CHAPTER 4

Configuration Interaction

4.1 Multiconfigurational Wave Functions and the Structure of the Full CI Matrix

4.1.1 Intermediate Normalization and an Expression for the Correlation Energy

Exercise 4.1

Obtain Eq.(4.12) from Eq.(4.11). It will prove convenient to use unrestricted summations.

Solution 4.1

Note that the index r must be included in the set $\{t,u,v\}$ and the index a must be included in the set $\{c,d,e\}$ for a matrix element of $\langle\Psi_a^r|\mathscr{H}|\Psi_{cde}^{tuv}\rangle$. Therefore, we find that

$$\sum_{\substack{c<d<e\\t<u<v}}\langle\Psi_a^r|\mathscr{H}|\Psi_{cde}^{tuv}\rangle c_{cde}^{tuv}=\frac{1}{(3!)^2}\sum_{\substack{cde\\tuv}}\langle\Psi_a^r|\mathscr{H}|\Psi_{cde}^{tuv}\rangle c_{cde}^{tuv}$$

$$\begin{aligned}=\frac{1}{(3!)^2}\Bigg[&\sum_{\substack{de\\uv}}\langle\Psi_a^r|\mathscr{H}|\Psi_{ade}^{ruv}\rangle c_{ade}^{ruv}+\sum_{\substack{de\\tv}}\langle\Psi_a^r|\mathscr{H}|\Psi_{ade}^{trv}\rangle c_{ade}^{trv}+\sum_{\substack{de\\tu}}\langle\Psi_a^r|\mathscr{H}|\Psi_{ade}^{tur}\rangle c_{ade}^{tur}\\&+\sum_{\substack{ce\\uv}}\langle\Psi_a^r|\mathscr{H}|\Psi_{cae}^{ruv}\rangle c_{cae}^{ruv}+\sum_{\substack{ce\\tv}}\langle\Psi_a^r|\mathscr{H}|\Psi_{cae}^{trv}\rangle c_{cae}^{trv}+\sum_{\substack{ce\\tu}}\langle\Psi_a^r|\mathscr{H}|\Psi_{cae}^{tur}\rangle c_{cae}^{tur}\\&+\sum_{\substack{cd\\uv}}\langle\Psi_a^r|\mathscr{H}|\Psi_{cda}^{ruv}\rangle c_{cda}^{ruv}+\sum_{\substack{cd\\tv}}\langle\Psi_a^r|\mathscr{H}|\Psi_{cda}^{trv}\rangle c_{cda}^{trv}+\sum_{\substack{cd\\tu}}\langle\Psi_a^r|\mathscr{H}|\Psi_{cda}^{tur}\rangle c_{cda}^{tur}\Bigg].\end{aligned}$$

Then, these dummy indices should be converted into the same one, viz.,

$$\begin{aligned}&\sum_{\substack{c<d<e\\t<u<v}}\langle\Psi_a^r|\mathscr{H}|\Psi_{cde}^{tuv}\rangle c_{cde}^{tuv}\\=\frac{1}{(3!)^2}\Bigg[&\sum_{\substack{cd\\tu}}\langle\Psi_a^r|\mathscr{H}|\Psi_{acd}^{rtu}\rangle c_{acd}^{rtu}+\sum_{\substack{cd\\tu}}\langle\Psi_a^r|\mathscr{H}|\Psi_{acd}^{tru}\rangle c_{acd}^{tru}+\sum_{\substack{cd\\tu}}\langle\Psi_a^r|\mathscr{H}|\Psi_{acd}^{tur}\rangle c_{acd}^{tur}\\&+\sum_{\substack{cd\\tu}}\langle\Psi_a^r|\mathscr{H}|\Psi_{cad}^{rtu}\rangle c_{cad}^{rtu}+\sum_{\substack{cd\\tu}}\langle\Psi_a^r|\mathscr{H}|\Psi_{cad}^{tru}\rangle c_{cad}^{tru}+\sum_{\substack{cd\\tu}}\langle\Psi_a^r|\mathscr{H}|\Psi_{cad}^{tur}\rangle c_{cad}^{tur}\\&+\sum_{\substack{cd\\tu}}\langle\Psi_a^r|\mathscr{H}|\Psi_{cda}^{rtu}\rangle c_{cda}^{rtu}+\sum_{\substack{cd\\tu}}\langle\Psi_a^r|\mathscr{H}|\Psi_{cda}^{tru}\rangle c_{cda}^{tru}+\sum_{\substack{cd\\tu}}\langle\Psi_a^r|\mathscr{H}|\Psi_{cda}^{tur}\rangle c_{cda}^{tur}\Bigg]\\=\frac{1}{(3!)^2}\times 9\sum_{\substack{cd\\tu}}\langle\Psi_a^r|\mathscr{H}|\Psi_{acd}^{rtu}\rangle c_{acd}^{rtu}=\frac{1}{(2!)^2}\sum_{\substack{cd\\tu}}\langle\Psi_a^r|\mathscr{H}|\Psi_{acd}^{rtu}\rangle c_{acd}^{rtu}=&\sum_{\substack{c<d\\t<u}}\langle\Psi_a^r|\mathscr{H}|\Psi_{acd}^{rtu}\rangle c_{acd}^{rtu}.\end{aligned}$$

Thus, we have proved that

$$\sum_{\substack{c<d<e\\ t<u<v}} \langle \Psi_a^r | \mathscr{H} | \Psi_{cde}^{tuv} \rangle c_{cde}^{tuv} = \sum_{\substack{c<d\\ t<u}} \langle \Psi_a^r | \mathscr{H} | \Psi_{acd}^{rtu} \rangle c_{acd}^{rtu}. \tag{4.1}$$

With this equation, it is clear that (4.12) can be obtained from (4.11).

