This chapter presents a qualitative treatment of molecular orbitals for chemical bonding (covalent bonds) using the simplest molecule, $H_2^+$. 

$H + H^+ \longrightarrow H_2^+$

$H_2^+$ is more stable than widely separated H atom and an H+ ion because of the delocalization of the electron over the molecule and localization of the electron in the region between the two nuclei.

As the participant atomic species come together to form a bond the energy of the molecule move through a minimum energy position (equilibrium bond distance = bond length).

Covalent bond resembles the superposition of charge distribution (valence electrons) among individual atoms - delocalization. Core electrons remain localized on individual atoms.

Molecular wave function; 

$\psi_{\text{molecule}} = \psi(r_1, r_2, ..., r_n, R_1, R_2, ..., R_m)$

The Born-Oppenheimer approximation

The nuclei have much larger masses in comparison to electron mass and will have a negligibly small velocity. Born-Oppenheimer takes advantage of this fact and makes the assumption that since the nuclei are much heavier in mass compared to the electron, their motion can be ignored while solving the electronic Schrödinger equation.

That is, the nuclei are assumed to be stationary while electrons move around it.

Therefore the motion of the nuclei and the electrons can be separated. The nuclear-nuclear motion/reputation issues can be treated independently.

The Born-Oppenheimer approximation simplifies the handling of the Schrödinger equation for a molecule.
Solve electron motion for a given set of $R_i$'s.

Electronic energy (Kinetic + Potential), $E_{el}$

\[ E_{nuc} \]

\[ E_{total} = E_{el} + E_{nuc} \]

**Molecular Orbitals**

Once electronic energy $E_{el}$ and wave functions (molecular orbitals) are solved with SE for a given nuclear configuration $R_{AB}$, the nuclear repulsion energy is then added for a given nuclear configuration $R_{AB}$ on top of $E_{el}$ to obtain the total energy at $R_{AB}$.

Change $R_{AB}$ and repeat the process.

**LCAO-MO Model – H₂**

The spaces in which electrons can reside in a molecule (MO) extends over the molecule. Molecular orbital description of chemical bond is based on the principle that $\psi_{el} = \psi$ can be written as a linear combination of atomic orbitals on individual atoms LCAO in the molecule.

For the simplest molecule, the simplest MO is constructed by the LC of the AOs $\phi_a$ and $\phi_b$ (basis functions) coming from atoms $H_a$ and $H_b$.

\[ \psi_i = c_a \phi_a + c_b \phi_b \]

an approximation

The next step is to solve for coefficients $c_i$ by the variation method, minimize $<\psi>$ value.

Expression for $<\psi>$:

\[ <\psi> = \frac{\int \psi^* \hat{H} \psi \, dr}{\int \psi^* \psi \, dr} \]
(e) = \frac{(c_a)^2 \int \phi_a^* \hat{H} \phi_a \, d\tau + (c_b)^2 \int \phi_b^* \hat{H} \phi_b \, d\tau + 2c_ac_b \int \phi_a \phi_b \, d\tau}{(c_a)^2 \int \phi_a^* \phi_a \, d\tau + (c_b)^2 \int \phi_b^* \phi_b \, d\tau + 2c_ac_b \int \phi_a \phi_b \, d\tau}

Assumptions:
\int \phi_a^* \hat{H} \phi_a \, d\tau = \int \phi_b^* \hat{H} \phi_b \, d\tau \quad \text{and} \quad \int \phi_a \phi_b \, d\tau = \int \phi_b \phi_a \, d\tau

Bra–ket notation
\langle \phi_a^* | \hat{H} | \phi_b \rangle \quad \text{and} \quad \langle \phi_b^* | \hat{H} | \phi_a \rangle = \langle \phi_a^* | \phi_b \rangle

Assumption valid for homonuclear di-atomics.

