Fermi’s Golden Rule: \( W_{i \rightarrow f} = \frac{2\pi}{\hbar} |V_{fi}|^2 n(E_f) \) = transition probability per unit time from state \( i \) to state \( f \).

We have started the process of applying FGR to the spontaneous emission of electric dipole radiation (a.k.a. E1 radiation) by atomic electrons. There are two concepts embedded in this sentence that are still new to us:

1. **Spontaneous emission**: This is the process by which an excited quantum state can decay all on its own down to a state of lower energy, emitting EM radiation as it does so. We know that this happens (in lightbulbs for example), but how does it happen? We’ve already mentioned the answer in lecture: the spontaneous emission of EM waves is really stimulated emission with the stimulating radiation coming from the vacuum. The ground state of the vacuum — of empty space — has non-zero <EM field energy>, just like the ground state of particle an \( \infty \) well has non-zero <kinetic energy>.

2. **E1 radiation**: Is the lowest order in the multipole expansion of EM radiation. (If this multipole expansion is not familiar to you from PHYS 436, no worries; I’m just mentioning it in case it is familiar.) E1 radiation is totally dominant when the wavelength of the radiation is much greater than the size of the system and when magnetic fields can be ignored. As we discussed, these conditions hold for the vast majority of interactions between EM waves and atomic electrons.

Those are the concepts, what’s left is the derivation of a formula for the rate of spontaneous emission. We will accomplish this derivation using Fermi’s Golden Rule. Below is a preview of what we will find. The items you need today are in boldface.

As we will see, E1 radiation consists of an oscillating perturbation \( H' = V(r)\left[ e^{i\omega t} + e^{-i\omega t} \right] \) caused by an approximately uniform electric field \( \vec{E}_0 \), i.e. for \( V(\vec{r}) = -q\vec{E}_0 \cdot \vec{r} \).

The ingredients of FGR for E1 radiation from electrons are:

- The transition matrix element \( V_{fi} \) is non-zero only when the selection rules at right are satisfied. ———— ———— ———— ————
- For incoherent E1 radiation, i.e. when polarization is randomly oriented, \( |V_{fi}|^2 = \frac{E_0^2 q^2}{3} \left| \langle f | \vec{r} | i \rangle \right|^2 = \frac{E_0^2 q^2}{3} \left| \vec{r}_{fi} \right|^2 \)
- The density of states is \( n(E_f) = \frac{L^3 \omega^2}{\pi^2 \hbar c^3} = \) # of available photon states of frequency \( \omega \) per unit energy.

If we plug these ingredients into FGR and set \( |\omega_i| = |\omega_f| = |E_i - E_j| / \hbar \) (the resonance condition for the absorption/emission of a photon of energy \( \hbar \omega \)), we will obtain the following spontaneous-emission rate.

It is so hugely important that it gets a special name and symbol:

\[
A = \frac{\omega_f^3 q^2 |\vec{r}_{fi}|^2}{3\pi \varepsilon_0 \hbar c^3} = \text{Einstein’s } A \text{ coefficient where } \omega_{if} = \frac{E_i - E_f}{\hbar} \text{ as usual}
\]

This “\( A \)” is the transition probability / second (aka transition rate) for an atom in state \( i \) to go to state \( f \) via the spontaneous emission of E1 radiation. IT REALLY SHOULD BE LABELLED \( A_{i\rightarrow f} \).

We’ll call it \( A_{i\rightarrow f} \) when it improves clarity.

Since “\( A \)” is the rate of spontaneous transition from a state \( i \) to a state \( f \), it is precisely related to the natural lifetime \( \tau \) of state \( i \), i.e. how long it will remain in state \( i \) before dropping down to state \( f \). The relationship is :
\[ \tau = \frac{1}{A} \] = lifetime of state \( i \) = time for the \# of atoms in state \( i \) to drop by factor \( 1/e \)

To be exact, this lovely relation is for the lifetime of state \( i \) under the transition \( i \rightarrow f \) for a specific final state \( f \) (since “A” refers to both a specific initial state and a specific final state). Usually, for a given initial state \( i \) there is a very dominant transition \( i \rightarrow f \) 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:

\[ \tau_i = \frac{1}{\sum_f A_{i \rightarrow f}} \]

i.e. the rates \( A_{i \rightarrow f} \) add, not the lifetimes, which makes total sense. ☺

Problem 2 : Various Elements

(a) List the ground-state electronic configurations and the \( L \), \( S \), and \( J \) quantum numbers for the following atoms: Li (\( Z=3 \)), B (\( Z=5 \)), N (\( Z=7 \)), Na (\( Z=11 \)), K (\( Z=19 \)).

