

Modern Quantum Chemistry, Szabo & Ostlund

HW

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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 Size of full CI matrix

$$C_{72}^{42} = 164307576757973059488 \approx 1.64 \times 10^{20} \tag{2.2.16}$$

The number of singly excited determinants

$$42 \times 30 = 1260 \tag{2.2.17}$$

The number of doubly excited determinants

$$C_{42}^2 C_{30}^2 = 374535 \tag{2.2.18}$$

2.3 Operators and Matrix Elements

2.3.1 Minimal Basis H₂ Matrix Elements

Ex 2.8

$$\begin{aligned}
\langle \Psi_{12}^{34} | h(1) | \Psi_{12}^{34} \rangle &= \frac{1}{2} \langle \chi_3(\mathbf{x}_1) \chi_4(\mathbf{x}_2) - \chi_3(\mathbf{x}_2) \chi_4(\mathbf{x}_1) | h(1) | \chi_3(\mathbf{x}_1) \chi_4(\mathbf{x}_2) - \chi_3(\mathbf{x}_2) \chi_4(\mathbf{x}_1) \rangle \\
&= \frac{1}{2} (\langle \chi_3 | h(1) | \chi_3 \rangle - 0 - 0 + \langle \chi_4 | h(1) | \chi_4 \rangle) \\
&= \frac{1}{2} (\langle \chi_3 | h(1) | \chi_3 \rangle + \langle \chi_4 | h(1) | \chi_4 \rangle)
\end{aligned} \tag{2.3.1}$$

thus

$$\langle \Psi_{12}^{34} | \mathcal{O}_1 | \Psi_{12}^{34} \rangle = \langle 3 | h | 3 \rangle + \langle 4 | h | 4 \rangle \tag{2.3.2}$$

$$\begin{aligned}
\langle \Psi_0 | h(1) | \Psi_{12}^{34} \rangle &= \frac{1}{2} \langle \chi_1(\mathbf{x}_1) \chi_2(\mathbf{x}_2) - \chi_2(\mathbf{x}_2) \chi_1(\mathbf{x}_1) | h(1) | \chi_3(\mathbf{x}_1) \chi_4(\mathbf{x}_2) - \chi_3(\mathbf{x}_2) \chi_4(\mathbf{x}_1) \rangle \\
&= \frac{1}{2} (0 - 0 - 0 + 0) \\
&= 0
\end{aligned} \tag{2.3.3}$$

thus

$$\langle \Psi_0 | \mathcal{O}_1 | \Psi_{12}^{34} \rangle = 0 \tag{2.3.4}$$

Similarly, we get

$$\langle \Psi_{12}^{34} | \mathcal{O}_1 | \Psi_0 \rangle = 0 \tag{2.3.5}$$

Ex 2.9 From Eq. (2.92) in textbook, we get

$$\langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle = \langle 1 | h | 1 \rangle + \langle 2 | h | 2 \rangle + \langle 12 | 12 \rangle - \langle 12 | 21 \rangle \quad (2.3.6)$$

From Ex 2.8, we get

$$\langle \Psi_0 | \mathcal{O}_1 | \Psi_{12}^{34} \rangle = \langle \Psi_{12}^{34} | \mathcal{O}_1 | \Psi_0 \rangle = 0 \quad (2.3.7)$$

thus

$$\begin{aligned} \langle \Psi_0 | \mathcal{H} | \Psi_{12}^{34} \rangle &= \langle \Psi_0 | \mathcal{O}_2 | \Psi_{12}^{34} \rangle \\ &= \frac{1}{2} \left\langle \chi_1(\mathbf{x}_1) \chi_2(\mathbf{x}_2) - \chi_1(\mathbf{x}_2) \chi_2(\mathbf{x}_1) \left| \frac{1}{r_{12}} \right| \chi_3(\mathbf{x}_1) \chi_4(\mathbf{x}_2) - \chi_3(\mathbf{x}_2) \chi_4(\mathbf{x}_1) \right\rangle \\ &= \langle 12 | 34 \rangle - \langle 12 | 43 \rangle \end{aligned} \quad (2.3.8)$$

$$\begin{aligned} \langle \Psi_{12}^{34} | \mathcal{H} | \Psi_0 \rangle &= \langle \Psi_{12}^{34} | \mathcal{O}_2 | \Psi_0 \rangle \\ &= \frac{1}{2} \left\langle \chi_3(\mathbf{x}_1) \chi_4(\mathbf{x}_2) - \chi_3(\mathbf{x}_2) \chi_4(\mathbf{x}_1) \left| \frac{1}{r_{12}} \right| \chi_1(\mathbf{x}_1) \chi_2(\mathbf{x}_2) - \chi_2(\mathbf{x}_2) \chi_1(\mathbf{x}_1) \right\rangle \\ &= \langle 34 | 12 \rangle - \langle 34 | 21 \rangle \end{aligned} \quad (2.3.9)$$

$$\begin{aligned} \langle \Psi_{12}^{34} | \mathcal{H} | \Psi_{12}^{34} \rangle &= \left\langle \Psi_{12}^{34} \left| h(1) + h(2) + \frac{1}{r_{12}} \right| \Psi_{12}^{34} \right\rangle \\ &= 2 \times \frac{1}{2} \langle \chi_3(\mathbf{x}_1) \chi_4(\mathbf{x}_2) - \chi_3(\mathbf{x}_2) \chi_4(\mathbf{x}_1) | h(1) | \chi_3(\mathbf{x}_1) \chi_4(\mathbf{x}_2) - \chi_3(\mathbf{x}_2) \chi_4(\mathbf{x}_1) \rangle \\ &\quad + \frac{1}{2} \left\langle \chi_3(\mathbf{x}_1) \chi_4(\mathbf{x}_2) - \chi_3(\mathbf{x}_2) \chi_4(\mathbf{x}_1) \left| \frac{1}{r_{12}} \right| \chi_3(\mathbf{x}_1) \chi_4(\mathbf{x}_2) - \chi_3(\mathbf{x}_2) \chi_4(\mathbf{x}_1) \right\rangle \\ &= \langle 3 | h | 3 \rangle + \langle 4 | h | 4 \rangle + \langle 34 | 34 \rangle - \langle 34 | 43 \rangle \end{aligned} \quad (2.3.10)$$

