3.1 Confinement in 1D

Consider free electrons confined in a one-dimensional potential well that extends from $x = 0$ to $x = L$.

a) Fixed boundary conditions:
Consider the case of confinement in an infinite potential well:

$V(x) = 0$ for
for $x \leq 0,\ x \geq L$

The general form of the solutions to the stationary Schrödinger equation for one electron is of the type:

$$\psi(x) = Ae^{ikx} + Be^{-ikx}$$

By imposing the boundary conditions, show that the wave functions that are solutions to the Schrödinger equation

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

are stationary waves.
Find the expression for the wave vectors, wave functions, and energies associated with them.
Graphically represent the energy of the electrons as a function of the wave number k.

b) Periodic boundary conditions:
Now consider the case of periodic boundary conditions:

$$\psi(x) = \psi(x + L)$$

In this case, the solutions to the Schrödinger equation are of the type (forward or backward waves):

$$\psi(x) = Ae^{ikx}$$

By imposing the periodic boundary conditions, find the expression for the wave vectors, wave functions, and energies associated with them.
Graphically represent the energy of electrons as a function of wave number.

c) Compare the results obtained.

3.1 Confinement in 1D - Solution

a) Fixed boundary conditions

By imposing boundary conditions, we obtain a condition on the coefficients and a condition on the values allowed for the wave number k:

$$\psi(0) = A + B = 0 \quad \Rightarrow \quad B = -A$$

$$\psi(L) = A\left(e^{ikL} - e^{-ikL}\right) = 0$$

$$A2i\sin(kL) = 0 \quad \Rightarrow \quad k_n = \frac{\pi}{L}n, \quad n \in \mathbb{N}, > 0$$

Wavefunctions:

$$\psi_n(x) = A\left(e^{ik_nx} - e^{-ik_nx}\right) = A\,2i\sin(k_nx) = A'\sin(k_nx)$$

Normalization:

$$1 = \int_0^L \psi^*(x)\psi(x)dx = |A'|^2\int_0^L \sin^2(k_nx)\,dx = |A'|^2\,\frac{L}{2}$$

$$\psi_n(x) = \sqrt{\frac{2}{L}}\sin(k_nx)$$

Energies:

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

b) Periodic boundary conditions:

