

5.61 Fall 2017
Problem Set #6

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

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

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 always

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

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

$$x_{v',v} \equiv \int dx \psi_{v'}^* \hat{x} \psi_v$$

integrals.

F. Using the value you found for $x_{v',v}$ write all of the E_0 -dependent values for $\widehat{\mathbf{H}}_{v',v}^{(1)}$ 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

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

G. Using $\frac{d^2 E_v}{dE_0^2}$ 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 $\{\psi_v^{(1)}\}$, compute μ_v using

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

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. Some Short Answer Questions

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

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

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

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

(i) \mathbf{a}^\dagger

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

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

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

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

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

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

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

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:

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

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

$$\omega = (k/\mu)^{1/2}$$

$$\tilde{\omega} = \frac{(k/\mu)^{1/2}}{2\pi c}$$

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

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

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

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 $(\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger)^3$ 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 $\tilde{\omega}\tilde{y} = 0$.]

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 $(\hat{\mathbf{a}} + \hat{\mathbf{a}}^\dagger)^4$ through second-order perturbation theory.

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 2nd 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?

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 .

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?

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

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, $\frac{dn}{dE}|_E$, 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.)

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

$$E_{10s} = \frac{-hc\mathfrak{R}_H}{10^2}, \quad \mathfrak{R}_H = 109679 \text{ cm}^{-1}.$$

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 .

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

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.

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

$$\begin{aligned} \lambda(r_{[n]}) &= \frac{h}{p(r_{[n]})} \\ \nu(r_{[n]}) &= p(r_{[n]})/m_e \\ \Delta t_{[n]} &= \frac{\lambda(r_{[n]})}{\nu(r_{[n]})}. \end{aligned}$$

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 $\psi_{n,\ell}^*(r_{[n]})\psi_{n,\ell}(r_{[n]})$ and $|\psi_{n,\ell}(r_{[n]})|$.

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]

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

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

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

$$n_\ell^* = n - \delta_\ell$$

where δ_ℓ is the “quantum defect.” n_ℓ^* can be determined empirically from

$$E_\infty - E_{n^*\ell} = \frac{hc\mathcal{R}}{n_\ell^{*2}}$$

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

and

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

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

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