

Week 6

Multi-electron Atoms and Molecules

6.1 Many-electron Atoms and Molecules

- 11/1: • Picking up from last time, since $Z = 2$ for helium,

$$\left. \frac{dE}{d\lambda} \right|_{\lambda=0} = \frac{5}{8}Z = \frac{5}{4}$$

- Additionally,

$$E_{\text{He}} = -Z^2 + \frac{5}{8}Z = -4 + \frac{5}{4} = -2.75 \text{ a.u.}$$

- The first equality is the ground state energy of two-electron atoms or ions.

- Summary:

- Zeroth-order Perturbation Theory approximation: $E_0 = -4 \text{ a.u.}$
- First-order approximation: $E_0 + E' = -2.75 \text{ a.u.}$
- Second-order: $E_0 + E' + \frac{1}{2}E'' = -2.9077 \text{ a.u.}$
- Thirteenth-order: $-2.903\,724\,33 \text{ a.u.}$

- Variational calculation of Helium:

- Simplest: $\psi_0(12) = 1s(1)1s(2)$. Gives $E = -2.75 \text{ a.u.}$
- Trial ψ with one parameter: $\psi_0(1,2) = \tilde{1}s(1)\tilde{1}s(2)$, where $\tilde{1}s(1) = \sqrt{Z^3/\pi}e^{-Zr_1}$. Energy: $E = -2.8477 \text{ a.u.}$

- Ionization energy.

- Simplest approximation:

$$\begin{aligned} \text{IE} &= E_{\text{He}^+} - E_{\text{He}} \\ &= -2 - (-2.75) \\ &= 0.75 \text{ a.u.} \\ &= 1969 \text{ kJ/mol} \end{aligned}$$

- Exact number:

$$\begin{aligned} \text{IE} &= E_{\text{He}^+} - E_{\text{He}} \\ &= -2 - (-2.903\,724) \\ &= 0.9033 \text{ a.u.} \\ &= 2372 \text{ kJ/mol} \end{aligned}$$

- Optimal orbitals (Hartree-Fock): Optimizing the orbitals to lower the energy as much as possible.

- $\psi(12) = \phi(r_1)\phi(r_2)$.
- The orbital energies converge to

$$E_{\text{HF}} = -2.8617 \text{ a.u.}$$

- Allow the $\psi(12)$ to move beyond a simple product of orbitals (Hylleras (1930)).

- $\psi(r_1, r_2, r_{12}) = e^{-Zr_1}e^{-Zr_2}(1 + cr_{12})$.
- Accounting for the electron-electron repulsion (the **electron correlation energy**) gives us an energy much better than the Hartree-Fock calculation:

$$E = -2.8913 \text{ a.u.}$$

- Pekeris (1959): Did a variational calculation with 1078 parameters. Was working at IBM, who told him to do something with their newest computer that would be impressive to the world. Pekeris tackled this, and got

$$E = -2.903\,724\,375 \text{ a.u.}$$

which is even more accurate than 13th order perturbation theory.

- This value cannot be accurately measured to this precision in the laboratory. Additionally, relativistic quantum mechanics (using the Dirac equation of which the Schrödinger equation is only a part) predicts a value that diverges from this one around the fifth decimal point, and this is the experimentally verifiable value.
- This is important because scientists want to figure out how accurately can we account for the electron cusp.
- To summarize, the improvement tiers are
 1. H orbitals.
 2. MO picture (Hartree-Fock).
 3. Solution of the Schrödinger equation (electron correlation).
- Recall that the electron has spin (from the Stern-Gerlach and Uhlenbeck-Goudsmit experiments).

- This is analogous to orbital angular momentum:

$$\hat{L}^2 Y_{lm} = l(l+1)\hbar^2 Y_{lm} \qquad \hat{L}_z Y_{lm} = m\hbar Y_{lm}$$

- These two operators give rise to

$$\hat{S}^2 \sigma = s(s+1)\hbar^2 \sigma \qquad \hat{S}_z \sigma = m_s \hbar \sigma$$

where σ is the spin eigenfunction, s is the total spin angular momentum quantum number, and m_s is the spin quantum number.

- We have $\sigma = \alpha$ or $\sigma = \beta$ where α represents “up” and β represents “down.”
- $m_s = \pm 1/2$ where $s = 1/2$, so $m_s = -s, s$.
- Spin eigenfunctions are orthonormal, i.e.,

$$\int \alpha^* \alpha = \int \beta^* \beta = 1 \qquad \int \alpha^* \beta = \int \beta^* \alpha = 0$$

- Hence, each electron has four degrees of freedom (three spatial and one spin).
- This gives rise to a **spin orbital** $\psi(x, y, z, \sigma) = \phi(x, y, z)\sigma$, which is the product of the spin and spatial orbitals.
- In fact, our ability to calculate the energy of the helium atom was complete luck — we cannot calculate the energy of any other element on the periodic table without accounting for spin.

