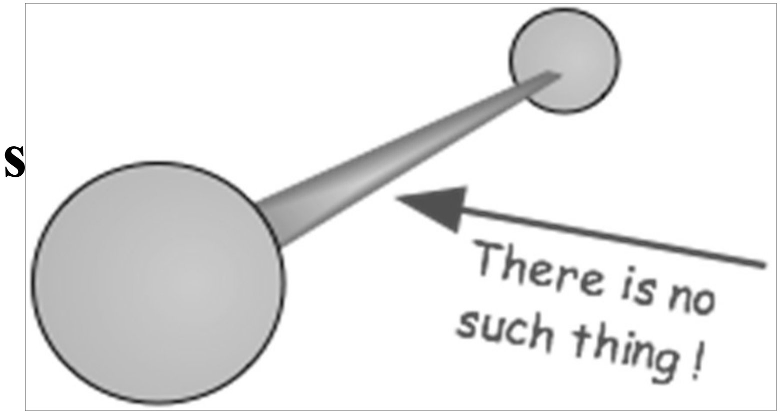
Chapter 4 The structure of diatomic molecules

- **What is a chemical bond?**

" It's only a *convenient fiction*, but let's pretend..."

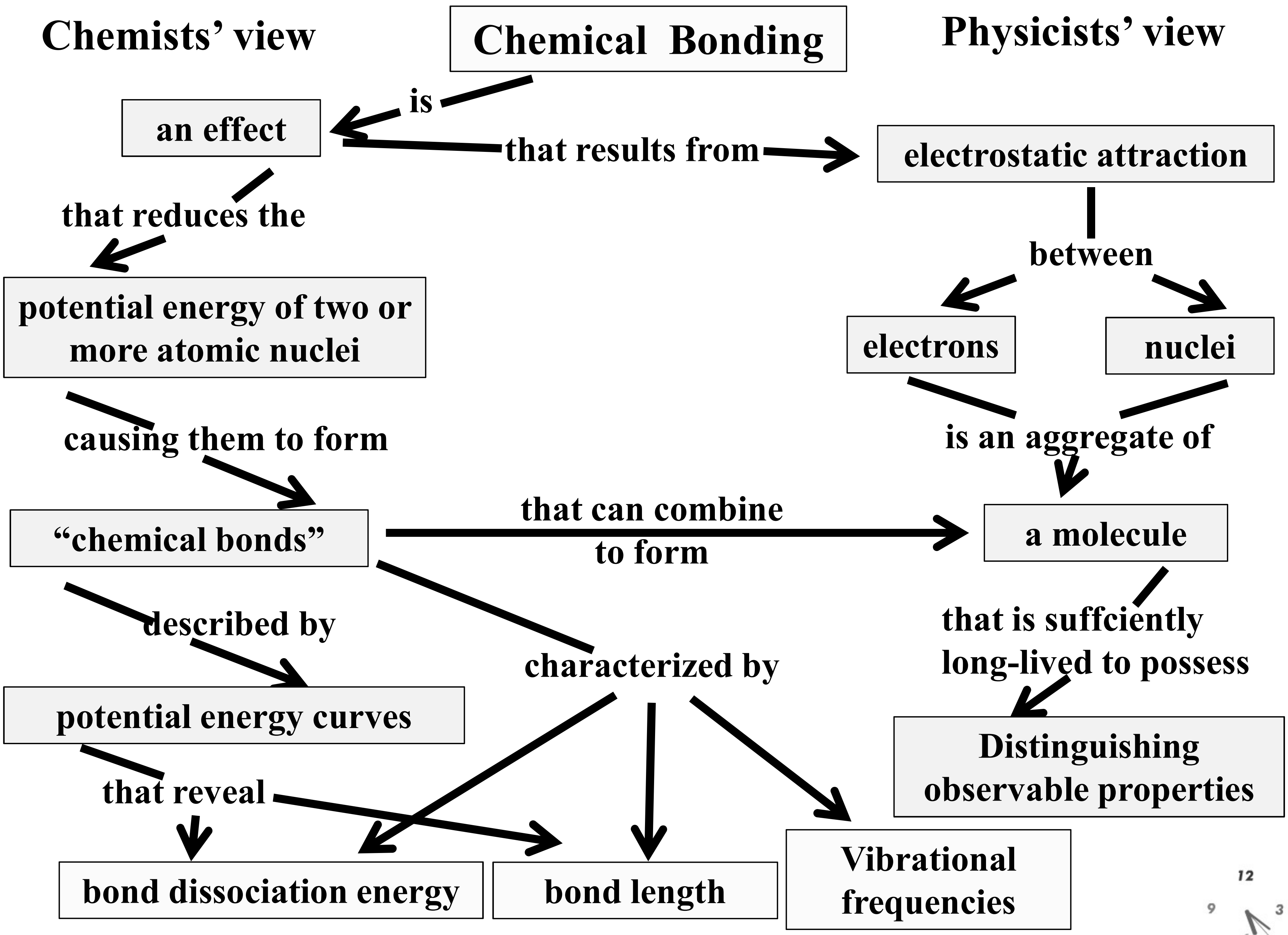
"SOMETIMES IT SEEMS to me that a bond between two atoms has become so real, so tangible, so friendly, that I can almost see it. Then I awake with a little shock, for a chemical bond is not a real thing. It does not exist. No one has ever seen one. No one ever can. It is a figment of our own imagination."

--C.A. Coulson (1910-1974)



It is more useful to regard a chemical bond as an *effect* that causes certain atoms to join together to form enduring structures that have unique physical and chemical properties.

Chemical bonding occurs when one or more electrons are simultaneously attracted to *two* nuclei.



Chemists’ view

Chemical Bonding

Physicists’ view

is

an effect

that results from

electrostatic attraction

that reduces the

between

potential energy of two or more atomic nuclei

electrons

nuclei

causing them to form

is an aggregate of

“chemical bonds”

that can combine to form

a molecule

described by

characterized by

that is suffciently long-lived to possess

potential energy curves

Distinguishing observable properties

that reveal

bond dissociation energy

bond length

Vibrational frequencies

Quantum mechanical theory for description of molecular structures and chemical bondings

- **Valence Bond (VB) Theory**

  a) Proposed by Heitler and London in1930s, further developments by Pauling and Slater et al.

  b) Finally programmed in later 1980s, e.g., ***XMVB3.0***

- **Molecular Orbital (MO) Theory**

  a) Proposed by Hund, Mulliken, Lennard-Jones et al. in 1930s.

  b) Further developments by Slater, Hückel and Pople et al.

  c) MO-based softwares are widely used nowadays, e.g., ***Gaussian***

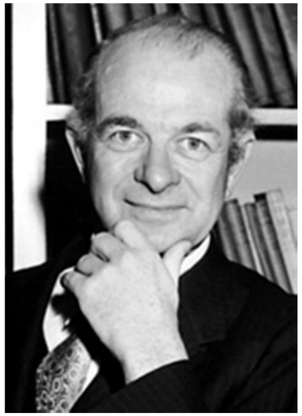
- **Density Functional Theory**

  a) Proposed by Kohn et al.

  b) DFT-implemented QM softwares are widely used, e.g., ***Gaussian***

Slater

Pauling



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卢嘉锡

Kohn

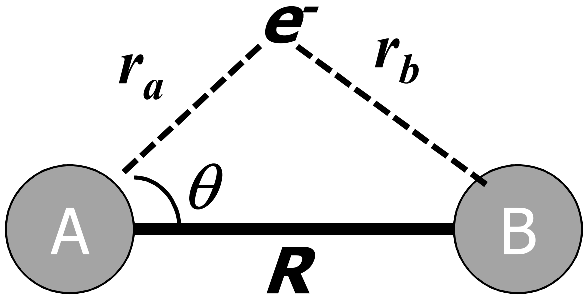
§ 1 Electronic structure of H_2^+ ion

1. Schrödinger equation of H_2^+

Born-Oppenheimer Approximation

- The electrons are much lighter than the nuclei.
- Nuclear motion is much slower than the electron motion.

→ ***Neglecting the motion of nuclei!***



($R_{expt.}$ = 106 pm)

The hamiltonian operator

$$\hat{H} = -\frac{1}{2}\nabla_e^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R}$$

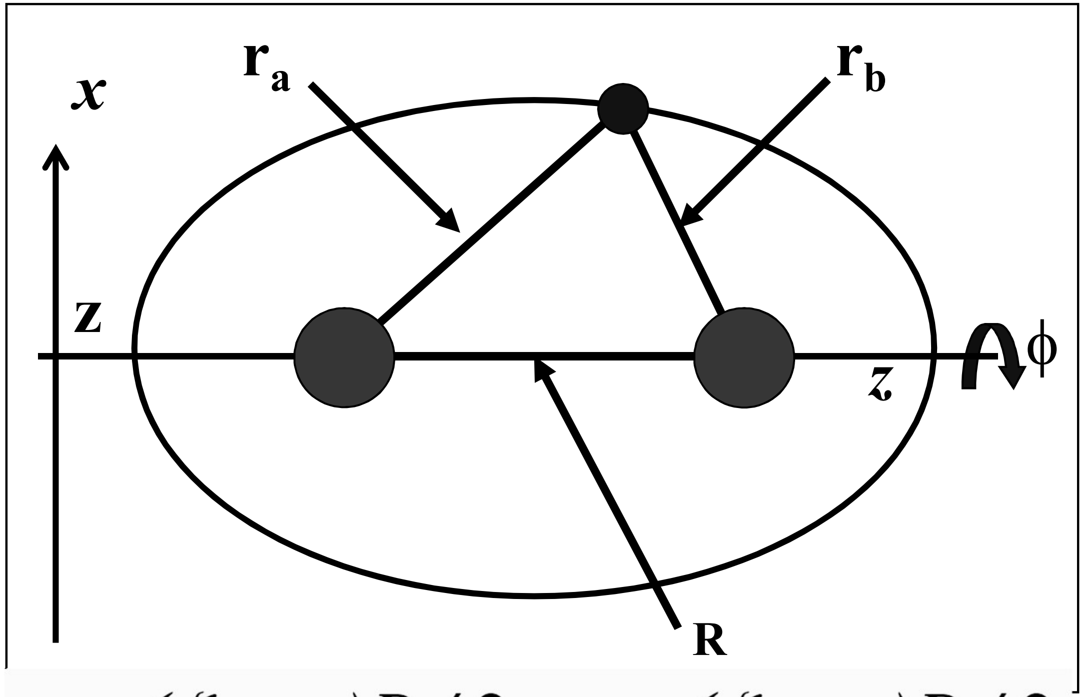
$$r_b = \sqrt{r_a^{\;2} + R^2 - 2r_aR\cos\theta}$$

Schrödinger equation of H_2^+

$$\hat{H}\psi = E\psi$$

Molecular Orbital Theory H_2^+

The schrödinger equation for H_2^+ can be solved exactly using ***confocal elliptical coordinates***:



$$r_a = (\xi + \eta)R/2 \quad r_b = (\xi - \eta)R/2$$

ξ (xi) = $(r_a+r_b)/R$

η (eta) = $(r_a-r_b)/R$

ϕ is a rotation around z

→ $R \leq (r_a+r_b) < \infty$

$-R \leq (r_a-r_b) \leq R$

$$\boxed{\begin{array}{c} 0 \leq \phi \leq 2\pi; \\ 1 \leq \xi \leq \infty; \\ -1 \leq \eta \leq 1 \end{array}}$$

$$\hat{H}(r_1, R)\psi(r_1, R) = E_e(R)\psi(r_1, R) \xrightarrow[\text{fixed}]{R} \hat{H}(r_1)\psi(r_1) = E\psi(r_1)$$

position of the electron!

Yet very TEDIOUS!

Molecular Orbital Theory

Molecular orbital (MO) of H_2^+

$$\Psi_{elec} = \underbrace{F(\xi,\eta)}_{\textbf{Radial part}}\underbrace{[(2\pi)^{-1/2}e^{im\phi}]}_{\textbf{Angular part}} \quad \boldsymbol{(m=0,\ \pm1,\ \pm2,\ \pm3,\ldots)}$$

- $\lambda = |m|$--orbital angular momentum quantum number.
- Each electronic level with $\lambda \neq 0$ is doubly degenerate, with $m = \pm|\lambda|$.
- *$m\hbar$ or m (in a.u.) -- the z-component of orbital angular momentum.*
- The one-electron wavefunction (MO) is no longer the eigenfunction of the operator L^2, but is the eigenfunction of L_z.

$$[\hat{L}^2, \hat{H}] \neq 0; \qquad\qquad [\hat{L}_z, \hat{H}] = 0$$

- Types of molecular orbitals are defined by the value of λ $(=|m|)$.

λ	0	1	2	3	4
letter	σ	π	δ	ϕ	γ

Type of MO (bond)

For diatomics,

$$\Psi_{elec} = F(\xi,\eta)(2\pi)^{-1/2} e^{im\phi}$$

$\lambda = |m|$ ($m = 0, \pm 1, \pm 2, \pm 3, \ldots$)

$\lambda = \|m\|$	**0**	**1**	**2**	**3**	**4**
letter	σ	π	δ	ϕ	γ

For atoms,

$$\Psi_{elec} = R_{n,l}(r)\Theta_{l,m_l}(\theta)\Phi_{m_l}(\phi)$$

Quantum numbers: n, l, m_l

l	**0**	**1**	**2**	**3**	**4**
letter	***s***	***p***	***d***	***f***	***g***

Quantum Number of Orbital angular momentum

- Atom: $\ell = 0, 1, 2, \ldots$ and the atomic orbitals are called: ***s, p, d***, etc.

  & each sublevel contains degenerate AOs with $m_l = l, \ldots, -l$.

- Diatomics: $\lambda = 0, 1, 2, \ldots$ and the molecular orbitals are: σ, π, δ, etc.

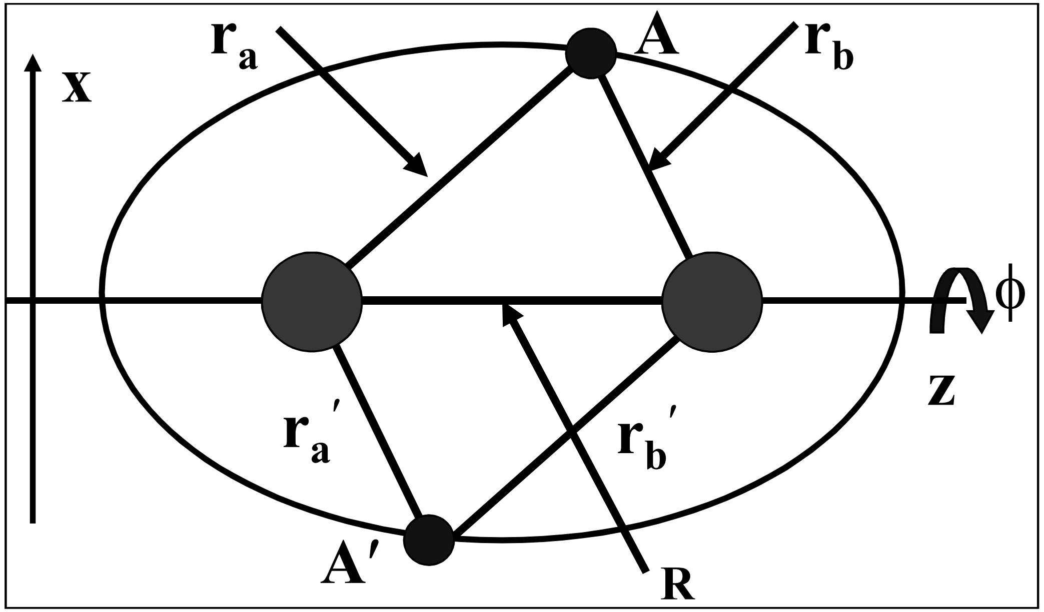
  & each level contains degenerate MOs with $m = \pm\lambda$.

Question: Supposing MO′s are composed of AO′s, what is the relationship between λ (MO) and l *(AO)*, or m (MO) and m_l *(AO)*?

Symmetry of MO

$$\Psi_{elec} = \sqrt{\frac{1}{2\pi}} F(\xi,\eta) e^{im\phi}$$

$$\xi = (r_a + r_b)/R$$
$$\eta = (r_a - r_b)/R$$



i) Inversion:

$$A(\xi, \eta, \phi) \xrightarrow{i} A'(\xi, -\eta, \phi+\pi) \qquad (r_a' = r_b,\ r_b' = r_a,\ \phi = \phi + \pi)$$

$$F(\xi,-\eta) = BF(\xi,\eta),\ B= +1 \text{ or } -1;$$

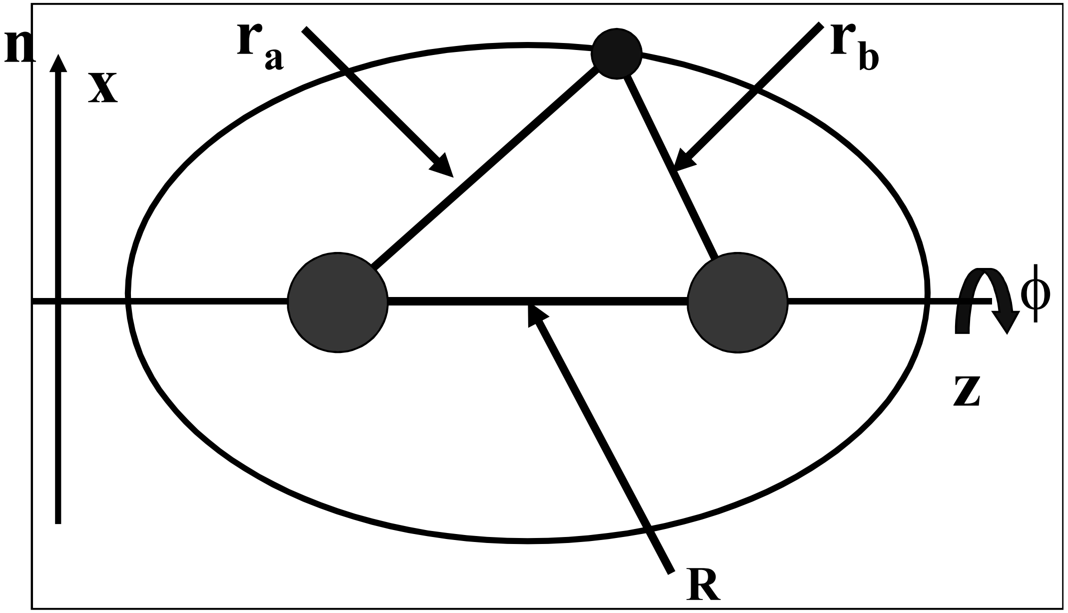
$$\hat{i}\Psi_m = \hat{i}[AF(\xi,\eta)e^{im\phi}] = AF(\xi,-\eta)e^{im(\phi+\pi)} = Be^{im\pi}\Psi_m = B'\Psi_m$$

Ψ_m is an eigenfunction of inversion with B′ = +1 or -1 !

- **B′ = 1, parity (even), (denoted g);**
- **B′ =-1, disparity (odd), (denoted u);**

Notation valid only for homonuclear diatomics!

Symmetry of MO wavefunction



$$\Psi_{elec} = \sqrt{\frac{1}{2\pi}} F(\xi,\eta) e^{im\phi}$$

$$\xi = (r_a + r_b)/R$$
$$\eta = (r_a - r_b)/R$$

ii) Reflection by the xz-plane.
(operator σ_{xz})

$$A(\xi, \eta, \phi) \xrightarrow{\sigma_{xz}} A'(\xi, \eta, -\phi)$$

$$(r_a' = r_a,\ r_b' = r_b,\ \phi = -\phi)$$

$$\sigma_{xz}\Psi_m = AF(\xi,\eta)e^{im(-\phi)} = [AF(\xi,\eta)e^{-im\phi}] = \Psi_{-m}$$

i.e. When $m \neq 0$, the molecular orbital wavefunction Ψ_m itself

is not an eigenfunction of σ_{xz}!

Types of Molecular Orbitals for H_2^+

$\psi_{elec} = F(\xi,\eta)\,(2\pi)^{-1/2}\,e^{im\phi}$

$\lambda = |m|$

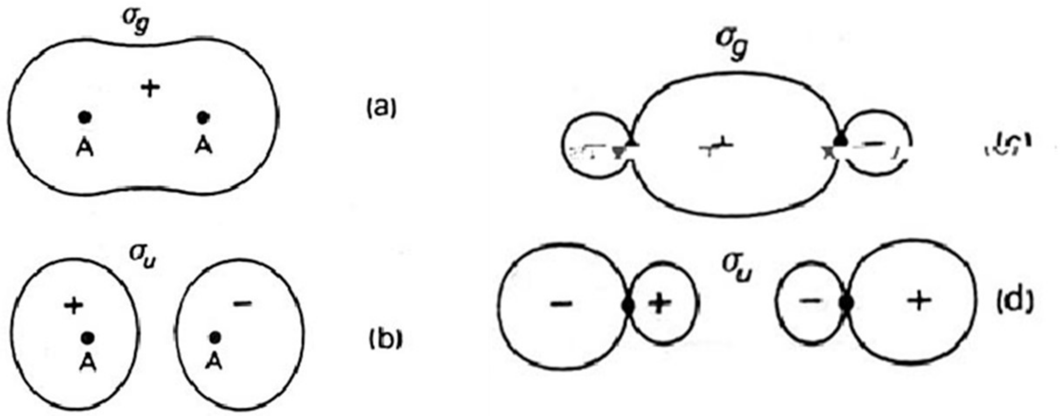
λ	0	1	2	3	4
letter	σ	π	δ	ϕ	γ

- Parity of molecular orbital (upon inversion): **(g ~ even, u ~ odd)**

i) $\lambda = 0$

σ-type

Real!



Bonding

Antibonding

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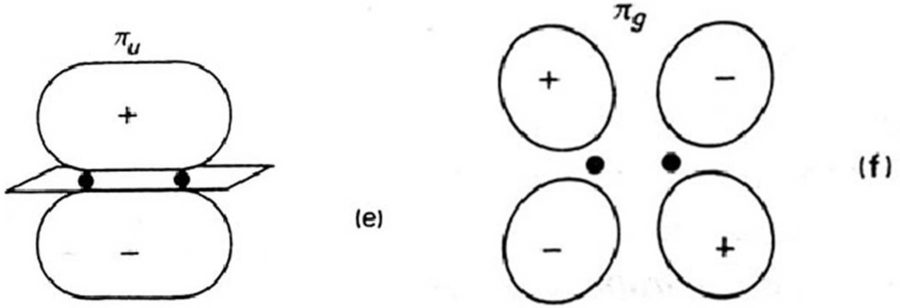
ii) $\lambda = 1$ Originally in complex form, but can be expressed in real form!

π-type **After being transformed into real form:**



Bonding **Antibonding**

Questions

1. **When we deal with a many-electron diatomic molecule, what problem will we encounter?**

2. What will we encounter when dealing with a many-electron many-atom molecule?

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{n}\nabla^{2}(i) + \sum_{i=1}^{n}\sum_{N}\left(-\frac{1}{r_{N}(i)}\right) + \sum_{N \neq M}\frac{1}{R_{NM}} + \sum_{i \neq j}\frac{1}{r_{ij}}$$

It is implausible to attain direct solution of the Schrödinger equation of such many-electron system!

Mean-field approximation (independent electron approx.) → variation theorem & LCAO-MO & HF-SCF

2. The Variation Theorem

Given a system whose Hamiltonian operator $\hat{H}$ is time-independent and whose lowest-energy eigenvalue is E_1, if ϕ is any normalized, well-behaved function of coordinates of the system's particles that satisfies the boundary conditions of the problem, then

$$< E >= \int \phi^* \hat{H} \phi d\tau \geq E_1 \qquad (\int \phi^* \phi d\tau = 1)$$

- The variation theorem allows us to calculate the upper bond for the system's ground-state energy.

To prove the variation theorem, ϕ is supposed to be expanded in terms of the complete, orthonormal set of eigenfunctions $\{\psi_k\}$ of the Hamiltonian operator $\hat{H}$, ***i.e.,***

$$\phi = \sum_k a_k \psi_k$$

where $\hat{H}\psi_k = E_k \psi_k, \quad \int \psi_k^* \psi_j d\tau = \delta_{kj} \ , \quad E_k \ \geq E_1 \ (\mathrm{k} \geq 1)$

i) In case ϕ is normalized, we have

$$\boxed{1 = \int \phi^* \phi d\tau} = \int (\sum_k a_k^* \psi_k^*)(\sum_j a_j \psi_j) d\tau$$

$$\delta_{kj} = 1 \quad (\mathrm{k} = \mathrm{j})$$

$$= 0 \quad (\mathrm{k} \neq \mathrm{j})$$

$$= \sum_k \sum_j a_k^* a_j \int \psi_k^* \psi_j d\tau = \sum_k \sum_j a_k^* a_j \delta_{kj} = \sum_k |a_k|^2$$

$$\therefore < E >= \int \phi^* \hat{H} \phi d\tau = \int (\sum_k a_k^* \psi_k^*) \hat{H} (\sum_j a_j \psi_j) d\tau$$

$$= \sum_k \sum_j a_k^* a_j E_j \delta_{kj} = \sum_k |a_k|^2 E_k \geq E_1 \quad (= \sum_k |a_k|^2 E_1)$$

ii) In case ϕ is not normalized, let $\varphi = N\phi$. Then we have

$$1 = \int \varphi^* \varphi d\tau = N^2 \int (\sum_k a_k^* \psi_k^*)(\sum_j a_j \psi_j) d\tau$$

$$= N^2 \sum_k |a_k|^2 \Rightarrow \int \phi^* \phi d\tau = \sum_k |a_k|^2 = 1/N^2$$

$$< E >= \int \varphi^* \hat{H} \varphi d\tau$$

$$= \int \phi^* \hat{H} \phi d\tau / \int \phi^* \phi d\tau \geq E_1$$

ϕ ----- a trial variation function (normalized)

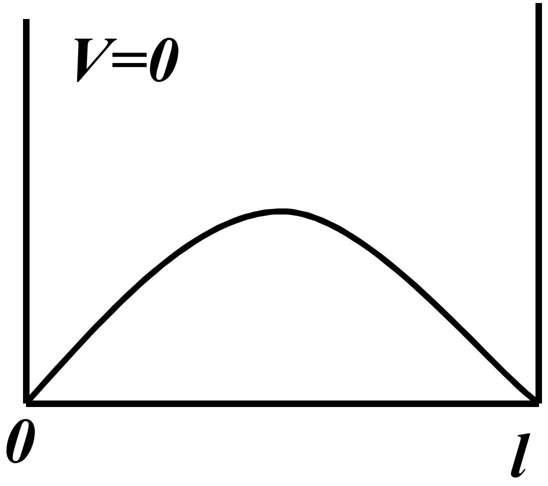
$$< E >= \int \phi^* \hat{H} \phi d\tau \geq E_1$$ ***variational integral***

- The lower the value of the variational integral, the closer the trial variational function to the real eigenfunction of ground state.
- To arrive at a good approximation to the ground-state energy ***E_1***, we try many trial variational functions and look for the one that gives the lowest value of the variational integral.

This offers an approximation to approach the solution for a complex system!

Example: Devise a trial variation function for the ground state of the particle in a one-dimensional box of length ***l***.

A simple function that has the properties of the ground state is the parabolic function:



$$\boxed{\phi = x(l-x)}$$ for $0 < x < l$

$$\Rightarrow \int \phi^* \hat{H} \phi d\tau = -\frac{\hbar^2}{2m}\int_0^l (lx - x^2)\frac{d^2}{dx^2}(lx - x^2)dx = \frac{\hbar^2 l^3}{6m}$$

$$\int \phi^* \phi d\tau = \int_0^l x^2(l-x)^2 dx = l^5/30$$

$$(\because \hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2})$$

$$< E >= \frac{\int \phi^* \hat{H} \phi d\tau}{\int \phi^* \phi d\tau} = \frac{5h^2}{4\pi^2 ml^2} \geq \frac{h^2}{8ml^2}$$

Parabolic—抛物线

3. Linear Variation Functions

$$\phi = c_1 f_1 + c_2 f_2 + \dots + c_n f_n = \sum_{i=1}^{n} c_i f_i$$

$f_1, f_2, \dots f_n$ are linearly independent, but not necessarily eigenfunctions of any operators.

Based on the variation theorem, the coefficients are regulated by the minimization routine so as to obtain the wavefunction that corresponds to the minimum energy. This is taken to be the wavefunction that closely approximates the ground state.

$$< E >= \frac{\int \phi^* \hat{H} \phi d\tau}{\int \phi^* \phi d\tau} \geq E_0$$

Real Ground-state Energy

$$\varepsilon =< E >$$

To minimize ε, make $\partial\varepsilon / \partial c_i = 0$

$\Rightarrow \{ \partial\varepsilon / \partial c_i = 0 \}$ (a total of n equations of $\{c_i\}$)

$$\Rightarrow \{\varepsilon_j, \phi_j = \sum_{i=1}^{n} c_i^j f_i\} \ (j = 1,2,\dots, \text{ n})$$

Example $\phi = c_1\psi_1 + c_2\psi_2 \qquad E = \dfrac{\int \phi^* \hat{H} \phi d\tau}{\int \phi^* \phi d\tau}$

c_1, c_2 and E to be solved by the variation theorem!

$$x = \int \phi^* \phi d\tau = \int (c_1\psi_1 + c_2\psi_2)^* (c_1\psi_1 + c_2\psi_2) d\tau$$

$$= \int (c_1^2\psi_1^*\psi_1 + c_1c_2\psi_1^*\psi_2 + c_1c_2\psi_2^*\psi_1 + c_2^2\psi_2^*\psi_2) d\tau$$

$$= \int (c_1{}^2\psi_1^*\psi_1 + 2c_1c_2\psi_1^*\psi_2 + c_2{}^2\psi_2^*\psi_2) d\tau$$

$$= c_1{}^2 S_{11} + 2c_1c_2S_{12} + c_2{}^2 S_{22} \qquad Let\ S_{ij} = \int \psi_i^* \psi_j d\tau = S_{\mathrm{ji}}$$

Overlap integral!

$$= c_1{}^2 + 2c_1c_2S_{12} + c_2{}^2 \qquad (\because S_{11} = S_{22} = 1)$$

ψ_1 and ψ_2 are normalized functions

$$y = \int \phi^* \hat{H} \phi d\tau = \int (c_1\psi_1 + c_2\psi_2)^* \hat{H} (c_1\psi_1 + c_2\psi_2) d\tau$$

$$= \int \ (c_1{}^2\psi_1^*\hat{H}\psi_1 + c_1c_2\psi_1^*\hat{H}\psi_2 + c_1c_2\psi_2^*\hat{H}\psi_1 + c_2{}^2\psi_2^*\hat{H}\psi_2) d\tau$$

$$= c_1^2 H_{11} + 2c_1c_2H_{12} + c_2^2 H_{22} \qquad (H_{ij} = H_{ji} = \int \psi_i^* \hat{H} \psi_j d\tau)$$

$$\therefore E = \frac{\int \phi^* \hat{H} \phi d\tau}{\int \phi^* \phi d\tau} = \frac{c_1{}^2 H_{11} + 2c_1 c_2 H_{12} + c_2{}^2 H_{22}}{c_1{}^2 S_{11} + 2c_1 c_2 S_{12} + c_2{}^2 S_{22}} = \frac{y}{x}$$

$$To\ make\ \ E \Rightarrow E_0, \text{ we have } 0 = \frac{\partial E}{\partial c_1} = \frac{1}{x}\frac{\partial y}{\partial c_1} - \frac{y}{x^2}\frac{\partial x}{\partial c_1}$$

$$\Rightarrow \frac{1}{x}(2c_1 H_{11} + 2c_2 H_{12}) - \frac{y}{x^2}(2c_1 S_{11} + 2c_2 S_{12}) = 0$$

$$\Rightarrow (c_1 H_{11} + c_2 H_{12}) - \frac{y}{x}(c_1 S_{11} + c_2 S_{12}) = 0$$

$$\Rightarrow (c_1 H_{11} + c_2 H_{12}) - E(c_1 S_{11} + c_2 S_{12}) = 0$$

$$\Rightarrow (H_{11} - ES_{11})c_1 + (H_{12} - ES_{12})c_2 = 0 \qquad (1)$$

Similarly, by making $\partial \mathbf{E}/\partial \mathbf{c_2} = \mathbf{0}$, we have

$$(H_{21} - ES_{21})c_1 + (H_{22} - ES_{22})c_2 = 0 \qquad (2)$$

$\phi = c_1\psi_1 + c_2\psi_2$ **Trial function**

Now we have two secular equations

$$\begin{aligned}(H_{11} - ES_{11})c_1 + (H_{12} - ES_{12})c_2 &= 0 \quad (1)\\ (H_{21} - ES_{21})c_1 + (H_{22} - ES_{22})c_2 &= 0 \quad (2)\end{aligned}$$

Secular equations

that can be express in the matrix form:

$$\begin{pmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

As $\boldsymbol{c_1, c_2 \neq 0}$, the **secular equations thus** demand the corresponding **secular determinant** to be zero, i.e.,

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$$

Secular determinant

$$(H_{11} - ES_{11})(H_{22} - ES_{22}) - (H_{21} - ES_{21})(H_{12} - ES_{12}) = 0 \quad (3)$$

- The algebraic equation ***(3)*** has ***2*** roots, E_1 and E_2.
- Substituting E_1 into the secular equations, a set of $\{c_1, c_2\}$ as well as the corresponding $\phi_1 = c_1\psi_1 + c_2\psi_2$ can be obtained.
- Substituting E_2 into the seqular equations, a set of $\{c_1, c_2\}$ as well as the corresponding ϕ_2 can be obtained.

Thus, the variational process gives two different energy E_1 and E_2, and two different sets of $\{c_1, c_2\}$ ➔ ϕ_1 and ϕ_2.

In general, for a linear variation function $\phi = c_1\psi_1 + c_2\psi_2 + \dots + c_n\psi_n$

we have the secular equations (in matrix form)

$$\begin{pmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & \cdots & H_{1n}-ES_{1n} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & \cdots & H_{2n}-ES_{2n} \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ H_{n1}-ES_{n1} & H_{n2}-ES_{n2} & \cdots & H_{nn}-ES_{nn} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \cdot \\ \cdot \\ c_n \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \cdot \\ \cdot \\ 0 \end{pmatrix}$$

and

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & \dots & H_{1n}-ES_{1n} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & \dots & H_{2n}-ES_{2n} \\ \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \dots & \cdot \\ H_{n1}-ES_{n1} & H_{n2}-ES_{n2} & \dots & H_{nn}-ES_{nn} \end{vmatrix} = 0$$

Secular determinant

This algebraic equation has ***n*** roots, which can be shown to be real. Arranging these roots in the order: $\mathbf{E_1 \leq E_2 \leq \dots \leq E_n}$.

Remarks on the linear variational process

- From the variation theorem, we know that the lowest value of root (**W_1**) is the upper bound for the system's real ground-state energy (**E_1**), i.e., $E_1 \leq W_1$

- Moreover, it is provable that the linear variation method provides upper bounds to the energies of the lowest ***n*** states of the system.

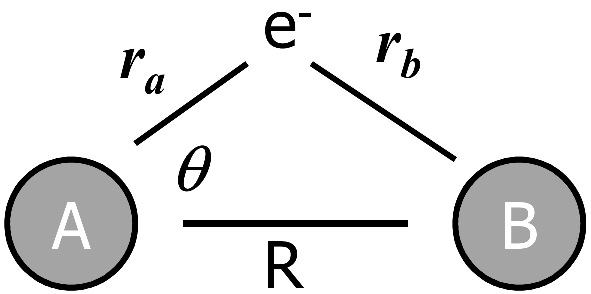
$$E_2 \leq W_2,\ E_3 \leq W_3, \dots ,\ E_n \leq W_n,$$

- We use these roots $\{W_i\}$ as approximations to the energies of the lowest ***n*** states $\{E_i\}$.

- If approximations to the energies of more states are wanted, we add more functions f_k $(k > n)$ into to the trial function ϕ. $(\phi = \Sigma c_i f_i)$

- Addition of more functions f_k can be shown to increase the accuracy of the calculated energies $\{W_i\}$.

3. The approximate solution of H_2^+



$$\hat{H} = -\frac{1}{2}\nabla_e^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R}$$

$$1s_A = e^{-r_a}/\sqrt{\pi} \qquad = \psi_a$$ **1s AO of A atom!**

$$1s_B = e^{-r_b}/\sqrt{\pi} \qquad = \psi_b$$ **1s AO of B atom!**

Let $$\phi = c_a\psi_a + c_b\psi_b$$

Trial function for the MO of H_2^+

(Linear combination of atomic orbitals into molecular orbital i.e., LCAO-MO, widely used!)

Now begin the variation process!

$$E = \frac{\int \phi^* \hat{H} \phi d\tau}{\int \phi^* \phi d\tau}$$ **&** $$\frac{\partial E}{\partial c_a} = \frac{\partial E}{\partial c_b} = 0$$

$$\phi = c_a\psi_a + c_b\psi_b \Rightarrow \text{The secular equations :}$$

$$(H_{aa} - ES_{aa})c_a + (H_{ab} - ES_{ab})c_b = 0$$

$$(H_{ba} - ES_{ba})c_a + (H_{bb} - ES_{bb})c_b = 0$$

→ **Secular determinant**

$$\Rightarrow \begin{vmatrix} H_{aa} - ES_{aa} & H_{ab} - ES_{ab} \\ H_{ba} - ES_{ba} & H_{bb} - ES_{bb} \end{vmatrix} = 0$$

$$\because \psi_a \text{ has the same form as } \psi_b, \quad \therefore H_{aa} = H_{bb}, \ H_{ab} = H_{ba}$$

$$\Rightarrow (H_{aa} - ES_{aa})^2 = (H_{ab} - ES_{ab})^2$$

$$\Rightarrow H_{aa} - ES_{aa} = \pm(H_{ab} - ES_{ab})$$

i) If $H_{aa} - ES_{aa} = -(H_{ab} - ES_{ab})$

$$\Rightarrow E_1 = \frac{H_{aa} + H_{ab}}{S_{aa} + S_{ab}} = \frac{\alpha + \beta}{1 + S}$$

ii） If $H_{aa} - ES_{aa} = H_{ab} - ES_{ab}$

$$\Rightarrow E_2 = \frac{H_{aa} - H_{ab}}{S_{aa} - S_{ab}} = \frac{\alpha - \beta}{1 - S}$$

Note: $\boldsymbol{S_{aa} = S_{bb} = 1}$

& define

$\boldsymbol{H_{aa} = H_{bb} = \alpha \quad (< \ 0)}$

$\boldsymbol{H_{ab} = H_{ba} = \beta \quad (< \ 0)}$

$\boldsymbol{S_{ab} = S_{ba} = S}$

Substitute E_1 into the secular equations,

$$(\alpha - E)c_a + (\beta - ES)c_b = 0 \quad (1)$$

$$(\beta - ES)c_a + (\alpha - E)c_b = 0 \quad (2)$$

$$\Rightarrow (\alpha - \frac{\alpha+\beta}{1+S})c_a + (\beta - \frac{\alpha+\beta}{1+S}S)c_b = 0$$

$$\Rightarrow (\alpha S - \beta)c_a + (\beta - \alpha S)c_b = 0$$

$$\Rightarrow c_a - c_b = 0 \Rightarrow c_a = c_b$$

$$\therefore \phi_1 = c_a\psi_a + c_b\psi_b = c_a(\psi_a + \psi_b)$$

Yet, c_a remains unknown! However, the wavefunction should be normalized, i.e.,

$$\int \phi_1^* \phi_1 d\tau = 1$$

$$nomalization\ condition: \quad \int \phi_1^* \phi_1 d\tau = 1$$

$$\Rightarrow \int (c_a(\psi_a + \psi_b))^* c_a(\psi_a + \psi_b) d\tau = 1$$

$$\Rightarrow \int [c_a^2 \psi_a^2 + 2c_a^2 \psi_a \psi_b + c_a^2 \psi_b^2] d\tau = 1$$

$$\Rightarrow 2c_a^2(1+S) = 1 \Rightarrow c_a = 1/\sqrt{2(1+S)}$$

$$\Rightarrow \phi_1 = (\psi_a + \psi_b)/\sqrt{2(1+S)}$$

Similarly, substituting E_2 into the secular equations, we have

$$c_a + c_b = 0 \Rightarrow c_a = -c_b$$

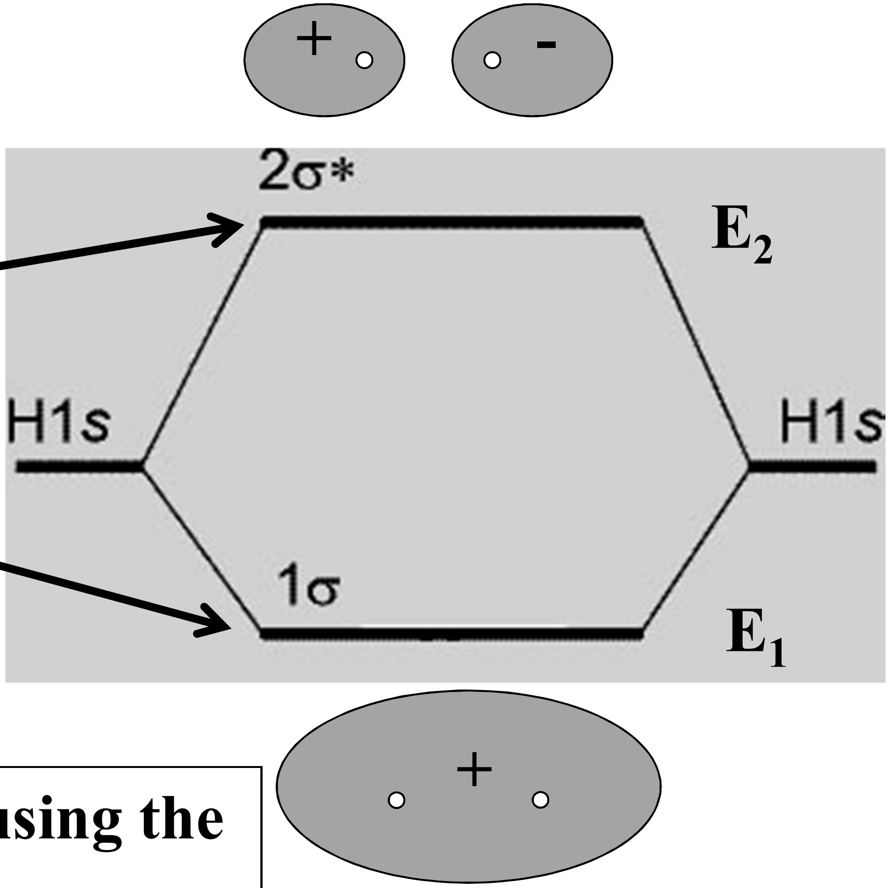
$$\Rightarrow \phi_2 = c_a \psi_a + c_b \psi_b = c_a(\psi_a - \psi_b)$$

$$\xrightarrow{\textit{\textbf{Normalization}}} \quad \phi_2 = (\psi_a - \psi_b)/\sqrt{2(1-S)}$$

Now we have

$$E_2 = \frac{\alpha - \beta}{1 - S}, \ \phi_2 = \frac{(\psi_a - \psi_b)}{\sqrt{2(1-S)}}$$

$$E_1 = \frac{\alpha + \beta}{1 + S}, \ \phi_1 = \frac{(\psi_a + \psi_b)}{\sqrt{2(1+S)}}$$



($E_1 < E_2$)

Can we simplify the process by using the molecular symmetry?

