

Lecture 27: Homonuclear Diatomic Molecules-II

The material in this lecture covers the following in Atkins.

14 Molecular structure

Molecular Orbital Theory

14.5 The structure of diatomic molecules

(f) The structures of homonuclear diatomic molecules

14.5 More about notation

(a) parity

(b) Term Symbols

Lecture on-line

Homonuclear diatomic molecules (PowerPoint)

Homonuclear diatomic molecules (PDF)

Handout for this lecture

Audio-visuals on-line

**Shape of molecular orbitals in homonuclear diatomic molecules
(PowerPoint)(From the Wilson Group,***)**

**Shape of molecular orbitals in homonuclear diatomic molecules
(PDF)(From the Wilson Group,***)**

**Composition of orbitals in homonuclear molecules
(6 MB MBQuick-Time with music)**

(A must from the Wilson Group,***)**

**The Occupation of homonuclear diatomic orbitals
(PowerPoint)(From the Wilson Group,***)**

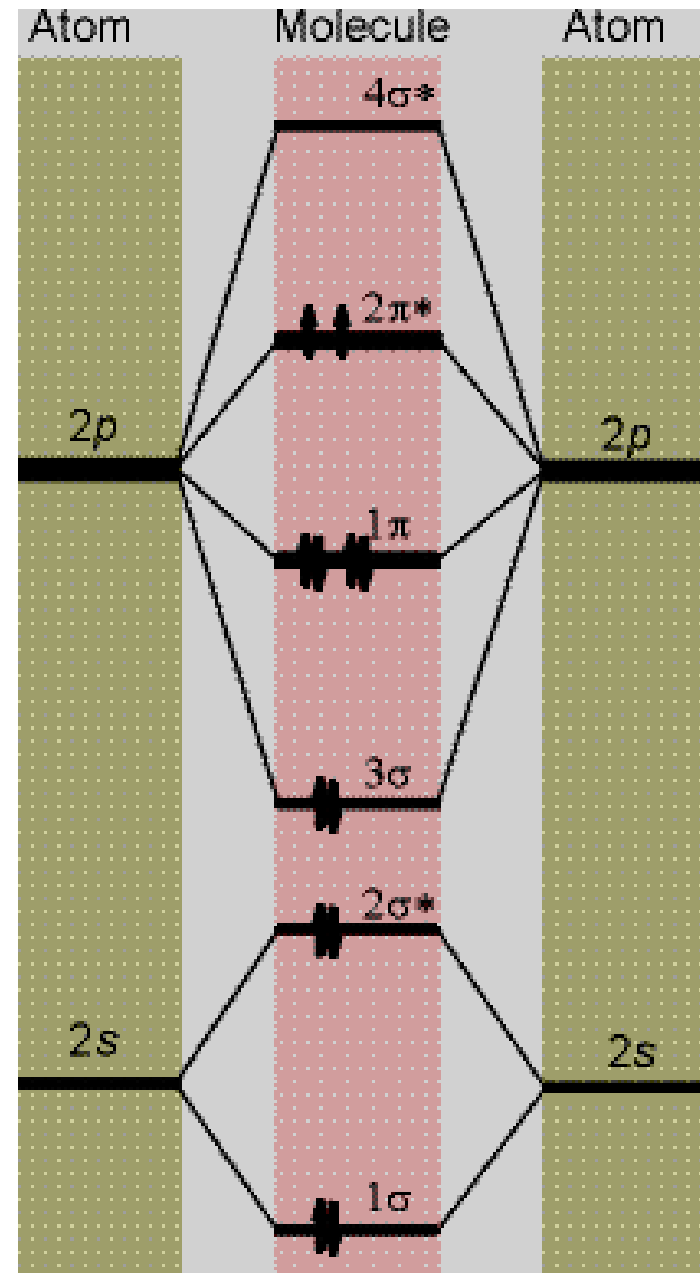
**The Occupation of homonuclear diatomic orbitals(PDF)
(From the Wilson Group,***)**

Molecular Orbital Theory

At the start of the second row Li-N we have mixing of $2s$ and $2p_{\sigma}$

The result is that $2\sigma^*$ is pushed down in energy whereas 3σ is raised

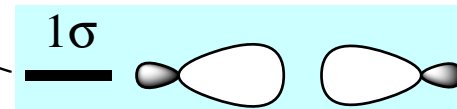
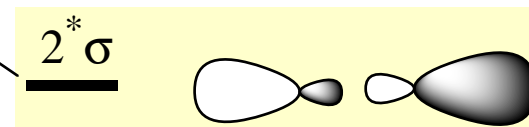
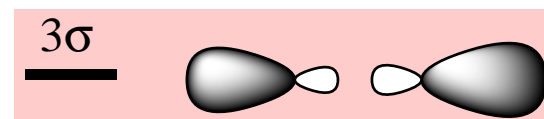
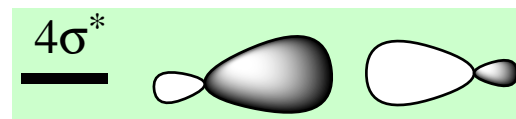
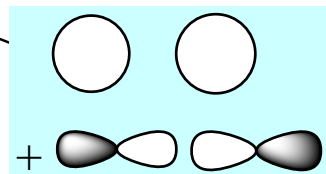
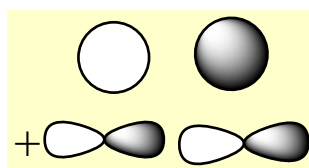
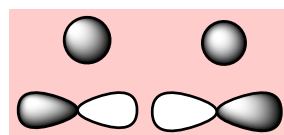
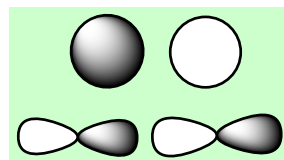
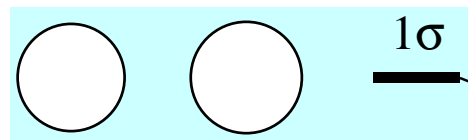
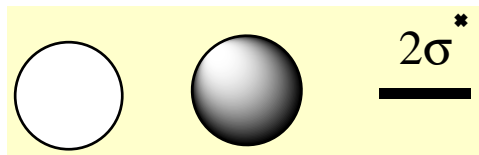
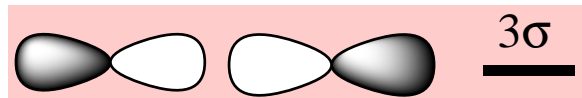
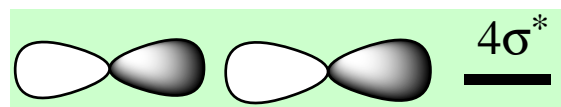
Diatomics



