ChemE 2200 – Applied Quantum Chemistry Lecture 10

Today:

Free-Electron Model, continued.

Electrical Conductivity: Metals and Superconductors

The Band Theory for Solids

Defining Question:

How can two electrons with the same wavenumber have different energy?

Reading for Today's Lecture:

Electrons in Solids, pp. 11-15.

Reading for Quantum Lecture 11:

Electrons in Solids, pp. 15-18.

S. C. Johnson Information Session

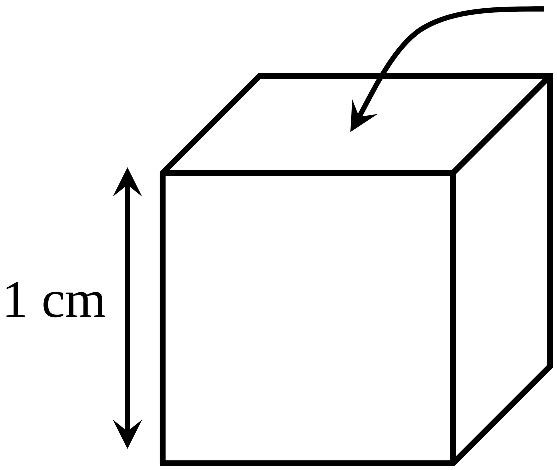
Summer Internships in Marketing,
Research & Development, Engineering

Today: 165 Statler, 5:00 p.m.

Hosted by Max Krakauer (B.S. ChemE 2012)

Recap

The Free-Electron Model of Solids



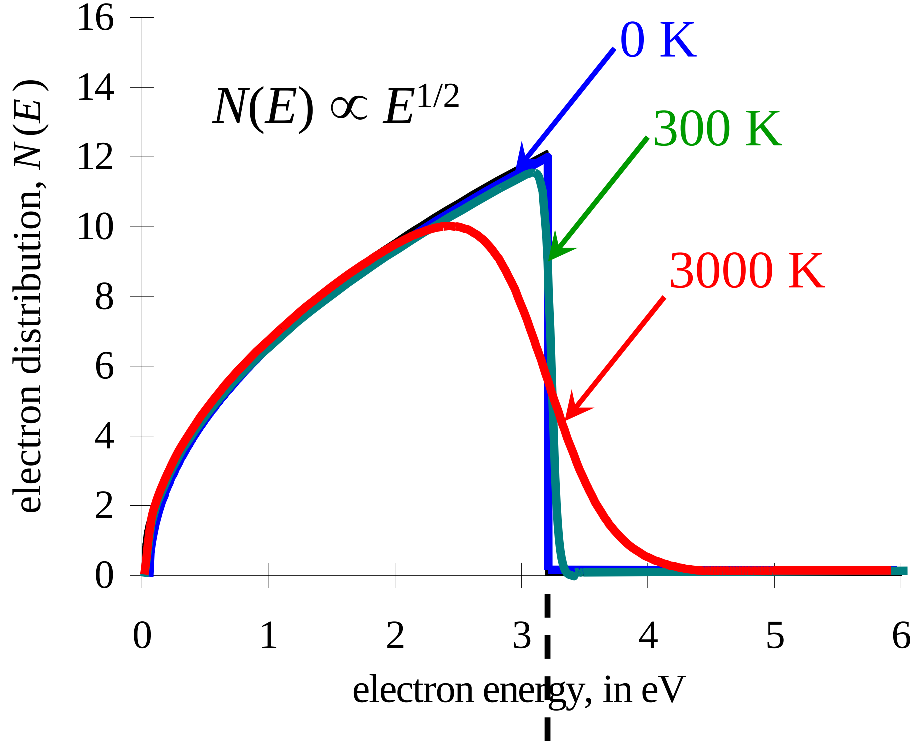
~ 10^{22} valence electrons

electrons are particles in a box $\quad E_{n_x n_y n_z} = \dfrac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$

$= 3.7 \times 10^{-15}$ eV

$= 6 \times 10^{-34}$ J

characteristic spacing
between energy levels
is *extremely* small.



Fermi level $\equiv E_F$

area under curve $\propto E_F^{3/2}$

area under curve =
number of electron states

number of electrons =
2×number of electron states

This is the 1st of two
key plots for the
Free-Electron Model.

The Electron Wavenumber

To analyze electrical conductivity, we need the net motion of the electrons.

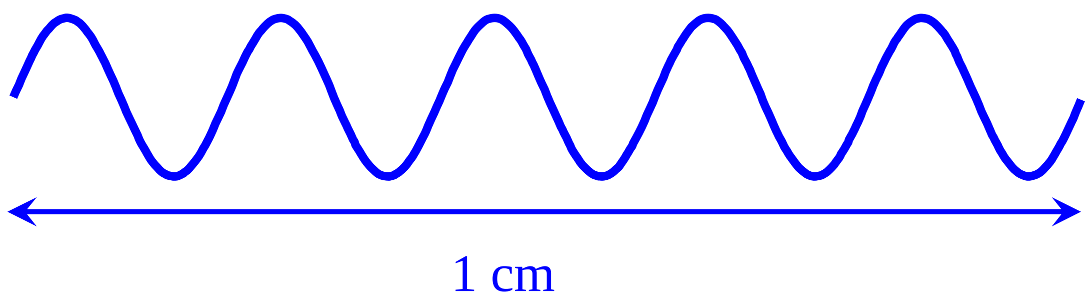
How to calculate net electron motion from electron energies?   Velocities!

Because there is no potential in the box, each electron's energy is its kinetic energy.

$$E = \frac{1}{2}mv^2$$

For $v_x > 0$, the electron is moving to the right.   For $v_x < 0$, the electron is moving to the left.

Physicists prefer electron wavenumber to describe electron motion.



9 nodes $\Rightarrow n_x = 10$

$$k_x = \frac{(2\pi)(\frac{1}{2}n_x)}{L}$$

$$k_x = \frac{\pi n_x}{L}$$

$$\text{wavenumber} = k_x = \frac{5\text{ cycles}}{1\text{ cm}} = \frac{5\,(2\pi\text{ radians})}{1\text{ cm}} = \frac{10\pi}{\text{cm}}$$

$$\text{wavelength} = \lambda = \frac{1\text{ cm}}{5\text{ cycles}} = 0.2\text{ cm}$$

$$\left.\right\} \quad k_x = \frac{2\pi}{\lambda}$$

The Electron Wavenumber vs. the Photon Wavenumber

$$\text{electron wavenumber} = k = \frac{2\pi}{\text{wavelength}} = \frac{2\pi}{\lambda} \qquad [k] = \frac{\text{radians}}{\text{cm}} \qquad 1 \text{ cycle} = 2\pi \text{ radians}$$

cf. photon wavenumber. velocity = speed of light for photons (photon rest mass = 0).

$$\text{photon wavenumber} = \tilde{v} = \frac{1}{\text{wavelength}} = \frac{1}{\lambda} \qquad [\tilde{v}] = \frac{\text{cycles}}{\text{cm}}$$

$$\tilde{v} = \frac{\text{frequency}}{c} = \frac{v}{c}$$

See Lecture Q4, slide 10.

The Electron Wavenumber and Electron Energy

$$k_x = \frac{2\pi}{\lambda} = \frac{\pi n_x}{L}$$

Express electron velocity in terms of wavenumber.   Start with the de Broglie wavelength.

$$\lambda = \frac{h}{p} = \frac{h}{m_e v}$$

Solve for velocity: $v_x = \dfrac{h}{m_e \lambda} = \dfrac{h}{m_e \dfrac{2\pi}{k_x}} = \dfrac{h}{2\pi}\dfrac{k_x}{m_e}$

$$v_x = \frac{\hbar k_x}{m_e}$$

Electron energy is entirely kinetic: $E = \dfrac{1}{2} m_e v^2 = \dfrac{1}{2} m_e \left(\dfrac{\hbar k_x}{m_e}\right)^2 = \dfrac{\hbar^2 k_x^2}{2 m_e}$