H_2^+ has an inversion center. The bonding and antibonding orbitals should be symmetric and asymmetric, respectively, upon inversion, i.e.,

$$\phi_{sym} = c(\psi_a + \psi_b); \ \phi_{asym} = c'(\psi_a - \psi_b) \xrightarrow[\text{normalization}]{} \textbf{c and c}'$$

$$\longrightarrow E_{sym} = \int \phi_{sym} * \hat{H} \phi_{sym} d\tau, E_{asym} = \int \varphi_{asym} * \hat{H} \varphi_{asym} d\tau$$

Overlap integral

$$S_{ab} = \int \psi_a^* \psi_b d\tau$$

$$R_{ab} = \infty,\ S_{ab} = 0; \quad R_{ab} = 0,\ S_{ab} = 1$$

Coulombic integral

$$H_{aa} = \int \psi_a^* \hat{H} \psi_a d\tau; \qquad \hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R}$$

$$H_{aa} = \int \psi_a^* \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R}\right)\psi_a d\tau$$

Internuclear repulsion

$$= \underline{\int \psi_a^* \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_a}\right)\psi_a d\tau} + \underline{\int \psi_a^* \frac{1}{R} \psi_a d\tau} - \underline{\int \psi_a^* \frac{1}{r_b} \psi_a d\tau}$$

$$= E_H + \underline{\left(\frac{1}{R} - \int \frac{1}{r_b} \psi_a^2 d\tau\right)} = E_H + \underline{J} \qquad (J \approx 5.5\% E_H)$$

$$\therefore \alpha = H_{aa} = E_H + J \approx E_H$$

The attractive energy of electron of H_a by the nucleas of H_b.

Ground-state energy of H_a atom

Electrostatic interaction exerted by the nucleas of H_b to H_a atom.

resonance integral 交换积分

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R}$$

$$H_{ab} = \int \psi_a^* \hat{H} \psi_b d\tau$$

$$= \int \psi_a^* (-\frac{1}{2}\nabla^2 - \frac{1}{r_b}) \psi_b d\tau + \int \psi_a^* (-\frac{1}{r_a} + \frac{1}{R}) \psi_b d\tau$$

$$= \int \psi_a^* E_b \psi_b d\tau + \frac{1}{R} \int \psi_a^* \psi_b d\tau - \int \frac{1}{r_a} \psi_a^* \psi_b d\tau$$

$$= \underline{E_H S_{ab}} + (\frac{S_{ab}}{R} - \int \frac{1}{r_a} \psi_a^* \psi_b d\tau) = E_H S_{ab} + K = \beta$$

$$\frac{S_{ab}}{R} - \int \frac{1}{r_a} \psi_a^* \psi_b d\tau = K$$

negative

The stabilization of chemical bonding ($S_{ab} > 0$) upon the nucleas of H_b approaching H_a atom.

$$\alpha = H_{aa} = E_H + J \quad (\approx E_a)$$
$$\beta = H_{ab} = E_H S_{ab} + K$$

$$S_{ab} = \int \psi_a^{*} \psi_b d\tau = S$$

$$E_1 = \frac{H_{aa} + H_{ab}}{1 + S_{ab}} = \frac{\alpha + \beta}{1 + S}$$

$$E_2 = \frac{H_{aa} - H_{ab}}{1 - S_{ab}} = \frac{\alpha - \beta}{1 - S}$$

$$E_1 = \frac{E_H + J + E_H S_{ab} + K}{1 + S_{ab}} = E_H + \frac{J + K}{1 + S}$$

Note: *J, K* < *0*

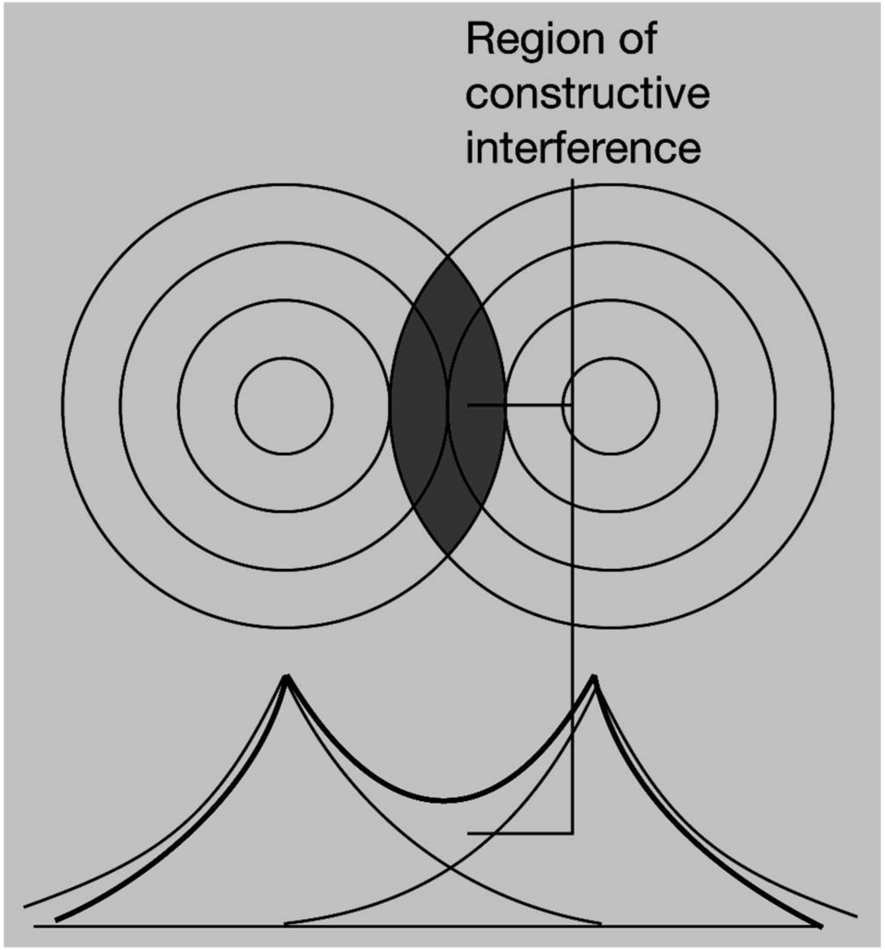
Ground-state energy of H_2^+

$$E_2 = E_H + \frac{J - K}{1 - S}$$

$$H + H^{+} \rightarrow H_2^{+} + E_b \quad \Rightarrow \quad E_b = E_1 - E_H = \frac{J + K}{1 + S}$$

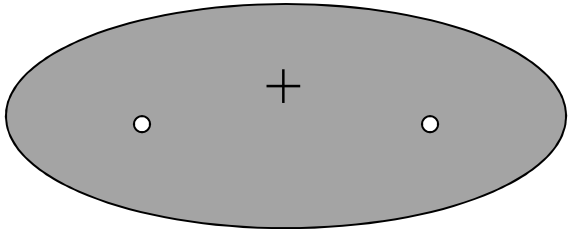
Molecular Orbital Theory

H_2^+



A representation of the constructive interference that occurs when two H 1*s* orbitals overlap and form a bonding σ orbital.

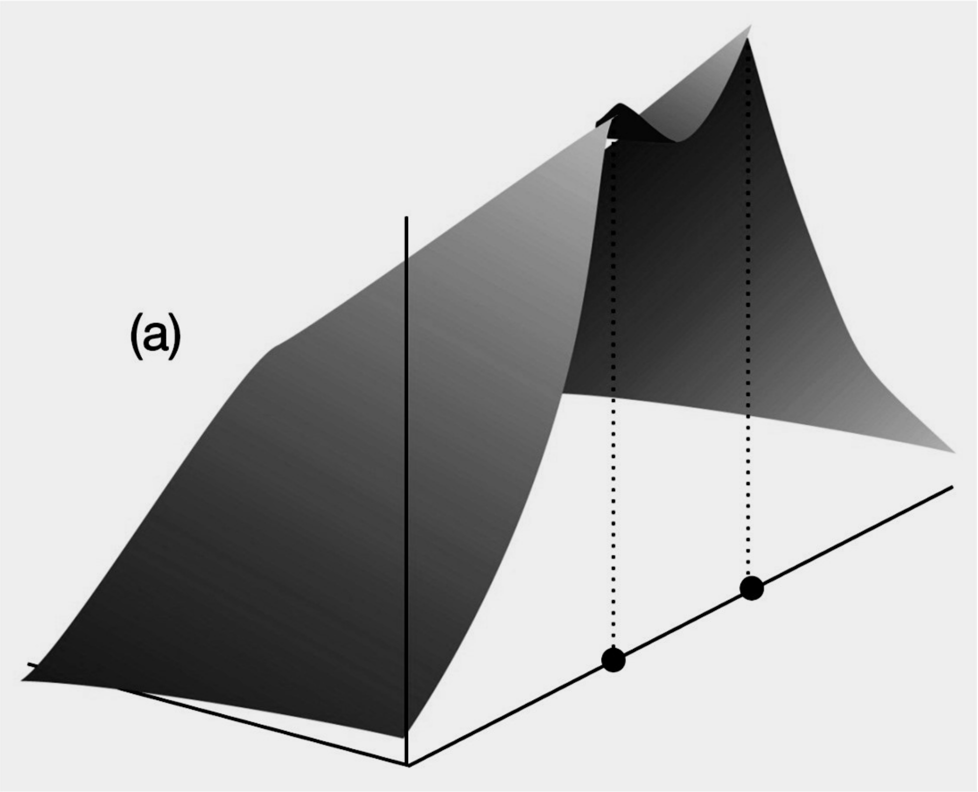
$$\phi_1 = \frac{1}{\sqrt{2(1+S_{ab})}}(\psi_a + \psi_b)$$



σ_{1s}

Molecular Orbital Theory

H_2^+



The electron density calculated by forming the square of the wavefunction. Note the accumulation of electron density in the internuclear region.

$$\phi_1 = \frac{1}{\sqrt{2(1+S_{ab})}}(\psi_a + \psi_b)$$

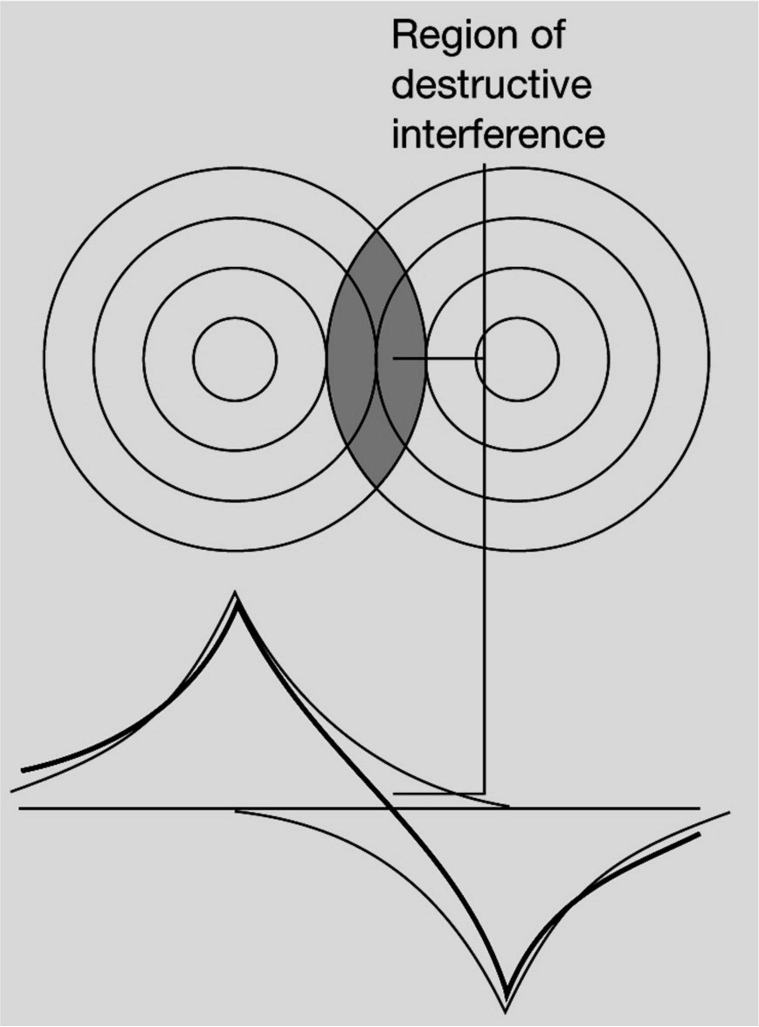
Electron density distribution:

$$\rho(\phi_1) = |\phi_1|^2 = \phi_1^* \phi_1 = (\psi_a^2 + \psi_b^2 + 2\psi_a\psi_b) / [2(1+S_{ab})]$$

$$\text{with} \quad \int \rho(\phi_1) d\tau = 1$$

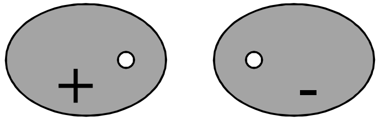
Molecular Orbital Theory

H_2^+



A representation of the destructive interference that occurs when two H1*s* orbitals overlap and form an antibonding σ* orbital.

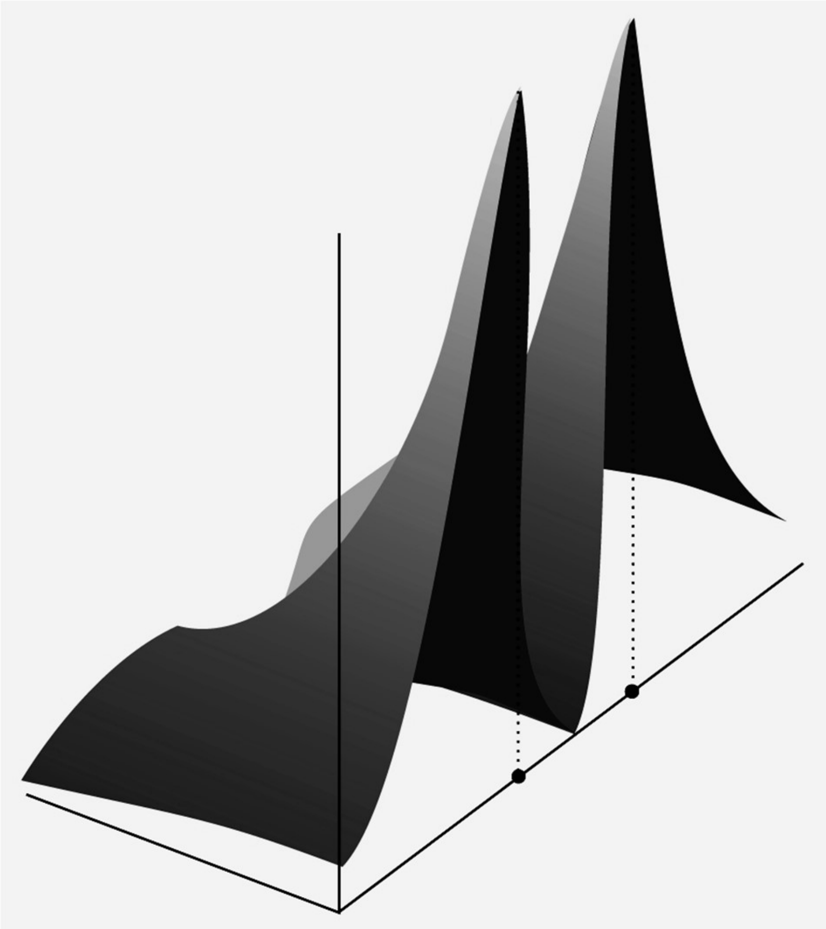
$$\phi_2 = \frac{1}{\sqrt{2(1-S_{ab})}}(\psi_a - \psi_b)$$



σ_{1s}^*

Molecular Orbital Theory

H_2^+



The electron density calculated by forming the square of the Wavefunction. Note the elimination of electron density from the internuclear region.

$$\phi_2 = \frac{1}{\sqrt{2(1-S_{ab})}}(\psi_a - \psi_b)$$

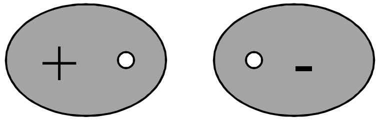
Its density distribution function (or probability distribution function):

$$\rho(\phi_2) = \phi_2^{*}\phi_2 = (\psi_a^{2} + \psi_b^{2} - 2\psi_a\psi_b)/[2(1-S_{ab})]$$

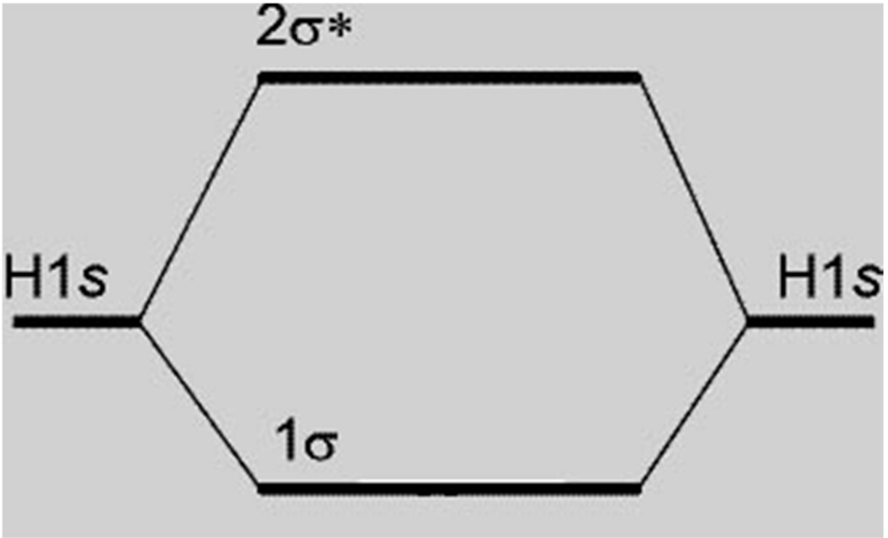
It is provable that this MO has no electron density at the midpoint of the H-H bond (i.e., the value of this function is zero at the midpoint`

Molecular Orbital Theory

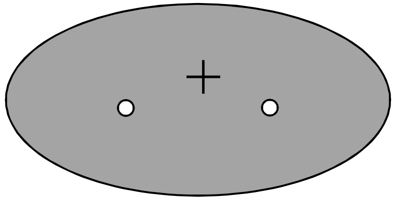
H_2^+



$$E_2 = \frac{\alpha - \beta}{1 - S}$$



A molecular orbital energy level diagram for orbitals constructed from the overlap of H1*s* orbitals; the separation of the levels corresponds to that found at the equilibrium bond length.



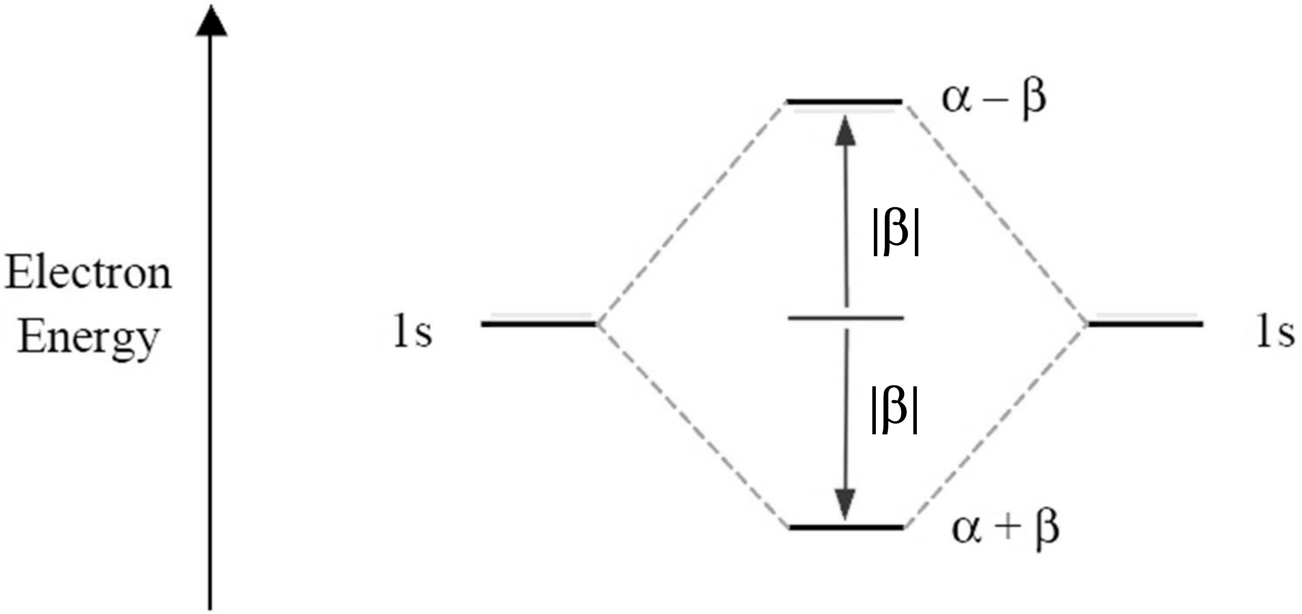
$$E_1 = \frac{\alpha + \beta}{1 + S}$$

(1) The Simplest Solution

Let **S=0** (i.e., Hückel approx.)

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0 \quad \Longrightarrow$$

$$\boxed{\begin{aligned} &(\alpha - E)^2 - \beta^2 = 0 \\ &\Rightarrow E - \alpha = \pm\beta \\ &\Rightarrow E_+ = \alpha + \beta, \qquad E_- = \alpha - \beta \end{aligned}}$$



(2) The More Realistic Solution **$S \neq 0$**

$$(\alpha - E)^2 - (\beta - ES)^2 = 0$$

$$\Rightarrow E - \alpha = \pm(\beta - ES)$$

$$\Rightarrow E(1 \pm S) = \alpha \pm \beta$$

$$\Rightarrow E_+ = \frac{\alpha + \beta}{1 + S}, \qquad E_- = \frac{\alpha - \beta}{1 - S}$$

So, the energy of the bonding molecular orbital is $E_+ = \frac{(\alpha + \beta)}{(1 + S)}$

The energy of the antibonding molecular orbital is $E_- = \frac{(\alpha - \beta)}{(1 - S)}$

$$E_+ = \frac{(\alpha + \beta)}{(1+S)} \;\; = \alpha + \frac{(\beta - S\alpha)}{(1+S)}$$

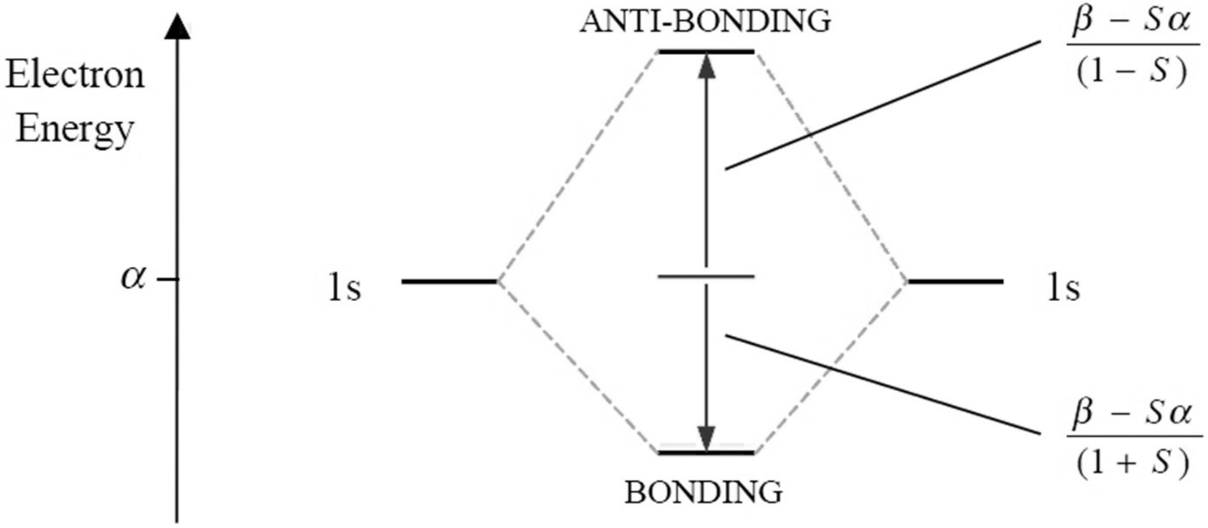
$$E_- = \frac{(\alpha - \beta)}{(1-S)} \;\; = \alpha - \frac{(\beta - S\alpha)}{(1-S)}$$

Note: β-Sσ < 0

When S>0 (bonding) ➔ 1+S > 1-S ➔

$$\boxed{\left|\frac{\beta - S\alpha}{1+S}\right| < \left|\frac{\beta - S\alpha}{1-S}\right|}$$

Generally the antibonding orbital is more strongly antibonding than the bonding orbital is bonding!



How to get the high-energy MO′s of H_2^+

- **It is expected that the high-energy MO’s of H_2^+ consist of the high-energy AO’s of the two H atoms.**
- **It is possible to get the high-energy MO’s of H_2^+ by including the high-energy AO’s of the two H atoms into the trial function.**

Trial function for the MO of H_2^+

$$\phi = [c_{1sa} f_{1sa} + c_{2sa} f_{2sa} + c_{2pxa} f_{2pxa} + \ldots]$$

AO’s of atom a.

$$+ [c_{1sb} f_{1sb} + c_{2sb} f_{2sb} + c_{2pxb} f_{2pxb} + \ldots]$$

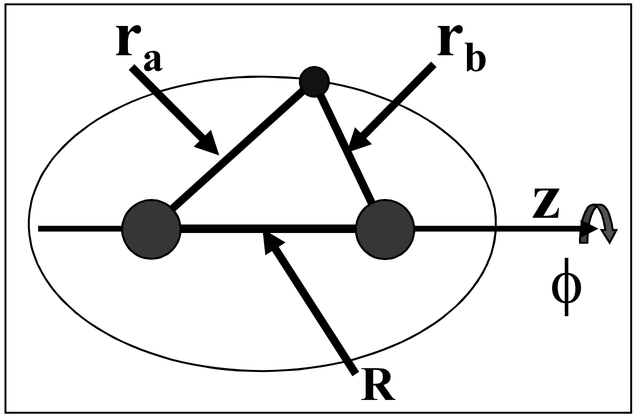
AO’s of atom b.

Summary

1. H_2^+ (confocal elliptical coordinates)

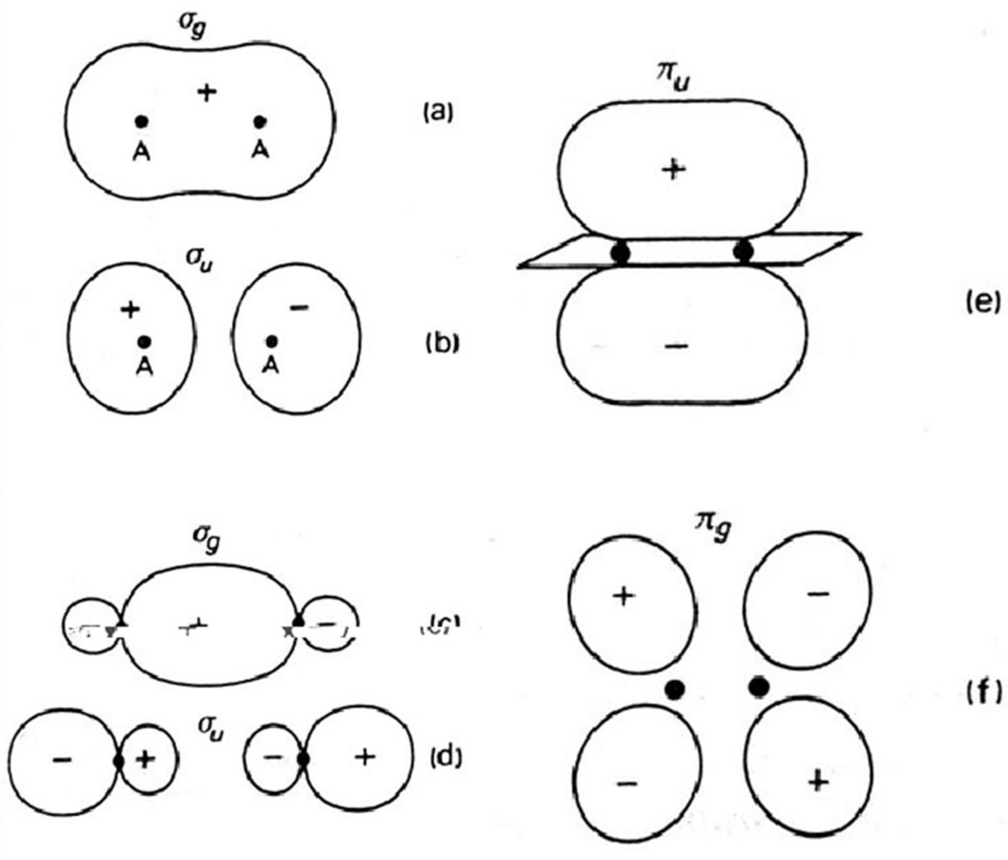
$$\psi_{elec} = F(\xi,\eta)\cdot[(2\pi)^{-1/2}e^{im\phi}]$$

$$\xi = (r_a+r_b)/R$$
$$\eta = (r_a-r_b)/R$$



$\lambda = \vert m\vert$	*0*	*1*	*2*	*3*	*4*
letter	σ	π	δ	ϕ	γ

σ π



Born-Oppenheimer Approx.

The Hamilton operator

$$\hat{H} = -\frac{1}{2}\nabla_e^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R}$$

Schrödinger equation:

$$\hat{H}\psi = E\psi$$

2. The Variation Theorem

Given a system whose Hamiltonian operator Ĥ is time-independent and whose lowest-energy eigenvalue is E_1, if ϕ is any normalized, well-behaved function of coordinates of the system's particles that satisfies the boundary conditions of the problem, then

$$< E >= \int \phi^* \hat{H} \phi d\tau \geq E_1 \qquad (\int \phi^* \phi d\tau = 1)$$

- The variation theorem allows us to calculate the upper bond for the system's ground-state energy.

3. Linear Variation Functions

A linear variation function is a linear combination of *n* linearly independent functions f_1, f_2, ...f_n.

$$\phi = c_1 f_1 + c_2 f_2 + \ldots + c_n f_n = \sum_{j=1}^{n} c_j f_j$$

Following the variation theorem, the coefficients ***{c***

$$< E >= \frac{\int \phi^* \hat{H} \phi d\tau}{\int \phi^* \phi d\tau} \geq E_0$$

$$\varepsilon =< E >$$

Minimizing ε leads to *n* secular equations, $\{\partial\varepsilon/\partial c_i = 0\}$.

Suppose the following trial wavefunction for a QM system

$$\phi = c_1\psi_1 + c_2\psi_2 + \ldots + c_n\psi_n$$

By employing the variation theorem, we have ***n*** secular equations:

$$\begin{array}{lr}
(H_{11} - ES_{11})c_1 + (H_{12} - ES_{12})c_2 + \ldots(H_{1n} - ES_{1n})c_n = 0 & (1) \\
(H_{21} - ES_{21})c_1 + (H_{22} - ES_{22})c_2 + \ldots(H_{2n} - ES_{2n})c_n = 0 & (2) \\
 & \\
(H_{n1} - ES_{n1})c_1 + (H_{n2} - ES_{n2})c_2 + \ldots(H_{nn} - ES_{nn})c_n = 0 & (n)
\end{array}$$

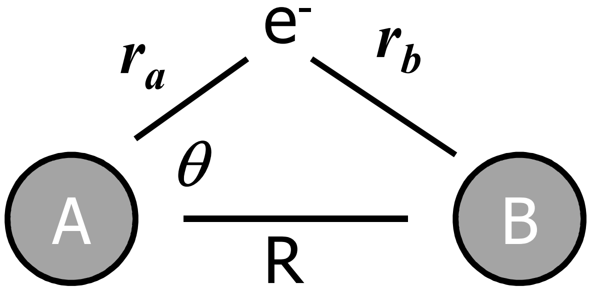
Which demand the following secular determinant being ***zero***,

$$\begin{vmatrix}
H_{11} - ES_{11} & H_{12} - ES_{12} & \ldots & H_{1n} - ES_{1n} \\
H_{21} - ES_{21} & H_{22} - ES_{22} & \ldots & H_{2n} - ES_{2n} \\
. & . & \ldots & . \\
. & . & \ldots & . \\
H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \ldots & H_{nn} - ES_{nn}
\end{vmatrix} = 0 \rightarrow \{E_j\} \rightarrow \{c_i^j\} \rightarrow \boxed{\phi_j = \sum_{i=1}^{n} c_i^{\ j}\psi_i}$$

(j = 1,2, …, n)

The algebraic equation has ***n*** roots, which can be shown to be real.
Arranging these roots in order of increasing value: $\boldsymbol{E_1 \leq E_2 \leq \ldots \leq E_n}$.

3. The solution of H_2^+



For H_2^+ that is :

$$1s_A = \frac{e^{-r_a}}{\sqrt{\pi}} \qquad = \psi_a$$

$$1s_B = \frac{e^{-r_b}}{\sqrt{\pi}} \qquad = \psi_\text{b}$$

$$\phi = c_a\psi_a + c_b\psi_b$$

Trial function for the MO of H_2^+

Note: We have as many linear combinations as we have atomic orbitals, i.e., {ψ_1, …, ψ_n} ➔ {ϕ_1, …, ϕ_n} with

$$\phi_j = \sum_{i=1}^{n} c_i^j \psi_i$$

$$\phi = c_a\psi_a + c_b\psi_b$$

→ **Secular equations,**

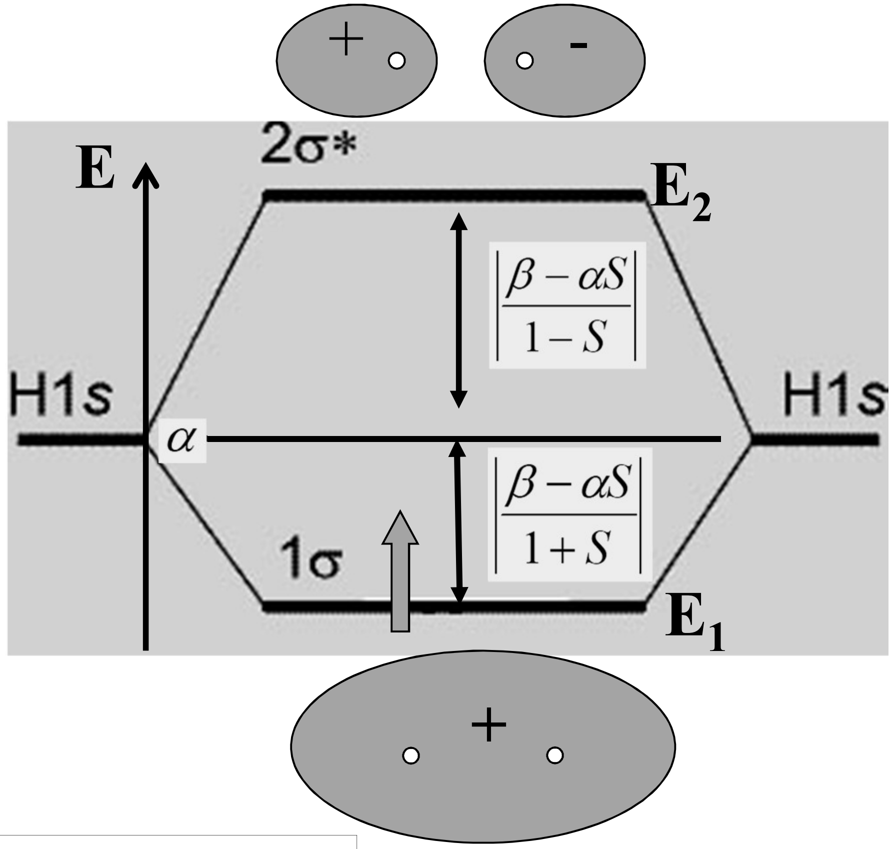
$$\begin{vmatrix} H_{aa} - ES_{aa} & H_{ab} - ES_{ab} \\ H_{ba} - ES_{ba} & H_{bb} - ES_{bb} \end{vmatrix} = 0$$

$$E_1 = \frac{\alpha+\beta}{1+S} = \alpha + \frac{\beta - \alpha S}{1+S}$$

$$E_2 = \frac{\alpha-\beta}{1-S} = \alpha - \frac{\beta - \alpha S}{1-S}$$

$$\phi_1 = \frac{1}{\sqrt{2(1+S)}}(\psi_a + \psi_b)$$

$$\phi_2 = \frac{1}{\sqrt{2(1-S)}}(\psi_a - \psi_b)$$



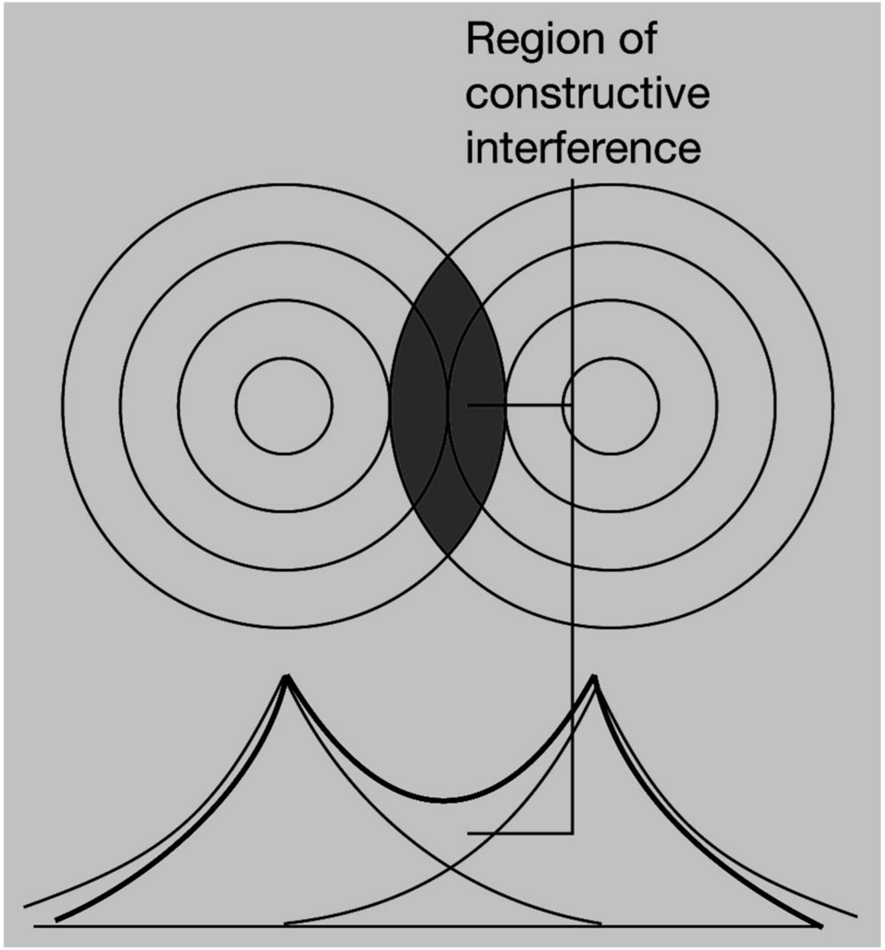
$\alpha = H_{aa} = H_{bb}$ **Coulombic integral**

$\beta = H_{ab} = H_{ba}$ **Resonance integral**

$S = S_{ab} = S_{ba}$ **Overlap integral**

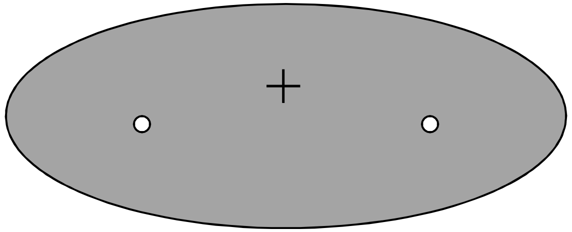
Molecular Orbital Theory

H_2^+



A representation of the constructive interference that occurs when two H 1*s* orbitals overlap and form a bonding σ orbital.

