What’s a chemical bond?
Chemical Bonding

Quantum mechanical theory for description of molecular structures and chemical bondings

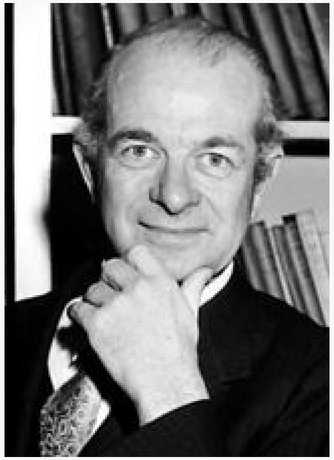
- **Molecular Orbital (MO) Theory**
  a) Proposed by Hund, Mulliken, Lennard-Jones et al. in 1930s.
  b) Further developments by Slater, Hückel and Pople et al.
  c) MO-based softwares are widely used nowaday, e.g., Gaussian

- **Valence Bond (VB) Theory**
  a) Proposed by Heitler and London 1930s, further developments by Pauling and Slater et al.
  b) Programmed in later 1980s, e.g., latest development--XMVB!

- **Density Functional Theory**
  a) Proposed by Kohn et al.
  b) DFT-implemented QM softwares are widely used, e.g., Gaussian.

Slater

Pauling



Kohn

↓

卢嘉锡

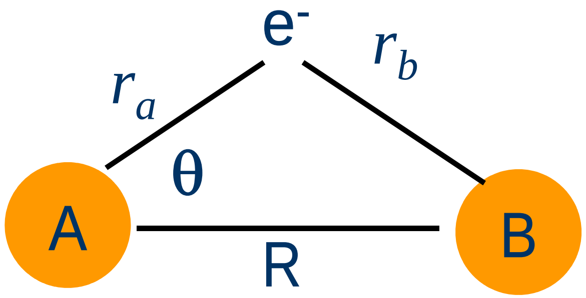
Chapter 4 The structure of diatomic molecules

§ 1 Treatment of variation method for the H_2^+ ion

1. Shroedinger equation of H_2^+

Born-Oppenheimer Approximation

- The electrons are much lighter than the nuclei.
- Nuclear motion is slow relative to the electron motion.



The Hamiltonian operator

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

Where r_a and r_b are related by:

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

Shroedinger equation of H_2^+

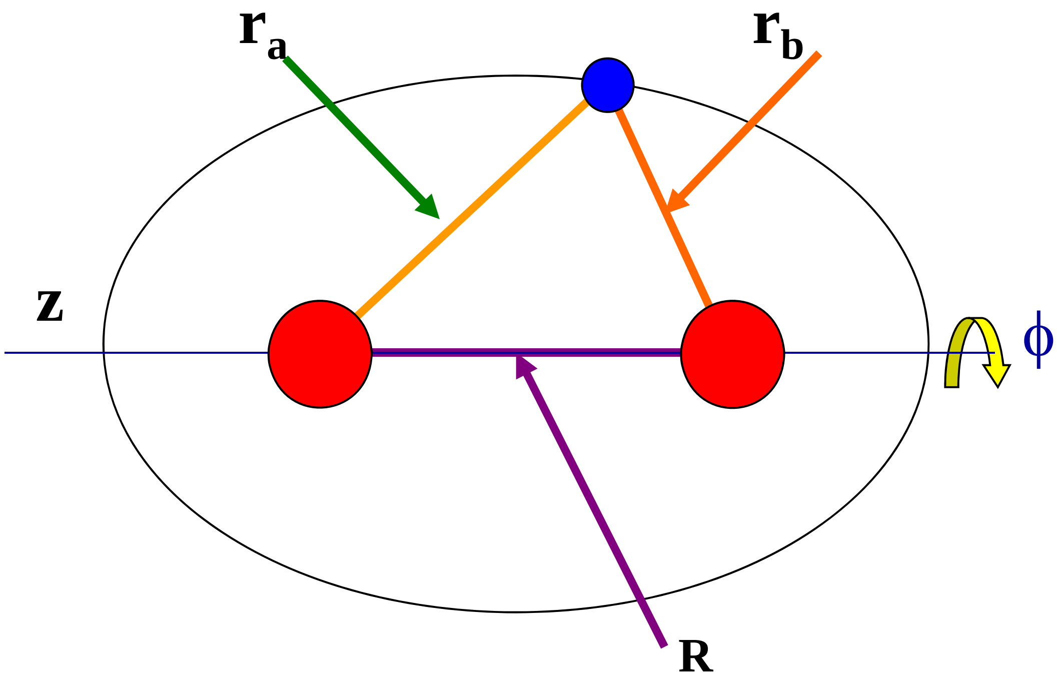
$$\hat{H}\psi = E\psi$$

Molecular Orbital Theory H_2^+

We could now solve: $\hat{H}(r_1,R)\psi(r_1,R) = E_e(R)\psi(r_1,R)$

This is possible but tedious

H_2^+ can be solved exactly using confocal elliptical coordinates:



$\xi = (r_a+r_b)/R$
$\eta = (r_a-r_b)/R$
ϕ is a rotation around z

$0 \le \phi \le 2\pi$;
$1 \le \xi \le \infty$;
$-1 \le \eta \le 1$

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

where $m=0, \pm 1, \pm 2, \pm 3, \ldots$

The associated quantum number is λ. → orbital angular momentum

$$\lambda = |m|$$

Each electronic level with $m \neq 0$ is doubly degenerate, i.e. $+|m|, -|m|$

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

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

λ	**0**	**1**	**2**	**3**	**4**
letter	σ	π	δ	ϕ	γ

H_2^+ : r_0 = 2 Bohr
E_b = 2.71 eV

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,

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

Proof

$$\phi(\varepsilon \ge E_0) \quad \text{its} \quad ground \quad state \ (\psi_0 \to E_0)$$

ψ_1, ψ_2, ψ_3 …consist of an orthogonal normalized set of wavefunctions

$$\phi = \sum_i c_i \psi_i$$

$$\hat{H}\psi_i = E_i \psi_i \qquad\qquad E_i \ge E_0$$

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

$$\int \phi^* \hat{H} \phi d\tau = \int \sum_i c_i^* \psi_i^* \hat{H} \sum_j c_j \psi_j d\tau = \sum_i c_i^* \sum_j c_j \int \psi_i^* \hat{H} \psi_j d\tau$$

$$= \sum_i \sum_j c_i c_j \int \psi_i^* E_j \psi_j d\tau = \sum_i \sum_j c_i c_j E_j \int \psi_i^* \psi_j d\tau$$

$$\int \phi^* \phi d\tau = \int \sum_i c_i^* \psi_i^* \sum_j c_j \psi_j d\tau = \sum_i c_i^* \sum_j c_j \int \psi_i^* \psi_j d\tau$$

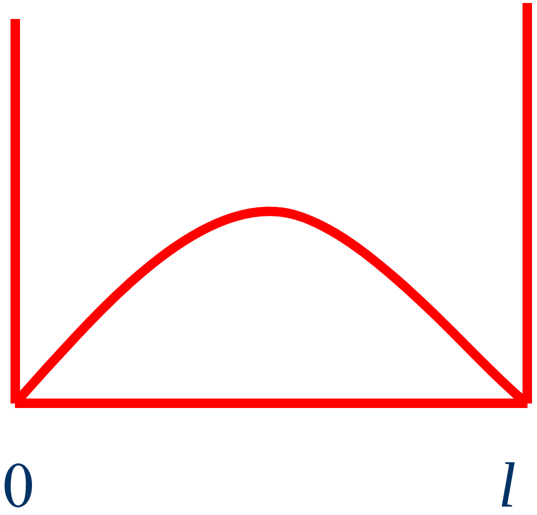
$$= \sum_i \sum_j c_i c_j \delta_{ij}$$

$$\varepsilon =< E >= \frac{\sum_i \sum_j c_i c_j E_j \int \psi_i^* \psi_j d\tau}{\sum_i \sum_j c_i c_j \delta_{ij}} = \frac{\sum_i |c_i|^2 E_j}{\sum_i |c_i|^2} \ge \mathrm{E}_0$$

Example: **Devise a trial variation function for 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:

$$\phi = x(l-x)$$ for 0≤x ≤*l*



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

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

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

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 $\frac{\partial \varepsilon}{\partial c_i} = 0$

Example

$$\phi = c_1\psi_1 + c_2\psi_2 \qquad \varepsilon = \frac{\int \phi^* \hat{H}\phi d\tau}{\int \phi^* \phi d\tau}$$

$$S_{ij} = \int \psi_i^* \psi_j d\tau = [S_{ij}]^*$$

$$= \int \psi_i \psi_j^* d\tau = S_{ji}$$

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

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

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

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

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

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

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

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

$$let \qquad \varepsilon = \frac{c_1{}^2 H_{11} + 2c_1c_2H_{12} + c_2{}^2 H_{22}}{c_1{}^2 S_{11} + 2c_1c_2S_{12} + c_2{}^2 S_{22}} = \frac{y}{x}$$

$$make \qquad \varepsilon \Rightarrow E_0$$

$$0 = \frac{\partial \varepsilon}{\partial c_1} = \frac{1}{x}\frac{\partial y}{\partial c_1} - \frac{y}{x^2}\frac{\partial x}{\partial c_1}$$

$$= \frac{1}{x}(2c_1H_{11} + 2c_2H_{12}) - \frac{y}{x^2}(2c_1S_{11} + 2c_2S_{12})$$

$$(2c_1H_{11} + 2c_2H_{12}) - \frac{c_1{}^2 H_{11} + 2c_1c_2H_{12} + c_2{}^2 H_{22}}{c_1{}^2 S_{11} + 2c_1c_2S_{12} + c_2{}^2 S_{22}}(2c_1S_{11} + 2c_2S_{12}) = 0$$

$$(2c_1H_{11} + 2c_2H_{12}) - E(2c_1S_{11} + 2c_2S_{12}) = 0$$

$$(c_1H_{11} + c_2H_{12}) - E(c_1S_{11} + c_2S_{12}) = 0$$

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

$$same \qquad as$$

$$0 = \frac{\partial \varepsilon}{\partial c_2}$$

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

$$seqular \qquad equation$$

$$made \qquad equation \qquad resolved(c_1, c_2 \neq 0)$$

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

$$get \qquad E \Rightarrow get \qquad c_1, c_2 \Rightarrow get \qquad \phi$$

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: $E_1 \leq E_2 \leq \ldots \leq E_n$.

- From the variation theorem, we know that the lowest value of root (W_1) is the upper bound for the system's ground-state energy.

$$\mathbf{E_1 \leq W_1}$$

- Moreover, it can be proved that the linear variation method provides upper bounds to the energies of the lowest n states of the system.

