Chemistry 2

Lecture 1

Quantum Mechanics in Chemistry

THE UNIVERSITY OF SYDNEY

Your lecturers

8am

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12pm

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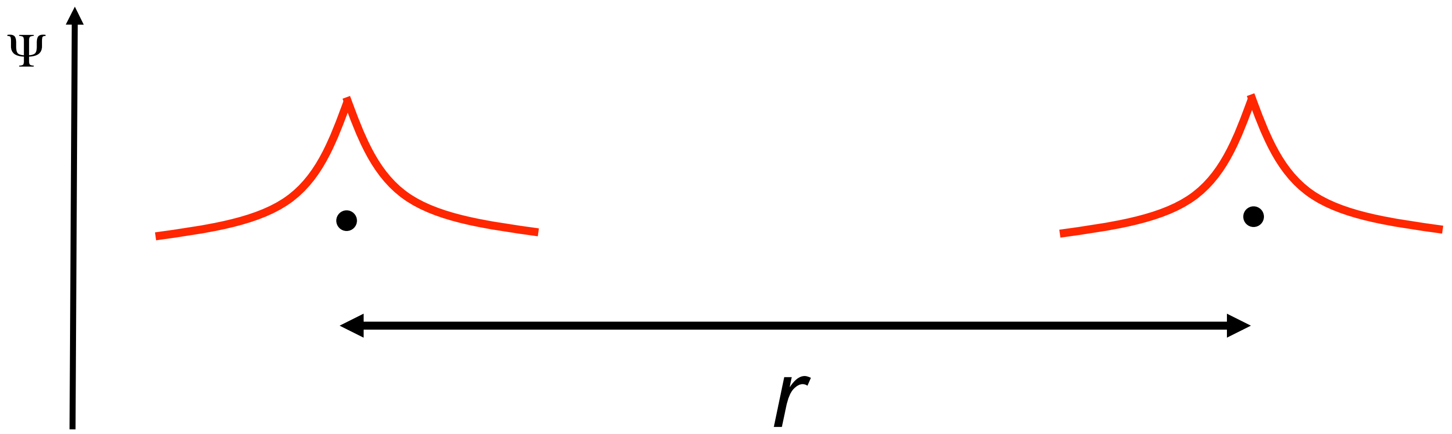
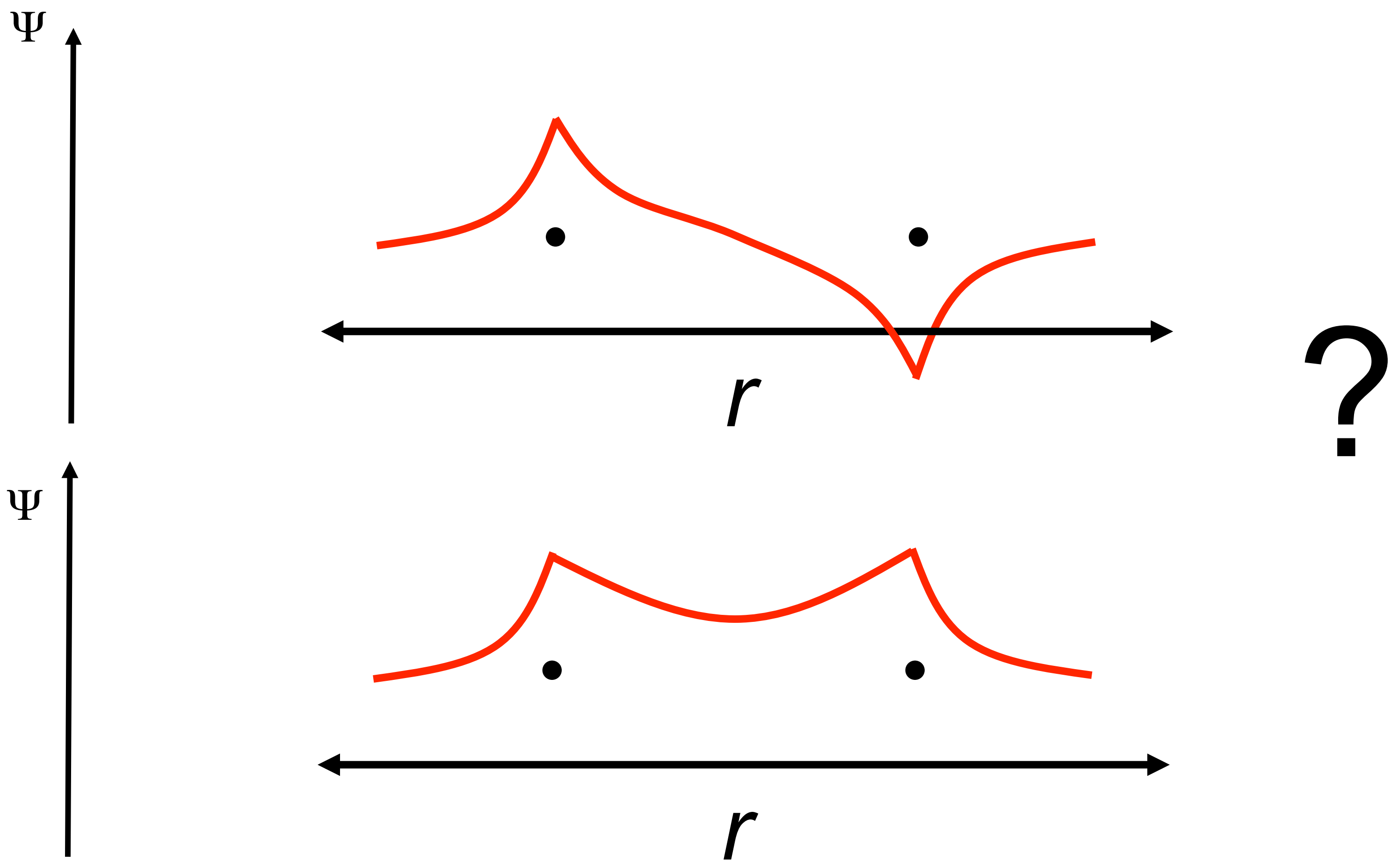
Revision – H_2^+

- Near each nucleus, electron should behave as a 1s electron.
- At dissociation, 1s orbital will be exact solution at each nucleus

