

Advanced Engineering Physics

Unit 2 : Quantum Mechanics

I. Fundamentals of Quantum Mechanics

1. Introduction to Quantum Concepts

- **de-Broglie Hypothesis:**
 - **Core Concept:** In quantum mechanics, particles such as electrons possess wave-like properties. The fundamental connection between the mechanical momentum of a particle and its quantum wavelength is given by the de Broglie relation.
 - **Formula:** The relation is mathematically expressed as $p = h/\lambda$, where p is the momentum of the particle and λ is its quantum wavelength.
 - **Application:** This relation explains phenomena such as the quantum zero-point correction to energy; if an atom is confined by fixed boundaries, its quantum wavelength λ is determined by those boundaries, which in turn dictates its kinetic energy via $p^2/2M = (h/\lambda)^2/2M$.
- **Heisenberg Uncertainty Principle:**
 - **Core Concept:** While the standard $\Delta x \Delta p \geq \hbar/2$ derivation is not explicitly derived in the provided excerpts, the textbooks heavily emphasize the energy-time manifestation of the uncertainty principle.
 - **Examples in the Text:**
 - **Lifetime Broadening:** In resonant tunneling through double barriers, the finite lifetime of a bound state causes an "uncertainty principle broadening" of the energy level, meaning the resonance becomes a peak with an energy width rather than a perfectly sharp line.
 - **Quasiparticle Definition:** As the energy of an electron approaches the Fermi energy (ϵ_F), the uncertainty in its energy ($\Delta\epsilon$) goes to zero as the second power of ϵ , which ensures that quasiparticles remain strictly well-defined near the Fermi surface.

2. The Wave Function and its Properties

- **Physical Significance of the Wave Function:**
 - **Core Definition:** In quantum mechanics, the state of a particle is described by a wave function, denoted as ψ . The physical significance of this wave function lies in determining where the particle is likely to be found.
 - **Probability Density Formula:** The probability density ρ of a particle at a given location is calculated as the absolute square of the wave function:
$$\rho = \psi^* \psi = |\psi|^2.$$

- **Theoretical Breakdown (Traveling vs. Standing Waves):**
 - For a pure traveling wave of the form $\psi = \exp(ikx)$, the probability density evaluates to $\rho = \exp(-ikx) \exp(ikx) = 1$. This means the charge density of a free-traveling electron is perfectly constant throughout space.
 - However, for standing waves (such as those formed at Brillouin zone boundaries in a crystal lattice), the probability density is not constant; it piles up either on the positive ion cores or in the spaces between them, which is the fundamental origin of energy bandgaps.

3. Postulates of Quantum Mechanics

- **Operators:**
 - **Core Concept:** In quantum theory, classical physical observables (like momentum or energy) are represented by mathematical operators that act upon the wave function.
 - **Momentum Operator:** The linear momentum p is represented by the differential operator $-i\hbar \frac{d}{dx}$ in one dimension, or $-i\hbar \nabla$ in three dimensions.
 - **Hamiltonian (Energy) Operator:** By substituting the momentum operator into the classical kinetic energy equation ($p^2/2m$), the Hamiltonian operator for a free electron is constructed as $\mathcal{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$.
- **Eigenvalues and Eigenfunctions:**
 - **Core Definition:** When an operator is applied to a special vector (or wave function) and results in the *exact same* vector multiplied by a scalar constant, that vector is called an **eigenvector** (or **eigenfunction/eigenstate**), and the scaling constant is called the **eigenvalue**.
 - **In the Schrödinger Wave Equation:** The wave equation is written as $\mathcal{H}\psi_n = \epsilon_n\psi_n$. Here, the solutions ψ_n are the eigenfunctions (often called "orbitals" for a one-electron system), and the allowed energy levels ϵ_n are the eigenvalues.
 - **In Quantum Computing:** Quantum gates act as operators. For example, if the Pauli X gate is applied to the $|+\rangle$ state, the result is $|+\rangle = |+\rangle$. Thus, $|+\rangle$ is an eigenstate of the X gate with an eigenvalue of 1. Similarly, $|-\rangle = -|-\rangle$, making $|-\rangle$ an eigenstate with an eigenvalue of -1 .
- **Expectation Value:**
 - **Core Concept:** Because quantum mechanics relies on probabilities, the exact outcome of a single measurement cannot always be predicted; instead, we calculate the "expectation value," which represents the average or expected value of physical properties over many measurements.
 - **Formula & Example:** The expectation value of the momentum for an electron in a specific Bloch state k is calculated by integrating the momentum operator over the volume of the charge distribution: $p = \int d\psi_k^* (-i\hbar \nabla) \psi_k$.