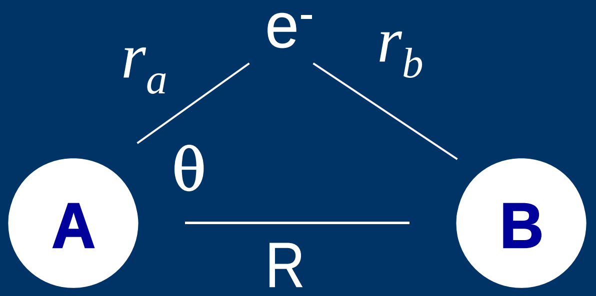
$$\mathbf{E_2 \leq W_2, \; E_3 \leq W_3, \ldots , E_n \leq W_n}$$

- We use the roots as approximations to the energies of the lowest states.

- If approximation to the energies of more states are wanted, we add more functions f_k to the trial function ϕ.

- The addition of more functions f_k can be shown to increase the accuracy of the previously calculated energies.

3. The solution of H_2^+



For H_2^+ that is :

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

$$1s_B = \frac{e^{-r_b}}{\sqrt{\pi}} = \psi_b$$

Note : we have as many linear combinations as we have atomic orbitals

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

Trial function

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

seqular *equation*

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

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

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

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

if $H_{aa} - ES_{aa} = -(H_{ab} - ES_{ab})$

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

if $H_{aa} - ES_{aa} = H_{ab} - ES_{ab}$

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

substituting E_1 *to seqular equation*

$$(H_{aa} - ES_{aa})c_a + (H_{ab} - ES_{ab})c_b = 0 \qquad (1)$$

$$(H_{ba} - ES_{ba})c_a + (H_{bb} - ES_{bb})c_b = 0 \qquad (2)$$

$$S_{aa} = S_{bb} = 1$$

$$(H_{aa} - \frac{H_{aa} + H_{ab}}{1 + S_{ab}})c_a + (H_{ab} - \frac{H_{aa} + H_{ab}}{1 + S_{ab}} S_{ab})c_b = 0$$

$$(H_{aa}(1 + S_{ab}) - (H_{aa} + H_{ab}))c_a + (H_{ab}(1 + S_{ab}) - (H_{aa} + H_{ab})S_{ab})c_b = 0$$

$$(H_{aa}(1 + S_{ab}) - (H_{aa} + H_{ab}))c_a + (H_{ab}(1 + S_{ab}) - (H_{aa} + H_{ab})S_{ab})c_b = 0$$

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

$$c_a - c_b = 0 \qquad c_a = c_b$$

$$\varphi_1 = c_a\psi_a + c_b\psi_b = c_a(\psi_a + \psi_b)$$

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

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

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

$$2c_a{}^2(1 + S_{ab}) = 1$$

$$\therefore \qquad c_a = \frac{1}{\sqrt{2(1+S_{ab})}}$$

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

$substituting \quad E_2 \quad to \quad seqular \quad equation$

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

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

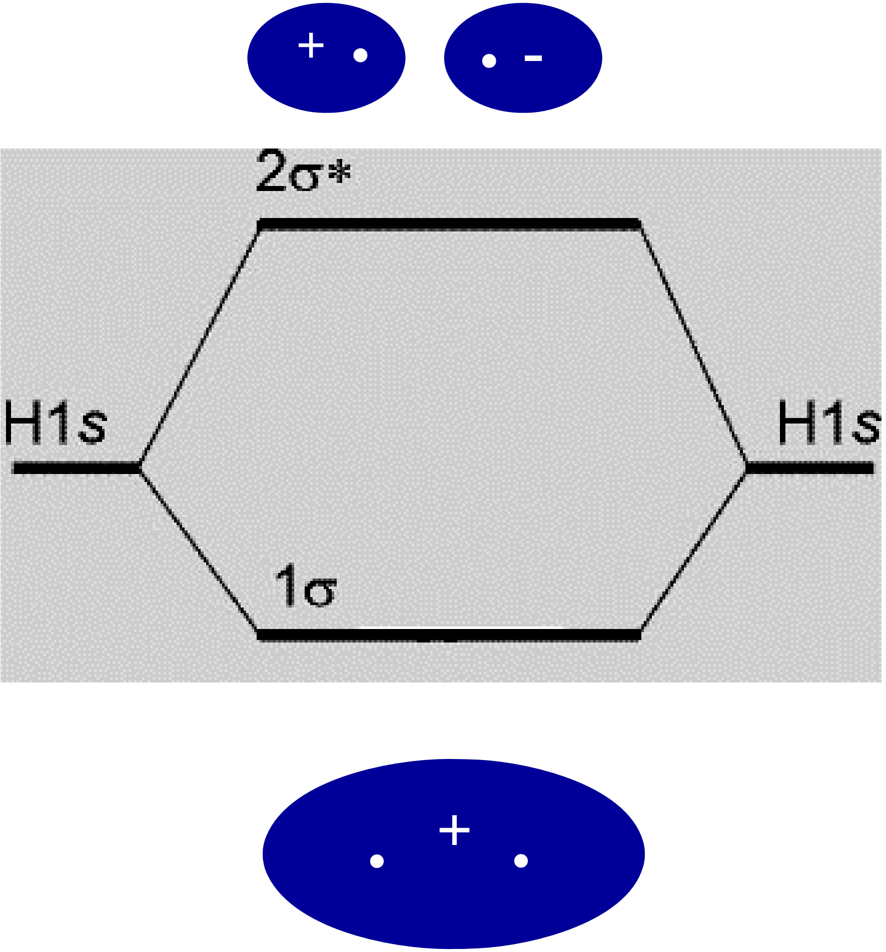
$$\phi_2 = \frac{1}{\sqrt{2(1-S_{ab})}}(\psi_a - \psi_b)$$

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

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

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

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



Overlap integral

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

Coulombic integral

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

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

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

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

$$= E_H + \underline{\frac{1}{R} - \int \psi_a^{*} \frac{1}{r_b} \psi_a d\tau} = E_H + J$$

$$J \approx 5.5\% E_H$$

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

Resonance integral

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

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

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

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

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

$$= E_H S_{ab} + K$$

$$= \beta$$

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

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

$$H_{ab} = E_H S_{ab} + K = \beta$$

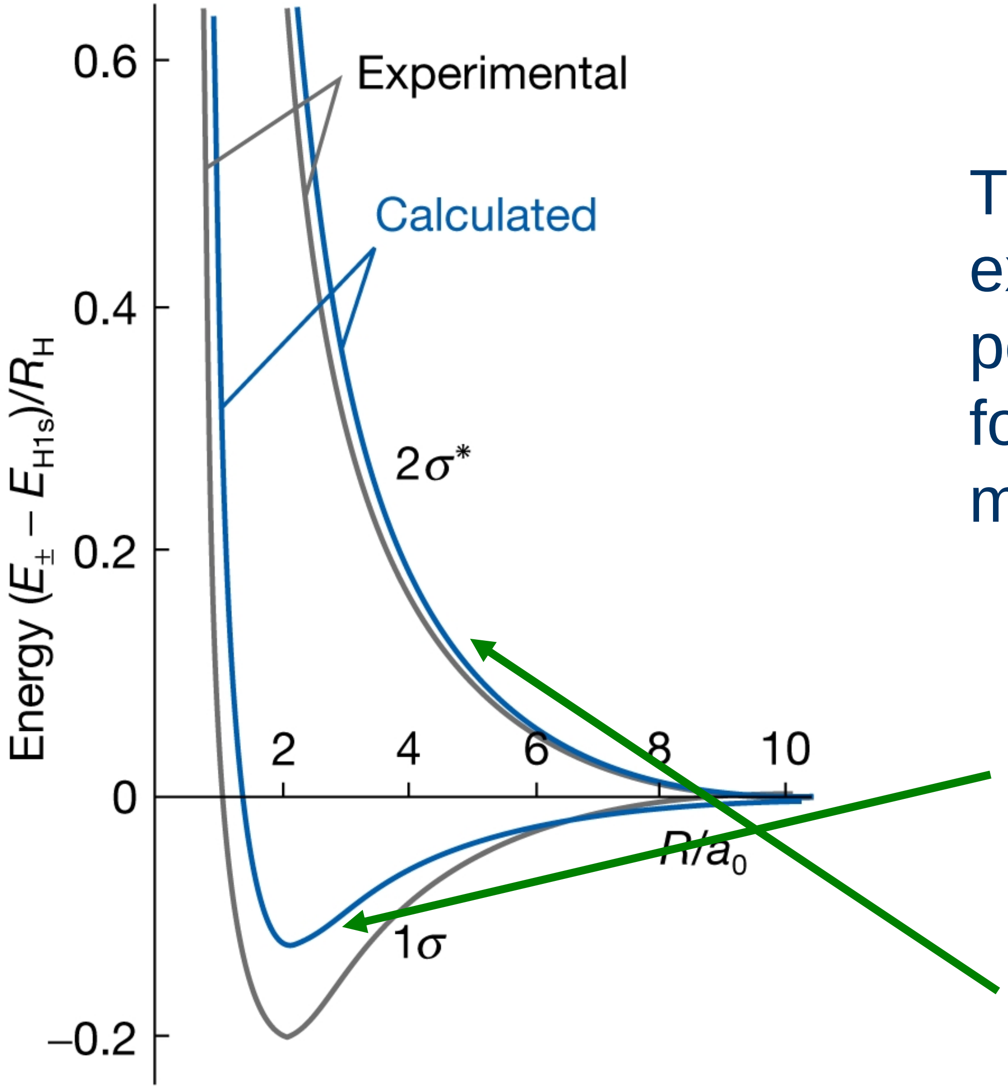
$$E_a = \frac{H_{aa} + H_{ab}}{1 + S_{ab}}$$

$$E_b = \frac{H_{aa} - H_{ab}}{1 - S_{ab}}$$

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

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

H_2^+



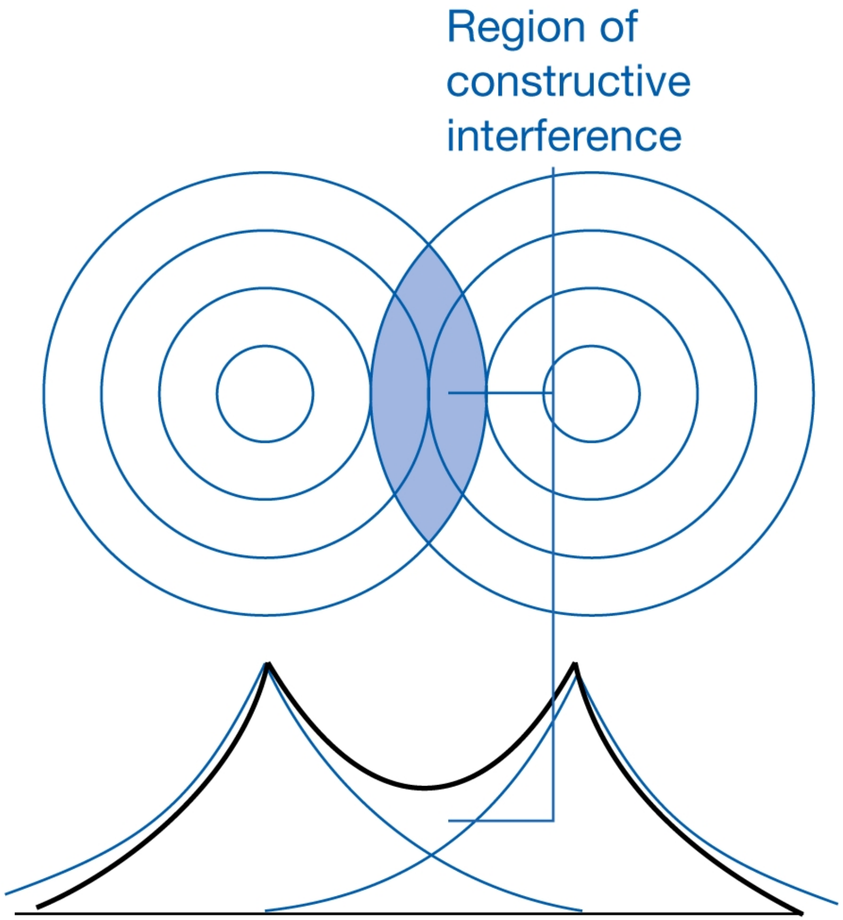
The calculated and experimental molecular potential energy curves for a hydrogen molecule-ion.