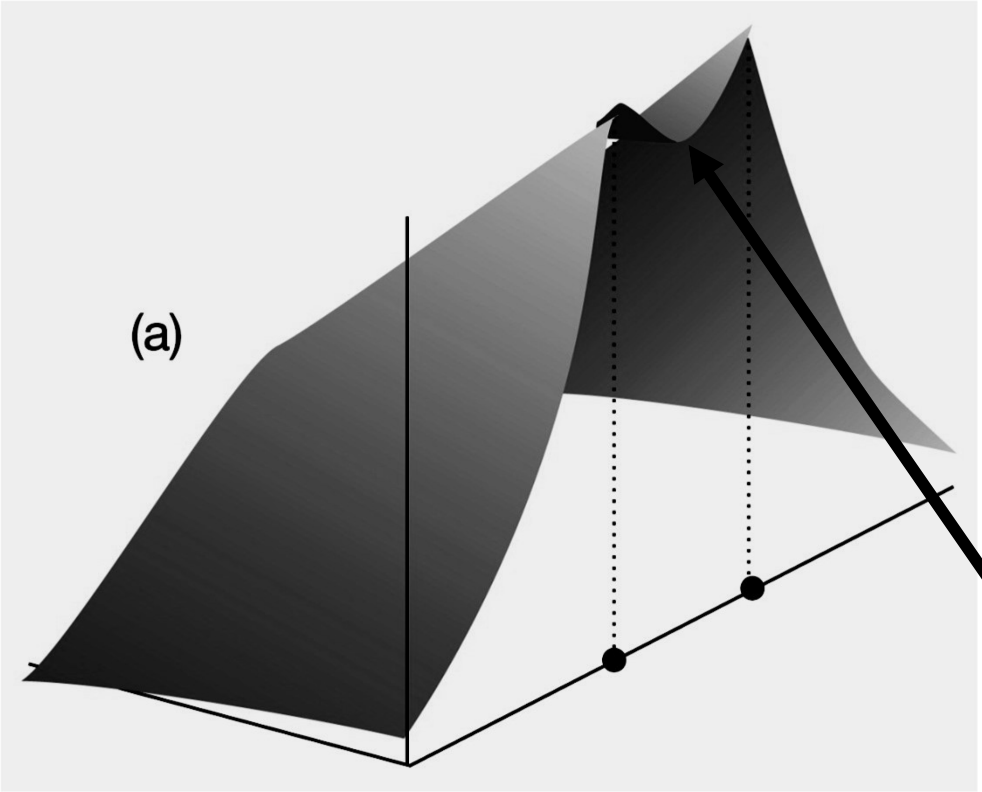
$$\phi_1 = \frac{1}{\sqrt{2(1+S_{ab})}}(\psi_a + \psi_b)$$



σ_s

Molecular Orbital Theory

H_2^+



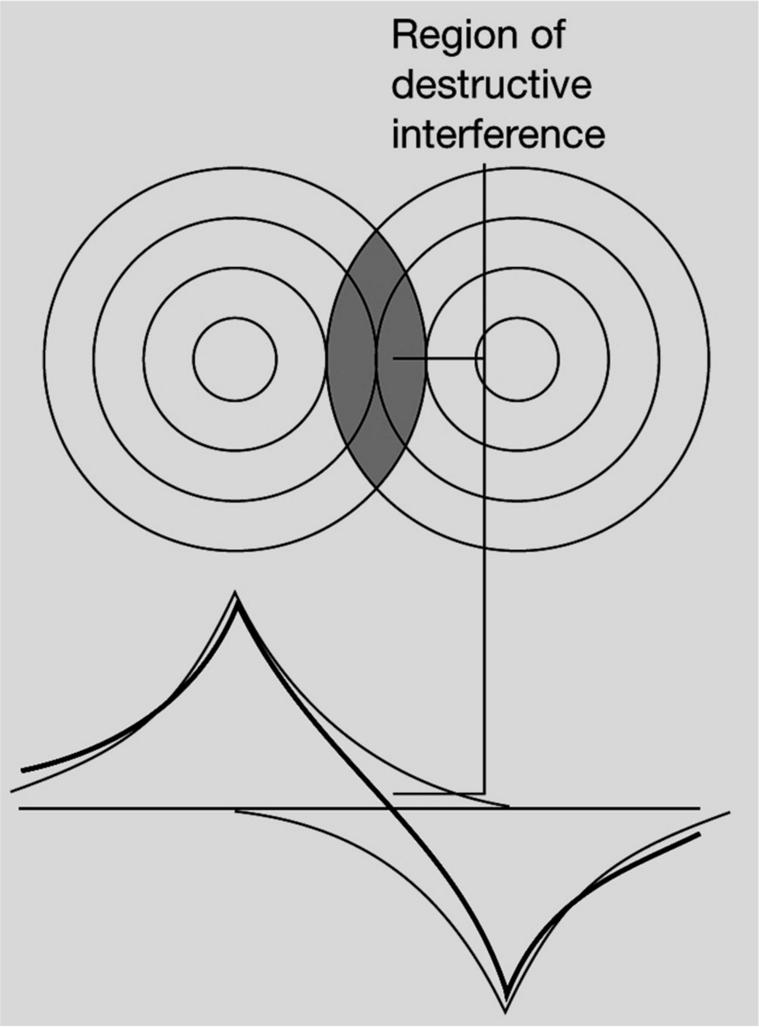
The electron density calculated by forming the square of the wavefunction.
Note the accumulation of electron density in the internuclear region.

$$\phi_1 = \frac{1}{\sqrt{2(1+S_{ab})}}(\psi_a + \psi_b)$$

$$\rho(\phi_1) = \phi_1^* \phi_1 = \frac{1}{2(1+S)}(\psi_a{}^2 + \psi_b{}^2 + 2\psi_a\psi_b)$$

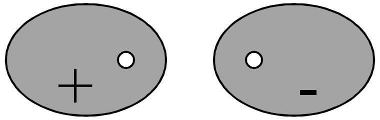
Molecular Orbital Theory

H_2^+



A representation of the destructive interference that occurs when two H1*s* orbitals overlap and form an antibonding σ* orbital.

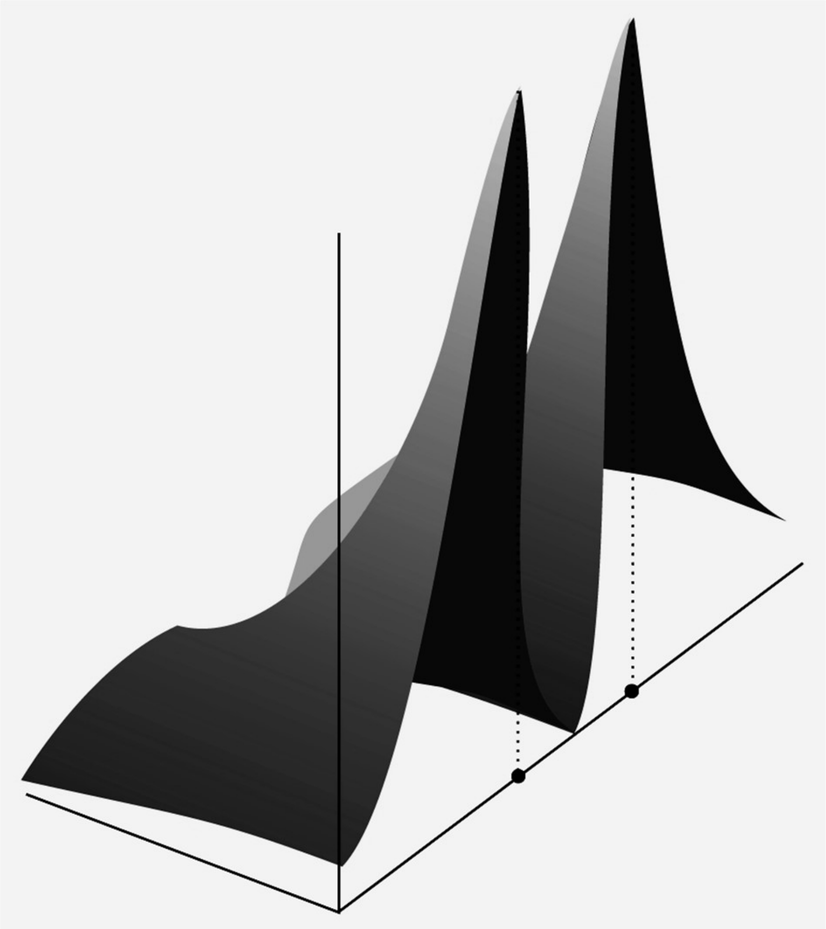
$$\phi_2 = \frac{1}{\sqrt{2(1-S_{ab})}}(\psi_a - \psi_b)$$



$\sigma_s{}^*$

Molecular Orbital Theory

H_2^+



The electron density calculated by forming the square of the Wavefunction. Note the elimination of electron density from the internuclear region.

$$\phi_2 = \frac{1}{\sqrt{2(1-S_{ab})}}(\psi_a - \psi_b)$$

$$\rho(\phi_2) = \phi_2^*\phi_2 = \frac{1}{2(1-S)}(\psi_a{}^2 + \psi_b{}^2 - 2\psi_a\psi_b)$$

The nature of chemical bonding

Atomic orbitals overlap

$\Downarrow$

Concentration of electronic density around the midpoint

$\Downarrow$

Electronic delocalization: from 1 nucleus to 2 nuclei

$\Downarrow$

$$\mathbf{T}\downarrow,\quad \mathbf{V}_{\mathbf{Ne}}\downarrow \quad\rightarrow\quad \mathbf{E}\downarrow$$

Overall stabilization upon chemical bonding!

§ 2 Molecular orbital theory and diatomic molecules

1. Molecular orbital (MO) theory

a. **Mean-Field approximation**: Every electron in a molecule is supposed to move in an average potential field exerted by the nuclei and other electrons.

~~separation of variables!~~

Potential energy operator for a *n*-electron molecule:

$$\hat{V}_{total} = \hat{V}_{total}^{N-e} + \hat{V}_{total}^{N-N} + \hat{V}_{total}^{e-e} = \sum_{i}\sum_{N}\frac{1}{r_{iN}} + \sum_{N<M}\frac{1}{R_{NM}} + \sum_{i<j}\frac{1}{r_{ij}}$$

Mean-field approximation

$$\hat{V}_{total} = \hat{V}_{total}^{N-e} + \hat{V}_{total}^{N-N} + \hat{V}_{total}^{e-e} \approx \sum_{i=1}^{n}\hat{V}_{i}$$

Mean field exerted on electron ***i*** by all nuclei and other electrons.

$$\Rightarrow \hat{H} = \hat{T}_{total} + \hat{V}_{total} = \sum_{i=1}^{n}\hat{T}_{i} + \sum_{i=1}^{n}\hat{V}_{i} = \sum_{i=1}^{n}\hat{h}(i)$$

$$\& \ \hat{h}(i) = \hat{T}_{i} + \hat{V}_{i}$$

Accordingly, the total wavefunction can be approximately expressed as the product of single-particle wavefunctions,

$$\Psi(1,2,\ldots n) = \prod_i \phi_i(i) = \phi_1(1)\phi_2(2)\ldots\phi_n(n)$$

$$\hat{H}\Psi = \sum_{i=1}^{n} \hat{h}(i)[\phi_1(1)\phi_2(2)\ldots\phi_n(n)] = E\Psi$$

Separation of variables

$$\hat{h}(i)\phi_i = \varepsilon_i\phi_i \qquad \& \;\; E = \sum_{i=1}^{n}\varepsilon_i$$

Energy of the *i*th *e*

Single-particle eigenequation!

- **$\{\phi_i\}$ are a set of one-electron wavefunctions describing the motion of *n* electrons within a molecule, thus are called *Molecular Orbitals*.**

b. The formation of molecular orbital (MO).

- The atomic orbitals of all atoms within a molecule form a set of ***basis***, $\{\varphi_j\}$ ($j = 1, 2, \ldots,$), for the construction of MO’s.

- The MO’s can be approximated by the linear combination of atomic orbitals (LCAO).

$$\boxed{MO: \ \phi = \sum_j c_j \varphi_j \qquad (\varphi_j : j\text{th AO})}$$

LCAO-MO

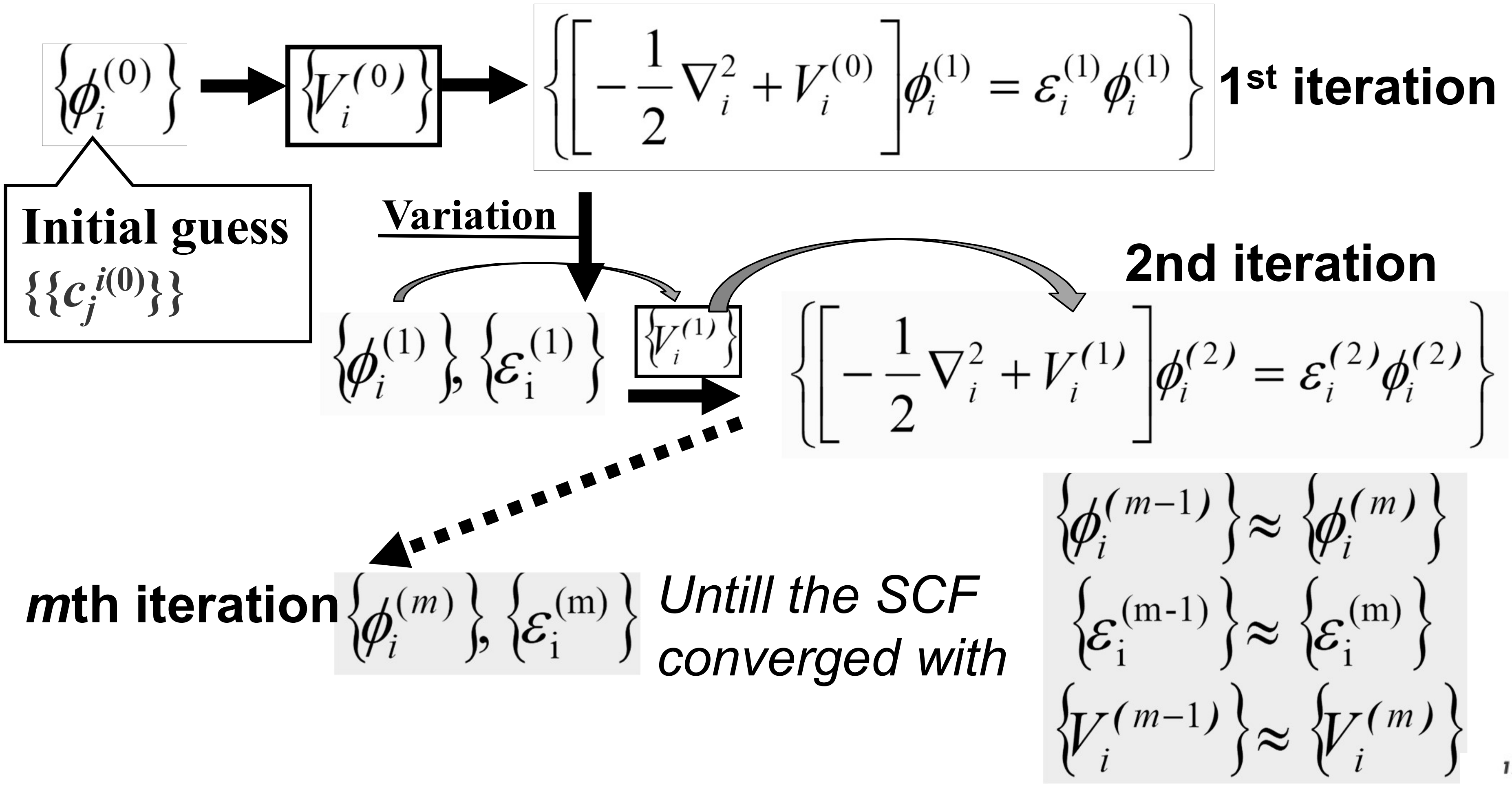
To be determined by the variation theorem!

- The Schrödinger equation can be approximately solved by using the ***Variation theorem*** in combination with the **HF-SCF** method!

Process of HF-SCF:

LCAO-MO

$$MO: \quad \phi_i = \sum_j c_j^i \varphi_j \qquad (\varphi_j : j\text{th AO})$$



$$\left\{\phi_i^{(0)}\right\} \rightarrow \boxed{\left\{V_i^{(0)}\right\}} \rightarrow \left\{\left[-\frac{1}{2}\nabla_i^2 + V_i^{(0)}\right]\phi_i^{(1)} = \varepsilon_i^{(1)}\phi_i^{(1)}\right\}$$

1st iteration

Initial guess
$\{\{c_j^{i(0)}\}\}$

Variation

$$\left\{\phi_i^{(1)}\right\}, \left\{\varepsilon_\mathrm{i}^{(1)}\right\} \quad \boxed{\left\{V_i^{(1)}\right\}} \rightarrow \left\{\left[-\frac{1}{2}\nabla_i^2 + V_i^{(1)}\right]\phi_i^{(2)} = \varepsilon_i^{(2)}\phi_i^{(2)}\right\}$$

2nd iteration

***m*th iteration** $\left\{\phi_i^{(m)}\right\}, \left\{\varepsilon_\mathrm{i}^{(\mathrm{m})}\right\}$

Untill the SCF converged with

$$\left\{\phi_i^{(m-1)}\right\} \approx \left\{\phi_i^{(m)}\right\}$$

$$\left\{\varepsilon_\mathrm{i}^{(\mathrm{m-1})}\right\} \approx \left\{\varepsilon_\mathrm{i}^{(\mathrm{m})}\right\}$$

$$\left\{V_i^{(m-1)}\right\} \approx \left\{V_i^{(m)}\right\}$$

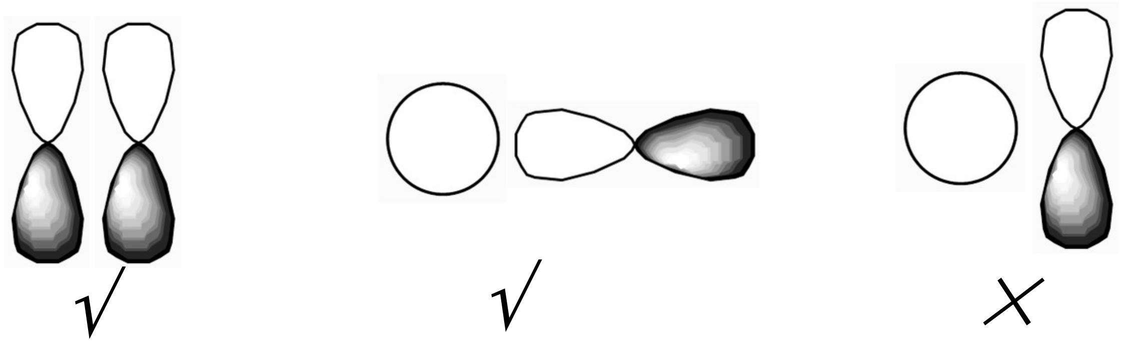
Computer makes the SCF process readily accessible!

The formation of molecular orbital (MO):

Qualitatively, there are three basic requirements for AO’s to form a bonding MO (i.e., mathematically to have remarkable $|c_j|$ values for the AO′s that constitute a MO!).

The AOs to form a bonding MO should

- **have comparable energy,**
- **have compatible symmetry,**
- **be able to have maximum overlap.**



Why should the AOs have comparable energy?

$$\phi = c_a\psi_a + c_b\psi_b \quad \Rightarrow$$

$$\begin{pmatrix} H_{aa} - ES_{aa} & H_{ab} - ES_{ab} \\ H_{ba} - ES_{ba} & H_{bb} - ES_{bb} \end{pmatrix} \begin{pmatrix} \mathrm{c_a} \\ \mathrm{c_b} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \Rightarrow$$

$$\begin{vmatrix} H_{aa} - E & H_{ab} - ES_{ab} \\ H_{ba} - ES_{ba} & H_{bb} - E \end{vmatrix} = 0 \quad \left(\because \begin{matrix} S_{aa} = 1 \\ S_{bb} = 1 \end{matrix}\right)$$

$$\text{if} \quad H_{aa} \approx E_a, H_{bb} \approx E_b, H_{ab} = \beta, S_{ab} \approx 0$$

$$E_1 = \frac{1}{2}[(E_a + E_b) - \sqrt{(E_b - E_a)^2 + 4\beta^2}\,]$$

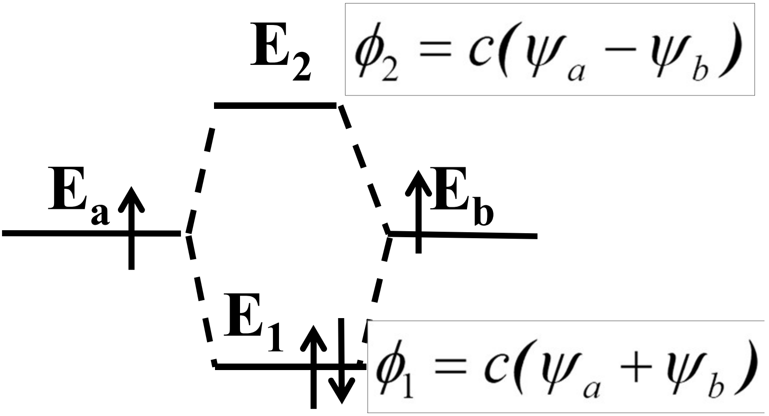
$$E_2 = \frac{1}{2}[(E_a + E_b) + \sqrt{(E_b - E_a)^2 + 4\beta^2}\,]$$

i) If $E_b = E_a$,

$E_1 = E_a - |\beta|$, $E_2 = E_b + |\beta|$

Bonding MO stabilized!

$$E_{bind} = 2E_1 - (E_a + E_b)$$
$$= -2|\beta|$$



$$\phi_2 = c(\psi_a - \psi_b)$$

$$\phi_1 = c(\psi_a + \psi_b)$$

ii) However, if $(E_b - E_a) >> |\beta|$, then $E_1 \approx E_a$, $E_2 \approx E_b$

-----nonbonding at all!

Why should the AOs have comparable energy?

$$\phi = c_a\psi_a + c_b\psi_b \quad \Rightarrow$$

$$\begin{pmatrix} H_{aa} - ES_{aa} & H_{ab} - ES_{ab} \\ H_{ba} - ES_{ba} & H_{bb} - ES_{bb} \end{pmatrix}\begin{pmatrix} \mathrm{c_a} \\ \mathrm{c_b} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \Rightarrow$$

$$\begin{vmatrix} H_{aa} - E & H_{ab} - ES_{ab} \\ H_{ba} - ES_{ba} & H_{bb} - E \end{vmatrix} = 0 \quad \left(\because \begin{matrix} S_{aa} = 1 \\ S_{bb} = 1 \end{matrix}\right)$$

$$if \;\; H_{aa} \approx E_a, H_{bb} \approx E_b, H_{ab} = \beta, S_{ab} \approx 0$$

$$E_1 = \frac{1}{2}[(E_a + E_b) - \sqrt{(E_b - E_a)^2 + 4\beta^2}\,]$$

$$E_2 = \frac{1}{2}[(E_a + E_b) + \sqrt{(E_b - E_a)^2 + 4\beta^2}\,]$$

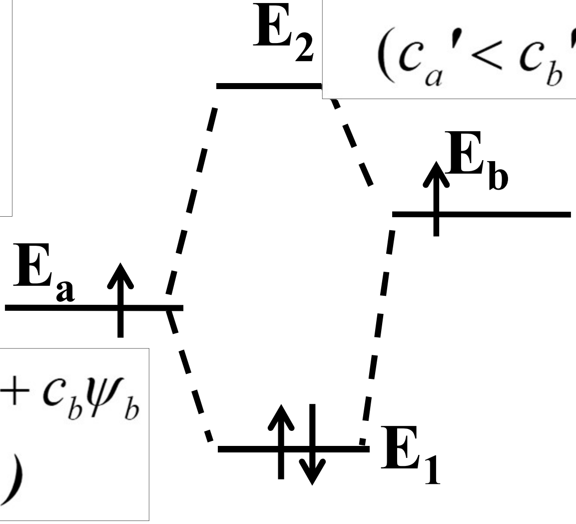
iii) In case E_a and E_b are comparable (E_b-$E_a \approx 0$) and $E_b > E_a$,

$$E_1 \approx \frac{1}{2}(E_a + E_b) - |\beta|$$

$$E_2 \approx \frac{1}{2}(E_a + E_b) + |\beta|$$

$$\phi_2 = c_a'\psi_a - c_b'\psi_b$$

$$(c_a' < c_b')$$



$$\phi_1 = c_a\psi_a + c_b\psi_b$$

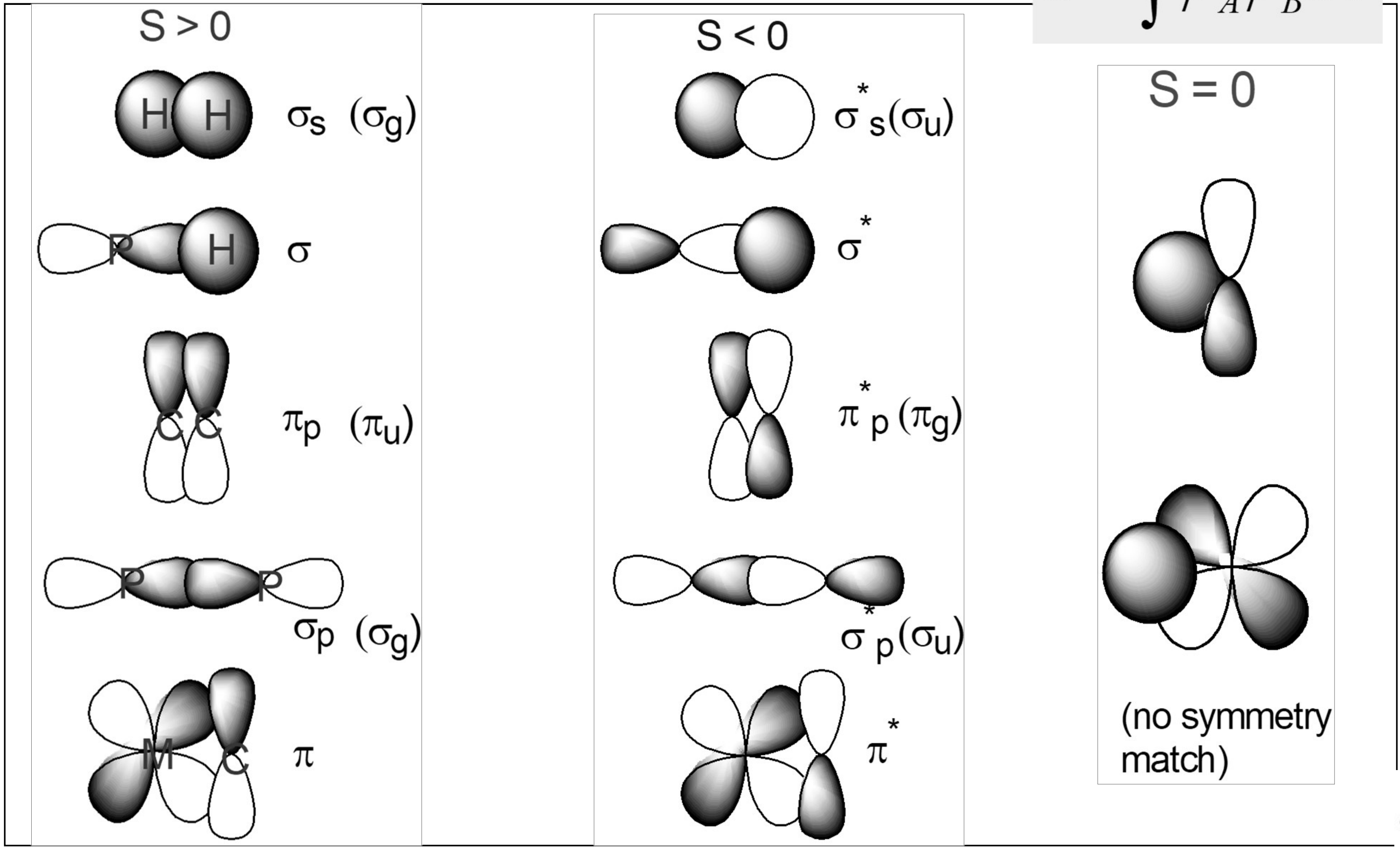
$$(c_a > c_b)$$

Polar bond with more electron density around atom ***a***.

Why should the AOs have compatible symmetry?

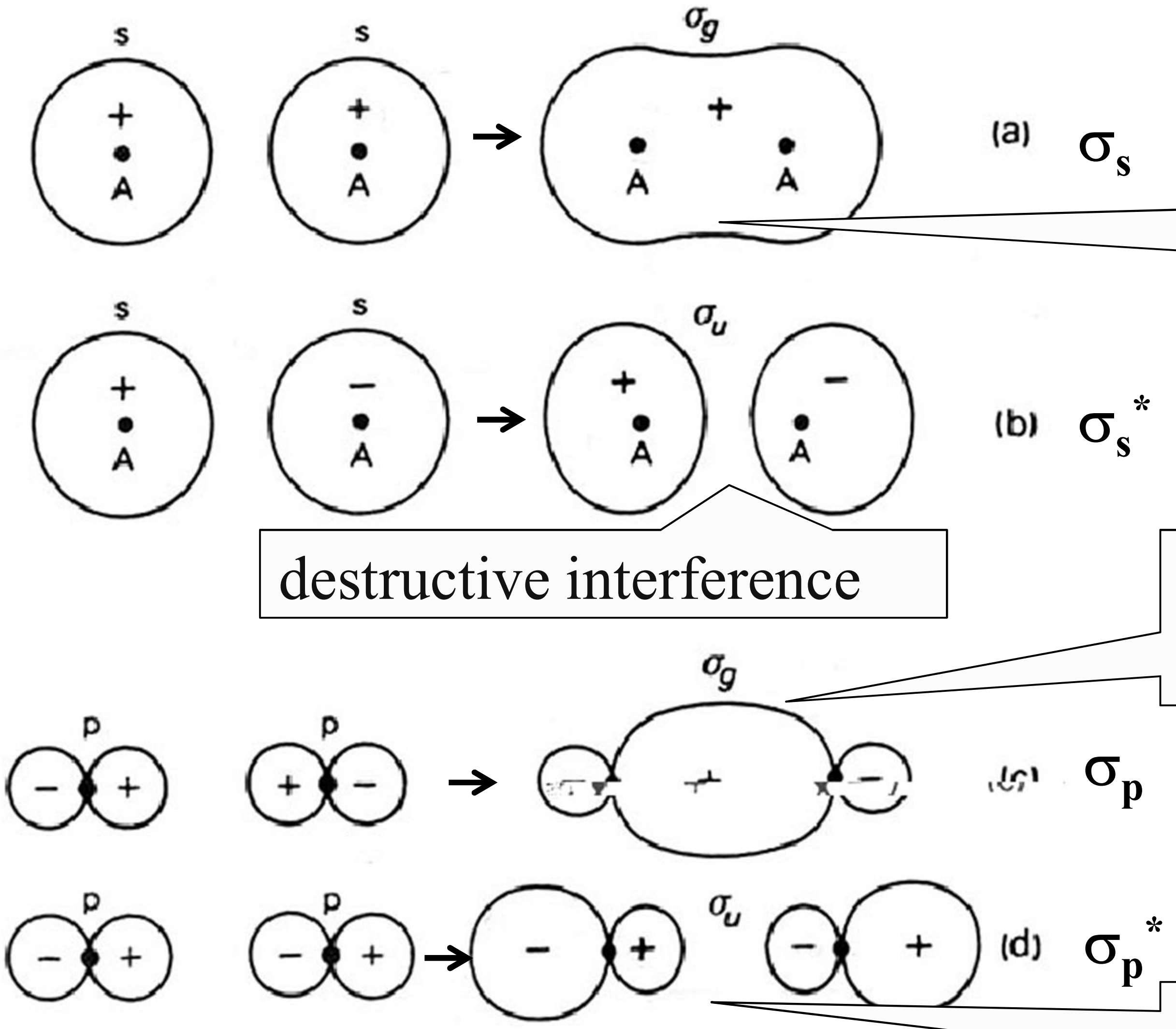
The overlap integral ***S*** may be positive (bonding), negative (antibonding) or zero (non-bonding interaction).

$$S = \int \psi_A^* \psi_B \, d\tau$$



2. The characteristic distribution and classification of molecular orbital

a. σ-orbital and σ-bond of homonuclear diatomics



σ_s

No nodal surface

Constructive interference

σ_s^*

One nodal surface

destructive interference

Constructive interference

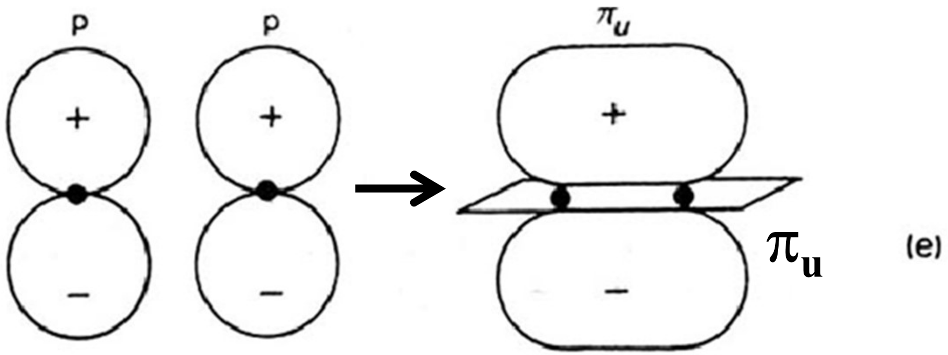
σ_p

σ_p^*

destructive interference

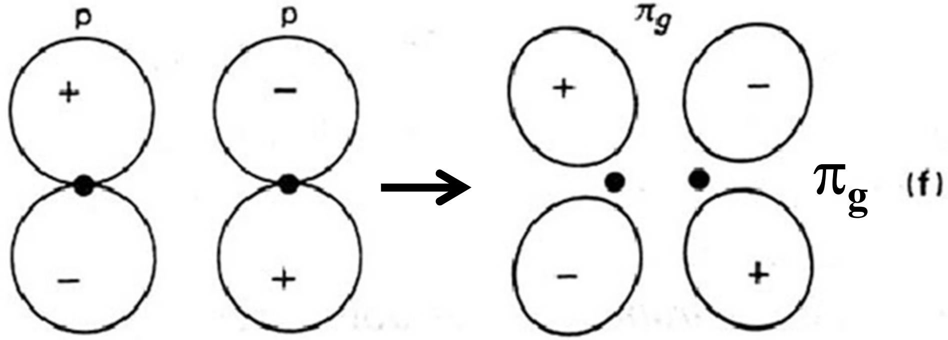
2. The characteristic distribution and classification of molecular orbital

b. π-orbital and π-bond of homonuclear diatomics



p_π + p_π

- One nodal surface.
- "***u***"-disparity, i.e., anti-symmetric upon inversion.



p_π - p_π

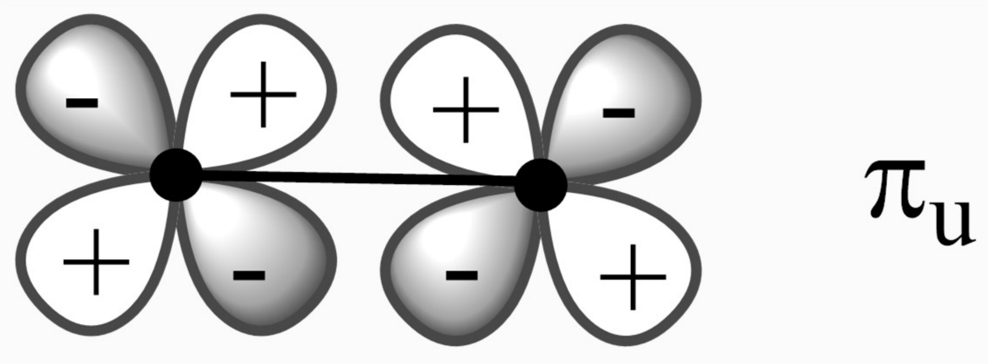
- Two nodal surfaces.
- "***g***"-parity, i.e., symmetric upon inversion.

- "***g***" & "***u***": only used when exists an inversion center!
- The complex form of π-type MO's :

$$p_{+1} + p_{+1} \rightarrow \pi_{+1} \ \& \ p_{-1} + p_{-1} \rightarrow \pi_{-1}$$

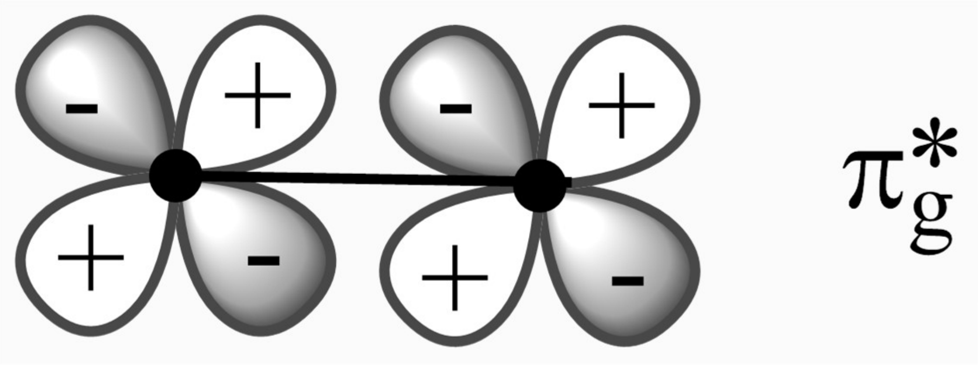
b. π-orbital and π-bond of homonuclear diatomics

$\mathbf{d}_{\pi} \pm \mathbf{d}_{\pi}$



Bonding

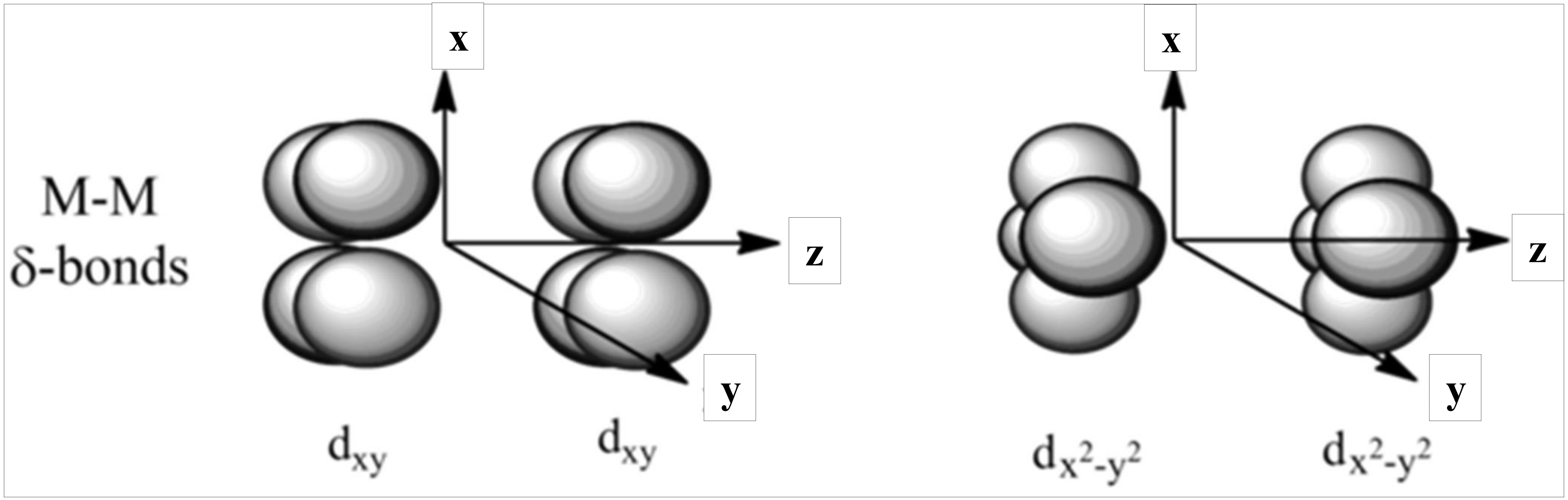
π_u Asymmetric upon inversion.



Antibonding

π_g^* Symmetric upon inversion.

c. δ-orbital and δ-bond of homonuclear diatomics



δ_g δ_g

- Similar to the corresponding *d*-orbital, bonding δ-orbital has two orthogonal nodal surfaces.
- Antibonding δ-orbital has three nodal surfaces.

Note：These π- and δ-orbitals are plotted in real form, which can be linear combination of their original complex form!

