Chapter 6 – Chemical Bonding

* Diatomic Molecules & Lewis Structures
   **-** Diatomic molecules include: H_2, N_2, O_2, F_2, Cl_2, Br_2, or I_2
    - Lewis proposed that electrons are shared between neighboring atoms and thereby
        form bonds - this type of bond is called a <u>covalent bond</u>
        -- each atom wants to be like a noble gas and noble gases have eight electrons in
          their highest energy shell
        -- <u>octet rule</u>: atoms in group IA - VIIA tend to form bonds which result in eight
          electrons
    - <u>valence electrons</u>: the electrons which are most readily available for bonding
        -- e.g. F - $\underbrace{1s^2}_{core}\underbrace{2s^2 2p^5}_{valence}$ (v.e. = 7) and S - $\underbrace{1s^2 2s^2 2p^6}_{core}\underbrace{3s^2 3p^4}_{valence}$ (v.e. = 6)

        -- general trends:
            --- Group 1A has 1 v.e. (H - Cs)
            --- Group 2A has 2 v.e. (Be - Ba)
            --- Group 3A has 3 v.e. (B - In)
            --- Group 4A has 4 v.e. (C - Sn)
             --- Group 5A has 5 v.e. (N - Sb)
            --- Group 6A has 6 v.e. (O - Se)
            --- Group 7A has 7 v.e. (F - I)
            --- Group 8A has 8 v.e. (He - Xe)
    - Lewis structures - show how atoms in a molecule are bonded and take into
        account the <u>lone pairs</u> (pairs of electron which belong to a particular atom and
        don't take part in bonding to other atoms)
   -- Ex: O_2, N_2

