

Representation of E,k for 1-D Material

$$E = \frac{\hbar^2 k^2}{2m}; k = \frac{\sqrt{2mE}}{\hbar}$$

$$\frac{dE}{dk} = \frac{\hbar^2 k}{m}$$

$$N = \frac{2k_F L}{\pi}$$

$$g(E) = \frac{dN}{dE} \frac{dk}{dE} \frac{1}{L} = \frac{2}{\pi} \frac{m}{\hbar^2 k} = \frac{\sqrt{2m}}{\pi \hbar} E^{-\frac{1}{2}}$$

$g(E)$ =density of states=number of electron states per energy per length

$$n = \frac{N}{L} = \frac{2k_F}{\pi} = \frac{2\sqrt{2mE_F}}{\hbar\pi} \text{ or } k_F = \frac{n\pi}{2}$$

- n , the electron density, the number of electrons per unit length is determined by the crystal structure and valence
- n determines the energy and velocity of the highest occupied electron state at $T=0$

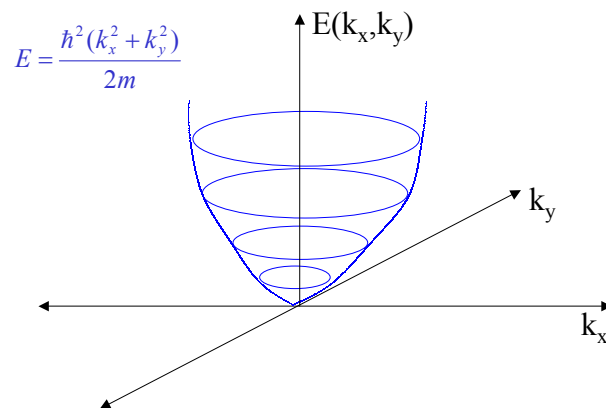


3.225

© E. Fitzgerald-1999

1

Representation of E,k for 2-D Material

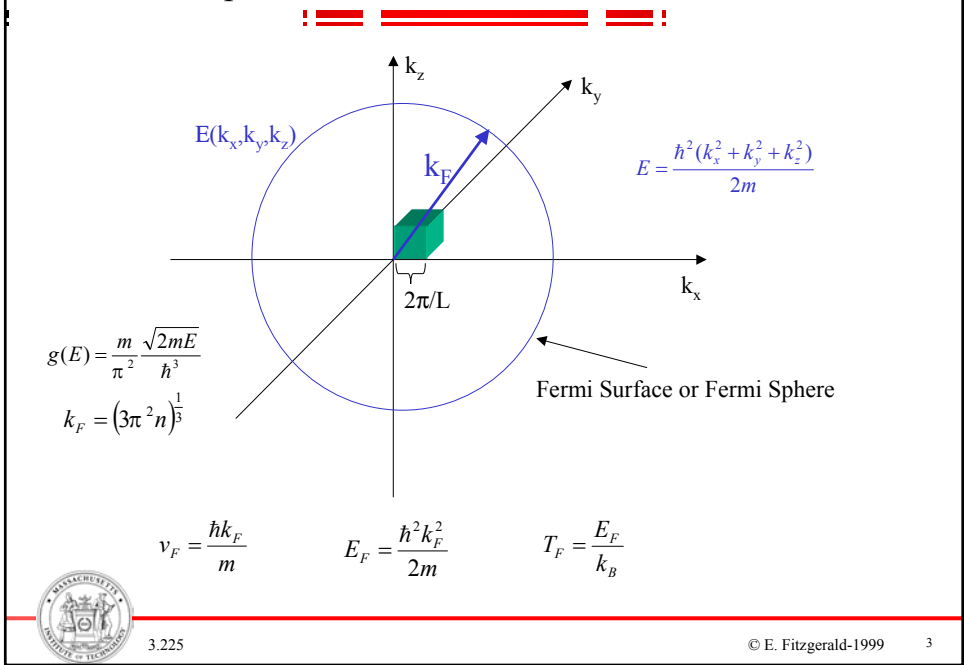


3.225

© E. Fitzgerald-1999

2

Representation of E,k for 3-D Material



So how have material properties changed?

