Phys 487 Discussion 13 – Spectroscopic Lines

Fermi's Golden Rule for transition probability / time:

$$W_{i\to f} = \frac{2\pi}{\hbar}\left|V_{fi}\right|^2 n(E_f)$$

Einstein A coefficient for spontaneous emission of E1 radiation:

$$\boxed{A_{i\to f} = \frac{\omega_{if}^3 e^2 \left|\vec{r}_{fi}\right|^2}{3\pi\varepsilon_0 \hbar c^3}} \quad \text{with } \omega_{if} \equiv \frac{E_i - E_f}{\hbar}, \quad \vec{r}_{fi} \equiv \left\langle \psi_f \left| \vec{r} \right| \psi_i \right\rangle$$

For the electron making the transition

(a) $\Delta l = \pm 1$
(b) $\Delta m_l = 0, \pm 1$

For the atom as a whole

(a) $\Delta S = 0$
(b) $\Delta L = 0, \pm 1$ ($L = 0 \leftrightarrow L' = 0$ forbidden)
(c) $\Delta M_L = 0, \pm 1$
(d) $\Delta J = 0, \pm 1$ ($J = 0 \leftrightarrow J' = 0$ forbidden)
(e) $\Delta M_J = 0, \pm 1$

Both of these quantities give you a transition probability / second (aka **transition rate**) for an atom in state i to go to state f. Since A is the rate of *spontaneous* transition from a state i to a state f, it is precisely related to the **natural lifetime τ** of state i, *i.e.* how long it will remain in state i before dropping down to state f. The relationship is :

$$\boxed{\tau = \frac{1}{A}} = \textbf{lifetime} \text{ of state } i = \text{time for the \# of atoms in state } i \text{ to drop by factor } 1/e$$

To be exact, this is the lifetime of state i under the transition $i \to f$ for a specific final state f. Usually, for a given initial state i there is a very dominant transition $i \to f$ that is much more probable (higher rate) than all the others, but if there are several final states to which state i can decay, the lifetimes add as follows :

$$\boxed{\tau_i = \frac{1}{\sum_f A_{i\to f}}}$$ i.e. <u>the rates $A_{i\to f}$ add, not the lifetimes</u>, which makes total sense. ☺

Problem 1 : Lifetime of hydrogen $n = 2$ states *adapted from Griffiths 9.11* [1]

It's time to get some *numbers* into our work, since we are now know how to calculate the actual stability of an electron in an excited atomic state. Calculate the lifetime, in seconds, for each of the four $n = 2$ states of hydrogen.

▶ HINT 1: First <u>list</u> the four $n = 2$ states of hydrogen. How many quantum numbers do you need to specify each state? For a single particle with spin, it's 5 … but here you can ignore the spin quantum numbers $s = ½$ and $m_s = \pm ½$ because the E1 radiation rate A doesn't depend on spin. (In other words, you will get the same answer for different states of m_s, so you can ignore ignore m_s in your calculation.) While you're at it, list the <u>ground state</u> quantum numbers too: you will be calculating the transition rates from each of the $n = 2$ excited states to the ground state. The answers to this first hint are in the footnote for you to check before you continue.

▶ HINT 2: You will need to evaluate matrix elements of the form $\langle \psi_{100} \mid x \mid \psi_{200} \rangle$, $\langle \psi_{100} \mid y \mid \psi_{211} \rangle$, and so on. Remember that $x = r \sin\theta \cos\phi$, $y = r \sin\theta \sin\phi$, $z = r \cos\theta$. As often happens when evaluating quantum matrix elements, <u>most of the integrals are ZERO</u>, so scan them before you start calculating (as always!). The E1 **selection rules** in the box above are also a useful way to identify some of the transition matrix elements that are going to be zero. In the end, as long as you treat m=±1 as a single case (by using the symbol ±), you should have <u>ONLY TWO</u> non-zero integrals to do. Once you have identified them, check the footnote before integrating to make sure you have found the right two.

