

X-Ray Scattering by a Free Electron

X-rays are electromagnetic radiation, and as such manifest both wave and particle properties:

X-ray waves have wavelengths and frequencies of the order of $\lambda \approx 1 \text{ \AA} = 10^{-10} \text{ m}$ and

$\omega = 2\pi\nu = 2\pi c/\lambda \approx 2 \times 10^{19} \text{ s}^{-1}$; X-ray photons have Planck-Einstein energies $E_\gamma = h\nu = hc/\lambda$

and de Broglie momenta $p_\gamma = h/\lambda$, where $h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$ is Planck's constant. X-rays with $\lambda = 1 \text{ \AA}$ have $E_\gamma = 1.988 \times 10^{-25} \text{ J}$ or $V = E_\gamma/q_e = 12.4 \text{ keV}$, where $q_e = 1.602 \times 10^{-19} \text{ C}$ is the electron charge. Corresponding to the dualistic wave/particle nature of X-rays, there are two types of X-ray scattering by electrons: Thomson scattering via electromagnetic wave-electron interactions, and Compton scattering via photon-electron collisions.

Thomson Scattering. If a linearly polarized, monochromatic, plane wave X-ray beam is incident on a stationary free electron with charge e and mass m , the oscillating electric field

$E = E_0 e^{i(\omega t - \delta)}$ of the incident X-ray wave exerts a Coulombic driving force ($F = qE$) on the electron that causes it to oscillate at the same frequency as the incident radiation. By Newton's second law of motion ($F = ma$) the equation of motion for the driven harmonic oscillation of the electron is then

$$ma = q_e E = e E_0 e^{i(\omega t - \delta)},$$

and the electron experiences the oscillating acceleration

$$a = \frac{e}{m} E_0 e^{i(\omega t - \delta)} = a_0 e^{i(\omega t - \delta)}.$$

Since an accelerated charge emits electromagnetic radiation, the oscillating electron becomes a new source of X-rays that radiate spherically in all directions and have the same frequency as the incident X-rays. Effectively, the electron scatters the incident X-ray beam in all directions.

According to classical electrodynamical theory, the electromagnetic radiation at a point at \vec{r} far from a charge q that experiences an acceleration \vec{a} has an electric field component

$$\mathcal{E} = -\frac{qa \sin \alpha}{c^2 r},$$

where c is the speed of light and α is the angle between \vec{a} and \vec{r} . So, if a linearly-polarized, monochromatic X-ray beam is incident on a free stationary electron, and the scattered radiation is observed at a position \vec{r} , far from the electron, in the equatorial plane through the electron's original at-rest position and perpendicular to its oscillation direction, *i.e.*, perpendicular to the incident beam polarization direction, then $\alpha = 90^\circ$, $\sin \alpha = 1$, and the electric field component of the scattered radiation has amplitude

$$\mathcal{E}_0 = -\frac{qa_0}{c^2 r} = -\frac{q}{c^2 r} \frac{e}{m} E_0 = -\left(\frac{e^2}{mc^2} \right) \frac{E_0}{r}.$$

In the present case of forced oscillation of a free electron, although $q = e$ is a negative charge, the product $qe = e^2$ is positive, and the negative sign means that the scattered radiation is 180° or π out of phase with the incident radiation, *i.e.*, there is a 180° phase change – a phase flip or phase reversal – upon scattering.

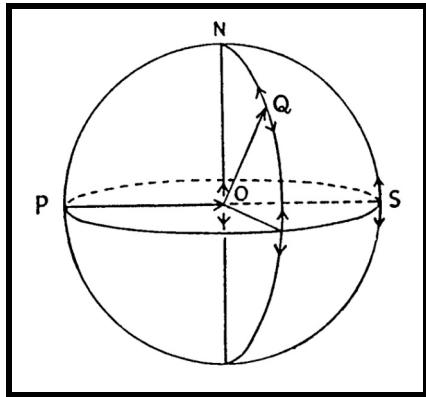


Figure copied from James (1982).

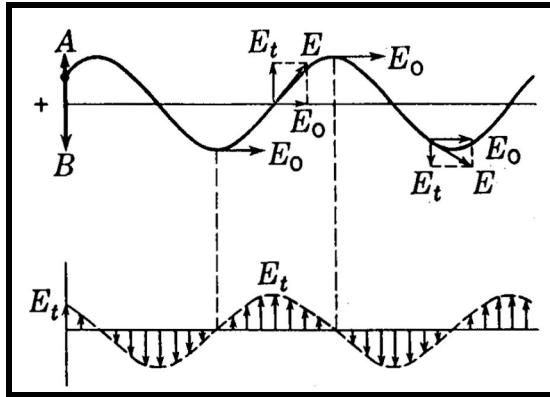


Figure copied from Jenkins and White (1957).

X-rays incident from point P on an electron at the origin O are scattered spherically in all directions. The amplitude of the scattered wave at any observation point such as S or Q is perpendicular to the radius from O to the point, and the phase of the scattered wave with respect to the meridian through the observation point is opposite the phase of the incident wave with respect to the polar axis through the origin. The incident wave and the forced oscillation of the electron have the same frequency, but the phase of the electron oscillation lags $\pi/2$ behind the phase of the incident wave, and the phase of the scattered wave lags $\pi/2$ behind the phase of the electron oscillation. Hence, the phase of the scattered wave lags π behind, i.e., is opposite the phase of the incident wave.

The physics of X-ray scattering by a free electron was first analyzed in terms of classical electromagnetic theory by J.J. Thomson (1856-1940), the discoverer of the electron, and the

constant factor in the scattered-to-incident amplitude ratio, $\frac{\mathcal{E}_o}{E_0} = -\left(\frac{e^2}{mc^2}\right)\frac{1}{r} = -\frac{r_e}{r}$, is called the

Thomson scattering length of the classical electron. By dimensional analysis,

$$r_e = \frac{e^2}{mc^2} = \frac{\text{charge}^2}{\text{mass} \cdot \text{velocity}^2} = \frac{\text{charge}^2}{\text{mass} \cdot \text{distance}^2 \cdot \text{time}^{-2}} = \frac{\text{force}}{\text{mass} \cdot \text{time}^{-2}} = \frac{\text{acceleration}}{\text{time}^{-2}} = \text{distance},$$

and the constant has dimension length (as it must, because multiplying it by $1/r$ gives the dimensionless ratio $-\mathcal{E}_0/E_0$). For historical reasons, the Thomson scattering length is also called the *classical electron radius*, since for a uniform distribution of charge equal to the electron charge, q_e , confined to a sphere with mass equal to the electron rest mass, m_e , the sphere radius, r_e , results from equating the electrostatic potential energy of the charge distribution, $q_e V = q_e^2/r_e$, and the relativistic energy, $m_e c^2$, equivalent to the electron rest mass.

Converting from Gaussian cgs units to SI mks units (in which $1 \text{ C} = 1 \text{ A} \cdot \text{s}$), the value of the Thomson scattering length or classical electron radius is

$$r_e = \frac{e^2}{mc^2} = \frac{1}{4\pi\epsilon_0} \frac{q_e^2}{m_e c^2} = 2.818 \times 10^{-15} \text{ m},$$

where $q_e = 1.602 \times 10^{-19} \text{ C}$ and $m_e = 9.107 \times 10^{-31} \text{ kg}$ are, respectively, the charge and rest mass of the electron, $c = 2.998 \times 10^8 \text{ m} \cdot \text{s}^{-1}$ is the speed of light in free space, and the quantity $(4\pi\epsilon_0)^{-1} = 8.988 \times 10^9 \text{ C}^{-2} \cdot \text{N} \cdot \text{m}^2$ is the constant of proportionality in Coulomb's law,

$F = (4\pi\epsilon_0)^{-1} q_1 q_2 / r_{12}^2$, in which $\epsilon_0 = 1/(\mu_0 c^2) = 8.854 \times 10^{-12} \text{ C}^2 \cdot \text{N}^{-1} \cdot \text{m}^{-2}$ is the electric permittivity of free space, derived from the defined magnetic permeability of free space, $\mu_0 \equiv 4\pi \times 10^{-7} \text{ C}^{-2} \cdot \text{N} \cdot \text{s}^2$.

Because r_e is so small, the scattered-to-incident amplitude ratio $-\mathcal{E}_0/E_0 = r_e/r$ implies that an electron scatters only a tiny fraction of X-radiation incident on it. At a distance from the electron of only a nanometer, the amplitude ratio is only $r_e/r = 2.8 \times 10^{-15} \text{ m}/10^{-9} \text{ m} \approx 10^{-6}$, yet we observe and measure X-ray scattering at sample to detector distances of tens of centimeters because even a tiny material sample contains a huge number of electrons, e.g., in just 1 μg of carbon there are $10^{-6} \text{ g} \times \frac{1 \text{ mol}}{12 \text{ g}} \times \frac{6.023 \times 10^{23} \text{ atoms}}{1 \text{ mol}} \times \frac{6 \text{ electrons}}{\text{atom}} \approx 3 \times 10^{17} \text{ electrons}$.

Compton scattering. Thomson scattering, which accounts for most X-ray scattering by electrons, is elastic, i.e., the incident and scattered X-rays have the same wavelength; and it is the Thomson scattering of electromagnetic X-ray waves without change in wavelength that produces the interference effects responsible for diffraction of X-rays by crystals. A small part, however, of the total scattering of X-rays by matter is inelastic in that some of the scattered X-rays have longer wavelengths than the incident X-rays, because, in the manner of a billiard ball collision, with total energy and total momentum are conserved, energy is transferred from the incident X-ray photon to the electron, and both the photon and the electron are scattered at angles that depend on the size of the photon wavelength change, i.e., on the size of the photon-to-electron energy transfer. In crystallographic X-ray diffraction measurements of Bragg reflection peaks due to coherent, elastic Thomson scattering, the incoherent, inelastic Compton scattering appears as diffuse, uniform background under the peaks.

