Chapter 41
Atomic structure

1. The hydrogen atom
2. The Zeeman effect
3. Electron spin
4. Many electron atoms and the exclusion principle
5. X-ray spectra

Atomic structure

- Atomic structure of an atom is the result of solving the Schrodinger equation for that atom.
- Most of the sciences of chemistry and semiconductor physics rise from this procedure.
- More quantization appear during the process of solving the Schrodinger equation.
- Bohr model deficiencies
  - Only good for hydrogen and hydrogen-like atoms.
  - Provides no insight to the process of emission & absorption of radiation
  - Mixed the concepts of classical physics and quantum mechanics
  - Predicted wrong magnetic properties for the hydrogen atom.
  - Assumed a localized position for the electron.

Schrodinger equation for the hydrogen atom I

The 3-dimensional version of the Schrodinger equation:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi\left(x,y,z\right)}{\partial x^2}+\frac{\partial^2\psi\left(x,y,z\right)}{\partial y^2}+\frac{\partial^2\psi\left(x,y,z\right)}{\partial z^2}\right)+U\left(x,y,z\right)\psi\left(x,y,z\right)=E\psi\left(x,y,z\right)$$

Most of the atomic problems are spherically symmetric and the potential depends only on the distance of the particles from the center of symmetry or $r=\sqrt{x^2+y^2+z^2}$.

and we have $U(x,y,z)=U\left(r\right)$:

The Coulomb potential has the form:

$$U\left(r\right)=-\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$

For such a potential the wavefunction is product of three functions each function of only one variable $\psi(x,y,z)=R\left(r\right)\Theta\left(\theta\right)\Phi\left(\phi\right)$

When we insert this solution into the Schrodinger equation we get 3 separate equations each depending only on one variable which is an enormous simplification.

Schrodinger equation for the hydrogen atom II

The separate wave functions forming the ψ should satisfy different conditions

$$\psi(x,y,z) = R(r)\Theta(\theta)\Phi(\phi)$$

$\lim_{r\to\infty} R(r)$ since the particle is somewhere in the vicinity of the nucleus

$$\Phi(\phi + 2\pi) = \Phi(\phi)$$

$$\Theta(\theta + 2\pi) = \Theta(\theta)$$

Both $\Theta(\theta)$ and $\Phi(\phi)$ have to stay finite for all values of θ and ϕ

Without solving the equations we state the form of the three functions

$R(r) \propto e^{-\alpha r}$ and $\Theta(\theta)$ contains polynomials in powers of sinθ and cosθ

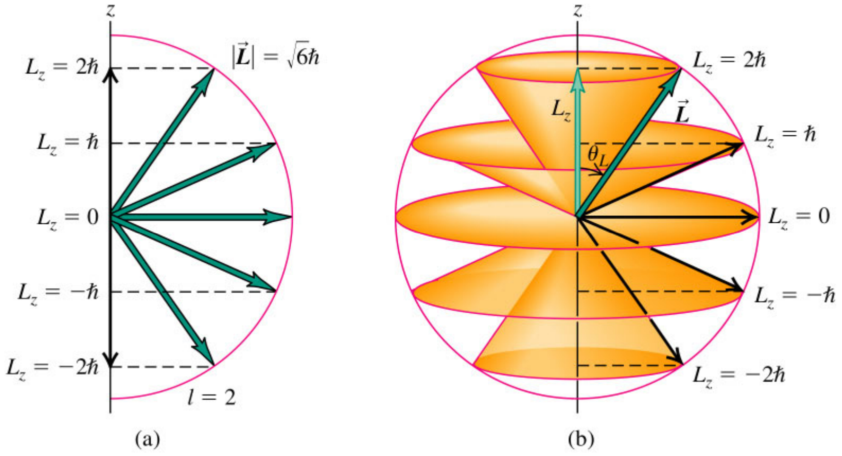
$\Phi(\phi) \propto e^{im_l\phi}$ where $m_l = 0, \pm 1, \pm 2, \ldots$

While serching for the solutions that satisfy the boundary conditions we impose conditions that lead to quantum numbers. The energy levels are then:

$\boxed{E_n = -\frac{1}{(4\pi\varepsilon_0)^2}\frac{m_r e^4}{2n^2\hbar^2} = -\frac{13.60eV}{n^2}}$, $n = 1, 2, 3, ..$ is the principal quantum number.

This result is compatible with Bohr model's result but does not have limitations of it. We can use this approach for an atom with any number of electrons.

Angular momentum



In classical mechanics:

The angular momentum is defined as

$$\vec{L} = \vec{r} \times \vec{p} = m\vec{r} \times \vec{v}$$

Which is a vector quantity and its magnitude is:

$$|L| = \left| m\vec{r} \times \vec{v} \right| = r_{\perp} p$$

It is the component of the momentum in a direction perpendicular to the direction of motion.

You can think of the linear momentum as what pushes the object forward and angular momentum what takes the object out of its linear path and move it around a curved trajectory.

In quantum mechanics magnitude of the orbital angular momentum is quantized as a result of confinement of the electron in the potential field of the nucleus and is given by:

$$L = \sqrt{l(l+1)}\hbar \qquad (l = 0, 1, 2, \ldots n\text{-}1)$$

$\vec{L}$'s accurate direction can not be determined due to uncertainty principle but the magnitude of its z component is given by:

$$L_z = m_l \hbar \qquad (m_l = 0, \pm 1, \pm 2, \ldots, \pm l)$$

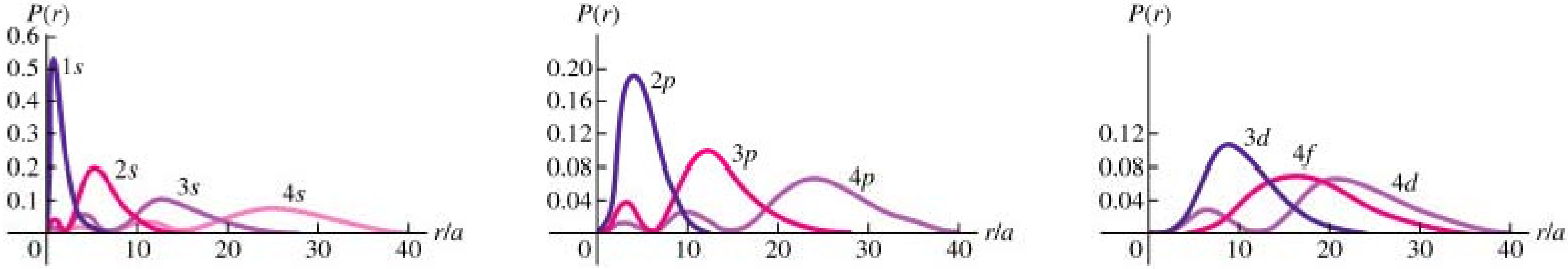
Radial probability distribution functions P(r) as a function of r/a

