

Quantum Bound States

INFINITE POTENTIAL WELL

To solve the TISE for an infinite potential well shown on the figure below, we recall the step potential solution (see resource <http://nanohub.org/resources/4934>) and examine the solution in region 2 when $E < V_0$ (the evanescent wave) of the form:

$$\psi_2(x) = \frac{2k_1}{k_1 + i\kappa_2} A^{(1)} e^{-\kappa_2 x} \rightarrow |\psi_2(x)| = \frac{2k_1}{\sqrt{k_1^2 + \kappa_2^2}} e^{-\kappa_2 x} = 2\sqrt{\frac{E}{V_0 - E}} e^{-\kappa_2 x} .$$

In the limit $V_0 \rightarrow \infty$, it is obvious that $|\psi_2(x)| \rightarrow 0$ for any value of $x \geq 0$. Therefore, we can say that in this limit, the wavefunction vanishes at the boundary of the infinite potential step. We can generalize this by saying that the wavefunction vanishes at $x = \pm L/2$ for the infinite well problem.

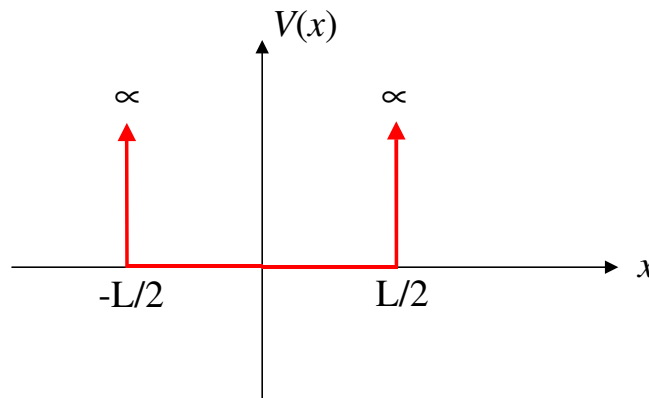


Figure 1. Infinite potential well.

Notes:

➤ The solution of the TISE for this type of potential constitutes a bound-state problem. A significant difference between continuum and bound-state problems follows from the fundamental difference between the nature of these states, i.e.

(a) the type of boundary conditions that they satisfy:

$$|\psi(x,t)|^2 \xrightarrow{x \rightarrow \pm\infty} 0 \text{ at all times } \rightarrow \text{bound states}$$

$$|\psi(x,t)|^2 \xrightarrow{x \rightarrow \pm\infty} 0 \text{ at any particular time } t \rightarrow \text{unbound states}$$

(b) Energy spectrum:

bound states \rightarrow discrete energy spectrum

unbound states \rightarrow continuous energy spectrum

- A major difficulty in solving the TISE for bound states is that we do not know the allowed quantized energies in advance. We must find these by solving for the Hamiltonian eigenfunctions that obey the appropriate boundary conditions:

$$\begin{aligned}\Psi_E(x) &\rightarrow 0, x \rightarrow \pm\infty \\ \int_{-\infty}^{\infty} \Psi_E^*(x)\Psi_E(x)dx &= 1\end{aligned}$$

Solution to the particle in the box problem:

Since the particle is free inside the box, we can write the general solution to the TISE in this region as:

$$\Psi(x) = Ae^{ikx} + Be^{-ikx} = C \cos(kx) + D \sin(kx)$$

For this wavefunction to be a proper wavefunction, it must satisfy the two boundary conditions at $x=-L/2$ and $x=L/2$. The one at $x=L/2$ leads to:

$$C \cos(kL/2) + D \sin(kL/2) = 0 \Rightarrow \begin{cases} C = 0, & \frac{kL}{2} = n\pi \rightarrow k_n = \frac{2n\pi}{L}, \quad n = 1, 2, 3, \dots \\ D = 0, & \frac{kL}{2} = (2n-1)\frac{\pi}{2} \rightarrow k_n = \frac{(2n-1)\pi}{L}, \quad n = 1, 2, 3, \dots \end{cases}$$

The top solution leads to odd parity wavefunctions $\Psi_o(x)$, and the bottom one to even parity wavefunctions $\Psi_e(x)$, of the form:

$$\begin{cases} \Psi_o(x) = \sqrt{\frac{2}{L}} \sin\left[\frac{2n\pi}{L}x\right] \\ \Psi_e(x) = \sqrt{\frac{2}{L}} \cos\left[\frac{(2n-1)\pi}{L}x\right] \end{cases}$$

Important:

The discussion presented in this section suggests that the wavevector of the particle in an infinite potential well is quantized, i.e. the spatial functions that satisfy the boundary conditions imposed by the potential exist only for discrete values of the wavevectors which, in turn, leads to discrete energy spectrum:

$$k_n = \frac{n\pi}{L} \rightarrow E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2 \pi^2}{2mL^2} n^2 = n^2 E_1,$$

where E_1 is the energy of the lowest allowed energy level, also known as the ground state. The list of allowed stationary-state energies is called **energy spectrum**.

FINITE POTENTIAL WELL

- Consider the ground state of an infinite potential well. The energy corresponding to this state equals to

$$E_1 = \frac{\hbar^2 \pi^2}{2mL^2}$$

Now, let's look at the final well solution to the TISE shown schematically on Figure 2. Due to the finite height of the well, there is a spilling of the wavefunction in the classically-forbidden region. To first order, the spilling of the wavefunction can be explained as having a wider well with effective width $\lambda > L$. This, in turn leads to a lower value for the ground state of a finite well when compared to the infinite well solution. In the limit, when the barrier height approaches zero and $\lambda \rightarrow \infty$, we therefore arrive at the continuum problem.

