and a great success of the quantum theory was to predict the correct energy levels that led to these spectra.

But the theory is more powerful still. Not only does it tell us the energies of the transitions, it also tells us

- the probability per second that the transition occurs (and a photon is emitted)
  i.e., the rate
- what transitions are and are not allowed. It turns out that not every possible transition between atomic states happens; the theory tells us which ones can & cannot happen. The results are called "selection rules"

We'll discuss both. First, a practical comment about how we test these things experimentally. We can measure the transition rate, the prediction for which tells us the number of photons/unit time, by looking at the intensity of the spectral lines (remember intensity ∝ number of photons). We can check the selection rules simply by seeing whether a particular line is there or not.

On to what the theory says. We need a couple of assumptions to begin with (they're not really assumptions but are beyond our scope).

- It turns out that classically oscillating electric dipoles give rise to radiation, and you can calculate the rate of emission.

- We can obtain the quantum mechanical result by picturing something similar (the dipole is the electron-nucleus system). What we need to make it quantitative (besides the classical result) is the fact that we can treat the atom in transition as a superposition of the initial and final states.

Look at the probability density of the superposition of the states ψ_i and ψ_f. ψ_i + ψ_f are energy eigenstates, so each has its own time dependence e^{-iEt}. The total wave function is

$$\Psi = c_i \psi_i e^{-iE_i t} + c_f \psi_f e^{-iE_f t}$$

with c_i & c_f some constants (we don't actually need to know what they are). The probability density is

→

$$\Psi^* \Psi = |c_i|^2 |\psi_i|^2 + |c_f|^2 |\psi_f|^2$$
$$+ c_i^* c_f \psi_i^* \psi_f e^{+i(E_i - E_f)t} + c_i c_f^* \psi_i^* \psi_f e^{-i(E_i - E_f)t}$$

⇒ the cross terms have time dependence. Not only that, but they're oscillating with exactly the frequency that corresponds to the transition between the states! Now we complete the picture by noting that the probability density is large where the electron is likely to be found (or, equivalently you can think of the prob. density as proportional to the charge density. The charge distribution is oscillating ⇔ it looks (on average) like an oscillating dipole.

Now back to the transition rate. Classically, the rate of emission of photons (= prob/time the atom undergoes the transition) is

$$R = \text{const} * \nu^3 p^2$$

where ν is the frequency of the photon and p is the amplitude of the dipole moment.

Aside: There's a slight contradiction here – classically, there's no such thing as a photon. What we really did was take the classical result

for the energy radiated per unit time, and divided by the energy per photon $h\nu$.

Now to interpret this quantum mechanically, we simply substitute for the dipole moment its expectation value. The atom's electric dipole moment (viz., the moment of the electron w.r.t. the fixed nucleus at the origin) is

$$\vec{p} = -e\vec{r}$$

Now the trick is, we use the expectation value of this in the mixed state:

$$\bar{p} = \int \bar{\Psi}^* (-e\vec{r}) \bar{\Psi} \, d^3x$$

$$= |c_i|^2 \int \psi_i^* (-e\vec{r}) \psi_i \, d^3x + |c_f|^2 \int \psi_f^* (-e\vec{r}) \psi_f \, d^3x$$

$$+ c_i^* c_f e^{i(E_i - E_2)t} \int \psi_i^* (-e\vec{r}) \psi_f \, d^3r$$

$$+ c_i c_f^* e^{-i(E_i - E_2)t} \int \psi_f^* (-e\vec{r}) \psi_i \, d^3r$$

Now, we want the oscillating part (because we want the dipole to oscillate so it can radiate), so we could argue that we only want the last two terms + we can ignore the first two. Turns out the first two are zero anyway, because they're odd.

(Also, the last two terms are complex conjugates of each other.) They correspond to transitions in both directions.

Now in the classical case, the p that goes in the rate formula is the amplitude of the oscillations. The analogous thing here is the part that multiplies the oscillating exponential. We'll absorb C_i + C_f into the overall constant + define

$$P_{fi} \equiv \left| \int \psi_f^* (-e\vec{r})\, \psi_i \, d^3r \right|$$

magnitude includes mag. of vector

which is the relevant term for transition from the initial state to the final state. Notice that if we took all possible initial + final states, we could form all the P_{fi} into a matrix. Hence P_{fi} is called the matrix element of the electric dipole moment between the initial + final states.

