A first-principles theory of x-ray Faraday effects

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Abstract. We present a first-principles theory of x-ray Faraday effects. Initially we calculate the difference in absorption rate for right and left circularly polarized incident radiation. From this we are able to define an effective dielectric tensor that can be used to calculate magneto-x-ray properties. This work is based on a fully relativistic scattering-theory description of the electronic structure of magnetic materials. The theory is illustrated by a calculation of the Faraday rotation and induced ellipticity in linearly polarized light incident at the K edge of iron. Recent experiments compare favourably with the theory.

Currently the availability of tunable intense x-ray sources has generated great interest in using x-rays to study magnetism in condensed matter [1]. In particular several types of spectroscopy have been performed or proposed that are intrinsically relativistic in nature. Among the most important of these are magnetic x-ray scattering [2], magnetic resonance scattering [3,4] and circular dichroism in absorption [5–9] and fluorescence [10]. A recent series of experiments by Siddons, Hart and co-workers [11–13] has demonstrated the analogue of several magneto-optical effects in the x-ray region of the electromagnetic spectrum. However, development of these into a probe of the magnetic properties of matter has been hampered because a satisfactory theory of magneto-x-ray effects has not been developed. It has not been clear what these effects tell us about the electronic structure of materials. In this paper we present a first-principles quantitative theory of these effects, and discuss what they tell us about electrons in itinerant magnets. Firstly we review the calculation of x-ray absorption rates, then we discuss how to use such calculations to evaluate Faraday rotation and induced ellipticity.

A fully relativistic theory for describing the absorption of x-rays by electrons in solids has been developed by Ebert and co-workers [6, 14, 15] based upon the work of Durham [16], in order to describe the x-ray dichroism experiments pioneered by Schütz *et al* [5]. In short, their expression for the probability per unit time that the absorption of a photon of wavevector q, polarization λ, and energy $\hbar\omega$ induces a transition from a core state into the unoccupied conduction band is

$$W_i^{q\lambda}(\omega) = -\frac{1}{\Gamma} \int \mathrm{d}^3 r \int \mathrm{d}^3 r' \, \psi_i^+(r) X_{q\lambda}(r) \,\mathrm{Im}\, G(r, r'; E_i+\omega) X_{q\lambda}^+(r')\psi(r')\Theta(E_i+\omega-\tilde{E}_\mathrm{F})$$

(1)

In this equation E_i is the energy of the core state ψ_i, which is a Dirac spinor. E_F is the Fermi energy. The Θ function ensures that the excited electron can only occupy energetically acceptable empty conduction band states. In a fully relativistic theory the interaction operator $X_{q\lambda}$ is given by

$$X_{q\lambda}(r) = -e\alpha \cdot A(r) = -e\alpha \cdot a_\lambda \mathrm{e}^{\mathrm{i}(q \cdot r + \omega t)} + \mathrm{HC}.$$

(2)

Here α are the standard Dirac matrices and $A(r)$ represents the vector potential corresponding to the x-ray photon. Right (left) circularly polarized x-rays are described by $a_\lambda = (1/\sqrt{2})(1, i, 0)$ $(a_\lambda = (1/\sqrt{2})(1, -i, 0))$. $G(r, r', E)$ is a 4×4 bispinor Dirac Green function describing the conduction band. To compute the Green function we have used the *very efficient relativistic multiple scattering* KKR *method of Strange et al* [17]. Although this method has proved very efficient for calculating the results of spectroscopies, it should be borne in mind that correlation is only included within the local density approximation with all the limitations that implies. Furthermore, core-hole effects are completely neglected within this theory. Despite these approximations band-theory-based methods of describing spectroscopies have proved very successful [16].

