# Announcements

- Mid-term exam: 01/29, 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, , Monday 28, room , pm

# Lecture 5 Topics

- Most probable value r vs. expectation value r
- Invariance and conservations
- 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

# Most probable vs. expectation value

Expectation Value r $\langle r \rangle = \int_0^\infty r \cdot r^2 R_{n,l}(r)^2 dr$

Most probable r Value $\frac{dP(r)}{dr} = \frac{d r^2 R_{n,l}(r)^2}{dr} = 0$

# Most probable vs. expectation value

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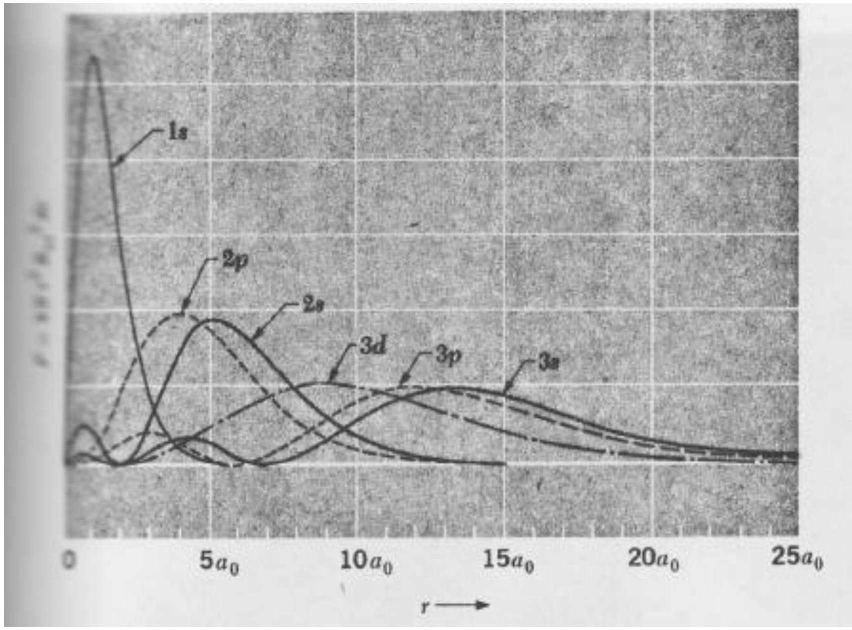
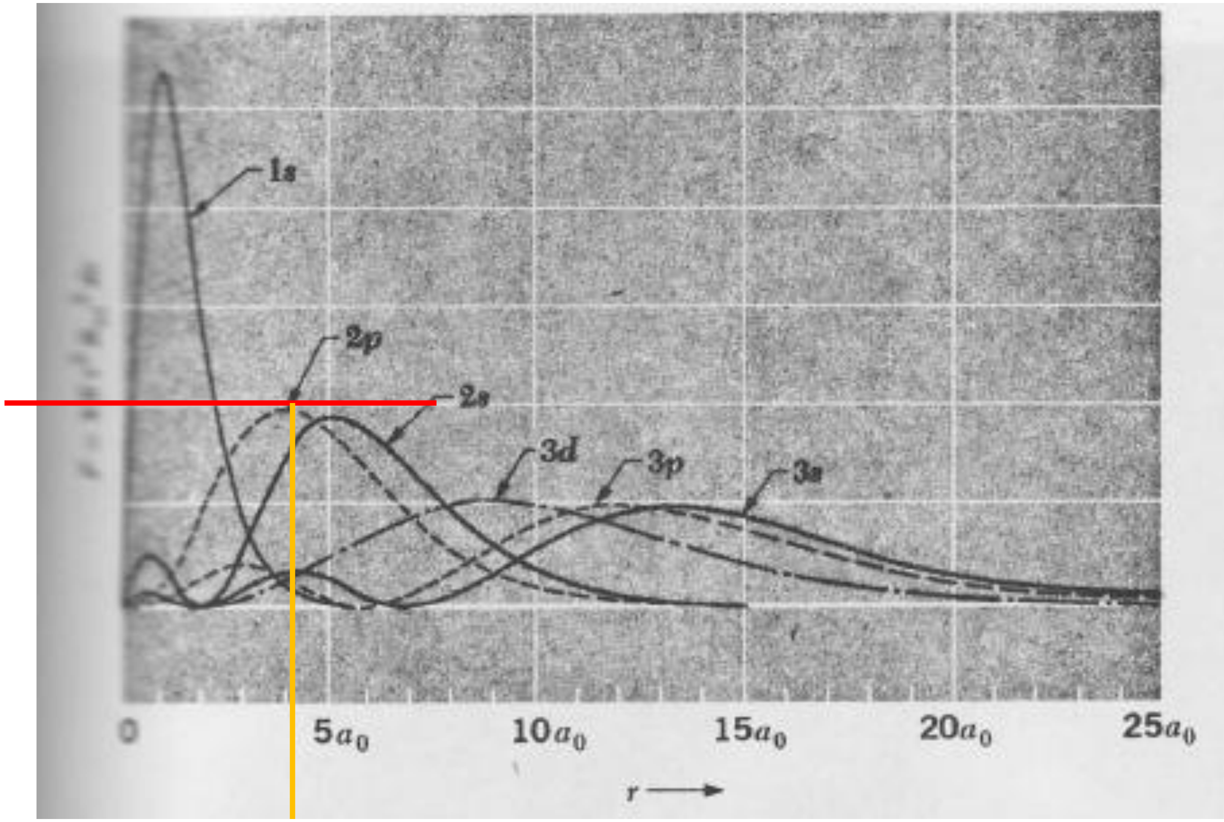
Most probable r Value $\frac{dP(r)}{dr} = \frac{d r^2 R_{n,l}(r)^2}{dr} = 0$

$$n = 2, l = 1 \rightarrow R_{21} = \frac{1}{(2a_0)^{\frac{3}{2}}} \frac{r}{\sqrt{3}a_0} e^{-\frac{r}{2a_0}}$$



