NANO 703-Notes

Chapter 14-Dynamical diffraction

More relativity

We need some mathematical tools to develop a physical theory of electron diffraction. Ideal crystals are infinite things, so there will be some infinities lingering about. Usually, the infinite quantity only exists at a point in space - either direct or reciprocal - so we get finite numbers for things that we measure. And when we adjust our theory later for real, imperfect crystals, the infinite things become finite.

Starting with a relation from Ch. 1 for a relativistic electron:

$$\sqrt{(pc)^2 + (m_0c^2)^2} = mc^2$$

where $mc^2 = E + m_0c^2$. In a crystal, we need to include the potential energy $e\Phi(\mathbf{r})$ from the crystal potential. This causes the momentum to vary with position.

$$\sqrt{[p(\mathbf{r})c]^2 + \left(m_0c^2\right)^2} = mc^2 + e\Phi(\mathbf{r})$$

I have chosen to stick with the previously defined expression for m above, even though, strictly speaking, it includes the spatially varying potential energy term, too. Although the value mc^2 is on the order of tens or hundreds of KeV, $e\Phi(\mathbf{r})$ is on the order of a few tens of eV, at most. So

$$mc^2 \gg |e\Phi(\mathbf{r})|$$

This allows us to approximate

$$[mc^2 + e\Phi(\mathbf{r})]^2 \approx (mc^2)^2 + 2(mc^2)\cdot e\Phi(\mathbf{r})$$

Now

$$[p(\mathbf{r})c]^2 + \left(m_0c^2\right)^2 \approx (mc^2)^2 + 2(mc^2)\cdot e\Phi(\mathbf{r})$$

We had defined the following energy before

$$E_{nr} = \left(\frac{m + m_0}{2m}\right)\cdot E$$

This was selected to write the wavelength in non-relativistic form, while still including relativistic effects:

$$\lambda = \frac{h}{\sqrt{2mE_{nr}}}$$

Now we have

$$\frac{p(\mathbf{r})^2}{2m} - e\Phi(\mathbf{r}) = E_{nr}$$

Wave equation

Quantum mechanics uses operators that are often linked to measurable quantities. The one for energy is the Hamiltonian:

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} - e\Phi(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2 - e\Phi(\mathbf{r})$$

Now we can write the time-independent Schrodinger equation:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - e\Phi(\mathbf{r})\right]\psi(\mathbf{r}) = E_{nr}\cdot\psi(\mathbf{r})$$

This can be a written as something that is more obviously wave equation, if we rearrange things a bit. First, let's define a "structure function"

$$U(\mathbf{r}) = \frac{2me}{h^2}\Phi(\mathbf{r})$$

We already know the electron's wave number is $k = \sqrt{2mE_{nr}}/h$, so

$$\left[\nabla^2 + 4\pi^2\left(k^2 + U(\mathbf{r})\right)\right]\psi(\mathbf{r}) = 0$$

Bloch-wave solutions

The crystal potential is periodic, so the structure function is, too: $U(\mathbf{r}+\mathbf{r}_{uvw}) = U(\mathbf{r})$. This means we can write it as a Fourier series:

$$U(\mathbf{r}) = \sum_{\mathbf{g}} U_{\mathbf{g}} \mathrm{e}^{2\pi i \mathbf{g}\cdot\mathbf{r}}$$

The Fourier coefficients are just

$$U_{\mathbf{g}} = \frac{2me}{h^2}\Phi_{\mathbf{g}}$$

Putting this into the wave equation:

$$\left[\nabla^2 + 4\pi^2\left(k^2 + \sum_{\mathbf{g}} U_{\mathbf{g}} \mathrm{e}^{2\pi i \mathbf{g}\cdot\mathbf{r}}\right)\right]\psi(\mathbf{r}) = 0$$

Bloch considered solutions of the form:

$$\psi^{(j)}(\mathbf{r}) = u^{(j)}(\mathbf{r})\cdot \mathrm{e}^{2\pi i \mathbf{k}^{(j)}\cdot\mathbf{r}}$$

where the $u^{(j)}$ are also periodic:

$$u^{(j)}(\mathbf{r}) = \sum_{\mathbf{g}} C_{\mathbf{g}}^{(j)} \mathrm{e}^{2\pi i \mathbf{g}\cdot\mathbf{r}}$$

Given a suitable set of wave vectors $\mathbf{k}^{(j)}$, we can always find some coefficients $C_{\mathbf{g}}^{(j)}$ that are solutions to the wave equation. We call these solutions Bloch waves:

$$\psi^{(j)}(\mathbf{r}) = \sum_{\mathbf{g}} C_{\mathbf{g}}^{(j)} \mathrm{e}^{2\pi i\left[\mathbf{k}^{(j)}+\mathbf{g}\right]\cdot\mathbf{r}}$$

Structure function

The Fourier coefficients of the structure function are related to the structure factors $F_{\mathbf{g}}$ that we defined before. We can start be relating the $U_{\mathbf{g}}$ to the Fourier transform of the unit-cell potential times the Fourier components of the crystal function.

$$U_{\mathbf{g}} = \frac{2me}{h^2} \cdot \phi(\mathbf{g}) \cdot X_{\mathbf{g}}$$

where

$$\phi(\mathbf{g}) = \sum_{m \text{ atoms}} \phi^{(m)}(g) \mathrm{e}^{-2\pi i \mathbf{g} \cdot \mathbf{d}^{(m)}}$$

Recall that

$$f^{(m)}(\mathbf{g}) \equiv \frac{2\pi me}{h^2} \int_{\mathbf{r}} \phi^{(m)}(\mathbf{r}) \mathrm{e}^{2\pi i \mathbf{g} \cdot \mathbf{r}} \cdot d^3 r$$

so

$$f^{(m)}(g) = \frac{2\pi me}{h^2} \phi^{(m)}(g)$$

which showed up in the structure factors:

$$F_{\mathbf{g}} = \sum_{m \text{ atoms}} f^{(m)}(g) \mathrm{e}^{-2\pi i \mathbf{g} \cdot \mathbf{d}^{(m)}}$$

Putting in the appropriate factors:

$$F_{\mathbf{g}} = \frac{2\pi me}{h^2} \phi(\mathbf{g})$$

Now we have

$$U_{\mathbf{g}} = \frac{F_{\mathbf{g}} \cdot X_{\mathbf{g}}}{\pi}$$

We had shown that

$$X_{\mathbf{g}} = \begin{cases} \frac{1}{v}, & \mathbf{g} = \text{an RLV} \\ 0, & \mathbf{g} = \text{otherwise} \end{cases}$$

In other words, the Fourier coefficients of the structure function are just the structure factors divided by the unit-cell volume, with a π thrown in for good measure.