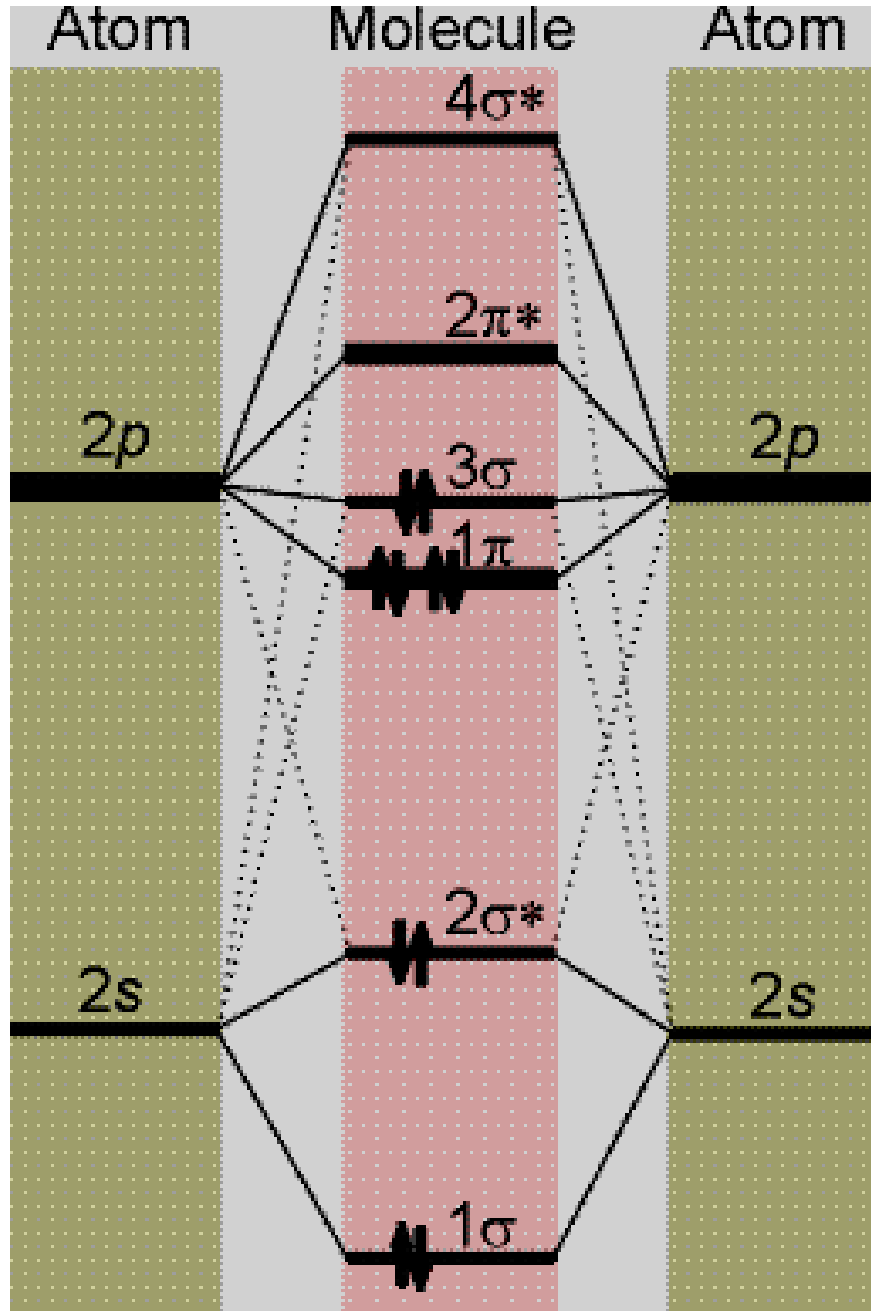
Molecular Orbital Theory

The effect of interactions between 2s and 2p

Diatomics



Molecular Orbital Theory



Diatomics

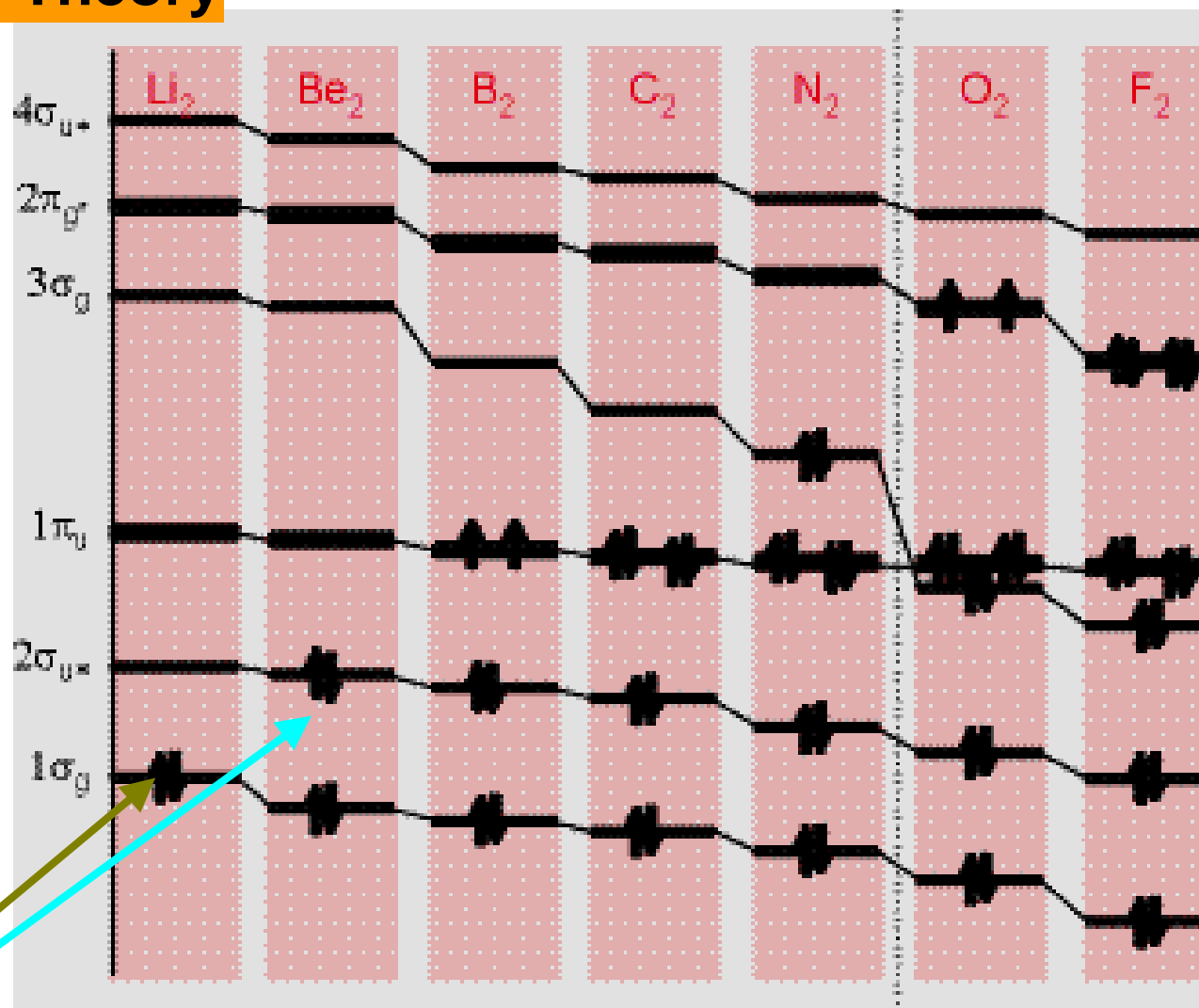
An alternative molecular orbital energy level diagram for homonuclear diatomic molecules.

