ECE 536 – Integrated Optics and Optoelectronics
Lecture 5 – February 1, 2022

Spring 2022

Tu-Th 11:00am-12:20pm

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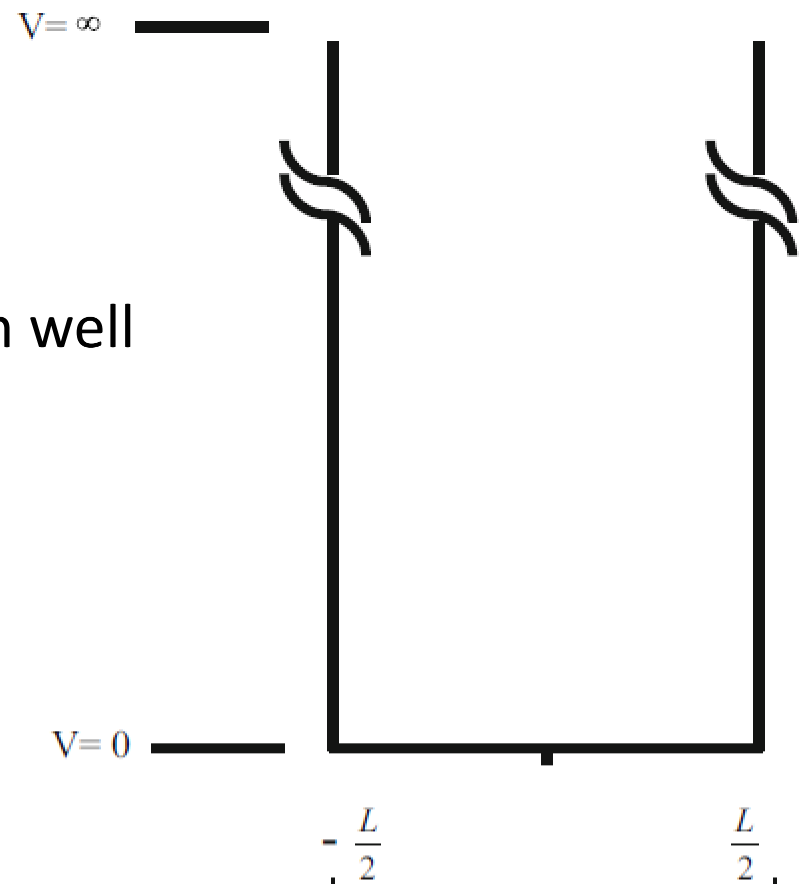
Lecture 5 Outline

- Some more quantum mechanics refresher
- Density of States in different dimensionalities
- Perturbation theory in quantum mechanical applications
- Time-independent Perturbation
- Time-dependent perturbation and Fermi Golden rule

Quantum wells are very important in optoelectronics

Infinite quantum well



Region I

$x \leq -\frac{L}{2}$

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

Region II

$-\frac{L}{2} \leq x \leq \frac{L}{2}$

$\Psi(x) = Ce^{ikx} + De^{-ikx}$

Region III

$x \geq \frac{L}{2}$

$\Psi(x) = Fe^{ikx} + Ge^{-ikx}$

Infinite quantum well – The solution in each region has the form of two counter-propagating plane waves

$$\Psi(x) = Ae^{ikx} + Be^{-ikx}, \quad \text{where} \quad k = \sqrt{\frac{2m^*}{\hbar^2}(E - V)}$$

The constants A and B are determined by applications of boundary conditions. In Region 1 and 3, *k* is purely imaginary (evanescent wave) and there is only a forward wave in region 3 and a backward wave in region 1. However, because the potential is infinite, there is no wave penetration and the wave function must be zero at the boundaries of the well.

Solution:

$$k = \frac{n\pi}{L} \qquad E_n = \frac{n^2\pi^2\hbar^2}{2L^2m^*}$$

Combination of the two waves give a cosine standing wave for odd integer and a sine standing wave for even integer

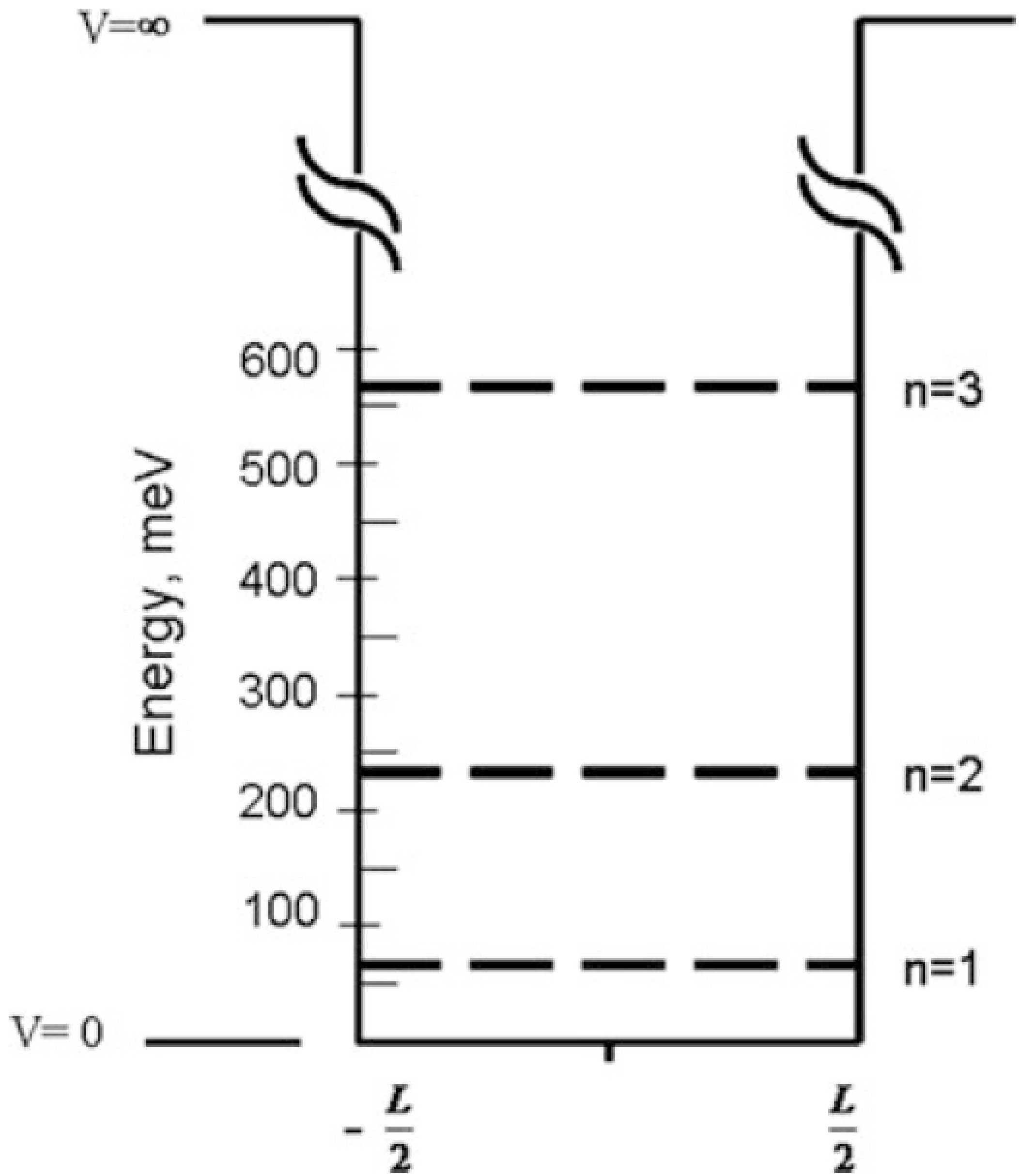
$$\Psi(x) = C\cos\left(\tfrac{\pi}{L}x\right) \qquad \int_{-\frac{L}{2}}^{\frac{L}{2}} C^2\cos^2\left(\frac{\pi}{L}x\right)dx = 1, \quad C = \sqrt{\frac{2}{L}}$$

$$\Psi(x) = \begin{cases} \sqrt{\frac{2}{L}}\cos\left(\frac{n\pi}{L}x\right), & \mathrm{n} = 1, 3, 5, \ldots \\ \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right), & \mathrm{n} = 2, 4, 6, \ldots \end{cases}$$

Example

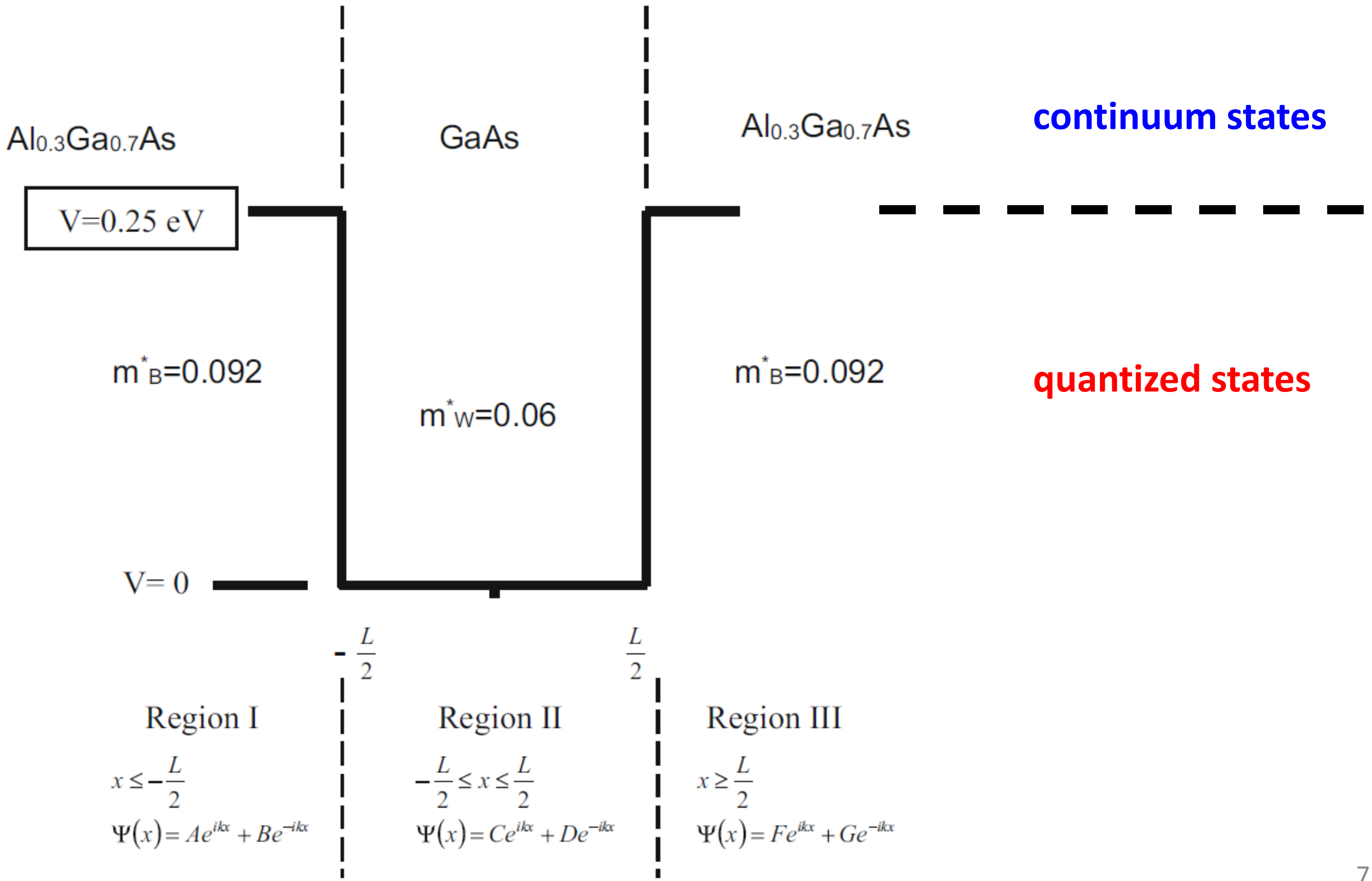
$L = 10$ nm

$m = 0.066\, m_o$



Finite square well

$$-\frac{\hbar^2}{2m^*}\frac{d^2}{dx^2}\Psi(x)+V(x)\Psi(x)=E_n\Psi(x)\qquad V(x)=\begin{cases}V_0, & \text{for} \quad |x|\le \frac{L}{2}\\ 0, & \text{for} \quad |x|>\frac{L}{2}\end{cases}$$



Boundary conditions

(i) continuity of the wavefunction across the boundary.
(ii) continuity of the electric current across the boundary.

