5.61 Fall 2017
Problem Set #5

1. Phase Ambiguity

When one uses $\hat{\mathbf{a}}, \hat{\mathbf{a}}^\dagger$ and $\widehat{N}$ operators to generate all Harmonic Oscillator wavefunctions and calculate all integrals, it is easy to forget what the explicit functional forms are for all of the $\psi_v(x)$. In particular, is the innermost (near x_-) or outermost (near x_+) lobe of the ψ_v always positive? Use $\hat{\mathbf{a}}^\dagger = 2^{-1/2}\left(\widehat{\tilde{x}} - i\,\widehat{\tilde{p}}\right)$ to show that the *outermost* lobe of all $\psi_v(x)$ is always positive, given that

$$\psi_v(x) = [v!]^{-1/2}(\hat{\mathbf{a}}^\dagger)^v\psi_0(x)$$

and that $\psi_0(x)$ is a positive Gaussian. Apply $\hat{x}$ and $-i\hat{p}$ to the region of $\psi_0(x)$ near $x_+(E_0)$ to discover whether the region of $\psi_1(x)$ near $x_+(E_1)$ is positive or negative.

A Note about Phase Ambiguity

When one uses $\hat{\mathbf{a}}, \hat{\mathbf{a}}^\dagger$ and $\widehat{N}$ operators to generate all Harmonic Oscillator wavefunctions and calculate all integrals, it is easy to forget what the explicit functional forms are for all of the $\psi_v(x)$. In particular, is the innermost (near x_-) or outermost (near x_+) lobe of the ψ_v always positive? Use $\hat{\mathbf{a}}^\dagger = 2^{-1/2}\left(\widehat{\tilde{x}} - i\widehat{\tilde{p}}\right)$ to show that the outermost lobe of all $\psi_v(x)$ is always positive, given that

$$\psi_v(x) = [v!]^{-1/2}(\hat{\mathbf{a}}^\dagger)^v\psi_0(x)$$

and that $\psi_0(x)$ is a positive Gaussian. Apply $\hat{x}$ and $k - i\hat{p}$ to the region of $\psi_0(x)$ near $x_+(E_0)$ to discover whether the region of $\psi_1(x)$ near $x_+(E_1)$ is positive or negative.

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2. Anharmonic Oscillator

The potential energy curves for most stretching vibrations have a form similar to a Morse potential

$$V_M(x) = D[1 - e^{-\beta x}]^2 = D[1 - 2e^{-\beta x} + e^{-2\beta x}].$$

Expand in a power series

$$V_M(x) = D\left[\beta^2 x^2 - \beta^3 x^3 + \frac{7}{12}\beta^4 x^4 + \dots\right].$$

In contrast, most bending vibrations have an approximately quartic form

$$V_Q(x) = \frac{1}{2}kx^2 + bx^4.$$

Here is some useful information:

$$\hat{x}^3 = \left(\frac{\hbar}{2\mu\omega}\right)^{3/2} (\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger)^3$$
$$\hat{x}^4 = \left(\frac{\hbar}{2\mu\omega}\right)^{2} (\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger)^4$$
$$\omega = (k/\mu)^{1/2} \qquad \text{[radians/second]}$$
$$\widetilde{\omega} = \frac{(k/\mu)^{1/2}}{2\pi c} \qquad [\text{cm}^{-1} \text{ if } c = 3.0 \times 10^{10} \text{ cm/second}]$$
$$(\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger)^3 = \hat{\mathbf{a}}^3 + 3(\widehat{N}+1)\hat{\mathbf{a}} + 3\widehat{N}\hat{\mathbf{a}}^\dagger + \hat{\mathbf{a}}^{\dagger 3}$$
$$(\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger)^4 = \hat{\mathbf{a}}^4 + \hat{\mathbf{a}}^2[4\widehat{N}-2] + [6\widehat{N}^2 + 6\widehat{N} + 3] + \hat{\mathbf{a}}^{\dagger 2}(4\widehat{N}+6) + \hat{\mathbf{a}}^{\dagger 4}$$
$$\widehat{N} = \hat{\mathbf{a}}^\dagger \hat{\mathbf{a}}.$$

