

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

Ex 2.15

$$\begin{aligned} \langle \Psi | \mathcal{H} | \Psi \rangle &= \frac{1}{N!} \left\langle \sum_{n=1}^{N!} (-1)^{p_n} \mathcal{P}_n \{ \chi_i(1) \chi_j(2) \cdots \chi_k(N) \} \left| \sum_{c=1}^N h(c) \right| \sum_{m=1}^{N!} (-1)^{p_m} \mathcal{P}_m \{ \chi_i(1) \chi_j(2) \cdots \chi_k(N) \} \right\rangle \\ &= \frac{1}{N!} \sum_{n=1}^{N!} \sum_{m=1}^{N!} (-1)^{p_n+p_m} \sum_{c=1}^N \langle \mathcal{P}_n \{ \chi_i(1) \chi_j(2) \cdots \chi_k(N) \} | h(c) | \mathcal{P}_m \{ \chi_i(1) \chi_j(2) \cdots \chi_k(N) \} \rangle \end{aligned} \quad (2.3.26)$$

Since the integral inside equals 0 when $\mathcal{P}_n \neq \mathcal{P}_m$,

$$\langle \Psi | \mathcal{H} | \Psi \rangle = \frac{1}{N!} \sum_{n=1}^{N!} (-1)^{p_n+p_n} (\varepsilon_i + \varepsilon_j + \cdots + \varepsilon_k) = \varepsilon_i + \varepsilon_j + \cdots + \varepsilon_k \quad (2.3.27)$$

Ex 2.16 Suppose

$$c = \langle K^{HP} | \mathcal{H} | L \rangle = \left\langle K^{HP} \left| \mathcal{H} \right| \sum_{m=1}^{N!} (-1)^{p_m} \mathcal{P}_m L^{HP} \right\rangle \quad (2.3.28)$$

thus

$$\langle K | \mathcal{H} | L \rangle = \sum_{n=1}^{N!} (-1)^{p_n} \left\langle \mathcal{P}_n K^{HP} \left| \mathcal{H} \right| \sum_{m=1}^{N!} (-1)^{p_m} \mathcal{P}_m L^{HP} \right\rangle \quad (2.3.29)$$

2.3.5 Transition from Spin Orbitals to Spatial Orbitals

Ex 2.17

$$\begin{aligned} |1\rangle &= |\psi_1 \alpha\rangle & |2\rangle &= |\psi_1 \beta\rangle \\ |3\rangle &= |\psi_2 \alpha\rangle & |4\rangle &= |\psi_2 \beta\rangle \end{aligned} \quad (2.3.30)$$

thus

$$\begin{aligned} \mathbf{H} &= \begin{pmatrix} \langle 1 | h | 1 \rangle + \langle 2 | h | 2 \rangle + \langle 12 | 12 \rangle - \langle 12 | 21 \rangle & \langle 12 | 34 \rangle - \langle 12 | 43 \rangle \\ \langle 34 | 12 \rangle - \langle 34 | 21 \rangle & \langle 3 | h | 3 \rangle + \langle 4 | h | 4 \rangle + \langle 34 | 34 \rangle - \langle 34 | 43 \rangle \end{pmatrix} \\ &= \begin{pmatrix} 2(1|h|1) + (11|11) & (12|12) \\ (21|21) & 2(2|h|2) + (22|22) \end{pmatrix} \end{aligned} \quad (2.3.31)$$

Ex 2.18

$$\begin{aligned}
|\langle ab || rs \rangle|^2 &= (\langle ab || rs \rangle - \langle ab || sr \rangle)^* (\langle ab || rs \rangle - \langle ab || sr \rangle) \\
&= \langle rs || ab \rangle \langle ab || rs \rangle - \langle rs || ab \rangle \langle ab || sr \rangle - \langle sr || ab \rangle \langle ab || rs \rangle + \langle sr || ab \rangle \langle ab || sr \rangle \\
&= [ra|sb][ar|bs] - [ra|sb][as|br] - [sa|rb][ar|bs] + [sa|rb][as|br] \\
&= [ar|bs]^2 - 2[ar|bs][as|br] + [as|br]^2
\end{aligned} \tag{2.3.32}$$

Let's calculate $E_0^{(2)}$ term by term.