Properties of Bloch waves (I)

The Bloch waves should really be viewed as quantum states. For our given set of wave vectors $\mathbf{k}^{(j)}$, we have a collection of coefficients $C_{\mathbf{g}_1}^{(j)}$, $C_{\mathbf{g}_2}^{(j)}$, etc. There is an underlying matrix problem here, where a

column vector containing the coefficients describes the quantum state. Dirac's "bra-ket" notation is a useful way to represent the state (as well as the matrix):

$$\left|\psi^{(j)}\right\rangle = \begin{pmatrix} C_0^{(j)} \\ C_{\mathbf{g}_1}^{(j)} \\ C_{\mathbf{g}_2}^{(j)} \\ . \\ . \\ . \end{pmatrix}, \quad \left\langle\psi^{(j)}\right| = \left\{\left[C_0^{(j)}\right]^* \quad \left[C_{\mathbf{g}_1}^{(j)}\right]^* \quad \left[C_{\mathbf{g}_2}^{(j)}\right]^* \quad . \quad . \quad .\right\}$$

Quantum states are associated with probabilities, and we usually want them to be normalized:

$$1 = \left\langle\psi^{(j)}\middle|\psi^{(j)}\right\rangle = \sum_{\mathbf{g}} \left|C_{\mathbf{g}}^{(j)}\right|^2$$

Because the Bloch sates are all solutions of the same linear differential equation, they are orthogonal:

$$0 = \left\langle\psi^{(j)}\middle|\psi^{(j')}\right\rangle;\ j \neq j'$$

Properties of Bloch waves (II)

The Bloch waves form an orthonormal set, so we can collect them into a matrix:

$$V = \begin{pmatrix} C_{\mathbf{g}_1}^{(1)} & C_{\mathbf{g}_1}^{(2)} & \cdots \\ C_{\mathbf{g}_2}^{(1)} & C_{\mathbf{g}2}^{(2)} & \\ \vdots & & \ddots \end{pmatrix} = \begin{pmatrix} \left|\psi^{(1)}\right\rangle & \left|\psi^{(2)}\right\rangle & \ldots \end{pmatrix}$$

The so-called Hermitian adjoint is:

$$V^\dagger = \begin{pmatrix} \left\langle\psi^{(1)}\right| \\ \left\langle\psi^{(2)}\right| \\ \vdots \end{pmatrix}$$

These satisfy, $V^\dagger V = I$ and $(V^T)^\dagger V^T = I$. By the way, what are the transposes?:

$$V^T = \begin{pmatrix} C_{\mathbf{g}_1}^{(1)} & C_{\mathbf{g}_2}^{(1)} & \cdots \\ C_{\mathbf{g}_1}^{(2)} & C_{\mathbf{g}2}^{(2)} & \\ \vdots & & \ddots \end{pmatrix} = \begin{pmatrix} \left|\psi_{g_1}\right\rangle & \left|\psi_{g_2}\right\rangle & \cdots \end{pmatrix}, \text{ and } (V^T)^\dagger = \begin{pmatrix} \left\langle\psi_{\mathbf{g}_1}\right| \\ \left\langle\psi_{\mathbf{g}2}\right| \\ \vdots \end{pmatrix}$$

Apparently, the sets of $\mathbf{g}$ components of the Bloch waves also form an orthonormal set

$$\left\langle\psi_{\mathbf{g}}\middle|\psi_{\mathbf{g}}\right\rangle = \sum\nolimits_j \left|C_{\mathbf{g}}^{(j)}\right|^2 = 1$$

$$\left\langle\psi_{\mathbf{g}'}\middle|\psi_{\mathbf{g}}\right\rangle = \sum\nolimits_j \left[C_{\mathbf{g}'}^{(j)}\right]^* \cdot C_{\mathbf{g}}^{(j)} = 0, \quad (\mathbf{g}' \neq \mathbf{g})$$

This is nice for when we want to think about actual diffracted beams, rather than abstract Bloch waves.

Total wave function

Which of these many Bloch waves gives our wave function in the crystal? Well, in general, the total wave function in the crystal is a linear combination of Bloch waves:

$$\psi(\mathbf{r}) = \sum_j \varepsilon^{(j)} \psi^{(j)}(\mathbf{r})$$

where the coefficients $\varepsilon^{(j)}$ are called the "excitation amplitudes" of the Bloch waves. To find them, we need to know something about our incident beam, particularly at the top (entrance) surface of the TEM foil. Once we have done that, we can write the total wave function as a set of diffracted beams:

$$\begin{aligned}\psi(\mathbf{r}) &= \sum_j \varepsilon^{(j)} \sum_{\mathbf{g}} C_{\mathbf{g}}^{(j)} e^{2\pi i\left[\mathbf{k}^{(j)}+\mathbf{g}\right]\cdot\mathbf{r}} \\ &= \sum_{\mathbf{g}} \sum_j \varepsilon^{(j)} C_{\mathbf{g}}^{(j)} e^{2\pi i\left[\gamma^{(j)}-\mathbf{s}_{\mathbf{g}}\right]\cdot\mathbf{r}} e^{2\pi i(\mathbf{k}+\mathbf{g}+\mathbf{s}_{\mathbf{g}})\cdot\mathbf{r}} \\ \psi(\mathbf{r}) &= \sum_{\mathbf{g}} \Psi_{\mathbf{g}}(\mathbf{r}) e^{2\pi i \mathbf{k}_{\mathbf{g}}\cdot\mathbf{r}}\end{aligned}$$