$$P(r) \sim r^2 R^2(r)$$

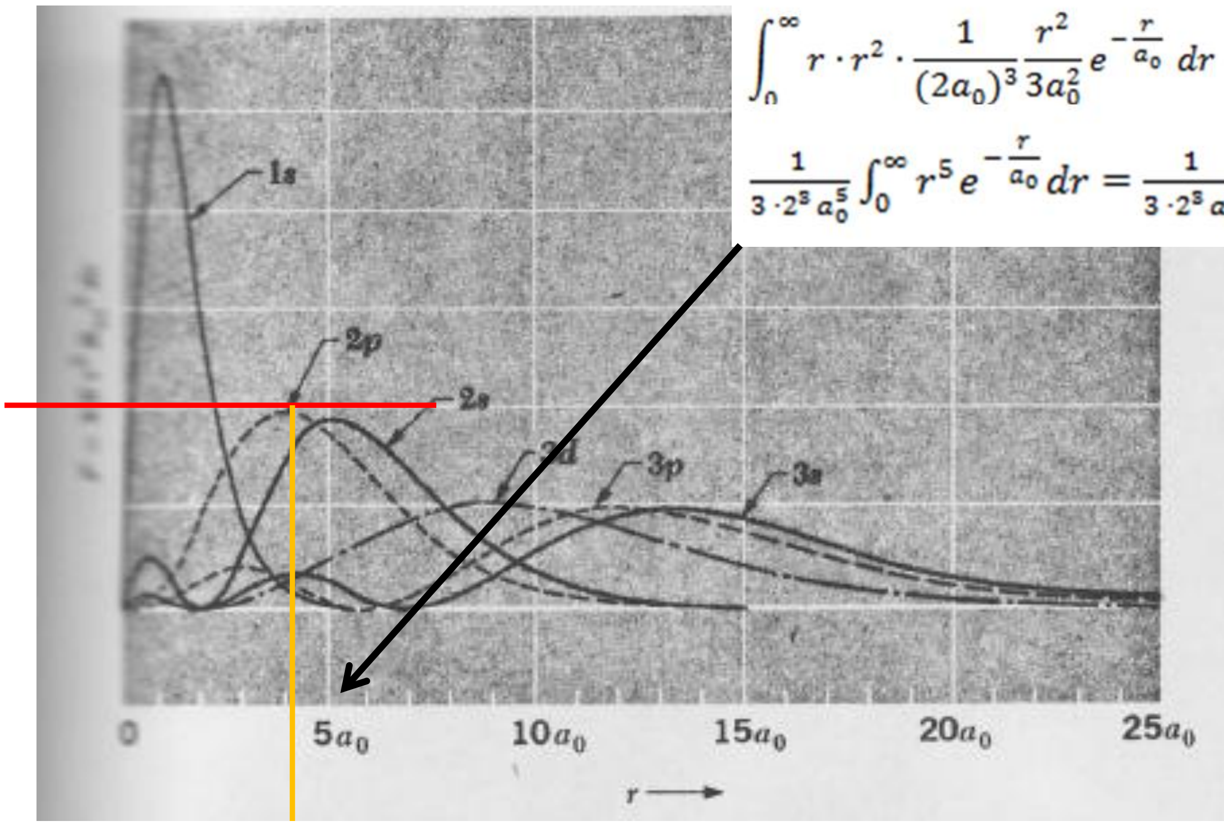


# $P(r) \sim r^2 R^2(r)$

$$\langle r \rangle = \int_0^\infty r \cdot r^2 R_{n,l}(r)^2 dr$$

$$\int_0^\infty r \cdot r^2 \cdot \frac{1}{(2a_0)^3} \frac{r^2}{3a_0^2} e^{-\frac{r}{a_0}} dr$$

$$\frac{1}{3 \cdot 2^3 a_0^5} \int_0^\infty r^5 e^{-\frac{r}{a_0}} dr = \frac{1}{3 \cdot 2^3 a_0^5} 5!\, a_0^6 = 5\, a_0$$



# Invariance and Conservation

H = T (Kinetic) +U (Potential)

$$H(x,y,z) = H(x+a, y+b, z+c)$$

Trsnalationally invariant → Linear momentum conservation

$$H(r,\theta,\phi) = H(r,\theta+a,\phi+b)$$

Rotationally invariant → Angular momentum conservation

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$$H(r, \theta, \phi) = H(r, \theta + a, \phi + b)$$

Rotationally invariant → Angular momentum conservation

$$\mathrm{H}\psi_{n,l,m_l} = E_n\psi_{n,l,m_l}$$

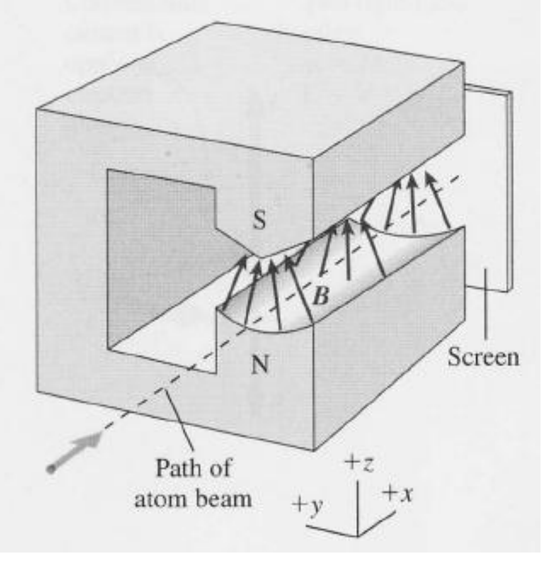
$$\mathrm{L}^2\psi_{n,l,m_l} = l(l+1)\hbar^2\psi_{n,l,m_l}$$

$$\mathrm{L_z}\psi_{n,l,m_l} = m_l\hbar\psi_{n,l,m_l}$$

# 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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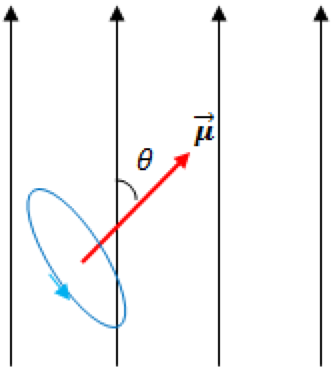


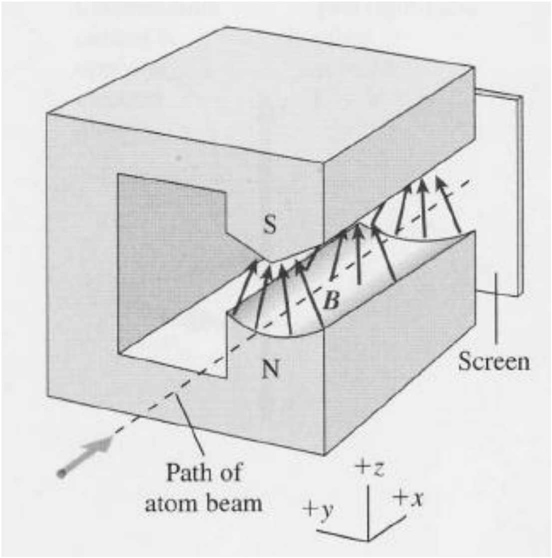


$$\mu = i(\pi r^2) = -e\left(\frac{v}{2\pi r}\right)(\pi r^2) = -e\left(\frac{vr}{2}\right) = -\frac{eL}{2m}$$

Magnetic dipole moment

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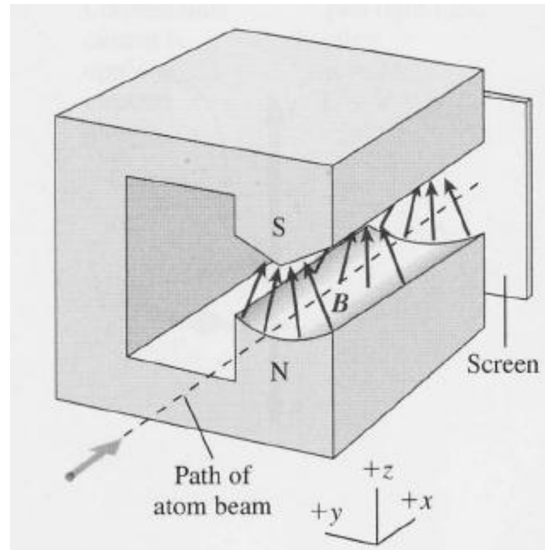


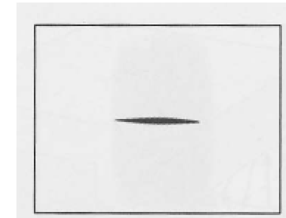

$\ell = 0$ expectation

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

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

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

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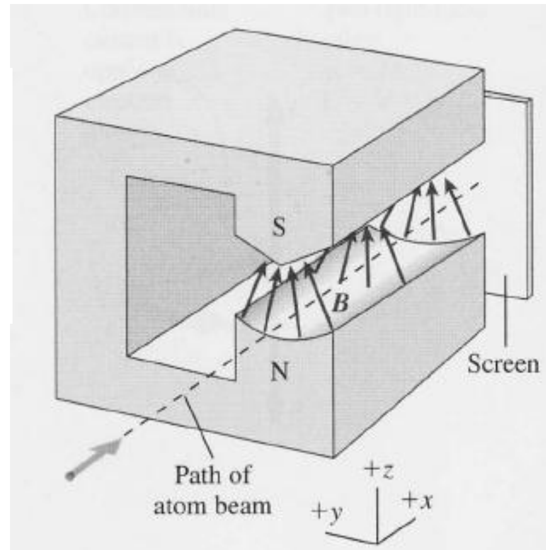
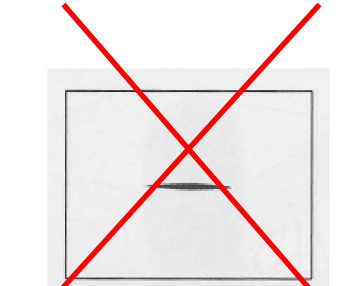
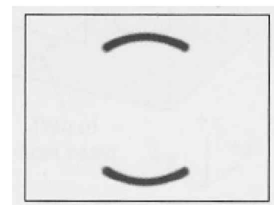