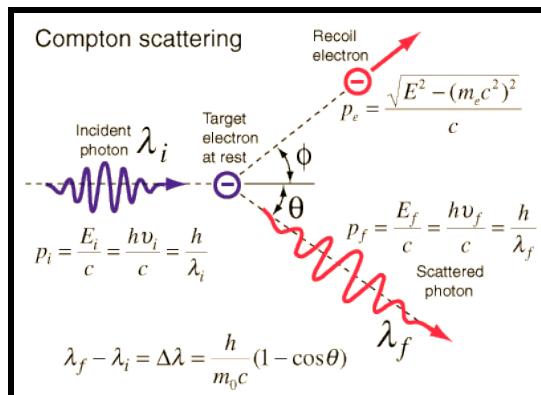


Illustration copied from Nave (2006). <http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/compeq.html#c1>.

X-Ray Scattering by a Bound Atomic Electron

If a linearly polarized, monochromatic X-ray beam is incident on an atom, the oscillating electric field of the electromagnetic radiation forces both the nucleus and the electrons surrounding it to oscillate with the same frequency as the incident X-rays. The atom becomes an assembly of oscillating dipoles in which the relatively massive nucleus ($m_p/m_e = 1836$) can be regarded as being stationary and each oscillating electron experiences a Hooke's law restoring force ($F = -kx$) equal to the net resultant of the force of attraction to the nucleus screened by the forces of repulsion from the other electrons.

The equation of motion for the forced harmonic oscillation of an electron in an atom is then

$$m \frac{d^2x}{dt^2} = -kx + eE_0 e^{i(\omega t - \delta)}.$$

This differential equation has a solution of the form

$$x = x_0 e^{i(\omega t - \delta)}$$

for the oscillatory displacement, and differentiation gives the oscillatory velocity and acceleration,

$$\begin{aligned} v &= \frac{dx}{dt} = i\omega x_0 e^{i(\omega t - \delta)} \\ a &= \frac{dv}{dt} = \frac{d^2x}{dt^2} = -\omega^2 x_0 e^{i(\omega t - \delta)}. \end{aligned}$$

Substitution into the equation of motion gives

$$\begin{aligned} -m\omega^2 x_0 e^{i(\omega t - \delta)} &= -kx_0 e^{i(\omega t - \delta)} + eE_0 e^{i(\omega t - \delta)} \\ x_0 (k - m\omega^2) &= eE_0, \end{aligned}$$

which yields the electron's oscillation amplitude,

$$x_0 = \frac{eE_0}{k - m\omega^2} = \frac{eE_0}{m\left(\frac{k}{m} - \omega^2\right)} = \frac{eE_0}{m(\omega_0^2 - \omega^2)},$$

or, after changing signs in the numerator and denominator,

$$x_0 = -\frac{eE_0}{m(\omega^2 - \omega_0^2)},$$

where the quantity introduced as

$$\omega_0 = \sqrt{\frac{k}{m}}$$

is the natural vibration frequency of the dipole oscillator corresponding to the net binding force ($F = -kx = -m\omega_0^2 x$) exerted on the electron by the nucleus as screened by the other electrons.

The oscillating electron's acceleration is then

$$a = -\omega^2 x_0 e^{i(\omega t - \delta)} = \frac{eE_0 \omega^2}{m(\omega^2 - \omega_0^2)} e^{i(\omega t - \delta)} = a_0 e^{i(\omega t - \delta)},$$

and, from the classical theory of electrodynamics, the radiation scattered to a position \vec{r} in the equatorial plane of the dipole oscillator, which is perpendicular to the X-ray polarization direction, has amplitude

$$\mathcal{E}_0 = -\frac{ea_0}{c^2 r} = -\left(\frac{e^2}{mc^2}\right) \frac{E_0}{r} \frac{\omega^2}{(\omega^2 - \omega_0^2)}.$$

Therefore, at unit distance, in units of minus the Thomson scattering length of a free classical electron, the scattering factor for a bound atomic electron is

$$f_e = \frac{\mathcal{E}_0(\text{bound})}{\mathcal{E}_0(\text{free})} = \frac{\omega^2}{\omega^2 - \omega_0^2} = \frac{1}{1 - \left(\frac{\omega_0}{\omega}\right)^2},$$

where, again, ω is the frequency of the incident and scattered X-rays and ω_0 is the natural vibration frequency of the nucleus-electron dipole oscillator

Note that in the high-frequency limit with $\omega \gg \omega_0$, which is commonly case, the scattering factor is independent of frequency, and *the scattering by a bound atomic electron is to a good approximation the same as the scattering by a free electron.*

Since atomic electrons move around the nucleus with speeds much less than of the speed of light, they appear, from the point of view of incident X-rays, to be stationary. For example, in a Bohr atom, the condition for a stable electron orbit is that the centripetal force of nuclear attraction balances the tangential centrifugal force of orbital revolution, i.e.,

$$\frac{Ze^2}{r^2} = \frac{mv^2}{r},$$

$$Ze^2 = (mvr)v,$$

and the orbital angular momentum is quantized,

$$L = mvr = \frac{nh}{2\pi}, \quad n = 1, 2, 3, \dots.$$

Thus, the speed of an electron in the ground-state, first Bohr orbit in a hydrogen atom is,

$$v = \frac{Ze^2}{L} = Ze^2 \frac{2\pi}{nh} \Big|_{Z=1, n=1} = \left(\frac{1}{4\pi\epsilon_0}\right) q_e^2 \frac{2\pi}{h} \\ = \frac{(8.988 \times 10^9 \text{ C}^{-2} \cdot \text{N} \cdot \text{m}^2) \times (1.602 \times 10^{-19} \text{ C})^2 \times 2\pi}{6.626 \times 10^{-34} \text{ J} \cdot \text{s}} = 2.2 \times 10^6 \text{ m} \cdot \text{s}^{-1} = 0.007 c.$$

less than 1% of the speed of light. Even in the extreme case of a uranium atom with $Z = 90$, the speed of the lowest energy electron, in the first Bohr orbit, is only $\sim 0.6 c$.

Not only are atomic electrons generally moving much more slowly than electromagnetic waves, but the oscillatory displacement of an electron imparted by the oscillating electric field of an incident X-ray wave is very small. In the high frequency limit with $\omega \gg \omega_0$ the amplitude of electron oscillation per unit amplitude of incident X-rays is

$$x_0 = \frac{eE_0}{m(\omega^2 - \omega_0^2)} = \left(\frac{1}{4\pi\epsilon_0} \right) \frac{q_e E_0}{m_e \omega_x^2}$$

$$= \frac{(8.988 \times 10^9 \text{ C}^{-2} \cdot \text{N} \cdot \text{m}^2)(1.602 \times 10^{-19} \text{ C})(1 \text{ C} \cdot \text{m}^{-2})}{(9.107 \times 10^{-31} \text{ kg})(\sim 20 \times 10^{18} \text{ s}^{-1})^2} \approx 4 \times 10^{-14} \text{ m} = 4 \times 10^{-4} \text{ \AA},$$

which is a tiny fraction of an atomic diameter.

Thus all-in-all, *in the high-frequency limit with $\omega \gg \omega_0$, for atoms with $Z \lesssim 20$, normal scattering of X-rays by a bound atomic electron is independent of frequency or wavelength, and is, to a fair approximation, the same as the scattering by a stationary free electron.*

Dispersion Effects in X-Ray Scattering

In the special case that the X-ray frequency ω happens to be, or is tuned to be, close to the dipole oscillator's natural vibration frequency ω_0 , *resonant absorption due to the frequency matching* causes the electron oscillation amplitude $x_0 = (e/m)E_0\omega^2/(\omega^2 - \omega_0^2)$ to become very large. The amplitude does not, however, become infinite at $\omega = \omega_0$ because there is a small damping effect due to the energy loss to classical radiation by the oscillating electron.

Taking the damping force to be proportional the electron's velocity ($F = -k'v$), the electron's equation of motion in the damped, driven harmonic oscillator is

$$m \frac{d^2x}{dt^2} = -k' \frac{dx}{dt} - kx + eE_0 e^{i(\omega t - \delta)}.$$

Recalling that the restoring force constant was defined as

$$k = m\omega_0^2,$$

and defining the damping force constant as

$$k' = m\gamma,$$

the equation of motion can be rewritten as

$$\frac{d^2x}{dt^2} = -\gamma \frac{dx}{dt} - \omega_0^2 x + \frac{e}{m} E_0 e^{i(\omega t - \delta)}.$$

This differential equation too has a solution of the form

$$x = x_0 e^{i(\omega t + \delta)},$$

and differentiation and substitution gives

$$\begin{aligned} -\omega^2 x_0 e^{i(\omega t - \delta)} &= -i\gamma\omega x_0 e^{i(\omega t - \delta)} - \omega_0^2 x_0 e^{i(\omega t - \delta)} + \frac{e}{m} E_0 e^{i(\omega t - \delta)} \\ x_0 (\omega^2 - \omega_0^2 - i\gamma\omega) &= -\frac{e}{m} E_0 \\ x_0 &= -\frac{eE_0}{m(\omega^2 - \omega_0^2 - i\gamma\omega)}. \end{aligned}$$

With this oscillation amplitude, the oscillating acceleration of the electron is

$$a = -\omega^2 x_0 e^{i(\omega t - \delta)} = a_0 e^{i(\omega t - \delta)} = \frac{eE_0\omega^2}{m(\omega^2 - \omega_0^2 - i\gamma\omega)} e^{i(\omega t - \delta)};$$

the amplitude of radiation scattered to a point at \vec{r} in the equatorial plane of the oscillator is

$$\mathcal{E}_0 = -\frac{qa_0}{c^2 r} = -\left(\frac{e^2}{mc^2}\right) \frac{E_0}{r} \frac{\omega^2}{(\omega^2 - \omega_0^2 - i\gamma\omega)};$$

and, with the resonance damping correction included, the X-ray scattering factor for a bound atomic electron is

$$f_e = \frac{\mathcal{E}_0(\text{bound})}{\mathcal{E}_0(\text{free})} = \frac{\omega^2}{\omega^2 - \omega_0^2 - i\gamma\omega} = \frac{1}{1 - \left(\frac{\omega_0}{\omega}\right)^2 - \frac{i\gamma}{\omega}}.$$

For a free electron, $\omega_0 = \gamma = 0$ and $f_e = 1$ in units of minus the Thomson scattering length.

