

Why tight binding works

In tight binding one ^{approximates} ~~takes~~ the Bloch wavefunction as

$$\psi_k = \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \left(\sum_n b_n \phi_n(\vec{r} - \vec{R}) \right)$$

atomic orbitals

One can show (see A+M chpt 10 pgs 187-188) that the exact Bloch eigenstate can always be written in the form

$$\psi_k(\vec{r}) = \sum_{\vec{R}} e^{i\vec{k} \cdot \vec{R}} \phi(\vec{r} - \vec{R})$$

for some suitable function $\phi(\vec{r})$. This $\phi(\vec{r})$ is called the Wannier function

The tight binding approximation is then built on the assumption that the Wannier function $\phi(\vec{r})$ can be well approximated by a linear combination of atomic orbitals.

In principle the complete set of eigenfunctions of the atomic Hamiltonian H_{at} form a complete basis set of functions ~~in forms~~ such that any function (and so in particular the Wannier function) can be written as a linear combination of these atomic eigenfunctions. But for this to be a complete basis we need to include the continuum of ionized atomic eigenstates as well as the

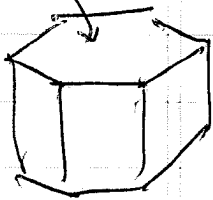
discrete bound atomic orbitals $\varphi_n(\vec{r})$.

The tight binding approximation then consists of neglecting the ionized atomic eigenstates when trying to expand the Wannier function $\phi(\vec{r})$. It works well when $\phi(\vec{r})$ is well localized i.e. when $\phi(\vec{r})$ decays quickly to zero as $|\vec{r}| \rightarrow \infty$.

Spin-orbit interaction

We have seen in both the weak potential approx and the tight binding approx, that there may remain degeneracies in the band structure at certain points of high symmetry (for example in prob 3 of HW 4)

$S_K = 0$, no gap



1st BZ
hcp

An example would be the absence of the expected energy gap at the top and bottom faces of the 1st BZ for hcp crystals, due to the vanishing of the geometric structure factor S_K on these faces

In such case, in the heavier elements, the degeneracy may be lifted (i.e. an energy gap, appear) due to the effects of the spin-orbit interaction.

In principle there is always an interaction between the intrinsic electron spin with its own magnetic moment $\vec{\mu}$ (due to intrinsic spin) and its motion in the electric field of the ions

$$\delta H_{so} \approx g \vec{\mu} \cdot (\vec{v} \times \vec{E})$$

$\vec{B}$ in local rest frame of electron

$\vec{E}$ is from ionic potential

If one includes $\hat{H}_{so}$ in the single electron Hamiltonian, one can no longer ignore the coupling between electron spin state and real space wave function (as we have been doing). One needs to consider linear combinations of both different spatial orbitals and spin states, this doubling the number of functions used in the tight binding expansion for ψ_k .

When one includes $\hat{H}_{so}$ one finds that symmetry induced band degeneracies can be lifted.

This effect is most noticeable in heavier elements where the atomic electric field $\vec{E}$ is stronger.

Real metals

Monovalent Metals

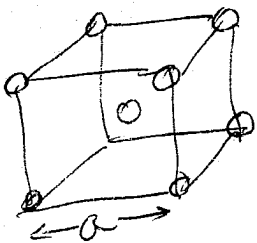
(1A) <u>Alkali's</u> (bcc)	(1B) <u>Nobel's</u> (fcc)
Li $[1s^2]2s^1$	—
Na $[Ne]3s^1$	—
K $[Ar]4s^1$	Cu $[Ar]3d^{10}4s^1$
Rb $[Kr]5s^1$	Ag $[Kr]4d^{10}5s^1$
Cs $[Xe]6s^1$	Au $[Xe]4f^{14}5d^{10}6s^1$

Rare Earth configuration is tightly bound core. electrons here are in very low lying, narrow, filled tight binding bands. Can generally ignore them.

