5.61 Fall 2017
Problem Set #5 Solutions

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 ψ_v always positive? Use $\mathbf{\hat{a}}^\dagger = 2^{-1/2}\left(\hat{\tilde{x}} - i\,\hat{\tilde{p}}\right)$ 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.

<u>Solution:</u>
We know that

$$\psi_v(x) = [v!]^{-1/2}(\mathbf{\hat{a}}^\dagger)^v\psi_0(x) \tag{1.1}$$

And plugging in for $\mathbf{\hat{a}}^\dagger$ gives us

$$\psi_v(x) = [v!]^{-1/2}(2^{-1/2}[\hat{\tilde{x}} - i\hat{\tilde{p}})^v\psi_0(x) \tag{1.2}$$

or, after putting the momentum operator into position space

$$\psi_v(x) = [v!]^{-1/2}\left(2^{-1/2}\left[\hat{\tilde{x}} - \hbar\frac{\partial}{\partial x}\right]\right)^v\psi_0(x). \tag{1.3}$$

For large values of x, the $\hat{\tilde{x}}$ operator should give a large, positive value. The derivative of a positive gaussian in this region should be negative and very small (and will contribute positively due to the negative sign in the equation). And the ψ_0 itself is defined as a positive gaussian and is therefore positive over all space. Therefore, because all terms are positive for very large x values, the far right lobe should be positive.

> <u>A Note about 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 $\mathbf{\hat{a}}^\dagger = 2^{-1/2}\left(\hat{\tilde{x}} - i\hat{\tilde{p}}\right)$ to show that the outermost lobe of all $\psi_v(x)$ is always positive, given that
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> $$\psi_v(x) = [v!]^{-1/2}(\mathbf{\hat{a}}^\dagger)^v\psi_0(x)$$
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> 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.

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

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

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:

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

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 $\widetilde{\omega y} = 0$.]

Solution:

We can interpret a Morse potential as a perturbation of a perfect harmonic oscillator. These perturbations are the higher order terms in the power expansion of the potential. Considering only the terms of order 4 or less and defining $\omega_0 = \sqrt{2D\beta^2/m}$, we have

$$H^{(0)} = \frac{p^2}{2m} + \frac{m\omega_0^2}{2}x^2 \tag{2.1}$$

$$H^{(1)} = -D\beta^3 x^3 + \frac{7D}{12}\beta^4 x^4. \tag{2.2}$$

The zero-order energies are those for a harmonic oscillator with frequency ω_0

$$E_v^{(0)} = \hbar\omega_0(v + 1/2) \tag{2.3}$$

To calculate the first-order corrections it's necessary to rewrite the perturbation term $H^{(1)}$ in terms of raising and lowering operators.

$$\begin{aligned}
H^{(1)} &= -D\beta^3 x^3 + \frac{7D}{12}\beta^4 x^4 && (2.4)\\
&= -D\beta^3\left(\frac{\hbar}{2m\omega_0}\right)^{3/2}(\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger)^3 + \frac{7D}{12}\beta^4\left(\frac{\hbar}{2m\omega_0}\right)^2(\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger)^4 && (2.5)\\
&= -\frac{\hbar^{3/2}D^{1/4}\beta^{3/2}}{2^{9/4}m^{3/4}}(\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger)^3 + \frac{7\hbar^2\beta^2}{96m}(\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger)^4 && (2.6)
\end{aligned}$$

The first-order corrections are the integrals $H_{v,v}^{(1)}$. In the equation above, the cubic term has selection rules $\Delta v = \pm 3, \pm 1$, and so it will not contribute to the first-order corrections. Expanding the quartic term and keeping only those parts that have a selection rule $\Delta v = 0$ (i.e. those terms which have two $\hat{\mathbf{a}}$'s and two $\hat{\mathbf{a}}^\dagger$'s), we arrive at

$$\begin{aligned}
E_v^{(1)} = H_{v,v}^{(1)} &= \frac{7\hbar^2\beta^2}{96m}\int dx \psi_v^\star[6\widehat{N}^2 + 6\widehat{N} + 3]\psi_v && (2.7)\\
&= \frac{7\hbar^2\beta^2}{96m}(6v^2 + 6v + 3) && (2.8)\\
&= \frac{7\hbar^2\beta^2}{16m}(v^2 + v + 1/2) && (2.9)\\
&= \frac{7\hbar^2\beta^2}{16m}(v + 1/2)^2 + \frac{7\hbar^2\beta^2}{64m}. && (2.10)
\end{aligned}$$

