

ME597/PHYS57000

Fall Semester 2009

Lecture 01

Course Overview

Discuss Syllabus

Introduction to Basic Quantum Mechanics

Energy States in Periodic Crystals

Quick Review of Quantum Mechanics

Conservation of Energy
(Hamilton-Jacobi; 1834): $E = PE + KE = U + \frac{p^2}{2m}$

Planck (1901), Einstein (1905): $E = hf = \hbar\omega$

de Broglie (1923): $p = \frac{h}{\lambda} = \frac{h}{2\pi} \frac{2\pi}{\lambda} = \hbar k$

Wave-like
properties of
matter

Hamilton believed that mechanics was the zero-wavelength limit of wave propagation, so why not represent matter by a wave?

Schrödinger introduces a matter-wave Ψ , but what is the appropriate wave equation?

Schrödinger's *ansatz* (complex wave function!!!) in 1D:

$$\Psi = Ae^{(ik_x x - \omega t)}$$

$$\frac{\partial}{\partial t} \Psi = -i\omega \Psi$$

$$\frac{\partial}{\partial x} \Psi = ik_x \Psi$$

$$\frac{\partial^2}{\partial x^2} \Psi = -k_x^2 \Psi$$

$$i\hbar \frac{\partial}{\partial t} \Psi = \left[U(x) - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right] \Psi$$

$$E\Psi = \left[U(x) + \frac{\hbar^2 k_x^2}{2m} \right] \Psi$$

$$E\Psi = \left[U(x) + \frac{p_x^2}{2m} \right] \Psi$$

When applied to the hydrogen atom: $U(x) \rightarrow U(r) = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$

The calculated values of E exactly matched Bohr's results from 1911!

What is physical interpretation of Ψ ? Max Born (1926):

P = Probability that particle is in volume dV

$$P = \int_V [\Psi\Psi^*] dV = \int_V |\Psi|^2 dV$$

Ψ is probability amplitude and $\Psi\Psi^*$ (or $|\Psi|^2$) is probability density

Noble Prizes in Physics:

- 1918 Planck
- 1921 Einstein
- 1922 Bohr
- 1929 de Broglie
- 1933 Schrödinger
- 1954 Born

Quick Review of Quantum Mechanics

- Focus on energies, not equation of motion
- Wave-Particle duality - de Broglie matter-waves
- Emphasize particle (electron) wavefunction, $\Psi(x,y,z)$
- Wavefunction Ψ is complex
- $|\Psi(x,y,z) \Psi^*(x,y,z)|$ gives probability of finding particle at (x,y,z)
- 3D Schrödinger's time dependent equation (1926):

$$-\frac{\hbar^2}{2m_e} \nabla^2 \Psi(\vec{r}, t) + U(\vec{r}) \Psi(\vec{r}, t) = i\hbar \frac{\partial \Psi}{\partial t}(\vec{r}, t) = E\Psi$$

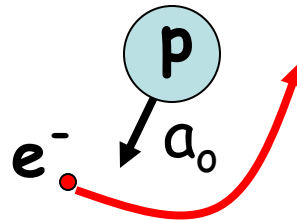
The Hydrogen Atom

e^-

Attractive Force *via*
Coulomb's Law

p

We now know that
 $a_0 \sim 0.0529 \text{ nm}$
 (52.9 pm)
 $(5.29 \times 10^{-11} \text{ m})$