Current carried by one electron

$$I = -qv = -q\frac{m^*v}{m^*} = -q\frac{\hbar k}{m^*} = iq\frac{\hbar}{m^*}\frac{d}{dx}\Psi(x)$$

Trick: Substitute crystal momentum with quantum-mechanical momentum operator

Boundary condition conserving electric current

$$\frac{1}{m_W^*}\frac{d}{dx}\Psi_{regionII}(x)_{x=\frac{L}{2}} = \frac{1}{m_B^*}\frac{d}{dx}\Psi_{regionIII}(x)_{x=\frac{L}{2}}$$

Application of Boundary conditions

$$\boxed{x = \frac{L}{2}}$$

$$Ce^{ik\frac{L}{2}} + De^{-ik\frac{L}{2}} = Fe^{-\kappa\frac{L}{2}}$$

$$\frac{ik}{m_W^*}\left(Ce^{ik\frac{L}{2}} - De^{-ik\frac{L}{2}}\right) = -\frac{\kappa}{m_B^*}Fe^{-\kappa\frac{L}{2}}.$$

$$\frac{ik}{m_W^*}\left(Ce^{ikL} - D\right) = -\frac{\kappa}{m_B^*}\left(Ce^{ikL} + D\right)$$

$$Ce^{ikL}\left(\kappa m_W^* + ikm_B^*\right) + D\left(\kappa m_W^* - ikm_B^*\right) = 0$$

$$\boxed{x = -\frac{L}{2}}$$

Using the same procedure

$$Ce^{-ikL}\left(\kappa m_W^* - ikm_B^*\right) + D\left(\kappa m_W^* + ikm_B^*\right) = 0$$

$$Ce^{ikL}\left(\kappa m_W^* + ikm_B^*\right) + D\left(\kappa m_W^* - ikm_B^*\right) = 0$$

$$Ce^{-ikL}\left(\kappa m_W^* - ikm_B^*\right) + D\left(\kappa m_W^* + ikm_B^*\right) = 0$$

Solution exists if the determinant of coefficients is zero

$$2i\left(\kappa m_W^*\right)^2 \sin(kL) + 4ikm_B^*\kappa m_W^* \cos(kL) - 2i\left(km_B^*\right)^2 \sin(kL) = 0$$

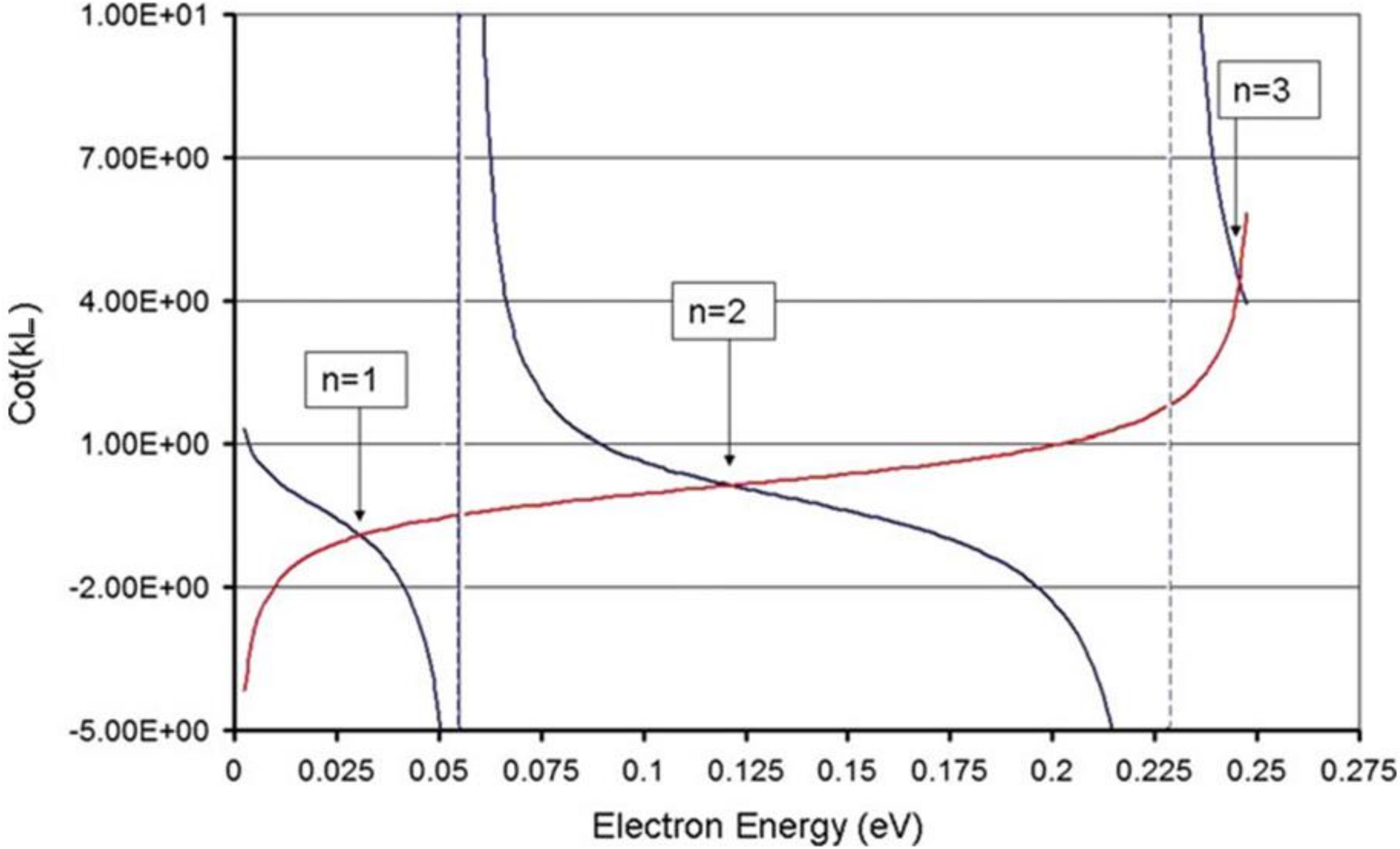
$$\downarrow$$

$$\cot(kL) = \frac{\left(km_B^*\right)^2 - \left(\kappa m_W^*\right)^2}{2km_B^*\kappa m_W^*}$$

$$k = \frac{\sqrt{2m_W^* E}}{\hbar}$$

$$\kappa = \frac{\sqrt{2m_B^*\left(V_0 - E\right)}}{\hbar}$$

The equation gives the energy of the quantized states in the well. It can be solved by numerical iteration to a desired accuracy. It can also be solved graphically.



$L = 10$ nm

$\cot(kL)$

$$\frac{\left(km_B^*\right)^2 - \left(\kappa m_W^*\right)^2}{2km_B^*\kappa m_W^*}$$

Comparison between wells

$L = 10$ nm

	V_0	m^*_B	m^*_W	E_1 (eV)	E_2(eV)	E_3 (eV)
Infinite well	∞	–	0.066	0.056	0.223	0.502
Finite well	0.25 eV	0.092	0.066	0.03	0.121	0.245

In many practical situations relevant for optoelectronics, quantum wells have only several energy levels.

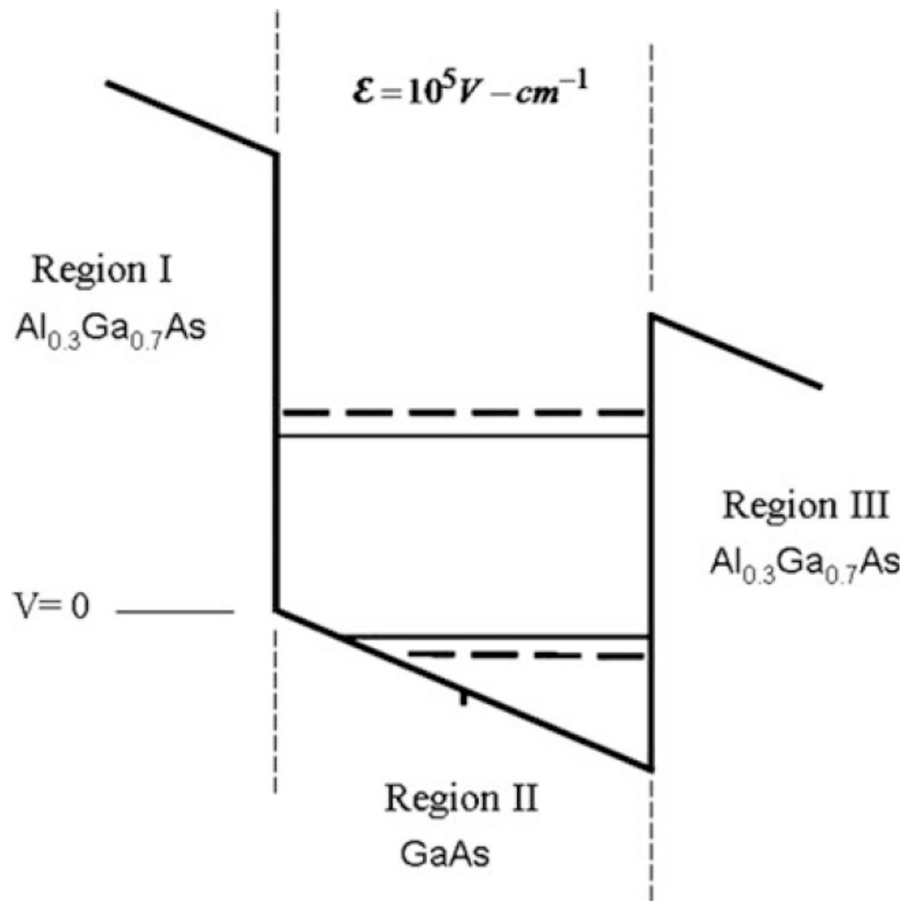
In realistic conditions, there is a field across quantum well, due to applied potentials, differences in electron affinity between the heterostructure materials which define the well, and to the charge distribution associated with the wave functions and with ionized impurities, as well.

The time-independent Schrödinger equation should be solved simultaneously with the Poisson equation for a self-consistent solution.

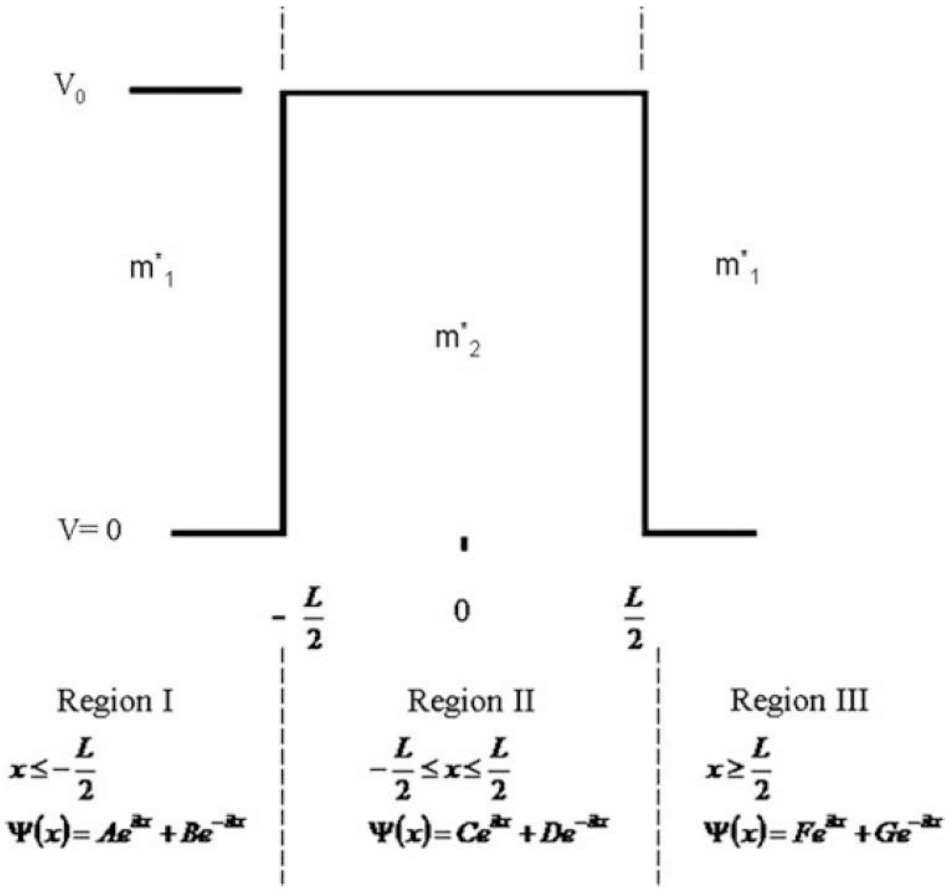
In addition, there may be onset of quantum Stark effect which tends to separate energy levels in confined spaces when an electric field is applied. The energy shift can be calculated by perturbation theory.

