

## An Aside on Bloch Functions

Something that has been bothering me all along so far is the use of "free electron" wavefunctions in the theory produced by the artifice of periodic boundary conditions. It has bothered me because at the boundaries of the crystal, periodicity is broken and the basic problem more resembles the "particle in a box" problem with its solution in terms of standing waves.

The answer to this concern seems to lie in the idea of Bloch functions. The following notes are taken from "Electronic Structure" by Martin.

Any perfect crystal has a potential function,  $V(\vec{r})$ , that is periodic with the direct lattice. That is,  $V(\vec{r}) = V(\vec{r} + \vec{d})$  where  $\vec{d}$  is a direct lattice vector. If  $V(\vec{r})$  is periodic in  $\vec{d}$ , then  $\psi(\vec{r})$  must also be periodic in  $\vec{d}$ . Proof is as follows:

$$\text{Given } \nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0$$

with  $V(\vec{r}) = V(\vec{r} + \vec{d})$ ,

~~Let  $\psi_1$  and  $\psi_2$  be two solutions such that~~

~~$$\psi_1(\vec{r}) = A_1 f_1(\vec{r}) + A_2 f_2(\vec{r})$$~~

~~$$\psi_2(\vec{r}) = B_1 f_1(\vec{r}) + B_2 f_2(\vec{r})$$~~



Bloch's Theorem states: Given  $\nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0$

If  $V(\vec{r} + \vec{d}) = V(\vec{r}) \quad \forall \vec{d}$ , then

$$\psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} U_{n\vec{k}}(\vec{r})$$

where

$$U_{n\vec{k}}(\vec{r}) = U_{n\vec{k}}(\vec{r} + \vec{d}).$$

Stated another way, The eigenstates of  $H = -\hbar^2 \nabla^2 / 2m + V(\vec{r})$  can be chosen such that associated with each  $\psi$  is a wavevector  $\vec{k}$  such that

$$\boxed{\psi(\vec{r} + \vec{d}) = e^{i\vec{k} \cdot \vec{d}} \psi(\vec{r})}$$

Proof (from ~~Ashcroft~~ Ashcroft & Mermin)

For each Bravais lattice vector  $\vec{d}$  define a translation operator  $T_{\vec{d}}$  such that for any function  $f(\vec{r})$

$$T_{\vec{d}} f(\vec{r}) = f(\vec{r} + \vec{d}).$$

Since the Hamiltonian is periodic

$$T_{\vec{d}}(H\psi) = H(\vec{r} + \vec{d})\psi(\vec{r} + \vec{d}) = H(\vec{r})\psi(\vec{r} + \vec{d}) = HT_{\vec{d}}\psi$$

Since this must hold for any function  $\psi$ ,

$$T_{\vec{d}} H = H T_{\vec{d}}$$

In addition,

$$\begin{aligned} T_{\vec{d}} T_{\vec{d}'} \psi(\vec{r}) &= T_{\vec{d}} \psi(\vec{r} + \vec{d}') = \psi(\vec{r} + \vec{d}' + \vec{d}) \\ &= T_{\vec{d}'} T_{\vec{d}} \psi(\vec{r}) \end{aligned}$$

$$\text{Therefore, } T_{\vec{d}} T_{\vec{d}'} = T_{\vec{d}'} T_{\vec{d}} = T_{\vec{d} + \vec{d}'}$$

Therefore,  $T_{\vec{d}}$  for all Bravais lattice vectors  $\vec{d}$  and the Hamiltonian,  $H$ , form a set of commuting operators.



Since  $T_d$  and  $H$  commute, they share a set of eigenfunctions. [Proof: Let  $A$  and  $B$  commute and let  $A u_n = a_n u_n$ . Then  $BA u_n = a_n B u_n$ . Likewise,  $AB u_n = BA u_n$  (because  $A$  &  $B$  commute) and so  $AB u_n = a_n B u_n$ . Now,  $B u_n$  must be an eigenfunction of  $A$  and, therefore, can differ from  $a_n u_n$  only by a multiplicative constant. Thus,  $B u_n = b_n u_n$ . Hence,  $u_n$  is an eigenfunction of both  $A$  and  $B$ ]

