Ch. 9 Atomic Physics

References:

1. Young & Freedman, “University Physics”, 13th ed. Ch. 41

2. Halliday et al., “Principles of Physics”, 9th ed. Ch. 39, 40

Outline

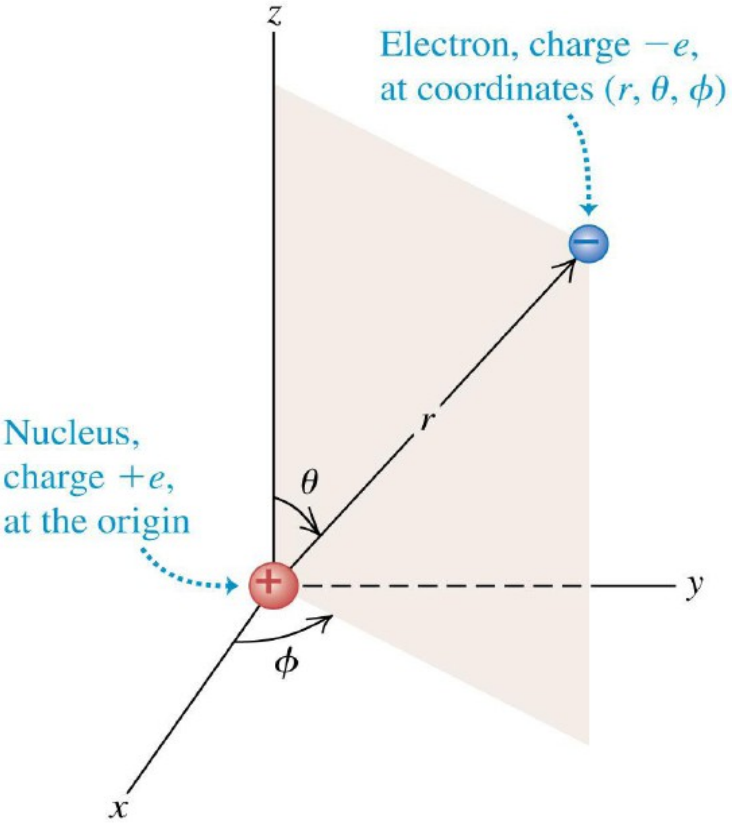
9.1 The Hydrogen Atom
9.2 The Zeeman Effect
9.3 Electron Spin
9.4 Many-Electron Atoms
9.5 X-Ray Spectra

9.1 The Hydrogen Atom

Recall: Schrödinger equation in spherical coordinates:

$$-\frac{\hbar^2}{2m}\left\{\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi)+\frac{1}{r^2\sin\theta}\left[\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]\right\}+U\psi=E\psi$$

where $U(r)=-\frac{1}{4\pi\epsilon_0}\frac{e^2}{r}$



The problem can be solved by separation of variables. We shall only outline the procedure and summarize the results:

Let $\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$

Schrödinger equation => 3 separate equations

$$\frac{d^2\Phi}{d\phi^2} + m_l^2\Phi = 0 \qquad \text{(Eq.1)}$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left[l(l+1) - \frac{m_l^2}{\sin^2\theta}\right]\Theta = 0 \qquad \text{(Eq.2)}$$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[\frac{2m}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r} + E\right) - \frac{l(l+1)}{r^2}\right]R = 0 \qquad \text{(Eq.3)}$$

where l and m_l are constants

1. (Eq.1) => $\Phi(\phi) = A e^{i m_l \phi}$

The wave function must be single value at a given point:

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

=> $m_l = 0, \pm 1, \pm 2, \ldots$

2. (Eq.2) is called the Legendre's equation and has solutions only if *l* is an integer and satisfies:

$$l \geq |m_l|$$

3. The radial function *R* must approach zero at large *r*. (Eq.3) has solutions if the energy levels satisfy:

$$E_n = -\frac{1}{(4\pi\epsilon_0)^2} \frac{m e^4}{2 n^2 \hbar^2} = -\frac{13.6\ \text{eV}}{n^2}$$

where the integer $n \geq l + 1$

Energy levels of a hydrogen atom:

$$E_n = -\frac{1}{(4\pi\epsilon_0)^2}\frac{me^4}{2n^2\hbar^2} = -\frac{13.6\ \mathrm{eV}}{n^2}$$ (same as Bohr model)

Principal quantum number n :

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

Orbital quantum number l :

$$l = 0, 1, 2, \ldots, n-1$$

Magnetic quantum number m_l :

$$m_l = 0, \pm 1, \pm 2, \ldots \pm l$$

$$(-l, -l+1, \ldots, l-1, l)$$

- ***Quantization of Orbital Angular Momentum***

It can be shown (in a formal QM course) that l is related to the magnitude of the orbital angular momentum by

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

The permitted values of the component of $\boldsymbol{L}$ in a given direction (e.g., z-component) is

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

Note:

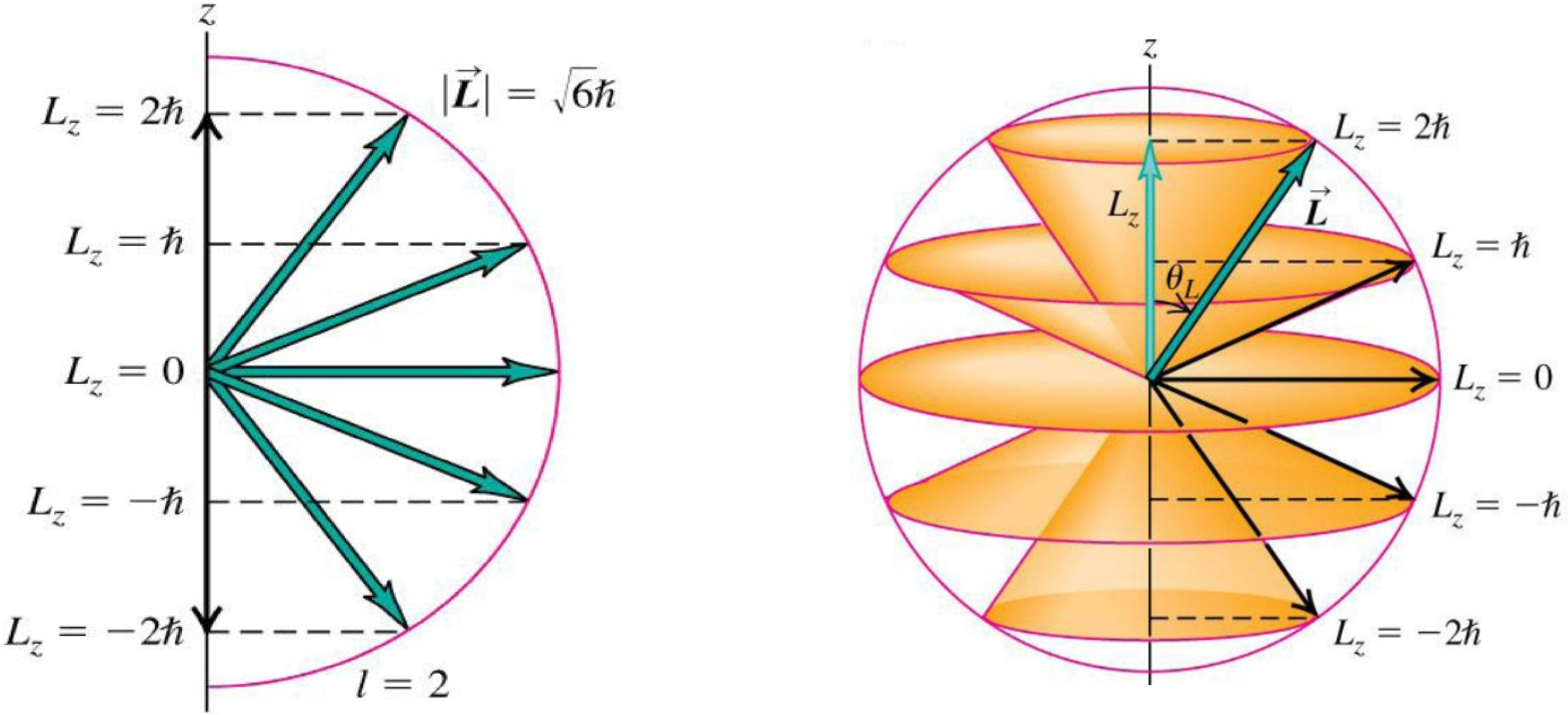
1. $l = 0$ => $L = 0$

   $l = 0$ state has no orbital angular momentum.
   The $l = 0$ wave function is spherically symmetric (depends only on r).

2. $|L_z|$ is always less than L

Example: $l = 2$

$$L = \sqrt{l(l+1)}\hbar = \sqrt{6}\hbar \approx 2.45\hbar$$
$$L_z = m_l \hbar = -2\hbar, -\hbar, 0, \hbar, 2\hbar$$



Minimum angle $\theta_L = \cos^{-1}(L_z / L) = 35.3^{\mathrm{o}}$

- ***Quantum Number Notation***

The wave function depends on n, l, m_l :

$$\psi_{n l m_l}(r, \theta, \phi) = R_{n l}(r)\,\Theta_{l m_l}(\theta)\, e^{i m_l \phi}$$

The energy depends only on n : $E_n = -\dfrac{13.6\ \mathrm{eV}}{n^2}$

=> In general, for each energy level E_n, there is more than one distant state having the same energy (Degeneracy).

Examples:

1. Ground level (n = 1)

=> l = 0, m_l = 0

=> a unique wavefunction ψ_{100}

2. First excited level (n = 2)

$$\Rightarrow \quad \begin{array}{ll} l=0 \;, & m_l=0 \\ l=1 \;, & m_l=-1,0,1 \end{array}$$

=> four distant wavefunctions

$$\begin{array}{l} \psi_{200} \\ \psi_{21-1}, \psi_{210}, \psi_{211} \end{array}$$

The orbital quantum number l are often labeled with letters:

$l = 0$: s states (sharp)
$l = 1$: p states (principal)
$l = 2$: d states (diffuse)
$l = 3$: f states (fundamental)
$l = 4$: g states
$l = 5$: h states
… and so on alphabetically

Examples:

1. (n=1, l=0) is called 1s state

2. (n=4, l=3) is called 4f state

The radial extent of the wave function increases with n, and we can speak of a region of space associated with a particular value of n as a shell:

n = 1: K shell
n = 2: L shell
n = 3: M shell
n = 4: N shell
… and so on alphabetically

Examples:

n	l	m_l	Spectroscopic notation	Shell
1	0	0	1s	K
2	0	0	2s	L
2	1	-1, 0, 1	2p	L
3	0	0	3s	M
3	1	-1, 0, 1	3p	M
3	2	-2, -1, 0, 1, 2	3d	M

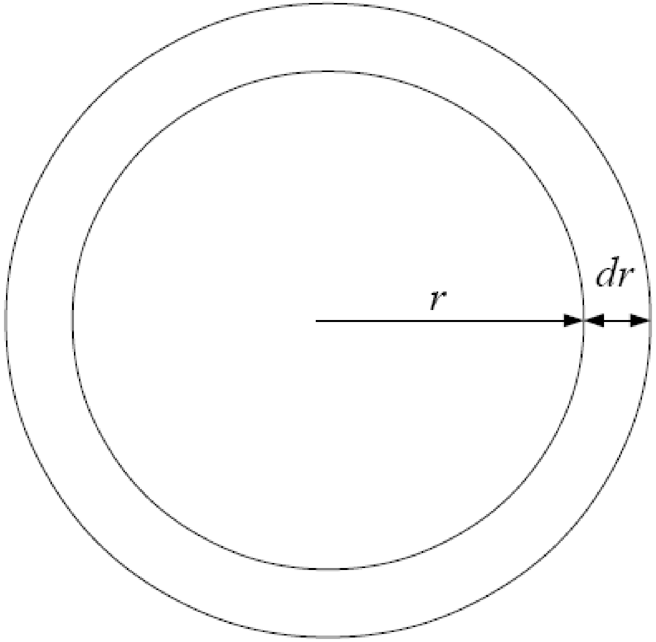
For each n, different l correspond to different subshells.

The L shell (n=2) contains the 2s and 2p subshells.

