

Lecture 28 — Helium Atom & Electron-Electron Repulsion

Reading: Engel 4th ed., Chapter 10 (Sections 10.1–10.3)

Learning Objectives

- Write the Hamiltonian for two-electron and many-electron atoms
- Explain why the many-electron Schrödinger equation cannot be solved exactly
- Apply the orbital approximation and interpret its limitations
- Use variational methods and perturbation theory for the helium atom
- Define shielding and effective nuclear charge

1. The Helium Atom Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

Term	Physics
$-\frac{\hbar^2}{2m_e}\nabla_i^2$	Kinetic energy of electron i
$-\frac{Ze^2}{4\pi\epsilon_0 r_i}$	Attraction of electron i to nucleus ($Z = 2$)
$+\frac{e^2}{4\pi\epsilon_0 r_{12}}$	Electron-electron repulsion

The electron-electron repulsion term $e^2/(4\pi\epsilon_0 r_{12})$ makes this problem **analytically unsolvable** because $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ couples the coordinates of both electrons.

[!NOTE] **Concept Check 28.1** In the helium atom Hamiltonian, the r_{12} term represents the repulsion between the two electrons. Why does this single term prevent us from solving the Schrödinger equation exactly?

2. The Orbital Approximation

Zeroth-Order Approach: Ignore e^2/r_{12}

Without repulsion, the Hamiltonian separates:

$$\hat{H}^{(0)} = \hat{h}_1 + \hat{h}_2$$

Each electron moves independently in a hydrogen-like orbital with $Z = 2$:

$$\psi^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = \phi_{1s}(\mathbf{r}_1) \phi_{1s}(\mathbf{r}_2)$$

$$E^{(0)} = -Z^2 \times 13.6 \text{ eV} \times 2 = -4 \times 13.6 \times 2 = -108.8 \text{ eV}$$

Experimental: $E = -79.0 \text{ eV}$. The discrepancy (-29.8 eV) is entirely due to the neglected electron-electron repulsion — it is enormous and cannot be ignored.

First-Order Perturbation Theory

Treat $\hat{V}_{ee} = e^2/(4\pi\epsilon_0 r_{12})$ as a perturbation:

$$E^{(1)} = \langle \psi^{(0)} | \hat{V}_{ee} | \psi^{(0)} \rangle = \frac{5}{8} Z \times 13.6 \text{ eV} = +34.0 \text{ eV}$$

$$E_{\text{total}} = -108.8 + 34.0 = -74.8 \text{ eV}$$

Better, but still 5% off from the experimental value.

3. The Variational Method

Variational Principle

For any trial wavefunction ψ_{trial} :

$$E_{\text{trial}} = \frac{\langle \psi_{\text{trial}} | \hat{H} | \psi_{\text{trial}} \rangle}{\langle \psi_{\text{trial}} | \psi_{\text{trial}} \rangle} \geq E_{\text{exact}}$$

The trial energy is always an **upper bound** to the true ground-state energy. We optimize parameters in ψ_{trial} to minimize E_{trial} .

Effective Nuclear Charge

Use $\psi_{\text{trial}} = \phi_{1s}^{Z_{\text{eff}}}(\mathbf{r}_1) \phi_{1s}^{Z_{\text{eff}}}(\mathbf{r}_2)$ with Z_{eff} as a variational parameter.

Result: $Z_{\text{eff}} = Z - 5/16 = 1.6875$

$$E_{\text{var}} = -77.5 \text{ eV}$$

The effective nuclear charge is less than $Z = 2$ because each electron **screens** (shields) the other from the nucleus.

Understanding Shielding

Each electron, on average, partially neutralizes the nuclear charge seen by the other electron. The concept of **effective nuclear charge** $Z_{\text{eff}} = Z - \sigma$ (where σ is the shielding constant) is central to understanding the periodic table.

[!NOTE] **Concept Check 28.2** The variational method for helium yields an effective nuclear charge $Z_{\text{eff}} \approx 1.69$. Why is this value significantly lower than the actual nuclear charge $Z = 2$?

4. Shielding and Penetration in Many-Electron Atoms

The Orbital Approximation for N Electrons

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \approx \phi_1(\mathbf{r}_1) \phi_2(\mathbf{r}_2) \cdots \phi_N(\mathbf{r}_N)$$

Each electron moves in an **effective potential** created by the nucleus and the average distribution of all other electrons.

Consequences: Lifting the l -Degeneracy

In hydrogen, E depends only on n . In multi-electron atoms, **shielding depends on l** :

- s electrons: significant probability near the nucleus \rightarrow penetrate through inner shells \rightarrow feel higher $Z_{\text{eff}} \rightarrow$ lower energy
- p electrons: less penetration \rightarrow more shielded \rightarrow higher energy
- d electrons: even less penetration \rightarrow even more shielded \rightarrow higher energy

Result: For a given n : $E_{ns} < E_{np} < E_{nd} < E_{nf}$

This explains the filling order and the structure of the periodic table.

Key Equations Summary

Equation	Expression
He Hamiltonian	$\hat{H} = \hat{h}_1 + \hat{h}_2 + e^2/(4\pi\epsilon_0 r_{12})$
Zeroth-order energy	$E^{(0)} = -2Z^2(13.6 \text{ eV})$
First-order correction	$E^{(1)} = (5Z/8)(13.6 \text{ eV})$
Variational principle	$E_{\text{trial}} \geq E_{\text{exact}}$
Effective nuclear charge (He)	$Z_{\text{eff}} = Z - 5/16$
Orbital energy ordering	$E_{ns} < E_{np} < E_{nd}$ (multi-electron)

Recent Literature Spotlight

"Imaging the Square of the Correlated Two-Electron Wave Function of a Hydrogen Molecule" *M. Waitz, D. Metz, J. Lower, C. Schober, M. Kircher, et al.*, *Science*, **2022**, 376, 260–264. [DOI](#)

This experiment imaged the correlated two-electron wave function of H₂ following double ionization and Coulomb explosion. By measuring the momenta of both electrons simultaneously, the authors reconstructed the two-particle probability density $|\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2$ — providing a direct visualization of electron correlation and entanglement that goes beyond the independent-particle model taught in this lecture for helium.

Practice Problems

- Helium energies.** Calculate the zeroth-order, first-order perturbation, and variational energies for He. Compare each to the experimental value of -79.0 eV .
- Lithium.** Write the Hamiltonian for the lithium atom ($Z = 3$, 3 electrons). How many electron-repulsion terms are there?
- Effective nuclear charge.** Using Slater's rules, estimate Z_{eff} for the $2p$ electron in nitrogen ($Z = 7$). How does this compare to the $2s$ electron?

Next lecture: The Hartree-Fock Self-Consistent Field Method