Molecular Structure

談論到分子結構的兩個重要理論:

1. VB Theory (Valence Bond Theory):
引用 σ bond, π bond, promotion 及hybridization 觀念來解釋分子 的電子結構.

2. MO Theory (Molecular Orbital Theory):
基本觀念如同AO (Atomic Orbital), MO認為 wavefN是 spreads over all the atoms in a molecular.

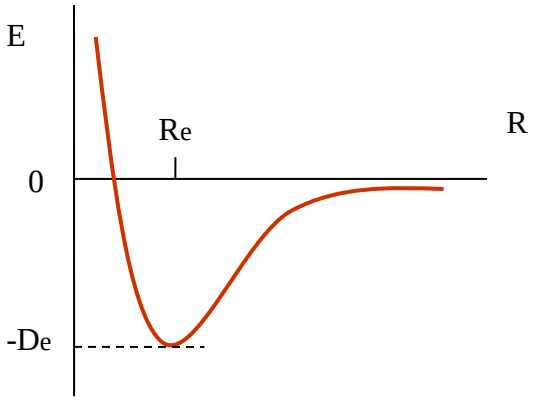
可用來描述固態分子的電子結構，電導性及半導性.

Born-Oppenheimer Approximation.

目前Schrödinger equation只能解一個particle的case ，所以對H原子 or (hydrogenic atoms)可以得到精密的能階及orbital的解。然而對最簡單的分子 H_2^+ (因其具有三個particles，2個H核及一個e^-)，仍無法解，幸好有Born-Oppenheimer approximation的提出，如下:

B-O approximation:
由於原子核的質量遠大於電子，相對於電子而言移動很慢(可視為是stationary)，因此可以假想原子核是被固定在某特定的核距R (nuclei are being fixed at arbitrary separation R)，只有單一個電子(H_2^+ case)在此核距下所形成的位能，在Schrödinger equation的建構下，可解出該電子的wavefN,在ground state該approximation還算不會有太大誤差，但在excited state就不適用。

依據B-O app.可先選一特定核距R，解Schrödinger equation，得到電子能量，再改變另一核距R’ ，再解Schrödinger equation，算出該核距下電子的能量，如此不斷可算出多個R值下的電子能量，畫出如下圖:

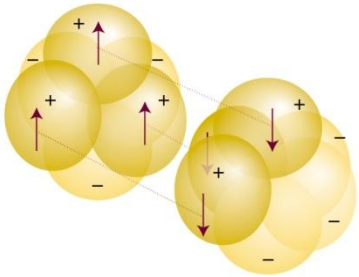


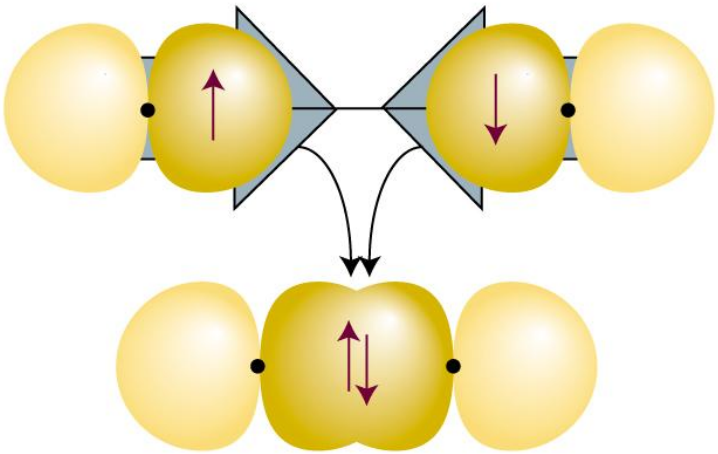
說明 “how the energy of the molecule varies with bond length”.稱為 “Molecular potential energy curve”(因為我們是假設原子核是不動的，不具任何動能)，由該圖可得R_e，D_0(bond dissociation energy)及 D_e(the depth of the minimum (well))。

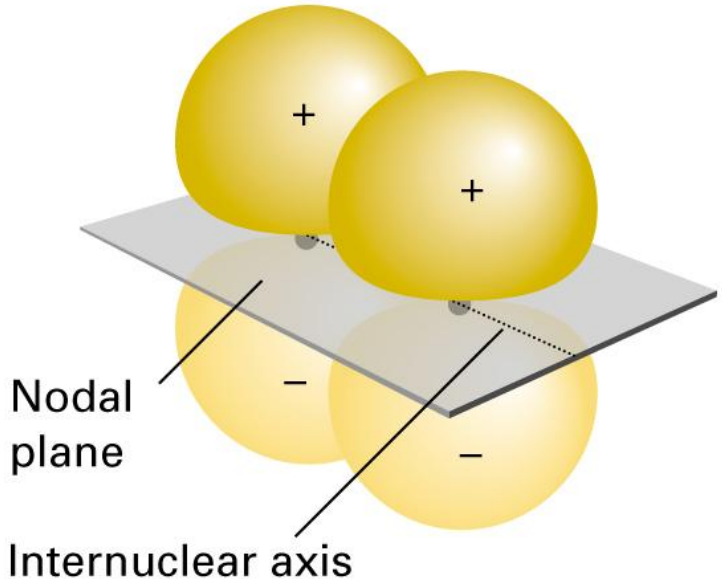
VB 理論

Nitrogen, N_2

$$2s^2 2p_x^1 2p_y^1 2p_z^1.$$







A σ bond is then formed by spin pairing between the two electrons in the two *$2p_z$ orbitals.*

The remaining *2p orbitals cannot merge to give σ bonds as they do not have cylindrical* symmetry around the internuclear axis. Instead, they merge to form two π bonds. A ***π bond*** *arises from the spin pairing of electrons in two p orbitals that* approach side-by-side.