$$E_1 = E_H + \frac{J + K}{(1 + S)}$$

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

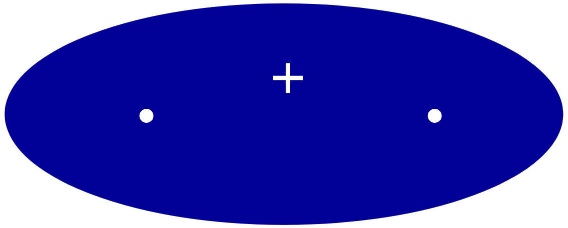
Molecular Orbital Theory

$\mathbf{H_2^+}$



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

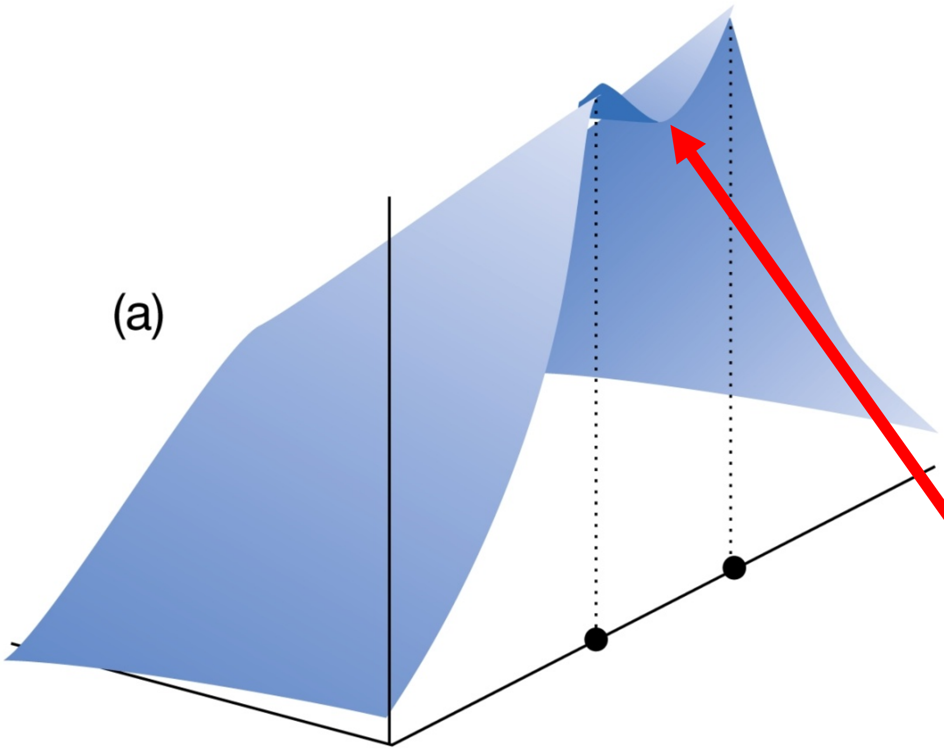
$$\phi_1 = \frac{1}{\sqrt{2(1+S_{ab})}}(\psi_a + \psi_b)$$



σ_s

Molecular Orbital Theory

H_2^+

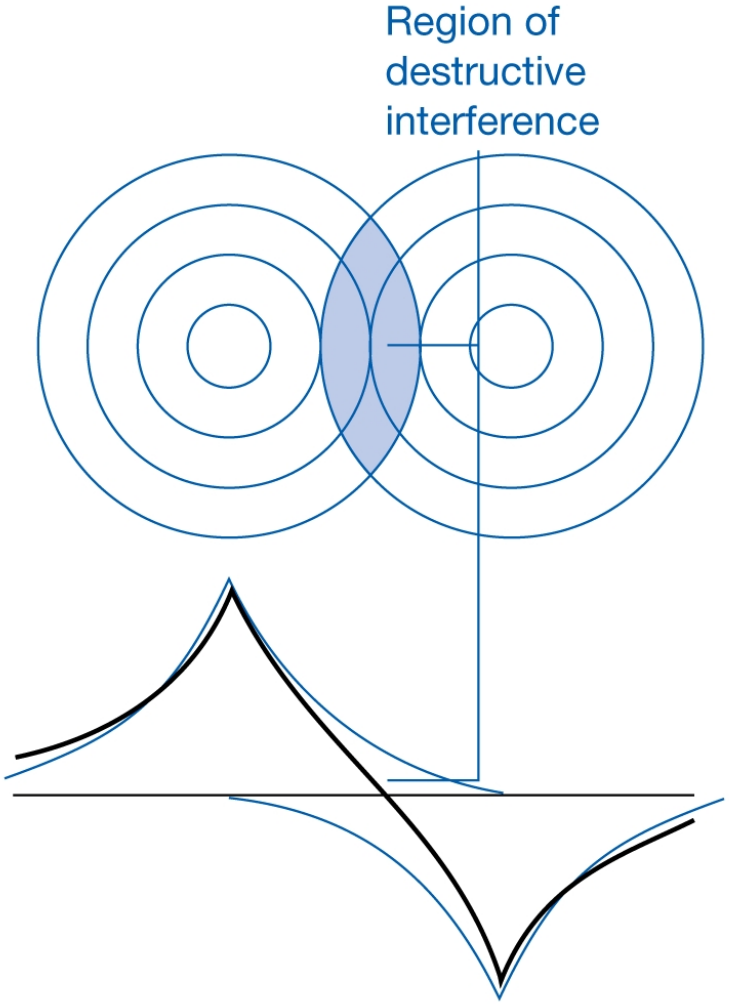


The electron density calculated by forming the square of the wavefunction.
Note the accumulation of electron density in the internuclear region.

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

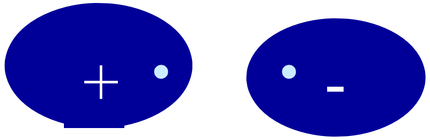
Molecular Orbital Theory

H_2^+



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

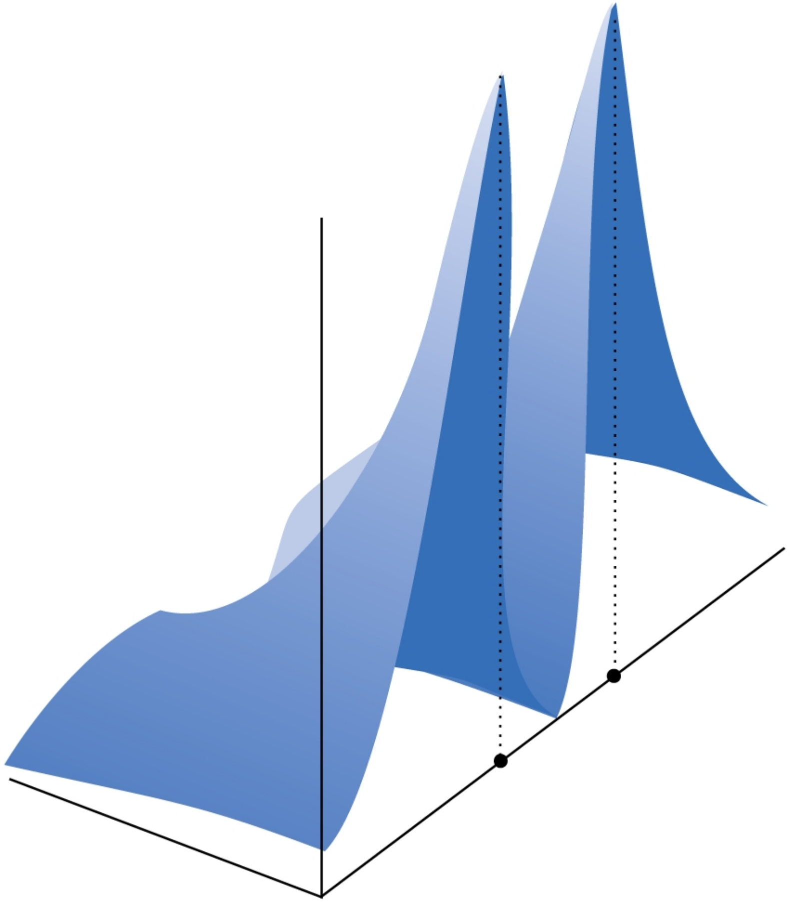
$$\phi_2 = \frac{1}{\sqrt{2(1-S_{ab})}}(\psi_a - \psi_b)$$



σ_s^*

Molecular Orbital Theory

H_2^+

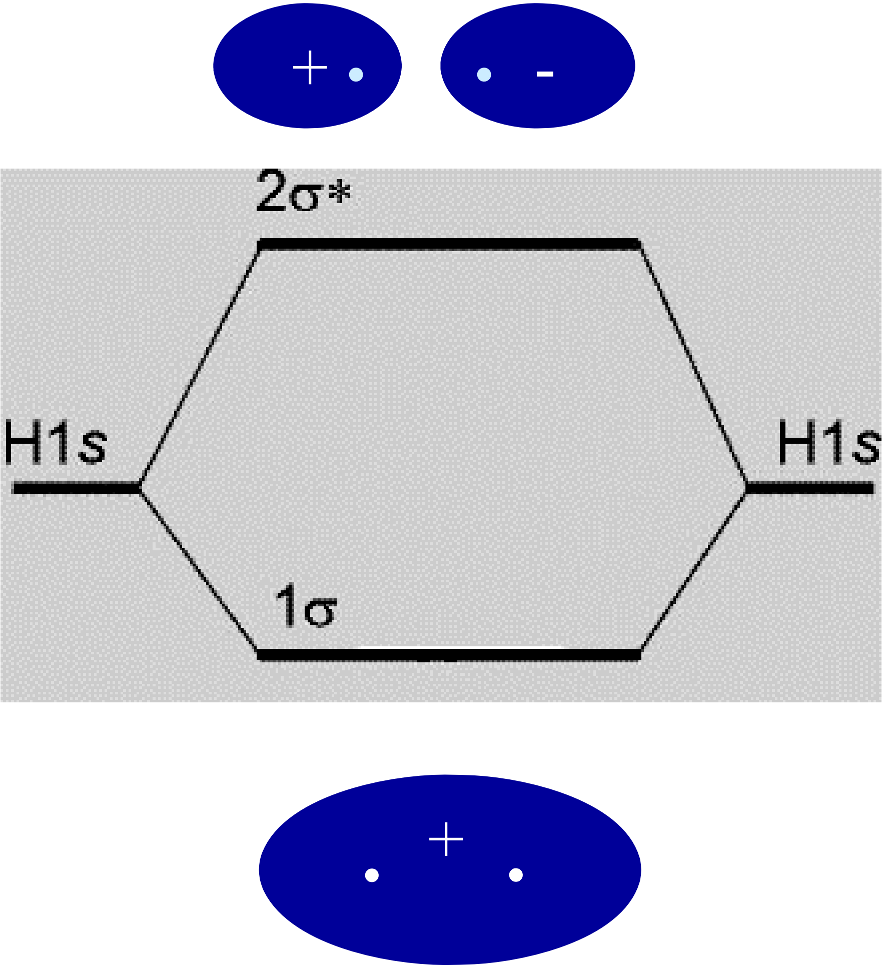


The electron density calculated by forming the square of the wavefunction. Note that the elimination of electron density from the internuclear region.