The second-order term is a bit more complicated. We will make the simplification of only considering the second-order contributions from the cubic term in the potential (this is reasonable because in real systems quartic terms are generally an order of magnitude smaller than cubic terms). The second order correction to the energies is

$$E_v^{(2)} = \sum_{v' \neq v} \frac{\left|H_{v',v}^{(1)}\right|^2}{E_v^{(0)} - E_{v'}^{(0)}} \tag{2.11}$$

where

$$\begin{aligned}
H_{v',v}^{(1)} &= -\frac{\hbar^{3/2}D^{1/4}\beta^{3/2}}{2^{9/4}m^{3/4}}\int dx \psi_{v'}(\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger)^3\psi_v && (2.12)\\
&= -\frac{\hbar^{3/2}D^{1/4}\beta^{3/2}}{2^{9/4}m^{3/4}}\int dx \psi_{v'}[\hat{\mathbf{a}}^3 + 3(\widehat{N} + 1)\hat{\mathbf{a}} + 3\widehat{N}\hat{\mathbf{a}}^\dagger + \hat{\mathbf{a}}^{\dagger 3}]\psi_v. && (2.13)
\end{aligned}$$

The selection rules for this integral are $\Delta v = \pm 1, \pm 3$. Evaluating it in the second-order correction sum yields 4 terms:

$$E_v^{(2)} = \frac{\hbar^3 D^{1/2}\beta^3}{2^{9/2}m^{3/2}}\frac{1}{\hbar\omega_0}\left[\frac{(v^3-3v^2+2v)}{3}+\frac{3v^3}{1}+\frac{3(v^3-3v^2+3v+1)}{-1}+\frac{(v^3+6v^2+11v+6)}{-3}\right] \tag{2.14}$$

$$= \frac{-\hbar^2\beta^2}{32m}[-12v^2-12v-5] \tag{2.15}$$

$$= \frac{3\hbar^2\beta^2}{8m}[v^2+v+5/12] \tag{2.16}$$

$$= \frac{3\hbar^2\beta^2}{8m}(v+1/2)^2+\frac{\hbar^2\beta^2}{6m}. \tag{2.17}$$

Okay! Now we've done the hard work, let's make the final connections. First let's add up all of the perturbation corrections to the energy levels:

$$E_v = E_v^{(0)}+E_v^{(1)}+E_v^{(2)} \tag{2.18}$$

$$= [\hbar\omega_0(v+1/2)]+\left[\frac{7\hbar^2\beta^2}{16m}(v+1/2)^2+\frac{7\hbar^2\beta^2}{64m}\right]+\left[\frac{3\hbar^2\beta^2}{8m}(v+1/2)^2+\frac{\hbar^2\beta^2}{6m}\right] \tag{2.19}$$

$$= \frac{53}{192}\frac{\hbar^2\beta^2}{m}+\hbar\omega_0(v+1/2)+\frac{13}{16}\frac{\hbar^2\beta^2}{m}(v+1/2)^2 \tag{2.20}$$

Compare this to the "dumb" (i.e. *a priori* un-insightful) power series expansion of the energy levels (which we would measure experimentally),

$$E_v = hc[\tilde{\omega}(v+1/2)-\tilde{\omega}\tilde{x}(v+1/2)^2+\tilde{\omega}\tilde{y}(v+1/2)^3+\ldots] \tag{2.21}$$

Matching powers of $(v+1/2)$, we can determine the following relations between the experimentally determined molecular constants ($\tilde{\omega}$, $\tilde{\omega}\tilde{x}\ldots$) and the potential curve parameters (the information we actually care about).

$$hc\tilde{\omega} = \hbar\omega_0 \tag{2.22}$$

$$-hc\tilde{\omega}\tilde{x} = \frac{13}{16}\frac{\hbar^2\beta^2}{m} \tag{2.23}$$

$$hc\tilde{\omega}\tilde{y} = 0 \tag{2.24}$$

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.

