PHYS3022 Applied Quantum Mechanics Problem Set 5 Due: 22 March 2019 (Friday).
"T+2 = 25 March 2019"

All problem sets should be handed in not later than 5pm on the due date. Drop your assignments in the PHYS3022 box outside Rm.213.

Please work out the steps of the calculations in detail. Discussions among students are highly encouraged, yet it is expected that we do your homework independently.

5.0 **Reading Assignment.** For atomic transitions, including (stimulated) absorption, stimulated emission and spontaneous emission, see *Modern Physics* (e.g. by Taylor, Zafiratos, Dubson; and by Harris) for the big picture and physical ideas. We discussed time-dependent perturbation theory. The discussion follows that in *Introduction to Quantum Mechanics* by Griffiths, and *An Introduction to Theory and Applications of Quantum Mechanics* by Yariv. We applied the theory to transition rates, Einstein's A and B coefficients, and the life time of excited states. We started to discuss the Physics of Molecules. The first part introduces the general QM problem of a molecule and the very clever Born-Oppenheimer approximation, which separates the molecular QM problem into two parts. The electronic part takes the nuclei as fixed (in principle should try different nuclei separations). The results include a preferred separation (bond length) and the the electronic wavefunction provides the chemical bond, which in turn gives the spring that model a bond about which the nuclei vibrate and rotate. The electronic part is usually handled by LCAO (linear combination of atomic orbitals). See the chapter on molecules in *Modern Physics* (e.g. by Taylor, Zafiratos, Dubson; and by Harris) for physics contents. We treated the QM in LCAO more completely. The discussion on MO follows that in *Physical Chemistry* by McQuarrie and *Quantum Chemistry and Spectrocopy* by Thomas Engel.

Time-dependent Perturbation Theory and Atom-light Interaction

5.1 **Deriving the equation for $da_i(t)/dt$ for a 3-state system - Practicing your QM manipulation**

Background: In developing the time-dependent perturbation theory (in class and in class notes), we focused on a two-state system and developed the equation(s) for the time evolution of the coefficients $da_i(t)/dt$ for $i = 1, 2$.

Let's consider a 3-state system, with states labelled 1,2, and 3. In the presence of $\hat{H} = \hat{H}_0 + \hat{H}'(t)$, where $\hat{H}'(t)$ has a time-dependence (as well as a spatial dependence), the general form of the wavefunction is

$$\Psi(x,t) = \sum_{i=1,2,3} a_i(t)\ \psi_i(x) e^{-iE_i t/\hbar} \tag{1}$$

where the effects of $\hat{H}'(t)$ is put into the time-dependence of the coefficients and ψ_i and E_i are eigenstates and eigenvalues of the $\hat{H}_0$ part of the Hamiltonian.

(a) **Substitute** Eq. (1) into the time-dependence Schrödinger Equation and **obtain** the equations governing da_1/dt, da_2/dt, and da_3/dt. [Note that the equations are (i) general, and (ii) applicable to any initial conditions.]

(b) For the initial condition $a_1(0) = 1$, $a_2(0) = 0$, and $a_3(0) = 0$, **write down** the equations for obtaining $a_1(t)$, $a_2(t)$, and $a_3(t)$ to the lowest order (also called leading order) in $\hat{H}'(t)$.

5.2 **The form of $|a_2(t)|^2$ for transitions from state 1 to a group of final states**

Background: Let's go back to 2-state system as discussed in class. After getting $da_2(t)/dt$ and assuming $a_1(t) \approx 1$, we obtained the following expression for an incident EM waves polarized in the z-direction, i.e., $\vec{\mathcal{E}}_0 = \mathcal{E}_0\hat{z}$. After integration over time from 0 (when $\hat{H}'(t)$ is switched on) to time t, we obtained

$$\begin{aligned} |a_2(t)|^2 &= e^2\mathcal{E}_0^2|z_{21}|^2 \frac{\sin^2[\frac{1}{2\hbar}(E_2 - E_1 - \hbar\omega)t]}{(E_2 - E_1 - \hbar\omega)^2} \\ &= \frac{e^2\mathcal{E}_0^2}{\hbar^2}|z_{21}|^2 \frac{\sin^2[\frac{1}{2}(\omega_{21} - \omega)t]}{(\omega_{21} - \omega)^2} \end{aligned} \tag{2}$$

where $\omega_{21} = (E_2 - E_1)/\hbar$ is set by the energy difference between the initial state "1" and final state "2". Eq. (2) works for **monochromatic light** of angular frequency ω polarized in the $\hat{z}$-direction for a transition **from one initial state "1" to one final state "2"**. It is the starting point for deriving several other results.

