

Quantum Mechanics

Week 9

Mark Benazet Castells
mbenazet@ethz.ch

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Pre-Reading Note

Dear Students,

Welcome to the course on Quantum Mechanics. As part of your learning resources, I will prepare a series of educational materials and sheets designed to complement the lectures.

Please note that these materials are **abridged versions** of the content from the textbook *"Introduction to Quantum Mechanics By David J. Griffiths"*. They have been tailored to align with the class schedule and topics, providing you with concise summaries and key points for each topic covered.

It's important to understand that these sheets are **not standalone resources**. They are intended to be used in conjunction with the class material. For a deeper understanding and a more comprehensive view of each topic, I strongly encourage you to refer to the mentioned textbook.

The book provides detailed explanations, examples, and insights that go beyond the scope of our summaries. It will be an invaluable resource for you to solidify your understanding of Quantum Mechanics.

I cannot guarantee neither correctness nor completeness of the script. Please report any mistake directly to me.

Have fun with Quantum Mechanics!

Best regards,

Mark Benazet Castells

1 Two-Particle Systems

In quantum mechanics, a two-particle system extends the concept of a single-particle system by including interactions and correlations between two distinct particles. The state of such a system is described by a wavefunction $\psi(x_1, x_2)$, where x_1 and x_2 represent the positions of the first and second particle, respectively. This section delves into the mathematical formulation of such systems.

1.1 Wavefunction and Probability Density

The wavefunction for two particles is expressed as:

$$\Psi(\vec{r}_1, \vec{r}_2, t) \quad (1)$$

where $\Psi(\vec{r}_1, \vec{r}_2, t)$ is a function of the individual particles position and time. The probability density for a two-particle quantum system is then given by:

$$P(\vec{r}_1, \vec{r}_2, t) = |\Psi(\vec{r}_1, \vec{r}_2, t)|^2 \quad (2)$$

which provides the likelihood of simultaneously finding particle #1 in a volume element $d^3\vec{r}_1$ around position \vec{r}_1 and particle #2 in a volume element $d^3\vec{r}_2$ around position \vec{r}_2 .

1.2 Hamiltonian of the System

The Hamiltonian operator, which encompasses both kinetic and potential energy, is formulated as:

$$\hat{H} = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(x_1, x_2) \quad (3)$$

Here, the first two terms represent the kinetic energies of each particle, with m_1 and m_2 being their respective masses. The term $V(x_1, x_2)$ denotes the potential energy that includes any interactions between particles.

1.3 Schrödinger Equation for Two-Particle Systems

The Schrödinger equation for the system is written as:

$$\hat{H}\psi(x_1, x_2) = E\psi(x_1, x_2) \quad (4)$$

Solving this equation gives the energy eigenvalues and eigenfunctions, which describe the quantized states of the system.

2 Approach to Solving Two-Particle Problems

For a two-particle system, the complexity of the Schrödinger equation can often be reduced by transforming the problem into center of mass and relative coordinates. This approach simplifies the potential and kinetic energy terms and allows for the separation of the wave function into two parts: one that describes the motion of the center of mass and another that describes the relative motion of the particles.

2.1 Center of Mass and Relative Distance Formulation

The center of mass \vec{R} for two particles of masses m_1 and m_2 at positions \vec{r}_1 and \vec{r}_2 is given by:

$$\vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2} \quad (5)$$

The relative position vector \vec{r} is defined as:

$$\vec{r} = \vec{r}_1 - \vec{r}_2 \quad (6)$$

2.2 Reduced and Total Mass Calculations

The total mass M and the reduced mass m_r are important for describing the dynamics of the two-particle system. They are defined as:

$$M = m_1 + m_2 \quad (7)$$

$$m_r = \frac{m_1 m_2}{m_1 + m_2} \quad (8)$$

These masses play a crucial role in the separation of the Schrödinger equation.

2.3 Wave Function Separation Techniques

By expressing the kinetic energy operators in terms of the center of mass and relative coordinates, the Schrödinger equation can be separated into two independent equations. The wave function $\Psi(\vec{r}_1, \vec{r}_2, t)$ can be written as a product of the wave functions for the center of mass $\Psi_R(\vec{R}, t)$ and the relative motion $\psi_r(\vec{r}, t)$:

$$\Psi(\vec{r}_1, \vec{r}_2, t) = \Psi_R(\vec{R}, t) \cdot \psi_r(\vec{r}, t) \quad (9)$$

and the hamiltonian becomes:

$$\hat{H} = -\frac{\hbar^2}{2M} \nabla_R^2 - \frac{\hbar^2}{2m_r} \nabla_r^2 + V(\vec{r}) \quad (10)$$

Solving the Schrödinger equation for these two separate wave functions yields solutions that account for the motion of both the center of mass and the relative motion of the two particles.