$$\begin{aligned}
(E_0^{(2)})_1 &= \frac{1}{4} \sum_{abrs} \frac{[ar|bs]^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \\
&= \frac{1}{4} \sum_{a,b}^{N/2} \sum_{r,s=N/2+1}^K \frac{[ar|bs]^2 + [\bar{a}\bar{r}|bs]^2 + [ar|\bar{b}\bar{s}]^2 + [\bar{a}\bar{r}|\bar{b}\bar{s}]^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \\
&= \sum_{a,b}^{N/2} \sum_{r,s=N/2+1}^K \frac{[ar|bs]^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \\
&= \sum_{a,b}^{N/2} \sum_{r,s=N/2+1}^K \frac{\langle ab || rs \rangle \langle rs || ab \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}
\end{aligned} \tag{2.3.33}$$

$$\begin{aligned}
(E_0^{(2)})_2 &= \frac{1}{4} \sum_{abrs} \frac{-2[ar|bs][as|br]}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \\
&= -\frac{1}{2} \sum_{a,b}^{N/2} \sum_{r,s=N/2+1}^K \frac{[ar|bs][as|br] + [\bar{a}\bar{r}|\bar{b}\bar{s}][\bar{a}\bar{s}|\bar{b}\bar{r}]}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \\
&= -\sum_{a,b}^{N/2} \sum_{r,s=N/2+1}^K \frac{[ar|bs][as|br]}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \\
&= -\sum_{a,b}^{N/2} \sum_{r,s=N/2+1}^K \frac{\langle ab || rs \rangle \langle rs || ba \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}
\end{aligned} \tag{2.3.34}$$

$$\begin{aligned}
(E_0^{(2)})_3 &= \frac{1}{4} \sum_{abrs} \frac{[as|br]^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} = \frac{1}{4} \sum_{abrs} \frac{[ar|bs]^2}{\varepsilon_a + \varepsilon_b - \varepsilon_s - \varepsilon_r} \\
&= \sum_{a,b}^{N/2} \sum_{r,s=N/2+1}^K \frac{\langle ab || rs \rangle \langle rs || ab \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s}
\end{aligned} \tag{2.3.35}$$

thus,

$$E_0^{(2)} = \sum_{a,b}^{N/2} \sum_{r,s=N/2+1}^K \frac{\langle ab || rs \rangle (2 \langle rs || ab \rangle - \langle rs || ba \rangle)}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \tag{2.3.36}$$

2.3.6 Coulomb and Exchange Integrals

Ex 2.19

$$J_{ii} = (ii|ii) = K_{ii} \tag{2.3.37}$$

$$J_{ij}^* = \langle ij || ij \rangle^* = \langle ij || ij \rangle = J_{ij} \tag{2.3.38}$$

$$K_{ij}^* = \langle ij || ji \rangle^* = \langle ji || ij \rangle = \langle ij || ji \rangle = K_{ij} \tag{2.3.39}$$

$$J_{ij} = (ii|jj) = (jj|ii) = J_{ji} \tag{2.3.40}$$

$$K_{ij} = (ij|ji) = (ji|ij) = K_{ji} \tag{2.3.41}$$

Ex 2.20 For real spatial orbitals

$$K_{ij} = (ij|ji) = (ij|ij) = (ji|ji) \quad (2.3.42)$$

$$K_{ij} = \langle ij | ji \rangle = \langle ii | jj \rangle = \langle jj | ii \rangle \quad (2.3.43)$$

Ex 2.21

$$\mathbf{H} = \begin{pmatrix} 2(1|h|1) + (11|11) & (12|12) \\ (21|21) & 2(2|h|2) + (22|22) \end{pmatrix} = \begin{pmatrix} 2h_{11} + J_{11} & K_{12} \\ K_{12} & 2h_{22} + J_{22} \end{pmatrix} \quad (2.3.44)$$

Ex 2.22

$$E_{\uparrow\downarrow}^{HP} = \left\langle \Psi_{\uparrow\downarrow}^{HP} \left| h(1) + h(2) + \frac{1}{r_{12}} \right| \Psi_{\uparrow\downarrow}^{HP} \right\rangle = (1|h|1) + (2|h|2) + (11|22) = h_{11} + h_{22} + J_{12} \quad (2.3.45)$$

$$E_{\downarrow\downarrow}^{HP} = \left\langle \Psi_{\downarrow\downarrow}^{HP} \left| h(1) + h(2) + \frac{1}{r_{12}} \right| \Psi_{\downarrow\downarrow}^{HP} \right\rangle = (1|h|1) + (2|h|2) + (11|22) = h_{11} + h_{22} + J_{12} \quad (2.3.46)$$

2.3.7 Pseudo-Classical Interpretation of Determinantal Energies

Ex 2.23 a.-g. can be obtained immediately with definition.

