Diffraction Methods in Chemistry

University of Cambridge Part II Natural Sciences Tripos

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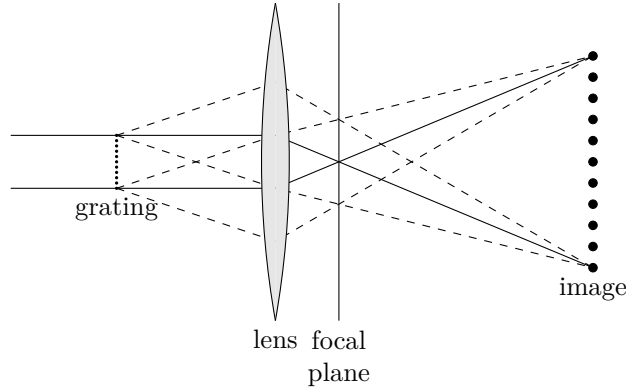
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Acknowledgements

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Figure 1.1: A magnified image of the diffraction grating is formed using a convex lens to focus the diffraction pattern.

1 Diffraction

It might be familiar from physics that if you shine a beam of light on a diffraction grating, then a diffraction pattern will emerge. If you put a lens after the diffracted beam, they may be brought to a focus, and a magnified image of the diffraction grating will be seen, as shown in the figure.

Atoms in a crystal are, in some sense, very fine gratings. Can we use a similar method to image the atoms in a crystal directly? However, to form a diffraction pattern, we need the wavelength of the light to be in roughly the same length scale as the pattern we are trying to image. The atoms are in the length scales of Angstroms ($10^{-10}\,\mathrm{m}$), therefore, we need to use X-ray for diffractions at atomic length scales. However, there is no lens for X rays (because lenses are made of atoms too), so the imaging process does not work. What we have to do is to measure the intensity of the diffracted beams at different directions, and infer the atomic structure mathematically.

This is, however, a hard thing to do. We will spend the vast majority of our lectures on how to translate the diffracted beam intensities to atomic structure.

1.1 Addition of Electromagnetic Waves

X-rays are electromagnetic waves, so they are described by Maxwell's equations, from which we can infer that the electromagnetic fields are essentially just oscillating electric and magnetic fields, travelling in some direction $\mathbf{k}$ (the magnitude of $\mathbf{k}$ also encodes the wavelength via $|k| = 2\pi/\lambda$) with the speed of light c.[1] We will label the distance as x along the direction of propagation of the

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[1]In free space, $\rho = 0$ and $\mathbf{J} = 0$, so by Maxwell's equations

$$\boldsymbol{\nabla} \times (\boldsymbol{\nabla} \times \mathbf{E}) = -\boldsymbol{\nabla} \times \frac{\partial \mathbf{B}}{\partial t} = -\frac{\partial}{\partial t}(\boldsymbol{\nabla} \times B) = -\frac{\partial}{\partial t}\left(\mu_0 \epsilon_0 \frac{\partial \mathbf{E}}{\partial t}\right) = -\mu_0 \epsilon_0 \frac{\partial^2 \mathbf{E}}{\partial t^2}\,. \tag{1.1}$$

By vector calculus identities, we also have

$$\boldsymbol{\nabla} \times (\boldsymbol{\nabla} \times \mathbf{E}) = \boldsymbol{\nabla}(\boldsymbol{\nabla} \cdot \mathbf{E}) - \nabla^2 \mathbf{E} = -\nabla^2 \mathbf{E}\,, \tag{1.2}$$

and hence

$$\nabla^2 \mathbf{E} = \mu_0 \epsilon_0 \frac{\partial^2 \mathbf{E}}{\partial t^2}\,. \tag{1.3}$$

This is the wave equation, with wave speed $c = 1/\sqrt{\mu_0 \epsilon_0}$, with general complex solution

$$\mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)} \tag{1.4}$$

for $\mathbf{E} \in \mathbb{C}$ and $\mathbf{k}^2 c^2 = \omega^2$. By Maxwell's equations, we also have

$$\frac{\partial \mathbf{B}}{\partial t} = -\boldsymbol{\nabla} \times \mathbf{E} = -i\mathbf{k} \times \mathbf{E}\,, \tag{1.5}$$
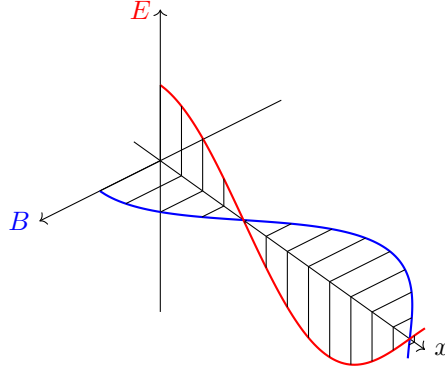
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Figure 1.2: Electromagnetic wave propagating in space.

electromagnetic wave $\mathbf{k}$, and consider the wave at some fixed time t. Then the electric (or equivalently the magnetic) field strength is given by

$$\psi(x) = A \sin\left(\frac{2\pi x}{\lambda} + \phi\right) , \tag{1.7}$$

where the real number A is the amplitude and ϕ is the phase offset. However, it turns out that when considering oscillations, it is always easier to use complex numbers, so we will alternatively see the electric field as the real part of the complex wave

$$\psi(x) = A \exp\left(\frac{2\pi i x}{\lambda}\right) , \tag{1.8}$$

where $A = |A|\, e^{i\phi}$ is now complex and includes both the amplitude $|A|$ and the initial phase offset ϕ.
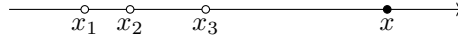
Now what happens if we have multiple sources, each sending off magnetic waves of the same frequencies but with different amplitudes and phases? Let's consider the simple 1D case, where n sources are located at x_j. We will let all three sources to have a zero initial phase[2], so that the resulting wave at point x due to source j is given by

$$\psi_j(x) = A_j \exp\left(\frac{2\pi i (x - x_j)}{\lambda}\right) , \tag{1.9}$$

where A_j is real because we have a zero initial phase. We will denote the phase of the wave due to source j at x as

$$\phi_j = \frac{2\pi(x - x_j)}{\lambda} . \tag{1.10}$$

Then to work out the total wave, we only need to sum up the contributions from each sources to get

$$\Psi_{\text{res}}(x) = \sum_j A_j \exp\left(i\phi_n\right) . \tag{1.11}$$

It is easy to see that the phase angle of the resultant amplitude is

$$\Phi_{\text{res}} = \tan^{-1}\left[\frac{\sum_j A_j \sin\phi_j}{\sum_j A_j \cos\phi_j}\right] . \tag{1.12}$$

and so

$$\mathbf{B} = \frac{\mathbf{k}}{\omega} \times \mathbf{E} . \tag{1.6}$$

Therefore, $\mathbf{E}$ and $\mathbf{B}$ are both transverse wave that are in the same phase but perpendicular to each other.

[2]It is a trivial generalisation for the sources to have different non-zero initial phases. We make such assumption because this is the only situation we will need for later discussion, and it makes my diagram cleaner. It is actually also trivial to generalise it to 3D by replacing $x - x_j$ with $\|\mathbf{x} - \mathbf{x}_j\|$ in all the expressions below.
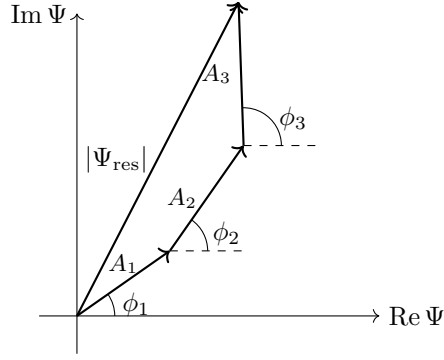
Now what if we move the measuring point x by an amount of δx? This will increase the phases of the wave from all the sources by

$$\delta\phi = \frac{2\pi\delta x}{\lambda}\,. \tag{1.13}$$

The net result is that the resultant magnitude of the combined wave does not change, but the phase changes by $\delta\phi$, as

$$\Psi'_{\text{res}}(x) = \sum_j A_j \exp(i(\phi_n + \delta\phi)) = e^{i\delta\phi} \sum_j A_j \exp(i\phi_n)\,. \tag{1.14}$$

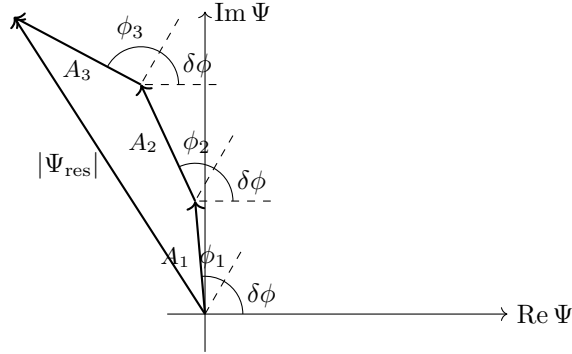Figure 1.3: Movement of the measuring point results in a change of measured phase only.

What if we change the position of one of the sources x_k? This will in general lead to a change in the phase ϕ_k. Now both the phase and the amplitude of the resulting wave is different.
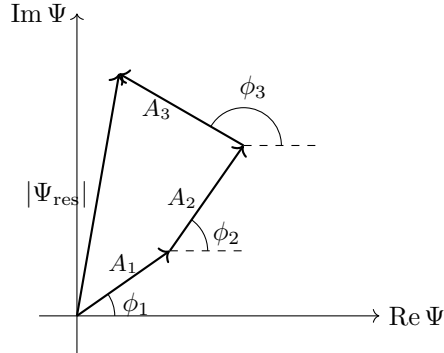

Figure 1.4: A change in the position of one of the sources leads to a change in both the magnitude and the phase measured.
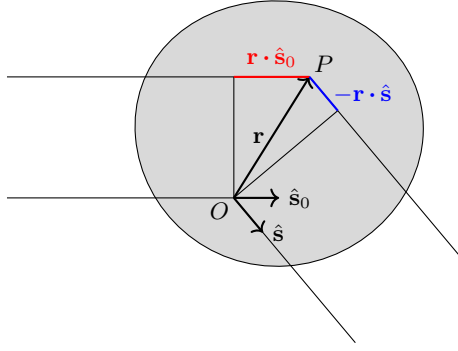
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Figure 1.5: Path difference for diffractions in a general object.

1.2 Diffraction of an Object

We would now like to consider the diffraction of an extended object. Suppose we have parallel incident beams from the direction $\hat{\mathbf{s}}_0$ illuminating the whole object, and we are measuring the diffracted beam at some distant point Q. The dimension of this object is small compared to its distance to the measuring point Q so we can sensibly say that Q is at direction $\hat{\mathbf{s}}$ for all points in the object.[3] To produce the diffraction pattern, we need to sum up the radiation scattered from all the points in the object. To do this, we first pick an arbitrary origin O in the object, and we need to figure out the intensity and phase difference between the beams diffracted in direction $\hat{\mathbf{s}}$ from O and from any other point P with position vector $\mathbf{r}$.

From figure 1.5, it is easy to see that the beam diffracted from P and O has a path difference

$$\Delta x = \mathbf{r} \cdot \hat{\mathbf{s}}_0 - \mathbf{r} \cdot \hat{\mathbf{s}} \,. \tag{1.15}$$

In particular, a positive path difference means that the beam from P falls behind the beam from O, leading to a negative phase difference, so

$$\Delta \phi = -\frac{2\pi \Delta x}{\lambda} = \frac{2\pi \mathbf{r} \cdot (\hat{\mathbf{s}} - \hat{\mathbf{s}}_0)}{\lambda} \,. \tag{1.16}$$

The amplitude of the beam diffracted from O and P may also be different, since the object may be inhomogeneous. Let $A(\mathbf{r})$ be a real function representing the diffraction amplitude, then by integrating over all points, the wave measured at point Q is

$$\Psi(\hat{\mathbf{s}}) = \int \mathrm{d}^3 \mathbf{r} \, A(\mathbf{r}) \exp\left(\frac{2\pi i \mathbf{r} \cdot (\mathbf{s} - \mathbf{s}_0)}{\lambda}\right) \,. \tag{1.17}$$

We can define the *scattering vector* $\mathbf{S}$ by

$$S := \frac{\hat{\mathbf{s}} - \hat{\mathbf{s}}_0}{\lambda} \,. \tag{1.18}$$

It is a vector bisecting the incident and diffracted beam, as shown in the figure below. If we define the angle of deflection to be 2θ, then the length of the scattering vector is

$$\|\mathbf{S}\| = \frac{2 \sin \theta}{\lambda} \,. \tag{1.19}$$

The scattering vector has dimension $[\mathrm{L}]^{-1}$, so it exists in the reciprocal space, which might be familiar from Part IB Chemistry A.[4] This allows us to simplify our expression of the measured wave as

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[3]This type of diffraction is known as *Fraunhofer diffraction*. If you are observing near the diffracting object, then the diffraction is *Fresnel diffraction*.

[4]In some derivation, one uses *momentum transfer vector* $\mathbf{Q}$ defined by

$$\mathbf{Q} = \frac{2\pi(\hat{\mathbf{s}} - \hat{\mathbf{s}}_0)}{\lambda} \,. \tag{1.20}$$
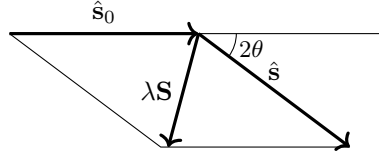
instead of $\mathbf{S}$.

Figure 1.6: Construction of the scattering vector.

$$\Psi(\mathbf{S}) = \int d^3\mathbf{r}\, A(\mathbf{r}) \exp\left(2\pi i\mathbf{r}\cdot\mathbf{S}\right). \tag{1.21}$$

1.3 Diffraction of X-rays from Electrons

We will now consider how X-rays interacts with matter. The interaction generally fall into two categories.

- *Elastic scattering.* This is our main focus. In an *elastic scattering*, or *Thomson scattering*, there is no net transfer of energy from the photon to the material. It can be think of as some kind of resonance of the atomic electrons. When X-rays pass through the material, the oscillating electric field causes the atomic electrons to oscillate, which in turn emit X-rays in all directions. The incoming and outgoing rays retain a non-random phase relationship and are said to be *coherent.*

- *Inelastic processes. Inelastic processes* involve energy transfer from the incoming X-rays to electrons in atoms. The simplest example is photoelectron emission, where an X-ray photon providing energy for an atom to eject a core-shell electron. The photons are then re-emitted with lower energy in an incoherent fashion. This incoherence means that they cannot interfere with each other to produce diffraction patters. Other processes of this type may result from interaction with valence shell electrons or vibrations, all being incoherent. We are therefore not interested in inelastic processes at this stage — we will return to this later.

The quantitative description of Thomson scattering strictly only applies to free electrons, but the results are found to be generally applicable to crystals under normal scattering conditions. Crucially, the amplitude of X-rays diffracted from some point is proportional to the local electron density $\rho(\mathbf{r})$. Therefore,

$$\Psi(\mathbf{S}) = \int d^3\mathbf{r}\, \sigma\rho(\mathbf{r}) \exp(2\pi i\mathbf{r}\cdot\mathbf{S}), \tag{1.22}$$

where σ is the scattering power of a single electron. We can divide through this constant of proportionality to obtain the *structure factor* $F(\mathbf{S})$ given by

$$F(\mathbf{S}) = \int d^3\mathbf{r}\, \rho(\mathbf{r}) \exp\left(2\pi i\mathbf{r}\cdot\mathbf{S}\right). \tag{1.23}$$

Mathematically, $F(\mathbf{S})$ is the *Fourier transform* of the electron density $\rho(\mathbf{r})$.

