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.

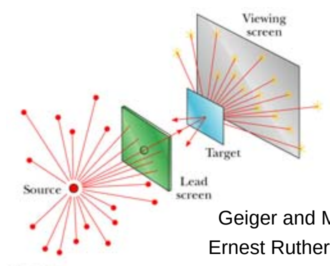
The spectra of atoms provide information about the energies of the electron in the atom.

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.

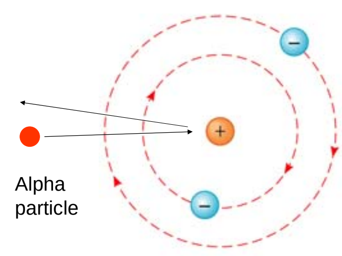
Atomic structure



Geiger and Marsden
Ernest Rutherford 1911

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.

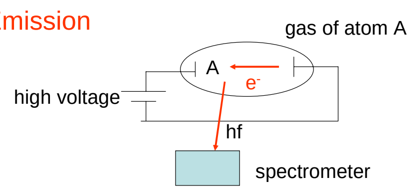
Planetary model of the atom



Scattering from a small compact nucleus

Atomic spectra

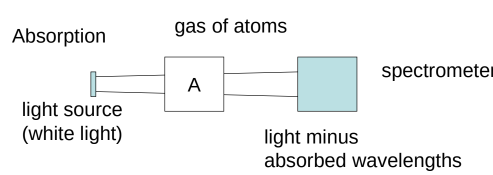
Emission



Excitation e^- (fast) + A -> e^- (slow) + A^*

Emission A^* -> A + hf

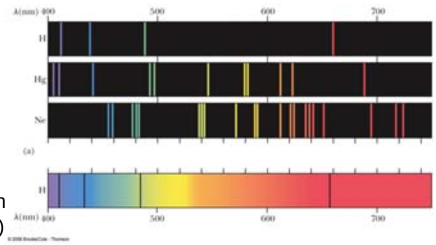
Atomic Spectra



Atomic Spectra

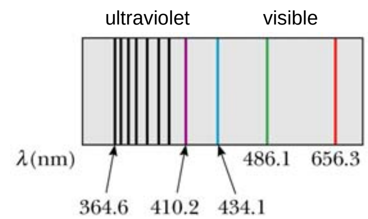
Emission

Absorption
(dark lines)



Discrete spectral lines are observed.

Balmer series for Hydrogen



Lowest λ　　Highest λ

A series of peaks closer together (continuum) at low λ

Rydberg Constant

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

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

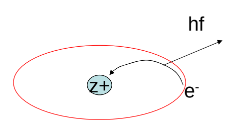
Rydberg Constant $R_H = 1.0973732 \times 10^7\ m^{-1}$

n = 3,4, 5 .... 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.



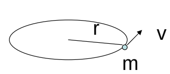
Planetary Model of the atom

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 h/2π = $\hbar$ (called h bar)

$L = mvr = n\hbar$

n=1, 2, 3 ....



h has units of angular momentum

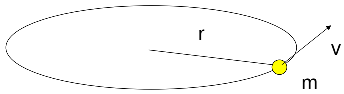
$$mvr \Rightarrow (kg)\left(\frac{m}{s}\right)(m) \Rightarrow \frac{kg \cdot m^2}{s}$$

$$h \Rightarrow J \cdot s \Rightarrow \left(\frac{kgm^2}{s^2}\right) \cdot s \Rightarrow \frac{kg \cdot m^2}{s}$$

Angular momentum of a tennis ball

$L = n\hbar$ is quantized. What is n for the ball?