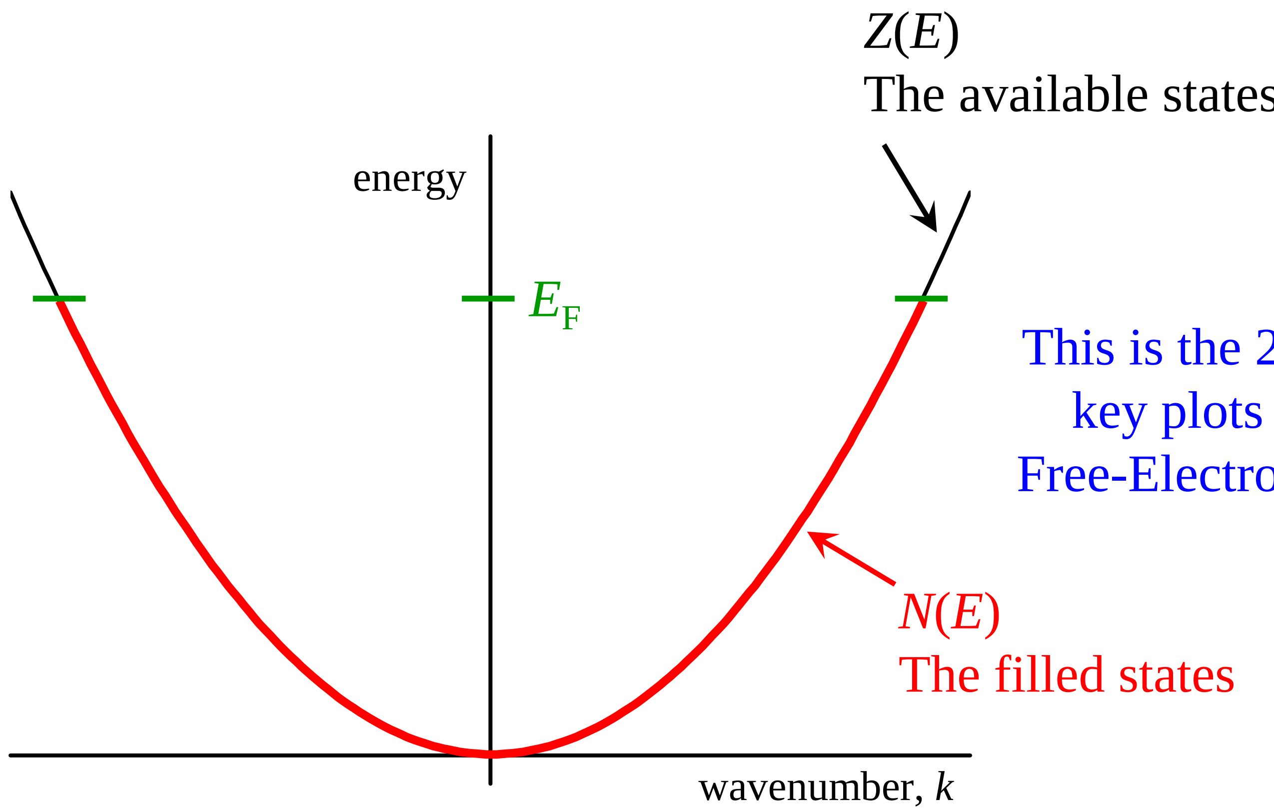
Particle in a 1-D box: $E = \dfrac{h^2}{8 m_e L^2} n_x^2 = \dfrac{h^2}{8 m_e \cancel{L^2}} \left(\dfrac{k_x \cancel{L}}{\pi}\right)^2 = \left(\dfrac{h}{2\pi}\right)^2 \dfrac{k_x^2}{2 m_e} = \dfrac{\hbar^2 k_x^2}{2 m_e}$ ✓

The Electron Wavenumber and Electron Energy

$$E = \frac{\hbar^2 k_x^2}{2m_e}$$

$$v_x = \frac{\hbar k_x}{m_e}$$

a parabola:



This is the 2nd of two key plots for the Free-Electron Model.

$$\sum k_x = 0$$

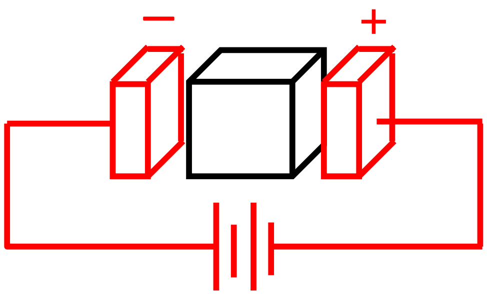
No net electron flow.

No electric current.

Electrical Current; Net Electron Flow

Electrical current requires: (1) a driving force: an electric potential

(2) empty states with wavenumbers close to occupied states.



Electromotive force = (electron charge) × (electric field)

$$F_{\text{emf}} = m_e a = m_e \frac{dv_x}{dt} = \hbar \frac{dk_x}{dt}$$

electrons accelerate without limit?!

No. Electrons collide with the lattice of nuclei (not explicit in the Free Electron model).

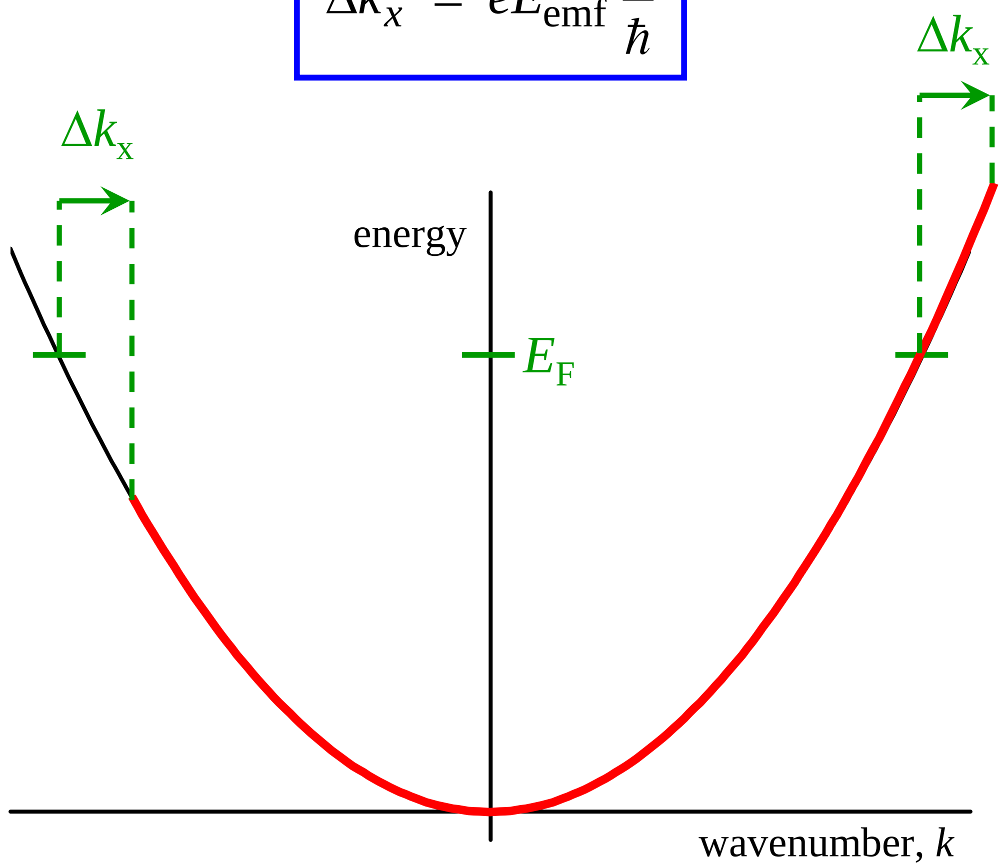
At steady state, the electromotive force balances the electrical resistivity.

For electrons that collide with the lattice on average every τ seconds,

$$\Delta k_x = eE_{\text{emf}} \frac{\tau}{\hbar}$$

Free-Electron Model Predicts Metallic Conductivity

$$\Delta k_x = eE_{\text{emf}} \frac{\tau}{\hbar}$$



$$\sum k_x > 0$$

Electric field causes net flow of electrons; an electric current.

Even the smallest applied electric field induces electric current. Metals!

The Free-Electron Model also predicts Superconductivity. See *Electrons in Solids*, pp 8-9.

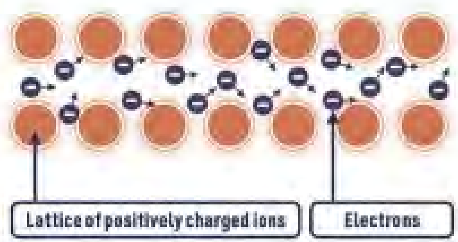
The science of superconductors

PERIODIC GRAPHICS

Superconducting materials, capable of conducting electricity without resistance, have fascinated scientists for over a century. Here we examine what they are, how they've been found, and how we use them.

What are superconductors?

When we pass electrical current through a conducting solid, electrons collide with themselves and the lattice of ions in the solid, causing resistance. At low temperatures, there are fewer vibrations, fewer collisions, and lower resistance.



In superconducting materials, electrical resistance drops to zero if they are cooled below a critical temperature (T_c) that is far below room temperature. In some superconductors, this resistance drop happens because electrons pair up and flow together, overcoming resistance. Scientists still don't know exactly how superconductivity happens in some types of superconductors.

The lattice is distorted by the first electron, creating a region of positive charge that pulls the second electron through.

A short history of superconductors

1911 The first superconductor

Physicist Heike Kamerlingh Onnes discovers superconductivity in mercury in 1911 by cooling it with liquid helium. Other scientists find superconductivity in other metals in subsequent years.

Name	Hg: Mercury	Pb: Lead
T_c	-269.2°C	-265.9°C

1986 High-temperature superconductors

J. Georg Bednorz and K. Alex Müller discover superconductivity in a copper oxide ceramic. C. W. Chu modifies this copper oxide to make a superconductor with a critical temperature achievable using liquid nitrogen as a coolant.