Notice that we have introduced a new vector $\boldsymbol{\gamma}^{(j)} \equiv \mathbf{k}^{(j)} - \mathbf{k}$. We ended up with diffracted beams that vary in amplitude as functions of position in the crystal. (We had previously only considered the amplitudes outside of the crystal, where we expect them to be constant.) In the crystal they are

$$\Psi_{\mathbf{g}}(\mathbf{r}) \equiv \sum_j \varepsilon^{(j)} C_{\mathbf{g}}^{(j)} e^{2\pi i\left[\gamma^{(j)}-\mathbf{s}_{\mathbf{g}}\right]\cdot\mathbf{r}}$$

Boundary condition(s) (I)

For various fundamental reasons related to the interpretation of the wave function, at the foil entrance surface, we must have:

i) $\psi(\mathbf{r})$ continuous and

ii) $\hat{\mathbf{n}}\cdot\nabla\psi(\mathbf{r})$ continuous

We can pick the foil entrance surface to be the plane $z = 0$, with its normal direction as $\hat{\mathbf{n}} = -\hat{\mathbf{z}}$. It is usually adequate to assume that wave function above the sample is a plane wave, i.e. the incident beam:

$$\psi(\mathbf{r}) = e^{2\pi i \mathbf{k}\cdot\mathbf{r}}$$

This is suitable for analyzing the transmitted wave, by ignoring any backscattered waves, but it limits us to satisfying condition i) only. Then we have:

$$e^{2\pi i \mathbf{k}\cdot\mathbf{r}}\Big|_{z=0} = \sum_j \varepsilon^{(j)} \left\{ \sum_{\mathbf{g}} C_{\mathbf{g}}^{(j)} e^{2\pi i\left[\mathbf{k}^{(j)}+\mathbf{g}\right]\cdot\mathbf{r}} \right\}\Big|_{z=0}$$

Canceling the common factor:

$$1 = \sum_j \varepsilon^{(j)} \left\{ \sum_{\mathbf{g}} C_{\mathbf{g}}^{(j)} e^{2\pi i\left[\boldsymbol{\gamma}^{(j)}+\mathbf{g}\right]\cdot\mathbf{r}} \right\}\Big|_{z=0}$$

Boundary condition(s) (II)

Notice that

$$1 = \sum_j \varepsilon^{(j)} C_{\mathbf{0}}^{(j)} \mathrm{e}^{2\pi i \boldsymbol{\gamma}^{(j)} \cdot \mathbf{r}} \Big|_{z=0}$$
$$0 = \sum_j \varepsilon^{(j)} \left\{ \sum_{\mathbf{g} \neq \mathbf{0}} C_{\mathbf{g}}^{(j)} \mathrm{e}^{2\pi i \left[\boldsymbol{\gamma}^{(j)} + \mathbf{g} \right] \cdot \mathbf{r}} \right\} \Big|_{z=0}$$

Apparently,

$$\mathrm{e}^{2\pi i \boldsymbol{\gamma}^{(j)} \cdot \mathbf{r}} \big|_{z=0} = 1$$

So we must have

$$\boldsymbol{\gamma}^{(j)} \cdot \mathbf{r} \big|_{z=0} = 0$$

From this we can conclude that $\boldsymbol{\gamma}^{(j)} = -\gamma^{(j)} \hat{\mathbf{n}}$.

$$1 = \sum_j \varepsilon^{(j)} C_{\mathbf{0}}^{(j)}$$
$$0 = \sum_{\mathbf{g} \neq \mathbf{0}} \mathrm{e}^{2\pi i \mathbf{g} \cdot \mathbf{r}} \big|_{z=0} \left[\sum_j \varepsilon^{(j)} C_{\mathbf{g}}^{(j)} \right]$$

Based on the orthonormality of the Bloch waves, we have found the excitation amplitudes:

$$\varepsilon^{(j)} = \left[C_{\mathbf{0}}^{(j)} \right]^*$$

Diffracted beam amplitudes

Let's put everything we have together. The total wave function in the crystal can be written two ways:

$$\psi(\mathbf{r}) = \sum_j \varepsilon^{(j)} \psi^{(j)}(\mathbf{r}) = \sum_{\mathbf{g}} \Psi_{\mathbf{g}}(\mathbf{r}) \mathrm{e}^{2\pi i (\mathbf{k} + \mathbf{g} + \mathbf{s}_{\mathbf{g}}) \cdot \mathbf{r}}$$

Notice that the excitation amplitudes of the Bloch waves are constants, whereas the amplitudes of the diffracted beams are not:

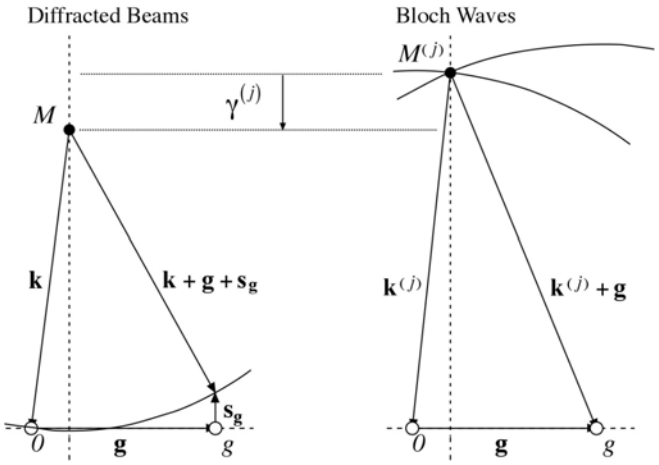
$$\Psi_{\mathbf{g}}(\mathbf{r}) = \sum_j \varepsilon^{(j)} C_{\mathbf{g}}^{(j)} \mathrm{e}^{2\pi i \left[\mathbf{k}^{(j)} - \mathbf{k} - \mathbf{s}_{\mathbf{g}} \right] \cdot \mathbf{r}} = \sum_j \varepsilon^{(j)} C_{\mathbf{g}}^{(j)} \mathrm{e}^{2\pi i \left[\boldsymbol{\gamma}^{(j)} - \mathbf{s}_{\mathbf{g}} \right] \cdot \mathbf{r}}$$