- ***Electron Probability Distributions***

Consider the special case where the normalized wave function ψ depends only on r (eg, l=0 state):

Define: Radial distribution probability

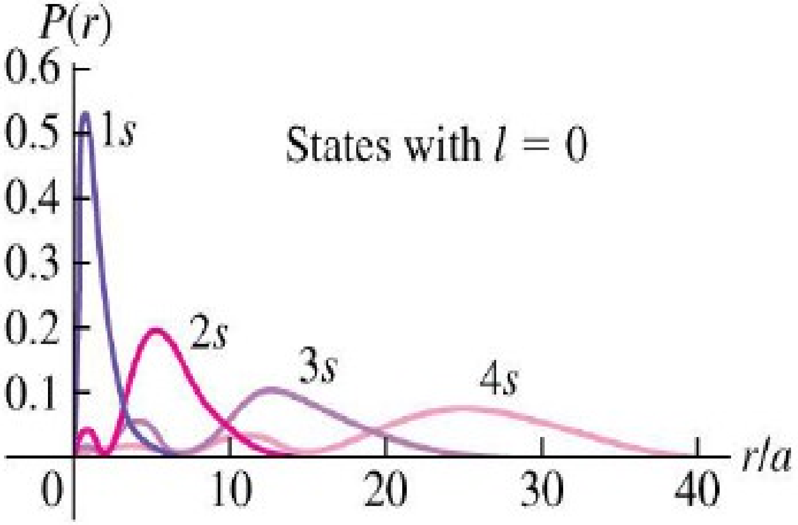


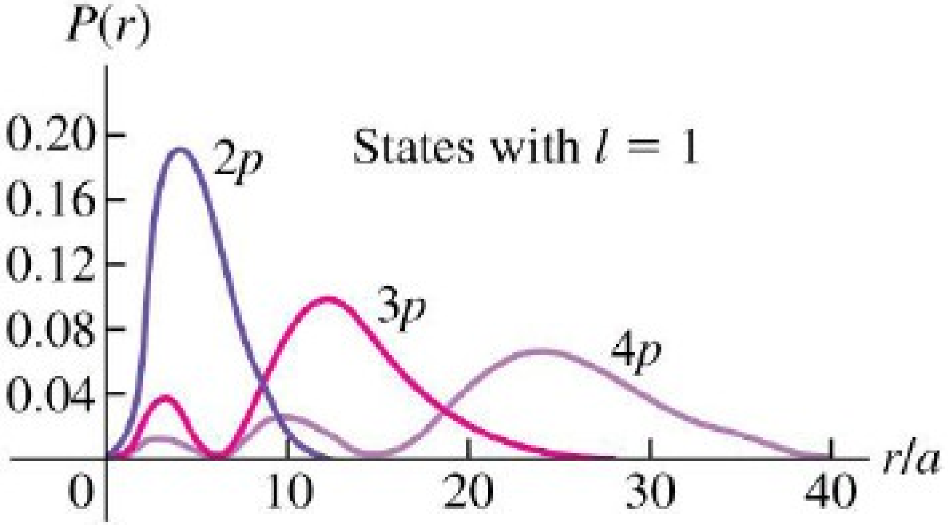
$$\boxed{P(r)\,dr = |\psi(r)|^2\, dV = |\psi(r)|^2\, 4\pi r^2\, dr}$$

Probability of finding the electron in the range (r, $r + dr$)

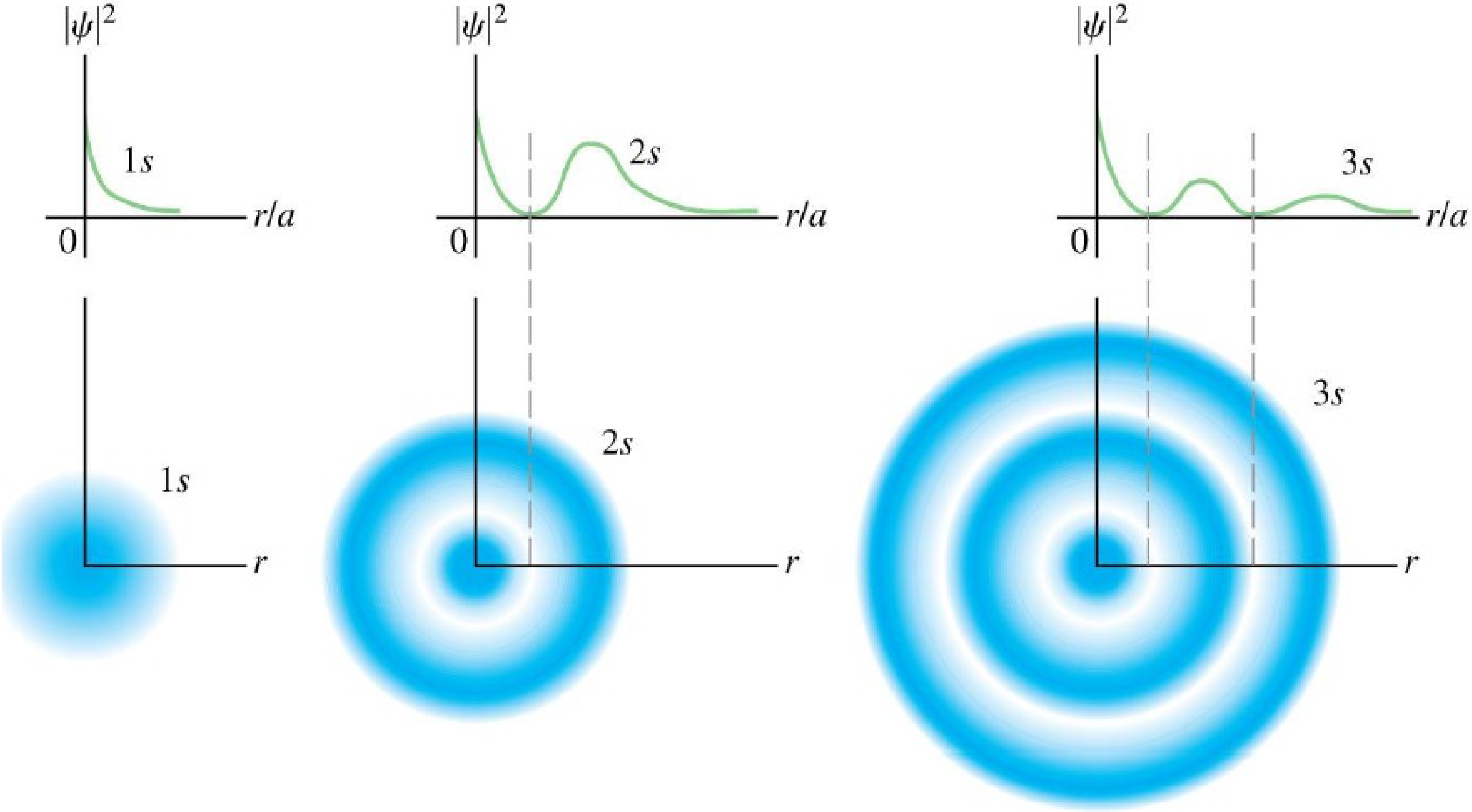
Remark: For ψ that depends also on θ and ϕ, we use the value of $|\psi|^2$ averaged over all angles

Examples:

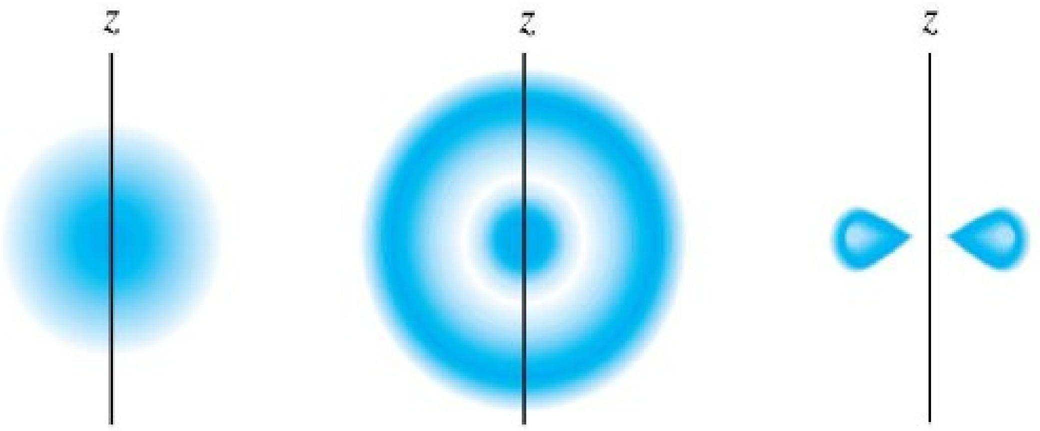




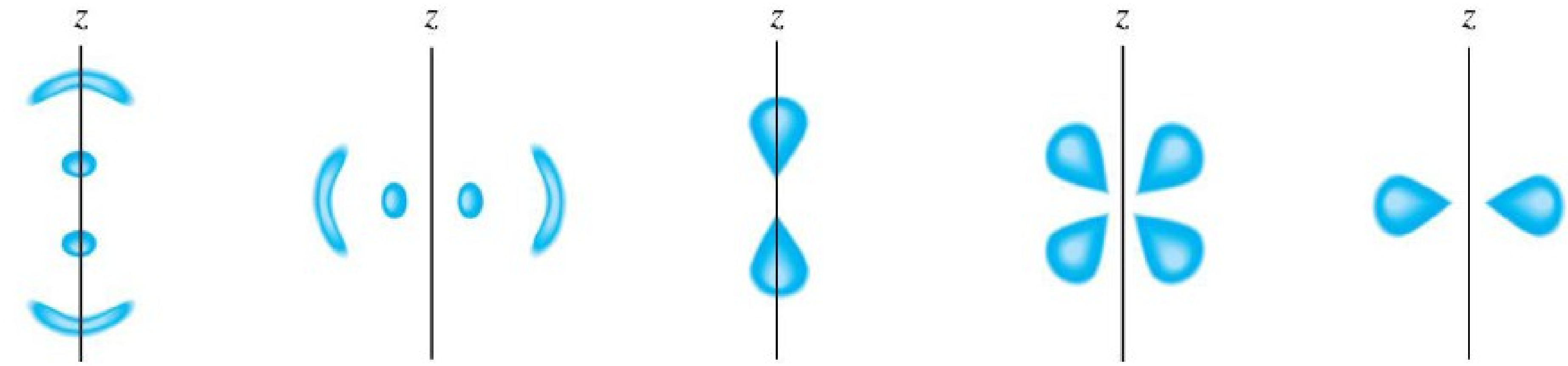
$$a = \frac{\epsilon_0 h^2}{\pi m e^2} = 5.29 \times 10^{-11}\,\mathrm{m}$$ (Bohr radius)


$|\psi|^2$
1s
0
r/a
$|\psi|^2$
2s
0
r/a
$|\psi|^2$
3s
0
r/a
1s
r
2s
r
3s
r

Cross sections of $|\psi|^2$:



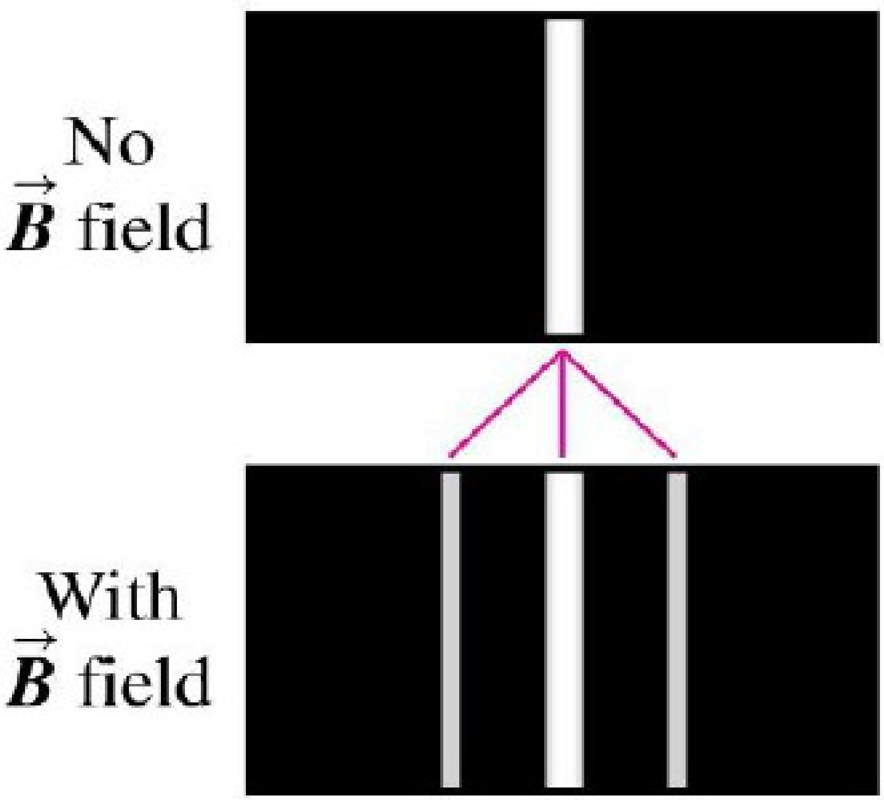
$1s, m_l = 0$ $2s, m_l = 0$ $2p, m_l = \pm 1$ $2p, m_l = 0$



