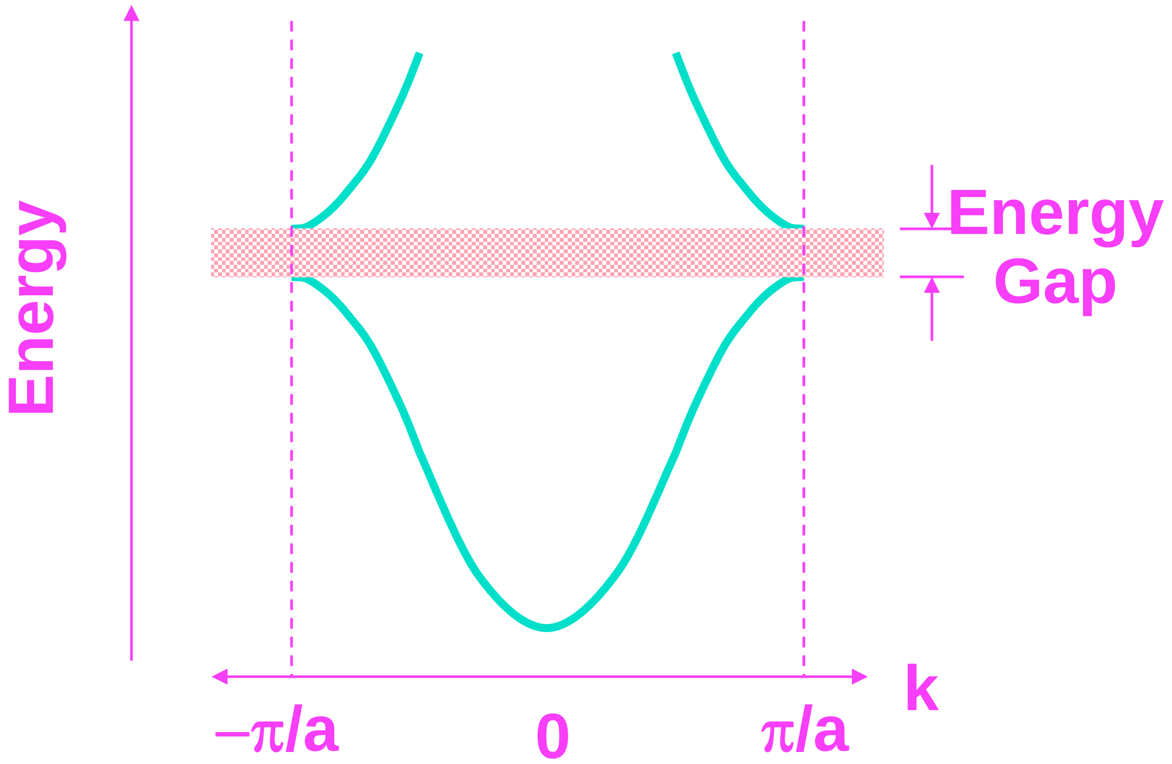
Lecture 14: Energy Bands for Electrons in Crystals (Kittel Ch. 7)



Outline

- **Recall the solution for the free electron gas (Jellium)**

  Simplest model for a metal
  Free electrons in box of size L x L x L
  (artificial but very useful)
  Schrodinger equation can be solved
  States classified by k with $E(\mathbf{k}) = (\hbar^2/2m)\,|\,\underline{\mathbf{k}}\,|^2$
  Periodic boundary conditions convenient:
  Leads to k_x = integer x $(2\pi/L)$, etc.
  Pauli Exclusion Principle, Fermi Statistics

- **Questions:**

  Answered in the next few lectures

  Why are some materials insulators, some metals?
  What is a semiconductor? What makes them useful?

- **Electrons in crystals**

  First step - NEARLY free electrons in a crystal
  Simple picture - Bragg diffraction leads to standing waves at the Brillouin Zone boundary and to energy gaps

- **(Read Kittel Ch 7)**

Questions for understanding materials:

- **Why are most elements metallic - special place of semiconductors between metals and insulators**

