HOMEWORK ASSIGNMENT 7
QUANTUM MECHANICS
DUE APR 10, 2008

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1a. *Derive Equations (7.7) and (7.8) in Schatz and Ratner.*

Solution. Substitution of (7.6) into (7.5) yields

$$\Psi_{\mathrm{wp}}(x,t)=\int_{-\infty}^{\infty} dk\,\sqrt{\frac{a}{2\pi^{3/2}}}e^{-a^2(k-k_0)^2/2}e^{ikx}e^{-i\hbar k^2t/2m}$$

We must write the combined exponents in the form $-(Ak+B)^2+C$ in order to perform the integration. That is, we write

$$-\Big(\frac{a^2}{2}+\frac{i\hbar t}{2m}\Big)k^2+(a^2k_0+ix)k-\frac{a^2k_0^2}{2}=-A^2k-2ABk-B^2+C,$$

so

$$A=\sqrt{\frac{a^2}{2}+\frac{i\hbar t}{2m}},\qquad B=-\frac{a^2k_0+ix}{2A},\qquad C=B^2-\frac{a^2k_0^2}{2}.$$

By substituting $u=Ak+B$ we know that $\int_{-\infty}^{\infty}dk\,e^{-(Ak+B)^2}=(1/A)\int_{-\infty}^{\infty}du\,e^{-u^2}=\sqrt{\pi}/A$, provided that the real part of A^2 is positive. Hence

$$\begin{aligned}\Psi_{\mathrm{wp}}(x,t)&=\sqrt{\frac{a}{2\pi^{3/2}}}\int_{-\infty}^{\infty}dk\,e^{-(Ak+B)^2+C}=\sqrt{\frac{a}{2\pi^{3/2}}}\,\frac{\sqrt{\pi}}{A}\,e^{C}\\&=\pi^{-1/4}\sqrt{a}\Big(a^2+\frac{i\hbar t}{m}\Big)^{-1/2}\exp\Big(\frac{(a^2k_0+ix)^2}{2(a^2+i\hbar t/m)}-\frac{a^2k_0^2}{2}\Big)\\&=\pi^{-1/4}\Big(a+\frac{i\hbar t}{ma}\Big)^{-1/2}\exp\Big(\frac{a^4k_0^2+2a^2k_0ix-x^2-a^2k_0^2(a^2+i\hbar t/m)}{2(a^2+i\hbar t/m)}\Big)\\&=\pi^{-1/4}\Big(a\Big(1+\frac{i\hbar t}{ma^2}\Big)\Big)^{-1/2}\exp\Big(\frac{2a^2k_0ix-x^2-ia^2k_0^2\hbar t/m}{2a^2(1+i\hbar t/ma^2)}\Big).\qquad(*)\end{aligned}$$

The pre-exponential term, therefore, is exactly as (7.7). The argument of the exponential in (7.7) is

$$-\frac{(x-\hbar k_0t/m)^2}{2a^2(1+i\hbar t/ma^2)}+ik_0x-\frac{i\hbar t}{2ma^2},$$

which cannot be reduced to the one in $(*)$. A correct expression along the lines of (7.7) requires that the rightmost term be $k_0^2a^2$ times bigger:

$$\begin{aligned}-\frac{(x-\hbar k_0t/m)^2}{2a^2(1+i\hbar t/ma^2)}+ik_0x-\frac{ik_0^2\hbar t}{2m}&=\frac{-x^2+2x\hbar k_0t/m-\hbar^2k_0^2t^2/m^2+(a^2+i\hbar t/m)(2ik_0x-ik_0^2\hbar t/m)}{2a^2(1+i\hbar t/ma^2)}\\&=\frac{-x^2+2a^2ik_0x-ia^2k_0^2\hbar t/m}{2a^2(1+i\hbar t/ma^2)},\end{aligned}$$

which matches the last line of $(*)$.

