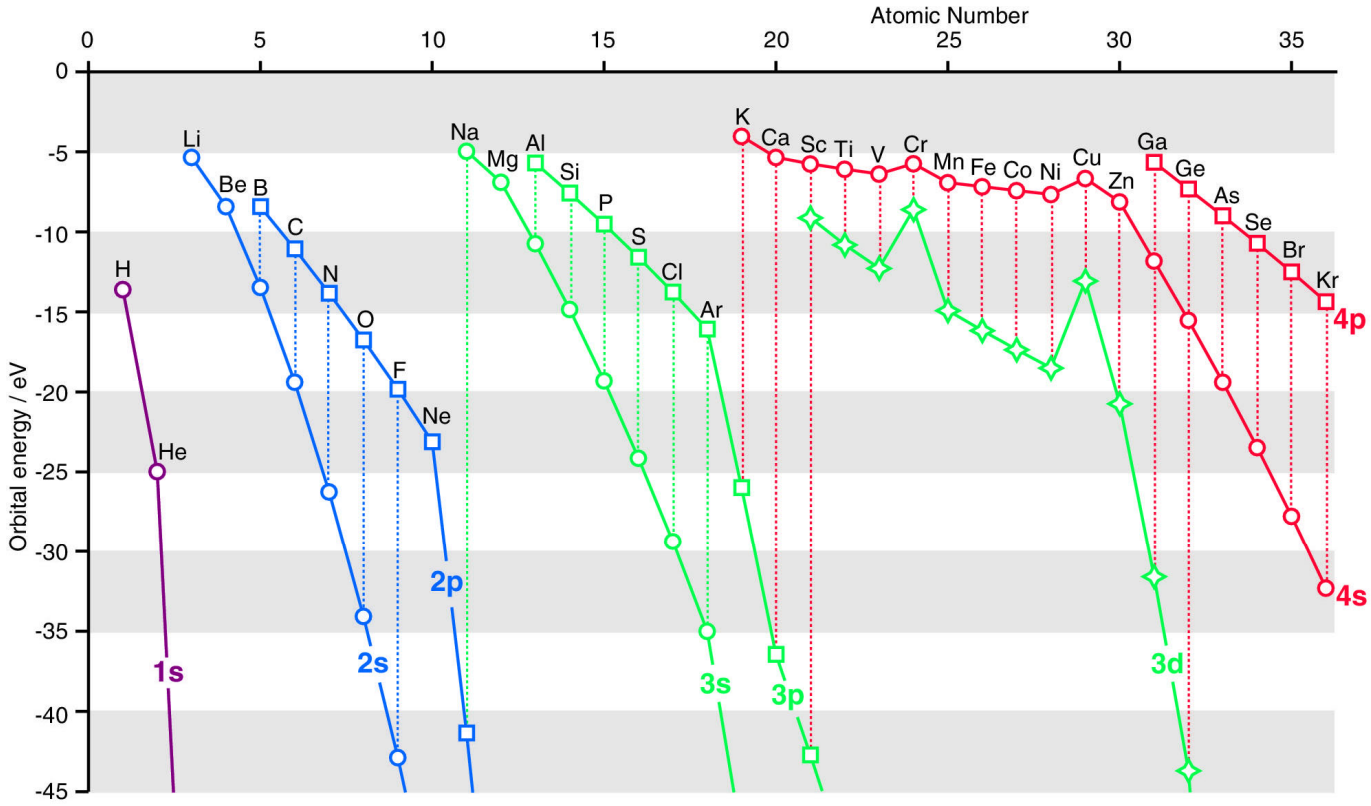
Orbital Energies

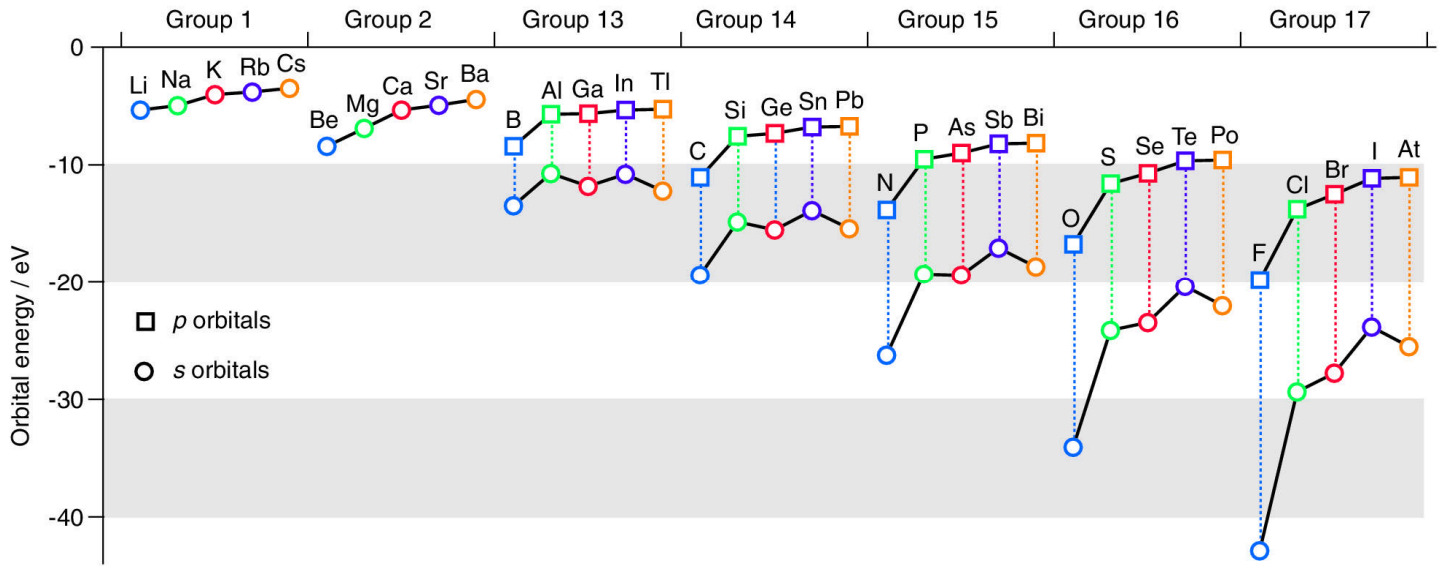
(-)Orbital Energies



- Sc to Zn: 3d electrons added effectively screens 4s electrons
- Ga to Kr: 4p electrons ineffective screen for 4s
- 2s and 2p: Successive electrons added do not screen each other very well