One thing we did was the case of a **non-monochromatic light source** with a spread in the angular frequencies. In that case, we summed up their contributions to $|a_2(t)|^2$ and found

$$|a_2(t)|^2 = \frac{\pi e^2}{\epsilon_0\hbar^2}|z_{21}|^2\, t\, U(\omega_{21}) \tag{3}$$

and hence the transition probability per unit time (rate) per atom as

$$\lambda_{1\to 2} = \frac{\pi e^2}{\epsilon_0\hbar^2}|z_{21}|^2\, U(\omega_{21}) \tag{4}$$

where $U(\omega_{21})$ is the energy density of the incident energy right at the frequency ω_{21} defined by $(E_2 - E_1)/\hbar$. In going from Eq. (2) to Eq. (3), we looked at the time-dependent function in Eq. (2) as a function of ω for a fixed ω_{21} (i.e. given two states). Eq. (4) is also related to Einstein's B coefficient.

Your Action: Let's start from Eq. (2) again. We consider the case of a **monochromatic incident light** at ω with energy density $U(\omega)$. In many real systems, it so happens that starting from **an initial state** "1", the **transitions can go to a group of final states**. This will be the case of many degenerate final states. This happens readily in a solid. This is the physical scenario for you to work out here.

In this case, the time-dependent function in Eq. (2) can be regarded as a function of ω_{21} at fixed ω (and time t). Make a sketch of that function as a function of ω_{21}. The physical scenario under consideration implies that there is a spread in ω_{21} among the possible final states. There is a function called the **density of states** (in physics) where $g(\omega_{21})d\omega_{21}$ gives the number of states with the quantity $(E_2 - E_1)/\hbar$ falling within the interval ω_{21} to $\omega_{21} + d\omega_{21}$. By summing up the contributions from possible transitions (possible final states and many of them), **derive** an expression for $|a_2(t)|^2$ and **show** that the answer is linear in time t. Hence, **obtain** an expression for $\lambda_{1\to group\ of\ states}$ and **show** that the answer picks up $g(\omega)$ (i.e., the number of states with $(E_2 - E_1)/\hbar$ right at the incident frequency $\hbar\omega$. [Remark: The answer is another popular form of what is called the Fermi Golden rule.]

5.3 **Hydrogen atom's explicit "Matrix element" for transitions and selection rules** (Closely related to SQ19 in Week 8)

A key result of time-dependent perturbation theory is that a transition from a state 1 (or initial state) to a state 2 (or final state) occurs with a probability depending on a spatial integral

$$a_2(t) \propto \overline{\mathbf{r}_{2p_z,1s}} = \int \psi^*_{final}(\mathbf{r})\ \mathbf{r}\ \psi_{initial}(\mathbf{r})\ d^3r \tag{5}$$

together with a complicated function of time that gives the energy criterion (see Problem 5.2). Here, $\mathbf{r} = \vec{r}$. Eq. (5) comes from the interaction between the atom's **electric dipole moment** and the **incident light**, which is the most important mechanism. The integral is usually handled numerically for atoms and molecules. For the simplest case of a hydrogen atom, it is possible to evaluate it analytically. This integral plays an important role for stimulated processes AND spontaneous emission. The integral is a vector and at the end what it matters is the dot product of this vector and the electric field. The integral also governs which transitions are allowed and which not, i.e., the **selection rules**.

We know that for hydrogen, the transition between 1s and 2p is allowed. There are several 2p states. So let's be concrete. Consider the transition between the $2p_z$ state of $m_\ell = 0$ and the $1s$ ground state. Thus, $\psi_{2,1,0}(\mathbf{r})$ is the final state and $\psi_{1,0,0}(\mathbf{r})$ is the initial state. [In SQ19, TA considered transition between $(1,0,0)$ and $(2,1,1)$ states.]