Based on reasoning discussed before, a common choice for the excitation-error vector is $\mathbf{s}_{\mathbf{g}} = -s_g \hat{\mathbf{n}}$. Now we just have a 1-D problem:

$$\Psi_{\mathbf{g}}(\mathbf{r}) \rightarrow \Psi_{\mathbf{g}}(z) = \sum_j \varepsilon^{(j)} C_{\mathbf{g}}^{(j)} \mathrm{e}^{2\pi i \left[\gamma^{(j)} - s_{\mathbf{g}} \right] \cdot z}$$

The nice thing is that the $\gamma^{(j)}$ (which we don't have a name for, yet) and the excitation error $\mathbf{s}_{\mathbf{g}}$ are just reciprocal-space lengths measured along *z* now:

$$\gamma^{(j)} \cdot \mathbf{r} = \gamma^{(j)} \cdot z \text{ and } \mathbf{s}_{\mathbf{g}} \cdot \mathbf{r} = s_g \cdot z$$



Solving for the Bloch-wave coefficients

Our particular Bloch waves are solutions of:

$$\left[\nabla^2 + 4\pi^2\left(K^2 + \sum_{\mathbf{g}\neq 0} U_{\mathbf{g}} e^{2\pi i \mathbf{g}\cdot\mathbf{r}}\right)\right]\psi(\mathbf{r}) = 0$$

where

$$K^2 \doteq k^2 + U_0 \left(\approx k^2\right)$$

Let's break this down term-by-term. The first term is:

$$\nabla^2\psi^{(j)}(\mathbf{r}) = -4\pi^2 \sum_{\mathbf{g}} C_{\mathbf{g}}^{(j)} \left(\mathbf{k}^{(j)} + \mathbf{g}\right)^2 e^{2\pi i\left[\mathbf{k}^{(j)}+\mathbf{g}\right]\cdot\mathbf{r}}$$

Now we have

$$\sum_{\mathbf{g}} \left\{\left[k^2 - \left(\mathbf{k}^{(j)} + \mathbf{g}\right)^2\right] + \sum_{\mathbf{h}\neq 0} U_{\mathbf{h}} e^{2\pi i \mathbf{h}\cdot\mathbf{r}}\right\} C_{\mathbf{g}}^{(j)} e^{2\pi i\left(\mathbf{k}^{(j)}+\mathbf{g}\right)\cdot\mathbf{r}} = 0$$

Rearranging the sums

The trick to solving for Bloch waves is to group terms that have the same phase factors. We can break the expression into two terms:

$$\sum_{\mathbf{g}} \left\{\left[k^2 - \left(\mathbf{k}^{(j)} + \mathbf{g}\right)^2\right] C_{\mathbf{g}}^{(j)} e^{2\pi i \mathbf{g}\cdot\mathbf{r}}\right\} + \sum_{\mathbf{g}'} \left\{C_{\mathbf{g}'}^{(j)} \sum_{\mathbf{h}\neq 0} U_{\mathbf{h}} e^{2\pi i(\mathbf{h}+\mathbf{g}')\cdot\mathbf{r}}\right\} = 0$$

then judiciously reindex:

$$\mathbf{h}' = \mathbf{h} + \mathbf{g}'$$
$$\mathbf{h} = \mathbf{h}' - \mathbf{g}'$$
$$\mathbf{h} = \mathbf{0} \rightarrow \mathbf{h}' = \mathbf{g}'$$

So we can write the structure function part as

$$\sum_{\mathbf{h}\neq\mathbf{0}} U_{\mathbf{h}} e^{2\pi i(\mathbf{h}+\mathbf{g}')\cdot\mathbf{r}} = \sum_{\mathbf{h}'\neq\mathbf{g}} U_{\mathbf{h}'-\mathbf{g}'} e^{2\pi i \mathbf{h}'\cdot\mathbf{r}}$$

Now we have

$$\sum_{\mathbf{g}}\left\{\left[k^2-\left(\mathbf{k}^{(j)}+\mathbf{g}\right)^2\right]C_{\mathbf{g}}^{(j)}\mathrm{e}^{2\pi i\mathbf{g}\cdot\mathbf{r}}\right\}+\sum_{\mathbf{g}'}\left\{C_{\mathbf{g}'}^{(j)}\sum_{\mathbf{h}\neq\mathbf{g}'}U_{\mathbf{h}-\mathbf{g}'}\mathrm{e}^{2\pi i\mathbf{h}\cdot\mathbf{r}}\right\}=0$$

At this point we can identify terms with the same exponents:

$$\left[k^2-\left(\mathbf{k}^{(j)}+\mathbf{g}\right)^2\right]C_{\mathbf{g}}^{(j)}+\sum_{\mathbf{h}\neq\mathbf{g}}U_{\mathbf{g}-\mathbf{h}}C_{\mathbf{h}}^{(j)}=0$$

At this point we are dealing only with the coefficients $C_{\mathbf{g}}^{(j)}$ and the wave vectors $\mathbf{k}^{(j)}$.

Rewriting the sum

Let's try to simplify some more. First, using $\mathbf{k}^{(j)}=\mathbf{k}+\boldsymbol{\gamma}^{(j)}$:

$$\left(\mathbf{k}^{(j)}+\mathbf{g}\right)^2=\left[(\mathbf{k}+\mathbf{g})+\boldsymbol{\gamma}^{(j)}\right]^2=(\mathbf{k}+\mathbf{g})^2+2(\mathbf{k}+\mathbf{g})\cdot\boldsymbol{\gamma}^{(j)}+\gamma^{(j)2}$$

Next, using $k=|\mathbf{k}+\mathbf{g}+\mathbf{s}_{\mathbf{g}}|$

$$k^2=(\mathbf{k}+\mathbf{g}+\mathbf{s}_{\mathbf{g}})^2=(\mathbf{k}+\mathbf{g})^2+2(\mathbf{k}+\mathbf{g})\cdot\mathbf{s}_{\mathbf{g}}-s_{\mathbf{g}}{}^2$$

