Announcements

- Mid-term exam: 01/28, Tue, in class
  - Chapters 7 and 8
  - Open book and open lecture notes but no personal notes
  - More conceptual
  - simple calculations if any.
  - Review session, , Friday, room , pm
  - Change in office hours? Moving Monday to?

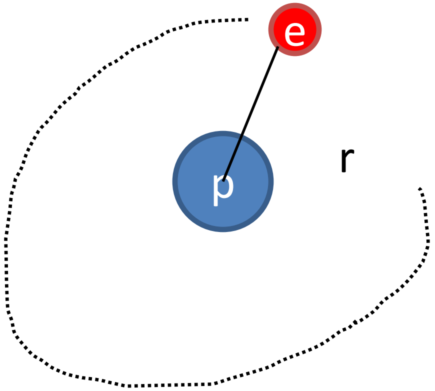
Lecture 5 Topics

- Hydrogen like atoms
- Connection to Hydrogen Spectra
- Why orbital angular momentum is not enough?
- Spin angular momentum
- Four quantum numbers
- Total angular momentum
- LS coupling
- Wave function for a system of particles
  - Identical particles
  - Exclusion principle for fermions
- Multi-electron atoms
  - Energy levels by n
  - Energy levels by l at a given n
  - Energy levels by electron symmetric and antisymmetric configurations at a given l and n

Hydrogen atom

- Potential created by Coulomb interactions between electron (-*e*) and proton (+*e*)

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



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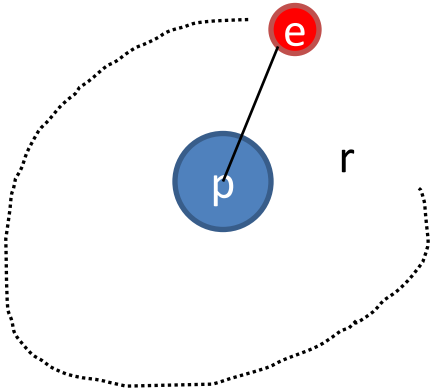


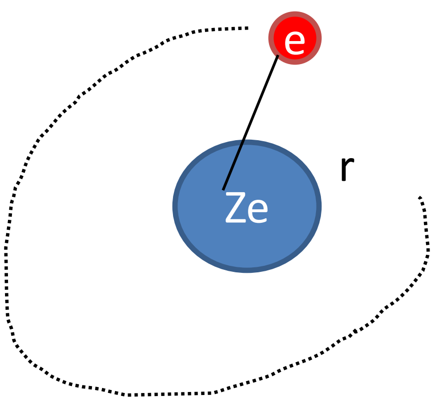
$$\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi) = R_{n,l}\Theta_{l,m_l}\Phi_{m_l}$$

$$\text{where } \Theta_{l,m_l}\Phi_{m_l} = \mathbf{Y}_l^{m_l} \text{ (Spherical harmonics)}$$

- Principal quantum number, $n = 1, 2, 3, \ldots$
- Orbital quantum number, $l = 0, 1, 2, \ldots (n-1)$ where l =1(*s*), =2(*p*), =3(*d*), =4 (*f*), *etc.*
- Magnetic quantum number, $m_l = 0, \pm 1, \pm 2, \ldots \pm l$

Hydrogen-like ions

- Potential created by Coulomb interactions between electron (-*e*) and positively-charged nucleus (+Z*e*)



$$U(r) = \frac{1}{4\pi\varepsilon_0}\frac{-e^2}{r} \longrightarrow U(r) = -\frac{1}{4\pi\varepsilon_0}\frac{e \cdot Ze}{r} = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$$

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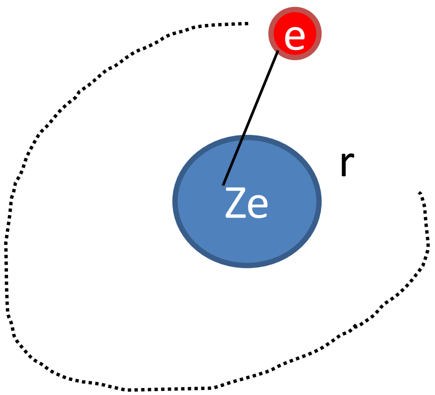

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Examples: He^{+}, Li^{++}, Be^{+++}

What changes to known hydrogen atom solutions?

Three quantum numbers

- Principal quantum number: *n*

$$E_n = -\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2}\left(\frac{1}{n^2}\right) = -\left(\frac{e^2}{8\pi\varepsilon_0}\right)\left(\frac{me^2}{4\pi\varepsilon_0\hbar^2}\right)\left(\frac{1}{n^2}\right) =$$

$$-\left(\frac{e^2}{8\pi\varepsilon_0 a_0}\right)\left(\frac{1}{n^2}\right) = -13.6\ eV\left(\frac{1}{n^2}\right)$$

$$L^2 = l(l+1)\hbar^2$$

$$L_z = m_l\hbar$$

- Orbital quantum number: $l = 0, 1, 2, \ldots (n\text{-}1)$
- Magnetic quantum number: $m_l = 0, \pm 1, \pm 2, \ldots \pm l$

$$\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi) = R_{n,l}\Theta_{l,m_l}\Phi_{m_l}$$

where $\Theta_{l,m_l}\Phi_{m_l} = \mathbf{Y}_l^{m_l}$ (Spherical harmonics)

$$\text{Bohr radius } a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2} \qquad (= 0.529\ A)$$

