

PH102, 2014W, Lecture Notes: January 21, Tues, Class 5

Orbital and spin angular momentum quantization, LS coupling, and Periodic table

Objectives:

- Define what the Spin angular momentum represents and how it is quantized.
- Define the total angular momentum, how it is quantized, and how it is related to L and S.
- Understand what LS coupling represents and how it is done.
- Understand Pauli exclusion principle and apply it to bosons and fermions
- Recognize patterns in the periodic table and connect them to underlying causes.

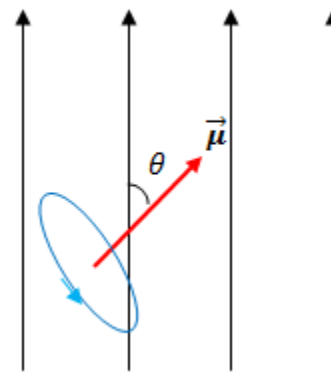
Why Spin?

An electron revolving around a nucleus in an atom can be considered as a minute current loop and has a magnetic field of a magnetic dipole $\vec{\mu}$. In an external \vec{B} (magnetic) field, the potential of the magnetic dipole can be defined as:

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

↑

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



Why? The magnetic moment of a current loop is

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

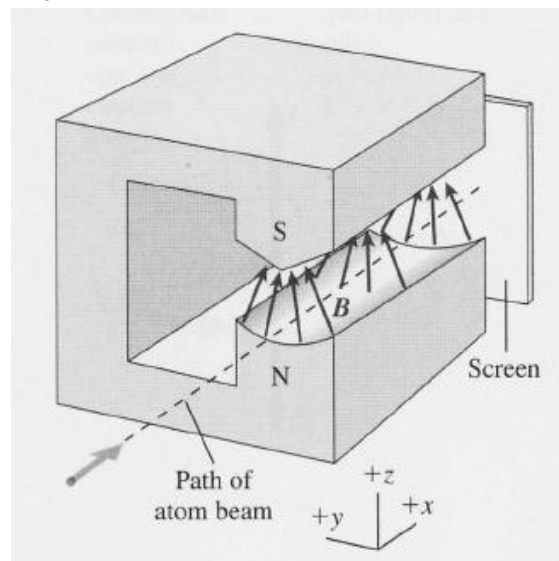
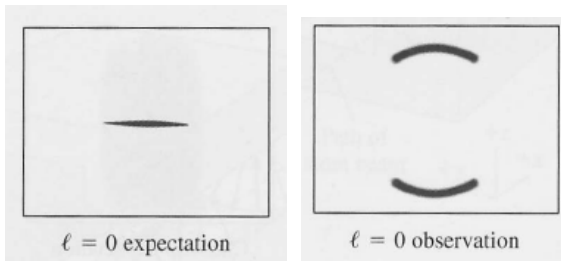
The force exerting on the magnetic dipole is

$$F = -\nabla (-\vec{\mu} \cdot \vec{B}) = -\left(\frac{e}{2m}\right) L_z \frac{\partial B_z}{\partial z} \hat{z} = -\left(\frac{e}{2m}\right) (m_l \hbar) \frac{\partial B_z}{\partial z} \hat{z} \quad \text{where } m_l = -l, \dots, +l.$$

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

In a uniform \vec{B} field, there is no force exerting on the magnetic dipole. In a non-uniform \vec{B} field, the force varies by m_l .

If $l=0 \rightarrow m_l = 0 \rightarrow$ no orbital motion \rightarrow no magnetic moment \rightarrow one spectral line



However, the Stern-Gerlach experiment shows that two

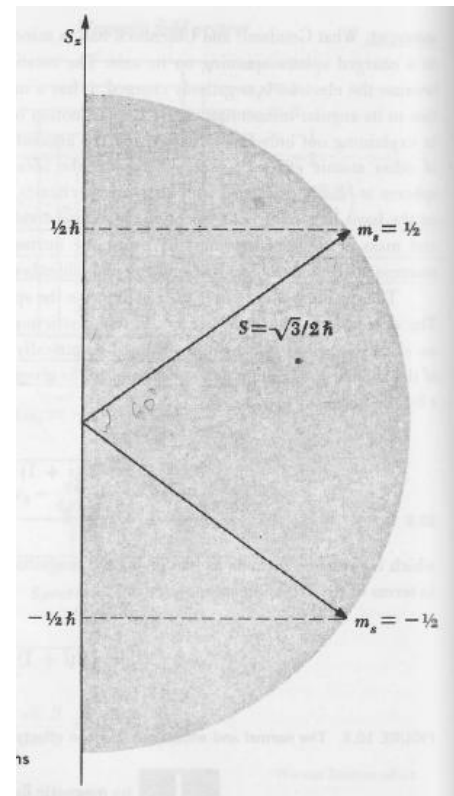
split lines are present when $l=0$.