6.2 Many-electron Atoms and Molecules / Spin

- 11/3: • **Spin orbital:** A spatial orbital augmented with a spin eigenfunction. *Given by*

$$\psi(x, y, z, \sigma) = \phi(x, y, z)\sigma$$

- Key idea: Electrons are indistinguishable, i.e., if $\psi(1, 2, \dots, N)$ where each number represents the three spatial coordinates of an electron, the N electrons in ψ must be indistinguishable.
- There are two possible ways to achieve *mathematical* indistinguishability.

1. We can require that

$$\psi(1, 2, 3, \dots, N) = \psi(2, 1, 3, \dots, N)$$

- Essentially, this is a symmetric permutation of all pairs of particles.

2. We can alternatively require that

$$\psi(1, 2, 3, \dots, N) = -\psi(2, 1, 3, \dots, N)$$

- Because the probability is invariant to the sign (think about taking the modulus squared and how that eliminates sign considerations).
- Essentially, this is an antisymmetric permutation of all pairs of particles.

- Experimental observation shows two types of particles in nature.

1. Bosons (symmetric permutations).
2. Fermions (antisymmetric permutations).

- Electrons are Fermions.

- Prob = $\psi^*(1, 2, \dots, N)\psi(1, 2, \dots, N)$ tells us the probability of finding the N electrons at the positions specified by 1 through N .

- Example (helium):

- We had $\psi(1, 2) = 1s\alpha(1)1s\beta(2)$.
- But since the electrons are distinguishable here, we have to make them indistinguishable by letting

$$\begin{aligned}\psi(1, 2) &= 1s\alpha(1)1s\beta(2) - 1s\alpha(2)1s\beta(1) \\ &= 1s(1)1s(2)[\alpha(1)\beta(2) - \alpha(2)\beta(1)]\end{aligned}$$

- Here, we've separated out the spatial and spin parts.

- How to represent antisymmetry.

- Grassmann Wedge Product (1850s): Herman de Grassmann was studying linear algebra and would learn about higher dimensional spaces in his dreams.
- de Grassman says

$$\psi(1, 2) = 1s\alpha(1) \wedge 1s\beta(2)$$

$$\frac{1}{2!}(1s\alpha(1)1s\beta(2) - 1s\alpha(2)1s\beta(1))$$

where \wedge is the wedge product, a tensor product.

- We can normalize the above by substituting $\sqrt{2!}$ for $2!$.

- Slater determinant (1930): Took

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

- We now consider lithium.

- Let's put 3 electrons in a single orbital:

$$\psi(1, 2, 3) = 1s\alpha(1) \wedge 1s\beta(2) \wedge 1s\beta(3)$$

- $1s\beta(2) \wedge 1s\beta(3)$ will vanish as per Grassmann algebra since the electrons have the same spin state. In general, $\phi \wedge \phi = 0$.

- Thus, in general,

$$\psi(1, 2, 3) = \sqrt{3!}(1s\alpha(1) \wedge 1s\beta(2) \wedge 2s\alpha(3))$$

or, using the Slater determinant,

$$\psi(1, 2, 3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s\alpha(1) & 1s\beta(1) & 2s\alpha(1) \\ 1s\alpha(2) & 1s\beta(2) & 2s\alpha(2) \\ 1s\alpha(3) & 1s\beta(3) & 2s\alpha(3) \end{vmatrix}$$

- **Pauli exclusion principle:** Each electron must occupy a distinct spin orbital, that is, it must have a distinct set of 4 quantum numbers n, l, m, m_s .

- Emerges naturally from the quantum mechanics as per the above.

- What if electrons were bosons?

- Then

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

where \vee is the bosonic operator, i.e., the symmetric wedge product, which denotes the positive sum of all permutations.

- We have

$$\begin{aligned} \phi(1) \vee \phi(2) &= \phi(1)\phi(2) + \phi(2)\phi(1) \\ &= 2\phi(1)\phi(2) \end{aligned}$$

- Thus, we could put an infinite number of electrons in the same orbital (all electrons could occupy the same orbital) if electrons were bosons, and our shell structure would disintegrate.

- Everything would also merge; we could not form matter as we know it.

- Sodium atoms are bosons.