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.,

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

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

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

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, $\Delta = 0.78865\,\text{a.u.}$ 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

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

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

Thus, we have proved that γ is a Hermitian matrix.