When the spin angular momentum is considered, then the electron in the atomic beam in the experiment can be solved by replacing $-\vec{\mu}$ with $\vec{\mu}_s = -\frac{e}{2m}\vec{S}$

$F = -\nabla(-\vec{\mu} \cdot \vec{B}) = -\left(\frac{e}{2m}\right)S_z \frac{\partial B_z}{\partial z} \hat{z} = -\left(\frac{e}{m}\right)(m_s \hbar) \frac{\partial B_z}{\partial z} \hat{z}$ where $m_s = \pm \frac{1}{2} \rightarrow$ two lines justified!

To account for this, an intrinsic angular momentum called Spin (S) was introduced by Goudsmit and Uhlenbeck in 1925:

- The intrinsic angular momentum is one of fundamental properties of a particle such as mass and charge.
 - Fermions (Half-integral spin): Electron, proton, neutron, neutrino, and Omega = $\frac{1}{2}$
 - Bosons (integral spin): pion and alpha particle = 0
 - Bosons: Photon, Deuteron = 1
- Magnitude of \vec{S} , $|\vec{S}| = \sqrt{s(s+1)} \hbar$
 (e.g. electron $|\vec{S}| = \frac{\sqrt{3}}{2} \hbar$)
- Direction is quantized by $S_z = m_s \hbar$ where $m_s = -s, \dots, -s+1, \dots, s-1, s$ (e.g. electron $-1/2$ and $1/2$)
- A given particle has intrinsic magnetic dipole moment due to its intrinsic angular momentum:
 $\vec{\mu}_s = g \frac{q}{2m} \vec{S}$ (e.g. electron $\vec{\mu}_s = -\frac{e}{m} \vec{S}$)
- Spin is not classical, so an analogy of rotating its own axis does not properly describe it.
- Now the wave function for the Schrodinger Equation can be completely described using four quantum numbers, n, l, m_l, m_s .



OR

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

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

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

- Spin should increase the degeneracy in the hydrogen atom. The number of states with the same n would increase the degeneracy from n^2 to $2n^2$. But, due to interactions between orbital and spin angular momentums, degeneracy can be broken.

- Photon's Spin is 1. When an atom undergoes a transition in which a photon is produced, there is a limit on how much the atom's angular momentum can change: no more than 1, which creating selection rules for spectral emissions.

Spin-Orbit Coupling (Spin-Orbit Interaction) OR LS Coupling

In a weak external magnetic field where the external magnetic field does not overwhelm the magnetic field internal to the atom, we do not observe separate quantization of \vec{L} and \vec{S} . Rather, we observe the combined angular momentum:

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

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

$$J_z = m_j \hbar \quad \text{where } m_j = -j, -j+1, \dots, j-1, j$$

$$J_z = L_z \pm S_z$$

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

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

$$L_z = m_l \hbar \quad \text{where } m_l = -l, -l+1, \dots, l-1, l$$

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

$$S_z = m_s \hbar \quad \text{where } m_s = -s, -s+1, \dots, s-1, s$$

- In a strong magnetic field, LS coupling breaks. In that case, \vec{L} and \vec{S} are independently quantized.
- Good quantum numbers refer to quantities which can be assigned simultaneously to describe a quantum system at any time. In a weak B field, n, l, j, m_j are good quantum numbers. In a strong B field, n, l, m_l , and m_s are good quantum numbers.
- The effect of LS coupling is very small compared to the electron energies allowed in the hydrogen atom around $2 \times 10^{-5} \text{ eV}$. (compare this with -13.6 eV).--> the effect is observed in the fine structure of hydrogen spectral lines. When L and S are aligned, the energy is slightly higher than when L and S are anti-aligned.