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

Molecular Orbital Theory

H_2^+



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.

§ 2 Molecular orbital theory and diatomic molecules

1. Molecular orbital (MO) theory

a. Every electron in a molecule is in an average potential field of the nuclei and the other electrons.

The state of electron i is described by the ψ_i wavefunction.

------- the one-electron wavefunction

$$\varphi(1,2,\ldots n) = \psi_1(1)\psi_2(2)\ldots\psi_n(n)$$

$$\hat{H} = \sum_i \hat{H}_i$$

$$\hat{H}_i\psi_i = E_i\psi_i$$

b. The formation of molecular orbital (MO).

The MO may be approximated from the linear combination of atomic orbitals (LCAO).

Three basic requirements in the formation of MO:

* The AOs should have comparable energy, have compatible symmetry and be able to have maximum overlap.

The building-up principle in molecules:

Pauli exclusion principle, the minimum energy principle and Hund’s rule.

Why should the AOs should have comparable energy?

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

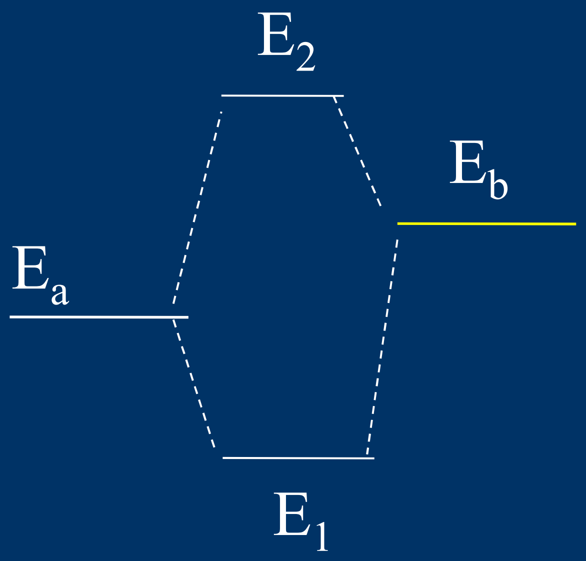
$$seqular \quad equation$$

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

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

