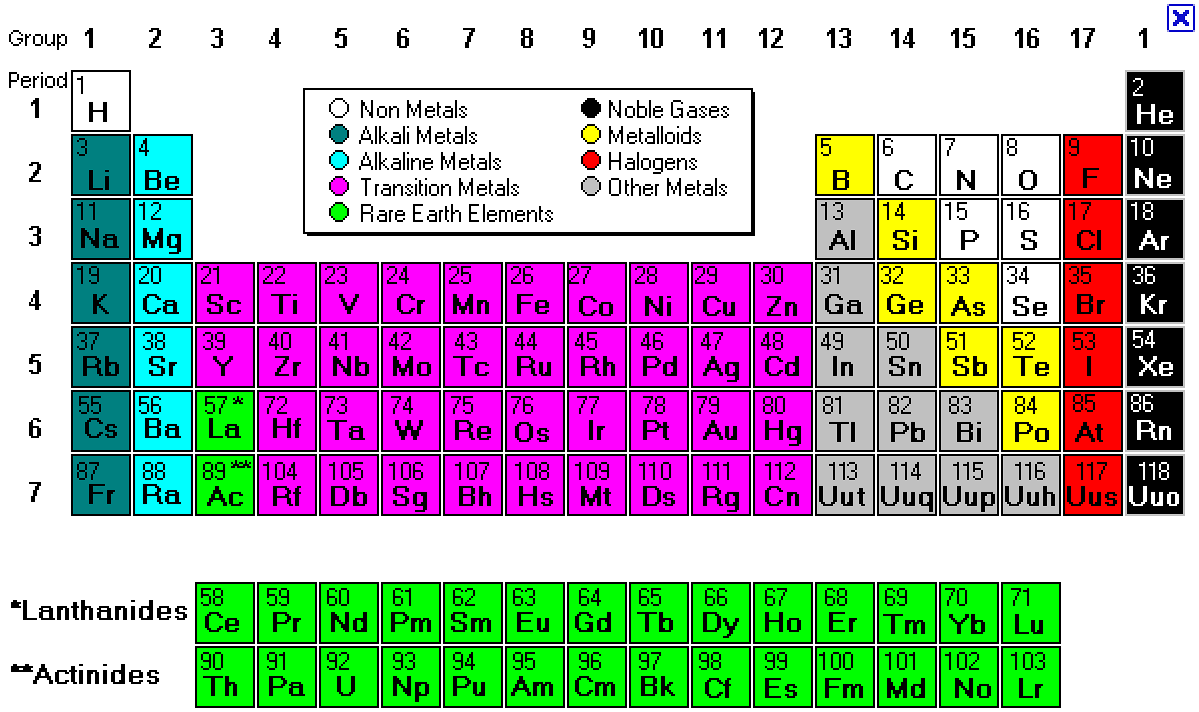
PH102, 2012W, Lecture Notes: January 27, Fri, Class 8



Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	1
Period 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

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 → 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 → 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 $\psi_I or\ \psi_{II}\ is\ right,$ we combine both wave functions in such a way that meet

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

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

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

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

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

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 $\psi_{Anti-Symmetric}$→ Exclusion principle applies.

- When $n = n', \psi_{Anti-Symmetric} = 0.$ → this cannot be the case → 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

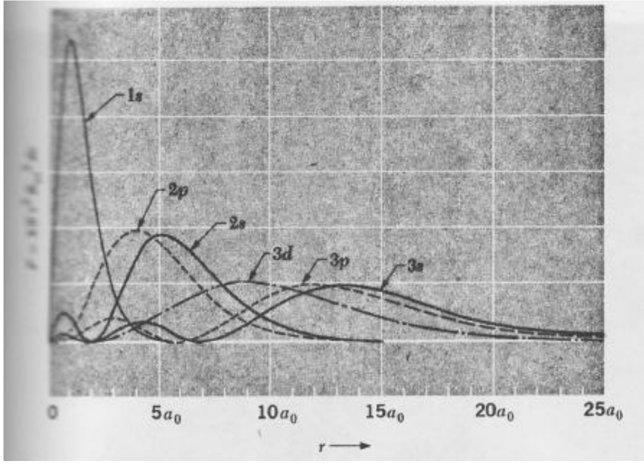
Two basic rules to determine the electron configuration in many-electron atoms:

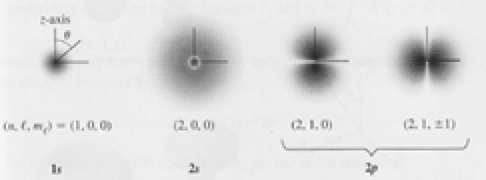
- A system of particles is stable when its total energy is a minimum
- Only one electron can exist in any particular quantum state in an atom (exclusion principle).

Determining what quantum state has lower energy?

