Suggested Reading: McQuarrie, Chapters 8.4–8.5

1. Harmonic Oscillator Subject 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

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

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 $x_{\min}$, $V(x_{\min})$, 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

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

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. Some Short Answer Questions

A. Evaluate the following integrals for ψ_{JM} eigenfunctions of $\mathbf{J}^2$ and $\mathbf{J}_z$.

(i) $\int \psi_{22}^* \left(\widehat{\mathbf{J}}^+\right)^4 \psi_{2,-2} d\tau$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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.

A Note about Phase Ambiguity

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

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

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.

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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 $E_{n,\ell}$:

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

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 nth level (by iterating E until the quantization condition is satisfied);

(ii) how many energy levels lie at or below E; 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.)

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.

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

Parts **F** through **J** are *optional*

The next sequence of questions 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

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

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:

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

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

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

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

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 $\left|\psi_{n,\ell}\left(r_{[n]}\right)\right|$.

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]

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

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

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

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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