Exercise 4.2

Using the secular determinant approach show that the lowest eigenvalue of the matrix

$$\begin{pmatrix} 0 & K_{12} \\ K_{12} & 2\Delta \end{pmatrix}$$

is given by Eq.(4.23).

Solution 4.2

The introduction of the secular determinant approach is demonstrated in the page 18. The matrix in the exercise 4.2 is denoted as H, then

$$\det(H - \varepsilon I) = \begin{vmatrix} -\varepsilon & K_{12} \\ K_{12} & 2\Delta - \varepsilon \end{vmatrix} = \varepsilon^2 - 2\Delta\varepsilon - K_{12}^2 = 0,$$

The discriminant Δ_E of this quadratic equation is

$$\Delta_E = 4\Delta^2 - 4 \times (-K_{12}^2) = 4(\Delta^2 + K_{12}^2)$$

Thus, the root are

$$E_1 = \Delta + \sqrt{\Delta^2 + K_{12}^2}, \quad E_2 = \Delta - \sqrt{\Delta^2 + K_{12}^2}.$$

Therefore, the lowest root is the correlation energy, viz.,

$$E_{\text{corr}} = \Delta - \sqrt{\Delta^2 + K_{12}^2}. \tag{4.2}$$

Exercise 4.3

Calculate the coefficient of the double excitation (c) in the intermediate normalized CI wave function at R = 1.4 a.u., using the STO-3G integrals given in Appendix D. Show analytically that as $R \to \infty$, $c \to -1$, and hence that at large distances the Hartree-Fock ground state and the doubly excited configuration have equal weight in the CI ground state. Finally, show that the CI wave function, when normalized to unity, becomes (at $R = \infty$)

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

where ϕ_1 and ϕ_2 are atomic orbitals on centers one and two, respectively.

Solution 4.3

When $R = 1.4.$ a.u., we know that

$$\begin{array}{lll} \varepsilon_1 = -0.5782\,\text{a.u.}, & \varepsilon_2 = 0.6703\,\text{a.u.}, & J_{11} = 0.6746\,\text{a.u.}, \\ J_{12} = 0.6636\,\text{a.u.}, & J_{22} = 0.6975\,\text{a.u.}, & K_{12} = 0.1813\,\text{a.u.} \end{array}$$

Firstly, with (4.20), we calculate 2Δ at $R = 1.4.$ a.u., viz.,

$$2\Delta = [2(\varepsilon_2 - \varepsilon_1) + J_{11} + J_{22} - 4J_{12} + 2K_{12}] = 1.5773\,\text{a.u.}$$

In other words, $\Delta = 0.78865$ a.u. Thus, the correlation energy E_{corr} at $R = 1.4.$ a.u. is

$$E_{\text{corr}} = \Delta - \sqrt{\Delta^2 + K_{12}^2} = -0.02057\,\text{a.u.}.$$

Therefore,

$$c = \frac{K_{12}}{E_{\text{corr}} - 2\Delta} = \frac{0.1813\,\text{a.u.}}{-0.02057\,\text{a.u.}. - 1.5773\,\text{a.u.}.} \approx -0.1135. \tag{4.3}$$

Indeed, we can find that

$$\Delta = \varepsilon_2 - \varepsilon_1 + \frac{1}{2}J_{11} + \frac{1}{2}J_{22} - 2J_{12} + K_{12} = h_{22} - h_{11} - \frac{1}{2}J_{11} + \frac{1}{2}J_{12}.$$

It is clear that

$$\lim_{R\to\infty}\Delta = \lim_{R\to\infty}\left[h_{22} - h_{11} + \frac{1}{2}J_{22} - \frac{1}{2}J_{11}\right] = E(\text{H}) - E(\text{H}) + \frac{1}{4}(\phi_1\phi_1|\phi_1\phi_1) - \frac{1}{4}(\phi_1\phi_1|\phi_1\phi_1) = 0.$$

Thus,

$$\begin{aligned}\lim_{R\to\infty} c &= \lim_{R\to\infty}\frac{K_{12}}{E_{\text{corr}} - 2\Delta} = \lim_{R\to\infty}\frac{K_{12}}{\Delta - \sqrt{\Delta^2 + K_{12}^2} - 2\Delta} = \lim_{R\to\infty}\frac{-K_{12}}{\Delta + \sqrt{\Delta^2 + K_{12}^2}} \\ &= -\lim_{\Delta\to 0}\frac{1}{\frac{\Delta}{K_{12}} + \sqrt{1 + \left(\frac{\Delta}{K_{12}}\right)^2}} = -\lim_{x\to 0}\frac{1}{x + \sqrt{1+x^2}} = -1.\end{aligned}$$

This conclusion means that at large distances the Hartree-Fock ground state Ψ_0 and the doubly excited configuration $\Psi_{1\bar{1}}^{2\bar{2}}$ have equal weight in the CI ground state Φ, viz.,

$$\lim_{R\to\infty}|\Phi\rangle = |\Psi_0\rangle - |\Psi_{1\bar{1}}^{2\bar{2}}\rangle = |\psi_1\bar{\psi}_1\rangle - |\psi_2\bar{\psi}_2\rangle.$$

