Why tight binding works

In tight binding one approximates the Bloch wave function as

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

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

\[ \psi_k (\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \phi (\mathbf{r} - \mathbf{R}) \]

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

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

In principle, the complete set of eigenfunctions of the atomic Hamiltonian form a complete basis set of functions in terms 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 $\varphi_n(r)$.

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

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 effect of the spin-orbit interaction.

In principle there is always an interaction between the intrinsic electron spin with Néel-Vinrnan magnetic moment $\mu_s$ (due to intrinsic spin) and its motion in the electric field of the ions.

$$\delta H_{So} = g \mu_s \left( \mathbf{L} \times \mathbf{E} \right)$$

$\mathbf{E}$ is in local rest frame of electron

$\mathbf{E}$ is from ionic potential
If one includes ST50 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, thus doubling the number of functions used in the tight binding expansion for \( y_e \).

When one includes ST50, one finds that symmetry induced band degeneracies can be lifted.

This effect is most noticeable in heavier elements where the ionic electric field is stronger.
Real metals

Monovalent metals

<table>
<thead>
<tr>
<th>(1A) Alkali's</th>
<th>(bcc)</th>
<th>(1B) Noble's</th>
<th>(fcc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>[1s^22s^2]</td>
<td></td>
<td>[Ar]</td>
</tr>
<tr>
<td>Na</td>
<td>[Ne]3s\textsuperscript{1}</td>
<td></td>
<td>\</td>
</tr>
<tr>
<td>K</td>
<td>[Ar]4s\textsuperscript{1}</td>
<td>Cu</td>
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<tr>
<td>Rb</td>
<td>[Kr]5s\textsuperscript{1}</td>
<td>Ag</td>
<td>\</td>
</tr>
<tr>
<td>Cs</td>
<td>[Xe]6s\textsuperscript{1}</td>
<td>Au</td>
<td>\</td>
</tr>
</tbody>
</table>

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

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

\[
\frac{4}{3} \pi \frac{k_F^3}{4\pi^2} = \frac{k_F^3}{3\pi^2} = n = \frac{2}{a^3}
\]

- side of unit cell

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

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

\[
\Rightarrow k_F = \left(\frac{3}{4\pi}\right)^{1/3}\left(\frac{2\pi}{a}\right) = \frac{1}{420}\left(\frac{2\pi}{a}\right)
\]

one half of side of unit cell in real lattice.

Unit cell of RL has side of length \( \frac{4\pi}{a} \)
1st BZ in Wigner-Seitz cell of FCC lattice of unit cell size \( \frac{\sqrt{2}}{a} \).

Nearest neighbor is \( \frac{2 \sqrt{2}}{a} \), \( \sqrt{\left(\frac{1}{2}\right)^2 + \left(\frac{1}{2}\right)^2} \) away, so shortest distance to surface of 1st BZ is

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

2 bisect R-L vector to get dist to Bragg plane.

So \( \frac{k_F}{k_0} = \frac{0.620}{0.707} = 0.877 \). Fermi surface goes 0.877 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 \( O(U^2) \).

This is the case. Sommerfeld model is essentially good in explaining Alkalis (Li not clear) (charge density wave?)

\( \frac{1}{Rw} \text{ vs } \frac{1}{E_F} \): Li, Na, K, Rb, Cs

-1/Rw nec \( 8, 1.2, 1.1, 1.0, 0.9 \)

(Charge density waves?)

Magnetoresistance also follows \( \gamma \) field dependent than other materials (Sommerfeld give indp of \( \gamma \))

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

\[
\gamma = \frac{\pi^2}{3} \left( \frac{k_B^2}{E_F} \right) n
\]

\( \gamma \) measures \( g(E_F) \)

\( \gamma \) free electron \( \gamma \) exprpt

<table>
<thead>
<tr>
<th>( g(E_F) ) Measures</th>
<th>( \gamma ) Free Electron</th>
<th>( \gamma ) Exprpt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>1.8</td>
<td>4.2</td>
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<tr>
<td>Na</td>
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<td>3.5</td>
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<tr>
<td>K</td>
<td>4.0</td>
<td>4.4</td>
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<tr>
<td>Rb</td>
<td>4.6</td>
<td>5.8</td>
</tr>
<tr>
<td>Cs</td>
<td>6.3</td>
<td>7.7</td>
</tr>
</tbody>
</table>

See also
Noble Metals (fcc)

As in alkalis, rare earth core is tightly bound and 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 electrons per B-lattice site)

turns out 6 bands are enough. 5 lowest bands completely filled, 6th band half full. Bands look like 5 narrow bands (d-like tight binding) and one (s-band) nearly free electron like. However, the nearly free electron 5-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.

\[ \frac{k_F^3}{3\pi^2} = \frac{q}{a^3} \]

\[ k_F = \frac{6\,2\,6 \times 10^{16} \, \text{cm}^{-3}}{(2\pi a)^3} = 0.782 \times 10^{16} \text{ cm}^{-3} \]

(4 atoms in unit cell)

