

# The Variation Principle

The energy calculated using an approximate wavefunction cannot be less than the true energy of the system.

If  $\chi$  is a trial function,

$$\frac{\langle \chi | \hat{H} | \chi \rangle}{\langle \chi | \chi \rangle} = \mathcal{E} \geq E_{\text{exact}} = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

For example, suppose  $\chi$  is a linear combination of exact eigenfunctions of  $\hat{H}$ ,

$$\chi = \sum_i c_i \psi_i \quad \text{with} \quad \hat{H} \psi_i = E_i \psi_i$$

Then

$$\begin{aligned} \langle \chi | \hat{H} | \chi \rangle &= \sum_j \sum_i c_j^* c_i \langle \psi_j | \hat{H} | \psi_i \rangle \\ &= \sum_j \sum_i c_j^* c_i E_i \langle \psi_j | \psi_i \rangle \\ &= \sum_i c_i^* c_i E_i \end{aligned}$$

But since  $c_i^* c_i = c_i^2 \geq 0$  for real coefficients, and  $E_i \geq E_0$

$$\frac{\langle \chi | \hat{H} | \chi \rangle}{\langle \chi | \chi \rangle} = \frac{\sum_i c_i^2 E_i}{\sum_i c_i^2} \geq E_0$$

Note: There are other types of variational parameters, in addition to coefficients of linear combination.

# $H_2^+$ : LCAO-MO Approach

## Linear Combination of Atomic Orbitals

$H_2^+$  :  $\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R_{ab}}$       only one electron

Assume  $\Psi = c_a a + c_b b$  where  $a, b$  are H 1s wavefunctions

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{c_a^2 \langle a | \hat{H} | a \rangle + 2c_a c_b \langle a | \hat{H} | b \rangle + c_b^2 \langle b | \hat{H} | b \rangle}{c_a^2 \langle a | a \rangle + 2c_a c_b \langle a | b \rangle + c_b^2 \langle b | b \rangle}$$
$$= \frac{c_a^2 \alpha + 2c_a c_b \beta + c_b^2 \alpha}{c_a^2 + 2c_a c_b S + c_b^2}$$

where  $\alpha = \langle a | \hat{H} | a \rangle = \langle b | \hat{H} | b \rangle$       a Coulomb integral

$\beta = \langle a | \hat{H} | b \rangle = \langle b | \hat{H} | a \rangle$       a resonance integral

$S = \langle a | b \rangle = \langle b | a \rangle$       the overlap integral

Coulomb integral  $\alpha = \langle a | -\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R_{ab}} | a \rangle$

$$= E_{1s} - \langle a | \frac{1}{r_b} | a \rangle + 1/R_{ab}$$

H atom      el.-nucl.      nuclear  
energy      attraction      repulsion

Resonance integral  $\beta = (E_{1s} + 1/R_{ab})S - \langle a | \frac{1}{r_b} | b \rangle < 0$

## $H_2^+$ : LCAO-MO Approach – 2

The **Variation Principle** is used to find the optimum  $c_a$  and  $c_b$ :

setting 
$$\left. \begin{array}{l} \frac{\partial E}{\partial c_a} = 0 \\ \frac{\partial E}{\partial c_b} = 0 \end{array} \right\} \Rightarrow \begin{array}{l} c_a(\alpha - E) + c_b(\beta - SE) = 0 \\ c_a(\beta - SE) + c_b(\alpha - E) = 0 \end{array}$$

