PHYS3022 APPLIED QUANTUM MECHANICS

SAMPLE QUESTIONS FOR DISCUSSION IN WEEK 9 EXERCISE CLASSES (15 - 19 March 2021)

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. **You should attend one exercise class session per week.** You are encouraged to think about (or work out) the sample questions before attending exercise class and ask the TA questions.

Reminder – Please be reminded that the Mid-term Examination will be held on 20 March 2021 (Saturday) morning at 10am - 12noon in SC L1 and SC L2. Those who cannot possibly come to campus physically will do an online invigilated exam at around the same time.

Progress: In Week 8, we started to discuss atomic transitions, which is an initial value problem in the presence of a **time-dependent Hamiltonian**. The form of $\hat{H}'(\mathbf{r},t)$ in the electric dipole mechanism was introduced. **Time-dependent perturbation theory** was discussed and we arrived at a formula for $a_2(t)$, which is the probability amplitude of finding the system (the atom) to be in an energy eigenstate "2" given that the system was in an energy eigenstate "1" before $\hat{H}'(\mathbf{r},t)$ started to affect the system. We will see the big consequences of this single formula. It gives the selection rules, energy criteria for transitions to occur, stimulated absorption and stimulated emission rates. Spontaneous emission is harder to understand within Schrödinger QM, but we will see how Einstein's A and B coefficients (related to spontaneous emission and stimulated processes) are related and hence the spontaneous emission rate can also be obtained.

SQ18 - First-order perturbation theory - a slow motion analysis [Optional for Exam Purposes]
SQ19 - Electric dipole matrix elements, forbidden and allowed transitions in hydrogen atom between $n = 1$ and $n = 2$ states

SQ18 *First-order perturbation theory - a slow motion analysis* [Optional for Exam Purposes]

In the classnotes (an Appendix in the Light-Matter Interaction Module), time-dependent perturbation theory was discussed. Using a general equation for $da_2(t)/dt$, etc., we claimed that plugging the zeroth-order solutions on the RHS of the equation will give the first-order perturbation theory for $da_2(t)/dt$ and that the zeroth-order solutions are the given initial conditions. The goal of the Appendix is to arrive at Eq. (13) in the class notes from which stimulated emission and absorption follow. Here, TA will fill in the argument of tracking the order of the theory.

The starting point is Eq. (A8) in the Appendix. To set up the counting of the order, we write the problem in hand $\hat{H} = \hat{H}_0 + \hat{H}'(\mathbf{r},t)$ as $\hat{H} = \hat{H}_0 + \lambda\hat{H}'(\mathbf{r},t)$, with λ being a parameter tracing the order of the theory. The $\lambda = 1$ case is our problem. Plugging the exact expression

$$\Psi(\mathbf{r},t) = \sum_n a_n(t) e^{-iE_n t/\hbar}\psi_n(\mathbf{r}) \,, \tag{1}$$

where the time-dependent coefficients $a_n(t)$ carry all the effects of $\hat{H}'(\mathbf{r},t)$, into the time-dependent Schrödinger equation (TDSE), we arrive at

$$i\hbar\frac{da_2(t)}{dt} = a_1(t)\, e^{i(E_2-E_1)t/\hbar}\int \psi_2^*[\lambda\hat{H}']\psi_1 d^3r + a_2(t)\int \psi_2^*[\lambda\hat{H}']\psi_2 d^3r \tag{2}$$

and

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

where λ is explicitly included to count the order. Here, we simplified the problem to consider only two states. Eq. (2) and Eq. (3) are **exact** and they are **equivalent to TDSE**.

