

Bound-Bound and Bound-Free Transitions

From general issues of transition rates we'll move to specifics. As before, we'll start out with qualitative issues, then we'll actually do a derivation of the bound-bound oscillator strength for hydrogen, to see how things work in detail.

There are two types of atomic transition: one in which an electron moves from one bound state to another (bound-bound transitions), and one in which an electron moves from a bound state to an ionized state (a bound-free transition). **Ask class:** qualitatively, what effect does this have on a spectrum, say if these transitions absorb a background continuum? A bound-bound transition is between two sharply defined states of energy, hence it is significant only over a small range of energies. Thus, bound-bound transitions give *lines*: potentially large changes in the specific intensity, but over a narrow energy range. A bound-free transition is *not* sharply defined in energy, since in principle the ionized electron can have anywhere from zero energy (if it was barely ionized) to a large energy (if it was ejected with a large kinetic energy). There is a minimum energy, that required to ionize the electron in the first place. Therefore, the characteristic of a bound-free transition in a spectrum is an *edge*: no absorption below some energy, then a sharp onset in the absorption above that critical energy. As we'll see, the absorption decreases above the critical energy.

Ask class: why, do they think, is it that lines and edges have such a fundamental role in the understanding of astronomy, whereas although continuum spectra are useful they give much less certain interpretations? The key is that line and edge spectra have very precisely defined special energies and their interpretation is clearly atomic (or molecular in some cases). Therefore, the starting place is known, and deviations (redshifts, line broadening, etc.) can be interpreted in terms of the astrophysics. It is amusing that in 1825, Augustus Comte (a positivist philosopher) used the composition of stars as an example of something that could never be known. In his lifetime, however, spectroscopy was already being used for that very purpose.

In practice, however, there are difficulties to surmount. **Ask class:** If handed a spectrum that has a number of lines and edges, how would they go about learning things from it? The first step is to identify the transitions responsible for those lines and edges. **Ask class:** how can this be done? In principle, one has a list of rest-frame line and edge energies, then one "simply" shifts these until they match the spectrum. This is even done in practice, but sometimes there are complications. For example the spectrum of absorption lines from a quasar (typically at high redshift) can include lines from intervening clouds at several redshifts, so there is a blend one must disentangle. In addition, when high redshifts are involved or there are lots of lines, the correct identification isn't always obvious. One reason that, e.g., the doublet line for Mg II is often used is that it has specific line ratios that make its identification more secure.

Anyway, suppose that you've managed to identify the elements and transitions responsible for each line and edge. **Ask class:** how do you then proceed to deriving physical information about the system? This is where the information content of the lines and edges is remarkable. In the next class we'll go over line broadening in particular, but the point is that if you know the energies, then the line strength give you lots of clues as to the temperature, density, composition, magnetic field strengths, and many other things.

You do have to be careful. In the early part of the 20th century, people looked at stars, particularly the Sun, and were tempted to conclude that it was mainly made of heavy metals such as iron. After all, most of the lines were due to metals. However, in her thesis work Cecilia Payne showed that it isn't so; the Sun and other stars are primarily made up of hydrogen and helium. **Ask class:** if so, why do we mainly see metal lines? It's because hydrogen and helium are often ionized in stars; in addition, the lowest-energy transitions are usually high enough in energy that it isn't easy to excite them in stellar photospheres. Only by careful modeling was Payne able to conclude correctly that light elements dominate the composition of stars.

For most lines or edges, the complications are sufficient that it is best to measure the properties in a laboratory. For the simplest atoms, though, numerical calculations do pretty well, and for single-electron (hydrogen-like) atoms one can even do the calculations analytically. We're going to do an example now in detail, because it is helpful to see how such a calculation is carried out in its full glory.

Collecting some formulae from previous lectures, we get

$$g_i f_{if} = \sum \frac{2}{3} \frac{m}{\hbar} \omega_{if} |\mathbf{r}_{fi}|^2, \quad (1)$$

where g_i is the statistical weight of the initial state and the sum is over degenerate levels of the initial and final states. Here

$$|\mathbf{r}_{fi}|^2 \equiv \left| \int \psi_f^* \mathbf{r} \psi_i d^3\mathbf{r} \right|^2. \quad (2)$$

Let's compute the electric dipole transition strength from the $n = 1$ state of hydrogen to the $n = 2$ state of hydrogen. **Ask class:** What does this mean about the initial quantum numbers (n, l, m) and the final quantum numbers (n', l', m') ? For some value of n , the quantum number l can take on values from 0 to $n - 1$, so the initial state must have $l = 0$. The final state can in principle have $l = 0$ or $l = 1$, but for an electric dipole transition $\Delta l = \pm 1$ so the final state must have $l = 1$. Finally, the azimuthal quantum number m takes on values from $-l$ to $+l$, so in the initial state $m = 0$ and in the final state $m = -1, 0$, or 1 . Therefore, the transition is from $(1, 0, 0)$ to $(2, 1, -1)$, $(2, 1, 0)$, or $(2, 1, 1)$. The wave

functions are

$$\begin{aligned}\psi_{100} &= \pi^{-1/2} a_0^{-3/2} e^{-r/a_0} \\ \psi_{21-1} &= r^{-1} R_{21} Y_{1-1} \\ \psi_{210} &= r^{-1} R_{21} Y_{10} \\ \psi_{211} &= r^{-1} R_{21} Y_{11} .\end{aligned}\tag{3}$$

Here $R_{21} = 2^{-3/2} a_0^{-5/2} 3^{-1/3} r^2 e^{-r/2a_0}$ and Y_{lm} are the spherical harmonics. Note a property of the radial wavefunctions: for $l = 0$, there is a peak at $r = 0$, but for $l > 0$ the probability of $r = 0$ is zero. That makes sense; if in classical physics a particle in a central potential has nonzero angular momentum, it can't be at the origin, and the same is true in quantum mechanics.

