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Scattering of X-Rays

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$$\mathcal{H} = \sum_j \frac{1}{2m}\left(\underline{p}_j - \frac{e}{c}\underline{A}(\underline{r}_j)\right)^2 + \sum_{ij} V(r_{ij}) - \frac{e\hbar}{2mc}\sum_j \underline{s}_j \cdot \nabla \times \underline{A}(\underline{r}_j)$$

$$- \frac{e\hbar}{2(mc)^2}\sum_j \underline{s}_j \cdot \left(\underline{E}(\underline{r}_j) \times (\underline{p}_j - \frac{e}{c}\underline{A}(\underline{r}_j)\right) \qquad (1)$$

$$+ \sum_{\lambda \underline{k}} \hbar\omega k \left(c^+(\underline{k}\lambda)c(\underline{k}\lambda) + \frac{1}{2}\right)$$

This Hamiltonian contains terms of order $(\frac{v}{c})^2$. We will treat scattering to that order. By doing this we are able to take electronic bound states into account more easily.

The purpose of these derivations is to account for magnetic scattering of photons by magnetization densities in matter as discussed by Platzman and Tzoar (P.R.B 2, 3556 (1970)) and by de Bergevin and Brunel (Acta Cryst. A37, 314 (1981)). These authors derived magnetic scattering by taking the non-relativistic limit of Compton scattering from free electrons. There are, however, interesting phenomena which arise from electron binding which are important.

In the course of deriving formulas for magnetic scattering, we produce general formulas which contain, in appropriate limits, virtually all scattering phenomena (in the "kinematic", or Born approximation) for electro-magnetic radiation, including Thomson, Rayleigh, Bragg, thermal diffuse, and Raman scattering, and anomalous dispersion. Obviously such a general expression needs much

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work to particularize, but it has the advantage of indicating which terms are important in different limits. The principal results are eq. (13) and (15).

The Hamiltonian in (1) contains the radiation field, the electrons, and interaction terms. The vector potential $\underline{A}(\underline{r})$ is linear in photon creation and annililation operators so that scattering occurs in second order for terms linear in $\underline{A}$, and in first order for quadratic terms.

In the spin-orbit term in (1),

$$\underline{E} = -\nabla\phi - \frac{1}{c}\mathring{\underline{A}},$$

where ϕ is the Coulomb potential. Since this term is already of order $(\frac{V}{c})^2$ we will omit linear terms in $\underline{A}$ and keep only the quadratic ones and those independent of $\underline{A}$, so that

$$-\frac{e\hbar}{2(mc)^2}\sum_j \underline{s}_j\cdot\left(\underline{E}(\underline{r}_j)\times(\underline{p}_j - \frac{e}{c}\underline{A}(\underline{r}_j)\right) \to -\frac{e\hbar}{2(mc)^2}\left[\sum_j \underline{s}_j\cdot\left(-\nabla\phi_j \times \underline{p}_j\right)\right.$$
$$\left. - \sum_j \underline{s}_j\cdot\frac{e}{c^2}\left(\mathring{\underline{A}}(\underline{r}_j)\times\underline{A}(\underline{r}_j)\right)\right] \qquad (2)$$

The first term is the ordinary spin-orbit coupling term for electrons, while the second gives spin dependent scattering.

We can now write

$$\mathcal{H} = \mathcal{H}_o + \mathcal{H}_R + \mathcal{H}', \qquad (3)$$

with

$$\mathcal{H}_o = \sum_j \frac{1}{2m}\underline{p}^2{}_j + \sum_{ij} V(\underline{r}_{ij}) + \frac{e\hbar}{2(mc)^2}\sum_j \underline{S}_j\cdot(\nabla\phi_j \times \underline{p}_j) \qquad (4)$$

