Valence, Oxidation Number, and Formal Charge

- Terms such as valence, oxidation number and formal charge appear frequently in both elementary and advanced chemistry texts.
- However, it is evident from the literature that these terms are often viewed to be synonymous and that conclusions pertaining to such an interpretation may be misleading.

➢ ***Valence***

Number of electrons that an atom uses in bonding.

➢ ***Oxidation number***

The charge remaining on an atom when all ligands are removed ***heterolytically*** in their closed form, with the electrons being transferred to the more electronegative partner *(homonuclear bonds do not contribute to the oxidation number).*

➢ ***Formal charge***

The charge remaining on an atom when all ligands are removed ***homolytically***.

➢ ***Coordination number***

The number of atoms bonded to the atom of interest.

Valence

- Two of the most important factors that provide a first order evaluation of the nature of a covalent molecule are the *electron count (cf. the octet & eighteen-electron rules)* and the *valence* of each atom.

- Whereas the term electron count is self-evident *(i.e., the total number electrons in the valence shell of an atom in a molecule)* and used consistently, the word *valence (aka valency)* has many uses:

  - *valence electrons*

  - *valence bond theory*

  - *valence shell electron pair repulsion theory (VSEPR)*

  - *bond-valence model*

    … the valence of a particular atom is expressed in terms of a sum of the valences of individual bonds, which in turn are calculated using empirically parameterized equations that require knowledge of the bond lengths from crystallography.

  - *covalency*

    … refers to the formation of a covalent bond.

  - *electrovalency or ionic valency*

    … refers to complete electron transfer to form ions, with *positive electrovalency* being used to express the number of electrons released by an element, while *negative electrovalency* describes the number of electrons added.)

- But when used on its own, *to what does valence refer?*

- In view of the relationship between the valence of an atom and the molecular formulae of its compounds, the valence of an atom is often described as its ***combining power***, a phrase that was first introduced by Frankland (1852) with respect to his *atomicity* concept.

- Frankland's *atomicity* was later named *quantivalenz* by Hofmann (1865) and subsequently abbreviated to *valenz* by Kekulé (1867) and Wichelhaus (1868).

- Sidgwick's classic 1927 book on *The Electronic Theory of Valency* states that "Valency is a general term used to describe the power which atoms possess of combining with one another to form molecules".

- The valence of an atom in a covalent molecule is simply the number of electrons that an atom has used in bonding.

- Mathematically, the valence of an atom in a molecule is equal to the difference between

  (i) the number of valence electrons in the free atom (i.e., the group valence) and

  (ii) the number of nonbonding electrons on the atom in the molecule.

Valence = 'number of electrons in valence shell of free atom'

- 'number of nonbonding electrons on atom in molecule'

- If the valence is less than the group valence, it indicates that there are nonbonding electrons on the atom.

- Knowledge of the valence of an atom in a molecule is important because it tells us

  1. whether the atom has enough electrons to support the number of atoms attached via 2-center, 2-electron bonds.

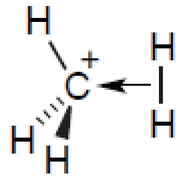
  2. whether any electrons remain on the atom and are available for subsequent reactivity.

  e.g., the valence of nitrogen in NH_3 is 3, which indicates that there is a pair of electrons on nitrogen that may be used to coordinate additional groups (such as BH_3 or H^+).

- In transition-metal chemistry, knowledge of the number of non-bonding electrons, i.e., the d^n configuration, is paramount because it is an important component in determining the **magnetic properties** and **electronic spectroscopy** of a molecule.

- If the valence of the atom appears to be greater than the group valence, it indicates that either the bonding cannot be described in terms of 2-center, 2-electron bonds but rather involves 3-center, 2-electron bonds.

- An example of such a species with 3-center, 2-electron bonds is CH_5^+.



3-center, 2-electron bond

8-electron configuration
oxidation number = −2
valence = 4

- As originally employed, the valence of an atom (A) refers to its combining power relative to that of hydrogen; as such, ***the valence of an atom in a molecule is explicitly and readily indicated by the molecular formula of the hydride AH_n***.

  e.g., the nitrogen atom in NH_3 has a valence of 3.

- However, valence has been taken to be synonymous with oxidation number, number of bonds and coordination number.

- The origin of this confusion can be readily seen by consideration of the ***neutral AH_n hydrides for which the valence, magnitude of the oxidation number, number of bonds, and coordination number each have the same value, n.***

  e.g., the nitrogen atom in NH_3 has a valence of 3, an oxidation number of -3, 3 bonds, and a coordination number of 3.

- However, this relationship is purely coincidental !

  e.g., consider $[NH_4]^+$ for which the nitrogen atom has used all five of its valence electrons (there are no lone pair electrons) and is pentavalent, but its oxidation number is -3, the number of bonds is 4, and the coordination number is 4.

Valence & Oxidation Number

- The oxidation number of an atom in a molecule is based on a formalism that forces a covalent compound to possess complete ionic character and may be defined as

  Oxidation number = ‘charge on compound’ - ‘charge on ligands’

  note: an exception are homonuclear bonds, in which case the bond is broken homolytically and a single electron is transferred to each atom.

- In many cases, the charges assigned to simple monoatomic ligands do not vary from compound to compound.
- A notable exception is provided by hydrogen for which ***both H^+ and H^- have permissible closed-shell configurations*** ($1s^0$ and $1s^2$, respectively). In this case, the charge assigned to hydrogen is determined by the relative electronegativity of the atom to which it is attached.
- It is important to emphasize that the derived charge does not correspond to the charge on the atom in the molecule, but is **hypothetical**.
- In this regard, it is unfortunate that the oxidation number is often described as a “formal charge” because this term has a very distinct and different meaning to that of oxidation number.

- In many situations, the valence of an atom in a molecule may be coincidentally equal to its oxidation number.
- There are several factors that cause this relationship to break down. Specifically, valence and oxidation number are not the same when either

(i) ***homonuclear element–element bonds are present***

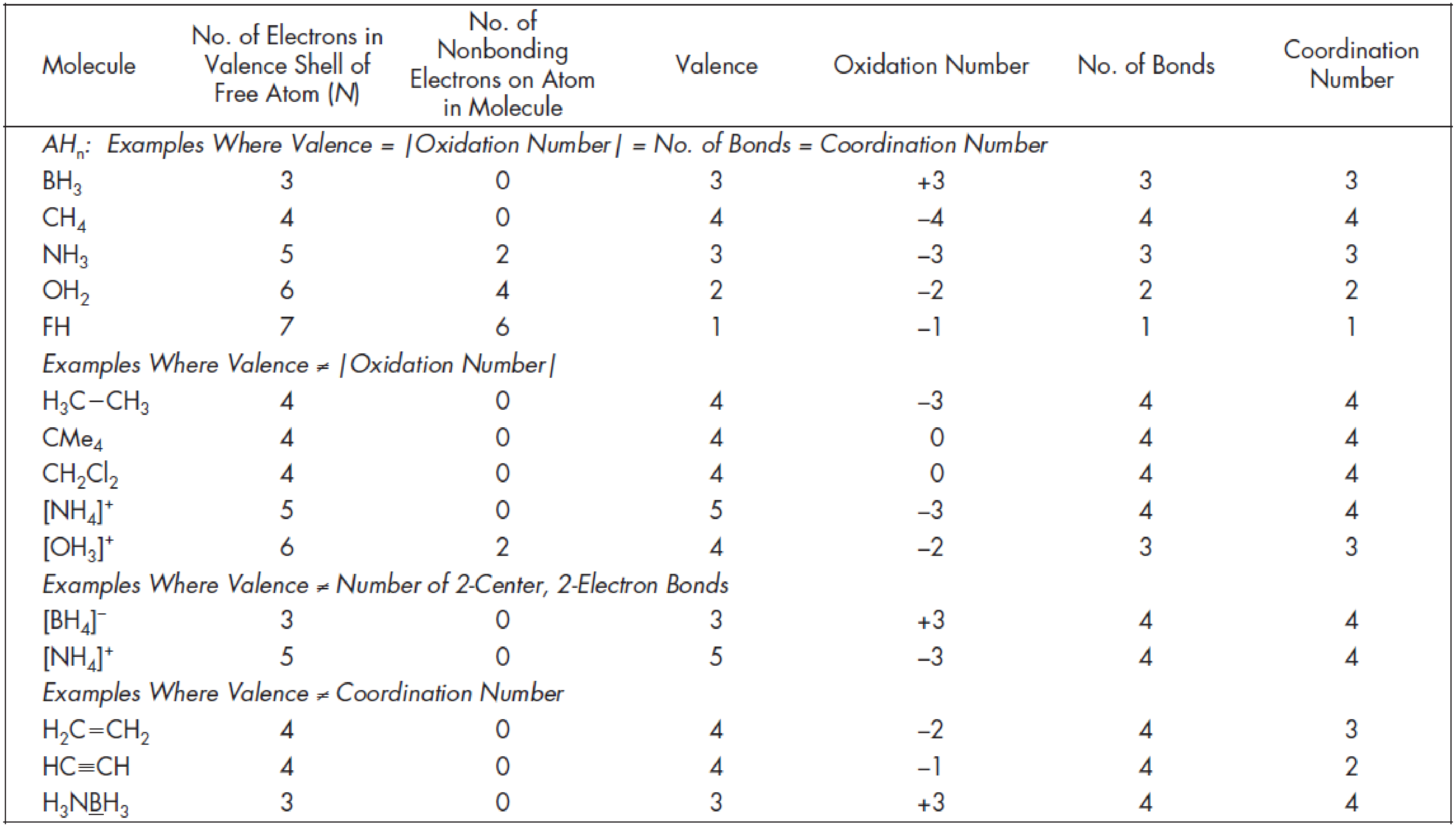
e.g., the valence of the central carbon in CMe_4 is four, but the oxidation number is zero because homonuclear element–element bonds are neglected in the determination of oxidation number.

(ii) ***the ligands attached to the atom of interest are dissociated with opposite charges***

e.g., the valence of carbon in CH_2Cl_2 is four, but the oxidation number is zero because, in terms of electronegativity differences with respect to carbon, H is viewed as H^+ and Cl is viewed as Cl^-.