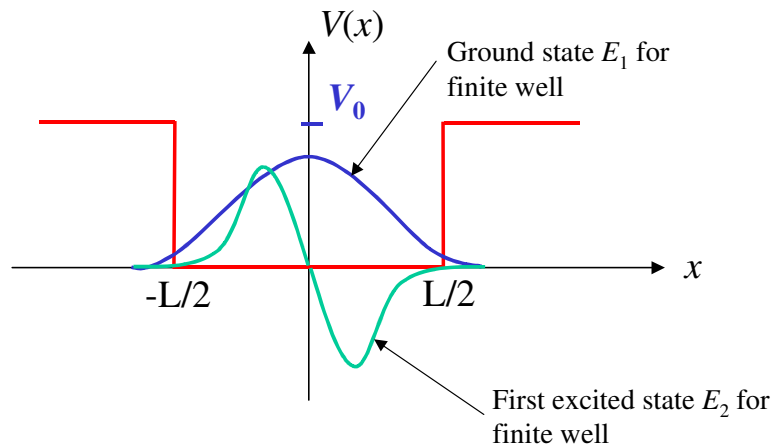


Figure 2. A sketch of the wavefunctions for the lowest two energy levels for a finite well.

- An additional observation that follows from this figure is that the ground state wavefunction remains to be an even function, i.e. the parity of the states does not change. Therefore, the even and odd solutions of the TISE have the following form:

$$\psi_e(x) = \begin{cases} Ae^{kx}, & x \leq -L/2 \\ B \cos(kx), & -L/2 < x < L/2 \\ Ae^{-kx}, & x \geq L/2 \end{cases}, \quad \psi_o(x) = \begin{cases} Ae^{kx}, & x \leq -L/2 \\ B \sin(kx), & -L/2 < x < L/2 \\ -Ae^{-kx}, & x \geq L/2 \end{cases}$$

where

$$k = \sqrt{\frac{2mE}{\hbar^2}} \quad \text{and} \quad \kappa = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}.$$

- Due to the **symmetry of the potential**, we do not need to impose four boundary conditions at the two boundaries. The two boundary conditions at one of the two boundaries are sufficient to determine the energy levels corresponding to the even and odd-parity functions. This can further be simplified by introducing the single **boundary condition on the logarithmic derivative**

$$d\left[\ln \psi^{(1)}(x)\right]_{x=x_0} = d\left[\ln \psi^{(2)}(x)\right]_{x=x_0}$$

In the above expression, $\psi^{(1)}(x)$ and $\psi^{(2)}(x)$ are the general solutions in regions 1 and 2 for some piecewise constant potential, and x_0 represents the boundary between the two regions. It is straightforward to show that the equality of the logarithmic derivatives at the matching point reduces to the two conditions we have used for step-potentials, namely continuity and smoothness of the wavefunction at the matching point.

- The application of the logarithmic boundary condition at $x=-L/2$ leads to the following results for the even and odd-parity functions:

(a) Even parity function:

$$\frac{1}{A \exp\left(-\frac{\kappa L}{2}\right)} A \kappa \exp\left(-\frac{\kappa L}{2}\right) = \frac{1}{B \cos\left(-\frac{kL}{2}\right)} (-Bk) \sin\left(-\frac{kL}{2}\right)$$

$$\downarrow$$

$$\kappa = k \tan\left(\frac{kL}{2}\right)$$

(b) Odd parity function:

$$\frac{1}{A \exp\left(-\frac{\kappa L}{2}\right)} A \kappa \exp\left(-\frac{\kappa L}{2}\right) = \frac{1}{B \sin\left(-\frac{kL}{2}\right)} (Bk) \cos\left(-\frac{kL}{2}\right)$$

$$\downarrow$$

$$\kappa = -k \cot\left(\frac{kL}{2}\right)$$

Discussion:

The condition on the allowed wavevectors for the even parity functions that are solutions of the TISE can be rewritten as:

$$\tan(\xi) = \sqrt{\frac{\beta^2}{\xi^2} - 1} = f(\xi),$$

where

$$\beta = \frac{L}{2} \sqrt{\frac{2mV_0}{\hbar^2}} \quad \text{and} \quad \xi = \frac{L}{2} \sqrt{\frac{2mE}{\hbar^2}}.$$

Similar expressions can be obtained for the odd parity functions, i.e. in this case one needs to solve the implicit equation

$$-\cot(\xi) = \sqrt{\frac{\beta^2}{\xi^2} - 1} = f(\xi) .$$

The solution of these implicit equations can be obtained by using either the graphical solution method (see the figures below) or using, for example, the Newton-Raphson method. An important conclusion that follows from the graphical solution method is that, in the limit of infinitely-small height of the well ($\beta \rightarrow 0$), there will be only one solution to the TISE and the energy of that level will coincide with the top of the well. This is also clear from the graphical solution to the problem.

