Week 7

Molecular Spectroscopy and Group Theory

7.1 Hydrogen Molecule

11/8:
- Reviews what would happen if electrons were bozons.
  - 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 bozon.
  - 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.
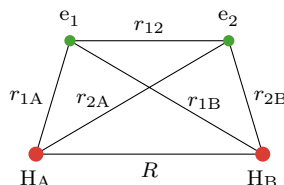- Consider the Boron atom:
  - It has 5 electrons.
  - It's electron configuration is $1s^2 2s^2 sp^1$.
  - It's wave function is
  $$\psi(12345) = 1s\alpha(1) \wedge 1s\beta(2) \wedge 2s\alpha(3) \wedge 2s\beta(4) \wedge 2p\alpha(5)$$
    - ▪ Recall that this is not the exact wave function; this is 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 $i, j = A, B, 1, 2$ and $i \neq j$ is r_{ij}.
 – Hamiltonian:
$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R}$$

- This is pretty complicated.

- Thus, let's start with the hydrogen molecular ion ($H_2{}^+$).
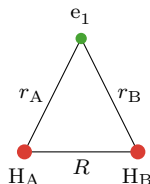
Figure 7.2: $H_2{}^+$ distances.

 – Hamiltonian:
$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$$

 – 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).
$$\psi(1) = c_1 1s_A + c_2 1s_B$$

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

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

solves for E.

– We have that

$$H_{\text{AA}} = H_{\text{BB}} = \int d\vec{r}\, 1s_{\text{A}}^* \hat{H} 1s_{\text{A}} = \int d\vec{r}\, 1s_{\text{B}}^* \hat{H} 1s_{\text{B}}$$

$$H_{\text{AB}} = H_{\text{BA}} = \int d\vec{r}\, 1s_{\text{A}}^* \hat{H} 1s_{\text{B}} = \int d\vec{r}\, 1s_{\text{B}}^* \hat{H} 1s_{\text{A}}$$

$$S_{\text{AA}} = S_{\text{BB}} = \int d\vec{r}\, 1s_{\text{A}}^* 1s_{\text{A}} = \int d\vec{r}\, 1s_{\text{B}}^* 1s_{\text{B}}$$

$$S_{\text{AB}} = S_{\text{BA}} = \int d\vec{r}\, 1s_{\text{A}}^* 1s_{\text{B}} = \int d\vec{r}\, 1s_{\text{B}}^* 1s_{\text{A}}$$

– We can show that

$$H_{\text{AA}} = H_{\text{BB}} = E_{1s} + J$$
$$H_{\text{AB}} = H_{\text{BA}} = E_{1s}\mathbb{S} + K$$

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

$$J = \int d\vec{r}\, 1s_{\text{A}}^* \left(-\frac{1}{r_{\text{B}}} + \frac{1}{R} \right) 1s_{\text{A}}$$

and K is the **exchange integral**

$$K = \int d\vec{r}\, 1s_{\text{B}}^* \left(-\frac{1}{r_{\text{B}}} + \frac{1}{R} \right) 1s_{\text{A}}$$

