

Molecular-Orbital Theory

You have to explain the following statements:

- 1- Helium is monatomic gas.
- 2- Oxygen molecule has a permanent magnetic dipole moment.
- 3- Oxygen is paramagnetic gas.
- 4- Most homonuclear diatomic gases are diamagnetic.
- 5- He_2 , Be_2 and Ne_2 are not stable molecules.
- 6- He_2^+ and He_2^- exist!

Hydrogen-ion molecules: This is formed by the combination of hydrogen atom containing one electron and hydrogen ion having no electron. Therefore, this ion has only one electron.

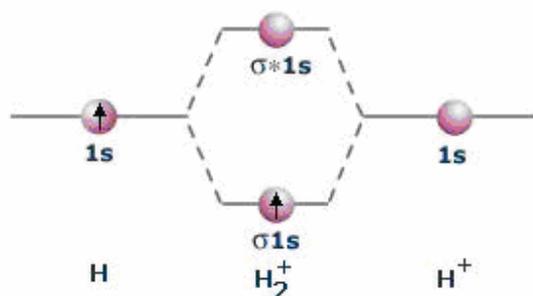


Figure 1 - Molecular orbital energy level diagram for H_2^+ - ion

The electronic configuration of the molecule is: $\text{H}_2^+ : (\sigma_g 1s)^1$

Bond order = $\frac{1}{2} (\# \text{ of bonding } e^- - \# \text{ of antibonding } e^-)$

The bond order in H_2^+ is : $\frac{1}{2}(1-0) = \frac{1}{2}$

1- The positive value of bond order indicates that the molecule is **stable**.

2- The presence of **unpaired electron** in the molecule indicates that it is **paramagnetic molecule**.

The stability of the ion as well as its paramagnetic character has been confirmed experimentally.

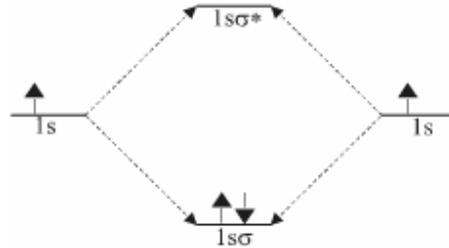
The bond length of H_2^+ ion is larger than that of H_2 molecule (bond length $\text{H}_2^+ = 104\text{pm}$; $\text{H}_2 = 47\text{pm}$)

while its bond dissociation energy is less than that of H_2 molecule (bond dissociation energy $\text{H}_2^+ = 269 \text{ KJ mol}^{-1}$, $\text{H}_2 = 458 \text{ KJ mol}^{-1}$). This clearly supports the fact that bond in H_2^+ ion is, weaker than that in H_2 molecule.

The He_2 molecule has four electrons, two in the bonding state $\sigma_g 1s$ and two in the antibonding state $\sigma_u^* 1s$; that is, $(\sigma_g 1s)^2 (\sigma_u^* 1s)^2$. The result is that **no stable configuration is produced**. This explains why **helium is a monatomic gas (Not a molecule)**. However, an excited He_2 molecule

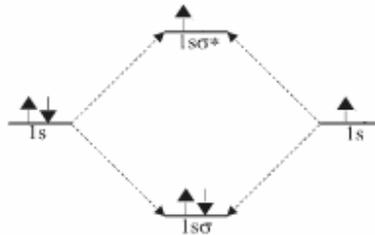
may be formed if one of the $\sigma_u^* 1s$ electrons is excited to the bonding state $\sigma_g 2s$, resulting in $(\sigma_g 1s)^2 (\sigma_u^* 1s) \sigma_g 2s$.

Hydrogen (H_2)



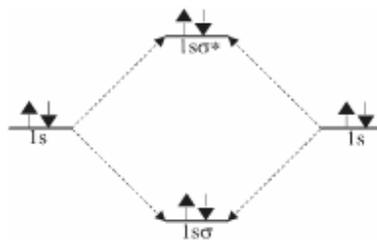
$$\text{Bond order} = \frac{1}{2} (\# \text{ of bonding } e^- - \# \text{ of antibonding } e^-) = \frac{2-0}{2} = 1.$$

Helium Ion (He_2^+)



The bond order for the helium ion molecule is $\frac{2-1}{2} = \frac{1}{2}$, i.e., He_2^+ does exist.

Helium (He_2)



The bond order for the helium molecule is $\frac{2-2}{2} = 0$, i.e., He_2 does not exist. **This explains why helium is a monatomic gas.**

Electronic Configuration of Homonuclear Diatomic Molecules

Molecule	Configuration								Dissociation energy, eV	Bond length, Å	Ground state
	$\sigma_{g,1s}$	σ_{g}^*1s	$\sigma_{g,2s}$	σ_{g}^*2s	$\pi_{g,2p}$	$\sigma_{g,2p}$	π_{g}^*2p	σ_{g}^*2p			
H ₂ ⁺	↑								2.65	1.06	² Σ _g
H ₂	↑↓								4.48	0.74	¹ Σ _g
He ₂ ⁺	↑↓	↑							3.1	1.08	² Σ _g
He ₂	↑↓	↑↓							Not stable		¹ Σ _g
Li ₂	↑↓	↑↓	↑↓						1.03	2.67	¹ Σ _g
Be ₂	↑↓	↑↓	↑↓	↑↓					Not stable		¹ Σ _g
B ₂	↑↓	↑↓	↑↓	↑↓	↑↑				3.6	1.59	³ Σ _g
C ₂	↑↓	↑↓	↑↓	↑↓	↑↑↓↓				3.6	1.31	¹ Σ _g
N ₂	↑↓	↑↓	↑↓	↑↓	↑↑↓↓	↑↓			7.37	1.09	¹ Σ _g
O ₂	↑↓	↑↓	↑↓	↑↓	↑↑↓↓	↑↓	↑↑		5.08	1.21	³ Σ _g
F ₂	↑↓	↑↓	↑↓	↑↓	↑↑↓↓	↑↓	↑↑↓↓		2.8	1.44	¹ Σ _g
Ne ₂	↑↓	↑↓	↑↓	↑↓	↑↑↓↓	↑↓	↑↑↓↓	↑↓	Not stable		¹ Σ _g

