

Two-center Integrals in Fourier Space

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2022-09-01

Evaluating Overlap Integral in Fourier Space I

Suppose $\chi_{l,m}(\mathbf{r})$ is a molecular orbital of the form:

$$\chi_{l,m}(\mathbf{r}) = f_l(r) \cdot Y_l^m(\hat{\mathbf{r}}) \quad (1)$$

where $f_l(r)$ is the radial part and Y_l^m is the **complex** spherical harmonics. The Fourier transform of $\chi_{l,m}(\mathbf{r})$ is a function of the same form:

$$\tilde{\chi}_{l,m}(\mathbf{k}) = i^l g_l(k) \cdot Y_l^m(\hat{\mathbf{k}}) \quad (2)$$

where $g_l(k)$ is the spherical Bessel transform (SBT) of $f_l(r)$.

$$g_l(k) = \sqrt{\frac{2}{\pi}} \int_0^\infty j_l(kr) f_l(r) r^2 dr \quad (3)$$

The overlap integral of two different such orbitals can then be written as

$$S(R) = \langle \chi_{l_1,m_1}(\mathbf{r}) | \chi_{l_2,m_2}(\mathbf{r} - \mathbf{R}) \rangle = \int \chi_{l_1,m_1}^*(\mathbf{r}) \chi_{l_2,m_2}(\mathbf{r} - \mathbf{R}) d\mathbf{r} \quad (4)$$

$$= \int \tilde{\chi}_{l_1,m_1}^*(\mathbf{k}) \tilde{\chi}_{l_2,m_2}(\mathbf{k}) e^{-i\mathbf{k} \cdot \mathbf{R}} d\mathbf{k} \quad (5)$$

Remember that the plane wave can be expanded in spherical waves

$$e^{i\mathbf{k} \cdot \mathbf{R}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l i^l j_l(kR) Y_l^{m*}(\hat{\mathbf{k}}) Y_l^m(\hat{\mathbf{R}}) \quad (6)$$

Inserting Eq. (6) into Eq. (5), one get

$$S(R) = 8 \sum_{l=0}^{\infty} \sum_{m=-l}^l i^{-l_1+l_2-l} \int g_{l_1}(k) Y_{l_1}^{m_1*}(\hat{\mathbf{k}}) g_{l_2}(k) Y_{l_2}^{m_2}(\hat{\mathbf{k}}) j_l(kR) Y_l^{m*}(\hat{\mathbf{k}}) Y_l^m(\hat{\mathbf{R}}) k^2 dk d\Omega \quad (7)$$

$$= 8 \sum_{l=0}^{\infty} \sum_{m=-l}^l i^{-l_1+l_2-l} (-1)^{m_1+m} \mathcal{G}(l_1, l_2, l, -m_1, m_2, -m) Y_l^m(\hat{\mathbf{R}}) \int_0^{\infty} g_{l_1}(k) g_{l_2}(k) j_l(kR) k^2 dk \quad (8)$$

where \mathcal{G} is the **Gaunt coefficients**¹ and can be obtained by by recursion from Clebsch–Gordan coefficients.

$$\mathcal{G}(l_1, l_2, l_3, m_1, m_2, m_3) = \int_0^{\pi} \int_0^{2\pi} Y_{l_1}^{m_1}(\hat{\mathbf{k}}) Y_{l_2}^{m_2}(\hat{\mathbf{k}}) Y_l^m(\hat{\mathbf{k}}) \sin \theta d\theta d\phi \quad (9)$$

- Note that $Y_l^{m*}(\theta, \phi) = (-1)^m Y_l^{-m}(\theta, \phi)$ in Eq. (8).
- The integral over k in Eq. (8) is the inverse spherical Bessel transform of $g_{l_1}(k) g_{l_2}(k)$.
- Note that in practice **real** spherical harmonics $Y_{l,m}(\theta, \phi)$ are used, which does not affect the validity of any of previous equations, but the Gaunt coefficients should be modified accordingly.

¹<https://www.theoretical-physics.net/dev/math/spherical-harmonics.html#gaunt-coefficients>

The Gaunt coefficients are related to Wigner-3j symbol by

$$\mathcal{G}(l_1, l_2, l_3, m_1, m_2, m_3) = \sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \quad (10)$$

and obey the following symmetry rules:²

- invariant under space reflection, i.e.

$$\mathcal{G}(l_1, l_2, l_3, m_1, m_2, m_3) = \mathcal{G}(l_1, l_2, l_3, -m_1, -m_2, -m_3) \quad (11)$$

- invariant under any permutation of the columns, i.e.

$$\begin{aligned} \mathcal{G}(l_1, l_2, l_3, m_1, m_2, m_3) &= \mathcal{G}(l_3, l_1, l_2, m_3, m_1, m_2) = \mathcal{G}(l_2, l_3, l_1, m_2, m_3, m_1) \\ &= \mathcal{G}(l_3, l_2, l_1, m_3, m_2, m_1) = \mathcal{G}(l_1, l_3, l_2, m_1, m_3, m_2) \\ &= \mathcal{G}(l_2, l_1, l_3, m_2, m_1, m_3) \end{aligned} \quad (12)$$

- non-zero only for even sum of the l_i , i.e. $l_1 + l_2 + l_3 = 2n$ for $n \in \mathbb{N}$
- non-zero for l_1, l_2, l_3 fulfilling the triangle relation, i.e. $|l_1 - l_2| \leq l_3 \leq l_1 + l_2$.
- non-zero for $m_1 + m_2 + m_3 = 0$

As a result, the sum in Eq. (8) reduces to: $\sum_{l=0}^{\infty} \sum_{m=-l}^l \Rightarrow \sum_{l=|l_1-l_2|}^{l_1+l_2} \sum_{m=-l}^l \delta_{m, m_2-m_1}$

²<https://docs.sympy.org/latest/modules/physics/wigner.html>

Thank you!