

Chemistry 2000 Slide Set 1: Introduction to the molecular orbital theory

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Review: quantum mechanics of atoms

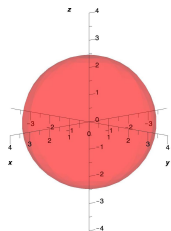
Hydrogenic atoms

- The hydrogenic atom (one nucleus, one electron) is **exactly solvable**.
- The solutions of this problem are called **atomic orbitals**.
- The square of the orbital wavefunction gives a **probability density** for the electron, i.e. the probability per unit volume of finding the electron near a particular point in space.

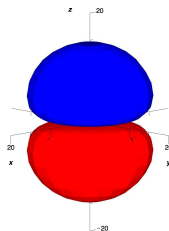
Review: quantum mechanics of atoms

Hydrogenic atoms (continued)

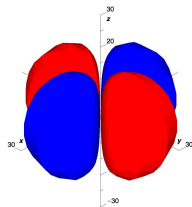
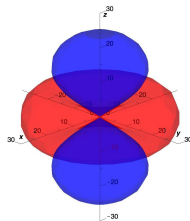
Orbital shapes:



1s



2p

 $3d_{x^2-y^2}$  $3d_{z^2}$

Review: quantum mechanics of atoms

Multielectron atoms

Consider He, the simplest multielectron atom:

- Electron-electron repulsion makes it impossible to solve for the electronic wavefunctions exactly.
- A fourth quantum number, m_s , which is associated with a new type of angular momentum called **spin**, enters into the theory.
For electrons, $m_s = \frac{1}{2}$ or $-\frac{1}{2}$.
- Pauli exclusion principle: No two electrons can have identical sets of quantum numbers.

Consequence: Only two electrons can occupy an orbital.

The quantum mechanics of molecules

- H_2^+ is the simplest possible molecule:
 - two nuclei
 - one electron

- Three-body problem: no exact solutions

- However, the nuclei are more than 1800 times heavier than the electron, so the electron moves much faster than the nuclei.

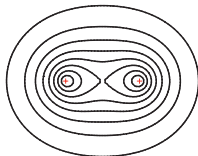
Born-Oppenheimer approximation

- Treat the nuclei as if they are immobile and separated by R to solve for the electron's wavefunction (**molecular orbital**) and orbital (electronic) energy.

In a single-electron molecule,

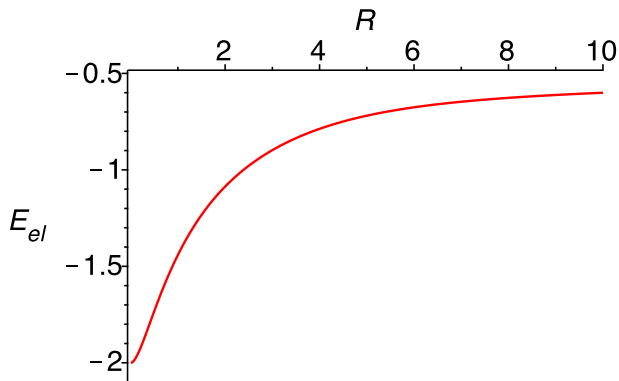
Orbital energy = electron kinetic energy + electron-nuclear attraction

- This problem can be solved exactly because of the single electron and simple (cylindrically symmetric) geometry.
- Ground-state molecular orbital:



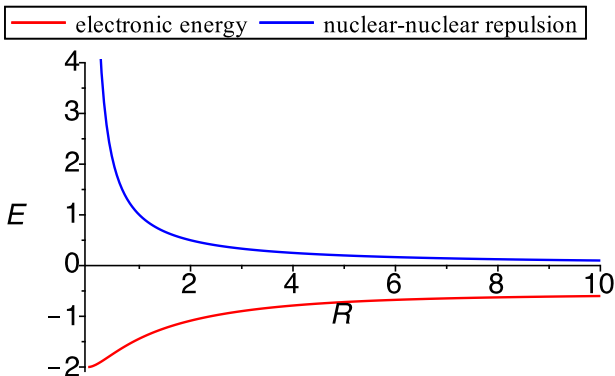
Born-Oppenheimer approximation (continued)

The orbital (electronic) energy depends on R (distance between nuclei):



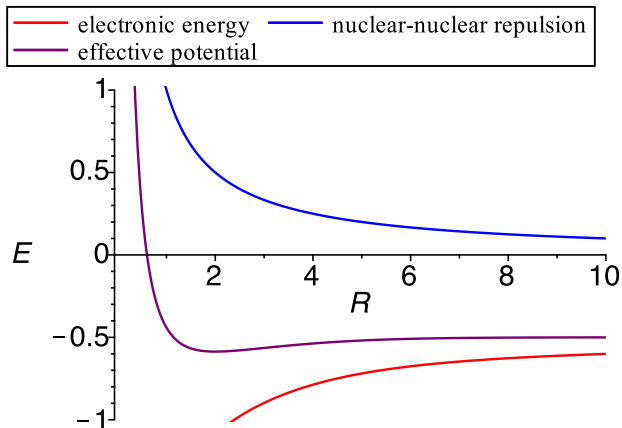
Born-Oppenheimer approximation (continued)

