electrons - a preview

The above argument for X-rays is true for any waves. In particular it is also true for
particle waves (where $\mathbf{p} = \hbar \mathbf{k}$ gives the quantum
wave vector $\mathbf{k}$) provided one assumes the collisions
of the particle with the crystal are elastic (i.e.
the particle only exchanges momentum but not energy to
the crystal). If one shot a high energy electron
into the crystal, one could see electron diffraction
patterns with Bragg peaks. Such electrons would
scatter only if the tip of the wave vector $\mathbf{k}$ lay
on a Bragg plane.

What about a conduction electron inside the metal?
In the absence of the periodic con potential, the
electron state would be a plane wave $e^{i\mathbf{k} \cdot \mathbf{r}}$.
When we turn on the con potential, such a plane
wave would scatter if $\mathbf{R}$ lay on a Bragg plane.
But in the presence of the con potential, $e^{i\mathbf{k} \cdot \mathbf{R}}$
no longer an exact eigenstate. We will see
that the eigenstates in the presence of the con potential
is a mixture of $e^{i\mathbf{k} \cdot \mathbf{r}}$ plus all the states
$e^{i(\mathbf{k}+\mathbf{R}) \cdot \mathbf{r}}$ into which it can be scattered by a
Bragg plane. From perturbation theory in
quantum mechanics, the extent to which the
scattered state $e^{i(\mathbf{k}+\mathbf{R}) \cdot \mathbf{r}}$ mixes into the
free electron state $e^{i\mathbf{k} \cdot \mathbf{r}}$ is determined by
the "energy denominator" \( \frac{1}{E(k) - E(k-k)} \).

Hence states \( e^{iK\cdot \vec{r}} \) where \( \vec{r} \) is far from any Bragg plane (and so where \( \frac{1}{E(k) - E(k-k)} \) is small) are very little changed from the free-electron plane wave state. It is only states \( e^{iK\cdot \vec{r}} \) where \( \vec{r} \) lies close to a Bragg plane that there will be a strong mixing in of the scattered state \( e^{i(k-k) \cdot \vec{r}} \) and the resulting wavefunction is noticeably different from the free-electron state (it will look like a reflected standing wave).

This explains why metals with valence \( Z = 1 \) are so well described by the free-electron model. When \( Z = 1 \), the Fermi surface lies away from all Bragg planes, so all electron states have little Bragg scattering and the electron states are a very good approximation.

For simplicity, consider a single cubic B.L. with lattice constant \( a \) and valence \( Z = 1 \). The B.L. has a 1st Brillouin Zone with volume \( \left( \frac{2\pi}{a} \right)^3 \)

The Fermi wave vector \( k_F \) is given by

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

\[
k_F = (3\pi^2 n)^{1/3}
\]

For \( Z = 1 \), conduction electron density is \( n = 1/a^3 \).
\[ k_F = \left( \frac{3\pi^2}{a^2} \right)^{1/3} \quad \text{and} \quad \frac{4\pi k_F^3}{a} = \frac{3.09}{a} < \frac{\pi}{a} \]

and so the Fermi surface lies entirely within the 1st Brillouin Zone. All electron states with the Fermi surface are therefore close to free electron-like, since they are not near any Bragg planes.

Note: Volume in k-space of Fermi sphere is
\[ \frac{4}{3} \pi k_F^3 = 4\pi^3 m = \frac{1}{2} \frac{2\pi^3}{a} = \frac{1}{2} \text{vol } 1^{st} \text{ B.Z.} \]

This is in general true for any B.Z.

\[ \Rightarrow \text{ for } z = 1, \text{ the Fermi surface always lies entirely within 1st B.Z. occupies a volume in k-space equal to } \frac{1}{2} \text{ the volume of the 1st B.Z.} \]

If \( z = 2 \) however, the conduction electron density \( m = \frac{2}{a^3} \) and Fermi surface will in general cut out across the surface of the 1st B.Z.

The electron states at the B.Z. surface will not be free electron-like and there is now the possibility for more complicated behavior.
X-ray scattering from Bragg with basis

We saw that the amplitude of the scattered X-ray will be proportional to

\[ \sum e^{i \tilde{k} \cdot \tilde{r}_i} \text{ where } \tilde{k} = \tilde{k} - \tilde{k}' \]

This vanishes when \( \tilde{k} = 0 \) in \( \text{R} \).\text{L.}.

The above calculation viewed scattering as scattering off the identical Wigner-Seitz cells that can be constructed about each Bragg site \( \tilde{r}_i \). These W-S cells are all identical so they scatter the same. But we did not need to assume anything about the ions contained in each such W-S cell. There might be a single ion at \( \tilde{r}_i \) or the might be several ions at positions \( \tilde{r}_i + \tilde{d}_j \), \( j = 1, \ldots, n \), in which case the crystal is a Bragg with a basis.

