

Modern Quantum Chemistry, Szabo & Ostlund

HW

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4 Configuration Interaction

4.1 Multiconfigurational Wave Functions and the Structure of Full CI Matrix

4.1.1 Intermediate Normalization and an Expression for the Correlation Energy

Ex 4.1 If $a \notin \{c, d, e\}$ and $r \notin \{t, u, v\}$,

$$\langle \Psi_a^r | \mathcal{H} | \Psi_{cde}^{tuv} \rangle = 0 \quad (4.1.1)$$

Let's suppose $a = e$, thus

$$\langle \Psi_a^r | \mathcal{H} | \Psi_{cde}^{tuv} \rangle = \langle \Psi_a^r | \mathcal{H} | \Psi_{acd}^{vtu} \rangle \quad (4.1.2)$$

if $r \neq v$, this term will still be zero, thus

$$\sum_{c < d < e, t < u < v} c_{cde}^{tuv} \langle \Psi_a^r | \mathcal{H} | \Psi_{cde}^{tuv} \rangle = \sum_{c < d, t < u} c_{acd}^{rtu} \langle \Psi_a^r | \mathcal{H} | \Psi_{acd}^{rtu} \rangle \quad (4.1.3)$$

Ex 4.2

$$\begin{vmatrix} -E_{\text{corr}} & K_{12} \\ K_{12} & 2\Delta - E_{\text{corr}} \end{vmatrix} = 0 \quad (4.1.4)$$

$$-E_{\text{corr}}(2\Delta - E_{\text{corr}}) - K_{12}^2 = 0 \quad (4.1.5)$$

$$E_{\text{corr}} = \frac{2\Delta \pm \sqrt{4\Delta^2 + 4K_{12}^2}}{2} = \Delta \pm \sqrt{\Delta^2 + K_{12}^2} \quad (4.1.6)$$

choosing the lowest eigenvalue,

$$E_{\text{corr}} = \Delta - \sqrt{\Delta^2 + K_{12}^2} \quad (4.1.7)$$

Ex 4.3 At $R = 1.4$,

$$\begin{aligned} \Delta &= \varepsilon_2 - \varepsilon_1 + \frac{1}{2}(J_{11} + J_{22}) - 2J_{12} + K_{12} \\ &= 0.6703 + 0.5782 + \frac{1}{2}(0.6746 + 0.6975) - 2 \times 0.6636 + 0.1813 \\ &= 0.78865 \end{aligned} \quad (4.1.8)$$

$$E_{\text{corr}} = \Delta - \sqrt{\Delta^2 + K_{12}^2} = 0.78865 - \sqrt{0.78865^2 + 0.1813^2} = -0.020571 \quad (4.1.9)$$

$$c = \frac{E_{\text{corr}}}{K_{12}} = \frac{-0.020571}{0.1813} = -0.1135 \quad (4.1.10)$$

As $R \rightarrow \infty$, $\varepsilon_2 - \varepsilon_1 \rightarrow 0$, all 2e integrals $\rightarrow \frac{1}{2}(\phi_1\phi_1|\phi_1\phi_1)$, thus

$$\lim_{R \rightarrow \infty} \Delta = 0 + \lim_{R \rightarrow \infty} \left[\frac{1}{2}(J_{11} + J_{22}) - 2J_{12} + K_{12} \right] = 0 \quad (4.1.11)$$

$$\lim_{R \rightarrow \infty} E_{\text{corr}} = - \lim_{R \rightarrow \infty} K_{12} \quad (4.1.12)$$

$$\lim_{R \rightarrow \infty} c = \lim_{R \rightarrow \infty} \frac{E_{\text{corr}}}{K_{12}} = -1 \quad (4.1.13)$$

As $R \rightarrow \infty$, the full CI wave function will be

$$|\Phi_0\rangle = |\Psi_0\rangle - |\Psi_{11}^{2\bar{2}}\rangle = |\psi_1\bar{\psi}_1\rangle - |\psi_2\bar{\psi}_2\rangle \quad (4.1.14)$$

