Quantization of Atomic Energy Levels

Atomic Spectra

The first real clues to the true nature and structure of atoms\(^1\) were provided by atomic spectra. Decades before Rutherford developed his model of the atom and Planck advanced his quantum theory of blackbody radiation, it was known that atomic gases (elements) exhibited discrete or line\(^2\) spectra. Such gases, when heated to a high enough temperature or are submitted to an electrical discharge, will emit visible light. When this light is passed through a diffraction grating or prism, one finds that only certain sharply defined wavelengths are emitted. In addition to the visible wavelengths, there are infrared and ultraviolet “lines” as well. These wavelengths make up the emission spectrum of the atom of which the gas is composed. If white light (continuous spectrum of wavelengths) is passed through a cool atomic gas, the continuous spectrum of the white light is found to be crossed by dark lines at specific wavelengths. This indicated that these specific wavelengths were being absorbed by the atoms of the gas. For a single gas of atoms, the lines in the absorption spectrum coincide exactly with lines in the emission spectrum. Hence, the atom emits light at the same specific wavelengths as it absorbs light. Moreover, each atomic gas was found to have a unique emission spectrum, which suggests that the spectrum is connected with the structure of the atom.\(^3\)

As you recall, Rutherford conceived of the planetary model of the atom based upon his alpha-particle experiments. However, this model atom is inherently unstable because of the continuous emission of electromagnetic radiation by the accelerating electrons.

In 1913, Niels Bohr proposed a model of the atom that was spectacularly successful in explaining the spectra of one-electron, or hydrogen-like, atoms. The model was based upon Rutherford’s model, but in a bold step, Bohr departed from the classical theory of radiation that was the demise of the Rutherford model. The elements of Bohr’s model can be summarized in four postulates.

(1) The Coulomb (electrostatic) attraction between an electron and the nucleus provides the centripetal force necessary for a dynamically stable circular orbit. [Classical]

(2) The permitted orbits are those in which the angular momentum of the electron is an integer multiple of \(\hbar\), i.e., \(L = n\hbar\), where \(\hbar = h/2\pi\) and \(n = 1, 2, 3, \ldots\). [Non-classical]

(3) An electron moving in a permitted stable orbit does not radiate. [Non-classical]

(4) Emission or absorption of radiation occurs only when an electron makes a transition between stable orbits. [Non-Classical]

Postulate 2 came about as a result of Bohr’s application of the Correspondence Principle, which says that in the limit of large orbits and large energies where classical physics is valid, quantum

---

\(^1\) Mechanical Universe Video “Atoms”, Ch. 20
\(^2\) “Line” here represents an image of the slit used in spectroscope or spectrometer.
\(^3\) Show emission and absorption spectra
calculations must agree with classical ones. In the macroscopic world where classical physics holds, the angular momentum is a continuous variable. Starting from this regime, Bohr was able to show that the angular momentum was quantized according to postulate 2.

The 3rd postulate is a simple assertion that circumvents the classical radiation problem. The 4th postulate connects with Planck’s quantum theory in which energy levels of atoms (oscillators) are quantized and emission or absorption of radiant energy occurs in discrete amounts corresponding to the energy difference between two levels.

We now utilize the Bohr model to derive an expression for the energy of the electron in a one-electron atom.

**Bohr Theory**

We assume the nucleus has positive charge \(+Ze\) and is infinitely massive (as far as the electron is concerned) and therefore undergoes no motion. We shall discuss corrections for the finite mass of the nucleus later. We also assume the electron is non-relativistic.

Equating the electric force to the centripetal force gives

\[
\frac{kZe^2}{r^2} = \frac{mv^2}{r},
\]

or,

\[
\frac{kZe^2}{r} = mv^2.
\]

In the preceding, \(k = 1/4\pi\varepsilon_0\).

The kinetic energy of the electron \(K = \frac{1}{2}mv^2\), which from Eq. (6.2) is given by

\[
K = \frac{1}{2}mv^2 = \frac{kZe^2}{2r}.
\]

Now, the electric potential energy \(U\) of the electron is given by \(U = -kZe^2/r\). The total mechanical energy \(E\) of the electron is then

\[
E = K + U = -\frac{kZe^2}{2r}.
\]

Note that \(E\) is negative because the electron is bound, i.e., energy must be supplied to remove the electron from the atom. Now to determine \(E\), we need to find \(r\). To do this, we invoke the second postulate:

\[
L = n\hbar, \quad n = 1, 2, 3...
\]

For an electron in a circular orbit about the nucleus, \(L = mvr\). Thus, using Eq. (6.5), we find that
\[ v = \frac{n\hbar}{mr}. \] (6.6)

Substituting for \( v \) in Eq. (6.2) yields
\[ \frac{kZe^2}{r} = m \left( \frac{n^2\hbar^2}{m^2r^2} \right), \]
or,
\[ r_n = \frac{n^2\hbar^2}{mkZe^2}, \quad n = 1, 2, 3, \ldots \] (6.7)

Thus, the quantization of the angular momentum leads to the quantization of the orbits.

