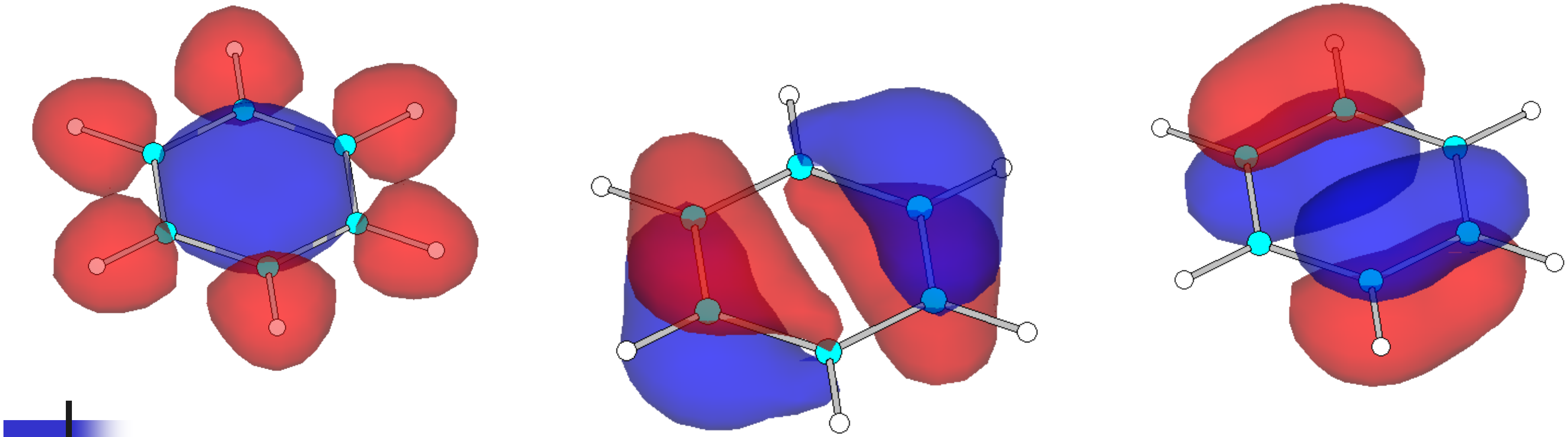

CHEMISTRY 2000

Topic #1: Bonding – What Holds Atoms Together?

Fall 2020

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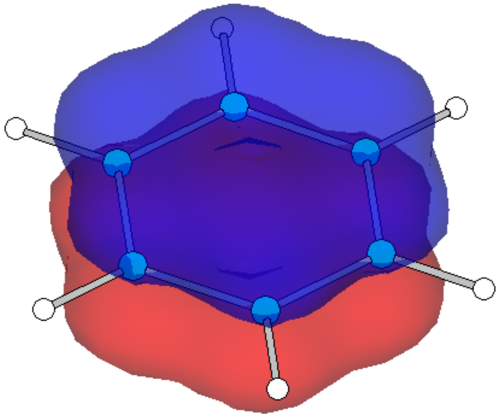
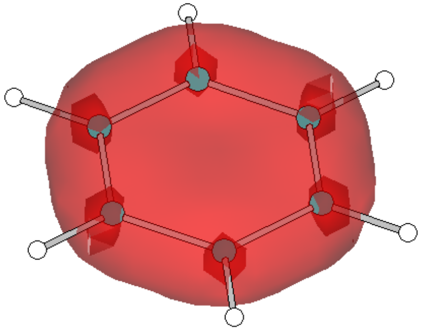
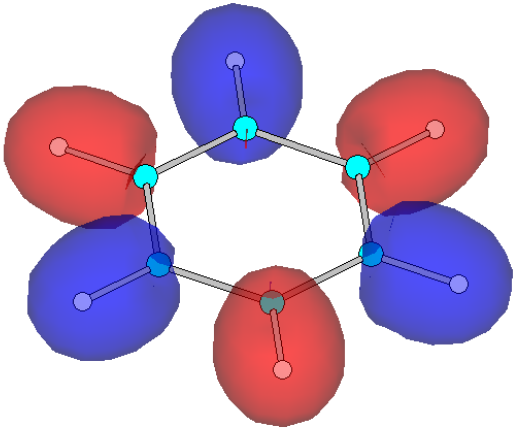
See Exercise 2.3







Why Do Bonds Form?