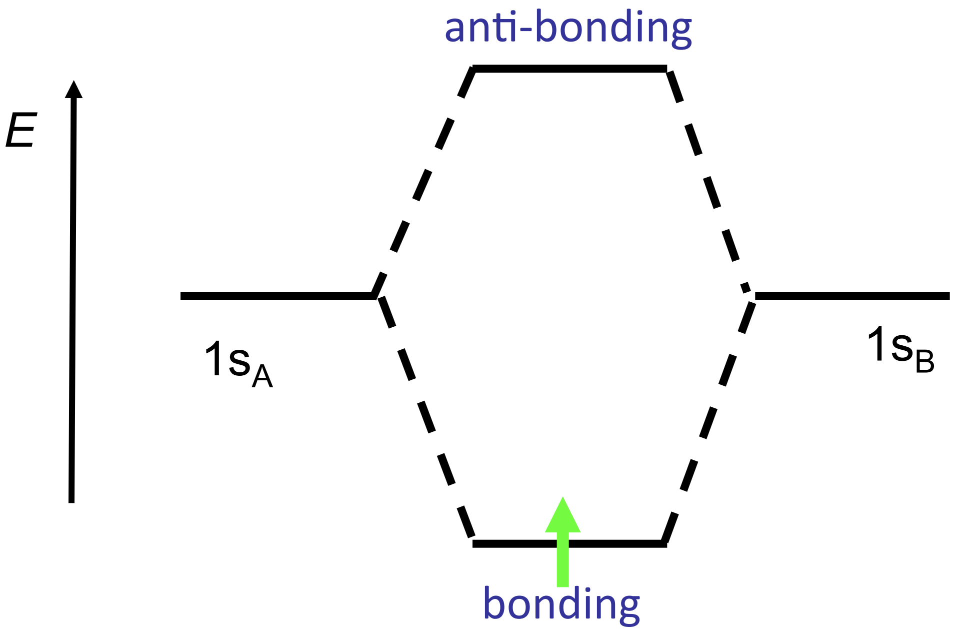


Revision – H_2^+

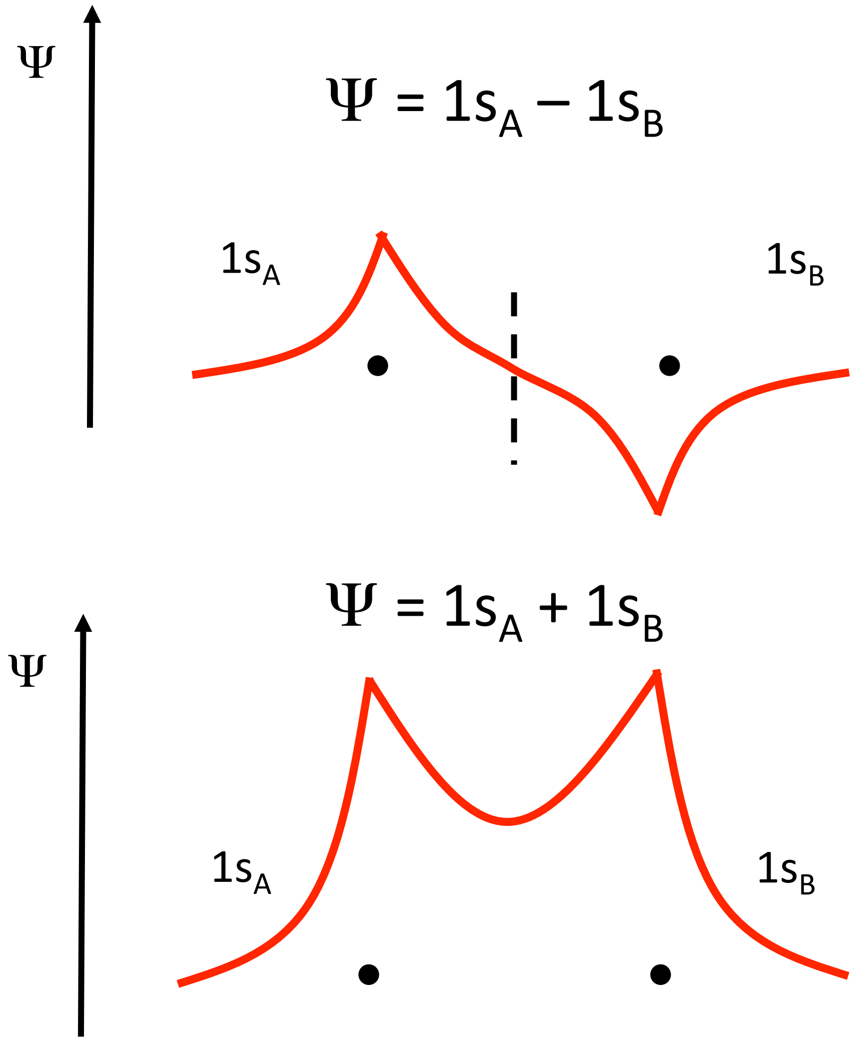
- At equilibrium, we have to make the lowest energy possible using the 1s functions available



Revision – H_2^+

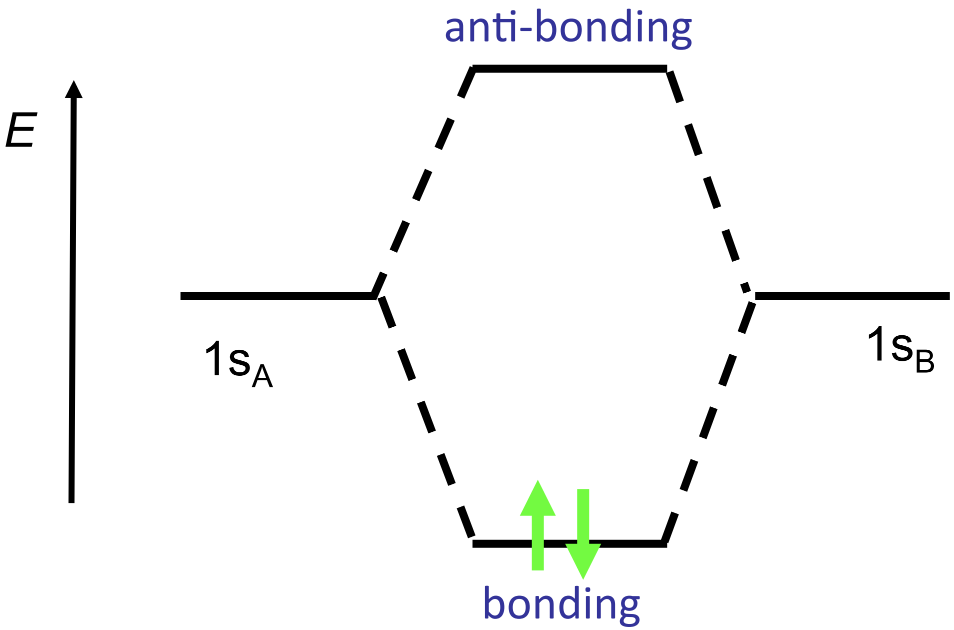


E
anti-bonding
$1s_A$
$1s_B$
bonding



Ψ
$\Psi = 1s_A - 1s_B$
$1s_A$
$1s_B$
Ψ
$\Psi = 1s_A + 1s_B$
$1s_A$
$1s_B$

Revision – H_2



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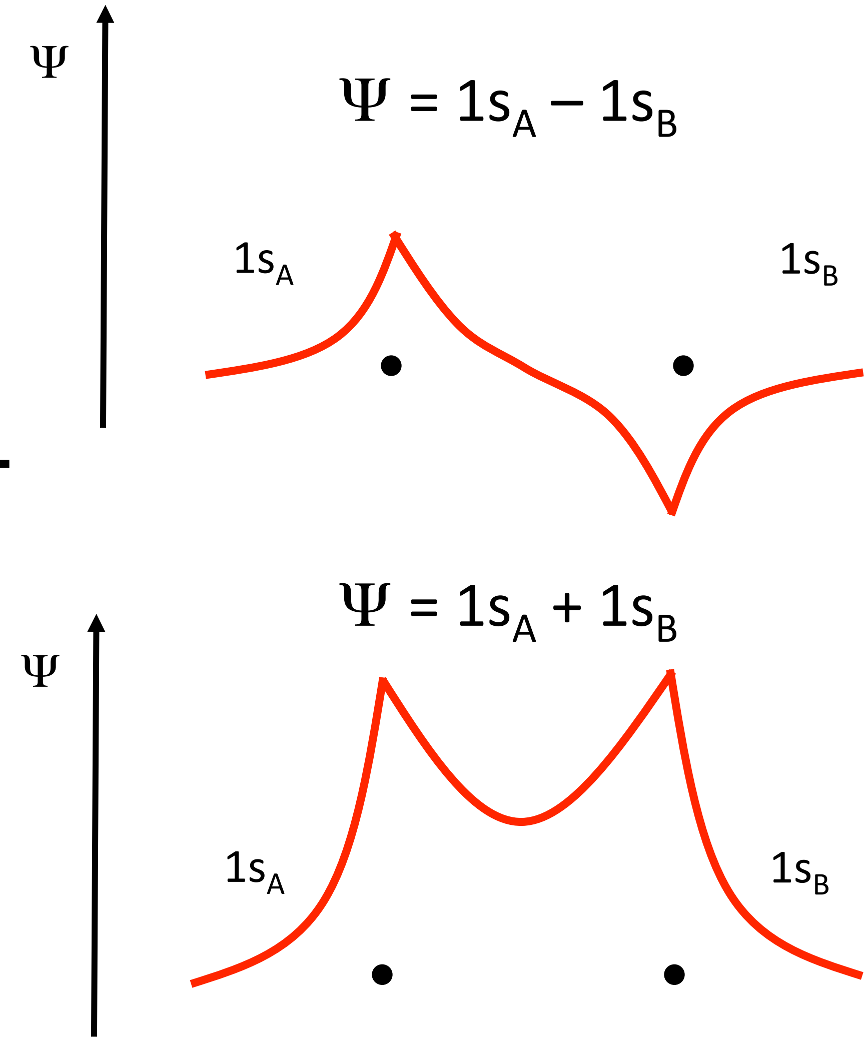