Let $P(r)$ be the radial probability distribution function of a particle with a normalized wavefunction ψ where $\int_{\text{entire space}} |\psi|^2\, dV = 1$

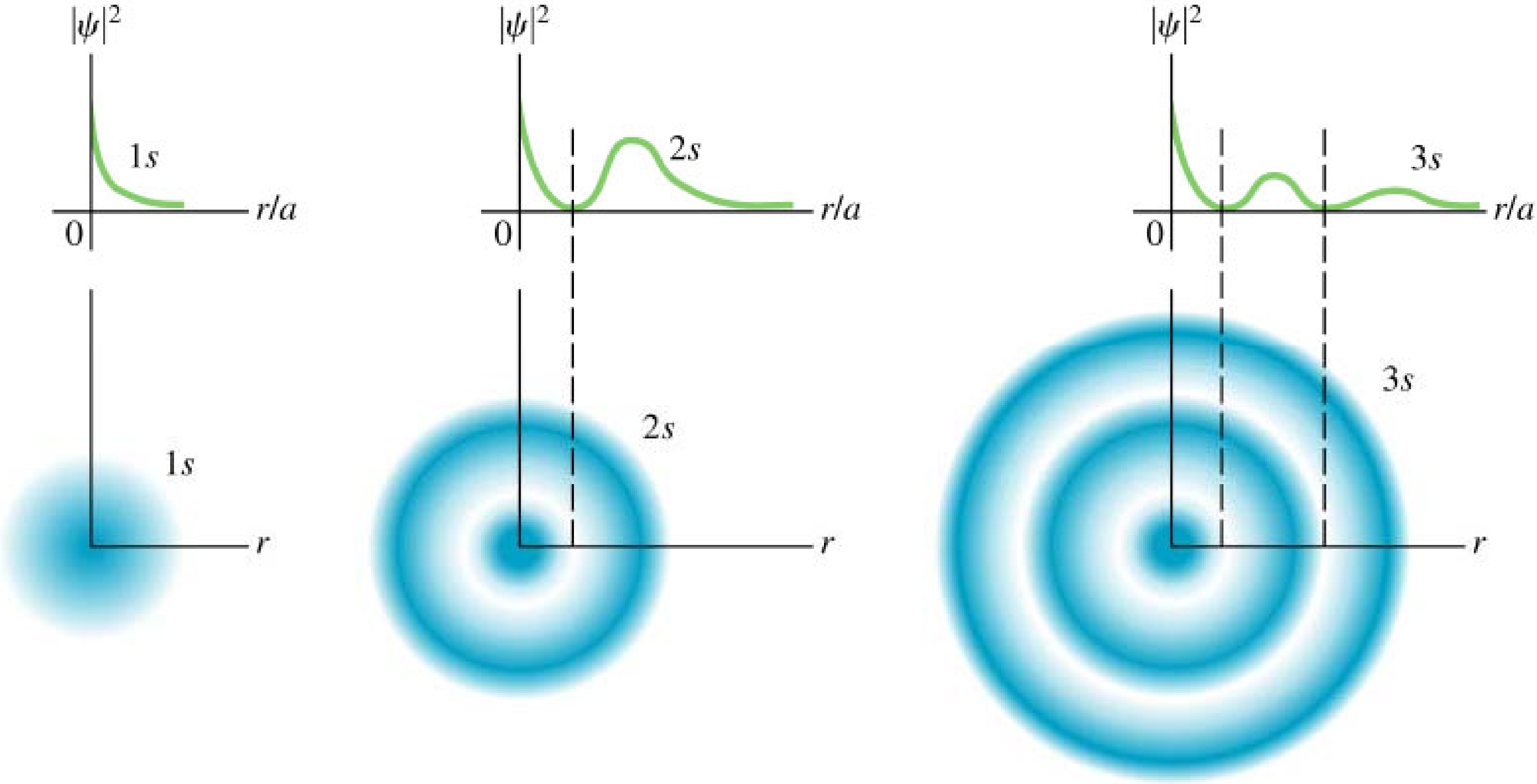
probability of finding the particle in a volume dV of space surrounded by two spheres of radius r and $r + dr$ is

$$\left.\begin{aligned} P(r)\,dr &= |\psi|^2\, dV \\ dV &= 4\pi r^2 dr \end{aligned}\right\} P(r)\,dr = |\psi|^2\, 4\pi r^2 dr$$

Usuallly the distance is expressed in units of $a = \dfrac{\varepsilon_0 h^2}{\pi m_r e^2} = 5.29\times10^{-11}$m, the smallest distance between the nucleus and the elctron in the Bohr model.

