

# Chemistry 2

## Lecture 1

### *Quantum Mechanics in Chemistry*



## Your lecturers



**8am**  
Asaph Widmer-Cooper

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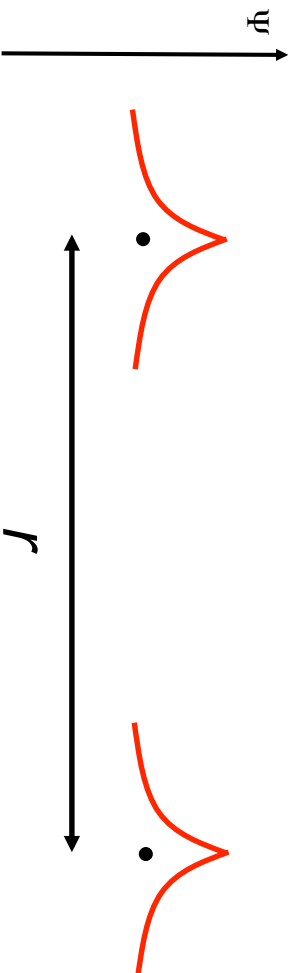


**12pm**  
Adam Bridgeman

Room 543A  
adam.bridgeman@sydney.edu.au

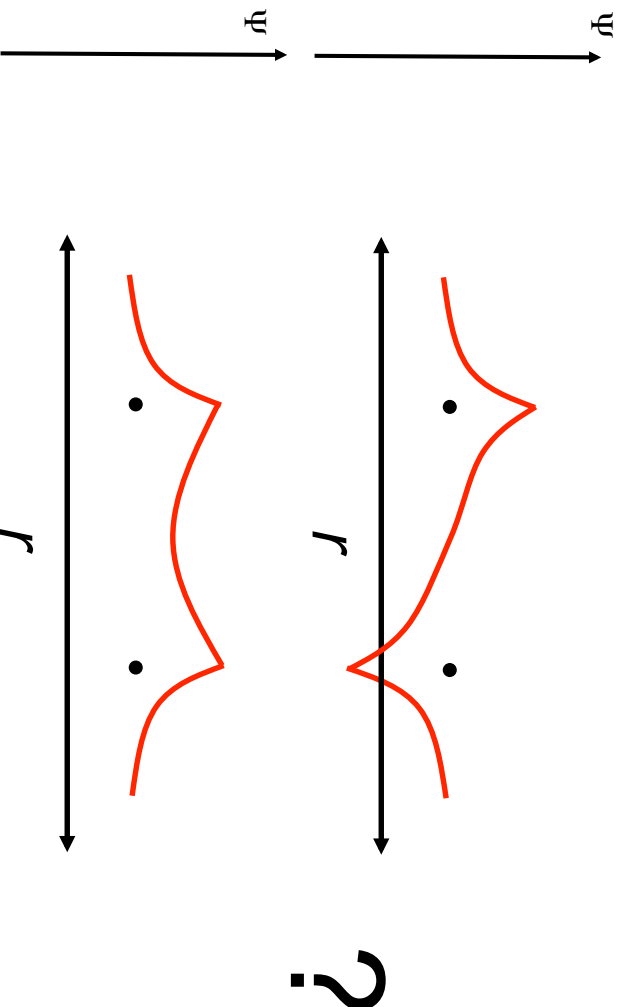
## Revision – $H_2^+$

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

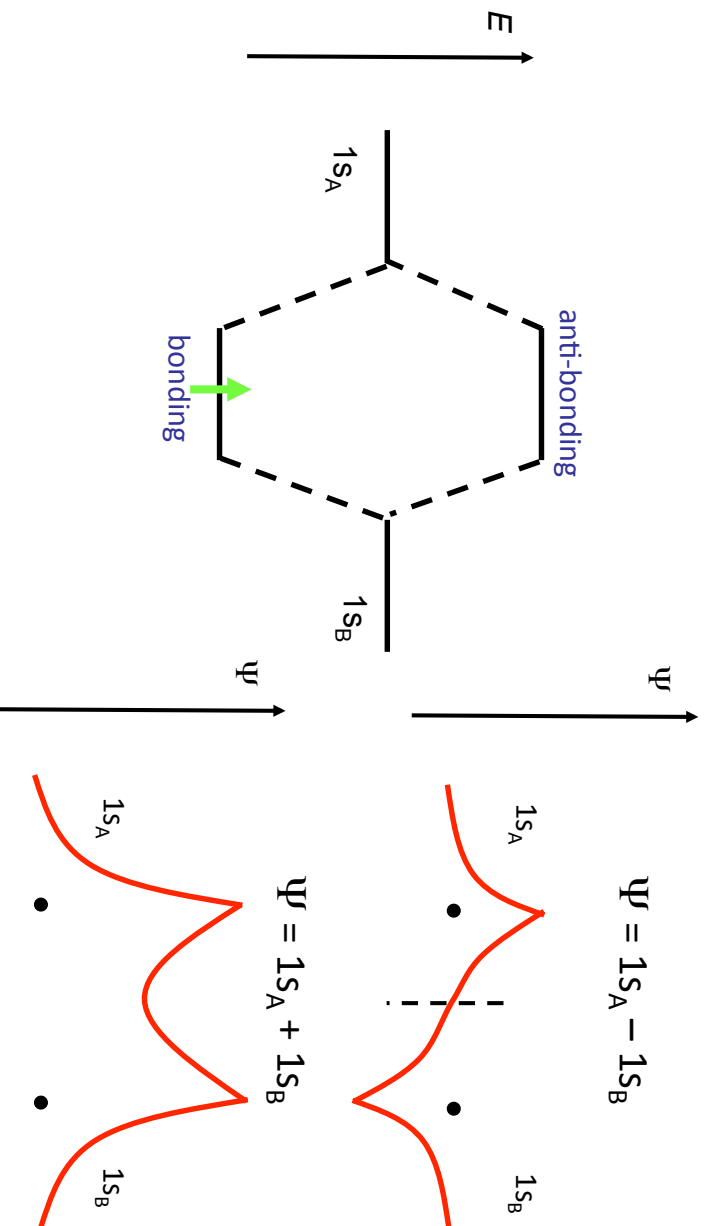


## Revision – $H_2^+$

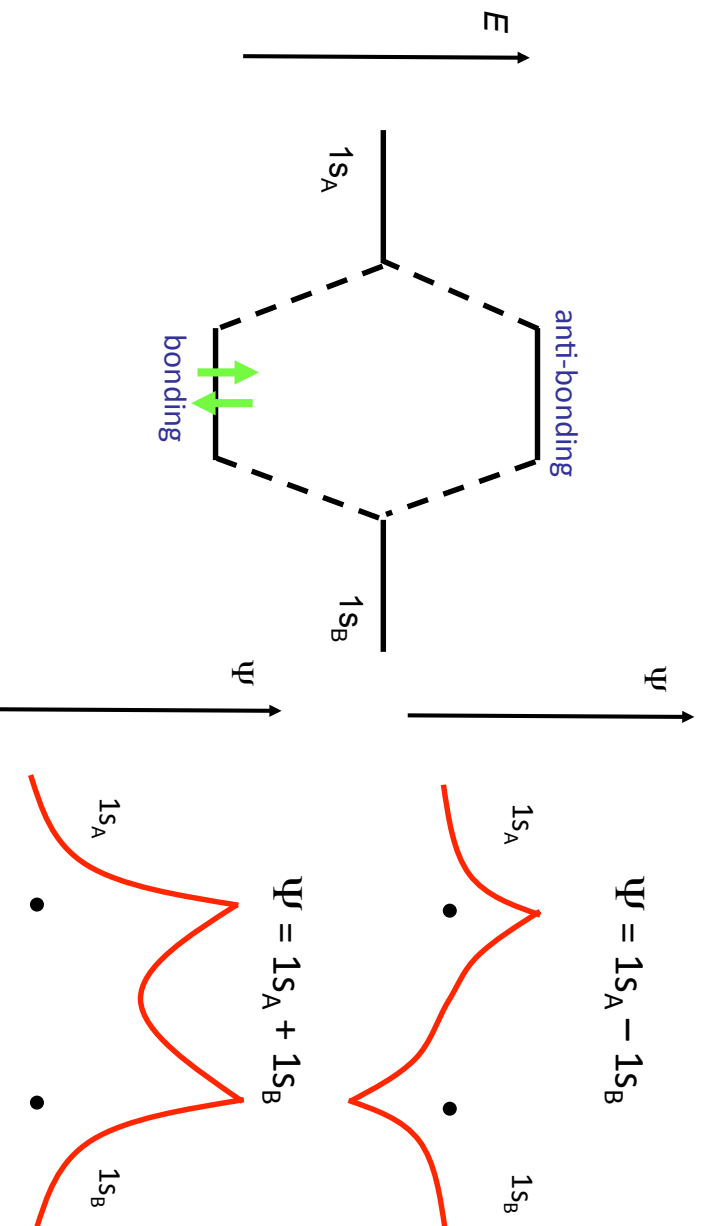
- At equilibrium, we have to make the lowest energy possible using the 1s functions available



