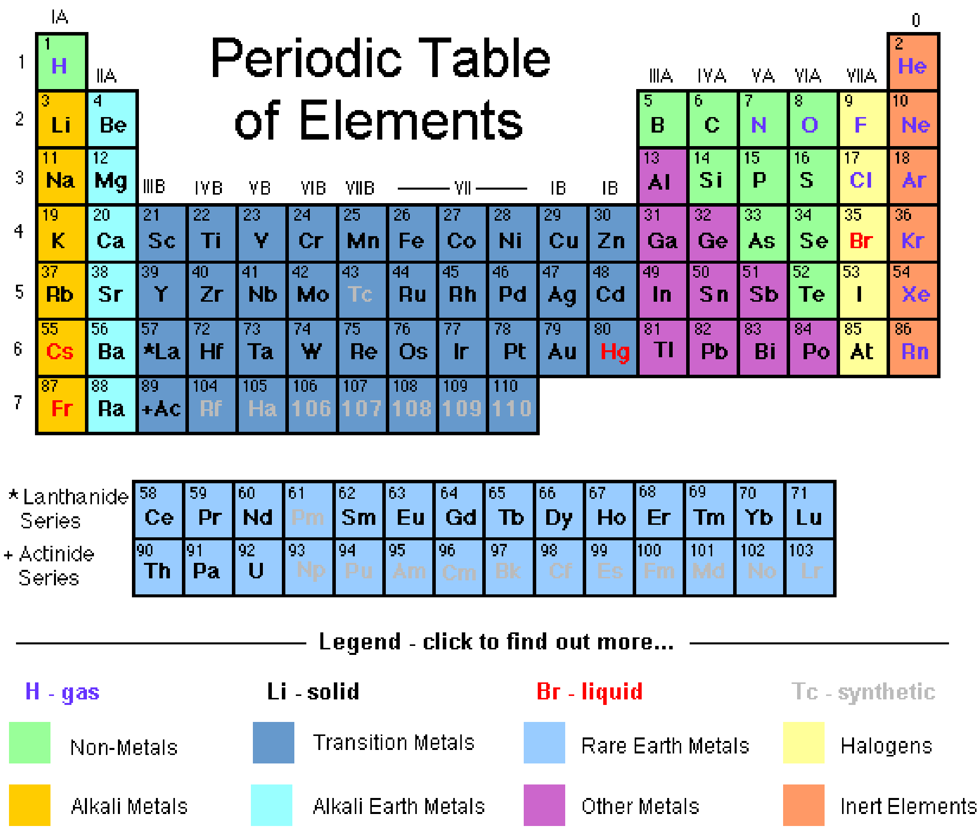
Lecture 5

Building-up principle of the electron shell for larger atoms. Electronic configurations and ground state terms. Hund's rules.



Pauli principle does not allow for two atomic electrons with the same quantum numbers, therefore each next electron will have to have at least one quantum number [n, ℓ, m_ℓ, m_s] different from all the other ones. We will use ↑ for m_s=1/2 and ↓ for m_s=-1/2.

List of distinct sets of quantum number combinations in order of increasing n and ℓ:

	n	ℓ	m_ℓ	m_s
1s	1	0	0	↑
1s	1	0	0	↓
2s	2	0	0	↑
2s	2	0	0	↓
2p	2	1	-1	↑
2p	2	1	0	↑
2p	2	1	1	↑
2p	2	1	-1	↓
2p	2	1	0	↓
2p	2	1	1	↓

1s shell (2 electrons)

2s subshell (2 electrons)

2p subshell (6 electrons)

Maximum number of electrons in a subshell

$$\underbrace{-\ell \le m_\ell \le \ell}_{2\ell+1}$$

$$\underbrace{m_s = \tfrac{1}{2} \text{ or } -\tfrac{1}{2}}_{2(2\ell+1)}$$

Shells with the same n but different l (2s, 2p) may be referred to as either shells or subshells. There are 2 electrons in n=1 shell and 8 electrons in n=2 shell.

