Modern Quantum Chemistry, Szabo & Ostlund HW

wsr

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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

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

thus

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

Ex 4.6

a.

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

b.

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

Ex 4.7

a.

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

while

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

$\therefore$

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

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

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

we can write

$$|{}^1\Phi_0\rangle = \sum_{i}^{K}\sum_{j}^{K} C_{ij}\left|\psi_i\bar{\psi}_j\right\rangle \tag{4.4.14}$$

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

4.6 Truncated CI and the Size-consistency Problem

Ex 4.10

$$\begin{aligned}\langle\Psi_0\,|\,\mathscr{H}\,|\,1_1\bar{1}_12_1\bar{2}_1\rangle &= \langle 1_2\bar{1}_2\,\|\,2_1\bar{2}_1\rangle\\ &= \langle 1_2\bar{1}_2\,|\,2_1\bar{2}_1\rangle - \langle 1_2\bar{1}_2\,|\,\bar{2}_12_1\rangle\\ &= [1_22_1|\bar{1}_2\bar{2}_1] - [1_2\bar{2}_1|\bar{1}_22_1]\\ &= (1_22_1|1_22_1)\\ &= 0\end{aligned} \tag{4.6.1}$$

$$\begin{aligned}\langle 2_1\bar{2}_11_2\bar{1}_2\,|\,\mathscr{H}\,|\,1_1\bar{1}_12_1\bar{2}_1\rangle &= \langle 2_1\bar{2}_11_2\bar{1}_2\,|\,\mathscr{H}\,|\,2_1\bar{2}_11_1\bar{1}_1\rangle\\ &= \langle 1_2\bar{1}_2\,\|\,1_1\bar{1}_1\rangle\\ &= \langle 1_2\bar{1}_2\,|\,1_1\bar{1}_1\rangle - \langle 1_2\bar{1}_2\,|\,\bar{1}_11_1\rangle\\ &= [1_21_1|\bar{1}_2\bar{1}_1] - [1_2\bar{1}_1|\bar{1}_21_1]\\ &= (1_21_1|1_21_1)\\ &= 0\end{aligned} \tag{4.6.2}$$

$$\begin{aligned}\langle 1_1\bar{1}_12_2\bar{2}_2\,|\,\mathscr{H}\,|\,1_1\bar{1}_12_1\bar{2}_1\rangle &= \langle 2_2\bar{2}_2\,\|\,2_1\bar{2}_1\rangle\\ &= \langle 2_2\bar{2}_2\,|\,2_1\bar{2}_1\rangle - \langle 2_2\bar{2}_2\,|\,\bar{2}_12_1\rangle\\ &= [2_22_1|\bar{2}_2\bar{2}_1] - [2_2\bar{2}_1|\bar{2}_22_1]\\ &= (2_22_1|2_22_1)\\ &= 0\end{aligned} \tag{4.6.3}$$

Ex 4.11

$$\frac{{}^NE_{\rm corr}({\rm DCI})}{N} = \frac{\Delta - (\Delta^2 + NK_{12}^2)^{1/2}}{N} \tag{4.6.4}$$

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

N	${}^NE_{\rm corr}({\rm DCI})/N$
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 $|2_1\bar{2}_12_2\,\delta 2_2\rangle$.

$$\langle\Psi_0\,|\,\mathscr{H}\,|\,2_1\bar{2}_12_2\bar{2}_2\rangle = 0 \tag{4.6.5}$$

$$\begin{aligned}\langle 2_1\bar{2}_11_2\bar{1}_2\,|\,\mathscr{H}\,|\,2_1\bar{2}_12_2\bar{2}_2\rangle &= \langle 1_2\bar{1}_2\,\|\,2_2\bar{2}_2\rangle\\ &= \langle 1_2\bar{1}_2\,|\,2_2\bar{2}_2\rangle - \langle 1_2\bar{1}_2\,|\,\bar{2}_22_2\rangle\\ &= [1_22_2|\bar{1}_2\bar{2}_2] - [1_2\bar{2}_2|\bar{1}_22_2]\\ &= (12|12)\\ &= K_{12}\end{aligned} \tag{4.6.6}$$

$$\begin{aligned}\langle 1_1\bar{1}_12_2\bar{2}_2\,|\,\mathscr{H}\,|\,2_1\bar{2}_12_2\bar{2}_2\rangle &= \langle 1_1\bar{1}_1\,\|\,2_1\bar{2}_1\rangle\\ &= \langle 1_1\bar{1}_1\,|\,2_1\bar{2}_1\rangle - \langle 1_1\bar{1}_1\,|\,\bar{2}_12_1\rangle\\ &= [1_12_1|\bar{1}_1\bar{2}_1] - [1_1\bar{2}_1|\bar{1}_12_1]\\ &= (12|12)\\ &= K_{12}\end{aligned} \tag{4.6.7}$$

