8.1 Atomic Physics

Atomic Spectra
Bohr Model
  Extensions of the Bohr model
  X-ray emission
Electrons in Atoms
  Quantum numbers
  Pauli Exclusion Principle

Atomic spectra and atomic structure.
The spectra of atoms provide information about the energies of the electron in the atom. Sharp peaks at discrete wavelengths indicate that only specified energies are allowed in the atom. For the Hydrogen atom the Bohr theory explains the energies in a simple manner based on a quantization of angular momentum. The quantization is explained by the de Broglie theory in terms of standing waves for the electron.

Atomic structure

The scattering of alpha particles (He\(^{2+}\)) nuclei from a thin gold foil. The back scattering of a few alpha particles showed that the nucleus is a small compact object.

Planetary model of the atom

Scattering from a small compact nucleus

Atomic spectra

Emission

\[ \text{Emission: } A + e^- + A^* \rightarrow A + e^- \rightarrow A + h\nu \]

Geiger and Marsden
Ernest Rutherford 1911

At the source of A

Alpha particle

At the target

Emission spectrometer

Absorption

At the source (white light)

light minus absorbed wavelengths

Spectrometer
Atomic Spectra

Discrete spectral lines are observed.

Balmer series for Hydrogen

A series of peaks closer together (continuum) at low $\lambda$.

Rydberg Constant

The Balmer series could be analyzed mathematically in terms of an empirical equation.

\[ \frac{1}{\lambda} = R_H \left( \frac{1}{2^2} - \frac{1}{n^2} \right) \]

Rydberg Constant $R_H = 1.0973732 \times 10^7 \text{ m}^{-1}$

$n = 3, 4, 5, \ldots \ldots$ Integers larger than 2.

Disagreement with classical theory

Classical physics for the planetary model of the atom predicts that the energy of the electron can have any value - cannot explain discrete spectral lines.

The classical theory could not explain the stability of the atom, why the electron does not fall into the nucleus radiating energy.

Bohr Theory

1. Electrons move in circular orbits.
2. Only specified atomic energy levels are allowed.
3. Energy is emitted when electron go from one energy level to another.
4. The orbital angular momentum of the electron is “quantized” in units of $\hbar/2\pi = \hbar/2$ (called h bar)

\[ L = mvr = n\hbar \]

$n=1, 2, 3 \ldots \ldots$

Bohr Theory

\[ mvr \Rightarrow (kg \cdot \frac{m}{s}) \Rightarrow kg \cdot m^2 \]

\[ h \Rightarrow J \cdot s \Rightarrow \frac{kgm^2}{s} \Rightarrow \frac{kg \cdot m^2}{s} \]
Angular momentum of a tennis ball

\[ L = mvr = (0.1\text{kg})(2\text{m/s})(0.5\text{m}) = 0.1 \text{kgm}^2\text{s}^{-1} = 0.1 \text{J}\cdot\text{s} \]

\( n \) is so large that \( L \) appears continuous

Angular momentum of a typical electron in an atom

\[ L = mvr = (9.1\times10^{-31}\text{kg})(10^7\text{m/s})(0.1\times10^{-9}\text{m}) = 9 \times 10^{-24} \text{J}\cdot\text{s} \]

\( n \) is much smaller. Quantization is apparent

Classical dynamics

For central force (hydrogen atom)

\[ F = ma \Rightarrow k_e \frac{e^2}{r^2} = \frac{mv^2}{r} \]

\( r \) is a function of \( v \) but any value of \( r \) is allowed

Bohr theory for hydrogen atom

Classical energies

any value of \( r \) is allowed

Bohr model

Only values of \( r \) are allowed that follow the quantization condition

\[ mvr = n\hbar \]

\( n = 1, 2, 3, \ldots \) integers

angular momentum is quantized

Results from Bohr theory

Only specific values of \( r \) are allowed that depend on universal constants

\[ r_n = \frac{n^2 \hbar^2}{m_e k_e e^2} \]

\( n = 1, 2, 3, \ldots \) integers

radius increases as \( n^2 \)

For \( n = 1 \)

\[ r_1 = \frac{(1)^2(1.05\times10^{-34}\text{J}\cdot\text{s})}{(9.1\times10^{-31}\text{kg})(8.9\times10^9\text{NmC}^{-1})(1.6\times10^{-19}\text{C})^2} = 5.3 \times 10^{-11}\text{m} \]

Size of the Hydrogen atom in the ground state

0.053 nm

Total Energies

Classical

\[ E = KE + PE = -\frac{k_e e^2}{2r} \]

Total energy varies as \( 1/r \)

Bohr

\[ E_n = -\frac{m_e k_e^2}{2n^2} \left(\frac{1}{n}\right) \]

Total energy of allowed states with \( n = 1, 2, 3, \ldots \) varies as \( 1/n^2 \)
Excited state energy levels

Energy levels are quantized (proportional to $1/n^2$)

$$E_n = \frac{m_k e^4}{2\hbar^2 n^2} = -\frac{13.6}{n^2} \text{eV}$$

Emission energies

$$\Delta E = E_{final} - E_{initial} = 13.6 \left(\frac{1}{n_{final}^2} - \frac{1}{n_{initial}^2}\right)$$

$$\hbar \omega_{max} = 13.6 \text{eV}$$

Predicts spectral lines in the ultraviolet (Lyman series) and infrared (Paschen series), maximum energies, continuum.

