Hyperspherical Harmonic Expansions of Potential $1/r_{jt}$ of Molecular Systems

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The expansion coefficient C_{lLl}^{O} of Coulomb potential $1/r_{jt}$ of molecular systems in hyperspherical harmonics is derived in detail, and the explicit expression is given.

Keywords expansion of potential $1/r_{jt}$, molecular system, hyperspherical harmonics, expansion coefficient

Introduction

In solving Schrödinger equation directly in irregular hyperspherical coordinates, it is an essential step to calculate the matrix elements of Coulomb potential $1/r_{jt}$ with hyperspherical bases. To do this, it is often needed to expand $1/r_{jt}$ in hyperspherical harmonics. Whitten[1] has expanded $1/r_{12}$ of helium atom in D functions, the bases of U_2 group representation. Fabre[2] and Avery[3] have exposited the expansion of $1/r_{12}$ in detail. And we[4] have ever derived the expansion of $1/r_{12}$ of atomic systems in hyperspherical harmonics. But these expansions are for atomic systems.

For molecular systems, there are more than one atomic centers, and it is needed to transform the Cartesian coordinates to Jacobi coordinates and describe the hyperspherical harmonics in terms of the later. Potential $1/r_{jt}$ should be expanded in hyperspherical harmonics derived from Jacobi coordinates. In this paper, the explicit expression of the expansion of $1/r_{jt}$ is derived.

Distance vector r_{jt}

Jacobi coordinates

For molecular systems of $N+1$ particles with Cartesian coordinates $\boldsymbol{x}_1, \boldsymbol{x}_2, \cdots, \boldsymbol{x}_N$, they can be transformed to Jacobi coordinates by the following method:

$$\xi_1 = \sqrt{\frac{m_2 m_1}{M_2}}(\boldsymbol{x}_2 - \boldsymbol{x}_1)$$

$$\xi_2 = \sqrt{\frac{m_3 M_2}{M_3}}\left(\boldsymbol{x}_3 - \frac{m_1\boldsymbol{x}_1 + m_2\boldsymbol{x}_2}{M_2}\right)$$

$$\cdots\cdots$$

$$\xi_{j-1} = \sqrt{\frac{m_j M_{j-1}}{M_j}}\left(\boldsymbol{x}_j - \frac{\sum_{i=1}^{j-1} m_i\boldsymbol{x}_i}{M_{j-1}}\right)$$

$$\cdots\cdots$$

$$\xi_N = \sqrt{\frac{m_{N+1} M_N}{M_{N+1}}}\left(\boldsymbol{x}_{N+1} - \frac{\sum_{i=1}^{N} m_i\boldsymbol{x}_i}{M_N}\right) \tag{1}$$

where $m_1, m_2, \cdots, m_{N+1}$ are the masses of the particles, and

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$$M_j = m_1 + m_2 + \cdots + m_j \quad (2)$$

is the mass sum of j particles. The non-relativistic Schrödinger equation is

$$\left\{-\frac{1}{2}\sum_j \nabla_j^2 + \sum_{i<j}\sum \frac{Z_iZ_j}{r_{ij}}\right\}\Psi = E\Psi \quad (3)$$

where the Laplacian operators are in Jacobi coordinates.

$$\boldsymbol{r}_{jt} = \boldsymbol{x}_t - \boldsymbol{x}_j$$

In order to express the distance vector $\boldsymbol{r}_{jt}$ in terms of the Jacobi coordinates, we reverse Eq. (1), and define

$$\omega_{j-1} = \sqrt{\frac{M_j}{m_jM_{j-1}}} \quad (4)$$

$$\boldsymbol{x}_2 - \boldsymbol{x}_1 = \omega_1\boldsymbol{\xi}_1$$

$$\boldsymbol{x}_3 - \frac{m_1\boldsymbol{x}_1 + m_2\boldsymbol{x}_2}{M_2} = \omega_2\boldsymbol{\xi}_2$$

$$\cdots\cdots$$

$$\boldsymbol{x}_j - \frac{\sum_{i=1}^{j-1} m_i\boldsymbol{x}_i}{M_{j-1}} = \omega_{j-1}\boldsymbol{\xi}_{j-1} \quad (5)$$

$$\cdots\cdots$$

$$\boldsymbol{x}_t - \frac{\sum_{i=1}^{t-1} m_i\boldsymbol{x}_i}{M_{t-1}} = \omega_{t-1}\boldsymbol{\xi}_{t-1}$$

$$\cdots\cdots$$

$$\boldsymbol{x}_{N+1} - \frac{\sum_{i=1}^{N} m_i\boldsymbol{x}_i}{M_N} = \omega_N\boldsymbol{\xi}_N$$

