Modern Quantum Chemistry, Szabo & Ostlund HW

wsr

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Contents

5 Pair and Coupled-pair Theories

5.1 The Independent Electron Pair Approximation

Ex 5.1

a.

$$
\begin{aligned}
{}^1E_{\text{corr}}(\text{FO}) &= \frac{|\langle 1\bar{1} \,\|\, 2\bar{2}\rangle|^2}{\varepsilon_1 + \varepsilon_1 - \varepsilon_2 - \varepsilon_2} \\
&= \frac{|\langle 1\bar{1} \,|\, 2\bar{2}\rangle - \langle 1\bar{1} \,|\, \bar{2}2\rangle|^2}{2\varepsilon_1 - 2\varepsilon_2} \\
&= \frac{|[12|\bar{1}\bar{2}] - [1\bar{2}|\bar{1}2]|^2}{2\varepsilon_1 - 2\varepsilon_2} \\
&= \frac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)}
\end{aligned}
\tag{5.1.1}
$$

b.

$$
\begin{aligned}
{}^1E_{\text{corr}} &= \Delta - \Delta\sqrt{1 + \frac{K_{12}^2}{\Delta^2}} \\
&= \Delta - \Delta\left(1 + \frac{K_{12}^2}{2\Delta^2}\right) \\
&= -\frac{K_{12}^2}{2\Delta}) \\
&\approx \frac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)}
\end{aligned}
\tag{5.1.2}
$$

Ex 5.2 From Eq. 5.9a and 5.9b in the textbook, we get

$$
\sum_{t<u} c_{1_i\bar{1}_i}^{tu} \left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{1_i\bar{1}_i}^{tu} \right\rangle = e_{1_i\bar{1}_i}
\tag{5.1.3}
$$

$$
\left\langle \Psi_{1_i\bar{1}_i}^{rs} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_0 \right\rangle + \sum_{t<u} \left\langle \Psi_{1_i\bar{1}_i}^{rs} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_{1_i\bar{1}_i}^{tu} \right\rangle c_{1_i\bar{1}_i}^{tu} = e_{1_i\bar{1}_i} c_{1_i\bar{1}_i}^{rs}
\tag{5.1.4}
$$

$\therefore$

$$
c_{1_i\bar{1}_i}^{2_i\bar{2}_i} \left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i} \right\rangle = e_{1_i\bar{1}_i}
\tag{5.1.5}
$$

$$
\left\langle \Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_0 \right\rangle + \sum_{t<u} \left\langle \Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_{1_i\bar{1}_i}^{tu} \right\rangle c_{1_i\bar{1}_i}^{tu} = e_{1_i\bar{1}_i} c_{1_i\bar{1}_i}^{2_i\bar{2}_i}
\tag{5.1.6}
$$

(5.1.5) gives

$$
K_{12} c_{1_i\bar{1}_i}^{2_i\bar{2}_i} = e_{1_i\bar{1}_i}
\tag{5.1.7}
$$

(5.1.6) gives

$$
K_{12} + \sum_{jk} \left\langle \Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_{1_i\bar{1}_i}^{2_j\bar{2}_k} \right\rangle c_{1_i\bar{1}_i}^{2_j\bar{2}_k} = e_{1_i\bar{1}_i} c_{1_i\bar{1}_i}^{2_i\bar{2}_i}
\tag{5.1.8}
$$

Since

$$
\left\langle \Psi_{1_i\bar{1}_i}^{2_i\bar{2}_i} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_{1_i\bar{1}_i}^{2_j\bar{2}_k} \right\rangle c_{1_i\bar{1}_i}^{2_j\bar{2}_k} = \begin{cases} 2\Delta & j = k = i \\ 0 & j = k \neq i \\ 0 & i = j = \neq k \end{cases}
\tag{5.1.9}
$$

we have

$$
K_{12} + 2\Delta c_{1_i\bar{1}_i}^{2_i\bar{2}_i} = e_{1_i\bar{1}_i} c_{1_i\bar{1}_i}^{2_i\bar{2}_i}
\tag{5.1.10}
$$

Ex 5.3

$$^2E_{\text{corr}}(\text{FO}) = \sum_i \frac{|\langle 1_i \bar{1}_i \| 2_i \bar{2}_i \rangle|^2}{\varepsilon_1 + \varepsilon_1 - \varepsilon_2 - \varepsilon_2}$$

$$= 2 \times \frac{K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)}$$

$$= \frac{K_{12}^2}{(\varepsilon_1 - \varepsilon_2)} \tag{5.1.11}$$

5.1.1 Invariance under Unitary Transformations: An Example

Ex 5.4

$$|a\bar{a}b\bar{b}\rangle = 2^{-1/2}\big(|1_1\bar{a}b\bar{b}\rangle + |1_2\bar{a}b\bar{b}\rangle\big)$$

$$= 2^{-1}\big(|1_1\bar{1}_1 b\bar{b}\rangle + |1_1\bar{1}_2 b\bar{b}\rangle + |1_2\bar{1}_1 b\bar{b}\rangle + |1_2\bar{1}_2 b\bar{b}\rangle\big)$$

$$= 2^{-2}(|1_1\bar{1}_1 1_1\bar{1}_1\rangle - |1_1\bar{1}_1 1_1\bar{1}_2\rangle - |1_1\bar{1}_1 1_2\bar{1}_1\rangle + |1_1\bar{1}_1 1_2\bar{1}_2\rangle$$
$$+ |1_1\bar{1}_2 1_1\bar{1}_1\rangle - |1_1\bar{1}_2 1_1\bar{1}_2\rangle - |1_1\bar{1}_2 1_2\bar{1}_1\rangle + |1_1\bar{1}_2 1_2\bar{1}_2\rangle$$
$$+ |1_2\bar{1}_1 1_1\bar{1}_1\rangle - |1_2\bar{1}_1 1_1\bar{1}_2\rangle - |1_2\bar{1}_1 1_2\bar{1}_1\rangle + |1_2\bar{1}_1 1_2\bar{1}_2\rangle$$
$$+ |1_2\bar{1}_2 1_1\bar{1}_1\rangle - |1_2\bar{1}_2 1_1\bar{1}_2\rangle - |1_2\bar{1}_2 1_2\bar{1}_1\rangle + |1_2\bar{1}_2 1_2\bar{1}_2\rangle)$$

$$= 2^{-2}(2|1_1\bar{1}_1 1_1\bar{1}_1\rangle + 2|1_1\bar{1}_1 1_2\bar{1}_2\rangle - 2|1_1\bar{1}_2 1_1\bar{1}_2\rangle - 2|1_1\bar{1}_2 1_2\bar{1}_1\rangle)$$

$$= 2^{-2}(2|1_1\bar{1}_1 1_2\bar{1}_2\rangle - 2|1_1\bar{1}_1 1_2\bar{1}_2\rangle)$$

$$= |1_1\bar{1}_1 1_2\bar{1}_2\rangle \tag{5.1.12}$$

Ex 5.5

$$\langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_{a\bar{a}}^{**} \rangle = 2^{-1/2}\big(\langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_{a\bar{a}}^{r\bar{r}} \rangle + \langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_{a\bar{a}}^{s\bar{s}} \rangle\big)$$

$$= 2^{-1/2}\left(2 \times \frac{1}{2}K_{12}\right)$$

$$= 2^{-1/2}K_{12} \tag{5.1.13}$$

$$\langle \Psi_{a\bar{a}}^{**} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{a\bar{a}}^{**} \rangle = 2^{-1}(\langle \Psi_{a\bar{a}}^{r\bar{r}} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{a\bar{a}}^{r\bar{r}} \rangle + \langle \Psi_{a\bar{a}}^{r\bar{r}} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{a\bar{a}}^{s\bar{s}} \rangle$$
$$+ \langle \Psi_{a\bar{a}}^{s\bar{s}} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{a\bar{a}}^{r\bar{r}} \rangle + \langle \Psi_{a\bar{a}}^{s\bar{s}} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{a\bar{a}}^{s\bar{s}} \rangle)$$

$$= 2^{-1}\Bigg[\left(2h_{11} + 2h_{22} + \frac{1}{2}J_{11} + \frac{1}{2}J_{22} + 2J_{12} - K_{12}\right) - (4h_{11} + 2J_{11})$$

$$+ \frac{1}{2}J_{22} + \frac{1}{2}J_{22}$$

$$+ \left(2h_{11} + 2h_{22} + \frac{1}{2}J_{11} + \frac{1}{2}J_{22} + 2J_{12} - K_{12}\right) - (4h_{11} + 2J_{11})\Bigg]$$

$$= 2^{-1}\left(-2h_{11} + 2h_{22} - \frac{3}{2}J_{11} + J_{22} + 2J_{12} - K_{12}\right) \times 2$$

$$= -2h_{11} + 2h_{22} - \frac{3}{2}J_{11} + J_{22} + 2J_{12} - K_{12} \tag{5.1.14}$$

