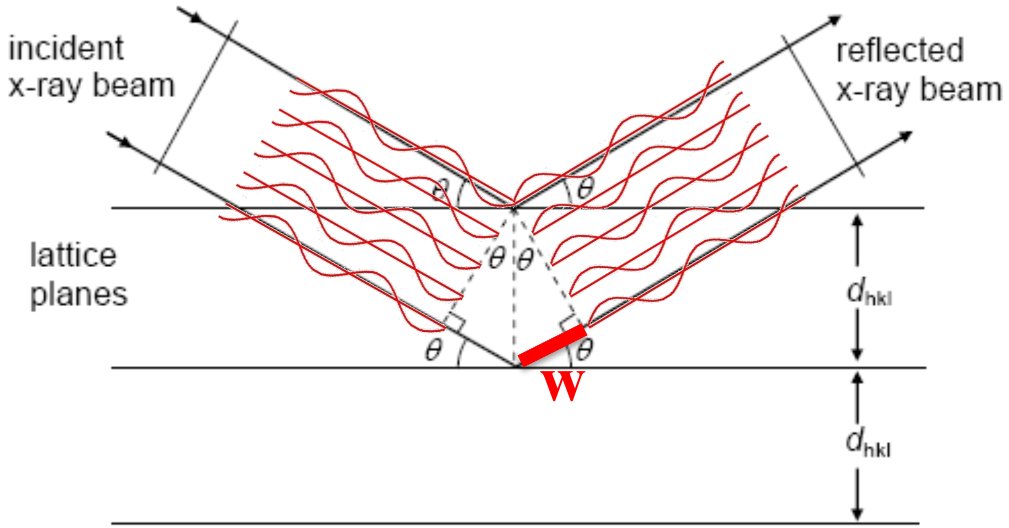
Structural Biology Methods

Fall 2024

Lecture #2

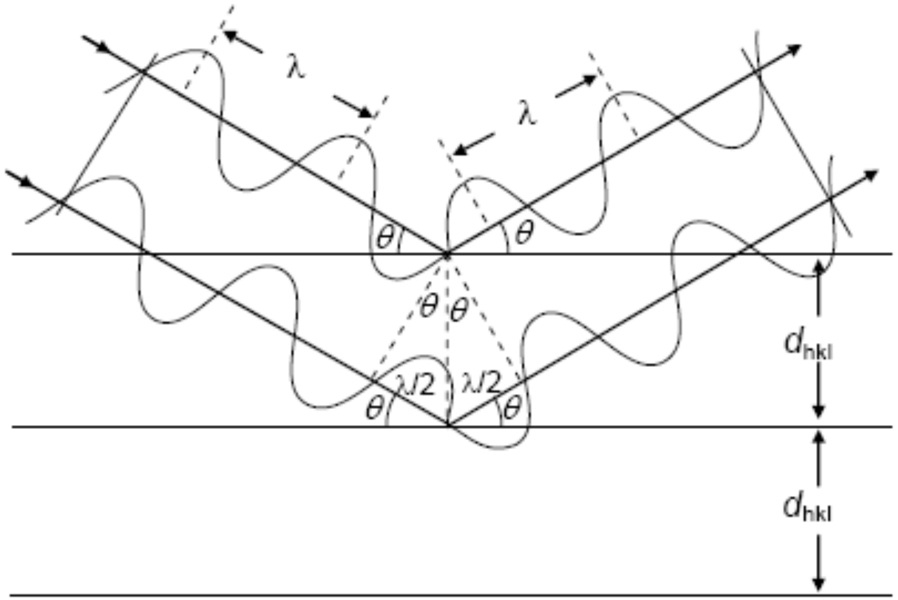
There is NO PHASE DIFFERENCE if the path differences are equal to whole number multiplies of wavelength



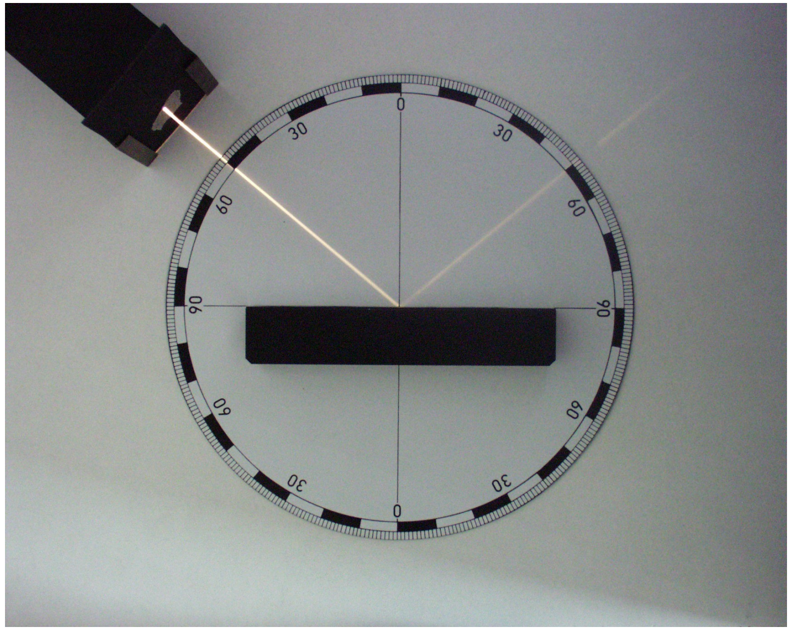
$$\sin\theta = \mathbf{w}/d$$
$$2\mathbf{w} = n\lambda$$

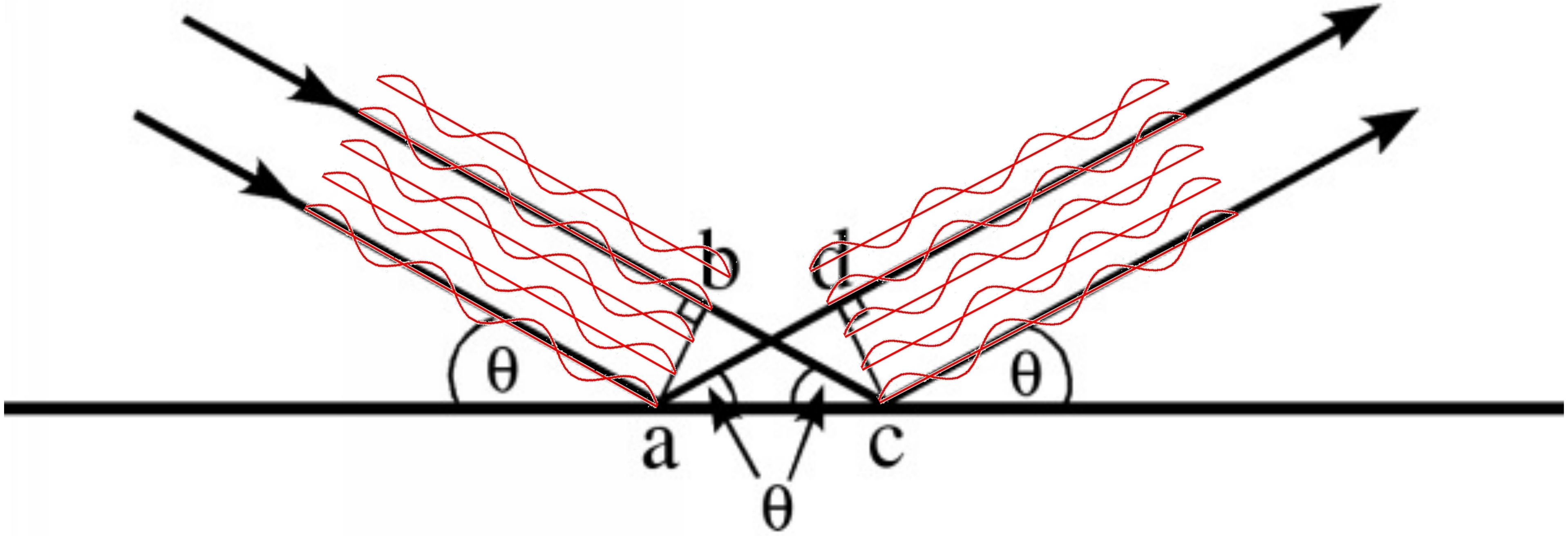
Bragg’s law:

$$\boxed{n\lambda = 2d\sin\theta}$$

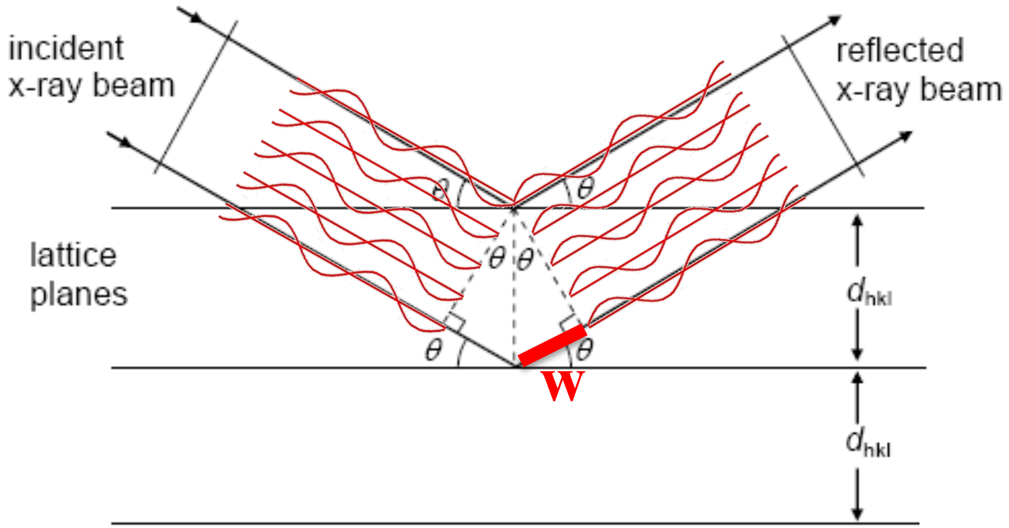


There is no path and PHASE DIFFERENCE when rays reflect from a plane





There is NO PHASE DIFFERENCE if the path differences are equal to whole number multiplies of wavelength

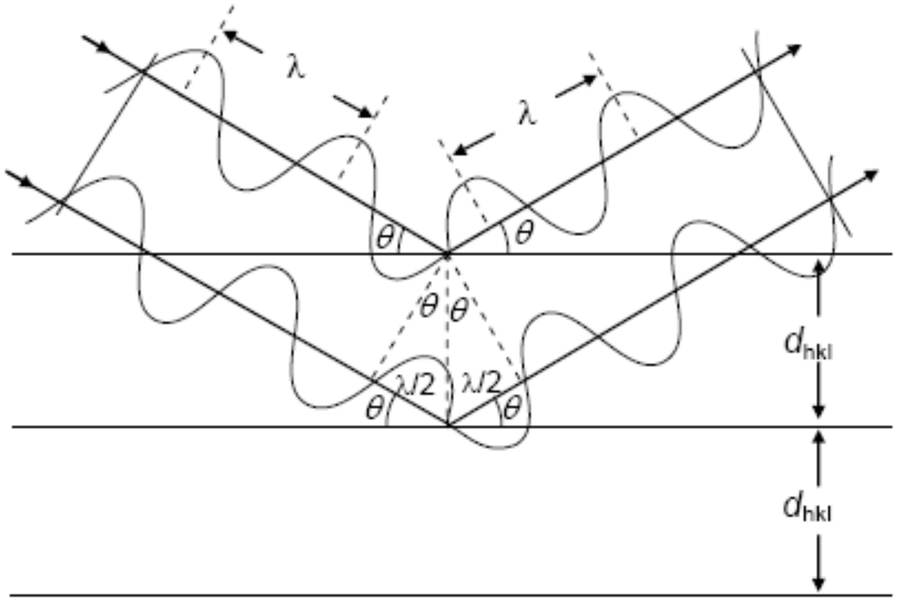


$\sin\theta = \mathbf{w}/d$

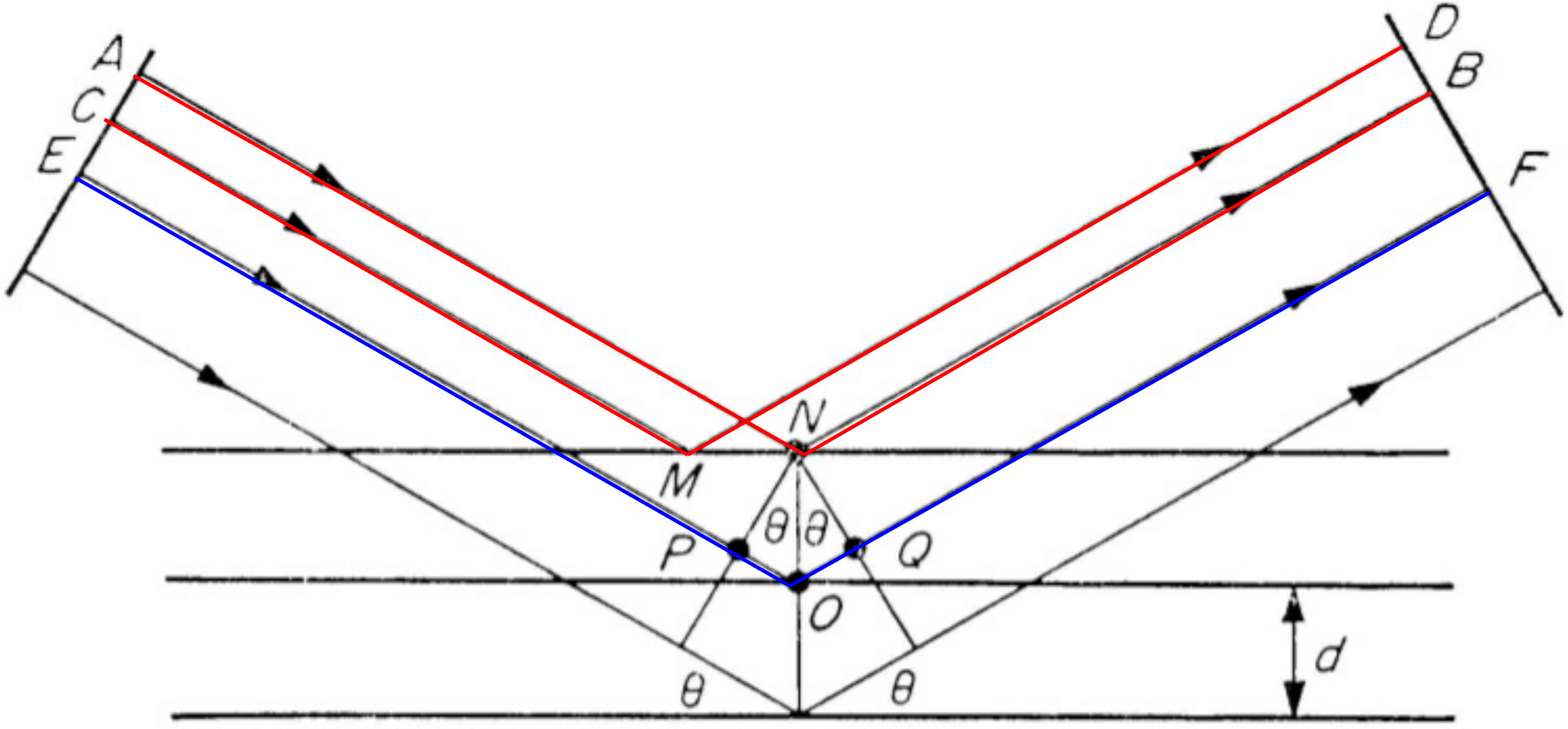
$2\mathbf{w} = n\lambda$

Bragg' s law:

$$\boxed{n\lambda = 2d\sin\theta}$$



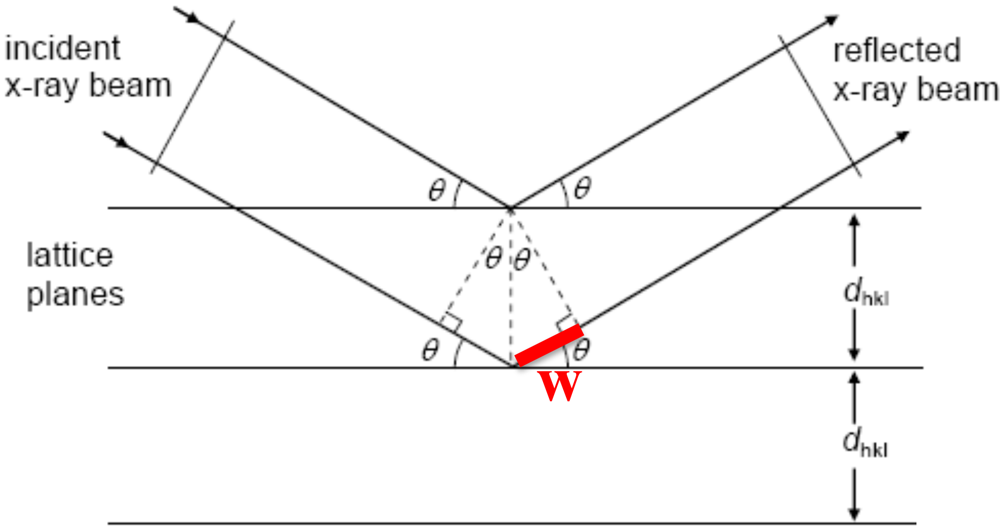
$$n\lambda = 2d\sin\theta$$

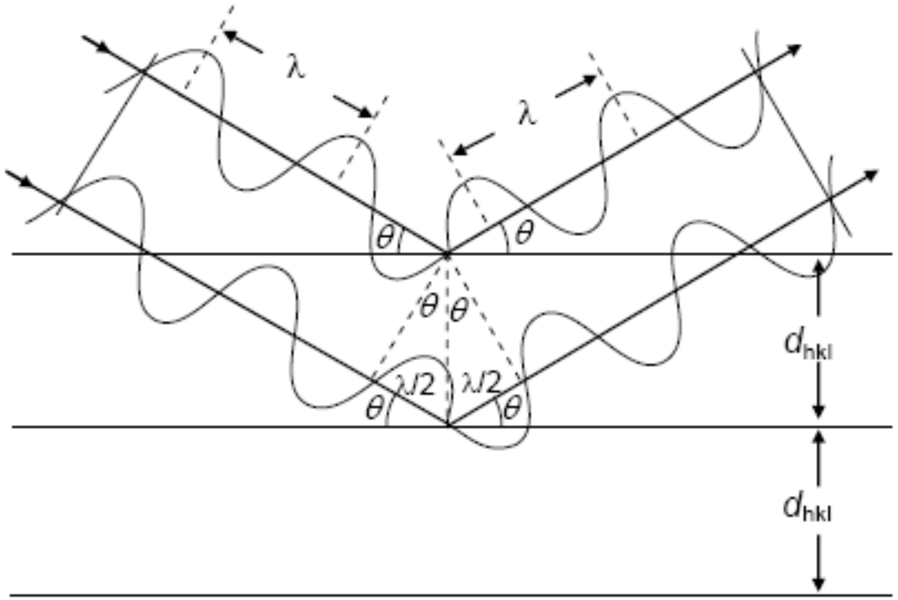


There is NO PHASE DIFFERENCE if the path differences are equal to prime number multiples of wavelength (λ)

Bragg's law:

$$\boxed{n\lambda = 2d\sin\theta}$$

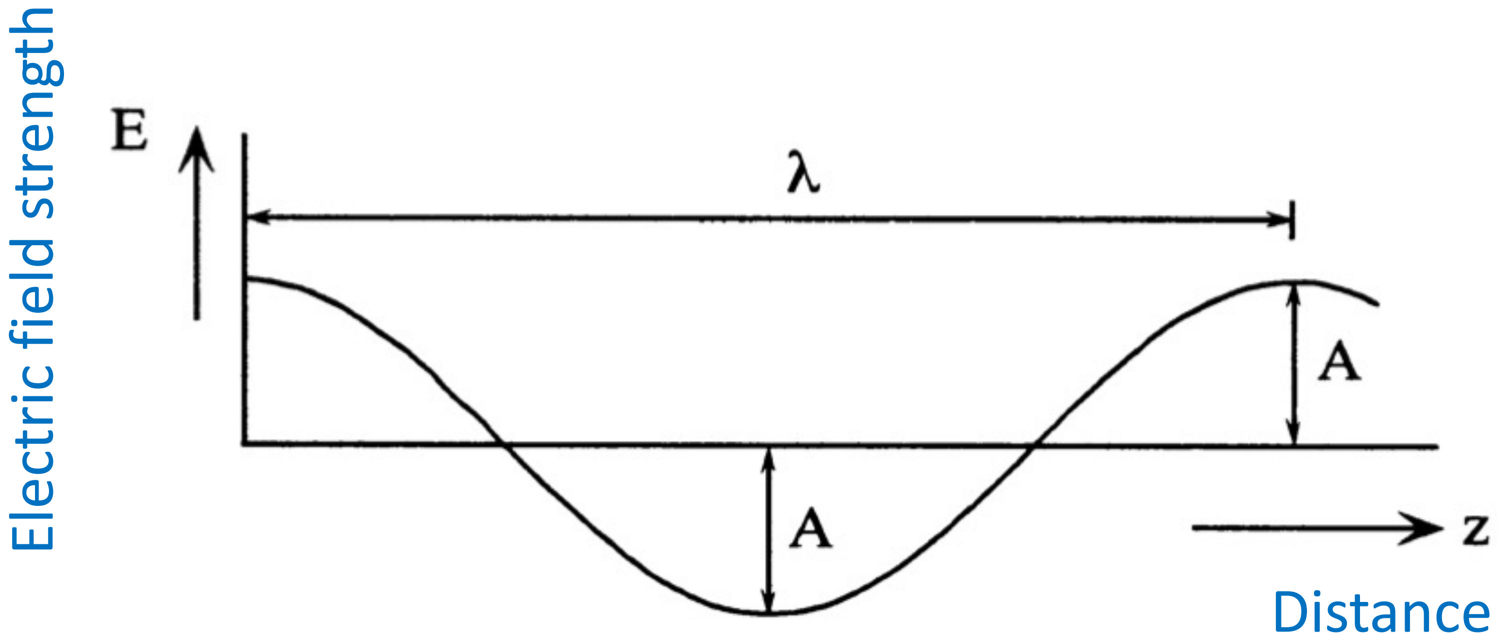




$\sin\theta = w/d$

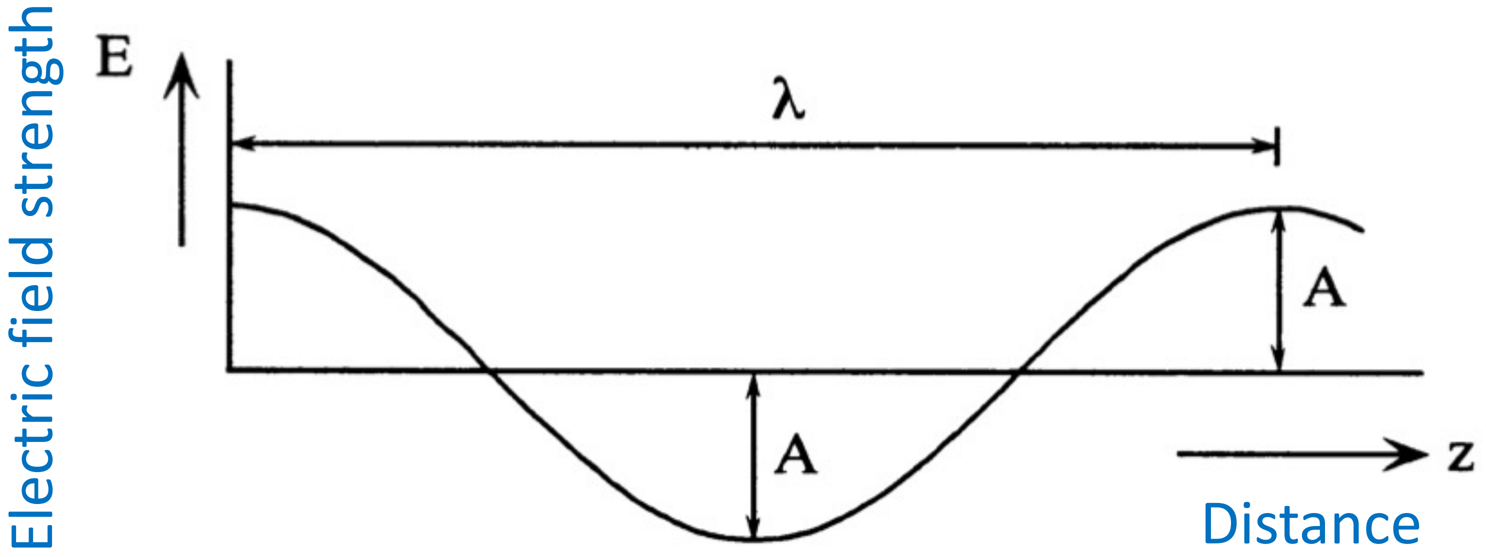
$2w = n\lambda$

Electromagnetic wave

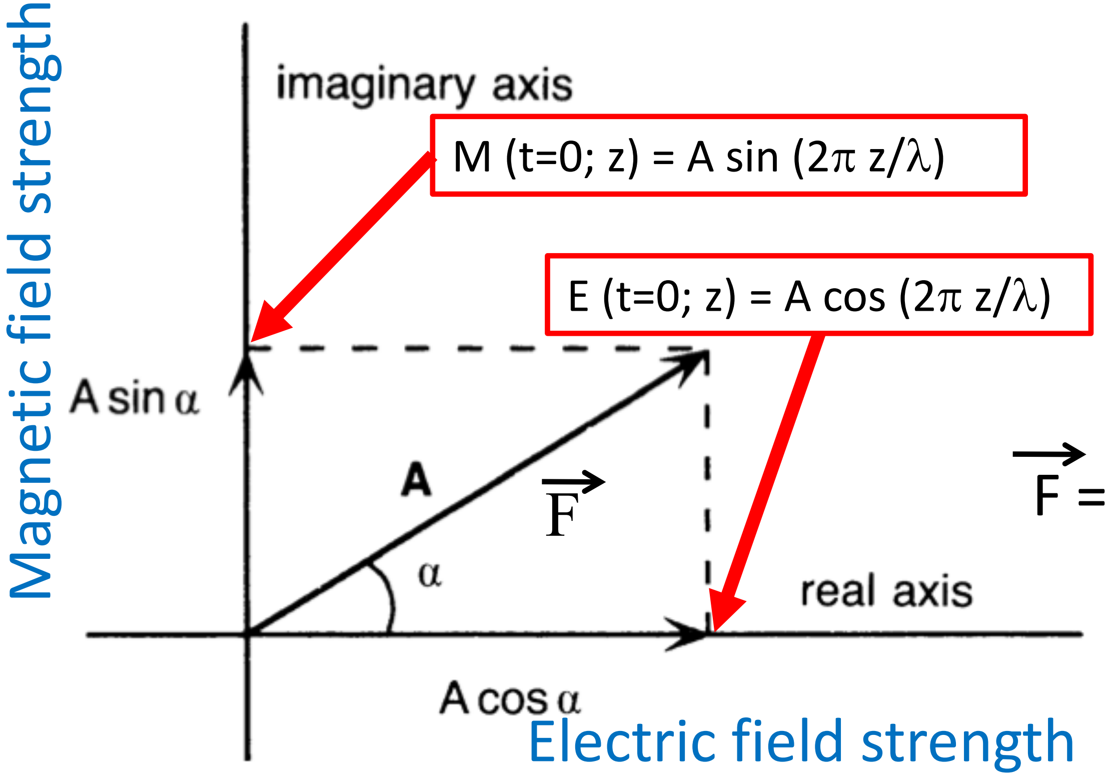


E – electric field strength
t – time
z – position
A – amplitude
λ – wavelength
2π – to convert relative distance to angles

