

Li: bonding via s orbitals      Be: bonding via sp hybrids

Transition Metals: s, p, d electrons important in bonding

{  $E_F$  rarely lies half-way up ladder }  
 {  $\Delta E$  not constant }

Density of states  $Z(E)$ ,  $p(E)$  not constant.  
 (states between  $E$ ,  $E+dE$ )

$p \propto$  no. of states at  $E$  \* spacing  
 (degeneracy)

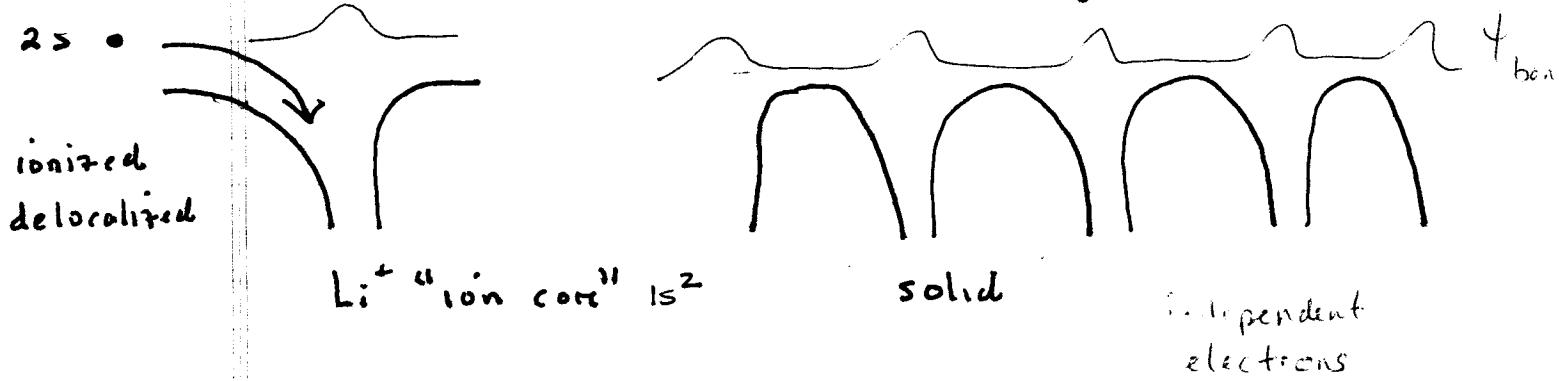
(SKIP)

Typically  $p$  goes up with increasing  $E$ . (H-atom example)