Using the Ansatz for the wavefunction, we find

$$Ae^{ikx} = Ae^{ik(x+L)}$$

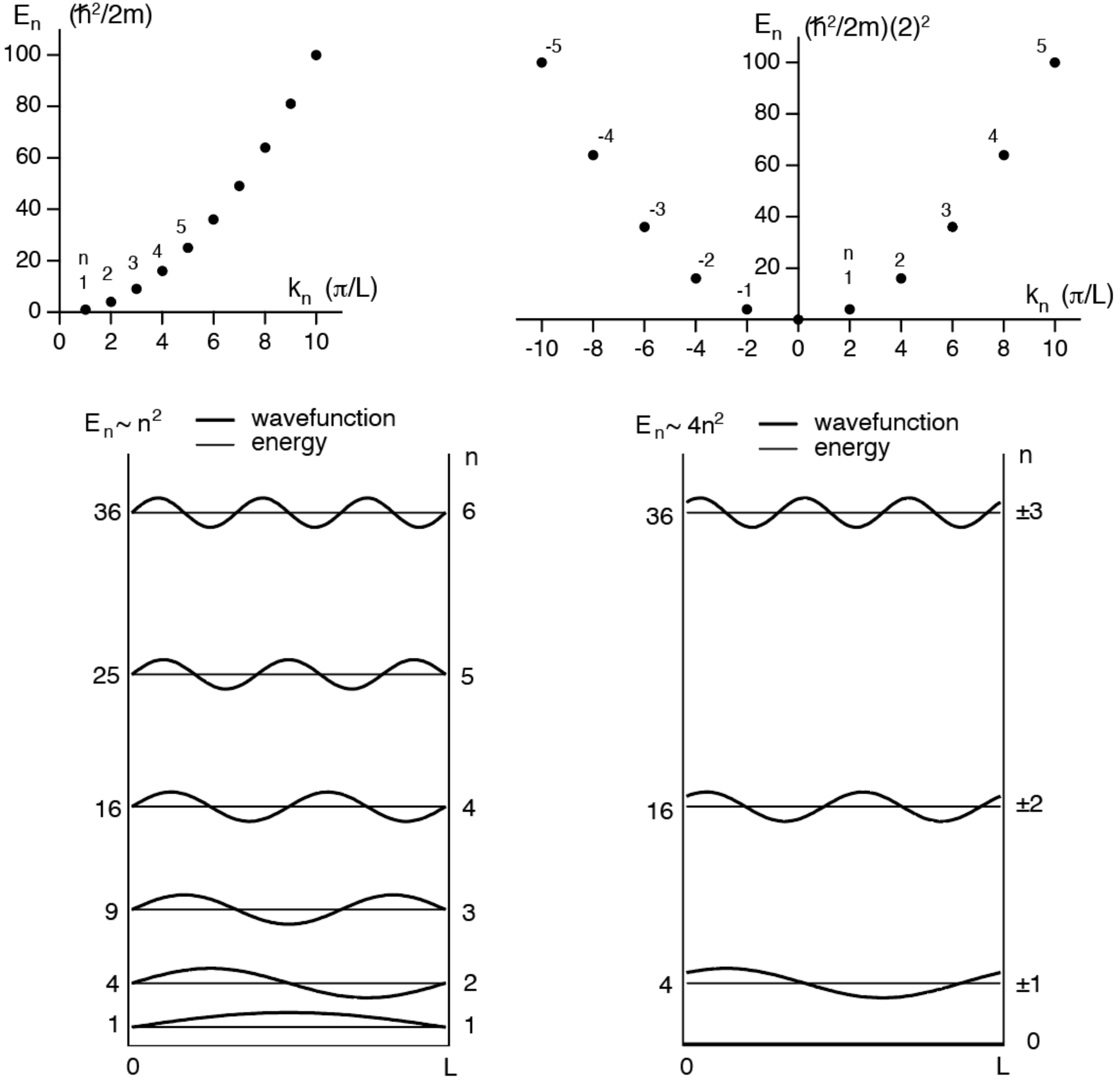
Wavefunctions and normalization

$$\psi_n(x) = \sqrt{\frac{1}{L}}e^{ik_nx}$$

Energies:

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

3.1 Confinement in 1D - Solution



c) Comparison

Allowed wave vectors:
in (a) positive multiples of π/L
in (b) positive and negative multiples of $2\pi/L$ and zero

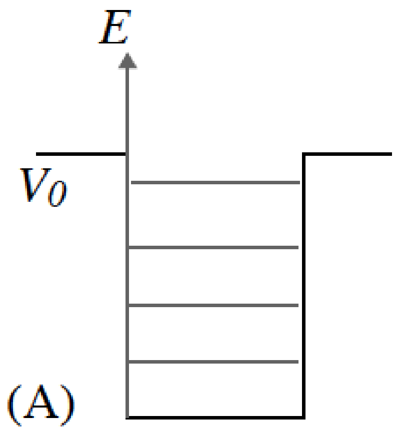
Energy level spacing:
in (a) the difference in energy between states is smaller than in (b)

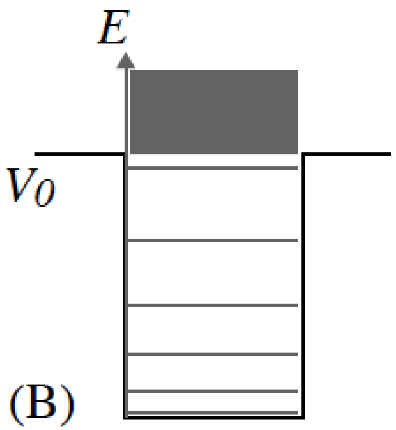
Energy level degeneracy:
in (a) the levels are not degenerate (each k_n corresponds to a different energy E_n);
in (b) the levels are doubly degenerate (except for $n = 0$)

3.2 1D-finite potential well

Which of these diagrams represents the energy levels of an electron in a 1D **finite** potential well? Explain.

Qualitatively, what do you expect as effects of a finite potential (instead of infinite) on the energy levels?


