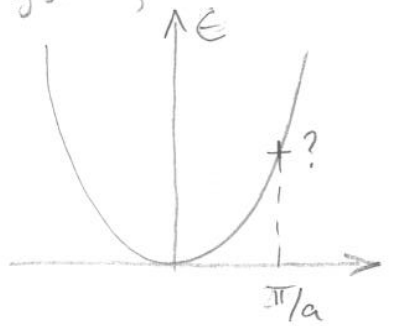


7.1 Electron Bands

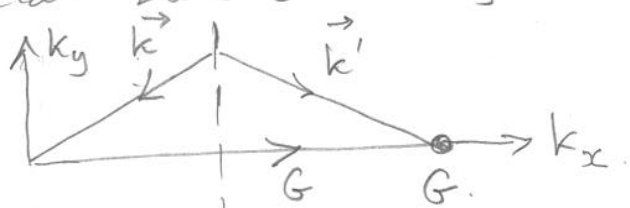
Our free-electron picture completely ignored the crystal, which we will now reintroduce.



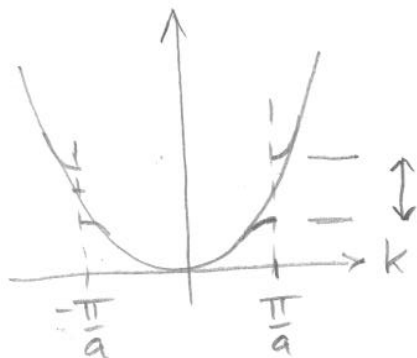
We saw $k_F \sim 2\pi / \text{typical spacing}$
2 electrons/atom means higher k_F still. We will definitely reach zone boundary.

\vec{k} here represents the k -vector of an electron wave function, but it is not different from any other wave, and will undergo elastic scattering or diffraction in a periodic crystal lattice.

Recall Zone Boundary definition.



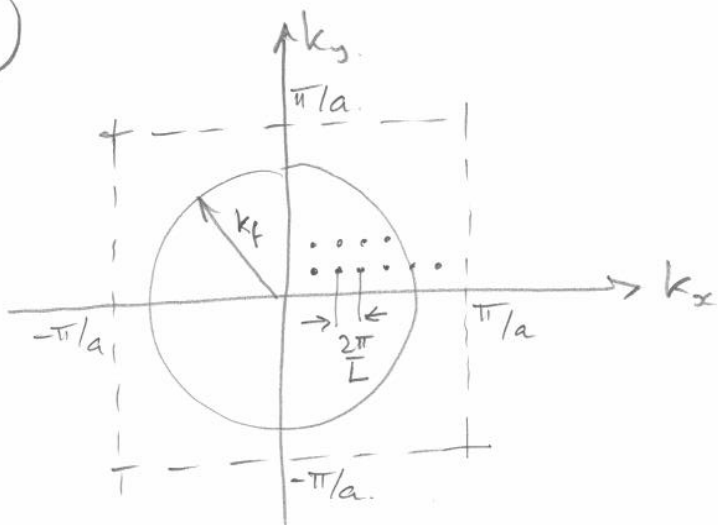
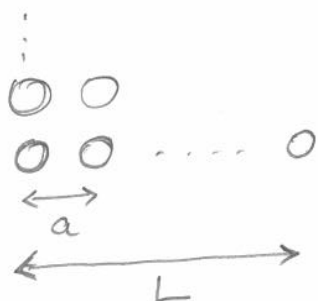
ZB is locus of points satisfying $\vec{k}' - \vec{k} = \vec{G}$
So all electron k 's that lie on (or near) the ZB will give rise to a strong wave k' coupled to it via the (reciprocal) lattice.



$E_g = \text{gap energy}$
Band gap opens at ZB.
- responsible for metal/insulator behaviour.

63a

7.0 Counting of States.



Finite sized crystal:

$$N = \text{no. of atoms} = \left(\frac{L}{a}\right)^3$$

No. of states inside First Brillouin Zone (FBZ)

$$N' = \left(\frac{\pi/a \times 2}{2\pi/L}\right)^2 = \left(\frac{L}{a}\right)^3 = N.$$

So no. of states = no. of atoms. General result

Two electrons per state \Rightarrow fills $\frac{1}{2}$ B.Z.

Sphere fits inside cube; true in almost all cases.

Valency = 1. No effect of zone boundary

Valency = 2. Will reach Z.B.

Metal or insulator? will depend on what happens at the zone boundary.

7.2 Calculation of E_g

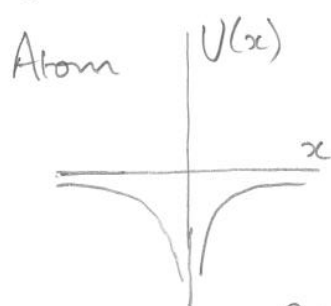
In the presence of strong scattering the $k = \pm \pi/a$ states are equal in amplitude. One state is reflected back and forth into the other and leads to a standing wave:

$$\psi(+)=e^{i\frac{\pi}{a}x}+e^{-i\frac{\pi}{a}x}=2\cos\frac{\pi}{a}x$$

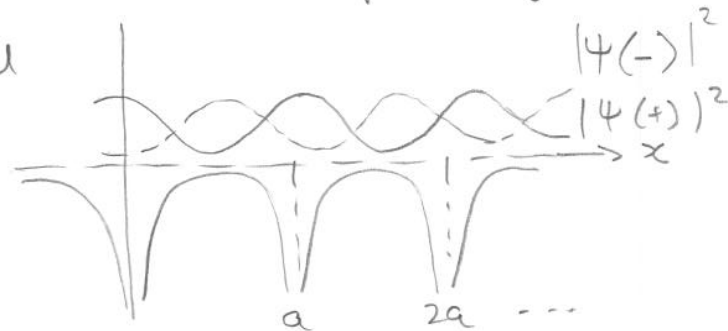
$$\psi(-)=e^{i\frac{\pi}{a}x}-e^{-i\frac{\pi}{a}x}=2i\sin\frac{\pi}{a}x$$

We are considering 1D case or k_x in 3D.

Atomic cores of the lattice contribute a potential $U(x)$, which we no longer neglect.



Crystal



eg Coulomb Potential.

The "nearly-free electron" model considers this $U(x)$ to be a perturbation on the FEG picture.

$$\mathcal{H}\psi = \left(-\frac{\hbar^2}{2m} \nabla^2 + U(\vec{r}) \right) \psi = E\psi = (\mathcal{H}_0 + \mathcal{H}')\psi$$

The energy is obviously lower for $\psi(+)$ than $\psi(-)$ because the maximum probability falls on top of the low potential regions of the crystal.

$|\psi(-)|^2$ is a maximum in between the ions.

If $U(x)$ is a perturbation, called \mathcal{H}' , then the energy change from the unperturbed state

$$\text{is } \Delta E = \int \psi^* \mathcal{H}' \psi dx = \int |\psi|^2 U(x) dx.$$

$$\text{so } E_g = \int U(x) [|\psi(+)|^2 - |\psi(-)|^2] dx$$

↑ unperturbed wave function

(65)

7.3 Fourier expansion of $U(x)$

The power of the reciprocal lattice is that it is the natural basis for Fourier analysis of periodic functions. Central concept in electronic band structure calculations. In 1D:

$$U(x) = \sum_n U_n e^{in \frac{2\pi}{a} x} = \sum_{n>0} U_n \cos n \frac{2\pi}{a} x$$

In the second step we assumed U is symmetric and ignore the $n=0$ offset term.

19.02.07 II U_n are a set of coefficients, U_G $G = \frac{2\pi}{a} n$

one number for every recip. lattice point in 3D. Fourier expansion makes evaluation of E_g easy:

$$E_g = \frac{1}{a} \int_0^a \sum U_n \cos n \frac{2\pi}{a} x \left(\underbrace{\cos^2 \frac{\pi}{a} x - \sin^2 \frac{\pi}{a} x}_{\cos \frac{2\pi}{a} x} \right) dx$$

$$\cos^2 \theta - \sin^2 \theta = \cos 2\theta$$

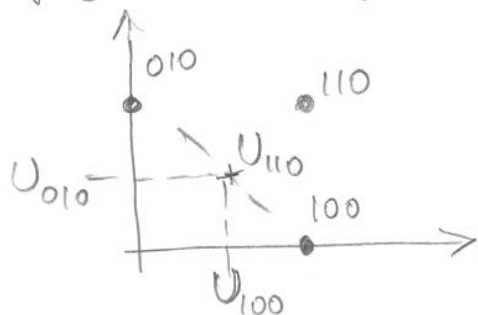
$$\text{Integral} = 0 \quad \text{for } n=0, 2, 3, \dots$$

$$= \frac{a}{2} \quad \text{for } n=1$$

$E_g = U_1$ Gap = first Fourier coef of potential

This result is completely accurate, but it only works for the gap at the ZB. Elsewhere, all the coefs of the Fourier series are important

By generalisation of this argument, the magnitude of the gap due to the \vec{G} reciprocal lattice vector is $U_{\vec{G}}$



65a

3. Consider a divalent metal with a two-dimensional square lattice, of lattice parameter a .

(a) For the *free* electron case, make sketches showing the electron energy as a function of wavevector for wavevectors along the lines from $\mathbf{k} = (0, 0)$ to $(\pi/a, 0)$, from $\mathbf{k} = (0, 0)$ to $(\pi/a, \pi/a)$, and from $\mathbf{k} = (\pi/a, 0)$ to $(\pi/a, \pi/a)$.