Now, we can write
\[ r_n = \frac{n^2\hbar^2}{mkZe^2} = \frac{n^2a_B}{Z}, \]
where
\[ a_B = \frac{\hbar^2}{mkZe^2} \] (6.8)

is defined to be the Bohr radius. Its value is \( a_B = 0.0529 \text{ nm} \).

Substituting for \( r \) in the expression for \( E \) yields
\[ E_n = -\frac{kZe^2}{2Z^2} = -Z^2 \left( \frac{ke^2}{2a_B} \right) \frac{1}{n^2}, \]
or,
\[ E_n = -\frac{1}{n^2} Z^2 \left( \frac{mk^2e^4}{2\hbar^2} \right), \quad n = 1, 2, 3, \ldots \] (6.9)

Hence, we see that energy quantization results from the quantization of angular momentum. Eq. (6.9) applies to all one-electron atoms, for example, hydrogen \((Z = 1)\); \( \text{He}^+ \) \((Z = 2)\); \( \text{Li}^{2+} \) \((Z = 3)\), and so on. Let us specifically consider the case of hydrogen \((Z = 1)\). Then,
\[ E_n = -\frac{1}{n^2} \left( \frac{mk^2e^4}{2\hbar^2} \right), \quad n = 1, 2, 3, \ldots \quad (Z = 1) \] (6.10)

Let us define the Rydberg energy:
\[ E_R = \frac{mk^2e^4}{2\hbar^2}. \] (6.11)

Thus, for hydrogen, the allowed energies are given by
\[ E_n = -\frac{E_R}{n^2}. \quad n = 1, 2, 3 \ldots \] (6.12)

The value of the Rydberg energy \( E_R = 13.6 \text{ eV} \).
According to the 4th postulate, energy is emitted or absorbed by the atom when there is a transition between energy states. In other words, a transition between energy states is accompanied by the emission or absorption of a photon of energy precisely equal to the difference between the energies of the two states.

Consider the emission process for hydrogen. The atom is initially in a higher energy state and makes a transition to a lower energy state, with a photon being emitted. By energy conservation, we have

\[ E_{ph} = hf = \frac{hc}{\lambda} = E_i - E_f. \]  

(6.13)

Now,

\[ E_i - E_f = \frac{E_R}{n_i^2} - \left( -\frac{E_R}{n_f^2} \right) = E_R \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right). \]  

(6.14)

From Eqs. (6.13) and (6.14), we find

\[ \frac{1}{\lambda} = \frac{E_R}{hc} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right). \]  

(6.15)

Let us define the Rydberg constant \( R = \frac{E_R}{hc} \). Then Eq. (6.15) becomes

\[ \frac{1}{\lambda} = R \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \]  

(6.16)

\( Z = 1 \)

The value of the Rydberg constant is 0.0110 nm\(^{-1}\).

Eq. (6.16) gives us the wavelengths of all the possible photons that can be emitted when a hydrogen atom makes a transition from a higher energy state (larger \( n \)) to be a lower energy state (smaller \( n \)). In other words, it predicts the wavelengths of all the lines of the emission (and absorption) spectrum of hydrogen. The wavelengths predicted by Eq. (6.16) are in excellent agreement with experimental results.

The lowest-energy state of an atom is called the ground state. Clearly, in the Bohr atom, the ground state corresponds to \( n = 1 \) (most negative energy). For hydrogen, the ground-state energy is \( E_1 = -\frac{E_R}{1^2} = -13.6 \text{ eV} \). The \( n = 2 \) level is called the first excited state. Its energy is \( E_2 = -\frac{E_R}{2^2} = -3.4 \text{ eV} \). The \( n = 3 \) level is the second excited state, and so forth.

The atomic energy states are often schematically depicted as an energy level diagram. Each level corresponds to the energy of an electron state. Arrows show the transitions between levels. Absorption of a photon is indicated by an arrow pointing from a lower to a higher energy level. Emission of a photon is indicated by an arrow from a higher to a lower energy level. These energy level diagrams allow one to conveniently depict different spectral series, which are groups of transitions, each of which contains transitions that terminate at the same
energy level. For example, the Balmer series, which contains the well known visible lines of the
hydrogen spectrum, consists of transitions in which the initial energy levels have \( n_i > 2 \) and the
final energy level in all cases is \( n_f = 2 \). For the Balmer Series (emission),
\[
\frac{1}{\lambda} = R \left( \frac{1}{2^2} - \frac{1}{n_i^2} \right). \quad \text{(Balmer Series, hydrogen)} \quad (6.17)
\]
When \( n_i = 3 \) in Eq. (6.17), one finds that \( \lambda = 656 \) nm, which corresponds to the red line.