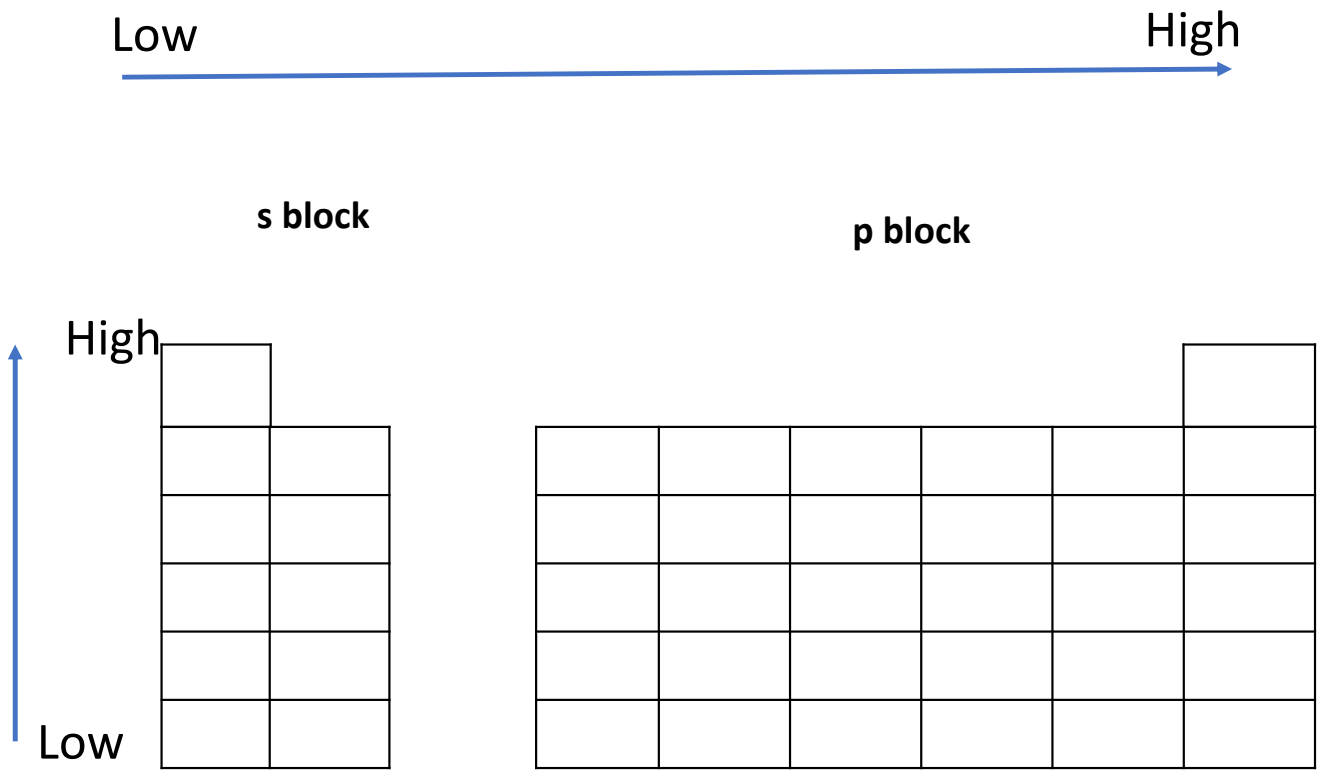
Orbital Energy Variation

Orbital Energy ~ Z_{eff}^2/n^2



Down the group (-)orbital energy decreases- n^2 dominates

(-)Orbital Energies (generally!!!)



Trends : Bonding between elements (Non-metals)

The Effect of Orbital Size and Energy Mismatch

- When two different elements combine, the size of interacting AO's and energies will differ
- Size of AO's determine strength of bonds as well as the nature
- When orbital energies are closely matched, equal sharing of electrons lead to "covalent" bond
