Lecture 6

Schrödinger Equation and relationship to electron motion in crystals

Reading:

Notes and Brennan Chapter 2.0-2.4, 7.4, 8.0-8.2 and 2.5-2.6

Schrödenger Equation

So how do we account for the wavelike nature of small particles like electrons?

Schrödenger Equation:

- In "Electrical Properties of Materials", Solymar and Walsh point out that. Like the 5 Postulates, there are NO physical assumptions available to "derive" the Schrödenger Equation

- Just like Newton's law of motion, F=ma, and Maxwell's equations, the Schrödenger Equation was proposed to explain several observations in physics that were previously unexplained. These include the atomic spectrum of hydrogen, the energy levels of the Planck oscillator, non-radiation of electronic currents in atoms, and the shift in energy levels in a strong electric field.

In Schrödinger's fourth paper he ends with:

" I hope and believe that the above attempt will turn out to be useful for explaining the magnetic properties of atoms and molecules, and also the electric current in the solid state".

Schrödenger Equation

So how do we account for the wavelike nature of small particles like electrons?

Schrödenger Equation:

- Lets start with the Classical Hamiltonian and substitute in the operators that correspond to the classical state variables.

$$KE + PE = E_{Total}$$

Potential electron moves through

Kinetic energy "operator"

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

Energy "operator"

Schrödenger Equation

To solve the Schrödinger equation one must make an assumption about the wave function. Lets assume the wave function has separate spatial and temporal components:

$$* \quad \phi(x,y,z,t) = \Psi(x,y,z)w(t)$$

Plugging this (*) into the Schrödinger equation and dividing both sides by (*) we arrive at:

$$\left(-\frac{\hbar^2}{2m}\frac{\nabla^2\Psi(x,y,z)}{\Psi(x,y,z)}+V\right) = i\hbar\frac{1}{w(t)}\frac{\partial w(t)}{\partial t}$$

Since the left hand side varies only with position, and the right hand side varies only with time, the only way these two sides can equate is if they are equal to a constant (we will call this constant, total energy, E). Thus, we can break this equation into two equations:

$$\left(-\frac{\hbar^2}{2m}\frac{\nabla^2\Psi}{\Psi}+V\right) = E \qquad\qquad E = i\hbar\frac{1}{w}\frac{\partial w}{\partial t}$$

Consider first the time variable version (right side) then later we will examine the spatially variable portion. This will give us time variable solutions and, later, a separate spatially variable solution.

Schrödenger Equation

Consider the time variable solution:

$$E = i\hbar \frac{1}{w}\frac{\partial w}{\partial t}$$

$$\frac{\partial w}{\partial t} = -\left(i\frac{E}{\hbar}\right)w$$

$$\boxed{\begin{array}{c} w(t) = e^{\left(-\left(i\frac{E}{\hbar}\right)t\right)} \quad \text{or} \quad w(t) = e^{(-i\omega t)} \\ where\ \mathrm{E} = \hbar\omega \end{array}}$$

This equation expresses the periodic time nature of the wave equation.

Introduction to Quantum Mechanics

Consider the space variable solution:

$$\left(-\frac{\hbar^2}{2m}\frac{\nabla^2\Psi}{\Psi}+V\right)=E$$

The combined "operator" is called the Hamiltonian

$$\left(-\frac{\hbar^2}{2m}\nabla^2+V\right)\Psi=E\Psi$$

$$\hat{H}\Psi=E\Psi$$

momentum "operator"

$$\left(\frac{1}{2m}\left(-j\hbar\nabla\right)^2+V\right)\Psi=E\Psi$$

$$\left(\frac{\hat{p}^2}{2m}+\hat{V}\right)\Psi=E\Psi$$

Kinetic Energy + Potential Energy = Total Energy

Classically, momentum, p=mv and kinetic energy is ½ (mv^2) = ½ $(p^2)/m$

Introduction to Quantum Mechanics

Consider a specific solution for the free space (no electrostatic potential, V=0) wave solution is (electron traveling in the +x direction in 1D only):

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\Psi = E\Psi$$

$$\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + E\Psi = 0$$

$$\boxed{\begin{gathered}\Psi(x) = Ae^{ikx} + Be^{-ikx}\\ \text{where k} = \frac{2\pi}{\lambda} = \sqrt{\frac{2mE}{\hbar^2}} \text{ or E} = \frac{\hbar^2 k^2}{2m}\end{gathered}}$$

Since we have to add our time dependent portion (see (*) previous) our total solution is:

$$\Psi = \Psi(x)w(t) = Ae^{-i(\omega t - kx)} + Be^{-i(\omega t + kx)}$$

This is a standard wave equation with one wave traveling in the +x direction and one wave traveling in the –x direction. Since our problem stated that the electron was only traveling in the +x direction, B=0.

Classically, momentum, p=mv and kinetic energy is ½ (mv^2) = ½ (p^2)/m

Introduction to Quantum Mechanics

An interesting aside: What is the value of A?

Since Ψ is a probability,

$$\int_{-\infty}^{\infty}\left[\Psi^{*}\Psi dx\right]=1$$

$$\int_{-\infty}^{\infty} Ae^{ikx}Ae^{-ikx}dx=1$$

$$\int_{-\infty}^{\infty} A^{2}e^{ikx-ikx}dx=1$$

$$\int_{-\infty}^{\infty} A^{2}dx=1$$

This requires A to be vanishingly small (unless we restrict our universe to finite size) and is the same probability for all x and t. More importantly it brings out a quantum phenomena: If we know the electrons momentum, p or k, we can not know it's position! This is a restatement of the uncertainty principle:

$$\Delta p \, \Delta x \geq \hbar/2$$

Where Δp is the uncertainty in momentum and Δx is the uncertainty in position

Wave Packet Discussion on Board:

Introduction to Quantum Mechanics

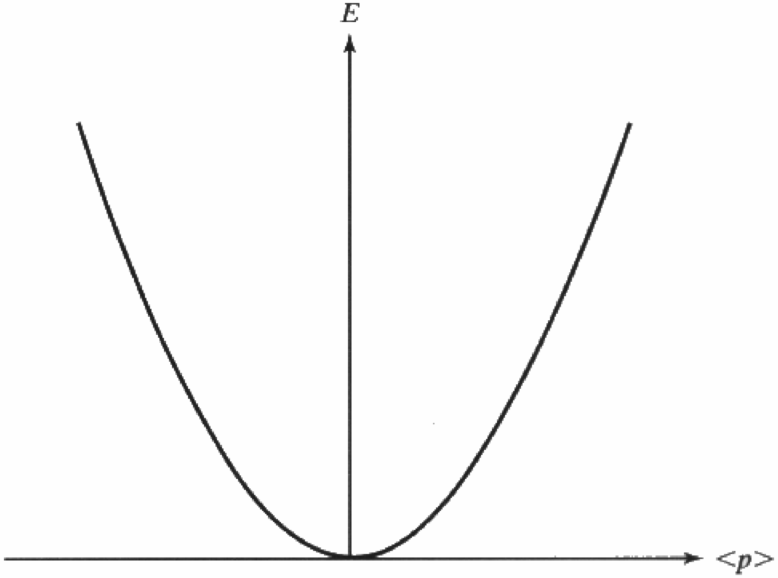
The solution to this free particle example brings out several important observations about the dual wave-particle nature of our universe:

$$\Psi = \Psi(x)w(t) = Ae^{-i(\omega t - kx)}$$

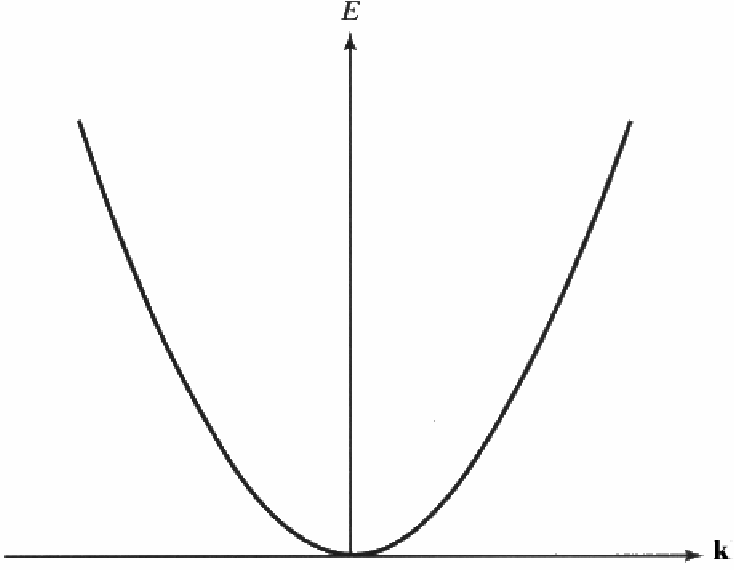
- •While particles act as waves, their charge is carried as a particle. I.e. you can only say that there is a "probability" of finding an electron in a particular region of space, but if you find it there, it will have all of it's charge there, not just a fraction.
- •Energy of moving particles follows a square law relationship:

$$E = \frac{\hbar^2 k^2}{2m} = \frac{\langle p \rangle^2}{2m}$$

Neudeck and Pierret Fig 2.3



Energy–momentum relationship for a free particle.



Energy–momentum relationship for a free particle.

Classically, momentum, p=mv and kinetic energy is $(mv^2)/2 = (p^2)/2m$

Introduction to Quantum Mechanics

What effect does this "E-k" square law relationship have on electron velocity and mass?

The group velocity (rate of energy delivery) of a wave is:

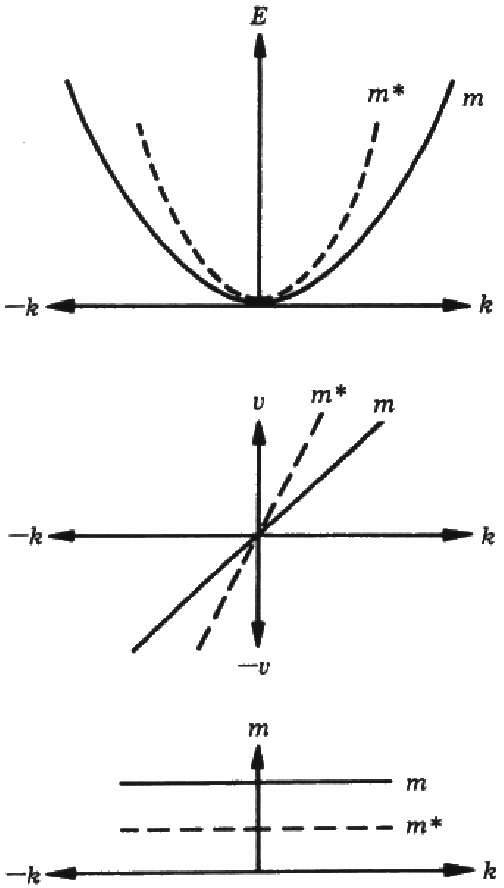
$$v_g \equiv \frac{dE}{dp} = \frac{1}{\hbar}\frac{dE}{dk}$$

So the "speed" of an electron in the direction defined by **p** is found from the slope of the E-k diagram.

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

$$m^* = \hbar^2 \left(\frac{d^2 E}{dk^2} \right)^{-1}$$

So the "effective mass" of an electron is related to the local inverse curvature of the E-k diagram



E–k diagram for a free electron with mass *m* (solid line) and a smaller mass, *m**. The parabolic *E–k* diagram leads to a linear *v* versus *k* relation and a constant mass.

Note: Brennan section 8.1 rigorously derives the equation for v_g and m^*

Figure after Mayer and Lau Fig 12.2

What effect does an electrostatic potential have on an electron?

Consider the electron moving in an electrostatic potential, V_o. The wave solution is (electron traveling in the +x direction in 1D only):

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\Psi = E\Psi$$

$$\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + \left(E - V_o\right)\Psi = 0$$

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

$$\text{where k} = \frac{2\pi}{\lambda} = \sqrt{\frac{2m\left(E - V_o\right)}{\hbar^2}} \text{ or E} = \frac{\hbar^2 k^2}{2m} - V_o$$

Since we have to add our time dependent portion (see (*) previous) our total solution is:

$$\Psi = \Psi(x)w(t) = Ae^{-i\left(\omega t - kx\right)} + Be^{-i\left(\omega t + kx\right)}$$

This is, again, a standard wave equation with one wave traveling in the +x direction and one wave traveling in the –x direction. Since our problem stated that the electron was only traveling in the +x direction, B=0.

When the electron moves through an electrostatic potential, for the same energy as in free space, the only thing that changes is the "wavelength" of the electron.