Note that as $R \to \infty$, from (3.236) and (3.237), we find that

$$\lim_{R\to\infty}\psi_1 = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2), \quad \lim_{R\to\infty}\psi_2 = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2).$$

Thus,

$$\begin{aligned}\lim_{R\to\infty}|\psi_1\bar{\psi}_1\rangle &= \frac{1}{2}|(\phi_1 + \phi_2)(\bar{\phi}_1 + \bar{\phi}_2)\rangle = \frac{1}{2}\left(|\phi_1\bar{\phi}_1\rangle + |\phi_1\bar{\phi}_2\rangle + |\phi_2\bar{\phi}_1\rangle + |\phi_2\bar{\phi}_2\rangle\right), \\ \lim_{R\to\infty}|\psi_2\bar{\psi}_2\rangle &= \frac{1}{2}|(\phi_1 - \phi_2)(\bar{\phi}_1 - \bar{\phi}_2)\rangle = \frac{1}{2}\left(|\phi_1\bar{\phi}_1\rangle - |\phi_1\bar{\phi}_2\rangle - |\phi_2\bar{\phi}_1\rangle + |\phi_2\bar{\phi}_2\rangle\right),\end{aligned}$$

and then

$$\lim_{R\to\infty}|\Phi\rangle = \lim_{R\to\infty}|\psi_1\bar{\psi}_1\rangle - \lim_{R\to\infty}|\psi_2\bar{\psi}_2\rangle = |\phi_1\bar{\phi}_2\rangle + |\phi_2\bar{\phi}_1\rangle$$

Thus, at $R = \infty$, the normalized CI wave function is

$$\lim_{R\to\infty}|\Phi\rangle = \lim_{R\to\infty}\frac{1}{\langle\Phi_0|\Phi_0\rangle}|\Phi_0\rangle = \frac{1}{\sqrt{2}}\left(|\phi_1\bar{\phi}_2\rangle + |\phi_2\bar{\phi}_1\rangle\right). \tag{4.4}$$

We have proved two conclusions at $R = \infty$, the equal weight of the Hartree-Fock ground state Ψ_0 and the doubly excited configuration $\Psi_{1\bar{1}}^{2\bar{2}}$, and the form of normalized CI wave function.

4.2 Doubly Excited CI

4.3 Some Illustrative Calculations

4.4 Natural Orbitals and the One-Particle Reduced Density Matrix

Exercise 4.4

Show that γ is a Hermitian matrix.

Solution 4.4

Firstly, we find that $\gamma(\boldsymbol{x}_1, \boldsymbol{x}_1')$ is Hermite, viz.,

$$\begin{aligned}\gamma^*(\boldsymbol{x}_1, \boldsymbol{x}_1') &= \left(N \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{x}_2 \cdots \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{x}_N \Phi^*(\boldsymbol{x}_1, \boldsymbol{x}_2, \cdots, \boldsymbol{x}_N)\Phi(\boldsymbol{x}_1', \boldsymbol{x}_2, \cdots, \boldsymbol{x}_N)\right)^* \\ &= N \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{x}_2 \cdots \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{x}_N \Phi^*(\boldsymbol{x}_1', \boldsymbol{x}_2, \cdots, \boldsymbol{x}_N)\Phi(\boldsymbol{x}_1, \boldsymbol{x}_2, \cdots, \boldsymbol{x}_N) = \gamma(\boldsymbol{x}_1', \boldsymbol{x}_1).\end{aligned}$$

Thus,

$$\begin{aligned}\gamma_{ji}^* &= \left(\int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{x}_1 \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{x}_1' \chi_j^*(\boldsymbol{x}_1)\gamma(\boldsymbol{x}_1, \boldsymbol{x}_1')\chi_i(\boldsymbol{x}_1')\right)^* = \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{x}_1 \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{x}_1' \chi_i^*(\boldsymbol{x}_1')\gamma^*(\boldsymbol{x}_1, \boldsymbol{x}_1')\chi_j(\boldsymbol{x}_1) \\ &= \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{x}_1 \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{x}_1' \chi_i^*(\boldsymbol{x}_1')\gamma(\boldsymbol{x}_1', \boldsymbol{x}_1)\chi_j(\boldsymbol{x}_1) = \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{x}_1 \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{x}_1 \chi_i^*(\boldsymbol{x}_1)\gamma(\boldsymbol{x}_1, \boldsymbol{x}_1')\chi_j(\boldsymbol{x}_1') = \gamma_{ij}.\end{aligned}$$

Hence we have proved that γ is a Hermitian matrix.

Exercise 4.5

Show that $\mathrm{tr}(\gamma) = N$.

Solution 4.5

$$\begin{aligned}N &= \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{x}_1 \rho(\boldsymbol{x}_1) = \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{x}_1 \gamma(\boldsymbol{x}_1, \boldsymbol{x}_1) = \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{x}_1 \sum_{i=1}^N \sum_{j=1}^N \chi_i(\boldsymbol{x}_1)\gamma_{ij}\chi_j^*(\boldsymbol{x}_1) \\ &= \sum_{i=1}^N \sum_{j=1}^N \gamma_{ij} \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{x}_1 \chi_i(\boldsymbol{x}_1)\chi_j^*(\boldsymbol{x}_1) = \sum_{i=1}^N \sum_{j=1}^N \gamma_{ij}\delta_{ij} = \sum_{i=1}^N \gamma_{ii} = \mathrm{tr}(\gamma).\end{aligned}$$

