

Quantum Mechanics

Week 7

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1 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

2 Introduction to Quantum Mechanics in 3D

Quantum mechanics in three dimensions (3D) expands the understanding of quantum phenomena beyond one-dimensional approximations. It allows for a more realistic representation of quantum systems, such as atoms and molecules.

2.1 Time-Dependent Schrödinger Equation in 3D

The Time-Dependent Schrödinger Equation (TDSE) in 3D is fundamental for describing the dynamics of quantum systems. It is expressed as:

$$i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}, t) + V(\vec{r}, t) \Psi(\vec{r}, t), \quad (1)$$

where $\Psi(\vec{r}, t)$ is the wave function, \vec{r} is the position vector, t is time, and $V(\vec{r}, t)$ is the potential energy. The TDSE in 3D allows for the exploration of complex quantum systems in realistic scenarios. We solve for the stationary states by decoupling the variables for example in cartesian coordinates:

$$\Psi(\vec{r}, t) = X(x) \times Y(y) \times Z(z) \times \varphi(t) \quad (2)$$

2.2 Operators in Quantum Mechanics

Operators are mathematical entities in quantum mechanics that correspond to measurable physical quantities. In 3D, the most significant operators include:

- **Momentum Operator:** $\hat{p} = -i\hbar \nabla$, representing the momentum of the particle.
- **Hamiltonian Operator:** $\hat{H} = \frac{\hat{p}^2}{2m} + V(\vec{r})$, the total energy operator, combining kinetic and potential energies.

2.3 Laplacian in Spherical Coordinates

The Laplacian operator plays a pivotal role in quantum mechanics, especially in systems with spherical symmetry. Its expression in spherical coordinates (r, θ, ϕ) is given by:

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right) \quad (3)$$

The spherical coordinates provide a natural framework to describe such systems, with r representing the radial distance, θ the polar angle, and ϕ the azimuthal angle.

The volume element for this system is given by $d^3\vec{r} = r^2 \sin(\theta) dr d\theta d\phi$.

We are going to make the assumption that the solutions $\psi_n(r, \theta, \varphi)$ can be separated into Radial $R(r)$ and Angular $Y(\theta, \varphi)$ parts. Then the solution becomes:

$$\psi_n(r, \theta, \varphi) = R(r) \times Y(\theta, \varphi) \quad (4)$$

3 Angular Equation

Spherical harmonics are mathematical functions that arise in solving the angular part of the Schrödinger Equation for systems with spherical symmetry. They are crucial in describing the angular distribution of a quantum particle's probability density.

3.1 Mathematical Formulation

Spherical harmonics, denoted as $Y_\ell^m(\theta, \phi)$, are defined as:

$$Y_\ell^m(\theta, \varphi) = \Theta(\theta) \times \Phi(\varphi) \quad (5)$$

$$= AP_\ell^m(\cos \theta) \times \exp(im\varphi) \quad (6)$$

$$= (-1)^{\frac{m+|m|}{2}} \sqrt{\frac{(2\ell+1)(\ell-|m|)!}{4\pi(\ell+|m|)!}} P_\ell^m(\cos \theta) e^{im\varphi}, \quad (7)$$

where $P_\ell^m(\cos \theta)$ are the associated Legendre polynomials, ℓ is the azimuthal quantum number, and m is the magnetic quantum number.