(A)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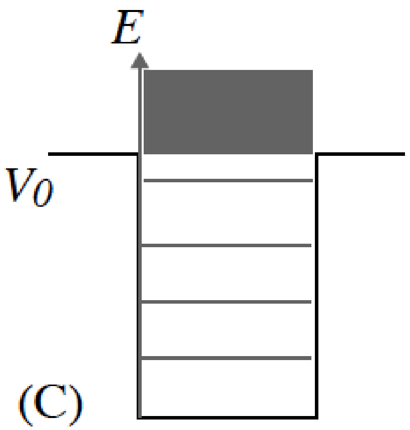
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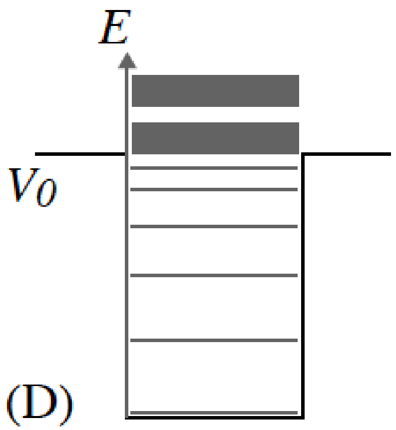
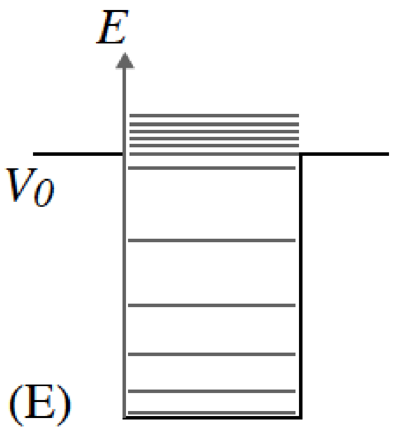
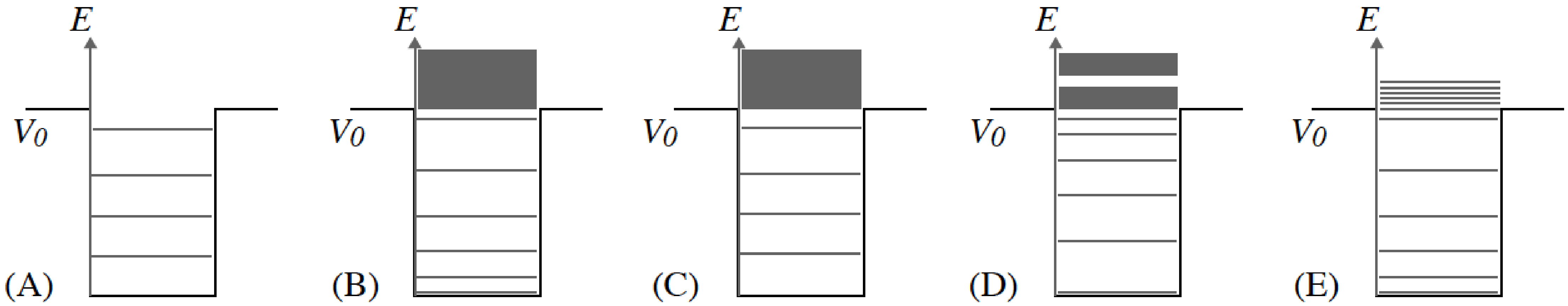

(D)


(E)

3.2 1D-finite potential well - Solution

This is scheme B. It is the only one in which the energy levels have an n^2-type dependence (the levels spread apart as the energy increases), and for which, for $E > V_0$, we have a continuum of energies.

In a finite well, there is a finite number of confined states and a continuum of states for energies higher than V_0.
The wavefunctions are not strictly confined, meaning that they leak out (tunneling). Qualitatively this corresponds to a larger well, i.e., the energies are lower. The dependence on n^2 is not perfectly respected (the higher the energy of the state, the lower the barrier seen by the electron, the higher the tunneling). This can be represented as a well becoming larger for higher states.



3.3 Density of states

In the lecture we have shown that the density of states for a 3D bulk material has the following dependence on energy: $D_{\mathrm{3D}}(E) \propto \sqrt{E}$

Find the complete expression knowing that the volume of the solid is $L^3 = V$, and considering that each state can accommodate two electrons (spin degeneracy)

$$D_{\mathrm{3D}}(E) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$$

Consider now a strictly 2D system. The density of states is constant: $D_{\mathrm{2D}}(E) \propto \ const.$

Find the complete expression knowing that the "volume" = area of the 2D-solid is $L^2 = \mathrm{A}$, and considering that each state can accommodate two electrons (spin degeneracy)

$$D_{\mathrm{2D}}(E) = \frac{A}{\pi}\frac{m}{\hbar^2}$$

Finally, consider a strictly 1D system. Its density of states is $D_{\mathrm{1D}}(E) \propto 1/\sqrt{E}$.

