Lecture 5

Homonuclear Diatomic Molecules

- Making MO Energy Level Diagrams Easy

- Making MO Theory Easy

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Objectives – a fundamental understanding

- **Wave mechanics / Atomic orbitals**
    - The flaws in classical quantum mechanics (the Bohr Model) in the treatment of electrons
    - Wave mechanics and the Schrödinger equation
    - Representations of atomic orbitals including wave functions
    - Electron densities and radial distribution functions
    - Understanding shielding and penetration in terms of the energies of atomic orbitals

- **Bonding**
    - Revision of VSEPR and Hybridisation
    - Linear combination of molecular orbitals (LCAO), bonding / antibonding
    - Labelling of molecular orbitals (s, p and g, u)
    - Homonuclear diatomic MO diagrams
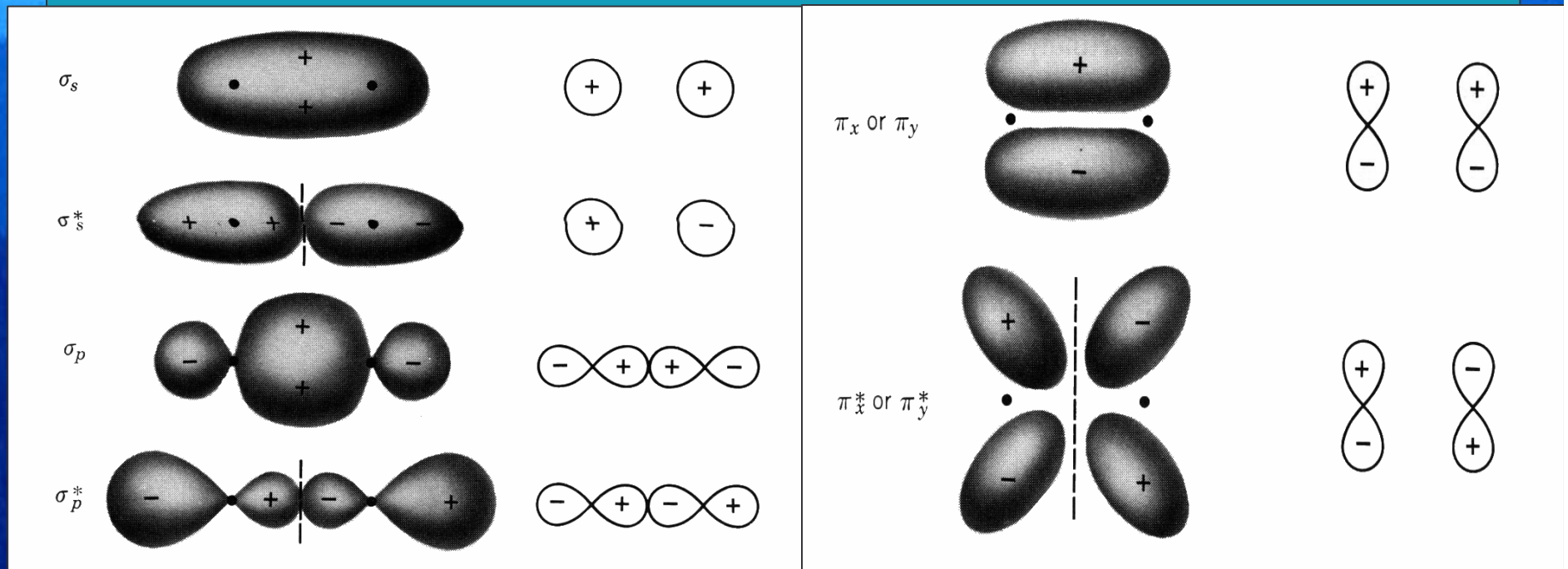   - MO diagrams for Inorganic Complexes

2nd row Homonuclear Diatomics

- Li_2, Be_2, B_2, C_2, N_2, O_2, F_2, Ne_2

  Bonding and antibonding interactions are possible between $1s$, $2s$ and $2p$ on one atom with the other

  σ bonding $\quad s - s$

  $\qquad\qquad p_z - p_z$

  π bonding $\qquad p_x - p_x$

  $\qquad\qquad\qquad p_y - p_y$

Energy level diagram for O_2

- *2s* and *2p* energies sufficiently spaced no mixing
- Simple picture of the MO

$6\sigma^*_u$

$4\sigma^*_u$

$2\pi^*_g$

$2\pi^*_g$

$2p$

$2p$

$1\pi_u$

$1\pi_u$

$5\sigma_g$

$3\sigma_g$
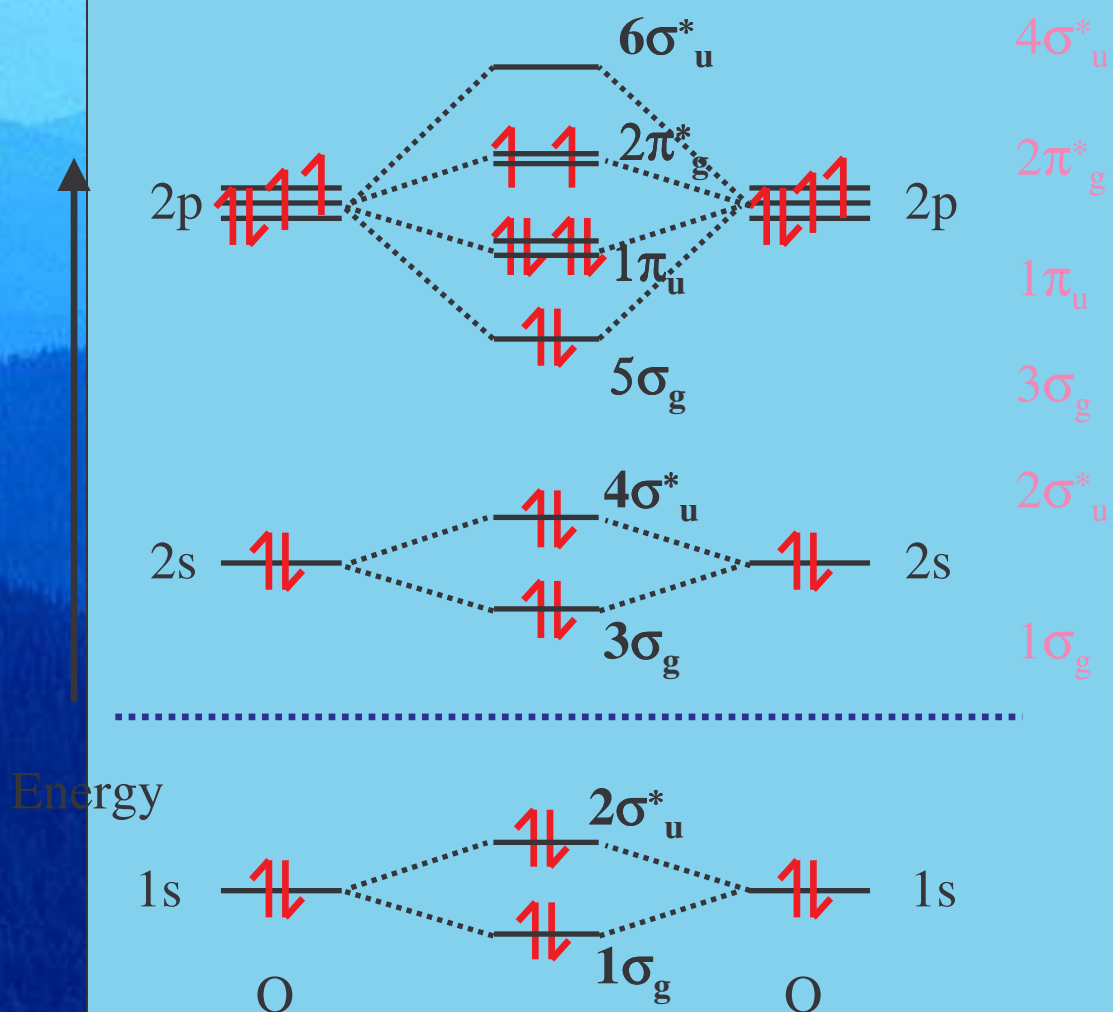
Unpaired electrons
→Paramagnetic

Label MOs starting from the bottom usually discount core electrons - only valence orbitals important for bonding

$4\sigma^*_u$

$2\sigma^*_u$

$2s$

$2s$

$3\sigma_g$

$1\sigma_g$

Energy

$2\sigma^*_u$

$1s$

$1s$

$1\sigma_g$

O

O

1*s* AO's very small → very small overlap in lower levels (small ΔE)

Other possible interactions

σ interactions between *s* and p_z can be important

– Depend on the energy difference between 2*s* and 2p_z

– The larger the energy difference (like in O_2) the less likely the interaction

- How does the energy of the 2s and 2p vary with Z (shielding / penetration)