\int \phi_a^* \hat{H} \phi_a \, d\tau = H_{aa} \quad \text{interaction energy electron a to nucleus a}
\int \phi_b^* \hat{H} \phi_b \, d\tau = H_{bb} \quad \text{interaction energy nucleus a to nucleus b}
\int \phi_a \phi_b \, d\tau = S_{ab} = 1 \quad \text{overlap of a.o. of atom A}
\int \phi_b \phi_a \, d\tau = S_{ba} \quad \text{overlap of a.o. of A and a.o. of B}

Exchange integral; \( H_{ab} < 0 \)
Overlap integral; \( 0 < S_{ab} < 1 \)

\begin{align*}
\text{Overlap integral:} \quad & H_{ab} = \int \phi_a^* \hat{H} \phi_b \, d\tau \leq 0 \\
\text{Overlap integral:} \quad & S_{ab} = \int \phi_a \phi_b \, d\tau > 0
\end{align*}

not in individual atoms!!

Determining the lowest energy use the variation method.

Differentiation of \( <e> \) expression w.r.t the \( c_i \) parameters and equating to zero (to find coefficients);

\begin{align*}
(2c_a + 2c_b S_{ab}) e &= 2c_a H_{uu} + 2c_b H_{vb} \\
(2c_a + 2c_b S_{ab}) e &= 2c_b H_{vb} + 2c_a H_{uu}
\end{align*}

\begin{align*}
c_a(H_{uu} - e) + c_b(H_{vb} - eS_{ab}) &= 0 \\
c_a(H_{vb} - eS_{ab}) + c_b(H_{vb} - e) &= 0
\end{align*}

Secular equations

\begin{align*}
\left| \begin{array}{ccc}
H_{uu} - e & H_{ub} - eS_{ab} \\
H_{ab} - eS_{ab} & H_{vb} - e
\end{array} \right| &= 0 \quad \text{Secular determinant}
\end{align*}

The order of the determinant depends on (equal to) the # AO s of the basis set used.

For non-trivial solution the determinant;

\begin{align*}
H_{uu} - e &
H_{ub} - eS_{ab} \\
H_{vb} - e &
H_{vb} - eS_{ab}
\end{align*}

Negative < 0, positive > 0

Overlap integral

The larger the overlap (wavefunctions in phase) lower the energy of the system \( <e> \), more stable is the covalent bond.
Expand the determinant:

Yields a polynomial in \( \varepsilon \), solution of which will give the energies of the system.

\[
\varepsilon = \frac{1}{2} - \frac{1}{2S_{ab}} |H_{aa} + H_{bb} + 2S_{ab}H_{ab}| \pm \sqrt{\left(\frac{1}{4}H_{aa}^2 + \frac{1}{4}H_{bb}^2 + \frac{1}{4}H_{ab}^2 + \frac{1}{4}S_{ab}^2H_{aa} + \frac{1}{4}S_{ab}^2H_{bb} + \frac{1}{4}S_{ab}^2H_{ab} - 2H_{ab}(H_{dd} + 2S_{ab}H_{ab} - 2S_{ab}^2H_{bb})\right)}
\]

For the homonuclear diatomic,

\[
\varepsilon_1 = \frac{H_{aa} + H_{ab}}{1 + S_{ab}} \quad \text{and} \quad \varepsilon_2 = \frac{H_{aa} - H_{ab}}{1 - S_{ab}}
\]

For homonuclear diatomic,

\[
\begin{align*}
H_{aa} &= H_{bb} < 0 \\
H_{ab} &= 0
\end{align*}
\]

Makes \( \varepsilon_2 > \varepsilon_1 \).

Substituting \( \varepsilon \) in secular equations we get information about the coefficients.

and \( c_a = c_b \) for \( \varepsilon_1 \)

\( c_a = -c_b \) for \( \varepsilon_2 \)

MO energy diagram

[equal coefficients].

Secular determinant:

\[
\begin{vmatrix}
H_{aa} - \varepsilon & H_{ab} - S_{ab}\varepsilon \\
H_{ab} - S_{ab}\varepsilon & H_{bb} - \varepsilon
\end{vmatrix} = 0
\]

homonuclear diatomic

\[
\begin{vmatrix}
H_{aa} - \varepsilon & H_{ab} - S_{ab}\varepsilon \\
H_{ab} - S_{ab}\varepsilon & H_{bb} - \varepsilon
\end{vmatrix} = 0
\]

expanding \( (H_{aa} - \varepsilon)^2 - (H_{ab} - S_{ab}\varepsilon)^2 = 0 \)

Taking the root:

\[
(H_{aa} - \varepsilon) = \pm (H_{ab} - S_{ab}\varepsilon)
\]