APPENDIX D: PERIODIC TABLE OF THE ELEMENTS

Group I	Group II	Transition elements										Group III	Group IV	Group V	Group VI	Group VII	Group 0
H 1 1.0079 $1s^1$																	**He** 2 4.0026 $1s^2$
Li 3 6.94 $2s^1$	**Be** 4 9.012 $2s^2$				Symbol Atomic mass*	C 6 12.011 $2p^2$	Atomic number Electron configuration					**B** 5 10.81 $2p^1$	**C** 6 12.011 $2p^22$	**N** 7 14.007 $2p^3$	**O** 8 15.999 $2p^4$	**F** 9 18.998 $2p^5$	**Ne** 10 20.18 $2p^6$
Na 11 22.990 $3s^1$	**Mg** 12 24.305 $3s^2$											**Al** 13 26.982 $3p^1$	**Si** 14 28.086 $3p^2$	**P** 15 30.974 $3p^3$	**S** 16 32.06 $3p^4$	**Cl** 17 35.453 $3p^5$	**Ar** 18 39.948 $3p^6$
K 19 39.098 $4s^1$	**Ca** 20 40.08 $4s^2$	**Sc** 21 44.956 $3d^14s^2$	**Ti** 22 47.90 $3d^24s^2$	**V** 23 50.94 $3d^34s^2$	**Cr** 24 51.996 $3d^54s^1$	**Mn** 25 54.938 $3d^54s^2$	**Fe** 26 55.847 $3d^64s^2$	**Co** 27 58.933 $3d^74s^2$	**Ni** 28 58.71 $3d^84s^2$	**Cu** 29 63.546 $3d^{10}4s^1$	**Zn** 30 65.38 $3d^{10}4s^2$	**Ga** 31 69.72 $4p^1$	**Ge** 32 72.59 $4p^2$	**As** 33 74.922 $4p^3$	**Se** 34 78.96 $4p^4$	**Br** 35 79.904 $4p^5$	**Kr** 36 83.80 $4p^6$
Rb 37 85.467 $5s^1$	**Sr** 38 87.62 $5s^2$	**Y** 39 88.906 $4d^15s^2$	**Zr** 40 91.22 $4d^25s^2$	**Nb** 41 92.906 $4d^45s^1$	**Mo** 42 95.94 $4d^54s^1$	**Tc** 43 98.9 $4d^55s^2$	**Ru** 44 101.07 $4d^75s^1$	**Rh** 45 102.906 $4d^85s^1$	**Pd** 46 106.4 $4d^{10}$	**Ag** 47 107.868 $4d^{10}5s^1$	**Cd** 48 112.41 $4d^{10}5s^2$	**In** 49 114.82 $5p^1$	**Sn** 50 118.69 $5p^2$	**Sb** 51 121.75 $5p^3$	**Te** 52 127.60 $5p^4$	**I** 53 126.90 $5p^5$	**Xe** 54 131.30 $5p^6$
Cs 55 132.905 $6s^1$	**Ba** 56 137.33 $6s^2$	57–71†	**Hf** 72 178.49 $5d^26s^2$	**Ta** 73 180.95 $5d^36s^2$	**W** 74 183.85 $5d^46s^2$	**Re** 75 186.207 $5d^56s^2$	**Os** 76 190.2 $5d^66s^2$	**Ir** 77 192.22 $5d^76s^2$	**Pt** 78 195.09 $5d^96s^1$	**Au** 79 196.966 $5d^{10}6s^1$	**Hg** 80 200.59 $5d^{10}6s^2$	**Tl** 81 204.37 $6p^1$	**Pb** 82 207.2 $6p^2$	**Bi** 83 208.980 $6p^3$	**Po** 84 (209) $6p^4$	**At** 85 (210) $6p^5$	**Rn** 86 (222) $6p^6$
Fr 87 (223) $7s^1$	**Ra** 88 226.025 $7s^2$	89–103‡	**Rf** 104 (261) $6d^27s^2$	**Ha** 105 (260) $6d^37s^2$	106 (263)	107 (262)	108 (265)	109 (266)									

† LANTHANIDE SERIES	**La** 57 139.906 $5d^16s^2$	**Ce** 58 140.12 $4f^26s^2$	**Pr** 59 140.908 $4f^36s^2$	**Nd** 60 144.24 $4f^46s^2$	**Pm** 61 (145) $4f^56s^2$	**Sm** 62 150.4 $4f^66s^2$	**Eu** 63 151.96 $4f^76s^2$	**Gd** 64 157.25 $5d^14f^76s^2$	**Tb** 65 158.925 $4f^96s^2$	**Dy** 66 162.50 $4f^{10}6s^2$	**Ho** 67 164.930 $4f^{11}6s^2$	**Er** 68 167.26 $4f^{12}6s^2$	**Tm** 69 168.934 $4f^{13}6s^2$	**Yb** 70 173.04 $4f^{14}6s^2$	**Lu** 71 174.967 $5d^14f^{14}6s^2$	(Lanthanide
‡ ACTINIDE SERIES	**Ac** 89 (227) $6d^17s^2$	**Th** 90 232.038 $6d^27s^2$	**Pa** 91 231.039 $5f^26d^17s^2$	**U** 92 238.029 $5f^36d^17s^2$	**Np** 93 237.048 $5f^46d^17s^2$	**Pu** 94 (244) $5f^67s^2$	**Am** 95 (243) $5f^77s^2$	**Cm** 96 (247) $5f^76d^17s^2$	**Bk** 97 (247) $5f^86d^17s^2$	**Cf** 98 (251) $5f^{10}7s^2$	**Es** 99 (253) $5f^{11}7s^2$	**Fm** 100 (257) $5f^{12}7s^2$	**Md** 101 (258) $5f^{13}7s^2$	**No** 102 (259) $5f^{14}7s^2$	**Lr** 103 (260) $6d^17s^2$	(Actinide

* Average value based on the relative abundance of isotopes on earth. For unstable elements, the mass of the most stable isotope is given in brackets.