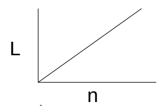
r= 0.5 m
m = 0.1 kg
v= 2 m/s



$$L = mvr = (0.1kg)(2m/s)(0.5m) = 0.1\frac{kgm^2}{s} = 0.1J\cdot s$$

$$\hbar = \frac{h}{2\pi} = \frac{6.6x10^{-34}J\cdot s}{2\pi} = 1.05x10^{-34}J\cdot s$$

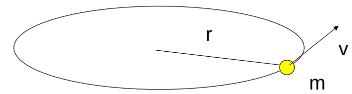
$$n = \frac{L}{\hbar} = \frac{0.1J\cdot s}{1.0x10^{-34}J\cdot s} = 10^{33}$$



n is so large that L appears continuous

Angular momentum of a typical electron in an atom

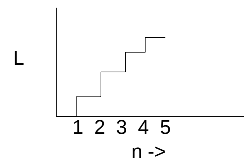
m=$9.1x10^{-31}$kg
r =0.1 x10^{-9} m
v=10^7 m/s



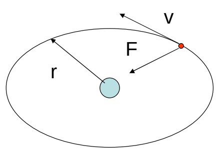
$$L = mvr = (9.1x10^{-31}kg)(10^7 m/s)(0.1x10^{-9}m) = 9x10^{-34}J\cdot s$$

$$n = \frac{L}{\hbar} = \frac{9x10^{-34}J\cdot s}{1.05x10^{-34}J\cdot s} \approx 9$$

L is much smaller.
Quantization is apparent



Classical dynamics
For central force (hydrogen atom)



v increases as r decreases

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

$$r = \frac{k_e e^2}{mv^2}$$

r is a function of v

but any value of r is allowed

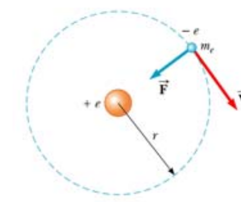
Bohr theory for hydrogen atom

Classical energies

any value of r is allowed

Bohr model

Only values of r are allowed that follow the quanization condition



$$mvr = n\hbar$$

n= 1, 2, 3, ... integers

angular momentum is quantized

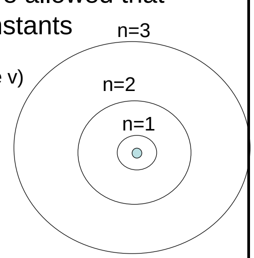
Results from Bohr theory

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

$$r_n = \frac{n^2\hbar^2}{m_e k_e e^2}$$ (eliminate v)

n=1, 2, 3, ... integers

radius increases as n^2



For n=1

$$r_1 = \frac{(1)^2(1.05x10^{-34}Js)}{(9.1x10^{-31}kg)(8.9x10^9 NmC^{-2})(1.6x10^{-19}C)^2} = 5.3x10^{-11}m$$

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

$$E_n = -\frac{m_e k_e^2 e^4}{2\hbar^2}\left(\frac{1}{n^2}\right)$$

Total energy of allowed states with n=1, 2, 3, ----- varies as $1/n^2$

Excited state energy levels

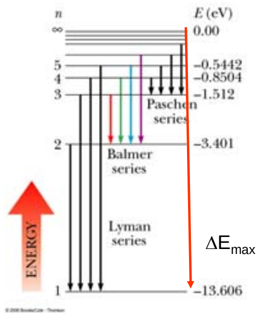
Energy levels are quantized (proportional to $1/n^2$)

$$E_n = -\frac{m_e k_e^2 e^4}{2\hbar^2}\left(\frac{1}{n^2}\right) = -\frac{13.6}{n^2}\text{eV}$$

Emission energies

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

hf_{max} =13.6 eV



ΔE_{max}

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

Agreement with Rydberg equation

$$\frac{1}{\lambda} = \frac{\Delta E}{hc} = \frac{m_e k_e^2 e^4}{4\pi c\hbar^3}\left(\frac{1}{n_{final}^2} - \frac{1}{n_{initial}^2}\right)$$

