Semi Classical Radiation Theory of X-ray Scattering

The force of an electromagnetic field on an electron is known as the Lorentz force. In cgs units for a single electron in a vacuum the force is,

\[ F = eE + \frac{e}{c}v \times H \]  \hspace{1cm} (1)

where \( E \) and \( H \) are the electric and magnetic field vectors of the electromagnetic wave and \( v \) is the velocity of the electron upon which the field acts. It is convenient to express both \( E \) and \( H \) in terms of a vector potential \( A \) and a scalar potential \( \phi \). Then,

\[ E = -\frac{1}{c} \frac{\partial A}{\partial t} - \nabla \phi \] \hspace{1cm} (2)

\[ H = \nabla \times A. \] \hspace{1cm} (3)

The equations of Maxwell for a single charged particle in a vacuum have the simple form:

\[ \nabla \times E = -\frac{1}{c} \frac{\partial H}{\partial t} \] \hspace{1cm} (4)

\[ \nabla \cdot H = 0 \] \hspace{1cm} (5)

\[ \nabla \times H = \frac{1}{c} \frac{\partial E}{\partial t} \] \hspace{1cm} (6)

\[ \nabla \cdot E = 0. \] \hspace{1cm} (7)

With substitution of eqns. (2) and (3) into eqn. (6) one obtains,

\[ \nabla \times (\nabla \times A) = -\frac{1}{c^2} \frac{\partial^2 A}{\partial t^2} - \frac{1}{c} \frac{\partial \nabla \phi}{\partial t} \] \hspace{1cm} (8)

From the vector identity,

\[ a \times (b \times c) = (a \cdot b)c - (b \cdot a)c, \] \hspace{1cm} (9)

the left hand side of (8) may be reexpressed as,

\[ \nabla \times (\nabla \times A) = \nabla(\nabla \cdot A) - \nabla^2 A. \] \hspace{1cm} (10)
Also if (2) is substituted into eqn. (7), one obtains,
\[
- \frac{1}{c} \frac{\partial (\nabla \cdot \mathbf{A})}{\partial t} - \nabla^2 \phi = 0
\]  
(11)

Together, eqns. (8), (10) and (11) give us a set of differential equations which can be solved for explicit relations of the vector potential, \( \mathbf{A} \), and scalar potential, \( \phi \). We transform \( \mathbf{A} \) and \( \phi \) to a new vector and scalar potential, \( \mathbf{A}_0 \) and \( \phi_0 \), respectively, by means of the Guage transformation,
\[
\mathbf{A}_0 = \mathbf{A} - \nabla \psi
\]  
(12)
\[
\phi_0 = \phi + \frac{1}{c} \frac{\partial \psi}{\partial t}
\]  
(13)

and choose the scalar \( \psi \) such that,
\[
\nabla \cdot \mathbf{A} = \nabla^2 \psi.
\]  
(14)
The choice of \( \psi \) in (14) is often called the Coulomb Gauge. With the Coulomb Gauge from (14), eqn. (11) simplifies to
\[
\nabla^2 \phi = 0
\]  
(15)
which is Poisson's equation,
\[
\nabla^2 \phi = -4\pi \rho
\]
with zero charges, (ie \( \rho = 0 \)). If \( \phi \) is continuous over a region of space and vanishes at the boundaries, (15) implies that \( \phi \) is zero everywhere in the region. In this case the eqns. (8) and (10) become the familiar wave equation for \( \mathbf{A} \)
\[
\nabla^2 \mathbf{A} - \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} = 0.
\]  
(16)
The solution to (16) is of the form,
\[
\mathbf{A}(\mathbf{r}, t) = \mathbf{A}(0) \exp[i(k \cdot \mathbf{r} - \omega t)]
\]  
(17)
with
\[
i = \sqrt{-1}.
\]
The Lorentz force law, given by (1), may now be written as
\[
\mathbf{F} = \frac{d\mathbf{p}}{dt} = -e \frac{\partial \mathbf{A}}{\partial t} + \frac{e \hbar i}{cm} \nabla \times (\nabla \times \mathbf{A})
\]  
(18)
where use has been made of the quantum mechanical representation for $v$ in eqn. (1). With the use of (8) (10) and (16), eqn. (18) may be simplified to read

$$\frac{dp}{dt} = -\frac{e}{c} A - \frac{\hbar i}{mc^2} \frac{\partial A}{\partial t}.$$  \hfill (19)

Eqn. (19) may be integrated to get,

$$p(t) - p(0) = -\frac{e}{c} [A(r, t) - A(r, 0)]$$

$$+ \frac{\hbar i}{mc^2} \left[ \frac{\partial A(r, t)}{\partial t} \right]_{t=t} - \left. \frac{\partial A(r, t)}{\partial t} \right|_{t=0}. \hfill (20)$$

From the plane wave field in (17), eqn. (20) may be expressed as,

$$p(t) - p(0) = -\frac{e}{c} \left[ 1 + \frac{\hbar \omega}{mc^2} \right] [A(r, t) - A(r, 0)] \hfill (21)$$

In (21) the term, $\hbar \omega/mc^2$, is due to the magnetic field contribution, which is usually small. Evidently eqn. (21) states that an electron at rest at time $t = 0$ will attain a momentum $p(t)$ in time $t$ by the action of the vector potential at the point $r$.

