Problem Set 3. Mostly Spectroscopy.

1. The energies of the 2s, $2p_x$, $2p_y$, and $2p_z$ eigenfunctions of the Hydrogen atom are the same. **Show that any wavefunction with the form**

$$\Psi(\mathbf{r}) = a_{2s}\Psi_{2s}(\mathbf{r}) + a_{2p_x}\Psi_{2p_x}(\mathbf{r}) + a_{2p_u}\Psi_{2p_u}(\mathbf{r}) + a_{2p_z}\Psi_{2p_z}(\mathbf{r})$$

   is also an eigenfunction of the Hydrogen atom Hamiltonian. (This is, very roughly, the justification for "hybrid orbitals.")

2. A McMaster scientist interested in the pollution from steel mills uses the characteristic 248 nm absorption of SO_3 to determine its concentration in air at ambient temperature and pressure (T = 300 K; p = 1 bar). The time-correlation she postulates for pressure broadening is

$$P_{none}(t) = e^{-\frac{\kappa Pt}{\sqrt{T}}}$$

   with the constant κ determined from the collision theory of gasses,

$$\kappa = 4\sigma_{SO_3}^2\sqrt{\frac{\pi N_A}{M_{SO_3}}}$$

   where σ_{SO_3} is the collision diameter of SO3, M_{SO_3} is the molecular mass, and N_A is Avogadro's number. She estimates the collision diameter from the van der Waals b coefficient, using $\sigma = \left(\frac{3b}{2\pi N_A}\right)^{1/3}$, and looks up b (.1 L/mol) for SO_3.

   a. **If pressure broadening were dominant, what would be the width of the spectral line that she observes?**
   b. **If Doppler broadening were dominant, what would be the width of the spectral line that she observes.**
   c. **Which is the dominant effect here?**

3. We used time-dependent perturbation theory to derive the response of a system to a time-varying perturbation that was added to the Hamiltonian, $V(\tau,t)$. Suppose that this variation were, instead, time-independent. (Equivalently, the frequency of the perturbation is zero.) **Show that the first-order change in ground-state energy, when $\hat{H}$ is changed to $\hat{H} + V(\tau)$, is**

$$E_0(\hat{H} + V) - E_0(V) = \langle \Psi_0 | V(\tau) | \Psi_0 \rangle.$$

4. For a source with a broad and uniform band of frequencies, the relative intensity of two spectral absorption lines may be estimated from

$$I_{f,f'} = \frac{W_{f',i}}{W_{f,i}} \approx \left(\frac{\langle \Psi_{f'} | x | \Psi_i \rangle}{\langle \Psi_f | x | \Psi_i \rangle}\right)^2$$

   Consider the ground state ($i = 0$) of the one-dimensional particle with unit mass in a box of unit length. **Compute the relative absorptivity of the higher excited states ($f' = 3,4,5,\dots$)** **compared to the first excitation ($f = 2$).** (That is, calculate $I_{2,f'}$.) **Do the absorption lines become stronger or weaker as the transition energy increases? Can you give a simple pictorial explanation for this effect?**

5-7. This is a "classic" problem, wherein we relate what we have learned about spectroscopy to describe the populations of energy levels. This analysis actually dates all the way back to Einstein, who laid the groundwork for the discovery of the laser in 1917.

Let i denote the initial state of a system and f denote its final state; we assume the initial state has lower energy than the final state. Suppose the system is in equilibrium with an electromagnetic (=light) field, so that the number of molecules in the initial state, N_i, and the number of molecules in the final state, N_f. The rate at which molecules are excited from the initial state to the final state in the presence of light with energy density $g(\hbar\omega)$ should be proportional to the energy density of the light and the number of molecules in the initial state. Einstein wrote the constant of proportionality as B_{fi}, and so the excitation rate is

$$\text{rate of absorbance} = B_{fi} \cdot g\left(\hbar\omega_{fi}\right)N_i \tag{1}$$

We have noted that the rate of stimulated emission is the same as the rate of "stimulated" absorbance. Consequently, the rate of stimulate emission will be proportional to the energy density and the number of molecules in the final state, with the same constant of proportionality, $B_{if} = B_{fi}$. Thus

$$\text{rate of stimulated emission} = B_{fi} \cdot g\left(\hbar\omega_{fi}\right)N_f \tag{2}$$

As anyone who has ever done a spectrum (even looked at the sun) knows, however, a molecule is quite capable of fluorescing even in the total absence of incident radiation. This process, known as spontaneous emission of light,[1] is clearly independent of the energy density in the incident light field and is proportional to the number of molecules in the excited state. Of course, the constant of proportionality is probably different from the proportionality constant for stimulated emission, since the two processes are fundamentally different. So we write the constant of proportionality as A_{fi} and have.

$$\text{rate of spontaneous emission} = A_{if}N_f \tag{3}$$

A_{fi} and B_{fi} are called the Einstein rate coefficients. Clearly, both coefficients are positive. There is, obviously, no such thing as "spontaneous absorption."[2]

5a. Derive a formula for B_{fi} from Fermi's Golden Rule.

