[magnetic form factors of atoms] The magnetic form factor of unpaired electrons in the l^n electronic configuration

The magnetic form factor is the Fourier transform of the magnetization density, spin and orbital contributions included, of the ion within a solid-state environment. We assume the effects of neighboring atoms are weak so that the magnetization density retains the features of the l^n electronic configuration of the ion. For transition-metal ions the orbital contributions often are small (e.g., quenched by crystal-field effects) or expected to follow the free-ion character. In any case the spin magnetization can be calculated reasonably accurately by several methods. In the evaluation of the matrix elements of the $\left|\theta JM\right\rangle$ states of the wavefunctions, we anticipate functions of spherical harmonics and spherical Bessel functions will appear in the calculation of the angular and radial components, respectively. Moreover, the formulism should take advantage of the symmetry properties of the l^n $(l = p, d, f)$ configurations. An important consequence is that the magnetic scattering amplitude is determined by matrix elements of even-order electric and odd-order magnetic multipoles, whose order of multipolarity k is less than or equal to $2l$+1. Some theoretical treatments resort to the dipolar approximation at the outset, expecting comparisons with experimental data collected at small neutron wavevector $\vec{\mathbf{Q}}$.

Stassis and Deckman.(1976) start from a general expression of the magnetic form factor

$$f_{mag}\left(\vec{\mathbf{Q}}\right) = \left(|\gamma| r_0\right)\vec{\sigma}\cdot\vec{\mathbf{J}}_{\perp}, \tag{1}$$

where γ =-1.91 is the neutron magnetic moment in nuclear magnetons, r_0 is the classical electron radius, $\vec{\sigma}$ is the Pauli matrix, and $\vec{\mathbf{J}}_{\perp}$ is a dimensionless operator which is the Fourier transform of the current density operator, $\vec{\mathbf{j}}\left(\vec{\mathbf{r}}_e\right)$ given by (4.29a) and (4.29b):

$$\vec{\mathbf{J}}_{\perp} = -i\left(\frac{m}{e\hbar Q}\right)\vec{\mathbf{Q}}\times\left\langle f\left|\int d^3\vec{\mathbf{r}}_e\vec{\mathbf{j}}\left(\vec{\mathbf{r}}_e\right)\exp\left(i\vec{\mathbf{Q}}\cdot\vec{\mathbf{r}}_e\right)\right|i\right\rangle, \tag{2}$$

and $\left\langle i\right|$ and $\left\langle f\right|$ are the initial and final state, respectively, of the neutron-atom system, denoted as $\left|i \,\text{or}\, f\right\rangle = \sum_{\theta JM} a\left(\theta JM\right)\left|\theta JM\right\rangle$. The authors realize that the matrix element in (2) is the same expression as in quantum theory of radiation, either in relativistic or non-relativistic treatment. Therefore, the operator can be evaluated by the well-established method of multipole expansion. The symmetry properties of the l^n electronic configuration are heeded by the *Racah tensor* algebra and the radial single-electron wavefunctions can be calculated by the *Hartree-Fock* or *Dira-Fock* methods.

Here, we outline the key steps of the calculations.

1. The transverse magnetization current density operator is expanded in multipole moments

$$\vec{\mathbf{j}}_{\perp} = \sum_{k,m}\left(\frac{8\pi}{2k+1}\right)^{1/2}\left[\vec{\mathbf{X}}^*_{km}(\hat{\mathbf{Q}})\left\langle f\left|T^{(e)}_{km}\right|i\right\rangle - i\left(\hat{\mathbf{Q}}\times\vec{\mathbf{X}}^*_{km}(\hat{\mathbf{Q}})\right)\left\langle f\left|T^{(m)}_{km}\right|i\right\rangle\right], \tag{3}$$

where $\vec{\mathbf{X}}_{km}(\hat{\mathbf{Q}})$ denotes the special vector spherical harmonic $\vec{\mathbf{Y}}^m_{k,k,1}(\hat{\mathbf{Q}})$, and

$$T_{km}^{(e)} = i^k \left[2\pi\left(2k+1\right)\right]^{1/2} \frac{1}{2\mu_B Q^2} \int \left[\vec{\nabla} \times \left(j_k(Qr)\vec{\mathbf{X}}_{km}(\hat{\mathbf{r}})\right)\right] \cdot j(\vec{\mathbf{r}}) d^3\vec{\mathbf{r}} \tag{4}$$

$$T_{km}^{(m)} = i^k \left[2\pi\left(2k+1\right)\right]^{1/2} \frac{1}{2\mu_B Q} \int j_k(Qr)\vec{\mathbf{X}}_{km}(\hat{\mathbf{r}}) \cdot j(\vec{\mathbf{r}}) d^3\vec{\mathbf{r}} \tag{5}$$

are the electric and magnetic multipole operators, respectively.

2. Substituting the spin and orbital magnetization density currents, (4.29a) and (4.29b) into (4) and (5), the matrix elements of the multipole operators are evaluated by means of the Racah tensor method. The magnetic form factor amounts to

$$\begin{aligned} f_{mag}(\vec{\mathbf{Q}}) &= \left(|\gamma| r_0\right)\vec{\sigma} \cdot \vec{\mathbf{J}}_{\perp} \\ &= \sum_{\substack{\theta JM \\ \theta' J' M'}} a^*\left(\theta JM\right) a\left(\theta' J' M'\right) f_{\theta' J' M'}^{\theta JM}(\vec{\mathbf{Q}}), \end{aligned} \tag{6}$$

where $f_{\theta' J' M'}^{\theta JM}(\vec{\mathbf{Q}})$ is the scattering amplitude for the transition $\theta JM \to \theta' J' M'$.

