Modern Quantum Chemistry, Szabo & Ostlund HW

wsr

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Contents

7 The 1-Particle Many-body Green's Function

7.1 Green's Function in Single-Particle Systems

Ex 7.1

$$\mathbf{V} = \mathbf{G}_0(E)^{-1} - \mathbf{G}(E)^{-1} \tag{7.1.1}$$

thus

$$\begin{aligned}\mathbf{G}_0(E)\mathbf{V}\mathbf{G}(E) &= \mathbf{G}_0(E)[\mathbf{G}_0(E)^{-1} - \mathbf{G}(E)^{-1}]\mathbf{G}(E) \\ &= \mathbf{G}(E) - \mathbf{G}_0(E)\end{aligned} \tag{7.1.2}$$

i.e.

$$\mathbf{G}(E) = \mathbf{G}_0(E) + \mathbf{G}_0(E)\mathbf{V}\mathbf{G}(E) \tag{7.1.3}$$

Ex 7.2

a. When $x = 0$,

$$\begin{aligned}\frac{\mathrm{d}^2}{\mathrm{d}x^2}|x|\bigg|_{x=0} &= \lim_{\epsilon\to 0} \frac{\frac{\mathrm{d}|x|}{\mathrm{d}x}\Big|_{x=\epsilon} - \frac{\mathrm{d}|x|}{\mathrm{d}x}\Big|_{x=-\epsilon}}{2\epsilon} \qquad (\epsilon > 0) \\ &= \lim_{\epsilon\to 0}\frac{1-(-1)}{2\epsilon} \\ &= \infty\end{aligned} \tag{7.1.4}$$

otherwise,

$$\begin{aligned}\frac{\mathrm{d}^2}{\mathrm{d}x^2}|x| &= \frac{\mathrm{d}^2}{\mathrm{d}x^2}[x\ \mathrm{sgn}(x)] \\ &= \frac{\mathrm{d}}{\mathrm{d}x}[1\times \mathrm{sgn}(x) + x \times 0] \\ &= 0\end{aligned} \tag{7.1.5}$$

b.

$$\begin{aligned}\int_{-\infty}^{\infty} \frac{\mathrm{d}^2}{\mathrm{d}x^2}|x|\mathrm{d}x &= \int_{-\infty}^{\infty} \mathrm{d}\left(\frac{\mathrm{d}}{\mathrm{d}x}|x|\right) \\ &= \frac{\mathrm{d}}{\mathrm{d}x}|x|\bigg|_{-\infty}^{\infty} \\ &= 1-(-1) \\ &= 2\end{aligned} \tag{7.1.6}$$

thus

$$\frac{\mathrm{d}^2}{\mathrm{d}x^2}|x| = 2\delta(x) \tag{7.1.7}$$

c.

$$\begin{aligned}\frac{\mathrm{d}^2}{\mathrm{d}x^2}a(x) &= \frac{\mathrm{d}^2}{\mathrm{d}x^2}\frac{1}{2}\int_\alpha^\beta \mathrm{d}x'|x-x'|b(x') \\ &= \frac{\mathrm{d}^2}{\mathrm{d}x^2}\frac{1}{2}\int_\alpha^x \mathrm{d}x'(x-x')b(x') + \frac{\mathrm{d}^2}{\mathrm{d}x^2}\frac{1}{2}\int_x^\beta \mathrm{d}x'[-(x-x')]b(x') \\ &= \frac{\mathrm{d}}{\mathrm{d}x}\frac{1}{2}\int_\alpha^x \mathrm{d}x' b(x') - \frac{\mathrm{d}}{\mathrm{d}x}\frac{1}{2}\int_x^\beta \mathrm{d}x' b(x') \\ &= \frac{1}{2}b(x) - \frac{1}{2}[-b(x)] \\ &= b(x)\end{aligned} \tag{7.1.8}$$

Ex 7.3

$$
\begin{aligned}
\left(E+\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\right)G_0(x,x',E) &= \left(E+\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\right)\frac{1}{\mathrm{i}(2E)^{1/2}}\,\mathrm{e}^{\mathrm{i}(2E)^{1/2}|x-x'|} \\
&= \frac{E}{\mathrm{i}(2E)^{1/2}}\,\mathrm{e}^{\mathrm{i}(2E)^{1/2}|x-x'|} + \frac{1}{2}\frac{1}{\mathrm{i}(2E)^{1/2}}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\,\mathrm{e}^{\mathrm{i}(2E)^{1/2}|x-x'|} \\
&= \frac{E}{\mathrm{i}(2E)^{1/2}}\,\mathrm{e}^{\mathrm{i}(2E)^{1/2}|x-x'|} + \frac{1}{2}\frac{1}{\mathrm{i}(2E)^{1/2}}\frac{\mathrm{d}}{\mathrm{d}x}\left[\mathrm{e}^{\mathrm{i}(2E)^{1/2}|x-x'|}\,\mathrm{i}(2E)^{1/2}\frac{\mathrm{d}}{\mathrm{d}x}|x-x'|\right] \\
&= \frac{E}{\mathrm{i}(2E)^{1/2}}\,\mathrm{e}^{\mathrm{i}(2E)^{1/2}|x-x'|} + \frac{1}{2}\left[\mathrm{e}^{\mathrm{i}(2E)^{1/2}|x-x'|}\,\mathrm{i}(2E)^{1/2}\left(\frac{\mathrm{d}}{\mathrm{d}x}|x-x'|\right)^2 + \mathrm{e}^{\mathrm{i}(2E)^{1/2}|x-x'|}\,\frac{\mathrm{d}^2}{\mathrm{d}x^2}|x-x'|\right] \\
&= \frac{E}{\mathrm{i}(2E)^{1/2}}\,\mathrm{e}^{\mathrm{i}(2E)^{1/2}|x-x'|} + \frac{1}{2}\,\mathrm{e}^{\mathrm{i}(2E)^{1/2}|x-x'|}\left[\mathrm{i}(2E)^{1/2}\times 1 + 2\delta(x-x')\right] \\
&= \mathrm{e}^{\mathrm{i}(2E)^{1/2}|x-x'|}\left[\frac{E}{\mathrm{i}(2E)^{1/2}} + \frac{-E}{\mathrm{i}(2E)^{1/2}} + \delta(x-x')\right] \\
&= \mathrm{e}^{\mathrm{i}(2E)^{1/2}|x-x'|}\,\delta(x-x') \\
&= \delta(x-x')
\end{aligned} \tag{7.1.9}
$$