How can we understand that some materials are insulators or semiconductors?

- To answer this question we must consider electrons in a crystal
- The key is the quantum wave nature of electrons in a crystal

A great success of quantum theory in the 1920's and 1930's

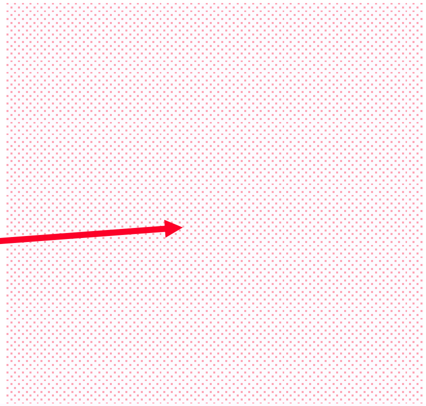
- The nuclei are arranged in a periodic crystalline array

This changes the energies of the electrons and leads to different behavior in different crystals

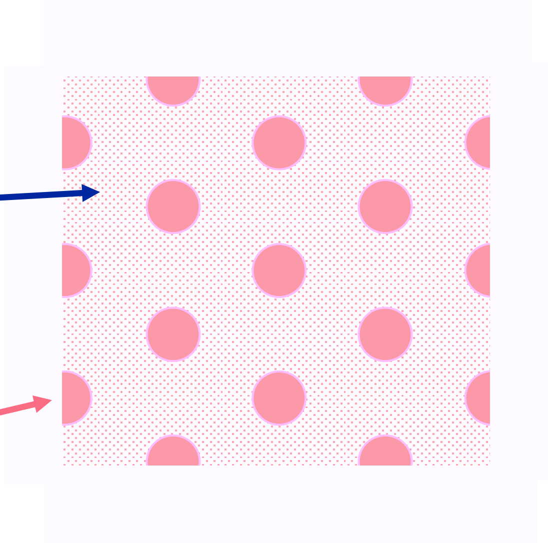
- Here we will see the basic effects
- Next time – a more complete derivation

Understanding Electrons in Crystals

- **Electron Gas**
  Simplest possible model for a metal - electrons are completely "free of the nuclei" - nuclei are replaced by a smooth background -- "Electrons in a box"



- **Real Crystal -**
  Potential variation with the periodicity of the crystal



Attractive (negative) potential around each nucleus

Schrodinger Equation

- Basic equation of Quantum Mechanics

$$[\, -(\hbar^2/2m)\nabla^2 + V(\underline{\mathbf{r}})\,]\,\Psi(\underline{\mathbf{r}}) = E\,\Psi(\underline{\mathbf{r}})$$

where

m = mass of particle

$V(\underline{\mathbf{r}})$ = potential energy at point $\underline{\mathbf{r}}$

$\nabla^2 = (d^2/dx^2 + d^2/dy^2 + d^2/dz^2)$

E = eigenvalue = energy of quantum state

$\Psi(\underline{\mathbf{r}})$ = wavefunction

$n(\underline{\mathbf{r}}) = |\Psi(\underline{\mathbf{r}})|^2$ = probability density

- Key Point for electrons in a crystal: The potential $V(\underline{\mathbf{r}})$ has the periodicity of the crystal

Schrodinger Equation

- How can we solve the Schrodinger Eq.

$$[- (\hbar^2/2m)\nabla^2 + V(\mathbf{r})]\, \Psi(\mathbf{r}) = E\, \Psi(\mathbf{r})$$

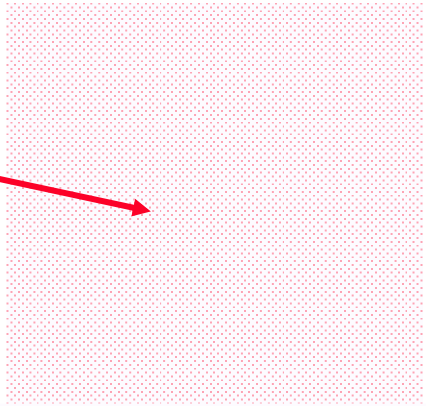
where $V(\mathbf{r})$ has the periodicity of the crystal?