In order to emphasize that the frequency dependence in the resonant scattering factor is a correction to the frequency-independent normal scattering factor, the resonant scattering factor may be rewritten as

$$f_e = \frac{\omega^2}{\omega^2 - \omega_0^2 - i\gamma\omega} = 1 + \left(\frac{\omega_0^2 + i\gamma\omega}{\omega^2 - \omega_0^2 - i\gamma\omega} \right) \approx 1 + \left(\frac{\omega_0^2}{\omega^2 - \omega_0^2 - i\gamma\omega} \right),$$

where to obtain the rightmost expression the imaginary term could be neglected in the numerator because $\gamma \ll \omega$; but, if by accident or design $\omega \approx \omega_0$, the imaginary term cannot be neglected

in the denominator. For classical radiation-loss damping it can be shown that $\gamma = \frac{2}{3} \left(\frac{e^2}{mc^2} \right) \frac{\omega^2}{c}$,

so that if $\lambda \approx 1 \text{ \AA}$, $\omega = 2\pi c/\lambda \approx 2 \times 10^{19} \text{ s}^{-1}$, then $\gamma \approx 2.5 \times 10^{15} \text{ s}^{-1}$ and $\gamma/\omega \approx 10^{-4}$.

Multiplying numerator and denominator of f_e by the complex conjugate of the denominator in order to put the imaginary term in the numerator gives

$$\begin{cases} f_e = f'_e + if''_e = \frac{\omega^2(\omega^2 - \omega_0^2) + i\gamma\omega^3}{(\omega^2 - \omega_0^2)^2 + \gamma^2\omega^2} \approx 1 + \left[\frac{\omega_0^2(\omega^2 - \omega_0^2) + i\gamma\omega\omega_0^2}{(\omega^2 - \omega_0^2)^2 + \gamma^2\omega^2} \right] \\ f'_e = \frac{\omega^2(\omega^2 - \omega_0^2)}{(\omega^2 - \omega_0^2)^2 + \gamma^2\omega^2} \approx 1 + \left[\frac{\omega_0^2(\omega^2 - \omega_0^2)}{(\omega^2 - \omega_0^2)^2 + \gamma^2\omega^2} \right] \\ f''_e = \frac{\gamma\omega^3}{(\omega^2 - \omega_0^2)^2 + \gamma^2\omega^2} \approx \frac{\gamma\omega\omega_0^2}{(\omega^2 - \omega_0^2)^2 + \gamma^2\omega^2} \end{cases} \quad \begin{cases} f_e = f'_e + if''_e = |f_e| e^{i\delta} \\ |f_e| = \sqrt{(f'_e)^2 + (f''_e)^2} \\ \delta = \tan^{-1} \left(\frac{f''_e}{f'_e} \right). \end{cases}$$

Note that the real part of the complex-valued scattering factor $f_e = f'_e + if''_e$ might be negative or positive according to

$$\begin{cases} f'_e < 0 & \text{if } \omega < \omega_0, \\ f'_e > 0 & \text{if } \omega > \omega_0; \end{cases}$$

however, the coefficient of the imaginary part is intrinsically positive

$$f''_e > 0.$$

Thus, it is as if the damped resonant scattering phenomenon that occurs if $\omega \approx \omega_0$ corresponds to, in effect, an elastic X-ray absorption and re-emission that translate to, in effect, a time lag that produces a phase advance $\delta = \tan^{-1}(f''/f')$ with $0 \leq \delta < \pi$.

It is in the sense of their frequency or wavelength dependence that the *damped resonant scattering effects* observable when $\omega \approx \omega_0$ are referred to as *dispersion effects*, i.e., refraction effects that are different for different wavelengths, like the refractive bending of visible light by a glass prism that disperses white light into its spectrum of colors.

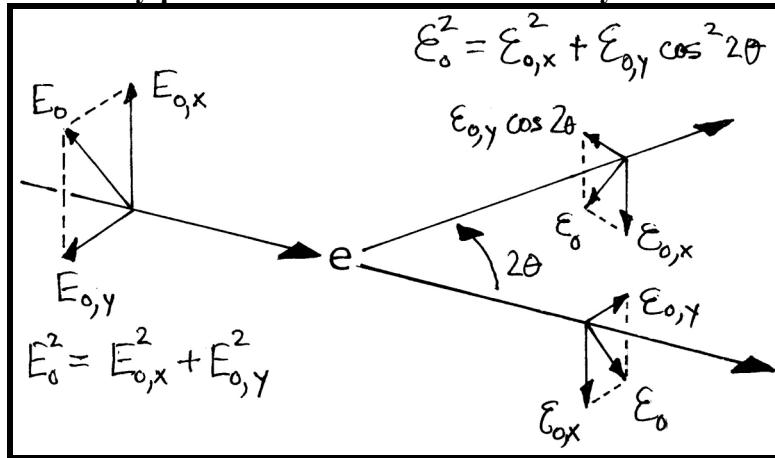
The dispersion effects due to damped resonant scattering are commonly referred to as *anomalous dispersion*, or *anomalous diffraction*, or *anomalous scattering*, since they are not normally observed, but rather are observed only when the incident radiation frequency is close to a scattering electron's natural absorption frequency. In this sense, the dispersion effects are not "normal", but there is nothing "abnormal" or "anomalous" about them; they are entirely natural resonance, or resonant absorption, effects.

Polarization Effects in X-Ray Scattering

To this point, the discussion of X-ray scattering by an electron has assumed a linearly polarized incident beam, and has considered only the scattering in an equatorial plane perpendicular to the incident beam polarization direction.

Scattering by an electron of an unpolarized beam was analyzed by J.J. Thomson by first considering a single, but arbitrary, direction of linear polarization resolved into its components perpendicular and parallel to the plane of scattering as in the figure below, and then averaging over all polarization directions $0 \leq \varphi < 2\pi$ around the beam direction.

Scattering of a linearly polarized beam with an arbitrary direction of polarization



In a linearly polarized beam incident along the z axis, the electric field amplitude in any particular direction and its x and y components obey

$$E_0^2 = E_{0,x}^2 + E_{0,y}^2 .$$

and, in the beam forward scattered at zero scattering angle along the z axis,

$$\mathcal{E}_0^2 = \mathcal{E}_{0,x}^2 + \mathcal{E}_{0,y}^2 .$$

At a point at distance R from the electron,

$$\mathcal{E}_0 = -\left(\frac{e^2}{mc^2}\right)\frac{1}{R} E_0 ,$$

and similarly for its x and y components, where the negative sign is present because $\vec{\mathcal{E}}_0$ and its x and y components are antiparallel to \vec{E}_0 and its x and y components due to the phase flip that occurs on scattering.,

For consistency with notation to be introduced later, the scattering angle between the incident beam and a scattered beam is denoted 2θ where θ is the angle that the incident and scattered beams each make with the bisector of the scattering angle. Then with respect to the forward scattered beam at zero scattering angle, the beam scattered at an angle 2θ to a point at a distance R from the electron has amplitude components $\mathcal{E}_{0,x}$ and $\mathcal{E}_{0,y} \cos 2\theta$, and the resultant scattered amplitude for the given, particular polarization direction is

$$\mathcal{E}_0^2 = \mathcal{E}_{0,x}^2 + \mathcal{E}_{0,y}^2 \cos^2 2\theta = \left(\frac{e^2}{mc^2} \right)^2 \frac{1}{R^2} (E_{0,x}^2 + E_{0,y}^2 \cos^2 2\theta) .$$

Finally, averaging the squared x - and y -amplitude components over $0 \leq \varphi < 2\pi$ polarization directions around the scattered beam direction gives

$$\langle E_{0,x}^2 \rangle = E_0^2 \langle \cos^2 \varphi \rangle = \langle E_{0,y}^2 \rangle = E_0^2 \langle \sin^2 \varphi \rangle = \frac{1}{2} E_0^2 ,$$

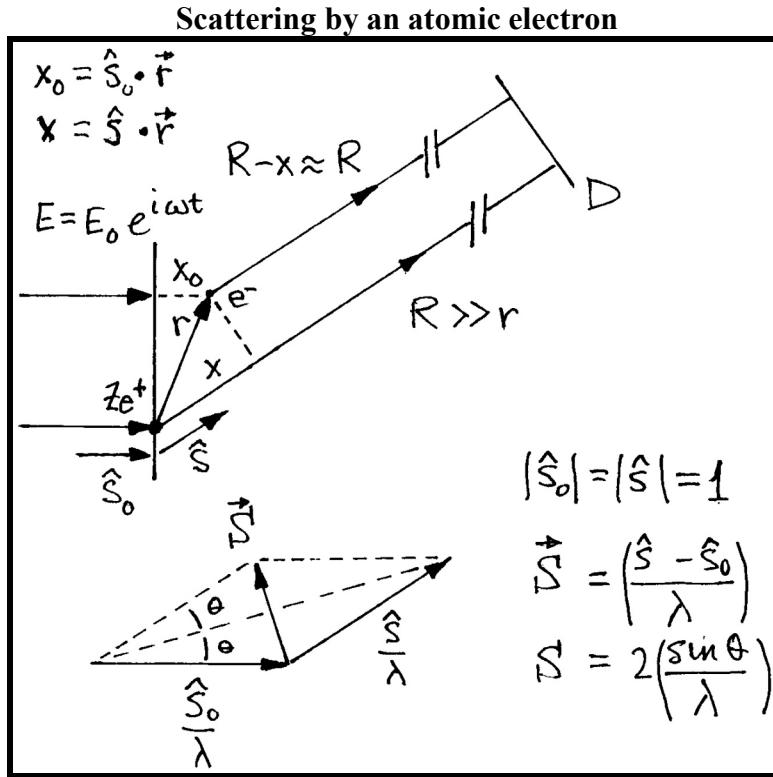
and thence the relative intensity of Thomson scattering of an unpolarized X-ray beam by a classical electron is

$$\frac{I_{2\theta}}{I_0} = \frac{\mathcal{E}_0^2}{E_0^2} = \left(\frac{e^2}{mc^2} \right)^2 \frac{1}{R^2} \left(\frac{1}{2} + \frac{1}{2} \cos^2 2\theta \right) ,$$

in which the factor $\left(\frac{1}{2} + \frac{1}{2} \cos^2 2\theta \right)$ is called the *polarization factor*.