Yields

\[
\begin{align*}
\varepsilon_1 &= \frac{H_{aa} + H_{ab}}{1 + S_{ab}} \\
\varepsilon_2 &= \frac{H_{aa} - H_{ab}}{1 - S_{ab}}
\end{align*}
\]

Substituting the energy values in;

\[
\begin{align*}
c_a(H_{aa} - \varepsilon) + c_b(H_{ab} - S_{ab}\varepsilon) &= 0 \\
c_a(H_{ab} - S_{ab}\varepsilon) + c_b(H_{bb} - \varepsilon) &= 0
\end{align*}
\]

Gives the coefficients after normalization

\[
\begin{align*}
c_a &= \frac{1}{\sqrt{2} + 2S} \quad \text{for } \varepsilon_1 \\
c_b &= \frac{1}{\sqrt{2} - 2S} \quad \text{for } \varepsilon_2 \text{ and } c_b = -c_a
\end{align*}
\]

and the wavefunctions

\[
\begin{align*}
\psi_1 &= c_a\phi_a + c_b\phi_b = \frac{1}{\sqrt{2} + 2S} (\phi_a + \phi_b) \quad \text{for } \varepsilon_1 \\
\psi_2 &= c_a\phi_b - c_b\phi_a = \frac{1}{\sqrt{2} - 2S} (\phi_a - \phi_b) \quad \text{for } \varepsilon_2
\end{align*}
\]

Penetration into forbidden region increases
Low energy states
Valence orbitals
Weakly bound

States (atom)

High energy states
Core orbitals
Strongly bound states

Overlap

Constructive interference of wave functions leads to bonding.

Particles (electrons) would share space on both atoms.

\[ \psi_g = c_1(\phi_{n\ell_1} + \phi_{n\ell_2}) \]
\[ \psi_u = c_2(\phi_{n\ell_1} - \phi_{n\ell_2}) \]
\[ \phi_{\text{HOMO}} = \frac{1}{\sqrt{2}}(\psi_g + \psi_u) e^{-\frac{\xi}{\alpha}} \]

Symmetry classification of MOs:
\[ g \] symmetric (about center of molecule)
\[ u \] antisymmetric

In MOs electron is delocalized.

Localization in bonding MO
Molecular Orbitals: Homonuclear Diatomic Molecules

Molecular orbitals are spaces in a molecule electrons could reside.

The wave function for MOs are constructed as linear combinations of atomic orbitals of the atoms involved LCAO-MO.

The extent to which each orbital from an atom contribute to the MO is related to the square of the respective coefficient.

$$\psi_j = \sum_{i=1}^{N} c_{ij} \phi_i$$

The MOs have shapes and spatial extents.

The MOs of homonuclear diatomics are divided into two groups with regard to two symmetry operations. (g or u symmetry, w.r.t. center of molecule indicated)

1. Rotation about nuclear (z) axis - rotation do not change MO - $\sigma$ symmetry.

2. MO has a nodal plane in the molecular axis – $\pi$ symmetry.

Only AOs of the same symmetry can form MOs.

Bonding – in phase (same sign)

Anti-bonding – out of phase

No bonding of any sort.

Further, the AOs involved should have comparable energies as well to form bonds. (to get a significant coefficient) in the LCAO-MO:

$$\psi_j = \sum_{i=1}^{N} c_{ij} \phi_i$$

Note the * antibonding orbital; high energy counterpart of bonding orbital.
Notation: MO homonuclear diatomic molecules

\[ 3\sigma_u^* \]

bonding/antibonding

\[ p.q.n., n \text{ of the AO.} \]

\[
\begin{align*}
\text{H}_2 & \quad \left(1\sigma_g\right)^2 \\
\text{He}_2 & \quad \left(1\sigma_g\right)^2 \left(1\sigma_u^*\right)^2
\end{align*}
\]

Minimal basis set sufficient for diatomics.
Closed-Shell Molecular Orbital Coefficients - H₂

**MO:**

<table>
<thead>
<tr>
<th>MO</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy (eV)</td>
<td>-15.50632</td>
<td>-15.50495</td>
<td>-1.40847</td>
<td>-0.72753</td>
<td>-0.54859</td>
</tr>
</tbody>
</table>