Suppose we have a Bragg with a basis, and all the ions are identical (e.g.: C ions in a diamond structure). In this case no only is the scattering off each W-S cell the same, but the scattering of each individual ion is the same.
We would then conclude that the scattered amplitude is proportional to

$$\sum_{i} \frac{\hat{n}_i}{\Delta k} e^{i \Delta k \cdot (\vec{R}_i + \vec{d}_i)} = \sum_{i} e^{i \Delta k \cdot \vec{R}_i} \frac{n_i}{\Delta k} e^{i \Delta k \cdot \vec{d}_i}$$

Again the vanishes unless $\Delta k = \vec{k}$ in R.L., because of the first term. The 2nd term tells how the amplitude is modulated at different $\vec{k}$ due to the specific positions of the ions within the W-S cell.

Define

$$S_k = \sum_{j} \frac{\hat{n}_j}{\Delta k} e^{i \vec{k} \cdot \vec{d}_j}$$

"geometric structure factor"
Example: Regard bcc as sc with a two point basis
\[ \mathbf{d}_1 = 0, \quad \mathbf{d}_2 = \frac{\alpha}{2} (\hat{x} + \hat{y} + \hat{z}) \]

Primitive vectors for sc are:
\[ \mathbf{a}_1 = a \hat{x}, \quad \mathbf{a}_2 = a \hat{y}, \quad \mathbf{a}_3 = a \hat{z} \]

Primitive vectors for sc RL are:
\[ \mathbf{b}_1 = \frac{2\pi}{a} \hat{x}, \quad \mathbf{b}_2 = \frac{2\pi}{a} \hat{y}, \quad \mathbf{b}_3 = \frac{2\pi}{a} \hat{z} \]

RL vector \( \mathbf{R} = \frac{2\pi}{a} (n_1 \hat{x} + n_2 \hat{y} + n_3 \hat{z}) \)
\( n_1, n_2, n_3 \) integers

Geometric form factor is:
\[ S_{\mathbf{K}} = e^{i \mathbf{R} \cdot \mathbf{d}_1} + e^{i \mathbf{R} \cdot \mathbf{d}_2} = 1 + e^{i \pi (n_1 + n_2 + n_3)} \]

\[ = \begin{cases} 2 & \text{if } n_1 + n_2 + n_3 \text{ even} \\ 0 & \text{if } n_1 + n_2 + n_3 \text{ odd} \end{cases} \quad \text{no Bragg peaks here!} \]

For \( \bullet \), \( S_{\mathbf{K}} = 2 \)
For \( \circ \), \( S_{\mathbf{K}} = 0 \implies \text{Bragg peak vanishes} \)

Removing the sites for \( \bullet \) with \( \mathbf{K} = 0 \), we see that we are left with an fcc RL with unit cell of length \( \frac{4\pi}{a} \).

But this is just what we expect for a bcc direct lattice! So all is consistent.
Diamond lattice - fcc with 2-point basis

$$ b_1 = \frac{2\pi}{a} (y + \frac{z}{2} - x) $$

$$ b_2 = \frac{2\pi}{a} (\frac{z}{2} + x - y) $$

$$ b_3 = \frac{2\pi}{a} (x + y - z) $$

$$ A_1 = 0, \quad A_2 = \frac{3}{4} (x + y + z) $$

$$ S_K = 1 + e^{\pm 2\pi i (n_1 + n_2 + n_3)} \quad \text{for } K = n_1 b_1 + n_2 b_2 + n_3 b_3 $$

$$ n_1 + n_2 + n_3 = \begin{cases} 
2m & \text{for } n_1 = \text{even} \quad m \geq 0 \quad \text{twice even} \\
2m + 1 & \text{for } n_1 = \text{odd} \quad \text{odd} \\
0 & \text{for } n_1 + n_2 + n_3 = 2(2m+1) \quad \text{twice odd} 
\end{cases} $$

A+M fig 6.12
Suppose now we have a lattice with a basis but different types of ions occupy the basis sites, for example, the NaCl or zinc-blend structure.

Now the angular factor $f(q, \theta)$, which gives the modulation of the scattered wave on observation angle, can be different for the different type of ions. The structure factor should thus include this. We can define

$$ S_K = \sum_{j=1}^{n} f_j(R) e^{i \vec{R} \cdot \vec{d}_j} $$

as a point basis.

Scattered amplitude $\sim e^{i \chi R} \sum e^{i \vec{R} \cdot \vec{R}_j} S(\vec{R})$

$f_j(R)$ is called the atomic form factor and depends on the momentum transfer $\vec{R} = \vec{k} - \vec{k'}$. It is determined by the internal structure of the ion at site $\vec{d}_j$ in the basis. $f_j$ is the same for identical types of ions.

For a simple model of dipole radiation

$$ f_d(R) \sim -\frac{1}{2} \int d^3 \vec{r} \ e^{-i \vec{R} \cdot \vec{r}} \ \rho(\vec{r}) $$

$\rho(\vec{r})$ is the charge density of the ion at $\vec{d}_j$.

$S_K$ will not vanish for small $R$. For small $R$, above is just $i \vec{R} \cdot \Delta \mu (\text{dipole moment})$. 