Molecular Orbital Theory

MO Overview

- Comes from quantum mechanics.
- Quantum mechanics gives the allowed energy levels for electrons in atoms/ions. We know these as 1s, 2p, 3d, 4f, etc designations.
- In MO theory, use quantum mechanics to give the allowed energy levels for the electrons in molecules.
- We will concentrate on applying MO theory to diatomic molecules only. The theory is to complicated for polyatomic molecules.
- The MO energy levels are designated as sigma (σ) and pi (π), similar to the terminology used in hybrid orbital theory.

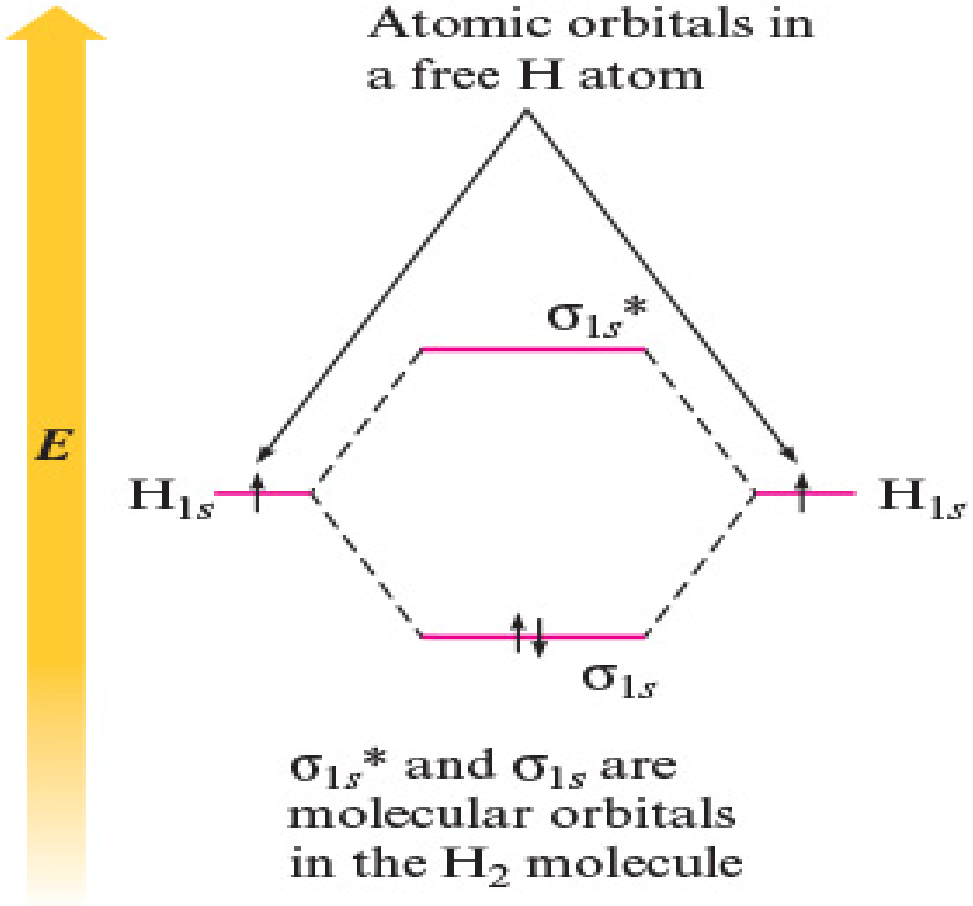
Characteristics of Molecular Orbital Theory

- Only valence orbitals are used to construct the molecular orbitals.
- Orbitals are conserved. The number of molecular orbitals will be equal to the number of valence atomic orbitals used to construct them.
- Each molecular orbital can hold two electrons, but the spins must be opposite.
- Atomic orbitals are wave functions. When atomic orbitals are added together to form molecular orbitals, they can add together constructively or destructively. Constructive addition forms bonding orbitals which are lower in energy than the atomic orbitals, while destructive addition forms antibonding orbitals which are higher in energy.

MO diagram for H_2

H: $1s^1$

H_2: 2 total valence electrons



MO Energy Diagram for H_2

- H:$1s^1$; when bringing two 1s orbitals together to form the bonding orbitals in H_2, two molecular orbitals are formed. Since 1s orbitals combine head-to-head, the MOs are sigma (σ) bonds.

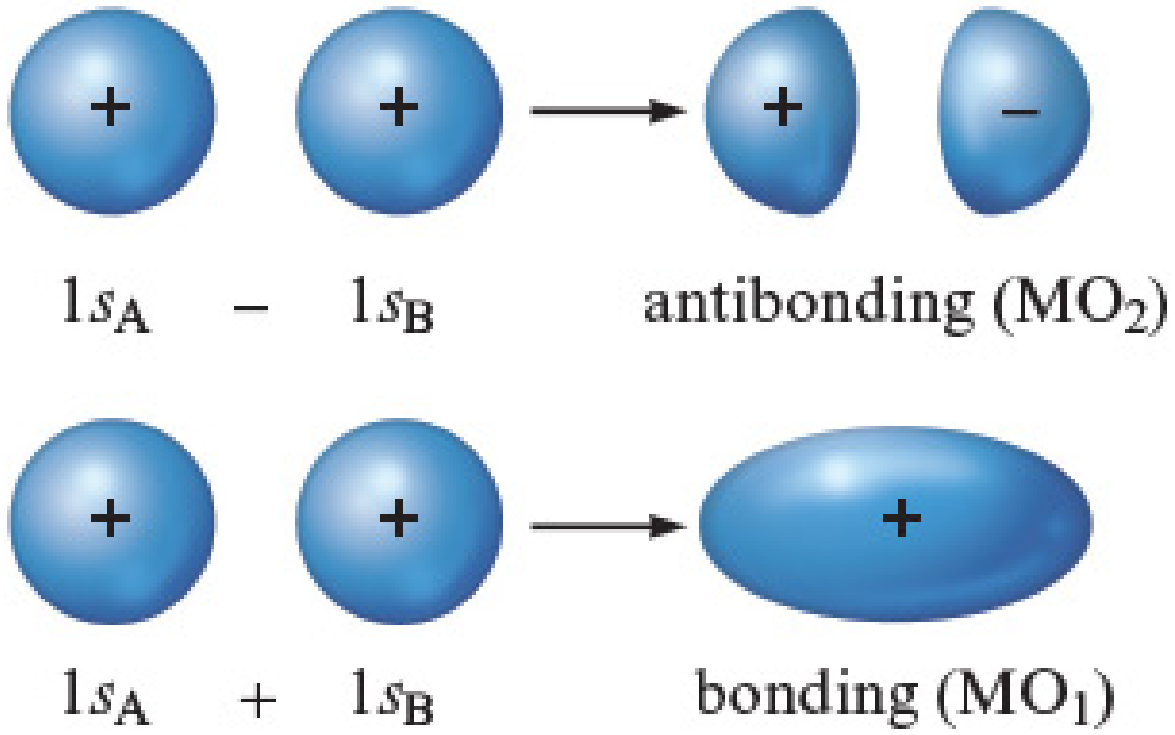
MO Energy Diagram for H_2

- One of the sigma bonding orbitals is lower in energy than the 1s atomic orbitals and is called a bonding MO. Here the 1s orbital from each H atom are in-phase with each other for constructive addition. Bonding MOs are always lower in energy than the atomic orbitals from which they are formed.