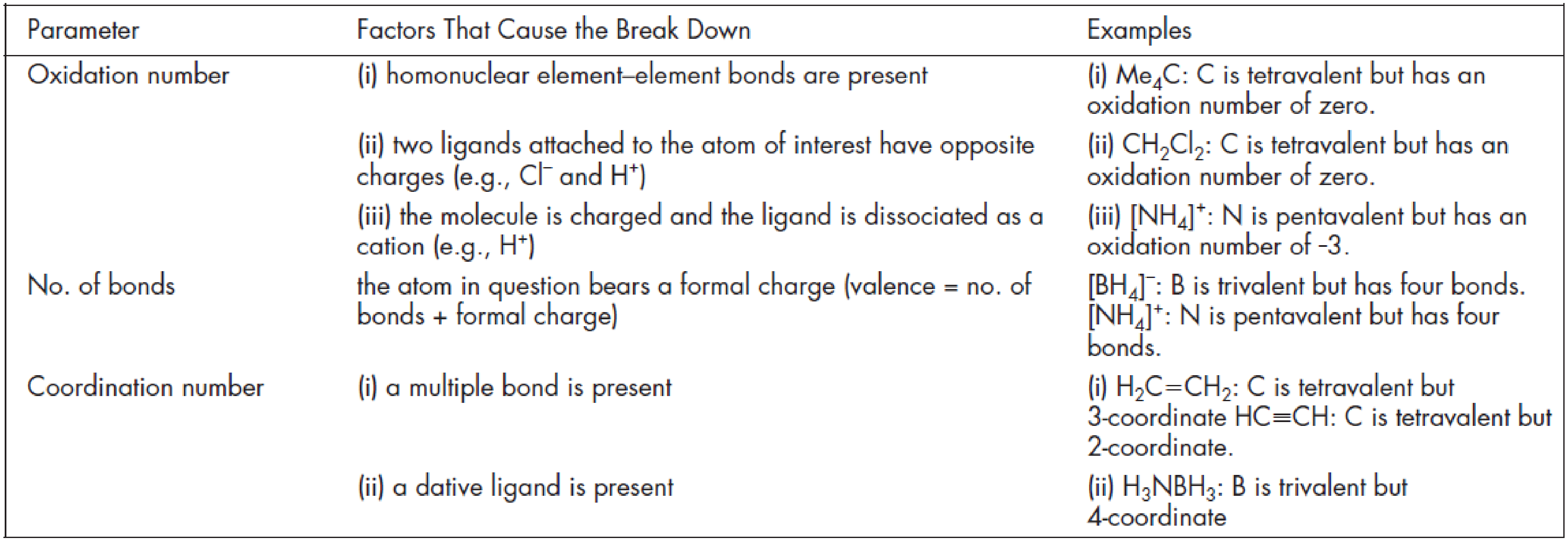
(iii) ***the molecule is charged and the ligand is dissociated as a cation***,

e.g., H^+ , the valence of nitrogen in NH_4^+ is five, but its oxidation number is -3.



Molecule	No. of Electrons in Valence Shell of Free Atom (*N*)	No. of Nonbonding Electrons on Atom in Molecule	Valence	Oxidation Number	No. of Bonds	Coordination Number
AH_n: Examples Where Valence = |Oxidation Number| = No. of Bonds = Coordination Number						
BH_3	3	0	3	+3	3	3
CH_4	4	0	4	–4	4	4
NH_3	5	2	3	–3	3	3
OH_2	6	4	2	–2	2	2
FH	7	6	1	–1	1	1
Examples Where Valence $\neq$ |Oxidation Number|						
$H_3C{-}CH_3$	4	0	4	–3	4	4
CMe_4	4	0	4	0	4	4
CH_2Cl_2	4	0	4	0	4	4
$[NH_4]^+$	5	0	5	–3	4	4
$[OH_3]^+$	6	2	4	–2	3	3
Examples Where Valence $\neq$ Number of 2-Center, 2-Electron Bonds						
$[BH_4]^-$	3	0	3	+3	4	4
$[NH_4]^+$	5	0	5	–3	4	4
Examples Where Valence $\neq$ Coordination Number						
$H_2C{=}CH_2$	4	0	4	–2	4	3
$HC{\equiv}CH$	4	0	4	–1	4	2
$H_3N\underline{B}H_3$	3	0	3	+3	4	4

- Comparison of the valence, oxidation number, number of bonds, and coordination number for some simple molecules.



Parameter	Factors That Cause the Break Down	Examples
Oxidation number	(i) homonuclear element–element bonds are present	(i) Me_4C: C is tetravalent but has an oxidation number of zero.
	(ii) two ligands attached to the atom of interest have opposite charges (e.g., Cl^- and H^+)	(ii) CH_2Cl_2: C is tetravalent but has an oxidation number of zero.
	(iii) the molecule is charged and the ligand is dissociated as a cation (e.g., H^+)	(iii) $[NH_4]^+$: N is pentavalent but has an oxidation number of -3.
No. of bonds	the atom in question bears a formal charge (valence = no. of bonds + formal charge)	$[BH_4]^-$: B is trivalent but has four bonds. $[NH_4]^+$: N is pentavalent but has four bonds.
Coordination number	(i) a multiple bond is present	(i) $H_2C{=}CH_2$: C is tetravalent but 3-coordinate $HC{\equiv}CH$: C is tetravalent but 2-coordinate.
	(ii) a dative ligand is present	(ii) H_3NBH_3: B is trivalent but 4-coordinate

- Examples of situations where the equivalence of valence to the magnitude of oxidation number, number of bonds, and coordination number break down.

Valence & Number of Bonds

- The equivalence between valence and number of 2-center, 2-electron bonds for molecules of the type AH_n breaks down when the atom in question bears a formal charge.

  e.g., consider the series of isoelectronic molecules BH_4^-, CH_4, and NH_4^+; while each of the molecules exhibits four bonds to the central atom, the valences of B, C, and N are 3, 4, and 5, respectively.

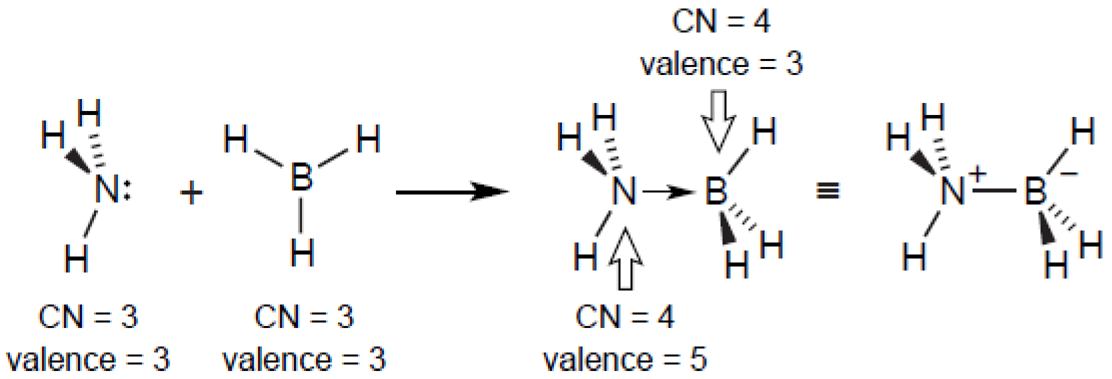
  Valence = 'number of bonds' + 'formal charge'

- As such, it is evident that, for neutral molecules of the type AH_n, the coincidental equivalence between valence and number of bonds is a consequence of the central atom bearing no formal charge.

Valence & Coordination Number *(CN)*

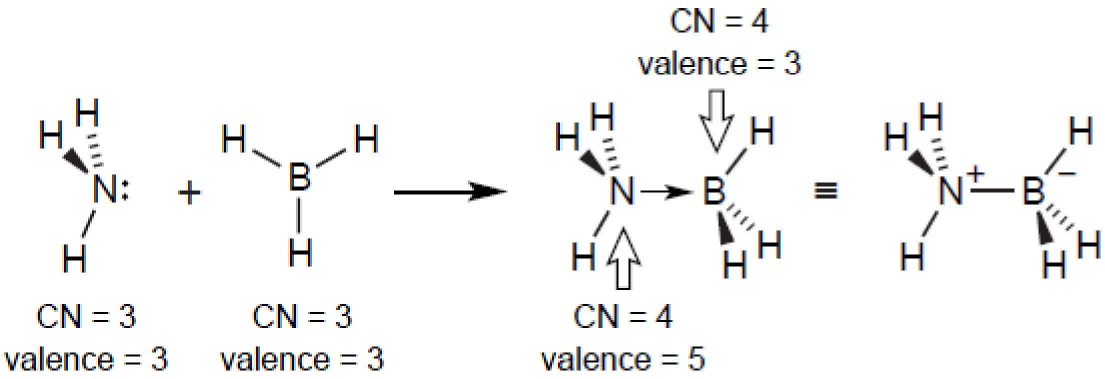
- The coordination number (CN) is simply defined as the number of atoms attached to the atom of interest in a molecule.For neutral molecules of the type AH_n the CN of A is *n* and is equivalent to its valence.
- ***The equivalence between valence and coordination number breaks down when a multiple bond is present.***

  e.g., consider the series of molecules $H_3C–CH_3$, $H_2C{=}CH_2$, and $HC{\equiv}CH$. The valence of carbon in each molecule is 4, but the CNs are 4, 3, and 2, respectively.
- In essence, when the central atom uses more than one of its electrons to bond to another atom, the coordination number of the central atom is reduced from the value of its valence.
- Likewise, the relationship between valence and CN breaks down when the bond is a dative covalent bond where one of the atoms provides both electrons.



e.g., the valence of B in three-coordinate BH_3 and four-coordinate H_3N-BH_3 is each 3.

- From the opposite perspective, it is evident that the valence of the coordinating atom of a dative ligand increases by two units when it coordinates to a Lewis acidic site.
- Thus, while the nitrogen in NH_3 is trivalent, it becomes pentavalent once it uses its lone pair upon coordinating to a Lewis acid (e.g., BH_3 or H^+).