Equation (7.8) is correct as written; it is the absolute square of either (7.7) or $(*)$, since all the letters stand for real numbers, and the sum of the argument of the exponential in either (7.7) or $(*)$ with its complex conjugate equals

$$-\frac{(x-\hbar k_0 t/m)^2}{2a^2}\left(\frac{1}{1+i\hbar t/ma^2}+\frac{1}{1-i\hbar t/ma^2}\right)=-\frac{(x-\hbar k_0 t/m)^2}{a^2(1+\hbar^2t^2/m^2a^4)}.$$

1b,c. *Using the expression for the wavefunction given in (7.7), derive an expression for the expectation value of the Hamiltonian, x, x^2, p and p^2.*

Taking the pre-exponential factor from $(*)$ and the argument of the exponential from two lines above that, we rewrite the wave function as

$$\Psi(x,t)=Ke^{-(x-u)^2/(2v^2)},$$

where

$$K=\pi^{-1/4}\left(a\left(1+\frac{i\hbar t}{ma^2}\right)\right)^{-1/2}\exp\left(-\frac{a^2k_0^2}{2}\right),\qquad u=ia^2k_0,\qquad v^2=a^2+i\hbar t/m.$$

Then

$$\frac{\partial}{\partial x}\Psi=-\frac{x-u}{v^2}\Psi,\qquad \frac{\partial^2}{\partial x^2}\Psi=\frac{x^2-2ux+u^2-v^2}{v^4}\Psi. \tag{†}$$

Now recall from (7.8) that $|\Psi|^2=Qe^{-(x-\mu)^2/(2\sigma^2)}$, with

$$Q=\pi^{-1/2}\left(a^2+\frac{\hbar^2t^2}{m^2a^2}\right)^{-1/2},\quad \mu=\frac{\hbar k_0 t}{m},\quad \sigma^2=\frac{1}{2}\left(a^2+\frac{\hbar^2t^2}{m^2a^2}\right).$$

From the well-known moments of the Gaussian function we get

$$\begin{aligned}\langle\Psi|\Psi\rangle &= \textstyle\int|\Psi|^2dx=1,\\ \langle x\rangle = \langle\Psi|x|\Psi\rangle &= \textstyle\int x|\Psi|^2dx=\mu,\\ \langle x^2\rangle = \langle\Psi|x^2|\Psi\rangle &= \textstyle\int x^2|\Psi|^2dx=\sigma^2+\mu^2.\end{aligned}$$

Together with (†), this yields

$$\begin{aligned}\langle p\rangle &= i\hbar\frac{\mu-u}{v^2}=i\hbar\frac{\hbar k_0t/m-ia^2k_0}{a^2+i\hbar t/m}=\hbar k_0,\\ \langle p^2\rangle &= -\hbar^2\frac{\sigma^2+\mu^2-2u\mu+u^2-v^2}{v^4}=\hbar^2\left(k_0^2+\frac{1}{2a^2}\right),\\ \langle\Delta p^2\rangle &= \langle p^2\rangle-\langle p\rangle^2=\frac{\hbar^2}{a^2},\\ \langle\Delta x^2\rangle &= \langle x^2\rangle-\langle x\rangle^2=\sigma^2=\frac{1}{2}\left(a^2+\frac{\hbar^2t^2}{m^2a^2}\right),\\ \langle H\rangle &= \frac{1}{2m}\langle p^2\rangle=\frac{\hbar^2}{2m}\left(k_0^2+\frac{1}{a^2}\right)\end{aligned}$$

(for the last line we used the condition $V=0$, so the Hamiltonian is simply the kinetic energy). At $t=0$ we have $\langle\Delta x^2\rangle\langle\Delta p^2\rangle=\frac{1}{2}a^2\hbar^2/2a^2=(\hbar^2/2)^2$.