bcc) Alkalies - If we assume the single conduction electron moves completely freely in metal, the Fermi surface is a sphere of radius k_F

$$\frac{4}{3}\pi \frac{k_F^3}{4\pi^3} = \frac{k_F^3}{3\pi^2} = n = \frac{2}{a^3} \quad \leftarrow \text{side of unit cell}$$

↑ density of ions



$$k_F = (6\pi^2)^{1/3} \frac{1}{a} = \left(\frac{6\pi^2}{(2\pi)^3}\right)^{1/3} \left(\frac{2\pi}{a}\right) = \left(\frac{3}{4\pi}\right)^{1/3} \left(\frac{2\pi}{a}\right)$$

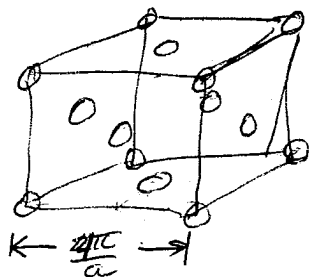
unit cell has 2 atoms $\Rightarrow n = \frac{2}{a^3}$

$$\Rightarrow k_F = \left(\frac{3}{4\pi}\right)^{1/3} \left(\frac{2\pi}{a}\right) = 0.620 \left(\frac{2\pi}{a}\right)$$

one half of side of unit cell in recip lattice.

unit cell of RL has side of length $\frac{4\pi}{a}$

1st BZ is Wigner-Seitz cell of fcc lattice of unit cell size $\frac{4\pi}{a}$



nearest neighbor is $\frac{4\pi}{a} \sqrt{(\frac{1}{2})^2 + (\frac{1}{2})^2}$ away, so shortest distance to surface of 1st BZ is

$$k_0 = \frac{1}{2} \sqrt{\frac{1}{4} + \frac{1}{4}} \left(\frac{4\pi}{a} \right) = 0.707 \left(\frac{2\pi}{a} \right)$$

$\uparrow$ bisect R-L vector to get dist to Bragg plane

so $\frac{k_F}{k_0} = \frac{.620}{.707} = .877$ ~~the~~ fermi surface goes .877 of the way to closest pt on zone boundary

If weak potential, approx good, expect fermi surface to be very spherical - since not near Bragg plane (zone boundary) corrections to free electrons are only $O(U^2)$

That is the case. Sommerfeld model is ~~extremely~~ good in explaining Alkali's (Li not clear) (charge density wave?)

	Li	Na	K	Rb	Cs
$-1/R_{\text{Hall}} \text{ rec}$	.8	1.2	1.1	1.0	0.9

$\frac{1}{R_H}$

(Charge density waves?)

magnetoresistance also ~~shows little~~ is less ¹⁷ field dependent than other materials (Sommerfeld gives indep of H)

Low temp specific heat $C_v = \gamma T + O(T^3)$

Free elec

$$\gamma = \frac{\pi^2}{2} \left(\frac{k_F}{E_F} \right)^2 n$$

γ measures $g(E_F)$

	γ free electron	γ expt
Li	1.8	4.2
Na	2.6	3.5
K	4.0	4.7
Rb	4.6	5.8
Cs	5.2	7.7

$$\gamma = \frac{\pi^2}{3} kT g(E_F)$$

in general

~~Noble~~ Noble Metals (fcc)

as in Alkalis, rare earth core is tightly bound + can be ignored. (also 4f electrons of Au)

Conduction electrons are the 11 $d^{10}s^1$ electrons.

⇒ need 6 bands at least (each band holds 2 elec's per B-lattice site)

turns out 6 bands are enough. 5 lowest bands completely filled, 6th band half full. ^{at any given k} Bands look like 5 narrow bands (d-like tight binding) and one

(s-band) nearly free electron like. However the nearly free electron s-band is mixed with narrow d-bands.