Atomic Scattering Factors

Consider a monochromatic, linearly polarized, plane wave X-ray beam incident on an atom, in particular on an atomic electron at \vec{r} from the nucleus in a plane perpendicular to the polarization direction.



If at the nucleus $Z e^+$ the incident plane wave is described by $E = E_0 \exp(i\omega t)$, then at the electron e^- at \vec{r} from the nucleus the wave is phase-shifted and described by

$$E = E_0 \exp(i\omega t') = E_0 \exp\left[i\omega\left(t - \frac{x_0}{c}\right)\right] = E_0 \exp\left[i\left(\omega t - \frac{2\pi}{\lambda}x_0\right)\right],$$

where the adjusted time $t' = t - (x_0/c)$ and the phase shift $\delta = -\omega x_0/c = -2\pi x_0/\lambda$ are due to the incident wave path length difference,

$$x_0 = \hat{s}_0 \cdot \vec{r},$$

which is the length of the projection of the electron position vector \vec{r} onto the unit direction vector of the incident beam \hat{s}_0 .

Consider next an observation point on a distant detector, at \vec{R} from the nucleus with $R \gg r$ in a plane through the nucleus and perpendicular to the polarization direction $\pm \vec{E}_0$ of the incident wave. A beam scattered from \vec{r} to \vec{R} travels a wave path of length $R - x \approx R$, where the scattered wave path length difference,

$$x = \hat{s} \cdot \vec{r},$$

is the length of the projection of \vec{r} onto the unit direction vector of the scattered beam \hat{s} .

The total wave path length from the wave front incident at the nucleus to \vec{R} via \vec{r} is then $x_0 + R - x = \hat{s}_0 \cdot \vec{r} + R - \hat{s} \cdot \vec{r}$, and, according to classical electromagnetic theory, with respect to the wave incident at the nucleus, the scattered wave at \vec{R} is described by

$$\begin{aligned}\frac{\mathcal{E}}{E_0} &= -\left(\frac{e^2}{mc^2}\right) \frac{1}{R} \exp\left\{i\left[\omega t - \frac{2\pi}{\lambda}(\hat{s}_0 \cdot \vec{r} + R - \hat{s} \cdot \vec{r})\right]\right\} \\ &= -\left(\frac{e^2}{mc^2}\right) \frac{1}{R} \exp\left[i\left(\omega t - \frac{2\pi}{\lambda}R\right)\right] \exp\left[2\pi i\left(\frac{\hat{s} - \hat{s}_0}{\lambda}\right) \cdot \vec{r}\right] \\ \frac{\mathcal{E}}{E_0} &= -\left(\frac{e^2}{mc^2}\right) \frac{1}{R} \exp\left[i\left(\omega t - \frac{2\pi}{\lambda}R\right)\right] \exp(2\pi i \vec{S} \cdot \vec{r}),\end{aligned}$$

where the quantity,

$$\vec{S} = \left(\frac{\hat{s} - \hat{s}_0}{\lambda}\right),$$

introduced in the last equation is called the *scattering vector*.

As shown in the illustration above, in the isosceles vector triangle defined by $\frac{\hat{s}}{\lambda} - \frac{\hat{s}_0}{\lambda} = \vec{S}$, the vectors \hat{s}_0 and \hat{s} each make an angle θ with the perpendicular bisector of \vec{S} , so that the *scattering angle* is

$$2\theta = \cos^{-1}(\hat{s}_0 \cdot \hat{s}), \quad |\hat{s}_0| = |\hat{s}| = 1,$$

and the length of the scattering vector is

$$S = |\vec{S}| = 2\left(\frac{\sin\theta}{\lambda}\right).$$

Supposing an atom is supposed to consist of Z classical electrons moving about the nucleus with instantaneous positions $\{\vec{r}_j | j = 1, 2, \dots, Z\}$ at time t , the instantaneous total atomic scattering can be described by the superposition of Z one-electron scattered waves, each with the same frequency as the incident radiation, and the same one-electron Thomson scattering length, but a different phase shift $\delta_j = 2\pi \vec{S} \cdot \vec{r}_j = 2\pi(\hat{s} - \hat{s}_0) \cdot \vec{r}_j / \lambda$ due to differences among the $\hat{s}_0 \cdot \vec{r}_j$ incident wave path lengths to, and the $\hat{s} \cdot \vec{r}_j$ scattered wave path lengths from, each electron j . The result of the wave superposition for the Z -electron atomic scattering is then

$$\frac{\mathcal{E}}{E_0} = -\left(\frac{e^2}{mc^2}\right) \frac{1}{R} \exp\left[i\left(\omega t - \frac{2\pi}{\lambda}R\right)\right] \sum_{j=1}^Z \exp(2\pi i \vec{S} \cdot \vec{r}_j),$$

in which the whole composite factor preceding the summation is the same for all Z electrons, while the Z -term summation represents the net Z -electron phase shift.

To this point, the electron has been treated as a classical point charge particle. To allow for the non-classical, quantum mechanical description of an atomic electron in terms of its wavefunction

$\psi(\vec{r})$, which is a standing wave solution of the time-independent Schrödinger wave equation,

$$\hat{\mathcal{H}}\psi = \left[-\frac{\hbar^2}{8\pi^2 m} \nabla^2 + V(\vec{r}) \right] \psi(\vec{r}) = U\psi ,$$

each individual electronic point charge particle at \vec{r}_j is replaced by a continuous probability density distribution of electronic charge density $\rho_j(\vec{r}) = |\psi_j(\vec{r})|^2$, which has dimensions of electrons per unit volume, and which when integrated over the (in principle, infinite) atomic volume gives $\int_V \rho_j(\vec{r}) d^3\vec{r} = 1$ electron.

The appropriate quantum mechanical replacement gives

$$\frac{\mathcal{E}}{E_0} = -\left(\frac{e^2}{mc^2} \right) \frac{1}{R} \exp \left[i \left(\omega t - \frac{2\pi}{\lambda} R \right) \right] \sum_{j=1}^Z \int_V \rho_j(\vec{r}) \exp(2\pi i \vec{S} \cdot \vec{r}) d^3\vec{r} ,$$

in which each j^{th} term in the summation is a volume integral that represents the scattering factor for the j^{th} electron,

$$f_j(\vec{S}) = \int_V \rho_j(\vec{r}) \exp(2\pi i \vec{S} \cdot \vec{r}) d^3\vec{r} ,$$

in units of minus the Thomson scattering length of a classical free electron. The atomic scattering factor for an atom a containing Z_a electrons is then the sum of the scattering factors of its Z_a electrons,

$$f_a(\vec{S}) = \sum_{j=1}^{Z_a} f_j(\vec{S}) = \sum_{j=1}^{Z_a} \int_V \rho_j(\vec{r}) \exp(2\pi i \vec{S} \cdot \vec{r}) d^3\vec{r} ,$$

and, since each $\rho_j(\vec{r})$ integrates to one electron,

$$\lim_{S \rightarrow 0} f_a(S) = Z_a$$

Atomic scattering factors have been computed and tabulated for the free atoms and stable monatomic ions of all the chemical elements using spherically symmetric or spherically averaged radial electron density distributions computed from atomic wavefunctions obtained from, e.g., Hartree-Fock self-consistent-field, quantum mechanical calculations.

The scattering factor expression,

$$f(\vec{S}) = \int_V \rho(\vec{r}) \exp(2\pi i \vec{S} \cdot \vec{r}) d^3\vec{r} ,$$

where

$$\vec{S} = (\hat{s} - \hat{s}_0)/\lambda, \quad |\hat{s}_0| = |\hat{s}| = 1, \quad 2\theta = \cos^{-1}(\hat{s}_0 \cdot \hat{s}), \quad |\vec{S}| = S = 2(\sin \theta)/\lambda ,$$

is a fundamental relationship in diffraction physics, and it is important to remember that the physical origin of the scattering factor expression is wave interference in the superposition of waves scattered with different phase shifts, $2\pi \vec{S} \cdot \vec{r} = 2\pi (\hat{s} - \hat{s}_0) \cdot \vec{r} / \lambda$, due to the differences among the incident wave path lengths $\hat{s}_0 \cdot \vec{r}$ to, and scattered wave path lengths $\hat{s} \cdot \vec{r}$ from, each volume element $dV = d^3\vec{r}$ of the scattering density distribution $\rho(\vec{r})$.

