Review of the isotope effect in the hydrogen spectrum

1 Balmer and Rydberg Formulas

By the middle of the 19th century it was well established that atoms emitted light at discrete wavelengths. This is in contrast to a heated solid which emits light over a continuous range of wavelengths. The difference between continuous and discrete spectra can be readily observed by viewing both incandescent and fluorescent lamps through a diffraction grating.

Around 1860 Kirchoff and Bunsen discovered that each element has its own characteristic spectrum. The next several decades saw the accumulation of a wealth of spectroscopic data from many elements. What was lacking though, was a mathematical relation between the various spectral lines from a given element. The visible spectrum of hydrogen, being relatively simple compared to the spectra of other elements, was a particular focus of attempts to find an empirical relation between the wavelengths of its spectral lines. In 1885 Balmer discovered that the wavelengths λ_n of the then nine known lines in the hydrogen spectrum were described to better than one part in a thousand by the formula

$$\lambda_n = 3646 \times n^2/(n^2-4) \text{ Å (angstrom)}, \tag{1}$$

where $n = 3, 4, 5, \ldots$ for the various lines in this series, now known as the Balmer series. (1 angstrom $= 10^{-10}$ m.) The more commonly used unit of length on this scale is the nm (10^{-9} m), but since the monochromator readout is in angstroms, we will use the latter unit throughout this write-up.

In 1890 Rydberg recast the Balmer formula in more general form as

$$1/\lambda_n = R(1/2^2 - 1/n^2) \tag{2}$$

where again $n = 3, 4, 5, \ldots$ and R is known as the Rydberg constant. For reasons to be explained later, its value depends on the mass of the nucleus of the particular isotope of the atom under consideration. The value for hydrogen from current spectroscopic data is

$$R_{\rm H} = 109677.5810\,{\rm cm}^{-1}[1],$$

and the current value for an infinitely heavy nucleus is

$$R_\infty = 109737.31568525(73)\ {\rm cm}^{-1}[2].$$

A generalization of the Rydberg formula to

$$1/\lambda = R_{\rm H}\left[\left(\frac{1}{n_1^2}\right) - \left(\frac{1}{n_2^2}\right)\right] \tag{3}$$

suggested that other series may exist with n_1 taking on the values $1, 3, 4, 5, \ldots$, subject to the restriction that $n_2 > n_1$. This proved to indeed be the case. In 1906 Lyman measured the ultraviolet spectrum of hydrogen and found the series, now bearing his name, corresponding to $n_1 = 1$. In 1908 Paschen measured the infrared spectrum of hydrogen and discovered the series, now bearing his name, corresponding to $n_1 = 3$. Figure 1 shows some of the lines in these series. The vertical axis in this figure is linear in energy (given in units of electron-volts, or eV, at the right), so you can get some sense of the relative energies of the different series.

