

EC(MS)574A1 Physics of Semiconductor Materials

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Fundamentals of Quantum Mechanics

- Quantum mechanics is the basic mathematical formalism used to study the objects (electrons, holes, phonons, photons) that are important to understand the properties of semiconductor materials and electronic/optoelectronic devices.
 - We will look at the reasons why classical mechanics cannot be used to describe electrons and holes.
 - We will develop the basic QM theory by using an axiomatic approach based on postulates.
 - We will apply the theory to study the electrical and optical properties of semiconductors.

The limit of classical mechanics

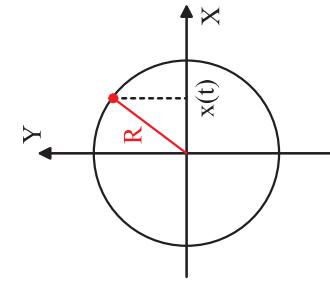
- The simplest way of studying the motion of rigid body in classical mechanics is to use Newton's equations.

$$\frac{d\vec{r}}{dt} = \frac{\vec{p}}{m} \quad \frac{d\vec{p}}{dt} = -\nabla V = \vec{F}$$

The solution describes a trajectory in phase space $p_x(t)$, $p_y(t)$, $p_z(t)$, $x(t)$, $y(t)$, $z(t)$, that for given initial condition is unique.

- At each instant the three components of the vector position \vec{r} and the momentum $\vec{p} = m\vec{v}$ are known with infinite precision.
- At the beginning of 1900 a series of experiment showed that this picture is not always applicable to study the motion of atomic scale particle, like electrons. (G.I. Taylor 1909)
- We start looking at a simple classical system: The Harmonic Oscillator.
- Readings: Branden-Joachain 1.2, 1.3, 1.6

I - An Important Example



In particular:

$$x(t) = R \cos(\omega t + \phi)$$

and the second derivative is given by:

$$\frac{d^2x(t)}{dt^2} = -\omega_0^2 R \cos(\omega_0 t + \phi)$$

and

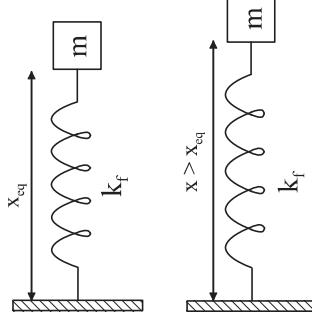
$$\frac{d^2x(t)}{dt^2} = -\omega_0^2 x(t)$$

Consider a ball tied to a rope moving on a circumference of constant radius R and constant angular frequency ω_0 . The trajectory of the ball is given by: $\vec{r}(t) = x(t)\hat{i} + y(t)\hat{j}$.

This is the well known equation that describes the **Simple Harmonic Oscillator (SHO)**.

II - Another Important Example

As we move the mass left or right, a force exerted by the spring will try to take the system back at the equilibrium position. This force is:



$$\frac{d^2x(t)}{dt^2} = -\omega_0^2(x - x_{eq})$$

Consider a mass m on an ideal spring where:
described by a force constant k_f .
The other side of the spring in fixed
by an immovable boundary.

$$\omega_0 = \sqrt{\frac{k_f}{m}}$$

is the the natural frequency.

$$\omega_0 = \sqrt{\frac{k_f}{m}}$$

III - Some Important Quantities

The potential energy $V(x)$ is given by:

$$V(\hat{x}) = - \int F dx = k_f \int \hat{x} dx$$

(\hat{x} is the variation around x_{eq})

$$V(\hat{x}) = \frac{1}{2}k_f\hat{x}^2 = \frac{1}{2}m\omega_0^2\hat{x}^2$$

The kinetic energy $T(\hat{x})$ is given by:

$$T(x) = \frac{p^2}{2m}$$

And the total energy $E = T(\hat{x}) + V(\hat{x})$ is a constant of the motion.

$$E = \frac{p^2}{2m} + \frac{1}{2} m \omega_0^2 \hat{x}^2 = \text{const}$$

interval - Some Important Quantities

$$V(\hat{x}) = \frac{1}{2} m \omega_0^2 (x - x_{eq})^2$$

At equilibrium ($x = x_{eq}$) the potential energy is zero, and the kinetic energy is maximum.

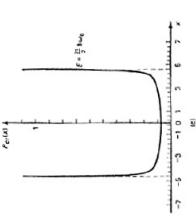
The **classical turning points (CTP)** are those values x_{ctp} of the coordinate for which the kinetic energy is zero and the potential energy is maximum. At these point the particle slows down, stops and turns around.

As a result during a period of oscillation, the particle is more likely to be found near the CTPs where its velocity is the smallest.

Classical Probability Density - I

- To be able to define a probability we have to select an ensemble of identical and non interacting systems that we observe.
 - Since any number of identical classical systems in the same state will always give the same measurement results, we select one of the systems as representative.
 - We measure at random times the position of the particle in the representative systems and define:
 $P_c(x)dx =$ Probability of finding the particle in a position between x and $x + dx$.
 - Since for the SHO $T_0 = 2\pi/\omega_0$ the in the time (period) required to complete a full oscillation, then:
 $P_c(x)dx = t/T_0$ is the fraction of the period the particle spends in an interval dx around the point x .

Classical Probability Density - II



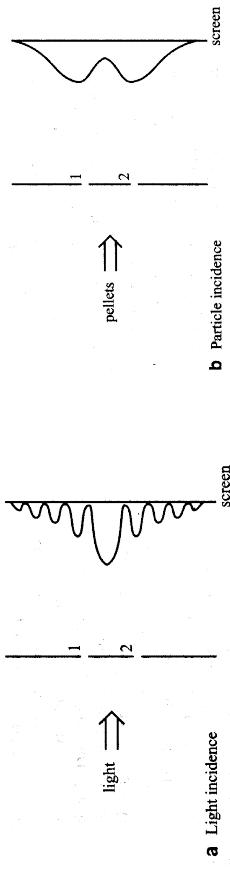
The classical probability can be compute to be (Homework-1):

$$P_{cl}(x)dx = \frac{\sqrt{m\omega_0^2}}{\pi} \frac{1}{\sqrt{2E - m\omega_0^2 x^2}} dx$$

It shows that the SHO is less likely to be found at $x = 0$ where it moves more rapidly, on the contrary, it is more likely to be found where it moves more slowly.

Classical probability density for tree energies: a) $E = 1/2\hbar\omega_0$, $n=0$; b) $E = 3/2\hbar\omega_0$, $n=1$; c) $E = 21/2\hbar\omega_0$, $n=10$

The Two-slit Diffraction Experiment



When the two slits are illuminate by a plane wave, the characteristic diffraction pattern is formed. This is a behavior expected from a wavelike excitation.

!!! Electrons behave like wave and particle at the same time and this depends on the measurement setup.

The same experiment is now performed with electrons. A very faint source is used so that one electron at the time is counted with a detector at either slit A or B (particle). If the experiment is run for a long time, a diffraction pattern similar to the wavelike excitation is observed.

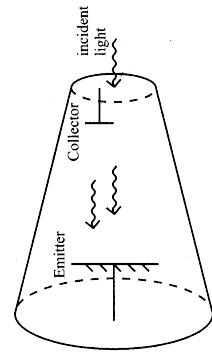
The limit of the Electromagnetic Theory

- As we know from electromagnetic theory light propagates in waves according to Maxwell's equations and the wave equation.

$$\nabla^2 \vec{E} + \mu\epsilon \frac{\partial \vec{E}}{\partial t} = 0$$

- Note that in this formulation the energy flow per unit area is determined by the Poynting vector: $\vec{P} \approx \vec{E} \times \vec{H}$ and it can assume a continuum of values and it is independent of the frequency.
- The photoelectric effect was the first experimental evidence that light can behave both like a wave or a particle depending on the measurement conditions.
- This confirmed Einstein's prediction of the existence of the quanta of light, i.e. the photon and Planck's black body theory.

The Photoelectric Effect



- Quantum Mechanical:

- As the intensity doubles the number of photons doubles but their energy remains the same. there is a fixed energy absorbed by electrons.
- The energy of each photon is $h\nu$. The energy changes on in discrete amount. If $h\nu$ is not large enough (frequency threshold) no electrons are emitted.
- Absorption of energy is instantaneous.

- Classical:

- Energy of the light depend directly on the light intensity.
- No frequency dependence is observed.
- Absorption of energy takes a finite time.

Summary

Remark

Several other experiments (Compton effect, tunneling, stability of the atom structure, ..) shows that in case of atomic size particles the laws of classical mechanics do not provide a correct description of the physics.

Remark

At the same time other experimental evidence shows that the electromagnetic radiation has both a wavelike and a particle nature (photon).

Remark

The quantum mechanical description of the atomic world will move away from a rigid description of either wave or particle, to introduce a more complex formalism that makes room for both.

Summary

Remark

This description is based on complex (for real objects !) wavefunctions and the introduction of the concept of probability to describe the motion of atomic particle.

The Indetermination Principle

- From the evidence of the electron diffraction experiment we have seen that the classical law that describe the particle trajectory no longer explain the physics.
 - It is important then to understand under which conditions the concept of trajectory can be used and what are its limitations.
 - Is the classical assumption that all the variables of motion can be be measured simultaneously at the same time still valid?
 - Let us look again the experiment electron diffraction experiment and consider the case in which the slit has a size $x \pm \Delta x$.
 - How would the electron diffraction pattern change? What does this mean in terms of the other "variables of motion" of the electron?

The Indetermination Principle

- From the diffraction experiment we obtain that $\Delta p_x \Delta x \approx p \lambda$.
 - The more precisely we try to localize the electron in space, by defining the x position, the larger is the diffraction pattern, that is a larger indetermination on the momentum.
 - A question is on order .. what is the wavelength associated with an electron? From the empirical relation introduced by DeBroglie we have that $\lambda = h/p$, where h is the Plank's constant.

Remark

- In conclusion more precisely we can say:

$$\triangle \rho_x \triangle x \simeq \hbar$$

That is the Heisenberg's indetermination principle.

Fundamentals of Quantum Mechanics

- There are several possible way of introducing quantum mechanics. The most immediate is based on postulates. These are facts that we assume as true and we build the rest of theory on it.
 - The formulation of these postulates is based on the experimental evidence, some of which has been presented.

Postulate - 1 Wavefunctions

- To each physical system, for example an ensemble of quantum particle like electrons or holes, can be associated a *wavefunction* or *state function*. This is a complex quantity and contains all the information concerning the ensemble.
- The wavefunction $\Psi(\vec{r}, t)$ has the following properties. It is square integrable (L^2 function):

$$\int |\Psi(\vec{r}, t)|^2 d\vec{r} < \infty$$

$$\int |\Psi(\vec{r}, t)|^2 d\vec{r} = 1$$

Remark

The square value of the wavefunction has the meaning of *position probability density*.

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

Momentum Space Wavefunctions

Instead of using a description of the system based on the real space wavefunction $\Psi(\vec{r}, t)$, one could used the momentum space wavefunction $\Phi(\vec{p}, t)$. As before:

$$\int |\Phi(\vec{p}, t)|^2 d\vec{p} = 1$$

and:

$$\Pi(\vec{p}, t) = |\Phi(\vec{p}, t)|^2$$

has the meaning of *position probability density in momentum space*. In other words the probability of finding the momentum particle in a volume $d\vec{p}$ around \vec{p} . The *momentum space* and *real space* wavefunctions are related by the Fourier transform.

$$\Phi(\vec{p}, t) = \frac{1}{(2\pi\hbar)^{3/2}} \int e^{-i\frac{1}{\hbar}(\vec{p}\cdot\vec{r})} \Psi(\vec{r}, t) d\vec{r}$$

Postulate - 2 Superposition Principle

There exist a *superposition principle*, the dynamical states of two quantum systems are linearly superposable. If $\Psi_1(\vec{r}, t)$ is a wavefunction associated to one of the possible states of the system and $\Psi_2(\vec{r}, t)$ is another one, then their linear combination:

$$\Psi_3(\vec{r}, t) = c_1 \Psi_1(\vec{r}, t) + c_2 \Psi_2(\vec{r}, t)$$

is itself another state describing the system. Where c_1 and c_2 are complex numbers. The relative phase of the two wavefunction is important because of the interference. It is important to remember that only to $|\Psi(\vec{r}, t)|^2$ is associated a physical meaning. If we consider $|\Psi_3(\vec{r}, t)|^2$ we have:

$$|\Psi_3(\vec{r}, t)|^2 = |c_1 \Psi_1(\vec{r}, t)|^2 + |c_2 \Psi_2(\vec{r}, t)|^2 + 2 \operatorname{Re} \left\{ c_1 c_2^* \Psi_1(\vec{r}, t) |\Psi_2(\vec{r}, t)| e^{i[\alpha_1 - \alpha_2]} \right\}$$

Where α_1 and α_2 are the phases of $\Psi_1(\vec{r}, t)$ and $\Psi_2(\vec{r}, t)$. (See also Sec. 2.1)

Postulate - 3 Operators

With every dynamical variable is associated a linear operator. If A is a linear operator associated to the observable \mathcal{A} , then

$$A(\Psi_1(\vec{r}, t) + \Psi_2(\vec{r}, t)) = A\Psi_1(\vec{r}, t) + A\Psi_2(\vec{r}, t)$$

The quantization is performed by replacing the conjugate variables \vec{r}_i and \vec{p}_j with the respective operators $\hat{\vec{r}}_i$ and $-\imath\hbar\nabla_{\vec{p}_j}$ (See also Sec. 3.3 and 3.9).

Table: Observables - Operator correspondence

observable	operator
position coordinate x	\vec{r}
position vector \vec{r}	$i\hbar \frac{\partial}{\partial \vec{x}}$
x component of vector momentum p_x	$-i\hbar \frac{\partial}{\partial \vec{r}}$
momentum \vec{p}	$-\frac{\hbar^2}{2m} \nabla^2$
kinetic energy $T = \frac{\vec{p}^2}{2m}$	$\sqrt{\vec{r}, t}$
potential energy $V(\vec{r}, t)$	$V(\vec{r}, t)$
total energy $H = \frac{\vec{p}^2}{2m} + V(\vec{r}, t)$	$H = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}, t)$

Postulate - 4 Observable Measurements

The only results of precise measurement of the dynamical variable \mathcal{A} is one of the eigenvalues a_n of the operator A associated to \mathcal{A} . Eigenvalues are obtained from the solution of the eigenvalue problem:

$$\nabla \psi_n(\vec{r}, t) = a_n \psi_n(\vec{r}, t)$$

The functions $\psi_n(\vec{r}, t)$ are said to be the eigenfunction of the system and represent a complete orthonormal set (CON). The set of all the eigenvalues of an operator is called the *spectrum* of the operator. The spectrum can be discrete, continuous or a mix of the two. The outcome of a measurement on a physical observable must produce a real number. Consequently the operators associated to dynamical variables are Hermitian, and their eigenvalues real or $a_n^* = a_n$. In other words we can say that the operator is Hermitian if

$$\int \psi_n(\vec{r}, t)^* A \phi_n(\vec{r}, t) d\vec{r} = \int (A \psi_n(\vec{r}, t))^* \phi_n(\vec{r}, t) d\vec{r}$$

Postulate - 5 Expectation Values

The expectation values of a series of measurement on a dynamical variable \mathcal{A} on an ensemble of systems described by the state function $\Psi(\vec{r}, t)$ is given by

$$\langle \mathcal{A} \rangle = \frac{\int \Psi(\vec{r}, t)^* \Lambda \Psi(\vec{r}, t) d\vec{r}}{\int \Psi(\vec{r}, t)^* \Psi(\vec{r}, t) d\vec{r}}$$

It should always be remembered that $\langle \mathcal{A} \rangle$ is not the average of a classical statistical distribution of the dynamical variable \mathcal{A} between the systems being measured. Each system is identical and in the same state described by state function $\Psi(\vec{r}, t)$.