Example: Voltage drop of 0.1 V across the 10 nm well examined earlier, cause an electric field of 10^5 V cm^{-1} .

The estimate for shift in energy caused by Stark effect is about 2 meV.



Tunneling



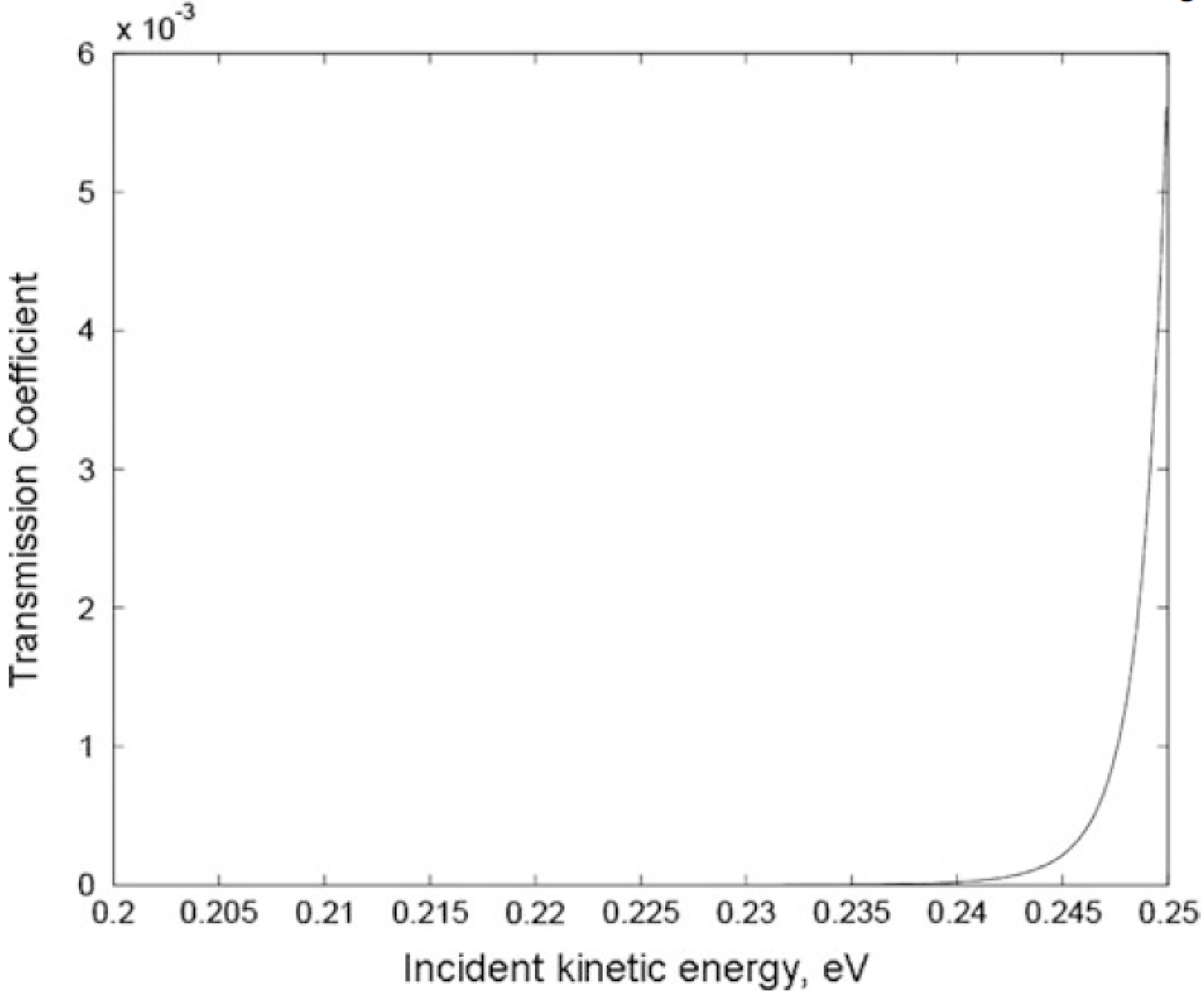
Transmission coefficient – analytical result for rectangular well

$$T = \frac{1}{\cosh^2(\kappa L) + \left(\frac{1}{4}\right)\left(\frac{\kappa m_1^*}{k m_2^*} - \frac{k m_2^*}{\kappa m_1^*}\right)^2 \sinh^2(\kappa L)}$$

Tunneling

Case I $m_1^* = m_2^* = 9 \times 10^{-31}$ kg

the barrier width is 10 nm and the barrier height is 0.25 eV



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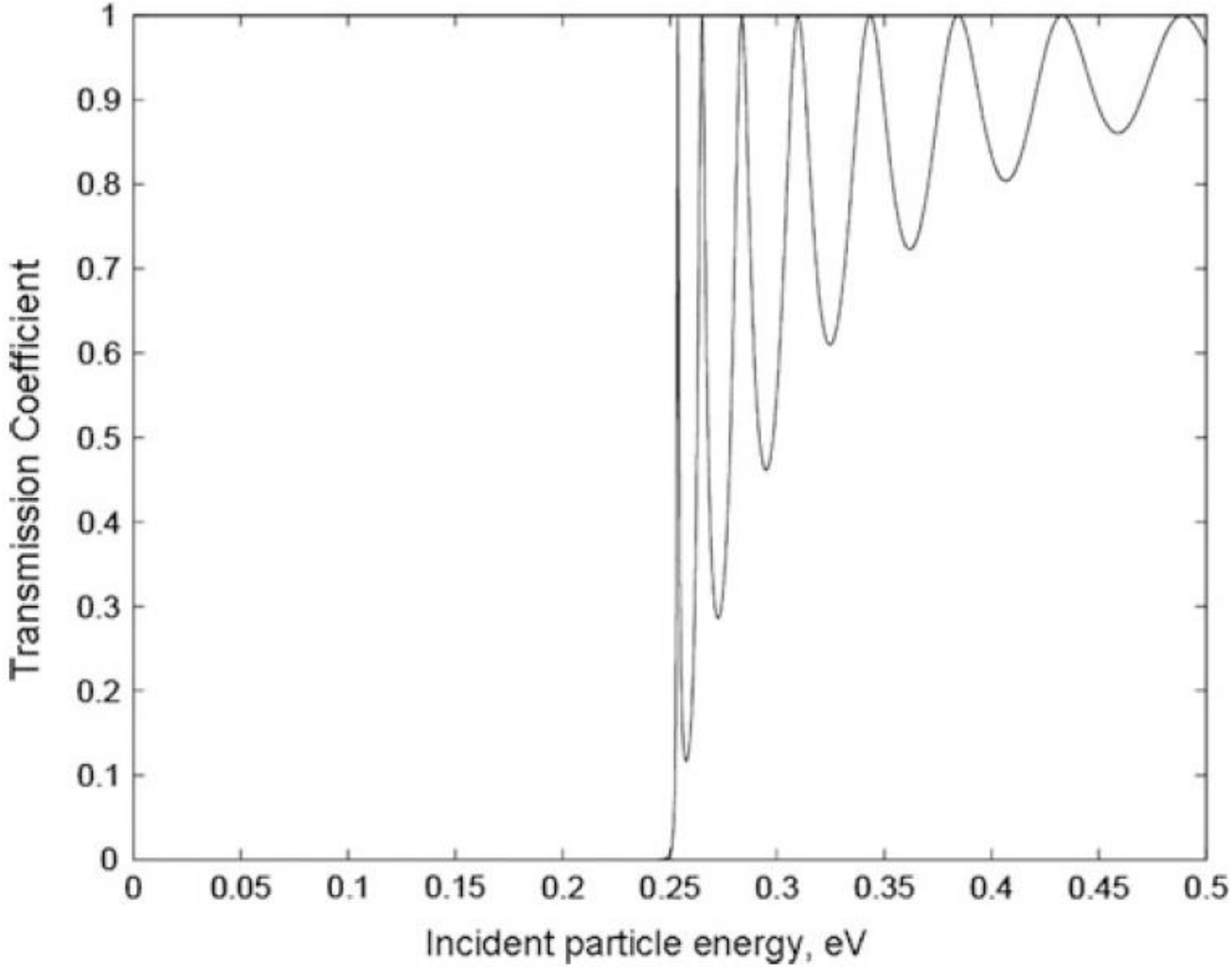
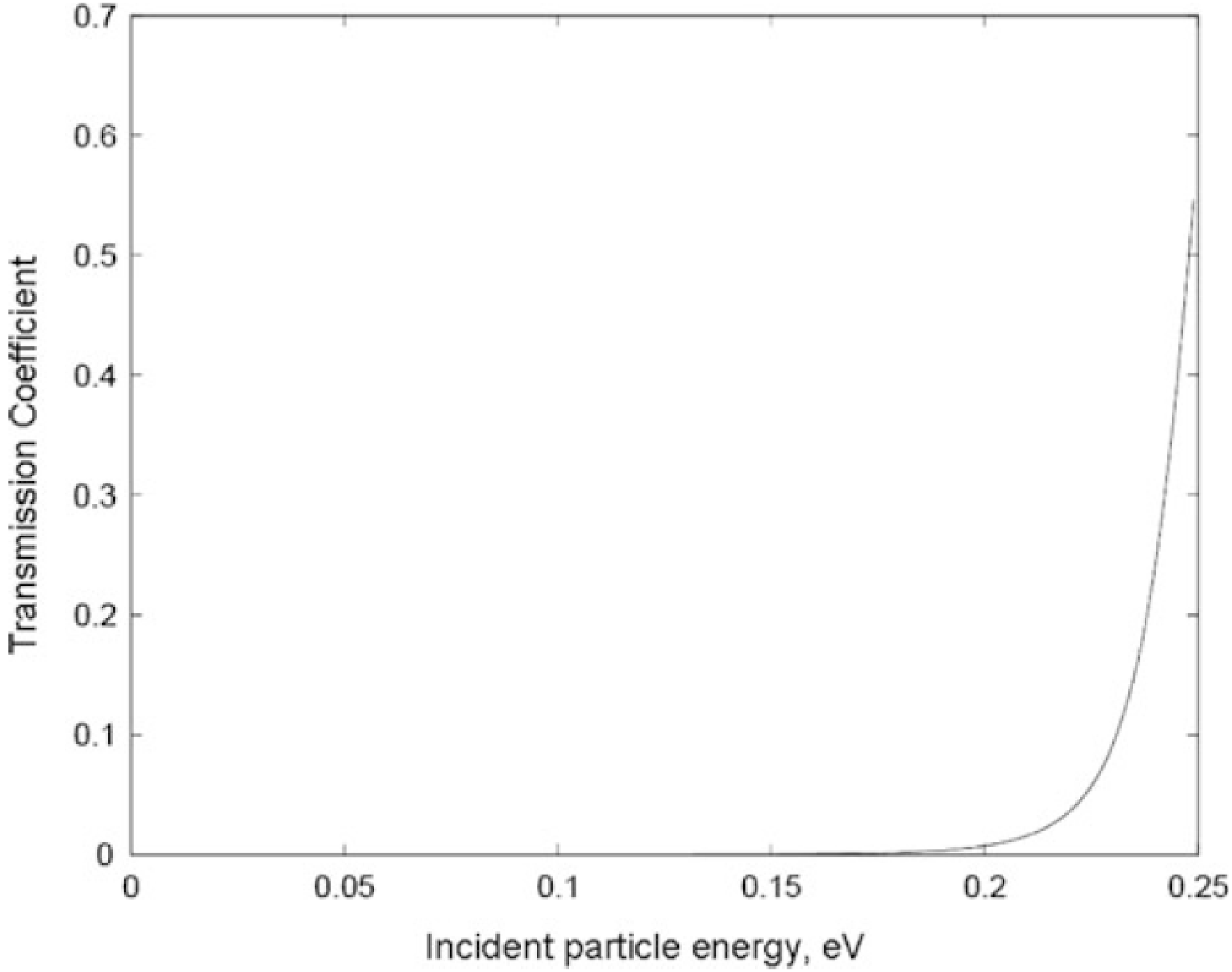


Tunneling

Case II $m_1^* \neq m_2^*$ $m_1^* = 9 \times 10^{-31}$ kg. $m_2^* = 0.066 m_1^*$.

the barrier width is 10 nm and the barrier height is 0.25 eV



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Case II $m_1^* \neq m_2^*$ $m_1^* = 9 \times 10^{-31}$ kg. $m_2^* = 0.066 m_1^*$.