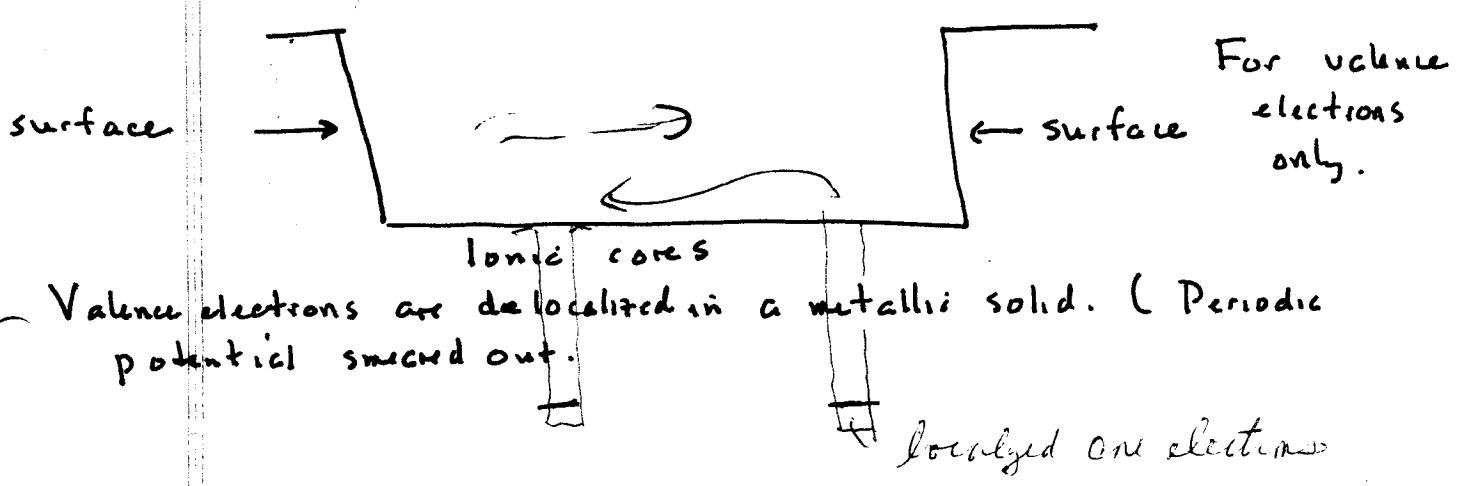
$E_F$  changed?  
 by adsorbate

Valence Electrons: Free Electron JELLIUM MODEL

Consider an electron and  $Li^+$  (or any metal ion)



We approximate periodic potential by particle-in-a-box:



Valence electrons are delocalized in a metallic solid. (Periodic potential smeared out.)

# Simplistic Procedure

1-D Use electron in a macroscopic box with  $\infty$  walls

$$E_n = \frac{n^2 h^2}{8mL^2} = \frac{n^2 \hbar^2 \pi^2}{2mL^2} \quad n = 1, 2, 3, 4, \dots$$

$$\Psi_n(x) = \sqrt{2/L} \sin \frac{n\pi x}{L} \quad \text{independent particles except for Pauli Princ.}$$

Physicists like to use  $k_x = \frac{p_x}{\hbar} = \frac{h}{\hbar \lambda} = \frac{2\pi}{\lambda}$   $\lambda = \frac{h}{p}$   
 momentum; wave vector

$$\bar{V}=0 \quad E = \frac{p_x^2}{2m} = \frac{\hbar^2 k_x^2}{2m} \Rightarrow k_x^2 = \frac{n^2 \pi^2}{L^2} \quad k_x = \frac{n\pi}{L} = \frac{2\pi}{\lambda_n}$$

$$\Psi_n(x) = A \sin k_x x = A \sin \frac{2\pi x}{\lambda_n} \quad \lambda_n = \frac{2L}{n}$$

(or  $k_x$ )

3-D  $E = E_x + E_y + E_z = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2)$

$$L_x = L_y = L_z = L$$

$$E = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2}{2m} k^2$$

$$k_x = \frac{n_x \pi}{L} \text{ etc.}$$

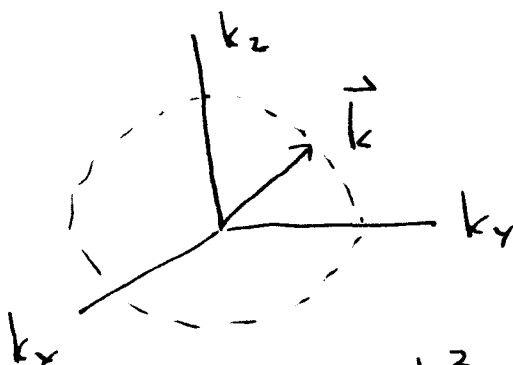
(discrete barely)

$$\Psi = A \sin k_x x \sin k_y y \sin k_z z \quad A = \sqrt{\frac{2^3}{V}}$$

Count number of levels up to a given  $k_{\max}$ : (or  $n_{\max}$ )

$$k^2 = k_x^2 + k_y^2 + k_z^2$$

"momentum space"



1 state  $\leftrightarrow$  8 boxes

No. levels through  $k_{\max}$

$$= \frac{\frac{4}{3} \pi k_{\max}^3}{(2\pi/L)^3}$$

2:  $k_x, -k_x$  etc.  
not independent states

$$N_{\text{levels}} = \frac{\pi}{6} \frac{k_{\text{max}}^3}{(\pi/L)^3} = \frac{V}{6\pi^2} k_{\text{max}}^3$$

$$N_{\text{levels}} = \frac{V}{6\pi^2} \left( \frac{2mE_F}{\hbar^2} \right)^{3/2} = \frac{1}{2} N_{\text{electrons}}$$

$$E_F = \frac{\hbar^2 k_{\text{max}}^2}{2m}$$

↑↓  
(= 1/2 N<sub>states</sub>)

$$k_{\text{max}}^2 = \frac{2mE_F}{\hbar^2} \quad N_{\text{elec}} = \frac{V}{3\pi^2} \left( \frac{2mE_F}{\hbar^2} \right)^{3/2}$$

$$N_{\text{elec}} = \frac{1}{3\pi^2} \left( \frac{8\pi^2 m}{\hbar^2} \right)^{3/2} V E_F^{3/2}$$

$$= \frac{\pi}{3} \left( \frac{8m}{\hbar^2} \right)^{3/2} V E_F^{3/2}$$

keep on board

$$E_F^{3/2} = \frac{3}{\pi} \underbrace{\frac{N_{\text{elec}}}{V}}_{\rho_{\text{elec}}} \left( \frac{\hbar^2 4\pi^2}{8me} \right)^{3/2} *$$