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$$\mathcal{H}_R = \sum_{\underline{k}\lambda} \omega_{\underline{k}} \left(c^{+}(\underline{k}\lambda)\, c(\underline{k}\lambda) + \frac{1}{2} \right) \tag{5}$$

$$\mathcal{H}' = \underbrace{\frac{e^2}{2mc^2} \sum_j A^2(\underline{r}_j)}_{\mathcal{H}'_1} - \underbrace{\frac{e}{mc} \sum_j \underline{A}(\underline{r}_j) \cdot p_j}_{\mathcal{H}'_2} - \underbrace{\frac{e\hbar}{mc} \sum_j S_j \cdot \nabla \times \underline{A}(\underline{r}_j)}_{\mathcal{H}'_3}$$

$$+ \underbrace{\frac{e\hbar}{2(mc)^2} \cdot \frac{e}{c^2} \cdot \sum_j \underline{S}_j \cdot (\underline{\mathring{A}}(\underline{r}_j) \times \underline{A}(\underline{r}_j))}_{\mathcal{H}'_4} \tag{6}$$

$$\equiv \mathcal{H}'_1 + \mathcal{H}'_2 + \mathcal{H}'_3 + \mathcal{H}'_4 \tag{7}$$

$\mathcal{H}'_1$ and $\mathcal{H}'_4$ are quadratic in $\underline{A}$, while $\mathcal{H}'_2$ and $\mathcal{H}'_3$ are linear.

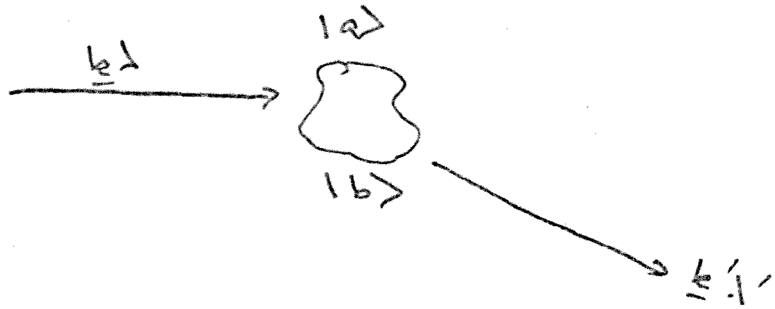
The vector potential $\underline{A}$ is expanded as

$$\underline{A}(\underline{r}) = \sum_{\underline{q}\sigma} \left(\frac{2\pi\hbar c^2}{V\omega_q} \right)^{1/2} \underline{\varepsilon}(\underline{q}\sigma)\, c(\underline{q}\sigma)\, e^{i\underline{q}\cdot\underline{r}} + \varepsilon^{*}(\underline{q}\sigma)\, c^{+}(\underline{q}\sigma)\, e^{-i\underline{q}\cdot r} \tag{8}$$

V is a quantization volume, which drops out of any physical expression. The index $\sigma(=1,2)$ labels the two polarizations of each wave $\underline{q}$ and $\underline{\varepsilon}(\underline{q}\sigma)$ is the corresponding unit polarization vector. Because of the transversality of the waves,

$$\underline{q} \cdot \underline{\varepsilon}(\underline{q}\sigma) = 0. \tag{9}$$

Scattering cross-sections are calculated by assuming that initially the solid (or system) is in a quantum state $|a\rangle$ which is an eigenstate of $\mathcal{H}_o$ with energy E_a, and that there is a single photon with wave vector $\underline{k}$ and polarization λ present. We then calculate the probability of a transition induced by $\mathcal{H}'$ to a state $|b\rangle$ with photon $k'\lambda'$:



The transition probability/unit time is given by the "golden rule" (to second order)

$$W = \frac{2\pi}{\hbar}\left|\langle f|\mathcal{H}'|i\rangle + \Sigma \frac{\langle f|\mathcal{H}'|n\rangle\langle n|\mathcal{H}'|i\rangle}{E_i - E_n}\right|^2 \delta(E_i - E_n)$$

$$|i\rangle = |a;\underline{k}\lambda\rangle; \quad |f\rangle = |b;\underline{k}'\lambda'\rangle$$

$$E_i = E_a + \hbar\omega_k; \quad E_f = E_b + \hbar\omega_{k'} \tag{10}$$

Only $\mathcal{H}'_1$ and $\mathcal{H}'_4$ contribute to the first order term, and only $\mathcal{H}'_2$ and $\mathcal{H}'_3$ to second order.