Since

$$\psi_1 = \frac{1}{\sqrt{2(1 + S_{12})}}(\phi_1 + \phi_2) \quad (4.1.15)$$

$$\psi_2 = \frac{1}{\sqrt{2(1 - S_{12})}}(\phi_1 - \phi_2) \quad (4.1.16)$$

we get

$$|\psi_1\bar{\psi}_1\rangle = \frac{1}{2(1+S_{12})}(|\phi_1\bar{\phi}_1\rangle + |\phi_1\bar{\phi}_2\rangle + |\phi_2\bar{\phi}_1\rangle + |\phi_2\bar{\phi}_2\rangle) \quad (4.1.17)$$

$$|\psi_2\bar{\psi}_2\rangle = \frac{1}{2(1-S_{12})}(|\phi_1\bar{\phi}_1\rangle - |\phi_1\bar{\phi}_2\rangle - |\phi_2\bar{\phi}_1\rangle + |\phi_2\bar{\phi}_2\rangle) \quad (4.1.18)$$

As $R \rightarrow \infty$, $S_{12} \rightarrow 0$, thus

$$|\Phi_0\rangle = |\psi_1\bar{\psi}_1\rangle - |\psi_2\bar{\psi}_2\rangle = \frac{1}{2}(|\phi_1\bar{\phi}_2\rangle + |\phi_2\bar{\phi}_1\rangle) \quad (4.1.19)$$

Renormalize it, we get

$$|\Phi_0\rangle = \frac{1}{\sqrt{2}}(|\phi_1\bar{\phi}_2\rangle + |\phi_2\bar{\phi}_1\rangle) \quad (4.1.20)$$

4.2 Doubly Exited CI

4.3 Some Illustrative Calculations

4.4 Natural Orbitals and the 1-Particle Reduced DM

Ex 4.4

$$\gamma_{ij} = \int d\mathbf{x}_1 d\mathbf{x}'_1 \chi_i^*(\mathbf{x}_1) \gamma(\mathbf{x}_1, \mathbf{x}'_1) \chi_j(\mathbf{x}'_1) \quad (4.4.1)$$

$$\begin{aligned} \gamma_{ji}^* &= \int d\mathbf{x}_1 d\mathbf{x}'_1 \chi_j(\mathbf{x}_1) \gamma^*(\mathbf{x}_1, \mathbf{x}'_1) \chi_i^*(\mathbf{x}'_1) \\ &= \int d\mathbf{x}'_1 d\mathbf{x}_1 \chi_j(\mathbf{x}'_1) \gamma^*(\mathbf{x}'_1, \mathbf{x}_1) \chi_i^*(\mathbf{x}_1) \\ &= \int d\mathbf{x}'_1 d\mathbf{x}_1 \chi_j(\mathbf{x}'_1) \gamma(\mathbf{x}'_1, \mathbf{x}_1) \chi_i^*(\mathbf{x}_1) \\ &= \gamma_{ij} \end{aligned} \quad (4.4.2)$$

$\therefore \gamma$ is Hermitian.

Ex 4.5

$$\begin{aligned} \langle \Phi | \Phi \rangle &= \frac{1}{N} \int d\mathbf{x}_1 \gamma(\mathbf{x}_1, \mathbf{x}_1) \\ &= \int d\mathbf{x}_1 \sum_{ij} \chi_i(\mathbf{x}_1) \gamma_{ij} \chi_j^*(\mathbf{x}_1) \\ &= \frac{1}{N} \sum_{ij} \left[\int d\mathbf{x}_1 \chi_j^*(\mathbf{x}_1) \chi_i(\mathbf{x}_1) \right] \gamma_{ij} \\ &= \frac{1}{N} \sum_{ij} \delta_{ji} \gamma_{ij} \\ &= \frac{1}{N} \text{tr } \gamma \end{aligned} \quad (4.4.3)$$

thus

$$\text{tr } \gamma = N \quad (4.4.4)$$

Ex 4.6

a.