requires that

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

**Secular Determinant**

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

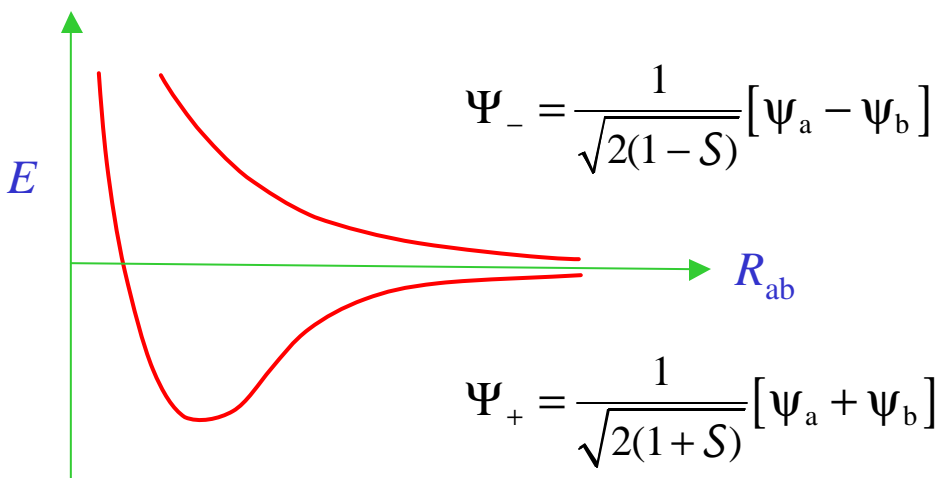
$$E^0 = \frac{\alpha + \beta}{1 + S} \quad E^* = \frac{\alpha - \beta}{1 - S}$$

$$c_a = c_b$$

$$c_a = -c_b$$

These equations can be solved by using the normalization condition:

$$\langle \Psi | \Psi \rangle = c_a^2 + 2c_a c_b S + c_b^2 = 1$$



# H<sub>2</sub> : LCAO-MO Approach

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

$$= \hat{h}_0(1) + \hat{h}_0(2) + \frac{1}{r_{12}} - \frac{1}{R_{ab}} \quad \text{where } \hat{h}_0 \text{ is the 1-e Hamiltonian for H}_2^+$$

Start by ignoring  $1/r_{12}$  (independent electron approach):

$$\Psi \approx \psi_i(1)\psi_j(2)\Phi_{\text{spin}} \quad \text{where } \psi_i \text{ are H}_2^+ \text{ functions.}$$

e.g. for ground state H<sub>2</sub>,  $\Psi_0 = \psi_+(1)\psi_+(2)\frac{1}{\sqrt{2}}[\alpha\beta - \beta\alpha]$

where  $\psi_+\psi_+ = \frac{1}{2(1+S)}[\underbrace{\psi_a\psi_a + \psi_b\psi_b}_{\text{ionic H}^+\text{H}^- + \text{H}^-\text{H}^+} + \underbrace{\psi_a\psi_b + \psi_b\psi_a}_{\text{covalent}}]$

Ionic configurations are weighted too highly!

Configuration Interaction corrects this by mixing in some excited states, such as  $\sigma^*\sigma^*$

$$\Psi_{\text{C.I.}} = \frac{1}{2(1+S)}[\psi_+\psi_+ + \lambda\psi_-\psi_-]\Phi_{\text{spin}}$$

Treat  $1/r_{12}$  as a perturbation to the simplified problem:

$$E = 2E(\text{H}_2^+) + \langle \Psi_0 | \frac{1}{r_{12}} | \Psi_0 \rangle - 1/R_{ab}$$

# Bond Formation in M.O. Theory

The results of calculations on simple molecules can be extended as general rules to more complicated systems.

Thus, to form a strong bond:

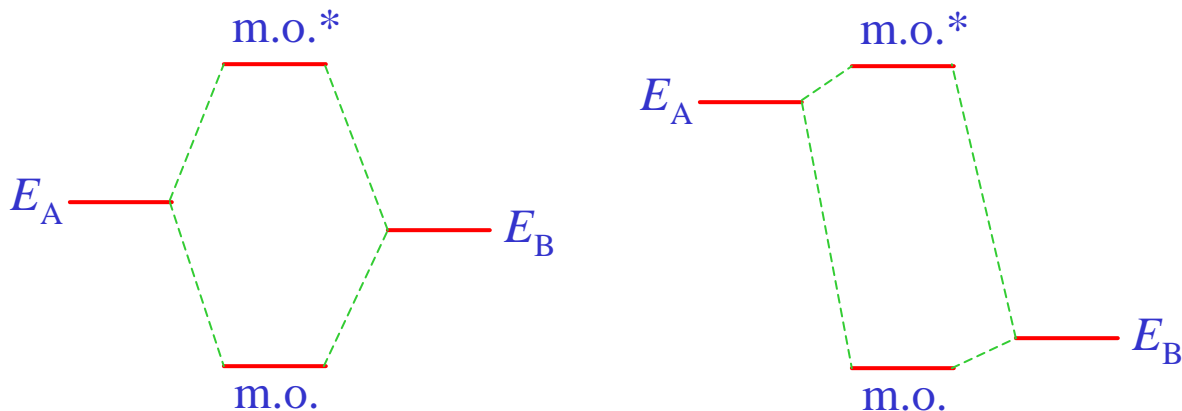
- ◆ Orbitals must have the same symmetry with respect to rotation about the internuclear axis. Otherwise  $S = 0$
- ◆ Orbitals must not be too small or too diffuse. Otherwise  $S$  will be too small. Valence shell electrons are most effective, with strengths roughly  $\sigma > \pi > \delta$
- ◆ Orbitals must be of similar energy. Otherwise...

