Lecture 4

Molecular Orbital Theory

Suggested reading: Chapter 2
"Which of course is the only reason to win a Nobel Prize, to be able to park on campus."
Saul Perlmutter, Nobel Laureate in Physics 2011
1954 Nobel Prize: Linus Pauling
Linus Pauling

He may not have delivered the most enigmatic chemistry lectures, but...

- Won 2 nobel prizes (Chemistry & Peace prize)
- At 21, graduated from Oregon State University
- At 26, started as a professor at Caltech
- Published 50 papers in his first five years
- One was: "The nature of the chemical bond. III. The transition from one extreme bond type to another." JACS 54 (1932)
Three key contributions:

1) Molecular orbital theory & Hybridization of atomic orbitals
2) Tetravalency of the carbon atom
   C: 1s^22s^22p^2
3) Electronegativity and relationships between ionic and covalent bonding
Nobel prize winner Linus Pauling was distinctly sceptical about his work: He would stand on those platforms and declare, "Danny Shechtman is talking nonsense. There is no such thing as quasicrystals, only quasi-scientists." Danny Shechtman, Nobel Laureate in Chemistry 2011
Molecular orbital theory of bonding

• The electron energy in each H atom is -13.6 eV below vacuum.

• What happens to the energy levels as the H-atoms approach each other?

• **Technique:** Solve Schrödinger equation, using the potential energy for the coupled electrons.
Molecular Force

\[ F_N = F_A + F_R \]

- Net Force when \( F_N = 0 \)
- Equilibrium when \( F_N = 0 \)
- \( r_0 = \text{bond length} \)
Potential energy, $V(r)$

- $V_0$: bond energy or cohesive energy (energy required to separate the two atoms)

- In general: $V(r) = -\frac{A}{r^n} + \frac{B}{r^m}$

Qual question: Why do materials expand upon heating?
Potential energy, $V(r)$

Due to thermal energy, the atoms will have vibrational kinetic energy. At a temperature $T$, the bond will be stretched and compressed by an amount corresponding to the kinetic energy of the atoms. A pair of atoms will be vibrating between $B$ and $C$, with an average separation of $A$ ($A > r_0$).
Back to Quantum (but not for long!)

Schrodinger equation: \[ \nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0 \]

Potential: \[ V(r) = -\frac{A}{r^n} + \frac{B}{r^m} \]

Molecular energies \( E \)

If bond formation is favorable, the energy of the system will be lower than the energy of the isolated atoms.
Bonding & Antibonding orbitals

Two H atoms, both in their 1s state. As they approach, their wavefunctions begin to overlap.
**Bonding & Antibonding orbitals**

Formation of molecular orbitals - bonding and antibonding ($\psi_\sigma$ and $\psi_{\sigma^*}$) when two H atoms approach each other. The two electrons pair their spins and occupy the bonding orbital $\psi_\sigma$. 

![Diagram showing bonding and antibonding orbitals for two hydrogen atoms](image-url)
H-H bond: Electron probability distribution

(a) Electron probability distributions for bonding and antibonding orbitals, $\psi_\sigma$ and $\psi_{\sigma^*}$.

(b) Lines representing contours of constant probability (darker lines represent greater relative probability).
Linear combination of atomic orbitals

Two identical atomic orbitals $\psi_{1s}$ on atoms $A$ and $B$ can be combined linearly in two different ways to generate two separate molecular orbitals $\psi_\sigma$ and $\psi_{\sigma^*}$

$\psi_\sigma$ and $\psi_{\sigma^*}$ generated from a linear combination of atomic orbitals (LCAO)

Wavefunction around $A$  

$\psi_\sigma = \psi_{1s}(r_A) + \psi_{1s}(r_B)$

Wavefunction around $B$  

$\psi_{\sigma^*} = \psi_{1s}(r_A) - \psi_{1s}(r_B)$
Energy of $\psi_\sigma$ and $\psi_{\sigma^*}$ found using the time-independent Schrödinger equation (TISE) vs. the interatomic separation $R$. 

**SYSTEM**
- 2 H-Atoms
- 2 Electrons
- 1 Electron/Atom
- 1 Orbital/Atom

**Graphical Representation**
- $E_\sigma(a)$ vs. $a$
- $E_{\sigma^*}(R)$ vs. $R = \infty$
- Bonding Energy between $E_\sigma(a)$ and $E_{\sigma^*}(R)$
Molecular orbital energy level diagram

\[ E_{\sigma}^* \]

Bonding energy (dissociation energy) = 4.5 eV

H atom

H₂ molecule

H atom
Two He atoms have four electrons. When He atoms come together, two of the electrons enter the $E_\sigma$ level and two the $E_{\sigma^*}$ level, so the overall energy is greater than two isolated He atoms (since $|E_{\text{antibonding}}| \gg |E_{\text{bonding}}|$). Therefore, He-He does not exist!
Key Concepts

1. The number of molecular orbitals will be equal to the number of atomic orbitals.

2. The Pauli exclusion principle limits the number of electrons that can occupy any molecular orbital to two. Those electrons must be paired.