Localized Particles Result in Quantized Energy/Momentum: Infinite Square Well

First a needed tool: Consider an electron trapped in an energy well with infinite potential barriers. The reflection coefficient for infinite potential was 1 so the electron can not penetrate the barrier.

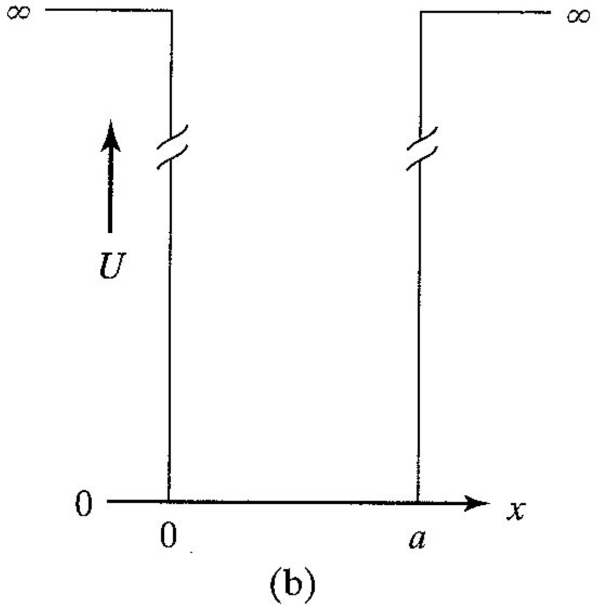
$$\left(-\frac{\hbar^2}{2m}\nabla^2+V\right)\Psi=E\Psi$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2}-E\Psi=0$$

$$\frac{\partial^2\Psi}{\partial x^2}+k^2\Psi=0$$

$$\text{General Solution: }\ \Psi(x)=A\sin(kx)+B\cos(kx)$$

$$\text{where k}=\frac{2\pi}{\lambda}=\sqrt{\frac{2mE}{\hbar^2}}\ \text{or E}=\frac{\hbar^2k^2}{2m}$$



After Neudeck and Pierret Figure 2.4a

Boundary Conditions:

$$\Psi(0)=0\ \Rightarrow\ \mathrm{B}=0$$

$$\Psi(\mathrm{a})=0\ \Rightarrow\ \mathrm{Asin(ka)}=0\ \Rightarrow\ \mathrm{k}=\frac{\mathrm{n}\pi}{\mathrm{a}}\ \text{for n}=\pm1,\pm2,\pm3...$$

$$\Psi_n(x)=A_n\sin\left(\frac{n\pi x}{a}\right)\ \text{and}\ \mathrm{E_n}=\frac{n^2\pi^2\hbar^2}{2ma^2}$$

Localized Particles Result in Quantized Energy/Momentum: Infinite Square Well

What does it mean?

$$\Psi_n(x) = A_n \sin\left(\frac{n\pi x}{a}\right) \quad \text{and} \quad \mathrm{E_n} = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

A standing wave results from the requirement that there be a node at the barrier edges (i.e. BC's: $\Psi(0)=\Psi(a)=0$). The wavelength determines the energy. Many different possible "states" can be occupied by the electron, each with different energies and wavelengths.

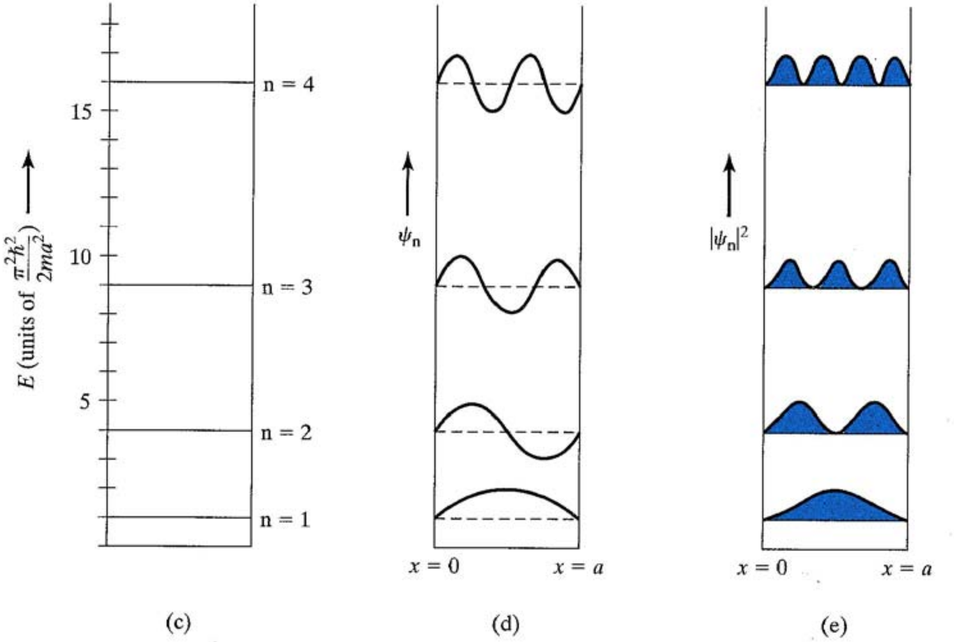


Figure 2.4 Particle in an infinitely deep one-dimensional potential well. (a) Spatial visualization of the particle confinement. (b) The assumed potential energy versus position dependence. (c) First four allowed energy levels. (d) Wavefunctions and (e) $|\psi|^2$ associated with the first four energy levels. $|\psi|^2$ is proportional to the probability of finding the particle at a given point in the potential well.

After Neudeck and Pierret Figure 2.4c,d,e

Localized Particles Result in Quantized Energy/Momentum: Infinite Square Well

What does it mean?

$$\Psi_n(x) = A_n \sin\left(\frac{n\pi x}{a}\right) \text{ and } \mathrm{E_n} = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

Solution for much larger "a". Note: offset vertically for clarity.

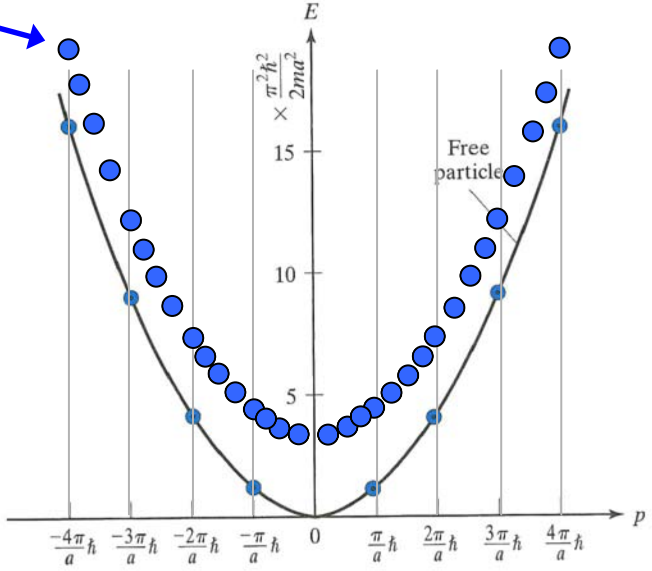


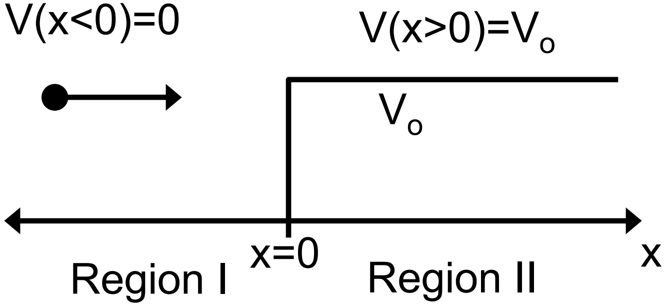
Figure 2.5 Allowed infinite-well particle energy versus counterpropagating wave momentum (discrete points) referenced against the free particle E–$\langle p \rangle$ relationship.

Recall, a free particle has E ~k^2. Instead of being continuous in k^2, E is discrete in n^2! I.e. the energy values (and thus, wavelengths/k) of a confined electron are quantized (take on only certain values). Note that as the dimension of the "energy well" increases, the spacing between discrete energy levels (and discrete k values) reduces. In the infinite crystal, a continuum same as our free particle solution is obtained.

After Neudeck and Pierret Figure 2.5

What about an electrostatic potential step?

Consider the electron incident on an electrostatic potential barrier, V_o. The wave solution (1D only):



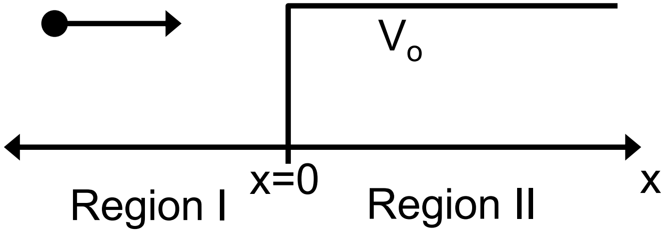
We have already solved these in regions I and II. The total solution is:

$$\Psi_I = \Psi_I(x)w_I(t) = A_I e^{-i(\omega t - k_I x)} + B_I e^{-i(\omega t + k_I x)}$$

$$\Psi_{II} = \Psi_{II}(x)w_{II}(t) = A_{II} e^{-i(\omega t - k_{II} x)} + B_{II} e^{-i(\omega t + k_{II} x)}$$

$$\text{where } k_I = \frac{2\pi}{\lambda_I} = \sqrt{\frac{2mE}{\hbar^2}} \quad \text{and} \quad k_{II} = \frac{2\pi}{\lambda_{II}} = \sqrt{\frac{2m(E - V_o)}{\hbar^2}}$$

What about an electrostatic potential step?



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$$\Psi_I = \Psi_I(x)w_I(t) = A_I e^{-i(\omega t - k_I x)} + B_I e^{-i(\omega t + k_I x)}$$

$$\Psi_{II} = \Psi_{II}(x)w_{II}(t) = A_{II} e^{-i(\omega t - k_{II} x)} + B_{II} e^{-i(\omega t + k_{II} x)}$$

$$\text{where } \mathrm{k_I} = \frac{2\pi}{\lambda_I} = \sqrt{\frac{2mE}{\hbar^2}} \quad \text{and} \quad \mathrm{k_{II}} = \frac{2\pi}{\lambda_{II}} = \sqrt{\frac{2m(E - V_o)}{\hbar^2}}$$

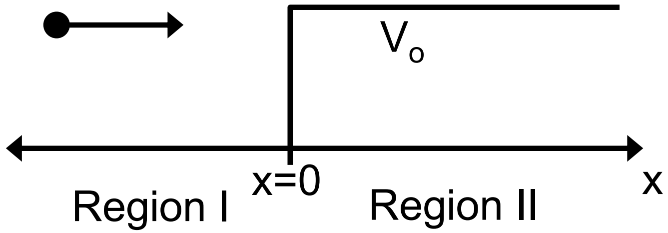
When the "wave" is incident on the barrier, some of it is reflected, some of it is transmitted. However, since there is nothing at x=+∞ to reflect the wave back, B_{II}=0.

$$\Psi_I = \overbrace{A_I e^{-i(\omega t - k_I x)}}^{\text{Incident Wave}} + \overbrace{B_I e^{-i(\omega t + k_I x)}}^{\text{Reflected Wave}} \qquad \Psi_{II} = \overbrace{A_{II} e^{-i(\omega t - k_{II} x)}}^{\text{Transmitted Wave}}$$

Energy is conserved across the boundary so,

$$\overbrace{\hbar\varpi_I = E_{incident} = \frac{\hbar^2 k_I^2}{2m}}^{\text{Incident Wave}} = \overbrace{E_{reflected} = \hbar\varpi_I}^{\text{Reflected Wave}} = \overbrace{E_{transmitted} = \frac{\hbar^2 k_{II}^2}{2m} + V_o = \hbar\varpi_{II}}^{\text{Transmitted Wave}}$$

What about an electrostatic potential step?