Question for the class: what is the total number of electrons in n=3 and n=4 shells?

n=3: 3s [2], 3p[6], 3d[10], so 18
n=4: 4s [2], 4p[6], 4d[10], 4f[14], so 18+14=32

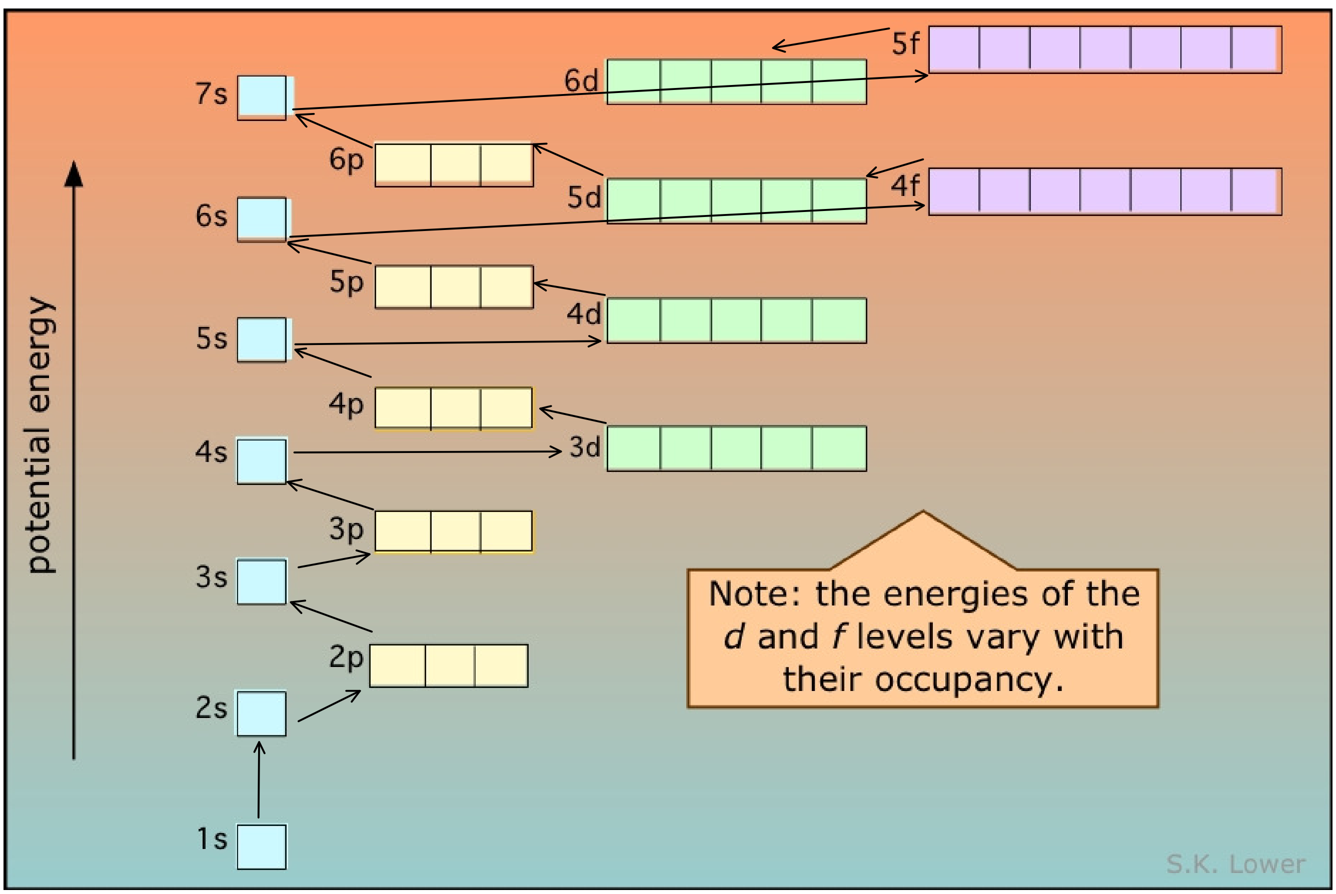
One can also arrive to this as follows: $2\sum_{\ell=0}^{n-1}(2\ell+1) = 2n^2$