As remarked in the text, this diagram should be used for diatomics up to and including N_2 .

Molecular Orbital Theory

Diatomics

The variation of the orbital energies of Period 2 homonuclear diatomics. The g and u labels are explained later (Section 14.6a).



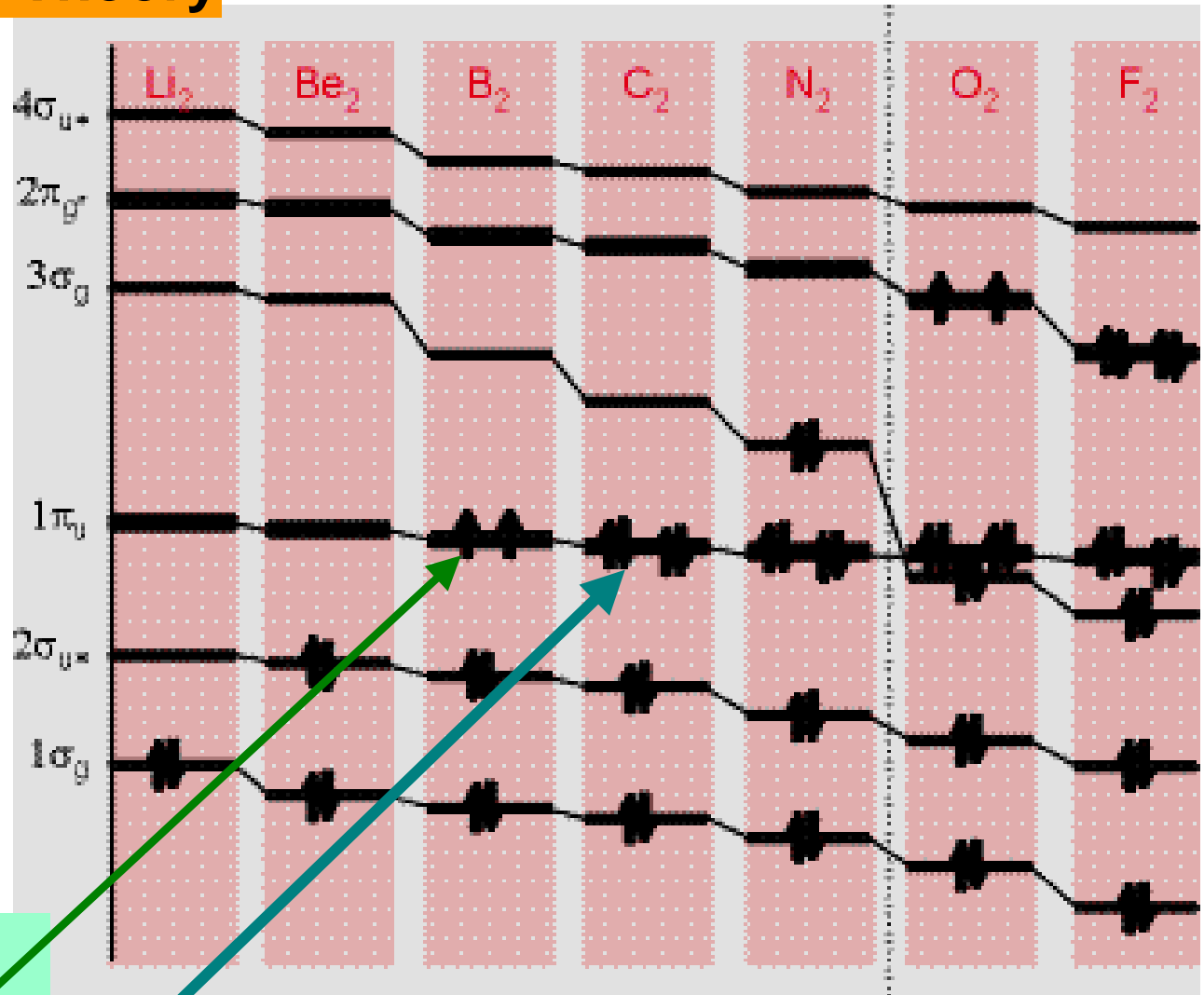
Fill up from below

Li: $2s^1$ Be: $2s^2$

Molecular Orbital Theory

Diatomics

The variation of the orbital energies of Period 2 homonuclear diatomics. The g and u labels are explained later (Section 14.6a).