LaBaCuO	Lanthanum barium copper oxide	-243.1°C
YBaCuO	Yttrium barium copper oxide	-180.1°C

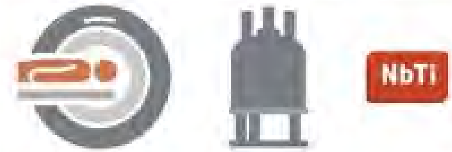
1993 Current record holder

Scientists make the highest-temperature superconductor at ambient pressure to date. Room-temperature superconductors remain elusive.

HgBaCaCuO	Mercury barium calcium copper oxide	-140.1°C

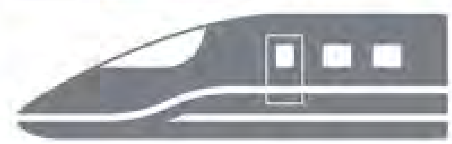
Superconductor applications

MRI scanners and NMR machines



Magnetic resonance imaging (MRI) machines in hospitals use electromagnets made from superconducting niobium-titanium (Nb-Ti) wire. Liquid helium cools the wire to superconducting temperatures. Nuclear magnetic resonance machines, which analyze organic compounds, work similarly.

Superconducting maglev trains



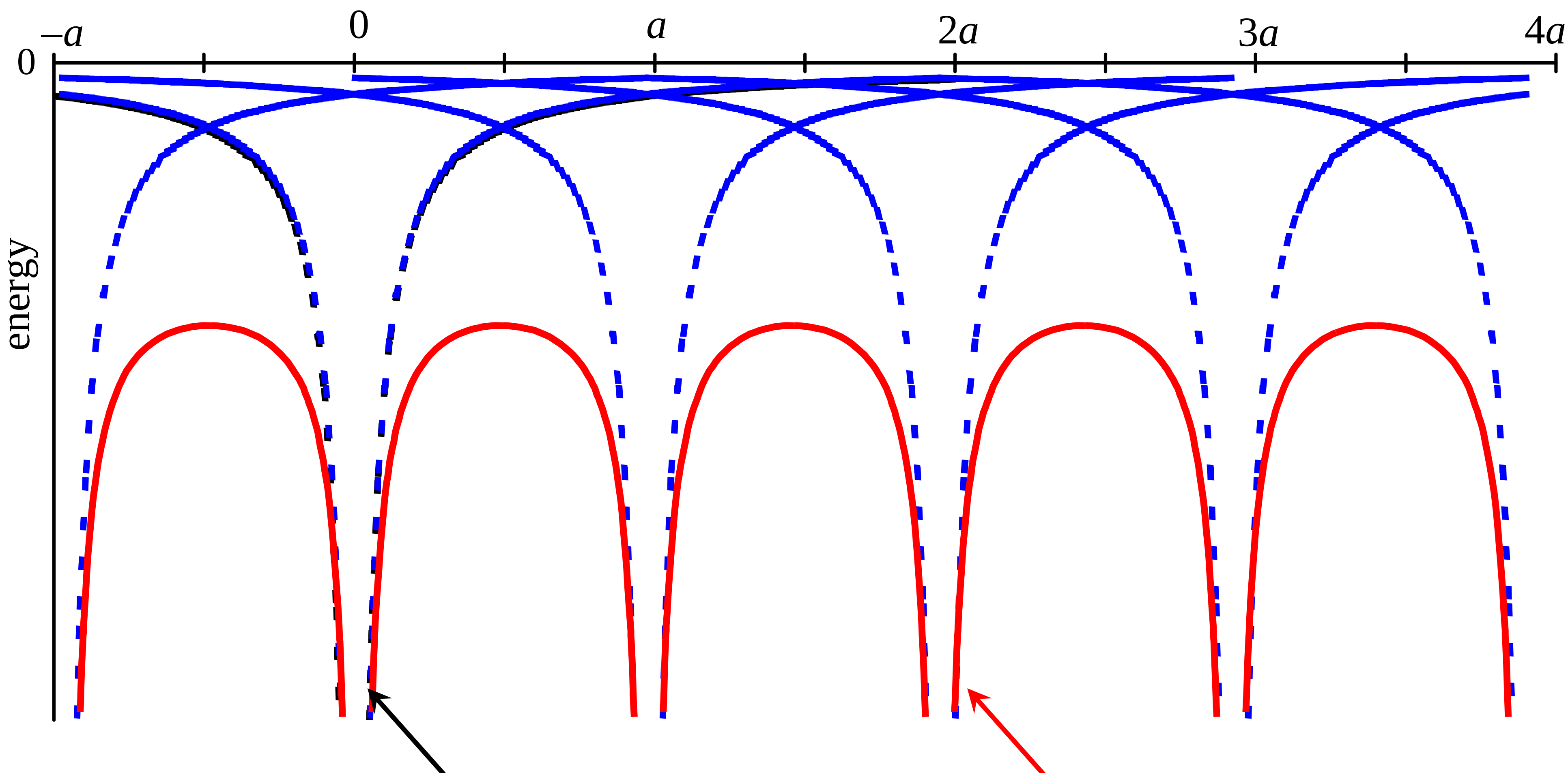
Superconducting magnetic levitation railways in Japan use Nb-Ti magnets on trains to induce a current in the metal coils positioned under the tracks and drive the train forward.

Particle accelerators

Superconducting Nb-Ti or niobium-tin magnets in particle accelerators such as the Large Hadron Collider generate the magnetic fields and electric fields needed to steer and accelerate particles.

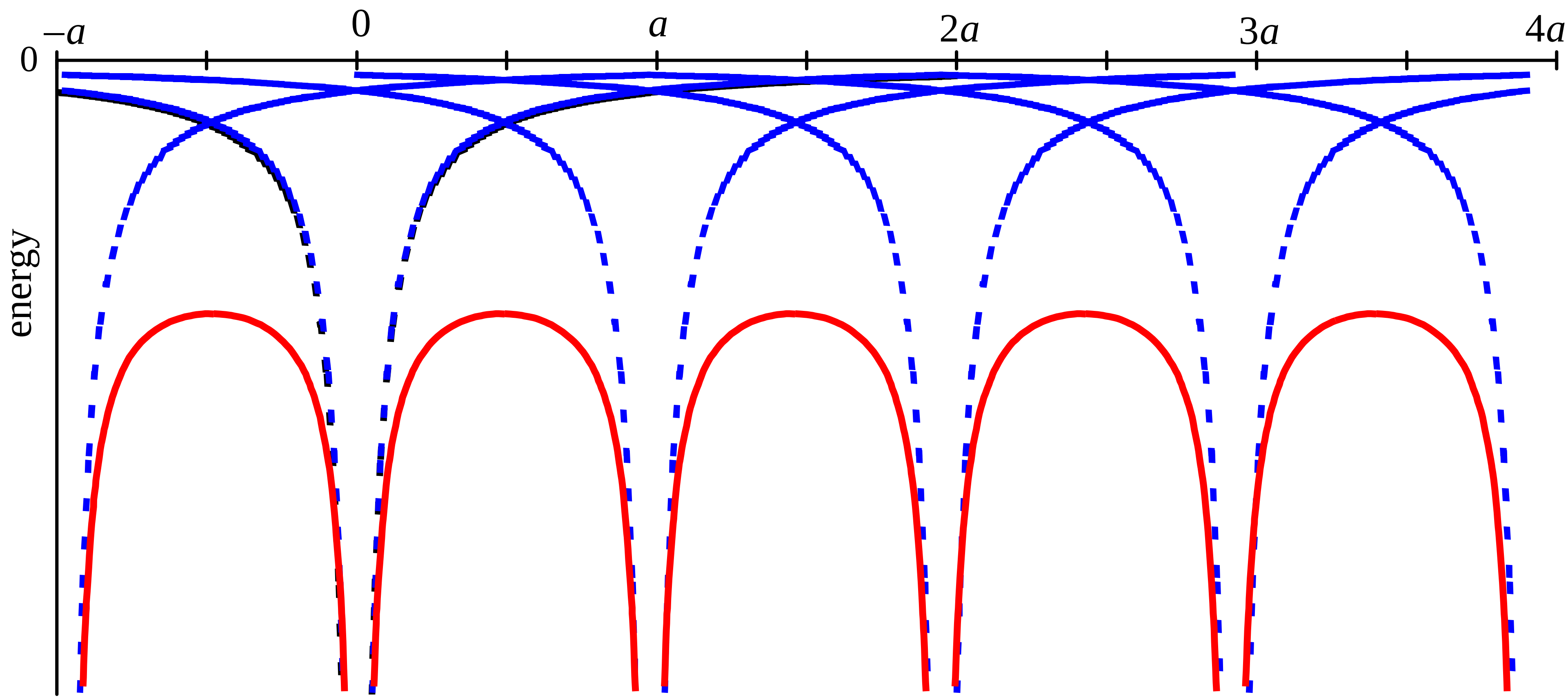
The Band Theory of Solids

Add an electric potential to represent the atomic ions.