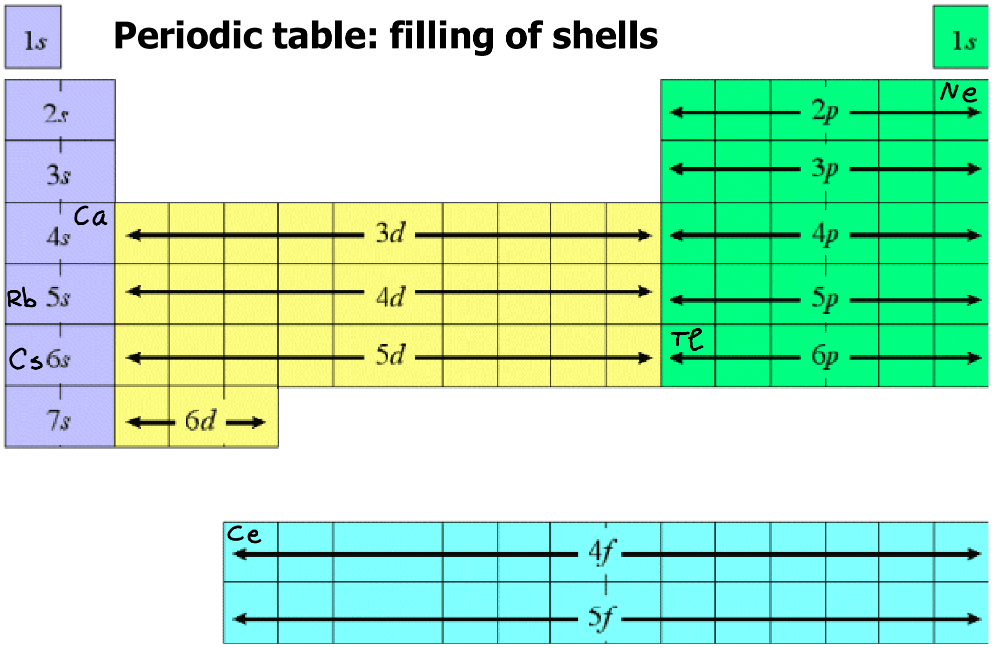
for ↑ and ↓

n=1 2
n=2 8
n=3 18
n=4 32
n=5 50
Σ110

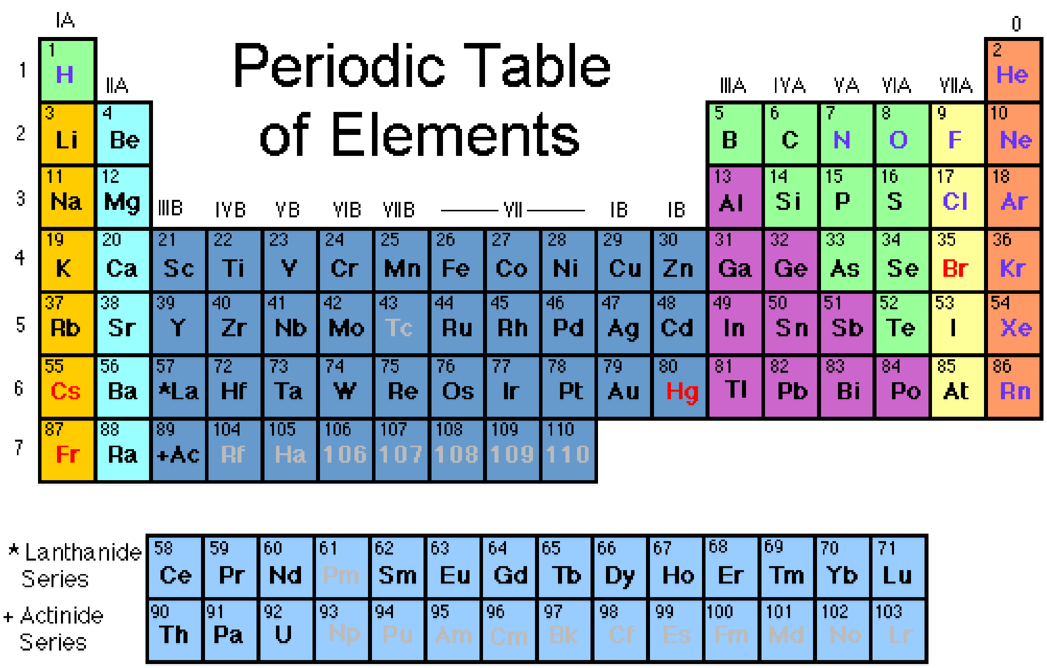
How do these shells get filled in a periodic table, i.e. what are electronic configurations and terms for ground states of all elements in the periodic table?