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

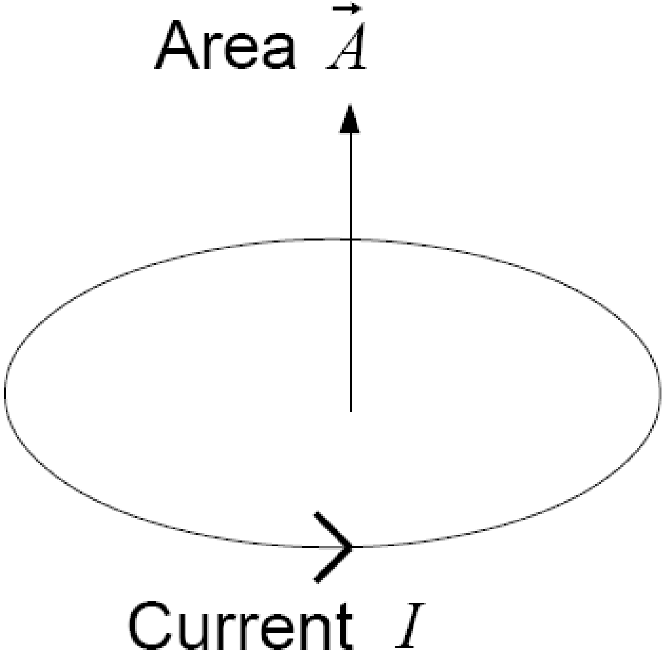
9.2 The Zeeman Effect

When an excited gas is placed in a B-field, the field splits individual spectral lines into sets of three lines.



• *Magnetic Moment of an Orbiting Electron*

A current loop defines a magnetic (dipole) moment:

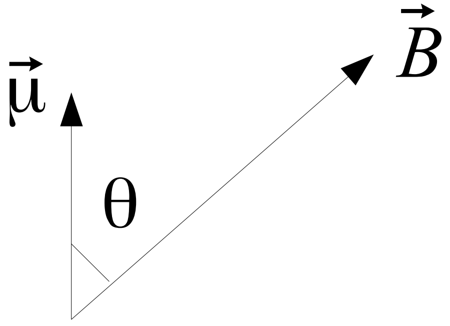


$$\vec{\mu} = I\vec{A}$$

When a magnetic moment is placed in a B-field:

=> Potential energy

$$U = -\vec{\mu}\cdot\vec{B} = -\mu B\cos\theta$$



Note: U is min when $\theta = 0$

Now consider the current loop produced by an electron in circular orbit:

speed

$$I = \frac{e}{T} = \frac{e\,v}{2\pi r}$$

orbit radius

Magnetic moment $\mu = I\,A = \frac{e\,v}{2\pi r}(\pi r^2) = e\,v\,r/2$

Angular momentum $L = m\,v\,r$

=> $\mu = \frac{e}{2m} L$

Note: The ratio $\frac{\mu}{L} = \frac{e}{2m}$ is called gyromagnetic ratio.

Note: Electron charge is negative ($-e$), the current is in a direction opposite to the electron motion

=> μ and L are in opposite directions

$$\boxed{\vec{\mu} = -\frac{e}{2m}\vec{L}}$$

(Magnetic moment associated with electron motion)

Let the B-field be along the +z axis:

$$U = -\vec{\mu}\cdot\vec{B} = -\mu_z B$$

=> $$U = -\left(-\frac{e}{2m}L_z\right)B$$

Recall: Quantization of angular momentum

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

$$\boxed{U = m_l \frac{e\hbar}{2m} B = m_l \mu_B B}$$

(Orbital magnetic interaction energy)

where $\mu_B \equiv e\hbar/2m$ (Bohr magneton)

The B-field shifts the energy of each orbital state by:

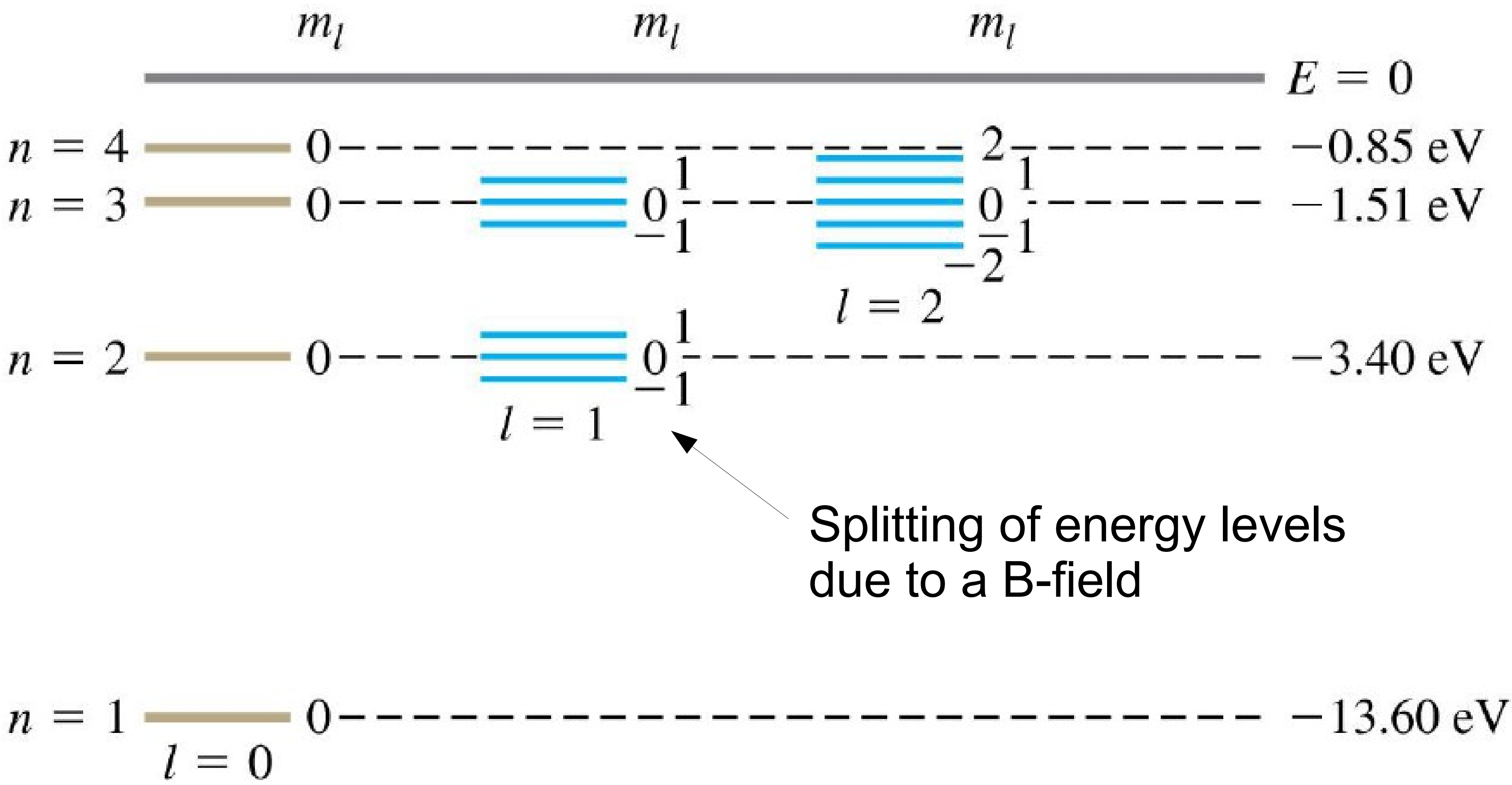
$$U = m_l \mu_B B \qquad (m_l = 0, \pm 1, \pm 2, \ldots, \pm l)$$

For each l, there are (2l+1) states. Without the B-field, they have the same energy (ie, they are degenerate).

In a B-field, they are split into (2l+1) distinct energy levels ; adjacent levels differ in energy by

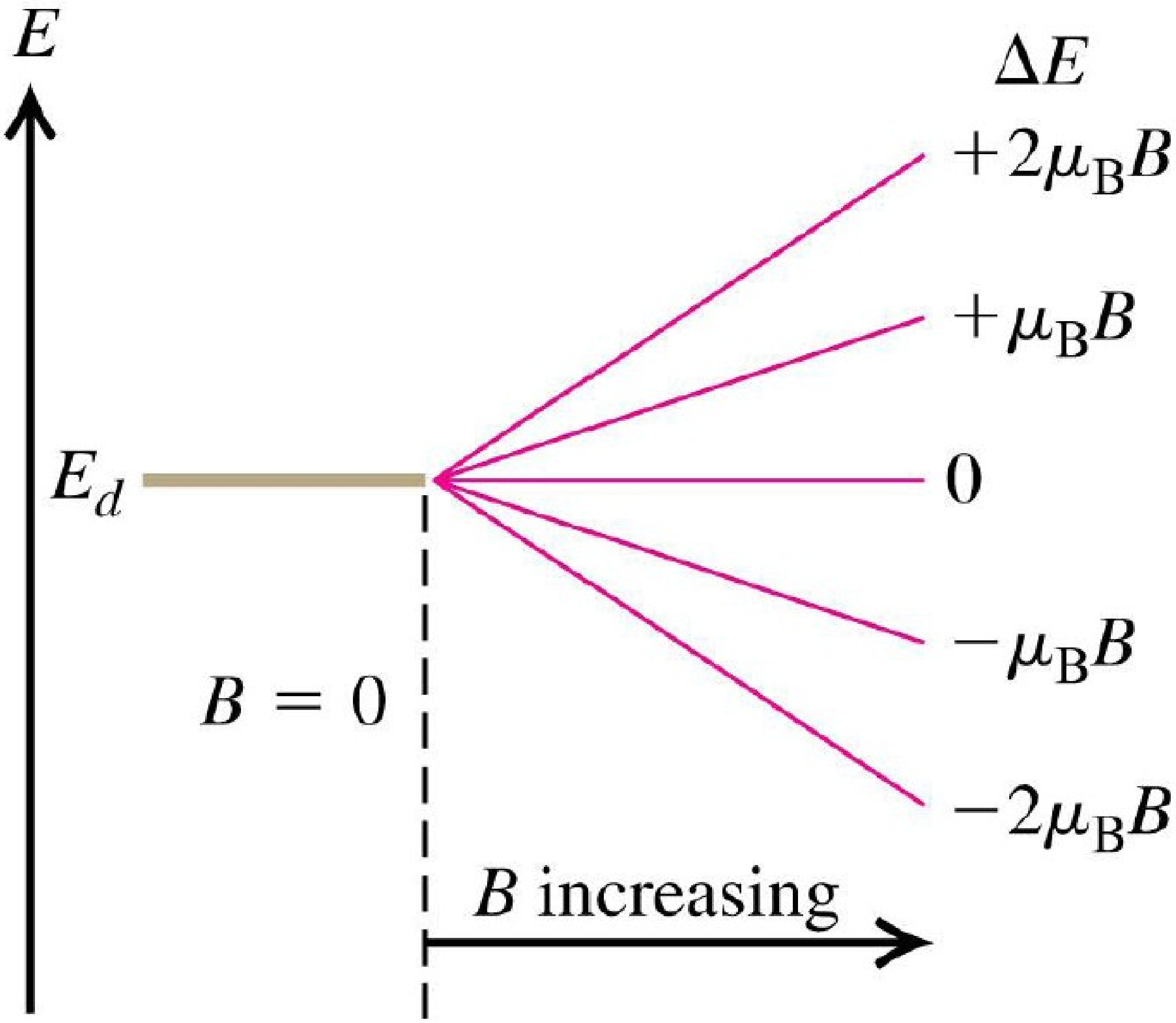
$$\Delta U = \mu_B B$$

Energy levels for hydrogen:

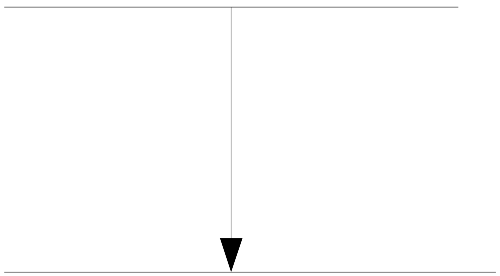


Splitting of energy levels due to a B-field

Example: d state (l=2)



