5.61 Fall 2017
Problem Set #6 Solutions

1. Harmonic Oscillator Subjected to Perturbation by an Electric Field

This problem is related to the example discussed in Lecture #19 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

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

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

$$V(x) = \frac{1}{2}kx^2 + E_0 ex \quad (e > 0 \text{ by definition}).$$

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

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

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

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

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

Solution:

The total potential, including the interaction with the electric field is

$$V(x) = \frac{m\omega^2}{2}x^2 + E_0 ex. \tag{1.1}$$

We find its minimum to be

$$\frac{dV}{dx} = m\omega^2 x + E_0 e = 0 \tag{1.2}$$

$$\Rightarrow x_{\text{min}} = \frac{E_0 e}{m\omega^2}, \tag{1.3}$$

$$V(x_{\text{min}}) = \frac{m\omega^2}{2}\frac{E_0^2 e^2}{m^2\omega^2} - \frac{E_0^2 e^2}{m\omega^2} \tag{1.4}$$

$$= \frac{E_0^2 e^2}{2m\omega^2}. \tag{1.5}$$

Defining the displacement from the minimum $x' = x - x_{\text{min}}$, we arrive at

$$V(x') = \frac{m\omega^2}{2}\left(x' - \frac{E_0 e}{m\omega^2}\right)^2 + E_0 e\left(x' - \frac{E_0 e}{m\omega^2}\right) \tag{1.6}$$

$$= \frac{m\omega^2}{2}x'^2 - \frac{E_0^2 e^2}{2m\omega^2}. \tag{1.7}$$

Thus, we see that the system is still harmonic! All we have done is to shift the minimum position and minimum energy, but the potential is still quadratic. The harmonic frequency ω remains unchanged.

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

Solution:

Since the potential now is a harmonic oscillator with frequency ω and a constant offset, we can easily write down the energy levels:

$$E_v = \hbar\omega(v + 1/2) - \frac{E_0^2 e^2}{2m\omega^2}. \tag{1.8}$$

Try not to mix up the fact that we use the letter E for both energy and electric field (an unfortunate, but common convention!). Note that the electric field strength only shifts the offset of each level. The spacing between levels ($\hbar\omega$) remains unchanged.

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?

Solution:

The polarizability for the v^{th} level is given by

$$\begin{aligned}
\alpha_v &= -\frac{d^2 E_v}{dE_0^2} && (1.9)\\
&= -\frac{d^2}{dE_0^2}\left(\hbar\omega(v+1/2) - \frac{E_0^2 e^2}{2m\omega^2}\right) && (1.10)\\
&= +\frac{e^2}{m\omega^2}. && (1.11)
\end{aligned}$$

This value is independent of v, so each level has the same polarizability.

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 $\mu(E_0)$?

Solution:

A second (and in this circumstance equivalent) definition of α is

$$\mu_v(E_0) - \mu_v(E=0) = \alpha_v E_0, \tag{1.12}$$

which let's us solve for $\mu_v(E_0)$, the dipole moment of state v as a function of field strength. Substituting our known expressions from above, we get

$$\begin{aligned}
\mu_v(E_0) - \left(-e\left\langle x\right\rangle_{v,Ek=0}\right) &= \frac{e^2}{m\omega^2}E_0 && (1.13)\\
\mu_v(E_0) - 0 &= -ex_{\text{min}} && (1.14)\\
\mu_v(E_0) &= -ex_{\text{min}}. && (1.15)
\end{aligned}$$

This makes physical sense. The electric field pulls the oscillator to a new equilibrium position x_{min}. The dipole moment of the state is always qx. For the oscillator, the expectation value of x is the minimum position for any state, yielding our result $-ex_{\text{min}}$.

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

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

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

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

integrals.

Solution:

We now treat the problem as a perturbation of a harmonic oscillator with perturbation term

$$\widehat{\mathbf{H}}^{(1)} = E_0 e\hat{x}, \tag{1.16}$$

where

$$\hat{x} = \left(\frac{\hbar}{2m\omega}\right)^{1/2} (\hat{\boldsymbol{a}} + \hat{\boldsymbol{a}}^{\dagger}) \tag{1.17}$$

Non-zero integrals that involve $\hat{x}$ can be readily evaluated:

$$\begin{aligned} x_{v',v} &= \int dx \psi^{\star}_{v'} \hat{x} \psi_v && (1.18)\\ &= \left(\frac{\hbar}{2m\omega}\right)^{1/2} \int dx \psi^{\star}_{v'} (\hat{\boldsymbol{a}} + \hat{\boldsymbol{a}}^{\dagger}) \psi_v && (1.19)\\ &= \left(\frac{\hbar}{2m\omega}\right)^{1/2} \int dx \psi^{\star}_{v'} \left(v^{1/2}\psi_{v-1} + (v+1)^{1/2}\psi_{v+1}\right) && (1.20) \end{aligned}$$

$$\begin{aligned} \Rightarrow x_{v+1,v} &= \left(\frac{\hbar}{2m\omega}\right)^{1/2} (v+1)^{1/2} && (1.21)\\ x_{v-1,v} &= \left(\frac{\hbar}{2m\omega}\right)^{1/2} v^{1/2} && (1.22) \end{aligned}$$

