Modern Quantum Chemistry, Szabo & Ostlund
HW

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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,

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

Ex 2.5

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

2.2.4 The Hartree-Fock Approximation

2.2.5 The Minimal Basis 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