---

[1] **Q1**: The 4 excited states of hydrogen in the $n = 2$ shell are $|nlm\rangle = |200\rangle, |21{+}1\rangle, |210\rangle, |21{-}1\rangle$, and the ground state is $|100\rangle$
… The only two non-zero matrix elements are $\langle\, 100 \,|\, x \,|\, 21{\pm}1 \,\rangle$ and $\langle\, 100 \,|\, y \,|\, 21{\pm}1 \,\rangle$.
… You should get the <u>same</u> lifetime of 1.6×10^{-9} s for three of the excited states, and an <u>infinite</u> lifetime for the fourth state.
… The state with the infinite lifetime — i.e. the state that is stable against E1 transitions to the ground state — is $|200\rangle$.

▶ Check your results at the **NIST database**, this time in the "**Lines**" section. (During our atomic structure weeks, we consulted the "Levels" section; now that we are calculating transition rates, we need the other half of the database.) Type in "H 0" for neutral hydrogen, then have a look at the results. It takes a couple of minutes to figure out what you're looking at, but it is well worth it! Two things in particular to note:

• You will find the 1.6×10^{-9} s lifetime you calculated, but it will be *upside down* : A^{-1} is listed, not A. Why? From last week's discussion, and repeated in the introductory summary above, **rates add, not lifetimes**.

• Find the transition for which you calculated an infinite lifetime. Is there really a completely stable excited state of the hydrogen atom? No … compare the lifetime in the database for the E1-forbidden state to the three E1-allowed ones, and have a look at the notation in red to see why the state is not completely stable.

Problem 2 : Multiple Decay Routes *adapted from Griffiths 9.14* [2]

An electron in the $|nlm\rangle = |300\rangle$ state of hydrogen decays by a sequence of E1 transitions to the ground state.

(a) What decay routes are open to it? By "decay route" we mean something like this:

$$|300\rangle \rightarrow |nlm\rangle \rightarrow |n'l'm'\rangle \rightarrow \ldots \rightarrow |100\rangle$$

▶ GUIDANCE: The electron's energy must drop when spontaneous emission occurs. In the Bohr model of the hydrogen atom, the electron's energy only depends on the principal quantum number n, and in this question you may assume that n changes by at least one unit with each emission. You calculated numerous corrections to the Bohr model (notably the fine structure = spin-orbit + relativistic correction), so you know that different l states with the same n don't have *exactly* the same energy, but the fine structure correction is small (smaller than E_{Bohr} by a factor of about $\alpha^2 \approx 10^{-4}$, if you recall), and the decay probability per unit time, A, is proportional to the CUBE of $\omega_{if} = (E_i - E_f)/\hbar$, so transitions between fine-structure-separated levels are GREATLY suppressed compared to those with $\Delta n \geq 1$.

(b) If you had a bottle full of atoms in this state, what fraction of them would decay via each route?

(c) What is the lifetime of this state?

▶ HINT: Once it's made the first transition, it's no longer in the state $|300\rangle$, so only the first step in each sequence is relevant when computing the lifetime. When there is more than one decay route open, the **rates add, not the lifetimes**.

---

[2] **Q2**: (a) HINTs: The $|\Delta l| = 1$ selection rule makes it impossible to go *directly* from $|300\rangle$ to $|100\rangle$, and the hint tells us that we may assume $\Delta n \geq 1$ for each step, so the decay routes must have EXACTLY ONE INTERMEDIATE STATE, with $n = 2$ … There are only three allowed intermediate states … Answer: the allowed intermediate states are $|200\rangle$ and $|21\pm1\rangle$
(b) The transition rates A = transition probability / second are the same from $|300\rangle$ to all three intermediate states
$\therefore$ ⅓ of the atoms will decay by each route.
(c) $\tau = 1.58 \times 10^{-7}$ s