Note that if the wave-function is normalized then we can write:

$$\langle \mathcal{A} \rangle = \int \Psi(\vec{r}, t)^* \Lambda \Psi(\vec{r}, t) d\vec{r}$$

Hermitian Operators

An operator \mathcal{A} that represent a physical observable \mathcal{A} need to have real eigenvalues. Since the eigenvalue spectrum is the collection of all the possible measurement outcomes, the expectation values of a physical observable \mathcal{A} must be real. Consequently we can write:

$$\langle \mathcal{A} \rangle = \int \Psi(\vec{r}, t)^* A \Psi(\vec{r}, t) d\vec{r}$$

and

$$\langle \mathcal{A} \rangle^* = \int \Psi(\vec{r}, t) (\mathbf{A} \Psi(\vec{r}, t))^* d\vec{r}$$

and since for a physical observable

$\langle A \rangle = \langle A \rangle^*$

then

$$\int \Psi^*(\vec{r}, t) A \Psi(\vec{r}, t) d\vec{r} = \int (A \Psi(\vec{r}, t))^* \Psi(\vec{r}, t) d\vec{r}$$

I - The Dirac's Notation

Dirac introduced a very compact notation to describe the operation of quantum mechanical quantities. It used the so called $\langle \text{bra} | | \text{ket} \rangle$. In this case we will indicate:

$$\langle \Psi_1 | \Psi_2 \rangle = \int \Psi_1(\vec{r})^* \Psi_2(\vec{r}) d\vec{r}$$

the symbol $\langle \Psi_1 |$ is called the *bra* and $| \Psi_2 \rangle$ the *ket*. From the definition we can also write:

$$\langle \Psi_1 | \Psi_2 \rangle = \langle \Psi_2 | \Psi_1 \rangle^*$$

We can also define the operation of multiplication by a constant and the distribution property:

$$\begin{aligned}\langle \Psi_1 | c\Psi_2 \rangle &= c \langle \Psi_1 | \Psi_2 \rangle \\ \langle c\Psi_1 | \Psi_2 \rangle &= c^* \langle \Psi_1 | \Psi_2 \rangle \\ \langle \Psi_1 | c\Psi_2 + d\Psi_3 \rangle &= c \langle \Psi_1 | \Psi_2 \rangle + d \langle \Psi_1 | \Psi_3 \rangle\end{aligned}$$

II - The Dirac's Notation

Two state functions are said to be orthogonal if their scalar product is zero,

$$\langle \Psi_1 | \Psi_2 \rangle = 0$$

and the normalization conditions becomes:

$$\langle \Psi_1 | \Psi_1 \rangle = 1$$

The eigenvalue problem for an operator A is written as:

$$A|\Psi_n\rangle = a_n|\Psi_n\rangle$$

and the expectation value of the dynamical variable \mathcal{A} is:

$$\langle \mathcal{A} \rangle = \frac{\langle \Psi | A | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

The definition of Hermitian operator can be written as:

$$\langle \Psi | A | \Phi \rangle = \langle \Psi | (A\Phi) \rangle = \langle (A\Psi) | \Phi \rangle = \langle \Phi | (A\Psi) \rangle^*$$

Postulate - 6 CON Set Expansion

A wavefunction $\Psi(\vec{r}, t)$ representing any dynamical state can be represented as a linear combination of the CON eigenfunctions set $\{\psi_n(\vec{r}, t)\}$ of the operator A, that is associated with the dynamical variable A.

$$\Psi(\vec{r}, t) = \sum_n c_n \psi_n(\vec{r}, t)$$

The expansion coefficient c_n can be found using the orthonormality relation

$$\int \psi_m^*(\vec{r}, t) \Psi(\vec{r}, t) d\vec{r} = \sum_n c_n \int \psi_m(\vec{r}, t)^* \psi_n(\vec{r}, t) d\vec{r} = \sum_n c_n \delta_{n,m} = c_m$$

The physical meaning of the expansion coefficient:

$$P_n = |c_n|^2 = \left| \int \psi_n(\vec{r}, t)^* \psi(\vec{r}, t) d\vec{r} \right|^2 \quad (0)$$

is the *probability amplitude*, i.e. the probability of finding at time t the system in the state $\psi_n(\vec{r}, t)$ as a result of a measurement.

I - Matrix Representation of operators

Consider again the eigenvalue equation,

$$A\Psi_n(\vec{r}, t) = a_n \Psi_n(\vec{r}, t)$$

where A is an Hermitian operator, or given two state function Ψ and Φ we have, $\langle \Psi | (A\Phi) \rangle = \langle (A\Psi) | \Phi \rangle$. Then the eigenvalues a_n are real number.

Let us know consider a CON set of wavefunctions $\{\psi_n\}$ where n can be finite of infinite. Accordingly to postulate 5 any wavefunction can be expanded in terms of a orthonormal set, then $\Psi(\vec{r}, t) = \sum_n c_n \psi_n(\vec{r}, t)$. We can say the c_n are a representation of $\Psi(\vec{r}, t)$ in the basis $\{\psi_n\}$. Consider now a linear and Hermitian operator A, and let A operate on $\Psi(\vec{r}, t)$ producing another wavefuntion $\Phi(\vec{r}, t)$, then $\Phi(\vec{r}, t) = A\Psi(\vec{r}, t)$. We can expand $\Phi(\vec{r}, t)$ in terms of $\{\psi_n\}$ and we have:

$$\Phi(\vec{r}, t) = \sum_m d_m \psi_m(\vec{r}, t) \quad (1)$$

II - Matrix Representation of operators

The expansion coefficients can be written as

$$d_m = \langle \psi_m | \Phi \rangle = \langle \psi_m | A | \Psi \rangle = \langle \psi_m | A | \sum_n c_n \psi_n \rangle \quad (2)$$

follows that

$$d_m = \sum_n \langle \psi_m | A | \psi_n \rangle c_n = \sum_n A_{m,n} c_n \quad (3)$$

then the *matrix elements* $A_{m,n}$ transform the $\{\psi_n\}$ of $\Psi(\vec{r}, t)$ into the one of $\Phi(\vec{r}, t)$. Since, the coefficients d_m that uniquely define $\Phi(\vec{r}, t)$ are related through the matrix elements to c_m that uniquely define $\Psi(\vec{r}, t)$, then we can say that the operator A is completely specified by the set of matrix elements $A_{m,n}$,

$$A_{m,n} = \langle \psi_m | A | \psi_n \rangle \quad (4)$$

Clearly the matrix representation of an operator depends on the chosen basis set.

Postulate - 7 Dynamical Behavior

The time evolution of the wavefunction describing a quantum system is determined by the time dependent Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}, t) = H\Psi(\vec{r}, t)$$

where H is the total hamiltonian of the system.

The hamiltonian H represent the physical observable total energy. In general we write:

Schrödinger equation

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

In its general form the potential energy operator $V(\vec{r}, t)$ will depend on time. For example in the case of an oscillating electromagnetic field coupled to the system.

The Schrödinger Equation

We have seen that the time evolution of the state of the quantum mechanical system is described by the Schrödinger equation:

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

This is in general a PDE, and a solution is a function of four coordinates, three spatial and time. The hamiltonian H represent the physical

Consider first the case where the potential energy operator only depends on the spatial coordinates but not on time; observable total energy.

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

We can try to solve is by using separation of variables.

The Schrödinger Equation - I Separation of Variables

We can write the solution as:

$$\Psi(\vec{r}, t) = \psi(\vec{r})\phi(t)$$

Substituting we obtain:

$$ih\psi(\vec{r})\frac{\partial}{\partial t}\phi(t) = \phi(t)\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right)\psi(\vec{r})$$

Dividing RHS and LHS by $\psi(\vec{r})\phi(t)$ we have:

$$ih\frac{1}{\phi(t)}\frac{\partial}{\partial t}\phi(t) = \frac{1}{\psi(\vec{r})}\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right)\psi(\vec{r})$$

this means that the LHS is a function only of time and the RHS only of space. Or:

$$g(t) \equiv f(\vec{r})$$

this means that the two sides have to be equal to a constant

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The Schrödinger Equation - II Separation of Variables

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + (V(\vec{r}) - E)\psi(\vec{r}) = 0$$

According to postulate 4 every time we perform a measurement of energy on a quantum mechanical a system described by the state function $\Psi(\vec{r})$ the result we obtain is a value among the spectrum E_n and because we have measured it the system has collapsed on one of the states of the CON set $\{\psi_n(\vec{r})\}$.

The Schrödinger Equation - I Free Particle

Consider a free particle $[V(\vec{r}) = 0]$ moving in one dimension:

$$-\frac{\hbar^2}{2m}\frac{\partial}{\partial x}\psi(x) - E\psi(x) = 0$$

the solution is:

$$\psi(x) = A e^{i k x} + B e^{-i k x} \quad (5)$$

where:

$$k = \sqrt{\frac{2mE}{\hbar^2}}$$

Let us assume that because of the boundary conditions in (5) $A = 1$ and $B = 0$, then

$$\psi(x) = e^{i k x} \quad (6)$$

This means that if an electron (or a quantum mechanical particle) in not subjected to an external force, then it is described as a plane wave. Note that the eigenvalue spectrum is a continuum as if it would be for a classical particle.

The Schrödinger Equation - II Free Particle

Furthermore we have $|\psi(x)|^2 = 1 \forall x$ and this means the probability to find the particle is 1 in all the points of the space. This means the uncertainty on the position is infinite.
Note that the time dependent solution for this problem is readily written as:

$$\psi(x) = e^{\frac{i}{\hbar} [p_x x - E t]} \quad (7)$$

Consider again equation (6), is this wavefunction normalized? How would you compute the normalization coefficient?

III Free Particle - Momentum Eigenvalues

What are the possible values of the momentum? To answer the question we need to solve the eigenvalue problem:

$$P_x \psi(x) = p_x \psi(x) \quad \rightarrow \quad -i\hbar \frac{\partial}{\partial x} \psi(x) = p_x \psi(x)$$

or

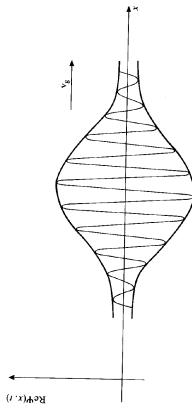
$$p_x = \hbar k$$

Example II - Wavewacket

The wavefunction in equation (6) describe a particle that has definite value of momentum and energy but is completely delocalized in space. To describe a particle partially localized in space we can use a superposition of free particle states.

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \frac{i}{\hbar} [p_x x - E t] \phi(p_x) dp_x \quad (8)$$

The (envelope) function $\phi(p_x)$ is in general complex (magnitude and phase) and give the amplitude of the component with momentum p_x .



Example II - Wavewacket

The center of the wavepacket is determined by:

$$\left[\frac{d[p_{\times}x - E t]}{dp_{\times}} \right]_{p_{\times}=p_0} = 0 \quad (9)$$

And moves with the group velocity:

$$\nu_g = \left[\frac{dE(p_x)}{dp_x} \right]_{p_x=p_0} \quad (10)$$

I Conservation of the Probability Density

From classical electrodynamics we have a continuity equation for charge:
written as:

$$\nabla \bullet \vec{J} + \frac{\partial \rho}{\partial t} = 0$$

What can we say about the probability density (or charge density distribution)?

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

Let us start from the Schrödinger and multiply the left and right terms by $\Psi^*(\vec{r}, t)$:

$$-\frac{\hbar^2}{2m} \Psi^*(\vec{r}, t) \nabla^2 \Psi(\vec{r}, t) + \Psi^*(\vec{r}, t) V(\vec{r}, t) \Psi(\vec{r}, t) = i\hbar \Psi^*(\vec{r}, t) \frac{\partial}{\partial t} \Psi(\vec{r}, t) \quad (11)$$

II Conservation of the Probability Density

take the complex conjugate

$$-\frac{\hbar^2}{2m}\Psi(\vec{r},t)\nabla^2\Psi^*(\vec{r},t) + \Psi(\vec{r},t)V(\vec{r},t)\Psi^*(\vec{r},t)$$

$$= -i\hbar\Psi(\vec{r},t)\frac{\partial}{\partial t}\Psi^*(\vec{r},t)$$
(12)

and subtract equation the second equation from the first:

$$-\frac{\hbar^2}{2m} \left[\Psi^*(\vec{r}, t) \nabla^2 \Psi(\vec{r}, t) - \Psi(\vec{r}, t) \nabla^2 \Psi^*(\vec{r}, t) \right] = i\hbar \left[\Psi^*(\vec{r}, t) \frac{\partial}{\partial t} \Psi(\vec{r}, t) + \Psi(\vec{r}, t) \frac{\partial}{\partial t} \Psi^*(\vec{r}, t) \right]$$

since:

$$\Psi^*(\vec{r}, t) \frac{\partial}{\partial t} \Psi(\vec{r}, t) + \Psi(\vec{r}, t) \frac{\partial}{\partial t} \Psi^*(\vec{r}, t) = \frac{\partial}{\partial t} (\Psi^*(\vec{r}, t) \Psi(\vec{r}, t))$$

III Conservation of the Probability Density

we have:

$$\frac{\hbar^2}{2m} [\Psi^*(\vec{r}, t) \nabla^2 \Psi(\vec{r}, t) - \Psi(\vec{r}, t) \nabla^2 \Psi^*(\vec{r}, t)] + i\hbar \frac{\partial}{\partial t} (\Psi^*(\vec{r}, t) \Psi(\vec{r}, t)) = 0$$

Using the vector identity:

$$\nabla \bullet (\phi \vec{A}) = \vec{A} \bullet \nabla \psi + \phi \nabla \bullet \vec{A}$$

with $\vec{A} = \nabla \phi$ we have:

$$\Psi^*(\vec{r}, t) \nabla^2 \Psi(\vec{r}, t) - \Psi(\vec{r}, t) \nabla^2 \Psi^*(\vec{r}, t) = \nabla \bullet [\Psi^*(\vec{r}, t) \nabla \Psi(\vec{r}, t) - \Psi(\vec{r}, t) \nabla \Psi^*(\vec{r}, t)]$$

Consequently we can write:

$$\frac{\partial}{\partial t} (\Psi^*(\vec{r}, t) \Psi(\vec{r}, t)) + \frac{\hbar}{2m_i} \nabla \bullet [\Psi^*(\vec{r}, t) \nabla \Psi(\vec{r}, t) - \Psi(\vec{r}, t) \nabla \Psi^*(\vec{r}, t)]$$

IV Conservation of the Probability Density

Notice that if we define the probability current density as:

$$\vec{J} = \frac{\hbar}{2m_i} [\psi^*(\vec{r}, t) \nabla \psi(\vec{r}, t) - \psi(\vec{r}, t) \nabla \psi^*(\vec{r}, t)]$$

we obtain the continuity equation for the probability density:

$$i\hbar \frac{\partial}{\partial t} \mathbf{P}(\vec{r}, t) + \nabla \cdot \vec{\mathbf{J}} = 0$$

I - Operators, Commutation Relations and Uncertainty

Consider the operator $\hat{x}p_x$, and compute the expectation value of the observable product of position and momentum $\langle \hat{x}p_x \rangle$

$$\langle x p_x \rangle = \int_{-\infty}^{+\infty} \Psi^*(x, t) x \left(-i \hbar \frac{\partial}{\partial x} \right) \Psi(x, t) dx$$

Integrating by parts we have:

$$\langle x \rho_x \rangle = [-i\hbar \times \Psi^*(x,t) \Psi(x,t)]_{-\infty}^{+\infty} + i\hbar \int_{-\infty}^{+\infty} \Psi^*(x,t) \frac{\partial}{\partial x} (\times \Psi(x,t)) dx$$

since $|\Psi(x, t)| \rightarrow 0$ as $x \rightarrow \pm\infty$,

II - Operators, Commutation Relations and Uncertainty

then:

$$\begin{aligned} \langle x p_x \rangle &= i \hbar \int_{-\infty}^{+\infty} \psi^*(x, t) x \frac{\partial}{\partial x} \psi(x, t) dx + \\ &i \hbar \int_{-\infty}^{+\infty} \psi^*(x, t) \psi(x, t) dx \end{aligned}$$

or:

$$\langle x p_x \rangle = \langle x p_x \rangle^* + i \hbar$$

The operator $x p_x$ is evidently not hermitian since its expectation value is not real. Similarly we can find that:

$$\langle p_x x \rangle = \langle p_x x \rangle^* - i \hbar$$

Consequently the order in which the operators are applied counts and $x p_x$ has different expectation values than $p_x x$, or as it is said they do not commute.

III - Operators, Commutation Relations and Uncertainty

Given two operators A and B, the commutator of A and B is defined as:

$$[A, B] = AB - BA \quad \rightarrow \quad AB = BA$$

then the two operators are said to commute.

In general:

$$[x, \rho_x] = [y, \rho_y] = [z, \rho_z] = i\hbar$$

I - Commutating Operators and Eigenfunctions

Let us assume that \mathcal{A} and \mathcal{B} are two observables represented by the operators A and B , and assume there exist a complete set $\{\psi_n\}$ of eigenfunctions that is simultaneously eigenfunction of A and B . Then A and B are said to be *compatible*, and their associated eigenvalues a_n and b_n are given by:

$$A\psi_n = a_n \psi_n \quad B\psi_n = b_n \psi_n$$

Also we have:

$$AB\psi_n = A b_n \psi_n = b_n A \psi_n = b_n \partial_n \psi_n = BA\psi_n$$

Consequently if we have a state function $\Psi(x, t)$ this can be expanded using the basis set $\{\psi_n\}$, then:

$$(AB - BA)\Psi(x, t) = \sum_n c_n(AB - BA)\psi_n = 0$$

and

II - Commutating Operators and Eigenfunctions

$$(AB - BA) = [A, B] = 0$$

the two operators commute and the the converse is also true

Commutating Operators

Two operators that commute have a set of CON eigenfunctions $\{\psi_n\}$ in common.

Commutator

$$[A, B] = (AB - BA)$$

Commutator Algebra

We also have the simple rules that are easy to prove:

$$\begin{aligned} [A, B] &= -[B, A] \\ [A, B + C] &= [A, B] + [A, C] \\ [A, BC] &= [A, B]C + B[A, C] \\ [A, [B, C]] + [B, [C, A]] + [C, [A, B]] &\equiv 0 \end{aligned}$$

These are useful to manipulate sequences of operators.