NO *s* and *p* mixing

2p

2s

YES *s* and *p* mixing

Energy

Li   Be   B   C   N   O   F   Ne

- Gap increases – *2p* more effectively shielded as 2s is pulled toward an ever increasing nuclear charge - critical point between O and N

MO diagram for N_2

- *2s* and *2p* energies sufficiently close for interaction → more complex
  - 1σ and 2σ shift to lower energy
  - 3σ and 4σ shifted to high energy
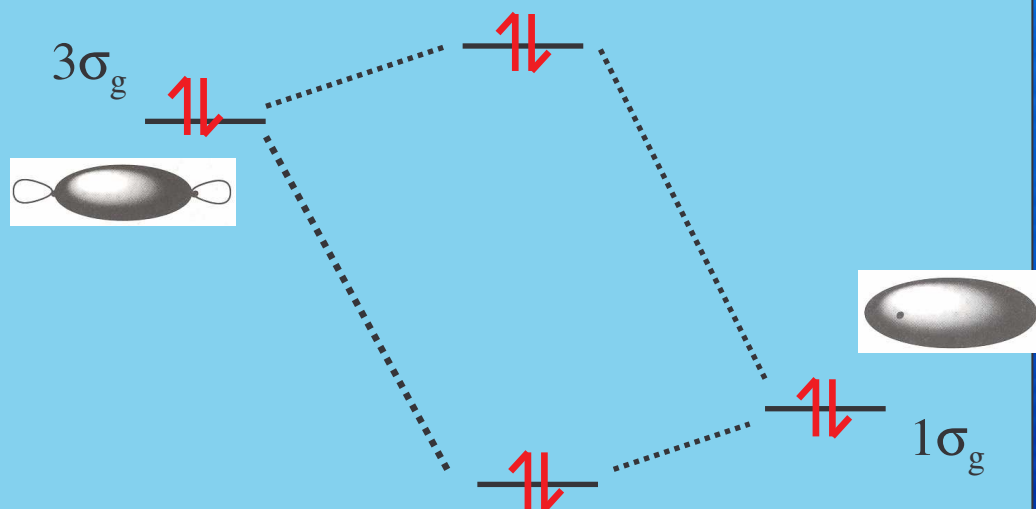 - 3σ now above 1π
  - π levels unaffected
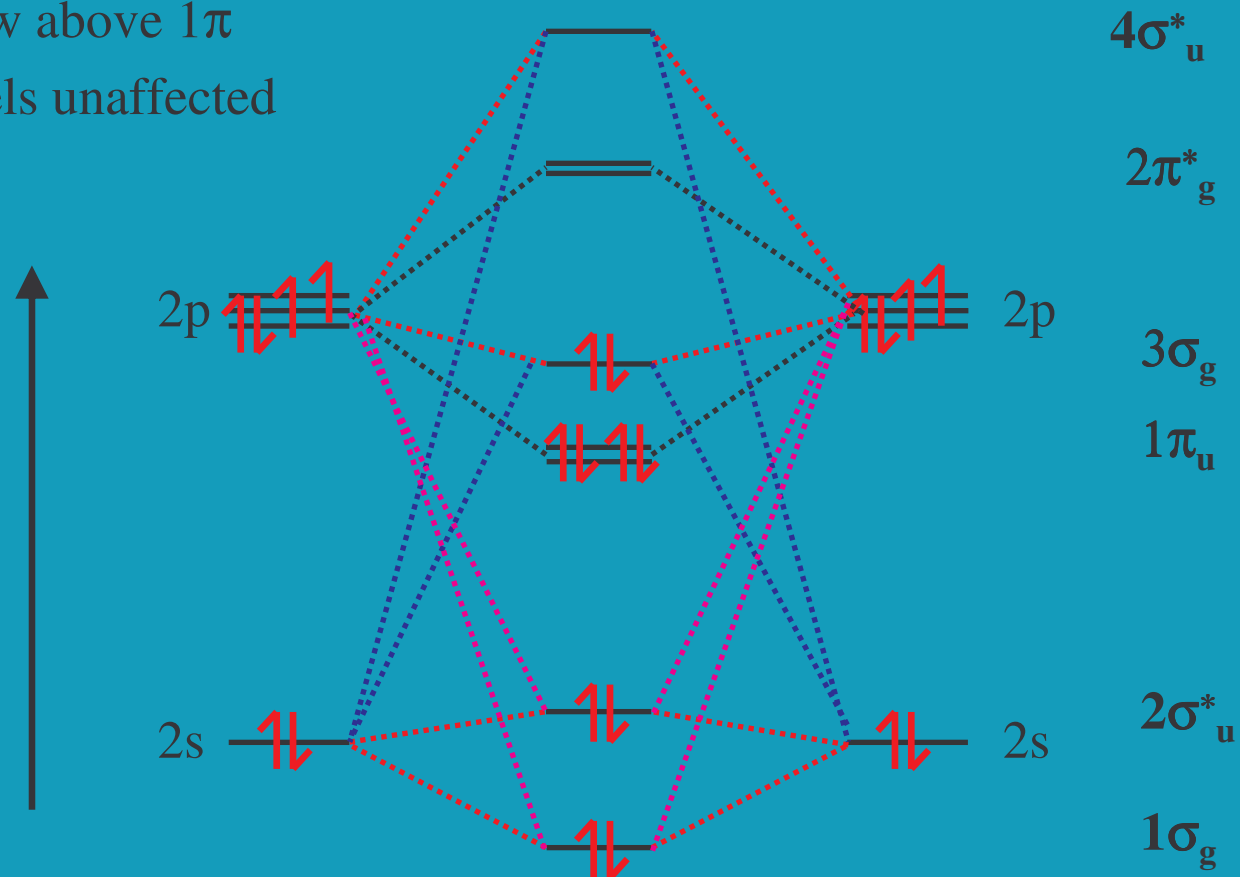
σ interactions in N_2

- Take basic model for oxygen – no *s and p* interaction - and apply changes to examine how the **MO's** can interact
  - π and σ cannot interact – zero overlap → π level remain the same
  - Examine σ –σ interactions

$4\sigma^*_u$

$2\pi^*_u$

2p

$1\pi_g$

$3\sigma_g$

$2\sigma^*_u$

2s

$1\sigma_g$
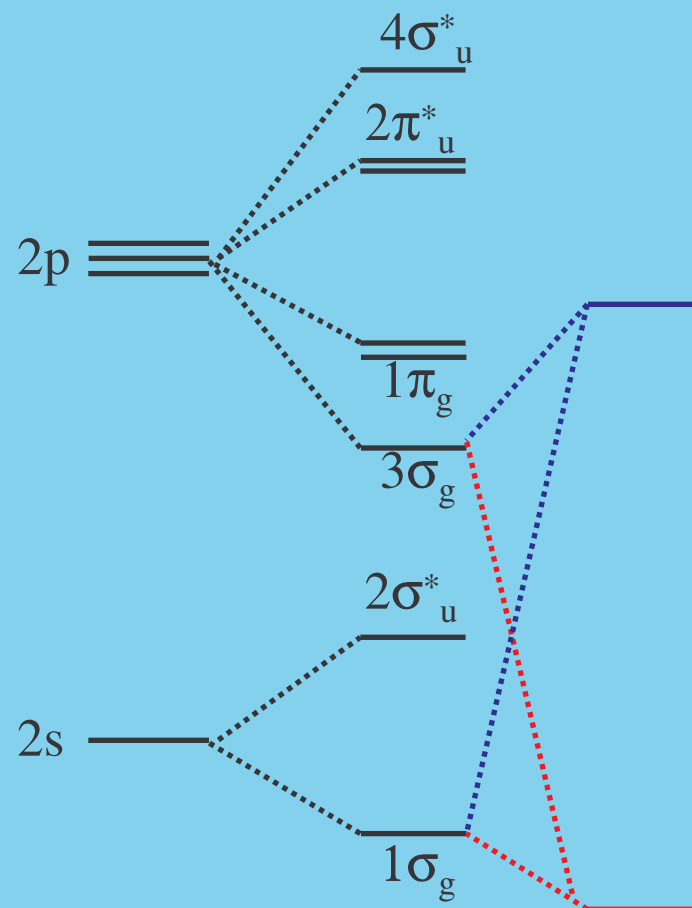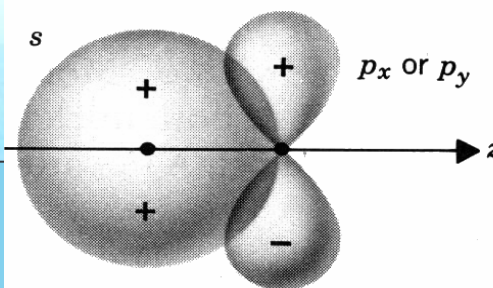
Bonding interactions can interact with each other $1\sigma_g$ and $3\sigma_g$