[4]

(b) If the crystal potential is

$$U(x, y) = -U_0 \cos\left(\frac{2\pi(x+y)}{a}\right),$$

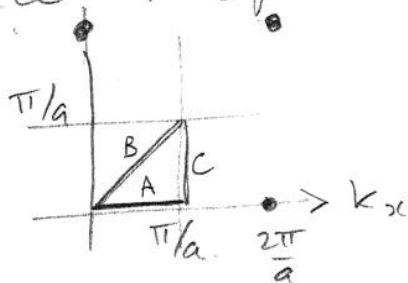
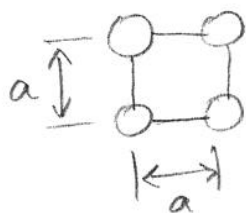
write down an estimate of the energy gaps at $\mathbf{k} = (\pi/a, 0)$ and $\mathbf{k} = (\pi/a, \pi/a)$.

[4]

(c) Taking the estimate of the gap to be exact, derive a condition for the material to be metallic.

[6]

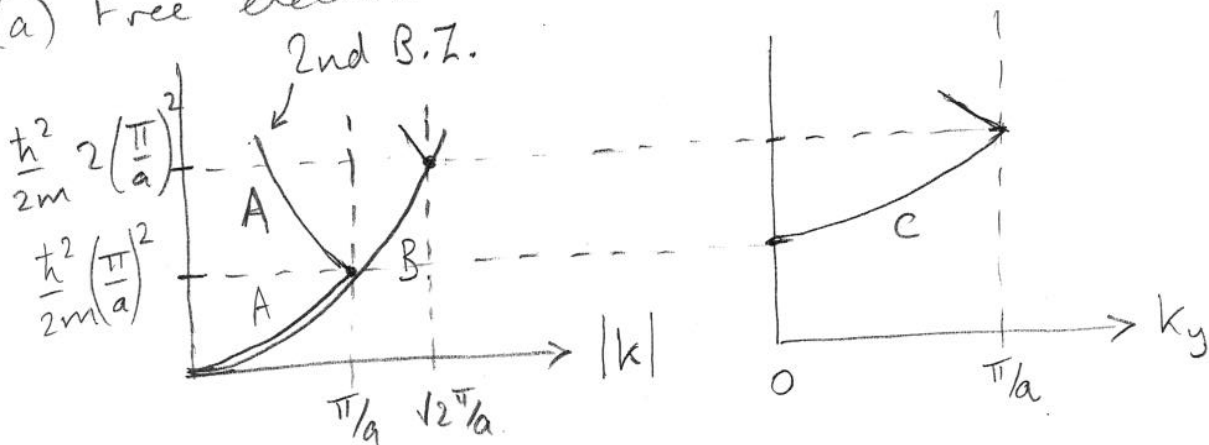
3. Divalent metal has 2 electrons / atom.
 Square lattice \rightarrow square recip. lattice



Three lines of recip space A, B, C

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

(a) Free electron case:



(b) Energy gap = Fourier coefficient of $U(\vec{r})$.
 Standing wave at $k = (\pi/a, 0)$ and $(\pi/a, \pi/a)$.

$$E_g = \int U(x,y) [|\psi(+)|^2 - |\psi(-)|^2] dx dy.$$

at $k = (\pi/a, 0)$:

$$[|\psi(+)|^2 - |\psi(-)|^2] = \left. \begin{aligned} &\cos^2 \frac{\pi}{a} x - \sin^2 \frac{\pi}{a} x \\ &= \cos \frac{2\pi}{a} x \end{aligned} \right\} \times \frac{2}{a^2} \text{ to normalize.}$$

$$E_g = \iint_0^a -U_0 \cos \frac{2\pi}{a} (x+y) \cos \frac{2\pi}{a} x \frac{2}{a^2} dx dy.$$

$$\left(\cos \frac{2\pi}{a} x \cos \frac{2\pi}{a} y - \sin \frac{2\pi}{a} x \sin \frac{2\pi}{a} y \right)$$

= 0 unpaired integral in y each term.

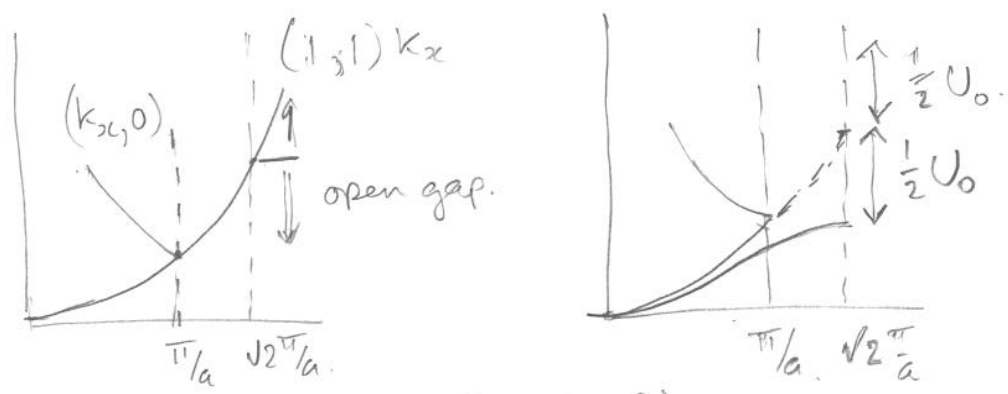
at $k = (\pi/a, \pi/a)$:

$$[|\psi(+)|^2 - |\psi(-)|^2] = \cos^2 \frac{\pi}{a} (x+y) - \sin^2 \frac{\pi}{a} (x+y) \\ = \cos \frac{2\pi}{a} (x+y)$$

$$E_g = \iint_0^a -U_0 \cos \frac{2\pi}{a} (x+y) \cos \frac{2\pi}{a} (x+y) \frac{2}{a^2} dx dy.$$

$$= -U_0 \cos^2 \frac{2\pi}{a} (x+y) \rightarrow \frac{1}{2} \text{ on average.}$$

(c) Metallic when band overlaps are removed:



Condition: $\frac{\hbar^2}{2m} \left(\left(\sqrt{2} \frac{\pi}{a} \right)^2 - \left(\frac{\pi}{a} \right)^2 \right) = \frac{1}{2} U_0.$

$$\Rightarrow \frac{\hbar^2}{m} \left(\frac{\pi}{a} \right)^2 = U_0$$

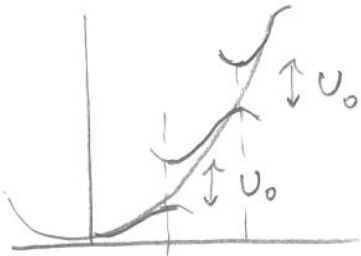
7.4 Kronig - Penney model

$U(x) = \delta$ -function, weight = U_0

$U_G = U_0$ same for all Fourier coeffs.

All band gaps are the same size.

Exact evaluation in Kittel to show shape of bands



23.02.09 II

7.5 Bloch Theorem

Important theorem concerning general form of the solution of the Schrödinger equation in a periodic potential:

$$\psi(\vec{r}) = \underbrace{u_k(\vec{r})}_{\text{periodic}} \underbrace{e^{i\vec{k}\cdot\vec{r}}}_{\text{wave, as in free-electron}}$$

periodic wave, as in free-electron

20.02.06 II

$$u_k(\vec{r} + \vec{T}) = u_k(\vec{r})$$

Simple proof for non-degenerate case:

Assume wave function satisfies periodic boundary conditions: 1D case, easily generalised.