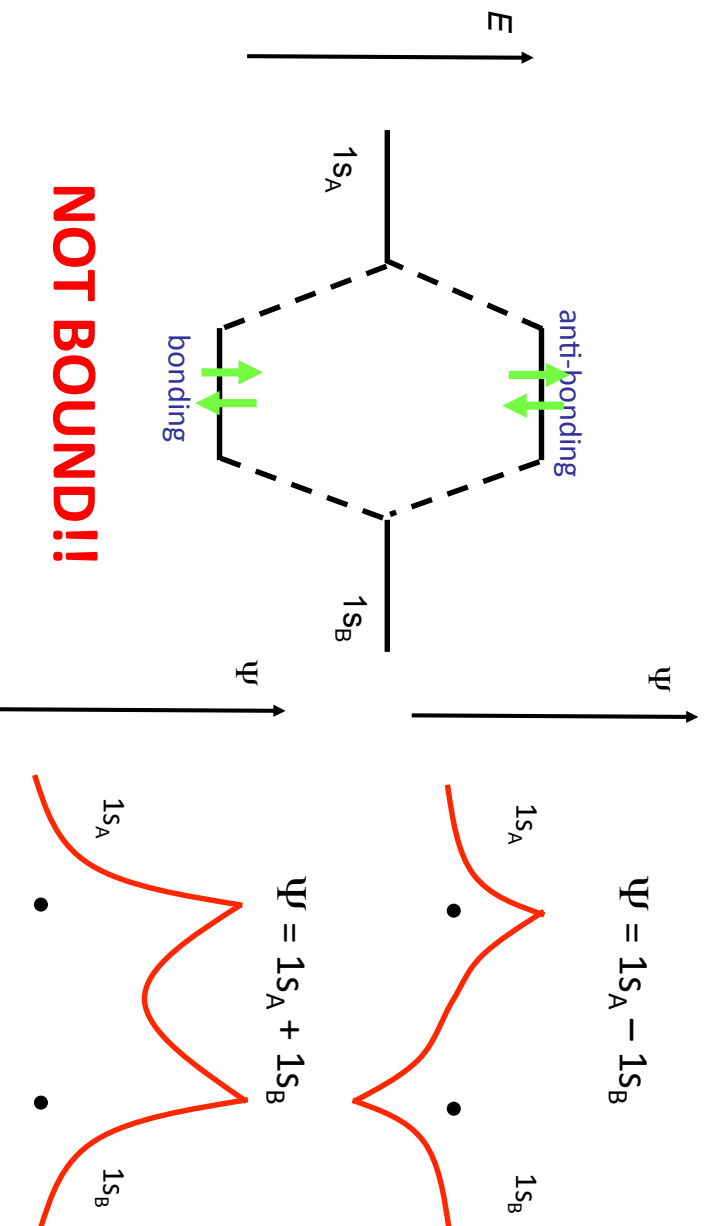
# Revision – $H_2^+$



# Revision – $H_2$



# Revision – He<sub>2</sub>



## 2<sup>nd</sup> row homonuclear diatomics

- Now what do we do? So many orbitals!



## Interacting orbitals

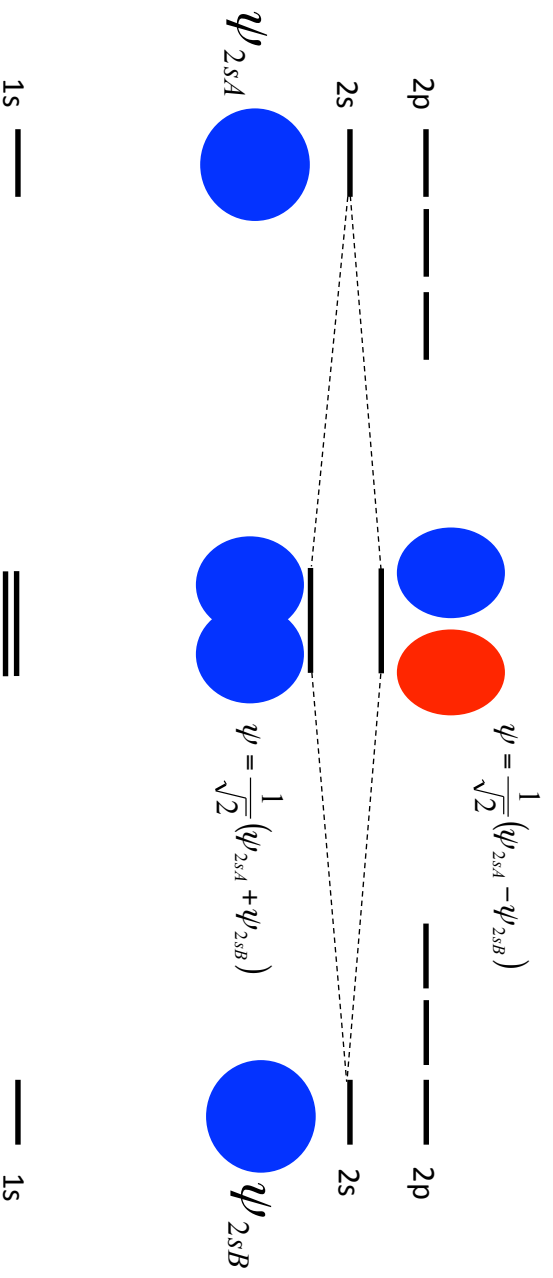
Orbitals can interact and combine to make new approximate solutions to the Schrödinger equation. There are two considerations:

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  $\beta$** . We will show how beta is calculated in a later lecture.

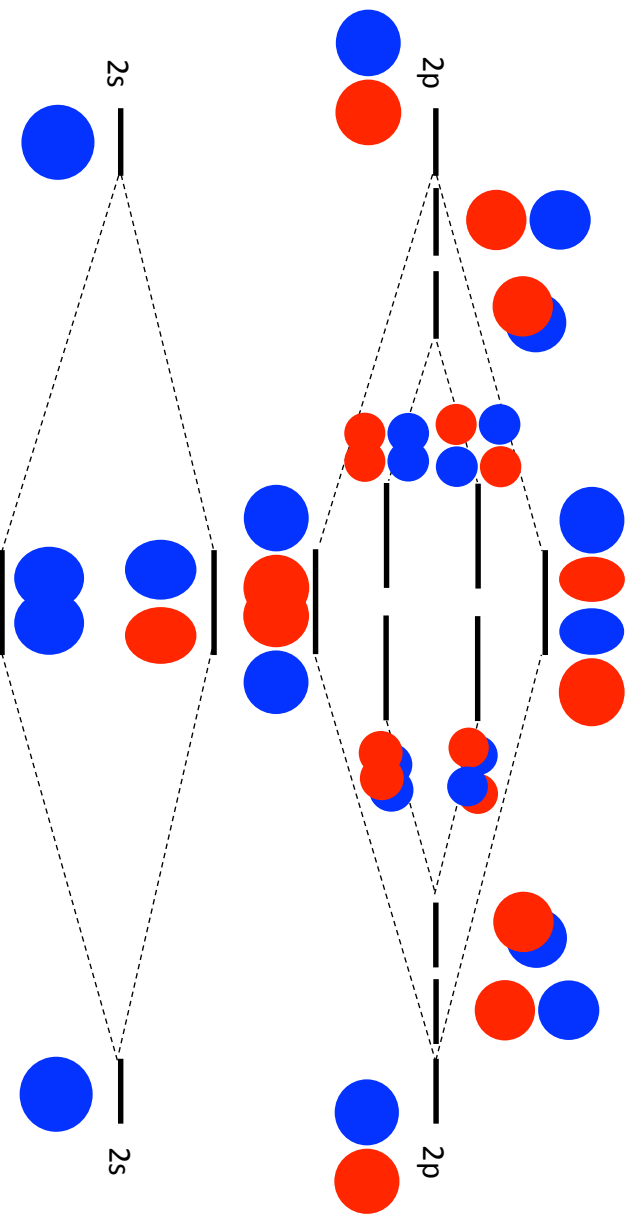
1. Orbitals interact proportionally to the inverse of their energy difference. Orbitals of the same energy interact completely, yielding completely mixed linear combinations.

## Interacting orbitals

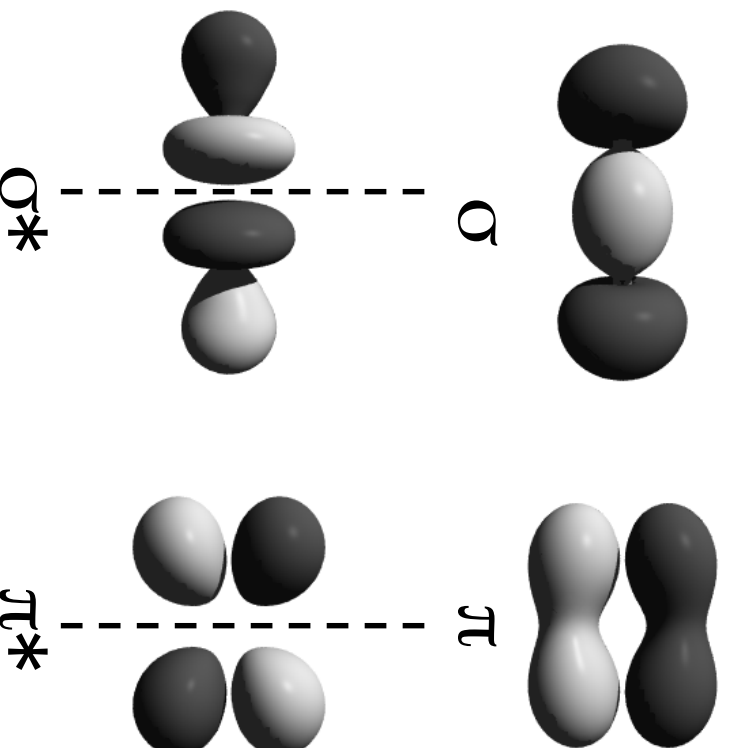
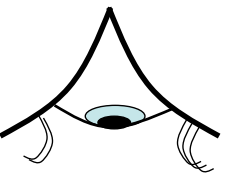


