

# Molecular structure

- To understand how atoms connect together to form molecules.
- How these chemical bonds lead to chemical reactions.
- Theory of the formation of the chemical bond. – molecular orbital (the more established ) and valence bond theories.

# The Born Openheimer approximation:

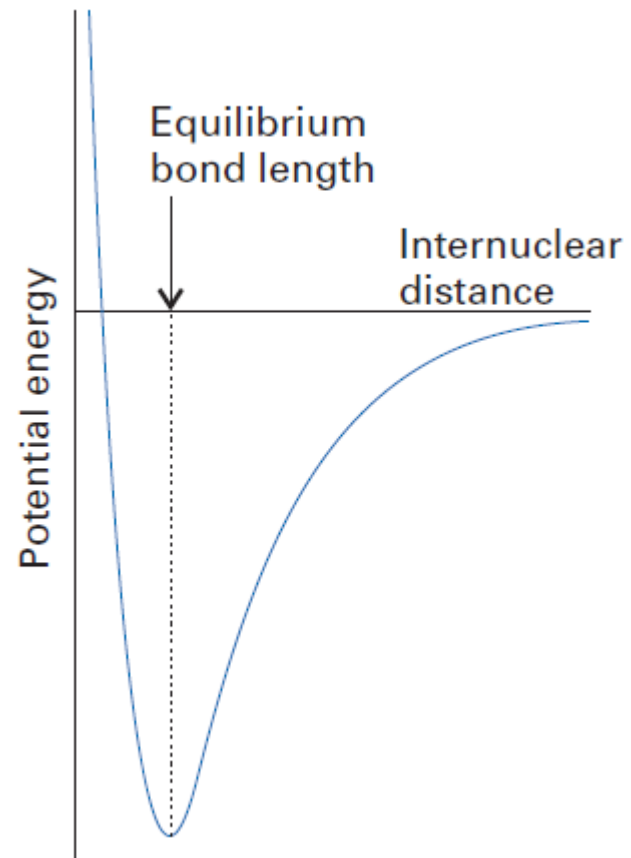
- Simplest molecule  $H_2^+$  Can be solved adiabatically. The nuclei are much heavier and slower.
- We can solve the Schrodinger eqn. for the electrons in the quasi static frame of the nuclei.
- After a time enables motion of the nuclei, the calculation is repeated.

# This enables the construction of molecular potential energy curve.

- In a diatomic molecule it is a curve.

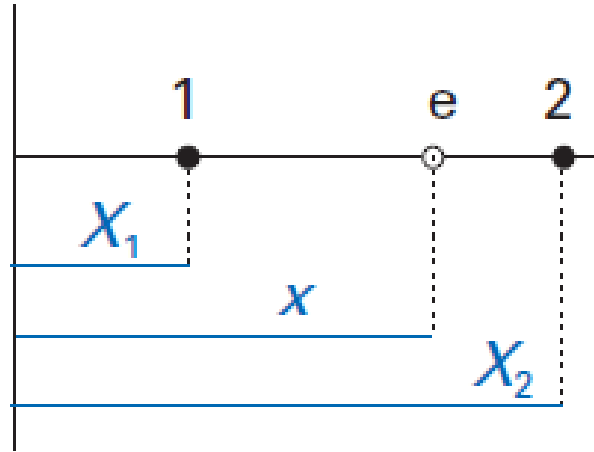
In a polyatomic molecule – it is a surface.

- \* BO approximation – very reliable in ground state calculations.



# Formulation of the BO approximation:

- A one dimensional approximation – motion restricted in the  $z$  direction:



- The Hamiltonian is:

$$H = -\frac{\hbar^2}{2m_e} \frac{\partial^2}{\partial z^2} - \sum_{j=1,2} \frac{\hbar^2}{2m_j} \frac{\partial^2}{\partial Z_j^2} + V(z, Z_1, Z_2)$$

- In a simpler form:

$$H = T_e + T_N + V$$

# BO approximation- separation of variables.

- The Schrodinger equation:

$$H\Psi(z, Z_1, Z_2) = E\Psi(z, Z_1, Z_2)$$

- We try to find a solution of the form:

$$\Psi(z, Z_1, Z_2) = \psi(z; Z_1, Z_2)\chi(Z_1, Z_2)$$

- $\Psi$  – electronic wavefunction,  $\chi$  – nuclear wavefunction.
- The notation  $\psi(z; Z_1, Z_2)$  - means dependence on  $z$  at given nuclear coordinates  $Z_1, Z_2$ . For each pair of  $Z_1, Z_2$  we calculate a different  $\Psi$

# Thus the Hamiltonian is:

$$H\psi\chi = \chi T_e\psi + \psi T_N\chi + V\psi\chi + W = E\psi\chi$$

All the terms are separated except W which

is:

$$W = - \sum_{j=1,2} \frac{\hbar^2}{2m_j} \left( 2 \frac{\partial\psi}{\partial Z_j} \frac{\partial\chi}{\partial Z_j} + \frac{\partial^2\psi}{\partial Z_j^2} \chi \right)$$

$\Psi$  is dependent on  $Z_i$  but the nuclear mass is large and therefore  $W$  is small.

We solve the approximate Hamiltonian:

$$\chi T_e\psi + \psi T_N\chi + V\psi\chi = E\psi\chi$$

After rearrangement:  $\psi T_N\chi + (T_e\psi + V\psi)\chi = E\psi\chi$

# Solution:

- As a first step we write:

$$T_e\psi + V\psi = E_e(Z_1, Z_2)\psi$$

- Namely to solve the electronic Schrodinger eqn. for specific  $Z_1, Z_2$ .
- Potential  $V$  depends on the fixed locations of the two nuclei.
- $E_e(Z_1, Z_2)$  – electronic contribution to the total energy of the molecule + internuclear repulsion – gives a point of the molecular potential energy curve.

# Substitution gives:

- $\psi T_N \chi + E_e \psi \chi = E \psi \chi$

- Eliminating  $\psi$  gives:

$$T_N \chi + E_e \chi = E \chi$$

- $E_e$  is the molecular potential and  $E$  is the total molecular energy within the Born Oppenheimer approximation.
- Writing the electron Schrodinger eqn in a simpler form gives  $H\psi = E\psi$   $H = -\frac{\hbar^2}{2m_e} \nabla^2 + V$
- $V$  – electron potential + nuclear repulsion,  
 $E$  – total energy + nuclear repulsion.



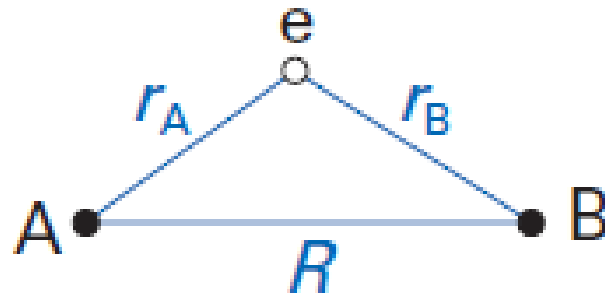
# An application: the hydrogen molecule-ion

- Even after making the BO approximation – there is only one molecule that can be solved exactly:  $\text{H}_2^+$

- The Hamiltonian:

$$H = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B} + \frac{e^2}{4\pi\epsilon_0 R}$$

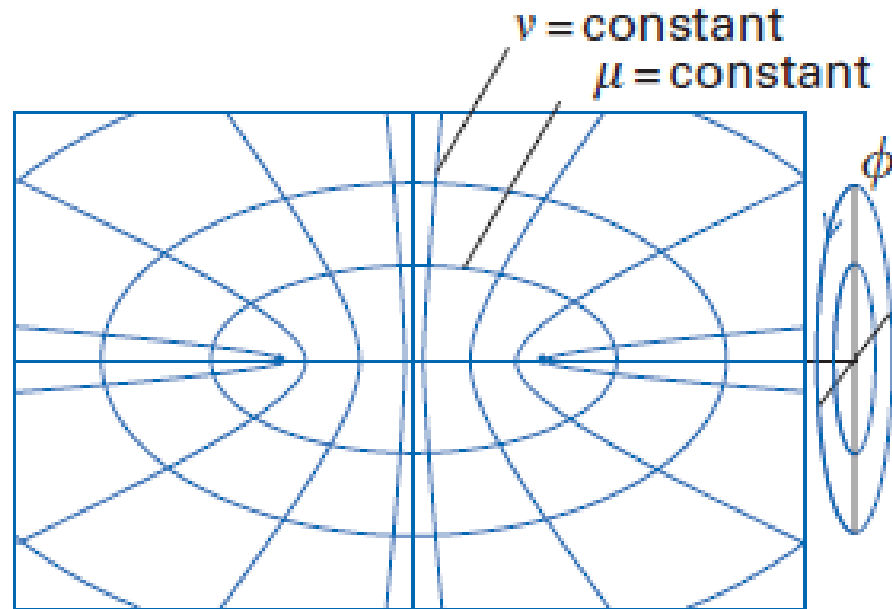
- The coordinates are defined by



# $H_2^+$ has only one electron.

- In the H atom the Schrodinger eqn. is solvable in spherical coordinates.
- In  $H_2^+$  it is solvable in ellipsoidal coordinates:

Where:  $\mu = \frac{r_A + r_B}{R}$      $\nu = \frac{r_A - r_B}{R}$      $\phi$  is the azimuthal angle around the internuclear axis



# Solution:

- The two nuclei lie at the foci of ellipses of constant  $\mu$ .
- The wave function (molecular orbital) spreads over these two nuclei.
- The exact molecular orbital – very complicated – another approximation is needed.
- The solution gives potential energy curves:

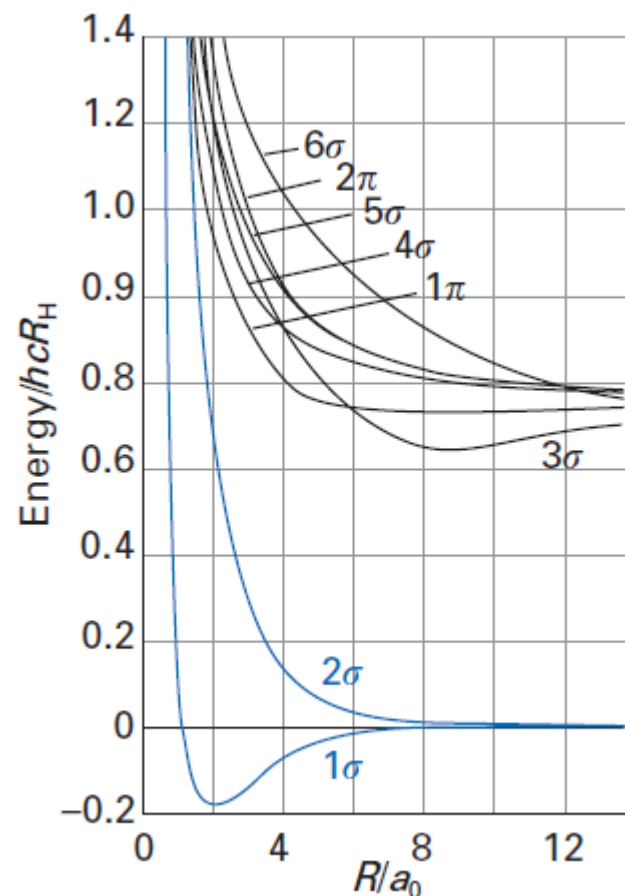
# As with the atomic orbitals:

there are many molecular orbitals –  
depending on  $R$ :

- We shall concentrate on  
the 2 lower ones.

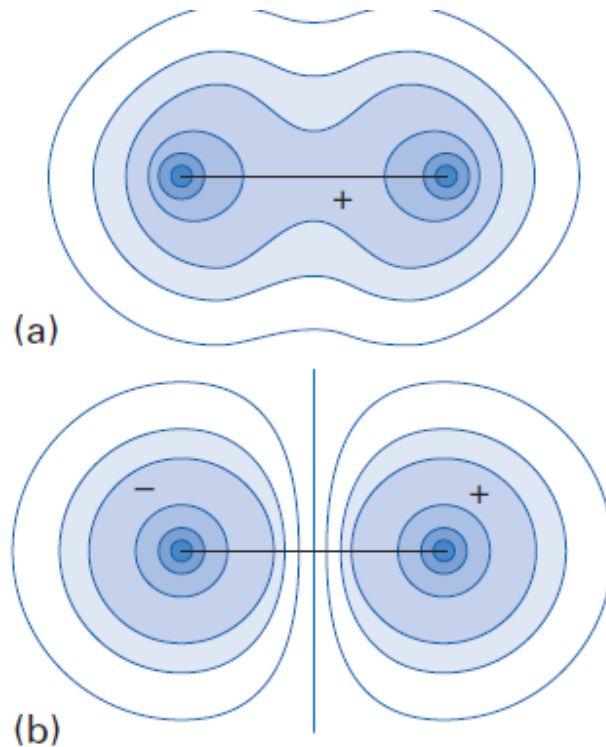
Steep rise at small  $R$   
nuclear – nuclear  
repulsion.

The lower curve – a  
minimum close to  $R=2a_0$



# The energy is compared with the ground state of H atom

- The energy of the minimum of ground state is:  
-  $0.20hcR_H$  (2.7 eV). In agreement with the experimental result:- 2.648 eV . The structure of the lowest wavefunctions explains the difference:



# The energy of the molecular orbital:

- The lower orbital – the electron can interact with both nuclei in the zone between them – lower energy – Opposite to the higher one.
- Other things that affect the orbital's energy:
- In the bonding orbital –  $R$  is smaller, and electrons are removed from the outer parts close to the nuclei. The Kinetic energy is larger.
  - Disadvantages of the bonding orbitals.
- The benefit of the potential energy overcomes.
- The opposite is true for the antibonding orbital.

# Molecular orbital theory.

- For other molecules, it is necessary to make another approximation – using the well characterized atomic orbitals.
- **Linear combination of atomic orbitals:**
- Close look on the exact solutions of  $\text{H}_2^+$  reveals that they are similar to:

$$\psi_+ \approx \phi_a + \phi_b \quad \psi_- \approx \phi_a - \phi_b$$

Where  $\phi$  are the 1s atomic orbitals.

It is possible to view it as constructive and destructive interferences of the 2 wavefunction.

# A partial justification:

- Looking at the Hamiltonian when the electron is close to nucleus A and  $r_A \ll r_B$ ,

$$H = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} + \frac{e^2}{4\pi\epsilon_0 R}$$

- Apart from the final constant term this is the Hamiltonian of H atom A. The same for B.
- This behavior is captured by the linear combination described above.
- A more formal attitude leads to the same conclusion:



# Variation principle:

- Suppose the system is described by the Hamiltonian  $H$ .  $E_0$  is the lowest eigenvalue.
- We make a conjecture that the wavefunction is  $\psi_{\text{trial}}$ .
- We calculate the Rayleigh ratio:

$$\mathcal{E} = \frac{\int \psi_{\text{trial}}^* H \psi_{\text{trial}} d\tau}{\int \psi_{\text{trial}}^* \psi_{\text{trial}} d\tau} \quad \text{The variation theorem}$$

says that:      for any  $\psi_{\text{trial}}$ ,  $\mathcal{E} \geq E_0$

- The equality holds only if the trial function is identical to the true ground state wavefunction of the system.

