Lecture 1: Introduction, Level Spacing and Density of States

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1a. When was the field of mesoscopic physics born? (which decade)
The field of mesoscopic physics was born in 1980s.

1b. Which development made the field possible?
The field of mesoscopic physics became possible due to several key developments:

1. **Advances in Nanofabrication Techniques:**
   The ability to fabricate structure at nano meter scale like, quantum dot, nano-wires by using ebeam-lithography and molecular beam epitaxy.

2. **Discovery of Quantum Effects in Small Systems:**
   The observation of quantum phenomena, such as , quantum tunneling, discrete energy levels and quantum confinement in this small system (Quantum dots, nano wires) demonstrated the behavior of electrons.

3. **Development of Low-Temperature Measurement Techniques:** Many masoscopic phenomena like coulomb blockade and quantum coherence, are only observable at low temperature. The development of cryogenic techniques and dilution refrigerators enabled to study these effects experimentally.

2a. Which fundamental equation is used to calculate the level spacing?
The time independent Schrödinger equation:

$$\left[E_s + \frac{(p_x + eBy)^2}{2m} + \frac{p_y^2}{2m} + U(y)\right]\Psi(x,y) = E\Psi(x,y) \tag{1}$$

$$\textbf{where} \quad p_x = -i\hbar\frac{\partial}{\partial x} \quad \text{and} \quad p_y = -i\hbar\frac{\partial}{\partial y} \tag{2}$$

From time independent Schödinger equation we got fundamental Equation for Level Spacing. The energy levels of a quantum harmonic oscillator are given by:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \quad \text{where } n = 0, 1, 2, 3, \ldots$$

The energy level spacing is defined as:

$$\Delta E = E_{n+1} - E_n$$

Substituting the energy expression:

$$\Delta E = \left(n + 1 + \frac{1}{2}\right)\hbar\omega - \left(n + \frac{1}{2}\right)\hbar\omega$$

$$\Delta E = \hbar\omega$$

Thus, the fundamental equation used to determine the level spacing is:

$$\Delta E = \hbar\omega$$

2.b What are the eigenvalues of an one-dimensional harmonic oscillator with V(x) = 1/2 m ω^2 x^2?

0.0.1 Method

Now, the time independent Schrödinger equation will be:

$$\frac{1}{2m}\left[\left(\frac{\hbar}{i}\frac{d}{dx}\right)^2 + (m\omega x)^2\right]\psi = E\psi. \tag{3}$$

The idea is to *factor* the term in square brackets. If these were *numbers*, it would be easy:

$$u^2 + v^2 = (u - iv)(u + iv). \tag{4}$$

Here, however, u and v are *operators*, and operators do not, in general, **commute** (uv is not the same as vu).

$$a_\pm \equiv \frac{1}{\sqrt{2m}}\left(\frac{\hbar}{i}\frac{d}{dx} \pm im\omega x\right). \tag{5}$$

$$\begin{aligned}
(a_- a_+)f(x) &= \frac{1}{2m}\left(\frac{\hbar}{i}\frac{d}{dx} - im\omega x\right)\left(\frac{\hbar}{i}\frac{d}{dx} + im\omega x\right)f(x) && (6)\\
&= \frac{1}{2m}\left(\frac{\hbar}{i}\frac{d}{dx} - im\omega x\right)\left(\frac{\hbar}{i}\frac{d}{dx} + im\omega x\right)f(x) && (7)\\
&= \frac{1}{2m}\left[-\hbar^2\frac{d^2}{dx^2} + \hbar m\omega\frac{d}{dx}(xf) - \hbar m\omega x\frac{d}{dx} + (m\omega x)^2 f\right] && (8)\\
&= \frac{1}{2m}\left[\left(\frac{\hbar}{i}\frac{d}{dx}\right)^2 + (m\omega x)^2 + \hbar m\omega\right]f(x). && (9)
\end{aligned}$$

[use, $d(xf)/dx = x(df/dx) + f$]

$$a_- a_+ = \frac{1}{2m}\left[\left(\frac{\hbar}{i}\frac{d}{dx}\right)^2 + (m\omega x)^2\right] + \frac{1}{2}\hbar\omega. \tag{10}$$

There's an extra term $(1/2)\hbar\omega$. However, if we pull this over to the other side, the Schrödinger equation becomes

$$(a_- a_+ - \frac{1}{2}\hbar\omega)\psi = E\psi. \tag{11}$$

The ordering of the factors a_+ and a_- is important here; the same argument, with a_+ on the left, yields

$$a_+ a_- = \frac{1}{2m}\left[\left(\frac{\hbar}{i}\frac{d}{dx}\right)^2 + (m\omega x)^2\right] - \frac{1}{2}\hbar\omega. \tag{12}$$

Thus,

$$a_- a_+ - a_+ a_- = \hbar\omega. \tag{13}$$

and the Schrödinger equation can also be written

$$(a_+ a_- + \frac{1}{2}\hbar\omega)\psi = E\psi. \tag{14}$$

Now, here comes the crucial step: I claim that *if ψ satisfies the Schrödinger equation, with energy E, then $a_+\psi$ satisfies the Schrödinger equation with energy* $(E + \hbar\omega)$. Proof:

$$\begin{aligned}(a_+ a_- + \frac{1}{2}\hbar\omega)(a_+\psi) &= (a_+ a_- a_+ + \frac{1}{2}\hbar\omega a_+)\psi \\ &= a_+(a_- a_+ + \frac{1}{2}\hbar\omega)\psi \\ &= a_+[(a_- a_+ - \frac{1}{2}\hbar\omega)\psi + \hbar\omega\psi] \\ &= a_+(E\psi + \hbar\omega\psi) = (E + \hbar\omega)(a_+\psi). \quad \text{QED}\end{aligned} \tag{15}$$