        -- O_2 is connected by a double bond where as N_2 is connected by a triple

*Are the bonding electrons in NO^+ shared equally?
    - <u>polar covalent bonds</u>: when the electrons forming a bond between two atoms are
        shared unequally
        -- they are drawn more closely to the more electronegative atom
        -- change in electronegativity between atoms leads to a bond which is polarized
    - <u>electronegativity</u>: an atom's ability to attract electrons
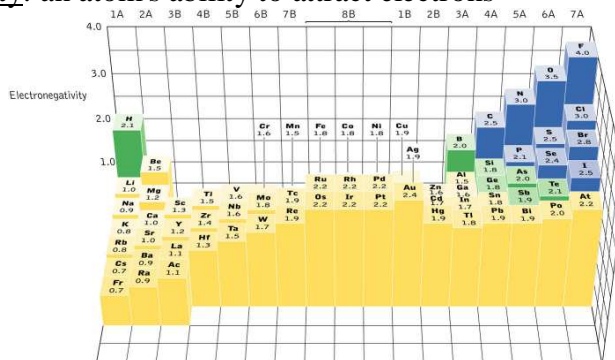
-- draw the trend
-- In HBr, which end is more electron rich? Br since it is more EN
-- when the EN difference between 2 atom is 2 or greater the bond is considered
   ionic - which means the more EN atom has possession of the bonding
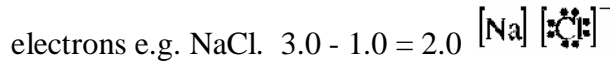
    electrons e.g. NaCl. 3.0 - 1.0 = 2.0 $[Na] [\ddot{\ddot{Cl}}]^-$
-- Which of the following pairs of elements form the most polar bond?
      a.) O & S: 3.5 - 2.5 = 1.0
      b.) Be & Cl: 3.0 - 1.5 = 1.5
      c.) N & H: 3.0 - 2.0 = 1.0
      d.) C & F: 4.0 - 2.5 = 1.5
- periodic trends
  -- atomic radius
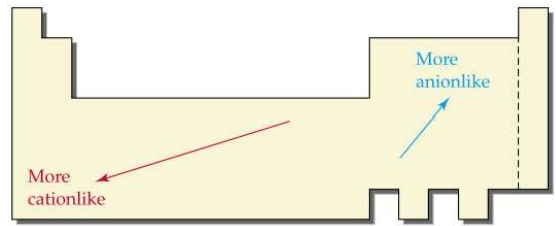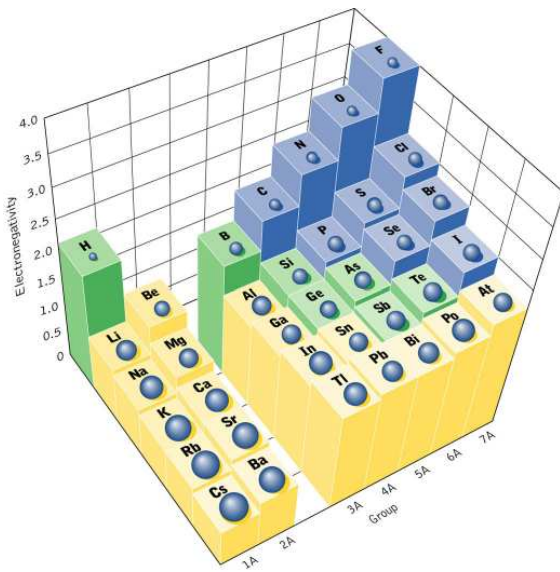
    --- show trend
    --- if the electrons are held more tightly by an atom then it makes sense if
   that the atomic radius would be smaller
  -- ionization energy
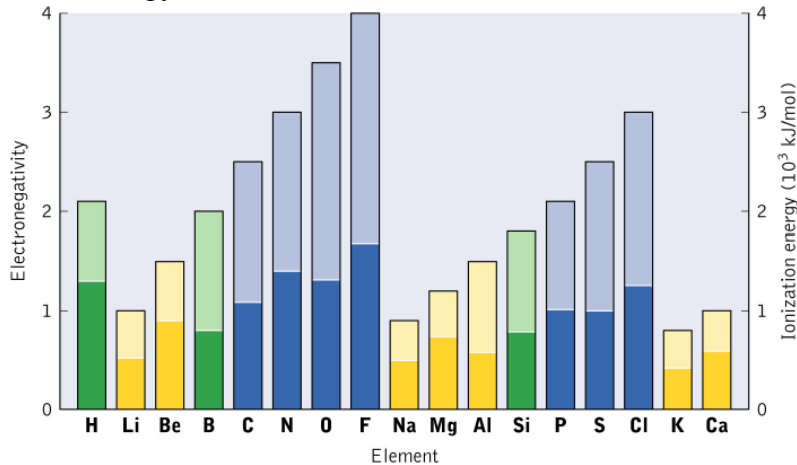
--- amount of energy required to remove an electron: $X \rightarrow X^+ + e^-$
--- several factors:
---- the EN an atom is the more energy it takes to remove an electron
---- if removing an electron makes an atom obtain a noble gas configuration it will take less energy - e.g. the alkali metals
---- if removing an electron will lead to a half filled (e.g. O) or empty subshell (e.g. B) then it will take less energy
-- <u>electron affinity</u> - in simple terms it's the attraction between an electron and an atom: $X + e^- \rightarrow X^-$
--- technically it is the energy change that occurs when a mole of gaseous atoms combine with a mole of electrons - creating a -1 ion
--- several factors:
---- when the addition of an electron will lead to a noble gas configuration then the atom will have a very high EA (e.g. halogens)
---- when the addition of an electron will lead to half-filled subshell then the atom will have a higher EA (e.g. C & Si)

*Lewis Structures
- ozone: an <u>allotrope</u> of oxygen (O_3 vs O_2)
-- an allotropes are occur when there are two or more different forms of the same elements
-- they have very different physical and chemical properties
- drawing Lewis structures (e.g. CO_2)
Step 1: Draw the skeleton such that the least EN element is in the middle (exception is H_2O)
O$-$C$-$O
Step 2: Determine the number of valence electrons (H)
H = 2*6 + 4 = 16
Step 3: Determine the number of electrons needed to make an octet for each element (N)
Exceptions: alkali (need only 2 e-'s) an alkaline earth metals (need 4 e-'s) and boron (needs 6 e'-s) and H (needs 2 e-'s)
N = 3*8 = 24
Step 4: Calculate the number of electrons which will be shared in the molecule (S)
S = (N-H) = 24 - 16 = 8
Step 5: Cal culate the number of bonds: S/2 = 8/2 = 4
Step 6: add the bonds to the skeleton
O=C=O
Step 7: Add the non-bonding electrons to the structure as lone pairs
:Ö=C=Ö:
the lone pairs go to the O-atoms in order to make them octets
- Example exercises: Draw the Lewis structures of the following: $CHCl_3$, HCN, OH$^-$.
$CHCl_3$
Step 1: Draw the skeleton

$$\begin{array}{c} \text{Cl} \\ | \\ \text{H}-\text{C}-\text{Cl} \\ | \\ \text{Cl} \end{array}$$
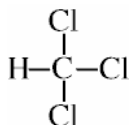
Step 2: Determine (H)

H = 3*7 + 4 +1 = 26

Step 3: Determine (N)
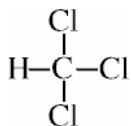
N = 2 + 4*8 = 34

Step 4: Calculate (S)