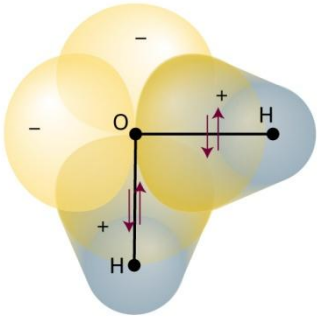
同樣以VB理論用於H_2O分子時，

O　提供2p軌域2個valence e-（互成90度）

H　提供1s軌域與O中一個p軌域結合

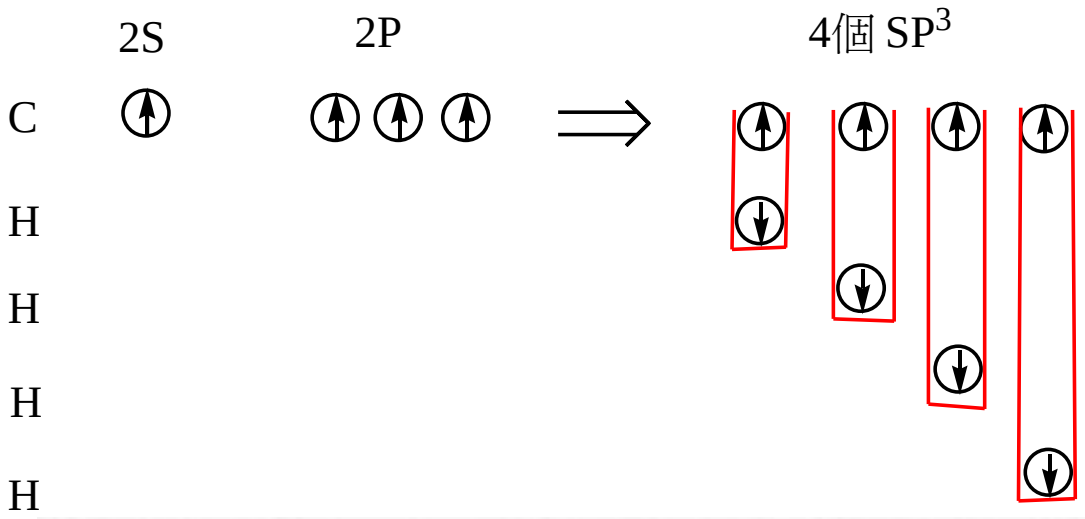
H　提供1s軌域與O中另一個p軌域結合

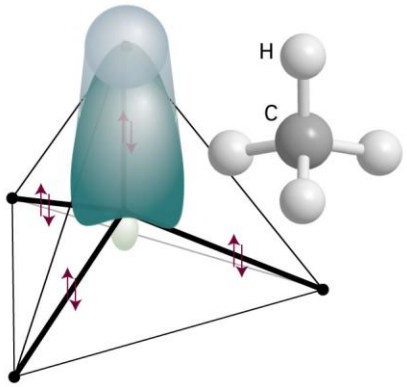
p^2鍵結



但CH_4分子，則必須提升C原子中的2s軌域電子到2p，同時hybridized。

∴不但promotion，同時hybridization。





$$h_1 = s + p_x + p_y + p_z \qquad h_2 = s - p_x - p_y + p_z$$
$$h_3 = s - p_x + p_y - p_z \qquad h_4 = s + p_x - p_y - p_z$$

$$\psi = h_1(1)A(2) + h_1(2)A(1)$$

A hybrid orbital has enhanced amplitude in the internuclear region, which arises from the constructive interference between the *s orbital and the positive lobes of the P* orbitals

As a result, the bond strength is greater than for a bond formed from an s or *p orbital alone. This increased bond strength is another factor that helps* to repay the promotion energy.

