Class 27: The Bohr model for the atom

Hydrogen line spectra
When excited by an electric discharge, a hydrogen gas emits light at a set of discrete wavelengths. Four strong lines are seen in the visible part of the spectrum at wavelengths 656.3, 486.1, 434.0 and 410.2 nm. Balmer in 1885 discovered an empirical formula for these wavelengths plus some strong UV lines observed in hot stars

\[ \lambda = 364.705 \frac{n^2}{n^2 - 4} \text{ nm, } n = 3, 4, 5, \ldots \]  

(Note here the wavelength is for measurements made in vacuum.) By writing the Balmer formula in terms of wave number, rather than wavelength, Rydberg proposed in 1888 a more general formula

\[ \frac{1}{\lambda} = R_H \left( \frac{1}{n_0^2} - \frac{1}{n^2} \right), \quad n = n_0 + 1, n_0 + 2, n_0 + 3, \ldots, \]

where \( R_H \) is a constant, now known as the Rydberg constant for hydrogen. The numerical value is \( R_H = 1.09678 \times 10^7 \text{ m}^{-1} \). The corresponding wavelength is 91.1763 nm.

Over the following 25 years or so, series of lines corresponding to different values of \( n_0 \) were discovered.

<table>
<thead>
<tr>
<th>( n_0 )</th>
<th>Series name</th>
<th>Discovered</th>
<th>Longest wavelength in the series in nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Lyman</td>
<td>1906 - 1914</td>
<td>121.6 (UV)</td>
</tr>
<tr>
<td>2</td>
<td>Balmer</td>
<td>656.5</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Paschen</td>
<td>1908</td>
<td>1875 (IR)</td>
</tr>
<tr>
<td>4</td>
<td>Brackett</td>
<td>1922</td>
<td>4050 (IR)</td>
</tr>
<tr>
<td>5</td>
<td>Pfund</td>
<td>1924</td>
<td>7460 (IR)</td>
</tr>
<tr>
<td>6</td>
<td>Humphreys</td>
<td>1953</td>
<td>12400 (IR)</td>
</tr>
</tbody>
</table>

At the time of Rydberg’s discovery, there was no physical explanation for his formula.

The Bohr model
In the Rutherford model for the atom, the electrons reside outside the positively charge nucleus, and hence are accelerated by the Coulomb force. According to classical physics, the electrons must radiate electromagnetic waves. The energy loss would result in the electrons spiraling into the nucleus.

At this time Niels Bohr was contemplating how Planck’s quantum nature of radiation ideas could be applied to atomic spectra, and in particular the Rydberg formula for hydrogen. Bohr pictured the electron in hydrogen orbiting the central atomic nucleus. In 1915 he postulated a number of general assumptions:
a) Atoms have ‘stationary states’ of definite total energy. In these stationary states, the electrons do not radiate.

b) Emission or absorption of electromagnetic radiation occurs only in transitions from one stationary state to another. The frequency of the electromagnetic radiation is proportional to the energy difference of the two states, and the constant of proportionality is Planck’s constant.

c) Classical physics describes the dynamical equilibrium of the atom in a stationary state but does not describe transitions between stationary states.

d) The mean value of the kinetic energy of the electron – nucleus system is quantized. For a circular orbit, Bohr pointed out that the quantization of kinetic energy was equivalent to the angular momentum of the system being an integer multiple of $\hbar$.

To derive the Rydberg formula for hydrogen from Bohr’s assumptions, we will assume that the central nucleus is fixed. For an electron of mass $m$ moving with speed $v$ in a circular orbit of radius $r$, its angular momentum about the nucleus is

$$ L = mvr. \quad (27.2) $$

According to assumption d), $L = mvr = nh$, where the integer $n$ is called the principal quantum number.

According to assumption c), we can apply Newton’s second law to the motion of the electron. The Coulomb force provides the centripetal acceleration. Hence

$$ k \frac{e^2}{r^2} = \frac{m v^2}{r}. \quad (27.3) $$

The orbital velocity is then given by

$$ v^2 = k \frac{e^2}{mr}. \quad (27.4) $$

Using the quantization of angular momentum to eliminate $v$, we find that only certain values of the orbital radius are allowed:

$$ r = n^2 \frac{\hbar}{kme^2} = n^2 a_0, \quad (27.5) $$

where

$$ a_0 = \frac{\hbar^2}{kme^2} \quad (27.6) $$

is called the Bohr radius. Its numerical value is $a_0 = 0.0529$ nm.