- However, large difference of energies between Aos can still give rise to strong bonds
- In extreme cases an electron transfer can give rise to an "ionic" bond

Size mismatch between orbitals

Molecule	H_2	HLi	HNa	HK	HRb	HCs
Bond strength kJ/mol	436	238	186	175	167	175

Generally, if two similar valance orbital of approximately same energy combine, the smaller the orbital, the stronger the bond

π-Bonding

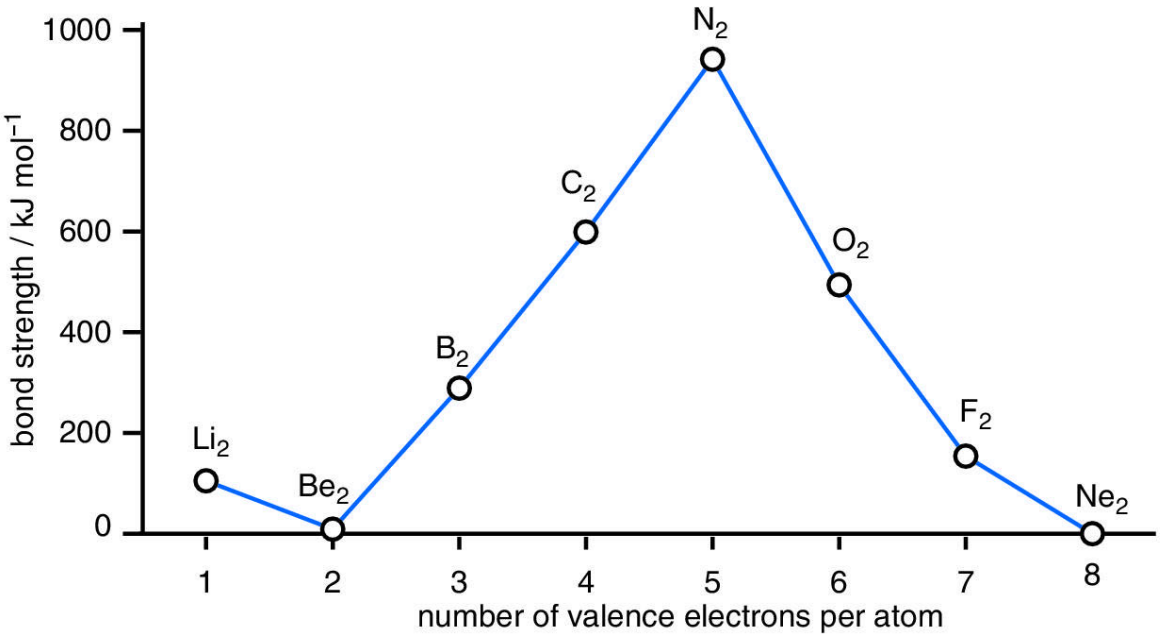
π-bonds are more susceptible to size of orbitals