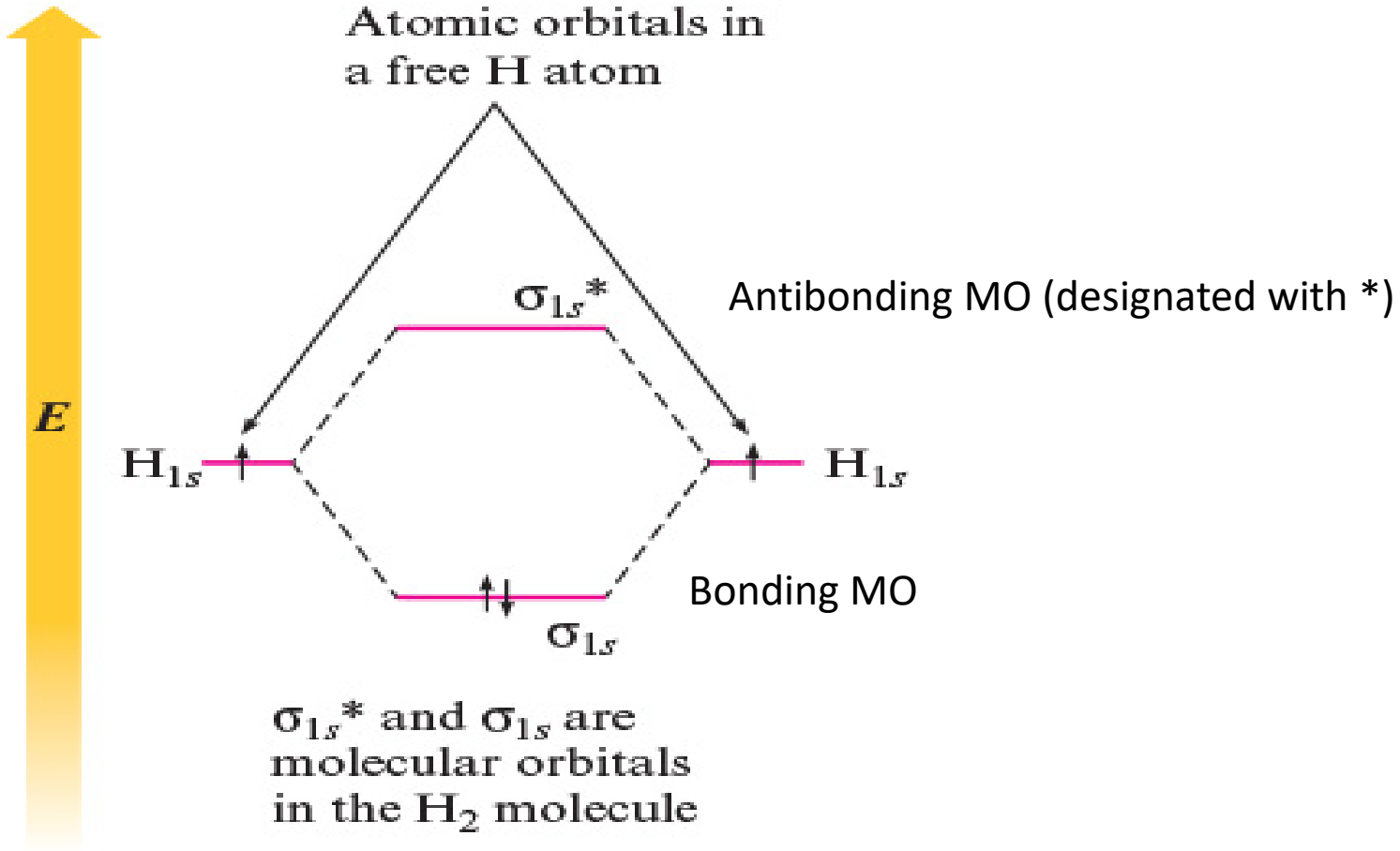
MO Energy Diagram for H_2

- One of the sigma bonding orbitals is lower in energy than the 1s atomic orbitals and is called a bonding MO. Here the 1s orbital from each H atom are in-phase with each other for constructive addition. Bonding MOs are always lower in energy than the atomic orbitals from which they are formed.
- The second bonding orbital is higher in energy than the 1s orbitals and is called an antibonding orbital. Here the 1s orbitals are out-of-phase with each other for destructive addition. Antibonding MOs are always higher in energy than the atomic orbitals.

Combining 1s orbitals in phase vs out of phase



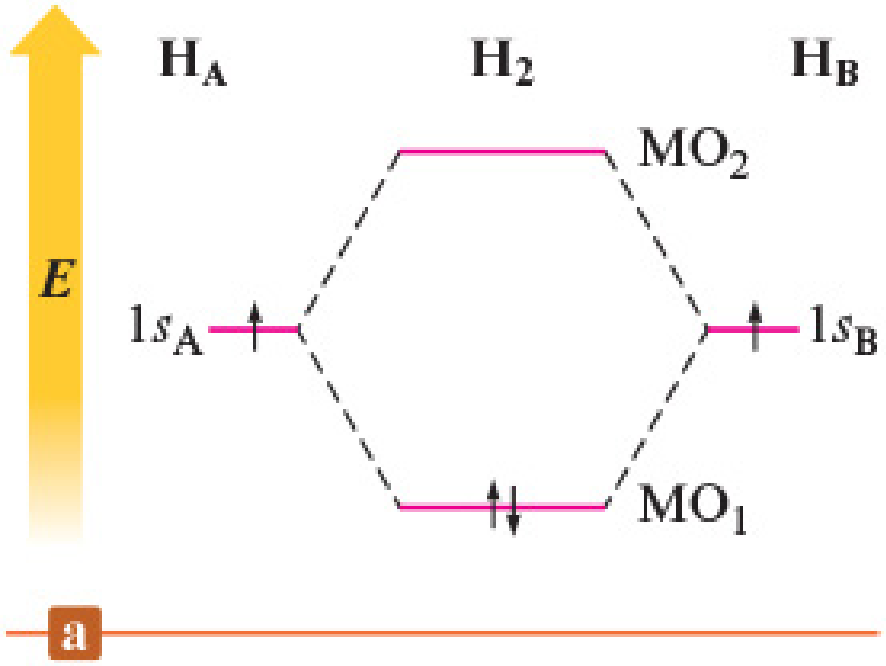
MO diagram for H_2



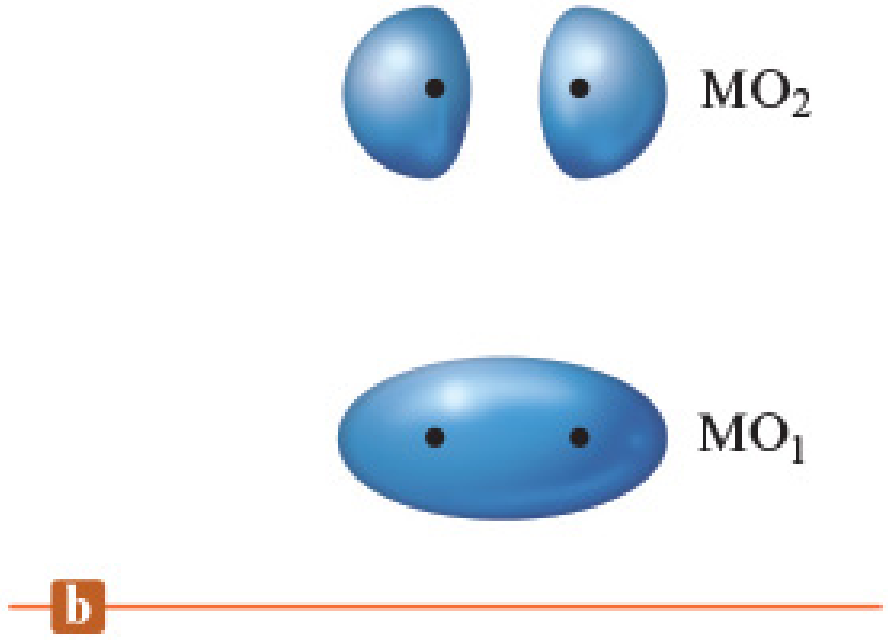
Bonding vs Antibonding Orbitals

- When bonding orbitals form, the MO orbital has most of the electron density between the two nuclei. Since the bonding electrons are attracted to two different nuclei, it is lower in energy that the atomic orbitals used to form it.
- When antibonding orbitals form, most of the electron density is located outside of the two nuclei. Antibonding orbitals are always higher in energy than the atomic orbitals.