$\ell = 0$ expectation


$\ell = 0$ observation

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

$\vec{B} = B_z \hat{z}$

Since $L_z = m_l \hbar$

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

# Spin Angular Momentum

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

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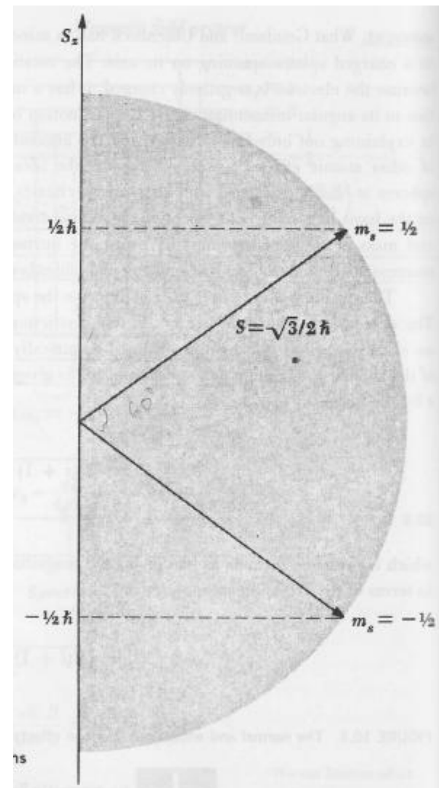
$$m_s = -s, . -s + 1, \ldots s - 1, s$$



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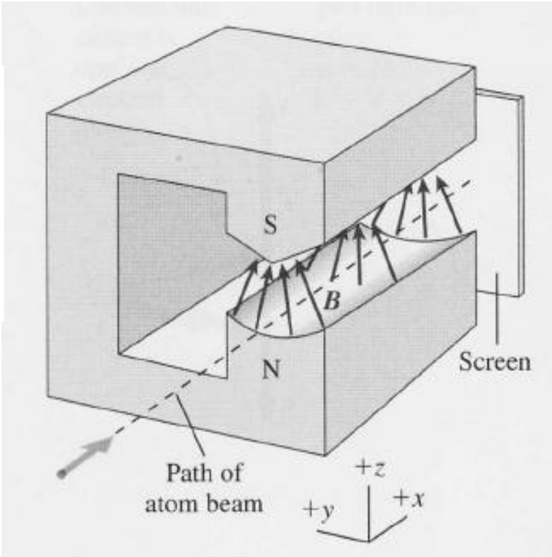
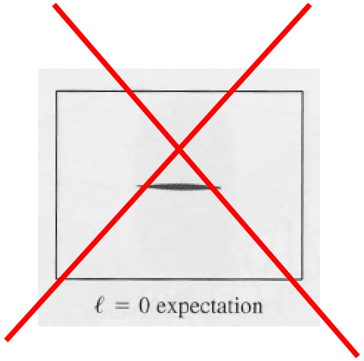
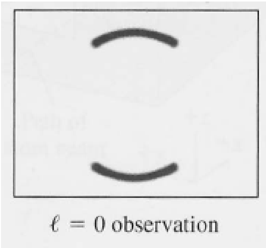
Since $\vec{\mu} = -\left(\frac{e}{2m}\right)\vec{L}$

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



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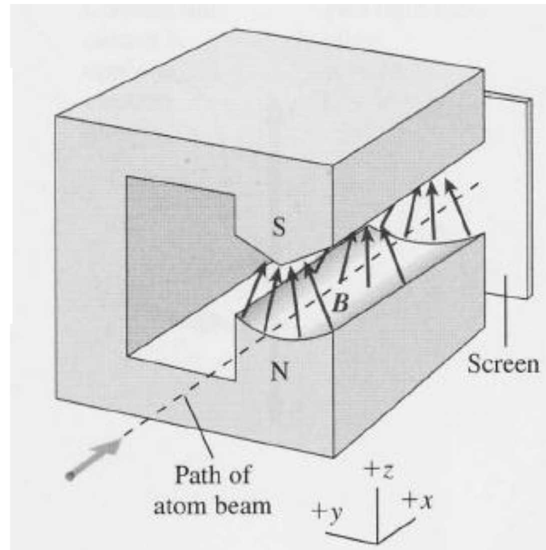
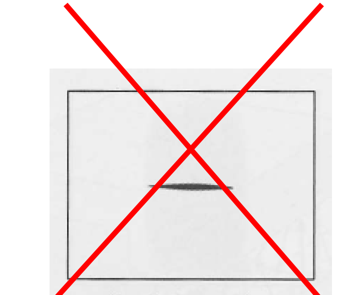
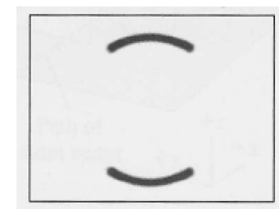




ℓ = 0 expectation


ℓ = 0 observation

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

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

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

$$|\vec{J}| = \sqrt{j(j+1)}\hbar \qquad where\ j = |l-s|, |l-s|+1, \ldots |l+s|-1, |l+s|$$

$$J_z = m_j\hbar \qquad \text{where } m_j = -j, -j+1, \ldots, j-1, j$$

$$J_z = L_z \pm S_z$$

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

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

$$L_z = m_l\hbar \qquad where\ m_l = -l, -l+1, \ldots l-1, l$$

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

$$S_z = m_s\hbar \qquad where\ m_s = -s, -s+1, \ldots s-1, s$$

# 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

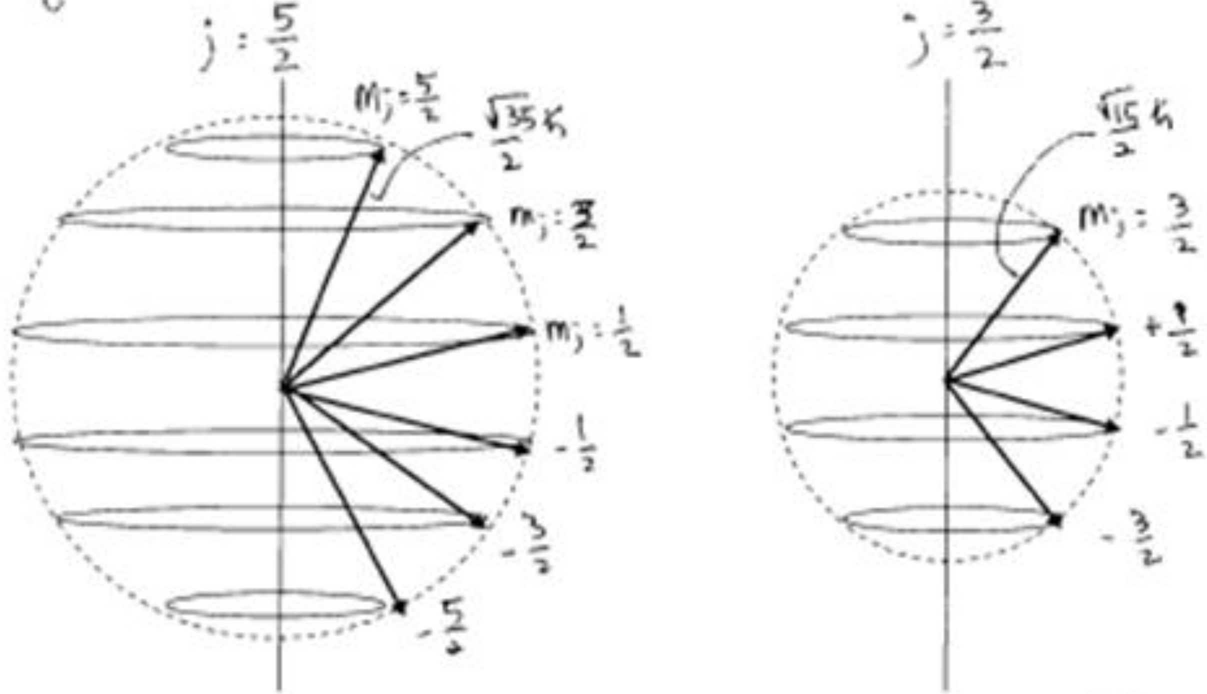
$$\text{for } j=\frac{5}{2}\rightarrow m_j = -\frac{5}{2},-\frac{3}{2},-\frac{1}{2},+\frac{1}{2},+\frac{3}{2},+\frac{5}{2} \quad |\vec{J}| = \sqrt{j(j+1)}\hbar = \sqrt{\frac{5}{2}\frac{7}{2}}\hbar = \frac{\sqrt{35}}{2}\hbar$$

6 possible states (2*j*+1)