(a) Writing $\mathbf{r} = x\hat{x} + y\hat{y} + z\hat{z} = r\sin\theta\cos\phi\ \hat{x} + r\sin\theta\sin\phi\ \hat{y} + r\cos\theta\ \hat{z}$, **evaluate the integral** in Eq. (5) explicitly for $\psi_{final}(\mathbf{r}) = \psi_{210}(\mathbf{r})$ and $\psi_{initial}(\mathbf{r}) = \psi_{100}(\mathbf{r})$. **Give** your answer in terms of the Bohr radius a_B. You should note that the answer is a vector.

(b) For (stimulated) absorption, consider an external field $\vec{\mathcal{E}} = \mathcal{E}\hat{z}$, i.e. incident light linearly polarized in z-direction. The perturbative term $\hat{H}'$ in the Hamiltonina is the dot product of the electric dipole moment $\vec{\mu}$ and the field, $-\vec{\mu}\cdot\vec{\mathcal{E}}$, which in turn is proportional to the dot product of $\overline{\mathbf{r}_{2p_z,1s}}$ and the field $\vec{\mathcal{E}}$. **Argue that** such a linearly polarized light can stimulate an absorption and thus the transition between 1s and 2p$_z$. **State** your result in terms of a selection rule.

(c) Now consider light propagating in the z-direction, i.e., the propagation vector $\vec{k} \parallel \hat{z}$. Thus, its electric field is on the x-y plane. In particular, circularly polarized light with its polarization (meaning: direction of $\vec{\mathcal{E}}$) specified by $\mathbf{e}^{+} \propto (\hat{x} + i\hat{y})$ or $\mathbf{e}^{-} \propto (\hat{x} - i\hat{y})$ has its electric field rotating with time (note that there is an time factor $e^{-i\omega t}$ in the field that gives the rotating behavior) at a fixed point in space. **Show** that circularly polarized light **cannot** lead to the 1s to 2p$_z$ transition. [Remark: SQ19 showed that $\mathbf{e}^{+} \propto (\hat{x} + i\hat{y})$ circularly polarized light can stimulate a transition from ψ_{100} to ψ_{211}. Thus, skillfully using the polarization of incident light can selectively induce transitions and thus put atoms into a particular excited state.]

Physics of Molecules

5.4 Selection rule: Transitions between harmonic oscillator states.

Let's rewrite Eq. (5) as

$$a_2(t) \propto \overline{\vec{\mu}_{fi}} = \int \psi^{*}_{final}(\mathbf{r})\ \vec{\mu}\ \psi_{initial}(\mathbf{r})\ d^3r \tag{6}$$

where we emphasized that it is the **electric dipole moment matrix element** that matters and $\vec{\mu}$ is the electric dipole moment (a vector).

This expression is **general**. It can be applied to different forms of initial and final states. Here, let's consider the initial and final states being 1D **harmonic oscillator states**. Such state carries a quantum number n. Practically, we need to consider transitions between one harmonic oscillator state n and another state n' in molecular physics. In Problem Set 2, we did integrals of x and x^2 between harmonic oscillator states. You may make use of the results in Problem Set 2.

The **Physical Situation** is: A particle experiences a potential energy function $U(x) \approx U(x_0) + \frac{1}{2}k(x-x_0)^2$ for $x \approx x_0$, and thus x_0 the classical equilibrium position where $U(x_0)$ is the minimum.

Thus, harmonic oscillator physics enters. The initial and final states in Eq. (6) are harmonic oscillator states $\psi_n(x - x_0)$. Depending on whether the particle is charged (and another particle at the origin is charged or not), there may be an electric dipole moment $\vec{\mu}$ that behaves like

$$\mu(x \approx x_0) = \mu_0 + \left.\frac{d\mu}{dx}\right|_{x=x_0} (x - x_0) \tag{7}$$

where μ_0 is a constant (e.g. $\mu_0 = qx_0$ for a charge $-q$ at $x = 0$ and a charge $+q$ at $x = x_0$) and the second term is a Taylor expansion about $x = x_0$ (e.g. gives how μ changes as the charge $+q$ oscillates about $x = x_0$). The vector sign is omitted because in 1D it is understood to be along the $\hat{x}$-direction.