Remark: This trick only works for two particle systems.

3 Distinguishability in Quantum Systems

3.1 Distinguishable Particles

For distinguishable particles, their individual wavefunctions do not interfere, and the combined system's wavefunction is a simple product of the individual wavefunctions. If $\psi_a(\vec{r}_1)$ is the wavefunction for particle 1 and $\psi_b(\vec{r}_2)$ for particle 2, then the combined wavefunction is either $\psi_a(\vec{r}_1) \cdot \psi_b(\vec{r}_2)$ or $\psi_b(\vec{r}_1) \cdot \psi_a(\vec{r}_2)$, depending on which particle is in which state.

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_a(\vec{r}_1)\psi_b(\vec{r}_2) \quad \text{or} \quad \psi(\vec{r}_1, \vec{r}_2) = \psi_b(\vec{r}_1)\psi_a(\vec{r}_2) \quad (11)$$

3.2 Indistinguishable Particles

For indistinguishable particles like electrons, the situation is more subtle. The combined wavefunction must either be completely symmetric or completely antisymmetric under the exchange of particle positions to comply with the symmetrization postulate. For two particles, the symmetric and antisymmetric wavefunctions are given by:

$$\psi_+(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} [\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) + \psi_a(\vec{r}_2)\psi_b(\vec{r}_1)] \quad (12)$$

$$\psi_-(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} [\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_a(\vec{r}_2)\psi_b(\vec{r}_1)] \quad (13)$$

This implies that the spatial wavefunction is a linear combination of the two possible states for each particle.

3.3 Wavefunction Solutions and Particle Statistics

The wavefunctions ψ_+ and ψ_- significantly affect the statistical behaviors and energy states of particles. They define distinct spatial regions for the particles with ψ_+ often corresponding to a lower energy state due to constructive interference, while ψ_- is associated with higher energy states due to destructive interference. This energy differentiation is a result of the quantum mechanical exchange interaction.

The term "exchange force" inaccurately suggests a classical force, akin to electromagnetism or the strong nuclear force, which involve particle exchange like photons and gluons. In reality, this "force" is a quantum effect unique to particles that cannot be distinguished from one another. It's a result of the symmetries within their wavefunctions, not an exchange of force carriers, and should be interpreted through quantum mechanics principles.

4 Wavefunction Symmetry

The wavefunction of a system of identical particles must be either symmetric or antisymmetric under the exchange of any two particles. This symmetry requirement arises from the indistinguishable nature of identical particles in quantum mechanics. A symmetric wavefunction remains unchanged under the exchange, whereas an antisymmetric wavefunction changes its sign.

$$\psi_{\text{symmetric}}(x_1, x_2) = \psi_{\text{symmetric}}(x_2, x_1) \quad (14)$$

$$\psi_{\text{antisymmetric}}(x_1, x_2) = -\psi_{\text{antisymmetric}}(x_2, x_1) \quad (15)$$

4.1 Role of the Exchange Operator in Particle Swapping

The exchange operator, denoted by \hat{P} , is an operator that swaps the positions of two particles in the wavefunction. The action of \hat{P} on a wavefunction characterizes its symmetry:

$$\hat{P}\psi(x_1, x_2) = \psi(x_2, x_1) \quad (16)$$

4.2 Exchange Symmetry and Its Implications

The exchange operator's commutation with the Hamiltonian, $[\hat{P}, \hat{H}] = 0$, implies that the Hamiltonian \hat{H} and the exchange operator \hat{P} are compatible. They share the same eigenfunctions, ψ_+ and ψ_- , which are stationary states, making \hat{P} a conserved quantity. We can also clearly see that the exchange operator has either ± 1 as eigenvalues.

$$\hat{P}\psi_+ = +1\psi_+ \quad (17)$$

$$\hat{P}\psi_- = -1\psi_- \quad (18)$$

5 Overall Symmetry in Quantum Mechanics

In quantum systems, the overall wavefunction, $\psi(x, s)$, which describes the state of a multi-particle system, is a product of its spatial part, $\psi_{\pm}(r)$, and its spin part, $\chi(s)$. The symmetry of $\psi(x, s)$ depends on the type of particles involved.

