

Introduction to Molecular Structure

Molecular Orbital Theory, LCAO, Hydrogen Molecule, Hückel Method

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Outline

- 1 Born-Oppenheimer Approximation
- 2 Molecular Orbital Theory
- 3 MOT Applied to H₂
- 4 MOT for Diatomic Molecules
- 5 MOT for Polyatomic Molecules
- 6 Conjugated π -Systems
- 7 The Hückel Approximation

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Born-Oppenheimer Approximation

Introduction

- Even a simple system like the H_2^+ ion has a complex Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{\hbar^2}{2m_p} (\nabla_A^2 + \nabla_B^2) + V(\vec{r}; \vec{R}_A, \vec{R}_B)$$

where:

- m_e is the electron mass, and m_p is the proton mass.
- ∇^2 acts on electron's coordinates
- ∇_A^2 and ∇_B^2 act on the nuclei
- $V(\vec{r}; \vec{R}_A, \vec{R}_B) = -\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{|\vec{r}-\vec{R}_A|} + \frac{1}{|\vec{r}-\vec{R}_B|} + \frac{1}{|\vec{R}_A-\vec{R}_B|} \right)$
- Impossible to solve for the wave function if we are to consider all three particles together.
- **BO approximation:** m_p is at least $1000m_e \rightarrow$ treat the nuclei as fixed
- This *decouples* electronic and nuclear degrees of freedom.

Born-Oppenheimer approximation

Separation of Variables

- Propose a solution

$$\Psi(\vec{r}, \vec{R}_A, \vec{R}_B) = \psi(\vec{r}; \vec{R}_A, \vec{R}_B)\chi(\vec{R}_A, \vec{R}_B)$$

- Substituting this into the full Schrödinger equation yields two equations:

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + V(\vec{r}; \vec{R}_A, \vec{R}_B) \right] \psi(\vec{r}; \vec{R}_A, \vec{R}_B) = E_e \psi(\vec{r}; \vec{R}_A, \vec{R}_B)$$

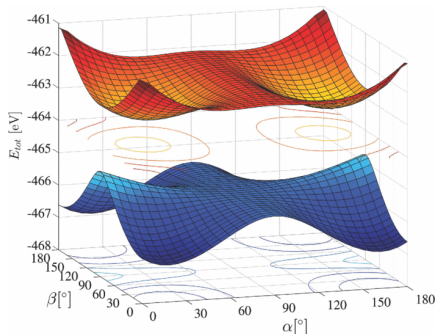
$$\left[-\frac{\hbar^2}{2m_p} (\nabla_A^2 + \nabla_B^2) + E_e \right] \chi(\vec{R}_A, \vec{R}_B) = E \chi(\vec{R}_A, \vec{R}_B)$$

- After we solve the first equation for the fixed nuclei, we can solve the second equation with E_e .

Born-Oppenheimer approximation

Potential Energy Surface

- We notice that $E_e = E_e(\vec{R}_A, \vec{R}_B)$ for both the ground state and excited states.
- Assuming that excited levels do not cross, we can view this function as a *potential energy surface* on which electrons move.



Ground and 1st excited states of the molecule formaldehyde for two angles.

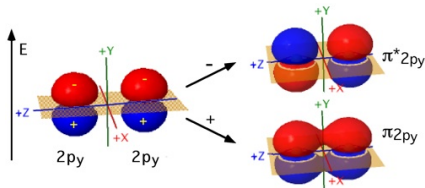
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Molecular Orbital Theory

Linear Combination of Atomic Orbitals (LCAO)

- Molecular Orbital Theory (MOT) describes the formation of molecular orbitals (MOs) from atomic orbitals (AOs).



- An *atomic orbital*, in this context, is an orbital that was obtained by solving the Schrödinger equation for an isolated atom, localized on that atom.

