

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.