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We can apply our probability current density concept,

$$\rho \equiv \Psi^*(r)\Psi(r) \qquad \vec{j} = \frac{\hbar}{2mi}\left(\Psi^*(r)\vec{\nabla}\Psi(r) - \Psi(r)\vec{\nabla}\Psi^*(r)\right) \qquad \vec{\nabla}\bullet\vec{j} + \frac{\partial\rho}{\partial t} = 0$$

to define transmission, T, and reflection coefficients, R, such that the transmission and reflection probability is

$$T^*T \equiv \left|\frac{J_{transmitted}}{J_{incident}}\right| \quad and \quad R^*R \equiv \left|\frac{J_{reflected}}{J_{incident}}\right|$$

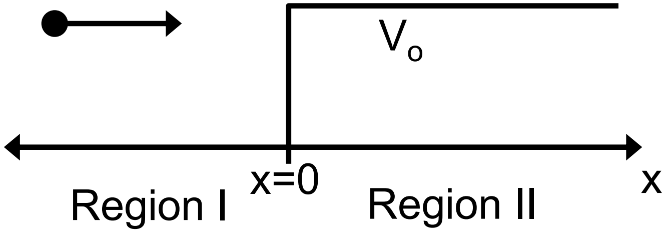
$$J_{Incident} = \frac{\hbar}{2mi}\left(\Psi_I^*\frac{d\Psi_I}{dx} - \Psi_I\frac{d\Psi_I^*}{dx}\right) = \frac{\hbar}{2mi}\left((+ik_I)A_I^* e^{+i(\omega t - k_I x)} A_I e^{-i(\omega t - k_I x)} - (-ik_I)A_I e^{-i(\omega t - k_I x)} A_I^* e^{+i(\omega t - k_I x)}\right)$$

$$J_{Incident} = \frac{\hbar}{2mi}\left(i2k_I A_I A_I^*\right)$$

Similarly,

$$J_{Transmitted} = \frac{\hbar}{2mi}\left(i2k_{II} A_{II} A_{II}^*\right) \quad \text{and} \quad J_{\mathrm{Re}\,flected} = -\frac{\hbar}{2mi}\left(i2k_I B_I B_I^*\right)$$

What about an electrostatic potential step?



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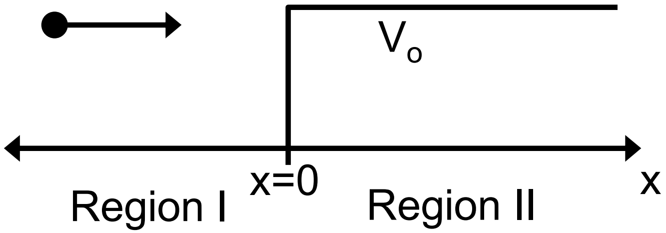
Thus,

$$T^*T \equiv \left|\frac{J_{transmitted}}{J_{incident}}\right| \quad and \quad R^*R \equiv \left|\frac{J_{reflected}}{J_{incident}}\right|$$

$$T^*T = \left|\frac{k_{II}\left(A_{II}A_{II}^*\right)}{k_I\left(A_IA_I^*\right)}\right| \quad \text{and} \quad R^*R = \frac{k_I\left(B_IB_I^*\right)}{k_I\left(A_IA_I^*\right)} = \frac{\left(B_IB_I^*\right)}{\left(A_IA_I^*\right)}$$

This transmission probability is dramatically different from that quoted in *MANY* quantum mechanics texts INCLUDING Brennan's. The above form (based on current flow) is valid for all cases, but the bottom form is valid for only $E \geq V_o$. Before we consider the case of $E < V_o$, it is worth considering where the error in these text (including ours) comes from.

What about an electrostatic potential step?



Consider a different approach...

$$\Psi_I = \Psi_I(x)w_I(t) = A_I e^{-i(\omega t - k_I x)} + B_I e^{-i(\omega t + k_I x)}$$

$$\Psi_{II} = \Psi_{II}(x)w_{II}(t) = A_{II} e^{-i(\omega t - k_{II} x)} + B_{II} e^{-i(\omega t + k_{II} x)}$$

$$\text{where } k_I = \frac{2\pi}{\lambda_I} = \sqrt{\frac{2mE}{\hbar^2}} \quad \text{and} \quad k_{II} = \frac{2\pi}{\lambda_{II}} = \sqrt{\frac{2m(E - V_o)}{\hbar^2}}$$

When the "wave" is incident on the barrier, some of it is reflected, some of it is transmitted. However, since there is nothing at x=+∞ to reflect the wave back, B_{II}=0.

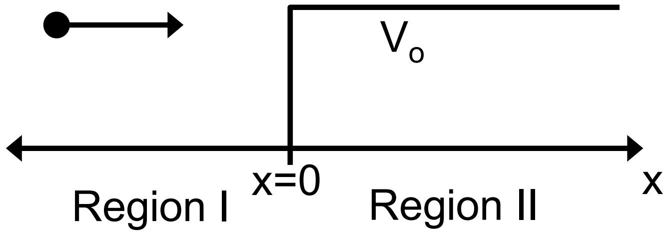
***If we use the simpler boundary condition,* ψ is a wave, both ψ and it's first derivative must be continuous across the boundary at x=0 for all time, t. Thus,**

$$\Psi_I(x=0) = \Psi_{II}(x=0) \quad \text{and} \quad \frac{\partial \Psi_I(x=0)}{\partial x} = \frac{\partial \Psi_{II}(x=0)}{\partial x}$$

$$\Rightarrow$$

$$A_I + B_I = A_{II} \quad \text{and} \quad ik_I(A_I - B_I) = ik_{II}A_{II}$$

What about an electrostatic potential step?



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$$A_I + B_I = A_{II}$$

$$and$$

$$ik_I\left(A_I - B_I\right) = ik_{II}A_{II}$$

$$ik_I\left(A_I - B_I\right) = ik_{II}\left(A_I + B_I\right)$$

$$ik_I\left(1 - \frac{B_I}{A_I}\right) = ik_{II}\left(1 + \frac{B_I}{A_I}\right)$$

$$\frac{B_I}{A_I} = \left(\frac{ik_I - ik_{II}}{ik_I + ik_{II}}\right)$$

We can define a "reflection coefficient" as the amplitude of the reflected wave relative to the incident wave,

$$R \equiv \frac{B_I}{A_I} = \frac{k_I - k_{II}}{k_I + k_{II}} \quad \text{and } R^* R \equiv \left|\frac{B_I}{A_I}\right|^2 = \left|\frac{k_I - k_{II}}{k_I + k_{II}}\right|^2$$

Same as previous case.

What about an electrostatic potential step?

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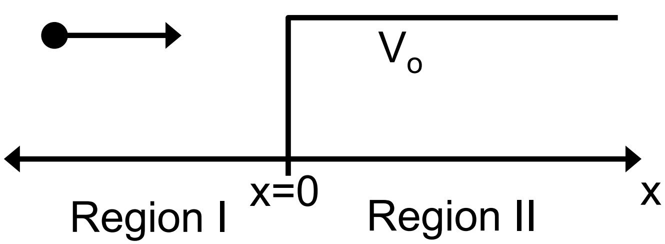

And likewise, we can define a transmission coefficient as the amplitude of the transmitted wave relative to the incident wave, $T=A_{II}/A_I$

$$A_I + B_I = A_{II}$$

and

$$ik_I\left(A_I - B_I\right) = ik_{II}A_{II}$$

$$ik_I\left(A_I - \left(A_{II} - A_I\right)\right) = ik_{II}A_{II}$$

$$ik_I\left(2A_I\right) = ik_{II}A_{II} + ik_I A_{II}$$

$$T = \frac{A_{II}}{A_I} = \frac{2k_I}{k_I + k_{II}} \quad \text{and} \quad T^*T = \left|\frac{A_{II}}{A_I}\right|^2 = \left|\frac{2k_I}{k_I + k_{II}}\right|^2$$

Notice that this approach is missing the factor (k_{II}/k_I). <u>**BIG ERROR! For this erroneous approach, $T^*T + R^*R \neq 1$.**</u>

$$k_I = \frac{2\pi}{\lambda_I} = \sqrt{\frac{2mE}{\hbar^2}} \quad \text{and} \quad k_{II} = \frac{2\pi}{\lambda_{II}} = \sqrt{\frac{2m(E-V)}{\hbar^2}}$$

What about an electrostatic potential step?

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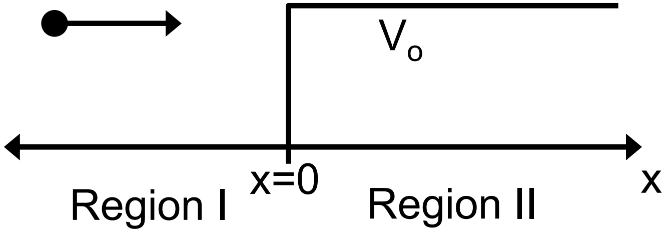

Final details:

$$T^*T = \frac{k_{II}\left(A_{II}A_{II}^*\right)}{k_I\left(A_I A_I^*\right)} \quad \text{and} \quad R^*R = \frac{\left(B_I B_I^*\right)}{\left(A_I A_I^*\right)}$$

$$\text{Since } \frac{\mathrm{A_{II}}}{\mathrm{A_I}} = \frac{2\mathrm{k_I}}{\mathrm{k_I} + \mathrm{k_{II}}} \quad \text{and} \quad \mathrm{T^*T} = \left|\frac{\mathrm{k_{II}}}{\mathrm{k_I}}\left(\frac{2\mathrm{k_I^*}}{\mathrm{k_I^*} + \mathrm{k_{II}^*}}\right)\left(\frac{2\mathrm{k_I}}{\mathrm{k_I} + \mathrm{k_{II}}}\right)\right|$$

$$\mathrm{T^*T} = \left|\frac{4\mathrm{k_{II}}}{\mathrm{k_I}}\left(\frac{1}{\left|1 + \frac{\mathrm{k_{II}}}{\mathrm{k_I}}\right|^2}\right)\right|$$

$$\mathrm{R^*R} = \left|\frac{\mathrm{k_I} - \mathrm{k_{II}}}{\mathrm{k_I} + \mathrm{k_{II}}}\right|^2$$

$$\mathrm{T^*T} + \mathrm{R^*R} = 1$$

$$\mathrm{k_I} = \frac{2\pi}{\lambda_I} = \sqrt{\frac{2mE}{\hbar^2}} \quad \text{and} \quad \mathrm{k_{II}} = \frac{2\pi}{\lambda_{II}} = \sqrt{\frac{2m(E-V)}{\hbar^2}}$$

What about an electrostatic potential step?

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Consider 2 cases: Case 1: E>V

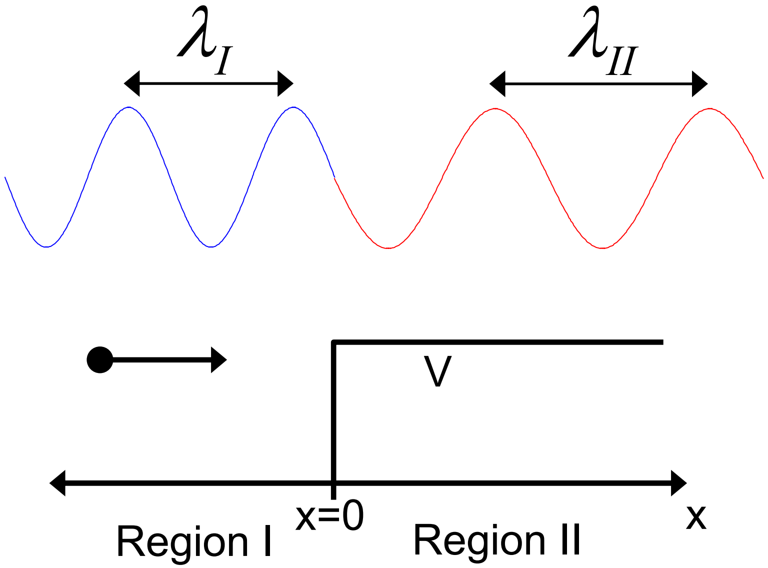
Both k_I and k_{II} are real and thus, the particle travels as a wave of different wavelength in the two regions.

However, R*R is finite. Thus, even thought the electron has an energy, E, greater than V it will have a finite probability of being reflected by the potential barrier.

If E>>V, this probability of reflection reduces to ~0 ($k_I \rightarrow k_{II}$)

$$R^*R \equiv \left|\frac{B_I}{A_I}\right|^2 = \left|\frac{k_I - k_{II}}{k_I + k_{II}}\right|^2$$

$$T^*T = \left|\frac{4k_{II}}{k_I}\left(\frac{1}{\left|1 + \frac{k_{II}}{k_I}\right|^2}\right)\right|$$



$$k_I = \frac{2\pi}{\lambda_I} = \sqrt{\frac{2mE}{\hbar^2}} \quad \text{and} \quad k_{II} = \frac{2\pi}{\lambda_{II}} = \sqrt{\frac{2m(E-V)}{\hbar^2}}$$

What about an electrostatic potential step?

cont'd...

Case 2: E<V

k_I is real but k_{II} is imaginary. When an imaginary k_{II} is placed inside our exponential, $e^{(ik_{II}x)}$, a decaying function of the form, $e^{(-ax)}$ results in region II.

