PHYS3022 APPLIED QUANTUM MECHANICS

SAMPLE QUESTIONS FOR DISCUSSION IN WEEK 11 EXERCISE CLASSES (13 - 17 April 2020)

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.** You are encouraged to think about (or work out) the sample questions before attending exercise class and ask the TA questions.

Progress: In Week 10, we discussed the physics behind the interaction of light with atoms in the electric dipole mechanism. The interaction term is time-dependent $\hat{H}'(t)$. The question is an initial value problem, i.e. given that the atom is in some initial state ψ_i, what is the probability of finding the atom to be in a final state ψ_f after the interaction term is switched on for a time duration t. QM gives the answer and it is related to the phenomena of (stimulated) absorption and stimulated emission. It is one theory for the two stimulated phenomena. Schrödinger quantum mechanics cannot treat the vacuum (no light) properly and so the spontaneous emission process is harder to explain. In Week 11, we will discuss Einstein's 1917 A and B coefficients. Einstein's A-coefficient is related to spontaneous emission and the B-coefficient is related to stimulated absorption and stimulated emission. There is a relation between the A and B coefficients. Since QM can calculated the B-coefficient, therefore all a sudden we also know what to get the A-coefficient by QM. It follows that they follow the same selection rules. Leaving an atom unattended at an excited state, it will de-excite to lower energy states without any external influence, i.e. spontaneous emission. Thus Einstein's A-coefficient is related to the life time τ of an excited state. Therefore, we can calculate the life time of an excited state using quantum mechanics. The ideas of long life time states (metastable states) and stimulated emission are essential for understanding how laser works. We will leave atomic physics at this point. Students who want to learn more atomic physics can move on to read *Atomic Physics* by C.J. Foot [you have the knowledge of first 7 chapters out of 13 chapters of this MSc level textbook] and *Quantum Chemistry* by D. McQuarrie [you have about 2/3 of this beginning postgraduate level book for physical chemistry students].

SQ25 - Quantum mechanics gives quantitatively the life time of hydrogen 2p state (follow up see also SQ24)
SQ26 - If stimulated absorption and stimulated emission processes were the only possible processes...
SQ27 - Population inversion is an out of equilibrium situation

SQ25 *Life time of hydrogen 2p state - Quantum Mechanics is quantitative!*

In SQ24 (last week), TA calculated the vector $\overline{\mathbf{r}_{2p,1s}}$ for a hydrogen atom. This quantity gets into the transition rates of stimulated processes and therefore related to Einstein's B coefficient. But Einstein's A coefficient is proportional to the B coefficient. So it is possible to calculate the A coefficient and the life time of an excited state. This SQ illustrates that Quantum Mechanics allows us to **calculate** measurable quantities **quantitatively**. The example here is the life time of a hydrogen 2p state using the result in SQ23.

The flow of ideas is as follows: QM gives the stimulated emission/absorption transition rate $\lambda_{2\to1}$. In 1917, Einstein introduced his B and A coefficients. The A coefficient is related to spontaneous emission (difficult to handle within Schrödinger's QM) and the B coefficient is related to stimulated processes. In QM, the formula of $\lambda_{2\to1}$ for stimulated processes gives a formula of the B-coefficient. Einstein gave a relation between the A-coefficient and the B-coefficient. Therefore, we can obtain a QM formula for the A-coefficient too. The life time of an excited state is how long on average it will last if it is "undisturbed". The life time τ of an excited state is related to spontaneous emission and the A-coefficient through $1/A$. In summary, $\lambda_{2\to 1}$ (QM) $\to$ formula of B-coefficient $\to$ formula of A-coefficient via relation between A-coefficient and B-coefficient (Einstein) $\to$ lifetime $\tau = 1/A$.

A word on experiments. The spectral lines are not infinitely sharp. The natural line shape of spectral lines comes from the finite life time of an excited time, with the line width related to $1/\tau$ and thus τ can be obtained by spectroscopy.

Here, we consider the life time of a 2p state of hydrogen atom. We will make use of the result in SQ24 to get at the life time of the 2p state of $(2, 1, +1)$. For spontaneous emission, it can make a transition to the ground state (final state) of $(1, 0, 0)$. In this case, the matrix element involved is $\overline{\mathbf{r}_{1s,2p}}$ (from 2p to 1s) rather than $\overline{\mathbf{r}_{2p,1s}}$ evaluated in SQ24. But we need no work to obtain it.

(a) Actually we did the matrix element in SQ24. By referring to SQ24, **give** $\overline{\mathbf{r}_{1s,2p}}$ without doing any calculation. Note that it is a vector.