**Reduced Mass**

In the derivation of the energy of the electron in a one-electron atom, we made the assumption
that the nucleus is infinitely massive and does not move. Though this is a reasonable
approximation given the fact that \( m_e \approx m_p / 2000 \), spectroscopy is a very precise science and the
discrepancy in the wavelength due to the infinite mass assumption can be detected. Hence, to
make our formulas more accurate, we must account for the finite mass of the nucleus and its
motion. We use problem 5.21, Taylor, Zafiratos, and Dubson, 2nd ed. as a vehicle to accomplish
this. [Show diagram in class; diagram in the textbook.]

First, we note that the center of mass (CM) of the hydrogen atom is unaccelerated since the net
external force on the atom is zero. Hence, we can place the CM at rest in an appropriate inertial
frame. The proton and electron orbit about the stationary CM. We assume the proton and
electron orbit the CM rigidly, so they have a common angular velocity \( \omega \). Further, let us take the
origin to be at the proton's position.

(a) The position of the CM is given by
\[
\vec{r}_{CM} = \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{m_1 + m_2}. \\
\vec{r}_p = |\vec{r}_{CM}| = \frac{m_p (0) + m_e r}{m_p + m_e} = \left( \frac{m_e}{m_p + m_e} \right) r. \quad \text{(i)}
\]
\[
r_e = r - r_p = \left( 1 - \frac{m_e}{m_p + m_e} \right) r = \left( \frac{m_p}{m_p + m_e} \right) r. \quad \text{(ii)}
\]

(b)
\[
v_p = r_p \omega. \quad v_e = r_e \omega.
\]
\[
K = K_e + K_p = \frac{1}{2} m_e r_e^2 \omega^2 + \frac{1}{2} m_p r_p^2 \omega^2
\]
\[
= \frac{1}{2} \omega^2 \left[ \frac{m_e m_p^2 r^2}{(m_e + m_p)^2} + \frac{m_p m_e^2 r^2}{(m_e + m_p)^2} \right] = \frac{1}{2} r^2 \omega^2 \left( \frac{m_p m_e}{m_e + m_p} \right)
\]
\[
= \frac{1}{2} \mu r^2 \omega^2, \quad \text{(iii)}
\]

where
\[ \mu = \frac{m_e m_p}{m_e + m_p} \]

is the reduced mass.

[Notice that the only difference between the above expression for \( K \) and the fixed-proton result is that \( \mu \) has replaced \( m_e \). Also, note that \( \mu = 0.9995 m_e \) for hydrogen.]

(c) The electrostatic force exerted on the proton is \( F = \frac{k e^2}{r^2} \).

The centripetal force \( \frac{m_p v_p^2}{r_p} = \frac{m_p r_p^2 \omega^2}{r_p} = m_p r_p \omega^2 \).

But \( r_p = \frac{m_r}{m_p + m_e} \).

So \( m_p r_p \omega^2 = r_p = \frac{m_p m_e r \omega^2}{m_p + m_e} = \mu r \omega^2 \).

Equating the electrostatic force to the centripetal force gives \( \mu r \omega^2 = \frac{k e^2}{r^2} \). ----- (iv)

The same result is obtained for the electron.

(d) The potential energy is given by \( U = -\frac{k e^2}{r} \).

Using Eq. (iv), we can write \( U = -\frac{k e^2}{r} = -\mu r^2 \omega^2 \). But \( K = \frac{1}{2} \mu r^2 \omega^2 \). Hence, \( K = -\frac{1}{2} U \).

\[ E = K + U = \frac{1}{2} U = -\frac{k e^2}{2r} \].

(e)

\[ L = L_c + L_p = m_p r_p v_p + m_e r_e v_e = m_p r_p^2 \omega + m_e r_e^2 \omega \]

\[ = \omega \left[ m_p \left( \frac{m_r}{m_p + m_e} \right)^2 + m_e \left( \frac{m_r}{m_p + m_e} \right)^2 \right] = \mu r^2 \omega. \]

(f) It is clear that correcting the previously derived result only entails replacing \( m_e \) by \( \mu \). Thus, the Rydberg energy becomes
\[ E_R = \frac{\mu k^2 e^4}{2\hbar^2}. \] (6.18)