Table 9.2 Calculated barriers to rotation (kJ mol^{-1}) about various π bonds

2*p*–2*p* overlap	barrier	2*p*–3*p* overlap	barrier	3*p*–3*p* overlap	barrier
$H_2C{=}CH_2$	274	$H_2C{=}SiH_2$	149	$H_2Si{=}SiH_2$	105
$H_2C{=}NH$	265	$H_2C{=}PH$	180	$H_2Si{=}PH$	120
$HN{=}NH$	251	$HN{=}PH$	185	$HP{=}PH$	142

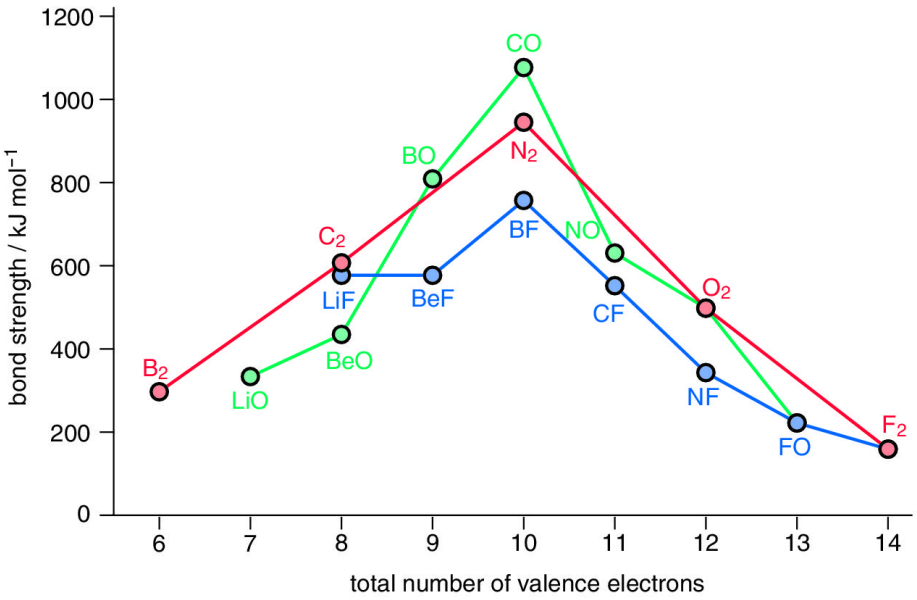
The rapid fall-off in strength of the π-bonding accounts for the fact that it is often preferred between period 2 elements