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[1]   What exactly is spontaneous emission? It is a quantum effect, and if we had used a quantum theory for light the phenomenon of spontaneous emission would have fallen out of the theory very naturally. Essentially, every field has a "zero-point" oscillation, and this is true even of the vacuum. The "vacuum oscillation" is associated with the creation and annihilation of a particle (or particles) in time, and can occur so long as the energy times the duration for which the particles exist is suitably small. More precisely, one has that $\Delta E \Delta t \geq \frac{\hbar}{2}$. So that a photon can "be created" provided it is "destroyed" again quickly enough. If the photon, however, stimulates a transition during its fleeting existence, after the "stimulating" photon has disappeared, the "stimulated" photon will still exist. Voila, "spontaneous" emission.

[2]   This is not quite true, but it doesn't matter for our purposes.

We can write the rate of change for the number of atoms in the initial and final states in terms of the Einstein coefficients.

$$\frac{dN_i}{dt} = -B_{fi} g\left(\hbar\omega_{fi}\right) N_i + B_{fi} g\left(\hbar\omega_{fi}\right) N_f + A_{fi} N_f \tag{4}$$

$$\frac{dN_f}{dt} = +B_{fi} g\left(\hbar\omega_{fi}\right) N_i - B_{fi} g\left(\hbar\omega_{fi}\right) N_f - A_{fi} N_f \tag{5}$$

5b.   Comparing Eqs. (4) and (5), why is $N_i > N_f$?

At equilibrium, $\frac{dN_i}{dt} = \frac{dN_f}{dt} = 0$. Setting Eqs. (4) and (5) equal to one another,

$$-B_{fi} g\left(\hbar\omega_{fi}\right) N_i + B_{fi} g\left(\hbar\omega_{fi}\right) N_f + A_{fi} N_f = B_{fi} g\left(\hbar\omega_{fi}\right) N_i - B_{fi} g\left(\hbar\omega_{fi}\right) N_f - A_{fi} N_f \tag{6}$$

$$\frac{N_f}{N_i} = \frac{B_{fi} g\left(\hbar\omega_{fi}\right)}{B_{fi} g\left(\hbar\omega_{fi}\right) + A_{fi}} \tag{7}$$

5c.   Suppose the light source is very intense, so that $B_{fi} g\left(\hbar\omega_{fi}\right)$ is much larger than A_{fi}. Show that

$$\frac{N_f}{N_i} \approx 1 - \frac{A_{fi}}{B_{fi} g\left(\hbar\omega_{fi}\right)} \tag{8}$$

5d.   Explain why, in a very intense light source, there is essentially no net absorbance of radiation. That is, why will light of frequency ω_{fi} shine "right through" a sample if it is strong enough.

We would like to find an expression for A_{fi}, but we don't want to have to do it the "right way" and consider the quantum theory of light. One way to do this is to put our system in an oven. (I.e., we put our system inside a black body.) Then, the relative populations of the final and initial states are given by the Boltzmann distribution, so

$$\frac{N_f}{N_i} = e^{-\hbar\omega_{fi}/kT} \tag{9}$$

where k is Boltzmann's constant and T is the absolute temperature. The other unknown in Eq. (7) is the energy density of the light source. However, the molecule is in an oven, so the light source is the black-body radiation from the oven's walls and, assuming these are also at temperature T (that is, our oven is perfectly insulated), we can use the black-body radiation law

$$g\left(\hbar\omega_{fi}\right) = \frac{2\hbar\omega_{fi}^3}{\pi c^3} \cdot \left[e^{\hbar\omega_{fi}/kT} - 1\right]^{-1} \tag{10}$$

Substituting these results into Eq. (7) gives

$$e^{-\hbar\omega_{fi}/kT} = \frac{B_{fi}\frac{2\hbar\omega_{fi}^3}{\pi c^3}\cdot\left(e^{\hbar\omega_{fi}/kT}-1\right)^{-1}}{B_{fi}\frac{2\hbar\omega_{fi}^3}{\pi c^3}\cdot\left(e^{\hbar\omega_{fi}/kT}-1\right)^{-1}+A_{fi}}$$

$$e^{\hbar\omega_{fi}/kT} = 1 + \frac{A_{fi}}{B_{fi}\frac{2\hbar\omega_{fi}^3}{\pi c^3}\cdot\left(e^{\hbar\omega_{fi}/kT}-1\right)^{-1}} \tag{11}$$

