12.12: Intensity Rules

Now, we know, from Section [s12.8], that when we take electron spin and spin-orbit coupling into account the degeneracy of the six $2P$ states of the hydrogen atom is broken. In fact, these states are divided into two groups with slightly different energies. There are four states characterized by the overall angular momentum quantum number $j = 3/2$—these are called the $2P_{3/2}$ states. The remaining two states are characterized by $j = 1/2$, and are thus called the $2P_{1/2}$ states. The energy of the $2P_{3/2}$ states is slightly higher than that of the $2P_{1/2}$ states. In fact, the energy difference is

$$\Delta E = -\frac{\alpha^2}{16} E_0 = 4.53 \times 10^{-5} \text{ eV}. \tag{12.12.1}$$

Thus, the wavelength of the spectral line associated with the $2P \to 1S$ transition in hydrogen is split by a relative amount

$$\frac{\Delta\lambda}{\lambda} = \frac{\Delta E}{\hbar\omega} = 4.4 \times 10^{-6}. \tag{12.12.2}$$

Note that this splitting is much greater than the natural line-width estimated in Equation ([e13.144a]), so there really are two spectral lines. How does all of this affect the rate of the $2P \to 1S$ transition?

Well, we have seen that the transition rate is independent of spin, and hence of the spin quantum number m_s, and is also independent of the quantum number m. It follows that the transition rate is independent of the z-component of total angular momentum quantum number $m_j = m + m_s$. However, if this is the case then the transition rate is plainly also independent of the total angular momentum quantum number j. Hence, we expect the $2P_{3/2} \to 1S$ and $2P_{1/2} \to 1S$ transition rates to be the same. However, there are four $2P_{3/2}$ states and only two $2P_{1/2}$ states. If these states are equally populated—which we would certainly expect to be the case in thermal equilibrium, because they have almost the same energies—and given that they decay to the $1S$ state at the same rate, it stands to reason that the spectral line associated with the $2P_{3/2} \to 1S$ transition is twice as bright as that associated with the $2P_{1/2} \to 1S$ transition.

Contributors and Attributions

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