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 an electric field, where

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

and the perturbed wavefunctions are

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

<u>Solution:</u>

We can now evaluate integrals of the perturbation term:

$$\widehat{\mathbf{H}}^{(1)}_{v',v} = E_0 e x_{v',v} \tag{1.23}$$

$$= \begin{cases} E_0 e \left(\frac{\hbar}{2m\omega}\right)^{1/2} (v+1)^{1/2} & v' = v+1 \\ E_0 e \left(\frac{\hbar}{2m\omega}\right)^{1/2} v^{1/2} & v' = v-1 \\ 0 & \text{else} \end{cases} \tag{1.24}$$

Using these values, we evaluate the first and second order corrections to the energies

$$E_v = E_v^{(0)} + E_v^{(1)} + E_v^{(2)}. \tag{1.25}$$

The first order term is a diagonal ($v' = v$) integral of the perturbation term

$$E_v^{(1)} = \widehat{\mathbf{H}}^{(1)}_{v',v} \tag{1.26}$$

$$= 0 \qquad \text{for all } v. \tag{1.27}$$

We see that there is strictly no first order shift to the energies. Now we move onto the second order correction

$$E_v^{(2)} = \sum_{v'} \frac{\left|\widehat{H}^{(1)}_{v',v}\right|^2}{E_v^{(0)} - E_{v'}^{(0)}} \tag{1.28}$$

$$= \frac{\left|\widehat{H}^{(1)}_{v-1,v}\right|^2}{E_v^{(0)} - E_{v-1}^{(0)}} + \frac{\left|\widehat{H}^{(1)}_{v+1,v}\right|^2}{E_v^{(0)} - E_{v+1}^{(0)}} \tag{1.29}$$

$$= \frac{\frac{E_0^2 e^2 \hbar v}{2m\omega}}{\hbar\omega} + \frac{\frac{E_0^2 e^2 \hbar (v+1)}{2m\omega}}{-\hbar\omega} \tag{1.30}$$

$$= \frac{E_0^2 e^2}{2m\omega^2}(v - v - 1) \tag{1.31}$$

$$= \frac{E_0^2 e^2}{2m\omega^2}. \tag{1.32}$$

The perturbed energies are thus

$$E_v = E_v^{(0)} + E_v^{(1)} + E_v^{(2)} \tag{1.33}$$

$$= \hbar\omega(v + 1/2) - \frac{E_0^2 e^2}{2m\omega^2}. \tag{1.34}$$

Note that the second-order perturbation theory expression matches the exact result from part **B**.

Let's now compute $\psi_v^{(1)}$, the correction to the zero-order wavefunctions. We begin with the definition of the first order correction

$$\psi_v^{(1)} = \sum_{v' \neq v} \frac{\widehat{\mathbf{H}}^{(1)}_{v',v}}{E_v^{(0)} - E_{v'}^{(0)}} \psi_{v'}^{(0)}. \tag{1.35}$$

$$= \frac{\widehat{\mathbf{H}}^{(1)}_{v-1,v}}{E_v^{(0)} - E_{v-1}^{(0)}} \psi_{v-1}^{(0)} + \frac{\widehat{\mathbf{H}}^{(1)}_{v+1,v}}{E_v^{(0)} - E_{v+1}^{(0)}} \psi_{v+1}^{(0)} \tag{1.36}$$

$$= E_0 e \left(\frac{\hbar}{2m\omega}\right)^{1/2} \left(\frac{v^{1/2}}{\hbar\omega} \psi_{v-1}^{(0)} + \frac{(v+1)^{1/2}}{-\hbar\omega} \psi_{v+1}^{(0)}\right) \tag{1.37}$$

$$= \left(\frac{E_0^2 e^2}{2m\hbar\omega^3}\right)^{1/2} \left(v^{1/2}\psi_{v-1}^{(0)} - (v+1)^{1/2}\psi_{v+1}^{(0)}\right). \tag{1.38}$$

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

Solution:

Re-evaluating the polarizability, we obtain

$$\alpha = \frac{d^2E_v}{dE_0^2} \tag{1.39}$$

$$= \frac{e^2}{m\omega^2}, \tag{1.40}$$

exactly the result we obtained earlier. Everything is thus far consistent.

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**?

Solution: Using the perturbed wavefunctions, let's calculate the induced dipole moment of each state μ_v

$$\mu_v = q \langle x \rangle_v = -e \int dx \left(\psi_v^{(0)\star} + \psi_v^{(1)\star}\right) \hat{x} \left(\psi_v^{(0)} + \psi_v^{(1)}\right) \tag{1.41}$$

$$= -e \left(\frac{\hbar}{2m\omega}\right)^{1/2} \int dx \left(\psi_v^{(0)\star} + \psi_v^{(1)\star}\right) \left(\hat{\boldsymbol{a}} + \hat{\boldsymbol{a}}^\dagger\right) \left(\psi_v^{(0)} + \psi_v^{(1)}\right) \tag{1.42}$$

$$= -e \left(\frac{\hbar}{2m\omega}\right)^{1/2} \left(\frac{E_0^2 e^2}{2m\hbar\omega^3}\right)^{1/2} (2v - 2(v+1)) \tag{1.43}$$

$$= E_0 \frac{e^2}{m\omega^2} = -ex_{\min}. \tag{1.44}$$

Once again, the perturbation theory result agrees with the exact result.