7.2   The Hydrogen Molecular Ion

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

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

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

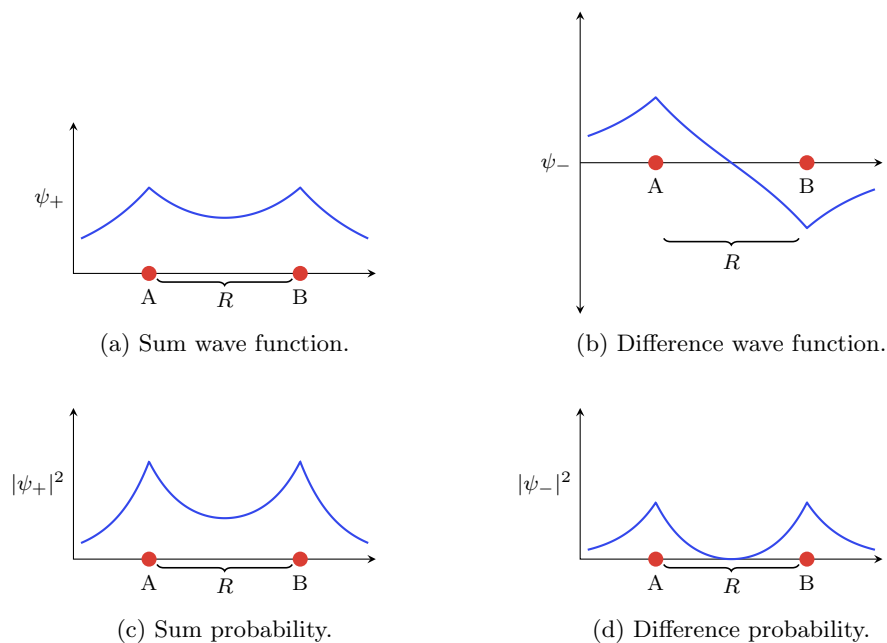$$|c_1| = |c_2| = k$$

- Therefore,

$$\psi_{\pm} = k(1s_{\text{A}} \pm 1s_{\text{B}})$$

(a) Sum wave function.

(b) Difference wave function.

(c) Sum probability.

(d) Difference probability.

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.
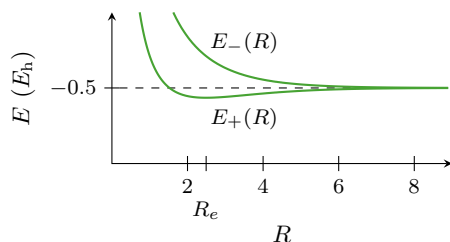

Figure 7.4: Potential energy surface of the hydrogen molecular ion.

- 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

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

where $\hat{H}_{\text{electr}}$ 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. $\mathbb{H}\vec{c} = E\mathbb{S}\vec{c}$ 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!
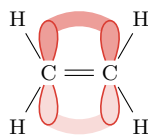
- Example: Ethene.

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 $\alpha \pm \beta = E_{\mp}$.
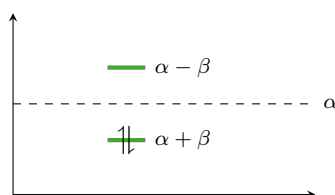- This yields the following energy diagram.

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

$$
\psi_{\alpha+\beta} = 2p_{z_A} + 2p_{z_B} \qquad\qquad \psi_{\alpha-\beta} = 2p_{z_A} - 2p_{z_B}
$$

  ■ 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

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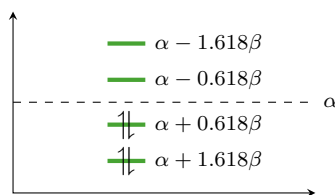$$

- 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

    $$0 = x^6 - 5x^4 + 6x^2 - 1$$
    $$= y^3 - 5y^2 + 6y - 1$$

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

7.4 Office Hours (Mazziotti)

- How does the asymptotic analysis guarantee us the $n = 1$ solution, from Problem Set 5.1e?

    - $n = 1$ dominates in the asymptotic analysis, especially among the ground states.

- Math that we're using?

    - We're doing a lot of linear algebra, ordinary differential equations, and partial differential equations (boundary condition differential equations). Typically eliptic boundary conditions.
    - Eigenvalue equations, determinants, etc.
    - We're in a Hilbert space. Hilbert spaces are subsets of the Banach spaces, so all of that linear algebra applies.
    - Differential equations in a subspace can be rewritten as eigenvalue equations?
    - Ties into real analysis and complex analysis with $e^{i\phi}$.
    - The Grassmann algebra is a piece of classical mathematics that plays in.
    - Point groups and spin groups fall under abstract algebra; more specifically, Lie algebra.

7.5 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.

- We seek to find $E_\pm$ by taking the quotient the integrals $\int d\mathbf{r}\, \psi_\pm^* \hat{H} \psi_\pm$ and $\int d\mathbf{r}\, \psi_\pm^* \psi_\pm$.

- Considering $\int d\mathbf{r}\, \psi_\pm^* \psi_\pm$ first, we are lead to define the **overlap integral**.