$3\sigma_g$

$1\sigma_g$

Thus $1\sigma_g$ goes down in energy and $3\sigma_g$ goes up in energy

s p_x or p_y

$+$ $+$

$+$

$-$

z

σ* interactions in N$_2$

- Now examine the anti-bonding interaction ($2\sigma*$ and $4\sigma*$)

$4\sigma^*$

$4\sigma^*_u$

$2\pi^*_u$

2p

$1\pi_g$

$3\sigma_g$

$2\sigma^*_u$

2s

$1\sigma_g$

$2\sigma^*$

Thus $2\sigma^*_u$ goes down in energy and $4\sigma^*_u$ goes up in energy

For bonding with anti-bonding ($1\sigma - 4\sigma*$ or $2\sigma* - 3\sigma$) the sign changes on one wave function → zero overlap.
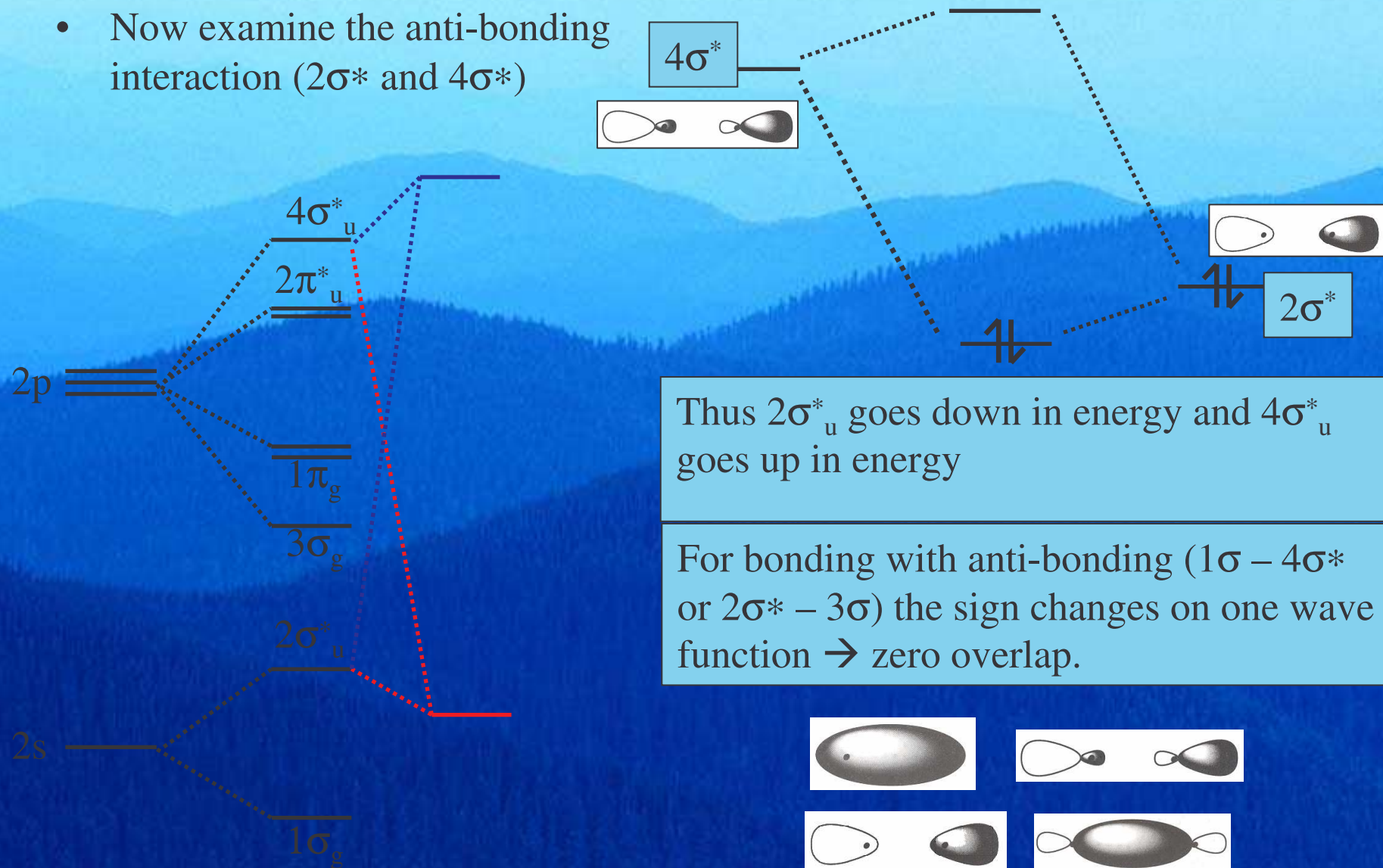
MO diagrams for 2nd row diatomics

- The effect of the overlap between *2s* and *2p* is greatest for the Li. The MO diagram changes systematically as you go across the periodic table
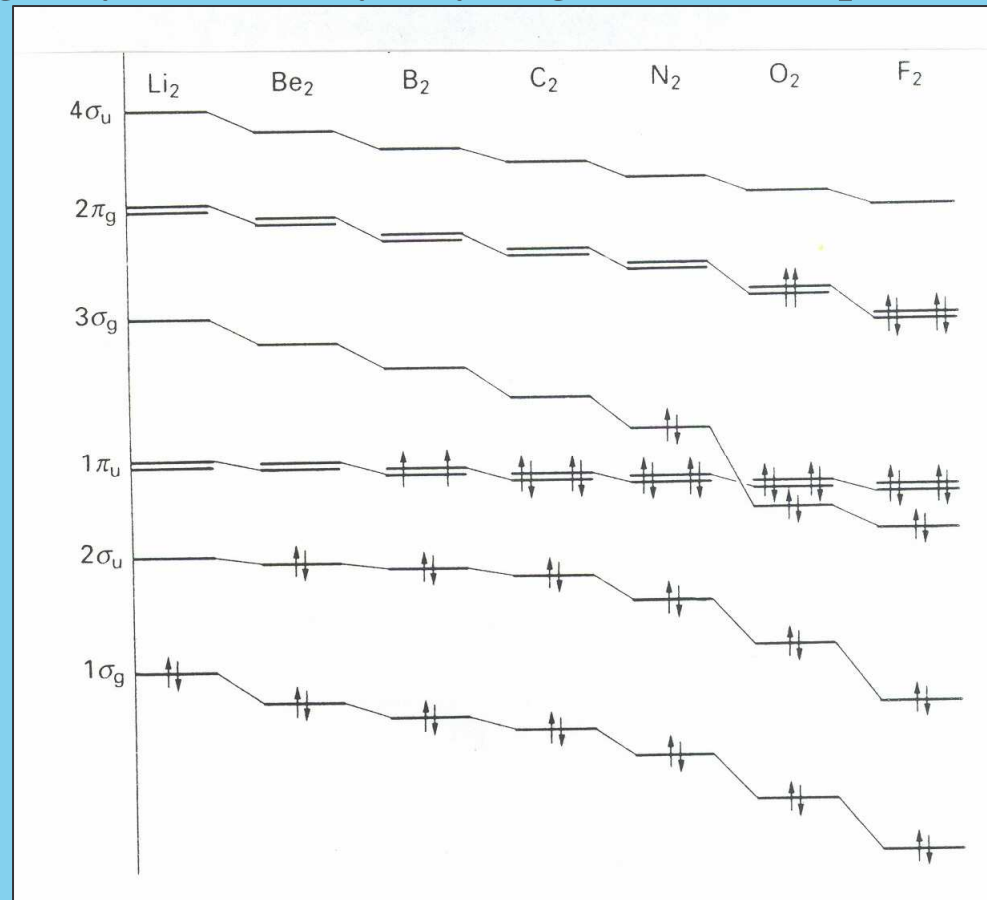
- *s – p* mixing → B$_2$ – paramagnetic and C$_2$ diamagnetic

MO diagram for CO

- Same orbitals as homonuclear diatomics isoelectronic with N_2
  - different energies give rise to significant *2s - 2p* mixing
  - As heteronuclear diatomic the orbitals have either C or O character

4σ   C-O anti - bonding (more C)

2π*   π∗ (uneven – more carbon)

3σ   Primarily carbon (p_z)

1π   π bond (uneven – more oxygen)

2σ   Primarily oxygen (p_z)

1σ   C-O bonding interaction (more O)