Adding electrons of same spin to different π - orbitals before spin-pairing

Li:
2s¹

Be:
2s²

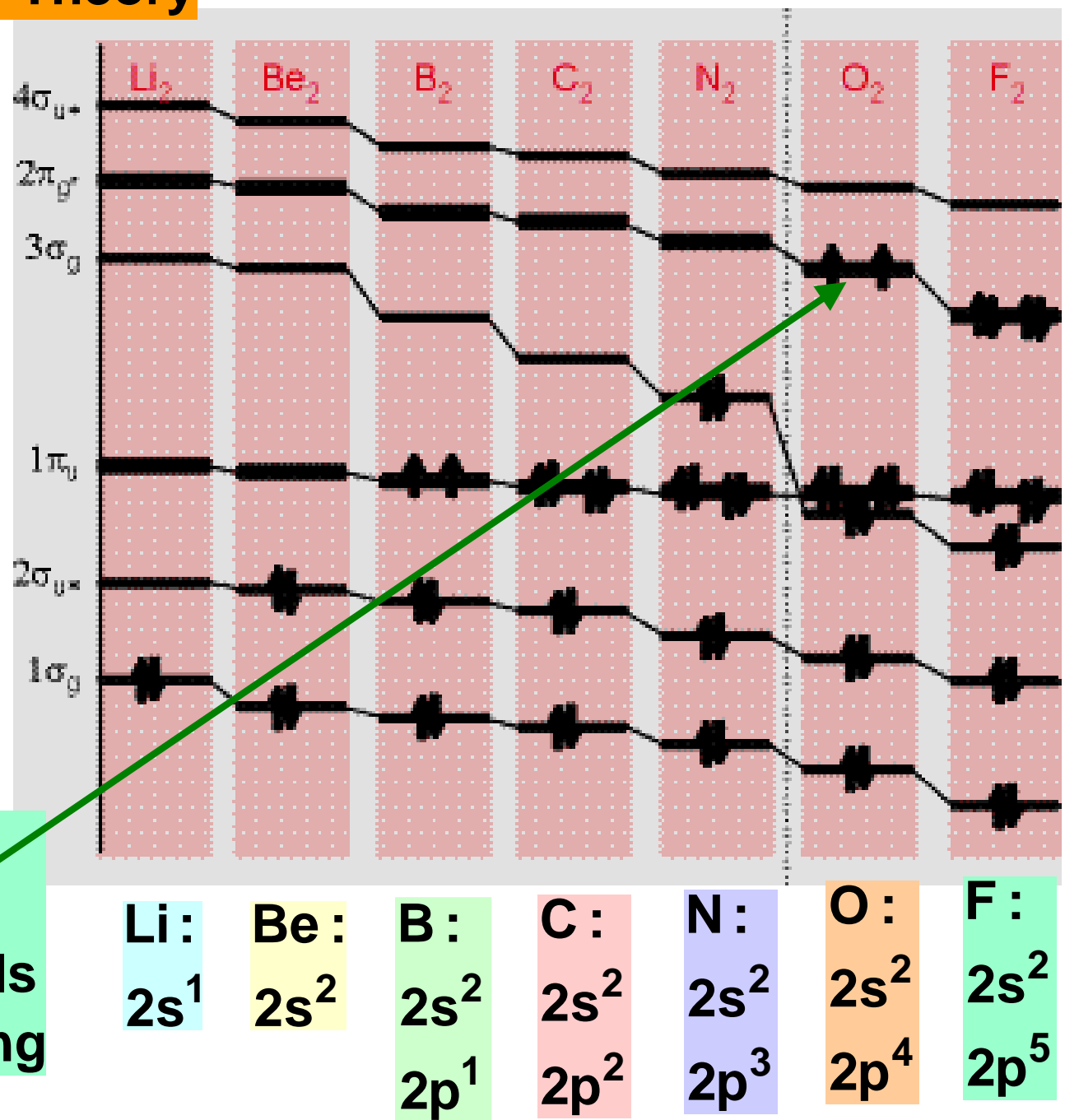
B:
2s²
2p¹

C:
2s²
2p²

Molecular Orbital Theory

Diatomics

The variation of the orbital energies of Period 2 homonuclear diatomics. The g and u labels are explained later (Section 14.6a).



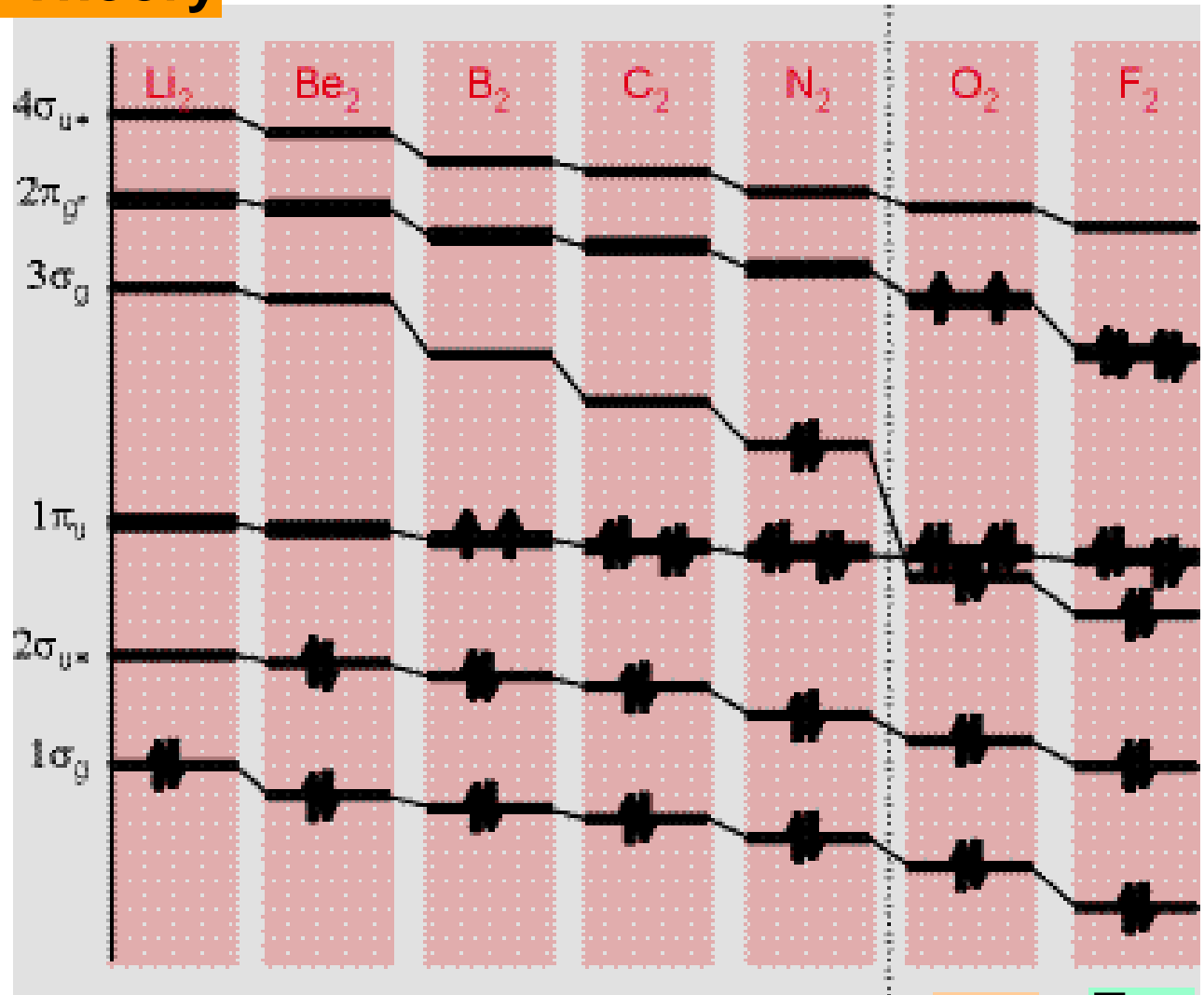
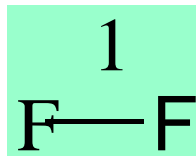
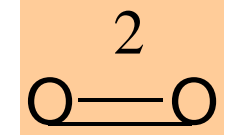
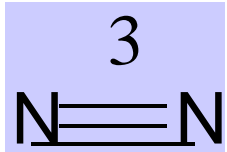
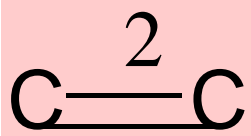
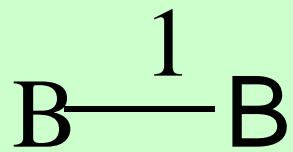
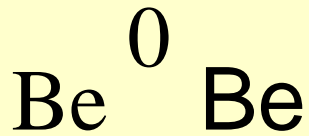
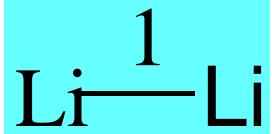
Adding electrons of same spin to different π -orbitals before spin-pairing