- **Overlap integral**: The following integral, which is only significant where there is a large overlap between the two hydrogenlike atomic orbitals. *Denoted by S. Given by*

$$S = \int d\mathbf{r}\, nl_A^* nl_B = \int d\mathbf{r}\, nl_B^* nl_A = \int d\mathbf{r}\, nl_A nl_B$$

(a) Small overlap.   (b) Large overlap.

Figure 7.8: Overlap integral vs. internuclear distance.

  - As $R \to 0$, $S \to 1$. As $R \to \infty$, $S \to 0$.

- The overlap integral when $nl = 1s$ can be evaluated analytically, giving

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

- The overlap integral allows us to express $\int d\mathbf{r}\, \psi_\pm^* \psi_\pm$ in the following convenient form.

$$\int d\mathbf{r}\, \psi_+^* \psi_+ = \int d\mathbf{r}\, (1s_A^* + 1s_B^*)(1s_A + 1s_B)$$
$$= \int d\mathbf{r}\, 1s_A^* 1s_A + \int d\mathbf{r}\, 1s_A^* 1s_B + \int d\mathbf{r}\, 1s_B^* 1s_A + \int d\mathbf{r}\, 1s_B^* 1s_B$$
$$= 1 + S + S + 1$$
$$= 2(1 + S)$$

- It follows that the normalized $\psi_\pm$ are

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

11/14:
- We now look to evaluate the integral $\int d\mathbf{r}\, \psi_+^* \hat{H} \psi_+$.

- To begin, we have that

$$\int d\mathbf{r}\, \psi_+^* \hat{H} \psi_+ = \int d\mathbf{r}\, (1s_A^* + 1s_B^*) \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right)(1s_A + 1s_B)$$
$$= \int d\mathbf{r}\, (1s_A^* + 1s_B^*) \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) 1s_A$$
$$+ \int d\mathbf{r}\, (1s_A^* + 1s_B^*) \left(-\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) 1s_B$$
$$= \int d\mathbf{r}\, (1s_A^* + 1s_B^*) \left(E_{1s} - \frac{1}{r_B} + \frac{1}{R} \right) 1s_A$$
$$+ \int d\mathbf{r}\, (1s_A^* + 1s_B^*) \left(E_{1s} - \frac{1}{r_A} + \frac{1}{R} \right) 1s_B$$
$$= \int d\mathbf{r}\, \left(E_{1s} - \frac{1}{r_B} + \frac{1}{R} \right) 1s_A^* 1s_A + \int d\mathbf{r}\, \left(E_{1s} - \frac{1}{r_B} + \frac{1}{R} \right) 1s_B^* 1s_A$$
$$+ \int d\mathbf{r}\, \left(E_{1s} - \frac{1}{r_B} + \frac{1}{R} \right) 1s_A^* 1s_B + \int d\mathbf{r}\, \left(E_{1s} - \frac{1}{r_B} + \frac{1}{R} \right) 1s_B^* 1s_B$$
$$= E_{1s} \cdot 1 + \int d\mathbf{r}\, \left(-\frac{1}{r_B} + \frac{1}{R} \right) 1s_A^* 1s_A + E_{1s} \cdot S + \int d\mathbf{r}\, \left(-\frac{1}{r_B} + \frac{1}{R} \right) 1s_B^* 1s_A$$
$$+ E_{1s} \cdot 1 + \int d\mathbf{r}\, \left(-\frac{1}{r_B} + \frac{1}{R} \right) 1s_A^* 1s_B + E_{1s} \cdot S + \int d\mathbf{r}\, \left(-\frac{1}{r_B} + \frac{1}{R} \right) 1s_B^* 1s_B$$
$$= 2E_{1s}(1 + S)$$
$$+ \int d\mathbf{r}\, \left(-\frac{1}{r_B} + \frac{1}{R} \right) 1s_A^* 1s_A + \int d\mathbf{r}\, \left(-\frac{1}{r_B} + \frac{1}{R} \right) 1s_B^* 1s_A$$
$$+ \int d\mathbf{r}\, \left(-\frac{1}{r_B} + \frac{1}{R} \right) 1s_A^* 1s_B + \int d\mathbf{r}\, \left(-\frac{1}{r_B} + \frac{1}{R} \right) 1s_B^* 1s_B$$

where $E_{1s} = -E_h/2$ is the ground-state energy of the hydrogen atom (the energy corresponding to the $1s_A$ wave function).