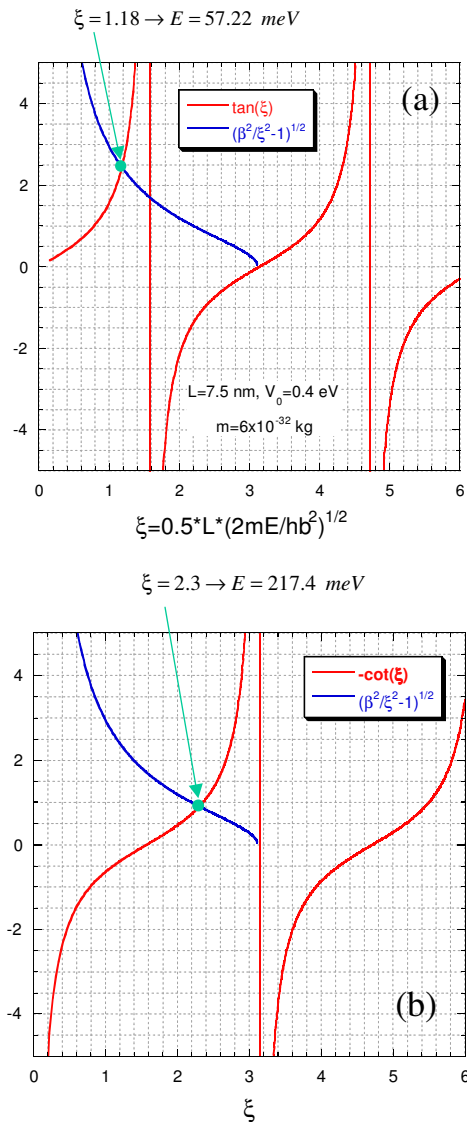


Figure 3. The even and the odd solutions of a finite well problem. There are two bound states in the well, one corresponding to the even function and the other to the odd function. Case (a) corresponds to the even function solutions, and case (b) corresponds to the odd solutions.

The graphical solution results for the bound states are 57.22 and 217.4 meV. The numerical solution to the same problem, using the scheme described in details in later section gives $E_1=57.3$ and $E_2=218.5$ meV, which is in excellent agreement with the graphical analysis. The shape of the wavefunctions corresponding to these two energy levels is shown in Fig. 4a. Also shown in this figure is the solution to the 1D TISE for an energy value that is not an eigenstate (Fig. 4b). It is important to note that, even though the wavefunction is continuous, it does not satisfy the smoothness condition (the wavefunction does not have continuous derivative).

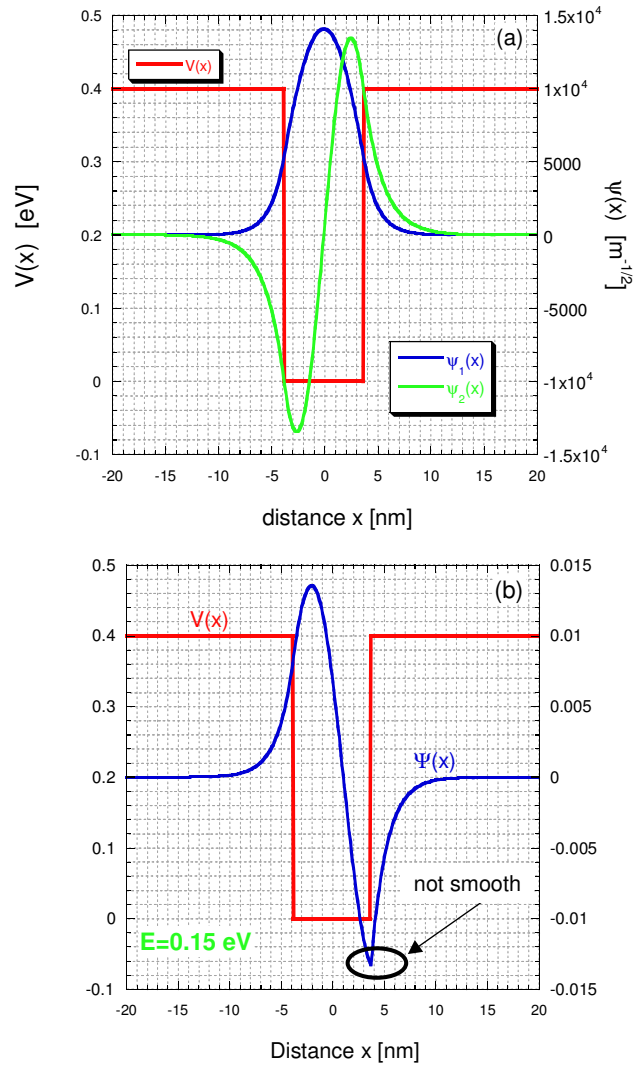


Figure 4. (a) The shape of the eigenfunctions corresponding to the bound states of a finite well. (b) Solution of the 1D Schrödinger equation for energy that does not correspond to an eigenstate.

For this problem, one can also plot the transmission coefficient $T(E)$ for particle energies $E > V_0 = 0.4$ V. Following the approach described for a step potential, with little bit more algebra, one arrives at the following expression for the transmission coefficient $T(E)$

$$T(E) = \left[1 + \frac{(k_1^2 - k_2^2)}{4k_1^2 k_2^2} \sin^2(k_2 L) \right]^{-1},$$

where

$$k_1^2 = \frac{2m(E - V_0)}{\hbar^2} \quad \text{and} \quad k_2^2 = \frac{2mE}{\hbar^2}.$$

The variation of the transmission coefficient with energy is shown in Fig. 5. From the results shown, it is clear that the transmission coefficient equals one for the following condition:

$$k_2 L = n\pi \rightarrow E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2 = 0.1014 n^2,$$

which gives $E_1 = 0.1014$, $E_2 = 0.4056$, $E_3 = 0.9126$ and $E_4 = 1.622$ eV. These values are consistent with the results deduced from Fig. 5.