We need to take the difference:

$$\left(\mathbf{k}^{(j)}+\mathbf{g}\right)^2-k^2=2(\mathbf{k}+\mathbf{g})\cdot\left(\boldsymbol{\gamma}^{(j)}-\mathbf{s}_{\mathbf{g}}\right)+\gamma^{(j)2}+s_{\mathbf{g}}{}^2$$

So we now have

$$\left[2(\mathbf{k}+\mathbf{g})\cdot\left(\boldsymbol{\gamma}^{(j)}-\mathbf{s}_{\mathbf{g}}\right)+\gamma^{(j)2}+s_{\mathbf{g}}{}^2\right]C_{\mathbf{g}}^{(j)}=\sum_{\mathbf{h}\neq\mathbf{g}}U_{\mathbf{g}-\mathbf{h}}C_{\mathbf{h}}^{(j)}$$

High-energy approximation

Some of these quantities are much bigger than others. In particular, $\gamma^{(j)2}$ and $s_{\mathbf{g}}{}^2$ are tiny. Also, we assumed g was perpendicular to $\hat{\mathbf{n}}$, so

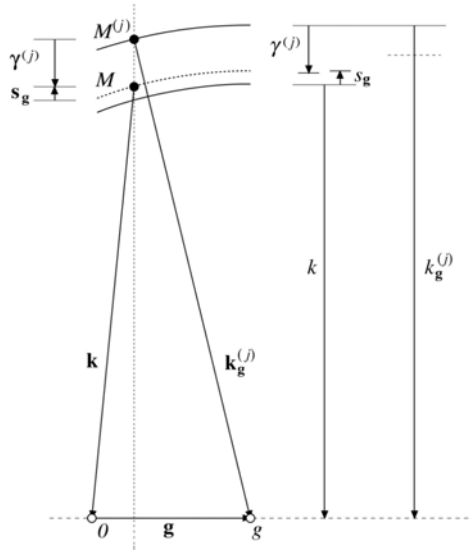
$$\left(\mathbf{k}^{(j)}+\mathbf{g}\right)^2-k^2\approx 2\mathbf{k}\cdot\left(\boldsymbol{\gamma}^{(j)}-\mathbf{s}_{\mathbf{g}}\right)$$

If the incident beam is tilted, we need to consider $\mathbf{k}\cdot\hat{\mathbf{n}}=k\cdot\cos\phi$. Then

$$2\mathbf{k}\cdot\left(\boldsymbol{\gamma}^{(j)}-\mathbf{s}_{\mathbf{g}}\right)=2k\cdot\cos\phi\cdot\left(\gamma^{(j)}-s_{\mathbf{g}}\right)$$

For now, let's just say $\phi=0$. We have

$$2k\cdot\left(\gamma^{(j)}-s_{\mathbf{g}}\right)C_{\mathbf{g}}^{(j)}=\sum_{\mathbf{h}\neq\mathbf{g}}U_{\mathbf{g}-\mathbf{h}}C_{\mathbf{h}}^{(j)}$$



Extinction distance

We can rearrange the preceding equation to give

$$s_\mathbf{g} C_\mathbf{g}^{(j)} + \sum_{\mathbf{h}\neq\mathbf{g}} \left(\frac{1}{2\xi_{\mathbf{g}-\mathbf{h}}} \right) C_\mathbf{h}^{(j)} = \gamma^{(j)} C_\mathbf{g}^{(j)}$$

Here we have used the "extinction distance":

$$\xi_{\mathbf{g}-\mathbf{h}} = \frac{k}{U_{\mathbf{g}-\mathbf{h}}} = \frac{\pi v}{\lambda F_{\mathbf{g}-\mathbf{h}}}$$

This quantity has units of length (check for yourself). We will later see that it can be thought of as the characteristic length over which diffraction into a particular channel occurs. In dynamical theory, we need to know its value associating any two beams, such as *g* and *h* (with RLVs $\mathbf{g}$ and $\mathbf{h}$, respectively). But we are often mainly interested in how one of the beams couples to the direct beam (*0)*, when we would need to know:

$$\xi_\mathbf{g} = \frac{\pi v}{\lambda F_\mathbf{g}}$$

Eigenvalue problem

Can we make this more complicated? Well, another way to write the above expression is in matrix form

$$\tilde{A} \left| \psi^{(j)} \right\rangle = \gamma^{(j)} \left| \psi^{(j)} \right\rangle$$

If we think of $\tilde{A}$ as an operator, this has the form of an eigenvalue problem. $\tilde{A}$ can be expressed in matrix notation as:

$$\tilde{\mathrm{A}} = \begin{pmatrix} s_0 & \frac{1}{2\xi_{\mathbf{g}_1}} & . & \frac{1}{2\xi_{\mathbf{g}_{n-1}}} \\ \frac{1}{2\xi_{\mathbf{g}_1}} & s_{\mathbf{g}_1} & . & \frac{1}{2\xi_{\mathbf{g}_{n-1}-\mathbf{g}_1}} \\ . & . & . & . \\ \frac{1}{2\xi_{\mathbf{g}_{n-1}}} & \frac{1}{2\xi_{\mathbf{g}_1-\mathbf{g}_{n-1}}} & . & s_{\mathbf{g}_{n-1}} \end{pmatrix}$$

The eigenvalue problem generates a system of equations that can be solved for the eigenvalues $\gamma^{(j)}$ and the coefficients $C_{\mathbf{g}}^{(j)}$. Notice that the number of Bloch waves involved is the same as the number of diffracted beams. So if we want to include many diffracted beams, we will need many Bloch waves. This is usually best done on a computer. The process of solving an eigenvalue problem in matrix form is sometimes called diagonalization, and most data analysis programs (e.g., Matlab, Igor) have those routines built in.