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

4 possible states

-L.S coupling--

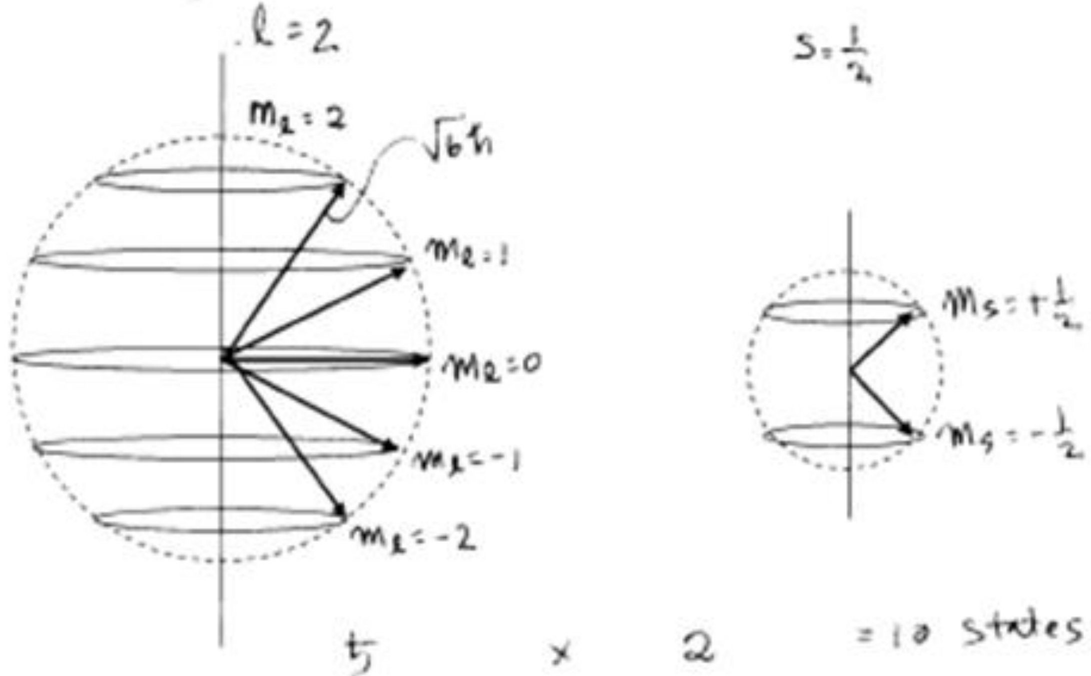



6 + 4 = 10 states

# 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-



# Periodic Table

| Period \ Group | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 1 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 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 | 57 * La | 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 | 89 ** Ac | 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 |

- Non Metals
- Alkali Metals
- Alkaline Metals
- Transition Metals
- Rare Earth Elements
- Noble Gases
- Metalloids
- Halogens
- Other Metals

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Lanthanides | 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 | 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 |

# What we know so far:

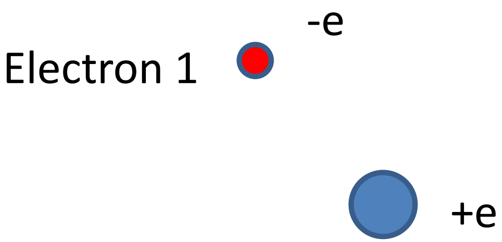
- Number of electrons in each atom
- Electrons should be in one of the orbitals determined by *n*, *l*, and $m_l$
- n limits what types of l orbitals an electron can occupy.
- Each l orbital has 2l+1 possible $m_l$ states:
  - *s* orbital = 1
  - *p* orbital = 2 x 1 + 1 = 3
  - *d* orbital = 2 x 2 + 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 $n$

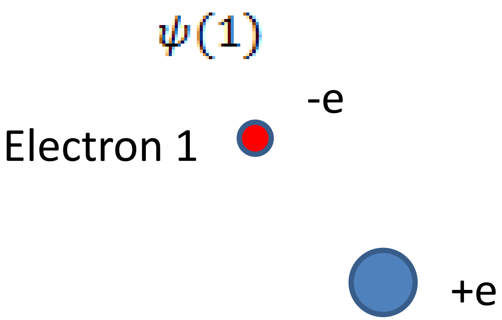
# Identical particles

$\psi(1)$




Hydrogen atom

# Identical particles

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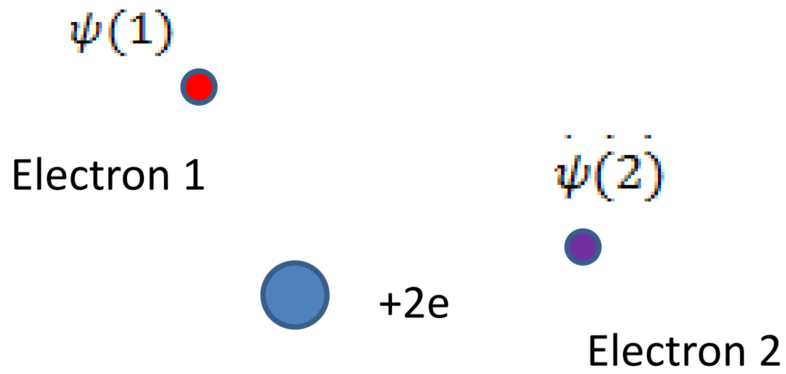
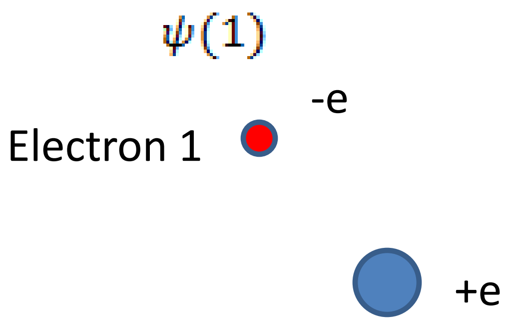



Helium atom

$$\psi(1,2) = \psi(1)\psi(2)$$

# Identical particles

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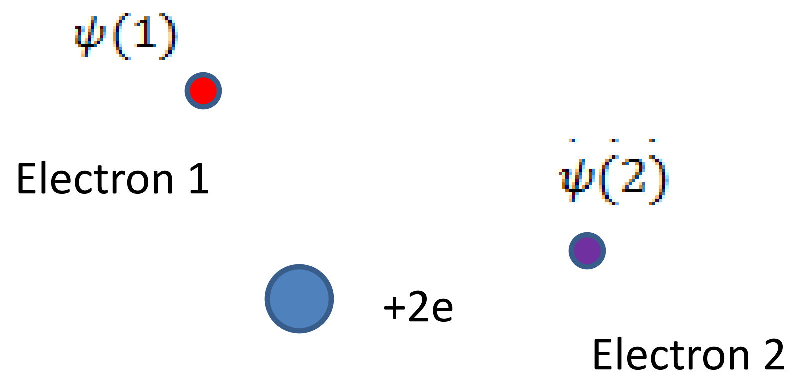
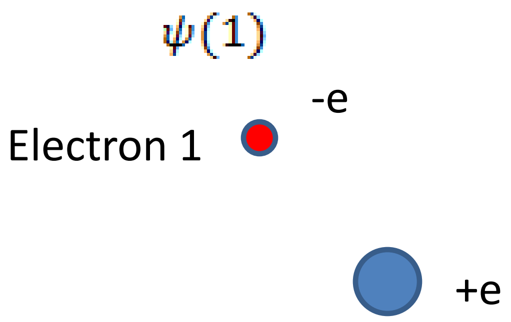



Helium atom

$$\psi(1,2) = \psi(1)\psi(2)$$

After exchanging two particles

# Identical particles

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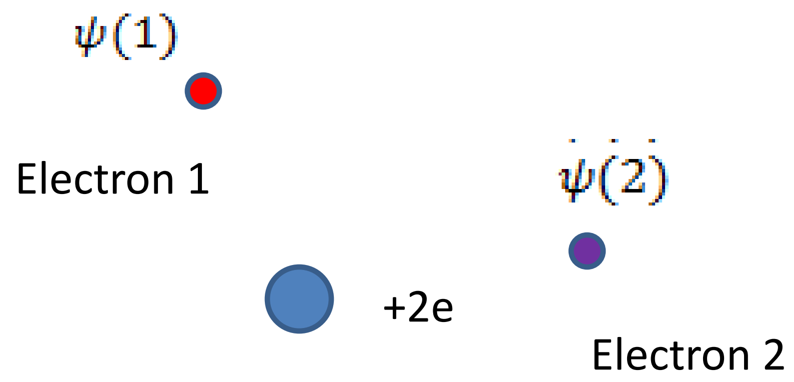