Definition 1.1. Let $f : \mathbb{R}^n \to \mathbb{C}$ be a function. The *Fourier transform* of f is $\mathcal{F}[f] \equiv \tilde{f} : \mathbb{R}^n \to \mathbb{C}$ given by[5]

$$\tilde{f}(\mathbf{k}) := \int d^n\mathbf{x}\, f(\mathbf{x})e^{2\pi i\mathbf{k}\cdot\mathbf{x}}. \tag{1.25}$$

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[5]You might be more familiar with the Fourier transform defined as

$$\tilde{f} = \frac{1}{\sqrt{2\pi}} \int dx\, f(x)e^{-ikx}, \tag{1.24}$$

where the normalisation factor of $1/\sqrt{2\pi}$ may or may not be there. It is just a matter of convention. However, this difference in convention is annoying since it results in slight tweaks in a lot of formulae.

Theorem 1.2. Let $\tilde{f}(\mathbf{k})$ be the Fourier transform of $f(\mathbf{x})$. The *inverse Fourier transform* that converts $\tilde{f}$ back to f is given by

$$f(\mathbf{x}) = \mathcal{I}[\tilde{f}(\mathbf{k})] := \int \mathrm{d}^3\mathbf{k}\,\tilde{f}(\mathbf{k})e^{-2\pi i\mathbf{k}\cdot\mathbf{x}}\,. \tag{1.26}$$

Proof.

$$
\begin{aligned}
\mathcal{F}[\tilde{f}](\mathbf{x}) &= \int \mathrm{d}^n\mathbf{k}\,e^{-2\pi i\mathbf{k}\cdot\mathbf{x}}\int \mathrm{d}^3\mathbf{s}\,e^{2\pi i\mathbf{k}\cdot\mathbf{s}}f(\mathbf{s})\\
&= \int \mathrm{d}^n\mathbf{s}\,f(\mathbf{s})\int \mathrm{d}^n\mathbf{k}\,e^{2\pi ik\cdot(\mathbf{s}-\mathbf{x})}\\
&= \int \mathrm{d}^n\mathbf{s}\,f(\mathbf{s})\delta(\mathbf{s}-\mathbf{x})\\
&= f(\mathbf{x})\,.
\end{aligned}
\tag{1.27}
$$

$\square$

Hence to convert the $F(\mathbf{S})$ back to $\rho(\mathbf{r})$, one simply needs to perform the inverse Fourier transform

$$\rho(\mathbf{r}) = \int \mathrm{d}^3\mathbf{S}\,F(\mathbf{S})\exp(-2\pi i\mathbf{r}\cdot\mathbf{S})\,. \tag{1.28}$$

This means that if we can determine the $F(\mathbf{S})$, then we can easily reconstruct the electron density in a material, no matter how complex the structure is. (1) Measure the phases and the amplitudes of the diffracted beams. (2) Divide by single-electron scattering power σ to get $F(\mathbf{S})$. (3) Do the inverse Fourier transform to obtain $\rho(\mathbf{S})$. Simple as that! Three steps to solve any chemical structure in the world!

This should be the happy ending of our story on X-ray diffraction.

2 The Phase Problem and the Patterson Function

2.1 The Phase Problem

If the problem is really that simple, then this would be a one-lecture course instead of a 12-lecture one. There is a huge issue. We cannot measure the phase of an X-ray.

To measure the magnitude and the phase of an electromagnetic wave, we would use an antenna. However, this requires the antenna to have its dimensions comparable to the radiation wavelength. The X-ray we used for diffraction is at atomic length scale — that's why we can see the diffraction, but it is impossible to make an antenna at atomic length scale since antennas should be made from atoms! All we can measure in a diffraction experiment is the number of X-ray photons encountered in a given time, which is the diffracted *intensity*. This is proportional to $I = |F(\mathbf{S})|^2$. The phase information is completely lost. This is referred to as the *phase problem* in diffraction.

Now the question is: is getting the correct phase important? If using a wrong phase of the diffracted beam has little impact on the electron density calculated, then this would not be a huge problem. We can calculate the modulus of $F(\mathbf{S})$ by taking the square root of the intensity, and just plug in some random phases to calculate $\rho(\mathbf{r})$. However, it turns out that getting the correct phase is extremely important — it even plays a more important role than the magnitude to some extent. This can be illustrated by the following little experiment.

Instead of doing Fourier transform of a electron density function, we do a Fourier transform on a picture. A black and white picture is also a function of the pixels, where the values of the function is the gray scale. We can transform it into the frequency domain, and then transform it back, and we get the original image. However, if we use some randomly generated phase values to replace the correct phase values in the Fourier transform of the image, and we transform it back, we see a complete mess. This is what will happen if we use random phase value for the structure factor — we will get no valuable information. If fact, if we use some random value for the magnitudes of the Fourier transform, with the correct phase values, we can still vaguely see the shape of a cat.

(a) Correct magnitude + correct phase
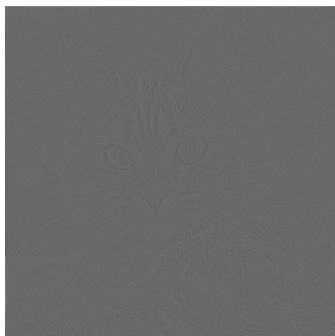
(b) Random magnitude + correct phase
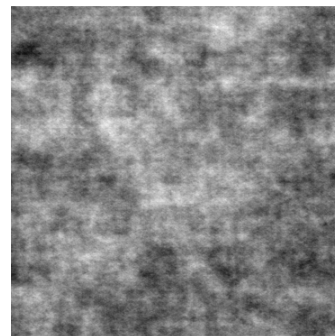
(c) Correct magnitude + random phase

Figure 2.1: The effect of using the wrong phases and magnitudes in an inverse Fourier transform.

Just for fun, we can extend this experiment further. We have two images: one is a benzene and one is a cat. What will happen if we use the magnitude value of one figure with the phase value of the other? The result is in (2.2), and you can see it is the phase that determines what we will see.

Moral: phase is important, but we can't measure it. The main task of structure determination using X-ray diffraction is to deduce the phases of the structure factor. This is what we will spend the remaining 11-lectures worths of time on.
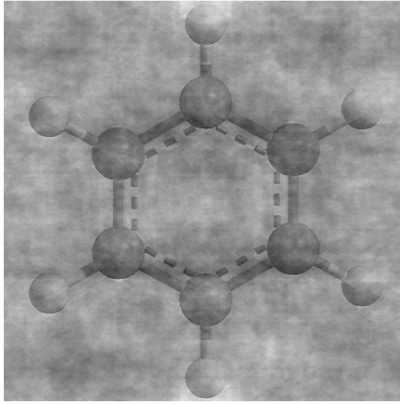
(a) Magnitude of cat + phase of benzene

(b) Magnitude of benzene + phase of cat

Figure 2.2: Phases govern what we see in an inverse Fourier transform. If you use the phases of a benzene, you see a benzene. If you use the phases of a cat, you see a cat.

2.2 Patterson Function

Since all what we can get from measuring a diffraction pattern is the intensity $I(\mathbf{S}) = |F(\mathbf{S})|^2$, let's see what its inverse Fourier transform gives us anyway.

Before doing that, let's first introduce convolution and correlation.

Definition 2.1. For two functions $f, g : \mathbb{R}^n \to \mathbb{C}$, their *convolution* is

$$(f * g)(\mathbf{x}) := \int \mathrm{d}^n \mathbf{s}\, f(\mathbf{s}) g(\mathbf{x} - \mathbf{s}) \,, \tag{2.1}$$

and their *correlation* is

$$(f \otimes g)(\mathbf{x}) := \int \mathrm{d}^n \mathbf{s}\, f(\mathbf{s})^* g(\mathbf{x} + \mathbf{s}) \,. \tag{2.2}$$
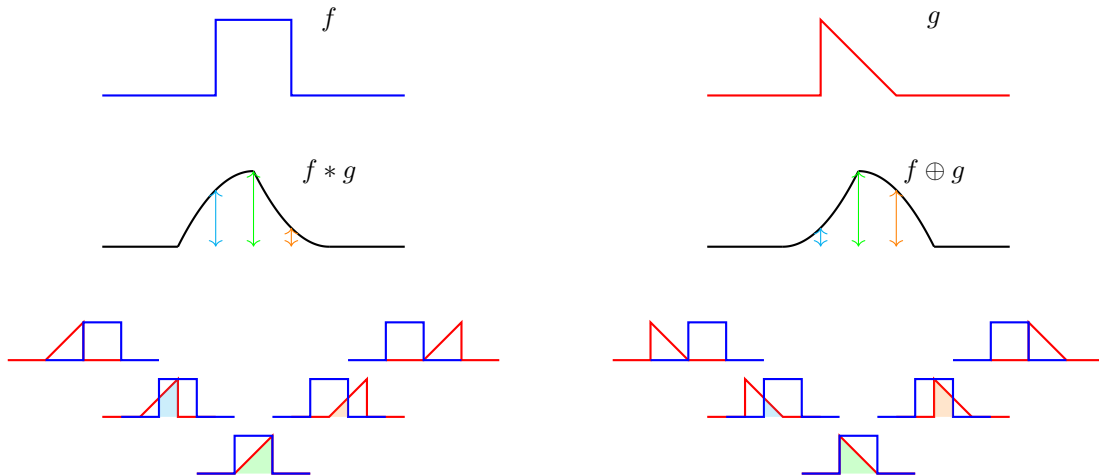

Figure 2.3: Graphic explanation of convolution and correlation.

Theorem 2.2 (Convolution theorem). The Fourier transform of a convolution if the product of Fourier transform.

$$\mathcal{F}[f * g] = \mathcal{F}[f]\mathcal{F}[g] \,. \tag{2.3}$$

Proof.

$$\mathcal{F}[f * g](\mathbf{k}) = \int d^n\mathbf{x} \, e^{2\pi i \mathbf{k} \cdot \mathbf{x}} \int d^n\mathbf{s} \, f(\mathbf{s})g(\mathbf{x} - \mathbf{s})$$

$$= \int d^n\mathbf{s} \, f(\mathbf{s}) \int d^n\mathbf{x} \, e^{2\pi i \mathbf{k} \cdot \mathbf{x}} g(\mathbf{x} - \mathbf{s})$$

$$= \int d^n\mathbf{s} \, f(\mathbf{s}) \int d^n\mathbf{u} \, e^{2\pi i \mathbf{k} \cdot (\mathbf{u} + \mathbf{s})} g(\mathbf{u}) \qquad \text{define } \mathbf{u} = \mathbf{x} - \mathbf{s}$$

$$= \int d^n\mathbf{s} \, e^{2\pi i \mathbf{k} \cdot \mathbf{s}} f(\mathbf{s}) \int d^n\mathbf{u} \, e^{2\pi i \mathbf{k} \cdot \mathbf{u}} g(\mathbf{u})$$

$$= \tilde{f}(\mathbf{k})\tilde{g}(\mathbf{k}) \, . \tag{2.4}$$

$\square$

Theorem 2.3. Conversely, the Fourier transform of a product fg is the convolution of their fourier transforms

$$\mathcal{F}[fg] = \mathcal{F}[f] * \mathcal{F}[g] \, . \tag{2.5}$$

Proof.

$$\mathcal{F}[fg](\mathbf{k}) = \int d^n\mathbf{x} \, e^{2\pi i \mathbf{k} \cdot \mathbf{x}} f(\mathbf{x})g(\mathbf{x})$$

$$= \int d^n\mathbf{x} \, e^{2\pi i \mathbf{k} \cdot \mathbf{x}} f(\mathbf{x}) \int d^n\boldsymbol{\ell} \, e^{-2\pi i \boldsymbol{\ell} \cdot \mathbf{x}} \tilde{g}(\boldsymbol{\ell})$$

$$= \int d^n\boldsymbol{\ell} \, \tilde{g}(\boldsymbol{\ell}) \int d^n\mathbf{x} \, e^{2\pi i \mathbf{x} \cdot (\mathbf{k} - \boldsymbol{\ell})} f(\mathbf{x})$$

$$= \int d^n\boldsymbol{\ell} \, \tilde{g}(\boldsymbol{\ell}) \tilde{f}(\mathbf{k} - \boldsymbol{\ell})$$

$$= \tilde{f} * \tilde{g}(\mathbf{k}) \, . \tag{2.6}$$

$\square$

We see a beautiful duality here. Product in the real domain is the convolution in the Fourier domain, and *vice versa*.

Theorem 2.4 (Wiener–Khinchin theorem). The Fourier transform of the autocorrelation of a function is its *power spectral intensity*.

$$\mathcal{F}[f \otimes f] = \left| \tilde{f} \right|^2 \, . \tag{2.7}$$

Proof.

$$\mathcal{F}[f \otimes f](\mathbf{k}) = \int d^n\mathbf{x} \, e^{2\pi i \mathbf{k} \cdot \mathbf{x}} \int d^n\mathbf{s} \, f^*(\mathbf{s})f(\mathbf{x} + \mathbf{s})$$

$$= \int d^n\mathbf{s} \, f^*(\mathbf{s}) \int d^n\mathbf{x} \, e^{2\pi i \mathbf{k} \cdot \mathbf{x}} f(\mathbf{x} + \mathbf{s})$$

$$= \int d^n\mathbf{s} \, f^*(\mathbf{s}) \int d^n\mathbf{u} \, e^{2\pi i \mathbf{k} \cdot (\mathbf{u} - \mathbf{s})} f(\mathbf{u}) \qquad \text{define } \mathbf{u} = \mathbf{x} + \mathbf{s}$$

$$= \int d^n\mathbf{s} \, e^{-2\pi i \mathbf{k} \cdot \mathbf{s}} f^*(\mathbf{s}) \int d^n\mathbf{u} \, e^{2\pi i \mathbf{k} \cdot \mathbf{u}} f(\mathbf{u})$$

$$= \tilde{f}^*(\mathbf{k})\tilde{f}(\mathbf{k}) = \left| \tilde{f}(\mathbf{k}) \right|^2 \, . \tag{2.8}$$

$\square$

Finally, if we apply both sides on the Wiener–Khinchin theorem, we get

$$\mathcal{I}\left[|\tilde{f}|^2\right] = f \otimes f. \tag{2.9}$$

We can apply this to our diffraction intensity! We previously identified the structure factor to be the Fourier transform of the electron density, $F(\mathbf{S}) = \mathcal{F}[\rho(\mathbf{x})]$, and the diffraction intensity is exactly $I(\mathbf{S}) = |F(\mathbf{S})|^2$. Therefore, the inverse Fourier transform of the diffraction intensity is exactly the autocorrelation of the electron density!

$$\mathcal{I}[I(\mathbf{S})] = \rho \otimes \rho(\mathbf{r}). \tag{2.10}$$

We often call this the *Patterson function*, denoted $P(\mathbf{r})$.

