Overlap Integrals in Momentum Space

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Evaluting Overlap Integral in Momentum Space I

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

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

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:

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

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

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

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

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

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

Remember that the plane wave can be expanded in spherical waves

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

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

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

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

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

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

- 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.

$$S(R) = 8\sum_{l=0}^{\infty}\sum_{m=-l}^{l} i^{-l_1+l_2-l}\mathcal{G}'(l_1,l_2,l,m_1,m_2,m)\,Y_{l,m}(\hat{\mathbf{R}})\int_0^{\infty} g_{l_1}(k)g_{l_2}(k)j_l(kR)\;k^2\mathrm{d}k \tag{10}$$

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

Gaunt Coefficients Properties I

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

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

and obey the following symmetry rules:[2]

1. invariant under space reflection, i.e.

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

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

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

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. $|l_1 - l_2| \leqslant l \leqslant l_1 + l_2$.
5. non-zero for $m_1 + m_2 + m_3 = 0$

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

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

$$Y_{l,m}(\theta,\phi) = \sum_{n=0}^{2l+1} U^l_{m,n} Y_l^{n-l}(\theta,\phi) \tag{14}$$

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

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

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

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. $|l_1-l_2|\leqslant l\leqslant l_1+l_2$.
5. non-zero for $m_1+m_2+m_3\neq 0$

[2] https://docs.sympy.org/latest/modules/physics/wigner.html

Thank you!