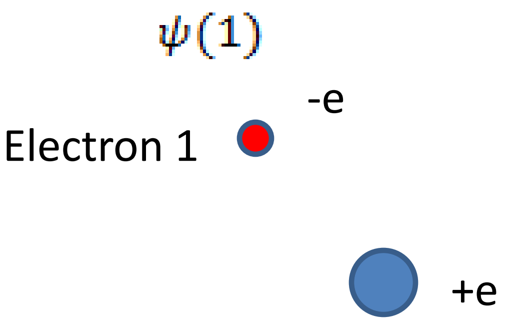

Helium atom

$$\psi(1,2) = \psi(1)\psi(2)$$

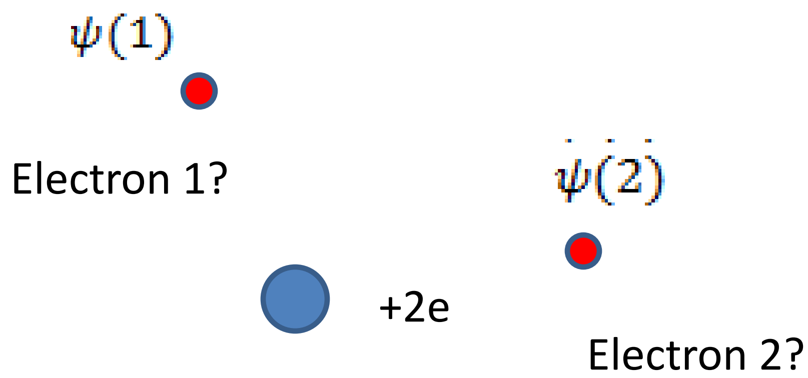
After exchanging two particles

$$\psi(2,1) = \psi(2)\psi(1)$$

# Identical particles




Hydrogen atom




Helium atom

$$|\psi(1,2)|^2 = |\psi(2,1)|^2$$

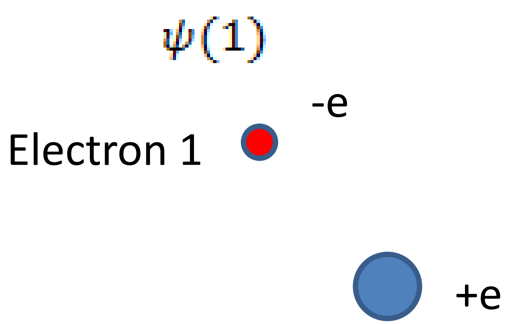
$$\psi(1,2) = \psi(1)\psi(2)$$

$$\psi(1,2) = \psi(2,1)$$
$$\psi(1,2) = -\psi(2,1)$$

After exchanging two particles

$$\psi(2,1) = \psi(2)\psi(1)$$

# Identical particles

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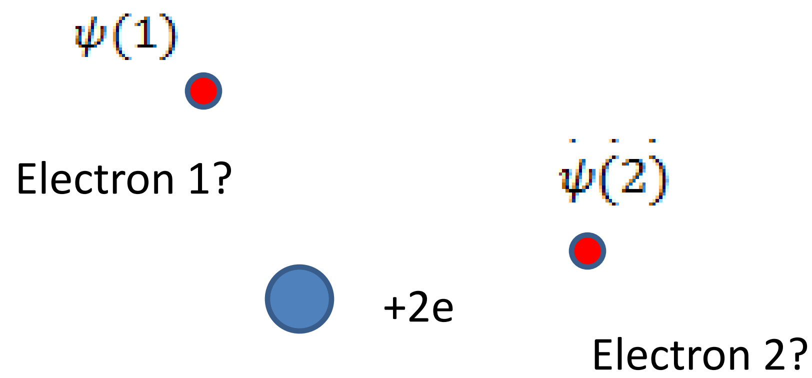


Helium atom

$$|\psi(1,2)|^2 = |\psi(2,1)|^2$$

$$\psi(1,2) = \psi(2,1)$$ → Symmetric under exchange operation

$$\psi(1,2) = -\psi(2,1)$$ → Anti-symmetric

When Particle 1 is in $n$ state and Particle 2 is in $n'$ state

$$\psi_I = \psi_n(1)\psi_{n'}(2)$$

When Particle 2 is in $n$ state and Particle 1 is in $n'$ state

$$\psi_{II} = \psi_n(2)\psi_{n'}(1)$$

$$|\psi(1,2)|^2 = |\psi(2,1)|^2$$

$$\psi_{Symmetric} = \frac{1}{\sqrt{2}}[\psi_n(1)\psi_{n'}(2) + \psi_n(2)\psi_{n'}(1)]$$

$$\psi_{Anti-Symmetric} = \frac{1}{\sqrt{2}}[\psi_n(1)\psi_{n'}(2) - \psi_n(2)\psi_{n'}(1)]$$

# Bosons

$$\psi_{Symmetric}\ satisfies\ \psi(1,2) = \psi(2,1)$$

- Systems of bosons are described by wave functions that are symmetric upon the exchange of any pair of bosons.
- Bosons are integer spin particles such as
  - Photon (s=1) Deuteron (s=1)
  - Pion (s=0)
  - Helium nucleus (alpha particle; s=0)
- Bosons can occupy the same quantum state.

# Fermions

$$\psi_{Anti-Symmetric}\ satisfies\ \psi(1,2) = -\psi(2,1)$$

- Systems of fermions are described by wave functions that reverse sign upon the exchange of any pair of electrons.
- Fermions' spin numbers are half-integer:
  - Electron, proton, and neutron = ½
- If $n = n', \psi_{Anti-Symmetric} =$ ???

$$\psi_{Anti-Symmetric} = \frac{1}{\sqrt{2}}[\psi_n(1)\psi_{n'}(2) - \psi_n(2)\psi_{n'}(1)]$$

# Fermions

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- If

$$n = n', \psi_{Anti-Symmetric} = 0.$$

$$\psi_{Anti-Symmetric} = \frac{1}{\sqrt{2}}[\psi_n(1)\psi_{n'}(2) - \psi_n(2)\psi_{n'}(1)]$$

Two fermions of the same type cannot occupy the same quantum state in an isolated system.

→ Exclusion Principle

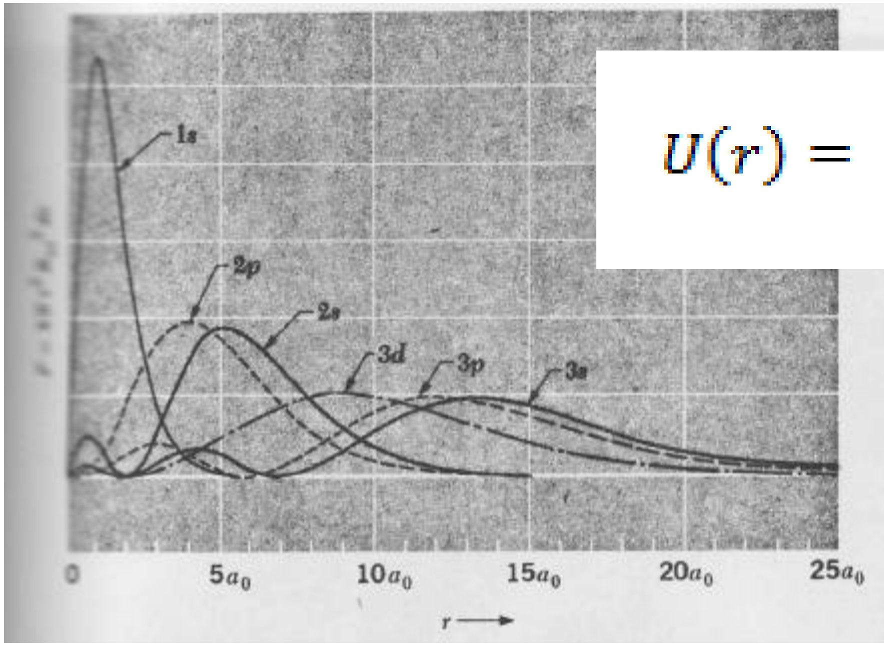
# Periodic Table: Two basic rules

- A system of particles is stable when its total energy is a minimum
- Only one electron can exist in any particular quantum state in an atom (exclusion principle).