MO Diagram for H_2



Energy diagram



Electron probability distribution

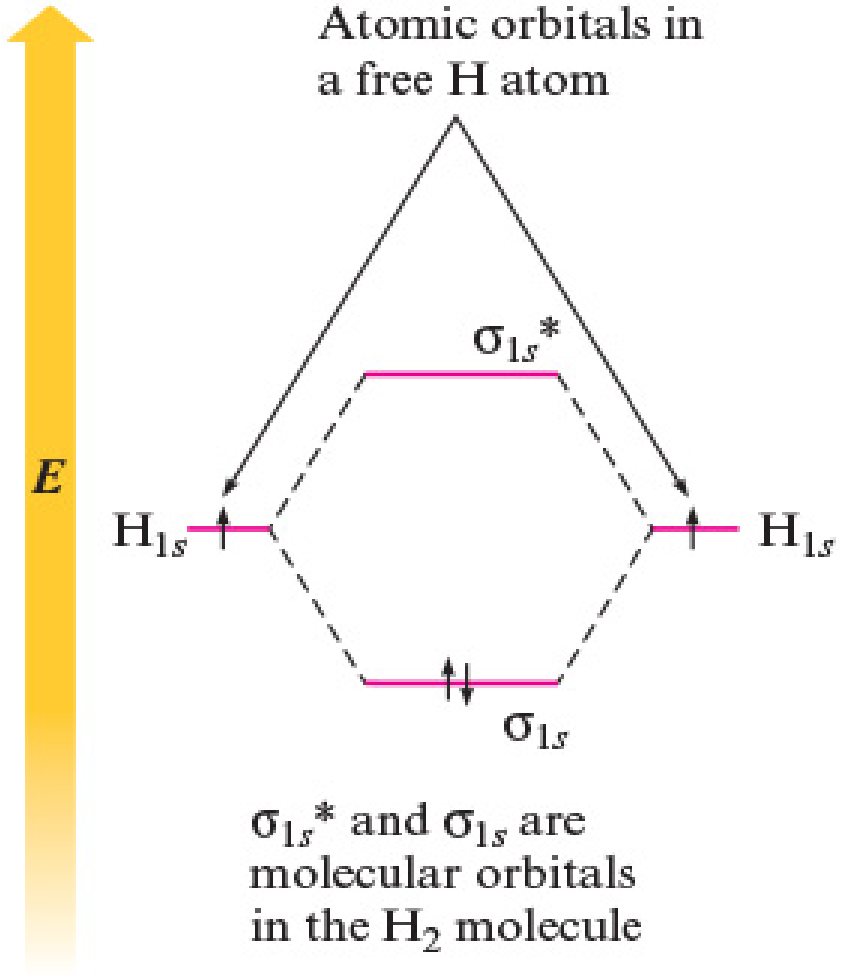
Why does H_2 form?

Answer: The electrons in the H_2 molecule are overall lower in energy than the separate 1s orbitals for two individual H atoms.

Can assign a number to calculate if the MO diagram for some species is lower in energy than the separate atomic orbitals. It is called bond order.

Bond order = $\frac{\text{number of bonding electrons} - \text{number of antibonding electrons}}{2}$

Bond Order Calculation for H_2



Bond order =

$$\frac{\text{number of bonding electrons} - \text{number of antiobonding electrons}}{2}$$

Bond order = $\frac{2-0}{2} = 1$

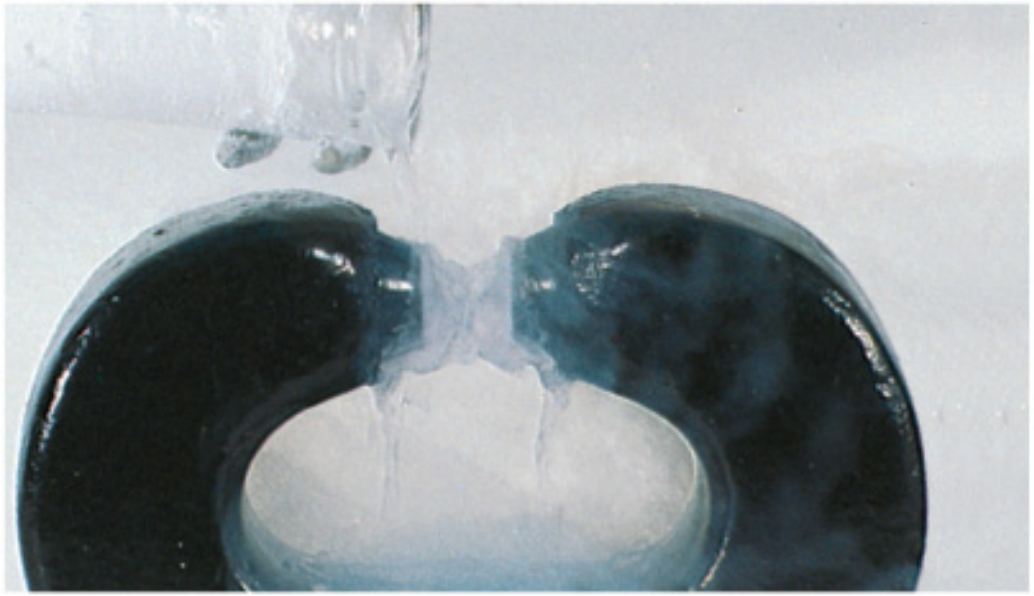
Note: if bond order > 0, the species is energetically favorable to form. If bond order = 0, the molecule will not form. Here, bond order = 1, so H_2 is an energetically stable molecule and can form.

H_2: $(\sigma_{1s})^2$

Paramagnetic or Diamagnetic

- MO theory can also predict whether a molecule will be attracted into a magnetic field (paramagnetic) or if a molecule is repelled by a magnetic field (diamagnetic).