Molecular Orbital Theory

Diatomics

Bond orders :

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



Li:
2s¹

Be:
2s²

B:
2s²
2p¹

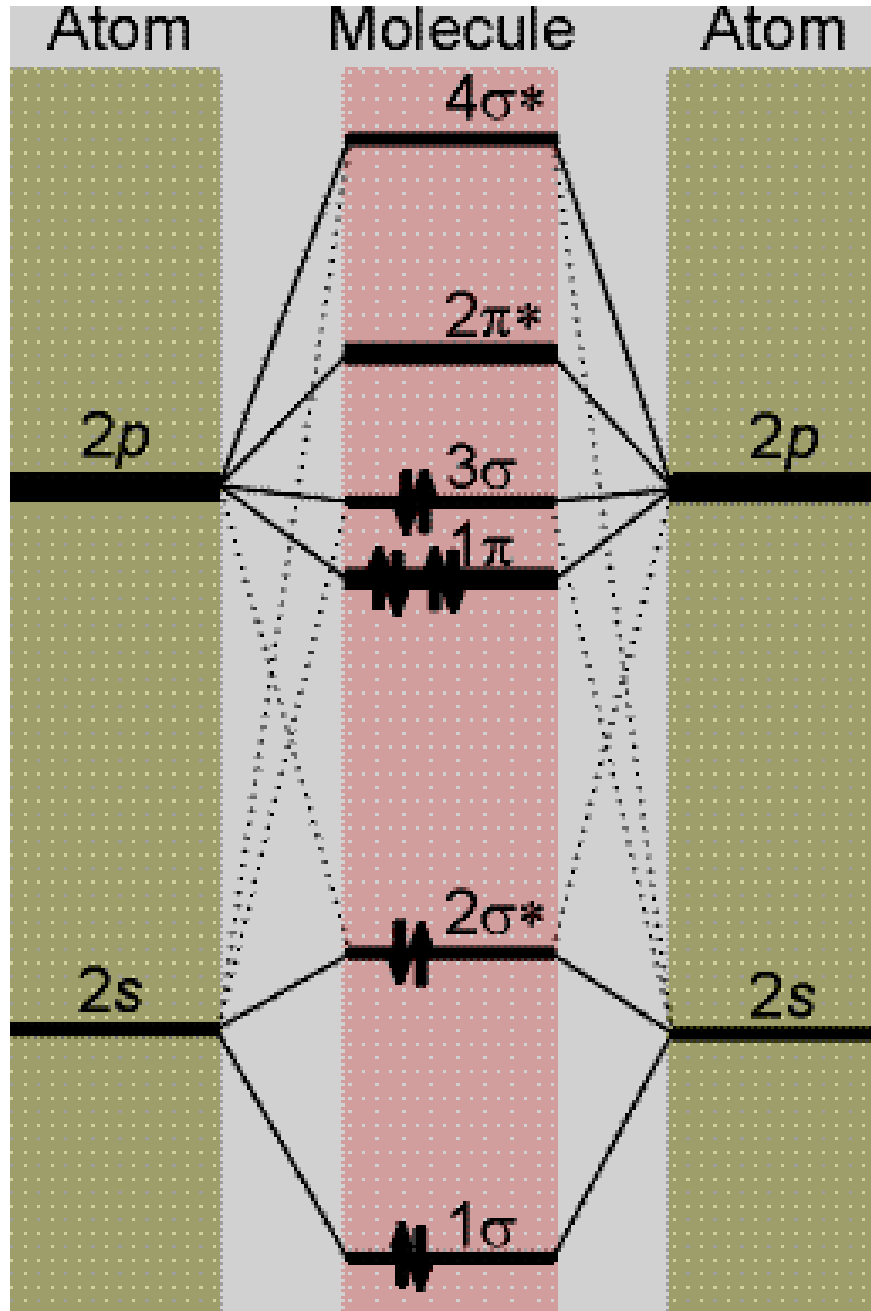
C:
2s²
2p²

N:
2s²
2p³

O:
2s²
2p⁴

F:
2s²
2p⁵

Molecular Orbital Theory

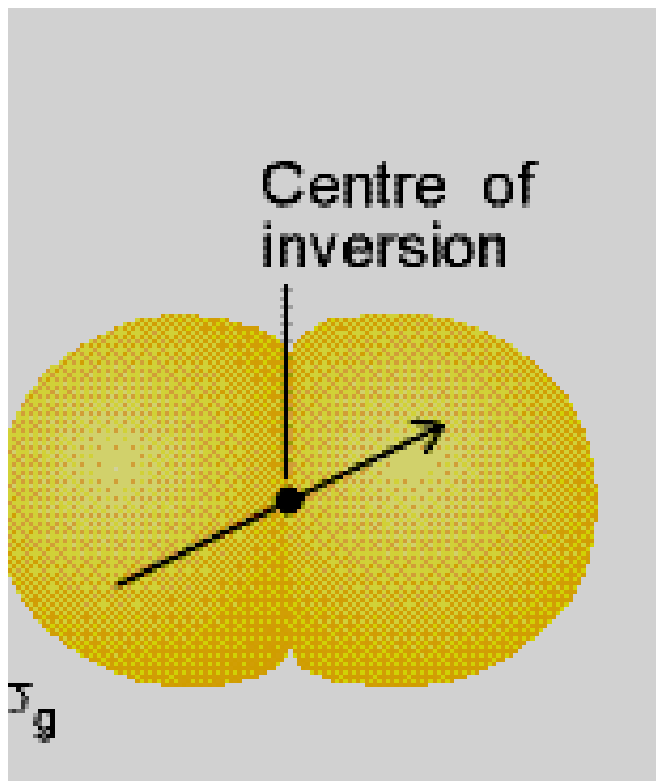


Diatomics

An alternative molecular orbital energy level diagram for homonuclear diatomic molecules.

