

Quantum Mechanics

Week 11

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Pre-Reading Note

Dear Students,

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

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

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

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

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

Have fun with Quantum Mechanics!

Best regards,

Mark Benazet Castells

1 Free Electron Model

The Free Electron Model is a pivotal concept in solid state physics, providing crucial insights into the behavior of conduction electrons in metallic solids. This model simplifies the complex electron-lattice interactions in a solid by approximating electrons as free particles within an infinite potential well.

1.1 Energy in a 3D Infinite Square Well

In the Free Electron Model, the electrons are considered to be confined within a three-dimensional (3D) infinite potential well, representing the boundaries of the solid. This is a significant extension from the one-dimensional case, involving a more complex spatial consideration.

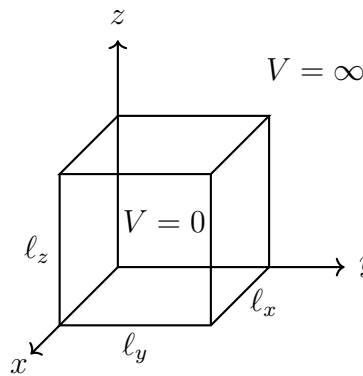


Figure 1: 3D Infinite Square Well

In this model, the solutions to the Schrödinger equation reveal quantized energy levels, uniquely defined by a set of three quantum numbers (n_x, n_y, n_z) . These quantum numbers represent the electron's state in each spatial dimension within the well. The energy levels, a direct consequence of quantum confinement, are given by:

$$E_{n_x, n_y, n_z} = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_x^2}{\ell_x^2} + \frac{n_y^2}{\ell_y^2} + \frac{n_z^2}{\ell_z^2} \right), \quad (1)$$

where ℓ_x , ℓ_y , and ℓ_z represent the dimensions of the well in the respective x , y , and z directions, and m is the electron mass.

The eigenstates, or the wavefunctions associated with these energy levels, are described by:

$$\psi_{n_x, n_y, n_z} = \sqrt{\frac{8}{\ell_x \ell_y \ell_z}} \sin\left(\frac{n_x \pi}{\ell_x} x\right) \sin\left(\frac{n_y \pi}{\ell_y} y\right) \sin\left(\frac{n_z \pi}{\ell_z} z\right), \quad (2)$$

where \hbar is the reduced Planck constant. The normalization factor $\sqrt{\frac{8}{\ell_x \ell_y \ell_z}}$ ensures that the probability density integrated over the entire well is equal to one.

Remark: This model simplifies the electron dynamics by neglecting spin and electron-electron interactions, focusing on the spatial quantization aspect of electron behavior in a solid.

1.2 Transformation to \mathbf{k} -space

In solid state physics, the wave vector \mathbf{k} plays a crucial role in describing electron states within periodic potentials, typical in crystal lattices. This vector is closely related to the electron's momentum and provides an insightful framework for understanding electron behavior in these environments.

The wave vector \mathbf{k} is defined as follows:

$$\mathbf{k} = k_x \vec{e}_x + k_y \vec{e}_y + k_z \vec{e}_z, \quad (3)$$

with each component k_i given by

$$k_i = \frac{n_i \pi}{\ell_i}, \quad \text{for } i \in \{x, y, z\}, \quad (4)$$

where n_i are the quantum numbers for each spatial dimension, and ℓ_i represent the dimensions of the potential well. The magnitude of the wave vector \mathbf{k} is then calculated as:

$$k^2 = k_x^2 + k_y^2 + k_z^2. \quad (5)$$

Substituting these expressions for \mathbf{k} into the energy equation, we redefine the energy levels in terms of the wave vector:

$$E(\mathbf{k}) = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2 k^2}{2m}, \quad (6)$$

where \hbar is the reduced Planck constant and m is the electron mass.

The k -space lattice, which graphically represents these quantized states, is an essential tool for visualizing the possible electron states in a crystal lattice.