Now we put this back into the expression for the rate (p. 5.33). To get the overall constant we have to use - you guessed it - quantum electrodynamics (QED). The result is

$$R = \frac{16\pi^3 \nu^3 P_{fi}^2}{3\epsilon_0 h c^3}$$

QED also gives a picture of how the atom gets into the mixed state + the transition happens

in the first place. What happens is that the atoms can sort of resonate if there's an electromagnetic field component of the right frequency (corresponding to the energy difference between the levels) around - remember light is just an oscillating EM field. There are two cases of interest

- stimulated emission, when an EM field is applied to the atom. The rate turns out to be proportional to the intensity of the applied field, so an intense field gives a high rate. This is the idea behind the laser ("light amplification by stimulated emission of radiation")
- spontaneous emission, where there's no applied field. Like other quantized systems, the EM field has a zero point energy, some of which includes the appropriate field vibrations. (The usual picture in QED is that virtual photons are always popping in and out of the vacuum. They can only exist for a time determined by the uncertainty princ.: $\Delta E \Delta t \sim \hbar$.)

Not surprisingly, stimulated emission happens at a much higher rate than spontaneous emission.

Now let's come back to the matrix element P_{fi} and see where selection rules come from. The matrix has elements P_{fi} whose squares determine the rate of the corresponding transition. If the

matrix element is zero, the transition doesn't happen! So the matrix also tells us which rates are allowed and which aren't. Which matrix elements are zero depends on the quantum numbers of the relevant states.

> Selection rules are just conditions on the quantum numbers of the initial and final states for which the matrix element is not zero, i.e. the transition is allowed.

Now, the transitions we're talking about are electric dipole transitions (there are other kinds, like magnetic dipole, but they have smaller probabilities), and they have selection rules

$$\Delta l = \pm 1$$
$$\Delta j = 0, \pm 1$$

and no other transitions are allowed. Let's look at each in turn

(1) $\Delta l = \pm 1$ & parity

We can get this one directly from parity considerations. Remember when we introduced parity (p. 3.32) and we said that if the potential is symmetric with respect to space reflection, i.e.

$$V(-\vec{r}) = V(\vec{r})$$

then the sol'ns to the time-indep. Schrödinger eqn have definite parity:

$$\psi(-\vec{r}) = +\psi(\vec{r}) \quad \text{even parity}$$

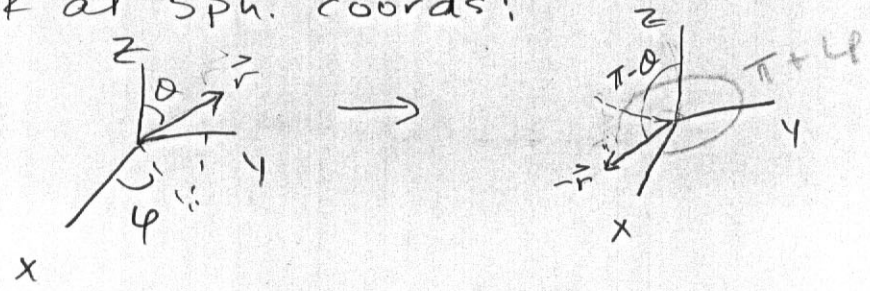
$$\text{or} \quad \psi(-\vec{r}) = -\psi(\vec{r}) \quad \text{odd parity.}$$

Although we didn't mention it explicitly, this holds for the hydrogen atom. The potential V only depends on the magnitude of $\vec{r}$, so $V(\vec{r}) = V(-\vec{r})$. That means the eigenfunctions we found also have definite parity under space reflection.

To see what the parity is for a given $\psi_{n\ell m_\ell}(r, \theta, \varphi)$ we have to figure out what $\vec{r} \to -\vec{r}$ means for the spherical coords. In cartesian coords it's just

$$x \to -x, \quad y \to -y, \quad z \to -z$$

Look at sph. coords:



The space reflection gives

$$r \to r \qquad \theta \to \pi - \theta \qquad \varphi \to \pi + \varphi$$

If we stick this into the H eigenfunctions, we find

$$\psi_{n\ell m_\ell}(-\vec{r}) = \psi_{n\ell m_\ell}(r, \pi-\theta, \pi+\varphi)$$

$$= (-1)^\ell \psi_{n\ell m_\ell}(\vec{r}, \theta, \varphi) = (-1)^\ell \psi_{n\ell m_\ell}(\vec{r})$$

The parity is determined, only by the orbital angular momentum quantum number ℓ.

