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.

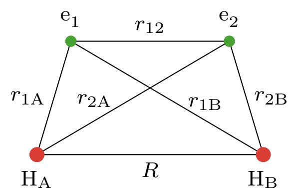

Figure 7.1: H_2 distances.

  - 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 $i, j = \mathrm{A}, \mathrm{B}, 1, 2$ and $i \neq j$ is r_{ij}.
  - Hamiltonian:
$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{1}{r_{1\mathrm{A}}} - \frac{1}{r_{1\mathrm{B}}} - \frac{1}{r_{2\mathrm{A}}} - \frac{1}{r_{2\mathrm{B}}} + \frac{1}{r_{12}} + \frac{1}{R}$$

- This is pretty complicated.

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

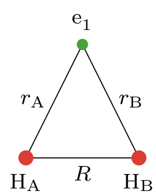

Figure 7.2: ${H_2}^+$ distances.

  - Hamiltonian:
$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r_\mathrm{A}} - \frac{1}{r_\mathrm{B}} + \frac{1}{R}$$
  - 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).
$$\psi(1) = c_1 1s_\mathrm{A} + c_2 1s_\mathrm{B}$$
    - Albeit simple, this wave function gives pretty good results.
  - By the variational principle, $\mathbb{H}\vec{c} = E\mathbb{S}\vec{c}$, or
$$\begin{vmatrix} H_\mathrm{AA} - ES_\mathrm{AA} & H_\mathrm{AB} - ES_\mathrm{AB} \\ H_\mathrm{BA} - ES_\mathrm{BA} & H_\mathrm{BB} - ES_\mathrm{BB} \end{vmatrix} = 0$$

    solves for E.

- We have that

$$
\begin{aligned}
H_{\text{AA}} = H_{\text{BB}} &= \int \mathrm{d}\vec{r}\, 1s_{\text{A}}^* \hat{H} 1s_{\text{A}} = \int \mathrm{d}\vec{r}\, 1s_{\text{B}}^* \hat{H} 1s_{\text{B}} \\
H_{\text{AB}} = H_{\text{BA}} &= \int \mathrm{d}\vec{r}\, 1s_{\text{A}}^* \hat{H} 1s_{\text{B}} = \int \mathrm{d}\vec{r}\, 1s_{\text{B}}^* \hat{H} 1s_{\text{A}} \\
S_{\text{AA}} = S_{\text{BB}} &= \int \mathrm{d}\vec{r}\, 1s_{\text{A}}^* 1s_{\text{A}} = \int \mathrm{d}\vec{r}\, 1s_{\text{B}}^* 1s_{\text{B}} \\
S_{\text{AB}} = S_{\text{BA}} &= \int \mathrm{d}\vec{r}\, 1s_{\text{A}}^* 1s_{\text{B}} = \int \mathrm{d}\vec{r}\, 1s_{\text{B}}^* 1s_{\text{A}}
\end{aligned}
$$

- We can show that

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

  where J is the **Coulomb integral**

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

  and K is the **exchange integral**

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

7.2 Chapter 9: The Chemical Bond — Diatomic Molecules

From McQuarrie and Simon (1997).

- 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

$$\psi_{\pm} = c_1 1s_{\mathrm{A}} \pm c_2 1s_{\mathrm{B}}$$

  where $1s_{\mathrm{A,B}}$ 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* $\boldsymbol{S}$. *Given by*

$$S = \int \mathrm{d}\mathbf{r}\, nl_{\mathrm{A}}^* nl_{\mathrm{B}} = \int \mathrm{d}\mathbf{r}\, nl_{\mathrm{B}}^* nl_{\mathrm{A}} = \int \mathrm{d}\mathbf{r}\, nl_{\mathrm{A}} nl_{\mathrm{B}}$$

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

Figure 7.3: 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 $R \to 0$, $S \to 1$. As $R \to \infty$, $S \to 0$.
- The overlap integral when $nl = 1s$ can be evaluated analytically, giving

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

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

$$\psi_{\pm} = \frac{1}{\sqrt{2(1 \pm S)}}(1s_{\mathrm{A}} \pm 1s_{\mathrm{B}})$$