Find the complete expression knowing that the "volume" = length of the 1D-solid is L, and considering that each state can accommodate two electrons (spin degeneracy)

$$D_{\mathrm{1D}}(E) = \frac{L}{\pi}\left(\frac{2m}{\hbar^2}\right)^{1/2} E^{-1/2}$$

3.3 Density of states - Solution

$$D(E) = \frac{dN}{dE} = \frac{dN}{dk}\frac{dk}{dE}$$

$\frac{dk}{dE}$ is the same for all dimensions: $E = \frac{\hbar^2 k^2}{2m} \rightarrow \frac{dE}{dk} = \frac{\hbar^2 k}{m} \rightarrow \frac{dk}{dE} = \frac{m}{\hbar^2 k}$ $\qquad k = \frac{\sqrt{2mE}}{\hbar}$

$\frac{dN}{dk}$ depends on the dimensionality. We need to consider the number of states dN between k and $k + dk$.

For the 3D case: volume of the spherical shell of thickness dk divided by the volume associated to each wavevector:

$$dN = 4\pi k^2 dk \cdot \frac{V}{(2\pi)^3}$$

For the 2D case: $dN = 2\pi k\, dk \cdot \frac{A}{(2\pi)^2}$

For the 1D case: $dN = dk \cdot \frac{L}{2\pi}$

Multiplying the two terms and replacing k with E where needed, one find the desired expressions.

3.4 Quantum dot shape

The zero-point energy of a cubic QD of lateral size d is lower than the one of a spherical QD of diameter d.

Can you explain qualitatively why?

3.4 Quantum dot shape

The zero-point energy of a cubic QD of lateral size d is lower than the one of a spherical QD of diameter d.

It’s because the sphere has a smaller volume $V = (\pi/6)d^3$ than the cube $V = d^3$.

3.5 Degeneracy of states in quantum dots

Write the wave functions for two electrons having the same energy but different quantum numbers and different spatial distribution for the electrons, in a quantum dot (a cube with side L).

Hints:
remember that variables can be separated
just give the dependence on k_x, k_y, k_z (no need to find the normalization)

3.5 Degeneracy of states in quantum dots - Solution

Wave function

$$\Psi(x,y,z) = \psi(x)\psi(y)\psi(z) \sim \sin(xk_{n_x})\sin\left(yk_{n_y}\right)\sin(zk_{n_z})$$

The allowed values for $k_{n_i} = n_i \frac{\pi}{L}$ with $n_i \in \mathbb{N}, > 0$

The energy levels are of the form

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

For example:

$n_x = 1, n_y = 1, n_z = 2$

and

$n_x = 1, n_y = 2, n_z = 1$

are two sets of quantum numbers that correspond to different wave functions

$$\Psi(x,y,z) \sim \sin\left(x\frac{\pi}{a}\right)\sin\left(y\frac{\pi}{a}\right)\sin\left(z\frac{2\pi}{a}\right)$$

$$\Psi(x,y,z) \sim \sin\left(x\frac{\pi}{a}\right)\sin\left(y\frac{2\pi}{a}\right)\sin\left(z\frac{\pi}{a}\right)$$

but have the same energy $E_{1,1,2} = E_{1,2,1} = 6\frac{\hbar^2\pi^2}{2mL^2}$

3.6 CdSe quantum dots

Estimate the number of atoms contained in CdSe spherical QDs of diameter

- $d = 4.5$ nm
- $d = 3.4$ nm
- $d = 1.5$ nm

knowing that the volume of a unit cell in the CdSe wurtzite structure is $V_{cell} = 0.11$ nm^3 and that there are 4 atoms per unit cell.

3.6 CdSe quantum dots - Solution

- $d = 4.5$ nm

$V = \frac{4}{3}\pi\frac{d^3}{8} = 47.7$ nm^3

Number of atoms = $\frac{V}{V_{cell}}4 = 1735$

- $d = 3.4$ nm

$V = \frac{4}{3}\pi\frac{d^3}{8} = 20.6$ nm^3

Number of atoms = $\frac{V}{V_{cell}}4 = 748$

- $d = 1.5$ nm

$V = \frac{4}{3}\pi\frac{d^3}{8} = 1.77$ nm^3

Number of atoms = $\frac{V}{V_{cell}}4 = 64$