Do we need to formulate a quantum mechanical treatment of the effect of electromagnetic radiation on electrons? Is it necessary to quantize the radiation field? Are relativistic corrections to the scattering formalism important? For the present lecture we will neglect relativistic effects. It will be shown that the concept of the photon is not essential to arrive at a correct non-relativistic treatment of X-ray scattering. A number of critiques on the limitations of semi-classical radiation theory have been published. One possible reference is a paper by Nesbet [R. K. Nesbet, *Phys. Rev. Letters* **27**, 553 (1971)].

The momentum operator for an electron is normally given by

$$p = \frac{\hbar}{i} \nabla$$

but it was shown previously that an electron undergoes a change in momentum due to the action of an electromagnetic field. Following eqn. (21), one can write the total momentum of the electron as

$$p = -i\hbar \nabla - \frac{e}{2e} [A^*(r, t) + A(r, t)]. \hfill (22)$$
Notice that the classical operator, \( A(r, t) \), is expressed in an Hermitean form before adding it to the orbital momentum operator. With (22), the Hamiltonian can be expressed as,

\[
\mathcal{H} = \frac{1}{2m} \left[ -i\hbar \nabla - \frac{e}{2c} (A^* + A) \right] \cdot \left[ -i\hbar \nabla - \frac{e}{2c} (A^* + A) \right] + V(r).
\]

(23)

For an \( N \) electron system, the total kinetic energy is a sum over the terms from (23):

\[
\sum_{j=1}^{N} \left[ -i\hbar \nabla_j - \frac{e}{2c} [A^*(r_j, t) + A(r_j, t)] \right]^2
\]

Before the Hamiltonian from (23) can be used in the Schrödinger equation, an explicit form of the vector potential \( A \) must be specified. The solution of Maxwell’s wave equation for a plane wave is \( A(0) \exp[i(k \cdot r - \omega t)] \), where \( A(0) \) is the electric field perpendicular to the direction of propagation \( k \). In a scattering experiment, two fields need to be considered. The incident field:

\( A_i(0) \exp[i(k_i \cdot r - \omega t)] \)

and the field produced by the scattering process:

\( A_s(0) \exp[i(k_s \cdot r - \omega t)] \)

Thus the field acting on the electron is,

\[
A(r, t) = A_i(0) \exp[i(k_i \cdot r - \omega t)] + A_s(0) \exp[i(k_s \cdot r - \omega t)]
\]

(24)

In eqn. (24), the scattered wave is a plane wave. How does (24) compare to a form for an outgoing spherical wave? An outgoing spherical wave which is observed at \( R \) from the center of the scattering system has the approximate form

\[
\left( \frac{\exp(i|k_s| |R|)}{|R|} \right) \exp(i k_s \cdot r)
\]

where \( r \) defines a point within the scatterer with \( |R| \gg |r| \) and \( |R - r| \) is the distance between the point of observation and the
position of the electron. The part of the wave which depends on the field is in the form of a plane wave as has been assumed. We define,

\[ A_i(0) = E_i^i \hat{n}_{i}^{\alpha} \exp(i\mathbf{k}_i \cdot \mathbf{R}) \] (25)

and

\[ A_s(0) = E_s^s \hat{n}_s^{\alpha} \frac{\exp(i|\mathbf{k}| |\mathbf{R}|)}{|\mathbf{R}|} \] (26)

where \( E_i^i \) and \( E_s^s \) are the magnitudes of the electric fields in the incident \((i)\) and scattered \((s)\) directions with respective polarizations \( \hat{n}_i^{\alpha} \) and \( \hat{n}_s^{\alpha} \). The term

\[ \frac{\exp(i|\mathbf{k}| |\mathbf{R}|)}{|\mathbf{R}|} \]

represents an outgoing spherical wave. The gauge guarantees that the field is polarized perpendicular to the direction of propagation; it has transverse polarization. The polarization can be subdivided into a component in the scattering plane \((id est, \text{the plane which contains both the wavevectors } \mathbf{k}_i \text{ and } \mathbf{k}_s)\) and a component perpendicular to the scattering plane.

One can set up the experiment with two possible choices for the initial polarization and two possible choices for the polarization of the scattered radiation. Often times one has an unpolarized source of X-rays. In this case, one must sum over all final state polarizations and an average over the initial polarizations. For polarization in the scattering plane we will denote \( \alpha \) as \( \parallel \) and when normal to the plane, \( \alpha \) is \( \perp \). For elastic and coherent scattering (the case for X-ray diffraction),

\[ \omega = \omega' \]

and

\[ |\mathbf{k}_i| = |\mathbf{k}_s|. \]

The vector potential operator is,

\[ \mathbf{A}(r, t) = \frac{1}{2} \left[ A_i(0)\hat{n}_i^{\alpha} \exp(i\mathbf{k}_i \cdot \mathbf{r}) + A_s(0)\hat{n}_s^{\alpha} \exp(i\mathbf{k}_s \cdot \mathbf{r}) \right] \] (27)

where \( \alpha \) is \( \parallel \) or \( \perp \).