Paramagnetic Substance – attracted to an applied magnetic field



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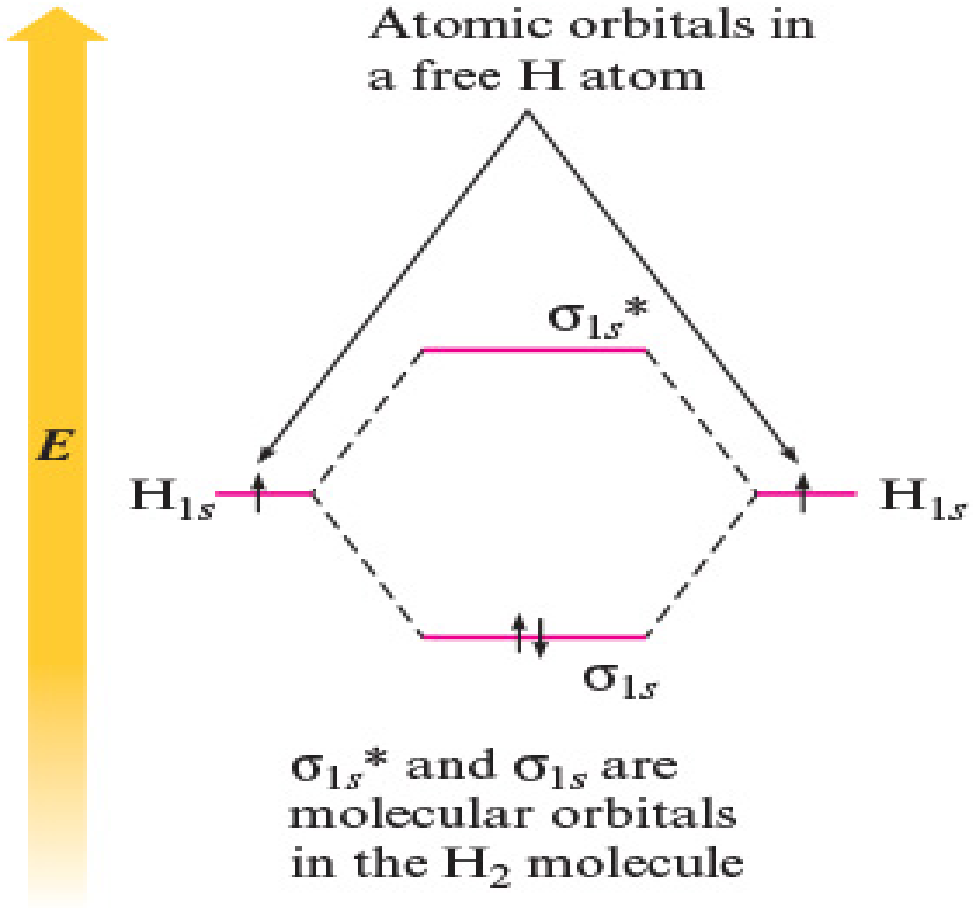
Paramagnetic or Diamagnetic

- MO theory can also predict whether a molecule will be attracted into a magnetic field (paramagnetic) or if a molecule is repelled by a magnetic field (diamagnetic).
- If a molecule has only paired electrons in the MO diagram, then the molecule is diamagnetic. If the molecule has unpaired electrons in the MO diagram, then the molecule is paramagnetic.
- H_2 is diamagnetic since all electrons in the MO diagram are paired.

MO diagram for H_2

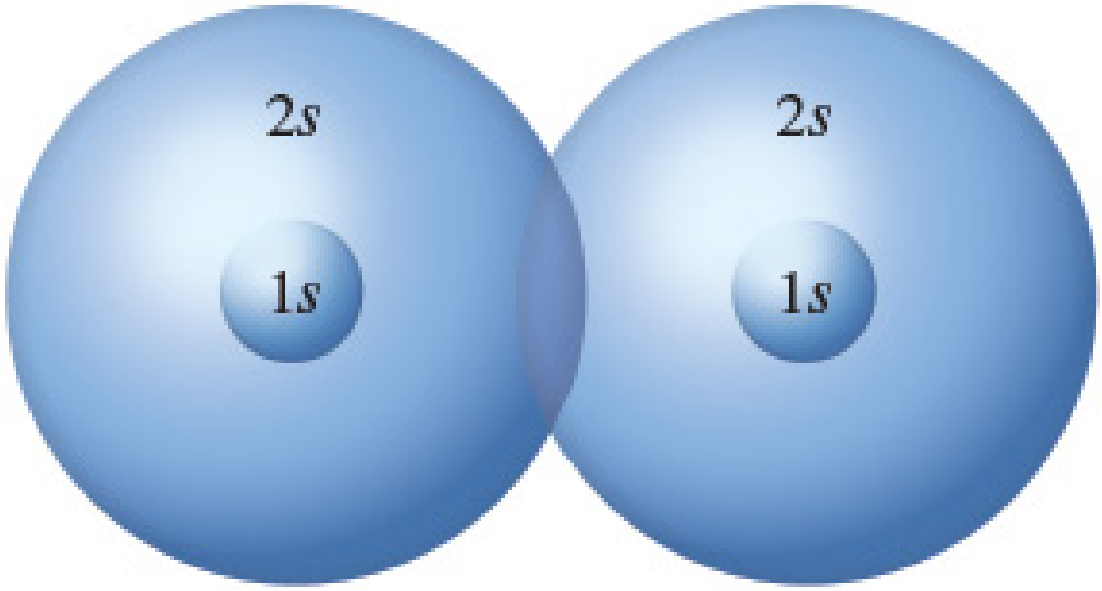


Electrons are paired in the MO diagram for H_2, so H_2 is diamagnetic.

Questions

- Why doesn't He_2 form?
- In theory, can H_2^- form? If so, what is its bond order and is it paramagnetic or diamagnetic?
- What is the MO diagram for Li_2? The electron configuration for lithium is: $1s^2 2s^1$.

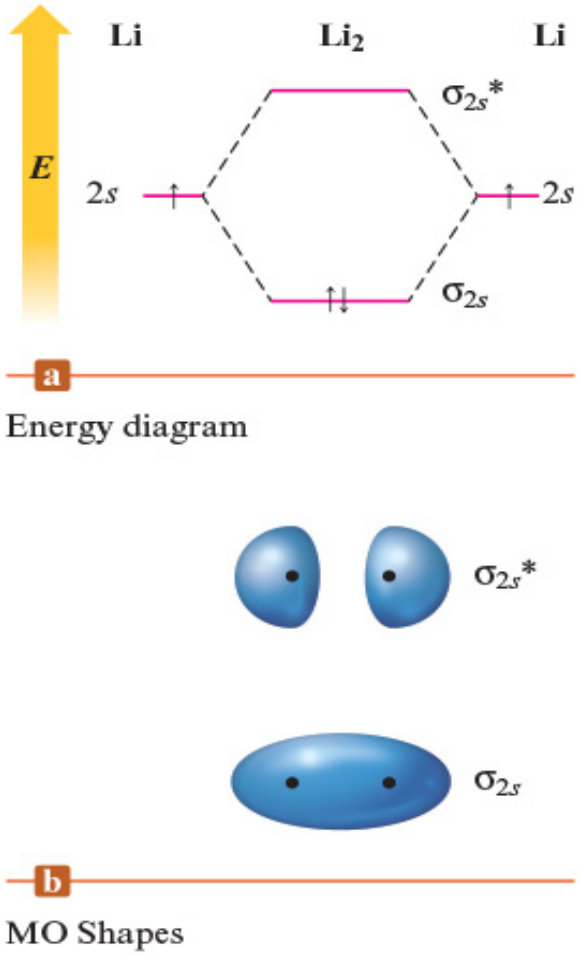
Bonding in Lithium



Inner core orbitals are assumed not to participate in bonding (too close to the nucleus to overlap). Assume only valence orbitals are close enough to each other to combine. For Li, assume only 2s orbitals are involved in bond formation.