## *(First year) MO diagram*

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

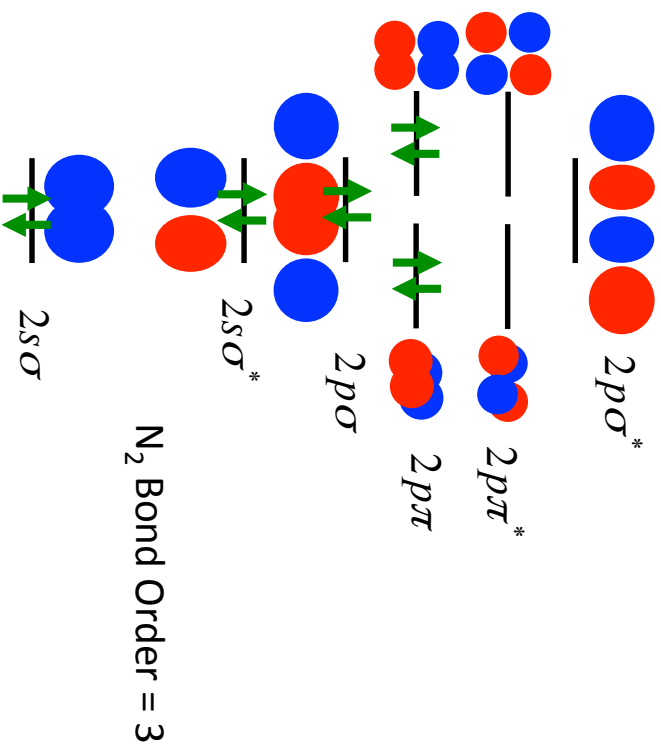


## *Molecular Orbital Theory - Revision*



# Molecular Orbital Theory - Revision

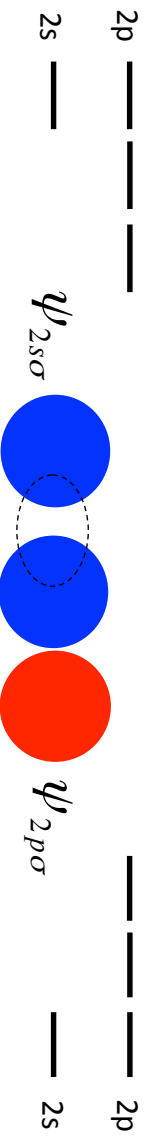
- Can predict bond strengths qualitatively



## Interacting orbitals

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

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



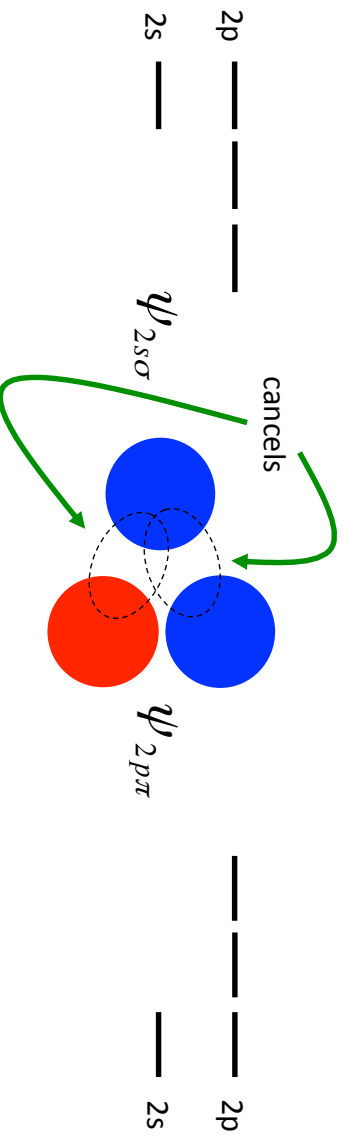
The 2s orbital on one atom *can* interact with the 2p from the other atom, but since they have different energies this is a smaller interaction than the 2s-2s interaction. We will deal with this later.