Two-beam condition

There are a few simple cases that we actually solve by hand, though, such as when only the direct beam (*0*) and one diffracted beam (*g*) are involved. This "two-beam" condition is important when the diffracted beam is strongly excited (its planes are near the Bragg condition), which allows us to ignore other, weaker beams. With only *0* and g included, the total wave function in the crystal is:

$$\psi(\mathbf{r}) = \left[\Psi_0(z) + \Psi_{\mathbf{g}}(z)\cdot \mathrm{e}^{2\pi i(\mathbf{g}+\mathbf{s})\cdot\mathbf{r}}\right]\cdot \mathrm{e}^{2\pi i\mathbf{k}\cdot\mathbf{r}}$$

In the Bloch-wave basis, this is

$$\psi(\mathbf{r}) = \varepsilon^{(1)}\psi^{(1)}(\mathbf{r}) + \varepsilon^{(2)}\psi^{(2)}(\mathbf{r})$$

The two Bloch waves can be written out:

$$\psi^{(1)}(\mathbf{r}) = C_0^{(1)}\mathrm{e}^{2\pi i\mathbf{k}^{(1)}\cdot\mathbf{r}} + C_{\mathbf{g}}^{(1)}\mathrm{e}^{2\pi i\left[\mathbf{k}^{(1)}+\mathbf{g}\right]\cdot\mathbf{r}} = \left(C_0^{(1)} + C_g^{(1)}\mathrm{e}^{2\pi i\mathbf{g}\cdot\mathbf{r}}\right)\mathrm{e}^{2\pi i\gamma^{(1)}z}\mathrm{e}^{2\pi i\mathbf{k}\cdot\mathbf{r}}$$
$$\psi^{(2)}(\mathbf{r}) = C_0^{(2)}\mathrm{e}^{2\pi i\mathbf{k}^{(2)}\cdot\mathbf{r}} + C_{\mathbf{g}}^{(1)}\mathrm{e}^{2\pi i\left[\mathbf{k}^{(2)}+\mathbf{g}\right]\cdot\mathbf{r}} = \left(C_0^{(2)} + C_g^{(2)}\mathrm{e}^{2\pi i\mathbf{g}\cdot\mathbf{r}}\right)\mathrm{e}^{2\pi i\gamma^{(2)}z}\mathrm{e}^{2\pi i\mathbf{k}\cdot\mathbf{r}}$$

Since our illumination is a plane wave, the excitation amplitudes are

$$\varepsilon^{(1)} = \left[C_0^{(1)}\right]^*,\ \varepsilon^{(2)} = \left[C_0^{(2)}\right]^*$$

It is somewhat simpler if the structure factor is real:

$$F_{-\mathbf{g}} = \left(F_{\mathbf{g}}\right)^* = F_{\mathbf{g}}$$

Then $U_{\mathbf{g}} = U_{-\mathbf{g}}$, so we abbreviate $\xi_{\mathbf{g}} = \xi_{-\mathbf{g}} = \xi$. There is only one non-zero excitation error, so $s_{\mathbf{g}} = s$. Now the matrix is:

$$\tilde{\mathrm{A}} = \begin{pmatrix} 0 & \frac{1}{2\xi} \\ \frac{1}{2\xi} & s \end{pmatrix}$$

We have to solve for

$$\left|\psi^{(1)}\right\rangle = \begin{pmatrix} C_0^{(1)} \\ C_g^{(1)} \end{pmatrix} \text{ and } \left|\psi^{(2)}\right\rangle = \begin{pmatrix} C_0^{(2)} \\ C_g^{(2)} \end{pmatrix}$$

Solving the two-beam condition

This all amounts to a 2 × 2 eigenvalue problem:

$$\begin{pmatrix} 0 & \frac{1}{2\xi} \\ \frac{1}{2\xi} & s \end{pmatrix} \begin{pmatrix} C_0 \\ C_g \end{pmatrix} = \gamma \begin{pmatrix} C_0 \\ C_g \end{pmatrix}$$

The usual way to solve this is by subtracting the right side from the left side:

$$\left(\tilde{A} - \gamma \tilde{1}\right) \cdot \begin{pmatrix} C_0 \\ C_g \end{pmatrix} = 0 \cdot \begin{pmatrix} C_0 \\ C_g \end{pmatrix}$$

The solutions must satisfy

$$\det \begin{pmatrix} -\gamma & \frac{1}{2\xi} \\ \frac{1}{2\xi} & s - \gamma \end{pmatrix} = 0$$

This gives a quadratic expression:

$$\gamma^2 - s\gamma - \left(\frac{1}{2\xi}\right)^2 = 0$$

The two solutions have different eigenvalues:

$$\gamma^{(1,2)} = \frac{s \pm \sqrt{s^2 + \frac{1}{\xi^2}}}{2}$$

There is a pair of coefficients for each of the two states:

$$\begin{pmatrix} 0 & \frac{1}{2\xi} \\ \frac{1}{2\xi} & s \end{pmatrix} \begin{pmatrix} C_0^{(1,2)} \\ C_g^{(1,2)} \end{pmatrix} = \gamma^{(1,2)} \begin{pmatrix} C_0^{(1,2)} \\ C_g^{(1,2)} \end{pmatrix}$$

Special case, strong beam

Let's just consider the strong-beam case first, that is $s = 0$. Now:

$$\gamma^{(1)} = \frac{1}{2\xi} \text{ and } \gamma^{(2)} = -\frac{1}{2\xi}$$

Then we find the coefficients for the two cases:

$$\begin{pmatrix} 0 & \frac{1}{2\xi} \\ \frac{1}{2\xi} & 0 \end{pmatrix} \begin{pmatrix} C_0^{(1,2)} \\ C_{\mathbf{g}}^{(1,2)} \end{pmatrix} = \pm\frac{1}{2\xi} \begin{pmatrix} C_0^{(1,2)} \\ C_{\mathbf{g}}^{(1,2)} \end{pmatrix}, \left|\psi^{(1,2)}\right\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm 1 \end{pmatrix}$$

Finally, we identify the $\varepsilon^{(j)}$ values:

$$\varepsilon^{(1)} = \frac{1}{\sqrt{2}} \text{ and } \varepsilon^{(2)} = \frac{1}{\sqrt{2}}$$