$$E(t = 0; z) = A \cos 2\pi \frac{z}{\lambda}$$

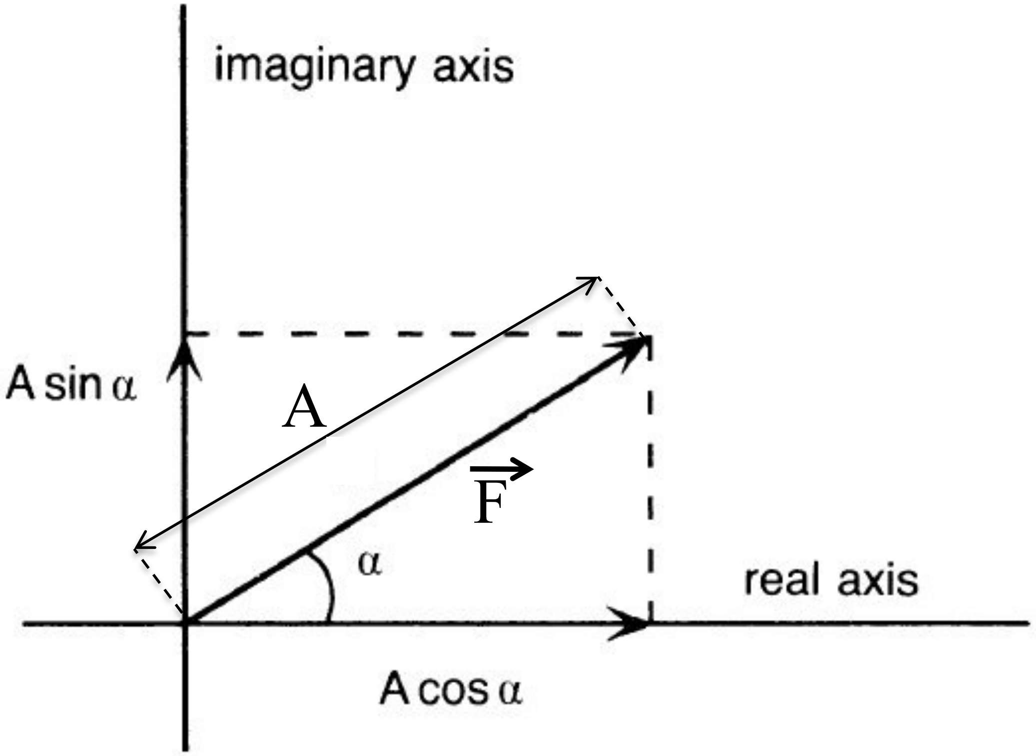


$E\ (t=0;\ z) = A \cos\ (2\pi\ z/\lambda)$



$$\vec{F} = A \cos(2\pi\ z/\lambda) + i\ A \sin(2\pi\ z/\lambda)$$

Wave as a vector



A - wave amplitude

α - wave phase angle

$$\vec{F} = A\cos\alpha + i\,A\sin\alpha$$

$$\vec{F} = A\exp(i\alpha)$$

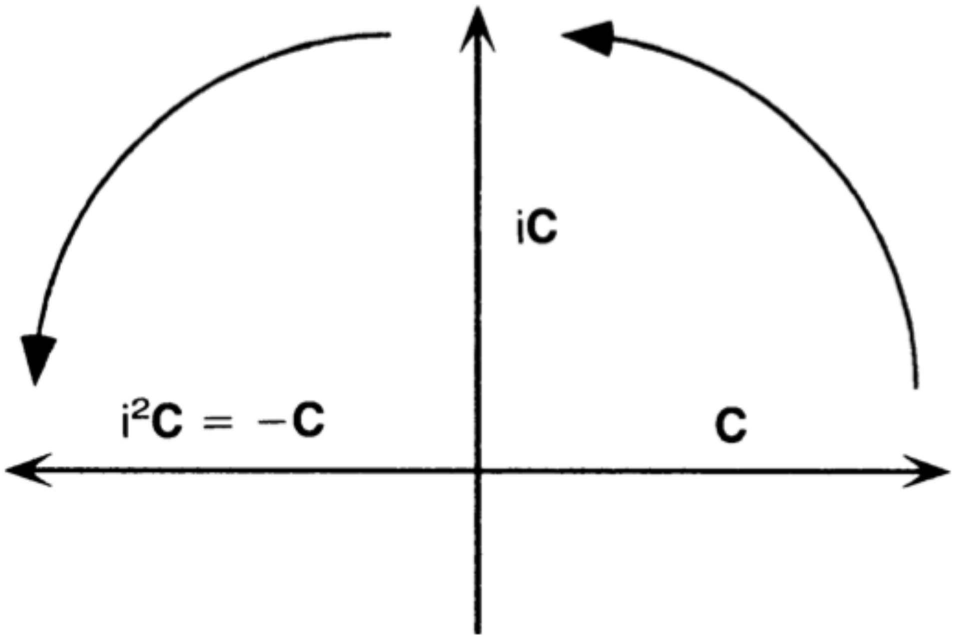


Figure 4.3. Multiplication of a vector **C** in the Argand diagram by i simply means rotating **C** 90° counterclockwise. Therefore, $i^2\mathbf{C} = -\mathbf{C}$.

$$i = \sqrt{-1}$$

$$A \cos \alpha + iA \sin \alpha$$

$$A \cos \alpha + iA \sin \alpha = A \exp[i\alpha]$$

$$A \cos \alpha + iA \sin \alpha = A \exp[i\alpha]$$

Properties of Exponential Terms

We will not prove that $A \cos \alpha + iA \sin \alpha = A \exp[i\alpha]$. You must know, however, the properties of exponential terms:

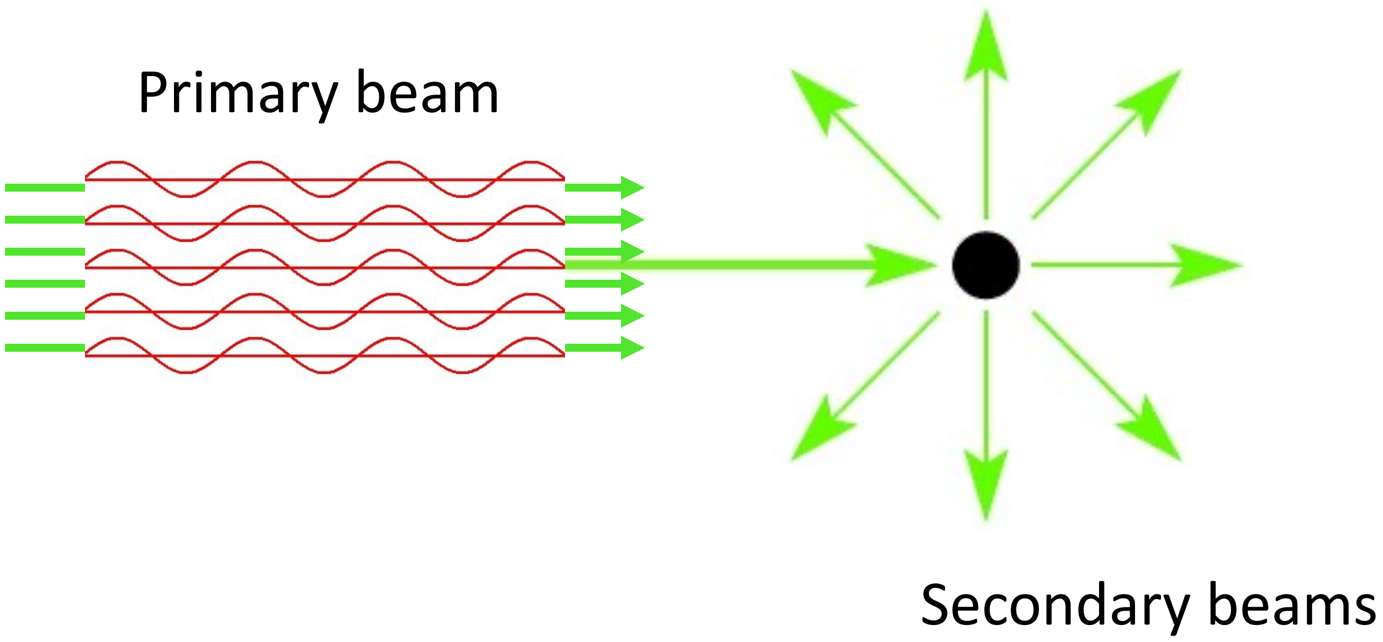
$$\exp[a]\exp[b] = \exp[a+b]; \qquad \frac{\exp[a]}{\exp[b]} = \exp[a-b];$$

$$\exp[k \cdot a] = \{\exp[a]\}^k; \qquad \exp[0] = 1;$$

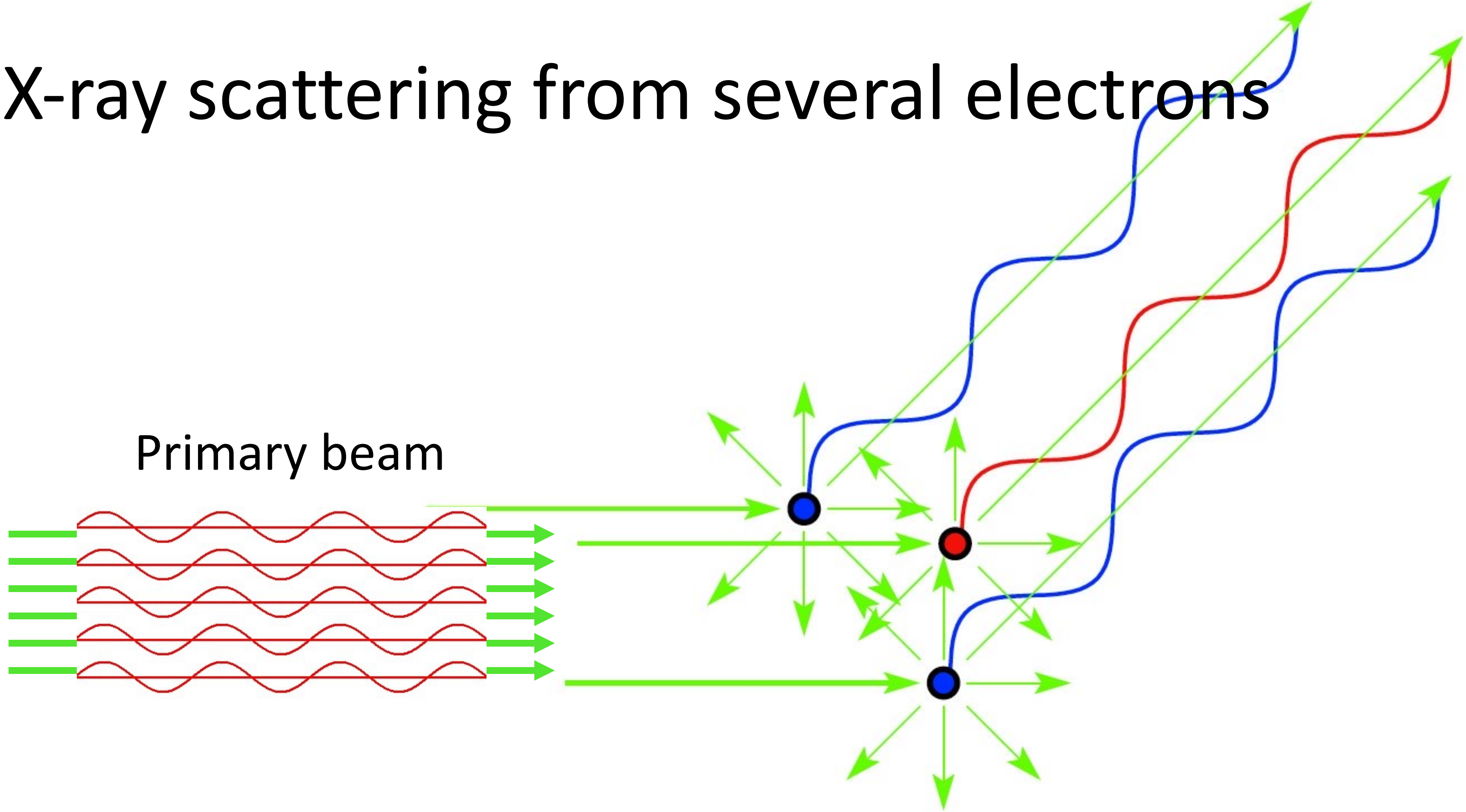
$$\exp[a] \to +\infty \text{ for } a \to +\infty;$$

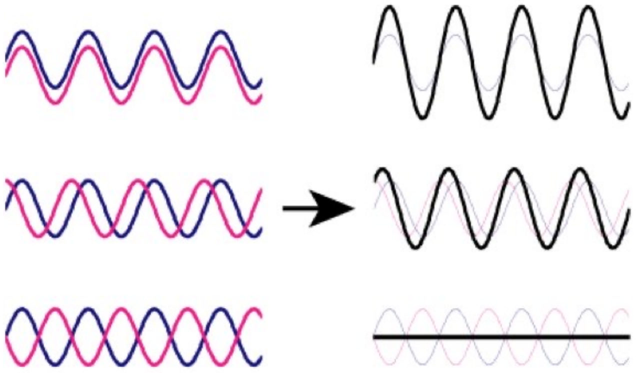
$$\exp[a] \to 0 \text{ for } a \to -\infty.$$

X-rays scatter from electrons in all directions



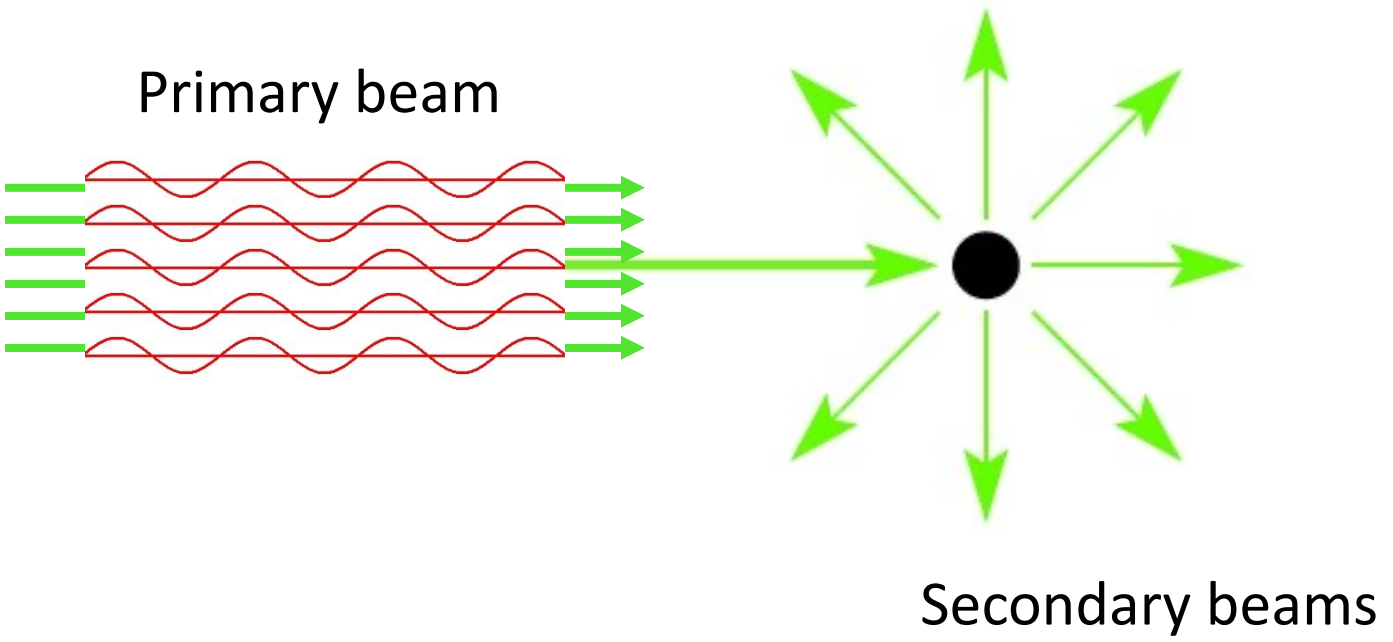
X-ray scattering from several electrons



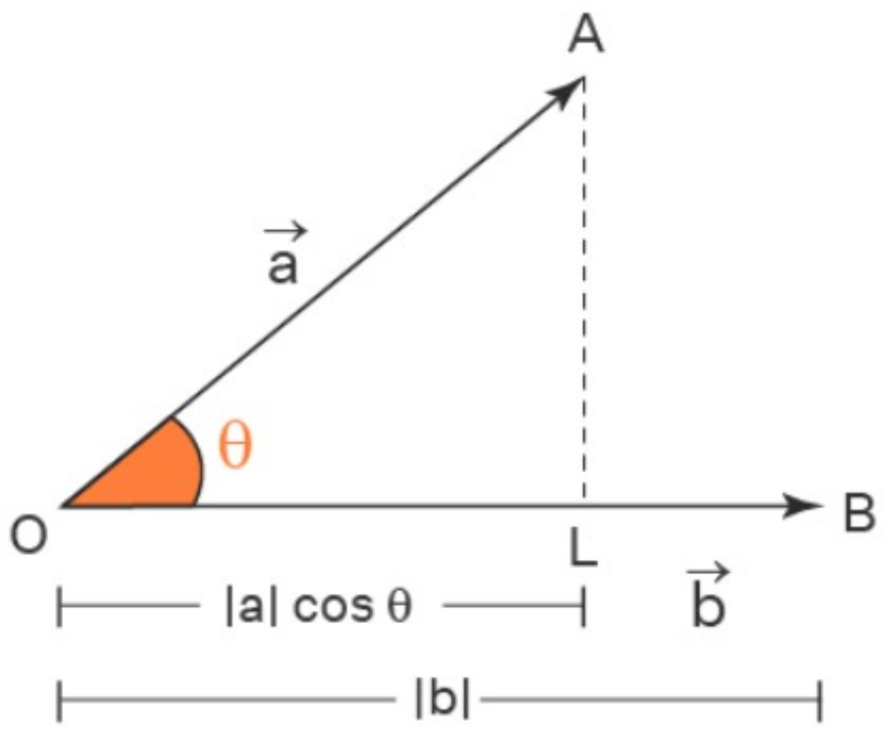


When do electrons scatter "in phase" so that waves add constructively?