To get the total energy of the molecule, we need to also consider the nuclear-nuclear repulsion:

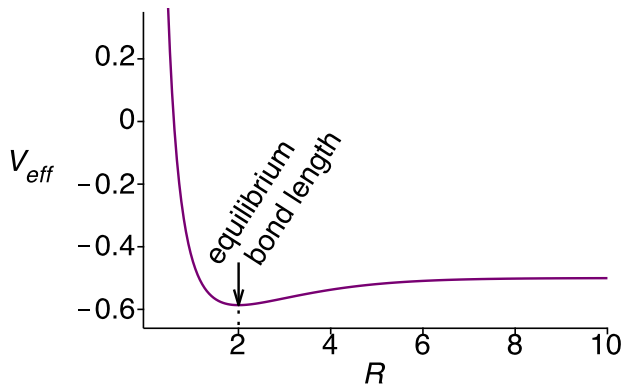


Born-Oppenheimer approximation (continued)

The sum of the electronic (orbital) and nuclear-nuclear repulsion energies is the **effective potential energy** experienced by the nuclei:



Equilibrium bond length



$$F = -\frac{dV_{eff}}{dR}$$

Key lessons learned from H_2^+

- 1 Electrons in molecules do **not** belong to particular atoms. Rather, electrons occupy **molecular orbitals** which extend over the entire molecule.
As with atomic orbitals, we can have several molecular orbitals (occupied or unoccupied).
- 2 The energy of a molecular orbital depends on the positions of the nuclei (on the separation R in a diatomic molecule).
- 3 There is an equilibrium geometry (a point where the forces are zero or, equivalently, a point of minimum energy).
This geometry defines the bond lengths from which we get (for example) covalent atomic radii.

The molecular orbitals of H₂

- When we add a second electron, it becomes impossible to solve the electronic Schrödinger equation exactly.
(We had the same problem with the helium atom.)
- In order to gain some insight into the molecular orbitals (MOs) of H₂, consider the following limits:
 - If the separation between the nuclei, R , is large, then we should have the equivalent of two hydrogen atoms, i.e.

$$\text{MO} \rightarrow 1s_A \oplus 1s_B$$



- If we imagine pushing the nuclei together, we would have two electrons and a single centre of positive charge with charge $+2$, i.e. the equivalent of a helium atom. Then

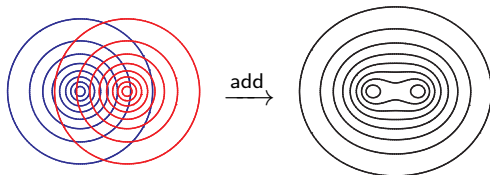
$$\text{MO} \rightarrow 1s(\text{He})$$

LCAO-MO theory

- Since the MO can be described in terms of atomic orbitals (AOs) in some special limits, we **may** be able to **approximate** the MOs of H_2 using AOs at any internuclear separation.

LCAO-MO: This term applies to an approximate MO constructed as a **Linear Combination of Atomic Orbitals**.

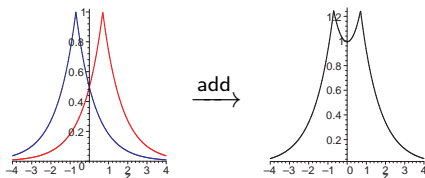
- For the H_2 ground-state MO,



Note: Here, colors are used to distinguish the AOs from the two atoms, not to indicate phases.

Sigma bonding orbital

- Here is a plot of the atomic and molecular orbital wavefunctions along the bonding (z) axis:



- This is a **sigma (σ) bonding orbital**.

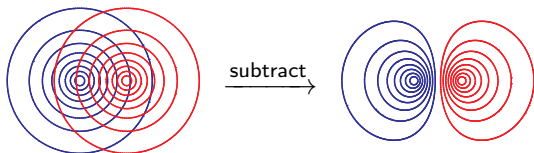
Characteristics:

Bonding: lots of electron density (square of orbital wavefunction) between the two nuclei

Sigma symmetry: rotationally symmetric about the bonding axis (same symmetry as a cylinder)

Sigma antibonding orbital

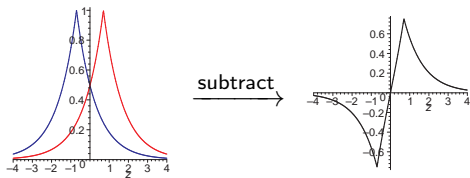
- Adding the AOs is **not** the only way to combine them.
- The only physical requirement is that we treat the two nuclei symmetrically since they are identical.
- We can also **subtract** the AOs.