- ***Selection Rules***



Initial State (n, l, m_l)

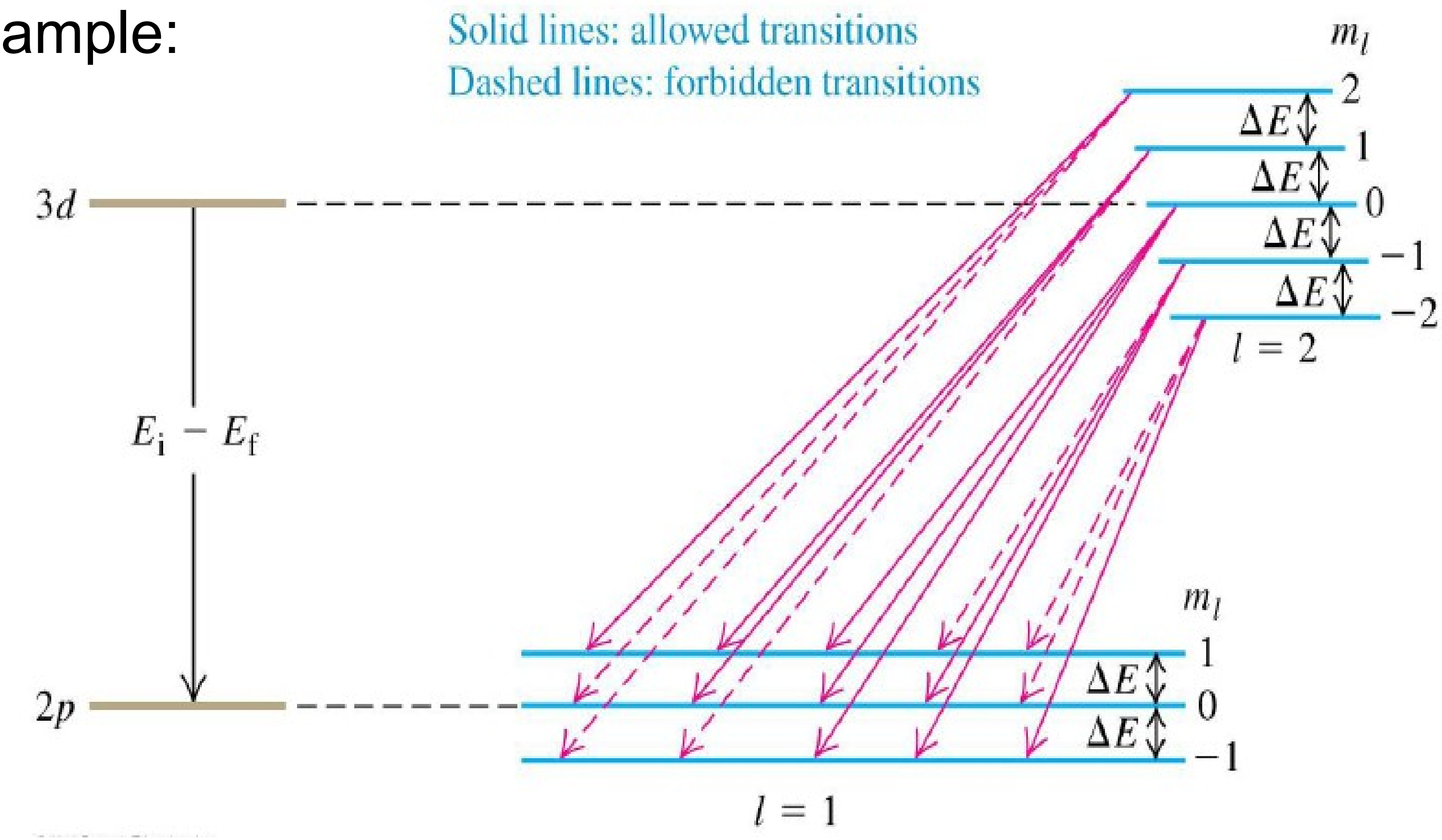
Final state (n', l', m_l')

Not all transitions from initial to final states are allowed because of a restriction associated with conservation of angular momentum.

$$\boxed{\begin{array}{l} \Delta l = \pm 1 \\ \Delta m_l = 0, \pm 1 \end{array}}$$

Selection rule

Example:



The allowed transitions => only 3 possible photon energies

Note: The splitting of a spectral line into 3 components due to the orbital motion of the electron is called normal Zeeman effect.

9.3 Electron Spin

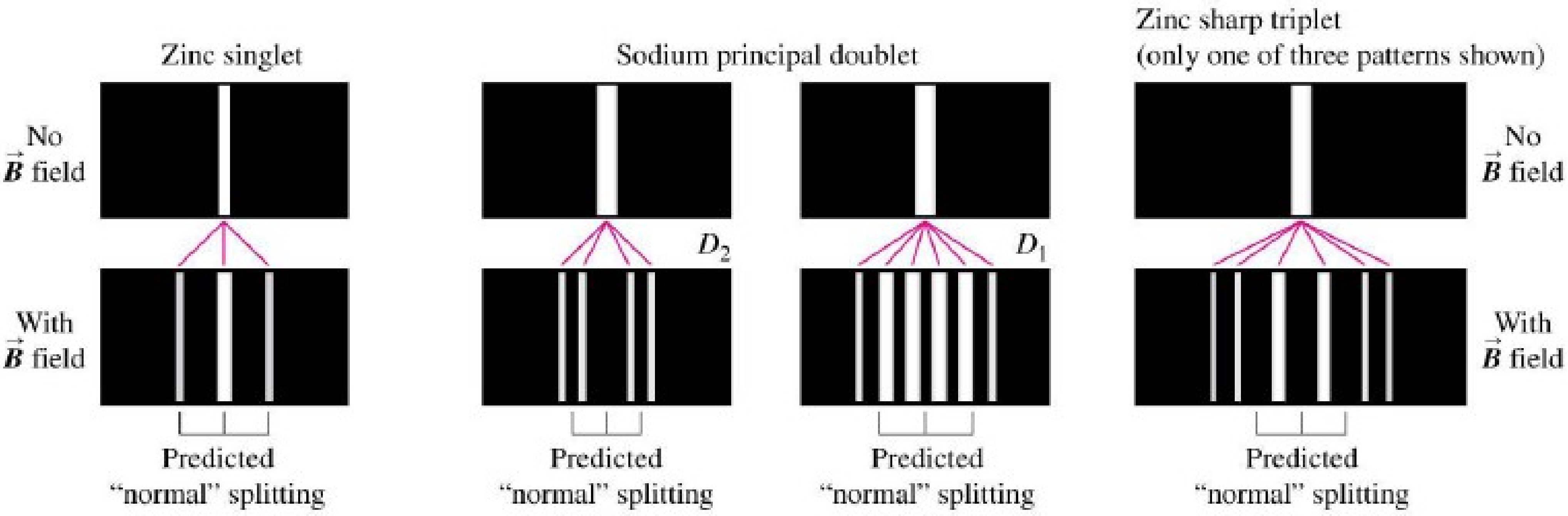
Observations =>

(1) Many spectral lines actually consist of two closely seperate lines

(2) It is expected that each spectral line should be split into 3 components in the presence of a B-field (normal Zeeman effect). However, this is not always the case

The quantum theory we have developed so far cannot explained these observations!

Normal and anomalous Zeeman effects:

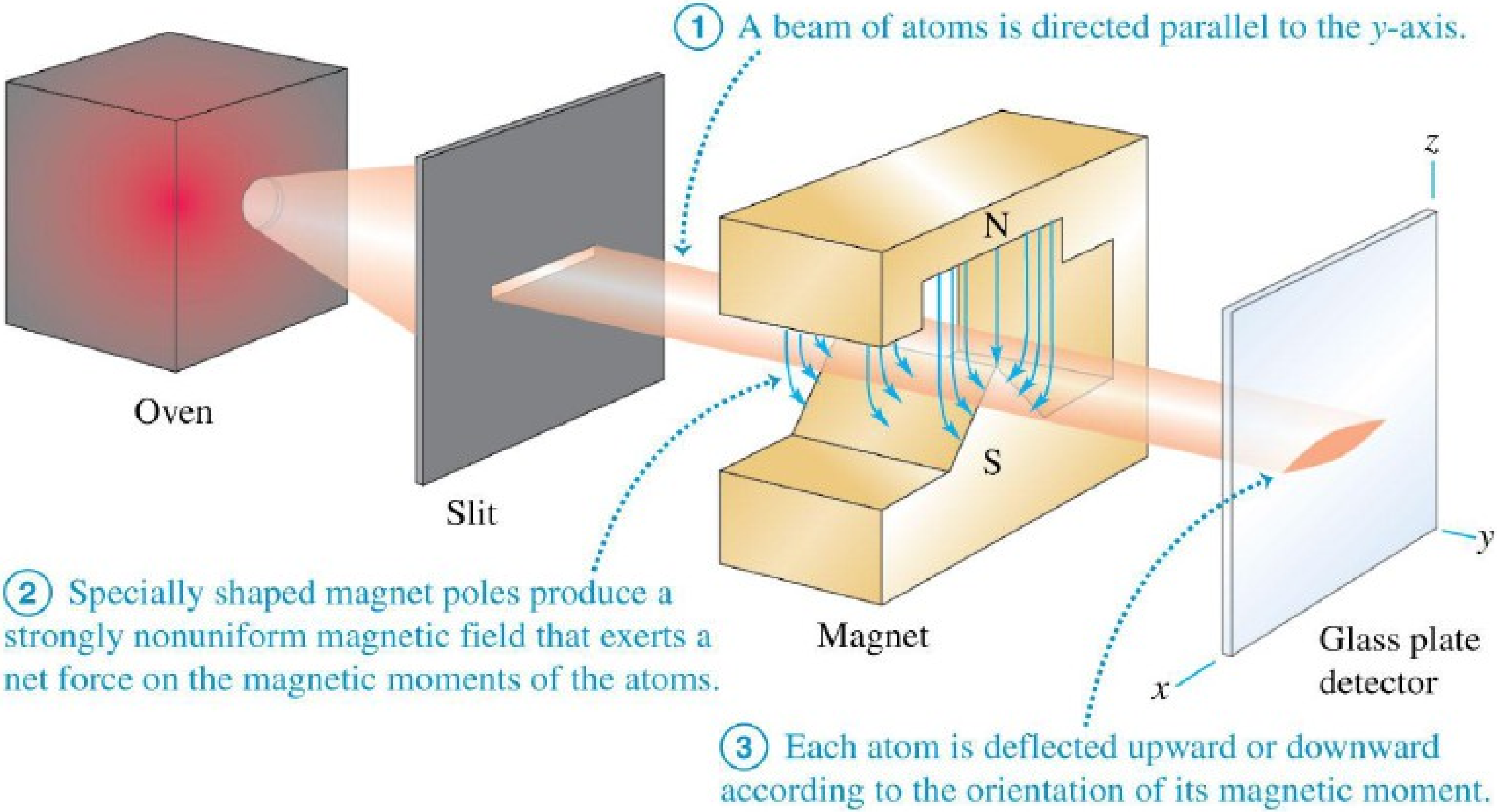


Normal pattern:
Experiment agrees with predicted "normal" splitting.

Anomalous patterns: Experiment does not agree with predicted "normal" splitting.

- ***The Stern-Gerlach Experiment***

(Otto Stern & Walter Gerlach 1922)



① A beam of atoms is directed parallel to the *y*-axis.

② Specially shaped magnet poles produce a strongly nonuniform magnetic field that exerts a net force on the magnetic moments of the atoms.

③ Each atom is deflected upward or downward according to the orientation of its magnetic moment.

- ***Spin Quantum Numbers***

In 1925, Samuel Goudsmit and George Uhlenbeck proposed that every electron has an intrinsic angular momentum (spin).