Since  $T_d$  and  $H$  share a set of eigenfunctions, we have

$$H \psi = E \psi$$

$$T_d \psi = C(\bar{d}) \psi$$

The eigenvalues  $C(\bar{d})$  are related because

$$T_{d'} T_d \psi = C(\bar{d}) T_{d'} \psi = C(\bar{d}) C(\bar{d}') \psi$$

$$\text{and } T_{d'} T_d \psi = T_{d'+d} \psi = C(\bar{d} + \bar{d}') \psi$$

$$\text{Therefore, } C(\bar{d} + \bar{d}') = C(\bar{d}) C(\bar{d}')$$

Now let  $\bar{d} = n_1 \bar{a}_1 + n_2 \bar{a}_2 + n_3 \bar{a}_3$  where the  $\bar{a}_i$  are primitive vectors for the Bravais lattice.

$C(\bar{a}_i)$  may always be written as  $C(\bar{a}_i) = e^{2\pi i \chi_i}$  for suitably chosen  $\chi_i$ . Therefore,

$$\begin{aligned} C(\bar{d}) &= e^{2\pi i \chi_1} e^{2\pi i \chi_2} e^{2\pi i \chi_3} = C(\bar{a}_1)^{n_1} C(\bar{a}_2)^{n_2} C(\bar{a}_3)^{n_3} \\ &= e^{i \mathbf{k} \cdot \bar{d}} \end{aligned}$$



## Scattering by Defects

provided that

$$\vec{k} = \chi_1 \vec{b}_1 + \chi_2 \vec{b}_2 + \chi_3 \vec{b}_3$$

$$\text{and } \vec{b}_i \cdot \vec{a}_j = 2\pi \delta_{ij}$$

(i.e., The  $\vec{b}_i$  are reciprocal lattice vectors)

Therefore,

$$T_{\vec{a}} \psi = \psi(\vec{r} + \vec{a}) = c(\vec{a}) \psi = e^{i\vec{k} \cdot \vec{a}} \psi(\vec{r}) \quad \text{QED}$$

So, Bloch's Theorem  $\psi(\vec{r} + \vec{a}) = e^{i\vec{k} \cdot \vec{a}} \psi(\vec{r})$  is proven.

If  $\vec{g}$  is a lattice wavevector,  $S(\vec{g})$  is still unity.

How Since  $\psi(\vec{r})$  is periodic in the lattice, then

each solution of the Schrodinger equation must

satisfy a boundary condition that is also periodic

in the direct lattice of the crystal. This is

because  $\psi$  must be the same at physically equivalent

points in the crystal. Thus, it follows that

because of the periodicity of  $V(\vec{r})$ , use of

periodic boundary conditions is okay.

From this, it follows that since

$$\psi(\vec{k}, \vec{r}) = \mu(\vec{k}, \vec{r}) e^{i\vec{k} \cdot \vec{r}}$$

(where  $\mu(\vec{k}, \vec{r})$  is called the modulating function)

is a solution to Schrodinger's equation with periodic

boundary conditions,  $\psi$  takes on the form of

a modulated plane wave - "scattering"



## Scattering by Defects

The example he treated was a vacancy at lattice site  $\vec{r}_0$ .

The structure factor of (6-5) describing the pseudopotential must omit this ion as follows:

$$S(\vec{g}) = \frac{1}{N_0-1} \sum_i' e^{-i\vec{g} \cdot \vec{r}_i}$$

where the prime indicates skipping the missing ion at  $\vec{r}_0$ .

If  $\vec{g}$  is a lattice wavevector,  $S(\vec{g})$  is still unity.

However, the atomic volume is now  $\Omega/(N_0-1)$  and

since  $W_0$  depends on  $\Omega_0$ , the matrix element

$\langle \vec{k}+\vec{g} | W^0 | \vec{k} \rangle$  will now be different. If  $N_0$  is enormous,

this won't be much of a change.

