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Expansion of inverse-power intermolecular atom–atom potentials

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Abstract. A potential of the form $r^{-2\nu}$ is expanded for $\nu > 0$ and $R > \rho$, where $\boldsymbol{R} = \boldsymbol{r}+\boldsymbol{\rho}$ and $\boldsymbol{\rho} = \boldsymbol{r}_1 - \boldsymbol{r}_2$. The expansion is in spherical harmonics of the spherical polar angle coordinates of $\boldsymbol{r}_1$, $\boldsymbol{r}_2$ and $\boldsymbol{R}$, and powers of r_1/R and r_2/R. Coefficients for the Legendre expansion of Gegenbauer polynomials are given in a simple closed form. The potential expansion is also expressed in a rotationally invariant form.

1. Introduction

The Lennard-Jones potential is an inverse-power potential that describes part of the intermolecular atom–atom interactions. Inverse-power potentials can be written in the form $r^{-2\nu}$ with $\nu > 0$ where r is the atom–atom distance. Thus the Lennard-Jones (6–12) potential, for example, is given by $\nu = 3$ and $\nu = 6$, and the Coulomb potential is given by $\nu = \frac{1}{2}$.

For the treatment of non-spherical molecules it is desirable to be able to expand these potentials in spherical harmonics of the spherical polar angle coordinates of the vectors $\boldsymbol{r}_1, \boldsymbol{r}_2$ and $\boldsymbol{R}$ defined in figure 1. This allows one to distinguish the spherical and various non-spherical components of the potential in an explicit manner. Furthermore, such an expansion can be expressed in terms of rotationally invariant quantities.

An expansion of $r^{-2\nu}$ has been given by Prigogine (1957) but it contains a number of serious errors that are considered at the end of this paper. Recently Dixon and Lacroix (1973) derived a one-centre expansion ($r_2 = 0$) for $r^{-2\nu}$ with 2ν = integer. This ν restriction is physically reasonable but unnecessary, and the derivation presented by Dixon and Lacroix is somewhat laborious, requiring separate treatment of the 2ν = odd and 2ν = even cases.

The two-centre expansion ($r_2 \neq 0$), of which the one-centre expansion is a special case, can be derived for arbitrary $\nu > 0$ using the Legendre expansion of Gegenbauer polynomials and angular momentum methods. In § 2 of this paper symmetry principles that dictate the general form of the expansion are briefly considered. The derivation of the $r^{-2\nu}$ expansion is presented in § 3 and special cases are considered in § 4. An invariant form of the expansion is presented in § 5 and the Prigogine expansion is discussed in § 6.

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2. Symmetry principles

Spherical harmonics form a complete orthogonal set for expanding a function of $\boldsymbol{r}$ in the spherical polar angle coordinates of $\boldsymbol{r}_1, \boldsymbol{r}_2$ and $\boldsymbol{R}$. A scalar function $f(r)$ must be invariant under rotations of the coordinate system and also under the parity transformation $\boldsymbol{r} \to -\boldsymbol{r}$, ie $(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{R}) \to (-\boldsymbol{r}_1, -\boldsymbol{r}_2, -\boldsymbol{R})$. Therefore $f(r)$ can be expanded in the following way (Brink and Satchler 1962):

$$f(r) = \sum_{l_1=0}^{\infty} \sum_{l_2=0}^{\infty} \sum_{m_1=-l_1}^{l_1} \sum_{m_2=-l_2}^{l_2} \sum_{LM} F_{l_1 l_2 L}(r_1, r_2, R) \times \begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & M \end{pmatrix} C_{l_1 m_1}(\Omega_1) C_{l_2 m_2}(\Omega_2) C_{LM}(\Omega_R) \tag{1}$$

subject to the restriction

$$F_{l_1 l_2 L}(r_1, r_2, R) = 0 \tag{2}$$

unless $l_1 + l_2 + L =$ even. The Wigner 3-j coefficient in (1) vanishes unless

$$m_1 + m_2 + M = 0,$$
$$|l_1 - l_2| \leqslant L \leqslant l_1 + l_2. \tag{3}$$

The conditions (2) and (3) restrict L to values given by

$$L = l_1 + l_2 - 2\sigma, \tag{4}$$

$$\sigma = 0, 1, 2, \ldots, \min(l_1, l_2). \tag{5}$$

The $C_{lm}(\Omega)$ in (1) are the renormalized spherical harmonics as defined by Brink and Satchler (1962):

$$C_{lm}(\Omega) = C_{lm}(\theta, \phi) = [4\pi/(2l+1)]^{1/2} Y_{lm}(\theta, \phi)$$

and $\Omega_1, \Omega_2, \Omega_R$ denote the spherical polar angles specifying the orientations of $\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{R}$ in the arbitrary space-fixed coordinate system.