Exercise 4.6

Consider the one-electron operator

$$\mathscr{O}_1 = \sum_{i=1}^N h(i).$$

a. Show that

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

where the notation $[\quad]_{\boldsymbol{x}_1' = \boldsymbol{x}_1}$ means that $\boldsymbol{x}_1'$ is set equal to $\boldsymbol{x}_1$ after $h(\boldsymbol{x}_1)$ has operated on $\gamma(\boldsymbol{x}_1, \boldsymbol{x}_1')$.

b. Show that

$$\langle \Phi | \mathscr{O}_1 | \Phi \rangle = \mathrm{tr}(\mathbf{h}\gamma)$$

where

$$h_{ij} = \langle i | h | j \rangle = \int \mathrm{d}\boldsymbol{x}_1 \chi_i^*(\boldsymbol{x}_1) h(\boldsymbol{x}_1) \chi_j(\boldsymbol{x}_1).$$

Thus the expectation value of any one-electron operator can be expressed in terms of the one-matrix.

Solution 4.6

a. From the definition of $\mathscr{O}_1$, we find that

$$\begin{aligned}\langle \Phi | \mathscr{O}_1 | \Phi \rangle &= \langle \Phi | \sum_{i=1}^N h(i) | \Phi \rangle \\ &= \sum_{i=1}^N \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{x}_1 \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{x}_2 \cdots \int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{x}_N \Phi^*(\boldsymbol{x}_1, \boldsymbol{x}_2, \cdots, \boldsymbol{x}_N) h(\boldsymbol{x}_i) \Phi(\boldsymbol{x}_1, \boldsymbol{x}_2, \cdots, \boldsymbol{x}_N)\end{aligned}$$

Considering that the different integral variables $\mathrm{d}\boldsymbol{x}_1$ and $\mathrm{d}\boldsymbol{x}_i$ $(i \neq 1)$ have the same integral range,

it is clear that

$$\begin{aligned}\langle\Phi|\mathscr{O}_1|\Phi\rangle &= \langle\Phi|\sum_{i=1}^{N} h(i)|\Phi\rangle \\ &= N\int_{\mathbb{R}^3}\mathrm{d}\boldsymbol{x}_1\int_{\mathbb{R}^3}\mathrm{d}\boldsymbol{x}_2\cdots\int_{\mathbb{R}^3}\mathrm{d}\boldsymbol{x}_N\Phi^*(\boldsymbol{x}_1,\boldsymbol{x}_2,\cdots,\boldsymbol{x}_N)h(\boldsymbol{x}_1)\Phi(\boldsymbol{x}_1,\boldsymbol{x}_2,\cdots,\boldsymbol{x}_N) \\ &= \int_{\mathbb{R}^3}\mathrm{d}\boldsymbol{x}_1 h(\boldsymbol{x}_1)\times N\int_{\mathbb{R}^3}\mathrm{d}\boldsymbol{x}_2\cdots\int_{\mathbb{R}^3}\mathrm{d}\boldsymbol{x}_N\Phi^*(\boldsymbol{x}_1,\boldsymbol{x}_2,\cdots,\boldsymbol{x}_N)\Phi(\boldsymbol{x}_1,\boldsymbol{x}_2,\cdots,\boldsymbol{x}_N) \\ &= \int_{\mathbb{R}^3}\mathrm{d}\boldsymbol{x}_1 h(\boldsymbol{x}_1)\rho(\boldsymbol{x}_1) = \int_{\mathbb{R}^3}\mathrm{d}\boldsymbol{x}_1 h(\boldsymbol{x}_1)\gamma(\boldsymbol{x}_1,\boldsymbol{x}_1) = \int_{\mathbb{R}^3}\mathrm{d}\boldsymbol{x}_1\left[h(\boldsymbol{x}_1)\gamma(\boldsymbol{x}_1,\boldsymbol{x}_1')\right]_{\boldsymbol{x}_1'=\boldsymbol{x}_1}.\end{aligned}$$

b. From the former issue, we know that

$$\begin{aligned}\langle\Phi|\mathscr{O}_1|\Phi\rangle &= \int_{\mathbb{R}^3}\mathrm{d}\boldsymbol{x}_1 h(\boldsymbol{x}_1)\gamma(\boldsymbol{x}_1,\boldsymbol{x}_1) = \int_{\mathbb{R}^3}\mathrm{d}\boldsymbol{x}_1 h(\boldsymbol{x}_1)\sum_{i=1}^{N}\sum_{j=1}^{N}\chi_i(\boldsymbol{x}_1)\gamma_{ij}\chi_j^*(\boldsymbol{x}_1) \\ &= \sum_{i=1}^{N}\sum_{j=1}^{N}\gamma_{ij}\int_{\mathbb{R}^3}\mathrm{d}\boldsymbol{x}_1\chi_i(\boldsymbol{x}_1)h(\boldsymbol{x}_1)\chi_j^*(\boldsymbol{x}_1) = \sum_{i=1}^{N}\sum_{j=1}^{N}\gamma_{ij}h_{ji} = \mathrm{tr}(\gamma\mathbf{h}) = \mathrm{tr}(\mathbf{h}\gamma).\end{aligned}$$

The last step uses the conclusion of exercise 1.4(a).

Exercise 4.7

Recall that in second quantization a one-electron operator is

$$\mathscr{O}_1 = \sum_{ij}\langle i|h|j\rangle a_i^\dagger a_j.$$

a. Show that

$$\gamma_{ij} = \langle\Phi|a_j^\dagger a_i|\Phi\rangle.$$

b. Show that the matrix elements of γ^{HF} are given by Eq.(4.40).