If  $|\alpha_A - \alpha_B|$  is large, and  $S$  is small,

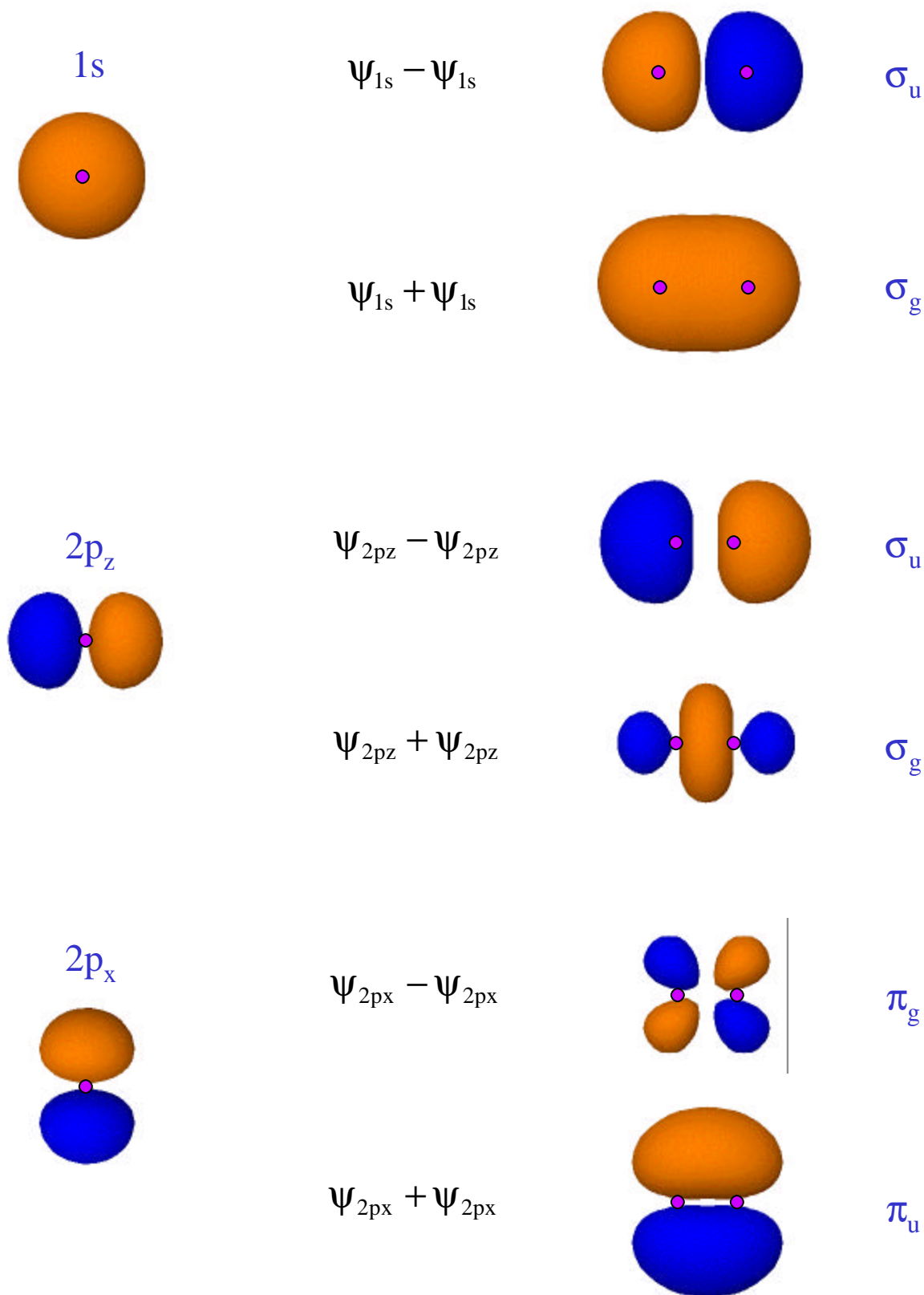
$$\begin{vmatrix} \alpha_A - E & \beta - SE \\ \beta - SE & \alpha_B - E \end{vmatrix} = 0$$