The above Table shows the electronic configuration of the homonuclear diatomic molecules up to Ne₂. The table also indicates the binding energy and the bond length of the ground state of these molecules. Some interesting features can be seen in his table. In general, molecular binding results when two electrons with opposite spins concentrate in the region between the two combining atoms; that is, they occupy bonding molecular orbitals. This, however, is not a strict rule, since Li₂ has only three electrons, and in B₂ and O₂, the last pair of electrons are in π – orbitals and their spins are parallel instead of opposed. This characteristic of B₂ and O₂ is due to the fact that π – orbitals can accommodate up to four electrons, two with spin up and two with spin down, while these molecules have only two electrons in that energy level. From the atomic case we recall that the repulsion among the electrons favors the most antisymmetric space wave function. This requires the most symmetric spin wave function according to the exclusion principle, which means in this case that the two electrons have their spins parallel. Since the resultant spin of O₂ is one, the oxygen molecule has a permanent magnetic dipole moment,

thereby explaining why Oxygen is a paramagnetic gas, while most homonuclear diatomic gases are diamagnetic. We may also expect that the stability of the molecule will depend on the relative number on the relative bonding and antibonding pairs of electrons. For example, we have indicated that He_2 has the same number of bonding and antibonding pairs of electrons and is not stable. The same happens to Be_2 therefore both molecules are unstable. On the other hand, the stability of N_2 , O_2 , F_2 and N_2 (as measured by the dissociation energy) decreases because the difference between bonding and antibonding pairs for these molecules is a 2, 1, and 0, respectively.

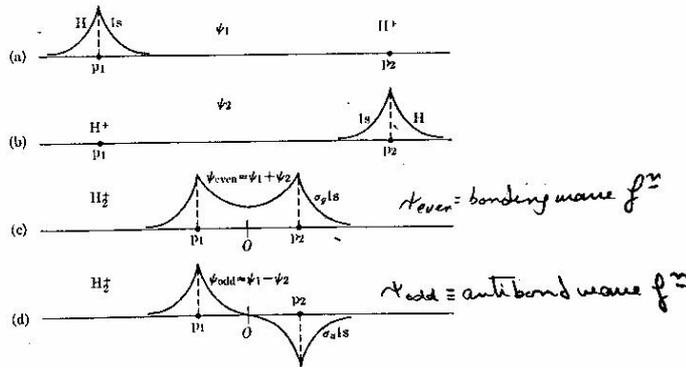


Fig. 5-4. Even and odd molecular orbitals in H_2^+ .

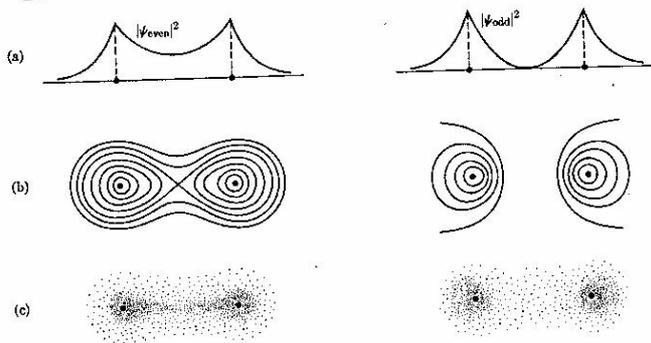


Fig. 5-5. Probability density for even and odd molecular orbitals in H_2^+ . (a) Distribution along the lines joining the protons; (b) and (c) distribution in a plane containing the two protons.

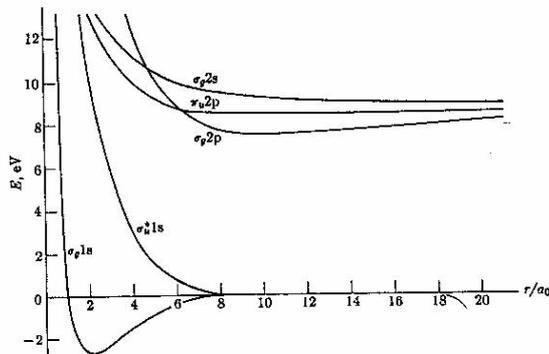
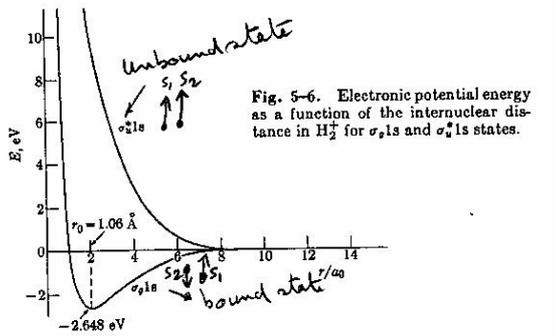


Fig. 5-7. Electron potential energies in H_2^+ for the ground state and some excited states.