Solution 4.7

a. We can use the conclusion in exercise 4.6(b), viz.,

$$\mathrm{tr}(\mathbf{h}\gamma) = \sum_{ij}h_{ij}\gamma_{ji} = \langle\Phi|\mathscr{O}_1|\Phi\rangle.$$

With the second quantization form, we find that

$$\sum_{ij}h_{ij}\gamma_{ji} = \langle\Phi|\mathscr{O}_1|\Phi\rangle = \sum_{ij}\langle\Phi|a_i^\dagger a_j|\Phi_1\rangle h_{ij} \Leftrightarrow \sum_{ij}\left[\langle\Phi|a_i^\dagger a_j|\Phi\rangle - \gamma_{ji}\right]h_{ij} = 0.$$

For any system, this equation holds true, which means that terms h_{ij} are linearly independent. Thus,

$$\gamma_{ji} = \langle\Phi|a_i^\dagger a_j|\Phi\rangle, \tag{4.5}$$

which equals $\gamma_{ij} = \langle\Phi|a_j^\dagger a_i|\Phi\rangle$.

b. If i belongs to unoccupied, $a_i|\Phi\rangle$ vanishes, and so does $\langle\Phi|a_j^\dagger$ if j belongs to unoccupied. If the indices i and j are occupied, viz., $i = a$ and $j = b$, with $a_a^\dagger|\Phi\rangle = 0$,

$$\gamma_{ab}^{\mathrm{HF}} = \langle\Phi|a_a^\dagger a_b|\Phi\rangle = \langle\Phi|(\delta_{ab} - a_b a_a^\dagger)|\Phi\rangle = \delta_{ab} - \langle\Phi|a_b a_a^\dagger|\Phi\rangle = \delta_{ab} - 0 = \delta_{ab}.$$

Thus, we have proved

$$\gamma_{ij}^{\mathrm{HF}} = \begin{cases}\delta_{ij}, & \text{iff } i,j\in\text{occupied},\\ 0, & \text{otherwise.}\end{cases}$$

Exercise 4.8

For the special case of a two-electron system, the use of natural orbitals dramatically reduces the size of the full CI expansion. If ψ_1 is the occupied Hartree-Fock spatial orbital and ψ_r, $r = 2, 3, ..., K$ are virtual spatial orbitals, the normalized full CI singlet wave function has the form

$$|^1\Phi_0\rangle = c_0|1\bar{1}\rangle + \sum_{r=2}^{K} c_1^r|^1\Psi_1^r\rangle + \frac{1}{2}\sum_{r=2}^{K}\sum_{s=2}^{K} c_{11}^{rs}|^1\Psi_{11}^{rs}\rangle$$

where the singly and doubly excited spin adapted configurations are defined in Subsection 2.5.2.

a. Show that $|^1\Phi_0\rangle$ can be cast into the form

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

where $\mathbf{C}$ is a symmetric $K \times K$ matrix.

b. Show that

$$\gamma(\boldsymbol{x}_1, \boldsymbol{x}_1') = \sum_{ij}(\mathbf{C}\mathbf{C}^\dagger)_{ij}\left(\psi_i(1)\psi_j^*(1') + \bar{\psi}_i(1)\bar{\psi}_j^*(1')\right).$$

c. Let $\mathbf{U}$ be the unitary transformation which diagonalizes $\mathbf{C}$

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

where $(\mathbf{d})_{ij} = d_i\delta_{ij}$. Show that

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

d. Show that

$$\gamma(\boldsymbol{x}_1, \boldsymbol{x}_1') = \sum_i d_i^2\left(\zeta_i(1)\zeta_i^*(1') + \bar{\zeta}_i(1)\bar{\zeta}_i^*(1')\right)$$

where

$$\zeta_i = \sum_k \psi_k U_{ki}.$$

Thus $\mathbf{U}$ diagonalizes the one-matrix, and hence ζ_i are natural spatial orbitals for the two-electron system.

e. Finally, since $\mathbf{C}$ is symmetric, $\mathbf{U}$ can be chosen as real. Show that in terms of the natural spatial orbitals, $|^1\Phi_0\rangle$ given in part (a) can be rewritten as

$$|^1\Phi_0\rangle = \sum_{i=1}^{K} d_i|\zeta_i\bar{\zeta}_i\rangle$$

and note that this expansion contains only K terms.

Solution 4.8

a. From (2.263) at the page 103 and Table 2.7 at the page 104, we know that

$$\begin{aligned}
|^1\Psi_1^r\rangle &= \frac{1}{\sqrt{2}}\left(|\Psi_1^{\bar{r}}\rangle + |\Psi_1^r\rangle\right) = \frac{1}{\sqrt{2}}\left(|1\bar{r}\rangle + |r\bar{1}\rangle\right), \\
|^1\Psi_{11}^{rr}\rangle &= |\Psi_{1\bar{1}}^{r\bar{r}}\rangle = |r\bar{r}\rangle, \\
|^1\Psi_{11}^{rs}\rangle &= \frac{1}{\sqrt{2}}\left(|\Psi_{1\bar{1}}^{r\bar{s}}\rangle + |\Psi_{1\bar{1}}^{s\bar{r}}\rangle\right) = \frac{1}{\sqrt{2}}\left(|r\bar{s}\rangle + |s\bar{r}\rangle\right), \forall r \neq s.
\end{aligned}$$