$$\begin{aligned}
\langle \Phi | \mathcal{O}_1 | \Phi \rangle &= \sum_i \langle \Phi | h(\mathbf{x}_1) | \Phi \rangle \\
&= N \int d\mathbf{x}_1 \int d\mathbf{x}_2 \cdots d\mathbf{x}_N \Phi^*(\mathbf{x}_1, \dots, \mathbf{x}_N) h(\mathbf{x}_1) \Phi(\mathbf{x}_1, \dots, \mathbf{x}_N) \\
&= N \frac{1}{N} \int d\mathbf{x}_1 [h(\mathbf{x}_1) \gamma(\mathbf{x}_1, \mathbf{x}'_1)]_{\mathbf{x}'_1 = \mathbf{x}_1} \\
&= \int d\mathbf{x}_1 [h(\mathbf{x}_1) \gamma(\mathbf{x}_1, \mathbf{x}'_1)]_{\mathbf{x}'_1 = \mathbf{x}_1}
\end{aligned} \tag{4.4.5}$$

b.

$$\begin{aligned}
\langle \Phi | \mathcal{O}_1 | \Phi \rangle &= \int d\mathbf{x}_1 [h(\mathbf{x}_1) \gamma(\mathbf{x}_1, \mathbf{x}'_1)]_{\mathbf{x}'_1 = \mathbf{x}_1} \\
&= \int d\mathbf{x}_1 [h(\mathbf{x}_1) \sum_{ij} \chi_i(\mathbf{x}_1) \gamma_{ij} \chi_j^*(\mathbf{x}'_1)]_{\mathbf{x}'_1 = \mathbf{x}_1} \\
&= \sum_{ij} \left[\int d\mathbf{x}_1 \chi_j^*(\mathbf{x}_1) h(\mathbf{x}_1) \chi_i(\mathbf{x}_1) \right] \gamma_{ij} \\
&= \sum_{ij} h_{ji} \gamma_{ij} \\
&= \sum_j (\mathbf{h}\boldsymbol{\gamma})_{jj} \\
&= \text{tr}(\mathbf{h}\boldsymbol{\gamma})
\end{aligned} \tag{4.4.6}$$

Ex 4.7

a.

$$\langle \Phi | \mathcal{O}_1 | \Phi \rangle = \sum_{ij} \langle i | h | j \rangle \langle \Phi | a_i^+ a_j | \Phi \rangle \tag{4.4.7}$$

while

$$\langle \Phi | \mathcal{O}_1 | \Phi \rangle = \sum_{ij} h_{ij} \gamma_{ji} \tag{4.4.8}$$

\therefore

$$\gamma_{ji} = \langle \Phi | a_i^+ a_j | \Phi \rangle \tag{4.4.9}$$

i.e.

$$\gamma_{ij} = \langle \Phi | a_j^+ a_i | \Phi \rangle \tag{4.4.10}$$

b.

$$\gamma_{ij}^{\text{HF}} = \langle \Psi_0 | a_j^+ a_i | \Psi_0 \rangle \tag{4.4.11}$$

If i is unoccupied, thus $\gamma_{ij}^{\text{HF}} = 0$ as we cannot annihilate electrons from it. If j is unoccupied, $\gamma_{ij}^{\text{HF}} = \delta_{ij} - \langle \Psi_0 | a_i a_j^+ | \Psi_0 \rangle = \delta_{ij} - \delta_{ij} = 0$.

Otherwise, when i, j are occupied, it's clear that $\gamma_{ij}^{\text{HF}} = \delta_{ij}$.