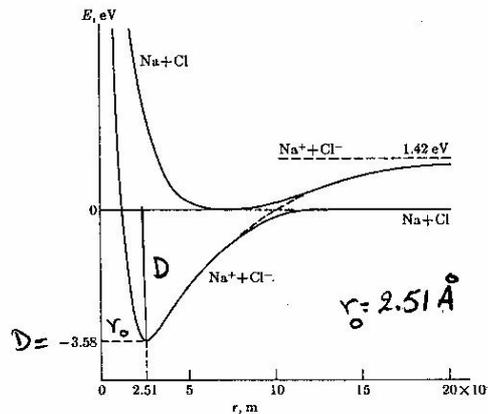


Fig. 5-14. Potential energy curves for NaCl and Na^+Cl^-

$r_0 \equiv$ equilibrium distance (at which the energy will be minimum)
 $D =$ dissociation energy of a molecule (energy needed to separate a molecule in its lowest energy state into its components)

The He_2 molecule has four electrons, two in the bonding state $\sigma_g 1s$ and two in the antibonding state $\sigma_u^* 1s$; that is, $(\sigma_g 1s)^2 (\sigma_u^* 1s)^2$. The result is that no stable configuration is produced. This explains why helium is a monatomic gas. However, an excited He_2 molecule may be formed if one of the $\sigma_u^* 1s$ electrons is excited to the bonding state $\sigma_g 2s$, resulting in $(\sigma_g 1s)^2 \sigma_u^* 1s \sigma_g 2s$.

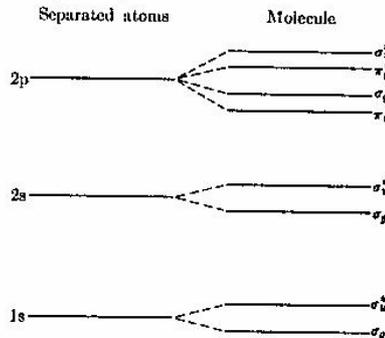


Fig. 5-11. Electronic energy levels in homonuclear diatomic molecules.

TABLE 5-2 Dissociation Energies D , Bond Lengths r_0 , and Electric Dipole Moments p of Some Diatomic Molecules*

Covalent				Ionic			
Molecule	D , eV	r_0 , Å	p , D	Molecule	D , eV	r_0 , Å	p , D
H_2	4.48	0.74	0	NaCl	3.58	2.51	8.5
Li_2	1.03	2.67	0	HCl	4.43	1.27	1.07
O_2	5.08	1.21	0	LiH	2.5	1.60	5.88
N_2	7.37	1.09	0	KBr	3.96	2.94	1.29
Cl_2	2.47	1.99	0	KF	5.9	2.55	8.60
HI	3.06	1.61	0.38	CsCl	3.76	3.06	9.97
CO	11.11	1.13	0.12	KCl	4.92	2.79	8.0
NO	5.3	1.15	0.15	KI	3.0	3.23	9.24

* The molecules are grouped according to the dominant character of the bond. Electric dipole moments are expressed in *debyes* (D). One D is 3.3×10^{-30} m C.

Ionic molecule \equiv polar molecule \equiv heteropolar (dissimilar)

Covalent bond \equiv homopolar bond

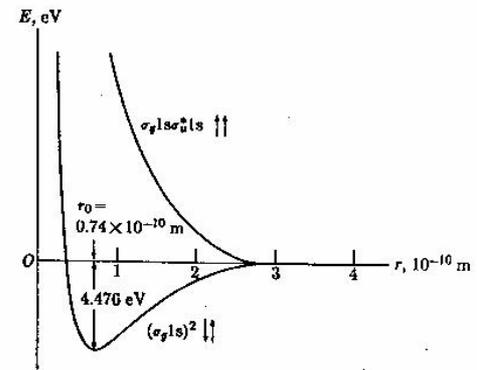


Fig. 5-13. Electronic potential energy as a function of internuclear separation for bonding and antibonding states in H_2 .

Introduction

Orbitals in molecules are not necessarily localized on atoms or between atoms as suggested in the valence bond theory.

Molecular orbitals can also be formed the LCAO where more than two atomic orbitals are used. (Technically, we can use all of the atomic orbitals in the LCAO.)

Linear combinations of orbitals result in the interference of waves. Both constructive and destructive interference may result.

Within a diatomic molecule, N atomic orbitals on atom 1 and N atomic orbitals on atom 2 result in 2N molecular orbitals.

In a practical sense, only those atomic orbitals that have similar energies and the appropriate symmetry can combine to form molecular orbitals.

These molecular orbitals are classified as **bonding orbitals**, **antibonding orbitals** or **nonbonding orbitals**.

Types of Molecular Orbitals

Bonding Orbitals

For the linear combination of only two atomic orbitals, the bonding orbital is constructed from adding the wavefunctions together.

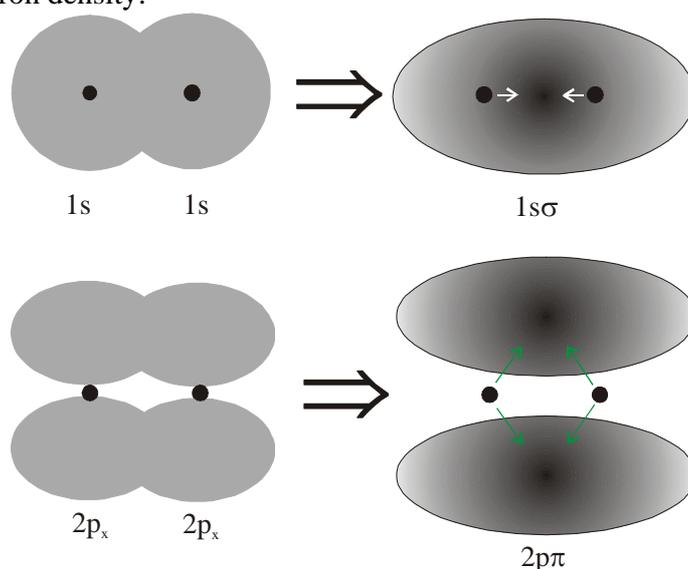
$$\Psi_{MO} = \Psi_{AO}(A) + \Psi_{AO}(B)$$

Thus, the probability density of the bonding orbital can be written as

$$\begin{aligned} |\Psi_{MO}|^2 &= |\Psi_{AO}(A)|^2 + |\Psi_{AO}(B)|^2 + 2\Psi_{AO}(A)\Psi_{AO}(B) \\ &= A^2 + B^2 + 2AB \end{aligned}$$

The 2AB term is the constructive interference of the overlap of the atomic orbitals.