- An energy diagram shows that a bond forms between two atoms if the overall energy of the system is lowered when the two atoms approach closely enough that the valence electrons experience attraction to both nuclei:

- It is important to consider both the attractive and repulsive forces involved!
- Also, remember that atoms are in constant motion above 0 K. Bonds are NOT rigid!

The Quantum Mechanics of H_2^+

- To get a better understanding of bonding, it's best to start with the simplest possible molecule, H_2^+. H_2^+ consists of:

- What forces do we need to consider?

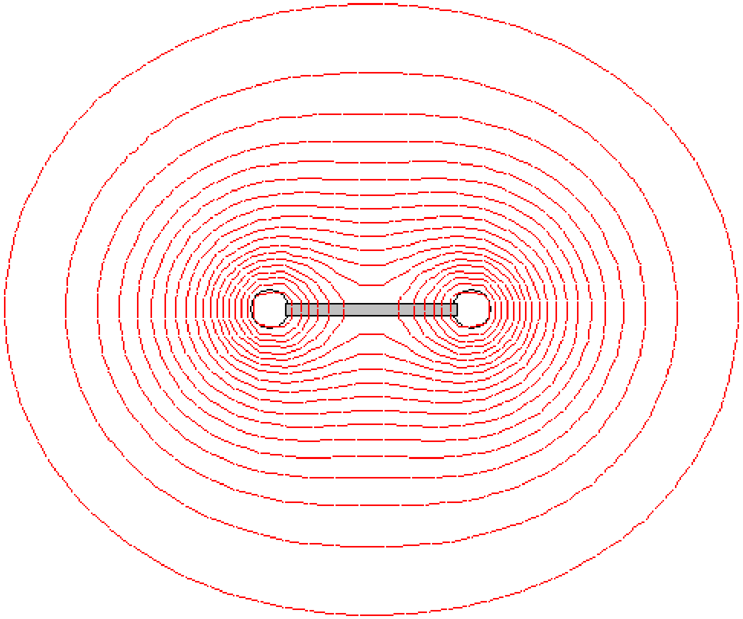
- This is a three-body problem, so there is no exact solution.
- The nuclei are much more massive than the electrons (1 u for a proton; 0.0005u for an electron). To simplify the problem, we use the **Born-Oppenheimer approximation**. We assume that the motion of the nuclei is negligible compared to the motion of the electrons and treat the nuclei as though they were immobile.

The Quantum Mechanics of H_2^+

- If we set the internuclear distance to R, we are then able to solve for the wavefunction of the electron in H_2^+ and its energy:

Electron energy = kinetic energy + electron-nuclear attraction

- This is possible because H_2^+ has only one electron and simple (cylindrically symmetric) geometry. The resulting ground-state orbital looks like this:



The Quantum Mechanics of H_2^+

- The energy of this ground state orbital depends on R.
- If we calculate the potential energy of the system (both the electron and the internuclear repulsion) at different values of R, we arrive at an energy diagram just like the one on the first page of your notes.

- Important Points to Note:
  - In H_2^+, the electron doesn't belong to either atom.
  - In H_2^+, the electron is in an orbital which spans the molecule – a **molecular orbital**!
  - Just as atoms have many atomic orbitals (1*s*, 2*s*, 2*p*, etc.), molecules can have many molecular orbitals. In H_2^+, the higher energy molecular orbitals are all empty.
  - The energy of a molecular orbital depends in part on the relative positions of the nuclei.

