X-ray Scattering from BL with basis

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

$$\sum_i e^{i \hat{\mathbf{k}} \cdot \mathbf{R}_i}$$

where $\Delta \mathbf{k} = \mathbf{k} - \mathbf{k}'$

This vanishes when $\Delta \mathbf{k} \neq \mathbf{K}$ in R.L.

The above calculation viewed scattering as scattering off the identical Wigner-Seitz cells that can be constructed about each BL site $\mathbf{R}_i$. 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 $\mathbf{R}_i$, or there might be several ions at positions $\mathbf{R}_i + \mathbf{d}_j$, $j = 1, \ldots, n$, in which case the crystal is a BL with a basis.

Suppose we have a BL with a basis, and all the ions are identical (e.g., C ions in a diamond structure). In this case not only is the scattering off each W-S cell the same, but the scattering off each individual ion is the same.
We would then conclude that the scattered amplitude is proportional to

$$\sum_i^\eta \sum_j^\xi e^{i\Delta k \cdot (\vec{R}_i + \vec{d}_j)} = \sum_i e^{i\Delta k \cdot \vec{R}_i} \sum_j e^{i\Delta k \cdot \vec{d}_j}$$

Again the vanishes unless \( \Delta k = \vec{0} \) in R.L., because of the first term. The 2nd term tells how the amplitude is modulated at different \( \vec{R} \) due to the specific positions of the ions within the W-S cell.

Define

$$S_k = \sum_j^\xi e^{i\vec{K} \cdot \vec{d}_j}$$

"geometric structure factor"
Example: Regard bcc as sc with a two point basis

\[ \mathbf{d}_1 = 0, \quad \mathbf{d}_2 = \frac{a}{2} (\hat{x} + \hat{y} + \hat{z}) \]

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

\( m, n_2, n_3 \) integer

Geometric form factor is

\[ S_K = e^{i \mathbf{R} \cdot \mathbf{d}_1} + e^{i \mathbf{R} \cdot \mathbf{d}_2} = 1 + e^{i \pi (n_1 + n_2 + n_3)} \]

\[ \begin{cases} \frac{2}{i} & \text{if } n_1 + n_2 + n_3 \text{ even} \\ 0 & \text{if } n_1 + n_2 + n_3 \text{ odd} \end{cases} \]

for \( n \neq 0 \) peaks here.

\[ S_K = \begin{cases} 2 & \text{for } \mathbf{R} = 0 \\ 0 & \text{Bragg peak vanishes} \end{cases} \]

Removing the sites for which \( S_K = 0 \) we see that we are left with an fcc RL with unit cell of length \( \frac{2 \pi}{a} \).

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

\( \Rightarrow \text{ RL or bcc} \)

\[
\begin{align*}
\vec{b}_1 &= \frac{2\pi}{a} (\hat{y} + \frac{1}{2} - \hat{x}) \\
\vec{b}_2 &= \frac{2\pi}{a} (\hat{y} + \frac{1}{2} - \hat{y}) \\
\vec{b}_3 &= \frac{2\pi}{a} (\hat{x} + \hat{y} - \hat{z}) \\
\vec{d}_1 &= 0, \quad \vec{d}_2 = \frac{a}{2} (\hat{x} + \hat{y} + \hat{z})
\end{align*}
\]

\[ S_K = 1 + e^{\frac{i}{2} \pi (n_1 + n_2 + n_3)} \quad \text{for } K = n_1 \vec{b}_1 + n_2 \vec{b}_2 + n_3 \vec{b}_3 \]

\[
\begin{cases} 
2 \quad n_1 + n_2 + n_3 = 2m \quad \text{for } m \text{ integer twice} \\
1 \pm 1 \quad n_1 + n_2 + n_3 = 2m+1 \quad \text{odd} \\
0 \quad n_1 + n_2 + n_3 = 2(2m+1) \quad \text{twice even}
\end{cases}
\]

Ass. 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 $f(\theta, \phi)$, 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

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

$n$ point basis

scattered amplitude $\sim e^{-i\vec{k} \cdot \vec{r}} \sum_{K} e^{i\vec{K} \cdot \vec{r}} S(\vec{K})$