S = (N-H) = 34 - 26 = 8

Step 5: Calculate the number of bonds: S/2 = 8/2 = 4

Step 6: add the bonds to the skeleton

$$\begin{array}{c} \text{Cl} \\ | \\ \text{H}-\text{C}-\text{Cl} \\ | \\ \text{Cl} \end{array}$$

Step 7: Add the non-bonding electrons to the structure as lone pairs

$$\begin{array}{c} :\ddot{\text{Cl}}: \\ | \\ \text{H}-\text{C}-\ddot{\text{Cl}}: \\ | \\ :\ddot{\text{Cl}}: \end{array}$$

the lone pairs go to the Cl-atoms in order to make them octets

HCN

Step 1: Draw the skeleton

H−C−N

Step 2: Determine (H)

H = 5+ 4 +1 = 10

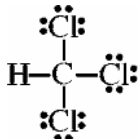Step 3: Determine (N)

N = 2 + 2*8 = 18

Step 4: Calculate (S)

S = (N-H) = 18 - 10 = 8

Step 5: Calculate the number of bonds: S/2 = 8/2 = 4

Step 6: add the bonds to the skeleton

H−C≡N

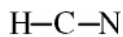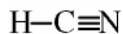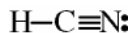Step 7: Add the non-bonding electrons to the structure as lone pairs

H−C≡N:

the lone pairs go to the N-atom in order to make them octets

OH⁻

Step 1: Draw the skeleton

H−O

Step 2: Determine (H)

H = 6+1+1 = 8

Step 3: Determine (N)

N = 2 + 8 = 10

Step 4: Calculate (S)

S = (N-H) = 10 - 8 = 2

Step 5: Calculate the number of bonds: S/2 = 2/2 = 1

Step 6: add the bonds to the skeleton

H—O

Step 7: Add the non-bonding electrons to the structure as lone pairs

H—$\ddot{\underset{..}{O}}\!\!:^{-}$

the lone pairs go to the O-atom in order to make them octets

*Resonance Lewis Structures

- <u>resonance structures</u>: Lewis structures with the same skeleton but different bonding arrangements

Example: Draw all the resonance structures for the azide (N_3^-) and nitronium (NO_2^+) ions

N_3^-

Step 1: Draw the skeleton

  N—N—N

Step 2: Determine (H)

  H = 3*5+1 = 16

Step 3: Determine (N)

  N = 3*8 = 24

Step 4: Calculate (S)

  S = (N-H) = 24 - 16 = 8

Step 5: Calculate the number of bonds: S/2 = 8/2 = 4

Step 6: add the bonds to the skeleton

  N—N≡N N≡N—N N=N=N

Step 7: Add the non-bonding electrons to the structure as lone pairs

$$\left[:\!\ddot{\underset{..}{N}}\!\!-\!N\!\equiv\!N\!:\right]^{-}\!\!\leftrightarrow\left[:\!N\!\equiv\!N\!-\!\ddot{\underset{..}{N}}\!:\right]^{-}\!\!\leftrightarrow\left[:\!\ddot{N}\!\!=\!N\!=\!\ddot{N}\!:\right]^{-}$$

NO_2^+

Step 1: Draw the skeleton

  O—N—O

Step 2: Determine (H)

  H = 5+2*6-1 = 16

Step 3: Determine (N)
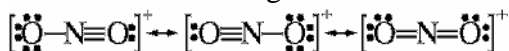
  N = 3*8 = 24

Step 4: Calculate (S)

  S = (N-H) = 24 - 16 = 8

Step 5: Calculate the number of bonds: S/2 = 8/2 = 4

Step 6: add the bonds to the skeleton

  O—N≡O O≡N—O O=N=O

Step 7: Add the non-bonding electrons to the structure as lone pairs

$$\left[:\!\ddot{\underset{..}{O}}\!\!-\!N\!\equiv\!O\!:\right]^{+}\!\!\leftrightarrow\left[:\!O\!\equiv\!N\!-\!\ddot{\underset{..}{O}}\!:\right]^{+}\!\!\leftrightarrow\left[:\!\ddot{O}\!\!=\!N\!=\!\ddot{O}\!:\right]^{+}$$

* Do all resonance forms of a molecule contribute equally?