The most probable r vale for the orbital *l* = *n* – 1

$r_{n,\ l=n-1\ (most\ probable)\ hydrogen} = n^2 a_0$

$r_{n,\ l=n-1\ (most\ probable)\ hydrogen} =$

$$E_{n\ hydrogen} = -\frac{m(e^2)e^2}{32\pi^2\varepsilon_0^2\hbar^2}\left(\frac{1}{n^2}\right) = -\left(\frac{e^2}{8\pi\varepsilon_0}\right)\left(\frac{me^2}{4\pi\varepsilon_0\hbar^2}\right)\left(\frac{1}{n^2}\right) = -\left(\frac{e^2}{8\pi\varepsilon_0 a_0}\right)\left(\frac{1}{n^2}\right) = -13.6\ eV\left(\frac{1}{n^2}\right)$$

$$E_{n\ hydrogenlike} =$$

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Bound energies are deeper by z^2 , the orbital most probably radii smaller by 1/z

Hydrogen atom spectral lines

$$E_n = -\frac{me^4}{2(4\pi\varepsilon_0)^2\hbar^2}\frac{1}{n^2} = -\frac{e^2}{8\pi\varepsilon_0}\ \frac{me^2}{4\pi\varepsilon_0\hbar^2}\frac{1}{n^2} = -\frac{e^2}{8\pi\varepsilon_0\, a_0}\ \frac{1}{n^2} = (-13.6\ \text{eV})\ \frac{1}{n^2}$$

$$\text{Where } a_0(Bohr\ Radius) = \frac{me^2}{4\pi\varepsilon_0\hbar^2} = 0.0529\ \text{nm} = 0.529\ \text{A}$$

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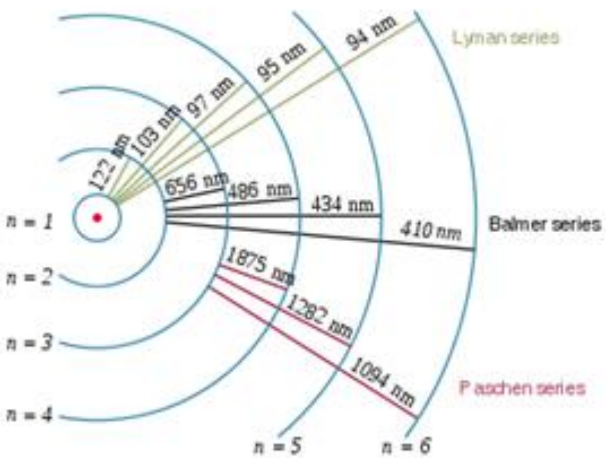