X-rays scatter from electrons in all directions



Dot product



$$a \,.\, b = |a|.|b| \cos\theta$$

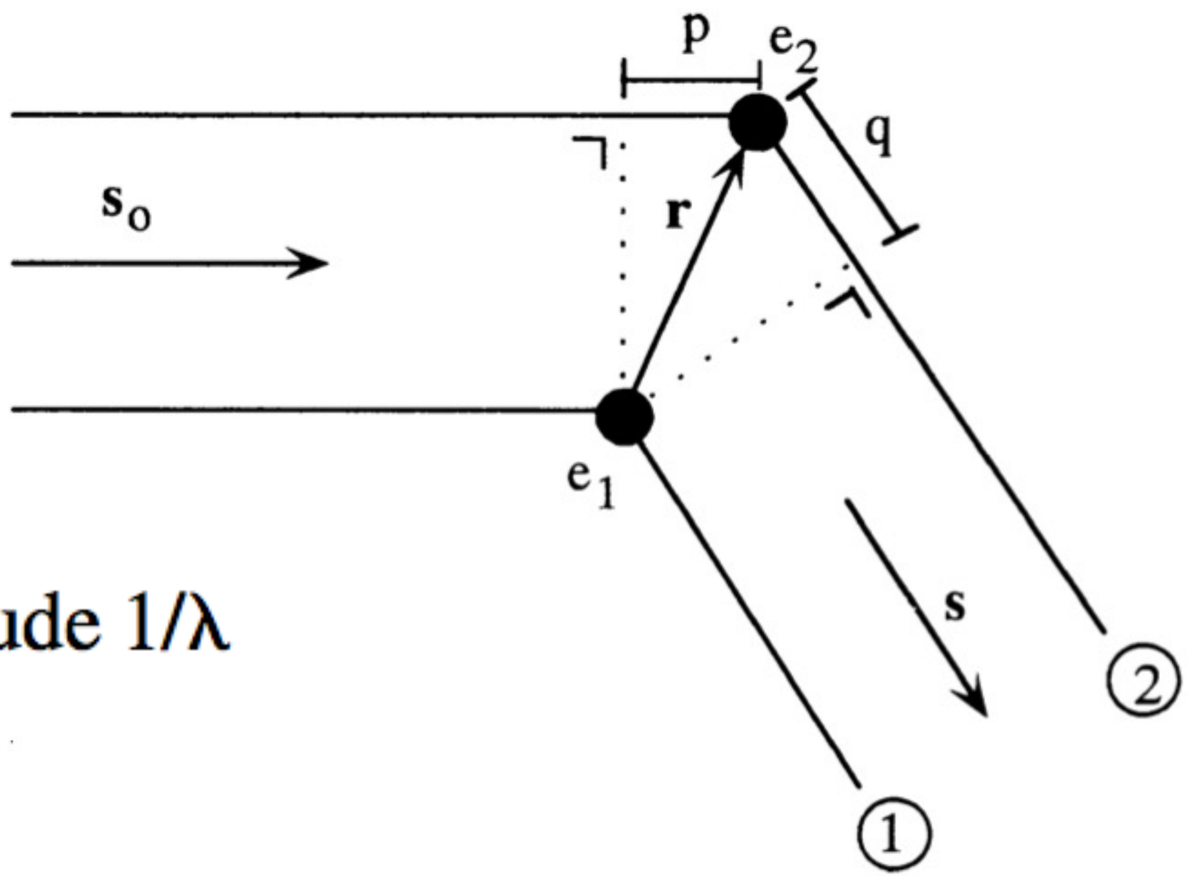
The Product of Two Vectors a and b

Let vectors **a** and **b**, with lengths $|a|$ and $|b|$, be inclined at an angle θ.

Scalar product: Their scalar product is the number $\mathbf{a} \cdot \mathbf{b} = ab \cos\,\theta$ and $\mathbf{a} \cdot \mathbf{b} = \mathbf{b} \cdot \mathbf{a}$.

System of two electrons

Figure 4.4. A system of two electrons: e_1 and e_2. The path difference between the scattered waves 1 and 2 is $p + q$.



$\mathbf{s}_0$ and $\mathbf{s}$ are wave vectors of magnitude $1/\lambda$

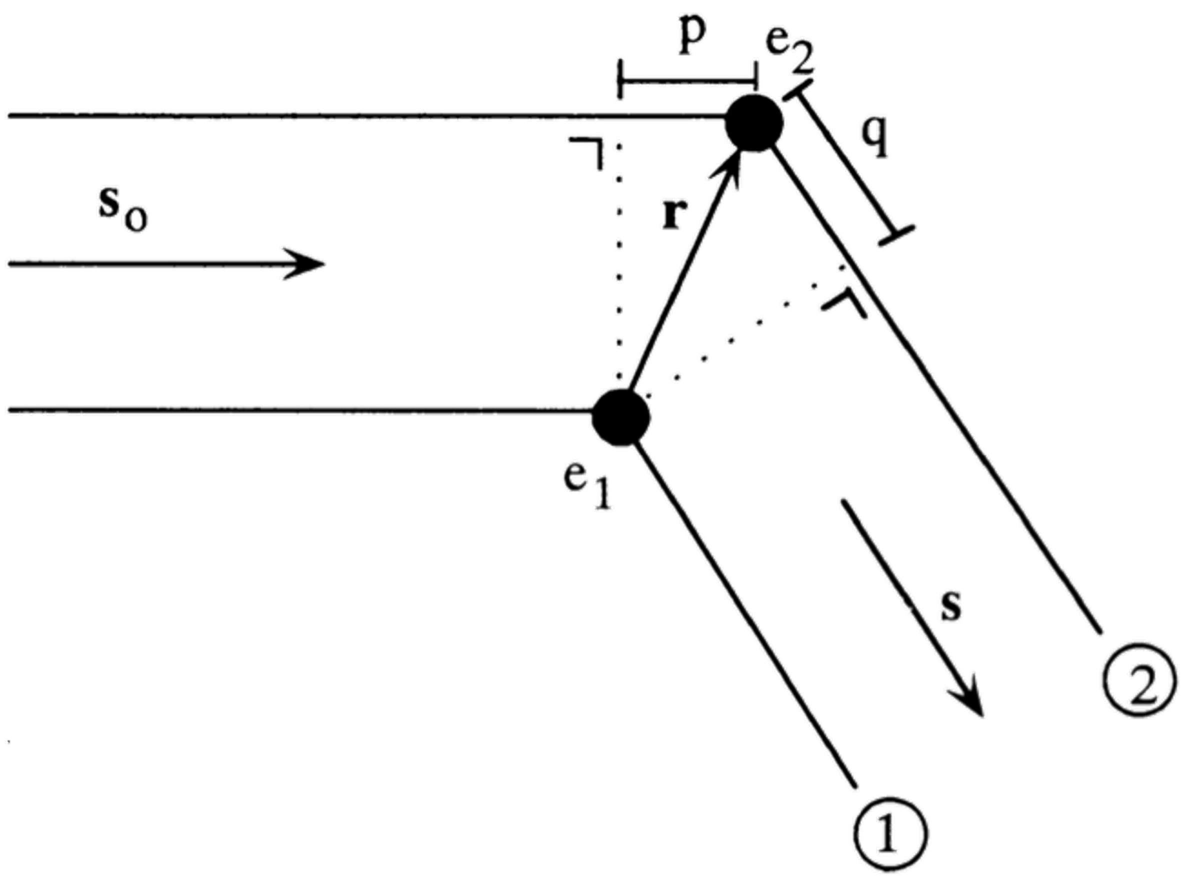
$$p = \lambda \cdot \mathbf{r} \cdot \mathbf{s}_0$$

$$q = -\lambda \cdot \mathbf{r} \cdot \mathbf{s}$$

minus sign is due to the fact that the projection of **r** on **s** has a direction opposite to **s**

$$p + q = \lambda \cdot \mathbf{r} \cdot (\mathbf{s}_0 - \mathbf{s}).$$

Figure 4.4. A system of two electrons: e_1 and e_2. The path difference between the scattered waves 1 and 2 is $p + q$.



The wave along electron e_2 is lagging behind in phase compared with the wave along e_1. With respect to wave 1, the phase of wave 2 is

$$-\frac{2\pi \mathbf{r} \cdot (\mathbf{s}_0 - \mathbf{s}) \cdot \lambda}{\lambda} = 2\pi \mathbf{r} \cdot \mathbf{S},$$

where

$$\mathbf{S} = \mathbf{s} - \mathbf{s}_0 \tag{4.1}$$

It is interesting to note that the wave can be regarded as being reflected against a plane with θ as the reflecting angle and $|S| = 2(\sin\theta)/\lambda$ (Figure 4.5). The physical meaning of vector **S** is the following: Because $\mathbf{S} = \mathbf{s} - \mathbf{s}_0$, with $|s| = |s_0| = 1/\lambda$, **S** is perpendicular to the imaginary "reflecting plane," which makes equal angles with the incident and reflected beam.

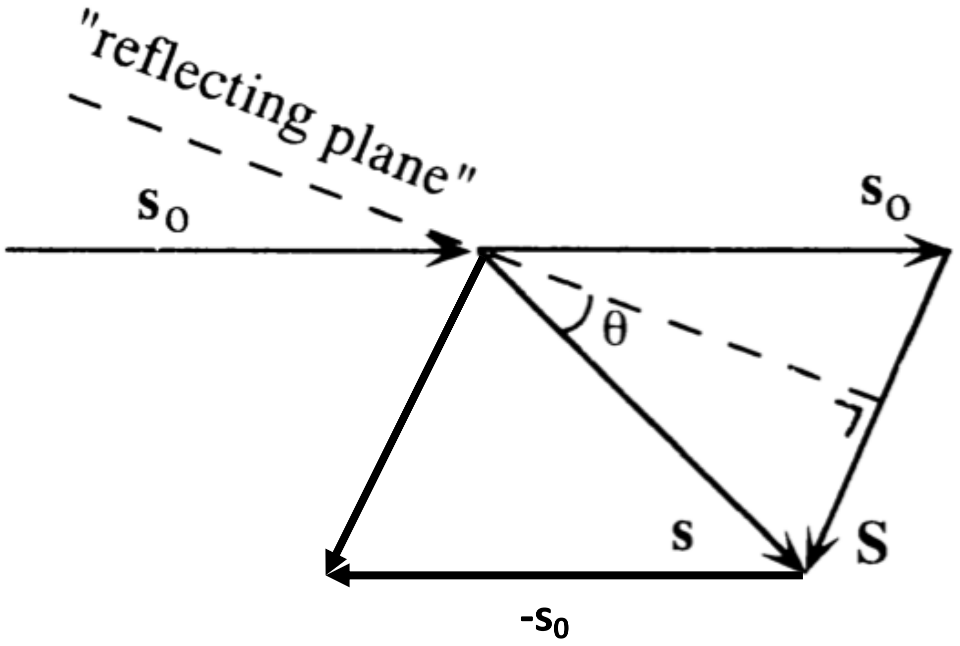
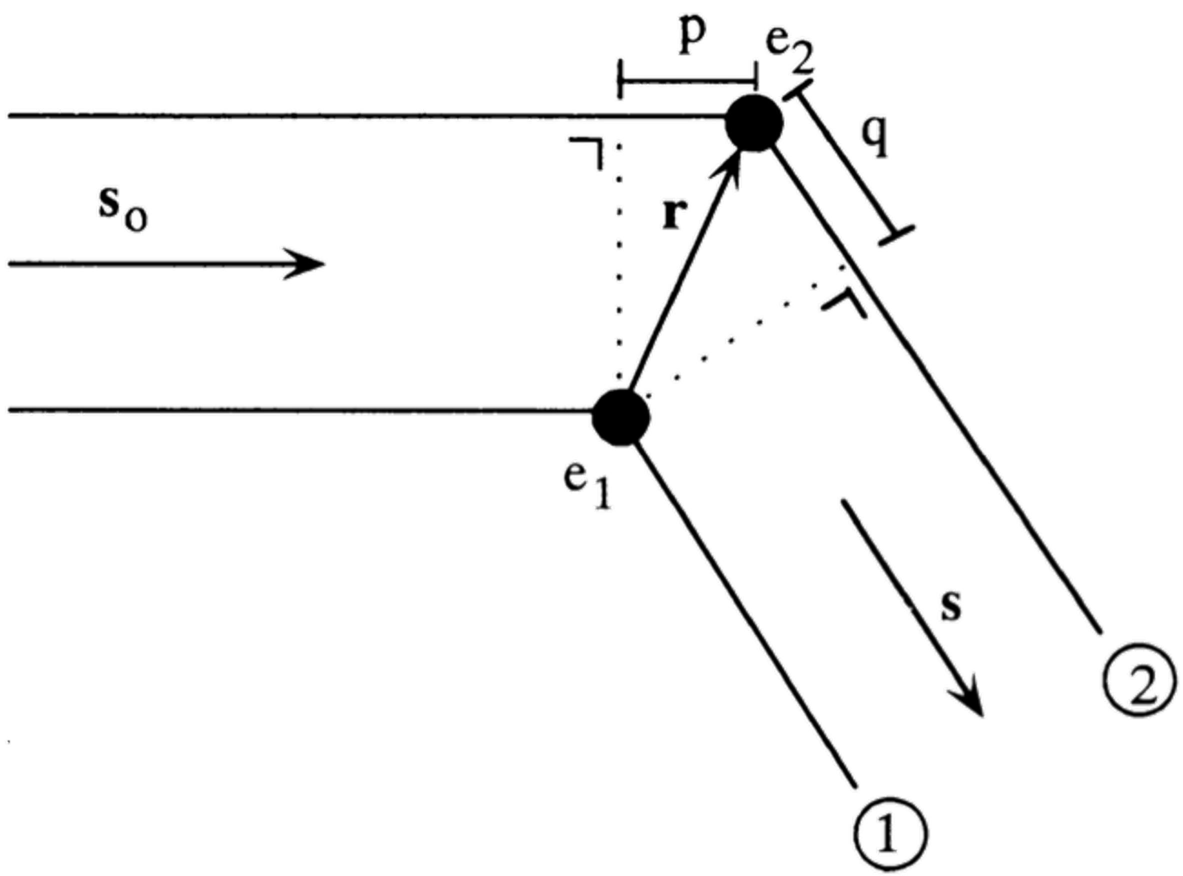


Figure 4.5. The primary wave, represented by $\mathbf{s}_0$, can be regarded as being reflected against a plane. θ is the reflecting angle. Vector **S** is perpendicular to this plane.

