

Week 7

Molecular Spectroscopy and Group Theory

7.1 Hydrogen Molecule

- 11/8: • Reviews what would happen if electrons were bosons.

– The wave function ψ of the lithium atom would be

$$\psi(123) = 1s\alpha(1) \vee 1s\alpha(2) \vee 1s\alpha(3)$$

– Reviews wedge products.

– Conclusion: All electrons could occupy the same orbital.

- A sodium atom (the nucleus and the electrons jointly) acts like a boson.

– At temperatures on the order of microkelvin, 10^{11} atoms have been placed in the same ground-state orbital.

– These substances are known as **Bose-Einstein condensates**.

– We use a magnetic field to confine the atoms to a harmonic potential. Since the atoms form a Gaussian curve at the bottom of said potential, they are all in the ground state (see Figure 3.3).

– Evaporative cooling and laser cooling allow you to reach such temperatures.

– Fermionic atoms cannot condense in such a way (because of the Pauli Exclusion Principle).

– Superconductivity is a condensation phenomena.

– Bose-Einstein condensates were predicted by Einstein in the 1930s but not experimentally verified until the 1990s.

– A very dilute gas was used here. In such a condition, the atoms feel the statistics force of the wedge product which forces them into such a state.

- Consider the Boron atom:

– It has 5 electrons.

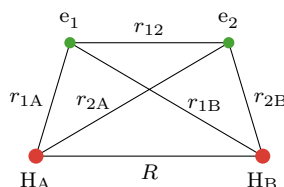
– It's electron configuration is $1s^2 2s^2 sp^1$.

– It's wave function is

$$\psi(12345) = 1s\alpha(1) \wedge 1s\beta(2) \wedge 2s\alpha(3) \wedge 2s\beta(4) \wedge 2p\alpha(5)$$

- Recall that this is not the exact wave function; this is still a product of hydrogenlike orbitals at the Hartree-Fock level.

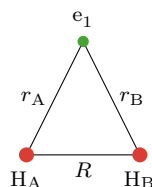
- More general wave functions can be used to obtain more accurate results.
- Consider the diatomic molecule H_2 .

Figure 7.1: H_2 distances.

- We have hydrogen atoms H_A and H_B , separated by a distance R .
- We have electrons e_1 and e_2 .
- The distance from object i to j where $i, j = \text{A}, \text{B}, 1, 2$ and $i \neq j$ is r_{ij} .
- Hamiltonian:

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{1}{r_{1\text{A}}} - \frac{1}{r_{1\text{B}}} - \frac{1}{r_{2\text{A}}} - \frac{1}{r_{2\text{B}}} + \frac{1}{r_{12}} + \frac{1}{R}$$

- This is pretty complicated.
- Thus, let's start with the hydrogen molecular ion (H_2^+).

Figure 7.2: H_2^+ distances.

- Hamiltonian:

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r_\text{A}} - \frac{1}{r_\text{B}} + \frac{1}{R}$$

- This *can* be solved exactly in cylindrical coordinates, but it's nasty.
- Thus, let's approximate with the following variational wave function (originally by Heitler and London in the 1960s).

$$\psi(1) = c_1 1s_\text{A} + c_2 1s_\text{B}$$

- Albeit simple, this wave function gives pretty good results.
- By the variational principle, $\mathbb{H}\vec{c} = E\mathbb{S}\vec{c}$, or

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

solves for E .

– We have that

$$\begin{aligned}H_{AA} &= H_{BB} = \int d\vec{r} 1s_A^* \hat{H} 1s_A = \int d\vec{r} 1s_B^* \hat{H} 1s_B \\H_{AB} &= H_{BA} = \int d\vec{r} 1s_A^* \hat{H} 1s_B = \int d\vec{r} 1s_B^* \hat{H} 1s_A \\S_{AA} &= S_{BB} = \int d\vec{r} 1s_A^* 1s_A = \int d\vec{r} 1s_B^* 1s_B \\S_{AB} &= S_{BA} = \int d\vec{r} 1s_A^* 1s_B = \int d\vec{r} 1s_B^* 1s_A\end{aligned}$$