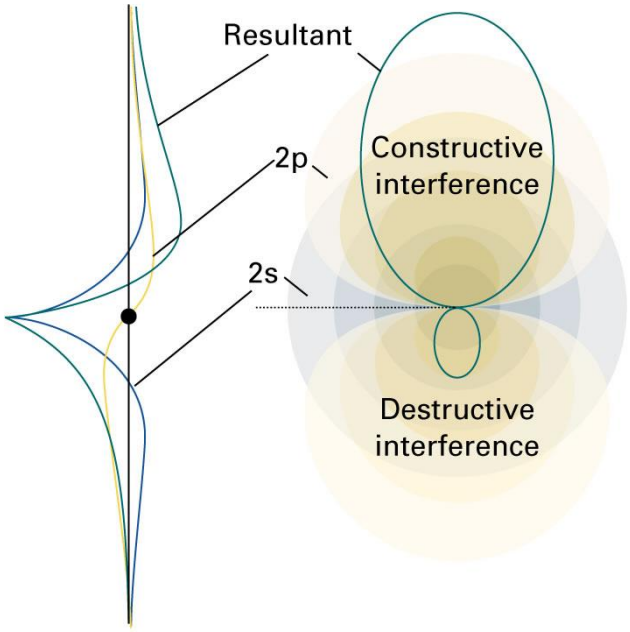


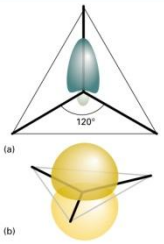
Table 10.1* Some hybridization schemes

Coordination number	Arrangement	Composition
2	Linear	sp, pd, sd
	Angular	sd
3	Trigonal planar	sp^2, p^2d
	Unsymmetrical planar	spd
	Trigonal pyramidal	pd^2
4	Tetrahedral	sp^3, sd^3
	Irregular tetrahedral	spd^2, p^3d, dp^3
	Square planar	p^2d^2, sp^2d
5	Trigonal bipyramidal	sp^3d, spd^3
	Tetragonal pyramidal	sp^2d^2, sd^4, pd^4, p^3d^2
	Pentagonal planar	p^2d^3
6	Octahedral	sp^3d^2
	Trigonal prismatic	spd^4, pd^5
	Trigonal antiprismatic	p^3d^3

* Source: H. Eyring, J. Walter, and G.E. Kimball, *Quantum chemistry*, Wiley (1944).

***sp2* hybrid orbitals:**

$$h_1 = s + 2^{1/2}p_y \qquad h_2 = s + (\tfrac{3}{2})^{1/2}p_x - (\tfrac{1}{2})^{1/2}p_y \qquad h_3 = s - (\tfrac{3}{2})^{1/2}p_x - (\tfrac{1}{2})^{1/2}p_y$$



***sp* hybrid orbitals:**

$$h_1 = s + p_z \qquad h_2 = s - p_z$$

以VSEPR (Valence Shell Electron Pair Repulsion)理論，認為這4個sp^3形成的面度應為4面體，同樣類似方法可用到過渡金屬中d軌域的鍵結，而有sp、sp^2、sp^3、dsp^3、d^2sp^3、……平面或八面體結構等。

這VB理論純粹用原子的valence electron及orbital，兩個原子軌域，兩個原子軌域成對結合形成bonding，雖然是形成分子，但仍然還是具備原子軌域的性質，簡單、方便、容易明瞭，常運用到有機及無機分子的鍵結說明。

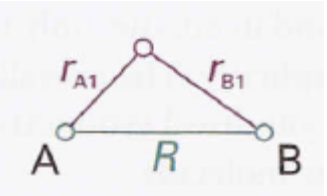
缺點:其比較沒有整體觀念，電子還是局部的散佈在原子與原子間。

Molecular orbital theory

In MO theory, it is accepted that electrons should not be regarded as belonging to particular bonds but should be treated as spreading throughout the entire molecule

ex: H_2^+

$$H = -\frac{\hbar^2}{2m_e}\nabla_1^2 + V \qquad V = -\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{A1}} + \frac{1}{r_{B1}} - \frac{1}{R}\right)$$



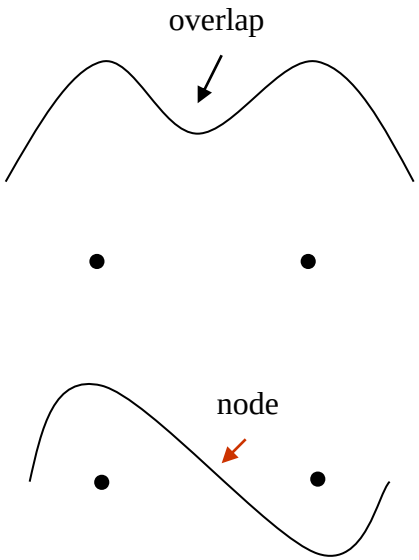
The one-electron wavefunctions obtained by solving the Schrodinger equation *are called molecular orbitals (MO).*

Problem: the solution cannot be extended to polyatomic systems.

LCAO-MO: $$\Psi_{MO} = \sum_i c_i \phi_i$$

, 其中ϕ_i 為 Atomic orbital, 由所求出的一組{Ci}就代表一個MO(Ψ_{MO}),而N個AO可以線性組合成N個MO,亦即有N組{Ci},這是近似真正MO的一種表示方法,具有AO的特質。

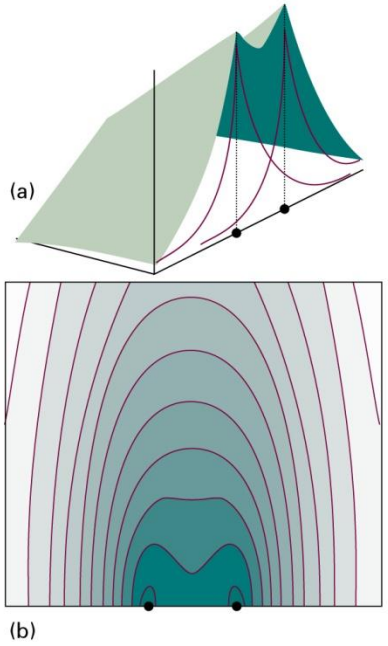
結果E_+比較低，代表ground state，ψ_{+H_2} 為ground state MO，畫出圖形



ψ_{+H_2} σ

ψ_{-H_2} σ^*

$\psi_{\pm} = N(A \pm B)$



Normalize the molecular orbital ψ_+ in eqn 11.7.

Method We need to find the factor N such that

$$\int \psi^* \psi \, d\tau = 1$$

To proceed, substitute the LCAO into this integral, and make use of the fact that the atomic orbitals are individually normalized.