Exercise: Identify the different total angular momentum states possible for $l = 2$ and $s = \frac{1}{2}$

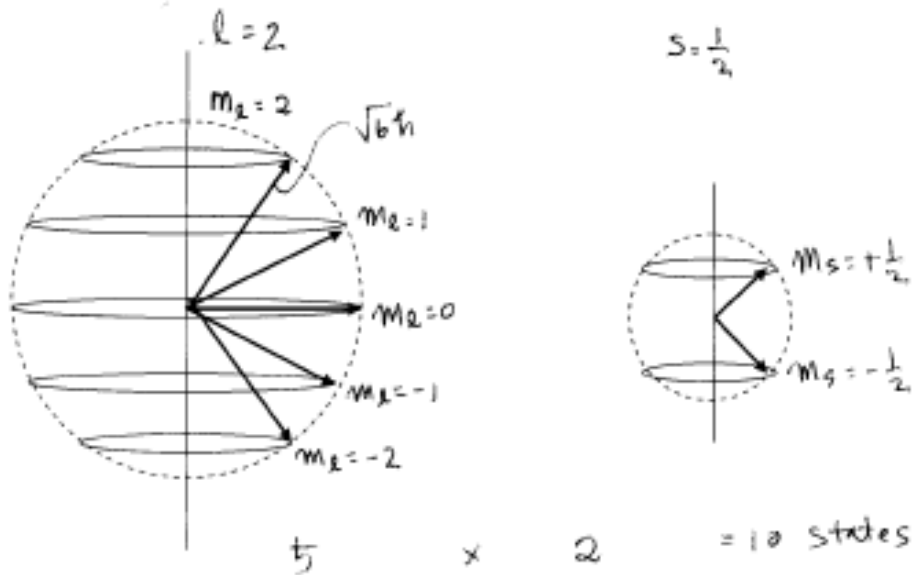
$$j \text{ can be } l + s \text{ or } l - s \rightarrow 2 + \frac{1}{2} \left(= \frac{5}{2} \right) \text{ or } 2 - \frac{1}{2} \left(= \frac{3}{2} \right)$$

- for $j = \frac{5}{2} \rightarrow m_j = -\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}, +\frac{5}{2}$ $|\vec{J}| = \sqrt{j(j+1)}\hbar = \sqrt{\frac{57}{2}}\hbar = \frac{\sqrt{35}}{2}\hbar \rightarrow$
6 possible states ($2j+1$)
- for $j = \frac{3}{2} \rightarrow m_j = -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}$ $|\vec{J}| = \sqrt{j(j+1)}\hbar = \sqrt{\frac{15}{2}}\hbar = \frac{\sqrt{15}}{2}\hbar \rightarrow$
4 possible states
- A total of 10 states are possible.

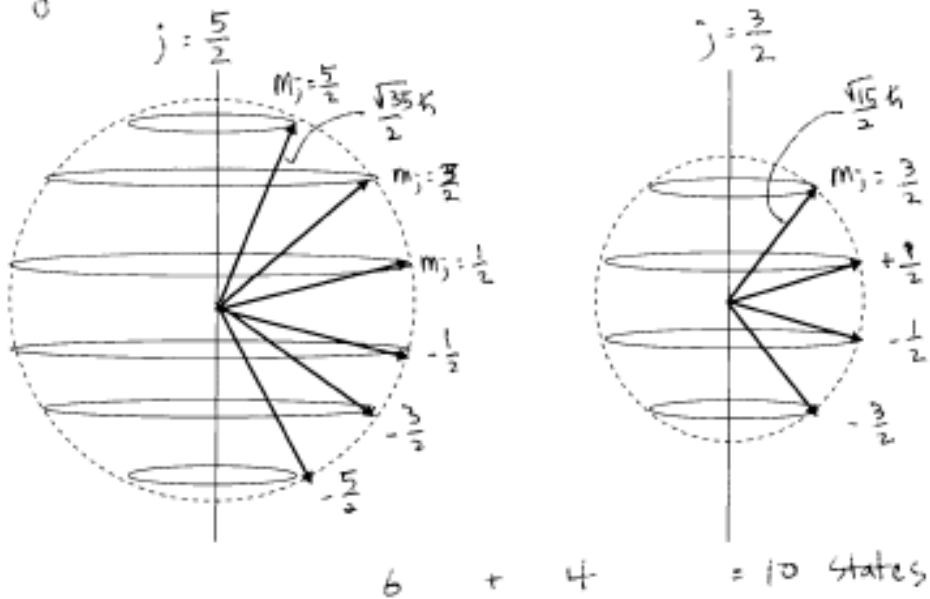
If we consider \vec{L} and \vec{S} separately,

- For $l = 2 \rightarrow 5$ states are possible
- For $s = \frac{1}{2} \rightarrow 2$ states are possible
- When adding $\vec{L} + \vec{S}$, a total of $5 \times 2 = 10$ states are possible. This number agrees to the number of states possible with J .

