

Modern Quantum Chemistry, Szabo & Ostlund

HW

WSR

May 30, 2021

Contents

7	The 1-Particle Many-body Green's Function	2
7.1	Green's Function in Single-Particle Systems	2
	Ex 7.1	2
	Ex 7.2	2
	Ex 7.3	3
	Ex 7.4	3
	Ex 7.5	3
	Ex 7.6	4
7.2	The 1-Particle Many-body Green's Function	5
7.2.1	The Self-Energy	5
	Ex 7.7	5
	Ex 7.8	5
7.2.2	The Solution of the Dyson Equation	5
7.3	Application of the Formalism to H_2 and HeH^+	5
	Ex 7.9	5
	Ex 7.10	7
	Ex 7.11	7
	Ex 7.12	8
7.4	Perturbation Theory and the Green's Function Method	9
	Ex 7.13	9
	Ex 7.14	9
	Ex 7.15	9
7.5	Some Illustrative Calculations	10
	Ex 7.16	10

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

7.1 Green's Function in Single-Particle Systems

Ex 7.1

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

thus

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

i.e.

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

Ex 7.2

a. When $x = 0$,

$$\begin{aligned} \left. \frac{d^2}{dx^2} |x| \right|_{x=0} &= \lim_{\epsilon \rightarrow 0} \frac{\left. \frac{d|x|}{dx} \right|_{x=\epsilon} - \left. \frac{d|x|}{dx} \right|_{x=-\epsilon}}{2\epsilon} \quad (\epsilon > 0) \\ &= \lim_{\epsilon \rightarrow 0} \frac{1 - (-1)}{2\epsilon} \\ &= \infty \end{aligned} \quad (7.1.4)$$

otherwise,

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

b.

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

thus

$$\frac{d^2}{dx^2} |x| = 2\delta(x) \quad (7.1.7)$$

c.

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

Ex 7.3

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

Ex 7.4

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

Let $x = x'$,

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

thus

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

Ex 7.5

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

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

Ex 7.6

a.

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

b. From

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

we get

$$\lim_{\varepsilon \rightarrow 0} \int_0^\infty dt i \frac{\partial G(x, x', t)}{\partial t} [-i e^{(iE-\varepsilon)t}] = \lim_{\varepsilon \rightarrow 0} \int_0^\infty dt \mathcal{H} G(x, x', t) [-i e^{(iE-\varepsilon)t}] \tag{7.1.16}$$

$$\begin{aligned}
 \lim_{\varepsilon \rightarrow 0} \int_0^\infty dt \frac{\partial G(x, x', t)}{\partial t} e^{(iE-\varepsilon)t} &= \int_0^\infty dt \mathcal{H} G(x, x', t) [-i e^{iEt}] \\
 &= \mathcal{H} G(x, x', E)
 \end{aligned} \tag{7.1.17}$$

thus

$$\lim_{\varepsilon \rightarrow 0} \left[G(x, x', t) e^{(iE-\varepsilon)t} \right]_{t=0}^\infty - \int_0^\infty dt G(x, x', t) e^{(iE-\varepsilon)t} (iE - \varepsilon) = \mathcal{H} G(x, x', E) \tag{7.1.18}$$

$$\begin{aligned}
 \mathcal{H} G(x, x', E) &= -G(x, x', 0) - iE \int_0^\infty dt G(x, x', t) e^{iEt} \\
 &= -G(x, x', 0) - iEG(x, x', E)/(-i) \\
 &= -\delta(x - x') + EG(x, x', E)
 \end{aligned} \tag{7.1.19}$$

\therefore

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

c.

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

$$\lim_{\varepsilon \rightarrow 0} \int_0^\infty dt e^{(iE-\varepsilon)t} i \frac{\partial}{\partial t} \mathcal{G}(t) = \lim_{\varepsilon \rightarrow 0} \int_0^\infty dt e^{(iE-\varepsilon)t} \mathcal{H} \mathcal{G}(t) \tag{7.1.22}$$

$$\lim_{\varepsilon \rightarrow 0} \left[e^{(iE-\varepsilon)t} \mathcal{G}(t) \right]_0^\infty - (iE - \varepsilon) \int_0^\infty dt e^{(iE-\varepsilon)t} \mathcal{G}(t) = \mathcal{H} \mathcal{G}(E) \tag{7.1.23}$$