2. *S&R Chapter 9 problem 1a. Given that*

$$\mu(q)=\mu(q_0)+(q-q_0)Q_0 \tag{1}$$

and

$$I(\omega)=2\,\mathrm{Re}\int_0^\infty\langle\mu(t)\mu(0)\rangle e^{-i\omega t}\,dt \tag{2}$$

and

$$m\ddot{q}=-\gamma m\dot{q}-m\omega_0^2(q-q_0)+R, \tag{3}$$

show that

$$I(\omega) = \frac{2\gamma\,\langle x_0^2\rangle\,\omega_0^2 Q_0^2}{(\omega^2-\omega_0^2)^2+\gamma^2\omega^2},$$

where x_0 is the value of $x := q - q_0$ at $t = 0$.

Solution. From (1) we have

$$\langle \mu(t)\mu(0)\rangle = \big\langle \big(\mu(q_0)+x(t)Q_0\big)\big(\mu(q_0)+x(0)Q_0\big)\big\rangle = \langle \mu(q_0)^2\rangle + \langle x(t)x(0)\rangle\, Q_0^2.$$

Hence, from (2),

$$I(\omega) = 2\,\mathrm{Re}\bigg(\int_0^\infty \big(\langle \mu(q_0)^2\rangle + \langle x(t)x(0)\rangle\, Q_0^2\big)e^{-i\omega t}\,dt\bigg).$$

Since $\int_0^\infty e^{-i\omega t}\,dt = -i/\omega$ is purely imaginary, the only surviving term is

$$I(\omega) = 2\,\mathrm{Re}\int_0^\infty \langle x(t)x(0)\rangle\, Q_0^2 e^{-i\omega t}\,dt,$$

which must be estimated by keeping in mind the classical differential equation (3) for the displacement. Dividing through by m and substituting $x = q - q_0$ this equation becomes

$$\ddot{x} = -\gamma\dot{x} - \omega_0^2 x + \text{constant},$$

To put this in a form that can be applied to the problem, we multiply by $x(0)$ and average, obtaining

$$\frac{d^2}{dt^2}\langle x(t)x(0)\rangle = -\gamma\frac{d}{dt}\langle x(t)x(0)\rangle - \omega_0^2\langle x(t)x(0)\rangle + \text{constant}, \tag{4}$$

It is tempting to solve this differential equation for $C(t) = \langle x(t)x(0)\rangle$; since it is linear with constant coefficients, it has an analytic solution involving exponentials of the form $e^{\frac{1}{2}(-\gamma^2\pm\sqrt{\gamma^2-4\omega})t}$, as can be seen from the characteristic equation. But we're after not so much C itself but its transform $\int_0^\infty e^{-i\omega t}C(t)\,dt$. So we set $s = i\omega$, which makes this integral into the Laplace transform of C:

$$I(\omega) = 2Q_0^2\,\mathrm{Re}\,C^L(s), \quad \text{with } s = i\omega. \tag{5}$$

Using the properties of the Laplace transform (for instance, Mathematica evaluates `LaplaceTransform[F′′[t],t,s]` as `s^2 LaplaceTransform[F[t],t,s] - s F[0]`), and using the initial condition $C(0) = \langle x_0^2\rangle$, we turn the differential equation (4) into a purely algebraic equation:

$$s^2C^L - s\langle x_0^2\rangle = -\gamma\,(sC^L - \langle x_0^2\rangle) - \omega_0^2 C^L$$

which can be solved to give

$$C^L = \frac{\langle x_0^2\rangle\,(s+\gamma)}{s^2+\omega_0^2+\gamma s}.$$

Now applying (5) we obtain

$$\begin{aligned}
I(\omega) &= 2Q_0^2\,\mathrm{Re}\,\frac{\langle x_0^2\rangle\,(i\omega+\gamma)}{\omega_0^2-\omega^2+\gamma i\omega}\\
&= 2Q_0^2\langle x_0^2\rangle\ \mathrm{Re}\,\frac{(i\omega+\gamma)(\omega_0^2-\omega^2-\gamma i\omega)}{|\omega_0^2-\omega^2+\gamma i\omega|^2}\\
&= 2Q_0^2\langle x_0^2\rangle\ \mathrm{Re}\,\frac{i\omega(\omega_0^2-\omega^2)+\gamma\omega^2+\gamma(\omega_0^2-\omega^2)-i\gamma^2\omega}{|\omega_0^2-\omega^2+\gamma i\omega|^2}\\
&= 2Q_0^2\langle x_0^2\rangle\,\frac{\gamma\omega_0^2}{(\omega_0^2-\omega^2)^{+}\gamma^2\omega^2}.
\end{aligned}$$