More on the Uncertainty Relations

Consider two dynamical variables \mathcal{A} and \mathcal{B} and $\langle A \rangle = \langle \Psi | A | \Psi \rangle$, $\langle B \rangle = \langle \Psi | B | \Psi \rangle$ the respective expectation values for a given state function Ψ . We define the uncertainty ΔA on the observable \mathcal{A} and \mathcal{B} as:

$$\Delta A = \sqrt{<(A - < A >^2)>} , \quad \Delta B = \sqrt{<(B - < B >^2)>}$$

it can be shown (homework) that:

$$\Delta A \Delta B \geq \frac{1}{2} |<[A,B]>|$$

Two non-commuting observables that are canonically conjugated then we have $[A, B] = i\hbar$ and:

$$\Delta A \Delta B \geq \frac{\hbar}{2}$$

As we have seen, for x and p_x we have $[x, p_x] = i\hbar$, consequently:

$$\Delta x \Delta p_x \geq \frac{\hbar}{2}$$

Classical Limit - The Ehrenfest Theorems

This theorem states that Newton's classical dynamics equations:

$$\frac{d\vec{r}}{dt} = \vec{p} - \vec{m}$$

and

$$\frac{dp'}{dt} = -\nabla V \quad (14)$$

are exactly satisfied by the expectation (*average*) values of the corresponding operators in quantum mechanics.

Note that in quantum mechanics we can not talk of trajectory in the classical sense and consequently we can not compute $d\vec{r}/dt$ or $d\vec{p}/dt$ but rather we can compute the rate of change of the expectation values of position $\langle \vec{r} \rangle$ and momentum $\langle \vec{p} \rangle$.

I - The Ehrenfest Theorems

If we start by computing the time derivative of the expectation values of the position coordinate x , we have:

$$\frac{d}{dt} < x > = \frac{d}{dt} \int \Psi(\vec{r}, t)^* x \Psi(\vec{r}, t) d\vec{r}$$

as shown in the additional materials, one obtains:

$$\frac{d}{dt} < x > = \frac{1}{m} \int \psi(\vec{r}, t)^* \left(-i\hbar \frac{\partial}{\partial_x} \right) \psi(\vec{r}, t) d\vec{r} = \frac{1}{m} < p_x >$$

which is the equivalent of equation 13:

First Ehrenfest Theorems

$$\frac{d}{dt} \langle x \rangle = \frac{1}{m} \langle p_x \rangle \quad \Leftrightarrow \quad \frac{d\vec{r}}{dt} = \frac{\vec{p}}{m} \quad (15)$$

II - The Ehrenfest Theorems

In the same way by considering the time derivative of the momentum (for example x component of \vec{P}) we have:

$$\frac{d}{dt} \langle p_x \rangle = \frac{d}{dt} \int \Psi(\vec{r}, t)^* \left(-i\hbar \frac{\partial}{\partial x} \right) \Psi(\vec{r}, t) d\vec{r}$$

With some manipulation, as shown in the supplementary material:

$$\frac{d}{dt} \langle p_x \rangle = \int \Psi(\vec{r}, t)^* \frac{\partial V(\vec{r}, t)}{\partial x} \Psi(\vec{r}, t) d\vec{r} = - \left\langle \frac{\partial V(\vec{r}, t)}{\partial x} \right\rangle$$

that is analogous to the classical equation 14.

Second Ehrenfest Theorems

$$\frac{d}{dt} \langle p_x \rangle = - \left\langle \frac{\partial V(\vec{r}, t)}{\partial x} \right\rangle \iff \frac{d\vec{p}}{dt} = -\nabla V \quad (16)$$

Generalization of the Ehrenfest Theorems

Consider an observable \mathcal{A} represented by an operator A , we can evaluated in Dirac's notation as:

$$\begin{aligned}\frac{d}{dt} \langle A \rangle &= \frac{d}{dt} \langle \Psi | A | \Psi \rangle \\&= \left\langle \frac{d}{dt} \Psi \left| A \right| \Psi \right\rangle + \left\langle \Psi \left| \frac{d}{dt} A \right| \Psi \right\rangle + \left\langle \Psi \left| A \right| \frac{d}{dt} \Psi \right\rangle \\&= \int_V \frac{d}{dt} \Psi^* A \Psi d\vec{r} + \int_V \Psi^* \frac{d}{dt} A \Psi d\vec{r} + \int_V \Psi^* A \frac{d}{dt} \Psi d\vec{r}\end{aligned}\quad (17)$$

The expression above contains the time derivative of the operator A. The value of this derivative depends on the representation used.

Representation in Quantum Mechanics

Schrödinger Representation

In the Schrödinger Representation the time dependence of the system is embedded in the wavefunctions $\Psi(\vec{r}, t)$ and the operators A are time-independent.

Heisenberg Representation

In the Heisenberg Representation the time dependence of the system is embedded in the operators $A(t)$ and wavefunctions $\Psi(\vec{r})$ are time-independent.

Interaction Representation

In the Interaction Representation the time dependence of the system is embedded both in the operators $A(t)$ and the wavefunctions $\Psi(\vec{r}, t)$.

Generalization of the Ehrenfest Theorems - II

As shown in the additional material we obtain:

$$\frac{d}{dt} \langle A \rangle = \left\langle \frac{d}{dt} A \right\rangle + \frac{1}{i\hbar} \langle [A, H] \rangle \quad (18)$$

Where H is the Hamiltonian of the system.

Conservation Laws

If the operators A commutes with the Hamiltonian H and it is time independent then $[A, H] = 0$. In this case:

$$\frac{d}{dt} \langle A \rangle = 0 \quad (19)$$

The observable \mathcal{A} is conserved.

Solvable Problems in Quantum Mechanics

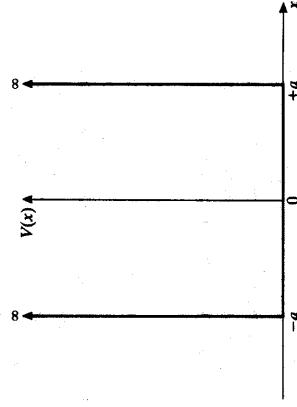
The Schrödinger equation can be solved in closed form only for a limited set of problems. This depends on the form of the Hamiltonian operator.

$$i\hbar \frac{\partial}{\partial t} \Psi(\vec{r}, t) = \hat{H}\Psi(\vec{r}, t) = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \Psi(\vec{r}, t)$$

If the potential energy is time-independent, the solution of equation 20 can be separated in a time dependent part and a spatial dependent part. The solution of the spatial dependent part provides the stationary states of the system. The situations where a solution can be found in a closed form are:

- Potential step (1D)
 - Potential barrier (1D)
 - Infinite potential square well (1-3D)
 - Square well (1D)
 - Harmonic oscillator (1-3D)
 - Periodic Potential (1D)
 - Central Potential, Hydrogen Atom. (

I - Infinite Potential Well



$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) - E \psi(x) = 0$$

the solution is:

$$\psi(x) = A e^{ikx} + B e^{-ikx}$$

also:

$$\psi(x) = A \cos(kx) + B \sin(kx)$$

where:

$$k = \sqrt{\frac{2mE}{\hbar^2}}$$

the boundary condition is:

$$\psi(x) = 0 \quad \text{for } |x| > a \quad \psi(x) = 0 \quad \text{for } x = \pm a$$

Consequently:

II - Infinite Potential Well

$$A \cos(kx) = 0$$

and

$$B \sin(kx) = 0$$

then

$$k_n = \frac{n\pi}{2a} = \frac{n\pi}{L}$$

where $L = 2a$. Then the solutions are:

$$\psi_n(x) = A_n \cos(k_n x) \quad \text{for } n = 1, 3, 5, 7, \dots$$

$$\psi_m(x) = B_m \sin(k_m x) \quad \text{for } m = 2, 4, 6, 8, \dots$$

The final wavefunctions are:

$$\psi_n(x) = \frac{1}{\sqrt{a}} \cos\left(\frac{n\pi}{2a} x\right) \quad \text{for } n = 1, 3, 5, 7, \dots$$

$$\psi_m(x) = \frac{1}{\sqrt{a}} \sin\left(\frac{n\pi}{2a} x\right) \quad \text{for } m = 2, 4, 6, 8, \dots$$

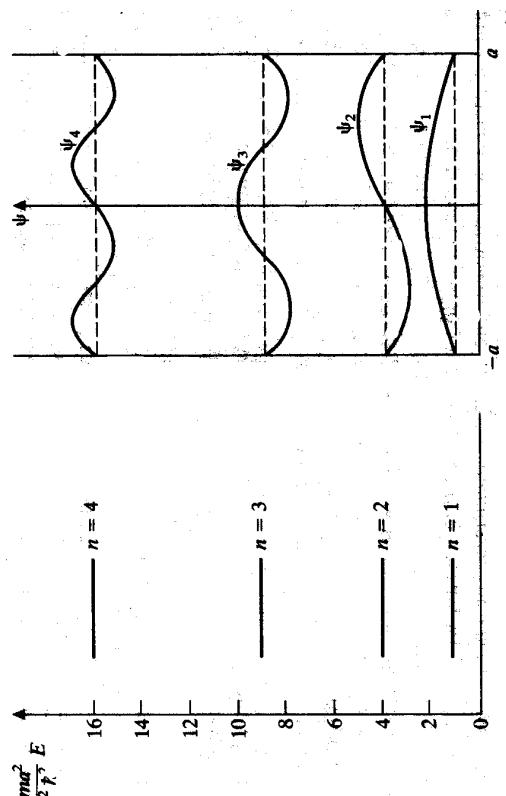
Consequently the possible energy that the particle can assume in the well are quantized.

$$E_n = \frac{\hbar^2 \pi^2 n^2}{8m a^2} = \frac{\hbar^2 \pi^2 n^2}{2m L^2}$$

using the normalization condition:

Note that there is only one eigenfunction for each energy level. 

Infinite Potential Well Wavefunctions



Infinite Potential Well Wavefunctions - Summary

Ground State Energy

There is a *non-zero* minimum energy $E_n = \hbar^2 \pi^2 / (8 m a^2)$, this energy increases as the well becomes narrower (reaction to confinement).

Uncertainty

The *zero point* energy is a direct consequence of the indetermination principle. In fact the uncertainty on the position is $\Delta x = a$ consequently the uncertainty on the momentum is $\Delta p_x = \hbar/a$ and a minimum energy of the order $\hbar^2 / (m a^2)$.

Eigenfunctions Nodes

The n th eigenfunction has $(n-1)$ nodes. The ground state never has a node.

Infinite Potential Well Wavefunctions - Summary

Eigenfunctions Orthogonality

Wavefunctions corresponding to two different energy eigenvalues E_n and E_m are orthogonal:

$$\int \psi_n^*(x) \psi_m(x) dx = 0 \quad n \neq m$$

Wavefunction Symmetry - Parity Operator

Note that for the solution of the previous example all the wavefunctions have a defined parity, they are either:

$$\begin{aligned}\psi_n(-x) &= \psi_n(x) && \text{even parity} \\ \psi_m(-x) &= -\psi_m(x) && \text{odd parity}\end{aligned}$$

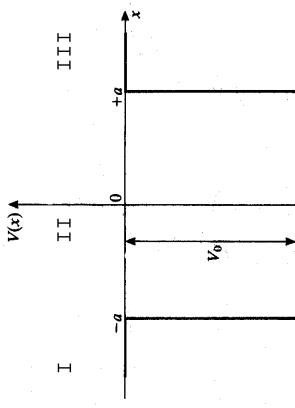
The wavefunctions possess a definite parity since the potential is symmetric respect the origin $x = 0$: $V(-x) = V(x)$. The Schrödinger equation does not change if $x \rightarrow -x$.

We can also define a parity operator such that the observable parity P represented by the operator P :

$$P \psi_n(x) = P \psi_n(x)$$

when applied to the eigenfunction give the eigenvalues $p = \pm 1$.

I - Finite Square Well



There are two region interfaces:
 $x = -a$ and $x = -a$, the continuity boundary conditions between two regions I and II are:

$$\psi_I(x_0) = \psi_{II}(x_0)$$

$$\frac{1}{m_I} \frac{\psi_I(x)}{dx} \Big|_{x=x_0} = \frac{1}{m_{II}} \frac{\psi_{II}(x)}{dx} \Big|_{x=x_0}$$

The second boundary condition is equivalent to use the continuity of the probability current density at the interface:

$$V(x) = \begin{cases} -\nabla_0 & |x| \leq a \\ 0 & |x| > a \end{cases}$$

Note that now the wavefunction for $|x| > a$ will no longer be 0.

$$\vec{J}_I^{\parallel} =$$

II - Finite Square Well

We consider two different situations for the solution of this problem:

$$a) = V_0 < E_i < 0 \text{ and } b) E_i > 0$$

c) Case a) For region II

$$\frac{d^2}{dx^2} \psi(x) + \alpha^2 \psi(x) = 0 \quad \alpha = \sqrt{\frac{2m}{\hbar^2}(V_0 - |E|)}$$

and for regions I and III

$$\frac{d^2}{dx^2} \psi(x) - \beta^2 \psi(x) = 0 \quad \beta = \sqrt{\frac{2m}{\hbar^2} |E|}$$

Since the potential is symmetric respect the origin then the wavefunctions need to have a definite parity. Then we can consider the solution only for $x > 0$. The even solutions are given by:

$$\psi(x) = A \cos(\alpha x) \quad 0 < x < a$$

$$\psi(x) = C e^{-\beta x} \quad x \geq a$$

III - Finite Square Well

Requiring that $\psi(x)$ and its first derivative be continuous at the interface located at $x = a$, we have two transcendental equations:

$$A \cos(\alpha a) = C e^{-\beta a} \quad -\alpha A \sin(\alpha a) = -\beta C e^{-\beta a}$$

or

$$\alpha \tan(\alpha a) = \beta \quad (20)$$

The odd solutions are given by:

$$\begin{aligned}\psi(x) &= B \sin(\alpha x) & 0 < x < a \\ \psi(x) &= C e^{-\beta x} & x \geq a\end{aligned}$$

Requiring that $\psi(x)$ and its first derivative be continuous at the interface located at $x = a$, we have the transcendental equation:

$$\alpha \cot(\alpha a) = -\beta \quad (21)$$

The energy level are computed solving equations 20 and 21.

IV - Finite Square Well

Setting $\xi = \alpha a$ and $\eta = \beta a$ we have

$$\xi \tan \xi = \eta \quad \xi \cot \xi = -\eta \quad (22)$$

Since ξ and η have to be positive and:

$$\xi^2 + \eta^2 = \gamma^2 = \sqrt{\frac{2 m V_0 a^2}{\hbar^2}}$$

We can find graphically the solutions by finding the intersection between the circles defined by $\xi^2 + \eta^2 = \gamma^2$ of radius γ and 22 for even and odd wavefunctions.

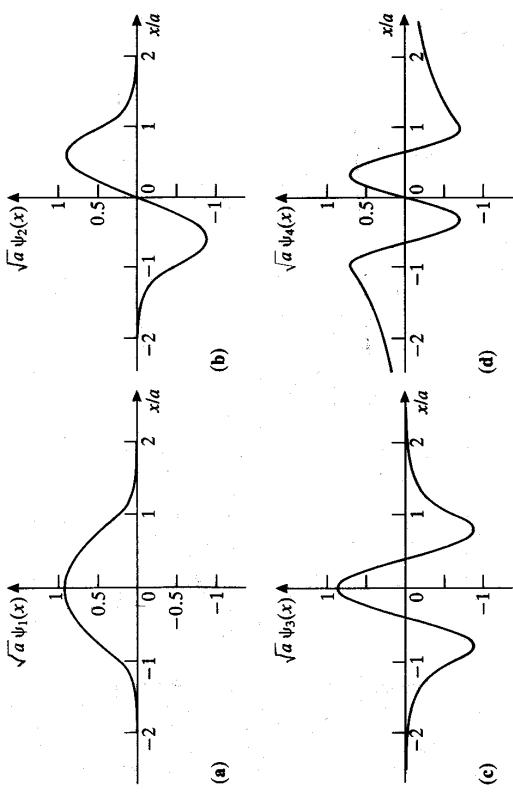
Bound States

The bound states are non-degenerate and their number is finite.

Symmetry

Even and odd states alternates in the energy scale.

Finite Square Well Wavefunctions - Bound States



Finite Square Well - Unbound States

Case b) $E > 0$

- For region I and III the solutions for the external regions $x < -a$ and $x > a$ are given by:

$$\psi(x) = \begin{cases} Ae^{ix} + Be^{-ix} \\ Ce^{-ix} \end{cases}$$

Where as usual $k = \sqrt{\frac{2mE}{\hbar^2}}$.

- For region II the solutions is written as:

$$\psi(x) = F e^{i\alpha x} + G e^{-i\alpha x}$$

where $\alpha = \sqrt{\frac{2m(V_0+E)}{h^2}}$

- The five constants A, B, C, F, G are computed by imposing the continuity of the wavefunction and its derivative at $x = -a$ and $x = a$.

