Classical Radiation Theory of X-ray Scattering

X-ray Scattering by an Atom

The text here is a continuation of the development of scattering by a single electron on pages one to three of the September 2, 2004 lecture. A major feature of the derivation is that the X-ray frequency of the electromagnetic field driving the single electron is much larger than the natural frequency of the electron, so that the restoring force of the electron is very small. For this case the polarizability of the electron was negative (see eqn. (5) of the September 2 lecture). The frequency of the X-ray, in radians per second, is related to the X-ray wavelength, \( \lambda \),

\[ \omega = 2\pi \nu = 2\pi c/\lambda \]

where \( c \) is the velocity of light. In terms of the X-ray wavelength, the polarizability is

\[ \alpha_e = -\frac{e^2}{mc^2} \left( \frac{\lambda}{2\pi} \right)^2. \]  

(1)

In mks units, \( e^2 \) is \( 2.3071 \times 10^{-28} \) J m, and \( mc^2 \) is \( 8.1871 \times 10^{-14} \) J which gives a value of \( 2.8180 \) fm for the classical radius of an electron. The square of this radius is the Thomson cross section for scattering of electromagnetic radiation by an electron

\[ \sigma_T = \left( \frac{e^2}{mc^2} \right)^2 \]  

(2)

the value of which is \( \approx 7.941 \) fm\(^2\). For unpolarized X-rays, we learned from equations (8) and (10) that the ratio of scattered to incident intensities is,

\[ \frac{I_e}{I_0} = \sigma_T \left( \frac{1 + \cos^2 2\theta}{2 |R|^2} \right) \]  

(3)

where in (3) \( 2\theta \) is the scattering angle between incident and scattered wave vectors and \( |R| \) is the distance from the electron to the point of observed scattered radiation (\( \sim 10^{15} \) fm). Notice that the scattering intensity, given by (3) is independent of the X-ray frequency.
The material below closely follows the development in Chapter III of the textbook *Theory of X-Ray Diffraction in Crystals* by Professor William H. Zachariasen. For a classical treatment of scattering by an atom with $z$ electrons, we will place the nucleus at the origin. For a given instant, the atomic electrons may be described by the position vectors,

$$r_1 \cdots r_j \cdots r_z.$$  

From the action of the field

$$E_0 \exp\left[ i (\omega t - \mathbf{k}_0 \cdot \mathbf{r}) \right]$$

where $\mathbf{k}_0$ is the wave vector of the incident X-ray, the electrons will be displaced by the amounts $x_j$ from their instantaneous positions. We take the X-ray frequency much larger than any natural frequency of the electrons in the atom so the restoring forces and the interaction between the electrons are neglected. Then the steady state solution for the displacement of electron $j$ is

$$x_j = \frac{e^2}{m\omega^2} E_0 \exp\left[ i (\omega t - \mathbf{k}_0 \cdot r_j) \right]. \quad (4)$$

The dipole moment $d_j$ for electron $j$ becomes

$$-e x_j = d_j \exp(i \omega t) \quad (5)$$

$$d_j = d_e \exp(-i\mathbf{k}_0 \cdot r_j) \quad (6)$$

The strength of the field at a point of observation, $\mathbf{R}$, where $|\mathbf{R}|$ is large compared to the wavelength and atomic dimensions, is obtained by taking the superposition of the fields due to the various electrons. With the use of eqn (7) from the September 2 lecture and (6), the electric field at point $\mathbf{R}$ is,

$$E_{at.} e^{i\omega t} = \sum_j (\mathbf{u}_j \times d_j) \times \mathbf{u}_j \frac{\omega^2}{c^2 R_j} e^{i(\omega t - \mathbf{k}_j \cdot \mathbf{R}_j)} \quad (7)$$

and a similar expression for the magnetic field. $\mathbf{R}_j$ is the radius vector from electron $j$ to the field point so that

$$\mathbf{R}_j = \mathbf{R} - r_j$$

with

$$\mathbf{R}_j = |\mathbf{R}_j| \mathbf{u}_j$$

2
and
\[ \mathbf{R} = |\mathbf{R}| \mathbf{u} \]

On may replace \( \mathbf{R}_j \) by \( \mathbf{R} \) and \( \mathbf{k}_j \) by \( \mathbf{k} \) in (7) with negligible error. Then we get,
\begin{align*}
\mathbf{E}_{\text{at.}} & = \mathbf{E}_e \sum_j e^{i \mathbf{K} \cdot \mathbf{r}_j} \quad (8) \\
\mathbf{K} & = \mathbf{k} - \mathbf{k}_0 \quad (9)
\end{align*}

where \( \mathbf{E}_e \) is the electric field of an oscillating electron and is given by the expression
\[ \mathbf{E}_e = (\mathbf{u} \times \mathbf{d}_e) \times \mathbf{u} \frac{\omega^2}{c^2} \exp(-i \mathbf{k} \cdot \mathbf{R}) \quad (10) \]