II. Schrödinger's Wave Equation & The 1D Box

1. Schrödinger's Time-Independent Wave Equation (Free Particle)

Core Definitions & Concepts:

- **The Model:** To understand the quantum behaviour of electrons in a solid, we begin by modeling a free electron gas in one dimension.
- **Momentum Operator:** In quantum mechanics, the linear momentum p of a particle is represented by the differential operator $-i\hbar \frac{d}{dx}$.
- **The Wave Equation:** By substituting the momentum operator into the classical kinetic energy expression ($p^2/2m$) and neglecting the potential energy, we arrive at the time-independent Schrödinger wave equation for a free particle. It is mathematically expressed as:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_n}{dx^2} = \epsilon_n \psi_n$$

- **Orbitals:** The solution to this wave equation, $\psi_n(x)$, is called an *orbital*. This term specifically denotes a quantum state solution for a system containing only one electron. The parameter ϵ_n represents the energy eigenvalue of the electron occupying that specific orbital.

2. Particle in a 1D Box

The Model and Boundary Conditions:

- **Physical Setup:** Imagine an electron of mass m perfectly confined to a one-dimensional line segment of length L . The ends of this line are bounded by infinite potential energy barriers.
- **Boundary Conditions:** Because the potential energy outside the box is infinite, the electron cannot exist there. Therefore, the wavefunction must drop exactly to zero at the walls of the box. Mathematically, this imposes the strict boundary conditions: $\psi_n(0) = 0$ and $\psi_n(L) = 0$.

Wavefunctions:

- **Sineline Solutions:** To satisfy the boundary conditions, the wavefunction must be a sineline standing wave that fits an exact, integral number n of half-wavelengths into the length L .
- **Expression:** The allowed wavefunctions take the form:

$$\psi_n = A \sin\left(\frac{n\pi x}{L}\right)$$

where A is a normalization constant and n is a positive integer representing the quantum number of the state.

Step-by-Step Derivation of Quantized Energy Levels (ϵ_n):

To find the discrete energy levels allowed for the confined electron, we must apply the Schrödinger wave equation to our wavefunction.

1. **First Derivative:** Differentiate the wavefunction ψ_n with respect to x :

$$\frac{d\psi_n}{dx} = A \left(\frac{n\pi}{L} \right) \cos \left(\frac{n\pi x}{L} \right)$$

.

2. **Second Derivative:** Differentiate again with respect to x :

$$\frac{d^2\psi_n}{dx^2} = -A \left(\frac{n\pi}{L} \right)^2 \sin \left(\frac{n\pi x}{L} \right)$$

.

Notice that the term $A \sin \left(\frac{n\pi x}{L} \right)$ is simply our original wavefunction ψ_n . So, we can rewrite this as:

$$\frac{d^2\psi_n}{dx^2} = - \left(\frac{n\pi}{L} \right)^2 \psi_n$$

.

3. **Apply the Wave Equation:** Substitute this second derivative back into the free-particle Schrödinger wave equation ($-\frac{\hbar^2}{2m} \frac{d^2\psi_n}{dx^2} = \epsilon_n \psi_n$):

$$-\frac{\hbar^2}{2m} \left(- \left(\frac{n\pi}{L} \right)^2 \psi_n \right) = \epsilon_n \psi_n$$

.