In evaluating the above expressions we worked in the (κ, m_j) representation. For interpreting the results it is more convenient to use the familiar (l, m, s) representation. The relation between the two representations is discussed in detail by Strange *et al* [18]. We used the theory and codes of Ebert [19] to calculate the core-level wavefunctions. Finally our calculations have been performed in the dipole approximation by taking $e^{iq \cdot r} \simeq 1$ in equation (2). From the above theory we are able to calculate the magnetic x-ray dichroism from

$$D(q, \omega) = \frac{W_i^{q+}(\omega) - W_i^{q-}(\omega)}{W_i^{q+}(\omega) + W_i^{q-}(\omega)}. \tag{3}$$

The theory of magneto-optical effects has been given by Argyres [20]. This theory is derived for dielectric media assuming that the wavelength of the radiation is large compared to the mean free path of the electrons in the medium. As stated by Ashcroft and Mermin [21] this is valid for optical and ultra-violet frequencies, but not for x-rays. Argyres showed that magneto-optical effects can be described in terms of the conductivity tensor $\tilde{\sigma}$. For the case of uniaxial symmetry with the magnetic moment parallel to the z-axis this can be written in the form

$$\tilde{\sigma}(\omega) = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & 0 \\ -\sigma_{xy} & \sigma_{xx} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix} \tag{4}$$

where all the tensor elements are complex, i.e. $\sigma_{ij}(\omega) = \sigma_{1ij}(\omega) + i\sigma_{2ij}(\omega)$. The optical conductivities for right and left circularly polarized light are

$$\sigma^{r,l}(\omega) = \sigma_{xx}(\omega) \pm i\sigma_{xy}(\omega). \tag{5}$$

It can be shown that the dielectric constant $\epsilon_{ij}(\omega)$ and complex refractive index $n^{r,l}(\omega)$ of a magnetic material can be written in terms of the elements of the conductivity tensor as

$$\epsilon_{ij}(\omega) = \delta_{ij} - \frac{4\pi i}{\omega}\sigma_{ij}(\omega) \tag{6}$$

$$n^{r,l}(\omega) = \sqrt{1 + 4\pi i\sigma^{r,l}(\omega)/\omega}. \tag{7}$$

Argyres [20] has shown that many magneto-optical effects can be determined from these quantities. For example the Faraday rotation and ellipticity are given by

$$\theta_f = \frac{\omega d}{2c} \text{Re}[n^r - n^l] \tag{8}$$

and

$$\epsilon_f = -\tanh\left(\frac{\omega d}{2c} \, \mathrm{Im}[n^r - n^l]\right) \tag{9}$$

respectively, where d is the thickness of the material.

From our point of view a very useful extension of the work of Argyres was worked out by Bennett and Stern [22]. Assuming that we have a unit volume of material and a photon of unit amplitude, the power transferred in the absorption process is given by

$$P^\lambda = \hbar\omega \sum_i W_i^{q\lambda}(\omega) \tag{10}$$

where the summation is over all possible processes that involve absorption of a photon of frequency ω, wavevector q and polarization λ. They showed that the real part of the diagonal element of the conductivity tensor is given by $\sigma_{1xx} = P^l + P^r$. Furthermore the imaginary part of the off-diagonal component of the conductivity tensor is given by $\sigma_{2xy} = P^l - P^r$. The imaginary part of the diagonal component and the real part of the off-diagonal component of the conductivity tensor can then be found using the Kramers–Kronig relations.

Equations (6)–(9) cannot be directly applied in the x-ray region of the spectrum. However using equations (1) and (10) it is possible to calculate the power absorbed for any frequency, and hence find σ_{1xx} and σ_{2xy} from first principles. The next step is to postulate the existence of a very dense free carrier effective dielectric medium which does satisfy the criteria for the equations (6)–(9) to hold and has a dielectric (and conductivity) tensor identical to that of our magnetic material. Such an approach has been suggested by the work of Pershan [23] and Strange and Gyorffy [24], although several authors have implied that equations (6)–(9) are not applicable at x-ray frequencies [21,26]. Nonetheless we have determined the dielectric constant and conductivity tensor at these frequencies for our effective dielectric medium. All magneto-x-ray effects in this medium will be identical to those in our original magnetic material. Finally we note that in a dielectric material the absorption coefficient for electromagnetic radiation of frequency ω is given by [26]

$$K^{r,l}(\omega) = \frac{\omega}{c} \, \mathrm{Im} \, \epsilon^{r,l} \tag{11}$$

where $\epsilon^{r,l} = \epsilon_{xx} \pm i\epsilon_{xy}$. In short, we are setting up an effective-medium theory in which the photon absorption rate of our effective medium is identical to that of the real material.

