

Overlap Integrals in Momentum Space

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Evaluating Overlap Integral in Momentum 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

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

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

Remember that the plane wave can be expanded in spherical waves

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

Evaluating Overlap Integral in Momentum Space II

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

$$S(\mathbf{R}) = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l i^{l_1-l_2-l} \int g_{l_1}(k) Y_{l_1}^{m_1*}(\hat{\mathbf{k}}) g_{l_2}(k) Y_{l_2}^{m_2}(\hat{\mathbf{k}}) j_l(kR) Y_l^{m*}(\hat{\mathbf{k}}) Y_l^m(\hat{\mathbf{R}}) k^2 dk d\Omega \quad (7)$$

$$= 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l i^{l_1-l_2-l} (-1)^{m_1+m} \mathcal{G}(l_1, l_2, l, -m_1, m_2, -m) Y_l^m(\hat{\mathbf{R}}) \int_0^{\infty} g_{l_1}(k) g_{l_2}(k) j_l(kR) k^2 dk \quad (8)$$

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

$$\mathcal{G}(l_1, l_2, l_3, m_1, m_2, m_3) = \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} Y_{l_1}^{m_1}(\theta, \phi) Y_{l_2}^{m_2}(\theta, \phi) Y_l^m(\theta, \phi) \sin \theta d\theta d\phi \quad (9)$$

- Note that $Y_l^{m*}(\theta, \phi) = (-1)^m Y_l^{-m}(\theta, \phi)$ from Eq. (7) to 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.

$$S(\mathbf{R}) = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l i^{l_1-l_2-l} \mathcal{G}'(l_1, l_2, l, m_1, m_2, m) Y_{l,m}(\hat{\mathbf{R}}) \int_0^{\infty} g_{l_1}(k) g_{l_2}(k) j_l(kR) k^2 dk \quad (10)$$

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

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

$$\mathcal{G}(l_1, l_2, l_3, m_1, m_2, m_3) = \sqrt{\frac{(2l_1 + 1)(2l_2 + 1)(2l_3 + 1)}{4\pi}} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \quad (11)$$

and obey the following symmetry rules:²

- ① invariant under space reflection, i.e.

$$\mathcal{G}(l_1, l_2, l_3, m_1, m_2, m_3) = \mathcal{G}(l_1, l_2, l_3, -m_1, -m_2, -m_3) \quad (12)$$

- ② invariant under any permutation of the columns, i.e.

$$\begin{aligned} \mathcal{G}(l_1, l_2, l_3, m_1, m_2, m_3) &= \mathcal{G}(l_3, l_1, l_2, m_3, m_1, m_2) = \mathcal{G}(l_2, l_3, l_1, m_2, m_3, m_1) \\ &= \mathcal{G}(l_3, l_2, l_1, m_3, m_2, m_1) = \mathcal{G}(l_1, l_3, l_2, m_1, m_3, m_2) \\ &= \mathcal{G}(l_2, l_1, l_3, m_2, m_1, m_3) \end{aligned} \quad (13)$$

- ③ non-zero only for even sum of the l_i , i.e. $l_1 + l_2 + l_3 = 2n$ for $n \in \mathbb{N}$
- ④ non-zero for l_1, l_2, l_3 fulfilling the triangle relation, i.e. $|l_1 - l_2| \leq l_3 \leq l_1 + l_2$.
- ⑤ non-zero for $m_1 + m_2 + m_3 = 0$

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

Gaunt Coefficients Properties II

Real and complex spherical harmonics can be inter-transformed with a **unitary** matrix U^l , i.e.

$$Y_{l,m}(\theta, \phi) = \sum_{n=0}^{2l+1} U_{m,n}^l Y_l^{n-l}(\theta, \phi) = \begin{cases} \frac{i}{\sqrt{2}}(Y_l^m - (-1)^m Y_l^{-m}) & \text{if } m < 0 \\ Y_l^0 & \text{if } m = 0 \\ \frac{1}{\sqrt{2}}(Y_l^{-|m|} + (-1)^m Y_l^m) & \text{if } m > 0 \end{cases} \quad (14)$$

The Gaunt coefficients defined with **real** spherical harmonics $Y_{l,m}$ can be written as

$$\mathcal{G}'(l_1, l_2, l_3, m_1, m_2, m_3) = \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} Y_{l_1, m_1}(\theta, \phi) Y_{l_2, m_2}(\theta, \phi) Y_{l_3, m_3}(\theta, \phi) \sin \theta d\theta d\phi \quad (15)$$

$$= \sum_{n_1=0}^{2l_1+1} \sum_{n_2=0}^{2l_2+1} \sum_{n_3=0}^{2l_3+1} U_{m_1, n_1}^{l_1} U_{m_2, n_2}^{l_2} U_{m_3, n_3}^{l_3} \mathcal{G}(l_1, l_2, l_3, n_1-l_1, n_2-l_2, n_3-l_3) \quad (16)$$

The properties of $\mathcal{G}'(l_1, l_2, l_3, m_1, m_2, m_3)$ are:

- ① **not** invariant under space reflection
- ② invariant under any permutation of the columns
- ③ non-zero only for even sum of the l_i , i.e. $l_1 + l_2 + l_3 = 2n$ for $n \in \mathbb{N}$
- ④ non-zero for l_1, l_2, l_3 fulfilling the triangle relation, i.e. $|l_1 - l_2| \leq l_3 \leq l_1 + l_2$.
- ⑤ zero for $m_1 < 0, m_2 < 0$ and $m_3 < 0$
- ⑥ if $m_1 > 0, m_2 > 0$ and $m_3 > 0$, then non-zero for $m_1 + m_2 + m_3 = 2n$ for $n \in \mathbb{N}$

Thank you!