4. **Solve for Energy:** Cancelling out the negative signs and the ψ_n from both sides, we isolate the final equation for the quantized energy levels:

$$\epsilon_n = \frac{\hbar^2}{2m} \left(\frac{n\pi}{L} \right)^2$$

.

Important Theoretical Breakdown:

- **Quantization:** This derivation proves that confinement strictly limits an electron to discrete, quantized energy states. The energy level ϵ_n grows quadratically with the quantum number n .
- **Zero-Point Energy:** Because n must be a positive integer (if $n = 0$, the wavefunction vanishes entirely, meaning there is no electron), the lowest possible energy state is $n = 1$. Therefore, an electron confined to a box can never have zero kinetic energy.

III. Electrons in a Periodic Potential (Band Theory)

1. Bloch's Theorem (Qualitative)

Core Concept & Definition:

- To understand why electrons can travel through a densely packed crystal without scattering off every ion, we must treat them as matter waves responding to a periodic potential.
- **Bloch's Theorem** states that the eigenfunctions of the wave equation for a periodic potential must be the product of a plane wave $\exp(i\mathbf{k}\cdot\mathbf{r})$ times a modulating function $u(\mathbf{r})$ that possesses the exact periodicity of the crystal lattice.
- **Mathematical Expression:** The wavefunction takes the specific form $\psi(\mathbf{r}) = u(\mathbf{r}) \exp(i\mathbf{k}\cdot\mathbf{r})$, where $u(\mathbf{r}) = u(\mathbf{r} + \mathbf{R})$ for any crystal lattice translation vector \mathbf{R} . This means the free-electron plane wave is only modulated by the periodic atomic arrangement.

2. Kronig-Penney Model (Qualitative)

The Square-Well Potential:

- To exactly solve the wave equation and illustrate band theory mathematically, the Kronig-Penney model utilizes a simplified, idealized **square-well array** to represent the periodic potential energy of the crystal lattice.
- By applying Bloch's theorem and the necessary boundary conditions (continuity of the wavefunction and its derivative), the model establishes a restrictive transcendental equation: $(P/a) \sin a + \cos a = \cos ka$.

E-k Diagram & Energy Gaps:

- Because the right side of the equation ($\cos ka$) is strictly bounded between -1 and $+1$, the equation only possesses travelling wave solutions for specific ranges of energy.
- If we plot the **E-k diagram** (energy versus wavenumber k), we visually observe forbidden energy ranges where no wavelike solutions exist. These **energy gaps** form precisely at the Brillouin zone boundaries (e.g., at $ka = \pi, 2\pi, \dots$).

3. Origin of Energy Gaps & Band Formation

Bragg Reflection:

- Physically, energy gaps are caused by the **Bragg reflection** of electron waves by the periodic array of ion cores in the crystal.
- At the Brillouin zone boundary (e.g., $k = \pi/a$), the wavevector perfectly satisfies the condition for Bragg diffraction. As a result, a wave travelling to the right is entirely reflected to the left, and vice versa. Free propagation is halted.

Standing Waves and Probability Density:

- Because the forward and reflected waves have equal amplitudes at the zone boundary, they superimpose to form **standing waves**, which do not carry momentum. Two distinct standing waves can be formed:

$$\psi(+)=e^{i\pi x/a}+e^{-i\pi x/a}=2\cos(\pi x/a)\text{ and }\psi(-)=e^{i\pi x/a}-e^{-i\pi x/a}=2i\sin(\pi x/a).$$

- The actual physical charge distribution is given by the probability density $|\psi|^2$.
 - $|\psi(+)|^2 \propto \cos^2(\pi x/a)$: This standing wave piles up negative electronic charge directly onto the positive ion cores. Because opposite charges attract, this configuration substantially **lowers** the electrostatic potential energy,.
 - $|\psi(-)|^2 \propto \sin^2(\pi x/a)$: This standing wave concentrates the electrons in the empty spaces exactly between the ion cores, resulting in a **higher** potential energy,.
- **The Bandgap Magnitude:** The energy gap E_g is exactly equal to the energy difference between these two distinct standing wave states ($\psi(-)$ and $\psi(+)$) at the zone boundary,.