1.03.10

$$\psi(x + Na) = \psi(x)$$

This can be made arbitrarily general by going to the limit $N \rightarrow \infty$.

Look for solutions that factorise to separate their lattice periodicity:

$$\psi(x+a) = C(x)\psi(x)$$

Given that $C(x)$ can be any function, this is still a general solution.

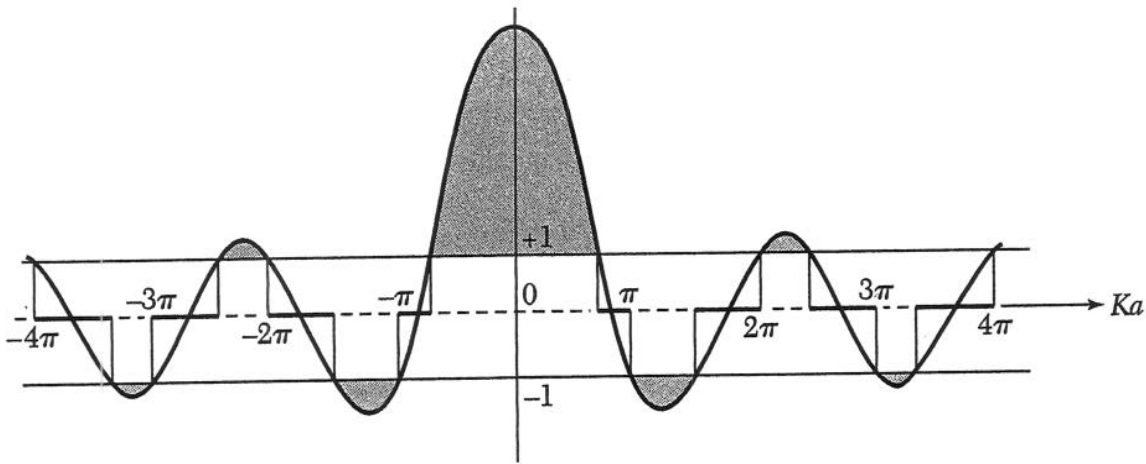


Figure 5 Plot of the function $(P/Ka) \sin Ka + \cos Ka$, for $P = 3\pi/2$. The allowed values of the energy e are given by those ranges of $Ka = (2m\epsilon/\hbar^2)^{1/2}a$ for which the function lies between ± 1 . For other values of the energy there are no traveling wave or Bloch-like solutions to the wave equation, so that forbidden gaps in the energy spectrum are formed.

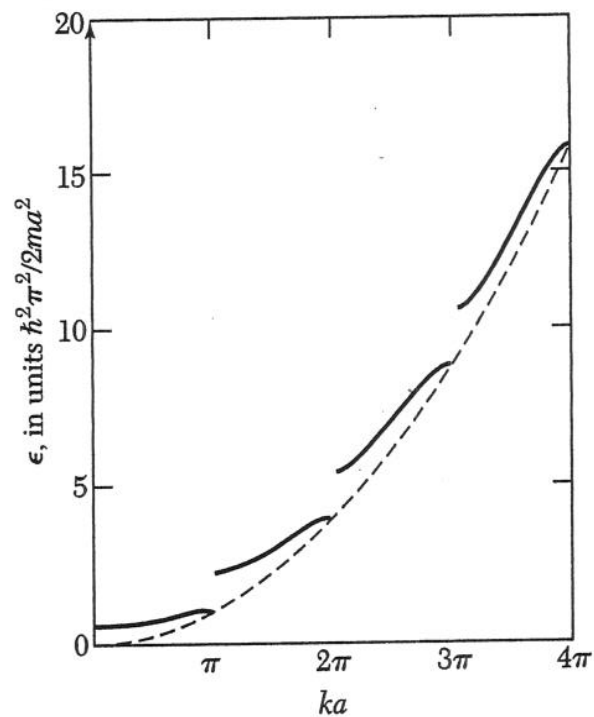


Figure 6 Plot of energy vs. wavenumber for the Kronig-Penney potential, with $P = 3\pi/2$. Notice the energy gaps at $ka = \pi, 2\pi, 3\pi \dots$

values of k . Let $U(x)$ denote the potential energy of an electron in a linear lattice of lattice constant a . We know that the potential energy is invariant under a crystal lattice translation: $U(x) = U(x + a)$. A function invariant under a crystal lattice translation may be expanded as a Fourier series in the reciprocal lattice vectors G . We write the Fourier series for the potential energy as

$$U(x) = \sum_G U_G e^{iGx} . \quad (22)$$

The values of the coefficients U_G for actual crystal potentials tend to decrease rapidly with increasing magnitude of G . For a bare coulomb potential U_G decreases as $1/G^2$.

(67)

Applying periodic boundary condition

$$\psi(x+Na) = C(x)^N \psi(x) = \psi(x)$$

So $C(x)^N = 1$ $C(x) = N$ -th root of unity

not even depending on x , necessarily. } $C(x)$ is like a wave

$$C(x) = e^{2\pi i s/N} \quad s = 0, 1, 2, \dots, N-1$$

So if we choose a function, for any s :

$$\psi(x) = u(x) e^{2\pi i s x / Na} \quad \text{with } u(x) \text{ periodic}$$

$$\begin{aligned} \psi(x+a) &= u(x+a) e^{2\pi i s (x+a) / Na} \\ &= \underbrace{u(x) e^{2\pi i s x / Na}}_{\psi(x)} \underbrace{e^{2\pi i s / N}}_{C(x)} \end{aligned}$$

This Bloch function satisfies the assumptions.

In the limit of large N , we consider the discrete variable $2\pi s / Na \rightarrow k$, a continuous variable.

$$\psi(x) = u(x) e^{ikx}$$

We have usually considered k to be of this form whenever we modeled a crystal with periodic boundary conditions

Note the Bloch functions are more general than strict periodic functions.

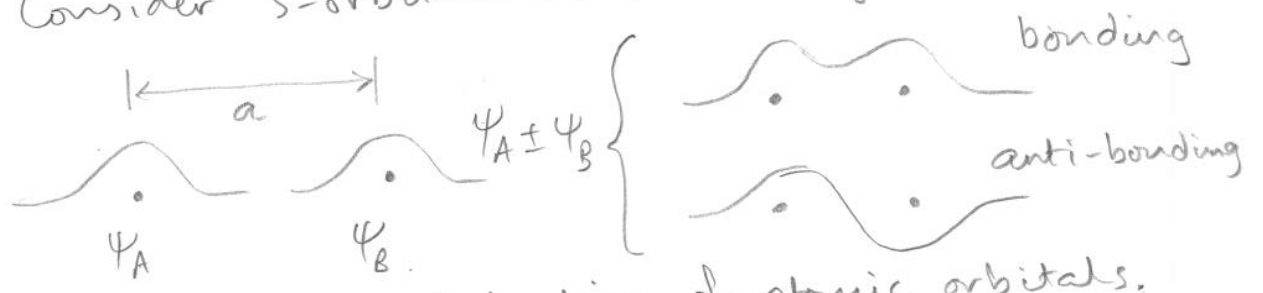
- Consider as repeating part modulated by a continuously varying phase that represents the wave.
- In 3D, the wave part has 3 components.
- Assemble into 'wave packets', just like plane waves, to represent localised particles.
- Accounts for fast-varying ψ inside atomic cores, but keeps long-range wave coherence.

7.7 Tight Binding [Kittel ch9]

One of three general methods discussed in Kittel ch9 for general band-structure calculation.

- Knowing Bloch's theorem, we no longer fear the deep-potential regions around the ions.
- Start with atomic picture, instead.
- Approach crystal from separated-ion limit.
- Chemical bonding picture; ok for metals, but very good for covalent crystals.

Consider s-orbitals on two neighbours

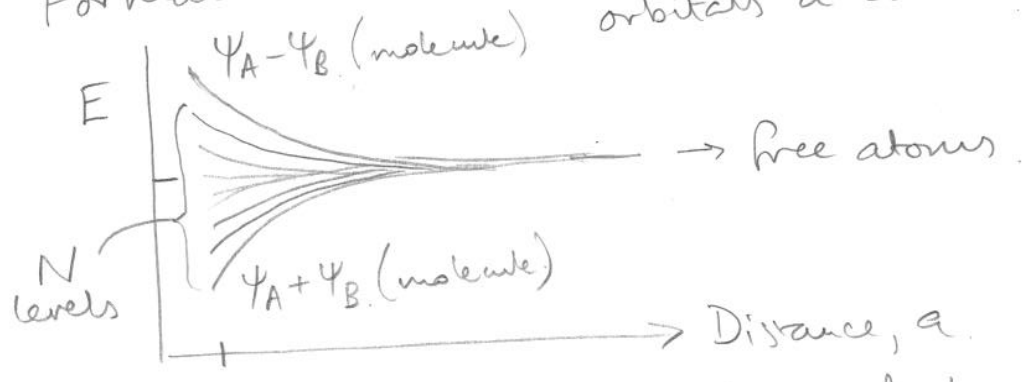


LCAO = linear combination of atomic orbitals.