Li MO diagram

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



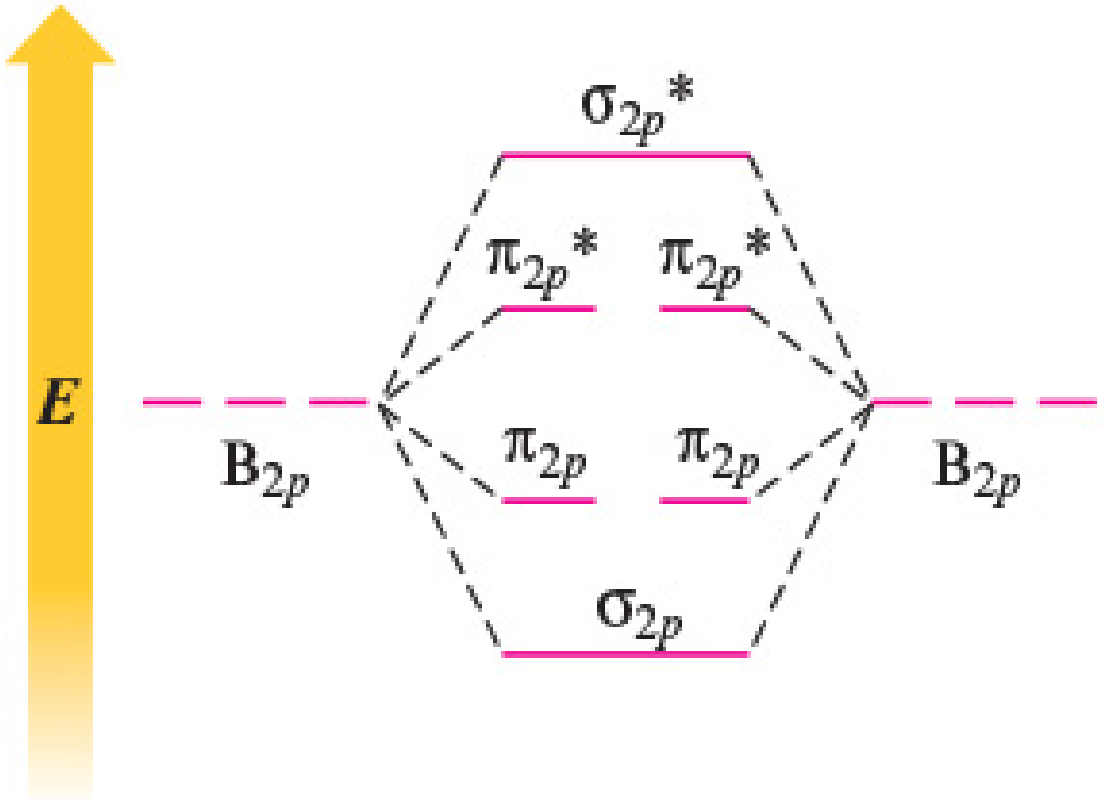
Only valence orbitals form MO orbitals.

B.O. = $\frac{2-0}{2}$ = 1; diamagnetic

Since B.O. > 0, yes Li_2 can form.

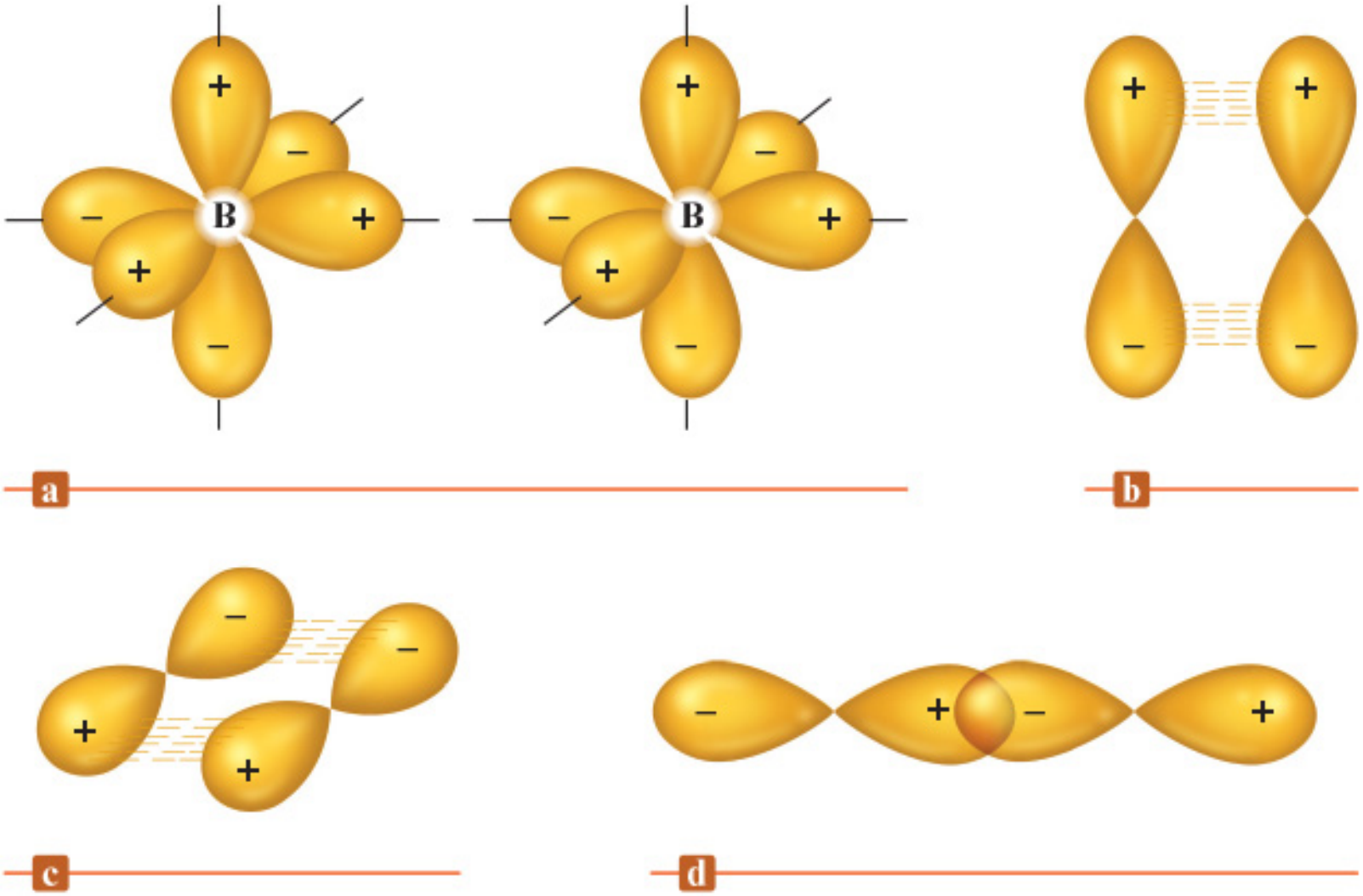
Li_2: $(\sigma_{2s})^2(\sigma_{2s}^*)^2$