3. The structure of homonuclear diatomic molecules

a. The ground-state electronic configuration

The ***aufbau*** (building-up) principle for ground state:

- Pauli exclusion principle (for Fermionic system)
- The minimum energy principle
- Hund's rule.

e.g., For a *n*-electron molecule

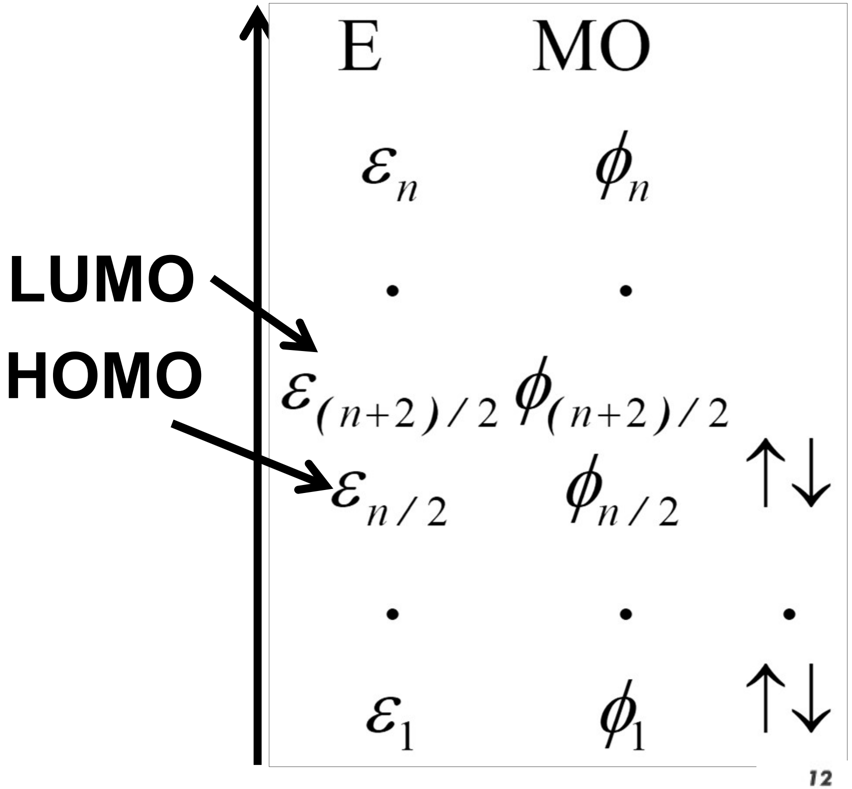
$$MO: \ \phi_i = \sum_{j=1}^{n} c_j^i \varphi_j \ (\varphi_j : j\text{th AO})$$

HF-SCF

$$\boldsymbol{MO: \{\phi_1, \phi_2, \ldots, \phi_i, \ldots, \phi_n\}}$$

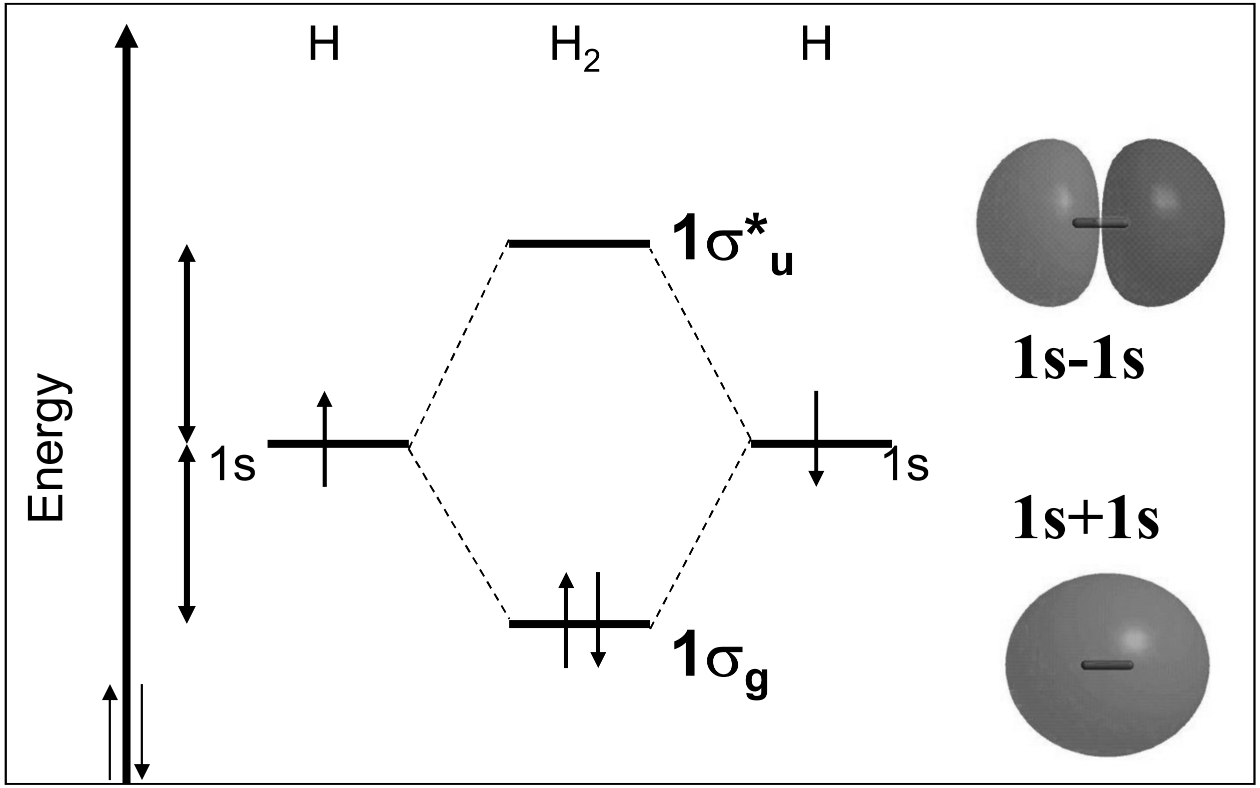
$$\boldsymbol{\{\varepsilon_1 < \varepsilon_2 < \ldots < \varepsilon_i < \ldots < \varepsilon_n\}}$$

(If $\varepsilon_i = \varepsilon_{i+1}$, the two MO's are degenerate!)



(n = even)

Diatomic molecules: The bonding in H_2



Electronic configuration:

H_2 $1\sigma_g^2$

H_2^+ $1\sigma_g^1$

Bond order :

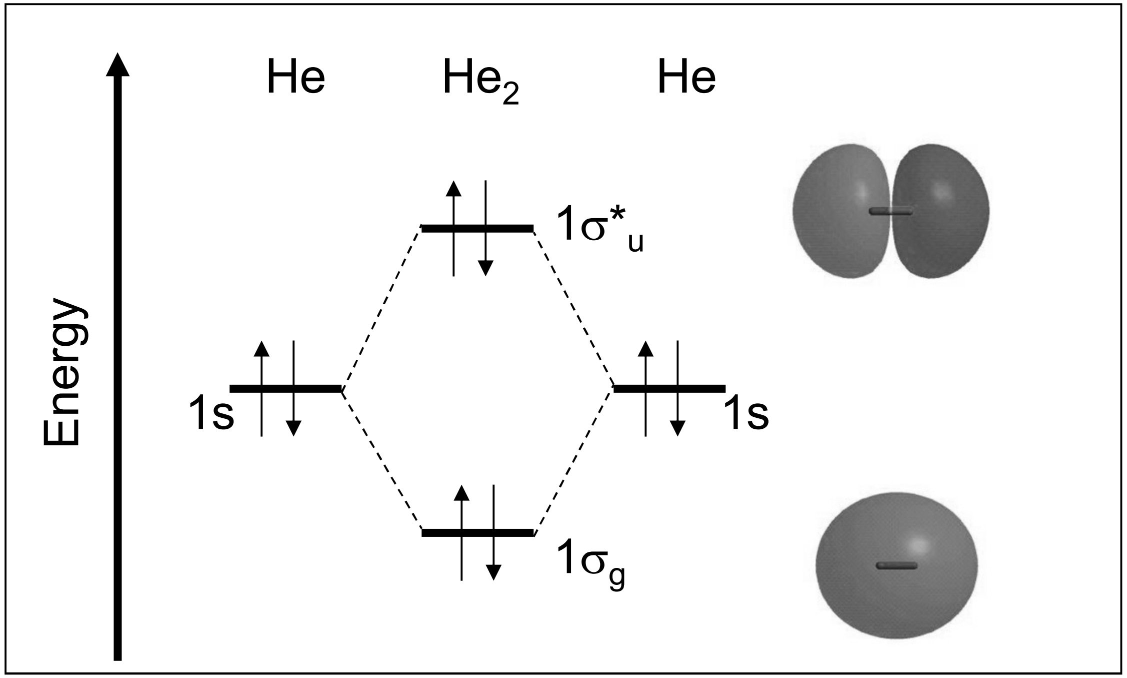
$$b = \frac{1}{2}(n - n^*)$$

n: Electrons in bonding orbitals

n*:Electrons in antibonding orbitals

$b(H_2^+) = 0.5$; $b(H_2)= 1$; $H + H \rightarrow H_2$ $\Delta E = -432$ kJ/mol.

Diatomic molecules: The bonding in He_2



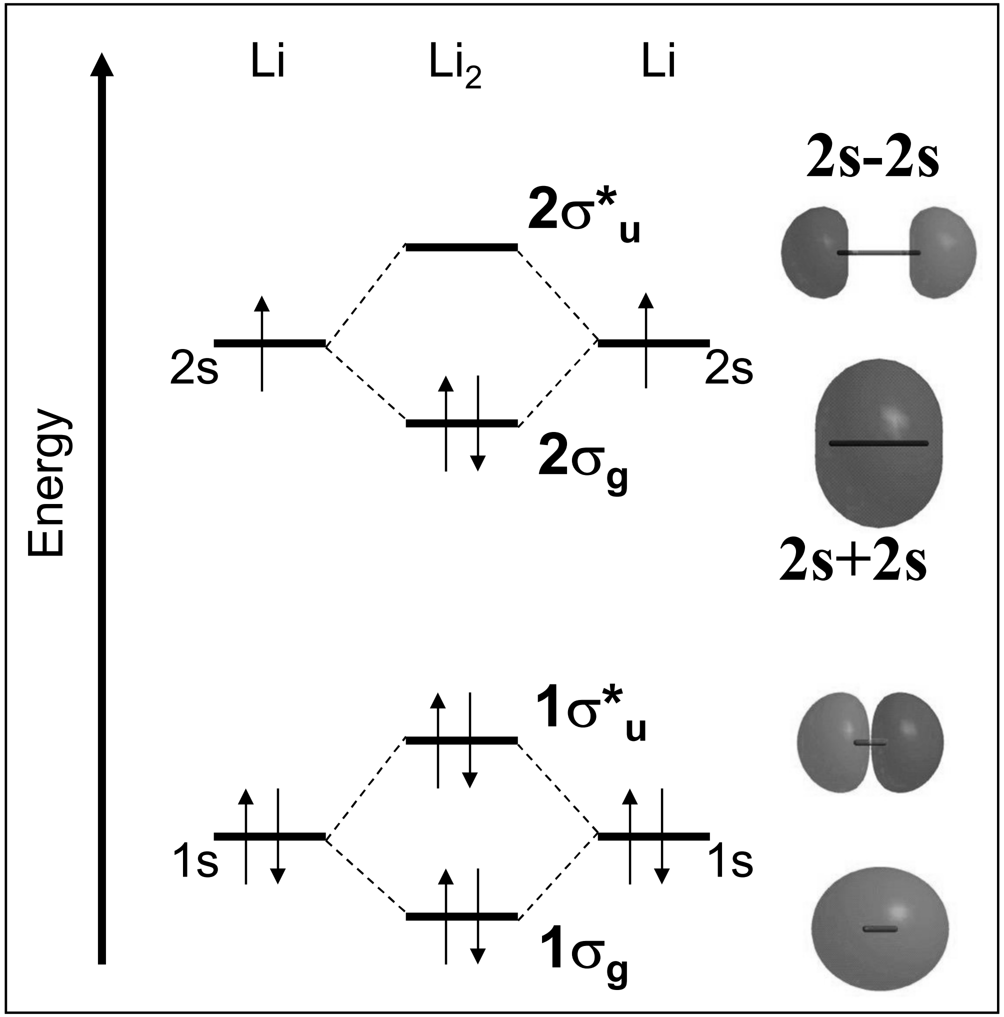
- The bond order (BO) of **He_2**: b = (2-2)/2 = 0 →

  He_2 does not exist as a covalently bounded molecule!

  Accordingly, the molecular form of He is a single atom!

- **He_2^+:** b = (2-1)/2 = 0.5, **exists!** **($1\sigma_g^2 1\sigma_u^{*1}$)**

Diatomic molecules:
Homonuclear Molecules of the Second Period



Electronic Configuration:

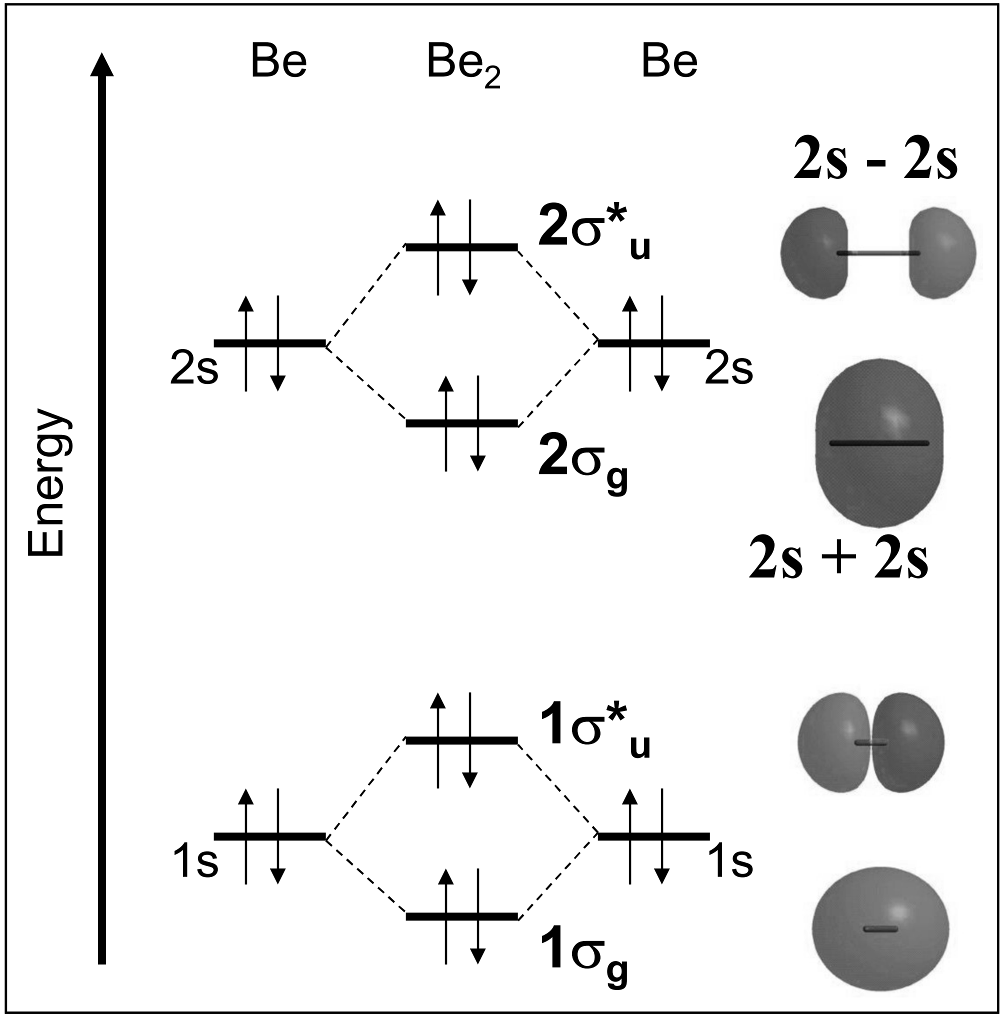
$(1\sigma_g)^2\ (1\sigma_u^*)^2\ (2\sigma_g)^2$

- $b(Li_2) = (4-2)/2 = 1$
- Li_2 could exist.
- $Li_2 \rightarrow Li + Li$

$\Delta E = 105$ kJ/mol

Diatomic molecules:

Homonuclear Molecules of the Second Period

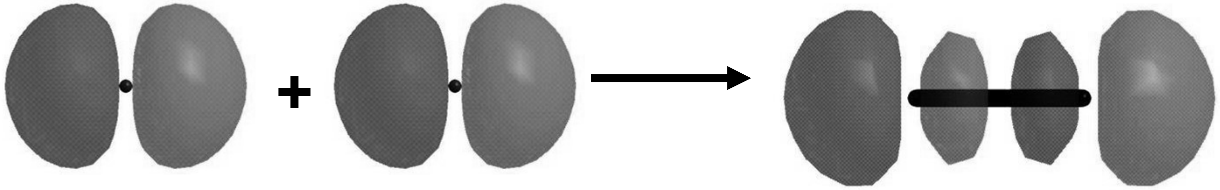


- b = (4-4)/2 = 0
- Be_2 could not exist!

The bonding in F_2

The combinations of σ symmetry:

i)

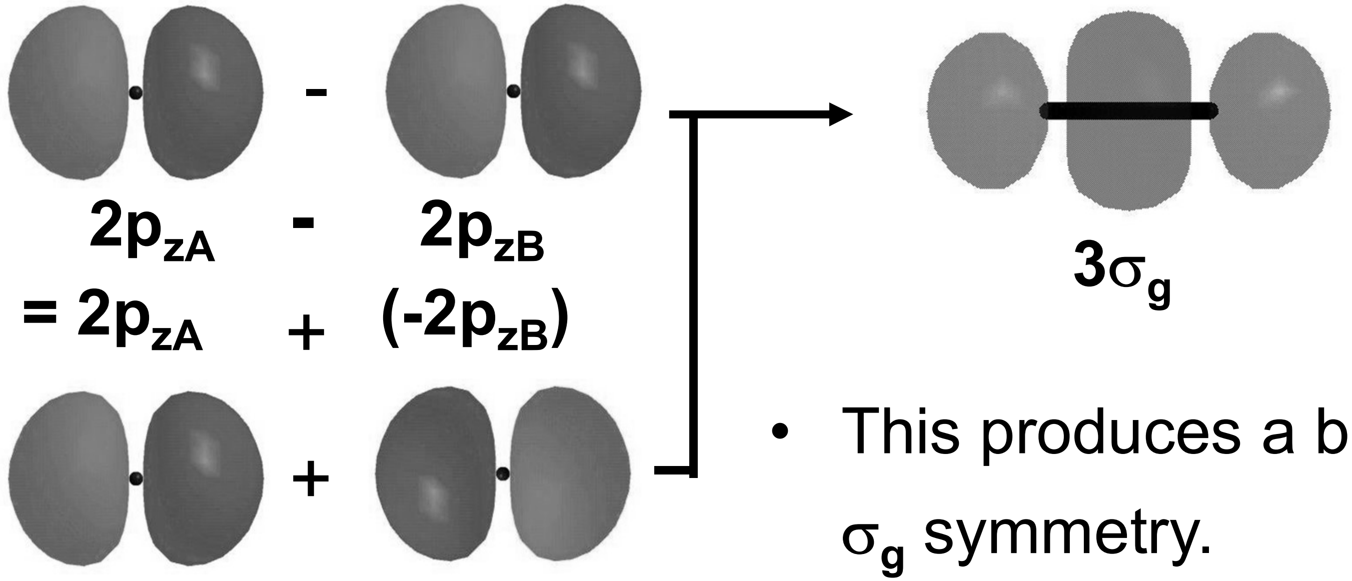


$2p_{zA}$ + $2p_{zB}$

$3\sigma^*_u$

- This produces an antibonding MO of σ^*_u symmetry.

ii)



$2p_{zA}$ - $2p_{zB}$

$= 2p_{zA}$ + $(-2p_{zB})$

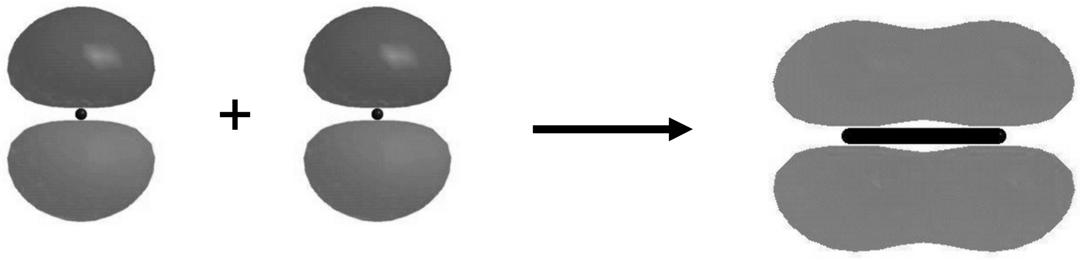
$3\sigma_g$

- This produces a bonding MO of σ_g symmetry.

The bonding in F_2

The first set of combinations of π symmetry:

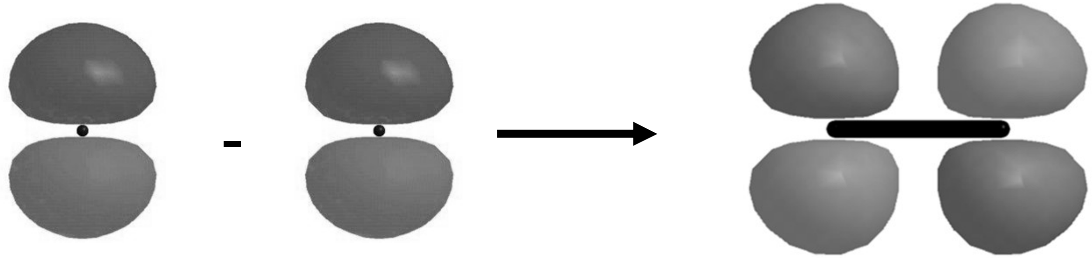
iii)



$\mathbf{2p_{yA}}$ $\mathbf{2p_{yB}}$ $\mathbf{1\pi_y}$

- bonding MO of π_u symmetry.

iv)



$\mathbf{2p_{yA}}$ $\mathbf{2p_{yB}}$ $\mathbf{1\pi^*_y}$

- antibonding MO of π^*_g symmetry.

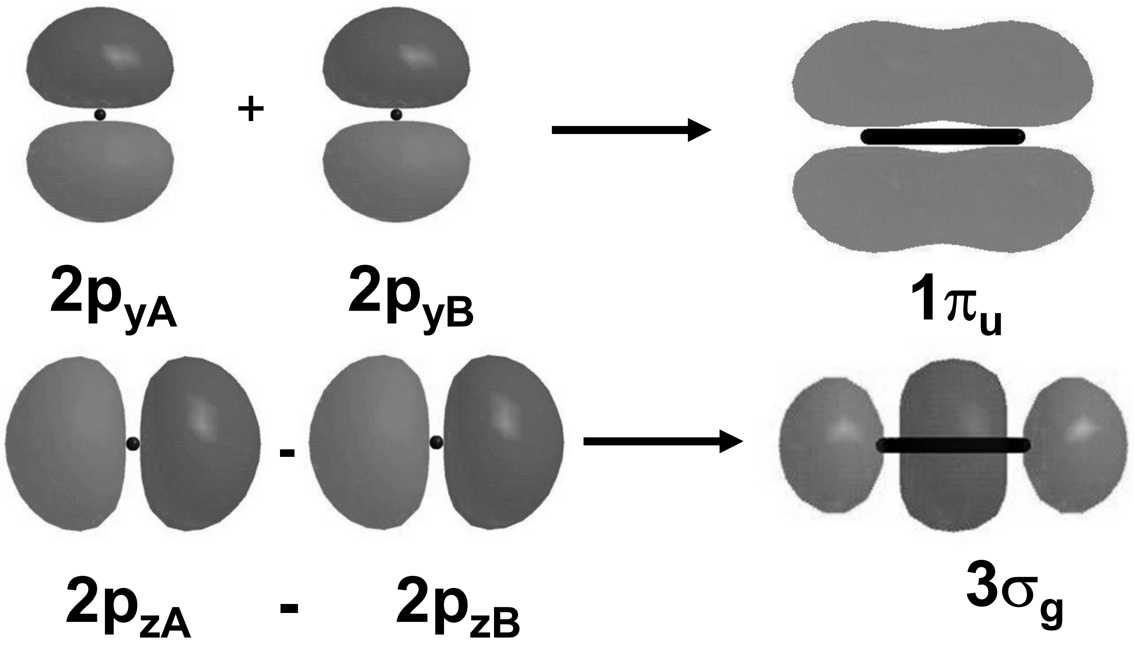
v&vi) Similarly, the combinations of two ***2p***$\boldsymbol{2p_x}$ AOs of the two atoms result in a bonding π_x MO and an antibonding π^*_x MO.

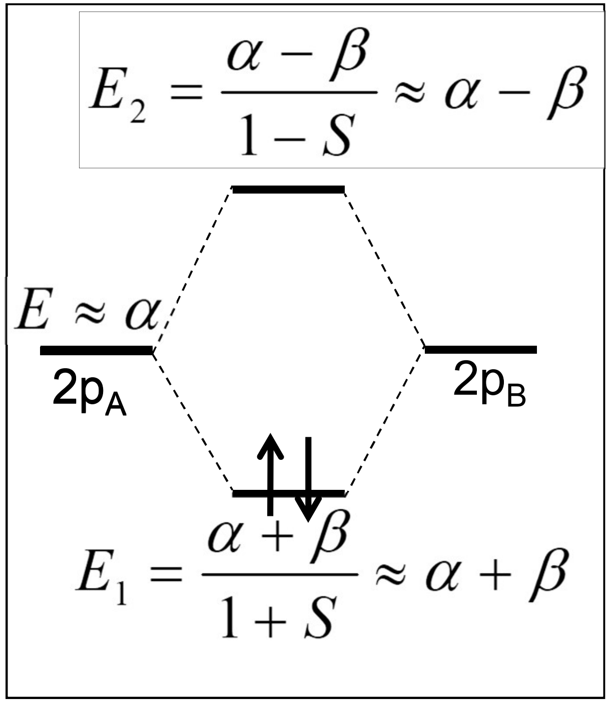
Note: For AO, $\mathbf{p_x = A(p_{+1} + p_{-1})}$ **&** $\mathbf{p_y = A'(p_{+1} - p_{-1})}$

For MO， $\mathbf{\pi_x = B(\pi_{+1} + \pi_{-1})}$ **&** $\mathbf{\pi_y = B'(\pi_{+1} - \pi_{-1})}$

The bonding in F_2

π_{2p} MO vs σ_{2p} MO.





$$E_2 = \frac{\alpha - \beta}{1 - S} \approx \alpha - \beta$$

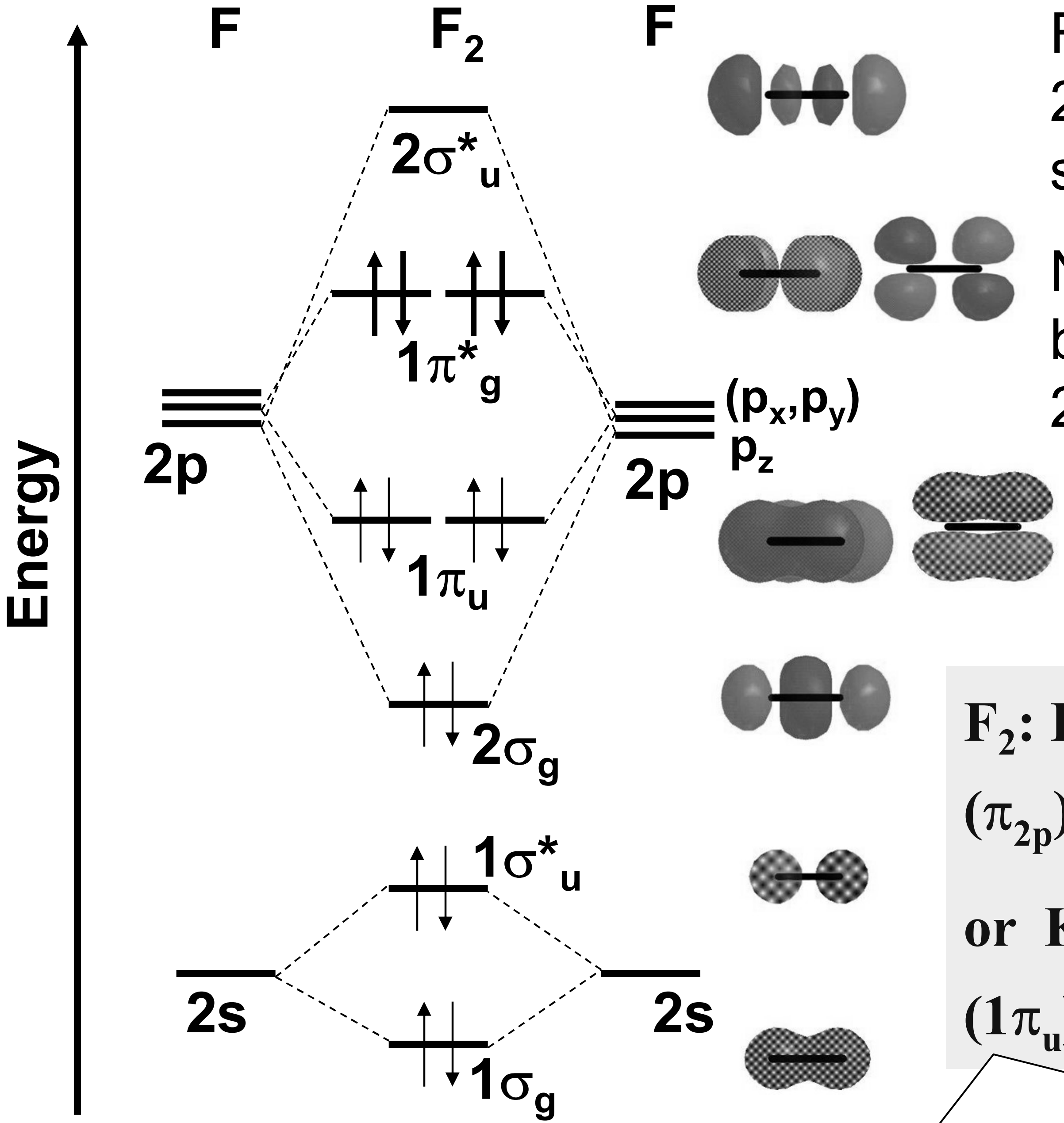
$$E_1 = \frac{\alpha + \beta}{1 + S} \approx \alpha + \beta$$

$$\Delta E = E_2 - E_1 \approx -2\beta$$

As $\beta_\sigma < \beta_\pi < 0$

➔ $\Delta E_\pi < \Delta E_\sigma$

➔ $E_\pi > E_\sigma$, $E_{\pi*} < E_{\sigma*}$



For oxygen and fluorine, 2p and 2s AO's are well separated in energy !

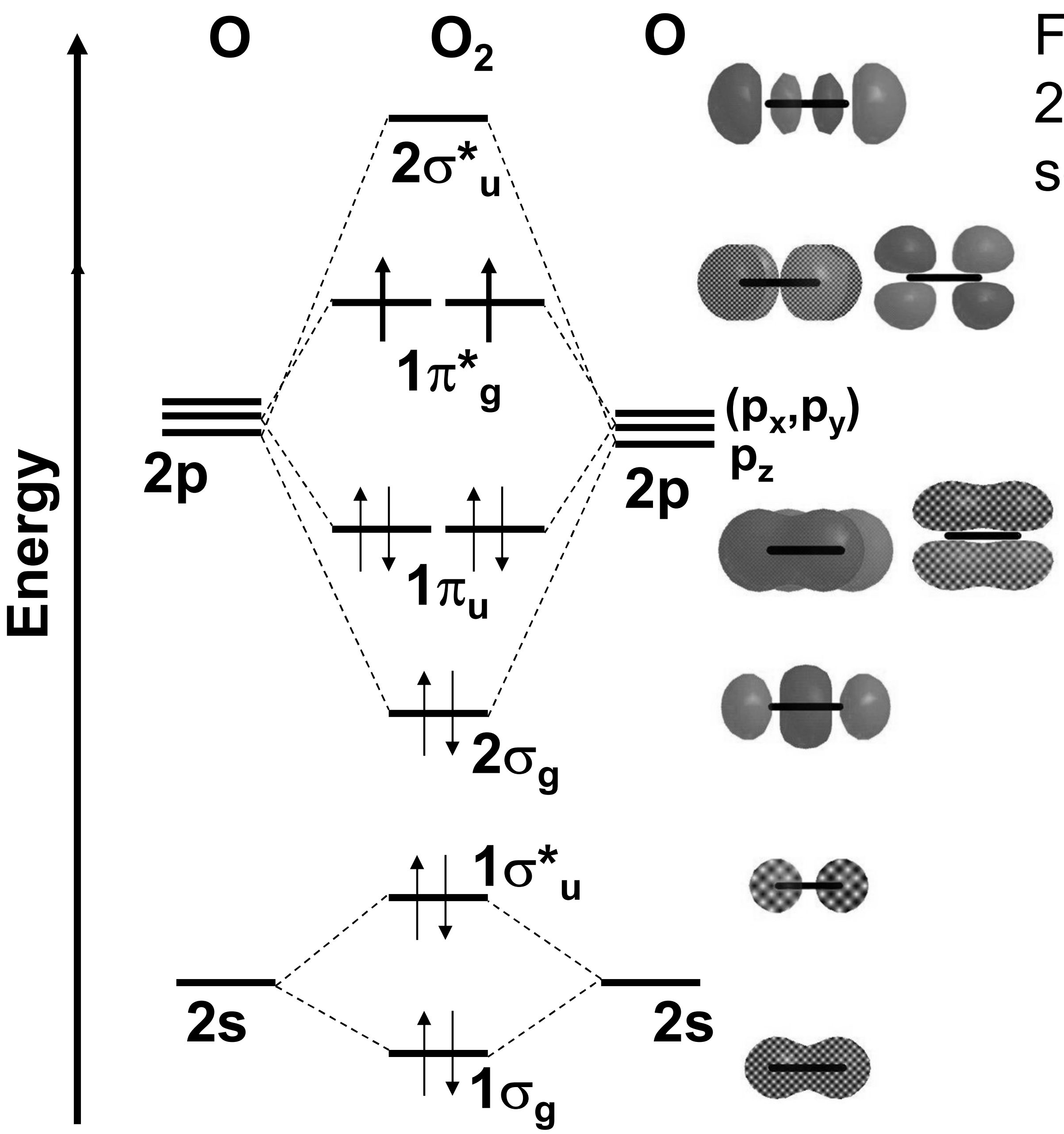
No need to consider the bonding between 2s and 2p AOs of different atoms

Bond order of F_2:
$b = (8-6)/2 = 1$

F_2: $KK(\sigma_{2s})^2 (\sigma^*_{2s})^2 (\sigma_{2p})^2 (\pi_{2p})^4 (\pi^*_{2p})^4$

or $KK(1\sigma_g)^2 (1\sigma^*_u)^2 (2\sigma_g)^2 (1\pi_u)^4 (1\pi^*_g)^4$

The latter notation is more reasonable and widely used!



For oxygen and fluorine, 2s and 2p AO's are well separated.

O_2: $KK(\sigma_{2s})^2 (\sigma^*_{2s})^2$

$(\sigma_{2p})^2 (\pi_{2p})^4 (\pi^*_{2p})^2$

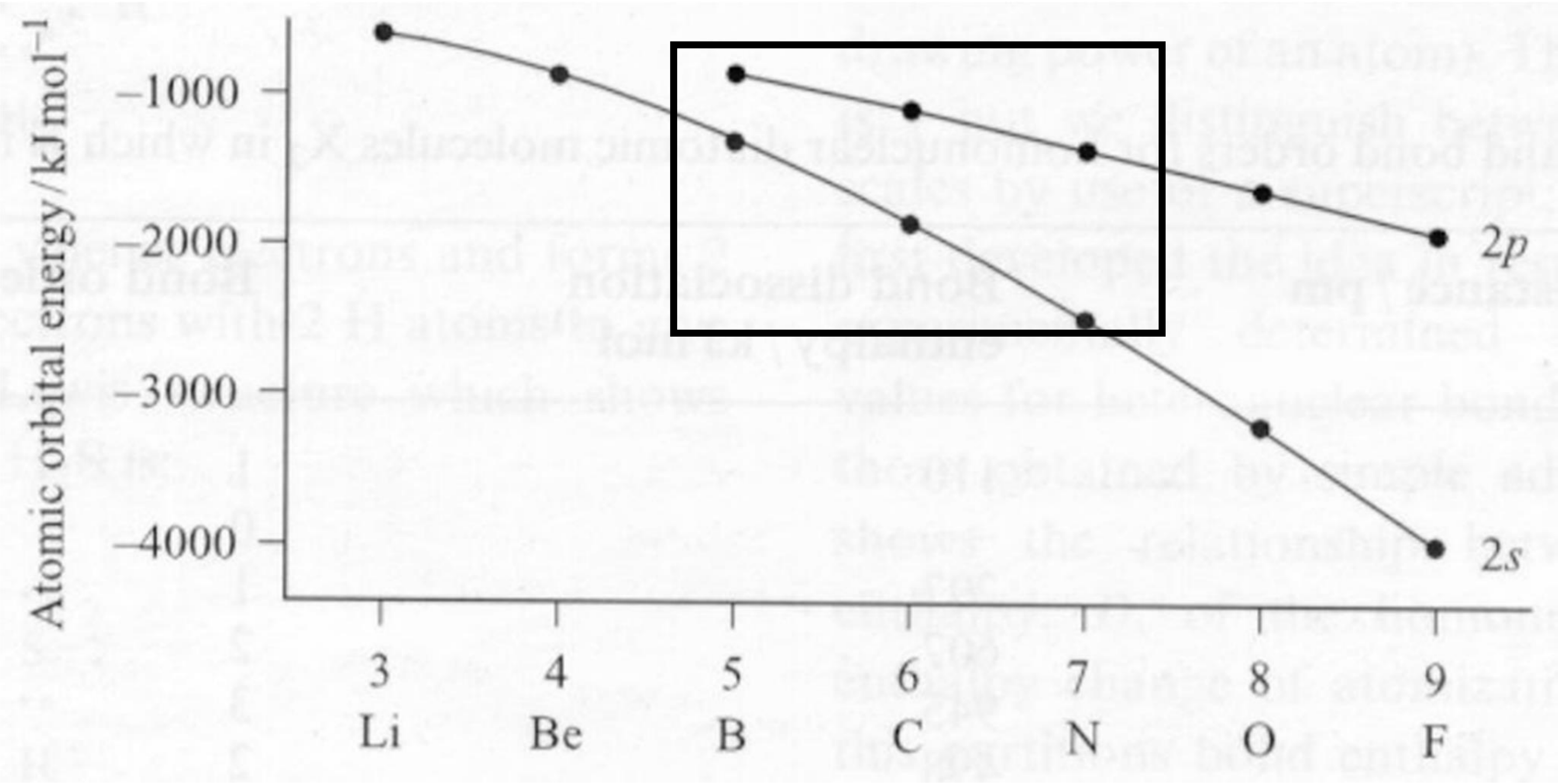
or $KK(1\sigma_g)^2 (1\sigma^*_u)^2$

$(2\sigma_g)^2 (1\pi_u)^4 (1\pi^*_g)^2$

Bond order of O_2:

b = (8-4)/2 =2

Mixing of s- and p-orbitals



For B, C and N, their 2s- and 2p-orbitals are close in energy and have non-negligible interatomic s,p-orbital interaction.

Accordingly, mixing of 2s- and 2p-orbitals should be considere

When does sp mixing occur?

B, C, and N all have ≤ 1/2 filled 2p orbitals

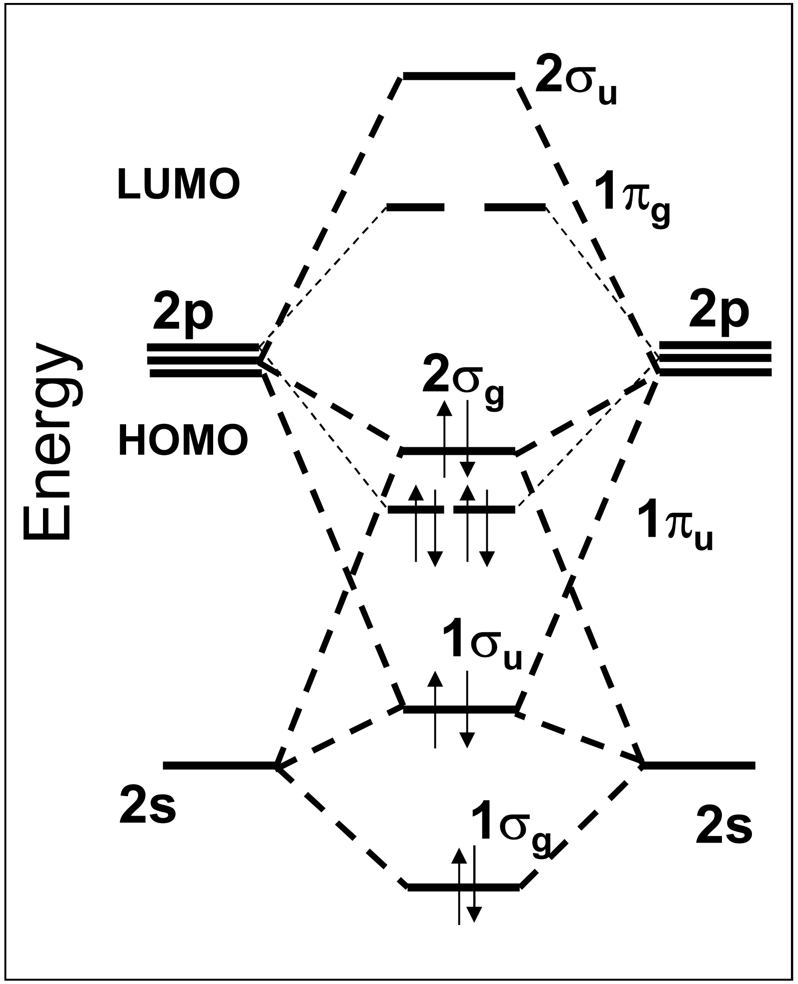
O, F and Ne all have ≥ 1/2 filled 2p orbitals.