The kinetic and potential energies are
\[ K = \frac{1}{2}mv^2 = \frac{1}{2}ke^2 = \frac{1}{2}\frac{k^2me^4}{n^2\hbar^2}, \]  
\[ U = -k\frac{e^2}{r} = -2K = -\frac{k^2me^4}{n^2\hbar^2}. \]

The total energy is

\[ E = K + U = -K = -\frac{1}{2}\frac{k^2me^4}{n^2\hbar^2}. \]

Hence the energy of a photon associated with a transition between states of quantum numbers \( n_0 \) and \( n \) is

\[ hf = \frac{k^2me^4}{2\hbar^2} \left( \frac{1}{n_0^2} - \frac{1}{n^2} \right). \]

Since \( \lambda f = c \), we obtain the Rydberg formula

\[ \frac{1}{\lambda} = k^2 \frac{me^4}{4\pi\varepsilon_0 c \hbar^2} \left( \frac{1}{n_0^2} - \frac{1}{n^2} \right). \]

To take into account the finite mass of the nucleus, \( m \) must be replaced by the reduced mass, which for hydrogen is

\[ \mu_H = \frac{mm_p}{m + m_p}. \]

where \( m_p \) is the mass of the proton. Hence

\[ R_H = k^2 \frac{\mu He^4}{4\pi\varepsilon_0 c \hbar^3}. \]

**The reduced mass**

Consider two mutually interaction particles of mass \( m_1 \) and \( m_2 \). Suppose that the strength of the interaction depends only on the distance between the two particles. In an inertial frame, the equations of motion of the particles are of form

\[ m_1 \frac{d^2\mathbf{r}_1}{dt^2} = \mathbf{F}(|\mathbf{r}_1 - \mathbf{r}_2|), \]

\[ m_2 \frac{d^2\mathbf{r}_2}{dt^2} = -\mathbf{F}(|\mathbf{r}_1 - \mathbf{r}_2|). \]

The position of mass \( m_1 \) relative to mass \( m_2 \) is
\[ \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2. \]  

Hence

\[
\frac{d^2 \mathbf{r}}{dt^2} = \frac{d^2 \mathbf{r}_1}{dt^2} - \frac{d^2 \mathbf{r}_2}{dt^2} = \frac{1}{m_1} \mathbf{F}\left(\mathbf{r}_1 - \mathbf{r}_2\right) + \frac{1}{m_2} \mathbf{F}\left(\mathbf{r}_1 - \mathbf{r}_2\right) = \left(\frac{1}{m_1} + \frac{1}{m_2}\right) \mathbf{F}\left(\mathbf{r}_1 - \mathbf{r}_2\right). \tag{27.16}
\]

This can be considered as the equation of motion of a single particle of mass \( \mu \) and position \( \mathbf{r} \) acted on by a force whose magnitude depends only on the magnitude of the particle’s position vector. The mass is the reduced mass

\[ \mu = \frac{m_1 m_2}{m_1 + m_2}. \tag{27.17} \]

Now further suppose that the positions of the two particles are measured in the center of mass frame. Then

\[ m_1 \mathbf{r}_1 + m_2 \mathbf{r}_2 = 0. \tag{27.18} \]

Since this holds for all time, we also have that

\[ m_1 \frac{d\mathbf{r}_1}{dt} + m_2 \frac{d\mathbf{r}_2}{dt} = 0. \tag{27.19} \]

In terms of \( \mathbf{r} \), we now have

\[ \mathbf{r}_1 = -\frac{m_2}{m_1 + m_2} \mathbf{r}, \quad \mathbf{r}_2 = -\frac{m_1}{m_1 + m_2} \mathbf{r}, \tag{27.20} \]

with similar expressions for the particle velocities.