(a) Let's consider only the constant μ_0 term. "**Evaluate**" the integral in Eq. (6) between different harmonic oscillator states.

(b) Let's consider the second term in the Taylor expansion in Eq. (7). **Write down** Eq. (6) for this term between different harmonic oscillator states. Hence, making use of previous results in Problem Set 2, **find the rule** that governs the initial and final states n and n' for allowed transitions. [Hint: You don't need to re-do the integrals, even you love to do them!]

[Remark: **Results in (a) and (b) are important! Take them with you.** They govern the transitions between vibrational states in molecules and how the interpretation of molecular spectrum. There is one complication. Part (a) says that a molecule with a **fixed and constant** electric dipole moment will not absorb (usually harmonic oscillator states have energy difference in the infrared) in IR range. Part (b) gives that if a molecule has an electric dipole moment that does not change as the atoms vibrate, then $\left.\frac{d\mu}{dx}\right|_{x=x_0} = 0$ and the molecule will not absorb through transitions between oscillator states. This is the case of a linear molecule of the form $-+-$ vibrating in the way that the two slightly negative parts stretches out in opposite directions on the line and back. Such vibrating **normal mode**, for example, will not lead to IR absorption. Part (b) also says when the electric dipole moment of a molecule **changes as it vibrates**, thus $\left.\frac{d\mu}{dx}\right|_{x=x_0} \neq 0$, then there will be transitions governed by the $(x - x_0$ term and the system is IR active. This is why CO_2 is greenhouse gas and O_2 is not. It is Quantum Mechanics at work!]

5.5 *KCl* - energetics

For two **ions** (not neutral atoms), an approximate expression for the potential energy as a function of the separation between the two ions is

$$PE = -\frac{e^2}{4\pi\epsilon_0 r} + \frac{b}{r^9} \tag{8}$$

(a) **Give** the physical meaning of the two terms. Obviously, $PE = 0$ when $r \to \cancel{0}$ $r \to \infty$. **What is the physical situation** that $r \to \cancel{0}$ refers to?

(b) **Sketch** PE as a function of r. $r \to \infty$

(c) Let $r = r_0$ be the separation that PE takes on the minimum value. **Express** the parameter b in terms of r_0.

(d) For *KCl* (potassium chloride), $r_0 = 2.79$ Å. **Calculate** PE of *KCl* at its equilibrium separation.

(e) If the ionization energy of 4.34 eV of potassium and electron affinity of 3.62 eV of chlorine are taken into account, **how would the sketch in part (b) be altered** so that zero energy refers to two neutral atoms far apart? **What would be** the estimate for the dissociation energy of *KCl*, which is the energy to break *KCl* into two neutral atoms far apart?

5.6 **From two ions to a solid: Adding up Coulombic terms in a 2D ionic crystal**

Consider a square lattice and put ions onto it so that a cation is surrounded by 4 anions and an anion is surrounded by 4 cations. It is meant to be an infinite lattice. The separation between nearest neighboring ions (lattice constant) is r_0.

(a) **Sketch** the array of oppositely charged ions to illustrate the arrangement.

(b) Sit on a cation (doesn't matter which one), then consider the coulomb energies due to the nearest anions (attractive), and then the next-nearest cations (repulsive), and then the next-next-nearest anions (attractive), and so on. **Show** that the coulomb energy u_c per ion can be expressed in the form

$$u_c = \frac{1}{2} \cdot \frac{e^2}{4\pi\epsilon_0 r_0} \text{(a series of alternating signs to be summed up)} \ , \tag{9}$$

and **give** the first 6 (minus, plus, minus, plus, minus, plus) terms at least.

Optional: NO bonus points Next, write a program to sum up the series to convergence (you need a way to generate the terms) and obtain a value. Is u_c positive or negative at the end, i.e., will it bind?

(c) **Not optional: Look up the value on the web.** The number is characteristic of the square lattice and it is called the Madelung constant. Different lattices have different Madelung constants. This is a section in solid state physics books.

(d) **Optional: NO bonus points** You did the square lattice. There are 5 possible 2D lattices, with the square lattice being the simplest one. Look up the other 4 lattices and work out the corresponding Madelung constants.