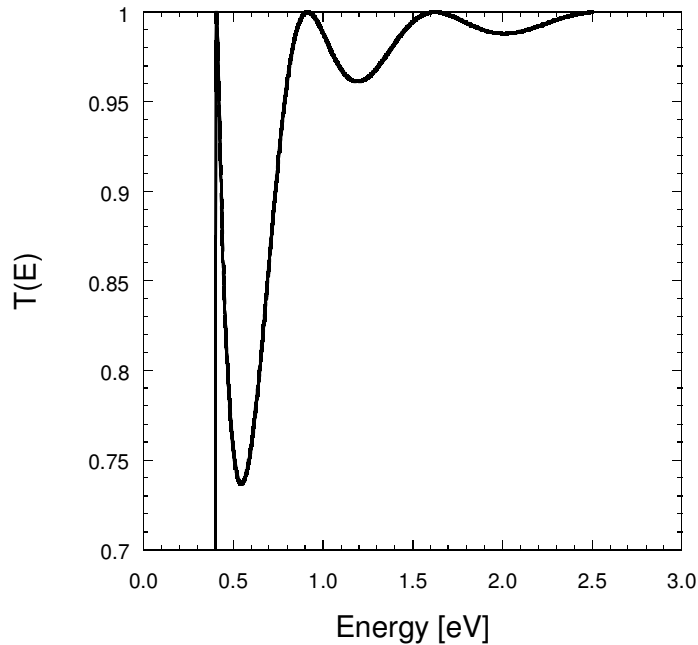


Figure 5. Variation of the transmission coefficient with energy for the quantum well problem from Figs. 8 and 9.

TRIANGULAR WELL SOLUTIONS

When an electric field is applied to the surface of a p -type semiconductor, such as occurs in a metal-oxide-semiconductor under bias, an n -type inversion layer is produced at the surface (see Fig. 6). When the bands are bent strongly, as in strong inversion, the potential well formed by the insulator-semiconductor surface and the electrostatic potential in the semiconductor can be narrow enough that quantum-mechanical effects become important. The motion of electrons in the direction perpendicular to the surface is constrained to remain within this potential well and, if the thickness of the well is comparable to the electronic wavelength, size effect quantization leads to widely spaced electron energy levels. These energy levels are then grouped into subbands, each of which corresponds to a particular quantized level of motion in the direction perpendicular to the surface. The same quantization effect occurs in quantum wells, heterostructures and superlattices. In the thermodynamic limit, the electrons are described by plane waves in the plane parallel to the interface. In MOS devices, such quantum effects play an important role even at room temperature, where the width of the inversion layer is of the same order of magnitude as the thermal wavelength of the carriers. Therefore, it becomes necessary to solve the Schrödinger equation for the subband energies and wavefunctions in order to study transport properties of inversion layer electrons.

The periodic crystal potential in the bulk of semiconducting materials is such that, for a given energy in the conduction band, the allowed electron wavevectors trace out a surface in \mathbf{k} -space. In the effective-mass approximation for silicon, these constant energy surfaces can be visualized as six equivalent ellipsoids of revolution (Fig. 6), whose major and minor axes are inversely proportional to the effective masses. A collection of such ellipsoids for different energies is referred to as a valley.

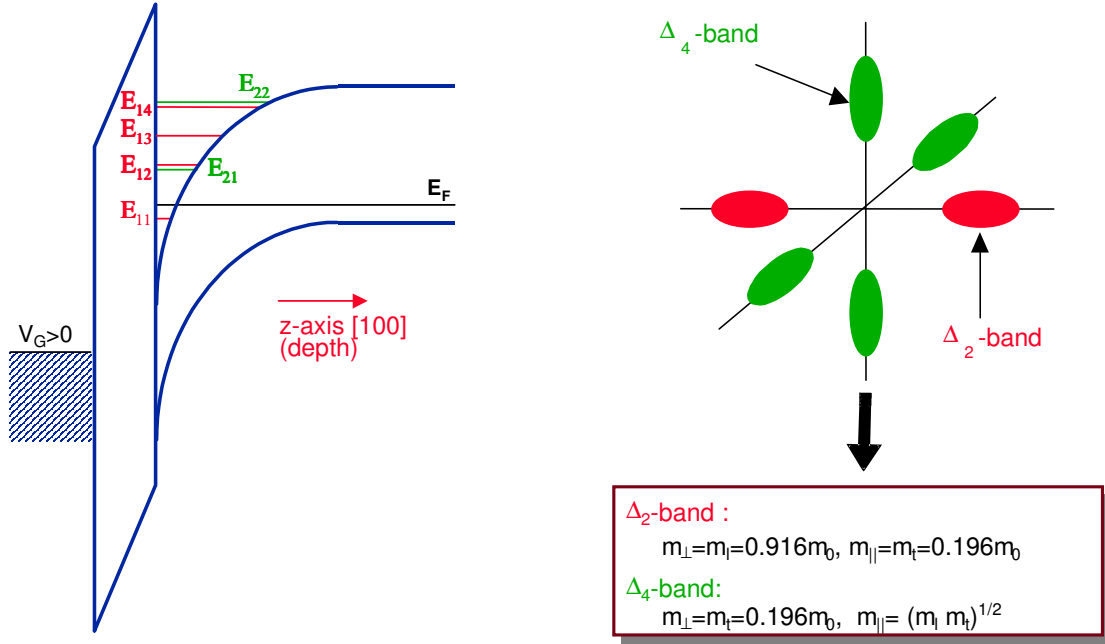


Figure 6. (left) Potential diagram for inversion of p -type semiconductor. (right) Constant-energy surfaces for the conduction-band of silicon showing six conduction-band valleys in the $\langle 100 \rangle$ direction of momentum space. The band minima, corresponding to the centers of the ellipsoids, are 85% of the way to the Brillouin-zone boundaries. The long axis of an ellipsoid corresponds to the longitudinal effective mass of the electrons in silicon m_l , while the short axes correspond to the transverse effective mass m_t .

