5.61 Fall 2017
Problem Set #4

1. 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 $\langle x \rangle_{t=0}$?

B. Compute and plot the time-dependences 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?

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2. Vibrational Transitions

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

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

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 constants and note that all $\psi_v(x)$ are real. You will need some definitions from Lecture Notes #9:

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

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 $\mu_2/\mu_1 = 1/10$ (do not worry about the units). Estimate the ratio $I_{2,0}/I_{1,0}$.

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3. More Wavepacket for Harmonic Oscillator

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

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 wavepackets.

4. Two-Level Problem

A. Algebraic Approach

$$\int \psi_1^* \widehat{H} \psi_1 d\tau = H_{11} = E_1$$
$$\int \psi_2^* \widehat{H} \psi_2 d\tau = H_{22} = E_2$$
$$\int \psi_2^* \widehat{H} \psi_1 d\tau = H_{12} = V$$

Find eigenfunctions:

$$\psi_+ = a\psi_1 + b\psi_2 \qquad \text{(must be normalized, } \psi_1, \psi_2 \text{ are orthonormal)}$$
$$\widehat{H}\psi_+ = E_+\psi_+$$
$$\psi_- = c\psi_1 + d\psi_2 \qquad \text{(must be normalized, and orthonormal to } \psi_+\text{)}$$
$$\widehat{H}\psi_- = E_-\psi_-$$

Use any brute force algebraic method (but not matrix diagonalization) to solve for E_+, E_-, a, b, c and d.

B. Matrix Approach

$$\mathbf{H} = \begin{pmatrix} E_1 & V \\ V^* & E_2 \end{pmatrix} = \begin{pmatrix} \overline{E} & 0 \\ 0 & \overline{E} \end{pmatrix} + \begin{pmatrix} \Delta & V \\ V^* & \Delta \end{pmatrix}$$
$$\overline{E} = \frac{E_1 + E_2}{2}$$
$$\Delta = \frac{E_1 - E_2}{2} < 0 \qquad \text{(assume } E_1 < E_2\text{)}$$

(i) Find the eigenvalues of **H** by solving the determinantal secular equation

$$0 = \begin{vmatrix} \Delta - E & V \\ V^* & -\Delta - E \end{vmatrix}$$
$$0 = -\Delta^2 + E^2 - |V|^2$$

(ii) *If you dare*, find the eigenfunctions (eigenvectors) of **H**. Do these eigenvectors depend on the value of $\overline{E}$?

(iii) Show that

$$E_+ + E_- = 2\overline{E} \text{ (trace of } \mathbf{H}\text{)}$$
$$(E_+)(E_-) = \begin{vmatrix} \Delta & V \\ V^* & -\Delta \end{vmatrix} \qquad \text{(determinant of } \mathbf{H}\text{)}$$

(iv) This is the most important part of the problem: If $|V| \ll \Delta$, show that $E_{\pm} = \overline{E} \pm \frac{|V|^2}{(E_2 - E_1)}$ by doing a power series expansion of $[\Delta^2 + |V|^2]^{1/2}]$. Also show that

$$\psi_+ \approx \alpha\psi_2 + \frac{|V|}{(E_2 - E_1)}\psi_1$$

where

$$\alpha = \left[1 - \left(\frac{|V|}{(E_2 - E_1)}\right)^2\right]^{1/2} \approx 1.$$

It is always a good strategy to show that ψ_+ belongs to E_+ (not E_-). This minimizes sign and algebraic errors.

C. You have derived the basic formulas of non-degenerate perturbation theory. Use this formalism to solve for the energies of the three-level problem:

$$\mathbf{H} = \begin{pmatrix} E_1^{(0)} & V_{12} & V_{13} \\ V_{12}^* & E_2^{(0)} & V_{23} \\ V_{13}^* & V_{23}^* & E_3^{(0)} \end{pmatrix}$$

$$\begin{aligned} \text{Let } E_1^{(0)} &= -10 \\ E_2^{(0)} &= 0 \\ E_3^{(0)} &= +20 \\ V_{12} &= 1 \\ V_{13} &= 2 \\ V_{23} &= 1 \end{aligned}$$

D. The formulas of non-degenerate perturbation theory enable a solution for the three approximate eigenvectors of $\mathbf{H}$ as shown below. Show that $\mathbf{H}$ is *approximately diagonalized* when you use ψ_1' below to evaluate $\mathbf{H}$:

$$\begin{aligned} \psi_1' &= \psi_1 + \frac{V_{12}}{E_1 - E_2}\psi_2 + \frac{V_{13}}{E_1 - E_3}\psi_3 \\ \psi_2' &= \psi_2 + \frac{V_{12}}{E_2 - E_1}\psi_1 + \frac{V_{13}}{E_2 - E_3}\psi_3 \\ \psi_3' &= \psi_3 + \frac{V_{13}}{E_3 - E_1}\psi_1 + \frac{V_{23}}{E_3 - E_2}\psi_2 \end{aligned}$$

This problem is less burdensome when you use numerical values rather than symbolic values for the elements of $\mathbf{H}$.