Thus,

$$|^1\Phi_0\rangle = c_0|1\bar{1}\rangle + \sum_{r=2}^{K}\frac{c_1^r}{\sqrt{2}}\left(|1\bar{r}\rangle + |r\bar{1}\rangle\right) + \frac{1}{2}\sum_{r=2}^{K} c_{11}^{rr}|r\bar{r}\rangle + \sum_{r=2}^{K}\sum_{\substack{s=2 \\ r>s}}^{K} c_{11}^{rs}\frac{1}{\sqrt{2}}\left(|r\bar{s}\rangle + |s\bar{r}\rangle\right).$$

From this equation, we find that the coefficients are

$$\begin{aligned}
C_{11} &= c_0, \\
C_{r1} = C_{1r} &= \frac{c_1^r}{\sqrt{2}}, \\
C_{rr} &= \frac{c_{11}^{rr}}{2}, \\
C_{rs} = C_{sr} &= \frac{c_{11}^{rs} + c_{11}^{sr}}{2}, \ \forall r \neq s,
\end{aligned}$$

which equals

$$|^1\Phi_0\rangle = \sum_{i=1}^{K}\sum_{j=1}^{K} C_{ij}|\psi_i\bar{\psi}_j\rangle, \tag{4.6}$$

where

$$C_{ij} = C_{ji}, \ \forall i, j \in \{1, 2, \cdots, K\}. \tag{4.7}$$

In other words, $\mathbf{C}$ is a symmetric $K \times K$ matrix.

b. Note that there are two electrons in this system,

$$\begin{aligned}
\gamma(\boldsymbol{x}_1, \boldsymbol{x}_1') &= 2\int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{x}_2 \Phi(\boldsymbol{x}_1, \boldsymbol{x}_2)\Phi^*(\boldsymbol{x}_1', \boldsymbol{x}_2) \\
&= 2\int_{\mathbb{R}^3} \mathrm{d}\boldsymbol{x}_2 \frac{1}{\sqrt{2}} \sum_{i=1}^{K}\sum_{j=1}^{K} C_{ij}\left[\psi_i(\boldsymbol{x}_1)\bar{\psi}_j(\boldsymbol{x}_2) - \psi_i(\boldsymbol{x}_2)\bar{\psi}_j(\boldsymbol{x}_1)\right] \\
&\qquad \times \frac{1}{\sqrt{2}} \sum_{k=1}^{K}\sum_{l=1}^{K} C_{kl}^*\left[\psi_k^*(\boldsymbol{x}_1')\bar{\psi}_l^*(\boldsymbol{x}_2) - \psi_k^*(\boldsymbol{x}_2)\bar{\psi}_l^*(\boldsymbol{x}_1')\right] \\
&= \sum_{i=1}^{K}\sum_{j=1}^{K}\sum_{k=1}^{K}\sum_{l=1}^{K} C_{ij}C_{kl}^* \\
&\quad \left[\psi_i(\boldsymbol{x}_1)\psi_k^*(\boldsymbol{x}_1')\int_{\mathbb{R}^3}\mathrm{d}\boldsymbol{x}_2\bar{\psi}_j(\boldsymbol{x}_2)\bar{\psi}_l^*(\boldsymbol{x}_2) - \psi_i(\boldsymbol{x}_1)\bar{\psi}_l^*(\boldsymbol{x}_1')\int_{\mathbb{R}^3}\mathrm{d}\boldsymbol{x}_2\bar{\psi}_j(\boldsymbol{x}_2)\psi_k^*(\boldsymbol{x}_2)\right. \\
&\quad \left. -\bar{\psi}_j(\boldsymbol{x}_1)\psi_k^*(\boldsymbol{x}_1')\int_{\mathbb{R}^3}\mathrm{d}\boldsymbol{x}_2\psi_i(\boldsymbol{x}_2)\bar{\psi}_l^*(\boldsymbol{x}_2) + \bar{\psi}_j(\boldsymbol{x}_1)\bar{\psi}_l^*(\boldsymbol{x}_1')\int_{\mathbb{R}^3}\mathrm{d}\boldsymbol{x}_2\psi_i(\boldsymbol{x}_2)\psi_k^*(\boldsymbol{x}_2)\right] \\
&= \sum_{i=1}^{K}\sum_{j=1}^{K}\sum_{k=1}^{K}\sum_{l=1}^{K} C_{ij}C_{kl}^*\left[\psi_i(\boldsymbol{x}_1)\psi_k^*(\boldsymbol{x}_1')\delta_{jl} + \bar{\psi}_j(\boldsymbol{x}_1)\bar{\psi}_l^*(\boldsymbol{x}_1')\delta_{ik}\right] \\
&= \sum_{i=1}^{K}\sum_{j=1}^{K}\sum_{k=1}^{K} C_{ij}C_{kj}^*\psi_i(\boldsymbol{x}_1)\psi_k^*(\boldsymbol{x}_1') + \sum_{i=1}^{K}\sum_{j=1}^{K}\sum_{l=1}^{K} C_{ij}C_{il}^*\bar{\psi}_j(\boldsymbol{x}_1)\bar{\psi}_l^*(\boldsymbol{x}_1') \\
&= \sum_{i=1}^{K}\sum_{j=1}^{K}\sum_{k=1}^{K} C_{ij}C_{jk}^\dagger\psi_i(\boldsymbol{x}_1)\psi_k^*(\boldsymbol{x}_1') + \sum_{i=1}^{K}\sum_{j=1}^{K}\sum_{k=1}^{K} C_{ji}C_{ik}^\dagger\bar{\psi}_j(\boldsymbol{x}_1)\bar{\psi}_k^*(\boldsymbol{x}_1') \\
&= \sum_{i=1}^{K}\sum_{j=1}^{K}\psi_i(\boldsymbol{x}_1)\psi_j^*(\boldsymbol{x}_1')\left(\sum_{k=1}^{K} C_{ik}C_{kj}^\dagger\right) + \sum_{i=1}^{K}\sum_{j=1}^{K}\bar{\psi}_i(\boldsymbol{x}_1)\bar{\psi}_j^*(\boldsymbol{x}_1')\left(\sum_{k=1}^{K} C_{ik}C_{kj}^\dagger\right) \\
&= \sum_{i=1}^{K}\sum_{j=1}^{K}(\mathbf{C}\mathbf{C}^\dagger)_{ij}\left(\psi_i(\boldsymbol{x}_1)\psi_j^*(\boldsymbol{x}_1') + \bar{\psi}_i(\boldsymbol{x}_1)\bar{\psi}_j^*(\boldsymbol{x}_1')\right).
\end{aligned}$$