The strong, two-beam solution

We now have

$$\psi^{(1)}(\mathbf{r}) = \left(\frac{1}{\sqrt{2}} + \frac{1}{\sqrt{2}} e^{2\pi i \mathbf{g}\cdot\mathbf{r}}\right) \cdot e^{\pi i z/\xi} \cdot e^{2\pi i \mathbf{k}\cdot\mathbf{r}} \text{ and } \psi^{(2)}(\mathbf{r}) = \left(\frac{1}{\sqrt{2}} - \frac{1}{\sqrt{2}} e^{2\pi i \mathbf{g}\cdot\mathbf{r}}\right) e^{-\pi i z/\xi} \cdot e^{2\pi i \mathbf{k}\cdot\mathbf{r}}$$

The total wave function in this case is:

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{2}} \psi^{(1)}(\mathbf{r}) + \frac{1}{\sqrt{2}} \psi^{(2)}(\mathbf{r})$$

A little reorganization gives:

$$\psi(\mathbf{r}) = \left[\cos(\pi z/\xi) + i \sin(\pi z/\xi) e^{2\pi i \mathbf{g}\cdot\mathbf{r}}\right] e^{2\pi i \mathbf{k}\cdot\mathbf{r}}$$

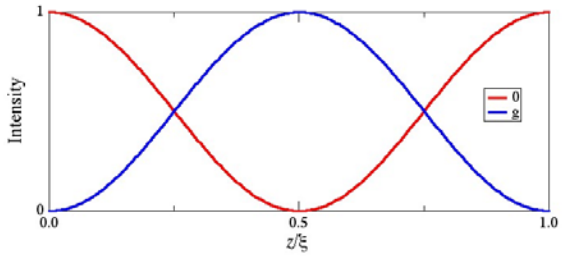
We can identify the beam amplitudes:

$$\Psi_0(z) = \cos(\pi z/\xi) \text{ and } \Psi_{\mathbf{g}}(z) = i \sin(\pi z/\xi)$$

Notice that $\Psi_{\mathbf{g}}$ has a $90°$ phase shift. The intensities are

$$|\Psi_0(z)|^2 = \cos^2(\pi z/\xi) \text{ and } |\Psi_{\mathbf{g}}(z)|^2 = \sin^2(\pi z/\xi)$$

We see that the intensity oscillates with thickness between *0* and *g* with a period of ξ.



The general two-beam solution

We might as well dive in and figure out the general two-beam case. The amplitudes are related by

$$\frac{1}{2\xi}C_{\mathbf{g}}^{(1,2)} = \gamma^{(1,2)}C_{\mathbf{0}}^{(1,2)} \text{ and } \frac{1}{2\xi}C_{\mathbf{0}}^{(1,2)} + sC_{\mathbf{g}}^{(1,2)} = \gamma^{(1,2)}C_{\mathbf{g}}^{(1,2)}$$

If we define $w \equiv s\xi$, these give:

$$2\xi\gamma^{(1,2)} = w \pm \sqrt{w^2+1}$$

Now we have the eigenvalues:

$$2\gamma^{(1,2)} = s \pm \sqrt{s^2 + \frac{1}{\xi^2}}$$

It is useful to normalize the Bloch waves:

$$\left(C_0^{(1,2)}\right)^2 + \left(C_{\mathbf{g}}^{(1,2)}\right)^2 = 1$$

This allows use to solve for the individual coefficients:

$$\left(C_0^{(1,2)}\right)^2 = \frac{1}{1+\left(w \pm \sqrt{w^2+1}\right)^2}$$

Next define $\cot\beta \doteq w$. We then have

$$\left(C_0^{(1,2)}\right)^2 = \frac{\sin^2\beta}{2 \mp 2\cos\beta}$$

These can be written

$$\left(C_0^{(1)}\right)^2 = \sin^2(\beta/2) \text{ and } \left(C_0^{(2)}\right)^2 = \cos^2(\beta/2)$$

The phases are arbitrary. We can pick

$$C_0^{(1)} = \sin(\beta/2) \text{ and } C_0^{(2)} = \cos(\beta/2)$$

Finding the Bloch waves

The coefficients satisfy

$$C_{\mathbf{g}}^{(1,2)} = 2\xi\gamma^{(1,2)}C_{\mathbf{0}}^{(1,2)}$$

We can write the factor in front as

$$2\xi\gamma^{(1,2)} = \frac{\cos(\beta) \pm 1}{\sin(\beta)}$$

So

$$\left|\psi^{(1)}\right\rangle = \begin{pmatrix} C_{\mathbf{0}}^{(1)} \\ C_{\mathbf{g}}^{(1)} \end{pmatrix} = \begin{pmatrix} \sin(\beta/2) \\ \cos(\beta/2) \end{pmatrix}$$
$$\left|\psi^{(2)}\right\rangle = \begin{pmatrix} C_{\mathbf{0}}^{(2)} \\ C_{\mathbf{g}}^{(2)} \end{pmatrix} = \begin{pmatrix} \cos(\beta/2) \\ -\sin(\beta/2) \end{pmatrix}$$

So the Bloch waves look like

$$\psi^{(1)}(\mathbf{r}) = \left[\sin(\beta/2) + \cos(\beta/2)\cdot e^{2\pi i \mathbf{g}\cdot\mathbf{r}}\right]\cdot e^{\pi i(s+s_{eff})z}\cdot e^{2\pi i \mathbf{k}\cdot\mathbf{r}}$$
$$\psi^{(2)}(\mathbf{r}) = \left[\cos(\beta/2) - \sin(\beta/2)\cdot e^{2\pi i \mathbf{g}\cdot\mathbf{r}}\right]\cdot e^{\pi i(s-s_{eff})z}\cdot e^{2\pi i \mathbf{k}\cdot\mathbf{r}}$$

In terms of Bloch waves, the general two-beam solution is

$$\psi(\mathbf{r}) = \sin(\beta/2)\cdot\psi^{(1)}(\mathbf{r})\cdot e^{2\pi i\gamma^{(1)}z} + \cos(\beta/2)\cdot\psi^{(2)}(\mathbf{r})\cdot e^{2\pi i\gamma^{(2)}z}$$