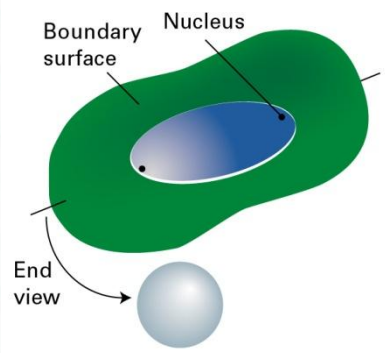
Answer When we substitute the wavefunction, we find

$$\int \psi^* \psi \, d\tau = N^2 \left\{ \int A^2 d\tau + \int B^2 d\tau + 2 \int AB \, d\tau \right\} = N^2(1 + 1 + 2S)$$

where $S = \int AB \, d\tau$. For the integral to be equal to 1, we require

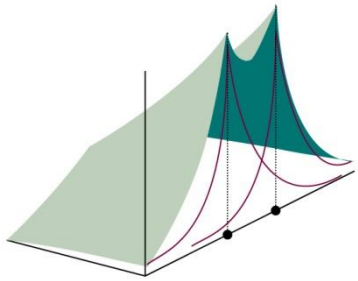
$$N = \frac{1}{\{2(1+S)\}^{1/2}}$$

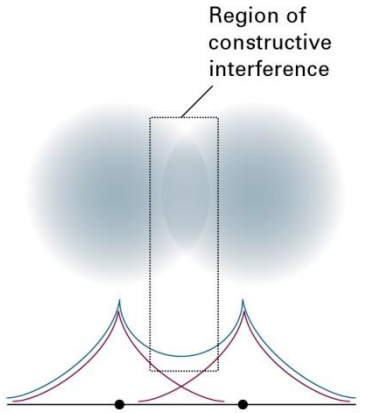
In H_2^+, $S \approx 0.59$, so $N = 0.56$.



$$\psi_+^2 = N^2(A^2 + B^2 + 2AB)$$

1 A^2, the probability density if the electron were confined to the atomic orbital A.
2 B^2, the probability density if the electron were confined to the atomic orbital B.
3 $2AB$, an extra contribution to the density.



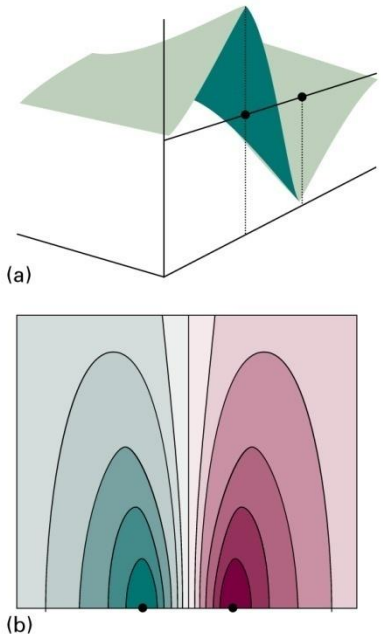


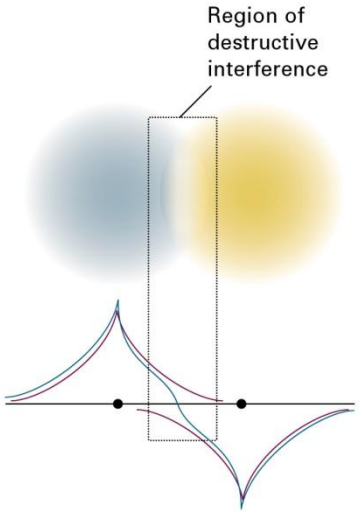
The enhancement **(finding the electron in the internuclear region)** can be traced to the constructive interference of the two atomic orbitals: each has a positive amplitude in the internuclear region, so the total amplitude is greater there than if the electron were confined to a single atomic orbital. (S = 0 for separate atoms, orthogonal)

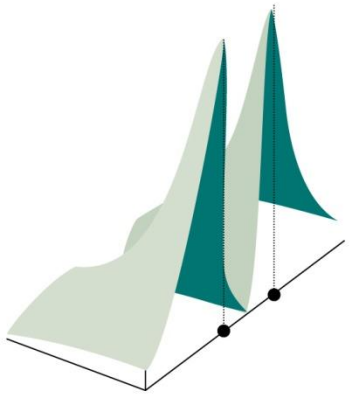
This conventional explanation, however, has been called into question, because shifting an electron away from a nucleus into the internuclear region *raises its potential energy. The modern (and still controversial)* explanation does not emerge from the simple LCAO treatment given here. It seems that, at the same time as the electron shifts into the internuclear region, the **atomic orbitals shrink**. This orbital shrinkage improves the electron-nucleus attraction more than it is decreased by the migration to the internuclear region, so there is a net lowering of potential energy. The kinetic energy of the electron is also modified because the curvature of the wavefunction is changed, but the change in kinetic energy is dominated by the change in potential energy.

$$\psi_-^2 = N^2(A^2 + B^2 - 2AB)$$

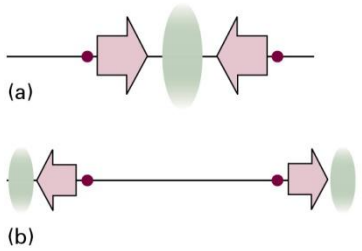
There is a reduction in probability density between the nuclei due to the *-2AB term*; in physical terms, there is destructive interference where the two atomic orbitals overlap.