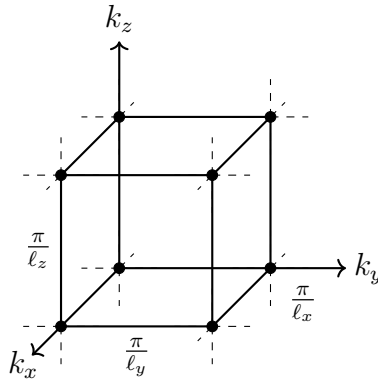


Figure 2: k -space lattice

The k -space lattice visually captures the arrangement of electron states, where each node, denoted by a filled circle, signifies a quantized state. The arrangement and spacing of these nodes reflect the quantized nature of electron states and are directly influenced by the dimensions of the potential well in real space.

1.3 Volume of States in k -space

In k -space, quantum states are represented as distinct points. The volume allocated to each of these states, denoted as V_k , is inversely proportional to the physical volume of the crystal in real space, V . This relationship is expressed mathematically as:

$$V_k = \frac{\pi^3}{V}, \quad (7)$$

where $V = \ell_x \ell_y \ell_z$ represents the volume of the crystal.

The concept of spin degeneracy, where each quantum state can accommodate two electrons with opposite spins, is an important consideration. Incorporating spin into the k -space model allows for a comprehensive understanding of the distribution and arrangement of electronic states in a material. This understanding is fundamental to analyzing the material's electronic properties, including its conductivity and band structure.

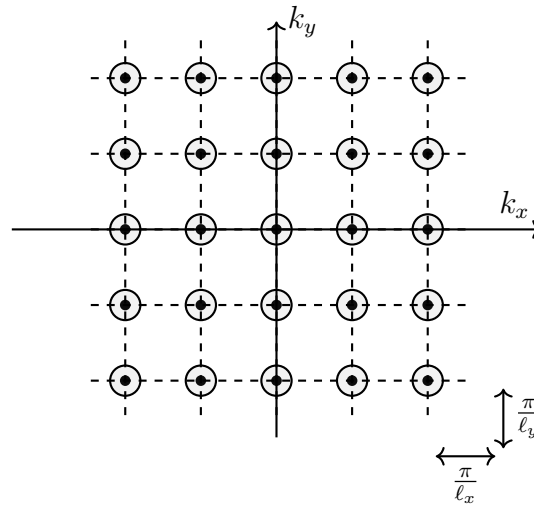


Figure 3: 2D k -space lattice with highlighted volume each state occupies.

The figure above demonstrates that in a two-dimensional representation, each dot corresponds to a quantum state occupying a square space in k -space. The area of each square is $\frac{\pi^2}{A}$, with $A = \ell_x \ell_y$ being the area of the 2D lattice cell. When extended to three dimensions, states are represented as occupying portions of a cubic volume in k -space, and the volume per state is $\frac{\pi^3}{V}$.

The Fermi sphere visualizes the occupied electron states in a metal at absolute zero temperature. Its volume, $V_{\text{Fermi sphere}}$, is computed based on the radius k_F . The equation for $V_{\text{Fermi sphere}}$ in k -space, considering only the positive octant due to symmetry, is:

$$V_{\text{Fermi sphere}} = \frac{1}{8} \cdot \frac{4}{3} \pi k_F^3, \quad (8)$$

highlighting the quantum states within the Fermi energy level. Since we focus on the positive octants where $k_{x,y,z} > 0$, only this segment of the Fermi sphere is relevant for our analysis.

In the 1D infinite square well, the wave function $\psi_n(x) = A \sin\left(\frac{n\pi x}{L}\right)$ is characterized by quantum number $n > 0$. Negative values of n lead to

$$\sin(-n\pi x/L) = -\sin(n\pi x/L),$$

indicating no new independent solutions. In three dimensions, the quantum numbers n_x, n_y, n_z map to positive wave vector components k_x, k_y, k_z . Therefore, the relevant portion of k -space is the first octant, where all k components are positive. This approach ensures no redundancy in the quantum states due to the symmetries in the lattice structure, accurately represented by:

$$k_n = \frac{n\pi}{L}, \quad n > 0. \quad (9)$$

Thus, only the positive octant of the Fermi sphere is relevant in 3D problems, ensuring unique quantum state accounting.

1.4 Fermi Energy

In the k -space, electrons fill up states up to a maximum wavevector k_F , defining the Fermi Level—the highest occupied energy state at absolute zero temperature, as stated above. This concept is pivotal for understanding the behavior of electrons in various materials.