<u>Solution:</u>

We approach the quartic bending potential in the same manner as above. First we find the perturbation theory expressions for the energy levels and manipulate them to be a power series in $(v+1/2)$, and then compare this to the experimental power series expansion of the vibrational energy levels.

Our Hamiltonian $H = H^{(0)} + H^{(1)}$, where

$$H^{(0)} = \frac{p^2}{2m} + \frac{m\omega^2}{2}x^2 \tag{2.25}$$

$$H^{(1)} = bx^4 = b\left(\frac{\hbar}{2m\omega}\right)^2 (\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger)^4 \tag{2.26}$$

with $\omega = \sqrt{k/m}$.

Our zero order energies are those of $H^{(0)}$ (a harmonic oscillator)

$$E_v^{(0)} = \hbar\omega(v+1/2). \tag{2.27}$$

The first order corrections will use the same expression as part **2.A**.

$$E_v^{(1)} = b\left(\frac{\hbar}{2m\omega}\right)^2 (6v^2 + 6v + 3) \tag{2.28}$$

$$= \frac{b}{24}\left(\frac{\hbar}{m\omega}\right)^2 (v+1/2)^2 + \frac{b}{96}\left(\frac{\hbar}{m\omega}\right)^2. \tag{2.29}$$

The second order correction will require a sum over states. The selection rules for the terms in this sum are (excluding $\Delta v = 0$) $\Delta v = \pm 2$, ± 4, leading to four non–zero terms

$$E_v^{(2)} = b^2\left(\frac{\hbar}{2m\omega}\right)^4 \left[\frac{(v)(v-1)(v-2)(v-3)}{4\hbar\omega} + \frac{(v-1)(v)(4v-2)}{2\hbar\omega}\right. \tag{2.30}$$

$$\left. + \frac{(v+2)(v+1)(4v+6)}{-2\hbar\omega} + \frac{(v+4)(v+3)(v+2)(v+1)}{-4\hbar\omega}\right] \tag{2.31}$$

$$= -\frac{b^2\hbar^3}{4m^4\omega^5}\left[v^3 + \frac{9}{2}v^2 + \frac{13}{2}v + 3\right] \tag{2.32}$$

$$= -\frac{b^2\hbar^3}{4m^4\omega^5}\left[(v+1/2)^3 + 3(v+1/2)^2 + \frac{11}{4}(v+1/2) + \frac{3}{4}\right] \tag{2.33}$$

Summing our zero-order energies with the first- and second-order corrections yields

$$E_v = \left[\frac{1}{16}\frac{b\hbar^2}{m^2\omega^2} - \frac{3}{16}\frac{b^2\hbar^3}{m^4\omega^5}\right] + \left[\hbar\omega - \frac{11}{16}\frac{b^2\hbar^3}{m^4\omega^5}\right](v+1/2) \tag{2.34}$$

$$+ \left[\frac{1}{24}\frac{b^2\hbar^2}{m^2\omega^3} - \frac{3}{4}\frac{b^2\hbar^3}{m^4\omega^5}\right](v+1/2) \tag{2.35}$$

$$+ \left[\frac{1}{4}\frac{b^2\hbar^3}{m^4\omega^5}\right](v+1/2)^3 \tag{2.36}$$

As before, the molecular constants from the empirical energy level power series in $(v+1/2)$

are related to the potential parameters by matching powers:

$$hc\tilde{\omega} = \hbar\omega - \frac{11}{16}\frac{b^2\hbar^3}{m^4\omega^5} \tag{2.37}$$

$$-hc\tilde{\omega}\tilde{x} = \frac{1}{24}\frac{b\hbar^2}{m^2\omega^2} - \frac{3}{4}\frac{b^2\hbar^3}{m^4\omega^5} \tag{2.38}$$

$$hc\tilde{\omega}\tilde{y} = \frac{1}{4}\frac{b^2\hbar^3}{m^4\omega^5}. \tag{2.39}$$

Note that when we treat the quartic term up through second-order perturbation theory it contributes to the linear, quadratic, and cubic terms in the $(v+1/2)$ power series. The first-order correction only contributes to the quadratic term (and all contribute to the constant offset).