- <u>formal charges</u>: used to access stability of a Lewis structure

 -- formal charge = H_{atom} - # of e-'s assigned to the atom

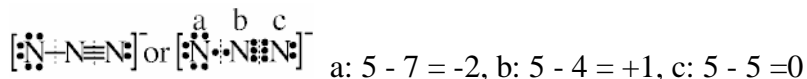 -- the more formal charges a structure possesses the less stable the structure is

 -- the less stable a structure the less it contributes to the bonding of the molecule

-- when a + charge is placed on a more EN atom in a structure than that structure is less stable
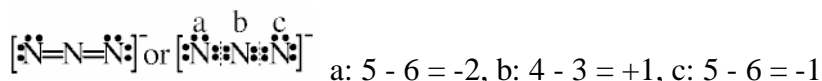
- Examples:

Which resonance structure(s) of the azide (N_3^-) and nitronium (NO_2^+) ions contributes the most to the true bonding picture.
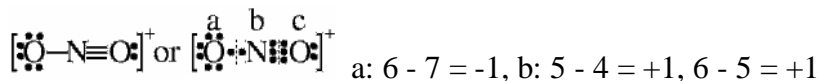
N_3^-

$$[:\ddot{N}{-}N{\equiv}N:]^- \text{ or } [:\overset{a}{\ddot{N}}{\cdot}{\cdot}\overset{b}{N}\overset{c}{\colonbox{N}}:]^-$$ a: 5 - 7 = -2, b: 5 - 4 = +1, c: 5 - 5 = 0

this is the same case for $[N{\equiv}N{-}\ddot{N}:]^-$

$$[:\ddot{N}{=}N{=}\ddot{N}:]^- \text{ or } [:\overset{a}{\ddot{N}}{\colon}{\colon}\overset{b}{N}{\colon}{\colon}\overset{c}{\ddot{N}}:]^-$$ a: 5 - 6 = -2, b: 4 - 3 = +1, c: 5 - 6 = -1
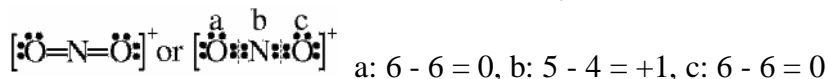
because it possesses the least number of formal charges the last structure contributes the most to the bonding of azide

NO_2^+

$$[:\ddot{O}{-}N{\equiv}O:]^+ \text{ or } [:\overset{a}{\ddot{O}}{\cdot}{\cdot}\overset{b}{N}\overset{c}{\colonbox{O}}:]^+$$ a: 6 - 7 = -1, b: 5 - 4 = +1, 6 - 5 = +1

the second structure is the same as this one, $[:O{\equiv}N{-}\ddot{O}:]^+$

$$[:\ddot{O}{=}N{=}\ddot{O}:]^+ \text{ or } [:\overset{a}{\ddot{O}}{\colon}{\colon}\overset{b}{N}{\colon}{\colon}\overset{c}{\ddot{O}}:]^+$$ a: 6 - 6 = 0, b: 5 - 4 = +1, c: 6 - 6 = 0
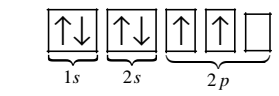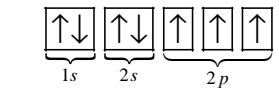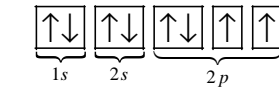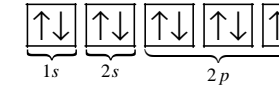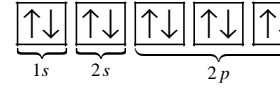
because the last structure does not place a + charge on the very EN O-atom and it possesses the lesser number of formal charges it contributes most to the bonding of nitronium

*You've heard of atomic orbitals – how are they related to molecules
- **when two atoms come together and create a bond - their atomic orbitals overlap and create molecular orbitals**
- <u>delocalized molecular orbitals</u>: combinations of atomic orbitals which are spread out over the entire molecule
- Recall: orbital diagrams from Chapter 3

Element	Electron Configuration (EC)	Orbital Diagram
H	$1s^1$	[↑] $1s$
He	$1s^2$	[↑↓] $1s$
Li	$1s^2 2s^1$	[↑↓] [↑] $1s$ $2s$
Be	$1s^2 2s^2$	[↑↓] [↑↓] $1s$ $2s$
B	$1s^2 2s^2 2p^1$	[↑↓] [↑↓] [↑][ ][ ] $1s$ $2s$ $2p$

C	$1s^2 2s^2 2p^2$	
N	$1s^2 2s^2 2p^3$	
O	$1s^2 2s^2 2p^4$	
F	$1s^2 2s^2 2p^5$	
Ne	$1s^2 2s^2 2p^6$	