- **Coulomb integral**: The following integral, which reflects both the charge density of the electron about nucleus A interacting with nucleus B via the Coulumb potential and the internuclear repulsion. *Denoted by J. Given by*

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

- **Exchange integral**: The following integral. *Also known as* **resonance integral**. *Denoted by* K. *Given by*

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

  - The exchange integral describes a purely quantum-mechanical effect; it has no analogy in classical mechanics.

- Using the definitions of the Coluomb and exchange integrals, we have that

$$\int d\mathbf{r}\, \psi_+^* \hat{H} \psi_+ = 2E_{1s}(1 + S) + 2J + 2K$$

- We can now determine a final expression for the energy E_+ corresponding to ψ_+.

$$\begin{aligned}
E_+ &= \frac{\int d\mathbf{r}\, \psi_+^* \hat{H} \psi_+}{\int d\mathbf{r}\, \psi_+^* \psi_+} \\
&= \frac{2E_{1s}(1 + S) + 2J + 2K}{2(1 + S)} \\
&= E_{1s} + \frac{J + K}{1 + S}
\end{aligned}$$

- The Coulomb and exchange integrals can be evaluated analytically, giving

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

  - Note that since the Coulomb integral is always positive, the exchange integral is entirely responsible for the existence of the chemical bond in $H_2{}^+$.
  - This highlights the importance of the quantum-mechanical nature of the chemical bond.

- **Bonding orbital**: A state that exhibits a stable chemical bond.

  - Example: ψ_+.

- **Antibonding orbital**: A state that leads to a repulsive interaction between the two nuclei for all internuclear distances.

  - Example: ψ_-.

- The bonding orbital $\psi_b = \psi_+$ describes the ground state of $H_2{}^+$, while the antibonding orbital $\psi_a = \psi_-$ describes an excited state.

- Note that we have only found two molecular orbitals (as opposed to the infinitely many hydrogenlike atomic orbitals) because we used a trial wave function that was the linear combination of only two atomic orbitals. We could use longer linear combinations to find more molecular orbitals, but for pedagogical reasons, we will limit ourselves to two for now.

- "Because ψ_b is the molecular orbital corresponding to the ground-state energy of $H_2{}^+$, we can describe the ground state of H_2 by placing two electrons with opposite spins in ψ_b, just as we placed two electrons in a $1s$ atomic orbital to describe the helium atom" (McQuarrie & Simon, 1997, p. 336).

- This leads to the Slater determinantal wave function

$$\psi = \frac{1}{\sqrt{2!}} \begin{vmatrix} \psi_b \alpha(1) & \psi_b \beta(1) \\ \psi_b \alpha(2) & \psi_b \beta(2) \end{vmatrix}$$

for H_2.

- As before, the spatial and spin parts of this two-electron wave function separate.

- It follows that the spatial molecular wave function is

$$\psi_{\text{MO}} = \psi_{\text{b}}(1)\psi_{\text{b}}(2)$$
$$= \frac{1}{2(1+S)}[1s_{\text{A}}(1) + 1s_{\text{B}}(1)][1s_{\text{A}}(2) + 1s_{\text{B}}(2)]$$

- **Linear combination of atomic orbitals-molecular orbitals method**: The method of constructing molecular wave functions by taking the product of molecular orbitals, which are in turn linear combinations of atomic orbitals. *Also known as* **LCAO-MO method**.

    - This is how we constructed ψ_{MO}, above.

- Knowing that ψ_{MO} is normalized, we have that

$$E_{\text{MO}} = \int d\mathbf{r}_1 \, d\mathbf{r}_2 \, \psi_{\text{MO}}^*(1,2)\hat{H}\psi_{\text{MO}}(1,2)$$

- **σ orbital**: An orbital that is symmetric about the internuclear axis.