Predicted MO diagram for p atomic orbitals



MO diagram for p atomic orbitals

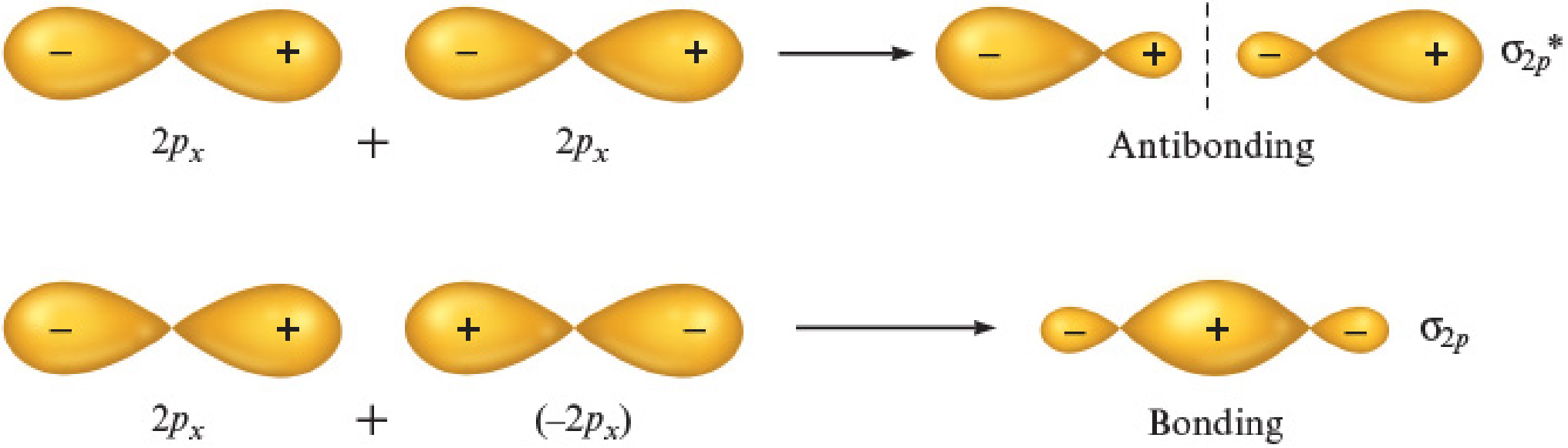
- p atomic orbitals can combine head-to-head or side-to-side.
- Head-to-head gives rise to sigma (σ) bonds.
- Side-to-side results in pi (π) bonds.



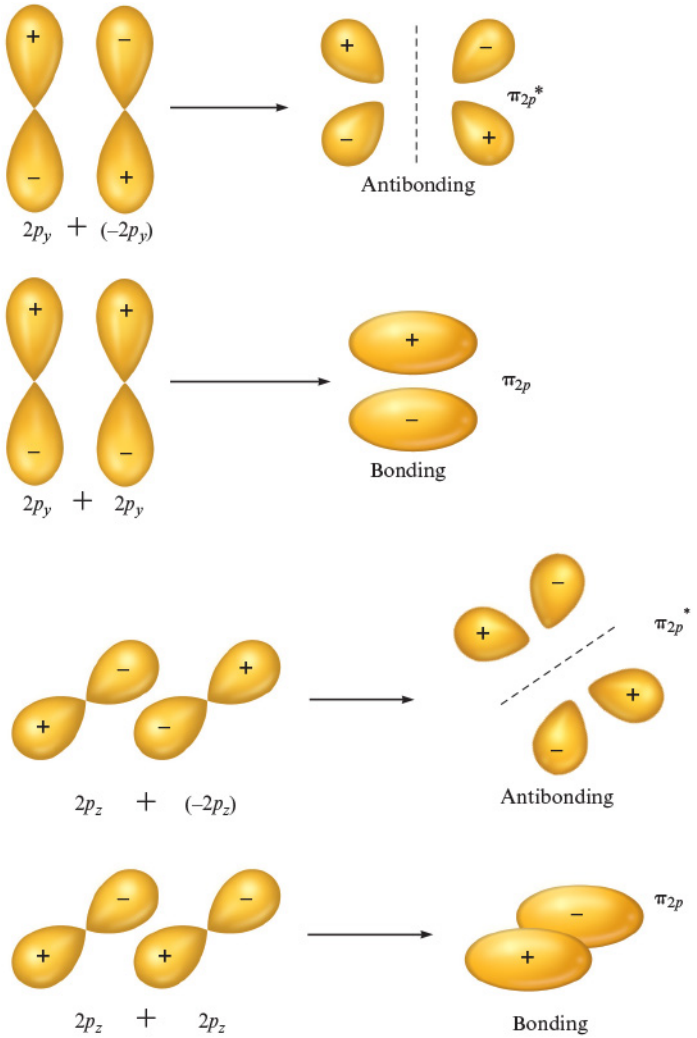
MO diagram for p atomic orbitals

- p orbitals overlap in-phase or out-of-phase.
- When in-phase, bonding orbitals form.
- When out-of-phase, antibonding orbitals result.

