Optional – Bonding

Molecular Orbital Theory

Molecular Orbital (MO) Theory

- In MO theory, we apply Schrödinger's wave equation to the molecule to calculate a set of **molecular orbitals**.
  - In practice, the equation solution is estimated.
  - We start with good guesses from our experience as to what the orbital should look like.
  - Then we test and tweak the estimate until the energy of the orbital is minimized.
- In this treatment, the electrons belong to the whole molecule, so the orbitals belong to the whole molecule.
  - Delocalization

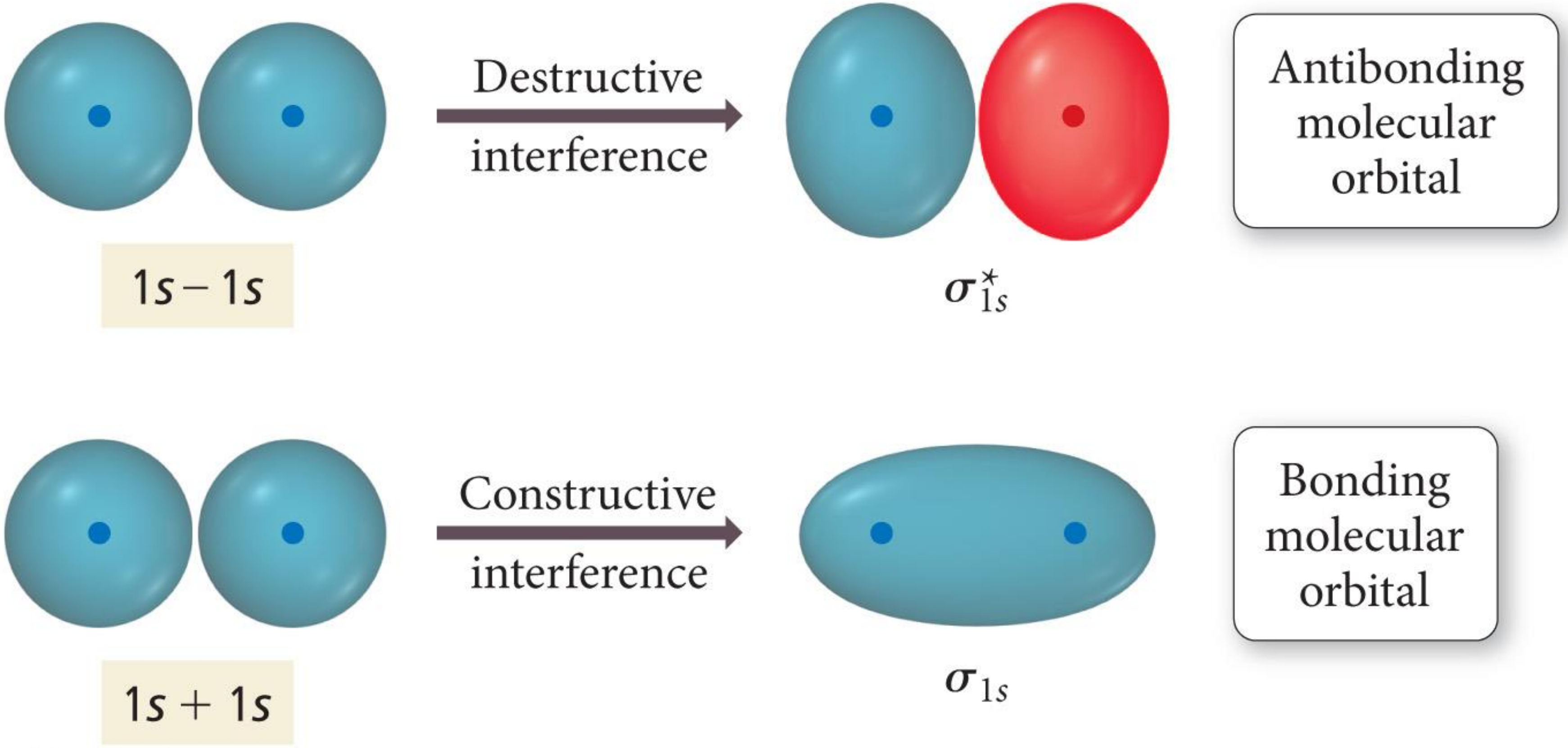
LCAO

- The simplest guess starts with the atomic orbitals of the atoms adding together to make molecular orbitals; this is called the **linear combination of atomic orbitals (LCAO)** method.
  - Weighted sum
- Because the orbitals are wave functions, the waves can combine either **constructively** or **destructively**.

Molecular Orbitals

- When the wave functions combine constructively, the resulting molecular orbital has less energy than the original atomic orbitals; it is called a **bonding molecular orbital**.
  - σ, π
  - – Most of the electron density between the nuclei
- When the wave functions combine destructively, the resulting molecular orbital has more energy than the original atomic orbitals; it is called an **antibonding molecular orbital**.
  - σ^*, π^*
  - – Most of the electron density outside the nuclei
  - – Nodes between nuclei