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

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

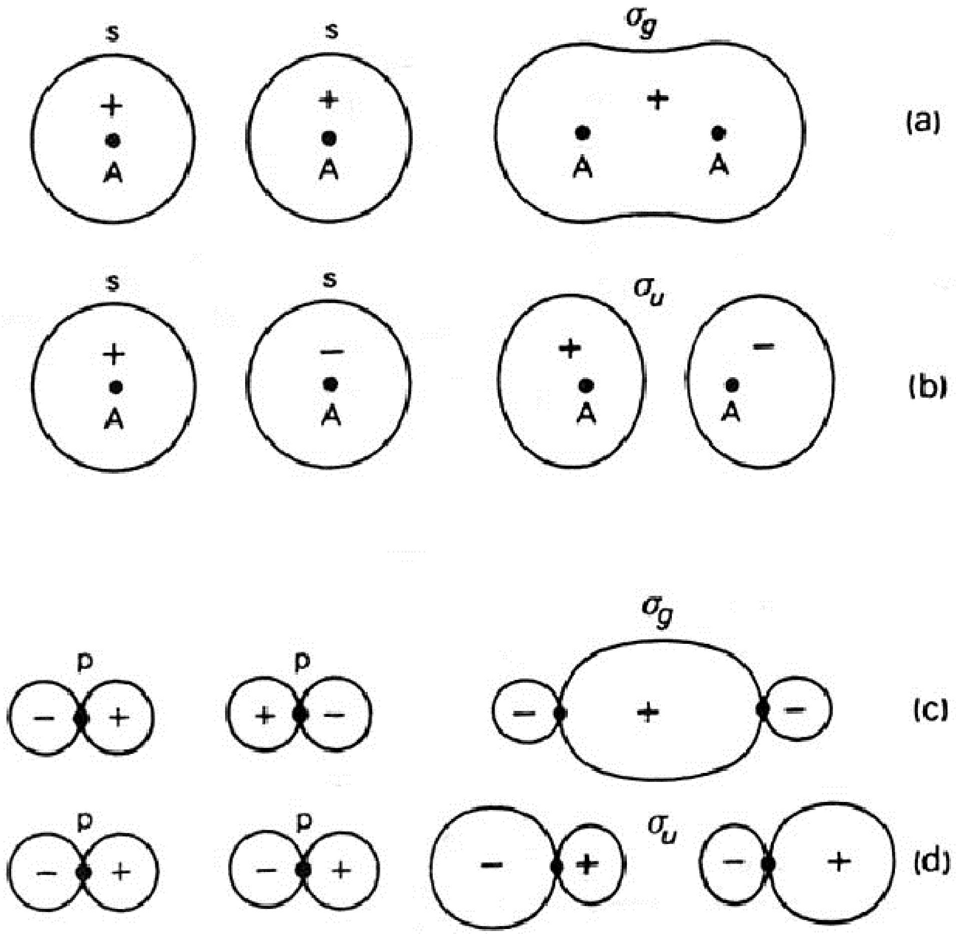


$(E_b-E_a)>>|\beta|$ => $E_1 \approx E_a$, $E_2 \approx E_b$

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

2. The characteristic distribution and classification of molecular orbitals

a. σ-orbital and σ-bond

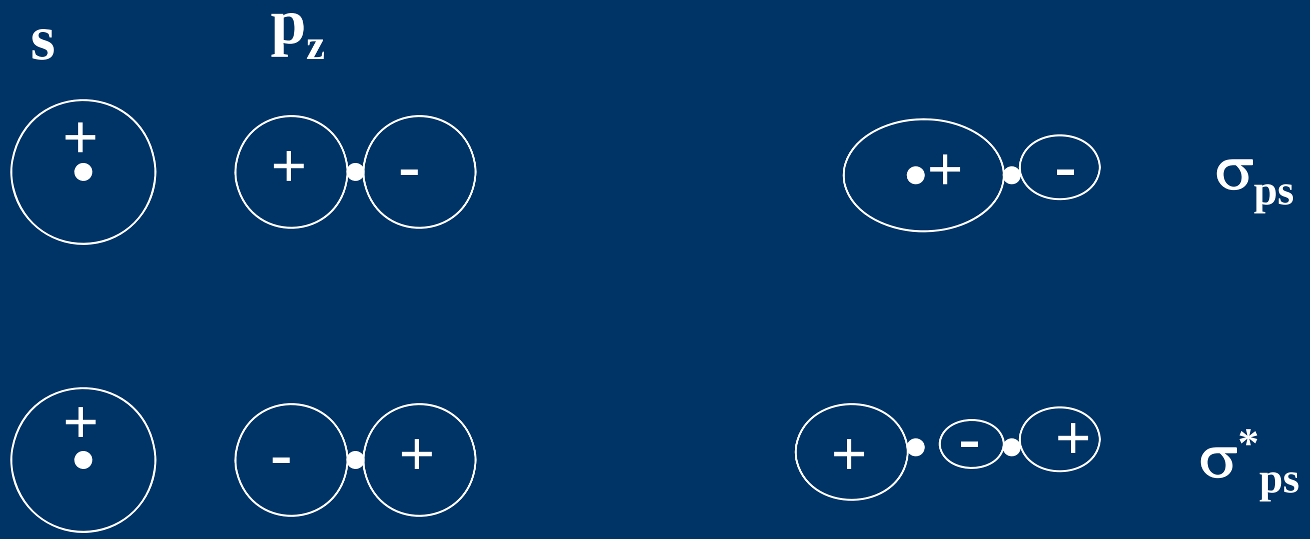


σ_s

$\sigma_s{}^*$

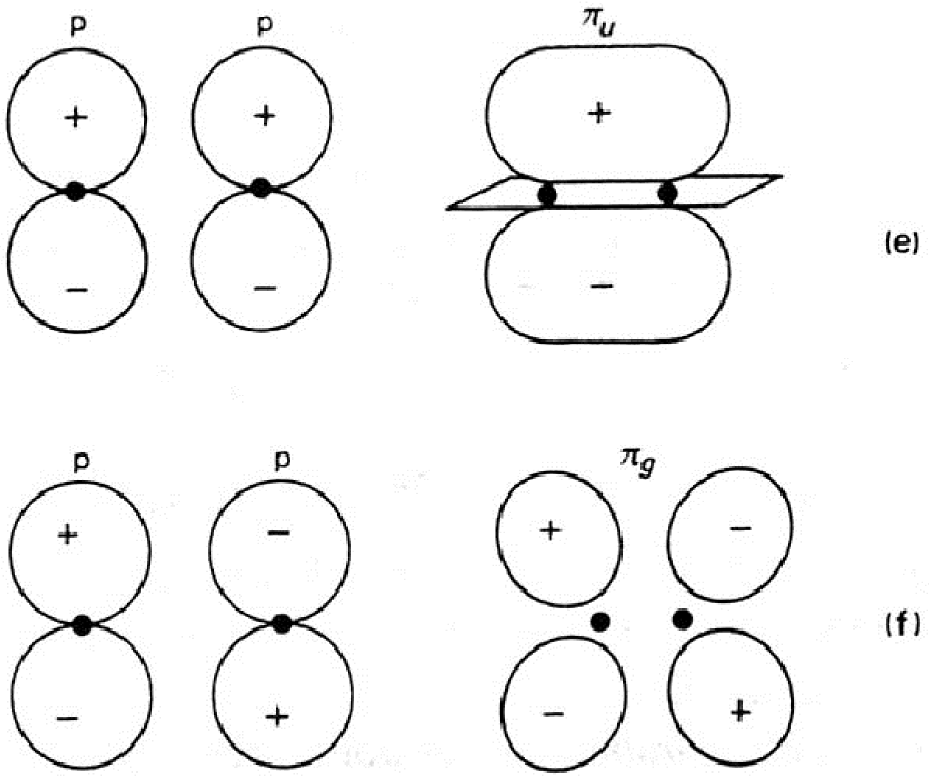
σ_p

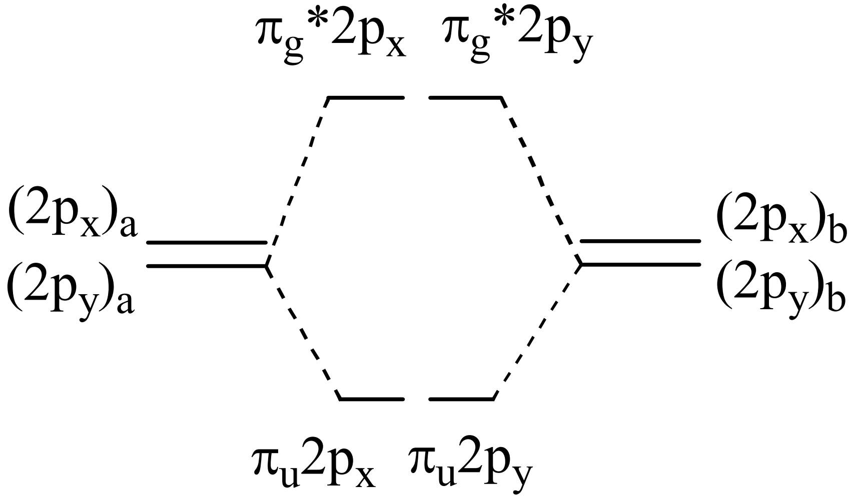
$\sigma_p{}^*$


s
p_z
+
+
-
σ_{ps}
+
+
-
+
-
+
+
-
+
σ^*_{ps}

2. The characteristic distribution and classification of molecular orbital

b. π-orbital and π-bond





$\pi_g{}^*2p_x$ $\pi_g{}^*2p_y$

$(2p_x)_a$
$(2p_y)_a$

$(2p_x)_b$
$(2p_y)_b$

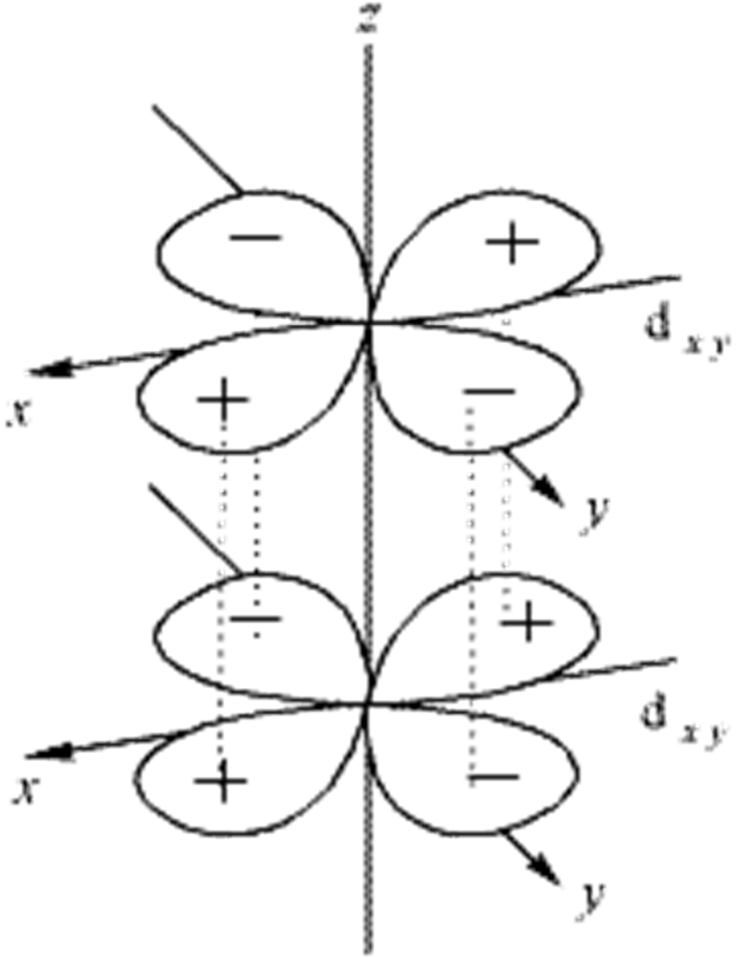
$\pi_u 2p_x$ $\pi_u 2p_y$

2. The characteristic distribution and classification of molecular orbital

c. δ-orbital and δ-bond

$Re_2Cl_8^{2-}$, $Mo_2Cl_8^{4-}$

^{75}Re: S^2d^5; Re^{3+}: d^4

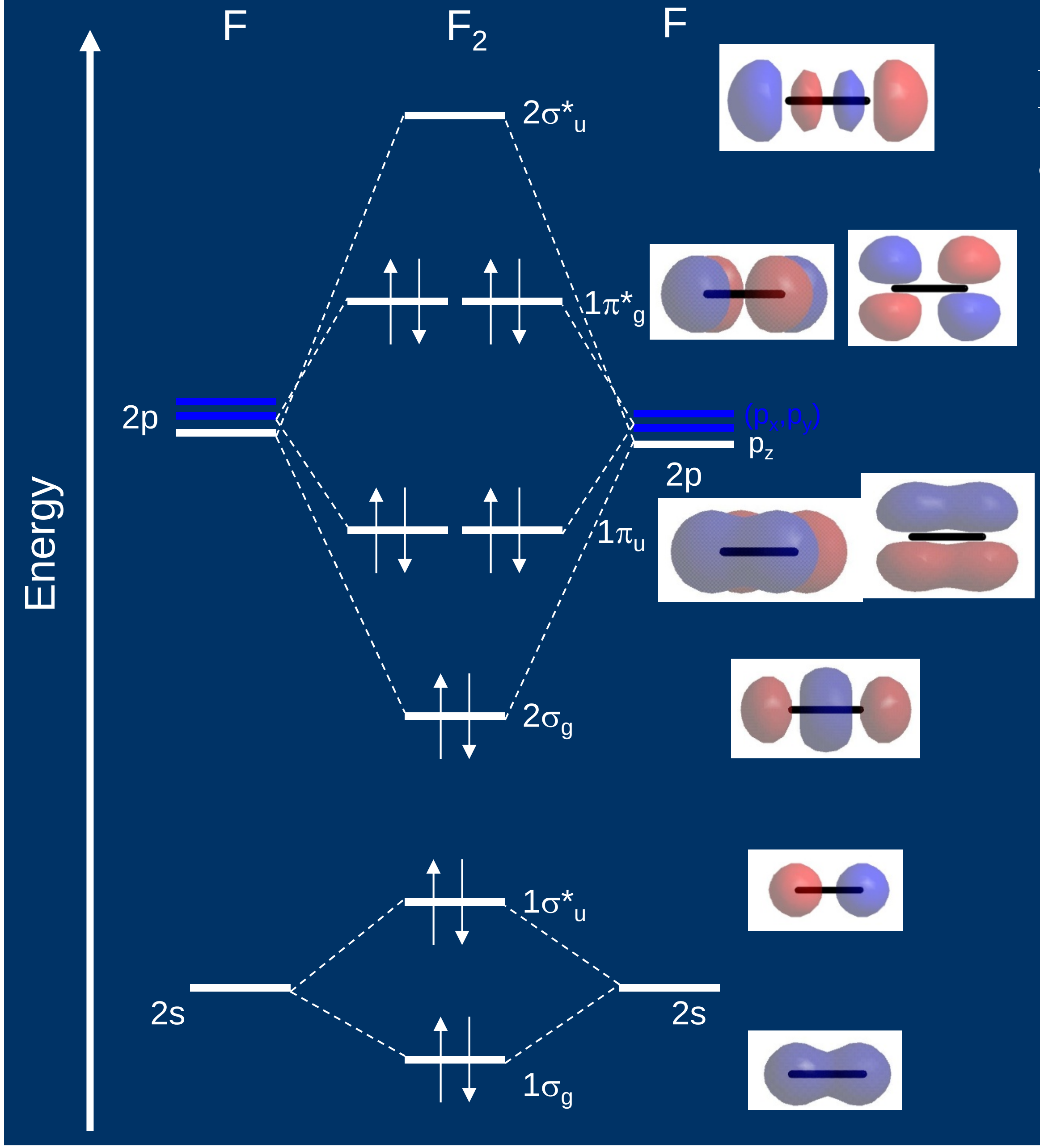


(a)

(b)

3. The structure of homonuclear diatomic molecules

a. The ground-state electronic configurations

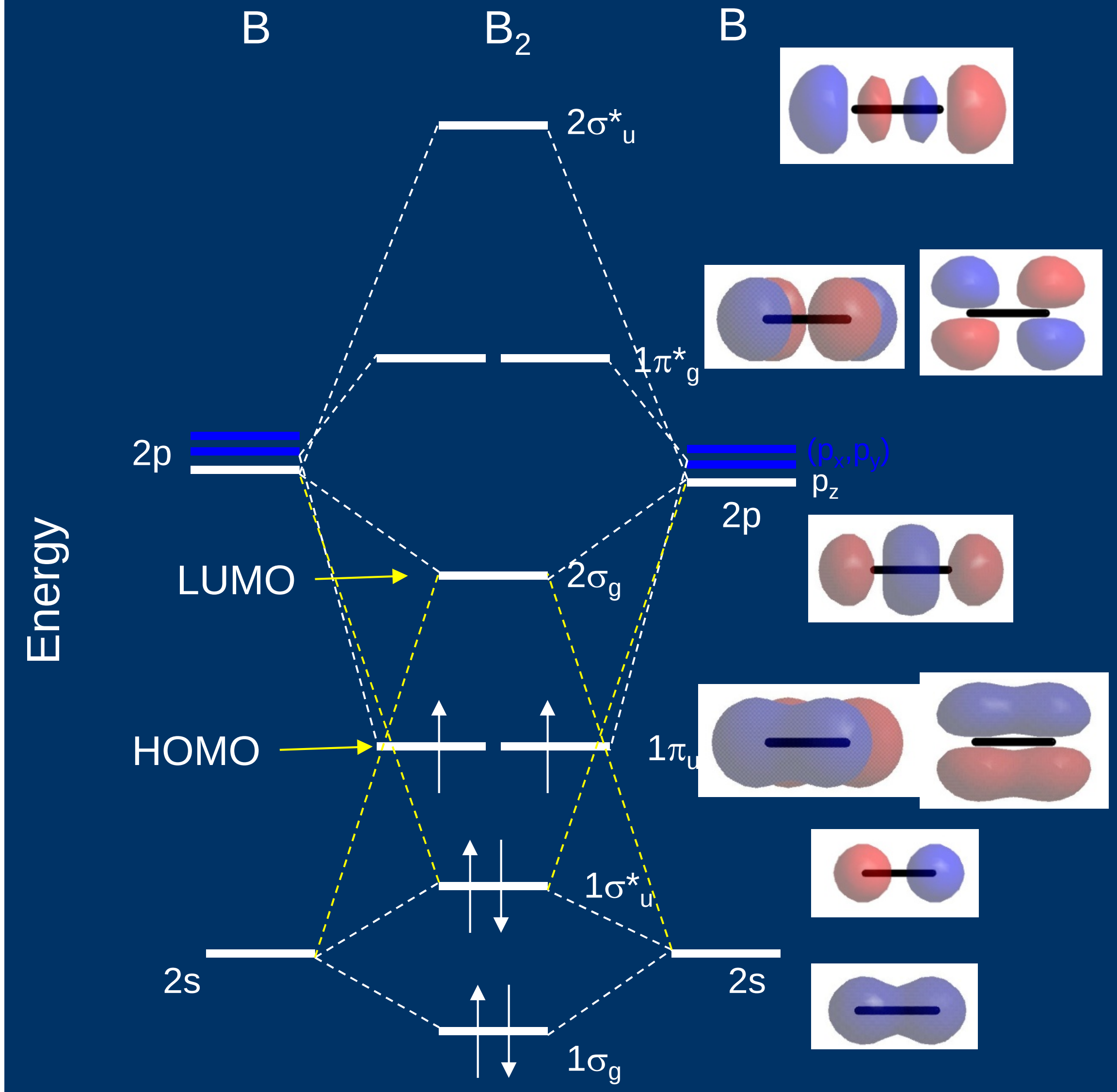


For oxygen and fluorine, 2p and 2s are well separated.