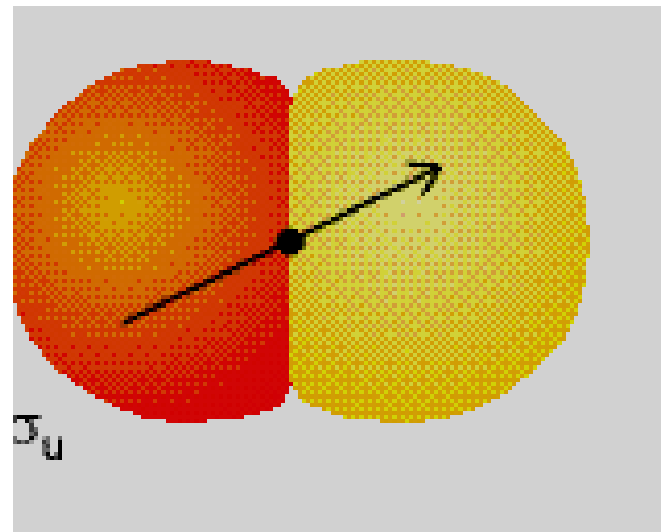
As remarked in the text, this diagram should be used for diatomics up to and including N_2 .

Molecular Orbital Theory



Diatomics

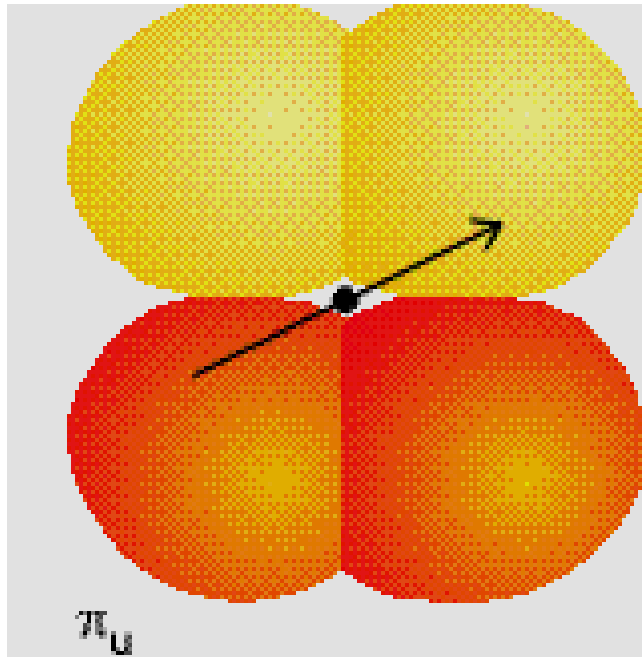
Parity of orbitals



The parity of an orbital is even (g) if its wavefunction is unchanged under inversion in the centre of symmetry of the molecule, but odd (u) if the wavefunction changes sign.

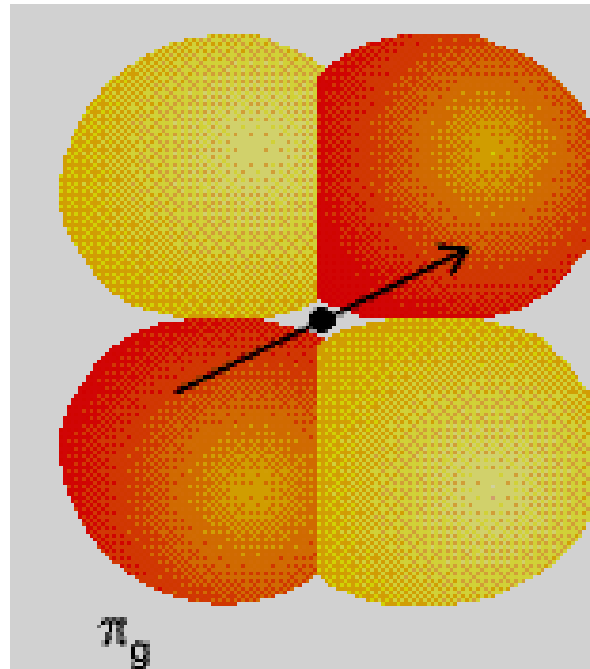
Heteronuclear diatomic molecules do not have a centre of inversion, so for them the g,u classification is irrelevant.

Molecular Orbital Theory



Diatomics

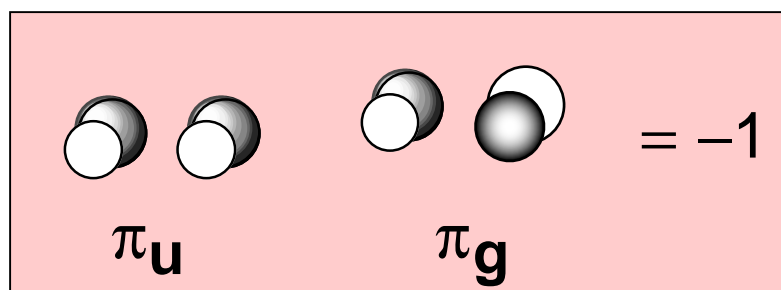
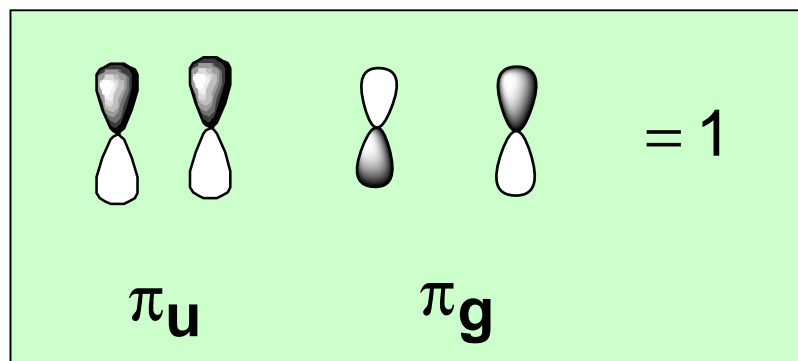
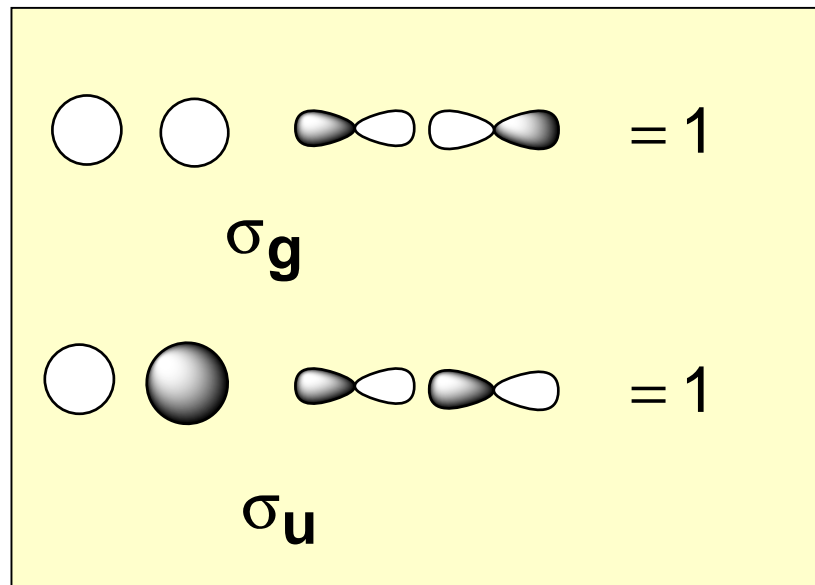
Parity of orbitals



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Heteronuclear diatomic molecules do not have a centre of inversion, so for them the g,u classification is irrelevant.