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

For a single model of dipole radiation

$$f_j(\vec{r}_j) \rightarrow -\frac{1}{2} \int d^3r e^{i\vec{K} \cdot \vec{r}} \rho_{\vec{r}}(\vec{r})$$

depend on $\overrightarrow{r}$

$S(\vec{K})$ will not in general vanish at any $\vec{K}$. for small $\vec{K}$, above is just $i\vec{K} \cdot \vec{r}$ (dipole moment).
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 ion potential, the electron state would be a plane wave $e^{i \mathbf{k} \cdot \mathbf{r}}$. When we turn on the ion potential, such a plane wave would scatter if $\mathbf{k}$ lay on a Bragg plane. But in the presence of the ion potential, $e^{i \mathbf{k} \cdot \mathbf{r}}$ is no longer an exact eigenstate. We will see that the eigenstates in the presence of the ion potential is a mixture of $e^{i \mathbf{k} \cdot \mathbf{r}}$ plus all the states $e^{i (\mathbf{k} \cdot \mathbf{R}) \cdot \mathbf{r}}$ into which it can be scattered by a Bragg plane. From perturbation theory in quantum mechanics, the extent to which the scattered state $e^{i (\mathbf{k} \cdot \mathbf{R}) \cdot \mathbf{r}}$ mixes into the free electron state $e^{i \mathbf{k} \cdot \mathbf{r}}$ is determined by...
the "energy denominator" $\frac{1}{E(k) - E(k-R)}$. Hence states $e^{i k \cdot r}$ where $k$ is far from any Bragg plane (and so where $\frac{1}{E(k) - E(k-R)}$ is small) are very little changed from the free electron plane wave state. It is only states $e^{i (k-R) \cdot r}$ where $k$ lies close to a Bragg plane that there will be a strong mixing in of the scattered state $e^{i (k-R) \cdot r}$ and the resulting eigenstate 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 free electron states are a very good approximation.

For simplicity, consider a simple cubic BZ with lattice constant a and valence $Z=1$. The RL has a 1st Brillouin zone with volume $\frac{4\pi^3}{a^3}$.

The Fermi wave vector $k_F$ is given by

$$\frac{4\pi^3}{3} k_F^3 = n$$

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

For $Z=1$, conduction electron density is $n = \frac{1}{a^3}$. 
\[ k_F = \left( \frac{3\pi^2}{a} \right)^{1/3} \quad \frac{4\pi}{a} \frac{m}{\hbar^2} \leq \frac{\pi}{a} \]

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

\[ \frac{4}{3} \pi k_F^3 = 4\pi^3 m = \frac{1}{2} \left( \frac{2\pi}{a} \right)^3 = \frac{1}{2} \text{ vol 1st B.Z.} \]

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 \( m = 2/a^3 \) and Fermi surface will no longer cut across the surface of the 1st B.Z. The electron states at the BZ surface will not be free electron-like and there is now the possibility for more complicated behavior.
Electrons in a crystal

When we discussed X-ray scattering we saw that the condition of constructive interference required that an incident wavevector $\mathbf{k}$ could only scatter into wavevectors $\mathbf{k}' = \mathbf{k} - \mathbf{R}$ where $\mathbf{R}$ was in the B.L.

For electrons in a crystal we expect similar behavior since our argument depended only on the wave nature of the scattering.

So a free electron plane wave state $e^{i\mathbf{k} \cdot \mathbf{r}}$ will get scattered into states $e^{-i\mathbf{k}' \cdot \mathbf{r}}$ with $\mathbf{k}' = \mathbf{k} - \mathbf{R}$. We therefore expect the eigenstates of an electron in the periodic atomic potential of the crystal will be a mixture of these scattered states

$$\psi_k(r) = \sum_k e^{i(k-k) \cdot r} \langle k | k - k \rangle$$

$$= e^{i\mathbf{k} \cdot \mathbf{r}} \sum_k e^{-i\mathbf{k} \cdot \mathbf{r}} \langle k | k - k \rangle$$

$$= e^{i\mathbf{k} \cdot \mathbf{r}} U_k(r) \quad \text{where} \quad U_k(r) = \sum_k e^{-i\mathbf{k} \cdot \mathbf{r}} \langle k - k | k \rangle$$