2.3 Illustrating the Patterson Function

The above derivation is a bit abstract. Let's do a simple 1D example of an electron density function with three peaks, modelling three atoms in a line, and see how its Patterson function look like.
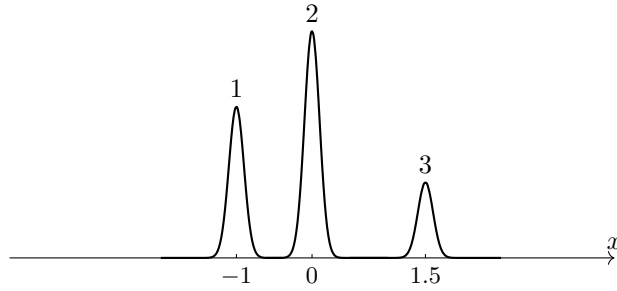

We put the three peaks at positions $x = -1$, $x = 0$ and $x = 1.5$ with weights 2, 3 and 1 respectively. From the definition of the Patterson function, which is the correlation of the electron density with itself

$$P(u) = \int \mathrm{d}x\, \rho(x)\rho(x + u), \tag{2.11}$$

we need to take another copy of electron density function, shift it by some distance u, and evaluate the integral of their product, which is roughly governed by how well do the peaks of the two functions overlap. Let's set u to a range of different values and see what happens.

- $u = -3$: First, when u is really small, the two function has almost no overlap, so at this value of u, $F(u) \approx 0$.
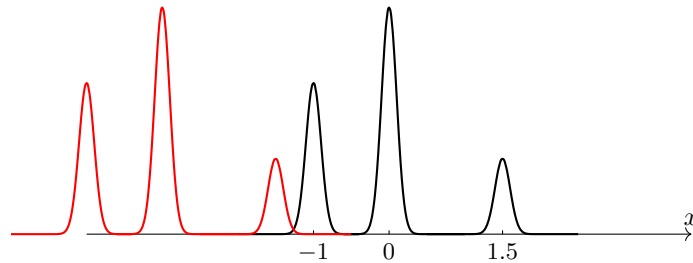

- $u = -2.5$: At this value of u, peak 1 and peak 3 just overlaps. Without the actual functional form of the peak, we can't evaluate this integral of their product, but since peak 1 has weight 2 and peak 3 has weight 1, we can roughly assign a relative weight of $2 \times 1 = 2$ to the Patterson function here.
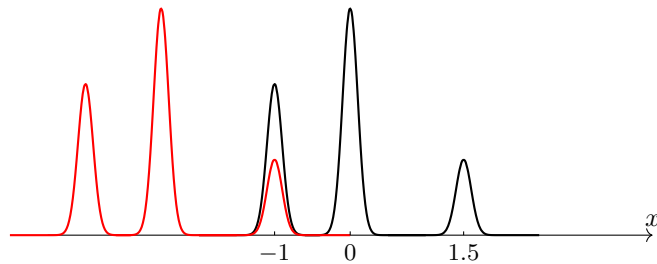
- $u = -1.5$: Now at this value of u, peak 3 and peak 2 overlaps, giving a peak in the Patterson function with relative weight $3 \times 1 = 3$.
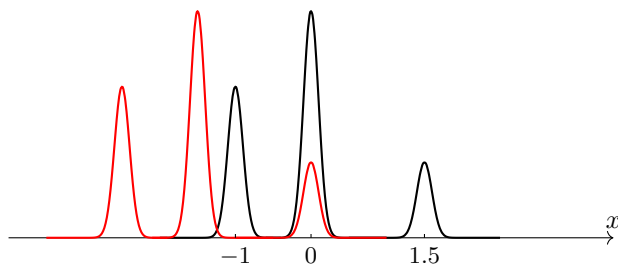
- $u = -1$: Peak 1 and peak 2 overlaps, giving a peak in the Patterson function with relative weight $2 \times 3 = 6$.
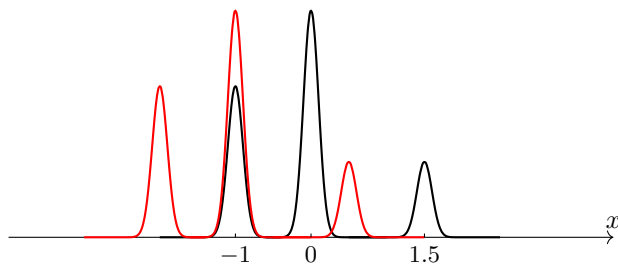
- $u = 0$: At this special value of u, the second function is not moved at all, so all the three peaks are perfectly aligned. This leads to a very large peak in the Patterson function with weight $2^2 + 3^2 + 1^2 = 14$.
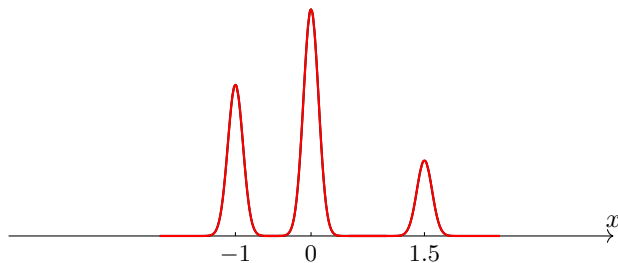
You can go further to check other values of u, but we should have done enough to discover a pattern. The Patterson function will have peaks at the values when the are two peaks in the electron density function align, which are exactly the "inter-peak" distances in the electron density. The relative weight of the peak in the Patterson function is the product of the weight of the peaks in the electron density.
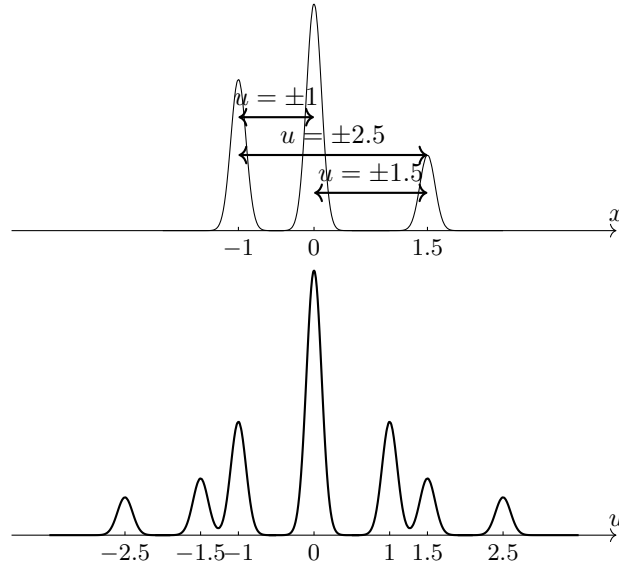
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Figure 2.4: Peaks in the Patterson function corresponds to the inter-peak vectors in the electron density function.

To conclude, let's summarise some features of the Patterson function:

1. The Patterson function is defined in the same space as $\rho(\mathbf{r})$ (as opposed to the structure factor defined in the reciprocal space), and it spans a range twice that spanned by $\rho(\mathbf{r})$.

2. The Patterson function is always centrosymmetric, even if $\rho(\mathbf{r})$ is not.

3. The maximum of the Patterson function occurs at $\mathbf{u} = \mathbf{0}$, and its value is

$$P(\mathbf{0}) = \int \mathrm{d}^3\mathbf{r}\, \rho^2(\mathbf{r}).\tag{2.12}$$

4. Local maxima in $P(\mathbf{u})$ occurs when peaks in $\rho(\mathbf{r})$ overlaps with those in $\rho(\mathbf{u}+\mathbf{r})$. This happens if the offset vector $\mathbf{u}$ is some peak↔peak vector in $\rho(\mathbf{r})$. If we take an atomic picture of the electron density, in which electron densities are concentrated on the atomic sites (we will formalise this latter), then peaks in $P(\mathbf{u})$ occurs when $\mathbf{u}$ is an *interatomic vector*.

5. If there are N peaks in $\rho(\mathbf{r})$, there are N^2 interatomic vectors. Of these, N will occur at $\mathbf{u} = \mathbf{0}$, corresponding to vectors of an atom pointing itself. Consequently, there will in general be $N^2 - N$ non-origin peaks in $P(\mathbf{u})$ (some of them may overlap as well).

6. For a function $\rho(\mathbf{r})$ consists of resolved peaks, the total weight (area) of the peak produced in $P(\mathbf{u})$ is proportional to the product of the weights of the peaks in $\rho(\mathbf{r})$ and $\rho(\mathbf{r} + \mathbf{u})$ producing it. If atoms in $\rho(\mathbf{r})$ and $\rho(\mathbf{r} + \mathbf{u})$ have atomic numbers Z_1 and Z_2, then the weight of the peaks in $P(\mathbf{u})$ will be proportional to $Z_1 Z_2$. Consequently, Patterson peaks involving heavy atoms (where Z_1 and/or Z_2 is large) will show up most clearly.

7. Peaks in $P(\mathbf{u})$ will be broadened than in $\rho(\mathbf{r})$, and peaks corresponding to vectors from light atoms may merge into a poorly-defined backgrounds.

Hence, as we will see later, the Patterson function will be helpful in locating heavy atoms in a structure.

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2.4 Patterson Function of a Molecule

Now consider a SO_3 molecule. For simplicity, we will make this problem 2 dimensional. The atomic number of S and O are 16 and 8 respectively, so the electron density function has one peak of weight 16, which we set at the origin, and three peaks of weight 6 at the same distance from the origin, separated by $120°$.
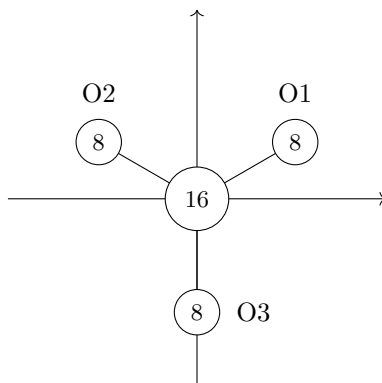

Figure 2.5: The electron density of a SO_3 molecule.
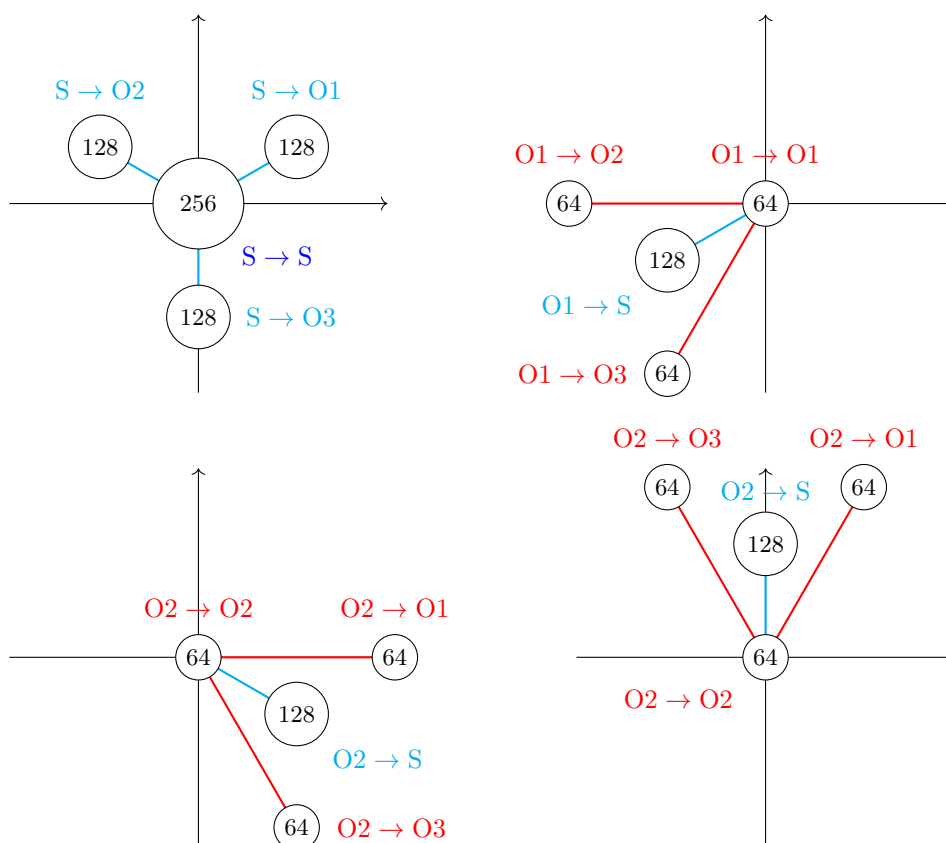
Figure 2.6: Interatomic vectors of SO_3.

To evaluate the Patterson function, we need to find all the interatomic vectors. Let's first consider vectors from the central S atom. There will be a self-vector $(S \rightarrow S)$ at the origin, with weight $16 \times 16 = 256$, and there will be three $S \rightarrow O$ vectors arranged symmetrically around origin, with weight $16 \times 8 = 128$ each. Their distance to the origin is the same as the $S - O$ bond length, which we will denote as r_1. Note that this looks like the molecule itself, with the S atom sitting at the origin.

Then consider the vectors from the atom O1. There will be a self vector (O1 $\to$ O1) at the origin, with weight $8 \times 8 = 64$. There are two other O $\to$ O vectors, O1 $\to$ O2 and O1 $\to$ O2, at $60°$ to each other, with weight 64 and length $\sqrt{3}r_1$. Bisecting these two is a S $\to$ O1 vector with weight 128 and length r_1. Note this again look like the molecule itself, but now with O1 sitting at the origin. Similarly, we can consider vectors from atoms O2 and O3 as well.

Then to construct the Patterson function, we only need to add these contributions up. The result is shown in the figure below.
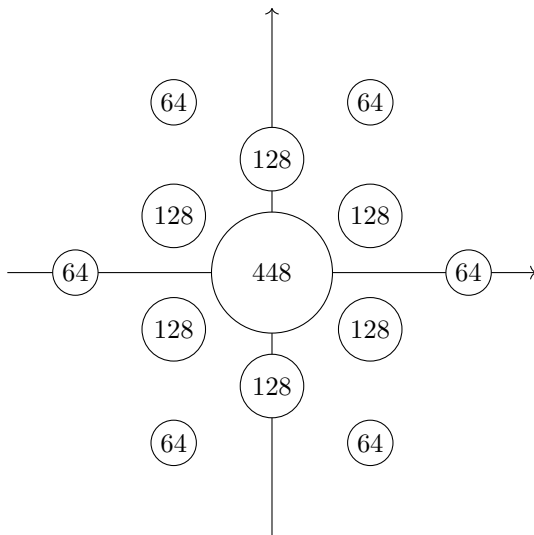

Figure 2.7: The Patterson function of a SO_3 molecule.

Some remarks:

- The weight of the origin is the sum of the squares the atomic numbers of all atoms.

- The Patterson function includes vectors between all atoms, not just between the chemically bonded ones.

- $P(\mathbf{u})$ must have a centre of symmetry at the origin, even though SO_3 does not have one. The point group of the SO_3 molecule is D_{3h}, and the centre of symmetry have upgraded the point group of the Patterson function to D_{6h}.

One can use the same principle to construct the Patterson of a 3D molecule. Below an example of the Patterson function of SO_4^{2-} ion, with T_d symmetry. The Patterson function has an extra inversion centre, so its point group is O_h.

2.5 The Patterson Function of Ideal Gas

We now move on to a more realistic case where these is a whole collection of molecule, and we will consider two extremes — an ideal gas and a crystalline solid.