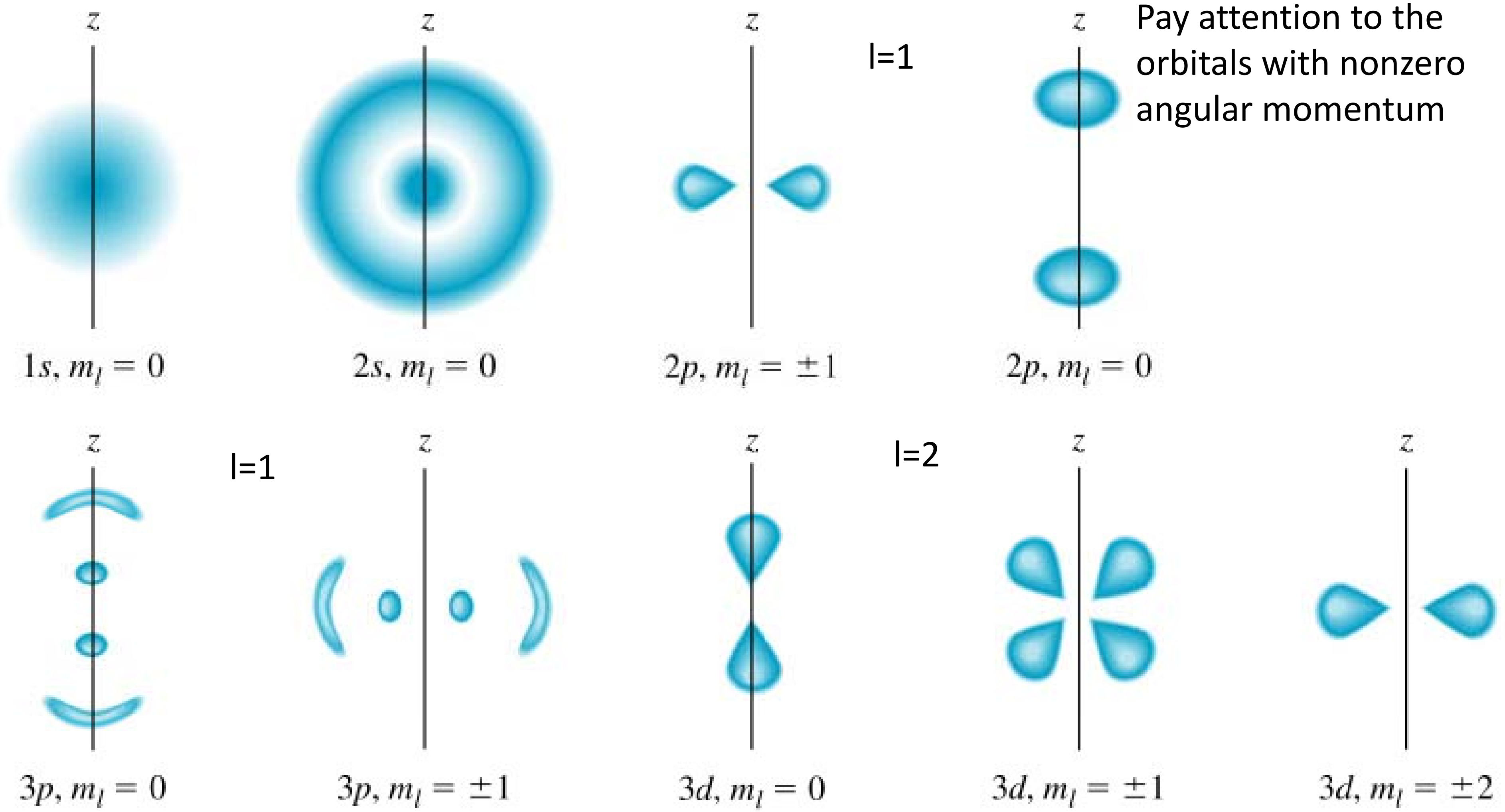


3-D probability distribution functions for the spherically symmetric wavefunctions of hydrogen atom (1s,2s,3s) with *l=0* & *L=0*



3-D probability distribution functions for hydrogen atom with different quantum numbers

Pay attention to the orbitals with nonzero angular momentum



l=1

$1s, m_l = 0$ $2s, m_l = 0$ $2p, m_l = \pm 1$ $2p, m_l = 0$

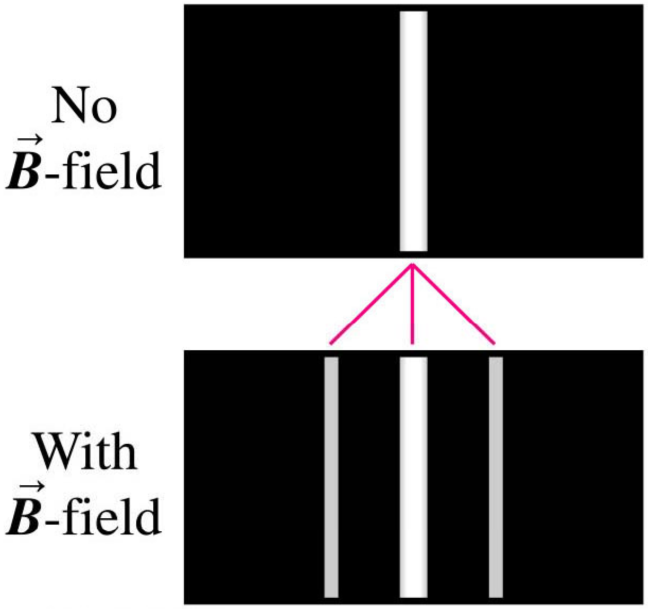
l=1

l=2

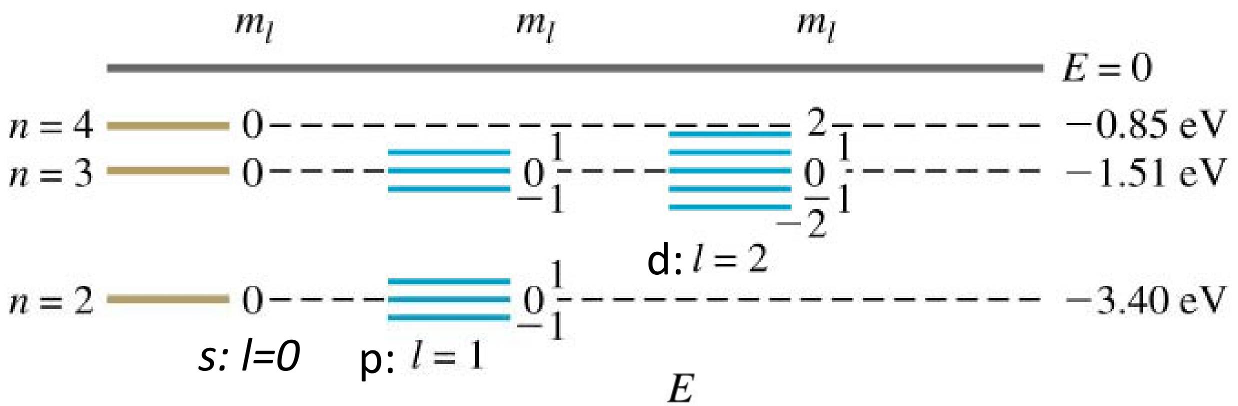
$3p, m_l = 0$ $3p, m_l = \pm 1$ $3d, m_l = 0$ $3d, m_l = \pm 1$ $3d, m_l = \pm 2$