A$_{II}$ can be complex

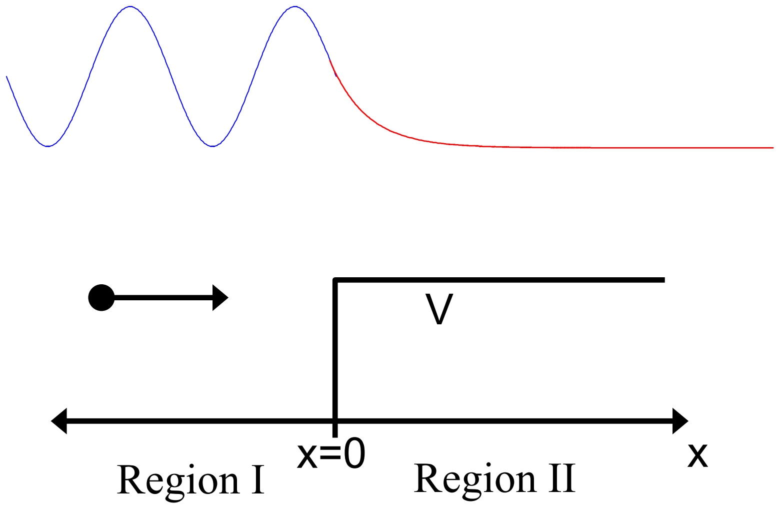
$$\Psi_{II} = \overbrace{A_{II} e^{-i(\omega t - k_{II} x)}}^{\textbf{Transmitted Wave}} = A_{II} e^{-(|k_{II}| x)} e^{-i\omega t}$$

However, T*T is now finite but evanescent. Evanescent waves carry no current (see homework). So even though the electron has an energy, E, less than V it will have a finite probability of being found within the potential barrier. The probability of finding the electron deep inside the potential barrier is ~0 due to the rapid decay of ψ.

$$R^*R \equiv \left|\frac{B_I}{A_I}\right|^2 = \left|\frac{k_I - i|k_{II}|}{k_I + i|k_{II}|}\right|^2 = \frac{z^*}{z} = 1$$

$$T^*T = 0$$

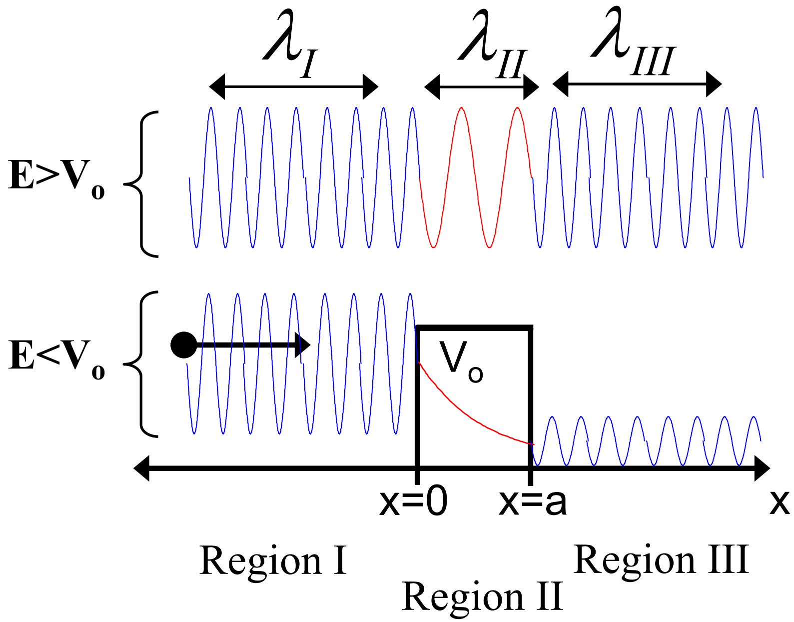
Due to $J_{Transmitted} = 0$



$$k_I = \frac{2\pi}{\lambda_I} = \sqrt{\frac{2mE}{\hbar^2}} \quad \text{and} \quad k_{II} = \frac{2\pi}{\lambda_{II}} = \sqrt{\frac{2m(E-V)}{\hbar^2}}$$

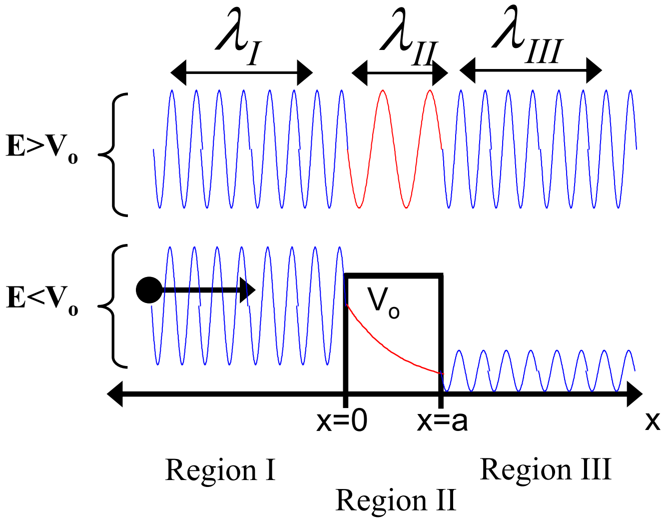
What about an electrostatic potential step?

Consider the following potential profile with an electron of energy $E<V_o$.



The electron has a finite probability to "tunnel" through the barrier and will do so if the barrier is thin enough. Once through, it will continue traveling on it's way.

What about an electrostatic potential step?



Consider the following potential profile with an electron of energy $E<V_o$.

$$\Psi_I = \overbrace{Ae^{-i(\omega t - k_1 x)}}^{\textbf{Incident Wave}} + \overbrace{Be^{-i(\omega t + k_1 x)}}^{\textbf{Reflected Wave from x=-a}}$$

$$\Psi_{II} = \overbrace{Ce^{-i(\omega t - k_2 x)}}^{\textbf{+x Wave Region II}} + \overbrace{De^{-i(\omega t + k_2 x)}}^{\textbf{Reflected Wave from x=+a}}$$

$$\Psi_{III} = \overbrace{Fe^{-i(\omega t - k_1 x)}}^{\textbf{Transmitted Wave}}$$

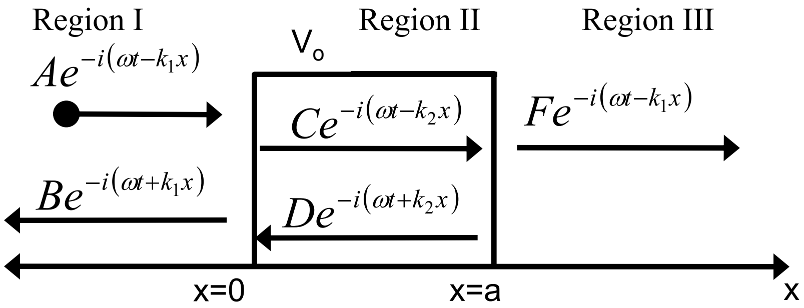
Energy is conserved across the boundary so,

$$\frac{\hbar^2 k_1^2}{2m} = E \qquad \frac{\hbar^2 k_2^2}{2m} = E - V_o \qquad \frac{\hbar^2 k_1^2}{2m} = E$$

$k_1 = \frac{2\pi}{\lambda_1} = \sqrt{\frac{2mE}{\hbar^2}}$ and $k_2 = \frac{2\pi}{\lambda_2} = \sqrt{\frac{2m(E-V)}{\hbar^2}}$

What about an electrostatic potential step?

As was found before for the currents,



$$J_{+I}=\frac{\hbar}{2mi}\left(\Psi^*_{+I}\frac{d\Psi_{+I}}{dx}-\Psi_{+I}\frac{d\Psi^*_{+I}}{dx}\right)=\frac{\hbar}{2mi}\left(\left(+ik_1\right)A^*e^{+i(\omega t-k_1x)}A\;e^{-i(\omega t-k_1x)}-\left(-ik_1\right)A\;e^{-i(\omega t-k_1x)}A^*e^{+i(\omega t-k_1x)}\right)$$

$$J_{+I}=\frac{\hbar}{2mi}\left(i2k_1AA^*\right)$$

Similarly,

$$J_{-I}=-\frac{\hbar}{2mi}\left(i2k_1BB^*\right)\quad\text{and}\quad J_{+II}=\frac{\hbar}{2mi}\left(i2k_2CC^*\right)\quad\text{and}\quad J_{-II}=-\frac{\hbar}{2mi}\left(i2k_2DD^*\right)\quad\text{and}\quad J_{+III}=\frac{\hbar}{2mi}\left(i2k_1FF^*\right)$$

Current continuity at the boundaries x = ± a implies,

$$J_{+I}+J_{-I}=J_{+II}+J_{-II}\quad\text{and}\quad J_{+II}+J_{-II}=J_{+III}$$

$$k_1AA^*+\left(-k_1BB^*\right)=k_2CC^*+\left(-k_2DD^*\right)\quad\text{and}\quad k_2CC^*+\left(-k_2DD^*\right)=k_1FF^*$$

Solving for $k_2CC^*+\left(-k_2DD^*\right)$ from the first equation and substituting into the second,

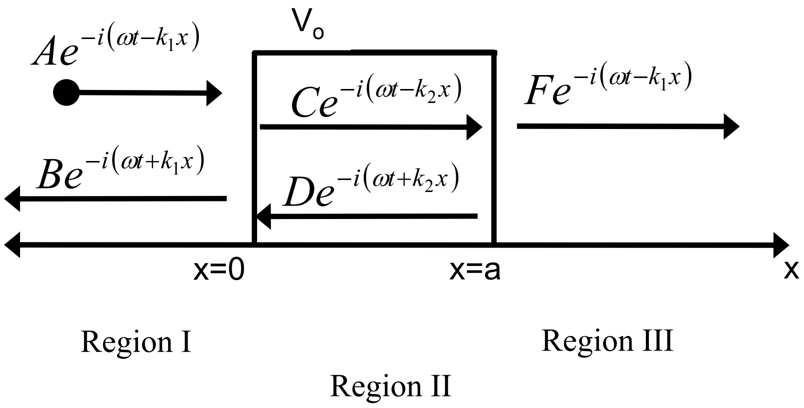
$k_1AA^*-k_1BB^*=k_1FF^*$ or rearranging and dividing through by k_1AA^*

$$1=\frac{BB^*}{AA^*}+\frac{FF^*}{AA^*}\quad\text{but,}$$

$$\quad\;\;\uparrow\qquad\;\;\uparrow$$

$$1=RR^*+TT^*\qquad\qquad\therefore\;\;\mathrm{T^*T}\equiv\left|\frac{\mathrm{F}}{\mathrm{A}}\right|^2\qquad\mathrm{R^*R}\equiv\left|\frac{\mathrm{B}}{\mathrm{A}}\right|^2$$

What about an electrostatic potential step?

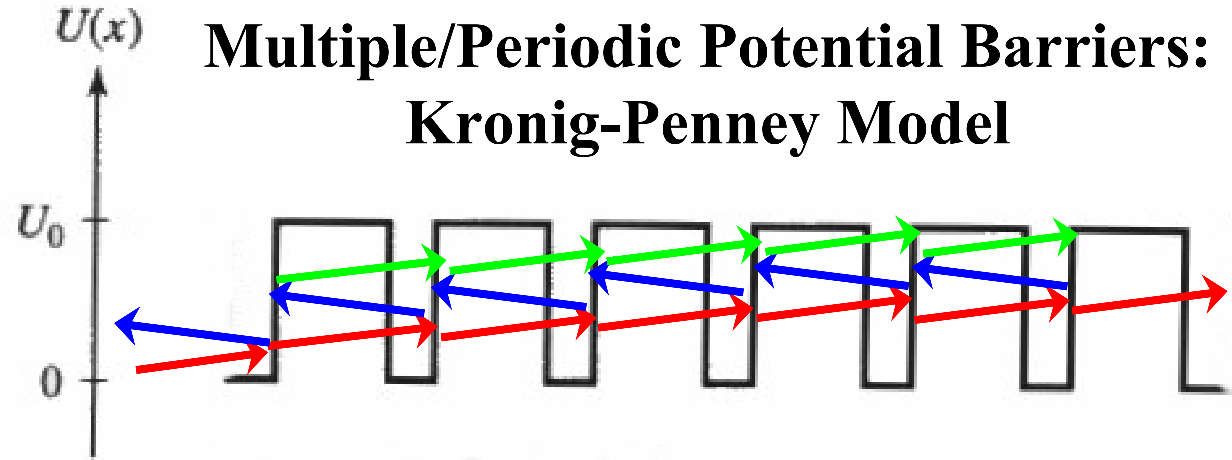


$$T^*T=?\qquad R^*R=?$$

Homework!