First, let's consider an ideal gas. There are no intermolecular forces, negligible molecular volumes, and we will assume that all molecules are perfectly rigid and geometrically identical. The Patterson peaks will have contribution from all molecules: both intermolecular vectors and intramolecular vectors. For the vectors pointing within a molecule, the interatomic vectors should be identical to that for a single molecule, multiplied by the total number of molecules that are present. But as we
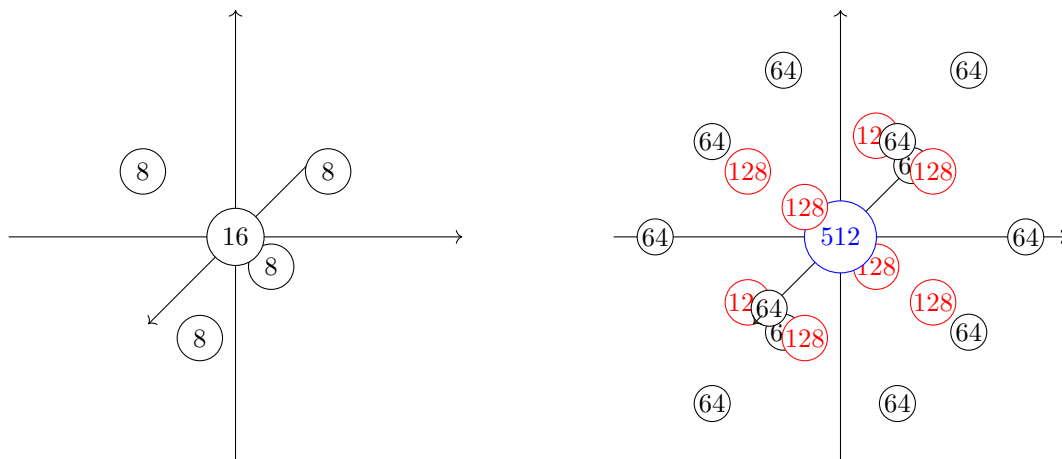
Figure 2.8: The electron density and the Patterson function of SO_4^{2-}.

are in the gas phase, we have another complexity. Due to the random molecular orientation, the Patterson function of an ideal gas appears as a spherically averaged version of the 3D Patterson that we constructed for one molecule. Thus, only the length of the interatomic vector is important, and we will plot the resulting Patterson function as a radial vector map. For example, for the SO_4^{2-} ideal gas (which apparently will not be ideal in reality), the radial Patterson function is shown in the figure below.[6]
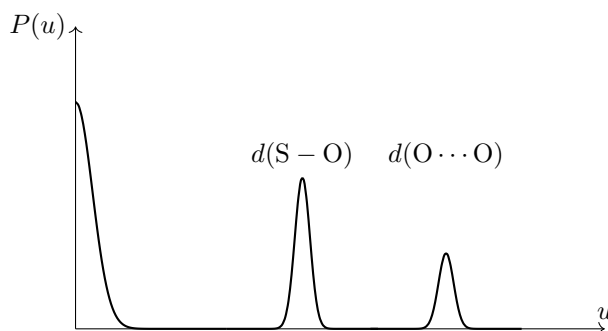

Figure 2.9: Intramolecular contribution to the radial Patterson function of SO_4^{2-}.

We then need to consider the intermolecular vectors. If the gas is indeed ideal with no intermolecular forces, then the positions and orientations of all molecules should be completely random at any time. Hence, all distances between molecules are equally possible, and soo the intermolecular vectors will sum over time to form a constant background. If we are going to inject a little bit of reality into this crude model, we can say that the molecules cannot be too close from each other, so this background is zero at small u.

As a result, in an ideal gas, the radial Patterson function has discernible peaks corresponding solely to the spherical averaged Patterson function of one molecule, superimposed on a featureless background. Non-ideal gases, liquid and non-crystalline solid will show similar radial Patterson function due their disorderedness. However, they may show local coordination peaks.

---

[6]As for the atomic wavefunction, you can choose to plot a radial Patterson function or a radial distribution function — we are being rather loose here since we are doing everything schematically. Anyway, the true weight of a peak is the integral of the 3D Patterson function.
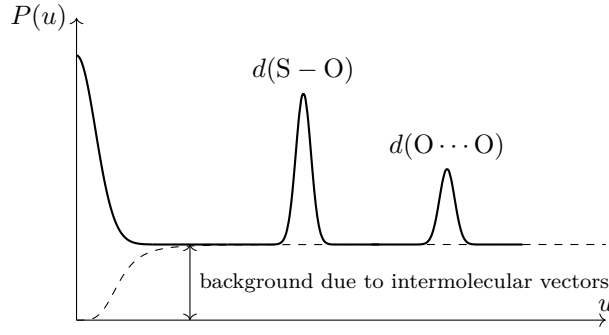
Figure 2.10: Radial Patterson function of SO_4^{2-} with both intermolecular and intramolecular contributions.

3 Diffraction from a Single Crystal

In the remainder of the course, we will focus almost exclusively on single crystals, since as we will see, we can develop robust methods to interpret single-crystal diffraction patterns.

3.1 Diffracted Intensity for a Single Crystal

We will first infer how the Patterson function of a crystal would look like — this shouldn't be too difficult due to the order in a crystal, and then we will perform the Fourier transform to try to figure out the form of its diffracted intensity.

We will consider a single crystal will unit cell vectors $\mathbf{a}, \mathbf{b}, \mathbf{c}$, with $N = N_a \times N_b \times N_c$ unit cells in total, where N_a, N_b, N_c are the number of cells along each direction.

Suppose the Patterson function of a single unit cell is $P_{\text{cell}}(\mathbf{u})$, then its Fourier transform will give the diffracted intensity from one unit cell, which we will call $|F_{\text{cell}}(\mathbf{S})|^2$.

$$|F_{\text{cell}}|^2 = \int \mathrm{d}^3\mathbf{u}\, e^{2\pi i \mathbf{u} \cdot \mathbf{S}} P_{\text{cell}}(\mathbf{u})\,. \tag{3.1}$$

The for our single crystal, there will be N such contributions to the diffracted intensities, so we get the intra-cell contribution $N |F_{\text{cell}}(\mathbf{S})|^2$.

Next consider the contribution to the Patterson function by inter-cell vectors pointing from each cell to the cell next to it along the $+\mathbf{a}$ direction. For each intra-cell vector $\mathbf{u}$, there must be such a inter-cell vector $\mathbf{u} + \mathbf{a}$, so the contribution to the Patterson function from this type of inter-cell vectors is $P_{\text{cell}}(\mathbf{u} + \mathbf{a})$. This contributes

$$\int \mathrm{d}^3\mathbf{u}\, P_{\text{cell}}(\mathbf{u} + \mathbf{a}) e^{2\pi i \mathbf{u} \cdot \mathbf{S}} \tag{3.2}$$

to the diffraction intensity. We can simplify this a bit further. By the change of variable $\mathbf{v} = \mathbf{u} + \mathbf{a}$, we have

$$\int \mathrm{d}^3\mathbf{u}\, P_{\text{cell}}(\mathbf{u} + \mathbf{a}) e^{2\pi i \mathbf{u} \cdot \mathbf{S}} = \int \mathrm{d}^3\mathbf{v}\, P_{\text{cell}}(\mathbf{v}) e^{2\pi i \mathbf{v} \cdot \mathbf{S}} e^{-2\pi i \mathbf{a} \cdot \mathbf{S}}$$
$$= |F_{\text{cell}}|^2\, e^{-2\pi i \mathbf{a} \cdot \mathbf{S}}\,. \tag{3.3}$$

However, there are only $(N_a - 1)N_b N_c$ cells has such a neighbouring cell one unit along $+\mathbf{a}$ direction, so its contribution to the diffraction intensity is

$$(N_a - 1)N_b N_c |F_{\text{cell}}|^2\, e^{-2\pi i \mathbf{a} \cdot \mathbf{S}}\,. \tag{3.4}$$

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Similarly, there are also contributions from inter-cell vectors pointing from a cell to the neighbouring cell along $-\mathbf{a}$ direction, which is

$$(N_a - 1)N_b N_c |F_{\text{cell}}|^2 e^{+2\pi i \mathbf{a} \cdot \mathbf{S}}. \tag{3.5}$$

The rest of the process is similar, there will be inter-cell vectors pointing from one cell to the cell $n_a \mathbf{a} + n_b \mathbf{b} + n_c \mathbf{c}$ away for any $-N_a < n_a < N_a$, $-N_b < n_b < N_b$, $-N_c < n_c < N_c$, contributing

$$(N_a - n_a)(N_b - n_b)(N_c - n_c)|F_{\text{cell}}|^2 e^{-2\pi i (n_a \mathbf{a} + n_b \mathbf{b} + n_c \mathbf{c}) \cdot \mathbf{S}} \tag{3.6}$$

to the total diffraction intensity. We need to sum all of these up, and we get a total diffraction intensity

$$
\begin{aligned}
I(\mathbf{S}) &= |F_{\text{cell}}|^2 \sum_{n_a = -N_a}^{N_a} \sum_{n_b = -N_b}^{N_b} \sum_{n_c = -N_c}^{N_c} (N_a - |n_a|)(N_b - |n_b|)(N_c - |n_c|)e^{-2\pi i (n_a \mathbf{a} + n_b \mathbf{b} + n_c \mathbf{c}) \cdot \mathbf{S}} \\
&= |F_{\text{cell}}|^2 \prod_{j \in \{a,b,c\}} \sum_{n_j = -N_j + 1}^{N_j - 1} (N_j - |n_j|)e^{-2\pi i n_j \mathbf{j} \cdot \mathbf{S}}.
\end{aligned}
\tag{3.7}
$$

The latter form is rather more compact, but less intuitive.[7]

A more Mathematical View

Consider the convolution of some function $f(\mathbf{r})$ with a Dirac delta $\delta(\mathbf{r} - \mathbf{a})$ with its peak at $\mathbf{r} = \mathbf{a}$.

$$f(\mathbf{r}) * \delta(\mathbf{r} - \mathbf{a}) = \int_{-\infty}^{\infty} d^3\mathbf{u}\, f(\mathbf{u})\delta(\mathbf{u} - (\mathbf{r} - \mathbf{a})) = f(\mathbf{r} - \mathbf{a}). \tag{3.8}$$

We see that its effect is to shift $f(\mathbf{r})$ by $\mathbf{a}$ — or in other words, it put a copy of $f(\mathbf{r})$ at position $\mathbf{a}$. A crystal is essentially a copy of ρ_{cell} at each lattice point[8]. This allows us to view the electron density of a crystal as the convolution of the lattice of Dirac delta functions with the electron density of a single unit cell:

$$\rho(\mathbf{r}) = \rho_{\text{cell}}(\mathbf{r}) * \rho_{\text{lattice}}(\mathbf{r}), \tag{3.9}$$

where

$$\rho_{\text{lattice}}(\mathbf{r}) = \sum_{n_a = 0}^{N_a - 1} \sum_{n_b = 0}^{N_b - 1} \sum_{n_c = 0}^{N_c - 1} \delta(\mathbf{r} - n_a \mathbf{a} - n_b \mathbf{b} - n_c \mathbf{c}) \tag{3.10}$$

is the lattice of delta functions (It is obviously not a electron density, but we will denote it as ρ anyway). A rather useful properties is the Patterson function of a convolution is the convolution of the Patterson functions,[9] and so

$$P(\mathbf{u}) = P_{\text{cell}}(\mathbf{u}) * P_{\text{lattice}}(\mathbf{u}). \tag{3.12}$$

---

[7]You might have noticed that the limits of the sum should be $\pm(N_j - 1)$ instead of N_j. We have included $n_j = \pm N_j$ into our sum since they contribute nothing and can make our formula slightly more compact.

[8]This is not quite accurate as a unit cell may contain more than one lattice point in non-primitive cell. This is not a crystallographic course so we will be rather loose here.

[9]This is perhaps not too obvious to prove using the integral definitions of these quantities. However, an important fact of electron density is that it is a real function, so $P(\mathbf{r}) = \rho(\mathbf{r}) \otimes \rho(\mathbf{r}) = \rho(\mathbf{r}) * \rho(-\mathbf{r})$. Then

$$
\begin{aligned}
P(\mathbf{r}) &= \rho(\mathbf{r}) * \rho(-\mathbf{r}) \\
&= [\rho_{\text{cell}}(\mathbf{r}) * \rho_{\text{lattice}}(\mathbf{r})] * [\rho_{\text{cell}}(-\mathbf{r}) * \rho_{\text{lattice}}(-\mathbf{r})] \\
&= [\rho_{\text{cell}}(\mathbf{r}) * \rho_{\text{cell}}(-\mathbf{r})] * [\rho_{\text{lattice}}(\mathbf{r}) * \rho_{\text{lattice}}(-\mathbf{r})] \\
&= P_{\text{cell}}(\mathbf{r}) * P_{\text{lattice}}(\mathbf{r})
\end{aligned}
\tag{3.11}
$$

by the commutativity and associativity of convolution (which are not that difficult to prove).

The Patterson function (autocorrelation) of the lattice of delta functions is

$$P_{\text{lattice}}(\mathbf{u}) = \sum_{n_a=-N_a}^{N_a} \sum_{n_b=-N_b}^{N_b} \sum_{n_c=-N_c}^{N_c} (N_a - |n_a|)(N_b - |n_b|)(N_c - |n_c|)\delta(\mathbf{r} - n_a\mathbf{a} - n_b\mathbf{b} - n_c\mathbf{c}). \quad (3.13)$$

Then by the convolution theorem, the diffracted intensity, which is the Fourier transform of the Patterson function, must be the product of the diffracted intensity of a unit cell $|F_{\text{cell}}(\mathbf{r})|^2$ with the Fourier transform of this Patterson function of the lattice, which is given by

$$I(\mathbf{S}) = \sum_{n_a=-N_a}^{N_a} \sum_{n_b=-N_b}^{N_b} \sum_{n_c=-N_c}^{N_c} (N_a - |n_a|)(N_b - |n_b|)(N_c - |n_c|)e^{-2\pi i(n_a\mathbf{a}+n_b\mathbf{b}+n_c\mathbf{c})\cdot\mathbf{S}}. \quad (3.14)$$

We have arrived at the same result.