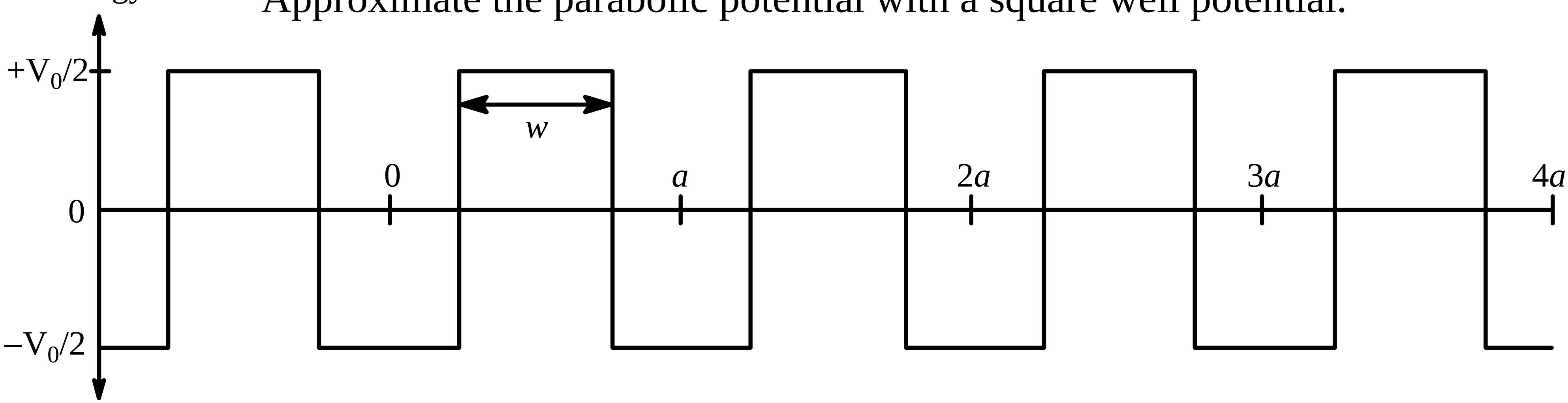


$$V(x) = \frac{-Ze^2}{4\pi\varepsilon_0}\frac{1}{x}$$

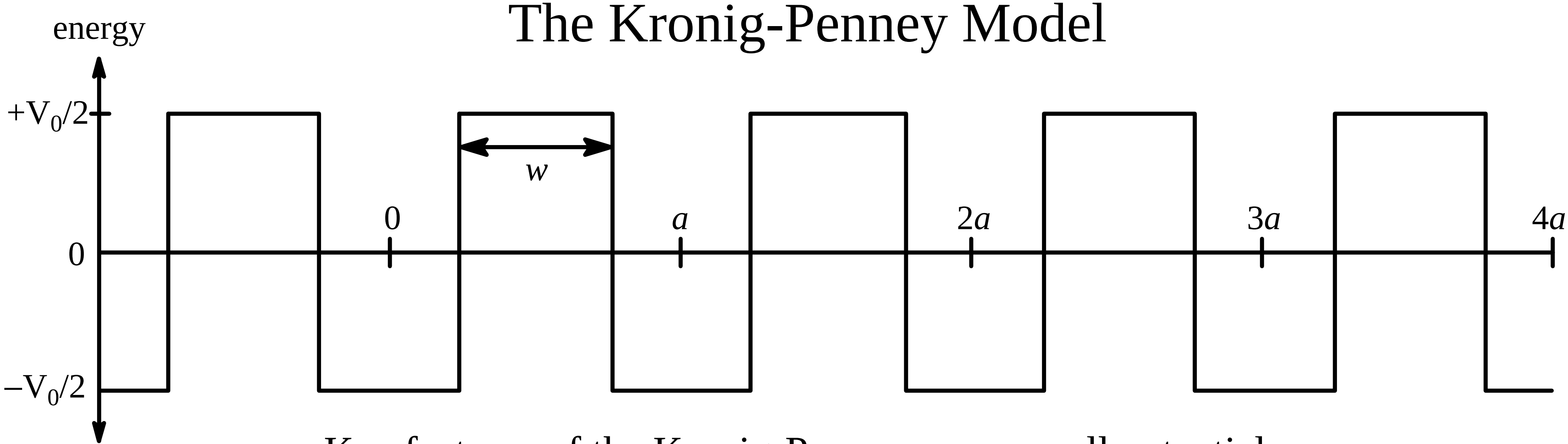
The Kronig-Penney Model



Approximate the parabolic potential with a square well potential.



The Kronig-Penney Model



Key features of the Kronig-Penney square well potential:

1. The potential is periodic. Period is set by atomic lattice spacing, *a*.

2. The potential near an atomic ion (nucleus + valence electrons) is lower than the potential between atomic ions.

3. Parameters V_0 and w can be adjusted to match electronic properties.

4. The potential yields a solvable Schrödinger equation.

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi \qquad \Rightarrow \qquad \psi(x) = u_k(x)e^{ikx}$$

Boundary conditions set wavenumber *k*:

$$\cos ka = \frac{V_0 wma}{\hbar^2}\frac{\sin \alpha a}{\alpha a} + \cos \alpha a \qquad \text{such that } \alpha = \frac{(2m_e E)^{1/2}}{\hbar}$$

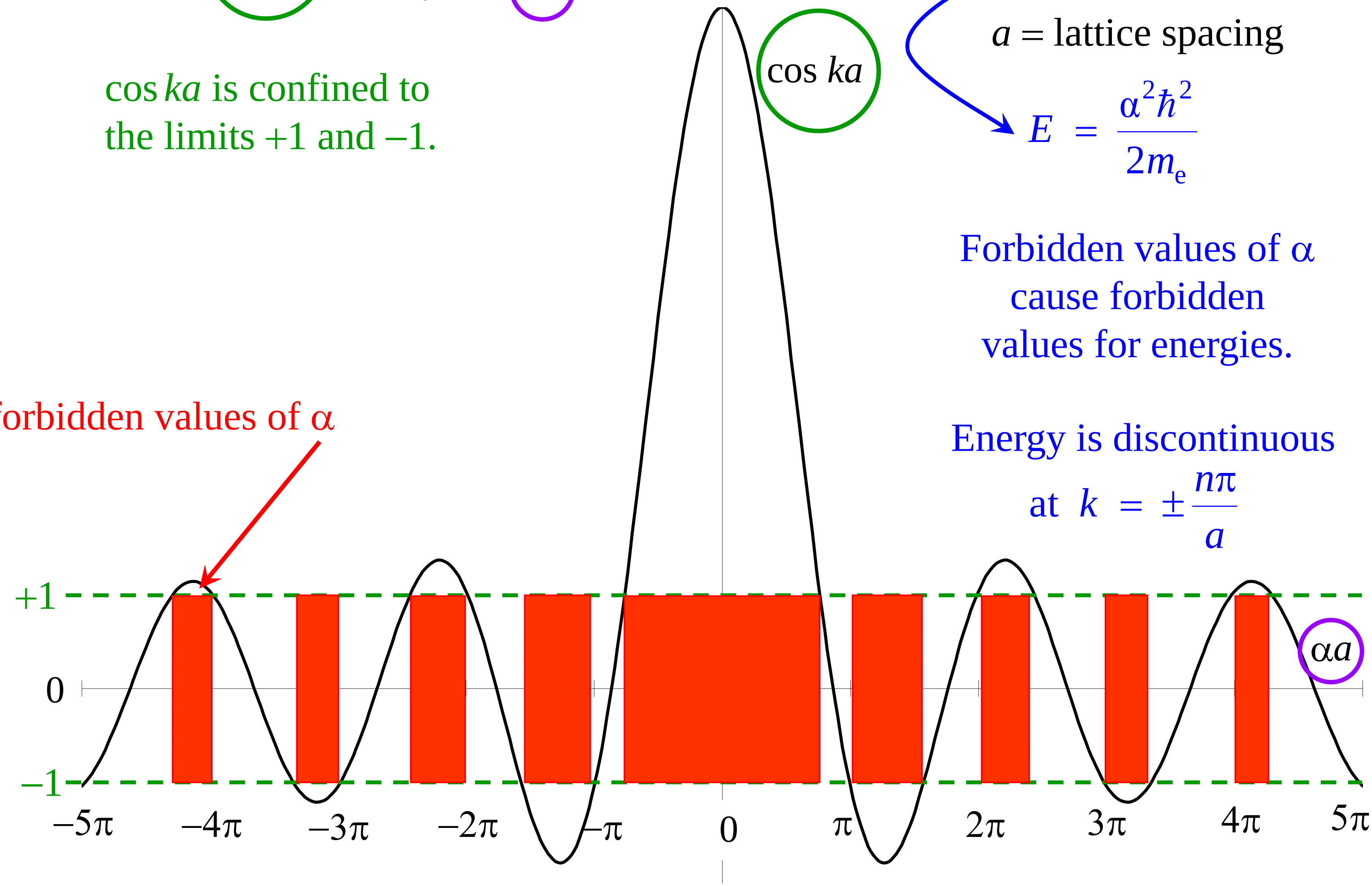
Kronig-Penney Model: Electron Wavenumbers

$$\cos ka = \frac{V_0 w m a}{\hbar^2}\frac{\sin \alpha a}{\alpha a} + \cos \alpha a \qquad \text{such that } \alpha = \frac{(2m_e E)^{1/2}}{\hbar}$$

a = lattice spacing

$$E = \frac{\alpha^2 \hbar^2}{2m_e}$$

cos *ka* is confined to the limits +1 and –1.

