) = \sum_l (i)^{l_1+l_2+l_3} (-1)^{l_1} [1] \frac{4\pi}{(2\pi)^{3/2}} \int_0^{\infty} dk k^2 \phi(k) j_{l_1}(kr_\alpha) j_{l_2}(kr_\beta) j_{l_3}(kR) \\ \times \sum_m \left[\frac{1}{4\pi} \int d\Omega_k C_{m_1}^{(l_1)}(\Omega_k) C_{m_2}^{(l_2)}(\Omega_k) C_{m_3}^{(l_3)}(\Omega_k) \right]^* C_{m_1}^{(l_1)}(\Omega_\alpha) C_{m_2}^{(l_2)}(\Omega_\beta) C_{m_3}^{(l_3)}(\Omega). \quad (\text{A4})$$

The integral between brackets is a special case of the one given in Eq. (2.13), because $C_m^{(l)}(\theta, \phi) = D_{0m}^{(l)}(\theta, \phi, -)$, and equals a product of two Wigner coefficients, one of which has all magnetic quantum numbers equal to zero. As a result only terms where $l_1 + l_2 + l_3$ is even appear in the summation and so $(-1)^{l_2+l_3}$ can be substituted for $(-1)^{l_1}$. Introduction of these two results into the above equation leads to

$$f(r_{\alpha\beta}) = \sum_l \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} (-1)^{l_2} [1] (i)^{l_1+l_2+l_3} \frac{4\pi}{(2\pi)^{3/2}} \int_0^{\infty} dk k^2 \phi(k) j_{l_1}(kr_\alpha) j_{l_2}(kr_\beta) j_{l_3}(kR) \\ \times \sum_m \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} C_{m_1}^{(l_1)}(\Omega_\alpha) C_{m_2}^{(l_2)}(\Omega_\beta) C_{m_3}^{(l_3)}(\Omega). \quad (\text{A5})$$

Now we direct our attention solely to the case of a two-center expansion for $\exp(-r_{\alpha\beta})$. The methods we use are very similar to those of Ref. 12. First we need the transform $\phi(k)$:

$$\begin{aligned}\phi(k) &= \frac{1}{(2\pi)^{3/2}} \int d\mathbf{r} \exp(-r) \exp(-i\mathbf{k} \cdot \mathbf{r}) \\ &= \frac{8\pi}{(2\pi)^{3/2}} \frac{1}{(k^2 + 1)^2}.\end{aligned}\quad (\text{A6})$$

After introduction of this into Eq. (A5), we obtain Eq. (3.3) in which

$$\begin{aligned}g_1(\infty | r_\alpha, r_\beta, R) &= (i)^{l_1+l_2+l_3} e^R \frac{4}{\pi} \int_0^\infty dk \frac{k^2}{(k^2 + 1)^2} \\ &\quad \times j_{l_1}(kr_\alpha) j_{l_2}(kr_\beta) j_{l_3}(kR).\end{aligned}\quad (\text{A7})$$

From the definition of the spherical Bessel function in Eq. (A3) we see that $j_l(-z) = (-1)^l j_l(z)$. As a result the integrand in Eq. (A7) is even for all terms in which $l_1 + l_2 + l_3$ is even. Because these are the only terms we need, we can substitute $\frac{1}{2} \int_{-\infty}^\infty dk$ for $\int_0^\infty dk$. Now we make use of the first equals sign in Eq. (A3) for the Bessel function whose variable has the largest value, which in our case is $j_{l_3}(kR)$. Then

$$\begin{aligned}g_1(\infty | r_\alpha, r_\beta, R) &= (i)^{l_1+l_2+l_3} e^R \frac{2}{\pi} \int_{-\infty}^\infty dk (-R)^{l_3} \left(\frac{1}{R} \frac{d}{dR} \right)^{l_3} \\ &\quad \times \frac{\sin(kR)}{R} \frac{k^{-l_3+1}}{(k^2 + 1)^2} j_{l_1}(kr_\alpha) j_{l_2}(kr_\beta).\end{aligned}\quad (\text{A8})$$