3.2 Few Spherical Harmonic Solutions

Table 1: The first few spherical harmonics, $Y_\ell^m(\theta, \varphi)$

Spherical Harmonic	Expression
Y_0^0	$\left(\frac{1}{4\pi}\right)^{1/2}$
Y_1^0	$\left(\frac{3}{4\pi}\right)^{1/2} \cos \theta$
$Y_1^{\pm 1}$	$\mp \left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{\pm i\phi}$
Y_2^0	$\left(\frac{5}{16\pi}\right)^{1/2} (3 \cos^2 \theta - 1)$
$Y_2^{\pm 1}$	$\mp \left(\frac{15}{8\pi}\right)^{1/2} \sin \theta \cos \theta e^{\pm i\phi}$
$Y_2^{\pm 2}$	$\left(\frac{15}{32\pi}\right)^{1/2} \sin^2 \theta e^{\pm 2i\phi}$
Y_3^0	$\left(\frac{7}{16\pi}\right)^{1/2} (5 \cos^3 \theta - 3 \cos \theta)$
$Y_3^{\pm 1}$	$\mp \left(\frac{21}{64\pi}\right)^{1/2} \sin \theta (5 \cos^2 \theta - 1) e^{\pm i\phi}$
$Y_3^{\pm 2}$	$\left(\frac{105}{32\pi}\right)^{1/2} \sin^2 \theta \cos \theta e^{\pm 2i\phi}$
$Y_3^{\pm 3}$	$\mp \left(\frac{35}{64\pi}\right)^{1/2} \sin^3 \theta e^{\pm 3i\phi}$

3.3 Properties and Applications

Spherical harmonics possess several important properties:

- They form a complete, orthonormal set over the sphere.
- They are eigenfunctions of the angular momentum operators \hat{L}^2 and \hat{L}_z .
- They are used in quantum mechanics to describe the angular part of wave functions in systems with spherical symmetry, such as atoms.

4 Radial Equation

In spherically symmetric potentials, while the angular part of the wave function is universal, the shape of the potential $V(r)$ uniquely affects the radial part. This distinction emerges in the separation of variables in the three-dimensional Schrödinger equation. For example, in the hydrogen atom, the radial part of the equation is specifically influenced by the form of $V(r)$:

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[V + \frac{\hbar^2}{2m} \frac{\ell(\ell+1)}{r^2} \right] u(r) = Eu, \quad (8)$$

where $u(r) = rR(r)$ is the radial wave function, E is the energy eigenvalue, $V(r)$ is the potential energy function, and ℓ is the angular momentum quantum number.

We can clearly see that our new V_{eff} is equal to the potential energy V and the centrifugal energy $\frac{\hbar^2}{2m} \frac{\ell(\ell+1)}{r^2}$.

4.1 Radial Solutions

The solutions to the radial equation for the hydrogen atom can be expressed in terms of the generalized Laguerre polynomials and are given by:

$$R_{n\ell}(r) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}} e^{-\frac{\rho}{2}} L_{n-\ell-1}^{2\ell+1}(\rho), \quad (9)$$

where n is the principal quantum number, a_0 is the Bohr radius, and $L_{n-\ell-1}^{2\ell+1}(x)$ are the associated Laguerre polynomials and $\rho = \frac{r}{na_0}$.

These radial solutions are characterized by the number of nodes in the wave function, which is $n - \ell - 1$. The nodes are the points where the wave function crosses zero, excluding the origin.

The total wave function, $\psi_n(r, \theta, \varphi) = R(r) \times Y(\theta, \varphi)$, represents the solution to the Time-Independent Schrödinger Equation (TISE) for spherically symmetric potentials.

Examples wave functions of Hydrogen

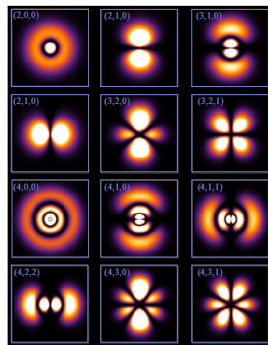
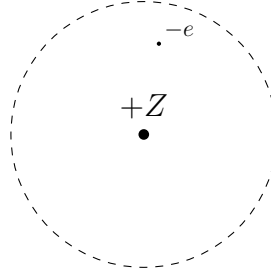


Figure 1: First hydrogen solutions

5 Hydrogen Atoms

Hydrogen atoms are characterized by a single electron orbiting a nucleus. The potential energy for these atoms is dominated by the Coulomb interaction between the electron and the nucleus.



5.1 Structure of the Hydrogen Atom

In a hydrogen atom, the nucleus, typically a proton, forms the center around which the electron orbits. The potential energy of the electron is given by the Coulomb potential:

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}, \quad (10)$$

where e is the electron charge, ϵ_0 is the vacuum permittivity, and r is the distance from the nucleus.