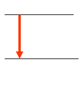
$$R = \frac{m_e k_e^2 e^4}{4\pi c\hbar^3}$$

$$R = \frac{9.109\text{x}10^{-31}(8.987\text{x}10^{9})^2(1.602\text{x}10^{-19})^4}{4\pi(2.997\text{x}10^{8})(1.054\text{x}10^{-34})^3} = 1.099\text{x}10^{7}\,\text{m}^{-1}$$

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

Example

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



n=3

n=2

n=1

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

$$\frac{1}{\lambda} = (1.097\text{x}10^{7}\text{m}^{-1})\left(\frac{1}{2^2} - \frac{1}{3^2}\right)$$

$$\frac{1}{\lambda} = 1.097\text{x}10^{7}\left(\frac{1}{4} - \frac{1}{9}\right) = 1.52\text{x}10^{6}\text{m}^{-1}$$

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

red line in Balmer series

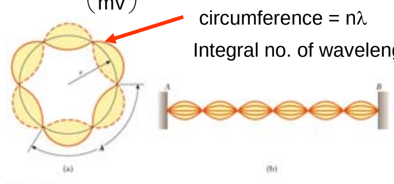
Explanation of Bohr theory in terms of the de Broglie wavelength

$$mvr = n\frac{h}{2\pi}$$ quantization of angular momentum

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

circumference = $n\lambda$

Integral no. of wavelengths.

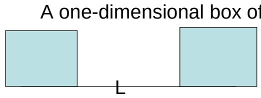


Quantization of angular momentum is equivalent to forming circular standing waves. (Constructive interference)

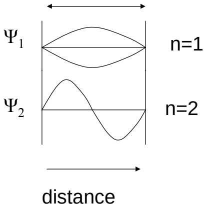
Particle in a Box (prob. 32)

A simple quantum model for a confined particle.

A one-dimensional box of length L



potential energy
U =0 inside the box,
U=∞ outside the box



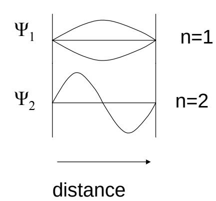
A particle in a box has wave properties of a standing wave on a string fixed at both ends.

Particle in a box

Find the kinetic energy of the particle in the box

The wavelength is

$$\lambda_n = \frac{2L}{n} = \frac{h}{p_n}$$



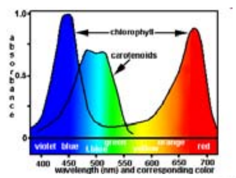
The energy is

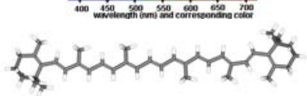
$$E_n = \frac{p_n^2}{2m} = \left(\frac{n^2h^2}{4L^2}\right)\frac{1}{2m} = \frac{n^2h^2}{8L^2m}$$

$$E_1 = \frac{h^2}{8L^2m}$$

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^+, Li^{2+} ....

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

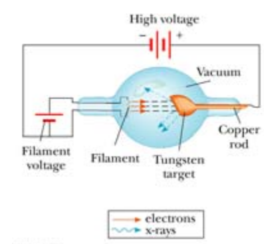
For this case the energy for each state is multiplied by $Z^2 = 4$

$$E_n = -\frac{m_e k_e^2 Z^2 e^4}{2\hbar^2}\left(\frac{1}{n^2}\right)$$

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

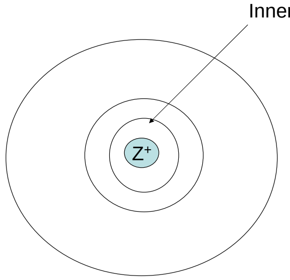
for He^+

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



A Bohr model for x-ray emission

Inner shell electrons



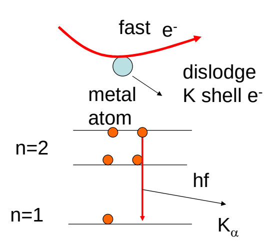
Energy from Bohr model

$$E_n = Z_{eff}^2(13.6)\frac{1}{n^2}$$

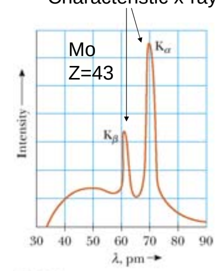
Z_{eff} is an effective charge of the nucleus due to screening.