[Notice that whereas the ordering of a_+ and a_- *does* matter, the ordering of $a_\pm$ and any *constants* (such as $\hbar$, ω, and E) does not.] By the same token, $a_-\psi$ is a solution with energy $(E - \hbar\omega)$:

$$\begin{aligned}(a_- a_+ - \frac{1}{2}\hbar\omega)(a_-\psi) &= a_-(a_+ a_- - \frac{1}{2}\hbar\omega)\psi \\ &= a_-[(a_+ a_- + \frac{1}{2}\hbar\omega)\psi - \hbar\omega\psi] \\ &= a_-(E\psi - \hbar\omega\psi) \\ &= (E - \hbar\omega)(a_-\psi).\end{aligned} \tag{16}$$

There must occur a "lowest rung" (let's call it ψ_0) such that

$$a_-\psi_0 = 0. \tag{17}$$

That is to say,

$$\frac{1}{\sqrt{2m}}\left(\frac{\hbar}{i}\frac{d\psi_0}{dx} - im\omega x\psi_0\right) = 0. \tag{18}$$

or

$$\frac{d\psi_0}{dx} = -\frac{m\omega}{\hbar}x\psi_0. \tag{19}$$

This differential equation for ψ_0 is easy to solve:

$$\int \frac{d\psi_0}{\psi_0} = -\frac{m\omega}{\hbar}\int x\,dx \quad \Rightarrow \quad \ln\psi_0 = -\frac{m\omega}{2\hbar}x^2 + \text{constant}, \tag{20}$$

so

$$\psi_0(x) = A_0 e^{-\frac{m\omega}{2\hbar}x^2}. \tag{21}$$

To determine the energy of this state, we plug it into the Schrödinger equation (in the form of Equation 14),

$$(a_+a_- + (1/2)\hbar\omega)\psi_0 = E_0\psi_0,$$

nd exploit the fact that $a_-\psi_0 = 0$. Evidently,

$$E_0 = \frac{1}{2}\hbar\omega. \tag{22}$$

(the ground state of the quantum oscillator), we simply apply the raising operator to generate the excited states:

$$\boxed{\psi_n(x) = A_n(a_+)^n e^{-\frac{m\omega}{2\hbar}x^2}, \quad \text{with} \quad E_n = \left(n + \frac{1}{2}\right)\hbar\omega.} \tag{23}$$

2c. Calculate the density of states for a small frequency ω. The density of states $g(E)$ is defined as the number of quantum states per unit energy interval:

$$g(E) = \frac{dN}{dE}$$

For a one-dimensional quantum harmonic oscillator, the energy levels are given by:

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

At large n, we approximate $n \approx \frac{E}{\hbar\omega}$, so the number of states up to energy E is:

$$N(E) \approx \frac{E}{\hbar\omega}.$$

Differentiating this with respect to E gives the density of states:

$$g(E) = \frac{d}{dE}\left(\frac{E}{\hbar\omega}\right) = \frac{1}{\hbar\omega}.$$

For small ω the level spacing $\hbar\omega$ becomes smaller, meaning the density of states increases. In the limit $\omega \to 0$ the density of states approaches infinity, resembling a continuous energy spectrum. Thus, for small ω.

2d. Compare the energy dependence of the d.o.s. with that of a particle in an one-dimensional box.

$$N = \int_0^{k_F} g_s \rho_{1D}(k) dk = g_s \frac{L}{\pi} k_F \tag{24}$$

or

$$k_F = N\frac{\pi}{g_s L} = \frac{N}{L}\frac{\pi}{g_s} = n\frac{\pi}{g_s} = n\frac{\pi}{2} \tag{25}$$

This immediately yields the Fermi energy

$$E_F \equiv \frac{\hbar^2}{2m}k_F^2 = \frac{\hbar^2}{2m}\left(\frac{N\pi}{2L}\right)^2 = \frac{\hbar^2}{2m}\left(n\frac{\pi}{2}\right)^2 \tag{26}$$

To calculate the *DOS in energy space*, $\rho_{1D}(E)$, we have to take into account the quadratic E-k relation, given by

$$k = \sqrt{\frac{2mE}{\hbar^2}} \tag{27}$$

and so one finds

$$\rho_{1D}(E) \equiv \frac{dN}{dE} = \frac{dN}{dk}\frac{dk}{dE} = \rho_{1D}(k) \cdot \sqrt{\frac{m}{2\hbar^2 E}} = \frac{g_s L}{\pi} \cdot \sqrt{\frac{m}{2\hbar^2}} \cdot \frac{1}{\sqrt{E}} \tag{28}$$

i.e. the 1-dimensional E-DOS follows an inverse square root dependence on energy.

For a quantum harmonic oscillator, the energy levels are given by:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega, \quad n = 0, 1, 2, \ldots$$

The energy spacing between adjacent levels is constant:

$$\Delta E = \hbar\omega.$$

The density of states is inversely proportional to $\hbar\omega$, meaning:

$$g(E) \propto \frac{1}{\hbar\omega}.$$

Thus, the difference is that the harmonic oscillator has a constant DOS, while the particle in a box has a DOS that decreases with energy.

2e. What would you take as the size L of the system when it is filled with 1000 non-interacting electrons?
For a one-dimensional system, the Fermi wavevector k_F is related to the number of electrons N by:

$$k_F = \frac{\pi n}{2}$$

where

$$n = \frac{N}{L}$$

is the electron density (number of electrons per unit length). For $N = 1000$ electrons, the Fermi wave-vector is:

$$k_F = \frac{\pi \cdot 1000}{2L}.$$

The size L of the system filled with 1000 non-interacting electrons is approximately:

$$L \approx \frac{1000 \cdot \pi}{2k_F}$$

where k_F is the Fermi wave-vector. The exact value of L depends on the specific Fermi energy or Fermi wave-vector of the system, which in turn depends on the material and confinement conditions.