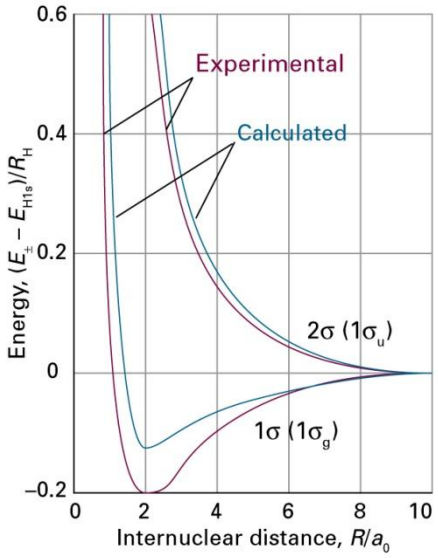






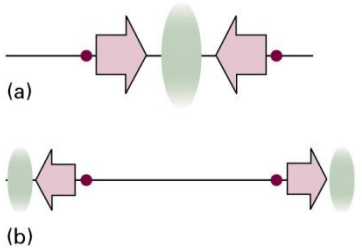
Bonding and antibonding comparison:





A bonding electron pulls two nuclei together, an antibonding electron pulls the nuclei apart

*antibonding orbital is **more antibonding** than the bonding orbital is bonding. This important conclusion* stems in part from the presence of the nucleus-nucleus repulsion: *this* contribution raises the energy of both molecular orbitals.



Notation

1. Antibonding *
2. Inversion symmetry: gerade and ungerade: $1\sigma_g$, $1\sigma^*_u$

More about notation

如同AO表示法，以小寫表示MO orbitals,(如σ_g, π_u，δ_g……)

以大寫表示在某一電子組態下的某一狀態(state)，如$^1\Sigma_g^+$, $^2\pi_u$, $^1\Delta_g$…

分子因具有對稱性，所以表示法隨不同對稱性而有不同符號，基本上與group theory中不同對稱性的point group中的 representation的符號是相同的，如非直線型分子，H_2O為C_{2v}對稱，其character table中的representation有a_1，b_1，a_2，b_2，(小寫表H_2O的MO)大寫 $^xA_1$, $^xB_1$, $^xB_2$代表在某電子組態下的total wavefN的state notation

Parity：專指對有對稱中心的分子而言，e.g. O_2，C_2H_6，C_6H_6…….

Inversion

以g 附加表示該MO對該對稱中心是對稱的
以u 附加表示該MO對該對稱中心是反對稱的

e.g. σ_g，π_u…
a_{1g}，b_{2u}….

若沒有對稱中心分子，如HCl，HCN，H_2O，CH_4……..

其MO就無此對稱性質：就不加 g或 u，如σ，π，a_1，b_1…

“ +”或” -”notation on term symbol . mirror

指 MO在 含分子平面的reflection, if 對稱then(+), if 反對稱 then (-).
專指直線形分子，且term symbol 為Σ者，才有 “+”或” -”的差別.

對 Π 或Δsymbol就不須 “+”或” -”，∵每個 Π orΔ皆代表 doubly degenerate.含蓋 “+”and ”-”，因此無表示意義。

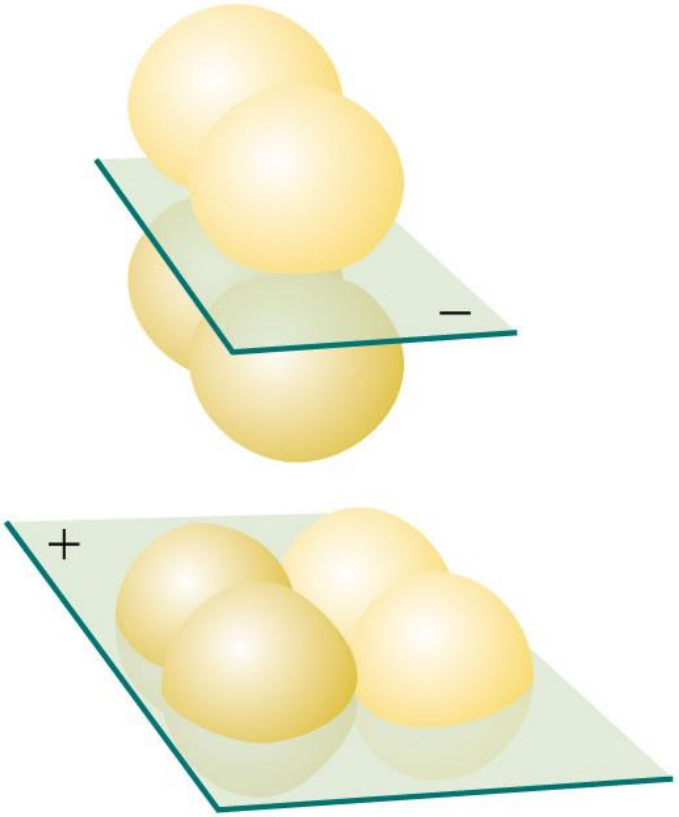


Fig. 14.2 The + or – on a term symbol refers to the overall symmetry of a configuration under reflection in a plane containing the two nuclei.