[Show Fig 15.4]

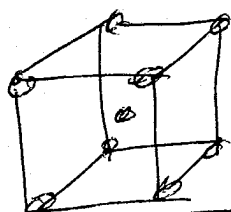
Fermi surface passes through 6th band (s-band) where it looks very free electron like - above narrow d-bands. Try free electron approx for the Fermi surface of half filled 6th band.

$$\frac{k_F^3}{3\pi^2} = \frac{4}{a^3}$$

As before, add 1 electron per site to 6th band

$$\Rightarrow k_F = \sqrt[3]{\frac{4\pi}{a^3}} \left(\frac{6}{4\pi}\right)^{1/3} \quad \left(\begin{array}{l} 4 \text{ atoms in} \\ \text{unit cell} \end{array} \right)$$

$$= 0.782 \left(\frac{2\pi}{a}\right)$$



$$k_{\text{small}} = \sqrt{\left(\frac{1}{2}\right)^2 + \left(\frac{1}{2}\right)^2 + \left(\frac{1}{2}\right)^2} \left(\frac{4\pi}{a}\right)$$

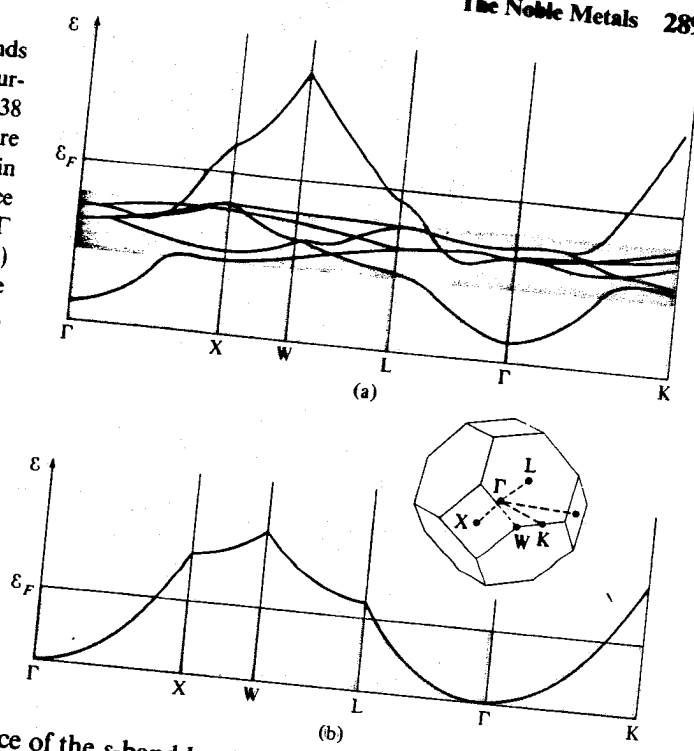
1st BZ is Wigner Seitz cell of bcc, closest pt

$$\text{on boundary from origin is at } k_0 = \frac{1}{2} \sqrt{\left(\frac{1}{2}\right)^2 + \left(\frac{1}{2}\right)^2 + \left(\frac{1}{2}\right)^2} \left(\frac{4\pi}{a}\right)$$

$$k_0 = \sqrt{\frac{3}{4}} \left(\frac{2\pi}{a}\right) = 0.866 \left(\frac{2\pi}{a}\right)$$

Figure 15.4

(a) Calculated energy bands in copper. (After G. A. Burdick, *Phys. Rev.* **129**, 138 (1963).) The ϵ vs. k curves are shown along several lines in the interior and on the surface of the first zone. (The point Γ is at the center of the zone.) The d -bands occupy the darkest region of the figure, whose width is about 3.5 eV. (b) The lowest-lying free electron energies along the same lines as in (a). (The energy scales in (a) and (b) are not the same.)