3a. Calculate the Fermi wavenumber k$_F$ for a two dimensional electron gas (2DEG), expressed in the electron concentration n. Do the same for 1D.
The units in which the electron "concentration" is expressed changes with the dimensionality of the system. To compare systems with different dimensionalities, the concentration can be expressed in the effective distance between electrons d$_{e-e}$ by assuming that each electron lives in a box of size d$_{e-e}$.

For 2D, It is common to use the periodic boundary conditions which require k_x and k_y to take on quantized values depending on the dimensions L_x and L_y of the sample (n_x and n_y are integers):

$$k_x = n_x\left(\frac{2\pi}{L_x}\right) \quad \text{and} \quad k_y = n_y\left(\frac{2\pi}{L_y}\right) \tag{29}$$

Thus the area in the $k_x - k_y$ plane 'occupied' by an individual state is given by (S: area of the conductor)

$$\frac{2\pi}{L_x} \times \frac{2\pi}{L_y} = \frac{4\pi^2}{S} \tag{30}$$

while the area enclosed by the circle is πk^2. Hence (for $E > E_s$):

$$N_T(E) = 2 \text{ (for spin)} \times \frac{\pi k^2}{4\pi^2/S} = S\frac{k^2}{2\pi} = \frac{mS}{\pi\hbar^2}(E - E_s) \tag{31}$$

This is the total number of states. The density of states per unit area per unit energy is given by:

$$N(E) = \frac{1}{S}\frac{d}{dE}N_T(E) = \frac{m}{\pi\hbar^2}\vartheta(E - E_s) \tag{32}$$

At equilibrium, the available states in a conductor are filled up according to the Fermi function:

$$f_0(E) = \frac{1}{1 + \exp\left(\frac{E-E_f}{k_BT}\right)} \tag{33}$$

There are two limits in which the Fermi function inside the band (E ¿ E,) can be simplified somewhat making it easier to perform numerical calculations. One is the high temperature or the non- degenerate limit $\exp\left(\frac{E_s-E_f}{k_BT}\right) \gg 1$ where

$$f_0(E) \approx \exp\left[-\frac{(E - E_f)}{k_BT}\right] \tag{34}$$

The other is the low temperature or the degenerate limit $\exp\left(\frac{E_s-E_f}{k_BT}\right) \ll 1$ where,

$$f_0(E) \approx \vartheta(E_f - E) \tag{35}$$

In this book, we will mainly be discussing degenerate conductors. To relate the equilibrium electron density n_s (per unit area) to the Fermi energy, we make use of the relation

$$n_s = \int N(E)f_0(E)dE \tag{36}$$

For degenerate conductors, it is easy to perform the integral to obtain

$$n_s = N_s(E_f - E_s) \quad \text{where} \quad N_s = \frac{m}{\pi\hbar^2} \tag{37}$$

where we have made use of Eqs. (32) and (35).

At low temperatures, the conductance is determined entirely by electrons with energy close to the Fermi energy. The wavenumber of such electrons is referred to as the Fermi wavenumber (k_f):

$$E_f - E_s = \frac{\hbar^2 k_f^2}{2m} \quad \Rightarrow \quad \hbar k_f = \sqrt{2m(E_f - E_s)} \tag{38}$$

Using Eq. (37), we can express the Fermi wavenumber in terms of the electron density:

$$k_f = \sqrt{2\pi n_s} \tag{39}$$

For 1D, The longest wave compatible with this condition forms a half wave spanning the length L, i.e. $\lambda_1 = 2L$: this forms the first or lowest (1D) eigenstate $|1\rangle$. The second state results for one full wave of wavelength fitting the length, i.e. with a wavelength $\lambda_2 = \frac{2L}{2} = L$. Similarly three half waves of wavelength $\lambda_3 = \frac{2L}{3}$ for the third state, etc. can be set up, i.e. in general for the state $|j\rangle$

$$\lambda_j = \frac{2L}{j} \qquad (j = 1, 2, 3, ...) \tag{40}$$

For the associated k-vector of the state $|j\rangle$ we thus find

$$k_j = \frac{2\pi}{\lambda_j} = \frac{j\pi}{L} \tag{41}$$

To see how we have to accommodate all the electrons available in the 1D-wire we need to see how many states there are within a certain range of k-values. From (41) we see that the k-vectors are equally spaced at intervals $\Delta k = \pi/L$, and so we obtain for the *density-of-states* or *DOS* in 1D k-space

$$\rho_{1D}(k) \equiv \frac{dN_k}{dk} = \frac{1}{\Delta k} = \frac{L}{\pi} \tag{42}$$

Now assume that the wire contains N electrons in total, that are uniformly distributed along the chain yielding a *linear* electron density $n = N/L$ (per unit length, i.e., in units m^{-1}).

To evaluate how many states are occupied by the N electrons we have to recognise that each k-state may contain more than one electron. We assume that the *degeneracy* is only 2-fold, with each k-state occupied by two electrons of opposite spin, denoted by the *spin-degeneracy* $g_s = 2$.

So, by integrating eq. (42) we immediately obtain the Fermi momentum k_F, which by definition equals the largest k value for any occupied state.

Thus,

$$N = \int_0^{k_F} g_s \rho_{1D}(k) dk = g_s \frac{L}{\pi} k_F \tag{43}$$

or

$$k_F = N \frac{\pi}{g_s L} = \frac{N}{L} \frac{\pi}{g_s} = n \frac{\pi}{g_s} = n \frac{\pi}{2} \tag{44}$$

From the Fermi wave vector k_F in eq. (41) we can derive the Fermi wavelength

$$\lambda_F = \frac{2\pi}{k_F} \sim \text{2-3 times the interelectron distance } d_{ee} \tag{45}$$

3b. Express the results for $\mathbf{k}_F$ in one, two and three dimensions in de-e and calculate the numerical value of the prefactors. Are you surprised that they are close to one?

