

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.

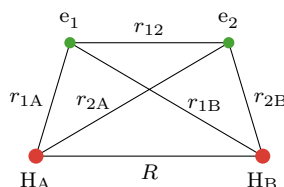
– It's electron configuration is $1s^2 2s^2 sp^1$.

– 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.

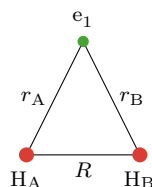
- More general wave functions can be used to obtain more accurate results.
- Consider the diatomic molecule H_2 .

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 $i, j = A, B, 1, 2$ 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

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

– We can show that

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

where 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**

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