Let the spin angular momentum of an electron be $\vec{S}$

The z-component: $\boxed{S_z = \pm \frac{1}{2}\hbar}$ (components of spin angular momentum)

Recall: $L = \sqrt{l(l+1)}\hbar$

Similarly, $S = \sqrt{s(s+1)}\hbar = \sqrt{\frac{3}{4}}\hbar$

where the spin quantum number s = 1/2

To label the state of the electron in a hydrogen atom, we need a new quantum number m_s to specify the spin orientation:

$$\psi_{n l m_l m_s}$$

The spin angular momentum can have $2s + 1 = 2$ orientations:

$$S_z = m_s \hbar \qquad \left(m_s = \pm 1/2\right)$$

Note:

$m_s = +1/2$ (spin up); $m_s = -1/2$ (spin down)

Recall: magnetic moment due to orbital motion

$$\vec{\mu}_{\text{orbit}} = -\frac{e}{2m}\vec{L}$$

The associated spin magnetic moment:

$$\vec{\mu}_{\text{spin}} = -2\frac{e}{2m}\vec{S}$$

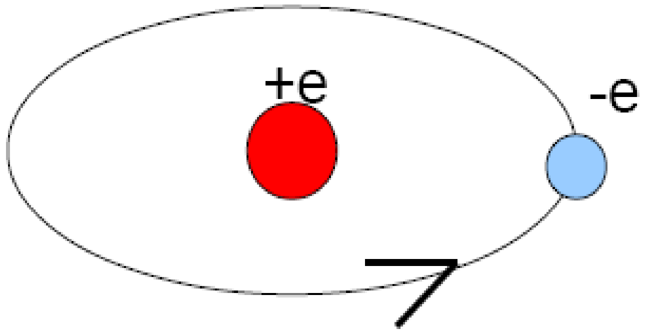
(Experiments show that this is not exactly 2, but 2.0023..., which is predicted by quantum electrodynamics (QED))

=> Total magnetic moment:

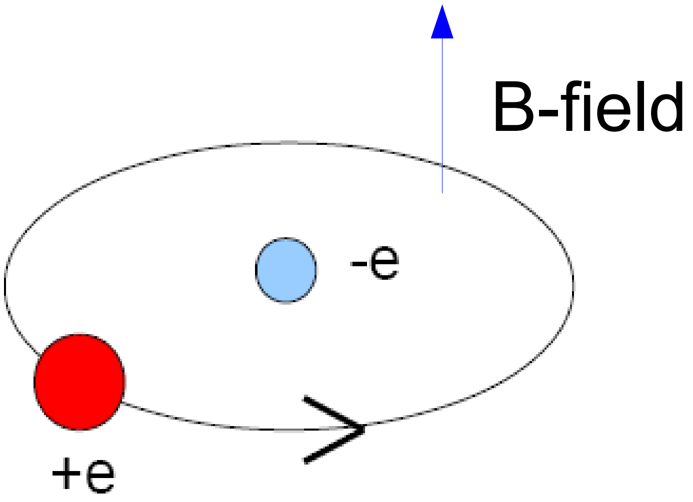
$$\boxed{\vec{\mu}_{\text{total}} = \vec{\mu}_{\text{orbit}} + \vec{\mu}_{\text{spin}} = -\frac{e}{2m}\left(\vec{L} + 2\vec{S}\right)}$$

Spin-Orbit Coupling

Spin magnetic moment => splitting of energy levels
(even when there is no external B-field)

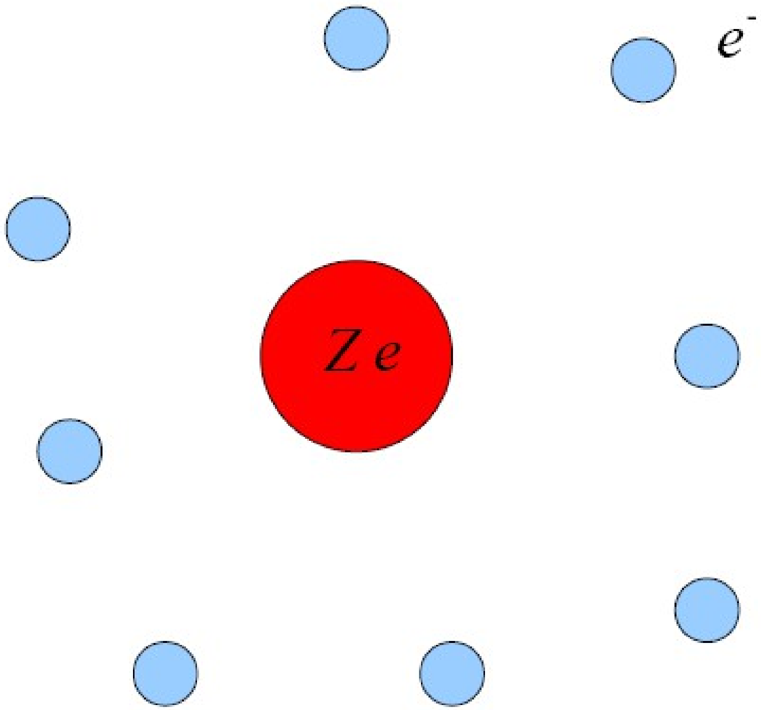


In the frame of
the atomic nucleus
(proton for H atom)



In the frame of the
electron
(The B-field is due to the moving
proton as seen by the electron)

9.4 Many-Electron Atoms



Z = atomic number

We can apply the Schrödinger equation to study this general atom, but the complexity of the analysis increases rapidly with Z.

- ***The Central-Field Approximation***

1. Consider each electron as moving independently in a potential due to the nucleus and the (Z-1) other electrons.

2. Consider the (Z-1) other electrons as a spherically symmetric charge cloud around the nucleus

Solve the Schrödinger equation for the one-electron wavefunction:

$$-\frac{\hbar^2}{2m}\left\{\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi)+\frac{1}{r^2\sin\theta}\left[\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]\right\}+\underset{\substack{\uparrow\\ \text{Spherically symmetric}}}{U(r)}\psi=E\psi$$

$U(r)$ does not depend on θ and ϕ

=> same solutions for the angular part as the H atom

=> label a state by $\left(n\,,l\,,m_l\,,m_s\right)$

Quantum numbers for the angular-momentum state

The allowed values are the same as the H atom:

$$\boxed{n\geq 1 \quad , \quad 0\leq l\leq n-1 \quad , \quad \left|m_l\right|\leq l \quad , \quad m_s=\pm\frac{1}{2}}$$

Note: In general, the energy of a state now depends on both n and l.

- ***The Pauli Exclusion Principle***

We would expect a gradual change in physical and chemical properties of atoms as Z increases.

But observations suggest properties of elements can vary widely from one to the next!

Example:

Element	Z	Properties
Fluorine (F)	9	Forms compounds by acquiring an extra electron
Neon (Ne)	10	Forms no compounds
Sodium (Na)	11	Forms compounds by losing an electron

In 1925, Pauli discovered the fundamental principle that governs the electronic configuration of multi-electron atoms.


Wolfgang Pauli
(1900-1958)

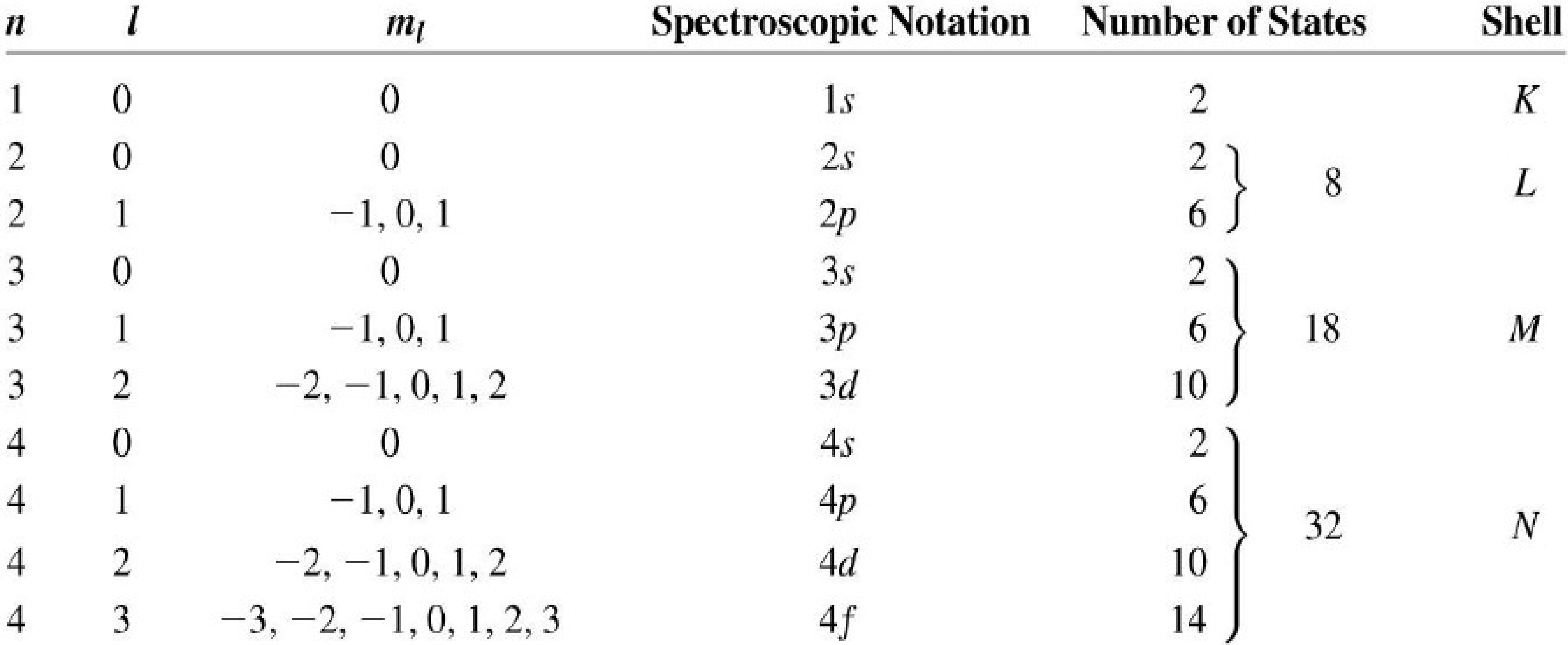
Pauli exclusion principle:

No two electrons can occupy the same quantum-mechanical state in a given system

ie, no two electrons in an atom can have the same values of (n, l, m_l, m_s)

Remark: In general, the exclusion principle applies to half-integral spin particles (Fermions).

Quantum states of electrons in the first four shells:



n	l	m_l	Spectroscopic Notation	Number of States		Shell
1	0	0	1s	2		K
2	0	0	2s	2	8	L
2	1	−1, 0, 1	2p	6		
3	0	0	3s	2	18	M
3	1	−1, 0, 1	3p	6		
3	2	−2, −1, 0, 1, 2	3d	10		
4	0	0	4s	2	32	N
4	1	−1, 0, 1	4p	6		
4	2	−2, −1, 0, 1, 2	4d	10		
4	3	−3, −2, −1, 0, 1, 2, 3	4f	14		

Note: Number of states = max number of electrons allowed

- ***The Periodic Table***

Ground-state electron configuration:

Hydrogen (H; Z = 1): $1s$

The single electron is in a state (n=1, l=0, m_l=0, m_s=±1/2)

Helium (He; Z = 2): $1s^2$

The two electrons are in 1s states, with opposite spins.

K shell is completely filled. Helium is a noble gas.

Note: The chemical properties of an atom are determined mainly by its outermost (valence) electrons.