3. Expansion of $(R/r)^{2\nu}$

It is assumed that

$$R > \rho, \tag{6}$$

an inequality that holds for all orientations of $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ if and only if

$$R > r_1 + r_2. \tag{7}$$

With the restriction (6), $(R/r)^{2\nu}$ can be expanded in Gegenbauer polynomials (Abramowitz and Stegun 1966):

$$\left(\frac{R}{r}\right)^{2\nu} = \sum_{n=0}^{\infty} C_n^{\nu}(\cos\theta) \left(\frac{\rho}{R}\right)^n \tag{8}$$

where θ is the angle between $\boldsymbol{\rho}$ and $\boldsymbol{R}$ (figure 1). The Gegenbauer polynomials are given by (Abramowitz and Stegun 1966)

$$C_n^\nu(\cos\theta) = \frac{1}{\Gamma(\nu)} \sum_{m=0}^{N} \frac{(-1)^m \Gamma(n+\nu-m)(2\cos\theta)^{n-2m}}{m!(n-2m)!} \tag{9}$$

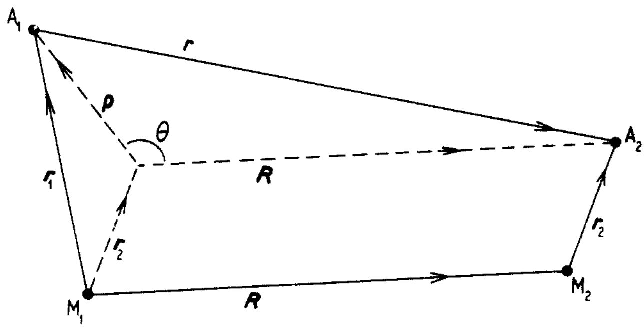

Figure 1. The vectors $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ give the positions of the atoms A_1 and A_2 relative to the molecular centres M_1 and M_2. The vectors $\boldsymbol{r}$ and $\boldsymbol{R}$ give the positions of A_2 and M_2 relative to A_1 and M_1, and $\boldsymbol{r} = \boldsymbol{R} - \boldsymbol{\rho} = \boldsymbol{R} - (\boldsymbol{r}_1 - \boldsymbol{r}_2)$.

where $N = [n/2]$. It is possible to expand $\cos^n\theta$ in Legendre polynomials:

$$\cos^n\theta = \sum_{m=0}^{N} b_{nm} P_{n-2m}(\cos\theta) \tag{10}$$

where the b_{nm} are given by (Abramowitz and Stegun 1966)

$$b_{nm} = (2n-4m+1)\int_0^1 dx\, x^n P_{n-2m}(x) = \frac{\surd(\pi)(2n-4m+1)n!}{2^{n+1}m!\Gamma(n-m+\frac{3}{2})}.$$

The Legendre expansion (10) is now applied to (9) to obtain the Legendre expansion for Gegenbauer polynomials:

$$C_n^\nu(\cos\theta) = \sum_{m=0}^{N} \sum_{L} \delta_{n-2m,L} d_{Lm}^\nu P_L(\cos\theta), \tag{11}$$

$$d_{Lm}^\nu = \frac{\surd(\pi)(L+\frac{1}{2})}{\Gamma(\nu)} \sum_{\lambda=0}^{m} \frac{(-1)^{m+\lambda}\Gamma(m+L+\lambda+\nu)}{\lambda!(m-\lambda)!\Gamma(L+\lambda+\frac{3}{2})}$$

$$= \frac{\surd(\pi)(L+\frac{1}{2})(-1)^m\Gamma(m+L+\nu)}{\Gamma(\nu)m!\Gamma(L+\frac{3}{2})} {}_2F_1(-m, m+L+\nu; L+\tfrac{3}{2}; 1). \tag{12}$$