Ex 7.4

$$
\begin{aligned}
\phi_n(x)\phi_n^*(x') &= \lim_{E\to E_n}(E-E_n)\frac{1}{\mathrm{i}(2E)^{1/2}}\left[\mathrm{e}^{\mathrm{i}(2E)^{1/2}|x-x'|} - \frac{\mathrm{e}^{\mathrm{i}(2E)^{1/2}(|x|+|x'|)}}{1+\mathrm{i}(2E)^{1/2}}\right] \\
&= \lim_{E\to -1/2}(E+1/2)\frac{1}{-1}\left[\mathrm{e}^{-|x-x'|} - \frac{\mathrm{e}^{-(|x|+|x'|)}}{1+\mathrm{i}(2E)^{1/2}}\right] \\
&= -\lim_{E\to -1/2}(E+1/2)\,\mathrm{e}^{-|x-x'|} + \lim_{E\to -1/2}(E+1/2)\frac{\mathrm{e}^{-(|x|+|x'|)}}{1+\mathrm{i}(2E)^{1/2}} \\
&= 0 + \lim_{E\to -1/2}(E+1/2)\frac{\mathrm{e}^{-(|x|+|x'|)}(1-\mathrm{i}(2E)^{1/2})}{(1+\mathrm{i}(2E)^{1/2})(1-\mathrm{i}(2E)^{1/2})} \\
&= \lim_{E\to -1/2}(E+1/2)\frac{\mathrm{e}^{-(|x|+|x'|)}(1-\mathrm{i}(2E)^{1/2})}{1+2E} \\
&= \frac{1}{2}\,\mathrm{e}^{-(|x|+|x'|)}(1-(-1)) \\
&= \mathrm{e}^{-(|x|+|x'|)}
\end{aligned} \tag{7.1.10}
$$

Let $x = x'$,

$$\phi_n^2(x) = \mathrm{e}^{-2|x|} \tag{7.1.11}$$

thus

$$\phi_n(x) = \mathrm{e}^{-|x|} \tag{7.1.12}$$

Ex 7.5

$$
\begin{aligned}
\mathscr{H}\,\phi &= \left[-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2} - \delta(x)\right]\mathrm{e}^{-|x|} \\
&= -\frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}x}\left[\mathrm{e}^{-|x|}\left(-\frac{\mathrm{d}}{\mathrm{d}x}|x|\right)\right] - \delta(x)\,\mathrm{e}^{-|x|} \\
&= \frac{1}{2}\left[-\mathrm{e}^{-|x|}(\frac{\mathrm{d}}{\mathrm{d}x}|x|)^2 + \mathrm{e}^{-|x|}\,\frac{\mathrm{d}^2}{\mathrm{d}x^2}|x|\right] - \delta(x)\,\mathrm{e}^{-|x|} \\
&= \frac{1}{2}\left[-\mathrm{e}^{-|x|} + \mathrm{e}^{-|x|}\times 2\delta(x)\right] - \delta(x)\,\mathrm{e}^{-|x|} \\
&= -\frac{1}{2}\,\mathrm{e}^{-|x|}
\end{aligned} \tag{7.1.13}
$$

thus the eigenvalue is $-\dfrac{1}{2}$.

Ex 7.6

a.

$$
\begin{aligned}
\mathrm{i}\,\frac{\partial}{\partial t}\phi(x,t) &= \mathrm{i}\int \mathrm{d}x'\,\frac{\partial G(x,x',t)}{\partial t}\psi(x') \\
&= \int \mathrm{d}x'\,\mathscr{H}\,G(x,x',t)\psi(x') \\
&= \mathscr{H}\,\phi(x,t)
\end{aligned} \tag{7.1.14}
$$

b. From

$$
\mathrm{i}\,\frac{\partial G(x,x',t)}{\partial t} = \mathscr{H}\,G(x,x',t) \tag{7.1.15}
$$

we get

$$
\lim_{\varepsilon\to 0}\int_0^\infty \mathrm{d}t\,\mathrm{i}\,\frac{\partial G(x,x',t)}{\partial t}[-\,\mathrm{i}\,\mathrm{e}^{(\mathrm{i}\,E-\varepsilon)t}] = \lim_{\varepsilon\to 0}\int_0^\infty \mathrm{d}t\,\mathscr{H}\,G(x,x',t)[-\,\mathrm{i}\,\mathrm{e}^{(\mathrm{i}\,E-\varepsilon)t}] \tag{7.1.16}
$$