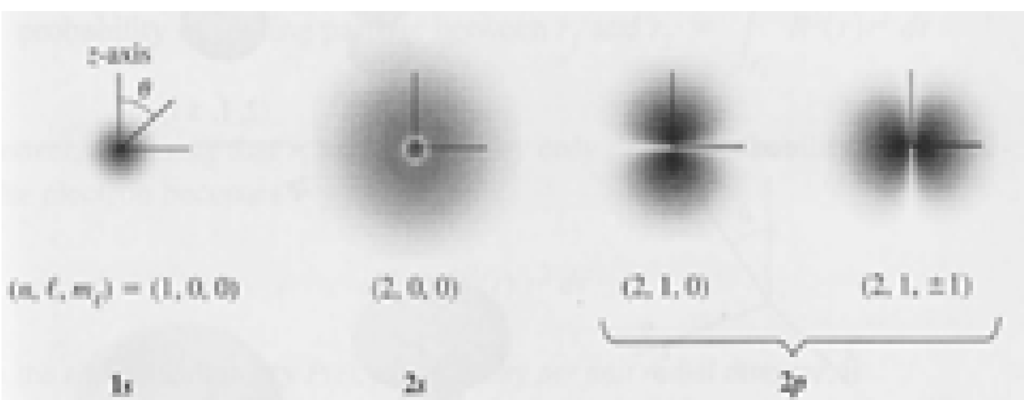
# Which quantum state has a lower energy?

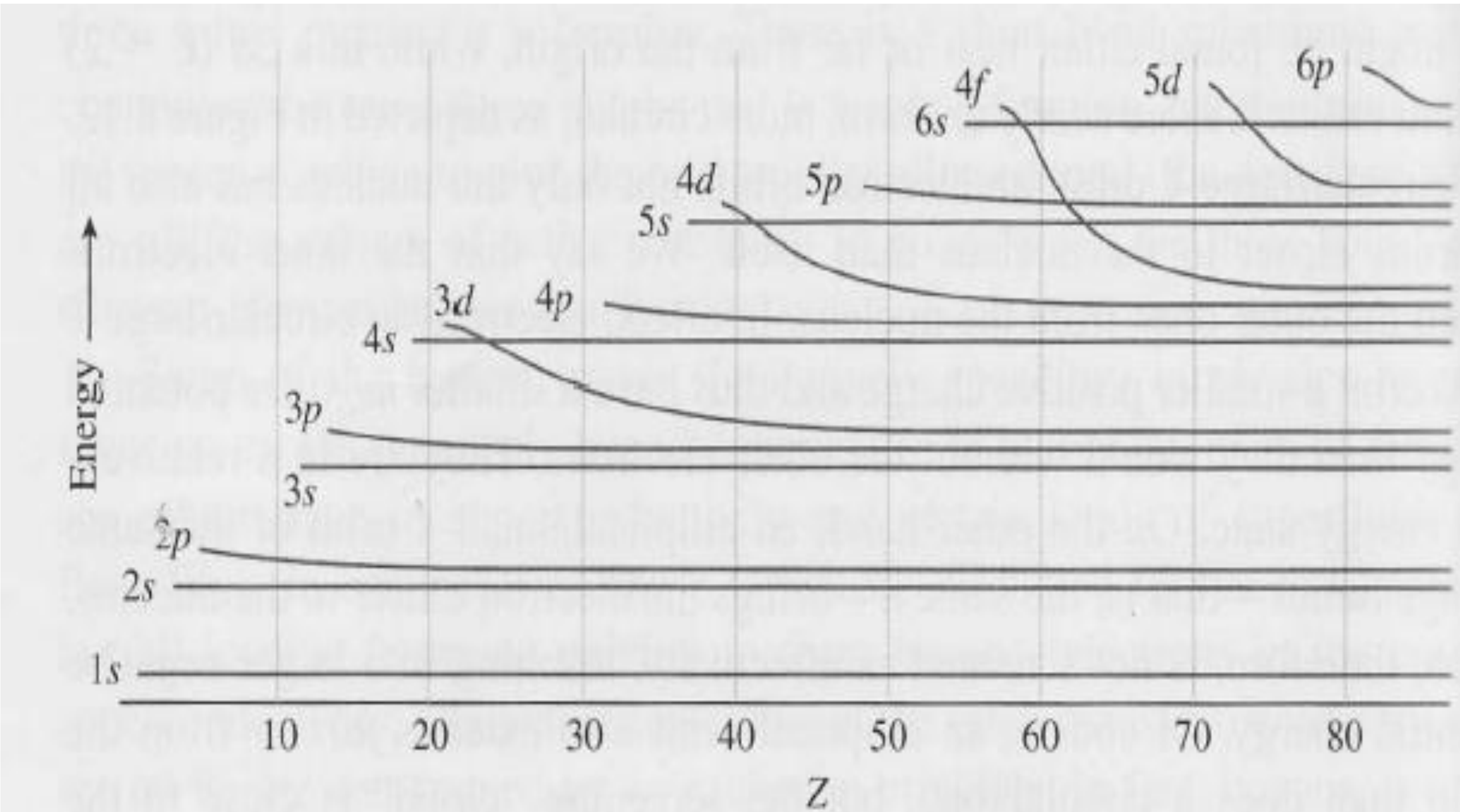
- When n is lower.
- With a given , when *l* is lower.
- With a given *l*, parallel spin arrangements lower energy.