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2. Some Short Answer Questions

A. Evaluate the following integrals for ψ_{JM} eigenfunctions of $\mathbf{J}^2$ and $\mathbf{J}_z$. *(i)* $\int \psi_{22}^* \left(\widehat{\mathbf{J}}^+\right)^4 \psi_{2,-2} d\tau$

Solution:

$$\int \psi_{22}^* \left(\hat{J}_+\right)^4 \psi_{2,-2} d\tau = \int \psi_{22}^* \sqrt{2(2+1) - (-2)(-2+1)} (\hat{J}_+)^3 \psi_{2,-1} d\tau \tag{2.1}$$

$$= \int \psi_{22}^* \sqrt{2(2+1) - (-2)(-2+1)} \sqrt{2(2+1) - (-1)(-1+1)} (\hat{J}_+)^2 \psi_{2,0} d\tau \tag{2.2}$$

$$= \int \psi_{22}^* \sqrt{2(2+1) - (-2)(-2+1)} \sqrt{2(2+1) - (-1)(-1+1)} \tag{2.3}$$

$$\times \sqrt{2(2+1) - (0)(0+1)} (\hat{J}_+) \psi_{2,1} d\tau \tag{2.4}$$

$$= \int \psi_{22}^* \sqrt{2(2+1) - (-2)(-2+1)} \sqrt{2(2+1) - (-1)(-1+1)} \tag{2.5}$$

$$\times \sqrt{2(2+1) - (0)(0+1)} \sqrt{2(2+1) - (1)(1+1)} \psi_{22} d\tau \tag{2.6}$$

$$= \sqrt{4} \times \sqrt{6} \times \sqrt{6} \times \sqrt{4} \int \psi_{22}^* \psi_{22} d\tau \tag{2.7}$$

$$= 24 \tag{2.8}$$

(ii) $\int \psi_{33}^* \left(\widehat{\mathbf{J}}^+\right)^4 \psi_{2,-1} d\tau$

Solution:

$$\hat{J}_+^3 \psi_{2,-1} = C\psi_{2,2} \tag{2.9}$$

for some constant C. One more application of $\hat{J}_+$ annihilates this state

$$\hat{J}_+ \psi_{2,2} = 0 \tag{2.10}$$

so

$$\int \psi_{3,3}^* \hat{J}_+^4 \psi_{2,-1} d\tau = 0. \tag{2.11}$$

(iii) $\int \psi_{33}^* \left(\widehat{\mathbf{J}}^+\right)^4 \psi_{3,-3} d\tau$

Solution:

$$\hat{J}_+^4 \psi_{3,-3} = C\psi_{3,1} \tag{2.12}$$

for some constant C. This is orthogonal to $\psi_{3,3}$ so

$$\int \psi_{3,3}^* \hat{J}_+^4 \psi_{3,-3} d\tau = 0. \tag{2.13}$$

B. Which of the following operators commutes with $\widehat{H} = \frac{1}{2}kx^2 + \frac{\hat{p}^2}{2\mu}$?

(i) $\mathbf{a}^\dagger$

Solution:

No.

$$[\widehat{\mathcal{H}}, \hat{\boldsymbol{a}}^\dagger] = [\hbar\omega(\widehat{N} + 1/2), \hat{\boldsymbol{a}}^\dagger] = [\hbar\omega[\widehat{N}, \hat{\boldsymbol{a}}^\dagger] = \hbar\omega \neq 0. \tag{2.14}$$

(ii) $\mathbf{a}^\dagger\mathbf{a}$

Solution:

Yes. This operator is $\widehat{N}$, which surely commutes with $\widehat{\mathcal{H}} = \hbar\omega(\widehat{N} + 1/2)$.

(iii) $\mathbf{a}\mathbf{a}^\dagger$

Solution:

Yes. This operator is $\widehat{N}+1$, which surely commutes with $\widehat{\mathcal{H}}$.

(iv) $\mathbf{a}\mathbf{a}\mathbf{a}\mathbf{a}^\dagger\mathbf{a}^\dagger\mathbf{a}^\dagger$

Solution:

Yes. Let this operator be called $\widehat{A}$.

$$\widehat{\mathcal{H}}\hat{A}\psi_v = (v+1)(v+2)(v+3)\widehat{\mathcal{H}}\psi_v = \hbar\omega(v+1/2)(v+1)(v+2)(v+3)\psi_v \tag{2.15}$$

and

$$\hat{A}\widehat{\mathcal{H}}\psi_v = \hat{A}\hbar\omega(v+1/2)\psi_v = \hbar\omega(v+1/2)(v+1)(v+2)(v+3)\psi_v \tag{2.16}$$

which implies that

$$\widehat{H}\hat{A} = \hat{A}\widehat{H}. \tag{2.17}$$

C. Is $\widehat{L}_+ = \widehat{L}_x + i\widehat{L}_y$ Hermitian?

Solution:

No

$$\widehat{L}_+^\dagger = \widehat{L}_x^\dagger - i\widehat{L}_y^\dagger = \widehat{L}_x - i\widehat{L}_y = \widehat{L}_- \neq \widehat{L}_+. \tag{2.18}$$

D. Is $2^{-1/2}[\psi_{LM_L} + \psi_{LM_L-1}]$ an eigenfunction of $\widehat{L}_+$? Explain.

Solution:

No. $\widehat{L}_+$ produces a linear combination of M_L+1 and M_L states, which cannot be the given state because it contains no M_L-1 state.

