FINE STRUCTURE OF A SPECTRAL LINE IN HYDROGEN

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 6.18.

As an example of the fine structure formula for hydrogen, we can work out the fine structure of one particular spectral line: the transition from $n=3$ to $n=2$ which occurs in the red portion of the visible spectrum. The fine structure formula is

$$E_n = E_{n0}\left[1-\frac{\alpha^2}{4n^2}\left(3-\frac{4n}{j+\frac{1}{2}}\right)\right] \tag{1}$$

$$= -\frac{13.6\text{ eV}}{n^2}\left[1-\frac{\alpha^2}{4n^2}\left(3-\frac{4n}{j+\frac{1}{2}}\right)\right] \tag{2}$$

where we've inserted the numerical value of the ground state energy $E_{10} = -13.6$ eV. The unperturbed energy is of course the same for all states with a given n, so we're interested in the fine structure correction term, which is

$$E_{nj1} = \frac{13.6\text{ eV}}{n^2}\frac{\alpha^2}{4n^2}\left(3-\frac{4n}{j+\frac{1}{2}}\right) \tag{3}$$

Since the fine structure depends only on the total angular momentum j, we can work out the possible starting and ending states. For $n=3$, $\ell=0,1,2$ and since $s=\frac{1}{2}$ always, the possible values of j are $j=\frac{1}{2},\frac{3}{2},\frac{5}{2}$ so there are 3 states with $n=3$. For $n=2$, $\ell=0,1$ and $j=\frac{1}{2},\frac{3}{2}$ so there are 2 states. Thus a total of $2\times3=6$ transitions are possible. The energy corrections for each state are (in eV):

$\lvert n,j\rangle$	E_{nj1} (eV)
$\left\lvert 3,\frac{1}{2}\right\rangle$	$-2.011717811\times10^{-5}$
$\left\lvert 3,\frac{3}{2}\right\rangle$	$-6.705726035\times10^{-6}$
$\left\lvert 3,\frac{5}{2}\right\rangle$	$-2.235242012\times10^{-6}$
$\left\lvert 2,\frac{1}{2}\right\rangle$	$-5.657956341\times10^{-5}$
$\left\lvert 2,\frac{3}{2}\right\rangle$	$-1.131591268\times10^{-5}$

To work out the frequencies of the transitions between these states, we use the formula $E = h\nu$ where E is the energy difference between the two states and h is Planck's constant (without the division by 2π implicit in $\hbar$). Planck's constant in the correct units is

$$h = 4.135667402 \times 10^{-15} \text{ eV} \cdot \text{sec} \tag{4}$$

The energy of the unperturbed photon is $E_{3,0} - E_{2,0} = 1.889$ eV and to that value we need to add the difference in the correction terms for each pair of states, which we read off the table above. We therefore get, with the transitions listed in increasing order of frequency:

From $\|n, j\rangle$	To $\|n, j\rangle$	ΔE_{nj1} (eV)	ν (Hz)	$\Delta\nu$ (Hz)
$\left\|3, \frac{1}{2}\right\rangle$	$\left\|2, \frac{3}{2}\right\rangle$	-8.80×10^{-6}	$4.567292053 \times 10^{14}$	-
$\left\|3, \frac{3}{2}\right\rangle$	$\left\|2, \frac{3}{2}\right\rangle$	4.61×10^{-6}	$4.567324481 \times 10^{14}$	3.2428×10^{9}
$\left\|3, \frac{5}{2}\right\rangle$	$\left\|2, \frac{3}{2}\right\rangle$	9.08×10^{-6}	$4.567335294 \times 10^{14}$	1.0813×10^{9}
$\left\|3, \frac{1}{2}\right\rangle$	$\left\|2, \frac{1}{2}\right\rangle$	3.65×10^{-5}	$4.567401504 \times 10^{14}$	6.6210×10^{9}
$\left\|3, \frac{3}{2}\right\rangle$	$\left\|2, \frac{1}{2}\right\rangle$	4.99×10^{-5}	$4.567433931 \times 10^{14}$	3.2428×10^{9}
$\left\|3, \frac{5}{2}\right\rangle$	$\left\|2, \frac{1}{2}\right\rangle$	5.43×10^{-5}	$4.567444744 \times 10^{14}$	1.0813×10^{9}

The unperturbed frequency is $4.567313339 \times 10^{14}$ Hz. The $\Delta\nu$ values are the differences in frequency of each line from the preceding line. The first transition produces a line with a lower frequency than the unperturbed one, while all other transitions produce higher frequencies. The fine structure really is 'fine', as the perturbations in the frequency amount to only about 10^{-5} of the unperturbed frequency.