# The Rayleigh–Ritz method

- The trial function is a linear combination of the basis eigenstates.

$$\psi_{\text{trial}} = \sum_i c_i \psi_i$$

- Only the coefficients (not the eigenstates) are variables.
- In this case the Rayleigh ratio is:

$$\mathcal{E} = \frac{\int \psi_{\text{trial}}^* H \psi_{\text{trial}} d\tau}{\int \psi_{\text{trial}}^* \psi_{\text{trial}} d\tau} = \frac{\sum_{i,j} c_i c_j \int \psi_i H \psi_j d\tau}{\sum_{i,j} c_i c_j \int \psi_i \psi_j d\tau} = \frac{\sum_{i,j} c_i c_j H_{ij}}{\sum_{i,j} c_i c_j S_{ij}}$$

We seek a minimum of the ratio:

- differentiation for each  $c_k$   $\partial \mathcal{E} / \partial c_k = 0$

We get:

$$\begin{aligned} \frac{\partial \mathcal{E}}{\partial c_k} &= \frac{\sum_j c_j H_{kj} + \sum_i c_i H_{ik}}{\sum_{i,j} c_i c_j S_{ij}} - \frac{\left( \sum_j c_j S_{kj} + \sum_i c_i S_{ik} \right) \sum_{i,j} c_i c_j H_{ij}}{\left( \sum_{i,j} c_i c_j S_{ij} \right)^2} \\ &= \frac{\sum_j c_j (H_{kj} - \mathcal{E} S_{kj})}{\sum_{i,j} c_i c_j S_{ij}} + \frac{\sum_i c_i (H_{ik} - \mathcal{E} S_{ik})}{\sum_{i,j} c_i c_j S_{ij}} = 0 \end{aligned}$$

# The secular equation:

- The expression is satisfied when the numerator vanishes. We solve the secular equation:

$$\sum_i c_i (H_{ik} - \mathcal{E} S_{ik}) = 0$$

- Returning to the LCAO method, For a non trivial solution, the secular determinant must vanish:  $|H - ES| = 0$
- Returning to the case of a basis set of 2 atomic orbitals:

# We get a 2x2 secular determinant

- $S$  is the overlap integral and:

$$S_{AA} = S_{BB} = 1 \quad S_{AB} = S_{BA} = S$$

- Also:  $H_{AA} = H_{BB} = \alpha$        $H_{AB} = H_{BA} = \beta$
- where  $\alpha$  is the molecular Coulomb integral and  $\beta$  is the resonance integral.
- The secular determinant is

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

- And its roots are:  $E_{\pm} = \frac{\alpha \pm \beta}{1 \pm S}$

# Using the secular equations:

- We get the coefficient of the normalized wave functions:

$$c_A = c_B \quad c_A = \frac{1}{\{2(1 + S)\}^{1/2}} \quad \text{for } E_+ = \frac{\alpha + \beta}{1 + S}$$

$$c_A = -c_B \quad c_A = \frac{1}{\{2(1 - S)\}^{1/2}} \quad \text{for } E_- = \frac{\alpha - \beta}{1 - S}$$

- Estimation of the Coulomb and resonance integrals:
- We use the abbreviation:
- $|\phi_A\rangle \rightarrow |A\rangle$  and  $|\phi_B\rangle \rightarrow |B\rangle$

# Coulomb and resonance integrals:

- Inserting the Hamiltonian:

$$\alpha = \langle A|H|A \rangle = E_{1s} - \frac{e^2}{4\pi\epsilon_0} \left\langle A \left| \frac{1}{r_B} \right| A \right\rangle + \frac{e^2}{4\pi\epsilon_0 R}$$

- We use the abbreviation:

$$j_0 = \frac{e^2}{4\pi\epsilon_0}$$

- Giving: 
$$\alpha = E_{1s} - j_0 \left\langle A \left| \frac{1}{r_B} \right| A \right\rangle + \frac{j_0}{R}$$

- $E_{1s}$  is observed because  $\phi_A$  is an eigenfunction of the atomic Hamiltonian:

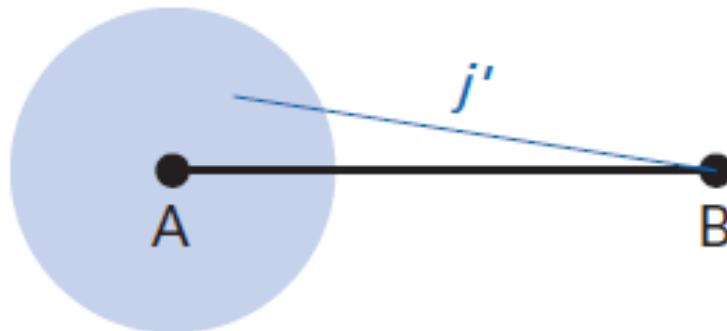
The second term is the interaction between electron A and the second nucleus B

- We use the abbreviation  $j'$  :

$$j' = j_0 \int \frac{\phi_A^2}{r_B} d\tau$$

- Total Coulomb energy:

$$\alpha = E_{1s} - j' + \frac{j_0}{R}$$



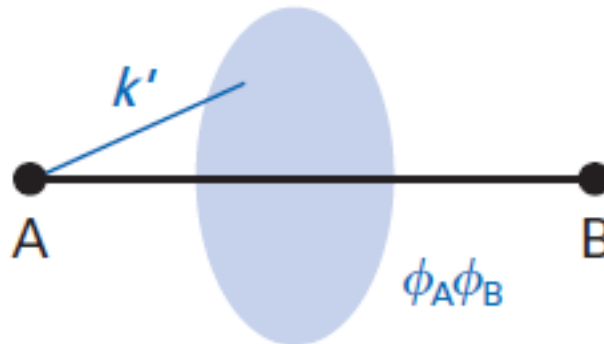


# The resonance integral $\beta$ :

- We use the fact that  $\phi_B$  is an eigenfunction for the Hydrogen atom B. We get:

$$\begin{aligned}\beta &= \langle A|H|B\rangle = E_{1s} \langle A|B\rangle - j_0 \left\langle A \left| \frac{1}{r_A} \right| B \right\rangle + \frac{j_0}{R} \langle A|B\rangle \\ &= \left( E_{1s} + \frac{j_0}{R} \right) S - k' \quad \text{where:} \quad k' = j_0 \int \frac{\phi_A \phi_B}{r_A} d\tau\end{aligned}$$

- $k'$  represents the interaction of the overlap charge density,  $-e\phi_A\phi_B$ , with nucleus A.



# Demonstration with the real s orbital:

- Evaluation of the overlap integral  $s$  and the integral  $j'$  in the hydrogen positive ion.
- The volume element in the ellipsoidal coordinate is:

$$d\tau = \frac{1}{8}R^3 (\mu^2 - v^2) d\mu dv d\phi$$

- Where the integral is within the limits:

$$1 \leq \mu \leq \infty, \quad -1 \leq v \leq 1, \quad \text{and} \quad 0 \leq \phi \leq 2\pi.$$

- We start with the atomic wavefunction:

$$\phi(r) = (Z^3/\pi a_0^3)^{1/2} e^{-Zr/a_0}$$

# The product of the 2 wave functions:

$$\phi_A(r_A)\phi_B(r_B) = \left(\frac{Z^3}{\pi a_0^3}\right) e^{-Z(r_A+r_B)/a_0} = \left(\frac{Z^3}{\pi a_0^3}\right) e^{-Z\mu R/a_0}$$

- The overlap integral:

$$S = \langle A|B \rangle = \frac{Z^3 R^3}{8\pi a_0^3} \int_0^{2\pi} \int_1^\infty \int_{-1}^1 (\mu^2 - v^2) e^{-Z\mu R/a_0} d\mu dv d\phi$$

- After integration over  $\phi$ :

$$= \frac{Z^3 R^3}{8\pi a_0^3} \times 2\pi \times \int_1^\infty \int_{-1}^1 (\mu^2 - v^2) e^{-Z\mu R/a_0} d\mu dv$$

- After integration over  $v$ :

$$= \frac{Z^3 R^3}{8\pi a_0^3} \times 2\pi \times \int_1^\infty \left(2\mu^2 - \frac{2}{3}\right) e^{-Z\mu R/a_0} d\mu$$

# Cont:

- The overlap integral is:

$$= \left\{ 1 + \frac{ZR}{a_0} + \frac{1}{3} \left( \frac{ZR}{a_0} \right)^2 \right\} e^{-ZR/a_0}$$

- The evaluation of  $j'$  is similar. We use:

$$\mu^2 - v^2 = (\mu + v)(\mu - v):$$

- **Recall:**

$$\mu = \frac{r_A + r_B}{R} \quad v = \frac{r_A - r_B}{R} \quad j' = j_0 \int \frac{\phi_A^2}{r_B} d\tau$$