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3. Anharmonic Oscillator

The potential energy curves for most stretching vibrations have a form similar to a Morse potential (x is displacement from equilibrium, written as Q in lecture).

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

Expand in a power series

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

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:

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

The power series expansion of the vibrational energy levels is

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

A. For a Morse potential, use perturbation theory to obtain the relationships between (D, β) and $(\tilde{\omega}, \tilde{\omega}\tilde{x}, \tilde{\omega}\tilde{y})$. Treat the $(\hat{\boldsymbol{a}} + \hat{\boldsymbol{a}}^\dagger)^3$ term through second-order perturbation theory and the $(\hat{\boldsymbol{a}} + \hat{\boldsymbol{a}}^\dagger)^4$ term only through first-order perturbation theory.

[**HINT**: you will find that $\tilde{\omega}\tilde{y} = 0$.]

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 series expansion of the potential. Considering only the terms of order 4 or less and defining $\omega_0 = \sqrt{2D\beta^2/m}$, we have

$$H^{(0)} = \frac{p^2}{2m} + \frac{m\omega_0^2}{2}x^2 \tag{3.1}$$

$$H^{(1)} = -D\beta^3 x^3 + \frac{7D}{12}\beta^4 x^4. \tag{3.2}$$

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

$$E_v^{(0)} = \hbar\omega_0(v + 1/2) \tag{3.3}$$

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

$$H^{(1)} = -D\beta^3 x^3 + \frac{7D}{12}\beta^4 x^4 \tag{3.4}$$

$$= -D\beta^3 \left(\frac{\hbar}{2m\omega_0}\right)^{3/2} (\hat{\boldsymbol{a}} + \hat{\boldsymbol{a}}^\dagger)^3 + \frac{7D}{12}\beta^4 \left(\frac{\hbar}{2m\omega_0}\right)^2 (\hat{\boldsymbol{a}} + \hat{\boldsymbol{a}}^\dagger)^4 \tag{3.5}$$

$$= -\frac{\hbar^{3/2} D^{1/4} \beta^{3/2}}{2^{9/4} m^{3/4}} (\hat{\boldsymbol{a}} + \hat{\boldsymbol{a}}^\dagger)^3 + \frac{7\hbar^2\beta^2}{96m} (\hat{\boldsymbol{a}} + \hat{\boldsymbol{a}}^\dagger)^4 \tag{3.6}$$

The first-order corrections are the integrals $H^{(1)}_{v,v}$. 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 $\hat{\boldsymbol{a}}$'s and two $\hat{\boldsymbol{a}}^\dagger$'s), we arrive at

$$E^{(1)}_v = H^{(1)}_{v,v} = \frac{7\hbar^2\beta^2}{96m} \int dx \psi^\star_v [6\widehat{N}^2 + 6\widehat{N} + 3]\psi_v \tag{3.7}$$

$$= \frac{7\hbar^2\beta^2}{96m}(6v^2 + 6v + 3) \tag{3.8}$$

$$= \frac{7\hbar^2\beta^2}{16m}(v^2 + v + 1/2) \tag{3.9}$$

$$= \frac{7\hbar^2\beta^2}{16m}(v + 1/2)^2 + \frac{7\hbar^2\beta^2}{64m}. \tag{3.10}$$

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

$$E^{(2)}_v = \sum_{v' \neq v} \frac{\left|H^{(1)}_{v',v}\right|^2}{E^{(0)}_v - E^{(0)}_{v'}} \tag{3.11}$$

where

$$H^{(1)}_{v',v} = -\frac{\hbar^{3/2} D^{1/4} \beta^{3/2}}{2^{9/4} m^{3/4}} \int dx \psi_{v'} (\hat{\boldsymbol{a}} + \hat{\boldsymbol{a}}^\dagger)^3 \psi_v \tag{3.12}$$

$$= -\frac{\hbar^{3/2} D^{1/4} \beta^{3/2}}{2^{9/4} m^{3/4}} \int dx \psi_{v'} [\hat{\boldsymbol{a}}^3 + 3(\widehat{N} + 1)\hat{\boldsymbol{a}} + 3\widehat{N}\hat{\boldsymbol{a}}^\dagger + \widehat{\;}\,3]\psi_v. \tag{3.13}$$