- molecular orbital diagrams
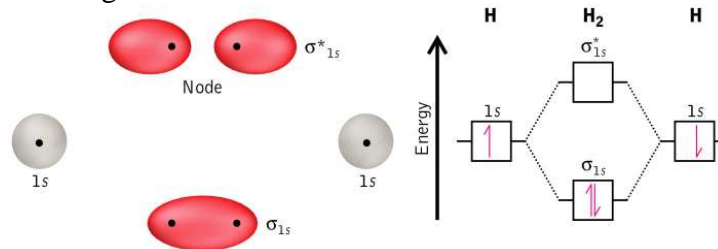
-- when atomic orbitals combine together they do so constructively and
destructively
-- when two s atomic orbitals combine they make a constructive σ_s bonding
orbital and a destructive σ_s^* anti-bonding orbital

- <u>bonding molecular orbitals</u>: create electron density between the two atomic nuclei
and thereby lower the energy and create a covalent bond
- <u>antibonding molecular orbitals</u>: reduce the electron density between the two atomic
nuclei and therefore destabilize the covalent bond
- Molecular Orbital Diagrams for diatomic hydrogen
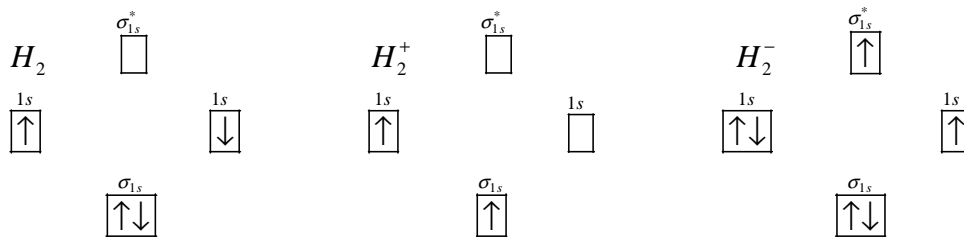
-- <u>bond order</u>: gives the stability of the bond btwn the two nuclei and tells us
whether we have a single, double, triple bond, or no bond

--- bond order $= \frac{1}{2}\left(\text{no. of bonding e-'s - no. of anti-bonding e-'s}\right)$

--- $H_2: \frac{1}{2}(2 - 0) = 1$ $H_2^+ : \frac{1}{2}(1 - 0) = \frac{1}{2}$ $H_2^1 : \frac{1}{2}(2 - 1) = \frac{1}{2}$
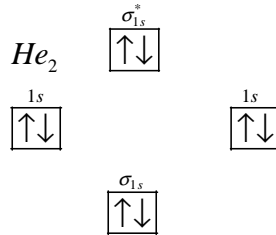
-- <u>paramagnetic vs. diamagnetic</u>
--- paramagnetic: when there are unpaired electrons in a system
(e.g. H_2^+ & H_2^-)

--- diamagnetic: when all electrons are paired (e.g. H_2)

-- molecular electronic configuration - show how the electrons are placed in the MOs
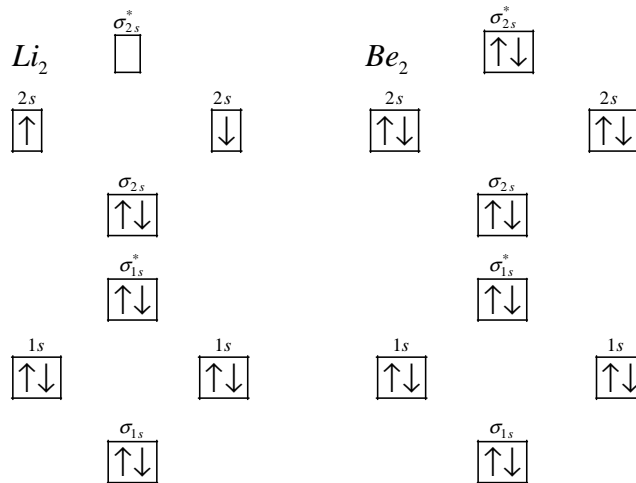
$$H_2 : \sigma_{1s}^2 \qquad H_2^+ : \sigma_{1s}^1 \qquad H_2^- : \sigma_{1s}^2 \sigma_{1s}^{*\,1}$$
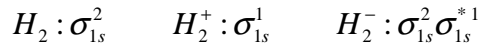
- Helium Molecular Orbital Diagram

He_2

σ_{1s}^* | ↑↓ |

1s | ↑↓ | 1s | ↑↓ |

σ_{1s} | ↑↓ |

-- bond order = 0 therefore this molecule does not form

-- diamagnetic compond

-- electronic configuration: $\sigma_{1s}^2 \sigma_{1s}^{*\,2}$

* What happens for higher level diatomics?