$$E \approx \alpha_A + \frac{\beta^2}{\alpha_A - \alpha_B}, \quad \alpha_B - \frac{\beta^2}{\alpha_A - \alpha_B}$$

$$\approx E_A + (\text{small term}), \quad E_B + (\text{small term})$$



# Molecular Orbitals of Diatomics



# Homonuclear Diatomics

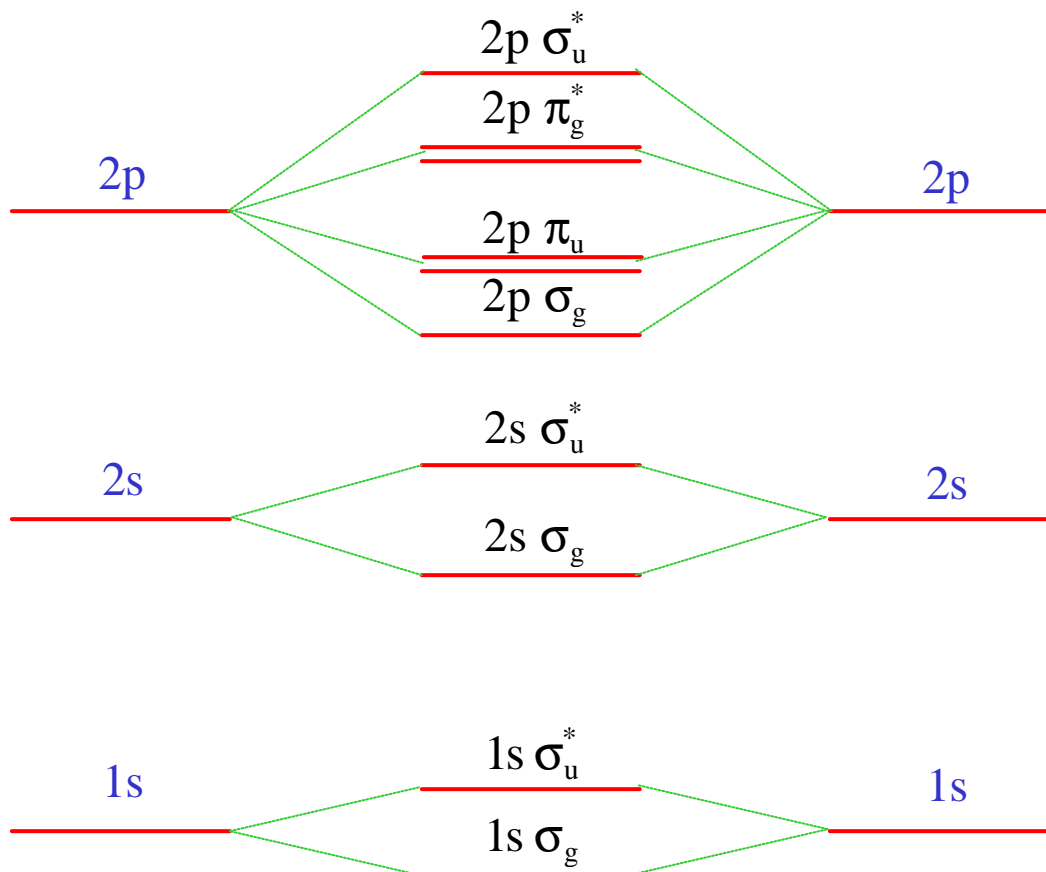
Molecular orbitals are classified as  $\sigma$ ,  $\pi$ ,  $\delta$ ,  $\phi$  according to their symmetry as viewed along the internuclear axis.