▶ HINT 1: It is implied that you should specify \( 2S+1LJ \) for the ground states of these atoms. (There is no other way to interpret the question that would give a unique answer for each atom! Realizing such things is often necessary for qual problems. :-))

▶ HINT 2: Hurray! An opportunity to recall all that wonderful atomic physics you mastered! This is a really good qual problem, we just couldn’t do it until now as it involves radiative transitions between atomic energy levels, which we are just now covering. To be exact, you could have done all parts of this problem except for (d) in our atomic physics section.

(b) The lowest frequency line in the absorption spectrum of Na is a doublet. What mechanism splits the corresponding pair of energy levels? The splitting between levels is proportional to \( < r^n > \) where \( r \) is the distance of the valence electron from the nucleus. What is the numerical value of \( n \)?

▶ JARGON BUSTING: A “doublet” in spectroscopy means a “line” that is actually two similar frequencies at which the atom likes to absorb or emit photons. A split line like a double generally refers to a transition between two orbitals (\( |nl> \) states) where one or both of them has an energy degeneracy that is split by some small correction. Also, when the question says “what is the lowest frequency line”, it means the lowest-frequency transition between the ground state and the orbital that is immediately above it in energy. This is somewhat sloppy language because you can find transitions of arbitrarily low frequency by moving an electron from e.g. an \( n = 10000 \) orbital to an \( n = 10001 \) orbital. (As \( n \) increases, the energy levels get closer together.)

▶ HINT 1: You can only figure out \( n \) once you know the mechanism that splits the energy levels. To figure out the mechanism, look at the electron configuration for the sodium ground state, then ask yourself: How many valence electrons does this atom have? What are the two lowest-lying energy orbitals, i.e. the states that are involved in this spectroscopic line? What mechanism do I know that could remove the degeneracy of one of those orbitals?

▶ HINT 2: Once you know the splitting mechanism, you may still have to hunt through notes / Griffiths / web to find the formula you need for \( n \). It’s not on our formula sheet, but I bet you can figure it out on your own!

(c) Consider potassium (\( Z=19 \)). Make a level diagram indicating the three lowest-lying states \( 2S+1LJ \) in energy order. (Check your result against the NIST database!) Then consider the effect of adding a weak magnetic field \( B \); this will further split the levels → how?

▶ HINT: You will get a new level diagram with \( M_J \) now specified as well; it should have 8 levels in total.
(d) On your 8-level diagram, indicate all the allowed transitions.

▶ JARGON BUSTING: “Allowed transition” means “E1 transition”, in almost every context. This is your first opportunity to read the box of E1 selection rules on the first page. We will derive them, but first, let’s apply them!

▶ HINT: You should find 10 allowed transitions.

**Problem 2: Positronium and Reduced Mass**  
*part of a Qual Problem*

In classical mechanics, two bodies with masses $m_1 \& m_2$ with a central force between them can be treated as one effective body with the reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2}.$$  

(Griffiths problem 5.1 goes through the proof. If you would like to work through it, you will see that the Schrödinger equation simplifies exactly as Lagrange’s equations did in CM, which is not surprising.)

Positronium is a hydrogen-like bound state made up of an electron and a positron. The two particles have the same mass, so treating them as one effective particle of mass $\mu$ in a fixed central force is a huge simplification: it turns a potentially-complicated 2-body problem into a 1-body system with the exact same structure as a 1-electron atom. We have already solved the 1-electron atom! Most excellent! → The reduced mass allows us to apply atomic results we already know to other systems.

(a) Estimate the binding energy of the ground state ($n = 1$) and the Lyman-α ($2p \rightarrow 1s$) transition wavelength for positronium.

(b) The lifetime for the decay from 2p to 1s for the hydrogen atom is 1.6 ns. Estimate the lifetime for the same decay in positronium.

**Problem 3: Reduced Mass: Atomic Corrections**  
*Griffiths 5.2*

We can use the reduced mass to correct for the motion of the nucleus in hydrogen: we simply replace the electron mass with the reduced mass for the (electron + proton) system.

(a) Find (to two significant digits) the percent error in the binding energy of hydrogen introduced by our use of $m$ instead of $\mu$.

(b) Find the separation in wavelength between the red “Balmer” lines ($n=3 \rightarrow n=2$) for hydrogen & deuterium.

(c) Suppose you wanted to confirm the existence of muonic hydrogen, in which the electron is replaced by a muon (same charge, same spin, but 207 times heavier). At what wavelength would you look for the “Lyman-α” line ($n=2 \rightarrow n=1$)?