In the September 9 lecture notes eqn (10) gave the amplitude of vibration of an electron which was forced by the electric field of an electromagnetic wave with circular frequency $\omega$. Under the action of the incident wave, the steady state moment at time $t$ is,

$$M = \frac{e^2}{m} \frac{E_0 e^{i \omega t}}{\omega_0^2 - \omega^2 + i \gamma \omega}.$$  \hspace{1cm} (1)

The axis of the resultant dipole oscillator is parallel to the direction of the incident electric vector $E$, which is given in the numerator of (1). The action of the magnetic field of the incident wave on the dipole motion is small and was neglected.

The oscillating dipole is the source of an electromagnetic wave of the same frequency. At a distance large compared to the amplitude of oscillation, the scattered wave is spherical, and its electric vector at a distance $R$ at a time $t$ at a point in the equatorial plane of the dipole is the moment of the dipole at time $t-|R|/c$ times $\omega^2/(c^2|R|)$. The amplitude $A$ of the scattered wave at unit distance in the equatorial plane is therefore

$$A = \frac{e^2}{mc^2} \frac{\omega^2 E_0}{\omega_0^2 - \omega^2 + i \gamma \omega}.$$  \hspace{1cm} (2)

The scattering factor of the dipole, $f$, is defined as the ratio of the amplitude scattered by the oscillator to that scattered by a free electron under the same conditions. The scattering by a free electron is (2) with the natural frequency, $\omega_0$, at zero and the damping factor, $\gamma$, also set to zero. Thus the scattered amplitude of the free electron in the equatorial plane at unit distance is,

$$A_e = -\frac{(e^2/mc^2)}{E_0}.$$  \hspace{1cm} (3)

The negative sign means that the wave scattered by the free electron in the forward direction has a phase opposite to that of the primary wave. The results from (2) and (3) give for the scattering factor of a dipole oscillator with natural frequency $\omega_0$ and for waves of frequency $\omega$,

$$f = \frac{\omega^2}{\omega^2 - \omega_0^2 - i \gamma \omega}.$$  \hspace{1cm} (4)
With the definition of $f$ in (4) the scattered wave is *opposed* in phase to the primary wave when $f$ is positive.

If $\omega \gg \omega_0$, $f$ is unity. If $\omega \ll \omega_0$, $f$ is negative, and the dipole then scatters a wave in phase with the primary wave and the amplitude is proportional to $\omega^2$. For the two extremes considered here the damping term, $\gamma \omega$, in the denominator is small and may be neglected. When $\omega \approx \omega_0$, the scattering factor becomes complex. This means that both amplitude and phase of the scattered radiation depend on the incident frequency.

Let’s suppose that an incident plane wave passes through a medium that contains a large number $N$ of similar dipoles per unit volume, each of which scatters a wave assumed to be in phase with the primary wave. This means the incident frequency is in a regime where $f$ is negative. By the method of Fresnel zones it can be shown that the waves scattered by the dipoles lying in any thin sheet of the medium parallel to the primary wave-front will combine to form a resultant wave the phase of which lags $\pi/2$ behind that of the primary wave. The successive additions of these small components $\pi/2$ out of phase with the primary wave cause the resultant transmitted wave to travel through the medium with a phase-velocity which is less than $c$, the speed of light in free space. This means the medium has a refractive index for the transmitted waves that differs from unity, For X-rays the refractive index $n$ is given in terms of the scattering factor $f$ by

$$n = 1 - \left(\frac{2\pi Ne^2}{m\omega^2}\right)f,$$  \hspace{1cm} (5)

When $\omega \ll \omega_0$, $f$ is negative so $n$ is greater than one and the phase-velocity of the scattered wave is less than $c$. But for $\omega \gg \omega_0$, the refractive index is less than unity and the phase-velocity of the transmitted wave is greater than $c$. At both these extremes there is no appreciable absorption of the radiation by the medium. The effect of scattering is a change in the phase-velocity of the transmitted wave. If $\omega$ is comparable to $\omega_0$, $f$ becomes complex as does the refractive index of the medium. The imaginary component is related to the conductivity of the medium or, more appropriately, to the absorption of the radiation by the medium.