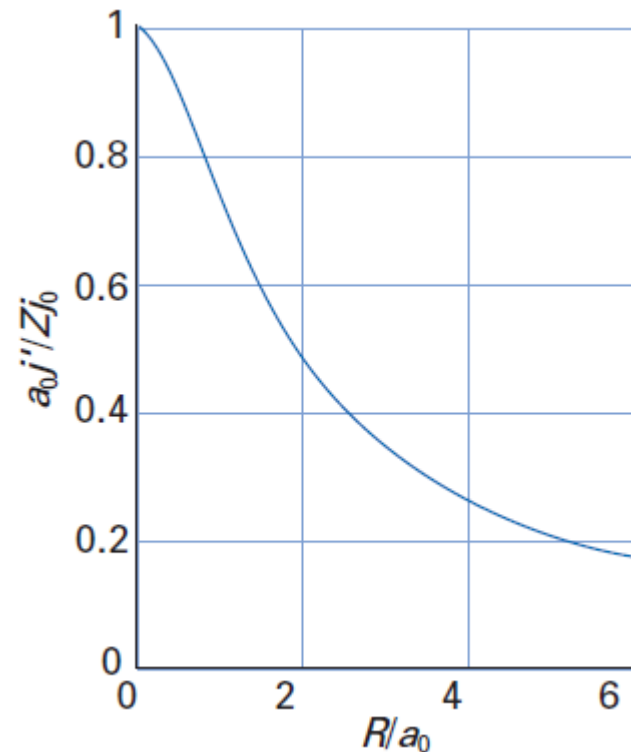
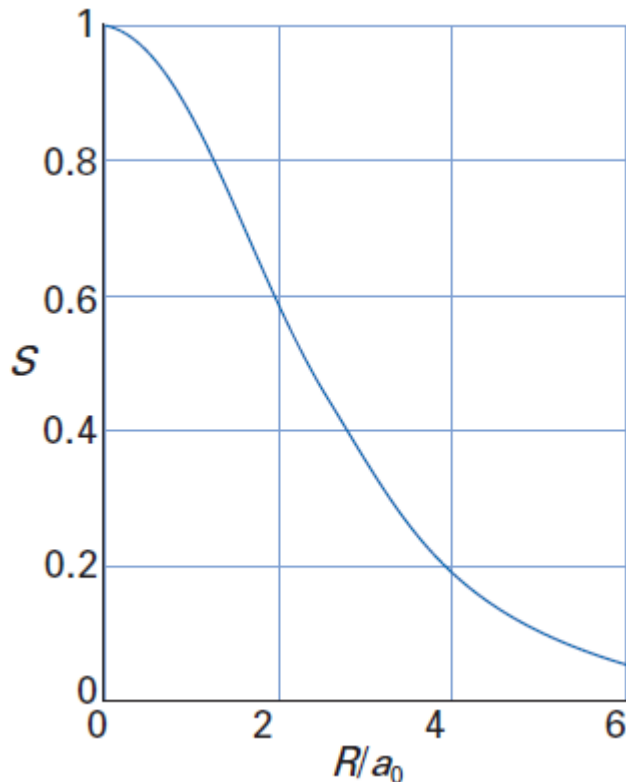
$$j' = \frac{j_0 Z^3}{\pi a_0^3} \int_0^{2\pi} \int_1^\infty \int_{-1}^1 \frac{\frac{1}{8} R^3 (\mu^2 - v^2) e^{-Z(\mu+v)R/2a_0}}{\frac{1}{2} R (\mu - v)} d\mu dv d\phi$$

# Cont:

- We get:

$$= \frac{1}{2} j_0 \left( \frac{Z}{a_0} \right)^3 R^2 \int_1^\infty \int_{-1}^1 (\mu + \nu) e^{-Z(\mu+\nu)R/2a_0} d\mu d\nu$$

$$= \frac{1}{R} j_0 \left\{ 1 - \left( 1 + \frac{ZR}{a_0} \right) e^{-2ZR/a_0} \right\}$$



# Recall:

- We had:  $k' = j_0 \int \frac{\phi_A \phi_B}{r_A} d\tau$
- If we use the expression of the real wavefunction we get:

$$k' = \frac{j_0}{a_0} \left\{ 1 + \frac{R}{a_0} \right\} e^{-R/a_0}$$

- $k'$  represents the interaction of the overlap charge density,  $e\phi_A\phi_B$ , with nucleus A.
- The energies of the two molecular orbitals:

$$E_+ = E_{1s} + \frac{j_0}{R} - \frac{j' + k'}{1 + S}$$

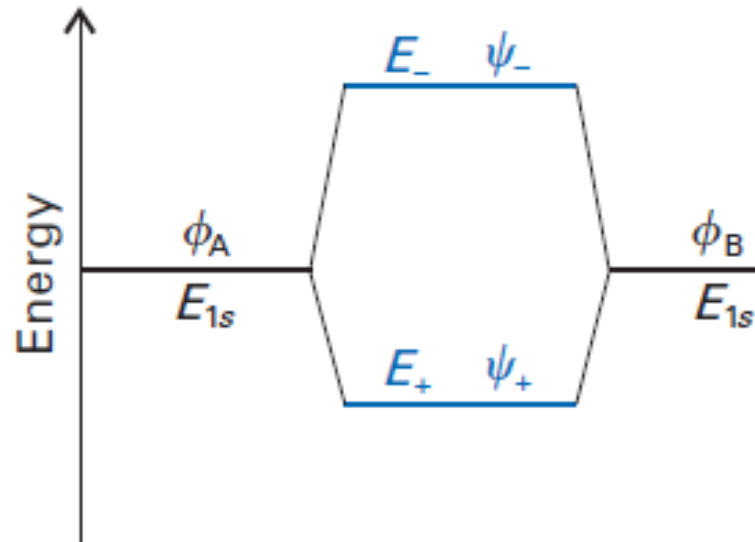
$$E_- = E_{1s} + \frac{j_0}{R} - \frac{j' - k'}{1 - S}$$

# Recall:

- $j'$  is the interaction between electron A and the second nucleus B.

and 
$$j_0 = \frac{e^2}{4\pi\epsilon_0}$$

The molecular orbital energy diagram:



# Bonding and antibonding molecular orbitals

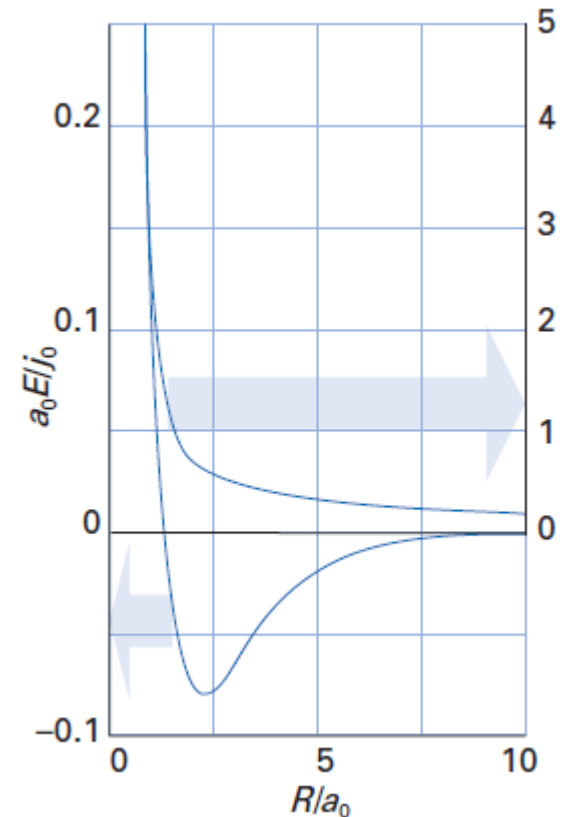
Both  $j'$  and  $k'$  are positive with  $j' > k'$

- \* The bonding orbital:  $\psi_+ = \phi_A + \phi_B$
- The antibonding orbital:  $\psi_- = \phi_A - \phi_B$
- In the bonding orbital the nuclei are pushed closer to each other. In the antibonding orbital – they are pushed away from each other.
- The energies are not symmetric. The nuclear repulsions are pushing up  $E_-$  more than  $E_+$  is pushed down.