3.2 The Reciprocal Lattice

Although we can't measure the structure factor, we can still work it out assuming we know $\rho(\mathbf{r})$ to see how it looks like for a single crystal. Using the above expression of the electron density as a convolution (3.9), we can directly take its Fourier transform and get the structure factor

$$\begin{aligned}
F(\mathbf{S}) &= F_{\text{cell}}(\mathbf{S})\mathcal{F}\left[\sum_{n_a=0}^{N_a-1}\sum_{n_b=0}^{N_b-1}\sum_{n_c=0}^{N_c-1} \delta(\mathbf{r} - n_a\mathbf{a} - n_b\mathbf{b} - n_c\mathbf{c})\right] \\
&= F_{\text{cell}}(\mathbf{S})\left[\sum_{n_a=0}^{N_a-1}\sum_{n_b=0}^{N_b-1}\sum_{n_c=0}^{N_c-1} e^{-2\pi i(n_a\mathbf{a}+n_b\mathbf{b}+n_c\mathbf{c})}\right] \\
&= F_{\text{cell}}(\mathbf{S}) \prod_{j\in\{a,b,c\}}\sum_{n_j=0}^{N_j-1} e^{-2\pi i n_j\mathbf{j}\cdot\mathbf{S}}. \quad (3.15)
\end{aligned}$$

We see a cute geometric series here! This allows to further simplify it

$$\begin{aligned}
F(\mathbf{S}) &= F_{\text{cell}}(\mathbf{S}) \prod_{j\in\{a,b,c\}} \frac{1 - \exp[-2\pi i N_j\mathbf{j}\cdot\mathbf{S}]}{1 - \exp[-2\pi i\mathbf{j}\cdot\mathbf{S}]} \\
&= F_{\text{cell}}(\mathbf{S}) \prod_{j\in\{a,b,c\}} \frac{\exp[-\pi i N_j\mathbf{j}\cdot\mathbf{S}]}{\exp[-\pi i\mathbf{j}\cdot\mathbf{S}]} \frac{\exp[\pi i N_j\mathbf{j}\cdot\mathbf{S}] - \exp[-\pi i N_j\mathbf{j}\cdot\mathbf{S}]}{\exp[\pi i\mathbf{j}\cdot\mathbf{S}] - \exp[-\pi i\mathbf{j}\cdot\mathbf{S}]} \\
&= F_{\text{cell}}(\mathbf{S}) \prod_{j\in\{a,b,c\}} \exp[-\pi i(N_j-1)\mathbf{j}\cdot\mathbf{S}]\frac{\sin(\pi N_j\mathbf{j}\cdot\mathbf{S})}{\sin(\pi\mathbf{j}\cdot\mathbf{S})} \quad (3.16)
\end{aligned}$$

Having the structure factor in this form, we can work out another expression of the diffraction intensity of single crystal

$$\begin{aligned}
I(\mathbf{S}) &= F(\mathbf{S})F^*(\mathbf{S}) \\
&= |F_{\text{cell}}(\mathbf{S})|^2 \prod_{j\in\{a,b,c\}} \frac{\sin^2(\pi N_j\mathbf{j}\cdot\mathbf{S})}{\sin^2(\pi\mathbf{j}\cdot\mathbf{S})} \\
&= |F_{\text{cell}}(\mathbf{S})|^2 \frac{\sin^2(\pi N_a\mathbf{a}\cdot\mathbf{S})}{\sin^2(\pi\mathbf{a}\cdot\mathbf{S})}\frac{\sin^2(\pi N_b\mathbf{b}\cdot\mathbf{S})}{\sin^2(\pi\mathbf{b}\cdot\mathbf{S})}\frac{\sin^2(\pi N_c\mathbf{c}\cdot\mathbf{S})}{\sin^2(\pi\mathbf{c}\cdot\mathbf{S})}. \quad (3.17)
\end{aligned}$$

This is somewhat easier to plot. To make the plotting easier, we will consider a 1D crystal of N units cell, so

$$\frac{I(S)}{|F_{\text{cell}}(S)|^2} = \frac{\sin^2(\pi NaS)}{\sin^2(\pi aS)}. \quad (3.18)$$

(a) $N = 3$ (b) $N = 7$ (c) $N = 25$
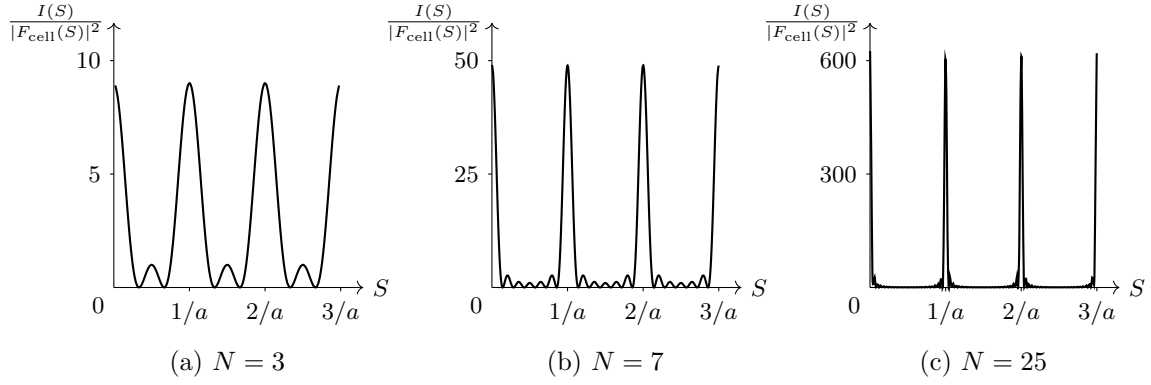
Let's plot this function at different values of N and see how they look like.

We see that the functions have principal maxima at $S = k/a$ for integer values of k, and there are $N - 2$ subsidiary maxima between the principal maxima. As we increase N, the principal maxima becomes too strong that we can no longer see the subsidiary maxima. We can see this by taking the limit

$$\lim_{S \to k/a} \frac{\sin^2(\pi N a S)}{\sin^2(\pi a S)} = \lim_{S \to k} \left(\frac{\sin N k \pi}{\sin k \pi} \right)^2 = \lim_{S \to k} \left(\frac{N \pi \cos N k \pi}{\pi \cos k \pi} \right)^2 = N^2 \,, \tag{3.19}$$

so the height of the principal maxima is N^2. Hence, in the limit of large N (in real-life crystals, $N \sim 10^{23}$), we can well-approximate the diffraction pattern of single crystals as discrete beams, separated by $1/a$.

Similarly, in a 3D crystals, the diffraction intensity will only be observable at discrete values of $\mathbf{S}$ separated by $1/\|\mathbf{a}\|$, $1/\|\mathbf{b}\|$ and $1/\|\mathbf{c}\|$. This forms what is called a *reciprocal lattice*, with lattice vectors $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$ given by

$$\mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{V} \qquad\qquad \mathbf{b}^* = \frac{\mathbf{c} \times \mathbf{a}}{V} \qquad\qquad \mathbf{c}^* = \frac{\mathbf{a} \times \mathbf{b}}{V} \,, \tag{3.20}$$

where $V = \mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})$ is the volume of the unit cell. We will only observe diffracted beams with

$$\mathbf{S} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \,, \tag{3.21}$$

i.e. on the reciprocal lattice points. We will show later that this corresponds to the same h, k, l as in the Miller planes in Bragg's description of diffraction which you might have seen if you take Part IA Material Sciences.

It is called the reciprocal lattice because it lives in the reciprocal space (Fourier domain). In fact, the reciprocal lattice is the Fourier transform of the real lattice. The unit of the reciprocal lattice vectors are length^{-1}, and their magnitudes are given by

$$\|\mathbf{a}\| = \frac{\|\mathbf{b}\| \|\mathbf{c}\| \sin \alpha}{V} \qquad \|\mathbf{b}\| = \frac{\|\mathbf{c}\| \|\mathbf{a}\| \sin \beta}{V} \qquad \|\mathbf{c}\| = \frac{\|\mathbf{a}\| \|\mathbf{b}\| \sin \gamma}{V} \,, \tag{3.22}$$

where α is the angle between $\mathbf{b}$ and $\mathbf{c}$, *etc.* This means that we can view the reciprocal lattice as "the lattice of periodicities in a crystal". To see this, let's consider all the possible set of repeated parallel planes that are compatible with the periodicity of the crystal. By being compatible with the periodicity, we require it to look identical in different unit cells, which requires the planes to intersect with the each edge of the lattice an integer amount of time. This allows us to define the *Miller indices* for repeated planes in crystals by specifying how many times the plane intersect with the edge of the cell in each direction. If we put the first plane at the origin and the second plane intersects the axes at $1/h$, $1/k$ and $1/l$ for $h, k, l \in \mathbb{Z}$, then we would label these planes as (hkl). Then this set of planes will intersect $\mathbf{a}$ axis h times, $\mathbf{b}$ axis k times and $\mathbf{c}$ axis l times.
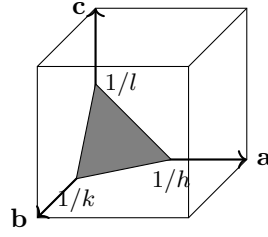
Figure 3.1: A (hkl) plane in a unit cell. There will be another $\max(h,k,l)$ planes parallel to this in this cell, intersecting $\mathbf{a}$ axis at $1/h, 2/h, \ldots, 1$, $\mathbf{b}$ axis at $1/k, 2/k, \ldots, 1$ and $\mathbf{c}$ axis at $1/l, 2/l, \ldots, 1$.
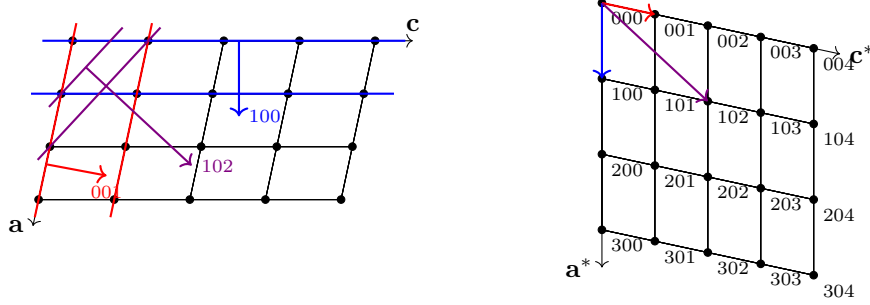

Figure 3.2: Constructing the reciprocal lattice using planes.

We can use these planes to construct the reciprocal lattice. Consider viewing the lattice along $\mathbf{b}$ direction, and constructing planes of $(h0l)$ types. For each set of plane, if we draw a vector perpendicular to these planes and magnitude reversely proportional to the interplanar spacing, then the end of these vectors will form the $(h0l)$ section of the reciprocal lattice.

By the definition of the reciprocal lattice vectors, it is easy to see that

$$\mathbf{i} \cdot \mathbf{j}^* = \delta_{ij} \,, \tag{3.23}$$

$i, j \in \{a, b, c\}$. Hence, by expanding $\mathbf{r} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c}$ and $\mathbf{S} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$, we can see that

$$\begin{aligned}
\mathbf{r} \cdot \mathbf{S} = {} & xh\mathbf{a} \cdot \mathbf{a}^* + xk\mathbf{a} \cdot \mathbf{b}^* + xl\mathbf{a} \cdot \mathbf{c}^* \\
& yh\mathbf{b} \cdot \mathbf{a}^* + yk\mathbf{b} \cdot \mathbf{b}^* + yl\mathbf{b} \cdot \mathbf{c}^* \\
& zh\mathbf{c} \cdot \mathbf{a}^* + zk\mathbf{c} \cdot \mathbf{b}^* + zl\mathbf{c} \cdot \mathbf{c}^* \\
= {} & xh + yk + lz \,.
\end{aligned} \tag{3.24}$$

Therefore for a single crystal, the structure factor can be rewritten as

$$F(h,k,l) = \int \mathrm{d}x \, \mathrm{d}y \, \mathrm{d}z \, \rho(x,y,z) e^{2\pi i (hx + ky + lz)} \,. \tag{3.25}$$

3.3 Bragg's Law

Here we present an alternative view of diffraction in a single crystal, which might be familiar from Part IA Material Sciences. We can think of the diffracted beam as being reflected by the planes in crystals, which are known as the Bragg's planes. The scattering vector is bisecting the incoming and outgoing rays, so it is perpendicular to those imaginary mirror planes. Now for a constructing interference to occur, we need the path difference of light reflected by consecutive Bragg planes to be an integer multiple of the wavelength, so
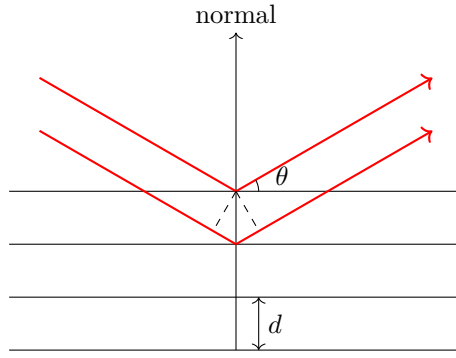
$$n\lambda = 2d \sin \theta \,, \tag{3.26}$$

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Figure 3.3: Diffraction using Bragg planes.

where θ is the angle between the planes and the beams, and d is the interplanar spacing. This factor of n can be omitted since diffraction from with $n > 1$ from a set of planes with spacing d is equivalent to diffraction with $n = 1$ from planes with spacing d/n, so we can instead think of them as being reflected from a high-order plane. For example, a $n = 4$ reflection from 100 planes is equivalent to a $n = 1$ reflection from 400 planes. Therefore, we have the Bragg's law

$$\lambda = 2d \sin \theta \tag{3.27}$$

for diffraction to be observed. We have defined $\|\mathbf{S}\| = 2 \sin \theta / \lambda$, and so $\|\mathbf{S}\| = 1/d$. This again shows why diffraction is only observed on reciprocal lattice points.

3.4 Practical Measurements of Single-Crystal X-Ray Diffraction

Suppose we are measuring the diffraction from a particular single crystal. Since a crystal has a defined orientation, a certain scattering vector $\mathbf{S} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ will appear in a well-defined direction relative to the crystal (perpendicular to the hkl planes). We can think the reciprocal lattice is attached to the crystal, and hence to measure a particular hkl diffraction, we need to arrange the incident beam to a particular direction relative to the crystal given by the Bragg's law. This require us to be able to flexibly adjust the relative orientation of the incident beam, the detector and the crystal.
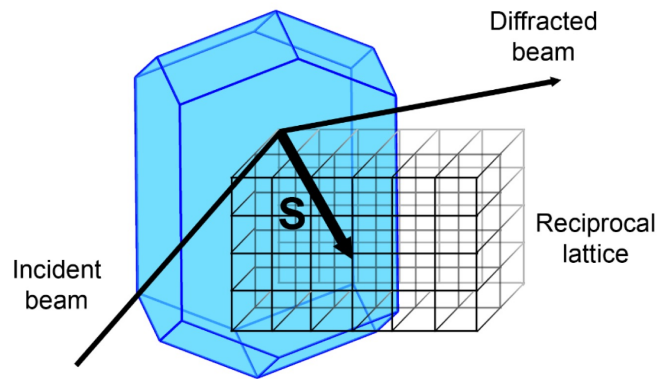

Figure 3.4: A schematic illustration of diffraction in a single crystal.

Practically, it is very difficult to move the X-ray source, so we have to move the crystal and the detector. If the source and the detector is making an angle 2θ, then this will correspond to a scattering vector of length $2 \sin \theta / \lambda$ and direction bisecting the the line from the crystal to the source
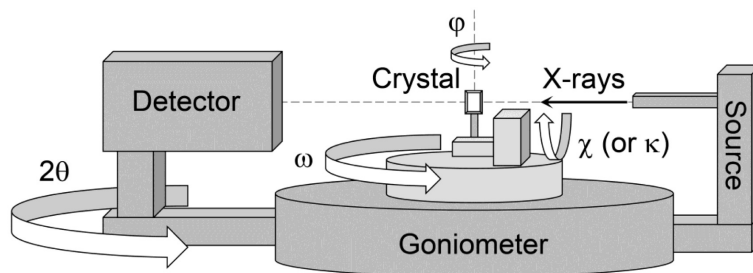
24

Figure 3.5: Apparatus to measure the X-ray diffraction of a single crystal practically.

and to the detector. If this scattering vector happens to hit one of the reciprocal lattice point, then we will see a non-zero diffracted intensity in the detector. To make that happen, we have to be able to freely rotate the crystal around all 3 directions, so that we are effectively moving the reciprocal lattice attached to the crystal. This is achieved using a *goniometer.*

The outcome of a single-crystal X-ray diffraction measurement can be conceptually divided into two parts.

1. *Geometrical information.* From the value of $\mathbf{S} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ we measured non-zero diffraction intensity, we can infer the reciprocal lattice vectors, and hence the real lattice vectors of the crystal. This can be done using only a small proportion of all the diffraction data, so only costs a few minutes.

2. *A list of diffracted intensity.* Once the geometry of the crystal in known, we can point the crystal and the detector only to where we know that there will be diffraction occurring. Then we can get a list of *hkl* values of measured diffracted beams and the corresponding diffraction intensities $|F(hkl)|^2$. To calculate the Patterson function (or the electron density if we somehow figure out the phases of the beams using methods that will be introduced latter), we need the structure factor of the whole reciprocal space. This is not practical to do since there will be some maximum $\|\mathbf{S}\|$ value we are able to reach, and the diffraction will be weak for high *hkl* values. What we can do is to measure as many diffracted peaks as possible. This is generally take hours, and hence X-ray diffraction is a slow technique, and the resulting structures are usually time-averaged.