To determine k_F , we equate the total volume of occupied states in k -space with the product of the total number of electrons and the volume per electronic state:

$$\left\{ \begin{array}{c} \text{Total Volume} \\ \text{of occupied} \\ \text{states in } k\text{-space} \end{array} \right\} = \left\{ \begin{array}{c} \text{Total number} \\ \text{of electrons} \end{array} \right\} \cdot \frac{1}{2} \cdot \left\{ \begin{array}{c} \text{Volume in} \\ k\text{-space per} \\ \text{electronic state} \end{array} \right\}.$$

Here, $N \cdot q$ represents the product of the total number of atoms and the number of free electrons per atom. $V_k = \frac{\pi^3}{V}$ is the volume in k -space for each electronic state, with $V = \ell_x \ell_y \ell_z$ being the crystal's real-space volume. The factor $\frac{1}{2}$ accounts for the two possible electron spins per state.

Plugging everything in we get:

$$\frac{1}{8} \cdot \frac{4}{3} \pi k_F^3 = Nq \cdot \frac{\pi^3}{2V}, \quad (10)$$

The Fermi wavevector k_F and consequently the Fermi energy E_F are given by:

$$k_F = \left(\frac{3\pi^2 Nq}{V} \right)^{1/3} \quad (11)$$

$$E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 Nq}{V} \right)^{2/3}. \quad (12)$$

The number of one-electron states at a specific energy E is given by:

$$N(E) = \frac{V}{6\pi^2} \left(\frac{2mE}{\hbar^2} \right)^{3/2}, \quad (13)$$

where V is the volume of the system, m is the electron mass, \hbar is the reduced Planck constant, and E is the energy.

The density of states $D(E)$, which represents the number of states available per unit energy interval, is derived as:

$$D(E) = \frac{dN}{dE} = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \sqrt{E}. \quad (14)$$

The density of states is essential for understanding various material properties, such as electrical conductivity and thermal characteristics, making it a key concept in solid-state physics.

Finally, the energy spacing at energy E can be calculated as:

$$\Delta E = \frac{1}{D(E)}, \quad (15)$$

where ΔE represents the average energy spacing between adjacent quantum states at energy E . The inverse of the density of states provides a measure of the average energy interval between adjacent states.

2 Potential Models

Free Electron Model is not universally applicable to all solids; consequently, it becomes necessary to explore alternative models that incorporate periodic potentials to accurately describe the behavior of electrons in such materials.

2.1 Periodic Potential

The electronic properties of crystals are fundamentally determined by the periodic potential that electrons experience within the crystal lattice. This periodic potential arises as a direct consequence of the crystal's structure and is mathematically represented as:

$$V(x) = V(x + a), \quad (16)$$

where a denotes the lattice constant, encapsulating the crystal's periodicity. This repetitive arrangement in the crystal lattice results in a corresponding periodicity in the potential energy landscape experienced by the electrons.

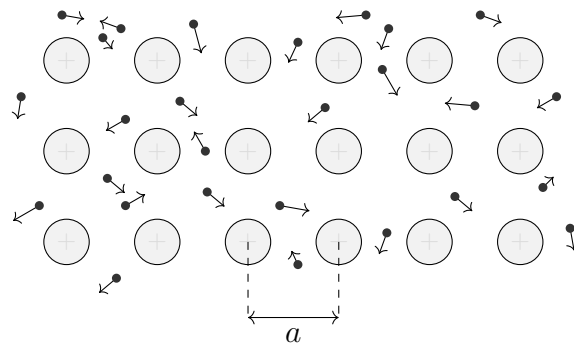


Figure 4: Valence Electrons moving through a regular crystal lattice

Electrons moving in the crystal lattice will experience a periodic potential due to the interactions with the nuclei of the atom and the core electrons moving fixed around the atom. These interactions are crucial in determining the electronic structure of the material.

A cornerstone of solid-state quantum theory is Bloch's theorem, which describes the behavior of electron wavefunctions in a periodic potential. According to this theorem, these wavefunctions, known as Bloch functions, take the form:

$$\psi(x + a) = e^{iKa} \psi(x), \quad K \in \mathbb{R}, \quad (17)$$

where $\psi(x)$ are the solutions to the one-dimensional Time-Independent Schrödinger Equation (TISE) and K is a real number, independent of x .