Eqn (8) represents the instantaneous amplitude of scattering at the point \( \mathbf{R} \); the corresponding intensity is obtained by multiplying with the complex conjugate and by the factor \( c/8\pi \). The quantity \( \mathbf{K} \cdot \mathbf{r}_j \) measures the phase difference between the radiation scattered by electron \( j \) and that scattered by an electron at the origin. Since X-ray wavelengths are comparable to the distances between the electrons, the phase differences are appreciable and cannot be ignored. The electrons in an atom are changing positions so rapidly that it is not possible to measure the instantaneous amplitude and intensity of the scattered radiation. We must work with averages of these quantities. To obtain the correct averages it is important to distinguish coherent from incoherent radiation. The immediate objective here is a study of X-ray diffraction effects in crystal lattices. Thus we will focus on the coherent part of the scattering by an atom—that is the part of the scattering which can have interference effects.

Let the motion of the various electrons be represented by distribution functions

\[ \rho_1 \cdots \rho_j \cdots \rho_z \]

such that \( \rho_j \, d^3 \mathbf{r}_j \) is the probability of finding electron \( j \) in the volume element \( d^3 \mathbf{r}_j \). We take all the functions \( \rho_j \) as independent of one another. In order to obtain the coherent scattering, the instantaneous amplitude of (8) is averaged over the variable position:
\begin{align*}
\phi_j & = \int \rho_j(\mathbf{r}_j) \exp(i \mathbf{K} \cdot \mathbf{r}_j) d^3 \mathbf{r}_j \quad (11) \\
\langle \mathbf{E}_{\text{at.}} \rangle & = \mathbf{E}_e \sum_j \phi_j. \quad (12)
\end{align*}
From (11) and (12) the intensity of the coherent scattering by the atom is,

$$I_{\text{coh.}} = I_e \left| \sum_j \phi_j \right|^2.$$  \hspace{1cm} (13)

By contrast the total X-ray scattering is obtained by averaging the instantaneous intensity,

$$I_{\text{tot.}} = I_e \int \int \sum_j \sum_k \rho_j \rho_k \exp \left[ i \mathbf{K} \cdot (\mathbf{r}_j - \mathbf{r}_k) \right] d^3 \mathbf{r}_j d^3 \mathbf{r}_k$$

$$= I_e \left( z + \sum_{j \neq k} \phi_k^* \phi_j \right)$$  \hspace{1cm} (14)

The total scattering is the sum of both coherent and incoherent X-ray scattering. Evidently the incoherent scattering will be,

$$I_{\text{inc.}} = I_e \left( z + \sum_{j \neq k} \phi_k^* \phi_j - \left| \sum_j \phi_j \right|^2 \right)$$

$$= I_e \left( z - \sum_j |\phi_j|^2 \right)$$  \hspace{1cm} (15)

As can be seen from (15), the incoherent scattering is $c/8\pi$ times the difference between the mean square and the squared mean amplitude.

The results obtained up to now can only be accepted if they can be confirmed by a quantum mechanical treatment of the scattering problem. Quantum theory predicts that X-rays scattered by an atom are partly coherent and partly incoherent. It turns out that the coherent part is predicted to have the same amplitude and intensity from both classical and quantum mechanical derivations. The incoherent part given by (15) is only an approximation to the quantum mechanical expression. A quantum perturbation treatment shows that the coherent and incoherent parts are due to distinctly different scattering processes. The incoherent, or Compton, scattering represents a distinct quantum process which involves a frequency shift—an inelastic scattering event. Because of its incoherence, the intensity of the Compton scattering from a crystal is due to the sum of the electrons (as in atoms) that make up the crystal. This type of scattering is independent of the crystal structure, \textit{id est}, the arrangement of the atoms is not important, but rather the bulk density and types of atoms determines the Compton scattering intensity.
The coherent scattering by an atom according to (11) and (12) may be interpreted as due to electrons smeared into continuous distributions which are represented by probability functions. The number of electrons per unit volume in this smeared atom is

$$\rho(r) = \sum_j \rho_j(r_j)$$  \hspace{1cm} (16)

A quantum mechanical derivation reveals that \( \rho \) is the one-electron distribution function and the \( \rho_j \) are products of the natural spin orbitals for the atom. At a more approximate, but adequate level of theory, the \( \rho_j \) may be represented with products of Hartree–Fock spin orbitals. The atomic scattering power of the atom is defined as the ratio of the amplitudes of the radiation scattered by the atom to that of an electron under the same conditions. The atomic form factor (atomic scattering power) is thus,

$$f(K) = \sum_j \phi_j = \int \rho(r) e^{iK \cdot r} d^3r$$  \hspace{1cm} (17)

Note that the atomic scattering factor in (17) is the Fourier transform of the atomic electron density function. The magnitude of \( K \) has a simple relation to the scattering angle, which we have defined as \( 2\theta \), and the wavelength of the X-ray.

$$|K| = K = 4\pi \sin \theta / \lambda$$  \hspace{1cm} (18)

The electron density function \( \rho \) is often given in spherical coordinates. For numerical evaluation of (17), it is convenient to expand the plane wave of the Fourier transform in spherical wavefunctions.