Thus, we have proved that

$$\gamma(\boldsymbol{x}_1, \boldsymbol{x}_1') = \sum_{i=1}^{K}\sum_{j=1}^{K}(\mathbf{C}\mathbf{C}^\dagger)_{ij}\left(\psi_i(\boldsymbol{x}_1)\psi_j^*(\boldsymbol{x}_1') + \bar{\psi}_i(\boldsymbol{x}_1)\bar{\psi}_j^*(\boldsymbol{x}_1')\right). \tag{4.8}$$

c. In fact, all d_i are real as all eigenvalues of a real symmetric matrix are real, thus $\mathbf{d}^\dagger = \mathbf{d}$, and

$$\mathbf{d}^2 = \mathbf{d}\mathbf{d}^\dagger = \mathbf{U}^\dagger\mathbf{C}\mathbf{U}(\mathbf{U}^\dagger\mathbf{C}\mathbf{U})^\dagger = \mathbf{U}^\dagger\mathbf{C}\mathbf{U}\mathbf{U}^\dagger\mathbf{C}^\dagger\mathbf{U} = \mathbf{U}^\dagger\mathbf{C}\mathbf{C}^\dagger\mathbf{U}. \tag{4.9}$$

d. From the former issue, we know

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

Thus, we find that

$$\begin{aligned}
\gamma(\boldsymbol{x}_1, \boldsymbol{x}_1') &= \sum_{i=1}^{K}\sum_{j=1}^{K}(\mathbf{C}\mathbf{C}^\dagger)_{ij}\left(\psi_i(\boldsymbol{x}_1)\psi_j^*(\boldsymbol{x}_1') + \bar{\psi}_i(\boldsymbol{x}_1)\bar{\psi}_j^*(\boldsymbol{x}_1')\right) \\
&= \sum_{i=1}^{K}\sum_{j=1}^{K}(\mathbf{U}\mathbf{d}^2\mathbf{U}^\dagger)_{ij}\left(\psi_i(\boldsymbol{x}_1)\psi_j^*(\boldsymbol{x}_1') + \bar{\psi}_i(\boldsymbol{x}_1)\bar{\psi}_j^*(\boldsymbol{x}_1')\right) \\
&= \sum_{i=1}^{K}\sum_{j=1}^{K}\sum_{k=1}^{K}\mathbf{U}_{ik}d_k^2\mathbf{U}_{kj}^\dagger\left(\psi_i(\boldsymbol{x}_1)\psi_j^*(\boldsymbol{x}_1') + \bar{\psi}_i(\boldsymbol{x}_1)\bar{\psi}_j^*(\boldsymbol{x}_1')\right) \\
&= \sum_{k=1}^{K} d_k^2\left(\sum_{i=1}^{K}\psi_i(\boldsymbol{x}_1)\mathbf{U}_{ik}\sum_{j=1}^{K}\psi_j^*(\boldsymbol{x}_1')\mathbf{U}_{jk}^* + \sum_{i=1}^{K}\bar{\psi}_i(\boldsymbol{x}_1)\mathbf{U}_{ik}\sum_{j=1}^{K}\bar{\psi}_j^*(\boldsymbol{x}_1')\mathbf{U}_{jk}^*\right).
\end{aligned}$$

Therefore, we define

$$\zeta_i = \sum_{k=1}^{K}\psi_k U_{ki},$$

and we obtain

$$\gamma(\boldsymbol{x}_1, \boldsymbol{x}_1') = \sum_{k=1}^{K} d_k^2\left(\zeta_k(\boldsymbol{x}_1)\zeta_k^*(\boldsymbol{x}_1') + \bar{\zeta}_k(\boldsymbol{x}_1)\bar{\zeta}_k^*(\boldsymbol{x}_1')\right) = \sum_{i=1}^{K} d_i^2\left(\zeta_i(\boldsymbol{x}_1)\zeta_i^*(\boldsymbol{x}_1') + \bar{\zeta}_i(\boldsymbol{x}_1)\bar{\zeta}_i^*(\boldsymbol{x}_1')\right). \tag{4.10}$$

We conclude thay U diagonalizes the one-matrix, and hence ζ_i are natural spatial orbitals for the two-electron system.