O_2: KK$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^2$

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

Molecular Orbital Theory



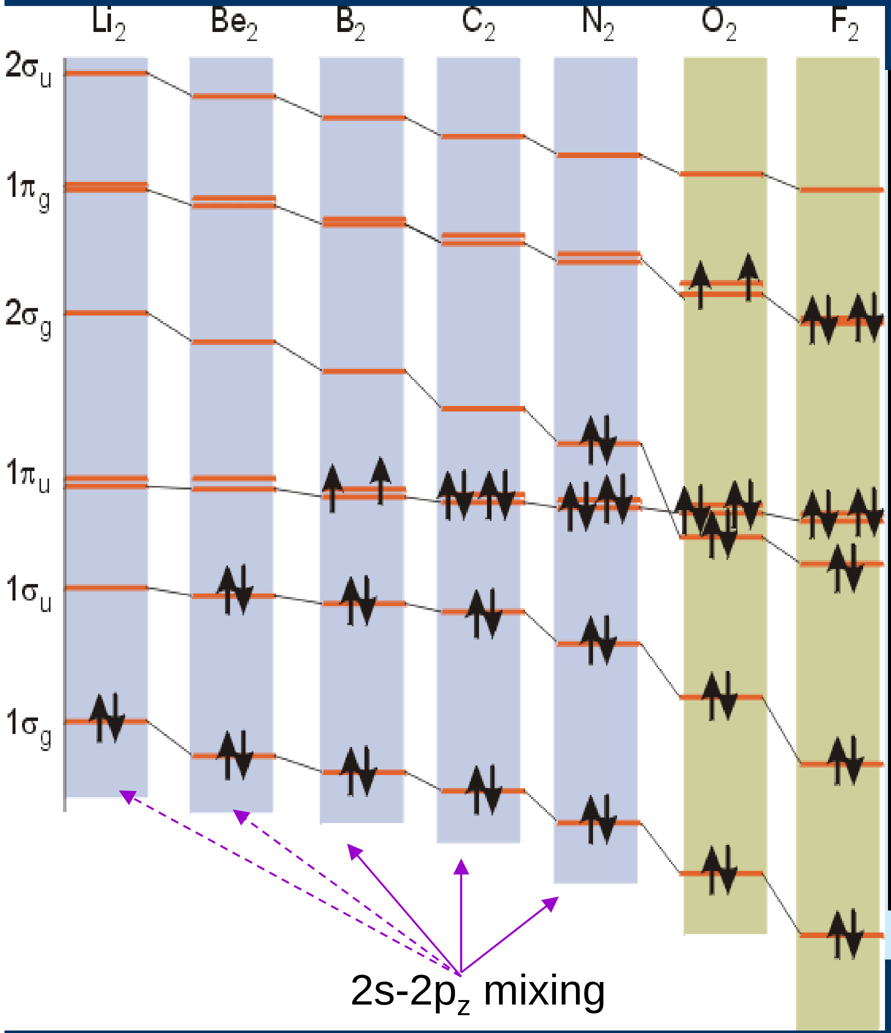
The effect of interactions between 2s and 2p.

At the start of the second row Li-N, we have mixing of 2s and 2p. The result is that $1\sigma_u$* is pushed down in energy whereas $2\sigma_g$ is raised.

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

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

Electronic configurations



2s-2p$_z$ mixing

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	$KK(\sigma_{g2s})^2\,(\sigma_{u2s})^2\,(\sigma_{g2p})^2\,(\pi_{u2p})^4\,(\pi_{g2p})^4$

3. The structure of homonuclear diatomic molecules

b. The bond order

Bond orders :

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

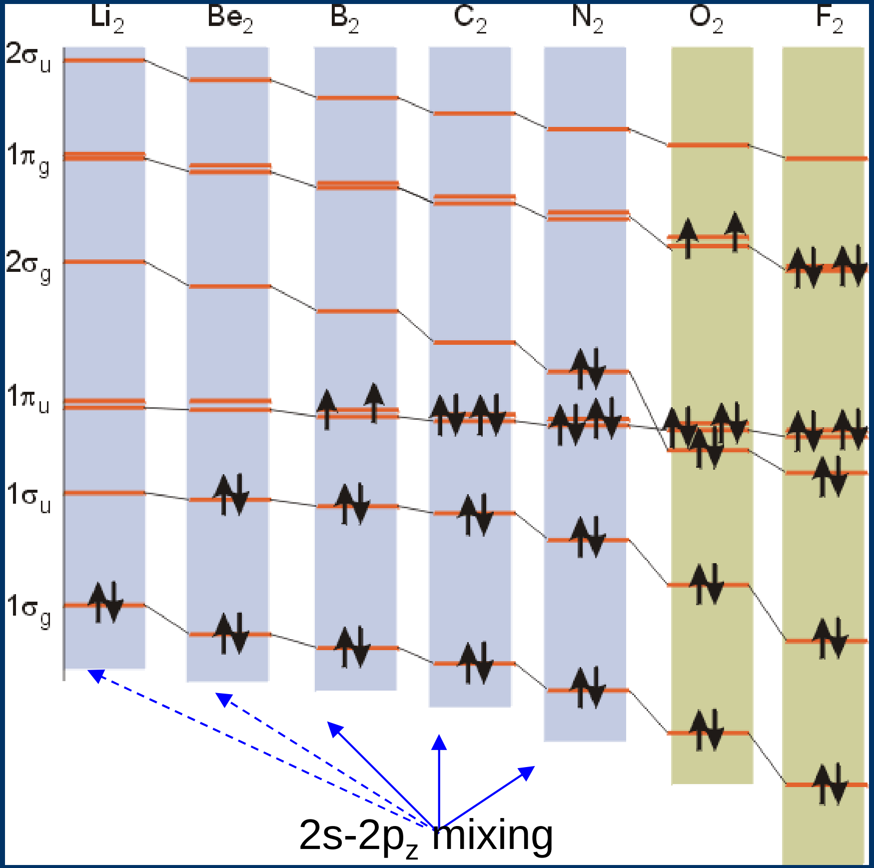
n: Electrons in bonding orbitals

n*: Electrons in antibonding orbitals

Diatomic molecules

Bond orders :

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



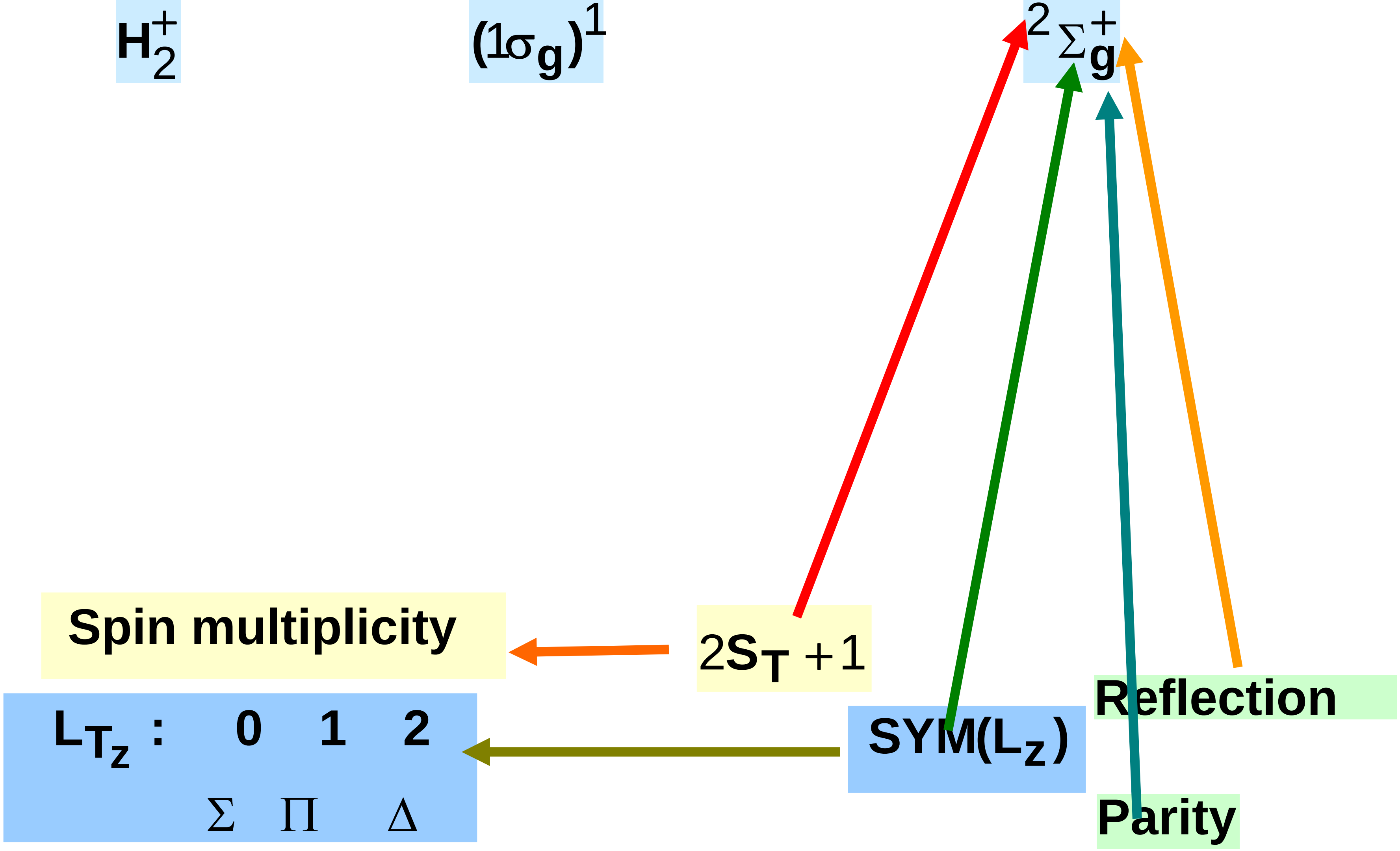
Molecule	Li$_2$	Be$_2$	B$_2$	C$_2$	N$_2$	O$_2$	F$_2$	Ne$_2$
Bond Order	1	0	1	2	3	2	1	0
Bond Length (Å)	2.67	n/a	1.59	1.24	1.01	1.21	1.42	n/a
Bond Energy (kJ/mol)	105	n/a	289	609	941	494	155	n/a
Diamagnetic (d)/ Paramagnetic (p)	d	n/a	p	d	d	p	d	n/a

