5.61 Fall 2013
Problem Set #5

Suggested Reading: McQuarrie, Pages 396-409

1. Harmonic Oscillator Subject to Perturbation by an Electric Field

This problem is related to the example discussed in Lecture #13.5 of a harmonic oscillator perturbed by an oscillating electric field. An electron is connected by a harmonic spring to a fixed point at $x = 0$. It is subject to a field–free potential energy

$$V(x) = \frac{1}{2}kx^2.$$

The energy levels and eigenstates are those of a harmonic oscillator where

$$\begin{aligned}\omega &= [k/m_e]^{1/2}\\ E_v &= \hbar\omega(v + 1/2)\\ \psi_v(x) &= (v!)^{-1/2}(\hat{\mathbf{a}}^\dagger)^v\psi_{v=0}(x).\end{aligned}$$

Now a constant electric field, E_0, is applied and $V(x)$ becomes

$$V(x) = \frac{1}{2}kx^2 + E_0ex \quad (e > 0 \text{ by definition}).$$

Note on dipole interactions and signs:

The interaction energy of a charge q located at position x in a uniform DC electric field E_0 is aways

$$H = -\mu E_0 = -E_0qx.$$

Note the negative sign! This means that when a dipole, $\vec{\mu} = q\vec{x}$, points along the same direction as an electric field, there is a *favorable* interaction (i.e. negative interaction energy).

For an electron, $q = q_{e^-} \equiv -e$, where e is the elementary charge and is *strictly positive*, making the electron's charge negative. Therefore, an electron in a field in the $+x$ direction has an interaction expressed as

$$H = -\vec{\mu}\cdot\vec{E}_0 = -E_0q_{e^-}x = -E_0(-e)x = +E_0ex.$$

As the electron's position x increases, its interaction energy with the field increases (assuming $E_0 > 0$, i.e. the field points in the $+x$ direction). This makes physical sense: we know from 8.02 that an electron likes to go *away* from the direction that the field points (and positive charges like to go *toward* the direction of the field).

You are going to approach this problem two ways:

(i) by a simple and exact way first, and then

(ii) by perturbation theory.

A. Solve for $x_{\min}$, $V(x_{\min})$, and $V(x')$ where $x' = x - x_{\min}$ for this harmonic oscillator in a constant electric field. Is the system still a harmonic oscillator? What is ω for this oscillator?

B. Write an expression for the energy levels as a function of the strength of the electric field.

C. One definition of the *polarizability*, α, is the second derivative of the energy with respect to the electric field

$$\alpha_v = -\frac{d^2 E_v}{dE_0^2}.$$

What is the value of α_v? Is it v–dependent?

D. Another definition of the polarizability is

$$\mu(E_0) - \mu(E = 0) = \alpha E_0$$

where μ is the electric dipole moment. Using this definition of α, what is $\mu(E_0)$?

E. Now let's approach this problem by perturbation theory. The zero-order energies and wavefunctions are those of the harmonic oscillator at $E_0 = 0$. The perturbation term is

$$\widehat{\mathbf{H}}^{(1)} = E_0 e\hat{x}$$

where $\hat{x}$ is the usual harmonic oscillator displacement coordinate. If

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

write a general formula for *all* of the non-zero

$$x_{v',v} \equiv \int dx \psi^\star_{v'} \hat{x} \psi_v$$

integrals.

F. Using the value you found for $x_{v',v}$ write all of the E_0–dependent values for $\widehat{\mathbf{H}}^{(1)}_{v',v}$ and then compute the energy levels of the harmonic oscillator perturbed by a electric field, where

$$E_v = E_v^{(0)} + E_v^{(1)} + E_v^{(2)}$$

and the perturbed wavefunctions are

$$\psi_v = \psi_v^{(0)} + \psi_v^{(1)}.$$

G. Using $\dfrac{d^2 E_v}{dE_0^2}$ compute the polarizability, α_v. Is the polarizability v–dependent? Does α_v agree with the value you obtained in part **C**?

H. Using the $\left\{\psi_v^{(1)}\right\}$, compute μ_v using

$$\mu_v = e \int dx \psi_v^\star \hat{x} \psi_v$$

where the ψ_v here are the perturbed ψ_v. Is μ v–dependent? Should it be v–dependent? Does it agree with the result you obtained in part **D**?

2. <u>Perturbation Theory for a Particle in a modified infinite box</u>

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

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

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

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

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. $V_0 < 0$.

3. Perturbation Theory for Harmonic Oscillator Tunneling Through a δ–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^{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 $H^{(1)}_{vv}$ 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. (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) $\Psi(x, t = 0) = 2^{-1/2}[\psi_0(x) + \psi_1(x)]$. 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. <u>Anharmonic Oscillator</u>

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

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

In contrast, most bending vibrations have an approximately quartic form

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

Here is some useful information:

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

The power series expansion of the vibrational energy levels is

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

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 $(\mathbf{\hat{a}} + \mathbf{\hat{a}}^\dagger)^3$ term through second–order perturbation theory and the $(\mathbf{\hat{a}} + \mathbf{\hat{a}}^\dagger)^4$ 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 $(\mathbf{\hat{a}} + \mathbf{\hat{a}}^\dagger)^4$ through second–order perturbation theory.

5. <u>Phase Ambiguity</u>

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 ψ_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.