# With a given , when *l* is lower

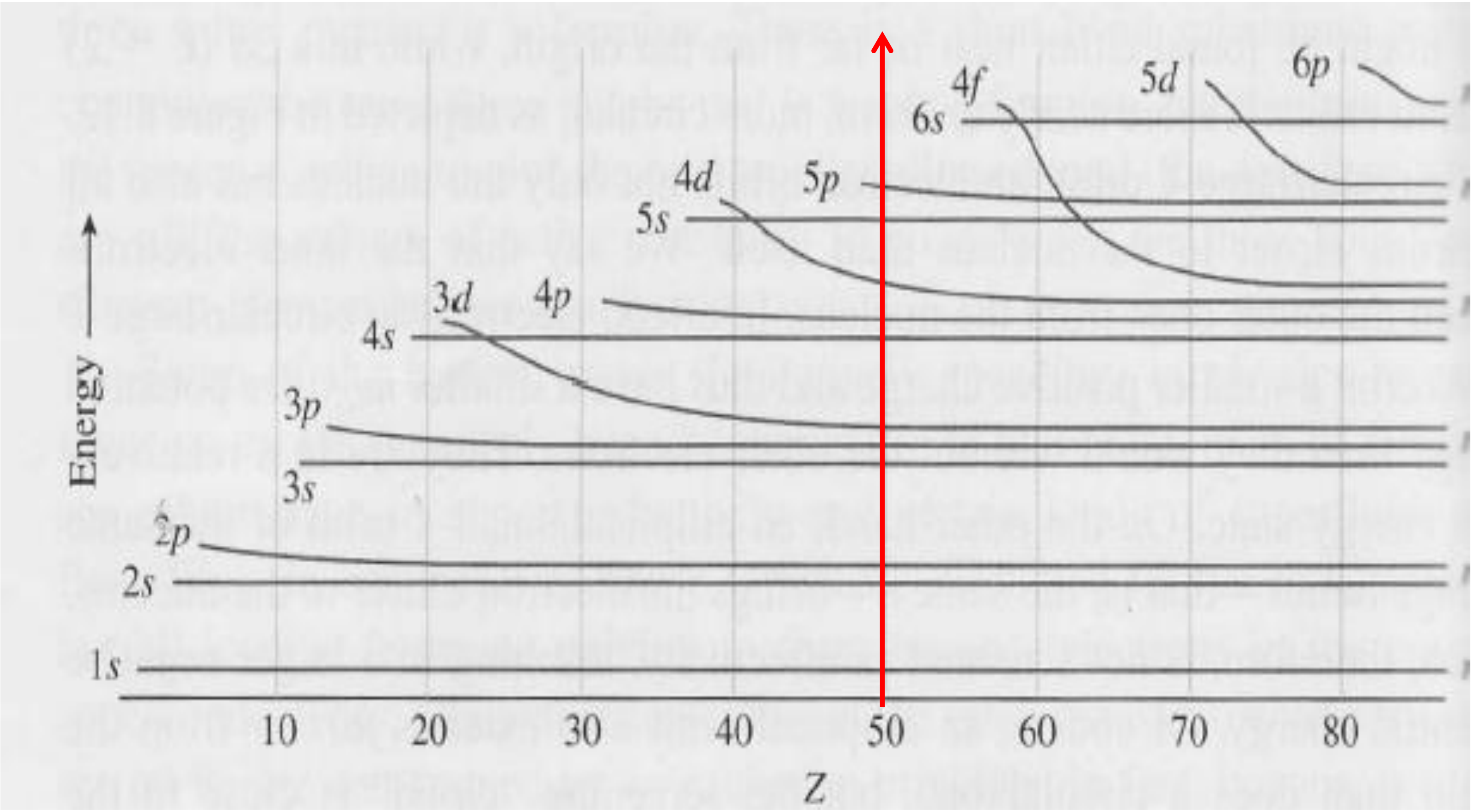



$$U(r) = \frac{1}{4\pi\varepsilon_0}\frac{(electron\ charge)(nucleus\ charge)}{r}$$





6p
5d
4f
6s
4d
5p
5s
3d
4p
4s
3p
3s
2p
2s
1s
Energy
10
20
30
40
50
60
70
80
Z


Energy
1s
2s
2p
3s
3p
4s
3d
4p
5s
4d
5p
6s
4f
5d
6p
10
20
30
40
50
60
70
80
Z

# With a given *l*, parallel spin arrangements lower energy.

wave function where electron 1 occupies n state and electron occupies n' state:

$$\psi(1,2) = \psi_{n\,n'}(1,2)\uparrow\uparrow$$

If we exchange electron 1 and electron 2, a wave function becomes

$$\psi(2,1) = \psi_{n\,n'}(2,1)\uparrow\uparrow$$

According to the exclusion principle,

$$\psi(1,2) = -\,\psi(2,1)$$

$$\psi_{n\,n'}(1,2)\uparrow\uparrow = -\psi_{n\,n'}(2,1)\uparrow\uparrow$$

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→ Lower Coulomb Interaction (by decreasing repulsive interaction between two electrons)

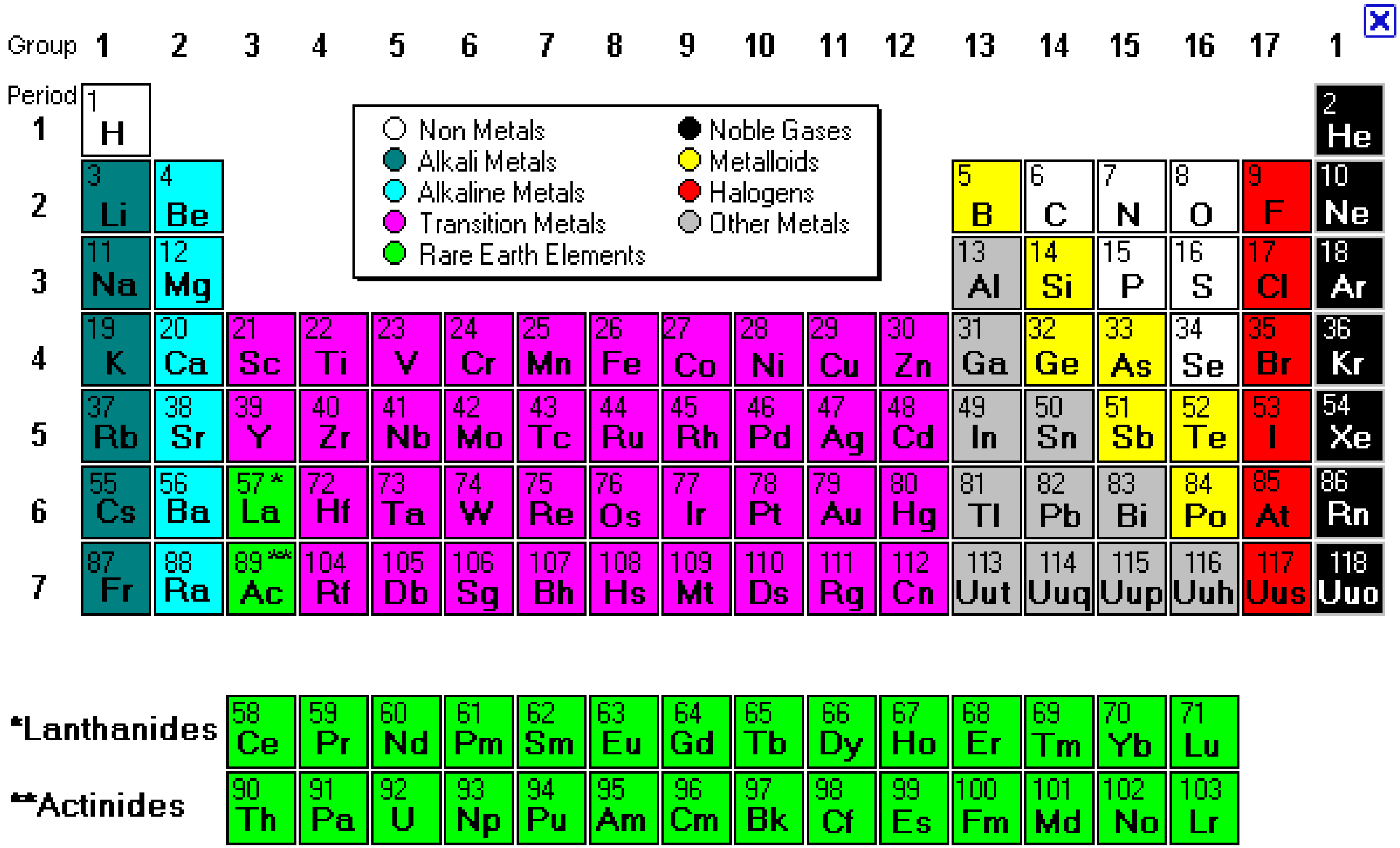
# P orbital spin arrangements

| | $p_x$ | $p_y$ | $p_z$ |
|---|---|---|---|
| Lower E | ↑ | | |
| | | | |
| | | | |
| | | | |
| | | | |
| Higher E | | | |