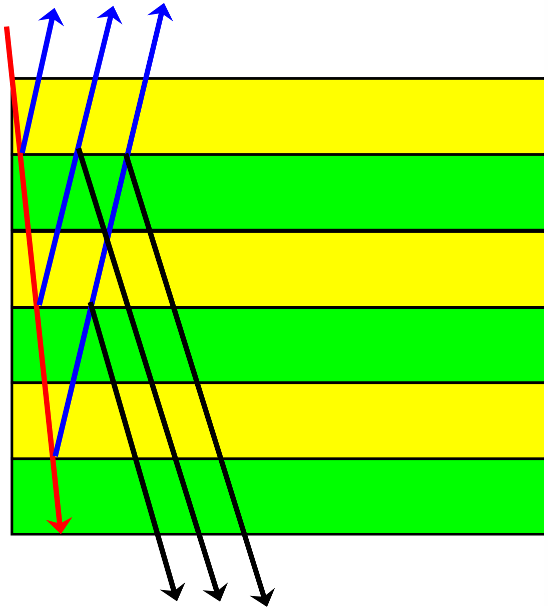
Hint: Use a combination of the continuity of the wave function and continuity of the probability density current (or equivalently in this case, the continuity of the derivative).

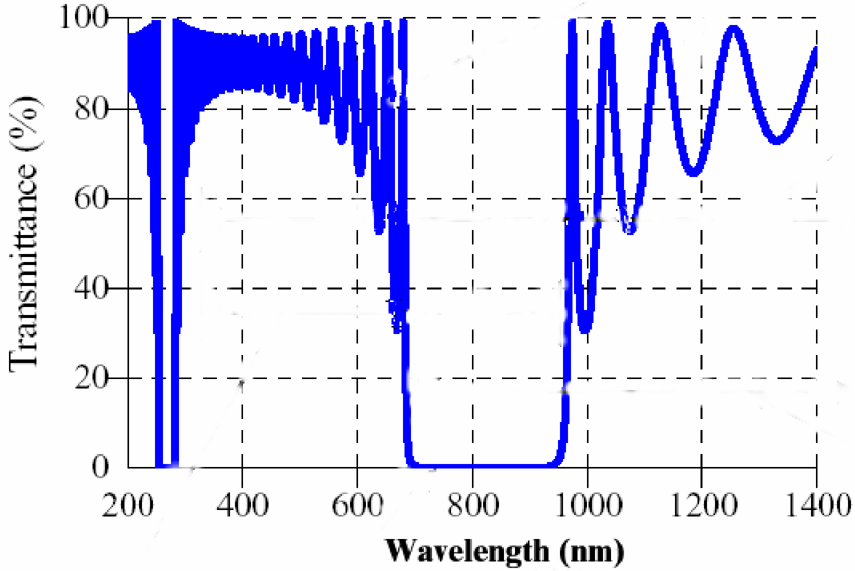
Multiple/Periodic Potential Barriers: Kronig-Penney Model

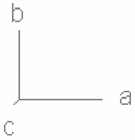


Resonant reflectance/transmission creates "standing waves" in the crystal. Only certain wavelengths (energies) can pass through the 1D crystal.

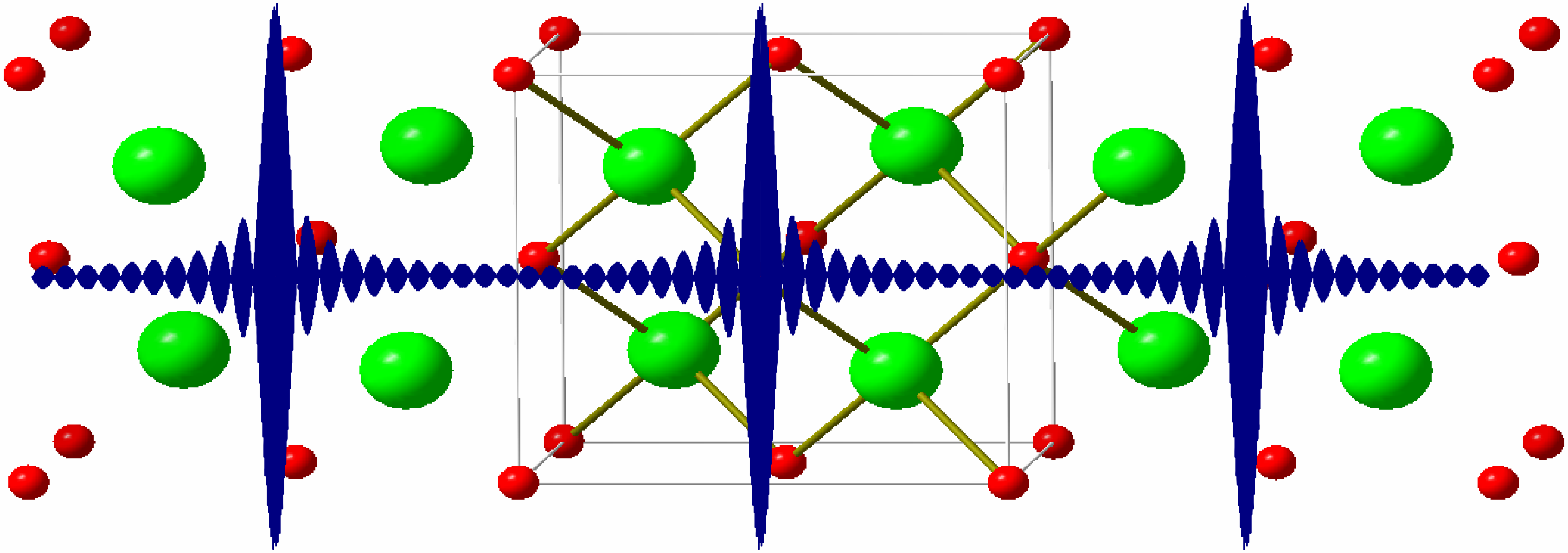
By analogy, a multiple layer optical coating has similar reflection/transmission characteristics. The result is the same, only certain wavelengths (energies) are transmitted through the optical stack. In a since, we have an "optical bandgap".







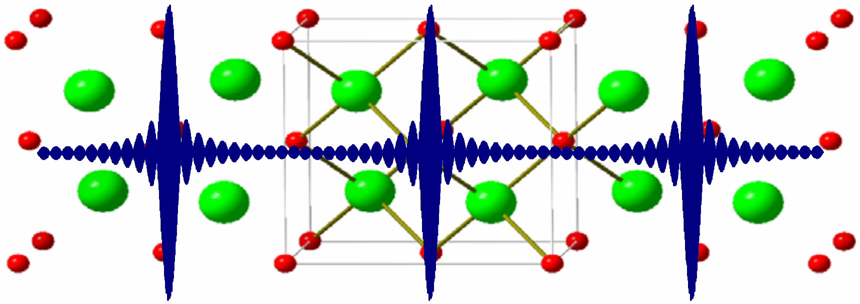
Now consider an periodic potential in 1D
Kronig-Penney Model: Bloch Functions Explained



Since each unit cell is indistinguishable from the next, the probability of finding an electron in one unit cell is identical to that of finding it in an adjacent unit cell.

The Bloch theorem states that since the potential repeats every "a" lengths, the magnitude of the wavefunction (but not necessarily the phase) must also repeat every "a" lengths. This is true because the probability of finding an electron at a given point in the crystal must be the same as found in the same location in any other unit cell.

Now consider an periodic potential in 1D Kronig-Penney Model: Bloch Functions Explained



To achieve this property, the MAGNITUDE of the wavefunction (but not necessarily the wavefunction) must have the same periodicity as the lattice. Thus, we choose a wavefunction that is modulated by the periodicity of the lattice.

$$\textit{Since } \mathrm{V(r+a)} = \mathrm{V(r)}$$

we choose plane waves modulated by a periodic function,

$$\Psi(\mathrm{r}) = \mathrm{e}^{\mathrm{ikr}} u_{\mathrm{nk}}(\mathrm{r}) \text{ where } u_{\mathrm{nk}}(\mathrm{r}) = u_{\mathrm{nk}}(\mathrm{r+a})$$

Thus,

$$\Psi(\mathrm{r+a}) = u_{\mathrm{nk}}(\mathrm{r+a})\mathrm{e}^{\mathrm{ik(r+a)}}$$

$$\Psi(\mathrm{r+a}) = \mathrm{e}^{\mathrm{ika}}\left[u_{\mathrm{nk}}(\mathrm{r})\mathrm{e}^{\mathrm{ikr}}\right] = \mathrm{e}^{\mathrm{ika}}\Psi(\mathrm{r}) \text{ or merely a phase shifted version of } \Psi(\mathrm{r})$$

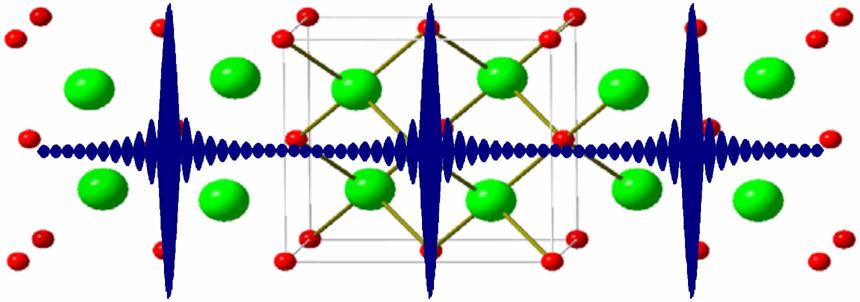
The wavefunction in one unit cell is merely a phase shifted version of the wavefunction in an adjacent unit cell.

Thus,

$$\Psi^*(\mathrm{r+a})\Psi(\mathrm{r+a}) = \mathrm{e}^{\mathrm{-ika}}\Psi^*(\mathrm{r})\mathrm{e}^{\mathrm{ika}}\Psi(\mathrm{r}) = \Psi^*(\mathrm{r})\Psi(\mathrm{r})$$

Thus, the probability of finding an electron in one unit cell is identical to that of finding it in an adjacent unit cell – as expected.

An Important Aside: Effect of Bloch Functions



Assuming a large number of unit cells in a material, N, the boundary condition for the system is Na translations must result in the wavefunction being translated to return to itself? (The probability at the material edges must be symmetric and equal).

$$\Psi(x+Na) = e^{ikNa}\Psi(x) = \Psi(x)$$

Thus,

$$e^{ikNa} = 1 \text{ so taking the Nth root,}$$

$$e^{ika} = 1^{\left(1/N\right)} = \left(e^{in2\pi}\right)^{\left(1/N\right)} = e^{\left(in2\pi/N\right)}$$

$$ka = \left(n2\pi/N\right)$$

So the allowed states of k are :

$$k = \frac{2\pi n}{Na}$$

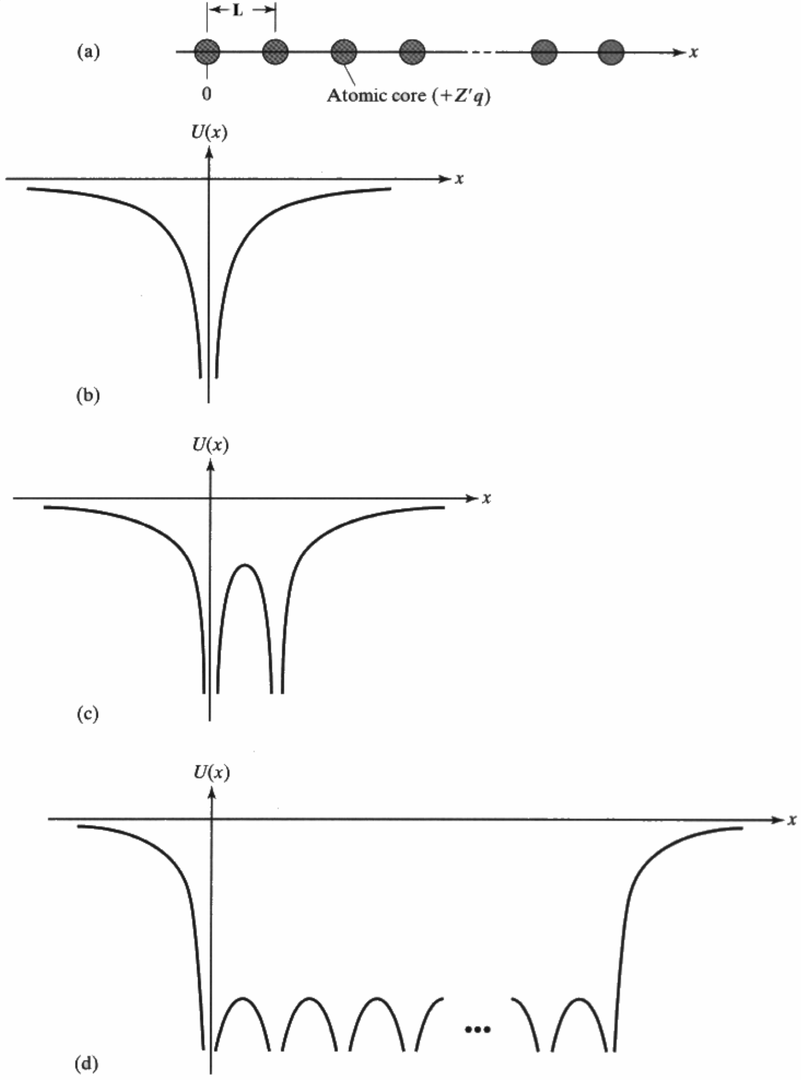
Thus, if N (the number of unit cells available) is very large, like in a semiconductor, the spacing between the allowed k-values (kn=2-kn=1 etc... are almost continuous, justifying the treatment of the k-states as a continuum.

