Modern Quantum Chemistry, Szabo & Ostlund HW

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Contents

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 $r \notin \{t, u, v\}$,

$$\left\langle \Psi_a^r \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{cde}^{tuv} \right\rangle = 0 \tag{4.1.1}$$

Let's suppose $a = e$, thus

$$\left\langle \Psi_a^r \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{cde}^{tuv} \right\rangle = \left\langle \Psi_a^r \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{acd}^{vtu} \right\rangle \tag{4.1.2}$$

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

$$\sum_{c<d<e, t<u<v} c_{cde}^{tuv} \left\langle \Psi_a^r \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{cde}^{tuv} \right\rangle = \sum_{c<d, t<u} c_{acd}^{rtu} \left\langle \Psi_a^r \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{acd}^{rtu} \right\rangle \tag{4.1.3}$$

Ex 4.2

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

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

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

choosing the lowest eigenvalue,

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

Ex 4.3 At $R = 1.4$,

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

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

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

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

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

$$\lim_{R \to \infty} E_{\text{corr}} = -\lim_{R \to \infty} K_{12} \tag{4.1.12}$$

$$\lim_{R \to \infty} c = \lim_{R \to \infty} \frac{E_{\text{corr}}}{K_{12}} = -1 \tag{4.1.13}$$

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

$$|\Phi_0\rangle = |\Psi_0\rangle - |\Psi_{1\bar{1}}^{2\bar{2}}\rangle = |\psi_1\bar{\psi}_1\rangle - |\psi_2\bar{\psi}_2\rangle \tag{4.1.14}$$

Since

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

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

we get

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

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

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

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

Renormalize it, we get

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

4.2 Doubly Exited CI

4.3 Some Illustrative Calculations

4.4 Natural Orbitals and the 1-Particle Reduced DM

Ex 4.4

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

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

$\therefore \boldsymbol{\gamma}$ is Hermitian.

Ex 4.5

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

thus

$$\operatorname{tr}\boldsymbol{\gamma} = N \tag{4.4.4}$$

Ex 4.6

a.

$$\langle \Phi \,|\, \mathscr{O}_1 \,|\, \Phi \rangle = \sum_i \langle \Phi \,|\, h(\mathbf{x}_1) \,|\, \Phi \rangle$$

$$= N \int d\mathbf{x}_1 \int d\mathbf{x}_2 \cdots d\mathbf{x}_N \Phi^*(\mathbf{x}_1, \cdots, \mathbf{x}_N) h(\mathbf{x}_1) \Phi(\mathbf{x}_1, \cdots, \mathbf{x}_N)$$

$$= N \frac{1}{N} \int d\mathbf{x}_1 [h(\mathbf{x}_1)\gamma(\mathbf{x}_1, \mathbf{x}_1')]_{\mathbf{x}_1'=\mathbf{x}_1}$$

$$= \int d\mathbf{x}_1 [h(\mathbf{x}_1)\gamma(\mathbf{x}_1, \mathbf{x}_1')]_{\mathbf{x}_1'=\mathbf{x}_1} \tag{4.4.5}$$

b.

$$\langle \Phi \,|\, \mathscr{O}_1 \,|\, \Phi \rangle = \int d\mathbf{x}_1 [h(\mathbf{x}_1)\gamma(\mathbf{x}_1, \mathbf{x}_1')]_{\mathbf{x}_1'=\mathbf{x}_1}$$

$$= \int d\mathbf{x}_1 [h(\mathbf{x}_1) \sum_{ij} \chi_i(\mathbf{x}_1)\gamma_{ij}\chi_j^*(\mathbf{x}_1')]_{\mathbf{x}_1'=\mathbf{x}_1}$$

$$= \sum_{ij} \left[\int d\mathbf{x}_1 \chi_j^*(\mathbf{x}_1) h(\mathbf{x}_1)\chi_i(\mathbf{x}_1) \right] \gamma_{ij}$$

$$= \sum_{ij} h_{ji}\gamma_{ij}$$

$$= \sum_j (\mathbf{h}\boldsymbol{\gamma})_{jj}$$

$$= \mathrm{tr}(\mathbf{h}\boldsymbol{\gamma}) \tag{4.4.6}$$

Ex 4.7

a.

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

while

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

$\therefore$

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

i.e.

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

b.

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

If i is unoccupied, thus $\gamma_{ij}^{\mathrm{HF}} = 0$ as we cannot annihilate electrons from it. If j is unoccupied,
$\gamma_{ij}^{\mathrm{HF}} = \delta_{ij} - \langle \Psi_0 \,|\, a_i a_j^+ \,|\, \Psi_0 \rangle = \delta_{ij} - \delta_{ij} = 0$.
Otherwise, when i, j are occupied, it's clear that $\gamma_{ij}^{\mathrm{HF}} = \delta_{ij}$.
Thus,