1st BZ is Wigner-Seitz cell of bcc, closest pt
on boundary from origin is at

\[ k_0 = \frac{1}{2}(\frac{\sqrt{3}a}{2})^2(\frac{\sqrt{3}a}{2})^2(\frac{4\pi}{a}) \]

\[ k_0 = \sqrt{\frac{3}{4}} \times \left(\frac{2\pi}{a}\right) = 0.866 \left(\frac{2\pi}{a}\right) \]
Figure 15.4
(a) Calculated energy bands in copper. (After G. A. Burdick, Phys. Rev. 129, 138 (1963).) The $\varepsilon$ vs. $k$ curves are shown along several lines in the interior and on the surface of the first zone. (The point $\Gamma$ 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 $\varepsilon_F$ at points where the resemblance to the free electron band is still quite recognizable. 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 any of the filled bands in the alkali metals.

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...
$\lambda_F / k_0 = 0.903 \Rightarrow \text{neutrally spherical might be expected}$

However, in this direction of closest approach (111), 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 [As van Alphen expects with $H$ in (111) direction have 2 periods corresponding to small area neck + wide area sphere]

Magneto- resistance shows dramatic effect on $\rho$ dependence with field integral with orientation of current cot open orbits.

Cu Ag Au

$-\frac{1}{(R \rho)_{\text{mea}}}$

$\delta_{\text{free electron}}$

1.2 1.5 1.5

$\delta_{\text{cub}}$

1.6 1.6 1.6

open orbits can cause problems?

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

$\frac{-1}{R_{\text{mea}}} = \frac{\text{mec}(1+\lambda)}{\text{mec}} = 1+\lambda > 1$ as above
es are closely related to contact is actually made shape shown in Figure I faces of the zone, but 1. The existence of these oscillations for magnetic determined by the extremal (1,6). The ratio of the two 111) cross sections. The free electron sphere sections to make contact with s. (b) Detailed cross sections separate metals. (D. Shoenberg is, Roy. Soc. 255, 85 (1962).) The modelled by a comparison with

<table>
<thead>
<tr>
<th>METAL</th>
<th>$A_{111}$ (BELLY)/$A_{111}$ (NECK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>27</td>
</tr>
<tr>
<td>Ag</td>
<td>51</td>
</tr>
<tr>
<td>Au</td>
<td>29</td>
</tr>
</tbody>
</table>

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 $A_{111}$(belly)/$A_{111}$(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!)
Figure 15.7
Indicating only a few of the surprisingly many types of orbits an electron can pursue in 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 repeated zone scheme.

Figure 15.8
The spectacular direct proportionality between the high magnetoresistance in c and the characteristic of the copper surface support open domains. The [100] and [011] directions of the copper crystal are indicated in the figure. As current flows in the direction perpendicular to the plane of the graph, the magnitude of the magnetic field is fixed at 18 gauss, and its direction is continuously rotated from [00] to [010]. The graph is a plot of $\rho(H) - \rho(0)$ vs. orientation of the field sample, which is very pure at temperature very low (4.2 K, the temperature of liquid helium) to insure the possible value for $\alpha_f$. Klauder and J. E. Ku, *The Fermi Surface, Ha and Webb*, eds., Wiley, New York, 1960.)
For Nibler, d-bands cause complications threshold occurs for exciting d-band electron up to conduction s-band unoccupied state. This for Cu occurs at \( \approx 2 \text{eV} \).

[Show Fig 15.11]

Absorption for Cu shows peak at \( \approx 2 \text{eV} \), correspondingly to a 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 range at about 4 eV.

Read about Divalent \((\text{hcp, fcc, bcc})\)

**Trivalent** Aluminium \((\text{fcc})\)

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

For free electrons with 3 conduction electrons,

1\(^{\text{st}}\) BZ completely full - Fermi surface box boundaries & 2nd, 3rd, 4th zones. In reduced zone scheme, 2nd zone contains holes, 3rd zone closed surface, in 3rd zone connected tubes, in 4th zone small pockets of electrons.

In Al potential causes pockets of electrons in 4\(^{th}\) zone.
Since 1st band completely full, need to put remaining electrons in 2nd + 3rd bands.

If $n$ is total conduction electron density

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

But also $n_e^I + n_h^II = \frac{2}{3}(\frac{n}{3}) \quad (\text{since 2nd conduction band also hold } \frac{2}{3} n \text{ electrons})$

\[ n_e^I - n_h^II = -\frac{n}{3} \]

Since hole orbits of 2nd band, and electron orbits of 3rd band are closed \( \Rightarrow \) Hall coefficient

\[ R = -\frac{1}{n_{eff} e c} \]

with \( n_{eff} = -\frac{n}{3} \). Explain anomalous sign of Hall effect

\[-\frac{1}{n_{ec} R_H \text{exp}} = 0.3 \approx -\frac{1}{3} \text{ predicted above!} \]

$z = 4$ Tetra-valent metals - Tin, Lead

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

Transition metals \( \uparrow \) Antimony

Rare earth metals \( \uparrow \) Arsenic