## Interacting orbitals

- 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

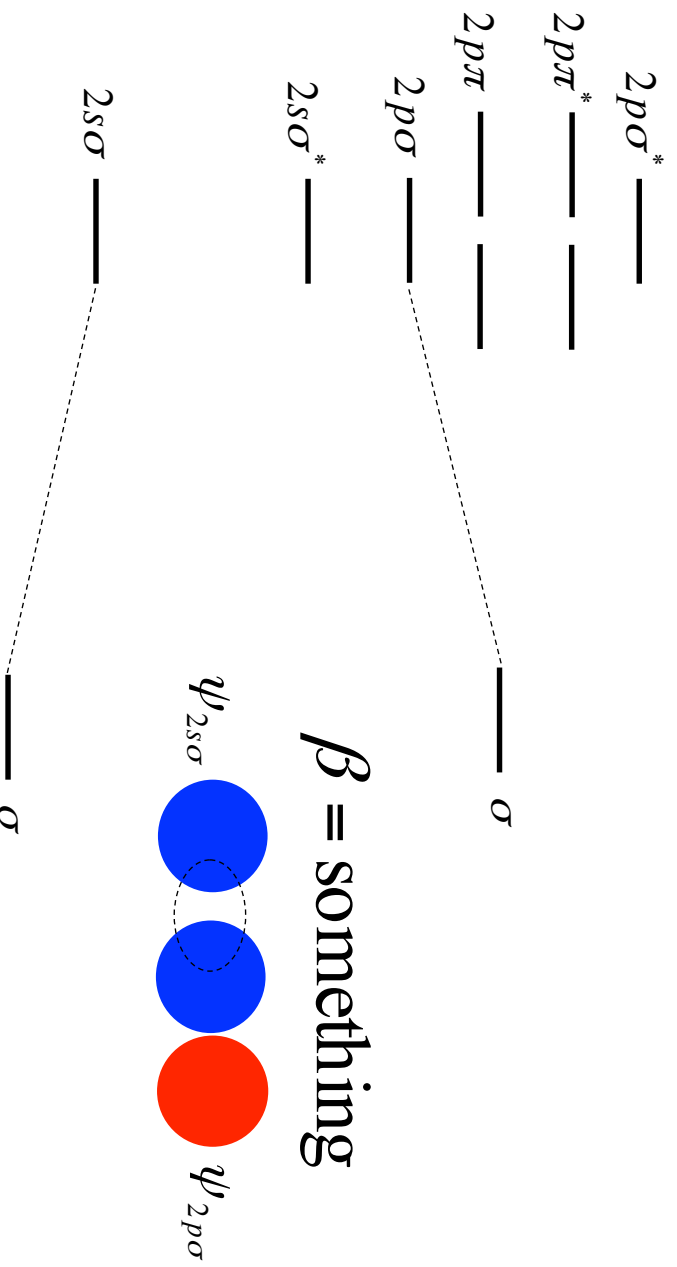
1s —

====

— 1s

## More refined MO diagram

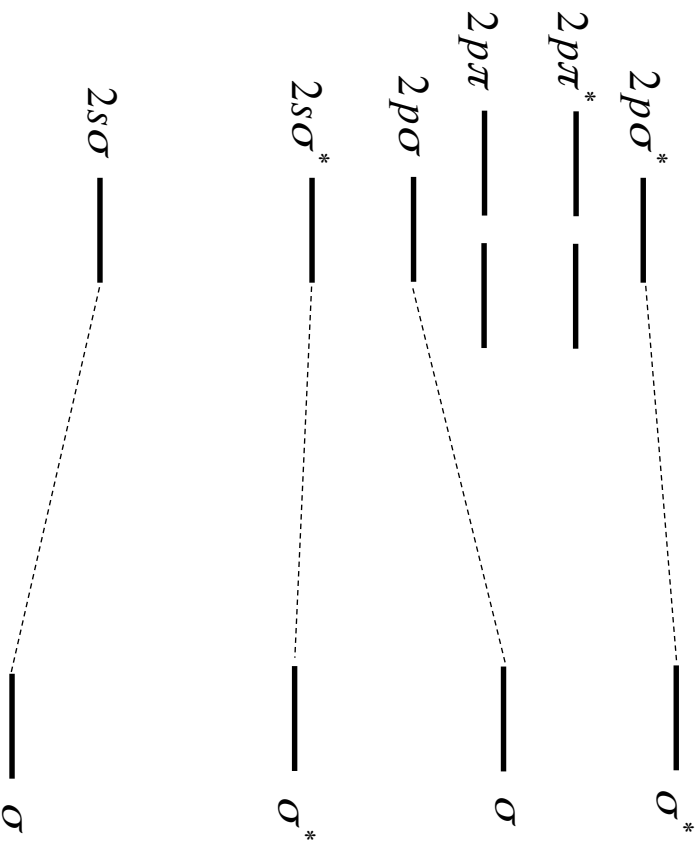
$\sigma$  orbitals can now interact





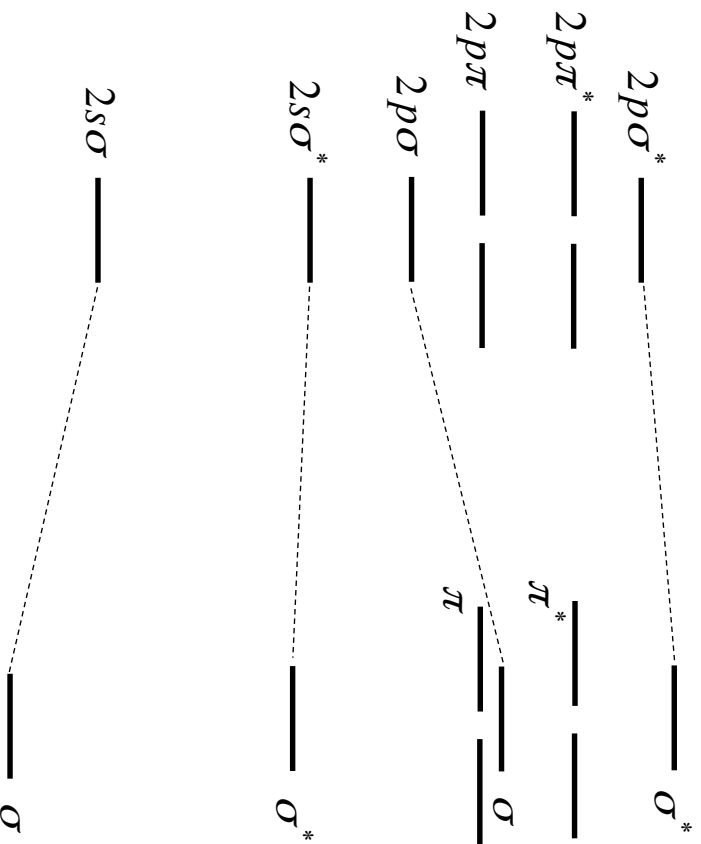
## More refined MO diagram

$\sigma^*$  orbitals can interact



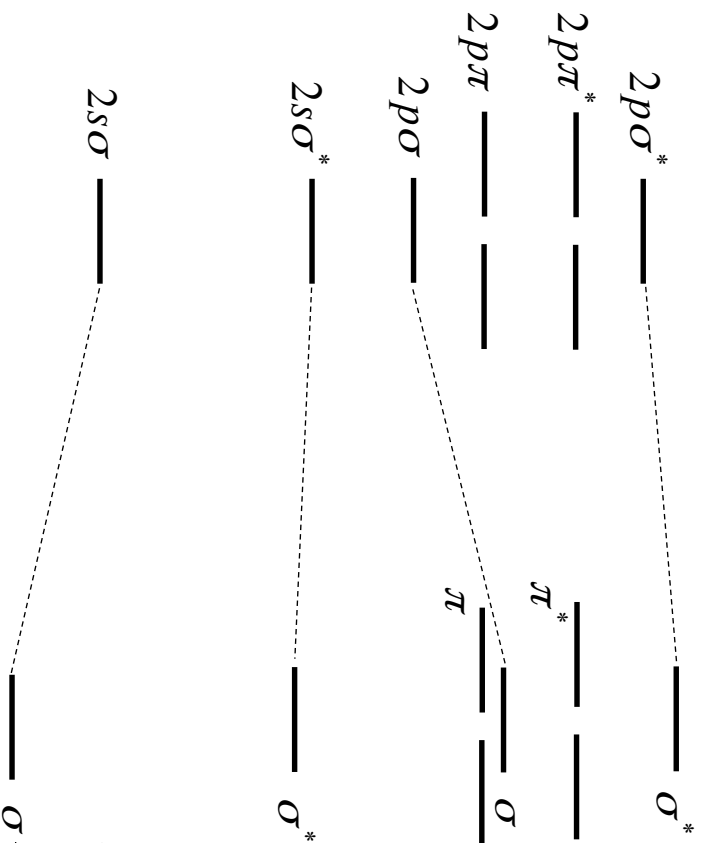
## More refined MO diagram

$\pi$  orbitals do not interact