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

$$E_v^{(2)} = \frac{\hbar^3 D^{1/2}\beta^3}{2^{9/2}m^{3/2}}\frac{1}{\hbar\omega_0}\left[\frac{(v^3-3v^2+2v)}{3}+\frac{3v^3}{1}+\frac{3(v^3-3v^2+3v+1)}{-1}+\frac{(v^3+6v^2+11v+6)}{-3}\right] \tag{3.14}$$

$$= \frac{-\hbar^2\beta^2}{32m}[-12v^2-12v-5] \tag{3.15}$$

$$= \frac{3\hbar^2\beta^2}{8m}[v^2+v+5/12] \tag{3.16}$$

$$= \frac{3\hbar^2\beta^2}{8m}(v+1/2)^2+\frac{\hbar^2\beta^2}{6m}. \tag{3.17}$$

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:

$$E_v = E_v^{(0)}+E_v^{(1)}+E_v^{(2)} \tag{3.18}$$

$$= [\hbar\omega_0(v+1/2)]+\left[\frac{7\hbar^2\beta^2}{16m}(v+1/2)^2+\frac{7\hbar^2\beta^2}{64m}\right]+\left[\frac{3\hbar^2\beta^2}{8m}(v+1/2)^2+\frac{\hbar^2\beta^2}{6m}\right] \tag{3.19}$$

$$= \frac{53}{192}\frac{\hbar^2\beta^2}{m}+\hbar\omega_0(v+1/2)+\frac{13}{16}\frac{\hbar^2\beta^2}{m}(v+1/2)^2 \tag{3.20}$$

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

$$E_v = hc[\tilde{\omega}(v+1/2)-\tilde{\omega}\tilde{x}(v+1/2)^2+\tilde{\omega}\tilde{y}(v+1/2)^3+\dots] \tag{3.21}$$

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

$$hc\tilde{\omega} = \hbar\omega_0 \tag{3.22}$$

$$-hc\tilde{\omega}\tilde{x} = \frac{13}{16}\frac{\hbar^2\beta^2}{m} \tag{3.23}$$

$$hc\tilde{\omega}\tilde{x} = 0 \tag{3.24}$$

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

Solution:

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

$$H^{(0)} = \frac{p^2}{2m} + \frac{m\omega^2}{2}x^2 \tag{3.25}$$

$$H^{(1)} = bx^4 = b\left(\frac{\hbar}{2m\omega}\right)^2 (\hat{\boldsymbol{a}} + \hat{\boldsymbol{a}}^\dagger)^4 \tag{3.26}$$

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

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

$$E_v^{(0)} = \hbar\omega(v+1/2). \tag{3.27}$$

The first order corrections will use the same expression as part **3.A** (Eqs. 3.8–3.10).

$$E_v^{(1)} = b\left(\frac{\hbar}{2m\omega}\right)^2 (6v^2+6v+3) \tag{3.28}$$

$$= \frac{3}{2}b\left(\frac{\hbar}{m\omega}\right)^2 (v+1/2)^2 + \frac{3}{8}b\left(\frac{\hbar}{m\omega}\right)^2. \tag{3.29}$$

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

$$E_v^{(2)} = b^2\left(\frac{\hbar}{2m\omega}\right)^4 \left[\frac{(v)(v-1)(v-2)(v-3)}{4\hbar\omega} + \frac{(v-1)(v)(4v-2)}{2\hbar\omega}\right. \tag{3.30}$$

$$\left. + \frac{(v+2)(v+1)(4v+6)}{-2\hbar\omega} + \frac{(v+4)(v+3)(v+2)(v+1)}{-4\hbar\omega}\right] \tag{3.31}$$

$$= -\frac{b^2\hbar^3}{4m^4\omega^5}\left[v^3 + \frac{9}{2}v^2 + \frac{13}{2}v + 3\right] \tag{3.32}$$

$$= -\frac{b^2\hbar^3}{4m^4\omega^5}\left[(v+1/2)^3 + 3(v+1/2)^2 + \frac{11}{4}(v+1/2) + \frac{3}{4}\right] \tag{3.33}$$

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

$$E_v = \left[\frac{3}{8}\frac{b\hbar^2}{m^2\omega^2} - \frac{3}{16}\frac{b^2\hbar^3}{m^4\omega^5}\right] + \left[\hbar\omega - \frac{11}{16}\frac{b^2\hbar^3}{m^4\omega^5}\right](v+1/2) \tag{3.34}$$

$$+ \left[\frac{3}{2}\frac{b\hbar^2}{m^2\omega^2} - \frac{3}{4}\frac{b^2\hbar^3}{m^4\omega^5}\right](v+1/2)^2 \tag{3.35}$$

$$- \left[\frac{1}{4}\frac{b^2\hbar^3}{m^4\omega^5}\right](v+1/2)^3 \tag{3.36}$$

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:

$$hc\tilde{\omega} = \hbar\omega - \frac{11}{16}\frac{b^2\hbar^3}{m^4\omega^5} \tag{3.37}$$

$$-hc\tilde{\omega}\tilde{x} = \frac{3}{2}\frac{b\hbar^2}{m^2\omega^2} - \frac{3}{4}\frac{b^2\hbar^3}{m^4\omega^5} \tag{3.38}$$

$$hc\tilde{\omega}\tilde{y} = -\frac{1}{4}\frac{b^2\hbar^3}{m^4\omega^5}. \tag{3.39}$$

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 both contribute to the constant offset).