$$
\begin{aligned}
\lim_{\varepsilon\to 0}\int_0^\infty \mathrm{d}t\frac{\partial G(x,x',t)}{\partial t}\,\mathrm{e}^{(\mathrm{i}\,E-\varepsilon)t} &= \int_0^\infty \mathrm{d}t\,\mathscr{H}\,G(x,x',t)[-\,\mathrm{i}\,\mathrm{e}^{\mathrm{i}\,Et}] \\
&= \mathscr{H}\,G(x,x',E)
\end{aligned} \tag{7.1.17}
$$

thus

$$
\lim_{\varepsilon\to 0}\left[G(x,x',t)\,\mathrm{e}^{(\mathrm{i}\,E-\varepsilon)t}\Big|_{t=0}^{\infty} - \int_0^\infty \mathrm{d}tG(x,x',t)\,\mathrm{e}^{(\mathrm{i}\,E-\varepsilon)t}(\mathrm{i}\,E-\varepsilon)\right] = \mathscr{H}\,G(x,x',E) \tag{7.1.18}
$$

$$
\begin{aligned}
\mathscr{H}\,G(x,x',E) &= -G(x,x',0) - \mathrm{i}\,E\int_0^\infty \mathrm{d}tG(x,x',t)\,\mathrm{e}^{\mathrm{i}\,Et} \\
&= -G(x,x',0) - \mathrm{i}\,EG(x,x',E)/(-\,\mathrm{i}) \\
&= -\delta(x-x') + EG(x,x',E)
\end{aligned} \tag{7.1.19}
$$

$\therefore$

$$
(E-\mathscr{H})G(x,x',E) = \delta(x-x') \tag{7.1.20}
$$

c.

$$
\begin{aligned}
\mathrm{i}\,\frac{\partial}{\partial t}\mathscr{G}(t) &= \mathrm{i}\,\frac{\partial}{\partial t}\,\mathrm{e}^{-\,\mathrm{i}\,\mathscr{H}\,t} \\
&= \mathrm{i}\,\mathrm{e}^{-\,\mathrm{i}\,\mathscr{H}\,t}(-\,\mathrm{i}\,\mathscr{H}) \\
&= \mathscr{H}\,\mathscr{G}(t)
\end{aligned} \tag{7.1.21}
$$

$$
\lim_{\varepsilon\to 0}\int_0^\infty \mathrm{d}t\,\mathrm{e}^{(\mathrm{i}\,E-\varepsilon)t}\,\mathrm{i}\,\frac{\partial}{\partial t}\mathscr{G}(t) = \lim_{\varepsilon\to 0}\int_0^\infty \mathrm{d}t\,\mathrm{e}^{(\mathrm{i}\,E-\varepsilon)t}\,\mathscr{H}\,\mathscr{G}(t) \tag{7.1.22}
$$

$$
\lim_{\varepsilon\to 0}\left[\mathrm{e}^{(\mathrm{i}\,E-\varepsilon)t}\,\mathscr{G}(t)\Big|_0^\infty - (\mathrm{i}\,E-\varepsilon)\int_0^\infty \mathrm{d}t\,\mathrm{e}^{(\mathrm{i}\,E-\varepsilon)t}\,\mathscr{G}(t)\right] = \mathscr{H}\,\mathscr{G}(E) \tag{7.1.23}
$$

$\therefore$

$$
\begin{aligned}
\mathscr{H}\,\mathscr{G}(E) &= \lim_{\varepsilon\to 0}\left[-\mathscr{G}(0) - (\mathrm{i}\,E-\varepsilon)\int_0^\infty \mathrm{d}t\,\mathrm{e}^{(\mathrm{i}\,E-\varepsilon)t}\,\mathscr{G}(t)\right] \\
&= -\mathscr{G}(0) + E\mathscr{G}(E) \\
&= -1 + E\mathscr{G}(E)
\end{aligned} \tag{7.1.24}
$$

thus

$$
\mathscr{G}(E) = \frac{1}{E-\mathscr{H}} \tag{7.1.25}
$$

7.2 The 1-Particle Many-body Green's Function

7.2.1 The Self-Energy

Ex 7.7

$$
\begin{aligned}
\Sigma_{ij}^{(2)}(E) &= \frac{1}{2}\sum_{ars}\frac{\langle rs \,\|\, ia\rangle \langle ja \,\|\, rs\rangle}{E+\varepsilon_a-\varepsilon_r-\varepsilon_s} + \frac{1}{2}\sum_{abr}\frac{\langle ab \,\|\, ir\rangle \langle jr \,\|\, ab\rangle}{E+\varepsilon_r-\varepsilon_a-\varepsilon_b} \\
&= \frac{1}{2}\sum_{ars}\frac{(\langle rs \,|\, ia\rangle - \langle rs \,|\, ai\rangle)(\langle ja \,|\, rs\rangle - \langle ja \,|\, sr\rangle)}{E+\varepsilon_a-\varepsilon_r-\varepsilon_s} + \frac{1}{2}\sum_{abr}\frac{(\langle ab \,|\, ir\rangle - \langle ab \,|\, ri\rangle)(\langle jr \,|\, ab\rangle - \langle jr \,|\, ba\rangle)}{E+\varepsilon_r-\varepsilon_a-\varepsilon_b}
\end{aligned} \tag{7.2.1}
$$

