

# Modern Quantum Chemistry, Szabo & Ostlund

## HW

WSF

May 5, 2021

## Contents

|          |   |          |
|----------|---|----------|
| <b>4</b> | <b>Configuration Interaction</b>  | <b>2</b> |
| 4.1      | Multiconfigurational Wave Functions and the Structure of Full CI Matrix . . . . . | 2        |
| 4.1.1    | Intermediate Normalization and an Expression for the Correlation Energy . . . . . | 2        |
|          | Ex 4.1 . . . . .  | 2        |
|          | Ex 4.2 . . . . .  | 2        |
|          | Ex 4.3 . . . . .  | 2        |
| 4.2      | Doubly Excited CI . . . . .   | 3        |
| 4.3      | Some Illustrative Calculations . . . . .  | 3        |
| 4.4      | Natural Orbitals and the 1-Particle Reduced DM . . . . .                          | 3        |
|          | Ex 4.4 . . . . .  | 3        |
|          | Ex 4.5 . . . . .  | 3        |
|          | Ex 4.6 . . . . .  | 3        |
|          | Ex 4.7 . . . . .  | 4        |
|          | Ex 4.8 . . . . .  | 4        |
| 4.5      | The MCSCF and the GVB Methods . . . . .   | 6        |
|          | Ex 4.9 . . . . .  | 6        |
| 4.6      | Truncated CI and the Size-consistency Problem . . . . .                           | 7        |
|          | Ex 4.10 . . . . .   | 7        |
|          | Ex 4.11 . . . . .   | 7        |
|          | Ex 4.12 . . . . .   | 7        |
|          | Ex 4.13 . . . . .   | 8        |
|          | Ex 4.14 . . . . .   | 8        |
|          | Ex 4.15 . . . . .   | 11       |

## 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

$$|\Phi_0\rangle = |\Psi_0\rangle - |\Psi_{11}^{22}\rangle = |\psi_1\bar{\psi}_1\rangle - |\psi_2\bar{\psi}_2\rangle \quad (4.1.14)$$

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

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

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.

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

#### 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

### 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.

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

i.e.

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

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

## 4.6 Truncated CI and the Size-consistency Problem

### Ex 4.10

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

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

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

### Ex 4.11

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

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

| $N$ | ${}^N E_{\text{corr}}(\text{DCI})/N$ |
|-----|--------------------------------------|
| 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  $|2_1 \bar{2}_1 2_2 \bar{2}_2\rangle$ .

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

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

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

$$\begin{aligned}\langle 2_1 \bar{2}_1 2_2 \bar{2}_2 | \mathcal{H} - E_0 | 2_1 \bar{2}_1 2_2 \bar{2}_2 \rangle &= 4h_{22} + 2J_{22} - 4h_{11} - 2J_{11} \\ &= 4\Delta\end{aligned}\quad (4.6.8)$$

thus the full CI equation is

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

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

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

**Ex 4.13**

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

$$\begin{aligned}{}^N E_{\text{corr}}(\text{DCI}) &= \Delta - \sqrt{\Delta^2 + N K_{12}^2} \\ &= \Delta - \Delta \sqrt{1 + \frac{N K_{12}^2}{\Delta^2}} \\ &\approx \Delta - \Delta \left( 1 + \frac{1}{2} \frac{N K_{12}^2}{\Delta^2} \right) \\ &\approx -\frac{1}{2} \frac{N K_{12}^2}{\Delta}\end{aligned}\quad (4.6.12)$$

**Ex 4.14**

a.

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

b.

$$c_0^2 = \frac{1}{1 + N c_1^2} \quad (4.6.14)$$

thus

$$1 - c_0^2 = \frac{N c_1^2}{1 + N c_1^2} \quad (4.6.15)$$



c.

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

d.

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

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

e.

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

while

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

thus

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

Since

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

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

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

| $N$ | ${}^N E_{\text{corr}}(\text{DCI})$ | ${}^N E_{\text{corr}}(\text{exact})$ | $\Delta E_{\text{Davidson}}$ |
|-----|------------------------------------|--------------------------------------|------------------------------|
| 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.

| $N$ | ${}^N E_{\text{corr}}(\text{DCI})/{}^N E_{\text{corr}}(\text{exact})$ | Error/% | $[{}^N E_{\text{corr}}(\text{DCI}) + \Delta E_{\text{Davidson}}]/{}^N E_{\text{corr}}(\text{exact})$ | 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

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

thus

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

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**

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

Since

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

we get

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