Because of the appearance of the Wigner coefficients as factors in Eq. (A5) we only need terms for which $l_1 + l_2 \geq l_3$. As a result $\sin(kR) k^{-l_3+1} (k^2 + 1)^{-2} j_{l_1}(kr_\alpha) j_{l_2}(kr_\beta) \sim k^{l_1+l_2-l_3+2}$ is not singular, which makes it possible to interchange $\int_{-\infty}^\infty dk$ and $(-R)^{l_3} (R^{-1} d/dR)^{l_3} R^{-1}$. The next step is to substitute $(i)^{-1} \exp(ikr)$ for $\sin(kR)$. This is allowed because $\int_{-\infty}^\infty dk \cos(kR) k^{-l_3+1} (k^2 + 1)^{-2} j_{l_1}(kr_\alpha) \times j_{l_2}(kr_\beta) = 0$ when $l_1 + l_2 + l_3$ is even. These operations result in

$$\begin{aligned}g_1(\infty | r_\alpha, r_\beta, R) &= (i)^{l_1+l_2+l_3} e^R (-R)^{l_3} \left(\frac{1}{R} \frac{d}{dR} \right)^{l_3} \frac{1}{R} \frac{2}{\pi i} \\ &\quad \times \int_{-\infty}^\infty dk \exp(ikr) \frac{k^{-l_3+1}}{(k^2 + 1)^2} j_{l_1}(kr_\alpha) j_{l_2}(kr_\beta).\end{aligned}\quad (\text{A9})$$

When $R > r_\alpha + r_\beta$, which we suppose is true, we can close the integration contour in the upper half of the complex plane. Now the integrand has two poles at $k = i$ and $k = -i$, both of second order. By taking $2\pi i$ times the residue at $k = i$ we find

$$\begin{aligned}g_1(\infty | r_\alpha, r_\beta, R) &= (i)^{l_1+l_2+l_3} e^R (-R)^{l_3} \left(\frac{1}{R} \frac{d}{dR} \right)^{l_3} \frac{4}{R} \\ &\quad \times \left[\frac{d}{dk} \frac{k^{-l_3+1}}{(k+i)^2} \exp(ikr) j_{l_1}(kr_\alpha) j_{l_2}(kr_\beta) \right]_{k=i}.\end{aligned}\quad (\text{A10})$$

Although tedious it is not difficult to evaluate the differentiation in Eq. (A10). From the definition (A3) we derive $dj_l(z)/dz = lj_l(z)/z - j_{l+1}(z)$. Using this, the definition of $\mathcal{K}_l(z)$ in Eq. (3.3), and the fact that $\mathcal{J}_l(z) = (i)^{-l} j_l(iz)$, we derive

$$\begin{aligned}g_1(\infty | r_\alpha, r_\beta, R) &= (-1) e^R [(l_1 + l_2 - l_3) \mathcal{J}_{l_1}(r_\alpha) \mathcal{J}_{l_2}(r_\beta) \mathcal{K}_{l_3}(R) \\ &\quad + r_\alpha \mathcal{J}_{l_1+1}(r_\alpha) \mathcal{J}_{l_2}(r_\beta) \mathcal{K}_{l_3}(R) + r_\beta \mathcal{J}_{l_1}(r_\alpha) \mathcal{J}_{l_2+1}(r_\beta) \\ &\quad \times \mathcal{K}_{l_3}(R) - R \mathcal{J}_{l_1}(r_\alpha) \mathcal{J}_{l_2}(r_\beta) \mathcal{K}_{l_3+1}(R)].\end{aligned}\quad (\text{A11})$$

This is simply another version of that given in Eq. (3.2), as follows directly from the recurrence relation $\mathcal{K}_{l_3+1}(z) - \mathcal{K}_{l_3-1}(z) = (2l_3 + 1) \mathcal{K}_{l_3}(z)/z$.

APPENDIX B: TWO-CENTER EXPANSION FOR $r_{\alpha\beta}^{-n}$

Now that we have a two-center expansion for $\exp(-r_{\alpha\beta})$, it is relatively easy to derive a two-center expansion for $r_{\alpha\beta}^{-n}$. To this end we insert the two-center expansion for $\exp(-xr_{\alpha\beta})$ into the following formula:

$$r_{\alpha\beta}^{-n} = \frac{1}{(n-1)!} \int_0^\infty dx x^{n-1} \exp(-xr_{\alpha\beta}).\quad (\text{B1})$$

We then find the required expansion in which

$$\begin{aligned}g_1(n | r_\alpha, r_\beta, R) &= \frac{R^n}{(n-1)!} \int_0^\infty dx x^{n-1} \exp(-xR) \\ &\quad \times g_1(\infty | xr_\alpha, xr_\beta, xR).\end{aligned}\quad (\text{B2})$$