Now consider an periodic potential in 1D
Kronig-Penney Model

Consider what potentials an electron would see as it moves through the lattice (limited to 1D for now). The electrostatic potential, V(x) is periodic such that V(x+L)=V(x).

We ***MUST*** have standing waves in the crystal that have a period equal to a multiple of the period of the crystal's electrostatic potential. (Similar to a multilayer antireflection coating in optics)

It is important to note that since, the wavefunction repeats each unit cell, we only have to consider what happens in one unit cell to describe the entire crystal. Thus, we can restrict ourselves to values of k such that –π/a to +π/a (implying ka ≤1 or (2π/λ)a≤1)



(a) One-dimensional crystalline lattice. (b–d) Potential energy of an electron inside the lattice considering (b) only the atomic core at $x = 0$, (c) the atomic cores at both $x = 0$ and $x = a$, and (d) the entire lattice chain.

After Neudeck and Peirret Fig 3.1

Now consider a periodic potential in 1D Kronig-Penney Model

Assumptions of Kronig-Penney Model:

- Simplifying the potential to that shown here:
- 1D only
- Assume electron is a simple plane wave of the form,

$$e^{ikx}$$

> ...modulated by a function with the same periodicity as the periodic crystalline potential, U(x)

- The crystalline potential is periodic, $U(x)=U(x+L)$
- Thus the wave function is a simple plain wave modulated by a function with the same periodicity as the periodic crystalline potential:

$$\Psi(x) = u_{nk}(x)e^{ikx}$$

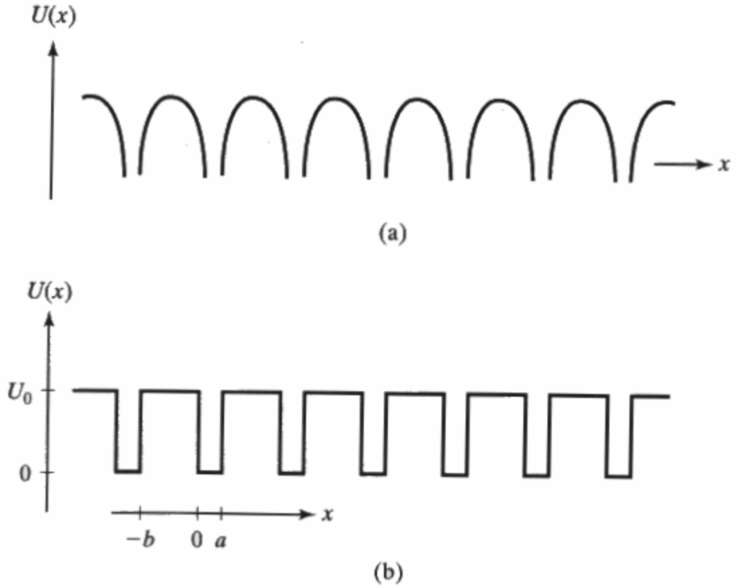


Figure 3.2 Kronig–Penney idealization of the potential energy associated with a one-dimensional crystalline lattice. (a) One-dimensional periodic potential. (b) Kronig–Penney model.

The question "how does the presence of a periodic potential effect the free electron" can thus be converted to the question "what effect on the electron does the changing of an electron's free state (plane wave) to a Bloch state"?

Neudeck and Peirret Fig 3.2

Kronig-Penney Model

For 0<x<a:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + \cancelto{0}{V}\right)\Psi = E\Psi$$

$$\frac{\partial^2\Psi}{\partial x^2} + \alpha^2\Psi = 0$$

$$\text{where } \alpha = \sqrt{\frac{2mE}{\hbar^2}}$$

$$\Psi_a(x) = A\sin(\alpha x) + B\cos(\alpha x)$$

For -b<x<0:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\Psi = E\Psi$$

$$\frac{\partial^2\Psi}{\partial x^2} + \beta^2\Psi = 0$$

$$\beta = i\sqrt{\frac{2m(E - U_o)}{\hbar^2}} \quad for\ \mathrm{E} > \mathrm{U_o}$$

$$\beta = \sqrt{\frac{2m(U_o - E)}{\hbar^2}} \quad for\ 0 < \mathrm{E} < \mathrm{U_o}$$

$$\Psi_b(x) = C\sin(\beta x) + D\cos(\beta x)$$

Kronig-Penney Model

For 0<x<a:

$$\Psi_a(x) = A\sin(\alpha x) + B\cos(\alpha x)$$

For -b<x<0:

$$\Psi_b(x) = C\sin(\beta x) + D\cos(\beta x)$$

Applying the following boundary conditions:

$$\left.\begin{aligned} &\Psi_a(x=0) = \Psi_b(x=0) \\ &\left.\frac{d\Psi_a(x)}{dx}\right|_{x=0} = \left.\frac{d\Psi_b(x)}{dx}\right|_{x=0} \end{aligned}\right\}$$

BC for continuous wave function at the boundary

$$\left.\begin{aligned} &\Psi_a(x=a) = e^{ik(a+b)}\Psi_b(x=-b) \\ &\left.\frac{d\Psi_a(x)}{dx}\right|_{x=a} = e^{ik(a+b)}\left.\frac{d\Psi_b(x)}{dx}\right|_{x=-b} \end{aligned}\right\}$$

BC for periodic wave function at the boundary

Kronig-Penney Model

Applying the boundary conditions, we get:

$$B = D$$

$$\alpha A = \beta C$$

$$A\sin(\alpha a) + B\cos(\alpha a) = e^{ik(a+b)}\left[-C\sin(\beta b) + D\cos(\beta b)\right]$$

$$\alpha A\cos(\alpha a) + \alpha B\sin(\alpha a) = e^{ik(a+b)}\left[\beta C\cos(\beta b) + \beta D\sin(\beta b)\right]$$

Eliminating the variables C and D using the above equations, we get:

$$A\left[\sin(\alpha a) + \left(\frac{\alpha}{\beta}\right)e^{ik(a+b)}\sin(\beta b)\right] + B\left[\cos(\alpha a) - e^{ik(a+b)}\cos(\beta b)\right] = 0$$

$$A\left[\alpha\cos(\alpha a) - \alpha e^{ik(a+b)}\cos(\beta b)\right] + B\left[-\alpha\sin(\alpha a) - \beta e^{ik(a+b)}\sin(\beta b)\right] = 0$$

This equation set forms a matrix of the form:

$$\begin{bmatrix} w & x \\ y & z \end{bmatrix}\begin{bmatrix} A \\ B \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

A and B are only non-zero (non-trivial solution) when the determinate of the above set is equal to zero.

Kronig-Penney Model

Taking the determinate and simplifying we get:

$$-\left(\frac{\alpha^2+\beta^2}{2\alpha\beta}\right)\sin(\alpha a)\sin(\beta b)+\cos(\alpha a)\cos(\beta b)=\cos\big(k(a+b)\big)$$

Plugging in the definitions for α and β we get:

$$\left(\frac{1-2\frac{E}{U_o}}{2\sqrt{\frac{E}{U_o}\left(\frac{E}{U_o}-1\right)}}\right)\sin\left(a\sqrt{\frac{2mU_o}{\hbar^2}}\sqrt{\frac{E}{U_o}}\right)\sin\left(b\sqrt{\frac{2mU_o}{\hbar^2}}\sqrt{\left(\frac{E}{U_o}-1\right)}\right)+\cos\left(a\sqrt{\frac{2mU_o}{\hbar^2}}\sqrt{\frac{E}{U_o}}\right)\cos\left(b\sqrt{\frac{2mU_o}{\hbar^2}}\sqrt{\left(\frac{E}{U_o}-1\right)}\right)=\cos\big(k(a+b)\big)\ \text{for E} > \text{U}_\text{o}$$

$$\left(\frac{1-2\frac{E}{U_o}}{2\sqrt{\frac{E}{U_o}\left(1-\frac{E}{U_o}\right)}}\right)\sin\left(a\sqrt{\frac{2mU_o}{\hbar^2}}\sqrt{\frac{E}{U_o}}\right)\sinh\left(b\sqrt{\frac{2mU_o}{\hbar^2}}\sqrt{\left(1-\frac{E}{U_o}\right)}\right)+\cos\left(a\sqrt{\frac{2mU_o}{\hbar^2}}\sqrt{\frac{E}{U_o}}\right)\cosh\left(b\sqrt{\frac{2mU_o}{\hbar^2}}\sqrt{\left(1-\frac{E}{U_o}\right)}\right)=\cos\big(k(a+b)\big)\ \text{for } 0 < \text{E} < \text{U}_\text{o}$$

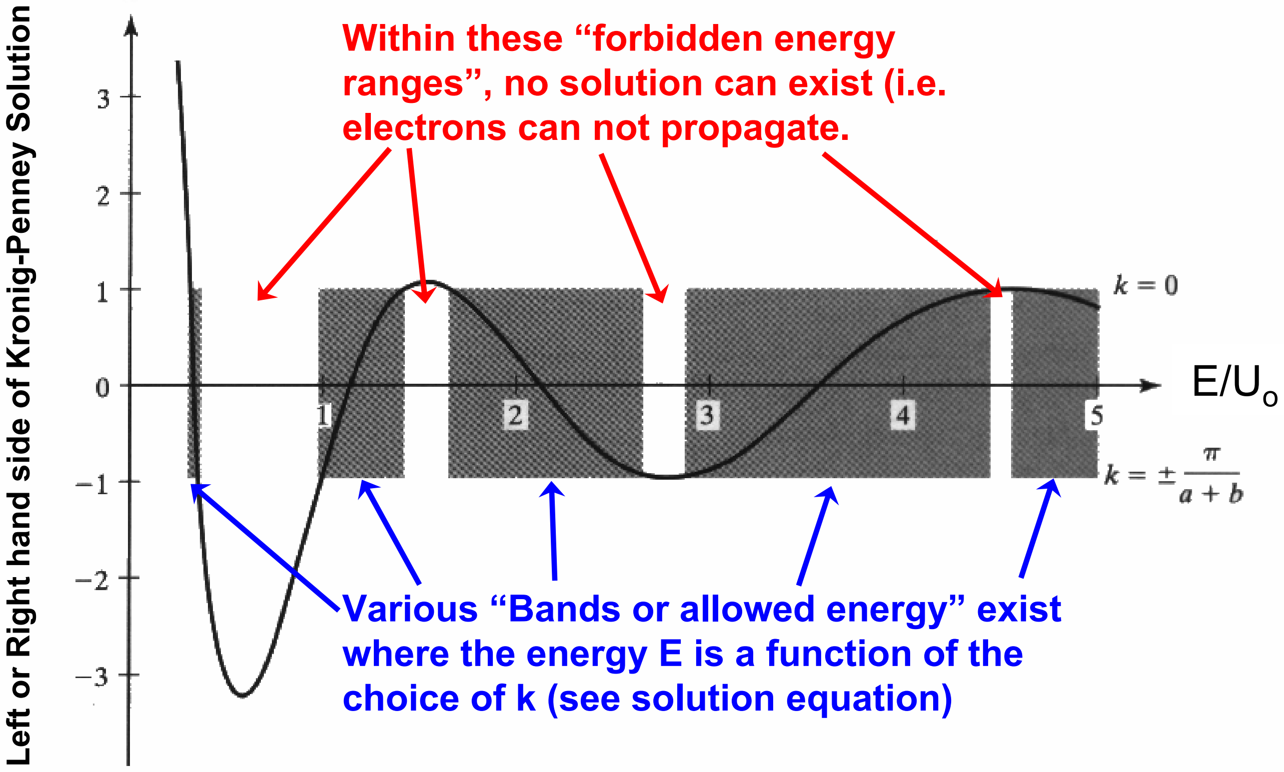
The right hand side is constrained to a range of +/- 1 and is a function of k only. The limits of the right hand side (+/- 1) occurs at k=0 and +/- π/(a+b) where a+b is the period of the crystal potential.