In the 1st summation:
To make the terms non-zero, the spin of r is fixed in the first and last term, and r, s, a are all fixed in the second and third term, thus

$$
\begin{aligned}
\text{the 1st term} &= \frac{1}{2}\sum_{ars}^{N/2}\frac{1}{E+\varepsilon_a-\varepsilon_r-\varepsilon_s}[2\langle rs \,|\, ia\rangle \langle ja \,|\, rs\rangle - \langle rs \,|\, ai\rangle \langle ja \,|\, rs\rangle - \langle rs \,|\, ia\rangle \langle ja \,|\, sr\rangle + 2\langle rs \,|\, ai\rangle \langle ja \,|\, sr\rangle] \\
&= \sum_{ars}^{N/2}\frac{1}{E+\varepsilon_a-\varepsilon_r-\varepsilon_s}[2\langle rs \,|\, ia\rangle \langle ja \,|\, rs\rangle - \langle rs \,|\, ia\rangle \langle ja \,|\, sr\rangle] \\
&= \sum_{ars}^{N/2}\frac{\langle rs \,|\, ia\rangle [2\langle ja \,|\, rs\rangle - \langle aj \,|\, rs\rangle]}{E+\varepsilon_a-\varepsilon_r-\varepsilon_s}
\end{aligned} \tag{7.2.2}
$$

Similarly,

$$
\Sigma_{ij}^{(2)}(E) = \sum_{ars}^{N/2}\frac{\langle rs \,|\, ia\rangle [2\langle ja \,|\, rs\rangle - \langle aj \,|\, rs\rangle]}{E+\varepsilon_a-\varepsilon_r-\varepsilon_s} + \sum_{abr}^{N/2}\frac{\langle ab \,|\, ir\rangle [2\langle jr \,|\, ab\rangle - \langle rj \,|\, ab\rangle]}{E+\varepsilon_r-\varepsilon_a-\varepsilon_b} \tag{7.2.3}
$$

Ex 7.8

$$
\begin{aligned}
[\mathbf{G}_0(E)]_{ij} &= \sum_m \frac{\left\langle {}^N\Psi_0 \,\middle|\, a_i^\dagger a_m \,\middle|\, {}^N\Psi_0 \right\rangle \langle a_m {}^N\Psi_0 \,|\, a_j \,|\, {}^N\Psi_0\rangle}{E - (\langle {}^N\Psi_0 \,|\, \mathscr{H} \,|\, {}^N\Psi_0\rangle - \langle a_m {}^N\Psi_0 \,|\, \mathscr{H} \,|\, a_m {}^N\Psi_0\rangle)} + \sum_p \frac{\langle {}^N\Psi_0 \,|\, a_j a_p^\dagger \,|\, {}^N\Psi_0\rangle \left\langle a_p^\dagger {}^N\Psi_0 \,\middle|\, a_i^\dagger \,\middle|\, {}^N\Psi_0 \right\rangle}{E + \left(\langle {}^N\Psi_0 \,|\, \mathscr{H} \,|\, {}^N\Psi_0\rangle - \left\langle a_p^\dagger {}^N\Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, a_p^\dagger {}^N\Psi_0 \right\rangle \right.} \\
&= \sum_m \frac{\delta_{im}\delta_{mj}}{E-\varepsilon_m} + 0 \\
&= \sum_m \frac{\delta_{ij}}{E-\varepsilon_m}
\end{aligned} \tag{7.2.4}
$$

7.2.2 The Solution of the Dyson Equation

7.3 Application of the Formalism to H_2 and HeH^+

Ex 7.9

a.

$$
{}^{N+1}\mathscr{E}_0 = {}^{N+1}E_0 + {}^{N+1}E_{\text{corr}} \tag{7.3.1}
$$

Since the ground state ($|1\bar{1}2\rangle$) of ${H_2}^-$ is of ungerade symmetry while the excited state ($|12\bar{2}\rangle$) is of gerade symmetry,

$$
{}^{N+1}E_{\text{corr}} = 0 \tag{7.3.2}
$$

thus

$$
\begin{aligned}
{}^{N+1}\mathscr{E}_0 - {}^{N}\mathscr{E}_0 &= {}^{N+1}E_0 - {}^{N}E_0 - {}^{N}E_{\text{corr}} \\
&= (2\varepsilon_1 + \varepsilon_2 - J_{11}) - (2\varepsilon_1 - J_{11}) - {}^{N}E_{\text{corr}} \\
&= \varepsilon_2 - {}^{N}E_{\text{corr}}
\end{aligned} \tag{7.3.3}
$$

$$
\begin{aligned}
{}^{N+1}\mathscr{E}_1 - {}^{N}\mathscr{E}_0 &= {}^{N+1}E_1 - {}^{N}E_0 - {}^{N}E_{\text{corr}} \\
&= (h_{11}h + 2h_{22} + 2J_{12} + J_{22} - K_{12}) - (2\varepsilon_1 - J_{11}) - {}^{N}E_{\text{corr}} \\
&= (\varepsilon_1 + 2\varepsilon_2 - 2J_{12} + K_{12} - J_{11} + J_{22}) - (2\varepsilon_1 - J_{11}) - {}^{N}E_{\text{corr}} \\
&= 2\varepsilon_2 - \varepsilon_1 - 2J_{12} + K_{12} + J_{22} - {}^{N}E_{\text{corr}}
\end{aligned} \tag{7.3.4}
$$

b.