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

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

$$\begin{aligned} {}^1E_{\text{corr}}(\text{exact}) &= \Delta - \sqrt{\Delta^2 + K_{12}^2} \\ &= \Delta - \Delta\sqrt{1 + \frac{K_{12}^2}{\Delta^2}} \\ &\approx \Delta - \Delta\left(1 + \frac{1}{2}\frac{K_{12}^2}{\Delta^2}\right) \\ &\approx -\frac{1}{2}\frac{K_{12}^2}{\Delta} \end{aligned} \tag{4.6.11}$$

$$\begin{aligned} {}^NE_{\text{corr}}(\text{DCI}) &= \Delta - \sqrt{\Delta^2 + NK_{12}^2} \\ &= \Delta - \Delta\sqrt{1 + \frac{NK_{12}^2}{\Delta^2}} \\ &\approx \Delta - \Delta\left(1 + \frac{1}{2}\frac{NK_{12}^2}{\Delta^2}\right) \\ &\approx -\frac{1}{2}\frac{NK_{12}^2}{\Delta} \end{aligned} \tag{4.6.12}$$

Ex 4.14

a.

$$\begin{aligned} {}^NE_{\text{corr}}(\text{DCI}) &= \Delta - \sqrt{\Delta^2 + NK_{12}^2} \\ &= \Delta - \Delta\sqrt{1 + \frac{NK_{12}^2}{\Delta^2}} \\ &= \Delta - \Delta\left(1 + \frac{1}{2}\frac{NK_{12}^2}{\Delta^2} - \frac{1}{8}\frac{N^2K_{12}^4}{\Delta^4} + \cdots\right) \\ &= -\frac{1}{2}\frac{NK_{12}^2}{\Delta} + \frac{1}{8}\frac{N^2K_{12}^4}{\Delta^3} + \cdots \end{aligned} \tag{4.6.13}$$

b.

$$c_0^2 = \frac{1}{1 + Nc_1^2} \tag{4.6.14}$$

thus

$$1 - c_0^2 = \frac{Nc_1^2}{1 + Nc_1^2} \tag{4.6.15}$$

c.

$$
\begin{aligned}
c_1 &= \frac{K_{12}}{{}^N E_{\text{corr}}(\text{DCI}) - 2\Delta} \\
&= \frac{K_{12}}{-\dfrac{1}{2}\dfrac{NK_{12}^2}{\Delta} + \dfrac{1}{8}\dfrac{N^2K_{12}^4}{\Delta^3} - 2\Delta + \cdots} \\
&= \frac{1}{-\dfrac{1}{2}\dfrac{NK_{12}}{\Delta} + \dfrac{1}{8}\dfrac{N^2K_{12}^3}{\Delta^3} - 2\dfrac{\Delta}{K_{12}} + \cdots} \\
&= -\frac{1}{2}\frac{K_{12}}{\Delta} + \cdots
\end{aligned} \tag{4.6.16}
$$

d.

$$
\Delta E_{\text{Davidson}} = (1 - c_0^2)\ {}^N E_{\text{corr}}(\text{DCI}) \tag{4.6.17}
$$

$$
\begin{aligned}
&= \frac{N(-K_{12}/2\Delta)^2}{1 + N(-K_{12}/2\Delta)^2}\left(-\frac{1}{2}\frac{NK_{12}^2}{\Delta} + \frac{1}{8}\frac{N^2K_{12}^4}{\Delta^3} + \cdots\right) \\
&= N\frac{K_{12}^2}{4\Delta^2}\left(-\frac{1}{2}\frac{NK_{12}^2}{\Delta} + \frac{1}{8}\frac{N^2K_{12}^4}{\Delta^3} + \cdots\right) \\
&= -\frac{N^2K_{12}^4}{8\Delta^3} + \cdots
\end{aligned} \tag{4.6.18}
$$

e.

$$
\begin{aligned}
\Delta E_{\text{Davidson}} &= (1 - c_0^2)\ {}^N E_{\text{corr}}(\text{DCI}) \\
&= \frac{Nc_1^2}{1 + Nc_1^2} NK_{12}c_1 \\
&= \frac{N^2K_{12}c_1^3}{1 + Nc_1^2}
\end{aligned} \tag{4.6.19}
$$

while

$$
c_1 = {}^N E_{\text{corr}}(\text{DCI})/NK_{12} \tag{4.6.20}
$$

thus

$$
\begin{aligned}
\Delta E_{\text{Davidson}} &= \frac{N^2K_{12}c_1^3}{1 + Nc_1^2} \\
&= \frac{[{}^N E_{\text{corr}}(\text{DCI})]^3/NK_{12}^2}{1 + [{}^N E_{\text{corr}}(\text{DCI})]^2/NK_{12}^2} \\
&= \frac{[{}^N E_{\text{corr}}(\text{DCI})]^3}{NK_{12}^2 + [{}^N E_{\text{corr}}(\text{DCI})]^2}
\end{aligned} \tag{4.6.21}
$$

Since

$$
{}^N E_{\text{corr}}(\text{DCI}) = \Delta - \sqrt{\Delta^2 + NK_{12}^2} \tag{4.6.22}
$$

$$
{}^N E_{\text{corr}}(\text{exact}) = N\left[\Delta - \sqrt{\Delta^2 + K_{12}^2}\right] \tag{4.6.23}
$$

The values of ${}^{N}E_{\mathrm{corr}}(\mathrm{DCI})$, ${}^{N}E_{\mathrm{corr}}(\mathrm{exact})$, $\Delta E_{\mathrm{Davidson}}$ for $N = 1, \cdots, 20, 100$ are as follows.

