Problem Set #2 – Time Independent Perturbation Theory

Due Tuesday, Feb. 8, 2011

Problem 1: The ro-vibrational spectrum of diatomic atoms (15 points)

   Consider a diatomic molecule. In the Born-Oppenheimer approximation such that the nuclei move much more slowly than the electrons, the nuclei see an effective static potential $U(r)$, where r is the relative coordinate. Making the usual separation of variables between center of mass of relative coordinates for this two-body problem, the Hamiltonian for the reduced mass μ is,

$$\hat{H} = \frac{\hat{p}_r^2}{2\mu} + \frac{\hbar^2 l(l+1)}{2\mu r^2} + U(\hat{r}).$$

Assuming an attractive potential for large separations and repulsive for short range, there can be bound states which form the molecule. The may appear as the figure below.
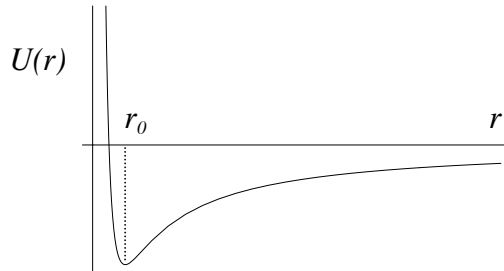
(a) Near r_0, the classical equilibrium point, the potential looks harmonic. Perform a Taylor series expansion to fourth order in $\delta r = r - r_0$, and show that the Hamiltonian has the form of a one-dimensional SHO, plus perturbation:

$$\hat{H} = \hat{H}_0 + \hat{H}_1,$$

$$\hat{H}_0 = \frac{\hat{p}_r^2}{2\mu} + \frac{1}{2}k(\delta\hat{r})^2 + \frac{\hbar^2 l(l+1)}{2\mu r_0^2} + U(r_0), \qquad\qquad \text{where } k = \left.\frac{d^2 U}{dr^2}\right|_{r=r_0}, etc.$$

$$\hat{H}_1 = \frac{1}{3}k'(\delta\hat{r})^3 + \frac{1}{4}k''(\delta\hat{r})^4 - \frac{\delta\hat{r}\,\hbar^2 l(l+1)}{\mu r_0^3} + \frac{3}{2}\frac{(\delta\hat{r})^2\,\hbar^2 l(l+1)}{\mu r_0^4},$$

and thus the zeroth order energy eigenvalues are: $E_{v,l}^{(0)} = \hbar\sqrt{\dfrac{k}{\mu}}\left(v + \dfrac{1}{2}\right) + \dfrac{\hbar^2 l(l+1)}{2\mu r_0^2} + U(r_0)$, with v

an integer (the vibration quantum number).

(b) Find the appropriate scale length x_0, and from this the energy scale, to make the
    dimensionless Hamiltonian (here in the position representation),

$$h = h_0 + h_1,$$

$$h_0 = -\frac{1}{2}\frac{d^2}{dy^2} + \frac{1}{2}y^2 + \frac{l(l+1)}{2r_0^2}\frac{1}{\sqrt{\mu k}} + \frac{U(r_0)}{\hbar}\sqrt{\frac{\mu}{k}},$$

$$h_1 = \frac{1}{3}k'\frac{y^3}{(k^5\mu)^{1/4}} + \frac{1}{4}k''\frac{y^4}{(k^3\mu)^{1/2}} - \frac{y\,l(l+1)}{r_0^3(k\mu)^{3/4}} + \frac{3}{2}\frac{y^2\,l(l+1)}{k\mu r_0^4},$$

where $y = \delta r / x_0$
and I have set, $\hbar \equiv 1$.

(c) Find the first order corrections to the energy levels as a function of v and l.
    Of the four terms in the sum h_1, the last two involve a coupling of the rotational and
    vibrational motion. The last in particular has a large contribution in first order and is called
    the "rotational-vibrational" interaction.

Consider the hydrogen diatomic molecule (H_2). Note that this molecule has no electric dipole
moment, so its vibration-rotation radiation is inhibited. However, the spectrum exists, and has
been seen in radio telescopes from H_2 in space and by laser spectroscopy of earth. The selection
rules for this radiation (as we will derive later in class) are $\Delta l = \pm 2$ and $\Delta v = \pm 2$.
The H_2 molecule has the following properties:

$$r_0 = 0.75\,\text{Å},\ k = 5.2\ \text{Newtons/cm},$$

bond strength = binding energy of molecule = 102 kilocalories/mole

The deuterium molecule D_2 has the same parameters except the bond strength is 104 kCal/mole.

(d) Calculate the wavelength of the $\Delta v = 2$ $\Delta l = 0$ line and the $\Delta v = 0$ $\Delta l = 2$ line in H_2 (excluding
the perturbations).