Since

$$\varepsilon_2 - \varepsilon_1 = h_{22} - h_{11} + 2J_{12} - K_{12} - J_{11} \tag{5.1.15}$$

we have

$$\langle \Psi_{a\bar{a}}^{**} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{a\bar{a}}^{**} \rangle = 2(\varepsilon_2 - \varepsilon_1) - 2J_{12} + K_{12} + \frac{1}{2}J_{11} + J_{22} \tag{5.1.16}$$

Ex 5.6 Since

$$|\Psi_{a\bar{b}}^{**}\rangle = 2^{-1/2}(|\Psi_{a\bar{b}}^{r\bar{s}}\rangle + |\Psi_{a\bar{b}}^{s\bar{r}}\rangle) \tag{5.1.17}$$

$$
\begin{aligned}
\langle\Psi_0\,|\,\mathscr{H}\,|\,\Psi_{a\bar{b}}^{**}\rangle &= 2^{-1/2}\big(\langle\Psi_0\,|\,\mathscr{H}\,|\,\Psi_{a\bar{b}}^{r\bar{s}}\rangle + \langle\Psi_0\,|\,\mathscr{H}\,|\,\Psi_{a\bar{b}}^{s\bar{r}}\rangle\big) \\
&= 2^{-1/2}\big(\langle a\bar{b}\,\|\,r\bar{s}\rangle + \langle a\bar{b}\,\|\,s\bar{r}\rangle\big) \\
&= 2^{-1/2}\big((ar|bs) + (as|br)\big) \\
&= 2^{-1/2}K_{12}
\end{aligned}
\tag{5.1.18}
$$

$$
\begin{aligned}
\langle\Psi_{a\bar{b}}^{**}\,|\,\mathscr{H}-E_0\,|\,\Psi_{a\bar{b}}^{**}\rangle &= 2^{-1}\big(\langle\Psi_{a\bar{b}}^{r\bar{s}}\,|\,\mathscr{H}-E_0\,|\,\Psi_{a\bar{b}}^{r\bar{s}}\rangle + \langle\Psi_{a\bar{b}}^{r\bar{s}}\,|\,\mathscr{H}-E_0\,|\,\Psi_{a\bar{b}}^{s\bar{r}}\rangle \\
&\quad + \langle\Psi_{a\bar{b}}^{s\bar{r}}\,|\,\mathscr{H}-E_0\,|\,\Psi_{a\bar{b}}^{r\bar{s}}\rangle + \langle\Psi_{a\bar{b}}^{s\bar{r}}\,|\,\mathscr{H}-E_0\,|\,\Psi_{a\bar{b}}^{s\bar{r}}\rangle\big) \\
&= 2^{-1}\bigg[\bigg(2h_{11} + 2h_{22} + \frac{1}{2}J_{11} + \frac{1}{2}J_{22} + 2J_{12} - K_{12}\bigg) - (4h_{11} + 2J_{11}) \\
&\quad + \frac{1}{2}J_{22} + \frac{1}{2}J_{22} \\
&\quad + \bigg(2h_{11} + 2h_{22} + \frac{1}{2}J_{11} + \frac{1}{2}J_{22} + 2J_{12} - K_{12}\bigg) - (4h_{11} + 2J_{11})\bigg] \\
&= \ldots \\
&= 2(\varepsilon_2 - \varepsilon_1) - 2J_{12} + K_{12} + \frac{1}{2}J_{11} + J_{22} \equiv 2\Delta'
\end{aligned}
\tag{5.1.19}
$$

Thus the equations determining $e_{a\bar{b}}$ are identical to that of $e_{a\bar{a}}$. Similarly, $e_{\bar{a}b}$ shares the same equations with them.

$\therefore\ e_{a\bar{b}} = e_{\bar{a}b} = e_{a\bar{a}}$.

Ex 5.7

a. As shown in Ex 5.5, 5.6

$$\langle\Psi_0\,|\,\mathscr{H}\,|\,\Psi_{a\bar{a}}^{**}\rangle = \langle\Psi_0\,|\,\mathscr{H}\,|\,\Psi_{a\bar{b}}^{**}\rangle = \langle\Psi_0\,|\,\mathscr{H}\,|\,\Psi_{\bar{a}b}^{**}\rangle = 2^{-1/2}K_{12} \tag{5.1.20}$$

$$\langle\Psi_{a\bar{a}}^{**}\,|\,\mathscr{H}-E_0\,|\,\Psi_{a\bar{a}}^{**}\rangle = \langle\Psi_{a\bar{b}}^{**}\,|\,\mathscr{H}-E_0\,|\,\Psi_{a\bar{b}}^{**}\rangle = \langle\Psi_{\bar{a}b}^{**}\,|\,\mathscr{H}-E_0\,|\,\Psi_{\bar{a}b}^{**}\rangle = 2\Delta' \tag{5.1.21}$$

Similarly, we get

$$\langle\Psi_0\,|\,\mathscr{H}\,|\,\Psi_{b\bar{b}}^{**}\rangle = 2^{-1/2}K_{12} \tag{5.1.22}$$

$$\langle\Psi_{b\bar{b}}^{**}\,|\,\mathscr{H}-E_0\,|\,\Psi_{b\bar{b}}^{**}\rangle = 2\Delta' \tag{5.1.23}$$

For the rest,

$$
\begin{aligned}
\langle\Psi_{a\bar{a}}^{**}\,|\,\mathscr{H}-E_0\,|\,\Psi_{b\bar{b}}^{**}\rangle &= 2^{-1}\big(\langle\Psi_{a\bar{a}}^{r\bar{r}}\,|\,\mathscr{H}-E_0\,|\,\Psi_{b\bar{b}}^{r\bar{r}}\rangle + \langle\Psi_{a\bar{a}}^{r\bar{r}}\,|\,\mathscr{H}-E_0\,|\,\Psi_{b\bar{b}}^{s\bar{s}}\rangle \\
&\quad + \langle\Psi_{a\bar{a}}^{s\bar{s}}\,|\,\mathscr{H}-E_0\,|\,\Psi_{b\bar{b}}^{r\bar{r}}\rangle + \langle\Psi_{a\bar{a}}^{s\bar{s}}\,|\,\mathscr{H}-E_0\,|\,\Psi_{b\bar{b}}^{s\bar{s}}\rangle\big) \\
&= 2^{-1}\big[\langle b\bar{b}\,\|\,a\bar{a}\rangle + 0 + 0 + \langle b\bar{b}\,\|\,a\bar{a}\rangle\big] \\
&= (ab|ab) \\
&= \frac{1}{2}J_{11}
\end{aligned}
\tag{5.1.24}
$$