- Li_2 & Be_2 MO diagrams

Li_2 σ_{2s}^* | | Be_2 σ_{2s}^* | ↑↓ |

2s | ↑ | 2s | ↓ | 2s | ↑↓ | 2s | ↑↓ |

σ_{2s} | ↑↓ | σ_{2s} | ↑↓ |

σ_{1s}^* | ↑↓ | σ_{1s}^* | ↑↓ |

1s | ↑↓ | 1s | ↑↓ | 1s | ↑↓ | 1s | ↑↓ |

σ_{1s} | ↑↓ | σ_{1s} | ↑↓ |

-- bond orders: Li_2: $\frac{1}{2}(4 - 2) = 1 \; or \; \frac{1}{2}(2 - 0) = 1$

Be_2: $\frac{1}{2}(4 - 4) = 0 \; or \; \frac{1}{2}(2 - 2) = 0$ therefore Be_2 DNE

-- both species are diamagnetic

-- electronic configuration: Li_2: $\sigma_{1s}^2 \sigma_{1s}^{*\,2} \sigma_{2s}^2$ and Be_2: $\sigma_{1s}^2 \sigma_{1s}^{*\,2} \sigma_{2s}^2 \sigma_{2s}^{*\,2}$

- <u>pi (π) orbitals</u>
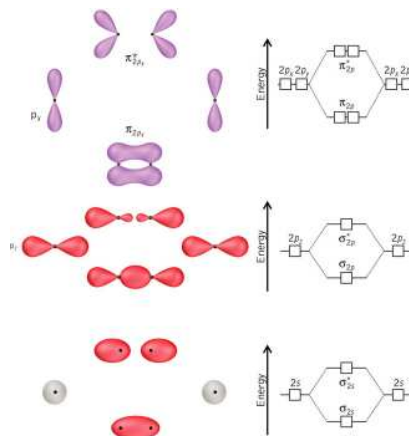
-- p atomic orbitals may overlap in two different ways

--- if only two lobes overlap then σ_{2p} & σ_{2p}^* molecular orbitals are formed

--- when all four lobes overlap then π_{2p} & π_{2p}^* molecular orbitals are made

-- depending upon the diatomic the MO ordering is different

- B_2, C_2, and N_2 MO diagrams

B_2 C_2 N_2
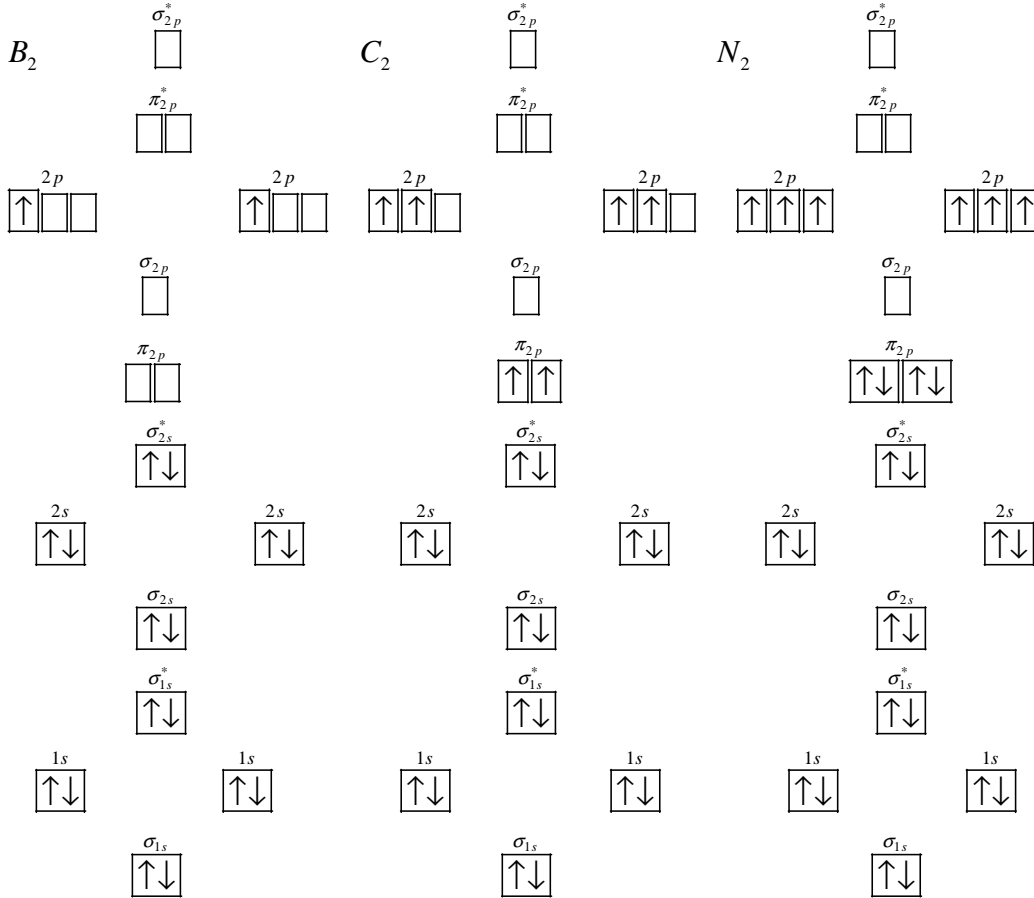
-- bond orders: B_2: $\frac{1}{2}(2 - 0) = 1$, C_2: $\frac{1}{2}(4 - 0) = 2$, N_2: $\frac{1}{2}(6 - 0) = 3$

