Expansion of potential $\frac{1}{r_{12}}$ of atomic systems in hyper-spherical harmonics

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The expansion coefficient C^{p}_{lLl} of Coulomb potential $\frac{1}{r_{12}}$ of atomic system in hyper-spherical harmonics is derived and the explicit expression is given.

Keywords Expansion of potential $\frac{1}{r_{12}}$, atomic system, hyper-spherical harmonics, expansion coefficient

Introduction

In calculating the matrix elements of potential $\frac{1}{r_{ij}}$ with hyperspherical bases, it is often needed to expand $\frac{1}{r_{ij}}$ in hyperspherical harmonics. Whitten[1] expanded $\frac{1}{r_{12}}$ of helium atom in D functions, the representation basis functions of U_2 group. Fabre[2] and Avery[3] exposited the expansion in detail although they did not give explicit expression of the expansion. But no explicit coefficient of the expansion is available.

In this paper we derive the explicit expression of the expansion of $\frac{1}{r_{12}}$. The explicit expression of the expansion of $\frac{1}{r_{ij}}$ can be obtained from the expansion of $\frac{1}{r_{12}}$ by permutation operation.[4]

Fourier transform

For an N-particle system the non-relativistic Schrödinger equation is

$$\left\{-\frac{1}{2}\sum_{i=1}^{N}\frac{1}{m_i}\nabla_i^2 + V - E\right\}\Psi = 0 \qquad (1)$$

where V is the interaction potential

$$V = -\sum_{i=1}^{N}\frac{Z_N}{r_i} + \sum_{i}\sum_{i<j}^{N}\frac{1}{r_{ij}}, \qquad (2)$$

and m_j (i = 1 to N) are the masses of particles. Defining the mass scaling coordinates

$$\underline{\zeta}_i = \sqrt{m_i}\,\underline{x}_i \qquad (3)$$

Eq. (1) becomes

$$\left\{-\frac{1}{2}\sum_{i=1}^{N}\nabla_{\zeta_i}^2 + V - E\right\}\Psi = 0 \qquad (4)$$

Eq. (4) can be considered as one-particle with unit mass moving in $3N$-dimension space.

The Fourier transform of $\frac{1}{r_{12}}$ is

$$\frac{1}{r_{12}} = \frac{1}{|\underline{x}_1 - \underline{x}_2|} = \frac{1}{2\pi^2}\int d^3k\,\frac{e^{i\underline{k}\cdot(\underline{x}_1-\underline{x}_2)}}{k^2}$$

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$$= \frac{1}{2\pi^2}\iint \mathrm{d}k\mathrm{d}\Omega_k e^{i\underline{k}\cdot\left(\frac{\underline{\xi}_1}{\sqrt{m_1}}-\frac{\underline{\xi}_2}{\sqrt{m_2}}\right)} \tag{5}$$

Introducing $3N$-dimensional vectors

$$\begin{aligned} \underline{\xi} &= (\underline{\xi}_1, \underline{\xi}_2, 0, 0, \cdots, 0) \\ \underline{K} &= (\underline{K}_1, \underline{K}_2, 0, 0, \cdots, 0) \end{aligned} \tag{6}$$

where

$$\begin{aligned} \underline{K}_1 &= \frac{1}{\sqrt{m_1}}\underline{k} \\ \underline{K}_2 &= -\frac{1}{\sqrt{m_2}}\underline{k} \end{aligned} \tag{7}$$

Eq. (5) is reduced to

$$\frac{1}{r_{12}} = \frac{1}{2\pi^2}\iint \mathrm{d}k\mathrm{d}\Omega_k e^{i\underline{K}\cdot\underline{\xi}} \tag{8}$$

In non-regular hyper-spherical harmonic function, the $D = 3N$ dimension vectors are first transformed to

$$\begin{aligned} \underline{\xi}_i &= \xi_i \hat{n}_{\xi_i} \\ \underline{K}_i &= K_i \hat{n}_{K_i} \qquad i = 1,2,\cdots N \end{aligned} \tag{9}$$

where $\hat{n}_{\xi_i}$ and $\hat{n}_{K_i}$ are the unit polar vectors of vectors $\underline{\xi}_i$ and $\underline{K}_i$, respectively. Eq. (7) shows that the direction of $\underline{K}_1$ is the same as that of $\underline{k}$, and that of $\underline{K}_2$ is in the opposite direction of $\underline{k}$.