The Molecular Orbitals of H_2

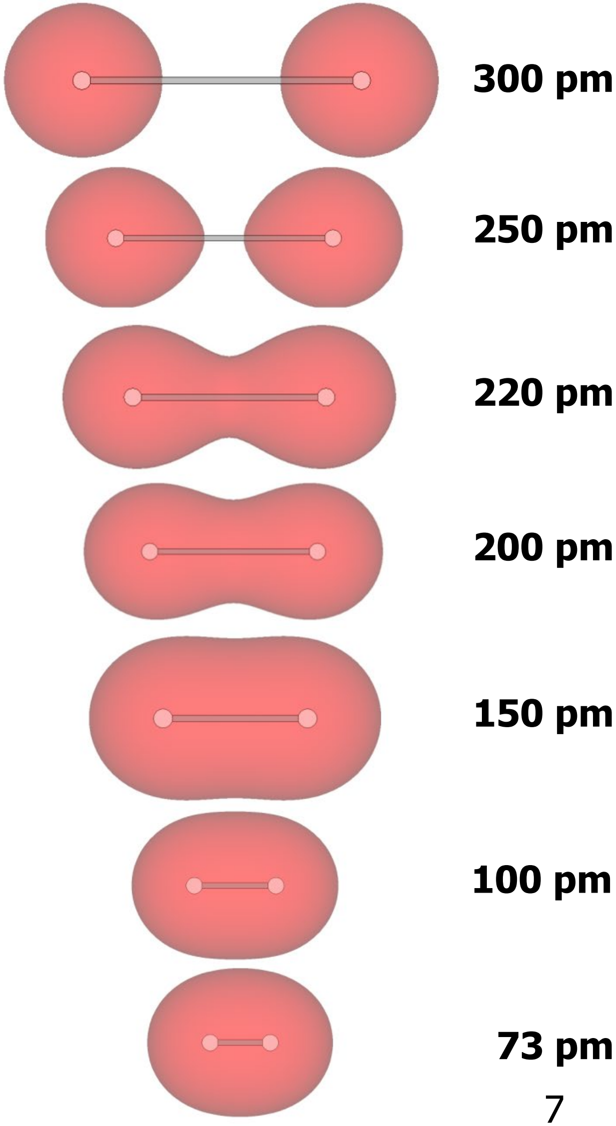
- Recall from CHEM 1000 that it was possible to solve the Schrödinger equation exactly for a hydrogen atom, but a helium atom had too many electrons. We encounter the same problem with H_2. While H_2^+ can be solved, as soon as a second electron is introduced, there are too many moving bodies and the wavefunction cannot be solved exactly. This does not mean we're finished with quantum mechanics! Instead, we make more approximations…

- So, what's a reasonable approximation? We know that, when two hydrogen atoms are far apart (i.e. R is large), they behave like two free hydrogen atoms:

If we were able to bring them together such that the nuclei overlapped (i.e. R = 0 pm), we would have ____________________

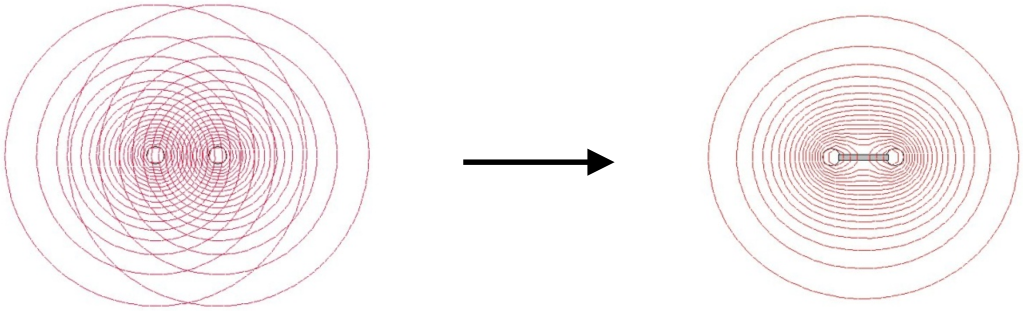
The Molecular Orbitals of H_2

- If we imagine the initially separate hydrogen atoms approaching each other (as in the diagram at the right), we see the electrons begin to “lean in” to begin making the H-H bond. What is responsible for this behaviour?



The Molecular Orbitals of H_2

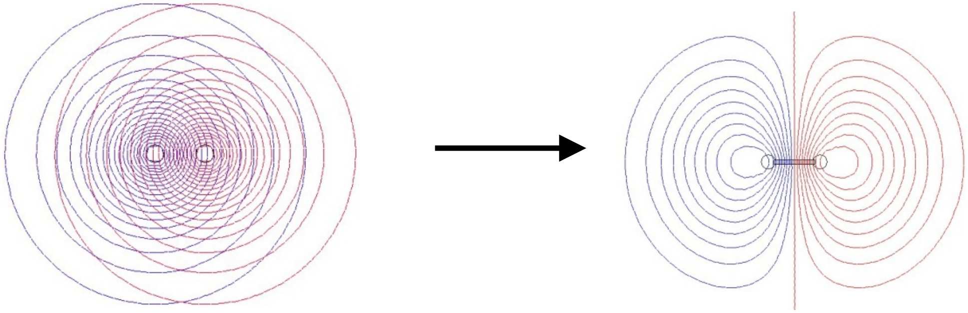
- The orbitals of a hydrogen molecule (R = ~74 pm) must be somewhere between those two extremes. We often approximate molecular orbitals by describing them as combinations of atomic orbitals. This is termed **Linear Combination of Atomic Orbitals** (LCAO) and gives an LCAO-MO such as that below:



- By adding the two atomic orbitals, we obtain a **sigma bonding orbital** (σ).
  - **Bonding:** lots of electron density between the two nuclei
  - **Sigma symmetry:** cylindrical symmetry (no visible change when the axis connecting the nuclei is spun; no node along that axis)

The Molecular Orbitals of H_2

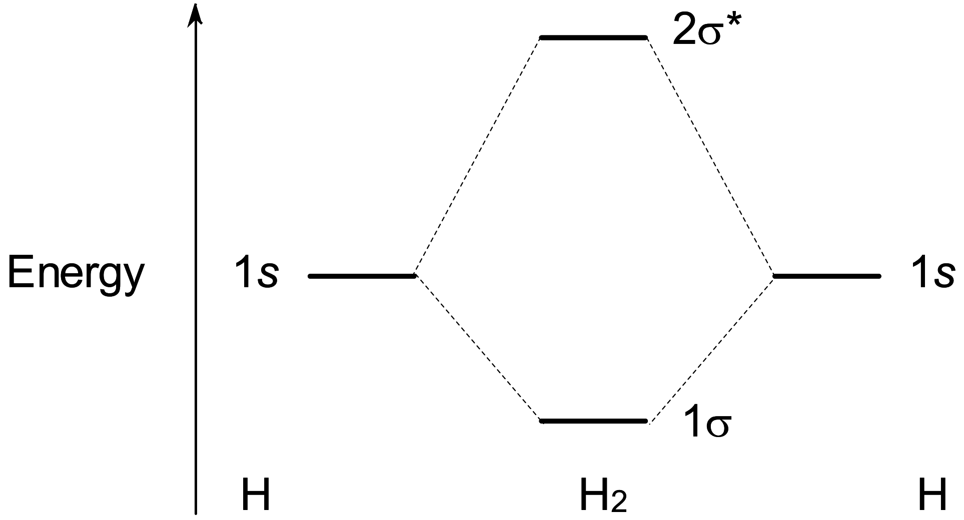
- We can also subtract the two atomic orbitals *(equivalent to adding them after inverting the phase of one – just as subtracting 5 is equivalent to adding -5)*:



- This is a **sigma antibonding orbital** (σ^*).
  - **Antibonding:** depleted electron density between the two nuclei *(look for a node perpendicular to the axis connecting the nuclei)*
  - **Sigma symmetry:** cylindrical symmetry (no visible change when the axis connecting the nuclei is spun; no node along that axis)

Molecular Orbital Diagram for H_2

- We can draw an energy level diagram showing molecular orbitals and the atomic orbitals from which they were derived. This is referred to as a molecular orbital diagram (**MO diagram**).



Note that the energy difference is larger between the atomic orbitals and the antibonding orbital than between the atomic orbitals and the bonding orbital.

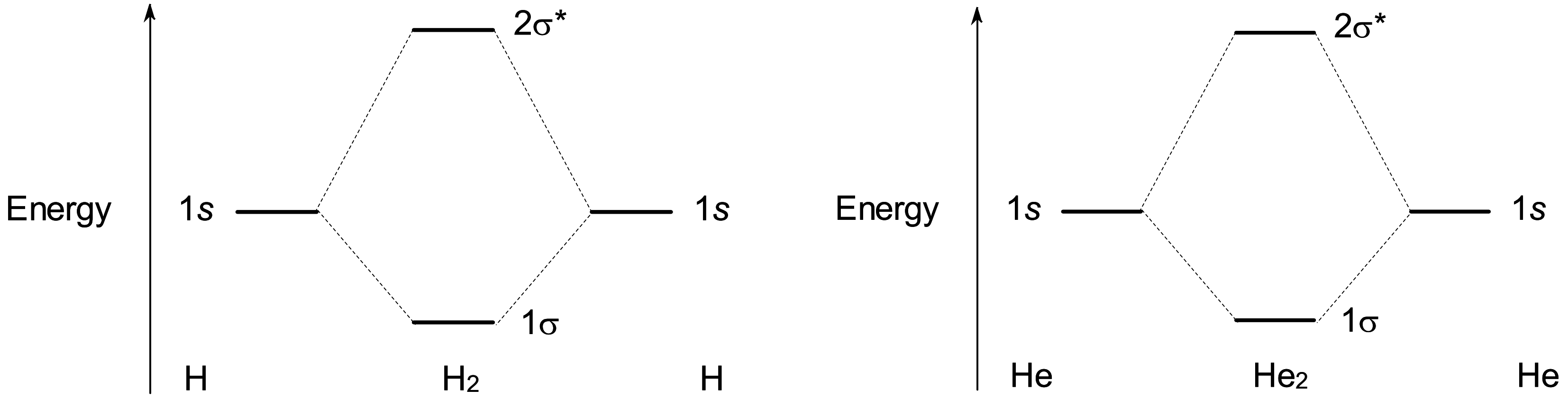
Molecular Orbital Diagram for H_2

- **MO diagrams** relate the energies of molecular orbitals to the atomic orbitals from which they were derived. If the total energy of the electrons is lower using molecular orbitals *(the middle column)*, the molecule forms. If the total energy of the electrons is lower using atomic orbitals *(the two outside columns)*, no molecule is formed.