- Difficult problem - This is the basis of current research in the theory of electrons in crystals

- We will consider simple cases as an introduction
  - One dimension
  - Nearly Free Electrons
  - Kronig-Penny Model

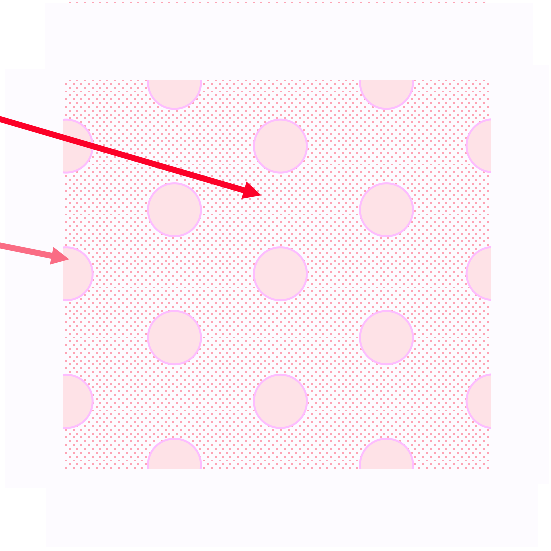
Next Step for Understanding Electrons in Crystals

- Simplest extension of the Electron Gas model



- Nearly Free electron Gas - Very small potential variation with the periodicity of the crystal

Very weak potentials with crystal periodicity



- We will first consider electrons in one dimension

Consider 1 dimensional example

- If the electrons can move freely on a line from 0 to L (with no potential),

0 **L**

then we have seen before that :

- Schrodinger Eq. In 1d with V = 0

$$-(\hbar^2/2m)\, d^2/dx^2\, \Psi(x) = E\, \Psi(x)$$

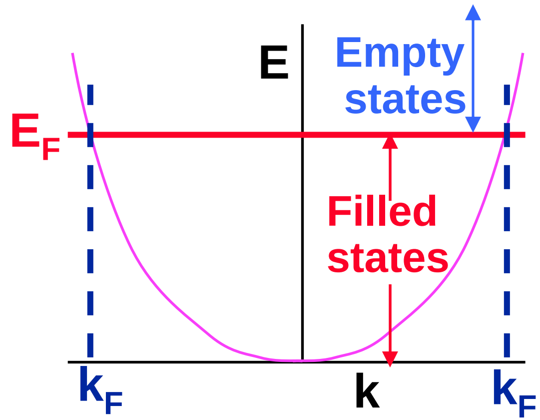
- If we have periodic boundary conditions ($\Psi(0) = \Psi(L)$) then the solution is:

$$\Psi(x) = L^{-1/2} \exp(ikx), \quad k = \pm m\, (2\pi/L), \quad m = 0,1,..$$

$$E(k) = (\hbar^2/2m)\, |k|^2$$

Electrons on a line

- For electrons in a box, the energy is just the kinetic energy
  $E(k) = (\hbar^2/2m)\, k^2$
- Values of k fixed by the box, $k = \pm m\, (2\pi/L)$, m = 0, 1, . . .



- The lowest energy state is for electrons is to fill the lowest states up to the Fermi energy E_F and Fermi momentum k_F – two electrons (spin up and spin down) in each state
- This is a metal – the electrons can conduct electricity as we described before

How can we understand that some materials are insulators or semiconductors?

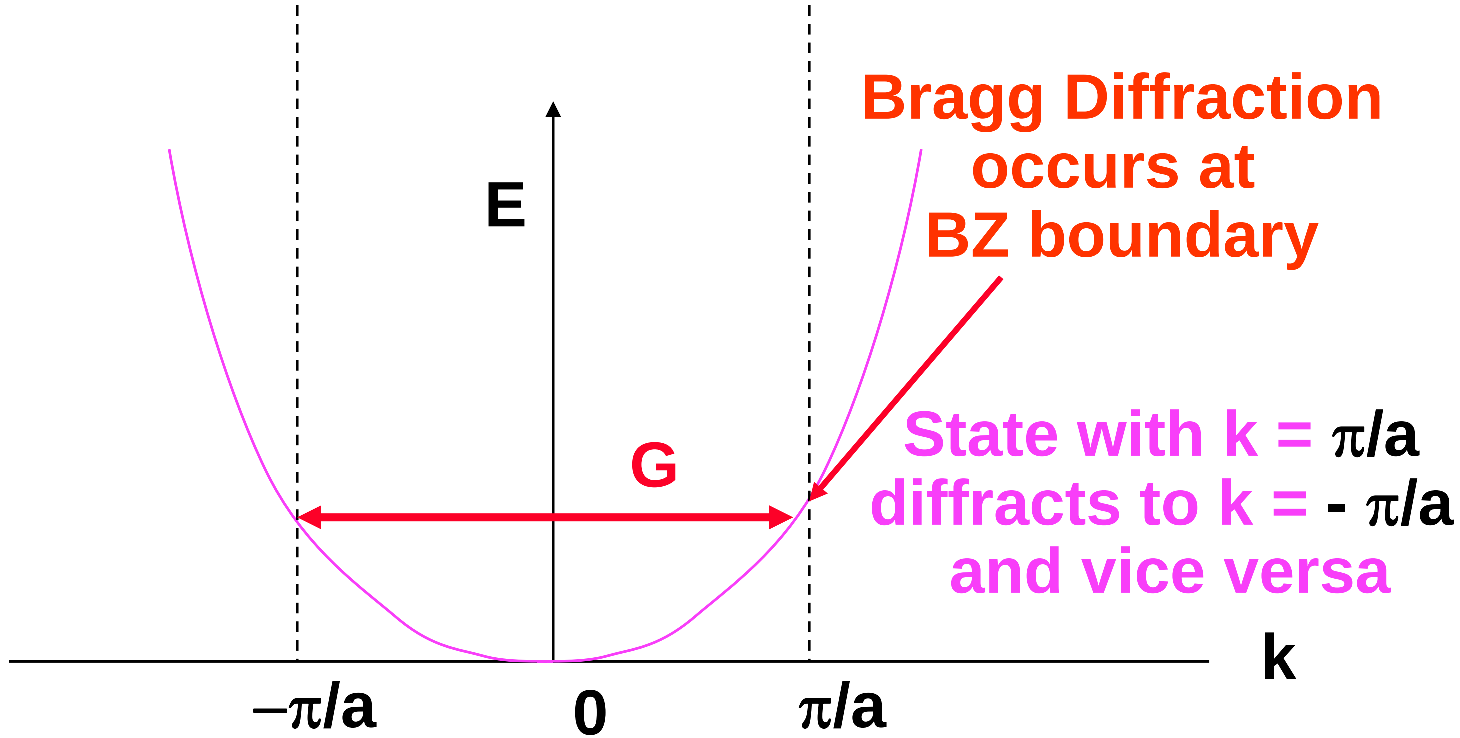
- To answer this question we must consider electrons in a crystal
- The nuclei are arranged in a periodic crystalline array