$$
\begin{aligned}
\varepsilon_{11}^{+} &= \varepsilon_1 + (\varepsilon_2 - \varepsilon_1) + \sqrt{(\varepsilon_2 - \varepsilon_1)^2 + K_{12}^2} \\
&\approx \varepsilon_1 + (\varepsilon_2 - \varepsilon_1) + \Delta - \Delta + \sqrt{\Delta^2 + K_{12}^2} \\
&= \varepsilon_1 + (\varepsilon_2 - \varepsilon_1) + \Delta - {}^{N}E_{\text{corr}} \\
&= \varepsilon_1 + (\varepsilon_2 - \varepsilon_1) + (\varepsilon_2 - \varepsilon_1) + \frac{1}{2}(J_{11} + J_{22}) - 2J_{12} + K_{12} - {}^{N}E_{\text{corr}} \\
&\approx 2\varepsilon_2 - \varepsilon_1 + J_{22} - 2J_{12} + K_{12} - {}^{N}E_{\text{corr}}
\end{aligned} \tag{7.3.5}
$$

thus

$$
\varepsilon_{11}^{+} \approx {}^{N+1}\mathscr{E}_1 - {}^{N}\mathscr{E}_0 \tag{7.3.6}
$$

c.

$$
E - \varepsilon_2 - \Sigma_{22}^{(2)}(E) = 0 \tag{7.3.7}
$$

$$
E - \varepsilon_2 - \frac{K_{12}^2}{E - \varepsilon_2 - 2(\varepsilon_1 - \varepsilon_2)} = 0 \tag{7.3.8}
$$

$\therefore$

$$
\begin{aligned}
\varepsilon_{22}^{\pm} &= \varepsilon_1 \pm \sqrt{(\varepsilon_1 - \varepsilon_2)^2 + K_{12}^2} \\
&= \varepsilon_2 - \left[(\varepsilon_2 - \varepsilon_1) \mp \sqrt{(\varepsilon_2 - \varepsilon_1)^2 + K_{12}^2}\right]
\end{aligned} \tag{7.3.9}
$$

d.

$$
\begin{aligned}
\varepsilon_{22}^{+} &= \varepsilon_2 - \left[(\varepsilon_2 - \varepsilon_1) - \sqrt{(\varepsilon_2 - \varepsilon_1)^2 + K_{12}^2}\right] \\
&\approx \varepsilon_2 - \left[\Delta - \sqrt{\Delta^2 + K_{12}^2}\right] \\
&= \varepsilon_2 - {}^{N}E_{\text{corr}} \\
&= {}^{N+1}\mathscr{E}_0 - {}^{N}\mathscr{E}_0
\end{aligned} \tag{7.3.10}
$$

$$
\begin{aligned}
\varepsilon_{22}^{-} &= \varepsilon_2 - \left[(\varepsilon_2 - \varepsilon_1) + \sqrt{(\varepsilon_2 - \varepsilon_1)^2 + K_{12}^2}\right] \\
&\approx \varepsilon_2 + \left[-(\varepsilon_2 - \varepsilon_1) - \Delta + \Delta - \sqrt{\Delta^2 + K_{12}^2}\right] \\
&= \varepsilon_2 - (\varepsilon_2 - \varepsilon_1) - \Delta - {}^{N}E_{\text{corr}} \\
&= \varepsilon_2 - (\varepsilon_2 - \varepsilon_1) - \left(\varepsilon_2 - \varepsilon_1 + \frac{1}{2}(J_{11} + J_{22}) - 2J_{12} + K_{12}\right) - {}^{N}E_{\text{corr}} \\
&= 2\varepsilon_1 - \varepsilon_2 - \left(\frac{1}{2}(J_{11} + J_{22}) - 2J_{12} + K_{12}\right) - {}^{N}E_{\text{corr}} \\
&\approx 2\varepsilon_1 - \varepsilon_2 - J_{11} + 2J_{12} - K_{12}) - {}^{N}E_{\text{corr}} \\
&= {}^{N}\mathscr{E}_0 - {}^{N-1}\mathscr{E}_1
\end{aligned} \tag{7.3.11}
$$

Ex 7.10 Since

$$\begin{aligned}\Sigma_{11}^{(2)}(\varepsilon_1) &= \frac{K_{12}}{\varepsilon_1 + \varepsilon_1 - 2\varepsilon_2} \\ &= \frac{K_{12}}{2(\varepsilon_1 - \varepsilon_2)}\end{aligned} \tag{7.3.12}$$

$$\begin{aligned}\Sigma_{11}^{(3)}(\varepsilon_1) &= \frac{K_{12}^2(J_{22} - 2J_{12} + K_{12})}{(\varepsilon_1 - 2\varepsilon_2 + \varepsilon_1)^2} + \frac{K_{12}^2(J_{11} - 2J_{12} + K_{12})}{(\varepsilon_1 - 2\varepsilon_2 + \varepsilon_1)(\varepsilon_1 - \varepsilon_2)} + \frac{K_{12}^2(2J_{12} - K_{12} - J_{11})}{4(\varepsilon_1 - \varepsilon_2)^2} \\ &= \frac{K_{12}^2(J_{22} - 2J_{12} + K_{12})}{4(\varepsilon_1 - \varepsilon_2)^2} + \frac{K_{12}^2(J_{11} - 2J_{12} + K_{12})}{2(\varepsilon_1 - \varepsilon_2)^2} + \frac{K_{12}^2(2J_{12} - K_{12} - J_{11})}{4(\varepsilon_1 - \varepsilon_2)^2} \\ &= \frac{K_{12}^2(J_{22} + J_{11} - 4J_{12} + 2K_{12})}{4(\varepsilon_1 - \varepsilon_2)^2}\end{aligned} \tag{7.3.13}$$