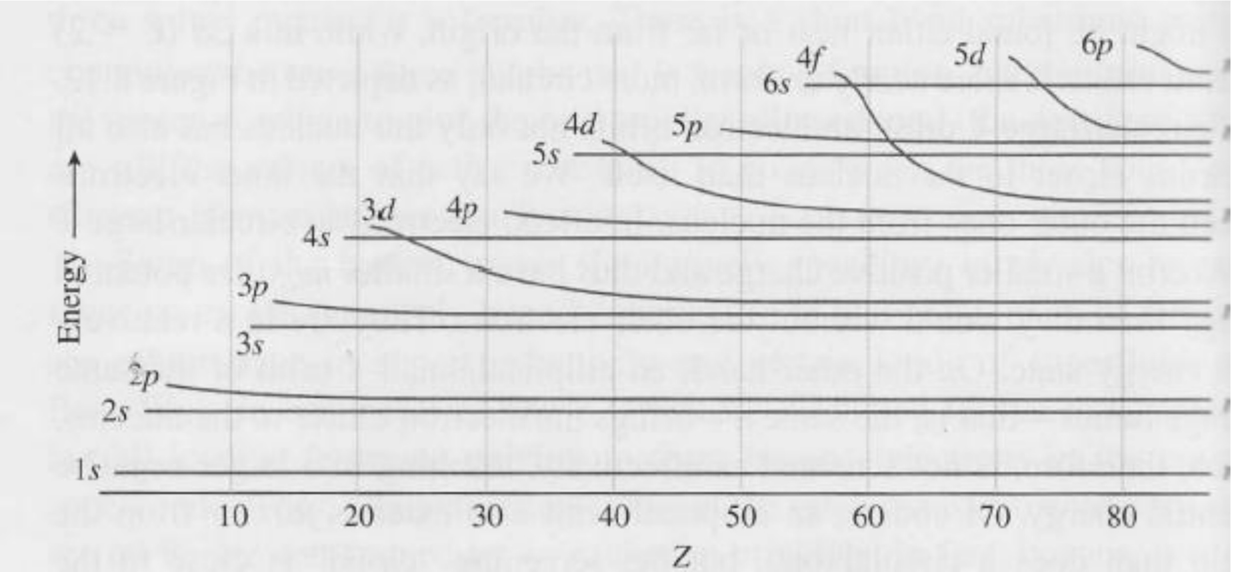
- When n is lower.
- With a given n, when *l* is lower.

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 potential energy, resulting in a lower energy state. This means that the energy of 2*s* is lower than that of 2*p*.





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., ↑↓, 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. ↑↓ = - ↓↑

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

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

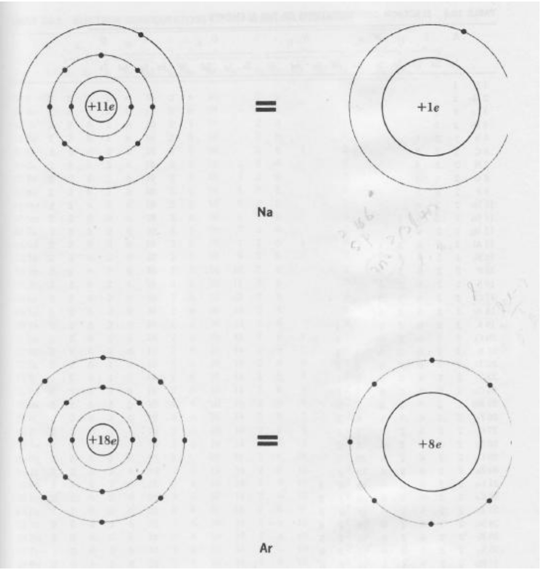
This allows two electrons to be in the same spatial quantum state, which will increase energy.

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:

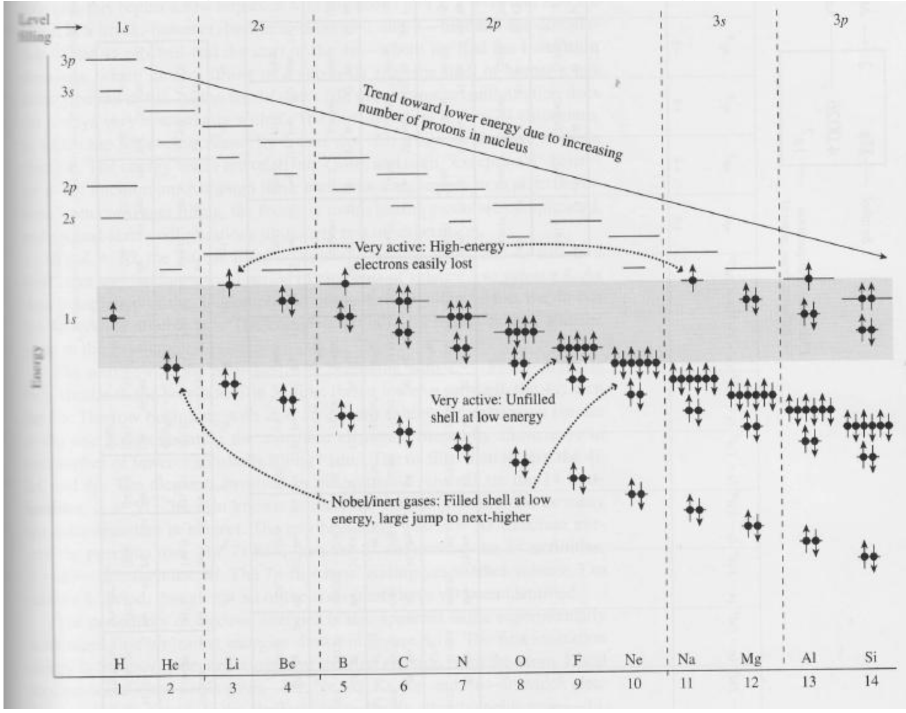
	p_x	p_y	p_z
Lower E	↑		
	↑	↑	
	↑	↑	↑
	↑↓	↑	↑
	↑↓	↑↓	↑
Higher E	↑↓	↑↓	↑↓

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 vey 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.

Figure 8.16 First ionization energies of the elements.