Using the elementary expression for the hypergeometric function ${}_2F_1$ (Abramowitz and Stegun 1966) and the relation $\Gamma(z)\Gamma(1-z) = \pi\,\mathrm{cosec}(\pi z)$, (12) reduces to

$$d_{Lm}^\nu = \frac{\surd(\pi)(L+\frac{1}{2})\Gamma(m+\nu-\frac{1}{2})\Gamma(m+L+\nu)}{\Gamma(\nu)\Gamma(\nu-\frac{1}{2})m!\Gamma(m+L+\frac{3}{2})}. \tag{13}$$

This result has not been given previously in the literature. It is immediately apparent from (13) that

$$d_{Lm}^{1/2} = \delta_{m0}. \tag{14}$$

Another simple case is $d_{Lm}^{3/2} = 2L+1$.

The Legendre polynomials $P_L(\hat{x}.\hat{y})$ satisfy the addition theorem (Brink and Satchler 1962)

$$P_L(\hat{x}.\hat{y}) = \sum_M C_{LM}(\Omega_x)C^*_{LM}(\Omega_y) \tag{15}$$

where $\hat{x}, \hat{y}$ are unit vectors and Ω_x, Ω_y their spherical polar angle coordinates. Equations (11) and (15) are now applied to (8), giving

$$\left(\frac{R}{r}\right)^{2\nu} = \sum_{L=0}^{\infty} \sum_M \sum_{m=0}^{\infty} d^\nu_{Lm} \left(\frac{\rho}{R}\right)^{2m} \left(\frac{\rho}{R}\right)^L C^*_{LM}(\Omega_\rho)C_{LM}(\Omega_R). \tag{16}$$

The $(\rho/R)^{2m}$ term in (16) is expanded in a binomial series and (10) and (15) are used to obtain

$$\left(\frac{\rho}{R}\right)^{2m} = \sum_{k=0}^{m} \sum_{q=0}^{K} \sum_{LM} \delta_{k-2q,L} \binom{m}{k} b_{kq}(-2\alpha_1\alpha_2)^k(\alpha_1^2+\alpha_2^2)^{m-k} C_{LM}(\Omega_1)C^*_{LM}(\Omega_2), \tag{17}$$

where

$$K = [k/2], \qquad \alpha_1 = r_1/R, \qquad \alpha_2 = r_2/R.$$

Dixon and Lacroix (1973) give a relatively complicated proof by induction for the expansion of the solid harmonics $\rho^L C_{LM}(\Omega_\rho)$ and their equation (1) is missing a phase factor $(-1)^l$. A simpler approach is to start with equation (10.1.47) of Abramowitz and Stegun (1966), noting that $\exp(i\boldsymbol{k}.\boldsymbol{\rho}) = \exp(i\boldsymbol{k}.\boldsymbol{r}_1)\exp(-i\boldsymbol{k}.\boldsymbol{r}_2)$. Using the spherical harmonic addition theorem (Brink and Satchler 1962) one then readily obtains the result

$$\begin{aligned} j_L(k\rho)C^*_{LM}(\Omega_\rho) = \sum_{\substack{L_1L_2\\M_1M_2}} & i^{L_1-L_2-L}(2L_1+1)(2L_2+1) \\ & \times \begin{pmatrix} L_1 & L_2 & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L_1 & L_2 & L \\ M_1 & M_2 & M \end{pmatrix} j_{L_1}(kr_1)j_{L_2}(kr_2)C_{L_1M_1}(\Omega_1)C_{L_2M_2}(\Omega_2) \end{aligned} \tag{18}$$

where j_L is the spherical Bessel function. Using the expression given by Brink and Satchler (1962) for the first 3-j coefficient in (18), it follows directly that

$$\begin{aligned} \rho^L C^*_{LM}(\Omega_\rho) &= \lim_{k\to 0} k^{-L}(2L+1)!!\, j_L(k\rho)C^*_{LM}(\Omega_\rho) \\ &= \sqrt{(2L+1)} \sum_{\substack{L_1L_2\\M_1M_2}} \delta_{L_1+L_2,L}(-1)^{L_1} \binom{2L}{2L_1}^{1/2} \\ &\quad \times \begin{pmatrix} L_1 & L_2 & L \\ M_1 & M_2 & M \end{pmatrix} r_1^{L_1}C_{L_1M_1}(\Omega_1)r_2^{L_2}C_{L_2M_2}(\Omega_2). \end{aligned} \tag{19}$$

Equation (19) has been given previously in the literature (Moshinsky 1959) and it is a simple matter to substitute the explicit expression for the 3-j coefficient in (19) to reproduce equation (1) of Dixon and Lacroix (1973).