- The interference results in an increase of electron density between the nuclei.
- Thus, the nuclei have greater attraction to each other, via their mutual attraction to the increased electron density.



Aside: $S = \int AB d\tau$ is called **overlap integral**.

Antibonding Orbitals

For the linear combination of only two atomic orbitals, the antibonding orbital is constructed from subtracting the wavefunctions together.

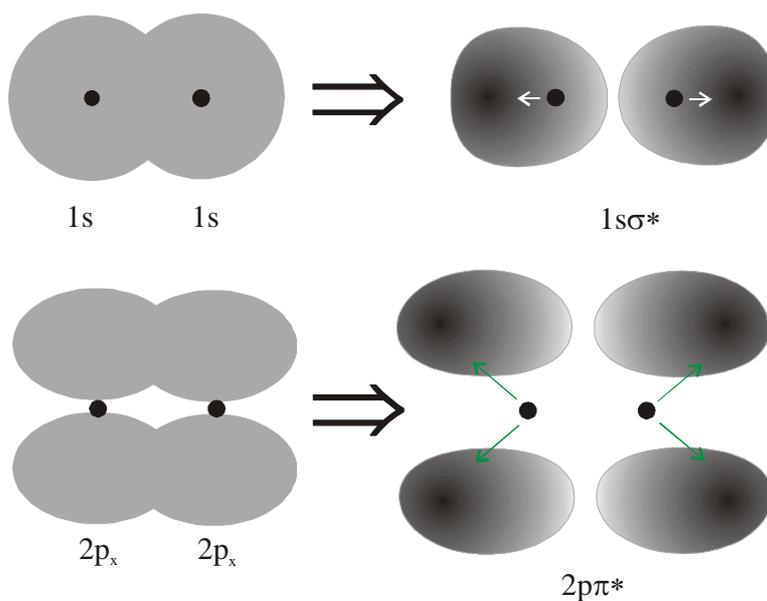
$$\Psi_{MO} = \Psi_{AO}(A) - \Psi_{AO}(B)$$

Thus, the probability density of the bonding orbital can be written as

$$\begin{aligned} |\Psi_{MO}|^2 &= |\Psi_{AO}(A)|^2 + |\Psi_{AO}(B)|^2 - 2\Psi_{AO}(A)\Psi_{AO}(B) \\ &= A^2 + B^2 - 2AB \end{aligned}$$

The $-2AB$ term is the destructive interference of the overlap of the atomic orbitals.

- The interference results in a decrease of electron density between the nuclei and increase of electron density away from the nuclei.
- Thus, the nuclei are drawn away from each other.



The energy increase of the antibonding orbital is slightly higher than the energy decrease of the bonding orbital.

$$E_{\pm} \propto \frac{1}{1 \pm S} \quad (S \text{ is the overlap integral})$$

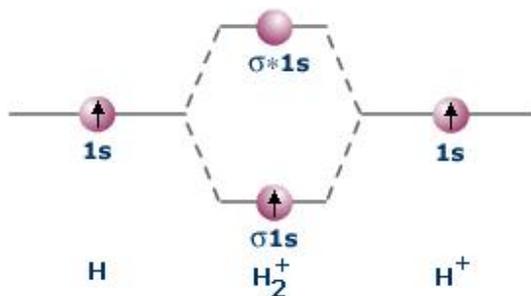
Example: Let $S = \frac{1}{4}$

$$E_{+} \propto \frac{1}{1+S} = \frac{1}{1+\frac{1}{4}} = \frac{1}{\frac{5}{4}} = \frac{4}{5} \quad E_{-} \propto \frac{1}{1-S} = \frac{1}{1-\frac{1}{4}} = \frac{1}{\frac{3}{4}} = \frac{4}{3}$$

Energy Level Diagrams of Diatomic Molecular Orbitals

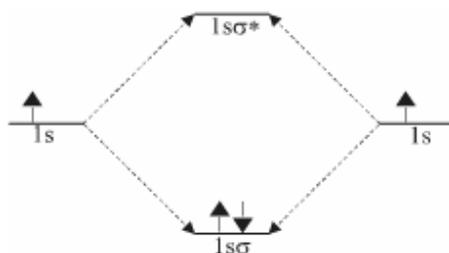
Homonuclear Diatomic Molecules

Hydrogen Ion H_2^+



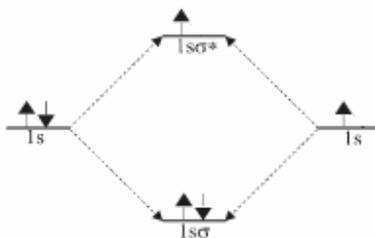
$$\text{Bond order} = \frac{1}{2} (\# \text{ of bonding } e^- - \# \text{ of antibonding } e^-) = \frac{1-0}{2} = \frac{1}{2}.$$

Hydrogen (H_2)