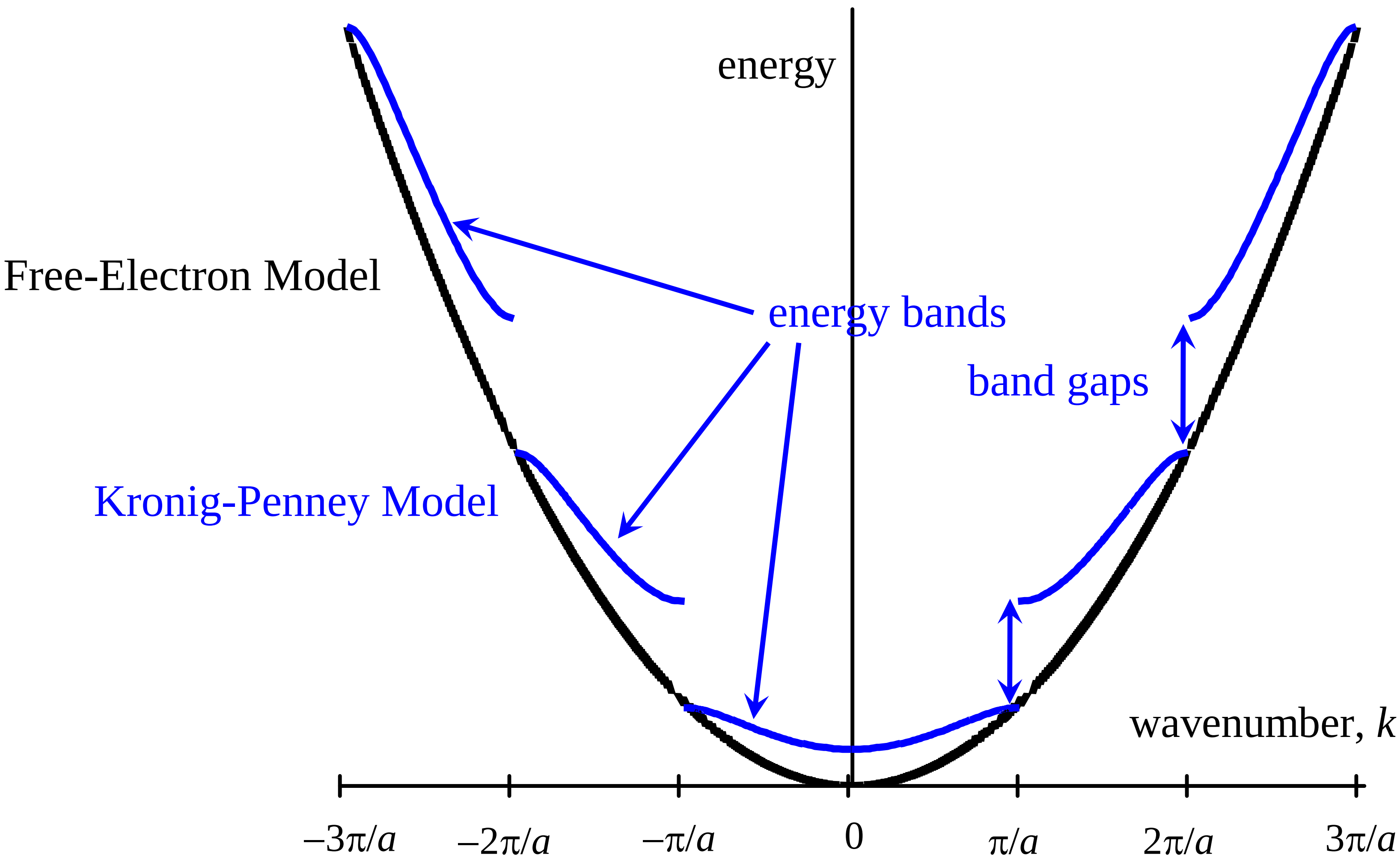


forbidden values of α

Forbidden values of α cause forbidden values for energies.

Energy is discontinuous at $k = \pm\frac{n\pi}{a}$

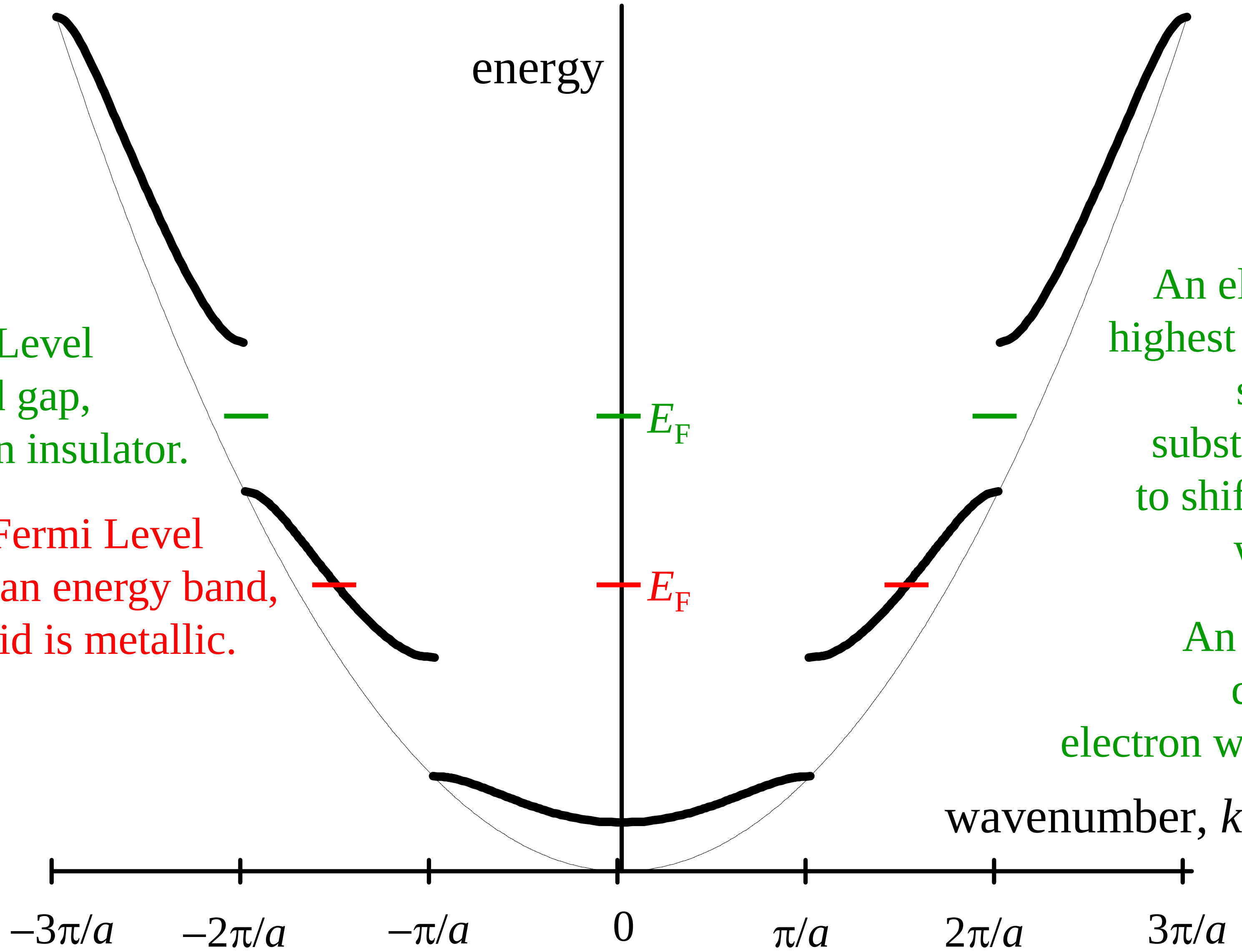
Kronig-Penney Model: Energy Bands and Band Gaps



Kronig-Penney Model: Metals and Insulators

If the Fermi Level lies in a band gap, the solid is an insulator.

If the Fermi Level lies in an energy band, the solid is metallic.



An electron in the highest filled energy state requires substantial energy to shift to a higher wavenumber.

An electric field does not shift electron wavenumbers.

Elements with an odd number of valence electrons – Li, Na, and Al – have Fermi Levels in energy *bands*: metals.

Elements with an even number of valence electrons – C and Si – have Fermi Levels in energy *gaps*: insulators and semiconductors.

Kronig-Penney Model: Why Energy Band Gaps?

