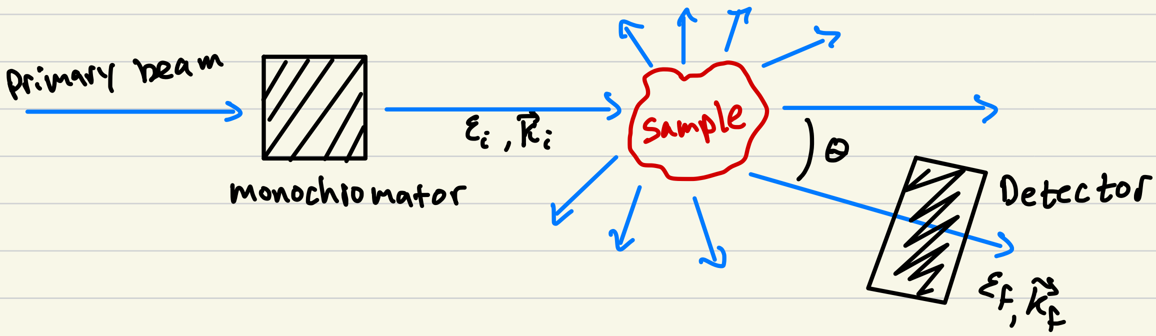
Probing crystals via scattering (G and P ch. X)

- In order to probe the structure and properties of crystals, many experiments involve scattering of electrons, photons, or neutrons

- Schematic setup for scattering measurements:



* Monochromator: selects particles with momentum $\hbar\vec{k}_i$ and energy ε_i
* Detector selects particles w/ $\hbar\vec{k}_f$, ε_f
* Information is derived from $\Delta\vec{k} = \vec{k}_f - \vec{k}_i$, $\Delta\varepsilon = \varepsilon_f - \varepsilon_i$

- Scattering particles:

* Photons: $\hbar\omega = \hbar c k = \hbar c \frac{2\pi}{\lambda} \Rightarrow \lambda = \frac{12398.5}{\hbar\omega}$ (λ in Å, ħω in eV)
  - For $\hbar\omega \sim 10-50$ keV, $\lambda \sim$ interatomic spacing
  - Interaction via electric field, amplitude of scattering related to Z

* Neutrons: $E = \frac{\hbar^2 k^2}{2M_n} = \frac{\hbar^2 4\pi^2}{2M_n \lambda^2} \Rightarrow \lambda = \frac{0.2862}{\sqrt{E}}$
  - For $\lambda \sim$ Å, $E \sim 80$ meV (similar to $k_B T$)
  - Elastic interaction for atoms, amplitude related to mass
  - Can also interact via magnetic interactions

* Electrons: $E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 4\pi^2}{2m\lambda^2} \Rightarrow \lambda = \frac{12.264}{\sqrt{E}}$

  - To get $\lambda \sim$ Å, $E \sim 150$ eV
  - Interact via coulomb interactions w/ atoms

- Key distinction: Elastic versus inelastic scattering

  * Elastic: Conserve energy and momenta in a scattering event
    - $\varepsilon_i = \varepsilon_f$, $|\vec{k}_i| = |\vec{k}_f|$

  * Inelastic: Energy and momenta lost to excitations in the crystal (e.g., phonons, magnons, electronic excitations)
    - $\Delta\varepsilon = \varepsilon_f - \varepsilon_i$ and $|\Delta\vec{k}| = |\vec{k}_f| - |\vec{k}_i|$ representative of excitation

- Elastic scattering of X-rays

  * Consider incident radiation beam frequency ω, propagation vector $\vec{k}_i$, polarization $\vec{e}_i$, amplitude E_0

    $$\vec{E}(\vec{r},t) = \vec{e}_i E_0 \, e^{i(\vec{k}_i \cdot \vec{r} - \omega t)}$$

  * Electron at $\vec{r}$ accelerated by field like

    $$m\ddot{\vec{u}} = -e\vec{E}(\vec{r},t) = -e\,\vec{e}_i E_0 \, e^{i(\vec{k}_i\cdot\vec{r} - \omega t)}$$