$U_k(r)$ is periodic on the Bravais lattice:

$$U_k(r + \mathbf{R}) = \sum_k e^{-i\mathbf{k} \cdot (r + \mathbf{R})} \langle k - k | k \rangle = \sum_k e^{i\mathbf{k} \cdot \mathbf{R}} e^{-i\mathbf{k} \cdot \mathbf{r}} \langle k - k | k \rangle$$

$$= \sum_k e^{-i\mathbf{k} \cdot \mathbf{r}} \langle k - k | k \rangle = U_k(r) \quad \text{since} \quad e^{-i\mathbf{k} \cdot \mathbf{R}} = 1 \quad \text{for all} \ \mathbf{R} \ \text{in B.L.}$$
The theorem yields Block's Theorem, which we prove more rigorously later.

The energy eigenstates of an electron in a potential with the periodicity of a Bragg lattice can be written in the form

\[ \Psi_k(\vec{r}) = e^{i \vec{k} \cdot \vec{r}} \Psi_k(\vec{r}) \]

where \( \Psi_k(\vec{r}+\vec{R}) = \Psi_k(\vec{r}) \) in periodic on the B.L.

An equivalent alternative statement of Block's theorem is

\[ \Psi_k(\vec{r}+\vec{R}) = e^{i \vec{k} \cdot \vec{R}} \Psi_k(\vec{r}) \]

If the wave vector \( \vec{k} \) lies exactly on the Bragg plane, directed by H.L. vector \( \vec{K} \), then the two free electron plane wave states \( \vec{k} \) and \( \vec{k} + \vec{K} = \vec{k}' \) are degenerate in energy, and so we expect they must mix equally in forming the new eigenstates in the presence of the periodic potential. Since we start with two states \( \vec{k}, \vec{k}' \) we should end up with two new states. If they mix equally, their relative coefficients should just be a phase factor \( e^{i \phi} \). Hence we expect the two eigenstates to have the form

\[ \Psi_1(\vec{r}) = e^{i \vec{k} \cdot \vec{r}} + e^{i \phi} e^{i \vec{k}' \cdot \vec{r}} \]
\[ \Psi_2(\vec{r}) = e^{i \vec{k} \cdot \vec{r}} + e^{i \phi} e^{i \vec{k}' \cdot \vec{r}} \]
The new eigenstates \( \Phi_1 \) and \( \Phi_2 \) should be orthogonal

\[
0 = \langle \Psi_1 | \Psi_2 \rangle = \int d^3r \ \Phi_1^*(\vec{r}) \Phi_2(\vec{r})
\]

\[
= \int d^3r \left[ e^{-i\vec{k}_1 \cdot \vec{r}} e^{i\phi_1} - i\vec{k}_1 \cdot \vec{r} \right] \left[ e^{i\vec{k}_2 \cdot \vec{r}} e^{i\phi_2} - i\vec{k}_2 \cdot \vec{r} \right]
\]

\[
= \int d^3r \left[ 1 + e^{i(\phi_2 - \phi_1)} + e^{-i\phi_1} e^{i(\vec{k}_2 - \vec{k}_1) \cdot \vec{r}} - i\vec{d}_1 \cdot \vec{r} \right]
\]

\[
= V \left[ 1 + e^{i(\phi_2 - \phi_1)} \right]
\]

= 0 \quad \text{only if} \quad \phi_2 - \phi_1 = \pi

\[
\begin{align*}
\vec{k}_1 & = k - \vec{k} \\
\vec{k}_1' & = k - \vec{k}
\end{align*}
\]

Write \( \vec{k}_1 = \vec{k}_1 + \vec{k}_1' \)

Then \( \vec{k}_1' = -\vec{k}_1 + \vec{k}_1' \)

So

\[
\Psi_1(\vec{r}) = e^{i\phi_1/2} e^{i\vec{k}_1' \cdot \vec{r}} \left[ e^{-i\phi_1/2} e^{i\vec{k}_1 \cdot \vec{r}} + e^{i\phi_2/2} e^{-i\vec{k}_1 \cdot \vec{r}} \right]
\]

\[
= e^{i\phi_1/2} e^{i\vec{k}_1' \cdot \vec{r}} \cos (\vec{k}_1 \cdot \vec{r} - \phi_1/2)
\]