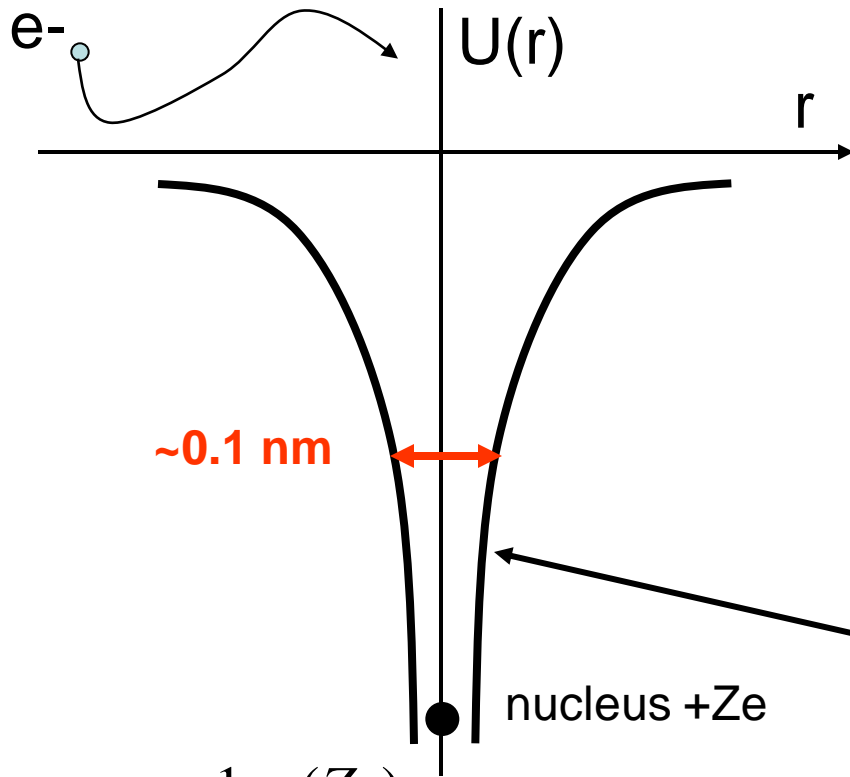


Electrically
Neutral H
Atom

	neutron	proton	electron
symbol	n	p	e^-
charge	0 (zero)	$+1.6 \times 10^{-19} \text{ C}$	$-1.6 \times 10^{-19} \text{ C}$
mass	$1.675 \times 10^{-27} \text{ kg}$	$1.673 \times 10^{-27} \text{ kg}$	$9.11 \times 10^{-31} \text{ kg}$

Note: 1 C = 1 Coulomb

Understanding atomic electron states



What are the allowed energies of an electron in this confining potential?

$$\Phi(r) = \frac{1}{4\pi\epsilon_0} \frac{(Ze)}{r} \text{ electrostatic potential (in volts)}$$

$$U(r) = \frac{1}{4\pi\epsilon_0} \frac{Ze(-e)}{r} = -\frac{Z}{4\pi\epsilon_0} \frac{e^2}{r} \text{ electrostatic potential energy (in joules)}$$

$$E_n = -\frac{Z^2 e^4 m}{32\pi^2 \epsilon_0 \hbar^2} \frac{1}{n^2} = -2.18 \times 10^{-18} \frac{Z^2}{n^2} \text{ (in joules)}$$