Equations (17), (19) and some Racah algebra manipulations are now applied to (16) to obtain

$$\left(\frac{R}{r}\right)^{2\nu} = \sum_{\substack{l_1l_2L\\m_1m_2M}} Q^\nu_{l_1l_2L}(\alpha_1,\alpha_2) \begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & M \end{pmatrix} C_{l_1m_1}(\Omega_1)C_{l_2m_2}(\Omega_2)C_{LM}(\Omega_R) \tag{20}$$

$$Q^{\nu}_{l_1 l_2 L}(\alpha_1, \alpha_2) = (2l_1+1)(2l_2+1)\sqrt{(2L+1)} \sum_{m=0}^{\infty} \sum_{k=0}^{m} \sum_{q=0}^{K} \sum_{L_1 L_2}$$
$$\times \alpha_1^{L_1+k} \alpha_2^{L_2+k} (\alpha_1^2+\alpha_2^2)^{m-k} d^{\nu}_{LM} \delta_{L_1+L_2,L} (-1)^{L_2} 2^k \binom{m}{k} \binom{2L}{2L_1}^{1/2}$$
$$\times b_{kq} W(l_1 l_2 L_1 L_2; Lk-2q) \begin{pmatrix} l_1 & L_1 & k-2q \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & L_2 & k-2q \\ 0 & 0 & 0 \end{pmatrix}. \tag{21}$$

Equation (20) is obviously of the form (1) and, because the 3-j coefficients in (21) vanish unless both l_1+L_1+k and l_2+L_2+k are even, (2) is also satisfied. Restricting L to values given by (4) and (5), it follows that

$$\lambda = l_2 - \sigma, \qquad \tau = l_1 - \sigma$$

are both non-negative integers. The 3-j and Racah (W) coefficients in (21) are special cases for which expressions are given by Brink and Satchler (1962).

Substituting these in (21), one obtains

$$Q^{\nu}_{l_1 l_2 L}(\alpha_1, \alpha_2) = (-1)^{\tau}(l_1+\tfrac{1}{2})(l_2+\tfrac{1}{2})(\tfrac{1}{2})^{2L+1}$$
$$\times [\pi(2L+2\sigma+1)!(2\lambda)!(2\tau)!/(2\sigma)!]^{1/2} \alpha_1^{l_1} \alpha_2^{l_2} \sum_{n_1=0}^{\lambda} \sum_{n_2=0}^{\tau}$$
$$\times \frac{(2n_1+2n_2+2\sigma+1)\Gamma(\sigma+n_1+\frac{1}{2})\Gamma(\sigma+n_2+\frac{1}{2})}{n_1!\,n_2!\,(\lambda-n_1)!\,(\tau-n_2)!\,\Gamma(l_1+n_1+\frac{3}{2})\Gamma(l_2+n_2+\frac{3}{2})}$$
$$\times \alpha_1^{2n_1} \alpha_2^{2n_2} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{(\sigma+n_1+n_2+2m+n)!\,d^{\nu}_{L\sigma+n_1+n_2+2m+n}}{m!\,n!\,\Gamma(\sigma+n_1+n_2+m+\frac{3}{2})}$$
$$\times (\alpha_1\alpha_2)^{2m} (\alpha_1^2+\alpha_2^2)^n. \tag{22}$$

4. Special cases

The spherical component of (20) is given by

$$Q^{\nu}_{000}(\alpha_1, \alpha_2) = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{(2m+n)!\,d^{\nu}_{0\,2m+n}}{(2m+1)!\,n!} (2\alpha_1\alpha_2)^{2m} (\alpha_1^2+\alpha_2^2)^n.$$

Setting $r_2 = 0$ in (16) one obtains the one-centre expansion

$$\left(\frac{R}{r}\right)^{2\nu} = \sum_{L=0}^{\infty} \sum_{M} \alpha_1^L C_{LM}(\Omega_1) C^*_{LM}(\Omega_R) \sum_{m=0}^{\infty} d^{\nu}_{Lm} \alpha_1^{2m}. \tag{23}$$

The generality and simplicity of (23) and (13) are to be compared with equations (15) and (22) of Dixon and Lacroix (1973).