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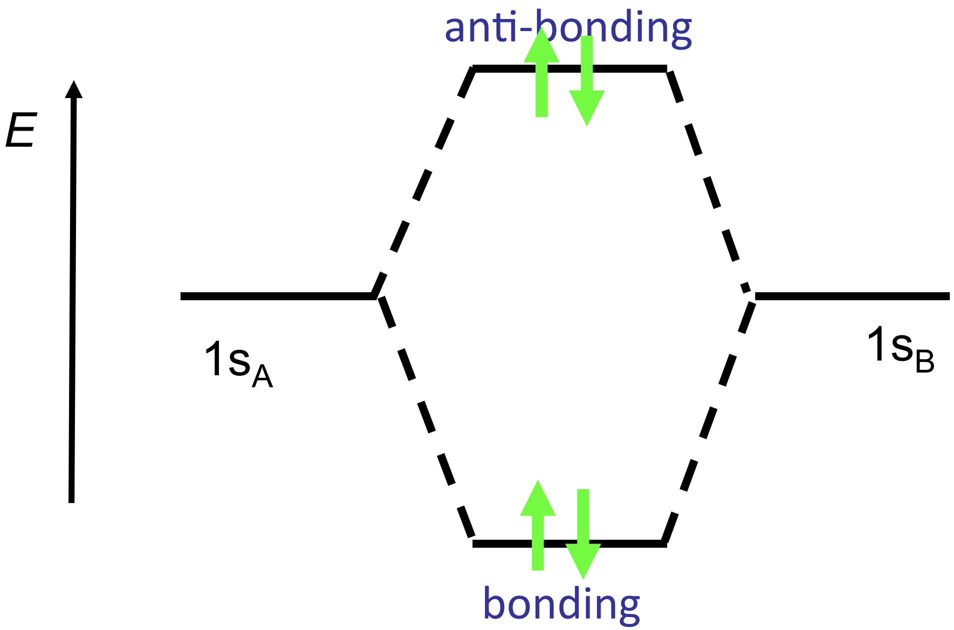
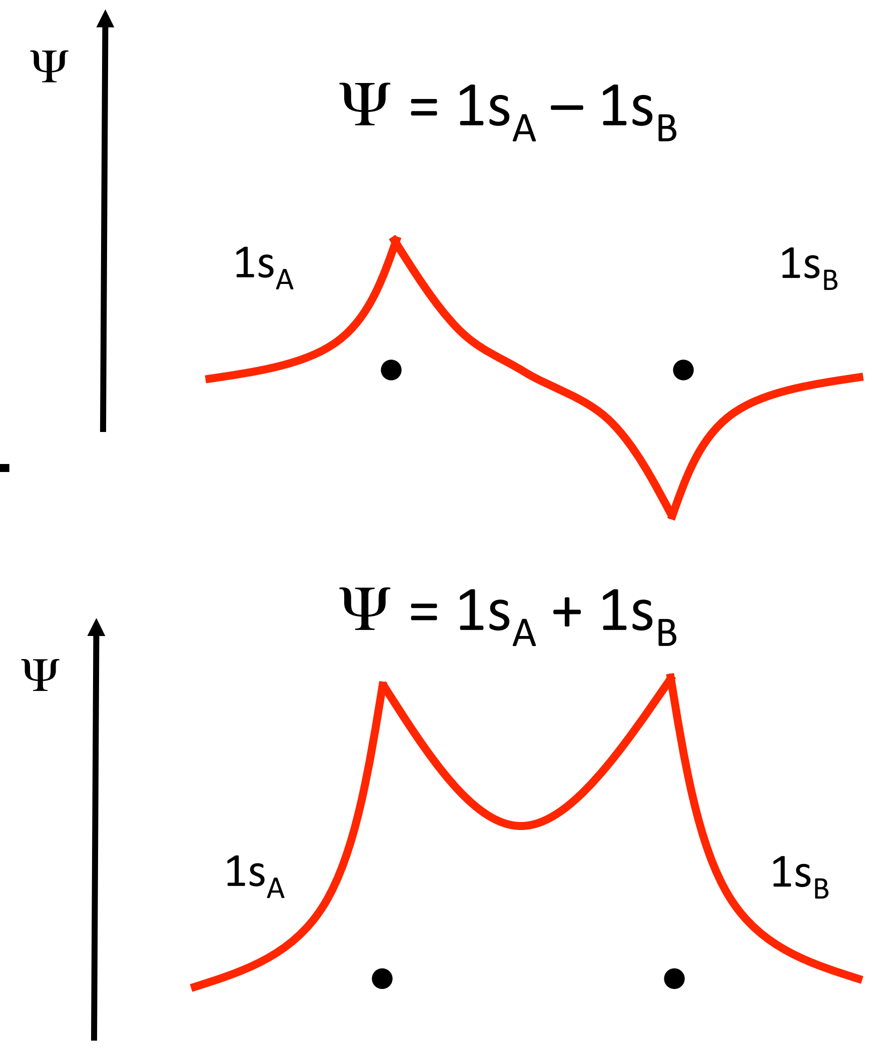
Revision – He_2



NOT BOUND!!



2nd row homonuclear diatomics

- Now what do we do? So many orbitals!