Similarly

\[
\Psi_2(\vec{r}) = e^{i\phi_2/2} e^{i\vec{k}_1' \cdot \vec{r}} \cos (\vec{k}_1 \cdot \vec{r} - \phi_2/2)
\]

\[
= e^{i\phi_2/2} e^{i\vec{k}_1' \cdot \vec{r}} \cos (\vec{k}_1 \cdot \vec{r} - \phi_2/2 - \pi)
\]

\[
= e^{i\phi_2/2} e^{-i\vec{k}_1' \cdot \vec{r}} 2\sin (\vec{k}_1 \cdot \vec{r} - \phi_2/2)
\]
\[ |\Psi_1(\mathbf{r})|^2 \sim \cos^2(\mathbf{k}_\parallel \cdot \mathbf{r} - \Phi/2) \]
\[ |\Psi_2(\mathbf{r})|^2 \sim \sin^2(\mathbf{k}_\parallel \cdot \mathbf{r} - \Phi/2) \]

\[ \text{probablity density} \]

Reflection from Bragg plane gives standing waves in direction \( n \) to \( \mathbf{K} \)

Since \( \mathbf{k}_\parallel = \frac{\mathbf{K}}{2} \), we have \( \mathbf{k}_\parallel \cdot \mathbf{r} = \frac{\mathbf{K} \cdot \mathbf{r}}{2} \) where \( n \) is an integer

\[ |\Psi_1(\mathbf{r})|^2 \text{ and } |\Psi_2(\mathbf{r})|^2 \text{ have the periodicity of the R.L.} \]
\[ = |\Psi_1(\mathbf{r} + \mathbf{K})|^2 = \cos^2(\mathbf{k}_\parallel \cdot (\mathbf{r} + \mathbf{K}) + \pi n - \Phi/2) = \cos^2(\mathbf{k}_\parallel \cdot \mathbf{r} - \Phi/2) \]
\[ = |\Psi_1(\mathbf{r})|^2 \]

The only difference between \( \Psi_1 \) and \( \Psi_2 \) is their relative phase shift of \( \frac{\pi}{2} \), which shifts the location of the peaks of \( |\Psi_1|^2 \text{ and } |\Psi_2|^2 \) relative to the positions of the ions. By symmetry we expect one of these, say \( \Psi_1 \), will have its peaks positioned at the same sites as the ions, while the other, \( \Psi_2 \), will have its peaks positioned in between the sites of the ions. For example, if \( \mathbf{K} \) is the smallest non-zero R.L. vector, \( |\mathbf{K}| = \frac{2\pi}{a} \) with \( a \) = separation between ions, we expect:

\[ \text{ions} \mathbf{K} \rightarrow \]

\[ <-|\Psi_1|^2 \]

\[ <-|\Psi_2|^2 \]
The spatial periodicity of \( \chi \) and \( \chi_2 \) is \( \lambda = \frac{2\pi}{k_{11}} = \frac{2\pi}{(k/2)} = \frac{2\pi}{k} = 2a \). The spatial periodicity of \( \chi_1^{1/2} \) and \\
\( \chi_2^{1/2} \) is therefore \( \frac{1}{2} \lambda = a \). Since \( \chi_1 \) and \( \chi_2 \) are \( \frac{\pi}{2} \) out of phase, then \( \chi_1^{1/2} \) and \( \chi_2^{1/2} \) are \( \pi \) out of phase, hence their relative peaks are separated by \( a/2 \) as in the diagram above.

Now when one turns on the attractive ionic potential, the state \( \chi_1 \) will have a lower energy than the state \( \chi_2 \) since \( \chi_1 \) has its peaks located at the ionic positions, where the interaction is strongest. While \( \chi_2 \) has its peaks intercell, the ions, where the interaction is weakest.

Hence we expect that the two states \( \chi_1 \) and \( \chi_2 \), which were degenerate in energy before turning on the ionic potential, now split in energy, with a finite energy gap between them, \( E_1 < E_2 \).

\[ \text{Ionic potential cause a gap to appear in the energy dispersion relation } E(k) \text{ whenever } k \text{ crosses a Bragg plane. Since the Brillouin zones are formed by the intersections of Bragg planes, gaps in } E(k) \text{ open as } k \text{ crosses the boundary of any Brillouin zone.} \]