- The Fermi velocity is much higher than kT even at $T=0!$ Pauli Exclusion raises the energy of the electrons since only 2 e- allowed in each level
- Only electrons near Fermi surface can interact, i.e. absorb energy and contribute to properties

$$T_F \sim 10^4 \text{K} \quad (T_{\text{room}} \sim 10^2 \text{K}),$$

$$E_F \sim 100 E_{\text{class}}, \quad v_F^2 \sim 100 v_{\text{class}}^2$$

Table 2.1
FERMI ENERGIES, FERMI TEMPERATURES, FERMI WAVE VECTORS, AND FERMI VELOCITIES FOR REPRESENTATIVE METALS*

ELEMENT	r_s/a_0	ϵ_F	T_F	k_F	v_F
Li	3.25	4.74 eV	5.51×10^4 K	$1.12 \times 10^8 \text{ cm}^{-1}$	$1.29 \times 10^8 \text{ cm/sec}$
Na	3.93	3.24	3.77	0.92	1.07
K	4.86	2.12	2.46	0.75	0.86
Rb	5.20	1.85	2.15	0.70	0.81
Cs	5.62	1.59	1.84	0.65	0.75
Cu	2.67	7.00	8.16	1.36	1.57
Ag	3.02	5.49	6.38	1.20	1.39
Au	3.01	5.53	6.42	1.21	1.40
Be	1.87	14.3	16.6	1.94	2.25
Mg	2.66	7.08	8.23	1.36	1.58
Ca	3.27	4.69	5.44	1.11	1.28
Sr	3.57	3.93	4.57	1.02	1.18
Ba	3.71	3.64	4.23	0.98	1.13
Nb	3.07	5.32	6.18	1.18	1.37
Fe	2.12	11.1	13.0	1.71	1.98
Mn	2.14	10.9	12.7	1.70	1.96
Zn	2.30	9.47	11.0	1.58	1.83
Cd	2.59	7.47	8.68	1.40	1.62
Hg	2.65	7.13	8.29	1.37	1.58
Al	2.07	11.7	13.6	1.75	2.03
Ga	2.19	10.4	12.1	1.66	1.92
In	2.41	8.63	10.0	1.51	1.74
Tl	2.48	8.15	9.46	1.46	1.69
Sn	2.22	10.2	11.8	1.64	1.90
Pb	2.30	9.47	11.0	1.58	1.83
Bi	2.25	9.90	11.5	1.61	1.87
Sb	2.14	10.9	12.7	1.70	1.96

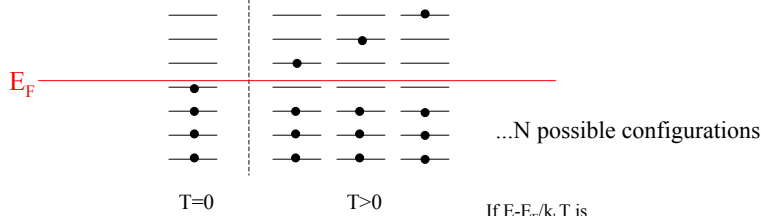
* The table entries are calculated from the values of r_s/a_0 given in Table 1.1 using $m = 9.11 \times 10^{-28}$ grams.



Effect of Temperature ($T>0$): Coupled electronic-thermal properties in conductors

- Electrons at the Fermi surface are able to increase energy: responsible for properties
- Fermi-Dirac distribution
- NOT Boltzmann distribution, in which any number of particles can occupy each energy state/level

Originates from:



$$f = \frac{1}{e^{\frac{(E-E_F)}{k_b T}} + 1}$$

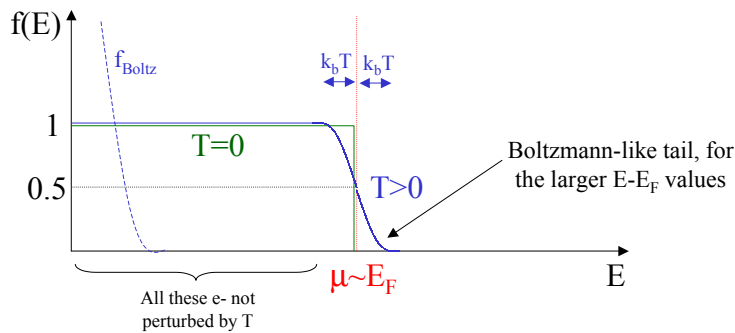
If $E-E_F/k_b T$ is large (i.e. far from E_F) then $f = e^{\frac{-(E-E_F)}{k_b T}}$