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$$\langle \Psi_{a\bar{a}}^{**} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{a\bar{b}}^{**} \rangle = 2^{-1} (\langle \Psi_{a\bar{a}}^{r\bar{r}} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{a\bar{b}}^{r\bar{s}} \rangle + \langle \Psi_{a\bar{a}}^{r\bar{r}} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{a\bar{b}}^{s\bar{r}} \rangle$$
$$+ \langle \Psi_{a\bar{a}}^{s\bar{s}} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{a\bar{b}}^{r\bar{s}} \rangle + \langle \Psi_{a\bar{a}}^{s\bar{s}} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{a\bar{b}}^{s\bar{r}} \rangle)$$
$$= 2^{-1} \big[\langle \bar{r}b \,\|\, \bar{a}\bar{s} \rangle - \langle r\bar{b} \,\|\, s\bar{a} \rangle + \langle s\bar{b} \,\|\, r\bar{a} \rangle - \langle \bar{s}b \,\|\, \bar{a}\bar{r} \rangle \big]$$
$$= 2^{-1} [(ra|bs) - (rs|ba) - (rs|ba) - (sr|ba) + (sa|br) - (sr|ba)]$$
$$= 2^{-1} [(ra|bs) + (sa|br) - 4(ab|sr)]$$
$$= 2^{-1} \left[2 \times \frac{1}{2} K_{12} - 4 \times \frac{1}{2} J_{12} \right]$$
$$= \frac{1}{2} K_{12} - J_{12} \tag{5.1.25}$$

Similarly, we get

$$\langle \Psi_{a\bar{b}}^{**} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{\bar{a}b}^{**} \rangle = \frac{1}{2} J_{11} \tag{5.1.26}$$

$$\langle \Psi_{a\bar{a}}^{**} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{\bar{a}b}^{**} \rangle = \langle \Psi_{b\bar{b}}^{**} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{a\bar{b}}^{**} \rangle = \langle \Psi_{b\bar{b}}^{**} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{\bar{a}b}^{**} \rangle = \frac{1}{2} K_{12} - J_{12} \tag{5.1.27}$$

thus the DCI equation is

$$\begin{pmatrix} 0 & 2^{-1/2}K_{12} & 2^{-1/2}K_{12} & 2^{-1/2}K_{12} & 2^{-1/2}K_{12} \\ 2^{-1/2}K_{12} & 2\Delta' & \frac{1}{2}J_{11} & \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}K_{12} - J_{12} \\ 2^{-1/2}K_{12} & \frac{1}{2}J_{11} & 2\Delta' & \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}K_{12} - J_{12} \\ 2^{-1/2}K_{12} & \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}K_{12} - J_{12} & 2\Delta' & \frac{1}{2}J_{11} \\ 2^{-1/2}K_{12} & \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}K_{12} - J_{12} & \frac{1}{2}J_{11} & 2\Delta' \end{pmatrix} \begin{pmatrix} 1 \\ c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = {}^2E_{\text{corr}}(\text{DCI}) \begin{pmatrix} 1 \\ c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} \tag{5.1.28}$$

b. By solving the DCI equation above (see `5-7.nb`), we get

$$^2E_{\text{corr}}(\text{DCI}) = \frac{2\Delta' + \frac{1}{2}J_{11} + 2(\frac{1}{2}K_{12} - J_{12}) - \sqrt{16(2^{-1/2}K_{12})^2 + [2\Delta' + \frac{1}{2}J_{11} + 2(\frac{1}{2}K_{12} - J_{12})]^2}}{2} \tag{5.1.29}$$

and

$$c_1 = c_2 = c_3 = c_4 = \frac{2\Delta' + \frac{1}{2}J_{11} + 2(\frac{1}{2}K_{12} - J_{12}) + \sqrt{16(2^{-1/2}K_{12})^2 + [2\Delta' + \frac{1}{2}J_{11} + 2(\frac{1}{2}K_{12} - J_{12})]^2}}{8 \times 2^{-1/2}K_{12}} \tag{5.1.30}$$

Since

$$2\Delta' = 2(\varepsilon_2 - \varepsilon_1) - 2J_{12} + K_{12} + \frac{1}{2}J_{11} + J_{22} \tag{5.1.31}$$

$$2\Delta = 2(\varepsilon_2 - \varepsilon_1) + J_{11} + J_{22} - 4J_{12} + 2K_{12} \tag{5.1.32}$$

we have

$$2\Delta = 2\Delta' + \frac{1}{2}J_{11} - 2J_{12} + K_{12} \tag{5.1.33}$$

$\therefore$

$$^2E_{\text{corr}}(\text{DCI}) = \frac{2\Delta - \sqrt{8K_{12}^2 + (2\Delta)^2}}{2}$$
$$= \Delta - \sqrt{2K_{12}^2 + \Delta^2} \tag{5.1.34}$$

$$c_1 = c_2 = c_3 = c_4 = \frac{2\Delta + \sqrt{8K_{12}^2 + (2\Delta)^2}}{4\sqrt{2}K_{12}}$$
$$= \frac{\Delta + \sqrt{2K_{12}^2 + \Delta^2}}{2\sqrt{2}K_{12}} \tag{5.1.35}$$

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Ex 5.8

$$E_{\text{corr}}(\text{FO}) = \sum_{A<B} \sum_{R<S} \frac{|\langle AB \,\|\, RS\rangle|^2}{\varepsilon_A + \varepsilon_B - \varepsilon_R - \varepsilon_S}$$

$$= \frac{|\langle a\bar{a} \,\|\, r\bar{r}\rangle|^2 + |\langle a\bar{a} \,\|\, r\bar{s}\rangle|^2 + |\langle a\bar{a} \,\|\, s\bar{r}\rangle|^2 + |\langle a\bar{a} \,\|\, s\bar{s}\rangle|^2}{\varepsilon_1 + \varepsilon_1 - \varepsilon_2 - \varepsilon_2} + \frac{|\langle a\bar{b} \,\|\, r\bar{r}\rangle|^2 + |\langle a\bar{b} \,\|\, r\bar{s}\rangle|^2 + |\langle a\bar{b} \,\|\, s\bar{r}\rangle|^2 + |\langle a\bar{b} \,\|\, s\bar{s}\rangle|^2}{\varepsilon_1 + \varepsilon_1 - \varepsilon_2 - \varepsilon_2}$$

$$+ \frac{|\langle b\bar{a} \,\|\, r\bar{r}\rangle|^2 + |\langle b\bar{a} \,\|\, r\bar{s}\rangle|^2 + |\langle b\bar{a} \,\|\, s\bar{r}\rangle|^2 + |\langle b\bar{a} \,\|\, s\bar{s}\rangle|^2}{\varepsilon_1 + \varepsilon_1 - \varepsilon_2 - \varepsilon_2} + \frac{|\langle b\bar{b} \,\|\, r\bar{r}\rangle|^2 + |\langle b\bar{b} \,\|\, r\bar{s}\rangle|^2 + |\langle b\bar{b} \,\|\, s\bar{r}\rangle|^2 + |\langle b\bar{b} \,\|\, s\bar{s}\rangle|^2}{\varepsilon_1 + \varepsilon_1 - \varepsilon_2 - \varepsilon_2}$$

$$= \frac{|(ar|ar)|^2 + |(ar|as)|^2 + |(as|ar)|^2 + |(as|as)|^2}{2(\varepsilon_1 - \varepsilon_2)} + \frac{|(ar|br)|^2 + |(ar|bs)|^2 + |(as|br)|^2 + |(as|bs)|^2}{2(\varepsilon_1 - \varepsilon_2)}$$

$$+ \frac{|(br|ar)|^2 + |(br|as)|^2 + |(bs|ar)|^2 + |(bs|as)|^2}{2(\varepsilon_1 - \varepsilon_2)} + \frac{|(br|br)|^2 + |(br|bs)|^2 + |(bs|br)|^2 + |(bs|bs)|^2}{2(\varepsilon_1 - \varepsilon_2)}$$

$$= \frac{\left|\frac{1}{2}K_{12}\right|^2 + 0 + 0 + \left|\frac{1}{2}K_{12}\right|^2}{2(\varepsilon_1 - \varepsilon_2)} + \frac{0 + \left|\frac{1}{2}K_{12}\right|^2 + \left|\frac{1}{2}K_{12}\right|^2 + 0}{2(\varepsilon_1 - \varepsilon_2)}$$

$$+ \frac{0 + 0 + \left|\frac{1}{2}K_{12}\right|^2 + \left|\frac{1}{2}K_{12}\right|^2}{2(\varepsilon_1 - \varepsilon_2)} + \frac{\left|\frac{1}{2}K_{12}\right|^2 + 0 + 0 + \left|\frac{1}{2}K_{12}\right|^2}{2(\varepsilon_1 - \varepsilon_2)}$$

$$= \frac{2K_{12}^2}{2(\varepsilon_1 - \varepsilon_2)} \tag{5.1.36}$$

Ex 5.9

a.