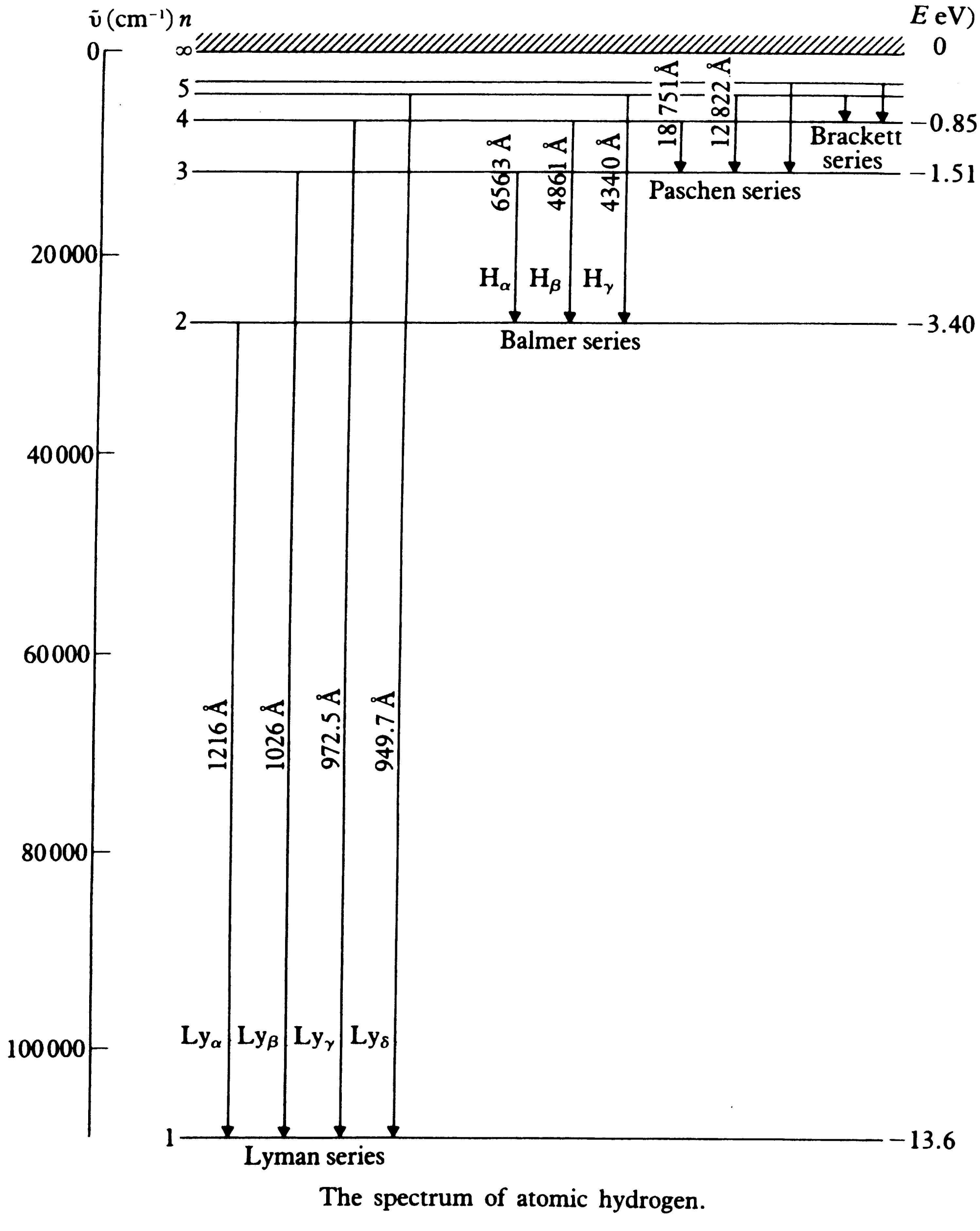

Figure 1: Energy level diagram of atomic hydrogen showing the transitions giving rise to the Lyman (IR), Balmer (visible) and Paschen (UV) spectra.

The remarkable success of the Rydberg formula in describing the spectrum of atomic hydrogen was in stark contrast to theoretical understanding of the atom in the early 1900's. Attempts to understand the emission of light at discrete wavelengths, or frequencies, using principles of classical mechanics and electrodynamics proved fruitless, as classical theory does not allow for an electron to circulate about a nucleus in a stable orbit. Rather, classical theory predicted that the negatively charged electron, circulating about the positive nucleus under the influence of a Coulomb potential, would emit radiation due to the centripetal acceleration associated with circular motion (recall that accelerating charges emit radiation). As the electron emitted radiation and lost energy, the orbit would shrink and eventually (in a predicted 10^{-12} seconds!) the electron would spiral into the nucleus, emitting a continuum of radiation in the process. The stability of atoms, and discrete atomic spectra clearly demonstrate that such a theory does not describe atomic behavior.

2 The Bohr Postulates

in 1913 the Danish physicist Niels Bohr, working at Ernest Rutherford's laboratory in Manchester, England, proposed a blend of classical and radically new ideas to describe atomic behavior. His three postulates were:

1. The electron moves in a circular orbit about the nucleus under the influence of the Coulomb potential, obeying the laws of classical mechanics;

2. In contrast to the infinite number of orbits allowed classically, the electron can occupy only orbits for which its orbital angular momentum is quantized in units of $\hbar$, i.e., L = orbital angular momentum $= n\hbar$ where $n = 1, 2, 3, \ldots$. Electrons are stable in such orbits, i.e., they have a well defined energy and do emit radiation even though they are undergoing centripetal acceleration. Bohr termed these orbits *stationary states*;

3. Radiation is emitted when an electron transitions from one stationary state to another. The energy of the radiation, $E = h\nu$, is equal to the difference in the energies of the initial and final stationary states.

