

Modern Quantum Chemistry, Szabo & Ostlund

HW

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August 31, 2019

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2 Many-electron Wave Functions and Operators

2.1 The Electronic Problem

2.1.1 Atomic Units

2.1.2 The B-O Approximation

2.1.3 The Antisymmetry or Pauli Exclusion Principle

2.2 Orbitals, Slater Determinants, and Basis Functions

2.2.1 Spin Orbitals and Spatial Orbitals

Ex 2.1 Consider $\langle \chi_k | \chi_m \rangle$. If $k = m$,

$$\langle \chi_{2i-1} | \chi_{2i-1} \rangle = \langle \psi_i^\alpha | \psi_i^\alpha \rangle \langle \alpha | \alpha \rangle = 1 \quad (2.2.1)$$

$$\langle \chi_{2i} | \chi_{2i} \rangle = \langle \psi_i^\beta | \psi_i^\beta \rangle \langle \alpha | \alpha \rangle = 1 \quad (2.2.2)$$

thus

$$\langle \chi_k | \chi_k \rangle = 1 \quad (2.2.3)$$

If $k \neq m$, three cases may occur as below

$$\langle \chi_{2i-1} | \chi_{2j-1} \rangle = \langle \psi_i^\alpha | \psi_j^\alpha \rangle \langle \alpha | \alpha \rangle = 0 \cdot 1 = 0 \quad (i \neq j) \quad (2.2.4)$$

$$\langle \chi_{2i-1} | \chi_{2j} \rangle = \langle \psi_i^\alpha | \psi_j^\beta \rangle \langle \alpha | \beta \rangle = S_{ij} \cdot 0 = 0 \quad (2.2.5)$$

$$\langle \chi_{2i} | \chi_{2j} \rangle = \langle \psi_i^\beta | \psi_j^\beta \rangle \langle \beta | \beta \rangle = 0 \cdot 1 = 0 \quad (i \neq j) \quad (2.2.6)$$

thus

$$\langle \chi_k | \chi_m \rangle = 0 \quad (k \neq m) \quad (2.2.7)$$

Overall,

$$\langle \chi_k | \chi_m \rangle = \delta_{km} \quad (2.2.8)$$

2.2.2 Hartree Products

Ex 2.2

$$\begin{aligned} \mathcal{H}\Psi^{HP} &= \sum_{i=1}^N h(i) \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) \cdots \chi_k(\mathbf{x}_N) \\ &= \varepsilon_i \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) \cdots \chi_k(\mathbf{x}_N) + \chi_i(\mathbf{x}_1) [\varepsilon_j \chi_j(\mathbf{x}_2)] \cdots \chi_k(\mathbf{x}_N) + \cdots + \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) \cdots [\varepsilon_k \chi_k(\mathbf{x}_N)] \\ &= (\varepsilon_i + \varepsilon_j + \cdots + \varepsilon_k) \Psi^{HP} \end{aligned} \quad (2.2.9)$$

2.2.3 Slater Determinants

Ex 2.3

$$\begin{aligned} \langle \Psi | \Psi \rangle &= \frac{1}{2} (\langle \chi_i | \chi_i \rangle \langle \chi_j | \chi_j \rangle - \langle \chi_i | \chi_j \rangle \langle \chi_j | \chi_i \rangle - \langle \chi_j | \chi_i \rangle \langle \chi_i | \chi_j \rangle + \langle \chi_j | \chi_j \rangle \langle \chi_i | \chi_i \rangle) \\ &= \frac{1}{2} (1 + 0 + 0 + 1) = 1 \end{aligned} \quad (2.2.10)$$

Ex 2.4 According to Ex. 2.2, we know that $\chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2)$ are an eigenfunction of \mathcal{H} and has the eigenvalue $\varepsilon_i \varepsilon_j$. Similarly, we have the same conclusion for $\chi_i(\mathbf{x}_2) \chi_j(\mathbf{x}_1)$.

For the antisymmetrized wave function,

$$\begin{aligned} \langle \Psi | \mathcal{H} | \Psi \rangle &= \frac{1}{2} (\langle \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) | \mathcal{H} | \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) \rangle - \langle \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) | \mathcal{H} | \chi_j(\mathbf{x}_1) \chi_i(\mathbf{x}_2) \rangle \\ &\quad - \langle \chi_j(\mathbf{x}_1) \chi_i(\mathbf{x}_2) | \mathcal{H} | \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) \rangle + \langle \chi_j(\mathbf{x}_1) \chi_i(\mathbf{x}_2) | \mathcal{H} | \chi_j(\mathbf{x}_1) \chi_i(\mathbf{x}_2) \rangle) \\ &= \frac{1}{2} (\varepsilon_i + \varepsilon_j - 0 - 0 + \varepsilon_i + \varepsilon_j) \\ &= \varepsilon_i + \varepsilon_j \end{aligned} \quad (2.2.11)$$

Ex 2.5

$$\begin{aligned}
\langle K | L \rangle &= \frac{1}{2} \langle \chi_i(\mathbf{x}_1) \chi_j(\mathbf{x}_2) - \chi_j(\mathbf{x}_1) \chi_i(\mathbf{x}_2) | \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2) - \chi_l(\mathbf{x}_1) \chi_k(\mathbf{x}_2) \rangle \\
&= \frac{1}{2} (\langle \chi_i | \chi_k \rangle \langle \chi_j | \chi_l \rangle - \langle \chi_i | \chi_l \rangle \langle \chi_j | \chi_k \rangle - \langle \chi_j | \chi_k \rangle \langle \chi_i | \chi_l \rangle + \langle \chi_j | \chi_l \rangle \langle \chi_i | \chi_k \rangle) \\
&= \frac{1}{2} (\delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk} - \delta_{jk} \delta_{il} + \delta_{jl} \delta_{ik}) \\
&= \delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk}
\end{aligned} \tag{2.2.12}$$

2.2.4 The Hartree-Fock Approximation

2.2.5 The Minimal Basis H₂ Model

Ex 2.6

$$\langle \psi_1 | \psi_1 \rangle = \frac{1}{2(1+S_{12})} (\langle \phi_1 | \phi_1 \rangle + 2 \langle \phi_1 | \phi_2 \rangle + \langle \phi_2 | \phi_2 \rangle) = \frac{2+2S_{12}}{2(1+S_{12})} = 1 \tag{2.2.13}$$

$$\langle \psi_2 | \psi_2 \rangle = \frac{1}{2(1-S_{12})} (\langle \phi_1 | \phi_1 \rangle - 2 \langle \phi_1 | \phi_2 \rangle + \langle \phi_2 | \phi_2 \rangle) = \frac{2-2S_{12}}{2(1-S_{12})} = 1 \tag{2.2.14}$$

$$\langle \psi_1 | \psi_2 \rangle = \frac{1}{2\sqrt{1+S_{12}}\sqrt{1-S_{12}}} (\langle \phi_1 | \phi_1 \rangle - \langle \phi_2 | \phi_2 \rangle) = 0 \tag{2.2.15}$$

2.2.6 Excited Determinants

2.2.7 Form of the Exact Wfn and CI

Ex 2.7

$$C_{72}^{42} = 164307576757973059488 \tag{2.2.16}$$