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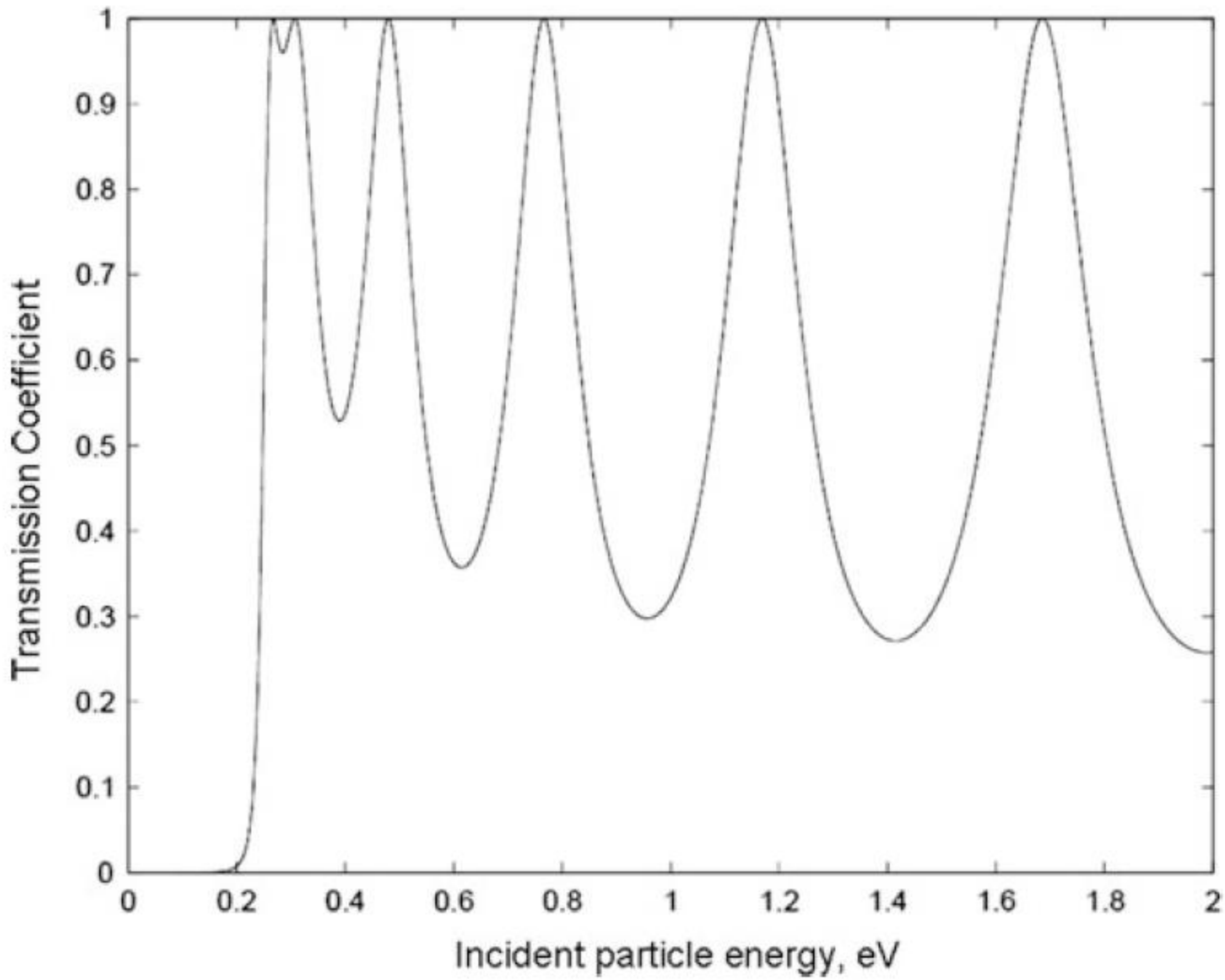
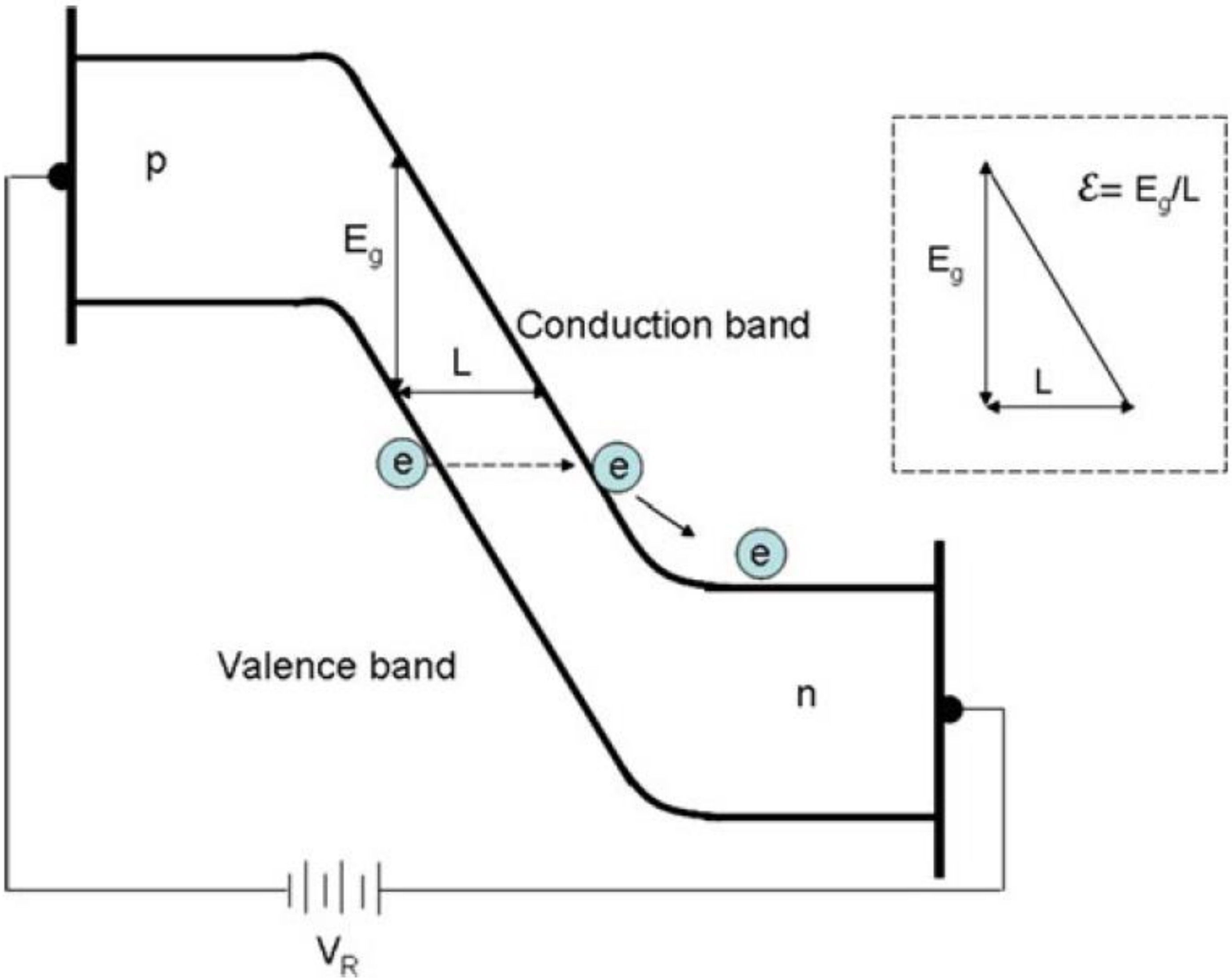


Tunneling in reverse biased p-n junctions



Simple model for tunneling current (GaAs)

tunneling current $$J_{Tunn} = nqv_{sat}$$

$$n = N_V T$$

$$v_{sat} = 1.2 \times 10^7 \text{ cm s}^{-1}$$

$$N_V = 4 \text{ valence electrons/atom} \times 8 \text{ atoms/unit-cell/unit-cell volume}$$
$$= 1.7 \times 10^{23} \text{ cm}^{-3}$$

transmission coefficient

$$T = \frac{1}{\cosh^2(\kappa L) + \left(\frac{1}{4}\right)\left(\frac{\kappa m_1^*}{k m_2^*} - \frac{k m_2^*}{\kappa m_1^*}\right)^2 \sinh^2(\kappa L)}$$

(Approximation: this is for a rectangular well. Well is actually triangular)

Simple model (GaAs)

electrons at the valence band edge have thermal energy

$$E = \frac{3}{2} k_B \overline{T} = \frac{\hbar^2 k^2}{2m^*}$$

where $\overline{T}$ is the temperature

barrier height $V_0 = E_g = 1.43 \text{ eV}$

approximate average wave vector in the forbidden gap

$$\kappa = \frac{1}{\hbar}\sqrt{2m^*\left(E_g - k_B\overline{T}\right)} \quad \text{and} \quad |\kappa| = 1.4 \times 10^9 \text{ m}^{-1} \gg |k|$$

width of the barrier

$$\mathcal{E} = \frac{E_g/q}{L} = \sqrt{\frac{2qN_D V}{\varepsilon\varepsilon_0}}, \quad \text{where} \quad V = V_{Applied} + \phi_{built-in}$$

(Assume one sided junction with $N_D = 10^{16}$ cm^{-3} and reverse bias V=-1 V)

$$L = \frac{E_G}{\sqrt{\frac{2qN_D V}{\varepsilon\varepsilon_0}}} = 2.7 \times 10^{-7} \text{ m}$$

Note: $\kappa L \gg 1$

Simple model (GaAs)

set effective masses $m_1^* = m_2^* = m^*$

approximate transmission coefficient since $\kappa L \gg 1$

$$T = \frac{1}{\cosh^2(\kappa L) + \left(\frac{1}{4}\right)\left(\frac{\kappa m_1^*}{k m_2^*} - \frac{k m_2^*}{\kappa m_1^*}\right)^2 \sinh^2(\kappa L)} \cong 16 e^{-2\kappa L}\left(\frac{k\kappa}{k^2+\kappa^2}\right)^2 \cong 16\left[\frac{k}{\kappa}\right]^2 e^{-2\kappa L}$$

also

$$\kappa L = \frac{E_G}{\hbar}\sqrt{\frac{2m^* E_G \varepsilon\varepsilon_0}{2qN_D V}} = C_0 V^{-\frac{1}{2}}$$

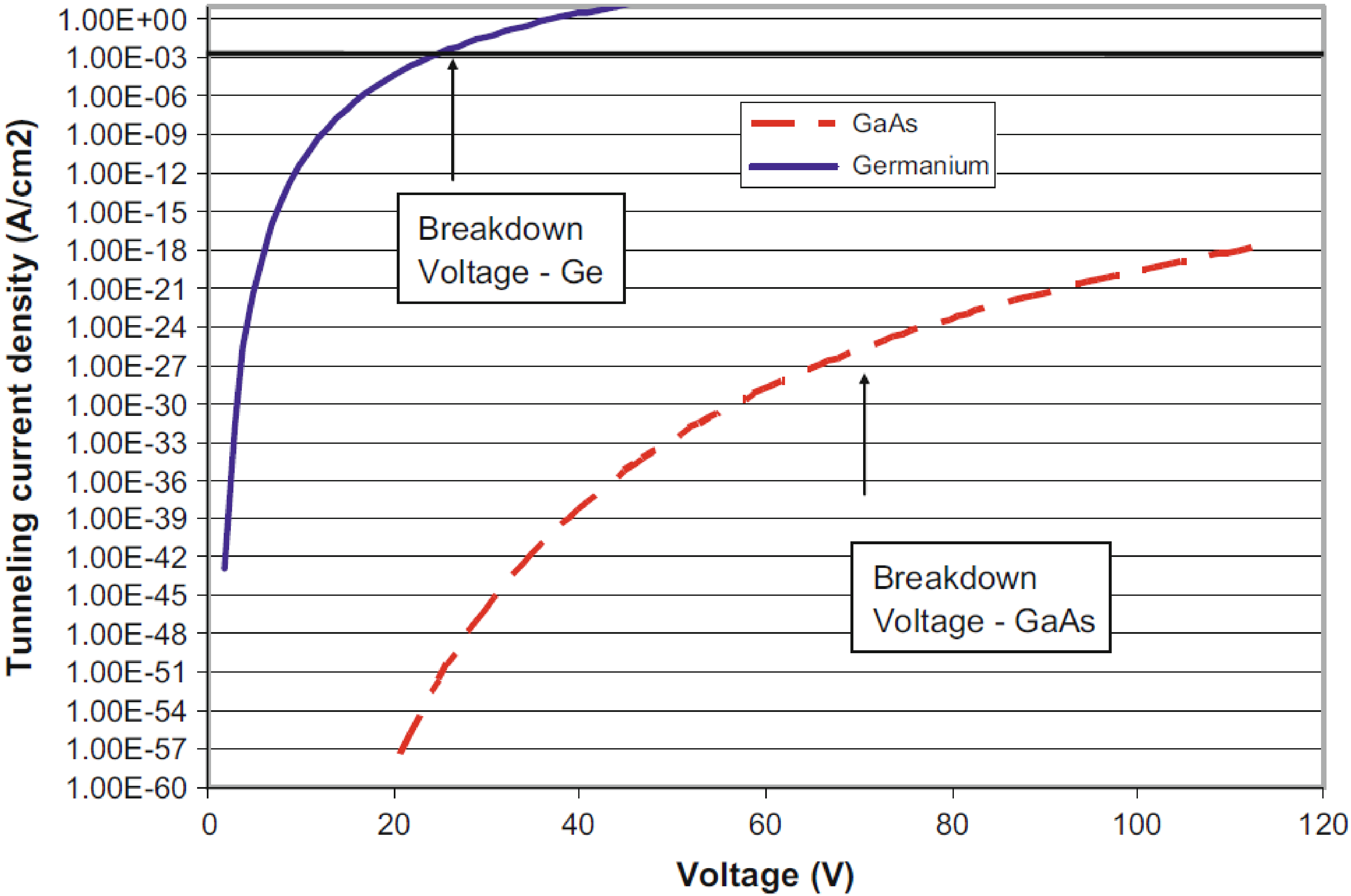
$$\left(\frac{k}{\kappa}\right)^2 \cong \frac{3k_B\overline{T}}{2E_g}, \text{ where } \overline{T} \text{ is the temperature}$$