Transforming to hyperspherical coordinates we write

$$\begin{aligned} \xi_N &= \xi\cos\eta_N \\ \xi_{N-1} &= \xi\sin\eta_N\cos\eta_{N-1} \\ &\cdots\cdots \\ \xi_i &= \xi\sin\eta_N\sin\eta_{N-1}\cdots\sin\eta_{i+1}\cos\eta_i \\ &\cdots\cdots \\ \xi_2 &= \xi\sin\eta_N\sin\eta_{N-1}\cdots\sin\eta_3\cos\eta_2 \\ \xi_1 &= \xi\sin\eta_N\sin\eta_{N-1}\cdots\sin\eta_3\sin\eta_2. \end{aligned} \tag{10}$$

Since $\xi_3, \xi_4, \cdots, \xi_N = 0$, we have

$$\eta_3 = \eta_4 = \cdots = \eta_N = \frac{\pi}{2} \tag{11}$$

and

$$\begin{aligned} \xi_2 &= \xi\cos\eta_2 \\ \xi_1 &= \xi\sin\eta_2 \\ \xi^2 &= \xi_1^2 + \xi_2^2 \end{aligned} \tag{12}$$

In the same way we can write

$$\begin{aligned} K_N &= K\cos\eta_N^{(K)} \\ K_{N-1} &= K\sin\eta_N^{(K)}\cos\eta_{N-1}^{(K)} \\ &\cdots\cdots \\ K_i &= K\sin\eta_N^{(K)}\sin\eta_{N-1}^{(K)}\cdots\sin\eta_{i+1}^{(K)}\cos\eta_i^{(K)} \\ &\cdots\cdots \\ K_2 &= K\sin\eta_N^{(K)}\sin\eta_{N-1}^{(K)}\cdots\sin\eta_3^{(K)}\cos\eta_2^{(K)} \\ K_1 &= K\sin\eta_N^{(K)}\sin\eta_{N-1}^{(K)}\cdots\sin\eta_3^{(K)}\sin\eta_2^{(K)} \end{aligned} \tag{13}$$

we also have

$$\eta_3^{(K)} = \eta_4^{(K)} = \cdots = \eta_N^{(K)} = 0 \tag{14}$$

and

$$\begin{aligned} K_2 &= K\cos\eta_2^{(K)} \\ K_1 &= K\sin\eta_2^{(K)} \\ K^2 &= K_1^2 + K_2^2 \end{aligned} \tag{15}$$

In conjunction with Eq. (7) we have

$$K^2 = \frac{k^2}{\mu} \tag{16}$$

where the reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{17}$$

Again,

$$\frac{k}{\sqrt{m_2}} = \frac{k}{\sqrt{\mu}}\cos\eta_2^{(K)}$$

or

$$\cos\eta_2^{(K)} = \sqrt{\frac{m_1}{m_1 + m_2}} \tag{18}$$

Thus, $\cos\eta_2^{(K)}$ is a constant dependent on the masses of the particles. In the case of $m_1 = m_2$, we have $\cos\eta_2^{(K)} = \frac{1}{\sqrt{2}}$.

Expansion in hyperspherical harmonics

Eq. (8) can be further expanded in hyperspherical harmonics:[3]

$$\begin{aligned} \frac{1}{r_{12}} &= \frac{1}{2\pi^2}\iint \mathrm{d}k\mathrm{d}\Omega_k \frac{(2\pi)^{\frac{D}{2}}}{(K\xi)^{\frac{D}{2}-1}} \sum_{|L|} i^L \Psi_{|L|}(\Omega)\Psi^*_{|L|}(\Omega_k) J_{\frac{D}{2}+L-1}(K\xi) \\ &= \sum_{|L|} C^D_{|L|}\Psi_{|L|}(\Omega) \end{aligned} \tag{19}$$

where $D=6$, $\Psi_{|L|}(\Omega)$ and $\Psi^*_{|L|}(\Omega)$ are hyperspherical harmonics in $\underline{\xi}$ and $\underline{K}$ spaces respectively, $|L|$ is a set of quantum numbers and L is the first one of the set. $J_{\frac{D}{2}+L-1}(K\xi)$ is spherical Bessel function, and

$$C^D_{|L|} = 2(2\pi)^{\frac{D}{2}-2} i^L \iint \mathrm{d}k\mathrm{d}\Omega_k \frac{1}{(K\xi)^{\frac{D}{2}-1}} \Psi^*_{|L|}(\Omega_k) J_{\frac{D}{2}+L-1}(K\xi) \tag{20}$$