– We can show that

$$\begin{aligned}H_{AA} &= H_{BB} = E_{1s} + J \\H_{AB} &= H_{BA} = E_{1s}S + K\end{aligned}$$

where E_{1s} is the energy of the $1s$ orbital of the hydrogen atom, J is the **Coulomb integral**

$$J = \int d\vec{r} 1s_A^* \left(-\frac{1}{r_B} + \frac{1}{R} \right) 1s_A$$

and K is the **exchange integral**

$$K = \int d\vec{r} 1s_B^* \left(-\frac{1}{r_B} + \frac{1}{R} \right) 1s_A$$

7.2 The Hydrogen Molecular Ion

11/10: • Continuing from last time, the determinant for the equation $\mathbb{H}\vec{c}_n = E_n S\vec{c}_n$ is

$$\begin{vmatrix} E_{1s} + J - E & E_{1s}S + K \\ E_{1s}S + K & E_{1s} + J - E \end{vmatrix}$$

- Therefore, the characteristic polynomial is a quadratic equation in E .
- Solving said quadratic gives us

$$E_{\pm} = E_{1s} + \frac{J \pm K}{1 \pm S}$$

where

$$J(R) = e^{-2R} \left(1 + \frac{1}{R} \right) \quad S(R) = e^{-R} \left(1 + R + \frac{R^2}{3} \right) \quad K(R) = \frac{S(R)}{R} - e^{-R}(1 + R)$$

- We then determine \vec{c}_n in the two different cases. But this yields

$$|c_1| = |c_2| = k$$

- Therefore,

$$\psi_{\pm} = k(1s_A \pm 1s_B)$$

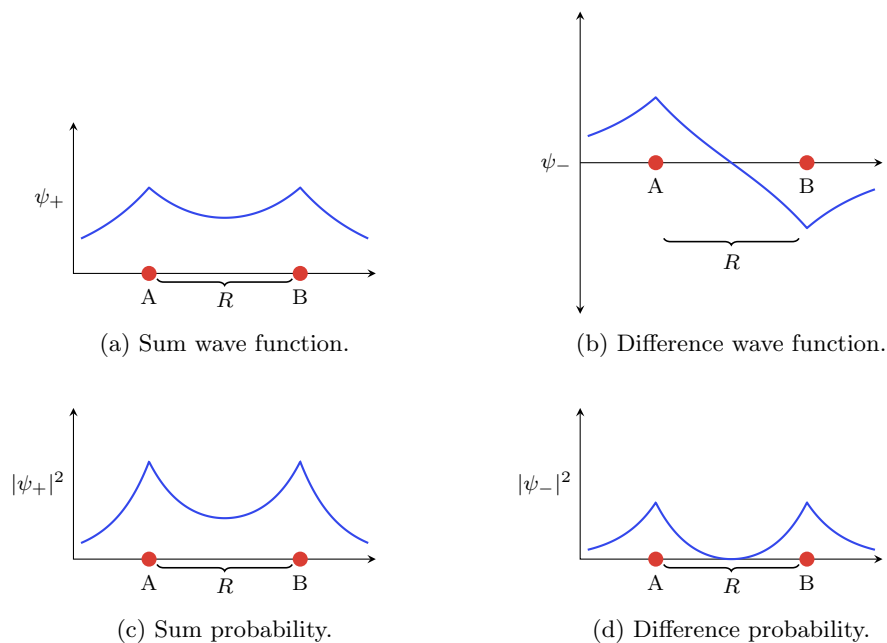


Figure 7.3: Hydrogen ion bonding.

- Note that in ψ_- , a node arises naturally from the quantum mechanics.
- Thus, ψ_+ is a bonding orbital and ψ_- is an antibonding orbital.
- We now consider the **potential energy surface** or **PES** of the molecule.

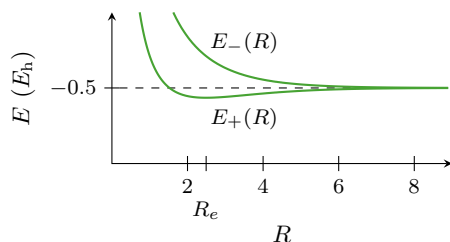


Figure 7.4: Potential energy surface of the hydrogen molecular ion.