Now, if  $\vec{g}$  is not a lattice wavevector, the structure factor is

$$S(\vec{g}) = \frac{1}{N_0-1} \sum_i' e^{-i\vec{g} \cdot \vec{r}_i} = \frac{1}{N_0-1} e^{-i\vec{g} \cdot \vec{r}_0} = \frac{e^{-i\vec{g} \cdot \vec{r}_0}}{N_0-1} \approx -\frac{1}{N_0}$$

Therefore, the vacancy creates a small matrix element

$-W_0/N_0$  which couples every pair of states

$$\langle \vec{k}+\vec{g} | W^0 | \vec{k} \rangle = -\frac{W_0}{N_0}, \quad \vec{g} \neq \text{lattice wavevector}$$

This coupling is referred to as "scattering"



At this point, Harrison trots out some scattering formulas. I don't understand what he did (perhaps I need to look at a text on electron transport).

Basically, though, he comes up with a scattering rate

$$\frac{1}{\tau} = \frac{\Omega_0 \hbar^m}{2\pi \hbar^3} \left( \frac{N_v}{N_u} \right) \int_0^\pi W_0^2 \cdot (1 - \cos \theta) d\theta$$

$$\frac{1}{\tau} = \frac{\Omega_0 \hbar^m}{2\pi \hbar^3} \left( \frac{N_v}{N_u} \right) \int_0^\pi W_0 (1 - \cos \theta) \sin \theta d\theta \quad (16-22)$$

where  $N_v = \#$  of vacancies and  $W_0$  is now a function of  $\theta$ . (see 16-7)

Well, he made a nice detour here, but I don't get "how this fits" yet. It looks like I need to study up on this business of transport theory ←

## Screening

This is the section where he starts to deal with the fact that the electron density,  $N$ , can not be uniform. His approach is to make another correction in the pseudo potential.

Rather than go with a self-consistent calculation, or use of perturbation theory, his approach is to make a couple of approximations -



He begins by noting that 16-2 is an inverse Fourier expansion and from that sets  $W^0(\vec{r})$  in terms of a Fourier series

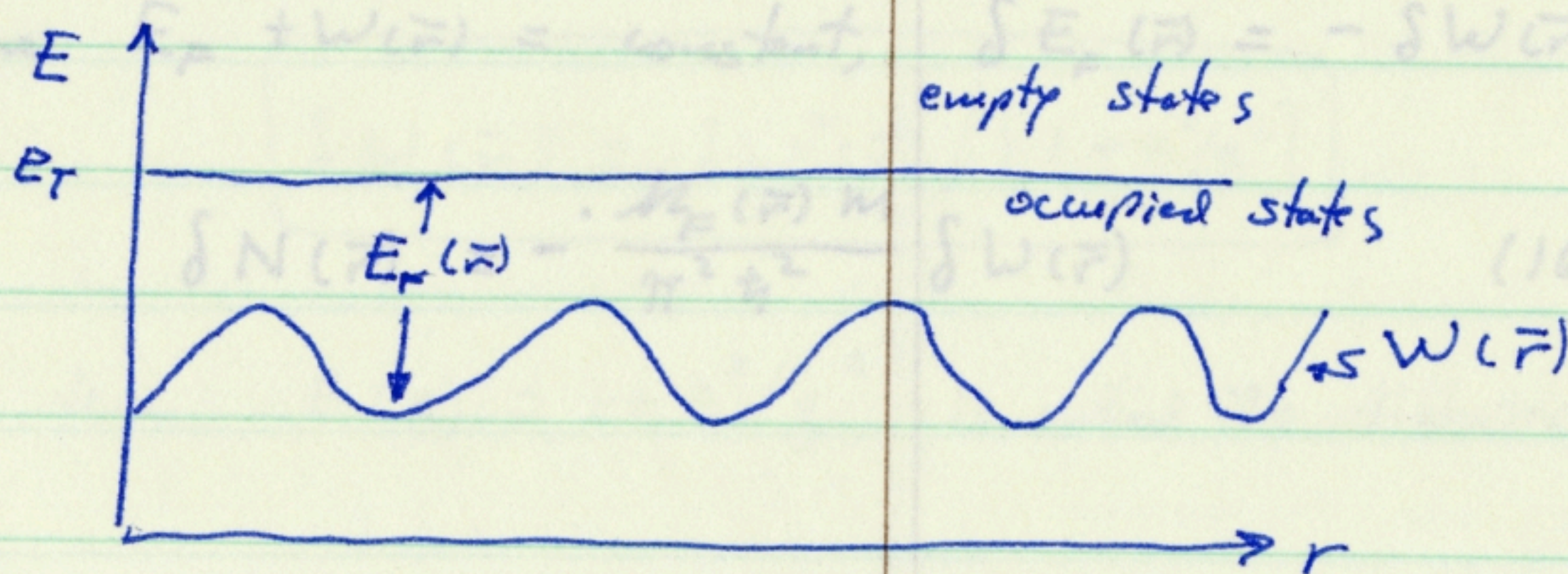
$$W^0(\vec{r}) = \sum_{\vec{g}} W_{\vec{g}}^0 e^{i\vec{g} \cdot \vec{r}} \quad (16-29)$$