We illustrate this approach to magneto-x-ray effects with a calculation of the Faraday rotation and induced ellipticity for linearly polarized x-rays incident at the K edge of ferromagnetic iron. This is chosen for two reasons. Firstly, our description of the electronic structure of iron is known to be reliable from previous calculations [6, 10]. Secondly, experimental results are readily available for the Faraday rotation in iron [12]. The absorption rates for iron for incident right and left circularly polarized radiation have been calculated and the dichroism given by equation (3) found. This has been broadened with a Lorentzian of width 0.8 eV to simulate core-hole lifetime effects. It is these broadened data which were used in the Kramers–Kronig relations to find σ_{2xx} and σ_{1xy}. This was because unbroadened data required an unrealistically large number of energy points for a converged Kramers–Kronig transformation. Equations (6) and (11) imply that the dichroism calculated from equations (1) and (11) should be identical. Of course, there is a Kramers–Kronig transformation between these two equations, but a comparison of the dichroism

calculated by each method is a stringent test of our numerical routines. In figure 1 we show the dichroism calculated using each method. These are not new results. Clearly the curves are identical on this scale and this lends strong support to our theory. This enables us to calculate the Faraday rotation and ellipticity from equations (8) and (9) with some confidence. The Faraday rotation has been further convoluted with a Gaussian of width 1.0 eV to allow for instrumental broadening etc and is shown in figure 2. Clearly, the final shape of the curve has a small dependence on the exact value of the broadening parameters chosen. The points in figure 2 are experimental values taken from [12] and they agree with the theory to the same level of accuracy that is usual in x-ray dichroism experiments. In figure 3 we show the Faraday ellipticity calculated from equation (9), this has not been broadened, so that a direct comparison with figure 1 can be made. Clearly the ellipticity follows the dichroism curve precisely and obeys the relation

$$\epsilon_f = D/2 \tag{12}$$

where ϵ_f has been normalized as the ellipticity per unit absorption. An analogous equation at optical frequencies has been discussed by Sato [25]. To our knowledge the ellipticity at x-ray energies has not been measured for iron.
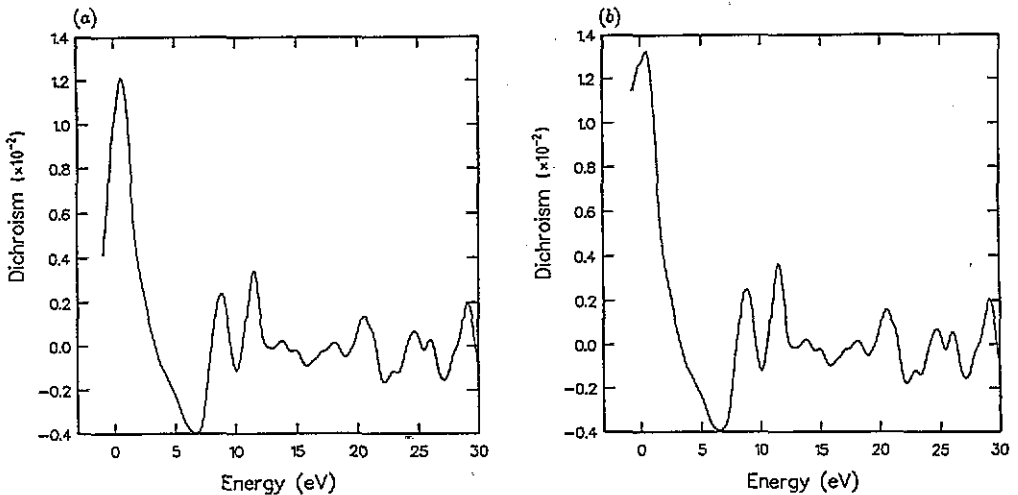

Figure 1. (a) The K edge magnetic x-ray dichroism calculated from first principles using equations (1) and (3). (b) The K edge magnetic x-ray dichroism calculated for our effective dielectric material using equations (11) and (3).

Obviously, once we have the effective dielectric (or conductivity) tensors it is a trivial task to go on to calculate other magneto-x-ray effects such as the magneto-x-ray Kerr effect (MXKE).