$$^2E_{\text{corr}}(\text{EN(L)}) = -\frac{\left|\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1}\right\rangle\right|^2}{\left\langle \Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1}\right\rangle} - \frac{\left|\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1}\right\rangle\right|^2}{\left\langle \Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_{1_1\bar{1}_1}^{2_1\bar{2}_1}\right\rangle}$$

$$= -\frac{K_{12}^2}{2\Delta} \times 2$$

$$= -\frac{K_{12}^2}{\Delta} \tag{5.1.37}$$

b.

$$^2E_{\text{corr}}(\text{EN(D)}) = e_{a\bar{a}} + e_{b\bar{b}} + e_{a\bar{b}} + e_{\bar{a}b}$$

$$= 2e_{a\bar{a}} + 2e_{a\bar{b}}$$

$$= -2\frac{|\langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_{a\bar{a}}^{**}\rangle|^2}{\langle \Psi_{a\bar{a}}^{**} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{a\bar{a}}^{**}\rangle} - 2\frac{\left|\langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_{a\bar{b}}^{**}\rangle\right|^2}{\langle \Psi_{a\bar{b}}^{**} \,|\, \mathscr{H} - E_0 \,|\, \Psi_{a\bar{b}}^{**}\rangle}$$

$$= -2\frac{\left|2^{-1/2}K_{12}\right|^2}{2\Delta'} - 2\frac{\left|2^{-1/2}K_{12}\right|^2}{2\Delta'}$$

$$= -\frac{K_{12}^2}{2\Delta'} \times 2$$

$$= -\frac{K_{12}^2}{\Delta'} \tag{5.1.38}$$

c.

$$^2E_{\text{corr}}^{\text{singlet}}(\text{EN(D)}) = e_{a\bar{a}} + e_{b\bar{b}} + e_{ab}^{\text{singlet}}$$

$$= -\frac{K_{12}^2}{2\Delta'} - \frac{\left|\langle \Psi_0 \,|\, \mathscr{H} \,|\, {}^B\Psi_{ab}^{rs}\rangle\right|^2}{\langle {}^B\Psi_{ab}^{rs} \,|\, \mathscr{H} - E_0 \,|\, {}^B\Psi_{ab}^{rs}\rangle}$$

$$= -\frac{K_{12}^2}{2\Delta'} - \frac{K_{12}^2}{2\Delta''} \tag{5.1.39}$$

d.

$$^2E_{\text{corr}}(\text{EN(L)}) = -0.04168 \tag{5.1.40}$$

$$^2E_{\text{corr}}(\text{EN(D)}) = -0.02755 \tag{5.1.41}$$

$$^2E_{\text{corr}}^{\text{singlet}}(\text{EN(D)}) = -0.02585 \tag{5.1.42}$$

thus EN pairs is not invariant to unitary transformations.

Ex 5.10

5.1.2 Some Illustrative Calculations

5.2 Coupled-pair Theories

5.2.1 The Coupled-cluster Approximation

5.2.2 The Cluster Expansion of the Wave Function

Ex 5.11 Eq. 5.49 gives

$$|\Phi_0\rangle = |1_1\bar{1}_11_2\bar{1}_2\rangle + c_{1_1\bar{1}_1}^{2_1\bar{2}_1}|2_1\bar{2}_11_2\bar{1}_2\rangle + c_{1_2\bar{1}_2}^{2_2\bar{2}_2}|1_1\bar{1}_12_2\bar{2}_2\rangle + c_{1_1\bar{1}_11_2\bar{1}_2}^{2_1\bar{2}_12_2\bar{2}_2}|2_1\bar{2}_12_2\bar{2}_2\rangle$$

$$= \left[1 + c_{1_1\bar{1}_1}^{2_1\bar{2}_1}a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1}a_{1_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2}a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2}a_{1_2} + c_{1_1\bar{1}_11_2\bar{1}_2}^{2_1\bar{2}_12_2\bar{2}_2}a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2}a_{1_2}a_{\bar{1}_1}a_{1_1}\right]|1_1\bar{1}_11_2\bar{1}_2\rangle \tag{5.2.1}$$

while

$$\exp\left(c_{1_1\bar{1}_1}^{2_1\bar{2}_1}a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1}a_{1_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2}a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2}a_{1_2}\right)|1_1\bar{1}_11_2\bar{1}_2\rangle$$

$$= \left[1 + \left(c_{1_1\bar{1}_1}^{2_1\bar{2}_1}a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1}a_{1_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2}a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2}a_{1_2}\right) + \left(c_{1_1\bar{1}_1}^{2_1\bar{2}_1}a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1}a_{1_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2}a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2}a_{1_2}\right)^2 + \cdots\right]|1_1\bar{1}_11_2\bar{1}_2\rangle \tag{5.2.2}$$

since we cannot annihilate or create any orbital twice, the terms over 3rd power must be zero, thus

$$\exp\left(c_{1_1\bar{1}_1}^{2_1\bar{2}_1}a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1}a_{1_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2}a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2}a_{1_2}\right)|1_1\bar{1}_11_2\bar{1}_2\rangle$$

$$= \left[1 + \left(c_{1_1\bar{1}_1}^{2_1\bar{2}_1}a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1}a_{1_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2}a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2}a_{1_2}\right) + \left(c_{1_1\bar{1}_1}^{2_1\bar{2}_1}a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1}a_{1_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2}a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2}a_{1_2}\right)^2\right]|1_1\bar{1}_11_2\bar{1}_2\rangle$$

$$= \left[1 + \left(c_{1_1\bar{1}_1}^{2_1\bar{2}_1}a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1}a_{1_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2}a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2}a_{1_2}\right) + \left(c_{1_1\bar{1}_1}^{2_1\bar{2}_1}a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1}a_{1_1}\right)^2 + \left(c_{1_2\bar{1}_2}^{2_2\bar{2}_2}a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2}a_{1_2}\right)^2$$

$$+ c_{1_1\bar{1}_1}^{2_1\bar{2}_1}c_{1_2\bar{1}_2}^{2_2\bar{2}_2}a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_1}a_{1_1}a_{\bar{1}_2}a_{1_2}\right]|1_1\bar{1}_11_2\bar{1}_2\rangle$$

$$= \left[1 + c_{1_1\bar{1}_1}^{2_1\bar{2}_1}a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1}a_{1_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2}a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2}a_{1_2} + c_{1_1\bar{1}_1}^{2_1\bar{2}_1}c_{1_2\bar{1}_2}^{2_2\bar{2}_2}a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_1}a_{1_1}a_{\bar{1}_2}a_{1_2}\right]|1_1\bar{1}_11_2\bar{1}_2\rangle$$

$$= \left[1 + c_{1_1\bar{1}_1}^{2_1\bar{2}_1}a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{\bar{1}_1}a_{1_1} + c_{1_2\bar{1}_2}^{2_2\bar{2}_2}a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_2}a_{1_2} + c_{1_1\bar{1}_11_2\bar{1}_2}^{2_1\bar{2}_12_2\bar{2}_2}a_{2_1}^\dagger a_{\bar{2}_1}^\dagger a_{2_2}^\dagger a_{\bar{2}_2}^\dagger a_{\bar{1}_1}a_{1_1}a_{\bar{1}_2}a_{1_2}\right]|1_1\bar{1}_11_2\bar{1}_2\rangle \tag{5.2.3}$$

