Computational Material Science
Part I

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Qualitative Molecular Orbital Theory (QMOT)

How to get the energy of the system?

Shrödinger equation: \( H\psi = E\psi \)

\[
\int \psi H \psi d\tau = \int \psi E \psi d\tau
\]

\[
E = \frac{\int \psi H \psi d\tau}{\int \psi \psi d\tau}
\]

H: Hamiltonian operator  \( \psi \): wavefunction  E: system energy
$H \psi = E \psi$

- What is in the Hamiltonian?

\[
H = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_k \frac{\hbar^2}{2m_k} \nabla_k^2 - \sum_i \sum_k \frac{e^2 Z_k}{r_{ik}} + \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_{k<l} \frac{e^2 Z_k Z_l}{r_{kl}}
\]

- Operator for kinetic energy of electron
- For kinetic energy of nucleus
- For attraction of the electrons to the nuclei
- For the interelectronic repulsions
- For the internuclear repulsions

Under the **Born-Oppenheimer approximation** (electrons respond to the motion of nucleus instantaneously, so assume fixed nuclear geometry when electronic energy is evaluated), this term is zero!
\[ H \psi = E \psi \]

- What is the electronic wave function of a system?

In the so-called molecular orbital theory

\[ \psi : \text{linear combination of atomic orbitals} \]

\[ \psi_1 = c_{11}\phi_1 + c_{12}\phi_2 + c_{13}\phi_3 + \cdots + c_{1N}\phi_N \]
\[ \psi_2 = c_{21}\phi_1 + c_{22}\phi_2 + c_{23}\phi_3 + \cdots + c_{2N}\phi_N \]
\[ \vdots \]
\[ \psi_N = c_{N1}\phi_1 + c_{N2}\phi_2 + c_{N3}\phi_3 + \cdots + c_{NN}\phi_N \]

\[ \psi_i = \sum_{j=1}^{N} c_{ij}\phi_j \]

\[ \psi : \text{molecular orbital} \]

\[ \phi : \text{atomic orbital wave function} \]
Ex: $H_2^+$

$$\psi_- = N_-(\phi_A - \phi_B)$$

$$\psi_+ = N_+(\phi_A + \phi_B)$$

$N$: normalization const.

$$\int \psi_+^2 d\tau = 1 = N_+^2 \int (\phi_A + \phi_B)^2 d\tau$$

$$\Rightarrow \frac{1}{N_+^2} = \int \phi_A^2 d\tau + 2 \int \phi_A \phi_B d\tau + \int \phi_B^2 d\tau = 2 + 2S_{AB}$$

Overlap integral $S_{AB}$

$$\therefore N_+ = \frac{1}{\sqrt{2 + 2S_{AB}}}$$

$$\int \psi_-^2 d\tau = 1$$

$$\Rightarrow N_- = \frac{1}{\sqrt{2 - 2S_{AB}}}$$
if \( \psi = \psi_+ \)

\[
E_+ = \frac{\int \psi^+ H \psi^+ d\tau}{\int \psi^+ \psi^+ d\tau} = N^2 \int (\phi_A + \phi_B)(\phi_A + \phi_B) d\tau
\]

\[
= \frac{1}{2 + 2S} \left[ \int \phi_A H_{\phi A} d\tau + \int \phi_A H_{\phi B} d\tau + \int \phi_B H_{\phi A} d\tau + \int \phi_B H_{\phi B} d\tau \right]
\]

let \( H_{AB} = \int \phi_A H_{\phi B} d\tau \)

\[
H_{AB} = H_{BA}
\]

\[ \therefore E_+ = \frac{2H_{AA} + 2H_{AB}}{2 + 2S} = \frac{H_{AA} + H_{AB}}{1 + S} \quad E_- = \frac{2H_{AA} - 2H_{AB}}{2 - 2S} = \frac{H_{AA} - H_{AB}}{1 - S} \]
If $S=0$

\[
E_+ = \frac{2H_{AA} + 2H_{AB}}{2 + 2S} = \frac{H_{AA} + H_{AB}}{1 + S}
\]

\[
E_- = \frac{2H_{AA} - 2H_{AB}}{2 - 2S} = \frac{H_{AA} - H_{AB}}{1 - S}
\]