The power series expansion of the vibrational energy levels is

$$E_v = hc\left[\widetilde{\omega}(v+1/2) - \widetilde{\omega x}(v+1/2)^2 + \widetilde{\omega y}(v+1/2)^3\right].$$

Hint: The goal of this problem is to relate information about the potential surface (i.e. D and β) to information about the energy level pattern we can obtain experimentally (i.e. $\tilde{\omega}$, $\tilde{\omega}\tilde{x}$, etc.). We make these connections via perturbation theory.

A. For a Morse potential, use perturbation theory to obtain the relationships between (D, β) and ($\widetilde{\omega}$, $\widetilde{\omega x}$, $\widetilde{\omega y}$). Treat the $(\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger)^3$ term through second–order perturbation theory and the $(\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger)^4$ term only through first order perturbation theory.
[**HINT**: you will find that $\widetilde{\omega y} = 0$.]

B. *Optional Problem*
For a quartic potential, find the relationship between ($\widetilde{\omega}$, $\widetilde{\omega x}$, $\widetilde{\omega y}$) and (k, b) by treating $(\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger)^4$ through second–order perturbation theory.

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3. Perturbation Theory for Harmonic Oscillator Tunneling Through a δ–function Barrier

$$V(x) = (k/2)x^2 + C\delta(x) \tag{3.1}$$

where $C > 0$ for a barrier. $\delta(x)$ is a special, infinitely narrow, infinitely tall function centered at $x = 0$. It has the convenient property that

$$\int_{-\infty}^{\infty} \delta(x)\psi_v(x)dx = \psi_v(0) \tag{3.2}$$

where $\psi_v(0)$ is the value at $x = 0$ of the v^{th} eigenfunction for the harmonic oscillator. Note that, for all $v =$ odd,

$$\int_{-\infty}^{\infty} \delta(x)\psi_{\text{odd}}(x)dx = 0 \tag{3.3}$$

A.
(i) The $\{\psi_v\}$ are normalized in the sense

$$\int_{-\infty}^{\infty} |\psi_v|^2 \, dx = 1 \tag{3.4}$$

What are the units of $\psi(x)$?

(ii) From Eq. (3.2), what are the units of $\delta(x)$?

(iii) $V(x)$ has units of energy. From Eq. (3.1), what are the units of the constant, C?

B. In order to employ perturbation theory, you need to know the values of all integrals of $\widehat{H}^{(1)}$

$$\widehat{H}^{(1)} \equiv C\delta(x) \tag{3.5}$$

$$\int_{-\infty}^{+\infty} \psi_{v'}(x)\widehat{H}^{(1)}\psi_v(x)dx = C\psi_{v'}(0)\psi_v(0) \tag{3.6}$$

$$\widehat{H}^{(0)}\psi_v(x) = \hbar\omega(v + 1/2)\psi_v(x). \tag{3.7}$$

Write general formulas for $E_v^{(1)}$ and $E_v^{(2)}$ (do not yet attempt to evaluate $\psi_v(0)$ for all even–v). Use the definitions in Eqs. (3.8) and (3.9).

$$E_v^{(1)} = H_{vv}^{(1)} \tag{3.8}$$

$$E_v^{(2)} = \sum_{v' \neq v} \frac{\left(H_{vv'}^{(1)}\right)^2}{E_v^{(0)} - E_{v'}^{(0)}} \tag{3.9}$$

C. The semi-classical amplitude of $\psi(x)$ is proportional to $[v_{\text{classical}}(x)]^{-1/2}$ where $v_{\text{classical}}(x)$ is the classical mechanical velocity at x

$$v_{\text{classical}}(x) = p_{\text{classical}}(x)/\mu = \frac{1}{\mu}[2\mu(E_v - V(x))]^{1/2}. \tag{3.10}$$