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

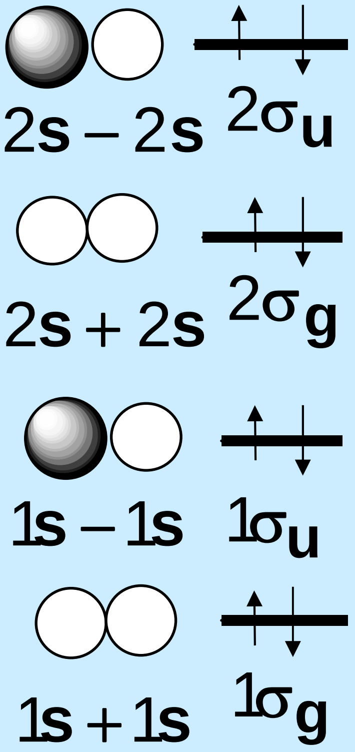
← SYM(L_z)

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

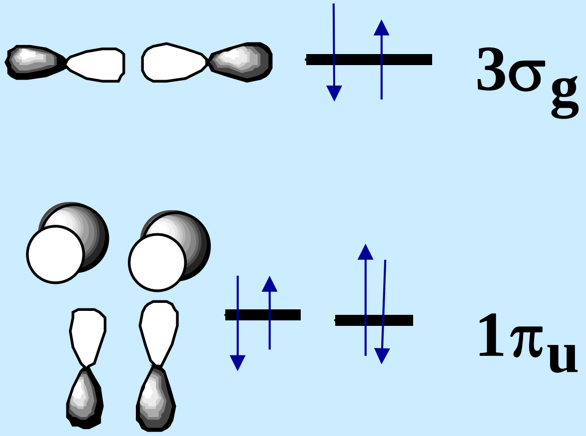
← SYM(L_z)

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

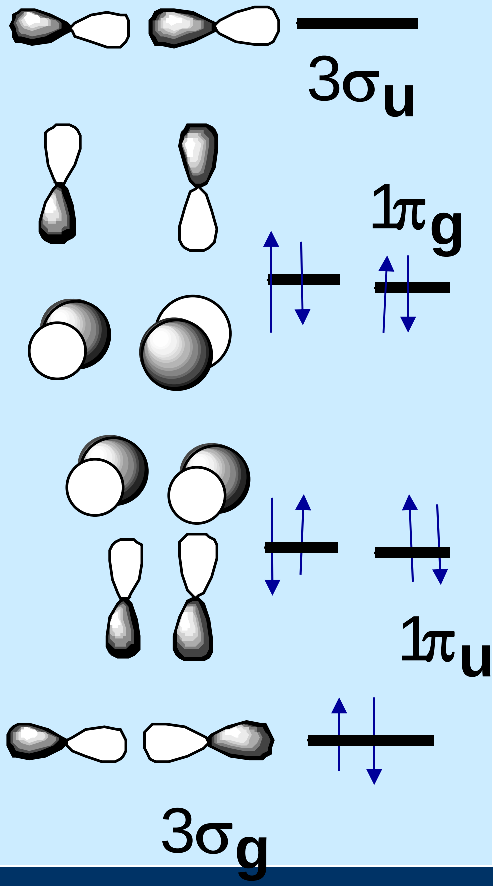
← $\mathrm{SYM}(L_z)$

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

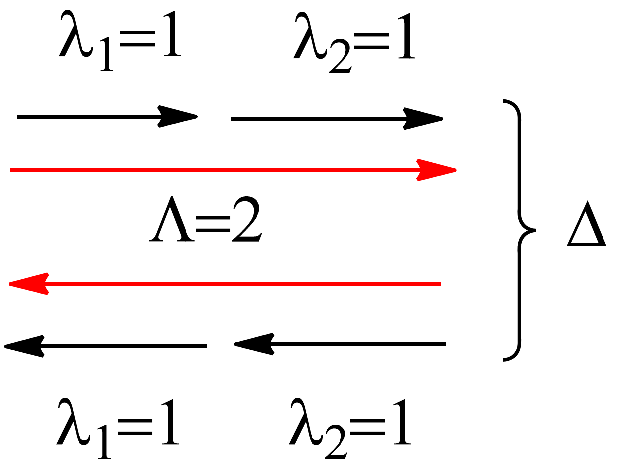
Σ Π Δ ← $\mathrm{SYM}(L_z)$

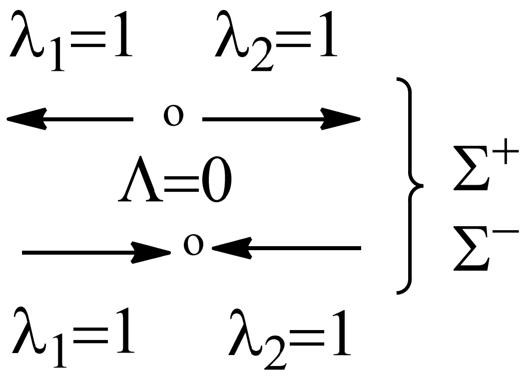
Reflection

Parity

O_2 $(1\pi_g)^2$ $^3\Sigma_g^-$ $^1\Delta_g$ $^1\Sigma_g^+$

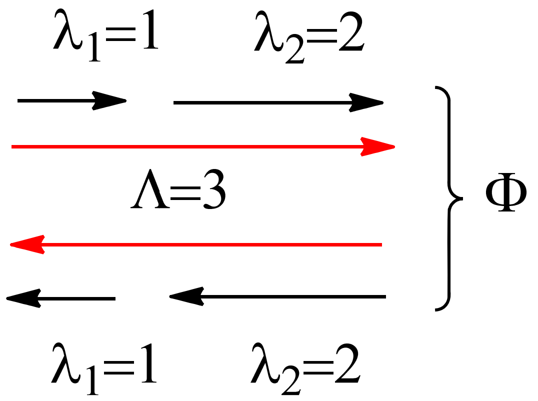
$(\pi\pi)$

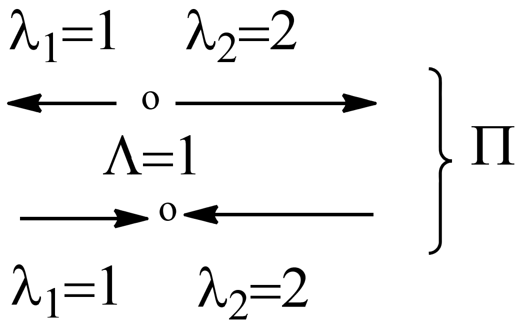




$^1\Delta$, $^3\Delta$, $^1\Sigma^+$, $^3\Sigma^+$, $^1\Sigma^-$, $^3\Sigma^-$

$(\pi\delta)$





$^1\Phi$, $^3\Phi$, $^1\Pi$, $^3\Pi$

Molecular-Orbital Configurations:

… N_2

$KK < 2\sigma_g < 2\sigma_u^* < 1\pi_u < 3\sigma_g < 1\pi_g^* < 3\sigma_u^* 2p$

O_2 …

$KK < 2\sigma_g < 2\sigma_u^* < 3\sigma_g < 1\pi_u < 1\pi_g^* < 3\sigma_u^* 2p$

MO Nomenclature for Homonuclear Diatomic Molecules

$\sigma_g 1s$	$\sigma_u^* 1s$	$\sigma_g 2s$	$\sigma_u^* 2s$	$\pi_u 2p$	$\sigma_g 2p$	$\pi_g^* 2p$	$\sigma_u^* 2p$
$1\sigma_g$	$1\sigma_u$	$2\sigma_g$	$2\sigma_u$	$1\pi_u$	$3\sigma_g$	$1\pi_g$	$3\sigma_u$

Properties of Homonuclear Diatomic Molecules in their Ground States

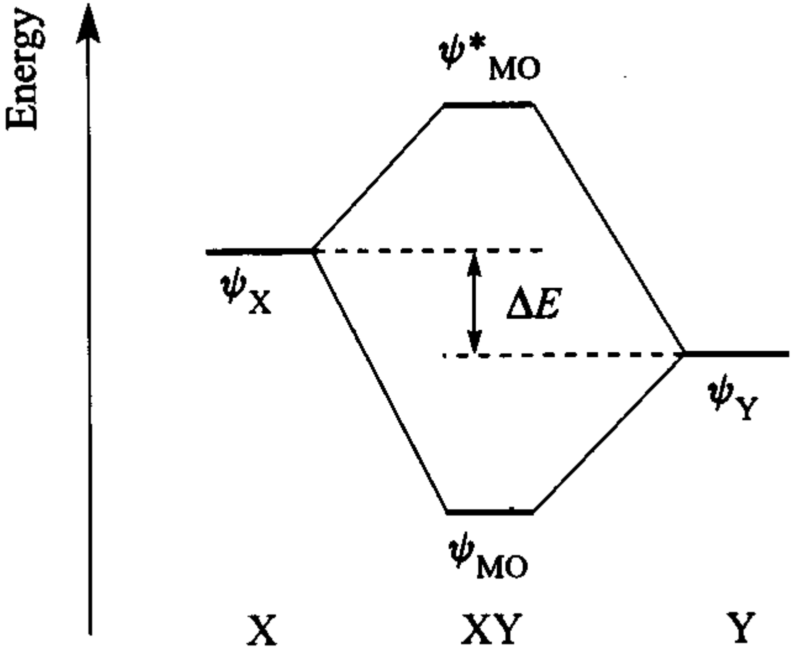
Species	Term	BO	De (eV)	Re (Å)
H_2^+	$^2\Sigma_g^+$	1/2	2.8	1.06
H_2	$^1\Sigma_g^+$	1	4.75	0.742
He_2^+	$^2\Sigma_u^+$	1/2	3	1.08
He_2	$^1\Sigma_g^+$	0	—	—
Li_2	$^1\Sigma_g^+$	1	1.1	2.67
Be_2	$^1\Sigma_g^+$	0	—	—
B_2	$^3\Sigma_g^-$ (?)	1	2.9	1.59
N_2^+	$^2\Sigma_g^+$	2.5	8.9	1.12
N_2	$^1\Sigma_g^+$	3	9.9	1.10
O_2^+	$^2\Pi_g$	2.5	6.8	1.12
O_2	$^3\Sigma_g^-$	2	5.2	1.21
F_2	$^1\Sigma_g^+$	1	1.6	1.42
Ne_2	$^1\Sigma_g^+$	0	—	—

4. The structure of heteronuclear diatomic molecules

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.