Note that the k dependence of the s -band levels, except where they approach the d -bands, bears a remarkable resemblance to the lowest free electron band for an fcc crystal (plotted in Figure 15.4b for comparison), especially if one allows for the expected modifications near the zone faces characteristic of a nearly free electron calculation (Chapter 9). Note also that the Fermi level lies far enough above the d -band for the s -band to intersect ϵ_F at points where the resemblance to the free electron band is still quite recognizable.⁴ Thus the calculated band structure indicates that for purposes of Fermi surface determination one might still hope for some success with a nearly free electron calculation. However, one must always keep in mind that not too far below the Fermi energy lurks a very complex set of d -bands, which can be expected to influence the metallic properties far more strongly than do any of the filled bands in the alkali metals.⁵

The Fermi surface for a single half-filled free electron band in an fcc Bravais lattice is a sphere entirely contained within the first Brillouin zone, approaching the surface of the zone most closely in the $\langle 111 \rangle$ directions, where it reaches 0.903 of the distance from the origin to the center of the hexagonal face. The de Haas-van Alphen

⁴ However, the Fermi level is close enough to the d -band to make the s -band nomenclature somewhat misleading for conduction band levels on the Fermi surface. A more precise specification of how s -like or d -like a level is must be based on a detailed examination of its wave function. In this sense most, but not all, levels at the Fermi surface are s -like.

⁵ Atomic ionization potentials provide a convenient reminder of the different roles played by the s and d electrons in the alkali and noble metals. To remove the first ($4s$) and then the second ($3p$) electron from potassium requires 4.34 and 31.81 eV, respectively. The corresponding figures for copper are 7.74 and 20.29 eV ($3d$).

$$= .782 / .866$$

195

$$k_F / k_0 = .903 \Rightarrow \text{neatly spherical might be expected}$$

However in this direction of closest approach $\langle 111 \rangle$, Fermi surface distorts from sphere to touch zone boundary + give neck. Fermi surface in repeated zone scheme is multiply connected with open orbits as well as closed orbits



de Haas van Alphen expts with H in $\langle 111 \rangle$ direction have 2 period corresp to small area neck + wide area sphere

[Show Fig 15.6
Fig 15.7]

Magnetoresistance shows dramatic effect ~~when~~ in H dependence ~~with~~ ~~the field direction~~ with orientation of current wrt open orbits

	Cu	Ag	Au	
$-1/(R_H)_{nec}$	1.5	1.3	1.5	$\left. \begin{array}{l} \leftarrow \text{open orbits can cause problems!} \\ \} \text{ not bad} \end{array} \right\}$
$\gamma_{free elect}$	1.2	1.5	1.5	
γ_{expt}	1.6	1.6	1.6	

$$R = \frac{-1}{m_{ec}(1+\lambda)} \quad \text{from single model}$$

$$\frac{-1}{R_{m_{ec}}} = \frac{m_{ec}(1+\lambda)}{m_{ec}} \approx 1+\lambda > 1 \quad \text{as above}$$

METAL	$A_{111}(\text{BELLY})/A_{111}(\text{NECK})$
Cu	27
Ag	51
Au	29

Although a distorted sphere, bulging out to make contact with the hexagonal zone faces, is still a fairly simple structure, when viewed in the repeated-zone scheme the noble metal Fermi surface reveals a variety of exceedingly complex orbits. Some of the simplest are shown in Figure 15.7. The open orbits are responsible for the very dramatic behavior of the magnetoresistance of the noble metals (Figure 15.8), whose