Finite Square Well - Unbound States

Solving for A,B, and C we can define a *Transmission Coefficient T* and a *Reflection Coefficient R*:

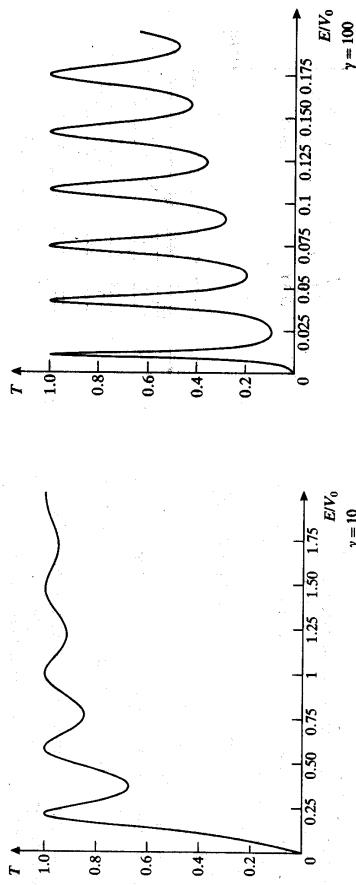
$$R = \frac{|B|^2}{|A|^2} \quad T = \frac{|C|^2}{|A|^2}$$

and clearly $R+T=1$.

$$R = \left[1 + \frac{4E(V_0 + E)}{V_0^2 \sin^2(\alpha/2a)} \right]^{-1} \quad T = \left[1 + \frac{V_0^2 \sin^2(\alpha/2a)}{4E(V_0 + E)} \right]^{-1}$$

and clearly $R+T=1$.

Finite Square Well Wavefunctions - Transmission Probability



Finite Square Well - Summary

Transmission Coefficient

The transmission coefficient is less than unity, as opposed to what happens in the case of a classical particle.

Minimum Transmission

The transmission peaks for which $T = 1$ occur at $\alpha L = n\pi$. The minima are reached when $\alpha L = (2n - 1)\pi/2$. Where as defined $\alpha = \sqrt{2mE/\hbar^2}$.

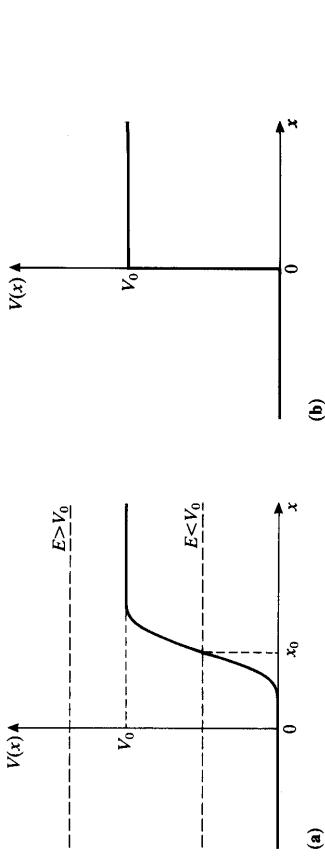
Resonance

Perfect transmission occurs when the dimension of the well L is equal to a integral of half-integral number of *de Broglie* electron wavelengths $2\pi/\alpha$ (Resonance).

Classical Limit

If $E \gg V$ then T becomes asymptotically equal to unity.

I - Potential Step



In this case we have again two distinct cases a) $V_0 < E < 0$ and b)

$$\frac{d^2}{dx^2} \psi(x) + k^2 \psi(x) = 0 \quad k = \sqrt{\frac{2m}{\hbar^2} E} \quad x < 0$$

$$\frac{d^2}{dx^2} \psi(x) + \kappa^2 \psi(x) = 0 \quad \kappa = \sqrt{\frac{2m}{\hbar^2} (V_0 - E)} \quad x > 0$$

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II - Potential Step

with solutions

$$\psi(x) = \begin{cases} A e^{i\kappa x} + B e^{-i\kappa x} & x < 0 \\ D e^{-i\kappa x} & x > 0 \end{cases}$$

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By using the boundary conditions on the wavefunction and its derivative we obtain:

$$\begin{aligned}\psi(x) &= 2A e^{i\alpha/2} \cos(kx - \alpha/2) & x < 0 \\ \psi(x) &= 2A e^{i\alpha/2} \cos(\alpha/2) e^{-kx} & x > 0\end{aligned}$$

$$\begin{aligned}\psi(x) &= 2A e^{i\alpha/2} \cos(kx - \alpha/2) & x < 0 \\ \psi(x) &= 2A e^{i\alpha/2} \cos(\alpha/2) e^{-kx} & x > 0\end{aligned}$$

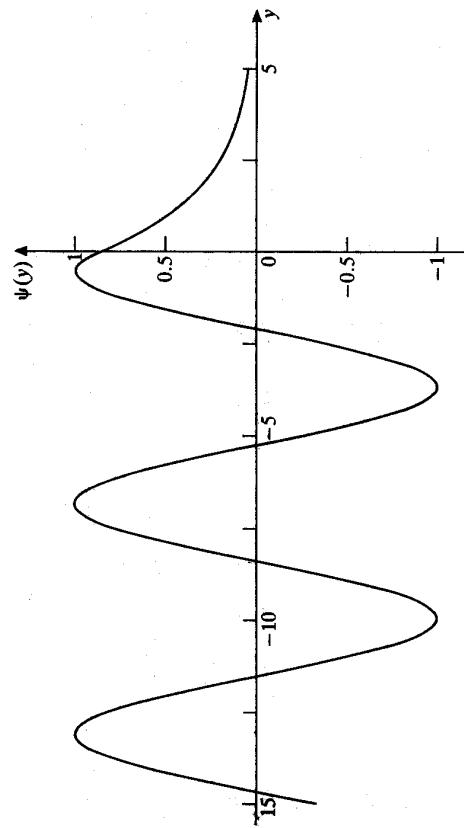
where:

$$\alpha = 2 \tan^{-1} \left[- \left(\frac{V_0}{E} - 1 \right)^{1/2} \right]$$

As in the case of the finite square well we can define a reflection coefficient for the potential step.

$$R = \frac{|B|^2}{|A|^2}$$

Potential Step - Wavefunctions



Reflection at the Step

Notice that the probability density on the left of the barrier:

$$P(x) = 4|A|^2 \cos^2(k_x - \alpha/2)$$

has an oscillatory behavior due to the interference of incident and reflected waves.

Under the barrier it becomes:

$$P(x) = |D|^2 e^{-2\kappa x}$$

There is a finite probability of finding the particle under the barrier, this is clearly impossible from the classical standpoint. Why do we have this?

$$\begin{aligned} \Delta x &\simeq \frac{1}{\kappa} \rightarrow \Delta p_x \geq \frac{\hbar}{\Delta x} \simeq \hbar\kappa = \sqrt{2m(V_0 - E)} \rightarrow \\ \rightarrow \Delta E &= \frac{\Delta^2 p_x}{2m} \geq (V_0 - E) \end{aligned}$$

The particle energy can no longer be said to be lower than V_0

Potential Step - Transmission Above the Barrier

Case b) We have $E > V_0$ then

$$\begin{aligned} \frac{d^2}{dx^2}\psi(x) + k^2\psi(x) &= 0 & k = \sqrt{\frac{2m}{\hbar^2}E} & x < 0 \\ \frac{d^2}{dx^2}\psi(x) + k'^2\psi(x) &= 0 & k' = \sqrt{\frac{2m}{\hbar^2}(E - V_0)} & x > 0 \end{aligned}$$

with solutions

$$\begin{aligned}\psi(x) &= A e^{i k x} + B e^{-i k x} & x < 0 \\ \psi(x) &= C e^{i k' x} + D e^{-i k' x} & x > 0\end{aligned}$$

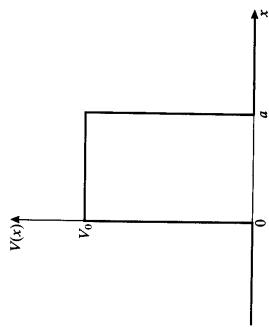
since there is no reflected wave once the particle has move to the region $x > 0$ then $D=0$ As before we can define a transmission and reflection coefficients:

$$R = \frac{|B|^2}{|A|^2} = \frac{(k-k')^2}{(k+k')^2} = \frac{\left[1 - \sqrt{1 - V_0/E}\right]^2}{\left[1 + \sqrt{1 - V_0/E}\right]^2}$$

Potential Step - Transmission Above the Barrier

$$T = \frac{|C|^2}{|A|^2} = \frac{4kk'}{(k+k')^2} = \frac{4\sqrt{1-V_0/E}}{\left[1+\sqrt{1-V_0/E}\right]^2}$$

Finite Width Potential Barrier



We are going to have as usual three solutions, on the left of the barrier, under the barrier and on the right of the barrier, and we will consider the case in which $E > V_0$ or $E \leq V_0$ for

$$\psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx} & x < 0 \\ Ce^{ikx} & x > a \end{cases}$$

As before we will define:

$$V(x) = \begin{cases} 0 & x < 0 \\ V_0 & 0 \leq x \leq a \\ 0 & x > a \end{cases} \quad R = \frac{|B|^2}{|A|^2} \quad T = \frac{|C|^2}{|A|^2}$$

Finite Width Potential Barrier - Tunneling |

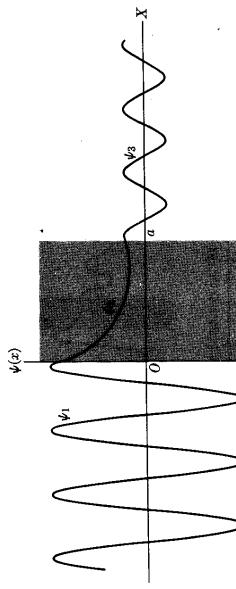
For $E \leq V_0$ then the solution for $0 \leq x \leq a$ is:

$$\psi(x) = F e^{\kappa x} + G e^{-\kappa x}$$

using the boundary conditions we have can compute the relations between the coefficients and determine the transmission and reflection coefficients:

$$R = \frac{|B|^2}{|A|^2} = \left[1 + \frac{4E(V_0 - E)}{V_0^2 \sinh^2(\kappa a)} \right]^{-1}$$

$$T = \frac{|C|^2}{|A|^2} = \left[1 + \frac{V_0^2 \sinh^2(\kappa a)}{4E(V_0 - E)} \right]^{-1}$$



Finite Width Potential Barrier - Tunneling II

Clearly there is a finite probability for the particle to *tunnel* under the barrier and appear on the other side. This effect is extremely important for a lot of practical applications in electronic devices, for example ohmic contact.

For $E > V_0$ then the solution for $0 \leq x \leq a$ is:

$$\psi(x) = F e^{i k' x} + G e^{-i k' x}$$

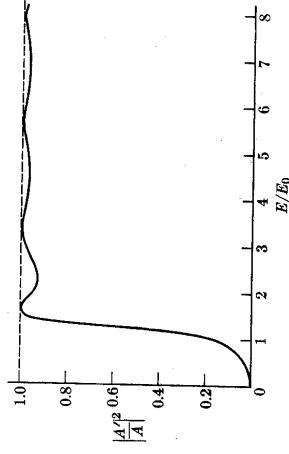
and as before we have can compute the relations between the coefficients and determine the transmission and reflection coefficients:

$$R = \frac{|B|^2}{|A|^2} = \left[1 + \frac{4 E (E - V_0)}{V_0^2 \sin^2(k' a)} \right]^{-1}$$

and

$$T = \frac{|C|^2}{|A|^2} = \left[1 + \frac{V_0^2 \sin^2(k' a)}{4 E (E - V_0)} \right]^{-1}$$

Finite Width Potential Barrier - Tunneling III



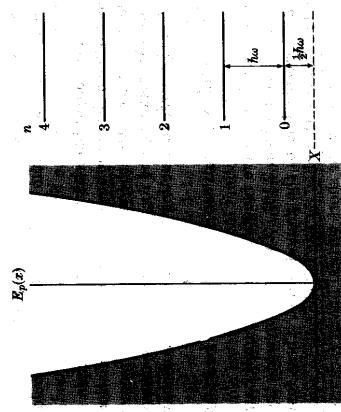
Transmission Minima

The transmission peaks for which $T = 1$ occur at $k' a = n\pi$. The minima is reached when $\alpha L = (2n - 1)\pi/2$, with $k' = \sqrt{2m(E - V_0)/\hbar^2}$.

Perfect Transmission

Perfect transmission occurs when the dimension of the well a is equal to a integral half-integer number of de Broglie wavelengths $2\pi/k'$ (Resonance).

I - The Linear Harmonic Oscillator



The potential is characterized by the spring constant k in analogy with the classical harmonic oscillator. We define:

$$\omega_0 = \sqrt{\frac{k}{m}}$$

and the quantity $\hbar\omega_0$ is the equivalent harmonic oscillator energy. We also define:

$$\beta = \sqrt{\frac{m\omega_0}{\hbar}}$$

The potential in this case has the form:

$$V(x) = \frac{1}{2} k x^2$$

II - The Linear Harmonic Oscillator

The Schrödinger equation becomes:

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) + \frac{1}{2}kx^2\psi(x) = E\psi(x)$$

This type of equation is not easily solved. Many techniques can be used, the usual one it to find a solution by series expansion. In this case the eigenvalues that one obtains are:

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega_0 \quad n = 0, 1, 2, 3, \dots$$

The wavefunctions are given by:

$$\psi_n(x) = N_n e^{-\beta^2 x^2/2} H_n(\beta x)$$

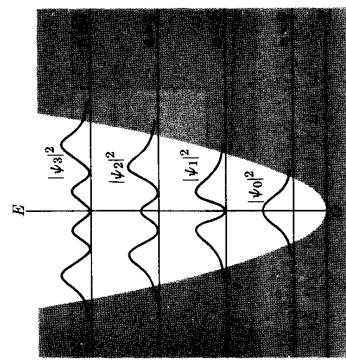
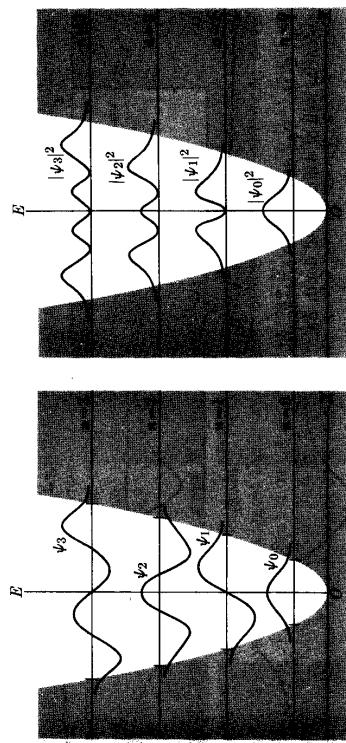
where N_n is a normalization constant and $H_n(\alpha x)$ is the Hermite polynomial of order n. These polynomial are a CON set of functions, defined as:

$$H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n e^\xi}{d\xi^n}$$

Hermite Polynomials and Wavefunctions

$$\begin{aligned} H_0(\xi) &= 1 \\ H_1(\xi) &= 2\xi \\ H_2(\xi) &= 4\xi^2 - 2 \end{aligned} \quad \begin{aligned} H_0(\xi) &= 1 \\ H_1(\xi) &= 2\xi \\ H_2(\xi) &= 4\xi^2 - 2 \end{aligned}$$

and the wavefunctions:



Wavefunctions Normalization

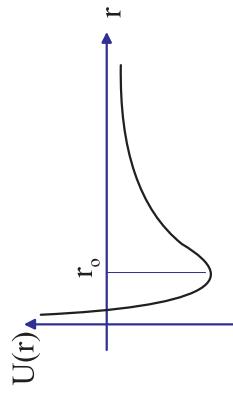
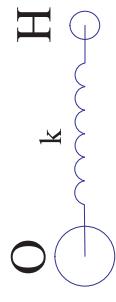
The normalization constant is obtained by requiring that the square of the absolute value of the wavefunction be 1. It is:

$$N_n = \sqrt{\frac{\beta}{\sqrt{\pi} 2^n n!}}$$

Consequently:

$$\psi_n(x) = \sqrt{\frac{\beta}{\sqrt{\pi} 2^n n!}} e^{-\beta^2 x^2/2} H_n(\alpha x)$$

Linear Harmonic Oscillator: Application to the H-O Molecule Vibration I



Consider the H-O molecule. The smaller Hydrogen atom is bounded to a larger Oxygen atom. The force between them can be expressed as:

$$\vec{F} = -\nabla U(\vec{r})$$

Where $U(\vec{r})$ is the potential energy.