2.3.2 Notations for 1- and 2-Electron Integrals

2.3.3 General Rules for Matrix Elements

Ex 2.10

$$\langle K | \mathcal{H} | K \rangle = \sum_m^N [m|h|m] + \frac{1}{2} \sum_m^N \sum_n^N \langle mn || mn \rangle = \sum_m^N [m|h|m] + \frac{1}{2} \sum_m^N \sum_n^N ([mm|nn] - [mn|nm]) \quad (2.3.11)$$

When $m = n$,

$$[mm|mm] - [mm|mm] = 0 \quad (2.3.12)$$

thus

$$\langle K | \mathcal{H} | K \rangle = \sum_m^N [m|h|m] + \frac{1}{2} \sum_m^N \sum_{n \neq m}^N ([mm|nn] - [mn|nm]) = \sum_m^N [m|h|m] + \sum_m^N \sum_{n > m}^N ([mm|nn] - [mn|nm]) \quad (2.3.13)$$

Ex 2.11

$$\begin{aligned} \langle K | \mathcal{H} | K \rangle &= \langle K | \mathcal{O}_1 + \mathcal{O}_2 | K \rangle = \sum_m^N [m|h|m] + \sum_m^N \sum_{n > m}^N \langle mn || mn \rangle \\ &= \langle 1 | h | 1 \rangle + \langle 2 | h | 2 \rangle + \langle 3 | h | 3 \rangle + \langle 12 || 12 \rangle + \langle 13 || 13 \rangle + \langle 23 || 23 \rangle \end{aligned} \quad (2.3.14)$$

Ex 2.12

$$\begin{aligned} \langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle &= \langle 1 | h | 1 \rangle + \langle 2 | h | 2 \rangle + \langle 12 || 12 \rangle \\ &= \langle 1 | h | 1 \rangle + \langle 2 | h | 2 \rangle + \langle 12 | 12 \rangle - \langle 12 | 21 \rangle \end{aligned} \quad (2.3.15)$$

$$\langle \Psi_0 | \mathcal{H} | \Psi_{12}^{34} \rangle = \langle 12 || 34 \rangle = \langle 12 | 34 \rangle - \langle 12 | 43 \rangle \quad (2.3.16)$$

$$\langle \Psi_{12}^{34} | \mathcal{H} | \Psi_0 \rangle = \langle 34 || 12 \rangle = \langle 34 | 12 \rangle - \langle 34 | 21 \rangle \quad (2.3.17)$$

$$\begin{aligned} \langle \Psi_{12}^{34} | \mathcal{H} | \Psi_{12}^{34} \rangle &= \langle 3 | h | 3 \rangle + \langle 4 | h | 4 \rangle + \langle 34 || 34 \rangle \\ &= \langle 3 | h | 3 \rangle + \langle 4 | h | 4 \rangle + \langle 34 | 34 \rangle - \langle 34 | 43 \rangle \end{aligned} \quad (2.3.18)$$

Which are exactly the same with Ex 2.9.

Ex 2.13 if $a = b, r = s$

$$\langle \Psi_a^r | \mathcal{O} | \Psi_b^s \rangle = \langle \Psi_a^r | \mathcal{O}_1 | \Psi_a^r \rangle = \sum_c^N \langle c | h | c \rangle - \langle a | h | a \rangle + \langle r | h | r \rangle \quad (2.3.19)$$

if $a = b, r \neq s$

$$\langle \Psi_a^r | \mathcal{O} | \Psi_b^s \rangle = \langle \Psi_a^r | \mathcal{O}_1 | \Psi_a^s \rangle = \langle r | h | s \rangle \quad (2.3.20)$$

if $a \neq b, r = s$

$$\langle \Psi_a^r | \mathcal{O} | \Psi_b^s \rangle = \langle \Psi_a^r | \mathcal{O}_1 | \Psi_b^r \rangle = \langle \Psi_a^r | \mathcal{O}_1 | -(\Psi_a^r)_b^a \rangle = -\langle b | h | a \rangle \quad (2.3.21)$$

if $a \neq b, r \neq s$

$$\langle \Psi_a^r | \mathcal{O} | \Psi_b^s \rangle = \langle \Psi_a^r | \mathcal{O}_1 | (\Psi_a^r)_{rb}^{as} \rangle = 0 \quad (2.3.22)$$

Ex 2.14

$${}^N E_0 = \sum_m^N \langle m | h | m \rangle + \sum_m^M \sum_{n>m}^M \langle mn || mn \rangle \quad (2.3.23)$$

$${}^{N-1} E_0 = \sum_{m \neq a}^N \langle m | h | m \rangle + \sum_{m \neq a}^M \sum_{n>m, n \neq a}^M \langle mn || mn \rangle \quad (2.3.24)$$

$${}^N E_0 - {}^{N-1} E_0 = \langle a | h | a \rangle + \sum_{b \neq a}^N \langle ab || ab \rangle \quad (2.3.25)$$

2.3.4 Derivation of the Rules for Matrix Elements