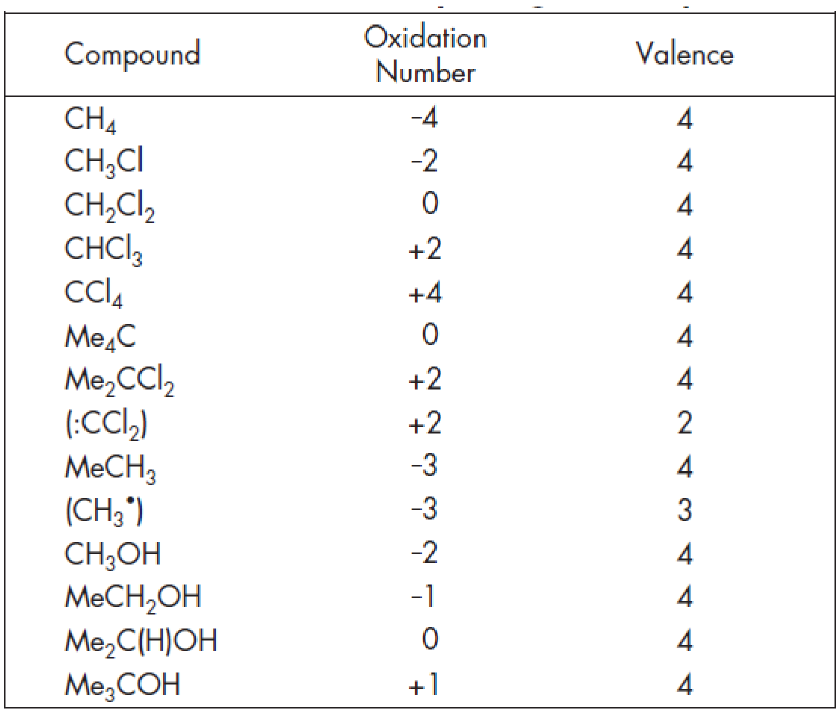


Using Valence & Oxidation Number To Provide Insight into the Nature of a Molecule

- It is pertinent to consider whether it is the valence or oxidation number that provides the greater insight into understanding the nature of a molecule.

1. The oxidation numbers of C span the range of -4 to +4.
2. Does the difference in the nature of CH_4 and CCl_4 warrant such a large change in oxidation number?

   e.g., CH_4 (ON = –4) is not a widely used reducing agent, and CCl_4 (ON = + 4) is not a widely used oxidizing agent.
3. CMe_4 (ON = 0) has little in common with CH_2Cl_2 (ON = 0).
4. As such, the large variation in oxidation states cannot be regarded as providing much insight into the nature of these molecules.



Compound	Oxidation Number	Valence
CH_4	-4	4
CH_3Cl	-2	4
CH_2Cl_2	0	4
$CHCl_3$	+2	4
CCl_4	+4	4
Me_4C	0	4
Me_2CCl_2	+2	4
$(:CCl_2)$	+2	2
$MeCH_3$	-3	4
$(CH_3^\bullet)$	-3	3
CH_3OH	-2	4
$MeCH_2OH$	-1	4
$Me_2C(H)OH$	0	4
Me_3COH	+1	4

- A further illustration of how oxidation number may offer little insight into the chemistry of a molecule is provided by the fact that both Me_2CCl_2 and $:CCl_2$ have an oxidation number of +2, but the chemistry of these molecules are very distinct.
- Thus, whereas Me_2CCl_2 is a stable species, the carbene $:CCl_2$ is only known to exist as a reactive intermediate.
- Likewise, the carbon atoms in both CH_3CH_3 and $CH_3^{\bullet}$ have an oxidation number of -3, but the former compound is a stable molecule while the latter is a highly reactive radical.

- In contrast, ***the valence of an atom in a molecule does provide useful information.*** Thus, with two exceptions, all of the compounds listed in previous table exhibit a valence of 4 for carbon, despite the fact that the oxidation numbers range from +4 to -4.
- The two exceptions are $:CCl_2$, with a valence of 2, and $CH_3^{\bullet}$ with a valence of 3. These exceptions are notable because they correspond to the two compounds that are not isolable under normal conditions.
- A further example is the oxidation number of the α-carbon atom in a series of alcohols.

  ON = -2 for CH_3OH

  ON = -1 for $MeCH_2OH$

  ON = 0 for $Me_2C(H)OH$

  ON = +1 for Me_3COH

  Each of the alcohols possess C in the same valence state and thereby reiterates the ability of valence to provide a greater appreciation of chemical reasonableness than does oxidation number.
- ***The valence of an atom in a molecule provides a much more meaningful criterion for evaluating the chemical reasonableness of a molecule than does the oxidation number.***
- Thus, while the concept of oxidation numbers is of use in certain situations, such as the balancing of redox equations, it is less fundamental than the underlying concept of valence and its use in evaluating the chemical reasonableness of a molecule is only successful when the oxidation number and valence of an atom in a molecule are coincidentally the same.

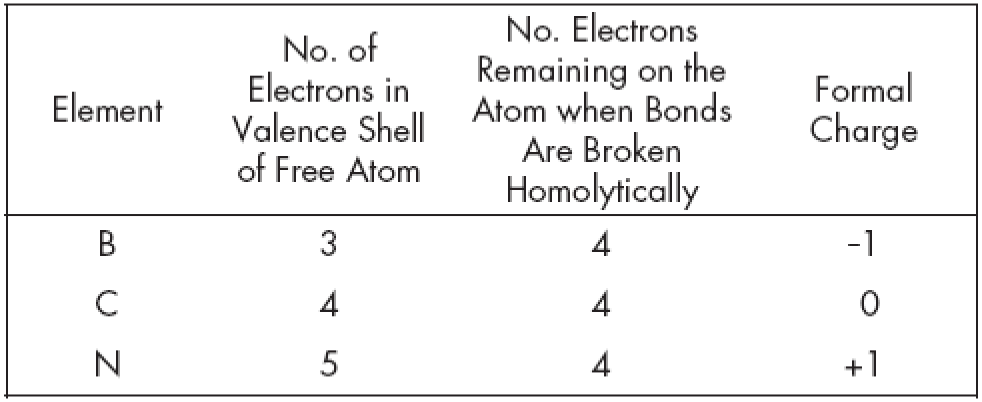
Knowledge of valence is essential because it allows one to ascertain whether
- the atom has enough electrons to support the number of atoms attached via 2-center, 2-electron bonds.

- Compare CH_4 and CH_5^+.
  - ➢ both contain C with an identical electronic configuration, ON = -4 and both obey the octet rule.
- However, the valence of C in CH_5^+ is 6 even though C only has 4 valence electrons indicating that there is something unusual about this molecule!
- Indeed, CH_5^+ is very unstable, but how could such a species exist if the valence of C were to be 6? Since the carbon atom in CH_4 does not have any electrons available for protonation (unlike the nitrogen atom in NH_3), the answer is quite simply provided by the fact that it is not the carbon atom itself that is protonated.
- Rather, it is the C-H bond that is protonated, thereby resulting in a 3-center, 2-electron interaction.
- With a 3-center, 2-electron interaction, CH_5^+ may be regarded as a dihydrogen complex of CH_3^+ and so the valence of the carbon in this species remains 4.
- Thus, because it is the C-H bond that is protonated, the carbon atom in CH_5^+ contributes only 4 valence electrons to bonding the 5 hydrogen atoms.

Knowledge of valence is essential because it allows one to ascertain whether

- any electrons remain on the atom and are available for subsequent reactivity.

- The use of valence to provide an indication of whether there are any electrons available on the atom for further bonding, is provided by consideration of NH_3.
- Thus, the valence of nitrogen in NH_3 is three, thereby indicating that there is a pair of electrons available for subsequent reactivity, such as protonation or coordination to a Lewis acid.



Element	No. of Electrons in Valence Shell of Free Atom	No. Electrons Remaining on the Atom when Bonds Are Broken Homolytically	Formal Charge
B	3	4	-1
C	4	4	0
N	5	4	+1

Calculation of formal charges for $(XH_4)^q$ (X = B, C, N; q = -1, 0, +1)

Comparison of Oxidation Number, Formal Charge, and “Actual” Charge

- The formal charge of an atom in a given Lewis structure is the charge it would possess if the electrons in each covalent bond were to be distributed equally between the two bonded atoms such that each partner receives one electron.

  i.e., homolytic cleavage

- The formal charge may, therefore, be defined as the difference between (i) the number of electrons in the free atom *(i.e., the group valence)* and (ii) the number of electrons remaining on the atom in a molecule when all bonds are broken homolytically.

  Formal charge = ‘number of electrons in valence shell of free atom

  – ‘number of electrons remaining after homolytic cleavage of all bonds’

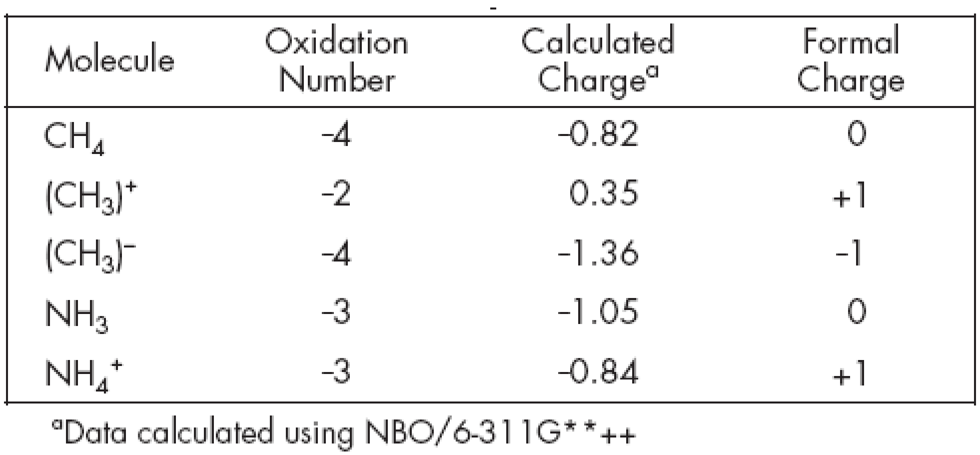
- Since each 2-center, 2-electron bond contributes one electron to the electron count of an atom in a molecule, the electron count is equal to the number of electrons in the valence shell of the free atom plus the number of covalent bonds, adjusted by the formal charge.

- Thus, the formal charge may also be expressed as:

  Formal charge = ‘number of electrons in valence shell of free atom’

  + ‘number of bonds’ – ‘electron count’

- While the concepts of oxidation number and formal charge are closely related in the sense that they both refer to a charge on an atom in a molecule, they have very different values because the charges are determined by two fundamentally different formalisms that respectively exaggerate the ionic and covalent character of the bonding.
- Does the “actual” charge on an atom in a covalent molecule correspond more closely to the oxidation number or the formal charge?



Molecule	Oxidation Number	Calculated Charge[a]	Formal Charge
CH_4	-4	-0.82	0
$(CH_3)^+$	-2	0.35	+1
$(CH_3)^-$	-4	-1.36	-1
NH_3	-3	-1.05	0
NH_4^+	-3	-0.84	+1

[a] Data calculated using NBO/6-311G**++

Electroneutrality Principle

"Stable complexes are those with structures such that each atom has only a small electric charge. Stable M-L bond formation generally reduces the positive charge on the metal as well as the negative charge and/or e- density on the ligand. The result is that the actual charge on the metal is not accurately reflected in its formal oxidation state"

- **Pauling**; *The Nature of the Chemical Bond, 3rd Ed.;1960, pg. 172.*

- Neither Oxidation Number or Formal Charge are accurate descriptions of electron density at the metal.
- Charge on an atom is typically considered to be less than ±1

  e.g., high oxidation state, early TM complexes are stabilized via π-donation shifting electron density from π-donor ligands to the metal. This in part accounts for the extreme oxophilicity of early TM.