4. Semi–Classical Treatment of H–Atom–Like Systems

The radial part of the **H**-atom Hamiltonian includes the effective potential

$$V_\ell(r) = -\frac{1}{r} + \frac{\ell(\ell+1)}{2r^2}.$$

The eigenfunctions and eigenvalues of this radial problem are obtained from a 2^{nd} order differential equation for $\chi_{n,\ell}(r) = rR_{n,\ell}(r)$

$$\left[\frac{-\hbar^2}{2\mu_H}\frac{d^2}{dr^2} - V_\ell(r)\right]\chi_{n,\ell}(r) = E_{n,\ell}\chi_{n,\ell}(r).$$

You are going to understand this problem using a semi-classical approximation, without actually solving the differential equation.

A. For a 1-dimensional problem (OK to choose $\ell = 0$), where $n = 0$ is the quantum number for the lowest energy level, what is the relationship between n and the number of internal nodes?

Solution:

If $\ell = 0$, $n =$ number of nodes

B. The de Broglie relationship, $\lambda = h/p$, may be generalized to a system where p is dependent on r, via the classical mechanical definition of $p(r)$

$$p(r) = [2m(E_{n\ell} - V_\ell(r))]^{1/2} = h/\lambda(r).$$

Thus the semi-classical wavelength is

$$\lambda(r) = h[2m(E_{n,\ell} - V_\ell(r))]^{-1/2}.$$

The following integral equation enables you to compute the number of semi-classical wavelengths between the turning points of the $V_\ell(r)$ at energy $E_{n,\ell}$:

$$\frac{1}{h}\int_{r_-(E_{n,\ell})}^{r_+(E_{n,\ell})} p_{E_{n,\ell}}(r)dr = \#\text{ of wavelengths}.$$

Justify this equation by reference to an infinite box of width a.

Solution:

$$E_n = \frac{n^2h^2}{8ma^2}$$

Between turning points, $V = 0$

$$p = \sqrt{2mE_n} = \sqrt{\frac{2mn^2h^2}{8ma^2}} = \frac{nh}{2a}$$

$$\boxed{\frac{1}{h}\frac{nh}{2a}\int_{-a/2}^{a/2} dr = \frac{nha}{2ha} = \frac{n}{2} = \text{ \# of wavelengths}}$$

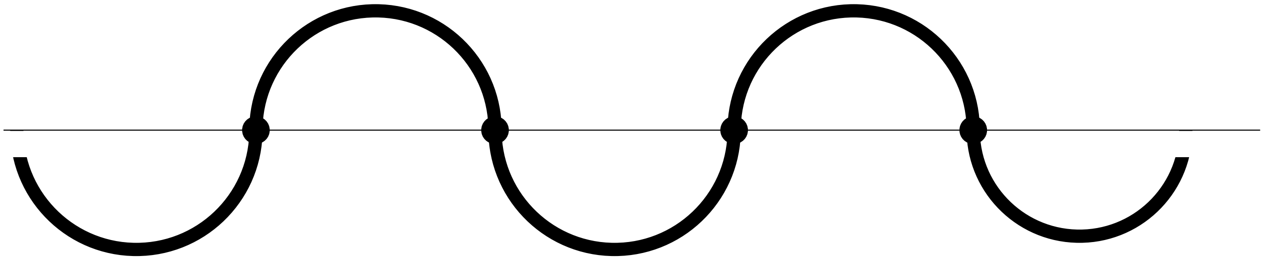
C. If the lowest energy level has quantum number $n = 0$ and $\psi_{n=0}(r)$ has zero internal nodes, then how many internal nodes does the $\psi_{n=4}(r)$ function have?

$\boxed{\text{4 nodes}}$

How many wavelengths fit between the turning points of $V_\ell(r)$ at $E_{n=4}$?

Solution:

There are four nodes, therefore the wavefunction must cross the r–axis 4 times, leading to $\frac{5}{2}$ wavelengths. Since n actually starts with 0 in this case, $n = 4$, corresponds to the 5th energy level. Therefore, the number of wavelengths matches with the formula derived in part **B**. Below is a qualitative picture (node spacing, magnitude of wavefunction, and the wavefunction as $r \to 0$ and $r \to \infty$ *are not* depicted in this cartoon).



D. There is a semi-classical quantization rule (corrected for tunneling of the wavefunction into the classically forbidden $E < V_\ell(r)$ regions)

$$\int_{r_-(E_n)}^{r_+(E_n)} p_E(r)dr = \frac{h}{2}(n + 1/2)$$

that tells you

(i) The energy of the n^{th} level (by iterating E until the quantization condition is satisfied);

(ii) how many energy levels lie at or below whatever value of E you choose;

and *(iii)* what is the density of states, $\frac{dn}{dE}\Big|_E$, or

$$\frac{n(E + dE) - n(E - dE)}{2dE}.$$

Use the semi-classical quantization condition to find the energy levels of a harmonic oscillator. (You have to evaluate a do-able integral.)

