Group Problems #22 - Solutions

Friday, October 21

Problem 1 *Ritz Combination Principle*

Show that the longest wavelength of the Balmer series and the longest two wavelengths of the Lyman series satisfy the *Ritz Combination Principle*.

The wavelengths corresponding to transitions between two energy levels in hydrogen is given by:

$$\lambda = \lambda_{limit} \frac{n^2}{n^2 - n_0^2}, \tag{1}$$

where $n_0 = 1$ for the Lyman series, $n_0 = 2$ for the Balmer series, and $\lambda_{limit} = 91.1$ nm for the Lyman series and $\lambda_{limit} = 364.5$ nm for the Balmer series. Inspection of this equation shows that the longest wavelength corresponds to the transition between $n = n_0$ and $n = n_0 + 1$. Thus, for the Lyman series, the longest two wavelengths are λ_{12} and λ_{13}. For the Balmer series, the longest wavelength is λ_{23}.

The Ritz combination principle states that certain pairs of observed frequencies from the hydrogen spectrum add together to give other observed frequencies. For this particular problem, we then have:

$$\begin{aligned}
\nu_{12} + \nu_{23} = \nu_{13} \quad &\Longrightarrow \quad h(\nu_{12} + \nu_{23}) = h\nu_{13} && (2)\\
&\Longrightarrow \quad hc\left(\frac{1}{\lambda_{12}} + \frac{1}{\lambda_{23}}\right) = hc\,\frac{1}{\lambda_{13}} && (3)\\
&\Longrightarrow \quad \frac{1}{\lambda_{12}} + \frac{1}{\lambda_{23}} = \frac{1}{\lambda_{13}}. && (4)
\end{aligned}$$

Inverting Eqn. 1 above gives:

$$\frac{1}{\lambda} = \frac{1}{\lambda_{limit}} \frac{n^2 - n_0^2}{n^2} = \frac{1}{\lambda_{limit}} \left(1 - \frac{n_0^2}{n^2}\right). \tag{5}$$

To calculate $1/\lambda_{12}$ and $1/\lambda_{13}$, we use the Lyman series numbers and find $1/\lambda_{12} = 3/(4 * 91.1) = 0.00823$ nm^{-1} and $1/\lambda_{13} = 8/(9 * 91.1) = 0.00976$ nm^{-1}. To compute $1/\lambda_{23}$, we use the Balmer series numbers and find $1/\lambda_{23} = 5/(9 * 364.5) = 0.00152$ nm^{-1}. Computing the left-hand-side of Eqn. 4 gives $1/\lambda_{12} + 1/\lambda_{23} = 0.00823 + 0.00152 = 0.00975$ nm^{-1}, which is equal to $1/\lambda_{13}$ within rounding error.

Problem 2 *The Rydberg Constant*

When an electron in an atom transitions between orbitals with principle quantum numbers n_1 and n_2, the emitted (or absorbed) photon has an energy

$$h\nu = |E_{n_1} - E_{n_2}|. \tag{6}$$

(a) Use Eq. (6) and the expression for the allowed electron energies, E_n, in the Bohr model to show that for *hydrogen* the emitted (or absorbed) photon has a wavelength

$$\begin{aligned} \lambda &= \frac{64\pi^3\epsilon_0^2\hbar^3 c}{m_e e^4}\left|\frac{n_1^2 n_2^2}{n_1^2 - n_2^2}\right| && (7) \\ &= \frac{1}{R_\infty}\left|\frac{n_1^2 n_2^2}{n_1^2 - n_2^2}\right|, && (8) \end{aligned}$$

where R_∞ is called the *Rydberg* constant.