Figure 4.4. A system of two electrons: e_1 and e_2. The path difference between the scattered waves 1 and 2 is $p + q$.



The wave along electron e_2 is lagging behind in phase compared with the wave along e_1. With respect to wave 1, the phase of wave 2 is

$$-\frac{2\pi\mathbf{r}\cdot(\mathbf{s}_0-\mathbf{s})\cdot\lambda}{\lambda}=2\pi\mathbf{r}\cdot\mathbf{S},$$

where

$$\mathbf{S}=\mathbf{s}-\mathbf{s}_0 \tag{4.1}$$

If we add the waves 1 and 2 in Figure 4.4, the Argand diagram shows two vectors, **1** and **2**, with equal length (amplitude) and a phase of $2\pi\mathbf{r}\cdot\mathbf{S}$ for wave **2** with respect to wave **1** (Figure 4.6). Vector **T** represents the sum of the two waves. In mathematical form: $\mathbf{T} = 1 + 2 = 1 + 1\exp[2\pi i\mathbf{r}\cdot\mathbf{S}]$ if the length of the vectors equals 1. So far we had the origin of this two-electron system in e_1.

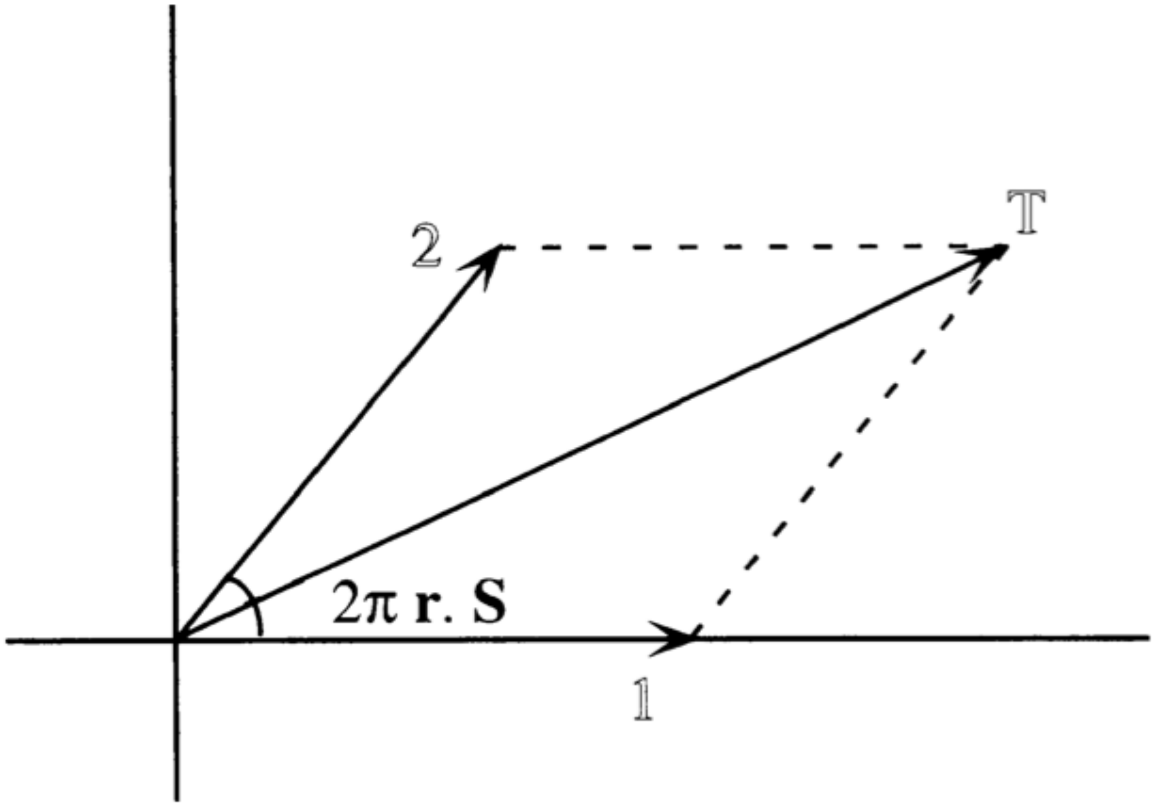


Figure 4.6. The summation of the two scattered waves in Figure 4.4 with the origin in electron e_1.

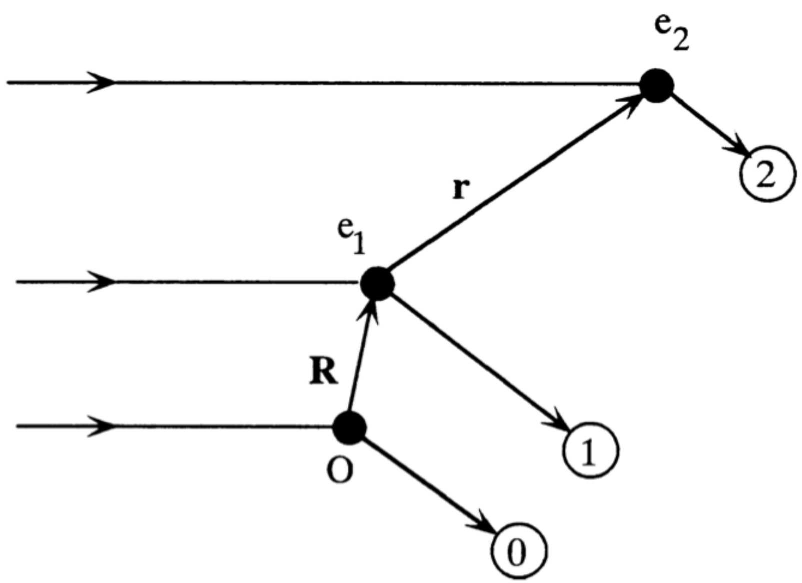


Figure 4.7. The origin, or reference point, for the scattered waves of the two-electron system is now located at O.

Suppose we move the origin over $-\mathbf{R}$ from e_1 to point O (Figure 4.7). Then we obtain the following: With respect to a wave **0**, wave **1** has a phase of $2\pi\mathbf{R}\cdot\mathbf{S}$, and wave **2** has a phase of $2\pi(\mathbf{r}+\mathbf{R})\cdot\mathbf{S}$ (Figure 4.8)

$$
\begin{aligned}
\mathbf{T} = 1 + 2 &= \exp[2\pi i \mathrm{R}\cdot\mathbf{S}] + \exp[2\pi i(\mathbf{r}+\mathrm{R})\cdot\mathbf{S}] \\
&= \exp[2\pi i \mathrm{R}\cdot\mathbf{S}]\{1 + \exp[2\pi i \mathbf{r}\cdot\mathbf{S}]\}
\end{aligned}
$$

Conclusion: A shift of the origin by $-\mathbf{R}$ causes an increase of all phase angles by $2\pi\mathbf{R}\cdot\mathbf{S}$. The amplitude and intensity (which is proportional to the square of the amplitude) of wave **T** do not change.

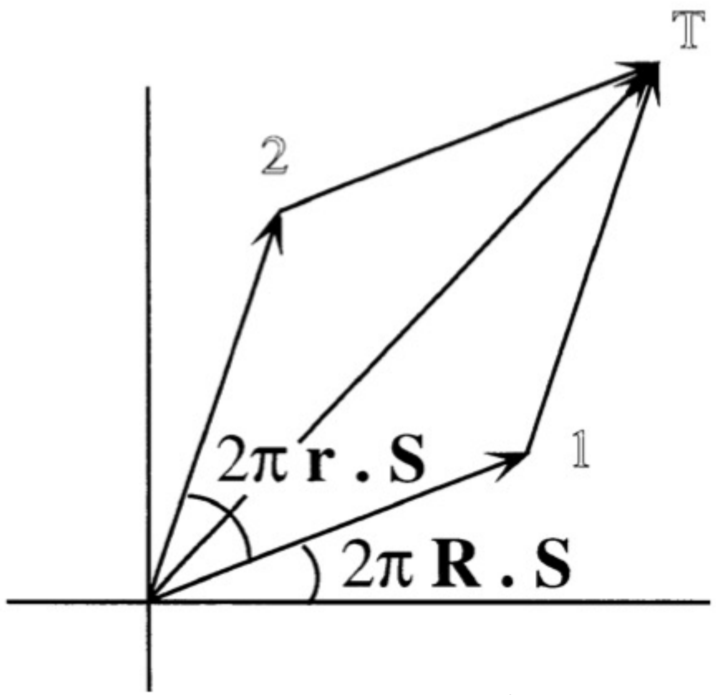


Figure 4.8. The summation of waves **1** and **2** with the origin of the two-electron system in position O.

Suppose we move the origin over $-\mathbf{R}$ from e_1 to point O (Figure 4.7). Then we obtain the following: With respect to a wave **0**, wave **1** has a phase of $2\pi\mathbf{R}\cdot\mathbf{S}$, and wave **2** has a phase of $2\pi(\mathbf{r}+\mathbf{R})\cdot\mathbf{S}$ (Figure 4.8)

$$\begin{aligned}\mathbf{T} = 1 + 2 &= \exp[2\pi i\mathrm{R}\cdot\mathbf{S}] + \exp[2\pi i(\mathbf{r}+\mathrm{R})\cdot\mathbf{S}]\\ &= \exp[2\pi i\mathrm{R}\cdot\mathbf{S}]\{1+\exp[2\pi i\mathbf{r}\cdot\mathbf{S}]\}\end{aligned}$$

Conclusion: A shift of the origin by $-\mathbf{R}$ causes an increase of all phase angles by $2\pi\mathbf{R}\cdot\mathbf{S}$. The amplitude and intensity (which is proportional to the square of the amplitude) of wave **T** do not change.

Scattering by an atom

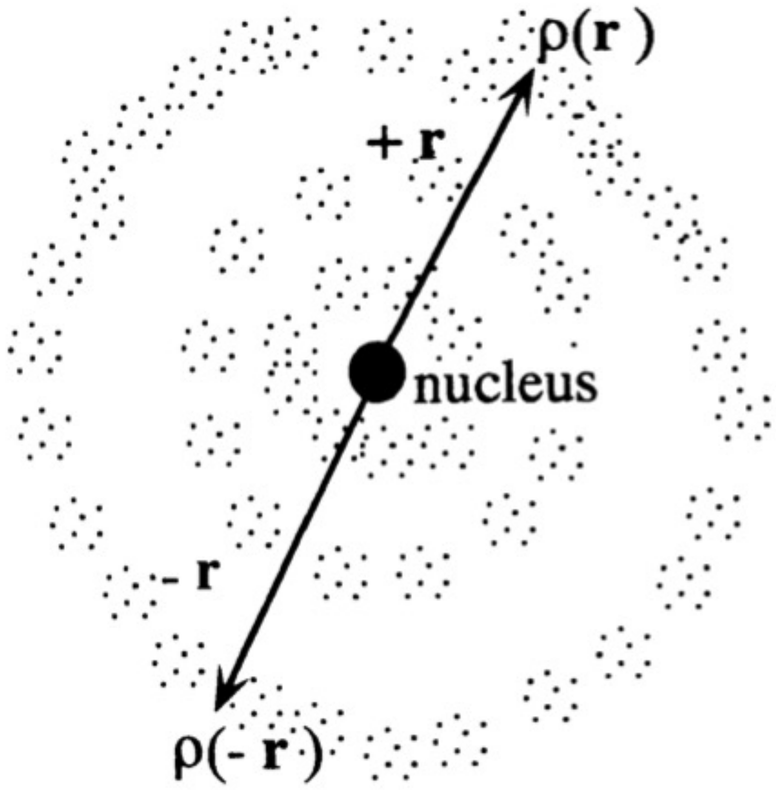


Figure 4.9. The electron cloud of an atom. $\rho(\mathbf{r})$ is the electron density. Because of the centrosymmetry, $\rho(\mathbf{r}) = \rho(-\mathbf{r})$.

$$f = \int_{\mathbf{r}} \rho(\mathbf{r}) \exp[2\pi i \mathbf{r} \cdot \mathbf{S}] \, d\mathbf{r}, \qquad (4.2)$$