# The molecular orbital energy curve:

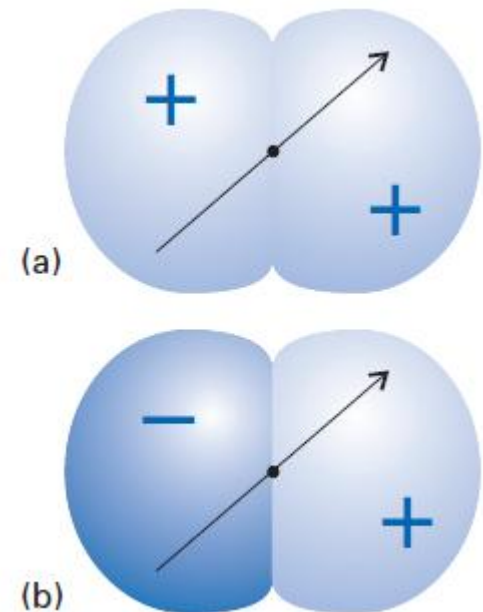
- A minimum close to:  $R = 2.5a_0$  (130 pm)
- With a depth of:  $0.13hcR_H$  (170 kJ mol<sup>-1</sup>)
- The agreement with experiment is not so good:  $2.0a_0$  (106 pm) and  $0.195hcR_H$  (255 kJ mol<sup>-1</sup>)
- The reason is that the approximation do not take into account the shrinking of the atomic orbitals around their nuclei.



# Parity of molecular orbitals:

- Like the atomic orbitals, the molecular orbitals differ by parity, which is used to mark them. (under inversion of the molecular coordinates).
- g – means even parity and u odd parity. Like with atomic orbitals the symmetry is important in selection rule.

The lowest 2 orbitals are:



# The hydrogen molecule:

- Adding another electron to the  $\text{H}_2^+$  ion.

The second electron creates a configuration  $1\sigma_g^2$  ( $\psi_+(1)\psi_+(2)$ ).

This is true only if the electron – electron repulsion can be ignored or included in an effective one electron potential (like the atomic central field approximation).

The true Hamiltonian:

$$H = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 r_{A1}} - \frac{e^2}{4\pi\epsilon_0 r_{B1}} \\ - \frac{e^2}{4\pi\epsilon_0 r_{A2}} - \frac{e^2}{4\pi\epsilon_0 r_{B2}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 R}$$

# Cont.

Is replaced by:

$$H = H_1 + H_2 + \frac{e^2}{4\pi\epsilon_0 R}$$

Where  $H_i$  depends only on the coordinates of the  $i$ -th electron only.

The spatial wave function  $\psi_+(1)\psi_+(2)$  is symmetric under exchange.

Thus the spin wavefunction should be antisymmetric with the form:

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

The electrons should be paired ( $\uparrow\downarrow$ ) to fill the molecular orbital:

# The molecular configuration is marked like the atomic one:

- Ground state configuration of  $H_2$ :  ${}^1\Sigma_g$

The superscript 1 is the spin multiplicity – corresponding to  $S=0$  (paired spin).

$\Sigma$  corresponds to s in atomic orbitals – No angular momentum – linear combination of two s orbitals.

Formally – we denote the component along the measurement axis as  $\lambda$ .

The total angular momentum in the molecular orbital is  $A = \lambda_1 + \lambda_2 = 0$ .

# The parity of the molecular orbital is

- Calculated by the parities of the individual orbitals:

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

- The full form of the H<sub>2</sub> ground state wavefunction:

$$\psi(1,2) = \psi_+(1)\psi_+(2)\sigma_-(1,2)$$

- The factor  $\sigma_-$  is the spin contribution:

$$\left(\frac{1}{2}\right)^{1/2} \{ \alpha(1)\beta(2) - \alpha(2)\beta(1) \}$$

# The lowest energy orbital of the H<sub>2</sub> atom:

- The expectation value of the ground state:

$$E = 2E_{1s} + \frac{j_0}{R} - \frac{2j' + 2k'}{1 + S} + \frac{j + 2k + m + 4l}{2(1 + S)^2}$$

- We have defined already  $j_0$ ,  $j'$  and  $k'$ . We define the 4 more integrals:

$$j = j_0 \int \phi_A(1)^2 \frac{1}{r_{12}} \phi_B(2)^2 d\tau_1 d\tau_2 = (AA|BB)$$

- The repulsion of a charge density of electron 1 on A with the charge density of electron 2 on B:

# The other integrals:

$$k = j_0 \int \phi_A(1)\phi_B(1) \frac{1}{r_{12}} \phi_A(2)\phi_B(2) d\tau_1 d\tau_2 = (AB|AB)$$

- The repulsion of the overlap charge density of electron 1 and the overlap charge density of electron 2:

$$l = j_0 \int \phi_A(1)^2 \frac{1}{r_{12}} \phi_A(2)\phi_B(2) d\tau_1 d\tau_2 = (AA|AB)$$

- The repulsion of the charge density of electron 1 on A with the overlap charge density of electron 2.

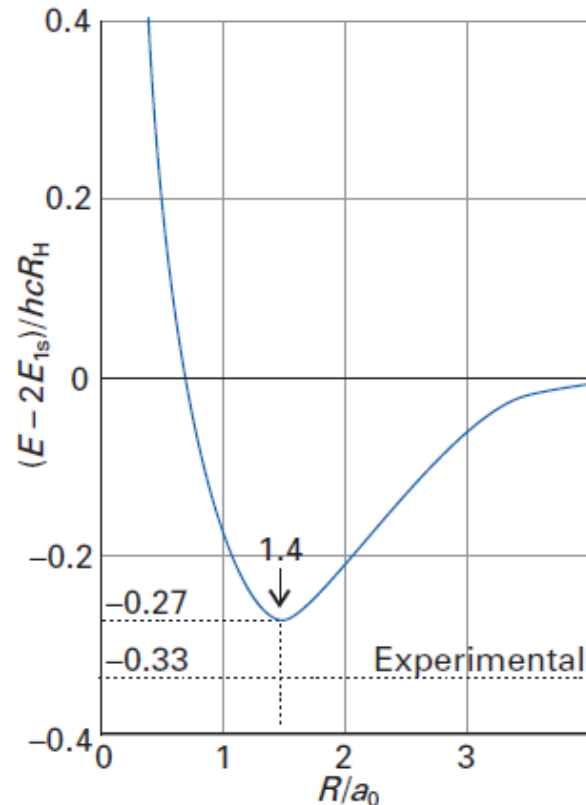


# Cont.

$$m = j_0 \int \phi_A(1)^2 \frac{1}{r_{12}} \phi_A(2)^2 d\tau_1 d\tau_2 = (AA|AA)$$

The repulsion of the charge density of electron 1 on A with the charge density of electron 2 also on A.

The molecular  
potential energy  
curve –depth:  
350 kJ mol<sup>-1</sup> (170 in H<sub>2</sub><sup>+</sup>)  
at 1,4a<sub>0</sub> (2.4 a<sub>0</sub> in H<sub>2</sub><sup>+</sup>)



# Quite good agreement with experiment.

- Improving accuracy can be reached with SCF calculations, and including electron correlation.

# Configuration interaction:

- Recall: The spin part of the wavefunction is:

$$\sigma_- = \left(\frac{1}{2}\right)^{1/2} \{\alpha(1)\beta(2) - \alpha(2)\beta(1)\}$$

- In the hydrogen molecule we take into account the 2 lowest levels. 3 configurations are possible:

$$1\sigma_g^2 \quad 1\sigma_g^1 1\sigma_u^1 \quad 1\sigma_u^2$$

- According to the Pauli principle the total wave function must be anti symmetric.

$$\Psi_1(1, 2; {}^1\Sigma_g) = \psi_+(1)\psi_+(2)\sigma_-(1, 2)$$

$$\Psi_2(1, 2; {}^1\Sigma_u) = \left(\frac{1}{2}\right)^{1/2} \{\psi_+(1)\psi_-(2) + \psi_+(2)\psi_-(1)\}\sigma_-(1, 2)$$

$$\Psi_3(1, 2; {}^1\Sigma_g) = \psi_-(1)\psi_-(2)\sigma_-(1, 2)$$

$$\Psi_4(1, 2; {}^3\Sigma_u) = \left(\frac{1}{2}\right)^{1/2} \{\psi_+(1)\psi_-(2) - \psi_+(2)\psi_-(1)\}\sigma_+(1, 2)$$