4. Effective Mass of Electron (m^*)

Core Concept & Physical Interpretation:

- An electron in a periodic potential accelerates in an applied electric or magnetic field as if it possesses an **effective mass (m^*)**, which can be larger, smaller, or even opposite in sign to the free electron mass,.
- **Physical Interpretation:** The effective mass accounts for the momentum transfer between the electron and the crystal lattice. The electron is subject to forces from both the external field and the internal lattice.

Step-by-Step Derivation from Group Velocity:

1. **Group Velocity:** The velocity of an electron wave packet is defined by the dispersion relation: $v_g = \frac{1}{\hbar} \frac{d\epsilon}{dk}$.
2. **Work-Energy Theorem:** The work done by an applied force F on an electron over a time interval dt is $d\epsilon = Fv_g dt$.
3. **Rate of Change of k :** Substituting v_g into the work equation gives $d\epsilon = F\left(\frac{1}{\hbar} \frac{d\epsilon}{dk}\right) dt$. Therefore, the rate of change of the wavevector is $\frac{dk}{dt} = \frac{F}{\hbar}$.
4. **Acceleration:** We differentiate v_g with respect to time to find the acceleration: $\frac{dv_g}{dt} = \frac{1}{\hbar} \frac{d}{dt} \left(\frac{d\epsilon}{dk} \right) = \frac{1}{\hbar} \frac{d^2\epsilon}{dk^2} \frac{dk}{dt}$.
5. **Final Formula:** Substituting $dk/dt = F/\hbar$ gives $\frac{dv_g}{dt} = \frac{1}{\hbar^2} \frac{d^2\epsilon}{dk^2} F$. Comparing this to Newton's second law ($a = F/m^*$), we obtain the precise formula for effective mass:

$$m^* = \frac{\hbar^2}{d^2\epsilon/dk^2}$$

Negative Effective Mass:

- Near the top of an energy band, the curvature $d^2\epsilon/dk^2$ is negative, resulting in a **negative effective mass**.
- Physically, as the electron is pushed toward the zone boundary by an external field, it undergoes increasing Bragg reflection. The momentum transferred *to the lattice* is larger than the momentum transferred *from the applied force*. Thus, pushing the electron forward actually causes its forward group velocity to decrease, acting as if its mass were negative.

5. Classification of Solids

Solids are classified into distinct categories based exclusively on how their allowed energy bands are occupied by electrons,.

- **Insulators:** The valence electrons exactly fill one or more allowed bands, which are separated from higher, entirely empty bands by a substantial forbidden energy gap,. Because every accessible state within the band is filled, an external electric field cannot change the total momentum of the electrons, meaning no electrical current can flow.
- **Semiconductors:** Their band occupancy is identical to that of insulators at absolute zero, but the forbidden energy gap is small enough that thermal excitation or impurities can populate the conduction band (or leave conducting holes in the valence band) at finite temperatures,.
- **Metals (Conductors):** One or more energy bands are only partly filled (typically between 10% and 90% filled). Because there are plenty of immediately adjacent empty energy states, electrons can easily gain momentum from an applied electric field.
- **Semimetals:** Materials (like bismuth or antimony) where the bottom of the conduction band edge is very slightly lower in energy than the top of the valence band. This creates a small band overlap in energy, leading to a small concentration of mobile electrons in the conduction band and holes in the valence band at absolute zero,.

IV. Nanomaterials and Quantum Confinement

1. Dimensionality Reduction

Core Definitions & Concepts:

- **Nanostructures:** Solids where spatial confinement occurs at the nanometer scale (typically between 1 and 100 nm). When the extent of a solid is reduced in one or more dimensions, its physical, electrical, magnetic, and optical properties are dramatically altered compared to the bulk material.
- **1D Systems (One-Dimensional):** Materials that are extended continuously in one macroscopic direction but are of nanometer scale in the two orthogonal directions.