TAs: Express the unknown coefficients order-by-order as:

$$a_1(t) = a_1^{(0)}(t) + \lambda a_1^{(1)}(t) + \lambda^2 a_1^{(2)}(t) + \cdots \tag{4}$$

$$a_2(t) = a_2^{(0)}(t) + \lambda a_2^{(1)}(t) + \lambda^2 a_2^{(2)}(t) + \cdots \tag{5}$$

where the superscripts "(0)", "(1)" track the order in $\hat{H}'$. For our purpose, we only need to retain up to $a_1^{(1)}(t)$ and $a_2^{(1)}(t)$. **Substitute** Eq. (4) and Eq. (5) into Eq. (2) and Eq. (3) to **obtain the equations** for $da_1^{(0)}/dt$, $da_2^{(0)}/dt$, $da_1^{(1)}/dt$, and $da_2^{(1)}/dt$. **Show that** the zeroth-order solutions are given by the initial conditions, and the zeroth-order solutions go into the RHS of the equations for $da_1^{(1)}/dt$ and $da_2^{(1)}/dt$.

Finally, for the special initial conditions of $a_1(0) = 1$ and $a_2(0) = 0$, **write down** the equation for $da_2^{(1)}(t)/dt$ and solve for $a_2(t)$ formally up to first-order. The result is Eq. (13) in the class notes.

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

From the key result of first-order time-dependent perturbation theory, there is an integral that involves the perturbation $\hat{H}'(\mathbf{r}, t) = e\mathbf{r} \cdot \mathbf{E}cos(\omega t) = e\mathbf{r} \cdot \hat{e}\mathcal{E}\cos(\omega t)$, where $\mathbf{r}$ is the position of the electron in the atom and $\hat{e}$ is the unit vector representing the polarization of the EM waves. When a system is initially in an eigenstate $\psi_{initial}$, only $\hat{H}'$ can take the system away from $\psi_{initial}$, and the governing equation of $a_2(t)$ has a spatial integral (see SQ18)

$$a_2(t) \propto \int \psi^*_{final}(\mathbf{r})\ \hat{H}'\ \psi_{initial}(\mathbf{r})\ d^3r \tag{6}$$

With the form of $\hat{H}'$, we have

$$a_2(t) \propto \overline{\mathbf{r}_{final,initial}} = \int \psi^*_{final}(\mathbf{r})\ \mathbf{r}\ \psi_{initial}(\mathbf{r})\ d^3r\ . \tag{7}$$

The integral on the RHS is a vector (to be dotted into $\hat{e}$ of the electric field). There is a function of time not shown here and it gives the energy criterion, i.e., $\hbar\omega$ must be right for the transition. In general, the integral in Eq. (7) is usually handled numerically for atoms and molecules. This is the "position 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. The integral plays an important role for stimulated processes AND spontaneous emission, as well as setting selection rules.

(a) Let's consider transitions in a hydrogen atom. By inspecting the integral

$$a_2(t) \propto \overline{\mathbf{r}_{2s,1s}} \equiv \int \psi^*_{2s}(\mathbf{r})\ \vec{r}\ \psi_{1s}(\mathbf{r})\ d^3r = \int \psi^*_{200}(\mathbf{r})\ \mathbf{r}\ \psi_{100}(\mathbf{r})\ d^3r \tag{8}$$

that would determine a transition between 1s and 2s states, **show that the integral vanishes** and thus the transition is not allowed (forbidden) by the electric dipole mechanism. In the process, **point out** that it is the angular (θ and ϕ) integrals that determine whether the integral vanishes or not, and the integral over r is usually not a problem.

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

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

Recall that there are several 2p states. 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.

(i) The integral in Eq. (9) 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 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). **Point out** that it is the $\hat{z}$-component of $\overline{\mathbf{r}_{2p,1s}}$ that matters. Hence, **discuss the condition** for the component $z_{2p,1s}$ to be non-zero. Hence, **argue that** such a linearly polarized light *cannot stimulate an absorption* from $\psi_{1,0,0}(\mathbf{r})$ to $\psi_{2,1,+1}(\mathbf{r})$. **Further discuss** that such a linearly polarized light cannot stimulate an *emission* from $(2, 1, +1)$ to the ground state $(1, 0, 0)$.

(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.]