

# Modern Quantum Chemistry, Szabo & Ostlund

## HW

WSR

August 10, 2020

### Contents

<b>7</b>	<b>The 1-Particle Many-body Green's Function</b>	<b>2</b>
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 . . . . .	6
	Ex 7.11 . . . . .	7
	Ex 7.12 . . . . .	7
7.4	Perturbation Theory and the Green's Function Method . . . . .	7
	Ex 7.13 . . . . .	7
	Ex 7.14 . . . . .	8
	Ex 7.15 . . . . .	8
7.5	Some Illustrative Calculations . . . . .	9
	Ex 7.16 . . . . .	9

## 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.**

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

**b.** From

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

we get

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

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

thus

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

$$\begin{aligned} \mathcal{H} G(x, x', E) &= -G(x, x', 0) - \mathrm{i} E \int_0^\infty dt G(x, x', t) e^{\mathrm{i} Et} \\ &= -G(x, x', 0) - \mathrm{i} E G(x, x', E) / (-\mathrm{i}) \\ &= -\delta(x - x') + E G(x, x', E) \end{aligned} \quad (7.1.19)$$

$\therefore$

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

**c.**

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

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

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

$\therefore$

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

thus

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

## 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 $\text{H}_2$ and $\text{HeH}^+$

**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  $\text{H}_2^-$  is of ungerade symmetry while the excited state ( $|1\bar{1}\bar{2}\rangle$ ) 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.**

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

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

$\therefore$

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

**Ex 7.10** Since

$$\begin{aligned}
\Sigma_{11}^{(2)}(\varepsilon_1) &= \frac{K_{12}}{\varepsilon_1 + \varepsilon_1 - 2\varepsilon_2} \\
&= \frac{K_{12}}{2(\varepsilon_1 - \varepsilon_2)}
\end{aligned} \tag{7.3.10}$$

$$\begin{aligned}
\Sigma_{11}^{(3)}(\varepsilon_1) &= \frac{K_{12}^2(J_{22} - 2J_{12} + K_{12})}{(\varepsilon_1 - 2\varepsilon_2 + \varepsilon_1)^2} + \frac{K_{12}^2(J_{11} - 2J_{12} + K_{12})}{(\varepsilon_1 - 2\varepsilon_2 + \varepsilon_1)(\varepsilon_1 - \varepsilon_2)} + \frac{K_{12}^2(2J_{12} - K_{12} - J_{11})}{4(\varepsilon_1 - \varepsilon_2)^2} \\
&= \frac{K_{12}^2(J_{22} - 2J_{12} + K_{12})}{4(\varepsilon_1 - \varepsilon_2)^2} + \frac{K_{12}^2(J_{11} - 2J_{12} + K_{12})}{2(\varepsilon_1 - \varepsilon_2)^2} + \frac{K_{12}^2(2J_{12} - K_{12} - J_{11})}{4(\varepsilon_1 - \varepsilon_2)^2} \\
&= \frac{K_{12}^2(J_{22} + J_{11} - 4J_{12} + 2K_{12})}{4(\varepsilon_1 - \varepsilon_2)^2}
\end{aligned} \tag{7.3.11}$$

thus

$$\Sigma_{11}^{(2)}(\varepsilon_1) = E_0^{(2)} \tag{7.3.12}$$

$$\Sigma_{11}^{(3)}(\varepsilon_1) = E_0^{(3)} \tag{7.3.13}$$

Similarly,

$$\begin{aligned}
\Sigma_{22}^{(2)}(\varepsilon_2) &= \frac{K_{12}}{\varepsilon_2 + \varepsilon_2 - 2\varepsilon_1} \\
&= \frac{K_{12}}{2(\varepsilon_2 - \varepsilon_1)}
\end{aligned} \tag{7.3.14}$$