thus

$$\Sigma_{11}^{(2)}(\varepsilon_1) = E_0^{(2)} \tag{7.3.14}$$

$$\Sigma_{11}^{(3)}(\varepsilon_1) = E_0^{(3)} \tag{7.3.15}$$

Similarly,

$$\begin{aligned}\Sigma_{22}^{(2)}(\varepsilon_2) &= \frac{K_{12}}{\varepsilon_2 + \varepsilon_2 - 2\varepsilon_1} \\ &= \frac{K_{12}}{2(\varepsilon_2 - \varepsilon_1)}\end{aligned} \tag{7.3.16}$$

$$\begin{aligned}\Sigma_{22}^{(3)}(\varepsilon_2) &= \frac{K_{12}^2(2J_{12} - K_{12} - J_{11})}{(\varepsilon_2 - 2\varepsilon_1 + \varepsilon_2)^2} + \frac{K_{12}^2(J_{22} - 2J_{12} + K_{12})}{(\varepsilon_2 - 2\varepsilon_1 + \varepsilon_2)(\varepsilon_1 - \varepsilon_2)} + \frac{K_{12}^2(J_{22} + K_{12} - 2J_{12})}{4(\varepsilon_1 - \varepsilon_2)^2} \\ &= \frac{K_{12}^2(2J_{12} - K_{12} - J_{11})}{4(\varepsilon_1 - \varepsilon_2)^2} - \frac{K_{12}^2(J_{22} - 2J_{12} + K_{12})}{2(\varepsilon_1 - \varepsilon_2)^2} + \frac{K_{12}^2(J_{22} + K_{12} - 2J_{12})}{4(\varepsilon_1 - \varepsilon_2)^2} \\ &= \frac{K_{12}^2(-J_{11} - J_{22} + 4J_{12} - 2K_{12})}{4(\varepsilon_1 - \varepsilon_2)^2}\end{aligned} \tag{7.3.17}$$

thus

$$\Sigma_{22}^{(2)}(\varepsilon_2) = -E_0^{(2)} \tag{7.3.18}$$

$$\Sigma_{22}^{(3)}(\varepsilon_2) = -E_0^{(3)} \tag{7.3.19}$$

Ex 7.11 From

$$\begin{pmatrix} h_{11} & h_{22} \\ h_{12} & h_{22} \end{pmatrix} \begin{pmatrix} 1 \\ c \end{pmatrix} =^{N-1} \mathscr{E}_0 \begin{pmatrix} 1 \\ c \end{pmatrix} \tag{7.3.20}$$

we get

$$h_{11} + h_{12}c =^{N-1} \mathscr{E}_0 \tag{7.3.21}$$

$$h_{12} + h_{22}c =^{N-1} \mathscr{E}_0 c \tag{7.3.22}$$

thus

$${}^{N-1}\mathscr{E}_0 = h_{11} + h_{12}\frac{h_{12}}{{}^{N-1}\mathscr{E}_0 - h_{22}} \tag{7.3.23}$$

$$h_{11} +^{N-1} E_R = h_{11} + h_{12}\frac{h_{12}}{h_{11} +^{N-1} E_R - h_{22}} \tag{7.3.24}$$

$$\begin{aligned}{}^{N-1}E_R &= \frac{h_{12}^2}{h_{11} +^{N-1} E_R - h_{22}} \\ &= \frac{|\langle 11 \,|\, 12\rangle|^2}{\varepsilon_1 - \varepsilon_2 - (J_{11} - 2J_{12} + K_{12}) +^{N-1} E_R}\end{aligned} \tag{7.3.25}$$

Ex 7.12

a.

$$|\Phi\rangle = |\Psi_0\rangle + c\,|\Psi_{\bar{1}}^{\bar{2}}\rangle \tag{7.3.26}$$

thus

$$\begin{pmatrix} 0 & \langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_{\bar{1}}^{\bar{2}} \rangle \\ \langle \Psi_0 \,|\, \mathscr{H} \,|\, \Psi_{\bar{1}}^{\bar{2}} \rangle & \langle \Psi_{\bar{1}}^{\bar{2}} \,|\, \mathscr{H} - {}^{N+1}E_0 \,|\, \Psi_{\bar{1}}^{\bar{2}} \rangle \end{pmatrix} \begin{pmatrix} 1 \\ c \end{pmatrix} = \left({}^{N+1}\mathscr{E}_0 - {}^{N+1}E_0 \right) \begin{pmatrix} 1 \\ c \end{pmatrix} \tag{7.3.27}$$

$\because$

$$\begin{aligned} \left\langle \Psi_0 \,\middle|\, \mathscr{H} \,\middle|\, \Psi_{\bar{1}}^{\bar{2}} \right\rangle &= h_{12} + \sum_{b=1,2} \langle \bar{1}b \,\|\, \bar{2}b \rangle \\ &= -\langle 11 \,|\, 12 \rangle + \langle 11 \,|\, 12 \rangle + \langle 12 \,|\, 22 \rangle \\ &= \langle 12 \,|\, 22 \rangle \end{aligned} \tag{7.3.28}$$