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

$$\begin{aligned} \Psi^*_{|L|}(\Omega_K) &= N_n^{\alpha,\beta}(\sin\eta_2^{(K)})^{l_1}(\cos\eta_2^{(K)})^{l_2} P_n^{\alpha,\beta}(\cos 2\eta_2^{(K)}) \\ &\times Y^*_{l_1\mu_1}(\Omega_{K_1}) Y^*_{l_2\mu_2}(\Omega_{K_2}) \end{aligned} \tag{21}$$

where $N_n^{\alpha,\beta}$ is the normalization constant, $P_n^{\alpha,\beta}(\cos 2\eta_2^{(K)})$ is Jacobi polynomial and

$$\begin{aligned} \alpha &= l_1 + \frac{1}{2} \\ \beta &= l_2 + \frac{1}{2} \end{aligned} \tag{22}$$

Eq. (20) can be written as

$$\begin{aligned} C^D_{|L|} &= 2(2\pi)^{\frac{D}{2}-2} i^L N_n^{\alpha,\beta}\left(\frac{m_2}{m_1+m_2}\right)^{\frac{l_1}{2}}\left(\frac{m_1}{m_1+m_2}\right)^{\frac{l_2}{2}} \\ &\times P_n^{l_1+\frac{1}{2},l_2+\frac{1}{2}}\left(\frac{m_1-m_2}{m_1+m_2}\right)\int \mathrm{d}k \frac{1}{(K\xi)^{\frac{D}{2}-1}} J_{\frac{D}{2}+L-1}(K\xi) \\ &\times \int \mathrm{d}\Omega_k Y^*_{l_1\mu_1}(\Omega_k) Y^*_{l_2\mu_2}(-\Omega_k). \end{aligned} \tag{23}$$

From Eq. (16) the integration over k can be written as (with $\rho = \frac{k\xi}{\sqrt{\mu}}$)

$$\begin{aligned} \int_0^\infty \mathrm{d}k \frac{1}{(K\xi)^{\frac{D}{2}-1}} J_{\frac{D}{2}+L-1}(K\xi) &= \frac{\sqrt{\mu}}{\xi}\int_0^\infty \mathrm{d}\rho \frac{1}{\rho^{\frac{D}{2}-1}} J_{\frac{D}{2}+L-1}(\rho) \\ &= \frac{\Gamma\left(\frac{L}{2}+\frac{1}{2}\right)}{2^{\frac{D}{2}-1}\Gamma\left(\frac{L}{2}+\frac{D}{2}-\frac{1}{2}\right)} \times \frac{\sqrt{\mu}}{\xi} \end{aligned} \tag{24}$$

The integral of the angular part can be easily carried out

$$\int d\Omega_k Y^*_{l_1\mu_1}(\Omega_k) Y^*_{l_2\mu_2}(-\Omega_k) = (-1)^{l_2}\int d\Omega_k Y^*_{l_1\mu_1}(\Omega_k) Y_{l_2\mu_2}(\Omega_k)$$
$$= (-1)^{l_2}\delta_{l_1,l_2}\delta_{\mu_1,\mu_2} \quad (25)$$

Since $L = 2n + l_1 + l_2$, Eq. (25) indicates that

$$i^L = (-1)^n. \quad (26)$$

Combining Eq. (23), (24), (25) and Eq. (26), we get the expression of the expansion coefficient $C^D_{|L|}$ as

$$C^D_{|L|} = \frac{2(2\pi)^{\frac{D}{2}-2}}{\xi}(-1)^n N_n^{l_1+\frac{1}{2},l_2+\frac{1}{2}}\left(\frac{\mu}{m_1+m_2}\right)^{\frac{l_1}{2}}$$
$$\times P_n^{l_1+\frac{1}{2},l_2+\frac{1}{2}}\left(\frac{m_1-m_2}{m_1+m_2}\right)\frac{\sqrt{\mu}\,\Gamma\left(\frac{L}{2}+\frac{1}{2}\right)}{2^{\frac{D}{2}-1}\Gamma\left(\frac{L}{2}+\frac{D}{2}-\frac{1}{2}\right)}\delta_{l_1,l_2}\delta_{\mu_1,\mu_2} = \frac{\overline{C^D_{n,l_1}}}{\xi} \quad (27)$$

and thus

$$\frac{1}{r_{12}} = \frac{1}{2\pi^2}\iint dk\, d\Omega_k e^{iK\cdot\xi} = \frac{1}{\xi}\sum_{n,l_1}\overline{C^D_{n,l_1}}\Psi_{n,l_1}(\Omega) \quad (28)$$

where $\overline{C^D_{n,l_1}}$ is the coefficient of $\frac{1}{\xi}$ in C^D_{n,l_1}.

Conclusion

In conclusion, we have expanded the Coulomb potential $\frac{1}{r_{12}}$ of atomic system in terms of hyper-spherical harmonics. We have expressed the expansion coefficient $C^D_{|L|}$ in terms of Jacobi polynomials.

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