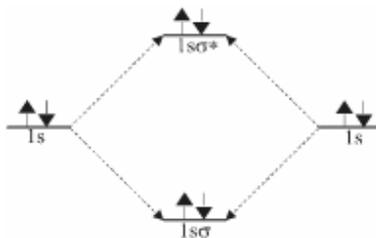
$$\text{Bond order} = \frac{1}{2} (\# \text{ of bonding } e^- - \# \text{ of antibonding } e^-) = \frac{2-0}{2} = 1.$$

Helium Ion (He_2^+)



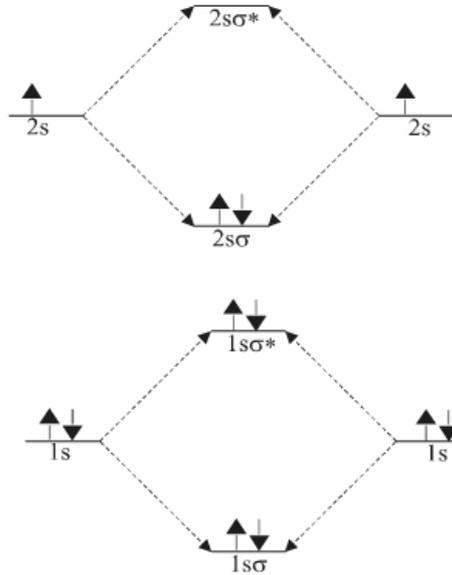
The bond order for the helium ion molecule is $\frac{2-1}{2} = 1$, i.e., He_2^+ does exist.

Helium (He_2)



The bond order for the helium molecule is $\frac{2-2}{2} = 0$, i.e., He_2 does not exist. ***This explains why helium is a monatomic gas.***

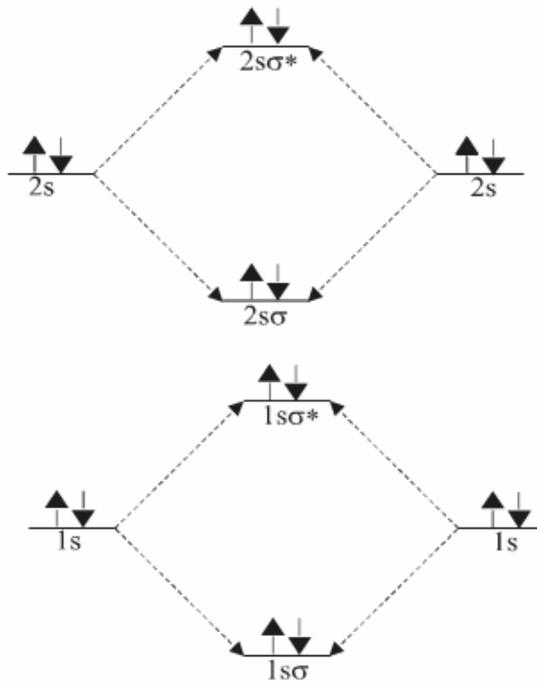
Lithium



Dilithium exists! (Though not as crystal!)

The bond order for the lithium molecule is one, i.e., 2 bonds – 1 antibond = 1 bond.

Beryllium



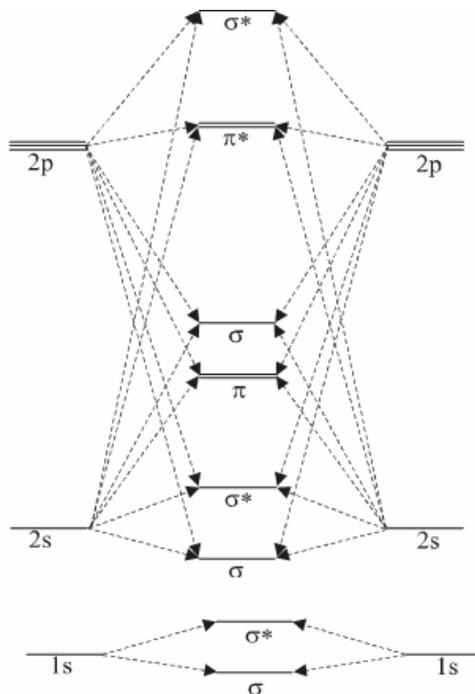
Diberyllium does not exist.

The bond order for the beryllium molecule is zero,

- i.e., 2 bonds – 2 antibonds = 0 bond.

Molecular Orbital Diagrams for Second Row Diatomic Molecules (Not needed)

B₂ through N₂



Notes:

For B through N, 2s and 2p are close enough in energy for hybridization to change the order of the molecular orbital energies.

B₂ bond is π bond?!? Also, B₂ is **paramagnetic**. The resultant spin of B₂ is 1.

- Molecular electronic structure also follows Hund's rules.

C₂ bonding is 2 π bonds. C₂ is **diamagnetic**.

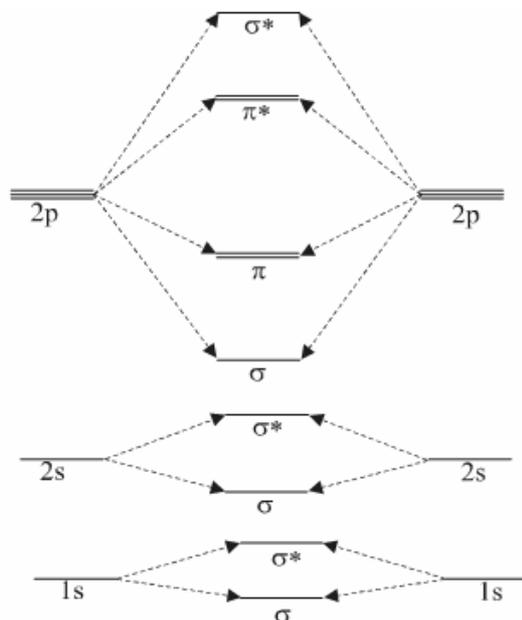
Note carbide ion, C₂²⁻ has triple bond.