- Separate -



-- L-S coupling --



Periodic Table

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
Period 1	1																	2	
1	H																		He
2	3	4											5	6	7	8	9	10	
	Li	Be											B	C	N	O	F	Ne	
3	11	12											13	14	15	16	17	18	
	Na	Mg											Al	Si	P	S	Cl	Ar	
4	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
5	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
6	55	56	57*	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	
	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
7	87	88	89**	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	
	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Uuq	Uup	Uuh	Uus	Uuo	

*Lanthanides	58	59	60	61	62	63	64	65	66	67	68	69	70	71
	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
**Actinides	90	91	92	93	94	95	96	97	98	99	100	101	102	103
	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

We need to find out how to put an electron as the atomic number increases in such a way that atoms in a certain group share similar chemical behaviors. If all electrons can occupy the same quantum state, then it is hard to imagine when a small change in the number of electrons gives rise to such distinct chemical behaviors with which we are familiar.

What is known:

- We know how many electrons each atom has
- We know electrons move in orbitals determined by n, l, m_l .
- We know energy level (n) limits what types of orbitals (l) an electron can be in
- We know each l orbital has $2l+1$ possible m_l states for an electron can occupy
- We know an electron has a spin resulting in 2 possible spin states for each of the $2l+1$ possible orbitals. Therefore, for each n , $2n^2$ different states exist.

We need to know rules for

- How to stack electrons across all orbitals \rightarrow exclusion principle: Pauli, “no two electrons in an atom can exist in the same quantum state” each electron must have a different set of quantum numbers (n, l, m_l , and m_s).
- How to construct wave functions when multiple electrons present surrounding one nucleus \rightarrow identical particle treatment

Identical Particles

If an electron's wave function is $\psi(1)$, another $\psi(2)$, another $\psi(3)$, etc.

The total wave function of the system of n particles can be represented as

$$\psi(1, 2, 3, \dots, n) = \psi(1)\psi(2)\psi(3) \dots \psi(n)$$

Let's consider a two particle system:

Particle 1's wave function = $\psi(1)$

Particle 2's wave function = $\psi(2)$

Consider Particles 1 and 2 are identical, there is no difference in probability density when exchanged

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

There are two ways to satisfy this condition:

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

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

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

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

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

We have no way of knowing whether ψ_I or ψ_{II} is right, we combine both wave functions in such a way that meet

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

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

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

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

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

Bosons of which spins are an integer satisfies $\psi_{Symmetric}$

- Systems of bosons are described by wave functions that are symmetric upon the exchange of any pair of **bosons**.

Fermions of which spins are halfinteger satisfies $\psi_{Anti-Symmetric} \rightarrow$ Exclusion principle applies.

- When $n = n'$, $\psi_{Anti-Symmetric} = 0$. \rightarrow this cannot be the case \rightarrow no two electrons can occupy the same quantum state.
- Systems of fermions are described by wave functions that reverse sign upon the exchange of any pair of electrons.
- The anti-symmetric state has a lower energy because two fermions are farther apart, reducing the repulsive energy between the two.
- The exclusion principle applies only two indistinguishable fermions, that is
 - Particles should be of the same fermion type

- Share the same space.

Periodic Table

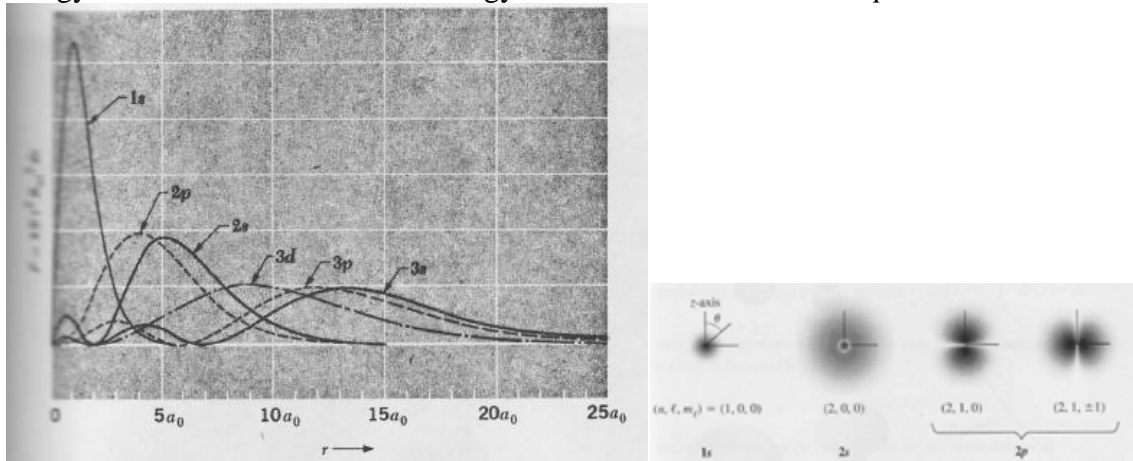
Two basic rules to determine the electron configuration in many-electron atoms:

- 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).