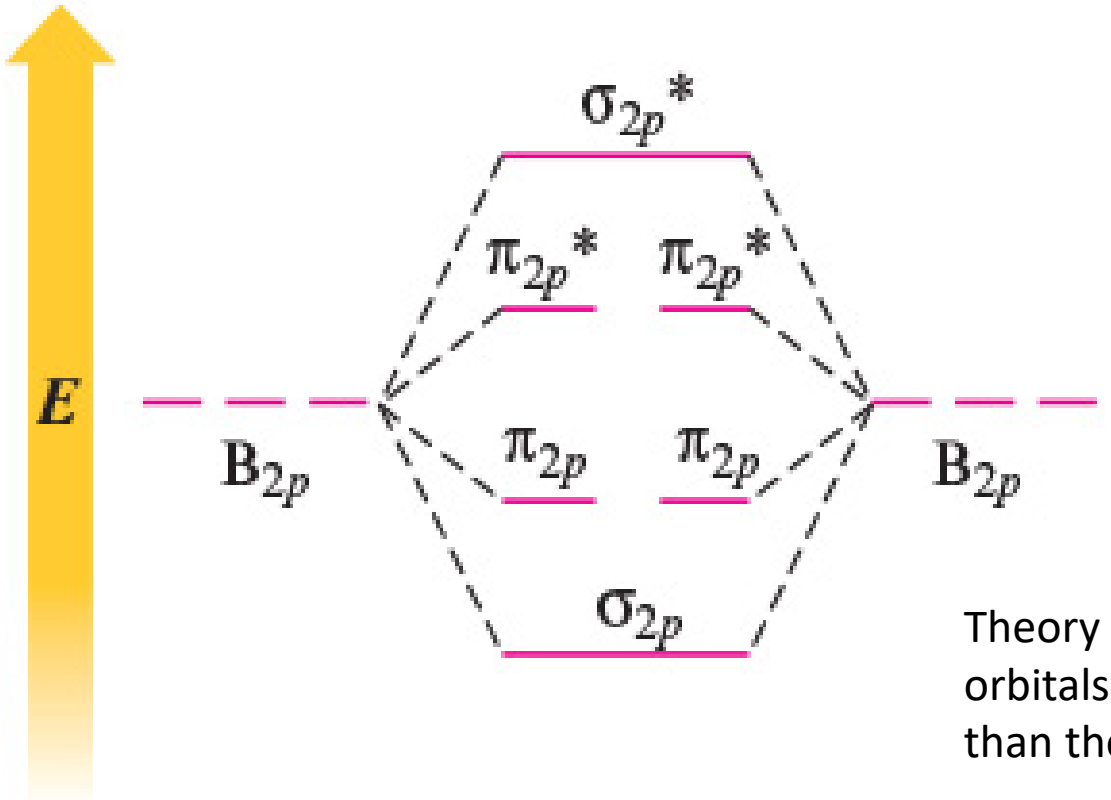
sigma bonding and antibonding orbitals



Pi (π) bonding vs antibonding orbitals



MO diagram for p atomic orbitals



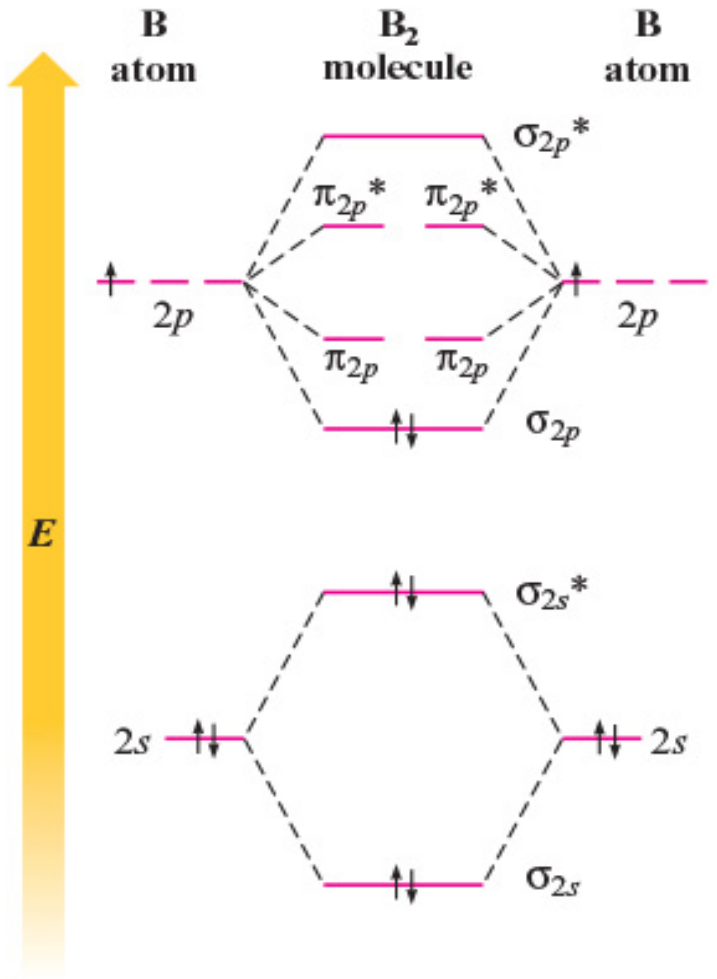
Theory predicts that σ bonding orbitals are lower in energy than the π bonding orbitals.

MO diagram for B_2

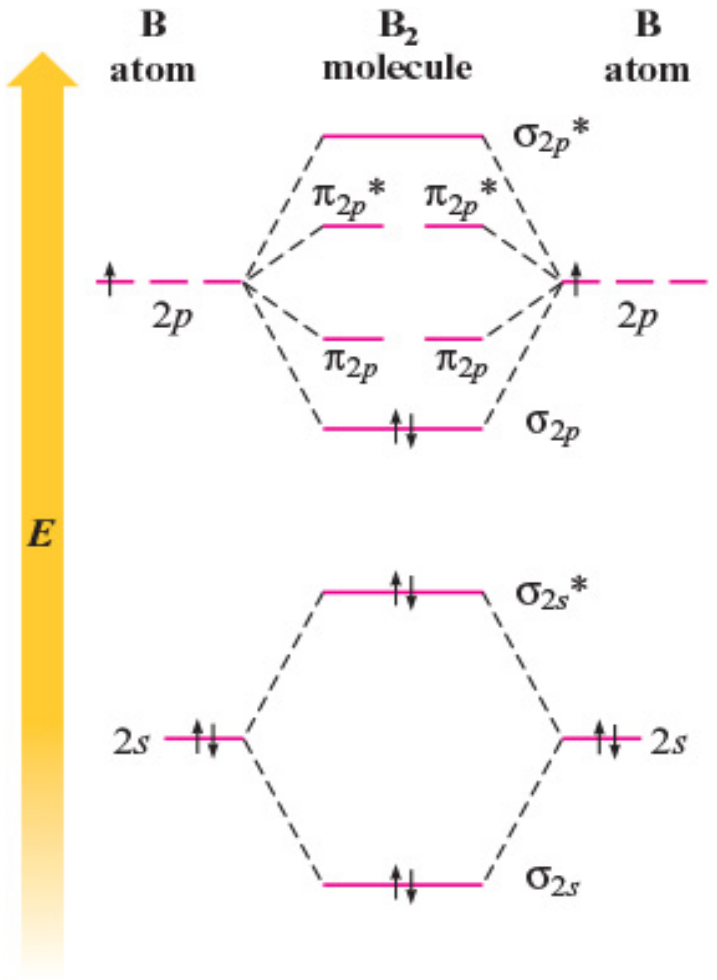
- B:$1s^2 2s^2 2p^1$
- Only worry about valence orbitals. So for B_2, we only worry about the 2s MO diagram and the 2p MO diagram.

B_2 MO diagram

B:$1s^2 2s^2 2p^1$



B_2 MO diagram



B.O. = $\frac{4-2}{2} = 1$

B_2 should form since B.O. > 0.

Note that we can ignore the 2s orbital diagram when calculating bond order since all MOs are filled.

B.O. = $\frac{2-0}{2} = 1$

Also predicts that B_2 is diamagnetic (all electrons in MO diagram are paired).

B_2 MO diagram issue

- Experiment agrees with a bond order of 1, but experiment shows that B_2 is paramagnetic, not diamagnetic.

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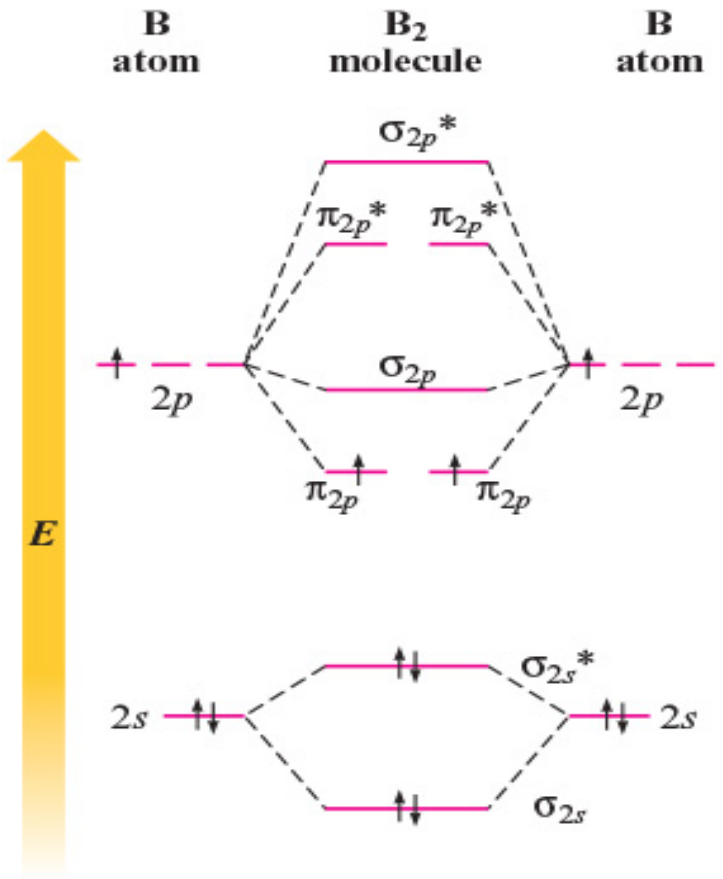
- Experiment agrees with a bond order of 1, but experiment shows that B_2 is paramagnetic, not diamagnetic.
- Solution: modify the model to explain the experimental data.

MO diagram to explain why B_2 is paramagnetic.



There is an apparent shift in energies between the sigma bonding and pi bonding orbitals. With the shift, B_2 still has a bond order of 1, but it is paramagnetic since it has unpaired electrons.

B.O. = $\frac{4-2}{2}$ = 1; paramagnetic

B_2: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^2$

When a model fails, we can throw out the entire model, or modify it to explain the data. Here we modify the model.