Interacting orbitals

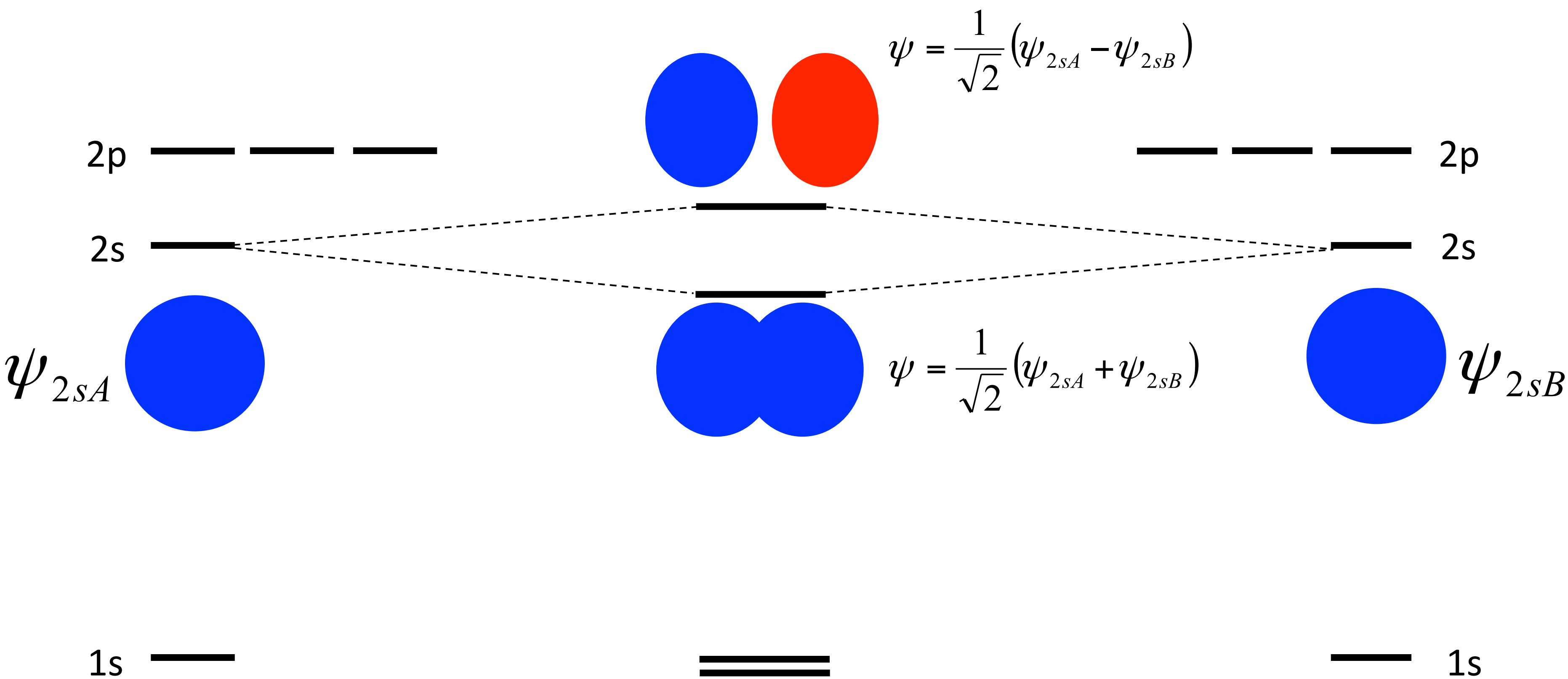
Orbitals can interact and combine to make new approximate solutions to the Schrödinger equation. There are two considerations:

1.Orbitals interact **inversely** proportionally to their **energy difference**. Orbitals of the same energy interact completely, yielding completely mixed linear combinations. In quantum mechanics, energy and frequency are related ($E=h\nu$). So, energy matching is equivalent to the phenomenon of **resonance**.

2.The extent of orbital mixing is given by the **resonance integral β**. We will show how beta is calculated in a later lecture.

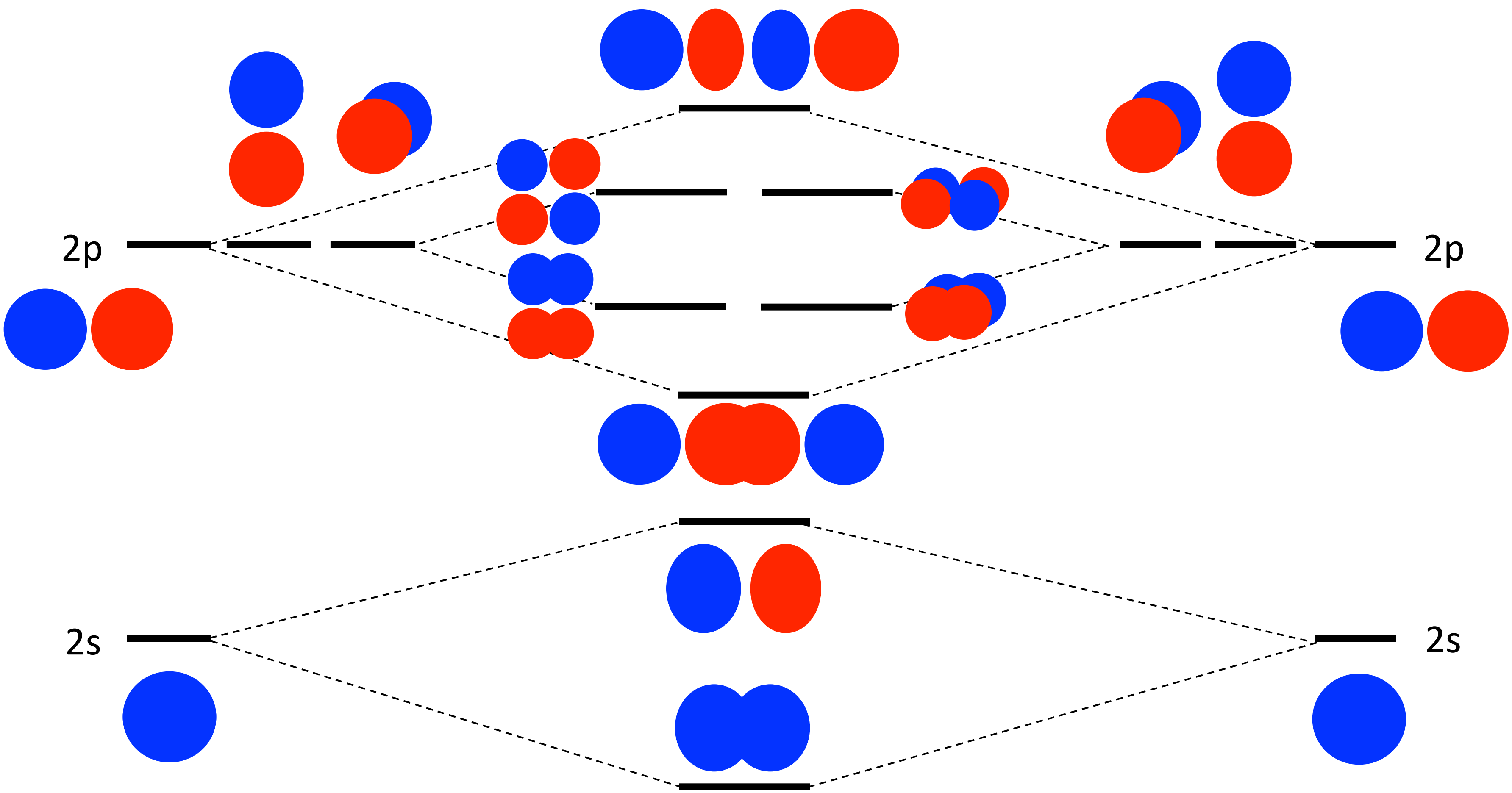
Interacting orbitals

1. Orbitals interact proportionally to the inverse of their energy difference. Orbitals of the same energy interact completely, yielding completely mixed linear combinations.