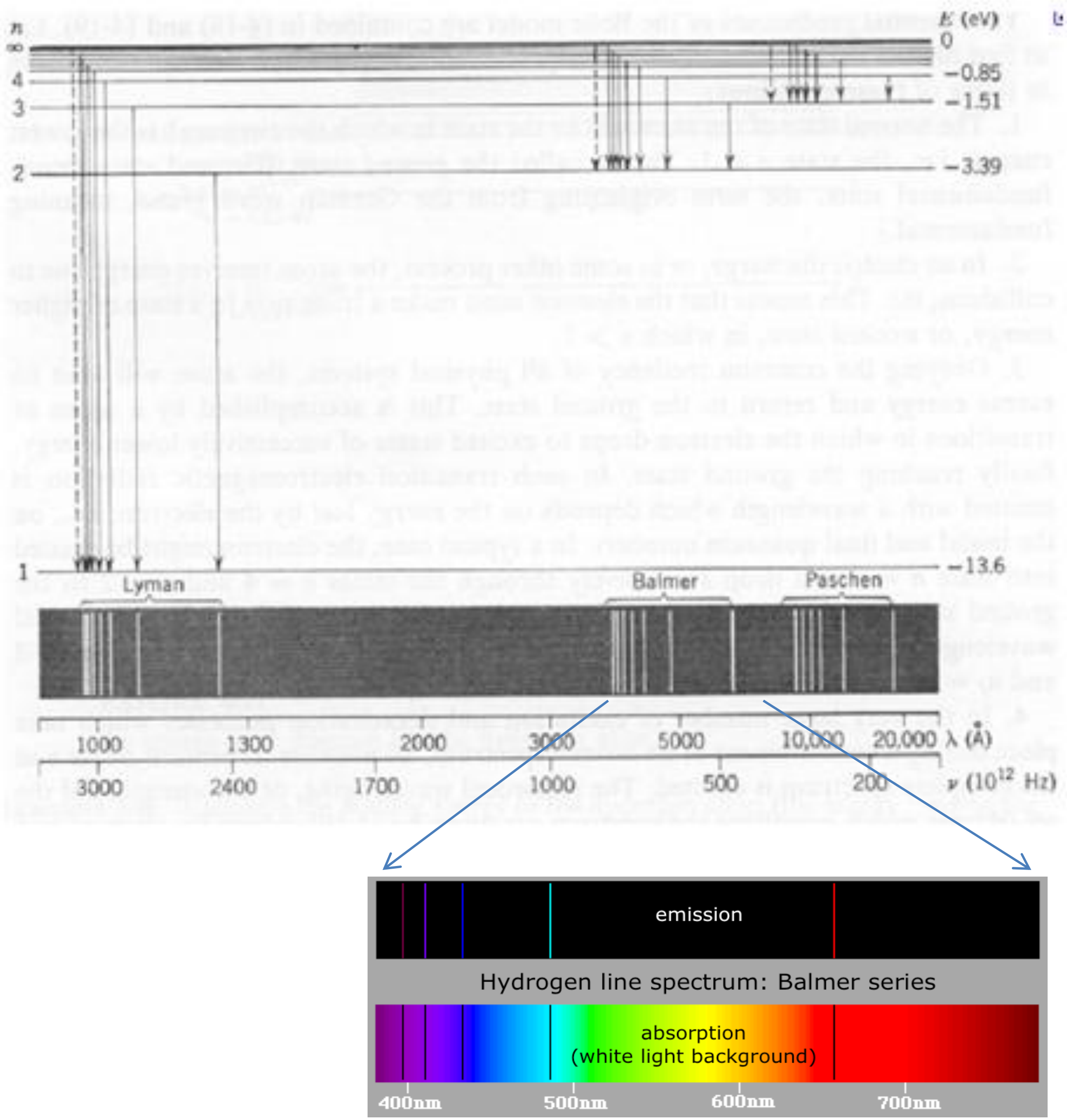

n
∞
4
3
2
1
E (eV)
0
−0.85
−1.51
−3.39
−13.6
Lyman
Balmer
Paschen
1000
1300
2000
3000
5000
10,000
20,000
λ (Å)
3000
2400
1700
1000
500
200
ν (10^{12} Hz)
emission
Hydrogen line spectrum: Balmer series
absorption
(white light background)
400nm
500nm
600nm
700nm

Hydrogen atom spectral lines

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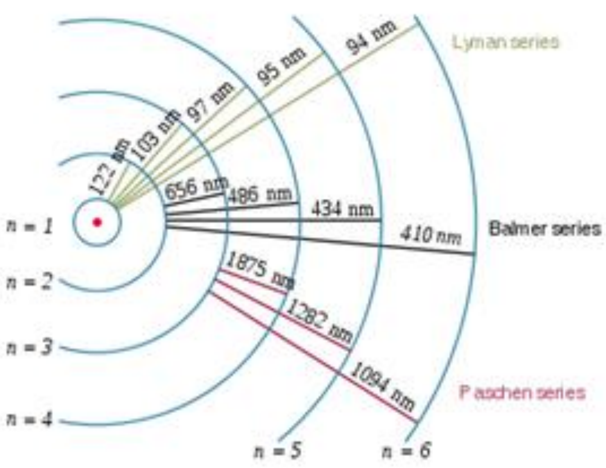
$$E_{photon} = \frac{hc}{\lambda} = E_{initial} - E_{final} = -\frac{me^4}{2(4\pi\varepsilon_0)^2\hbar^2}\left(\frac{1}{n_{final}^2} - \frac{1}{n_{initial}^2}\right)$$

$$\frac{1}{\lambda} = \frac{me^4}{2(4\pi\varepsilon_0)^2\hbar^2 hc}\left(\frac{1}{n_{final}^2} - \frac{1}{n_{initial}^2}\right) = 1.097\ x\ 10^7\ m^{-1}\left(\frac{1}{n_{final}^2} - \frac{1}{n_{initial}^2}\right)$$



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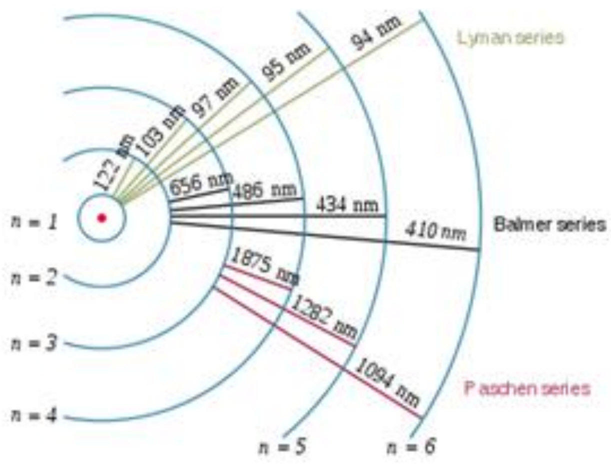


- When $n_{final} = 1$, *Lyman Series* (discovered between 1905-1914)
- When $n_{final} = 2$, *Balmer Series* (in 1885)
- When $n_{final} = 3$, *Pachen Series* (in 1908)
- When $n_{final} = 4$, *Brackett Series* (in 1922)
- When $n_{final} = 5$, *Pfund Series* (in 1924)
- When $n_{final} = 6$, *Humphreys Series* (in 1953)

Lyman Series (n_{final} = 1)

$n_{initial}$	λ (nm)
2	122
3	103
4	97.3
5	95.0
6	93.8
∞	91.2

Balmer Series (n_{final} = 2)

$n_{initial}$	λ (nm)
3	656
4	486
5	434
6	410
7	397
∞	365

Pachen Series ((n_{final} = 3)