\therefore

$$\begin{aligned}
 \mathcal{H} \mathcal{G}(E) &= \lim_{\varepsilon \rightarrow 0} \left[-\mathcal{G}(0) - (iE - \varepsilon) \int_0^\infty dt e^{(iE-\varepsilon)t} \mathcal{G}(t) \right] \\
 &= -\mathcal{G}(0) + E\mathcal{G}(E) \\
 &= -1 + E\mathcal{G}(E)
 \end{aligned} \tag{7.1.24}$$

thus

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

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

7.2.1 The Self-Energy

Ex 7.7

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

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

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

Similarly,

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

Ex 7.8

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

7.2.2 The Solution of the Dyson Equation

7.3 Application of the Formalism to H_2 and HeH^+

Ex 7.9

a.

$${}^{N+1}\mathcal{E}_0 = {}^{N+1}E_0 + {}^{N+1}E_{\text{corr}}\quad (7.3.1)$$

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,

$${}^{N+1}E_{\text{corr}} = 0\quad (7.3.2)$$

thus

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

$$\begin{aligned}
{}^{N+1}\mathcal{E}_1 - {}^N\mathcal{E}_0 &= {}^{N+1}E_1 - {}^NE_0 - {}^NE_{\text{corr}} \\
&= (h_{11}h + 2h_{22} + 2J_{12} + J_{22} - K_{12}) - (2\varepsilon_1 - J_{11}) - {}^NE_{\text{corr}} \\
&= (\varepsilon_1 + 2\varepsilon_2 - 2J_{12} + K_{12} - J_{11} + J_{22}) - (2\varepsilon_1 - J_{11}) - {}^NE_{\text{corr}} \\
&= 2\varepsilon_2 - \varepsilon_1 - 2J_{12} + K_{12} + J_{22} - {}^NE_{\text{corr}}
\end{aligned} \tag{7.3.4}$$

b.

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

thus

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

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.

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

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

Ex 7.10 Since

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

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

thus

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

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

Similarly,

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

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

thus

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

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

Ex 7.11 From

$$\begin{pmatrix} h_{11} & h_{22} \\ h_{12} & h_{22} \end{pmatrix} \begin{pmatrix} 1 \\ c \end{pmatrix} = {}^{N-1}\mathcal{E}_0 \begin{pmatrix} 1 \\ c \end{pmatrix} \quad (7.3.20)$$

we get

$$h_{11} + h_{12}c = {}^{N-1}\mathcal{E}_0 \quad (7.3.21)$$

$$h_{12} + h_{22}c = {}^{N-1}\mathcal{E}_0 c \quad (7.3.22)$$

thus

$${}^{N-1}\mathcal{E}_0 = h_{11} + h_{12} \frac{h_{12}}{{}^{N-1}\mathcal{E}_0 - h_{22}} \quad (7.3.23)$$

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

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

Ex 7.12

a.

$$|\Phi\rangle = |\Psi_0\rangle + c|\Psi_1^{\bar{2}}\rangle \quad (7.3.26)$$

thus

$$\begin{pmatrix} 0 & \langle \Psi_0 | \mathcal{H} | \Psi_1^{\bar{2}} \rangle \\ \langle \Psi_0 | \mathcal{H} | \Psi_1^{\bar{2}} \rangle & \langle \Psi_1^{\bar{2}} | \mathcal{H} - {}^{N+1}E_0 | \Psi_1^{\bar{2}} \rangle \end{pmatrix} \begin{pmatrix} 1 \\ c \end{pmatrix} = ({}^{N+1}\mathcal{E}_0 - {}^{N+1}E_0) \begin{pmatrix} 1 \\ c \end{pmatrix} \quad (7.3.27)$$

\therefore

$$\begin{aligned} \langle \Psi_0 | \mathcal{H} | \Psi_1^{\bar{2}} \rangle &= h_{12} + \sum_{b=1,2} \langle \bar{1}b | \bar{2}b \rangle \\ &= -\langle 11 | 12 \rangle + \langle 11 | 12 \rangle + \langle 12 | 22 \rangle \\ &= \langle 12 | 22 \rangle \end{aligned} \quad (7.3.28)$$

\therefore

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

Let

$${}^{N+1}E_R = {}^{N+1}\mathcal{E}_0 - {}^{N+1}E_0 \quad (7.3.30)$$

thus

$$\begin{aligned} {}^{N+1}\mathcal{E}_0 &= {}^{N+1}E_0 + {}^{N+1}E_R \\ &= {}^N E_0 + \varepsilon_2 + {}^{N+1}E_R \end{aligned} \quad (7.3.31)$$

b. Solving (7.3.29), we get

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

c.