$$e^{iK \cdot r} = \sum_{n=0}^{\infty} \sum_{k=0}^{n} i^n (2 - \delta_{0k})(2n + 1) \frac{(n-k)!}{(n+k)!} \times$$

$$\cos[k(\phi_K - \phi_r)] P_n^k(\eta_K) P_n^k(\eta_r) j_n(|K||r|)$$  \hspace{1cm} (19)

The function \( j_n \) in (19) is a spherical Bessel. Note that the vectors \( K \) and \( r \) are both represented in spherical coordinates. The surface harmonics in the plane wave expansion (19) make up a complete set in the space spanned by the solid angle, \( \Omega \), of a sphere. For the purposes at hand here, we’ll use them as real functions,

$$y_{nk\pm}(\Omega) = P_n^k(\eta) \begin{cases} \cos k\phi & \text{for } n k \to + \infty \\ \sin k\phi & \text{for } n k \to - \infty \end{cases}$$  \hspace{1cm} (20)
where $P_n^k$ is an unnormalized Associated Legendre function. The subscript notation of $k_+$ refers to the cosine of $k\phi$ and $k_-$ refers to the sine of $k\phi$. Integration of $\Omega$ over the full sphere,
\[
\int_{\Omega} d\Omega = \int_{-1}^{1} \int_{0}^{2\pi} d\phi d\Omega
\] (21)
gives $4\pi$ radians. The $y_{nk\pm}(\Omega)$ in (20) are a family of orthogonal functions on the surface of a sphere with the integration property,
\[
\int_{\Omega} y_{nk\pm}(\Omega)y_{lm\pm}(\Omega)d\Omega = \delta_{nm} \delta_{k\pm m\pm} \left[ \frac{2\pi(1 + \delta_{0k})(n + k)!}{(2n + 1)(n - k)!} \right]
\] (22)
Notice that if $y_{lm\pm}$, given by (20), is a basis for $\rho(r)$ in (17), then the plane wave expansion (19) filters out only a cos $m\phi_K$ if $+$, or a sin $m\phi_K$ if $-$, with $k = m$. Similarly, the integration over $\eta_r$ eliminates all other Associated Legendres but the $n = l$ one with argument $\eta_K$. Thus $y_{lm\pm}(\Omega_r)$ is transformed into $y_{lm\pm}(\Omega_K)$ via the relation,
\[
\int_{\Omega} y_{lm\pm}(\Omega_r) \left[ e^{i\mathbf{K} \cdot \mathbf{r}} / j_l(|\mathbf{K}|) \right] d\Omega_r = 4\pi i^l y_{lm\pm}(\Omega_K).
\] (23)
The projection properties of the plane wave given by (19) make it possible to use the same spherical surface harmonics in $r$ space and in $K$ space. For any density function that uses the $y_{lm\pm}$ as bases, the remaining parts are some types of radial functions, $\rho_l$ that depend on $|\mathbf{r}| = r$. The evaluation of (17) is completed by evaluating the radial form factor,
\[
f_l(K) = \int_{0}^{\infty} \rho_l(r) j_l(Kr)r^2 dr
\] (24)
If the atom has an electron density which is spherically symmetrical (an atom in an S state has this symmetry), then it has only the spherical surface harmonic, $y_{00\pm}(\Omega_r)$, which is unity over the whole sphere. The form factor for the atom will depend only on the magnitude of $\mathbf{K}$ and evaluation of (17) reduces to,
\[
f_0(K) = \int_{0}^{\infty} \rho(r) j_0(Kr)r^2 dr.
\] (25)
In (24) and (25) I’ve taken the liberty to use math italics for the radial variables,
\[
K = |\mathbf{K}| \text{ and } r = |\mathbf{r}|.
\]
The spherical Bessel,

\[ j_0(x) = \frac{\sin x}{x} \]  

To get you warmed up a bit, if a radial density function is a Slater type function (STF), \( r^n \exp(-\alpha r) \), then for \( l = 0 \), (24) has the explicit solution,

\[ f_{n,0}(K; \alpha) = \frac{(n + 2)!}{\alpha^{n+3}(1 + (K/\alpha)^2)^{n+2}} \times \]

\[ _2F_1\left(-\frac{n+1}{2}, -\frac{n}{2}; \frac{3}{2}; -\frac{K}{\alpha}\right) \]  

Since \( n \geq 0 \), the hypergeometric function in (27) is a finite polynomial.

The normalized ground state wavefunction for the hydrogen atom,

\[ \psi_{1s}(r) = \left( \frac{1}{\pi a_0^3} \right)^{1/2} \exp(-r/a_0) \]  

where \( a_0 \), the Bohr radius, is 52.9177 pm. Square the wavefunction to get the electron density function for a 1s H atom, use (23) and (27) to get an analytical function in \( K \) space for the H atom X-ray scattering factor. With the aid of (18) use the radial variable \( \sin \theta/\lambda \) rather than \( K \). Assume the wavelength of the X-ray is 100 pm; make a small table of \( f_H \) versus \( \sin \theta/\lambda \).