Thus,

$$\gamma_{ij}^{\text{HF}} = \begin{cases} \delta_{ij} & i, j \text{ are occupied} \\ 0 & \text{otherwise} \end{cases} \tag{4.4.12}$$

Ex 4.8

a. Since

$$|^1\Phi_0\rangle = c_0 |\psi_1\bar{\psi}_1\rangle + \sum_{r=2}^K c_1^r \frac{1}{\sqrt{2}} (|\psi_1\bar{\psi}_r\rangle + |\psi_r\bar{\psi}_1\rangle) + \frac{1}{2} \sum_{r=2}^K \sum_{s=2}^K c_{11}^{rs} \frac{1}{\sqrt{2}} (|\psi_r\bar{\psi}_s\rangle + |\psi_s\bar{\psi}_r\rangle) \quad (4.4.13)$$

we can write

$$|^1\Phi_0\rangle = \sum_i^K \sum_j^K C_{ij} |\psi_i\bar{\psi}_j\rangle \quad (4.4.14)$$

When one or two of i, j equals 1, it is clear that $C_{ij} = C_{ji}$. Otherwise, $c_{11}^{rs} = c_{11}^{sr}$. Thus, \mathbf{C} is symmetric.

b.

$$\begin{aligned} \gamma(\mathbf{x}_1, \mathbf{x}'_1) &= 2 \int d\mathbf{x}_2 \sum_{ij} C_{ij} \frac{1}{\sqrt{2}} (\psi_i(\mathbf{x}_1)\bar{\psi}_j(\mathbf{x}_2) - \psi_i(\mathbf{x}_2)\bar{\psi}_j(\mathbf{x}_1)) \sum_{kl} C_{kl}^* \frac{1}{\sqrt{2}} (\psi_k^*(\mathbf{x}'_1)\bar{\psi}_l^*(\mathbf{x}_2) - \psi_k^*(\mathbf{x}_2)\bar{\psi}_l^*(\mathbf{x}'_1)) \\ &= \sum_{ij} \sum_{kl} C_{ij} C_{kl}^* \int d\mathbf{x}_2 (\psi_i(\mathbf{x}_1)\bar{\psi}_j(\mathbf{x}_2) - \psi_i(\mathbf{x}_2)\bar{\psi}_j(\mathbf{x}_1)) (\psi_k^*(\mathbf{x}'_1)\bar{\psi}_l^*(\mathbf{x}_2) - \psi_k^*(\mathbf{x}_2)\bar{\psi}_l^*(\mathbf{x}'_1)) \\ &= \sum_{ij} \sum_{kl} C_{ij} C_{kl}^* [\psi_i(\mathbf{x}_1)\psi_k^*(\mathbf{x}'_1)\delta_{jl} + \bar{\psi}_j(\mathbf{x}_1)\bar{\psi}_l^*(\mathbf{x}'_1)\delta_{ik}] \\ &= \sum_{ij} \sum_k C_{ij} C_{kj}^* \psi_i(\mathbf{x}_1)\psi_k^*(\mathbf{x}'_1) + \sum_{ij} \sum_l C_{ij} C_{il}^* \bar{\psi}_j(\mathbf{x}_1)\bar{\psi}_l^*(\mathbf{x}'_1) \\ &= \sum_{ik} (\mathbf{C}\mathbf{C}^\dagger)_{ik} \psi_i(\mathbf{x}_1)\psi_k^*(\mathbf{x}'_1) + \sum_{jl} (\mathbf{C}^\dagger\mathbf{C})_{jl} \bar{\psi}_j(\mathbf{x}_1)\bar{\psi}_l^*(\mathbf{x}'_1) \\ &= \sum_{ij} (\mathbf{C}\mathbf{C}^\dagger)_{ij} \psi_i(\mathbf{x}_1)\psi_j^*(\mathbf{x}'_1) + \sum_{ij} (\mathbf{C}\mathbf{C}^\dagger)_{ji} \bar{\psi}_i(\mathbf{x}_1)\bar{\psi}_j^*(\mathbf{x}'_1) \\ &= \sum_{ij} (\mathbf{C}\mathbf{C}^\dagger)_{ij} [\psi_i(1)\psi_j^*(1') + \bar{\psi}_i(1)\bar{\psi}_j^*(1')] \end{aligned} \quad (4.4.15)$$

c.

