Now that we have an expression for \( n(\vec{r}) \) we need to determine how to solve for \( n_G \).

- Invoking constructive interference only when \( \Delta \vec{k} = \vec{G} \):
  - Inserting Fourier series expression for \( n(\vec{r}) \) and converting amplitude to intensity:
    - \( I(\Delta \vec{k}) \propto | \sum_G n_G \int V e^{i(\vec{G} - \Delta \vec{k}) \cdot \vec{r}} d\vec{r} |^2 \)
    - If \( \Delta \vec{k} = \vec{G} \) \( I \propto |n_G|^2 V^2 \) (note the complex exponential becomes \( e^0 = 1 \))
    - If \( \Delta \vec{k} \neq \vec{G} \) \( I = 0 \) (In short, the integral across \( \vec{r} \) when the complex exponential remains leads to destructive interference and no net intensity)
  - Can solve for \( n_G \) by using an inverse Fourier transform of \( n(\vec{r}) \):
    - \( n_{G,h,k,l} = \frac{1}{V_{cell}} \int_{cell} n(\vec{r}) e^{-i\vec{G}_{h,k,l} \cdot \vec{r}} d\vec{r} \) where \( \vec{G}_{h,k,l} \) denotes a specific \( G \) vector
    - Since we are invoking an infinitely periodic solid we can put a 1 over the volume term out front and integrate over just one unit cell
  - To check this, we can again insert the Fourier series for \( n(\vec{r}) \):
    - \( n_{G,h,k,l} = \frac{1}{V_{cell}} \sum_G \int_{cell} n_G e^{-i(\vec{G} - \vec{G}_{h,k,l}) \cdot \vec{r}} d\vec{r} \)
    - For this integral there is only one non-zero solution, when \( \vec{G} = \vec{G}_{h,k,l} \)
      - Same logic as above – when the exponent remains, the integration across \( \vec{r} \) leads destructive interference and a net zero value.
    - This gives \( n_{G,h,k,l} = \frac{1}{V_{cell}} \int_{cell} n_G e^{-i\vec{G}_{h,k,l} \cdot \vec{r}} d\vec{r} = \frac{1}{V_{cell}} n_{G,h,k,l} V_{cell} = n_{G,h,k,l} \) so we are on the right track. Now you can see why we have \( 1/V_{cell} \) out front as well.
  - With \( n_{G,h,k,l} = \frac{1}{V_{cell}} \int_{cell} n(\vec{r}) e^{-i\vec{G}_{h,k,l} \cdot \vec{r}} d\vec{r} \) the integral represents the scattering density within one unit cell, which we will call the **structure factor** \( S_{h,k,l} \).
- **Challenge:** We need to estimate \( n(\vec{r}) \) within the cell! With \( n(\vec{r}) \) established, we can predict intensities at the detector.

- **Approach:** Develop an approximation to \( n(\vec{r}) \) that doesn’t invoke any bonding, just the core electrons. Start with a coordinate system for atom positions, develop a local approximation for electron density, sum the densities.
- We will assume that the atoms don’t interact with each other and have their own local charge density of \( n_\alpha(\vec{r}) \) where this local vector \( \vec{r} \) points from the atom to some position vector \( \vec{r} \) and \( \vec{r}_\alpha \) points from the origin to atom \( \alpha \).
Then $\vec{r}' = \vec{r} - \vec{r}_\alpha$

Total $n(\vec{r})$ is then $\sum_\alpha n_\alpha(\vec{r} - \vec{r}_\alpha)$

This makes our structure factor equal to $S_{h,k,l} = \sum_\alpha \int_{\text{cell}} n_\alpha(\vec{r}') e^{-i\vec{g}_{h,k,l} \cdot \vec{r}} d\vec{r}$

We want to separate this into terms concerning $r_\alpha$ (where the atoms are centered) and $r'$ (the local change density associated with atom $\alpha$); to do so we multiply by $1 = e^{-i\vec{g}_{h,k,l} \cdot \vec{r}_\alpha} e^{i\vec{g}_{h,k,l} \cdot \vec{r}_\alpha}$.

This gives $S_{h,k,l} = \sum_\alpha e^{i\vec{g}_{h,k,l} \cdot \vec{r}_\alpha} \int_{\text{cell}} n_\alpha(\vec{r}') e^{-i\vec{g}_{h,k,l} \cdot \vec{r}'} d\vec{r}$

- The sum term includes $\vec{r}_\alpha$, which is where the atom is within the cell
- The integral term includes $\vec{r}'$ which gives a term called the atomic form factor, $f$

**Example 1:** One atom in cell at position $\vec{r}_\alpha = (0,0,0)$
- $\vec{g}_{h,k,l} \cdot \vec{r}_\alpha = 0$
- $S_{h,k,l} = f_{0,0,0} e^0 = f_{0,0,0}$ for all $h,k,l$
- So for every case where $\Delta \vec{k} = \vec{g}_{h,k,l}$ $l \propto |n_{\vec{g}_{h,k,l}}|^2 \propto |S_{h,k,l}|^2 \propto |f_0|^2$

**Example 2:** Cesium Chloride: Cs at (0,0,0), Cl at (1/2,1/2,1/2) within the cell
- Cesium atom gives $f_0$ as in previous example
- $S_{h,k,l} = f_{0,CS} + e^{-i\vec{g}_{h,k,l} \cdot \vec{r}_{Cl}} f_{0,Cl}$
- Chlorine atom gives $e^{-i\pi(h+k+l)}$ since $\vec{g}_i \cdot \vec{a}_j = 2\pi \delta_{ij}$ ($2 \times \frac{1}{2}$ yields unity…)
- This gives $S_{h,k,l} = f_{0,CS} + e^{-i\pi(h+k+l)} f_{0,Cl}$
- From Euler’s we know: $e^{-i\pi \text{ odd integer}} = -1$ and $e^{-i\pi \text{ even integer}} = 1$
- So $S_{h,k,l} = f_{0,CS} + f_{0,Cl}$ if $h+k+l=\text{even}$ and $S_{h,k,l} = f_{0,CS} - f_{0,Cl}$ if $h+k+l=\text{odd}$
- Moving $\Delta k$ out in reciprocal space (via shifting source/detector positions), we could pass through a set of $G= (h,0,0)$ points in reciprocal space. The first point, delta $k = G_{100}$ will be weak, the second point at $G_{200}$ will be strong, $G_{300}$ will be strong, etc.
If instead of CsCl, we considered a BCC cell (where the two $f$ are identical, we will see systematic absences of atoms as shown below in the $\bar{g}_3$ slice.

- **Practical application:** When we measure intensity, we lose the phase information in the amplitude at the detector. As such, we can’t simply take the inverse Fourier transform to obtain the scattering density.
- In practice, one guesses the structure, uses the structure factor to calculate the intensity pattern, compares that to experimental data and then changes the guess until experimental and calculated intensities match.
- Since it’s a fitting procedure rather than an exact transformation, there are the usual issues of initial guess choice, number of free parameters, local vs global minima, etc.