

# Quantum Mechanics

Week 8

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## Exercise Material



Webpage

# **Week 8**

**Review**

**Clicker Questions**

**Midterm Review**

**Exercises**

## Review of Last Week

- Any questions on last week's topics?
- Feedback on the previous session?

# Review

## Two-Particle Systems

### 1-Particle System

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(\vec{x})$$

$\Psi_n(\vec{x}, t)$  describes system

- Kinetic Energy of particle #1:  $-\frac{\hbar^2}{2m}\nabla^2$
- Potential Energy of particle #1:  $\hat{V}(\vec{x})$

## 2-Particle System

$$\hat{H} = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + \hat{V}(\vec{x}_1, \vec{x}_2)$$

$\Psi(\vec{x}_1, \vec{x}_2, t)$  describes system

- Kinetic Energy of particle #1:  $-\frac{\hbar^2}{2m_1}\nabla_1^2$
- Kinetic Energy of particle #2:  $-\frac{\hbar^2}{2m_2}\nabla_2^2$
- Potential Energy that includes any interactions between particles:  $\hat{V}(\vec{x}_1, \vec{x}_2)$

$P(\vec{x}_1, \vec{x}_2, t) = |\Psi(\vec{x}_1, \vec{x}_2, t)|^2$  provides the likelihood of simultaneously finding particle #1 and particle #2

## Solving the 2-Particle System

- Simplify the Schrödinger equation using center of mass and relative coordinates.

**Center of Mass ( $\vec{R}$ ):**

$$\vec{R} = \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{m_1 + m_2} \quad (1)$$

**Relative Position ( $\vec{r}$ ):**

$$\vec{r} = \vec{r}_1 - \vec{r}_2 \quad (2)$$



**Total Mass ( $M$ ):**

$$M = m_1 + m_2 \quad (3)$$

**Reduced Mass ( $m_r$ ):**

$$m_r = \frac{m_1 m_2}{m_1 + m_2} \quad (4)$$

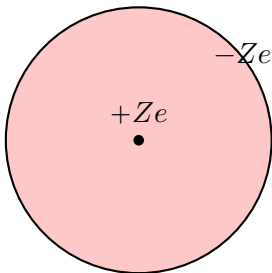
**Wave Function Separation:**

$$\Psi(\vec{r}_1, \vec{r}_2, t) = \Psi_R(\vec{R}, t) \cdot \psi_r(\vec{r}, t) \quad (5)$$

Which can be seen as separable solutions of the T.I.S.E.

## Multiple Particle System

Atom with  $Z$  protons and a single valence electron:



$$\hat{H} = \sum_{i=1}^Z \underbrace{\frac{-\hbar^2}{2m} \nabla_i^2 - \frac{1}{4\pi\epsilon_0} \frac{Ze^2}{r_i}}_{\text{Term 1}} + \underbrace{\frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{\substack{k=1 \\ k \neq i}}^Z \frac{e^2}{|r_i - r_k|}}_{\text{Term 2}}$$

- **(1) Kinetic and nucleus interaction:** Represents the energy due to electron kinetic energy and its interaction with the nucleus.
- **(2) Electron-electron repulsion:** Energy from electron repulsion in atoms, avoiding double counting with a 1/2 factor. This makes exact solutions to the TISE impossible, requiring approximations.

In order to get an easier solution, we will ignore the second term.  $\psi_{n,\ell,m_\ell,m_s}$

## Distinguishability in Quantum Mechanics

In Quantum Mechanics, any two identical particles (e.g., two electrons) are indistinguishable. Which means we have no way to tell them apart, they are exactly the same!