$n_{initial}$	λ (nm)
4	1870
5	1280
6	1090
7	1020
8	954
∞	820

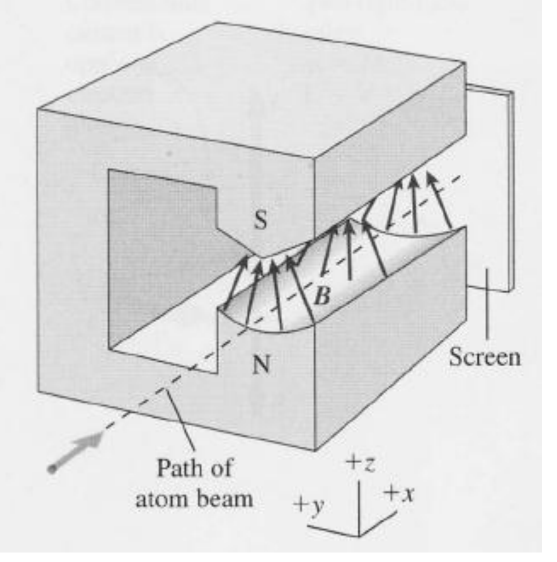
Degeneracies

n	l	m_l	E_n(eV)	$\|L\|$	L_z	ψ_{n,l,m_l} =	$R_{n,l}\mathbf{Y}_l^{m_l}$	degeneracies	Orbital name
1	0	0	-13.6	0	0	ψ_{100}	$R_{10}\mathbf{Y}_0^0$	Non-degenerate	1s
2	0	0	-3.40	0	0	ψ_{200}	$R_{20}\mathbf{Y}_0^0$	4 (=2^2)	2s
	1	-1		$\sqrt{2}\hbar$	$-\hbar$	ψ_{21-1}	$R_{21}\mathbf{Y}_1^{-1}$		2p
		0			0	ψ_{210}	$R_{21}\mathbf{Y}_1^0$		
		1			$+\hbar$	ψ_{211}	$R_{21}\mathbf{Y}_1^{+1}$		
3	0	0	-1.51	0	0	ψ_{300}	$R_{30}\mathbf{Y}_0^0$	9 (=3^2)	3s
	1	-1		$\sqrt{2}\hbar$	$-\hbar$	ψ_{31-1}	$R_{31}\mathbf{Y}_1^{-1}$		3p
		0			0	ψ_{310}	$R_{31}\mathbf{Y}_1^0$		
		1			$+\hbar$	ψ_{311}	$R_{31}\mathbf{Y}_1^1$		
	2	-2		$\sqrt{6}\hbar$	$-2\hbar$	ψ_{32-2}	$R_{32}\mathbf{Y}_2^{-2}$		3d
		--1			$-\hbar$	ψ_{32-1}	$R_{32}\mathbf{Y}_2^{-1}$		
		0			0	ψ_{320}	$R_{32}\mathbf{Y}_2^0$		
		1			$+\hbar$	ψ_{321}	$R_{32}\mathbf{Y}_2^1$		
		2			$+2\hbar$	ψ_{322}	$R_{32}\mathbf{Y}_2^2$		

Why not enough?

$$U = -\vec{\mu} \cdot \vec{B} = \left(\frac{e}{2m}\right) \vec{L} \cdot \vec{B} = \left(\frac{e}{2m}\right) L_z B_z$$

Since $\vec{\mu} = -\left(\frac{e}{2m}\right) \vec{L}$



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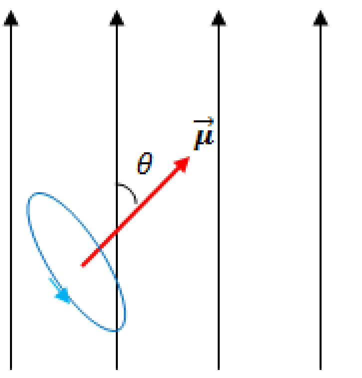

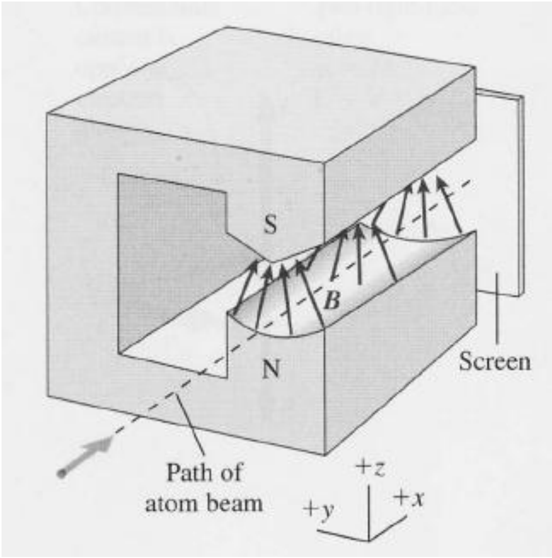

$$\mu = \frac{1}{2} q\, \mathbf{r} \times \mathbf{v} = -e\left(\frac{vr}{2}\right) = -\frac{eL}{2m}$$

Magnetic dipole moment

Why not enough?

$$U = -\vec{\mu}\cdot\vec{B} = \left(\frac{e}{2m}\right)\vec{L}\cdot\vec{B} = \left(\frac{e}{2m}\right)L_z B_z$$

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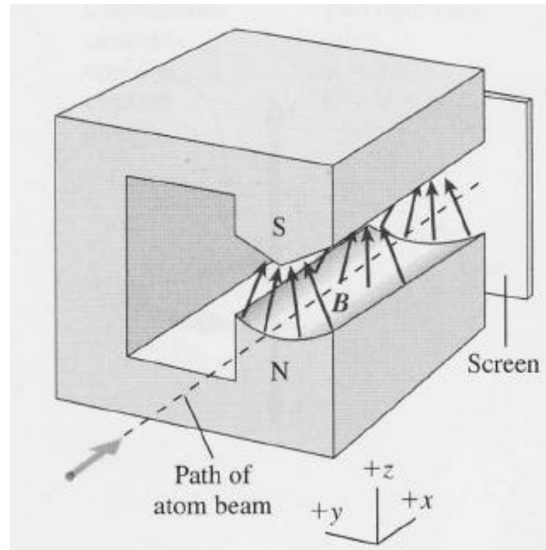

$$F = -\nabla\left(-\vec{\mu}\cdot\vec{B}\right) = -\left(\frac{e}{2m}\right)L_z\frac{\partial B_z}{\partial z}\hat{z} = -\left(\frac{e}{2m}\right)(m_l\hbar)\frac{\partial B_z}{\partial z}\hat{z}$$