Rule 1. The Pauli principle is obeyed.
Rule 2. The total energy of all electrons is minimum for atomic ground state.





$\ell = 0$	s
$\ell = 1$	p
$\ell = 2$	d
$\ell = 3$	f



Ne: $\underbrace{1s^2 2s^2 2p^6}_{10}$

Ca: $\underbrace{1s^2 2s^2 2p^6 3s^2 3p^6 4s^2}_{20}$

Rb: $\underbrace{[Ca]_{20}\ \underbrace{3d^{10} 4p^6 5s}_{17}}_{37}$

Class exercise: what are the ground-state electronic configurations for Cs (Z=55) and Tl (Z=81)?

Cs: $n = 1,2,3$ all filled : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ — 28

$n=4$: $4s^2 4p^6 4d^{10}$ — 18

$n=5$: $5s^2\ 5p^6$ — 8

$n=6$: $6s$ — 1

55, ok

Tl: all $n = 1,2,3,4$ filled (60 electrons) $\underbrace{1s^2 \ldots 4d^{10}}_{60}\ \underbrace{5s^2\ 5p^6\ 5d^{10}}_{18}\ \underbrace{6s^2 6p}_{3} = 81$ ok

Periodic table: filling of shells continued.

We now know how to write a configuration for a ground state of an atom. Next, how do we determine the ground state term, i.e. $^{2S+1}L_J$?

We have already done it for H and He. Li, Be, and B can be done in the same way.

Class exercise:

Write ground state terms $^{2S+1}L_J$ for Li (Z=3), Be (Z=4) and B(Z=5).

Li: $\underbrace{1s^2}\,2s$

$\left.\begin{array}{l} L=0 \\ S=0 \\ J=0 \end{array}\right\}$

$2s:\ s=1/2,\ \ell=0 \Rightarrow j=0$ $\boxed{^2S_{1/2}}$ (same as H)

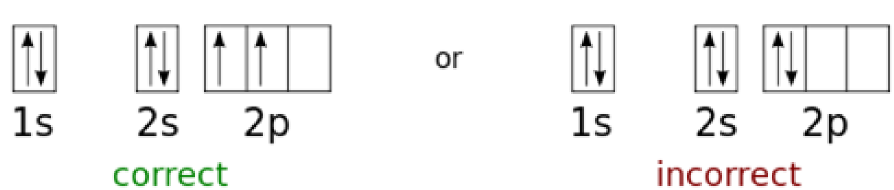
Fully filled shell or subshell can be excluded from consideration of the term since L=0, S=0, and J=0 for all closed subshells

Be: $1s^2 2s^2$ fully closed $s=0,\ l=0,\ j=0$ $\boxed{^1S_0}$ (as He)

B: $\underbrace{1s^2 2s^2}_{\text{fully filled}}\,2p$ $2p:\ \ell=1,\ s=\frac{1}{2} \Rightarrow j=\frac{1}{2},\ \frac{3}{2}$ $\boxed{^2P_{1/2}}$

lowest energy

The next atom is C and there are two possibilities below to place two p electrons:

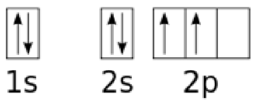


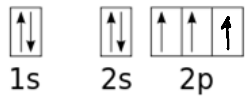
Here, **Rule 2: "The total energy of all electrons is minimum for atomic ground state"** comes into play. Parallel spin wave function is symmetric and corresponding spatial wave function is antisymmetric. Antisymmetric spatial wave function describes an electron distribution where electrons are further apart than for symmetric wave function. Then, the mutual Coulomb repulsion is smaller and energy is lower.