Application to the H-O Molecule Vibration II

$U(\vec{r})$ has a minimum corresponding to the bond length \vec{r}_0 . Around r_0 the potential $U(\vec{r})$ can be expanded in Taylor's series:

$$U(r) = U(r_0) + (r - r_0) \left. \frac{\partial U(r)}{\partial r} \right|_{r=r_0} + \frac{1}{2}(r - r_0)^2 \left. \frac{\partial^2 U(r)}{\partial r^2} \right|_{r=r_0} + \dots$$

Since $r = r_0$ is a minimum then

$$\left. \frac{\partial U(r)}{\partial r} \right|_{r=r_0} = 0$$

then around the equilibrium position the potential can be represented by (assuming $U(r_0) = 0$)

$$U(r) = \frac{1}{2}(r - r_0)^2 \left. \frac{\partial^2 U(r)}{\partial r^2} \right|_{r=r_0}$$

That is an harmonic oscillator with

$$k = \left. \frac{\partial^2 U(r)}{\partial r^2} \right|_{r=r_0}$$


The Linear Harmonic Oscillator Revisited (ODE Solution)

In this section we look in detail at the solution of the equation:

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) + \frac{1}{2} k x^2 \psi(x) = E \psi(x)$$

or:

$$-T(x) + V(x) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) + \frac{1}{2} m \omega_0^2 x^2 \psi(x) = E \psi(x)$$

that can be rewritten as:

$$\frac{d^2}{dx^2} \psi(x) - \frac{m \omega_0^2}{\hbar^2} x^2 \psi(x) + \frac{2mE}{\hbar^2} \psi(x) = 0 \quad (23)$$

we define:

$$\beta = \sqrt{\frac{m \omega_0}{\hbar}} \quad \text{and} \quad \xi = \beta x$$

II - The Linear Harmonic Oscillator Revisited

then

$$\frac{d}{dx} \rightarrow \frac{d}{d\xi} \frac{d\xi}{dx} = \beta \frac{d}{d\xi} \quad (24)$$

and

$$\frac{d}{dx^2} = \frac{d}{d\xi} \left(\frac{d}{dx} \right) = \frac{d}{d\xi} \left(\beta \frac{d}{d\xi} \right) \frac{d\xi}{dx} = \beta^2 \frac{d^2}{d\xi^2} \quad (25)$$

Substituting (24) and (25) in (23) we obtain:

$$\left[\frac{d}{d\xi^2} - \xi^2 + \epsilon \right] \psi(\xi) = 0 \quad (26)$$

and:

$$\epsilon = \frac{2E}{\hbar\omega_0}$$

Equation (26) is the Weber's equation, that has a well known solution.

We will derive the solution first studying the asymptotic behavior of (26) and solving it by using a power series expansion.

Solution of the Weber's Equation

Let us consider:

$$\left[\frac{d}{d\xi^2} - \xi^2 + \epsilon \right] \psi(\xi) = 0 \quad (27)$$

we want to determine a solution. The first thing it is normally done in the presence of a unknown ODE is to study the asymptotic behavior.

– **Asymptotic behavior:** $\xi \rightarrow \infty$

In this case we have that $\xi^2 \gg \epsilon$ and we can write:

$$\left[\frac{d}{d\xi^2} - \xi^2 \right] \chi(\xi) = 0 \quad (28)$$

And we have also assumed that as $\xi \rightarrow \infty$ then $\psi(\xi) \rightarrow \chi(\xi)$. The solution of equation (28) has the form:

$$\chi(\xi) = A e^{-\xi^2/2} + B e^{\xi^2/2} \quad (29)$$

We set $B = 0$ since $\xi(x)$ has to be bounded as $\xi \rightarrow \infty$.

II - Solution of the Weber's Equation

Consequently we have that: $\chi(\xi) = Ae^{-\xi^2/2}$, and the solution of (27) is:

We need now to factor out the asymptotic behavior and determine an ODE for $H(\xi)$. We can immediately see that:

$$\frac{d}{d\xi} \psi(\xi) = A \frac{dH(\xi)}{d\xi} e^{-\xi^2/2} - A \xi H(\xi) e^{-\xi^2/2} \quad (30)$$

二

$$\begin{aligned} \frac{d^2}{d\xi^2}\psi(\xi) &= A \frac{d^2H(\xi)}{d\xi^2} e^{-\xi^2/2} - 2A\xi \frac{dH(\xi)}{d\xi} e^{-\xi^2/2} \times \\ &\quad - A H(\xi) e^{-\xi^2/2} + A\xi^2 H(\xi) e^{-\xi^2/2} \end{aligned} \quad (31)$$

g (30) and (31) in (26) we have:

$$\frac{d^2H(\xi)}{d\xi^2} - 2\xi \frac{dH(\xi)}{d\xi} + (\epsilon - 1)H(\xi) = 0 \quad (32)$$

Substituting (30) and (31) in (26) we have:

$$\frac{d^2H(\xi)}{d\xi^2} - 2\xi \frac{dH(\xi)}{d\xi} + (\epsilon - 1)H(\xi) = 0 \quad (32)$$

That is the Hermite DE.

Solving Hermite's Equation Using Power Series

To solve equation (32) we expand the solution in power series.

$$H(\xi) = \sum_{j=0}^{\infty} c_j \xi^j \quad (33)$$

Once again:

$$\frac{dH(\xi)}{d\xi} = \sum_{j=1}^{\infty} jc_j \xi^{j-1} = \sum_{j=0}^{\infty} (j+1)c_{j+1}\xi^j \quad (34)$$

$$\frac{d^2 H(\xi)}{d\xi^2} = \sum_{j=2}^{\infty} j(j-1) c_j \xi^{j-2} = \sum_{j=0}^{\infty} (j+2)(j+1) c_{j+2} \xi^j \quad (35)$$

Substituting (34) and (36) in (32) we have:

$$\sum_{j=0}^{\infty} (j+2)(j+1)c_{j+2}\zeta^j - 2\xi \sum_{j=1}^{\infty} j c_j \zeta^{j-1} + (\epsilon - 1) \sum_{j=0}^{\infty} c_j \zeta^j = 0 \quad (36)$$

II - Solving Hermite's Equation Using Power Series

$$\sum_{j=0}^{\infty} (j+2)(j+1)c_{j+2}\xi^j - 2 \sum_{j=1}^{\infty} j c_j \xi^j + (\epsilon - 1) \sum_{j=0}^{\infty} c_j \xi^j = 0 \quad (37)$$

and, collecting ξ^j :

$$c_2 + (\epsilon - 1)c_0 + \sum_{j=0}^{\infty} [(j+2)(j+1)c_{j+2} - 2jc_j + (\epsilon - 1)c_j] \xi^j = 0 \quad (38)$$

For this expression to be zero it is needed that:

$$c_2 + (\epsilon - 1)c_0 = 0 \quad (39)$$

and

$$(j+2)(j+1)c_{j+2} - 2jc_j + (\epsilon - 1)c_j = 0 \quad (40)$$

or:

$$(41) \quad c_2 = (1 - \epsilon)c_0 \quad j = 0$$

III - Solving Hermite's Equation Using Power Series

and

$$c_{j+2} = \frac{2j + (1 - \epsilon)}{(j + 2)(j + 1)} c_j \quad j = 1, 2, 3, \dots \quad (42)$$

finally:

$$\frac{c_{j+2}}{c_j} = \frac{2j + (1 - \epsilon)}{(j + 2)(j + 1)} \quad (43)$$

- Note - I: Successive coefficients c_{j+2} and c_j are related by the recurrence relation (43).
- Note - II: The energy appears in the recurrence relation (43).
- Note - III: **Does the series converge?** Using the d'Alembert ratio test we have:

$$\frac{c_{j+2}\xi^{j+1}}{c_j\xi^j} = \frac{2j + (1 - \epsilon)}{(j + 2)(j + 1)} \xi^2 \quad j \rightarrow \infty \quad \frac{2\xi^2}{j} \rightarrow 0 \quad (44)$$

Consequently the series converges.

IV - Solving Hermite's Equation Using Power Series

What does the series converge to? To begin with we can assume c_0 and c_1 arbitrarily, and use the recurrence relation to determine the other coefficients. In this case we can write two expressions for $H(\xi)$, one for even:

$$H^e(\xi) = c_0 \left[1 + \frac{c_2}{c_0} \xi^2 + \frac{c_4}{c_2 c_0} \xi^4 + \dots \right] \quad (45)$$

and one for odd functions:

$$H^o(\xi) = c_1 \left[1 + \frac{c_3}{c_1} \xi + \frac{c_5}{c_3 c_1} \xi^5 + \dots \right] \quad (46)$$

Remembering that

$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!} \quad e^{x^2} = \sum_{n=0}^{\infty} \frac{x^{2n}}{n!} \quad (47)$$

we have that as $|\xi| \rightarrow \infty$, then $H(\xi) \rightarrow e^{\xi^2}$. Consequently:

$$\psi(\xi) = A H(\xi) e^{-\xi^2/2} = A e^{\xi^2} e^{-\xi^2/2} = A e^{\xi^2/2} \quad (48)$$

V - Solving Hermite's Equation Using Power Series

Consequently, as $|\xi| \rightarrow \infty$, $\psi(\xi)$ diverges and can not be normalized and as a result it is physically unacceptable. To obtain a viable solution we can enforce all the coefficients above a certain order, let us say j_{max} to be zero.

- If $c_j = 0$ for $j > j_{max}$ then $c_{j_{max}+2} = 0$, and using the recurrence relation we have: $\epsilon = 1 + 2j_{max}$
- Note - V: We have force the Hermite Series to be finite, we have
Hermite Polynomials:

$$H(\xi) = \sum_{j=0}^{j_{max}} c_j \xi^j \quad \epsilon = 2j_{max} - 1 \quad (49)$$

- Note - VI: Chosen a j_{max} we have:

$$\begin{aligned} j_{max} = 0 &\rightarrow \epsilon = 1 & H(\xi) = c_0 \\ j_{max} = 1 &\rightarrow \epsilon = 3 & H(\xi) = c_1 \xi \end{aligned}$$

and

VI - Solving Hermite's Equation Using Power Series

$$\begin{aligned}j_{max} &= 2 & \rightarrow \epsilon &= 5 & H(\xi) &= c_0 + c_1 \xi^2 \\j_{max} &= 3 & \rightarrow \epsilon &= 7 & H(\xi) &= c_1 + c_3 \xi^3\end{aligned}$$

Furthermore

$$\begin{aligned}c_2 &= \frac{1-\epsilon}{2} c_0 = \frac{1-5}{2} c_0 = -2c_0 \\c_2 &= \frac{2+(1-\epsilon)}{2\times 3} c_1 = \frac{2+1-7}{6} c_1 = -\frac{2}{3} c_1\end{aligned}$$

More in general if we use n to indicate the order of the Hermite polynomial we have:

$$\epsilon_n = 2n+1 = \frac{E_n}{\hbar\omega_0}$$

or:

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega_0$$

VII - Solving Hermite's Equation Using Power Series

Boundary Conditions

The requirement of square integrability (or boundary conditions if you want) has led to the energy quantization.

More on the Linear Harmonic Oscillator

Classical Turning Points

In correspondence to the classical turning points we have: $E_n = V(x_n)$, that is:

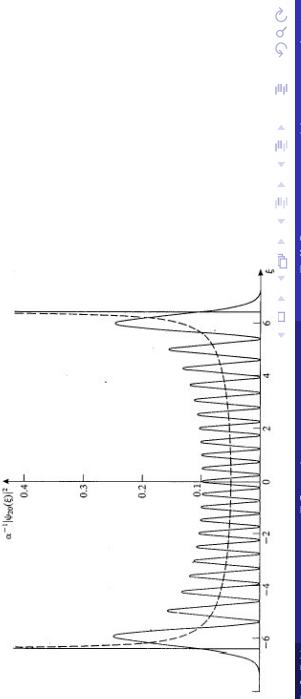
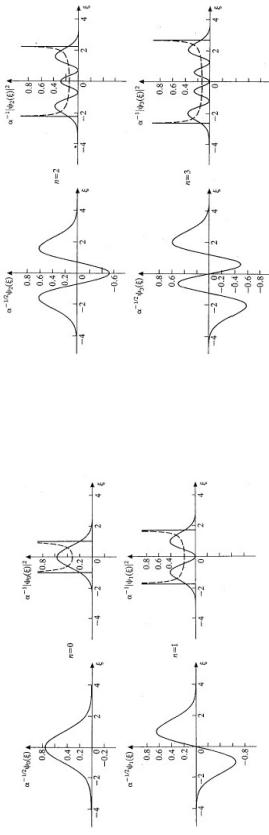
$$x_n = \pm \sqrt{\frac{2n+1}{\beta^2}}$$

More on the Linear Harmonic Oscillator

Probability Density $P_n(x)$

- a) The classical oscillator does not penetrate in the forbidden regions.
 - b) The QM oscillator can be found in the found in the classical forbidden regions.
 - c) The QM oscillator is more likely to be found at $x = 0$,
 - d) As n increases the probability density approached the classical one (correct classical limit or Principle of Correspondence)

Probability Density $P_n(x)$



Useful Integrals for the Linear Harmonic Oscillator

$$\begin{aligned} \beta &= \sqrt{\frac{m\omega_0}{\hbar}} \\ \int_{-\infty}^{\infty} \psi_n^*(x) \frac{d}{dx} \psi_m(x) dx &= \begin{cases} \beta \sqrt{\frac{n+1}{2}} & m = n+1 \\ -\beta \sqrt{\frac{n}{2}} & m = n-1 \\ 0 & \text{otherwise} \end{cases} \\ \int_{-\infty}^{\infty} \psi_n^*(x) x \frac{d}{dx} \psi_m(x) dx &= \begin{cases} \frac{1}{\beta} \sqrt{\frac{n+1}{2}} & m = n+1 \\ \frac{1}{\beta} \sqrt{\frac{n}{2}} & m = n-1 \\ 0 & \text{otherwise} \end{cases} \\ \int_{-\infty}^{\infty} \psi_n^*(x) x^2 \frac{d}{dx} \psi_m(x) dx &= \begin{cases} \frac{2n+1}{2\beta^2} & m = n \\ \frac{\sqrt{(n+1)(n+2)}}{2\beta^2} & m = n+2 \\ 0 & \text{otherwise} \end{cases} \end{aligned}$$

Schrödinger Equation Solutions in 3D

Consider the time independent Schrödinger equation solutions in 3D.

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi_n(\vec{r}) = E_n \psi_n(\vec{r}) \quad (50)$$

Depending on the particular form of $V(\vec{r})$ we will be able to solve Eq.(50) in a closed form. We will consider two cases that are quite important. The first is the quantum box, which is the simple example of a structure where all the coordinate of motion are quantized. In this case we have:

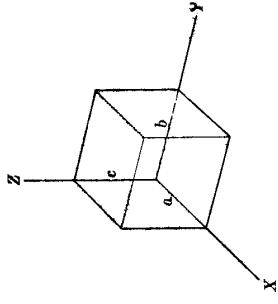
$$V(\vec{r}) = V_x(x) + V_y(y) + V_z(z)$$

The second case is the central potential, which represents the starting point for the study of atoms.

$$V(\vec{r}) = V_r(|\vec{r}|) V_{\theta,\phi}(\theta, \phi)$$

and where $V(\theta \phi) = 1$. In both cases we are able to solve Eq.(50) by separation of variables.

Quantum Box



Consider a box with sides of length a , b and c . Let's assume the potential $V(x, y, z) = 0$ inside the box and $V(x, y, z) = \infty$ outside the box. Consequently the wavefunction $\psi(x, y, z) = 0$ outside the box.

In this case we can solve by separation and we write:

$$\psi_n(\vec{r}) = X(x) Y(y) Z(z)$$

It is easy to show that we can write:

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V_x(x) \right] X(x) = E_{n_x} X(x)$$

II - Quantum Box

and

$$\begin{aligned} \left[-\frac{\hbar^2}{2m} \frac{d^2}{dy^2} + V_y(y) \right] Y(y) &= E_{n_y} Y(y) \\ \left[-\frac{\hbar^2}{2m} \frac{d^2}{dz^2} + V_z(z) \right] Z(z) &= E_{n_z} Z(z) \end{aligned}$$

and

$$E_{\eta_x, \eta_y, \eta_z} = E_{\eta_x} + E_{\eta_y} + E_{\eta_z}$$

$$E_{n_x} = \frac{\pi^2 \hbar^2}{2 m a^2} n_1^2 \quad E_{n_y} = \frac{\pi^2 \hbar^2}{2 m b^2} n_2^2 \quad E_{n_z} = \frac{\pi^2 \hbar^2}{2 m c^2} n_3^2$$

The combined solutions of the three equations is:

$$\psi(x, y, z) = C \sin\left(\frac{n_1 \pi x}{a}\right) \sin\left(\frac{n_2 \pi y}{b}\right) \sin\left(\frac{n_3 \pi z}{c}\right)$$

and C is the normalization constant

III - Quantum Box

If we consider a cubic box, $a=b=c$ than we have :

$$E_n = \frac{\pi^2 \hbar^2}{2 m a^2} (n_1^2 + n_2^2 + n_3^2)$$

different combinations of the values of n_1, n_2, n_3 give the same energy.

Notice that for each of these combinations the wavefunctions will be different. We refer to these wavefunctions as *degenerate* and their level of degeneracy.