Now

$$\boldsymbol{x}_t - \frac{\sum_{i=1}^{t-1} m_i\boldsymbol{x}_i}{M_{t-1}} = \omega_{t-1}\boldsymbol{\xi}_{t-1}$$

$$= \boldsymbol{x}_t - \frac{m_{t-1}}{M_{t-1}}\boldsymbol{x}_{t-1} - \frac{M_{t-2}}{M_{t-1}}\frac{\sum_{i=1}^{t-2} m_i\boldsymbol{x}_i}{M_{t-2}}$$

With the help of $\boldsymbol{x}_{t-1} - \frac{\sum_{i=1}^{t-2} m_i\boldsymbol{x}_i}{M_{t-2}} = \omega_{t-2}\boldsymbol{\xi}_{t-2}$, we can get $\boldsymbol{x}_t - \frac{\sum_{i=1}^{t-2} m_i\boldsymbol{x}_i}{M_{t-2}} = \omega_{t-1}\boldsymbol{\xi}_{t-1} + \frac{m_{t-1}\omega_{t-2}}{M_{t-1}}\boldsymbol{\xi}_{t-2}$. Going on, we get

$$\boldsymbol{x}_t - \boldsymbol{x}_j = \omega_{t-1}\boldsymbol{\xi}_{t-1} + \frac{m_{t-1}\omega_{t-2}}{M_{t-1}}\boldsymbol{\xi}_{t-2} + \frac{m_{t-2}\omega_{t-3}}{M_{t-2}}\boldsymbol{\xi}_{t-3} + \cdots + \frac{m_{j+1}\omega_j}{M_{j+1}}\boldsymbol{\xi}_j - \frac{M_{j-1}\omega_{j-1}}{M_j}\boldsymbol{\xi}_{j-1} \quad (6)$$

The distance vector $\boldsymbol{r}_{jt}$ is, therefore the linear combination of $(t-j)$ Jacobi vectors.

Fourier transform

The potential $\frac{1}{|\boldsymbol{x}_t - \boldsymbol{x}_j|}$ can be first Fourier transformed as[3]

$$\frac{1}{|\boldsymbol{x}_t - \boldsymbol{x}_j|} = \frac{1}{2\pi^2}\int d^3k\, \frac{e^{i\boldsymbol{k}\cdot(\boldsymbol{x}_t - \boldsymbol{x}_j)}}{k^2} = \frac{1}{2\pi^2}\int dk\, d\omega_k e^{i\boldsymbol{k}\cdot(\boldsymbol{x}_t - \boldsymbol{x}_j)} \quad (7)$$

where $\boldsymbol{k}$ is the 3-dimension reciprocal-space vector. Substituting (6) into (7) we get

$$\frac{1}{|\boldsymbol{x}_t - \boldsymbol{x}_j|} = \frac{1}{2\pi^2}\int dk\, d\omega_k e^{i\boldsymbol{k}\cdot(\omega_{t-1}\boldsymbol{\xi}_{t-1} + \cdots - \frac{M_{j-1}}{M_j}\omega_{j-1}\boldsymbol{\xi}_{j-1})} \quad (8)$$

Defining $3(t-j+1)$-dimensional vectors

$$\boldsymbol{\xi} = (\boldsymbol{\xi}_{j-1}, \boldsymbol{\xi}_j, \cdots, \boldsymbol{\xi}_{t-2}, \boldsymbol{\xi}_{t-1})$$

$$\boldsymbol{K} = (\boldsymbol{K}_{j-1}, \boldsymbol{K}_j, \cdots, \boldsymbol{K}_{t-2}, \boldsymbol{K}_{t-1})$$