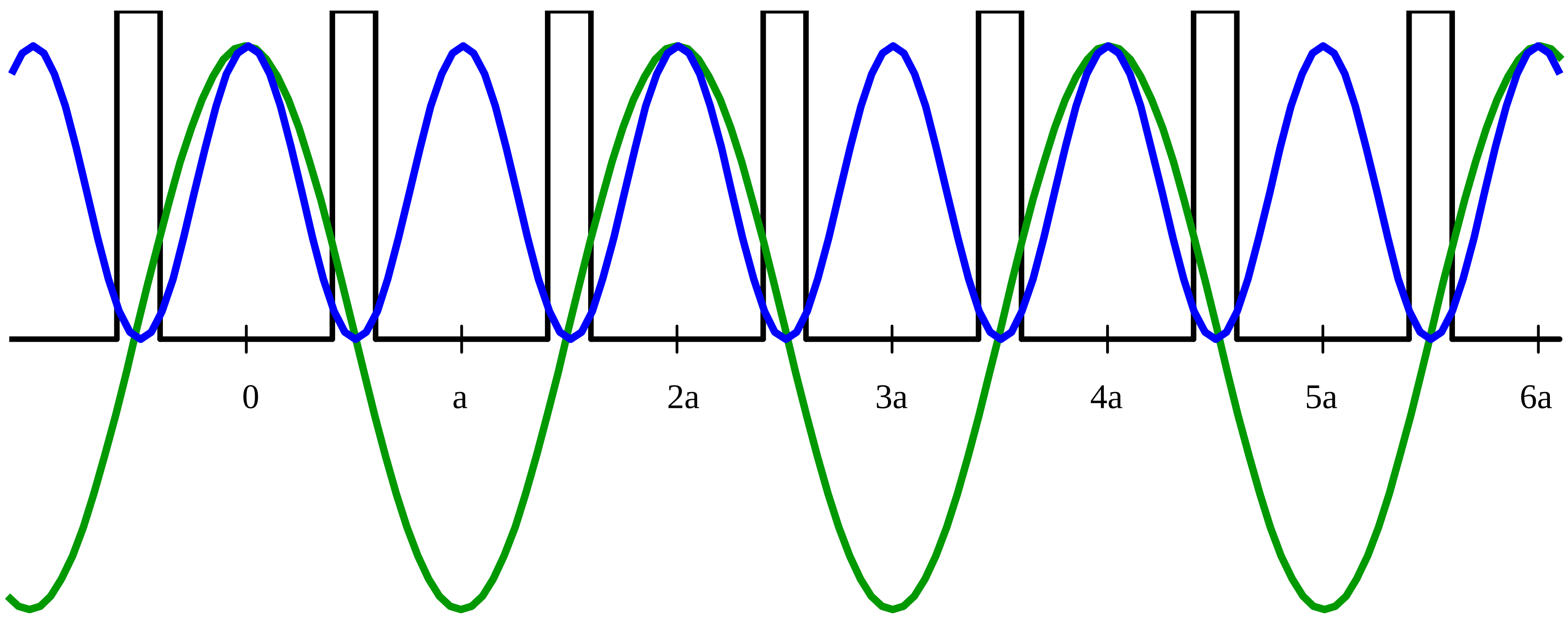
For the Free-Electron Model, $V = 0$ everywhere.

Energy increases monotonically with wavenumber k: $E = \frac{\hbar^2 k_x^2}{2m_e}$

Kronig-Penney potential:

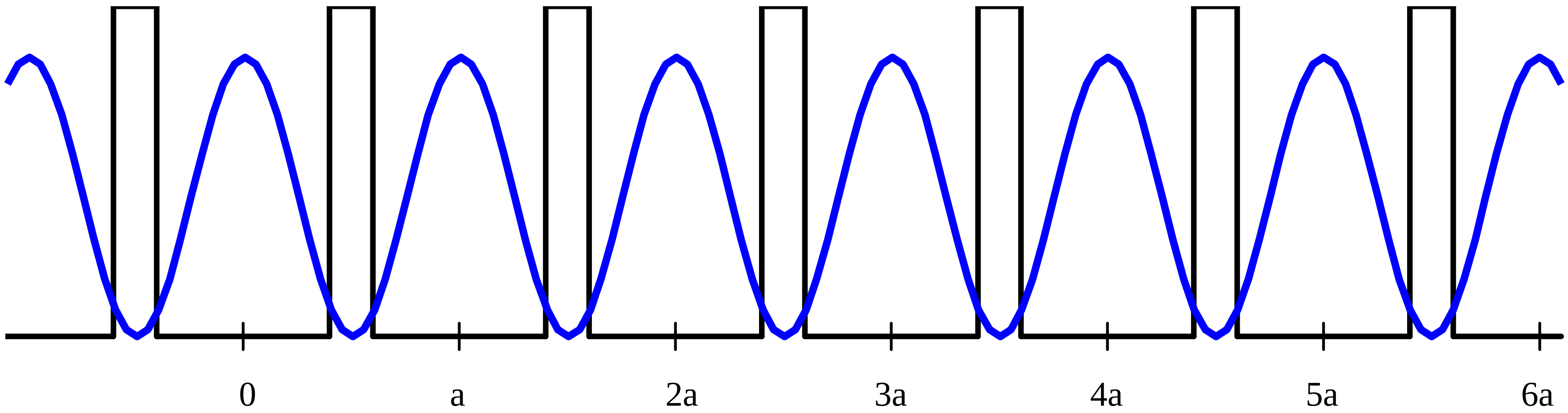
Consider an electron state with wavelength $\lambda = 2a$. $k = \frac{2\pi}{\lambda} = \frac{2\pi}{2a} = \frac{\pi}{a}$

probability amplitude, ψ probability density, $\psi^*\psi$

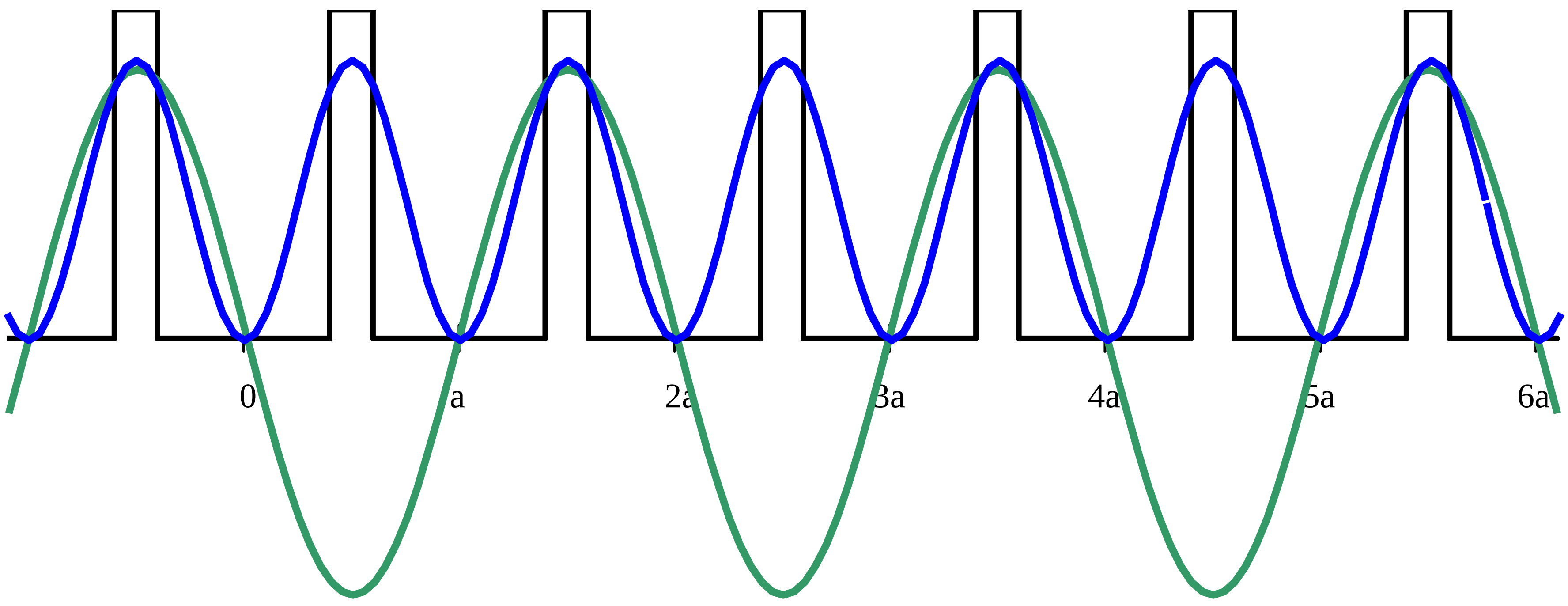


This electron with $k = \pi/a$ maximizes probability density in low potentials and minimizes probability density in high potentials.

Kronig-Penney Model: Why Energy Band Gaps?