- If two electrons are forced to be in the same atomic orbital, their energies go up.
- Accordingly, having > 1/2 filled *2p* orbitals raises the energies of 2p orbitals due to enhanced e -e repulsion.

- *sp*-mixing occurs when the n*s* and n*p* atomic orbitals are close in energy (≤ 1/2 filled 2*p* orbitals), which allows the ns (np) AO of one atom to interact strongly with both the ns and np AOs of another atom.

How does sp_z-mixing occur?

N_2: KK$(1\sigma_g)^2 (1\sigma_u)^2 (1\pi_u)^4 (2\sigma_g)^2$



sp-mixing = sp-hybridization !

$$\sigma_g(2s) = c_1(\phi_{2sA} + \phi_{2sB})$$

$$\sigma_g(2p) = c_2(\phi_{2pA} - \phi_{2pB})$$

sp-mixing

$$\sigma_g(2sp) = c_a\sigma_g(2s) \pm c_b\sigma_g(2p) =$$

$$c_1'(\phi_{2sA} + \phi_{2sB}) \pm c_2'(\phi_{2p_zA} - \phi_{2p_zB}) =$$

$$(c_1'\phi_{2sA} \pm c_2'\phi_{2p_zA}) + (c_1'\phi_{2sB} \mp c_2'\phi_{2p_zB})$$

sp_z-hybridization of AO's

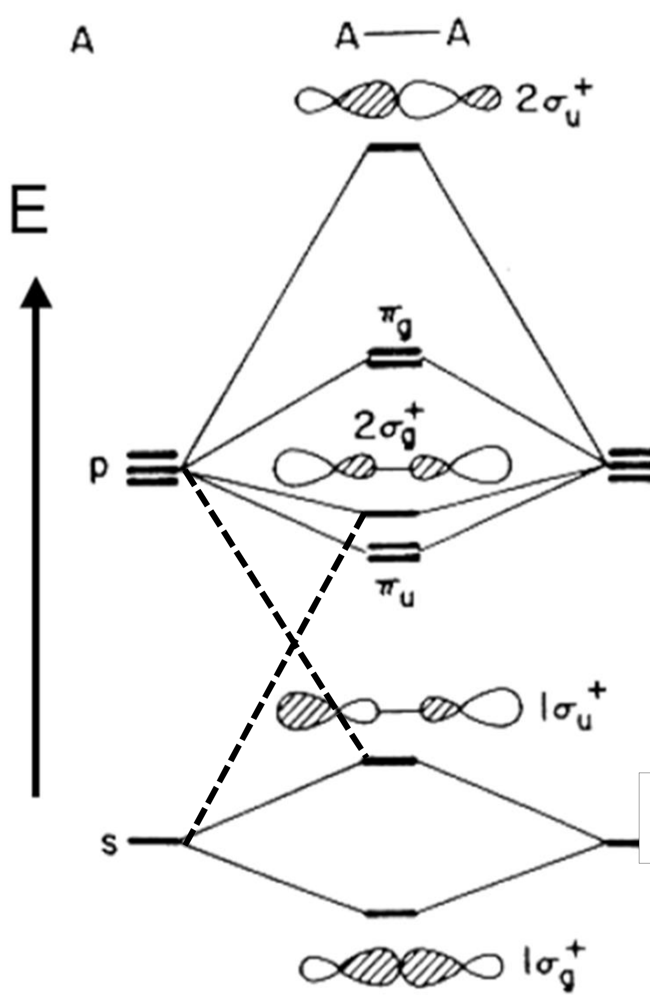
Similarly

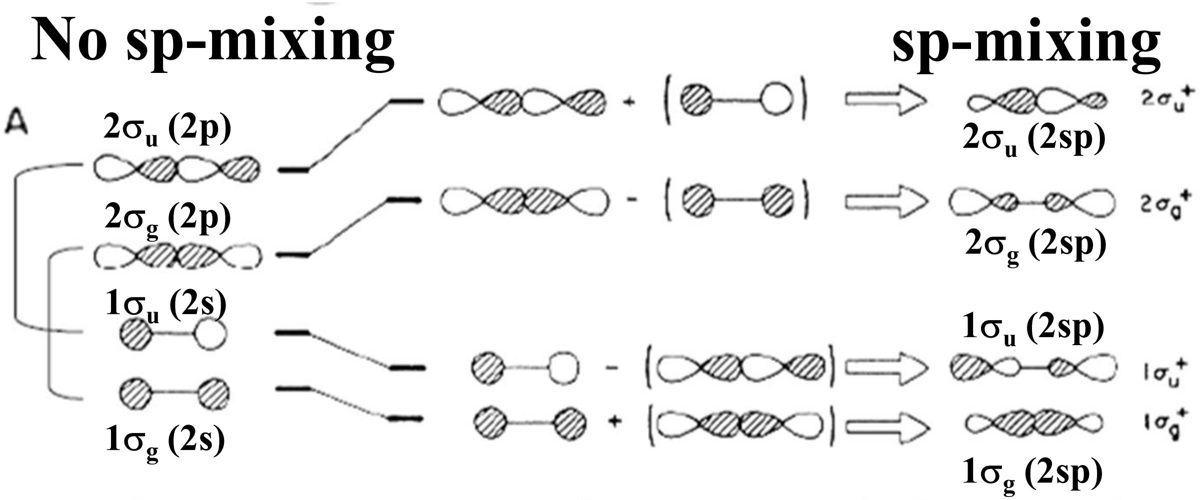
$$\sigma_u(2sp) = c_a\sigma_u(2s) \pm c_b\sigma_u(2p) =$$

$$(c_1'\phi_{2sA} \pm c_2'\phi_{2p_zA}) - (c_1'\phi_{2sB} \mp c_2'\phi_{2p_zB})$$

Both $2\sigma_g$ and $2\sigma_u$ are destabilized! → ***$E(2\sigma_g) > E(1\pi_u)$***

MO diagram with sp-mixing (for B_2, C_2, N_2 etc)





A more accurate depiction of the bonding takes into account mixing ☐ of MO's with the same symmetry (σ_g^+ & σ_u^+). The consequences of this 2nd order effect are:

The lower energy orbital is stabilized while *the higher energy orbital is destabilized.*

The s and p character of the σ MO's becomes mixed.

The mixing becomes more pronounced as the energy separation decreases.

Effects of sp_z-mixing

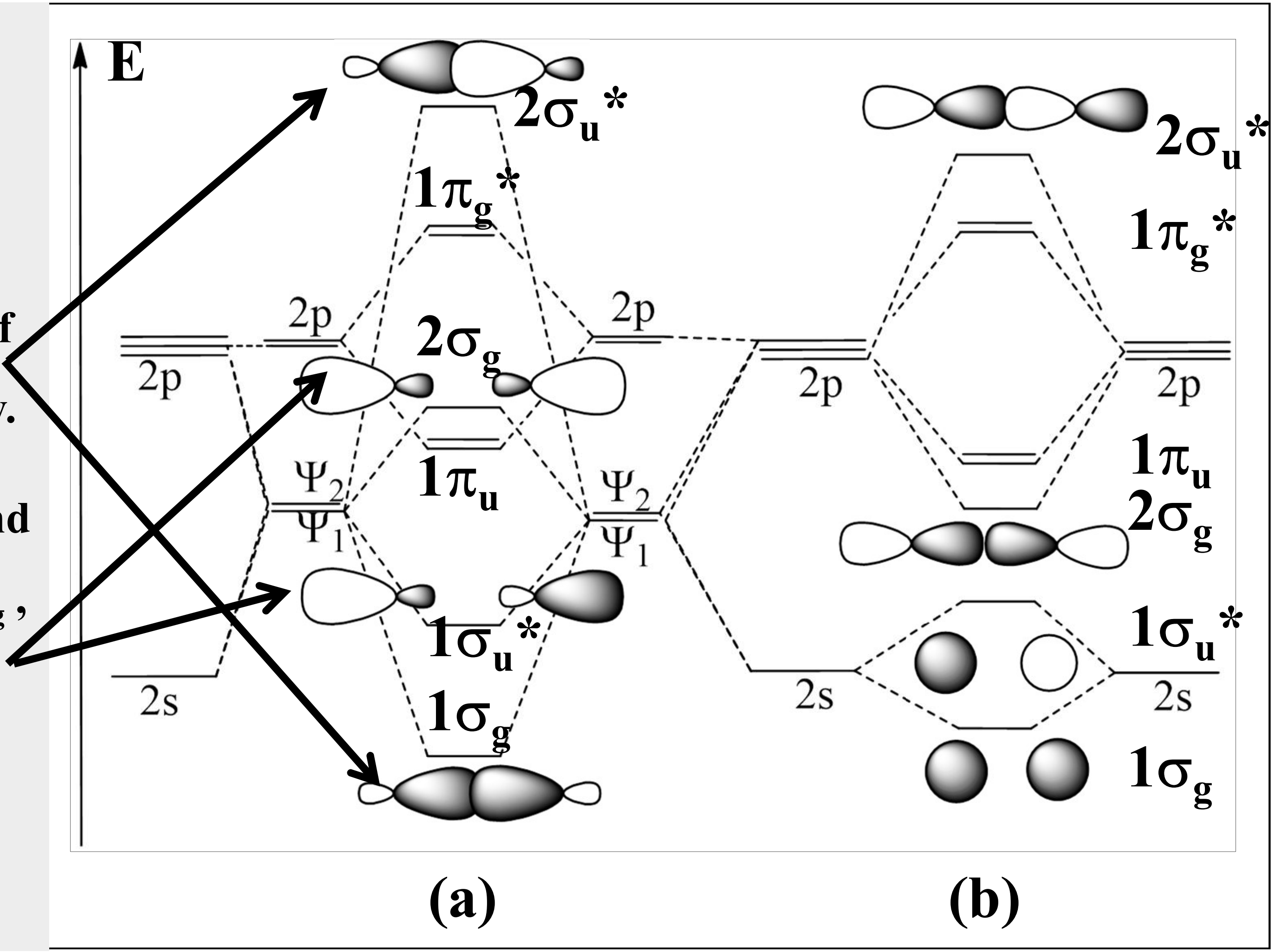
1) Mixing of σ-MO's with the same symmetry.

2) Enhance the bonding and antibonding nature of $1\sigma_g$ and $2\sigma_u$*, respectively.

3) Weaken the bonding and antibonding nature of $2\sigma_g$, $1\sigma_u$*, respectively.

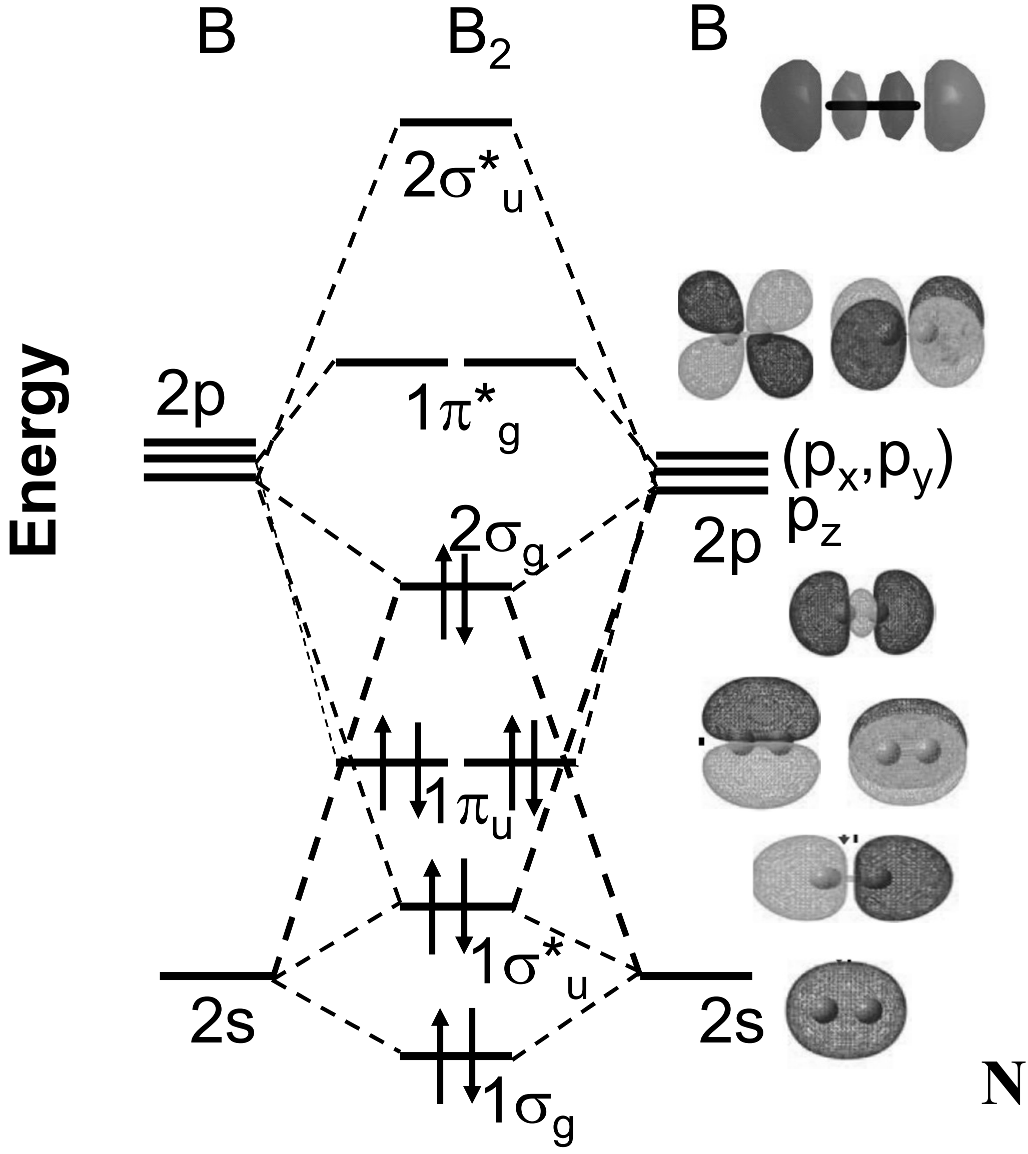
4) Stabilize $1\sigma_g$, $1\sigma_u$*.

5) Destabilize $2\sigma_g$, $2\sigma_u$*.



Energy diagram for X_2: (a) with and (b) without $2s$-$2p_z$ mixing. The 1s atomic orbitals are omitted.

Molecular Orbital Theory



At the start of the second row Li-N, we need to consider mixing of 2s and 2p.

B_2: $KK(1\sigma_g)^2\,(1\sigma_u)^2\,(1\pi_u)^2$

b =1

C_2: $KK(1\sigma_g)^2\,(1\sigma_u)^2\,(1\pi_u)^4$

b =2

N_2: $KK(1\sigma_g)^2\,(1\sigma_u)^2\,(1\pi_u)^4(2\sigma_g)^2$

b =3

H_2	2	$(\sigma_{g1S})^2$
He_2^+	3	$(\sigma_{g1s})^2\,(\sigma_{u1s})^1$
Li_2	6	$KK(1\sigma_g)^2$
B_2	10	$KK(1\sigma_g)^2\,(1\sigma_u)^2\,(1\pi_u)^2$
C_2	12	$KK(1\sigma_g)^2\,(1\sigma_u)^2\,(1\pi_u)^4$
N_2^+	13	$KK(1\sigma_g)^2\,(1\sigma_u)^2\,(1\pi_u)^4\,(2\sigma_g)^1$
N_2	14	$KK(1\sigma_g)^2\,(1\sigma_u)^2\,(1\pi_u)^4\,(2\sigma_g)^2$
O_2^+	15	$KK(\sigma_{g2s})^2\,(\sigma_{u2s})^2\,(\sigma_{g2p})^2\,(\pi_{u2p})^4\,(\pi_{g2p})^1$
O_2	16	$KK(\sigma_{g2s})^2\,(\sigma_{u2s})^2\,(\sigma_{g2p})^2\,(\pi_{u2p})^4\,(\pi_{g2p})^2$
F_2	18	$KK(\sigma_{g2s})^2\,(\sigma_{u2s})^2\,(\sigma_{g2p})^2\,(\pi_{u2p})^4\,(\pi_{g2p})^4$

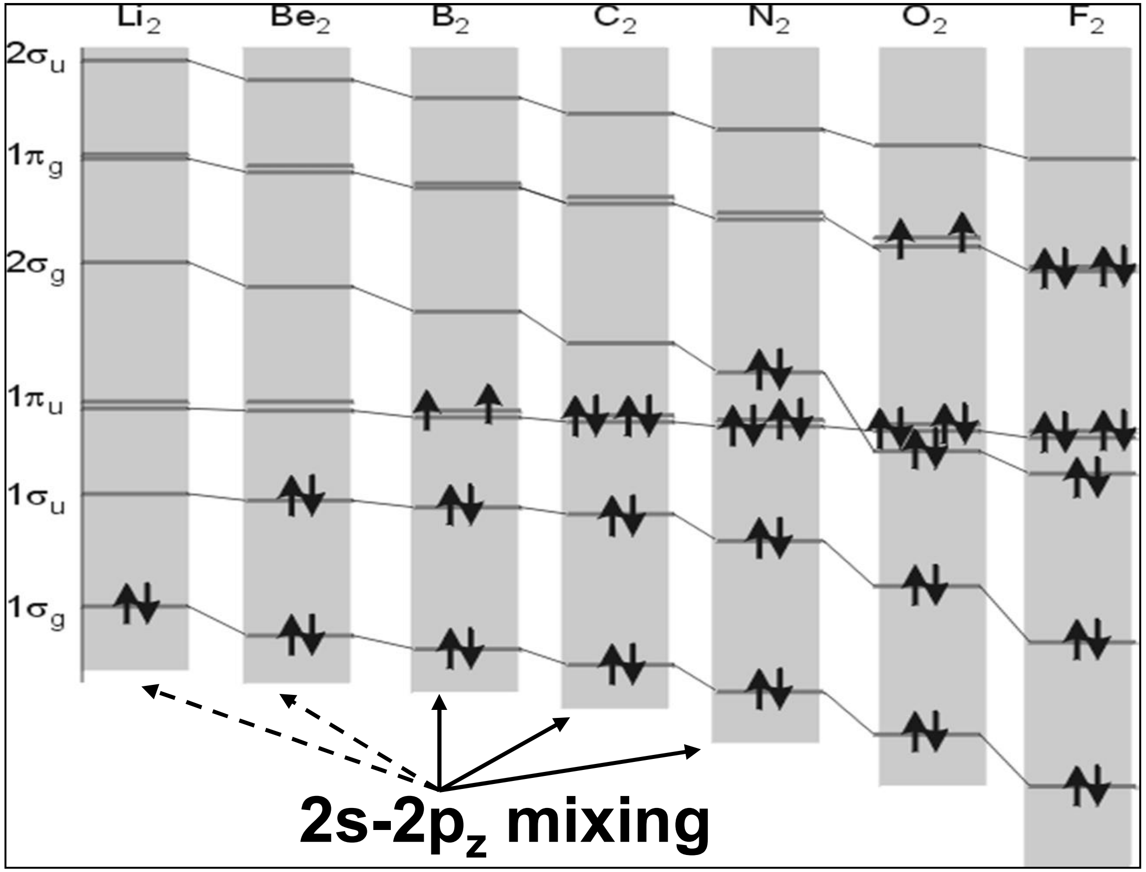
Diatomics

Bond orders :

$$b = \frac{1}{2}(n - n^*)$$

Paramagnetic:
unpaired electron(s)
EPR-active

Diamagnetic:
all electrons are paired!



Molecule	Li_2	Be_2	B_2	C_2	N_2	O_2	F_2	Ne_2
Bond Order	1	0	1	2	3	2	1	0
Bond Length (Å)	2.67	n/a	1.59	1.24	1.01	1.21	1.42	n/a
Bond Energy (kJ/mol)	105	n/a	289	609	941	494	155	n/a
Diamagnetic(d)/Paramagnetic(p)	d	n/a	p	d	d	p	d	

Magnetic moment of paramagnetic molecules

The magnetic moment ($\boldsymbol{\mu_m}$) of a paramagnetic molecule depends mainly on electron spin and can be given by

$$\mu_m = 2\sqrt{S(S+1)}\beta_e = \sqrt{n(n+2)}\beta_e$$

S: total electron spin quantum number $\because S = n/2$

n: the number of spin-unpaired electrons

$\boldsymbol{\beta_e}$: Bohr magneton.

e.g., for O_2 and B_2, ***n***=2, ***S*** =1 → $\mu_m = 2\sqrt{2}\beta_e$

Summary

§ 2 Molecular orbital theory and diatomic molecules

1. Molecular orbital (MO) theory

- **Independent Electron Model**: Every electron in a molecule is supposed to move in an average potential field exerted by the nuclei and other electrons. **(Independent Electron Approximation)!**

Schrödinger equation:	$\hat{H}\Psi(1,2,...n) = E\Psi(1,2,...,n)$
Wavefunction:	$\Psi(1,2,...n) = \phi_1(1)\phi_2(2)...\phi_n(n)$
Hamilton operator:	$\hat{H} = \sum_i \hat{h}_i\ ;\ \ (\hat{h}_i = -\frac{1}{2}\nabla_i^2 + V_i)$
One-electron wavefunctions and eigenequation:	$\hat{h}_i\phi_i = \varepsilon_i\phi_i;\qquad E = \sum_i \varepsilon_i$

Mean field exerted on e_i

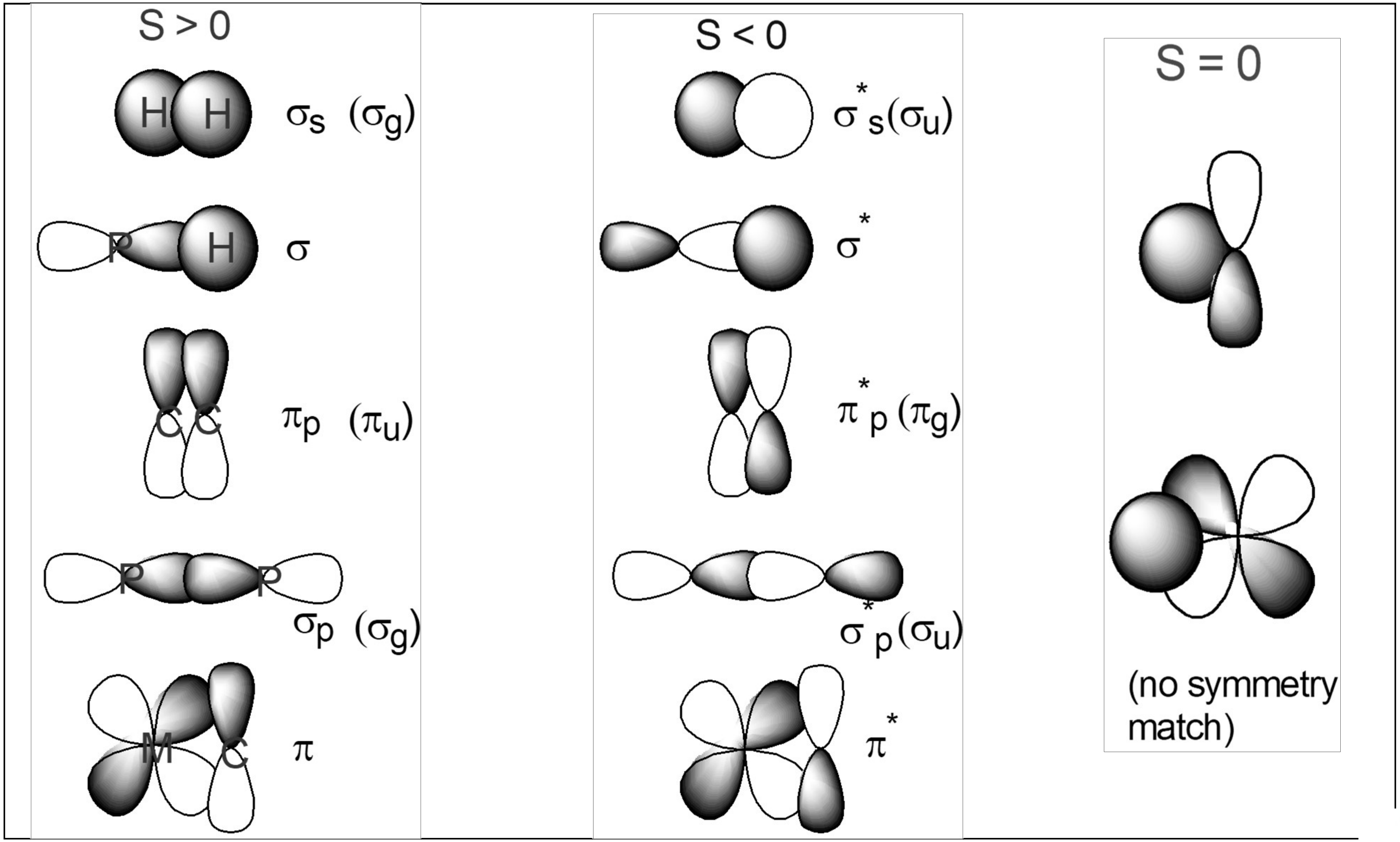
- **LCAO-MO:** $MO:\ \ \phi_i = \sum_j c_j\varphi_j \qquad (\varphi_j : j\text{th AO})$

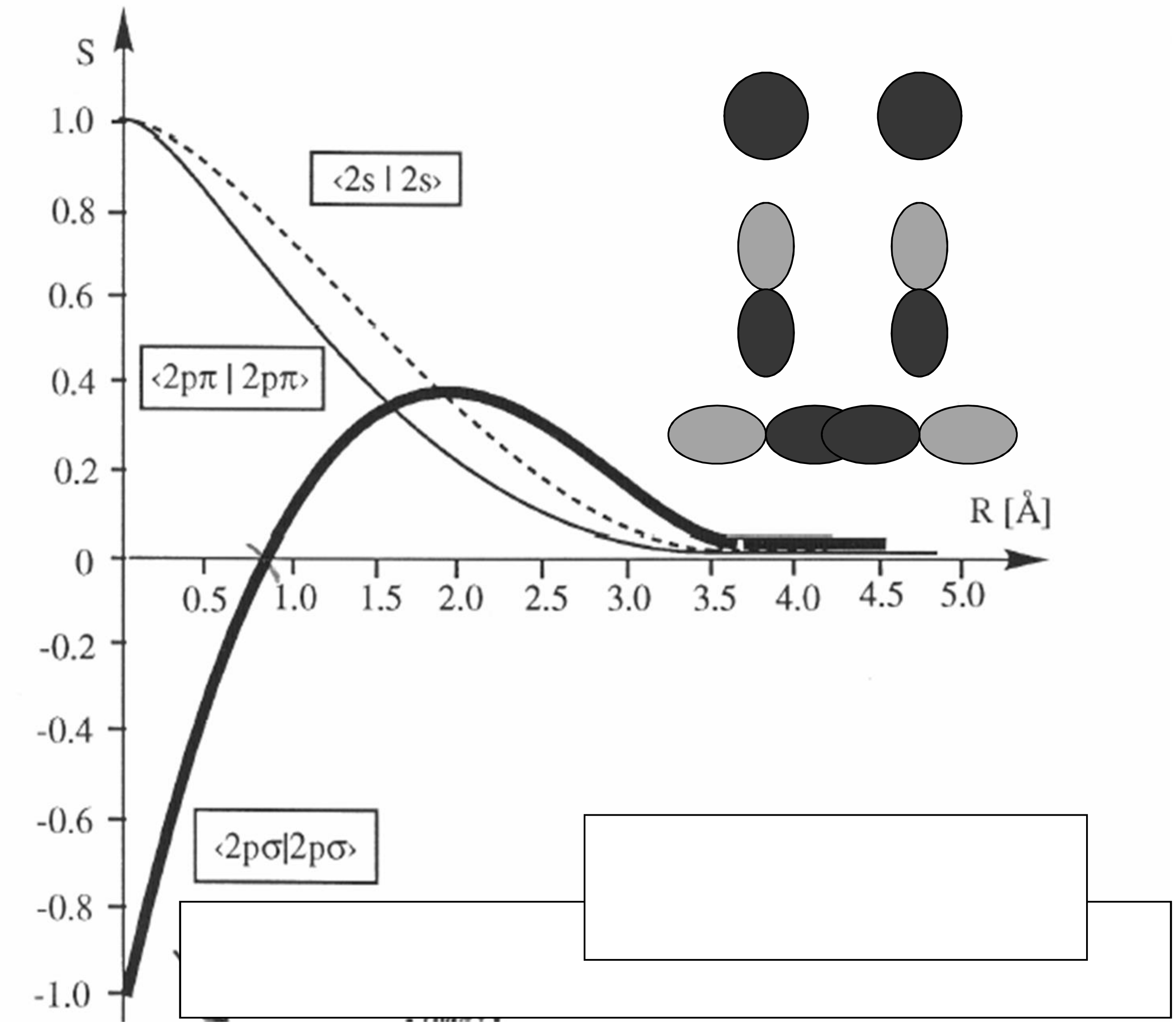
Atomic orbital overlap and bonding

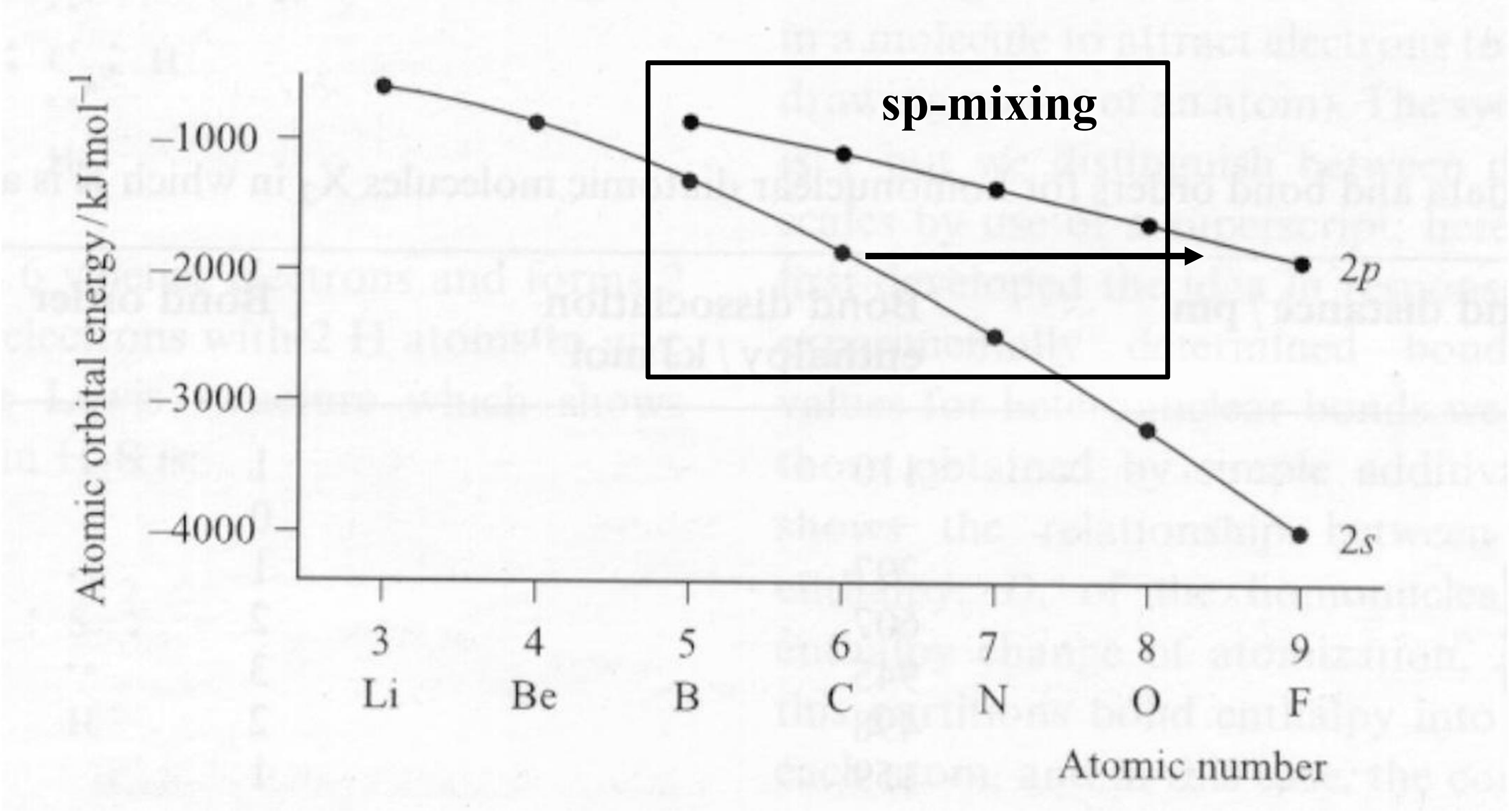
- Interaction between atomic orbitals leads to formation of covalent bonds only if the orbitals:
    - 1) are of the same symmetry;
    - 2) can overlap well;
    - 3) are of similar energy (less than 10-15 eV difference).
- Any two orbitals ψ_A and ψ_B can be characterized by the overlap integral S.
- Depending on the symmetry and the distance between two orbitals, the overlap integral S may be positive (bonding), negative (antibonding) or zero (non-bonding interaction).

The overlap integral S may be positive (bonding), negative (antibonding) or zero (non-bonding interaction).

$$S = \int \psi_A \psi_B dV$$

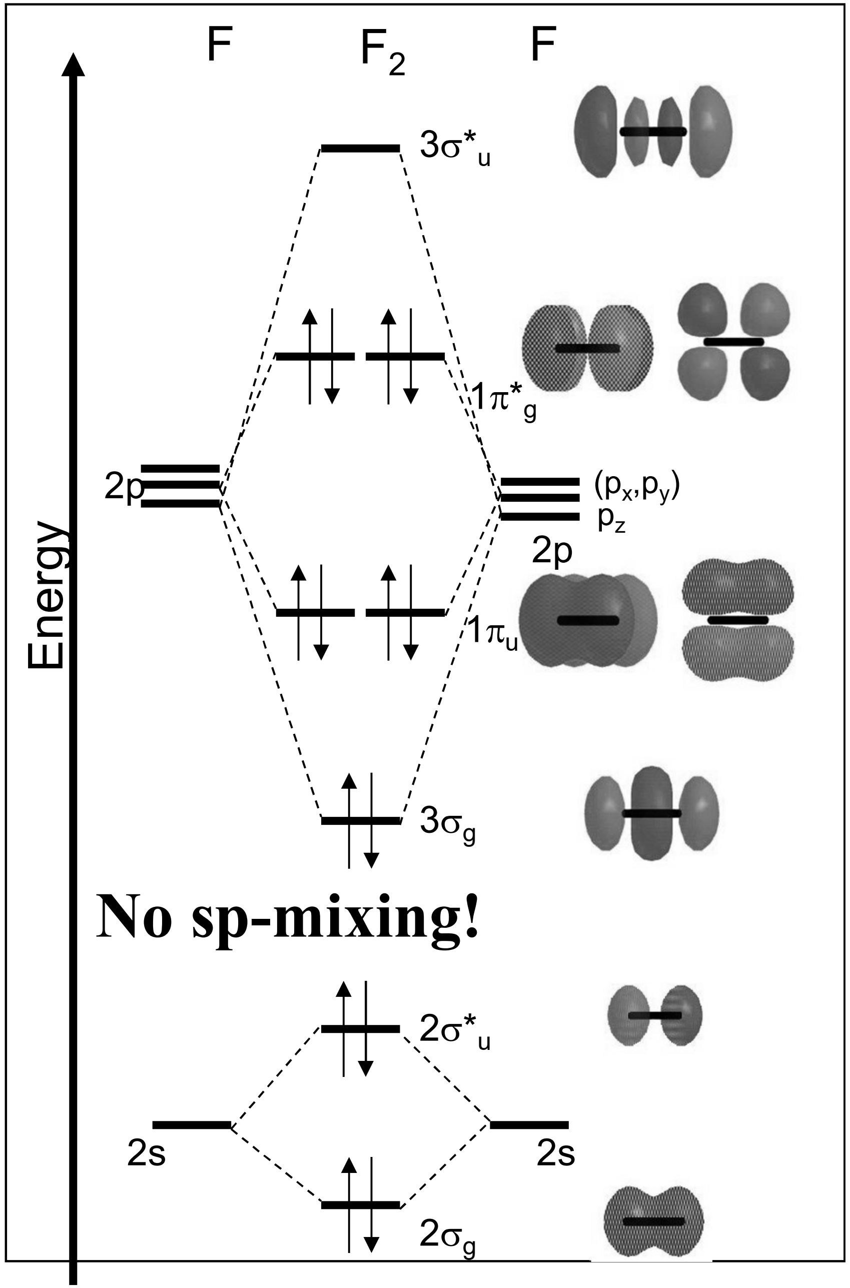



S
1.0
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
R [Å]
‹2s | 2s›
‹2pπ | 2pπ›
‹2pσ|2pσ›