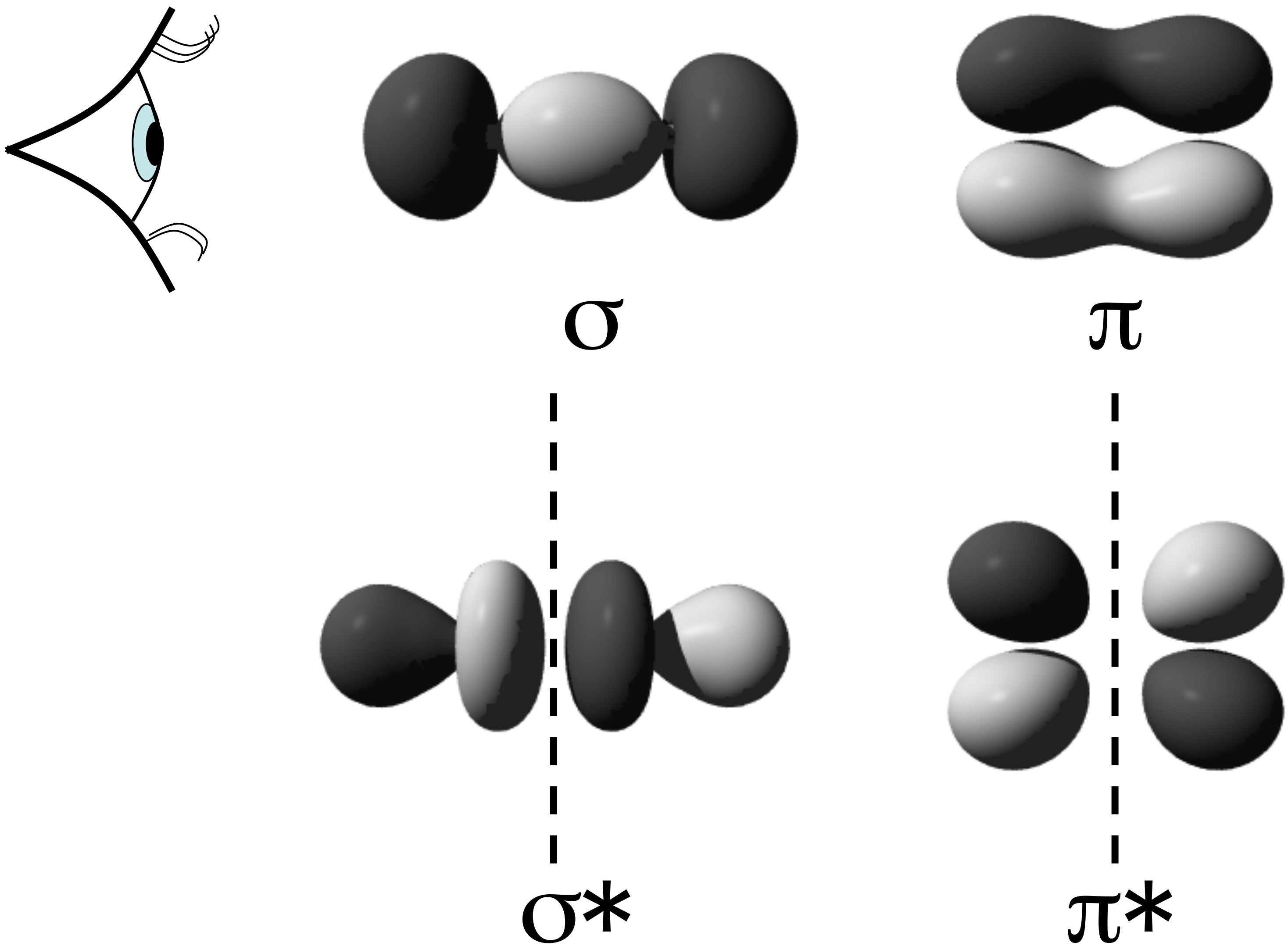


(First year) MO diagram

Orbitals interact *most* with the corresponding orbital on the other atom to make perfectly mixed linear combinations. (we ignore core).