The Coulomb potential is given by $\nu = \frac{1}{2}$, and substituting from (14) in (22) one readily obtains

$$Q^{1/2}_{l_1 l_2 L}(\alpha_1, \alpha_2) = (-1)^{l_1} \delta_{l_1+l_2,L} \sqrt{(2L+1)} \binom{2L}{2l_1}^{1/2} \alpha_1^{l_1} \alpha_2^{l_2}.$$

5. Invariant expansion

Fixed in each molecule is an intrinsic coordinate system. Usually the coordinates of a molecule's atoms are specified in this intrinsic coordinate system, and not in the arbitrary space-fixed coordinate system of the expansion (1). The orientations of $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ in their respective intrinsic coordinate systems are denoted by the spherical polar angles ω_1 and ω_2. If R_1 and R_2 are the rotations that carry the respective intrinsic coordinate systems into the arbitrary space-fixed coordinate system, the spherical harmonics in (1) are related to spherical harmonics of the intrinsic spherical polar angles by the rotational transformations (Brink and Satchler 1962)

$$C_{l_i m_i}(\Omega_i) = \sum_{m_i'} D^{l_i}_{m_i' m_i}(R_i) C_{l_i m_i'}(\omega_i) \qquad i = 1, 2. \tag{24}$$

If R_R is the rotation that carries $\boldsymbol{R}$ into the arbitrary space-fixed z axis, then

$$C_{LM}(\Omega_R) = D^L_{0M}(R_R). \tag{25}$$

Substituting from (24) and (25) in (1) one obtains

$$f(r) = \sum_{\substack{l_1 l_2 L \\ m_1 m_2}} G^{l_1 l_2 L}_{m_1 m_2}(r_1, r_2, R, \omega_1, \omega_2) \Phi^{l_1 l_2 L}_{m_1 m_2}(R_1, R_2, R_R),$$

$$G^{l_1 l_2 L}_{m_1 m_2}(r_1, r_2, R, \omega_1, \omega_2) = F_{l_1 l_2 L}(r_1, r_2, R) C_{l_1 m_1}(\omega_1) C_{l_2 m_2}(\omega_2), \tag{26}$$

$$\Phi^{l_1 l_2 L}_{m_1 m_2}(R_1, R_2, R_R) = \sum_{m_1' m_2' M'} \begin{pmatrix} l_1 & l_2 & L \\ m_1' & m_2' & M' \end{pmatrix} D^{l_1}_{m_1 m_1'}(R_1) D^{l_2}_{m_2 m_2'}(R_2) D^L_{0M'}(R_R). \tag{27}$$

In general the elements of the rotation matrix D are determined by three Euler angles for each of the rotations R_1, R_2 and R_R.

Rotations of the molecules or the vector $\boldsymbol{R}$ are reflected in changes of R_1, R_2 and R_R alone, the intrinsic quantities (26) being invariant under such rotations. However, for rotations of the arbitrary space-fixed coordinate system or of the complete two-molecule system, both (26) and (27) are invariant.

6. The Prigogine expansion

There are several typographical errors in the Prigogine derivation (Prigogine 1957) but the crucial error occurs in the step of taking only the $k = 0$ term of the expansion

$$C^{\nu-1/2}_m(\cos\phi) = \frac{1}{\Gamma(\nu-\frac{1}{2})^2} \sum_{k=0}^{m} \frac{\Gamma(\nu-\frac{1}{2}+k)\Gamma(\nu-\frac{1}{2}+m-k)}{k!(m-k)!} \cos[(m-2k)\phi] \tag{28}$$

in going from (13.4.10) to (13.4.12) (this numbering identifies equations in Prigogine 1957). Consequently (13.4.12) and the results derived therefrom are wrong. Even if the full expression (28) were used one still would not have a spherical harmonic expansion. Thus the approach of using the Gegenbauer polynomial addition theorem is a fruitless one. Prigogine also asserts that the expansion is valid for $r_1 < R$ and $r_2 < R$. The correct and more stringent restriction for the validity of the expansion for all orientations of $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ is given by (7).

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