    - Both $\psi_{\pm}$ are σ orbitals.
    - Molecular orbitals constructed from $1s$ orbitals are denoted by $\sigma 1s$.

- Distinguishing between $\sigma 1s$ bonding and antibonding orbitals.

    - We may let $\sigma 1s$ refer to ψ_+ and $\sigma^* 1s$ refer to ψ_-.
    - We may let $\sigma_g 1s$ refer to ψ_+ (g being short for "gerade" [the German word for even] since ψ_+ does not change sign under inversion) and $\sigma_u 1s$ refer to ψ_- (u being short for "ungerade" [the German word for odd] since ψ_- does change sign under inversion).
    - McQuarrie and Simon (1997) will favor the latter notation.

- $\sigma 2s$ molecular orbitals.

    - Of the form $2s_{\text{A}} \pm 2s_{\text{B}}$.
    - Have radial nodes about each nuclei (owing to the structure of the $2s$ hydrogenlike atomic orbital) in addition to the possible planar node in the middle of the molecule.
    - Have higher energies than $\sigma 1s$ MOs since they're associated with higher energy atomic orbitals. This can be demonstrated rigorously the same way we calculated the energies for the $\sigma 1s$ MOs.
    - In terms of energy, $\sigma_g 1s < \sigma_u 1s < \sigma_g 2s < \sigma_u 2s$.

- $2p$ molecular orbitals.

    - Choose the internuclear axis to be the z-axis.
    - $2p_{z_{\text{A}}} \pm 2p_{z_{\text{B}}}$ are cylindrically symmetric about the internuclear axis and are therefore $\sigma_u 2p_z$ and $\sigma_g 2p_z$ orbitals, respectively.
    - $2p_{x,y_{\text{A}}} \pm 2p_{x,y_{\text{B}}}$ are **π orbitals**, denoted $\pi_u 2p_{x,y}$ and $\pi_g 2p_{x,y}$, respectively.
    - $\pi_u 2p_x, \pi_u 2p_y$ and $\pi_g 2p_x, \pi_g 2p_y$ are degenerate pairs of orbitals since they are identical except for their spatial orientation.

- **π orbital**: A molecular orbital with one nodal plane that contains the internuclear axis.

- From Li_2 through N_2, the energy order is

$$\sigma_g 2s < \sigma_u 2s < \pi_u 2p_{x,y} < \sigma_g 2p_z < \pi_g 2p_{x,y} < \sigma_u 2p_z$$

- From O_2 through F_2, the energy order is

$$\sigma_g 2s < \sigma_u 2s < \sigma_g 2p_z < \pi_u 2p_{x,y} < \pi_g 2p_{x,y} < \sigma_u 2p_z$$

- Diatomic helium does not exist since the bonding and antibonding electrons cancel each other out, leaving only repulsive nuclei.

  - Bond order formalizes this notion.
  - Note that in 1993, Gentry and co. reported spectroscopic observations of He_2 in a gas-phase sample of helium of temperature $0.001\,K$, possessing by far the weakest chemical bond known.

- Note that since there is little difference between the electron densities of core electron-derived molecular orbitals, we need only consider electrons in the valence shell when discussing chemical bonding.

- We denote the filled $n = 1$ shell by K, e.g., the ground state electron configuration of Li_2 is $KK(\sigma_g 2s)^2$.

- MO theory accurately predicts that O_2 is paramagnetic.

  - MO theory also predicts bond orders of $2.5, 2, 1.5, 1$ for O_2^+, O_2, O_2^-, O_2^{2-}, respectively. This would suggest that bond length increases and bond energy decreases down this list, as we do indeed observe experimentally.

- McQuarrie and Simon (1997) provides data on the ground-state electron configuration, bond order, bond length, and bond energy for the homonuclear diatomics of lithium through neon.

- **Ionization energy**: The energy required to eject an electron from a molecule.

- **Photoelectron spectroscopy**: The measurement of the energies of the electrons ejected by radiation incident on gaseous molecules.