-- C_2 & N_2 are diamagnetic while B_2 is paramagnetic

- O_2 & F_2 - the order between σ_{2p} and π_{2p} reverses (e.g. $\sigma_{2p} < \pi_{2p}$)

O_2

F_2

σ_{2p}^*

π_{2p}^*

$2p$

π_{2p}

σ_{2p}

σ_{2s}^*

$2s$

σ_{2s}

σ_{1s}^*

$1s$
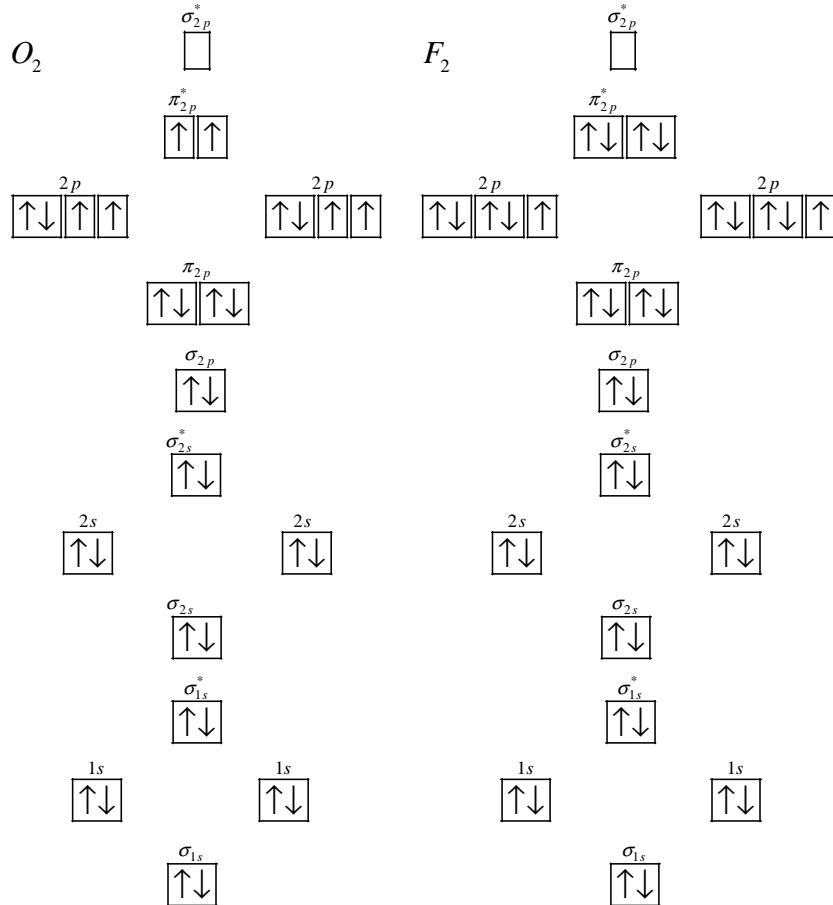
σ_{1s}

-- bond orders: O_2: $\frac{1}{2}(6-2)=2$, F_2: $\frac{1}{2}(6-4)=1$

-- F_2 is diamagnetic while O_2 is paramagnetic

-- this bond order agrees with the Lewis dot structure

* What about the aurora?
- colors of the aurora

N_2^* N_2 N_2^{+*} N_2^+

σ_{2p}^* π_{2p}^* σ_{2p} π_{2p} σ_{2s}^* σ_{2s}

Light emission 650–680 nm

Light emission 391–470 nm

A

B
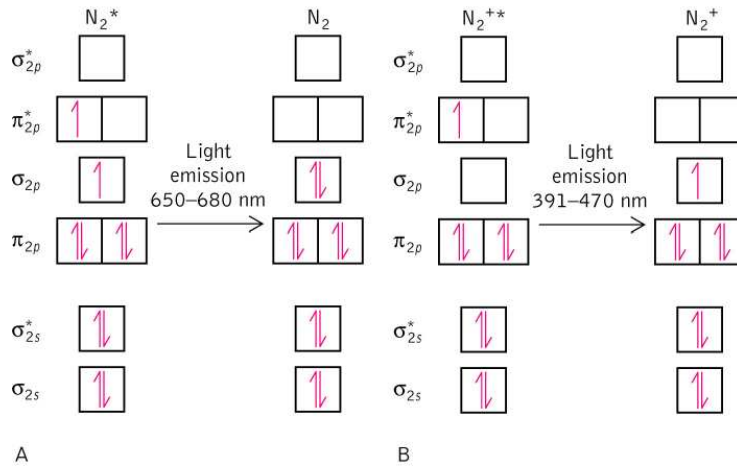
-- arise from emission of a photon when a molecule goes from an e.s. back down

10

to the g.s.

-- Ex: Draw the MO diagram for O_2^+ and a possible MO diagram for its e.s. O_2^{+*}.
What are the bond orders of each of these and are they diamagnetic or paramagnetic?

O_2^+

σ_{2p}^*
☐