Valence = ‘number of electrons in valence shell of free atom’
- ‘number of nonbonding electrons on atom in molecule’

Valence = ‘number of bonds’ + ‘formal charge’

Oxidation number = ‘charge on compound’ - ‘charge on ligands’

Formal charge = ‘number of electrons in valence shell of free atom
– ‘number of electrons remaining after homolytic cleavage of all bonds’

Formal charge = ‘number of electrons in valence shell of free atom’
+ ‘number of bonds’ – ‘electron count’

MO Theory

- MO theory assumes that electrons are delocalized across the molecular framework where a Linear Combination of Atomic Orbitals (LCAO) is invoked

$$\Psi_{\pm} = N\,(\Psi_A \pm \Psi_B)$$

- According to the Born interpretation, the probability electron density is proportional to Ψ^2

$$\Psi^2 = N^2\,(\Psi_A \pm \Psi_B)^2$$

σ bonding

- The probability electron density Ψ^2 of σ bond is thus proportional to
  1. The probability density of the electron confined to atom A, Ψ_A^2
  2. The probability density of the electron confined to atom B, Ψ_B^2
  3. The additional probability of finding the electron intermediate between A and B, $2\Psi_{AB}$

$$\Psi_+^2 = N^2\,(\Psi_A^2 + \Psi_B^2 + 2\Psi_{AB})$$

- The additional contribution from $2\Psi_{AB}$ is known as the **overlap density** and represents an enhancement of finding the electron in the internuclear distance.
- Thus electrons accumulate in regions of constructive orbital overlap between bonding nuclei and lowering the overall energy.

σ^* antibonding

- The probability electron density Ψ^2 of the σ^* antibonding orbital is thus proportional to
  1. The probability density of the electron confined to atom A, Ψ_A^2
  2. The probability density of the electron confined to atom B, Ψ_B^2
- The probability of finding the electron intermediate between A and B is now $-2\Psi_{AB}$ due to destructive interference in the internuclear region resulting in a node

$$\Psi_-^{\,2} = N^2 (\Psi_A^2 + \Psi_B^2 - 2\Psi_{AB})$$

- Occupation of the σ^* antibonding orbital thus decrease electron density in the internuclear region thus pushing the bonding nuclei apart, weakening the bond and raising the energy of the system.
- In fact the following relationship holds true

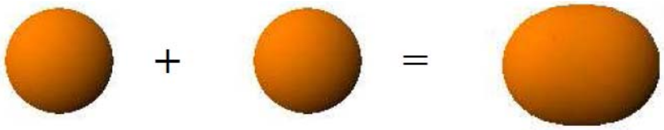
$$|E_- - E_A| > |E_+ - E_A|$$

thus the antibonding orbital is more antibonding than the bonding orbital is bonding.

MOs from 1*s* Orbitals
- Homonuclear Diatomic Molecules

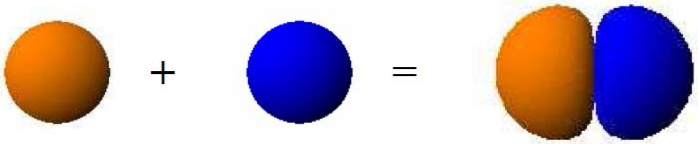
- Positive combination causes a build-up of electron density between the nuclei, resulting in a **sigma bonding MO (σ).**
- Negative combination results in a nodal plane between the nuclei, which works against bonding, resulting in a **sigma antibonding MO (σ*).**
- In general, number of MOs formed as LCAOs equals number of AOs used.

σ bonding MO



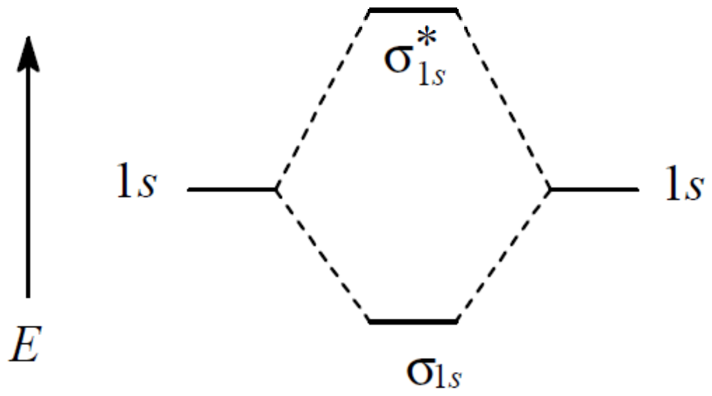
$$\Psi_{+} = a\Psi A + b\Psi B$$

σ* anti-bonding MO



$$\Psi_{-} = a\Psi A - b\Psi B$$

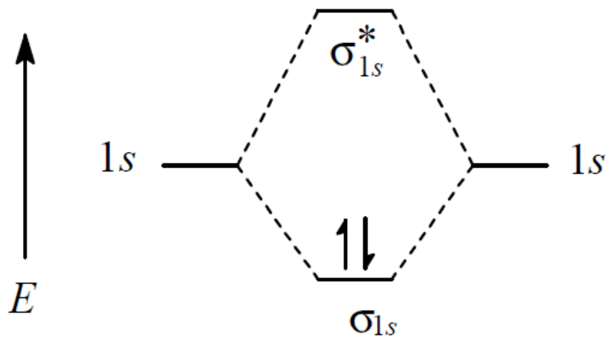
MO Energy Level Scheme
First Period Homonuclear Diatomic Cases



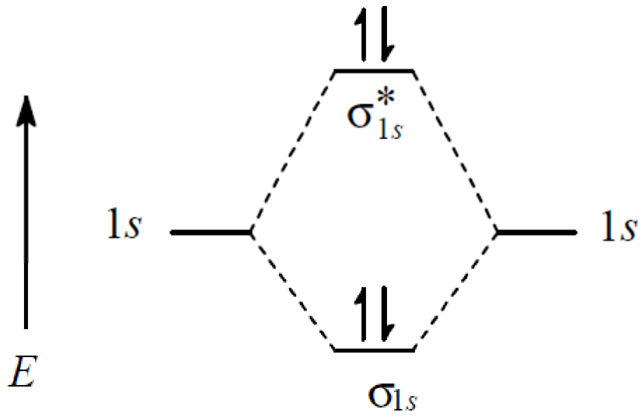
- Scheme is filled in the usual aufbau manner, following the Pauli exclusion principle and Hund's rule of maximum multiplicity (for the ground state).
- Bond order is defined as follows:

bond order = ½ (bonding *e's – antibonding e's)*

H_2 and He_2

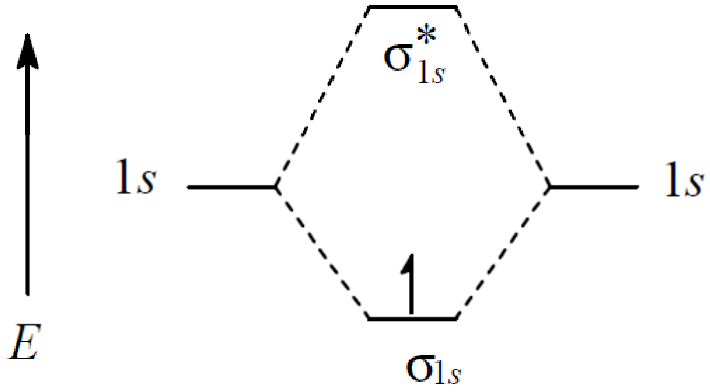


- H_2 bond order = ½(2 – 0) = 1

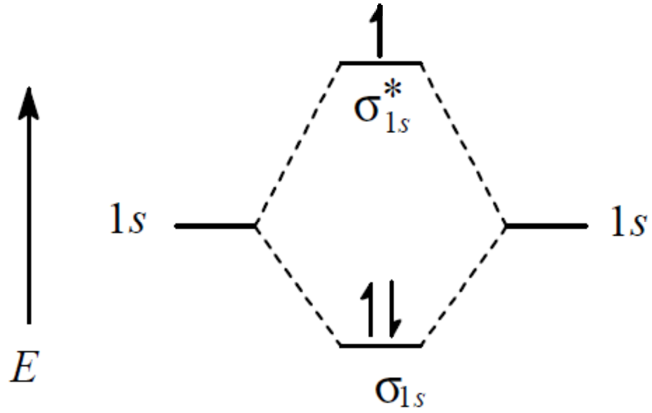


- He_2 bond order = ½(2 – 2) = 0
  (He2 does not exist.)

H_2^+ and He_2^+ ions



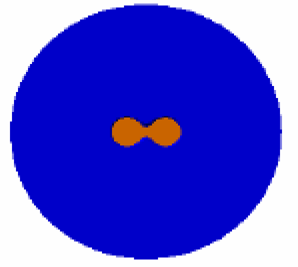
- H_2^+ bond order = ½(1 – 0) = ½



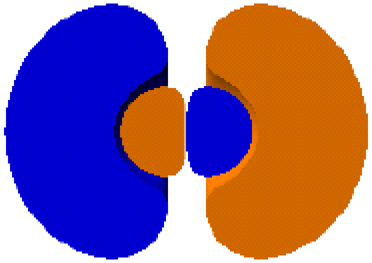
- He_2^+ bond order = ½(2 – 1) = ½

MOs for Second Period
Homonuclear Diatomic Molecules

- In general, atomic orbitals that are most similar in energy interact most effectively in forming MOs.
- MOs for second period diatomic molecules are combinations of the type 2*s ± 2s and 2p ± 2p.*