Σ若由σ orbital 組成，一定是Σ^+

若由π orbital 組成，一定是$\pi_+^1\pi_-^1 \Rightarrow {}^3\Sigma^-$

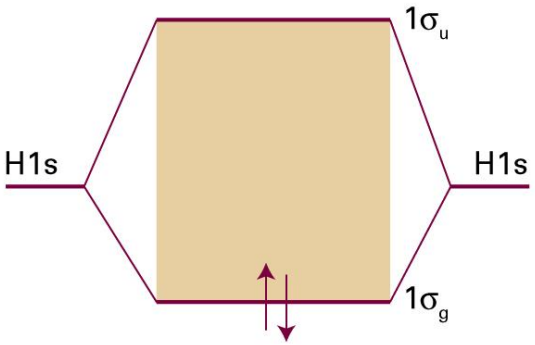
若orbital 全部填滿，一定是$^1\Sigma^+$

Selection rules:

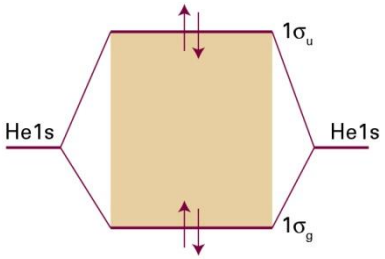
$$\Delta\Lambda = 0,\pm 1 \quad \Delta S = 0,$$

$$\Sigma^+ \leftrightarrow \Sigma^+,\ \Sigma^- \leftrightarrow \Sigma^-$$

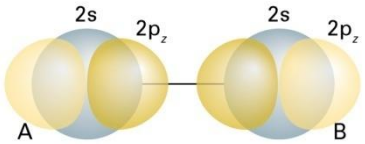
$$g \leftrightarrow u$$



H2分子軌域能階圖



He_2分子軌域能階圖



Example of σ bond from s and p orbitals

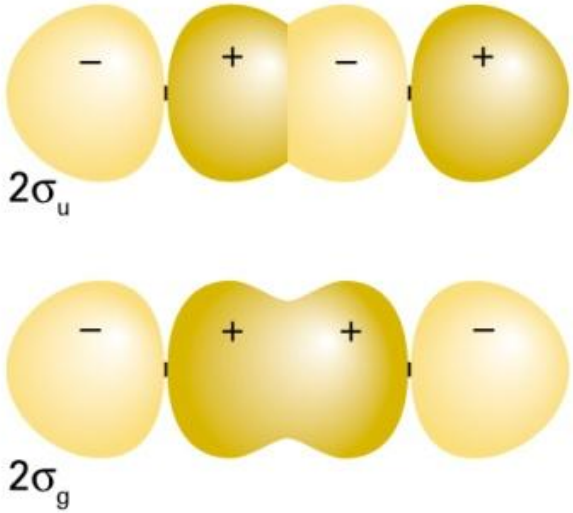
$$\psi = c_{A2s}\chi_{A2s} + c_{B2s}\chi_{B2s} + c_{A2p_z}\chi_{A2p_z} + c_{B2p_z}\chi_{B2p_z}$$

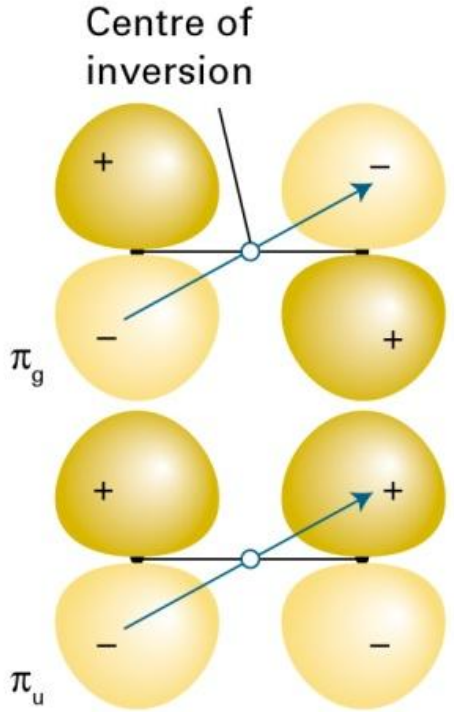
distinctly different energies between s and p,

$$\psi = c_{A2s}\chi_{A2s} + c_{B2s}\chi_{B2s} \qquad \psi = c_{A2p_z}\chi_{A2p_z} + c_{B2p_z}\chi_{B2p_z}$$