Clearly the Faraday ellipticity measures the same thing as dichroism. McWhan *et al* [27] have provided a deep and very transparent explanation of Faraday rotation and its relation to magnetic x-ray dichroism. They have shown that there is excellent agreement between the Kramers–Kronig transform of the experimentally obtained Faraday rotation and the magnetic dichroism and that both experiments can be described in terms of forward scattering amplitudes. The theory presented above is equivalent to this, but we have used
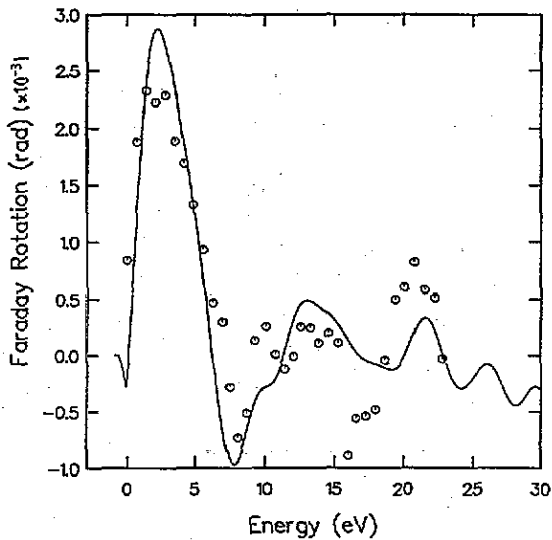
Figure 2. Faraday rotation of linearly polarized x-rays incident at the K edge of iron as a function of energy. The full line is the theoretical result, the points are experimental measurements from [12].
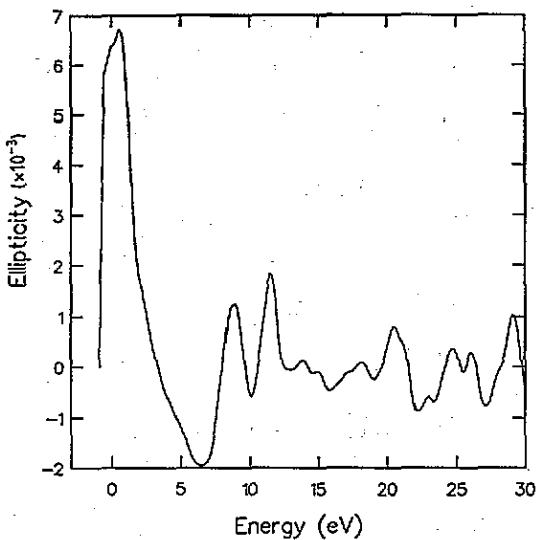

Figure 3. The induced ellipticity in linearly polarized x-rays incident at the K edge of iron as a function of energy calculated from equation (9). Compare this figure with figure 1.

the macroscopic conductivity tensor as the basic quantity from which spectroscopies can be calculated, in accordance with standard theory [27].

Now we have a reliable method for calculating magneto-x-ray effects in itinerant magnets we can ask what in the electronic structure of our magnetic material determines the size and energy dependence of magneto-x-ray phenomena.
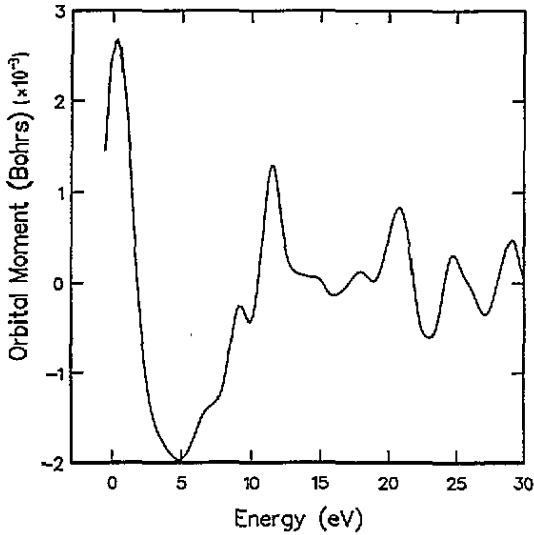
Figure 4. The $l = 1$ contribution to the orbital magnetic moment of Fe as a function of energy calculated from equation (13).
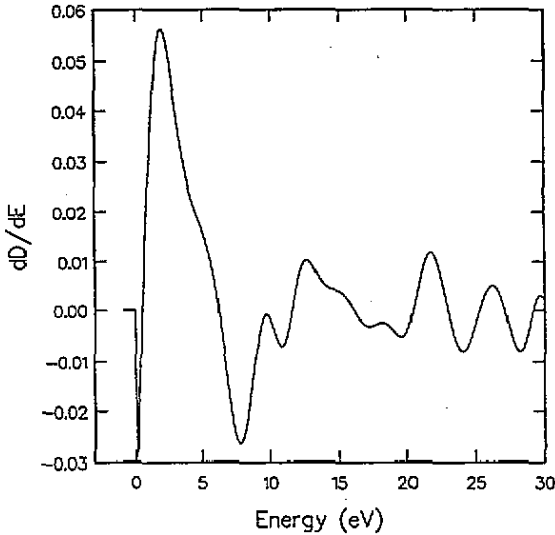