**Antibonding** interaction

nodal plane; where electrons will not reside

**Bonding** interaction

$\square E$ raising = $\square E$ lowering
In reality $S \neq 0$

★ For two degenerate orbitals

$$\frac{H_{AA} - H_{AB}}{1 - S}$$

$\Delta E_{raising} > 0$, $1 - S > 0$

$\Rightarrow SH_{AA} - H_{AB} > 0$

$$\Delta E_{raising} = \frac{H_{AA} - H_{AB} - H_{AA}}{1 - S}$$

$$\Delta E_{lowering} = H_{AA} - \frac{H_{AA} + H_{AB}}{1 + S}$$

$$\Delta E_{raising} - \Delta E_{lowering} = \frac{SH_{AA} - H_{AB}}{1 - S} - \frac{SH_{AA} - H_{AB}}{1 + S}$$

$$= (SH_{AA} - H_{AB}) \left( \frac{1}{1 - S} - \frac{1}{1 + S} \right)$$

$$= (SH_{AA} - H_{AB}) \left( \frac{2S}{1 - S^2} \right)$$

$> 0, > 0$
It is known that inert gas does not dimerize.

"close shell repulsion"
Consequence of filling electrons into **bonding** and **antibonding** orbitals:

**H₂⁺**

One-electron stabilization
R = 1.06 Å
Bond Energy = 61 kcal/mol

**H₂**

Two-electron stabilization
R = 0.74 Å
Bond Energy = 103 kcal/mol

**He₂⁺**

Three-electron stabilization
R = 1.08 Å
Bond Energy = 50 kcal/mol

**He₂**

Nonexistent
Repulsive four electron interaction

Notice the trends:
1. Electron in **bonding** orbital — bond length decreases; bond energy increases

2. Electron in **antibonding** orbital — bond length increases; bond energy decreases
For Na and Mg, 3s and 3p orbitals are very close in energy, unrealistic to treat as pure 3s cases.
Notice energies of bonding and antibonding orbitals may crossover. Therefore, simple QMOT results with limited molecular orbital interactions may not be correct!
For two nondegenerate orbitals

\[ \psi_{MO} = \phi_B - \lambda \phi_A \]

\[ \lambda \propto \frac{S_{AB}}{\Delta E} \]

\[ SE \propto \frac{S_{AB}^2}{\Delta E} \]

Rules in QMOT:

1) occupied orbital repel occupied orbital
2) S ≤, SE (Stabilization Energy) ≤
3) closer in energy, SE ≤
Occupied orbital interacts with unoccupied orbital => Lowering energy

HOMO–LUMO interaction important!

LUMO

Lowest Unoccupied

HOMO

Highest Occupied

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General rules for determining relative orbital energies

1. bonding < nonbonding < antibonding
2. $\sigma$ orbitals < $\pi$ orbitals < $\pi^*$ orbitals < $\sigma^*$ orbitals
3. AO energies decrease along a row of the periodic table. C 2p > N 2p > O 2p > F 2p =>
   $\sigma_{C-C} > \sigma_{C-N} > \sigma_{C-O} > \sigma_{C-F} ; \sigma^*_{C-C} > \sigma^*_{C-N} > \sigma^*_{C-O} > \sigma^*_{C-F}$
4. $\sigma_{C-I} > \sigma_{C-Br} > \sigma_{C-Cl} > \sigma_{C-F} ; \sigma^*_{C-F} > \sigma^*_{C-Cl} > \sigma^*_{C-Br} > \sigma^*_{C-I}$
Symmetry and orbital overlap
A: antisymmetric  S: symmetric

Wrong symmetry will result in zero overlap!
Wrong Symmetry!

(a) nonzero overlap
(b) nonzero overlap
(c) zero overlap
- Overlap integral $S$ vs $r$
- Overlap integral $S$ vs angle
Ex: \( H_4 \) (square)

Among interactions 1, 2, 3, and 4, which ones are valid?
Interactions 1 and 2

\[ S \neq 0 \]

\[ 4-3a \]

Will result in energy splitting!