Bloch's theorem implies that moving one lattice spacing results in the electronic wavefunction being the same, except for a phase factor e^{iKa} .

2.2 Periodic Boundary Conditions

In a real solid, the periodic potential $V(x)$ cannot extend indefinitely due to the finite size of the crystal. To address this limitation, we introduce periodic boundary conditions:

$$\psi(x) = \psi(x + Na),$$

where N represents the number of unit cells in the crystal lattice, and a is the lattice constant.

Under these conditions, Bloch's theorem is modified accordingly:

$$\psi(x) = e^{iKNa}\psi(x), \quad (18)$$

leading to the condition $e^{iKNa} = 1$ or equivalently $KNa = 2\pi j$, where j is an integer. Hence, the quantization of K becomes:

$$K = \frac{2\pi j}{Na}, \quad j \in \mathbb{Z},$$

where \mathbb{Z} denotes the set of all integers.

To model the periodic potential in the crystal, the One-Dimensional Dirac-Comb Model is often used, defined as:

$$V(x) = \alpha \sum_{j=0}^{N-1} \delta(x - ja), \quad (19)$$

where α is a strength constant and the delta functions are placed at each lattice point.

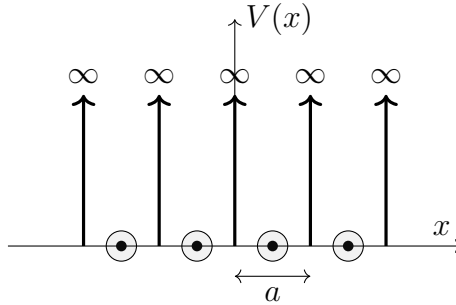


Figure 5: One-dimensional Dirac-Comb potential illustrating the periodic delta functions.

In regions where the potential $V(x)$ due to the Dirac comb is zero, the Time-Independent Schrödinger Equation (TISE) simplifies to the free particle equation:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi, \quad (20)$$

where ψ is the wave function, E is the energy of the particle, \hbar is the reduced Planck constant, and m is the mass of the particle. The general solution is:

$$\psi_1(x) = A \sin(kx) + B \cos(kx), \quad (21)$$

with the wave number k defined as:

$$k = \sqrt{\frac{2mE}{\hbar^2}}. \quad (22)$$

Bloch's theorem constrains the wave function's form within a periodic potential. For a cell to the left of the origin, we have:

$$\psi_2(x) = e^{-iKa} [A \sin(k(x+a)) + B \cos(k(x+a))], \quad -a < x < 0. \quad (23)$$

The wave function must be continuous at the crystal boundary $\psi_1(0) = \psi_2(0)$:

$$B = e^{-iKa} [A \sin(ka) + B \cos(ka)]. \quad (24)$$

However, the derivative exhibits a discontinuity due to the delta function's influence¹, manifesting as:

$$kA - e^{-iKa} kA \cos(ka) - B \sin(ka) = \frac{2m\alpha}{\hbar^2} B. \quad (25)$$

Solving for $A \sin(ka)$ gives us:

$$A \sin(ka) = [e^{iKa} - \cos(ka)] B. \quad (26)$$

This result, combined with the boundary conditions, leads to the crystalline energy bands condition:

$$\underbrace{\cos(Ka)}_{\text{LHS} \in [-1,1]} = \underbrace{\cos(ka) + \frac{m\alpha}{\hbar k} \cdot \sin(ka)}_{\text{RHS exceeds the range } [-1,1]} \quad (27)$$

where this equation relates the crystal wave number K to the particle wave number k and illustrates the conditions for allowed energy states (bands) and forbidden energy states (gaps) in the crystal.