  - Goes through how PES supports MO theory, as on Labalme (2021, p. 56).

- **Heteronuclear diatomic molecule**: A diatomic molecule in which the two nuclei are different.

- For heteronuclear diatomics whose constituent atoms' atomic numbers differ by 1 or 2, the scheme we used for homonuclear diatomics is good enough.

- For heteronuclear diatomics whose constituent atoms' atomic numbers differ greatly (e.g., HF), we need a new scheme.

  - Noting that the energy of the $1s$ atomic orbital of H is similar to the energy of the $2p$ atomic orbitals of F, we look for constructive and destructive interference and find that $1s_H$ and $2p_{z_F}$ interact nicely.
  - Thus, a first approximation the molecular orbital would be $\psi = c_1 1s_H + c_2 2p_{z_F}$.
  - Note that both MOs have σ symmetry.

- The scheme presented thus far is the simplest possible.

- More generally, we may create trial wave functions that include more and orbitals, minimizing the coefficients with the variational method along the way, until we reach the Hartree-Fock limit.

- **SCF-LCAO-MO wave function**: A wave function obtained from molecular orbitals that are linear combinations of atomic orbitals whose coefficients are determined by a self-consistent field method.

  - Such orbitals, obtained from many atomic orbitals, cannot be meaningfully classified as $\sigma 2s$ or $\pi 2p$, for example, so we classify them as the first σ_g orbital ($1\sigma_g$), the first σ_u orbital ($1\sigma_u$), and so on and so forth.
  - An SCF-LCAO-MO is only the same as a Hartree-Fock orbital if the SCF-LCAO-MO contains enough terms to reach the Hartree-Fock limit.

- **Hartree-Fock-Roothaan method**: The method for determining a SCF-LCAO-MO wave function.

- McQuarrie and Simon (1997) lists data on the Hartree-Fock limit vs. experimental calculations.

- Molecular term symbols.

- Excited states of molecules.

  – Consider H_2 with one electron in the $\sigma_g 1s$ orbital and one electron in the $\sigma_g 2s$ orbital. This species has a slightly longer bond length than ground state H_2.

7.6 Chapter 10: Bonding in Polyatomic Molecules

From McQuarrie and Simon (1997).

11/15:
- Consider BeH_2.

  – The two $Be-H$ bonds are equivalent with an angle of $180°$ between them
  – MOs are formed from orbitals that are similar in energy, so in addition to the $H(1s)$ and $Be(2s)$, throw in the energetically close $Be(2p)$.
  – We also add in a $2p$ orbital because we need the resultant molecular orbitals to point in opposite directions so as to explain the linear structure of the molecule, and directionality is not something the spherically symmetric $2s$ orbital can provide.
  – Thus, choose
  $$\psi_{Be-H} = c_1 \psi_{Be(2s)} + c_2 \psi_{Be(2p)} + c_3 \psi_{H(1s)}$$
  – The first two terms in the above linear combination can be thought of as representing a new **hybrid** "orbital" on beryllium.
  – The normalized sp hybrid orbitals are given by
  $$\psi_{sp} = \frac{1}{\sqrt{2}} (2s \pm 2p_z)$$
  where the z-axis is defined to be the internuclear $H-Be-H$ axis.
    ■ Note that sp hybrid orbitals concentrate electron density in one specific direction since the sign of the $2p$ wave function is different in the two direction ($\pm z$) but the sign of the $2s$ wave function is everywhere positive.

- **Hybrid orbital**: A linear combination of atomic orbitals on the same atom.