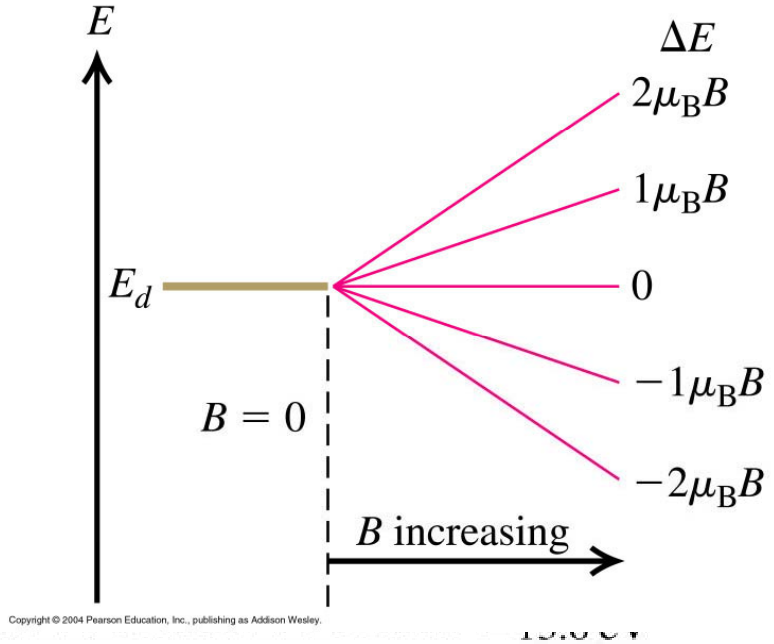
Zeeman Effect (1896): Splitting of the atomic spectral lines in presence of magnetic fields

- Splitting of the atomic energy levels leads to separation of the observed atomic spectral lines
- An atom is composed of charge in motion.
- Moving charges feel a force if placed in a magnetic field ***F***=*q**V**x**B***



Degenerate states share the same energy level with different magnetic quantum numbers





- ☐ If placed in a *B* field all *d* states that have the same *n* and the same energy will split to separate states with different energies.
- ☐ The amount of splitting is proportional to the magnitude of the B field

Magnitude of the Zeeman splitting External magnetic field B I

An orbiting electron has a magnetic moment of $\vec{\mu} = I\vec{A}$ where $|A| =$ area of the loop

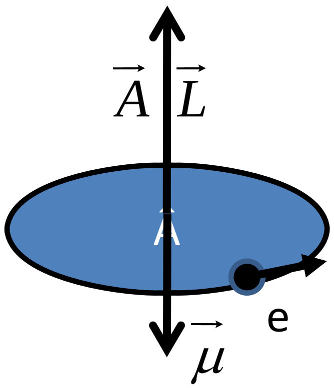
$\vec{\tau} = \vec{\mu} \times \vec{B}$ The torque exerted on a magnetic dipole in a magnetic field of $\vec{B}$

$U = \vec{\mu} \bullet \vec{B}$ The potential field felt by a magnetic dipole in a magnetic field of $\vec{B}$

For simplicity we use Bohr model. An electron orbiting in a circle of radius r around a stationary nucleus:

$$\left.\begin{array}{l} \left|\vec{A}\right| = \pi r^2 \hat{n} \rightarrow \vec{\mu} = I\vec{A} = \pi r^2 I\hat{n} \\ I = \dfrac{e}{T} = \dfrac{e}{v/2pr} = \dfrac{-ev}{2\pi r} \end{array}\right\} \vec{\mu} = \pi r^2 \frac{-ev}{2\pi r}\hat{n} \rightarrow \underbrace{\boxed{\vec{\mu} = -\frac{evr}{2}\hat{n}}}_{\text{For a current loop}}$$

The magnitude of the angular momentum is: $\left|L\right| = \left|m\vec{v} \times \vec{r}\right| = mvr$ in the direction of μ



$$\vec{\mu} = \frac{emvr}{2m}\hat{n} = -\frac{e\left|L\right|}{2m}\hat{n} \rightarrow \boxed{\vec{\mu} = -\frac{e\vec{L}}{2m}}$$

$\rightarrow$ The gyromagnetic ratio: $\boxed{\dfrac{\vec{\mu}}{\vec{L}} = -\dfrac{e}{2m}}$

Because of negative chage L and μ have opposite directions.

For Bohr model $L = n\hbar \rightarrow \left|\mu_n\right| = n\dfrac{e\hbar}{2m} = n\mu_B$

We give the name Bohr Magneton for $\boxed{\mu_B = \dfrac{e\hbar}{2m_e}} = 5.788\times10^{-5}\,\dfrac{eV}{T} = 9.274\times10^{-24}\,\dfrac{J}{T}$ or $A.m^2$

Bohr Magneton is the quantum of the magnetic moment for an electron in Bohr model.

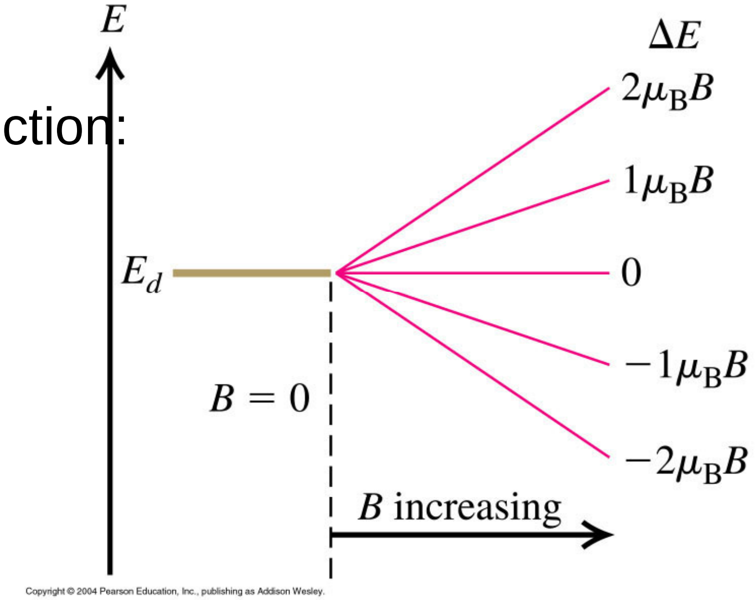
Magnitude of the Zeeman splitting External magnetic field B II

The Bohr model gives a correct gyromagnetic ratio but fails to predict correct magnetic interactions since it doe not provide correct numbers for the angular momentum of all energy levels.

Let us place an atom in a B-field in a $+z$ direction:

$$\left.\begin{aligned} U &= \vec{\mu}\bullet\vec{B} = -\mu_z B \\ \mu_z &= -\frac{e}{2m_e}L_z = -\frac{e\hbar}{2m_e}m_l \end{aligned}\right\}$$

$$\underbrace{\boxed{U = -\mu_z B = m_l\frac{e\hbar}{2m_e}B = m_l\mu_B B}}_{\text{Orbital magnetic interaction energy}} \left(m_l = 0, \pm 1, \pm 2, \ldots\right)$$



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When we place the atom in a magnetic field, the energy of the levels will be shifted by $\Delta E = U = m_l\mu_B B$.