Characteristic x-rays

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



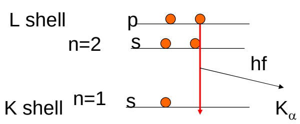
Characteristic x-rays



High energies due to high Z_{eff}^2

X-ray emission

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



L shell Z_{eff} =Z-3

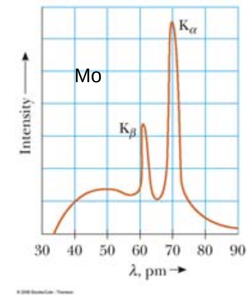
K shell Z_{eff} = Z-1

$$E_{(Lshell)} = -13.6(Z-3)^2\left(\frac{1}{2^2}\right)$$

$$E_{Kshell} = -13.6(Z-1)^2\left(\frac{1}{1^2}\right)$$

$\boxed{73\ \text{pm}}$

Calculated value
73 pm

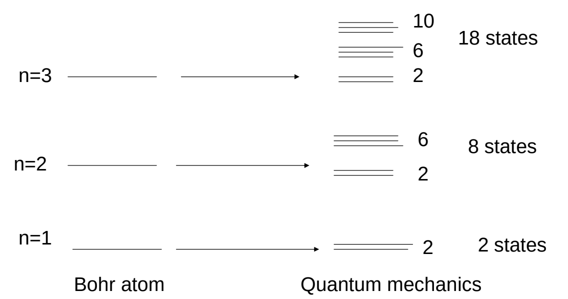


Electrons in atoms.

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.

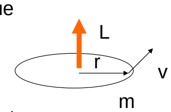
Quantum calculations show that more states are needed to describe the electrons in an atom



The number of states determined by quantum numbers.

Orbital angular momentum

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

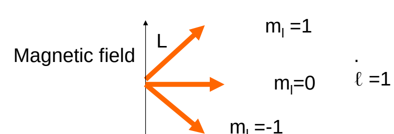


In quantum mechanics the values of the angular momentum are quantized and specified by a orbital angular momentum quantum no. ℓ

For an electron with a principle quantum no. n the value of ℓ ranges from 0 to n-1.

i.e. for n=2 , ℓ can have values of 0 and 1.

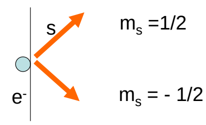
Orbital magnetic quantum number



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_l
The value of m_l ranges from – ℓ to + ℓ.

i.e. for ℓ=1, m_l 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 = +1/2 or -1/2

for an electron 2 spin states are possible $\pm$ 1/2

Atomic energy levels and quantum numbers.

	range of values
principle quantum number n	1, 2, 3, ...
angular momentum quantum number ℓ	0, 1 to n-1
orbital magnetic quantum number m_ℓ	$-\ell$,..to..$+\ell$
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, ℓ, m_l , m_s)
The number of states is determined by the set of possible quantum numbers.

Electronic states in an atom n=1,2 and 3

n	l	m_l	m_s	no. of states	no. n, l	no. n
1	0	0	$\pm$½	2	2	2
2	0	0	$\pm$½	2	2	8
2	1	-1	$\pm$½	2	6	
2	1	0	$\pm$½	2		
2	1	1	$\pm$½	2		
3	0	0	$\pm$½	2	2	18
3	1	-1	$\pm$½	2	6	
3	1	0	$\pm$½	2		
3	1	1	$\pm$½	2		
3	2	-2	$\pm$½	2	10	
3	2	-1	$\pm$½	2		
3	2	0	$\pm$½	2		
3	2	1	$\pm$½	2		
3	2	2	$\pm$½	2		

Pauli Exclusion Principle

No two electrons in an atom can have the same quantum number, n, l, m_l , 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

Shell and Subshell Notation

n	Shell Symbol	ℓ	Subshell Symbol
1	K	0	s
2	L	1	p
3	M	2	d
4	N	3	f
5	O	4	g
6	P	5	h
. . .		. . .	