OK  
max. occupied level

$$E_F = \frac{\hbar^2}{2me} \left( 3\pi^2 \rho_{\text{elec}} \right)^{2/3}$$

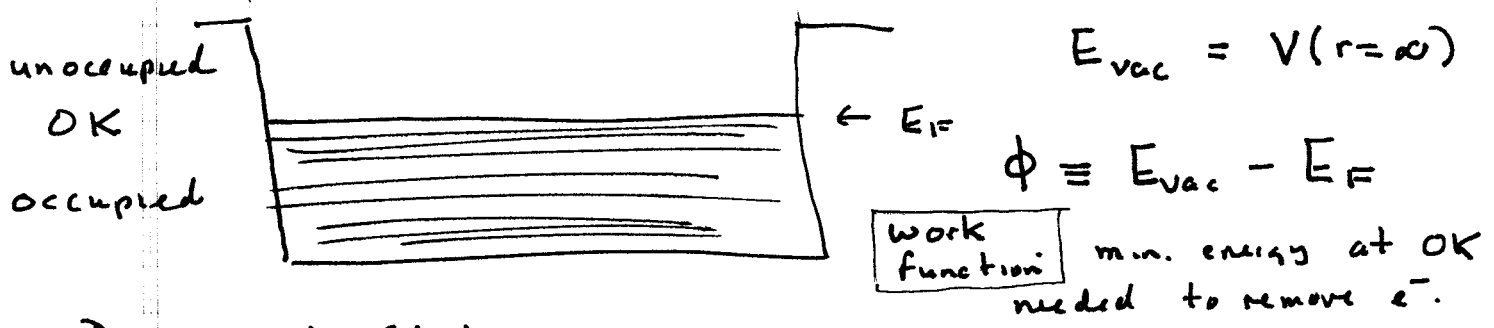
One valence electron per atom (Li.)

$$\rho_{\text{elec}} = \rho_{\text{atom}} \sim \sim 4.5 \times 10^{22} \frac{\text{elec}}{\text{cm}^3}$$

can estimate through bcc unit cell or bulk density

$$* E_F = \frac{\hbar^2 4\pi^2}{8me} \left( \frac{3}{\pi} \rho_{\text{elec}} \right)^{2/3}$$

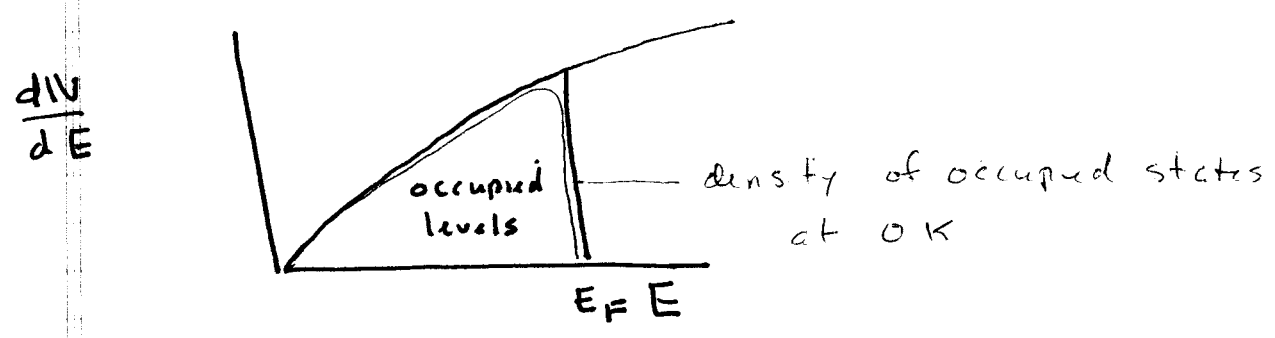
$\Rightarrow E_F \sim 7.5 \times 10^{-12} \text{ erg} = 4.7 \text{ eV}$