The antibonding orbital has higher energy than the bonding orbital:

- electron in the middle spends time near two nuclei, rather than one, in ψ_{A+B} .
- steep gradient of AB orbital means higher kinetic energy, in ψ_{A-B} state.

Formation of chemical bond: [p- and d-orbitals a bit more complicated]



21.02.06

N -atoms \rightarrow N combinations of bonding and antibonding \rightarrow N -level band.

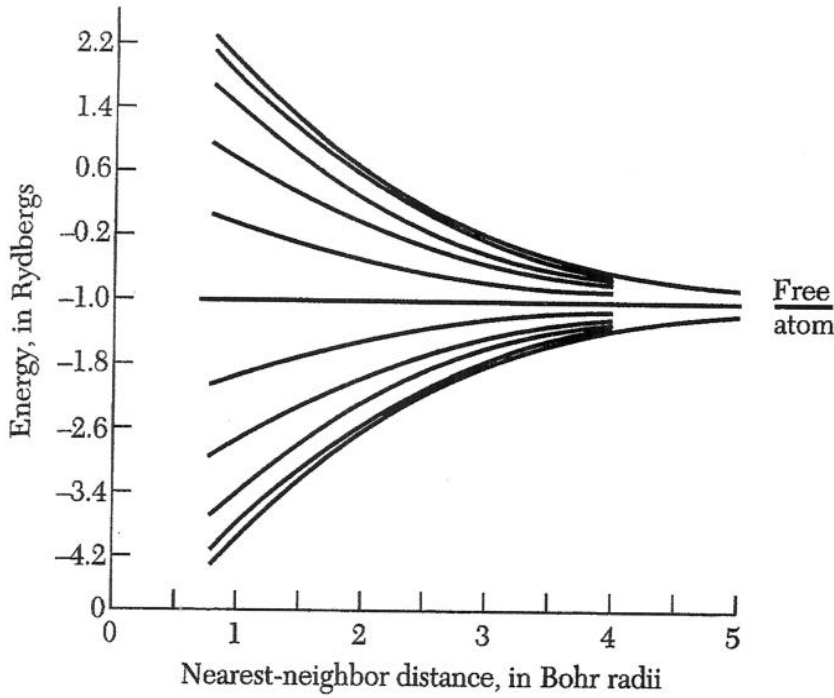


Figure 17 The 1s band of a ring of 20 hydrogen atoms; the one-electron energies are calculated in the tight-binding approximation with the nearest-neighbor overlap integral of Eq. (9).

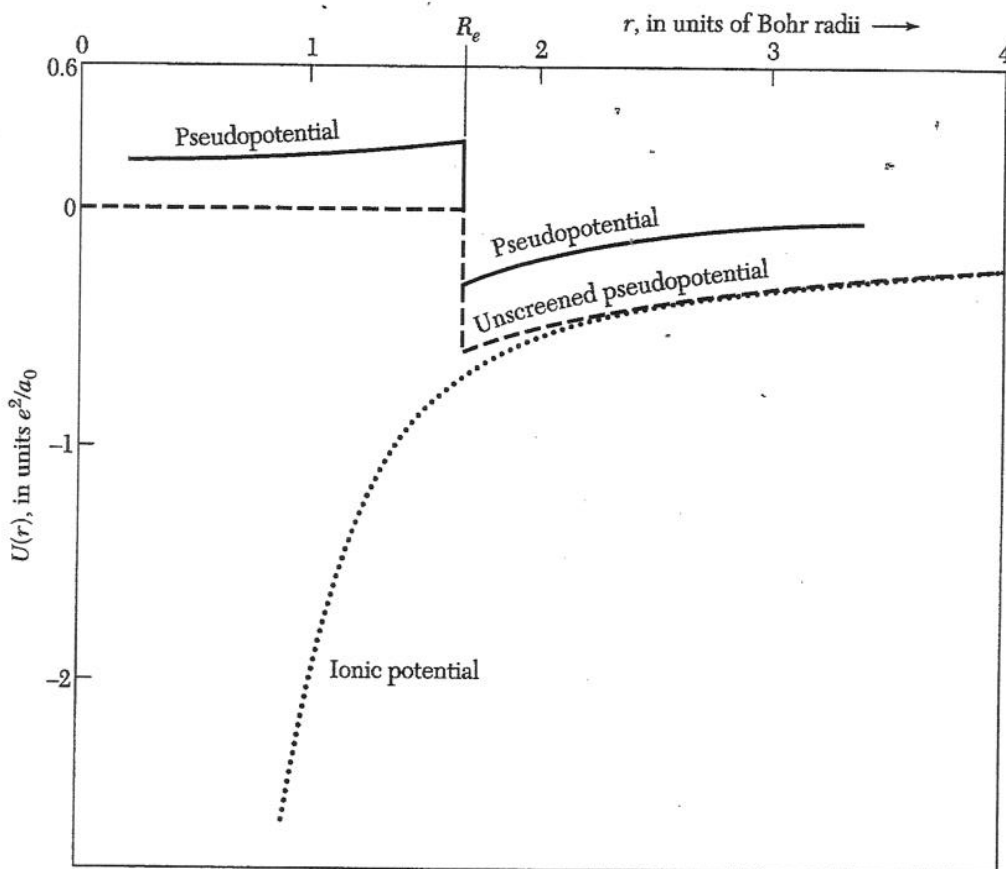


Figure 22a Pseudopotential for metallic sodium, based on the empty core model and screened by the Thomas-Fermi dielectric function. The calculations were made for an empty core radius $R_e = 1.66a_0$, where a_0 is the Bohr radius, and for a screening parameter $k_s a_0 = 0.79$. The dashed curve shows the assumed unscreened potential, as from (21). The dotted curve is the actual potential of the ion core; other values of $U(r)$ are -50.4 , -11.6 , and -4.6 , for $r = 0.15$, 0.4 , and 0.7 , respectively. Thus the actual potential of the ion (chosen to fit the energy levels of the free atom) is very much larger than the pseudopotential, over 200 times larger at $r = 0.15$.

7.8 Bloch tight-binding states. (LEAO)

Describe atomic state as $\phi(\vec{r})$.

Approximate wavefunction of electron in crystal:

$$\Psi_{\vec{k}}(\vec{r}) = \sum_j C_{\vec{k}j} \phi(\vec{r} - \vec{r}_j)$$

↑
coefficients

\vec{r}_j are the positions of all the sites in the lattice

We want $\Psi_{\vec{k}}$ to satisfy Bloch's theorem, for translations $\vec{r} \rightarrow \vec{r} + \vec{T}$ within the crystal, so we choose $C_{\vec{k}j}$ to resemble a wave:

$$C_{\vec{k}j} = e^{i\vec{k} \cdot \vec{r}_j}$$

Test this form under translation $\vec{r} \rightarrow \vec{r} + \vec{T}$:

$$\begin{aligned} \Psi_{\vec{k}}(\vec{r} + \vec{T}) &= \sum_j e^{i\vec{k} \cdot \vec{r}_j} \phi(\vec{r} + \vec{T} - \vec{r}_j) \\ &= e^{i\vec{k} \cdot \vec{T}} \sum_j e^{i\vec{k} \cdot (\vec{r}_j - \vec{T})} \phi(\vec{r} - (\vec{r}_j - \vec{T})) \\ &= e^{i\vec{k} \cdot \vec{T}} \Psi_{\vec{k}}(\vec{r}) \end{aligned}$$

Since the sum is over all lattice sites, we are allowed to offset by one site.