3. *S&R Chapter 9 problem 4.*

Here's what I can make of the problem. A molecule is in state i with energy $\mathscr{E}_i$ and can transition to state f with energy $\mathscr{E}_f$, by a collision with an atom which I'll suppose is helium for ease of reference. The distribution of He atoms according to k (= momentum divided by $\hbar$) is

$$P(k) = Ak^2 e^{-\hbar^2 k^2/2\mu k_B T},$$

where A is a normalization constant and μ is the mass of helium. We are interested in the rate of transition w from state i to f per unit time. This is given by the integral over all initial and final values of k (of helium atoms) of the golden-rule probability (4.66) of S&R, which takes the form

$$\frac{2\pi}{\hbar} |\langle i, k_i | V | f, k_f \rangle|^2 \delta(\mathscr{E}_i + \hbar^2 k_i^2/2\mu - \mathscr{E}_f - \hbar^2 k_f^2/2\mu)$$

since the energy of the molecule + He system in its initial state $|i, k_i\rangle$ is $\mathscr{E}_i + \hbar^2 k_i^2/2\mu$, and likewise for the final energy. (It is not clear to me what the potential V is meant to be.) The integral over k_i is weighed according to the probability $P(k_i)$. Everything so far is the justification of the bottom formula on page 229 of S&R, which is more clearly written as

$$w_{i\to f} = \frac{2\pi}{\hbar} \int \left(dk_i\, P(k_i) \int dk_f\, |\langle i, k_i | V | f, k_f \rangle|^2 \delta_{\Delta E}(\hbar\omega) \right),$$

where

$$\Delta E := \mathscr{E}_i + \hbar^2 k_i^2/2\mu - \mathscr{E}_f - \hbar^2 k_f^2/2\mu$$

is the location of the delta peak and $\hbar\omega$ is the intrinsic variable of the delta function. But

$$\delta(\omega\hbar) = 1/\hbar\delta(\omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{i\omega t}\, dt,$$

so

$$\delta_{\Delta E}(\hbar\omega) = \frac{1}{2\pi\hbar} e^{(\Delta E)t/\hbar} \int_{-\infty}^{\infty} e^{i\omega t}\, dt.$$

Hence

$$w_{i\to f} = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt \int dk_i\, P(k_i) \int dk_f\, |\langle i, k_i | V | f, k_f \rangle|^2 e^{(\Delta E)it/\hbar} e^{i\omega t}.$$

Now, the problem unfortunately does not define $V_{if}(t)$ and V_{fi}, so I'm just going to define them in a way that makes things work. Let $V_{i,k_i,f,k_f}(t) = \langle i, k_i | V | f, k_f \rangle$ with wavefunctions evolved to time t and let $\langle \cdots \rangle$ in the expression $\langle V_{if}(t) V_{fi} \rangle$ denote the ensemble average. The preceding display expression then equals

$$\begin{aligned}
&\frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt \int dk_i\, P(k_i) \int dk_f\, \langle i, k_i | V | f, k_f \rangle\, e^{(-\mathscr{E}_f - \hbar^2 k_f^2/2\mu)it/\hbar} \langle f, k_f | V | i, k_i \rangle\, e^{(\mathscr{E}_i + \hbar^2 k_i^2/2\mu)it/\hbar} e^{i\omega t}\, dt \\
&\quad = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt \int dk_i\, P(k_i) \int d_{k_f} dk_f\, V_{i,k_i,f,k_f}(t) V_{f,k_f,i,k_i}(0) e^{i\omega t} \\
&\quad = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt\, \langle V_{if}(t) V_{fi} \rangle\, e^{i\omega t},
\end{aligned}$$

as was to be shown.