**Eigenvalues:**

-0.59018, 0.70055

-16.05961, 19.06286

<table>
<thead>
<tr>
<th>Sg+</th>
<th>Su+</th>
<th>Sg+</th>
<th>Su+</th>
<th>Piu</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 H1</td>
<td>S 0.54587</td>
<td>1.24613</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 H2</td>
<td>S 0.54587</td>
<td>-1.24613</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note the change in energy hierarchy.
Electronic configuration, bond length (pm), bond order and bond energy (kJ mol⁻¹ of Li₂ to F₂ [σ₁s²σ¹s²]…

<table>
<thead>
<tr>
<th>Electronic configuration</th>
<th>Bond length</th>
<th>Bond energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-Li 2σ₂²</td>
<td>267</td>
<td>110</td>
</tr>
<tr>
<td>Be-Be 2σ₂²</td>
<td>exist?</td>
<td>exist?</td>
</tr>
<tr>
<td>B-B 2σ₂² 2σ¹s² 2π₂p²</td>
<td>159</td>
<td>290</td>
</tr>
<tr>
<td>C=C 2σ₂² 2σ¹s² 2π₂p²</td>
<td>124</td>
<td>602</td>
</tr>
<tr>
<td>N≡N 2σ₂² 2σ¹s² 2π₂p²</td>
<td>110</td>
<td>942</td>
</tr>
<tr>
<td>O=O 2σ₂² 2σ¹s² 2σ²p²</td>
<td>121</td>
<td>494</td>
</tr>
<tr>
<td>F-F 2σ₂² 2σ¹s² 2π₂p²</td>
<td>142</td>
<td>155</td>
</tr>
</tbody>
</table>

Delta bond:

Delta bonds (δ bonds) are covalent chemical bonds, where four lobes of one atom is involved with four lobes of the another atom.

This overlap leads to the formation of a bonding molecular orbital with two nodal planes which contains the internuclear axis and go through both atoms.

Molecular Orbitals: Hetero-nuclear Diatomic Molecules

E.g. HF - Energies of AOs unequal.

(mimal) basis functions - \( \phi_{\text{H}_1} \) and \( \phi_{\text{F}_2} \)

\[
\psi_1 = c_{1H}\phi_{\text{H}_1} + c_{1F}\phi_{\text{F}_2} \quad \text{and} \quad \psi_2 = c_{2H}\phi_{\text{H}_1} + c_{2F}\phi_{\text{F}_2}
\]

\[
\begin{align*}
\psi_1 &= -19.6 \text{ eV} \\
\psi_2 &= -10.3 \text{ eV}
\end{align*}
\]


Unequal coefficients.

Hetero-nuclear Diatomic Molecules

The AO energies of basis functions are unequal.

\[ \psi_1 = -19.6 \text{ eV} \quad \psi_2 = -10.3 \text{ eV} \]

Reminder: square of the coefficient is the contribution to electron probability distribution in the bond.

\[ \psi_1 = c_{11} \phi_{11} + c_{1F} \phi_{1F} \quad \psi_2 = c_{21} \phi_{21} + c_{2F} \phi_{2F} \]

\[ \int \psi_1^* \psi_2 \, d\tau = c_{11}^2 + c_{1F}^2 + 2c_{11}c_{1F}S_{HF} \]

\[ c_{1H}^2 = 0.34^2 = 0.12 \quad \text{Around H} \]

\[ c_{1F}^2 = 0.84^2 = 0.71 \quad \text{Around F} \]

\[ 2c_{11}c_{1F}S_{HF} = 0.17 \quad \text{Shared H and F} \]
Molecular Electrostatic Potential (MEP)

The potential felt by a test charge (unit positive) at various points in the molecule.

MEP is calculated by considering the positively charged nuclear framework and the negatively charged electron cloud of the molecule.

A negative MEP signifies attraction of a unit positive charge, therefore a negatively charged point in the molecule.

A positive MEP signifies repulsion of a unit positive charge, therefore a positively charged point in the molecule.

Electrostatic Potential Surfaces

Molecular electrical potential surfaces, illustrate the charge distributions of molecules three dimensionally.

The surface is a constant electron density surface.

The potential at the surface is mapped onto the surface. The surface (solid/transparent or mesh) is color coded according to the electrical potential.

Knowledge of the charge distributions can be used to determine how molecules interact with one another.