4.5 Many-electron Wave Functions

4.5.1. Hartree-product Wave Functions

- One-electron Shrodinger equation: $h_i \psi_i = \varepsilon_i \psi_i$
- Because the Hamiltonian operator defined is separable, its many electron eigenfunctions can be constructed as products of one-electron eigenfunctions.:

$$\psi_{HP} = \psi_1 \psi_2 \ldots \psi_N$$

"Hartree-product" wave function

Therefore, $H\psi_{HP} \Rightarrow H\psi_1\psi_2\ldots\psi_N = \left(\sum_{i=1}^{N} \varepsilon_i\right)\psi_{HP}$

energy eigenvalue of the many-electron wave function is simply the sum of the one-electron energy eigenvalues.

4.5.2 The Hartree Hamiltonian

- Accounts for electron-electron interactions in a confusing way, where they state that e^-s are in "non-interacting" system of electrons, where each e^- sees constant potential, which derived from other electrons, but their interaction is not accounted for instantaneously.

- If we were to sum up all of the one-electron eigenvalues for the operators h_i, which would give us the eigenvalue of our non-interacting Hamiltonian, we would double count the $e^- - e^-$ repulsion.

$$E = \sum_i \varepsilon_i - \frac{1}{2} \sum_{i \neq j} \underbrace{\iint \frac{|\psi_i|^2 |\psi_j|^2}{r_{ij}} \, dr_i \, dr_j}_{\text{"Coulomb integral"}}$$

4.5.3 Electron Spin and Antisymmetry

- all electrons are characterized by a spin quantum number (m_s)
- 2 eigenvalues possible: $\frac{\pm\hbar}{2}$;
- the spin eigenfunctions are orthonormal and are typically denoted as $\underbrace{\alpha \text{ and } \beta}_{\text{different from Hückel Theory.}}$
- m_s is a natural consequence of the application of relativistic quantum mechanics to the electron
- also Pauli exclusion principle comes from relativistic quantum mechanics

no 2 e^-s can have same set of quantum #s. ⇒ thus only 2 choices α or β in a MO

only 2 e^-s can be put in any MO

- electronic wave functions must <u>change sign</u> whenever the coordinates of two e^-s are interchanged. (antisymmetric wavefunction)

$$\underbrace{{}^3\Psi_{SD} = \frac{1}{\sqrt{2}}\left[\Psi_a(1)\alpha(1)\Psi_b(2)\alpha(2) - \Psi_a(2)\alpha(2)\Psi_b(1)\alpha(1)\right]}_{\text{Satisfies Pauli-Exclusion principle}}$$

this comes from Slater Determinants

4.5.4 Slater Determinants

The equation from previous section can be also described as

$$^{3}\Psi_{SD} = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_a(1)\alpha(1) & \psi_b(1)\alpha(1) \\ \psi_a(2)\alpha(2) & \psi_b(2)\alpha(2) \end{vmatrix}$$

This tells us that equation that we got in previous section was obtained by utilizing matrix

when you integrate this, you don't get term K_{ab}, classical coulomb repulsion b/w the e^- clouds in orbitals a and b.

4.5.5 The Hartree-Fock Self-consistent Field Method

The One-electron Fock operator for each e^-, i as:

$$f_i = -\frac{1}{2}\nabla_i^2 - \sum_k^{nuclei} \frac{Z_k}{r_{ik}} + V_i^{HF}\{j\}$$

Substitute Laplacian's equation/operator

HF potential $(2J_i - K_i)$

- HF method follows SCF procedure, just as Hartree method, where we first guess the orbital coefficients and then iterate to convergence.

- HF primary limitation is the one-electron nature of the Fock operators. All electron correlation is ignored.

- HF theory provides a very well defined energy, one which can be converged in the limit of an infinite basis set, and the difference b/w that converged E and reality is the e^- correlation E

- Flow chart of the HF SCF procedure is available on page 129 of the book.