We can write (4) in terms of a real and an imaginary component

$$f = f' + i f''$$  \hspace{1cm} (6)

where, based on (4),

$$f' = \frac{\omega^2(\omega^2 - \omega_0^2)}{(\omega^2 - \omega_0^2)^2 + \gamma^2\omega^2}$$  \hspace{1cm} (7)
According to classical optical theory the medium will have a linear absorption coefficient $\mu_0$ for waves of frequency $\omega$ via the relation,

$$\mu_0 = \left( \frac{4\pi N e^2}{m \omega c} \right) f''$$

(9)

From (8) and (9), the absorption per dipole of the medium for a wave with frequency $\omega$ is,

$$\mu_a(\omega) = \frac{4\pi e^2 \gamma}{mc} \frac{\omega^2}{(\omega^2 - \omega_0^2)^2 + \gamma^2 \omega^2}$$

(10)

From (8) it is clear that $f''$ is always positive. The imaginary part of $f$ denotes a component of scattering by the dipole with a phase which lags $\pi/2$ behind the primary wave. Dipoles lying in any thin sheet parallel to the primary wave-front produce a resultant wave with a phase retarded by $\pi/2$ behind that of the waves scattered by the individual dipoles in the sheet. Thus the retardation of the resultant scattered wave will be $\pi$, so that it opposes the primary wave. The effect of the imaginary component of $f$ will be to add to the resultant scattered wave a component which at each point of the medium is out of phase with the primary wave. Hence there is a progressive diminution in the amplitude of the transmitted wave, which is an absorption.

For a collection of electrons that respond to the external electromagnetic field independently, but with a natural frequency, $\omega_j$, and a damping constant, $\gamma_j$, for electron $j$, the steady-state solution for the displacement, (cf. eqn (4) in the September 9 lecture) is,

$$x_j = \frac{e}{m \omega^2} \frac{1}{1 - (\omega_j/\omega)^2 - i(\gamma_j/\omega)} E_0 e^{i(\omega t - k_0 r_j)}. \quad (11)$$

A comparison with the earlier development of an atomic scattering factor, eqn (17) from the September 6 lecture, suggests a sensible modification is,

$$f = \sum_j \frac{\phi_j}{1 - (\omega_j/\omega)^2 - i(\gamma_j/\omega)}. \quad (12)$$

In order to conform with the quantum mechanical picture of the atom, the electrons should be replaced with continuous bands of virtual classical oscillators. The $j$th electron in an atom has a series of levels completely occupied so
that transitions to the occupied levels are forbidden by the Pauli principle. The characteristic frequency of the electron must be associated with a transition from the normal state to an excited state of the continuum. We assume a frequency distribution function, $w_j$, of the corresponding oscillators from $\omega_j$ to $\infty$. The actual form of $w_j$ will depend on the transition probabilities.

We take $w_j(\omega')d\omega'$ as the number of virtual oscillators associated with the $jth$ electron in the range $\omega'$ to $\omega' + d\omega'$. With these distribution functions, the atomic form factor suggested by (12) is modified to,

$$f = \sum_j \phi_j \int_{\omega_j}^{\infty} \frac{w_j d\omega'}{1 - (\omega'/\omega)^2 - i(\gamma_j/\omega)}.$$  \hspace{1cm} (13)

At high frequencies for the X-ray, we expect $f$ to approach $f_0$, where

$$f_0 = \sum_j \phi_j.$$  \hspace{1cm} (14)