Hence:

$$W = \frac{2\pi}{h}\left|\langle b;\underline{k}'\lambda'|\mathcal{H}'_1+\mathcal{H}'_4|a;\underline{k}\lambda\rangle + {}_r \frac{\langle b;k'1'|\mathcal{H}'_2+\mathcal{H}'_3|n\rangle\langle n|\mathcal{H}'_2+\mathcal{H}'_3|a;k\lambda\rangle}{Ea + \hbar\omega_k - en}\right|$$

$$\times\ \delta(E_a - E_b + \hbar\omega_k - \hbar\omega_{k'}) \tag{11}$$

Assuming $\omega_k \simeq \omega_{k'}$ (i.e. that only low-lying excitations of the solid will be considered),

$$\langle b|\mathcal{H}'_1+\mathcal{H}'_4|a\rangle = \frac{2\pi\hbar c^2}{V\omega}\cdot\frac{e^2}{mc^2}$$

$$\times\left\{\langle b|\sum_j e^{i\underline{K}\cdot\underline{r}_j}|a\rangle\,\varepsilon'\cdot\varepsilon - i\frac{\hbar\omega}{mc^2}\langle b|\sum_j e^{i\underline{K}\cdot\underline{r}_j}\,\underline{S}_j|a\rangle\cdot(\underline{\varepsilon}'\times\underline{\varepsilon})\right\} \qquad (12)$$

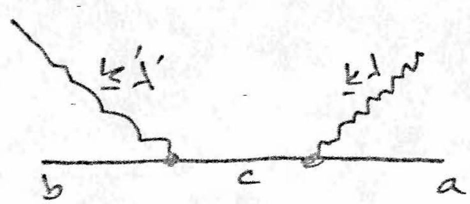
where $\varepsilon \equiv \varepsilon(\underline{k}\lambda)$ and $\underline{\varepsilon}' \equiv \underline{\varepsilon}(\underline{k}'\lambda')$, and $\underline{K} = \underline{k} - \underline{k}'$.

The first term gives the usual Thomson scattering expression, which depends on the Fourier transform of the electron density. $\sum e^{i\underline{k}\cdot\underline{r}_j}$. The second term, which is smaller than the first by $\frac{h\omega}{mc^2}$ ($mc^2 \sim .511$ MeV, so $\frac{h\omega}{mc^2} \sim .02$ for 10 keV x-rays) depends on the spin density Fourier transform $\sum_j e^{i\underline{k}\cdot\underline{r}_j}\,\underline{S}_j$.

In the limit of high energy photons the terms in $\mathcal{H}'_2$ and $\mathcal{H}'_3$ will give additional contributions of this sort, as will be seen.

In the second order terms, the intermediate states $|n\rangle$ fall in two classes: those in which the initial photon has been annihilated first, and those in which the final photon has first been created.

Diagramatically these are



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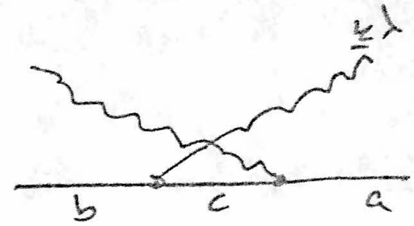

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Calculating the photon parts of these matrix elements and combining with (11) we get:

$$W = \frac{2\Pi}{\hbar}\left(\frac{2\Pi\hbar c^2}{V\omega}\right)^2 \cdot \left(\frac{e^2}{mc^2}\right)^2 \Bigg| \langle b|\sum_j e^{i\underline{k}\cdot\underline{r}_j}|a\rangle\ \varepsilon'\cdot\varepsilon$$

$$- i\frac{\hbar\omega}{mc^2}\langle b|\sum_j e^{i\underline{k}\cdot\underline{r}_j}\underline{S}_j\ |a\rangle \cdot (\underline{\varepsilon}' \times \varepsilon)$$