3.5 The Independent Atom Model

Although $\rho(\mathbf{r})$ is a continuous function, we are generally only interested in the positions and types of atoms. We will see how can we make further progress if we introduce an atomic picture.

We will make the following assumptions.

1. The electron density is not continuous, but instead gathered into isolated, individual atoms at fixed sites. The atoms are spherical.

2. All electrons are located within atoms. Delocalised electrons or electrons in chemical bonds that are between atoms are neglected.

This formalism is known as the *independent atom model* (IAM). The second assumption seems like a fairly suspicious one. As chemists, we all know that chemical structures are held together by chemical bonds, and covalent bonds definitely involve the sharing of atoms. However for most elements, the majority of electrons are core electrons, which indeed involves little in bonding and are very localised. An obvious exception is hydrogen — we will discuss more on hydrogen later.

Now, if we describe the electron density of a atom labelled n as a spherically symmetric function $\rho_{\text{atom},n}(\mathbf{r})$, then the total electron density in the crystal is

$$\rho(\mathbf{r}) = \sum_n \rho_{\text{atom},n}(\mathbf{r}) * \delta(\mathbf{r} - x_n\mathbf{a} - y_n\mathbf{b} - z_n\mathbf{c}), \tag{3.28}$$

where (x_n, y_n, z_n) is the fractional coordinate of atom n and the sum is taken over all atoms in the crystal. Now from the convolution theorem, the structure factor of the cell is

$$\begin{aligned}
F(\mathbf{S}) &= \mathcal{F}[\rho(\mathbf{r})] \\
&= \sum_n \mathcal{F}[\rho_{\text{atom},n}(\mathbf{r})]\mathcal{F}[\delta(\mathbf{r} - x_n\mathbf{a} - y_n\mathbf{b} - z_n\mathbf{c})] \\
&=: \sum_n f_n(\mathbf{S}) \exp(2\pi i \mathbf{r}_n \cdot \mathbf{S}) \\
&= \sum_n f_n(\mathbf{S}) \exp(2\pi i(hx_n + ky_n + lz_n)),
\end{aligned} \tag{3.29}$$

where the f_n is the Fourier transform of $\rho_{\text{atom},n}(\mathbf{r})$ called the *atomic scattering factor*. It can be seen as the diffraction of a single atom, and has unit of electrons. Since we assume $\rho_{\text{atom},n}(\mathbf{r})$ is spherically symmetric, $f(\mathbf{S})$ is spherically symmetric as well. Although some other more complicated model may apply (e.g. multipole expansion) to make both $\rho_{\text{atom},n}(\mathbf{r})$ and $f(\mathbf{S})$ not spherically symmetric, we shall not concern with these.

3.5.1 Atomic Scattering Factor

For the special case of $\mathbf{S} = \mathbf{0}$,

$$F(\mathbf{0}) = \sum f_n(\mathbf{0}) = \int dV\, \rho(\mathbf{r}). \tag{3.30}$$

For this to hold, we must have $f_n(\mathbf{0})$ equal to the total number of electrons in atom n. As $\mathbf{S}$ moves away from zero, the value of f_n must change to reflect the interference occurring between X-rays scattered from different positions within the atom's volume. Under the assumption that $f(\mathbf{S})$ is spherically symmetric, it is only dependent on $\|\mathbf{S}\| = (2\sin\theta)/\lambda$, so the scattering factor is usually fitted to parameterised function of $(\sin\theta)/\lambda$ as

$$f\left(\frac{\sin\theta}{\lambda}\right) = c + \sum_{i=1}^4 a_i \exp\left[-b_i\left(\frac{\sin\theta}{\lambda}\right)^2\right] \tag{3.31}$$

with nine tabulated parameters for each atom. These parameters are known as Cromer–Mann coefficients.

Some examples of spherically symmetric atomic scattering factors are shown in figure 3.6. We can see that $f(0)$ is equal to the number of electrons in the atom/ion. Heavier elements generally have larger atomic scattering factors. For species having the same number of electrons, if the atom/ion is larger, than the scattering factors drops off more quickly. This is because a bigger atom would induce a larger path difference in diffraction, and hence leads to lower f_n.[10]

These factors are derived quantum mechanically from atomic wavefunctions, which are effectively at $0\,\text{K}$. In practice, atoms in crystals are typically slightly displaced from their average position — this may be dynamic (due to thermal vibration) or static. This effectively makes the atom look larger, and hence the atomic scattering factor will drop off more quickly. This will put a extra *Debye–Waller factor*

$$e^{-8\pi^2 \langle u^2 \rangle \sin^2\theta/\lambda} \tag{3.32}$$

onto the atomic scattering factor at $0\,\text{K}$.

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[10]You can understand this by modelling the electron density in an atom as a Gaussian of width σ. Its Fourier transform (the scattering factor) will be a Gaussian of width σ^{-1}. Hence, if the atom is larger, then the scattering factor has smaller width. If we have a "point" atom, whose electron density is a delta function, then its Fourier transform is a constant, so the scattering factor will not drop off.
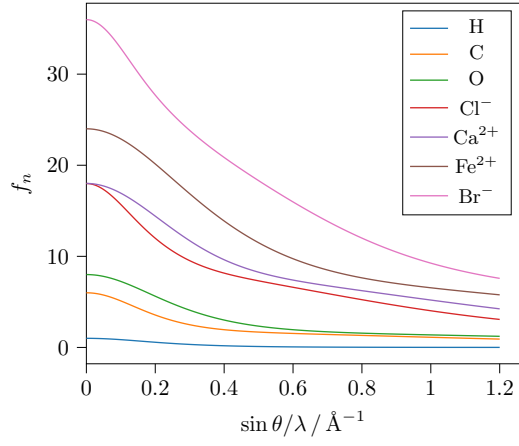
(a) Scattering factors of different species with different numbers of electrons.
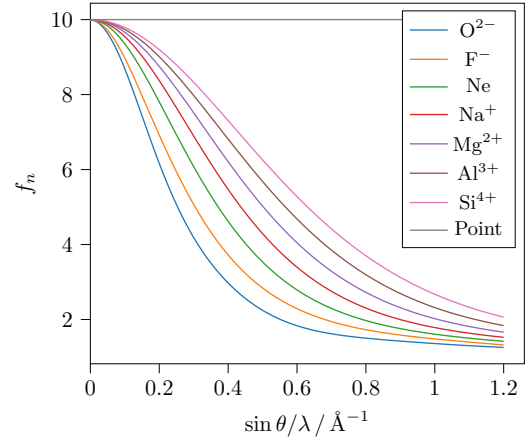
(b) Scattering factors of different species with the same number of electrons.

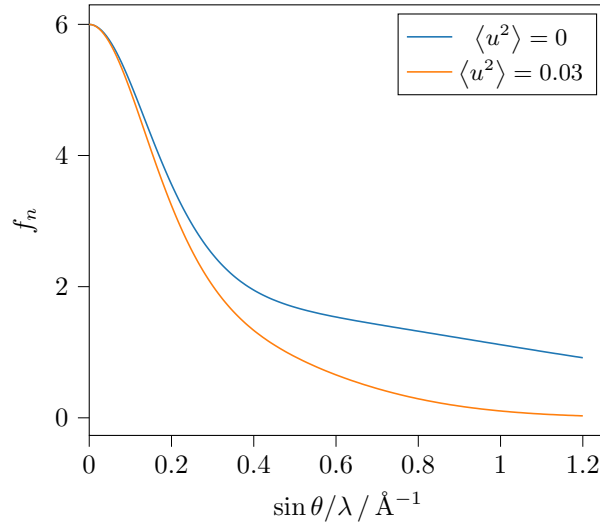Figure 3.6: Atomic scattering factors of different species.

Figure 3.7: The atomic scattering factor of C with and without isotropic displacement.

To conclude, under the independent atomic model, the structure factor of an atomic single crystal is

$$F(h, k, l) = \sum_n f_n \exp[2\pi i(hx_n + ky_n + lz_n)], \tag{3.33}$$

where n is taken over all atoms in the crystals. However, we have seen that $|F_{hkl}|^2 = N^2 |F_{\text{cell}}(hkl)|^2$, so the relative intensities of the diffracted beams are proportional to $|F_{\text{cell}}(hkl)|^2$. To solve for this, we only need to sum over all atoms in a unit cell

$$F_{\text{cell}}(h, k, l) = \sum_n f_n \exp[2\pi i(hx_n + ky_n + lz_n)]. \tag{3.34}$$

From now on we will drop the "cell" subscript, and we will always refer to F_{cell}. We see that this has now becomes a Fourier series. To figure out the electron density, we apply the inverse Fourier transform and we get

$$\rho(x, y, z) = \frac{1}{V_{\text{cell}}} \sum_h \sum_k \sum_l F_{hkl} \exp[-2\pi i(kx + ky + lz)], \tag{3.35}$$

where $1/V_{cell}$ is volume of the unit cell for normalisation.

4 Symmetry in Crystals

In the previous chapter, we have already exploited the translation symmetry of crystals, which is their defining properties. Typically, crystals also displays other types of symmetries, such as rotations, mirror planes and inversions *etc.* (although they do not have to). This leads us to something looks like *point groups* that describe the symmetry of molecules, but in crystals, we have additional translational symmetry, so they are instead known as *space groups*. Rather remarkably, there are only 230 possible 3D three groups — the number is finite, unlike for point groups where there can be an infinite number of them. This is because not all symmetry elements are compatible with the translational symmetry, leaving us with a limited possible combination of symmetry elements. The most famous example is probably that a crystal can never have a five-fold rotation axis[11].
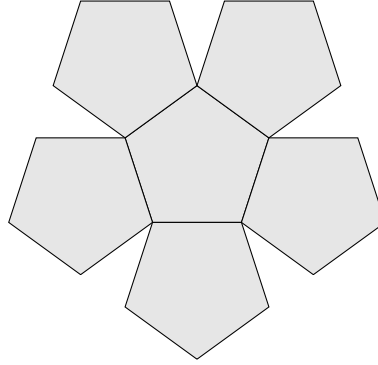

Figure 4.1: Five fold rotational symmetry is not compatible with translational symmetry.

Let's first see how various symmetry operators affect the diffraction patterns.

4.1 Symmetry Operations

4.1.1 Inversion Centre

Suppose there is a inversion centre in the crystal, then by translational symmetry there must be one in each unit cell. We set it to be the origin of the unit cell, then for each atom at (x_n, y_n, z_n), there must be the same atom at $(-x_n, -y_n, -z_n)$. Therefore, when calculating the structure factor, instead of summing over all N atoms in the unit cell, we can sum over the $N/2$ pairs:

$$
\begin{aligned}
F(hkl) &= \sum_{n=1}^{N/2} f_n \left[\exp[2\pi i(hx_n + ky_n + lz_n)] + \exp[-2\pi i(hx_n + ky_n + lz_n)] \right] \\
&= \sum_{n=1}^{N/2} 2f_n \cos[2\pi(hx_n + ky_n + lz_n)] . \\
&= \sum_{n=1}^{N} f_n \cos[2\pi(hx_n + ky_n + lz_n)] .
\end{aligned}
\tag{4.1}
$$

Two immediate consequences are

- The structure factor is always real (phase is 0 or π).

- $F(hkl) = F(\bar{h}\bar{k}\bar{l})$.

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[11]Something known as a *quasi-crystal* can, but it has no translational symmetry.

Therefore, the structure factor also shows a inversion symmetry, with point group symmetry (at least) C_i.

However, this is not something we can really exploit. This is because we can only measure $I(hkl) = |F(hkl)|^2$, or equivalently the modulus of the structure factor.

Theorem 4.1 (Friedel's law). For any crystal,

$$|F(hkl)| = \left|F(\bar{h}\bar{k}\bar{l})\right| . \tag{4.2}$$

Proof. This is because

$$
\begin{aligned}
F(\bar{h}\bar{k}\bar{l}) &= \sum_n f_n \exp[-2\pi i(hx_n + ky_n + lz_n)] \\
&= \left[\sum_n f_n \exp[2\pi i(hx_n + ky_n + lz_n)]\right]^* \\
&= F(hkl)^* .
\end{aligned}
\tag{4.3}
$$

They are complex conjugate, so they have the same modulus and diffraction intensity. $\qquad \square$

Therefore, the diffraction intensities of all crystals exhibit centres of inversion.

In practise, when describing a diffraction pattern, we often picture a reciprocal lattice with its lattice points scaled by the intensity of diffraction. This construction is called the *intensity-weighted reciprocal lattice*. The intensity-weighted reciprocal lattice of all crystals show a C_i point symmetry.

Aside: Intensity Statistics

However, it is possible to infer the presence of an inversion centre from the diffraction pattern base on the intensities. If a centre of symmetry is not present, then generally $F(hkl)$ would be a complex number, while if there is a centre of symmetry is present, $F(hkl)$ can only be a real number. A real $F(hkl)$ has a higher probability to have a modulus close to zero than a complex one, and so we have a higher change to observe weak $F(hkl)$ values if an inversion centre is present.

The above argument sounds a bit dubious. We can formalise it a little bit. Suppose the f_n values in a crystal follow some distribution with mean μ and variance σ^2, and the phase of each atom ϕ_n is somehow random (uniformly distributed) between 0 and 2π.