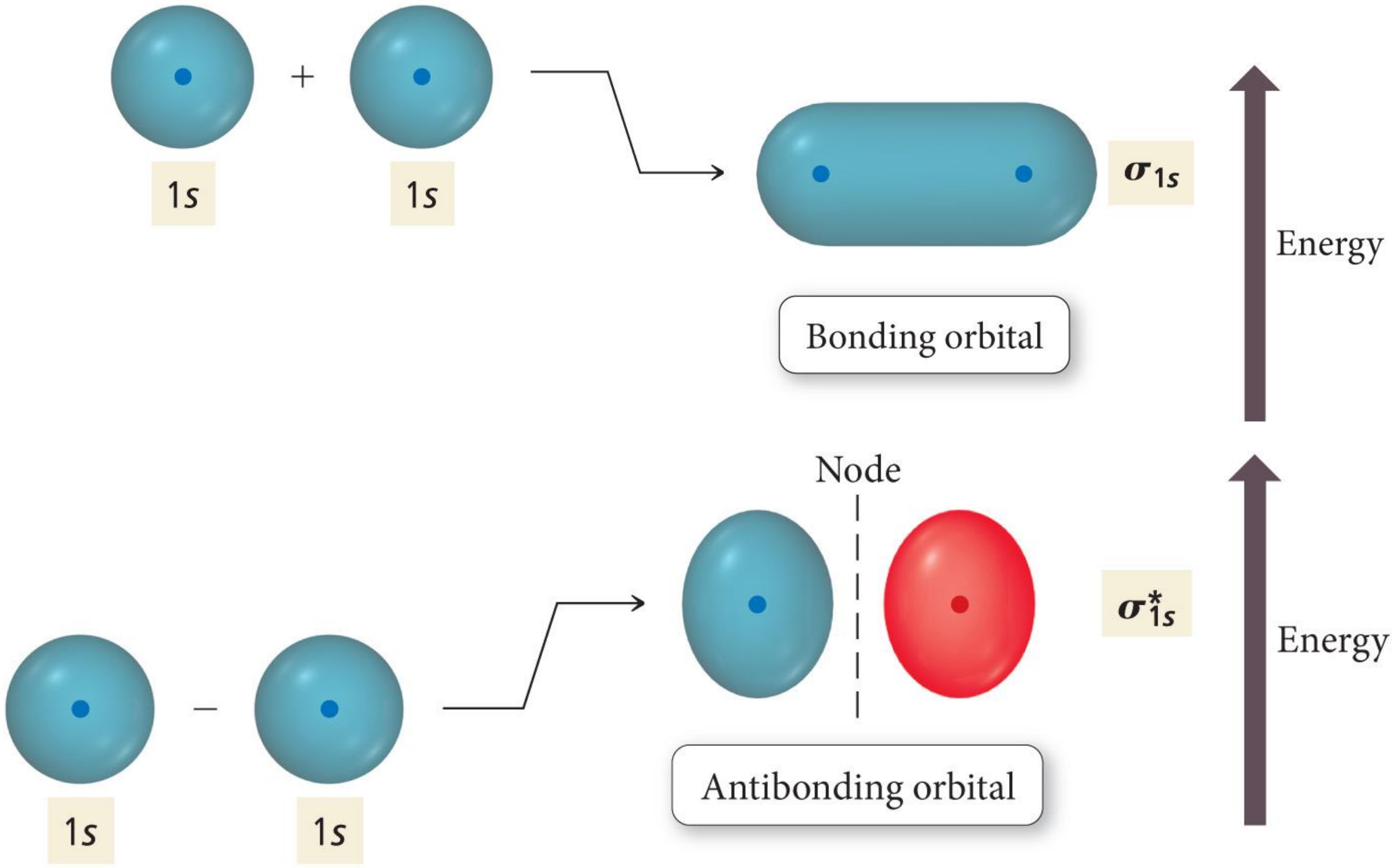
Interaction of 1s Orbitals



Molecular Orbital Theory

- Electrons in bonding MOs are stabilizing.
  - Lower energy than the atomic orbitals
- Electrons in antibonding MOs are destabilizing.
  - Higher in energy than atomic orbitals
  - Electron density located outside the internuclear axis
  - Electrons in antibonding orbitals cancel stability gained by electrons in bonding orbitals.

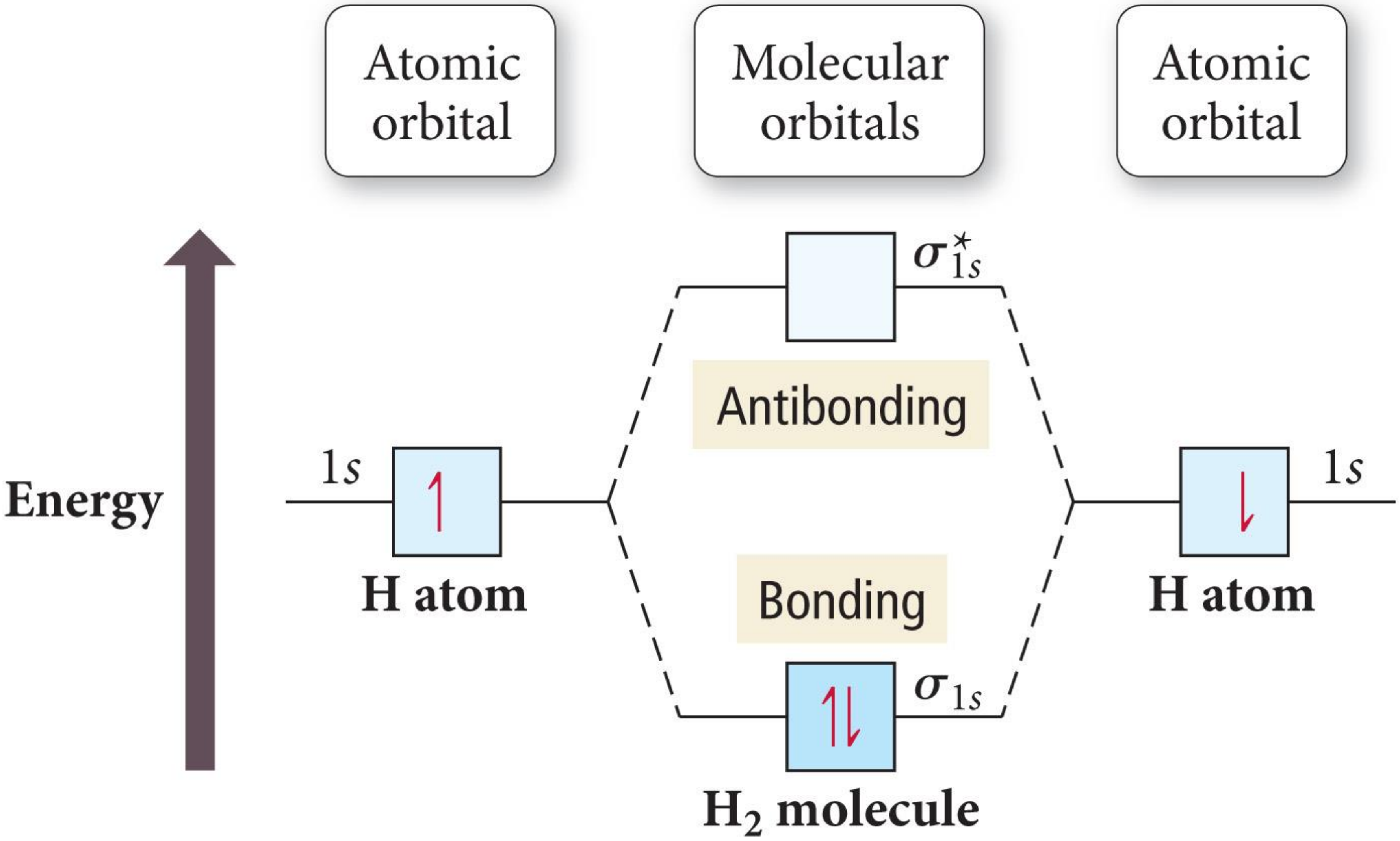
Energy Comparisons of Atomic Orbitals to Molecular Orbitals