$$A_{fi} = \frac{2\hbar\omega_{fi}^3}{\pi c^3}B_{fi}.$$

6. **The red-orange glow of hot hydrogen gas is due to the 3p-2s transition of the Hydrogen atom, $A_{fi} = 6.7\cdot 10^7\,\frac{1}{s}$. Compute $\frac{N_f}{N_i}$ and $\frac{A_{3p,2s}}{g(\hbar\omega)B_{3p,2s}}$ at $T = 300\,\text{\textdbend}K$, $T = 10{,}000\,\text{\textdbend}K$, and $T = 100{,}000\,\text{\textdbend}K$. What can you say about the relative rates of spontaneous emission, A_{fi} and stimulated emission, $B_{fi}g\left(\hbar\omega_{fi}\right)$ in the absence of incident light?**

How does a laser work? As a very simple case, we consider the "green line" for the Argon ion laser. This resembles a 3-level laser system, which is the simplest (but four-level lasers are more efficient) type of laser. The Argon ion is generated by a a high-voltage electric discharge, which ionizes the Argon atom and excites it to a high-energy state, which then relaxes to the $^4D_{5/2}$ state. This state then decays to the ground state $^2P_{3/2}$. However, because we have brought in a "third state" (the highly excited ion), we can achieve population inversion. This is helped by the fact that the excited state of interest decays very slowly (this is a spin-forbidden transition), so that A_{fi} is very small.

As an example that we can actually "solve", we might consider a three-level system like the one shown below, which (vaguely) resembles the intensity-determining features of a four-level laser like the Nd-YAG laser. In this case, the system is "pumped" with light of frequency ω_{31}, and then population inversion is achieved between the second and third states, causing a laser transition. We can write the rate coefficients as

$$\frac{dN_1}{dt} = -g\left(\hbar\omega_{31}\right)B_{31}N_1 + A_{21}N_2 + A_{31}N_3 + g\left(\hbar\omega_{31}\right)B_{31}N_3$$

$$\frac{dN_2}{dt} = A_{32}N_3 - A_{21}N_2 \tag{12}$$

$$\frac{dN_3}{dt} = g\left(\hbar\omega_{31}\right)B_{31}N_1 - A_{32}N_3 - A_{31}N_3 - g\left(\hbar\omega_{31}\right)B_{31}N_3$$

As before, at equilibrium $\frac{dN_1}{dt} = \frac{dN_2}{dt} = \frac{dN_3}{dt} = 0$. From the second equation we find that

$$\frac{N_3}{N_2} = \frac{A_{21}}{A_{32}} \tag{13}$$

Equation (13) is a general result, and can be easily understood (we probably could have guessed it). Clearly, we can have a laser only if $N_3 > N_2$, and it is best if N_3 is much greater than N_2 ($N_3 \gg N_2$).

7a. **From Eq. (13), what can you say about the relative spontaneous emission rates for the "higher" and "lower" energy states in a laser?**

7b. **Based on Eq. (13), why do laser lines usually correspond to "forbidden transitions."**

For example, except for the slight perturbation inflicted on the Nd^{3+} ion by the $Y_3Al_5O_{12}$ lattice, the popular Nd-YAG laser transition corresponding to A_{32} is electric dipole forbidden, magnetic dipole forbidden, electric quadrupole forbidden, and magnetic quadrupole forbidden, while the transition corresponding to A_{21} is electric dipole allowed.

8-10. Lifetime Broadening

Most of the effects that broaden spectral lines could be eliminated, in principle, by taking a spectrum at zero temperature and zero pressure and, in fact, high-resolution spectra are often taken under ultra-high vacuum conditions at liquid-helium temperatures. However, there is always a "homogeneous broadening" associated with spontaneous emission: there is no way to avoid the "decay time" associated with spontaneous emission, as it is an inherent property of the system.[3]

The rate of spontaneous decay is given by Eq. (11), and in order to relate this to expressions for homogeneous broadening we need to find the probability, $P(\tau)$ that a molecule in its excited state at $t = 0$ will still be in its excited state at $t = \tau$. The rate of transition is known from Eq. (5), and so the probability a molecule in its excited state at time $t = \tau$ "emits" to the ground state (or, more properly, state i), is proportional to the number of molecules in the excited state (which is proportional to $P(\tau)$ if the light source measuring the absorption spectrum is not very powerful), so we have

$$dP\left(\tau\right) = -A_{fi}P\left(\tau\right)d\tau \tag{1}$$

8. **Show that** $P(\tau) = e^{-A_{21}\tau}$ **.**

The natural lifetime of an excited state is defined as the time it takes for $P(\tau)$ to decay from $P(0) = 1$ to $P(\tau) = \frac{1}{e}$ in the absence of external fields. So the lifetime of a state is

$$\tau \equiv \frac{1}{A_{21}} \tag{2}$$

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[3] This is a lie. There is a weird quantum-mechanical result that says that if you constantly observe a system it can never change its state. For obvious reasons, it is called the "watched pot paradox." But "constantly observing" a system is extremely difficult and is not done in the context of chemical spectroscopy.

