5.61 Fall 2013
Problem Set #4

Suggested Reading: McQuarrie, Chapter 5

1. $\langle x \rangle_t$ and $\langle p_x \rangle_t$ follow Newton's Laws!

A. McQuarrie, page 187, Problem 4-43.

B. McQuarrie, page 188, Problem 4-44.

C. McQuarrie, page 250, Problem 5-35.

2. Survival Probabilities for Wavepacket in Harmonic Well

Let $V(x) = \frac{1}{2}kx^2$, $k = \omega^2\mu$, $\omega = 10$, $\mu = 1$.

A. Consider the three term $t = 0$ wavepacket

$$\Psi(x,0) = c\psi_1 + c\psi_3 + d\psi_2$$

Choose the constants c and d so that $\Psi(x,0)$ is both normalized and has the largest possible negative value of $\langle x \rangle$ at $t = 0$. What are the values of c and d and $\langle x \rangle_{t=0}$?
HINT: the only non-zero integrals of the form

$$x_{v,v+n} = \int dx \psi_v^* \hat{x} \psi_{v+n}$$

are those with $n = \pm 1$.

B. Compute and plot the time-dependence of $\langle \hat{x} \rangle$ and $\langle \hat{p} \rangle$. Do they satisfy Ehrenfest's theorem about motion of the "center" of the wavepacket?

C. Compute and plot the survival probability

$$P(t) = \left| \int dx \Psi^*(x,t)\Psi(x,0) \right|^2 .$$

Does *P(t)* exhibit partial or full recurrences or both?

D. Plot $\Psi^*(x,t_{1/2})\Psi(x,t_{1/2})$ at the time, $t_{1/2}$, defined as one half the time between t = 0 and the first full recurrence. How does this snapshot of the wavepacket look relative to the $\Psi^*(x,0)\Psi(x,0)$ snapshot? Should you be surprised?

3. Vibrational Transitions

The intensity of a transition between the initial vibrational level, v_i, and the final vibrational level, v_f, is given by

$$I_{v_f,v_i} = \left| \int \psi^{\star}_{v_f}(x)\hat{\mu}(x)\psi_{v_i}(x)dx \right|^2 ,$$

where $\mu(x)$ is the "electric dipole transition" moment function

$$\begin{aligned}\hat{\mu}(x) &= \mu_0 + \left.\frac{d\mu}{dx}\right|_{x=0}\hat{x} + \left.\frac{d^2\mu}{dx^2}\right|_{x=0}\frac{\hat{x}^2}{2} + \text{ higher-order terms} \\ &= \mu_0 + \mu_1\hat{x} + \mu_2\hat{x}^2/2 + \mu_3\hat{x}^3/6 + \ldots\end{aligned}$$

Consider only μ_0, μ_1, and μ_2 to be non-zero and note that all $\psi_v(x)$ are real. You will need some definitions from Lecture Notes #9:

$$\begin{aligned}\hat{x} &= \left(\frac{2\mu\omega}{\hbar}\right)^{-1/2}\left(\hat{\mathbf{a}} + \hat{\mathbf{a}}^{\dagger}\right) \\ \hat{\mathbf{a}}\psi_v &= v^{1/2}\psi_{v-1} \\ \hat{\mathbf{a}}^{\dagger}\psi_v &= (v+1)^{1/2}\psi_{v+1} \\ [\hat{\mathbf{a}}, \hat{\mathbf{a}}^{\dagger}] &= +1\end{aligned}$$

A. Derive a formula for all $v + 1 \leftarrow v$ vibrational transition intensities. The $v = 1 \leftarrow v = 0$ transition is called the "fundamental".

B. What is the expected ratio of intensities for the $v = 11 \leftarrow v = 10$ band ($I_{11,10}$) and the $v = 1 \leftarrow v = 0$ band ($I_{1,0}$)?

C. Derive a formula for all $v + 2 \leftarrow v$ vibrational transition intensities. The $v = 2 \leftarrow v = 0$ transition is called the "first overtone".