$\therefore$

$$\begin{pmatrix} 0 & \langle 12 \,|\, 22 \rangle \\ \langle 12 \,|\, 22 \rangle & \varepsilon_2 - \varepsilon_1 - 2J_{12} + K_{12} + J_{22} \end{pmatrix} \begin{pmatrix} 1 \\ c \end{pmatrix} = \left({}^{N+1}\mathscr{E}_0 - {}^{N+1}E_0 \right) \begin{pmatrix} 1 \\ c \end{pmatrix} \tag{7.3.29}$$

Let

$${}^{N+1}E_R = {}^{N+1}\mathscr{E}_0 - {}^{N+1}E_0 \tag{7.3.30}$$

thus

$$\begin{aligned} {}^{N+1}\mathscr{E}_0 &= {}^{N+1}E_0 + {}^{N+1}E_R \\ &= {}^{N}E_0 + \varepsilon_2 + {}^{N+1}E_R \end{aligned} \tag{7.3.31}$$

b. Solving (7.3.29), we get

$$\begin{aligned} {}^{N+1}E_R &= \frac{1}{2}\left(D - \sqrt{D^2 + 4\,\langle 12 \,|\, 22 \rangle^2} \right) \\ &\approx \frac{1}{2}\left(D - D\left(1 + 2\frac{\langle 12 \,|\, 22 \rangle^2}{D^2} \right) \right) \\ &= -\frac{\langle 12 \,|\, 22 \rangle^2}{D} \\ &\approx -\frac{\langle 12 \,|\, 22 \rangle^2}{\varepsilon_2 - \varepsilon_1} \\ &= \frac{\langle 12 \,|\, 22 \rangle^2}{\varepsilon_1 - \varepsilon_2} \end{aligned} \tag{7.3.32}$$

7.4 Perturbation Theory and the Green's Function Method

Ex 7.13

$$\begin{aligned} \left\langle {}^{N-1}\Psi_c \,\middle|\, \mathscr{V}^{N-1} \,\middle|\, {}^{N-1}\Psi_c \right\rangle &= \left\langle {}^{N-1}\Psi_c \,\middle|\, \sum_{i<j}^{N-1} r_{ij}^{-1} - \sum_{i}^{N-1} v_N^{\mathrm{HF}}(i) \,\middle|\, {}^{N-1}\Psi_c \right\rangle \\ &= \sum_{i<j}^{N-1} \left\langle {}^{N-1}\Psi_c \,\middle|\, r_{ij}^{-1} \,\middle|\, {}^{N-1}\Psi_c \right\rangle - \sum_{i}^{N-1} \left\langle {}^{N-1}\Psi_c \,\middle|\, v_N^{\mathrm{HF}}(i) \,\middle|\, {}^{N-1}\Psi_c \right\rangle \\ &= \frac{1}{2} \sum_{a\neq c} \sum_{b\neq c} \langle ab \,\|\, ab \rangle - \sum_{a\neq c} \sum_{b} \langle ab \,\|\, ab \rangle \\ &= -\frac{1}{2} \sum_{a\neq c} \sum_{b\neq c} \langle ab \,\|\, ab \rangle + \sum_{a\neq c} \langle ac \,\|\, ac \rangle \\ &= -\frac{1}{2} \left(\sum_{a} \sum_{b} \langle ab \,\|\, ab \rangle - \sum_{a} \langle ac \,\|\, ac \rangle - \sum_{b} \langle cb \,\|\, cb \rangle + \langle cc \,\|\, cc \rangle \right) + \sum_{a} \langle ac \,\|\, ac \rangle \end{aligned}$$

$$
\begin{aligned}
&= -\frac{1}{2}\left(\sum_a\sum_b \langle ab \,\|\, ab\rangle - 2\sum_a \langle ac \,\|\, ac\rangle + 0\right) + \sum_a \langle ac \,\|\, ac\rangle \\
&= -\frac{1}{2}\sum_a\sum_b \langle ab \,\|\, ab\rangle
\end{aligned} \tag{7.4.1}
$$

thus

$$
\left\langle {}^{N-1}\Psi_c \,\middle|\, \mathscr{V}^{N-1} \,\middle|\, {}^{N-1}\Psi_c \right\rangle = {}^{N}E_0^{(1)} \tag{7.4.2}
$$

Ex 7.14

$$
\begin{aligned}
{}^{N-1}\tilde{E}_R^{(2)}\binom{r}{a} &= -\sum_{ar} \frac{|\langle ac \,\|\, cr\rangle|^2}{\varepsilon_r - \varepsilon_a} \\
&= -\frac{|\langle 1\bar{1} \,\|\, \bar{1}2\rangle|^2}{\varepsilon_2 - \varepsilon_1} - \frac{|\langle \bar{1}1 \,\|\, 1\bar{2}\rangle|^2}{\varepsilon_2 - \varepsilon_1} \\
&= \frac{|\langle 1\bar{1} \,|\, \bar{1}2\rangle - \langle 1\bar{1} \,|\, 2\bar{1}\rangle|^2}{\varepsilon_1 - \varepsilon_2} \\
&= \frac{|\langle 1\bar{1} \,|\, 2\bar{1}\rangle|^2}{\varepsilon_1 - \varepsilon_2} \\
&= \frac{|\langle 11 \,|\, 12\rangle|^2}{\varepsilon_1 - \varepsilon_2}
\end{aligned} \tag{7.4.3}
$$

