Modern Quantum Chemistry, Szabo & Ostlund
HW

王石嵘

August 31, 2019

Contents

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 $k = m$,

$$\langle \chi_{2i-1} \,|\, \chi_{2i-1} \rangle = \langle \psi_i^\alpha \,|\, \psi_i^\alpha \rangle \langle \alpha \,|\, \alpha \rangle = 1 \tag{2.2.1}$$

$$\langle \chi_{2i} \,|\, \chi_{2i} \rangle = \left\langle \psi_i^\beta \,\middle|\, \psi_i^\beta \right\rangle \langle \alpha \,|\, \alpha \rangle = 1 \tag{2.2.2}$$

thus

$$\langle \chi_k \,|\, \chi_k \rangle = 1 \tag{2.2.3}$$

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

$$\langle \chi_{2i-1} \,|\, \chi_{2j-1} \rangle = \left\langle \psi_i^\alpha \,\middle|\, \psi_j^\alpha \right\rangle \langle \alpha \,|\, \alpha \rangle = 0 \cdot 1 = 0 \qquad (i \neq j) \tag{2.2.4}$$

$$\langle \chi_{2i-1} \,|\, \chi_{2j} \rangle = \left\langle \psi_i^\alpha \,\middle|\, \psi_j^\beta \right\rangle \langle \alpha \,|\, \beta \rangle = S_{ij} \cdot 0 = 0 \tag{2.2.5}$$

$$\langle \chi_{2i} \,|\, \chi_{2j} \rangle = \left\langle \psi_i^\beta \,\middle|\, \psi_j^\beta \right\rangle \langle \beta \,|\, \beta \rangle = 0 \cdot 1 = 0 \qquad (i \neq j) \tag{2.2.6}$$

thus

$$\langle \chi_k \,|\, \chi_m \rangle = 0 \qquad (k \neq m) \tag{2.2.7}$$

Overall,

$$\langle \chi_k \,|\, \chi_m \rangle = \delta_{km} \tag{2.2.8}$$

2.2.2 Hartree Products

Ex 2.2

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

2.2.3 Slater Determinants

Ex 2.3

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

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 $\mathscr{H}$ 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,

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

Ex 2.5

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

2.2.4 The Hartree-Fock Approximation

2.2.5 The Minimal Basis H_2 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 H_2 Matrix Elements

Ex 2.8

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

thus

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

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

thus

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

Similarly, we get

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

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

$$\langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_0 \rangle = \langle 1 \,|\, h \,|\, 1 \rangle + \quad \langle 2 \,|\, h \,|\, 2 \rangle + \langle 12 \,|\, 12 \rangle + \langle 12 \,|\, 21 \rangle \tag{2.3.6}$$