2.4 Second Quantization

2.4.1 Creation and Annihilation Operators and Their Anticommutation Relations

Ex 2.24 Since $a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = 0$, we have

$$(a_1^\dagger a_2^\dagger + a_2^\dagger a_1^\dagger) |K\rangle = 0 \quad (2.4.1)$$

for any $|K\rangle$.

Ex 2.25 Since $a_i a_j^\dagger + a_j^\dagger a_i = \delta_{ij}$, we have

$$(a_1 a_2^\dagger + a_2^\dagger a_1) |K\rangle = 0 \quad (2.4.2)$$

$$(a_1 a_1^\dagger + a_1^\dagger a_1) |K\rangle = |K\rangle \quad (2.4.3)$$

for any $|K\rangle$.

Ex 2.26

$$\langle \chi_i | \chi_j \rangle = \langle 0 | a_i a_j^\dagger | 0 \rangle = \langle 0 | \delta_{ij} - a_j^\dagger a_i | 0 \rangle = \delta_{ij} \quad (2.4.4)$$

where $|0\rangle$ is the vacuum state.

Ex 2.27 First, if $i \notin \{1, 2, \dots, N\}$ or $j \notin \{1, 2, \dots, N\}$,

$$\langle K | a_i^\dagger a_j | K \rangle = 0 \quad (2.4.5)$$

because inexistent electron cannot be annihilated.

Thus, $i, j \in \{1, 2, \dots, N\}$, and

$$\langle K | a_i^\dagger a_j | K \rangle = \delta_{ij} \langle K | K \rangle - \langle K | a_j a_i^\dagger | K \rangle \quad (2.4.6)$$

$\langle K | a_j a_i^\dagger | K \rangle$ would be 0 because χ_i is created twice. Thus,

$$\langle K | a_i^\dagger a_j | K \rangle = \delta_{ij} \quad (2.4.7)$$

Overall, $\langle K | a_i^\dagger a_j | K \rangle = 1$ when $i = j$ and $i \in \{1, 2, \dots, N\}$, but is 0 otherwise.

Ex 2.28

- a. That's obvious since inexistent electron cannot be annihilated.
b. That's obvious since an electron cannot be created twice.

c.

$$\begin{aligned}
a_r^\dagger a_a |\Psi_0\rangle &= a_r^\dagger a_a (-|\chi_a \cdots \chi_1 \chi_b \cdots \chi_N\rangle) \\
&= -a_r^\dagger |\cdots \chi_1 \chi_b \cdots \chi_N\rangle \\
&= -|\chi_r \cdots \chi_1 \chi_b \cdots \chi_N\rangle \\
&= |\chi_1 \cdots \chi_r \chi_b \cdots \chi_N\rangle \\
&= |\Psi_a^r\rangle
\end{aligned} \tag{2.4.8}$$

d. That's similar to 2.28.c.

e.

$$\begin{aligned}
a_s^\dagger a_b a_r^\dagger a_a |\Psi_0\rangle &= a_s^\dagger a_b a_r^\dagger (-|\chi_2 \cdots \chi_1 \chi_b \cdots \chi_N\rangle) \\
&= -a_s^\dagger a_b |\chi_r \chi_2 \cdots \chi_1 \chi_b \cdots \chi_N\rangle \\
&= -a_s^\dagger (-|\chi_2 \cdots \chi_1 \chi_r \cdots \chi_N\rangle) \\
&= |\chi_s \chi_2 \cdots \chi_1 \chi_r \cdots \chi_N\rangle \\
&= |\chi_1 \cdots \chi_r \chi_s \cdots \chi_N\rangle \\
&= |\Psi_{ab}^{rs}\rangle
\end{aligned} \tag{2.4.9}$$

\therefore

$$|\Psi_{ab}^{rs}\rangle = a_s^\dagger a_b a_r^\dagger a_a |\Psi_0\rangle = a_s^\dagger (-a_r^\dagger a_b) a_a |\Psi_0\rangle = a_r^\dagger a_s^\dagger a_b a_a |\Psi_0\rangle \tag{2.4.10}$$

f. That's similar to 2.28.e.

2.4.2 Second-Quantized Operators and Their Matrix Elements

Ex 2.29

$$\begin{aligned}
\langle \Psi_0 | \mathcal{O}_1 | \Psi_0 \rangle &= \sum_{ij} \langle i | h | j \rangle \langle 0 | a_2 a_1 a_i^\dagger a_j a_1^\dagger a_2^\dagger | 0 \rangle \\
&= \sum_{ij} \langle i | h | j \rangle \langle 0 | a_2 a_1 (\delta_{ij} - a_j^\dagger a_i) a_1^\dagger a_2^\dagger | 0 \rangle \\
&= \sum_i \langle i | h | i \rangle \langle 0 | a_2 a_1 a_1^\dagger a_2^\dagger | 0 \rangle - \sum_{ij} \langle i | h | j \rangle \langle 0 | a_2 a_1 a_j a_i^\dagger a_1^\dagger a_2^\dagger | 0 \rangle
\end{aligned} \tag{2.4.11}$$

The second terms must be 0 since $i \in 1, 2$.