Solution:

$$p(x) = \sqrt{2m(E_n - V(x))} \tag{4.1}$$

$$V(x) = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2 x^2 \tag{4.2}$$

Plugging Eq. (4.2) into Eq. (4.1)

$$p(x) = \sqrt{2m\left(E_n - \frac{1}{2}m\omega^2 x^2\right)}.$$

Turning points are when $E_n = V(x) = \frac{1}{2}m\omega^2 x^2$

$$x_+ = \sqrt{\frac{2E_n}{m\omega^2}}; \qquad x_- = -\sqrt{\frac{2E_n}{m\omega^2}}$$

$$\begin{aligned}
\int_{x_-(E_n)}^{x_+(E_n)} p_{E_n}(x)dx &= \int_{-\sqrt{\frac{2E_m}{m\omega^2}}}^{\sqrt{\frac{2E_n}{m\omega^2}}} \sqrt{2m\left(E_n - \frac{1}{2}m\omega^2 x^2\right)}dx \\
&= \int_{-\sqrt{\frac{2E_n}{m\omega^2}}}^{\sqrt{\frac{2E_n}{m\omega^2}}} \sqrt{2mE_n\left(1 - \frac{m\omega^2 x^2}{2E_n}\right)}dx \\
\text{Let } y^2 = \frac{m\omega^2 x^2}{2E_n} \longrightarrow dy &= \sqrt{\frac{m\omega^2}{2E_n}}dx
\end{aligned}$$

$$\int_{x_-(E_n)}^{x_+(E_n)} p_{E_n}(x)dx = \frac{2E_n}{\omega}\int_{-1}^{1}\sqrt{1-y^2}dy = \frac{E_n\pi}{\omega}.$$

Note: The above integral was evaluated by recognizing that $\sqrt{1-y^2}$ is the top half of the unit circle, and then simply dividing the area of a unit circle by 2.

$$\begin{aligned}
\int_{x_-(E_n)}^{x_+(E_n)} pE_n(x)dx = \frac{E_n\pi}{\omega} &= \frac{h}{2}\left(n + \frac{1}{2}\right) \\
E_n &= \hbar\omega\left(n + \frac{1}{2}\right).
\end{aligned}$$

These are the same energy levels that we have previously calculated using operator algebra for the harmonic oscillator.

E. What does the generalized de Broglie definition of $\lambda(r)$ tell you about the locations of nodes for $\ell = 0$ of the **H** atom?

(i) Compute the r value of the innermost internal node in $\chi_{n,\ell}(r)$ for $\ell = 0$, $n = 10$ and $n = 20$, where

$$E_{10s} = \frac{-hc\Re_H}{10^2}, \qquad \Re_H = 109679\ \text{cm}^{-1}.$$

This will show you that the innermost nodes for all $n \gtrsim 6$ members of any $n\ell$ Rydberg series occur at approximately the same value of r.

Solution:

$$\lambda(r) = \frac{h}{\sqrt{2m(E_{n\ell} - V_\ell(r)}}$$

Using atomic units, let $\hbar = m_e = 4\pi\epsilon_0 = e^- = 1$. Replace λ with $2r$ and $V_\ell(r)$ with $-\frac{1}{r}$:

$$\begin{aligned}
2r &= \frac{2\pi}{\sqrt{2\left(E_{n\ell} + \frac{1}{r}\right)}} \\
4r^2 &= \frac{(2\pi)^2}{2\left(E_{n\ell} + \frac{1}{r}\right)} \\
8r^2\left(E_{n\ell} + \frac{1}{r}\right) &= (2\pi)^2 \\
8E_{n\ell}r^2 + 8r - (2\pi)^2 &= 0 \\
r &= \frac{-8 \pm \sqrt{64 + 32E_{n\ell}(2\pi)^2}}{16E_{n\ell}} \\
E_{n_s} &= \frac{-hc\Re_H}{n^2} = \frac{1}{2n^2} \\
r &= \frac{-1 \pm \sqrt{1 + \pi^2\frac{1}{n^2}}}{\frac{1}{n^2}}
\end{aligned}$$

$\frac{1}{n^2} \ll 1$ when $n \geq 6$, therefore we can take a Taylor series expansion of our radical

$$\boxed{r = \frac{-1 \pm \left(1 + \frac{1}{2}\pi^2\frac{1}{n^2}\right)}{\frac{1}{n^2}} = \frac{\pi^2}{2}a_0}$$

Note that, because we were able to take a Taylor expansion, the radical due to the large energy denominator n does not appear in our final answer for the position of the first node. We can therefore conclude that the position of the first node is approximately independent of n, when $n \geq 6$.

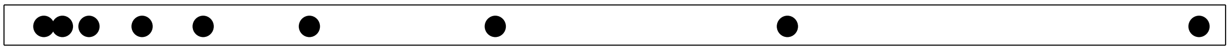
(ii) For $10s$, *sketch* the locations of all of the internal nodes. Which nodes are closest together and which are the furthest apart?