- *Examples:* Carbon nanotubes, quantum wires, and conducting polymers.
- **0D Systems (Zero-Dimensional):** Materials that are confined in all three orthogonal spatial dimensions.
 - *Examples:* Semiconductor nanocrystals (like CdSe), metal nanoparticles, and lithographically patterned quantum dots.

2. Concept of Discrete Energy Levels

Core Explanations:

- **Transformation from Continuous to Discrete:** In macroscopic 3D solids, electron energy levels form continuous bands. However, when dimensions are reduced to the nanoscale, the fundamental electronic and vibrational excitations become completely quantized.
- **Density of States:** For a finite-sized nanostructure, the density of states $D(\epsilon)$ cannot be represented by a continuous function. Instead, it transforms into a discrete sum of delta functions representing individual energy eigenstates:

$$D(\epsilon) = \sum_i \delta(\epsilon - \epsilon_i)$$

where the sum is taken over all the energy eigenstates of the system. This quantized density of states dictates the most important optical and electrical properties of the nanostructure.

3. Quantum Confinement

A. 1D Subbands and Van Hove Singularities

- **1D Subbands:** Consider a nanoscale wire continuous in the z direction but confined in the x and y planes. The energy eigenstates are given by:

$$\epsilon = \epsilon_{i,j} + \frac{\hbar^2 k^2}{2m}$$

where k is the wavevector in the z direction, and i, j are the quantum numbers labeling the discrete transverse energy states $\epsilon_{i,j}$ in the x, y plane. The overall dispersion relation consists of a series of these 1D subbands.

- **Van Hove Singularities:** The density of states for a specific 1D subband $D_{i,j}(\epsilon)$ is inversely proportional to the velocity of the electron and mathematically evaluates to:

$$D_{i,j}(\epsilon) \propto \frac{1}{(\epsilon - \epsilon_{i,j})^{1/2}}$$

This signifies that the density of states diverges (goes to infinity) exactly at each subband threshold ($\epsilon = \epsilon_{i,j}$). These sharp peaks in the density of states are called **Van Hove singularities**.

- **Physical Example:** In semiconducting carbon nanotubes, Van Hove singularities heavily dominate the optical absorption and emission spectra, as well as the tunneling conductance measured by a Scanning Tunneling Microscope (STM).

B. 0D Systems (Artificial Atoms / Quantum Dots)

- **Concept:** A system fully confined in all three dimensions exhibits completely discrete charge and electronic states. Because they behave optically and chemically like free atoms, 0D quantum dots are often referred to as **artificial atoms**.
- **Energy Level Formula:** For a simple model of an electron in an infinite spherical potential well of radius R , the eigenstates separate into angular parts (spherical harmonics $_{l,m}$) and radial parts $R_{n,l}$. The quantized energy levels are:

$$\epsilon_{n,l} = \frac{\hbar^2 \alpha_{n,l}^2}{2m^* R^2}$$

where m^* is the effective mass and $\alpha_{n,l}$ represents the n th zero of the l th spherical Bessel function.

- **Bandgap Tuning (Semiconductor Nanocrystals):** Based on the formula above, the energy $\epsilon_{n,l}$ is inversely proportional to R^2 . As the radius of a semiconductor nanocrystal (like CdSe) is reduced, the ground state energy of the electron increases and the hole energy decreases. Therefore, the bandgap grows significantly. By simply changing the physical radius R , the optical absorption and emission spectra can be tuned continuously across the visible spectrum.
- **Discrete Charge States (Coulomb Blockade):** If a 0D dot is relatively isolated, it possesses well-defined charge states. Adding a single electron to the dot requires an additional charging energy due to coulomb repulsion:

$$= \frac{e^2}{C}$$

where C is the capacitance of the dot. Because this charging energy often far exceeds the thermal energy $k_B T$, current flow is blocked (Coulomb blockade) unless a specific gate voltage is applied to align the electrochemical potentials, causing single electrons to hop on and off the dot in phenomena known as Coulomb oscillations.