Expression for k_F in Terms of d_{e-e}

The effective inter-electron distance d_{e-e} is given by:

$$d_{e-e} = n^{-1/D}$$

where n is the electron concentration and D is the system dimensionality.

1D Case

In one dimension, the electron concentration is:

$$n = \frac{2k_F}{\pi}$$

Solving for k_F:

$$k_F = \frac{\pi n}{2}$$

Expressing in terms of d_{e-e}:

$$k_F = \frac{\pi}{2d_{e-e}}$$

2D Case

In two dimensions, the electron concentration is:

$$n = \frac{k_F^2}{2\pi}$$

Solving for k_F:

$$k_F = \sqrt{2\pi n}$$

Expressing in terms of d_{e-e}:

$$k_F = \sqrt{2\pi}\frac{1}{d_{e-e}}$$

Numerical Values of the Prefactors

- $\frac{\pi}{2} \approx 1.57$ (1D)
- $\sqrt{2\pi} \approx 2.51$ (2D)

Interpretation

The prefactors are all close to 1, which is not surprising because d_{e-e} represents a characteristic length scale of the system. The differences arise from the geometric factors associated with different dimensionalities.

4. Graphene is recently discovered material, consisting of an one carbon atom thick layer. The atoms are positioned in a hexagonal lattice with a distance dCC = 1.4 Å between the atoms.
a. Each carbon atom has one free electron. Find the value for the Fermi energy and Fermi wavelength using the free electron model.

Graphene has a hexagonal lattice structure with a carbon-carbon bond distance:

$$d_{CC} = 1.4\,\text{Å} = 1.4 \times 10^{-10}\ \text{m}$$

Area of the Hexagonal Unit Cell

The area of a hexagonal unit cell is given by:

$$A_{\text{hex}} = \frac{3\sqrt{3}}{2} d_{CC}^2$$

Substituting $d_{CC} = 1.4 \times 10^{-10}$ m:

$$A_{\text{hex}} = \frac{3\sqrt{3}}{2} \times (1.4 \times 10^{-10})^2$$

$$\approx 5.24 \times 10^{-20}\ \text{m}^2$$

Electron Density n

Each unit cell contains 2 carbon atoms, with each atom contributing 1 free electron. Thus, the electron density n (number of electrons per unit area) is given by:

$$n = \frac{2}{A_{\text{hex}}}$$

Substituting $A_{\text{hex}} = 5.24 \times 10^{-20}$ m^2:

$$n = \frac{2}{5.24 \times 10^{-20}}$$

$$\approx 3.82 \times 10^{19} \text{ m}^{-2}$$

Fermi Wave Vector k_F in 2D

In two dimensions, the Fermi wave vector k_F is related to the electron density n by:

$$k_F = \sqrt{2\pi n}$$

Substituting $n \approx 3.82 \times 10^{19}$ m^{-2}:

$$k_F = \sqrt{2\pi \times 3.82 \times 10^{19}}$$
$$\approx 1.54 \times 10^{10} \text{ m}^{-1}$$

Fermi Energy E_F

The Fermi energy E_F is given by:

$$E_F = \frac{\hbar^2 k_F^2}{2m_e}$$

where:

- $\hbar = 1.054 \times 10^{-34}$ Js (reduced Planck's constant),
- $m_e = 9.11 \times 10^{-31}$ kg (electron mass).

Substituting $k_F \approx 1.54 \times 10^{10}$ m^{-1}:

$$E_F = \frac{(1.054 \times 10^{-34})^2 (1.54 \times 10^{10})^2}{2 \times (9.11 \times 10^{-31})}$$

$$\approx 1.36 \text{ eV}$$

Fermi Wavelength λ_F

The Fermi wavelength λ_F is related to k_F by:

$$\lambda_F = \frac{2\pi}{k_F}$$

Substituting $k_F \approx 1.54 \times 10^{10}$ m^{-1}:

$$\lambda_F = \frac{2\pi}{1.54 \times 10^{10}}$$

$$\approx 4.08 \times 10^{-10} \text{ m} = 4.08 \text{ Å}$$

b The band structure can also be calculated with a tight-binding model. Look up what the band structure E(k) is in this case. What is the effective mass?

1 Tight-binding Hamiltonian

Considering only nearest-neighbor hopping, the tight-binding Hamiltonian for graphene is

$$\hat{H} = -t \sum_{\langle ij \rangle} \left(\hat{a}_i^\dagger \hat{b}_j + \hat{b}_j^\dagger \hat{a}_i \right), \tag{46}$$

where i (j) labels sites in sublattice A (B), the fermionic operator $\hat{a}_i^\dagger$ ($\hat{a}_i$) creates (annihilates) an electron at the A site whose position is $\mathbf{r}_i$, and similarly for $\hat{b}_j^\dagger, \hat{b}_j$. We can rewrite the sum over nearest neighbors as

$$\sum_{\langle ij \rangle} (\hat{a}_i^\dagger \hat{b}_j + \hat{b}_j^\dagger \hat{a}_i) = \sum_{i \in A} \sum_{\boldsymbol{\delta}} (\hat{a}_i^\dagger \hat{b}_{i+\delta} + \hat{b}_{i+\delta}^\dagger \hat{a}_i), \tag{47}$$

where the sum over $\boldsymbol{\delta}$ is carried out over the nearest-neighbor vectors $\boldsymbol{\delta}_1, \boldsymbol{\delta}_2, \boldsymbol{\delta}_3$, and the operator $\hat{b}_{i+\delta}$ annihilates a fermion at the B site whose position is $\mathbf{r}_i + \boldsymbol{\delta}$.