    - Electron oscillates in the field, radiates electromagnetic waves at same freq. ω

    - Long distance $R \gg \lambda = 2\pi/k$ from radiating center:

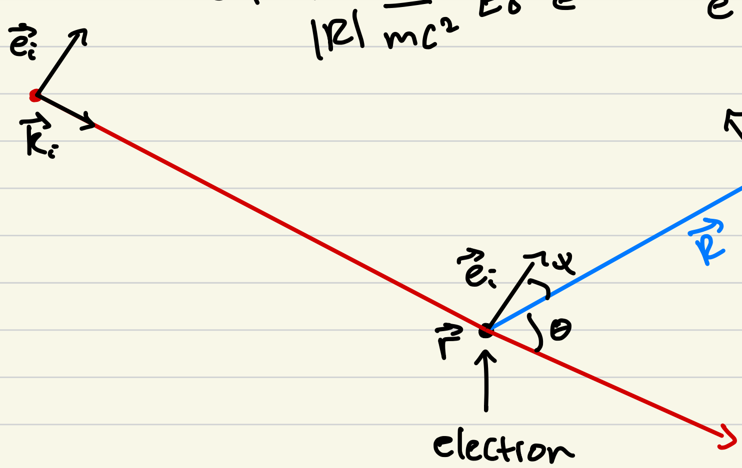
$$\vec{E}_s(\vec{R},t) = \vec{e}_f \frac{(-e)}{c^2 R}\, \ddot{\vec{u}}\left(t - \frac{R}{c}\right)\cdot \vec{e}_f$$

$$= \vec{e}_f \frac{1}{|R|}\frac{e^2}{mc^2} E_0 \, e^{i\vec{k}_i\cdot\vec{r}} \, e^{-i\omega(t-R/c)} \sin\psi$$

angle between $\vec{R}$ and $\vec{e}_i$

$$= \vec{e}_f \frac{1}{|R|}\frac{e^2}{mc^2} E_0 \, e^{i\vec{k}_i\cdot\vec{r}} \, e^{i(\vec{k}_f\cdot\vec{R})} \, e^{-i\omega t} \sin\psi$$

elastic scattering means $\frac{\omega}{c} = |\vec{k}_i| = |\vec{k}_f|$



- Take modulus squared to get intensity of scattered field:

$$I_s(\vec{R}) = I_0 \frac{1}{R^2}\left(\frac{e^2}{mc^2}\right)^2 \sin^2\psi$$

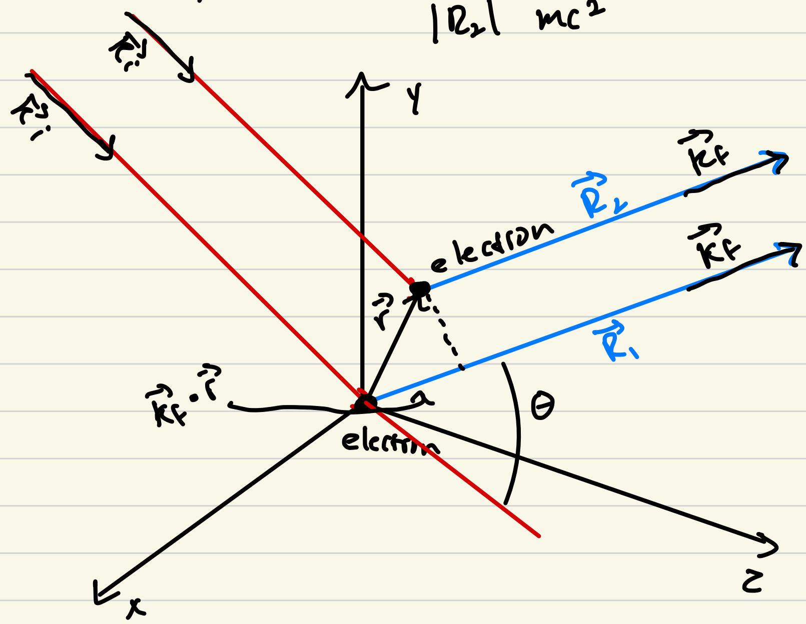
$\propto \frac{1}{m^2}$, so not sensitive to nuclei