Calculation of Atomic Scattering Factors from Atomic Wavefunctions

Each electron in an atom is described by a wavefunction that is expressible in spherical polar coordinates (see figure below) as a product of separable radial and angular functions,

$$\psi(\vec{r}) = \psi_{nlm}(r, \vartheta, \varphi) = R_{nl}(r)\Theta_l(\vartheta)\Phi_m(\varphi).$$

Spherically averaged, radial electron density distributions are given by

$$\begin{aligned}\rho(r) &= \int_{\varphi=0}^{2\pi} \int_{\vartheta=0}^{\pi} |\psi_{nlm}(r, \vartheta, \varphi)|^2 r^2 \sin \vartheta \, d\vartheta \, d\varphi \\ &= r^2 |R_{nl}(r)|^2 \int_{\vartheta=0}^{\pi} |\Theta_l(\vartheta)|^2 \sin \vartheta \, d\vartheta \int_{\varphi=0}^{2\pi} |\Phi_m(\varphi)|^2 \, d\varphi \\ &= r^2 |R_{nl}(r)|^2,\end{aligned}$$

where the last equality follows because as well as the wavefunction ψ the radial R , azimuthal Θ , and polar Φ functions are each normalized to unity, *i.e.*,

$$\int_0^\infty |R_{nl}(r)|^2 r^2 dr = 1, \quad \int_0^\pi |\Theta_l(\vartheta)|^2 \sin \vartheta \, d\vartheta = 1, \quad \int_0^{2\pi} |\Phi_m(\varphi)|^2 \, d\varphi = 1.$$

Spherical Polar Coordinates

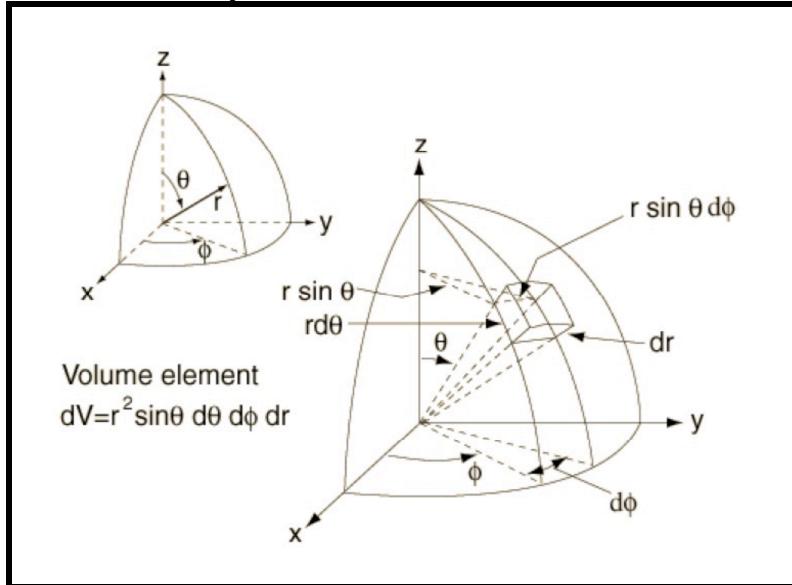


Figure copied from Nave (2005). <http://hyperphysics.phy-astr.gsu.edu/hbase/sphc.html>.

The spherical polar coordinates r, ϑ, φ are related to the corresponding Cartesian coordinates x, y, z according to

$$\begin{cases} r^2 = x^2 + y^2 + z^2 \\ \cos \vartheta = z/r \\ \sin \varphi = y/(r \sin \vartheta) \end{cases} \quad \begin{cases} x = r \sin \vartheta \cos \varphi \\ y = r \sin \vartheta \sin \varphi \\ z = r \cos \vartheta \end{cases} \quad dV = dx dy dz = dr r d\vartheta r \sin \vartheta d\varphi = r^2 \sin \vartheta dr d\vartheta d\varphi.$$

The quantum numbers,

$$n = 1, 2, 3, \dots \quad (K, L, M, \dots \text{ shells}),$$

$$l = 0, 1, 2, \dots, n \quad (s, p, d, f, g, h, \dots \text{ subshells}),$$

$$m = -l, \dots, -1, 0, +1, \dots, +l \quad (\text{orbitals}),$$

designate atomic orbitals (nlm), subshells (nl), and shells (n). Filled subshells, with each orbital doubly occupied, contain $2(2l+1)$ electrons, and the superposition sum of the orbital angular distributions in filled-subshells is spherically symmetric; thus, the notations $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, \dots$ each designate spherically symmetric filled subshells.

Spherical polar surface plots of the angular parts $\Omega_{lm}(\vartheta, \varphi) = \Theta_l(\vartheta)\Phi_m(\varphi)$ of the wavefunctions

$$\psi_{nlm}(r, \vartheta, \varphi) = R_{nl}(r)\Theta_l(\vartheta)\Phi_m(\varphi) \quad \text{for } n=1, 2, 3, 4, \quad l=n-1, \quad m=0, \pm 1, \dots, \pm l.$$

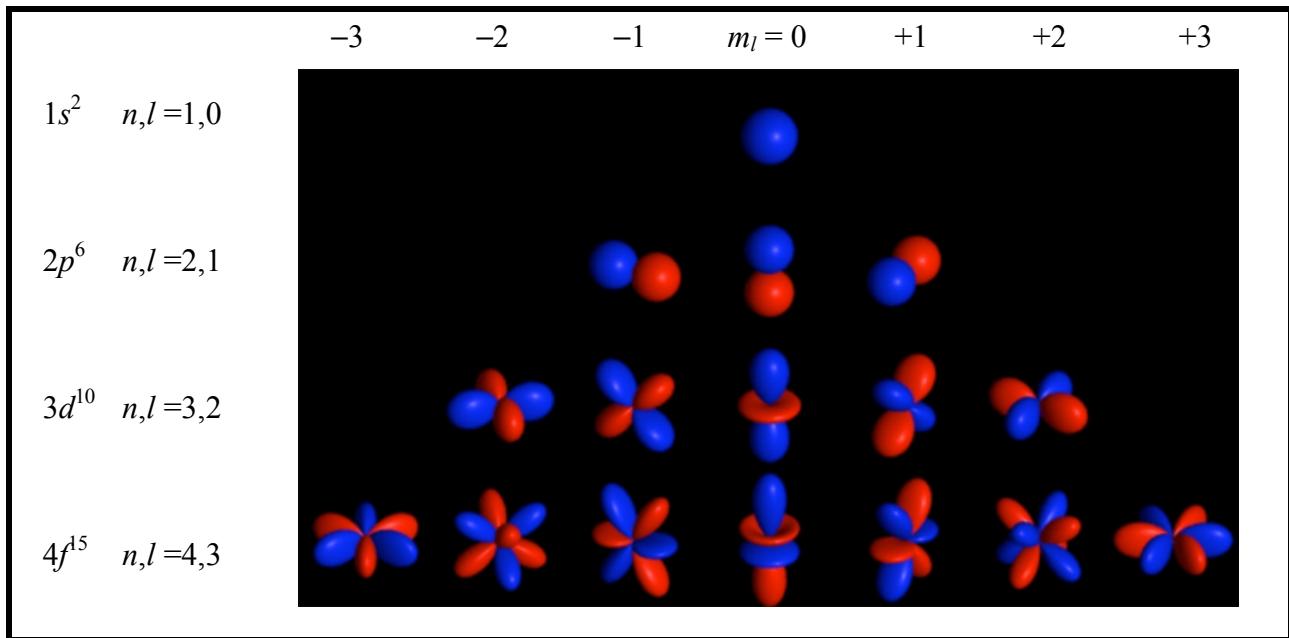


Image copied from <http://www.trinnov.com/images/sphericalHarm.jpg>

To calculate spherical atomic scattering factors,

$$f(S) = \int_V \rho(r) \exp(2\pi i \vec{S} \cdot \vec{r}) d^3 r = \int_{\varphi=0}^{2\pi} \int_{\vartheta=0}^{\pi} \int_{r=0}^{\infty} r^2 |R(r)|^2 \exp(2\pi i \vec{S} \cdot \vec{r}) \sin \vartheta dr d\vartheta d\varphi ,$$

the polar φ axis of the spherical polar coordinates system of the wavefunctions is conveniently taken to be along the scattering vector,

$$\vec{S} = (\hat{s} - \hat{s}_0)/\lambda ,$$

so that,

$$\vec{S} \cdot \vec{r} = S r \cos \vartheta$$

and

$$f(S) = \int_{\varphi=0}^{2\pi} \int_{\vartheta=0}^{\pi} \int_{r=0}^{\infty} r^2 |R(r)|^2 \exp(2\pi i S r \cos \vartheta) \sin \vartheta dr d\vartheta d\varphi .$$

The integration over φ gives

$$f(S) = 2\pi \int_{r=0}^{\infty} r^2 |R(r)|^2 \int_{\vartheta=0}^{\pi} \exp(2\pi i S r \cos \vartheta) \sin \vartheta d\vartheta dr,$$

and a change of variable,

$$u = 2\pi S r \cos \vartheta = a \cos \vartheta, \quad du = -a \sin \vartheta d\vartheta, \quad \sin \vartheta d\vartheta = -\frac{du}{a},$$

gives for the integration over ϑ

$$\begin{aligned} \int_{\vartheta=0}^{\pi} \exp(2\pi i S r \cos \vartheta) \sin \vartheta d\vartheta &= -\frac{1}{a} \int_{+a}^{-a} e^{iu} du = \frac{1}{a} \int_{-a}^{+a} e^{iu} du \\ &= \frac{1}{a} \int_{-a}^{+a} (\cos u + i \sin u) du = \frac{1}{a} (\sin u - i \cos u) \Big|_{-a}^{+a} = \frac{2 \sin a}{a} = \frac{2 \sin(2\pi S r)}{2\pi S r} \end{aligned}$$

[where the last equalities follow because $\sin(-x) = -\sin x$ and $\cos(-x) = \cos x$].