In this framework, the 1D Schrödinger equation for an electron residing in one of these valleys is of the form

$$\left[-\frac{\hbar^2}{2m_i^{\perp}} \frac{\partial^2}{\partial z^2} + V(z) \right] \psi_i(z) = E_i \psi_i(z)$$

where m_i^{\perp} is the effective mass normal to the semiconductor-oxide interface of the i -th subband from either the unprimed or primed ladder of subbands, and E_i and ψ_i are the energy level and the corresponding wavefunctions. For $\langle 100 \rangle$ crystal orientation the six equivalent minima of the bulk silicon conduction band split into two sets of subbands. The first set (Δ_2 -band) consists of the two equivalent valleys with in-plane effective mass $m_{\parallel}=0.19m_0$ and perpendicular effective mass $m_{\perp}=0.91m_0$. The second set (Δ_4 -band) consists of the four equivalent valleys with $m_{\parallel}=\sqrt{m_l m_t}=0.42m_0$ and $m_{\perp}=0.19m_0$. The energy levels associated with the Δ_2 -band comprise the so-called unprimed ladder of sub-bands, whereas those associated with the Δ_4 -band comprise the primed ladder of subbands.

To calculate the subband structure for the MOS capacitor, one needs to find the self-consistent solution of the Schrödinger equation, and of Poisson's equation

$$\frac{\partial}{\partial z} \left[\frac{1}{\epsilon(z)} \frac{\partial \phi}{\partial z} \right] = -e \left[N_D^+(z) - N_A^-(z) + p(z) - n(z) \right]$$

where $\phi(z)$ is the electrostatic potential, $\epsilon(z)$ is the dielectric constant, $N_D^+(z)$ and $N_A^-(z)$ are the ionized donor and acceptor concentrations, $n(z)$ and $p(z)$ are the electron and hole densities. Note that the potential energy term appearing in the Schrödinger equation is related to the potential $\phi(z)$ in the following manner: $V(z) = -e\phi(z) + const.$ The boundary conditions that one needs to impose are the following ones: $V(0) = 0$ and $V(\infty) \rightarrow 0$. In the analysis presented here, we assume that $z=0$ corresponds to the SiO_2/Si boundary. The quantum-mechanically calculated electron density is then given by:

$$n(z) = \sum_i N_i \psi_i^2(z) \quad ,$$

where N_i is the sheet-charge density corresponding to energy level E_i , and N_s is the total sheet charge density that is calculated using

$$N_s = \sum_i N_i = \sum_i \frac{m_i^{\parallel} k_B T}{\pi \hbar^2} \ln \left[1 + \exp \left(\frac{E_F - E_i}{k_B T} \right) \right]$$

When the Poisson equation is formally solved for this particular problem, one finds the solution

$$V_H(z) = V_d + V_i = \frac{e^2 N_A W}{\epsilon_{sc}} z \left(1 - \frac{z}{2W} \right) + \frac{e^2}{\epsilon_{sc}} \sum_i N_i \left[z - \int_0^z (z-x) \psi_i^2(x) dx \right],$$

for $z \leq W$, where W is the width of the depletion region. The first term represents the contribution from the fixed space charges whereas the second term represents the contribution from induced charges in the space-charge region (the so-called Hartree term). The width of the depletion layer is calculated to be

$$W = \sqrt{\frac{2\epsilon_{sc}\phi_d}{eN_I}} \quad ,$$

where $e\phi_d$ is the band bending shown in Fig. 7, given by

$$e\phi_d = (\epsilon_c - \epsilon_F)_{bulk} + (\epsilon_F - \epsilon_o) + \epsilon_o - \frac{e^2}{\epsilon_{sc}} \sum_i N_i z_i^{(av)} \quad .$$

In the above expression, $z_i^{(av)}$ is the average distance of the electrons that reside in the i -th subband from the interface, ϵ_c is the conduction band edge, and ϵ_o is the energy of the lowest subband.

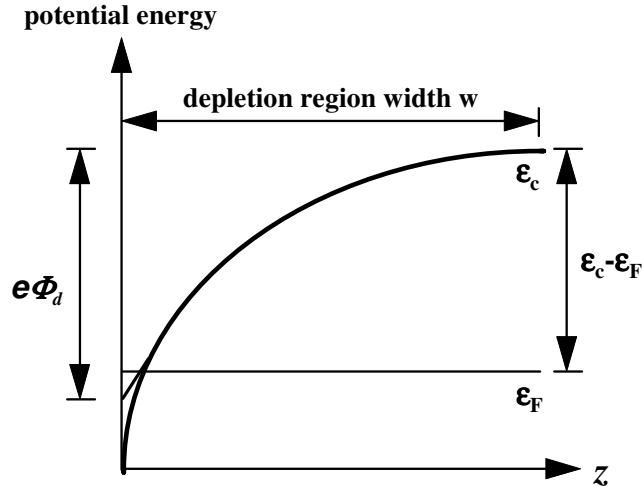


Figure 7. Schematic band-banding near the semiconductor-insulator interface, showing the nominal conduction-band edge (thick line) and the corresponding band-banding associated with the fixed depletion layer charge only (thin line).

To obtain self-consistent solution to this problem is a rather formidable task for students at this level. Because of this, in the rest of this section we will only describe ways to find approximate solutions. The explanation for the numerical solution of the 1D Schrödinger equation, without coupling to the 1D Poisson equation, is described in the next section. The simulation tool SCHRED used for obtaining numerical self-consistent results for MOS capacitors with p -type substrates and metal or poly-silicon gates, developed at Arizona State University, and donated to the Purdue Semiconductor Simulation Hub, can be accessed using the following link:

<http://nanohub.org/resources/schred> .

Follow this link to examine the capabilities of SCHRED. You need to read the user manual before you try to run SCHRED.