This is described by

Hund's first rule: for every atomic ground state, the total electron spin has maximum value tolerated by the Pauli principle.

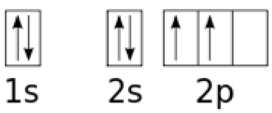
Thus, for carbon S=1 and for nitrogen S=3/2.



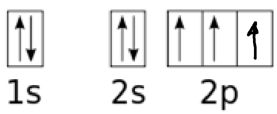


$m_s = 1/2 + 1/2 = 1 \Rightarrow$
S can not be less than 1

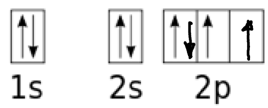
$m_s = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} \Rightarrow S = 3/2$ (can not be less than m_s)



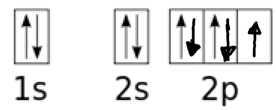
C $\quad {}^3P_0$



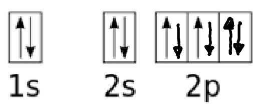
N $\quad {}^4S_{3/2}$



O $\quad {}^3P_2$



F $\quad {}^2P_{3/2}$

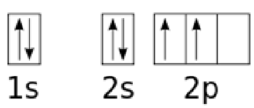


Ne $\quad {}^1S_0$ - fully filled

In general, terms can be determined by applying three Hund's rules.

Hund's second rule: for a given spin, the term with the largest value of the total orbital angular momentum quantum number L, consistent with overall antisymmetrization, has the lowest energy.

Carbon



S=0, L=1 as L=2 is symmetric
("top of the ladder" $M_L = L$ is symmetric)

Hund's third rule: if an outermost subshell is half-filled or less, the level with the lowest value of the total angular momentum J=|L-S| has the lowest in energy. If the outermost subshell is more than half-filled, the level with the highest value of J=L+S has the lowest energy.

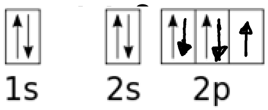
B: $\underbrace{1s^2\, 2s^2}_{\text{fully filled}},\ 2p$

2p: $l = 1,\ s = \frac{1}{2} \Rightarrow j = \frac{1}{2}, \frac{3}{2}$ $\quad \boxed{{}^2P_{1/2}}$

↑ lowest energy
shell less than 1/2 filled

Questions for the class:

1. Why J=3/2 for fluorine (Z=9) ground state (term ^2P **).**

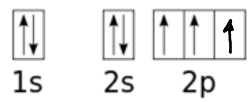


2p shell is more than half full, so j=l+1/2 according to third Hund's rule, as S=1/2 and L=1.

F $\quad ^2P_{3/2}$

2. Why nitrogen ground state is $^4S_{3/2}$ **?**

Nitrogen: $(1s)^2(2s)^2(2p)^3$



$S = 3/2$

spin state. Need antisymmetric spatial wave function with highest value of L.
It has to be L=0 for the following reason. Let's list all possible quantum numbers for three 2p electrons (all sets have to be different in at least one).

(we "number" them for convinience)

	1	2	3
n	2	2	2
l	1	1	1
s	1/2	1/2	1/2
m_s	1/2	1/2	1/2
m_l	−1	0	1

[so we can get $S = 3/2$ ↑↑↑] $M_S = 3/2$

$M_L = -1 + 0 + 1 = 0$

These must differ. We are not allowed to have two fermions with identical quantum numbers. Therefore, total M_L=0 and total L can only be 0 if M_L is fixed to 0.

$S = 3/2 \quad L = 0 \Rightarrow J = 3/2$ and ground state is $\boxed{^4S_{3/2}}$