2p

2s

C

2p

2s

O
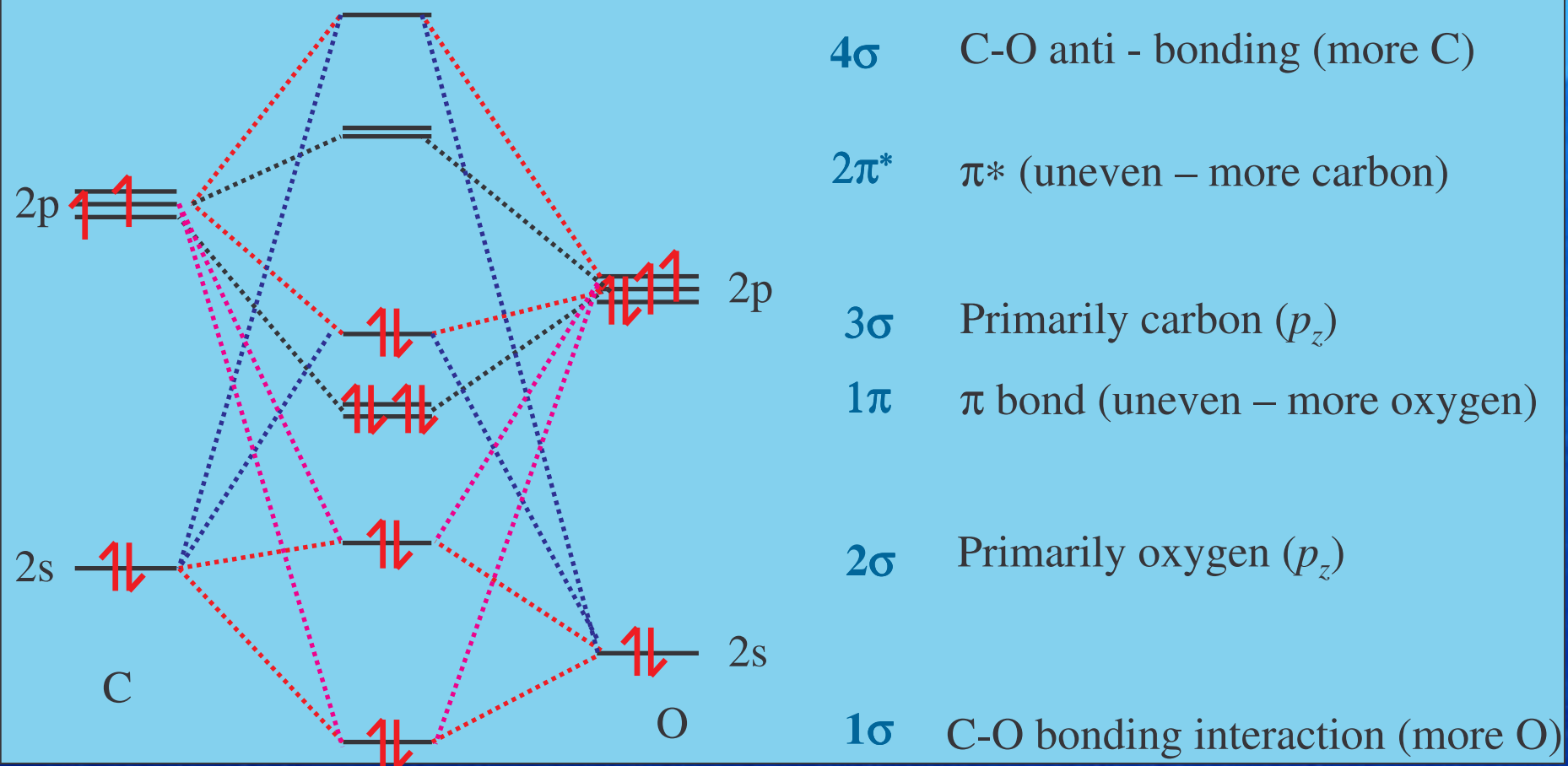
Homonuclear Diatomic MO energy diagrams

No mixing

Li_2 to O_2

Mixing

N_2 to Ne_2

$4\sigma^*_u$

$2\pi^*_g$

2p

$1\pi_u$

$3\sigma_g$

$2\sigma^*_u$

2s

$1\sigma_g$

$4\sigma^*_u$

$2\pi^*_g$

2p

$3\sigma_g$

2p

$1\pi_u$

$2\sigma^*_u$

2s

$1\sigma_g$

2s

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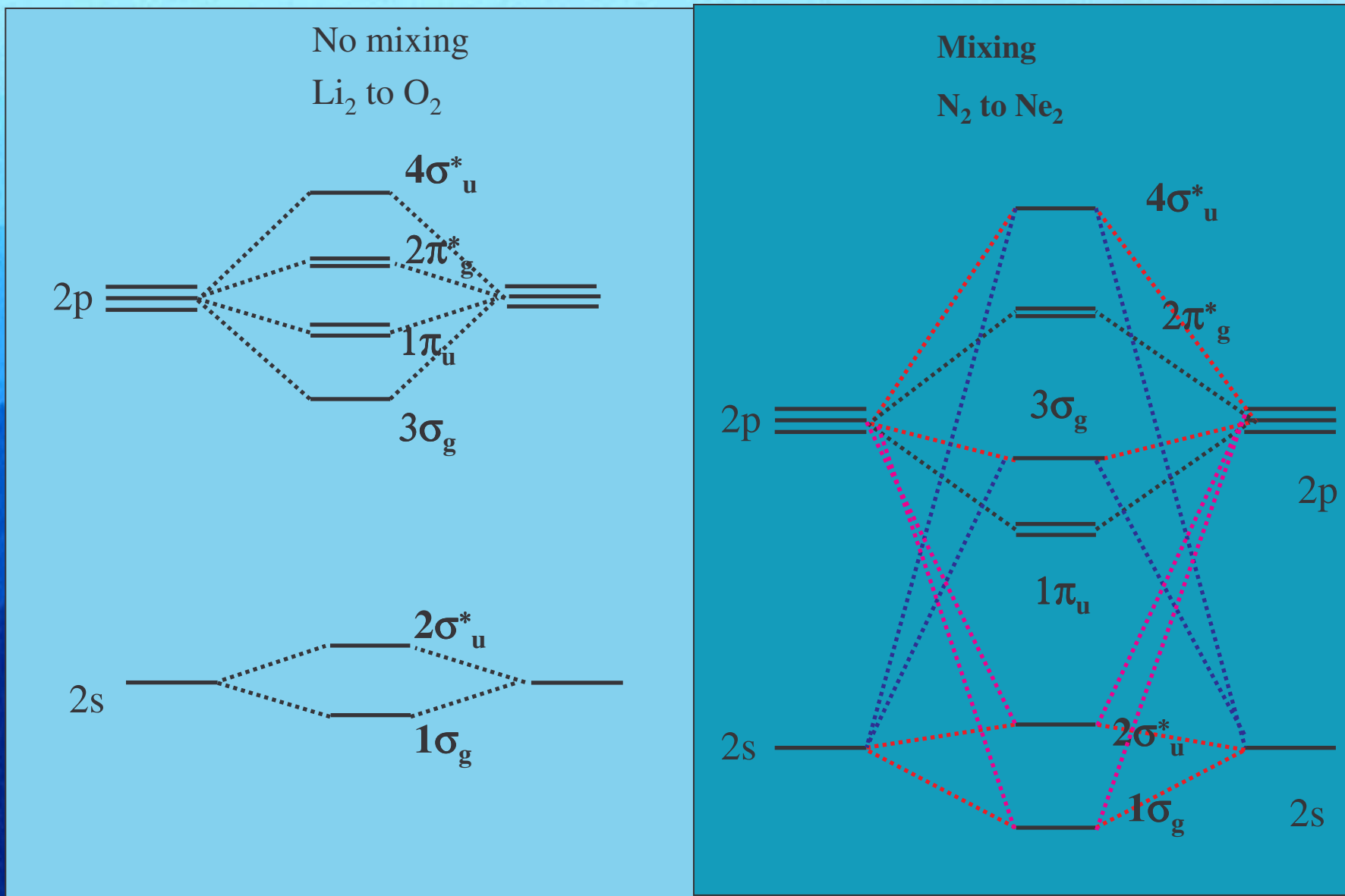
MO treatment of BeH$_2$

- VSEPR → linear molecule,   H – Be – H ⟶ Z
  - Be – $1s^2$ $2s^2$ $2p^0$ H – $1s^1$
  - Examine interaction of 6 AO with each other
  - 2 H $1s$, Be $2s$ and Be $2p_x$, Be $2p_y$ Be $2p_z$ → 6 MO's