Molecular Orbital Theory

Linear Combination of Atomic Orbitals (LCAO)

- In LCAO, we construct single-electron MO's as superpositions of atomic orbitals on all atoms involved

$$\Psi(\vec{r}) = \sum_i c_i \phi(\vec{r} - \vec{R}_i)$$

where i runs over all the atoms, and ϕ are the atomic orbitals.

- By placing this wave function into a Schrödinger equation and solving for the coefficients, we obtain *molecular orbitals*.
- This assumes a single orbital per atom \rightarrow can be extended.

Molecular Orbital Theory

Linear Combination of Atomic Orbitals (LCAO)

- Begin with the expansion for a molecular orbital ψ as a linear combination of atomic orbitals (LCAO) from multiple atoms:

$$\psi = \sum_i c_i \phi_i$$

- ψ is the molecular orbital.
 - ϕ_i is the atomic orbital on atom i (e.g., hydrogen 1s orbitals).
 - c_i are the coefficients determining the contribution of each atomic orbital.
- We aim to find the coefficients c_i by solving the Schrödinger equation:

$$\hat{H}\psi = E\psi$$

where \hat{H} is the molecular Hamiltonian, and E is its energy.

Molecular Orbital Theory

Linear Combination of Atomic Orbitals (LCAO)

- 1 Start by substituting the LCAO expansion into the Schrödinger equation:

$$\hat{H} \left(\sum_i c_i \phi_i \right) = E \left(\sum_i c_i \phi_i \right)$$

- 2 Multiply both sides by ϕ_j^* and integrate over all space:

$$\sum_i c_i \int \phi_j^* \hat{H} \phi_i d\vec{r} = E \sum_i c_i \int \phi_j^* \phi_i d\vec{r}$$

- 3 Define matrix elements:

$$H_{ij} = \int \phi_j^* \hat{H} \phi_i d\vec{r}, \quad S_{ij} = \int \phi_j^* \phi_i d\vec{r}$$

- H_{ij} is the Hamiltonian matrix element (Coulomb and exchange integrals).
- S_{ij} is the overlap matrix element.

Molecular Orbital Theory

Linear Combination of Atomic Orbitals (LCAO)

- The generalized secular equation obtained from the LCAO expansion can be written in matrix form:

$$\vec{H}\vec{c} = E\vec{S}\vec{c}$$

- \vec{H} is the Hamiltonian matrix with elements H_{ij} .
 - \vec{S} is the overlap matrix with elements S_{ij} .
 - \vec{c} is the vector of coefficients c_i .
- Solve the secular equation by finding the eigenvalues E and the corresponding eigenvectors \vec{c} :

$$\left| \vec{H} - E\vec{S} \right| = 0$$

This determinant gives the energy eigenvalues of the molecular orbitals.

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MOT Applied to H₂

LCAO Solution for H₂ Molecule

- ψ_{MO} approximated as a linear combination of two H 1s orbitals localized on atoms A and B .

$$\psi_{\text{MO}} = c_A\phi_A + c_B\phi_B$$

- Since the problem is very easy, we can construct the solutions by inspection.
- Two types of molecular orbitals arise:
 - Bonding molecular orbital: Constructive interference of the atomic orbitals ($\psi_+ = \phi_A + \phi_B$)
 - Anti-bonding molecular orbital: Destructive interference of the atomic orbitals ($\psi_- = \phi_A - \phi_B$)

MOT Applied to H₂

Solutions

- To determine the molecular orbital energies, we solve the Schrödinger equation:

$$\hat{H}\psi_{\text{MO}} = E\psi_{\text{MO}}$$

- For the LCAO approximation, we expand this equation as:

$$c_A\hat{H}\phi_A + c_B\hat{H}\phi_B = E(c_A\phi_A + c_B\phi_B)$$

- By multiplying from the left by ϕ_A^* and ϕ_B^* and integrating over all space, we obtain a system of linear equations:

$$c_A H_{AA} + c_B H_{AB} = E(c_A S_{AA} + c_B S_{AB})$$

$$c_A H_{BA} + c_B H_{BB} = E(c_A S_{BA} + c_B S_{BB})$$

- Here, H_{AA} , H_{AB} , etc. are the Hamiltonian matrix elements, and S_{AA} , S_{AB} , etc. are the overlap integrals:

$$H_{AA} = \int \phi_A^* \hat{H} \phi_A d\vec{r}$$

MOT Applied to H₂

Solutions

- The system of linear equations can be written in matrix form as:

$$\begin{pmatrix} H_{AA} - ES_{AA} & H_{AB} - ES_{AB} \\ H_{BA} - ES_{BA} & H_{BB} - ES_{BB} \end{pmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix} = 0$$