Thus,

$$\langle \Psi_0 | \mathcal{O}_1 | \Psi_0 \rangle = \sum_i \langle i | h | i \rangle \langle 0 | a_2 a_1 a_1^\dagger a_2^\dagger | 0 \rangle = \langle 1 | h | 1 \rangle + \langle 2 | h | 2 \rangle \tag{2.4.12}$$

Ex 2.30

$$\begin{aligned}
\langle \Psi_a^r | \mathcal{O}_1 | \Psi_0 \rangle &= \sum_{ij} \langle i | h | j \rangle \langle \Psi_0 | a_a^\dagger a_r a_i^\dagger a_j | \Psi_0 \rangle = \sum_{ij} \langle i | h | j \rangle \langle \Psi_0 | a_a^\dagger (\delta_{ri} - a_i^\dagger a_r) a_j | \Psi_0 \rangle \\
&= \sum_j \langle r | h | j \rangle \langle \Psi_0 | a_a^\dagger a_j | \Psi_0 \rangle - \sum_{ij} \langle i | h | j \rangle \langle \Psi_0 | a_a^\dagger a_i^\dagger a_r a_j | \Psi_0 \rangle \\
&= \sum_j \langle r | h | j \rangle \langle \Psi_0 | (\delta_{aj} - a_j a_a^\dagger) | \Psi_0 \rangle \\
&= \langle r | h | a \rangle \langle \Psi_0 | \Psi_0 \rangle - \sum_j \langle r | h | j \rangle \langle \Psi_0 | a_j a_a^\dagger | \Psi_0 \rangle \\
&= \langle r | h | a \rangle
\end{aligned} \tag{2.4.13}$$

Ex 2.31

$$\langle \Psi_a^r | \mathcal{O}_2 | \Psi_0 \rangle = \frac{1}{2} \sum_{ijkl} \langle ij | kl \rangle \langle \Psi_0 | a_a^\dagger a_r a_i^\dagger a_j^\dagger a_l a_k | \Psi_0 \rangle \quad (2.4.14)$$

while

$$\begin{aligned} \langle \Psi_0 | a_a^\dagger a_r a_i^\dagger a_j^\dagger a_l a_k | \Psi_0 \rangle &= \langle \Psi_0 | a_a^\dagger \delta_{ri} a_j^\dagger a_l a_k | \Psi_0 \rangle - \langle \Psi_0 | a_a^\dagger a_i^\dagger a_r a_j^\dagger a_l a_k | \Psi_0 \rangle \\ &= \delta_{ri} \left(\langle \Psi_0 | a_j^\dagger \delta_{ak} a_l | \Psi_0 \rangle - \langle \Psi_0 | a_j^\dagger a_k a_a^\dagger a_l | \Psi_0 \rangle \right) \\ &\quad - \left(\langle \Psi_0 | a_a^\dagger a_i^\dagger \delta_{rj} a_l a_k | \Psi_0 \rangle - \langle \Psi_0 | a_a^\dagger a_i^\dagger a_j^\dagger a_r a_l a_k | \Psi_0 \rangle \right) \\ &= \delta_{ri} \delta_{ak} \langle \Psi_0 | a_j^\dagger a_l | \Psi_0 \rangle - \delta_{ri} \delta_{al} \langle \Psi_0 | a_j^\dagger a_k | \Psi_0 \rangle \\ &\quad - \delta_{rj} \left(\langle \Psi_0 | a_i^\dagger \delta_{ak} a_l | \Psi_0 \rangle - \langle \Psi_0 | a_i^\dagger a_k a_a^\dagger a_l | \Psi_0 \rangle \right) + 0 \\ &= \delta_{ri} \delta_{ak} \langle \Psi_0 | a_j^\dagger a_l | \Psi_0 \rangle - \delta_{ri} \delta_{al} \langle \Psi_0 | a_j^\dagger a_k | \Psi_0 \rangle \\ &\quad - \delta_{rj} \delta_{ak} \langle \Psi_0 | a_i^\dagger a_l | \Psi_0 \rangle + \delta_{rj} \delta_{al} \langle \Psi_0 | a_i^\dagger a_k | \Psi_0 \rangle \end{aligned} \quad (2.4.15)$$