5.2.3 Linear CCA and the Coupled-Electron Pair Approximation

Ex 5.12

a. The diagonal elements of $\mathbf{D}$ is

$$\mathbf{D}_{rasb,rasb} = \langle\Psi_{ab}^{rs}|\mathscr{H}-E_0|\Psi_{ab}^{rs}\rangle \tag{5.2.4}$$

thus

$$E_{\text{corr}} = -\mathbf{B}^\dagger\mathbf{D}\mathbf{B}$$

$$= -\frac{\langle\Psi_0|\mathscr{H}|\Psi_{ab}^{rs}\rangle^\dagger\langle\Psi_0|\mathscr{H}|\Psi_{ab}^{rs}\rangle}{\langle\Psi_{ab}^{rs}|\mathscr{H}-E_0|\Psi_{ab}^{rs}\rangle}$$

$$= -\frac{|\langle\Psi_0|\mathscr{H}|\Psi_{ab}^{rs}\rangle|^2}{\langle\Psi_{ab}^{rs}|\mathscr{H}-E_0|\Psi_{ab}^{rs}\rangle} \tag{5.2.5}$$

which matches Eq. 5.15 and 5.16.

b.

5.2.4   Some Illustrative Calculations

5.3   Many-electron Theories with Single Particle Hamiltonians

Ex 5.13

$$C = \frac{-H_{11} + H_{22} - \sqrt{H_{11}^2 + 4H_{12}H_{21} - 2H_{11}H_{22} + H_{22}^2}}{2H_{12}} \tag{5.3.1}$$

$$
\begin{aligned}
\varepsilon_1 &= H_{11} + H_{12}C \\
&= H_{11} + \frac{-H_{11} + H_{22} - \sqrt{H_{11}^2 + 4H_{12}H_{21} - 2H_{11}H_{22} + H_{22}^2}}{2} \\
&= \frac{H_{11} + H_{22} - \sqrt{H_{11}^2 + 4H_{12}H_{21} - 2H_{11}H_{22} + H_{22}^2}}{2}
\end{aligned} \tag{5.3.2}
$$

while the eigenvalues of the matrix is

$$\frac{H_{11} + H_{22} \pm \sqrt{H_{11}^2 + 4H_{12}H_{21} - 2H_{11}H_{22} + H_{22}^2}}{2} \tag{5.3.3}$$

5.3.1   The Relaxation Energy via CI, IEPA, CEPA and CCA

Ex 5.14

a.

$$
\begin{aligned}
\langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_b^s \rangle &= \left\langle \Psi_0 \,\middle|\, \sum_i [h_0(i) + v(i)] \,\middle|\, \Psi_b^s \right\rangle \\
&= v_{bs}
\end{aligned} \tag{5.3.4}
$$

b.   Similarly

$$\langle \Psi_a^r \,|\, \mathscr{H} \,|\, \Psi_0 \rangle = v_{ra} \tag{5.3.5}$$

c.

$$
\begin{aligned}
\langle \Psi_a^r \,|\, \mathscr{H} - E_0 \,|\, \Psi_b^s \rangle &= \langle \Psi_a^r \,|\, \mathscr{H} \,|\, \Psi_b^s \rangle - E_0 \langle \Psi_a^r \,|\, \Psi_b^s \rangle \\
&= \begin{cases}
0 + 0 & a \neq b, r \neq s \\
v_{rs} + 0 & a = b, r \neq s \\
-v_{ba} + 0 & a \neq b, r = s \\
E_0 + \varepsilon_r^{(0)} + v_{rr} - \varepsilon_a^{(0)} - v_{aa} - E_0 & a = b, r = s
\end{cases} \\
&= \begin{cases}
0 & a \neq b, r \neq s \\
v_{rs} & a = b, r \neq s \\
-v_{ba} & a \neq b, r = s \\
\varepsilon_r^{(0)} + v_{rr} - \varepsilon_a^{(0)} - v_{aa} & a = b, r = s
\end{cases}
\end{aligned} \tag{5.3.6}
$$

d.   Since we cannot create or annihilate an orbital twice,

$$\langle \Psi_a^r \,|\, \mathscr{H} - E_0 \,|\, \Psi_{ab}^{rs} \rangle = \begin{cases} v_{bs} & a \neq b, r \neq s \\ 0 & \text{otherwise} \end{cases} \tag{5.3.7}$$

Ex 5.15

a.

$$\begin{aligned}
|\Phi_0\rangle =\ & a_1b_1 \cdot 0 + a_1b_2 \,|\chi_1^{(0)}\chi_2^{(0)}\rangle + a_1b_3 \,|\chi_1^{(0)}\chi_3^{(0)}\rangle + a_1b_4 \,|\chi_1^{(0)}\chi_4^{(0)}\rangle \\
& + a_2b_1 \,|\chi_2^{(0)}\chi_1^{(0)}\rangle + a_2b_2 \cdot 0 + a_2b_3 \,|\chi_2^{(0)}\chi_3^{(0)}\rangle + a_2b_4 \,|\chi_2^{(0)}\chi_4^{(0)}\rangle \\
& + a_3b_1 \,|\chi_3^{(0)}\chi_1^{(0)}\rangle + a_3b_2 \,|\chi_3^{(0)}\chi_2^{(0)}\rangle + a_3b_3 \cdot 0 + a_3b_4 \,|\chi_3^{(0)}\chi_4^{(0)}\rangle \\
& + a_4b_1 \,|\chi_4^{(0)}\chi_1^{(0)}\rangle + a_4b_2 \,|\chi_4^{(0)}\chi_2^{(0)}\rangle + a_4b_3 \,|\chi_4^{(0)}\chi_3^{(0)}\rangle + a_4b_4 \cdot 0 \\
=\ & (a_1b_2 - a_2b_1)\,|\chi_1^{(0)}\chi_2^{(0)}\rangle + (a_1b_3 - a_3b_1)\,|\chi_1^{(0)}\chi_3^{(0)}\rangle + (a_1b_4 - a_4b_1)\,|\chi_1^{(0)}\chi_4^{(0)}\rangle \\
& - (a_2b_3 - a_3b_2)\,|\chi_3^{(0)}\chi_2^{(0)}\rangle - (a_2b_4 - a_4b_2)\,|\chi_4^{(0)}\chi_2^{(0)}\rangle + (a_3b_4 - a_4b_3)\,|\chi_3^{(0)}\chi_4^{(0)}\rangle
\end{aligned} \tag{5.3.8}$$

thus, with intermediate normalization

$$\begin{aligned}
|\Phi_0\rangle = |\Psi_0\rangle &+ \frac{a_1b_3 - a_3b_1}{a_1b_2 - a_2b_1}\,|\Psi_2^3\rangle + \frac{a_1b_4 - a_4b_1}{a_1b_2 - a_2b_1}\,|\Psi_2^4\rangle \\
&- \frac{a_2b_3 - a_3b_2}{a_1b_2 - a_2b_1}\,|\Psi_1^3\rangle - \frac{a_2b_4 - a_4b_2}{a_1b_2 - a_2b_1}\,|\Psi_1^4\rangle + \frac{a_3b_4 - a_4b_3}{a_1b_2 - a_2b_1}\,|\Psi_{12}^{34}\rangle
\end{aligned} \tag{5.3.9}$$

$$\begin{aligned}
c_1^3 c_2^4 - c_1^4 c_2^3 &= -\frac{a_2b_3 - a_3b_2}{a_1b_2 - a_2b_1}\frac{a_1b_4 - a_4b_1}{a_1b_2 - a_2b_1} + \frac{a_2b_4 - a_4b_2}{a_1b_2 - a_2b_1}\frac{a_1b_3 - a_3b_1}{a_1b_2 - a_2b_1} \\
&= \frac{a_2a_4b_1b_3 + a_1a_3b_2b_4 - a_2a_3b_1b_4 - a_1a_4b_2b_3}{(a_1b_2 - a_2b_1)^2} \\
&= \frac{(a_1b_2 - a_2b_1)(a_3b_4 - a_4b_3)}{(a_1b_2 - a_2b_1)^2} \\
&= \frac{a_3b_4 - a_4b_3}{a_1b_2 - a_2b_1} \\
&= c_{12}^{34}
\end{aligned} \tag{5.3.10}$$

b.