- The x, y -axis units are Bohrs and Hartrees, respectively.
- The bound state only occurs in the bonding orbital; if the electron is excited to the antibonding orbital, the atoms will drift apart to ∞ to minimize energy.
- **Born-Oppenheimer approximation.**
 - Throughout this derivation, we neglected the kinetic energy of the nuclei.
 - Thus, technically the total Hamiltonian is

$$\hat{H}_{\text{tot}} = -\frac{\hbar^2}{2M}(\hat{\nabla}_A^2 + \hat{\nabla}_B^2) + \hat{H}_{\text{electr}}$$

where \hat{H}_{electr} is the Hamiltonian associated with Figure 7.2.

- We have assumed that the nuclei are fixed relative to the motion of the electrons. We can do this because $m_e/M \approx 10^{-3}$, i.e., the electrons travel much faster than the nuclei. Therefore, the kinetic energy of the electrons is more important.

- The wave functions of the nuclei (which do exist) are very sharp peaks, so the nuclei don't move much, so we may regard them as fixed.
- **Molecular orbital:** A linear combination of atomic orbitals. *Also known as MO.*
- Example (H_2):
 - $\psi_{\pm} = 1s_A \pm 1s_B$ (bonding and antibonding).
 - $\phi_{MO} = \phi_{1s_A} + \phi_{1s_B}$.
 - $\phi(12) = \phi_{MO}\alpha(1)\wedge\phi_{MO}\beta(2)$; thus, the MO diagram is connected back to the rigorous mathematics of Schrödinger.
- Filling rules: Fill the MOs that are lower in energy first.
- Example (C_2):
 - The MO diagram is identical to Figure III.17 from Labalme (2021) except that the σ_g corresponding to the $2p$ orbitals has higher energy than the π_u 's due to mixing.

7.3 Huckel Theory

11/12: • Reviews that diatomics with more electrons will have less mixing.

- **Bond order:** A measure of stability. *Given by*

$$BO = \frac{1}{2}[(\# \text{ of electrons in } BO_1) - (\# \text{ of electrons in } ABO_1)]$$

- For example, for C_2 , we will have $BO = \frac{1}{2}(8 - 4) = 2$.
- Huckel was a physicist/chemist from the 1930s who worked out the MO theory for conjugated molecules.
- Huckel's strategy.
 1. $\mathbb{H}\vec{c} = E\vec{S}\vec{c}$ becomes $\mathbb{H}\vec{c} = E\vec{c}$, where the only orbitals considered are the p_z orbitals.
 2. We let $\mathbb{S} = \mathbb{I}$, i.e., we assume all orbitals are orthonormal. $S_{ij} = \delta_{ij}$.
 3. $H_{ii} = \alpha$ (the energy of the electrons in p_z).
 - $H_{i,i+1} = H_{i+1,i} = \beta$ (interaction between adjacent p_z orbitals).
 - Everything else is zero!
- Example: Ethene.

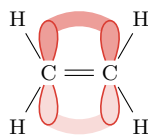


Figure 7.5: Ethene orbital diagram.

- The Hamiltonian matrix is

$$\mathbb{H} = \begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix}$$

- If we let $(\alpha - E)/\beta = x$, then

$$\begin{aligned} 0 &= \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} \\ &= \frac{1}{\beta^2} \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} \\ &= \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} \end{aligned}$$

- Thus, our characteristic polynomial is

$$\begin{aligned} 0 &= x^2 - 1 \\ &= (x + 1)(x - 1) \end{aligned}$$

so $x = \pm 1$.

- It follows from returning the substitution that $\alpha \pm \beta = E_{\mp}$.
- This yields the following energy diagram.

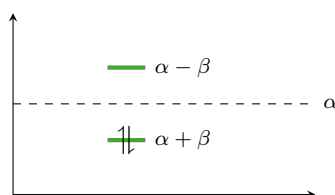


Figure 7.6: Ethene energy diagram.

- Note that the ground state MO is more stable than the 1-electron in each p_z orbital scenario; thus bonding occurs.
- It follows that

$$\psi_{\alpha+\beta} = 2p_{zA} + 2p_{zB} \qquad \psi_{\alpha-\beta} = 2p_{zA} - 2p_{zB}$$

■ Thus, $\psi_{\alpha+\beta}$ has π_u symmetry and $\psi_{\alpha-\beta}$ has π_g symmetry.

- Example: 1,3-butadiene.