3. Three types of molecular orbitals: bonding, antibonding, and nonbonding. Nonbonding: a MO that neither raises nor lowers the energy of the system. Typically, it consists of a single orbital on one atom (possibly because there is no atomic orbital of the correct symmetry for it to overlap on a neighboring atom).
A nearly non-bonding orbital arises in linear $\text{H}_3$

\[ \psi_a = \psi_{1s}(r_A) + \psi_{1s}(r_B) + \psi_{1s}(r_C) \]

\[ \psi_b = \psi_{1s}(r_A) - \psi_{1s}(r_C) \]

\[ \psi_c = \psi_{1s}(r_A) - \psi_{1s}(r_B) + \psi_{1s}(r_C) \]

Three molecular orbitals from three $\psi_{1s}$ atomic orbitals overlapping in three different ways.
A nearly non-bonding orbital arises in linear H₃.

The energies of the three molecular orbitals, labeled a, b, and c, in a system with three H atoms.
MOs with ‘s’ and ‘p’ atomic orbitals

$s$ orbitals are formed by allowing overlap between atomic orbitals that have cylindrical symmetry around the internuclear axis ($z$).
σ Orbitals

σ orbitals of homonuclear diatomic molecules are labeled “gerade” (“even”) or “ungerade” (“odd”) depending on their inversion symmetry.
π Orbitals

Two p orbitals can overlap to form a π orbital. The orbital has a nodal plane passing through the internuclear axis.
π Orbitals

Π orbitals are also labeled g or u depending on their inversion symmetry.

To determine inversion symmetry: start at an arbitrary point on the molecule, travel in a straight line through the center of the molecule, then continue an equal distance out on the other side of the center.
MOs with ‘d’ atomic orbitals (i.e., Hg$_2^{2+}$)

- With respect to the internuclear axis ($z$), $d_{z^2}$ has cylindrical symmetry
  → forms $\sigma$ molecular orbitals
MOs with ‘d’ atomic orbitals (i.e., Hg$_2^{2+}$)

- With respect to the internuclear axis (z), $d_{z^2}$ has cylindrical symmetry
  → forms $\sigma$ molecular orbitals

- When viewed along the internuclear axis (z), $d_{zx}$ and $d_{yz}$ look like p orbitals
  → form $\pi$ molecular orbitals
MOs with ‘d’ atomic orbitals (i.e., Hg$^{2+}$)
MOs with ‘d’ atomic orbitals (i.e., Hg$_2^{2+}$)

$\delta$ orbitals are formed by d-orbital overlap lacking cylindrical or “p” symmetry. The orbital has two mutually perpendicular nodal planes that intersect along the internuclear axis.
Example: Molecular nitrogen, \( \text{N}_2 \)

\[ \text{N: } 1s^22s^22p^3 \]

Start with outer-shell valence orbitals: 1 valence s orbital and 3 valence p orbitals

→ How many molecular orbitals?

Click for answer
Example: Molecular nitrogen, N₂

N: 1s²2s²2p³

Start with outer-shell valence orbitals: 1 valence s orbital and 3 valence p orbitals

→ How many molecular orbitals?

8

Half-Full pz

Half-Full px

Half-Full py
Example: Molecular nitrogen, $\text{N}_2$

The linear combination of the full 2s states looks much like $\text{He}_2$
Example: Molecular nitrogen, N₂

The half-full 2p orbitals will bond to form σ and π molecular orbitals.
Also, the p orbitals can interact with the s orbitals.
Example: Molecular nitrogen, N$_2$
Example: Molecular nitrogen, N₂

The electron configuration of N₂, with 10 valence electrons is:

\[1\sigma_g^21\sigma_u^21\pi_u^42\sigma_g^2\]

\(\pi^4\) is shorthand for the occupation of two different \(\pi\) orbitals.
The electron configuration of N2, with 10 valence electrons is:

\[ 1\sigma_g^2 1\sigma_u^2 1\pi_u^4 2\sigma_g^2 \]

\( \sigma_g \) is the HOMO for \( \text{N}_2 \): the “highest occupied molecular orbital”
Example: Molecular nitrogen, $N_2$

The electron configuration of $N_2$, with 10 valence electrons is:

$$1\sigma_g^21\sigma_u^21\pi_u^42\pi_g^2$$

$\pi_g$ is the LUMO for $N_2$: the “lowest unoccupied molecular orbital”

$\sigma_g$ is the HOMO for $N_2$: the “highest occupied molecular orbital”
Energies are determined by photoelectron spectroscopy