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

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

thus

$$\mathrm{tr}\,\boldsymbol{\gamma} = N \tag{4.4.4}$$

Ex 4.6

a.

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

b.

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

Ex 4.7

a.

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

while

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

$\therefore$

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

i.e.

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

b.

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

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

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

we can write

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

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.

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

c.

$$\mathbf{d} = \mathbf{U}^\dagger\mathbf{C}\mathbf{U} \tag{4.4.16}$$

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

Since $\mathbf{U}$ is unitary

$$\mathbf{d}^2 = \mathbf{d}\mathbf{d}^\dagger = \mathbf{U}^\dagger\mathbf{C}\mathbf{U}\mathbf{U}^\dagger\mathbf{C}^\dagger\mathbf{U} = \mathbf{U}^\dagger\mathbf{C}\mathbf{C}^\dagger\mathbf{U} \tag{4.4.18}$$

d. Since

$$\psi_k = \sum_i U_{ik}^\dagger\zeta_i \tag{4.4.19}$$

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

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

Ex 4.9

a.

$$\begin{aligned}
\langle u \,|\, u\rangle &= \frac{1}{a^2+b^2} \, \langle a\psi_A + b\psi_B \,|\, a\psi_A + b\psi_B\rangle \\
&= \frac{1}{a^2+b^2}(a^2+b^2) \\
&= 1
\end{aligned} \tag{4.5.1}$$

$$\begin{aligned}
\langle v \,|\, v\rangle &= \frac{1}{a^2+b^2} \, \langle a\psi_A - b\psi_B \,|\, a\psi_A - b\psi_B\rangle \\
&= \frac{1}{a^2+b^2}(a^2+b^2) \\
&= 1
\end{aligned} \tag{4.5.2}$$

$$\begin{aligned}
\langle u \,|\, v\rangle &= \frac{1}{a^2+b^2} \, \langle a\psi_A + b\psi_B \,|\, a\psi_A - b\psi_B\rangle \\
&= \frac{a^2-b^2}{a^2+b^2}
\end{aligned} \tag{4.5.3}$$

b.

$$\begin{aligned}
|\Psi_{\mathrm{GVB}}\rangle &= [2(1+S^2)]^{-1/2}[u(1)v(2)+u(2)v(1)]2^{-1/2}[\alpha(1)\beta(2)-\alpha(2)\beta(1)] \\
&= \left[2 + 2\left(\frac{a^2-b^2}{a^2+b^2}\right)^2\right]^{-1/2} (a^2+b^2)^{-1} \\
&\quad \times [(a\psi_A(1)+b\psi_B(1))(a\psi_A(2)-b\psi_B(2)) + (a\psi_A(2)+b\psi_B(2))(a\psi_A(1)-b\psi_B(1))] \\
&\quad \times 2^{-1/2}[\alpha(1)\beta(2)-\alpha(2)\beta(1)] \\
&= \left[2(a^2+b^2)^2 + 2\big(a^2-b^2\big)^2\right]^{-1/2}[2a^2\psi_A(1)\psi_A(2) - 2b^2\psi_B(1)\psi_B(2)] \times 2^{-1/2}[\alpha(1)\beta(2)-\alpha(2)\beta(1)] \\
&= \left[4(a^4+b^4)\right]^{-1/2}[2a^2\psi_A(1)\psi_A(2) - 2b^2\psi_B(1)\psi_B(2)] \times 2^{-1/2}[\alpha(1)\beta(2)-\alpha(2)\beta(1)] \\
&= \big(a^4+b^4\big)^{-1/2}[a^2\psi_A(1)\psi_A(2) - b^2\psi_B(1)\psi_B(2)] \times 2^{-1/2}[\alpha(1)\beta(2)-\alpha(2)\beta(1)]
\end{aligned} \tag{4.5.4}$$

i.e.

$$\begin{aligned}
|\Psi_{\mathrm{GVB}}\rangle &= \big(a^4+b^4\big)^{-1/2} a^2 \times 2^{-1/2}\psi_A(1)\psi_A(2)[\alpha(1)\beta(2)-\alpha(2)\beta(1)] \\
&\quad - \big(a^4+b^4\big)^{-1/2} b^2 \times 2^{-1/2}\psi_B(1)\psi_B(2)[\alpha(1)\beta(2)-\alpha(2)\beta(1)] \\
&= \big(a^4+b^4\big)^{-1/2} a^2 \, |\psi_A \bar{\psi}_A\rangle - \big(a^4+b^4\big)^{-1/2} b^2 \, |\psi_B \bar{\psi}_B\rangle
\end{aligned} \tag{4.5.5}$$

thus $|\Psi_{\mathrm{GVB}}\rangle$ is identical to $|\Psi^{\mathrm{MCSCF}}\rangle$.