Interaction between H $1s$ and Be $2s$ Interaction between H $1s$ and Be $2p_z$
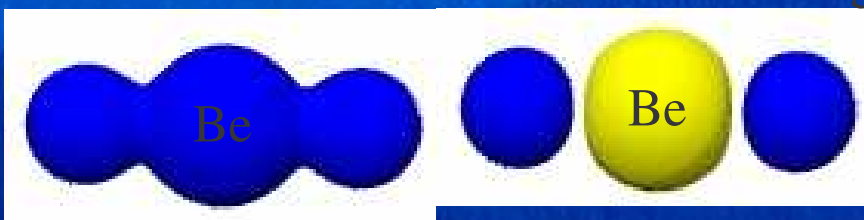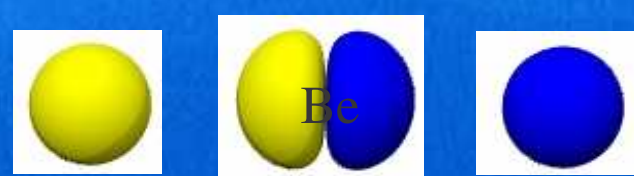
bonding   anti-bonding   bonding   anti-bonding
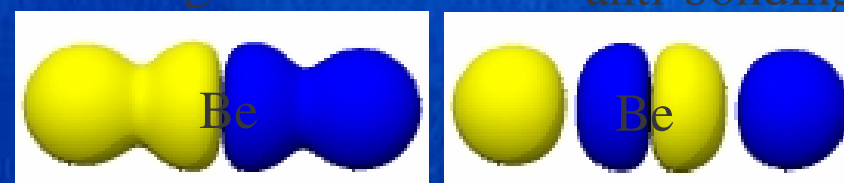
Each of these is delocalised over three atoms and can hold up to two electrons

p_x and p_y have zero overlap → non bonding

Energy level diagram for BeH$_2$

$4\sigma^*_u$

$3\sigma^*_g$

2p

Non bonding p_x and p_y

2s

$2\sigma_u$

$1\sigma_g$

Be   BeH$_2$ 2 H
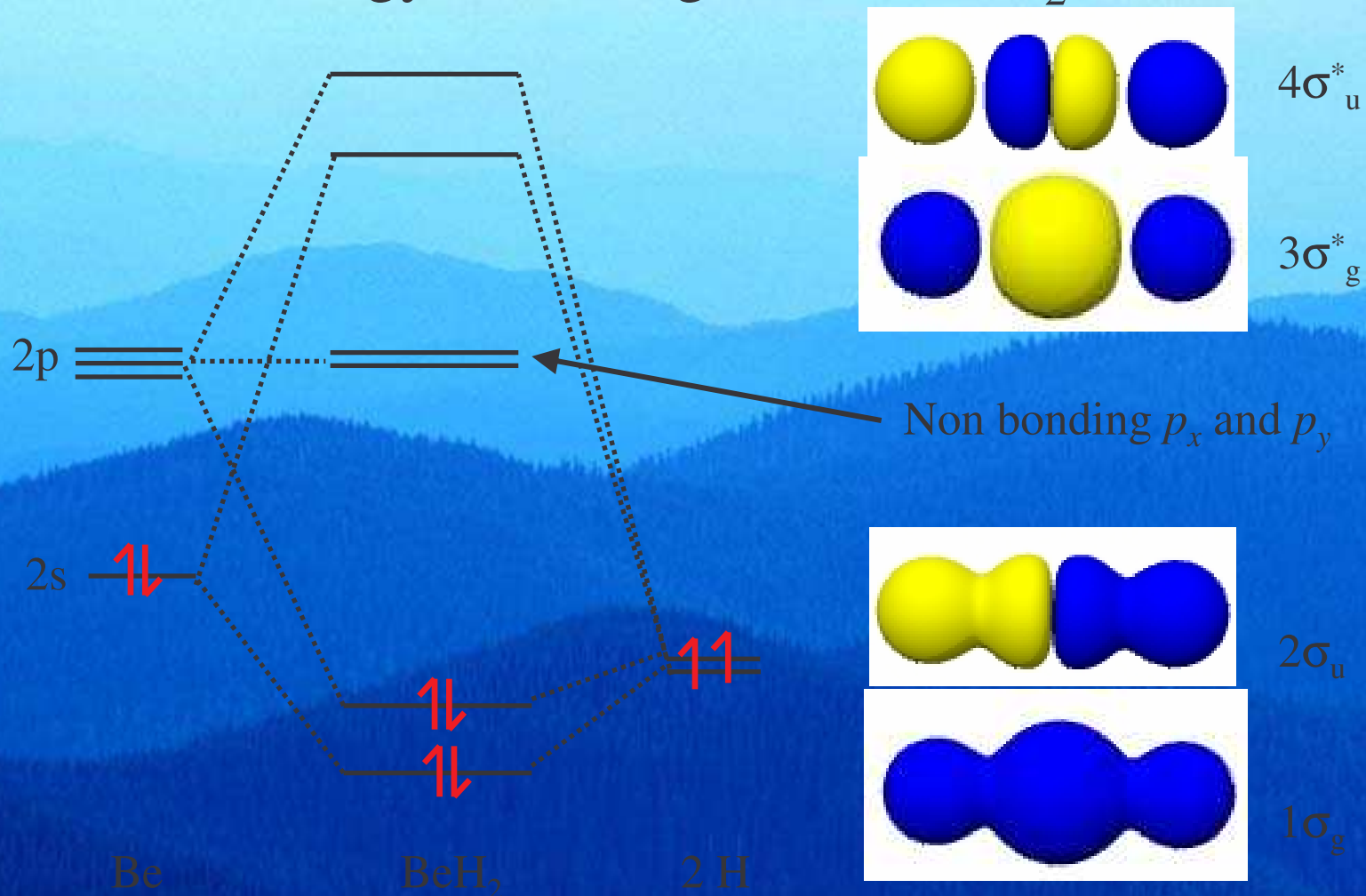
Compare these two MO's with no mixing of s and p orbitals with the localised model generated from two equivalent bonds formed via *sp* hybridization

Alternative approach

- Stepwise approach (ligands first)

H – Be – H $\longrightarrow$ Z

Mix hydrogen $1s$ orbitals first

$\rightarrow$ two Molecular orbitals
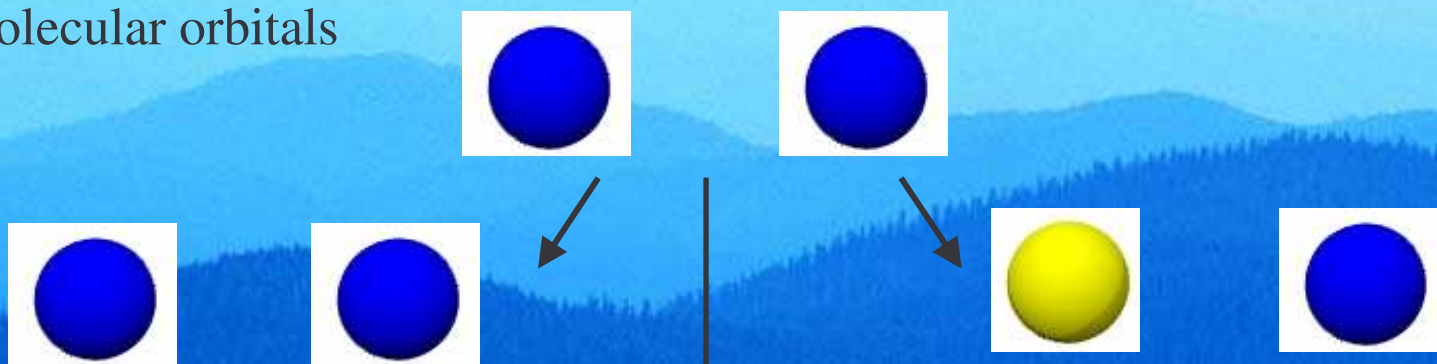
Then mix with Be s (zero overlap with p_z)

Then mix with Be p_z (zero overlap with s)
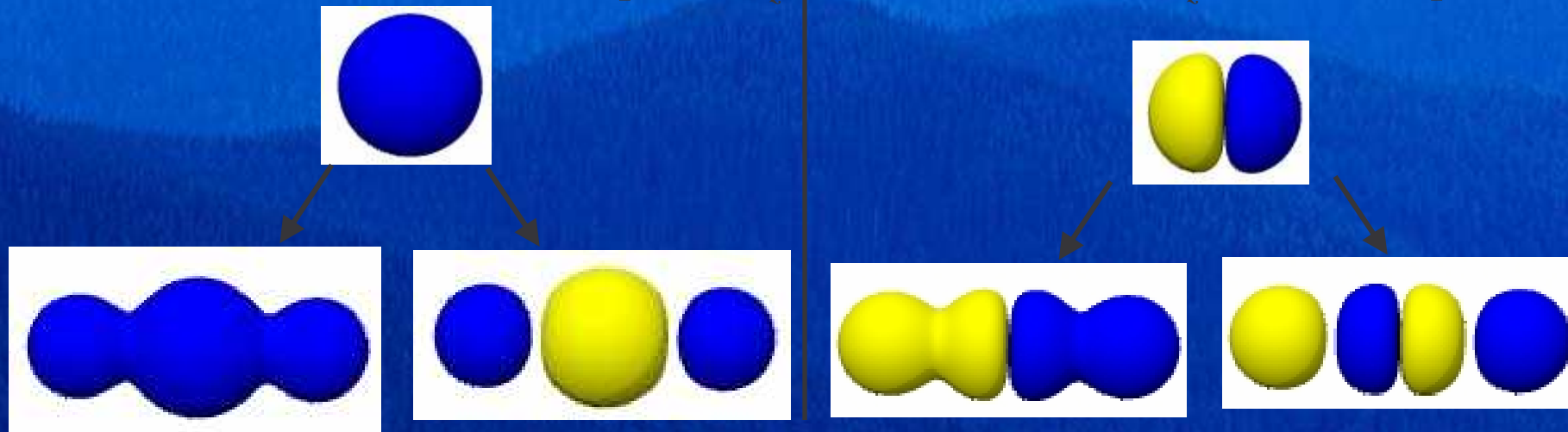
Alternative Route to energy level diagram for BeH$_2$