finally

$$\boxed{T \cong 16\left(\frac{3k_B\overline{T}}{2E_g}\right) e^{-2C_0 V^{-\frac{1}{2}}}}$$

$$\boxed{J_{tunneling} \cong 16 N_V q v_{sat}\left(\frac{3k_B\overline{T}}{2E_g}\right) e^{-2C_0 V^{-\frac{1}{2}}} \text{ amps}-\text{cm}^{-2}}$$

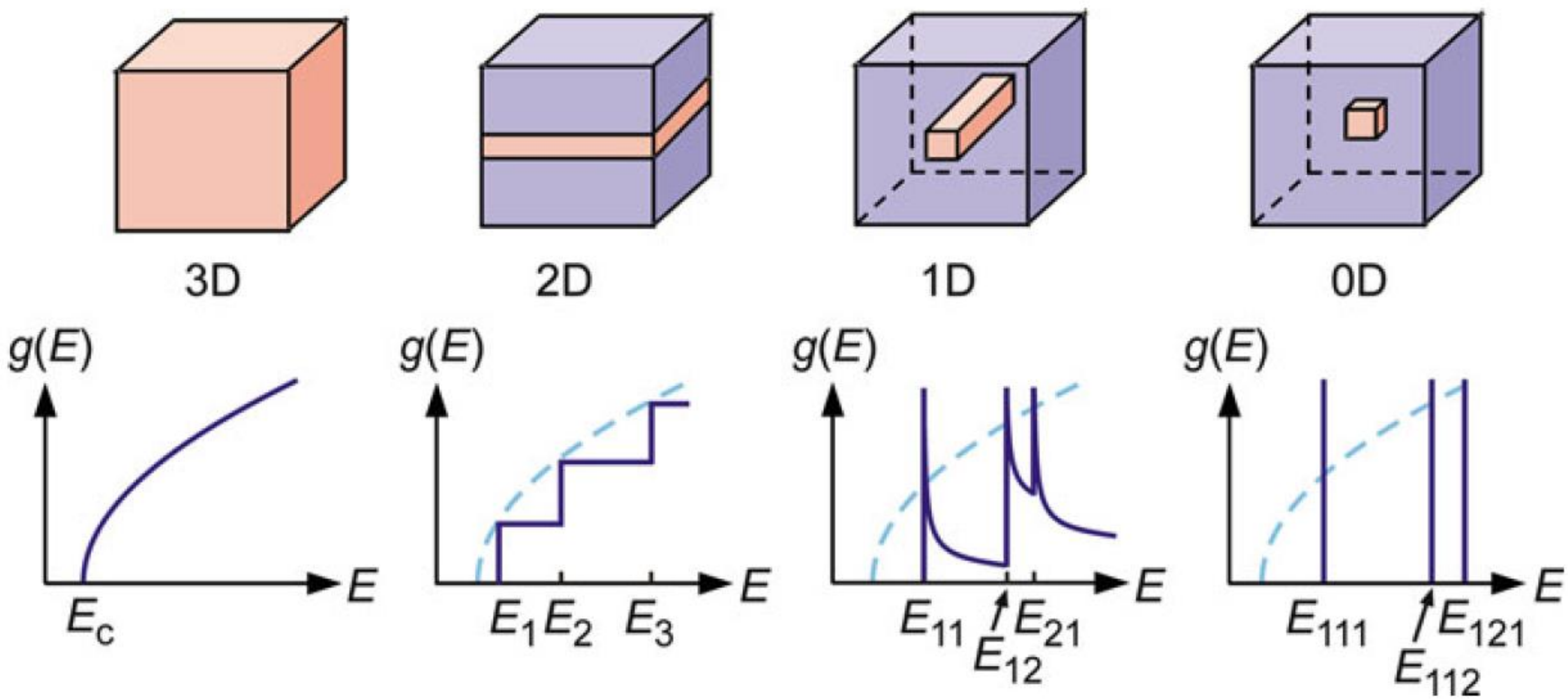
Result from a simple tunneling model



Density of States

$$g(E) \propto (E - E_0)^{d/2-1}$$

$$d = 1,\ 2,\ \text{or}\ 3$$



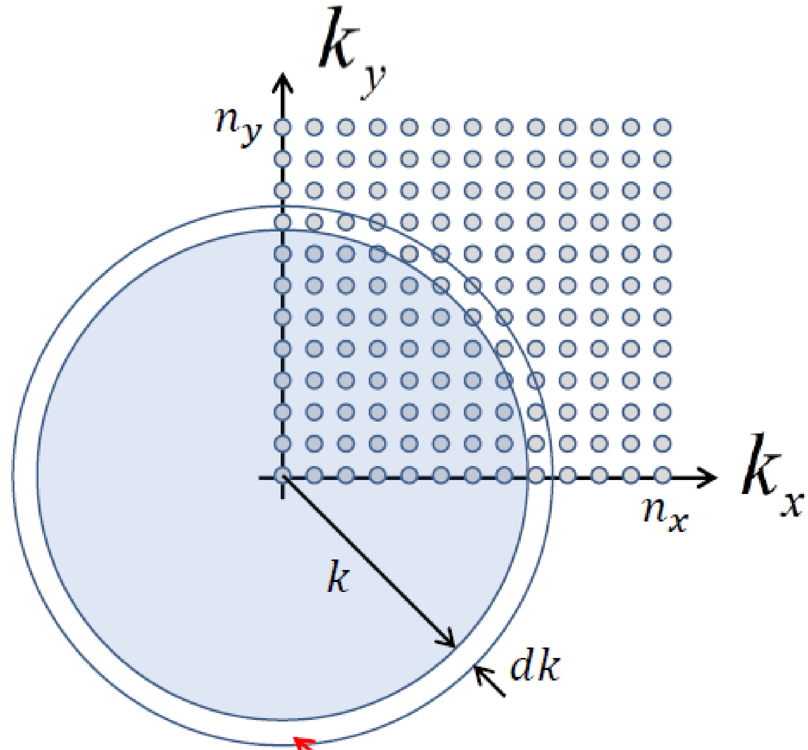
2D Density of States

$$\boxed{g(k)dk = \frac{2\pi k\ dk}{4\pi^2} = \frac{k\ dk}{2\pi}}$$

$$k = \frac{\sqrt{2m^* E}}{\hbar} \qquad dk = \frac{\sqrt{2m^*}}{\hbar}\frac{dE}{2\sqrt{E}}$$

$$\frac{k\ dk}{2\pi} = \frac{1}{2\pi}\frac{\sqrt{2m^* E}}{\hbar}\frac{\sqrt{2m^*}}{\hbar}\frac{dE}{2\sqrt{E}} = \frac{m^*}{2\pi}\frac{dE}{\hbar^2} = g(E)dE$$

$$\Rightarrow \quad g(E) = \underbrace{2}_{\text{spin}} \cdot \frac{m^*}{2\pi}\frac{1}{\hbar^2} = \frac{m^*}{\pi\hbar^2}$$



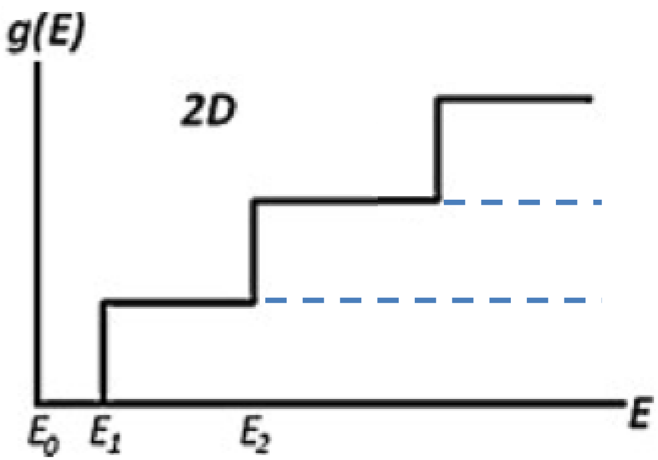
$\boxed{2\pi k\ dk}$

(area of annular region)

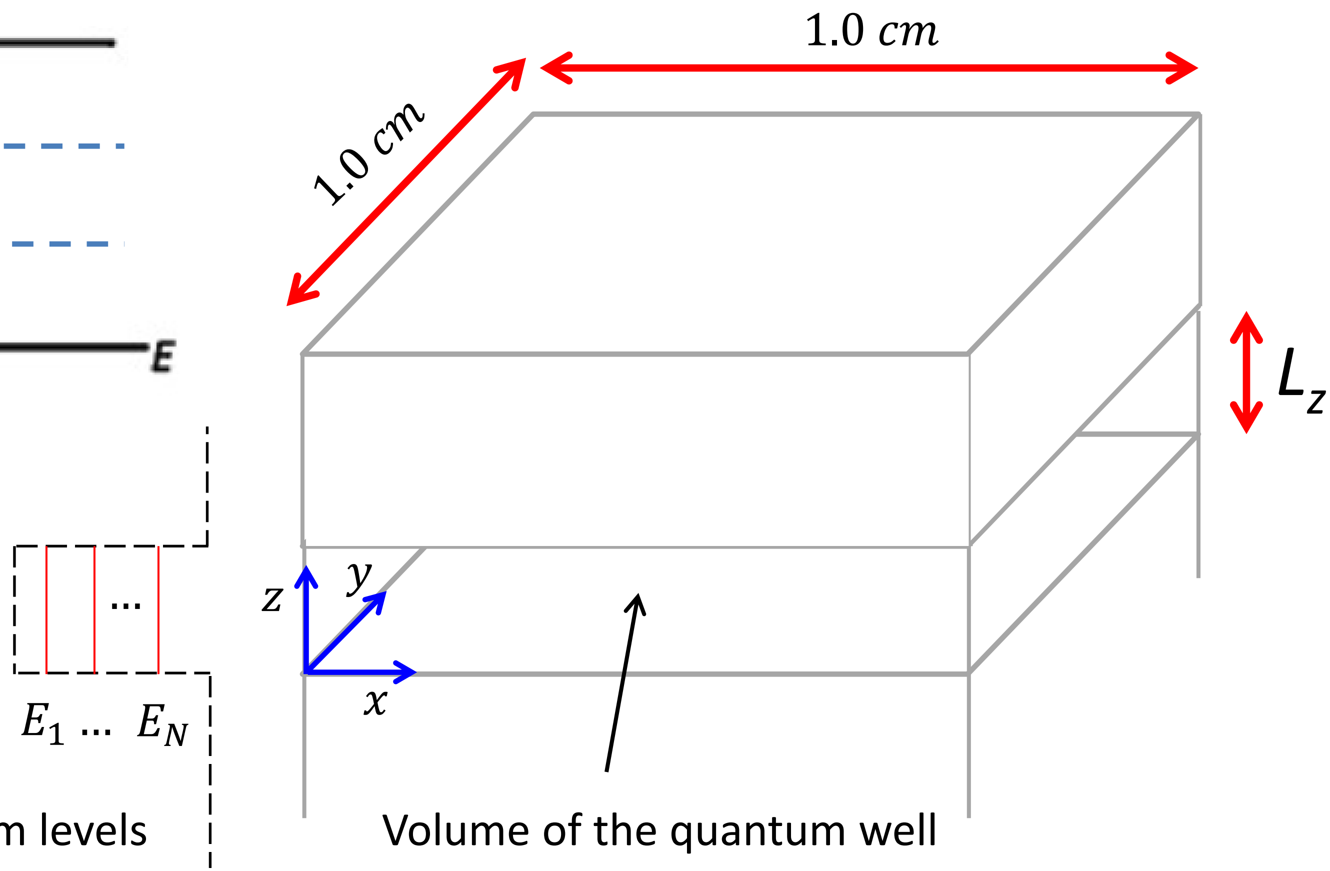
$\boxed{\frac{1}{4\pi^2}}$

(# allowed k-states per unit area)

A perfect 2D electron gas is approximated by a sheet of graphene, for instance. Often a quasi-2D electron gas is realized with a double heterojunction where a material with smaller bandgap is sandwiched between layers with larger bandgap, forming a quantum well of width L_z.