$$\mathbf{U}_{AA}^{-1} = \frac{1}{\det(\mathbf{U}_{AA})}\begin{pmatrix} b_2 & -b_1 \\ -a_2 & a_1 \end{pmatrix} \tag{5.3.11}$$

$$\begin{aligned}
(\mathbf{U}_{BA}\mathbf{U}_{AA}^{-1})_{11} &= \frac{1}{\det(\mathbf{U}_{AA})}(a_3b_2 - b_3a_2) \\
&= -\frac{a_2b_3 - a_3b_2}{a_1b_2 - a_2b_1} \\
&= c_1^3
\end{aligned} \tag{5.3.12}$$

5.3.2 The Resonance Energy of Polyenes in Hückel Theory

Ex 5.16

$$\mathbf{H} = \begin{pmatrix}
\alpha & \beta & 0 & 0 & 0 & \beta \\
\beta & \alpha & \beta & 0 & 0 & 0 \\
0 & \beta & \alpha & \beta & 0 & 0 \\
0 & 0 & \beta & \alpha & \beta & 0 \\
0 & 0 & 0 & \beta & \alpha & \beta \\
\beta & 0 & 0 & 0 & \beta & \alpha
\end{pmatrix} \tag{5.3.13}$$

the eigenvalues are

$$\alpha - 2\beta, \alpha - \beta, \alpha - \beta, \alpha + \beta, \alpha + \beta, \alpha + 2\beta \tag{5.3.14}$$

while from Eq. 5.131, we get

$$\varepsilon_i = \alpha + 2\beta \cos\frac{\pi i}{3} \quad (i = 0, \pm 1, \pm 2, 3) \tag{5.3.15}$$

i.e.
$$\{\varepsilon_i\} = \{\alpha + 2\beta, \alpha + \beta, \alpha + \beta, \alpha - \beta, \alpha - \beta, \alpha - 2\beta, \} \tag{5.3.16}$$
which is identical to those eigenvalues.

The total energy is
$$\mathscr{E}_0 = 2(\alpha + 2\beta + \alpha + \beta + \alpha + \beta) \tag{5.3.17}$$
$$= 6\alpha + 8\beta \tag{5.3.18}$$
which agrees with Eq. 5.132.

Ex 5.17   For Eq. 5.139
$$\langle i \,|\, j \rangle = \frac{1}{2}((\langle \phi_{2i-1}| + \langle \phi_{2i}|)(|\phi_{2j-1}\rangle + |\phi_{2j}\rangle)$$
$$= \frac{1}{2}(\delta_{2i-1,2j-1} + 0 + 0 + \delta_{2i,2j})$$
$$= \frac{1}{2}(\delta_{i,j} + \delta_{i,j})$$
$$= \delta_{i,j} \tag{5.3.19}$$
$\langle i^* \,|\, j^* \rangle$ is similar.

$$\langle i \,|\, j^* \rangle = \frac{1}{2}((\langle \phi_{2i-1}| + \langle \phi_{2i}|)(|\phi_{2j-1}\rangle - |\phi_{2j}\rangle)$$
$$= \frac{1}{2}(\delta_{2i-1,2j-1} - 0 + 0 - \delta_{2i,2j})$$
$$= \frac{1}{2}(\delta_{i,j} - \delta_{i,j})$$
$$= 0 \tag{5.3.20}$$
For Eq. 5.140
$$\langle i \,|\, h_{\text{eff}} \,|\, i \rangle = \frac{1}{2}((\langle \phi_{2i-1}| + \langle \phi_{2i}|)h_{\text{eff}}(|\phi_{2i-1}\rangle + |\phi_{2i}\rangle)$$
$$= \frac{1}{2}(\alpha + \beta + \beta + \alpha)$$
$$= \alpha + \beta \tag{5.3.21}$$

$$\langle i^* \,|\, h_{\text{eff}} \,|\, i^* \rangle = \frac{1}{2}((\langle \phi_{2i-1}| - \langle \phi_{2i}|)h_{\text{eff}}(|\phi_{2i-1}\rangle - |\phi_{2i}\rangle)$$
$$= \frac{1}{2}(\alpha - \beta - \beta + \alpha)$$
$$= \alpha - \beta \tag{5.3.22}$$

$$\langle i \,|\, h_{\text{eff}} \,|\, i \pm 1 \rangle = \frac{1}{2}((\langle \phi_{2i-1}| + \langle \phi_{2i}|)h_{\text{eff}}(|\phi_{2i-1\pm2}\rangle + |\phi_{2i\pm2}\rangle)$$
$$= \begin{cases} \frac{1}{2}(0 + 0 + \beta + 0) & + \\ \\ \frac{1}{2}(0 + \beta + 0 + 0) & - \end{cases}$$
$$= \beta/2 \tag{5.3.23}$$

$$\langle i^* \,|\, h_{\text{eff}} \,|\, (i \pm 1)^* \rangle = \frac{1}{2}((\langle \phi_{2i-1}| - \langle \phi_{2i}|)h_{\text{eff}}(|\phi_{2i-1\pm2}\rangle - |\phi_{2i\pm2}\rangle)$$
$$= \begin{cases} \frac{1}{2}(0 - 0 - \beta + 0) & + \\ \\ \frac{1}{2}(0 - \beta - 0 + 0) & - \end{cases}$$
$$= -\beta/2 \tag{5.3.24}$$

$$\langle i \,|\, h_{\text{eff}} \,|\, (i \pm 1)^* \rangle = \frac{1}{2}(\langle \phi_{2i-1} | + \langle \phi_{2i} |) h_{\text{eff}}(|\phi_{2i-1\pm2}\rangle - |\phi_{2i\pm2}\rangle)$$

$$= \begin{cases} \dfrac{1}{2}(0 - 0 + \beta - 0) \qquad + \\[2mm] \dfrac{1}{2}(0 - \beta + 0 - 0) \qquad - \end{cases}$$

$$= \pm \beta/2 \tag{5.3.25}$$

Ex 5.18

$$\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \overset{*}{1} \right\rangle = 2^{-1/2} \left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{2*} - \Psi_1^{3*} \right\rangle$$

$$= 2^{-1/2}[\beta/2 - (-\beta/2)]$$

$$= 2^{-1/2}\beta \tag{5.3.26}$$

$$\left\langle \overset{*}{1} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \overset{*}{1} \right\rangle = \frac{1}{2} \left\langle \Psi_1^{2*} - \Psi_1^{3*} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_1^{2*} - \Psi_1^{3*} \right\rangle$$

$$= \frac{1}{2}\left[\left\langle \Psi_1^{2*} - \Psi_1^{3*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{2*} - \Psi_1^{3*} \right\rangle - \left\langle \Psi_1^{2*} - \Psi_1^{3*} \,\middle|\, E_0 \,\middle|\, \Psi_1^{2*} - \Psi_1^{3*} \right\rangle\right]$$

$$= \frac{1}{2}[2(\alpha - \beta) - 2(-\beta/2) - 2E_0]$$

$$= \alpha - \beta/2 - E_0$$

$$= -\frac{3}{2}\beta \tag{5.3.27}$$

thus

$$2^{-1/2}\beta c = e_1 \tag{5.3.28}$$

$$2^{-1/2}\beta - \frac{3}{2}\beta c = e_1 c \tag{5.3.29}$$

the solutions are

$$c = \frac{-3 \pm \sqrt{17}}{2\sqrt{2}} \qquad e_1 = \frac{-3 \pm \sqrt{17}}{4}\beta \tag{5.3.30}$$

and we take

$$e_1 = \frac{-3 + \sqrt{17}}{4}\beta \tag{5.3.31}$$

Ex 5.19

a)

$$|\Psi_1\rangle = |\Psi_0\rangle + c_1 |\Psi_1^{1*}\rangle + c_2 |\Psi_1^{2*}\rangle + \cdots + c_n |\Psi_1^{n*}\rangle \tag{5.3.32}$$