$$\mathbf{d} = \mathbf{U}^\dagger \mathbf{C} \mathbf{U} \quad (4.4.16)$$

$$\mathbf{d}^\dagger = (\mathbf{U}^\dagger \mathbf{C} \mathbf{U})^\dagger = \mathbf{U}^\dagger \mathbf{C}^\dagger \mathbf{U} \quad (4.4.17)$$

Since \mathbf{U} is unitary

$$\mathbf{d}^2 = \mathbf{d}\mathbf{d}^\dagger = \mathbf{U}^\dagger \mathbf{C} \mathbf{U} \mathbf{U}^\dagger \mathbf{C}^\dagger \mathbf{U} = \mathbf{U}^\dagger \mathbf{C} \mathbf{C}^\dagger \mathbf{U} \quad (4.4.18)$$

d. Since

$$\psi_k = \sum_i U_{ik}^\dagger \zeta_i \quad (4.4.19)$$

$$\begin{aligned} \gamma(\mathbf{x}_1, \mathbf{x}'_1) &= \sum_{ij} (\mathbf{C}\mathbf{C}^\dagger)_{ij} [\psi_i(1)\psi_j^*(1') + \bar{\psi}_i(1)\bar{\psi}_j^*(1')] \\ &= \sum_{ij} (\mathbf{C}\mathbf{C}^\dagger)_{ij} \left[\sum_k U_{ki}^\dagger \zeta_k(1) \sum_l U_{lj}^{\dagger*} \zeta_l^*(1') + \sum_k U_{ki}^\dagger \bar{\zeta}_k(1) \sum_l U_{lj}^{\dagger*} \bar{\zeta}_l^*(1') \right] \\ &= \sum_k \sum_l \sum_{ij} U_{ki}^\dagger (\mathbf{C}\mathbf{C}^\dagger)_{ij} U_{jl} [\zeta_k(1)\zeta_l^*(1') + \bar{\zeta}_k(1)\bar{\zeta}_l^*(1')] \\ &= \sum_k \sum_l (\mathbf{U}^\dagger \mathbf{C} \mathbf{C}^\dagger \mathbf{U})_{kl} [\zeta_k(1)\zeta_l^*(1') + \bar{\zeta}_k(1)\bar{\zeta}_l^*(1')] \\ &= \sum_k \sum_l d_k^2 \delta_{kl} [\zeta_k(1)\zeta_l^*(1') + \bar{\zeta}_k(1)\bar{\zeta}_l^*(1')] \\ &= \sum_k d_k^2 [\zeta_k(1)\zeta_k^*(1') + \bar{\zeta}_k(1)\bar{\zeta}_k^*(1')] \end{aligned} \quad (4.4.20)$$

e.

$$\begin{aligned}
|{}^1\Phi_0\rangle &= \sum_i^K \sum_j^K C_{ij} |\psi_i \bar{\psi}_j\rangle \\
&= \sum_i^K \sum_j^K C_{ij} \left| \left(\sum_k U_{ki}^\dagger \zeta_k \right) \left(\sum_l U_{lj}^\dagger \bar{\zeta}_l \right) \right\rangle \\
&= \sum_i^K \sum_j^K \sum_k \sum_l U_{ki}^\dagger C_{ij} U_{jl} |\zeta_k \bar{\zeta}_l\rangle \\
&= \sum_k \sum_l d_k \delta_{kl} |\zeta_k \bar{\zeta}_l\rangle \\
&= \sum_k d_k |\zeta_k \bar{\zeta}_k\rangle
\end{aligned} \tag{4.4.21}$$

4.5 The MCSCF and the GVB Methods