Density of States

$\frac{dN_{states}}{dE} = ?$   $N(E) = \frac{\pi}{3} \left( \frac{8m}{h^2} \right)^{3/2} V E^{3/2} \quad (0-E)$

$\frac{dN_{states}}{dE} = \frac{\pi}{2} \left( \frac{8m}{h^2} \right)^{3/2} V E^{1/2}$



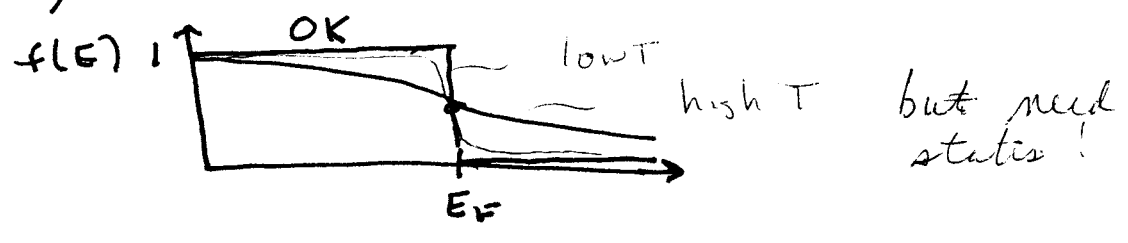
$T > 0K$  Fermi-Dirac Distribution Law

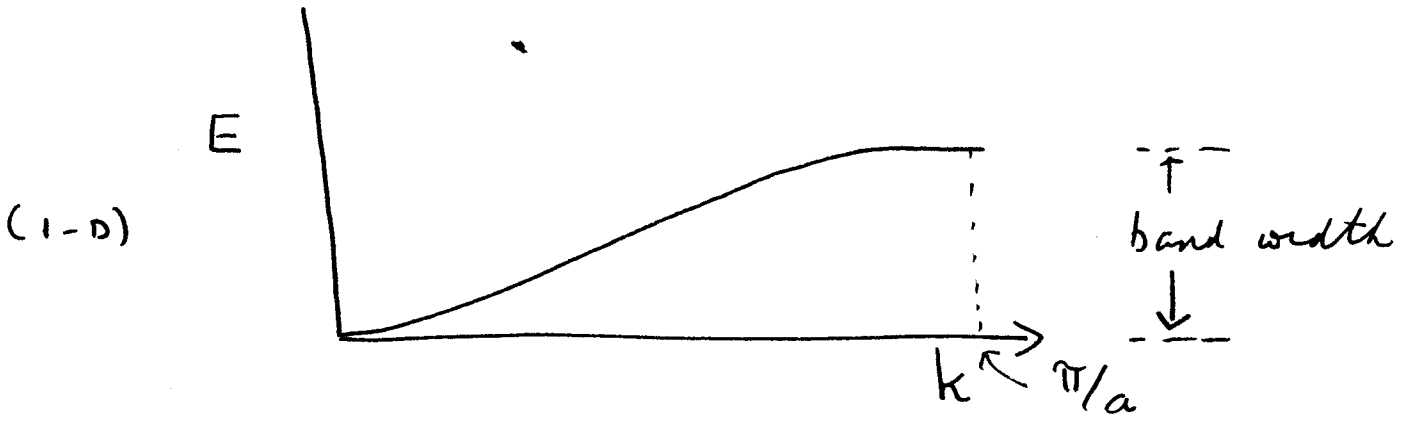
Electrons are Fermions ( $s = 1/2$ ) & do not obey normal Boltzmann statistics.

FD distribution Law:  $f(E) = \frac{1}{1 + e^{(E-\mu)/kT}}$   
fractional population per state