Homoatomic between A and B

$$\chi_{A2s} \pm \chi_{B2s} \qquad \chi_{A2p_z} \pm \chi_{B2p_z}$$



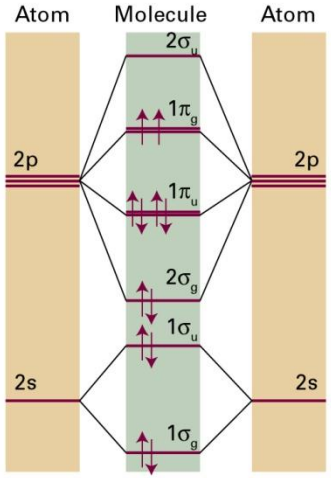


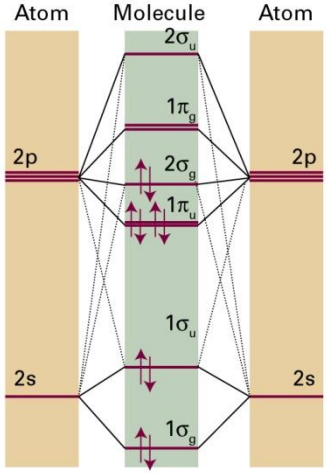
$\Phi_{\sigma}=2p_z+2p_z$

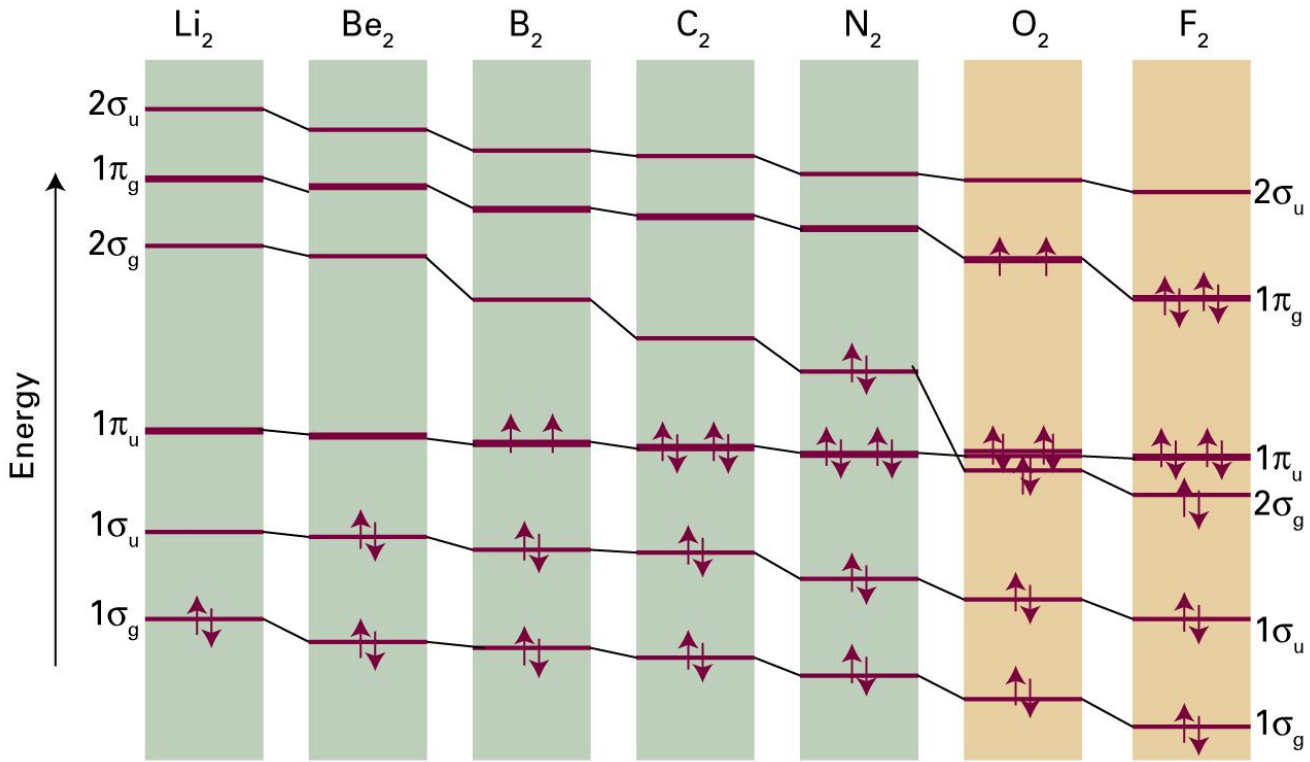
σ orbitals

$\Phi_{\pi}=2p_y+2p_y$, or, $=2p_x+2p_x$

π orbitals







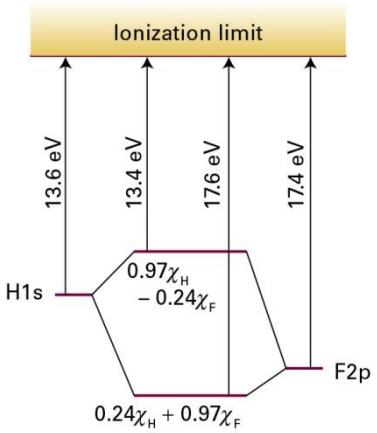
適用於0_2與F_2分子的分子軌域能階順序圖(molecular energy diagram)

3σ軌域隨著原子序增加而逐漸往下位移,主要是受到
質子正電荷的吸引使2s軌域層越往核靠近所以能量逐漸降低

Heteronuclear diatomic molecules

Polar bond: covalent bond between the atoms in a heteronuclear diatomic molecule is not shared evenly

$$\psi = c_A A + c_B B$$



The charge distribution in bonds is commonly discussed in terms of the electronegativity, *X*

Electronegativity: a measure of the power of an atom to attract electrons to itself when it is part of a compound.