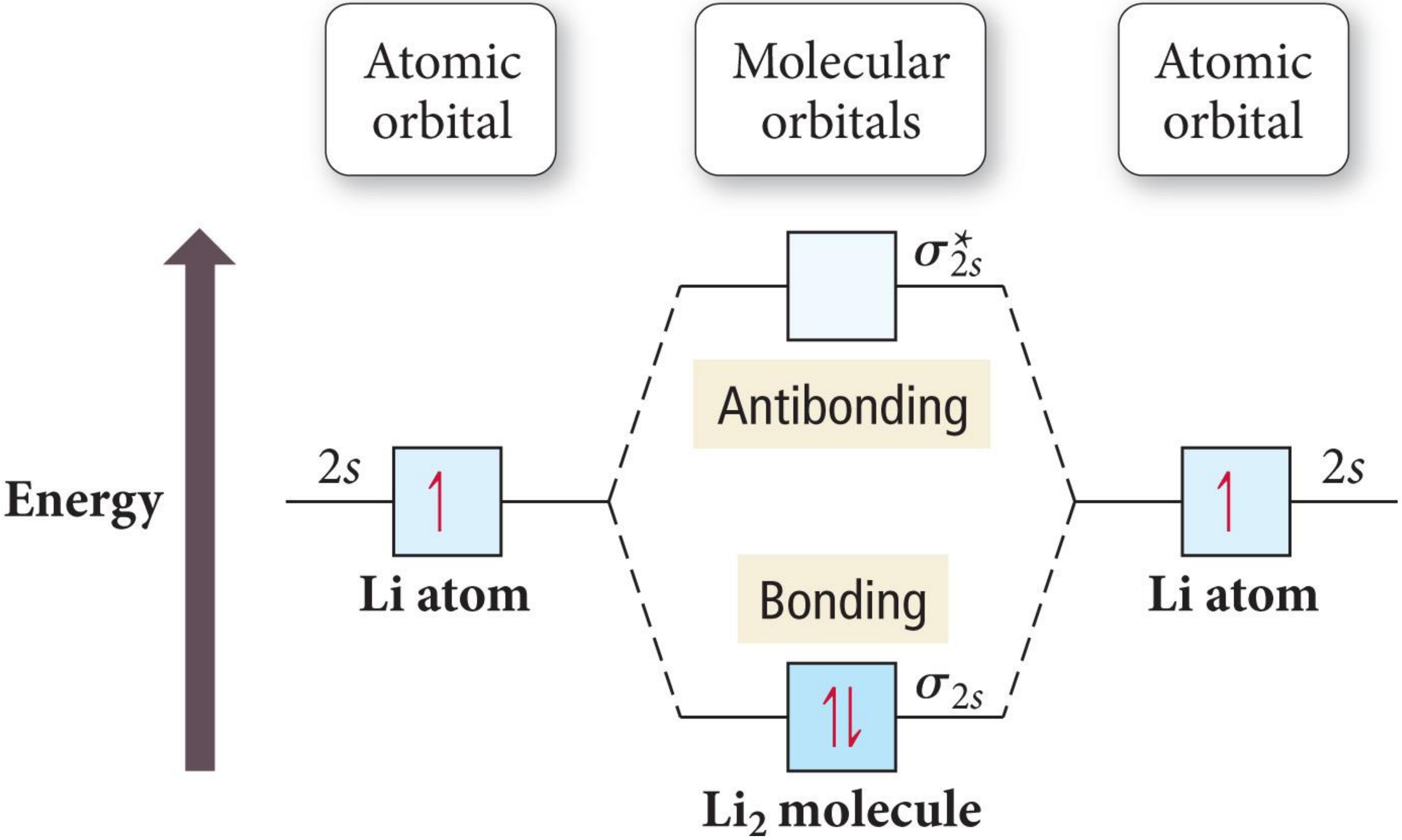
MO and Properties

- Bond order = difference between number of electrons in bonding and antibonding orbitals
  - Only need to consider valence electrons
  - May be a fraction
  - Higher bond order = stronger and shorter bonds
  - If bond order = 0, then bond is unstable compared to individual atoms and no bond will form.
- A substance will be paramagnetic if its MO diagram has unpaired electrons.
  - If all electrons paired, it is diamagnetic

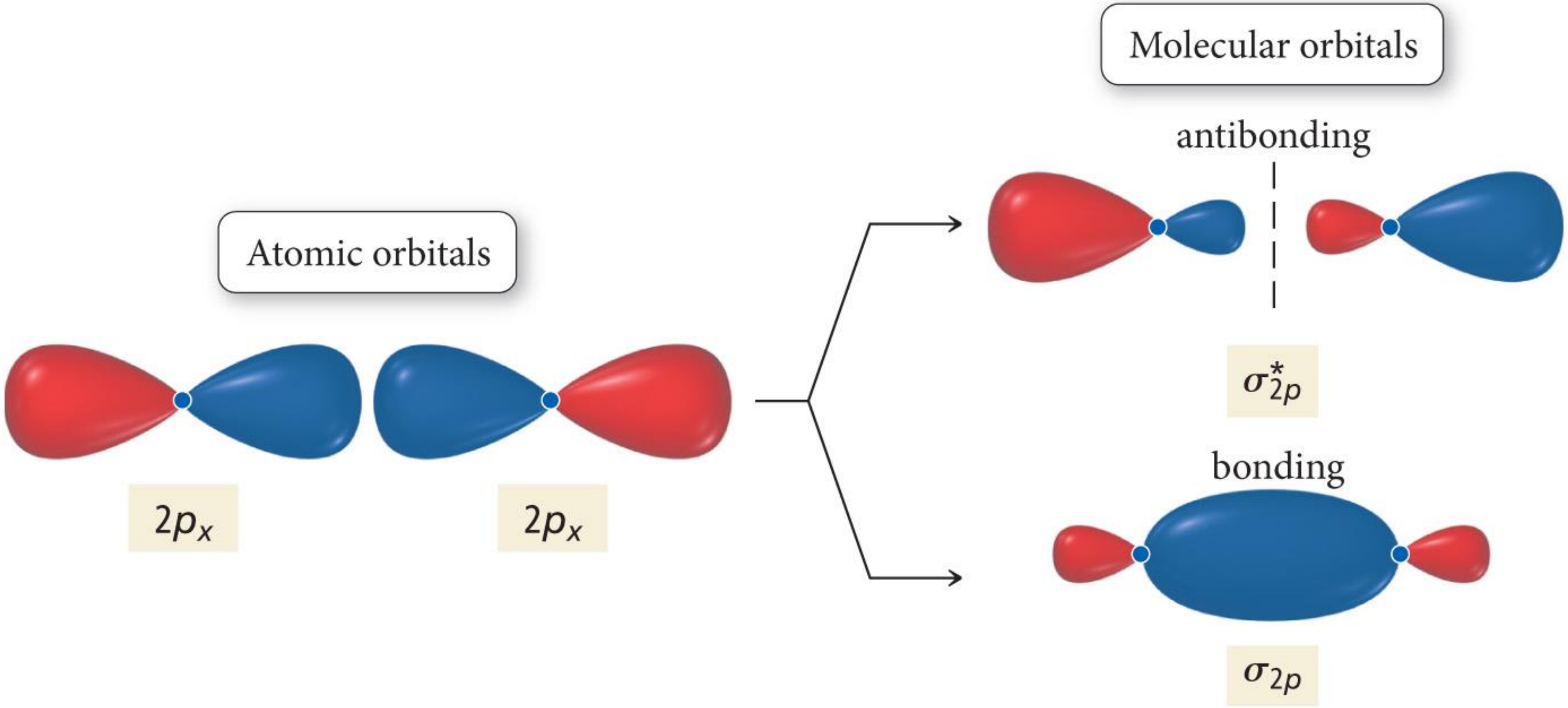
$$\text{Bond Order} = \frac{\#\,\text{Bonding Electrons} - \#\,\text{Antibonding Electrons}}{2}$$


Atomic orbital
Molecular orbitals
Atomic orbital
σ^*_{1s}
Antibonding
Energy
$1s$
H atom
Bonding
$1s$
H atom
σ_{1s}
H_2 molecule