For $m_l = 0$ states there is no shift

For $+m_l$ states there is a increase in energy of the state

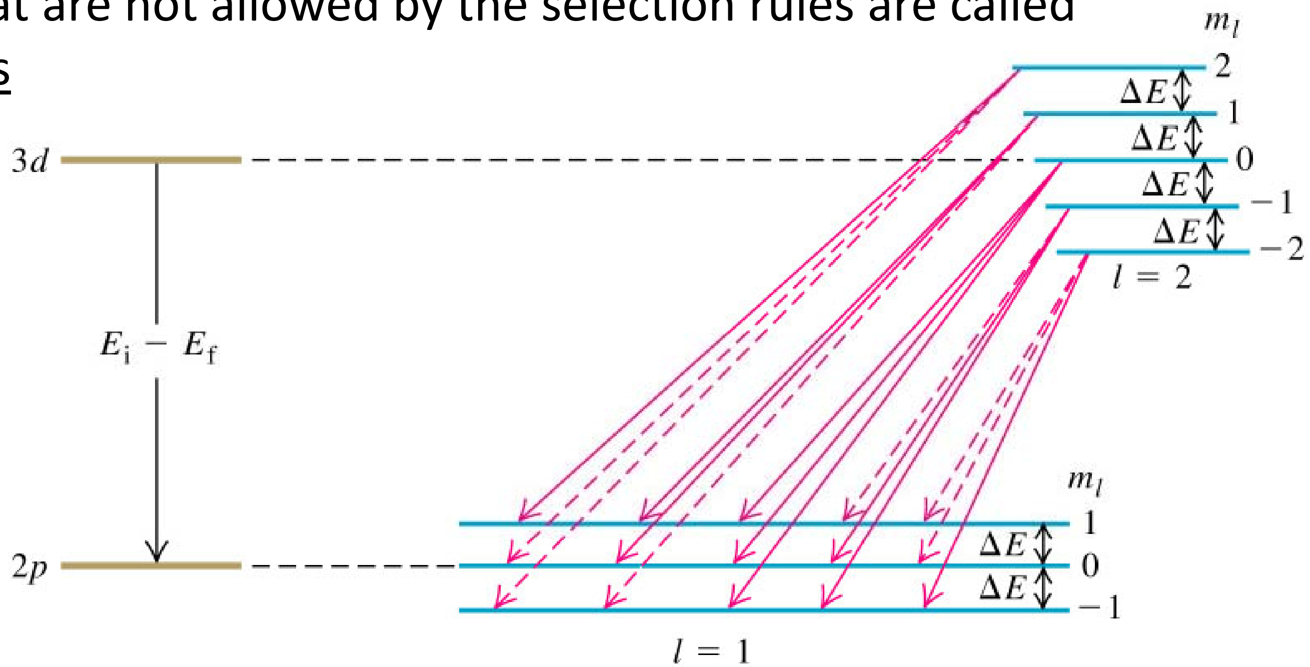
For $-m_l$ states there is a decrease in energy of the state

An atom in a magnetic field

- An atom with l=1 emits a photon of wavelength 600 nm and decays to l=0.
- If the atom is placed in a magnetic field of 2.00T determine the shifts in the energy levels and in the wavelengths of the emission spectra.

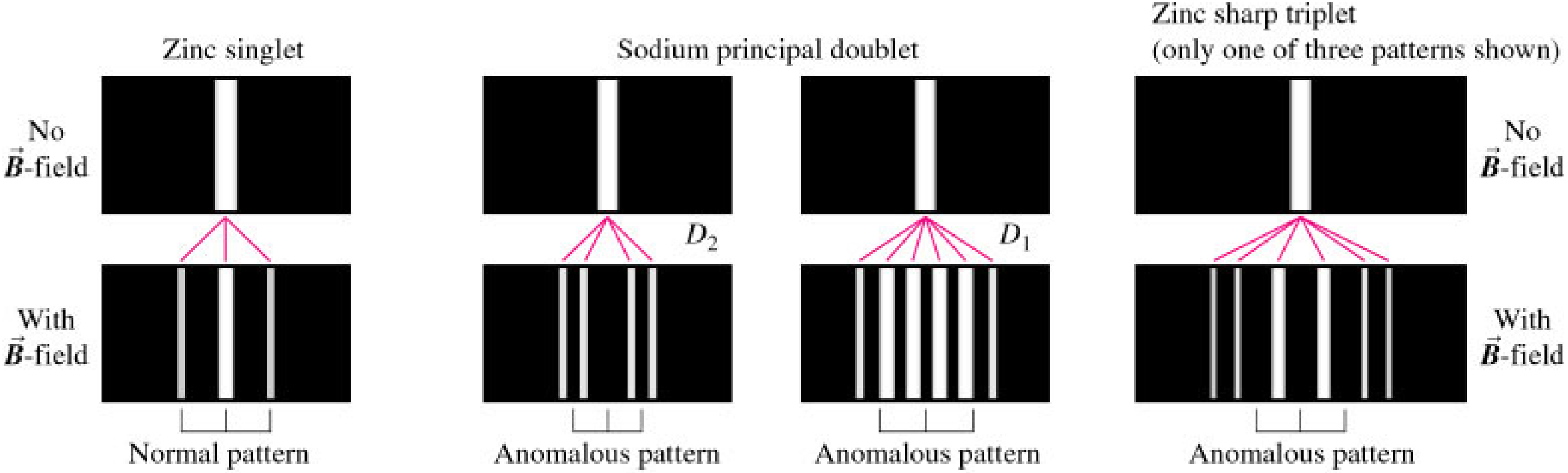
Selection rules

- Of all the possible transaction between the energy levels of an atom, only those are permitted that obey specific selection rules for quantum numbers.
- The selection rules are set by restrictions set by conservation laws (angular momentum, etc)
- Photon carries one unit of angular momentum (*h/2pi*) means in a transition
  - *l* must change by 1
  - m_l change by +/-1
- Those transitions that are not allowed by the selection rules are called <u>forbidden transitions</u>



Anomalous Zeeman effect

Equally spaced splitting of the energy levels was explained by the (normal) Zeeman effect.
Sometimes there was unequally spaced splittings that was not understood so they were called anomalous Zeeman effect.
Also splitting was observed in absence of external B field.
Closely spaced multiplets such as sodium doublets were not understood by regular Zeeman effect.
Splitting of the atomic gas in presence of magnetic field (Stern-Gerlach 1922) experiment suggstes half-integer angular momentum quantum numbers.



