Two-center Integrals in Fourier Space

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Evaluating Overlap Integral in Fourier Space I

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

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

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

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

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

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

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

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

$$\mathcal{G}(l_1,m_1,l_2,m_2,l,m) = \int_0^{\pi}\int_0^{2\pi} Y_{l_1}^{m_1}(\hat{\mathbf{k}})\;Y_{l_2}^{m_2}(\hat{\mathbf{k}})\;Y_l^{m}(\hat{\mathbf{k}})\,\mathrm{d}\theta\mathrm{d}\phi \tag{9}$$

- 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

Thank you!