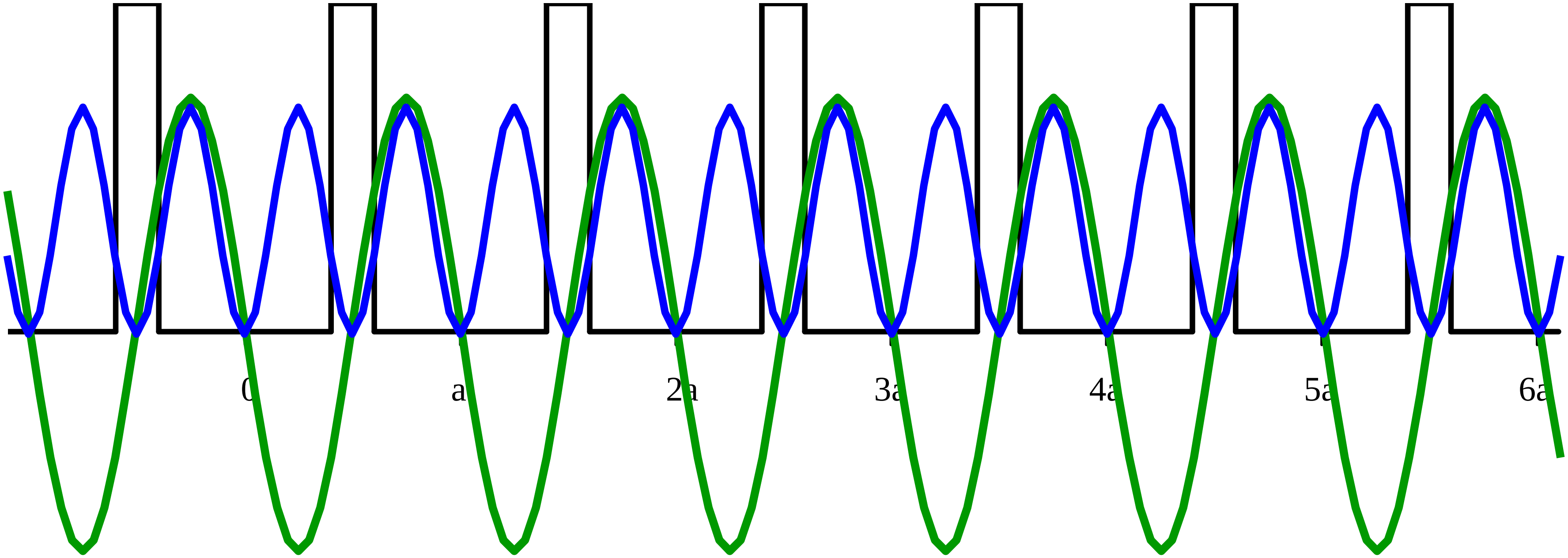
Consider a *different* electron state with wavelength $\lambda = 2a$. $k = \frac{2\pi}{\lambda} = \frac{2\pi}{2a} = \frac{\pi}{a}$

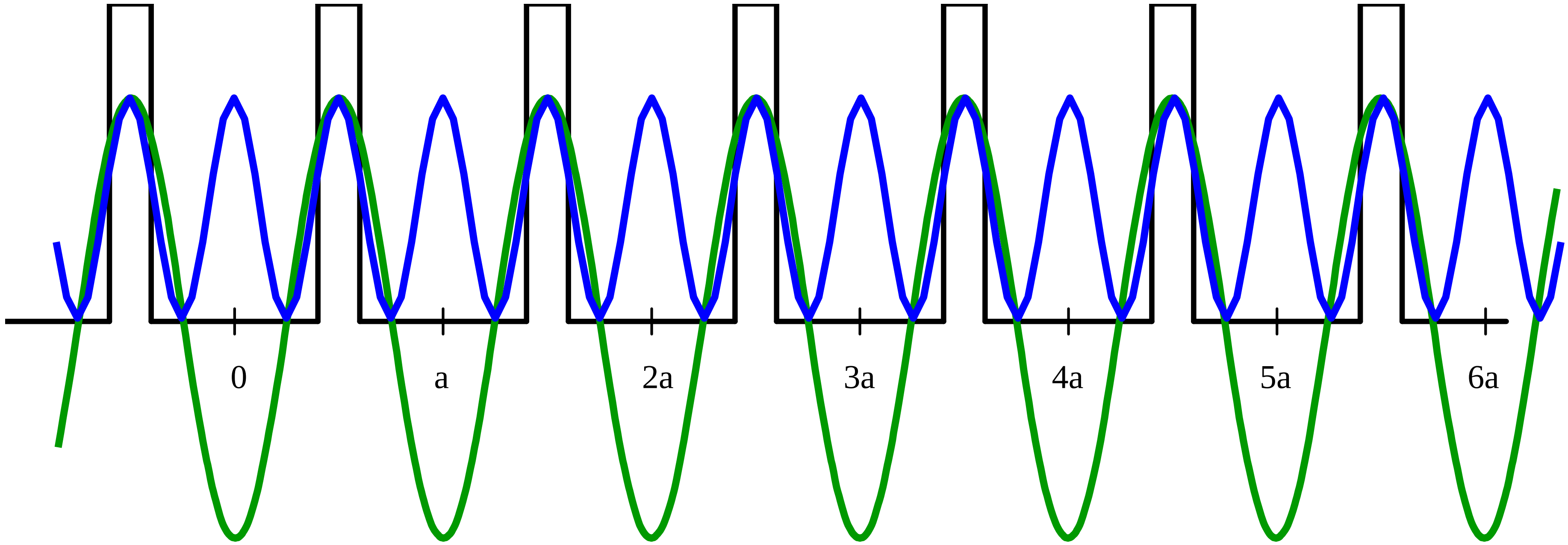


This electron with $k = \pi/a$ minimizes probability density in low potentials and maximizes probability density in high potentials.

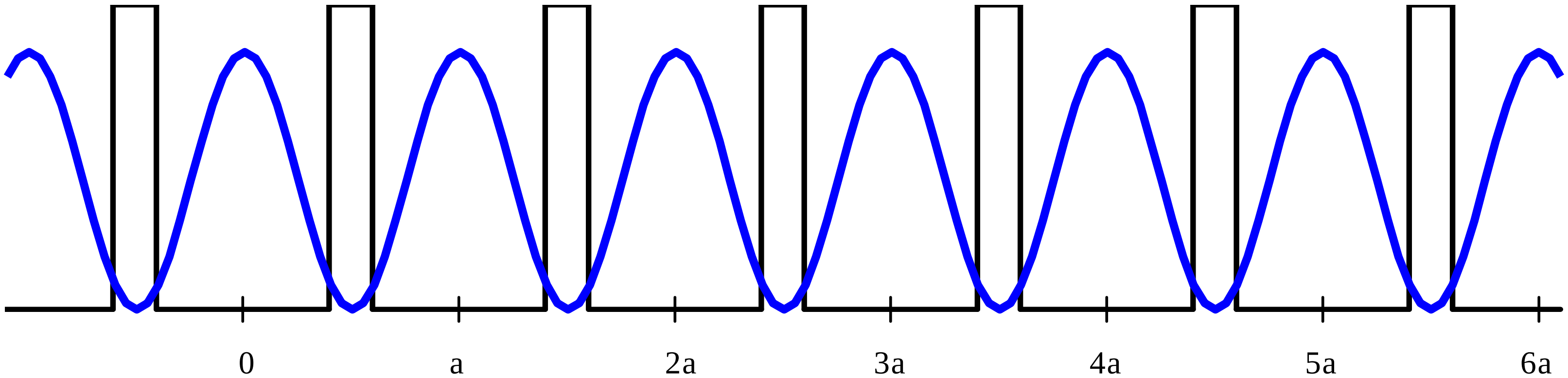
Kronig-Penney Model: Why Energy Band Gaps?

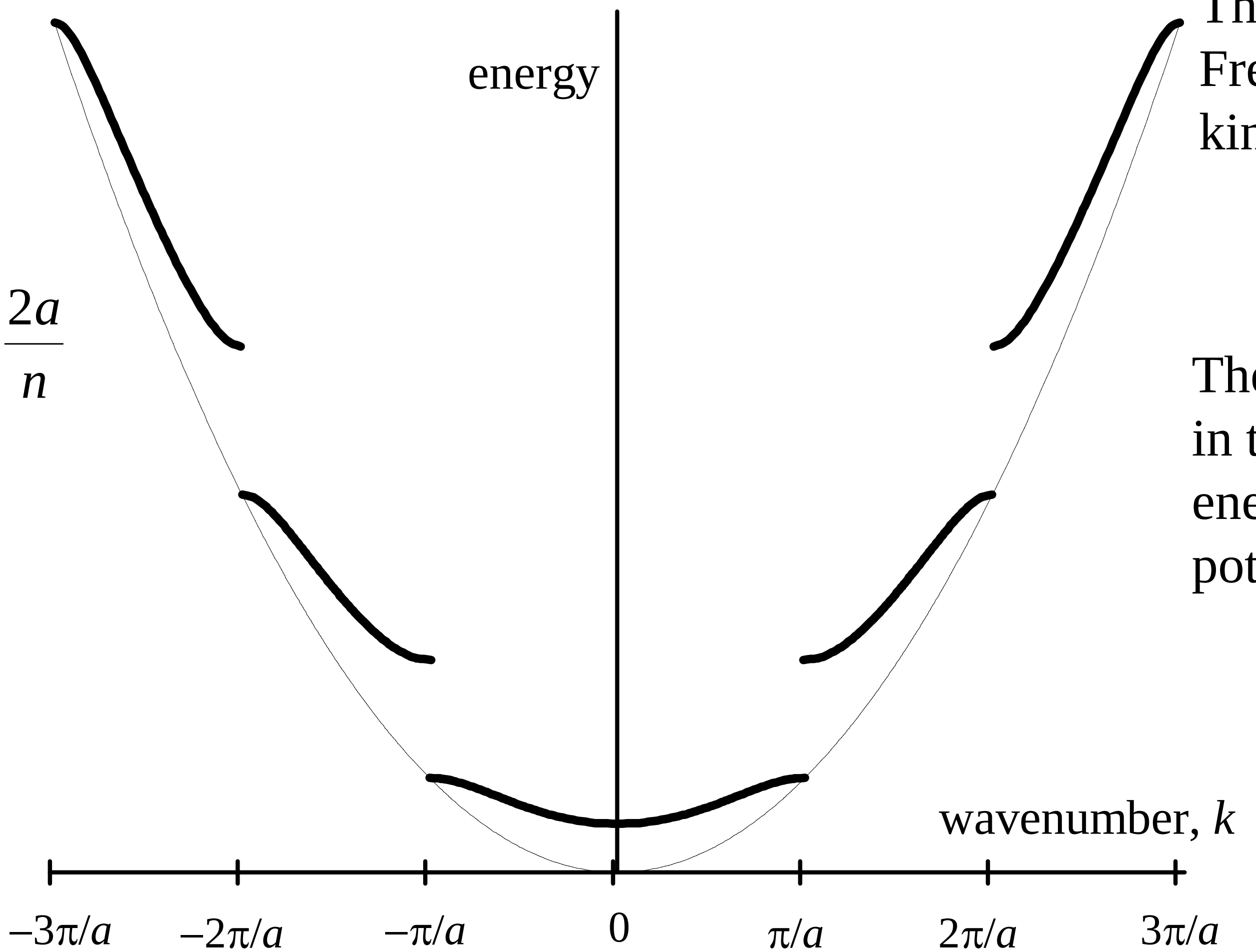
Consider electrons with wavelength $\lambda = a$. $\quad k = \frac{2\pi}{\lambda} = \frac{2\pi}{a}$