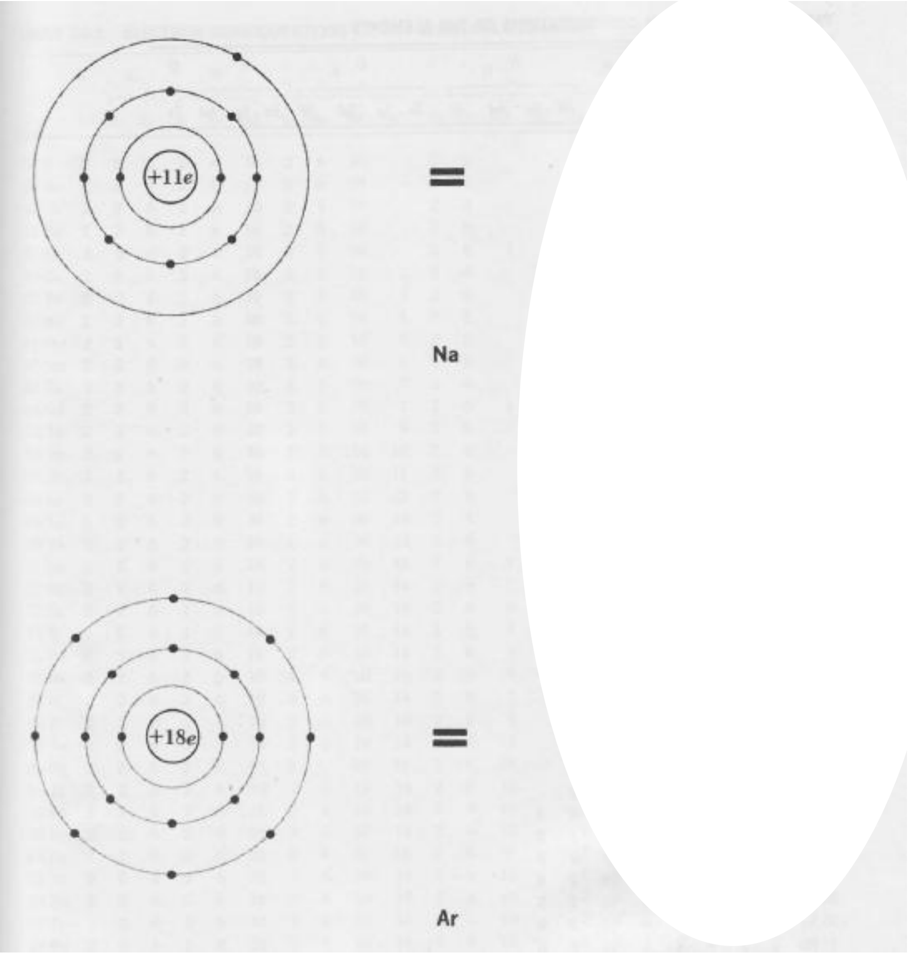
# P orbital spin arrangements

| | $p_x$ | $p_y$ | $p_z$ |
|---|---|---|---|
| Lower E | ↑ | | |
| | ↑ | ↑ | |
| | ↑ | ↑ | ↑ |
| | ↑↓ | ↑ | ↑ |
| | ↑↓ | ↑↓ | ↑ |
| Higher E | ↑↓ | ↑↓ | ↑↓ |

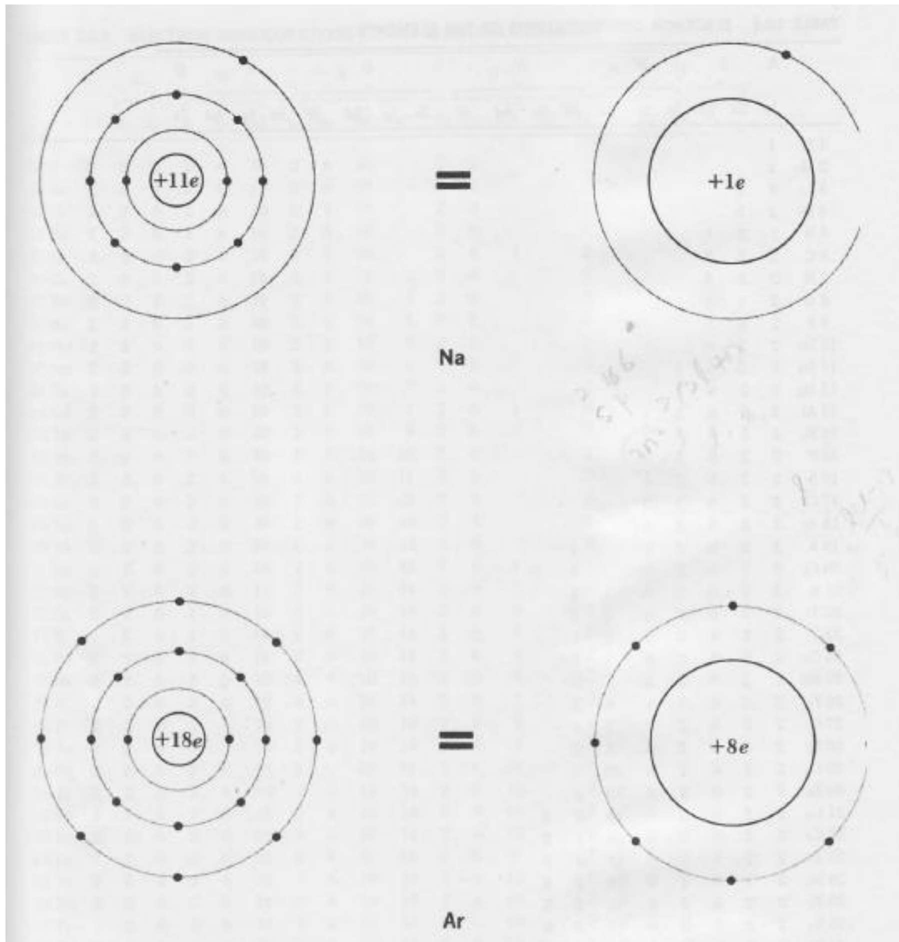
# Periodic Table



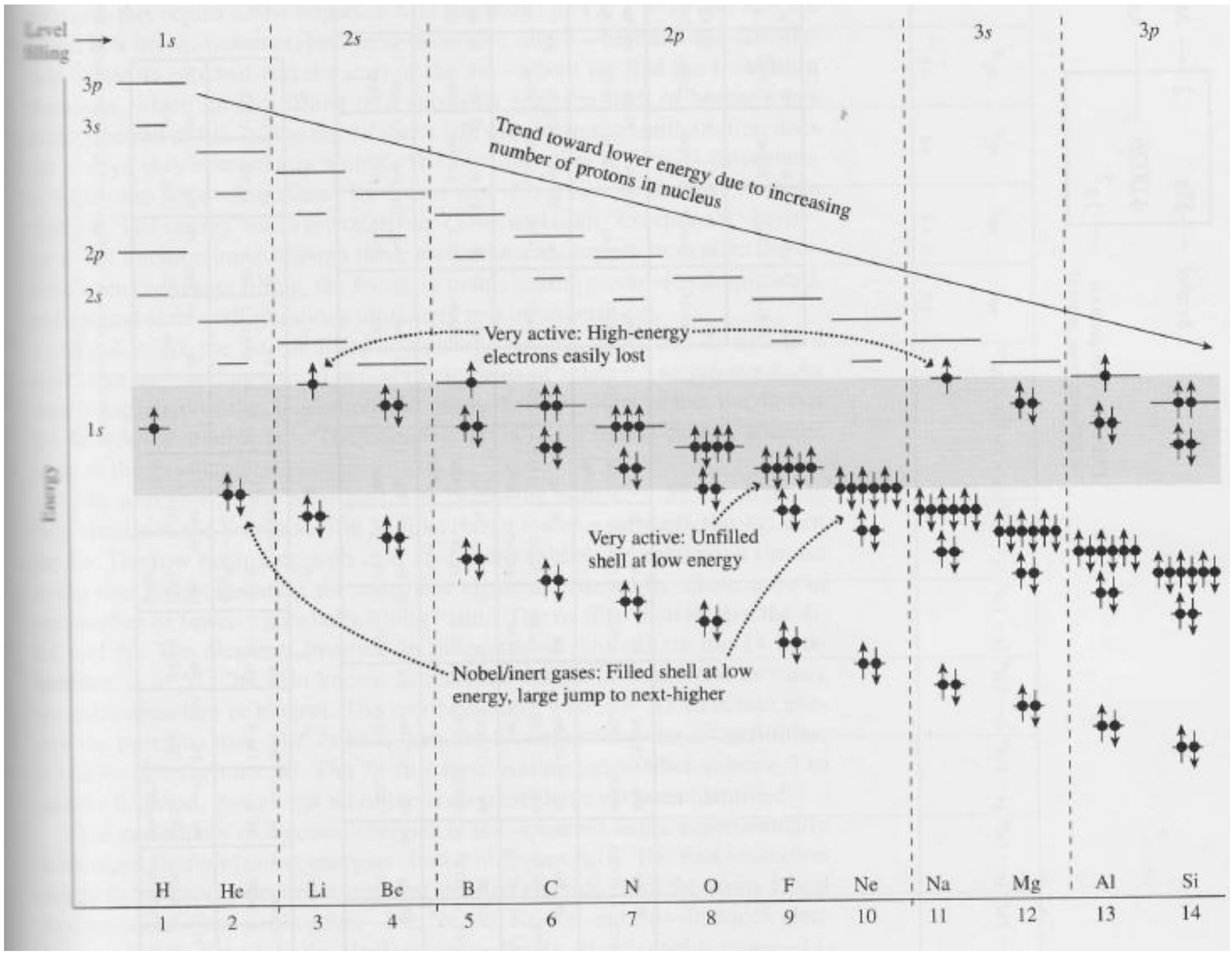
# Effective charge of the nucleus



# Effective charge of the nucleus



# Orbital Energy levels



# Ionization Energy

**Figure 8.16** First ionization energies of the elements.