$$+ \frac{\hbar^2}{m}\sum_c \sum_{ij}$$

$$\Bigg\{\frac{\langle b|(\underline{\varepsilon}'\cdot\underline{p}_i/\hbar - i(\underline{k}'\times\underline{\varepsilon}')\cdot\underline{S}_i)e^{i\underline{k}'\cdot\underline{r}_j}|c\rangle\langle c|\varepsilon\ \underline{p}_j + i(\underline{k}\times\underline{\varepsilon})\cdot\underline{S}_j)e^{i\underline{k}\cdot\underline{r}_j}|a\rangle}{E_a - E_c + \hbar\omega_k}$$

$$+\frac{\langle b|(\frac{\underline{\varepsilon}\cdot\underline{P}_j}{\hbar} + i(\underline{k}\times\underline{\varepsilon})\ \underline{S}_j)e^{i\underline{k}\cdot\underline{r}_j}|c\rangle\langle c|(\frac{\underline{\varepsilon}'\cdot\underline{p}_i}{\hbar} - i(\underline{k}'\times\underline{\varepsilon}')\ \underline{S}_i)e^{-i\underline{k}'\cdot r_i}|a\rangle}{E_a - E_c - \hbar\omega_{k'}}\Bigg|^2$$

$$\times\ \delta(E_a - E_b + \hbar\omega_k - \hbar\omega_{k'}) \qquad (13)$$

The cross-section is obtained from the transition probability by multiplying w by the density of final states and dividing by the incident flux:

$$\frac{d^2\sigma}{d\Omega' dE'} = W.\ \rho(E_f)/I_o$$

with $\rho(E_f) = \frac{V}{(2\Pi)^3}\ \frac{\omega^2_{k'}}{hc^3}$

and $I_o = \frac{c}{v}$,

$$\left(\frac{d^2\sigma}{d\Omega' dE'}\right)_{ab,\lambda\lambda} = \left(\frac{e^2}{mc^2}\right)\ \left(\frac{k'}{k}\right)\Bigg| \langle b|\sum_j e^{i\underline{k}.\underline{r}_j}|a\rangle\varepsilon'\cdot\varepsilon$$

$$- i \frac{\hbar\omega}{mc^2} \langle b|\sum_j e^{i\underline{k}\cdot\underline{r}_j}\underline{S}_j|a\rangle \cdot (\underline{\varepsilon}' \times \underline{\varepsilon})$$

$$+ \frac{\hbar^2}{m} \sum_c \sum_{ij}$$

$$\frac{\langle b|(\frac{\varepsilon' \cdot p_i}{\hbar} - i(\underline{k}' \times \underline{\varepsilon}')\cdot\underline{S}_i)e^{-i\underline{k}'\cdot\underline{r}i}|c\rangle\langle c|(\frac{\varepsilon\cdot p_j}{\hbar} + i(\underline{k}\times\underline{\varepsilon})\underline{S}_j)e^{i\underline{k}\cdot\underline{r}_j}|a\rangle}{E_a - E_c + \hbar\omega_k - i\Gamma e/2}$$

$$\left. + \frac{\langle b|(\frac{\underline{\varepsilon}\cdot\underline{p}_j}{\hbar} + i(\underline{k}\times\underline{\varepsilon})\cdot S_j)e^{i\underline{k}\,\underline{r}_j}|c\rangle\langle c|(\frac{\varepsilon'\cdot p_i}{\hbar} - i(\underline{k}'\times\underline{\varepsilon}')\cdot\underline{S}_i)e^{-i\underline{k}'\,\underline{r}i}|a\rangle}{E_a - E_c - \omega_{k'} - i\Gamma e/2} \right|^2$$

$$\times\ \delta(E_a - E_b - \hbar\omega_k - \hbar\omega_{k'}) \qquad (14)$$

Eq. (13) accounts for most x-ray scattering phenomena to order $\left(\frac{\hbar\omega}{mc^2}\right)^2$.

The first (Thomson) term gives the usual expression for Bragg scattering when $|b\rangle = |a\rangle$ and the periodicity of the lattice is accounted for. Anomalous dispersion effects occur when $\hbar\omega_k = E_a - E_c$ for some state $|c\rangle$, so that an energy denominator vanishes in (13). We have added a term $i\Gamma_c/2$ to the denominators in (13) to take into account the level width, which is important only very close to resonance. Eq. (13) also incudes spin-dependent resonance terms, which arise because of the $s \cdot (\nabla \times \underline{A})$ term in $\mathcal{H}'$.