Spin angular momentum

Goudsmidth-Uhlenbeck (1925) suggested additional motion for the electron spin simmilar to the classical idea of spinning spherical charge around itself.

So we should have additional angular momentum associated with this motion and it must be quantized.

This is analogous to the earth's motion around itself and the sun.

$S_z = m_s\hbar \quad m_s = \pm\frac{1}{2} \quad z$ allowed values of m_s and s_z for an electron

two possible orientaions: up and down.

$S = \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)}\hbar = \sqrt{\frac{3}{4}}\hbar$ magnitude of the spin angular momentum of an electron

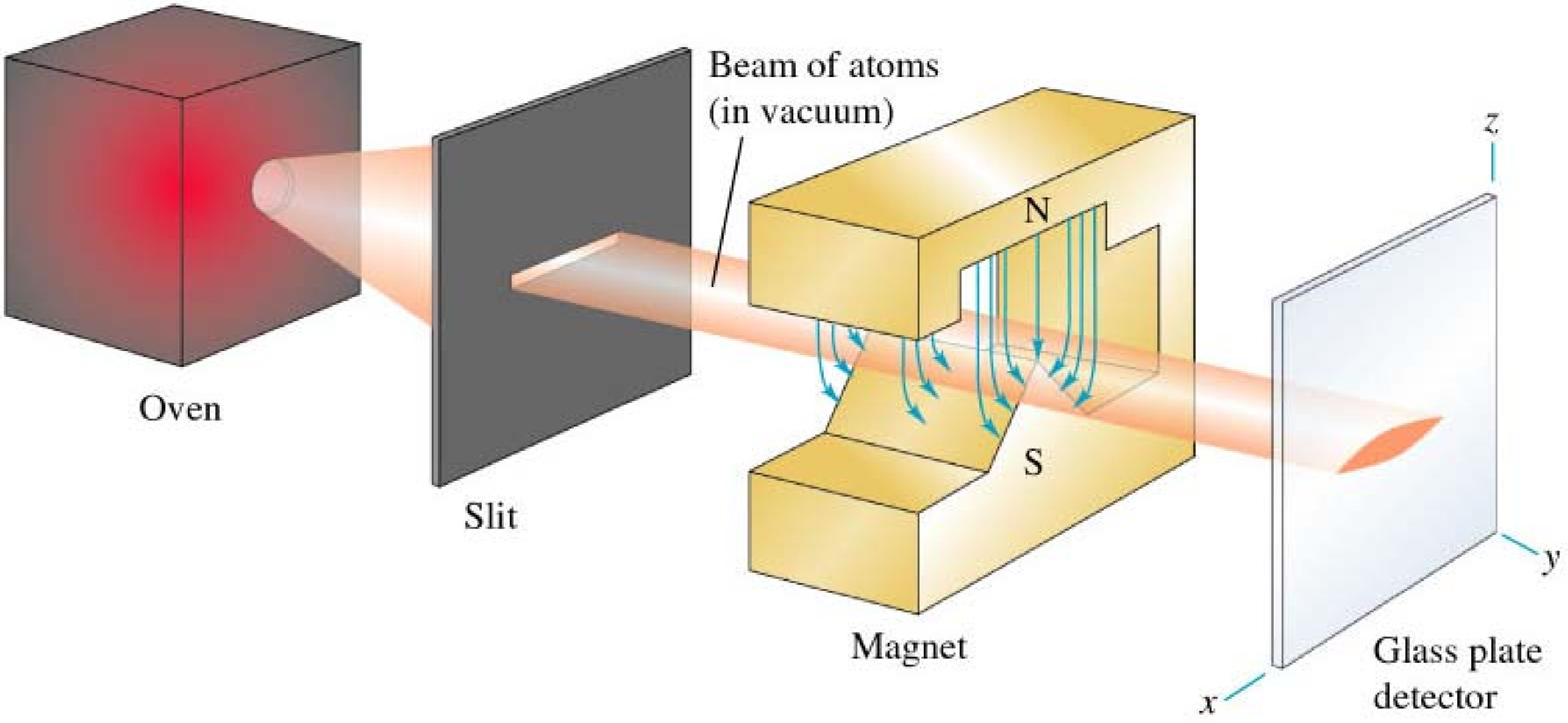
The z-component of the associated spin magnetic moment μ_z is related to S_z by

$\mu_z = -\left(2.00232\right)\frac{e}{2m}S_z$ and $U_s = -\boldsymbol{\mu}\bullet\mathbf{B}$

Paul Dirac (1928) developed the relativistic version of the Schrodinger equatiuon which solved the spin problem with gyromagnetic ration of $2\frac{e}{2m}$.

Quantumelectrodynamics (QED) 2 decades later explained the number to its higher sig figs.

Stern-Gerlach Experiment



Spin magnetic interaction energy

- Calculate the interaction energy for an electron in a l=0 state in a magnetic field with magnitude 2.00 T.

$$U_s = -\mu_z \bullet B$$

$$U_s = -\left(-2.00232\frac{e}{2m}\right)S_z B$$

$$U_s = -\left(-2.00232\frac{e}{2m}\right)\left(\pm\frac{1}{2}\right)B$$

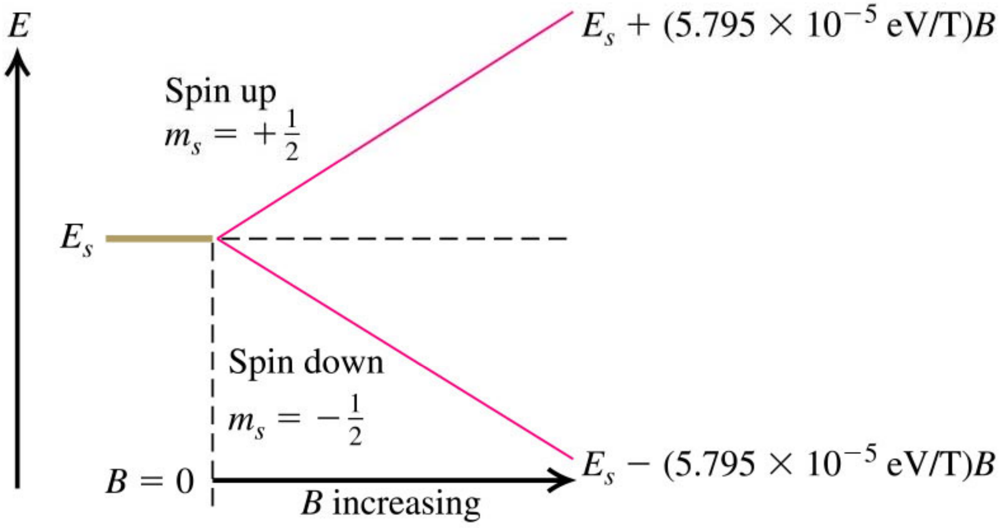
$$U_s = \pm 1.86\times10^{-23}\,J = \pm1.16\times10^{-5}\,eV$$