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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 $\psi(x)$?

Solution:
The normalization for the zero-order wavefunctions is given as

$$\int_{-\infty}^{\infty} |\psi_v|^2 dx = 1. \tag{3.5}$$

The right-hand side is dimensionless, so $|\psi_v|^2 dx$ must be dimensionless as well, implying that $|\psi_v|^2$ has units of reciprocal length $[\ell^{-1}]$, so ψ_v has units of $[\ell^{-1/2}]$.

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

Solution:
The δ function is defined by

$$\int_{-\infty}^{\infty} \delta(x)\psi_v(x)dx = \psi_v(0). \tag{3.6}$$

Therefore, $\delta(x)\psi_v(x)dx$ must have the same dimensions as $\psi_v(x)$ itself. That means that $\delta(x)dx$ is dimensionless, so $\delta(x)$ has dimensions of ℓ^{-1}.

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

Solution:
The perturbed harmonic oscillator potential is given as

$$V(x) = (k/2)x^2 + C\delta(x). \tag{3.7}$$

$C\delta(x)$ must have units of energy $[m\ell^2t^{-2}]$. We know that $\delta(x)$ has units of ℓ^{-1}, so C must have units of $[m\ell^3t^{-2}]$.

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

$$\widehat{H}^{(1)} \equiv C\delta(x) \tag{3.8}$$

$$\int_{-\infty}^{+\infty} \psi_{v'}(x)\widehat{H}^{(1)}\psi_v(x)dx = C\psi_{v'}(0)\psi_v(0) \tag{3.9}$$

$$\widehat{H}^{(0)}\psi_v(x) = \hbar\omega(v+1/2)\psi_v(x). \tag{3.10}$$

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. (3.11) and (3.12).

$$E_v^{(1)} = H_{vv}^{(1)} \tag{3.11}$$

$$E_v^{(2)} = \sum_{v' \neq v} \frac{\left(H_{vv'}^{(1)}\right)^2}{E_v^{(0)} - E_{v'}^{(0)}} \tag{3.12}$$

Solution:
All $\psi_v(x)$ with v odd are anti-symmetric functions with a node at $x = 0$, so

$$H_{v',v}^{(1)} = \begin{cases} 0 & v \text{ or } v' \text{ odd} \\ C\psi_{v'}(0)\psi_v(0) & v \text{ and } v' \text{ even} \end{cases} \tag{3.13}$$

The corrections to the energy levels are

$$E_v^{(1)} = H_{vv}^{(1)} = \begin{cases} 0 & v \text{ odd} \\ C\psi_v(0)^2 & v \text{ even} \end{cases} \tag{3.14}$$

$$E_v^{(2)} = \sum_{v' \neq v} \frac{\left(H_{v',v}^{(1)}\right)^2}{E_v^{(0)} - E_{v'}^{(0)}} \tag{3.15}$$

$$= \begin{cases} 0 & v \text{ odd} \\ \sum_{v' \neq v}^{v' \text{ even}} \frac{(C\psi_{v'}(0)\psi_v(0))^2}{\hbar\omega(v-v')} & v \text{ even} \end{cases} \tag{3.16}$$

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

$$v_{\text{classical}}(x) = p_{\text{classical}}(x)/\mu = \frac{1}{\mu}[2\mu(E_v - V(x))]^{1/2}. \tag{3.17}$$

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 $H_{vv}^{(1)}$ and $H_{vv'}^{(2)}$ on the vibrational quantum numbers, v and v'.

Solution:

A semi-classical argument estimates the amplitude of the even–v wavefunctions at the origin to be

$$\psi_v(0) \approx \left[\frac{(\omega/\pi)}{v_{\text{classical}}(0)}\right]^{1/2}, \text{ where} \tag{3.18}$$

$$v_{\text{classical}}(0) = \left[\frac{2\hbar\omega(v+1/2)}{\mu}\right]^{1/2} \tag{3.19}$$

$$\Rightarrow \psi_v(0) \approx \left[\frac{\omega\mu}{h\pi(v+1/2)}\right]^{1/4}. \tag{3.20}$$

Note that the amplitude at $x = 0$ decreases as $v_{\text{classical}}$ increases, as expected.