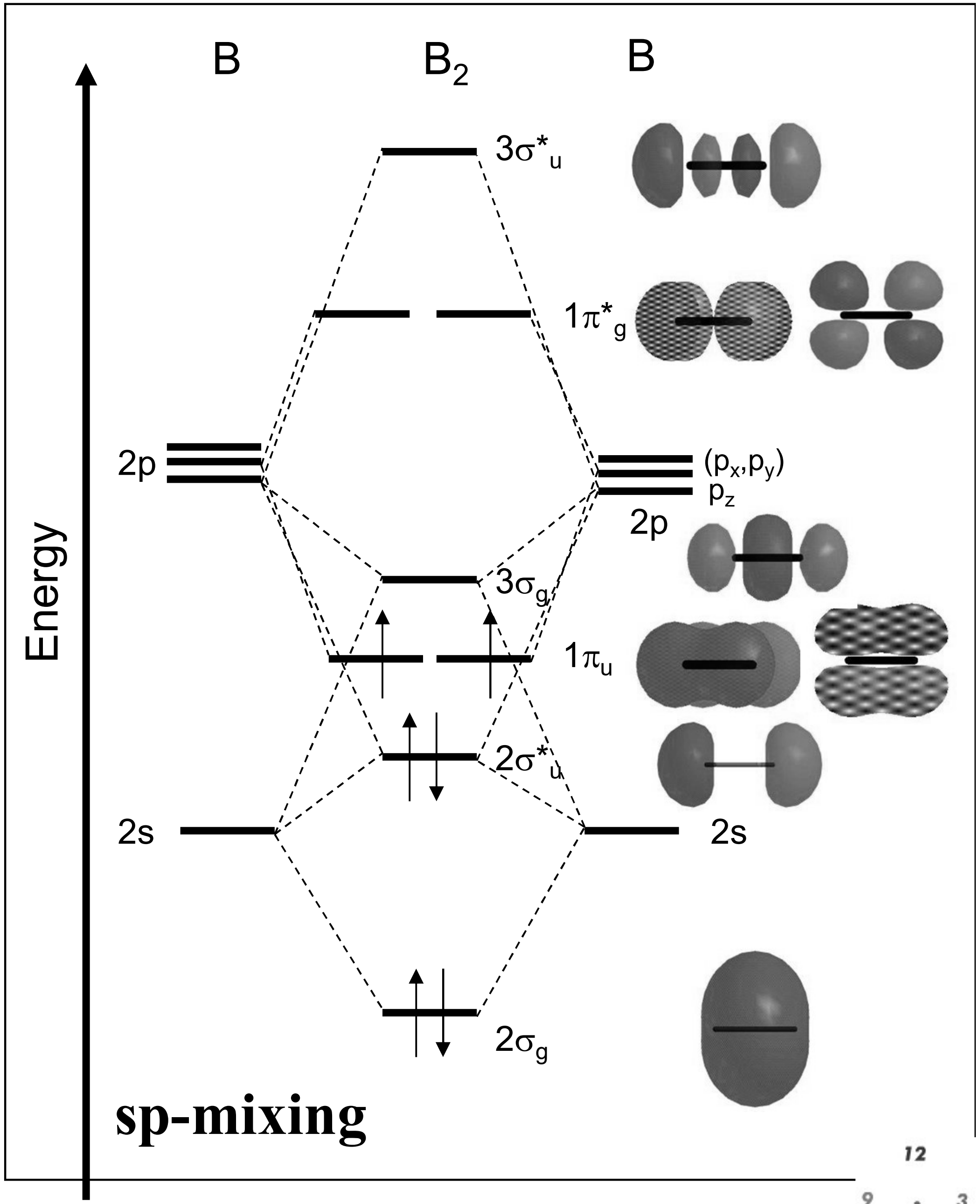

Atomic orbital energy / kJ mol^{-1}
–1000
–2000
–3000
–4000
2p
2s
3
Li
4
Be
5
B
6
C
7
N
8
O
9
F
Atomic number

sp-mixing

MO diagram for F_2

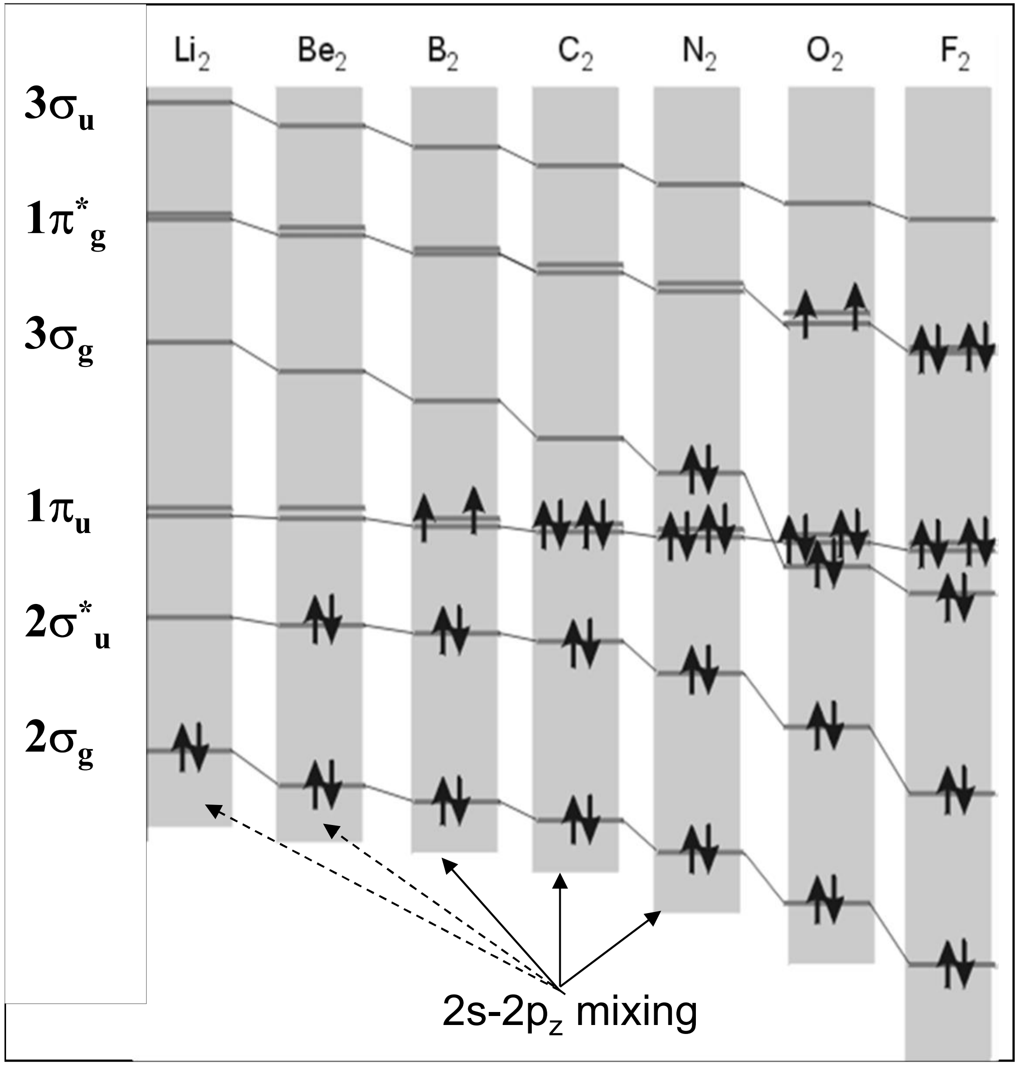


MO diagram for B_2

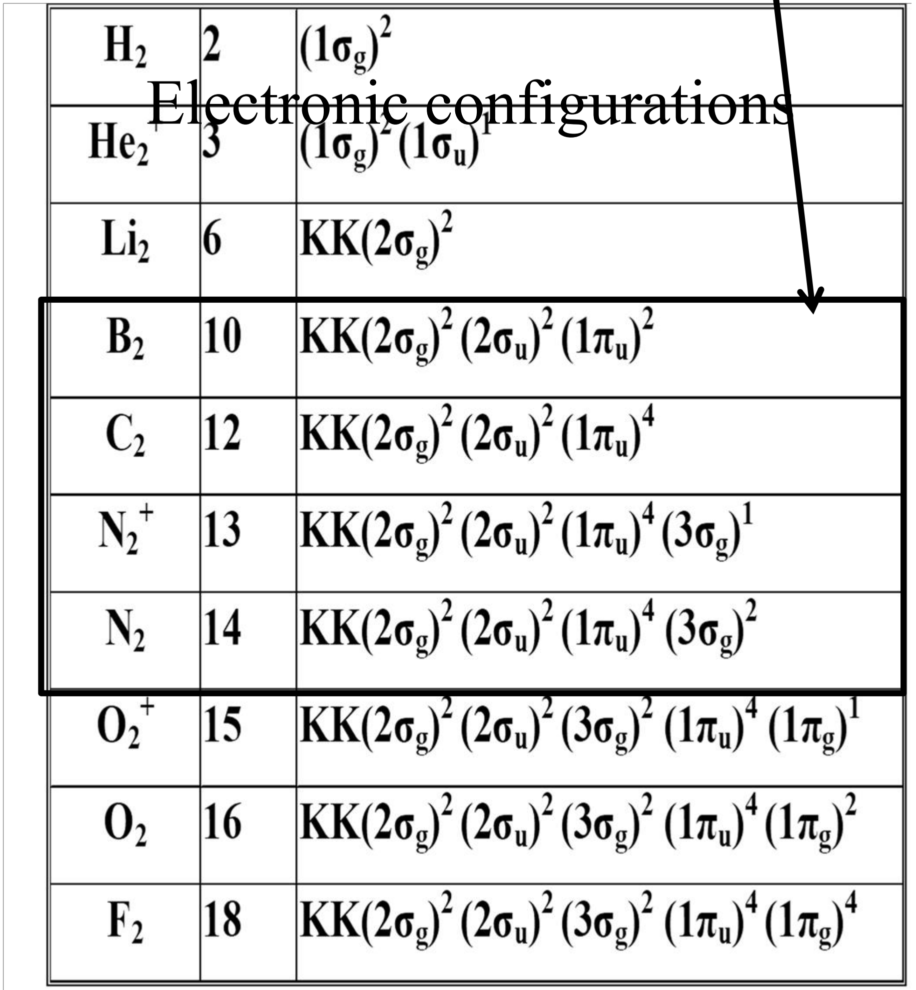


Homogeneous diatomic molecules

sp-mixing



Electronic configurations



H_2	2	$(1\sigma_g)^2$
He_2^+	3	$(1\sigma_g)^2(1\sigma_u)^1$
Li_2	6	$KK(2\sigma_g)^2$
B_2	10	$KK(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^2$
C_2	12	$KK(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4$
N_2^+	13	$KK(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^1$
N_2	14	$KK(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2$
O_2^+	15	$KK(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^1$
O_2	16	$KK(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^2$
F_2	18	$KK(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^4$

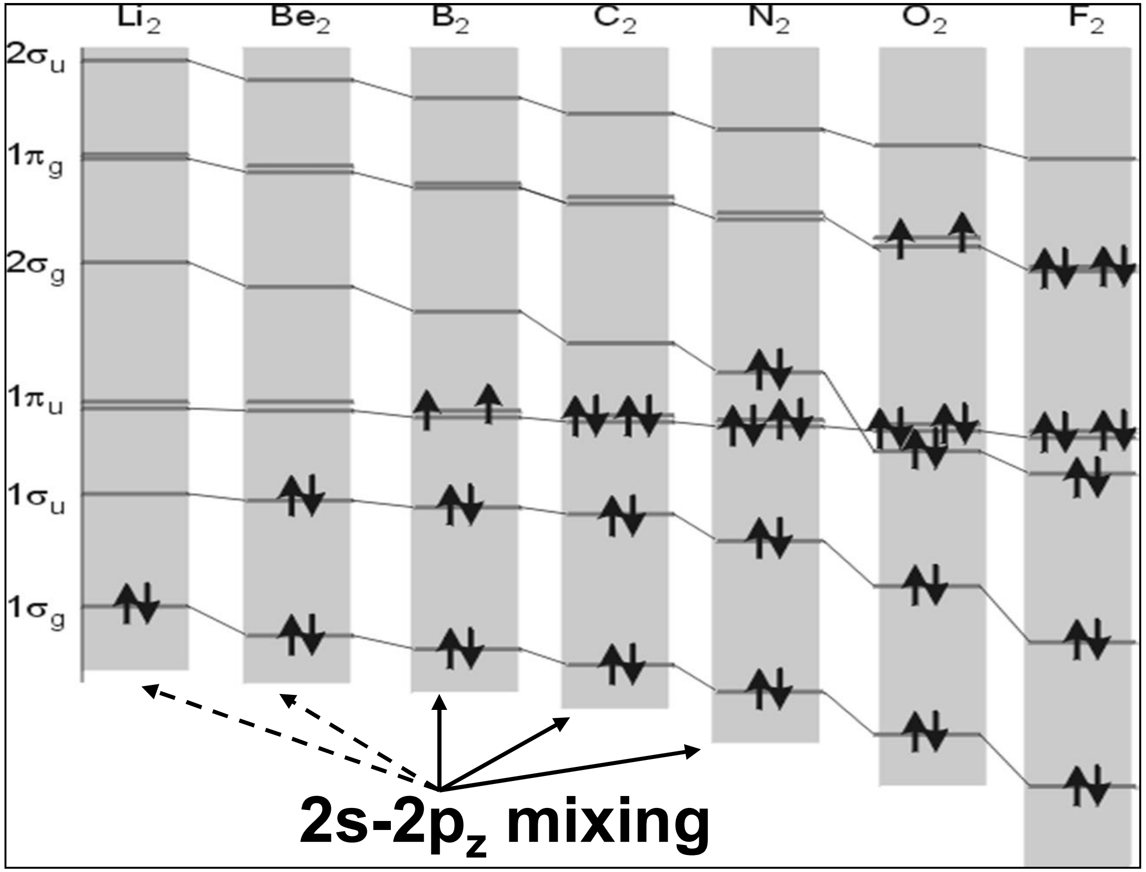
Diatomics

Bond orders :

$$b = \frac{1}{2}(n - n^*)$$

Paramagnetic:
unpaired electron(s)
EPR-active!

Diamagnetic:
all electrons are paired!



Molecule	Li$_2$	Be$_2$	B$_2$	C$_2$	N$_2$	O$_2$	F$_2$	Ne$_2$
Bond Order	1	0	1	2	3	2	1	0
Bond Length (Å)	2.67	n/a	1.59	1.24	1.01	1.21	1.42	n/a
Bond Energy (kJ/mol)	105	n/a	289	609	941	494	155	n/a
Diamagnetic(d)/Paramagnetic(p)	d	n/a	p	d	d	p	d	

Magnetic moment of paramagnetic molecules

The magnetic moment (μ_m) of a paramagnetic molecule depends mainly on electron spin and can be given by

$$\mu_m = 2\sqrt{S(S+1)}\beta_e = \sqrt{n(n+2)}\beta_e$$

S: total electron spin quantum number

n: the number of spin-unpaired electrons

β_e: Bohr magneton.

$$\because S = n \times (1/2)$$

E.g., for O_2 and B_2, n=2, S =1 → $\mu_m = 2\sqrt{2}\beta_e$

3. The structure of homonuclear diatomic molecules

c. The molecular spectroscopy – spectral term

1-electron wavefunction:

$$MO: \ \phi_i = \sum_j c_j^i \varphi_j \quad (\varphi_j : j\text{th AO})$$

Total wavefunction of a ***n***-electron system:

$$\Psi(1,2,\ldots n) = \phi_1(1)\phi_2(2)\ldots\phi_n(n)$$

- For a many-electron diatomic molecule, the operator for the axial component of the *total electronic orbital angular momentum* commutes with the Hamiltonian operator, possible eigenvalues of which can be $M_L\hbar$ ($M_L = 0, \pm 1, \pm 2$, …), with

$$M_L = \sum_{i=1}^{n} m(i)$$

- Now define $\Lambda = |M_L| = \left|\sum_i m(i)\right|$

- For $\Lambda \neq 0$, there are two possible values of M_L, $+/-\Lambda$.

- Now define *the total electronic spin **S*** as $\vec{\mathbf{S}} = \sum_{i=1}^{n} \vec{m}_s(i)$

whose magnitude has the possible values $S(S+1)^{1/2}\,\hbar$ (*S* –- total spin quantum number).

- The component of ***S*** along an axis has the possible values $M_s\hbar$, where $M_s = S, S-1, \ldots, -S+1, -S$.
- *Spin multiplicity = 2S +1.*
- A given set of *Λ* and ***S*** include 2(2S+1) (if $\Lambda \neq 0$) or (2S+1) (if $\Lambda = 0$) degenerate eigenstates!

Axial component of total orbital Angular momentum	$M_L = \sum_i m(i)$	$\Lambda = \lvert M_L \rvert$	$(M_L = +\Lambda, -\Lambda)$
Total spin	$\vec{S} = \sum_i \vec{m}_s(i)$	$S = \left\lvert \sum_i \vec{m}_s(i) \right\rvert$	$(M_S = +S, +S-1, \ldots -S+1, -S)$
	Vector	**Quantum number**	

Molecular Orbital Theory Diatomics Term symbols

Molecule	Configuration	Term symbol
H_2^+	$(1\sigma_g)^1$	$^2\Sigma_g^+$

$$\Lambda = \left|\sum_i m(i)\right|$$

$$S = \left|\sum_i m_s(i)\right|$$

Parity:

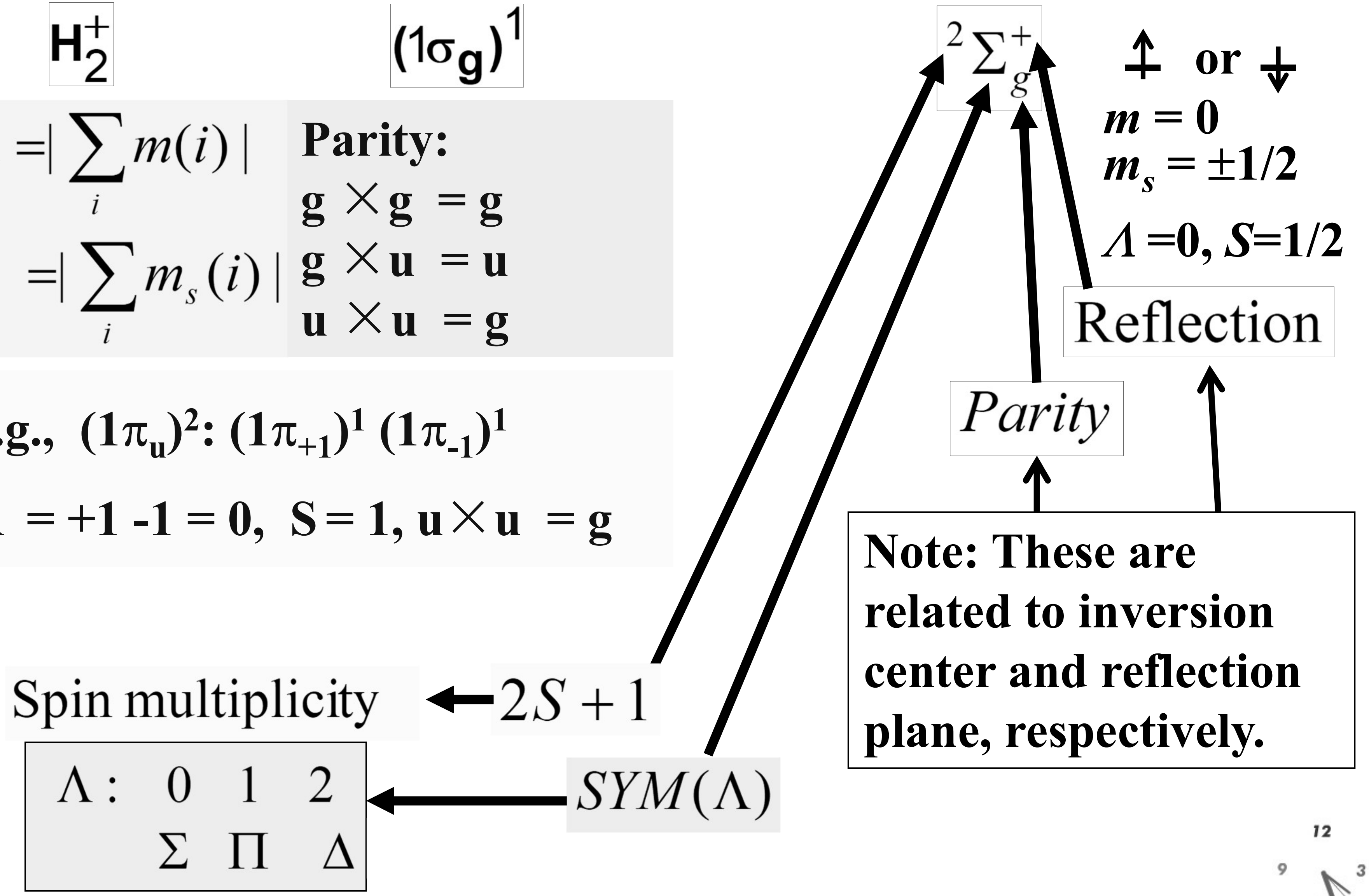
g × g = g

g × u = u

u × u = g

e.g., $(1\pi_u)^2$: $(1\pi_{+1})^1$ $(1\pi_{-1})^1$

Λ = +1 -1 = 0, S = 1, u × u = g



↑ or ↓

$m = 0$

$m_s = \pm 1/2$

$\Lambda = 0$, $S = 1/2$

Reflection

Parity

Note: These are related to inversion center and reflection plane, respectively.

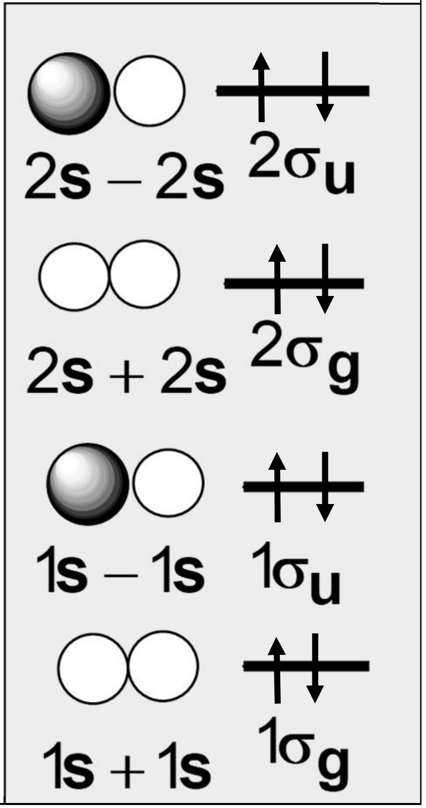
Spin multiplicity ← $2S+1$

$SYM(\Lambda)$

Λ:	0	1	2
	Σ	Π	Δ

Molecular Orbital Theory Diatomics Term symbols

Molecule	Configuration	Term symbol
H_2	$(1\sigma_g)^2$	$^1\Sigma_g^+$
H_2^-	$(1\sigma_g)^2(1\sigma_u)^1$	$^2\Sigma_u^+$
He_2	$(1\sigma_g)^2(1\sigma_u)^2$	$^1\Sigma_g^+$
Li_2	$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2$	$^1\Sigma_g^+$
Be_2	$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2$	$^1\Sigma_g^+$



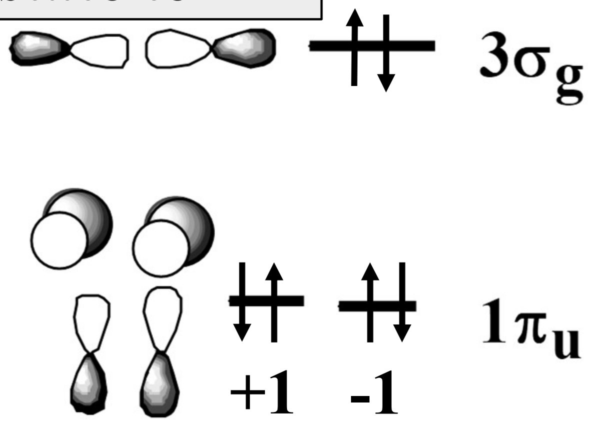
- For homonuclear diatomics, a closed-shell electronic configuration has ***S* = *0*** and ***Λ* =*0***, giving rise to the spectral term $\boxed{^1\Sigma_g^+}$.
- **The spectral terms of molecules with open shell(s) are determined by the electrons in the open shell(s)!**

Molecular Orbital Theory Diatomics Term symbols

Molecule	Configuration	Term symbol	
B_2	$\ldots\ (1\pi_u)^2$	$^3\Sigma_g^-$	$^1\Delta_g\ \ ^1\Sigma_g^+$
C_2	$\ldots\ (1\pi_u)^4$	$^1\Sigma_g^+$	
N_2^+	$\ldots\ (1\pi_u)^4(3\sigma_g)^1$	$^2\Sigma_g^+$	
N_2	$\ldots(1\pi_u)^4(3\sigma_g)^2$	$^1\Sigma_g^+$	

Excited states

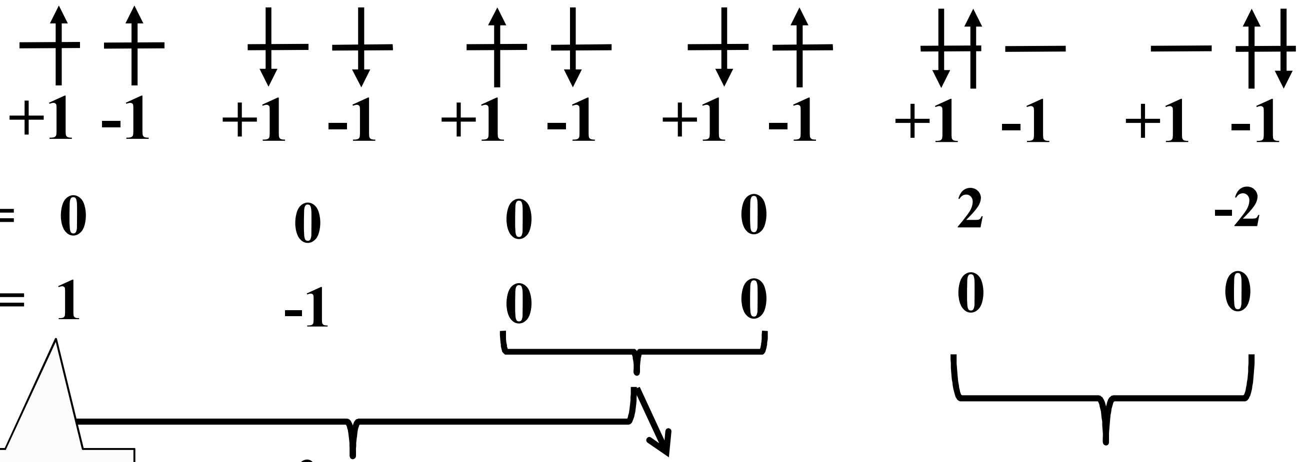
Ground-state term



- Note: $(1\pi_u)^2$ has a total of 6 (i.e., C_4^2) microstates!
- For equivalent electrons in an open shell (e.g., $\boxed{(1\pi_u)^2}$), Pauli exclusion principle & Hund's rule should be fulfilled to determine its ground term. (here $M_{Smax}=1 \rightarrow S=1$ & $M_{Lmax} = 0$)

For equivalent electrons in an open shell:

π_u^2 has in total $C_4^2 = 6$ microstates. (e.g., for B_2 and O_2)



m	+1 -1	+1 -1	+1 -1	+1 -1	+1 -1	+1 -1
$M_L =$	0	0	0	0	2	-2
$M_S =$	1	-1	0	0	0	0

M_{smax} → S =1 &
M_{Lmax} = 0 → L =0

$^3\Sigma_g^-$

$M_L = 0$
$M_S = 1, -1, 0$
$\Lambda = 0, S = 1$

$^1\Sigma_g^+$

$M_L = 0$
$M_S = 0$
$\Lambda = 0, S = 0$

$^1\Delta_g$

$M_L = 2, -2$
$M_S = 0$
$\Lambda = 2, S = 0$

The ground-state term includes the microstates that fulfills the minimum energy rule, Pauli exclusion & Hund’s rule.

(After-class reading: the following five pages!)

- **Electrons in a molecule are Fermions and indistinguishable!**

→ **The total electron wavefunctions of a many-e molecule should be antisymmetric upon permutation of any two electrons.**

- **e.g., for H_2 $^1\Sigma_g^+$**

Orbital part

$\uparrow\downarrow$ $1\sigma_g$

spin part

$$\Psi(1,2) = 1\sigma_g(1)1\sigma_g(2)\cdot[\underbrace{\alpha(1)\beta(2)-\alpha(2)\beta(1)}_{\text{Linear combination of two indistinguishable spin states}}]$$

Permutation:

$$\hat{P}_{12}\Psi(1,2) = \hat{P}_{12}\{1\sigma_g(1)1\sigma_g(2)[\alpha(1)\beta(2)-\alpha(2)\beta(1)]\}$$

$$= 1\sigma_g(2)1\sigma_g(1)[\alpha(2)\beta(1)-\alpha(1)\beta(2)] = -\Psi(1,2)$$

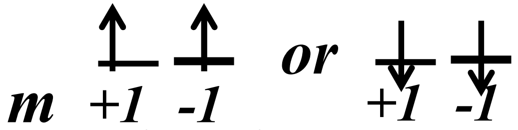
→ **Its orbital (spatial) part is symmetric upon permutation!**

→ **Thus its spin part has to be antisymmetric upon permutation to make the total wavefunction antisymmetric upon permutation**

- For equivalent electrons in an open shell (e.g., $\boxed{(\mathbf{1\pi_u})^2}$), Pauli exclusion principle & Hund's rule should be fulfilled to determine its ground-state term, for which $\mathbf{M_L = 0}$ ($\mathbf{\Lambda=0}$) and $\mathbf{M_S = \pm 1}$, 0($\mathbf{S=1}$).

i) For the cases of Λ**=0**, $\mathbf{M_L = 0}$ and **S= 1**, $\mathbf{M_S = \pm 1}$, the spin factor (inner-shell neglected) is symmetric upon permutation, i.e.,

$$\boxed{Ms = 1: \ \alpha(1)\alpha(2) \ \ or \ \ Ms = -1: \ \ \beta(1)\beta(2)}$$



The spatial part has to be asymmetric upon permutation, i.e.,

$$\boxed{\boldsymbol{\pi}_{+1}(1)\boldsymbol{\pi}_{-1}(2) - \boldsymbol{\pi}_{+1}(2)\boldsymbol{\pi}_{-1}(1)}$$

which is also asymmetric upon σ_v//z reflection; the superscript "–" refers to the eigenvalue of σ_v (e.g, σ(xz)) reflection. i.e.,

$$\begin{aligned}&\sigma_v[\boldsymbol{\pi}_{+1}(1)\boldsymbol{\pi}_{-1}(2) - \boldsymbol{\pi}_{+1}(2)\boldsymbol{\pi}_{-1}(1)] = [\boldsymbol{\pi}_{-1}(1)\boldsymbol{\pi}_{+1}(2) - \boldsymbol{\pi}_{-1}(2)\boldsymbol{\pi}_{+1}(1)]\\&= -[\boldsymbol{\pi}_{+1}(1)\boldsymbol{\pi}_{-1}(2) - \boldsymbol{\pi}_{+1}(2)\boldsymbol{\pi}_{-1}(1)]\end{aligned}$$

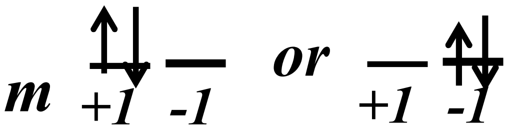
$$\because \sigma_{xz}\pi_m = \sigma_{xz}[AF(\xi,\eta)e^{im\phi}] = AF(\xi,\eta)e^{im(-\phi)} = \pi_{-m} \ \ (\mathrm{m} = + / - 1)$$

→ The total wavefunctions for $M_L = 0$ & $M_S = \pm 1$ (of $^3\Sigma_g^-$) are

$$\boxed{[\boldsymbol{\pi}_{+1}(1)\boldsymbol{\pi}_{-1}(2) - \boldsymbol{\pi}_{+1}(2)\boldsymbol{\pi}_{-1}(1)]\alpha(1)\alpha(2)} \ \ \mathbf{\&} \ \ \boxed{[\boldsymbol{\pi}_{+1}(1)\boldsymbol{\pi}_{-1}(2) - \boldsymbol{\pi}_{+1}(2)\boldsymbol{\pi}_{-1}(1)]\beta(1)\beta(2)}$$

ii) Similarly, for the case of $\mathbf{M_L = \pm 2}$ (Λ= **2**) and $\mathbf{Ms = 0}$ (**S = 0**),

The spatial part is definitely symmetric upon permutation, i. e.,



$$M_L = 2 : \boldsymbol{\pi}_{+1}(1)\boldsymbol{\pi}_{+1}(2) \quad or \quad M_L = -2 : \boldsymbol{\pi}_{-1}(1)\boldsymbol{\pi}_{-1}(2)$$

The spin factor has to be antisymmetric upon permutation, i. e.,

$$\alpha(1)\beta(2) - \alpha(2)\beta(1)$$

Neither spatial functions is the eigenfunction of σ_v(xz) reflection!

$$\sigma_v[\boldsymbol{\pi}_{+1}(1)\boldsymbol{\pi}_{+1}(2)] = \boldsymbol{\pi}_{-1}(1)\boldsymbol{\pi}_{-1}(2) \qquad \sigma_v[\boldsymbol{\pi}_{-1}(1)\boldsymbol{\pi}_{-1}(2)] = \boldsymbol{\pi}_{+1}(1)\boldsymbol{\pi}_{+1}(2)$$

$$\because \sigma_{xz}\pi_m = \sigma_{xz}[AF(\xi,\eta)e^{im\phi}] = AF(\xi,\eta)e^{im(-\phi)} = \pi_{-m} \quad (\mathrm{m} = + / - 1)$$

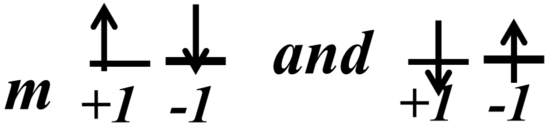
→ The total wavefunctions for $\mathbf{M_L = \pm 2}$ & $\mathbf{M_S = 0}$ (of ${}^1\Delta_g$) are

$$[\boldsymbol{\pi}_{+1}(1)\boldsymbol{\pi}_{+1}(2)][\alpha(1)\beta(2) - \alpha(2)\beta(1)] \qquad [\boldsymbol{\pi}_{-1}(1)\boldsymbol{\pi}_{-1}(2)][\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

Similarly, the spatial factor of the total wavefunction for the ground-state term ${}^2\Pi$ arising from $(\pi)^1$ or $(\pi)^3$ is not eigenfunction of σ_v reflection!

iii) For the two microstates with **M_L=0** and **Ms =0**,

The spin factor can be either antisymmetric or symmetric upon permutation, i.e.,



$\boxed{\alpha(1)\beta(2)-\alpha(2)\beta(1)}$ **or** $\boxed{\alpha(1)\beta(2)+\alpha(2)\beta(1)}$

a) If the spin factor is antisymmetric, the spatial part has to be symmetric upon permutation, i.e., $\boxed{\boldsymbol{\pi}_{+1}(1)\boldsymbol{\pi}_{-1}(2)+\boldsymbol{\pi}_{+1}(2)\boldsymbol{\pi}_{-1}(1)}$

$$\boxed{\sigma_v[\boldsymbol{\pi}_{+1}(1)\boldsymbol{\pi}_{-1}(2)+\boldsymbol{\pi}_{+1}(2)\boldsymbol{\pi}_{-1}(1)]=\boldsymbol{\pi}_{-1}(1)\boldsymbol{\pi}_{+1}(2)+\boldsymbol{\pi}_{-1}(2)\boldsymbol{\pi}_{+1}(1)}$$

which is also symmetric upon σ_v reflection; the superscript "+" refers to the eigenvalue of σ_v reflection. Thus the state described by the following wavefunction (**M_L=0**,**M_S=0**) belongs to **$^1\Sigma_g{}^+$,**

$$\boxed{[\boldsymbol{\pi}_{+1}(1)\boldsymbol{\pi}_{-1}(2)+\boldsymbol{\pi}_{+1}(2)\boldsymbol{\pi}_{-1}(1)]\cdot[\alpha(1)\beta(2)-\alpha(2)\beta(1)]}$$

---

b) If the spin factor is symmetric, the spatial factor has to be antisymmetric upon permutation, i.e., $\boxed{\boldsymbol{\pi}_{+1}(1)\boldsymbol{\pi}_{-1}(2)-\boldsymbol{\pi}_{+1}(2)\boldsymbol{\pi}_{-1}(1)}$

which is antisymmetric upon σ_v reflection. The derived state with the following wavefunction (**M_L=0**,**M_S=0**) belongs to **$^3\Sigma_g{}^-$.**

$$\boxed{[\boldsymbol{\pi}_{+1}(1)\boldsymbol{\pi}_{-1}(2)-\boldsymbol{\pi}_{+1}(2)\boldsymbol{\pi}_{-1}(1)]\cdot[\alpha(1)\beta(2)+\alpha(2)\beta(1)]}$$

Accordingly, without considering orbital-spin interaction, the electronic configuration π_u^2 contains a total of six quantum states differing in *(Λ, M_L; S, Ms)*, splitting into three energy levels, i.e., $^3\Sigma_g^-$, $^1\Delta_g$ and $^1\Sigma_g^+$:

1) The ground term $^3\Sigma_g^-$ has three degenerate quantum states described by the following sets of quantum numbers,

   (0, 0;1, 1), (0, 0;1, 0), (0, 0;1, -1)

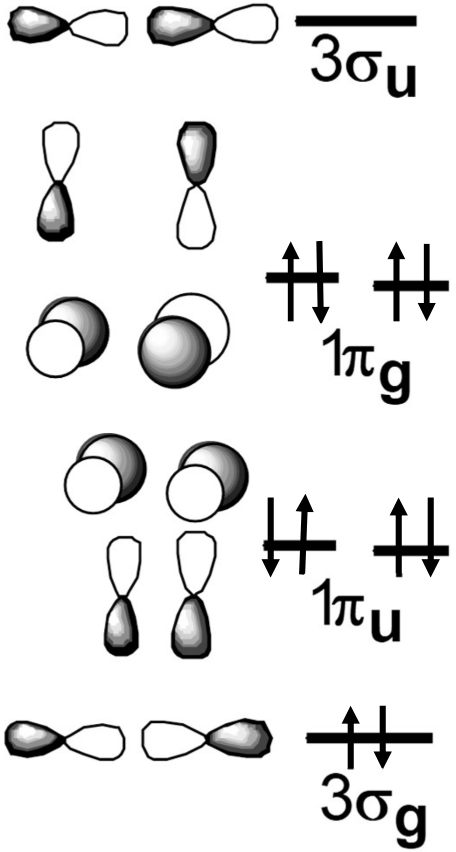
2) The first excited level, $^1\Delta_g$, has two degenerate quantum states, (1, 1;0, 0), (1, -1;0, 0).

3) The second excited level, $^1\Sigma_g^+$, has only one quantum state, (0,0;0,0)

Please derive the ground term of B_2^+

Molecular Orbital Theory Diatomics Term symbols

Molecule	Configuration	Term symbol
N_2^-	$(1\pi_u)^4(3\sigma_g)^2(1\pi_g)^1$	$^2\Pi_g$
O_2	$(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^2$	$^3\Sigma_g^-$ $^1\Delta_g$ $^1\Sigma_g^+$
F_2	$(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^4$	$^1\Sigma_g^+$
O_2^+	$(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^1$	$^2\Pi_g$



Spin multiplicity ← $2S_T + 1$

L_{T_z} :	0	1	2
	Σ	Π	Δ

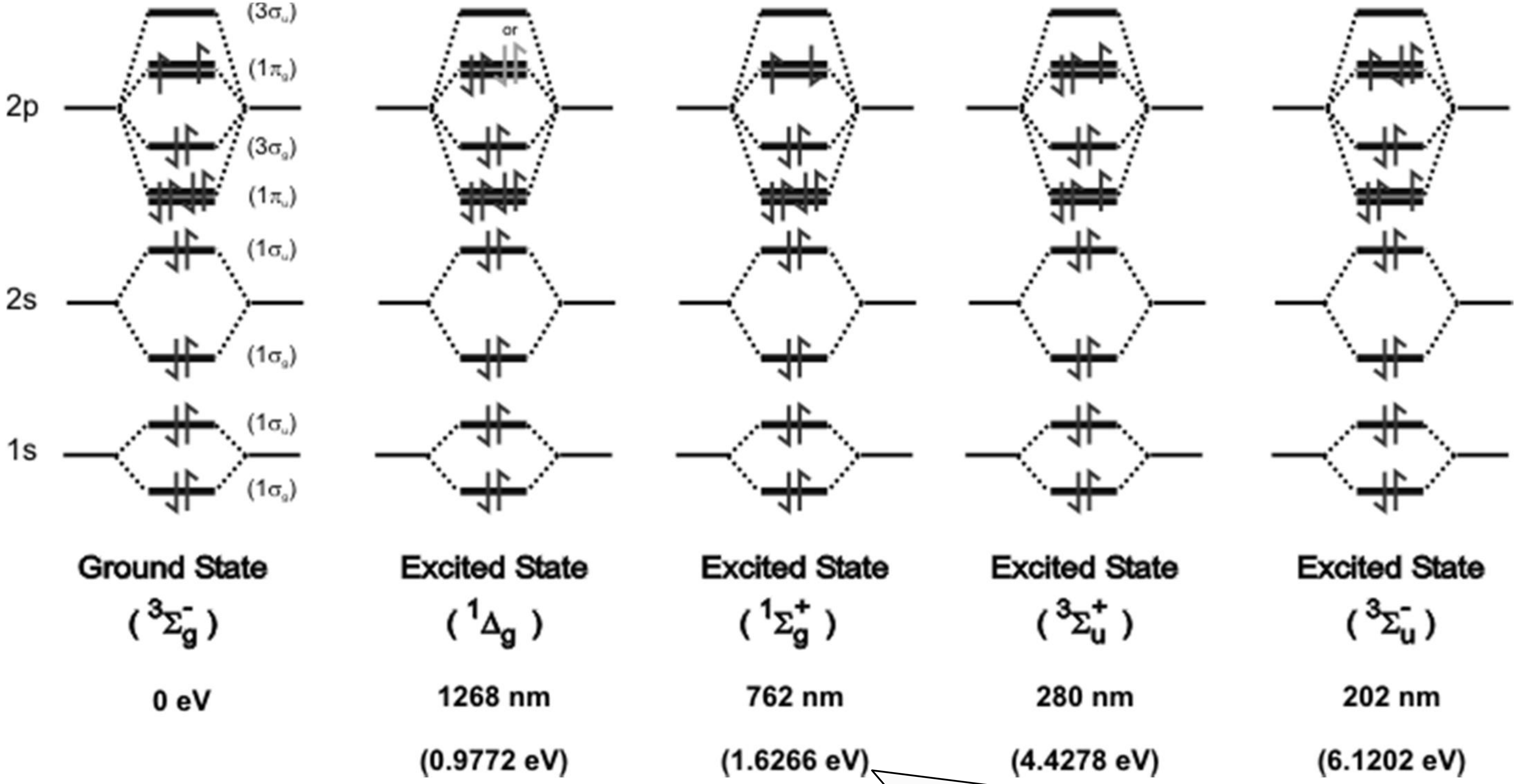
← $SYM(L_z)$

Reflection

Parity

- **Herein the "+"/"-" designations are only used for Σ terms!**

Electronic states of O_2



Caution: combination of two such microstates gives two eigenfunctions belong respectively to $^3\Sigma_g^-$ and $^1\Sigma_g^+$.

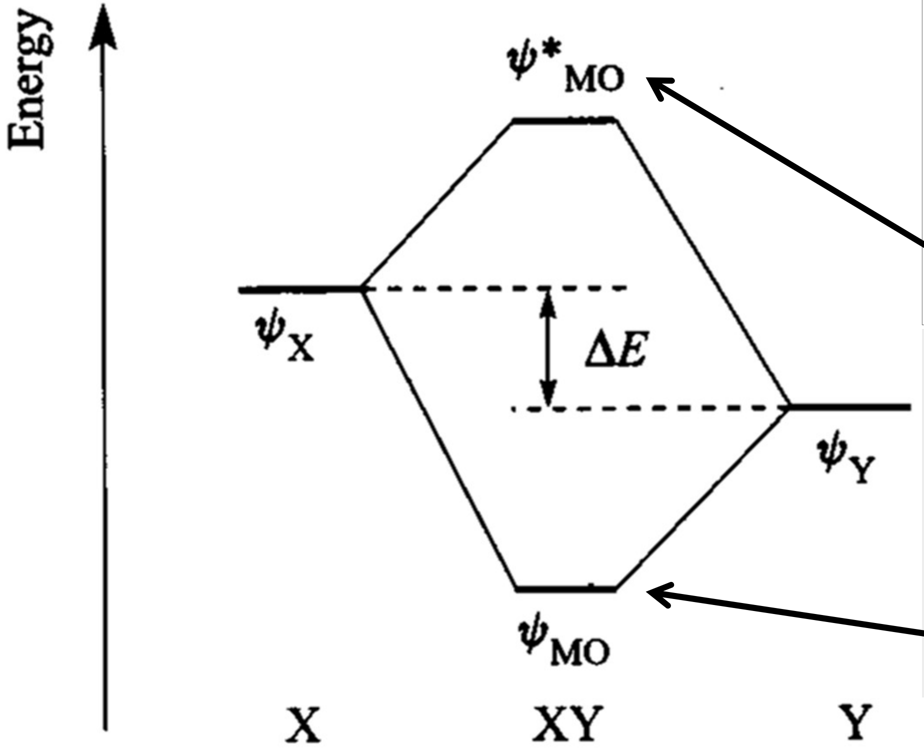
4. The structure of heteronuclear diatomic molecules

Differing from homonuclear diatomic molecules in the following aspects,

- **No inversion center → no parity of MOs**
- **Difference in electronegativity → polar MOs → polarity.**
- **MO′s no longer contain equal contributions from each AO.**

MO Theory for Heteronuclear Diatomics

- MO′s no longer contain equal contributions from each AO!
  - AO′s interact if symmetries are compatible.
  - AO′s interact if energies are close.
  - No interaction will occur if AO’s energies are too far apart. A nonbonding orbital will form.