# More refined MO diagram

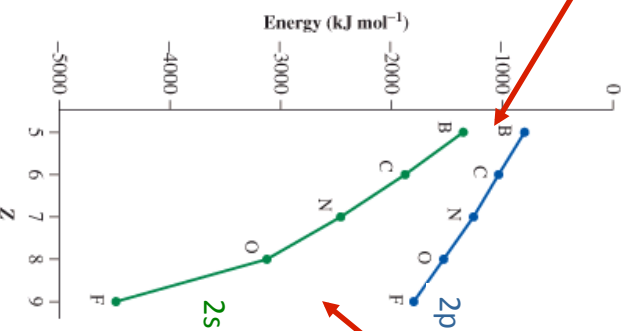
sp mixing



This new interaction energy  
Depends on  $\beta$  and the  
energy spacing between the  
 $2s\sigma$  and the  $2p\sigma$

## sp mixing

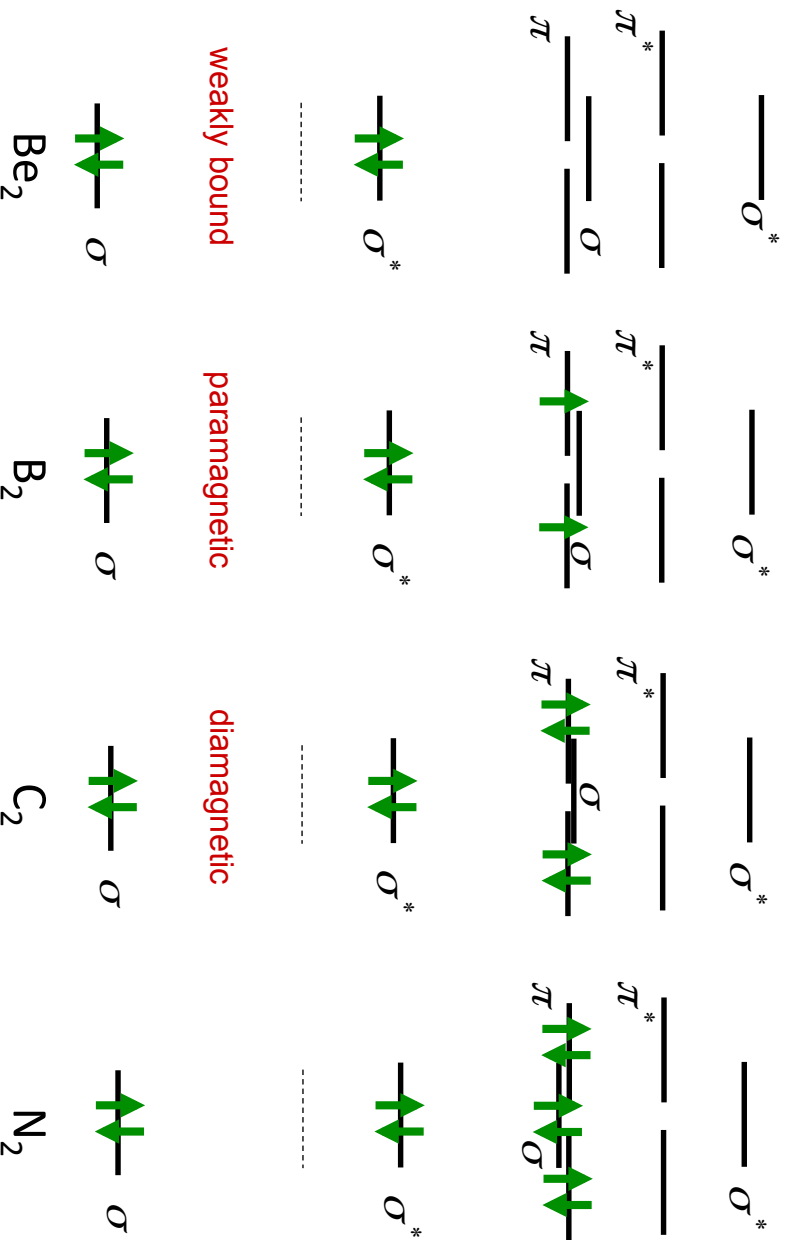
Smallest energy gap,  
and thus largest  
mixing between  $2s$   
and  $2p$  is for Boron.



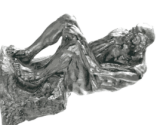
Largest energy gap, and  
thus smallest mixing  
between  $2s$  and  $2p$  is for  
Fluorine.

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

# sp mixing



## Learning outcomes



- Use the principle that the mixing between orbitals depends on the energy difference, and the resonance integral,  $\beta$ .
- Apply the separation of  $\sigma$  and  $\pi$  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  $\text{Li}_2$  than in  $\text{F}_2$ ?
2. How many core,  $\sigma$ -bonding, and  $\pi$ -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).