Interactions 3 and 4

\[ S = 0 \]

\[ 4-3c \]

No interaction!
More nodal plane, higher in energy

\[ \phi_1 = \sigma_{H_2}(1) + \sigma_{H_2}(2) \]
\[ \phi_2 = \sigma_{H_2}(1) - \sigma_{H_2}(2) \]
\[ \phi_3 = \sigma_{H_2}^*(1) + \sigma_{H_2}^*(2) \]
\[ \phi_4 = \sigma_{H_2}^*(1) - \sigma_{H_2}^*(2) \]

Figure 4.1. Construction of the MOs of square planar H₄.
When the side of the square is 1 Å, $S = 0.469$, $S' = 0.263$

$N_1 = 0.337$, $N_2 = N_3 = 0.582$, $N_4 = 0.877$
**Ex:** $H_4$ (rectangular)

This explains why cyclobutadiene is a closed-shell molecule and is rectangular.

Jahn-Teller effect: geometry distort to destroy degeneracy and get closed-shell species with lower energy.

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Figure 4.2. Construction of the MOs of rectangular $H_4$. 

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Ex: $H_3$ (linear)

Notice the population of $H_b$ is large in $\phi_1$ and $\phi_3$?

**Figure 4.3.** Construction of the MOs of linear $H_3$. 
Ex: $H_3$ (triangular)

Figure 4.5. Construction of the MOs of triangular $H_3$. 
Geometry and orbital correlation diagram

Experimentally, $H_3^+$ is found to be triangular and $H_3^-$ linear

- Orbital correlation diagram for bending $H_3$

**Figure 9.1.** Energetic evolution of the MOs of an $H_3$ unit on bending.
Now do you understand why $H_3^+$ is triangular and $H_3^-$ is linear?
Note: nuclear repulsion disfavor $\theta < 60^\circ$
- Rules for orbital correlation diagram

- Stabilization/destabilization of the MOs
  - bonding $\rightarrow$ antibonding $\rightarrow$ energy lowering
  - bonding $\rightarrow$ antibonding $\rightarrow$ energy increasing

- Conservation of orbital symmetry

- The non-crossing rule for MOs of the same symmetry
Ex: $H_4$ (linear)

More nodal plane, higher in energy

Figure 4.4. Construction of the MOs of linear $H_4$. 

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Ex: $H_6$ (hexagonal)

Figure 4.7. Construction of the MOs of hexagonal $H_6$. 

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Building up MOs of simple molecules

Ex: CH₂

Linear combination of H

ψ₁
ψ₂
ψ₃
ψ₄
ψ₅
ψ₆

Cₛ
Cₛ
- Same symmetry
  \( \Psi_1, \Psi_3, \Psi_4 \)
  closer in energy
  \( \Psi_2, \Psi_5 \)

- Energy difference between \( \pi_{\text{CH}_2} - \pi^*_{\text{CH}_2} \)
  smaller than
  \( \sigma_{\text{CH}_2} - \sigma^*_{\text{CH}_2} \)
  because of smaller overlap
"# of electrons in CH$_2$
4 + 1 + 1 = 6

Ψ$^4$ (n) is also of the same symmetry, should also interact with hydrogens

2nd order interaction"
- Three orbital interactions

\[ \varphi_1 = x_1 + x_2 + x_3 \]
\[ \varphi_2 = x_1 - x_2 + x_3 \]
\[ \varphi_3 = -x_1 - x_2 + x_3 \]

bonding, bonding

antibonding, bonding

antibonding, antibonding
- Nonequivalence of oxygen lone pairs in the water molecule

Photoelectron spectrum of water shows the lone pair orbitals are nonequivalent and are separated by 2.1 eV

Fig. 2.24. Orbital diagram showing (a) the symmetry-allowed interactions between the set of O 2p orbitals and the two H_2 orbitals (1+2) and (1-2) in the H_2O molecule. (b) The set of MOs in the H_2O molecule obtained from the interaction of the orbitals in (a). Note that the two lone-pair orbitals in H_2O are not degenerate.
- Another example of 2nd order interaction differences in electronic structure of F<sub>2</sub> and C<sub>2</sub>

F<sub>2</sub>: (1σ)<sup>2</sup>(1σ*)<sup>2</sup>(2σ)<sup>2</sup>(2σ*)<sup>2</sup>(3σ)<sup>2</sup>(1π)<sup>4</sup>(1π*)<sup>4</sup>

C<sub>2</sub>: (1σ)<sup>2</sup>(1σ*)<sup>2</sup>(2σ)<sup>2</sup>(2σ*)<sup>2</sup>(1π<sub>u</sub>)<sup>4</sup> why 3σ is not populated first?