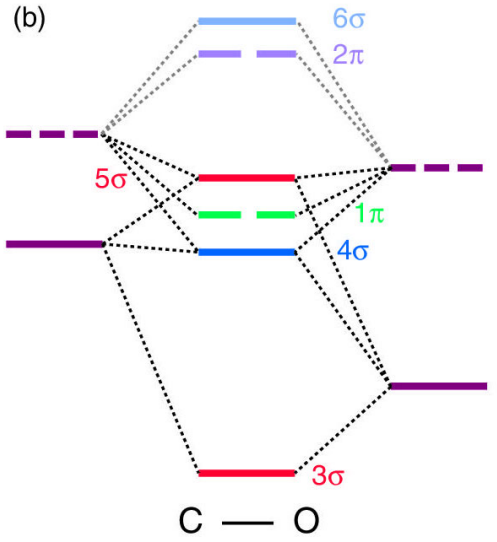
Recall: Bond Strength Variation Across Period



N_2 has enough electrons to fill all bonding MO while only one anti-bonding MO is filled

Bond strengths, measured in the gas phase of the period 2 heteronuclear diatomics



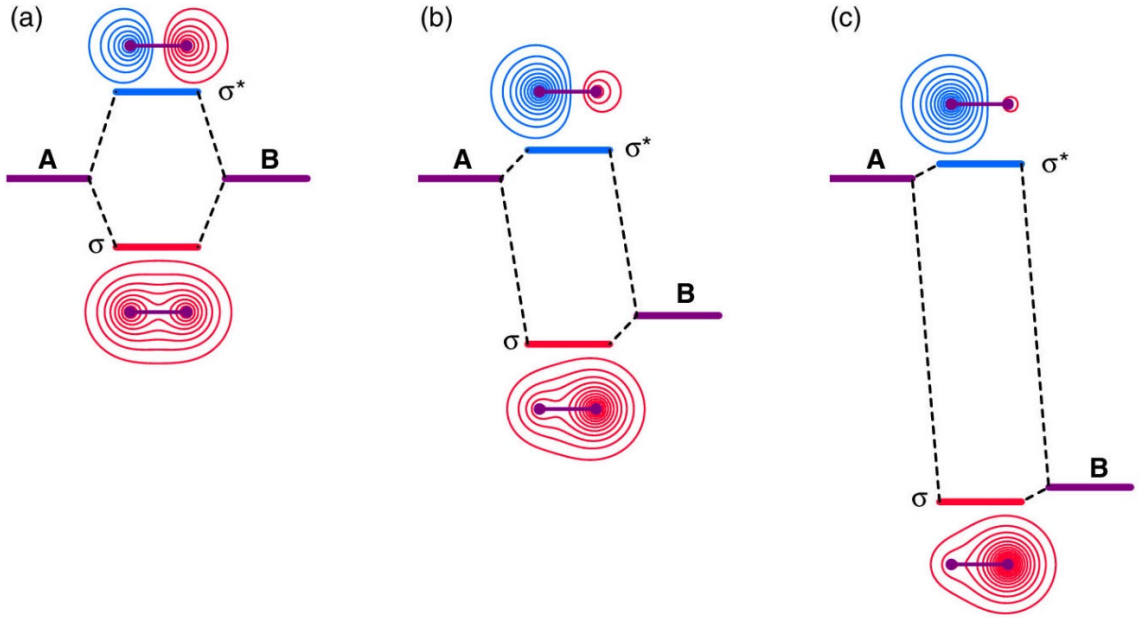


While the bond strengths follow the same the same trend for homonuclear diatomics, the nature of bonding substantially changes

