PHYSICAL REVIEW B VOLUME 61, NUMBER 22 1 JUNE 2000-II

Spin and orbital contributions to the magnetic scattering of neutrons

K. Ayuel and P. F. de Châtel
Department of Physics, University of Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands

(Received 13 December 1999)

The current densities in partially filled electron shells of free atoms or ions, when analyzed in terms of multipole expansions, do not carry signatures that would distinguish orbital and spin currents. The same holds for the orbital and spin contributions to elastic neutron scattering amplitude, which are related to Fourier transforms of the respective current densities. The pitfalls of the so-called dipole approximation, which appears to enable a distinction, are pointed out and errors involved are calculated for some free-ion and crystal-field states.

I. INTRODUCTION

In alloys and intermetallic compounds, rare earth atoms are mostly in their triply ionized state. Due to the localized nature of $4f$ states on the scale of interatomic distances, the ions occupy their free-ion ground states in the solid. The exchange interaction between ions and external magnetic fields only influence the relative occupancy of the $2J+1$ degenerate levels within the ground-state manifold[1] and weak crystal fields lead to significant mixing only within the set of the $2J+1$ states.

In the case of actinides and ambivalent rare-earths, the situation is not quite so simple, because one has to reckon with the admixture of ''divalent'' and ''tetravalent'' states, i.e., states involving deviating numbers of *f* electrons. In the formal description of such mixed-valence states *d* or *s* states also have to be included, because only isoelectronic configurations can be superposed in a meaningful way. As the *d* and *s* electrons are delocalized, the formation of bands and the concomitant quenching of orbital moments must be taken into account, irrespective of the direct overlap of *f* states, that is, the width of a pure, unhybridized *f* band.

Whereas the description of hybridization of strongly correlated *f* states with Bloch states remains a challenge for theorists, the reduction of the orbital momentum with respect to the Russell-Saunders value is generally considered to be a measure of such hybridization.[2] Therefore, the experimental determination of the orbital and spin moments *separately* is of crucial importance in the study of mixed-valent rare earth materials and some actinide compounds. Although, strictly speaking, neutrons cannot distinguish between orbital and spin magnetism, various assumptions and approximations have been used to extract such information from magnetic form factors measured by elastic neutron scattering. Most commonly, it is assumed that the magnetic ion is in its Russell-Saunders $|L,S,J,M_J\rangle$ ground state and the dipole approximation is applicable. If, as a further approximation, the contribution accounting for nonspherical distribution of the spin magnetism is neglected in the dipole term, the remaining contributions can be replaced by simple operator equivalents. The orbital contribution to the form factor is found then to be proportional to the expectations value of $\boldsymbol{\sigma}_n\cdot\mathbf{L}(\overline{j}_0+\overline{j}_2)$ and the spin contribution to $\boldsymbol{\sigma}_n\cdot\mathbf{S}\overline{j}_0$, where $\boldsymbol{\sigma}_n$ stands for the neutron's spin, $\mathbf{L}$ and $\mathbf{S}$ are the orbital and spin angular momentum operators, and $\overline{j}_0(q)$ and $\overline{j}_2(q)$ are Bessel transforms of the radial wave function [see below, Eq. (19)], which depend on the magnitude of the scattering vector $\mathbf{q}$.

Under the above assumption and within the approximations specified, what is customarily called the dipole approximation can be applied to the measured form factor. Fitting the latter with a linear combination of $\overline{j}_0(q)$ and $\overline{j}_2(q)$, the ratio of the coefficients of $\overline{j}_0(q)+\overline{j}_2(q)$ and $\overline{j}_0$, and hence the ratio μ_L/μ_S of the orbital and the spin moments can be deduced.