where  $W_{\vec{g}}^0 \triangleq \langle \vec{k} + \vec{g} | W^0(\vec{r}) | \vec{k} \rangle$ .

(16-24) can then be evaluated term by term.

The unscreened pseudopotential components are  $W_{\vec{g}}^0 e^{i\vec{g} \cdot \vec{r}}$ . He denotes the screened values by  $W_{\vec{g}} e^{i\vec{g} \cdot \vec{r}}$ . The game is to find  $W_{\vec{g}}$ .

The first approximation is to assume that wavelengths are long enough so that there are regions (in  $\vec{r}$ ?) where the potential is constant. In this case, the electrons would distribute themselves in each region so that the highest total energy would be the same in each region (equipartition of energy?).





With the total pseudopotential energy varying sinusoidally, the Fermi Kinetic energy must also vary in  $\vec{r}$  such that  $E_F(\vec{r}) + W(\vec{r}) = \text{constant}$ .

The local Fermi Kinetic energy leads to a local Fermi wave number,  $k_F(\vec{r})$ , which also varies as

$$\hbar^2 k_F(\vec{r}) / (2m) = E_F(\vec{r})$$

Thus, The electron density varies in  $\vec{r}$  by

$$N(\vec{r}) = k_F^3(\vec{r}) / (3\pi^2)$$

This is the Fermi-Thomas approximation.

The next approximation is that  $\Delta W(\vec{r})$  is small compared to  $E_F(\vec{r})$ . In this case, higher order terms in  $W(\vec{r})$  can be neglected relative to the first order terms. Taking derivative on the Fermi-Thomas approximation results in

$$\delta N(\vec{r}) = \frac{3 k_F^2(\vec{r})}{3\pi^2} \delta(k_F(\vec{r})) = \frac{k_F m}{\pi^2 \hbar^2} \delta E_F(\vec{r}).$$

Since  $E_F + W(\vec{r}) = \text{constant}$ ,  $\delta E_F(\vec{r}) = -\delta W(\vec{r})$  so

$$\delta N(\vec{r}) = - \frac{k_F(\vec{r}) m}{\pi^2 \hbar^2} \delta W(\vec{r}) \quad (16-26)$$

The term  $\epsilon(\vec{r}) = 1 + k_F^2 / \beta^2$  is called the dielectric function.



The next step is to go after the screening potential,  $\delta W(\vec{r}) - \delta W^0(\vec{r})$ , in terms of the electron density fluctuation. To do this, he invokes Poisson's equation,  $\nabla^2 V = -4\pi\rho$  where  $V$  = electrostatic potential and  $\rho$  = charge density, (cgs units). Since  $\rho = eN(\vec{r})$  and  $W = eV$ , Poisson's equation for the screening potential becomes

$$\nabla^2 [\delta W(\vec{r}) - \delta W^0(\vec{r})] = -4\pi e^2 \delta N(\vec{r}) \quad (16-27)$$

Now, the spatial dependence for all terms in (16-27) goes by  $e^{i\vec{q}\cdot\vec{r}}$  so  $\nabla^2 [\delta W(\vec{r}) - \delta W^0(\vec{r})] = -q^2 [\delta W(\vec{r}) - \delta W^0(\vec{r})]$  leading to

$$\begin{aligned} q^2 [\delta W(\vec{r}) - \delta W^0(\vec{r})] &= 4\pi e^2 \delta N(\vec{r}) \\ &= 4\pi e^2 \left[ -\frac{\hbar_F(\vec{r})m}{\pi^2 \hbar^2} \delta W(\vec{r}) \right] \end{aligned}$$