N₂ has triple bond. N₂ is diamagnetic.

Q: Which is more stable, N₂⁺ or N₂⁻?

A: Antibond stronger than bond; therefore N₂⁺ is predicted to be more stable.

O₂ through Ne₂



Notes:

O_2 bond is 1 σ and 1 π bond and the resultant spin is 1. Also, O_2 is paramagnetic.

F_2 bonding is σ bond. F_2 is diamagnetic.

Bond order of Ne_2 is zero. Ne atoms are not bound.

- Dimer does exist as van der Waals state.

- Ne_2^+ can exist.

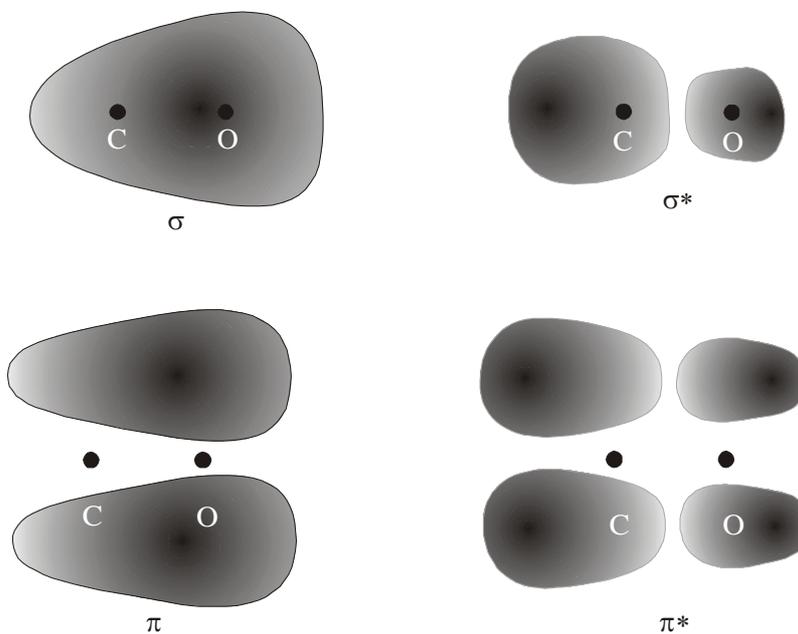
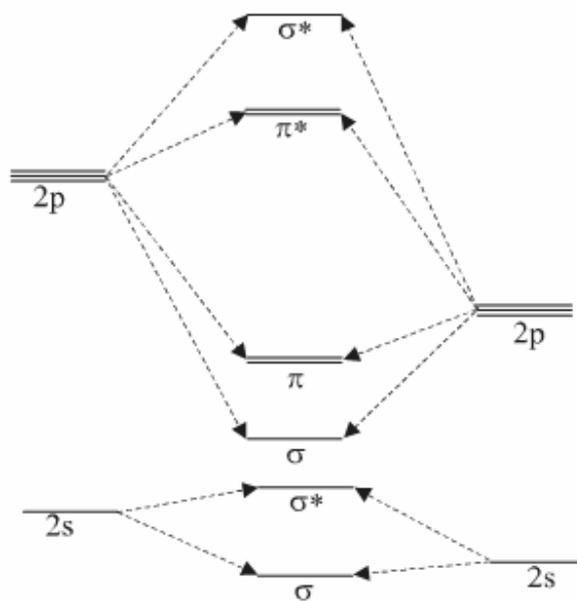
Q: According to MO theory, Ne_2^{2+} should be stable ion. Why haven't we heard of it until now?

A: I don't know.

Hypothesis: Neon is even more electronegative than fluorine.

Heteronuclear Diatomic Molecules

Energy of atomic orbitals is affected by effective nuclear charge.
More electronegative atom will draw electron density to itself in a bonding orbital.
Consider carbon monoxide as an example.



Note: Most electropositive atom has most anti-bonding density.

Term Symbols of Molecular States

Molecular Angular Momentum of Diatomic Molecules

Orbital Angular Momentum

The electron in a non-sigma bond experiences a cylindrically symmetric potential energy in contrast to an electron in an atomic non-s orbital that has a spherically symmetric potential energy.

The electron in a non-sigma bond has an angular momentum, L . However, because the electric field from the nuclei and the other electrons is not spherically symmetric, the angular is not well characterized.

However, for an electron in a non-sigma bond, the projection of the angular momentum upon the internuclear axis, M_L , is well characterized.

- To distinguish from the atomic M_L , the molecular M_L is given a new symbol, Λ .

Thus, the electronic state of a diatomic molecule is partially characterized by Λ .

$M_L \rightarrow \Lambda$	0	± 1	± 2	± 3
symbol	Σ	Π	Δ	Φ

Each electron contributes to the total orbital angular momentum thus

$$\Lambda = \Lambda_1 + \Lambda_2 + \dots$$

Each Λ state is doubly degenerate except the Σ state that has one state.

In other words, $E_{-\Lambda} = E_{\Lambda}$

A non-sigma bond electron has two directions to precess about the internuclear axis.

Spin Angular Momentum

The spin precesses about the internuclear axis since the magnetic moment of the electron tries to align itself with the magnetic field created by the "nuclei orbiting about the electron".

- This phenomenon could be referred to as molecular spin-orbit coupling.