Now evaluate the energy with Hamiltonian g_l :

$$\begin{aligned} \langle \vec{k} | g_l | \vec{k} \rangle &= \int \Psi_{\vec{k}}^*(\vec{r}) \cdot g_l \Psi_{\vec{k}}(\vec{r}) dV \leftarrow d^3\vec{r} \\ &= \sum_j \sum_m e^{i\vec{k} \cdot (\vec{r}_j - \vec{r}_m)} \langle \phi_m | g_l | \phi_j \rangle \end{aligned}$$

where $\phi_m = \phi(\vec{r} - \vec{r}_m)$

Now change variables to $\vec{p}_m = \vec{r}_m - \vec{r}_j$

$$\langle k | H_L | k \rangle = \sum_m e^{-i\vec{k} \cdot \vec{p}_m} N \int \phi^*(\vec{r} - \vec{p}_m) H_L \phi(\vec{r}) dV$$

H_L is periodic on lattice, so: \int is same for all j

\sum_m is now a sum over neighbours in lattice

To a good approximation we can keep only nearest neighbours of the same kind, for which the overlap integral will be the same:

$$\int \phi^*(\vec{r}) H_L \phi(\vec{r}) dV = -\alpha \quad [\alpha \text{ and } \gamma \text{ positive quantities}]$$
$$\int \phi^*(\vec{r} - \vec{p}) H_L \phi(\vec{r}) dV = -\gamma$$

\uparrow nearest neighbour, same for all
all others neglected. (spherical $\phi(\vec{r})$)

26.02.07 I

$$\frac{1}{N} \langle k | H_L | k \rangle = -\alpha - \gamma \sum_m e^{-i\vec{k} \cdot \vec{p}_m} = \epsilon_k$$

this is the final result.

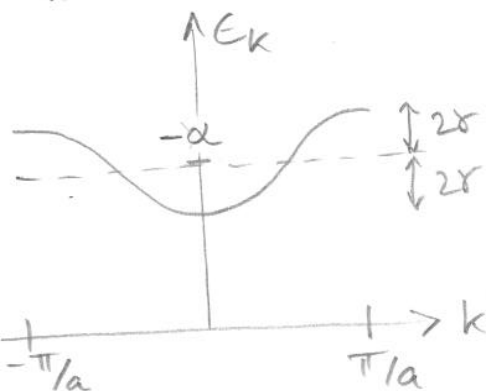
We have assumed that the orbitals themselves have not been distorted too badly by the overlap, so the linear combination is still valid.

7.9 Evaluation for special cases.

i) Simple cubic

Neighbours $p_m = (\pm a, 0, 0), (0 \pm a, 0), (0, 0 \pm a)$

$$\epsilon_k = -\alpha - 2\gamma (\cos k_x a + \cos k_y a + \cos k_z a)$$



$\rightarrow 4\gamma$ band width
 $\rightarrow 12\gamma$ at furthest point of zone, $(\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{a})$

2.03.09 II
25.02.08 II

ii) BCC structure.

8 neighbours at $(\pm \frac{a}{2}, \pm \frac{a}{2}, \pm \frac{a}{2})$

$$E_k = -\alpha - 8\gamma \cos \frac{k_x a}{2} \cos \frac{k_y a}{2} \cos \frac{k_z a}{2}$$

Width of band = 16γ

iii) FCC structure.

12 neighbours at $(\pm \frac{a}{2}, \pm \frac{a}{2}, 0)$ and permutations

$$E_k = -\alpha - 4\gamma (\cos \frac{k_x a}{2} \cos \frac{k_y a}{2} + \text{perms})$$

Width of band = $4 \times 3 \times 2 = 24\gamma$

27.02.06 I

7.9 Pseudopotential methods.

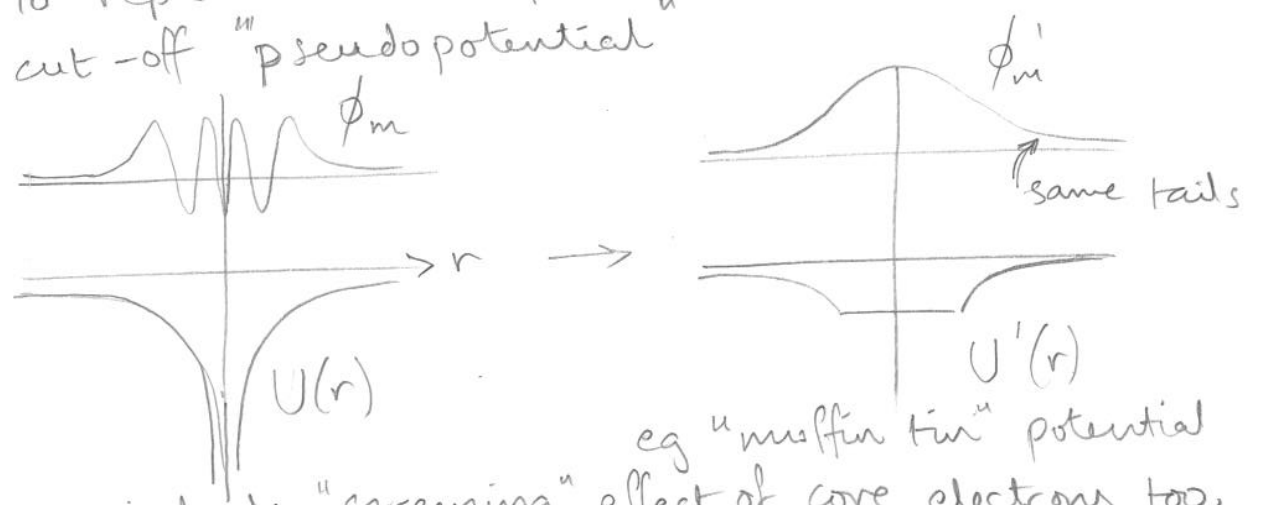
Especially for heavy elements, there is a lot of structure in the atomic functions ϕ_m :

5s orbital of Rb ($Z=37$) has 4 radial nodes
p- and d-orbitals have strong angular structure with \pm lobes.

The resulting Bloch waves will be unnecessarily complicated.

Only the very outer part of ϕ_m is important in the overlap integral γ : exponential tail.

It is found to be a very good approximation to replace the deep atomic potential by a cut-off "pseudopotential"



can include "screening" effect of core electrons too.

73a

ii) BCC structure

$$E_k = -\alpha - \gamma \sum_m e^{i\vec{k} \cdot \vec{r}_m} \left. \begin{array}{l} \left. \begin{array}{l} e^{\frac{ik_x a}{2}} e^{\frac{ik_y a}{2}} e^{\frac{ik_z a}{2}} \\ e^{-\frac{ik_x a}{2}} e^{\frac{ik_y a}{2}} e^{\frac{ik_z a}{2}} \end{array} \right\} \right. \\ \left. \begin{array}{l} + e^{\frac{ik_x a}{2}} e^{-\frac{ik_y a}{2}} e^{\frac{ik_z a}{2}} \\ + e^{\frac{ik_x a}{2}} e^{\frac{ik_y a}{2}} e^{-\frac{ik_z a}{2}} \end{array} \right\} \end{array}$$

pairs of terms:

$$2 \cos \frac{k_x a}{2} \left\{ e^{\frac{ik_y a}{2}} e^{\frac{ik_z a}{2}} + e^{-\frac{ik_y a}{2}} e^{\frac{ik_z a}{2}} + 2 \text{ more} \right\}$$

$$= 4 \cos \frac{k_x a}{2} \cos \frac{k_y a}{2} \left\{ e^{\frac{ik_z a}{2}} + e^{-\frac{ik_z a}{2}} \right\}$$

$$= 8 \cos \frac{k_x a}{2} \cos \frac{k_y a}{2} \cos \frac{k_z a}{2}$$

iii) FCC structure, 12 nearest neighbours

$$\vec{r}_m = \left(\pm \frac{a}{2} \pm \frac{a}{2} 0 \right) + \text{perms.}$$

$$E_k = -\alpha - \gamma \left\{ 4 \cos \frac{k_x a}{2} \cos \frac{k_y a}{2} + xz + yz \right\}$$



Small \vec{k}
overlaps in phase
like bonding orbital.

