22.6.5: iv. Review Exercise Solutions

Q1

Slater type orbitals (STOs) are "hydrogen-like" in that they have a normalized form of:

$$\left(\frac{2\xi}{a_0}\right)^{n+\frac{1}{2}}\left(\frac{1}{(2n)!}\right)^{\frac{1}{2}} r^{n-1}e^{\left(\frac{-\xi r}{a_0}\right)}Y_{l,m}(\theta,\phi),$$

where as gaussian type orbitals GTOs have the form:

$$N' x^a y^b z^c e^{(-\alpha r^2)},$$

where a, b, and c are quantum numbers each ranging from zero upward in unit steps. So, STOs give "better" overall energies and properties that depend on the shape of the wavefunction near the nuclei (e.g., Fermi contact ESR hyperfine constants) but they are more difficult to use (two-electron integrals are more difficult to evaluate; especially the 4- center variety which have to be integrated numerically). GTOs on the other hand are easier to use (more easily integrable) but improperly describe the wavefunction near the nuclear centers because of the so-called cusp condition (they have zero slope at R = 0, whereas 1s STOs have non-zero slopes there).