The projection of the spin, S , on the internuclear axis is M_S .

- To distinguish from the atomic M_S , the molecular M_S is given a new symbol, Σ .

- Note source of confusion: Σ can refer to a specific orbital angular momentum state or it can refer to the general total spin angular momentum.

Each electron contributes to the total spin angular momentum thus

$$\Sigma = \Sigma_1 + \Sigma_2 + \dots$$

$$\text{Multiplicity} = 2\Sigma + 1$$

The rules for multiplicity are the same as for atomic structure.

- filled orbital $\Sigma = 0$ multiplicity = 1 singlet
- half-filled orbital $\Sigma = 1/2$ multiplicity = 2 doublet
- two half-filled orbitals $\Sigma = 1$ multiplicity = 3 triplet

Introduction to Symmetry

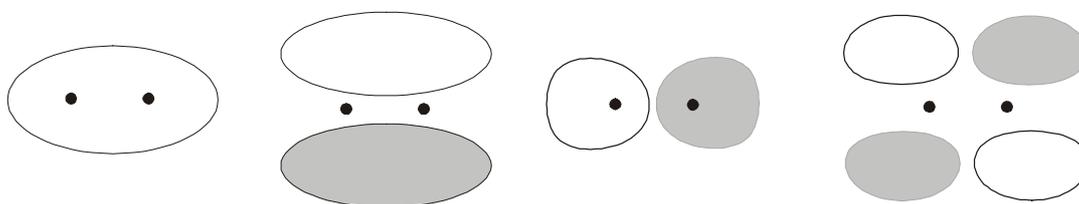
Parity

- g – **gerade** symmetric for inversion through center
- u – **ungerade** antisymmetric for inversion through center

Reflection

- + - reflection through plane containing internuclear axis is symmetric
- reflection through plane containing internuclear axis is antisymmetric

Consider the symmetries of the sigma and pi bonding and antibonding orbitals.



Parity	g	u	u	g
Reflection	+	-	+	-

When two or more electrons are in a molecular state, the total symmetry of the state is determined by multiplying the symmetries of the electrons together.

Multiplication rules for of parity and reflection symmetries

Parity

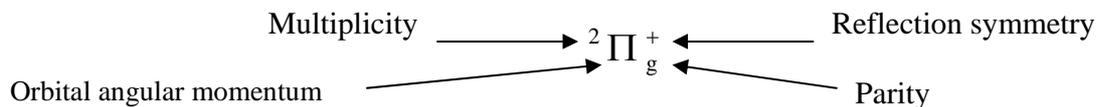
$$g \times g = g \quad g \times u = u \times g = u \quad u \times u = g$$

Reflection

$$(+)\times(+)= (+) \quad (+)\times(-)=(-)\times(+)=(-) \quad (-)\times(-)= (+)$$

Writing Term Symbols

Information available in a molecular term symbol



Writing an electron configuration as a term symbol.

1- For $H_2^+ \Rightarrow \sigma_g(1s)$, $2S+1 = 2 \times \frac{1}{2} + 1 = 2$, $m_\ell = 0 \Rightarrow \Lambda = 0 \Rightarrow \sigma_g(1s) \rightarrow {}^2\Sigma_g$

2- For $H_2 \Rightarrow \sigma_g^2(1s)$, $2S+1 = 2 \times 0 + 1 = 1$, $m_\ell = 0 \Rightarrow \Lambda = 0 \Rightarrow \sigma_g^2(1s) \rightarrow {}^1\Sigma_g$

Note : For closed shell $2S+1 = 2 \times 0 + 1 = 1$, $m_\ell = 0$

3- B_2 (each atom has five electrons $1s^2, 2s^2, 2p^1$)

The electron configuration for B_2 can be written as $(1s\sigma^2)(1s\sigma^{*2})(2s\sigma^2)(2s\sigma^{*2})(2p\pi^2)$
As in the atomic case, closed subshells do not contribute to the total angular momentum.

Two cases for electrons in the $2p\pi$ orbitals.

each electron is in different orbitals

$$\Lambda = \Lambda_1 + \Lambda_2 = 1 + (-1) = 0 \Rightarrow \Sigma \text{ state}$$

electron spins can be parallel or antiparallel

$$\Sigma = \Sigma_1 + \Sigma_2 = 1/2 + 1/2 = 1 \text{ or } \Sigma = \Sigma_1 + \Sigma_2 = 1/2 - 1/2 = 0$$

thus, possible terms are ${}^3\Sigma_g^+$ or ${}^1\Sigma_g^+$

both electrons in the same orbital

$$\Lambda = \Lambda_1 + \Lambda_2 = 1 + 1 = 2 \Rightarrow \Delta \text{ state}$$

electron spins can be antiparallel only (can't violate Pauli exclusion principle)

$$\Sigma = \Sigma_1 + \Sigma_2 = 1/2 - 1/2 = 0$$

thus, possible terms are ${}^1\Delta_g^+$

Using Hund's rules as with the atomic term symbols, the term with the highest multiplicity is the lowest energy. Thus the ground state term of B_2 is ${}^3\Sigma_g^+$

4- C_2 (each atom has six electrons $1s^2, 2s^2, 2p^2$) .

The ground state electron configuration for C_2 can be written as

$(1s\sigma^2)(1s\sigma^{*2})(2s\sigma^2)(2s\sigma^{*2})(2p\pi^4)$. Thus the term for the ground state is ${}^1\Sigma_g^+$.

However, consider excited state ${}^3\Sigma_u^+$. What is the electronic configuration for lowest possible excited state? How can we assign the molecular orbitals for the various electrons?