Energy	Combinations of n_1, n_2, n_3	Degeneracy, g
$3E_1$	(1, 1, 1)	1
$6E_1$	(2, 1, 1)(1, 2, 1)(1, 1, 2)	3
$9E_1$	(2, 2, 1)(2, 1, 2)(1, 2, 2)	3
$11E_1$	(3, 1, 1)(1, 3, 1)(1, 1, 3)	3
$12E_1$	(2, 2, 2)	1
$14E_1$	(1, 2, 3)(3, 2, 1)(2, 3, 1) (1, 3, 2)(2, 1, 3)(3, 1, 2)	6

Additional Topics

Problem

You should solve the problem for the free particle in 3D. Once you solve this problem consider the issue of the normalization of the wavefunction you obtain.

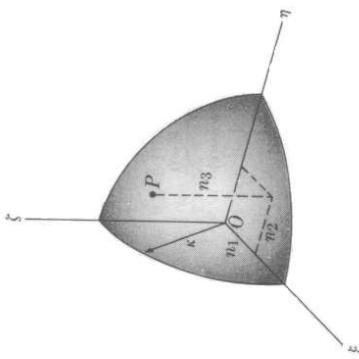
Problem

Solve the problem for the 3D harmonic oscillator. Determine the degeneracy for the case of the isotropic and anisotropic system. (The solutions are in Sec. 7.1 of the textbook.)

Quantum Box - Density of States

$$E_n = \frac{\pi^2 \hbar^2}{2m/l^2} (n_1^2 + n_2^2 + n_3^2)$$

If $L \rightarrow \infty$ then the spacing between two energy levels becomes very small, $\Delta E_n \rightarrow 0$. In principle when $L \rightarrow \infty$ the particle becomes free, since the box cover the entire space.



Consider a cubic box of side L. The energy levels are given by:

Since many level are degenerate and $\Delta E_n \rightarrow 0$ we can expect that in an interval dE there may be many energy levels that correspond to a set of $\{n_1, n_2, n_3\}$.

II - Density of States

Consider then the substitution of the three indexes $\{n_1, n_2, n_3\}$ with three continuous variables: ξ, η, ζ . If $\kappa^2 = \xi^2 + \eta^2 + \zeta^2$ then:

$$E(\kappa) = \frac{\pi^2 \hbar^2}{2 m L^2} \kappa^2$$

The number of states $N(E)$ between $E=0$ and E we find the volume od an octant of a sphere of radius κ , since $\{n_1 > 0, n_2 > 0, n_3 > 0\}$. We have:

$$N(E) = \frac{1}{8} \frac{4}{3} \pi \kappa^3 = \frac{\pi}{6} L^3 \left(\frac{2 m E}{\pi^2 \hbar^2} \right)^{3/2} = \frac{\sqrt{2}}{3\pi^2 \hbar^3} L^3 m^{3/2} E^{3/2} \quad (51)$$

The number of states between E and $E+dE$ is found differentiating equation 51:

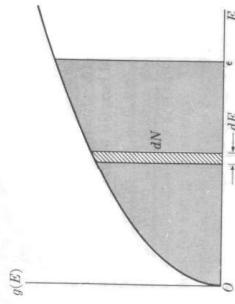
$$dN(E) = \frac{1}{\sqrt{2}\pi^2 \hbar^3} L^3 m^{3/2} E^{1/2} dE$$

III - Density of States

Finally the *density of states* per unit of volume between E and $E+dE$ is given by:

$$g(E) = \frac{1}{L^3} \frac{dN(E)}{dE} = \frac{1}{\sqrt{2\pi^2 \hbar^3}} m^{3/2} E^{1/2} = 4\pi \left(\frac{2m}{\hbar^3}\right)^{3/2} E^{1/2}$$

IV - Density of States



$$D(E) = \frac{1}{Jd} \frac{\partial N}{\partial E}$$

or $D(E)$ is the number of states at the energy E in the volume L^d . It can also be written in terms of k as:

$$D(E) = \frac{1}{I^d} \frac{\partial N}{\partial E} = \frac{1}{I^d} \frac{\partial N}{\partial k} \frac{\partial k}{\partial E}$$

$$\frac{\partial N}{\partial k} = 2 \frac{L^d}{(2\pi)^d}$$

In the limit case of an infinitely large and bos, that is a free particle, the density of states is proportional to the square root of the energy. More generally we can define the the density of states for a system of *dimensionality d* as:

Using the previous expression the density of states of systems of different dimensionality can be

Angular Momentum and Central Potential Problems

- We consider in this situation the case in which the potential depends only on the radial coordinate and does not have any angular dependence. We have $V(\vec{r}) = V(r)$. Note that in this case the force is a *central force*, i.e. directed along the radius, since $\vec{F} = -\nabla V$.
- Note that in this situation the net torque on the system is zero. In fact, since the torque is given by: $\vec{\tau} = \vec{F} \times \vec{r}$ and the momentum arm and the force are collinear, as a consequence $\vec{\tau} = 0$.
- Furthermore if no external torque is applied then the angular momentum is conserved. In classical mechanics the use of conservation law, allows to write the equation of motion of a system.
- A theorem exists that states that quantities that the conservation principles that come from particular symmetries are the same in classical and quantum mechanics.
- This means that the *observable* angular momentum is conserved in a quantum mechanical problem involving a central potential.

Angular Momentum Operator(s)

In classical mechanics the angular momentum is given by:

$$\vec{L} = \vec{r} \times \vec{p} = \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

For the principle of correspondence, the quantum mechanical operator for the momentum is given by:

$$\vec{L} = \vec{r} \times -i\hbar\nabla = -i\hbar$$

it is easy to show that

$$\vec{L} = L_x \vec{i} + L_y \vec{j} + L_z \vec{k}$$

where

II - Angular Momentum Operator(s)

The operators that represent the angular momentum components do not commute.

$$L_x = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$$

$$L_y = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)$$

$$L_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

The operator associated to the magnitude of the angular momentum is:

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

and in vector form

$$\vec{L} = -i\hbar(\vec{r} \times \nabla)$$

$$[L^2, L_x] = 0 \quad [L^2, L_y] = 0 \quad [L^2, L_z] = 0$$

III - Angular Momentum Operator(s)

- Only one component of the angular momentum can be measured with infinity precision.
 - In addition to one component the magnitude of the angular momentum can be measured.
 - The eigenfunction of an operator representing the one of the angular momentum components are not eigenfunctions of the others.
 - Note that in the case of a central potential, as we discussed the angular momentum is a constant of motion. If the operator \vec{L} commutes with the Hamiltonian then the angular momentum and the total energy can be known at all the times.
 - In this case the eigenvalues of the two quantities are said to be *good quantum numbers*.

Angular Momentum Operator in Polar Coordinates

Since we want to study problems involving a central potential, is more convenient to use polar coordinates $\{r, \theta, \phi\}$. This are related to the cartesian coordinates as follows:

$$x = r \sin\theta \cos\phi \quad y = r \sin\theta \sin\phi \quad z = r \cos\theta$$

with the limits:

$$0 \leq r < \infty \quad 0 \leq \theta \leq \pi \quad 0 \leq \phi \leq 2\pi$$

it is simple to show that

$$L_x = -i\hbar \left(-\sin\phi \frac{\partial}{\partial\theta} - \cot\theta \cos\phi \frac{\partial}{\partial\phi} \right)$$

$$L_z = -i\hbar \frac{\partial}{\partial\phi}$$

$$L_y = -i\hbar \left(\cos\phi \frac{\partial}{\partial\theta} - \cot\theta \sin\phi \frac{\partial}{\partial\phi} \right)$$

II - Angular Momentum Operator in Polar Coordinates

finally the operator for L^2 in polar coordinates is:

$$L^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]$$

Note that L_x , L_y , L_z and L^2 do not operate on r .

Examples

To determine the eigenfunctions and eigenvalues of L_z , We need to solve the eigenvalue equation:

$$L_z \Phi_m(\phi) = m\hbar \Phi_m(\phi) \quad -i\hbar \frac{\partial}{\partial\phi} \Phi_m(\phi) = m\hbar \Phi_m(\phi)$$

that has solutions:

$$\Phi_m(\phi) = \sqrt{\frac{1}{2\pi}} e^{im\phi} \quad \Phi_m(0) = \Phi_m(2\pi) \quad \rightarrow \quad m = 0, \pm 1, \pm 2, \dots$$

Schrödinger Equation in Polar Coordinates

In order to write the Schrödinger equation in polar coordinates for a central potential, we have first:

$$H = -\frac{\hbar}{2m} \rho^2 + V(r)$$

The momentum operator is then given by:

$$\vec{p} = -i\hbar \nabla = -i\hbar \left(\hat{r} \frac{\partial}{\partial r} + \hat{\phi} \frac{1}{r \sin\theta} \frac{\partial}{\partial \phi} + \hat{\theta} \frac{1}{r \partial \theta} \right)$$

and the unit vectors $\hat{r}, \hat{\phi}, \hat{\theta}$ are given by:

$$\begin{aligned}\hat{r} &= \sin\theta \cos\phi \hat{i} + \sin\theta \sin\phi \hat{j} + \cos\theta \hat{k} \\ \hat{\phi} &= -\sin\phi \hat{i} + \cos\phi \hat{j} \\ \hat{\theta} &= \cos\theta \cos\phi \hat{i} + \cos\theta \sin\phi \hat{j} - \sin\theta \hat{k}\end{aligned}$$

The spherical representation of \vec{L} is found as:

II - Schrödinger Equation in Polar Coordinates

$$\vec{L} = \vec{r} \times \vec{p} = -i\hbar \left(\hat{\phi} \frac{\partial}{\partial \phi} + \hat{\theta} \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \right)$$

and in from the product $\vec{L} \cdot \vec{L}$ we find:

$$L^2 = \vec{L} \cdot \vec{L} = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \phi} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$

As seen before L^2 commutes with any function or derivative of \vec{r} . Consequently L^2 commutes with $V(r)$ in the central potential case. Since \vec{L} is also independent of r then it commutes with $V(r)$ as well. To build the hamiltonian H we need to compute p^2 , now we note that:

$$L^2 = (\vec{r} \times \vec{p}) \cdot (\vec{r} \times \vec{p}) = r^2 p^2 - r(\vec{r} \cdot \vec{p}) \cdot \vec{p} + 2i\hbar \vec{r} \cdot \vec{p}$$

and

$$\vec{r} \cdot \vec{p} = -i\hbar r \frac{\partial}{\partial r}$$

III - Schrödinger Equation in Polar Coordinates

consequently

$$p^2 = \frac{L^2}{r^2} - \frac{\hbar^2}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right)$$

Note that this is only a function of r and L^2 . And consequently

$$H = \left[\frac{\rho^2}{2m} + V(r) \right] = \left[\frac{L^2}{2mr^2} - \frac{\hbar^2}{2mr^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + V(r) \right]$$

remembering that

$$[L, L^2] = 0 \quad [L^2, L^2] = 0$$

$$[H, L^2] = 0 \quad [H, L] = 0$$

This means that H and \vec{L} have a set of eigenstates in common, they satisfy two eigenvalue equations with the same eigenfunctions.

$$H\Psi = E\Psi \quad L^2\Psi = \lambda\hbar^2\Psi$$

III - Schrödinger Equation in Polar Coordinates

Finally the Schrödinger equation in polar coordinates is:

$$\left[\frac{L^2}{2mr^2} - \frac{\hbar^2}{2mr^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + V(r) \right] \Psi = E\Psi$$

Since L^2 depends only on ψ and θ we can think of finding a solution by writing:

$$\Psi(r, \phi, \theta) = R(r) Y(\phi, \theta)$$

and $Y(\phi, \theta)$ is the solution of the eigenvalue equation for L^2 . Notice also that:

$$\begin{aligned} L^2 \Psi(r, \phi, \theta) &= L^2 R(r) Y(\phi, \theta) = R(r) L^2 Y(\phi, \theta) = .. \\ R(r) \lambda \hbar^2 Y(\phi, \theta) &= \lambda \hbar^2 \Psi \end{aligned}$$

the we can substitute to $L^2 \Psi$ the term $\lambda h^2 \Psi$.

IV - Schrödinger Equation in Polar Coordinates

To solve Schrödinger equation in polar coordinates we need then to solve:

$$\left[\frac{\lambda \hbar^2}{2 m r^2} - \frac{\hbar^2}{2 m r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + V(r) \right] \Psi = E \Psi$$

We proceed by using separation of variables and we write:

$$\Psi(r, \phi, \theta) = R(r) Y(\phi, \theta)$$

Using the usual procedure we obtain two equations: one for the radial part of the and one for the angular part of the wavefunction.

Solution of the Schrödinger Equation by Separation of Variables

Using the usual procedure we obtain:

$$\left[-\frac{\hbar^2}{2mr^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\lambda \hbar^2}{2mr^2} + V(r) \right] R = ER$$

for the radial part and:

$$-\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\phi} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] Y = \lambda \hbar^2 Y$$

This second equation can be further separated by using:

$$Y(\phi, \theta) = \Theta(\theta) \Phi(\phi)$$

it is easily shown that for ϕ the equation is:

$$\frac{d^2}{d\phi^2}\Phi(\phi) + m^2\Phi(\phi) = 0$$

II - Solution of the Schrödinger Equation by Separation of Variables

which results in

$$\Phi_m(\phi) = C e^{im\phi}$$

Where $C=1$ for normalization and since $\Phi_m(\phi)$ has to be single-valued then

$$e^{im\phi} = e^{im(\phi+2\pi)}$$

the follows:

$$m = 0, \pm 1, \pm 2, \dots$$

As it can be seen easily these are eigenfunctions of L_z as well.

$$L_z \Phi_m(\phi) = -i\hbar \frac{\partial}{\partial \phi} e^{im\phi + 2\pi} = m\hbar e^{im\phi + 2\pi} = m\hbar \Phi_m(\phi)$$

The solutions for the second equation with unknown $\Theta(\theta)$ is more complex.

$$\frac{\sin^2 \theta}{\Theta} \left[\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \lambda \Theta \right] = m^2$$

III - Solution of the Schrödinger Equation by Separation of Variables

We consider two separate cases: when $m=0$ and $m\neq 0$.

If $m=0$ the equation becomes:

$$\frac{1}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) + \lambda\Theta = 0$$

This is the Legendre equation and has solutions only if:

$$\lambda = l(l+1)$$

with $l = 0, 1, 2, \dots$. Consequently

$$L^2\Theta(\theta) = \lambda\hbar^2\Theta(\theta) = l(l+1)\hbar^2\Theta(\theta)$$

Consequently the the functions $\Theta(\theta)$ are eigenfunctions of L^2 with eigenvalue $l(l+1)\hbar^2$. The solutions of the Legendre equation is once again a set of complete ortho-normal function called the Legendre Polynomials.

Legendre Polynomial

If we consider the change of variables:

$$\zeta = \cos\theta \quad d\zeta = -\sin\theta d\theta \quad F(\zeta) = \Theta(\theta)$$

the Legendre equation can be written as:

$$\frac{d}{d\zeta} \left[(1 - \zeta^2) \frac{dF}{d\zeta} \right] + \lambda F = 0$$

the solution of the Legendre equation can be written as:

$$P_l(\zeta) = \frac{1}{2^l l!} \frac{d^l}{d\zeta^l} (\zeta^2 - 1)^l$$

and the polynomials are:

$$\begin{aligned} P_0(\zeta) &= 1 & P_0(\cos\theta) &= 1 \\ P_1(\zeta) &= \zeta & P_1(\cos\theta) &= \cos\theta \\ P_2(\zeta) &= \frac{1}{2}(3\zeta^2 - 1) & P_2(\cos\theta) &= \frac{1}{2}(3\cos^2\theta - 1) \end{aligned}$$

II - Legendre Polynomial

the legendre polynomials are a CON set of functions:

$$\int_0^\pi P_l(\cos\theta) P_q(\cos\theta) \sin\theta \, d\theta = 0 \quad l \neq q$$

the normalization coefficient is found as:

$$\int_0^\pi |P_l(\cos\theta)|^2 \sin\theta d\theta = \frac{2}{2l+1}$$

Associate Legendre Polynomial

If $m \neq 0$ the solution depends both on l and m , in this case the general solution is found in terms of the associated Legendre polynomials. They are written as:

$$P_l^m(\zeta) = (1 - \zeta^2)^{m/2} \frac{d^m P_l(\zeta)}{d\zeta^m} = \frac{1}{2^l l!} (1 - \zeta^2)^{m/2} \frac{d^{l+m}}{d\zeta^{l+m}} (\zeta^2 - 1)^l$$

and they are a CON set as well. Notice that now we have:

$$\int_{-1}^{+1} |P_l^m(\zeta)|^2 d\zeta = \frac{2}{2l+1} \frac{(l+m)!}{(l-m)!}$$

Note:

- l can assume integer values from 0,1,2,...
- m can assume integer values ranging from $-l$ to $+l$

Spherical Harmonics

The complete solution of the angular part of the Schrödinger equation is given by:

$$Y_{lm}(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} (-1)^m e^{im\phi} P_l^m(\cos\theta)$$

These functions are called spherical harmonics, and are simultaneous eigenfunctions of the operator L^2 and L_z . They are orthogonal:

$$\int_0^{2\pi} \int_0^\pi Y_{lm}(\theta, \phi) Y_{qn}(\theta, \phi) d\Omega = \delta_{lq} \delta_{mn}$$

where $d\Omega = \sin\theta d\theta d\phi$.