Ex 7.15

$$
\begin{aligned}
{}^{N-1}\tilde{E}_R^{(2)}\binom{r}{a} &= \sum_{a\neq c}\sum_r \frac{\left|\left\langle {}^{N-1}\Psi_c \,\middle|\, \mathscr{V}^{N-1} \,\middle|\, {}^{N-1}\Psi_{ca}^{r} \right\rangle\right|^2}{\varepsilon_a - \varepsilon_r} \\
&= \sum_{a\neq c}\sum_r \frac{\left|\sum_{b\neq c} \langle ab \,\|\, rb\rangle - \sum_b \langle ab \,\|\, rb\rangle\right|^2}{\varepsilon_a - \varepsilon_r} \\
&= \sum_{a\neq c}\sum_r \frac{|\langle ac \,\|\, rc\rangle|^2}{\varepsilon_a - \varepsilon_r} \\
&= \sum_{a\neq c}\sum_r \frac{|\langle ac \,\|\, cr\rangle|^2}{\varepsilon_a - \varepsilon_r}
\end{aligned} \tag{7.4.4}
$$

$$
\begin{aligned}
{}^{N-1}\tilde{E}_R^{(2)}\binom{rs}{ab} &= \frac{1}{4}\sum_{a\neq c}\sum_{b\neq c}\sum_r\sum_s \frac{\left|\left\langle {}^{N-1}\Psi_c \,\middle|\, \mathscr{V}^{N-1} \,\middle|\, {}^{N-1}\Psi_{cab}^{rs} \right\rangle\right|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \\
&= \frac{1}{4}\sum_{a\neq c}\sum_{b\neq c}\sum_r\sum_s \frac{|\langle ab \,\|\, rs\rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \qquad (7.4.5) \\
&= \frac{1}{4}\sum_a\sum_b\sum_r\sum_s \frac{|\langle ab \,\|\, rs\rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} - \frac{1}{4}\sum_b\sum_r\sum_s \frac{|\langle cb \,\|\, rs\rangle|^2}{\varepsilon_c + \varepsilon_b - \varepsilon_r - \varepsilon_s} - \frac{1}{4}\sum_a\sum_r\sum_s \frac{|\langle ac \,\|\, rs\rangle|^2}{\varepsilon_a + \varepsilon_c - \varepsilon_r - \varepsilon_s} \\
&= \frac{1}{4}\sum_a\sum_b\sum_r\sum_s \frac{|\langle ab \,\|\, rs\rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} - \frac{1}{2}\sum_a\sum_r\sum_s \frac{|\langle ca \,\|\, rs\rangle|^2}{\varepsilon_a + \varepsilon_c - \varepsilon_r - \varepsilon_s} \\
&= {}^{N}E_0^{(2)} + \frac{1}{2}\sum_{a,r,s} \frac{|\langle rs \,\|\, ac\rangle|^2}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_c} \qquad (7.4.6)
\end{aligned}
$$

$$
\begin{aligned}
{}^{N-1}\tilde{E}_R^{(2)}\binom{cr}{ab} &= \frac{1}{2}\sum_{a\neq c}\sum_{b\neq c}\sum_{r}\frac{\left|\left\langle {}^{N-1}\Psi_c \,\middle|\, \mathscr{V}^{N-1} \,\middle|\, {}^{N-1}\Psi_{cab}^{cr}\right\rangle\right|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_c} \\
&= \frac{1}{2}\sum_{a\neq c}\sum_{b\neq c}\sum_{r}\frac{\left|\langle ab \,\|\, cr\rangle\right|^2}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_c} \\
&= -\frac{1}{2}\sum_{a\neq c}\sum_{b\neq c}\sum_{r}\frac{\left|\langle ab \,\|\, cr\rangle\right|^2}{\varepsilon_c+\varepsilon_r-\varepsilon_a-\varepsilon_b}
\end{aligned} \tag{7.4.7}
$$

7.5 Some Illustrative Calculations

Ex 7.16 For 2-electron system, in

$$
\mathrm{PRX} = -\frac{1}{2}\sum_{a\neq c}\sum_{b\neq c}\sum_{r}\frac{\left|\langle ab \,\|\, cr\rangle\right|^2}{\varepsilon_r+\varepsilon_c-\varepsilon_a-\varepsilon_b} \tag{7.5.1}
$$

a, b must be the same, thus $\langle ab \,\|\, cr\rangle = 0$, thus

$$
\mathrm{PRX} = 0 \tag{7.5.2}
$$

$$
\begin{aligned}
\mathrm{PRM} &= \frac{1}{2}\sum_{a,r,s}\frac{\left|\langle rs \,\|\, ca\rangle\right|^2}{\varepsilon_r+\varepsilon_s-\varepsilon_a-\varepsilon_c} \\
&= \frac{1}{2}\left(\frac{\left|\langle \bar{2}2 \,\|\, \bar{1}1\rangle\right|^2}{\varepsilon_2+\varepsilon_2-\varepsilon_1-\varepsilon_1}+\frac{\left|\langle 2\bar{2} \,\|\, \bar{1}1\rangle\right|^2}{\varepsilon_2+\varepsilon_2-\varepsilon_1-\varepsilon_1}\right) \\
&= \frac{1}{2}\times 2\frac{\left|\langle 22 \,\|\, 11\rangle\right|^2}{2(\varepsilon_2-\varepsilon_1)} \\
&= -\frac{K_{12}^2}{2(\varepsilon_1-\varepsilon_2)} \\
&= -{}^{N}E_0^{(2)}
\end{aligned} \tag{7.5.3}
$$