What about $|\mathbf{r}_{fi}|^2$? In classical physics one would think about this as $x^2 + y^2 + z^2$. You could also write this as $\frac{1}{2}|x + iy|^2 + \frac{1}{2}|x - iy|^2 + z^2$, and in quantum mechanics this becomes

$$|\mathbf{r}_{fi}|^2 = \frac{1}{2}|(x + iy)_{fi}|^2 + \frac{1}{2}|(x - iy)_{fi}|^2 + |z_{fi}|^2 .\tag{4}$$

It is convenient to do it this way because those particular combinations are expressible in terms of spherical harmonics:

$$\begin{aligned}x \pm iy &= r(8\pi/3)^{1/2} Y_{1\pm 1} \\ z &= r(4\pi/3)^{1/2} Y_{10} .\end{aligned}\tag{5}$$

Since the wavefunction is separable into radial and angular factors, one can do the integrals separately. Thus, the position matrix element can be written

$$|\mathbf{r}_{fi}|^2 = \frac{1}{18} a_0^{-8} \mathcal{R}^2 |\mathcal{A}|^2\tag{6}$$

where

$$\mathcal{R} \equiv \int_0^\infty r^4 e^{-3r/2a_0} dr = \left(\frac{2}{3}\right)^5 4! a_0^5\tag{7}$$

and

$$|\mathcal{A}|^2 \equiv \left| \int Y_{1m}^* Y_{11} d\Omega \right|^2 + \left| \int Y_{1m}^* Y_{10} d\Omega \right|^2 + \left| \int Y_{1m}^* Y_{1-1} d\Omega \right|^2 .\tag{8}$$

Ask class: what do we know about the properties of spherical harmonics? We know that they are orthonormal; therefore, for a given m , only one of the three terms above contributes, and that integral is 1. If we now perform the sum over $m = -1, 0, 1$ and multiply by 2 (the degeneracy of the original state), we get

$$g_i f_{if} = \frac{2^{17}}{3^{10}} \frac{a_0^2 m \omega_{if}}{\hbar} = \frac{2^{17}}{3^{10}} \frac{\hbar^3 \omega_{if}}{m e^4} .\tag{9}$$

Ask class: what is ω_{if} ? It's the frequency of the transition, which is E_{if}/\hbar , and the energy of the transition is 3/4 of the ionization energy from the ground state. Numerically, $\omega_{if} = (3/8) m e^4 / \hbar^3$, so finally

$$g_i f_{if} = \frac{2^{14}}{3^9} = 0.8324 .\tag{10}$$

Note that Table 10.1 in our book gives just f , which is 0.4162 because $g_i = 2$ for the 1s state.

Ask class: given this example, lead us through the steps to compute the oscillator strength from 1s to 2s. If we did this blindly, we would find that we came up with integrals like $\int Y_{10} d\Omega$, which vanish. This is simply a restatement of the electric dipole selection rule $\Delta l = \pm 1$.

What do we do if the final state is a continuum state, as in bound-free absorption? Instead of a final, precisely defined stationary state, we have an infinitude of them. We therefore have to consider a *differential* transition rate, from the bound state i to the continuum state f , for a free electron in the momentum range dp and solid angle $d\Omega$. Therefore, we need to take our original formula for the transition rate and multiply it by the number of states, which is equal to the density of states times $dpd\Omega$:

$$dw = \frac{4\pi^2 e^2}{m^2 c} \frac{\mathcal{J}(\omega)}{\omega^2} |\langle f | e^{i\mathbf{k}\cdot\mathbf{r}} \mathbf{1} \cdot \nabla | i \rangle|^2 \left[\frac{dn}{dpd\Omega} dpd\Omega \right]. \quad (11)$$

For a hydrogen-like atom (one electron) of nuclear charge Z , the total bound-free cross section (i.e., integrated over directions) from a state of principal quantum number n is

$$\sigma_{bf} = \left(\frac{64\pi n}{3\sqrt{3}Z^2} \right) \alpha a_0^2 (\omega_n/\omega)^3 g(\omega, n, l, Z), \quad \omega \geq \omega_n \quad (12)$$

where $\omega_n = \alpha^2 mc^2 Z^2 / (2\hbar n^2)$ is the ionization frequency and $g(\omega, n, l, Z)$ is the Gaunt factor. The form of the bound-free cross section is an abrupt rise at ω_n followed by a decline that is $\sim \omega^{-3}$ near threshold, but $\sim \omega^{-7/2}$ far from the threshold. Incidentally, in practice the ISM has bound-free edges from many different elements and species. This means that the overall bound-free opacity decreases a little slower than ω^{-3} , given that at high energies other contributions come in.