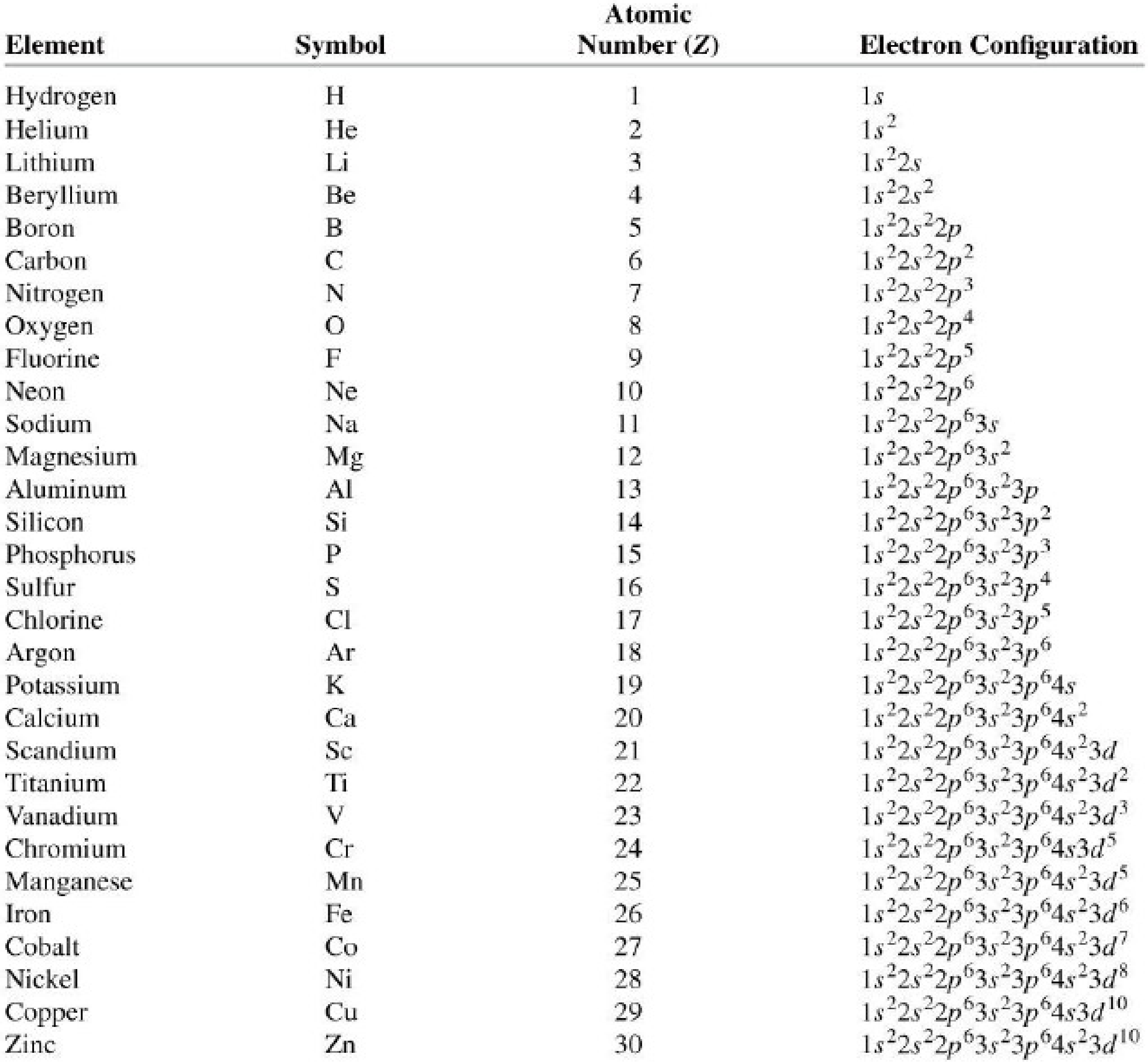
Lithium (Li; $Z = 3$): $1s^2 2s$

The $2s$ electron is loosely bound.

It is an alkali metal and forms ionic compound by losing an electron. It has a valence +1.

Beryllium (Be; $Z = 4$): $1s^2 2s^2$

The two valence electrons fill the s subshell of the L shell.
It is an alkaline earth element.



Element	Symbol	Atomic Number (Z)	Electron Configuration
Hydrogen	H	1	$1s$
Helium	He	2	$1s^2$
Lithium	Li	3	$1s^2 2s$
Beryllium	Be	4	$1s^2 2s^2$
Boron	B	5	$1s^2 2s^2 2p$
Carbon	C	6	$1s^2 2s^2 2p^2$
Nitrogen	N	7	$1s^2 2s^2 2p^3$
Oxygen	O	8	$1s^2 2s^2 2p^4$
Fluorine	F	9	$1s^2 2s^2 2p^5$
Neon	Ne	10	$1s^2 2s^2 2p^6$
Sodium	Na	11	$1s^2 2s^2 2p^6 3s$
Magnesium	Mg	12	$1s^2 2s^2 2p^6 3s^2$
Aluminum	Al	13	$1s^2 2s^2 2p^6 3s^2 3p$
Silicon	Si	14	$1s^2 2s^2 2p^6 3s^2 3p^2$
Phosphorus	P	15	$1s^2 2s^2 2p^6 3s^2 3p^3$
Sulfur	S	16	$1s^2 2s^2 2p^6 3s^2 3p^4$
Chlorine	Cl	17	$1s^2 2s^2 2p^6 3s^2 3p^5$
Argon	Ar	18	$1s^2 2s^2 2p^6 3s^2 3p^6$
Potassium	K	19	$1s^2 2s^2 2p^6 3s^2 3p^6 4s$
Calcium	Ca	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
Scandium	Sc	21	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d$
Titanium	Ti	22	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$
Vanadium	V	23	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$
Chromium	Cr	24	$1s^2 2s^2 2p^6 3s^2 3p^6 4s 3d^5$
Manganese	Mn	25	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$
Iron	Fe	26	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$
Cobalt	Co	27	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$
Nickel	Ni	28	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$
Copper	Cu	29	$1s^2 2s^2 2p^6 3s^2 3p^6 4s 3d^{10}$
Zinc	Zn	30	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$

Remark:

Argon (Ar; Z = 18): $1s^2 2s^2 2p^6 3s^2 3p^6$

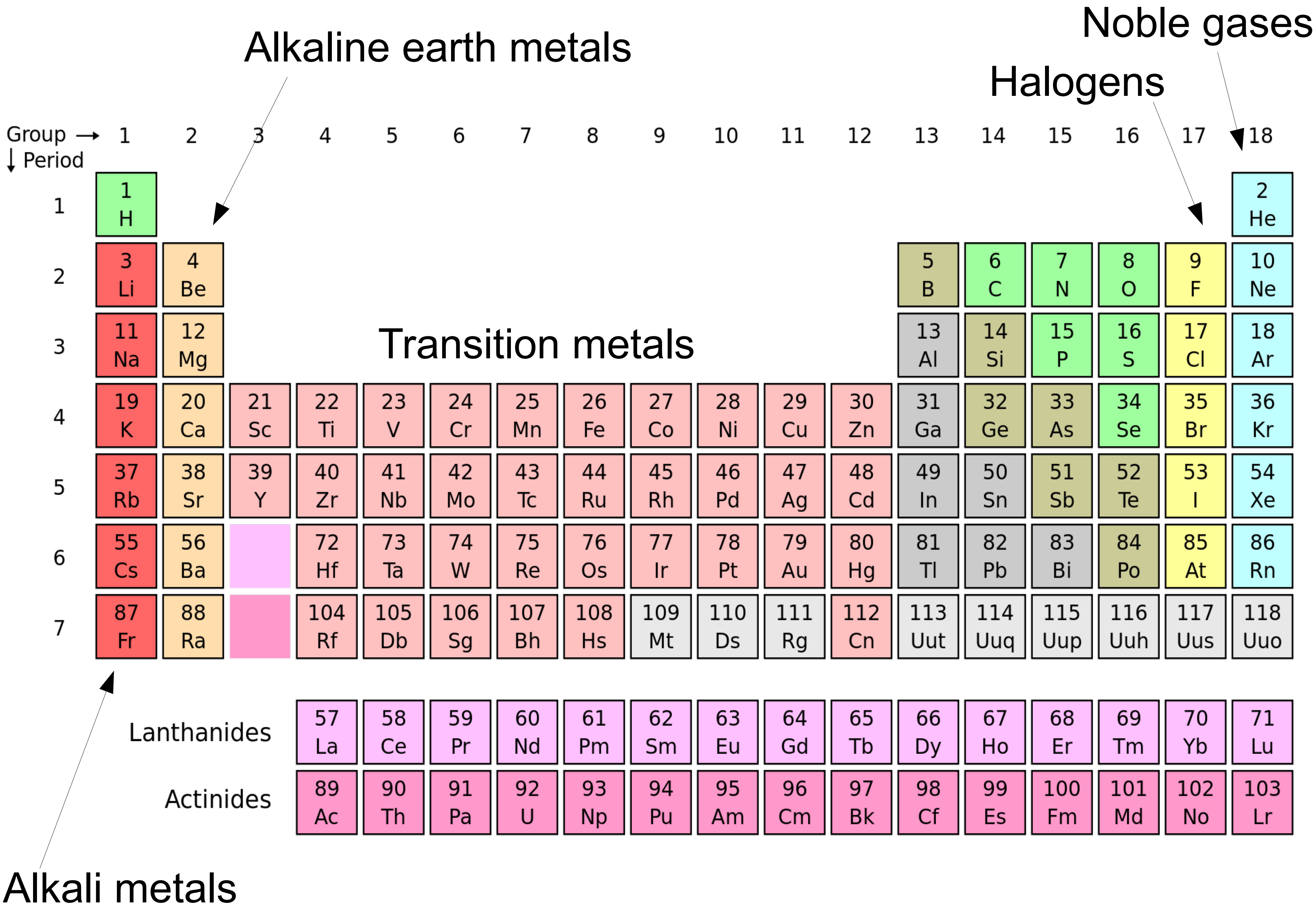
Potassium (K; Z = 19): $1s^2 2s^2 2p^6 3s^2 3p^6 4s$

(the electron goes to $4s$ state instead of $3d$ state because the energy is lower)

Calcium (Ca; Z = 20): $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

For $Z = 21 \longrightarrow 30$: one or two electrons in the $4s$ subshell and increasing number in the $3d$ subshell (they form the first transition series)

For $Z = 57 \longrightarrow 71$: one or two electrons in the $6s$ subshell but only partially filled $4f$ and $5d$ subshells



Noble gases

Alkaline earth metals

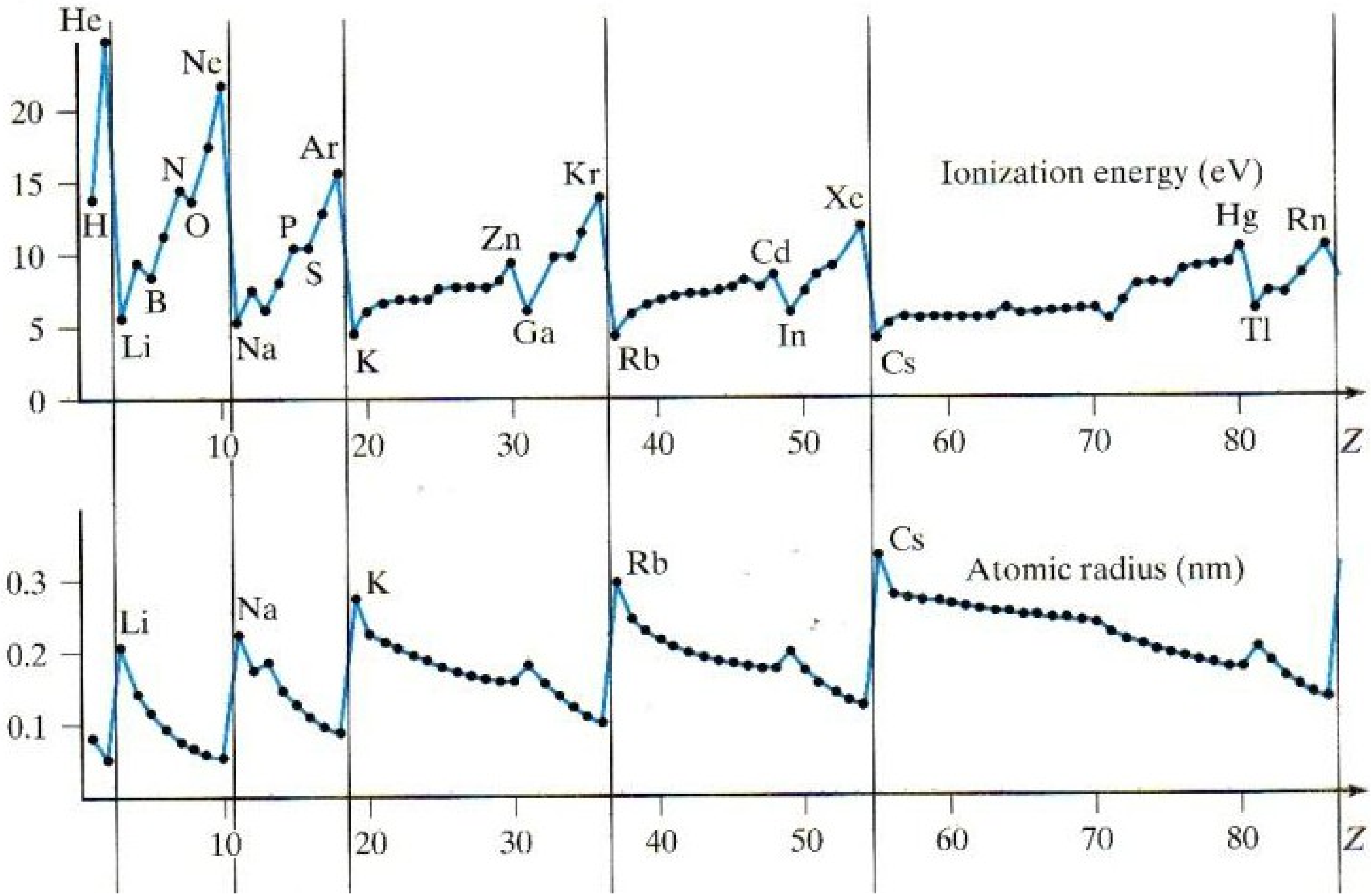
Halogens

Transition metals

Group → ↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
Lanthanides				57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides				89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