TABLE 28.3

Number of Electrons in Filled Subshells and Shells

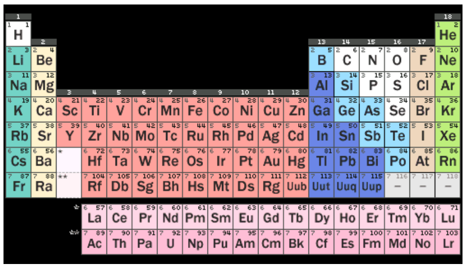
Shell	Subshell	Number of Electrons in Filled Subshell	Number of Electrons in Filled Shell
K ($n = 1$)	$s(\ell = 0)$	2	2
L ($n = 2$)	$s(\ell = 0)$	2	8
	$p(\ell = 1)$	6	
M ($n = 3$)	$s(\ell = 0)$	2	18
	$p(\ell = 1)$	6	
	$d(\ell = 2)$	10	
N ($n = 4$)	$s(\ell = 0)$	2	32
	$p(\ell = 1)$	6	
	$d(\ell = 2)$	10	
	$f(\ell = 3)$	14	

Periodic Table of the Elements

Dmitri Mendeleev (1834-1907)

noble gases

Z



2
10
18
36
54
86

Noble gas configurations

Noble gases have Filled Subshells

He Z= 2 $1s^2$

Ne Z=10 $1s^2$ $2s^2$ $2p^6$

Ar Z=18 $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$

Kr Z= 36 $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$ $4s^2$ $4p^6$

Noble gases have filled subshells

Stable, difficult to ionize A -> $A^+ + e^-$

TABLE 28.4

Electronic Configurations of Some Elements

Z	Symbol	Ground-State Configuration	Ionization Energy (eV)	Z	Symbol	Ground-State Configuration	Ionization Energy (eV)
1	H	$1s^1$	13.595	19	K	[Ar] $4s^1$	4.339
2	He	$1s^2$	24.581	20	Ca	$4s^2$	6.111
				21	Sc	$3d4s^2$	6.54
3	Li	[He] $2s^1$	5.390	22	Ti	$3d^24s^2$	6.83
4	Be	$2s^2$	9.320	23	V	$3d^34s^2$	6.74
5	B	$2s^22p^1$	8.296	24	Cr	$3d^54s^1$	6.76
6	C	$2s^22p^2$	11.256	25	Mn	$3d^54s^2$	7.432
7	N	$2s^22p^3$	14.545	26	Fe	$3d^64s^2$	7.87
8	O	$2s^22p^4$	13.614	27	Co	$3d^74s^2$	7.86
9	F	$2s^22p^5$	17.418	28	Ni	$3d^84s^2$	7.633
10	Ne	$2s^22p^6$	21.559	29	Cu	$3d^{10}4s^1$	7.724
				30	Zn	$3d^{10}4s^2$	9.391
11	Na	[Ne] $3s^1$	5.138	31	Ga	$3d^{10}4s^24p^1$	6.00
12	Mg	$3s^2$	7.644	32	Ge	$3d^{10}4s^24p^2$	7.88
13	Al	$3s^23p^1$	5.984	33	As	$3d^{10}4s^24p^3$	9.81
14	Si	$3s^23p^2$	8.149	34	Se	$3d^{10}4s^24p^4$	9.75
15	P	$3s^23p^3$	10.484	35	Br	$3d^{10}4s^24p^5$	11.84
16	S	$3s^23p^4$	10.357	36	Kr	$3d^{10}4s^24p^6$	13.996
17	Cl	$3s^23p^5$	13.01				
18	Ar	$3s^23p^6$	15.755				

Filled subshell configuration s^2 , p^6 , d^{10}