This changes the energies of the electrons and leads to different behavior in different crystals

- Here we will see the basic effects
- Next time – a more complete derivation

Electrons on a line with potential V(x)

- What happens if there is a potential V(x) that has the periodicity a of the crystal?
- An electron wave with wavevector k can suffer Bragg diffraction to $k \pm G$, with G any reciprocal lattice vector



Interpretation of Standing waves at Brillouin Zone boundary

- Bragg scattering at $k = \pi/a$ leads to the two possible standing waves. Each is a combination of the right and left going waves $\exp(i \pi x/a)$ and $\exp(-i \pi x/a)$:

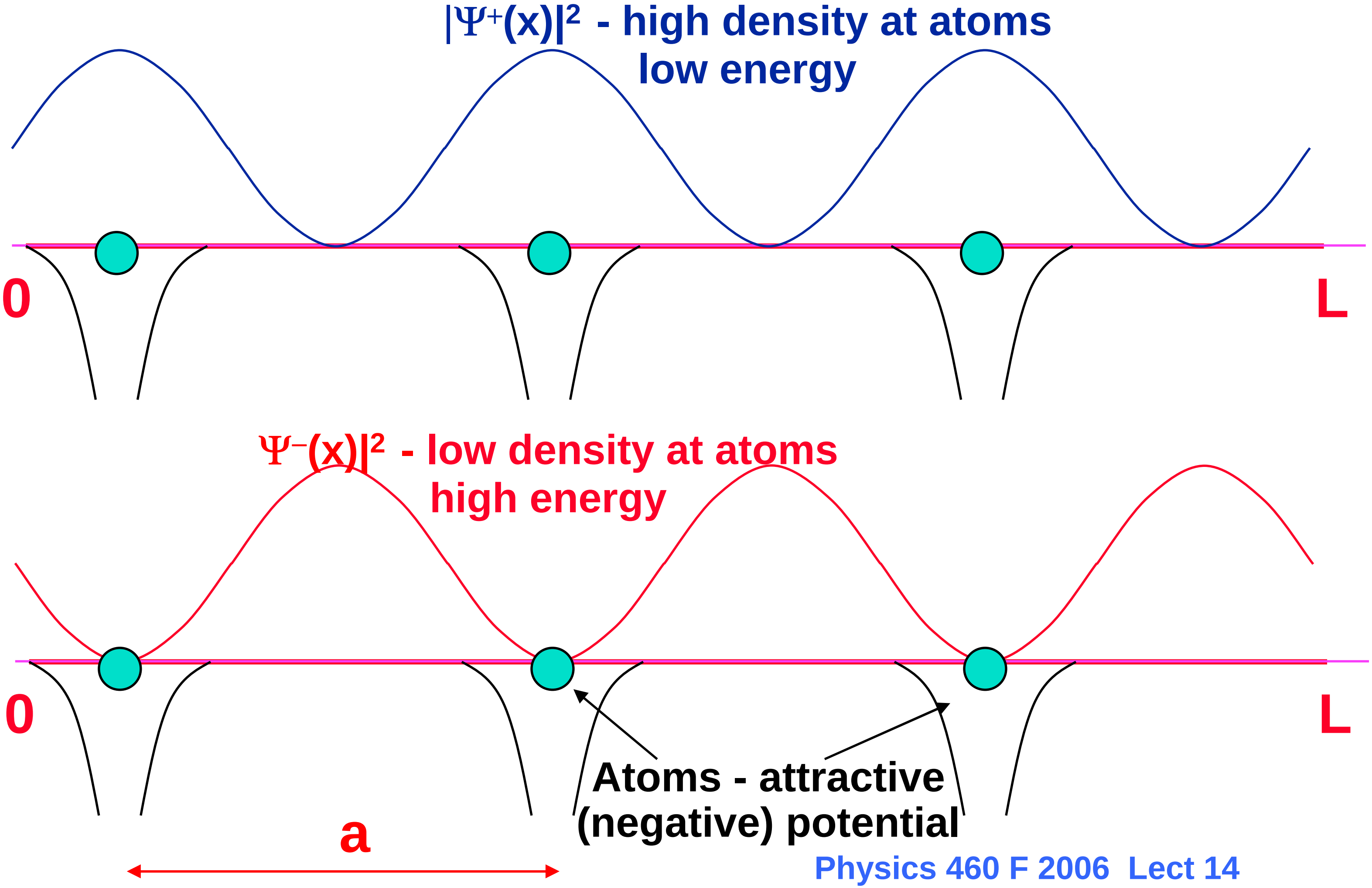
$$\Psi^{+}(x) = \exp(i \pi x/a) + \exp(-i \pi x/a) = 2 \cos(\pi x/a)$$
$$\Psi^{-}(x) = \exp(i \pi x/a) - \exp(-i \pi x/a) = 2i \sin(\pi x/a),$$