$\vec{B} = B_z\hat{z}$ Since $L_z = m_l\hbar$

$$m_l = -l, \ldots, +l.$$

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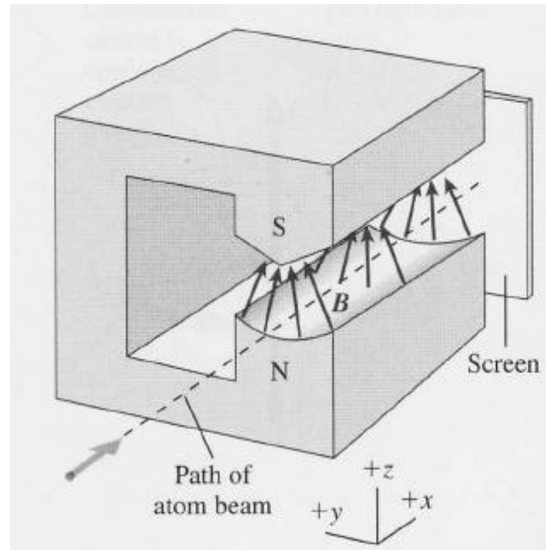

$\ell = 0$ expectation

$$F = -\nabla\left(-\vec{\mu} \cdot \vec{B}\right) = -\left(\frac{e}{2m}\right) L_z \frac{\partial B_z}{\partial z} \hat{z} = -\left(\frac{e}{2m}\right) (m_l \hbar) \frac{\partial B_z}{\partial z} \hat{z}$$

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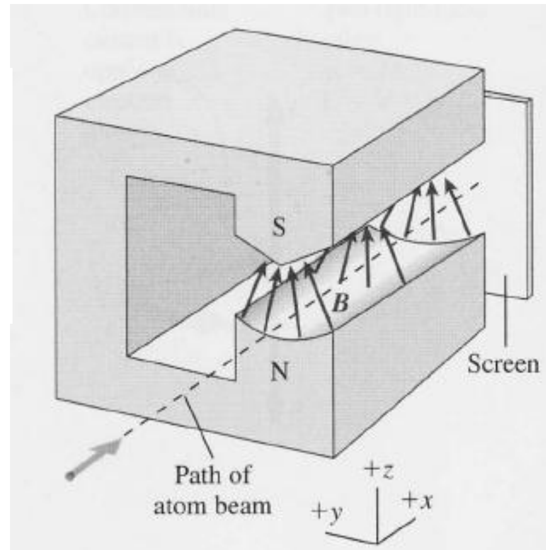

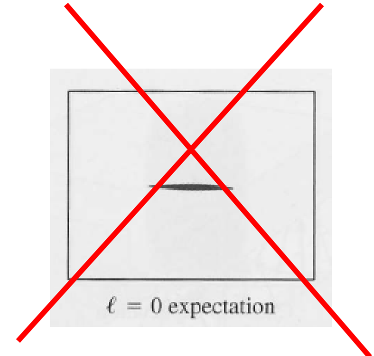

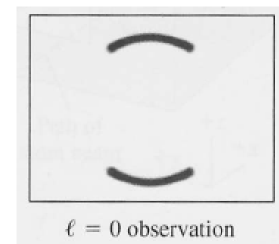

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Spin Angular Momentum

- Intrinsic property of a given particle
- Magnitude $|\vec{S}| = \sqrt{s(s+1)}\,\hbar$
- Direction $S_z = m_s \hbar$

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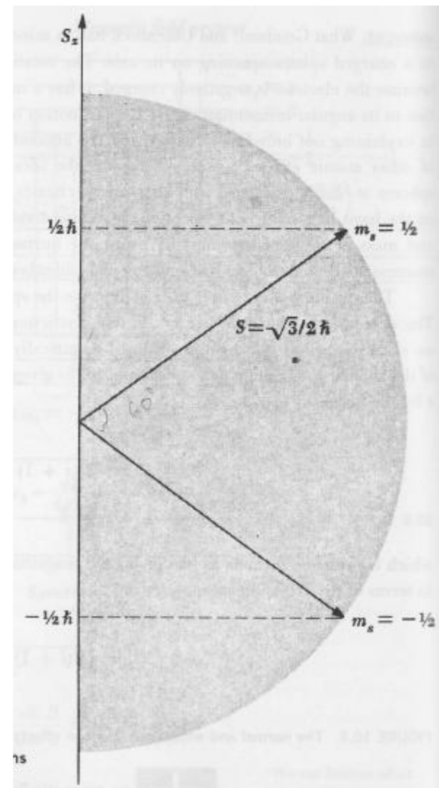
$$m_s = -s, -s+1, \ldots s-1, s$$



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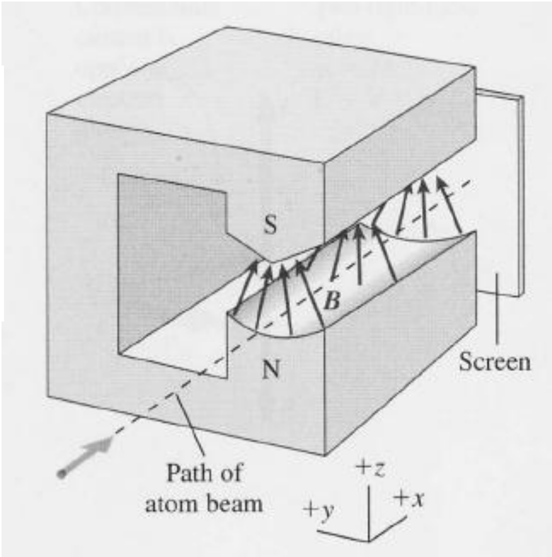
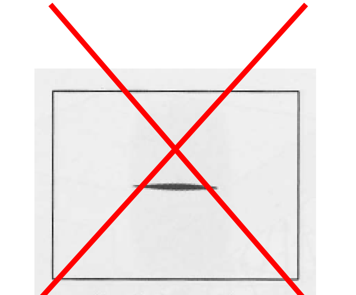
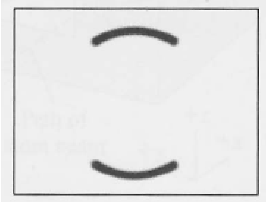
$$\vec{\mu}_s = -\frac{e}{2m}\vec{S}$$