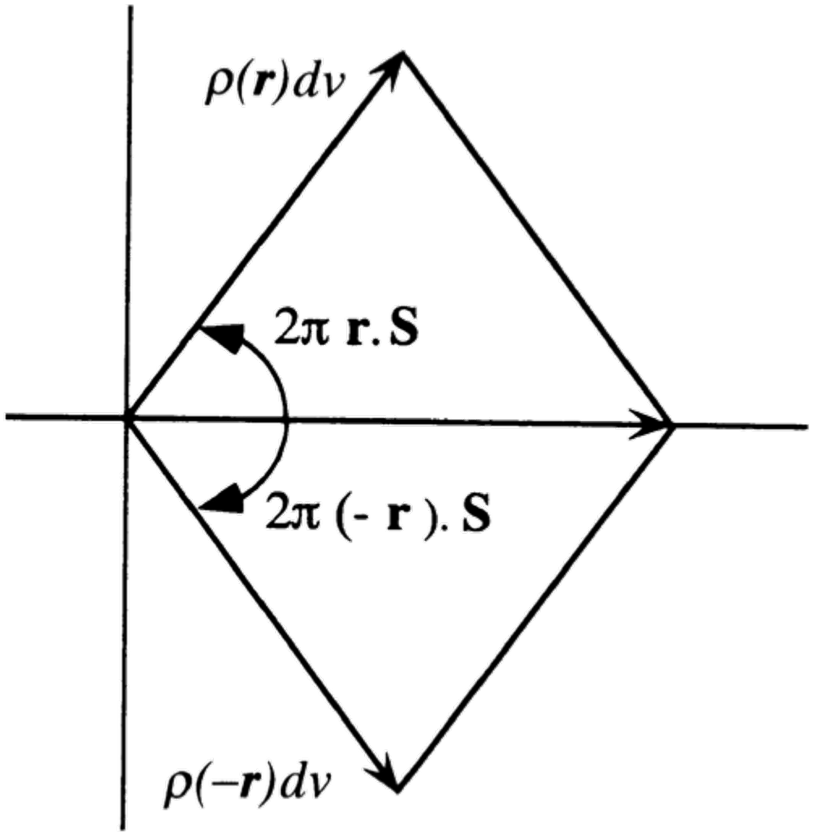
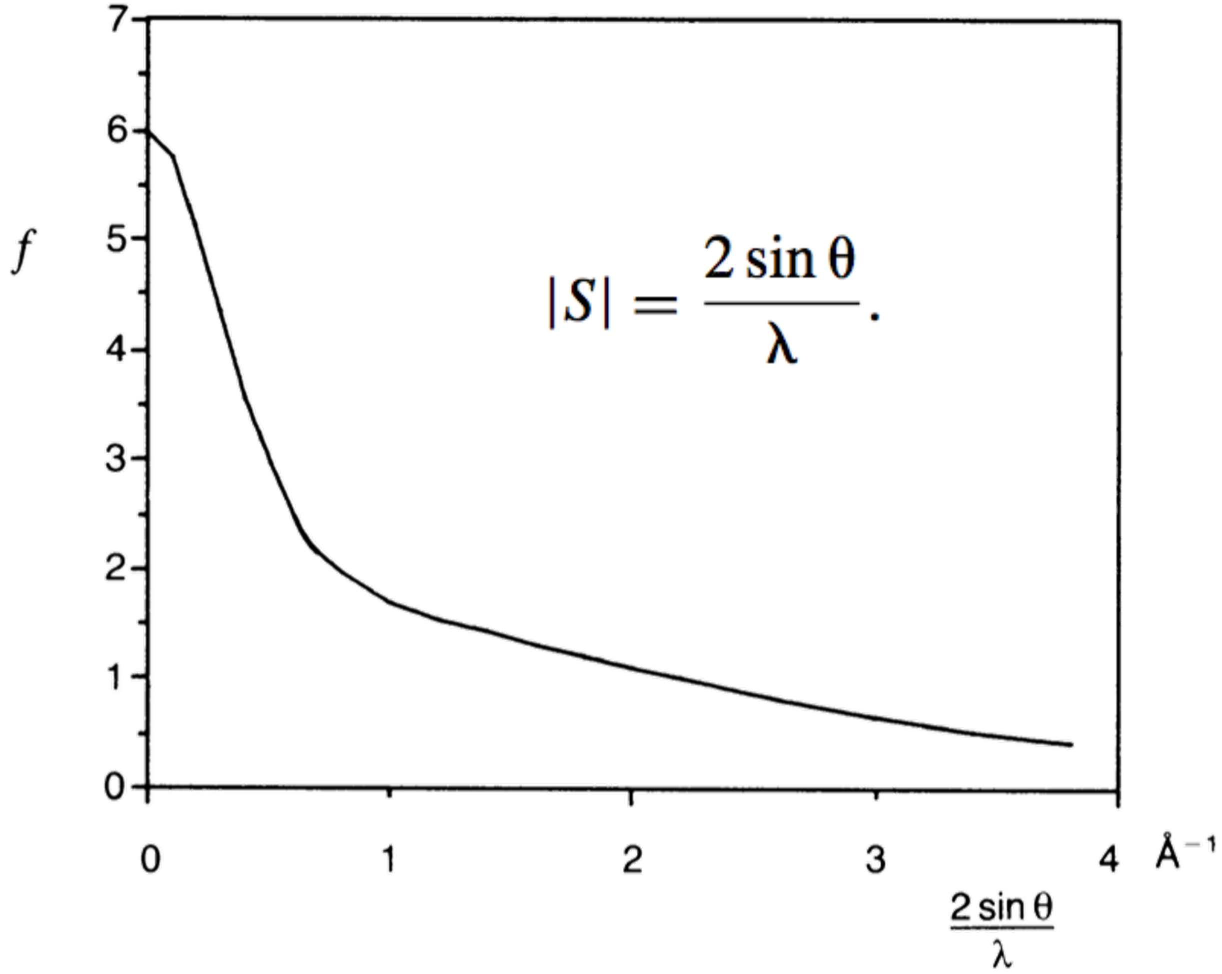


Figure 4.10. The scattering factor f of an atom is always real if we assume centrosymmetry of the electron cloud. The imaginary part of every scattering vector is compensated by the imaginary part of a vector with equal length but a phase angle of opposite sign.

$$f = \int_{\mathbf{r}} \rho(\mathbf{r}) \{\exp[2\pi i \mathbf{r} \cdot \mathbf{S}] + \exp[-2\pi i \mathbf{r} \cdot \mathbf{S}]\} \, d\mathbf{r}$$

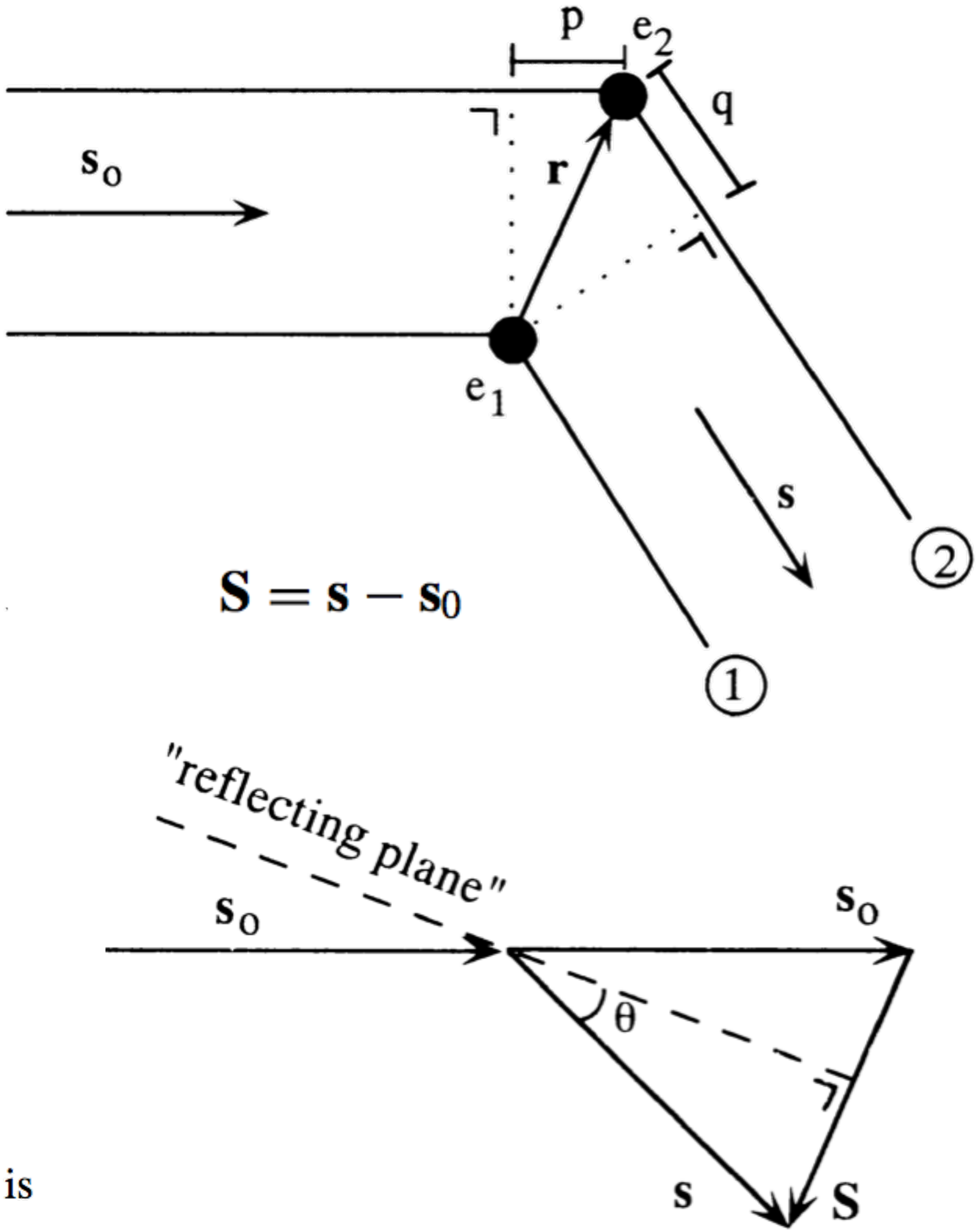
$$= 2 \int_{\mathbf{r}} \rho(\mathbf{r}) \cos[2\pi \mathbf{r} \cdot \mathbf{S}] \, d\mathbf{r}.$$

Scattering by an atom depends on the length of |S| (resolution)



$$|S| = \frac{2\sin\theta}{\lambda}.$$

Figure 4.11. The scattering factor f for a carbon atom as a function of $2(\sin\theta)/\lambda$. f is expressed as electron number, and for the beam with $\theta = 0$, $f = 6$.



$$\mathbf{S} = \mathbf{s} - \mathbf{s}_0$$

Scattering by a unit cell

Suppose a unit cell has n atoms at positions $\mathbf{r}_j$ ($j = 1, 2, 3, \ldots, n$) with respect to the origin of the unit cell (Figure 4.12). With their own nuclei as origins, the atoms diffract according to their atomic scattering factor f. If the origin is now transferred to the origin of the unit cell, the phase angles change by $2\pi\mathbf{r}_j \cdot \mathbf{S}$. With respect to the new origin, the scattering is given by

$$\mathbf{f}_j = f_j \exp[2\pi i \mathbf{r}_j \cdot \mathbf{S}],$$

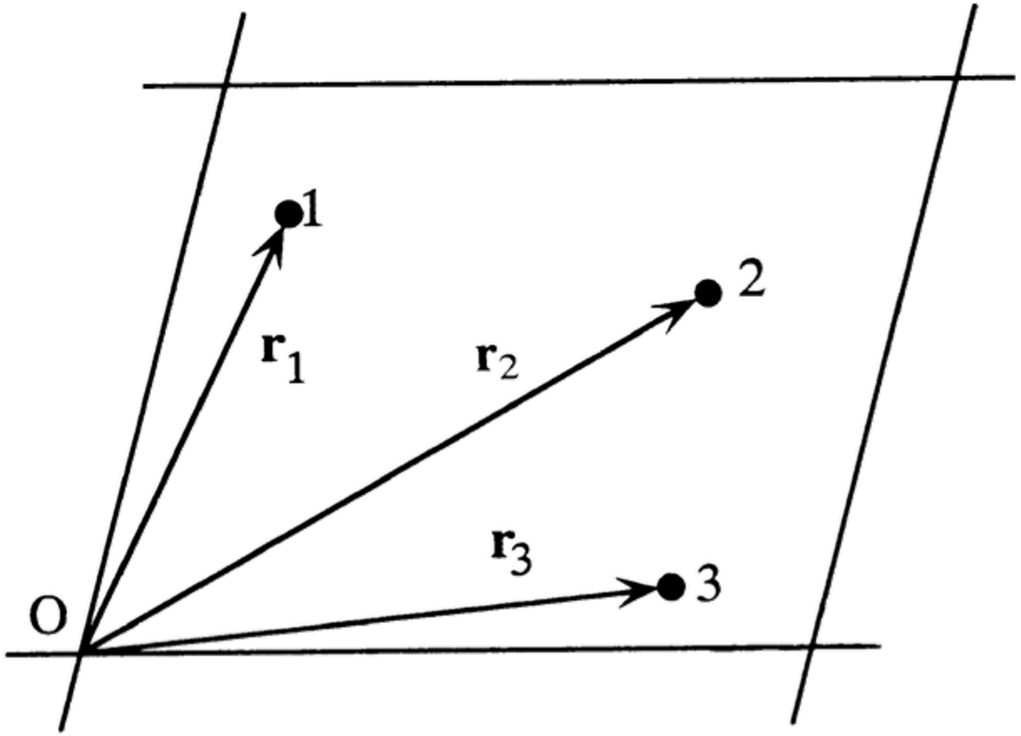


Figure 4.12. A unit cell with three atoms (1, 2, and 3) at positions $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{r}_3$.

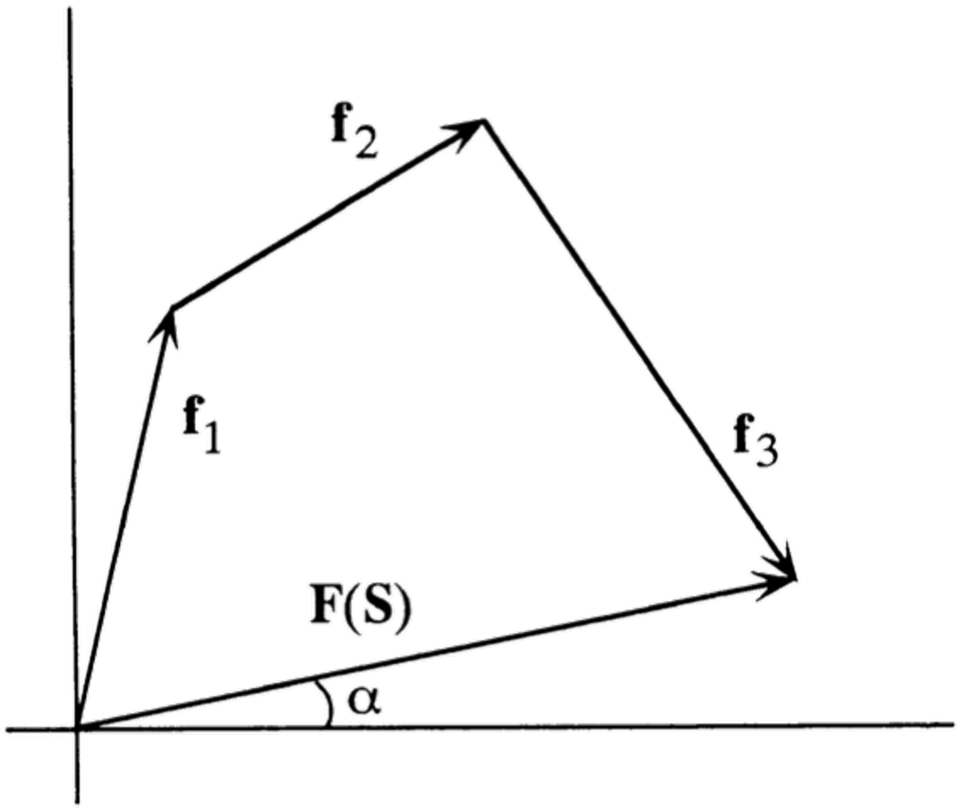


Figure 4.13. The structure factor **F(S)** is the sum of the scattering by the separate atoms in the unit cell.