The spherical atomic scattering factor is then

$$f(S) = 4\pi \int_0^{\infty} r^2 |R(r)|^2 \frac{\sin(2\pi S r)}{2\pi S r} dr, \quad S = 2 \left(\frac{\sin \theta}{\lambda} \right).$$

Radial electron density and scattering factor curves for K⁺ [Ar] 1s²2s²2p⁶3s²3p⁶ subshells

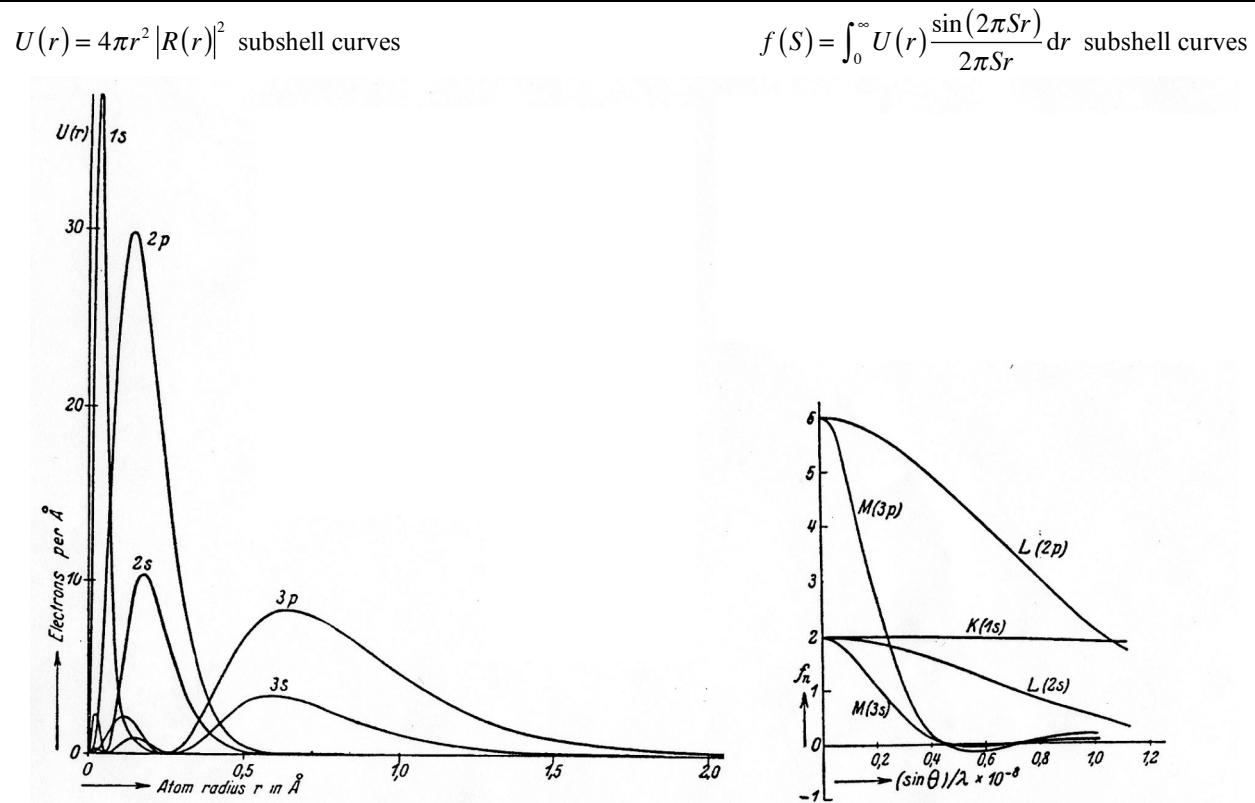


FIG. 43. Radial charge distribution for the different electron groups of K⁺
(James, *Ergebnisse der technischen Röntgenkunde*, vol. III, 1933)

FIG. 48. f-curves for the individual electron groups of K⁺
(James, *Ergebnisse der technischen Röntgenkunde*, vol. III, 1933)

Figures copied from James (1982).

Note that the spherical atomic scattering factor turns out to be real-valued, even though the integrand in the expression,

$$f(\vec{S}) = \int_V \rho(\vec{r}) \exp(2\pi i \vec{S} \cdot \vec{r}) d^3 r,$$

is formally complex-valued. This happens because a spherically symmetric or spherically averaged electron density distribution is *centrosymmetric*, i.e.,

$$\rho(-\vec{r}) = \rho(+\vec{r}).$$

If the density is centrosymmetric it can be written as

$$\rho(\vec{r}) = \frac{1}{2} [\rho(+\vec{r}) + \rho(-\vec{r})],$$

and the integrand,

$$\begin{aligned} \rho(\vec{r}) \exp(2\pi i \vec{S} \cdot \vec{r}) &= \frac{1}{2} [\rho(+\vec{r}) \exp(+2\pi i \vec{S} \cdot \vec{r}) + \rho(-\vec{r}) \exp(-2\pi i \vec{S} \cdot \vec{r})] \\ &= \frac{1}{2} \rho(\vec{r}) [\exp(+2\pi i \vec{S} \cdot \vec{r}) + \exp(-2\pi i \vec{S} \cdot \vec{r})] = \rho(\vec{r}) \cos(2\pi \vec{S} \cdot \vec{r}), \end{aligned}$$

can be seen to be real-valued, because the imaginary, (trigonometric) sine terms occur in pairs with opposite (algebraic) signs, $i \sin(2\pi \vec{S} \cdot \vec{r})$ and $i \sin(-2\pi \vec{S} \cdot \vec{r}) = -i \sin(2\pi \vec{S} \cdot \vec{r})$, which sum pairwise to zero. It follows that, with $\vec{S} \cdot \vec{r} = Sr \cos \vartheta$, the ϑ integration gives, as above,

$$\int_{\vartheta=0}^{\pi} \cos(2\pi Sr \cos \vartheta) \sin \vartheta d\vartheta = \frac{1}{a} \int_{-a}^{+a} \cos u du = \left[\frac{\sin u}{a} \right]_{-a}^{+a} = \frac{2 \sin a}{a} = \frac{2 \sin(2\pi Sr)}{2\pi Sr}.$$

Neutral atom scattering factor curves for H ($Z = 1$) through U ($Z = 90$)
 $f_Z(s)$ vs. $s = (\sin \theta)/\lambda$ and $d = \lambda/(2 \sin \theta)$ for $0 \leq s \leq 1.4 \text{ \AA}^{-1}$ and $\infty < d \leq 0.36$

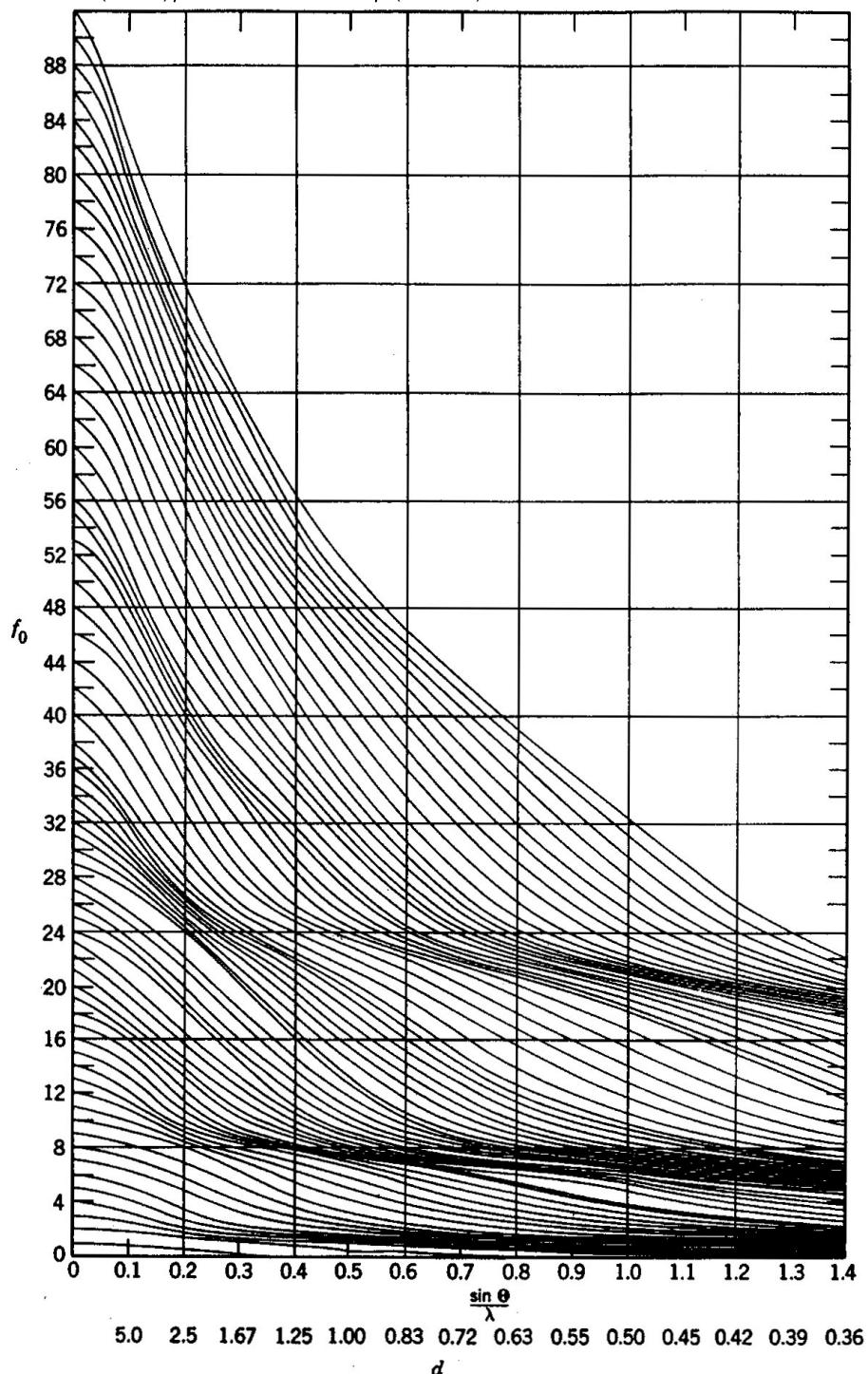


Fig. 3-13. Values of f_0 for neutral atoms. (Courtesy of Pauling and Sherman, *Z. Krist.*, 81, 1.)

Figure copied from Klug and Alexander (1954).