☐ Ψ_X makes a greater contribution to the Ψ^*_{MO}.

$\Psi^*_{MO} = C_X\Psi_X - C_Y\Psi_Y$; $(|C_X| > |C_Y|)$

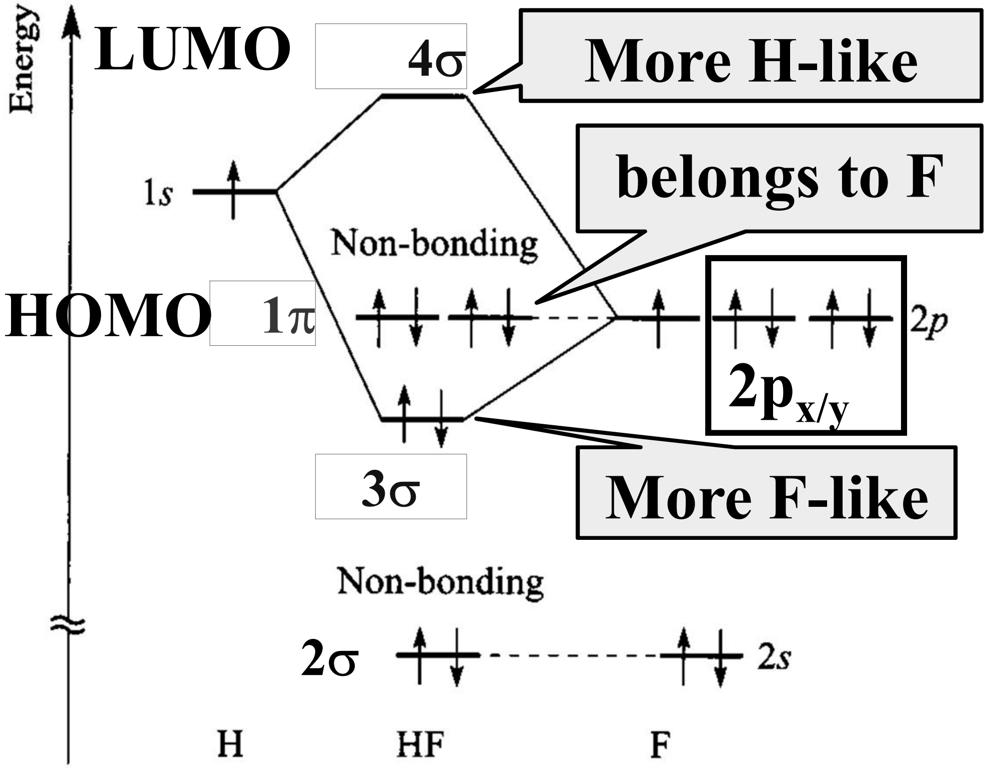
☐ Ψ_Y makes a greater contribution to the Ψ_{MO}.

$\Psi_{MO} = C_X\Psi_X + C_Y\Psi_Y$;$(|C_X| < |C_Y|)$

Example: HF (VE=8) $(1\sigma)^2 (2\sigma)^2 (3\sigma)^2 (1\pi)^4$

z ← H —— F

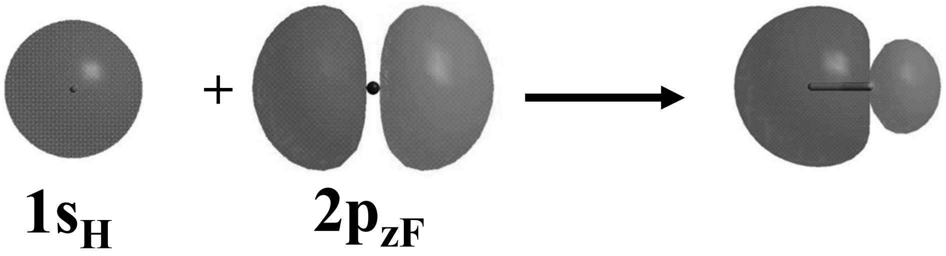
- The ***F 2s*** is much lower in energy than the ***H 1s*** so they do not mix.
  - → The ***F 2s*** orbital makes a non-bonding MO (2σ).
  - → So does the ***F 1s***. (1σ)

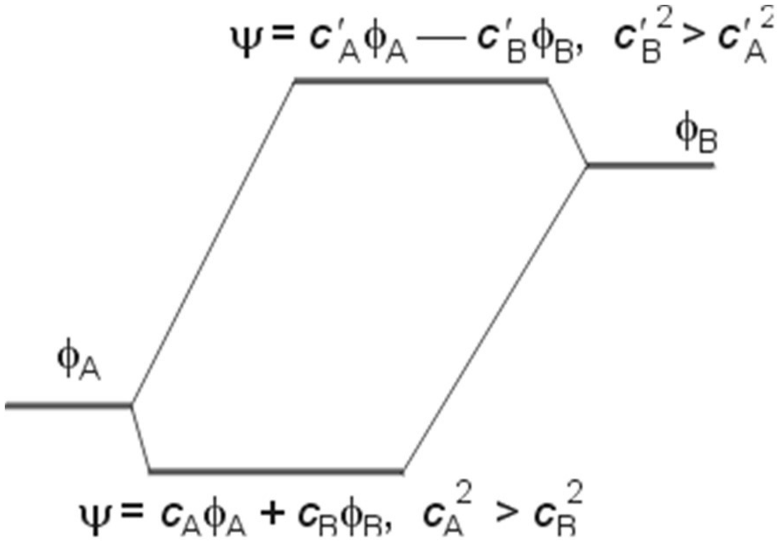


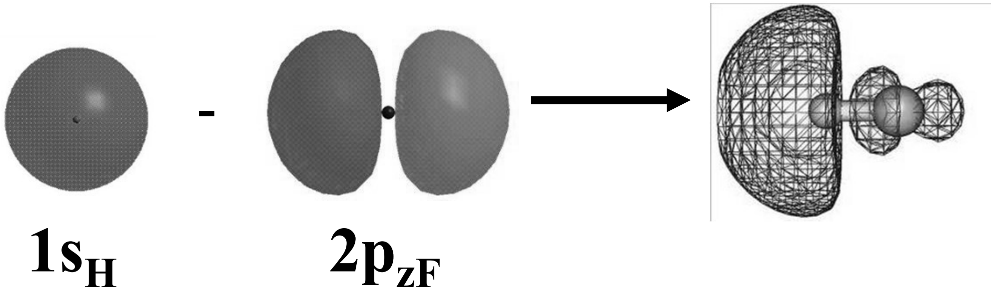
- **The *F 2p$_x$* and *2p$_y$*, finding no symmetry-matching AO in H, form non-bonding MO′s (1π).**

- **The *H 1s* and *F 2p$_z$* are close in energy and do interact to form a bonding MO (3σ) and an antibonding MO (4σ).**

$3\sigma = (\sqrt{0.1}\,1s_H + \sqrt{0.9}\,2p_{zF})$ **This bonding MO is more F-like!**







$4\sigma^* = (\sqrt{0.9}\,1s_H - \sqrt{0.1}\,2p_{zF})$ **This MO is more H-like.**

- **The occupied 3σ bonding MO of HF is thus strongly polar with the F-end being remarkably negative.**

- **The empty 4σ MO of HF is anti-bonding.**

- **The F atom in HF is F^-- like.**

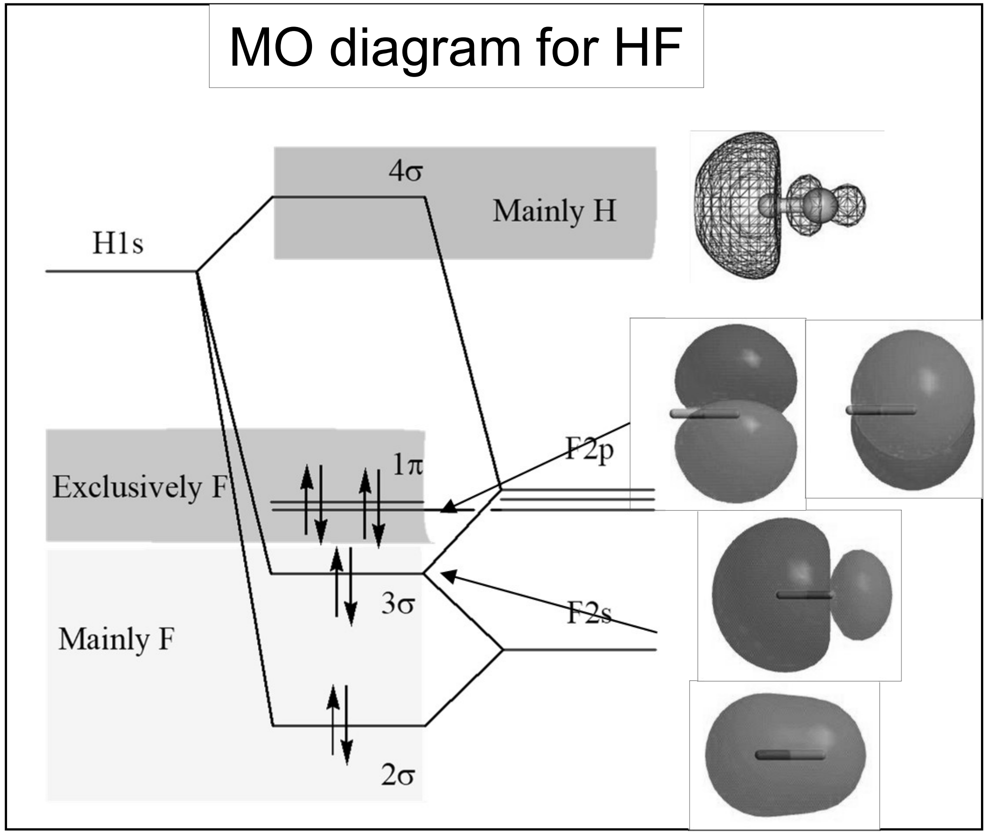
Atomic Orbital Energies and Symmetry Properties

Energy (au)					Symmetry
	H	Li	C	F	
1*s*	-0.5	-2.48	-11.33	-26.38	σ
2*s*		-0.20	-0.71	-1.57	σ
2*p*			-0.43	-0.73	σ and π

Atomic Configurations		**Ground-state Configurations**	
Li	**$1s^2 2s^1$**	**LiH**	**$1\sigma^2 2\sigma^2$**
C	**$1s^2 2s^2 2p^2$**	**CH**	**$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^1$**
F	**$1s^2 2s^2 2p^5$**	**HF**	**$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4$**

Bonding MO: 1) LiH-2σ, more H 1s-like;
2) CH-2σ, covalent; 3) FH-3σ, more F $2p_z$-like.

Heterogeneous diatomic molecules, HX



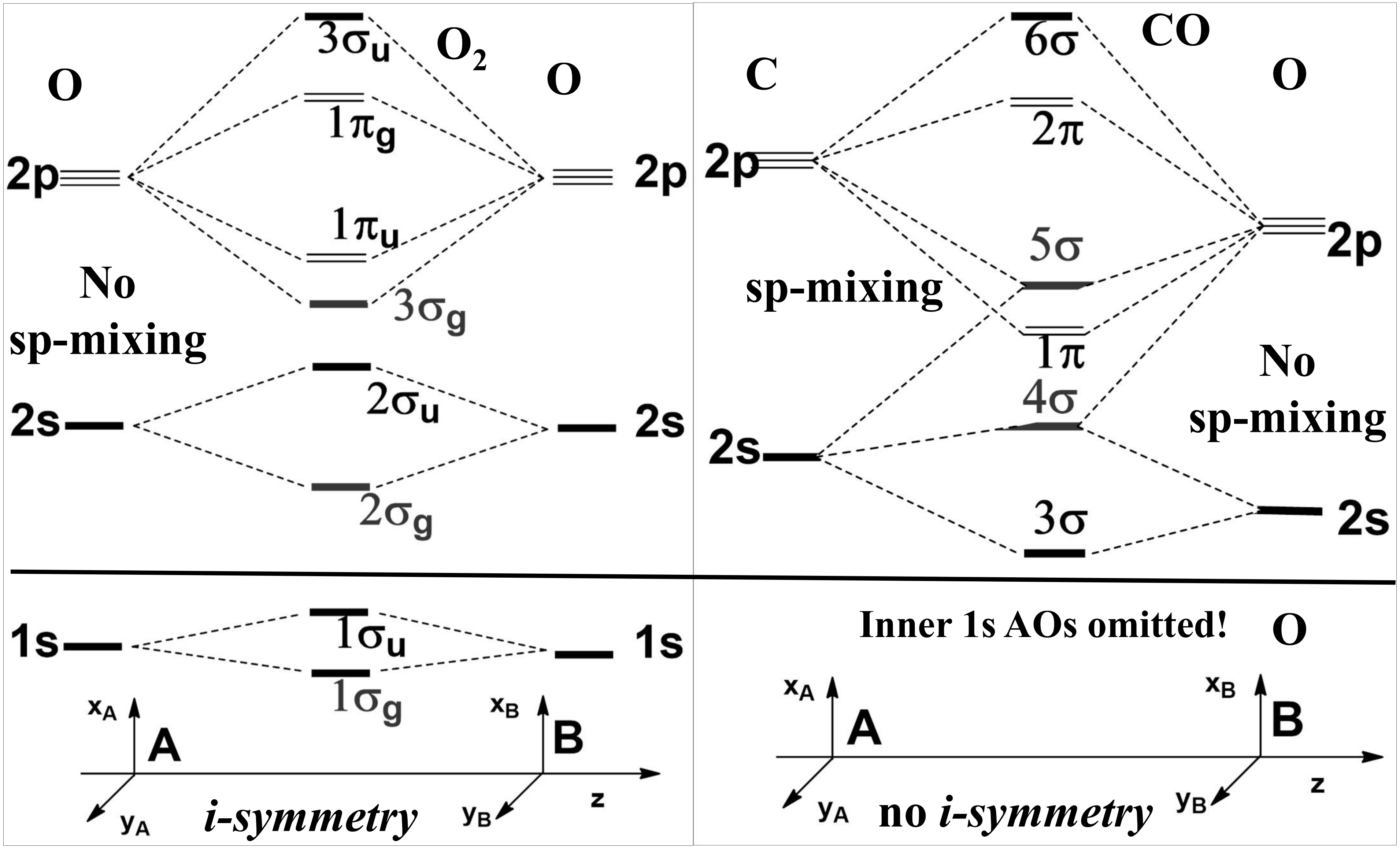
MO diagram for HF

Electronic configurations

LiH	**4**	**$K(2\sigma)^2$**
BeH	**5**	**$K(2\sigma)^2\,(3\sigma)^1$**
CH	**7**	**$K(2\sigma)^2\,(3\sigma)^2\,(1\pi)^1$**
NH	**8**	**$K(2\sigma)^2\,(3\sigma)^2\,(1\pi)^2$**
OH	**9**	**$K(2\sigma)^2\,(3\sigma)^2\,(1\pi)^3$**
HF	**10**	**$K(2\sigma)^2\,(3\sigma)^2\,(1\pi)^4$**

- The π **MOs in** such these **XH** molecules are non-bonding and **exclusively localized on the X atom**.
- **The 3σ bonding MO in HF, HO etc is highly polar** with the X-end being remarkably negative!
- In CH and NH: **2σ -bonding, 3σ - non-/weakly anti-bonding**

Simplified MO diagram of heteronuclear diatomic molecules



No sp-mixing

sp-mixing

No sp-mixing

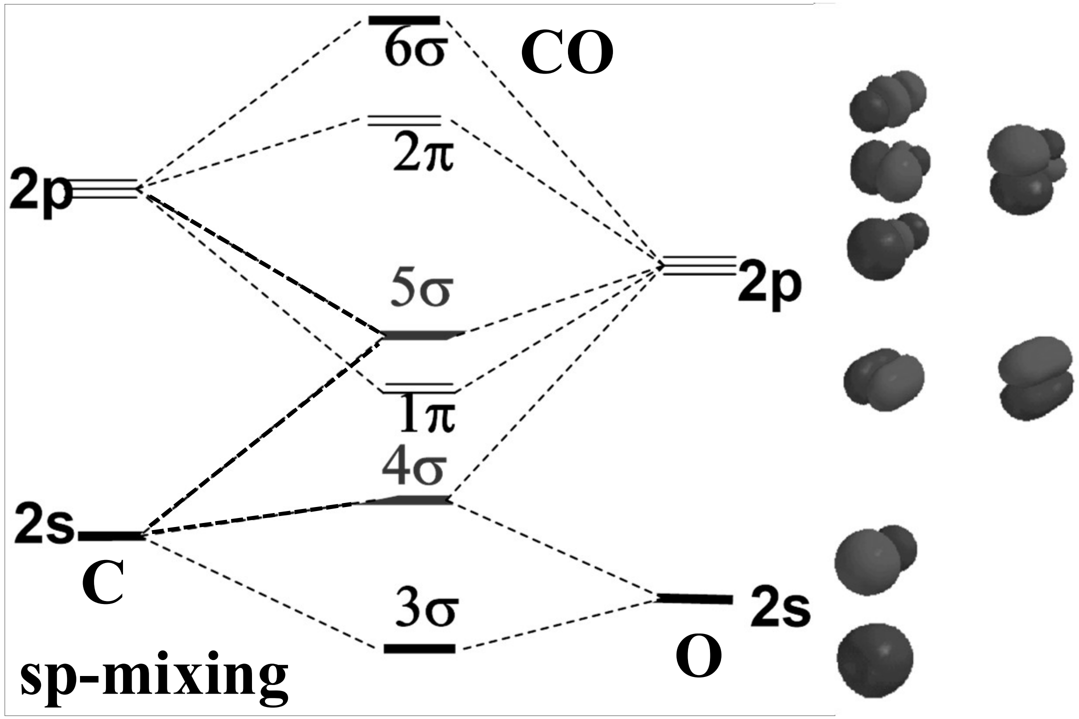
Inner 1s AOs omitted!

i-symmetry

no *i-symmetry*

A = B ⟷ **A ≠ B**

Heteronuclear diatomic molecules, YX



Isoelectronic rule:

The MO's bond formation and electronic configurations are similar among the isoelectronic diatomic molecules.

CO is isoelectronic with N_2!

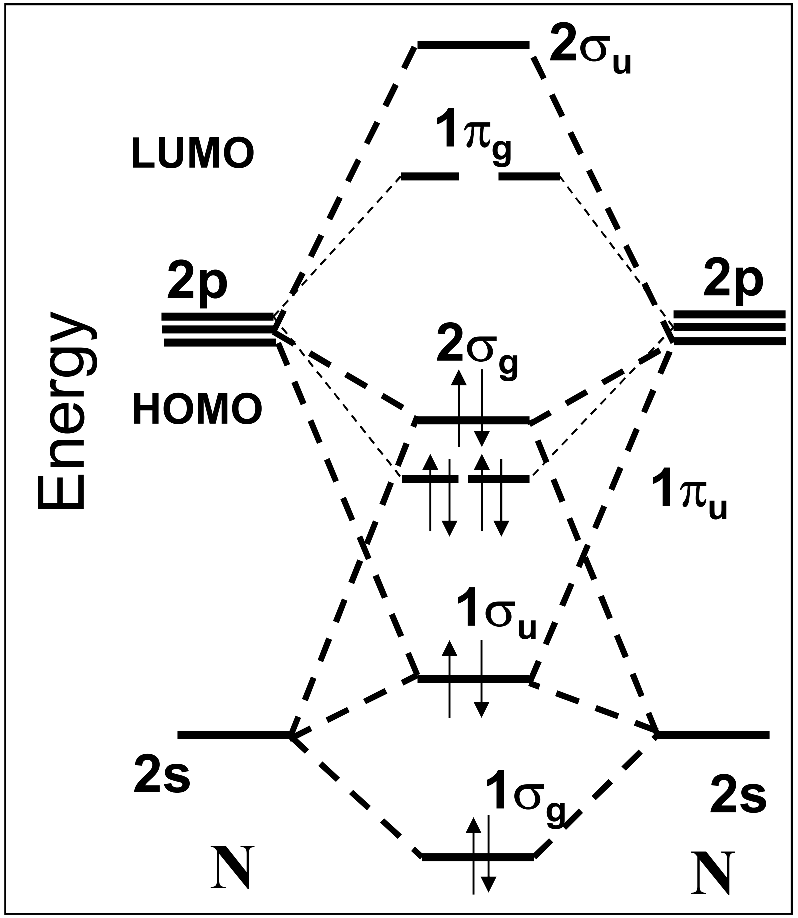
$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2$

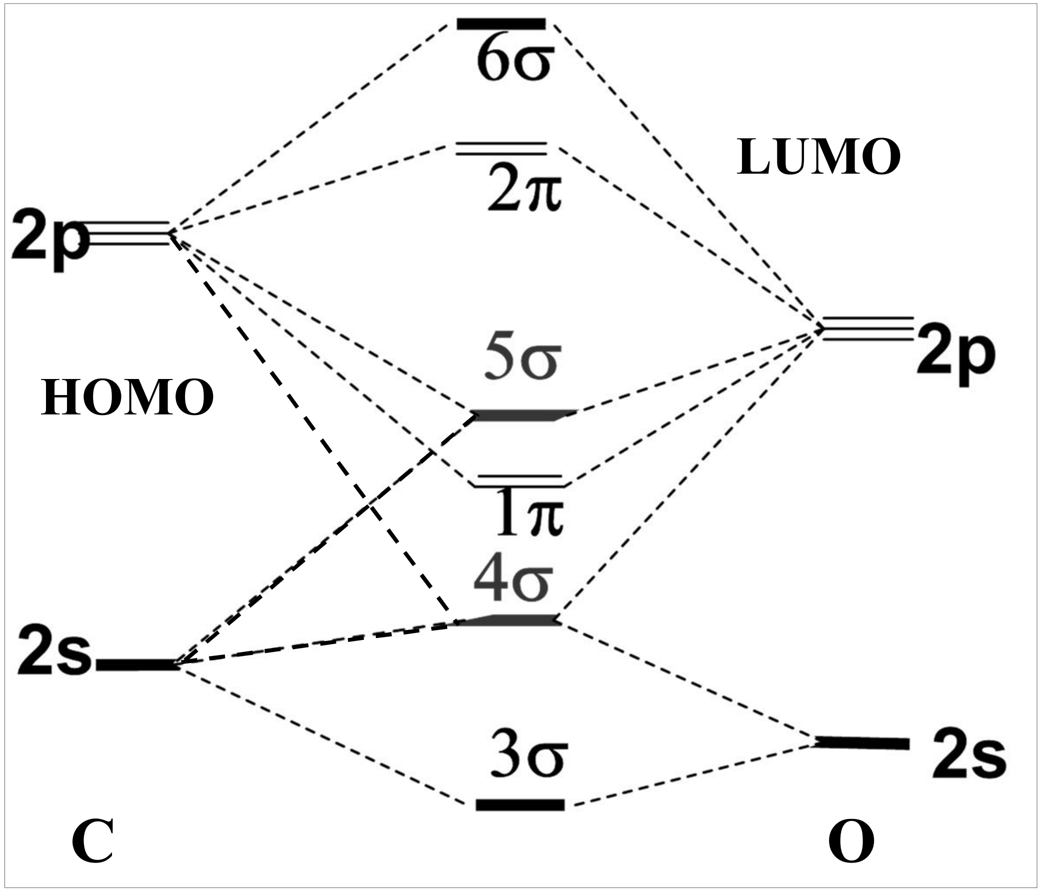
BeO	12	$KK(3\sigma)^2(4\sigma)^2(1\pi)^4$	like C_2
CN	13	$KK(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^1$	like N_2^+
CO	14	$KK(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2$	like N_2
NO	15	$KK(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2(2\pi)^1$	like O_2^+

CO is isoelectronic with N_2.

N_2: $KK(1\sigma_g)^2\ (1\sigma_u)^2\ (1\pi_u)^4\ (2\sigma_g)^2$

CO: $KK(3\sigma)^2\ (4\sigma)^2\ (1\pi)^4\ (5\sigma)^2$





However, for CO, its 5σ MO is more like a lone pair located at C atom, and is weakly antibonding!

The bonding in OH is quite similar to that of HF.

OH: K$(2\sigma)^2$ $(3\sigma)^2$ $(1\pi)^3$ $^2\Pi$ B.O. = 1

- $(2\sigma)^2$: Non-bonding MO (O 2s)
- $(3\sigma)^2$: bonding MO (O $2p_z$ + H 1s)
- $(1\pi)^3$: Non-bonding MOs (O $2p_x$, $2p_y$)

LiO: KK$(2\sigma)^2$ $(3\sigma)^2$ $(1\pi)^3$ $^2\Pi$

- $(2\sigma)^2$: Non-bonding MO (O 2s)
- $(3\sigma)^2$: bonding MO (O $2p_z$ + Li 2s)
- $(1\pi)^3$: Non-bonding or weakly bonding MOs (Mainly O2p_x, $2p_y$, with minor contribution from Li $2p_x$, $2p_y$.

B.O. ≥ 1 (Li, Be, sp-mixing)

BeO: KK$(2\sigma)^2$ $(3\sigma)^2$ $(1\pi)^4$

- $(2\sigma)^2$: Non-bonding MO (O 2s)
- $(3\sigma)^2$: bonding MO (O $2p_z$ + Be 2s)
- $(1\pi)^4$: Weakly bonding MOs (Mainly O2p_x, $2p_y$, with substantial contribution from Be $2p_x$, $2p_y$.

B.O. = 3 (2<B.O. <3)

- Be adopts $2s^12p^1$ in order to form BeO.

Molecule	electrons	electronic configuration	term	B.O.
LiH	4	$K(2\sigma)^2$	$^1\Sigma^+$	1
BeH	5	$K(2\sigma)^2\,(3\sigma)^1$	$^2\Sigma^+$	0.5
CH	7	$K(2\sigma)^2\,(3\sigma)^2\,(1\pi)^1$	$^2\Pi$	1
NH	8	$K(2\sigma)^2\,(3\sigma)^2\,(1\pi)^2$	$^3\Sigma^-$	1
OH	9	$K(2\sigma)^2\,(3\sigma)^2\,(1\pi)^3$	$^2\Pi$	1
HF	10	$K(2\sigma)^2\,(3\sigma)^2\,(1\pi)^4$	$^1\Sigma^+$	1
BeO, BN	12	$KK(3\sigma)^2\,(4\sigma)^2\,(1\pi)^4$	$^1\Sigma^+$	2
CN, BeF	13	$KK(3\sigma)^2\,(4\sigma)^2\,(1\pi)^4\,(5\sigma)^1$	$^2\Sigma^+$	2.5, 0.5
CO	14	$KK(3\sigma)^2\,(4\sigma)^2\,(1\pi)^4\,(5\sigma)^2$	$^1\Sigma^+$	3
NO	15	$KK(3\sigma)^2\,(4\sigma)^2\,(1\pi)^4\,(5\sigma)^2\,(2\pi)^1$	$^2\Pi$	2.5

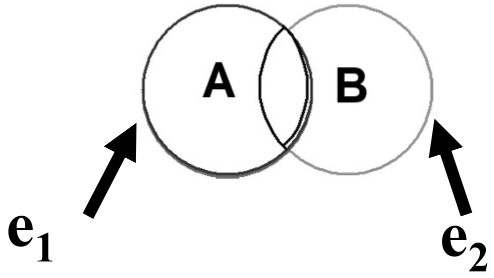
Please derive the spectral term of the first excited state of CH ?

Electronic configuration: $K(2\sigma)^2 (3\sigma)^1 (1\pi)^2)$

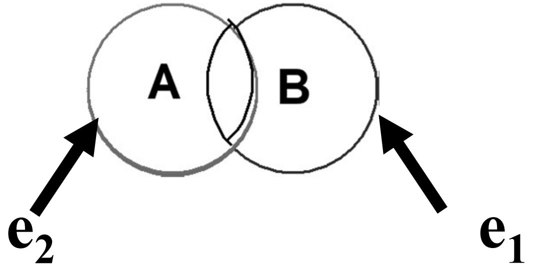
§ 3 Valence bond(VB) theory for the hydrogen molecule and comparison of VB theory with Molecular Orbital theory(MO)

In valence bond(VB) theory, each atom contributes an electron to form a covalent bond.

e.g., H_2



or



The Heitler-London treatment:

$f_1 = \mathbf{A(1)B(2)}$ & $f_2 = \mathbf{A(2)B(1)}$ **(two covalent VB structures)**

The trial variation function for the whole system:

$$\Psi = c_1 f_1 + c_2 f_2 = c_1\mathrm{A(1)B(2)} + c_2\mathrm{A(2)B(1)}$$

In case electron spin is concerned, the wavefunction is

$$\Psi(1,2)_{\mathrm{VB}} = \mathrm{N}[\mathrm{A}(1)B(2) + \mathrm{A}(2)B(1)] \times [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

VB theory solution of H_2

The hamilton operator

$$\hat{H} = (-\frac{1}{2}\nabla_1^2 - \frac{1}{r_{a1}}) + (-\frac{1}{2}\nabla_2^2 - \frac{1}{r_{b2}}) + (-\frac{1}{r_{a2}} - \frac{1}{r_{b1}} + \frac{1}{r_{12}} + \frac{1}{R})$$

$$= \hat{H}_a(1) + \hat{H}_b(2) + \hat{H}'$$

Schrödinger equation $\hat{H}\psi = E\psi$

Following the Variation Theorem, we have

$$E(c_1, c_2) = \frac{\int (c_1 f_1 + c_2 f_2)\hat{H}(c_1 f_1 + c_2 f_2) d\tau}{\int (c_1 f_1 + c_2 f_2)^2 d\tau}$$

$$\frac{\partial E}{\partial c_1} = \frac{\partial E}{\partial c_2} = 0$$

Then we have seqular equations and seqular determinant, the roots of which are

$$E_1 = \frac{H_{11} + H_{12}}{1 + S_{ab}^2} = 2E_H + \frac{Q + A}{1 + S_{ab}^2}; \qquad E_2 = \frac{H_{11} - H_{12}}{1 - S_{ab}^2} = 2E_H + \frac{Q - A}{1 - S_{ab}^2}$$

$$\Psi(1,2) = \frac{1}{\sqrt{2 \pm 2S_{ab}^2}}\left[A(1)B(2) \pm A(2)B(1)\right]$$

$$S_{ab} = \int A(1)B(2)d\tau = \int A(2)B(1)d\tau$$

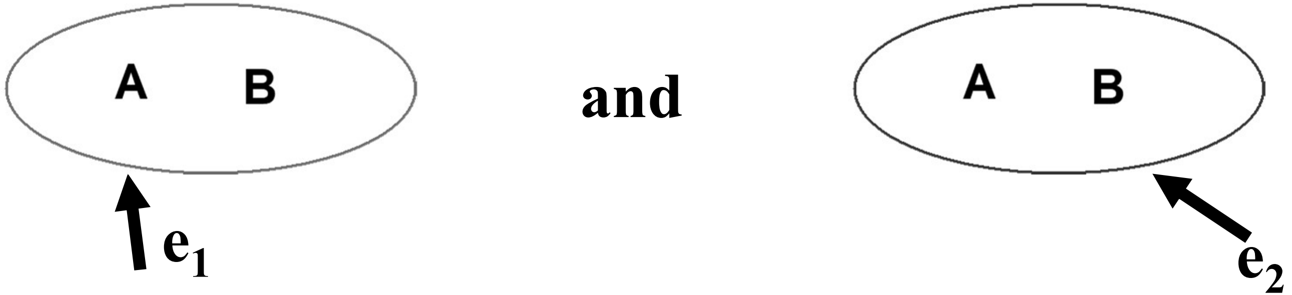
$$H_{11} = \int f_1\hat{H}f_1 d\tau = \int A(1)B(2)(\hat{H}_a + \hat{H}_b + \hat{H}')A(1)B(2)d\tau$$

$$= 2E_H + \int A(1)B(2)\hat{H}' A(1)B(2)d\tau = 2E_H + Q = H_{22}$$

$$H_{12} = \int f_1\hat{H}f_2 d\tau = \int A(1)B(2)(\hat{H}_a + \hat{H}_b + \hat{H}')A(2)B(1)d\tau$$

$$= 2E_H S_{ab}^2 + \int A(1)B(2)\hat{H}' A(2)B(1)d\tau = 2E_H S_{ab}^2 + A = H_{21}$$

In molecular orbital (MO) theory each electron moves over the whole molecule.



Both electrons can be on the same nuclei

Following the 1-particle approximation, variation theorem & SCF process give rise to a series of 1-e wavefunctions (MOs).

The bonding MO is $1\sigma_g = c[A + B]$

The LCAO-MO wavefunction for the H_2 ground state ($1\sigma_g^2$) is:

$$\Psi(1,2)_{MO} = N[1\sigma_g(1)][1\sigma_g(2)] \times [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

Spatial part $\Downarrow$ $\because 1\sigma_g(i) = c[A(i) + B(i)]$

$$\underbrace{\underset{H^-H^+}{A(1)A(2)} + \underset{H^+H^-}{B(1)B(2)}}_{\text{ionic terms}} + \underbrace{A(1)B(2) + A(2)B(1)}_{\text{covalent terms}}$$

QM treatments of H_2: MO vs. VB

- **Both treatments employ the variation theorem.**
- **Orbitals: VB-localized; MO-delocalized!**
- **Wavefunctions differ.**

$$\Psi(1,2)_{\mathrm{MO}} = \mathrm{N}[\mathrm{A}(1)+B(1)][\mathrm{A}(2)+B(2)]\times[\alpha(1)\beta(2)-\beta(1)\alpha(2)]$$

$$or = \mathrm{A}(1)\mathrm{A}(2) + B(1)B(2) + A(1)B(2) + \mathrm{A}(2)B(1) \quad (\text{spin - free})$$

H^-H^+ H^+H^- Covalent forms

Heitler-London VB treatment:

$$\Psi(1,2)_{\mathrm{VB}} = \mathrm{N}[\mathrm{A}(1)B(2)+\mathrm{A}(2)B(1)]\times[\alpha(1)\beta(2)-\beta(1)\alpha(2)]$$

$$or = \mathrm{A}(1)B(2) + \mathrm{A}(2)B(1) \qquad (\text{spin - free})$$

Only when the ionic valence structures are included can we have

$$\Psi_{VB} = \mathrm{A}(1)\mathrm{A}(2) + B(1)B(2) + A(1)B(2) + \mathrm{A}(2)B(1) \quad (\text{spin - free})$$

➔ The accuracy of VB treatment depends on how to enumerate possible VB structures!

Comparison of MO and VB theories

VB Theory

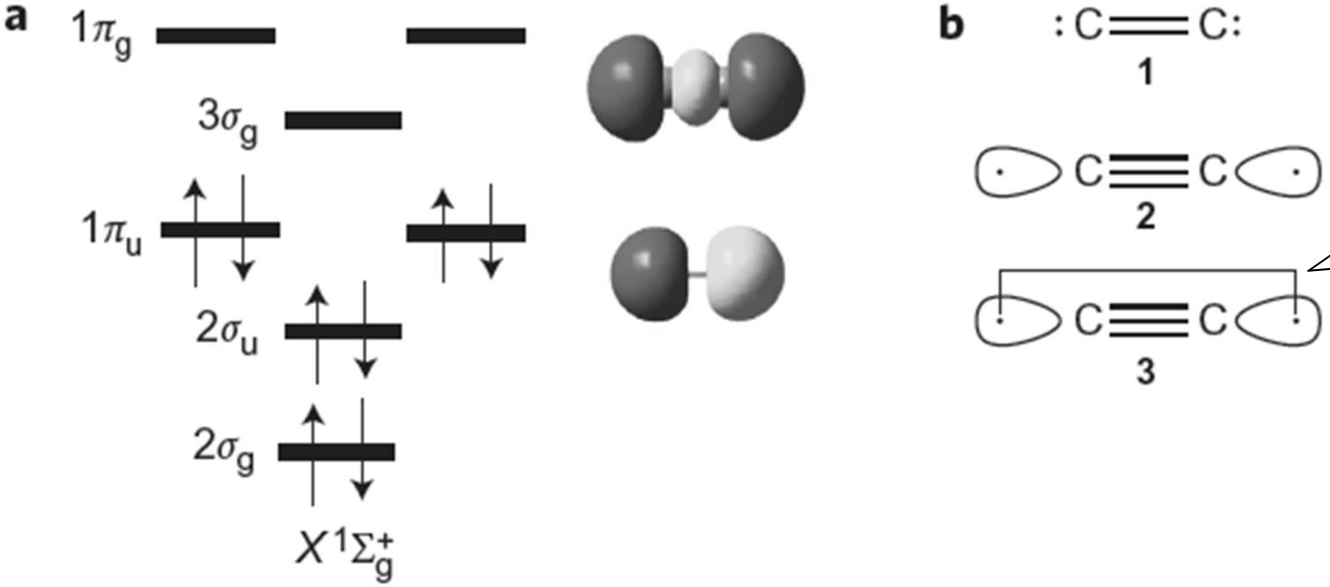
- The electrons in the molecule ***pair*** to accumulate density in the internuclear region.
- Electrons are ***localized*** (to specific bonds).
- Hybridization of atomic orbitals
- Basis of Lewis structures, resonance, and hybridization.
- Good theory for predicting molecular structure.

Molecular orbital theory

- Molecular orbitals are formed by the overlap and interaction of atomic orbitals.
- Electrons are “***delocalized”*** over molecular orbitals consisting of AOs.
- Electrons fill up the MO′s according to the *aufbau* principle.
- Give accurate bond dissociation energies, IP, EA, and spectral data.

Recent development: Quadruple bond in C_2 !

- Triple bond is conventionally considered as the limit for multiply bonded main group elements!
- Recently, high-level theoretical computations show that C_2 and its isoelectronic CN^+, BN and CB^- are bound by **a quadruple bond**.
- The fourth bond is an **‘inverted’ bond** with an bonding energy of 12-17 kcal/mol, stronger than a hydrogen bond.



“Inverted” bond!

P.F. Su, W. Wu, et al., Nat. Chem. 2012, 4, 195.

The End of This Chapter !

- 第二版： **pp. 111-112,**
  questions 4.8, 4.11, 4.19, and 4.21.
- 第三版： **p95-96,**
  questions 4.12, 4.15, 4.19, and 4.21.

Relationship between MO (λ,m) and its component AO(*l*,*m*)

$$\Psi_{elec} = (2\pi)^{-1/2} F(\xi,\eta) e^{im\phi}$$

$\lambda = \lvert m \rvert$	**0**	**1**	**2**	**3**	**4**
letter	σ	π	δ	ϕ	γ

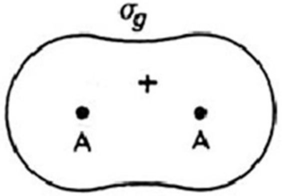
Now suppose MO can be composed of AO′s, i.e., $\Psi_{elec} = N[\phi_{nlm}(1) + \phi_{nlm}(2)]$

AO of atom 2

i) σ MO (λ =*0*, *m* = 0)

AO components

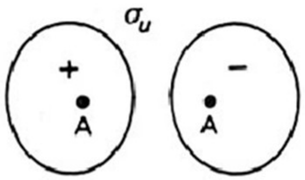
Bonding



(a)

ns (l=0,m_l=0) + ns (l=0,m_l=0)

Anti-bonding

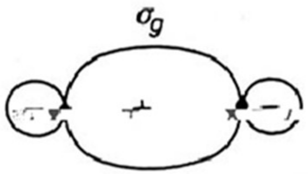


(b)

ns (l=0,m_l=0) – ns (l=0,m_l=0)

Note: Herein $p_0 = p_z$

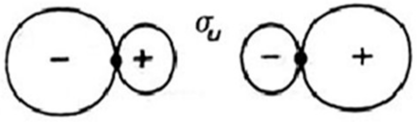
Bonding



ιc)

np_0 (l=1,m_l=0) – np_0 (l=1,m_l=0)

Anti-bonding



(d)

np_0 (l=1,m_l=0) + np_0 (l=1,m_l=0)

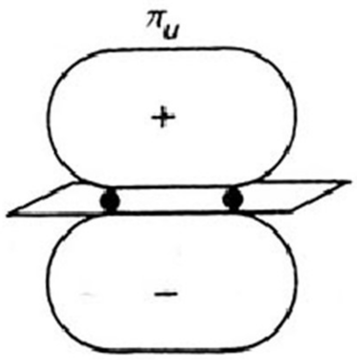
Relationship between MO (λ,m) and AO(l,m)

$$\Psi_{elec} = (2\pi)^{-1/2} F(\xi,\eta) e^{im\phi}$$

$\lambda = \lvert m \rvert$	0	1	2	3	4
letter	σ	π	δ	ϕ	γ

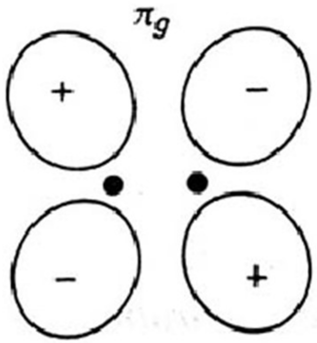
ii) π MO (m= ±1)

Bonding



(e) $n\mathrm{p}_{\pm1}$ $(l=1, m_l=\pm1) + n\mathrm{p}_{\pm1}$ $(l=1, m_l=\pm1)$

Anti-bonding



(f) $n\mathrm{p}_{\pm1}$ $(l=1, m_l=\pm1) - n\mathrm{p}_{\pm1}$ $(l=1, m_l=\pm1)$

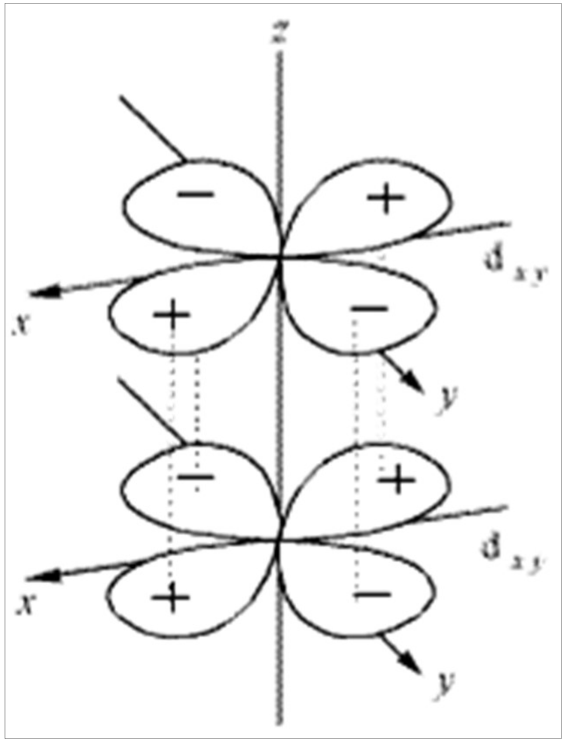
Relationship between MO (λ,m) and AO(*l*,*m*)

$$\Psi_{elec} = (2\pi)^{-1/2} F(\xi,\eta) e^{im\phi}$$

$\lambda = \|m\|$	0	1	2	3	4
letter	σ	π	δ	ϕ	γ

iii) δ MO (m=±2)

Bonding



$n\mathrm{d}_{\pm 2}\ (l=2, m_l=\pm 2) + n\mathrm{d}_{\pm 2}\ (l=2, m_l=\pm 2)$

Anti-Bonding

Not depicted!