Since

$$\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{1*} \right\rangle = 0 \tag{5.3.33}$$

$$\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{2*} \right\rangle = \beta/2 \tag{5.3.34}$$

$$\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{j*} \right\rangle = 0 \qquad (1 < j < n) \tag{5.3.35}$$

$$\left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{n*} \right\rangle = -\beta/2 \tag{5.3.36}$$

thus,

$$|\Psi_1\rangle = |\Psi_0\rangle + c\left|\overset{*}{1}\right\rangle \tag{5.3.37}$$

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$$\left|\overset{*}{1}\right\rangle = 2^{-1/2}\big(|\Psi_1^{2*}\rangle - |\Psi_1^{n*}\rangle\big) \tag{5.3.38}$$

As before, we get

$$\left\langle \Psi_0 \left| \mathscr{H} \right| \overset{*}{1} \right\rangle = 2^{-1/2}\beta \tag{5.3.39}$$

but

$$\begin{aligned}
\left\langle \overset{*}{1} \left| \mathscr{H} - E_0 \right| \overset{*}{1} \right\rangle &= \frac{1}{2}\big[\langle \Psi_1^{2*} - \Psi_1^{3*} \,|\, \mathscr{H} \,|\, \Psi_1^{2*} - \Psi_1^{3*}\rangle - \langle \Psi_1^{2*} - \Psi_1^{3*} \,|\, E_0 \,|\, \Psi_1^{2*} - \Psi_1^{3*}\rangle\big] \\
&= \frac{1}{2}[2(\alpha - \beta) - 2 \times 0 - 2E_0] \\
&= \alpha - \beta - E_0 \\
&= -2\beta
\end{aligned} \tag{5.3.40}$$

thus

$$e_1 = \left(-1 + \frac{\sqrt{6}}{2}\right)\beta \tag{5.3.41}$$

$$\begin{aligned}
E_R(\text{IEPA}) &= N e_1 \\
&= \left(-1 + \frac{\sqrt{6}}{2}\right)N\beta \\
&= 0.2247 N\beta
\end{aligned} \tag{5.3.42}$$

b) As $N = 10$,

$$|\Psi_1\rangle = |\Psi_0\rangle + c_1 |\Psi_1^{1*}\rangle + c_2 |\Psi_1^{2*}\rangle + c_3 |\Psi_1^{3*}\rangle + + c_4 |\Psi_1^{4*}\rangle + c_5 |\Psi_1^{5*}\rangle \tag{5.3.43}$$

As before, let

$$\left|\overset{*}{1}\right\rangle = 2^{-1/2}\big(|\Psi_1^{1*}\rangle - |\Psi_1^{5*}\rangle\big) \tag{5.3.44}$$

$$|\Psi_1\rangle = |\Psi_0\rangle + c_1 \left|\overset{*}{1}\right\rangle + c_3 |\Psi_1^{3*}\rangle + + c_4 |\Psi_1^{4*}\rangle \tag{5.3.45}$$

then the "particle" equations will be

$$\left\langle \Psi_0 \left| \mathscr{H} \right| \overset{*}{1} \right\rangle c_1 + \langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_1^{3*}\rangle c_3 + \langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_1^{4*}\rangle c_4 = e_1 \tag{5.3.46}$$

$$\left\langle \overset{*}{1} \left| \mathscr{H} \right| \Psi_0 \right\rangle + \left\langle \overset{*}{1} \left| \mathscr{H} \right| \Psi_1^{3*} \right\rangle c_3 + \left\langle \overset{*}{1} \left| \mathscr{H} \right| \Psi_1^{4*} \right\rangle c_4 + \left\langle \overset{*}{1} \left| \mathscr{H} - E_0 \right| \overset{*}{1} \right\rangle c_1 = e_1 c_1 \tag{5.3.47}$$

$$\langle \Psi_1^{3*} \,|\, \mathscr{H} \,|\, \Psi_0\rangle + \left\langle \Psi_1^{3*} \left| \mathscr{H} \right| \overset{*}{1} \right\rangle c_1 + \langle \Psi_1^{3*} \,|\, \mathscr{H} \,|\, \Psi_1^{4*}\rangle c_4 + \langle \Psi_1^{3*} \,|\, \mathscr{H} - E_0 \,|\, \Psi_1^{3*}\rangle c_3 = e_1 c_3 \tag{5.3.48}$$

$$\langle \Psi_1^{4*} \,|\, \mathscr{H} \,|\, \Psi_0\rangle + \left\langle \Psi_1^{4*} \left| \mathscr{H} \right| \overset{*}{1} \right\rangle c_1 + \langle \Psi_1^{4*} \,|\, \mathscr{H} \,|\, \Psi_1^{3*}\rangle c_3 + \langle \Psi_1^{4*} \,|\, \mathscr{H} - E_0 \,|\, \Psi_1^{4*}\rangle c_4 = e_1 c_4 \tag{5.3.49}$$

where

$$\left\langle \Psi_0 \left| \mathscr{H} \right| \overset{*}{1} \right\rangle = 2^{-1/2}\beta \tag{5.3.50}$$

$$\langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_1^{3*}\rangle = 0 \tag{5.3.51}$$

$$\langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_1^{4*}\rangle = 0 \tag{5.3.52}$$

$$\left\langle \overset{*}{1} \left| \mathscr{H} - E_0 \right| \overset{*}{1} \right\rangle = -2\beta \tag{5.3.53}$$

$$\left\langle \Psi_1^{3*} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_1^{3*} \right\rangle = \left\langle \Psi_1^{4*} \,\middle|\, \mathscr{H} - E_0 \,\middle|\, \Psi_1^{4*} \right\rangle = \alpha - \beta - E_0 = -2\beta \tag{5.3.54}$$

$$\left\langle \overset{*}{1} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{3*} \right\rangle = 2^{-1/2}\left[\left\langle \Psi_1^{2*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{3*} \right\rangle - \left\langle \Psi_1^{5*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{3*} \right\rangle \right]$$
$$= 2^{-1/2}(-\beta/2) \tag{5.3.55}$$

$$\left\langle \overset{*}{1} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{4*} \right\rangle = 2^{-1/2}\left[\left\langle \Psi_1^{2*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{4*} \right\rangle - \left\langle \Psi_1^{5*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{4*} \right\rangle \right]$$
$$= 2^{-1/2}(\beta/2) \tag{5.3.56}$$

$$\left\langle \Psi_1^{3*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_1^{4*} \right\rangle = -\beta/2 \tag{5.3.57}$$

thus

$$2^{-1/2}\beta c_1 = e_1 \tag{5.3.58}$$
$$2^{-1/2}\beta + 2^{-1/2}(-\beta/2)c_3 + 2^{-1/2}(\beta/2)c_4 + (-2\beta)c_1 = e_1 c_1 \tag{5.3.59}$$
$$2^{-1/2}(-\beta/2)c_1 + (-\beta/2)c_4 + (-2\beta)c_3 = e_1 c_3 \tag{5.3.60}$$
$$2^{-1/2}(\beta/2)c_1 + (-\beta/2)c_3 + (-2\beta)c_4 = e_1 c_4 \tag{5.3.61}$$