- Our determinant here will be

$$\begin{aligned} 0 &= \begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} \\ &= \begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} \\ &= x^4 - 3x^2 + 1 \\ &= y^2 - 3y + 1 \\ y &= \frac{3 \pm \sqrt{5}}{2} \\ x &= \pm 1.618, \pm 0.618 \end{aligned}$$

- Thus, our energy diagram will be

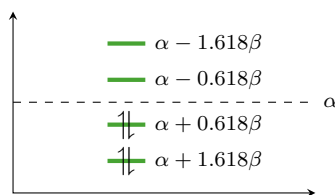


Figure 7.7: 1,3-butadiene energy diagram.

- This yields the bond order $BO = \frac{1}{2}(4 - 0) = 2$.
- Solving for the possible \vec{c} 's yields four wave function LCAOs analogous to the particle in a box wave functions (even function, odd function with one node, even function with two nodes, odd function with three nodes).
 - Thus, the Huckel approximation agrees with the approximation of four particles in a box.
- Example 3: 1,3,5-hexatriene.
 - Working out the determinant yields

$$\begin{aligned} 0 &= x^6 - 5x^4 + 6x^2 - 1 \\ &= y^3 - 5y^2 + 6y - 1 \end{aligned}$$

- Our energy diagram is as one might expect with 3 bonding orbitals and 3 antibonding orbitals.

7.4 Chapter 9: The Chemical Bond — Diatomic Molecules

From McQuarrie and Simon (1997).

- 11/8:
- Quantum mechanics was the first theory to explain why atoms combined to form a stable bond.
 - Since H_2^+ has the simplest chemical bond, we will discuss it in detail.
 - The ideas developed will be applicable to more complex molecules, motivating molecular orbitals.
 - Describes the Hamiltonian for H_2 , as in the discussion associated with Figure 7.1.
 - **Born-Oppenheimer approximation:** The approximation of neglecting the nuclear motion, allowing us to ignore $\nabla_{A,B}$ terms.
 - We can correct for the BO approximation using perturbation theory, but realistically we don't really need to (corrections are on the order of the mass ratio 10^{-3}).
 - **Molecular-orbital theory:** The method we will use to describe the bonding properties of molecules.
 - **Molecular orbital:** A single-electron wave function corresponding to a molecule.
 - Like we constructed atomic wave functions in terms of determinants involving atomic orbitals, we will construct molecular wave functions in terms of determinants involving molecular orbitals.
 - Note that H_2^+ is a stable, well-studied species in real life.
 - Although the Schrödinger equation for H_2^+ can be solved exactly within the BO approximation, the solutions are not easy to use and their mathematical form gives little physical insight into how and why bonding occurs.
 - Thus, we use approximate solutions that provide good physical insight and are in good agreement with experimental observations.

- As a first trial wave function $\psi(r_A, r_B; R)$, use

$$\psi_{\pm} = c_1 1s_A \pm c_2 1s_B$$

where $1s_{A,B}$ are the hydrogen atomic orbitals centered on nuclei A and B, respectively.

- By symmetry, $c_1 = c_2$ for H_2^+ .

- **LCAO molecular orbital:** A molecular orbital that is a linear combination of atomic orbitals.
- **Overlap integral:** The following integral. Denoted by S . Given by

$$S = \int d\mathbf{r} n l_A^* n l_B = \int d\mathbf{r} n l_B^* n l_A = \int d\mathbf{r} n l_A n l_B$$

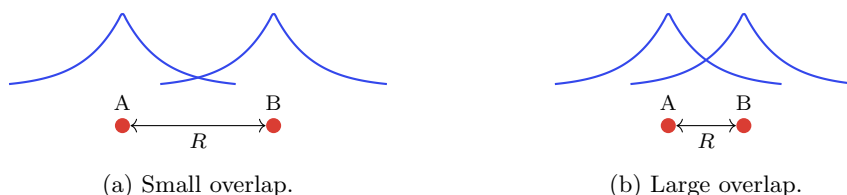


Figure 7.8: Overlap integral vs. internuclear distance.

- So named because it is only significant where there is a large overlap between the two hydrogenlike atomic orbitals.
- As $R \rightarrow 0$, $S \rightarrow 1$. As $R \rightarrow \infty$, $S \rightarrow 0$.
- The overlap integral when $nl = 1s$ can be evaluated analytically, giving

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

- It follows that the normalized ψ_{\pm} are

$$\psi_{\pm} = \frac{1}{\sqrt{2(1 \pm S)}} (1s_A \pm 1s_B)$$