$n\mathrm{d}_{\pm 2}\ (l=2, m_l=\pm 2) - n\mathrm{d}_{\pm 2}\ (l=2, m_l=\pm 2)$

* Subscription (g/u): the parity of one-electron wavefunction.

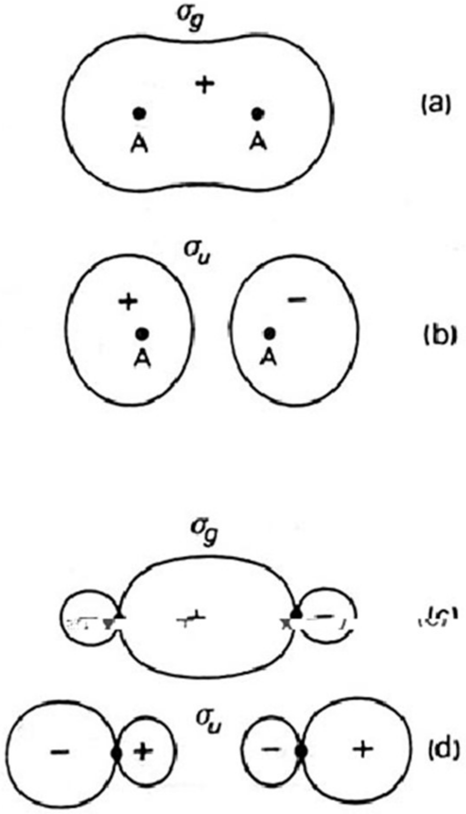
Summary

$$\boldsymbol{\psi_{elec} = F(\xi,\eta)\ (2\pi)^{-1/2}\ e^{im\phi}}$$

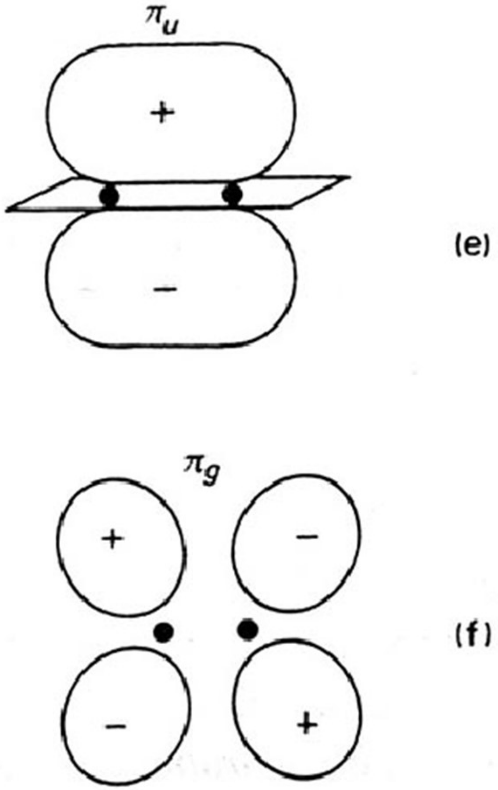
λ	0	1	2	3	4
letter	σ	π	δ	ϕ	γ

$\lambda = |\mathbf{m}|$

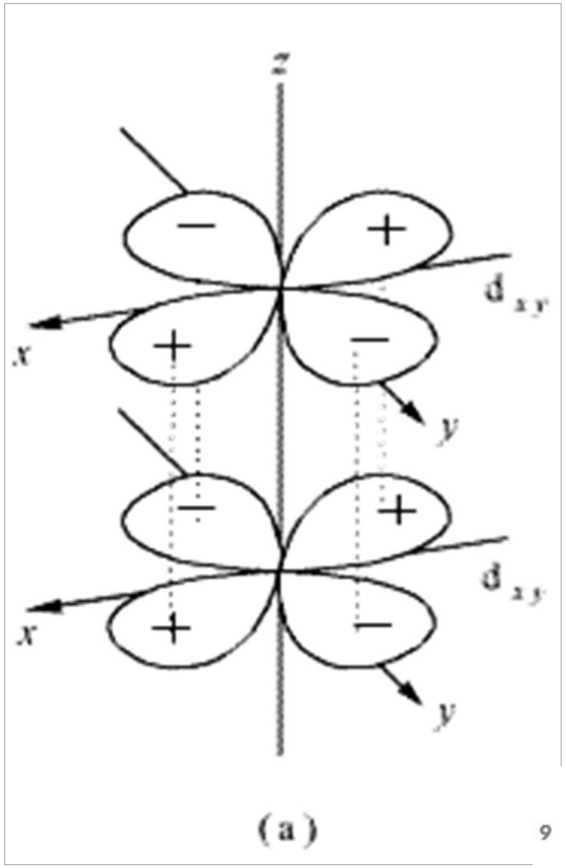
σ



π



δ



2. The Variation Theorem

For any well-behaved wavefunction ϕ, the average energy from the Hamiltonian of the system is always greater or close to the exact ground state energy (E_0) for that Hamiltonian,

$$<E>=\frac{\int \phi^* \hat{H} \phi d\tau}{\int \phi^* \phi d\tau} \geq E_0$$

3. Linear Variation Functions

$$\phi = c_1 f_1 + c_2 f_2 + \ldots + c_n f_n = \sum_{j=1}^{n} c_j f_j$$

A linear variation function is a linear combination of n linearly independent functions f_1, f_2, ...f_n.

Based on this principle, the parameters are regulated by the minimization routine so as to obtain the wavefunction that corresponds to the minimum energy. This is taken to be the wavefunction that closely approximates the ground state.

$$< E >= \frac{\int \phi^* \hat{H} \phi d\tau}{\int \phi^* \phi d\tau} \geq E_0$$

$$\varepsilon =< E >$$

adjusting the parameter, make $\dfrac{\partial \varepsilon}{\partial c_i} = 0$

$$\begin{array}{l} seqular \quad equation \\ made \quad equation \quad resolved(c_1, c_2 \neq 0) \\ \begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0 \\ get \quad E \Rightarrow get \quad c_1, c_2 \Rightarrow get \quad \phi \end{array}$$

The algebraic equation has 2 roots, E_1 and E_2.

$$\phi = c_1\psi_1 + c_2\psi_2 + \ldots + c_n\psi_n$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \ldots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \ldots & H_{2n} - ES_{2n} \\ . & . & \ldots & . \\ . & . & \ldots & . \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \ldots & H_{nn} - ES_{nn} \end{vmatrix} = 0$$

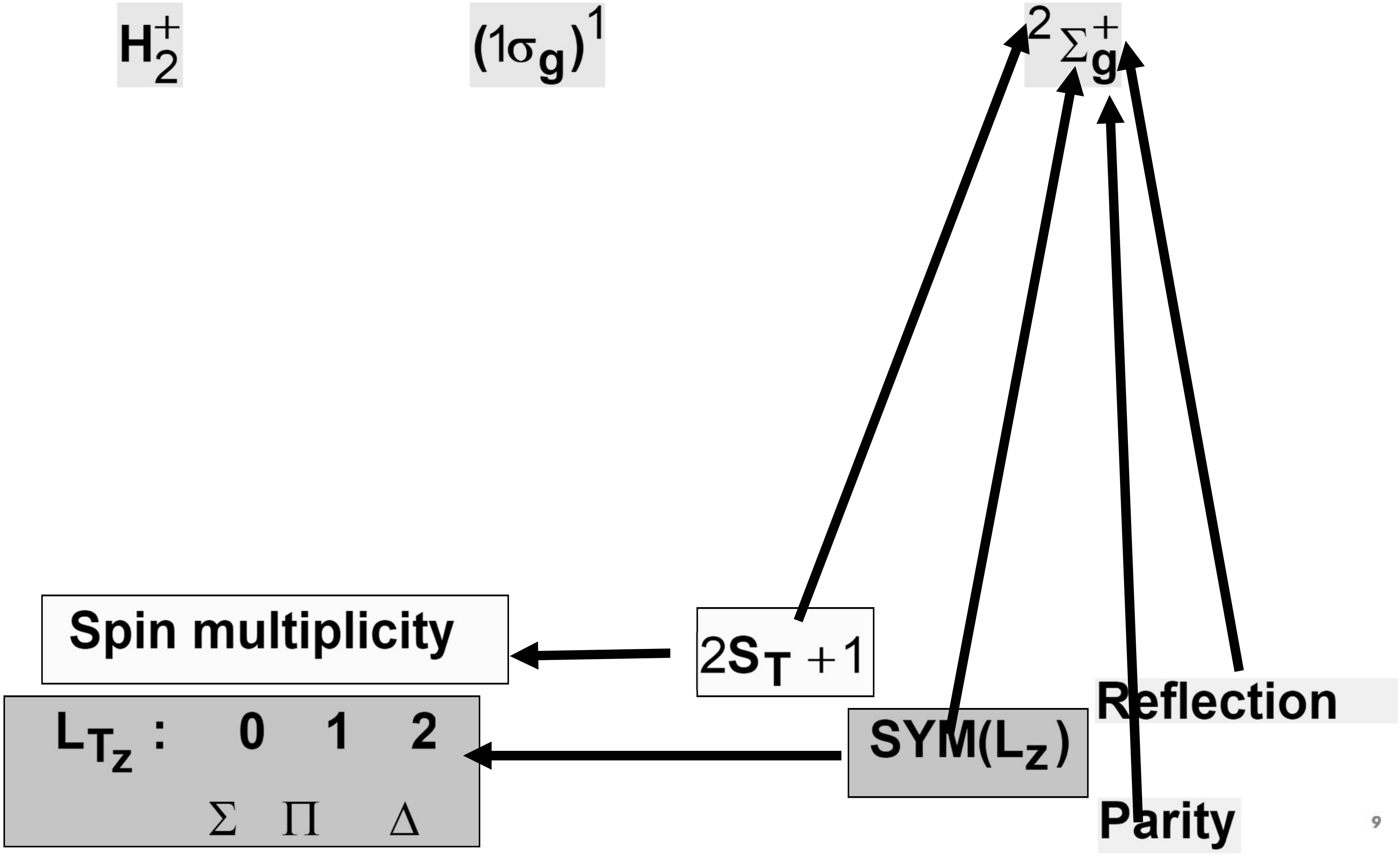
The algebraic equation has *n* roots, which can be shown to be real. Arranging these roots in order of increasing value: $E_1 \leq E_2 \leq \ldots \leq E_n$.

Summary

3. The structure of homonuclear diatomic molecules

c. The molecular spectroscopy - term

Molecular Orbital Theory Diatomics Term symbols



Molecule	Configuration	Term symbol
H_2^+	$(1\sigma_g)^1$	$^2\Sigma_g^+$

Spin multiplicity

$2S_T + 1$

L_{T_z} :	0	1	2
	Σ	Π	Δ

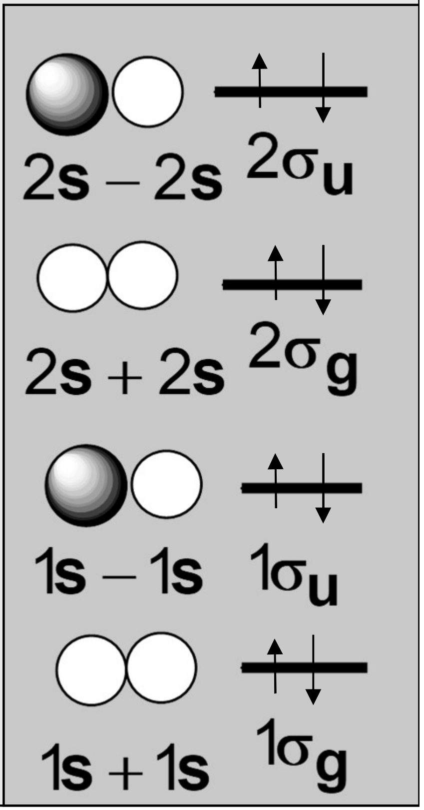
SYM(L_z)

Reflection

Parity

Molecular Orbital Theory Diatomics Term symbols

Molecule	Configuration	Term symbol
H_2	$(1\sigma_g)^2$	$^1\Sigma_g^+$
H_2^-	$(1\sigma_g)^2(1\sigma_u)^1$	$^2\Sigma_u^+$
He_2	$(1\sigma_g)^2(1\sigma_u)^2$	$^1\Sigma_g^+$
Li_2	$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2$	$^1\Sigma_g^+$
Be_2	$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2$	$^1\Sigma_g^+$



Spin multiplicity ← $2S_T + 1$

L_{T_z} : 0 1 2

Σ Π Δ

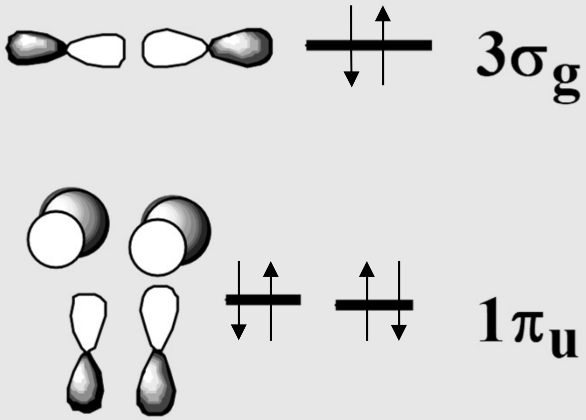
← $SYM(L_z)$

Reflection

Parity

Molecular Orbital Theory Diatomics Term symbols

Molecule	Configuration	Term symbol
B_2	$(1\pi_u)^2$	$^3\Sigma_g^-$ $^1\Delta_g$ $^1\Sigma_g^+$
C_2	$(1\pi_u)^4$	$^1\Sigma_g^+$
N_2^+	$(3\sigma_g)^1(1\pi_u)^4$	$^2\Sigma_g^+$
N_2	$(3\sigma_g)^2(1\pi_u)^4$	$^1\Sigma_g^+$



Spin multiplicity ← $2S_T + 1$

L_{T_z} : 0 1 2

Σ Π Δ

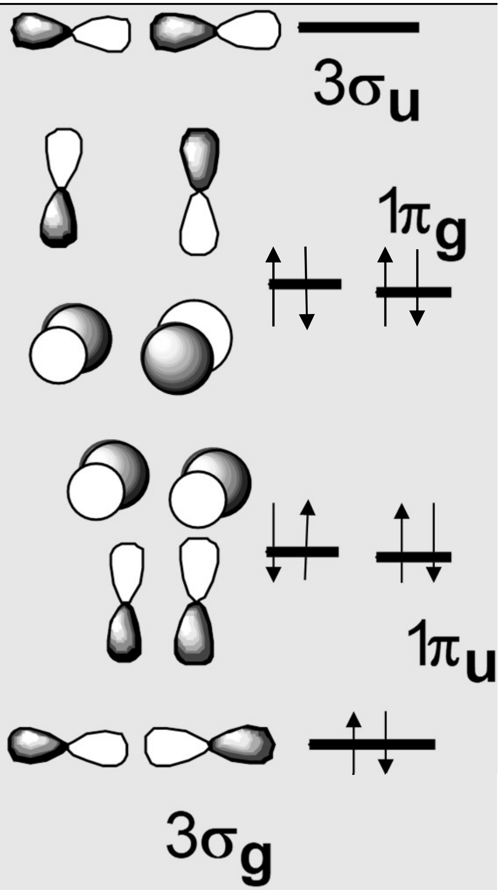
← $SYM(L_z)$

Reflection

Parity

Molecular Orbital Theory Diatomics Term symbols

Molecule	Configuration	Term symbol
N_2^-	$(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^1$	$^2\Pi_g$
O_2	$(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^2$	$^3\Sigma_g^-$ $^1\Delta_g$ $^1\Sigma_g^-$
F_2	$(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^4$	$^1\Sigma_g^+$



Spin multiplicity ← $2S_T + 1$

L_{T_z} :	0	1	2
	Σ	Π	Δ

← **SYM(L_z)**

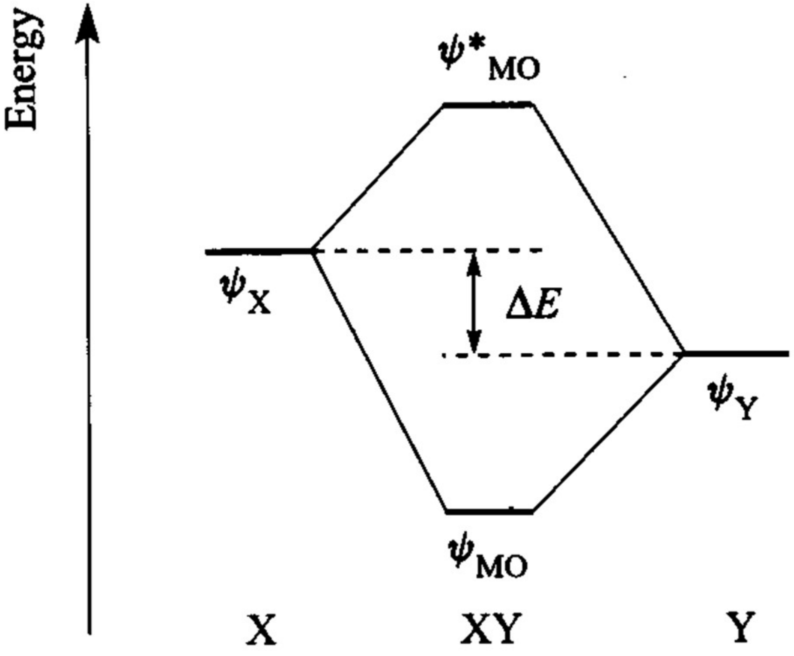
Reflection

Parity

Summary

MO Theory for Heteronuclear Diatomics

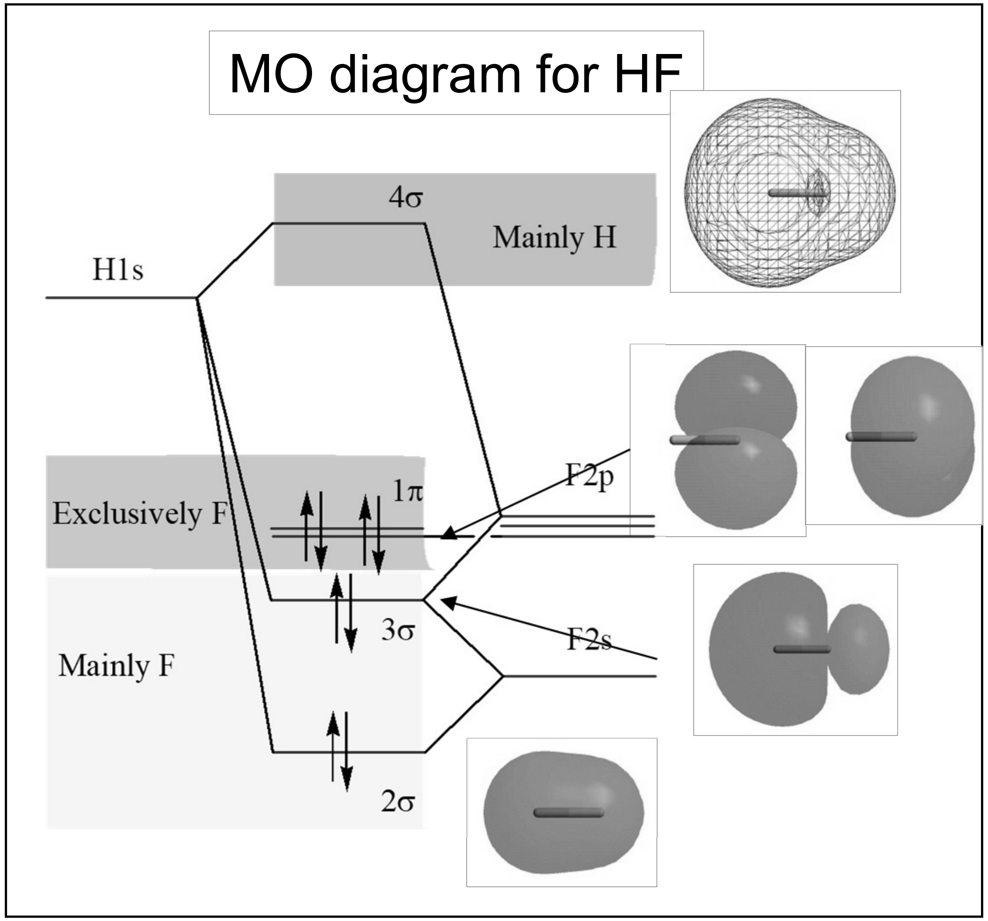
- MO′s will no longer contain equal contributions from each AO.
  - AO′s interact if symmetries are compatible.
  - AO′s interact if energies are close.
  - No interaction will occur if energies are too far apart. A nonbonding orbital will form.



Ψ_X makes a greater contribution to the Ψ^*_{MO}

Ψ_Y makes a greater contribution to the Ψ_{MO}

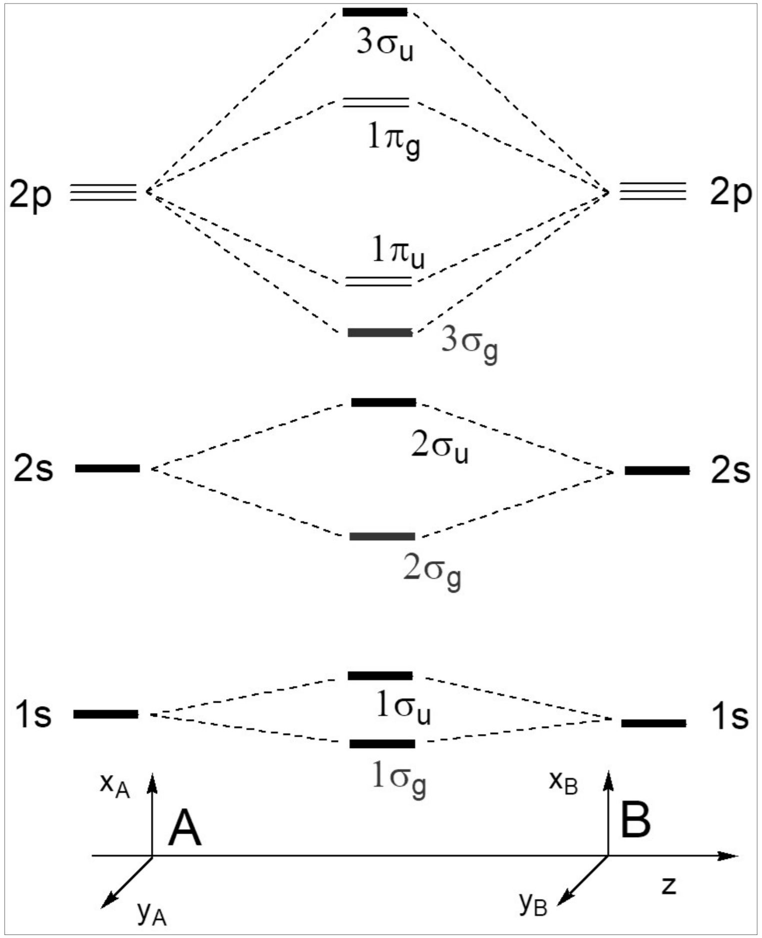
Heterogeneous diatomic molecules, HX

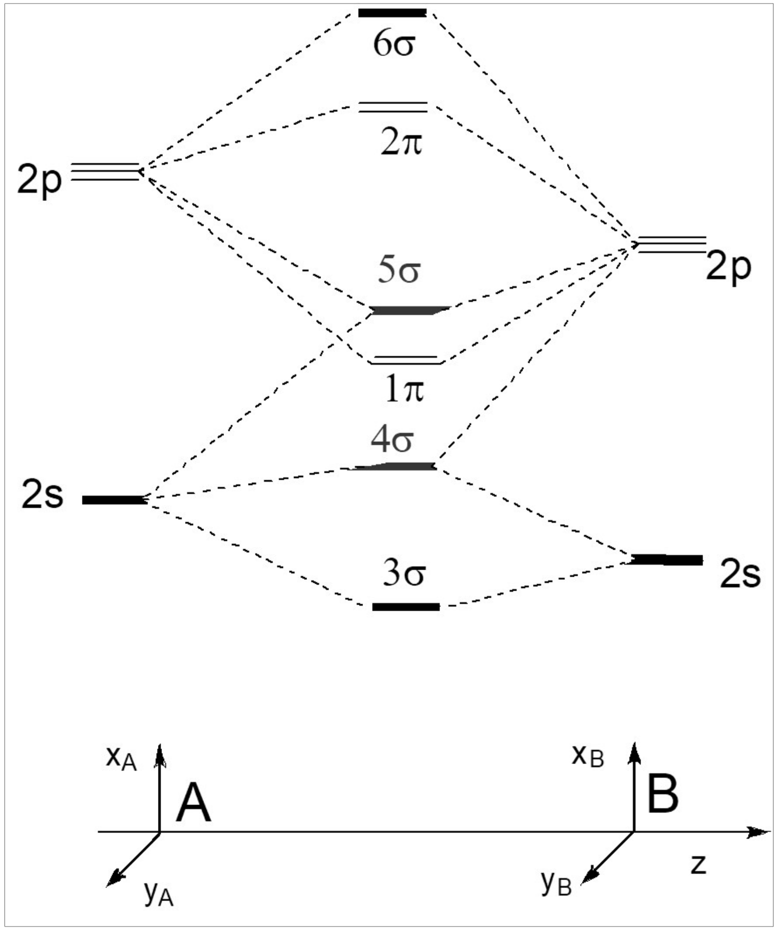


Electronic configurations

LiH	4	$K(2\sigma)^2$
BeH	5	$K(2\sigma)^2 (3\sigma)^1$
CH	7	$K(2\sigma)^2 (3\sigma)^2 (1\pi)^1$
NH	8	$K(2\sigma)^2 (3\sigma)^2 (1\pi)^2$
OH	9	$K(2\sigma)^2 (3\sigma)^2 (1\pi)^3$
HF	10	$K(2\sigma)^2 (3\sigma)^2 (1\pi)^4$

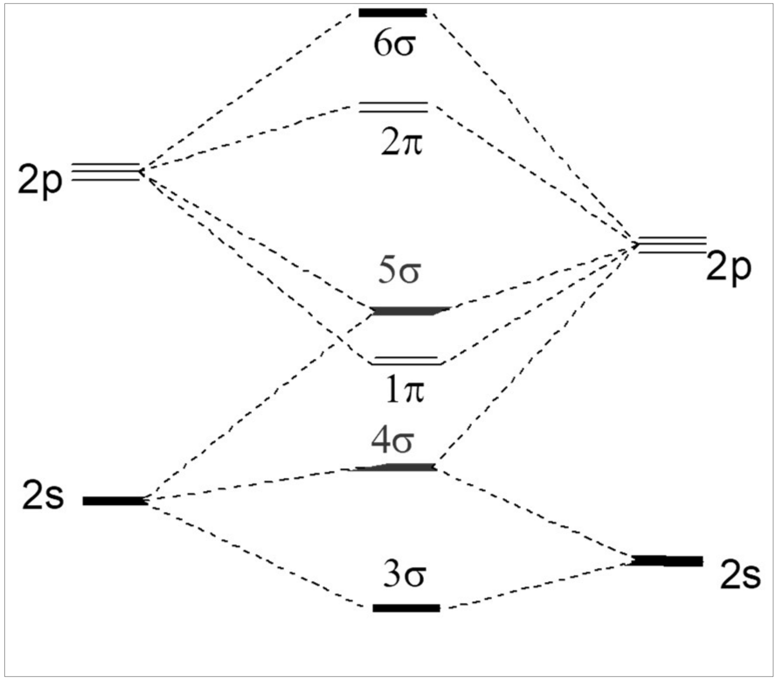
Simplified MO diagram of heteronuclear diatomic molecules





A = B ↔ **A ≠ B**

Heterogeneous diatomic molecules, YX



Isoelectronic rule:

The MO’s bond formation and electronic configurations are similar among the isoelectronic diatomic molecules.

CO is isoelectronic with N_2.

$KK(3\sigma)^2\,(4\sigma)^2\,(1\pi)^4\,(5\sigma)^2$

BeO	12	$KK(3\sigma)^2\,(4\sigma)^2\,(1\pi)^4$
CN	13	$KK(3\sigma)^2\,(4\sigma)^2\,(1\pi)^4\,(5\sigma)^1$
CO	14	$KK(3\sigma)^2\,(4\sigma)^2\,(1\pi)^4\,(5\sigma)^2$
NO	15	$KK(3\sigma)^2\,(4\sigma)^2\,(1\pi)^4(5\sigma)^2\,(2\pi)^1$

Molecule	**electrons**	**electronic configuration**	**term**
LiH	4	$K(2\sigma)^2$	$^1\Sigma^+$
BeH	5	$K(2\sigma)^2\,(3\sigma)^1$	$^2\Sigma^+$
CH	7	$K(2\sigma)^2\,(3\sigma)^2\,(1\pi)^1$	$^2\Pi$
NH	8	$K(2\sigma)^2\,(3\sigma)^2\,(1\pi)^2$	$^3\Sigma^-$
OH	9	$K(2\sigma)^2\,(3\sigma)^2\,(1\pi)^3$	$^2\Pi$
HF	10	$K(2\sigma)^2\,(3\sigma)^2\,(1\pi)^4$	$^1\Sigma^+$
BeO , BN	12	$KK(3\sigma)^2\,(4\sigma)^2\,(1\pi)^4$	$^1\Sigma^+$
CN , BeF	13	$KK(3\sigma)^2\,(4\sigma)^2\,(1\pi)^4\,(5\sigma)^1$	$^2\Sigma^+$
CO	14	$KK(3\sigma)^2\,(4\sigma)^2\,(1\pi)^4\,(5\sigma)^2$	$^1\Sigma^+$
NO	15	$KK(3\sigma)^2\,(4\sigma)^2\,(1\pi)^4\,(5\sigma)^2\,(2\pi)^1$	$^2\Pi$

Comparison of MO and VB theories

VB Theory

- Separate atoms are brought together to form molecules.
- The electrons in the molecule ***pair*** to accumulate density in the internuclear region.
- The accumulated electron density "holds" the molecule together.
- Electrons are ***localized*** (belong to specific bonds).
- Hybridization of atomic orbitals
- Basis of Lewis structures, resonance, and hybridization.
- Good theory for predicting molecular structure.

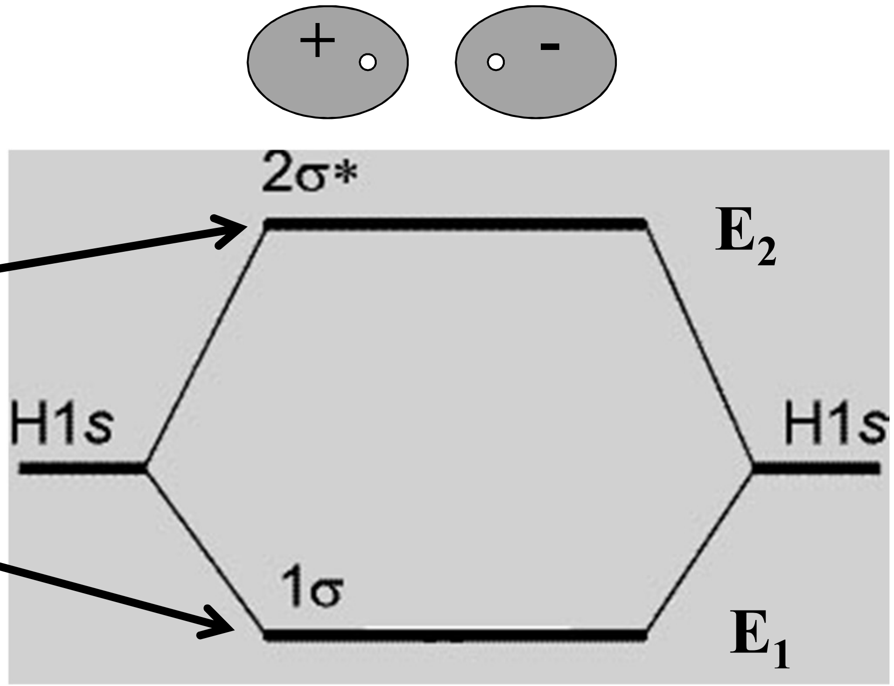
Molecular orbital theory

- Molecular orbitals are formed by the overlap and interaction of atomic orbitals.
- Electrons then fill the molecular orbitals according to the *aufbau* principle.
- Electrons are ***delocalized*** (don't belong to particular bonds, but are spread throughout the molecule).
- Can give accurate bond dissociation energies if the model combines enough atomic orbitals to form molecular orbitals.

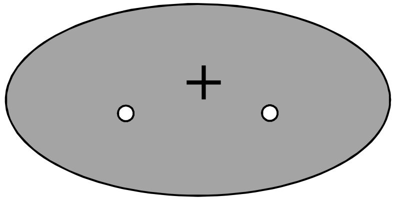
Now we have

$$E_2 = \frac{\alpha - \beta}{1 - S}, \ \phi_2 = \frac{(\psi_a - \psi_b)}{\sqrt{2(1-S)}}$$

$$E_1 = \frac{\alpha + \beta}{1 + S}, \ \phi_1 = \frac{(\psi_a + \psi_b)}{\sqrt{2(1+S)}}$$



($E_1 < E_2$)



Can we simplify the process by using the molecular symmetry?

H_2^+ is $D_{\infty h}$-symmetric. The bonding and antibonding orbitals should be symmetric and asymmetric, respectively, upon inversion, i.e.,

$$\phi_{sym} = c(\psi_a + \psi_b); \ \phi_{asym} = c'(\psi_a - \psi_b) \xrightarrow[\text{normalization}]{} \textbf{c and c'}$$

$$\longrightarrow \quad E_{sym} = \int \phi_{sym} * \hat{H} \phi_{sym} d\tau, E_{asym} = \int \varphi_{asym} * \hat{H} \varphi_{asym} d\tau$$

$$\phi_{sym} = c(\psi_a + \psi_b); \ \phi_{asym} = c'(\psi_a - \psi_b)$$

For the symmetric MO, normalization gives

$$1 = \int \phi_{sym} {}^* \phi_{sym} d\tau = c^2 \int (\psi_a + \psi_b)^2 d\tau$$

$$= c^2 \int (\psi_a^2 + \psi_b^2 + 2\psi_a \psi_b) d\tau = 2c^2 [1 + \int \psi_a \psi_b d\tau] = 2c^2 (1 + S_{ab})$$

$$\Rightarrow c = 1 / \sqrt{2(1 + S_{ab})}$$

Similarly, for the asymmetric MO, normalization gives

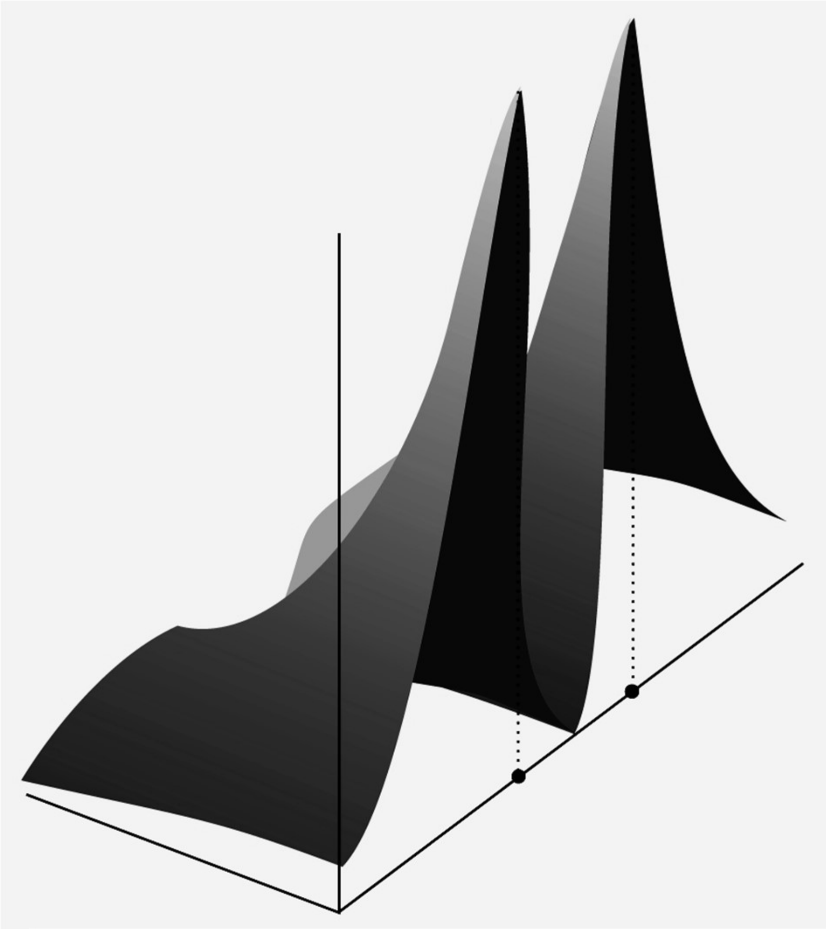
$$1 = \int \phi_{sym} {}^* \phi_{sym} d\tau = c^2 \int (\psi_a + \psi_b)^2 d\tau$$

$$= c^2 \int (\psi_a^2 + \psi_b^2 + 2\psi_a \psi_b) d\tau = 2c^2 [1 + \int \psi_a \psi_b d\tau] = 2c^2 (1 + S_{ab})$$

$$\Rightarrow c' = 1 / \sqrt{2(1 - S_{ab})}$$

Molecular Orbital Theory

H_2^+



The electron density calculated by forming the square of the Wavefunction. Note the elimination of electron density from the internuclear region.

$$\phi_2 = \frac{1}{\sqrt{2(1-S_{ab})}}(\psi_a - \psi_b)$$

Its density distribution function (or probability distribution function):

$$\rho(2) = \phi_2^* \phi_2 = (\psi_a^2 + \psi_b^2 - 2\psi_a \psi_b)/[2(1-S_{ab})]$$

It is provable that this MO has no electron density at the midpoint of the H-H bond (i.e., the value of this function is zero at the midpoint`

H_2^+

$$\phi_{1s}^{*} = \frac{1}{\sqrt{2(1-S_{ab})}}(\psi_a - \psi_b)$$

$$\rho(\phi_{1\mathrm{s}}^{*}) = (\phi_{1\mathrm{s}}^{*})^{*}\phi_{1\mathrm{s}}^{*} = (\psi_a{}^2 + \psi_b{}^2 - 2\psi_a\psi_b)/[2(1-S_{ab})]$$

Both ψ_a and ψ_b are 1s AO of H. Their values depend solely on the electron-nuclei distance. At the midpoint of H-H bond, $r_a=r_b = R_{H\text{-}H}/2$, thus we have

$$\psi_a\ (R/2) = \psi_b\ (R/2)$$

$$\Rightarrow \rho(\phi_{1\mathrm{s}}^{*})_{\mathrm{r}_a=r_b=R/2} = A[\psi_a{}^2(R/2) + \psi_b{}^2(R/2)$$
$$-2\psi_a(R/2)\psi_b(R/2)] = 0$$

Structural Chemistry

- Chapter 1. The basic knowledge of quantum mechanics
- 1.1. The naissance of quantum mechanics
- 1.2 The basic assumptions in quantum mechanics
- 1.3 Simple applications of quantum mechanics

- Chapter 2. The structure of atoms
- 2.1 The Schrödinger equation and its solution for one-electron
- 2.2 The physical significance of quantum number
- 2.3 The structure of multi-electron atoms
- 2.4 Atomic spectra and spectral term

- Chapter 3 The symmetry of molecules
- 3.1 Symmetry operations and symmetry elements
- 3.2 Point groups
- 3.3 The dipole moment and optical activity

- Chapter 4. Diatomic molecules
- 4.1 Treatment of variation method for the H_2^+ ion
- 4.2 Molecular orbital (MO) theory and diatomic molecules
- 4.3 Valence-bond (VB) theory and the structure of hydrogen molecule

Simple one-particle system → Solvable

- Particle in a Box
- Harmonic Oscillator
- Hydrogen Atom & H-like ions
- Rigid Rotor
- Hydrogen Molecule Ion

Complex system → not separable

For example: many-electron atom or molecule

An approximation to the real solution of a complex system: The variation theorem!