(e) Account for the difference in bond strength between the hydrogen and deuterium molecule.

Problem 2: The ac-Stark effect (15 points)

Suppose an atom is perturbed by a monochromatic electric field oscillating at frequency ω_L $\mathbf{E}(t) = E_z \cos(\omega_L t)\mathbf{e}_z$ (such as from a linearly polarized laser), rather than the dc-field studied in class. We know that such field can be absorbed and cause transitions between the energy levels; we will systematically study this effect later in the semester. The laser will also cause a *shift* of energy levels of the unperturbed states, known alternatively as the "ac-Stark shift", the "light shift", and sometimes the "Lamp shift" (don't you love physics humor). In this problem, we will look at this phenomenon is the simplest case that the field is near to resonance between the ground state $|g\rangle$ and some excited state $|e\rangle$, $\omega_L \approx \omega_{eg} \equiv (E_e - E_g)/\hbar$, so that we can ignore all other energy levels in the problem (the "two-level atom" approximation).

(i) <u>The classical picture</u>. Consider first the "Lorentz oscillator" model of the atom – a charge on a spring – with natural resonance ω_0.
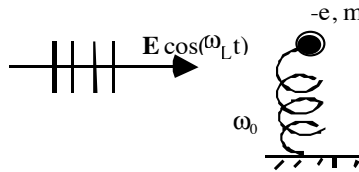
The Hamiltonian for the system is $H = \dfrac{p^2}{2m} + \dfrac{1}{2}m\omega_0^2 z^2 - \mathbf{d} \cdot \mathbf{E}(t)$, where $d = -ez$ is the dipole.

(a) Ignoring damping of the oscillator, use Newton's Law to show that the induced dipole moment is

$$\mathbf{d}_{induced}(t) = \alpha \mathbf{E}(t) = \alpha E_z \cos(\omega_L t),$$

where $\alpha = \dfrac{e^2/m}{\omega_0^2 - \omega_L^2} \approx \dfrac{-e^2}{2m\omega_0 \Delta}$ is the polarizability with $\Delta \equiv \omega_L - \omega_0$ the "detuning".

(b) Use your solution to show that the total energy store in the system is ,

$$H = -\frac{1}{2}d_{ind}(t)E(t) = -\frac{1}{2}\alpha E^2(t) \text{, or a time average value } \overline{H} = -\frac{1}{4}\alpha E_z^2$$

Note, the factor of 1/2 arise because energy is required to *create* the dipole.

(ii) Quantum picture. We consider the two-level atom described above. As we will derive later, the Hamiltonian for this system can be written in a time independent form (equivalent to the time-averaging done in the classical case)

$$\hat{H} = \hat{H}_{atom} + \hat{H}_{int} ,$$

where $\hat{H}_{atom} = -\hbar\Delta|e\rangle\langle e|$ is the "unperturbed" atomic Hamiltonian, and

$\hat{H}_{int} = -\dfrac{\hbar\Omega}{2}\big(|e\rangle\langle g| + |g\rangle\langle e|\big)$ is the dipole-interaction with $\hbar\Omega \equiv \langle e|\mathbf{d}|g\rangle \cdot \mathbf{E}$ (the Rabi frequency).

(a) Find the *exact* energy eigenvalues and eigenvectors for this simple two-dimensional Hilbert space and plot the levels as a function of Δ. These are known as the atomic "dressed states".

(b) Expand your solution in (a) to lowest nonvanishing order in Ω to find the perturbation to the energy levels. Under what condition is this expansion valid?

(c) Confirm your answer to (b) using perturbation theory. Find also the mean induced dipole moment (to lowest order in perturbation theory), and from this show that the atomic

polarizability, defined by $\langle\mathbf{d}\rangle = \alpha\mathbf{E}$ is $\alpha = \dfrac{-\big|\langle e|\mathbf{d}|g\rangle\big|^2}{\hbar\Delta}$, so that the second order perturbation

to the ground state is $E_g^{(2)} = -\dfrac{1}{4}\alpha E_z^2$ as in part (b).

(d) Show that the ratio of the polarizability calculated classical in (b) and the quantum expression in (c) has the form

$$f \equiv \dfrac{\alpha_{quantum}}{\alpha_{classical}} = \dfrac{\big|\langle e|z|g\rangle\big|^2}{\big(\Delta z^2\big)_{SHO}} , \text{ where } \big(\Delta z^2\big)_{SHO} \text{ the SHO zero point variance.}$$

This ratio is known as the oscillator strength.

Lessons:

- In lowest order perturbation theory an atomic resonance look just like a harmonic oscillator, with a correction factor given by the oscillator strength.
- Harmonic perturbations cause energy level shifts as well as absorption and emission.