MO Problems

- Write out the MO electron configuration for N_2. What is the bond order for N_2? Is it paramagnetic?
- Write out the MO electron configuration for O_2. What is the bond order for O_2? Is it paramagnetic?

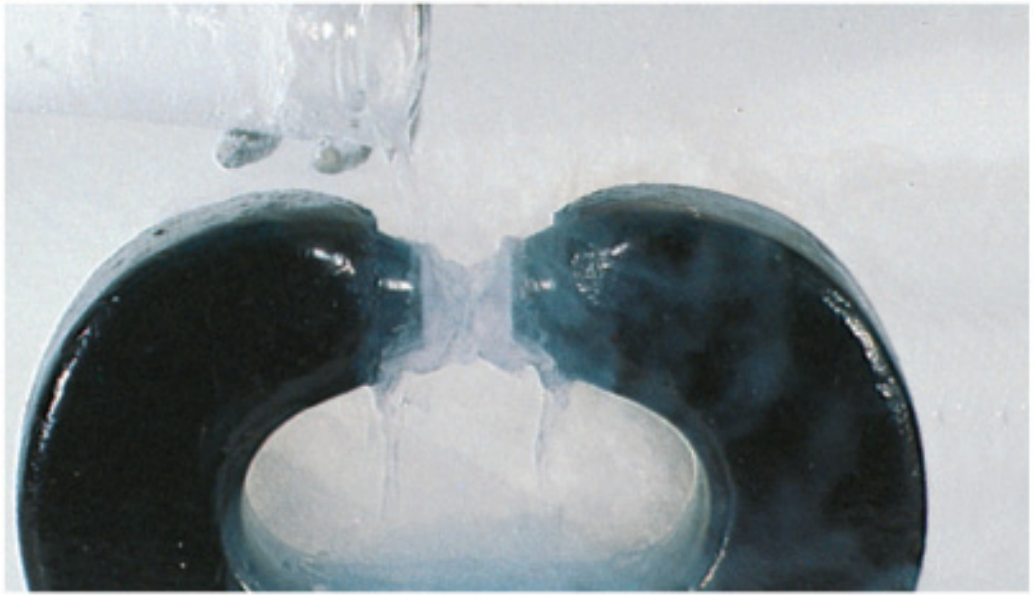
MO Problems

- Write out the MO electron configuration for N_2. What is the bond order for N_2? Is it paramagnetic?

N_2: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$ B.O. = $\frac{8-2}{2}$ = 3; diamagnetic

- Write out the MO electron configuration for O_2. What is the bond order for O_2? Is it paramagnetic?

Paramagnetic O_2



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MO Problems

- Write out the MO electron configuration for N_2. What is the bond order for N_2? Is it paramagnetic?

  N_2: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$ B.O. = $\frac{8-2}{2}$ = 3; diamagnetic

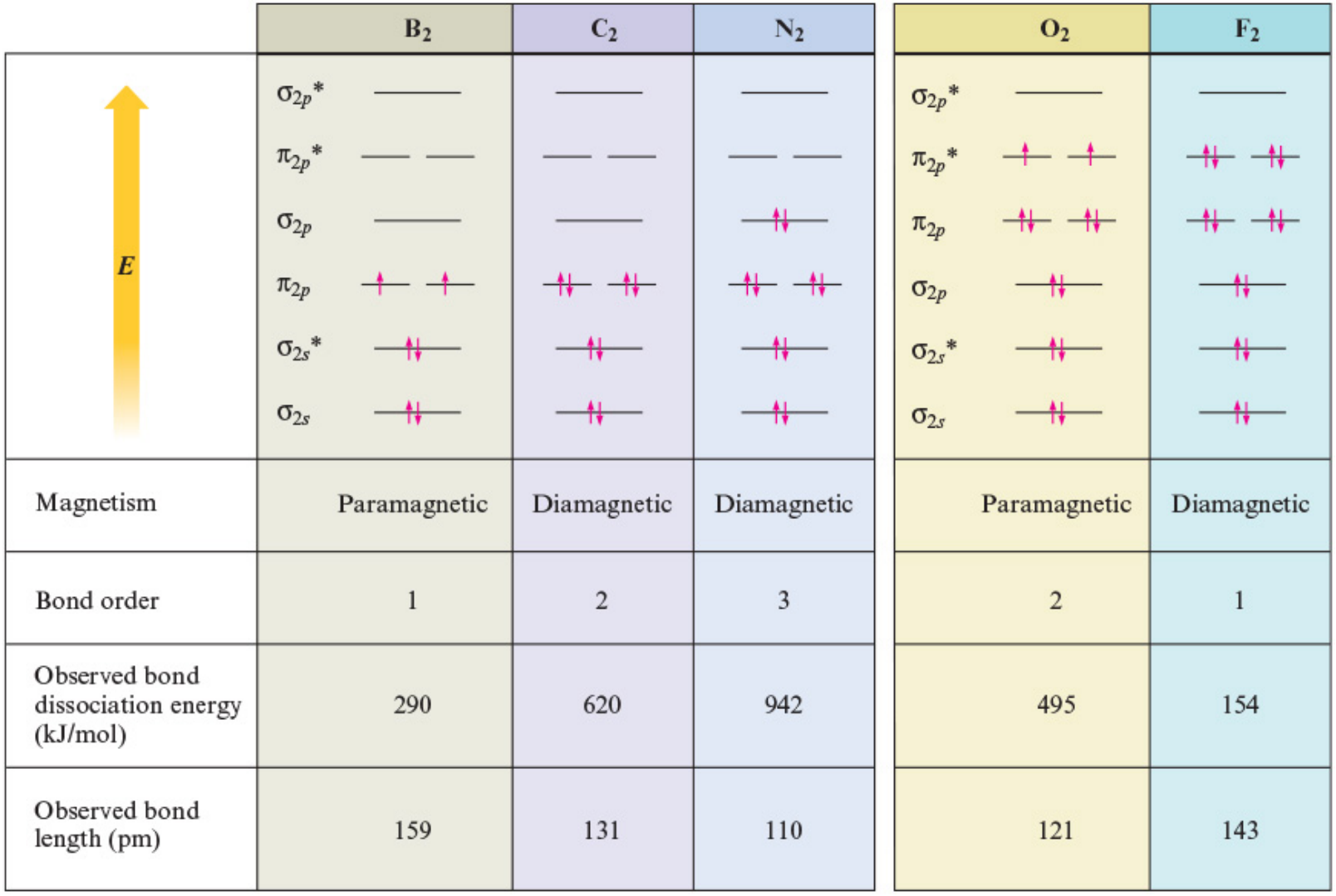
- Write out the MO electron configuration for O_2. What is the bond order for O_2? Is it paramagnetic?

  O_2: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2(\pi_{2p}^*)^2$ B.O. = $\frac{8-4}{2}$ = 2; paramagnetic

  or O_2: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2\ (\pi_{2p})^4(\pi_{2p}^*)^2$

More MO Problems

- Will the bond get stronger or weaker when an electron is removed from N_2? from O_2?
- Place the species CN^+, CN, and CN^- in order of increasing bond strength?
- Which has the higher ionization energy, O atoms or O_2 molecules?
- Which has the higher ionization energy, N atoms or N_2 molecules?



	B_2	C_2	N_2	O_2	F_2
Magnetism	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic
Bond order	1	2	3	2	1
Observed bond dissociation energy (kJ/mol)	290	620	942	495	154
Observed bond length (pm)	159	131	110	121	143

Fig 4.50 from text