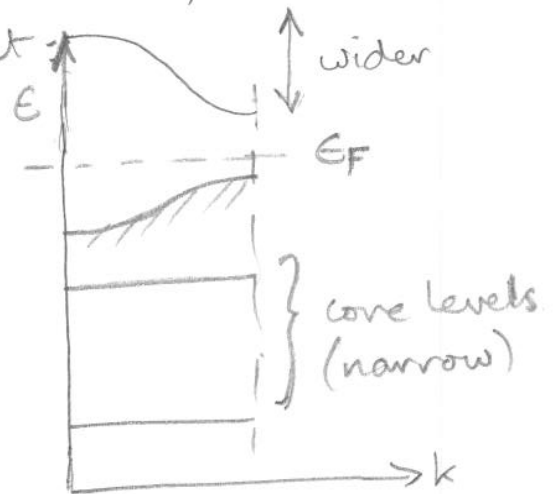
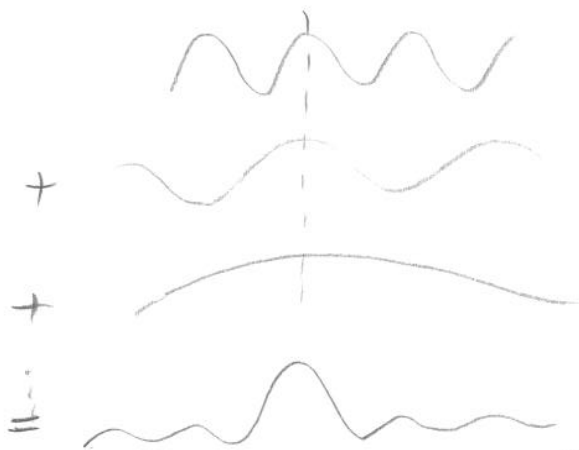
high \vec{k} : strong phase variation like antibonding.

7.10 Picture of k waves inside crystal.

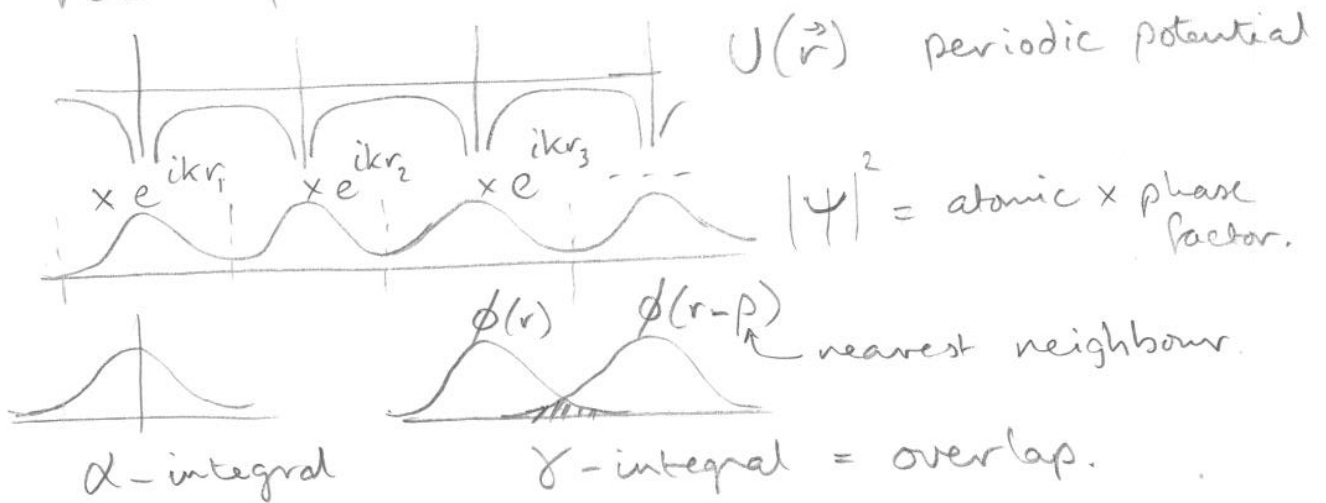
Bloch wave function we constructed

$$\Psi_k(\vec{r}) = \sum_{j=1}^N \underbrace{e^{ik \cdot \vec{r}_j}}_{\text{coefs}} \underbrace{\phi(\vec{r} - \vec{r}_j)}_{\substack{\uparrow \\ \text{only continuous } \vec{r}}}$$

- i) One electron over N nuclei [no Pauli repulsion].
- ii) Ground state spread as thinly as possible with all overlaps lowering energy. $k=0$
- iii) All states extend over entire crystal
- iv) All states orthogonal to each other. $\vec{k} \neq \vec{k}'$
- v) To construct something resembling a particle resembling a free electron, we have to construct wave packet



Actual wave functions "look" atomic; only their relative phase is wave-like.



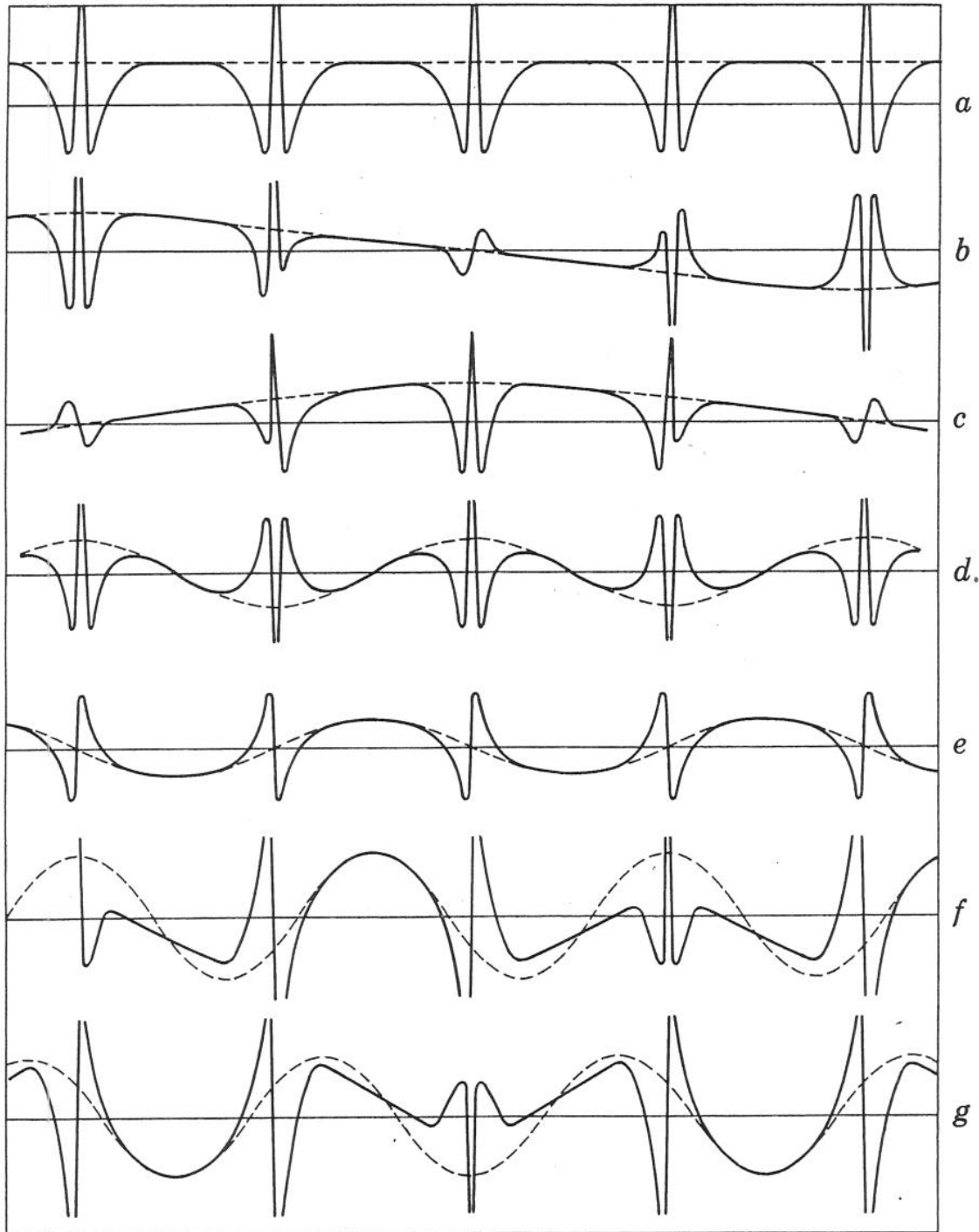
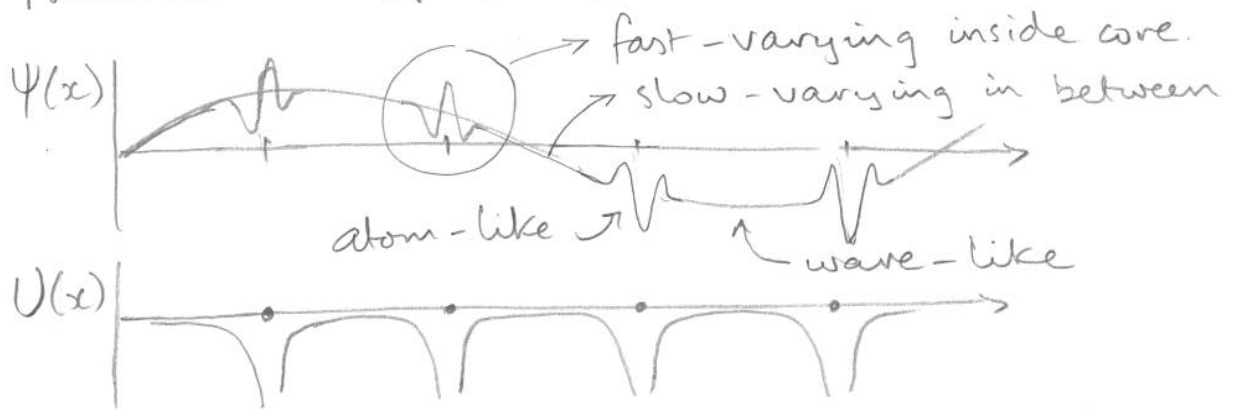


Fig. 31-9. Wave functions for conduction electrons, for sodium, as function of distance along a line in 111 direction, for a number of values of the wave vector k , starting with (a), representing the case $k = 0$. The dashed lines indicate the corresponding single plane wave which approximately represents the wave function in the region between atoms.