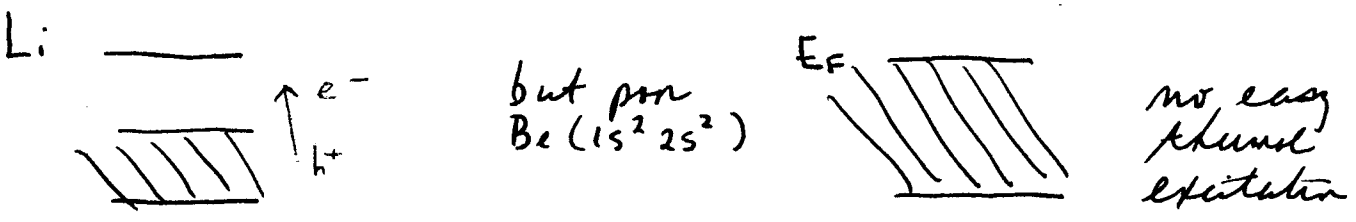
$T \approx 0K$   $f(E < E_F) = 1$   $f(E > E_F) = 0$   
 $\therefore \mu = E_F$  at 0K  $E_F \gg kT$

chemical potential



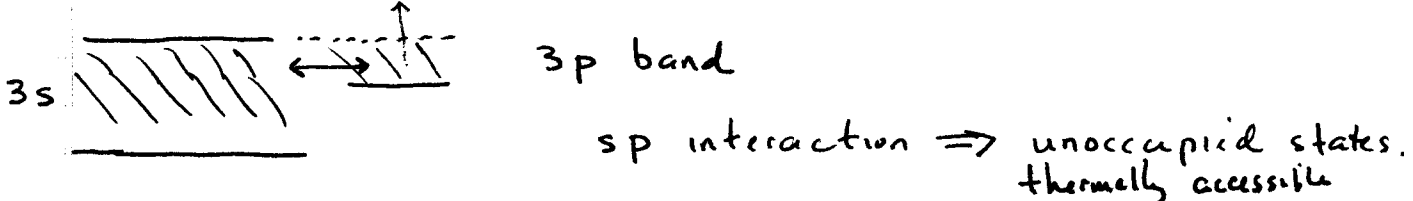


But, with a finite band, trouble ensues with our definition of conduction:

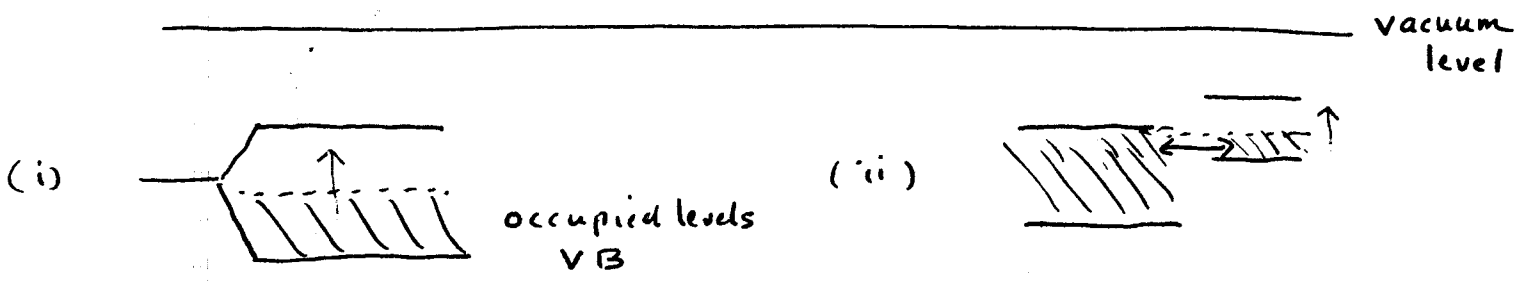


and what about magnesium?  $Mg (1s^2 2s^2 2p^6 3s^2)$   
 Valence

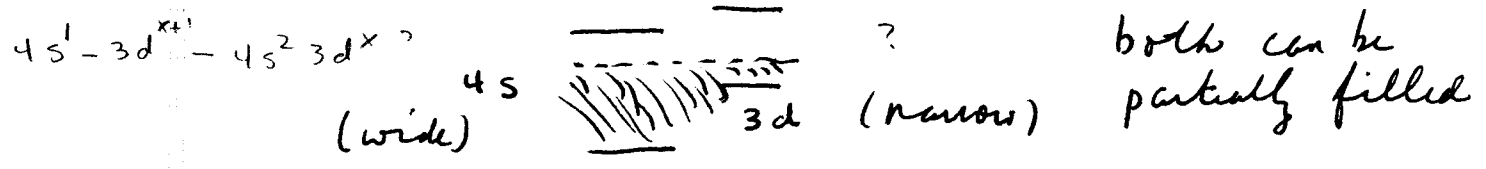
The solution lies with hybridization, or as physicists say, overlapping bands. Consider  $Mg$ :