Using

$$\hat{a}_i^\dagger = \frac{1}{\sqrt{N/2}} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}_i} \hat{a}_{\mathbf{k}}^\dagger, \tag{48}$$

where $N/2$ is the number of A sites, and similarly for $\hat{b}_{i+\delta}^\dagger$, we can write the tight-binding Hamiltonian for graphene (Eq. 46) as

$$\begin{aligned}
\hat{H} &= -\frac{t}{N/2} \sum_{i \in A} \sum_{\boldsymbol{\delta},\mathbf{k},\mathbf{k}'} \left[e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_i} e^{-i\mathbf{k}'\cdot\boldsymbol{\delta}} \hat{a}_{\mathbf{k}'}^\dagger \hat{b}_{\mathbf{k}} + \text{H.c.} \right] && (49) \\
&= -t \sum_{\boldsymbol{\delta},\mathbf{k}} \left(e^{-i\mathbf{k}\cdot\boldsymbol{\delta}} \hat{a}_{\mathbf{k}}^\dagger \hat{b}_{\mathbf{k}} + \text{H.c.} \right) && (50) \\
&= -t \sum_{\boldsymbol{\delta},\mathbf{k}} \left(e^{-i\mathbf{k}\cdot\boldsymbol{\delta}} \hat{a}_{\mathbf{k}}^\dagger \hat{b}_{\mathbf{k}} + e^{i\mathbf{k}\cdot\boldsymbol{\delta}} \hat{b}_{\mathbf{k}}^\dagger \hat{a}_{\mathbf{k}} \right), && (51)
\end{aligned}$$

where in the second line we have used

$$\sum_{i \in A} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_i} = \frac{N}{2} \delta_{\mathbf{k}\mathbf{k}'}. \tag{52}$$

We can therefore express the Hamiltonian as

$$\hat{H} = \sum_{\mathbf{k}} \Psi^\dagger h(\mathbf{k}) \Psi, \tag{53}$$

where

$$\Psi \equiv \begin{pmatrix} \hat{a}_{\mathbf{k}} \\ \hat{b}_{\mathbf{k}} \end{pmatrix}, \quad \Psi^\dagger \equiv (\hat{a}^\dagger_{\mathbf{k}} \quad \hat{b}^\dagger_{\mathbf{k}}). \tag{54}$$

and

$$\mathbf{h}(\mathbf{k}) \equiv -t \begin{pmatrix} 0 & \Delta_{\mathbf{k}} \\ \Delta^*_{\mathbf{k}} & 0 \end{pmatrix} \tag{55}$$

is the matrix representation of the Hamiltonian and

$$\Delta_{\mathbf{k}} \equiv \sum_{\boldsymbol{\delta}} e^{i\mathbf{k}\cdot\boldsymbol{\delta}}. \tag{56}$$

2 Energy bands

The eigenvalues of this matrix are $E_\pm = \pm\sqrt{\Delta_{\mathbf{k}}\Delta^*_{\mathbf{k}}}$. We can compute this by writing $\Delta_{\mathbf{k}}$ out more explicitly:

$$\begin{aligned}
\Delta_{\mathbf{k}} &= e^{i\mathbf{k}\cdot\boldsymbol{\delta}_1} + e^{i\mathbf{k}\cdot\boldsymbol{\delta}_2} + e^{i\mathbf{k}\cdot\boldsymbol{\delta}_3} && (57)\\
&= e^{i\mathbf{k}\cdot\boldsymbol{\delta}_3}\left[1 + e^{i\mathbf{k}\cdot(\boldsymbol{\delta}_1-\boldsymbol{\delta}_3)} + e^{i\mathbf{k}\cdot(\boldsymbol{\delta}_2-\boldsymbol{\delta}_3)}\right] && (58)\\
&= e^{-ik_xa}\left[1 + e^{i3k_xa/2}e^{i\sqrt{3}k_ya/2} + e^{i3k_xa/2}e^{-i\sqrt{3}k_ya/2}\right] && (59)\\
&= e^{-ik_xa}\left[1 + e^{i3k_xa/2}\left(e^{i\sqrt{3}k_ya/2} + e^{-i\sqrt{3}k_ya/2}\right)\right] && (60)\\
&= e^{-ik_xa}\left[1 + 2e^{i3k_xa/2}\cos\left(\frac{\sqrt{3}}{2}k_ya\right)\right]. && (61)
\end{aligned}$$

The energy bands are therefore given by

$$E_\pm(\mathbf{k}) = \pm\sqrt{1 + 4\cos\left(\frac{3}{2}k_xa\right)\cos\left(\frac{\sqrt{3}}{2}k_ya\right) + 4\cos^2\left(\frac{\sqrt{3}}{2}k_ya\right)}. \tag{62}$$

or, as it is sometimes written,

$$E_\pm(\mathbf{k}) = \pm t\sqrt{3 + f(\mathbf{k})}, \tag{63}$$

where

$$f(\mathbf{k}) = 2\cos(\sqrt{3}k_ya) + 4\cos\left(\frac{3}{2}k_xa\right)\cos\left(\frac{\sqrt{3}}{2}k_ya\right). \tag{64}$$

3 Dirac Points

The band structure has two distinct Dirac points (often labeled $\mathbf{K}$ and $\mathbf{K}'$) at the corners of the hexagonal Brillouin zone. Near these points, the energy dispersion is linear and can be approximated as:

$$E(\mathbf{k}) \approx \pm \hbar v_F |\mathbf{k}|, \tag{65}$$

where:

- $v_F \approx 10^6$ m/s is the Fermi velocity,
- $\mathbf{k}$ is measured relative to the Dirac point.