If the wavefunction changes sign upon inversion through a centre of symmetry, the orbital is labelled **u ungerade**;

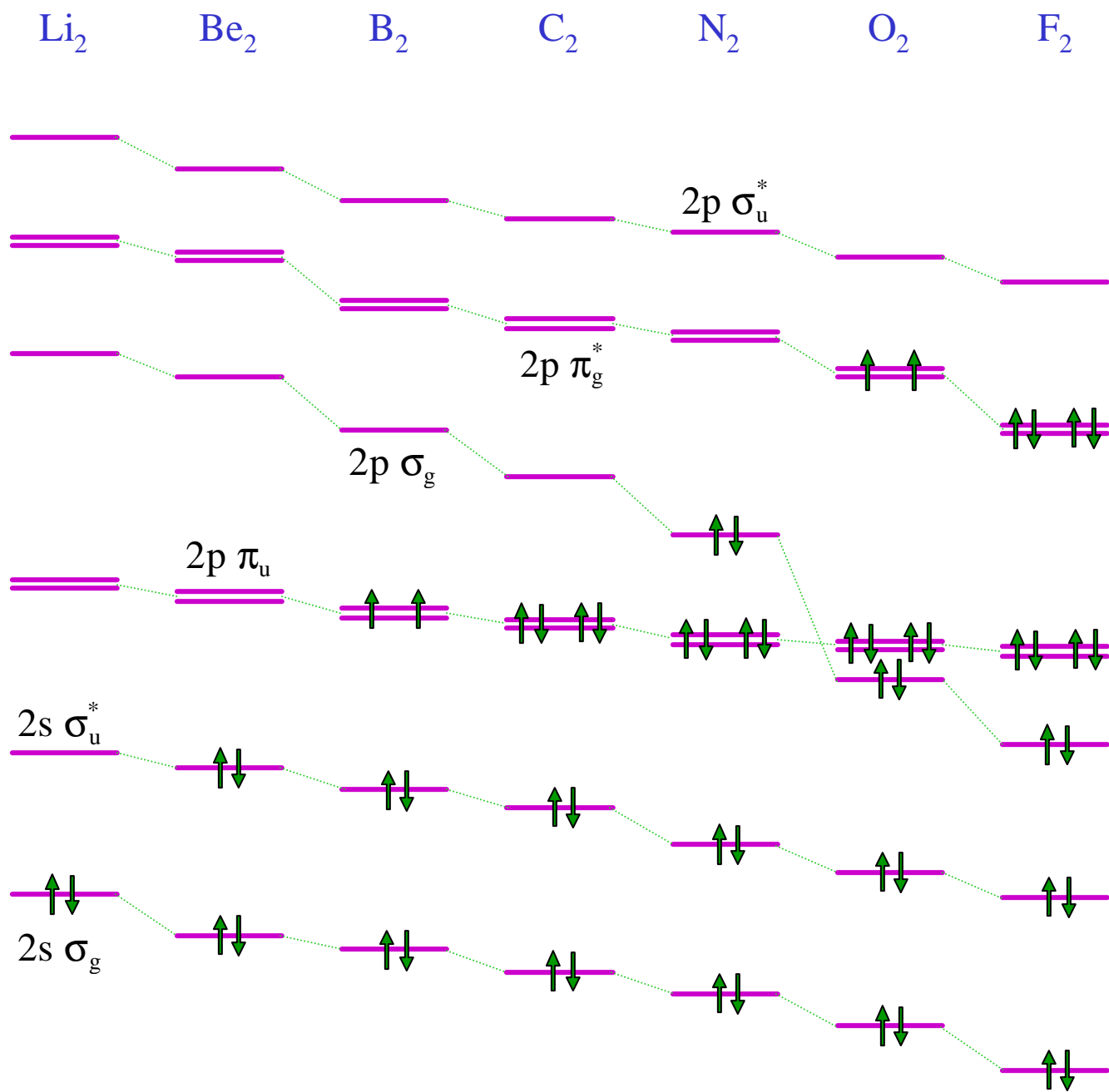
If the wavefunction does not change sign it is **g gerade**.

An atomic orbital that remains relatively unperturbed in a molecule (e.g. a lone pair) is labelled **n non-bonding**.

## Relative energies



# Homonuclear Diatomics – 2



All the above also have  $1s (\sigma_g)^2 (\sigma_u^*)^2$