Molecular Orbital Theory



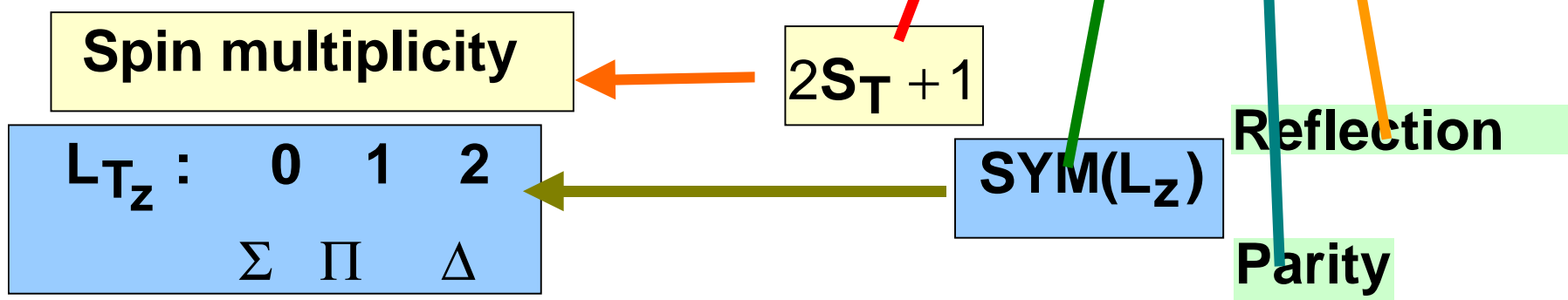
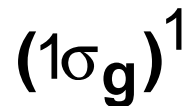
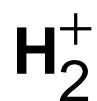
Diatomics

Reflection index

The \pm in a term symbol refers to the symmetry of an orbital when it is reflected in a plane containing the two nuclei.

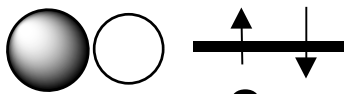
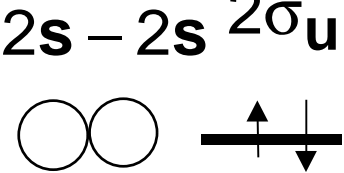
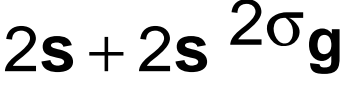
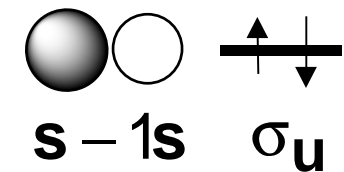
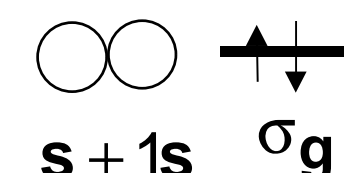
Molecular Orbital Theory Diatomics Term symbols

Molecule Configuration Term symbol



Molecular Orbital Theory Diatomics

Term symbols

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

Spin multiplicity

$$2S_T + 1$$

$L_{T_z} :$ 0 1 2

$\Sigma \quad \Pi \quad \Delta$

SYM(L_z)

Reflection

Parity

Molecular Orbital Theory Diatomics Term symbols

Molecule Configuration Term symbol

B_2

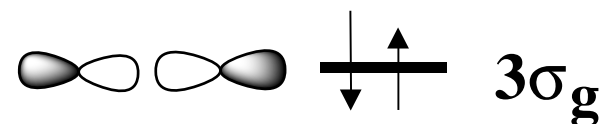
$(1\pi_u)^2$

$^3\Sigma_g^-$ Δ_g^+ Σ_g^+

C_2

$(1\pi_u)^4$

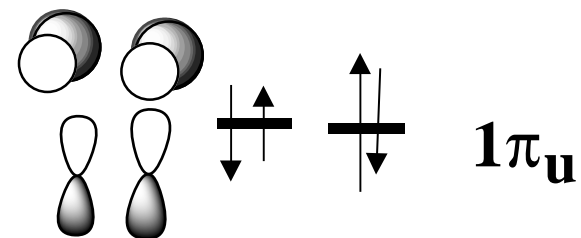
Σ_g^+



N_2^+

$(3\sigma_g)^1(1\pi_u)^4$

$^2\Sigma_g^+$



N_2

$(3\sigma_g)^2(1\pi_u)^4$

Σ_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^- $(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^1$

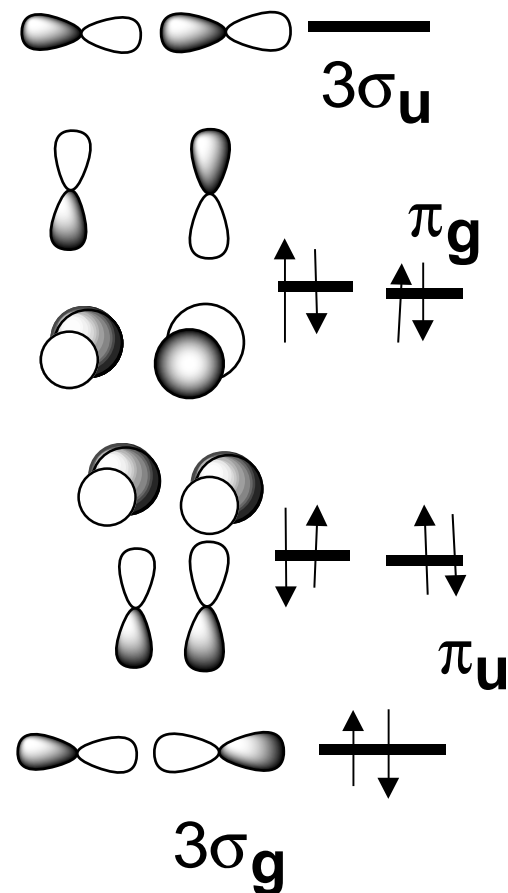
$^2\Pi_g^-$ $^2\Pi_g^+$

O_2 $(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^2$

$^3\Sigma_g^-$ Δ_g^+ Σ_g^-

F_2 $(3\sigma_g)^2(1\pi_u)^4(1\pi_g)^4$

Σ_g^-



Spin multiplicity

$$2S_T + 1$$

$L_{T_z} :$ 0 1 2

Σ Π Δ

SYM(L_z)