Eq. (8) can be written as

$$\frac{1}{|\boldsymbol{x}_t - \boldsymbol{x}_j|} = \frac{1}{2\pi^2}\int dk\, d\omega_k e^{i\boldsymbol{K}\cdot\boldsymbol{\xi}} \quad (9)$$

From Eq. (8) we get

$$\boldsymbol{K}_{j-1} = -\frac{M_{j-1}}{M_j}\omega_{j-1}\boldsymbol{k}$$

$$\boldsymbol{K}_j = \frac{m_{j+1}}{M_{j+1}}\omega_j\boldsymbol{k}$$

$$\cdots\cdots$$

$$\boldsymbol{K}_{t-2} = \frac{m_{t-1}}{M_{t-1}}\omega_{t-2}\boldsymbol{k}$$

$$K_{t-1}=\omega_{t-1}k \tag{10}$$

All the vectors K_j are in the same direction of k except K_{j-1}, which is in the opposite direction of k. The scalar K is

$$K=\theta_{jt}k \tag{11}$$

where

$$\theta_{jt}=\left\{\left(\frac{M_{j-1}}{M_j}\omega_{j-1}\right)^2+\left(\frac{m_{j+1}}{M_{j+1}}\omega_j\right)^2+\cdots+\left(\frac{m_{t-1}}{M_{t-1}}\omega_{t-2}\right)^2+\omega_{t-1}^2\right\}^{1/2} \tag{12}$$

Using Eq. (4), θ_{jt} can be written as

$$\theta_{jt}=\left\{\frac{M_{j-1}}{m_jM_j}+\frac{m_{j+1}}{M_{j+1}M_j}+\cdots+\frac{m_{t-1}}{M_{t-1}M_{t-2}}+\frac{M_t}{m_tM_{t-1}}\right\}^{1/2} \tag{13}$$

θ_{jt} is the function of the masses of particles only.

Hyperspherical harmonic expansion

Eq. (9) can be further expanded in hyperspherical harmonics[3]

$$\frac{1}{|x_t-x_j|}=\frac{1}{2\pi^2}\int dk d\omega_k\frac{(2\pi)^{\frac{D}{2}}}{(K\xi)^{\frac{D}{2}-1}}\sum_{|L|}i^{|L|}\Psi_{|L|}(\Omega)\cdot\Psi^*_{|L|}(\Omega_K)J_{\frac{D}{2}-1+L}(K\xi)=\sum_{|L|}C^D_{|L|}\Psi_{|L|}(\Omega) \tag{14}$$

where $D=3(t-j+1)$, $\Psi_{|L|}(\Omega)$ and $\Psi^*_{|L|}(\Omega_K)$ are hyperspherical harmonics in ξ and K spaces respectively, $|L|$ is a set of quantum numbers. $J_{\frac{D}{2}-1+L}(K\xi)$ is spherical Bessel function, and

$$C^D_{|L|}=2(2\pi)^{\frac{D}{2}-2}i^{|L|}\int dk d\omega_k\frac{1}{(K\xi)^{\frac{D}{2}-1}}\cdot\Psi^*_{|L|}(\Omega_K)J_{\frac{D}{2}-1+L}(K\xi) \tag{15}$$

The hyperspherical harmonic $\Psi^*_{|L|}(\Omega_K)$ is given by

$$\Psi^*_{|L|}(\Omega_K)=\left\{\prod_{i=j}^{t-1}N^{\alpha_i\beta_i}_{n_i}(\sin\eta_i^{(K)})^{\tau_{i-1}}(\cos\eta_i^{(K)})^{l_i}\cdot P^{\alpha_i\beta_i}_{n_i}(\cos2\eta_i^{(K)})Y^*_{l_iu_i}(\omega_k)\right\}\cdot Y^*_{l_{j-1}u_{j-1}}(-\omega_k) \tag{16}$$

where $N^{\alpha_i\beta_i}_{n_i}$ is the normalization constant, $P^{\alpha_i\beta_i}_{n_i}(\cos2\eta_i^{(K)})$ is Jacobi polynomial and

$$\beta_i=l_i+\frac{1}{2}$$
$$\alpha_i=\tau_{i-1}+\frac{D_i-3}{2}-1$$
$$\tau_i=2n_i+l_i+\tau_{i-1}\quad(\tau_1=l_1) \tag{17}$$