5.1 Wavefunction Symmetry for Bosons and Fermions

For bosons (particles with integer spin), the overall wavefunction is symmetric, while for fermions (particles with half-integer spin), it is antisymmetric. This distinction is crucial for understanding the physical properties of quantum systems.

$$\psi(x, s) = \psi_{\pm}(r) \cdot \chi(s) \begin{cases} \text{bosons} \rightarrow \text{symmetric} \\ \text{fermions} \rightarrow \text{antisymmetric} \end{cases} \quad (19)$$

5.2 Spin Combinations and Symmetry

The spin part of the wavefunction, $\chi(s)$, for a two-fermion system, can take several forms:

- Symmetric combinations (Triplet, $S = 1$):

$$\chi_{\text{triplet}}(s) = \begin{cases} \uparrow\uparrow & \text{(both spin up)} \\ \downarrow\downarrow & \text{(both spin down)} \\ \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) & \text{(one up or down)} \end{cases} \quad (20)$$

- Antisymmetric combination (Singlet, $S = 0$):

$$\chi_{\text{singlet}}(s) = \frac{1}{\sqrt{2}}(\uparrow\downarrow - \downarrow\uparrow) \quad (21)$$

5.3 Fermions and Wavefunction Symmetry

For fermions, the Pauli exclusion principle enforces that the overall wavefunction must be antisymmetric. Therefore, the spatial part, $\psi_{\pm}(r)$, must be matched with the appropriate spin symmetry:

- For a symmetric spatial wavefunction ψ_+ , the spin part must be antisymmetric (Singlet):

$$\psi(x, s)_{\text{antisymmetric}} = \psi_+ \cdot \chi_{\text{singlet}} \quad (22)$$

- For an antisymmetric spatial wavefunction ψ_- , the spin part must be symmetric (Triplet):

$$\psi(x, s)_{\text{antisymmetric}} = \psi_- \cdot \chi_{\text{triplet}} \quad (23)$$

6 Pauli Exclusion Principle

The Pauli Exclusion Principle is a fundamental tenet in quantum mechanics asserting that two identical fermions cannot simultaneously occupy the same quantum state. This principle is key to understanding the electronic structure of atoms and the stability of matter.

6.1 Conceptual Sketch

The principle prohibits identical fermions from sharing the same set of quantum numbers (n, ℓ, m_ℓ, m_s) , which define their state within a quantum system. This restriction is due to the requirement for the overall wavefunction of the fermions to be antisymmetric.

6.2 Mathematical Representation

For a two-fermion system, the antisymmetric wavefunction can be expressed as:

$$\psi_-(r_1, r_2) = C[\psi_{n_a, \ell_a, m_{\ell_a}, m_{s_a}}^a(r_1)\psi_{n_b, \ell_b, m_{\ell_b}, m_{s_b}}^b(r_2) - \psi_{n_b, \ell_b, m_{\ell_b}, m_{s_b}}^b(r_1)\psi_{n_a, \ell_a, m_{\ell_a}, m_{s_a}}^a(r_2)] \quad (24)$$

where C is a normalization constant, and r_1, r_2 are the positional variables of the two fermions. The subscript n, ℓ, m_ℓ, m_s represent the quantum numbers (principal, azimuthal, magnetic, and spin) for each fermion, which must differ to comply with the Pauli Exclusion Principle. If the two fermions attempt to occupy the same quantum state, then $\psi_-(r_1, r_2)$ becomes zero, indicating no physical solution and upholding the Pauli Exclusion Principle.

6.3 Implications for Quantum Systems

The principle results in the unique arrangement of electrons in atoms, adhering to a specific sequence of energy levels. This organization is responsible for the diverse chemical properties observed in elements and compounds. The exclusion principle also influences the density and phase of matter.

7 Final Wavefunction Formulation

The Pauli Exclusion Principle culminates in a specific formulation for the wavefunction of a fermion in a quantum system. The final expression integrates the radial, angular, and spin components, ensuring that the overall wavefunction adheres to the antisymmetry requirement for fermions:

$$\psi_{n,\ell,m_\ell,m_s} = A \cdot R_{n\ell}(r) \cdot Y_\ell^{m_\ell}(\theta, \varphi) \cdot |s, m_s\rangle \quad (25)$$

Here, A is the normalization constant, $R_{n\ell}(r)$ represents the radial part of the wavefunction, $Y_\ell^{m_\ell}(\theta, \varphi)$ denotes the spherical harmonics accounting for the angular part, and $|s, m_s\rangle$ signifies the spin state of the fermion.