- The normalized sp^2 hybrid orbitals are
$$\psi_1 = \frac{1}{\sqrt{3}} 2s + \sqrt{\frac{2}{3}} 2p_z \qquad\qquad \psi_2 = \frac{1}{\sqrt{3}} 2s - \frac{1}{\sqrt{6}} 2p_z + \frac{1}{\sqrt{2}} 2p_x$$
$$\psi_3 = \frac{1}{\sqrt{3}} 2s - \frac{1}{\sqrt{6}} 2p_z - \frac{1}{\sqrt{2}} 2p_x$$

- The normalized sp^3 hybrid orbitals are
$$\psi_1 = \frac{1}{2}(2s + 2p_x + 2p_y + 2p_z) \qquad\qquad \psi_2 = \frac{1}{2}(2s - 2p_x - 2p_y + 2p_z)$$
$$\psi_3 = \frac{1}{2}(2s + 2p_x - 2p_y - 2p_z) \qquad\qquad \psi_4 = \frac{1}{2}(2s - 2p_x + 2p_y - 2p_z)$$

- Bonding vs. lone pair electrons: H_2O.

- We could form bond orbitals out of the singly occupied $p_{y,z}$ orbitals of O, but this would predict a bond angle of 90°. Thus, we need hybrid orbitals.
- The bond angle in water is between that predicted using sp^2 hybrid orbitals and $2p$ orbitals.
- Since oxygen has two bonding and four lone pair electrons, we let

$$\psi = c_1 2s + c_2 2p_y + c_3 2p_z$$

- Determining the coefficients such that two orthogonal orbitals directed at an angle of 104.5° are generated yields

$$\psi_1 = 0.45 \cdot 2s + 0.71 \cdot 2p_y + 0.55 \cdot 2p_z \qquad \psi_2 = 0.45 \cdot 2s - 0.71 \cdot 2p_y + 0.55 \cdot 2p_z$$

- Physical interpretation of the normalization constants: c_i^2 is the fractional character of the ith orbital[1].
- ψ_1, ψ_2 accommodate the bonding electrons. Our unused hybrid orbital and unused $2p_x$ orbital accommodate the lone pair electrons as a linear combination (since symmetry necessitates that the two lone pair orbitals be equivalent).

- Why BeH_2 is linear but H_2O is bent.

  - Using a more general LCAO-MO with all relevant orbitals and solving yields a set of molecular orbitals.
  - Upon bending, the degeneracy of the π orbitals is lifted as the hydrogen orbitals move to intersect more with one specific side of the molecule.
  - Such changes are summarized by a **Walsh correlation diagram** (see Labalme (2021, p. 65)).
  - We want the minimal energy for however many electrons we have, and with the additional electrons of H_2O, it is more energetically favorable to bend then to remain linear.

- **Walsh correlation diagram**: A plot of the energy of a molecular orbital as a function of a systematic change in molecular geometry.

- **σ-bond framework**: The collection of all σ bonds in a molecule.

- **π-electron approximation**: The approximation of the delocalized π electrons of a conjugated polyene or benzene as moving in some fixed, effective, electrostatic potential due to the electrons in the σ framework.

  - Note that this can be rigorously developed from the Schrödinger equation.
  - We may write the wave function of the π orbital of ethene as

$$\psi_\pi = c_1 2p_{z_A} + c_2 2p_{z_B}$$

  - The diagonal entries in the corresponding secular determinant are **Coulomb integrals** and the off-diagonal entries are **resonance integrals**.
  - To evaluate the determinant, we either need to specify the Hamiltonian or come up with another approximation for the integrals.

- **Hückel molecular-orbital theory**: An approximation composed of the following three assertions.

  1. The overlap integrals $S_{ij} = \delta_{ij}$.
  2. All of the Coulomb integrals are assumed to be the same for all carbon atoms and are commonly denoted by α.

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[1] Think s-character, p-character.

3. The resonance integrals involving nearest-neighbor carbon atoms are assumed to be the same and are denoted by β.

- Once we calculate E from the reworked secular determinant, we plug in experimental values for α and β and go from there (no effective Hamiltonian needed).

- McQuarrie and Simon (1997) covers the same butadiene derivation from class.

  - Addendum: The total π-electronic energy of butadiene is

  $$E_\pi = 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta)$$
  $$= 4\alpha + 4.472\beta$$

  - Comparing this energy to the energy of two ethene molecules gives us the **delocalization energy**.
  - The molecular orbitals are given and their schematic diagrams drawn.

- McQuarrie and Simon (1997) treats benzene the same way. See Nocera Lectures 6-7 from Labalme (2021).