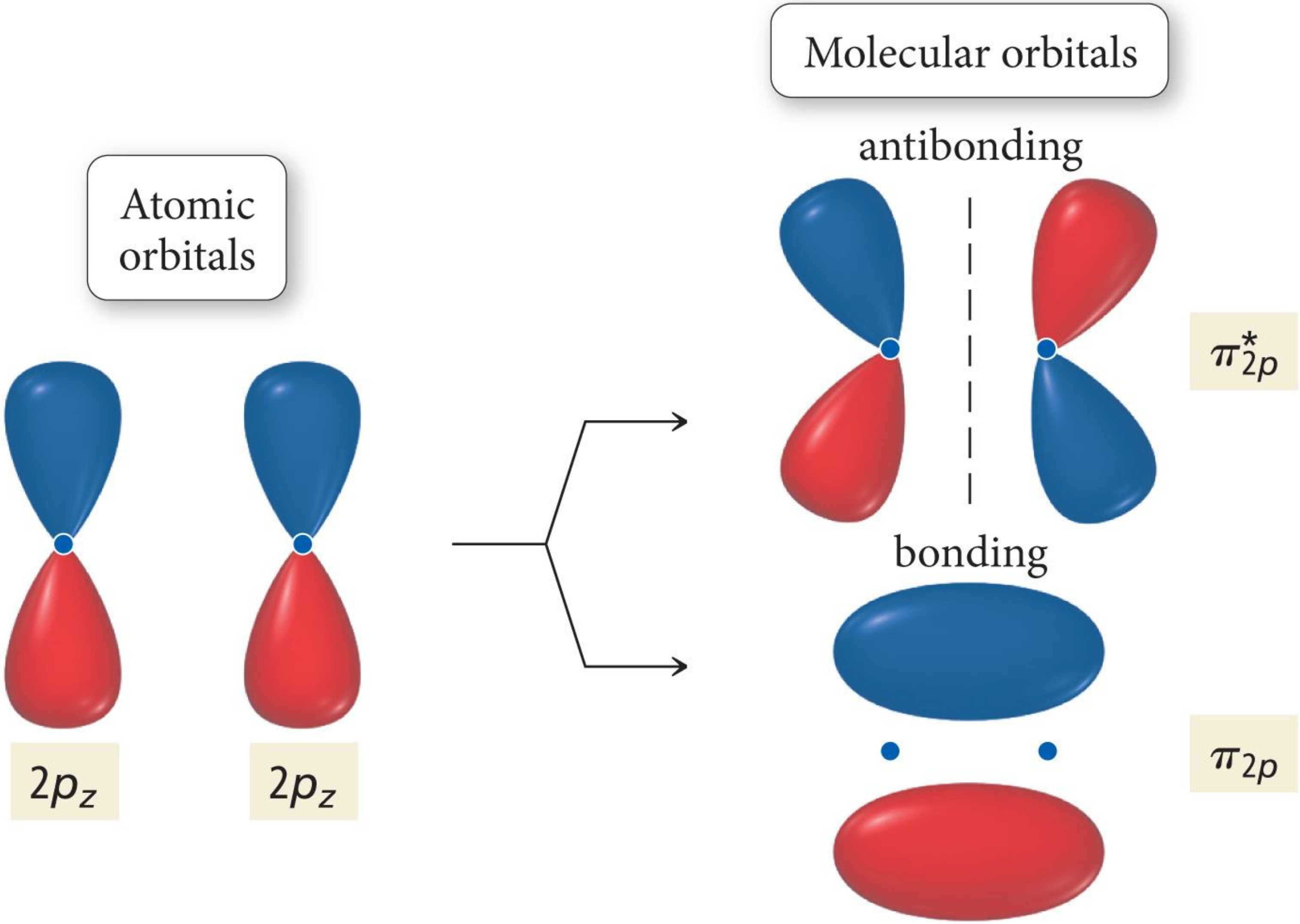
Period Two Homonuclear Diatomic Molecules