[See eqn(17) in the September 6 lecture.] We formally write (13) for an atom with anomalous scattering as,

$$f_{at}(K) = f_{at,0}(K) + \Delta f_{at}' + \imath \Delta f_{at}''$$ \hspace{1cm} (15)

with

$$\Delta f_{at}' = \sum_j \phi_j \int_{\omega_j}^{\infty} \frac{w_j(1 - (\omega'/\omega)^2)d\omega'}{(1 - (\omega'/\omega)^2 + (\gamma_j/\omega)^2)}.$$ \hspace{1cm} (16)

and

$$\Delta f_{at}'' = \sum_j \phi_j \int_{\omega_j}^{\infty} \frac{w_j(\gamma_j/\omega)d\omega'}{(1 - (\omega'/\omega)^2 + (\gamma_j/\omega)^2)}.$$ \hspace{1cm} (17)

In practice, the real and imaginary corrections to $f_0$ are taken for the forward scattering direction, i.e $K = 0$. The justification for this approximation is that the dominant contributor to $\Delta f'$ and $\Delta f''$ is the 1s electron in the atom, which has a highly localized density distribution about the nucleus. For most calculations in structural crystallography the atomic form factor is treated as a function which is isotropic in its dependence on $K$. Thus for open-shell atoms the atomic form factor used in a structure factor calculation is

$$f_{at}(K) = \left(\frac{1}{4\pi}\right) \int_{-1}^{1} \int_{0}^{2\pi} f(K) d\phi_{K} d\eta_{K}.$$ \hspace{1cm} (18)

Atomic form factors for the elements up to Pu ($Z = 94$) are tabulated in *International Tables for X-ray Crystallography Volume IV* J. A. Ibers and W. C.
Hamilton (eds.). Kynoch Press, 1974. The tabulations are of \( f_{at} \) as a function of \( \sin \theta/\lambda \ (\text{Å}^{-1}) \). In addition anomalous scattering factors for most of the elements at selected wavelengths (a selected \( \omega \)) are also tabulated.

The scattering factor for a crystallographic unit cell may be computed in a fashion similar to that for an atom, as done in the September 6 lecture [eg. see eqns (16) and (17)]. In the atom there was a continuous electron density distribution, \( \rho(\mathbf{r}) \), where the origin for \( \mathbf{r} \) is the atomic nucleus. The density of a cell is approximated as a superposition of spherical atoms; the so-called promolecule or independent atom model (IAM). With the IAM the cell electron density distribution is,

\[
\rho_{\text{cell}}(\mathbf{r}) = \sum_{k=1}^{N} \rho_{at}(\mathbf{r} - \mathbf{R}_k) \quad (19)
\]

for a crystallographic unit cell with \( N \) atoms. The \( k \)th atom resides at a site \( \mathbf{R}_k \) which is within the cell and is of microscopic dimensions \((10^{-1} \text{ to } 10^{+2} \text{ nm})\). The origin for \( \mathbf{r} \) in (19) is no longer an atomic nucleus, but rather the origin of the unit cell in a crystal. The atom electron density, \( \rho_{at}(\mathbf{r}_k) \), is for atom type \( at \). The cell scattering factor, corresponding to the density given by (19), is

\[
F(\mathbf{K}) = \sum_{k=1}^{N} f_{at,k}(K) \exp(i \mathbf{K} \cdot \mathbf{R}_k). \quad (20)
\]

\( F \) in (20) is commonly known as the structure factor in X-ray crystallography. Even if the \( f_{at} \) are real functions, \( F \) is in general complex. As can be seen in (20) the phase of \( F \) depends on the \( \mathbf{R}_k \), the atomic sites in the cell. The detailed values of the \( \mathbf{R}_k \) constitute a crystal structure. Notice how the structure factor \( F \) is due to coherent scattering by the atoms that make up the unit cell. If the atoms and their positions are known, then (20) provides a route for assigning phases to \( F \). The number of unique atoms in a crystallographic unit cell is generally less than \( N \). This is due to the symmetry elements of the space group to which the unit cell belongs. Sometimes, but not always, the symmetry of the crystal diffraction pattern is sufficient to assign the space group.

In the X-ray diffraction experiment, it is \(|F|^n\) which is measurable, rather than \( F \), where \( n \) is 1 or 2. Herein lies the phase problem for an X-ray crystal structure determination.