Note: Here the colors in the MO **do** represent different phases.

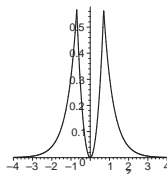
Sigma antibonding orbital (continued)

- Along the z axis, we have the following orbital wavefunctions:



Sigma antibonding orbital (continued)

- The electron density (square of the wavefunction) along the z axis has the following appearance:



- This is a **sigma antibonding (σ^*) orbital**.

Characteristics:

Antibonding: depleted electron density between the two nuclei

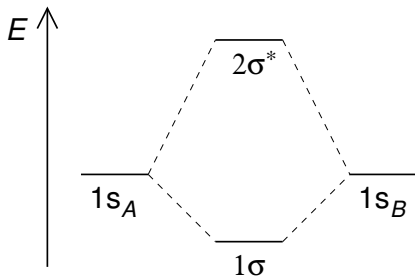
Sigma symmetry: rotationally symmetric about the bonding axis

MO diagrams

- An **MO diagram** shows the energies of the MOs of a molecule and (often) of the AOs they were generated from.

Rule: The number of MOs is equal to the number of AOs included in the calculation.

MO diagram for H_2 :



Orbital occupancy

- The same rules apply to filling MOs as do to AOs:
 - ① Fill them starting with the lowest energy orbital.
 - ② Only two electrons can occupy an orbital.
 - ③ Apply Hund's rule to the filling of degenerate MOs.
- Orbital occupancy for the ground state of H_2 : $(1\sigma)^2$
- There are also excited states, such as $(1\sigma)^1(2\sigma^*)^1$.
- Note from our MO diagram that the energy of the $2\sigma^*$ orbital is farther above the energy of the AOs than the 1σ is below.
 - The $(1\sigma)^1(2\sigma^*)^1$ configuration is not energetically favorable and should dissociate into $H + H$.

Effective potentials for many-electron molecules

- We can calculate an effective potential governing the motion of the nuclei for many-electron molecules using the Born-Oppenheimer approximation, much as we did for H_2^+ .
- There are however more terms in the electronic energy:

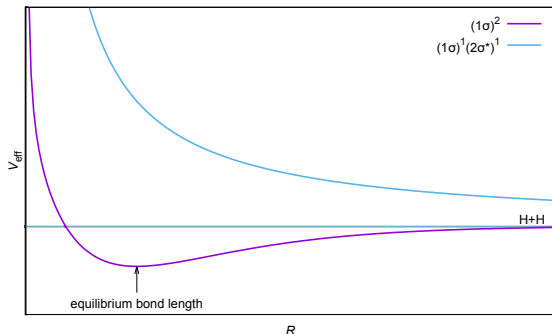
$$\text{Electronic energy} = \begin{pmatrix} \text{electron} \\ \text{kinetic} \\ \text{energies} \end{pmatrix} + \begin{pmatrix} \text{electron-electron} \\ \text{repulsion} \end{pmatrix} + \begin{pmatrix} \text{electron-nuclear} \\ \text{attraction} \end{pmatrix}$$

- We still have

$$V_{\text{eff}} = \text{electronic energy} + \text{nuclear-nuclear repulsion}$$

Effective potentials and orbital occupancy

- The stability or instability of a particular electronic configuration can also be connected to the shape of its effective potential energy curve:



Recall: $F = -dV_{\text{eff}}/dR$

Bond order and MO theory

General rule:

$$\text{Bond order} = \frac{1}{2} \left(\left\{ \begin{array}{c} \text{Number of} \\ \text{electrons in} \\ \text{bonding} \\ \text{orbitals} \end{array} \right\} - \left\{ \begin{array}{c} \text{Number of} \\ \text{electrons in} \\ \text{antibonding} \\ \text{orbitals} \end{array} \right\} \right)$$

Example: For the $\text{H}_2 (1\sigma)^2$ configuration,

$$\text{Bond order} = \frac{1}{2}(2 - 0) = 1.$$

Note that this agrees with the Lewis diagram bond order.

Example: For the $\text{H}_2 (1\sigma)^1(2\sigma^*)^1$ configuration,

$$\text{Bond order} = \frac{1}{2}(1 - 1) = 0.$$

He₂

- The ground state of an He₂ molecule would be $(1\sigma)^2(2\sigma^*)^2$.

$$\text{Bond order} = \frac{1}{2}(2 - 2) = 0.$$

That's the MO explanation why He₂ doesn't exist.

- However, He₂⁺ should be stable:
 - Ground-state electronic configuration $(1\sigma)^2(2\sigma^*)^1$
 - Bond order = $\frac{1}{2}(2 - 1) = \frac{1}{2}$
 - No equivalent Lewis diagram