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

Ex 4.8

a. Since

$$|{}^1\Phi_0\rangle = c_0\,|\psi_1\bar\psi_1\rangle + \sum_{r=2}^{K} c_1^r \frac{1}{\sqrt{2}}\left(|\psi_1\bar\psi_r\rangle + |\psi_r\bar\psi_1\rangle\right) + \frac{1}{2}\sum_{r=2}^{K}\sum_{s=2}^{K} c_{11}^{rs}\frac{1}{\sqrt{2}}\left(|\psi_r\bar\psi_s\rangle + |\psi_s\bar\psi_r\rangle\right) \qquad (4.4.13)$$

we can write

$$|{}^1\Phi_0\rangle = \sum_i^K \sum_j^K C_{ij}\,|\psi_i\bar\psi_j\rangle \qquad (4.4.14)$$

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.

$$\gamma(\mathbf{x}_1,\mathbf{x}_1') = 2\int d\mathbf{x}_2 \sum_{ij} C_{ij}\frac{1}{\sqrt{2}}\left(\psi_i(\mathbf{x}_1)\bar\psi_j(\mathbf{x}_2) - \psi_i(\mathbf{x}_2)\bar\psi_j(\mathbf{x}_1)\right)\sum_{kl} C_{kl}^*\frac{1}{\sqrt{2}}\left(\psi_k^*(\mathbf{x}_1')\bar\psi_l^*(\mathbf{x}_2) - \psi_k^*(\mathbf{x}_2)\bar\psi_l^*(\mathbf{x}_1')\right)$$

$$= \sum_{ij}\sum_{kl} C_{ij}C_{kl}^*\int d\mathbf{x}_2\left(\psi_i(\mathbf{x}_1)\bar\psi_j(\mathbf{x}_2) - \psi_i(\mathbf{x}_2)\bar\psi_j(\mathbf{x}_1)\right)\left(\psi_k^*(\mathbf{x}_1')\bar\psi_l^*(\mathbf{x}_2) - \psi_k^*(\mathbf{x}_2)\bar\psi_l^*(\mathbf{x}_1')\right)$$

$$= \sum_{ij}\sum_{kl} C_{ij}C_{kl}^*\left[\psi_i(\mathbf{x}_1)\psi_k^*(\mathbf{x}_1')\delta_{jl} + \bar\psi_j(\mathbf{x}_1)\bar\psi_l^*(\mathbf{x}_1')\delta_{ik}\right]$$

$$= \sum_{ij}\sum_{k} C_{ij}C_{kj}^*\psi_i(\mathbf{x}_1)\psi_k^*(\mathbf{x}_1') + \sum_{ij}\sum_{l} C_{ij}C_{il}^*\bar\psi_j(\mathbf{x}_1)\bar\psi_l^*(\mathbf{x}_1')$$

$$= \sum_{ik}(\mathbf{CC}^\dagger)_{ik}\psi_i(\mathbf{x}_1)\psi_k^*(\mathbf{x}_1') + \sum_{jl}(\mathbf{C}^\dagger\mathbf{C})_{lj}\bar\psi_j(\mathbf{x}_1)\bar\psi_l^*(\mathbf{x}_1')$$

$$= \sum_{ij}(\mathbf{CC}^\dagger)_{ij}\psi_i(\mathbf{x}_1)\psi_j^*(\mathbf{x}_1') + \sum_{ij}(\mathbf{CC}^\dagger)_{ji}\bar\psi_i(\mathbf{x}_1)\bar\psi_j^*(\mathbf{x}_1')$$

$$= \sum_{ij}(\mathbf{CC}^\dagger)_{ij}\left[\psi_i(1)\psi_j^*(1') + \bar\psi_i(1)\bar\psi_j^*(1')\right] \qquad (4.4.15)$$

c. Since $\mathbf{U}$ is unitary and $\mathbf{C}$ is symmetric,

$$\mathbf{d}^2 = \mathbf{U}^\dagger\mathbf{C}\mathbf{U}\mathbf{U}^\dagger\mathbf{C}\mathbf{U} = \mathbf{U}^\dagger\mathbf{C}\mathbf{C}\mathbf{U} = \mathbf{U}^\dagger\mathbf{C}\mathbf{C}^\dagger\mathbf{U} \qquad (4.4.16)$$

d. Since

$$\psi_k = \sum_i U_{ik}^\dagger\zeta_i \qquad (4.4.17)$$

$$\gamma(\mathbf{x}_1,\mathbf{x}_1') = \sum_{ij}(\mathbf{CC}^\dagger)_{ij}\left[\psi_i(1)\psi_j^*(1') + \bar\psi_i(1)\bar\psi_j^*(1')\right]$$

$$= \sum_{ij}(\mathbf{Ud}^2\mathbf{U}^\dagger)_{ij}\left[\sum_k U_{ki}^*\zeta_k(1)\sum_l U_{lj}\zeta_l^*(1') + \sum_k U_{ki}^*\bar\zeta_k(1)\sum_l U_{lj}\bar\zeta_l^*(1')\right]$$

$$= \sum_k\sum_m d_m^2\left[\zeta_k(1)\zeta_k^*(1') + \bar\zeta_k(1)\bar\zeta_k^*(1')\right]$$

$$(4.4.18)$$