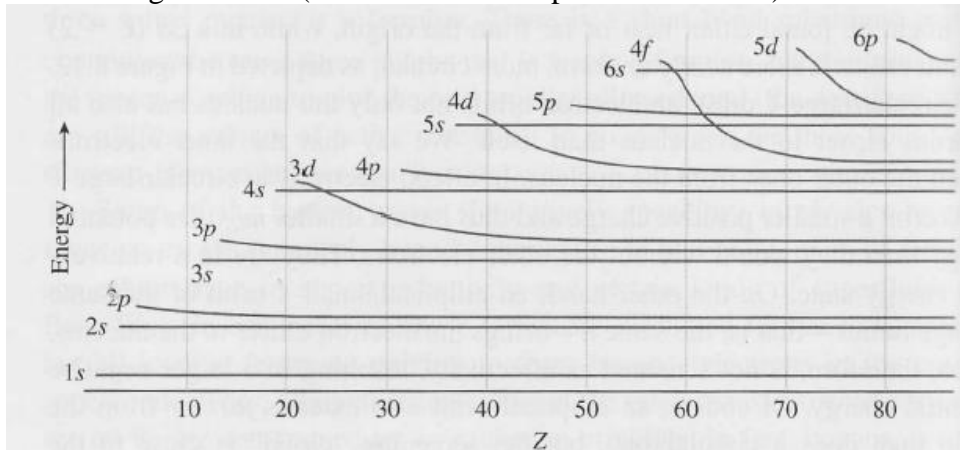
Determining what quantum state has lower energy?

- When n is lower.
- With a given n , when l is lower.

Why? At a given n state, a lower l state has less orbital kinetic energy and more radial energy. Therefore, more anti-nodes exist. This makes the probability density to fluctuate closer to and farther away from the nucleus. Since the Coulomb interaction is proportional to $1/r$, an electron in a lower l state will have a higher probability to get closer to the nucleus where the charge of the nucleus is less shielded by the inner electrons. That increases the magnitude of **attractive** potential energy, resulting in a lower energy state. This means that the energy of $2s$ is lower than that of $2p$.



The graph on the next page shows how energy levels align with l orbitals in different n states for a given atom (Z = the number of protons/electrons).



- With a given l , parallel spin arrangements lower energy.

Why? Let's consider two electrons in the $2p$ orbital. According to the exclusion principle since electrons are indistinguishable fermions in an atom, the wave function that describes both electrons should be antisymmetric.

When two electrons has a symmetric spin arrangement between electron 1 and electron 2, i.e. $\uparrow\uparrow$ or $\downarrow\downarrow$, we can write

a 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,

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

That is

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

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

If the two electrons are in the same spatial state, $n = n'$, then

$$\psi_{n n}(1,2) = -\psi_{n n}(2,1) = 0$$

Therefore, the electrons do not occupy the same spatial quantum state. This means that two electrons are farther apart, minimizing the repulsive Coulomb interaction between two electrons. Therefore, the energy is decreased.

If two electrons has an anti-symmetric spin arrangement between electron 1 and electron 2, i.e., $\uparrow\downarrow$, then we can write a wave function where electron 1 occupies n state and electron occupies n' state:

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

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

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

According to the exclusion principle,

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

That is

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

Since the spin quantum state is already antisymmetric arrangement, i.e. $\uparrow\downarrow = -\downarrow\uparrow$

We can have both electrons can have symmetric spatial quantum state arrangement

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

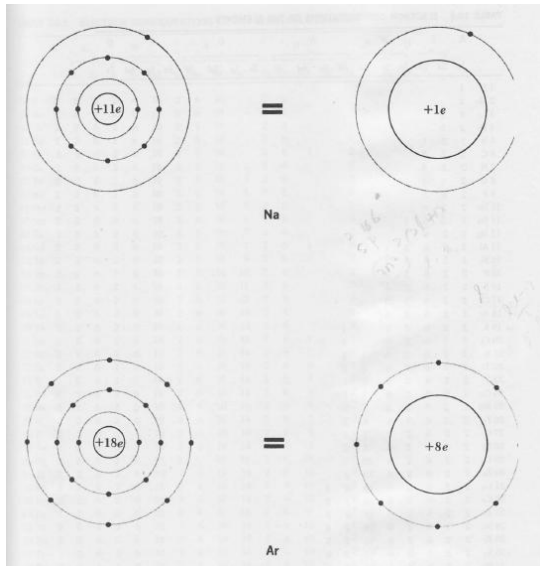
This allows two electrons to be in the same spatial quantum state, which will increase energy.

