PHYS3022 APPLIED QUANTUM MECHANICS

SAMPLE QUESTIONS FOR DISCUSSION IN WEEK 8 EXERCISE CLASSES (4 - 8 March 2019)

The Sample Questions are designed to serve several purposes. They either review what you have learnt in previous courses, supplement our discussions in lectures, or closed related to the questions in an upcoming Problem Set. Students should be able to do the homework problems independently after attending the exercise class. **You should attend one exercise class session.** You are encouraged to think about (or work out) the sample questions before attending exercise class and ask the TA questions.

Progress: In Week 7, we started to discuss how light and matter (atoms) interact. In particular, we focus on the context of atomic transitions. The problem is an initial value problem with a **time-dependent perturbation in the Hamiltonian**. The technique involes the **time-dependent perturbation theory** and its consequences include selection rules, energy criteria for transitions to occur, stimulated absorption and stimulated emission rates. At the end, QM can calculate what Einstein called his B coefficients. Spontaneous emission is harder to understand within Schrödinger QM but progress can be made via Einstein's A and B coefficients and how they are related. With QM telling us what the B coefficient is, the relation gives us Einstein's A coefficient related to spontaneous emission.

SQ18 - Full equations for da_1/dt and da_2/dt in a two-level system under the influence of $\hat{H}'(t)$
SQ19 - Electric dipole matrix elements, forbidden and allowed transitions in hydrogen atom between $n = 1$ and $n = 2$ states

SQ18 *Full equations for da_1/dt and da_2/dt in a two-level system under the influence of $\hat{H}'(t)$*

In class and class notes, we focused on the context of a two-state system (a state 1 and another state 2) with the initial conditions $a_1(0) = 1$ and $a_2(0) = 0$, i.e., it is certain that the system is in state 1 at time 0. The perturbation term $\hat{H}'(\vec{r}, t)$ is time dependent and spatial dependent, and it kicks in for $t > 0$. For the electric dipole mechanism, $\hat{H}'(\vec{r}, t) = e\vec{\mathcal{E}}_0 \cdot \vec{r} \cos \omega t$.

We then derived the following equation for da_2/dt (which is Eq. (17) in class notes on page LMI-I-30):

$$i\hbar \frac{da_2}{dt} = a_1(t) e^{\frac{i}{\hbar}(E_2 - E_1)t} \int \psi_2^* \hat{H}' \psi_1 d^3r + a_2 \int \psi_2^* \hat{H}' \psi_2 d^3r \tag{1}$$

We have not given explicitly the corresponding equation for da_1/dt in class notes.

(a) **Show** that the equation for da_1/dt is given by

$$i\hbar \frac{da_1}{dt} = a_1(t) \int \psi_1^* \hat{H}' \psi_1 d^3r + a_2(t) e^{\frac{i}{\hbar}(E_1 - E_2)t} \int \psi_1^* \hat{H}' \psi_2 d^3r \tag{2}$$

Equations (1) and (2) are exact, i.e., no approximations have been made so far. Note the parallelism between the two equations. [Thus, it will be easy to write down all equations even when there are more levels.]

Typically, the perturbation $\hat{H}'(\vec{r}, t)$ connects two **different** states, i.e., $\int \psi_n^* \hat{H}' \psi_n d^3r = 0$ in most problems. Under this condition, **write down** the set of equations for da_1/dt and da_2/dt.

(b) Zeroth-order approximation: Let's simply ignore everything about $\hat{H}'(\vec{r}, t)$. Argue that the zeroth-order results are simply $a_1(t) = 1$ and $a_2(t) = 0$. [Remark: This is what we expected in the absence of $\hat{H}'(t)$.]

(c) First-order approximation: Previously in perturbation theory, we saw that we need the zeroth-order results to get at the first-order results, and so on. In time dependent perturbation theory, it is the same. Plug the zeroth-order results into the two equations to **obtain** the first order results for $a_1(t)$ and $a_2(t)$ as

$$a_1(t) = 1 \ , \quad a_2(t) = -\frac{i}{\hbar}\int_0^t e^{\frac{i}{\hbar}(E_2-E_1)t'} \left(\int \psi_2^* \hat{H}'(\vec{r},t')\psi_1 d^3r\right) dt' \tag{3}$$

Note that the integral involving d^3r is a spatial integration and the result is a function of t'. Then, the integral involving dt' is over time and it gives $a_2(t)$ at the time t.

Eq. (3) is where we started in obtaining the selection rules, transition rates, and life time. Here, we show that explicitly we are working on first order time dependent perturbation theory.

[Remark: For those who want to develop the theory to 2nd order, plug the 1st order results into Eq. (1) and (2) to obtain $a_1(t)$ and $a_2(t)$ again.]

SQ19 *The integral that determines selection rules and Hydrogen atom's "Matrix element" for transitions between $n = 1$ and $n = 2$ states*

From SQ18, we see that when a system is initially in an eigenstate $\psi_{initial}$ of $\hat{H}_0$ (or $\hat{H}_{atom}$), the probability amplitude $a_{final}(t)$ of finding the system in another eigenstate ψ_{final} is related to a spatial integral:

$$a_{final}(t) \propto \int \psi_{final}^*(\mathbf{r})\ \hat{H}'(\vec{r},t)\ \psi_{initial}(\mathbf{r})\ d^3r \tag{4}$$

Here, we used $\mathbf{r}$ and $\vec{r}$ interchangeably. They mean the same thing. We focus on this spatial integral. For Atom-Light interaction, the most important mechanism is the interaction between the electric dipole moment $\vec{\mu}_{el}$ and the electric field $\vec{\mathcal{E}}$ in EM wave. Thus, $\hat{H}' = -\vec{\mu}_{el}\cdot\vec{\mathcal{E}} = -\vec{\mu}_{el}\cdot\vec{\mathcal{E}}_0\cos\omega t$. It follows from Eq. (4) that

$$a_{final}(t) \propto \int \psi_{final}^*(\mathbf{r})\ \vec{\mu}_{el}\ \psi_{initial}(\mathbf{r})\ d^3r \equiv [\vec{\mu}]_{fi} \tag{5}$$

Eq. (5) is the key to understand the selection rules under the electric dipole mechanism. It is the "**electric dipole matrix element**", as it is labelled by two indices (the initial i and final states f).

