2.2.1 Transition from spin states to spin-orbital states

All our development so far has treated spin states independently of the orbital part of the wavefunction. Now we will begin to unify the spatial and spin degrees of freedom by considering spin-orbital states, generalizations of spatial orbitals accounting for spin degrees of freedom.

Consider the HF energy of one natural bond & weak:

$E_0 = \langle \Phi_0 | H | \Phi_0 \rangle = \langle \Phi_0 | h | \Phi_0 \rangle + \langle \Phi_0 | g | \Phi_0 \rangle = \sum_{i=1}^{N} \langle \chi_i | h | \chi_i \rangle + \sum_{i<j}^{N} \langle \chi_i \chi_j | r_{12}^{-1} | \chi_i \chi_j \rangle - \langle \chi_i \chi_j | r_{12}^{-1} | \chi_j \chi_i \rangle$ (physicist notation) (chemist notation)

Recall:

$\langle \Phi_0 | h | \Phi_0 \rangle = \langle \Phi_0 | \Phi_0 \rangle \langle \chi_i | h | \chi_i \rangle$

$\langle \Phi_0 | g | \Phi_0 \rangle = \langle \Phi_0 | \Phi_0 \rangle \langle \chi_i \chi_j | r_{12}^{-1} | \chi_i \chi_j \rangle - \langle \chi_i \chi_j | r_{12}^{-1} | \chi_j \chi_i \rangle$

If $\Phi_0 = \langle \Phi_0 | \Phi_0 \rangle = \langle \chi_i | \chi_i \rangle \langle \chi_j | \chi_j \rangle + \langle \chi_i | \chi_j \rangle \langle \chi_j | \chi_i \rangle = \langle \chi_i | \chi_i \rangle \langle \chi_j | \chi_j \rangle$

For one-electron hamiltonian:

$\langle \Phi_0 | h | \Phi_0 \rangle = \langle \chi_i | h | \chi_i \rangle$

$\langle \Phi_0 | \Phi_0 \rangle \langle \chi_i | h | \chi_i \rangle$ (no dependency, one integral equals one, does not depend on spin)

$\langle \Phi_0 | h | \Phi_0 \rangle = \langle \chi_i | h | \chi_i \rangle$ (physicist)

$\langle \Phi_0 | h | \Phi_0 \rangle = \langle \chi_i | h | \chi_i \rangle$ (chemist)

Since:

$\langle \chi_i | h | \chi_i \rangle = \langle \chi_i | h | \chi_i \rangle$ $\langle \chi_i | h | \chi_i \rangle = \langle \chi_i | h | \chi_i \rangle$

$\langle \chi_i | h | \chi_i \rangle = \langle \chi_i | h | \chi_i \rangle$ $\langle \chi_i | h | \chi_i \rangle = 0$

the quantum indistinc is

$\therefore$ So no-cluster contribution to E_0 is: $2 \langle \Phi_0 | h | \Phi_0 \rangle$

So, the two-electron integral, or HF ground state energy:

$E_0 = -\langle \chi_i \chi_j | r_{12}^{-1} | \chi_i \chi_j \rangle - \langle \chi_i \chi_j | r_{12}^{-1} | \chi_j \chi_i \rangle$

$\langle \chi_i \chi_j | r_{12}^{-1} | \chi_i \chi_j \rangle = \langle \chi_i \chi_j | r_{12}^{-1} | \chi_j \chi_i \rangle$ $\langle \chi_i \chi_j | r_{12}^{-1} | \chi_i \chi_j \rangle =