Define a Hamiltonian Operator, H

$$H \equiv -\frac{\hbar^2}{2m_e} \nabla^2 + U(\vec{r})$$

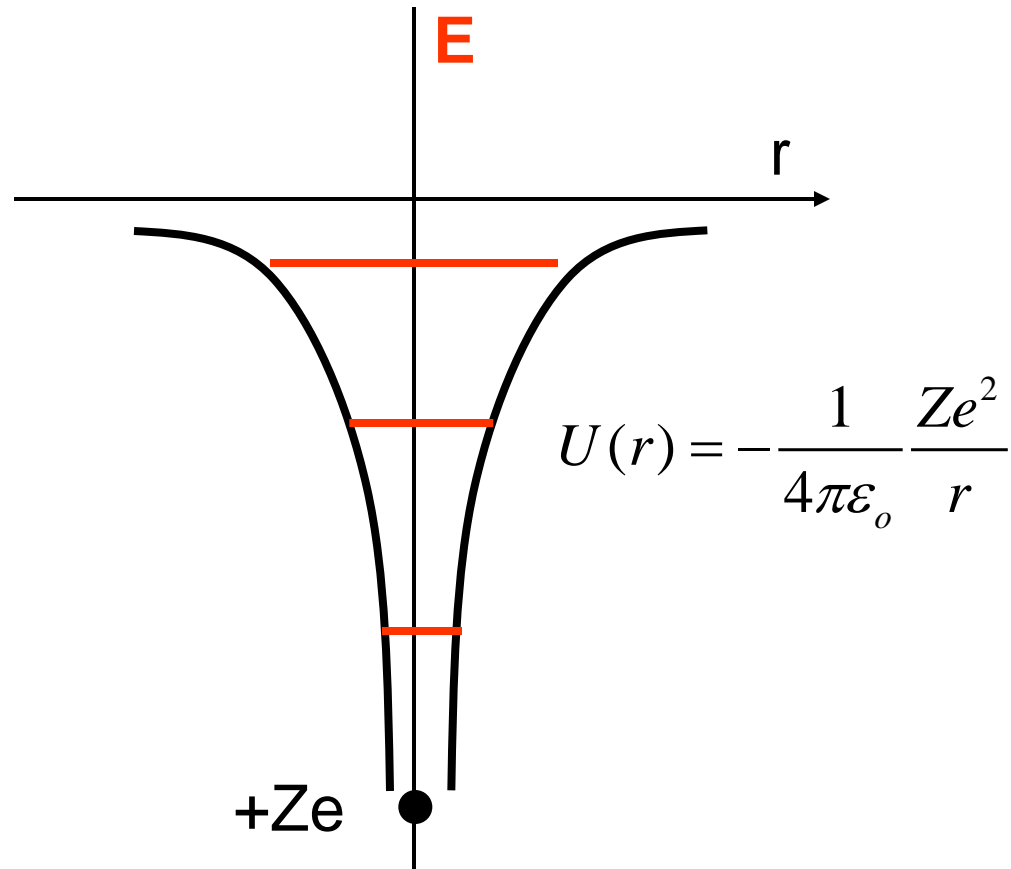
Then solve for Ψ

$$H\Psi = E\Psi$$

Probability of finding electron at position r is given by

$$\text{Probability} = \Psi(\vec{r})\Psi^*(\vec{r})$$

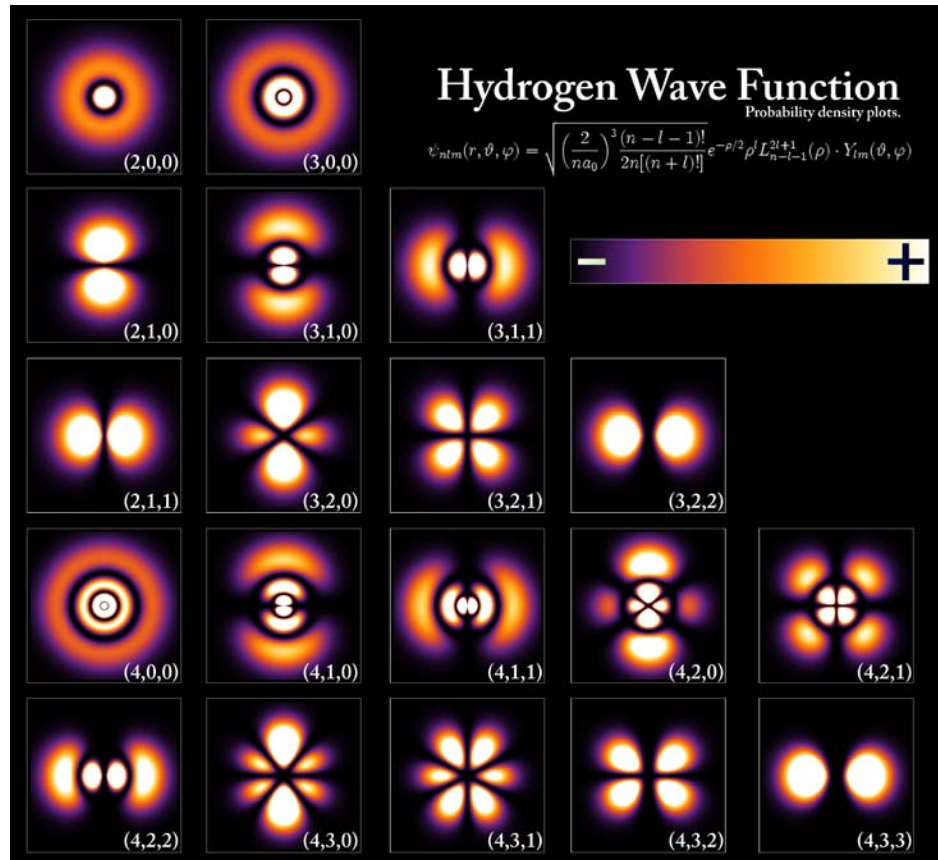
The consequences : Atomic Physics - all confined electron energies are quantized



Radial (3D) Schrödinger Equation

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \varphi} \frac{\partial}{\partial \varphi} \left(\sin \varphi \frac{\partial \psi}{\partial \varphi} \right) + \frac{1}{r^2 \sin^2 \varphi} \frac{\partial^2 \psi}{\partial \theta^2} + \frac{8\pi^2 m}{h^2} (E + V) \psi = 0$$

Remember these shapes



Source:
http://biomatics.org/index.php/Biological_Mathematics

A few links:

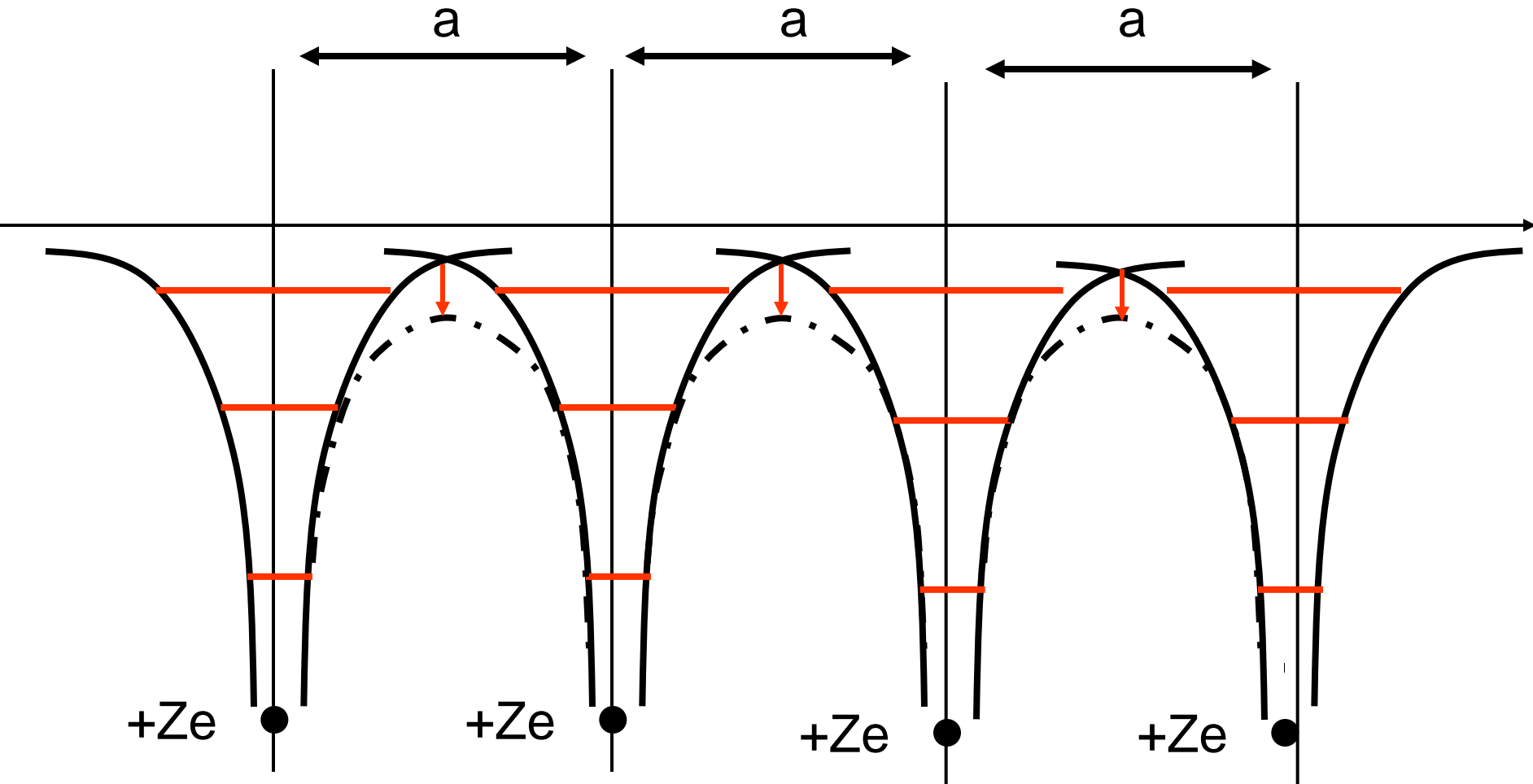
<http://www.orbitals.com/orb/orbtable.htm>

<http://qsad.bu.edu/applets/qexp/atomicexplorer.html>

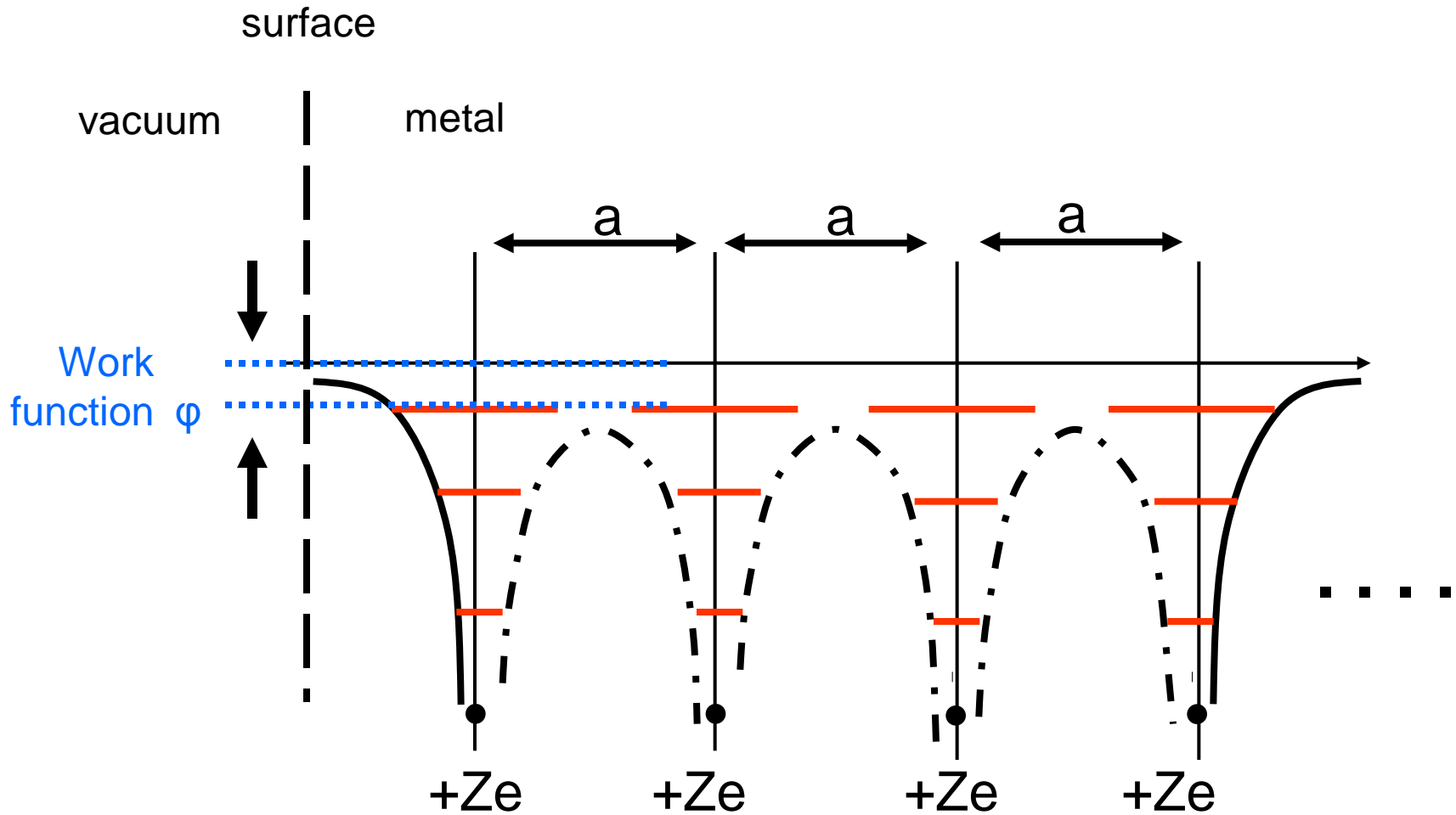
s-electrons: http://hogan.chem.lsu.edu/matter/chap26/animate2/an26_019.mov