Two Types of Metallic Conductors



$M^c$  Cash Transition metals are even more complex:



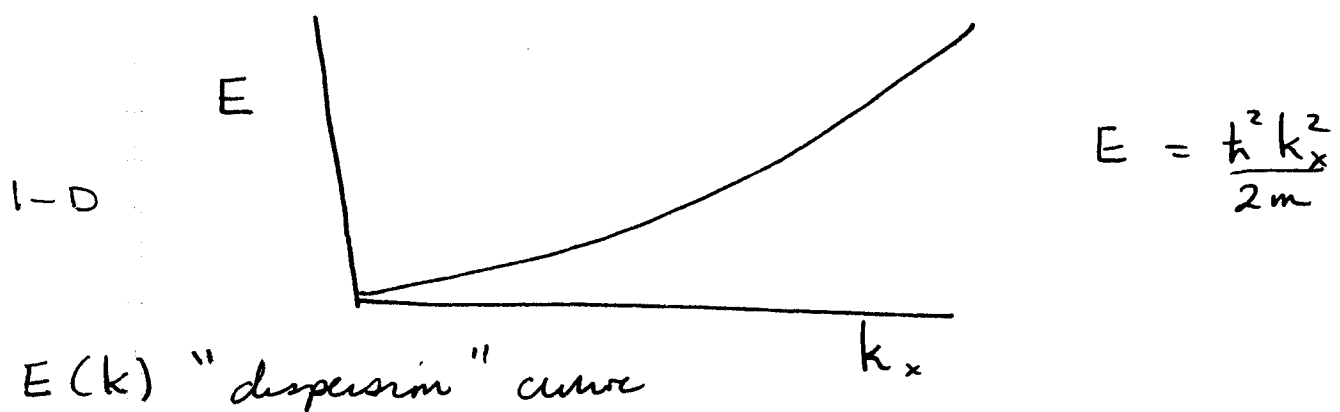
For  $T > 0K$ ,  $\mu = E_F \left[ 1 - \frac{\pi^2}{12} \left( \frac{k_B T}{E_F} \right)^2 \right]$

$T = 300K$   $E_F = 4 eV \Rightarrow \mu \sim E_F (0.99997)$

The formula comes from the definition that  $\mu = E$  at which  $f(E) = 0.5$  (see figure)

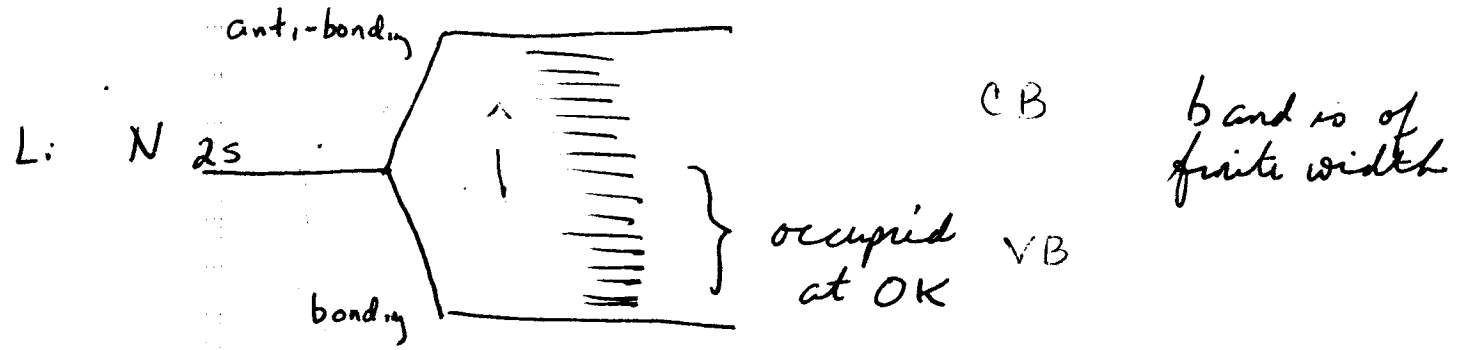
When electrons are thermally promoted to  $E > E_F$ , holes of  $(+)$  charge are created. The hole  $+ - e^-$  combination allows conduction in the presence of an applied electric field.