5.2 Energy Levels in the Hydrogen Atom

The allowed energy levels for a hydrogen atom are quantized, described by the Bohr formula:

$$E_n = \frac{1}{n^2} E_1 \quad (11)$$

$$= -\frac{1}{n^2} \frac{m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \quad (12)$$

$$= -13.6 \frac{1}{n^2} \text{ [eV]} \quad (13)$$

where n is the principal quantum number.

5.3 Degeneracy of Energy Levels

The energy levels in hydrogen atoms depend only on the principal quantum number n . For a given n , all states with $\ell = 0, \dots, n-1$ are degenerate, having the same energy. Additionally, for given n and ℓ , the $(2\ell+1)$ states with $m_\ell = -\ell, \dots, \ell$ are also degenerate.

$$\sum_{\ell=0}^{n-1} (2\ell+1) = n^2, \quad (14)$$

doubling if spin degeneracy is considered.

6 Quantum Numbers

Quantum numbers are fundamental to the quantum mechanical description of the states of an electron in an atom. They arise naturally from the solution to the Schrödinger equation and serve as "quantum addresses" that give detailed information about the energy and spatial distribution of an electron.

6.1 Principal Quantum Number (n)

The principal quantum number, denoted as n , defines the energy level of an electron in an atom. It is a positive integer ($n = 1, 2, 3, \dots$) and determines the size of the electron cloud and the energy associated with the electron's orbit. The energy levels are quantized and follow the relationship:

$$E_n = -\frac{Z^2}{n^2} E_1, \quad (15)$$

where E_1 is the energy of the ground state, and Z is the atomic number. In real life, n is crucial for understanding the electronic structure of atoms and the chemical properties they exhibit.

6.2 Azimuthal Quantum Number (ℓ)

The azimuthal (or angular momentum) quantum number, ℓ , determines the shape of the electron's orbital. It can take on any integer value from 0 to $n - 1$. Each value of ℓ corresponds to a specific type of orbital: s (sharp), p (principal), d (diffuse), and f (fundamental), with shapes ranging from spherical to more complex lobed structures. The value of ℓ is directly related to the orbital angular momentum of the electron, affecting the magnetic properties of atoms and their bonding behavior.

6.3 Magnetic Quantum Number (m_ℓ)

The magnetic quantum number, m_ℓ , describes the orientation of the angular momentum of an electron relative to an external magnetic field. It can take on any integer value between $-\ell$ and $+\ell$, including zero. This quantum number is responsible for the magnetic splitting of spectral lines, known as the Zeeman effect.

The quantum numbers together define the unique state of an electron in an atom, dictating not only the electron's energy but also its probable location within the atom.

7 Hydrogenic Atoms

Hydrogenic atoms are akin to the hydrogen atom but with a nucleus containing Z protons, resulting in a nuclear charge of Ze , where e is the elementary charge and Z is the atomic number.

7.1 Potential Change

The electrostatic potential energy $V(r)$ in a hydrogenic atom derives from Coulomb's law and reflects the attraction between the positively charged nucleus and the single electron:

$$V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r},$$

where ϵ_0 is the vacuum permittivity, and r is the distance from the nucleus.

7.2 Energy Levels

Altering the Coulombic potential changes the energy levels. The modified Rydberg formula for the energy E_n of the n th level in a hydrogenic atom is:

$$E_n = -\frac{Z^2 m e^4}{2\hbar^2 (4\pi\epsilon_0)^2 n^2} = Z^2 \frac{E_1}{n^2},$$

with m being the electron mass, \hbar the reduced Planck constant, and n the principal quantum number.

7.3 Radius

The radius r_n for the n th orbit is scaled by the inverse of the atomic number Z , indicating smaller orbits for larger nuclear charge:

$$r_n = \frac{n^2 \hbar^2}{Z m e^2} = n^2 \frac{a_0}{Z},$$

where a_0 is the Bohr radius, representing the probable distance for the electron in the ground state of a hydrogen atom.