He: $1s^2$, Ne: $1s^2 2s^2 2p^6$, and Ar: $1s^2 2s^2 2p^6 3s^2 3p^6$.

Transition to Crystalline Solids



Schematic $U(x)$ for a periodic 1D solid (exact):



Schematic $U(x)$ for a periodic solid (approximate)

Free electron
model



Nearly free
electron model

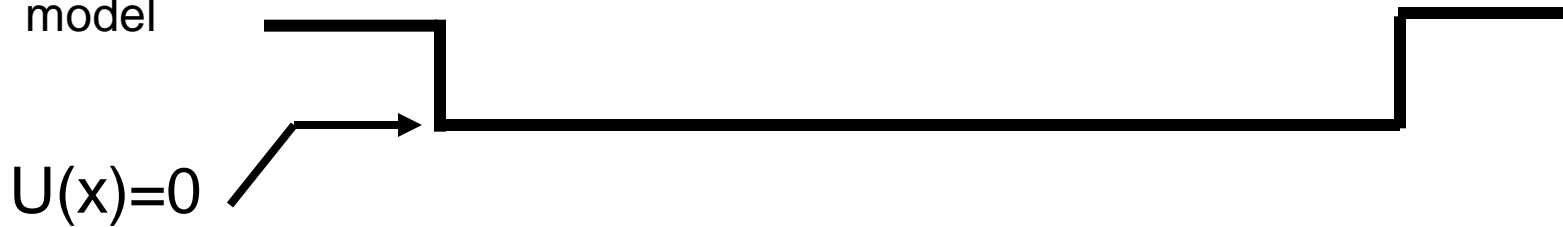


Kronig Penny
model



1D Free Electron Model

Free electron
model



$$-\frac{\hbar^2}{2m_e} \nabla^2 \Psi(\vec{r}, t) + U(\vec{r}) \Psi(\vec{r}, t) = i\hbar \frac{\partial \Psi}{\partial t}(\vec{r}, t) = E \Psi(\vec{r}, t)$$

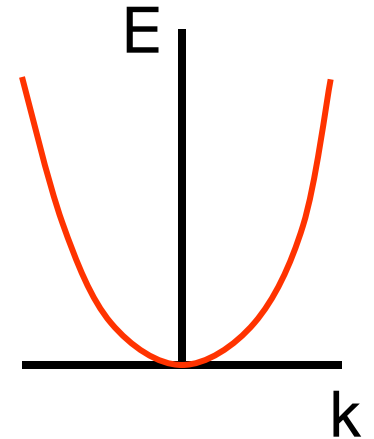
$$-\frac{\hbar^2}{2m_e} \nabla^2 \Psi(x, t) = E \Psi(x, t)$$

$$\text{let } \Psi(x) = A e^{ikx}$$

$$\nabla^2 \Psi = A(-k^2) e^{ikx} = -k^2 \Psi$$

$$\frac{\hbar^2 k^2}{2m_e} \Psi = E \Psi \Rightarrow E = \frac{\hbar^2 k^2}{2m_e} = \frac{p^2}{2m} \Rightarrow p = \hbar k$$