Kronig-Penney Model: Summary To Date





The parabola is the Free-Electron Model: kinetic energy only.

$$E = \frac{\hbar^2 k_x^2}{2m_e}$$

The additional energy in the Kronig-Penney energy bands is the potential energy.

Energy gaps at $\lambda = \dfrac{2a}{n}$

Energy gaps at

$$k = \frac{2\pi}{\lambda} = \frac{n\pi}{a}$$

Defining Question for Lecture 2.

How can two electrons with the same wavenumber have different energy?

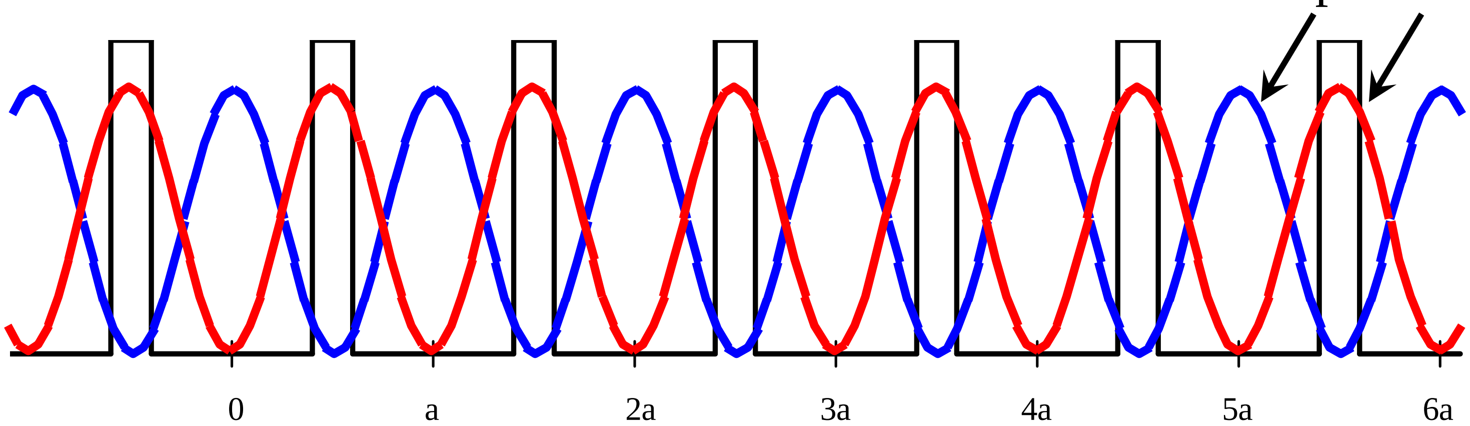
Wavenumber indicates the electron's *kinetic* energy. $E = \frac{\hbar^2 k_x^2}{2m_\mathrm{e}}$

For electrons with wavenumbers at the lattice spacing, $k = \frac{2\pi}{\lambda} = \frac{n\pi}{a}$

Electrons with high probability density at the positive atoms will have higher potential energy.

Electrons with high probability density between the positive atoms will have lower potential energy.

Recap: The Kronig-Penney Model



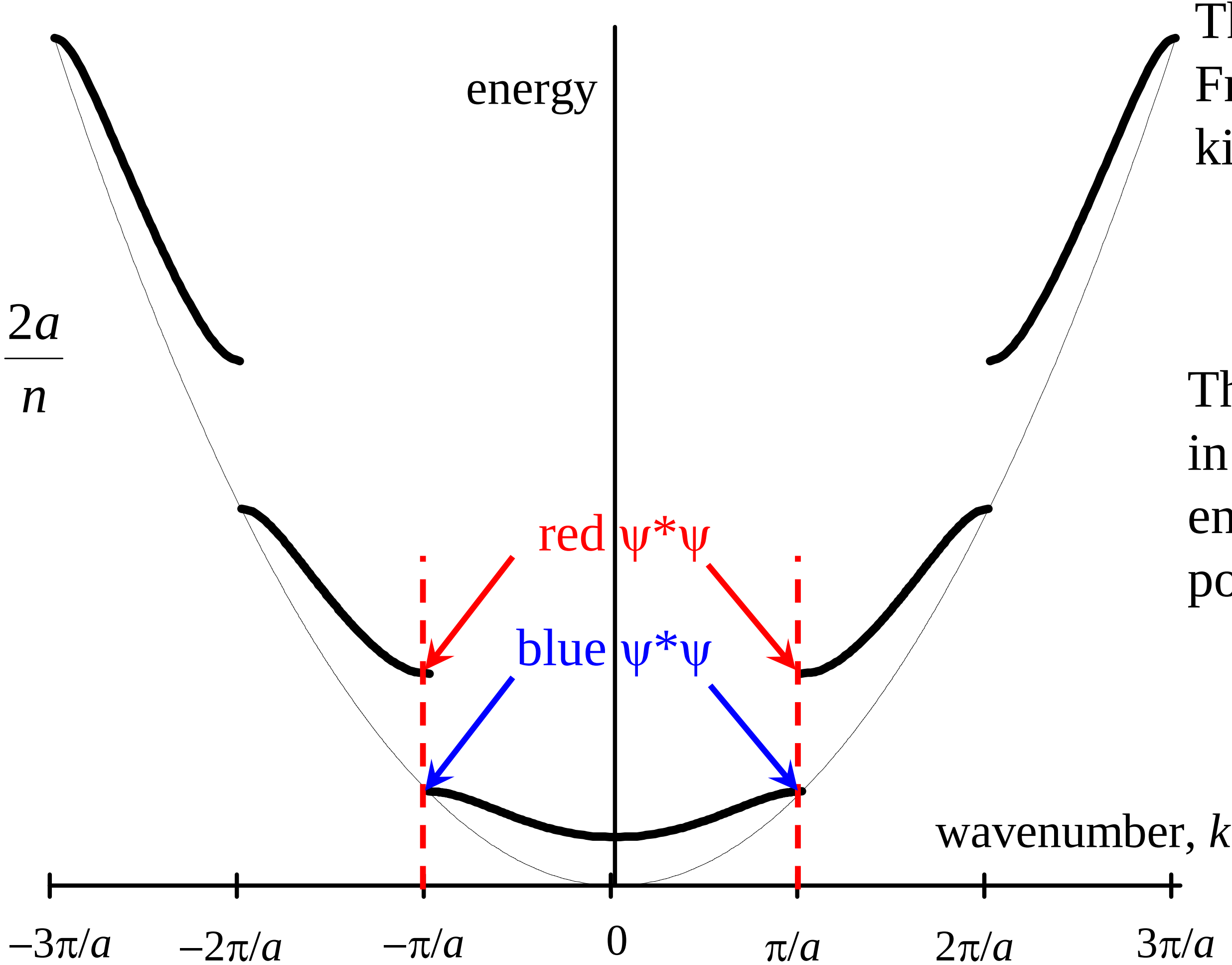
$\lambda = 2a,\ k = \pm\frac{\pi}{a}$

$\lambda = 2a,\ k = \pm\frac{\pi}{a}$

Energy gaps at $\lambda = \frac{2a}{n}$

Energy gaps at

$k = \frac{2\pi}{\lambda} = \frac{n\pi}{a}$



The parabola is the Free-Electron Model: kinetic energy only.

$$E = \frac{\hbar^2 k_x^2}{2m_e}$$

The additional energy in the Kronig-Penney energy bands is the potential energy.

Band gaps are a quantum mechanical phenomenon.