1 Slater-type orbitals

A real Slater-type orbital (STO) is defined as follows:

$$\chi_{nlm}(\zeta, \mathbf{r}) = N_n(\zeta) R_n(r, \zeta) S_{lm}(\theta, \phi) \tag{1}$$

where

$$N_n(\zeta) = \frac{(2\zeta)^{n+\frac{1}{2}}}{\sqrt{(2n)!}} \tag{2}$$

is the normalization factor,

$$R_n(r, \zeta) = r^{n-1} e^{-\zeta r} \tag{3}$$

is the radial part and $S_{lm}(\theta, \phi)$ is a real spherial harmonic.

2 Prolate spheroidal coordinates

For two-center integrals, it is more convenient to align the coordinate system of the two centers along the z-axis and use prolate spheroidal coordinates. In order to switch from spherical coordinates to the new coordinate system, we use the following identities:

$$\begin{aligned} r_a &= \frac{R(\mu+\nu)}{2}; \quad \cos\theta_a = \frac{1+\mu\nu}{\mu+\nu}; \quad \sin\theta_a = \frac{\sqrt{(\mu^2-1)(1-\nu^2)}}{\mu+\nu}; \\ r_b &= \frac{R(\mu-\nu)}{2}; \quad \cos\theta_b = \frac{1-\mu\nu}{\mu-\nu}; \quad \sin\theta_b = \frac{\sqrt{(\mu^2-1)(1-\nu^2)}}{\mu-\nu} \end{aligned} \tag{4}$$

Inside the integrals this change gives

$$\mathrm{d}V = \frac{R^3}{8}(\mu+\nu)(\mu-\nu)\mathrm{d}\mu\mathrm{d}\nu\mathrm{d}\phi \tag{5}$$

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3 Overlap integrals

The one-center overlap integrals

$$S_{nlm,n'l'm'}(\zeta, \zeta') = \int \chi^\star_{nlm}(\zeta, \mathbf{r}) \chi_{n'm'l'}(\zeta', \mathbf{r}) \mathrm{d}V \tag{6}$$

is the most straightforward molecular integrals and is readily evaluated in spherical coordinates. The integration of the radial part yields

$$\int_0^\infty R_n(\zeta, r) R_{n'}(\zeta', r) r^2 \mathrm{d}r = \frac{(n+n')!}{(\zeta+\zeta')^{n+n'+1}} \tag{7}$$

and using the orthonormality condition of the spherical harmonics, the analytical form of one-center overlap is

$$S_{nlm,n'l'm'}(\zeta, \zeta') = N_n(\zeta) N_{n'}(\zeta') \frac{(n+n')!}{(\zeta+\zeta')^{n+n'+1}} \delta_{ll'} \delta_{mm'} \tag{8}$$