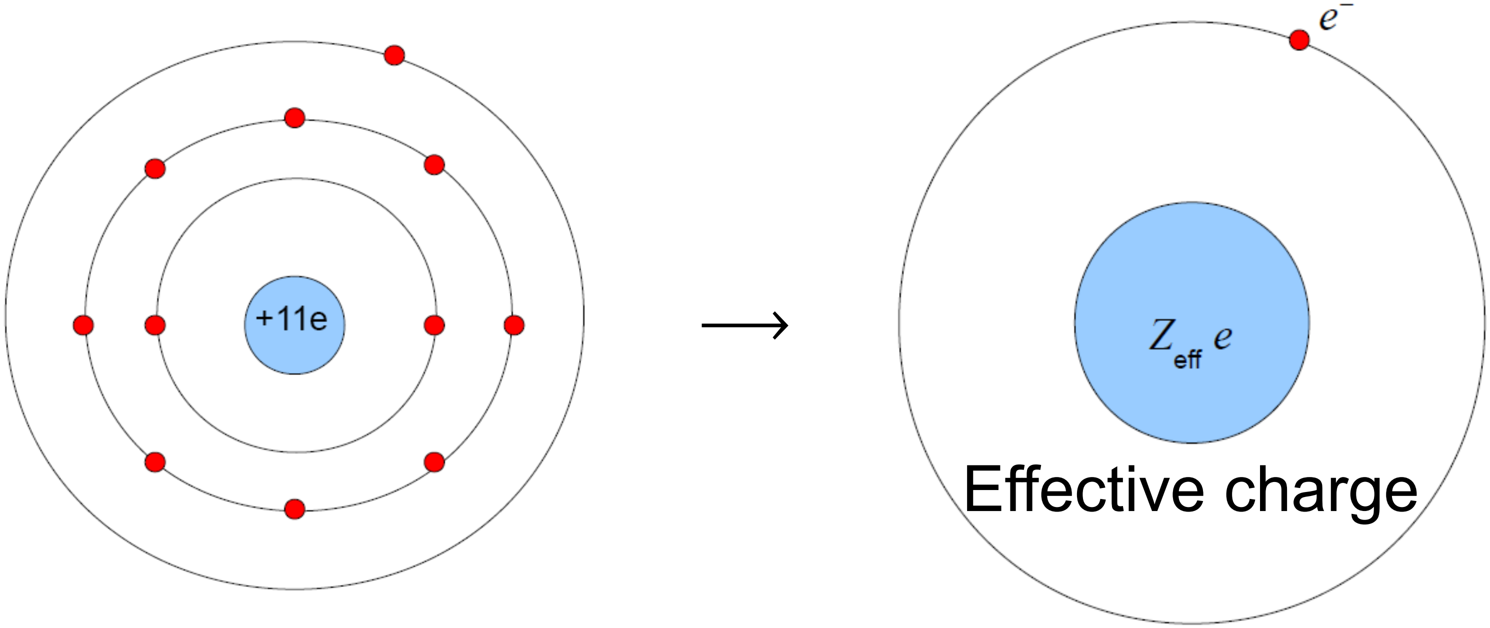
Alkali metals

Evidence for atomic shells:



- ***Screening***

Sodium (Na; Z = 11):



The charge of the nucleus is screened by the inner electrons.

$$\boxed{E_n = -\frac{Z_{\text{eff}}^2}{n^2}\left(13.6\ \text{eV}\right)}$$

(Energy levels with screening)

Example: The measured energy of a 3*s* state of Na = −5.138 eV

$$E_n = -\frac{Z_{\text{eff}}^2}{n^2}\left(13.6\ \text{eV}\right)$$

=> $$Z_{\text{eff}}^2 = -\frac{3^2\left(-5.138\ \text{eV}\right)}{\left(13.6\ \text{eV}\right)}$$

$$Z_{\text{eff}} = 1.84$$

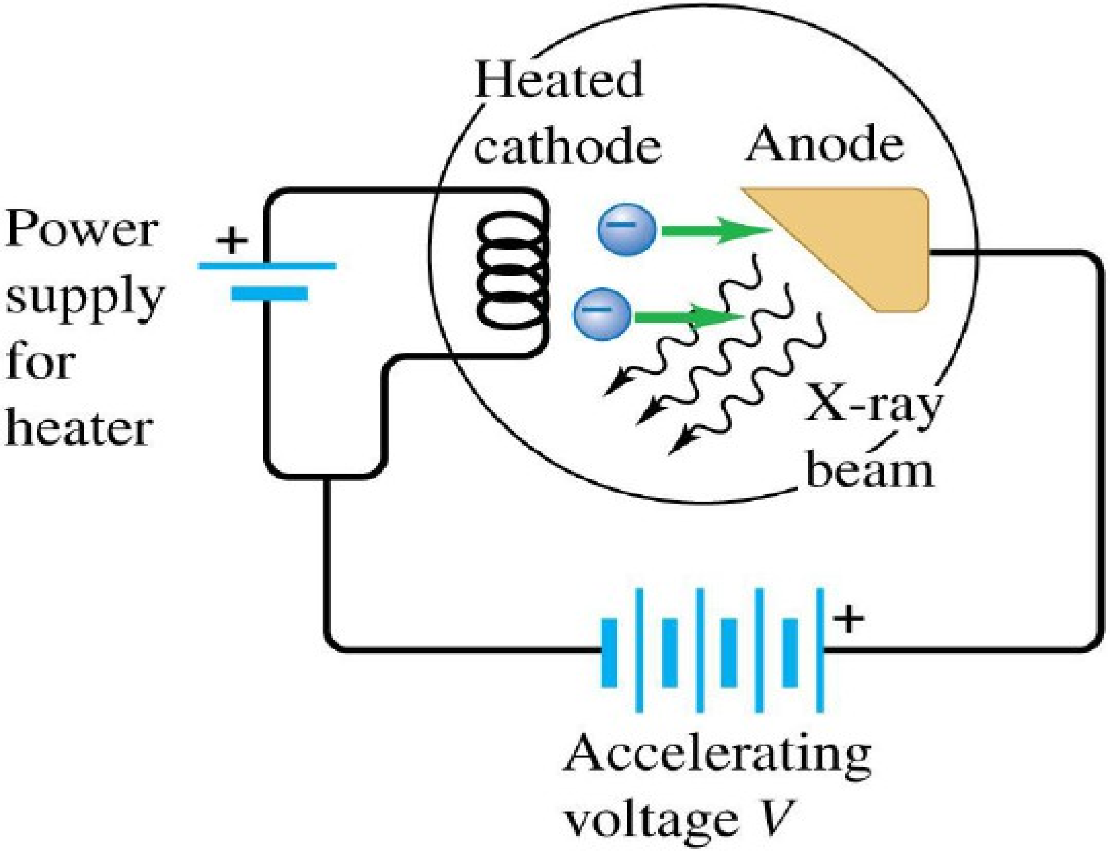
The effective charge attracting a 3*s* electron is 1.84 e

9.5 X-Ray Spectra

- ***X-Ray Production***

X-rays were first produced in 1895 by W. Röntgen

Typical wavelength: ~ 10^{-12} to 10^{-9} m



Two distinct processes are involved in X-ray emission:

1. Bremsstrahlung (German for "braking radiation")
   Electrons are slowed down or stopped by the target.

$$\boxed{eV = hf_{\max} = \frac{hc}{\lambda_{\min}}}$$

K.E. of the electron

Max. energy of a X-ray photon

2. The second process gives peaks in the X-ray spectrum at characteristic frequencies that depend on the target material.

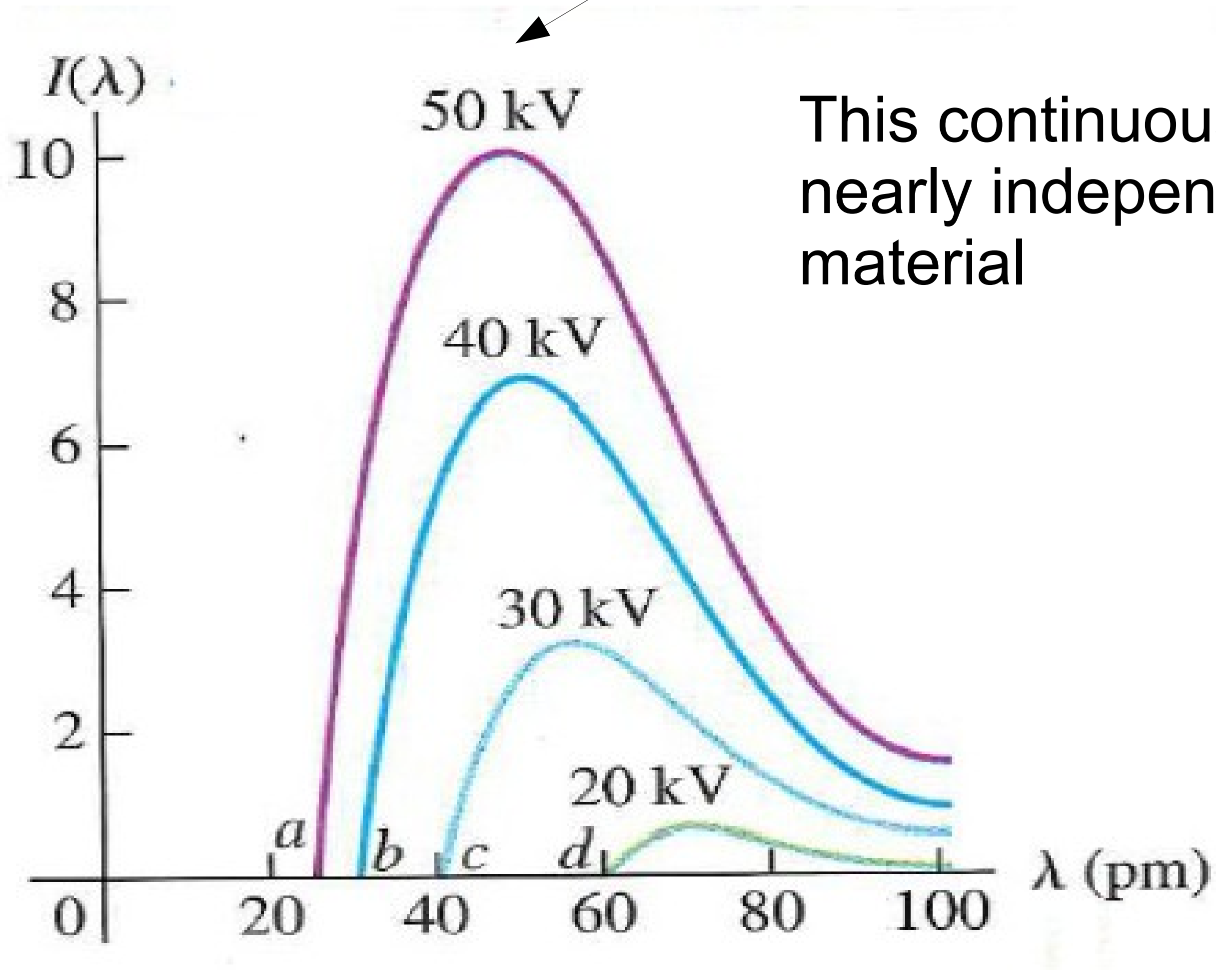
   Electron's energy is transferred to excite atoms.
   X-ray may be emitted when the atoms decay back to the ground state.