$$\begin{aligned} f_{\theta' J' M'}^{\theta JM}(\vec{\mathbf{Q}}) &= \left(|\gamma| r_0\right)\vec{\sigma} \cdot \langle \theta JM | \sum_{k,m} i^{k+1} \left(\frac{8\pi}{2k+1}\right)^{1/2} \\ &\times \left\{ \vec{\mathbf{X}}_{km}^*(\hat{\mathbf{Q}}) \left[R_2(k) W_m^{(0,k)k} + R_1(k,k) W_m^{(1,k)k}\right] - i\left(\vec{\mathbf{Q}} \times \vec{\mathbf{X}}_{km}^*(\hat{\mathbf{Q}})\right) \left[R_0(k) W_m^{(0,k)k} + \sum_{k'=k\pm1} R_1(k',k) W_m^{(1,k')k}\right] \right\} |\theta' J' M'\rangle. \end{aligned} \tag{7}$$

The R_0, R_1, and R_2 associate with radial integrals of spherical Bessel functions, and

$$\left\langle \theta JM \left| W_m^{(\kappa,k')k} \right| \theta' J' M' \right\rangle = (-)^{J-M} \begin{pmatrix} J & k & J' \\ -M & m & M' \end{pmatrix} \left(\theta J \left\| W^{(\kappa,k')k} \right\| \theta' J' \right). \tag{8}$$

The first term in the curly bracket of Eq. (7) corresponds to the electric multipole moments with $k = 2,4,...2l$ and the second term to the magnetic multipole moments with $k = 1,3,...2l+1$. Now the rest of the algebra such as the reduced matrix elements of the Racah double tensors, e.g., $\left(\theta J \left\| W^{(\kappa,k')k} \right\| \theta' J' \right)$, can be evaluated the Racah tensor method. The fact that the Racah double tensors are the generators of the groups $R_S(3)$, $R_L(3)$, $Sp(4l+1)$, and $R(2l+1)$ which are used to classify the $\left|\theta JM\right\rangle$ states, is advantageous. It permits the exploitation of the symmetry properties such as the selection rules applied to the reduced elements and the utilization of the reduced matrix elements for p^n, d^n and f^n, $n \le 2l+1$ already tabulated in the literature. So far the above treatment is general for magnetic transitions between Russel-Saunders states of nonrelativistic l^n configurations hence covers elastic and inelastic scattering. But it can be extended to mixed configurations and to relativistic atoms using effective multipole operators and relativistic radial integrals of the atomic wavefunctions.

3. Finally, the ionic magnetic form factor is obtained under the dipole approximation where all the electric multipole moments and magnetic multipoles higher than dipole ($m > 0$) in Eq. (7) are ignored. Higher multipole moments are required if detailed features over extended distances of a distribution function are to be described. Therefore, the dipole approximation is valid if the neutron scope, $\frac{1}{Q}$, is significantly larger than the radius of the orbital of the magnetic electrons. This is a good approximation for localized unpaired electrons such as those in *d*- and *f*-orbitals.

For elastic scattering, i.e., $\theta JM \to \theta JM$, the magnetic form factor takes a simple form

$$
\begin{aligned}
f_{\theta JM}^{\theta JM}(\vec{\mathbf{Q}}) &= (|\gamma| r_0) \sum_k \left(\frac{2}{k(k+1)} \right)^{1/2} P_k'(\cos\vartheta) \langle \theta JM | T_0^{(m)} | \theta JM \rangle \\
&= (|\gamma| r_0) \left\langle \theta JM \left| \sum_k i^{k+1} \left(\frac{2}{k(k+1)} \right)^{1/2} P_k'(\cos\vartheta) \left[R_0(k) W_0^{(0,k)k} + \sum_{k'=k\pm 1} R_1(k',k) W_0^{(1,k)k} \right] \right| \theta JM \right\rangle, \quad (9) \\
& k = 1, 3, \ldots 2l+1
\end{aligned}
$$

where $P_k'(\cos\vartheta) \equiv \dfrac{dP_k(\cos\vartheta)}{d(\cos\vartheta)}$ and ϑ is the angle between the magnetization direction (z-axis) and $\vec{\mathbf{Q}}$.

$$
R_0(k) = (-)^{k+1}(2l+1) \left[\frac{l(l+1)(2l+1)(2k+3)}{k} \right]^{1/2} \begin{pmatrix} l & k+1 & l \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} k+1 & 1 & k \\ l & l & l \end{Bmatrix} \left(\bar{j}_{k+1} + \bar{j}_{k-1} \right), \quad (10)
$$

$$
R_1(k',k) = (-)^l i^{k-k'-1}(2l+1) \left[\frac{(2k+1)(2k'+1)}{2} \right]^{1/2} \begin{pmatrix} k' & 1 & k \\ 0 & 1 & -1 \end{pmatrix} \begin{pmatrix} l & k' & l \\ 0 & 0 & 0 \end{pmatrix} \bar{j}_{k'}, \quad (11)
$$

$$
\bar{j}_k = \int_0^\infty r^2 \left(f(r) \right)^2 j_k(Q,r)\, dr. \quad (12)
$$

$(\ldots)$ and $\{\ldots\}$ are the 3-j and 6-j symbols, respectively, $f(r)$ is the one-electron radial wavefunction, and j_k is the spherical Bessel function.

The methodology has been applied by Stassis and Deckman to calculate the magnetic form factors of rare-earth ions and the result compared favorably with experimental data.

[Note: in the book, Eq. (4.30) is named twice for two different equations. The correct numbering should be: (4.29) → (4.29a), and the first (4.30) → (4.29b)]

Reference:

Stassis C. and H. W. Deckman (1976), “Magnetic scattering of neutron by atoms”, *J. Phys. C: Solid State Phys*. **9**, 2241.