free-electron $E(k)$



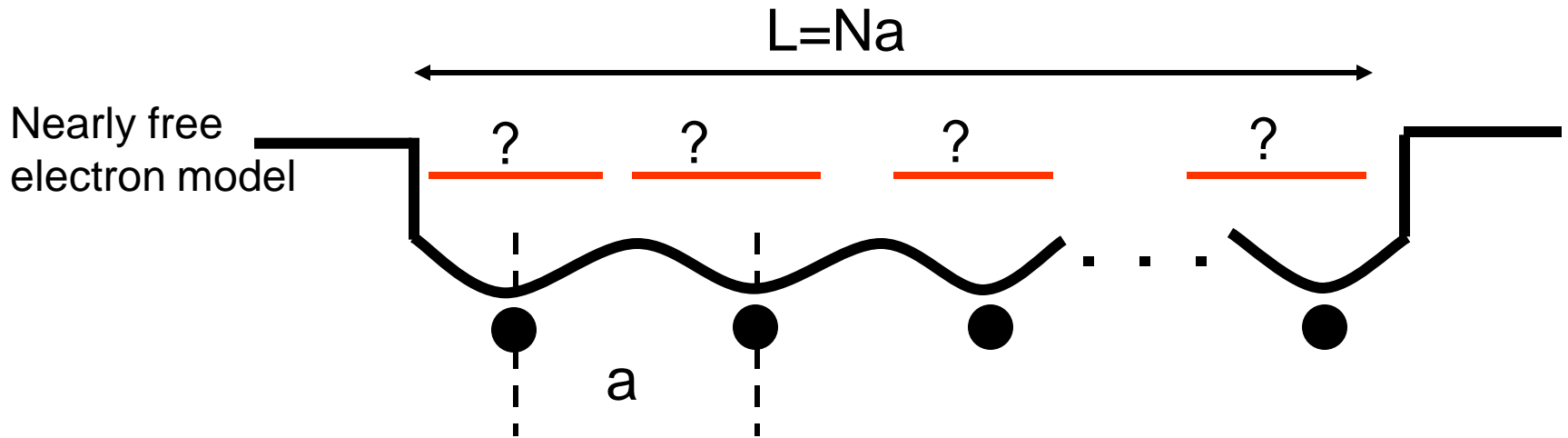
SUMMARY

In the free electron model, there are no restrictions on the “allowed” energies for an electron. The momentum of an electron is $\hbar k$.

The free electron model neglects electron-ion interactions and electron-electron interactions. It treats electrons as independent (uncharged) particles.

The free electron model explains heat capacity, magnetic susceptibility, electronic resistivity, and the electrodynamics of many metals reasonably well.