# Role of symmetry:

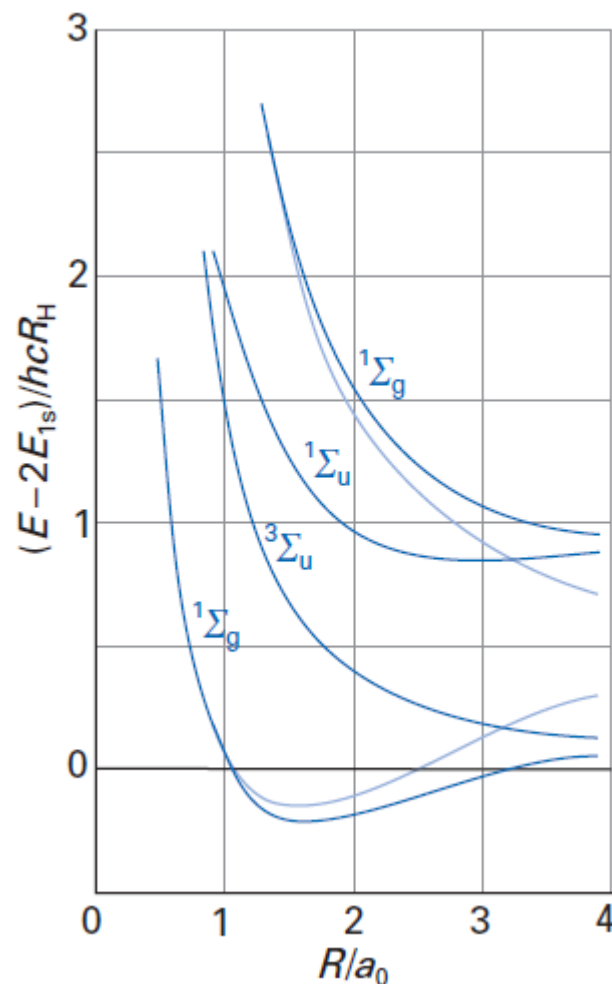
- Unlike the situation with atoms, in molecules the energy of the state can be changed by modifying the internuclear distance.
- This can lead to the possibility that 2 states with the same symmetry are degenerate.
- This will cause splitting of the states

# The energies of the 4 terms are:

\* The molecular potential energy curves:

- $\psi_1$  and  $\psi_3$  has the same symmetry ( $^1\Sigma_g$ ) they approach to the same energy as  $R \rightarrow \infty$ .

The result – configuration splitting as a result of creating a superposition of  $\psi_1$  and  $\psi_3$

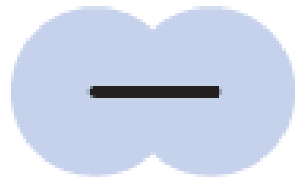


# Diatomic molecules

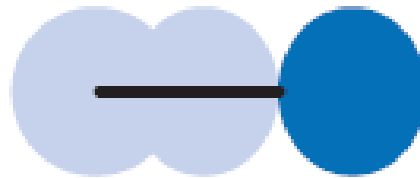
- Other homonuclear diatomic molecules are similar to the Hydrogen molecule.
- Construction of molecular orbitals - linear combinations of atomic orbitals with the same symmetry with respect to rotations about the inter-nuclear axis.
- Only orbitals of the same symmetry may have non-zero overlap ( $S \neq 0$ ) and contribute to bonding.
- This will be discussed in details:

# Example:

- When inter-nuclear species in the Z-direction –  $s$ ,  $p_z$ , and  $d_{z^2}$  have symmetry that enables formation of  $\sigma$  molecular orbital.



(a)



(b)

$P_x$  and  $P_y$  have the same symmetry and can form a molecular orbital with angular momentum ( $\pi$ ). Same thing can be done with

$d_{yz}$  and  $d_{zx}$



(c)



(d)

# Conditions for the formation of the chemical bond:

- Atomic orbitals must be neither too diffuse nor too compact. As an example in the second row, (1s,1s) overlap creates only a weak bond compared with (2s,2s).
- only overlap between orbitals of the valence shell normally can create a chemical bond.
- The energies of the orbitals should be similar:

We recall: The overlap between the WFs:

$$S_{AA} = S_{BB} = 1 \quad S_{AB} = S_{BA} = S$$



# Cont.

- And the energy terms:

$$H_{AA} = H_{BB} = \alpha \quad H_{AB} = H_{BA} = \beta$$

- $\alpha$  is the molecular Coulomb integral and  $\beta$  is the resonance integral:
- The secular determinant for 2 different atoms A and B is:

$$\begin{vmatrix} \alpha_A - E & \beta - ES \\ \beta - ES & \alpha_B - E \end{vmatrix} = 0$$

- With roots (when :  $|\alpha_A - \alpha_B| \gg \beta$ ,  $S = 0$ )

$$E_+ = \alpha_A - \frac{\beta^2}{\alpha_B - \alpha_A} \quad E_- = \alpha_B + \frac{\beta^2}{\alpha_B - \alpha_A}$$

# The observed molecular orbital:

- **Recall**  $\alpha_A$  and  $\alpha_B$  are defined by (for  $\alpha_A$ )

$$\alpha = \langle A|H|A \rangle = E_{1s} - \frac{e^2}{4\pi\epsilon_0} \left\langle A \left| \frac{1}{r_B} \right| A \right\rangle + \frac{e^2}{4\pi\epsilon_0 R}$$

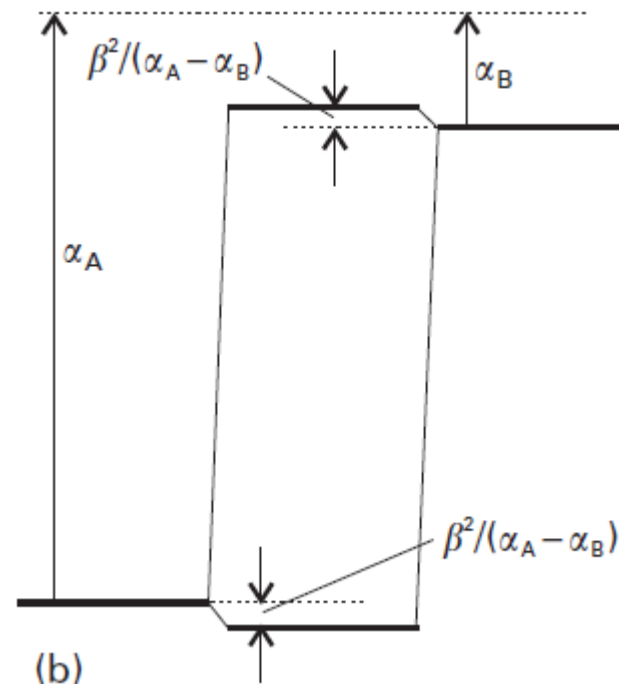
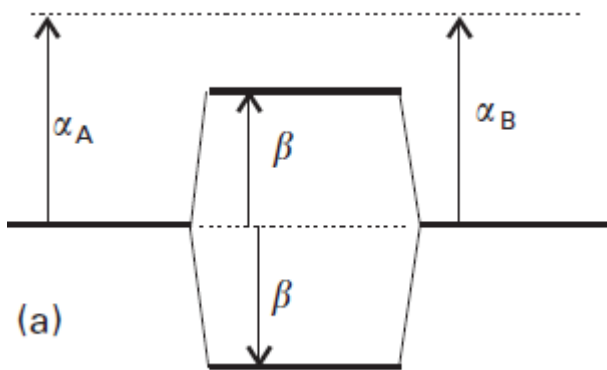
- This is the energy of atom A after adding
- the nuclear repulsion and subtracting the second term - corresponds to the energy between an electron density  $\phi_A^2$  and the second nucleus B

# The term $\beta$ :

- This is the sum of interactions with the overlap electrons:

$$\beta = \langle A|H|B \rangle = E_{1s} \langle A|B \rangle - j_0 \left\langle A \left| \frac{1}{r_A} \right| B \right\rangle + \frac{j_0}{R} \langle A|B \rangle$$

The observed potential is:



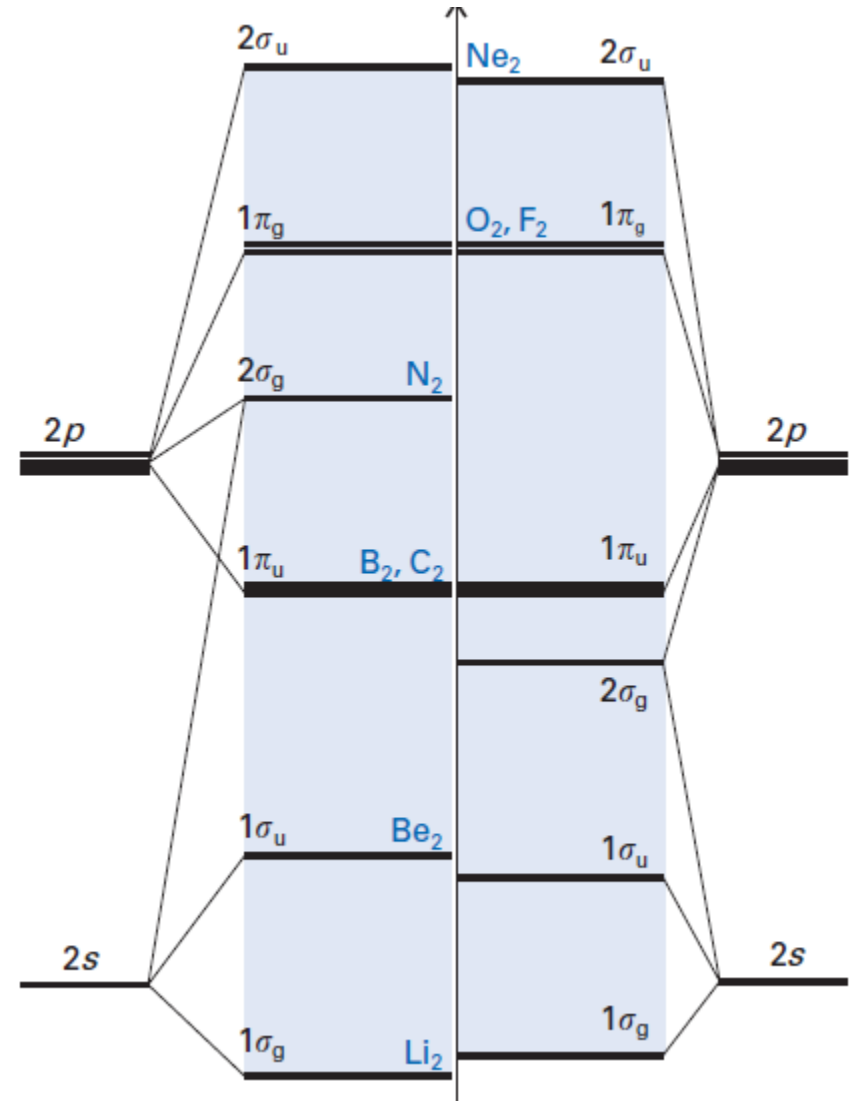
When A and B are the same (different).

# In the case the energy is much different

- Most of the density of state is in the neighborhood of atom A. The ground state molecular orbital is close to the atomic wave function A and the excited state – close to B.
- In the homonuclear molecule, the atomic orbitals of identical energy dominate the bonding (2s,2s) and (2p,2p).
- (2s,1s) and (2p, 1s) are negligible.
- (2s,2p) can not be ignored.

# Diatomic molecules of Second row in the periodic table:

Only valence electrons  
4 atomic orbitals – each atom – the S and  $p_z$  orbitals create  $\Sigma$  orbitals.  
 $P_x$  and  $P_y$  creates 2  
Pairs of degenerate  $\pi$  orbitals.  
Relative ordering is found experimentally – explained  
By more complicated theory



# Electron configuration of neutral diatomic molecules:

- Similar to filling electrons in atoms.
- Electrons fill the molecular orbital from low to high energy. 2 electrons for one orbital.
- With degenerate ( $\pi$ ) orbitals the two electrons fill 2 different orbitals first.
- Example -  $N_2$  10 valence electrons:



- $O_2$  - 12 valence electrons:



- $O_2$  – a triplet spin state.

# Angular momentum in molecular orbitals:

- Similar to atomic orbitals: for  $\sigma$  orbitals  $\lambda=0$ .
- For  $\pi$  orbitals it is possible to have 2 different linear combinations  $\rightarrow \pi_+ = \pi_x + \pi_y$  and  $\pi_- = \pi_x - \pi_y$  with  $\lambda=1$  and  $-1$  respectively.
- $\pi^4$  configuration contribute 0 to  $\lambda$ .
- $\pi^2$  configuration can contribute 0 or  $\pm 2$ .

0 with the structure  $(\pi_+^1 \pi_-^1)$

$\pm 2$  with the structure  $(\pi_+^2 \text{ or } \pi_-^2)$ , respectively.

The configuration

can be

$$\Sigma (|\Lambda| = 0) \text{ and } \Delta (|\Lambda| = 2)$$

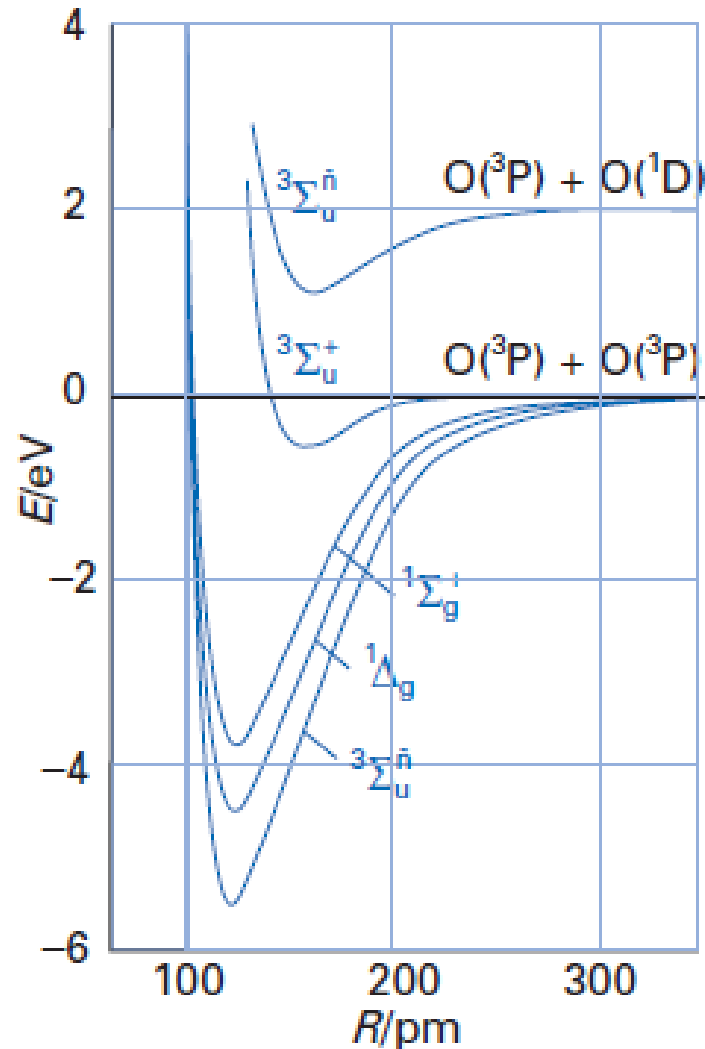
# Spin state in molecular orbitals:

- We expect that the two electrons will prefer to be in different orbitals (to minimize electron – electron repulsions:  $(\pi_+^1 \pi_-^1)$ )
- The ground state is expected to be  $\Sigma$ .  
Thus  $S$ =either 0 or 1 (1 is lower in energy).  
Thus we expect either  $^1\Sigma$  or  $^3\Sigma$  terms.  
In the  $\Delta$  molecular orbitals, in  $(\pi_+^2 \text{ or } \pi_-^2)$   
the spins must be paired thus  $S=0$  and the term is  $^1\Delta$ .