(b) What we need is $|\overline{\mathbf{r}_{1s,2p}}|^2$, which is a scalar. **Evaluate it** and give the answer in Bohr radius squared.

(c) Using the relation between the A and B coefficients, a formula for A-coefficient is obtained. The expression for spontaneous emission from an upper state 2 to a lower state 1 is

$$A = \frac{\omega^3}{3\pi\epsilon_0 c^3 \hbar}\, e^2 |r_{21}|^2 \tag{1}$$

It consists of three factors: a bunch of constants, ω^3 dependence, and $e^2|\overline{\mathbf{r}_{1s,2p}}|^2$ dependence. So, (i) **evaluate** the quantity $e^2|\overline{\mathbf{r}_{1s,2p}}|^2 = |\overline{\mu_{1s,2p}}|^2$ and give the result **in SI units**, i.e., in $\mathrm{C}^2\mathrm{m}^2$ where C is Coulomb and m is meter. This is related to the electric dipole moment squared. (ii) **Evaluate** ω_{21} (or simply call it ω) from the energy differences of the 2p and 1s states.

(d) For the 2p $(2, 1, +1)$ hydrogen state, $(1, 0, 0)$ is the *only* state that it can go via an allowed transition. This makes the calculation easier, as we don't need to consider several possible final states. The life time is given by $\tau = 1/A$. Thus we need to calculate A. There are some constants involving $\hbar$, c, and ϵ_0 in A. Plug in all the numbers to **find** A (in SI units) and the **lifetime** due to the electric dipole mechanism. The answer is a number in **seconds**. The result is worthy of remembering as it is typical of a state that can make a transition downward via electric dipole radiation. **You should appreciate that quantum mechanics works to give a precise number for a property of a quantum state.**

[Remarks: You just saw that typical life time is $\sim 10^{-9}$ s for states with allowed electric dipole transitions downward. If such a transition is forbidden (meaning "electric-dipole forbidden"), the life time becomes much longer. Physicists have manipulated atoms and measured some exceptionally long life time. For example, a metastable state in Mg was found to have a life time of 2050 seconds (see Jensen *et al.* Phys. Rev. Lett. **107**, 1130 (2011)). There are more extreme cases. When electric dipole transition is forbidden, then comes magnetic dipole, electric quadrupole, magnetic quadrupole, electric octupole processes, etc. An excited state in $^{172}\mathrm{Yb}^{+}$ ion was found to have a life time of 10 years via the electric octupole transition. See Roberts *et al.* in Phys. Rev. Lett. **78**, 1876 (1997). Of course, one needs to find a way to excite the atom to such a state before one can study it.]

SQ26 *If stimulated absorption and stimulated emission processes were the only possible processes...*

We derived from quantum mechanics that the stimulated absorption transition rate and the stimulated emission transition rate are the same between two states 1 and 2, under the same conditions.

If these are the only possible processes (simply forgot the fact that there is spontaneous emission), **write down** the dynamical equations dN_1/dt and dN_2/dt of atoms in the two states and **find** the numbers N_1 and N_2 when dynamical equilibrium is achieved.

[Remark: From your statistical physics course, you know that there are more atoms in the lower state 1 than in the higher state 2 (due to the Boltzmann factor). Don't worry. If we now put back the spontaneous emission process (that works to lower N_2 and increase N_1, things become consistent again. This idea is used in setting up the equations in discussing Einstein's A and B coefficients.]

SQ27 *Population inversion is an out of equilibrium situation*

We emphasized that one cannot populate a higher energy state 2 with more atoms than a lower state 1 by controlling the temperature with the system at thermal equilibrium (e.g. with a heat bath). There is a unreasonable (but common) misconception. One started with $T = 0$, then all atoms are in the lowest state 1. Now, increasing temperature a bit, some atoms will be excited to state 2. Increasing temperature, one may think that more atoms will be excited to state 2 and the number will keep on increasing. Therefore, "let's go to higher and higher temperature and we can get population inversion", sorry that's wrong.

The fact is that we always have $N_2 > N_1$ for equilibrium cases. The ratio is given by

$$\frac{N_2}{N_1} = e^{-(E_2-E_1)/kT} = e^{-\hbar\omega/kT} \tag{2}$$

Let's consider two states that emits a line of wavelength of 488.0 nm (nanometer) and that a population inversion such that $N_2 = 2N_1$ is achieved (by some other ways). Somehow, some people still insist on using Eq. (2), which is equilibrium physics, for this out of equilibrium situation. TA: **Evaluate** the corresponding "temperature". The answer comes out to be something very strange.

[Optional for students: For those who are learning (learned) statistical physics, think in terms of the number of microstates as the temperature increases from zero will help understand the physics.]