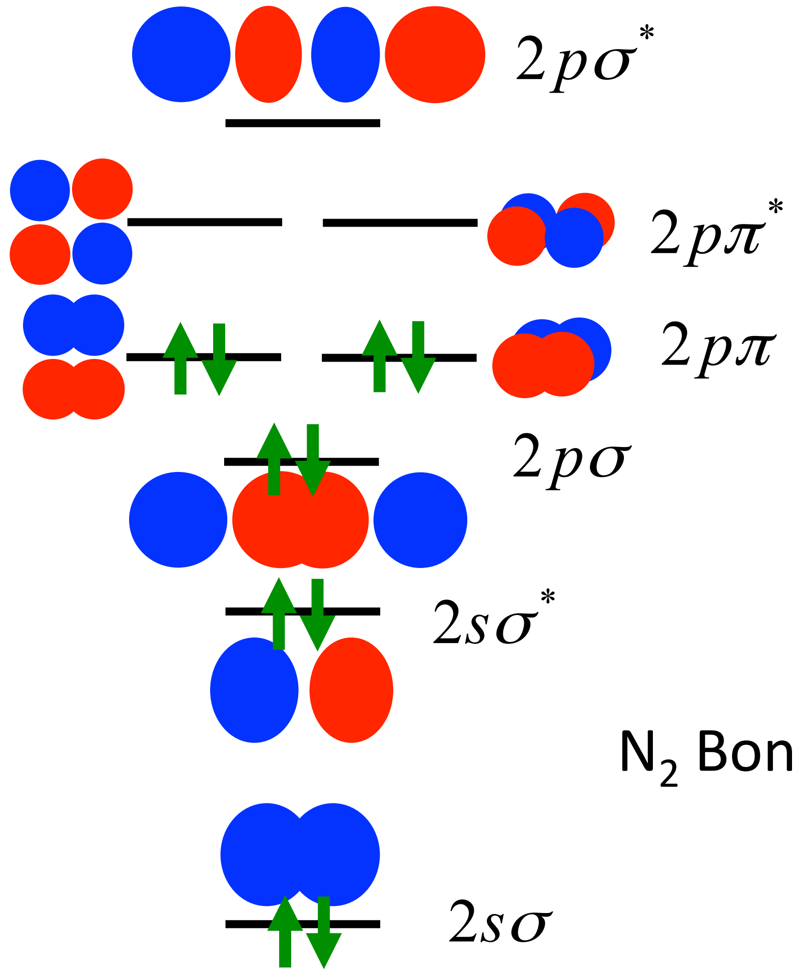


Molecular Orbital Theory - Revision



Molecular Orbital Theory - Revision

- Can predict bond strengths *qualitatively*



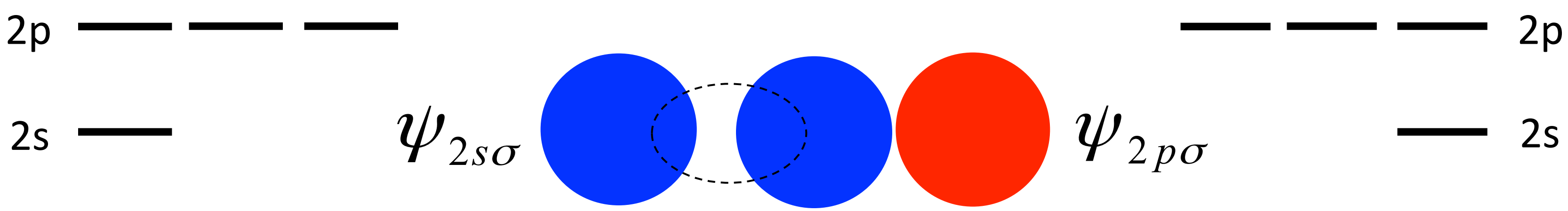
diamagnetic

N_2 Bond Order = 3

Interacting orbitals

1. The extent of orbital mixing is given by the integral

$$\beta = \text{something}$$

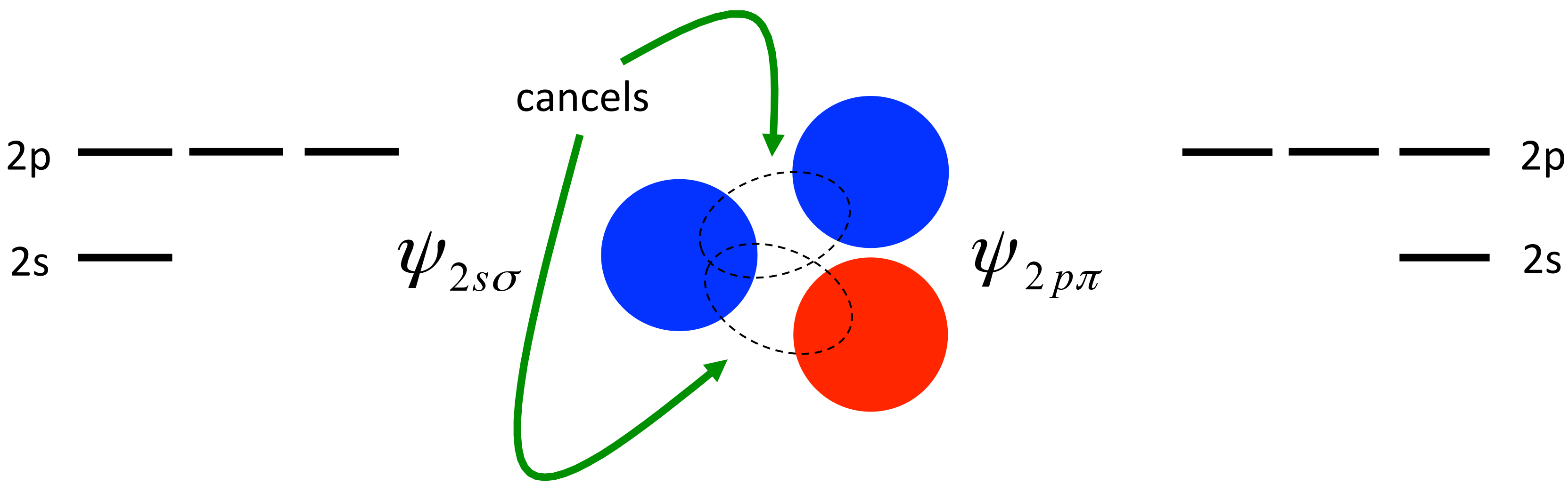


The 2s orbital on one atom *can* interact with the 2p from the other atom, but since they have different energies this is a smaller interaction than the 2s-2s interaction. We will deal with this later.

Interacting orbitals

1. The extent of orbital mixing is given by the integral

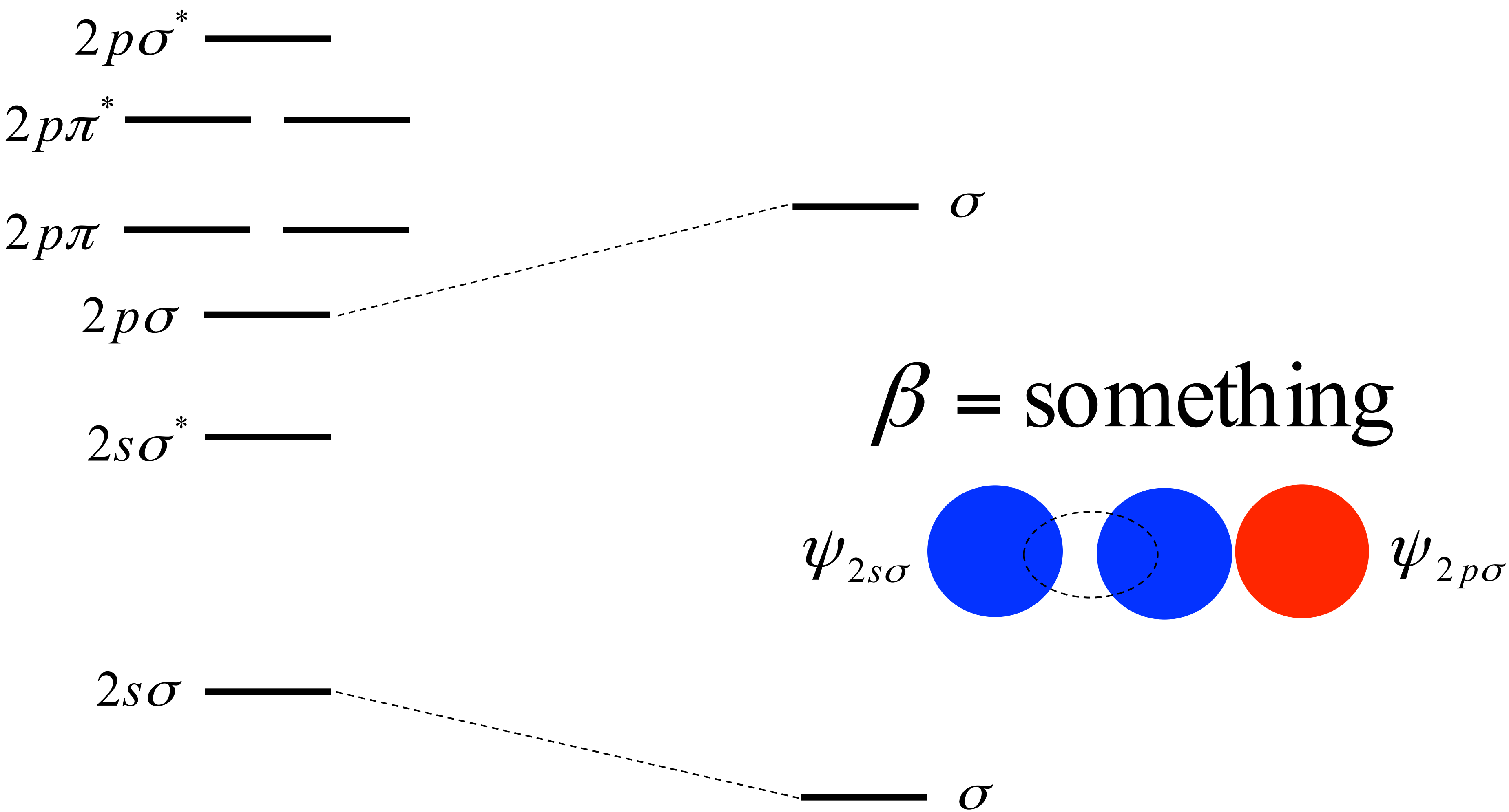
$$\beta = 0$$



There is no net interaction between these orbitals.
The positive-positive term is cancelled by the positive-negative term