- To fill a molecular orbital diagram with electrons, use the same rules as you would to fill in an atomic orbital diagram:
  - Fill ________________________________ first.
  - Pauli's exclusion principle still applies:
  - Hund's rule still applies:

Molecular Orbital Diagram for H_2

These diagrams are side by side for best use of space.
The energy of 1s(H) is NOT the same as the energy of 1s(He)!

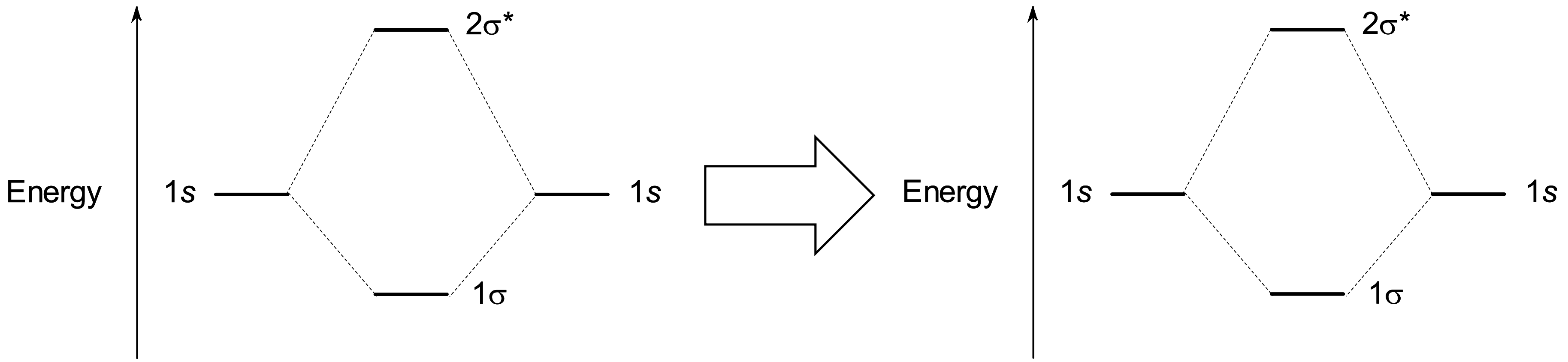


- Thus, the orbital occupancy for H_2 in the ground state is and the orbital occupancy for He_2 in the ground state is
- We can calculate bond orders for these two "molecules" from their MO diagrams:

$$\boxed{\text{bond order} = \frac{1}{2}\left(\#\,\text{bonding e}^- \; - \; \#\,\text{antibonding e}^-\right)}$$

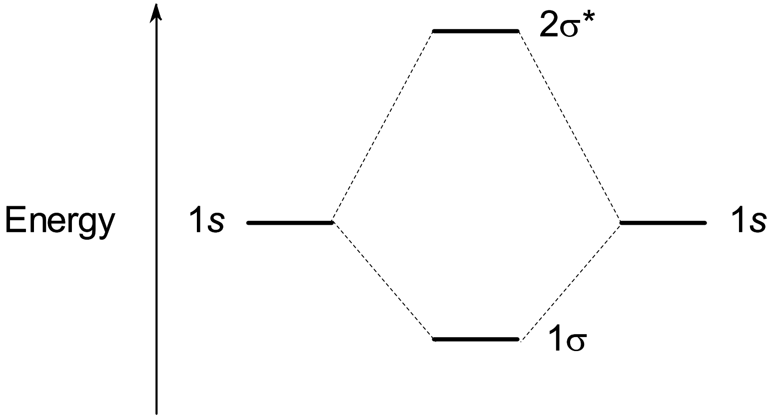
Applications of Molecular Orbital Diagrams

- If a molecule of H_2 was irradiated with light, exciting an electron from 1σ to $2\sigma^*$, what would happen?



Applications of Molecular Orbital Diagrams

- Should it be possible for H_2^- to exist?



- What about He_2^+?