

Lecture 34 — The H_2^+ Molecule Ion & LCAO-MO Theory

Reading: Engel 4th ed., Chapter 12 (Sections 12.1–12.3)

Learning Objectives

- Explain why chemical bonds form from a quantum-mechanical perspective
 - Set up the Schrödinger equation for H_2^+ and interpret its solutions
 - Construct molecular orbitals as linear combinations of atomic orbitals (LCAO)
 - Distinguish bonding (σ) and antibonding (σ^*) orbitals
 - Define and interpret the overlap, Coulomb, and resonance integrals
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1. Why Do Chemical Bonds Form?

A covalent bond forms when:

1. The total energy (electronic + nuclear repulsion) is **lower** than for separated atoms
2. This is achieved by electrons being shared between nuclei — occupying the **internuclear region**
3. The electron's potential energy is lowered (attracted to two nuclei instead of one) and the kinetic energy adjusts via a more diffuse wavefunction

[!NOTE] **Concept Check 34.1** In the formation of a chemical bond, the total energy must be lower than that of the separated atoms. Why does the accumulation of electron density between the two nuclei lead to a lower potential energy?

2. The H_2^+ Molecule Ion

The simplest molecule: one electron + two protons.

Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_A} - \frac{e^2}{4\pi\epsilon_0 r_B} + \frac{e^2}{4\pi\epsilon_0 R}$$

where r_A and r_B are electron-nucleus distances and R is the internuclear distance.

This problem can be solved exactly in ellipsoidal coordinates, giving:

- Equilibrium bond length: $R_e = 1.32 \text{ \AA} (2.49 a_0)$
 - Dissociation energy: $D_e = 2.79 \text{ eV}$
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3. LCAO-MO Approximation

The Trial Wavefunction

Construct MOs as linear combinations of atomic orbitals (AOs):

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

where $\phi_A = 1s_A$ and $\phi_B = 1s_B$ are hydrogen $1s$ orbitals centered on nuclei A and B.

Variational Calculation

Minimize E with respect to c_A and c_B . This gives the **secular equations**:

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

By symmetry ($H_{AA} = H_{BB}$), two solutions emerge:

Bonding Orbital (σ_{1s})

$$\psi_+ = \frac{1}{\sqrt{2(1+S)}}(\phi_A + \phi_B)$$

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

- Constructive interference in the internuclear region
- Electron density **accumulates** between nuclei
- Lower energy than individual AOs

Antibonding Orbital (σ_{1s}^*)

$$\psi_- = \frac{1}{\sqrt{2(1-S)}}(\phi_A - \phi_B)$$

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

- Destructive interference → **node** between nuclei
- Electron density is depleted from the internuclear region
- Higher energy than individual AOs

[!NOTE] **Concept Check 34.2** Describe the difference between a bonding Molecular Orbital (σ) and an antibonding Molecular Orbital (σ^*) in terms of electron density between the nuclei and the presence of nodes.

4. Key Integrals

Integral	Symbol	Definition	Physical Meaning
Overlap	$S = S_{AB}$	$\int \phi_A^* \phi_B d\tau$	Measure of AO overlap
Coulomb	H_{AA}	$\int \phi_A^* \hat{H} \phi_A d\tau$	Energy of electron in AO on nucleus A
Resonance (exchange)	H_{AB}	$\int \phi_A^* \hat{H} \phi_B d\tau$	Stabilization from delocalization

H_{AB} is **negative** (stabilizing) at equilibrium bond distance — this is what drives bonding.

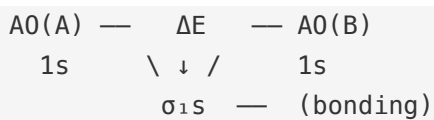
Overlap Integral

$$S(R) = e^{-R/a_0} \left(1 + \frac{R}{a_0} + \frac{R^2}{3a_0^2} \right)$$

$S = 1$ at $R = 0$, decreases exponentially, $S \rightarrow 0$ as $R \rightarrow \infty$.

5. Energy Diagram

σ^*_{1s} — (antibonding)
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The antibonding orbital is raised **more** than the bonding orbital is lowered (because the denominator $(1 - S) < (1 + S)$). This asymmetry has important consequences for understanding why He_2 doesn't form.

6. Symmetry Labels

Using the $D_{\infty h}$ point group for homonuclear diatomics:

MO	Symmetry label	Description
$\phi_A + \phi_B$	σ_g	Symmetric under inversion ($g = \text{gerade}$)
$\phi_A - \phi_B$	σ_u^*	Antisymmetric under inversion ($u = \text{ungerade}$)

The σ indicates cylindrical symmetry about the bond axis ($m_l = 0$).

Key Equations Summary

Equation	Expression
LCAO-MO	$\psi = c_A \phi_A + c_B \phi_B$
Bonding MO	$\psi_+ = (\phi_A + \phi_B) / \sqrt{2(1 + S)}$
Antibonding MO	$\psi_- = (\phi_A - \phi_B) / \sqrt{2(1 - S)}$
Secular determinant	$\det(H_{ij} - ES_{ij}) = 0$
Bonding energy	$E_+ = (H_{AA} + H_{AB}) / (1 + S)$

Recent Literature Spotlight

"The H_2^+ Molecular Ion Revisited: An Exact Benchmark for Approximations in Quantum Chemistry" M. Musiał, S. A. Kucharski, A. Gour, Journal of Chemical Theory and Computation, **2023**, 19, 4156–4167. [DOI](#)

H_2^+ , the simplest molecule (one electron, two protons), is the only molecular system whose electronic structure can be solved exactly. This benchmark study pushes coupled-cluster calculations on H_2^+ to extraordinary numerical accuracy, providing exact reference energies for calibrating all approximate electronic structure methods — from the LCAO-MO approach taught in this lecture to post-Hartree-Fock methods.

Practice Problems

1. **Overlap integral.** Calculate the overlap integral S for H_2^+ at $R = 2a_0$. Comment on whether this is "good" overlap.
 2. **Bond energy.** Explain qualitatively why $|E_- - H_{AA}| > |E_+ - H_{AA}|$ (antibonding destabilization exceeds bonding stabilization). What consequences does this have for He_2 ?
 3. **Symmetry labels.** Using the $D_{\infty h}$ character table, verify that $\phi_A + \phi_B$ transforms as σ_g and $\phi_A - \phi_B$ transforms as σ_u .
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Next lecture: Homonuclear Diatomic Molecules & MO Diagrams