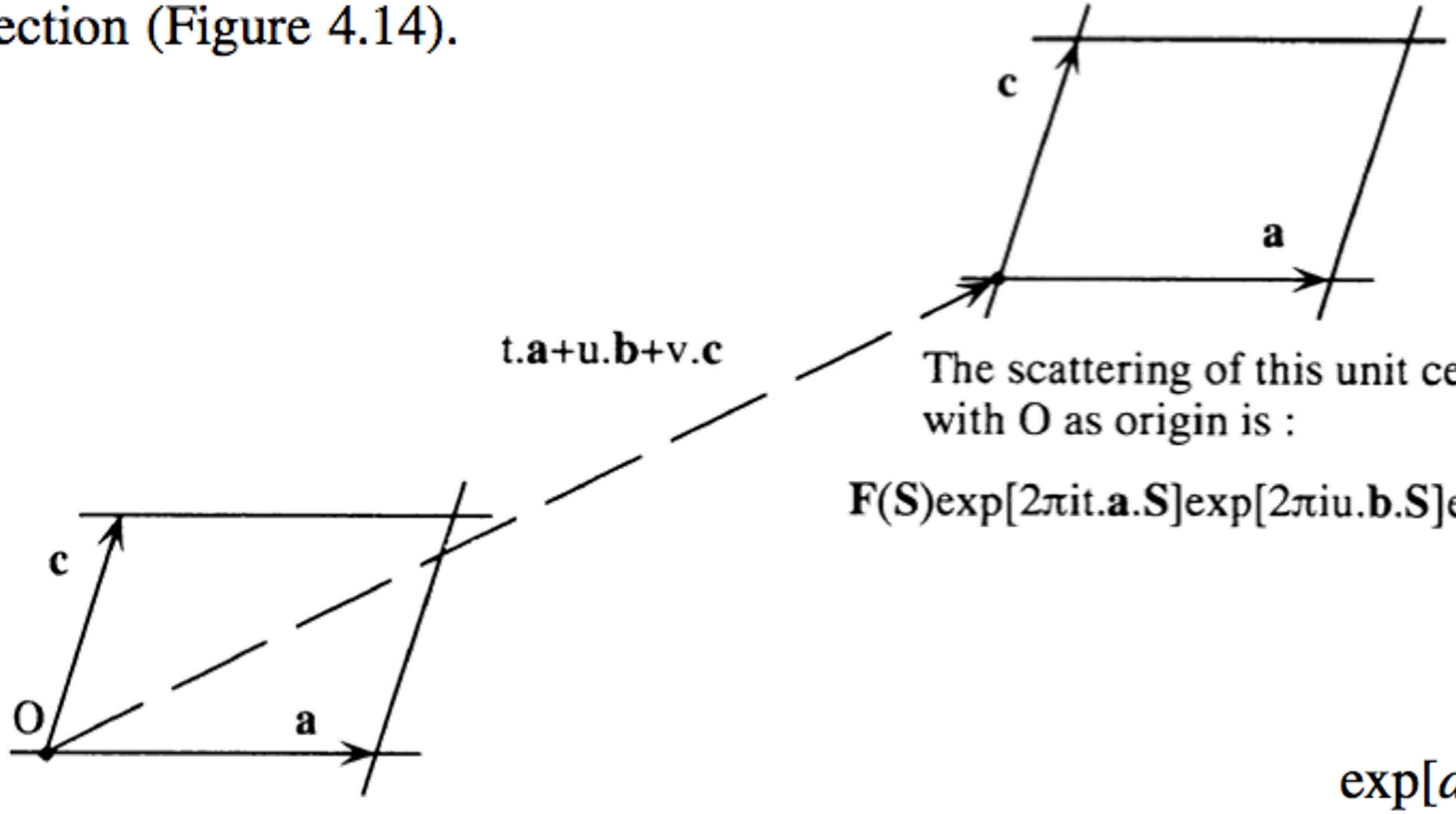
unit cell is

$$\mathbf{F}(\mathbf{S}) = \sum_{j=1}^{n} f_j \exp[2\pi i \mathbf{r}_j \cdot \mathbf{S}]. \tag{4.3}$$

F(S) is called the *structure factor* because it depends on the arrangement (structure) of the atoms in the unit cell (Figure 4.13).

Scattering by a crystal

Suppose that the crystal has translation vectors **a**, **b**, and **c** and contains a large number of unit cells: n_1 in the **a** direction, n_2 in the **b** direction, and n_3 in the **c** direction (Figure 4.14).



The scattering of this unit cell
with O as origin is :

F(**S**)exp[2πit.**a**.**S**]exp[2πiu.**b**.**S**]exp[2πiv.**c**.**S**]

$$\exp[a]\exp[b] = \exp[a+b]$$

The scattering of this unit cell

with O as origin is **F**(**S**)

Figure 4.14. A crystal contains a large number of identical unit cells. Only two of them are drawn in this figure.

To obtain the scattering by the crystal, we must add the scattering by all unit cells with respect to a single origin. We choose the origin O in Figure 4.14. For a unit cell with its own origin at position $t \cdot \mathbf{a} + u \cdot \mathbf{b} + v \cdot \mathbf{c}$, in which t, u, and v are whole numbers, the scattering is

$$\mathbf{F}(\mathbf{S}) \times \exp[2\pi i t \mathbf{a} \cdot \mathbf{S}] \times \exp[2\pi i u \mathbf{b} \cdot \mathbf{S}] \times \exp[2\pi i v \mathbf{c} \cdot \mathbf{S}].$$

The total wave $\mathbf{K}(\mathbf{S})$ scattered by the crystal is obtained by a summation over all unit cells:

$$\mathbf{K}(\mathbf{S}) = \mathbf{F}(\mathbf{S}) \times \sum_{t=0}^{n_1} \exp[2\pi i t \mathbf{a} \cdot \mathbf{S}] \times \sum_{u=0}^{n_2} \exp[2\pi i u \mathbf{b} \cdot \mathbf{S}] \times \sum_{v=0}^{n_3} \exp[2\pi i v \mathbf{c} \cdot \mathbf{S}].$$

The total wave **K(S)** scattered by the crystal is obtained by a summation over all unit cells:

$$\mathbf{K}(\mathbf{S}) = \mathbf{F}(\mathbf{S}) \times \sum_{t=0}^{n_1} \exp[2\pi i t\mathbf{a} \cdot \mathbf{S}] \times \sum_{u=0}^{n_2} \exp[2\pi i u\mathbf{b} \cdot \mathbf{S}] \times \sum_{v=0}^{n_3} \exp[2\pi i v\mathbf{c} \cdot \mathbf{S}].$$

Because n_1, n_2, and n_3 are very large, the summation $\sum_{t=0}^{n_1} \exp[2\pi i t\mathbf{a} \cdot \mathbf{S}]$ and the other two over u and v are almost always equal to zero unless $\mathbf{a} \cdot \mathbf{S}$ is an integer h, $\mathbf{b} \cdot \mathbf{S}$ is an integer k, and $\mathbf{c} \cdot \mathbf{S}$ is an integer l. This is easy to understand if we regard $\exp[2\pi i t\mathbf{a} \cdot \mathbf{S}]$ as a vector in the Argand diagram with a length of 1 and a phase angle $2\pi t\mathbf{a} \cdot \mathbf{S}$ (see Figure 4.15).

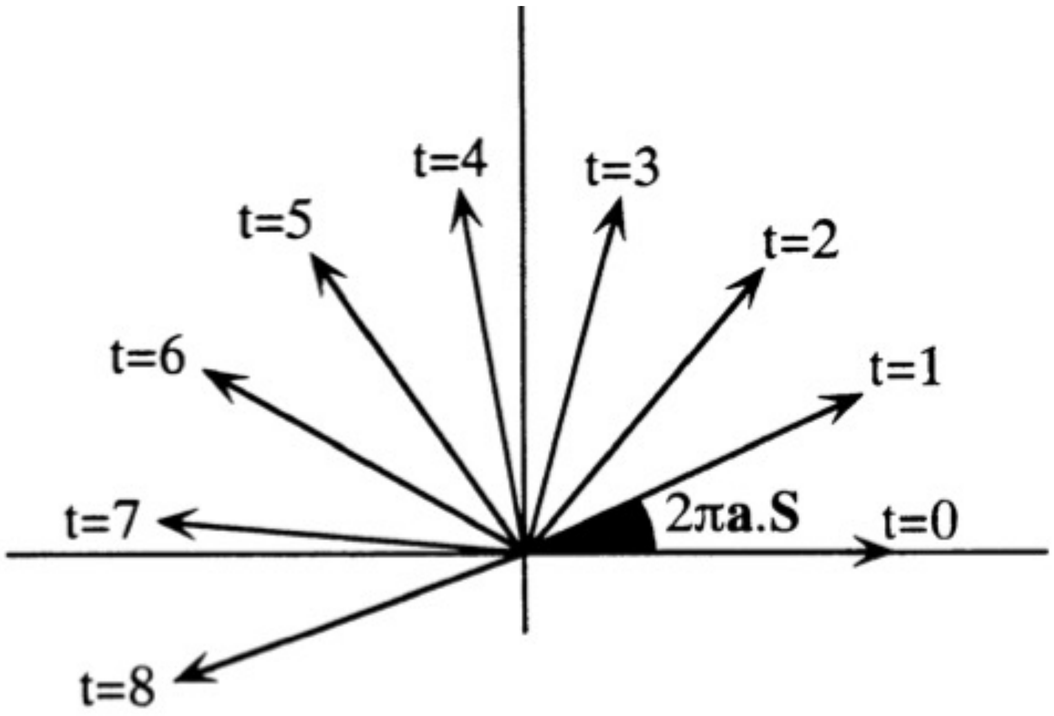
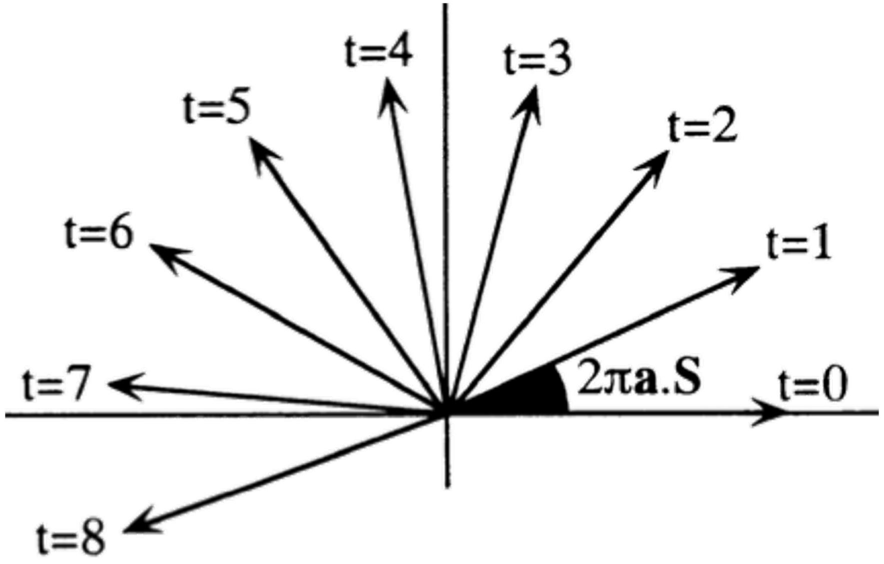


Figure 4.15. Each arrow represents the scattering by one unit cell in the crystal. Because of the huge number of unit cells and because their scattering vectors are pointing in different directions, the scattering by a crystal is, in general, zero. However, in the special case that $\mathbf{a} \cdot \mathbf{S}$ is an integer h, all vectors point to the right and the scattering by the crystal can be of appreciable intensity.



Conclusion: A crystal does not scatter X-rays, unless

$$\begin{aligned} \mathbf{a} \cdot \mathbf{S} &= h, \\ \mathbf{b} \cdot \mathbf{S} &= k, \\ \mathbf{c} \cdot \mathbf{S} &= l. \end{aligned} \tag{4.4}$$

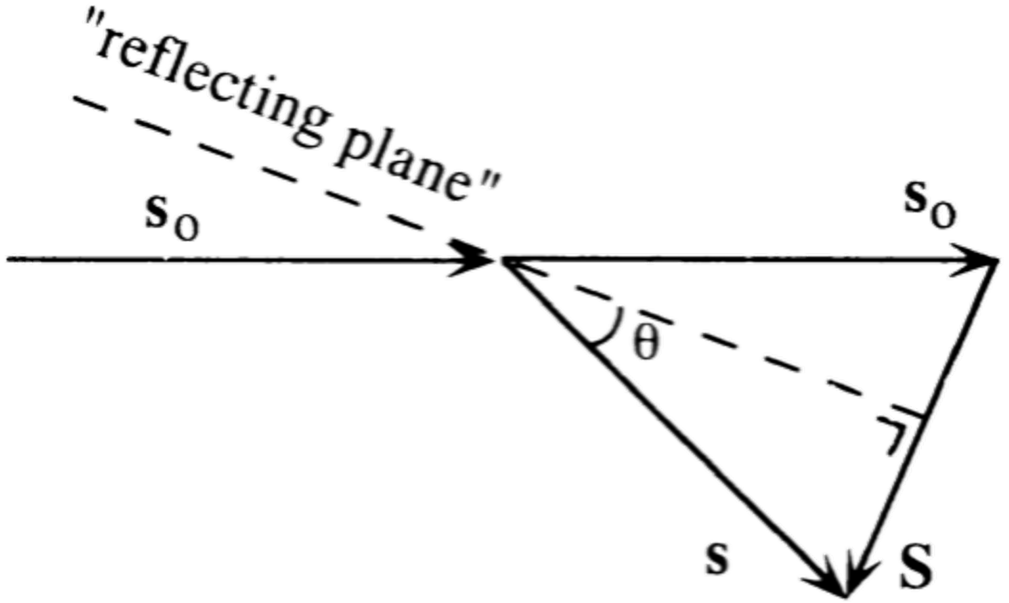
These are known as the Laue conditions. h, k, and l are whole numbers, either positive, negative, or zero. The amplitude of the total scattered wave is proportional to the amplitude of the structure factor $\mathbf{F}(\mathbf{S})$ and the number of unit cells in the crystal.