e. Now we convert $\mathbf{C}$ firstly,

$$\mathbf{C} = \mathbf{U}\mathbf{d}\mathbf{U}^\dagger \Leftrightarrow C_{ij} = \sum_{k=1}^{K}\mathbf{U}_{ik}d_k\mathbf{U}_{kj}^\dagger = \sum_{k=1}^{K}\mathbf{U}_{ik}d_k\mathbf{U}_{jk}^*$$

Thus we arrive at

$$|^1\Phi_0\rangle = \sum_{i=1}^{K}\sum_{j=1}^{K}C_{ij}|\psi_i\bar{\psi}_j\rangle = \sum_{i=1}^{K}\sum_{j=1}^{K}\sum_{k=1}^{K}\mathbf{U}_{ik}d_k\mathbf{U}_{jk}^*|\psi_i\bar{\psi}_j\rangle = \sum_{k=1}^{K}d_k|\zeta_k\bar{\zeta}_k\rangle = \sum_{i=1}^{K}d_i|\zeta_i\bar{\zeta}_i\rangle. \tag{4.11}$$

We find that this expansion contains only K terms.

4.5 The Multiconfiguration Self-Consistent Field (MCSCF) and Generalized Valence Bond (GVB) Methods

Exercise 4.9

Consider the transformation

$$u = \frac{1}{\sqrt{a^2+b^2}}\left(a\psi_A + b\psi_B\right),$$
$$v = \frac{1}{\sqrt{a^2+b^2}}\left(a\psi_A - b\psi_B\right).$$

a. Show that

$$\langle u|u\rangle = \langle v|v\rangle = 1$$

and

$$\langle u|v\rangle \equiv S = \frac{a^2-b^2}{a^2+b^2}.$$

b. Show that $|\Psi_{\mathrm{GVB}}\rangle$ in Eq.(4.52) can be rewritten as

$$|\Psi_{\mathrm{GVB}}\rangle = \frac{1}{\sqrt{a^4+b^4}}\left[a^2\psi_A(1)\psi_A(2) - b^2\psi_B(1)\psi_B(2)\right]\frac{1}{\sqrt{2}}\left(\alpha(1)\beta(2)-\alpha(2)\beta(1)\right)$$

and conclude that this is identical to $|\Psi_{\mathrm{MCSCF}}\rangle$ in Eq.(4.48) if

$$c_A = \frac{a^2}{\sqrt{a^4+b^4}},$$
$$c_B = -\frac{b^2}{\sqrt{a^4+b^4}}.$$

Solution 4.9

a.

$$\begin{aligned}\langle u|u\rangle &= \frac{1}{a^2+b^2}\left[a^2\langle\psi_A|\psi_A\rangle + ab\langle\psi_A|\psi_B\rangle + ab\langle\psi_B|\psi_A\rangle + b^2\langle\psi_B|\psi_B\rangle\right]\\ &= \frac{1}{a^2+b^2}\left[a^2\times 1 + ab\times 0 + ab\times 0 + b^2\times 1\right] = 1.\end{aligned} \tag{4.12}$$

$$\begin{aligned}S \equiv \langle u|v\rangle &= \frac{1}{a^2+b^2}\left[a^2\langle\psi_A|\psi_A\rangle - ab\langle\psi_A|\psi_B\rangle + ab\langle\psi_B|\psi_A\rangle - b^2\langle\psi_B|\psi_B\rangle\right]\\ &= \frac{1}{a^2+b^2}\left[a^2\times 1 - ab\times 0 + ab\times 0 - b^2\times 1\right] = \frac{a^2-b^2}{a^2+b^2}.\end{aligned} \tag{4.13}$$

b.

$$\begin{aligned}|\Psi_{\mathrm{GVB}}\rangle &= \frac{1}{\sqrt{2\left[1+(\frac{a^2-b^2}{a^2+b^2})^2\right]}}\left[\frac{1}{a^2+b^2}(a\psi_A(1)+b\psi_B(1))(a\psi_A(2)-b\psi_B(2))\right.\\ &\quad\left.+\frac{1}{a^2+b^2}(a\psi_A(2)+b\psi_B(2))(a\psi_A(1)-b\psi_B(1))\right]\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)-\alpha(2)\beta(1)\right]\\ &= \frac{a^2+b^2}{\sqrt{2\left[(a^2+b^2)^2+(a^2-b^2)^2\right]}}\times\frac{1}{\sqrt{2}\,(a^2+b^2)}\left[\alpha(1)\beta(2)-\alpha(2)\beta(1)\right]\\ &\quad\left[(a\psi_A(1)+b\psi_B(1))(a\psi_A(2)-b\psi_B(2))+(a\psi_A(2)+b\psi_B(2))(a\psi_A(1)-b\psi_B(1))\right]\\ &= \frac{1}{2\sqrt{2a^4+2b^4}}\left[2a^2\psi_A(1)\psi_A(2)-2b^2\psi_B(1)\psi_B(2)\right]\left[\alpha(1)\beta(2)-\alpha(2)\beta(1)\right]\\ &= \frac{1}{\sqrt{a^4+b^4}}\left[a^2\psi_A(1)\psi_A(2)-b^2\psi_B(1)\psi_B(2)\right]\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)-\alpha(2)\beta(1)\right]\end{aligned} \tag{4.14}$$

Thus,

$$c_A = \frac{a^2}{\sqrt{a^4+b^4}},\quad c_B = -\frac{b^2}{\sqrt{a^4+b^4}}.$$

4.6 Truncated CI and the Size-Consistency Problem