$4\sigma^*_u$

$3\sigma^*_g$

2p ⟵ Non bonding p_x and p_y

2s

$2\sigma_u$

$1\sigma_g$

Be   BeH$_2$ 2 H
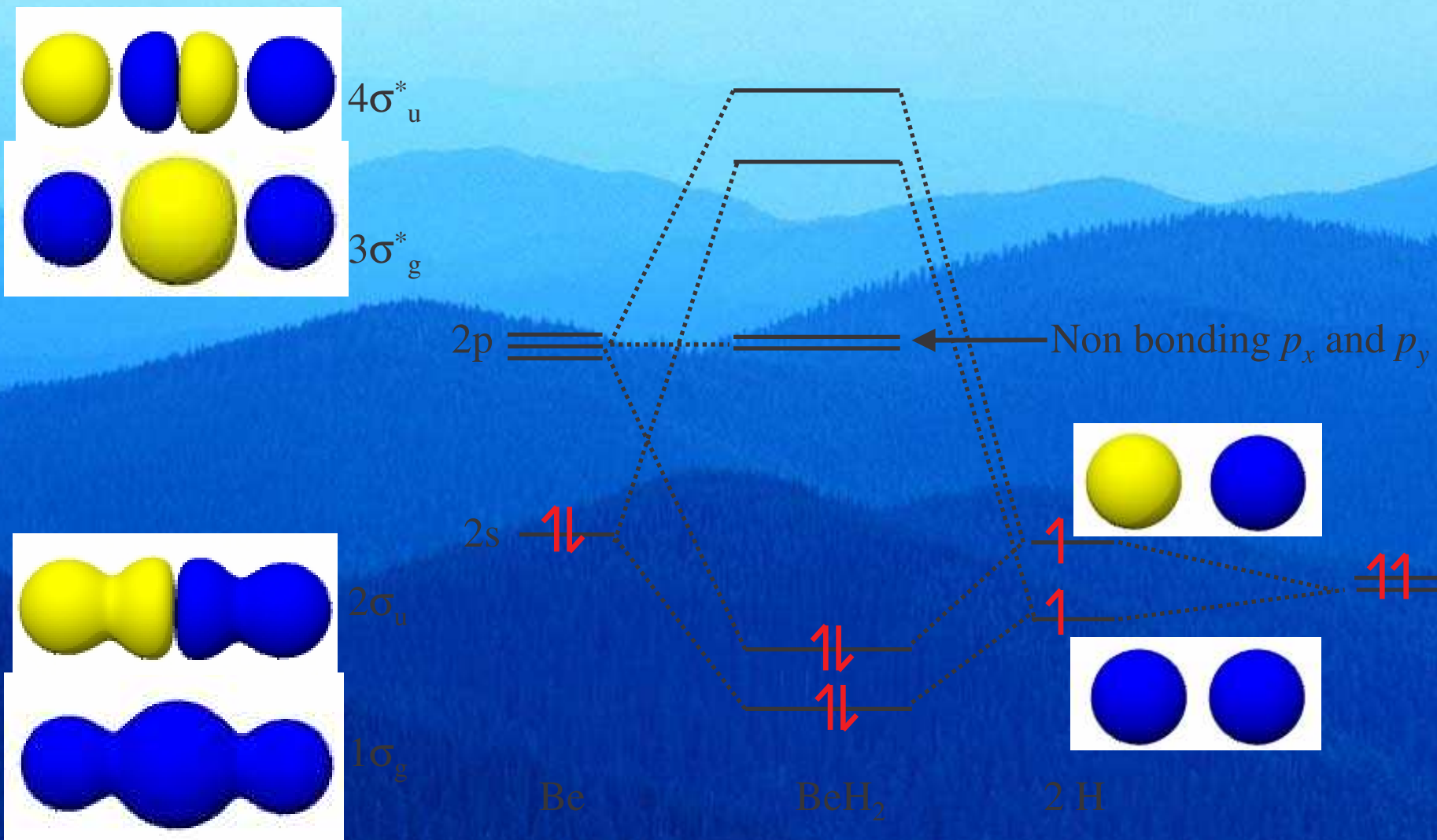
MO treatment of H_2O
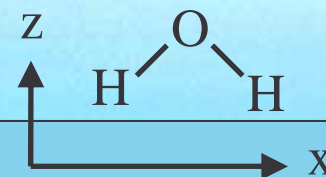
- H_2O is not linear – but why ?
  - We will examine the MOs for a non-linear tri-atomic and find out.
  - What orbitals are involved – 2 H $1s$ + O $2s$, O $2p_x$ O $2p_y$, and O $2p_z$

- Start by creating MO's from the hydrogen $1s$ orbitals.