$$\Sigma_{22}^{(2)}(\varepsilon_2) = \frac{\langle 12 | 22 \rangle^2}{\varepsilon_1 - \varepsilon_2} + \frac{K_{12}^2}{2(\varepsilon_2 - \varepsilon_1)} \quad (7.3.33)$$

\therefore

$$\begin{aligned} \varepsilon_2' &= \varepsilon_2 + \Sigma_{22}^{(2)}(\varepsilon_2) \\ &= {}^{N+1}\tilde{E}_R^{(2)} - {}^N E_0^{(2)} \end{aligned} \quad (7.3.34)$$

7.4 Perturbation Theory and the Green's Function Method

Ex 7.13

$$\begin{aligned}
\langle {}^{N-1}\Psi_c | \mathcal{V}^{N-1} | {}^{N-1}\Psi_c \rangle &= \left\langle {}^{N-1}\Psi_c \left| \sum_{i < j}^{N-1} r_{ij}^{-1} - \sum_i^{N-1} v_N^{\text{HF}}(i) \right| {}^{N-1}\Psi_c \right\rangle \\
&= \sum_{i < j}^{N-1} \langle {}^{N-1}\Psi_c | r_{ij}^{-1} | {}^{N-1}\Psi_c \rangle - \sum_i^{N-1} \langle {}^{N-1}\Psi_c | v_N^{\text{HF}}(i) | {}^{N-1}\Psi_c \rangle \\
&= \frac{1}{2} \sum_{a \neq c} \sum_{b \neq c} \langle ab || ab \rangle - \sum_{a \neq c} \sum_b \langle ab || ab \rangle \\
&= -\frac{1}{2} \sum_{a \neq c} \sum_{b \neq c} \langle ab || ab \rangle + \sum_{a \neq c} \langle ac || ac \rangle \\
&= -\frac{1}{2} \left(\sum_a \sum_b \langle ab || ab \rangle - \sum_a \langle ac || ac \rangle - \sum_b \langle cb || cb \rangle + \langle cc || cc \rangle \right) + \sum_a \langle ac || ac \rangle \\
&= -\frac{1}{2} \left(\sum_a \sum_b \langle ab || ab \rangle - 2 \sum_a \langle ac || ac \rangle + 0 \right) + \sum_a \langle ac || ac \rangle \\
&= -\frac{1}{2} \sum_a \sum_b \langle ab || ab \rangle
\end{aligned} \tag{7.4.1}$$

thus

$$\langle {}^{N-1}\Psi_c | \mathcal{V}^{N-1} | {}^{N-1}\Psi_c \rangle = {}^N E_0^{(1)} \tag{7.4.2}$$

Ex 7.14

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

Ex 7.15

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

$$\begin{aligned}
{}^{N-1}\tilde{E}_R^{(2)}\left(\begin{smallmatrix}rs\\ab\end{smallmatrix}\right) &= \frac{1}{4} \sum_{a \neq c} \sum_{b \neq c} \sum_r \sum_s \frac{|\langle {}^{N-1}\Psi_c | \mathcal{V}^{N-1} | {}^{N-1}\Psi_{cab}^{rs} \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \\
&= \frac{1}{4} \sum_{a \neq c} \sum_{b \neq c} \sum_r \sum_s \frac{|\langle ab || rs \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} \tag{7.4.5}
\end{aligned}$$

$$\begin{aligned}
&= \frac{1}{4} \sum_a \sum_b \sum_r \sum_s \frac{|\langle ab || rs \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} - \frac{1}{4} \sum_b \sum_r \sum_s \frac{|\langle cb || rs \rangle|^2}{\varepsilon_c + \varepsilon_b - \varepsilon_r - \varepsilon_s} - \frac{1}{4} \sum_a \sum_r \sum_s \frac{|\langle ac || rs \rangle|^2}{\varepsilon_a + \varepsilon_c - \varepsilon_r - \varepsilon_s} \\
&= \frac{1}{4} \sum_a \sum_b \sum_r \sum_s \frac{|\langle ab || rs \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_s} - \frac{1}{2} \sum_a \sum_r \sum_s \frac{|\langle ca || rs \rangle|^2}{\varepsilon_a + \varepsilon_c - \varepsilon_r - \varepsilon_s} \\
&= {}^N E_0^{(2)} + \frac{1}{2} \sum_{a,r,s} \frac{|\langle rs || ac \rangle|^2}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_c} \tag{7.4.6}
\end{aligned}$$

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

7.5 Some Illustrative Calculations

Ex 7.16 For 2-electron system, in

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

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

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

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