$\ell = 0$ expectation



$\ell = 0$ observation

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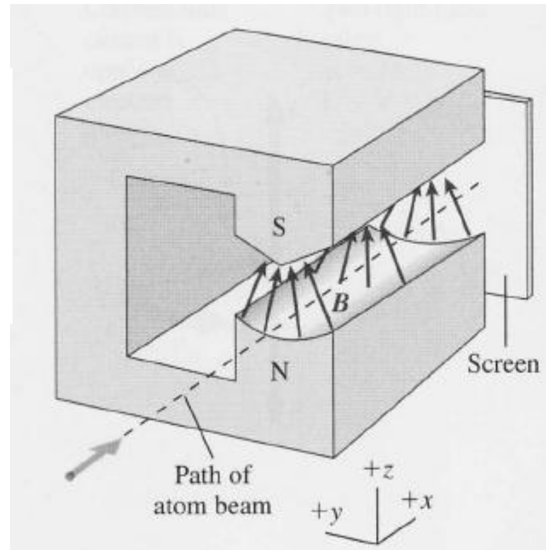
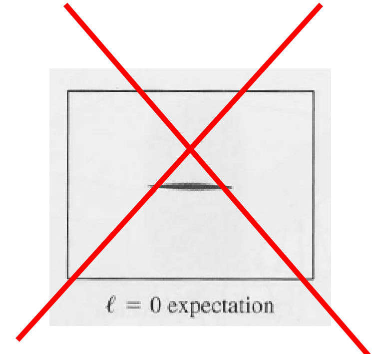
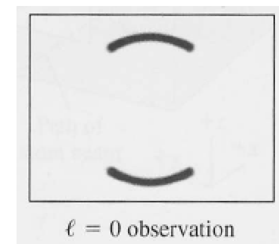
$$\vec{\mu}_s = -\frac{e}{2m}\vec{S}$$







$$F = -\nabla\left(-\vec{\mu} \cdot \vec{B}\right) = -\left(\frac{e}{2m}\right) S_z \frac{\partial B_z}{\partial z}\hat{z} = -\left(\frac{e}{m}\right)(m_s \hbar)\frac{\partial B_z}{\partial z}\hat{z}$$

$$m_s = \pm\frac{1}{2}$$

Two lines! For *l* = 0

Four quantum numbers

- Principal quantum number: *n*

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

$$|\vec{L}| = \sqrt{l(l+1)}\hbar$$
$$L_z = m_l\hbar$$

$$|\vec{S}| = \sqrt{s(s+1)}\hbar$$
$$S_z = m_s\hbar$$

- Orbital quantum number: $l = 0, 1, 2, \ldots (n\text{-}1)$
- Magnetic quantum number: $m_l = 0, \pm 1, \pm 2, \ldots \pm l$
- Spin quantum number: $m_s = -s, -s+1, \ldots s-1, s$

Wave functions

$$\psi_{n,l,m_l,m_s} = \psi_{n,l,m_l}(r,\theta,\phi)m_s$$

$$\psi_{n,l,m_l,+\frac{1}{2}} = \psi_{n,l,m_l}(r,\theta,\phi)\uparrow$$

$$\psi_{n,l,m_l,-\frac{1}{2}} = \psi_{n,l,m_l}(r,\theta,\phi)\downarrow$$

- Spin should increase the degeneracy when no magnetic field is present n^2 to $2n^2$
- With the magnetic field, degeneracy can be broken due to LS coupling.

Spin-Orbit Interaction

- In a weak external magnetic field, we observe the combined angular momentum

Total Angular Momentum ($\vec{J}$) $\vec{J} = \vec{L} + \vec{S}$

$$\overrightarrow{|J|} = \sqrt{j(j+1)}\hbar$$

$$J_z = m_j\hbar$$

$$J_z = L_z \pm S_z$$

$$m_j\hbar = m_l\hbar + m_s\hbar$$

$where\ j = |l-s|, |l-s|+1, \ldots |l+s|-1, |l+s|$

where $m_j = -j, -j+1, \ldots, j-1, j$

$$|\vec{J}| = \sqrt{j(j+1)}\hbar \qquad \text{where } j = |l-s|, |l-s|+1, \ldots |l+s|-1, |l+s|$$
$$J_z = m_j\hbar \qquad \text{where } m_j = -j, -j+1, \ldots, j-1, j$$
$$J_z = L_z \pm S_z$$
$$m_j\hbar = m_l\hbar + m_s\hbar$$

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

$$|\vec{S}| = \sqrt{s(s+1)}\hbar \qquad \text{where } s \text{ is a number intrinsic to a given particle}$$
$$S_z = m_s\hbar \qquad \text{where } m_s = -s, -s+1, \ldots s-1, s$$

Exercise *l*=2, *s*=1/2

- In a weak external magnetic field
  - Possible j values
  - Total angular momentum magnitude for each j
  - The number of possible states for each j

$$|\vec{J}| = \sqrt{j(j+1)}\hbar \qquad where\ j = |l-s|, |l-s|+1, \dots |l+s|-1, |l+s|$$
$$J_z = m_j\hbar \qquad \text{where } m_j = -j, -j+1, \dots, j-1, j$$
$$J_z = L_z \pm S_z$$
$$m_j\hbar = m_l\hbar + m_s\hbar$$