3.225

© E. Fitzgerald-1999 5

Fermi-Dirac Distribution: the Fermi Surface when $T>0$



Heat capacity of metal (which is \sim heat capacity of free e- in a metal):

$$c_v = \left(\frac{\partial U}{\partial T} \right)_v \quad U \sim \Delta E \cdot \Delta N \sim k_b T \cdot [g(E_F) \cdot k_b T] \sim g(E_F) \cdot (k_b T)^2 \quad U = \text{total energy of electrons in system}$$

$$c_v = \left(\frac{\partial U}{\partial T} \right)_v = 2 \cdot g(E_F) \cdot k_b^2 T \quad \text{Right dependence, very close to exact derivation}$$



3.225

© E. Fitzgerald-1999 6

Electrons in a Periodic Potential

- Rigorous path: $H\Psi = E\Psi$
- We already know effect: DeBroglie and electron diffraction
- Unit cells in crystal lattice are 10^{-8} cm in size
- Electron waves in solid are $\lambda = h/p \sim 10^{-8}$ cm in size
- Certain wavelengths of valence electrons will diffract!



Diffraction Picture of the Origin of Band Gaps

- Start with 1-D crystal again

1-D

$\lambda \sim a$

Take lowest order, $n=1$, and consider an incident valence electron moving to the right

$$k_i = \frac{\pi}{a}; \psi_i = e^{i\frac{\pi}{a}x}$$

Reflected wave to left: $k_o = -\frac{\pi}{a}; \psi_o = e^{-i\frac{\pi}{a}x}$

$$\Delta k = k_i - k_o = \frac{2\pi}{a}$$

$n\lambda = 2d \sin\theta$ $d=a, \sin\theta=1$

$n\lambda = 2a$

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

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

Total wave for electrons with diffracted wavelengths:

$$\psi = \psi_i \pm \psi_o$$

$$\psi_s = \psi_i + \psi_o = 2 \cos \frac{\pi}{a} x$$

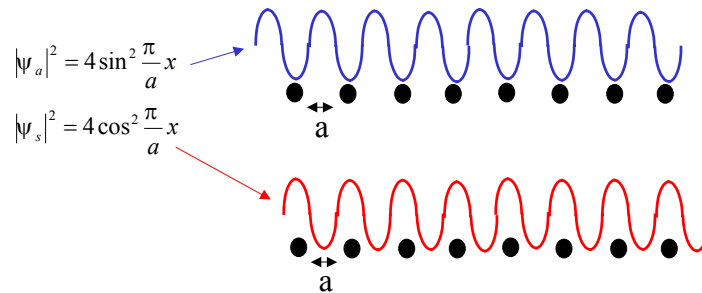
$$\psi_a = \psi_i - \psi_o = i 2 \sin \frac{\pi}{a} x$$



Diffraction Picture of the Origin of Band Gaps



Probability Density=probability/volume of finding electron= $|\psi|^2$



- Only two solutions for a diffracted wave
 - Electron density on atoms
 - Electron density off atoms
- No other solutions possible at this wavelength: no free traveling wave