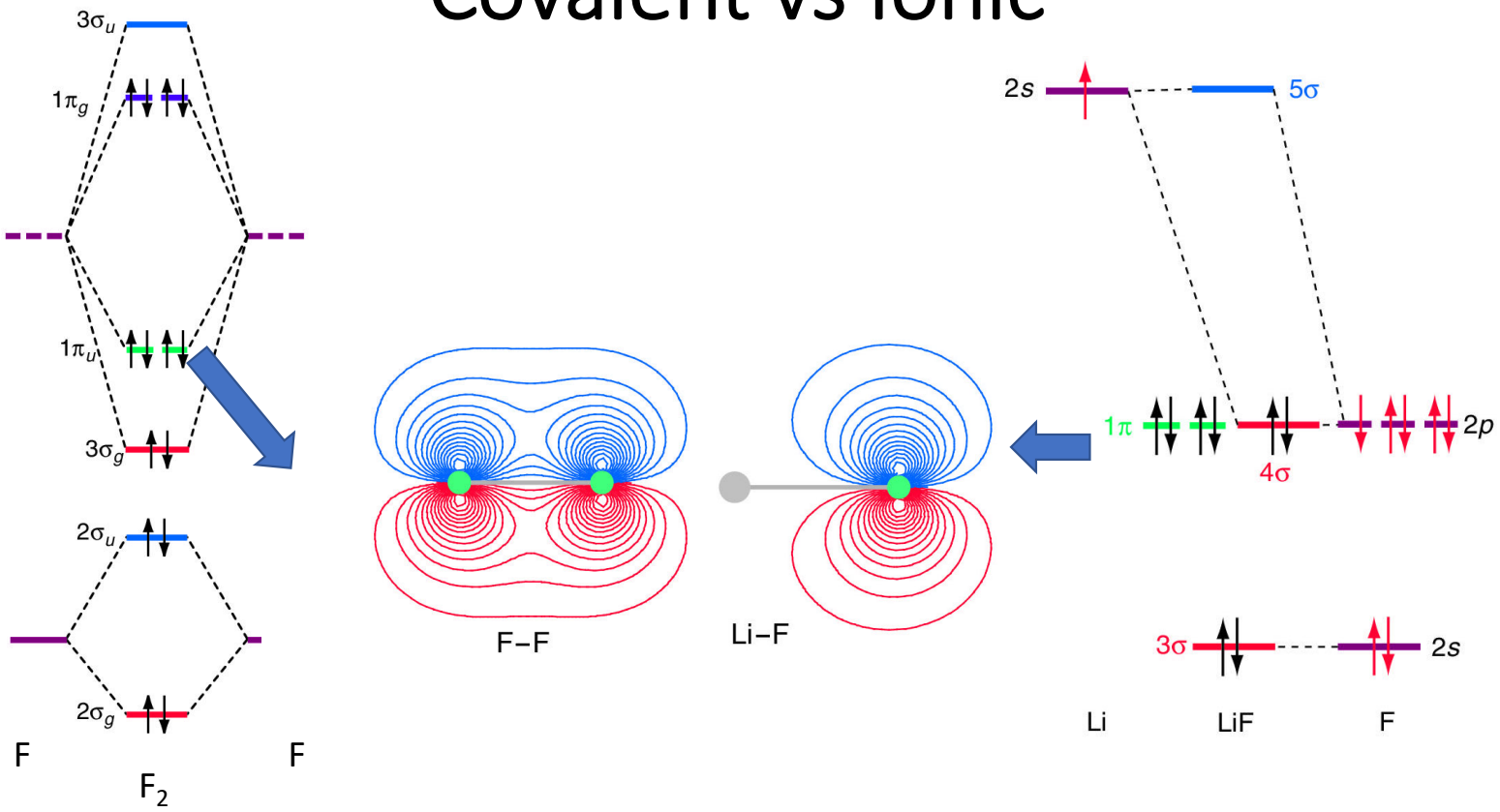
Covalent vs Ionic: Orbital Energy Differences

Orbital energy differences affects not only the strength but also the nature of the bonds

Recall:

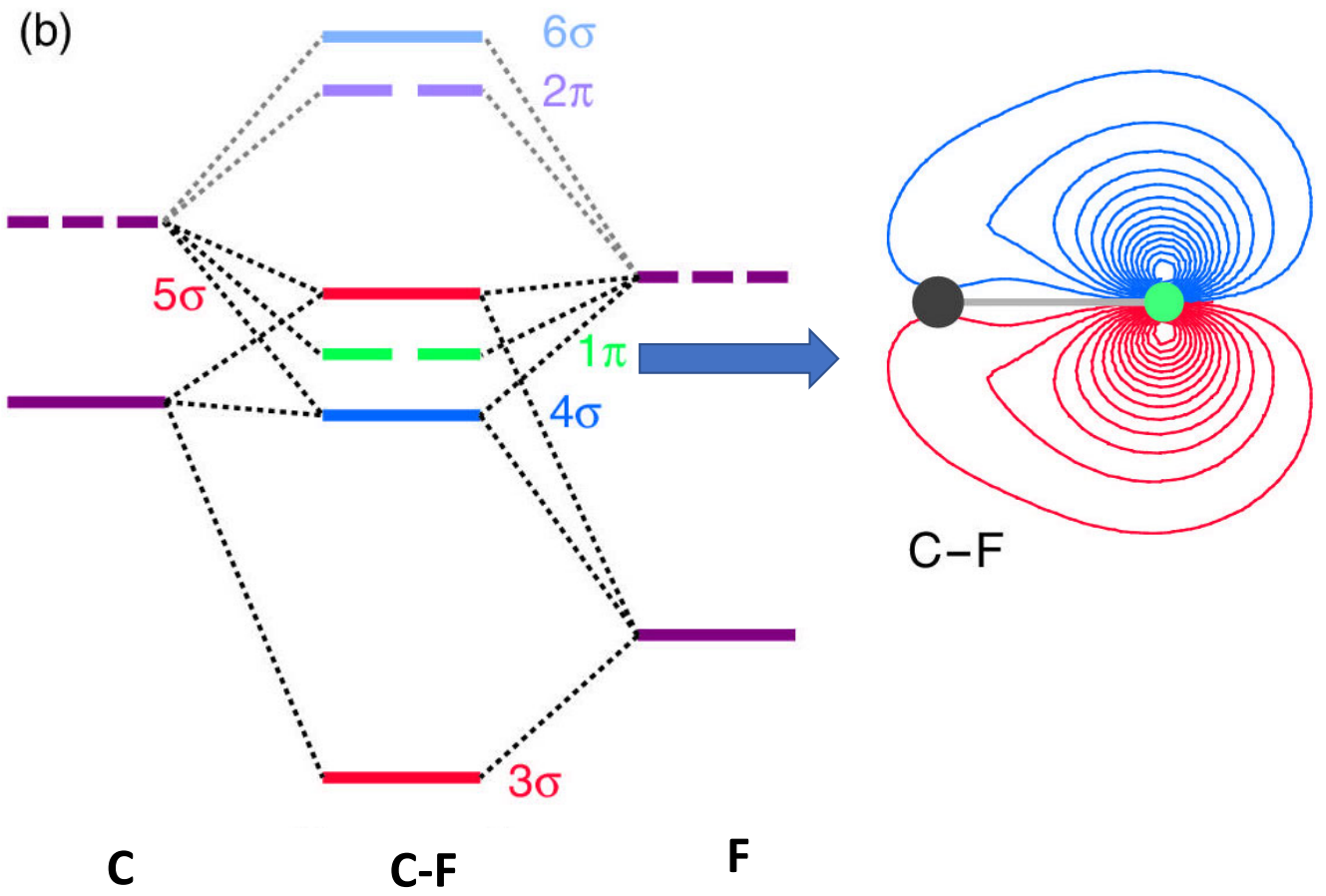


Covalent vs Ionic

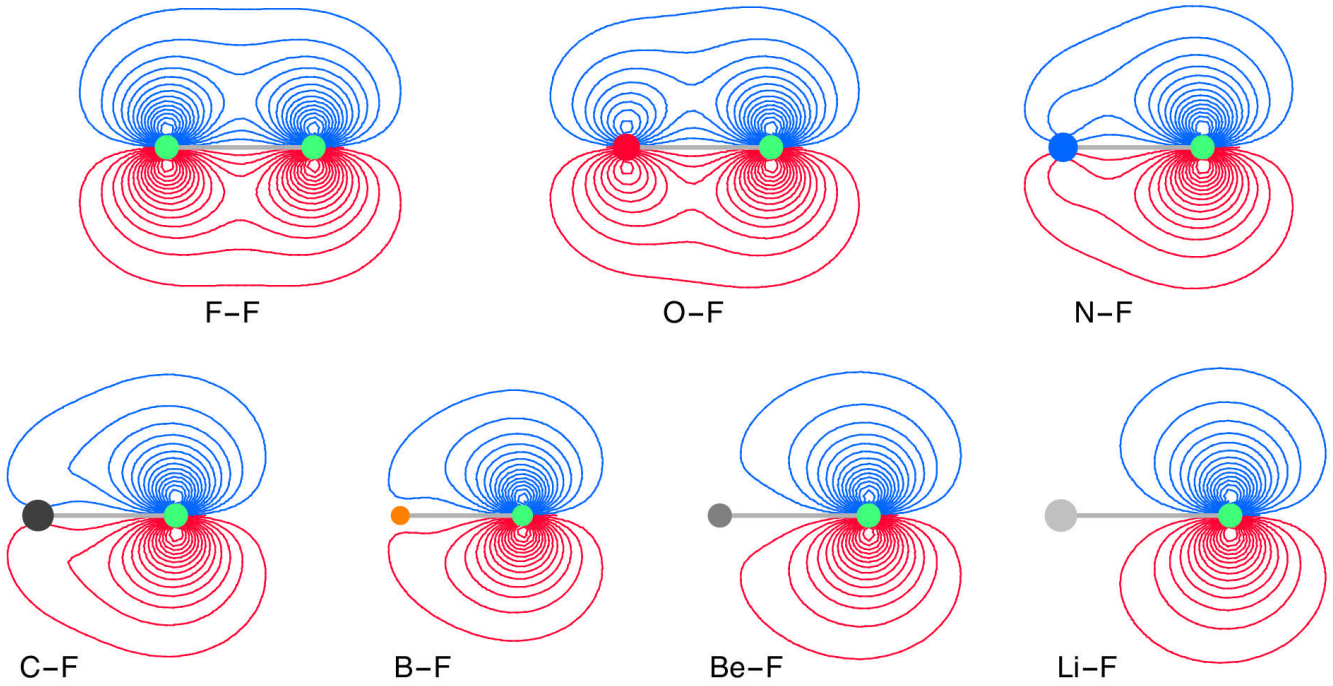


- The fractional charges are + 0.7 and - 0.7 on Li and F
- It require approximately 577 kJmol^{-1} (about 6 eV) to break Li-F bond