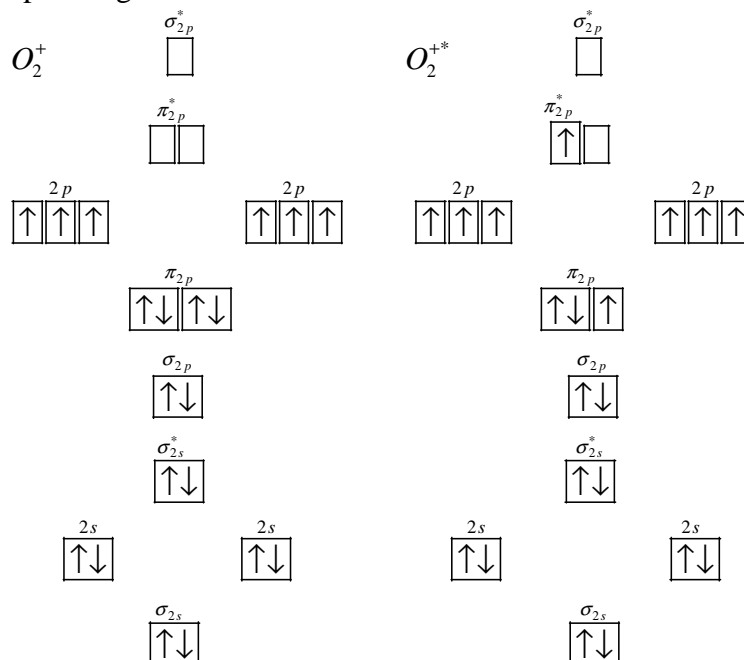| π_{2p}^*	
☐	☐

	2p						2p		
↑	↑	↑				↑	↑	↑

π_{2p}	
↑↓	↑↓

σ_{2p}
↑↓

σ_{2s}^*
↑↓

2s		2s
↑↓		↑↓

σ_{2s}
↑↓

O_2^{+*}

σ_{2p}^*
☐

π_{2p}^*	
↑	☐

	2p						2p		
↑	↑	↑				↑	↑	↑

π_{2p}	
↑↓	↑

σ_{2p}
↑↓

σ_{2s}^*
↑↓

2s		2s
↑↓		↑↓

σ_{2s}
↑↓

--- O_2^+ is diamagnetic where as O_2^{+*} is paramagnetic

--- bond orders: O_2^+: $\frac{1}{2}(6 - 0) = 3$, O_2^{+*}: $\frac{1}{2}(5 - 1) = 2$

* What else is out there?
- UV/visible spectroscopy - opposite from emission, a photon of light is absorbed from a molecule forcing it into an e.s.
- The amount of energy needed to excite an electron within a molecule to a higher molecular orbital is in the UV - visible range of electromagnetic radiate
- qualitative vs. quantitative analysis
    -- qualitative analysis: tells what compounds are present, but not how much
        --- e.g. IR spectroscopy
    -- quantitative analysis: tells us how much is present
        --- e.g. titrations