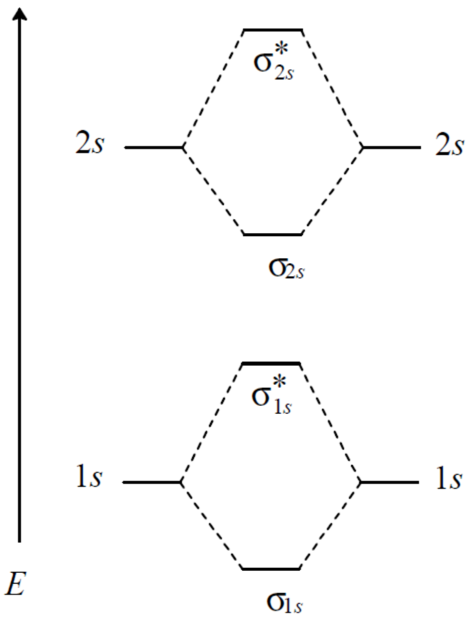


σ_{2s} **bonding MO**

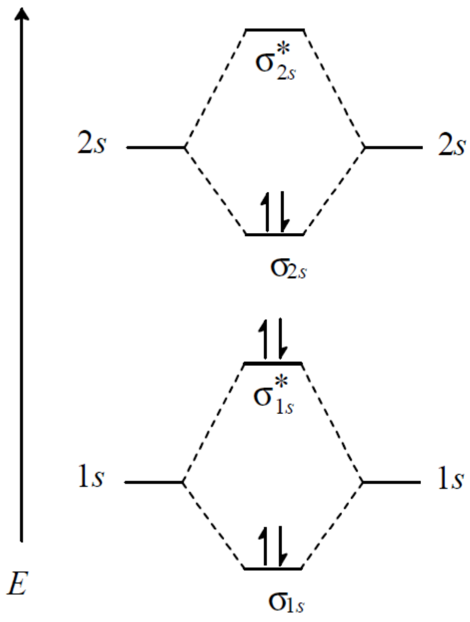


σ^{*}_{2s} **anti-bonding MO**

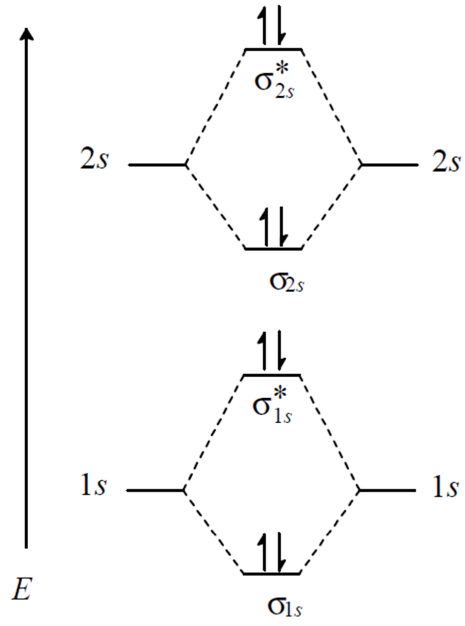
MO Energy Level Scheme for Li_2, Be_2, and Related Ions



Li_2



Be_2

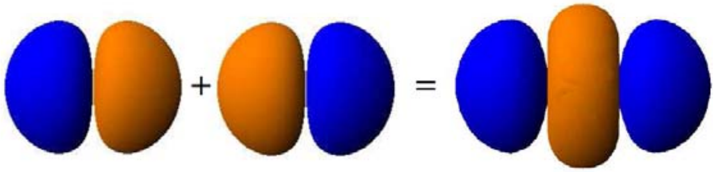


Li_2 bond order = ½(4 – 2) = 1

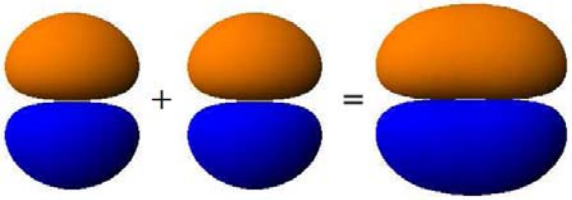
Be_2 bond order = ½(4 – 4) = 0

2p ± 2p MOs (σ and π)

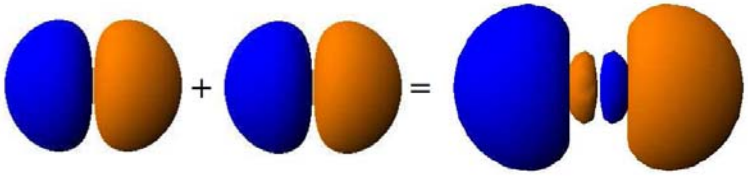
- Singly degenerate σ_{2p} and σ^*_{2p} bonding and antibonding MOs from $2p_z \pm 2p_z$
- Two degenerate π_{2p} bonding MOs, one from $2p_x + 2p_x$ and one from $2p_y + 2p_y$
- Two degenerate π^*_{2p} antibonding MOs, one from $2p_x - 2p_x$ and one from $2p_y - 2p_y$



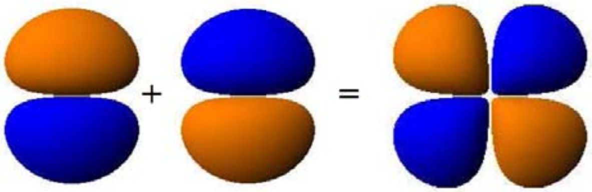
σ_{2p} bonding MO



π_{2p} bonding MO

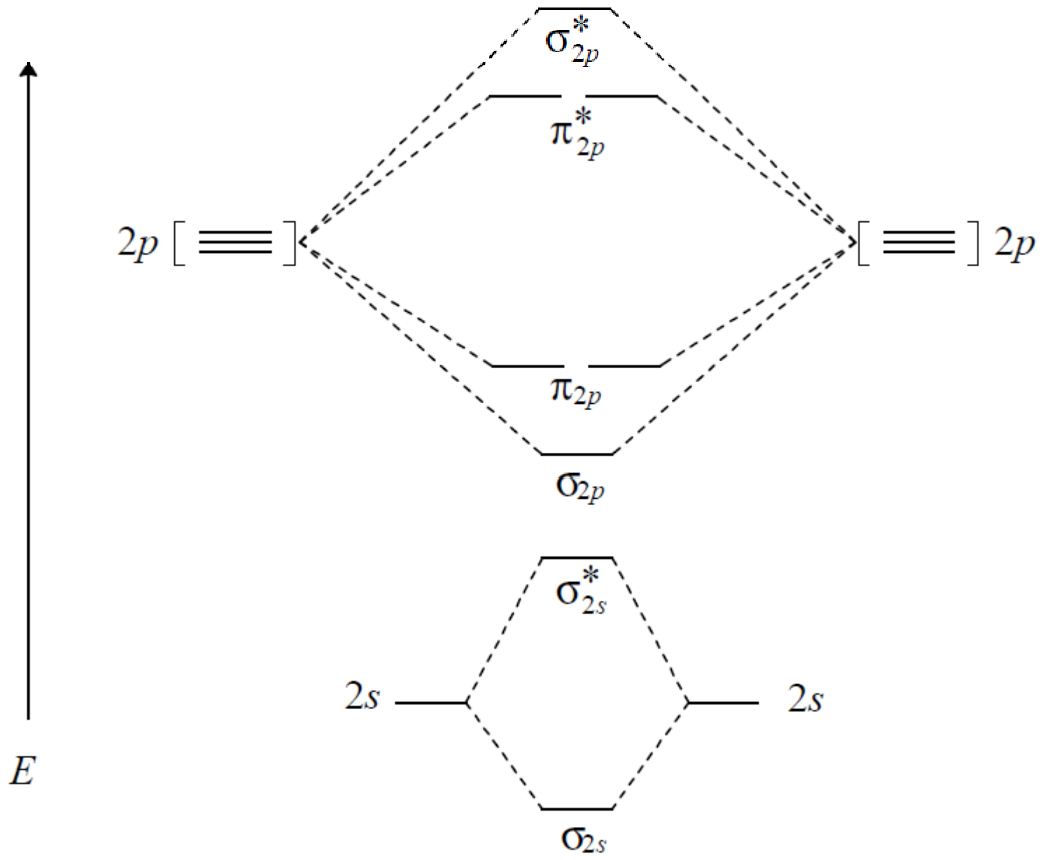


σ^*_{2p} antibonding MO



π^*_{2p} anti-bonding MO

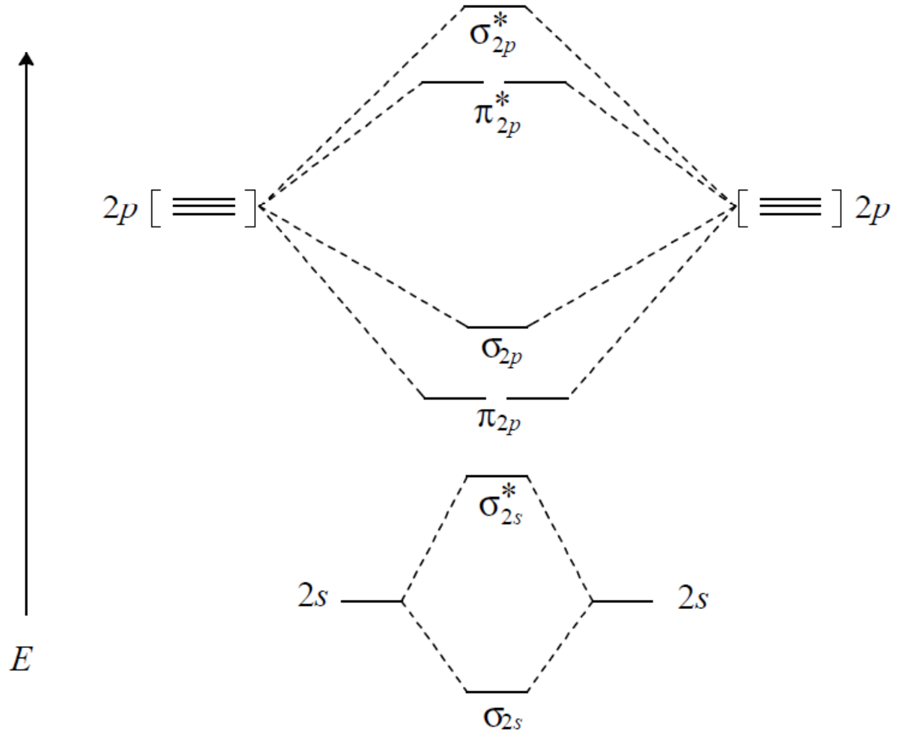
MO Scheme for O_2 through Ne_2 and Related Ions



- The core configuration levels σ_{1s} and σ^*_{1s} are omitted.