We define two parameters $z = ka$ and $\beta = \frac{m\alpha}{\hbar^2 k}$. Substituting these into the LHS of the equation, we obtain the following expression for the function $f(z)$:

$$f(z) = \cos(z) + \beta \frac{\sin(z)}{z}$$

To visualize the behavior of $f(z)$, particularly how it exceeds the range $[-1, 1]$, we plot it for a specific value of β . Setting $\beta = 10$, we examine the function $f(z) = \cos(z) + 10 \frac{\sin(z)}{z}$:

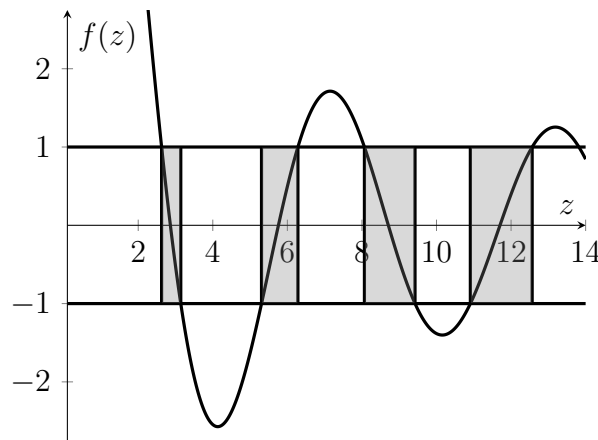


Figure 6: Visualization of the function $f(z)$ with $\beta = 10$.

¹This derivation can be found in Equation (2.128) of the third edition of *Introduction to Quantum Mechanics By David J. Griffiths*.

In this plot, the areas where the function are in the range $[-1, 1]$ are accentuated with shaded rectangles. These regions are critical in the formation of energy bands and gaps in solid-state physics, demonstrating the intervals where allowed energy states exist or are forbidden, respectively.

2.3 Energy Bands and Band Gaps

In solids, the TISE's solutions reflect the periodic nature of the potential. However, not all energy levels are permissible. The mathematical solution for the electron wave-functions in a periodic potential results in specific allowed and forbidden energy ranges. Specifically, there are instances where the solution's RHS exceeds, while the LHS does not, leading to only certain ranges of energy being allowed. This discrepancy creates distinct energy bands (allowed energy ranges) and band gaps (forbidden energy ranges).

- **Conductors:** Here, the valence band, containing bonding electrons, overlaps with the conduction band, allowing electrons to flow freely. This overlap results in minimal band gaps, enabling excellent electrical conductivity.
- **Semiconductors:** These materials have a small but finite band gap. At absolute zero, the valence band is full, and the conduction band is empty. Thermal energy at room temperature, quantified by $k_B T$, can excite electrons to the conduction band, enabling conductivity.
- **Insulators:** Characterized by a large band gap, insulators require a substantial amount of energy to transition electrons from the valence to the conduction band. This large gap leads to poor conductivity under normal conditions.

The band gap, defined as the energy difference between the top of the valence band (E_V) and the bottom of the conduction band (E_C), is a crucial parameter:

$$\text{Band Gap}(E_g) = E_C - E_V. \quad (28)$$

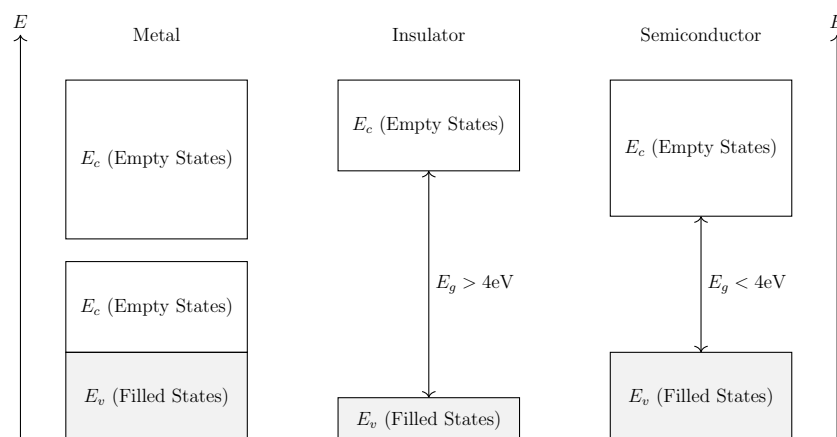


Figure 7: Energy levels for the three types of conductors

Remark: We focus exclusively on the transition bands, while acknowledging the presence of filled bands below and empty bands above.