Pauling: from bond dissociation energies, D

$$|\chi_A - \chi_B| = 0.102\{D(\text{A—B}) - \tfrac{1}{2}[D(\text{A—A}) + D(\text{B—B})]\}^{1/2}$$

Mulliken: from ionization energy: I

$$\chi_M = \tfrac{1}{2}(I + E_{ea})$$

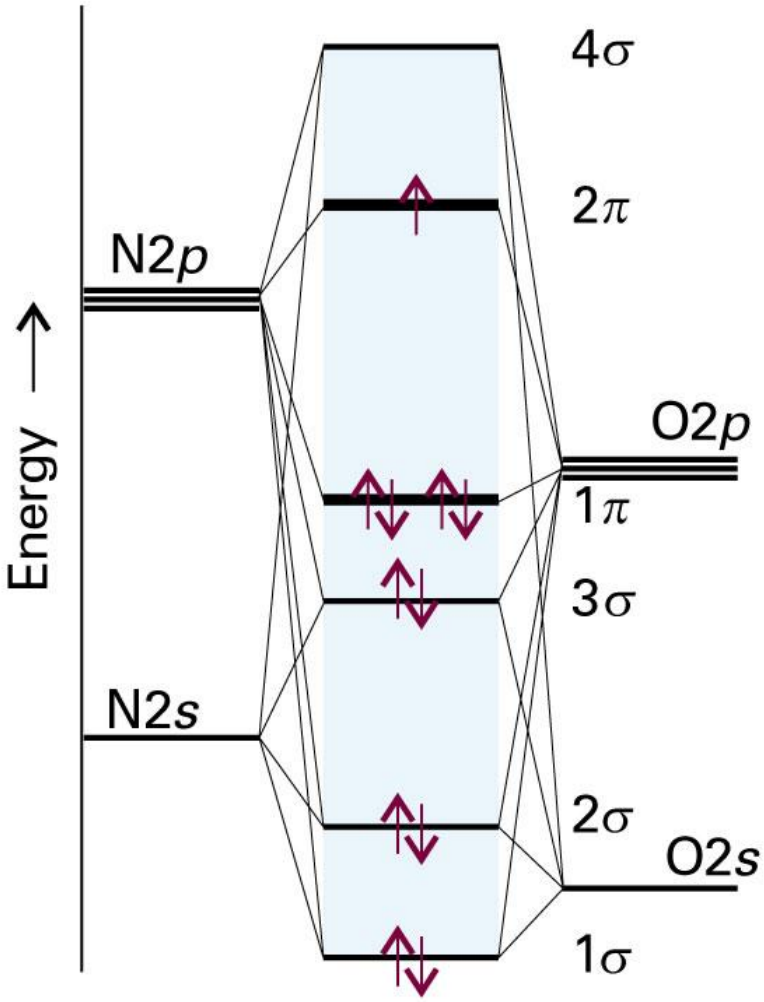


Fig. 11.37 The molecular orbital energy level diagram for NO.

bond order, *b*: $b = \frac{1}{2}(n - n^*)$

1 The greater the bond order, the shorter the bond.
2 The greater the bond order, the greater the bond strength.

Table 10.2* Bond lengths

Bond	Order	R_e/pm
HH	1	74.14
NN	3	109.76
HCl	1	127.45
CH	1	*114*
CC	1	*154*
CC	2	*134*
CC	3	*120*

* More values will be found in the *Data section*. Numbers in italics are mean values for polyatomic molecules.

Judge whether N_2^+ is likely to have a larger or smaller dissociation energy than N_2.

Method Because the molecule with the larger bond order is likely to have the larger dissociation energy, compare their electronic configurations and assess their bond orders.

Answer From Fig. 11.33, the electron configurations and bond orders are

N_2	$1\sigma_g^2 1\sigma_u^2 1\pi_u^4 2\sigma_g^2$	$b = 3$
N_2^+	$1\sigma_g^2 1\sigma_u^2 1\pi_u^4 2\sigma_g^1$	$b = 2\frac{1}{2}$

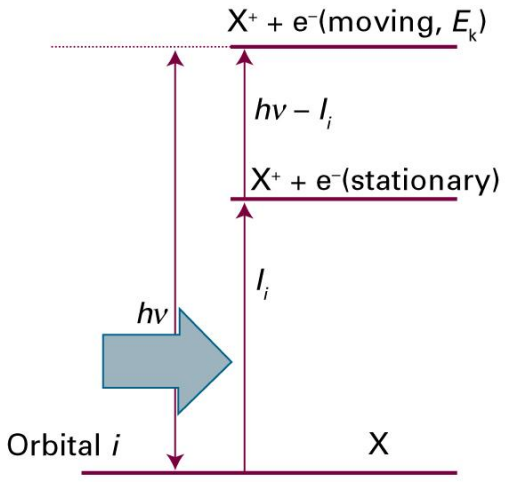
Because the cation has the smaller bond order, we expect it to have the smaller dissociation energy. The experimental dissociation energies are 945 kJ mol^{-1} for N_2 and 842 kJ mol^{-1} for N_2^+.

Table 10.3* Bond dissociation energies

Bond	Order	D_0/(kJ mol^{-1})
HH	1	432.1
NN	3	941.7
HCl	1	427.7
CH	1	*435*
CC	1	*368*
CC	2	*720*
CC	3	*962*

* More values will be found in the *Data section*. Numbers in italics are mean values for polyatomic molecules.

Photoelectron spectroscopy (PES) measures the ionization energies of molecules when electrons are ejected from different orbitals by absorption of a photon of the proper energy, and uses the information to infer the energies of molecular orbitals. (Similar to **atomic spectroscopy** to determine **atomic orbitals**)



Energy conservation: $h\nu = \frac{1}{2} m_e v^2 + I$

by measuring the kinetic energies ($1/2\ m_e v^2$) of the photoelectrons, and knowing v (hv), these ionization energies can be determined (I)
Koopman's theorm: $I = -\varepsilon$ (orbital energy)

Examples: USP (ultraviolet), XPS (X-ray), AES (Auger electron, e-gun)