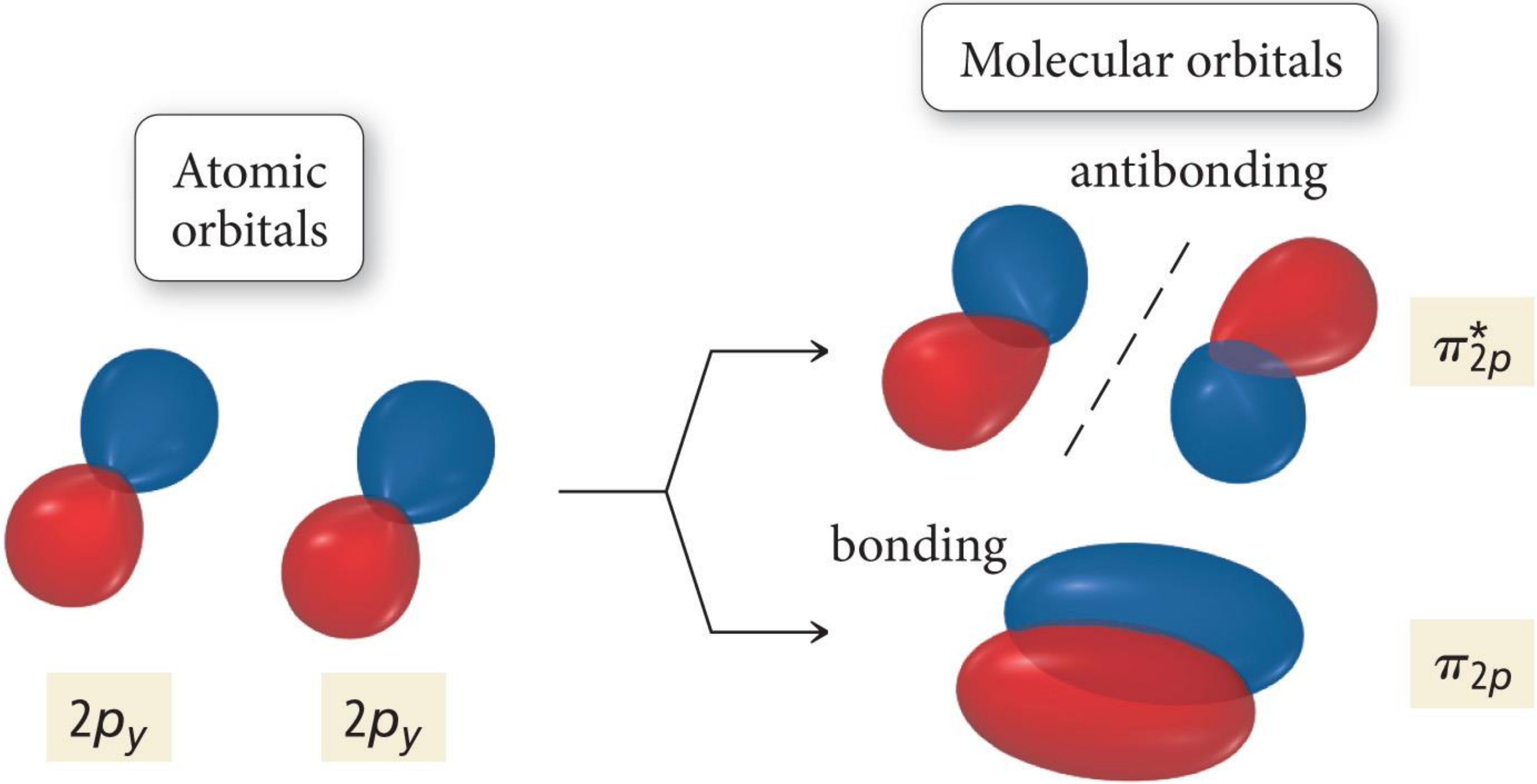
Interaction of *p* Orbitals

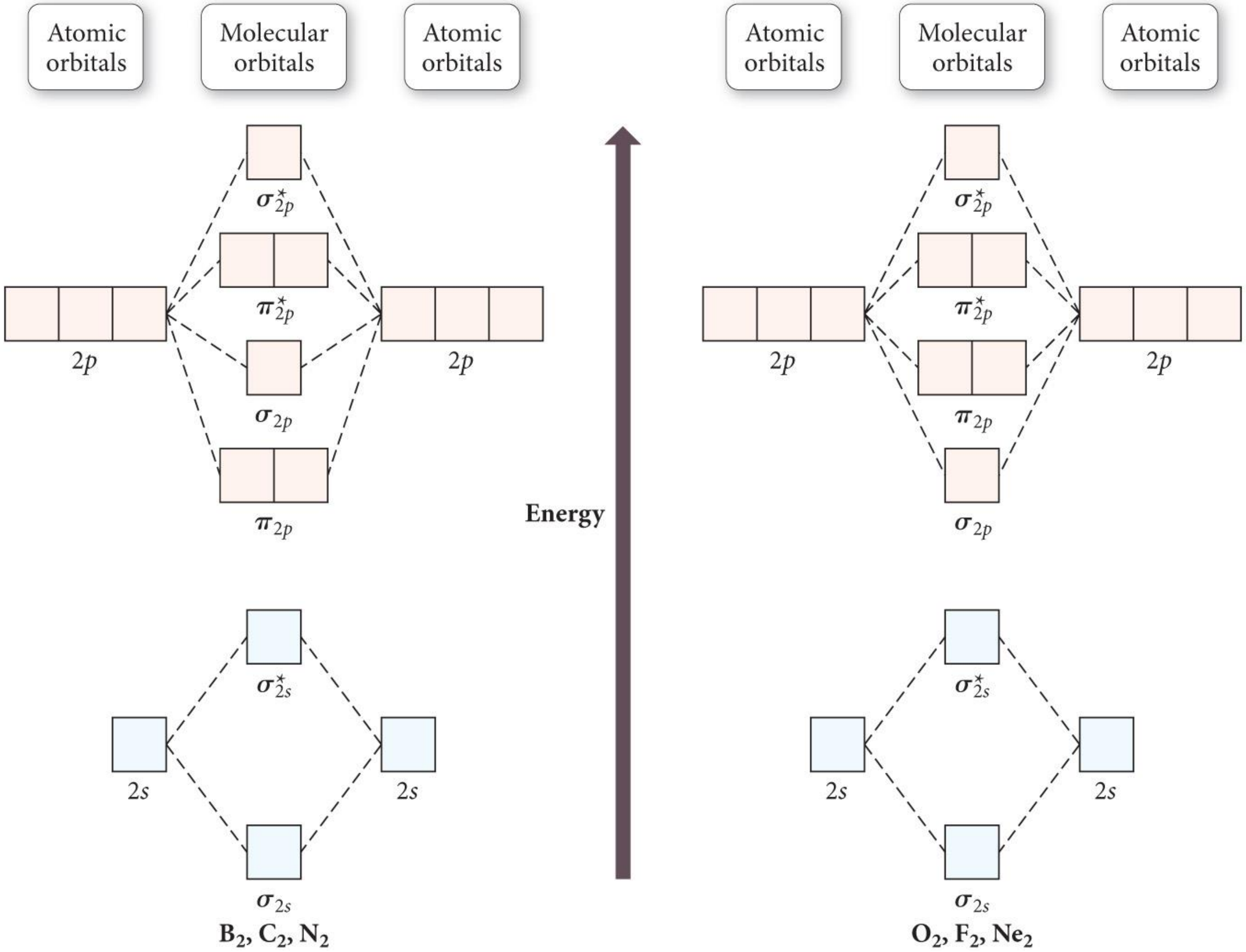


Interaction of *p* Orbitals



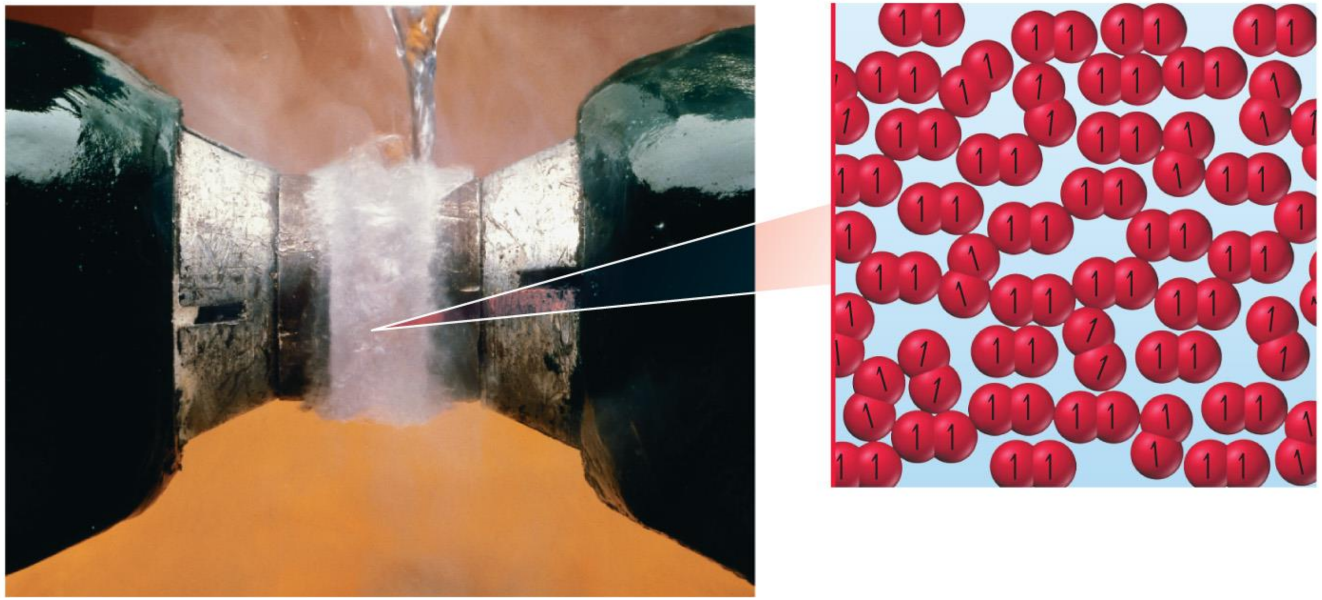
Interaction of *p* Orbitals



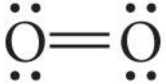

Atomic orbitals
Molecular orbitals
Atomic orbitals
σ^*_{2p}
π^*_{2p}
2p
2p
σ_{2p}
π_{2p}
σ^*_{2s}
2s
2s
σ_{2s}
B_2, C_2, N_2
Energy
Atomic orbitals
Molecular orbitals
Atomic orbitals
σ^*_{2p}
π^*_{2p}
2p
2p
π_{2p}
σ_{2p}
σ^*_{2s}
2s
2s
σ_{2s}
O_2, F_2, Ne_2