Agreement with Rydberg equation

$$\frac{1}{\lambda} = \frac{\Delta E}{hc} \frac{m_k e^4}{4\pi \hbar^2 n_{final}^2} \left(\frac{1}{n_{initial}^2} - \frac{1}{n_{final}^2}\right)$$

$$R = \frac{m_k e^4}{4\pi \hbar^2}$$

$$R = \frac{9.109 \times 10^{-7} (8.987 \times 10^{10}(1.602 \times 10^{-19}))^4}{4\pi (2.997 \times 10^8)(1.054 \times 10^{-34})^3} = 1.099 \times 10^7 \text{m}^{-1}$$

$$R_{measured} = 1.097 \times 10^7 \text{m}^{-1}$$

Example

Find the wavelength in the hydrogen emission spectrum for transition from $n=3$ to $n=2$.

$$n=3$$

$$\frac{1}{\lambda} = R \left(\frac{1}{n_{final}^2} - \frac{1}{n_{final}^2}\right)$$

$$\frac{1}{\lambda} = (1.097 \times 10^{10} \text{m}^{-1}) \left(\frac{1}{2^2} - \frac{1}{3^2}\right)$$

$$\frac{1}{\lambda} = 1.097 \times 10^{10} \left(\frac{1}{4} - \frac{1}{9}\right) = 1.52 \times 10^4 \text{m}^{-1}$$

$$\lambda = 6.56 \times 10^{-7} \text{m} = 656 \text{nm}$$

red line in Balmer series

Explanation of Bohr theory in terms of the de Broglie wavelength

$$mvr = \frac{\hbar}{2\pi}$$

quantization of angular momentum

$$2\pi = n \left(\frac{\hbar}{mv}\right) = n\lambda$$

circumference = $n\lambda$

Integral no. of wavelengths.

Quantization of angular momentum is equivalent to forming circular standing waves. (Constructive interference)

Particle in a Box (prob. 32)

A simple quantum model for a confined particle.

A one-dimensional box of length $L$

$$U = \begin{cases} 0 & \text{inside the box}, \\ \infty & \text{outside the box} \end{cases}$$

$$\Psi_1$$

$$\Psi_2$$

$$n=1$$

$$n=2$$

A particle in a box has wave properties of a standing wave on a string fixed at both ends.

$$E_n = \frac{p^2}{2m} \left(\frac{n^2\hbar^2}{4L^2}\right) = \frac{n^2\hbar^2}{8Lm}$$

The lowest energy state is not zero but gets lower for larger boxes
Pigment molecules

beta carotene – long molecule has absorption in the visible region. The excitation energy decreases when the electron is delocalized in a long molecule.

Bohr theory

Shows that the energy levels in the hydrogen atom are quantized.

Correctly predicts the energies of the hydrogen atom (and hydrogen like atoms.)

The Bohr theory is incorrect in that it does not obey the uncertainty principle. It shows electrons in well defined orbits.

Quantum mechanical theories are used to calculate the energies of electrons in atoms. (i.e. Shrödinger equation)

Extension of the Bohr Theory

Bohr theory can only be used to predict energies of Hydrogen-like atoms. (i.e. atoms with only one electron) This includes H, He+, Li2+ ....

For example He⁺ (singly ionized helium has 1 electron and a nucleus with a charge of Z = +2)

For this case the energy for each state is multiplied by 

\[ E_n = -\frac{m_k e^2}{2n^2} \] \[ E_n = -\frac{13.6(Z^2)^{-1}}{n^2} = -54.4 \left( \frac{1}{n^2} \right) \text{eV} \]

for He⁺

Characteristic X-rays are due to emission from heavy atoms excited by electrons

A Bohr model for x-ray emission

Inner shell electrons

Energy from Bohr model

\[ E_n = Z_{eff}^{-1} \frac{(13.6)}{n^2} \]

\( Z_{eff} \) is an effective charge of the nucleus due to screening.

A Bohr model for x-ray emission

Characteristic x-rays

The wavelength of characteristic x-ray peaks due to emission from high energy states of heavy atoms (high Z).