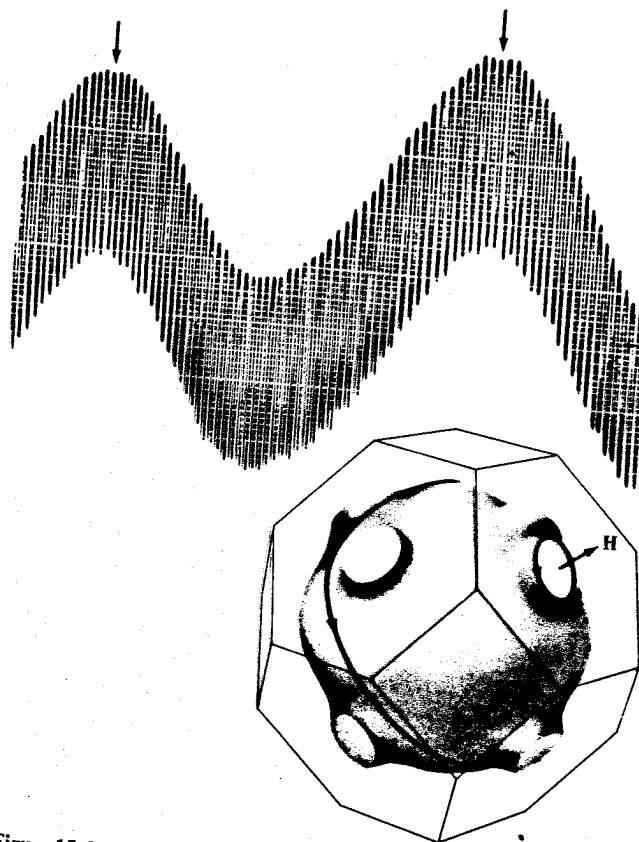


Figure 15.6
De Haas-van Alphen oscillations in silver. (Courtesy of A. S. Joseph.) The magnetic field is along a $\langle 111 \rangle$ direction. The two distinct periods are due to the neck and belly orbits indicated in the inset, the high-frequency oscillations coming from the larger belly orbit. By merely counting the number of high-frequency periods in a single low-frequency period (i.e., between the two arrows) one deduces directly that $A_{111}(\text{belly})/A_{111}(\text{neck}) = 51$. (Note that it is not necessary to know either the vertical or horizontal scales of the graph to determine this fundamental piece of geometrical information!)

es are closely related to
ontact is actually made
: shape shown in Figure
l faces of the zone, but
l. The existence of these
oscillations for magnetic
etermined by the extremal
5.6). The ratio of the two
al $\langle 111 \rangle$ cross sections:⁶

etals the free electron sphere
rections to make contact with
s. (b) Detailed cross sections
parate metals. (D. Shoenberg
is. *Roy. Soc.* 255, 85 (1962).) The
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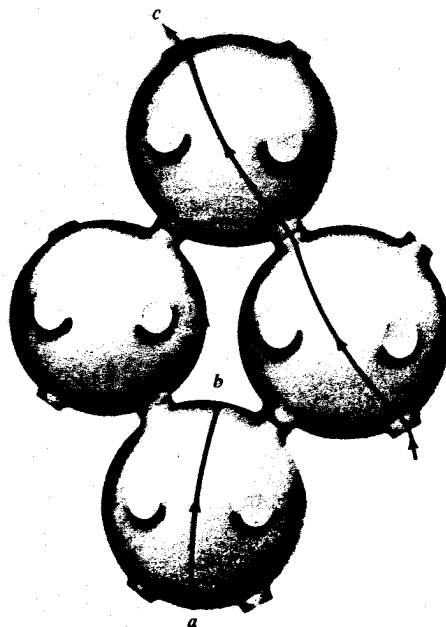


Figure 15.7

Indicating only a few of the surprisingly many types of orbits an electron can pursue in k -space when a uniform magnetic field is applied to a noble metal. (Recall that the orbits are given by slicing the Fermi surface with planes perpendicular to the field.) The figure displays (a) a closed particle orbit; (b) a closed hole orbit; (c) an open orbit, which continues in the general direction indefinitely in the reciprocal lattice.