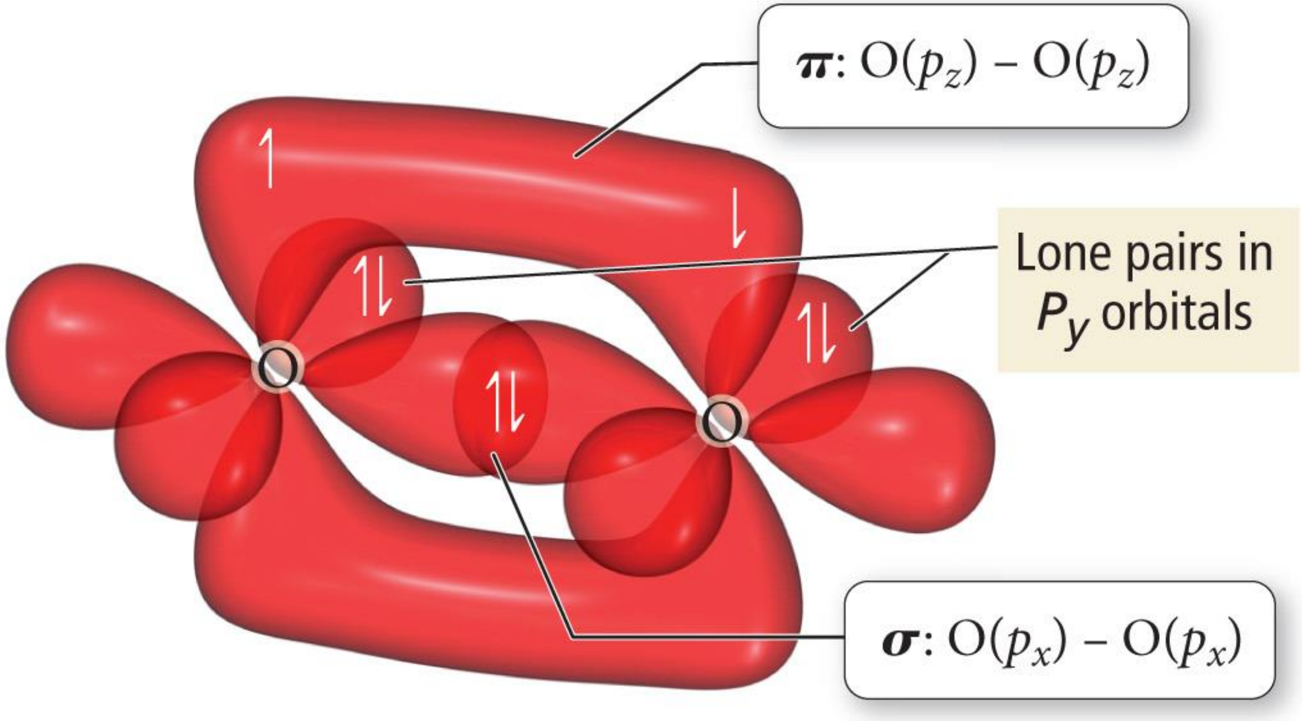
Diatomic O_2

- Dioxygen is paramagnetic.
- Paramagnetic material has unpaired electrons.
- Neither Lewis theory nor valence bond theory predict this result.



O_2 as Described by Lewis and VB Theory





π: O(p_z) – O(p_z)

Lone pairs in P_y orbitals

σ: O(p_x) – O(p_x)

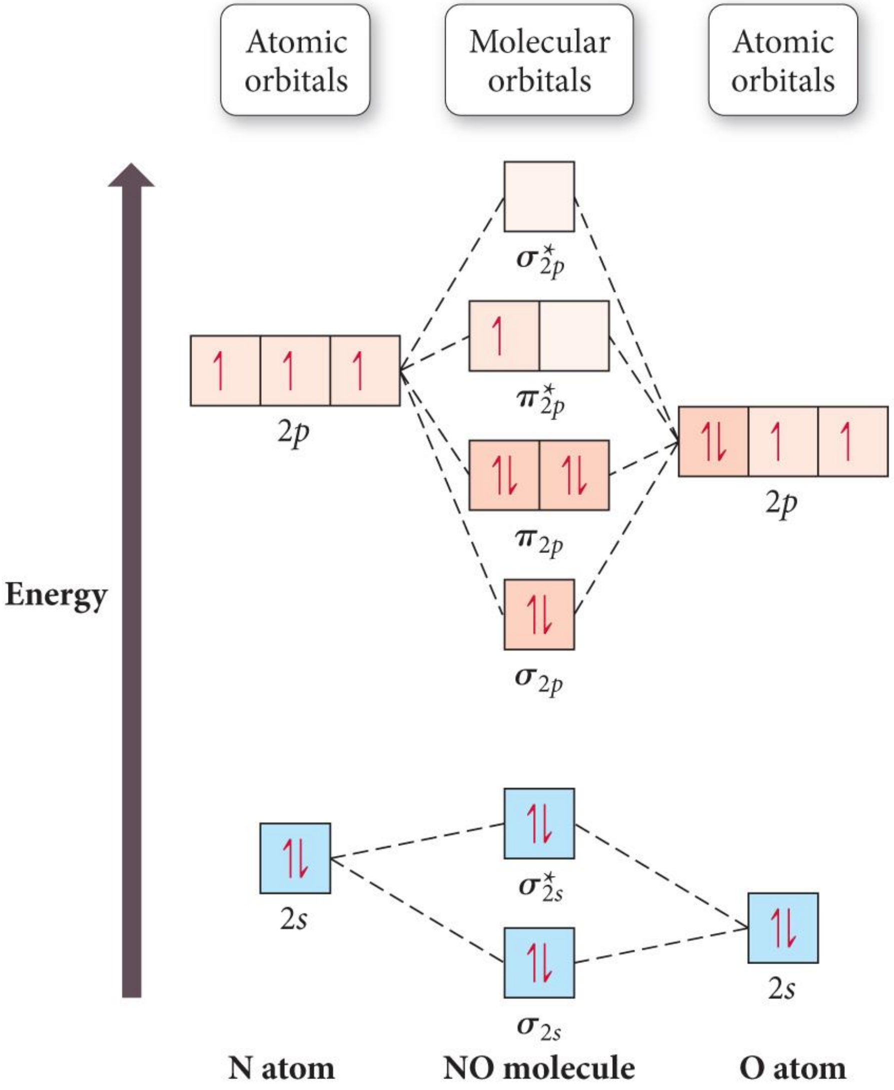
Heteronuclear Diatomic Molecules and Ions

- When the combining atomic orbitals are identical and of equal energy, the contribution of each atomic orbital to the molecular orbital is equal.
- When the combining atomic orbitals are different types and energies, the atomic orbital closest in energy to the molecular orbital contributes more to the molecular orbital.