or

$$\begin{pmatrix} 0 & 2^{-1/2}\beta & 0 & 0 \\ 2^{-1/2}\beta & -2\beta & 2^{-1/2}(-\beta/2) & 2^{-1/2}(\beta/2) \\ 0 & 2^{-1/2}(-\beta/2) & -2\beta & -\beta/2 \\ 0 & 2^{-1/2}(\beta/2) & -\beta/2 & -2\beta \end{pmatrix} \begin{pmatrix} 1 \\ c_1 \\ c_3 \\ c_4 \end{pmatrix} = e_1 \begin{pmatrix} 1 \\ c_1 \\ c_3 \\ c_4 \end{pmatrix} \tag{5.3.62}$$

the eigenvalues are

$$-\frac{5}{2}\beta \ \text{ or roots of } \ (2e_1/\beta)^3 + 7(2e_1/\beta)^2 + 9(2e_1/\beta) - 6 = 0 \tag{5.3.63}$$

rearrange the cubic equation, we get

$$4e_1^3 + 14\beta e_1^2 + 9\beta^2 e_1 - 3\beta^3 = 0 \tag{5.3.64}$$
$$e_1 = -2.4627\beta, -1.2760\beta, 0.2387\beta \tag{5.3.65}$$

so we take

$$e_1 = 0.2387\beta \tag{5.3.66}$$

Ex 5.20

$$\left\langle \overset{*}{1} \,\middle|\, \mathscr{H} \,\middle|\, \overset{*}{2} \right\rangle = \frac{1}{2}\left\langle \Psi_1^{2*} - \Psi_1^{3*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_2^{3*} - \Psi_2^{1*} \right\rangle$$
$$= -\frac{1}{2}\left\langle \Psi_1^{3*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_2^{3*} \right\rangle$$
$$= -\frac{1}{2}(-1)\left\langle 2 \,\middle|\, h_{\text{eff}} \,\middle|\, 1 \right\rangle$$
$$= -\frac{1}{2}(-1)\beta/2$$
$$= \beta/4 \tag{5.3.67}$$

$$\left\langle \overset{*}{1} \,\middle|\, \mathscr{H} \,\middle|\, \overset{*}{3} \right\rangle = \frac{1}{2}\left\langle \Psi_1^{2*} - \Psi_1^{3*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_3^{1*} - \Psi_3^{2*} \right\rangle$$
$$= -\frac{1}{2}\left\langle \Psi_1^{2*} \,\middle|\, \mathscr{H} \,\middle|\, \Psi_3^{2*} \right\rangle$$
$$= -\frac{1}{2}(-1)\beta/2$$
$$= \beta/4 \tag{5.3.68}$$

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$$\left\langle \overset{*}{2} \middle| \mathscr{H} \middle| \overset{*}{3} \right\rangle = \frac{1}{2} \left\langle \Psi_2^{3*} - \Psi_2^{1*} \middle| \mathscr{H} \middle| \Psi_3^{1*} - \Psi_3^{2*} \right\rangle$$

$$= -\frac{1}{2} \left\langle \Psi_2^{1*} \middle| \mathscr{H} \middle| \Psi_3^{1*} \right\rangle$$

$$= -\frac{1}{2}(-1)\beta/2$$

$$= \beta/4 \tag{5.3.69}$$

For SCI,

$$\sum_{bs} v_{bs} c_b^s = E_R(\text{SCI}) \tag{5.3.70}$$

$$v_{ra} + (\varepsilon_r^{(0)} + v_{rr})c_a^r + \sum_s v_{rs}c_a^s - (\varepsilon_a^{(0)} + v_{aa})c_a^r - \sum_b v_{ba}c_b^r = E_R(\text{SCI})c_a^r \tag{5.3.71}$$

thus

$$6c \left\langle \overset{*}{i} \middle| \mathscr{H} \middle| \Psi_0 \right\rangle = E_R(\text{SCI}) \tag{5.3.72}$$

$$\left\langle \overset{*}{i} \middle| \mathscr{H} \middle| \Psi_0 \right\rangle + c \left\langle \overset{*}{i} \middle| \mathscr{H} - E_0 \middle| \overset{*}{i} \right\rangle + \sum_{j \neq i} c \left\langle \overset{*}{j} \middle| \mathscr{H} \middle| \overset{*}{i} \right\rangle = E_R(\text{SCI})c \tag{5.3.73}$$

i.e.

$$6c \times 2^{-1/2}\beta = E_R(\text{SCI}) \tag{5.3.74}$$

$$2^{-1/2}\beta + c\left(-\frac{3}{2}\beta + 2 \times \beta/4\right) = E_R(\text{SCI})c \tag{5.3.75}$$

$\therefore$

$$6c \times 2^{-1/2}\beta = E_R(\text{SCI}) \tag{5.3.76}$$

$$2^{-1/2}\beta - c\beta = E_R(\text{SCI})c \tag{5.3.77}$$

the solutions are

$$E_R(\text{SCI}) = \frac{-1 \pm \sqrt{13}}{2}\beta \tag{5.3.78}$$

we take

$$E_R(\text{SCI}) = \frac{-1 + \sqrt{13}}{2}\beta \tag{5.3.79}$$

Ex 5.21 It's clear that

$$\left\langle \Psi_0 \middle| \mathscr{H} \middle| \overset{*}{i} \right\rangle = 2^{-1/2}\beta \tag{5.3.80}$$

while

$$\left\langle \overset{*}{i} \middle| \mathscr{H} - E_0 \middle| \overset{*}{j} \right\rangle = \left\langle \overset{*}{i} \middle| \mathscr{H} \middle| \overset{*}{j} \right\rangle - E_0\delta_{ij}$$

$$= \left\langle \Psi_i^{(i+1)*} - \Psi_i^{(i-1)*} \middle| \mathscr{H} \middle| \Psi_j^{(j+1)*} - \Psi_j^{(j-1)*} \right\rangle - E_0\delta_{ij} \tag{5.3.81}$$

If $i = j$,

$$\left\langle \overset{*}{i} \middle| \mathscr{H} - E_0 \middle| \overset{*}{j} \right\rangle = \frac{1}{2} \left\langle \Psi_i^{(i+1)*} - \Psi_i^{(i-1)*} \middle| \mathscr{H} \middle| \Psi_i^{(i+1)*} - \Psi_i^{(i-1)*} \right\rangle - E_0$$

$$= \frac{1}{2} \times 2(\alpha - \beta) - E_0$$

$$= -2\beta \tag{5.3.82}$$

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else,

$$\left\langle \overset{*}{i} \left| \mathscr{H} - E_0 \right| \overset{*}{j} \right\rangle = \frac{1}{2} \left\langle \Psi_i^{(i+1)*} - \Psi_i^{(i-1)*} \left| \mathscr{H} \right| \Psi_j^{(j+1)*} - \Psi_j^{(j-1)*} \right\rangle$$

$$= -\frac{1}{2} \left\langle \Psi_i^{(i+1)*} \left| \mathscr{H} \right| \Psi_j^{(j-1)*} \right\rangle - \frac{1}{2} \left\langle \Psi_i^{(i-1)*} \left| \mathscr{H} \right| \Psi_j^{(j+1)*} \right\rangle$$

$$= 0 \tag{5.3.83}$$

thus

$$\left\langle \overset{*}{i} \left| \mathscr{H} - E_0 \right| \overset{*}{j} \right\rangle = -2\beta \delta_{ij} \tag{5.3.84}$$

Similar to Ex. 5.20, the SCI equations are

$$Nc \times 2^{-1/2}\beta = E_R(\text{SCI}) \tag{5.3.85}$$

$$2^{-1/2}\beta + c(-2\beta + 0) = E_R(\text{SCI})c \tag{5.3.86}$$

$\therefore$

$$E_R(\text{SCI}) = \frac{-2 + \sqrt{2N+4}}{2}\beta = \left[\sqrt{1 + N/2} - 1\right]\beta \tag{5.3.87}$$