Exercise *l*=2, *s*=1/2

- In a weak external magnetic field
  - Possible j values
  - Total angular momentum magnitude for each j
  - The number of possible states for each j

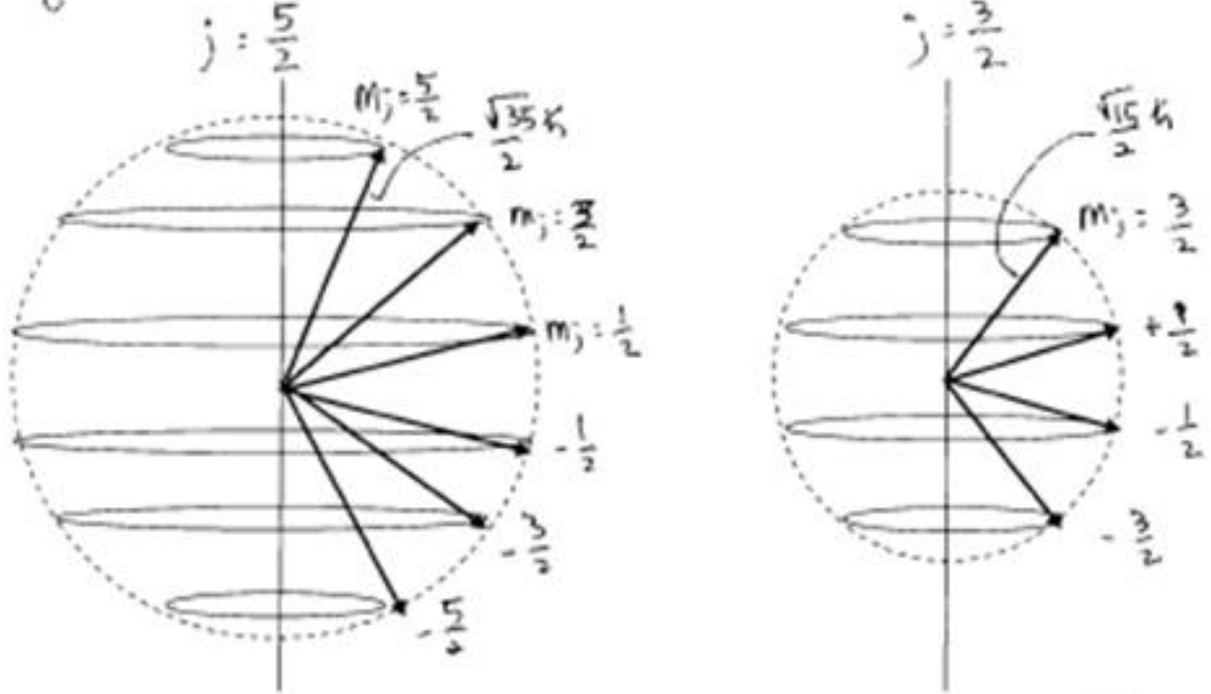
for $j = \frac{5}{2} \rightarrow m_j = -\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}, +\frac{5}{2}$ $\quad |\overrightarrow{J}| = \sqrt{j(j+1)}\hbar = \sqrt{\frac{5}{2}\frac{7}{2}}\hbar = \frac{\sqrt{35}}{2}\hbar$

6 possible states $(2j+1)$

for $j = \frac{3}{2} \rightarrow m_j = -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}$ $\quad |\overrightarrow{J}| = \sqrt{j(j+1)}\hbar = \sqrt{\frac{3}{2}\frac{5}{2}}\hbar = \frac{\sqrt{15}}{2}\hbar \rightarrow$