Figure 5. The derivative of the dichroism curve with respect to energy.

Schütz *et al* [5] have shown that if $m_l(E_f)$ and $n_l(E_f)$ are the partial magnetization and density of states, for the dipole-allowed value of the l quantum number, at the final-state energy E_f, it is often approximately true that $D(E_f) \propto m_l(E_f)/n_l(E_f)$. This approach would lead us to expect that the Faraday rotation will be large where the magnetic moment and/or the density of states is changing rapidly as a function of energy. There is a small contribution to the density of states of iron from (the dipole-allowed) $l = 1$ electrons just above the Fermi energy. This is a consequence of 4p–3d hybridization. As the 3d magnetic

moment and density of states are changing rapidly in the region a few electronvolts above the Fermi energy, so are those of the 4p electrons. Hence we expect the Faraday rotation in this region to be relatively large; our results in figure 2 are consistent with this.

A more sophisticated discussion of the role of the electronic structure in determining the magnetic x-ray dichroism has been presented by Thole *et al* [28, 29]. They have performed model calculations that show that if we neglect differences between spin–orbit-split matrix elements the magnetic dichroism is a direct measure of the orbital contribution to the magnetic moment. They have illustrated this with application to Ni and to Gd^{3+}. Here we calculate the orbital contribution to the magnetic moment within a first-principles-band theory approach using the method of Ebert *et al* [30].

$$\mu_{orb}(E) = -\frac{\mu_B}{\pi} \operatorname{Im} \operatorname{Tr} \tilde{\beta} \hat{L}_z G(r, r, E) \tag{13}$$

The dipole-allowed ($l = 1$) contribution to μ_{orb} is plotted as a function of energy in figure 4. Comparison of this with figures 1 and 3 confirms that the dichroism and ellipticity measure the orbital moment. There are small differences in the relative sizes of peaks between these figures, which are due to the correct inclusion of the matrix elements in the present calculation. Clearly, though, the present calculation confirms the theory of Thole *et al* [28] within an itinerant approach to the electronic structure. Figure 5 shows the derivative of the magnetic dichroism with respect to energy. Clearly this follows the Faraday rotation closely, and we can infer that the Faraday rotation is a measure of the rate of change of orbital moment, i.e. a large orbital moment brings about a rapid change in the x-ray Faraday rotation.

In summary then, the advances represented by this work are as follows. Firstly, we have shown that the theory of magneto-optical phenomena can be generalized to x-ray frequencies. Secondly we have combined first-principles electronic-structure methods and an effective-medium theory to provide a theory that is really complementary to the work of McWhan *et al* [27]. This work simply demonstrates the feasibility of performing calculations of Faraday rotation and ellipticity from first-principles band theory. This has been demonstrated by explicit calculation of the Faraday rotation and ellipticity for iron. To our knowledge, these effects have not been calculated from first principles at x-ray frequencies before. Good agreement with experiment has been found where results are available. Finally we have indicated what features of the electronic structure of an itinerant magnet are responsible for Faraday effects and shown that this is in agreement with the theory of Thole *et al* [28].

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