Unitary scattering factors $f_a(s)/Z_a$ vs. $s = (\sin \theta)/\lambda$ for selected 1(H) $\leq Z_a \leq 90$ (U)

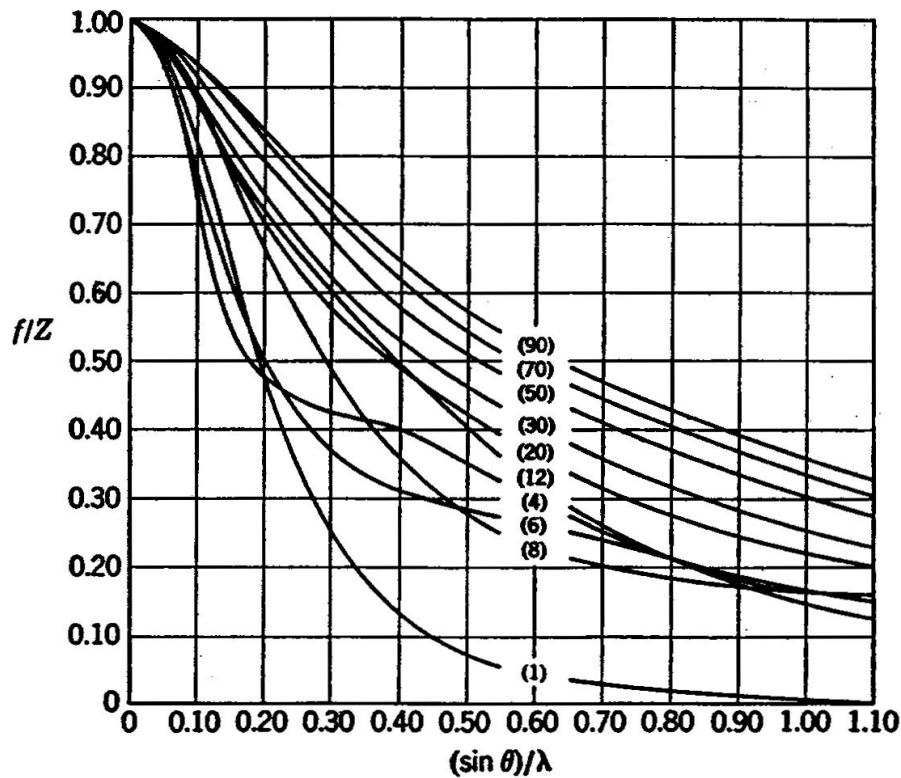


Fig. 20.

Variation of shapes of the curves of f/Z against $(\sin \theta)/\lambda$ for the chemical elements whose atomic numbers, Z , are given in parentheses. (After Harker and Kasper.²⁰)

Figure copied from Buerger (1960).

“Anomalous” Dispersion Corrections to Atomic Scattering Factors

As was shown above, damped resonant X-ray absorption and re-emission by a bound atomic electron causes the electron’s X-ray scattering factor to become complex-valued when the X-ray frequency ω is close to the natural frequency ω_0 of the nucleus-electron dipole oscillator.

Thus, in units of minus the Thomson scattering length, the general expression for the scattering factor of an individual electron with natural oscillation frequency ω_0 is

$$\begin{cases} f_e = \frac{\omega^2}{\omega^2 - \omega_0^2 - i\gamma\omega} = \frac{\omega^2(\omega^2 - \omega_0^2) + i\gamma\omega^3}{(\omega^2 - \omega_0^2)^2 + (\gamma\omega)^2} = f'_e + if''_e, \\ f'_e = \frac{\omega^2(\omega^2 - \omega_0^2)}{(\omega^2 - \omega_0^2)^2 + (\gamma\omega)^2}, \quad \begin{cases} f'_e > 0 & \text{if } \omega > \omega_0, \\ f'_e < 0 & \text{if } \omega < \omega_0, \end{cases} \\ f''_e = \frac{\gamma\omega^3}{(\omega^2 - \omega_0^2)^2 + (\gamma\omega)^2}, \quad f''_e > 0, \end{cases}$$

in which the imaginary term if'' can be neglected except when $\omega \approx \omega_0$, i.e., except near the resonant absorption frequency, or absorption edge.

For an atom with Z electrons, the corresponding general expression is

$$f(S, \omega) = f^0(S) + f'(\omega) + if''(\omega),$$

where

$$f^0(S) = 4\pi \sum_{j=1}^n \int_0^\infty r^2 |R(r)|^2 \frac{\sin(2\pi S r)}{2\pi S r} dr, \quad S = 2\left(\frac{\sin\theta}{\lambda}\right),$$

and

$$\begin{cases} f^0(S) + f'(\omega) = \sum_{j=1}^Z g_j \frac{\omega^2(\omega^2 - \omega_j^2)}{(\omega^2 - \omega_j^2)^2 + (\gamma\omega)^2} \approx \sum_{j=1}^Z g_j - \sum_{j=1}^Z g_j \frac{\omega^2}{\omega^2 - \omega_j^2}, \quad \sum_{j=1}^Z g_j \leq Z, \\ f''(\omega) = \sum_{j=1}^Z g_j \frac{\gamma\omega^3}{(\omega^2 - \omega_j^2)^2 + (\gamma\omega)^2}, \end{cases}$$

in which f^0 is the atomic scattering factor for dispersion-free or “normal” scattering, as calculated by Fourier transformation of the atomic electron density; and g_j is the oscillator strength, and ω_j is the natural oscillation frequency, for the j^{th} electron. Different electrons have different g_j and ω_j because they experience different net forces of nuclear attraction due to screening by the other $Z - 1$ electrons in the atom.

For practical calculations with dispersion corrected atomic scattering factors,

$$f = f^0 + f' + if'' = |f| e^{i\delta} = |f| (\cos\delta + i\sin\delta),$$

$$|f| = \sqrt{(f^0 + f')^2 + (f'')^2}, \quad \delta = \tan^{-1}\left(\frac{f''}{f^0 + f'}\right),$$

and values for the atomic scattering factor corrections f' and f'' have been tabulated as calculated from quantum mechanical scattering theory and/or measured in X-ray interferometry, refraction, scattering, and absorption spectroscopy experiments.

X-ray fluorescence measurements over a wavelength or frequency range of interest can give a crystal's linear absorption coefficient $\mu = \mu(\omega)$, $\omega = 2\pi c/\lambda$. Then, if resonant scattering is significant for only one kind of atom, with resonant frequency ω_0 at its absorption edge, the *optical theorem* gives

$$f''(\omega) = \frac{mc}{4\pi e^2} \omega \mu(\omega),$$

and from f'' values obtained over a sufficient range of frequencies, the *Kramers-Kronig transformation* gives

$$f'(\omega_0) = \frac{2}{\pi} \int_0^\infty \frac{\omega}{\omega^2 - \omega_0^2} f''(\omega) d\omega.$$

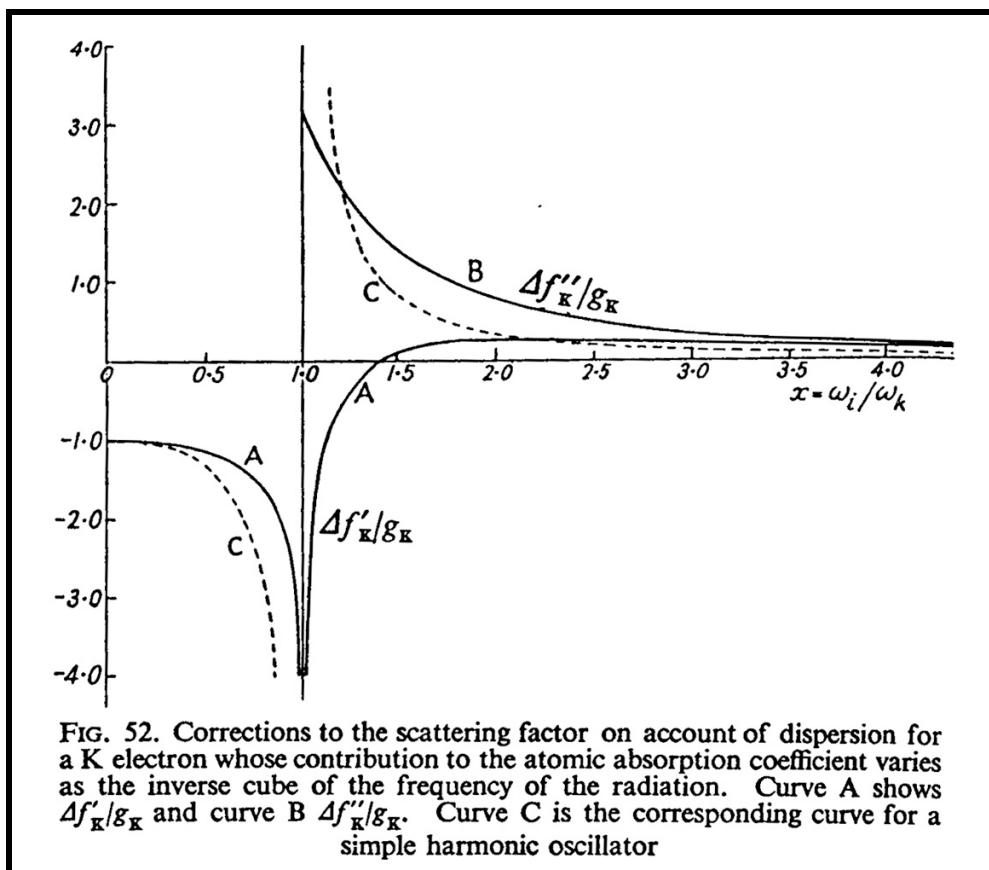


Figure copied from James (1982).