4 possible states

- L.S coupling --

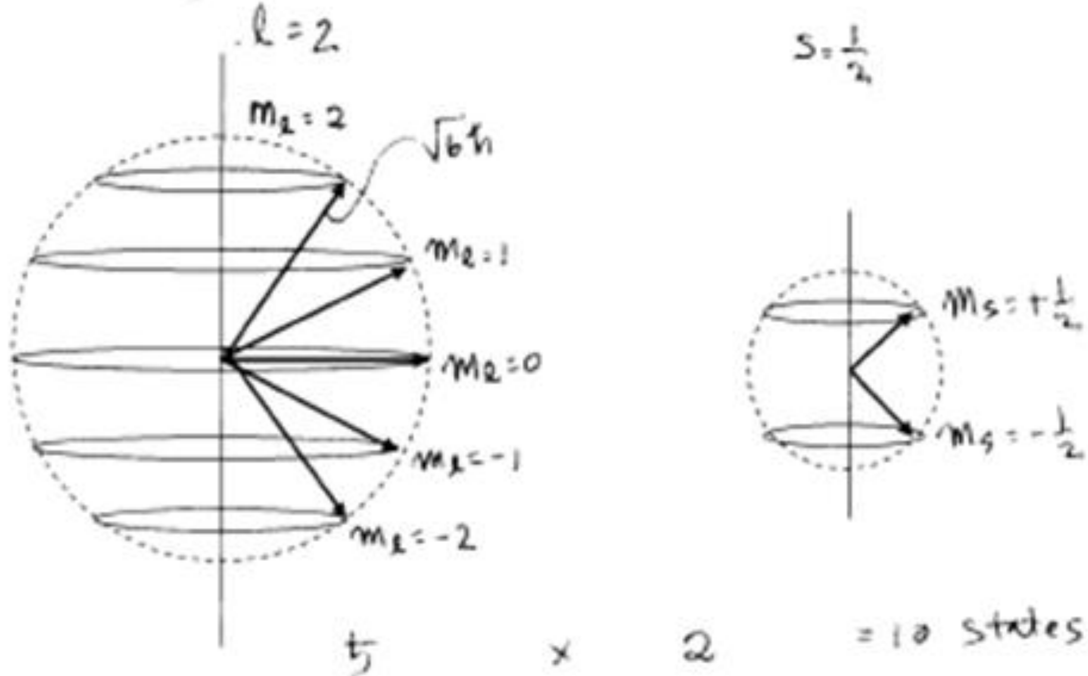


6 + 4 = 10 states

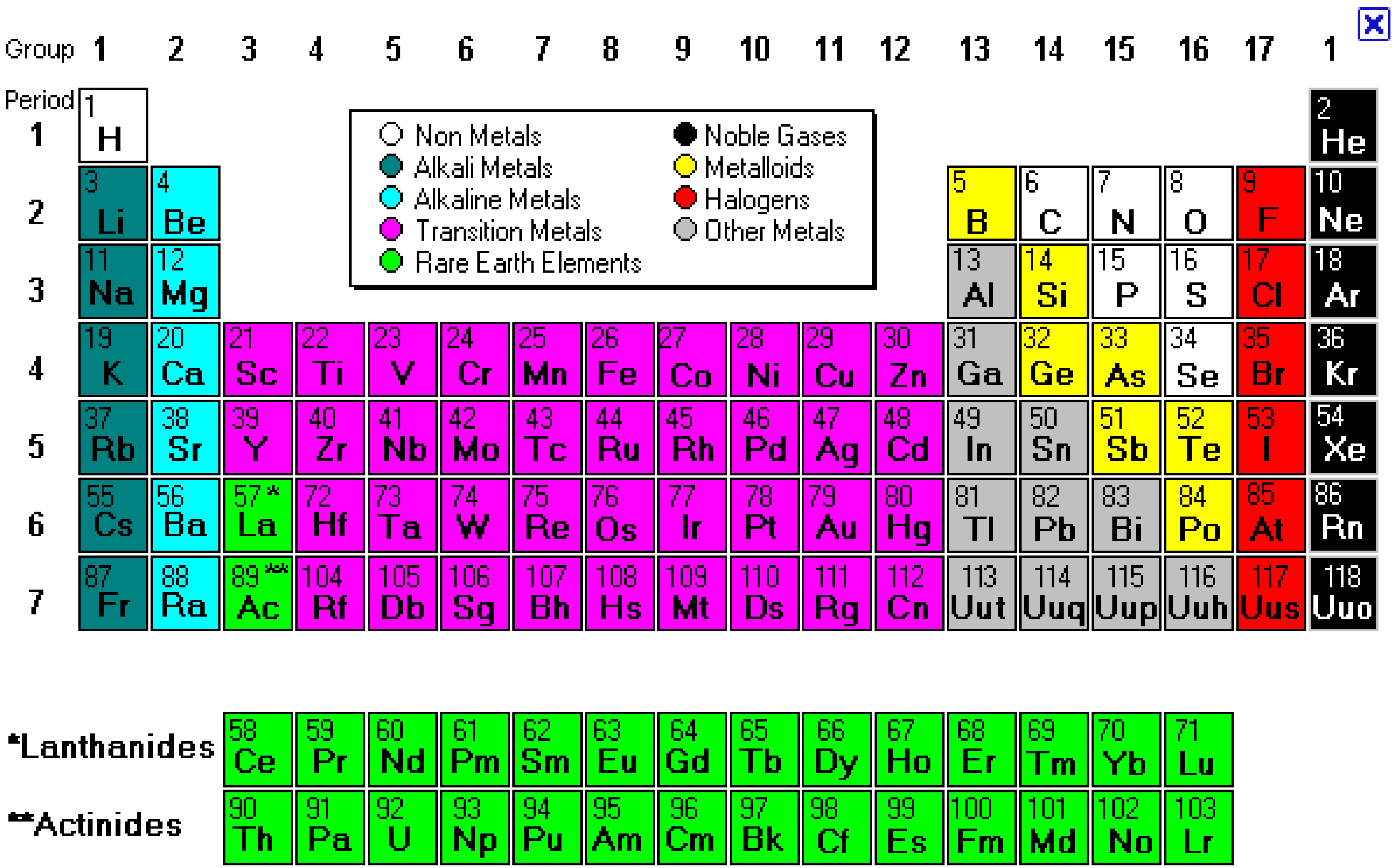
Exercise l=2, s=1/2

- In a strong external magnetic field
  - LS coupling breaks (LS coupling effect is very small)
  - L and S are independently quantized.

-separate-


$l = 2$
$m_l = 2$
$\sqrt{6}\hbar$
$m_l = 1$
$m_l = 0$
$m_l = -1$
$m_l = -2$
$s = \frac{1}{2}$
$m_s = +\frac{1}{2}$
$m_s = -\frac{1}{2}$
5 × 2 = 10 states

Periodic Table



What we know so far:

- Number of electrons in each atom
- Electrons should be in one of the orbitals determined by *n, l*, and m_l
- n limits what types of l orbitals an electron can occupy.
- Each l orbital has 2l+1 possible m_l states:
  - *s* orbital = 1
  - *p* orbital = 2 x 1 + 1 = 3
  - *d* orbital = 2 x 2 + 1 = 5
  - *f* orbital = 2 x 3 + 1 = 7
- Due to electron's spin where ½ and – ½ are possible, each m_l orbital can have two additional possible states.
- As a result, in each n, there are $2n^2$ possible states.

Questions

- How to construct a wave function with multi-electrons in an atom (wave function question)
- How to stack electrons across all possible orbitals? (energy question)
  - *n*
  - By *l* at a given *n*
  - By m_l at a given *l* and *n*