For density calculation



Volume of the quantum well

$$V = 1.0\ cm\ \times 1.0\ cm\ \times L_z$$

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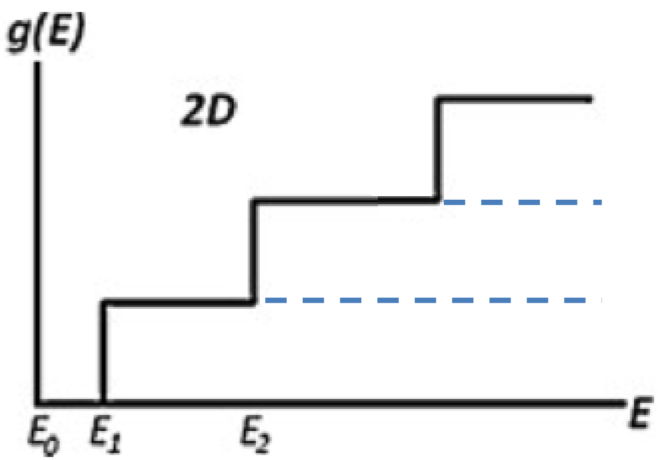
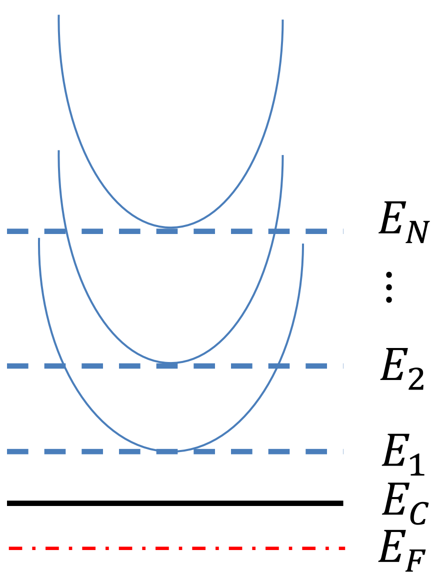


Carrier Density

$$n = \frac{2}{V}\sum_{\vec{k}} f(E) \rightarrow \sum_{m} \frac{2}{V}\sum_{k_x}\sum_{k_y} f(E)$$

separate quantized direction

Assume that each quantum level functions as a "virtual" conduction band level associated with a parabolic band for the transverse momentum (with x and y components)



$$E = E_m + \frac{\hbar^2}{2m_e^*} k_{t,m}^2$$

$$k_{t,m}^2 = \frac{2m_e^*}{\hbar^2}(E - E_m) \quad \text{for} \quad E \geq E_m$$

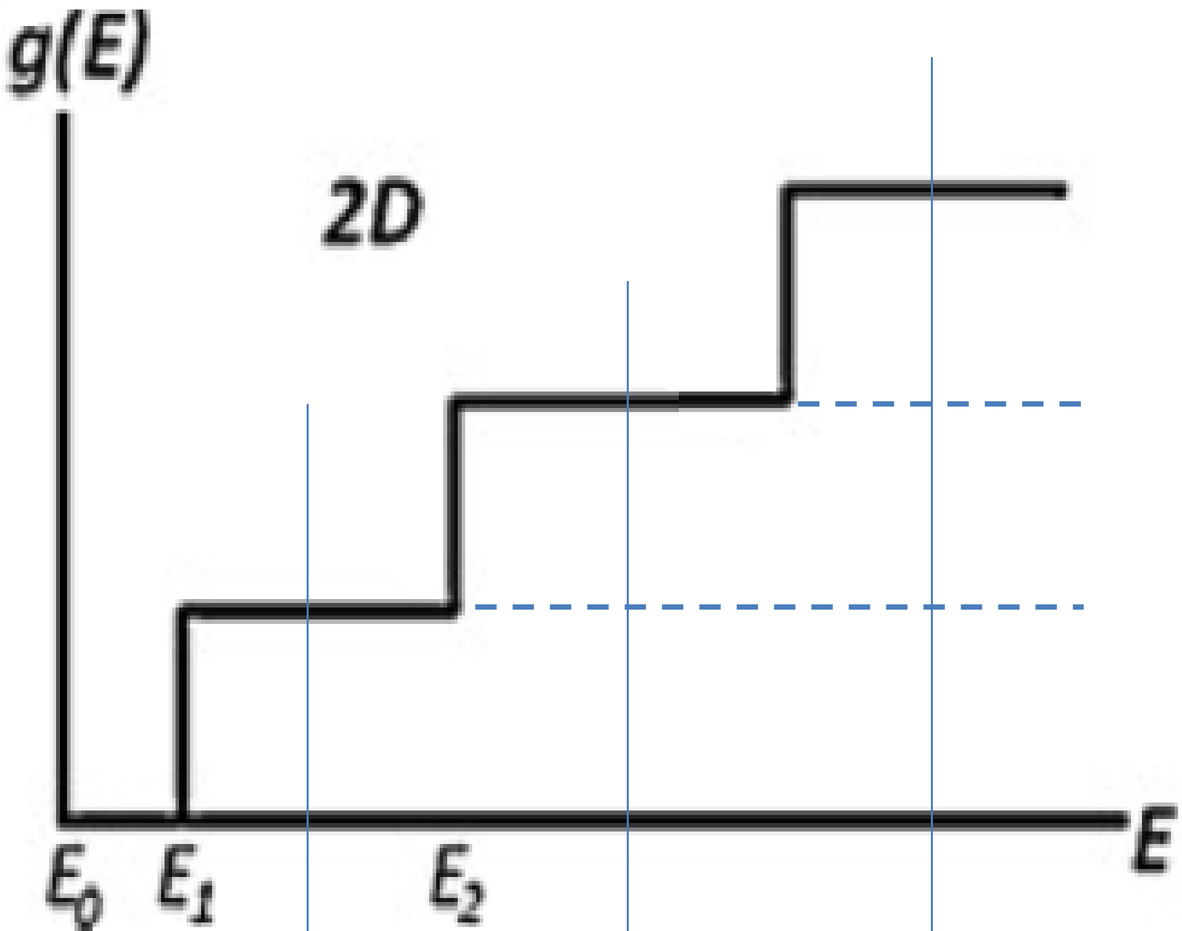
$$n = \sum_{m} \frac{2}{V} \sum_{k_x} \sum_{k_y} f(E) \ \rightarrow \ \sum_{m} \int_0^{\infty} 2 \frac{1}{4\pi^2 L_z} f(E)\, 2\pi k_{t,m}\, dk_{t,m}$$

$$k = \frac{\sqrt{2m^* E}}{\hbar} \qquad dk = \frac{\sqrt{2m^*}}{\hbar} \frac{dE}{2\sqrt{E}}$$

step function

$$\sum_{m} \int_0^{\infty} \frac{1}{\pi L_z} f(E)\, k_{t,m}\, dk_{t,m} = \ \sum_{m} \int_0^{\infty} \frac{m_e^*}{\pi L_z \hbar^2}\ H(E - E_m) f(E) dE$$

$$\int_0^{\infty} \frac{m_e^*}{\pi L_z \hbar^2} \sum_{m} H(E - E_m) \ \ f(E) dE$$



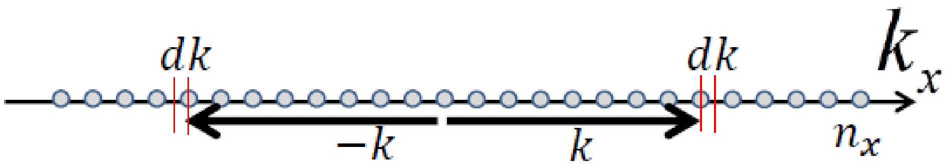
$$D(E) = \frac{m_e^*}{\pi L_z \hbar^2}$$

$$D(E) = \frac{2m_e^*}{\pi L_z \hbar^2}$$

$$D(E) = \frac{3m_e^*}{\pi L_z \hbar^2}$$

$$\cdots D(E) = \frac{n_z m_e^*}{\pi L_z \hbar^2}$$

1D Density of States



$$k = \frac{\sqrt{2m^* E}}{\hbar} \qquad dk = \frac{\sqrt{2m^*}}{\hbar}\frac{dE}{2\sqrt{E}}$$

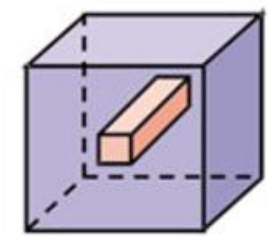
$\boxed{2dk}$

(length of increments *dk*)

$\boxed{\frac{1}{2\pi}}$

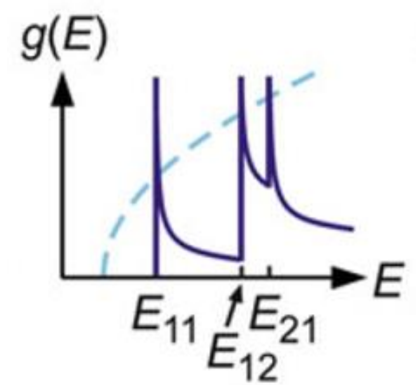
(# allowed k-states per unit length)

$$g(k)dk = \frac{2dk}{2\pi} = \frac{dk}{\pi}$$



1D

$$\frac{2dk}{2\pi} = \frac{1}{\pi}\frac{\sqrt{2m^*}}{\hbar}\frac{dE}{2\sqrt{E}} = g(E)\,dE$$



$$\boxed{g(E) = \underbrace{2}_{\text{spin}} \cdot \frac{1}{\pi}\frac{\sqrt{2m^*}}{\hbar}\frac{1}{2\sqrt{E}} = \frac{\sqrt{2m^*}}{\pi\hbar}\frac{1}{\sqrt{E}}}$$

Perturbation theory

Simple quantum mechanical problems (e.g. rectangular quantum well) can be solved exactly, either analytically or numerically. The majority of problems for general systems, however, cannot be solved exactly.

Perturbation theory is an approach to deal with those cases that can be considered ***small deformations*** of systems we can solve exactly. We are going to consider a Hamiltonian operator (for simplicity eigenvalues are non-degenerate)

$$\underbrace{\boldsymbol{H} = \boldsymbol{H}^{(0)}}_{\text{unperturbed Hamiltonian}} + \underbrace{\lambda}_{\text{small parameter}} \, \underbrace{H'}_{\text{perturbation potential}}$$

Consider the time-independent Schrödinger equation in short-hand form for the Hamiltonian operator $\boldsymbol{H} = \boldsymbol{H}^{(0)} + \lambda\boldsymbol{H}'$

$$\boldsymbol{H}\psi = E\psi$$

We assume that we can solve the equation for $H^{(0)}$ and that we know the corresponding eigenvalues and eigenfunctions.

$$H^{(0)}\varphi_n^{(0)} = E_n^{(0)}\varphi_n^{(0)}$$

Since λ is a small parameter, we can expand those solutions in series.

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \cdots$$
$$\psi = \psi^{(0)} + \lambda\psi^{(1)} + \lambda^2\psi^{(2)} + \cdots$$

After substitution into the Schrödinger equation of H, E and ψ we can define approximations of increasing order.

The Schrödinger equation becomes

$$\left(\boldsymbol{H}^{(0)} + \lambda \boldsymbol{H}'\right)\left(\psi^{(0)} + \lambda\psi^{(1)} + \lambda^2\psi^{(2)} + \cdots\right) =$$

$$= \left(E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \cdots\right)\left(\psi^{(0)} + \lambda\psi^{(1)} + \lambda^2\psi^{(2)} + \cdots\right)$$

$$\left(\boldsymbol{H}^{(0)} + \lambda \boldsymbol{H}'\right)\left[\sum_{q=0}^{\infty} \lambda^q \, \psi^{(q)}\right] = \left[\sum_{q'=0}^{\infty} \lambda^{q'} \, E^{(q')}\right] \left[\sum_{q=0}^{\infty} \lambda^q \, \psi^{(q)}\right]$$

We can solve now order by order in λ.