N	${}^{N}E_{\mathrm{corr}}(\mathrm{DCI})$	${}^{N}E_{\mathrm{corr}}(\mathrm{exact})$	$\Delta E_{\mathrm{Davidson}}$
1	-0.020571	-0.020571	-0.0002615
2	-0.040632	-0.041142	-0.0009954
3	-0.060219	-0.061713	-0.0021360
4	-0.079364	-0.082284	-0.0036282
5	-0.098095	-0.102855	-0.0054259
6	-0.116439	-0.123426	-0.0074900
7	-0.134419	-0.143997	-0.0097872
8	-0.152055	-0.164567	-0.0122891
9	-0.169367	-0.185138	-0.0149711
10	-0.186371	-0.205709	-0.0178120
11	-0.203084	-0.22628	-0.0207933
12	-0.219519	-0.246851	-0.0238991
13	-0.235691	-0.267422	-0.0271151
14	-0.251612	-0.287993	-0.0304291
15	-0.267292	-0.308564	-0.0338301
16	-0.282743	-0.329135	-0.0373084
17	-0.297975	-0.349706	-0.0408554
18	-0.312996	-0.370277	-0.0444636
19	-0.327814	-0.390848	-0.0481262
20	-0.342439	-0.411419	-0.0518370
100	-1.188450	-2.057090	-0.3571950

The values and errors of DCI energies and DCI energies with Davidson correction are as follows.

N	${}^{N}E_{\mathrm{corr}}(\mathrm{DCI})/{}^{N}E_{\mathrm{corr}}(\mathrm{exact})$	Error/%	$[{}^{N}E_{\mathrm{corr}}(\mathrm{DCI}) + \Delta E_{\mathrm{Davidson}}]/{}^{N}E_{\mathrm{corr}}(\mathrm{exact})$	Error/%
1	1.0000	0.00	1.0127	-1.27
2	0.9876	1.24	1.0118	-1.18
3	0.9758	2.42	1.0104	-1.04
4	0.9645	3.55	1.0086	-0.86
5	0.9537	4.63	1.0065	-0.65
6	0.9434	5.66	1.0041	-0.41
7	0.9335	6.65	1.0015	-0.15
8	0.9240	7.60	0.9986	0.14
9	0.9148	8.52	0.9957	0.43
10	0.9060	9.40	0.9926	0.74
11	0.8975	10.25	0.9894	1.06
12	0.8893	11.07	0.9861	1.39
13	0.8813	11.87	0.9827	1.73
14	0.8737	12.63	0.9793	2.07
15	0.8662	13.38	0.9759	2.41
16	0.8591	14.10	0.9724	2.76
17	0.8521	14.79	0.9689	3.11
18	0.8453	15.47	0.9654	3.46
19	0.8387	16.13	0.9619	3.81
20	0.8323	16.77	0.9583	4.17
100	0.5777	42.23	0.7514	24.86

f. From data of Saxe et al., we get

$$E_{\text{corr}}(\text{DCI}) = -0.139340 \qquad c_0 = 0.97938 \tag{4.6.24}$$

thus

$$\begin{aligned} \Delta E_{\text{Davidson}} &= (1 - c_0^2) E_{\text{corr}}(\text{DCI}) \\ &= (1 - 0.97938^2) \times (-76.129178) \\ &= -0.005687 \end{aligned} \tag{4.6.25}$$

thus

	correlation energy	error wrt full CI
DCI + Davidson	-0.145027	0.003181
DQCI	-0.145859	0.002349
Full CI	-0.148208	0

Ex 4.15

$$\begin{aligned} \langle \Psi_0 \,|\, \Phi_0 \rangle &= \prod_{i=1}^{N} \left[(1 + c^2)^{-1/2} \langle 1_i \bar{1}_i \,|\, 1_i \bar{1}_i \rangle + c(1 + c^2)^{-1/2} \langle 1_i \bar{1}_i \,|\, 2_i \bar{2}_i \rangle \right] \\ &= (1 + c^2)^{-N/2} \end{aligned} \tag{4.6.26}$$

Since

$$c = \frac{{}^1E_{\text{corr}}}{K_{12}} = \frac{-0.020571}{0.1813} = -0.1135 \tag{4.6.27}$$

we get

N	$\langle \Psi_0 \,|\, \Phi_0 \rangle$
1	0.9936
10	0.9380
100	0.5273