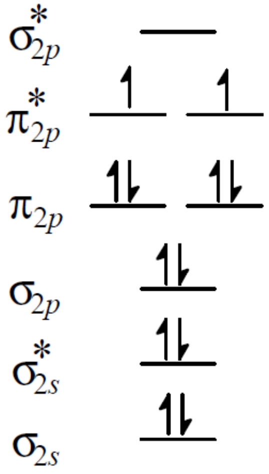
MO Scheme for B_2 through N_2 and Related Ions

- In diatomic molecules of the lighter elements B_2, C_2, and N_2, mixing between sigma-type MOs causes the σ^*_{2s} level to move down and the σ_{2p} level to move up in energy.
- The σ_{2p} level rises above that of π_{2p}.
- This results in the following scheme, in which the relative ordering $\pi_{2p} < \sigma_{2p}$ occurs:



MO Description of O_2 and Its Ions

- MO model predicts the observed paramagnetism, which VB theory cannot explain easily.



Formula	Configuration	Bond Order	$D(X_2)$ kJ/mol	$d(X–X)$ pm	Magnetic Property
O_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^2$	2	494	120.75	para
O_2^-	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^3$	1.5	395	135	para
O_2^{2-}	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^4$	1	126	149	dia
O_2^+	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^1$	2.5	643	111.6	para

Second Period Heteronuclear Diatomic Molecules

- MO scheme for homonuclear diatomic molecules can be adapted to describe bonding in heteronuclear diatomic molecules.

- The two atoms do not contribute equally to each MO.

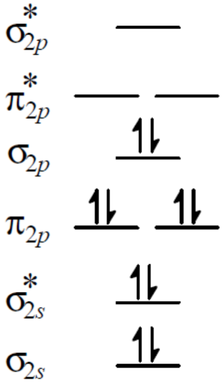
  - More electronegative element has lower energy AOs and makes a greater contribution to bonding MOs.

  - Less electronegative atom makes a greater contribution to antibonding MOs.

- Ordering of MOs energies in heteronuclear cases tends to be like lighter homonuclear cases: i.e., $\pi_{2p} < \sigma_{2p}$

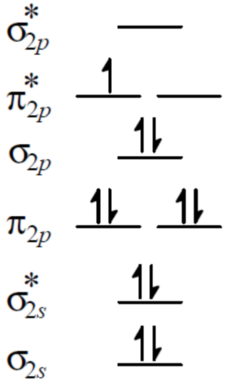
Heteronuclear Diatomic Molecules
Examples

- CO, CN⁻, NO⁺ (10 valence electrons, like N_2)



bond order = 3

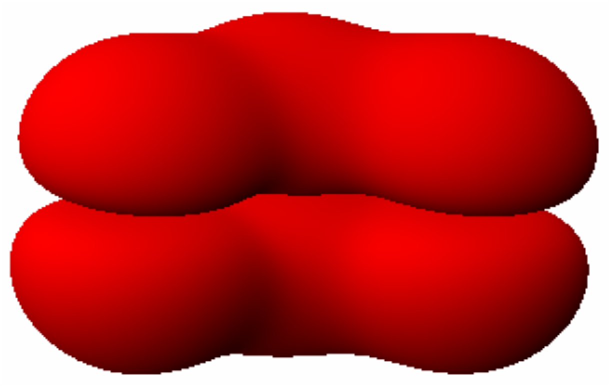
- NO (11-electron free radical, like O_2^+)



bond order = 2.5

MO Description of Pi-Delocalized Systems

- MO theory has no difficulty explaining the π-delocalized electron density implied by resonance forms, which VB theory cannot easily represent.



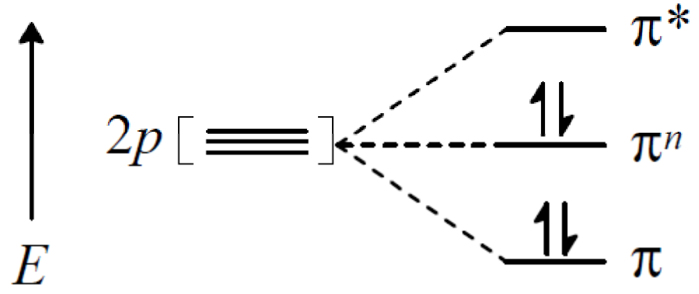
π electron density of O_3

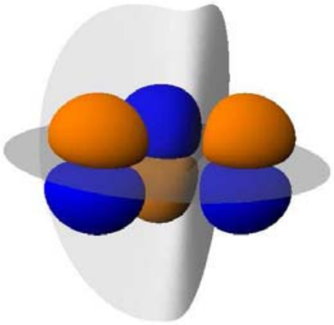
- The three 2*p orbitals perpendicular to the molecular plane* combine to form three π MOs:

1. π – bonding MO
2. π^n – *nonbonding MO*
3. π* – antibonding MO

- A non-bonding MO neither builds nor destroys bonding between the oxygen atoms.

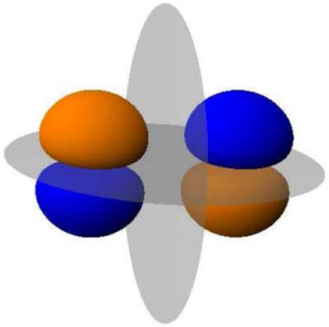
Pi MO Energy Level Scheme for O_3



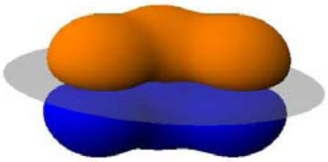


π^* – antibonding MO

- The π system has two pairs of electrons, one pair in the π MO, and the other in the π^n non-bonding MO.
- The configuration $(\pi)^2$ adds a bond order of 1 across the two O–O bonds (i.e., 0.5 to each bond).
- When this is added to the sigma bond between each oxygen pair, the O–O bond order becomes 1.5.
- The configuration $(\pi^n)^2$ neither adds nor subtracts from the overall strength of the bonds.



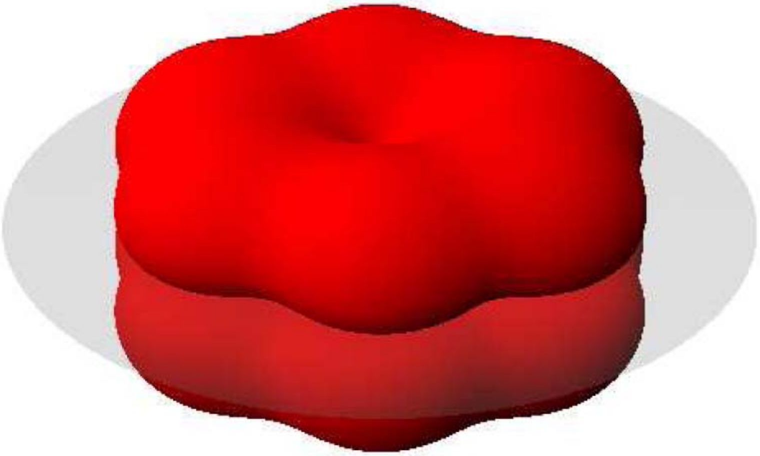
π^n – nonbonding MO



π – bonding MO

Pi MOs of Benzene, C_6H_6

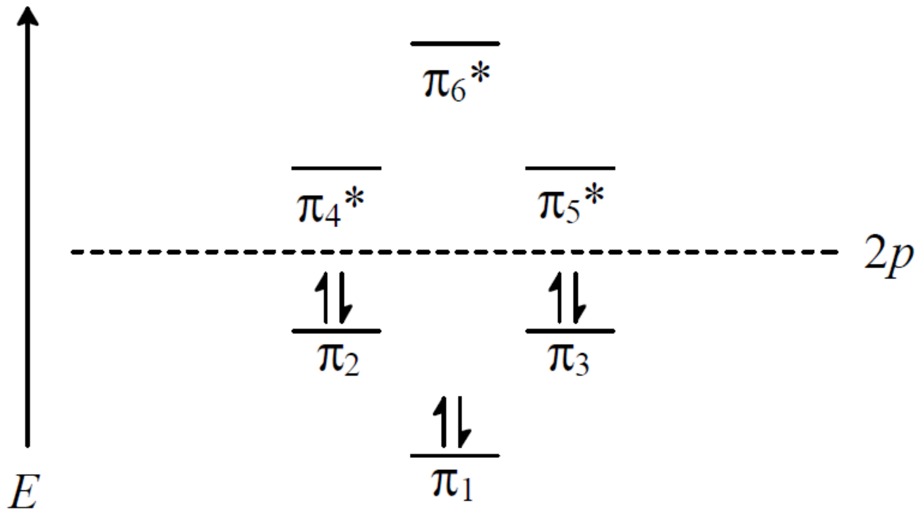
- C_6H_6, has three pairs of electrons delocalized in a π system extending around the hexagonal ring.

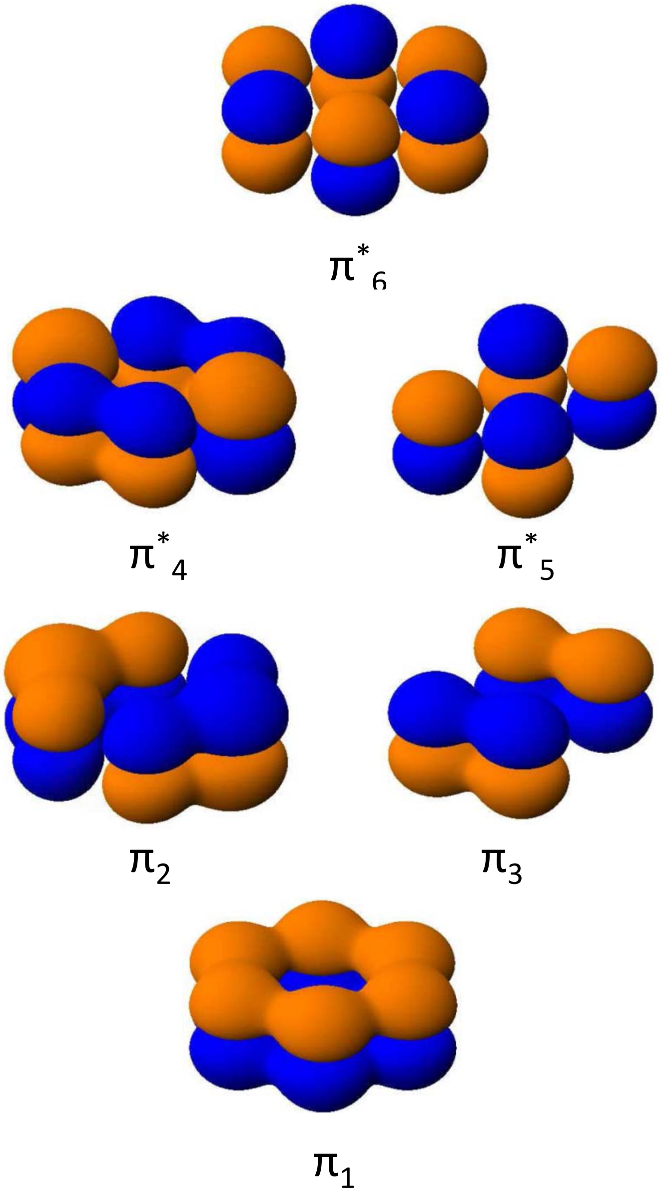


π electron density of C_6H_6

- The six 2*p orbitals perpendicular to the ring on the six carbon* atoms combine to form three bonding (π_1, π_2, π_3) and three antibonding (π_4*, π_5*, π_6*) MOs.