- However, it produces Li and F atoms in gas phase

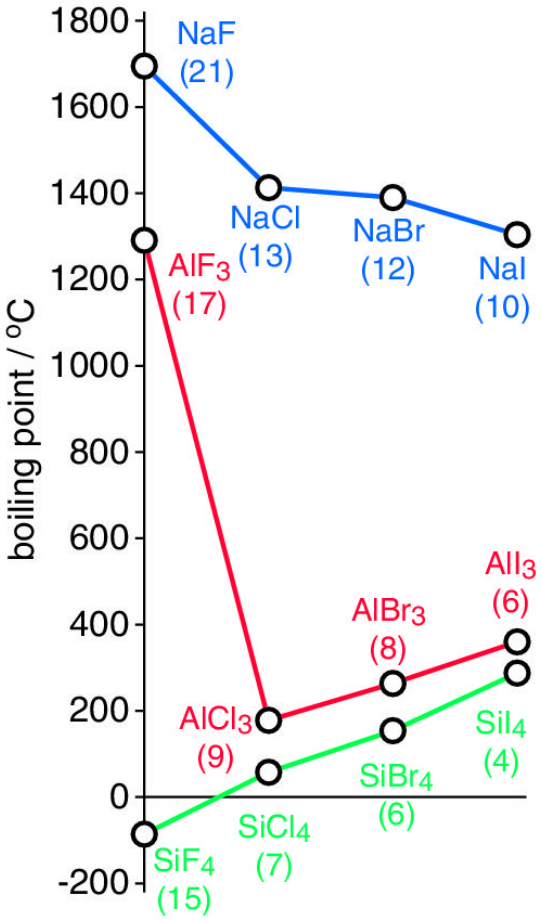
The C-F Bond



Covalent vs Ionic



Orbital Energy and Bond type



Van Arkel Diagram