$\cos\eta_i^{(K)}$ and $\sin\eta_i^{(K)}$ are cosine and sine of the hyperspherical angles of K-space. Let $j=2$, the $\cos\eta_i^{(K)}$ and $\sin\eta_i^{(K)}$ are defined through the following formula,

$$K_1=K\sin\eta_{t-1}^{(K)}\sin\eta_{t-2}^{(K)}\cdots\sin\eta_3^{(K)}\sin\eta_2^{(K)}$$
$$K_2=K\sin\eta_{t-1}^{(K)}\sin\eta_{t-2}^{(K)}\cdots\sin\eta_3^{(K)}\mathrm{con}\,\eta_2^{(K)}$$
$$\cdots\cdots$$
$$K_{t-2}=K\sin\eta_{t-1}^{(K)}\mathrm{con}\,\eta_{t-2}^{(K)}$$
$$K_{t-1}=K\mathrm{con}\,\eta_{t-1}^{(K)} \tag{18}$$

Solving for the cosines we have

$$\mathrm{con}\,\eta_{t-1}^{(K)}=\frac{K_{t-1}}{K},\ \mathrm{con}\,\eta_{t-2}^{(K)}=\frac{K_{t-2}}{\sqrt{K_1^2+\cdots+K_{t-2}^2}}$$
$$\cdots\cdots,\ \mathrm{con}\,\eta_2^{(K)}=\frac{K_2}{\sqrt{K_1^2+K_2^2}} \tag{19}$$

Together with Eqs. (10), (11) and (13) we use all the $\cos\eta_i^{(K)}(i=1,2,\cdots,t-1)$ are constants determined by the masses m_i of the particles. $C^D_{|L|}$ can therefore be written as

$$C^D_{|L|}=2(2\pi)^{\frac{D}{2}-2}i^{|L|}\left[\prod_{i=2}^{t-1}N^{\alpha_i\beta_i}_{n_i}(\sin\eta_i^{(K)})^{\tau_{i-1}}\cdot(\cos\eta_i^{(K)})^{l_i}P^{\alpha_i\beta_i}_{n_i}(\cos2\eta_i^{(K)})\right]\int dk\cdot\frac{1}{(K\xi)^{\frac{D}{2}-1}}J_{\frac{D}{2}-1+L}(K\xi)\int d\omega_kY^*_{l_2u_2}(\omega_k)\cdots Y^*_{l_{t-1}u_{t-1}}(\omega_k)Y^*_{l_1u_1}(-\omega_k) \tag{20}$$

Now, the k part can be easily integrated[3] (with $\rho = \theta_{2t}k\xi$)

$$\int \mathrm{d}k \frac{1}{(K\xi)^{\frac{D}{2}-1}} J_{\frac{D}{2}-1+L}(K\xi) = \frac{1}{\theta_{2t}\xi}\int \mathrm{d}\rho \frac{1}{\rho^{\frac{D}{2}-1}} J_{\frac{D}{2}-1+L}(\rho)$$
$$= \frac{\Gamma\left(\frac{L}{2}+\frac{1}{2}\right)}{2^{\frac{D}{2}-1}\Gamma\left(\frac{L}{2}+\frac{D}{2}-\frac{1}{2}\right)} \times \frac{1}{\theta_{2t}\xi} \tag{21}$$