intensity of incident field

- Now consider scattering from two electrons, one at $\vec{r}=0$, other at $\vec{r}\neq 0$:

$$\vec{r}=0 \;:\; \vec{E}_s(\vec{R}_1, t) = \vec{e}_f \frac{1}{|R_1|} \frac{e^2}{mc^2} E_0 e^{i(\vec{k}_f\cdot\vec{R}_1 - \omega t)} \sin\psi$$

$$\vec{r}\neq 0 \;:\; \vec{E}_s(\vec{R}_2, t) = \vec{e}_f \frac{1}{|R_2|} \frac{e^2}{mc^2} E_0 e^{i\vec{k}_i\cdot\vec{r}} e^{i(\vec{k}_f\cdot\vec{R}_2 - \omega t)} \sin\psi$$



- We see that $\vec{k}_f\cdot\vec{R}_2 = \vec{k}_f\cdot\vec{R}_1 - \vec{k}_f\cdot\vec{r}$

$$\vec{E}_s(\vec{R}_2, t) = \vec{e}_f \frac{1}{|R_2|} \frac{e^2}{mc^2} E_0 e^{i(\vec{k}_i - \vec{k}_f)\cdot\vec{r}} e^{i(\vec{k}_f\cdot\vec{R}_1 - \omega t)} \sin\psi$$

- If we take large $|R_1|, |R_2|$, $\frac{1}{|R_1|} \approx \frac{1}{|R_2|} \approx \frac{1}{R}$ ← average distance to detector

so $\vec{E}_s(\vec{R}_2, t) = \vec{E}_s(\vec{R}_1, t)\, e^{-i\Delta\vec{k}\cdot r}$

$\Delta\vec{k} = \vec{k}_f - \vec{k}_i$

- Sum of intensity from both:

$$I_s(R,\psi) = I_0 \frac{1}{R^2}\left(\frac{e^2}{mc^2}\right)^2 \left(1 + e^{-i\Delta\vec{k}\cdot\vec{r}}\right)^2 \sin\psi$$

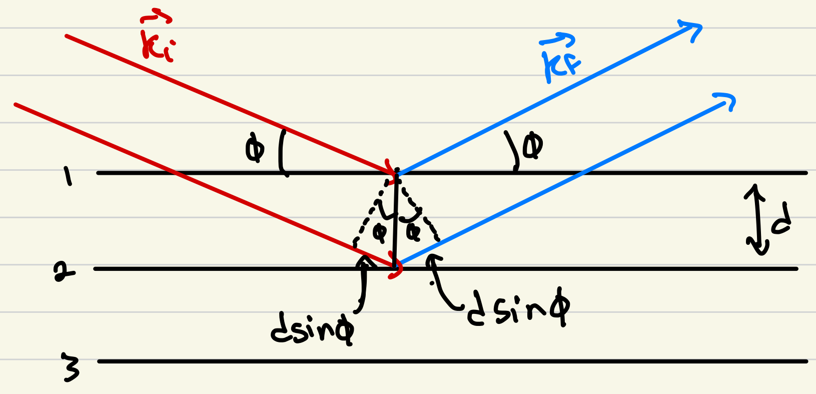
- Instead discrete point charges, if we had a continuous charge distribution,

$$I_s(R,\psi) = I_0 \frac{1}{R^2}\left(\frac{e^2}{mc^2}\right)^2 \Big[\underbrace{\int n_{el}(\vec{r})\, e^{-i\Delta\vec{k}\cdot\vec{r}}\, d\vec{r}}_{\text{Fourier transform of electronic density!}} \Big]^2 \sin\psi$$

* We have seen that scattering probes the Fourier transform of the electron density. What if $n_{el}(\vec{r})$ is periodic as in a crystal?
  - Fourier coefficients $F(\Delta k) = \int n_{el}(\vec{r})\, e^{-i\Delta\vec{k}\cdot r}\, d\vec{r}$ only nonzero if $\Delta\vec{k} = \vec{G}$ where $\vec{G}$ is a reciprocal lattice vector

    $\Rightarrow$ peaks in x-ray scattering give reciprocal lattice vectors!!

