5.61 Fall 2017
Problem Set #4

Suggested Reading: McQuarrie, Chapter 5

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-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?

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

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

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

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

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:

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

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 μ_2/μ_1 = 1/10 (do not worry about the units). Estimate the ratio $I_{2,0}/I_{1,0}$.

3. <u>More Wavepacket for Harmonic Oscillator</u>

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

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 wavepacket.

4. Two-Level Problem

A. Algebraic Approach

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

Find eigenfunctions:

$\psi_+ = a\,\psi_1 + b\psi_2$ (must be normalized, ψ_1,ψ_2 are orthonormal)

$\hat{H}\,\psi_+ = E_+\psi_+$

$\psi_- = c\psi_1 + d\psi_2$ (must be normalized and orthogonal to ψ_+)

$\hat{H}\,\psi_- = E_-\psi_-$

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

B. Matrix Approach

$$\mathbf{H} = \begin{pmatrix} E_1 & V \\ V^* & E_2 \end{pmatrix} = \begin{pmatrix} \bar{E} & 0 \\ 0 & \bar{E} \end{pmatrix} + \begin{pmatrix} \Delta & V \\ V^* & -\Delta \end{pmatrix}$$

$$\bar{E} = \frac{E_1 + E_2}{2}$$

$$\Delta = \frac{E_1 - E_2}{2} < 0 \qquad \text{(assume } E_1 < E_2\text{)}$$

(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 $\bar{E}$?

(iii) Show that

$$E_+ + E_- = 2\bar{E} \quad \text{(trace of } \mathbf{H}\text{)}$$

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

(iv) This is the most important part of the problem: If $|V| \ll \Delta$, show that $E_\pm = \bar{E} \pm \frac{|V|^2}{(E_2 - E_1)}$ 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:

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

Let $E_1^{(0)} = -10$

$E_2^{(0)} = 0$

$E_3^{(0)} = +20$

$V_{12} = 1$

$V_{13} = 2$

$V_{23} = 1$

D. The formulas of non-degenerate perturbation theory enable solution for the three approximate eigenvectors of **H**, as shown below. Show36 that **H** is *approximately diagonalized* when you use ψ_1' below to evaluate **H**:

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

This problem is less burdensome when you use numerical values rather than symbolic values for the elements of **H**.