It is easiest to use for $g_1(\infty | xr_\alpha, xr_\beta, xR)$ a somewhat modified version of the equation corresponding to Eq. (A10). The modification consists of substituting $(4i)^{-1} [d/dk f(k)]_{k=i}$ for $[d/dk kf(k)/(k+i)^2]_{k=i}$ and in making use of $[d/dk f(kx)]_{k=i} = (x/i) d/dx f(ix)$. When we also use the definition of $\mathcal{K}_l(z)$ in Eq. (3.3) and the fact that $\mathcal{J}_l(z) = (i)^{-l} j_l(iz)$ we find

$$\begin{aligned}g_1(\infty | xr_\alpha, xr_\beta, xR) &= (-1) \exp(xR) \frac{d}{dx} x \mathcal{J}_{l_1}(xr_\alpha) \mathcal{J}_{l_2}(xr_\beta) \mathcal{K}_{l_3}(xR).\end{aligned}\quad (\text{B3})$$

After introduction of Eq. (B3) into Eq. (B2) we see that the integral is nonsingular for all l_1, l_2, l_3 with $l_1 + l_2 \geq l_3$, only when $n \geq 2$. We now partially integrate the expression to find

$$\begin{aligned}g_1(n | r_\alpha, r_\beta, R) &= \frac{R^n}{(n-2)!} \int_0^\infty dx x^{n-1} \mathcal{J}_{l_1}(xr_\alpha) \\ &\quad \times \mathcal{J}_{l_2}(xr_\beta) \mathcal{K}_{l_3}(xR).\end{aligned}\quad (\text{B4})$$

Finally we introduce into this equation the power series for $\mathcal{J}_l(z)$ and $\mathcal{K}_l(z)$ [Eq. (3.3)]. We can easily derive the series for $\mathcal{J}_l(z)$ from the one for $j_l(z)$ by using $\mathcal{J}_l(z) = (i)^{-l} j_l(iz)$ and thereby we find $\mathcal{J}_l(z) = \sum_{m=0}^\infty z^{l+2m} \times [(2l+2m+1)!!(2m)!!]^{-1}$. After carrying out the integration we obtain an expression that will be equal to the one given in Eq. (3.2) if we can show that

$$\sum_{m_3=0}^{l_3} \frac{(l_3+m_3)! (k-m_3)!}{(l_3-m_3)! (2m_3)!} = \frac{(k+l_3)!}{(k-l_3)!} \cdot (k-l_3)!,\quad (\text{B5})$$

where $k = n - 2 + l_1 + l_2 + 2m_1 + 2m_2$.

The two-center expansion that we have derived in this Appendix was first derived by Yasuda and Yamamoto.² In their very complicated derivation they made use of the algebra of irreducible tensors. A similar expansion for finite $n \leq -2$ was given by Kay, Todd, and Silverstone.¹⁵

We will prove¹³ Eq. (B5) by recognizing it as a special case of the polynomial identity

$$R_l(z) = F_l(z) - \sum_{m=0}^l \binom{l+m}{m} \frac{1}{2^{l+m}} F_{l-m}(2z) = 0,\quad (\text{B6})$$

where

$$F_l(z) = \frac{1}{l!} (z+1)(z+2) \cdots (z+l), \quad l \geq 1,$$

$$F_0(z) = 1.$$

Introduction of $F_l[(k-l)/2] = (2^l l!)^{-1} (k+l)! / (k-l)!!$ and $F_{l-m}(k-l) = (k-m)! / [(k-l)!(l-m)!]$ into Eq. (B6) leads to Eq. (B5). The proof will be given by induction over l . Use will be made of $R_{k+1}(z) = R_k(z) + R_{k+1}(z-1)$ and of $R_l(-\frac{1}{2}) = 0$ for all l . The last identity can easily be shown to be true by using $F_{l-m}(-1) = \delta_{l,m}$ and $F_l(-\frac{1}{2}) = (1/l!)(2l-1)!!/2^l$. The first identity can be shown to be true by some clever manipulation of the sums and by repeated use of $F_{k+1}(z) - F_{k+1}(z-1) = F_k(z)$, which follows directly from the definition in Eq. (B6).

Then (1) $R_0(z) = 0$ and (2) the induction hypothesis $R_l(z) = 0$ leads to $R_{l+1}(z) = 0$. This can be seen as follows: From $R_l(z) = 0$, $R_{l+1}(-\frac{1}{2}) = 0$, and $R_{l+1}(z) = R_l(z) + R_{l+1}(z-1)$, one finds $R_{l+1}(\frac{1}{2}) = 0$ and by repetition $R_{l+1}(n - \frac{1}{2}) = 0$ for all n . The polynomial $R_{l+1}(z)$, which is of finite degree, then has an infinite number of zeros and therefore has to be equal to zero. Induction over l now completes the proof.

The expansion of $r_{\alpha\beta}^{-1}$ is well known in the literature (see Yasuda and Yamamoto³ and references given there) and we shall not rederive it here.

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