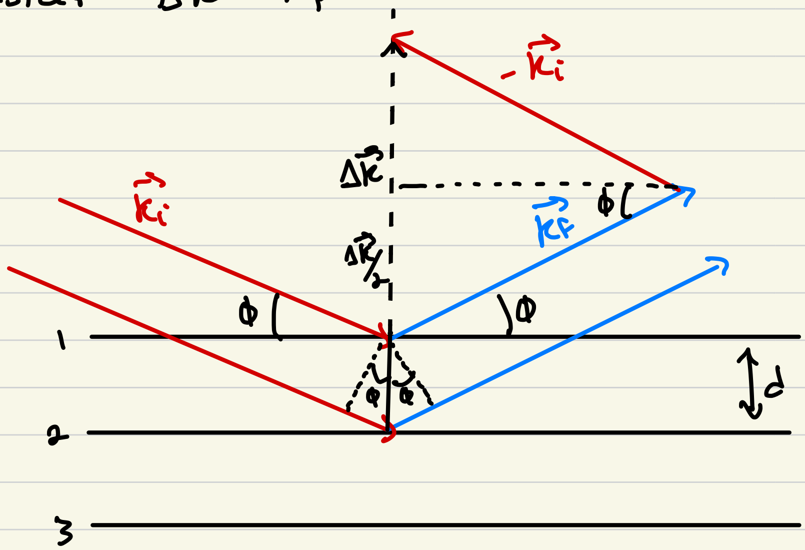
* Another way to see this: Bragg condition
  - Consider scattering off of lattice planes spaced by d:



  - Extra distance from scattering off of plane 2 is $2d\sin\phi$. So for constructive interference we need wavelength of incident light to be

$$n\lambda = 2d\sin\phi \quad , \quad n \in \mathbb{Z}$$

• Now consider $\Delta\vec{k} = \vec{k}_f - \vec{k}_i$



$$\sin\phi = \frac{\frac{|\Delta\vec{k}|}{2}}{|\vec{k}_f|} \Rightarrow |\Delta\vec{k}| = 2|\vec{k}_f|\sin\phi$$

Since we are considering elastic scattering,

$$|\vec{k}_i| = |\vec{k}_f| = \frac{\omega}{c} = \frac{2\pi}{\lambda} \Rightarrow |\Delta\vec{k}| = \frac{4\pi}{\lambda}\sin\phi = \frac{2\pi}{d}n$$

• so $\Delta\vec{k}$ is perpendicular to lattice planes and has magnitude $\frac{2\pi}{d}n$

$\Rightarrow \Delta\vec{k} = \vec{G}$!!!

- Thus by measuring diffraction peaks obtained by varying $\Delta\vec{k}$, can map out $\vec{G}_n$ and thus $\vec{G}_m$

* To map this out we can

• Shine light of various wavelengths (Laue method)

• shine monochromatic light, but rotate the sample (Bragg method)

• Use a "polycrystalline" sample with many crystallites with different orientations (powder method)

- So far we have just discussed where the peaks are, but information also is in relative intensities of peaks

* Consider $n_{el}(\vec{r})$ as made up of spherically symmetric contributions at each atomic site:

$$n_{el}(\vec{r}) = \sum_{\vec{t}_n} \sum_{\vec{d}_\nu} n_{a\nu}(\vec{r} - \vec{t}_n - \vec{d}_\nu)$$

↳ Works well core electron contribution, or crystals without significant covalent bonding