To derive purely magnetic scattering we assume $\omega_{k'} \sim \omega_k \gg (E_a - E_c)/\hbar$. Neglecting the latter terms in the denominators of the last two terms, these reduce to

$$\frac{\hbar^2}{m} \cdot \frac{1}{\hbar\omega} \sum_{ij}\langle b| \left[\frac{(\varepsilon'\cdot p_i}{\hbar} - i(\underline{k}'\times\underline{\varepsilon}')\cdot\underline{S}_i)e^{-i\underline{k}'\cdot\underline{r}_i}, (\frac{\underline{\varepsilon}\cdot\underline{p}_j}{\hbar} + i(\underline{k}\times\underline{\varepsilon})\,\underline{S}_j)e^{i\underline{k}\,\underline{r}_j}\right]|a\rangle$$

(15)

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where we have used closure to carry out the sum over c. The communtators in (14) are straight-forward but tedious. Evaluating them gives

$$- \frac{i\hbar\omega}{mc^2} \langle b| \sum_j e^{i\underline{k}\cdot\underline{r}_j}\, i\, \frac{\underline{k} \times \underline{p}_j}{\hbar k^2} \cdot (\underline{\varepsilon}' \times \underline{\varepsilon})\, |a\rangle$$

$$+ \langle b| \sum_j e^{i\underline{k}\cdot\underline{r}_j}\, \underline{S}_j\, |a\rangle \cdot \Big((-\underline{k}' \times \underline{\varepsilon}')\times(\underline{k} \times \underline{\varepsilon})$$

$$+ (\underline{k}' \times \varepsilon')(\underline{k}' \cdot \varepsilon) - (\underline{k} \times \underline{\varepsilon})(\underline{k} \cdot \underline{\varepsilon}') \Big),$$

and combining this with the other terms in (13) gives

$$\frac{d^2\sigma}{d\Omega' dE'}_{\substack{ab'\\ \lambda\lambda}} = \frac{e^2}{mc^2}^2 \frac{k'}{k}^2 \Big| \langle b|\sum_j e^{i\underline{k}\cdot r_j}|a\rangle\, (\underline{e}'\cdot \underline{e}')$$

$$- \frac{i\hbar\omega}{mc^2} \langle b| \sum_j e^{i\underline{k}\cdot\underline{r}j}\; i\,\frac{K\times P_j}{\hbar k^2}\cdot\underline{A}+\underline{S}_j\cdot B\; |a\rangle \Big|^2$$

$$\delta(E_a - E_b + \hbar\omega_k - \hbar\omega_k'), \qquad (16)$$

where $\underline{A} = \underline{\varepsilon}' \times \underline{\varepsilon}$

and $\underline{B} = \underline{\varepsilon}' \times \underline{\varepsilon} + (\hat{\underline{k}}' \times \underline{\varepsilon}')(\hat{\underline{k}}' \cdot \underline{\varepsilon})(\hat{\underline{k}} \times \underline{\varepsilon})(\hat{\underline{k}} \cdot \underline{\varepsilon}')$

$$- (\hat{\underline{k}}' \times \underline{\varepsilon}')\times(\hat{\underline{k}} \times \underline{\varepsilon})$$

Note: if circular polarization vectors are used as bases ε' should read $\varepsilon^*(\underline{k}'\lambda')$ in these expressions.