The density of electrons for each standing wave is:

$$|\Psi^{+}(x)|^2 = 4 \cos^2(\pi x/a)$$
$$|\Psi^{-}(x)|^2 = 4 \sin^2(\pi x/a)$$

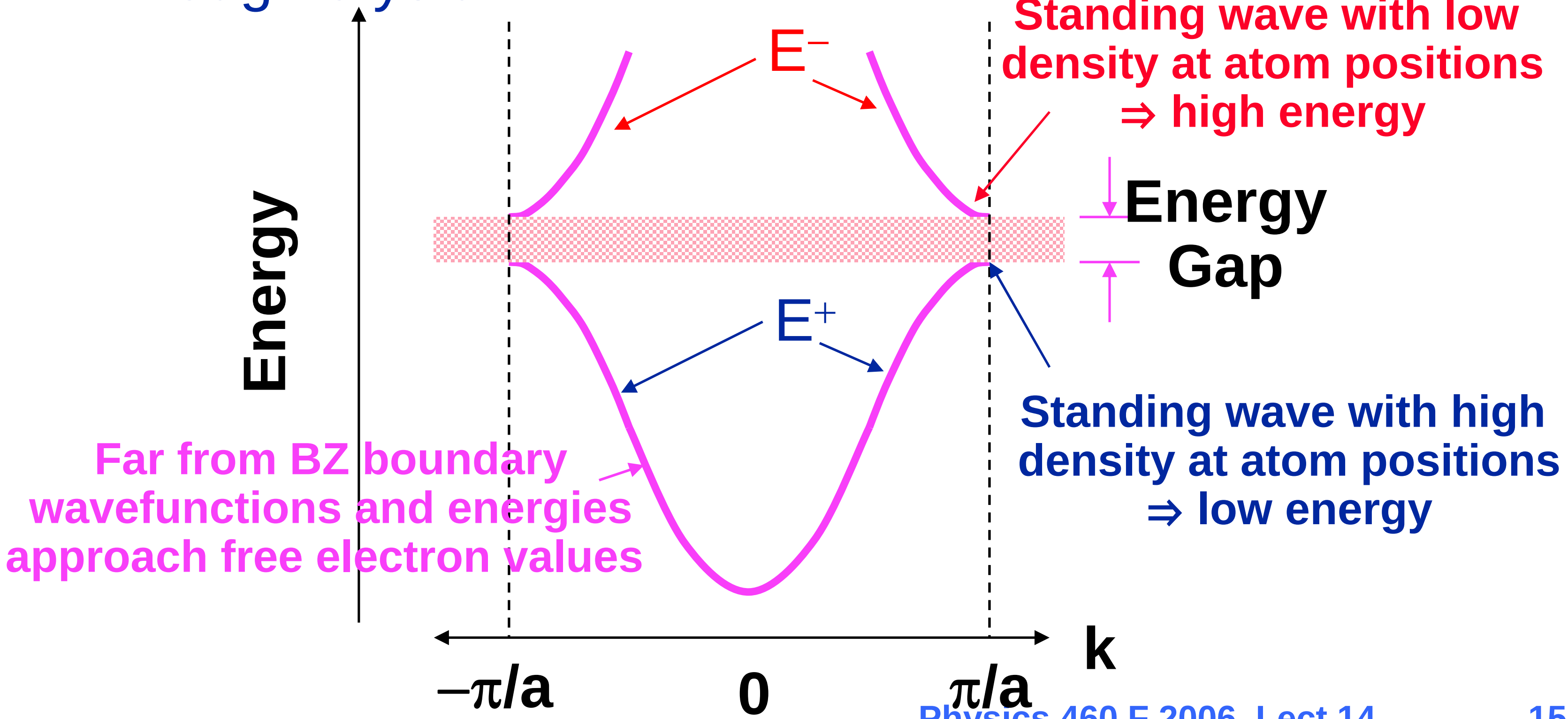
- (Recall standing phonon waves at the zone boundary)