We can now estimate the value of the integrals of the perturbation term

$$H_{vv}^{(1)} = C\psi_v(0)^2 \approx C\left[\frac{\omega\mu}{h\pi(v+1/2)}\right]^{1/2} \tag{3.21}$$

$$H_{v',v}^{(1)} = C\psi_{v'}(0)\psi_v(0) \approx C\left[\frac{\omega\mu}{h\pi(v+1/2)^{1/2}(v'+1/2)^{1/2}}\right]^{1/2} \tag{3.22}$$

We note that the diagonal terms ($v' = v$), are $\propto v^{-1/2}$ and the off-diagonal terms ($v' \neq v$) are $\propto (v'v)^{-1/4}$.

D. Make the assumption that all terms in the sum over v' (Eq. 3.12) 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?

Solution:
Making the assumption that only the $v' = v-2$, $v, v+2$ terms are non-negligible, we can calculate the perturbed energy levels of the v–even states.

$$E_v = E_v^{(0)} + E_v^{(1)} + E_v^{(2)} \tag{3.23}$$

$$\approx \hbar\omega(v+1/2) + C\left[\frac{\omega\mu}{h\pi(v+1/2)^{1/2}}\right]^{1/2}\left[\frac{1}{(v+1/2)^{1/4}} + \frac{1}{(v-3/2)^{1/4}} + \frac{1}{(v+5/2)^{1/4}}\right] \tag{3.24}$$

(Note: the $1/(v-3/2)^{1/4}$ term does not occur for $v = 0$).
The selection rules on the perturbation term do not affect the v-odd levels at all. The v-odd levels remain unperturbed. The v-even levels are all shifted up. The size of the shift decreases approximately as $v^{-1/2}$, decreasing slowly with increasing v.

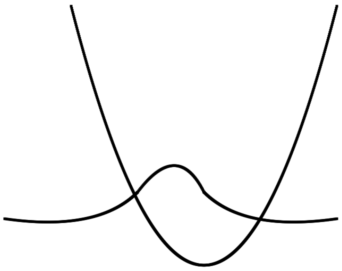
E. Estimate $E_1 - E_0$ and $E_3 - E_2$. Is the effect of the δ–function barrier on the level pattern increasing or decreasing with v?

Solution:
Since the shifts in the energy levels decreases as $\sim v^{-1/2}$, the shifts in the level differences will go down by $\sim v^{-3/2}$. Therefore we expect the $E_1 - E_0$ difference to be larger than the $E_3 - E_2$ difference.

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

Solution:

The time-dependence of this two-level superposition state's probability distribution



$\Psi^\star(x,t)\Psi(x,t)$ will exhibit oscillations at the frequency corresponding to the two-level energy difference $\omega - (E_1 - E_0)/\hbar$. As this motion causes the wavepacket to move back and forth through the barrier, this oscillation frequency is called the *tunneling frequency*.

G. *Compute* $\langle \hat{x} \rangle_t$ for the coherent superposition state in part **F**. Recall that

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

Solution:

To compute $\langle x \rangle_t$, we need expressions for the perturbed wavefunctions in terms of the zero-order harmonic oscillator wavefunctions

$$\psi_v = \psi_v^{(0)} + \sum_{v' \neq v} \frac{\mathbf{H}^{(1)}_{v',v}}{E_v^{(0)} - E_{v'}^{(0)}} \tag{3.25}$$

Odd-v wavefunctions are unperturbed, so $\psi_1 = \psi_1^{(0)}$, but we do need to calculate the energy of the perturbed ground state

$$\psi_0 = \psi_0^{(0)} + \sum_{v' \neq 0} \frac{\mathbf{H}^{(1)}_{v',0}}{E_0^{(0)} - E_{v'}^{(0)}} \psi_{v'}^{(0)} \tag{3.26}$$

$$= \psi_0^{(0)} + \frac{C\left[\frac{\omega\mu}{\hbar\pi(1/2)^{1/2}(5/2)^{1/2}}\right]}{-2\hbar\omega}\psi_2^{(0)} + \ldots \tag{3.27}$$