Eq. (15) gives the cross-section for scattering from magnetization densities. The magnetic terms are smaller by $\hbar\omega$ in amplitudes than the charge terms. An interference between magnetic and charge scattering can occur which will be of this same order. Because of the i in front of the magnetic term this interference will occur only if the polarization factors are complex (circular polarization) or if the structure is non-centrosymmetric. The pure charge scattering is larger than the pure magnetic scattering by a significant factor:

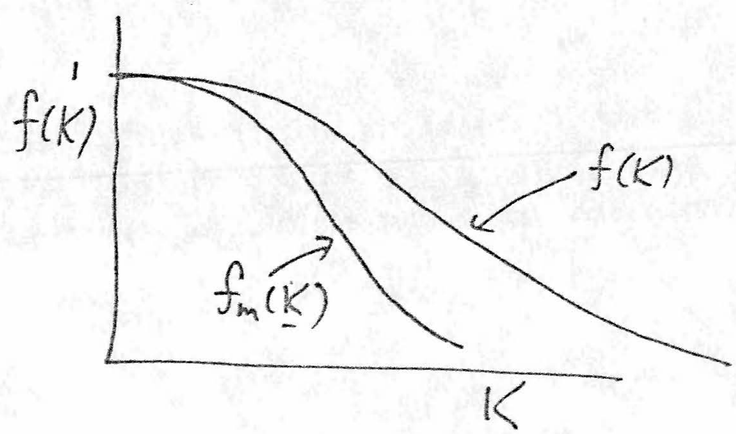
$$\frac{\sigma_{mag}}{\sigma_{charge}} \sim \left(\frac{\hbar\omega}{mc^2}\right)^2 \frac{N_m^2}{N^2} \langle \underline{S} \rangle^2 \frac{f_m^2}{f^2} \qquad (17)$$

where N_m is the number of magnetic electrons/atom, N the number of electrons/atom, and f_m and f are the magnetic and charge form factors.

For Fe and 10 keV photons

$$\frac{\sigma_{mag}}{\sigma_{charge}} \sim 4 \times 10^{-6} \langle S \rangle^2$$

Also, the magnetic form factor of an atom falls off more rapidly than the charge form factor because the magnetization density is more diffuse spatially than is the charge density:



This reduces the ratio even further, finally the factor ⟨5⟩, which goes to zero at the curve temperature is unity only at low temperatures.

By comparison, the cross-section for magnetic neutron scattering is:

$$\frac{d^2\sigma}{d\Omega dE} = \left(\frac{1.91e^2}{mc^2}\right)^2 \frac{k'}{k} \left|\langle b|\sum_j e^{i\underline{k}\cdot\underline{r}_j} \; \frac{i}{R}\; k x \underline{p}_j + K x(\underline{S}_j x K)\;|a\rangle\right|^2$$

$$\delta\left(E_b - E_a + \frac{h^2 k'^2}{2m_o} - \frac{h^2 k^2}{2m_o}\right) \qquad (18)$$

The ratio of magnetic terms for x-rays and __neutrons__ is approximately

$$\frac{I_o^{x\text{-}ray} \; x \; \sigma_{mag}^{x\text{-}ray}}{I_o^{neutron} \; \sigma_{mag}^{neutron}} \approx \frac{1}{4}\frac{h\omega}{mc^2}^2 \cdot \frac{I_o^{x\text{-}ray}}{I_o^{neutron}} \approx \frac{1}{4}\, 10^{-4}\, \frac{I_o^{x\text{-}ray}}{I_o^{neutron}}$$

Neutron sources can give $\sim 10^8$ neutrons/sec. on a sample. an x-ray source which gives $\sim 10^{12}$ photons/sec (monochromatic) will give comparable x-ray and neutron peaks.

The x-ray pure magnetic scattering should be observed in structures (like anti-ferromagnets or spirals) in which the Bragg peaks do not occur at the same point in K space as the much __longer__ charge scattering.

Note to that e.q., (15) shows a different polarization factor for spin and orbital terms, prohibiting the possibility of distinginshing spin and orbit magnetization densities.

Summary

There are many interesting effects which can be studied in the magnetic scattering of photons. This technique can compliment in some cases the neutron scattering measurements.

Among the experiments are measurements to study:

1. Long period modulated structures
2. Differences of spin and orbit magnetization density
3. Resonance effects i.e. spin dependent anomalous dispersion, which will give greater intensity and will give Bragg peaks at points in k space different from the charge peaks
4. Surfaces using the above resonance methods
5. Interference between magnetic and charge scattering using circular polarization.

The principal equations derived here are (13) and (15). A fuller discussion of all their properties will be given elsewhere.