Interpretation of Standing waves at Brillouin Zone boundary



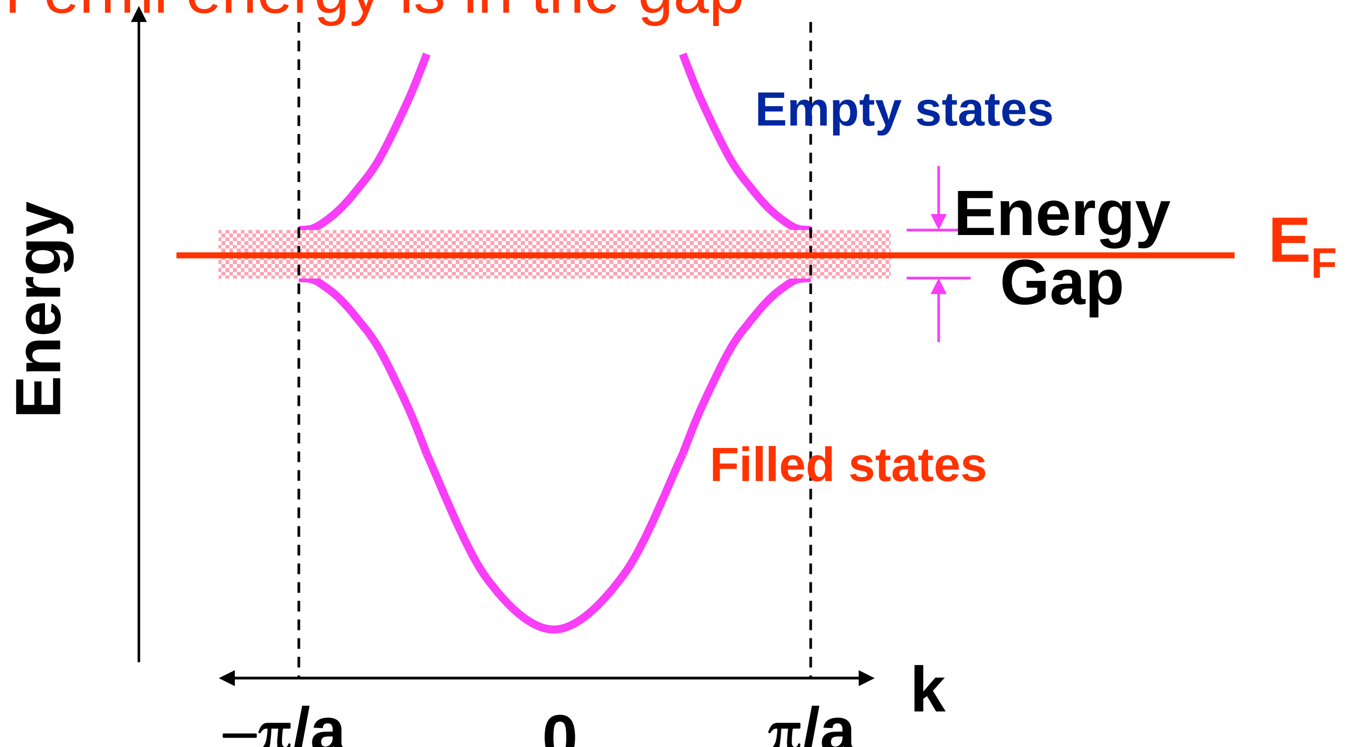
Nearly Free Electrons on a line

- Bands changed greatly only at zone boundary
  Standing wave at zone boundary
  Energy gap -- energies at which no waves can travel through crystal