Diffraction Conditions

In Section 4.3, we noted that vector $\mathbf{S}$ is perpendicular to a "reflecting" plane. With a chosen origin for the system, $\mathbf{r} \cdot \mathbf{S}$ is the same for all points in the reflecting plane. This is true because the projection of each $\mathbf{r}$ on $\mathbf{S}$ has the same length. Because $\mathbf{r} \cdot \mathbf{S}$ determines the phase angle, the waves from all points in a reflecting plane reflect in phase. Choose the origin of the system in the origin O of the unit cell. The waves from a reflecting plane through the origin have phase angle 0 ($\mathbf{r} \cdot \mathbf{S} = 0$). For a parallel plane with $\mathbf{r} \cdot \mathbf{S} = 1$, they are shifted by $1 \times 2\pi$, and so forth. All parallel planes with $\mathbf{r} \cdot \mathbf{S}$ equal to an integer are reflecting in phase and form a series of Bragg planes.

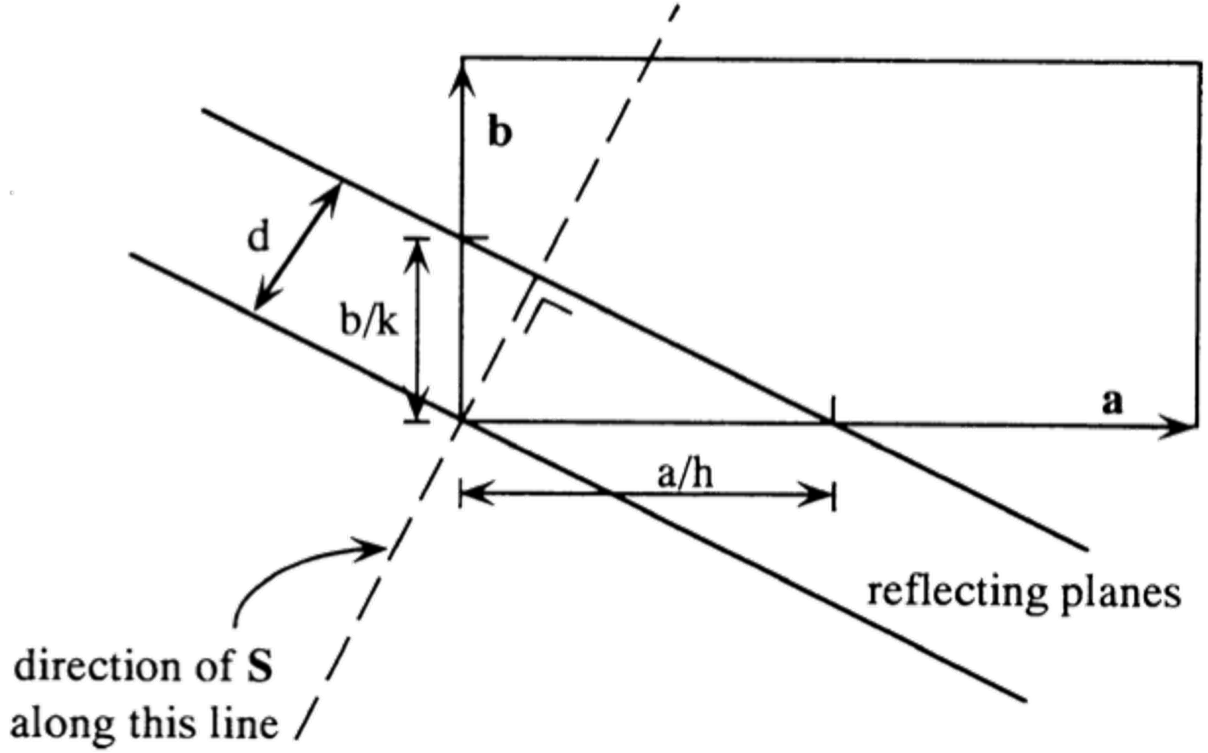
$$\mathbf{S} = \mathbf{s} - \mathbf{s}_0, \text{ with } |s| = |s_0| = 1/\lambda$$

$$|S| = 2(\sin\theta)/\lambda$$



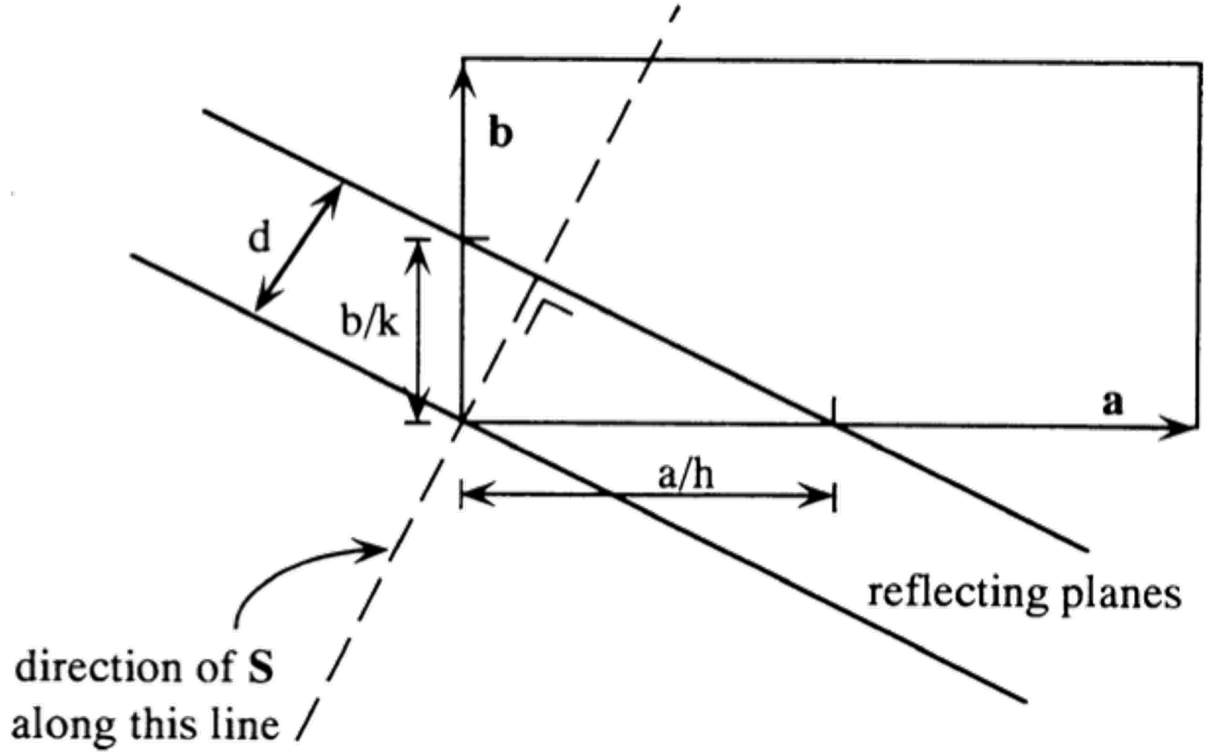
Bragg planes are identical to lattice planes

The plane with $\mathbf{r} \cdot \mathbf{S} = 1$ cuts the $\mathbf{a}$-axis at position $\mathbf{r} = \frac{\mathbf{a}}{\xi}$. Thus $\frac{\mathbf{a}}{\xi} \cdot \mathbf{S} = 1$. But from the Laue conditions we know that $\frac{\mathbf{a}}{h} \cdot \mathbf{S} = 1$. Therefore, $\xi = h$ and in the same way the reflecting plane cuts the $\mathbf{b}$-axis at $\mathbf{b}/k$ and the $\mathbf{c}$-axis at $\mathbf{c}/l$. The result is that the reflecting planes are the lattice planes.



The end points of the vectors $\mathbf{a}/h$, $\mathbf{b}/k$, and $\mathbf{c}/l$ form a lattice plane perpendicular to vector $\mathbf{S}$ (see the text). d is the distance between these lattice planes.

The projection of **a**/h on **S** has a length $1/|S|$, but this projection is also equal to the distance d between the lattice planes (Figure 4.16).



The end points of the vectors $\mathbf{a}/h$, $\mathbf{b}/k$, and $\mathbf{c}/l$ form a lattice plane perpendicular to vector **S** (see the text). d is the distance between these lattice planes.

$$1/|S| = d \text{ and } |S| = 2(\sin\theta)/\lambda \quad \Rightarrow \quad \frac{2d\sin\theta}{\lambda} = 1$$

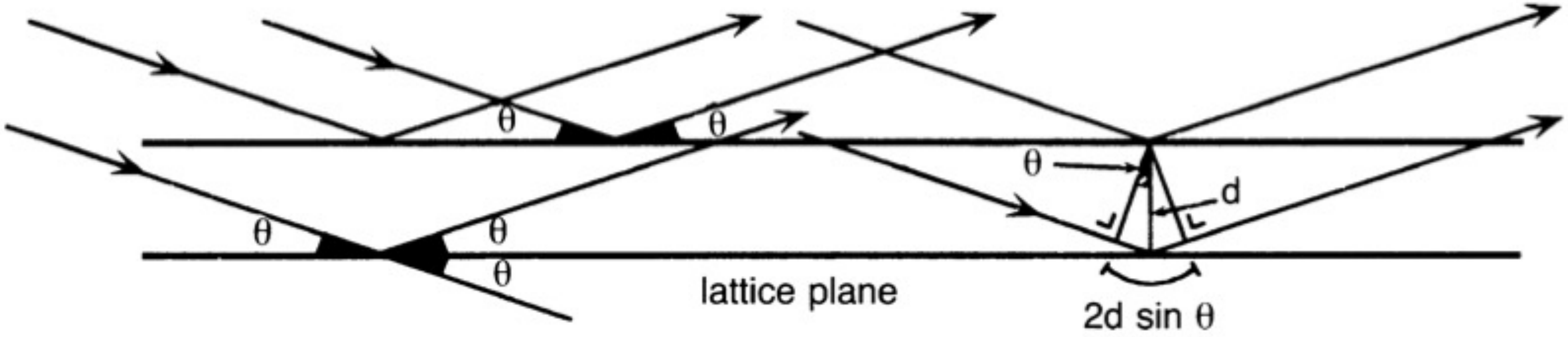


Figure 4.17. Two lattice planes are drawn separated by a distance d. The incident and the reflected beams make an angle θ with the lattice planes. Note that the beam is thus deflected through an angle of 2θ relative to its incident direction.

The incident and reflected beam make an equal angle with the plane (Figure 4.17). In a series of parallel reflecting planes (Bragg planes), the phase difference between the radiation from successive planes is 2π. The diffraction of X-rays by lattice planes can easily form the impression that only atoms on lattice planes contribute to the reflection. This is completely wrong! All atoms in the unit cell contribute to each reflection, atoms on lattice planes and in between. The advantage of lattice plane reflection and Bragg's law is that it offers a visual picture of the scattering process.

Reciprocal lattice and Ewald construction

There is a crystal lattice and a reciprocal lattice. The crystal lattice is real, but the reciprocal lattice is an imaginary lattice.

Question: What is the advantage of the reciprocal lattice?
Answer: With the reciprocal lattice, the directions of scattering can easily be constructed.

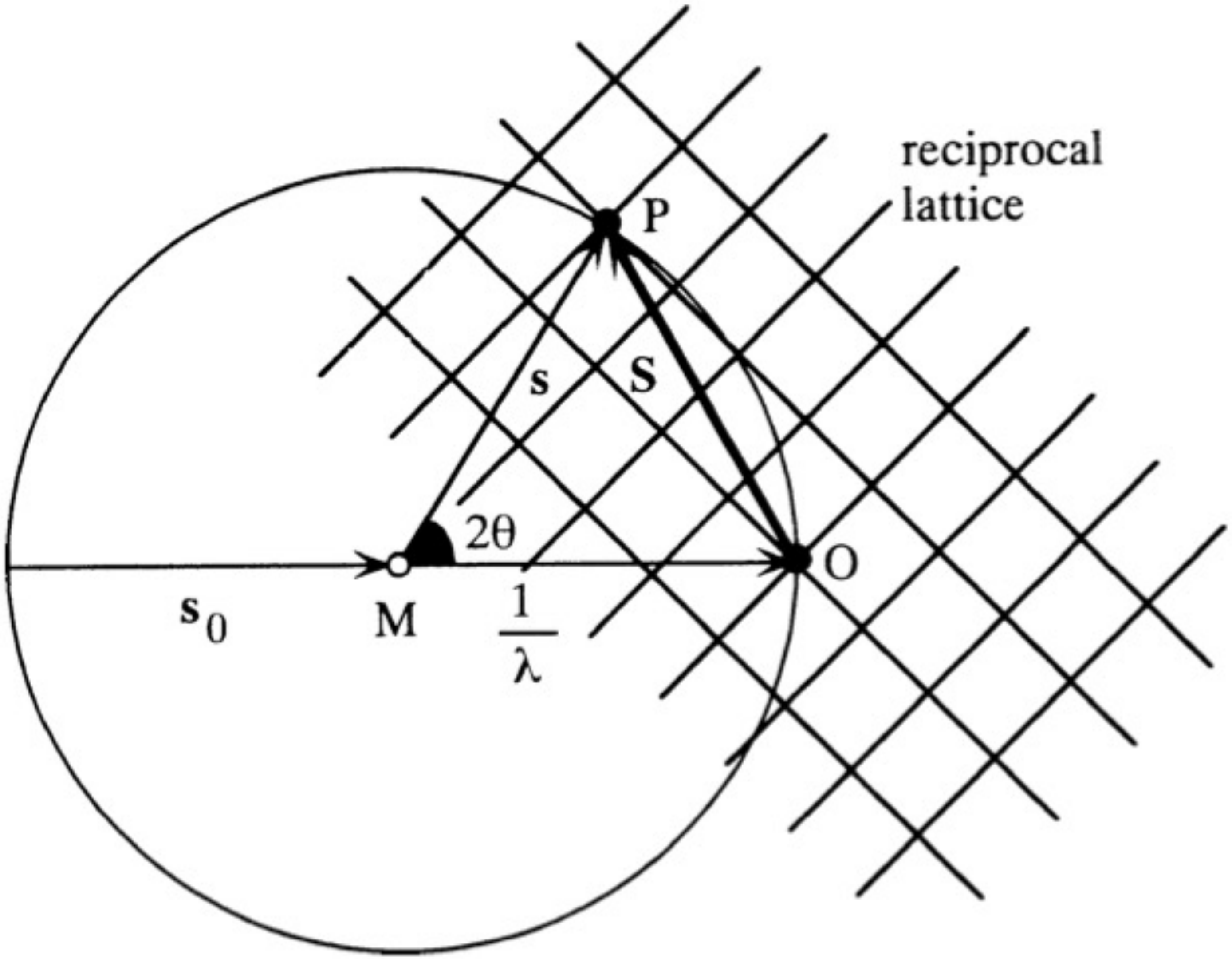


Figure 4.19. The Ewald sphere as a tool to construct the direction of the scattered beam. The sphere has radius $1/\lambda$. The origin of the reciprocal lattice is at O. $\mathbf{s}_0$ indicates the direction of the incident beam; $\mathbf{s}$ indicates the direction of the scattered beam.

Expected end of lecture #2