For spin up the + value

and for spin down the - value

E=$E_0 \pm U$

$$U_s = hc/\lambda \rightarrow \lambda = 10.68\mu$$



Spin-Orbit coupling: the fine structure

- As electron revolves around the positively charged nucleus in Bohr model, it sees a B field caused by the relative motion of the nucleus at its location. This causes the splitting of the energy levels without an external magnetic field.
- The effect is called Spin-Orbit coupling in the Schrodinger model which has interaction energy equal to dot product of the spin and orbital angular momentum vectors.
- This is effect is responsible for the splitting of doublets in Sodium spectrum

Total angular momentum: $\vec{J} = \vec{L} + \vec{S}$

Possible values for magnitude of the

J are given by: $J = \sqrt{j\left(j+1\right)}\hbar$

$j = l \pm \frac{1}{2}$ for a given l

When $j = l + \frac{1}{2}$ the $\vec{L} \& \vec{S}$ have

parallel z-componnets

When $j = l + \frac{1}{2}$ the $\vec{L} \& \vec{S}$ have

anti-parallel z-componnets

This splitting is called fine structre

Hyperfine structure

- Interaction of the magnetic dipole moment of the nucleus with the spin angular momentum or orbital angular momentum causes further splitings that is known as hyperfine structure.

- Example of hyperfine structure is splitting of the ground level of hydrogen atom by $5.9\text{x}10^{-6}$eV which leads to radio waves of 21 cm coming from all stars and is the base for radio-astronomy. We detect objects that are too cold to emit in the visible of IR.

The exclusion principle and Many electron atoms

In many electron atoms the electrons have the same quantum numbers as the hydrogen atom with two key differences.

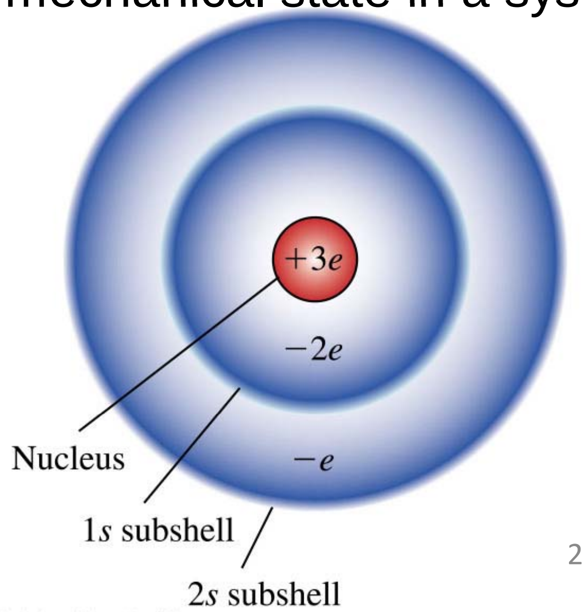
1) The effect of the screening of the potential of the nucleus by inner electrons as seen by the outer electrons. $E_n = -\frac{Z_{eff}^{\;2}}{n^2}(13.6eV)$ where $Z_{eff} \leq Z_{atom}$

And the quantum numbers are: $n \geq 1 \quad 0 \leq l \leq n-1 \quad |m_l| \leq l$

2) Pauli (1925) stated the <u>exclusion principle</u> as:

no two electrons can occupy the same quantum-mechanical state in a system, or <u>no two electrons can have the same</u> quantum-numbers(n, l, m_l, m_s) in an atom.

This justifies and explains the radical differences between the atoms that have small differences between their atomic number and the shape of the periodic table.



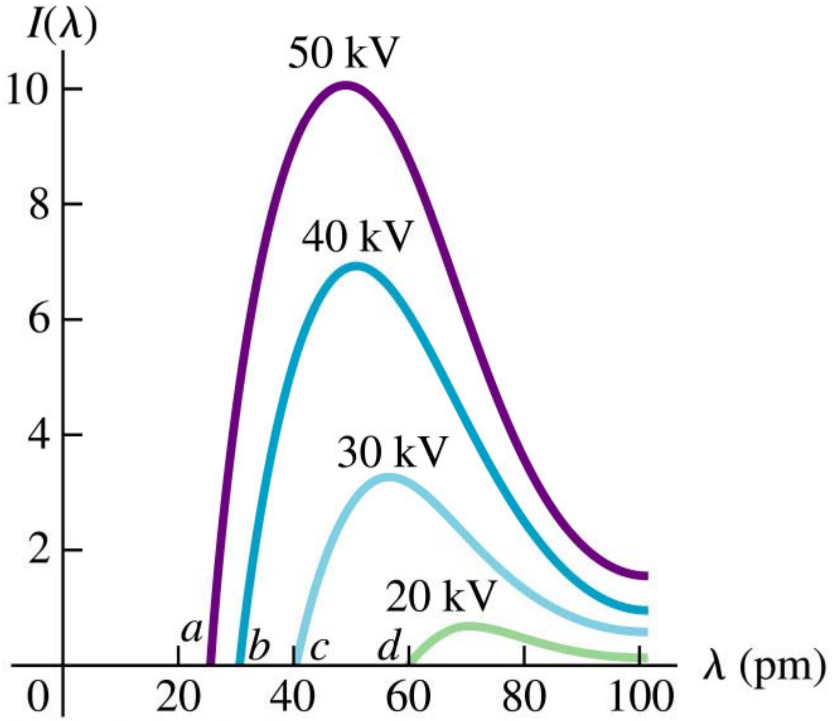
Periodic table and the quantum numbers (read on your own)

Determining Z_{eff}

Energies for a valence electron

Continuous X-ray spectra

- Accelerated beam of electrons with V_{ac} hitting surface of a target generating energetic photons.
- The minimum wavelength is determined by V_{ac}