4.6 Truncated CI and the Size-consistency Problem

Ex 4.10

$$\begin{aligned}\langle\Psi_0\,|\,\mathscr{H}\,|\,1_1\bar{1}_1 2_1\bar{2}_1\rangle &= \langle 1_2\bar{1}_2 \,\|\, 2_1\bar{2}_1\rangle\\ &= \langle 1_2\bar{1}_2\,|\,2_1\bar{2}_1\rangle - \langle 1_2\bar{1}_2\,|\,\bar{2}_1 2_1\rangle\\ &= [1_2 2_1|\bar{1}_2\bar{2}_1] - [1_2\bar{2}_1|\bar{1}_2 2_1]\\ &= (1_2 2_1|1_2 2_1)\\ &= 0\end{aligned}\tag{4.6.1}$$

$$\begin{aligned}\langle 2_1\bar{2}_1 1_2\bar{1}_2\,|\,\mathscr{H}\,|\,1_1\bar{1}_1 2_1\bar{2}_1\rangle &= \langle 2_1\bar{2}_1 1_2\bar{1}_2\,|\,\mathscr{H}\,|\,2_1\bar{2}_1 1_1\bar{1}_1\rangle\\ &= \langle 1_2\bar{1}_2 \,\|\, 1_1\bar{1}_1\rangle\\ &= \langle 1_2\bar{1}_2\,|\,1_1\bar{1}_1\rangle - \langle 1_2\bar{1}_2\,|\,\bar{1}_1 1_1\rangle\\ &= [1_2 1_1|\bar{1}_2\bar{1}_1] - [1_2\bar{1}_1|\bar{1}_2 1_1]\\ &= (1_2 1_1|1_2 1_1)\\ &= 0\end{aligned}\tag{4.6.2}$$

$$\begin{aligned}\langle 1_1\bar{1}_1 2_2\bar{2}_2\,|\,\mathscr{H}\,|\,1_1\bar{1}_1 2_1\bar{2}_1\rangle &= \langle 2_2\bar{2}_2 \,\|\, 2_1\bar{2}_1\rangle\\ &= \langle 2_2\bar{2}_2\,|\,2_1\bar{2}_1\rangle - \langle 2_2\bar{2}_2\,|\,\bar{2}_1 2_1\rangle\\ &= [2_2 2_1|\bar{2}_2\bar{2}_1] - [2_2\bar{2}_1|\bar{2}_2 2_1]\\ &= (2_2 2_1|2_2 2_1)\\ &= 0\end{aligned}\tag{4.6.3}$$

Ex 4.11

$$\frac{{}^N E_{\mathrm{corr}}(\mathrm{DCI})}{N} = \frac{\Delta - (\Delta^2 + N K_{12}^2)^{1/2}}{N}\tag{4.6.4}$$

From Ex 4.3, we get $\Delta = 0.78865$, $K_{12} = 0.1813$, thus

N	${}^N E_{\mathrm{corr}}(\mathrm{DCI})/N$
1	-0.02057
10	-0.01864
100	-0.01188

Ex 4.12

a. In addition to the matrix elements obtained in Eq. 4.56 in the textbook, we need to calculate the rest, i.e. those involving $|2_1\bar{2}_1 2_2\,\delta 2_2\rangle$.

$$\langle\Psi_0\,|\,\mathscr{H}\,|\,2_1\bar{2}_1 2_2\bar{2}_2\rangle = 0\tag{4.6.5}$$

$$\begin{aligned}\langle 2_1\bar{2}_1 1_2\bar{1}_2\,|\,\mathscr{H}\,|\,2_1\bar{2}_1 2_2\bar{2}_2\rangle &= \langle 1_2\bar{1}_2 \,\|\, 2_2\bar{2}_2\rangle\\ &= \langle 1_2\bar{1}_2\,|\,2_2\bar{2}_2\rangle - \langle 1_2\bar{1}_2\,|\,\bar{2}_2 2_2\rangle\\ &= [1_2 2_2|\bar{1}_2\bar{2}_2] - [1_2\bar{2}_2|\bar{1}_2 2_2]\\ &= (12|12)\\ &= K_{12}\end{aligned}\tag{4.6.6}$$

$$\begin{aligned}\langle 1_1\bar{1}_1 2_2\bar{2}_2\,|\,\mathscr{H}\,|\,2_1\bar{2}_1 2_2\bar{2}_2\rangle &= \langle 1_1\bar{1}_1 \,\|\, 2_1\bar{2}_1\rangle\\ &= \langle 1_1\bar{1}_1\,|\,2_1\bar{2}_1\rangle - \langle 1_1\bar{1}_1\,|\,\bar{2}_1 2_1\rangle\\ &= [1_1 2_1|\bar{1}_1\bar{2}_1] - [1_1\bar{2}_1|\bar{1}_1 2_1]\\ &= (12|12)\\ &= K_{12}\end{aligned}\tag{4.6.7}$$

$$\begin{aligned}\langle 2_1\bar{2}_1 2_2\bar{2}_2 \,|\, \mathscr{H} - E_0 \,|\, 2_1\bar{2}_1 2_2\bar{2}_2\rangle &= 4h_{22} + 2J_{22} - 4h_{11} - 2J_{11} \\ &= 4\Delta \end{aligned} \tag{4.6.8}$$

thus the full CI equation is

$$\begin{pmatrix} 0 & K_{12} & K_{12} & 0 \\ K_{12} & 2\Delta & 0 & K_{12} \\ K_{12} & 0 & 2\Delta & K_{12} \\ 0 & K_{12} & K_{12} & 4\Delta \end{pmatrix} \begin{pmatrix} 1 \\ c_1 \\ c_2 \\ c_3 \end{pmatrix} = {}^2E_{\text{corr}} \begin{pmatrix} 1 \\ c_1 \\ c_2 \\ c_3 \end{pmatrix} \tag{4.6.9}$$

e. Directly solve the full CI equation (see `4-11,12.nb`), we get the lowest eigenvalue

$${}^2E_{\text{corr}} = 2[\Delta - \sqrt{\Delta^2 + K_{12}^2}] \tag{4.6.10}$$

Ex 4.13