Including the electron-ion core interaction: the nearly free electron model



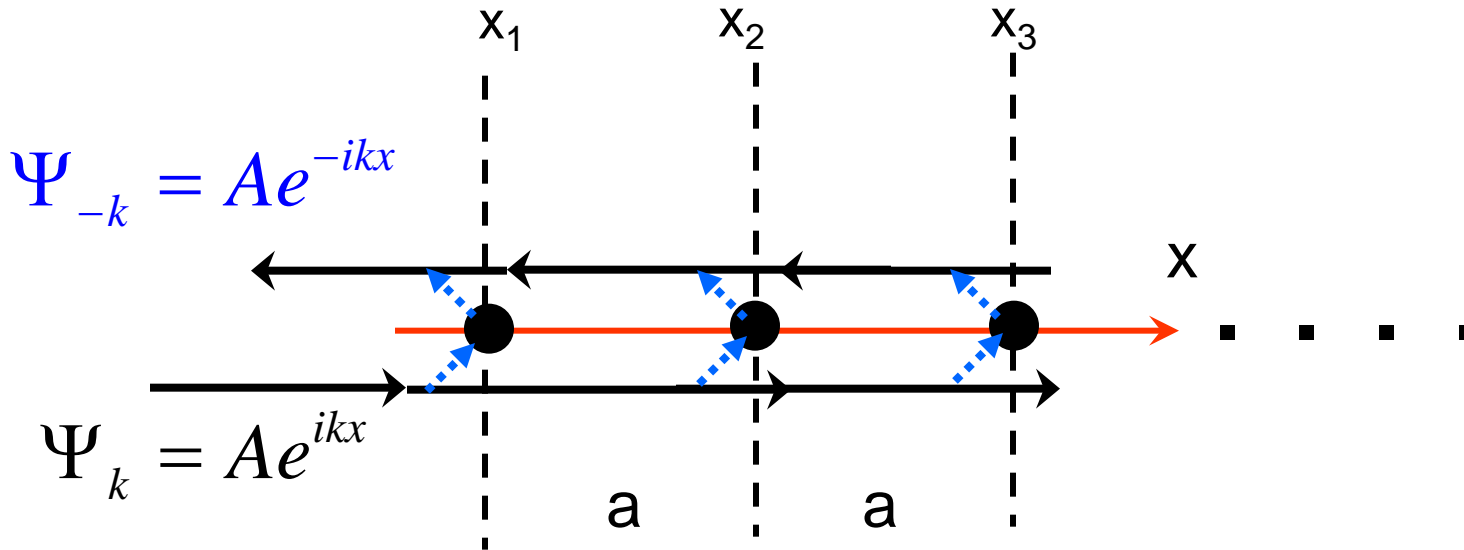
$$\text{Let } U(x) = U_0 \cos(Gx)$$

$$\text{where } G = \frac{2\pi}{a} \text{ with } a = \text{lattice constant}$$

$$\text{Note that } U(x) = U(x + a)$$

In the nearly free electron model,
something new happens - not all
solutions to Schrödinger's Equation will
propagate freely through a periodic
lattice!

Consider what happens if waves reflected at x_1, x_2, x_3, \dots constructively reinforce each other?



A full reflected wave will develop if the path difference ($2a$) between $(x_1, x_2); (x_2, x_3); \dots$ is $n\lambda$ where n is an integer **$n\lambda=2a$** ;

$n=1,2,3,\dots$


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

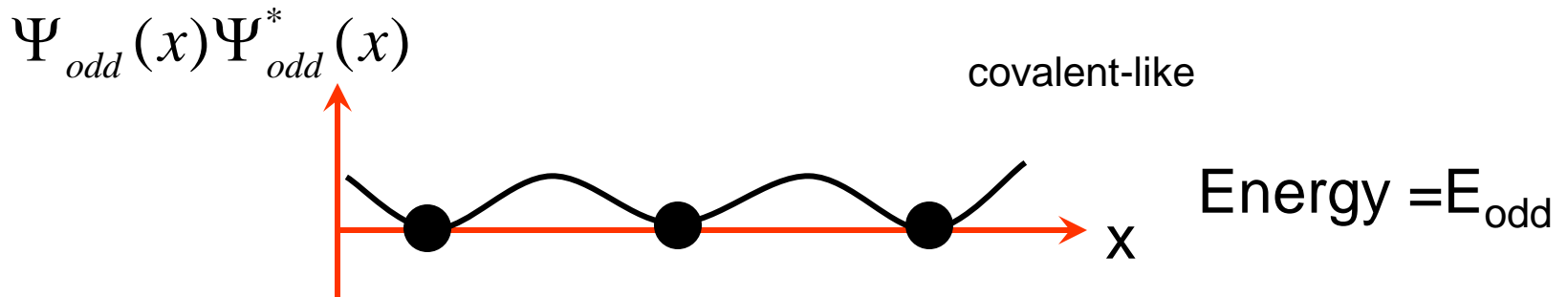
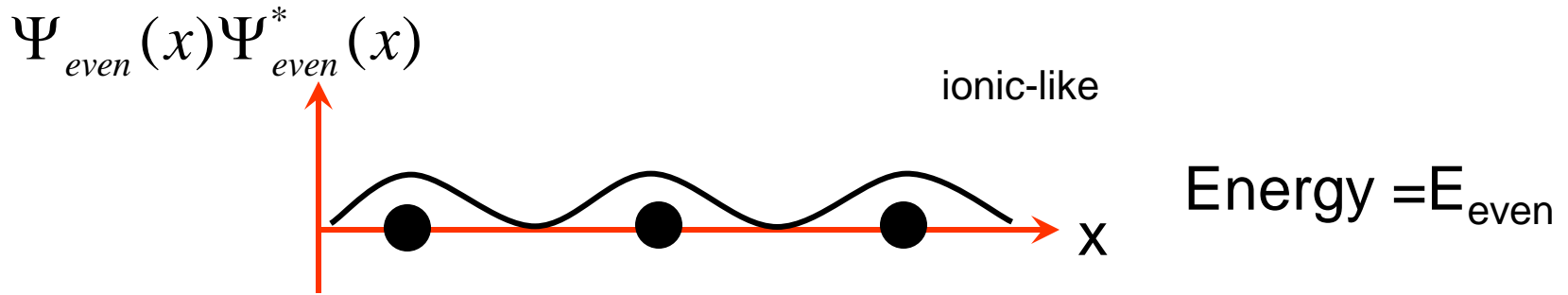
In what follows, let $n=1$

In general, the 1D crystal will develop waves traveling in the forward and backward directions. When Ψ has a k value that satisfies the constructive interference condition ($n\lambda=2a$), Ψ will no longer propagate through the lattice. The electron wavefunction will consist of two waves Ψ_k and Ψ_{-k} . These waves can combine in two ways (pick $n=1$):

$$\Psi_{\text{even}}(x) = Ae^{ikx} + Ae^{-ikx} = 2A \cos(kx) = 2A \cos\left(\frac{Gx}{2}\right)$$

$$\Psi_{\text{odd}}(x) = Ae^{ikx} - Ae^{-ikx} = i2A \sin(kx) = i2A \sin\left(\frac{Gx}{2}\right)$$


 specifies phase
of wave



KE is same for both waves: $KE = \frac{(\hbar k)^2}{2m}$

PE is different for each wave:

$$\langle U_{\text{even}} \rangle = \int_0^L U_o \cos^2(Gx) |\Psi_{\text{even}}(x)\Psi_{\text{even}}^*(x)| dx = \frac{U_o}{2}$$