(1) Airy functions

If the inversion layer contribution to the potential energy is negligible compared to the depletion layer contribution, for small values of z ($z \ll W$) one can approximate the potential energy profile by

$$V(z) \approx \frac{e^2 N_A W}{\epsilon_{sc}} z = eE_s z ,$$

where E_s is the electric field at the semiconductor-insulator interface ($z=0$). This is called the triangular-potential approximation. It leads to the Airy equation of the form

$$\frac{d^2 \Psi}{d\xi^2} - \xi \Psi(\xi) = 0, \quad \text{where} \quad \xi = z \left(\frac{2meE_s}{\hbar^2} \right)^{1/3} - \frac{2mE}{\hbar^2} \left(\frac{\hbar^2}{2meE_s} \right)^{2/3} .$$

The solutions of this equation are Airy functions $\text{Ai}(\xi)$, and the zeroes of the Airy functions are

$$\xi_n = - \left[\frac{3\pi}{2} \left(n - \frac{1}{4} \right) \right]^{2/3}, \quad n = 1, 2, 3, \dots$$

which occurs for $z=0$. This means that the energy levels can be calculated using

$$E_n = \left(\frac{\hbar^2}{2m} \right)^{1/3} \left[\frac{3\pi e E_s}{2} \left(n - \frac{1}{4} \right) \right]^{2/3}, \quad n = 1, 2, 3, \dots$$

The eigenvalues E_i are asymptotic values for large i , but they are amazingly close even for the ground state $n=1$. The exact eigenvalues for the three lowest states have $(n - 1/4)$ replaced by 0.7587, 1.7540, and 2.7525, respectively.

Example:

Calculate the energy levels for a triangular potential well by using the Airy function method. Use $N_s = 10^{12} \text{ cm}^{-2}$, $N_{depl} = 5 \times 10^{11} \text{ cm}^{-2}$, $\epsilon_{sc} = 11.8\epsilon_0$ and $m = 0.91m_0$. Plot the first five energy levels.

Solution:

The surface electric field equals to:

$$E_s = \frac{e}{\epsilon_{sc}} (N_s + N_{depl}) = 2.3 \times 10^7 \text{ (V / m)}$$

The Airy function method gives:

$$E_n = \left(\frac{\hbar^2}{2m} \right)^{1/3} \left[\frac{3\pi e E_s}{2} \left(n - \frac{1}{4} \right) \right]^{2/3} = 78.96 (n - 1/4)^{2/3} \text{ (meV)} ,$$

i.e., we have: $E_1=65.18 \text{ meV}$, $E_2=114.7 \text{ meV}$, $E_3=155 \text{ meV}$, $E_4=190.6 \text{ meV}$ and $E_5=223.1 \text{ meV}$. Note that the separation of the levels decreases because of the linear increase of the well width. The wavefunctions corresponding to these five energy levels are plotted in Figure 8.

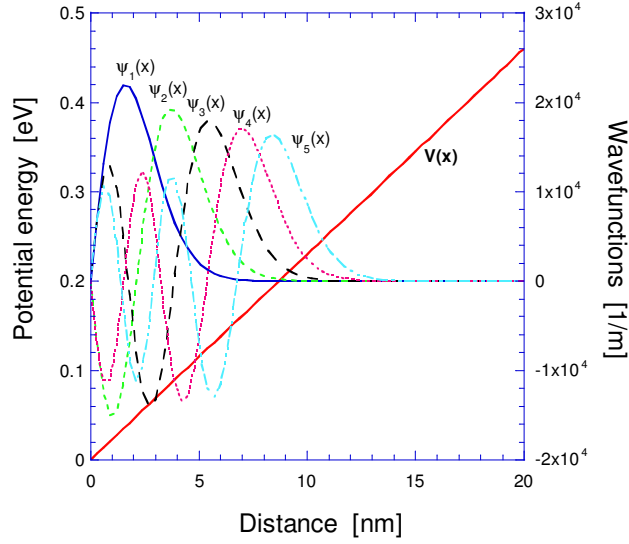


Figure 8: Eigenfunctions corresponding to the lowest five energy levels of a triangular potential well. Also shown in this figure is the shape of the confining potential.

(2) Variational Approach

The triangular-potential approximation is a reasonable approximation when there is little or no charge in the inversion layer, but fails when the inversion charge density is comparable to or greater than the depletion charge density $N_{depl} = N_I W$. At low temperatures and moderately high inversion charge densities and (100) orientation of the surface, only the lowest subband of the two equivalent valleys with longitudinal mass perpendicular to the interface is usually occupied. In this case, a variational approach gives a good estimate for the energy of the lowest subband. One can approximate the wavefunction of the lowest subband with some trial function. The trial function proposed by Fang and Howard is

$$\Psi_o(z) = \left(\frac{b^3}{2} \right)^{1/2} z e^{-bz/2}$$

where b is a parameter which is determined by minimizing the total energy of the system for given values of the inversion and depletion charges. The total energy per electron, the quantity that needs to be minimized, is then given by

$$E/N = \langle T \rangle + \langle V_d \rangle + \frac{1}{2} \langle V_i \rangle = \left(\frac{\hbar^2 b^2}{8m_z^*} \right) + \left(\frac{3e^2 N_{depl}}{\epsilon_{sc} b} - \frac{6e^2 N_I}{\epsilon_{sc} b^2} \right) + \frac{1}{2} \left(\frac{33e^2 N_s}{16\epsilon_{sc} b} \right)$$