(68)

Illustration of Bloch waves:



The $\Psi(x)$ doesn't have to be an exact solution of the Schrödinger equation inside every core, just within a mult. phase factor.

- Hybrid form, atomic-like $\Psi(x)$ near cores, and wave-like in between.

- We can now answer the riddle of why the electrons do not "see" the nuclei in a metal:

i) every nucleus has a large, localised potential function that strongly influences the wave,

ii) but every nucleus acts the same, giving the same phase shift to Ψ .

iii) added up over entire lattice, the phase shifts satisfy the long-range period- N constraint

- So, in a periodic lattice, the electrons move as (Bloch) waves, in invisible lattice.

- If one atom is out of position, the wrong size, or missing there will be a strong scattering event.

7.6 Bands in 3D

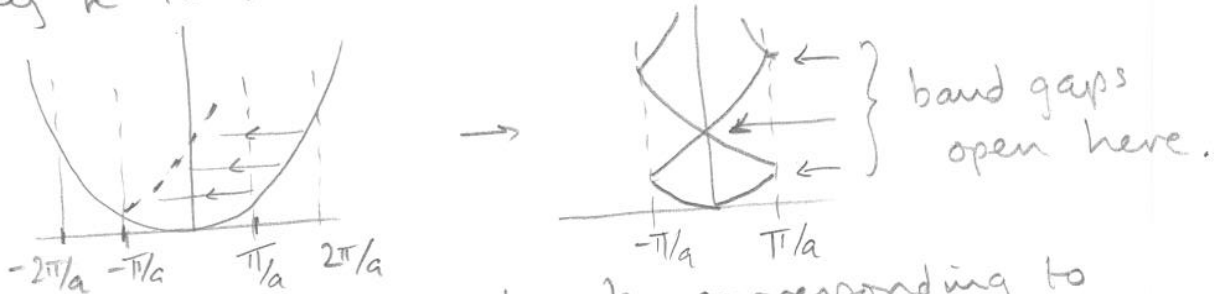
Even for free electrons, the combined effects of spherical energy contours and square geometrical reciprocal space leads to a complicated picture. [phonon case = identical state]

Reduced Zone Scheme[†] allows all (\vec{k}, E)

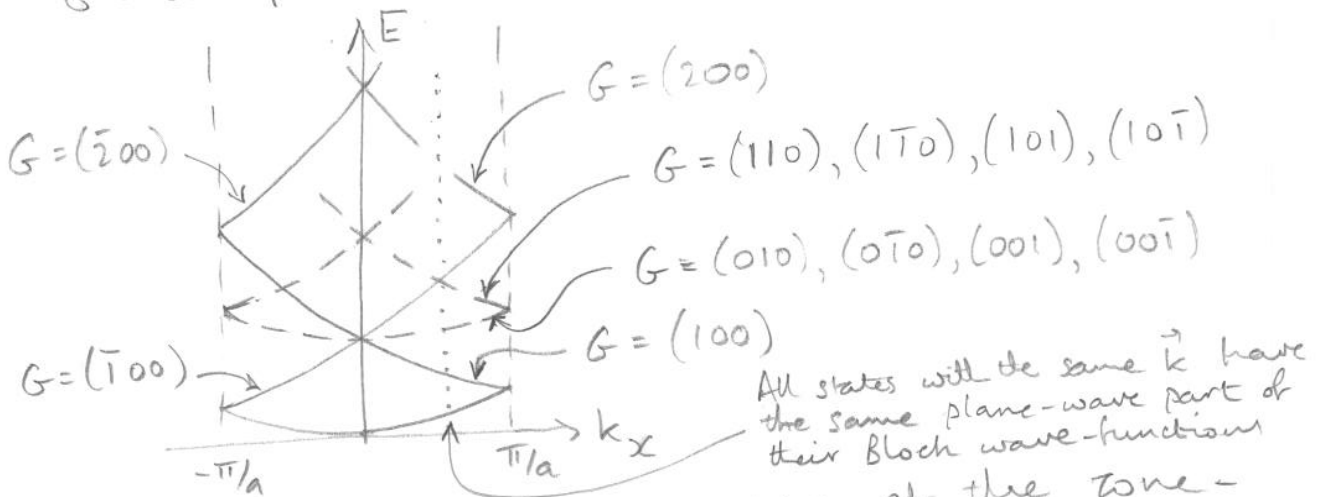
points to be mapped into the first B.Z. by redefining the Bloch factorisation: $k \rightarrow k+G$

$$\Psi_{k+G} = e^{i(k+G)\cdot\vec{r}} u(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \underbrace{\left(e^{iG\cdot\vec{r}} u(\vec{r}) \right)}_{\text{new periodic function}}$$

We can always subtract a nearby G from any \vec{k} to move back to first B.Z. In 1D:



In 3D we add more bands, corresponding to \vec{G} -components in the y- and z-directions.



In all cases, band gaps open at the zone-boundary and zone centre, with $E_g = U_G$

Gap = Fourier component of potential $U(\vec{r})$.

† All Bloch waves are equivalent to the one with \vec{k} in the FBZ. The energy $E_{\vec{k}}$ is periodic in \vec{k} for a Bloch wave.

