HYDROGEN ATOM: COINCIDENT SPECTRAL LINES

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Reference: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 4.47.

According to the Rydberg formula:

$$\frac{1}{\lambda}=R\left|\left(\frac{1}{n_i^2}-\frac{1}{n_f^2}\right)\right| \tag{1}$$

the wavelength λ of a spectral line in hydrogen is determined solely by the initial and final principal quantum numbers n_i and n_f. If we can find two distinct pairs of integers whose inverse squares have the same difference, then these two distinct transitions will give rise to the same spectral line. An example (given in the question in Griffiths) is the pairs $[6851,6409]$ and $[15283,11687]$. Clearly if we try to find other pairs by randomly picking integers and trying them out, it will likely take a very long time before we hit on an answer. We can get a clue as to how to find other pairs by analyzing the example given. For these two pairs, we can find their prime factors:

$$\begin{aligned}
6851 &= 13\times17\times31 && (2)\\
6409 &= 13\times17\times29 && (3)\\
15283 &= 17\times29\times31 && (4)\\
11687 &= 13\times29\times31 && (5)
\end{aligned}$$

Thus the first pair has two prime factors in common (13 & 17) and the second pair has 29 & 31 in common. In addition, each member of the first pair uses one of the prime factors of the second pair, and vice versa. In particular, if we let $a=31$, $b=29$, $c=17$ and $d=13$, then we can write

$$\begin{aligned}
\frac{1}{(bcd)^2}-\frac{1}{(acd)^2} &= \frac{1}{(abd)^2}-\frac{1}{(abc)^2} && (6)\\
\frac{a^2-b^2}{(abcd)^2} &= \frac{c^2-d^2}{(abcd)^2} && (7)\\
a^2-b^2 &= c^2-d^2 && (8)\\
(a+b)(a-b) &= (c+d)(c-d) && (9)
\end{aligned}$$

Therefore, the key to finding coincident spectral lines is finding pairs of integers that have the same difference of squares. The last line above is an aid to calculating these pairs.

Since we want the difference of squares to have (at least) two different pairs of factors, we can discard any differences of squares that are either prime, or have only two prime factors. We can pick values for a and b, calculate a^2-b^2 to see if it satisfies this condition, then use the other factors of a^2-b^2 to calculate c and d.

For example, if we pick $a=7$ and $b=5$, then $a^2-b^2=24$, and this difference has factors of 1, 2, 3, 4, 6, 8 and 12. We have already used 2 and 12 since $a+b=12$ and $a-b=2$, so we can pick, say, 4 and 6, choosing $c+d=6$ and $c-d=4$, so $c=5$ and $d=1$. Calculating the inverse squares as above, we get

$$\frac{1}{25^2}-\frac{1}{35^2}=\frac{1}{35^2}-\frac{1}{175^2} \tag{10}$$

so the two pairs that give the same wavelength λ are $[35,25]$ and $[175,35]$.

Note that not all pairs of factors found this way will work. In the above example, choosing $c+d=8$ and $c-d=3$ does not give integral values for c and d. The additional condition that must be satisfied is that the sum of the two factors must be even.

As another example, we can pick $a=11$ and $b=5$, giving $a^2-b^2=96$. Two other factors of 96 are 12 and 8, so $c+d=12$ and $c-d=8$, giving $c=10$ and $d=2$. The two pairs are $[220,100]$ and $[550,110]$, since

$$\frac{1}{100^2}-\frac{1}{220^2}=\frac{1}{110^2}-\frac{1}{550^2} \tag{11}$$