D. Typically $\left(\frac{2\mu\omega}{\hbar}\right)^{-1/2} = 1/10$ and $\mu_2/\mu_1 = 1/10$. Estimate the ratio $I_{2,0}/I_{1,0}$.

4. $\hat{\mathbf{a}}^{\dagger}, \hat{\mathbf{a}}$ Operators

A. Selection rules: state the v_f, v_i selection rule for the following integrals:

$$\int \psi_{v_f} \hat{O}p \psi_{v_i} dx$$

Where $\hat{O}p$ is

(i) $c_1(\mathbf{\hat{a}}^\dagger)^2\mathbf{\hat{a}}^3\mathbf{\hat{a}}^\dagger$

(ii) $c_2(\mathbf{\hat{a}})^{14}(\mathbf{\hat{a}}^\dagger)\mathbf{\hat{a}}(\mathbf{\hat{a}}^\dagger)^{10}$

(iii) $c_3\mathbf{\hat{a}}^\dagger\mathbf{\hat{a}}\mathbf{\hat{a}}^\dagger\mathbf{\hat{a}}\mathbf{\hat{a}}^\dagger\mathbf{\hat{a}}\mathbf{\hat{a}}^\dagger$

B. Values of integrals: Evaluate the following integrals (all obtained "by inspection")

(i) $\int \psi_{v+3}(\mathbf{\hat{a}}^\dagger)^4\mathbf{\hat{a}}\psi_v\, dx$

(ii) $\int \psi_v\mathbf{\hat{a}}\mathbf{\hat{a}}^\dagger\mathbf{\hat{a}}\mathbf{\hat{a}}^\dagger\psi_v dx$

(iii) $\int \psi_{10}(\mathbf{\hat{a}}^\dagger)\psi_0 dx$

C. $\hat{\tilde{x}} = 2^{-1/2}(\mathbf{\hat{a}} + \mathbf{\hat{a}}^\dagger)$
$\hat{\tilde{p}} = 2^{-1/2}i(\mathbf{\hat{a}} - \mathbf{\hat{a}})$

Evaluate the following integrals:

(i) $\int \psi_{v+4}\hat{\tilde{x}}^3\hat{\tilde{p}}^2\psi_v dx$

(ii) $\int \psi_{v+5}\hat{\tilde{x}}^3\hat{\tilde{p}}^2\psi_v dx$

(iii) $\int \psi_{10}\hat{\tilde{x}}^{10}\psi_0 dx$

(iv) Is $\int \psi_8\hat{\tilde{x}}^{10}\psi_0 dx$ nonzero? (If it is, do not bother to evaluate it.)

5. <u>More Wavepacket</u>

$$\sigma_x \equiv \left[\left\langle \hat{x}^2 \right\rangle - \left\langle \hat{x} \right\rangle^2\right]^{1/2}$$
$$\sigma_{p_x} \equiv \left[\left\langle \hat{p}^2 \right\rangle - \left\langle \hat{p} \right\rangle^2\right]^{1/2}$$
$$\Psi_{1,2}(x,t) = 2^{-1/2}\left[e^{-i\omega t}\psi_1 + e^{-2i\omega t}\psi_2\right]$$
$$\Psi_{1,3}(x,t) = 2^{-1/2}\left[e^{-i\omega t}\psi_1 + e^{-3i\omega t}\psi_3\right]$$

A. Compute $\sigma_x\sigma_{p_x}$ for $\Psi_{1,2}(x,t)$.

B. Compute $\sigma_x \sigma_{p_x}$ for $\Psi_{1,3}(x,t)$.

C. The uncertainty principle is

$$\sigma_x \sigma_{p_x} \geq \hbar/2.$$

The $\Psi_{1,2}(x,t)$ wavepacket is moving and the $\Psi_{1,3}(x,t)$ wavepacket is "breathing". Discuss the time dependence of $\sigma_x \sigma_{p_x}$ for these two classes of wavepacket.