Nearly-Free Electron Model



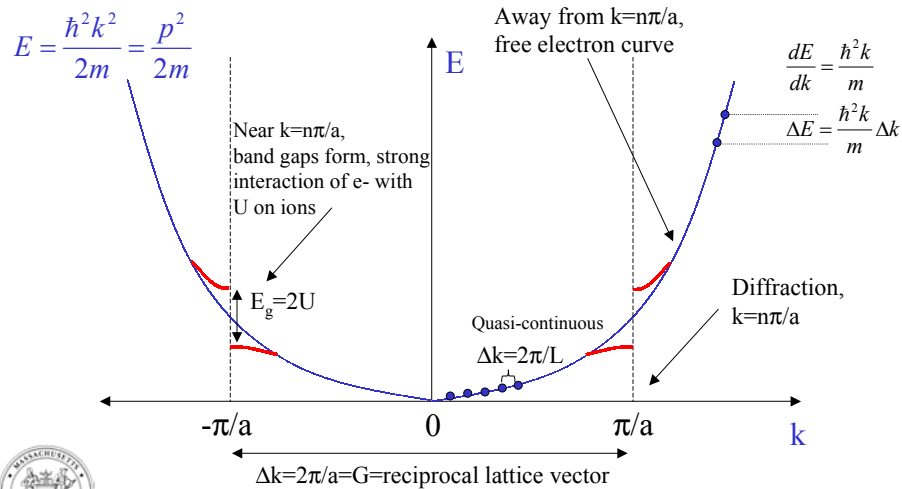
- Assume electrons with wave vectors (k 's) far from diffraction condition are still free and look like traveling waves and see ion potential, U , as a weak background potential
- Electrons near diffraction condition have only two possible solutions
 - electron densities between ions, $E = E_{\text{free}} - U$
 - electron densities on ions, $E = E_{\text{free}} + U$
- Exact solution using $H\Psi = E\Psi$ shows that E near diffraction conditions is also parabolic in k , $E \sim k^2$



Nearly-Free Electron Model (still 1-D crystal)

- states

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



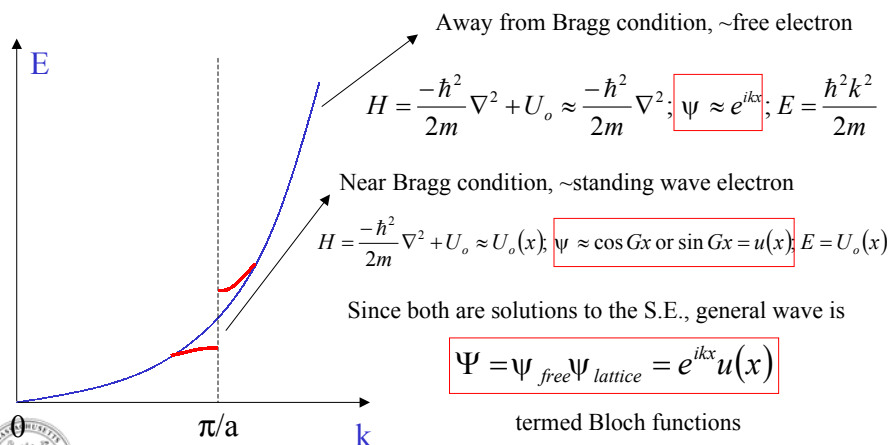
3.225

© E. Fitzgerald-1999

11

Electron Wave Functions in Periodic Lattice

- Often called 'Bloch Electrons' or 'Bloch Wavefunctions'



3.225

© E. Fitzgerald-1999

12

Block Theorem

- If the potential on the lattice is $U(r)$ (and therefore $U(r+R)=U(r)$), then the wave solutions to the S.E. are a plane wave with a periodic part $u(r)$ that has the periodicity of the lattice

$$\Psi(r) = e^{ik \cdot r} u(r)$$

$$u(r) = u(r + R)$$

Note the probability density spatial info is in $u(r)$:

$$\Psi^* \Psi = |\Psi_0|^2 u^*(r) \cdot u(r)$$

An equivalent way of writing the Bloch theorem in terms of Ψ :

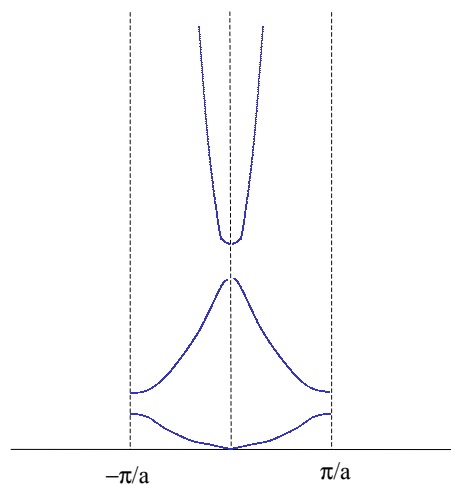
$$\Psi(r + R) = e^{ik(r+R)} u(r + R) = e^{ik(r+R)} \frac{\Psi(r)}{e^{ik \cdot r}}$$