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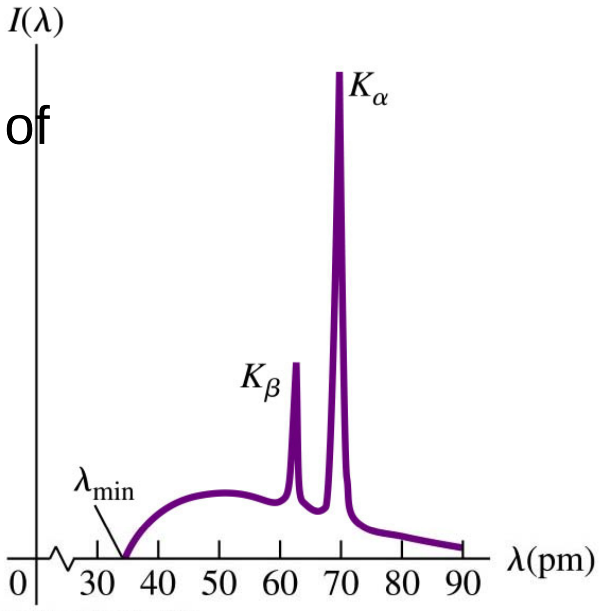
Moseley’s law

Mosley's law states that the frequency of a K_α $x-ray$ which is a result of an electron from and L shell with $n=2$ is dropping to an K-shell with n-1 from a target with atomic number of Z is

$$f = 2.48\times10^{15}\,Hz\left(z-1\right)^2$$

The characteristic x-ray spectra results from a transition to a hole in an inner energy level of an atom.



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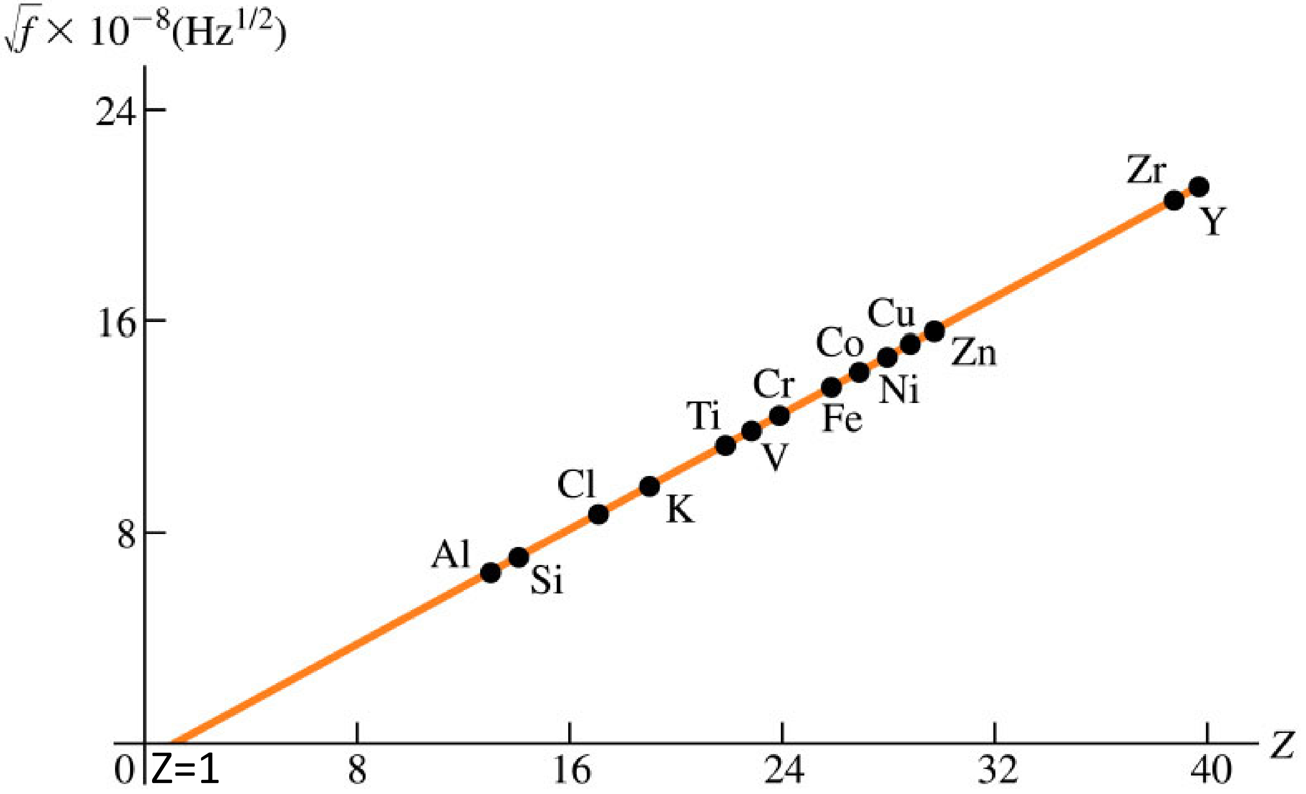
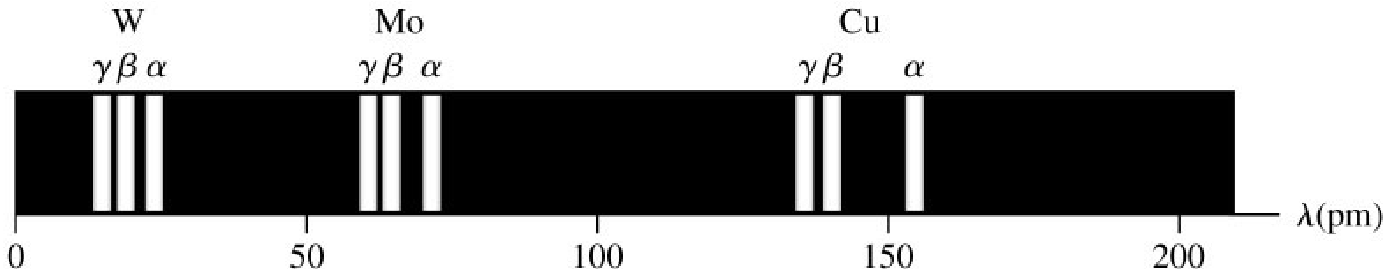
Graphic representation of the Mosley’s law

$$f = 2.48\times10^{15}\,Hz\left(z-1\right)^2$$

$$\sqrt{f} = \sqrt{2.48\times10^{15}\,Hz}\left(z-1\right)$$




W
γ β α
Mo
γ β α
Cu
γ β α
λ(pm)
0
50
100
150
200

X-ray absorption

- When energy of a beam of x-ray passing through a material matches the material's characteristic x-ray lines, we see increased absorption.
- Material are capable of absorbing whatever spectral lines they emit and vise versa.
- We can identify the material with their x-ray lines such as Kalpha