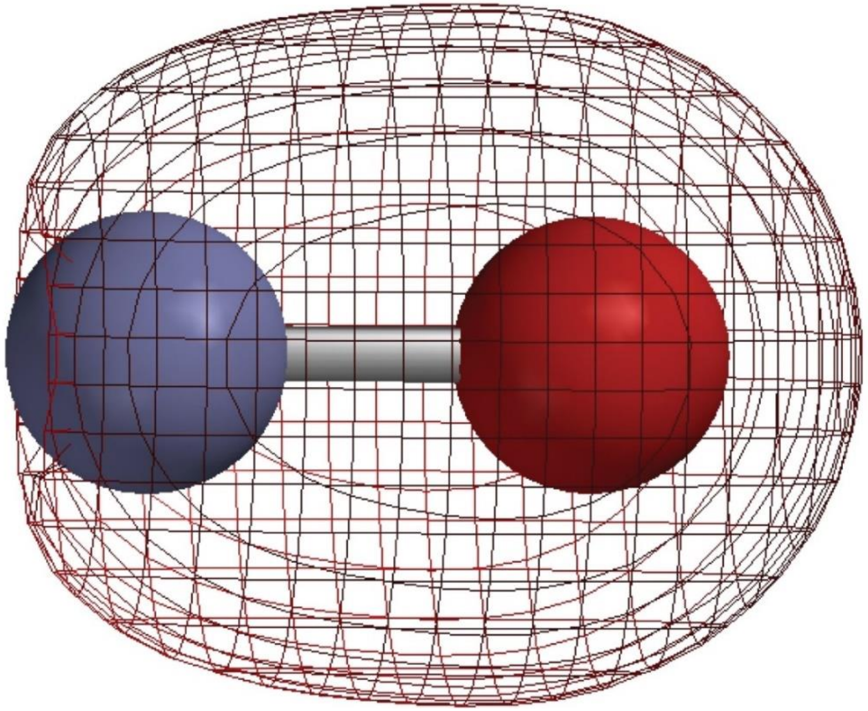
Heteronuclear Diatomic Molecules and Ions

- The more electronegative an atom is, the lower in energy are its orbitals.
- Lower energy atomic orbitals contribute more to the bonding MOs.
- Higher energy atomic orbitals contribute more to the antibonding MOs.
- Nonbonding MOs remain localized on the atom donating its atomic orbitals.

Second-Period Heteronuclear Diatomic Molecules



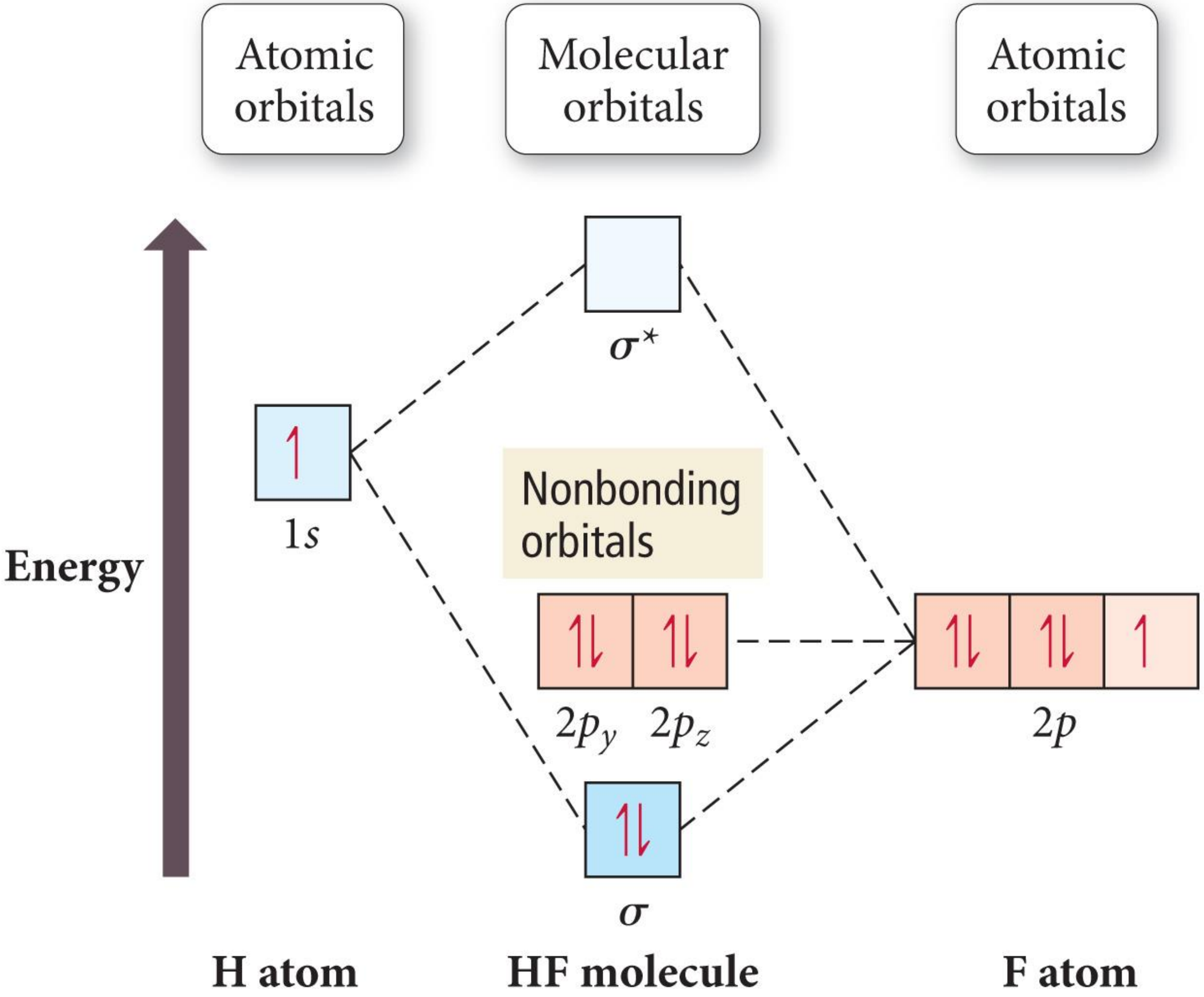
NO example



σ_{2s} bonding MO

shows more electron density near O because it is mostly O’s 2*s* atomic orbital.

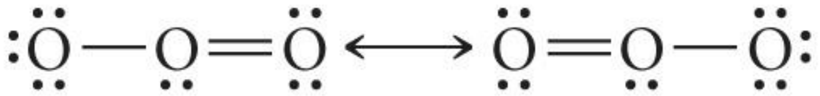
HF example


Atomic orbitals
Molecular orbitals
Atomic orbitals
Energy
σ*
1
1s
Nonbonding orbitals
1⇃ 1⇃
$2p_y$ $2p_z$
1⇃ 1⇃ 1
2p
1⇃
σ
H atom
HF molecule
F atom