The simple free electron model has its problems! According to this model, the band stretches to  $\infty$ :



$E(k)$  "dispersion" curve

But this is not possible. Remember our  $N$   $Li$  atoms:

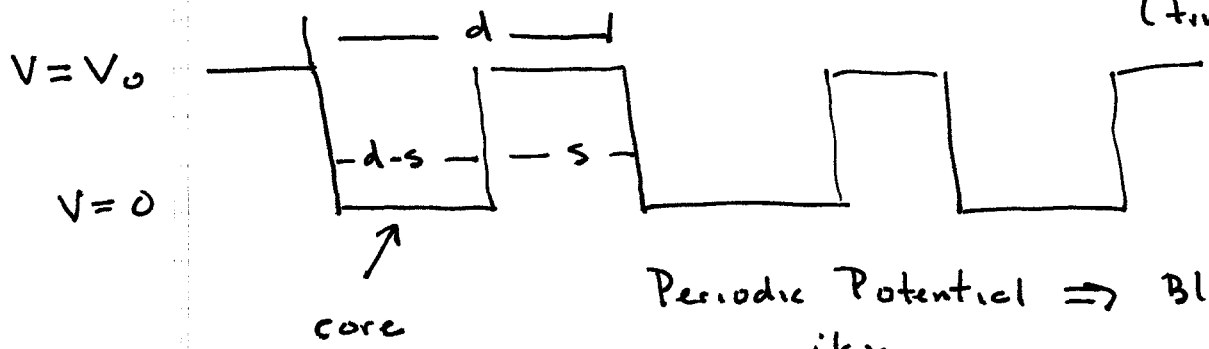


Another representation of this band in terms of  $k$  is

1-D Model  
Morrison et al.

Kronig - Penney Model

∞ Length  
(true continuous)



Periodic Potential ⇒ Bloch's theorem

$$\psi_{E,k}(x) = \underbrace{e^{ikx}}_{\text{plane wave}} \underbrace{u_{E,k}(x)}_{\text{periodic function}}$$

$$u_{E,k}(x + nd) = u_{E,k}(x)$$

periodic function  
invariant under  
translation by any  
lattice translation  
vector  $T = nd$

label for now (quantum "number")

$$V=0 \quad nd \leq x \leq nd + d-s$$

$$V=V_0 \quad \text{elsewhere}$$



$V=0$   
regions

$$\frac{d^2 \psi}{dx^2} + \frac{2m}{\hbar^2} E \psi_{E,k}(x) = 0$$

Is this  
correct?

$$\psi_{E,k}(x) = \left[ A e^{i\alpha(x-nd)} + B e^{-i\alpha(x-nd)} \right] e^{iknd}$$

$$\alpha = \sqrt{2mE/\hbar^2}$$

$V=V_0$

$$\psi_{E,k}(x) = \left[ C e^{\beta(x-nd)} + D e^{-\beta(x-nd)} \right] e^{iknd}$$

$$\beta = \frac{1}{\hbar} \sqrt{2m(V_0 - E)}$$

Now match boundary conditions at 2 adjacent boundaries.  
 $\psi, \psi'$  continuous ⇒ A, B, C, D



eigenvalue equation

$$\cos kd = \cos \alpha (d-s) \cosh \beta s$$

$$+ \frac{\beta^2 - \alpha^2}{2\alpha\beta} \sin \alpha (d-s) \sinh \beta s$$

E in  $\alpha, \beta$

exact

Exact?

Limiting Cases

$V_0 \rightarrow \infty$   $E \rightarrow \frac{\pi^2 \hbar^2}{2m_e (d-s)^2} n^2$  p in a box