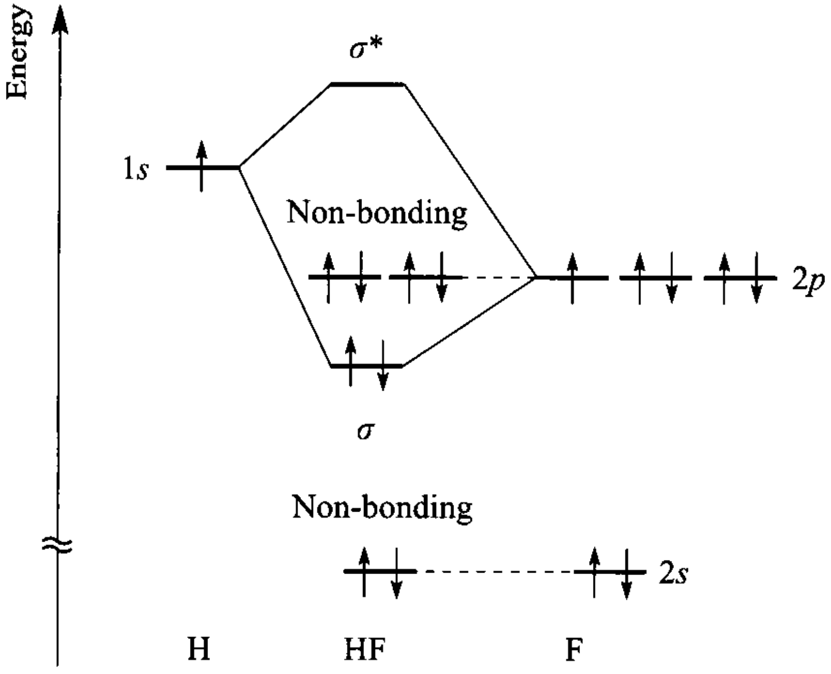
Ψ_X makes a greater contribution to the Ψ^*_{MO}



Ψ_Y makes a greater contribution to the Ψ_{MO}

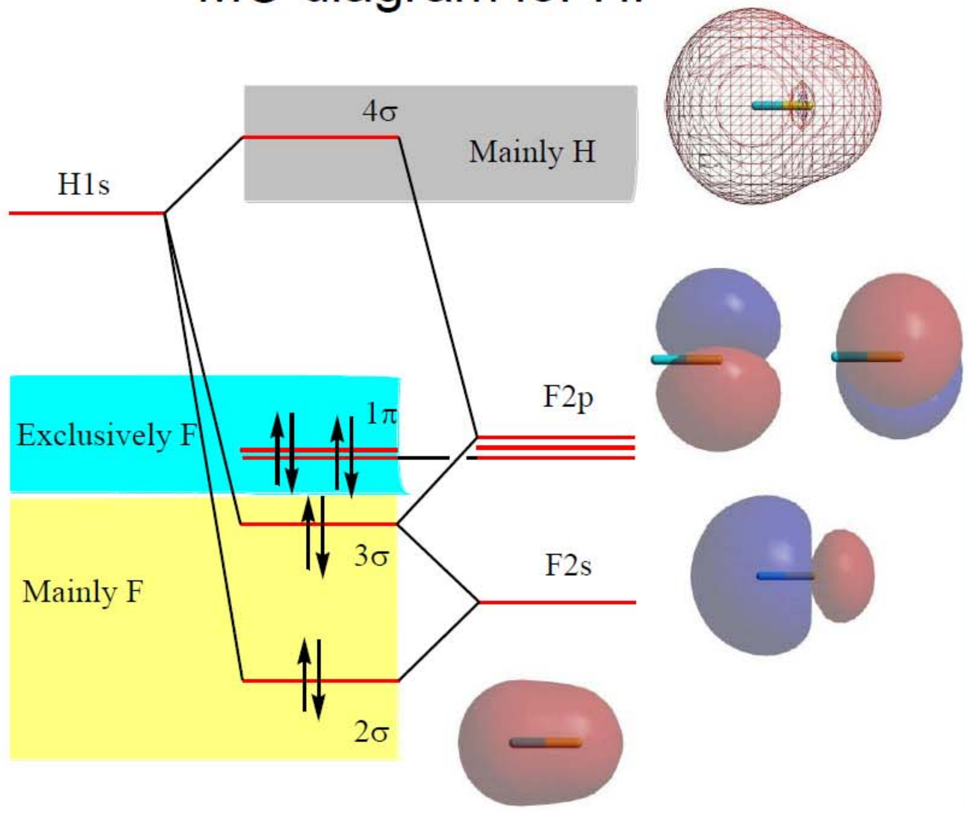
Example: HF

- 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.
  - We certainly don't have to worry about the F (1s) because is MUCH lower in energy.
- The H (1s) and F (2p)'s are close in energy and do interact.
  - The 2px and 2py don't have the appropriate symmetry though and therefore form nonbonding MO'S
  - Only the 2pz and 1s mix.



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

Heterogeneous diatomic molecules, HX



MO diagram for HF

Electronic configurations

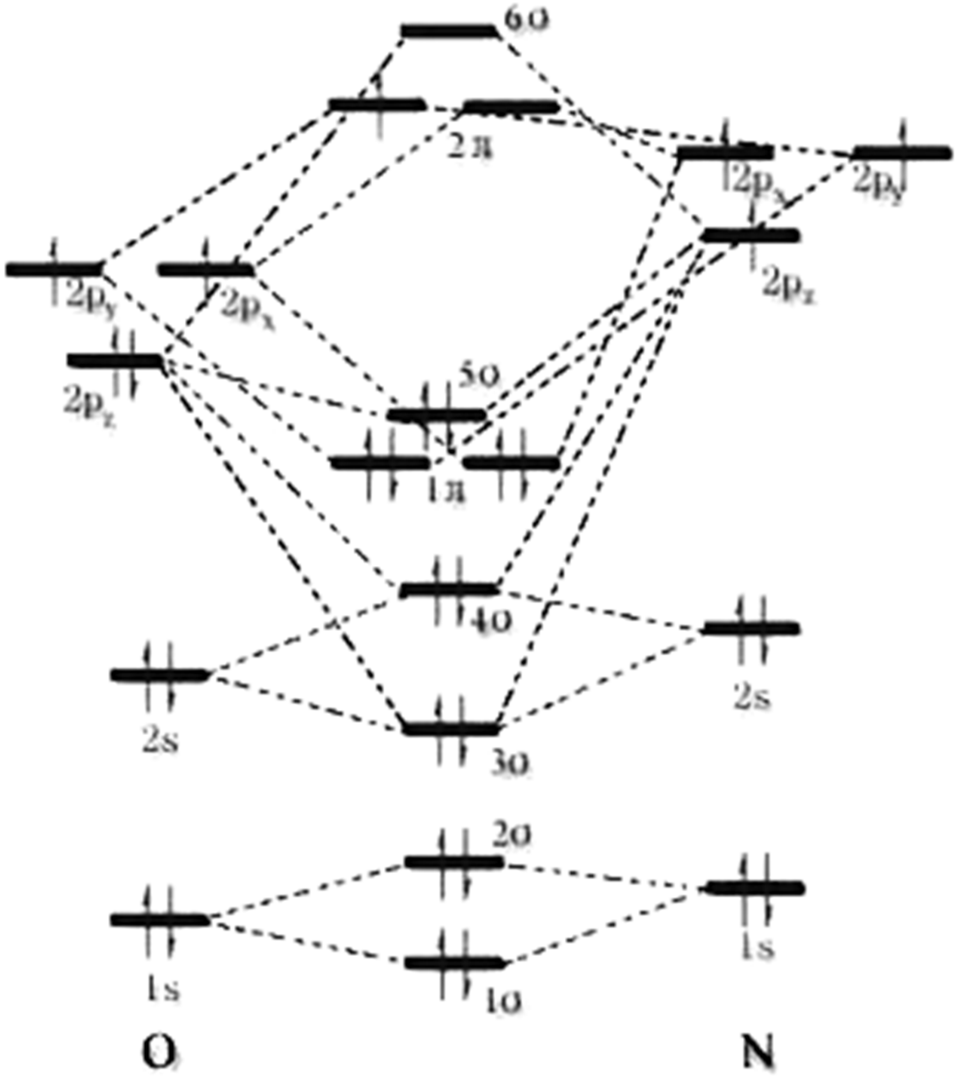
LiH	4	$K(2\sigma)^2$
BeH	5	$K(2\sigma)^2\,(3\sigma)^1$
CH	7	$K(2\sigma)^2\,(3\sigma)^2\,(1\pi)^1$
NH	8	$K(2\sigma)^2\,(3\sigma)^2\,(1\pi)^2$
OH	9	$K(2\sigma)^2\,(3\sigma)^2\,(1\pi)^3$
HF	10	$K(2\sigma)^2\,(3\sigma)^2\,(1\pi)^4$

Isoelectronic rule:

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

CO is isoelectronic with N_2.

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

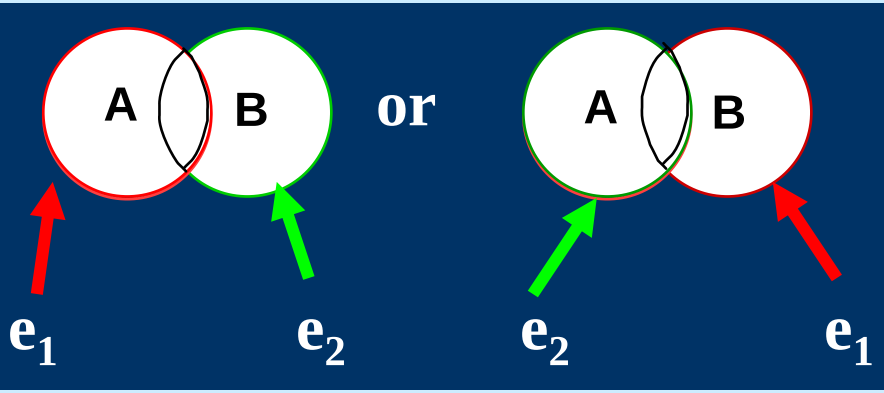


electronic configurations of NO

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

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

In valence bond(VB) theory we localized one electron to each.



The Heitler-London treatment:

f_1=A(1)B(2) f_2=A(2)B(1)

The trial variation function:

$\Psi = c_1 f_1 + c_2 f_1 = c_1 A(1)B(2) + c_2 A(2)B(1)$

We have the valence bond wavefunction

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

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

Both electrons can be on the same nuclei

The unnormalized LCAO-MO wave function for the H2 ground state is:

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

$$\Downarrow$$

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

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.
- Poor theory for obtaining quantitative bond dissocation energies. *(have been improved)*
- 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.