$$= \psi_0^{(0)} + C_2\psi_2^{(0)} + \ldots \tag{3.28}$$

We can now calculate the expectation value of x

$$\langle \tilde{x} \rangle_t = \frac{1}{2}\sqrt{\frac{\hbar}{2\mu\omega}} \int dx \left([\psi_0^{(0)\star} + C_2 \psi_2^{(0)\star} + \ldots] e^{+iE_0 t/\hbar} + \psi_1^{(0)\star} e^{+iE_1 t/\hbar} \right) \tag{3.29}$$

$$(\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger) \left([\psi_0^{(0)} + C_2 \psi_2^{(0)} + \ldots] e^{-iE_0 t/\hbar} + \psi_1^{(0)} e^{-iE_1 t/\hbar} \right) \tag{3.30}$$

$$= \frac{1}{2}\sqrt{\frac{\hbar}{2\mu\omega}} \int dx \Big[C_2 2^{1/2} \psi_1^{(0)\star} \psi_1^{(0)} e^{+i(E_1 - E_0)t/\hbar} + \psi_0^{(0)\star} \psi_0^{(0)} e^{-i(E_1 - E_0)t/\hbar} \tag{3.31}$$

$$+ \psi_1^{(0)\star} \psi_1^{(0)} e^{+i(E_1 - E_0)t/\hbar} + C_2 2^{1/2} \psi_2^{(0)\star} \psi_2^{(0)} e^{+i(E_0 - E_1)t/\hbar} \Big] \tag{3.32}$$

$$+ \text{orthogonal terms} \tag{3.33}$$

$$= \sqrt{\frac{\hbar}{2\mu\omega}} (1 + C_2 2^{1/2}) \cos(\omega_{10} t), \quad \text{where} \quad \omega_{10} = (E_1 - E_0)t/\hbar \tag{3.34}$$

The value of ω_{10} will be $\approx \omega$ plus additional perturbation corrections as determined in part **3D**. Note that the motion remains sinusoidal (why is this always true for a two-level superposition state?).

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?

Solution:

The tunneling rate for a superposition of two adjacent states will be proportional to the energy difference between them. As we saw in parts **3.D** and **3.E**, the difference in energy of the $v = 0$ and $v = 1$ level is smaller than the difference in energy between the $v = 2$ and $v = 3$ states (because lower–v states are pushed up more). Therefore the $v = 0, 1$ superposition will have a slower tunneling rate. Increasing the barrier height by increasing C will decrease the tunneling rates. It pushes up each even-v state closer to the unperturbed odd-v state above it. For example, the $v = 0, 1$ states will be closer together in energy and a superposition state of them will tunnel at a slower rate.

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

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

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

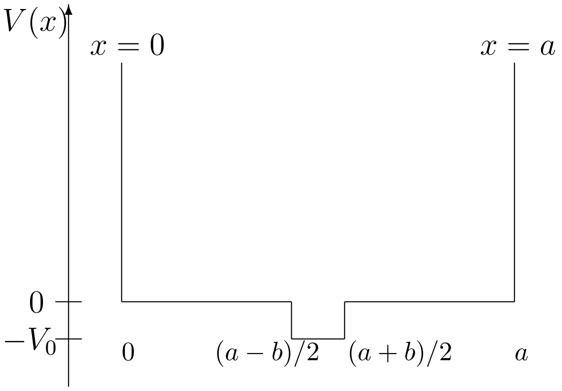
$$\widehat{\mathbf{H}}^{(1)} = V'(x)$$

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

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

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

Solution:



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

Solution:
$\psi_n^{(0)}$ and $E_n^{(0)}$ are the familiar PIB wavefunctions and energy levels:

$$\psi_n^{(0)} = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) \tag{4.1}$$
$$E_n^{(0)} = \frac{n^2h^2}{8ma^2} \tag{4.2}$$

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

$$\mathbf{H}^{(1)}_{nm} = \int dx \psi^{(0)}_n \widehat{\mathbf{H}}^{(1)} \psi^{(0)}_m ?$$

Solution:
The perturbation integrals are

$$\mathbf{H}^{(1)}_{nm} = \int dx \psi^{(0)}_n \widehat{\mathbf{H}}^{(1)} \psi^{(0)}_m \tag{4.3}$$

$$= \int dx \psi^{(0)}_n V'(x) \psi^{(0)}_m \tag{4.4}$$

Without evaluating any further, we can determine the selection rules for these integrals. We require that the integrand is symmetric (or has a symmetric part). Since $V'(x)$ is a symmetric function relative to the center of the box, this requires that the product of $\psi^{(0)}_n$ and $\psi^{(0)}_m$ must be symmetric. This requires that n and m are either both even or both odd.