The integral of the angular part is

$$\int \mathrm{d}\omega_k Y^*_{l_2u_2}(\omega_k) Y^*_{l_3u_3}(\omega_k) \cdots Y^*_{l_{t-1}u_{t-1}}(\omega_k) Y^*_{l_1u_1}(-\omega_k)$$
$$= (-1)^{l_1} \sum_{L_3=|l_2-l_3|}^{l_2+l_3} \cdots \sum_{L_{t-1}=|L_{t-2}-l_{t-1}|}^{l_{t-1}+L_{t-2}} (l_2l_3u_2u_3 \mid L_3U_3) \cdot$$
$$\sqrt{\frac{[l_2][l_3]}{4\pi[L_3]}} (l_2l_300 \mid L_30)(L_3l_4U_3u_4 \mid L_4U_4) \cdot$$
$$\sqrt{\frac{[L_3][l_4]}{4\pi[L_4]}} (L_3l_400 \mid L_40) \cdots (L_{t-2}l_{t-1}U_{t-2}u_{t-1}$$
$$\mid L_{t-1}U_{t-1}) \sqrt{\frac{[L_{t-2}][l_{t-1}]}{4\pi[L_{t-1}]}} (L_{t-2}l_{t-1}00 \mid L_{t-1}0) \cdot$$
$$\delta_{L_{t-1}, l_1} \delta_{U_{t-1}, u_1} \tag{22}$$

For Eq. (22) to be not zero identically, the sum of the quantum numbers, $L_i + l_{i+1} + L_{i+1}$ of the Wigner coefficients $(L_il_{i+1}00 \mid L_{i+1}0)$ $(i = 1, 2, \cdots, t-2)$, must be even. That is

$$l_2 + l_3 + \cdots l_{t-1} + 2(L_3 + L_4 + \cdots + L_{t-2}) + L_{t-1} = \text{even integer} \tag{23}$$

Since $L_{t-1} = l_1$, we have

$$l_1 + l_2 + \cdots l_{t-1} + 2(L_3 + L_4 + \cdots + L_{t-2}) = \text{even integer} \tag{24}$$

Because l_1, l_2, $\cdots$, l_{t-1}, L_3, L_4, $\cdots$, L_{t-2} are integers, Eq. (24) indicates

$$l_1 + l_2 + \cdots + l_{t-1} = \text{even integer} \tag{25}$$

This again indicates the quantum number L,

$$L = 2(n_2 + n_3 + \cdots + n_{t-1}) + l_1 + l_2 + \cdots + l_{t-1}$$

is even too, and we have

$$i^{|L|} = (-1)^{(n_2+n_3+\cdots+n_{t-1}) + \frac{1}{2}(l_1+l_2+\cdots+l_{t-1})} \tag{26}$$

The expansion coefficient C^D_L is

$$C^D_L = (-1)^{\left(\sum_{i=2}^{t-1} n_i + \frac{1}{2}\sum_{i=1}^{t-1} l_i\right)} 2(2\pi)^{\frac{D}{2}-2}(-1)^{l_1} \cdot$$
$$\left\{\prod_{i=2}^{t-1} N^{\alpha_i\beta_i}_{n_i} (\sin\eta_i^{(K)})^{\tau_{i-1}} (\mathrm{con}\,\eta_i^{(K)})^{l_i} \cdot\right.$$
$$\left. P^{\alpha_i\beta_i}_{n_i}(\mathrm{con}2\eta_i^{(K)})\right\} \left\{\frac{1}{\theta_{2t}\xi} \times \frac{\Gamma\left(\frac{L}{2}+\frac{1}{2}\right)}{2^{\frac{D}{2}-1}\Gamma\left(\frac{D}{2}+\frac{L}{2}-\frac{1}{2}\right)}\right\} \cdot$$
$$\sum_{i=3}^{t-1} \left\{\sqrt{\frac{[L_{i-1}][l_i]}{4\pi[L_i]}} (L_{i-1}l_iU_{i-1}u_i \mid L_iU_i) \cdot\right.$$
$$(L_{i-1}l_i00 \mid L_i0)\delta_{U_{t-1}, u_1} \tag{27}$$

and the expansion is

$$\frac{1}{r_{2t}} = \frac{1}{\xi} \sum_L \bar{C}^D_L \Psi_L(\Omega) \tag{28}$$

where $\bar{C}^D_L$ is the coefficient of $\frac{1}{\xi}$ in C^D_L.

Conclusion

In conclusion, the Coulomb potential $1/r_{jt}$ of molecular systems has been expanded in terms of hyperspherical harmonics and the expansion coefficient C^D_L has been expressed in terms of Jacobi polynomials.

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