The angular momentum of the system about the center of mass is

\[
\mathbf{L} = m_1 \mathbf{r}_1 \times \frac{d\mathbf{r}_1}{dt} + m_2 \mathbf{r}_2 \times \frac{d\mathbf{r}_2}{dt}
\]

\[
= m_1 \frac{m_2}{m_1 + m_2} \mathbf{r} \times \frac{m_2}{m_1 + m_2} \frac{d\mathbf{r}}{dt} + m_2 \frac{m_1}{m_1 + m_2} \mathbf{r} \times \frac{m_1}{m_1 + m_2} \frac{d\mathbf{r}}{dt}
\]

\[
= \frac{m_1 m_2}{m_1 + m_2} \mathbf{r} \times \frac{d\mathbf{r}}{dt}
\]

\[
= \mu \mathbf{r} \times \frac{d\mathbf{r}}{dt}.
\tag{27.21}
\]

This is the same as the angular momentum of a single particle of mass equal to the reduced mass at position \( \mathbf{r} \).
We now see that to generalize the Bohr model to a finite mass nucleus the electron mass must be replaced by the reduced mass in the quantization of angular momentum (see equation (27.2)) and in the Newton’s second law equation (27.3).

**De Broglie relation**

It is Bohr’s postulate (d) that lead de Broglie to formulate his relation between momentum and wavelength. If the electron in the hydrogen atom is to be represented by a wave, then the circumference of the orbit must be an integer number of wavelengths, i.e.

\[ n\lambda = 2\pi r. \quad (27.22) \]

Equation (27.2) can be written in terms of the electron momentum and radius of the orbit

\[ L = rp. \quad (27.23) \]

Bohr’s quantization condition gives that

\[ rp = n\hbar. \quad (27.24) \]

Eliminating \( r \) from equations (27.22) and (27.24), we find

\[ p = \frac{n\hbar}{r} = \frac{nh}{2\pi r} = \frac{h}{\lambda}. \quad (27.25) \]

which is the de Broglie relation.

**Ionization potential**

From equation (27.9), we see that the most tightly bound orbit occurs for \( n = 1 \). The minimum energy input needed to remove the electron from this ground state is called the ionization potential. The ionization potential for hydrogen is

\[ I_H = \frac{1}{2} \frac{k^2 \mu_H e^4}{\hbar^2} = 13.5984 \text{ eV}. \quad (27.26) \]

**Single electron ions**

For a single electron in an ion of nuclear charge \( Z e \), the analysis is the same as for the Bohr model of the hydrogen atom, except that \( e^2 \) must be replaced by \( Z e^2 \), and the appropriate reduced mass must used. In particular the Rydberg constant is

\[ R = k^2 \frac{\mu Z^2 e^4}{4\pi \epsilon_0 \hbar^2} = \frac{\mu}{\mu_H} Z^2 R_H, \quad (27.27) \]
where for a nucleus of mass $M$,

$$\mu = \frac{mM}{m + M}. \quad (27.28)$$

**The fine structure constant**

The ratio of the velocity of electron in the ground state to the speed of light in vacuum is

$$\alpha = \frac{v}{c} = k\frac{e^2}{\hbar}. \quad (27.29)$$

This dimensionless quantity occurs frequently in atomic physics, and elsewhere, and is called the fine structure constant. Its value is approximately $\alpha = 1/137$.

The quantized energies of the Bohr model and the Bohr radius can be written using the fine structure constant as

$$E_n = -\frac{1}{2} mc^2 \frac{\alpha^2}{n^2}, \quad (27.30)$$

and

$$a_0 = \frac{1}{\alpha mc}. \quad (27.31)$$

The Rydberg formula for hydrogen is

$$\frac{2\pi a_0}{\lambda} = \frac{\alpha \left( \frac{1}{n_0^2} - \frac{1}{n^2} \right)}{2}, \quad (27.32)$$

which reveals how the shortest possible wavelength of photons emitted by a transition in a hydrogen atom is related to the circumference of the orbit in the ground state.

One physical interpretation of the fine structure constant arises from consideration of the electron. The electron is a point-like charged particle with no structure. Interaction of the charge with its field leads to oscillations which replace the point with a charge distribution of some radius, $R$, The energy of the charge distribution is $E = ke^2/R$. Identifying $2\pi R$ with the de Broglie wavelength of an electron at rest, $mc^2 = hf = hc/R$. Hence the ratio of the energy of the charge distribution to the rest energy of the electron is $E/(mc^2) = ke^2/(hc) = \alpha$.

In the standard model of particle physics, $\alpha$ is the coupling constant determining the strength of the interaction between electrons and photons.