This linear dispersion relation is a hallmark of graphene and is responsible for its unique electronic properties, such as massless Dirac fermion behavior.

4 Effective Mass in Graphene

The effective mass m^* of electrons in a material is defined by the curvature of the energy bands:

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2}. \tag{66}$$

4.1 Near the Dirac Points

In graphene, the linear dispersion relation near the Dirac points implies that the second derivative $\frac{\partial^2 E}{\partial k^2}$ is zero. Therefore, the effective mass m^* is:

$$m^* = 0. \tag{67}$$

This means that electrons in graphene behave as massless Dirac fermions near the Dirac points, which is a unique feature of graphene's band structure.

4C. Find the density of states from the band structure. Compare the result to the results for a free electron gas.

The density of states $g(E)$ is defined as the number of states per unit energy per unit area. For a 2D system, the general formula for DOS is given by:

$$g(E) = \frac{dN}{dE}$$

where N is the number of states. **Number of States N:**

In 2D, the number of states with wave vector $|k| \leq k$ is given by:

$$N(k) = \frac{A}{(2\pi)^2} \cdot \pi k^2 = \frac{Ak^2}{4\pi},$$

where A is the area of the system.

Energy Relation:

From the linear dispersion relation:

$$E = \hbar v_F k,$$

we can express k in terms of E as:

$$k = \frac{E}{\hbar v_F}.$$

Substituting k into $N(k)$:

By substituting $k = \frac{E}{\hbar v_F}$ into $N(k)$, we get:

$$N(E) = \frac{A}{4\pi}\left(\frac{E}{\hbar v_F}\right)^2.$$

Density of States $g(E)$:

Differentiating $N(E)$ with respect to E:

$$g(E) = \frac{dN}{dE} = \frac{A}{2\pi}\frac{E}{(\hbar v_F)^2}.$$

The DOS per unit area is:

$$g(E) = \frac{E}{2\pi(\hbar v_F)^2}.$$

The DOS in graphene is linear in energy E, unlike the constant DOS in a 2D free electron gas.

Density of States for a 2D Free Electron Gas

For a 2D free electron gas, the energy dispersion is quadratic:

$$E(k) = \frac{\hbar^2 k^2}{2m}.$$

Number of States N The number of states with wave vector $|k| \leq k$ is:

$$N(k) = \frac{A}{(2\pi)^2} \cdot \pi k^2 = \frac{Ak^2}{4\pi}.$$

Energy Relation

From the quadratic dispersion relation:

$$E = \frac{\hbar^2 k^2}{2m},$$

we can express k in terms of E:

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

Substituting k into $N(k)$

$$N(E) = \frac{A}{4\pi}\left(\frac{2mE}{\hbar^2}\right).$$

Density of States $g(E)$

Differentiating $N(E)$ with respect to E:

$$g(E) = \frac{dN}{dE} = \frac{A}{2\pi}\frac{m}{\hbar^2}.$$

The DOS per unit area is:

$$g(E) = \frac{m}{\pi\hbar^2}.$$

The DOS for a 2D free electron gas is constant.

5a. Argue in which case the infinite square well describes reality the best: a metallic or a semiconducting material.

The **infinite square well** is a simplified quantum mechanical model used to describe the behavior of particles confined in a potential well with infinitely high walls. While it is an idealized model, it can provide insights into the electronic properties of materials. Let's analyze whether it describes **metallic** or **semiconducting** materials better.

1. Infinite Square Well Model

In the infinite square well model:

- Electrons are confined to a region of space with infinitely high potential barriers at the boundaries.
- The energy levels are quantized and given by:

  $$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2},$$

  where n is a positive integer (quantum number), m is the electron mass, and L is the width of the well.
- The wavefunctions are standing waves with nodes at the boundaries.

2. Comparison with Metallic Materials

Properties of Metals:

- Metals have a **partially filled conduction band**, meaning there are available states for electrons to move freely.
- The Fermi level lies within the conduction band, and electrons near the Fermi level can be excited to higher energy states with minimal energy input.

- The electronic states in metals are delocalized, and electrons behave as a "free electron gas."

Applicability of Infinite Square Well:

- The infinite square well model can describe the **quantization of energy levels** in confined systems, such as electrons in a thin metallic film or nanowire.
- However, metals are characterized by a **continuum of states** near the Fermi level, which is not fully captured by the discrete energy levels of the infinite square well.
- The model does not account for the **band structure** of metals, which is crucial for understanding their conductivity and other properties.

Conclusion for Metals:

The infinite square well model is not a good description of metallic materials because it oversimplifies the electronic structure and does not capture the continuum of states or the delocalized nature of electrons in metals.

3. Comparison with Semiconducting Materials

Properties of Semiconductors:

- Semiconductors have a **band gap** between the valence band (filled with electrons) and the conduction band (empty at zero temperature).
- The Fermi level lies within the band gap, and electrons need to be excited across the band gap to contribute to conduction.
- The electronic states in semiconductors are more localized compared to metals, especially in nanostructures like quantum dots or thin films.

Applicability of Infinite Square Well:

- The infinite square well model is better suited for describing **confined systems** such as quantum dots, nanowires, or thin semiconductor films, where electrons are spatially confined and exhibit quantized energy levels.
- In semiconductors, the discrete energy levels of the infinite square well can approximate the **quantum confinement effects** observed in nanostructures.
- The model can also describe the **formation of discrete states** within the band gap of semiconductors, which is relevant for understanding optical and electronic properties of nanostructures.

Conclusion for Semiconductors:

The infinite square well model is a better description for semiconducting materials, especially in nanostructures where quantum confinement effects dominate.