Two-beam result

I would like to know the amplitudes of *0* and *g* in the general case. We define an "effective" excitation error:

$$s_{eff} \equiv \sqrt{s^2 + \left(\frac{1}{\xi^2}\right)}$$

Notice that $s_{eff} \geq 0$. Now the eigenvalues can be written

$$\gamma^{(1,2)} \equiv \frac{s \pm s_{eff}}{2}$$

In terms of diffracted beams, the total wave function is

$$\psi(\mathbf{r}) = \left[\Psi_0(z) + \Psi_{\mathbf{g}}(z)\cdot e^{2\pi i(\mathbf{g}+\mathbf{s})\cdot\mathbf{r}}\right]\cdot e^{2\pi i \mathbf{k}\cdot\mathbf{r}}$$

So now we can find the direct- and diffracted-beam amplitudes:

$$\Psi_{\mathbf{0}}(z) = \left[\sin^2(\beta/2)e^{\pi i s_{eff} z} + \cos^2(\beta/2)e^{-\pi i s_{eff} z}\right]e^{\pi i s z} = \left[\cos(\pi s_{eff} z) - i\cos(\beta)\sin(\pi s_{eff} z)\right]e^{\pi i s z}$$
$$\Psi_{\mathbf{g}}(z) = \frac{1}{2}\sin\beta\cdot(e^{\pi i s_{eff} z} - e^{-\pi i s_{eff} z})\cdot e^{-2\pi i s z}\cdot e^{\pi i s z} = i\sin(\beta)\sin(\pi s_{eff} z)e^{-\pi i s z}$$

We are mostly done with the angle β at this point. Using

$$w = s\xi = \cot(\beta)$$

This gives

$$\sin(\beta) = \frac{1}{\sqrt{1+\cot^2(\beta)}} = \frac{1}{\sqrt{1+w^2}} = \frac{1}{s_{eff}\xi} \text{ and } \cos(\beta) = \frac{1}{\sqrt{1+\tan^2(\beta)}} = \frac{w}{\sqrt{1+w^2}} = \frac{s}{s_{eff}}$$

Finally,

$$\Psi_{\mathbf{0}}(z) = \left[\cos(\pi s_{eff} z) - i\left(\frac{s}{s_{eff}}\right)\sin(\pi s_{eff} z)\right] e^{\pi i s z}$$

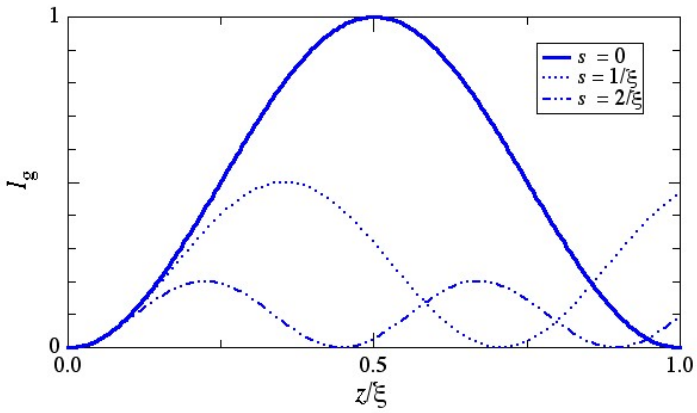
$$\Psi_{\mathbf{g}}(z) = \frac{i\sin(\pi s_{eff} z)}{s_{eff}\xi} e^{-\pi i s z}$$

Two-beam intensity

It is often only the intensity of the diffracted beam that we need:

$$I_{\mathbf{g}} = |\psi_{\mathbf{g}}|^2 = \left[\frac{\sin(\pi s_{eff} z)}{s_{eff}\xi}\right]^2$$

The quantity s_{eff} turns out to be a useful parameter here. We get the strong-beam result back when $s = 0$ (the Bragg condition). As the sample is tilted away from the Bragg condition, the intensity goes down overall and the period of oscillation in thickness gets shorter.



Howie-Whelan equations

It is possible to get rid of any reference to Bloch waves altogether by finding a system of equations that relates the various diffracted-beam amplitudes. Start with

$$\Psi_{\mathbf{g}}(z) = \sum_j \varepsilon^{(j)} C_{\mathbf{g}}^{(j)} e^{2\pi i\left[\gamma^{(j)} - s_{\mathbf{g}}\right]z}$$

Then take the derivative

$$\frac{d\Psi_{\mathbf{g}}}{dz} = \sum_j \left\{2\pi i\left[\gamma^{(j)} - s_{\mathbf{g}}\right]\right\} \varepsilon^{(j)} C_{\mathbf{g}}^{(j)} e^{2\pi i\left[\gamma^{(j)} - s_{\mathbf{g}}\right]z}$$

The Bloch waves satisfied:

$$\left(\gamma^{(j)} - s_{\mathbf{g}}\right) C_{\mathbf{g}}^{(j)} = \sum_{\mathbf{h}\neq\mathbf{g}} \left(\frac{1}{2\xi_{\mathbf{g}-\mathbf{h}}}\right) C_{\mathbf{h}}^{(j)}$$

So we can substitute the corresponding term in the derivative sum:

$$\frac{d\Psi_{\mathbf{g}}}{dz} = \sum_{\mathbf{h}\neq\mathbf{g}} \left(\frac{\pi i}{\xi_{\mathbf{g}-\mathbf{h}}} \right) \left[\sum_{j} \varepsilon^{(j)} C_{\mathbf{h}}^{(j)} e^{2\pi i (\gamma^{(j)} - s_{\mathbf{h}}) \cdot z} \right] \cdot e^{2\pi i (s_{\mathbf{h}} - s_{\mathbf{g}}) z}$$

We already know the quantity in square brackets, so substitute:

$$\frac{d\Psi_{\mathbf{g}}}{dz} = \sum_{\mathbf{h}\neq\mathbf{g}} \left(\frac{\pi i}{\xi_{\mathbf{g}-\mathbf{h}}} \right) \Psi_{\mathbf{h}} e^{2\pi i (s_{\mathbf{h}} - s_{\mathbf{g}}) z}$$

This system of equations is called the Howie-Whelan equations. The allow determination of diffracted-beam amplitudes without any reference to Bloch waves.