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

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