Characteristic x-rays

High energies due to high \( Z_{eff}^2 \)
X-ray emission

Calculate the wavelength for Kα x-ray emission of Mo (Z=42). The electron in the L shell must be in a l=1 (p state).

\[ Z_{eff} = Z - 1 \]

\[ \Delta E_{k_{α}} = -13.6(Z-3)\left(\frac{1}{n^2}\right) \]

\[ \Delta E_{l_{α}} = -13.6(Z-1)\left(\frac{1}{n^2}\right) \]

Calculated value: 73 pm

Electrons in atoms.

Electrons in atoms exist in discrete energy levels.

The pattern of energy levels which results from a quantum mechanical rule called the Pauli Exclusion Principle, is responsible for the periodicity in the chemical properties of the different elements as seen in the Periodic Table.

Orbital angular momentum

Classically the angular momentum L of an electron moving in a circle can have any value.

In quantum mechanics the values of the angular momentum are quantized and specified by an orbital angular momentum quantum no. \( \ell \).

For an electron with a principle quantum no. \( n \) the value of \( \ell \) ranges from 0 to \( n-1 \).

i.e. for \( n=2 \), \( \ell \) can have values of 0 and 1.

Orbital magnetic quantum number

Classically an electron moving in a circle is a current which results in a magnetic dipole along the direction of L. Classically, the dipole can have any orientation with respect to a field.

In quantum mechanics, only discrete orientations are allowed. The orientation are determined by the orbital magnetic quantum no. \( m_\ell \).

The value of \( m_\ell \) ranges from \( -\ell \) to \( +\ell \).

i.e. for \( \ell = 1 \), \( m_\ell \) can have values of -1, 0, and 1.
Spin magnetic quantum number

In quantum mechanics an electron has an intrinsic magnetic moment due to spin. The magnetic moment can have two orientations in a magnetic field determined by a spin quantum number $m_s$:

- $m_s = +\frac{1}{2}$ or $-\frac{1}{2}$

For an electron, 2 spin states are possible: $\pm \frac{1}{2}$.

At the atomic energy levels and quantum numbers.

- Principle quantum number $n$: range of values $1, 2, 3, \ldots$
- Angular momentum quantum number $\ell$: $0, 1$ to $n-1$
- Orbital magnetic quantum number $m_\ell$: $-\ell, \ldots, +\ell$
- Spin magnetic quantum number $m_s$: $-\frac{1}{2}$ or $+\frac{1}{2}$

The state of an electron is specified by the set of its quantum numbers $(n, \ell, m_\ell, m_s)$.

The number of states is determined by the set of possible quantum numbers.

Pauli Exclusion Principle

No two electrons in an atom can have the same quantum number, $n, \ell, m_\ell$, or $m_s$. To form an atom with many electrons, the electrons go into the lowest energy unoccupied state.

The periodic properties of the elements as shown in the Periodic Table can be explained by the Pauli Exclusion Principle by properties of filled shells.

Electrons in atoms- Shell Notation

**TABLE 28.1**

<table>
<thead>
<tr>
<th>Shell and Subshell Notation</th>
<th>Shell Symbol</th>
<th>Subshell Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>$\ell$</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>K</td>
<td>0</td>
</tr>
<tr>
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<td>L</td>
<td>1</td>
</tr>
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<td>3</td>
<td>M</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>N</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>O</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>P</td>
<td>5</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

*Electron configurations.*

**TABLE 28.3**

<table>
<thead>
<tr>
<th>Shell</th>
<th>Subshell</th>
<th>Number of Electrons in Filled Subshells</th>
<th>Number of Electrons in Filled Shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>K ($n = 1$)</td>
<td>s ($\ell = 0$)</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>L ($n = 2$)</td>
<td>s ($\ell = 0$)</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>M ($n = 3$)</td>
<td>s ($\ell = 0$)</td>
<td>2</td>
<td>18</td>
</tr>
<tr>
<td>N ($n = 4$)</td>
<td>s ($\ell = 0$)</td>
<td>2</td>
<td>32</td>
</tr>
</tbody>
</table>
Periodic Table of the Elements
Dmitri Mendeleev (1834-1907)

Noble gases

He  Z= 2  1s²
Ne  Z=10  1s²  2s²  2p⁶
Ar  Z=18  1s²  2s²  2p⁶  3s²  3p⁶
Kr  Z=36  1s²  2s²  2p⁶  3s²  3p⁶  3d¹⁰  4s²  4p⁶

Noble gas configurations
Noble gases have Filled Subshells

He  Z= 2  1s²
Ne  Z=10  1s²  2s²  2p⁶
Ar  Z=18  1s²  2s²  2p⁶  3s²  3p⁶
Kr  Z=36  1s²  2s²  2p⁶  3s²  3p⁶  3d¹⁰  4s²  4p⁶

Filled subshell configuration  s² ,  p⁶ ,  d¹⁰