- For non-trivial solutions, the determinant of the coefficient matrix must vanish. This leads to the secular determinant:

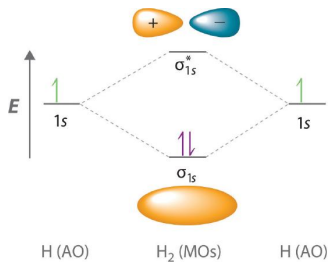
$$\begin{vmatrix} H_{AA} - ES_{AA} & H_{AB} - ES_{AB} \\ H_{BA} - ES_{BA} & H_{BB} - ES_{BB} \end{vmatrix} = 0$$

- Solving the secular determinant gives two energy eigenvalues E_+ and E_- , corresponding to the bonding and anti-bonding molecular orbitals, respectively:

$$E_{\pm} = \frac{H_{AA} + H_{BB}}{2} \pm \frac{\sqrt{(H_{AA} - H_{BB})^2 + 4H_{AB}^2}}{2}$$

MOT Applied to H₂

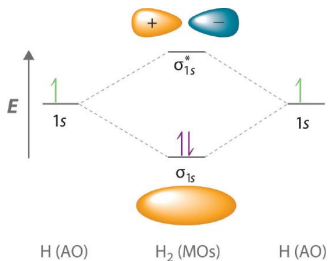
Interpretation of Bonding and Anti-Bonding Orbitals



- The bonding molecular orbital (ψ_+) has lower energy (E_+) than the anti-bonding molecular orbital (E_-).
- This energy difference leads to the stability of the H₂ molecule in its ground state.

MOT Applied to H₂

Interpretation of Bonding and Anti-Bonding Orbitals



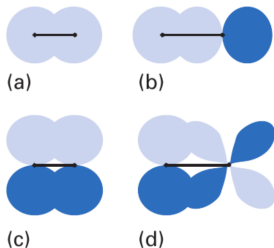
- The bonding orbital is characterized by a high electron density between the two nuclei, resulting in attractive interaction and bond formation.
- The anti-bonding orbital has a nodal plane between the nuclei, leading to repulsion.

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MOT for Diatomic Molecules

Choosing the Atomic Orbitals for LCAO

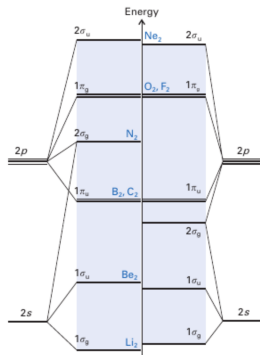


(a) and (b) σ orbitals
(c) and (d) π orbitals

- Must choose AOs of the same symmetry to avoid zero overlap.
 - s , p_z , and d_{z^2} \rightarrow σ orbitals
 - p_y , and p_z \rightarrow π orbitals
 - d_{yz} , and d_{zx} \rightarrow π orbitals
 - d_{xy} , and $d_{x^2-y^2}$ \rightarrow δ orbitals
- The AOs should not be too *diffuse* or too *compact*: e.g. $(1s, 1s)$ almost does not overlap but $(2s, 2s)$ does.
- The AOs should be close in energy: e.g. $(2s, 2s)$ and $(2p, 2p)$ dominate the bonding while $(2s, 1s)$ etc are too small.
- Construct MO diagrams for period 2 homonuclear diatomic molecules: N_2 , O_2 etc.