Pi MO Energy Level Scheme for C_6H_6





- Three pairs in bonding MOs add a total of three bond orders over six C–C linkages, or 0.5 for each.
- When this is added to the sigma bond between each carbon pair, the C–C bond order becomes 1.5.

Wave Equations of Molecules

- Approximate wave functions are sought by combining atomic wave functions for the bonded atoms.
- Several different approaches have been taken to constructing trial wave functions.

➢ Valence Bond (VB) - Heitler & London (1927)

$$\Psi_{\text{bond}} = \Psi_a \Psi_b$$

Hybrid orbitals - Pauling (1920s)

➢ Molecular Orbital (MO) - Hund, Mulliken (1920s)

$$\Psi_{\text{MO}} = a\,\Psi_A + b\,\Psi_B$$

LCAOs - Lennard-Jones (1929)

Normalization Requirement

- From the Copenhagen interpretation we associate the probability of finding the electron in a vanishingly small volume element (“a point”) as

$$P \propto \Psi^2$$

- The electron has unit probability over all space:

$$P = \int \Psi^2 \, d\tau = 1$$

- To ensure that any trial wave function, R, meets this criterion we generally must multiply by a *normalization constant, N,* such that

$$P = N^2 \int \Psi^2 \, d\tau = 1$$

- If Ψ is a solution to the Schrödinger equation, then so too is $N\Psi$*, and E in ,*$H(\Psi) = E(\Psi)$ *is unaffected.*

Normalization Requirement

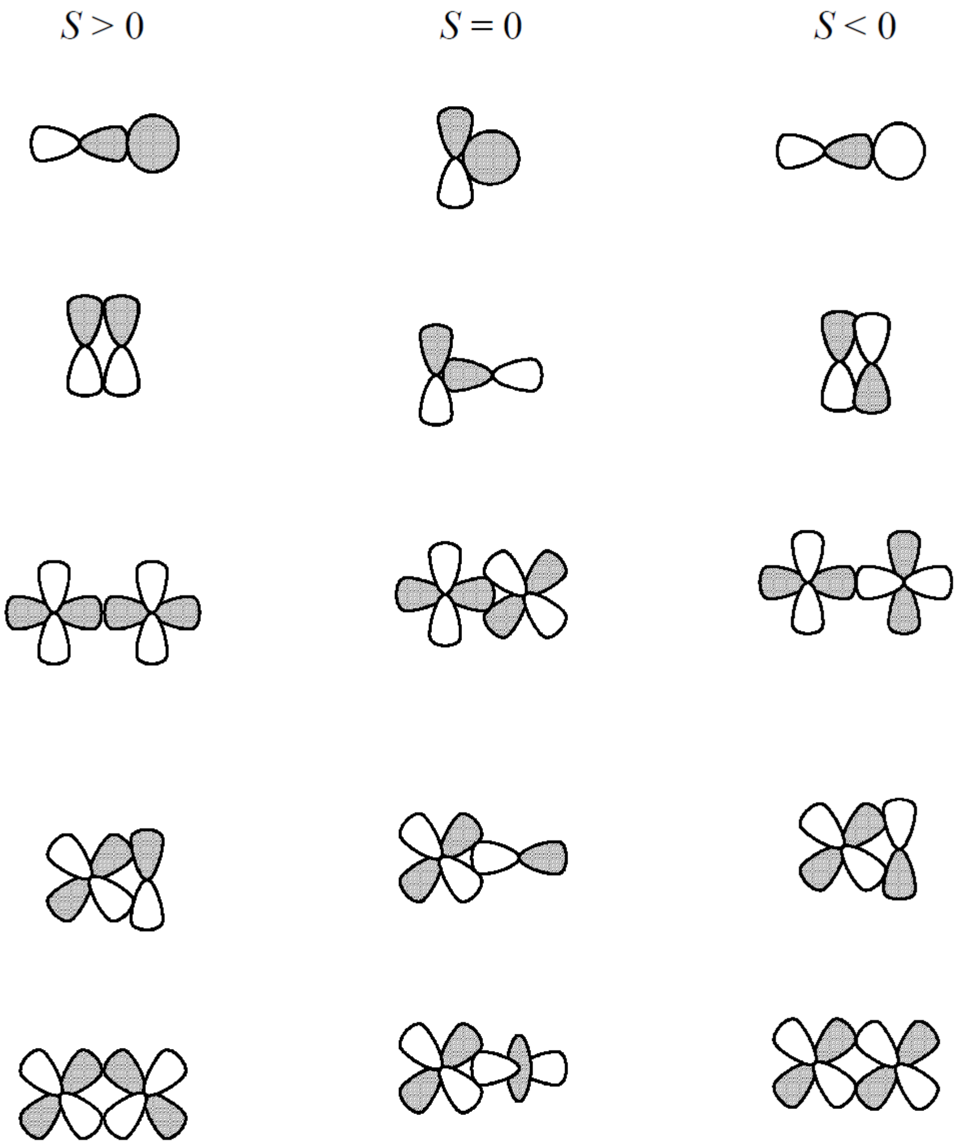
- When two orbitals on different atoms A and B overlap, the nature and effectiveness of their interaction is given by the Slater overlap integral

$$S = \int \Psi_A \Psi_B \, d\tau$$

which can be evaluated precisely only for H_2 .

- For our purposes we only need to recognize when certain interactions of orbitals have $S > 0$, $S = 0$, or $S < 0$
  - ➢ $S > 0$ – bonding interaction
  - ➢ $S = 0$ – nonbonding interaction
  - ➢ $S < 0$ – antibonding interaction
- The sense of S is evident from simple pictures of interacting orbitals.
  - ➢ $S > 0$ – reinforcing overlap between nuclei
  - ➢ $S = 0$ – equally reinforcing and cancelling overlaps
  - ➢ $S < 0$ – cancelling overlap between nuclei

Examples of $S > 0$, $S = 0$, and $S < 0$



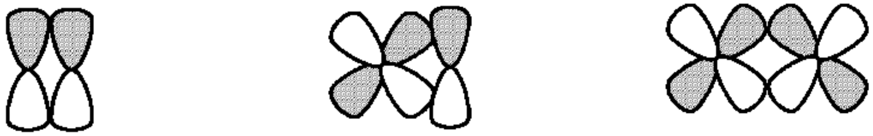
AO Shape and Symmetry

- All AOs with the same value of *l* have the same symmetry, regardless of *n*.
- As isolated orbitals, each type can be identified with a particular point group.
    - s = R_3
    - p = C_{4v}
    - d = D_{2h} ("cloverleaf") or D_{4h} (dz^2)
- Orbitals that have bonding combinations usually have the same kind of symmetry with respect to the internuclear axis.
- If a bonding combination can be identified for any pair of orbitals, there must also be an antibonding combination.
- Nonbonding orbitals are oriented relative to each other such that they do not have the same kind of symmetry relative to the internuclear axis.

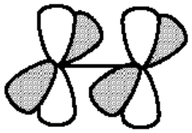
Symmetry Definition of Sigma, Pi, and Delta Interactions

- Sigma (σ) interactions are symmetrical relative to a C_2 axis collinear with the internuclear axis.

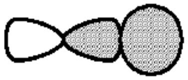
- Pi (π) interactions are anti-symmetric (Ψ changes sign) with respect to C_2 collinear with the internuclear axis and with respect to σ_v coplanar with the shared nodal plane.



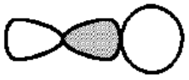
- Delta (δ) interactions are symmetric to C_2 and anti-symmetric to C_4 .



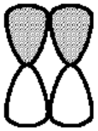
- Bonding and antibonding interactions of the same type have the same symmetry with respect to the internuclear axis.