4. Final Argument

The infinite square well model describes **semiconducting materials** better than metallic materials because:

- Semiconductors often exhibit **quantum confinement effects** in nanostructures, which are well-described by the discrete energy levels of the infinite square well.
- Metals, on the other hand, have a **continuum of states** near the Fermi level, which is not captured by the infinite square well model.
- The infinite square well is more applicable to systems where electrons are strongly confined, such as quantum dots or thin semiconductor films, rather than the delocalized electrons in metals.

Thus, the infinite square well model is more relevant for **semiconducting materials**, particularly in the context of nanoscale systems.

5b. Calculate the level spacing for a cubic gold cluster with size 1×1×1 and 10×10×10 nm^3 and compare this with its charging energy.

We calculate the **level spacing** and **charging energy** for two cubic gold clusters: one with size $1 \times 1 \times 1\,\text{nm}^3$ and another with size $10 \times 10 \times 10\,\text{nm}^3$.

1. Level Spacing in a Cubic Potential Well

The energy levels for an electron in a 3D infinite potential well (cubic box) are given by:

$$E_{n_x,n_y,n_z} = \frac{\hbar^2\pi^2}{2m_eL^2}(n_x^2 + n_y^2 + n_z^2),$$

where:

- n_x, n_y, n_z are positive integers (quantum numbers),
- L is the side length of the cubic box,
- m_e is the electron mass ($m_e \approx 9.11 \times 10^{-31}\,\text{kg}$),
- $\hbar$ is the reduced Planck's constant ($\hbar \approx 1.054 \times 10^{-34}\,\text{J s}$).

The **level spacing** ΔE is the energy difference between the ground state ($n_x = n_y = n_z = 1$) and the first excited state ($n_x = 2, n_y = n_z = 1$):

$$\Delta E = E_{2,1,1} - E_{1,1,1} = \frac{\hbar^2\pi^2}{2m_eL^2}(2^2 + 1^2 + 1^2 - 1^2 - 1^2 - 1^2) = \frac{3\hbar^2\pi^2}{2m_eL^2}.$$

2. Charging Energy

The **charging energy** E_C is the energy required to add an electron to the cluster. For a small metallic cluster, it is given by:

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

where:

- e is the elementary charge ($e \approx 1.602 \times 10^{-19}\,\mathrm{C}$),
- C is the capacitance of the cluster.

For a cubic cluster, the capacitance is approximated as:

$$C \approx 4\pi\epsilon_0 \frac{L}{2},$$

where L is the side length of the cube, and ϵ_0 is the vacuum permittivity ($\epsilon_0 \approx 8.854 \times 10^{-12}\,\mathrm{F\,m^{-1}}$).

Thus, the charging energy becomes:

$$E_C = \frac{e^2}{4\pi\epsilon_0 L}.$$

3. Calculations for $1 \times 1 \times 1\,\mathrm{nm}^3$ Gold Cluster

Level Spacing:

For $L = 1\,\mathrm{nm} = 1 \times 10^{-9}\,\mathrm{m}$:

$$\Delta E = \frac{3\hbar^2\pi^2}{2m_e L^2} = \frac{3(1.054 \times 10^{-34}\,\mathrm{J\,s})^2\pi^2}{2(9.11 \times 10^{-31}\,\mathrm{kg})(1 \times 10^{-9}\,\mathrm{m})^2}.$$

$$\Delta E \approx 1.13 \times 10^{-19}\,\mathrm{J} \approx 0.71\,\mathrm{eV}.$$

Charging Energy:

$$E_C = \frac{e^2}{4\pi\epsilon_0 L} = \frac{(1.602 \times 10^{-19}\,\mathrm{C})^2}{4\pi(8.854 \times 10^{-12}\,\mathrm{F\,m^{-1}})(1 \times 10^{-9}\,\mathrm{m})}.$$

$$E_C \approx 2.30 \times 10^{-19}\,\mathrm{J} \approx 1.44\,\mathrm{eV}.$$

4. Calculations for $10 \times 10 \times 10\,\mathrm{nm}^3$ Gold Cluster

Level Spacing:

For $L = 10\,\mathrm{nm} = 10 \times 10^{-9}\,\mathrm{m}$:

$$\Delta E = \frac{3\hbar^2\pi^2}{2m_e L^2} = \frac{3(1.054 \times 10^{-34}\,\mathrm{J\,s})^2\pi^2}{2(9.11 \times 10^{-31}\,\mathrm{kg})(10 \times 10^{-9}\,\mathrm{m})^2}.$$

$$\Delta E \approx 1.13 \times 10^{-21}\,\mathrm{J} \approx 0.0071\,\mathrm{eV}.$$

Charging Energy:

$$E_C = \frac{e^2}{4\pi\epsilon_0 L} = \frac{(1.602 \times 10^{-19}\,\mathrm{C})^2}{4\pi(8.854 \times 10^{-12}\,\mathrm{F\,m^{-1}})(10 \times 10^{-9}\,\mathrm{m})}.$$

$$E_C \approx 2.30 \times 10^{-20}\,\mathrm{J} \approx 0.144\,\mathrm{eV}.$$

5c. Calculate the values for $\mathbf{E}_F$ (in eV), $\mathbf{k}_F$ (in nm^{-1}) and $\mathbf{D}(\mathbf{E}_F)$ (in eV^{-1}) in both cases. Look up the values that you need.