Other Evidence for the Quantization of Energy Levels

(a) Characteristic X-rays

We have seen that when x-rays are produced by bombarding a target material with high-energy (keV) electrons, a continuous x-ray spectrum is produced (bremsstrahlung) along with discrete peaks that are characteristic of the target material. These discrete x-ray wavelengths are due to transitions involving the innermost \( (n = 1,2) \) electrons in the multielectron atom. (See diagram below.) A bombarding electron knocks out an inner electron, creating a vacancy. The atom is now in an excited state. To return to its lowest energy state, an electron from a higher energy state makes a transition to fill the vacancy at the lower level. This is accompanied by the emission of an x-ray photon.\(^4\) Electrons at the \( n = 1 \) level are traditionally called K electrons. Thus, a transition from the \( n = 2 \) level to the \( n = 1 \) level is called K\(_\alpha\) radiation, from the \( n = 3 \) level to the \( n = 1 \) level is called K\(_\beta\) radiation, etc. The group of transitions terminating at the K \((n = 1)\) level is called the K series. Transitions that terminate at the \( n = 2 \) level form the L series, and so forth.

From the Bohr model, one would predict that photon energies and frequencies are proportional to \( Z^2 \). [For a one-electron atom with nuclear charge \(+Ze\), \( E_{ph} = hf = Z^2 E_R \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \).] Moseley found that the K\(_\alpha\) and K\(_\beta\) radiation\(^5\) for many elements could be described by the relation

\[ f = a (Z - \delta)^2, \] (6.19)

---

\(^4\) Actually, a succession of transitions occur as vacancies are created at higher and higher energy levels. We are only concerned with the lowest levels, however.

\(^5\) Diagram of Moseley’s data, p. 92 Rohlf
where \( a \) is a constant and \( \delta \approx 1 \).

[Note that the x-ray lines are not single lines, but closely spaced lines. The higher levels are split by the spin-orbit interaction.]

The \((Z-1)^2\) dependence occurs because the charge of the nucleus is partially screened. Such screening effects are not accounted for in the Bohr theory. However, Moseley’s work represented strong evidence of the quantized nature of atomic energy levels, as predicted by Bohr.

**Franck-Hertz Experiment**

This experiment represented additional confirmation of the quantized atomic energy states predicted by the Bohr theory. Mercury vapor is bombarded with electrons of known energy. If the kinetic energy (KE) of the electrons is less than the energy required to excite an Hg atom from the ground state to the first excited state (first excitation energy), then electrons make only elastic collisions with the massive Hg atoms and very little KE is lost by the electrons (1 part in \(10^5\)). However, when the KE of the electrons is equal to the first excitation energy, an electron can give up all of its KE to an Hg atom in an inelastic collision, which excites the Hg atom to the first excited state. By comparing the KE of the electrons before and after collision, one can find the first excitation energy.

[Show diagram of apparatus and graph of plate current vs. grid voltage from textbook.]

The F-H apparatus consists of an Hg tube containing a cathode, a plate (collector), and an accelerating grid. Both the plate and grid are held at a positive potential with respect to the cathode, but the plate potential is slightly lower (\(\sim 0.5\) V) than the grid. This retarding potential prevents electrons with negligible KE from reaching the plate and thereby contributing to the plate current. Thus, when electrons make inelastic collisions with Hg atoms in the vicinity of the grid, the retarding potential prevents those electrons with negligible KE after collision from reaching the plate, and the plate current drops. For Hg, such a drop in plate current occurs at an accelerating voltage of 4.9 V, and integer multiples of this value. The drops in current at \(2\times4.9\) V, \(3\times4.9\) V, etc., are due to one electron suffering two or more inelastic collisions with Hg atoms before reaching the grid, where it undergoes a final inelastic collision and therefore cannot reach the plate. Hence, the first excitation energy of Hg should be 4.9 eV. This corresponded precisely with a 253.6-nm spectral line that appeared in the emission spectrum of the vapor. Since the inelastic collisions only occur when the bombarding electron has KE great enough to supply the 1st excitation energy to a Hg atom, one concludes that the energy states are indeed discrete, as predicted by the Bohr theory.

**Limitations of the Bohr Model**

Though the Bohr model was very successful in explaining the spectra of hydrogen-like atoms, it failed to explain the spectra and other properties of atoms with more than one electron. The

---

6 Each electron in the K shell partially shields or screens the nuclear charge for the other electron in the K shell.
reason is that the Bohr model could not properly account for the interactions among the electrons. We shall see that, in order to deal with multielectron atoms, the wave nature of the electrons has to be invoked. This really does not detract from the success of Bohr model, since its ultimate revelation – that atomic energy levels are quantized – is still valid.\footnote{Other limitations of Bohr model: (1) intensity of spectral lines; (2) Why is $L$ quantized?}