The purpose of this paper is to comment on the analysis of form factor data in the customary dipole approximation. In our considerations we shall relate the form factor to the current density, rather than the magnetization, as is customary. The ambiguity of the atomic magnetization $\mathbf{M}(\mathbf{r})$ and consequently, of its Fourier transform $\mathbf{M}(\mathbf{q})$, which is related to the neutron scattering amplitude, has been recognized[3] early and extensively discussed[4] and illustrated[5] recently. In these illustrations it appears that the use of $\mathbf{M}(\mathbf{r})$ to describe atomic magnetism has no merits over the use of the magnetic induction $\mathbf{B}(\mathbf{r})$, since the longitudinal (irrotational) component is not accessible to measurement by neutrons and $\mathbf{M}_\perp(\mathbf{r})=\mu_0^{-1}\mathbf{B}(\mathbf{r})$. Furthermore, $\mathbf{M}(\mathbf{r})$ functions obtained for different definitions of the magnetization as solutions of the differential equation

$$\nabla\times\mathbf{M}(\mathbf{r})=\mathbf{j}(\mathbf{r}), \tag{1}$$

which relates the magnetization $\mathbf{M}(\mathbf{r})$ to the current density $\mathbf{j}(\mathbf{r})$, turn out to be qualitatively different. The analysis of such functions can easily result in misleading physical interpretations, while they invariably exhibit some unphysical, contraintuitive features. So it is preferable to discuss the calculated or measured magnetic behavior of atoms in terms of physically uniquely defined quantities such as the current density and the magnetic field $\mathbf{B}$.

Trammell[6] was the first one to formulate the magnetic scattering of neutrons entirely in terms of current densities, using the Dirac velocity operator at the outset. Stassis and Deckman[7] followed this approach and showed that the magnetic scattering amplitude can be written as

0163-1829/2000/61(22)/15213(8)/$15.00

$$f(\mathbf{q})=i|\gamma|r_0\frac{1}{2\mu_B q^2}\boldsymbol{\sigma}\cdot\left(\mathbf{q}\times\left\langle f\left|\int\hat{\mathbf{j}}(\mathbf{r})e^{i\mathbf{q}\cdot\mathbf{r}}dV\right|i\right\rangle\right), \quad (2)$$

where r_0 is the classical electron radius. The vector product $\mathbf{q}\times\mathbf{j}(\mathbf{q})$, where $\mathbf{j}(\mathbf{q})$ is the Fourier transform of $\mathbf{j}(\mathbf{r})$, suggests a limitation of neutron scattering, which, apparently, has no access to the longitudinal component of $\mathbf{j}(\mathbf{q})$. However, this component is the Fourier transform of the irrotional component of $\mathbf{j}(\mathbf{r})$, which vanishes in the case of intra-atomic currents, for which $\operatorname{div}\mathbf{j}=0$. Atomic current densities are thus seen to be fully accessible to experimental observation.

In Sec. II, we go back to current densities, in search of characteristics distinguishing spin and orbital currents. In the expectation values in angular-momentum eigenstates no such characteristics are found. In Sec. III, the known[7] expressions for the neutron scattering amplitude due to orbital and spin currents are deduced from the corresponding current densities. Maintaining only the dipole term in the multipole expansion of the latter gives the proper dipole approximation, which is less restrictive than the customary dipole approximation described above. Section IV contains the discussion of $\overline{j_0}$ vs $\overline{j_2}$ analyses with inclusion of various contributions and concludes with cautionary remarks concerning the significance of the outcome of such analyses.

II. THE NATURE OF THE CURRENT DENSITY OF ATOMIC BOUND ELECTRONS

Instead of calculating the expectation value of the Fourier transform appearing in the scattering amplitude (2) directly, we shall first calculate the expectation value of the current density itself. Starting with the definition of the orbital current density in the nonrelativistic limit of the Dirac equation and performing a multipole expansion in terms of vector spherical harmonics[8] $\mathbf{Y}^{\mathcal{L}}_{\mathcal{L}'\mathcal{M}'}$, the orbital current density operator can be written in the following form:[9]

