Atomic Spectroscopy and Quantum Mechanics: Hydrogen Spectrum

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1 The Atomic Spectrum of Hydrogen

The atomic spectrum of hydrogen was the cornerstone of modern quantum mechanics *and* quantum electrodynamics (e.g. Lamb shift).

John Jacob Balmer was a Swiss mathematician and physicist. At age sixty, in 1855, he came up with an empirical formula that fitted the the wavelengths of the first *four* optical lines of hydrogen (Hα, Hβ, Hγ, Hδ)

$$\lambda = h\frac{n_2^2}{n_2^2 - n_1^2} \tag{1}$$

with $h = 3645.6\,\text{Å}$, $n_1 = 2$ and $n_1 = 3, 4, 5, ...$ He extrapolated and predicted that the fifth line ($n_1 = 7$), Hϵ, should lie at 3970 Å. This was verified immediately. This example shows that boldness can, at times, pay off.

Johannes Robert Rydberg was a Swedish physicist who primarily focused on studying the lines of alkali elements (Lithium, Potassium and Sodium) obtained by Liveing and Dewar. Rydberg preferred to work with wavenumbers and so, in 1885, he recast Angstrom's formula as well as generalized it

$$k = \frac{4}{B}\Big(\frac{1}{n^2} - \frac{1}{m^2}\Big), \qquad n = 1, 2, 3... \ \ \textit{and} \ \ m = 2, 3, 4... \tag{2}$$

Lyman, during the period 1906–1914, measured the UV lines and Paschen discovered lines (arising from $n = 4$) in the NIR in 1908. Further lines were discovered by Pfund (arising from $n = 5$) in 1924. Humphreys discovered lines in the microwave band in 1953 ($n = 6 \rightarrow 7, 8, ..$).

2 Bohr Planetary Model (1913)

In 1913, Bohr, following a visit to Manchester (where he learnt about Rutherford's atom model and also about the atomic spectrum of hydrogen) constructed a "planetary" model to explain the hydrogen spectrum. Bohr made the following assumptions: (1) the electron orbits the proton akin to a planet around the parent star and (2) the orbits were circular. He used the correspondence principle to associate the orbital energy to the lines radiated at long wavelengths. (3) The observed spectral lines were photons emitted as the electron descended from an upper orbit to a lower orbit. Since the lines were discrete only certain orbits were stable (or allowed). He postulated that (4) orbits with angular momentum which were a multiple of h did not suffer from radiation loss (as would be expected in the classical model).

The results of this model are summarized by the following equations:

$$k = RZ^2\Big(\frac{1}{n_1^2} - \frac{1}{n_2^2}\Big) \quad (3)$$

$$R = \frac{2\pi^2 m_e e^4}{ch^3} \quad (4)$$

$$a = a_0\frac{n^2}{Z} \quad (5)$$

$$a_0 = \frac{h^2}{4\pi^2} = 0.528\,\text{Å} \quad (6)$$

$$v/c = \alpha\frac{Z}{n} \quad (7)$$

$$\alpha = \frac{2\pi^2}{ch} = 1/137.29. \quad (8)$$

Here, Z is the charge of the nucleus, k is the wave number emitted by an electron as it jumps from energy level n_2 to level n_1 and a and v is the orbital radius and velocity of an electron in energy state n. R is the Rydberg constant, a_0 is the Bohr radius and α is the fine structure constant.

The limitations of the Bohr model were the following: (1) it could not explain the observed "fine structure" in the observed lines (doublets, triplets), (2) could not account for the intensities of the lines nor (3) explain the Zeeman effect (which was already discovered by then).

3 Sommerfeld Model (1916)

Sommerfeld noted that the Bohr model did not satisfy special relativity. In particular the mass of the electron will be dependent on the energy level (owing to velocity). Also he allowed for orbits which were elliptical. In all other respects Sommerfeld made the same assumptions as before.

First, we discuss the non-relativistic Sommerfeld model. There are two angular momenta associated with an elliptical orbit: angular (p_ϕ; quantum number k) and radial (p_r; quantum number r). The quantization requirement thus results in two quantum numbers already noted. For instance with $n = 3$, the azimuthal quantum number can be 1, 2, 3 and the radial quantum number is $r = n - k$. However, Sommerfeld excluded, noting that for r=0 the electron will collide with the nucleus excluded the quantum number $r = 0$. However, the energy levels, even in this model, depended only on n. Thus the non-relativistic Sommerfeld model could also not explain the fine structure seen in the spectral lines.

However, the relativistic model provided a plausible accounting for the fine structure seen in the hydrogen spectrum. The theory could not explain the intensities nor accurately account for the fine structure line wavelengths.

An additional improvement (the Wilson-Sommerfeld model) arose from the following consideration: while each orbit is in a plane there is no reason why all orbits should occupy the same plane. Another way of stating this fundamental point is that orbits need to be fully specified in 3-dimensional space. Thus there are three angular momenta: radial, azimuthal and polar. Each has to be quantized. This led to a new quantum number, m (the orientation of the ellipse with respect to an arbitrarily chosen z axis). This quantum number is restricted to $\pm 1, \pm 2, ..., \pm k$. Electrons circulating in an orbit have a magnetic momentum. Thus an external magnetic field can provide a natural z axis orientation. This model thus had a natural explanation for Zeeman splitting.

de Broglie, as a part of his 1924 thesis, proposed that even matter, like radiation, is also a wave. If so, stable orbits are identified as those with integer wavelengths.

4 Schrodinger's Model

In 1926, Schrodinger, accepting de Broglie's proposal that all material objects are waves, recast the equations of mechanics in terms of waves. We are all familiar with a particle in a box problem (which naturally gives rise to quantum states). The Hydrogen atom is like a a particle in a box but with a potential which is more complicated.

In this model the time-independent wave function of the electron is given by

$$\Psi(r, \theta, \phi) = R(r)P(\theta)F(\phi). \tag{9}$$

The quantum numbers with $R(r)$, $P(\theta)$ and $F(\phi)$ are n, l, m_l. The allowed values are

$$\begin{aligned} n &= 1, 2, 3... \\ l &= 0, 1, 2.., n - 1 \\ m_l &= -l, -l + 1, .., +l \end{aligned} \tag{10}$$

It should be noted that the energy levels in Schrodinger's model is exactly the same as in the Bohr model. The stationary orbits of Bohr were understood as orbits whose length had integer number of de Broglie wavelengths.

5 Spin

In 1922 Sterl & Gerlach reported experiments which led to the conclusion that electron (in this case the valence electron of Silver) had a spin of $s = 1/2h$ and an associated magnetic moment

$$\mu_{\mathbf{s}} = -g_s \mu_B \mathbf{s} \tag{11}$$

where $\mathbf{s}$ is the spin vector, $\mu_B = e\hbar/(2m_e c)$ is the Bohr magneton and $g \approx 2$. This then adds a number quantum number, m_2 which takes the value $\pm 1/2$. In 1925 Pauli proposed his famous "exclusion rule" which stated that no two electrons can have the same quantum numbers (more below).

6 Relativistic Formulation: Dirac (1928)

The fine structure lines were fully understood in the relativistic formulation of the equation of quantum mechanics by Dirac. In Dirac's formulation the spin and momentum are deeply coupled.

See §14.4 of Review of the Hydrogen atom by Luca Nanni.

7 Quantum Electrodynamics

Only with Quantum Electrodynamics (where even the field is quantized and there vacuum fluctuations) was the Lamb shift understood.