The first postulate is clearly based on classical theory; however the second and third postulates marked a radical departure from classical concepts. Applying these postulates to the hydrogen atom, Bohr's model predicted the total energy of an electron in a stationary state with orbital angular momentum $L = n\hbar$ to be

$$E_n = -\frac{mZ^2e^4}{(4\pi\varepsilon_0)^2 2\hbar^2}\frac{1}{n^2} \tag{4}$$

where m is the mass of electron, Z is the number of protons in the nucleus ($Z = 1$ for hydrogen) and e is the charge of the electron [3]. A transition from a state of higher energy to one of lower energy should result in the emission of radiation with energy

$$E_i - E_f = \frac{hc}{\lambda} = \frac{mZ^2e^4}{(4\pi\varepsilon_0)^2 2\hbar^2}\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right] \tag{5}$$

where $n_i\hbar$ and $n_f\hbar$ are the electron orbital angular momenta of the initial and final states, respectively. Comparing this formula with the Rydberg formula we find that R_{H} should be

$$R_{\mathrm{H}} = \frac{me^4}{8\varepsilon_0^2h^3c}\ .$$

That Bohr's theory resulted in an expression for the Rydberg constant in terms of fundamental constants was a great triumph as it allowed for evaluation of the above expression and comparison to the value derived from spectroscopic data. Then current values for m, e, h and c indicated good agreement between $R_{\rm H}$ calculated from Bohr's theory and experimentally derived values.

But doubters of Bohr's theory remained, with skepticism on the continent being particularly strong. His brother Harald wrote Bohr in the fall of 1913 from Göttingen, Germany, saying that the physicists there considered Bohr's model to be too "bold" and too "fantastic". Rutherford himself was skeptical, asking Bohr, "How does the electron decide what frequency it is going to vibrate (radiate) at when it passes from one stationary state to another? It seems to me that you would have to assume the electron knows beforehand where it is going to stop."

And skeptics were buttressed by new experimental results. Measurements of the spectral lines of singly ionized helium (one electron orbiting around a nucleus with two protons) showed that the ratio of the wavelengths of corresponding helium and hydrogen lines (same n_i and n_f) was not 1:4 as predicted by Bohr's formula, but rather 1:4.0016. (The ratio 1:4 results from increasing Z from one to two in the above expressions for the electron energy.) Bohr quickly revised his postulates, now requiring that the *total* angular momentum, the combined angular momentum of both the electron *and* the nucleus, be quantized in units of $\hbar$. The result of this requirement is that in the expression for the electron energy, the electron mass m must be replaced by the reduced mass μ,

$$\mu = mM/(M+m) \tag{6}$$

where M is the mass of the nucleus. This result is derived below. The expression for the radiation energy of hydrogen-like ions (i.e., one electron orbiting Z protons) is now

$$E_i - E_f = \frac{hc}{\lambda} = \frac{\mu_X Z^2 e^4}{(4\pi\varepsilon_0)^2 2\hbar^2}\left[\frac{1}{n_f^2} - \frac{1}{n_i^2}\right] \tag{7}$$

where μ_X is the reduced mass of atom X. According to Bohr's revised theory, the wavelength ratios between corresponding hydrogen and helium lines should be $4\mu_{\rm He}/\mu_{\rm H}$. It turns out that

$$\frac{\mu_{\rm He}}{\mu_{\rm H}} = 1.0004\ ,$$

(you may wish to verify this) resulting in complete agreement between theory and observation. When Einstein learned of this latest success of the Bohr theory, he responded: "This is an *enormous achievement*. The theory of Bohr must then be right."

The inclusion of the nuclear mass M into the equation for the spectral energies indicates that different isotopes of the same element should show different spectra, since these atoms would have different reduced mass. The existence of the isotope of hydrogen, deuterium, whose nucleus contains one neutron and one proton, was discovered by Harold Urey and his co-workers around 1930 using spectroscopic methods after they successfully produced samples of deuterium-enriched hydrogen by a distillation process [4]. Harold Urey was awarded the Nobel Prize in Chemistry in 1934, "for his discovery of heavy hydrogen."

3 Theory of the reduced-mass correction

Consider a classical system of two particles of mass M and m interacting via central forces (i.e., Coulomb or gravity). Let the position vector between the two particles be $\vec{r}$. When no external forces act on the system, the center of mass $\vec{\boldsymbol{R}}$ will be at rest with respect to some inertial reference frame S. The center of mass is defined as

$$\vec{\boldsymbol{R}} = \frac{M\vec{\boldsymbol{X}} + m\vec{\boldsymbol{x}}}{M+m} , \tag{8}$$

where $\vec{\boldsymbol{X}}$ and $\vec{\boldsymbol{x}}$ locate the particles of mass M and m with respect to the origin of S, and $\vec{\boldsymbol{x}} = \vec{\boldsymbol{X}} + \vec{\boldsymbol{r}}$. Since the center of mass is at rest with respect to S, a physically equivalent reference frame S' has its origin at the center of mass itself; in S', the center of mass of the system

$$\vec{\boldsymbol{R}}' = \frac{M\vec{\boldsymbol{X}}' + m\vec{\boldsymbol{x}}'}{M+m} = 0 . \tag{9}$$

