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

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

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

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

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

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

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

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

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

Renormalize it, we get

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

4.2 Doubly Exited CI

4.3 Some Illustrative Calculations

4.4 Natural Orbitals and the 1-Particle Reduced DM

Ex 4.4

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

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

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

Ex 4.5

$$\begin{aligned}
\operatorname{tr}\boldsymbol{\gamma} &= \sum_i \gamma_{ii} \\
&= \sum_i \int \mathrm{d}\mathbf{x}_1 \mathrm{d}\mathbf{x}_1' \chi_i^*(\mathbf{x}_1)\gamma(\mathbf{x}_1, \mathbf{x}_1')\chi_i(\mathbf{x}_1') \\
&= \sum_i \int \mathrm{d}\mathbf{x}_1 \mathrm{d}\mathbf{x}_1' \chi_i^*(\mathbf{x}_1)\chi_i(\mathbf{x}_1') N \int \mathrm{d}\mathbf{x}_2 \cdots \mathrm{d}\mathbf{x}_N \Phi^*(\mathbf{x}_1, \cdots, \mathbf{x}_N)\Phi(\mathbf{x}_1', \cdots, \mathbf{x}_N) \\
&= N \sum_i \int \mathrm{d}\mathbf{x}_2 \cdots \mathrm{d}\mathbf{x}_N \int \mathrm{d}\mathbf{x}_1 \chi_i^*(\mathbf{x}_1)\Phi^*(\mathbf{x}_1, \cdots, \mathbf{x}_N) \int \mathrm{d}\mathbf{x}_1' \chi_i(\mathbf{x}_1')\Phi(\mathbf{x}_1', \cdots, \mathbf{x}_N)
\end{aligned} \tag{4.4.3}$$

Since

$$\int \mathrm{d}\mathbf{x}_1' \chi_i(\mathbf{x}_1')\Phi(\mathbf{x}_1', \cdots, \mathbf{x}_N) = \int \mathrm{d}\mathbf{x}_1 \chi_i(\mathbf{x}_1)\Phi(\mathbf{x}_1, \cdots, \mathbf{x}_N) \tag{4.4.4}$$

we have

$$\begin{aligned}
\operatorname{tr}\boldsymbol{\gamma} &= N \sum_i \int \mathrm{d}\mathbf{x}_2 \cdots \mathrm{d}\mathbf{x}_N \int \mathrm{d}\mathbf{x}_1 \chi_i^*(\mathbf{x}_1)\Phi^*(\mathbf{x}_1, \cdots, \mathbf{x}_N) \int \mathrm{d}\mathbf{x}_1 \chi_i(\mathbf{x}_1)\Phi(\mathbf{x}_1, \cdots, \mathbf{x}_N) \\
&= N \sum_i \int \mathrm{d}\mathbf{x}_1 \chi_i^*(\mathbf{x}_1)\chi_i(\mathbf{x}_1) \int \mathrm{d}\mathbf{x}_1 \mathrm{d}\mathbf{x}_2 \cdots \mathrm{d}\mathbf{x}_N \Phi^*(\mathbf{x}_1, \cdots, \mathbf{x}_N)\Phi(\mathbf{x}_1, \cdots, \mathbf{x}_N) \\
&= N \sum_i \int \mathrm{d}\mathbf{x}_1 \chi_i^*(\mathbf{x}_1)\chi_i(\mathbf{x}_1)
\end{aligned} \tag{4.4.5}$$

Ex 4.6

a.

$$\begin{aligned}\langle \Phi \,|\, \mathscr{O}_1 \,|\, \Phi \rangle &= \sum_i \langle \Phi \,|\, h(\mathbf{x}_1) \,|\, \Phi \rangle \\ &= \sum_i \int \mathrm{d}\mathbf{x}_1 h(\mathbf{x}_1) \int \mathrm{d}\mathbf{x}_2 \cdots \mathrm{d}\mathbf{x}_N \Phi^*(\mathbf{x}_1, \cdots, \mathbf{x}_N)\Phi(\mathbf{x}_1, \cdots, \mathbf{x}_N) \\ &= \end{aligned} \tag{4.4.6}$$