• ***X-Ray Spectra***

Continuous spectrum of X-ray produced by a tungsten target:

X-ray intensity
(per unit wavelength)

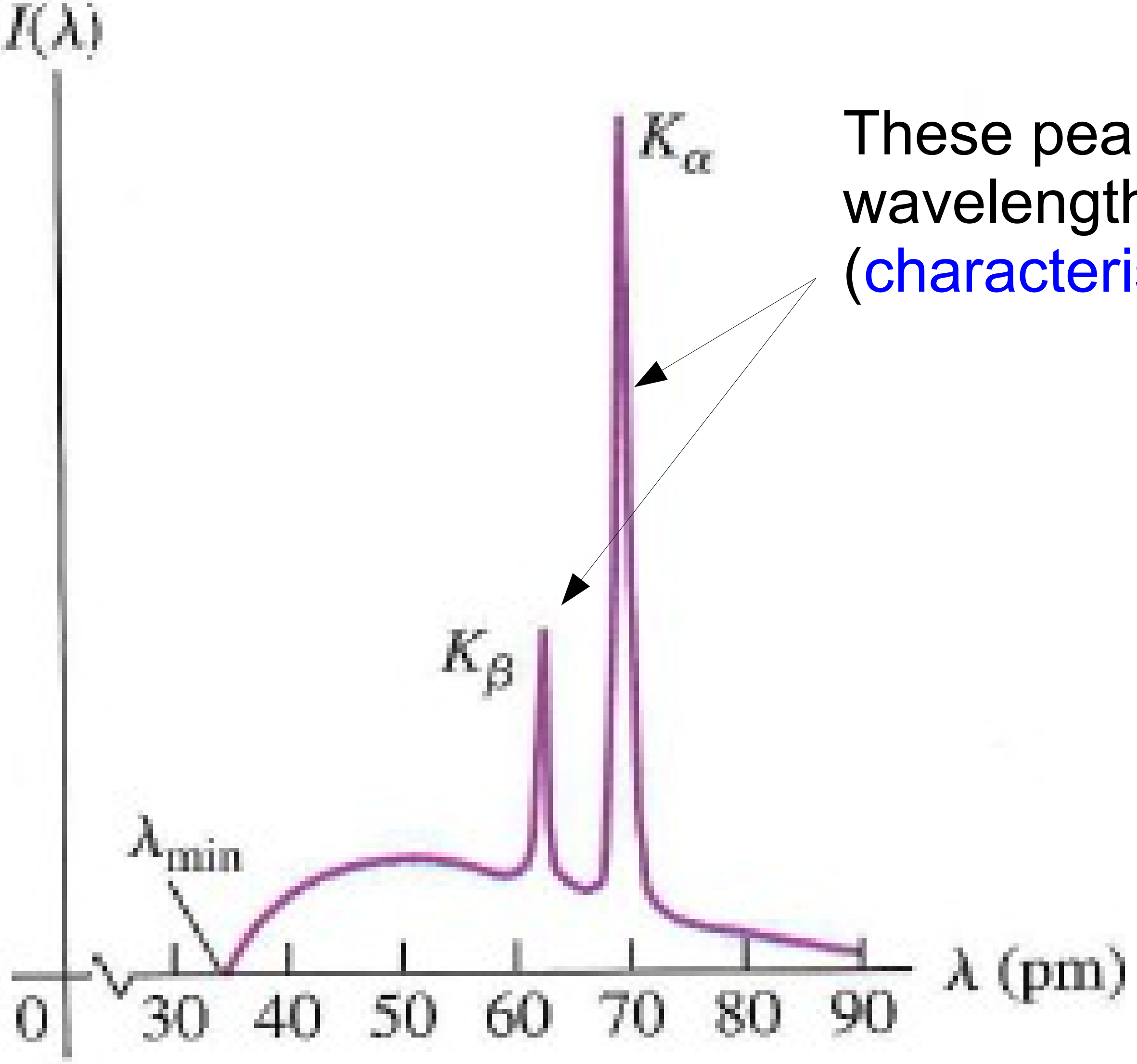
Voltage V



This continuous spectrum is nearly independent of the target material

1 pm = 10^{-12} m

Experiments also found sharp peaks superimposed on the continuous spectrum:



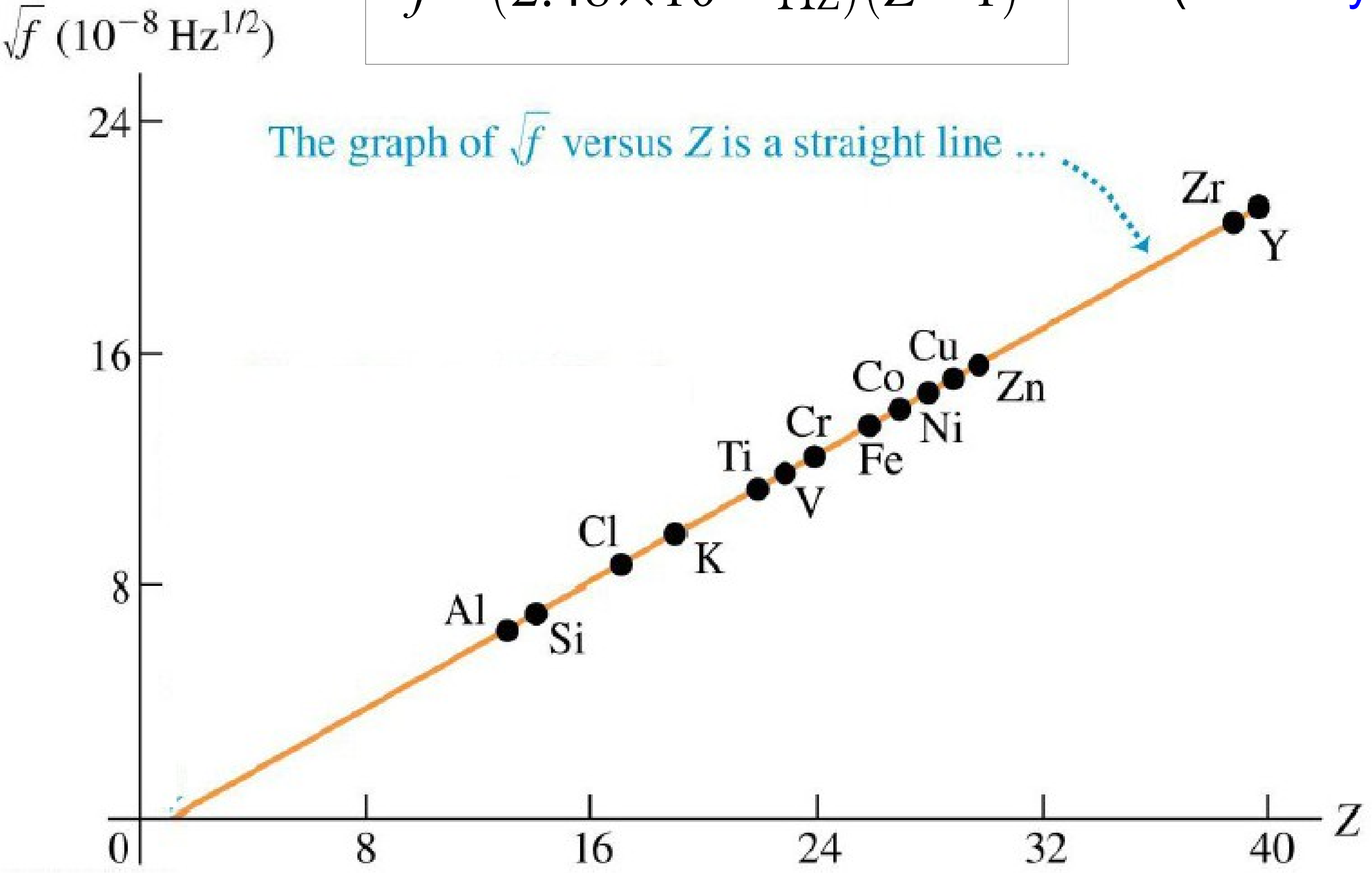
These peaks are at different wavelengths for different elements (characteristic X-ray spectrum)

• ***Moseley's Law and Atomic Energy Levels***

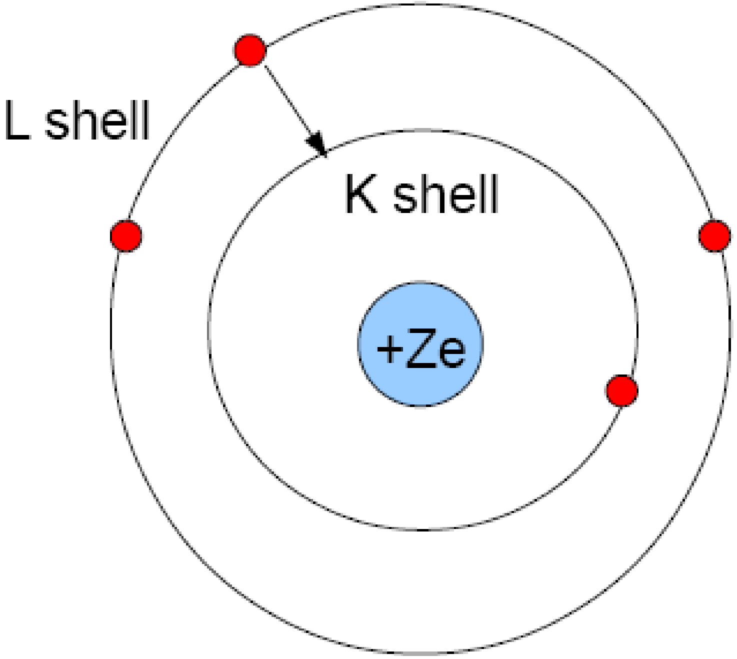
In 1913, Moseley found that the frequency of the K_α line satisfies :

$$f = (2.48\times10^{15}\ \text{Hz})(Z-1)^2$$

(Moseley's law)



K_α X-ray photon is emitted when an L-shell (n=2) electron drops down to fill a hole in the K shell (n=1):



Screening => initial energy $E_i \approx \frac{(Z-1)^2}{2^2}(13.6\ \text{eV})$

Final energy $E_f \approx \frac{(Z-1)^2}{1^2}(13.6\ \text{eV})$

Energy of K_α X-ray photon:

$$E_{\text{photon}} = E_i - E_f \approx (Z-1)^2 (10.2\ \text{eV})$$

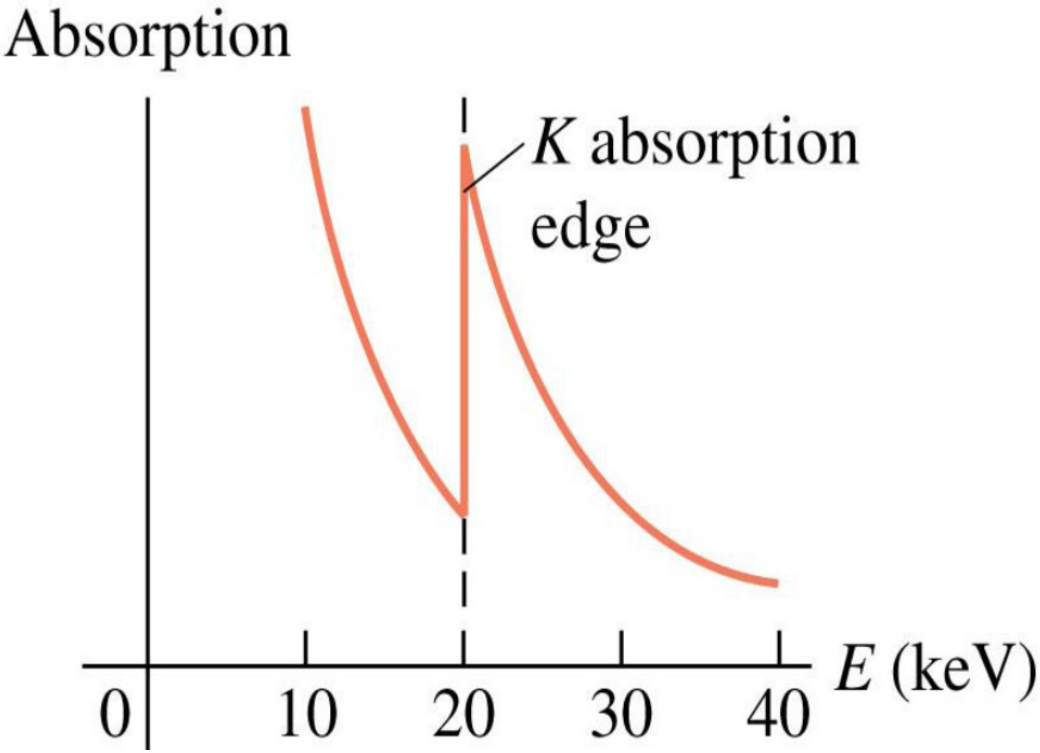
=> Frequency $f = \dfrac{E_{\text{photon}}}{h} = (2.47 \times 10^{15}\ \text{Hz})(Z-1)^2$

Remark: K series

K_α line: L shell (n=2) $\longrightarrow$ K shell
K_β line: M shell (n=3) $\longrightarrow$ K shell
K_γ line: N shell (n=4) $\longrightarrow$ K shell

- ***X-Ray Absorption Spectra***

A beam of X-ray is passed through a slab of molybdenum:



Energy of the X-ray photons

K absorption edge:
Photons with energy above this value can excite an electron from the K shell into an empty state.