The expression for the allowed energies in hydrogen is given by:

$$E_n = -\frac{1}{n^2}\frac{e^2}{8\pi\epsilon_0 a_0}, \text{ with } a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} \tag{9}$$

where n is an integer 1 or greater, ϵ_0 is the permittivity of free space, and a_0 is the so-called Bohr radius with m the mass and e the charge of an electron. The energy difference in Eqn. 6 is then given by:

$$h\nu = \frac{hc}{\lambda} = |E_{n_1} - E_{n_2}| = \frac{e^2}{8\pi\epsilon_0 a_0}\left|\frac{1}{n_2^2} - \frac{1}{n_1^2}\right| = \frac{e^2}{8\pi\epsilon_0 a_0}\left|\frac{n_1^2 - n_2^2}{n_1^2 n_2^2}\right|. \tag{10}$$

Inverting this equation and substituting for a_0 gives:

$$\begin{aligned} \lambda &= 8\pi\epsilon_0 a_0 \frac{hc}{e^2}\left|\frac{n_1^2 n_2^2}{n_1^2 - n_2^2}\right| && (11) \\ &= \frac{hc \cdot 8\pi\epsilon_0 \cdot 4\pi\epsilon_0\hbar^2}{e^2 \cdot me^2}\left|\frac{n_1^2 n_2^2}{n_1^2 - n_2^2}\right| && (12) \\ &= \frac{64\pi^3\epsilon_0^2\hbar^3 c}{me^4}\left|\frac{n_1^2 n_2^2}{n_1^2 - n_2^2}\right|, && (13) \end{aligned}$$

where we have used the identity $h = 2\pi\hbar$.

(b) What is the numerical value of $1/R_\infty$ (don't forget the units!)? You may want to use the *fine structure constant*, α in your calculation:

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} = \frac{1}{137}. \tag{14}$$

First of all, we see from Eq. 8 above that $1/R_\infty$ must have units of length. Comparing Eq. 8 and Eq. 13 gives:

$$\frac{1}{R_\infty} = \frac{64\pi^3\epsilon_0^2\hbar^3 c}{me^4} = \frac{16\pi^2\epsilon_0^2\hbar^2c^2}{e^4}\frac{4\pi\hbar c}{mc^2} \tag{15}$$

$$= \frac{1}{\alpha^2}\frac{2hc}{mc^2} = (137)^2\left(\frac{2\cdot 1240 \text{ eV nm}}{511\times 10^3 \text{ eV}}\right) \tag{16}$$

$$= 91.09 \text{ nm}. \tag{17}$$

(c) Find the wavelengths of the transitions from $n_1 = 3$ to $n_2 = 2$ and from $n_1 = 4$ to $n_2 = 2$. To which series do these two transitions belong?

Right away we see that the transition $n_1 = 3 \rightarrow n_2 = 2$ belongs to the Balmer series with $n_2 = n_0 = 2$. The transition $n_1 = 4 \rightarrow n_2 = 2$ also belongs to the Balmer series for the same reason. Using Eq. 8 and our value for $1/R_\infty$ gives:

$$\lambda_{23} = 91.09\left|\frac{9\cdot 4}{9-4}\right| = 656 \text{ nm} \tag{18}$$

$$\lambda_{24} = 91.09\left|\frac{16\cdot 4}{16-4}\right| = 486 \text{ nm}. \tag{19}$$

As a final note, we compare the phenomenological expression for the transition wavelengths, Eq. 1, and the expression derived from the Bohr model, Eq. 7. When $n_2 = 1$, then Eq. 7 becomes:

$$\lambda_{1,n_1} = 91.09\left|\frac{n_1^2}{n_1^2 - 1^2}\right|, \tag{20}$$

where n_1 is an integer larger than 1. This expression is precisely that for the transition wavelengths in the Lyman series, where $\lambda_{limit} = 91.09$ nm and $n_0 = 1$. Similarly, when $n_2 = 2$, we have:

$$\lambda_{2,n_1} = 91.09\left|\frac{n_1^2\cdot 4}{n_1^2 - 2^2}\right| = 364.4\left|\frac{n_1^2}{n_1^2 - 2^2}\right|, \tag{21}$$

where n_1 is now an integer larger than 2. This expression is exactly that for the transition wavelengths in the Balmer series, where $\lambda_{limit} = 364.4$ nm and $n_0 = 2$.