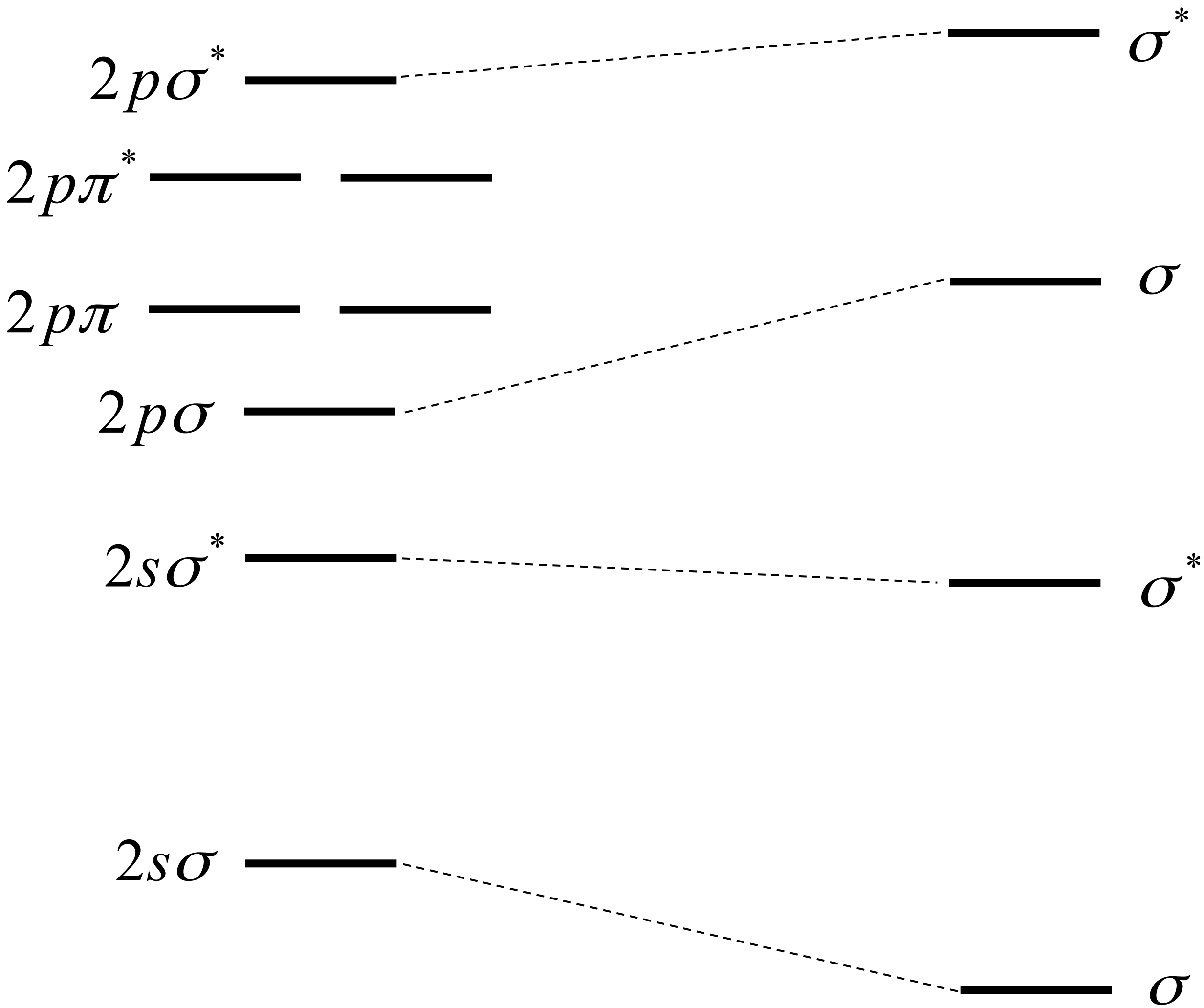
More refined MO diagram

σ orbitals can now interact



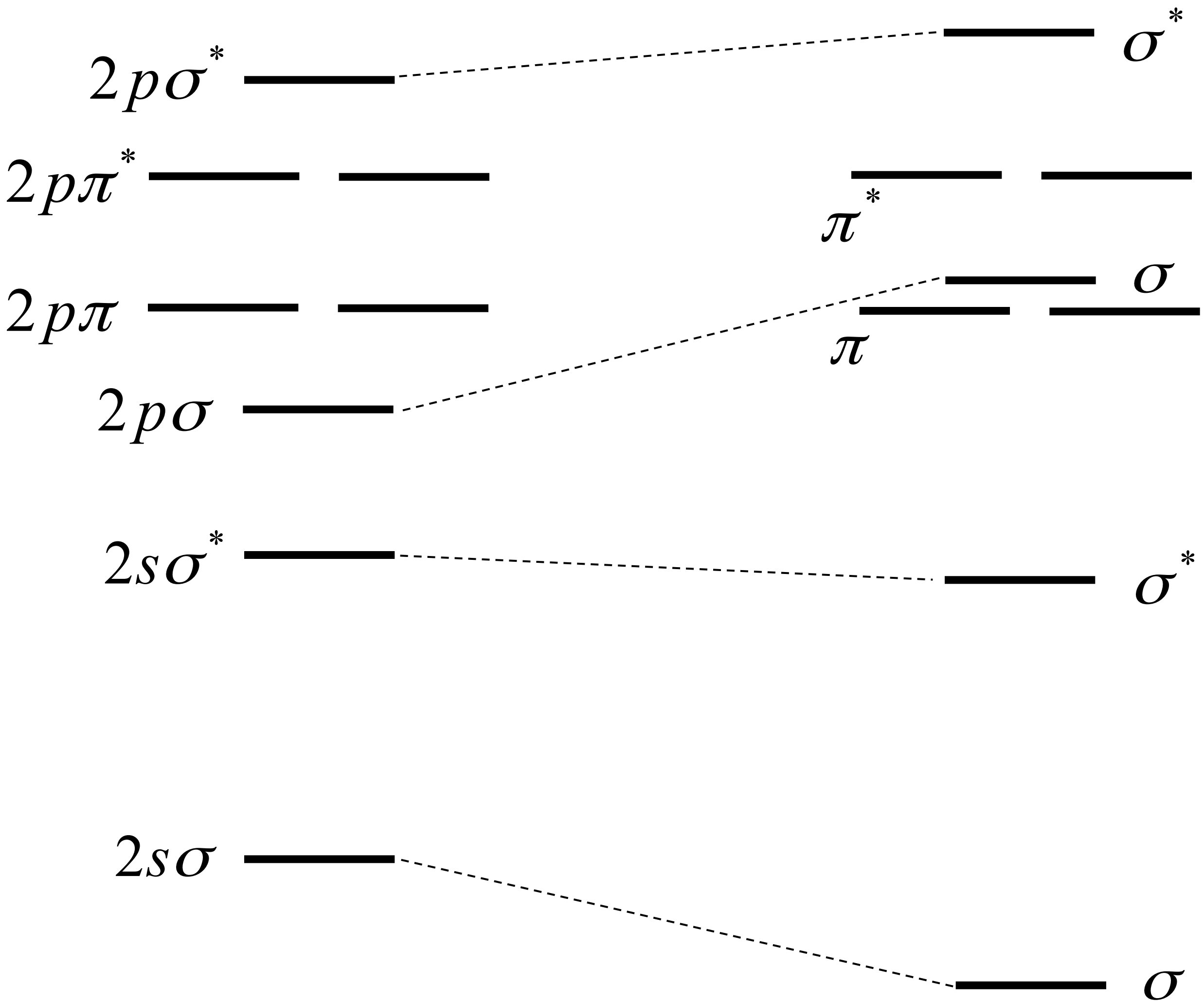
More refined MO diagram

σ* orbitals can interact



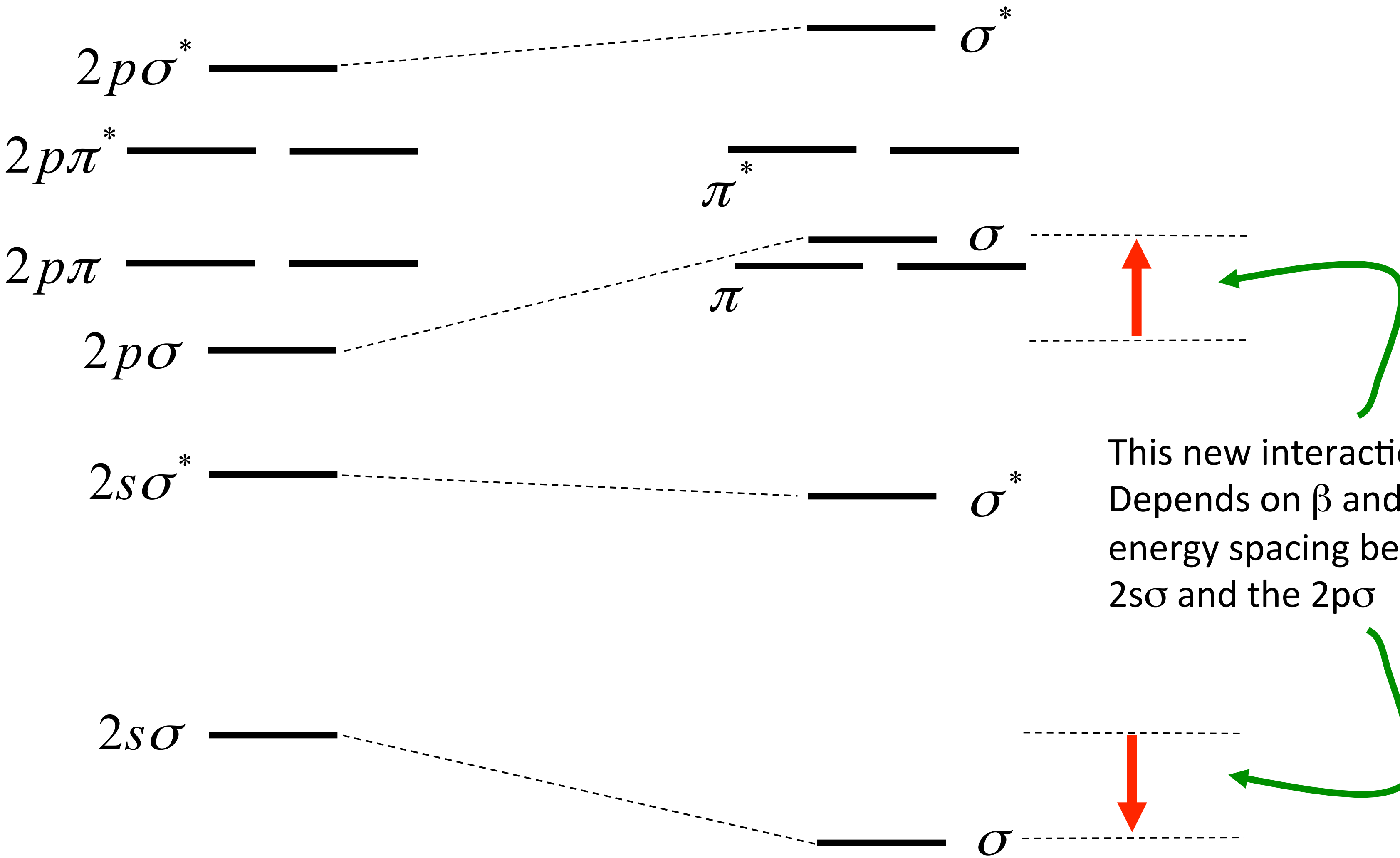
More refined MO diagram

π orbitals do not interact



More refined MO diagram

sp mixing

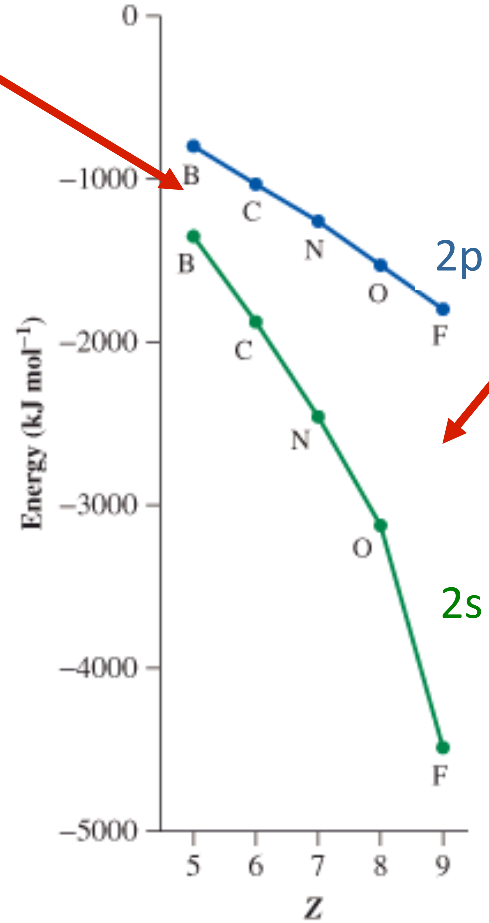


This new interaction energy Depends on β and the energy spacing between the 2sσ and the 2pσ

sp mixing

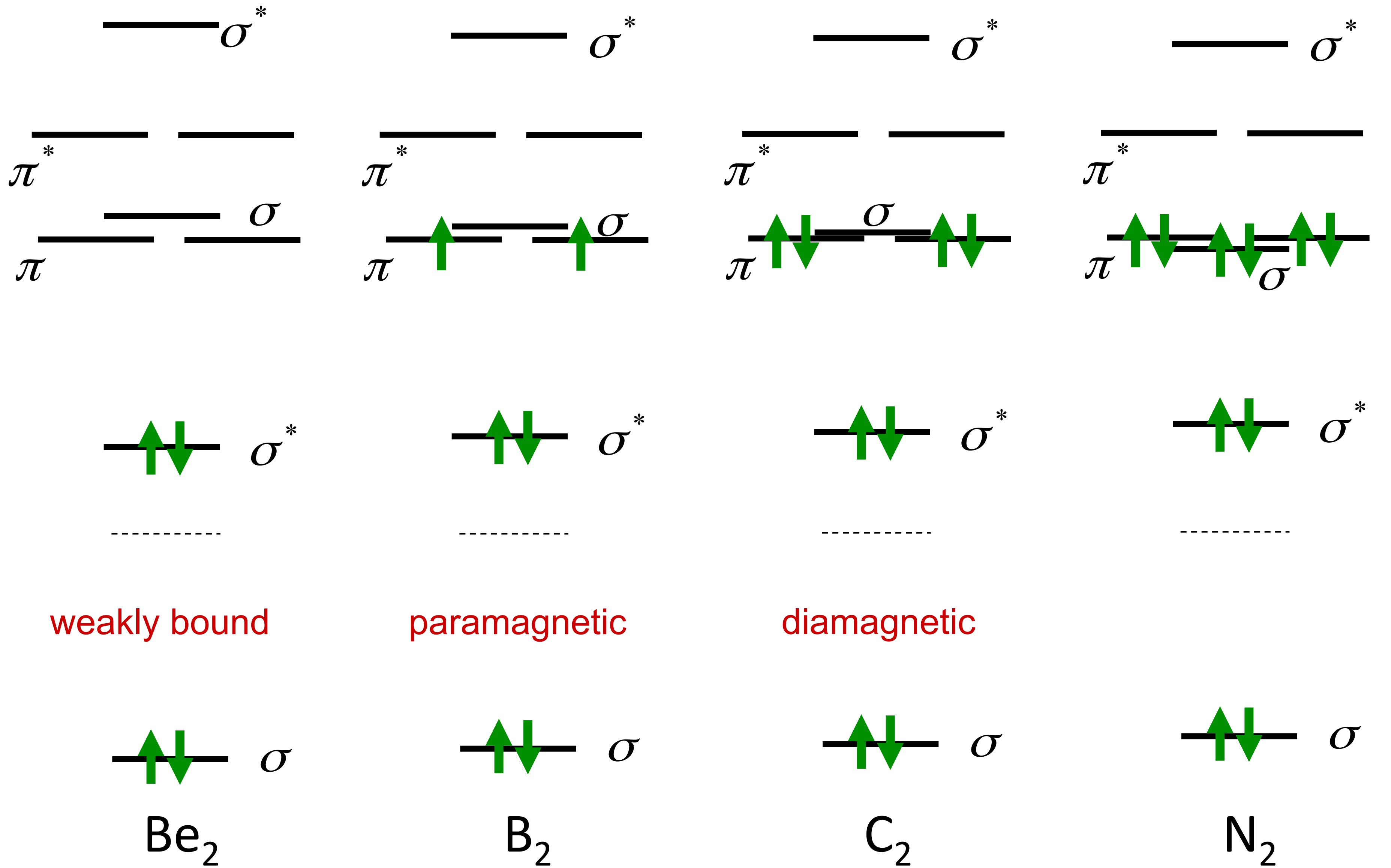
Smallest energy gap, and thus largest mixing between 2s and 2p is for Boron.

Largest energy gap, and thus smallest mixing between 2s and 2p is for Fluorine.



$$c.f.\ E_n = \frac{-\Re Z^2}{n^2}$$

sp mixing



Learning outcomes

- Use the principle that the mixing between orbitals depends on the energy difference, and the resonance integral, β.
- Apply the separation of σ and π bonding to describe electronic structure in simple organic molecules.
- Rationalize differences in orbital energy levels of diatomic molecules in terms of s-p mixing.

Next lecture

- Particle in a box approximation
  - solving the Schrödinger equation.

Week 10 tutorials

- Wavefunctions and the Schrödinger equation.

Practice Questions

1. Why is s-p mixing more important in Li_2 than in F_2?
2. How many core, σ-bonding, and π-electrons are there in
   a) acetylene
   b) ethylene
   c) benzene
   d) buckminsterfullerene

Check that your **total** number of electrons agrees with what is expected (6 per carbon, 1 per hydrogen).