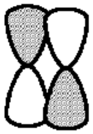
σ bonding



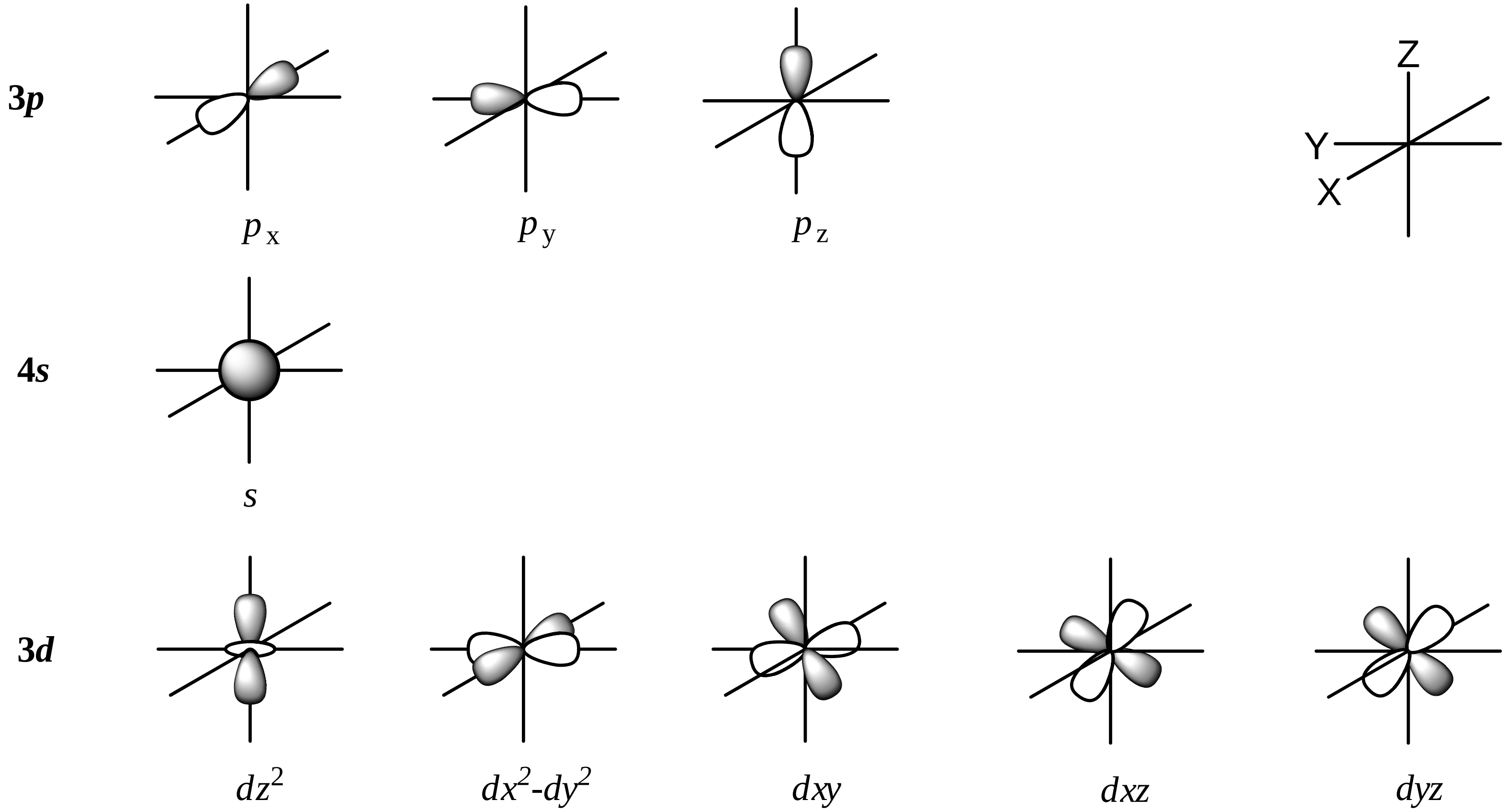
σ^* anti-bonding



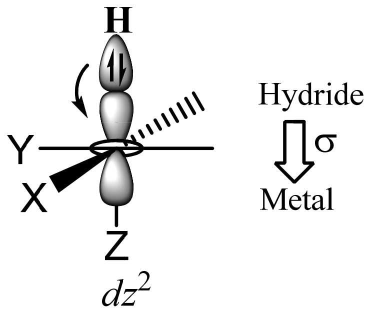
π bonding



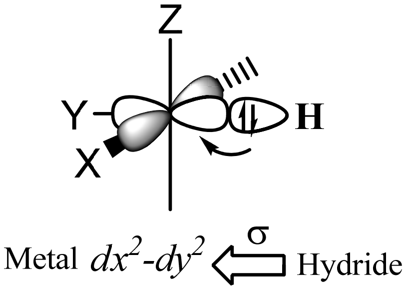
π^* anti-bonding


3*p*
p_x
p_y
p_z
Z
Y
X
4*s*
s
3*d*
dz^2
$dx^2\text{-}dy^2$
dxy
dxz
dyz

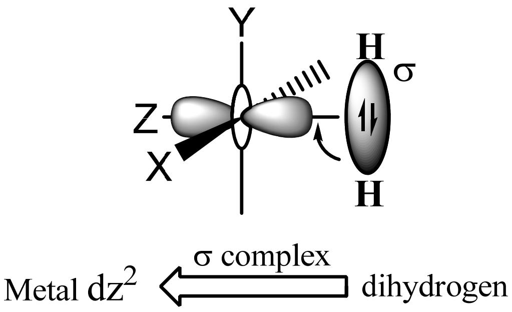
Metal Hydride

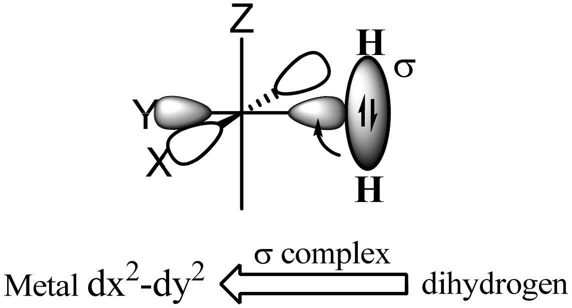


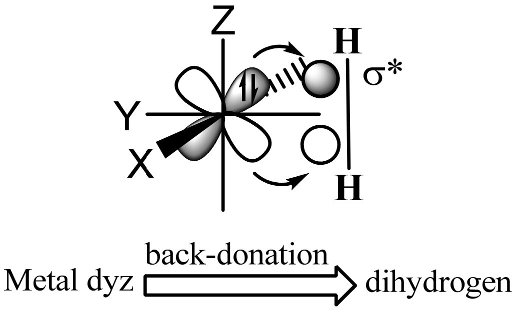
or



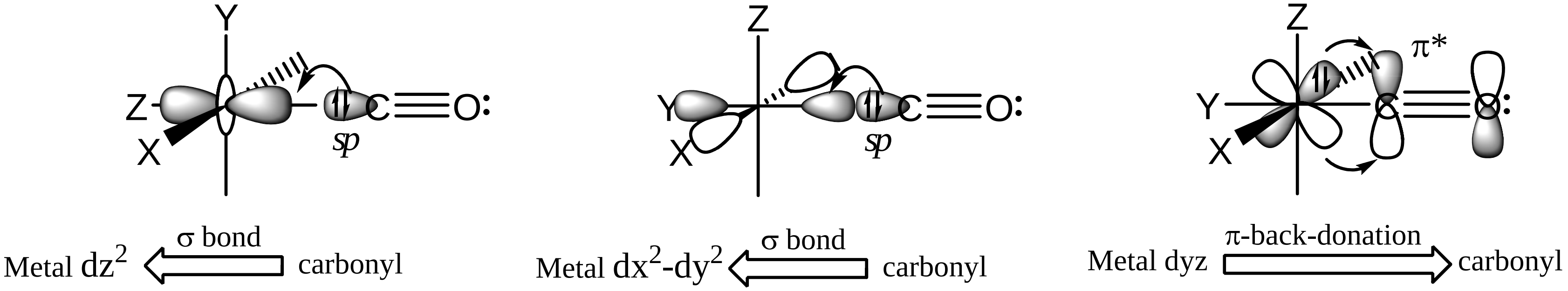
Metal Dihydrogen



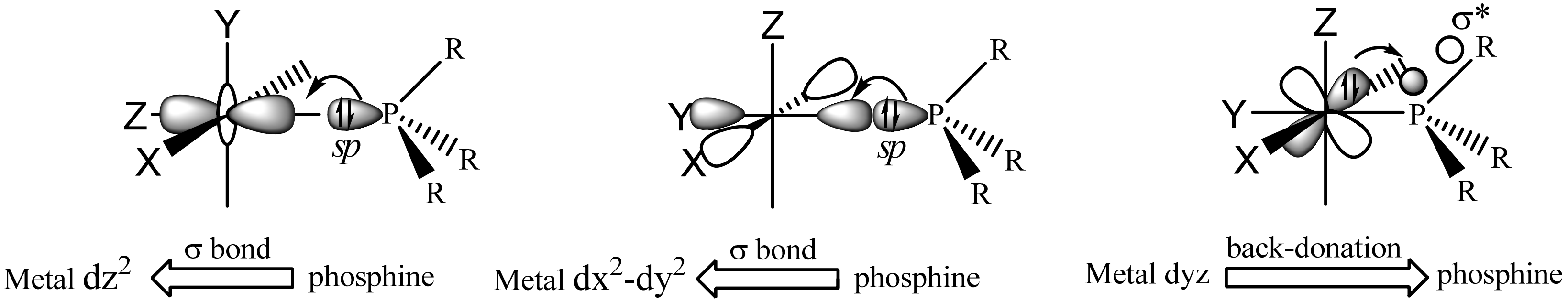




Metal Carbonyl

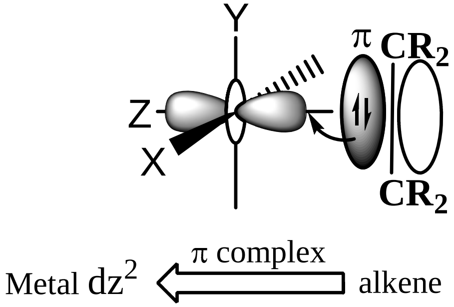


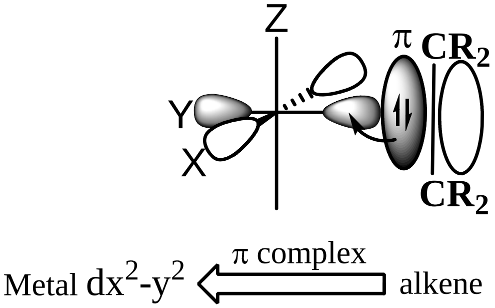
Metal Phosphine

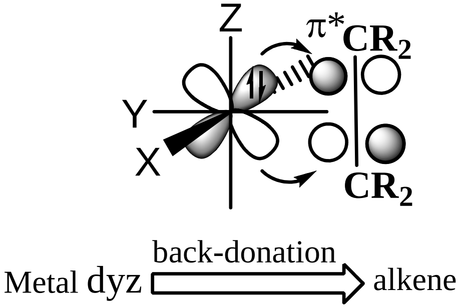


Z

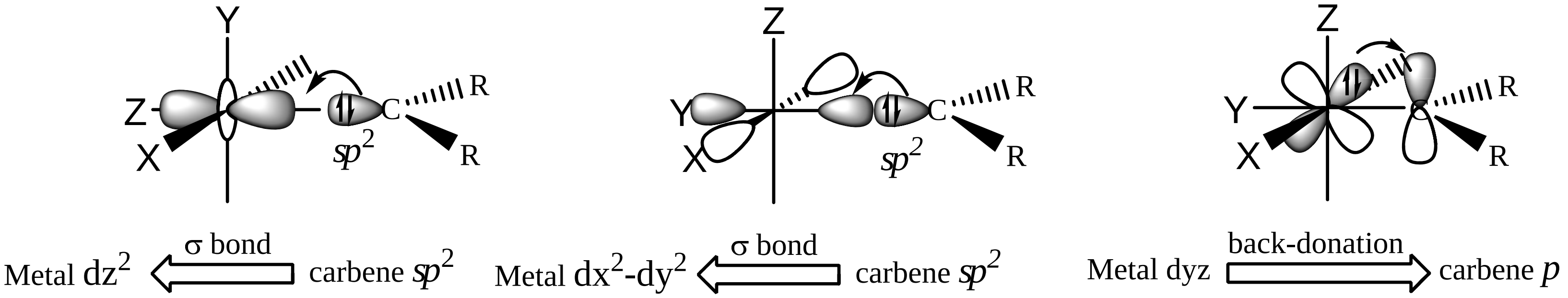
Metal Alkene







Fischer carbene



Schrock carbene