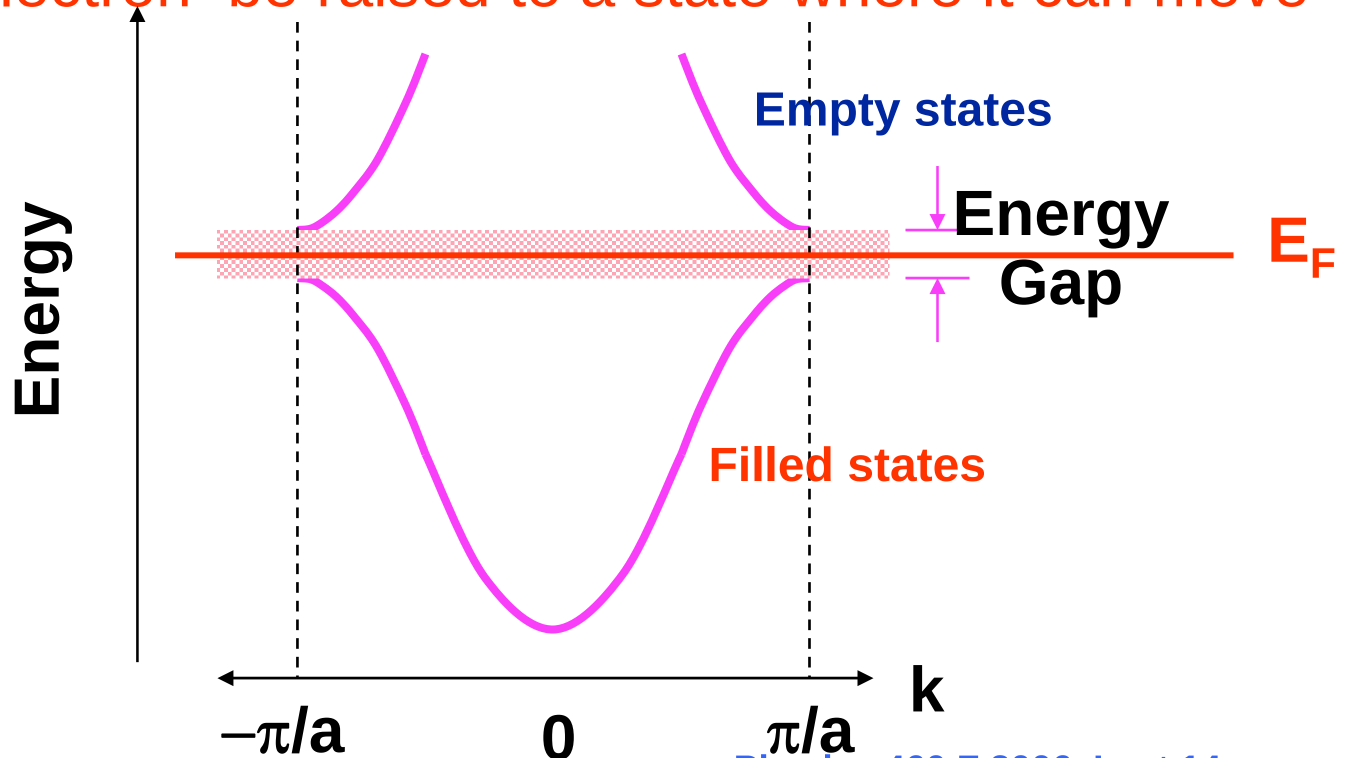
How does this help us understand that some materials are insulators or semiconductors?

- If there are just the right number of electrons to fill the lower band and leave the upper band(s) empty
- The Fermi energy is in the gap

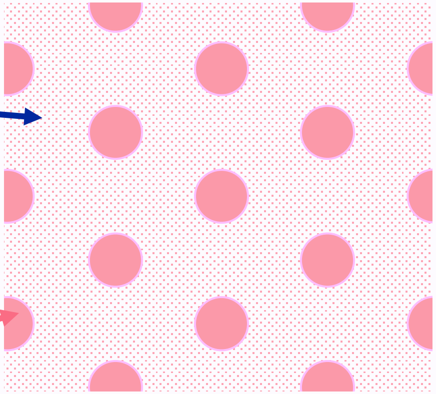


This is an insulator (or a semiconductors)!

- If the Fermi energy is in the gap, then the electrons are not free to move!
- Only if one adds an energy as as large as the gap can an electron be raised to a state where it can move



Summary I



- **Real Crystal -**
  Potential variation with the periodicity of the crystal

  Attractive (negative) potential around each nucleus

- **Potential leads to:**
  Electron bands - E(k) different from free electron bands
  Band Gaps

- **More next time on Consequences for crystals**

Summary II

- Electrons in crystals
  - Build upon the solution for free electrons
  - Consider “nearly free electrons” – first step in understanding electrons in crystals
- Simple picture of how Bragg diffraction leads to standing waves at the Brillouin Zone boundary and to energy gaps
- This is the basic idea for understanding why are some materials are insulators, some are metals, some are semiconductors
- In the following lectures, this will be developed and applied – especially for understanding semiconductors

Next time

- Bloch Theorem
  - Bloch states for electrons in crystals
  - Energy Bands
  - Band Gaps
- Kronig-Penny Model
- General solutions in Fourier Space
- Energy Bands and Band Gaps
  - Basis for understanding metals, insulators, and semiconductors
- (Read Kittel Ch 7)