MOT for Diatomic Molecules

MOT for Period 2 Homonuclear Diatomic Molecules



- Consider only the valence orbitals – the core orbitals are far too compact.
- Four σ orbitals from the four $2s$ – and $2p_z$ –orbitals: two antibonding, two bonding.
- Four π orbitals from the four p_y and p_z orbitals.
- The energy order is difficult to predict.
- Finally we fill the MOs with the number of electrons that we have.
 - HOMO: Highest occupied MO
 - LUMO: Lowest unoccupied MO.

MOT for Diatomic Molecules

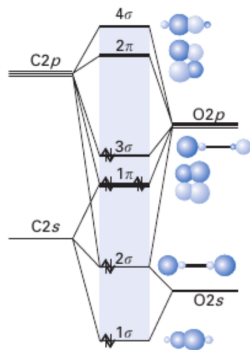
MOT for Heteronuclear Diatomic Molecules

- In the LCAO proposal for the MO

$$\psi = c_A\phi_A + c_B\phi_B$$

c_A and c_B is not the same anymore.

- In general, if A is more electronegative than B , $|c_A|^2 > |c_B|^2$ for bonding and $|c_A|^2 < |c_B|^2$ for antibonding.
- In the case of heteronuclear molecules, the AOs are different in energy \Rightarrow Bonding orbitals have lower energies, antibonding orbitals have higher energies due to weaker coupling.



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MOT for Polyatomic Molecules

Symmetry Adapted Linear Combinations (SALC)

- In forming the MO for polyatomic molecules, choosing symmetry-adapted linear combinations (SALCs) allows us to simplify the problem by using the symmetry properties of the molecule.
- The idea is to combine atomic orbitals in a way that respects the symmetry operations of the molecule.

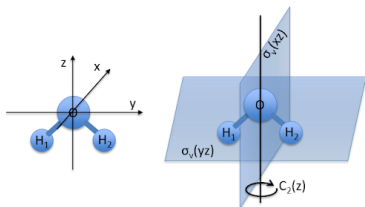
Mathematical Formulation

$$\Psi_i = \sum_j c_{ij} \phi_j$$

where Ψ_i is the SALC, ϕ_j are the atomic orbitals, and c_{ij} are the coefficients.

MOT for Polyatomic Molecules

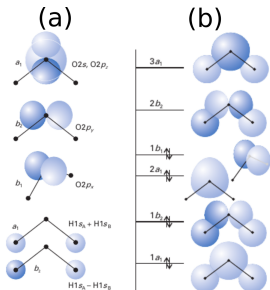
Example: H₂O Molecule



- H₂O has two mirror symmetries and a rotational symmetry by 180°, i.e. C_{2v} symmetry.
- Atomic orbitals of oxygen and hydrogen will combine to form molecular orbitals that respect this symmetry.

MOT for Polyatomic Molecules

Example: H₂O Molecule



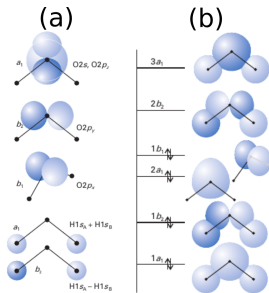
- Using H 1s, O 1s, O 2s and the three O 2p orbitals, construct three sets of states that have zero overlap \Rightarrow smaller matrices to deal with rather than a 6×6 matrix.
- Start with $O 2s$, $O 2p_x$, $O 2p_y$, $O 2p_z$, and two hydrogen orbitals:

$$\phi(A_1) = H1s_A + H1s_B$$

$$\phi(B_2) = H1s_A - H1s_B$$

MOT for Polyatomic Molecules

Example: H₂O Molecule



- Start with $O2s$, $O2p_x$, $O2p_y$, $O2p_z$, and two hydrogen orbitals:

$$\phi(A_1) = H1s_A + H1s_B$$

$$\phi(B_2) = H1s_A - H1s_B$$

- The SALCs for water are:

$$\psi(A_1) = c_1\phi(O2s) + c_2\phi(O2p_z) + c_3\phi(A_1)$$

$$\psi(B_1) = \phi(O2p_x)$$

$$\psi(B_2) = c_4\phi(O2p_y) + c_5\phi(B_2)$$

- Use these SALCs to construct the matrix, and obtain the MOs as shown in the Figure.