Hence $M\vec{\boldsymbol{X}}' = -m\vec{\boldsymbol{x}}'$. It is still true that $\vec{\boldsymbol{r}} = \vec{\boldsymbol{x}}' - \vec{\boldsymbol{X}}'$, since $\vec{\boldsymbol{x}}$ and $\vec{\boldsymbol{X}}$ are related to $\vec{\boldsymbol{x}}'$ and $\vec{\boldsymbol{X}}'$ by a simple translation. These two equations can be solved to yield

$$\vec{\boldsymbol{X}}' = -\frac{m}{m+M}\vec{\boldsymbol{r}} , \tag{10}$$

$$\vec{\boldsymbol{x}}' = \frac{M}{m+M}\vec{\boldsymbol{r}} . \tag{11}$$

In S' the energy of the two particle system is given by

$$E = \frac{1}{2}m\dot{x}'^2 + \frac{1}{2}M\dot{X}'^2 + V(r) , \tag{12}$$

where the "dot" notation indicates a derivative with respect to time and $V(r)$ is the potential energy between the two particles. Upon taking derivatives of Eqs. (10) and (11) and substituting the result into the energy equation one obtains

$$E = \frac{1}{2}\left(\frac{mM}{m+M}\right)\dot{r}^2 + V(r) . \tag{13}$$

Clearly, the expression in parenthesis in the above equation is the reduced mass μ, Eq. (6). An advantage of expressing the energy in terms of μ is that one transforms the problem of two particles of masses m and M into a problem of one particle of mass μ. A similar calculation shows that one can write the angular momentum about the center of mass in a similar way:

$$\vec{\boldsymbol{L}}' = \left(\vec{\boldsymbol{x}}' \times m\dot{\vec{\boldsymbol{x}}}'\right) + \left(\vec{\boldsymbol{X}}' \times M\dot{\vec{\boldsymbol{X}}}'\right) = \vec{\boldsymbol{r}} \times \mu\dot{\vec{\boldsymbol{r}}} . \tag{14}$$

In the Bohr model and in the subsequent Schrödinger theory, these classical results translate directly into their quantum equivalents.

4 The effect of the reduced mass on the spectrum

From a measurement of the wavelength difference for a given transition that produces a spectral line, you can derive the ratio of the masses of the hydrogen and deuterium atoms. The results for the three visible lines (the α, β and γ lines) can then be combined into a final result for the mass ratio.

The spectral lines are produced by a gas discharge lamp. In our setup, the lamp contains hydrogen enriched with deuterium so that both spectra are produced simultaneously. Enrichment of the hydrogen is necessary as the natural abundance of deuterium is about .015%.

From the Rydberg formula corrected for reduced mass, Eq. (7), we see that the wavelength of light emitted from a particular transition is inversely proportional to the reduced mass:

$$1/\lambda_X \propto \mu_X \ . \tag{15}$$

Because of this proportionality, we see that the nuclear masses of hydrogen and deuterium, M_{H} and M_{D}, are related to the different wavelengths of light produced by each isotope:

$$\frac{\lambda_{\mathrm{H}} - \lambda_{\mathrm{D}}}{\lambda_{\mathrm{H}}} = \frac{1/\mu_{\mathrm{H}} - 1/\mu_{\mathrm{D}}}{1/\mu_{\mathrm{H}}} = \frac{1 - M_{\mathrm{H}}/M_{\mathrm{D}}}{1 + M_{\mathrm{H}}/m} \ . \tag{16}$$

The mass M_{H} is, of course, just the mass of the proton M_p, and the ratio of the proton and electron masses is well known, $M_p/m = 1836.15$. Combining this with the results of your measurements, the ratio of the masses of the two nuclei, $M_{\mathrm{H}}/M_{\mathrm{D}}$ can easily be derived. By adding in electron masses, the mass ratio of the two isotopes can be derived and compared to established values,

$$\frac{M_{\mathrm{hydrogen}}}{M_{\mathrm{deuterium}}} = \frac{1.007825}{2.014102} = 0.500384 \ .$$

References

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