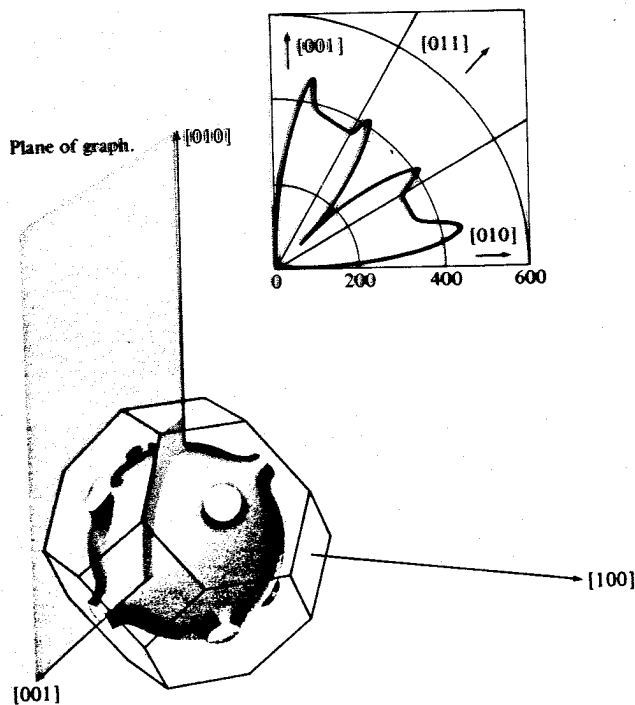


Figure 15.8

The spectacular directional dependence of the high magnetoresistance in copper is characteristic of a surface support. The [001] and [010] directions of the copper crystal are indicated in the figure, and the current flows in the direction perpendicular to the graph. The magnetic field in the plane of the graph has a fixed magnitude of 18 gauss, and its direction is continuously varied from [001] to [010]. The graph is a plot of

$$\frac{\rho(H) - \rho(0)}{\rho(0)}$$

vs. orientation of the field. The sample is very pure and the temperature is very low (4.2 K, the temperature of liquid helium) to insure the highest possible value for $\omega\tau$. (Klauder and J. E. Kuebler, *The Fermi Surface*, Harcourt and Webb, eds., Wiley, New York, 1960.)

For ~~most~~ Nobels, d-bands cause complications threshold occurs for exciting d-band electron up to conduction s-band unoccupied state. This for Cu occurs at λ where $h\nu \approx 2 \text{ eV}$.

[Show Fig 15.11]

Absorption for Cu shows peak at $\sim 2 \text{ eV}$, corresponding to λ in orange part of spectrum. This is why copper is red! Gold is yellow due to threshold at similar energy. Silver more complicated - threshold for d-band excitation + plasmon excitation merge at about 4 eV .

Read about Divalent - (hcp, fcc, bcc)

Trivalent Aluminium (fcc)

Fermi surface close to free electron sphere for fcc B-lattice with 3 conduction electrons per atom.

For free electrons with 3 conduction electrons, 1st BZ completely full - Fermi surface has branches in 2nd, 3rd, 4th zones. In reduced zone scheme, 2nd zone is closed surface, in 3rd zone, connected tubes, in 4th zone small pockets of electrons.

In Al potential ~~also~~ causes pockets of electrons in 4th zone (bands) exist in 2nd + 3rd zones (bands)

¹⁵⁷ per atom
 taking ² of the ³ electrons

Since 1st band completely full, need to put remaining ~~2~~ electrons in 2nd + 3rd bands.

If n is total conduction electron density

$$n_e^{\text{II}} + n_e^{\text{III}} = \frac{n}{3} \quad \left(\frac{2}{3}n \text{ in 1st band} \right)$$

But also $n_e^{\text{II}} + n_h^{\text{II}} = 2\left(\frac{n}{3}\right)$ (since 2nd band ~~can~~ also hold $\frac{2}{3}n$ electrons)

subtract
~~subtract~~

$$\Rightarrow \cancel{n_e^{\text{II}} + n_h^{\text{II}}} \Rightarrow n_e^{\text{III}} - n_h^{\text{II}} = -\frac{n}{3}$$

since hole orbits of 2nd band, and electron orbits of 3rd band are closed $\Rightarrow$ Hall coefficient

$$R_H = \frac{-1}{n_{\text{eff}} e c} \quad \text{with } n_{\text{eff}} = -\frac{n}{3} \cdot \text{Explains}$$

anomalous sign of Hall effect

$$-1/nec R_H \text{ exp} \quad -0.3 \quad \approx -1/3 \text{ predicted above!}$$

$Z=4$ Tetravalent metals - Tin Lead

$Z=5$ Semi metals, Graphite, As, Bi, Sb

Transition metals

Rare earth metals

↑ Antimony
 ↑ Arsenic