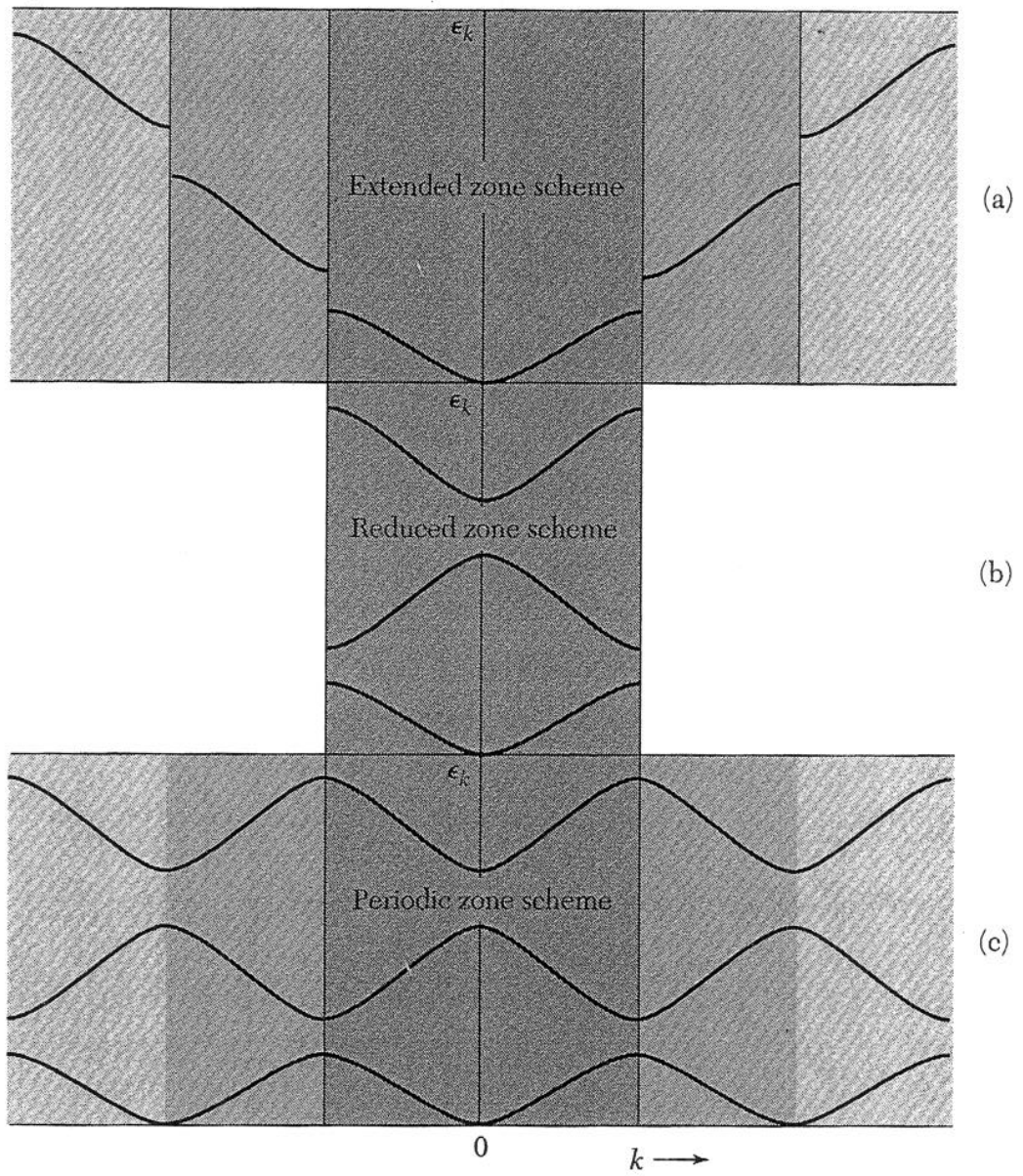


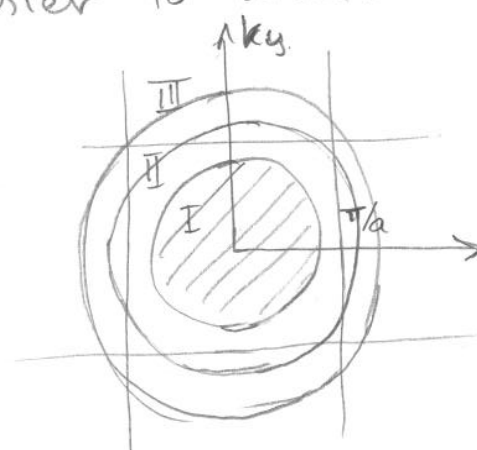
Figure 4 Three energy bands of a linear lattice plotted in (a) the extended (Brillouin), (b) reduced, and (c) periodic zone schemes.

(69a)

Fermi level surface in reduced zone scheme.

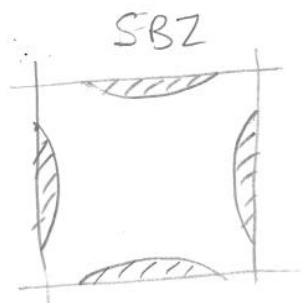
- i) FEG has spherical (circular) Fermi level.
- ii) When this falls outside, we construct geometric shape of "Fermi surface"

Easier to illustrate in 2D:



- I. Spherical surface entirely in FBZ.
- II. Partly entering 2nd Zone
- III: " " 3rd Zone

iii) Fold back into reduced zone scheme

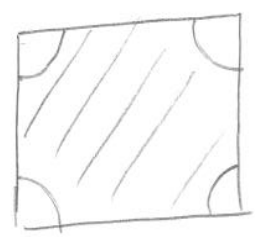
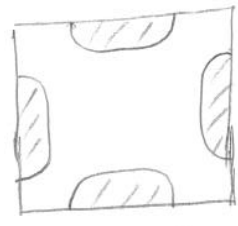


depends on E_F
= can fill up.

Case II

open band gaps at zone boundaries

$N_{atoms} = \left(\frac{L}{a}\right)^3$



iv) Counting of states. Simple cubic case

$2 \cdot \frac{4}{3} \pi k_F^3 / \left(\frac{2\pi}{L}\right)^3 = N_{sphere}$ radius k_F with degeneracy

$N_{atoms} = \left(\frac{2\pi}{a}\right)^3 / \left(\frac{2\pi}{L}\right)^3 = N_{cube}$ no of states in FBZ.

$\text{equal when } k_F = \frac{\pi}{a} \left(\frac{3}{\pi}\right)^{1/3} = 0.98 \frac{\pi}{a}$ = N atoms in sample.

1 electron/atom always fits in FBZ. (also FCC, BCC)

2 electrons/atom usually flows outside, but open band gap enough \rightarrow fills exactly.

(69b)

Important consequences for metal/insulator:

1 electron/atom = always metal!

2 electrons/atom can be insulator
(if band gap is wide enough)

Rule is general for crystal with basis:

odd electron count in basis = metal

even " " " usually insulator.

Semiconductors and insulators must
satisfy this even-counting rule.

2.03.09 I

Normally true for compound. that is neutral

Chemical rules \Leftrightarrow even count.
filled shells.

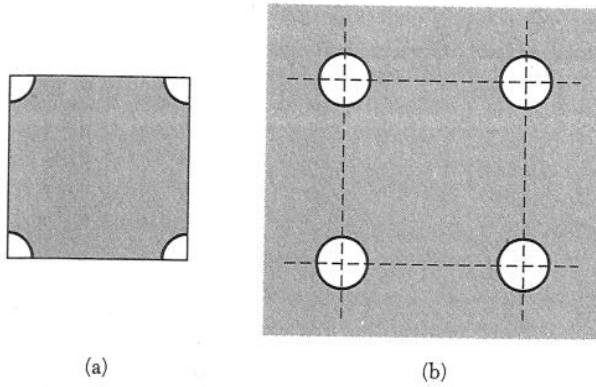


Figure 13 (a) Vacant states at the corners of an almost-filled band, drawn in the reduced zone scheme. (b) In the periodic zone scheme the various parts of the Fermi surface are connected. Each circle forms a holelike orbit. The different circles are entirely equivalent to each other, and the density of states is that of a single circle. (The orbits need not be true circles: for the lattice shown it is only required that the orbits have fourfold symmetry.)

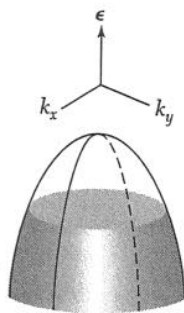


Figure 14 Vacant states near the top of an almost filled band in a two-dimensional crystal. This figure is equivalent to Fig. 12a.

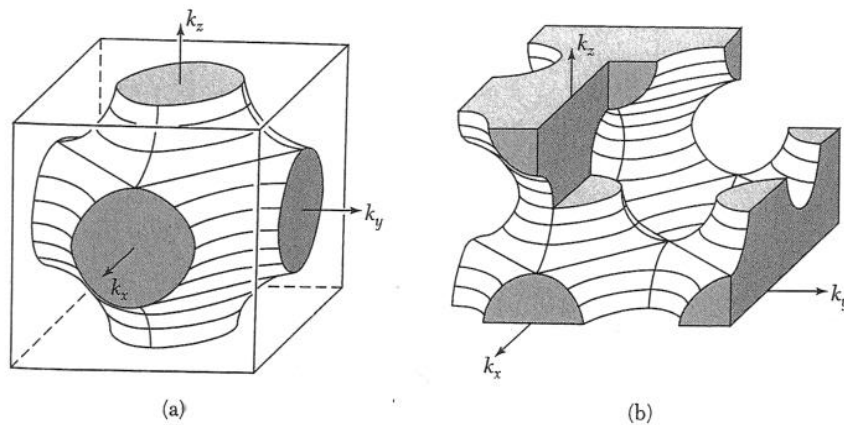


Figure 15 Constant energy surface in the Brillouin zone of a simple cubic lattice, for the assumed energy band $\epsilon_k = -\alpha - 2\gamma(\cos k_x a + \cos k_y a + \cos k_z a)$. (a) Constant energy surface $\epsilon = -\alpha$. The filled volume contains one electron per primitive cell. (b) The same surface exhibited in the periodic zone scheme. The connectivity of the orbits is clearly shown. Can you find electron, hole, and open orbits for motion in a magnetic field $B\hat{z}$? (A. Sommerfeld and H. A. Bethe.)

they are connected by a reciprocal lattice vector. Such an orbit is called an **open orbit**. Open orbits have an important effect on the magnetoresistance.

Vacant orbitals near the top of an otherwise filled band give rise to holelike orbits, as in Figs. 13 and 14. A view of a possible energy surface in three dimensions is given in Fig. 15.