$s \rightarrow \infty$   $E \rightarrow$  finite well

$$\cot [\alpha (d-s)] = \frac{\alpha^2 - \beta^2}{2\alpha\beta}$$

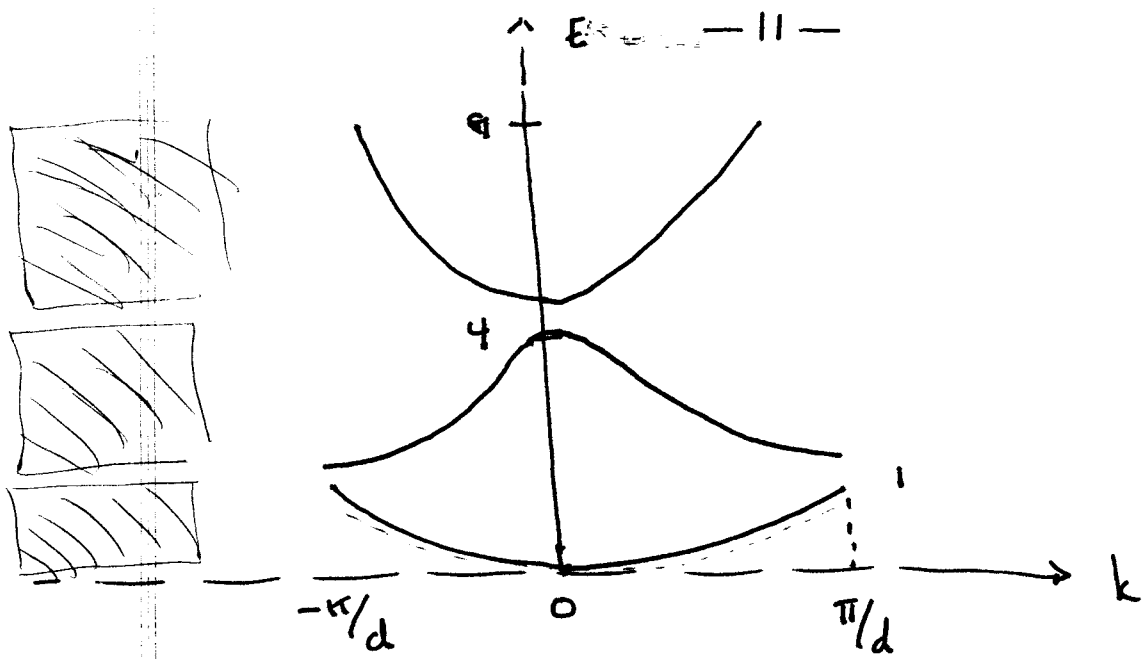
\* General Solution  $V_0 \rightarrow \infty$   $s \rightarrow 0$   $V_0 s$  constant



Three continuous bands:

- Band 1  $0.174 \leq E \leq 1$  in units of  $\frac{\pi^2 \hbar^2}{2m_e d^2}$
- gap 1
- Band 2  $1.37 \leq E \leq 4$
- gap 2
- Band 3  $4.49 \leq E \leq 9$

Eigenvalue  $E_1$  yields plot of  $E$  vs  $k$



First Brillouin Zone

Free electron approx

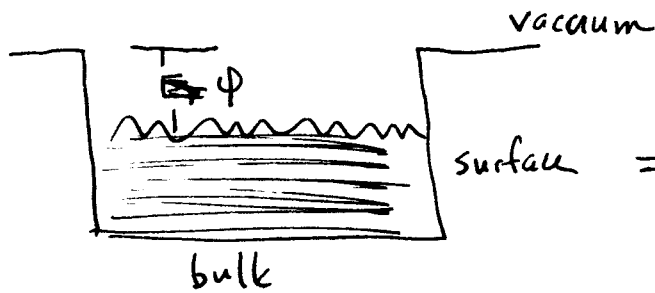
### The Metallic Surface

How do these bulk considerations relate to the surface?

Simple View:

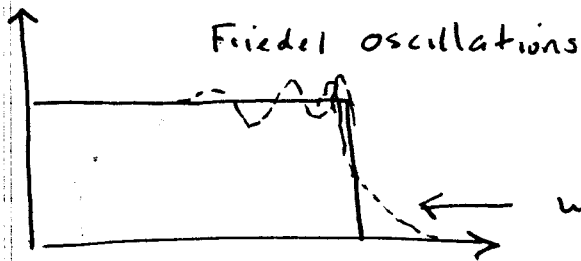
$$\phi = E_{vac} - E_F$$

diff. per?



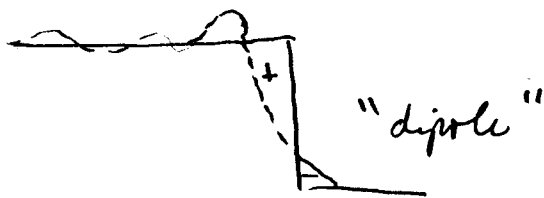
⇒ large electron density?

Electron Density



wave functions extend into vacuum

At surface



"dipole" adds contribution to work function

$$\phi = D - E_F \quad \text{dependent on plane}$$