Reflection

Parity

Molecular Orbital Theory Diatomics Comparing MO and VB Theory

For the hydrogen molecule



$A=1s_A$



$B=1s_B$

We have the valence bond wavefunction

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

Singlet

And the molecular orbital wavefunction

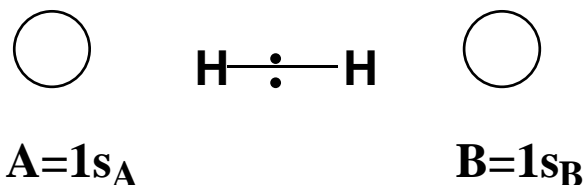
$$\Psi(1,2)_{\text{MO}} = \frac{1}{2} [\{A(1) + B(1)\}\{A(2) + B(2)\}] \times [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

Singlet

Molecular Orbital Theory

Diatomics

Comparing MO and VB Theory



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

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

The two wavefunctions have the same spin - part. Thus we need only compare space - parts

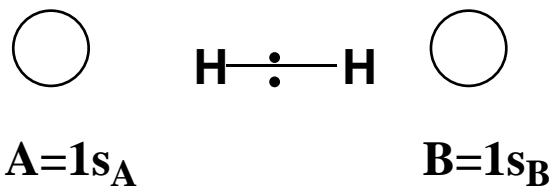
$$\Psi(1,2)_{\text{VB}} = \frac{1}{\sqrt{2}} [A(1)B(2) + A(2)B(1)]$$

$$\Psi(1,2)_{\text{MO}} = \frac{1}{2} [\{A(1) + B(1)\}\{A(2) + B(2)\}]$$

Molecular Orbital Theory

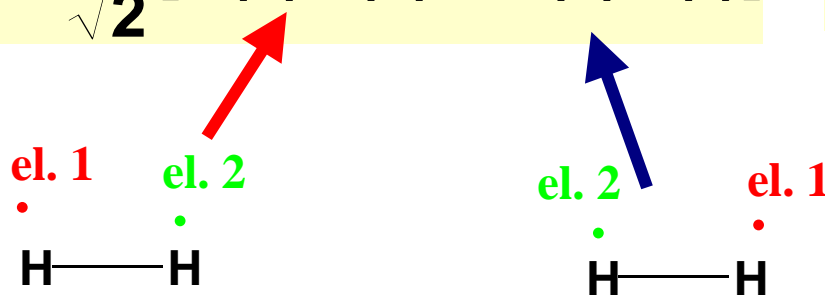
Diatomics

Comparing MO and VB Theory



$$\Psi(1,2)_{VB} = \frac{1}{\sqrt{2}} [A(1)B(2) + A(2)B(1)]$$

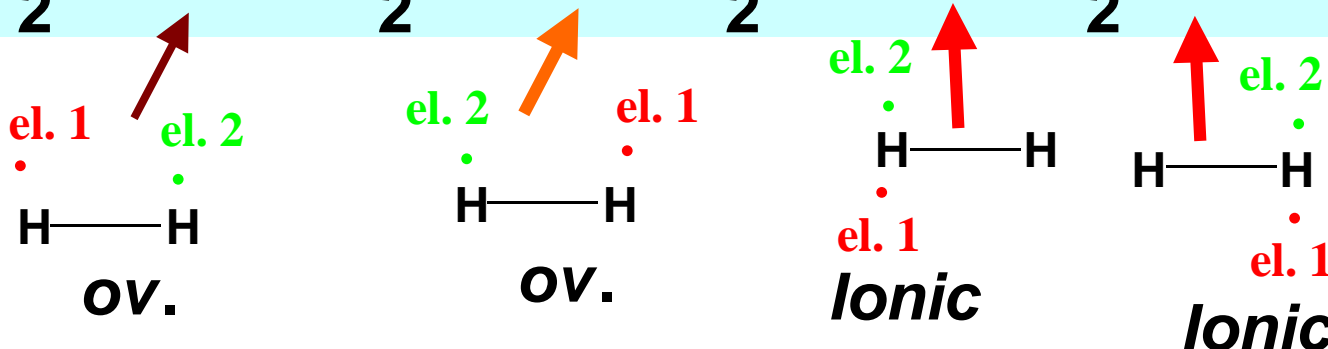
Both terms describe a covalent Bond



$$\Psi(1,2)_{MO} = \frac{1}{2} [\{A(1) + B(1)\}\{A(2) + B(2)\}]$$

$$= \frac{1}{2} A(1)B(2) + \frac{1}{2} B(1)A(2) + \frac{1}{2} A(1)A(2) + \frac{1}{2} B(1)B(2)$$

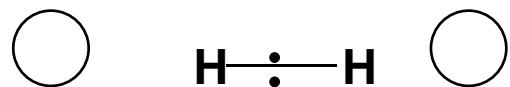
Equal mixture of ionic and covalent bond



Molecular Orbital Theory

Diatomics

Comparing MO and VB Theory



$A=1s_A$

$B=1s_B$

$$\begin{aligned}\Psi(1,2)_{\text{MO}} &= \frac{1}{2} \Psi(1,2)_{\text{VB}} + \frac{1}{2} \Psi(1,2)_{\text{ionic}} \\ &= \frac{1}{2} A(1)B(2) + \frac{1}{2} B(1)A(2) + \frac{1}{2} A(1)A(2) + \frac{1}{2} B(1)B(2)\end{aligned}$$

A better wavefunction would have different contributions from $\Psi(1,2)_{\text{VB}}$ and $\Psi(1,2)_{\text{ionic}}$

$$\Psi(1,2)_{\text{better}} = a \Psi(1,2)_{\text{VB}} + b \Psi(1,2)_{\text{ionic}}$$

Normally $|a^2| > |b^2|$

What you must learn from this lecture

The following refers to homonuclear molecules for elements from H to F and other main group elements.

. Understand (and recall) the energy ordering and qualitative composition of the orbitals

2. Be able to construct the electronic configuration using the Pauli exclusion principle and Hund's rule.

3. Understand the different parts of a term symbol for homonuclear diatomic molecules

4. Be able to determine the parity and reflection index of a molecule

5. be able to construct a term symbol from an electronic configuration

6. Understand the chemical difference between a VB wavefunction for H_2 and the corresponding MO function. Realize what would be a better wavefunction