0th order) $$H^{(0)}\psi^{(0)} = E_n^{(0)}\psi^{(0)}$$

This is the same as the unperturbed equation with solutions

$$\psi_n^{(0)} = \varphi_n^{(0)}$$

$$E_n^{(0)} = E_n^{(0)}$$

The wave functions are orthogonal so that

$$< \varphi_m^{(0)}|\varphi_n^{(0)} > = \int \varphi^*(\mathbf{r})\varphi(\mathbf{r})d^3r = \int |\varphi(\mathbf{r})|^2\, d^3r \ = \delta_{mn}$$

1st order)

$$\left(\boldsymbol{H}^{(0)} + \lambda \boldsymbol{H}'\right)\left(\psi^{(0)} + \lambda \psi^{(1)} \ldots\right) =$$
$$\left(E^{(0)} + \lambda E^{(1)} \ldots\right)\left(\psi^{(0)} + \lambda \psi^{(1)} \ldots\right)$$

$$\boldsymbol{H}^{(0)}\psi^{(0)} + \lambda \boldsymbol{H}'\psi^{(0)} + \boldsymbol{H}^{(0)}\lambda\psi^{(1)} + \lambda^2 \boldsymbol{H}'\psi^{(1)}$$
$$= E^{(0)}\psi^{(0)} + \lambda E^{(1)}\psi^{(0)} + E^{(0)}\lambda\psi^{(1)} + \lambda^2 E^{(1)}\psi^{(1)}$$

$$\cancel{\boldsymbol{H}^{(0)}\psi^{(0)}} + \lambda \boldsymbol{H}'\psi^{(0)} + \boldsymbol{H}^{(0)}\lambda\psi^{(1)} + \cancel{\lambda^2 \boldsymbol{H}'\psi^{(1)}}$$
$$= \cancel{E^{(0)}\psi^{(0)}} + \lambda E^{(1)}\psi^{(0)} + E^{(0)}\lambda\psi^{(1)} + \cancel{\lambda^2 E^{(1)}\psi^{(1)}}$$

$$\boldsymbol{H}^{(0)}\psi^{(1)} + \boldsymbol{H}'\psi^{(0)} = E^{(0)}\psi^{(1)} + E^{(1)}\psi^{(0)}$$

$$\left(\boldsymbol{H}^{(0)} - E^{(0)}\right)\psi^{(1)} + \left(\boldsymbol{H}' - E^{(1)}\right)\psi^{(0)} = 0$$

$$\left(\boldsymbol{H}^{(0)} - E^{(0)}\right)\psi^{(1)} = \left(E^{(1)} - \boldsymbol{H}'\right)\psi^{(0)}$$

The first order wave function perturbations $\psi^{(1)}$ can be expanded as linear combination of the unperturbed solutions, which are orthogonal with $< \varphi_m^{(0)} | \varphi_n^{(0)} > = \delta_{mn}$

$$\psi_n^{(1)} = \sum_m a_{mn}^{(1)} \varphi_m^{(0)}$$

$$\left(H^{(0)} - E_n^{(0)}\right) \psi_n{}^{(1)} = E^{(1)} \varphi_n{}^{(0)} - H' \varphi_n{}^{(0)}$$

After multiplying by $\varphi_m^{(0)*}$ and integrating over space ("inner" product)

$$E_n^{(1)} = H'_{nn} \qquad\qquad a_{mn}^{(1)} = \frac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}} \quad \text{with} \quad m \neq n$$

$$H'_{mn} = \int \varphi_m^{(0)*} H' \varphi_n^{(0)} \, d^3r$$

Enforce normalization of the "perturbed" wave functions

$$\int \left(\varphi_n^{(0)} + \sum_m a_{mn}^{(1)} \varphi_m^{(0)}\right)^* \left(\varphi_n^{(0)} + \sum_m a_{mn}^{(1)} \varphi_m^{(0)}\right) d^3r = 1$$

$$\int \varphi_n^{(0)*} \varphi_n^{(0)} d^3r + \int \varphi_n^{(0)*} \sum_m a_{mn}^{(1)} \varphi_m^{(0)} d^3r$$
$$+ \int \left(\sum_m a_{mn}^{(1)} \varphi_m^{(0)}\right)^* \varphi_n^{(0)} + \int \left(\sum_m a_{mn}^{(1)} \varphi_m^{(0)}\right)^* \sum_m a_{mn}^{(1)} \varphi_m^{(0)}\, d^3r \;= 1$$

We are free to choose norm and phase, so that the wave functions are normalized and the inner products with $\varphi_n^{(0)}$ are real numbers. This implies that to first order $a_{nn}^{(1)} = 0$.

[This means $\langle \psi^{(0)} | \psi^{(0)} \rangle = 1 \qquad \langle \psi^{(0)} | \psi^{(1)} \rangle = \langle \psi^{(1)} | \psi^{(0)} \rangle = 0$]

Finally, for first order perturbation we have

$$\psi_n = \varphi_n^{(0)} + \sum_{m \neq n} \frac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}} \varphi_n^{(0)}$$

$$E_n = E_n^{(0)} + H'_{nn}$$

2nd order) $\boldsymbol{H}^{(0)}\psi^{(2)} + \boldsymbol{H}'\psi^{(1)} = E^{(0)}\psi^{(2)} + E^{(1)}\psi^{(1)} + E^{(2)}\psi^{(0)}$

In terms of zero-order solutions

$$\psi_n^{(2)} = \sum_m a_{mn}^{(2)}\varphi_m^{(0)}$$

$$E_n^{(2)} = \sum_{m\neq n} a_{mn}^{(1)}H'_{mn} = \sum_{m\neq n}\frac{H'_{mn}H'_{nm}}{E_n^{(0)} - E_m^{(0)}}$$

$$a_{mn}^{(2)} = \sum_{k\neq n}\frac{H'_{mk}H'_{kn}}{\left(E_n^{(0)} - E_m^{(0)}\right)\left(E_n^{(0)} - E_k^{(0)}\right)} - \frac{H'_{mn}H'_{nn}}{\left(E_n^{(0)} - E_m^{(0)}\right)^2} \qquad \{m \neq n\}$$

We can again impose normalization and phase of the wave function at second order, which implies $\langle\psi^{(0)}|\psi^{(2)}\rangle = \langle\psi^{(2)}|\psi^{(0)}\rangle = -\frac{1}{2}\langle\psi^{(1)}|\psi^{(1)}\rangle$ or

$$a_{mn}^{(2)} = -\frac{1}{2}\sum_{m\neq n}\left|a_{mn}^{(1)}\right|^2$$

In terms of zero-order solutions, 2nd order perturbation results are

$$\psi_n = \varphi_n^{(0)} + \sum_{m\neq n} \frac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}} \varphi_n^{(0)}$$

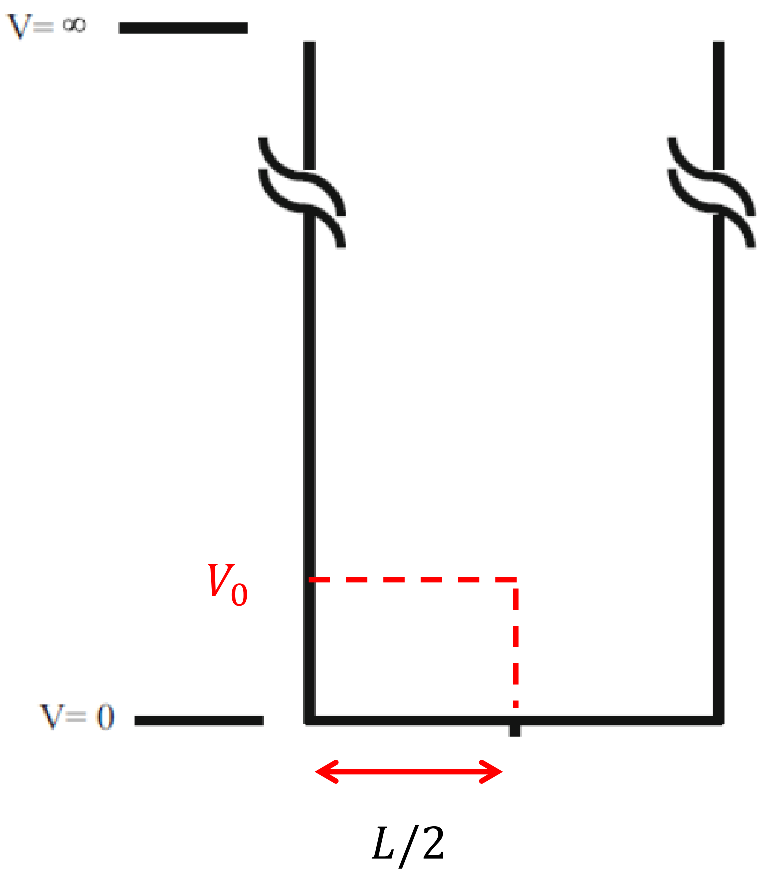
$$+ \sum_{m\neq n} \left\{ \left[\sum_{k\neq n} \frac{H'_{mk} H'_{kn}}{\left(E_n^{(0)} - E_m^{(0)}\right)\left(E_n^{(0)} - E_k^{(0)}\right)} - \frac{H'_{mn} H'_{nn}}{\left(E_n^{(0)} - E_m^{(0)}\right)^2} \right] \varphi_m^{(0)} - \frac{|H'_{mn}|^2}{2\left(E_n^{(0)} - E_m^{(0)}\right)^2} \varphi_n^{(0)} \right\}$$

$$E_n = E_n^{(0)} + H'_{nn} + \sum_{m\neq n} \frac{|H'_{nm}|^2}{E_n^{(0)} - E_m^{(0)}}$$

Simple example

Starting from an infinite quantum well, apply a potential perturbation as in the figure:

$$H' = V_0 \qquad 0 < x < L/2$$



$$E_n^{(1)} = H'_{nn} = \int \varphi_m^{(0)*} H' \varphi_n^{(0)} \, d^3r$$

With reference $x = 0$ set on the left wall, the wave functions are

$$\varphi_n^{(0)} = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \, dx$$

$$E_n^{(1)} = \frac{2}{L} \int_0^{L/2} V_0 \sin^2 n\pi x \, L$$

$$= \frac{2V_0}{L} \left\{ -\frac{1}{2\frac{n\pi}{a}} \cos \frac{n\pi x}{L} \sin \frac{n\pi x}{L} + \frac{x}{2} \right\}_0^{L/2} = \frac{2V_0}{L} \frac{L}{4} = \frac{V_0}{2}$$

$$E_n \approx E_n^{(0)} + \frac{V_0}{2}$$

$$\boxed{\int \sin^2(ax) \, dx = -\frac{1}{2a} \cos(ax) \sin(ax) + \frac{x}{2}}$$

Time-dependent perturbation theory

Consider a physical system described by a time-independent Hamiltonian (assumed to be discrete and non-degenerate)

$$H_0\, \varphi_n = E_n \varphi_n$$

Suppose that at $t = 0$ a time-dependent perturbation is applied to the system

$$H(t \geq 0) = H_0 + \lambda\, H'$$

where the parameter $\lambda \ll 1$. The system is initially in the state φ_i which is an eigenstate of H_0 with eigenvalue E_i.

We are looking for the first-order approximation of the probability $P_{ij}(t)$ of finding the system in another eigenstate φ_f of H_0 at time t.