The first term represents the expected value of the kinetic energy of the electron, while the second and third terms correspond to the average potential energies of the electron interacting with the depletion and inversion charge. The factor 1/2 prevents double counting of the electrons. After some algebra, one finds that the value of b that minimizes the average energy per electron equals to

$$b = \left(\frac{12m_z^* e^2 N^*}{\hbar^2 \epsilon_{sc}} \right)^{1/3}$$

where

$$N^* = N_{depl} + \frac{11}{32} N_s$$

The energy of the lowest state is found after a straightforward calculation to be

$$\epsilon_o = \langle T \rangle + \langle V_d \rangle + \langle V_i \rangle$$

and the inversion charge contribution to the potential energy (Hartree term) reduces to

$$V_i(z) = \frac{e^2}{\epsilon_{sc}} \sum_i N_i \left[\frac{3}{b} (1 - e^{-bz}) - ze^{-bz} \left(2 + \frac{1}{2} bz \right) \right]$$

Numerical solution of the 1D Schrödinger equation

There are various ways in which one can solve the eigenvalue problem numerically. The simplest one is the shooting method that will be explained in the context of the example shown in Fig. 9 representing an arbitrary potential energy profile. For simplicity, one usually assumes that the potential becomes infinite at some points $z = z_{\min}$ and $z = z_{\max}$ which means that the boundary conditions for the solutions of the Schrödinger equation are $\psi(z_{\min}) = \psi(z_{\max}) = 0$. The proper choice of these limit points depends upon the particular problem that one is solving. For example, in the silicon inversion layer, $z_{\min} = 0$, whereas z_{\max} can be any arbitrary point in the depletion layer that is far enough from the interface, so that we can assume with certainty that the wavefunction has vanished.

The idea of the shooting method is as follows. If one is looking for a bound state, it starts with some small trial eigenvalue ϵ . Upon integrating toward larger z from z_{\min} , one can generate a solution $\psi^<(z)$, which increases exponentially through the classically forbidden region and then oscillates beyond the left turning point in the classically allowed region. The integration becomes numerically unstable if one continues the integration past the right turning point, due to the admixture of the undesirable exponentially

growing solution. Therefore, for each energy value, one generates a second solution $\psi^>(z)$, by integrating from z_{\max} to some smaller values. To determine whether the energy that one chooses at the beginning is an eigenvalue, one has to compare $\psi^<(z)$ and $\psi^>(z)$ at some matching point z_m . Since both $\psi^<(z)$ and $\psi^>(z)$ satisfy a homogeneous equation, their normalization can always be chosen so that the two functions are equal at z_m . An eigenvalue is then signaled by equality of the derivatives at the matching point. If one approximates the derivatives by their simplest finite-difference approximations, discussed later in the text, an equivalent condition is that

$$f = \frac{1}{\psi} [\psi^<(z_m - h) - \psi^>(z_m - h)] = 0 \quad ,$$

where h is the step-size. The quantity ψ can be either the value of $\psi^<$ at z_m , or the maximum of $\psi^<$ or $\psi^>$. If this condition is satisfied, then one has found the eigenvalue. Otherwise, one needs to increase the energy and repeat the previously mentioned steps. The use of a bisection method can be very effective in fast location of the eigenvalues.

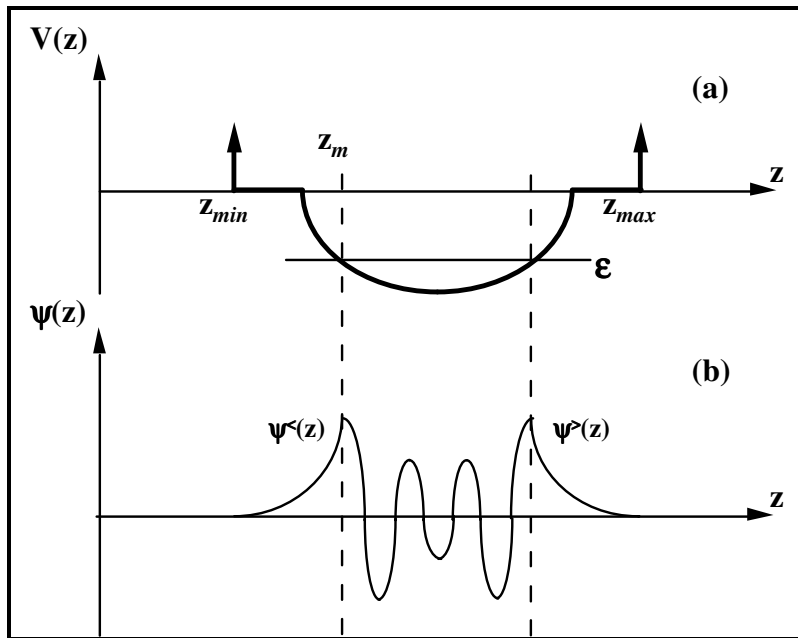


Figure 9. (a) Schematic potential used in the discussion for the shooting method. (b) Form of the solutions $\psi^<$ and $\psi^>$ at an arbitrary energy. The left turning point is used as a matching point. When ϵ is an eigenvalue, the derivative is continuous at the matching point.

In the remaining part of this section, we explain how one can numerically integrate the 1D Schrödinger equation. If some arbitrary function is known at some equidis-

tant node points (as shown in Figure 10), one can use Taylor series expansion to represent the first and second derivatives of this function in terms of the values of the function at the node points.

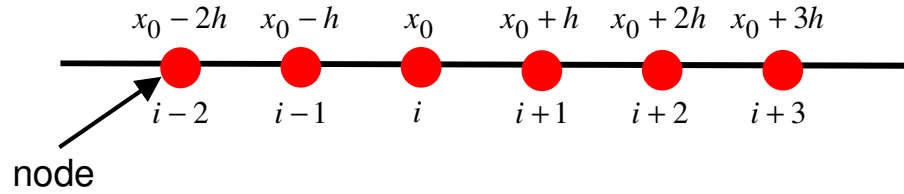


Figure 10. One-dimensional equidistant mesh.