=> energy raised because of mixing of 2σ and 3σ (\(\therefore\) same symmetry)
- Combine CH$_2$ and CH$_2$ to get CH$_2$=CH$_2$

The lone pairs (n) form a $\sigma$ bond and the $\pi$ orbitals form a $\pi$ bond

Net bonding with 12 electrons:
1 $\sigma$ bond
1 $\pi$ bond
Walsh diagram for correlating linear and bent $AH_2$

- Walsh diagram provides rationales for
  - Linear $BeH_2$, $BH_2^+$ (4 e$^-$)
  - Bent $CH_2$ (6 e$^-$)
  - Bent $H_2O$ (8 e$^-$)

a. i) weak bonding between
   H…H lost
   ii) stabilization from p orbital lost
b. i) H moves to maximum overlap
   ii) out of phase H…H become further apart
c. loses s character
Ex: cyclopropane

Poor alignment of p orbitals can explain strain, good e⁻ donor ability (high HOMO), and substituent effect

Do you find the resemblance between cyclopropane MOs and H₃ MOs?
Preferred structure of:

It is known that the cation part is planar:

- Favored
- Not favored

or

favored

not favored
Structure of

\[
\begin{align*}
\text{favored} &: C_1-C_2 \text{ longer than w/o the cation part} \\
\text{disfavored} &: C_2-C_3 \text{ shorter}
\end{align*}
\]

How do you rationalize?

\[
\begin{align*}
\text{Hint: empty orbital interact with filled orbital} \\
\text{Hint: electron flows out of bonding orbital} \Rightarrow \text{lengthen bonds} \\
\text{electron flows out of antibonding} \Rightarrow \text{shorten bonds}
\end{align*}
\]
π systems and conjugation

π Electrons are less tightly held than the σ electrons, often responsible for the electrical and optoelectrical properties of a material.

Ex: CH$_2$=CH$_2$

Antisymmetrical with respect to molecular plane.
- In the excited state, the geometry may relax to different conformation

No energy destabilization caused by orbital interaction
- Conjugation (C=C-C=C-…….)

• CH₃-CH₂-CH=CH₂ + H₂ → CH₃-CH₂-CH₂-CH₃  ΔH = -30.2 kcal/mol

• CH₂=CH-CH₂-CH=CH₂ + 2 H₂ → CH₃-CH₂-CH₂-CH₂-CH₃  ΔH = -60.4 kcal/mol  
  (unconjugated diene)

• CH=CH-CH=CH₂ + 2 H₂ → CH₃-CH₂-CH₂-CH₃  ΔH = -56.5 kcal/mol  
  (conjugated diene)

\[
\begin{align*}
\text{CH}_2 & \quad \text{CH} & \quad \text{CH} & \quad \text{CH}_2 \\
1.34 \, \text{Å} & & 1.48 \, \text{Å} & & 1.34 \, \text{Å} \\
\text{CH}_3 & & \quad \text{CH}_3 \\
1.53 \, \text{Å} & &
\end{align*}
\]

Why conjugated diene more stable than unconjugated diene?  Why C-C bond shorter in conjugated diene?
4 \pi electrons

Notice the center bond has net bonding character

Total energy of butadiene is lower than 2 isolated system (ex: 2+3)
Butadiene in reality: not linear

**Trans** is more stable than **cis**.

*Hint: Use orbital correlation diagram to rationalize it.*
*Or, think about steric effect*
Lewis structure and bond localization

Molecular orbital (delocalized in nature) is useful, but sometimes it is easier to think in terms of localized orbitals!

Localized orbitals can represent electron density in a conceptually useful way and give concise picture of orbital interactions for the local structure of interest. However, keep in mind that localized orbitals are not eigenfunctions, not orthogonal to each other, and cannot be used in correlations with physical observables such as photoelectron spectra.