Solution:

10s will have 9 total nodes. We have already calculated the position of the first node. To determine the position of the second node, we must set $\lambda = r$.

$$
\begin{aligned}
r &= \frac{2\pi}{\sqrt{2\left(E_{n\ell}+\frac{1}{r}\right)}} \\
r^2 &= \frac{(2\pi)^2}{2\left(E_{n\ell}+\frac{1}{r}\right)} \\
2r^2\left(E_{n\ell}+\frac{1}{r}\right) &= (2\pi)^2 \\
2E_{n\ell}r^2 + 2r - (2\pi)^2 &= 0 \\
r &= \frac{-1 \pm \sqrt{1+8\pi^2\frac{1}{n^2}}}{\frac{1}{n^2}} \\
r_{\text{second node}} &= \frac{-1 \pm \left(1+\frac{4}{2}\pi^2\frac{1}{n^2}\right)}{\frac{1}{n^2}} = 2\pi^2 a_0 \\
r_{\text{third node}} &= \frac{-1 \pm \left(1+\frac{9}{2}\pi^2\frac{1}{n^2}\right)}{\frac{1}{n^2}} = \frac{9}{2}\pi^2 a_0
\end{aligned}
$$

Clearly, node spacing increases with node number.



The next sequence of questions (parts **F** through **J**) are *optional.* They will lead you to estimate the amplitudes of the lobes of $|\psi_{n\ell}(r)|^2$ between each pair of adjacent nodes.

F. The classical mechanical oscillator period for each $n\ell$ level may be estimated from

$$\tau_{n,\ell} = \frac{h}{E_{n+1/2,\ell} - E_{n-1/2,\ell}}.$$

Estimate the oscillation period for the $10s$ state.

Solution:

$$\tau_{n\ell} = h\left(\frac{10.5^2}{-hc\Re_H} + \frac{9.5^2}{hc\Re_H}\right) = \frac{500}{c\Re_H} = 152\ fs.$$

G. Derive the time required for a classical electron to travel from the $(n-1)^{\text{th}}$ to the $(n+1)^{\text{th}}$ internal node with reference to the equations below:

$$r \text{ of the n}^{\text{th}} \text{ node is denoted as } r_{[n]}$$

$$\lambda\left(r_{[n]}\right) = \frac{h}{p\left(r_{[n]}\right)}$$

$$\nu\left(r_{[n]}\right) = p\left(r_{[n]}\right)/\,m_e$$

$$\Delta t_{[n]} = \frac{\lambda\left(r_{[n]}\right)}{\nu\left(r_{[n]}\right)}.$$

Solution:

$$\Delta t_{[n]} = \frac{\lambda(r_{[n]})}{v(r_{[n]})} = \frac{hm_e}{p(r_{[n]})^2} = \frac{h}{2\left(E_{n\ell} - V_\ell(r)\right)}$$

H. The *probability* of finding a classical particle moving at positive velocity between the $(n-1)^{\text{th}}$ and $(n+1)^{\text{th}}$ nodes is

$$\frac{\Delta t_{[n]}}{\tau_{n,\ell}}.$$

$\lambda^*_{n,\ell}(r)\lambda_{n,\ell}(r)$ is an oscillatory function, oscillating between 0 and twice the node–to–node probability. Estimate $\psi^*_{n,\ell}\left(r_{[n]}\right)\psi_{n,\ell}\left(r_{[n]}\right)$ and $\left|\psi_{n,\ell}\left(r_{[n]}\right)\right|$.

Solution:

$$\psi_{n\ell}^{*}\left(r_{[n]}\right)\psi_{n\ell}\left(r_{[n]}\right) \propto \frac{\Delta t_{[n]}}{2\tau_{n\ell}} = \frac{E_{n+\frac{1}{2}\ell} - E_{n-\frac{1}{2}\ell}}{2(E_{n\ell} - V_{\ell}(r))}$$

I. How would you use the results that you have derived here to estimate the expectation value of r^k for any value of k [**HINT**: a sum of each node-to-node region]

$$\left\langle r^k \right\rangle = \int_{-\infty}^{\infty} \psi_{n,\ell}^{*} r^k \psi_{n,\ell} dr?$$

Solution

No solution given.

J. For non-hydrogenic atoms, it is possible to replace the Rydberg equation (integer-n) by

$$E_{n^*,\ell} = -\frac{hc\Re}{n_{\ell}^{*2}}$$
$$n_{\ell}^{*} = n - \delta_{\ell}$$

where δ_{ℓ} is the "quantum defect." n_{ℓ}^{*} can be determined empirically from

$$E_{\infty} - E_{n^*\ell} = \frac{hc\Re}{n_{\ell}^{*2}}$$
$$n^* = \left[\frac{hc\Re}{E_{\infty} - E_{n^*\ell}}\right]^{1/2}$$

and

$$[E_{n^*\ell} - E_{n^*\ell-1}] \approx \frac{2hc\Re}{\left(n_{\ell}^{*}\right)^3}.$$

Are these semi-classical equations sufficient to *approximate* the expected values of all properties of all Rydberg states of all atoms?

Solution

No solution given.

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