Let  $\boxed{\kappa^2 \triangleq 4e^2 \hbar_F(\vec{r})m/(\pi \hbar^2)}$ . Then

$$q^2 \delta W(\vec{r}) - q^2 \delta W^0(\vec{r}) = -\kappa^2 \delta W(\vec{r})$$

or

$$\boxed{\delta W(\vec{r}) = \delta W^0(\vec{r}) / [1 + \kappa^2/q^2]} \quad (16-28)$$

The term  $\epsilon(q) = 1 + \kappa^2/q^2$  is called the dielectric function.



Harrison points out that when the long-wavelength approximation is removed, the dielectric function, as calculated from perturbation theory, becomes

$$\epsilon(q) = 1 + \frac{me^2}{2\pi k_F q^2} \left[ \frac{1-\eta^2}{2\eta} \ln \left| \frac{1+\eta}{1-\eta} \right| + 1 \right] \quad (16-31)$$

where

$$\eta = q/2k_F$$

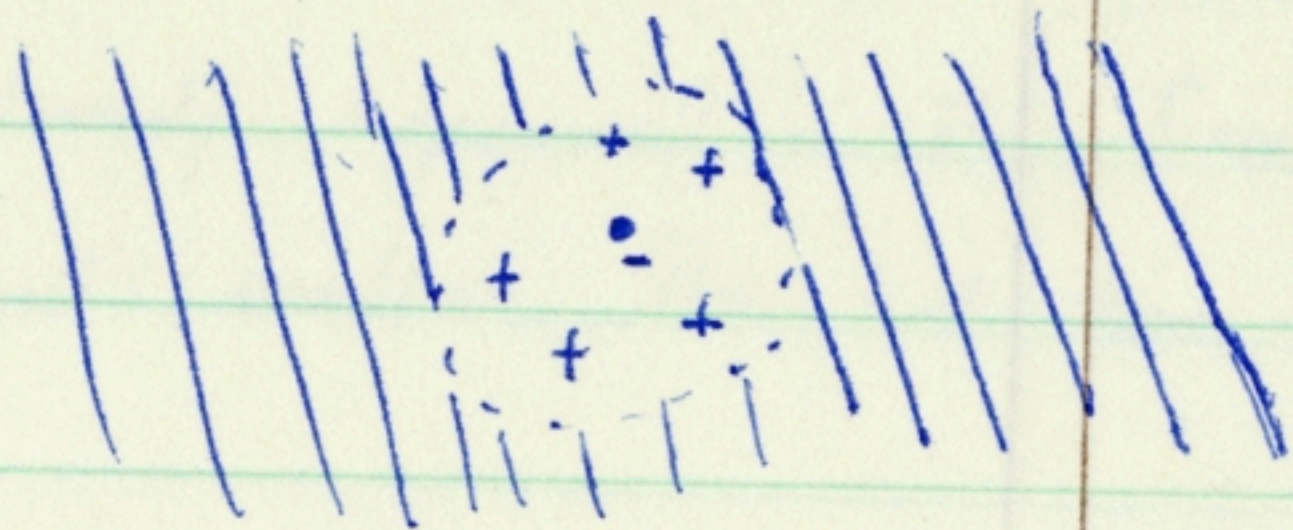
The general form  $\delta W(\vec{r}) = \frac{\delta W^0(\vec{r})}{\epsilon(q)}$  is the form seen earlier in computing the  $W_0$  of (16-7).

### An Aside on Screening

The physical basis of screening arises from the Coulomb and exchange (spin) interactions among the electrons in the electron gas. This discussion comes from chapter 1 of Inkson (Many Body Theory of Solids).

Considered semi-classically, the electrons in the electron gas tend to repel each other. The Coulomb interaction is repulsive and so is the exchange interaction between electrons of the same energy.

Therefore, each electron creates a "hole" around itself



and allows the ions to screen out and cancel the electric field due to the other electrons.