$$\Psi(r + R) = e^{ik \cdot R} \Psi(r)$$



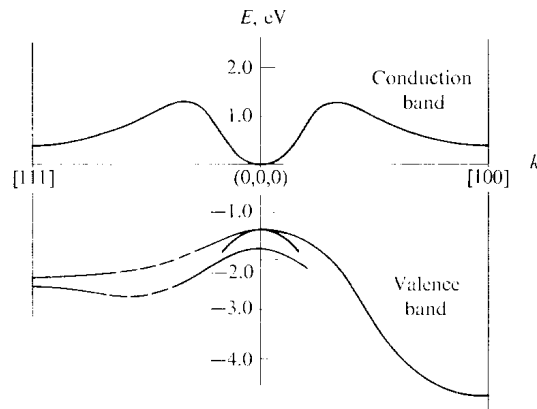
Reduced-Zone Scheme

- Only show $k=\pm\pi/a$ since all solutions represented there



Real Band Structures

- GaAs: Very close to what we have derived in the nearly free electron model
- Conduction band minimum at $k=0$: **Direct Band Gap**



3.225

© E. Fitzgerald-1999

15

Review of H atom

$$\psi = R(r)\Theta(\theta)\Phi(\phi)$$

$$H\psi = E\psi$$

Do separation of variables; each variable gives a separation constant

ϕ separation yields m_l

θ gives ℓ

r gives n

After solving, the energy E is a function of n

$$E = \frac{-\mu Z^2 e^4}{(4\pi\epsilon_0)^2 2\hbar^2 n^2} = -\frac{13.6\text{eV}}{n^2}$$

m_l and ℓ in Φ and Θ give Ψ the shape
(i.e. orbital shape)

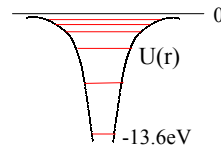
The relationship between the separation constants (and therefore the quantum numbers are:)

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

$$\ell=0,1,2,\dots,n-1$$

$$m_l = -\ell, -\ell+1, \dots, 0, \dots, \ell-1,$$

$$(m_s = + \text{ or } - 1/2)$$



3.225

© E. Fitzgerald-1999

16

Relationship between Quantum Numbers

TABLE 7-1. Possible Values of l and m_l for $n = 1, 2, 3$

n	1		2		3			
l	0	0	1		0	1		2
m_l	0	0	-1, 0, +1		0	-1, 0, +1		-2, -1, 0, +1, +2
Number of degenerate eigenfunctions for each l	1	1	3		1	3		5
Number of degenerate eigenfunctions for each n	1	4		9				
	s		s		p		d	

Origin of the periodic table

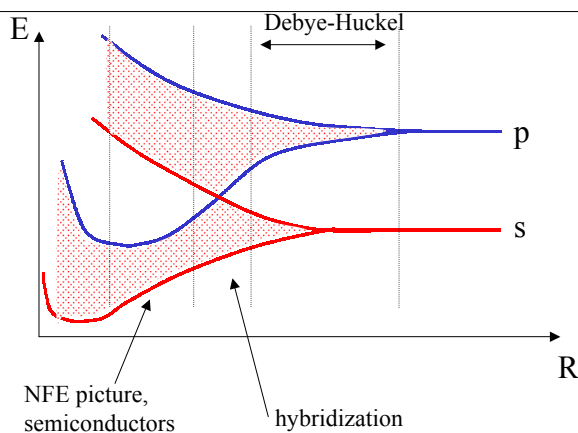


3.225

© E. Fitzgerald-1999 17

Bonding and Hybridization

- Energy level spacing decreases as atoms are added
- Energy is lowered as bonding distance decreases
- All levels have E vs. R curves: as bonding distance decreases, ion core repulsion eventually increases E



3.225

© E. Fitzgerald-1999 18