Electron Density of Gold (n)

Gold has a face-centered cubic (FCC) structure with a lattice constant:

$$a = 4.08\,\text{Å}$$

The electron density is given by:

$$n = \frac{4}{a^3} \approx \frac{4}{(4.08 \times 10^{-10}\,\mathrm{m})^3} \approx 5.90 \times 10^{28}\,\mathrm{m^{-3}}.$$

Effective Mass of Electrons in Gold (m^*)

For gold, the effective mass is close to the free electron mass:

$$m^* \approx m_e = 9.11 \times 10^{-31}\,\mathrm{kg}.$$

Fermi Energy E_F

The Fermi energy for a 3D free electron gas is given by:

$$E_F = \frac{\hbar^2}{2m^*}\left(3\pi^2 n\right)^{\frac{2}{3}}.$$

Substituting the values:

$$E_F = \frac{(1.054 \times 10^{-34}\,\mathrm{J\,s})^2}{2 \times 9.11 \times 10^{-31}\,\mathrm{kg}}\left(3\pi^2 \times 5.90 \times 10^{28}\,\mathrm{m^{-3}}\right)^{\frac{2}{3}}.$$

$$E_F \approx 5.53\,\mathrm{eV}.$$

Fermi Wave Vector k_F

The Fermi wave vector is given by:

$$k_F = \left(3\pi^2 n\right)^{\frac{1}{3}}.$$

Substituting the values:

$$k_F = \left(3\pi^2 \times 5.90 \times 10^{28}\,\mathrm{m}^{-3}\right)^{\frac{1}{3}}.$$

$$k_F \approx 1.20 \times 10^{10}\,\mathrm{m}^{-1} = 12.0\,\mathrm{nm}^{-1}.$$

Density of States at the Fermi Level $D(E_F)$

The density of states at the Fermi level for a 3D free electron gas is:

$$D(E_F) = \frac{m^*}{\pi^2 \hbar^3} \cdot 2m^* E_F.$$

Substituting the values:

$$D(E_F) = \frac{9.11 \times 10^{-31}\,\mathrm{kg}}{\pi^2 (1.054 \times 10^{-34}\,\mathrm{J\,s})^3} \cdot 2(9.11 \times 10^{-31}\,\mathrm{kg})(5.53\,\mathrm{eV} \times 1.602 \times 10^{-19}\,\mathrm{J\,eV}^{-1}).$$

$$D(E_F) \approx 1.14 \times 10^{47}\,\mathrm{J}^{-1}\,\mathrm{m}^{-3} \approx 1.82 \times 10^{22}\,\mathrm{eV}^{-1}\,\mathrm{cm}^{-3}.$$

Results for Both Clusters

$1 \times 1 \times 1$ nm^3 Cluster

- **Fermi energy** (E_F): $5.53\,\mathrm{eV}$
- **Fermi wave vector** (k_F): $12.0\,\mathrm{nm}^{-1}$
- **Density of states at** E_F ($D(E_F)$): $1.82 \times 10^{22}\,\mathrm{eV}^{-1}\,\mathrm{cm}^{-3}$

$10 \times 10 \times 10$ nm^3 Cluster

- **Fermi energy** (E_F): $5.53\,\mathrm{eV}$
- **Fermi wave vector** (k_F): $12.0\,\mathrm{nm}^{-1}$
- **Density of states at** E_F ($D(E_F)$): $1.82 \times 10^{22}\,\mathrm{eV}^{-1}\,\mathrm{cm}^{-3}$

5d. Find the level spacing and density of states for a spherical gold cluster with radius R. See p129 of introduction to quantum mechanics by Griffiths and use a computer to find the roots. Compare the results to the cubic case. Does the exact shape of the system matter when calculating the density of states?

To find the level spacing and density of states for a spherical gold cluster with radius R, we solve the Schrödinger equation for a particle confined in a spherical potential well. The steps are as follows:

1. Solving the Schrödinger Equation for a Spherical Well

For a spherical potential well of radius R, the Schrödinger equation in spherical coordinates is:

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi$$

The solutions are given by spherical Bessel functions $j_l(kr)$, where $k = \sqrt{2mE}/\hbar$. The boundary condition requires that the wavefunction vanishes at $r = R$, so:

$$j_l(kR) = 0$$

The roots of the spherical Bessel functions $j_l(x)$ determine the allowed energy levels. Let $x_{n,l}$ be the n-th root of $j_l(x)$. Then:

$$k_{n,l} = \frac{x_{n,l}}{R}$$

The corresponding energy levels are:

$$E_{n,l} = \frac{\hbar^2}{2m}\left(\frac{x_{n,l}}{R}\right)^2$$

2. Level Spacing

The level spacing ΔE is the difference in energy between adjacent levels. For a spherical well, the spacing depends on the quantum numbers n and l. For large n and l, the spacing can be approximated as:

$$\Delta E \approx \frac{\hbar^2}{2m}\left(\frac{x_{n+1,l} - x_{n,l}}{R}\right)^2$$

The roots $x_{n,l}$ can be computed numerically using a computer (e.g., Python, MATLAB, or Mathematica).

3. Density of States

The density of states $g(E)$ is the number of states per unit energy interval. For a spherical well, the density of states can be approximated by counting the number of states with energy less than E. This involves summing over all quantum numbers n and l such that $E_{n,l} \leq E$.

For large E, the density of states for a 3D system scales as:

$$g(E) \propto \sqrt{E}$$

This is similar to the cubic case, as the density of states depends on the dimensionality of the system rather than its exact shape.

4. Comparison to the Cubic Case

For a cubic potential well of side length L, the energy levels are:

$$E_{n_x,n_y,n_z} = \frac{\hbar^2\pi^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2)$$

The density of states for a cubic well also scales as $\sqrt{E}$ in 3D. Thus, the density of states is similar for both spherical and cubic systems, as long as they are both 3D.

5. Does the Exact Shape Matter?

The exact shape of the system does not significantly affect the density of states in the limit of large systems (large R or L). The density of states is primarily determined by the dimensionality of the system (e.g., 3D for both spherical and cubic wells). However, for small systems or specific energy ranges, the shape can influence the level spacing and degeneracies of the states.