We also have:

$$Y_{00}(\theta, \phi) = \frac{1}{\sqrt{4\pi}} \quad Y_{10}(\theta, \phi) = \sqrt{\frac{3}{4\pi}} \cos\theta \quad Y_{1\pm 1}(\theta, \phi) = \pm \sqrt{\frac{3}{8\pi}} e^{\pm i\theta} \sin\theta$$

II - Spherical Harmonics

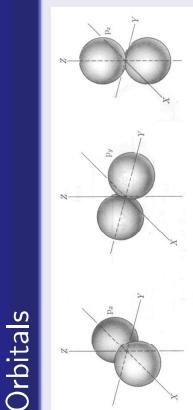
Angular Functions Corresponding to L^2 and L_z

l	m_l	Angular function	l	$ m_l $	Angular function
0	0	$Y_{00} = 1/\sqrt{4\pi}$	0	0	$s = 1/\sqrt{4\pi}$
0	0	$Y_{10} = \sqrt{3/4\pi} \cos \theta$	1	0	$p_z = \sqrt{3/4\pi} \cos \theta$
1	± 1	$Y_{1\pm 1} = \mp \sqrt{3/8\pi} \sin \theta e^{\pm i\phi}$	1	1	$p_x = \sqrt{3/4\pi} \sin \theta \cos \phi$ $p_y = \sqrt{3/4\pi} \sin \theta \sin \phi$
0	0	$Y_{20} = \frac{1}{2}\sqrt{5/4\pi} (3 \cos^2 \theta - 1)$		0	$d_{3z^2-2} = \sqrt{5/16\pi} (3 \cos^2 \theta - 1)$
2	± 1	$Y_{2\pm 1} = \mp \sqrt{15/8\pi} \sin \theta \cos \theta e^{\pm i\phi}$	2	1	$d_{xz} = \sqrt{15/4\pi} \sin \theta \cos \theta \cos \phi$ $d_{yz} = \sqrt{15/4\pi} \sin \theta \cos \theta \sin \phi$
	± 2	$Y_{2\pm 2} = \frac{1}{2}\sqrt{15/2\pi} \sin^2 \theta e^{\pm 2i\phi}$	2	2	$d_{x^2-y^2} = \sqrt{15/4\pi} \sin^2 \theta \cos 2\phi$ $d_{xy} = \sqrt{15/4\pi} \sin^2 \theta \sin 2\phi$

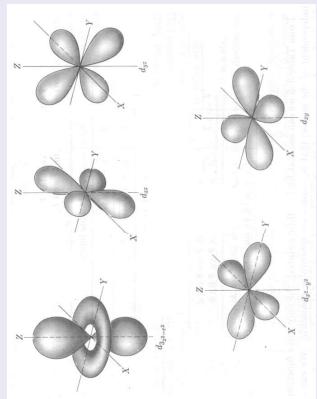
Angular Functions Corresponding to L^2 and L_z^2

l	$ m_l $	Angular function
0	0	$s = 1/\sqrt{4\pi}$
	0	$p_z = \sqrt{3/4\pi} \cos \theta$
1	1	$\begin{aligned} p_x &= \sqrt{3/4\pi} \sin \theta \cos \phi \\ p_y &= \sqrt{3/4\pi} \sin \theta \sin \phi \end{aligned}$
	0	$d_{3z^2-r^2} = \sqrt{5/16\pi} (3 \cos^2 \theta - 1)$
2	1	$\begin{aligned} d_{zx} &= \sqrt{15/4\pi} \sin \theta \cos \theta \cos \phi \\ d_{zy} &= \sqrt{15/4\pi} \sin \theta \cos \theta \sin \phi \end{aligned}$
	2	$\begin{aligned} d_{z^2-r^2} &= \sqrt{15/4\pi} \sin^2 \theta \cos 2\phi \\ d_{xy} &= \sqrt{15/4\pi} \sin^2 \theta \sin 2\phi \end{aligned}$

III - Spherical Harmonics



d-Orbitals



Prof. Enrico Bellotti (ECE and MSE @ BU) Fall Semester 2024 V.3 133 / 168

Solution of the Schrödinger Equation by Separation: Radial Equation

Using the usual procedure of separating the variables we have seen that we can write the radial part as:

$$\left[-\frac{\hbar^2}{2m r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{l(l+1)\hbar^2}{2m r^2} + V(r) \right] R_E(r) = E R_E(r)$$

Notice that this depends on the quantum number l , where $l(l+1)\hbar^2$ is the eigenvalue of the operator L^2 but not m .

Repulsive Centrifugal Barrier

The term:

$$V_{\text{eff}}(r) = \frac{l(l+1)\hbar^2}{2m r^2} + V(r)$$

can be seen as an effective potential, where $V(r)$ is the usual potential term, whereas $\frac{l(l+1)\hbar^2}{2m r^2}$ represents the *repulsive centrifugal barrier*.

II - Schrödinger Equation by Separation: Radial Equation

If we write:

$$u(r)_{EI} = r R_{EI}(r)$$

the we can write the radial part as:

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + V_{eff}(r) \right] u_E(r) = E u_E(r)$$

which has the form of the standard Schrödinger equation,

The solution of the Schrödinger in spherical polar coordinates can be written as:

$$\Psi_{E^m}(r, \phi, \theta) \equiv R_E(r) Y_{lm}(\phi, \theta)$$

The normalization of the wavefunction requires that:

$$\int |\Psi_{Em}(r, \phi, \theta)|^2 d\vec{r} = 1$$

III - Schrödinger Equation by Separation: Radial Equation

and:

$$|\Psi_{Elm}(r, \phi, \theta)|^2 d\vec{r} = |R_{EI}(r)|^2 |Y_{lm}(\phi, \theta)|^2$$

$$\int_0^{\infty} r^2 dr \int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\phi |\Psi_{Elm}(r, \phi, \theta)|^2 = 1$$

since:

$$\int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\phi |Y_m(r, \phi, \theta)|^2 = 1$$

then

$$\int_0^\infty |R_{EI}(r)|^2 r^2 dr = 1$$

Free Particle in 3D Spherical Coordinates

Remember that in the case of the solution of the free particle problem in 1D the solutions we obtained where simultaneous eigenfunctions of the Hamiltonian and the linear momentum operator. If we set $V(r)=0$ for a problem described in terms of spherical coordinates we obtain the solutions that are simultaneous eigenfunctions of the Hamiltonian, and the L^2 and L_Z operators. We write the radial equation for this case as follows:

$$\left[\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{l(l+1)}{r^2} + k^2 \right] R_{EI}(r) = 0$$

The regular solution of this equation is of the type:

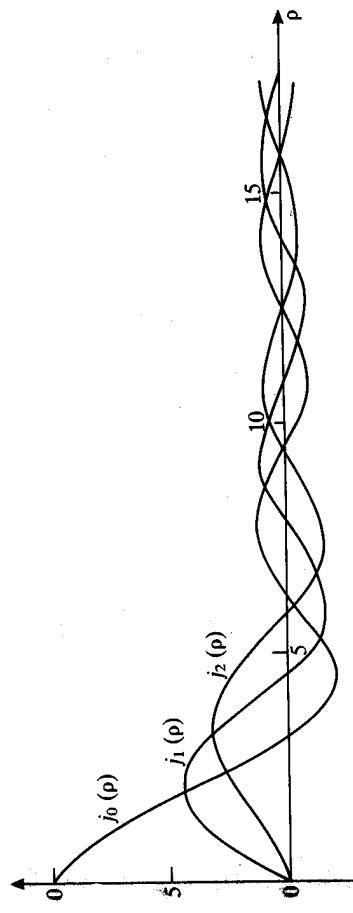
$$R_{EI}(r) = C j_l(kr)$$

where $j_l(x)$ is the spherical bessel function of order l , and:

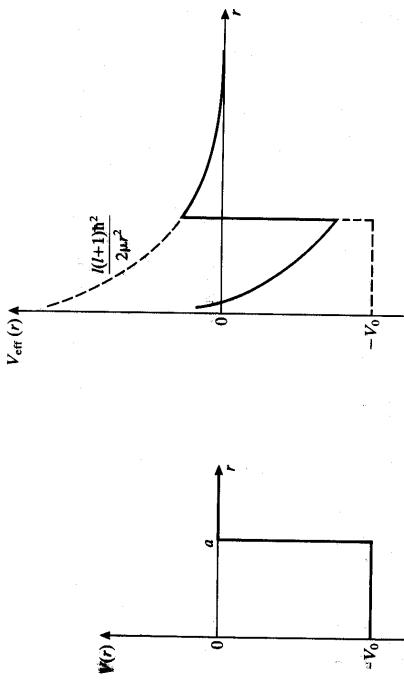
$$j_l(x) = \sqrt{\frac{\pi}{2x}} J_{l+1/2}(x)$$

where $J_{l+1/2}(x)$ is the bessel function of order $l+1/2$.

Spherical bessel Functions



Spherical Potential Well



In this case the central potential is not zero but

$$V(r) = \begin{cases} 0 & r \geq r_0 \\ -V_0 & 0 < r < r_0 \end{cases}$$

Spherical Potential Well: Interior Solution

As before we are going to have an interior $0 < r < r_0$ and an exterior $r \geq r_0$ solution and the two have to satisfy the usual boundary conditions at the well edge.

For $0 < r < r_0$ the Schrödinger equation is:

$$\left[-\frac{\hbar^2}{2m} \left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) - \frac{l(l+1)}{r^2} \right] R_E(r) = E R_E(r)$$

The only possible solution is:

$$R_E(r) = A_j j_l(Kr)$$

and $K = \sqrt{-(2m/\hbar^2)(E + V_0)}$.

Spherical Potential Well: Exterior Solution

$$\left[-\frac{\hbar^2}{2m} \left(\frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) - \frac{l(l+1)}{r^2} \right] R_{EI}(r) = (E + V_0) R_{EI}(r)$$

The solution is:

$$R_{EI}(r) = B [j_l(i\lambda r) + i n_l(i\lambda r)] = B h_l^{(1)}(i\lambda r)$$

Where $\lambda = \sqrt{-(2m/\hbar^2)E}$ and $n_l(x)$ is the spherical Neumann function.
We also have that:

$$h_0^{(1)}(i\lambda r) = -\frac{1}{\lambda r} e^{-\lambda r} \quad h_1^{(1)}(i\lambda r) = i \left(\frac{1}{\lambda r} + \frac{1}{\lambda^2 r^2} \right) e^{-\lambda r}$$

The energy level are then computed by solving the transcendental equation:

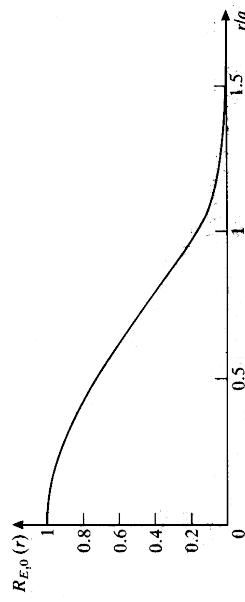
$$\left[\frac{\frac{dj_l(Kr)}{dr}}{j_l(Kr)} \right]_{r=a} = \left[\frac{\frac{dh_l^{(1)}(i\lambda r)}{dr}}{h_l^{(1)}(i\lambda r)} \right]_{r=2} = \frac{\alpha}{\lambda}$$

Spherical Potential Well: Exterior Solution II

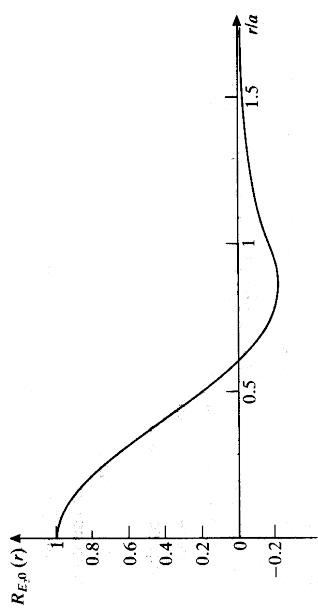
in case of $l = 0$ this is written as:

$$K \cot(Ka) = -\lambda$$

This equation can be solved in the same way the similar problem for the one-dimensional square well was approached.



Spherical Potential Well: Exterior Solution III



The Hydrogen Atom

For an ion with charge Z the central potential has the form:

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

where Ze is the nucleus charge and r the distance between the nucleus and the electron. If we define, as before, the radial equation solution as: $R(r) = u(r)/r$ then the radial equation becomes:

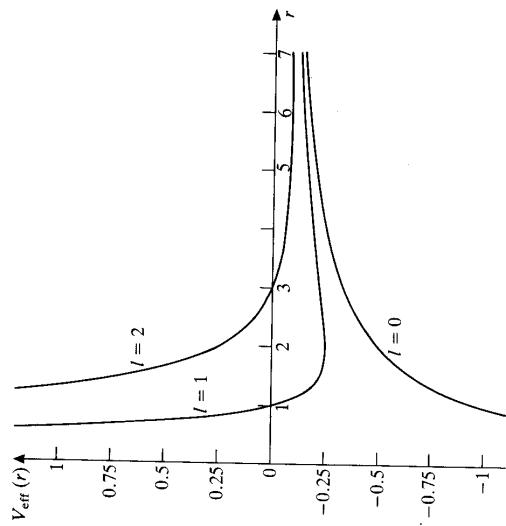
$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2\mu r^2} + V(r) \right] u_E(r) = E u_E(r)$$

The effective potential is:

$$V_{eff}(r) = -\frac{Ze^2}{(4\pi\epsilon_0)r} + \frac{\hbar^2 l(l+1)}{2\mu r^2}$$

Where μ is the reduced mass. The confinement potential depends on the orbital angular momentum and for $l = 0$ then $V_{eff}(r) \leq 0 \forall r$.

Effective Confining Potential for the Hydrogenic Atom



The Hydrogen Atom: Radial Wavafuctions

With a suitable change of variables (see Bransden-Joachain pp.332) to dimension less quantities this equation becomes:

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2\rho^2} - \frac{1}{\rho} \right] u = \varepsilon u$$

The solution of this equation can be obtained by using a power series expansion and requires that:

$$\varepsilon = -\frac{1}{2n^2}$$

and

$$E_n = -\frac{1}{2n^2} \frac{Z^2 e^2 m}{\hbar^2}$$

for the hydrogen atom $Z = 1$ and we have:

$$E_n = -\frac{13.06}{n^2} \text{eV} \quad (52)$$

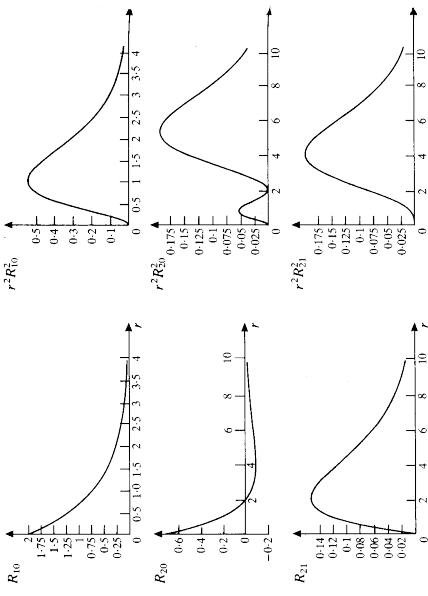
The ground state (when $n = 1$) of the hydrogen atom has a binding energy of -13.602 eV.

The Hydrogen Atom: Radial Wavefunctions II

The corresponding radial wavefunctions are computed by a series expansion.

$$\begin{aligned}R_1(r) &= \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0} \\R_{2,0,0}(r) &= \frac{1}{4\sqrt{2}\pi} \left(\frac{Z}{a_0}\right)^{3/2} \left(1 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0} \\R_{2,1,0}(r) &= \frac{1}{4\sqrt{2}\pi} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0} \cos\theta \\R_{2,1,\pm 1}(r) &= \frac{1}{8\sqrt{2}\pi} \left(\frac{Z}{a_0}\right)^{3/2} \left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0} \sin\theta e^{\pm i\phi}\end{aligned}$$

The Hydrogen Atom: Radial Wavefunctions III



Note: $r^2 R_{nl}^2(r)$ is the probability of finding the electron between r and $r+dr$.

The Hydrogen Atom: Summary

- The energy eigenvalues provided by Eq.(52) depend only on the principal quantum number n . This is always the case for a potential that has a dependence of r^{-1} .
 - For the 3D square well (in spherical coordinate) seen before the energy eigenvalue depends both on n and l .
 - In the case of alkali atoms (one valence electrons) the potential is not completely r^{-1} because of the presence of the core electrons.
 - To have better agreement with the experimental measurement several corrections have to be included (relativistic and nuclear effects).
 - As we have seen solving the central potential problem, the value of n sets a limit on the maximum value of l , in other words:

$$0 \leq l \leq n-1$$

The Hydrogen Atom: Quantum Numbers

More in general since the solution of the Schrödinger equation for the hydrogen atom is a three dimensional problem, three different coordinates of motion have to be known. These three coordinates are represented by the three quantum numbers n (for r), l (for θ) and m (for ϕ).