The left hand side is NOT constrained to +/- 1 and is a function of energy only.

Kronig-Penney Model

The right hand side is constrained to a range of +/- 1 and is a function of k only. The limits of the right hand side (+/- 1) occurs at k=0 to +/- π/(a+b).

The left hand side is NOT constrained to +/- 1 and is a function of energy only.



Within these "forbidden energy ranges", no solution can exist (i.e. electrons can not propagate.

Various "Bands or allowed energy" exist where the energy E is a function of the choice of k (see solution equation)

Graphical determination of allowed electron energies. The left-hand side of the Eqs. (3.18) Kronig–Penney model solution is plotted as a function of $\xi = E/U_0$. The shaded regions where $-1 \le f(\xi) \le 1$ identify the allowed energy states for the specific case where,

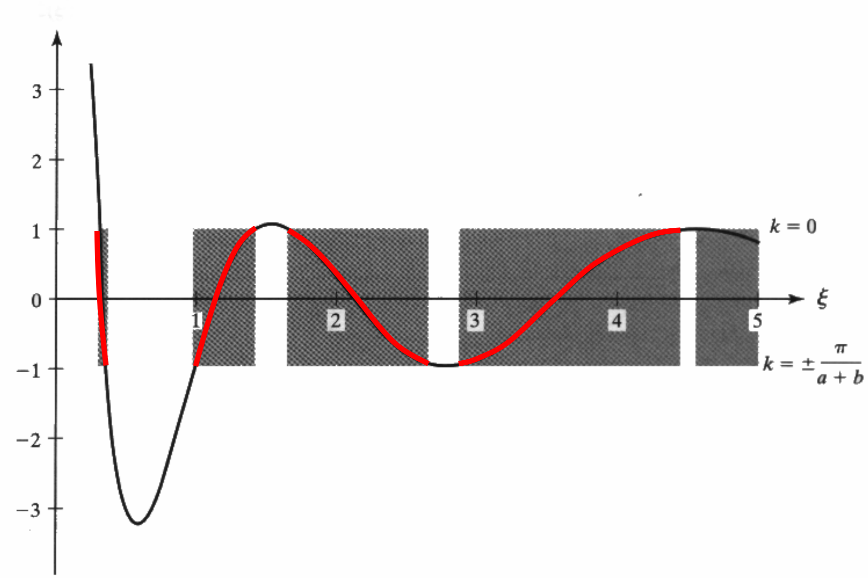
$$a\sqrt{\frac{2mU_o}{\hbar^2}} = b\sqrt{\frac{2mU_o}{\hbar^2}} = \pi$$

Kronig-Penney Model

Replotting the previous result in another form recognizing the lower k limit is shared by + and – π/(a+b) while the upper limit is for k=0.

There are at most 2 k-values for each allowed energy, E

The slope, dE/dK is zero at the k-zone boundaries at k=0, k= – π/(a+b) and k= + π/(a+b) Thus we see that the velocity of the electrons approaches zero at the zone boundaries. This means that the electron trajectory/momentum are confined to stay within the allowable k-zones.



Graphical determination of allowed electron energies. The left-hand side of the Eqs. (3.18) Kronig–Penney model solution is plotted as a function of $\xi = E/U_0$. The shaded regions where $-1 \le f(\xi) \le 1$ identify the allowed energy states ($\alpha_0 a = \alpha_0 b = \pi$).

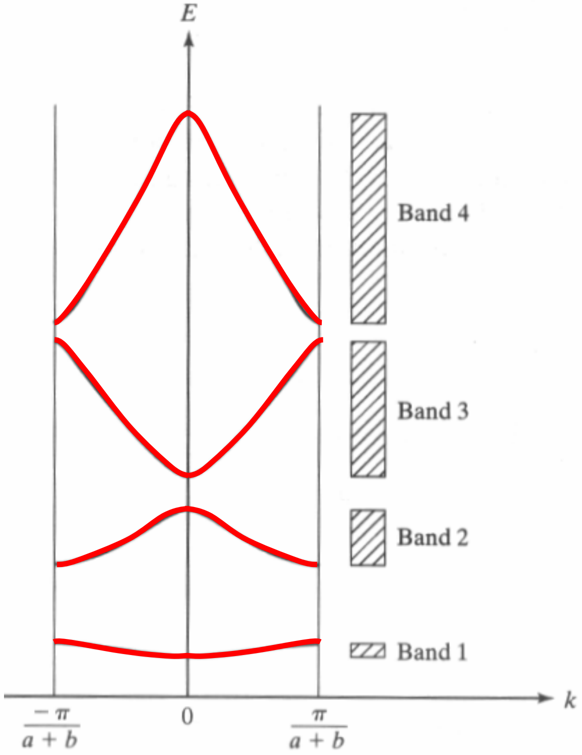


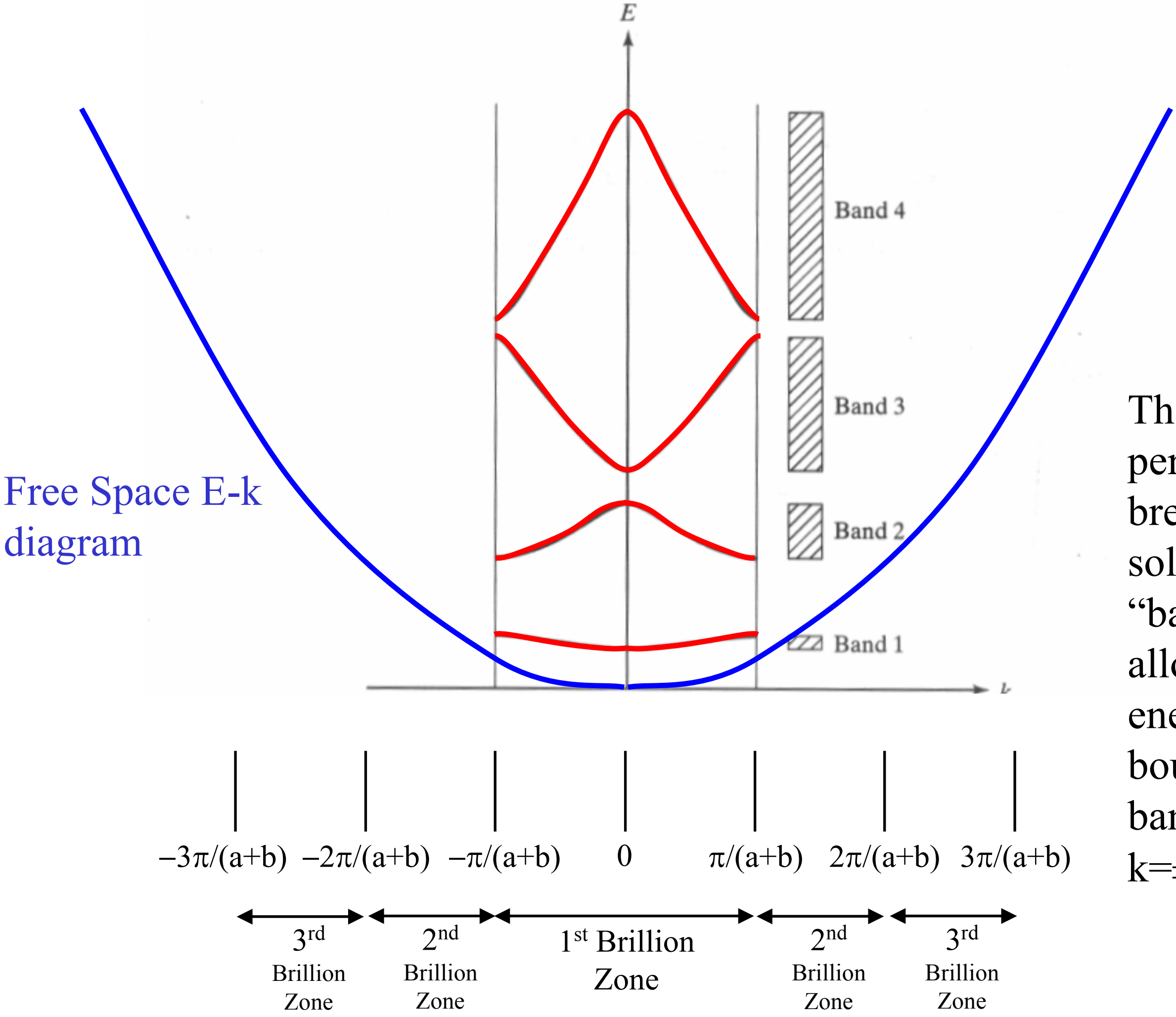
Figure 3.5 Reduced-zone representation of allowed E-k states in a one-dimensional crystal

Note: k-value solutions differing by 2π/(a+b) are indistinguishable

Figures after Neudeck and Peirret

Kronig-Penney Model

Replotting the previous result in another form ...



Free Space E-k diagram

3rd Brillion Zone

2nd Brillion Zone

1st Brillion Zone

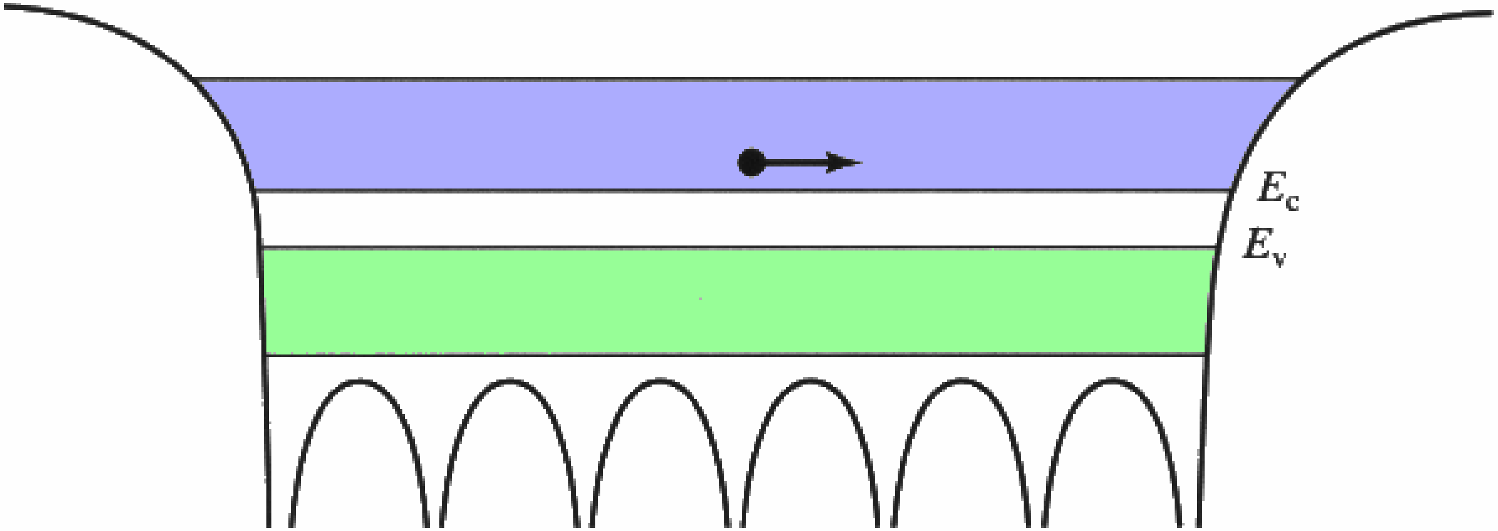
2nd Brillion Zone

3rd Brillion Zone

The presence of the periodic potential breaks the “free space solution” up into “bands” of allowed/disallowed energies. The boundaries of these bands occurs at k=±π/(a+b)

Note: k-value solutions differing by 2π/(a+b) are indistinguishable. Also due to animations printed version does not reflect same information.

Now consider an periodic potential in 1D
Kronig-Penney Model



Visualization of a conduction band electron moving in a crystal.

After Neudeck and Peirret Fig 4.1

What is the Importance of k-Space Boundaries at k=(+/-)π/a?