If there is a centre of inversion, then

$$F = \sum_n f_n \cos \phi_n . \tag{4.4}$$

$\cos \phi_n$ has a mean 0 and variance $\frac{1}{2}$. By central limit theorem, if N is large, then F is a Gaussian with expectation value of

$$\mathbb{E}[F] = N\mathbb{E}[f_n \cos \phi_n] = N\mathbb{E}[f_n]\mathbb{E}[\cos \phi_n] = 0 \tag{4.5}$$

and variance

$$
\begin{aligned}
\mathrm{Var}[F] &= N \, \mathrm{Var}[f_n \cos \phi_n] \\
&= N \left[(\mathrm{Var}[f_n] + \mathbb{E}[f_n]^2)(\mathrm{Var}[\phi_n] + \mathbb{E}[\phi_n]^2) - \mathbb{E}[f_n]^2\mathbb{E}[\phi_n]^2\right] \\
&= \frac{N}{2}(\sigma^2 + \mu^2) .
\end{aligned}
\tag{4.6}
$$

Let's denote this variance σ_F^2, then the for the centrosymmetric case, the probability distribution function of $|F|$ is

$$g(x) = \frac{2}{\sigma_F \sqrt{2\pi}} \exp\left[-\frac{x^2}{2\sigma_F^2}\right], \qquad x \geq 0. \tag{4.7}$$

If there is not a symmetry of inversion, however, then

$$F = \sum_n f_n (\cos\phi_n + i\sin\phi_n). \tag{4.8}$$

The real and imaginary part of F is then follows the same Gaussian distribution as the central symmetric case, with mean 0 and variance σ_F^2. However, this is a 2D Gaussian. The probability density function of $|F|$ is then

$$h(x) = \int_0^{2\pi} \mathrm{d}\theta \, x \frac{1}{2\pi\sigma_F^2} \exp\left[-\frac{x^2}{2\sigma_F^2}\right]$$
$$= \frac{x}{\sigma_F^2} \exp\left[-\frac{x^2}{2\sigma_F^2}\right]. \tag{4.9}$$

It has vanishing probability density to be close to 0.
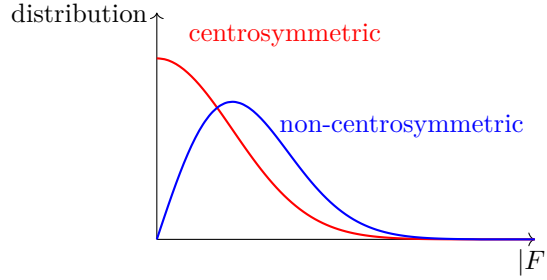
4.1.2 Mirror Plane

Consider a mirror plane perpendicular to $\mathbf{b}$ axis passing through the origin. This relates a atom at (x, y, z) to another at $(x, -y, z)$. The structure factor can be simplified to

$$F(hkl) = \sum_{n=1}^{N/2} f_n [\exp[2\pi i(hx_n + ky_n + lz_n)] + \exp[2\pi i(hx_n - ky_n + lz_n)]]$$
$$= \sum_{n=1}^{N} f_n \cos(2\pi k y_n) \exp[2\pi i(hx_n + lz_n)]. \tag{4.10}$$

Cosine is a even function, so

$$F(hkl) = F(h\bar{k}l), \tag{4.11}$$

and $|F(hkl)|^2 = |F(h\bar{k}l)|^2$. Therefore intensity-weighted reciprocal lattice will also have a mirror plane perpendicular to $\mathbf{b}^*$ axis. Combined with the i symmetry of Friedel pairs, we have

$$|F(hkl)|^2 = |F(h\bar{k}l)|^2 = |F(\bar{h}k\bar{l})|^2 = |F(\bar{h}\bar{k}\bar{l})|^2, \tag{4.12}$$

and so the intensity-weighted reciprocal lattice will have a C_{2h} symmetry. Note that i and σ_h generates the C_2 symmetry.
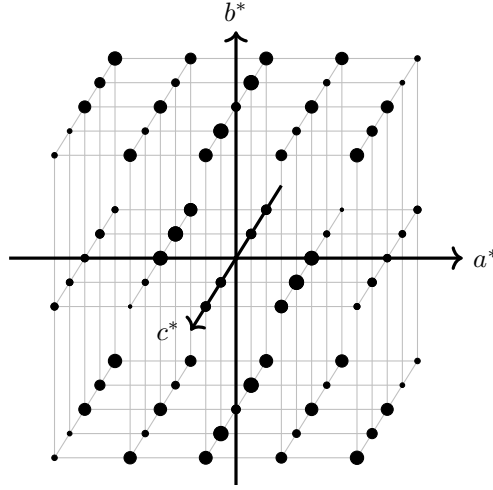
Figure 4.2: A intensity-weighted reciprocal lattice with C_{2h} symmetry.

4.1.3 Rotation Axes

Now let's consider the effect of a rotation axis. A m-fold rotation axis will rotate atoms by $2\pi/m$ radians around the defined axis. For simplicity, we will only consider the 2-fold axis. We set the axis such that the rotation axis passes through the origin and is parallel to the **b** axis of the unit cell, so that for each atom at (x_n, y_n, z_n), there is also a same atom at $(-x, y, -z)$. In this case, we may simplify the structure factor to

$$F(hkl) = \sum_n^{N/2} f_n[\exp[2\pi i(hx_n + ky_n + lz_n)] + \exp[2\pi i(-hx_n + ky_n - lz_n)]]$$

$$= \sum_n^{N} f_n \cos[2\pi(hx_n + lz_n)] \exp[2\pi i k y_n]. \tag{4.13}$$

Therefore,

$$F(hkl) = F(\bar{h}k\bar{l}). \tag{4.14}$$

The intensity-weighted reciprocal lattice therefore also has a 2-fold rotation axis along $\mathbf{b}^*$. Again, the Friedel's law still applies, so

$$|F(hkl)|^2 = |F(h\bar{k}l)|^2 = |F(\bar{h}k\bar{l})|^2 = |F(\bar{h}\bar{k}\bar{l})|^2. \tag{4.15}$$

Therefore the intensity-weighted reciprocal lattice has a C_{2h} point group symmetry (formally known as the *Laue group*), as i and C_2 further generates a σ_h symmetry.

Finally, note that if a crystal structure exhibits a 2-fold rotation axis along one direction, or a mirror plane perpendicular to some direction, this axis must be perpendicular to two of the lattice vectors, otherwise the rotated cell will have a different orientation, and the translational symmetry will be broken. For example, if a 2-fold axis is parallel to **b**, then **b** must be perpendicular to both **a** and **c**. This means that the structure is at least *monoclinic*, meaning that two of the unit-cell angles must be 90°. By convention, we usually choose $\alpha = \gamma = 90°$ and $\beta \neq 90°$ (although it could be that $\beta = 90°$, but then we will classify the crystal to have a higher symmetry e.g. *orthorhombic*).

4.1.4 Screw Axes

The fact that crystals are infinitely extended through the space leads us to some extra symmetry elements that are not present in point groups. Specifically, we can combine rotations or reflections with translations.

A n_m-screw axis stands for a rotation of $2\pi/n$ around the axis, and then a translation of m/n times the length of the lattice vector in that direction. We will only consider the 2-fold screw axis 2_1, and we will make the axis coincide with the **b** vector. This is a rotation of 180° along **b**, and then translate by $\mathbf{b}/2$, relating (x, y, z) to $(-x, \frac{1}{2} + y, -z)$. The resulting structure factor is

$$F(hkl) = \sum_{n=1}^{N/2} f_n \exp(2\pi i k y_n)[\exp[2\pi i(hx_n + lz_n)] + (-1)^k \exp[-2\pi i(hx_n + lz_n)]]$$

$$= \sum_{n=1}^{N} f_n \exp(2\pi i k y_n) \times \begin{cases} \cos[2\pi(hx_n + lz_n)] & \text{if } k \text{ is even} \\ i\sin[2\pi(hx_n + lz_n)] & \text{if } k \text{ is odd.} \end{cases} \tag{4.16}$$

Consequently,

$$F(hkl) = \begin{cases} F(\bar{h}k\bar{l}) & \text{if } k \text{ is even} \\ -F(\bar{h}k\bar{l}) & \text{if } k \text{ is odd,} \end{cases} \tag{4.17}$$

but it either case,

$$\left|F(hkl)\right|^2 = \left|F(\bar{h}k\bar{l})\right|^2 . \tag{4.18}$$

Combining with the Friedel pair relationship, we see that the 2_1 screw axis has exactly the same effect on the symmetry of the diffracted intensity as the 2-fold rotation axis, both having C_{2h}.

Moreover, if we consider the spacial case of $h = l = 0$, then the structure factor for $0k0$ reduces to

$$F(0h0) = \sum_{n}^{N/2} f_n \exp(2\pi i k y_n)[1 + (-1)^k] = \begin{cases} \sum_{n}^{N} f_n \exp(2\pi i k y_n) & \text{if } k \text{ is even} \\ 0 & \text{if } k \text{ is odd.} \end{cases} \tag{4.19}$$

The structure factors for all $0k0$ beams are zero if k is odd — this result is independent of the atomic coordinates and is purely originated from symmetry. This is known as a *systematic absence*. The pattern of the systematic absence depends on the direction of the screw axis:

- 2_1 axis parallel to **a**: $(h00)$ absent for odd h.

- 2_1 axis parallel to **b**: $(0k0)$ absent for odd k.

- 2_1 axis parallel to **c**: $(00l)$ absent for odd l.

We have a good explanation for this. Consider a 2_1 axis along **b**. If we project the 3D crystal structure into one dimension along **b**, i.e. we are not caring the x and z coordinates, the presence of a 2_1 screw axis doubles the periodicity along **b** direction, and hence the periodicity in the reciprocal lattice will be halved. This is exactly what a $0k0$ beam is detecting: as reflections from a $(0k0)$ Bragg's plane has contributions from all x and z coordinates for a certain y value, it is only able to tell the periodicity along y direction, and it finds that things are repeating twice as often.

4.1.5   Glide Planes

A glide plane is a mirror plane reflection followed by a translation one half of the lattice. We will consider a c-glide perpendicular to b, which is a reflection about a mirror plane perpendicular to b followed by a translation of $\frac{1}{2}\mathbf{c}$, relating atoms at (x, y, z) and $x, -y, \frac{1}{2} + z$. The structure factor equation becomes

$$F(hkl) = \sum_{n}^{N/2} f_n \exp[2\pi i(hx_n + lz_n)][\exp(2\pi i k y_n) + (-1)^l \exp(2\pi i k y_n)]$$

$$= \sum_{n}^{N} f_n \exp[2\pi i(hx_n + lz_n)] \times \begin{cases} \cos(2\pi k y_n) & \text{if } l \text{ is even} \\ i\sin(2\pi k y_n) & \text{if } l \text{ is odd.} \end{cases} \tag{4.20}$$

This means that

$$F(hkl) = \begin{cases} F(h\bar{k}l) & \text{if } l \text{ is even} \\ -F(h\bar{k}l) & \text{if } l \text{ is odd,} \end{cases} \tag{4.21}$$

but it either case,

$$\left|F(hkl)\right|^2 = \left|F(h\bar{k}l)\right|^2 . \tag{4.22}$$

The glide plane produces a mirror plane in the diffraction pattern, just as a normal mirror plane would do, and combining with Friedel pair relation, the diffraction pattern again has a C_{2h} symmetry.

Consider $k = 0$, the structure factor reduces to

$$F(h0l) = \begin{cases} \sum_n^N f_n \exp[2\pi i(hx_n + lz_n)] & \text{if } l \text{ is even} \\ 0 & \text{if } l \text{ is odd.} \end{cases} \tag{4.23}$$

Therefore, a c-glide perpendicular to b produces systematic absences of $F(h0l)$ for odd l. We again have a good explanation to it: we set k to 0 so the beam is ignorant of us changing the y coordinate by reflection, and now the translation of $\frac{1}{2}\mathbf{c}$ doubles the periodicity along c directions, so the reciprocal lattice is doubled in length in that direction.

To conclude the systematic absence for glide planes:
Glide plane perpendicular to a:

- b-glide: $(0kl)$ absent if k odd.

- c-glide: $(0kl)$ absent if l odd.

- n-glide: $(0kl)$ absent if $k+l$ odd. (*n*-glide means translation by a half in both y and z directions)

Glide plane perpendicular to b:

- a-glide: $(h0l)$ absent if h odd.

- c-glide: $(h0l)$ absent if l odd.

- n-glide: $(h0l)$ absent if $h + l$ odd.

Glide plane perpendicular to c:

- a-glide: $(hk0)$ absent if h odd.

- b-glide: $(hk0)$ absent if k odd.

- n-glide: $(hk0)$ absent if $h + k$ odd.

4.2 Lattice Types

In some cases, it is more preferable to define a unit cell that is not primitive, i.e. containing more than one lattice points. This is possibly because the non-primitive unit cell has a higher symmetry, or it allows the symmetry elements to align with the axes of the unit cell.

There are in total four types of 3D unit cells. The first type is *primitive*, denoted P, where the lattice points are at the corners of the cells only, so that there is only one lattice point in the unit cell. It is also possible for a cell to also contain lattice points in the centre of two opposite faces. This is conventionally chosen to be the ab face, so this type of cell is known as *C-centred*. Another possibility is to contain a second lattice point at the centre of the cell, and this is known as *body-centred* or *I-centred*. Finally, we can have lattice points at the centres of all unit-cell faces, which is known as *face-centred* or *F-centred*.

(a) mirror plane perpendicular to b.
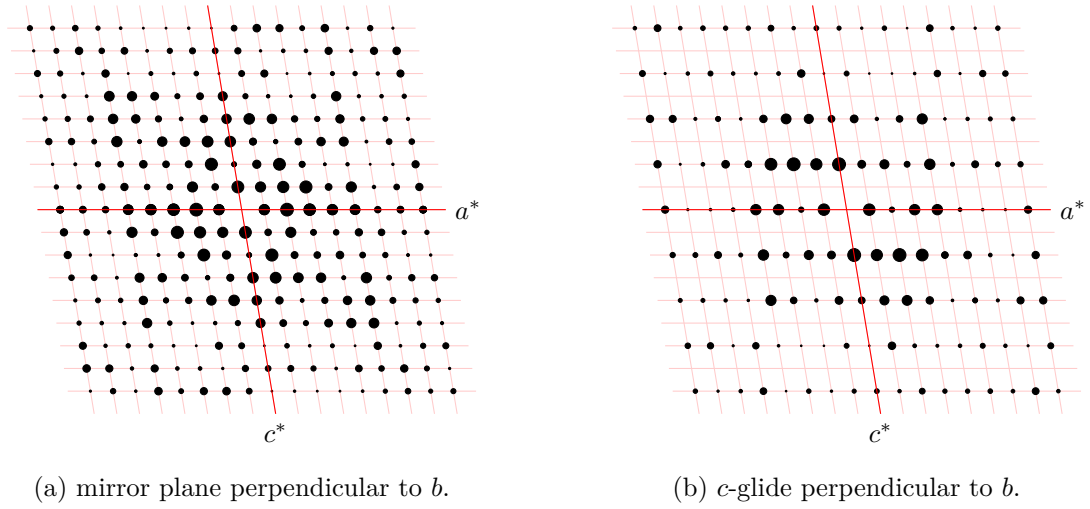

(b) c-glide perpendicular to b.

Figure 4.3: Schematic $(h0l)$ slices of the intensity-weighted reciprocal lattice. We see that glide planes create systematic absences, while mirror planes do not.
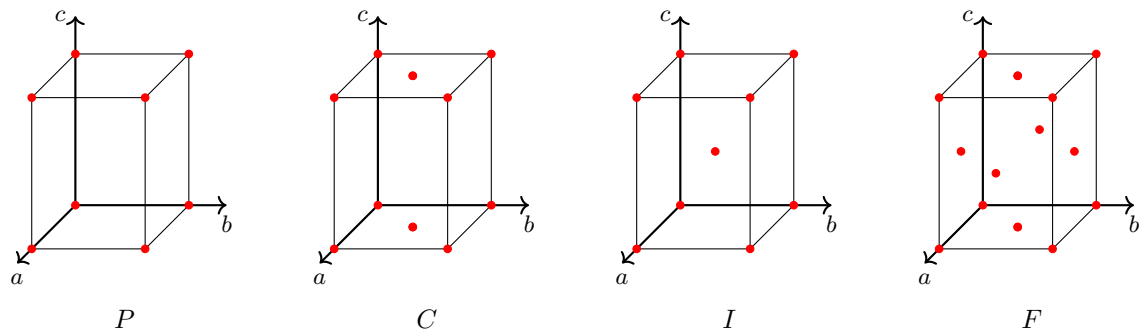

Figure 4.4: Types of unit cell centring.

Since non-primitive unit cells contain more than one lattice points, they also have systematic absences, which can be worked out using the same way as we did before.

- P: No systematic absences.

- C: (hkl) absent if $h + k = 2n + 1$.

- I: (hkl) absent if $h + k + l = 2n + 1$.

- F: (hkl) absent unless h, k, l are all odd or all even.

Heuristically, the reciprocal lattice of a P and a C lattices are themselves, the reciprocal lattice of an I lattice is a larger F lattice, and the reciprocal lattice of an F lattice is a larger I lattice.

By using a non-primitive cell, we are choosing to describe the real lattice with longer lattice vectors, so the reciprocal lattice vectors are correspondingly shorter. We are therefore using smaller reciprocal unit cells than a primitive reciprocal unit cell. Hence, systematic absences must arise.