If particles are **distinguishable** (Proton and an electron), then

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_a(\vec{r}_1) \cdot \psi_b(\vec{r}_2) \text{ or } \psi_b(\vec{r}_1) \cdot \psi_a(\vec{r}_2)$$

If particles are **indistinguishable**, then

$$\begin{cases} \psi_+(\vec{r}_1, \vec{r}_2) = C [\psi_a(\vec{r}_1) \cdot \psi_b(\vec{r}_2) + \psi_b(\vec{r}_1) \cdot \psi_a(\vec{r}_2)] \\ \psi_-(\vec{r}_1, \vec{r}_2) = C [\psi_a(\vec{r}_1) \cdot \psi_b(\vec{r}_2) - \psi_b(\vec{r}_1) \cdot \psi_a(\vec{r}_2)] \end{cases}$$

⇒ The solution is a linear combination. Which state is for which particle?

## Introduction to Exchange Symmetry

- The exchange operator  $\hat{P}$  swaps the positions of two particles within a quantum state.
- It is described mathematically by:

$$\hat{P}f(\vec{r}_1, \vec{r}_2) = f(\vec{r}_2, \vec{r}_1)$$

- Compatibility with Hamiltonian  $\hat{H}$ :

$$[\hat{P}, \hat{H}] = 0$$

- $\hat{P}$  and  $\hat{H}$  share the same eigenfunctions, suggesting  $\hat{P}$  is a conserved quantity.

- Symmetric Wavefunction ( $\psi_+$ ):

$$\hat{P}\psi_+ = +1\psi_+$$

- Antisymmetric Wavefunction ( $\psi_-$ ):

$$\hat{P}\psi_- = -1\psi_-$$

- Physical implications:

- $\psi_+$  results in particles being closer together.
- $\psi_-$  results in particles being further apart.
- Different energies due to exchange interaction, influencing bonding and antibonding states.

## Symmetry of Wavefunctions for Identical Particles

The symmetry of the overall wavefunction for identical particles is determined by their spin:

$$\left\{ \begin{array}{ll} \text{Bosons (integer spin):} & \text{Symmetric} \\ \text{Fermions (half-integer spin):} & \text{Antisymmetric} \end{array} \right.$$

relative to the exchange of any two particles.

$$\text{Overall Wavefunction: } \psi_{\pm}(r) \cdot \chi(s)$$

Spin combinations ( $\chi(s)$ ) and symmetry:

$$\left\{ \begin{array}{ll} \text{both spin up} & \uparrow\uparrow \\ \text{both spin down} & \downarrow\downarrow \\ \text{one up, one down} & \frac{1}{\sqrt{2}} (\uparrow\downarrow + \downarrow\uparrow) \text{ (Symmetric)} \\ \text{one up, one down} & \frac{1}{\sqrt{2}} (\uparrow\downarrow - \downarrow\uparrow) \text{ (Antisymmetric)} \end{array} \right.$$

- Three symmetric combinations (**Triplet**,  $S = 1$ )
- One antisymmetric combination (**Singlet**,  $S = 0$ )

**Note:** The singlet and triplet states have different energies.



For electrons (fermions), the overall wavefunction must be antisymmetric, leading to possible combinations:

$$\psi_+ \cdot (\text{Singlet}), \quad \psi_- \cdot (\text{Triplet})$$

## Pauli's Exclusion Principle

Two identical fermions can never be in the exact same quantum state (same  $n, \ell, m_\ell, m_s$ ) and still have an antisymmetric wavefunction.

## Mathematical Representation of Fermion Wavefunctions

The general form for the wavefunction of a fermion (in a radial spherical symmetric potential) in quantum mechanics is:

$$\psi_{n,\ell,m_\ell,m_s} = A \cdot R_{n\ell}(r) \cdot Y_\ell^{m_\ell}(\theta, \varphi) \cdot |s, m_s\rangle$$

Components of the wavefunction:

- $R_{n\ell}(r)$ : Radial part of the wavefunction
- $Y_\ell^{m_\ell}(\theta, \varphi)$ : Spherical harmonics
- $|s, m_s\rangle$ : Spin state

The overall wavefunction contains most of the eigenfunctions of the different operators, allowing measurement of the operator within the overall wavefunction.

## Clicker Questions

## Midterm Review

## Exercises

### Exercise 1

Very long, focus on b and c

## Exercise 2

Good to understand spatial symmetries.

## Exercise 3

Extra, would try or do with the solutions.