9a. **Referring to your notes on homogeneous broadening in the notes, show that the line shape is given by**

$$I(\omega) \equiv \sum_{i=0}^{\infty} \sum_{f=0}^{\infty} \frac{p_i}{8\pi} \left| \left\langle \Phi_f \left| \hat{\mu}_x \right| \Phi_i \right\rangle \right|^2 \left(\frac{(A_{21})}{A_{21}^2 + (\omega - \omega_{fi})^2} - \frac{(A_{21})}{A_{21}^2 + (\omega + \omega_{fi})^2} \right). \tag{3}$$

If we assume that the initial state is the ground state ($i = 0$), that the incident light is very weak (so $p_0 \approx 1$ and $p_f \approx 0$), we find that

$$I(\omega) \equiv \frac{1}{8\pi} \left| \left\langle \Phi_f \left| \hat{\mu}_x \right| \Phi_i \right\rangle \right|^2 \left(\frac{(A_{f0})}{A_{f0}^2 + (\omega - \omega_{fi})^2} - \frac{(A_{f0})}{A_{f0}^2 + (\omega + \omega_{fi})^2} \right). \tag{4}$$

9b. **Plot Eq. (4), assuming that the "pre-factor" is equal to $\frac{1}{\pi}$.**

The full-width at half-maximum of the spectral line you just plotted is
$$2A_{21} = \frac{2}{\tau} \tag{5}$$
Putting the molecule in any external field at all with broaden the line further and shorten the lifetime of the excited state. The error in frequency of the excited state, then, is always greater than
$$\Delta\omega \geq 2A_{21} = \frac{2}{\tau} \tag{6}$$
and so the energy uncertainty in the spectral line satisfies the inequality
$$\Delta E \equiv \hbar \Delta\omega \geq \hbar \frac{2}{\tau}$$
$$\tau \Delta E \geq \frac{\hbar}{2} \tag{7}$$
Equation (7) is sometimes called the "energy-time" Heisenberg uncertainty principle but it should be clear that it is really just a manifestation of the fundamental relationship from the Fourier transform, which is usually stated
$$\Delta t \cdot \Delta\nu \geq \frac{1}{2} \tag{8}$$
One of the most important uses of spectral states with long lifetimes is the laser, as discussed in the previous problem. Another important use is in the measurement of time. The *definition* of a second is that the time it takes for 9192631770 periods of the oscillation associated with the hyperfine splitting in the ^{133}Cs atom. (This is the basis of the "atomic clocks" used in satellite positioning systems.)

Clearly, in order to define a "second" in this way we must know the frequency of an oscillation very accurately, and this can only be done if width of the spectral line corresponding to a transition is very, very small.

The longest lived electronic excited state we know of is the $^2F_{7/2}$ to $^2S_{1/2}$ transition for

$^{172}Yb^+$, which has a characteristic wavelength of $467\ nm$ and a lifetime of about 8.4 years. (The

transition is electric *octupole* allowed.) According to Eq. (8), we should be able to measure the frequency of the transition with an error of only about

$$\Delta\nu \approx \tfrac{1}{2\tau} \qquad\qquad (9)$$

and, in practice, we can do slightly better than this.

10a. **Approximate the inherent uncertainty in the frequency of the $^2F_{7/2}$ to $^2S_{1/2}$ transition. What is the relative error in the frequency of the transition?**

10b. **What is the inherent error in the period of this oscillation? How many oscillations are there (roughly) per second? What is the theoretical limit on the accuracy with which the number of oscillations per second can be measured?**

10c. **What is the approximate error in the wave length? What is the relative error in the wavelength? (You can compute this by computing the wavelength for $\nu + \Delta\nu$ and ν, and comparing.)**

We can compare this transition to a (typical) transition in $^{172}\text{Yb}^+$. For example, the $^2P_{1/2}$ to $^2S_{1/2}$ transition has a wavelength of 369 nm and a lifetime of 8 ns.

10d. **Approximate the inherent uncertainty in the frequency of the $^2P_{1/2}$ to $^2S_{1/2}$ transition.**

10e. **What is the approximate absolute error in the wave length in this transition?**

Note that states with long lifetimes have "very pure" frequencies and wavelengths—they give very monochromatic light. This is yet another reason why, in designing lasers, one tends to prefer states with long lifetimes as the "initial state" for stimulated emission.