4.3 Space Groups and Equivalent Positions

An identification of the lattice type together with a collection of symmetry operators defines a *space group*. It describes the symmetry of a crystal, just as a point group describes the symmetry of a molecules, but we have an extra translational symmetry described by the lattice type.

For example, let's consider the most common space group $P2_1/c$, where its name stands for primitive lattice, a 2_1 screw axis $\parallel b$ and a c-glide $\perp b$. These symmetry elements also create a centre of inversion. By convention, we set the inversion centre to be the origin, so that the 2_1 axis is at $(0, y, 1/4)$ and the c-glide is at $(x, 1/4, z)$. This collection of symmetry operators produces a set of coordinates that are related to each others, known as the *general equivalent positions* (GEPs). The GEPs for $P2_1/c$ are shown in the figure below.
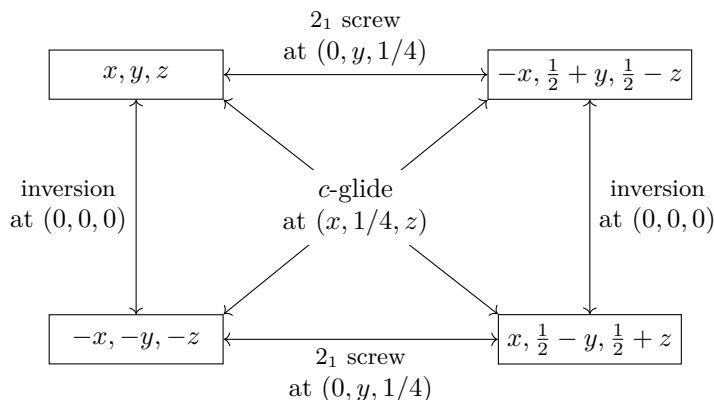

Figure 4.5: General equivalent positions in the $P2_1/c$ space group.

Therefore, there exists a minimal set of atomic coordinates that need to be specified to describe the whole unit cell (and hence the entire crystal structure), which is known as the *asymmetric unit*. The coordinates of the other atoms in the cell can be obtained by applying the symmetry elements in the space group.

However, notice that there are some special coordinates in the $P2_1/c$ group that do not produce a group of four distinct coordinates when the symmetry operators are applied. An example is $(0, 0, 0)$, for which you will only obtain two distinct coordinates $(0, 0, 0)$ and $(0, 1/2, 1/2)$ when applying the symmetry elements. Such positions are called the *special equivalent positions*. They arise because the coordinate coincide with the point group elements (centre of symmetry in this case), so it is not
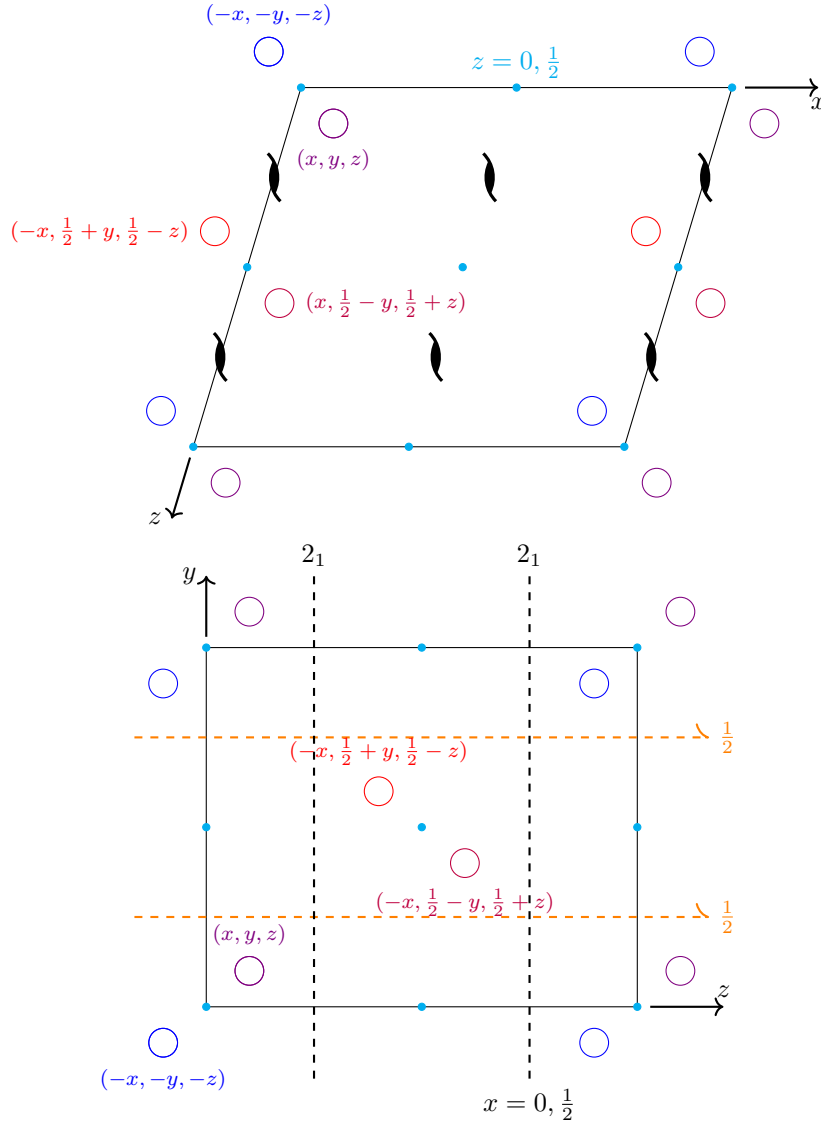
Figure 4.6: View of $P2_1/c$ space group unit cell along y axis and x axis. Note that extra symmetry elements arise automatically such that they appear twice as often as the lattice points.
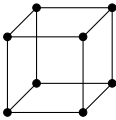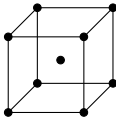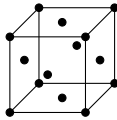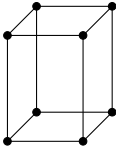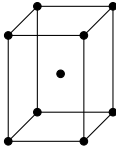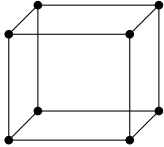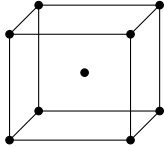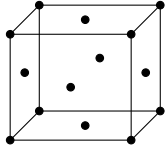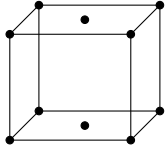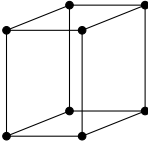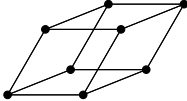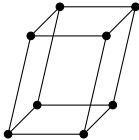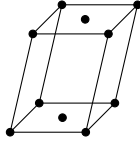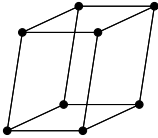
moved by those symmetry elements. Similarly, if a rotation axis or a mirror plane is present in some space group, there will be a whole line and a whole plane of special equivalent positions, respectively.

4.4 Determining Space Group

Having obtained a diffraction patter from the experiment, we should be able to easily determine the space group. First, by observing the reciprocal cell geometry, we should be able to infer the lattice vectors a, b, c and there angles α, β and γ. Then by observing the general (hkl) systematic absences, we can infer the lattice type (P, I, F or C). This will give us one of the 14 possible types of 3D lattice, known as the *Bravais lattices*.

Having determined the lattice type, we can then identify the symmetry elements in the crystal. If the intensity-weighted reciprocal lattice exhibits a C_{2h} symmetry, then there will be a C_2 axis or a mirror plane in the structure. If there are other systematic absences, then there will be glide planes

Table 1: The 14 Bravais lattices.

Crystal system	P	I	F	C
Cubic $a = b = c$ $\alpha = \beta = \gamma = 90°$				
Tetragonal $a = b \neq c$ $\alpha = \beta = \gamma = 90°$				
Orthorhombic $a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$				
Hexagonal $a = b \neq c$ $\alpha = \beta = 90°, \gamma = 120°$				
Trigonal $a = b = c$ $\alpha = \beta = \gamma \neq 90°$				
Monoclinic $a \neq b \neq c$ $\alpha = \gamma = 90°, \gamma \neq 90°, 120°$				
Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90°$				

or screw axes. We can identify the presence of inversion centres from intensity statistics.

In practice, this can be easily done using automated programs. However, for a genuine experiment, there will be measurement errors, or there might be ambiguity on whether a diffraction is too small or it is really absent. Hence, all of these assessment indicate probable space groups rather than a concrete assessment.

4.5 Symmetry in Patterson Functions

Symmetry also allows us to identify atomic coordinates directly from patterson function. Suppose we have confirmed that a crystal has a space group $P2_1/c$ from diffraction pattern, we then know that

the crystal must have the same atom at the following general equivalent positions:

$$(a): (x, y, z) \qquad (b): (-x, \tfrac{1}{2} + y, \tfrac{1}{2} - z) \qquad (c): (x, \tfrac{1}{2} - y, \tfrac{1}{2} + z) \qquad (d): (-x, -y, -z) \,.$$

This results in 16 interatomic vectors in the Patterson function: four of them are self-vectors at the origin, an the remaining twelve are non-origin vectors. Since each $A \to B$ vector will be accompanied by a $A \leftarrow B$ in reverse, these will comprise six centrosymmetric pairs:

(i) $(a) \leftrightarrow (b)$: $\pm(2x, -\tfrac{1}{2}, -\tfrac{1}{2} + 2z)$,

(ii) $(a) \leftrightarrow (c)$: $\pm(0, -\tfrac{1}{2} + 2y, -\tfrac{1}{2})$,

(iii) $(a) \leftrightarrow (d)$: $\pm(2x, 2y, 2z)$,

(iv) $(b) \leftrightarrow (c)$: $\pm(-2x, 2y, -2z)$,

(v) $(b) \leftrightarrow (d)$: $\pm(0, \tfrac{1}{2} + 2y, \tfrac{1}{2})$,

(vi) $(c) \leftrightarrow (d)$: $\pm(2x, \tfrac{1}{2}, \tfrac{1}{2} + 2z)$.

As the structure is periodic, there will be the same atom 1 unit away along any coordinate, so we can shift any coordinate by ± 1. Consequently, vector (i) is actually identical to (vi), and (ii) is identical to (v). Therefore, for the space group $P2_1/c$, we actually have two pairs of doubly-weighted peaks at $\pm(2x, \tfrac{1}{2}, \tfrac{1}{2} + 2z)$, $\pm(0, \tfrac{1}{2} + 2y, \tfrac{1}{2})$ and two pairs of singly-weighted peaks at $\pm(2x, 2y, 2z)$ and $\pm(-2x, 2y, -2z)$. Those peaks in the Patterson functions are easy to locate because of their special forms (0 or $\tfrac{1}{2}$ in some coordinates). By identifying the coordinates of these peaks in the Patterson function, we can directly work out the coordinate of these atoms.

Note that since the Patterson function only give distinct peaks for interatomic vectors between heavy atoms, this usually only allow us to work out the coordinate of the heavy atoms in the structure. However, this is usually a very important first step for a complete structure determination. Having known this initial information, we have three complementary methods to determine the coordinates of the rest of the methods. They are the *heavy atom method*, *isomorphous replacement* and *anomalous scattering*.

4.6 The Heavy Atom Method

Suppose of the N atoms in the unit cell, we know the coordinate of the M heavy atoms of them e.g. from Patterson function. We can split the structure factor into a contribution of heavy atoms and the contribution of the rest of the atoms.

$$
\begin{aligned}
F(hkl) &= \sum_{n=1}^{N} f_n \exp[2\pi i(kx_n + ky_n + lz_n)] \\
&= \sum_{n \text{ heavy}} f_n \exp[2\pi i(kx_n + ky_n + lz_n)] + \sum_{n \text{ rest}} f_n \exp[2\pi i(kx_n + ky_n + lz_n)] \\
&= F_{\text{heavy}}(hkl) + F_{\text{rest}}(hkl) \,.
\end{aligned}
\tag{4.24}
$$

From experiment, we can only measure $|F(hkl)|$, not $\Phi(hkl)$. But since we know the coordinate of the M heavy atoms, we can calculate

$$F_{\text{heavy}} = \sum_{n=1}^{M} f_n \exp[2\pi i(kx_n + ky_n + lz_n)] \,. \tag{4.25}$$

In particular, we know both the amplitude and the phase of the heavy atom contribution. Since the diffracting power of an atom f_n, is proportional to the number of electrons, which is in turn proportional to the atomic number, heavy atom contributions tends to dominate in $F(hkl)$.

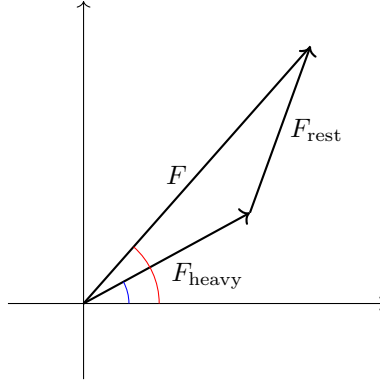$$|F_{\text{heavy}}(hkl)| \overset{?}{\gg} |F_{\text{rest}}(hkl)| \,.$$

Figure 4.7: We can use Φ_{heavy} (blue) to approximate Φ (red).

This allows us to argue that hopefully $\Phi(hkl)$ is close to $\Phi_{\text{heavy}}(hkl)$, so we can use it as an estimate of $\Phi(hkl)$. This allows us to combine the measured $|F(hkl)|$ and calculated $F_{\text{heavy}}(hkl)$ to get an estimate of the structure factor

$$F(hkl) = |F(hkl)| \exp[i\Phi(hkl)] \overset{?}{\approx} |F(hkl)| \exp[i\Phi_{\text{heavy}}(hkl)]. \tag{4.26}$$

Having obtained approximate $F(hkl)$ values, we can perform the inverse Fourier transform to get an approximated electron density

$$\rho(x, y, z) = \mathcal{I}[|F(hkl)| \exp[i\Phi(hkl)]] \tag{4.27}$$

$$\approx \mathcal{I}[|F(hkl)| \exp[i\Phi_{\text{heavy}}(hkl)]] \tag{4.28}$$

$$= \frac{1}{V_{\text{cell}}} \sum_{h,k,l} |F(hkl)| \exp[i\Phi_{\text{heavy}}(hkl) - 2\pi(hx + ky + lz)]. \tag{4.29}$$

This seems to be very crude so far, probably only slightly better than just guessing random Φ values. However, we will usually find that we are getting sufficiently close to the true ρ such that we can identify some peaks other than those due to the heavy atoms. If this is the case, we know some extra coordinates of some atoms. We can include them in our set of "heavy" atoms when calculating Φ_{heavy} — this will generally mean a better approximation of the true phase. A further inverse transform will give us a better approximation to the true electron density from which, hopefully, more atomic positions can be deduced. The iteration process can be repeated until all of the atoms are found. At this stage Φ_{heavy} will be Φ exactly, and we have completely solved the structure.
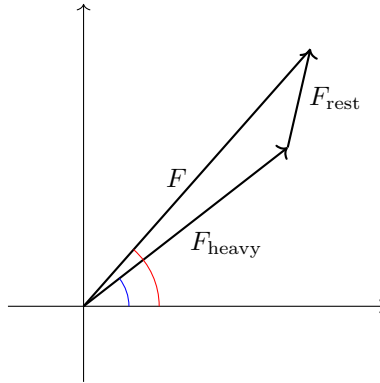

Figure 4.8: A refined approximation of Φ by including more atoms in the set of known 'heavy' atoms.

5 Phase Determining Methods

6 Direct Method and Others