According to Ex. 2.27, we have

$$\begin{aligned} \langle \Psi_a^r | \mathcal{O}_2 | \Psi_0 \rangle &= \frac{1}{2} \left(\sum_{jl} \langle rj | al \rangle \langle \Psi_0 | a_j^\dagger a_l | \Psi_0 \rangle - \sum_{jk} \langle rj | ka \rangle \langle \Psi_0 | a_j^\dagger a_k | \Psi_0 \rangle \right. \\ &\quad \left. - \sum_{il} \langle ir | al \rangle \langle \Psi_0 | a_i^\dagger a_l | \Psi_0 \rangle + \sum_{ik} \langle ir | ka \rangle \langle \Psi_0 | a_i^\dagger a_k | \Psi_0 \rangle \right) \\ &= \frac{1}{2} \left(\sum_j^N \langle rj | aj \rangle - \sum_j^N \langle rj | ja \rangle - \sum_i^N \langle ir | ai \rangle + \sum_i^N \langle ir | ia \rangle \right) \\ &= \sum_j^N \langle rj | aj \rangle - \sum_j^N \langle rj | ja \rangle \\ &= \sum_j^N \langle rj || aj \rangle \end{aligned} \quad (2.4.16)$$

2.5 Spin-adapted Configurations

2.5.1 Spin Operators

Ex 2.32

a)

$$\hat{\mathbf{s}}_+ |\alpha\rangle = (\hat{\mathbf{s}}_x + i\hat{\mathbf{s}}_y) |\alpha\rangle = \left(\frac{1}{2} + i\frac{i}{2} \right) |\beta\rangle = 0 \quad (2.5.1)$$

$$\hat{\mathbf{s}}_+ |\beta\rangle = (\hat{\mathbf{s}}_x + i\hat{\mathbf{s}}_y) |\beta\rangle = \left(\frac{1}{2} - i\frac{i}{2} \right) |\alpha\rangle = |\alpha\rangle \quad (2.5.2)$$

$$\hat{\mathbf{s}}_- |\alpha\rangle = (\hat{\mathbf{s}}_x - i\hat{\mathbf{s}}_y) |\alpha\rangle = \left(\frac{1}{2} - i\frac{i}{2} \right) |\beta\rangle = |\beta\rangle \quad (2.5.3)$$

$$\hat{\mathbf{s}}_- |\beta\rangle = (\hat{\mathbf{s}}_x - i\hat{\mathbf{s}}_y) |\beta\rangle = \left(\frac{1}{2} + i\frac{i}{2} \right) |\alpha\rangle = 0 \quad (2.5.4)$$

b)

$$\hat{\mathbf{s}}_+ \hat{\mathbf{s}}_- = (\hat{\mathbf{s}}_x + i\hat{\mathbf{s}}_y)(\hat{\mathbf{s}}_x - i\hat{\mathbf{s}}_y) = \hat{\mathbf{s}}_x^2 + \hat{\mathbf{s}}_y^2 + i(\hat{\mathbf{s}}_y \hat{\mathbf{s}}_x - \hat{\mathbf{s}}_x \hat{\mathbf{s}}_y) = \hat{\mathbf{s}}_x^2 + \hat{\mathbf{s}}_y^2 + \hat{\mathbf{s}}_z \quad (2.5.5)$$

$$\hat{\mathbf{s}}_- \hat{\mathbf{s}}_+ = (\hat{\mathbf{s}}_x - i\hat{\mathbf{s}}_y)(\hat{\mathbf{s}}_x + i\hat{\mathbf{s}}_y) = \hat{\mathbf{s}}_x^2 + \hat{\mathbf{s}}_y^2 + i(\hat{\mathbf{s}}_x \hat{\mathbf{s}}_y - \hat{\mathbf{s}}_y \hat{\mathbf{s}}_x) = \hat{\mathbf{s}}_x^2 + \hat{\mathbf{s}}_y^2 - \hat{\mathbf{s}}_z \quad (2.5.6)$$

thus,

$$\hat{\mathbf{s}}^2 = \hat{\mathbf{s}}_x^2 + \hat{\mathbf{s}}_y^2 + \hat{\mathbf{s}}_z^2 = \hat{\mathbf{s}}_+ \hat{\mathbf{s}}_- - \hat{\mathbf{s}}_z + \hat{\mathbf{s}}_z^2 \quad (2.5.7)$$

$$= \hat{\mathbf{s}}_- \hat{\mathbf{s}}_+ + \hat{\mathbf{s}}_z + \hat{\mathbf{s}}_z^2 \quad (2.5.8)$$

Ex 2.33