Table: Allowed set of Quantum Numbers for the Hydrogen Atom

n	I	m
1	0	0
2	0	0
3	-1, 0, +1	0
3	1	-1, 0, +1
4	2	-2, -1, 0, +1, +2
4	0	0
4	1	-1, 0, +1
4	2	-3, -2, -1, 0, +1, +2, +3

Spin Angular Momentum

- Studying the central potential problem we defined the quantum mechanical operator for the angular momentum (magnitude and its projection along the z-axis of the system) and we applied it to the study of the Hydrogen atom. Unfortunately this description is incomplete.
 - After a series of experiments performed by Stern and Gerlach in 1921, Goudsmit and Uhlenbeck proposed that in order to interpret correctly the experimental results an *intrinsic angular momentum*, denoted by S of the must be introduced.
 - This *intrinsic angular momentum* is responsible for an *intrinsic magnetic moment* given by:
$$\vec{M}_s = -g_s \mu_B (\vec{S} / \hbar)$$

Where g_s is the *spin gyromagnetic ratio* and μ_B is the *Bohr magneton*.

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Approximation Methods

- In many situations of practical importance the Schrödinger can not be solved in closed form. In these cases even an approximation of the solution has to be determined.
 - It is then important to be able to have the possibility of computing, an approximate solution and the degree of accuracy of the approximation itself.
 - Several approximation methods have been developed and they can be divided in two groups:

In particular we will look at stationary and time dependent perturbation theory.

Time-Independent Perturbation Theory

Let us assume that the hamiltonian of a system can be expressed as:

$$H = H_0 + \lambda H' \quad (53)$$

where H_0 is the hamiltonian of the unperturbed system and H' is the perturbation. The parameter $0 \leq \lambda \leq 1$ allows to change the strength of the perturbation. We suppose that the solution of the unperturbed problem is known:

$$H_0\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)} \quad (54)$$

and we want to find an approximation of the real solution of the problem:

$$H\psi_n = E_n\psi_n \quad (55)$$

Non-degenerate perturbation

Let us consider first the case where the eigenvalue is not degenerate. In this case to each eigenvalue corresponds only one eigenfunction. Suppose now we can expand both the eigenvalues and eigenfunctions in power series of the parameter λ .

$$E_n = \sum_j \lambda^j E_n^{(j)} \quad (56)$$

with the condition that:

$$\lim_{\lambda \rightarrow 0} E_n = E_n^{(0)} \quad \lim_{\lambda \rightarrow 0} \psi_n = \psi_n^{(0)} \quad (57)$$

Substituting into equation (55) we obtain:

$$(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots) (\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots) = (H_0 + \lambda H') (\psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \dots) = \quad (58)$$

II - Non-degenerate perturbation

we then obtain,

$$\begin{aligned}
 & H_0\psi_n^{(0)} + H_0\lambda\psi_n^{(1)} + H_0\lambda^2\psi_n^{(2)} + \dots \\
 & + \lambda H'\psi_n^{(0)} + \lambda^2 H'\psi_n^{(1)} + \lambda^3 H'\psi_n^{(2)} + \dots = \\
 & E_n^{(0)}\psi_n^{(0)} + \lambda E_n^{(0)}\psi_n^{(1)} + \lambda^2 E_n^{(0)}\psi_n^{(2)} + \dots \\
 & + \lambda E_n^{(1)}\psi_n^{(0)} + \lambda^2 E_n^{(1)}\psi_n^{(1)} + \lambda^3 E_n^{(1)}\psi_n^{(2)} + \dots \\
 & + \lambda^2 E_n^{(2)}\psi_n^{(0)} + \lambda^3 E_n^{(2)}\psi_n^{(1)} + \lambda^4 E_n^{(2)}\psi_n^{(2)} + \dots
 \end{aligned} \tag{59}$$

now we need to equate the coefficients of equal power on both sides of equation 59 for different powers of λ . For λ^0 we have the unperturbed system:

$$H_0\psi_n^{(0)} = E_n^0\psi_n^{(0)}, \tag{60}$$

III - Non-degenerate perturbation

for λ we have:

$$H_0\psi_n^{(1)} + H'\psi_n^{(0)} = E_n^{(0)}\psi_n^{(1)} + E_n^{(1)}\psi_n^{(0)} \quad (61)$$

and for λ^2 we have:

$$H_0\psi_n^{(2)} + H'\psi_n^{(1)} = E_n^{(0)}\psi_n^{(2)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(2)}\psi_n^{(0)} \quad (62)$$

The expressions for all the λ^n coefficients can be computed accordingly.
The first order correction can be computed multiplying equation (69) by $\psi_n^{(0)*}$ and integrating over the space. We have:

$$\begin{aligned} & \int \psi_n^{(0)*} H_0 \psi_n^{(1)} d\vec{r} + \int \psi_n^{(0)*} H' \psi_n^{(0)} d\vec{r} = \\ & \int \psi_n^{(0)*} E_n^{(0)} \psi_n^{(1)} d\vec{r} + \int \psi_n^{(0)*} E_n^{(1)} \psi_n^{(0)} d\vec{r} \end{aligned} \quad (63)$$

IV - Non-degenerate perturbation

from this we obtain that the first order correction is:

$$E_n^{(1)} = \int \psi_n^{(0)*} H' \psi_n^{(0)} d\vec{r}$$

NOTE! - The first order correction to a non-degenerate level due to the presence of an hamiltonian H' is only dependent on the wavefunctions of the unperturbed system.

Operating in the same way we can get the second order correction and we have:

$$E_n^{(2)} = \int \psi_n^{(0)*} (H' - E_n^{(1)}) \psi_n^{(1)} d\vec{r}$$

It can be seen that the computation of the second order correction requires the knowledge of the first order energy correction and the first order correction for the wavefunction. Similarly:

$$E_n^{(3)} = \int \psi_n^{(1)*} (H' - E_n^{(1)}) \psi_n^{(1)} d\vec{r} - 2 E_n^{(2)} \int \psi_n^{(0)*} \psi_n^{(1)} d\vec{r}$$

V - Non-degenerate perturbation

The second step is to find the first order approximation for the wavefunction. We can write the $\psi_n^{(1)}$ as:

$$\psi_n^{(1)} = \sum_k a_{n,k}^{(1)} \psi_k^{(0)} \quad (64)$$

Substituting equation (66) in (69), multiplying by $\psi_j^{(0)*}$ and integrating over the coordinates we have:

$$a_{-i}^{(1)}(E_i^{(0)} - E_n^{(0)}) + H'_n = E_n^{(1)}\delta_{in} \equiv 0 \quad (65)$$

for $l = n$ we obtain again equation (64) and for $l \neq n$ then

$$a_{n,l}^{(1)} = \frac{H'_{l,n}}{E_l^{(0)} - E_n^{(0)}} \quad (66)$$

with

$$H'_{l,n} = \int \psi_l^{(0)*} H' \psi_n^{(0)} d\vec{r}$$

VI - Non-degenerate perturbation

The coefficient $a_{n,n}^{(1)}$ can not be computed using equation (66). The second order wavefunctions can be obtained computing the expansion coefficients:

$$\psi_n^{(2)} = \sum_k a_{n,k} \psi_k^{(0)} \quad (67)$$

Substituting equation (69) in (69), using (66), multiplying by $\psi_j^{(0)*}$ and integrating over the coordinates we have:

$$\hat{a}_{n,l}^{(2)}(E_l^{(0)} - E_n^{(0)}) + \sum_k H_{l,k}^j \hat{a}_{n,k}^{(1)} - E_n^{(1)} a_{n,l}^{(1)} - E_n^{(1)} \delta_{l,n} = 0 \quad (68)$$

-- for $l = n$ we obtain:

$$E_n^{(2)} = \sum_{k \neq n} \frac{H'_{n,k} H'_{k,n}}{E_n^{(0)} - E_k^{(0)}} = \sum_{k \neq n} \frac{|H'_{n,k}|^2}{E_n^{(0)} - E_k^{(0)}}$$

VII - Non-degenerate perturbation

Higher Order Corrections

The second Order correction is obtained summing over all the states with $k \neq n$, these are called *intermediate states*.

In general we can write for $\lambda = 1$:

$$E_n = E_n^{(0)} + H'_{n,n} + \sum_{k \neq n} \frac{|H'_{n,k}|^2}{E_n^{(0)} - E_k}$$

-- for $l \neq n$ we have:

$$a_{n,l}^{(2)} = \frac{1}{E_n^{(0)} - E_l^{(0)}} \sum_{k \neq n} \frac{H'_{l,k} H'_{k,n}}{E_n^{(0)} - E_k^{(0)}} - \frac{H'_{n,n} H'_{l,n}}{(E_n^{(0)} - E_l^{(0)})^2} - \frac{a_{n,n}^{(1)}}{\partial_{n,n}} \frac{H'_{l,n}}{E_n^{(0)} - E_l^{(0)}}$$

Notice that the coefficient $a_{n,n}^{(2)}$ can not be computed using equation (69).

Evaluation of the Diagonal Terms $a_{n,n}^{(j)}$

As seen before the diagonal terms $a_{n,n}^{(j)}$ can not be determined from:

$$H_0 \psi_n^{(1)} + H' \psi_n^{(0)} = E_n^{(0)} \psi_n^{(1)} + E_n^{(1)} \psi_n^{(0)} \quad (69)$$

Since the coefficients $a_{n,n}^{(j)}$ are left indeterminate by the previous calculations they can be chosen accordingly to different criteria:

- Can be chosen so the that perturbed wavefunction is normalized:
 $\langle \psi_n | \psi_n \rangle = 1$. In this case we obtain:

$$a_{n,n}^{(1)} + a_{n,n}^{(1)*} = 0 \quad (70)$$

This means that the real part of $a_{n,n}^{(1)}$ has to be 0. Similarly:

$$a_{n,n}^{(2)} + a_{n,n}^{(2)*} + \sum_k |a_{n,k}^{(1)}|^2 = 0 \quad (71)$$

that is an equation of the real part of $a_{n,n}^{(2)}$. Notice that the imaginary part of the $a_{n,n}^{(j)}$ is still undetermined.

II – Evaluation of the Diagonal Terms $a_{n,n}^{(j)}$

Since this will only introduce phase factor, without loss of generality we can assume that it is zero. Then we have:

$$\psi_n^{(1)} = \sum_{l \neq n} \frac{|H'_{l,n}|}{E_n^{(0)} - E_l^{(0)}} \psi^{(0)}$$

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$$\psi_n^{(2)} = \sum_{l \neq n} \left[\sum_{k \neq n} \frac{H'_{l,k} H'_{k,n}}{(E_n^{(0)} - E_l^{(0)})(E_n^{(0)} - E_k^{(0)})} - \frac{H'_{n,n} H'_{l,n}}{E_n^{(0)} - E_l^{(0)}} \right] - \frac{1}{2} \sum_{k \neq n} \frac{|H'_{k,n}|^2}{(E_n^{(0)} - E_k^{(0)})} \psi_n^{(0)}$$

The $a_{n,n}^{(j)}$ can also be chosen so the $a_{n,n}^{(j)} = 0$. In this case the first correction $\psi_n^{(1)}$ is similar to what found before. Not so for the higher order corrections

Degenerate Perturbation

- In many situations, to a single energy eigenvalue $E_n^{(0)}$ correspond more than one eigenfunctions $\psi_{nr}^{(0)}$. In general we will consider a degeneracy, or $r = 1, 2, \dots, \alpha$.
- For example the hydrogen atom when $n=2$ and $l=0, 1$ and $m=0, +1, -1$. In this case when the perturbation is removed or $\lambda \rightarrow 0$ to which one of the eigenfunction the systems tends to.
 - We will assume the all the degenerate $\psi_{nr}^{(0)}$ are orthogonal
 $\langle \psi_{nr}^{(0)} | \psi_{ns}^{(0)} \rangle = \delta_{rs}$.
 - We will assume the all the degenerate eigenfunctions are orthogonal
With the eigenfunctions of the other eigenvalues $\langle \psi_{nr}^{(0)} | \psi_{mr}^{(0)} \rangle = \delta_{nm}$.

II - Degenerate Perturbation

As before we expand the perturbed wavefunction as:

$$\psi_{nr} = \chi_{nr}^{(0)} + \lambda \psi_{nr}^{(1)} + \lambda^2 \psi_{nr}^{(2)} + \dots \quad (40)$$

where $\chi_{nr}^{(0)}$ is the correct zero-order function, and the eigenvalue:

$$E_{nr} = E_n^{(0)} + \lambda E_{nr}^{(1)} + \lambda^2 E_{nr}^{(2)} + \dots \quad (41)$$

The first order correction is given by:

$$H_0\psi_{nr}^{(1)} + H'\chi_{nr}^{(0)} = E_n^{(0)}\psi_{nr}^{(1)} + E_n^{(1)}\chi_n^{(0)} \quad (42)$$

NOTE - the correct zero-order $\chi_{nr}^{(0)}$ is itself a linear combination of the unperturbed wavefunctions:

$$\chi_{nr}^{(0)} = \sum_{s=1}^{\alpha} c_{rs} \psi_{ns}^{(0)} \quad (43)$$

and $r = 1, 2, \dots, \alpha$.

III - Degenerate Perturbation

Since $\langle \psi_{nu}^{(0)} | \psi_{ks}^{(0)} \rangle = 0$ when $k \neq n$ and $E_k^{(0)} = E_n^{(0)}$ if $k = n$ we finally have:

$$\sum_{s=1}^{\alpha} c_{rs} [H'_{nu,ns} - E_{nr}^{(1)} \delta_{us}] = 0 \quad (47)$$

This is a linear homogeneous equation for the α unknowns $c_{r1}, c_{r2}, \dots, c_{r\alpha}$. For a non-trivial solution the determinant has to be zero. In other words:

$$\det |H'_{nu,ns} - E_{nr}^{(1)} \delta_{us}| = 0 \quad (48)$$

Equation (48), aka *secular equations* has α roots: $E_{n1}^{(1)}, E_{n2}^{(1)}, \dots, E_{n\alpha}^{(1)}$. If all these roots are different then the *degeneracy has been completely lifted*. Otherwise the *degeneracy has been partially lifted*. In many cases where the degeneracy still persist then the perturbing hamiltonian has some common symmetries with the unperturbed one.

NOTE - When the $E_{n1}^{(1)}, E_{n2}^{(1)}, \dots, E_{n\alpha}^{(1)}$ are known we can compute the $c_{r1}, c_{r2} \dots$

IV - Degenerate Perturbation

NOTE - The procedure we have followed has produced nothing else than a linear combination of unperturbed functions $\psi_{nr}^{(0)}$ that gives the correct zero-order $\chi_{nr}^{(0)}$ perturbation. For this particular combination $H'_{nu,ns} = \langle \chi_{nr}^{(0)} | \chi_{ns}^{(0)} \rangle$ is diagonal respect to r and s and the elements on the diagonal are the $E_{n1}^{(1)}, E_{n2}^{(1)}, \dots, E_{n\alpha}^{(1)}$.

NOTE - If $H'_{nu,ns} = \langle \psi_{nr}^{(0)} | \psi_{ns}^{(0)} \rangle$ is already diagonal in r and s, then the unperturbed wave-functions are already correct to first order and $E_{nr}^{(1)} = H'_{nr,nr}$. In this case the degeneracy is immaterial.

- **Doubly Degenerate Energy Level**

In this case:

$$\begin{bmatrix} H'_{11} - E_r^{(1)} & H'_{12} \\ H'_{21} & H'_{22} - E_r^{(1)} \end{bmatrix} \begin{bmatrix} c_{r1} \\ c_{r2} \end{bmatrix} = 0$$

V - Degenerate Perturbation

The secular equation is:

$$\begin{vmatrix} H'_{11} - E_r^{(1)} & H'_{12} \\ H'_{21} & H'_{22} - E_r^{(1)} \end{vmatrix} = 0$$

The energy corrections are computed as:

$$E_1^{(1)} = \frac{1}{2}(H'_{11} - H'_{22}) + \frac{1}{2}[(H'_{11} - H'_{22})^2 + 4|H'_{12}|^2]^{1/2} \quad (49)$$

and

$$E_2^{(1)} = \frac{1}{2}(H'_{11} - H'_{22}) - \frac{1}{2}[(H'_{11} - H'_{22})^2 + 4|H'_{12}|^2]^{1/2} \quad (50)$$

and the expansion coefficients c_{r1} and c_{r2} are computed from the secular equation:

$$\frac{c_{r1}}{c_{r2}} = -\frac{H'_{12}}{H'_{11} - E_r^{(1)}} = -\frac{H'_{22} - E_r^{(1)}}{H'_{21}} \quad (51)$$

where $r=1,2$ and imposing the normalization condition:

VI - Degenerate Perturbation

to obtain:

$$\chi_1^0 = c_{11}\psi_1^{(0)} + c_{12}\psi_2^{(0)} \quad (53)$$

and

$$\chi_2^0 = c_{21}\psi_1^{(0)} + c_{22}\psi_2^{(0)} \quad (54)$$