**5.61 Fall 2017**
**Problem Set #5**

Suggested Reading: McQuarrie, Pages 396-409

## 1. Phase Ambiguity

When one uses $\mathbf{\hat{a}}, \mathbf{\hat{a}}^\dagger$ 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 $\psi_v$ always positive? Use $\mathbf{\hat{a}}^\dagger = 2^{-1/2}\left(\widehat{\tilde{x}} - i\,\widehat{\tilde{p}}\right)$ to show that the *outermost* lobe of all $\psi_v(x)$ is always positive, given that

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

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.

## 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

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

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:

$$\hat{x}^3 = \left(\frac{\hbar}{2\mu\omega}\right)^{3/2}(\mathbf{\hat{a}} + \mathbf{\hat{a}}^\dagger)^3$$

$$\hat{x}^4 = \left(\frac{\hbar}{2\mu\omega}\right)^{2}(\mathbf{\hat{a}} + \mathbf{\hat{a}}^\dagger)^4$$

$$\omega = (k/\mu)^{1/2} \qquad \text{[radians/second]}$$

$$\widetilde{\omega} = \frac{(k/\mu)^{1/2}}{2\pi c} \qquad [\text{cm}^{-1} \text{ if } c = 3.0 \times 10^{10} \text{ cm/second}]$$

$$(\mathbf{\hat{a}} + \mathbf{\hat{a}}^\dagger)^3 = \mathbf{\hat{a}}^3 + 3(\widehat{N}+1)\mathbf{\hat{a}} + 3\widehat{N}\mathbf{\hat{a}}^\dagger + \mathbf{\hat{a}}^{\dagger 3}$$

$$(\mathbf{\hat{a}} + \mathbf{\hat{a}}^\dagger)^4 = \mathbf{\hat{a}}^4 + \mathbf{\hat{a}}^2[4\widehat{N} - 2] + [6\widehat{N}^2 + 6\widehat{N} + 3] + \mathbf{\hat{a}}^{\dagger 2}(4\widehat{N} + 6) + \mathbf{\hat{a}}^{\dagger 4}$$

$$\widehat{N} = \mathbf{\hat{a}}^\dagger\mathbf{\hat{a}}.$$

The power series expansion of the vibrational energy levels is

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

**A.** For a Morse potential, use perturbation theory to obtain the relationships between $(D, \beta)$ and $(\widetilde{\omega}, \widetilde{\omega}\widetilde{x}, \widetilde{\omega}\widetilde{y})$. 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 $\widetilde{\omega}\widetilde{y} = 0$.]

**B.** *Optional Problem*

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

## 3. Perturbation Theory for Harmonic Oscillator Tunneling Through a $\delta$–function Barrier

$$V(x) = (k/2)x^2 + C\delta(x) \tag{1}$$

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

$$\int_{-\infty}^{\infty} \delta(x)\psi_v(x)dx = \psi_v(0) \tag{2}$$

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

$$\int_{-\infty}^{\infty} \delta(x)\psi_{\text{odd}}(x)dx = 0 \tag{3}$$

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

$$\int_{-\infty}^{\infty} |\psi_v|^2\, dx = 1 \tag{4}$$

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

**(ii)** From Eq. (2), what are the units of $\delta(x)$?

**(iii)** $V(x)$ has units of energy. From Eq. (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 $\widehat{H}^{(1)}$

$$\widehat{H}^{(1)} \equiv C\delta(x) \tag{5}$$

$$\int_{-\infty}^{+\infty} \psi_{v'}(x)\widehat{H}^{(1)}\psi_v(x)dx = C\psi_{v'}(0)\psi_v(0) \tag{6}$$

$$\widehat{H}^{(0)}\psi_v(x) = \hbar\omega(v+1/2)\psi_v(x). \tag{7}$$

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. (8) and (9).

$$E_v^{(1)} = H_{vv}^{(1)} \tag{8}$$

$$E_v^{(2)} = \sum_{v' \neq v} \frac{\left(H_{vv'}^{(1)}\right)^2}{E_v^{(0)} - E_{v'}^{(0)}} \tag{9}$$

**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 $x$

$$v_{\text{classical}}(x) = p_{\text{classical}}(x)/\mu = \frac{1}{\mu}[2\mu(E_v - V(x))]^{1/2}. \tag{10}$$

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 $x_+(E_v)$.

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

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

**D.** Make the assumption that all terms in the sum over $v'$ (Eq. (9)) except the $v, v+2$ and $v, v-2$ terms are negligibly small. Determine $E_v = E_v^{(0)} + E_v^{(1)} + E_v^{(2)}$ and comment on the qualitative form of the vibrational energy level diagram. Are the odd–$v$ levels shifted at all from their $E_v^{(0)}$ values? Are the even–$v$ levels shifted up or down relative to $E_v^{(0)}$? 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 $\delta$–function barrier on the level pattern increasing or decreasing with $v$?

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

**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 $C$?

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

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

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

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

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

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. $V_0 < 0$.