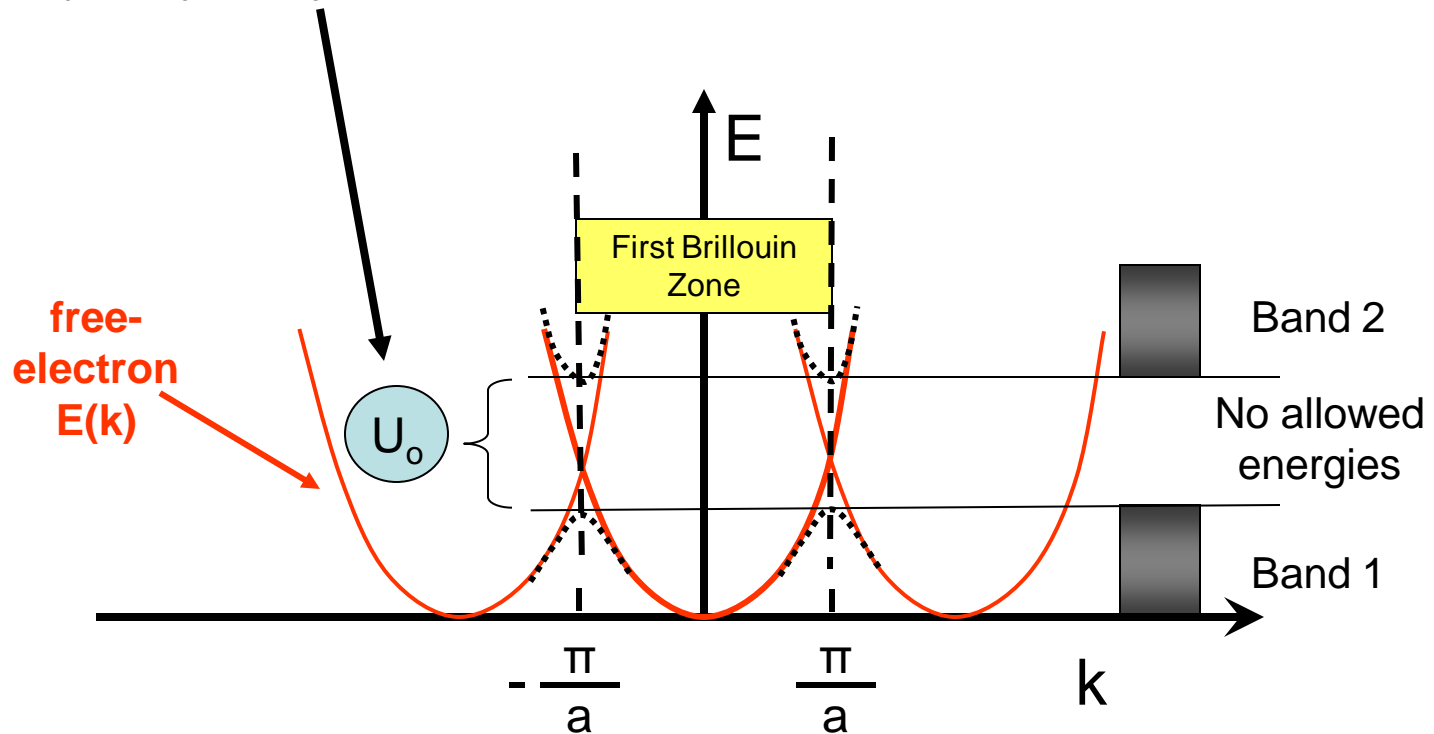
$$\langle U_{\text{odd}} \rangle = \int_0^L U_o \cos^2(Gx) |\Psi_{\text{odd}}(x)\Psi_{\text{odd}}^*(x)| dx = -\frac{U_o}{2}$$

At $k = \pm \frac{G}{2} = \pm \frac{\pi}{a}$, we have

$$\text{Energy} = E_e = \frac{(\hbar k)^2}{2m} + \frac{U_o}{2}$$

$$\text{Energy} = E_o = \frac{(\hbar k)^2}{2m} - \frac{U_o}{2}$$

$$\Delta E = E_e - E_o = U_o$$



SUMMARY

In the nearly free electron model, including a simple sinusoidal model for the electron-ion interaction opens up “gaps” in the allowed energy states.

The nearly free electron model explains the difference between metals, insulators and semiconductors reasonably well.