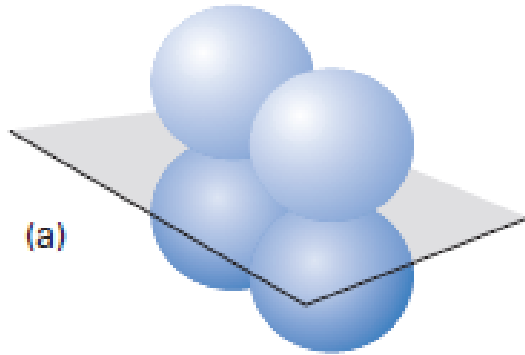
# The experimental molecular potential curve of $O_2$ :

- Some of the terms could be identified:

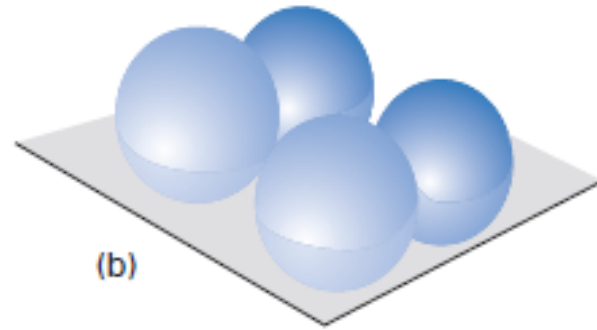


# Molecular symmetry:

- Another parameter in the term is the symmetry with respect to reflection in the plane that contains the molecular axis.



$\pi^+$



- Each  $\sigma$  orbital is +1 in this operation.
- In  $\pi$  orbitals, it is +1 or -1. Thus the overall symmetry is  $(+1) \cdot (-1) = -1$ .
- Marked as a superscript letter in the term:
- The ground state of the  $O_2$  molecule is  $3\Sigma_{g^-}$ .

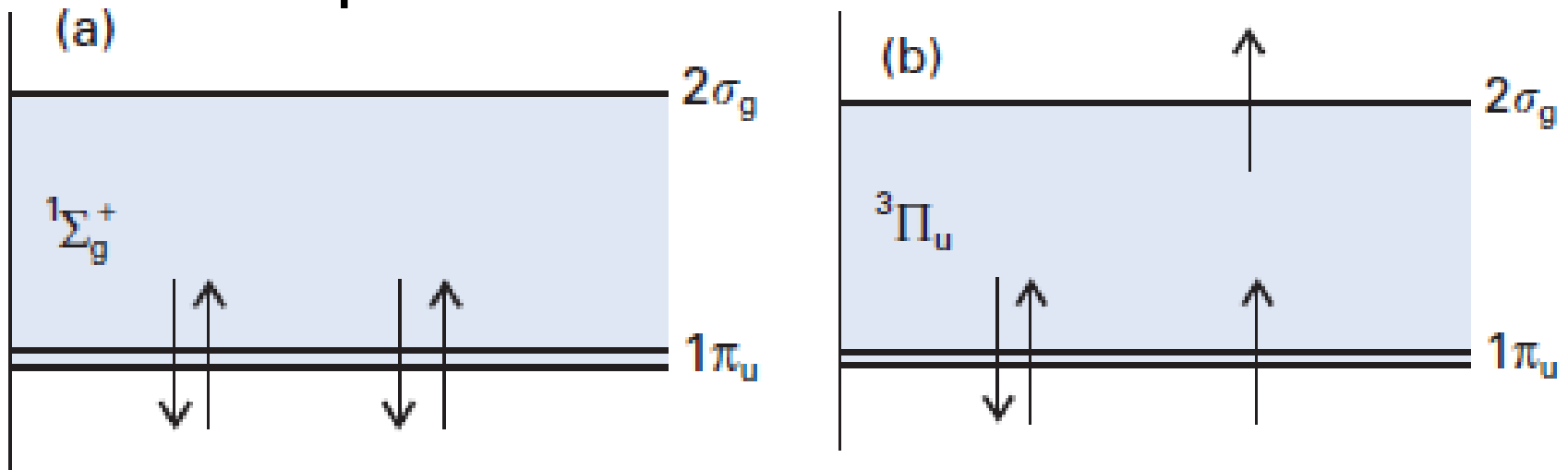
# The case of $C_2$ :

- Each C atom – 4 valence electrons.

A straightforward application of the building up principle suggest the ground state configuration:



However, spin correlation plays a role here too: It is possible to have b instead of a:



# Cont.

- An excitation to a higher energy orbital is possible to minimize electron – electron repulsion.
- The resulting ground state configuration:
- $1\sigma_g^2 1\sigma_u^2 1\pi_u^3 2\sigma_g^1$  a  $\bar{3}\Pi_u$  term.
- Minimization of energy due to spin correlation is possible if  $1\pi_u$  and  $2\sigma_g$  are close enough.

# Heteronuclear diatomic molecules:

- When two different atoms form the molecule, the molecular orbital is not uniform and is of the form:  $\psi = c_A\phi_A + c_B\phi_B$
- $|c_A|^2 = |c_B|^2$  no longer true.
- Rule of thumb: if A is more electronegative than B – in bonding orbitals  $|c_A|^2 > |c_B|^2$  ( $C_A$  and  $C_B$  – the same sign), in antibonding orbitals: ( $C_A$  and  $C_B$  – opposite sign):  $|c_A|^2 < |c_B|^2$
- A second feature: Unless the atomic energies are close, the shift of energy in the molecular orbitals (compared to the atomic) is smaller.

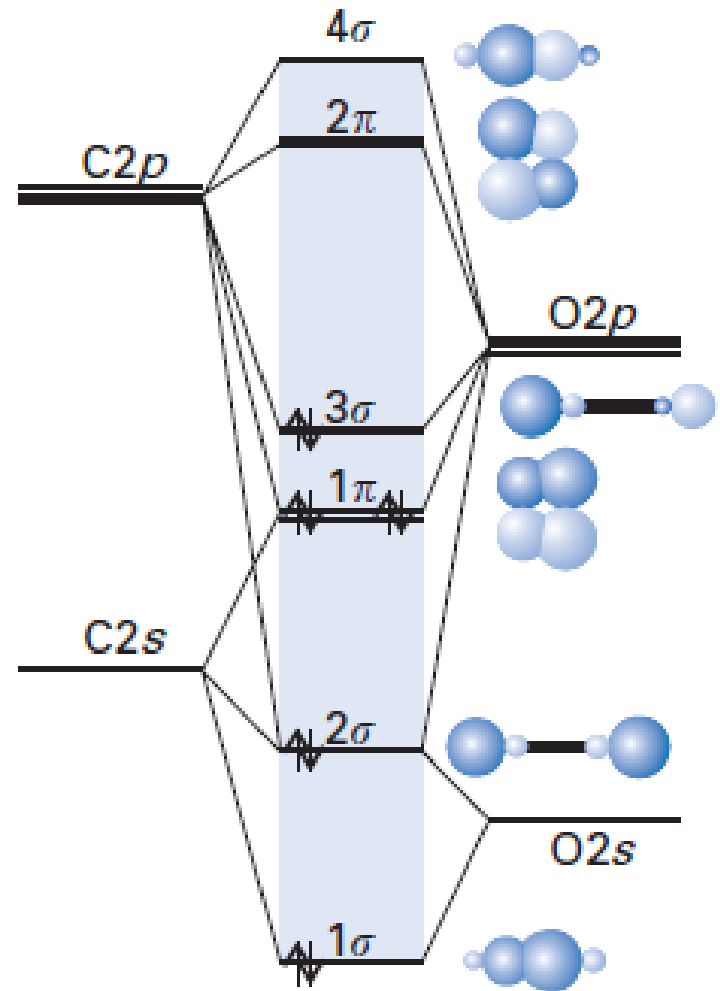
# Example – CO molecule:

- Molecular orbitals of Carbon monoxide:  
10 valence electrons  
Parity (g,u) not relevant.

The ground state is:



$3\sigma$  is the highest occupied molecular orbital (HOMO) is in a nonbonding orbital.



# Cont.

- The LUMO (lowest unoccupied molecular orbital) is  $2\pi$ .
- Both orbitals are close to the source atomic orbitals – the molecule easily accepts or give electrons.
- This causes the chemical reactivity of CO. – to create complex compounds such as  $\text{Ni}(\text{CO})_4$  and leads to very high chemical reactivity (poison).

There are several techniques to calculate exact energies and charge distributions.

# Molecular orbital theory of polyatomic molecules:

- In a similar way to diatomic molecules:

$$\psi = \sum_r c_r \phi_r$$

- Sum of atomic orbitals.
- In polyatomic molecules, the symmetry is important to choose which atomic orbitals to include in the linear combination:



# Symmetry adapted linear combinations:

- Consider the H<sub>2</sub>O molecule – 2 equivalent H atoms.