Fourier Transform Relationships

According to the mathematical form of the scattering factor expression,

$$f(\vec{S}) = \int_V \rho(\vec{r}) \exp(2\pi i \vec{S} \cdot \vec{r}) d^3 r,$$

the atomic scattering factor for X-rays is the inverse *Fourier transform* of the atomic electron density distribution. Mathematical shorthand notation for the relationship is

$$f(\vec{S}) = \hat{\mathcal{F}}^{-1}[\rho(\vec{r})].$$

Fourier transformation is a mathematical operation that relates pairs of functions, and a pair of functions $f(x)$ and $g(u)$ are related by Fourier transformation if

$$\begin{cases} g(u) = \int_{-\infty}^{+\infty} f(x) \exp(-2\pi i ux) dx = \hat{\mathcal{F}}[f(x)] \\ f(x) = \int_{-\infty}^{+\infty} g(u) \exp(+2\pi i ux) du = \hat{\mathcal{F}}^{-1}[g(u)]. \end{cases}$$

By an arbitrary convention, it is said that $g(u)$ is the forward Fourier transform, or simply the Fourier transform, of $f(x)$, and that $f(x)$ is the reverse Fourier transform, or Fourier inverse, of $g(u)$. The complex exponential quantities in the Fourier transformation formulae, $\exp(-2\pi i ux)$ and $\exp(+2\pi i ux)$, which must have arguments of opposite sign, are referred to as the *kernels* of, respectively, the forward and reverse Fourier transformations; i.e., the exponential argument in the kernel has the negative sign for the forward Fourier transformation operator $\hat{\mathcal{F}}$, and the positive sign that for the Fourier inversion operator $\hat{\mathcal{F}}^{-1}$. The kernels are, so to speak, bridges between the dual domains of the functions $f(x)$ and $g(u)$, and the variables x and u that constitute the two domains have reciprocal dimensions, so that the exponential arguments are, as they must be, dimensionless. If x is a “real-space” variable, then u is a “reciprocal space” variable. The Fourier transformation operators $\hat{\mathcal{F}}$ and $\hat{\mathcal{F}}^{-1}$ that relate the two spaces mean: multiply the function by the appropriate kernel and then integrate the product over the whole domain of the function.

The mathematics of Fourier transformation occurs in many areas of physics: It was discovered or invented in the 19th century by Jean-Baptiste Joseph Fourier as part of his development of his theory of heat; today it appears in the relationships between the frequency and time domains in electronics, infrared spectroscopy, and nuclear magnetic resonance spectroscopy; it is centrally important in computational image analysis and information theory; and in diffraction analyses of the ultrastructure of matter, Fourier analysis relates measurements of X-ray, electron, or neutron scattering patterns to the submicroscopic architecture of the atomic, molecular, and crystal structures responsible for the radiation scattering.

The Fourier transform relationship between the atomic electron density distribution and the atomic scattering factor for X-rays is then, in standard notation,

$$\begin{cases} f(\vec{S}) = \int_{V_r} \rho(\vec{r}) \exp(+2\pi i \vec{S} \cdot \vec{r}) d^3 r = \hat{\mathcal{F}}^{-1}[\rho(\vec{r})] \\ \rho(\vec{r}) = \int_{V_s} f(\vec{S}) \exp(-2\pi i \vec{S} \cdot \vec{r}) d^3 \vec{S} = \hat{\mathcal{F}}[f(\vec{S})], \end{cases}$$

where

$$\vec{S} = (\hat{s} - \hat{s}_0)/\lambda, \quad |\hat{s}_0| = |\hat{s}| = 1, \quad 2\theta = \cos^{-1}(\hat{s}_0 \cdot \hat{s}), \quad |\vec{S}| = S = 2(\sin\theta)/\lambda.$$

In this Fourier transform relationship, the physical origin of the transform kernel is wave interference in the superposition of scattered waves with different phase shifts

$2\pi(\hat{s} - \hat{s}_0) \cdot \vec{r}/\lambda = 2\pi\vec{S} \cdot \vec{r}$ due to different differences in path lengths $\hat{s}_0 \cdot \vec{r}$ to, and $\hat{s} \cdot \vec{r}$ from, each point in the atomic electron density distribution; the physical origin of the transform integration is the volume summation over all points of the distribution.

An exactly analogous relationship exists between the unit cell electron density distribution $\rho(xyz)$ in crystal or xyz or direct space and the unit cell scattering factor or crystal structure factor F_{hkl} in diffraction or hkl or reciprocal space. Indeed, that relationship is the basis for mapping electron density distributions in atoms, molecules, and crystals from measurements of X-ray scattering, and can be said to be the “fundamental theorem of structural crystallography” for determining the atomic architecture of matter.

In a nutshell, in customary notation, with vectors denoted by boldface type instead of by super-arrows,

$$\left\{ \begin{array}{l} F_{\mathbf{h}} = F_{hkl} \xrightleftharpoons[\hat{\mathcal{F}}^{-1}]{\hat{\mathcal{F}}} \rho(xyz) = \rho(\mathbf{r}) \\ \left\{ \begin{array}{l} F_{\mathbf{h}} = \int_V \rho(\mathbf{r}) \exp(+2\pi i \mathbf{h} \cdot \mathbf{r}) d^3\mathbf{r} = \sum_{a=1}^N f_a(\mathbf{h}) \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_a) = |F_{\mathbf{h}}| e^{i\varphi_{\mathbf{h}}} \\ \rho(\mathbf{r}) = \frac{1}{V_{\text{cell}}} \sum_{\mathbf{h}}^{\infty} F_{\mathbf{h}} \exp(-2\pi i \mathbf{h} \cdot \mathbf{r}) = \frac{1}{V_{\text{cell}}} \sum_{\mathbf{h}}^{\infty} |F_{\mathbf{h}}| \cos(\varphi_{\mathbf{h}} - 2\pi \mathbf{h} \cdot \mathbf{r}), \end{array} \right. \end{array} \right. \left\{ \begin{array}{l} F_{-\mathbf{h}} = |F_{\mathbf{h}}| \\ \varphi_{-\mathbf{h}} = -\varphi_{\mathbf{h}} \end{array} \right.$$

$$\text{where } \left\{ \begin{array}{l} \mathbf{r} = \sum_{i=1}^3 r^i \mathbf{a}_i = x \mathbf{a} + y \mathbf{b} + z \mathbf{c}, \quad V_{\text{cell}} = \mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}), \quad \circlearrowleft \\ \mathbf{h} = \sum_{i=1}^3 h_i \mathbf{a}^{*i} = h \mathbf{a}^{*i} + k \mathbf{b}^{*i} + l \mathbf{c}^{*i}, \quad \mathbf{a}^{*i} = \frac{\mathbf{b} \times \mathbf{c}}{V_{\text{cell}}}, \quad \circlearrowleft \\ |\mathbf{h}| = d_{hkl}^{*i} = \frac{1}{d_{hkl}} = 2 \left(\frac{\sin \theta_{hkl}}{\lambda} \right) \\ \mathbf{a}^{*i} \cdot \mathbf{a}_j = \delta_i^j = \begin{cases} 0, & i \neq j \\ 1, & i = j \end{cases} \\ \mathbf{h} \cdot \mathbf{r} = hx + ky + lz \end{array} \right.$$

$$\text{and } |F_{hkl}| \propto \sqrt{I_{hkl}}$$

$$I_{hkl} = \frac{E_{hkl} \omega}{I_0} = k |F_{hkl}|^2 ALp = \left(\frac{e^2}{mc^2} \right)^2 \lambda^3 \left(\frac{v_{\text{xtal}}}{V_{\text{cell}}} \right)^2 |F_{hkl}|^2 \left[\int_{v_{\text{xtal}}} e^{-\mu(t_0 + t_1)} dv \right] \frac{1}{\sin 2\theta} \left(\frac{1}{2} + \frac{1}{2} \cos^2 2\theta \right)$$

References and Bibliography

- Buerger, M.J. (1960). *Crystal Structure Analysis*. New York: John Wiley and Sons, Inc.
- Compton, A.H., and Allison, S.K. (1935). X-Rays in Theory and Experiment. London: Macmillan and Co., Ltd.
- Dushek, O., and Kuzmin, S.V. (2004). The fields of a moving charge: A new derivation from Jefimenko's equations. *Eur. J. Phys.* **25**, 343-350.
- Feynman, R.P., Leighton, R.B., and Sands, M. (1963). *The Feynman Lectures on Physics*, Vol. I, Ch. 28, Vol. II, Ch. 21. Reading, Massachusetts: Addison-Wesley Publishing Company.
- Gisin, F., and Pantic-Tanner, Z. (2002). How to Div Grad Kink and Curl Electrons....
<http://www.ieee.org/organizations/pubs/newsletters/emcs/winter02/how.html>
- Huang, F.-K. (2006). National Taiwan Normal University JAVA Virtual Physics Laboratory.
<http://www.phy.ntnu.edu.tw/ntnujava/>
- James, R.W. (1982). *The Optical Principles of the Diffraction of X-Rays*. Woodbridge, Connecticut: Ox Bow Press.
- Janah, A.R., Padmanabhan, T., and Singh, T.P. (1988). On Feynman's formula for the electromagnetic field of an arbitrarily moving charge. *Am. J. Phys.* **56**(11), 1036-1038.
- Jenkins, F.A., and White, H.E. (1957). *Fundamentals of Optics*. New York: McGraw-Hill Book Co., Inc.
- Klug, H.P., and Alexander, L.E. (1954). *X-Ray Diffraction Procedures*. New York: John Wiley and Sons, Inc.
- Nave, C.R. (2005). *Hyperphysics*. Department of Physics and Astronomy, Georgia State University. <http://hyperphysics.phy-astr.gsu.edu/hbase/hph.html> . See also *Hypermath*.
<http://hyperphysics.phy-astr.gsu.edu/hbase/hmat.html#hmat>
- Sears, F.W. (1951). *Electricity and Magnetism*. Reading, Massachusetts: Addison-Wesley Publishing Co., Inc.
- Sears, F.W. (1958). *Optics*. Reading, Massachusetts: Addison-Wesley Publishing Co., Inc.
- Siltec (2004). Computer Animations of Physical Processes. <http://physics.nad.ru/start.htm>
- Warren, B.E. (1990). *X-Ray Diffraction*. New York: Dover Publications, Inc.
- Weisstein, E. (2006). *Eric Weisstein's World of Physics*. Wolfram Research.
<http://scienceworld.wolfram.com/physics/topics/InterferencePhenomena.html>