* Then, we have:

$$F(\Delta\vec{k}) = \sum_{\vec{t}_n} \sum_{\vec{d}_\nu} \int e^{-i\Delta\vec{k}\cdot r} n_{a\nu}(\vec{r} - \vec{t}_n - \vec{d}_\nu)\, d\vec{r}$$

$$= \sum_{\vec{t}_n} \sum_{\vec{d}_\nu} \int e^{-i\Delta\vec{k}\cdot\vec{r}} e^{-i\Delta\vec{k}\cdot(\vec{t}_n + d_\nu)} e^{i\Delta\vec{k}\cdot(\vec{t}_n + d_\nu)} n_{a\nu}(\vec{r} - \vec{t}_n - \vec{d}_\nu)\, d\vec{r}$$

$$= \sum_{\vec{t}_n} \sum_{\vec{d}_\nu} \int e^{-i\Delta\vec{k}\cdot(\vec{r} - \vec{t}_n - \vec{d}_\nu)} e^{-i\Delta k\cdot(\vec{t}_n + \vec{d}_\nu)} n_{a\nu}(\vec{r} - \vec{t}_n - \vec{d}_\nu)\, d\vec{r}$$

$$= \sum_{\vec{t}_n} e^{-i\Delta\vec{k}\cdot\vec{t}_n} \sum_{\vec{d}_\nu} e^{-i\Delta\vec{k}\cdot\vec{d}_\nu} \underbrace{\int e^{-i\Delta\vec{k}\cdot\vec{r}} n_{a\nu}(\vec{r})\, d\vec{r}}_{f_{a\nu}(\Delta\vec{k})}$$

$f_{a\nu}(\Delta\vec{k}) \rightarrow$ "atomic form factors"

- Still have Laue condition for $f_{a\nu}$ to be nonzero only if $\Delta\vec{k} = \vec{G}$

- Once Laue condition is satisfied, get crystal "structure factors":

$$F(\vec{G}) = N \sum_{\vec{d}_\nu} e^{-i\vec{G}\cdot\vec{d}_\nu} f_{a\nu}(\vec{G})$$

- If all atoms are the same, we can factor f out from the sum:

$$F(\vec{G}) = N f_a(\vec{G}) \underbrace{\sum_{\vec{d}_\nu} e^{-i\vec{G}\cdot\vec{d}_\nu}}_{\text{geometrical structure factor}}$$

* Take as an example diamond structure

- FCC with basis $\vec{d}_1 = 0$, $\vec{d}_2 = a/4\,(1,1,1)$
- $\vec{g}_1 = \frac{2\pi}{a}(-1,1,1)$ $\quad \vec{g}_2 = \frac{2\pi}{a}(1,-1,1)$ $\quad \vec{g}_3 = \frac{2\pi}{a}(1,1,-1)$
- general $G_m = m_1\vec{g}_1 + m_2\vec{g}_2 + m_3\vec{g}_3$. Note that $G_m = \frac{2\pi}{a}(h_1, h_2, h_3)$ where h_1, h_2, h_3 are all even or all odd
- $S(\vec{G}) = e^{-i\vec{G}\cdot\vec{d}_1} + e^{-\vec{G}\cdot\vec{d}_2} = 1 + e^{-i\pi(h_1+h_2+h_3)/2}$

$$S(\vec{G}) = \begin{cases} 1-i & \text{if } h_1, h_2, h_3 \text{ are odd and } h_1+h_2+h_3 = 4n+1 \\ 1+i & \text{if } h_1, h_2, h_3 \text{ are odd and } h_1+h_2+h_3 = 4n+3 \\ 2 & \text{if } h_1, h_2, h_3 \text{ are even and } h_1+h_2+h_3 = 4n \\ 0 & \text{if } h_1, h_2, h_3 \text{ are even and } h_1+h_2+h_3 = 4n+2 \end{cases}$$

- So reciprocal lattice vectors with h_1, h_2, h_3 odd have the same $|S(G)|^2$
- even h_1, h_2, h_3 with $h_1 + h_2 + h_3 = 4n+2$ are "forbidden", i.e., will be very weak in diffraction experiments

* In reality, densities associated with atoms are not spherically symmetric, so these rules are approximate.