At $x = 0$, $v_{\text{classical}}(0) = \left[\frac{2\hbar\omega(v+1/2)}{\mu}\right]^{1/2}$. The proportionality constant for $\psi(x)$ is obtained from the ratio of the time it takes to move from x to $x + dx$ to the time it takes to go from $x_-(E_v)$ to $x_+(E_v)$, which is 1/2 of the period of oscillation.

$$\psi(0)^2 dx = \frac{dx/v_{\text{classical}}(0)}{\tau_v/2}$$
$$= \frac{2dx}{v_{\text{classical}}(0)(h/\hbar\omega)} = \frac{2\omega dx}{2\pi v_{\text{classical}}(0)}$$
$$\psi_v(0) \approx \left[\frac{(\omega/\pi)}{v_{\text{classical}}(0)}\right]^{1/2} \qquad \text{for even-}v$$

Use this semi-classical evaluation of $\psi_v(0)$ to estimate the dependence of $H^{(1)}_{vv}$ and $H^{(2)}_{vv'}$ on the vibrational quantum numbers, v and v'.

D. Make the assumption that all terms in the sum over v' (Eq. 3.9) except the $v, v+2$ and $v, v-2$ terms are negligibly small. Determine $E_v = E^{(0)}_v + E^{(1)}_v + E^{(2)}_v$ and comment on the qualitative form of the vibrational energy level diagram. Are the odd–v levels shifted at all from their $E^{(0)}_v$ values? Are the even–v levels shifted up or down relative to $E^{(0)}_v$? How does the size of the shift depend on the vibrational quantum number?

E. Estimate $E_1 - E_0$ and $E_3 - E_2$. Is the effect of the δ–function barrier on the level pattern increasing or decreasing with v?

F. Sketch (freehand) the superposition state, $\Psi(x, t = 0) = 2^{-1/2}[\psi_0(x) + \psi_1(x)]$. Predict the qualitative behavior of $\Psi^\star(x, t)\Psi(x, t)$.

The time-dependence of this two-level superposition state's probability distribution
G. *Compute* $\langle \hat{x} \rangle_t$ for the coherent superposition state in part **F**. Recall that

$$x_{v+1,v} = \text{(some known constants)} \int \psi_{v+1}(\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger)\psi_v dx.$$

H. Discuss what you expect for the qualitative behavior of $\langle \hat{x} \rangle_t$ for the $v = 0, 1$ superposition vs. that of the $v = 2, 3$ superposition state. How will the right↔left tunneling rate depend on the value of C?

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4. Perturbation Theory for a Particle in a modified infinite box

$$\widehat{\mathbf{H}}^{(0)} = \hat{p}^2/2m + V^{(0)}(x)$$

$$V^{(0)}(x) = \infty \qquad x < 0, x > a$$
$$V^{(0)}(x) = 0 \qquad 0 \leq x \leq a$$

$$\widehat{\mathbf{H}}^{(1)} = V'(x)$$

$$V'(x) = 0 \qquad x < \frac{a-b}{2}, x > \frac{a+b}{2}$$
$$V'(x) = -V_0 \qquad \frac{a-b}{2} < x < \frac{a+b}{2}, V_0 > 0$$

where $a > 0$, $b > 0$, and $a > b$.

A. Draw $V^{(0)}(x) + V'(x)$.

B. What are $\psi_n^{(0)}(x)$ and $E_n^{(0)}$?

C. What is the selection rule for non-zero integrals

$$\mathbf{H}_{nm}^{(1)} = \int dx \psi_n^{(0)} \widehat{\mathbf{H}}^{(1)} \psi_m^{(0)}?$$

D. Use

$$\sin A \sin B = \frac{1}{2}\left[\cos(A-B) - \cos(A+B)\right]$$

and

$$\int dx \cos Cx = \frac{1}{C} \sin Cx$$

to compute $E_n = E_n^{(0)} + E_n^{(1)} + E_n^{(2)}$ for $n = 0$, 1, 2, and 3 and limiting the second-order perturbation sums to $n \leq 5$.

E. Now reverse the sign of V_0 and compare the energies of the $n = 0$, 1, 2, 3 levels for $V_0 > 0$ vs. $V_0 < 0$.