$$\begin{aligned}
\Sigma_{22}^{(3)}(\varepsilon_2) &= \frac{K_{12}^2(2J_{12} - K_{12} - J_{11})}{(\varepsilon_2 - 2\varepsilon_1 + \varepsilon_2)^2} + \frac{K_{12}^2(J_{22} - 2J_{12} + K_{12})}{(\varepsilon_2 - 2\varepsilon_1 + \varepsilon_2)(\varepsilon_1 - \varepsilon_2)} + \frac{K_{12}^2(J_{22} + K_{12} - 2J_{12})}{4(\varepsilon_1 - \varepsilon_2)^2} \\
&= \frac{K_{12}^2(2J_{12} - K_{12} - J_{11})}{4(\varepsilon_1 - \varepsilon_2)^2} - \frac{K_{12}^2(J_{22} - 2J_{12} + K_{12})}{2(\varepsilon_1 - \varepsilon_2)^2} + \frac{K_{12}^2(J_{22} + K_{12} - 2J_{12})}{4(\varepsilon_1 - \varepsilon_2)^2} \\
&= \frac{K_{12}^2(-J_{11} - J_{22} + 4J_{12} - 2K_{12})}{4(\varepsilon_1 - \varepsilon_2)^2}
\end{aligned} \tag{7.3.15}$$

thus

$$\Sigma_{22}^{(2)}(\varepsilon_2) = -E_0^{(2)} \tag{7.3.16}$$

$$\Sigma_{22}^{(3)}(\varepsilon_2) = -E_0^{(3)} \tag{7.3.17}$$

**Ex 7.11** From

$$\begin{pmatrix} h_{11} & h_{22} \\ h_{12} & h_{22} \end{pmatrix} \begin{pmatrix} 1 \\ c \end{pmatrix} = {}^{N-1}\mathcal{E}_0 \begin{pmatrix} 1 \\ c \end{pmatrix} \tag{7.3.18}$$

we get

$$h_{11} + h_{12}c = {}^{N-1}\mathcal{E}_0 \tag{7.3.19}$$

$$h_{12} + h_{22}c = {}^{N-1}\mathcal{E}_0 c \tag{7.3.20}$$

thus

$${}^{N-1}\mathcal{E}_0 = h_{11} + h_{12} \frac{h_{12}}{{}^{N-1}\mathcal{E}_0 - h_{22}} \tag{7.3.21}$$

$$h_{11} + {}^{N-1}E_R = h_{11} + h_{12} \frac{h_{12}}{h_{11} + {}^{N-1}E_R - h_{22}} \tag{7.3.22}$$

$$\begin{aligned}
{}^{N-1}E_R &= \frac{h_{12}^2}{h_{11} + {}^{N-1}E_R - h_{22}} \\
&= \frac{|\langle 11 | 12 \rangle|^2}{\varepsilon_1 - \varepsilon_2 - (J_{11} - 2J_{12} + K_{12}) + {}^{N-1}E_R}
\end{aligned} \tag{7.3.23}$$

**Ex 7.12**

## 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**

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

**Ex 7.15**

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

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

$$\begin{aligned}
{}^{N-1}\tilde{E}_R^{(2)}\left(\begin{smallmatrix} cr \\ ab \end{smallmatrix}\right) &= \frac{1}{2} \sum_{a \neq c} \sum_{b \neq c} \sum_r \frac{|\langle {}^{N-1}\Psi_c | \mathcal{V}^{N-1} | {}^{N-1}\Psi_{cab}^{cr} \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_c} \\
&= \frac{1}{2} \sum_{a \neq c} \sum_{b \neq c} \sum_r \frac{|\langle ab \| cr \rangle|^2}{\varepsilon_a + \varepsilon_b - \varepsilon_r - \varepsilon_c} \\
&= -\frac{1}{2} \sum_{a \neq c} \sum_{b \neq c} \sum_r \frac{|\langle ab \| cr \rangle|^2}{\varepsilon_c + \varepsilon_r - \varepsilon_a - \varepsilon_b}
\end{aligned} \tag{7.4.6}$$



## 7.5 Some Illustrative Calculations

**Ex 7.16** For 2-electron system, in

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

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

$$\text{PRX} = 0 \quad (7.5.2)$$

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