The Schrödinger equation is

$$i\hbar \frac{\partial}{\partial t}\psi(\mathbf{r},t) = H\,\psi(\mathbf{r},t) = (H_0 + \lambda H')\psi(\mathbf{r},t)$$

We assume to know the time-dependent solution for the unperturbed Hamiltonian

$$i\hbar \frac{\partial}{\partial t}\varphi_n(\mathbf{r},t) = H_0\,\varphi_n(\mathbf{r},t)$$

$$\varphi_n(\mathbf{r},t) = \varphi_n(\mathbf{r})e^{-iE_n t/\hbar}$$

Expand $\psi(\mathbf{r},t)$ in terms of the unperturbed eigensolutions

$$\psi(\mathbf{r},t) = \sum_n a_n(t)\,\varphi_n(\mathbf{r})e^{-iE_n t/\hbar}$$

dove $|a_n(t)|^2$ is probability for the electron to be in state n at t

Substitute the expansion in Schrödinger equation

$$i\hbar \frac{\partial}{\partial t}\left(\sum_n a_n(t)\, \varphi_n(\mathbf{r})\, e^{-iE_n t/\hbar}\right)$$

$$= (H_0 + \lambda H')\left(\sum_n a_n(t)\, \varphi_n(\mathbf{r})\, e^{-iE_n t/\hbar}\right)$$

First term of equation above

$$i\hbar \sum_n \frac{da_n(t)}{dt}\varphi_n(\mathbf{r})\; e^{-iE_n t/\hbar} + \underbrace{i\hbar \sum_n a_n(t)\frac{d}{dt}\left(\varphi_n(\mathbf{r})\; e^{-iE_n t/\hbar}\right)}_{\boxed{H_0\, \varphi_n(\mathbf{r},t)}}$$

$$\Downarrow$$

$$\sum_n \frac{da_n(t)}{dt}\varphi_n(\mathbf{r})\; e^{-iE_n t/\hbar} = -\frac{i}{\hbar}\sum_n \lambda H'(\mathbf{r},t)a_n(t)\,\varphi_n(\mathbf{r})\; e^{-iE_n t/\hbar}$$

$$\sum_n \frac{da_n(t)}{dt}\varphi_n(\mathbf{r})\ e^{-iE_nt/\hbar} = -\frac{i}{\hbar}\sum_n \lambda H'(\mathbf{r},t)a_n(t)\ \varphi_n(\mathbf{r})\ e^{-iE_nt/\hbar}$$

Take inner product with $\varphi_m^*(\mathbf{r})$

$$\frac{da_m(t)}{dt} = -\frac{i}{\hbar}\ \lambda\sum_n a_n(t)\ H'_{mn}(t)\ e^{-i(E_m-E_n)t/\hbar}$$

$$H'_{mn}(t) = \int \varphi_m^*(\mathbf{r})\ H'(\mathbf{r},t)\varphi_n(\mathbf{r})\ \boldsymbol{d^3r}$$

Now write the coefficients in the form of a power series

$a_n(t) = a_n^{(0)}(t) + \lambda a_n^{(1)}(t) + \lambda^2 a_n^{(2)}(t) + \cdots$

We seek the solution to first order in λ.

$$\frac{da_m(t)}{dt} = -\frac{i}{\hbar}\,\lambda \sum_n a_n(t)\, H'_{mn}(t)\, e^{-i(E_m - E_n)t/\hbar}$$

$$a_n(t) = a_n^{(0)}(t) + \lambda a_n^{(1)}(t) + \lambda^2 a_n^{(2)}(t) + \cdots$$

We have

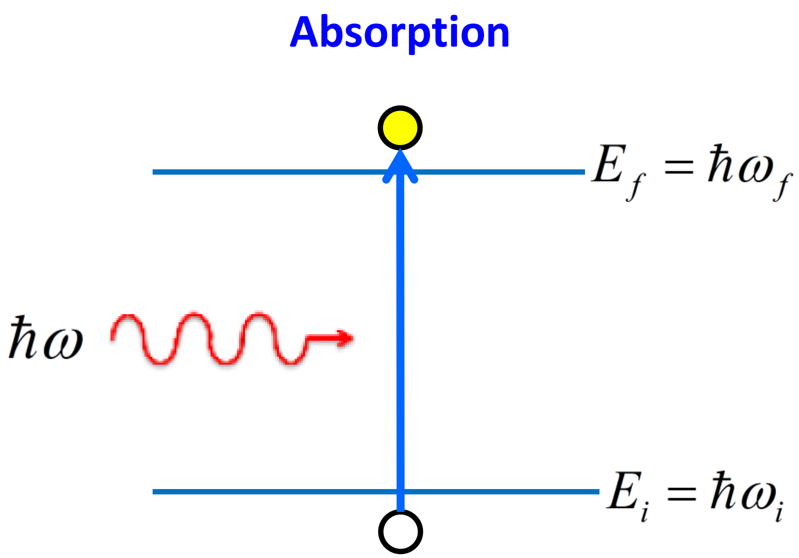
$$\frac{da_m^{(0)}}{dt} = 0$$

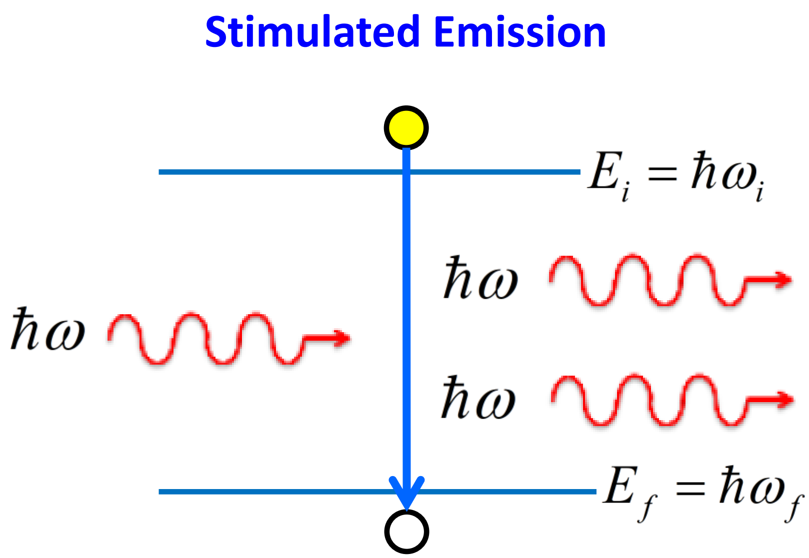
$$\frac{da_m^{(1)}(t)}{dt} = -\frac{i}{\hbar} \sum_n a_n^{(0)}(t)\, H'_{mn}(t)\, e^{-i(E_m - E_n)t/\hbar}$$

$$\frac{da_m^{(2)}(t)}{dt} = -\frac{i}{\hbar} \sum_n a_n^{(1)}(t)\, H'_{mn}(t)\, e^{-i(E_m - E_n)t/\hbar}$$

Fermi Golden Rule

We will use the main results of time-dependent perturbation theory to determine the **transition probability from one state to another**, due to an external perturbation.





The electron is at state " i " initially. The zeroth-order solutions are constant and electron stays in that state in absence of perturbation

$$a_i^{(0)}(t) = 1$$

$$a_m^{(0)}(t) = 0 \qquad m \neq i$$

The first order solution is obtained from

$$\boxed{\omega_{mi} = \frac{E_m - E_i}{\hbar}}$$

$$\frac{da_m^{(1)}(t)}{dt} = -\frac{i}{\hbar} H'_{mi}(t)\ e^{-i(E_m-E_i)t/\hbar} = -\frac{i}{\hbar} H'_{mi}(t)\ e^{-i\omega_{mi}t}$$

Assume time-dependent perturbation (e.g., photons) with form

$$H'(\mathbf{r},t) = H'_m(\mathbf{r})e^{-i\omega t} + H'^{+}_m(\mathbf{r})e^{i\omega t}$$

$$H'_{mi}(t) = \int \varphi_m^*(\mathbf{r})\, H'(\mathbf{r},t)\varphi_i(\mathbf{r})\, d^3r = H'_{mi}e^{-i\omega t} + H'^{+}_{mi}e^{i\omega t}$$

$$\boldsymbol{\omega_{fi} = \frac{E_f - E_i}{\hbar}}$$

Initial state $n = i$

$$\frac{da_m^{(1)}(t)}{dt} = -\frac{i}{\hbar} H'_{mi}(t)\ e^{-i\omega_{mi}t}$$
$$= -\frac{i}{\hbar}\left(H'_{mi}\ e^{i(\omega_{mi}-\omega)t} + H'^{+}_{mi}\ e^{i(\omega_{mi}+\omega)t}\right)$$

Integrate equation between **0** and ***t*** for a final state $m = f$

$$a_f^{(1)}(t) = -\frac{1}{\hbar}\left[H'_{fi}\frac{e^{i(\omega_{fi}-\omega)t} - 1}{\omega_{fi} - \omega} + H'^{+}_{fi}\frac{e^{i(\omega_{fi}+\omega)t} - 1}{\omega_{fi} + \omega}\right]$$

The associated probability is

$$\left|a_f^{(1)}(t)\right|^2 = \frac{1}{\hbar^2}\left[H'_{fi}\frac{e^{i(\omega_{fi}-\omega)t} - 1}{\omega_{fi} - \omega} + H'^{+}_{fi}\frac{e^{i(\omega_{fi}+\omega)t} - 1}{\omega_{fi} + \omega}\right]^2$$

$$\left|a_f^{(1)}(t)\right|^2 = \frac{1}{\hbar^2}\left[H'_{fi}\frac{e^{i(\omega_{fi}-\omega)t}-1}{\omega_{fi}-\omega} + H'^{+}_{fi}\frac{e^{i(\omega_{fi}+\omega)t}-1}{\omega_{fi}+\omega}\right]^2$$

Using $\sin x = \frac{1}{2i}\left(e^{ix} - e^{-ix}\right)$

$$e^{-i(\omega_{fi}-\omega)t} - 1 = 2i\, e^{i\frac{(\omega_{fi}-\omega)t}{2}} \sin\frac{(\omega_{fi}-\omega)t}{2}$$

$$\left|a_f^{(1)}(t)\right|^2 = \frac{4\left|H'_{fi}\right|^2}{\hbar^2}\frac{\sin^2\frac{(\omega_{fi}-\omega)t}{2}}{\left(\omega_{fi}-\omega\right)^2} + \frac{4\left|H'^{+}_{fi}\right|^2}{\hbar^2}\frac{\sin^2\frac{(\omega_{fi}+\omega)t}{2}}{\left(\omega_{fi}+\omega\right)^2} + \cancel{\cdots}$$

drop cross term

$$\left|a_f^{(1)}(t)\right|^2 = \frac{4\left|H'_{fi}\right|^2}{\hbar^2}\frac{\sin^2\frac{\left(\omega_{fi}-\omega\right)t}{2}}{\left(\omega_{fi}-\omega\right)^2} + \frac{4\left|H'^{+}_{fi}\right|^2}{\hbar^2}\frac{\sin^2\frac{\left(\omega_{fi}+\omega\right)t}{2}}{\left(\omega_{fi}+\omega\right)^2}$$

For a sufficiently long interaction time

$$\frac{\sin^2\left(\frac{x}{2}t\right)}{x^2} \rightarrow \frac{\pi t}{2}\,\delta(x)$$

$$\left|a_f^{(1)}(t)\right|^2 = \frac{2\pi t}{\hbar^2}\left|H'_{fi}\right|^2\delta\left(\omega_{fi}-\omega\right) + \frac{2\pi t}{\hbar^2}\left|H'^{+}_{fi}\right|^2\delta\left(\omega_{fi}+\omega\right)$$

$$\left|a_f^{(1)}(t)\right|^2 = \frac{2\pi t}{\hbar^2}\left|H'_{fi}\right|^2\delta\left(\omega_{fi} - \omega\right) + \frac{2\pi t}{\hbar^2}\left|H'^{+}_{fi}\right|^2\delta\left(\omega_{fi} + \omega\right)$$

Using the property $\delta(\hbar\omega) = \delta(\omega)/\hbar$ the transition rate is given by

$$W_{i\to f} = \frac{d}{dt}\left|a_f^{(1)}(t)\right|^2$$

$$W_{i\to f} = \frac{2\pi}{\hbar}\left|H'_{fi}\right|^2\delta\left(E_f - E_i - \hbar\omega\right) + \frac{2\pi}{\hbar}\left|H'^{+}_{fi}\right|^2\delta\left(E_f - E_i + \hbar\omega\right)$$

$$\left|a_f^{(1)}(t)\right|^2 = \frac{2\pi t}{\hbar^2}\left|H'_{fi}\right|^2 \delta(\omega_{fi} - \omega) + \frac{2\pi t}{\hbar^2}\left|H'^{+}_{fi}\right|^2 \delta(\omega_{fi} + \omega)$$

Using the property $\delta(\hbar\omega) = \delta(\omega)/\hbar$ the transition rate is given by

$$W_{i\to f} = \frac{d}{dt}\left|a_f^{(1)}(t)\right|^2$$

energy conserving delta functions

$$W_{i\to f} = \frac{2\pi}{\hbar}\left|H'_{fi}\right|^2 \delta(E_f - E_i - \hbar\omega) + \frac{2\pi}{\hbar}\left|H'^{+}_{fi}\right|^2 \delta(E_f - E_i + \hbar\omega)$$

$E_f = E_i + \hbar\omega$

$E_f = E_i - \hbar\omega$

absorption of a photon

emission of a photon

Reading Assignments:

Chapter 3 of Chuang's book