Therefore, electrons fill the same l state symmetrically first until all l orbitals are filled.

For example, in filling out p orbitals: 3 p orbitals to fill:

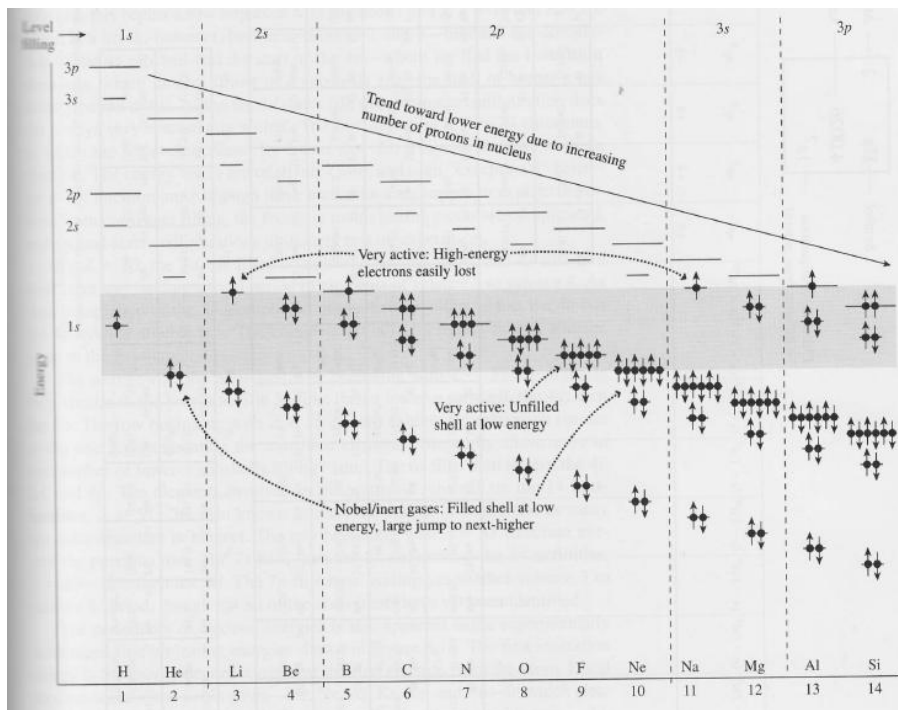
	p_x	p_y	p_z
Lower E	↑		
	↑	↑	
	↑	↑	↑
	↑↓	↑	↑
Higher E	↑↓	↑↓	↑
	↑↓	↑↓	↑↓

Effective charge of the nucleus due to the screening of inner shell electrons:



Electron shielding in Na and AR atoms. Each outer electron in an Ar atom is acted upon by an effective nuclear charge 8 times greater than that acting upon the outer electron in a Na atom, even though the outer electrons in both cases are in the $n=3$ shell.

- Chemical behaviors are determined by the number of valence electrons (= the number of electrons in the highest energy level allowed in a ground state of an atom).
- Noble gas: He ($Z=2$, $n=1$ shell filled), Ne ($Z=10$, $n=2$ shell filled), Ar ($Z=18$, $n=3$, $3s$ and $3p$ shell filled), Kr ($Z=36$, $3s$, $3p$, $3d$, $4s$, $4p$ filled), Xe ($Z=54$, $4s$, $4p$, $4d$, $5s$ and $5p$ filled), Rn ($Z=86$, $4s$, $4p$, $4d$, $4f$, $5s$, $5p$, $5d$, $6s$, $6p$ filled). Chemically inert.
- When there is one valence electron exists or one vacancy exists in the outermost shell, atoms become very active.
- As Z increases, the Coulomb interaction increases between the nucleus and the electrons, resulting in deeper energy levels (lower energy levels).



- Ionization energy: how much energy is necessary to take out one electron from an atom. It is very difficult to get rid of an electron when the shell is filled. It is very easy when fewer electrons exist in the outermost shell.