In the special case of a single electron (e.g. hydrogen atom), $\vec{\mu}_{el} = -e\vec{r}$. A transition from an initial (state 1) to a final state (state 2) occurs with a probability amplitude proportional to a spatial integral given by

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

The integral is a **vector**. There is a dot product with the field $\vec{\mathcal{E}}$ to give a scalar. The integral is usually handled numerically for atoms and molecules. This is the "position matrix element" (also related to the momentum matrix element) that determines $a_2(t)$. The probability of a transition from state 1 to state 2 after $\hat{H}'$ is applied for a time t is $|a_2(t)|^2$.

For the hydrogen atom, **the integral can be evaluated analytically**. This integral plays an important role for stimulated processes AND spontaneous emission, as well as setting selection rules. We have encountered such integrals in a previous problem on atomic polarizability.

(a) Let's consider transitions in a hydrogen atom. Consider a transition from 1s to 2s. By inspecting the integral

$$a_2(t) \propto \overline{\mathbf{r}_{2s,1s}} \equiv \int \psi_{2s}^*(\mathbf{r})\, \mathbf{r}\, \psi_{1s}(\mathbf{r})\, d^3r = \int \psi_{200}^*(\mathbf{r})\, \mathbf{r}\, \psi_{100}(\mathbf{r})\, d^3r \ , \tag{7}$$

show that it vanishes and thus the transition is not allowed (forbidden) by the electric dipole mechanism.

[Remark: If one can excite a hydrogen atom to the 2s state by some way, it cannot relax back to 1s by spontaneous emission via the electric dipole mechanism. It implies that the 2s state has a longer life time than the other excited states. It is a meta-stable state.]

(b) For hydrogen atom, the transition between 1s and 2p is allowed. In this case, the integral that matters is

$$a_2(t) \propto \overline{\mathbf{r}_{2p,1s}} \equiv \int \psi_{2p}^*(\mathbf{r})\, \mathbf{r}\, \psi_{1s}(\mathbf{r})\, d^3r \tag{8}$$

Recall that there are several 2p states because $m_\ell = +1, 0, -1$. So let's be concrete. Consider the transition between the 1s ground state and 2p state of $m_\ell = +1$ for which the angular part is $Y_{11}(\theta, \phi)$. Thus, $\psi_{2,1,+1}(\mathbf{r})$ is the final state and $\psi_{1,0,0}(\mathbf{r})$ is the initial state. The integral in Eq. (8) for this transition becomes

$$a_2(t) \propto \overline{\mathbf{r}_{2p,1s}} \equiv \int \psi_{211}^*(\mathbf{r})\, \mathbf{r}\, \psi_{100}(\mathbf{r})\, d^3r \tag{9}$$

(i) In Eq. (9), the integral is a vector because $\mathbf{r}$ is a vector. Explicitly, writing

$$\mathbf{r} = x\hat{x} + y\hat{y} + z\hat{z} = r\sin\theta\cos\phi\ \hat{x} + r\sin\theta\sin\phi\ \hat{y} + r\cos\theta\ \hat{z} \ , \tag{10}$$

evaluate the integral in Eq. (9). It is important to note that the answer is a vector and in general complex. [TA: Give the answer in unit of the Bohr radius.]

(ii) For (stimulated) absorption, consider an external field $\vec{\mathcal{E}} = \mathcal{E}\hat{z}$, i.e., the incident light is linearly polarized in z-direction (so the propagating direction is not z). The perturbative term in the Hamiltonian $\hat{H}' = -\vec{\mu}_{el} \cdot \vec{\mathcal{E}}$ implies that it is the $\hat{z}$-component of $\overline{\mathbf{r}_{2p,1s}}$ that matters. **Argue** that such a linearly polarized light *cannot* stimulate an absorption from $\psi_{1,0,0}(\mathbf{r})$ to $\psi_{2,1,+1}(\mathbf{r})$. **Discuss** that such a linearly polarized light cannot stimulate an *emission* from $(2, 1, +1)$ to the ground state $(1, 0, 0)$. **Further discuss** the condition for the component $z_{2p,1s}$ to be non-zero for transitions between 1s and 2p states.

(iii) Now consider circularly polarized light. Let the propagation direction be the z-direction. From EM theory, its electric field is on the x-y plane. In particular, a circularly polarized light with its polarization specified by $\mathbf{e}^+ \propto (\hat{x} + i\hat{y})$ has its electric field rotating with time at a fixed point in space (note that there is an time factor $e^{-i\omega t}$ in the field that gives the rotating behavior). Now let's do QM. **Show** that such a circularly polarized light can indeed stimulate a transition between $\psi_{1,0,0}(\mathbf{r})$ and $\psi_{2,1,+1}(\mathbf{r})$.

[Implication: Skillfully using circularly polarized light can selectively induce transitions and thus put atoms into a particular excited state. In recent years, techniques in cold atom physics (cooling atoms down to nano-Kelvin) also use circularly polarized light to induce selected transitions.]