The procedure for obtaining the finite-difference representation of the first and second derivatives on a uniform mesh is outlined below:

- Use Taylor series expansion of an arbitrary function $f(x)$:

$$\begin{aligned} f(x_0 + h) &= f(x_0) + h \left. \frac{\partial f}{\partial x} \right|_{x=x_0} + O(h^2) & f_{i+1} &\approx f_i + h \left. \frac{\partial f}{\partial x} \right|_i \\ f(x_0 - h) &= f(x_0) - h \left. \frac{\partial f}{\partial x} \right|_{x=x_0} + O(h^2) & f_{i-1} &\approx f_i - h \left. \frac{\partial f}{\partial x} \right|_i \end{aligned} \quad \rightarrow$$

In the above expressions h is the mesh size, and $O(h^2)$ is the truncation error. On the right, we have used a short-hand notation for the node values. Subtracting the second expression from the first one gives the centered finite difference expression for the first derivative at node point i :

$$\left. \frac{\partial f}{\partial x} \right|_i = \frac{f_{i+1} - f_{i-1}}{2h}$$

- Using the same arguments, we can also derive the finite-difference approximation for the second derivatives:

$$\left. \frac{d^2 f}{dx^2} \right|_i = \frac{d}{dx} \left(\left. \frac{df}{dx} \right|_i \right) = \frac{f'_{i+1/2} - f'_{i-1/2}}{h} = \frac{1}{h} \left[\frac{f_{i+1} - f_i}{h} - \frac{f_i - f_{i-1}}{h} \right] = \frac{f_{i+1} - 2f_i + f_{i-1}}{h^2}$$

- Once we have the finite-difference approximation for the second derivative, we can utilize this result to obtain the finite-difference approximation of the 1D Schrödinger equation:

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + V(x)\psi(x) = E\psi(x) \rightarrow \frac{d^2 \psi}{dx^2} + k^2(x)\psi(x) = 0 \quad ,$$

where

$$k^2(x) = \frac{2m}{\hbar^2} [E - V(x)] .$$

A simple substitution of the previously derived result for the second derivative gives:

$$\psi_{i+1} + (h^2 k_i^2 - 2)\psi_i + \psi_{i-1} = 0 .$$

- Having derived the finite-difference approximation for the 1D TISE, we can now utilize the forward and backward integration schemes, to get $\psi^>$ and $\psi^<$:

(a) forward-integration scheme:

$$\psi_{i+1} = (2 - h^2 k_i^2)\psi_i - \psi_{i-1}$$

(b) backward integration scheme:

$$\psi_{i-1} = (2 - h^2 k_i^2)\psi_i - \psi_{i+1}$$

- The initialization of the wavefunctions goes as follows: If $x=0$ ($i=0$) and $x=x_{max}$ ($i=N$) are the boundary points of our integration domain, at which we can assume with certainty that the wavefunction has vanished, then

$$\psi_0 = 0, \quad \psi_N = 0 .$$

One also needs to use some small values at the neighboring node points ($i=1$ and $i=N-1$), such as

$$\psi_1 = \psi_{N-1} = 10^{-9}$$

to ensure that we get the non-trivial solution. When performing the numerical integration from the left and from the right, to avoid overflow and underflow, one has to renormalize the wavefunctions if they exceed some predetermined maximum value.

- The eigenvalue is signaled if, for a given energy E , the second derivative is continuous, i.e. the function

$$f = \frac{1}{h\psi_i} [\psi_{i_{m-1}}^> - \psi_{i_{m-1}}^<]$$

goes to zero (this signals smoothness of the wavefunction). It is important to point out that before one evaluate f , it is necessary to match the solutions at the turning point i_m , to ensure continuity of the wavefunction. The energy variation of f is shown in the figure below. These results were obtained for a finite quantum well from Figure 8 ($L=7.5$ nm, $V_0=0.4$ V and $m=6 \times 10^{-32}$ kg). Notice that the zero's of f coincide with the values for the energy levels that we obtained using the graphical solution method.

Important note:

The graphical solution method gives only the eigenvalues for a finite square well, whereas the numerical method gives us simultaneously the eigenvalues and the corresponding eigenfunctions for an arbitrary confining potential.

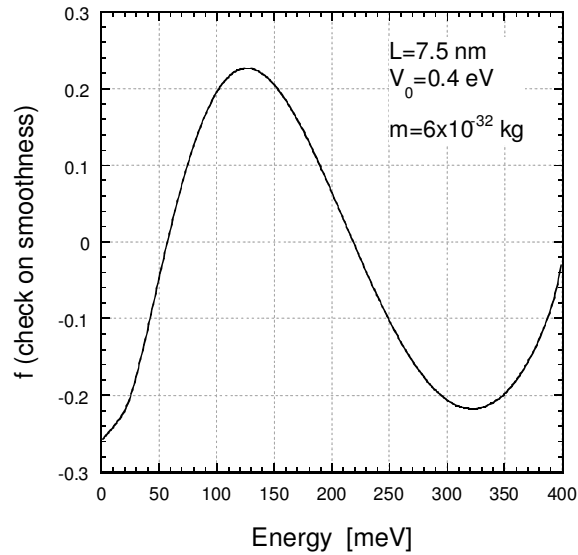


Figure 11: Energy dependence of the function f for a finite potential well, that checks the smoothness of the eigenfunctions. The zero's of f denote the energy eigenvalues for the finite potential well from Figure 3.