Now let's go back to the matrix elements P_{fi}. We have

$$P_{fi} = \left| \int \psi^*_{n\ell m_\ell}(-e\vec{r})\, \psi_{n'\ell'm'_\ell}\, d^3r \right|$$

$\psi^*_{n\ell m_\ell}$ has parity $(-1)^\ell$, $\vec{r}$ has parity (-1), and $\psi_{n'\ell'm'_\ell}$ has $(-1)^{\ell'}$. The net parity is then

$$(-1)^{\ell+\ell'-1}$$

If the power is odd, the integrand is odd and the integral is zero. If the power is even, the matrix element is nonzero. Therefore ℓ must change by an odd number for a transition to occur. We

cannot have $\Delta\ell = 0, \pm 2, \pm 4 \ldots$

We can have $\boxed{\Delta l = \pm 1}$, and as far as parity is concerned we can have changes in l by other odd numbers too. We'll see that a constraint on the change in total angular momentum prevents the other odd changes.

(2) $\Delta j = 0, \pm 1$

Turns out from QED that in an electric dipole transition the photon carries away 1 unit of angular momentum. Now angular momentum is conserved, but addition of angular momentum works in a funny way (see P246) such that the change in the quantum number j of the atomic state must be

$$\boxed{\Delta j = 0, \pm 1}$$

Since s can't change for the electron, this also eliminates $\Delta l = \pm 3, \pm 5$, etc. leaving only $\Delta l = \pm 1$.

Note that prohibited transitions can usually take place in some other way (e.g. from an oscillating magnetic dipole), but with a very small probability

Now as an example let's look at what happens to selection rules for electric dipole transitions in a strong magnetic field. When there's a strong field, as you know from the homework, the spin-orbit coupling can be ignored and m_ℓ & m_s become good quantum numbers again.

Ex Show that in an external field, there's a selection rule $\Delta m_\ell = 0, \pm 1$. We just need to show that the matrix element is only nonzero for these Δm_ℓ.

So $P_{fi} = \left| \int \psi_f^* (-e\vec{r}) \psi_i \, d^3x \right|$

$$= \left| \int \psi_{(n\ell m)_f} (-e\vec{r}) \psi_{(n\ell m)_i} r^2 dr \, d\cos\theta \, d\varphi \right|$$

Now the interesting thing that involves m_ℓ is the φ-dependent part of P_{fi}, which we can write as

$$\vec{I} \equiv \int_0^{2\pi} \Phi_f^*(\varphi) \hat{r} \Phi_i(\varphi) \, d\varphi \qquad \& \; \Phi = e^{im_\ell \varphi}$$

Note that we've pulled out the factor of $-e$, and that $\vec{I}$ is a vector quantity. We'll look at its components individually. Remember

$$z = r\cos\theta$$
$$x = r\sin\theta\cos\varphi$$
$$y = r\sin\theta\sin\varphi$$

So $$I_z = r\cos\theta \int_0^{2\pi} e^{i(m_i - m_f)\varphi}\, d\varphi$$

Since we can write $e^{iax} = \cos ax + i\sin ax$, we have

$$I_z = r\cos\theta \left\{ \int_0^{2\pi} \cos[(m_i - m_f)\varphi]\, d\varphi + i\int_0^{2\pi} \sin[(m_i - m_f)\varphi]\, d\varphi \right\}$$

Now each of these integrals integrates over 1 cycle of the function, which means each gives 0 (you can also show this by explicity evaluating the integrals).

So it looks like I_z doesn't contribute. But what if $m_f = m_i$? Then the arguments of the sin & cos are zero, $e^{i(m_f - m_i)\varphi} = 1$, and

$$I_z = r\cos\theta \int_0^{2\pi} d\varphi = 2\pi r\cos\theta \neq 0$$

$$\Rightarrow \int_0^{2\pi} e^{iax}\, dx = \begin{cases} 0, & a \neq 0 \\ 2\pi, & a = 0 \end{cases}$$

So: I_z gives a contribution only if $\Delta m = 0$.

On to I_x:

$$I_x = r\sin\theta \int_0^{2\pi} \cos\varphi\, e^{i(m_i - m_f)\varphi}\, d\varphi$$

We can use our result for $\int e^{iax}\, dx$ if we write $\cos\varphi$ in terms of exponentials: $\cos\varphi = \frac{e^{i\varphi} + e^{-i\varphi}}{2}$

So

$$I_x = \frac{r\sin\theta}{2}\left[\underbrace{\int_0^{2\pi} e^{i(m_i - m_f + 1)\varphi}\, d\varphi}_{=0 \text{ unless } m_i - m_f = -1} + \underbrace{\int e^{i(m_i - m_f - 1)\varphi}\, d\varphi}_{=0 \text{ unless } m_i - m_f = +1}\right]$$

$\Rightarrow I_x$ gives a contribution only if $\Delta m_\ell = \pm 1$

Similarly you can show that I_y only gives a contribution if $\Delta m_\ell = \pm 1$

$\therefore \vec{I}$ can only contribute for $\Delta m_\ell = 0, \pm 1$

end of ex.