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

Solution:
We will now explicitly calculate the perturbation integrals in order to evaluate the first and second-order corrections to the energy levels.

$$\mathbf{H}^{(1)}_{nm} = \int dx \psi^{(0)}_n V'(x) \psi^{(0)}_m \tag{4.5}$$

$$= \int_{\frac{a-b}{2}}^{\frac{a+b}{2}} dx \psi^{(0)}_n (-V_0) \psi^{(0)}_m \tag{4.6}$$

$$= -V_0 \int_{\frac{a-b}{2}}^{\frac{a+b}{2}} dx \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right) \sqrt{\frac{2}{a}} \sin\left(\frac{m\pi}{a}x\right) \tag{4.7}$$

$$= -V_0 \frac{2}{a} \int_{\frac{a-b}{2}}^{\frac{a+b}{2}} dx \sin\left(\frac{n\pi}{a}x\right) \sin\left(\frac{m\pi}{a}x\right) \tag{4.8}$$

$$= \frac{-V_0}{a} \int_{\frac{a-b}{2}}^{\frac{a+b}{2}} dx \left[\cos\left(\frac{(n-m)\pi}{a}x\right) - \cos\left(\frac{(n+m)\pi}{a}x\right)\right] \tag{4.9}$$

$$= \frac{-V_0}{\pi} \left[\frac{\sin\left(\frac{(n-m)\pi}{a}x\right)}{n-m} - \frac{\sin\left(\frac{(n+m)\pi}{a}x\right)}{n+m}\right]_{\frac{a-b}{2}}^{\frac{a+b}{2}} \tag{4.10}$$

The first-order corrections are equal to these integrals when $n = m$. For $n = 1, 2, 3$, they are

$$E^{(1)}_1 = -V_0 \left(b/a + \frac{\sin b\pi/a}{\pi}\right) \tag{4.11}$$

$$E^{(1)}_2 = -V_0 \left(b/a - \frac{\sin 2b\pi/a}{2\pi}\right) \tag{4.12}$$

$$E^{(1)}_3 = -V_0 \left(b/a + \frac{\sin 3b\pi/a}{3\pi}\right) \tag{4.13}$$

The second-order corrections are equal to the sum

$$E^{(2)}_n = \sum_{m \neq n} \frac{\left|\mathbf{H}^{(1)}_{mn}\right|^2}{E^{(0)}_n - E^{(0)}_m} \tag{4.14}$$

Limiting the infinite sum to $m \leq 5$ and remembering our selection rule for the perturbation integrals, we obtain

$$E^{(2)}_1 = \frac{\left|\mathbf{H}^{(1)}_{31}\right|^2}{-8h^2/8ma^2} + \frac{\left|\mathbf{H}^{(1)}_{51}\right|^2}{-24h^2/8ma^2} + \ldots \tag{4.15}$$

$$E^{(2)}_2 = \frac{\left|\mathbf{H}^{(1)}_{42}\right|^2}{-12h^2/8ma^2} + \ldots \tag{4.16}$$

$$E^{(2)}_3 = \frac{\left|\mathbf{H}^{(1)}_{13}\right|^2}{+8h^2/8ma^2} + \frac{\left|\mathbf{H}^{(1)}_{53}\right|^2}{-16h^2/8ma^2} + \ldots, \tag{4.17}$$

where $\left|\mathbf{H}_{mn}^{(1)}\right|^2$ is evaluated from Eq. (4.10).

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. $V_0 < 0$.

Solution:

The effect of switching the sign of V_0 will change the perturbation from being a "well in the box" to a "hill in the box". We expect the energies to be perturbed upward. This can easily be seen by the form of the first-order corrections in Eqs. (4.11)-(4.13). Switching the sign of the perturbation will simply switch the sign of the first order corrections.

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