- Taking the in-phase pair first – the result will interact with the O $2s$ and O $2p_z$ (zero overlap with O $2p_x$ and O $2p_y$)
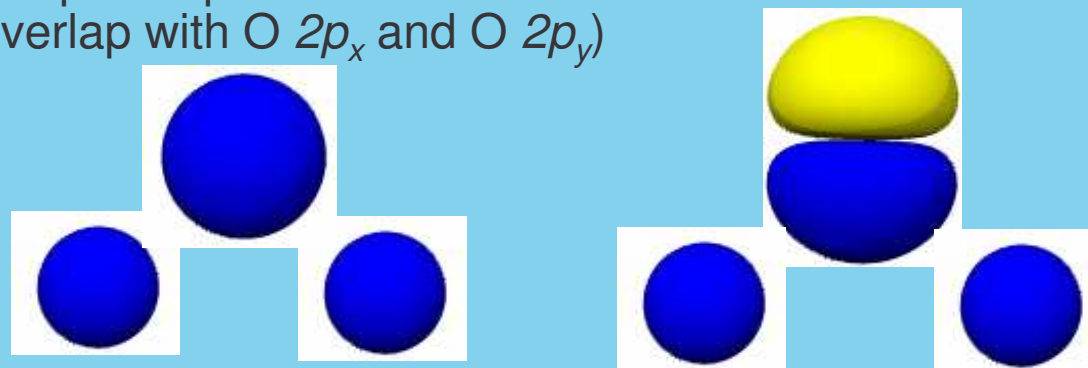
- Problem - this is mixing three orbitals → must produce three molecular orbitals
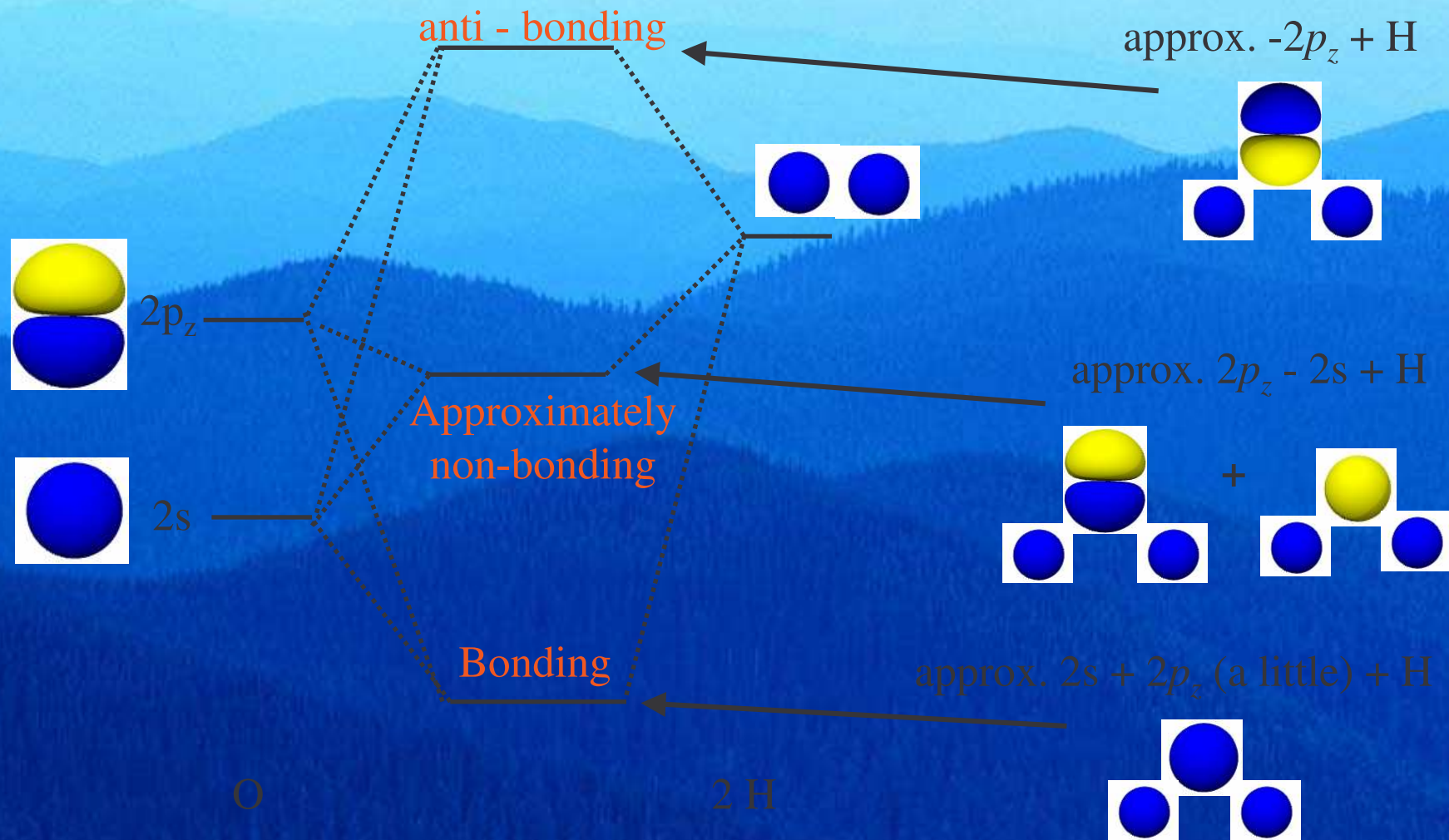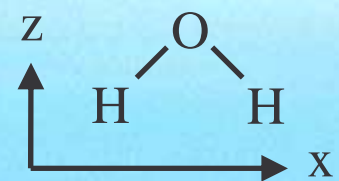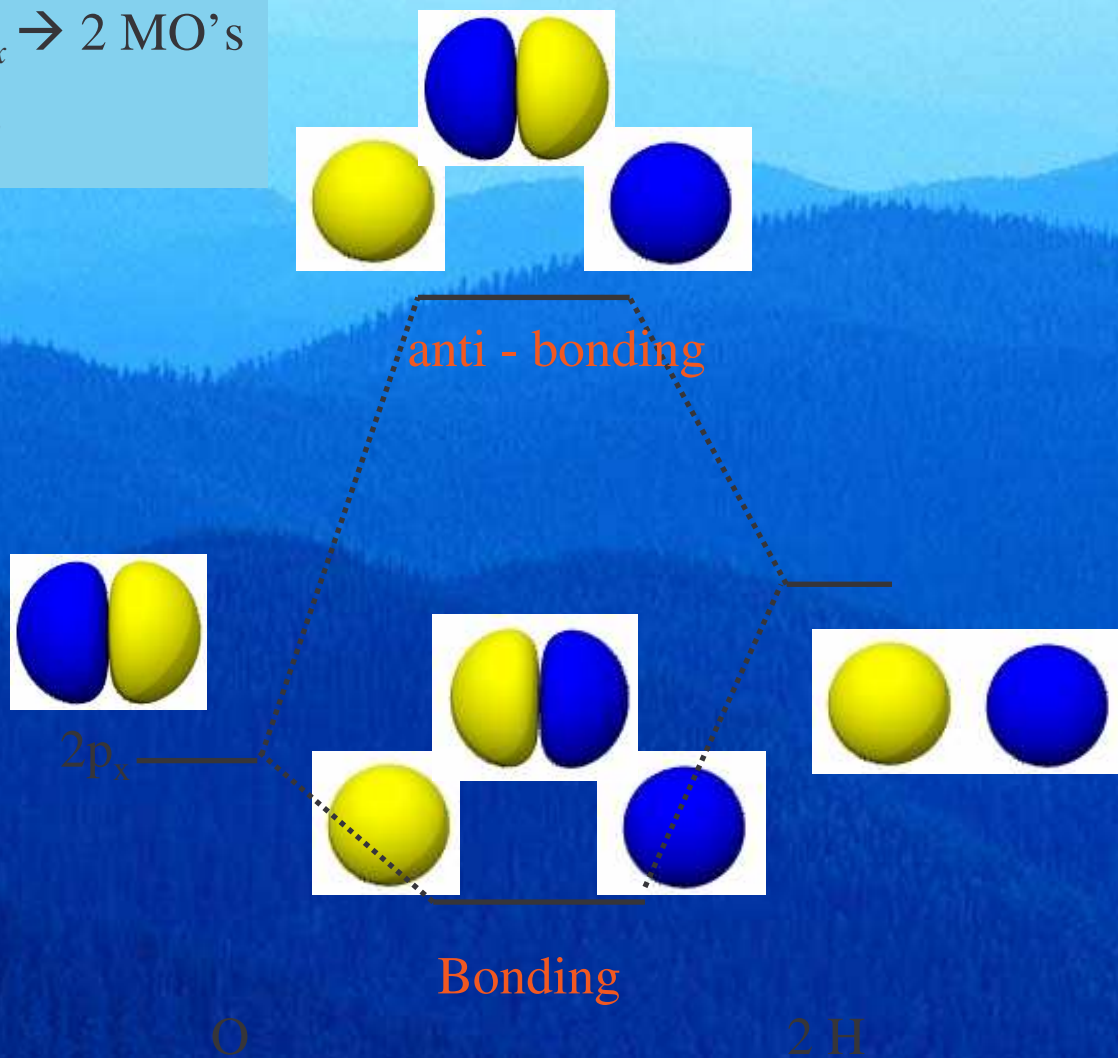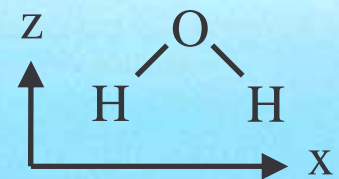
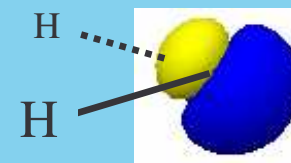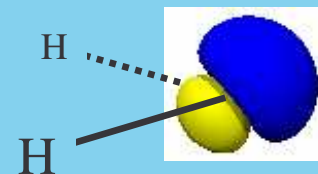# Energy level diagram for H_2O
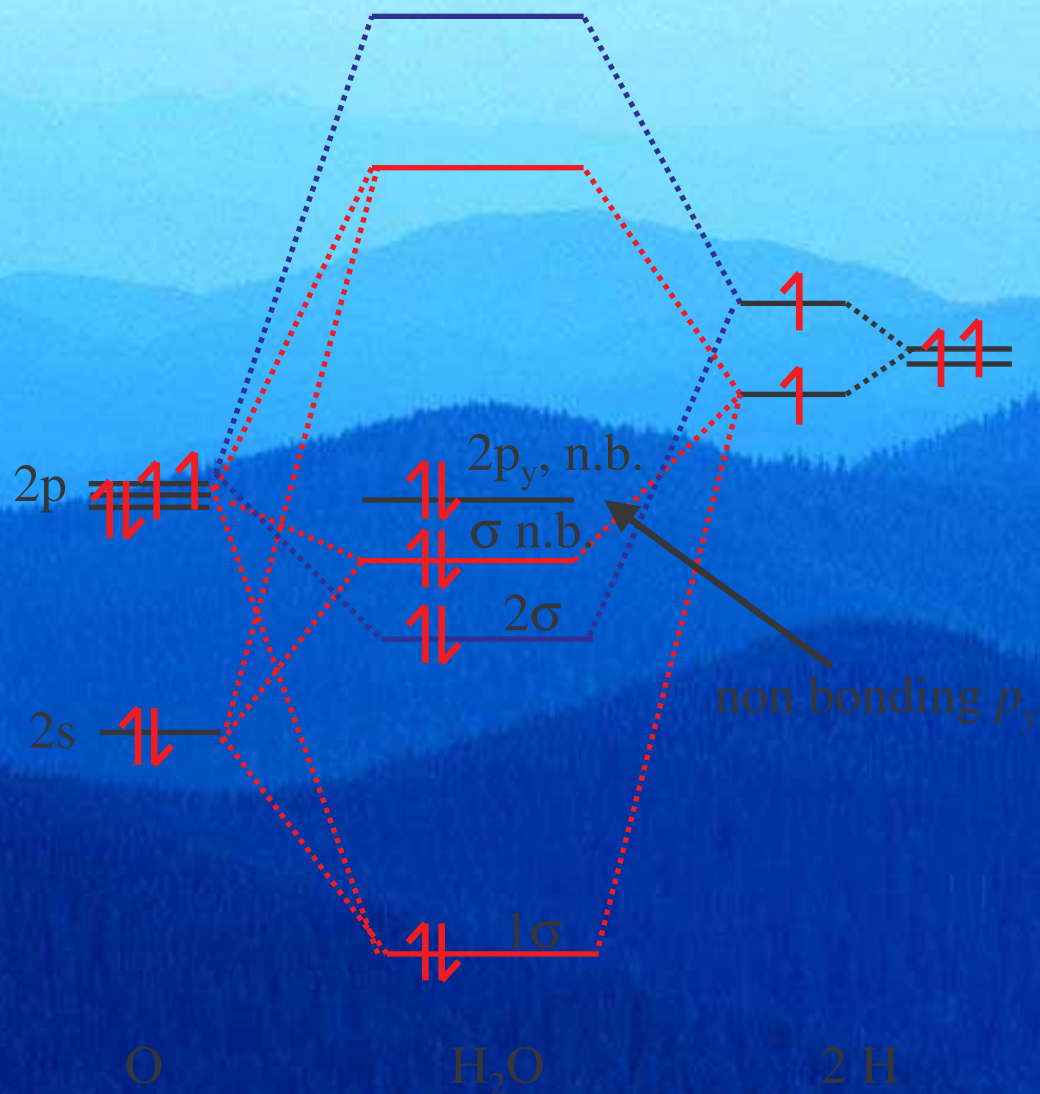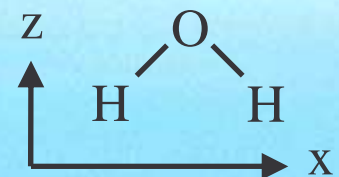
There are not two lone pairs !
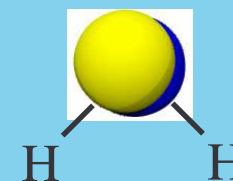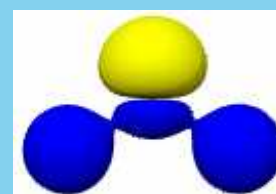
Slightly bonding Pz
Non bonding Py