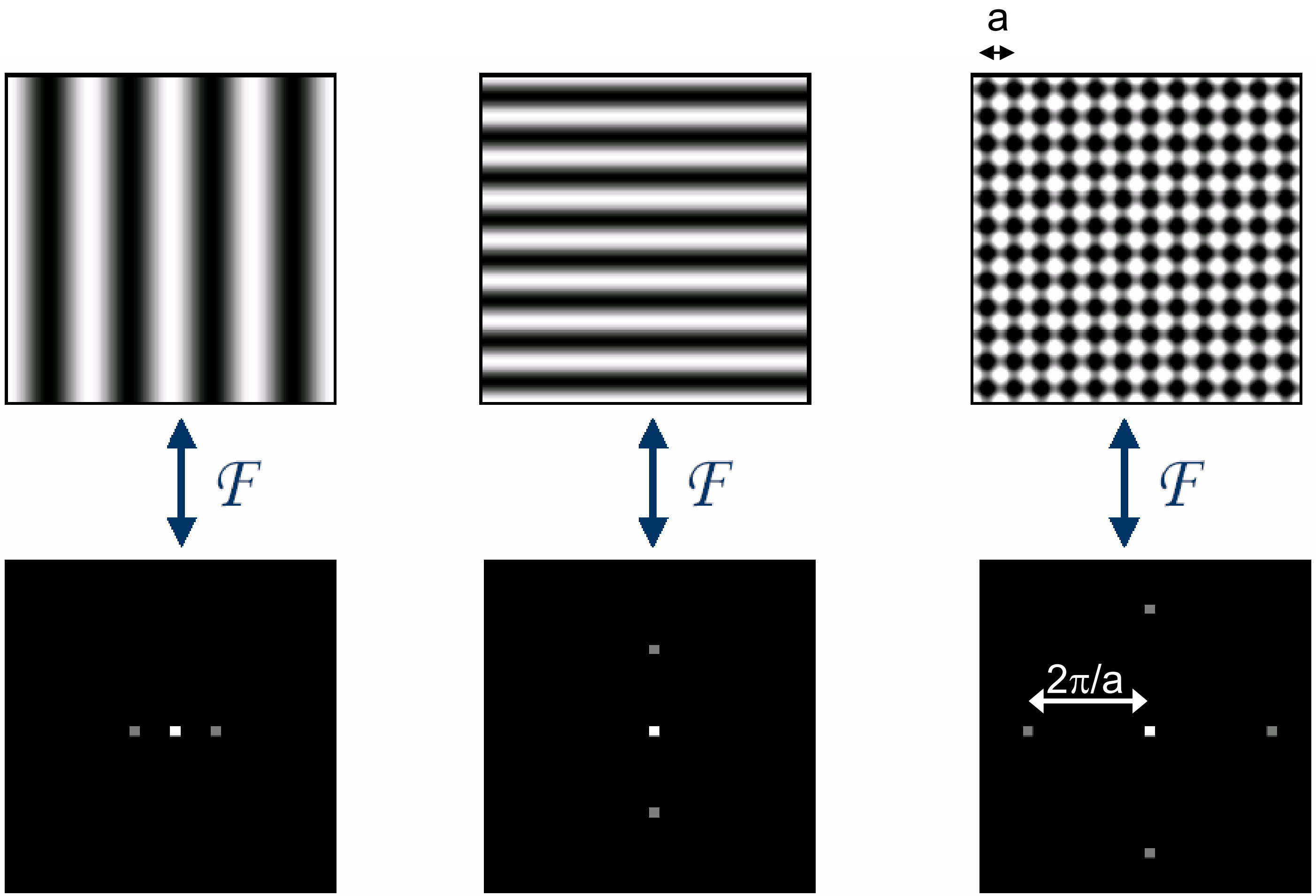
Crystal Structures, Brillouin Zones and Bragg Reflection

Concept of a Reciprocal Space

(Related to the Fourier Transform)

Real Space

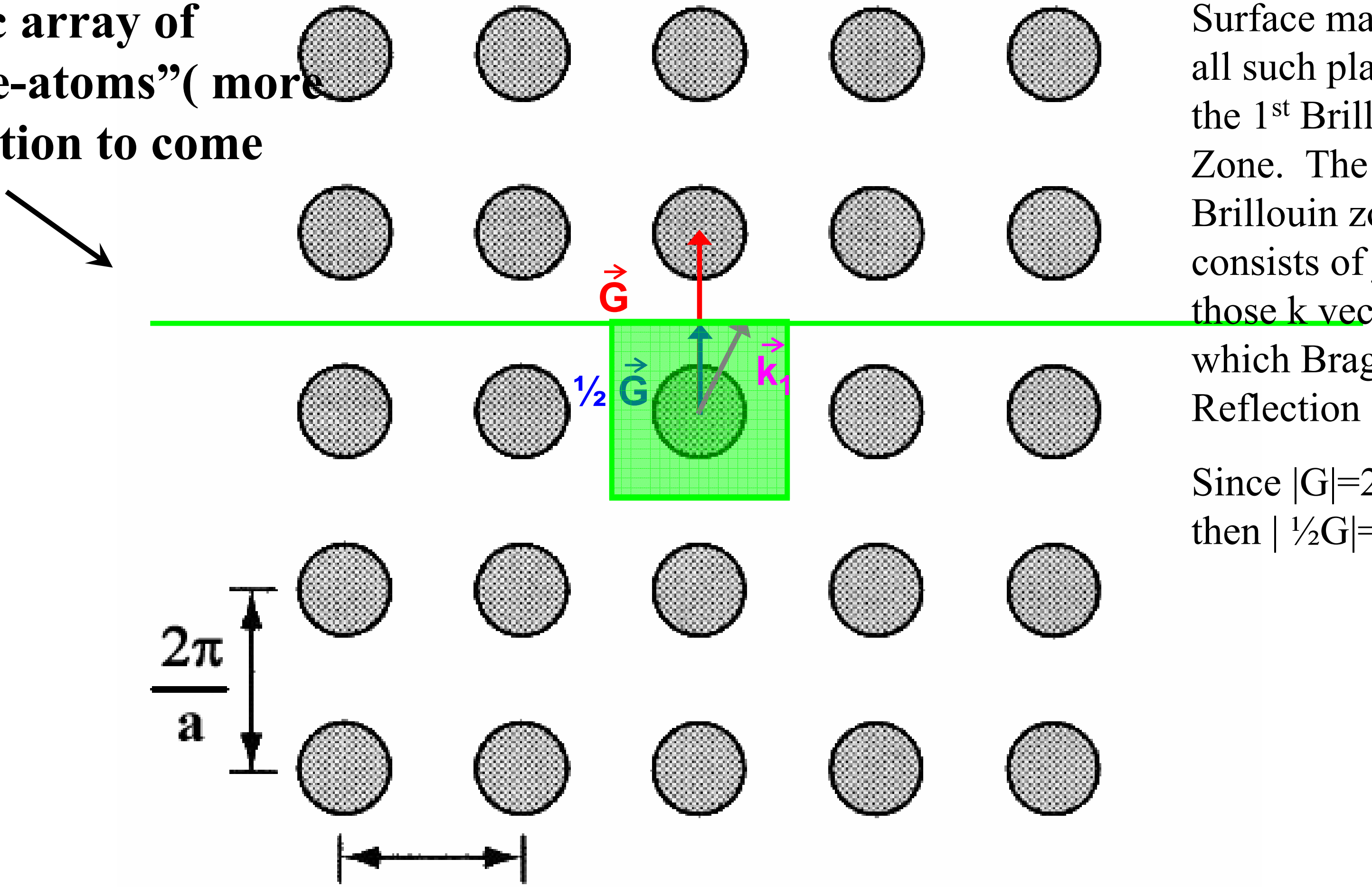
Reciprocal Space



Importance of k-Space Boundaries at k=(+/-)π/a
Crystal Structures, Brillouin Zones and Bragg Reflection

$$\vec{k}_1 \bullet \frac{1}{2}\vec{G} = \left|\frac{1}{2}\vec{G}\right|^2 \equiv \text{Bragg Reflection Condition for total internal reflection}$$

The crystal *reciprocal lattice* consists of a periodic array of "inverse-atoms"(more explanation to come later).



Surface made from all such planes is the 1st Brillouin Zone. The Brillouin zone consists of just those k vectors for which Bragg Reflection occurs.

Since |G|=2π/a then | ½G|=π/a

Importance of k-Space Boundaries at k=(+/-)π/a
Crystal Structures, Brillouin Zones and Bragg Reflection

$$\Psi(x)_{\text{for k}=\frac{\pi}{\text{a}}} \approx e^{\frac{i\pi x}{a}} + e^{-\frac{i\pi x}{a}} \text{ or } e^{\frac{i\pi x}{a}} - e^{-\frac{i\pi x}{a}}$$

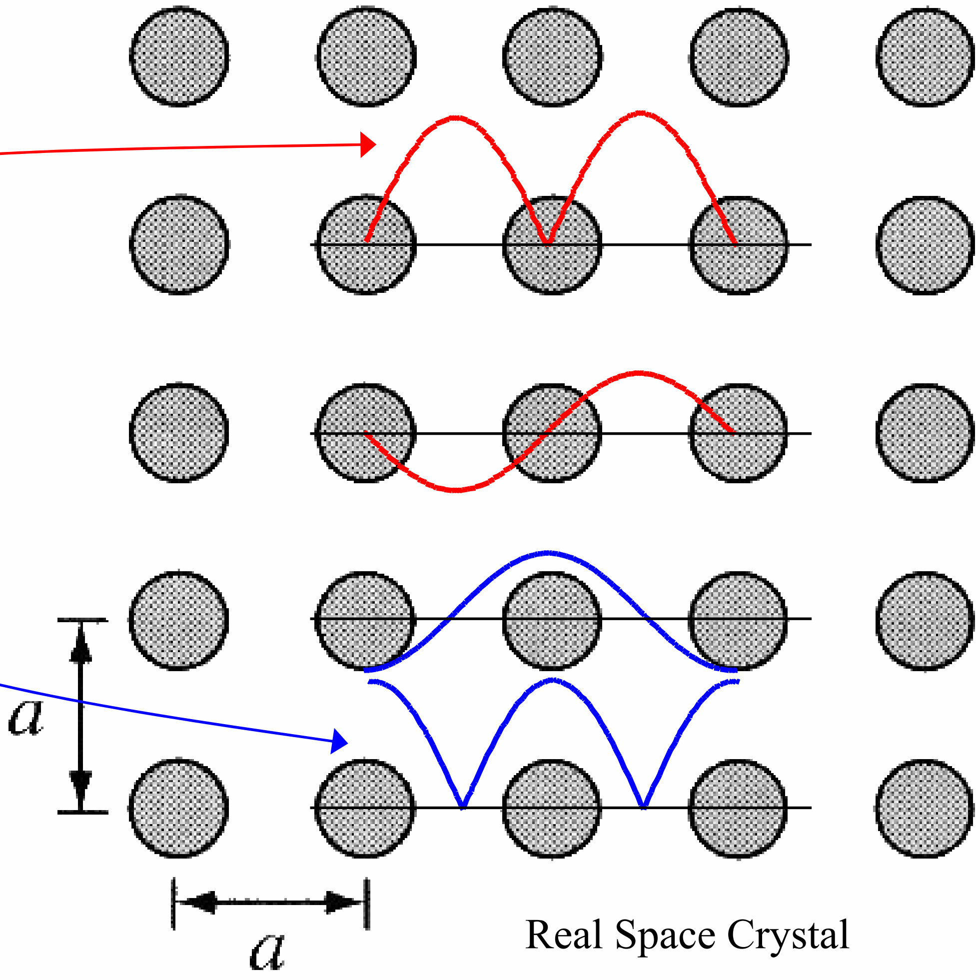
Thus,

$$\Psi(x)_{\text{for k}=\frac{\pi}{\text{a}}} \propto \cos\left(\frac{\pi \text{x}}{\text{a}}\right) \text{ or } \sin\left(\frac{\pi \text{x}}{\text{a}}\right)$$

Thus,

$$\Psi^{*}(x)\Psi(x)_{\text{for k}=\frac{\pi}{\text{a}}} \propto \cos^{2}\left(\frac{\pi \text{x}}{\text{a}}\right) \text{ or } \sin^{2}\left(\frac{\pi \text{x}}{\text{a}}\right)$$

Electrons are represented by "standing waves" of wavefunctions localized near the atom cores (i.e. valence electrons) and as far away from the cores as possible (i.e. free electrons). Given the different potential energies in both of these regions, the energies of the electrons away from the atom cores is higher. This is one explanation for the origin of the energy bandgap.



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