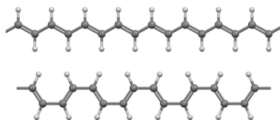
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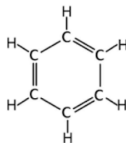
Conjugated π -Systems

Separation of π and σ systems

Polyacetylene



Benzene



- Special class of polyatomic molecules: polyenes and arenes.
- The π and σ systems are completely separate and non-interacting.

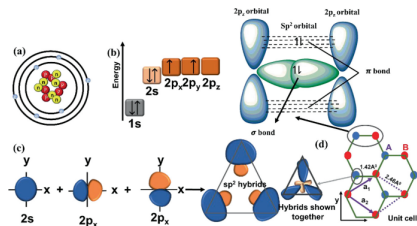
Conjugated π -Systems

A Famous Example: Graphene

- Graphene consists of a 2D honeycomb lattice of carbon atoms
- In-plane bonds: sp^2 hybridization

$$\psi_{sp^2} = \frac{1}{\sqrt{3}} (\phi_{2s} + \phi_{2p_x} + \phi_{2p_y})$$

- The π system: Superposition of $2p_z$ AOs ϕ_{2p_z} .



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The Hückel Approximation

Introduction

- Hückel theory provides a simple approach to study π -electron systems.
- In Huckel theory, only p -orbitals are considered for forming molecular orbitals.
- The Huckel secular determinant for a conjugated molecule is:

$$|H - ES| = 0$$

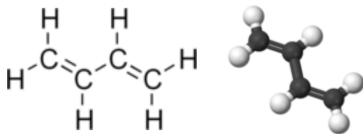
- The method makes a series of assumptions to simplify the calculations.

The Hückel Approximation

Assumptions

- All overlap integrals are set equal to zero unless the orbitals are the same and localized on the same atom: $S_{ij} = \delta_{ij}$.
- All diagonal elements of the Hamiltonian matrix are given the same value: $H_{ii} = \alpha$ with $\alpha < 0$
- All off-diagonal elements of the hamiltonian are set equal to zero except for those between neighbouring atoms, all of which are set equal to β .

Example: π MOs of 1,3-butadiene C_4H_6



The Hückel Approximation

Example: Butadiene

- We begin by constructing the secular determinant for butadiene with four carbon atoms in the π -system:

$$\det \begin{pmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{pmatrix} = 0$$

where:

- α is the Coulomb integral (on-site energy),
 - β is the resonance integral (hopping parameter),
 - E is the energy eigenvalue we are solving for.
- Each diagonal element corresponds to $\alpha - E$, and the off-diagonal elements represent nearest-neighbor interactions between atoms.

The Hückel Approximation

Example: Butadiene

- The solutions are: $E = \alpha \pm \frac{\sqrt{3 \pm \sqrt{5}}}{2} \beta$
- The orbitals are

$$\begin{aligned}\psi_1 &= 0.372\phi_A + 0.602\phi_B + 0.602\phi_C + 0.372\phi_D \\ \psi_2 &= -0.602\phi_A - 0.372\phi_B + 0.372\phi_C + 0.602\phi_D \\ \psi_3 &= -0.602\phi_A + 0.372\phi_B + 0.372\phi_C - 0.602\phi_D \\ \psi_4 &= 0.372\phi_A - 0.602\phi_B + 0.602\phi_C - 0.372\phi_D\end{aligned}$$

where A , B , C , and D refer to the four C atoms in the molecule.

- ϕ_1 , and ϕ_2 have a higher density in the bonding region and are therefore lower energy while ϕ_3 , and ϕ_4 have lower density and higher energy.