Very different to the VB concept of two identical sp^3 filled orbital

MO theory correct.

$2p_y$, n.b.
σ n.b.
2σ

non bonding p_y

1σ

2p

2s

O H_2O 2 H

Comparison of H_2O and BeH_2

- Both cases of XA_2 → same MO – different No of electrons
  - Bonding MO's as a function of A-X-A bond angle

BeH₂   linear

BH₂   131°

CH₂ (t) 134°

CH₂ (s) 102°

NH₂   103°

OH₂   105°

90°   H₂O   CH₂(T)   180°
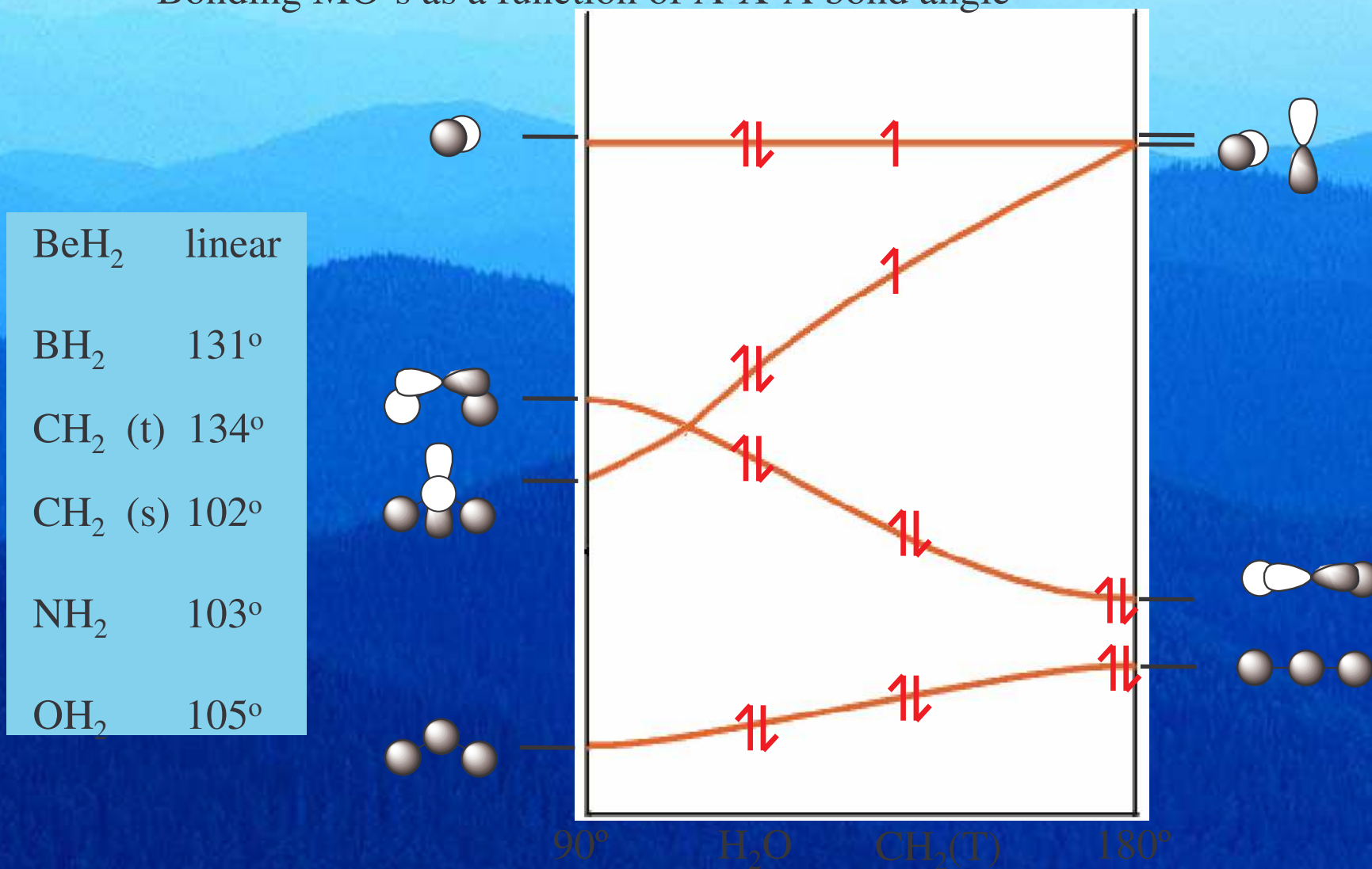
π MO's of Benzene

- π bonding is more important for reactivity –independent of σ (zero overlap)
  - six p_x orbitals → combine to form six MO's

  - Lowest energy – all in phase
  - Degenerate levels (1 nodal plane → 2 nodes)
  - Degenerate levels (2 nodal planes → 4 nodes)
  - Highest energy – all out of phase
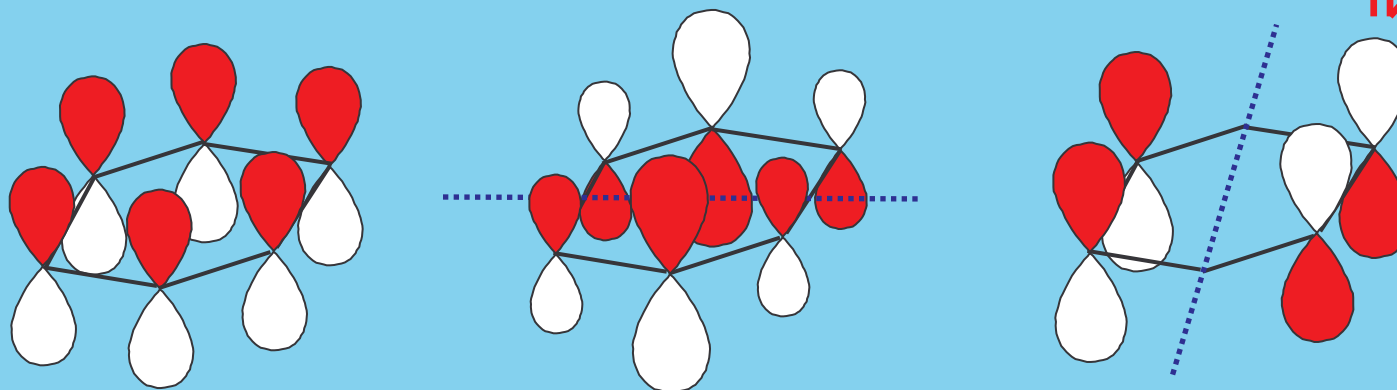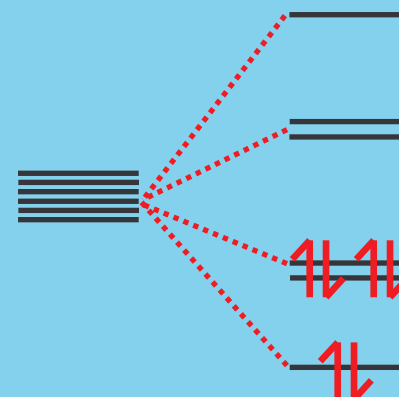
  - 2 electron per MO spread over 6 atoms

  - Compare with Lewis structure
  - has to resort to resonance structures to explain benzene