Polyatomic Molecules

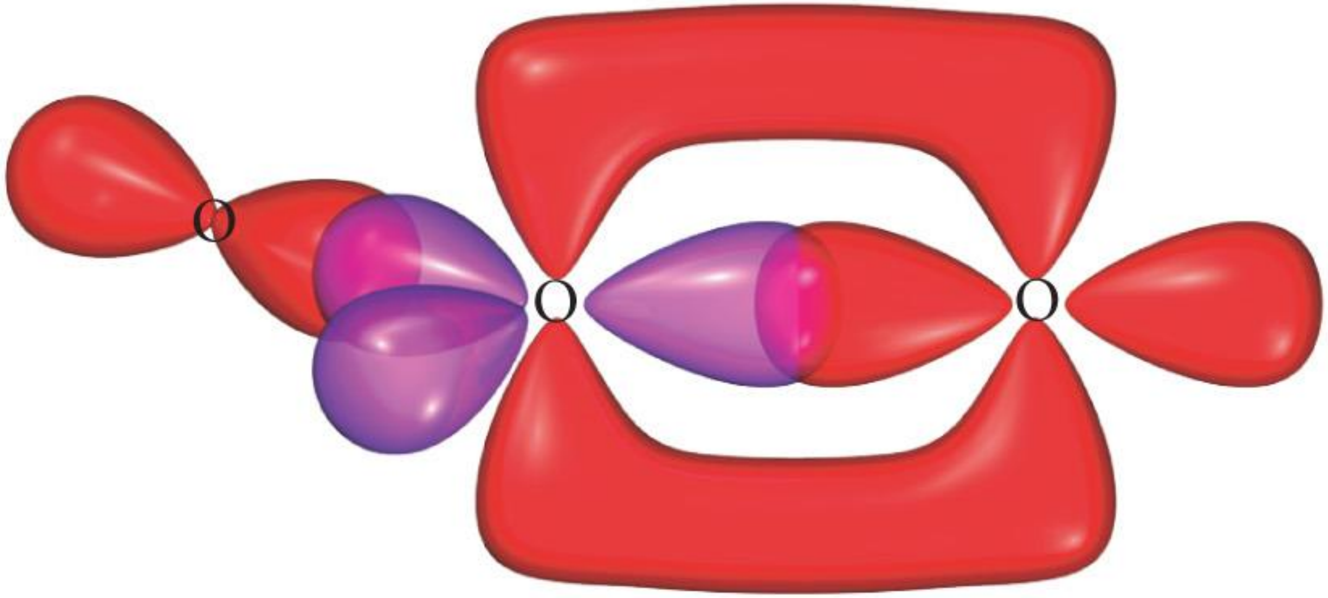
- When many atoms are combined together, the atomic orbitals of all the atoms are combined to make a set of molecular orbitals, which are delocalized over the entire molecule.
- Gives results that better match real molecule properties than either Lewis or valence bond theories.

Ozone, O_3



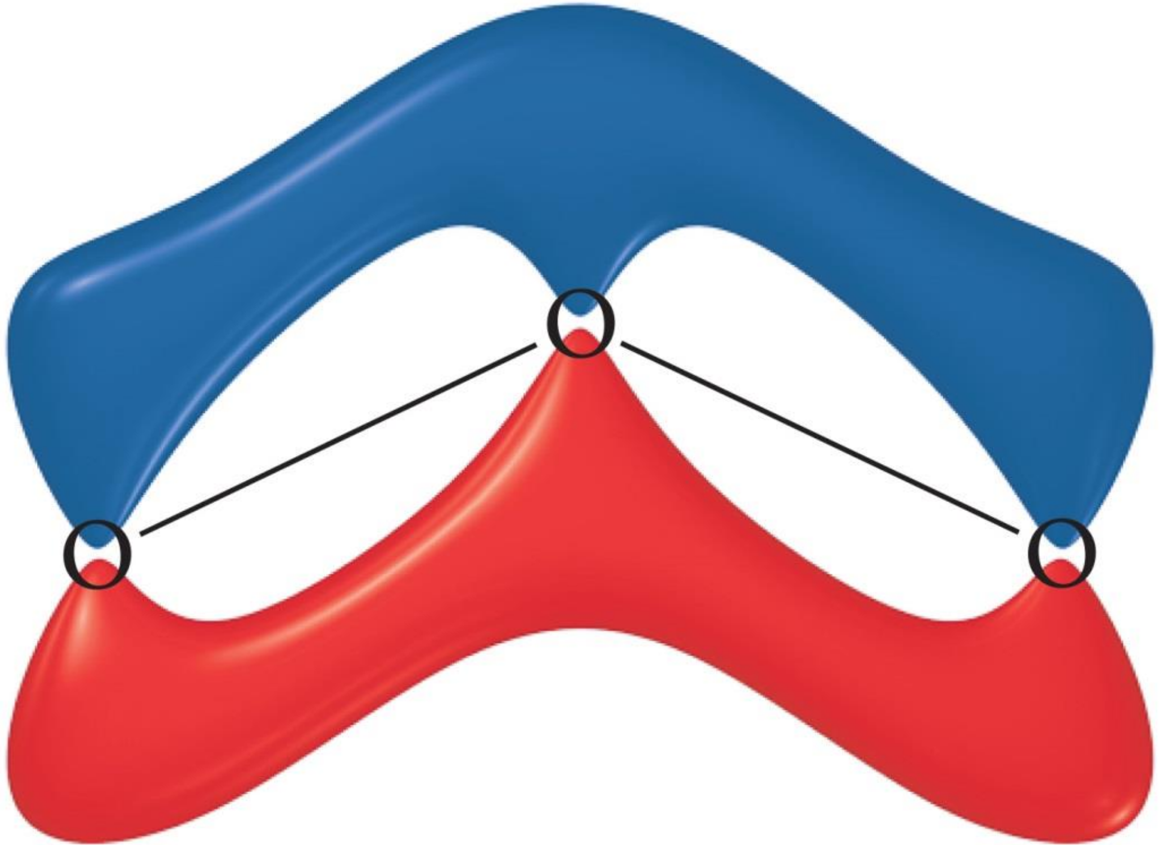
$$:\ddot{\underset{..}{O}}-\underset{..}{O}=\ddot{\underset{..}{O}} \longleftrightarrow \ddot{\underset{..}{O}}=\underset{..}{O}-\ddot{\underset{..}{O}}:$$

Lewis structure



Valence bond model

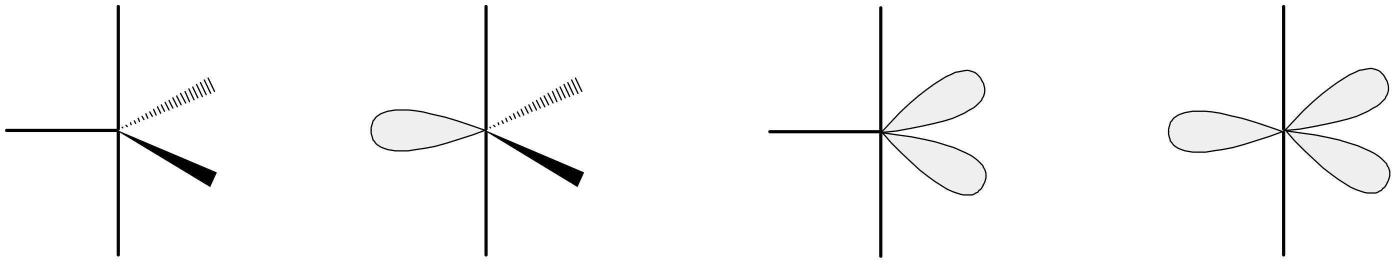
Ozone, O_3



Hybridization Involving "*d*" Orbitals

Beginning with elements in the third row, "*d*" orbitals may also hybridize, but they no longer think this is how it happens

sp^3d = **five** hybrid orbitals of equal energy



sp^3d^2 = **six** hybrid orbitals of equal energy