The Σ state implies that $\Lambda = 0$. At this point, let us consider that a single electron has been excited to a π^* orbital.

$$\Lambda = 0 \Rightarrow \Lambda_1 + \Lambda_2 = 0 \Rightarrow \Lambda_1 = 1 \quad \Lambda_2 = -1$$

Note that the above could be true if the electron is excited to a higher π orbital as well.

multiplicity = 3 implies that $\Sigma = 1 \Rightarrow \Sigma_1 = \Sigma_2 = 1/2$

The one electron remaining in the π orbital has an ungerade parity and negative reflection symmetry.

Thus, the electron in the unknown orbital must be gerade parity and negative reflection symmetry.

$$u \times ? = u \Rightarrow ? = g \qquad (-) \times (?) = (+) \Rightarrow (?) = (-)$$

Since the π^* orbital has gerade parity and negative reflection symmetry, it is possible that the ${}^3\Sigma_u^+$ implies the electron configuration $(1s\sigma^2)(1s\sigma^{*2})(2s\sigma^2)(2s\sigma^{*2})(2p\pi^3)(2p\pi^{*1})$.

However, ambiguity exists in the term symbol.

The electron configuration, $(1s\sigma^2)(1s\sigma^{*2})(2s\sigma^2)(2s\sigma^{*2})(2p\pi^3)(3p\pi^{*1})$, would also result in a term of ${}^3\Sigma_u^+$. To unambiguously assign electronic structure, more information is needed.

The term symbols of molecular states are very convenient when studying electronic spectroscopy. The selection rules of electronic spectroscopy are dependent on the symmetry changes of the states. Thus having the term symbols will allow us to quickly identify between which states transitions can occur.

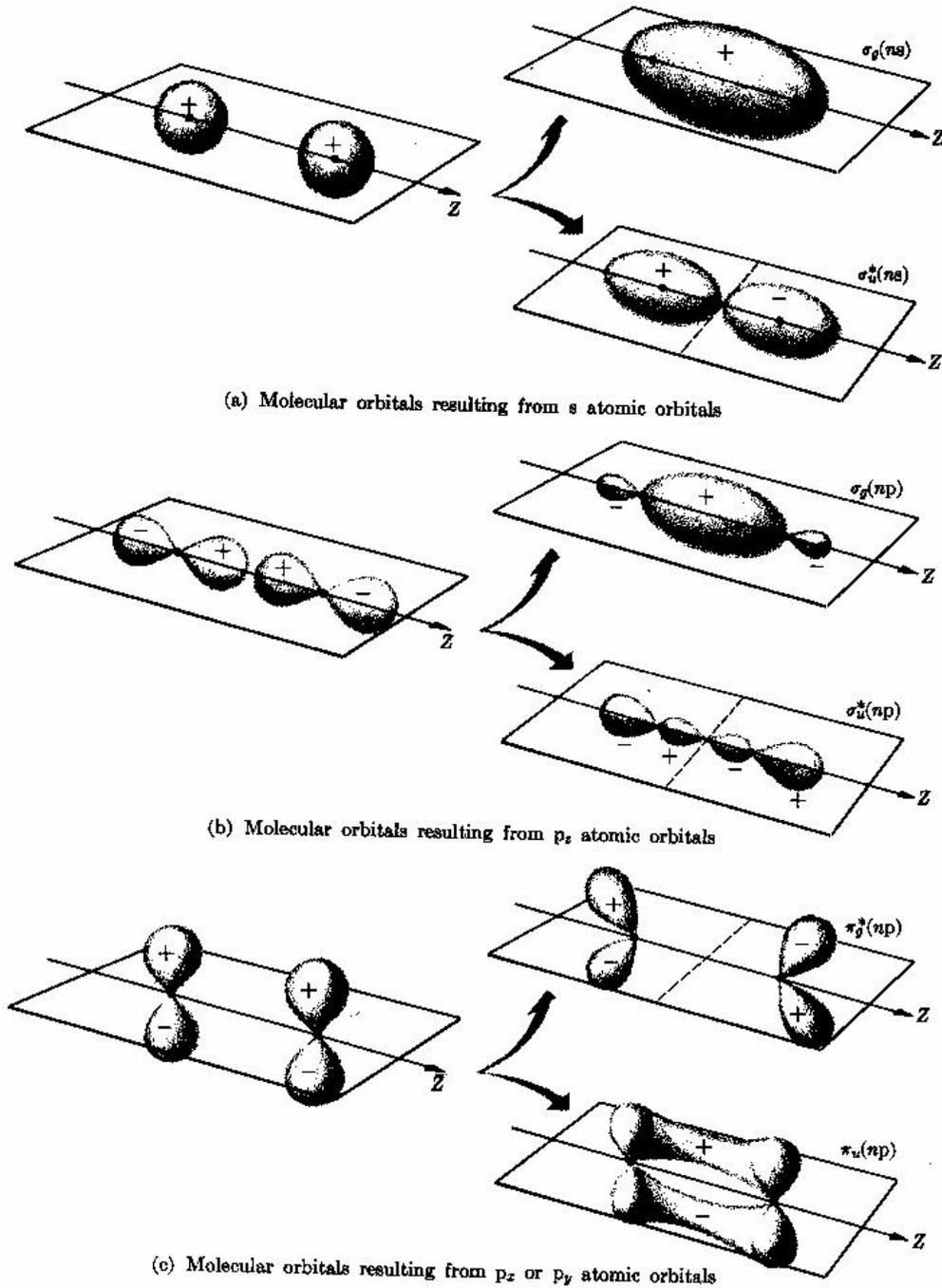


Fig. 5-10. Molecular orbitals in homonuclear diatomic molecules.