$$\hat{\mathbf{j}}^{o}(\mathbf{r})=\mu_B\sum_{\mathcal{L}\mathcal{L}'\mathcal{M}'}(-1)^{\mathcal{M}'}(\hat{j}^{o})^{(\mathcal{L}')}_{\mathcal{M}'}(\mathcal{L})\mathbf{Y}^{\mathcal{L}}_{\mathcal{L}'-\mathcal{M}'}(\mathbf{e}_r), \quad (3)$$

where $(\hat{j}^{o})^{(\mathcal{L}')}_{\mathcal{M}'}(\mathcal{L})$ are components of irreducible tensor operators of rank $\mathcal{L}'$ and $\mathbf{e}_r$ is the unit vector pointing in the direction of $\mathbf{r}$. The matrix elements of $(\hat{j}^{o})^{(\mathcal{L}')}_{\mathcal{M}'}(\mathcal{L})$ between the eigenstates within the same shell, i.e., within an (n,l) manifold, vanish, unless $\mathcal{L}'=\mathcal{L}$.

Similarly, the spin density operator can be expanded as

$$\hat{\boldsymbol{\sigma}}(\mathbf{r})=\frac{\mu_B}{r^2}\delta(\hat{r}'-r)\sum_{\mathcal{L}\mathcal{L}'\mathcal{M}'}(-1)^{\mathcal{L}-\mathcal{L}'+\mathcal{M}'}$$
$$\times[\hat{Y}^{(\mathcal{L})}\otimes\hat{\sigma}^{(1)}]^{(\mathcal{L}')}_{\mathcal{M}'}\mathbf{Y}^{\mathcal{L}}_{\mathcal{L}'-\mathcal{M}'}(\mathbf{e}_r), \quad (4)$$

where $[\hat{Y}^{(\mathcal{L})}\otimes\hat{\sigma}^{(1)}]^{(\mathcal{L}')}_{\mathcal{M}'}$ is a component of the rank $\mathcal{L}'$ irreducible product of the tensor operators $\hat{\mathbf{Y}}^{(\mathcal{L})}$ and $\hat{\boldsymbol{\sigma}}^{(1)}$ and $\hat{\boldsymbol{\sigma}}^{(1)}$ is the vector composed of the Pauli spin matrices.

Both $\hat{\mathbf{j}}^{o}(\mathbf{r})$ and $\hat{\boldsymbol{\sigma}}(\mathbf{r})$ being single-particle operators, their matrix elements between Russell-Saunders spin-orbit coupled eigenstates $|\theta JM\rangle$ of n-electron shells can be written in terms of Racah double tensors $W^{(k',k'')}$ and $W^{(k',k'')k}$ as[9]

$$\langle\theta JM_J|\hat{\mathbf{j}}^{o(n\text{-electrons})}|\theta'J'M_J'\rangle=\sqrt{2}\mu_B\frac{R^2_{nl}}{r}(-1)^{l+1}(2l+1)\sum_{\mathcal{L}\mathcal{M}}(-1)^{\mathcal{M}}\sqrt{\frac{(2l+\mathcal{L}+2)(2l-\mathcal{L}+1)}{4\pi}}\begin{pmatrix} l & \mathcal{L} & l+1\\ 0 & 0 & 0\end{pmatrix}$$
$$\times\langle\theta JM_J|W^{(0,\mathcal{L})\mathcal{L}}_{\mathcal{M}}|\theta'J'M_J'\rangle\mathbf{Y}^{\mathcal{L}}_{\mathcal{L}-\mathcal{M}} \quad (5)$$

and

$$\langle\theta JM_J|\hat{\boldsymbol{\sigma}}^{(n\text{-electrons})}|\theta'J'M_J'\rangle=(-1)^{l+\mathcal{M}+1}\frac{\mu_B}{\sqrt{2\pi}}(2l+1)R^2_{nl}\sum_{\mathcal{L}}\sum_{\mathcal{L}'=\mathcal{L}\pm1}\begin{pmatrix} l & \mathcal{L}' & l\\ 0 & 0 & 0\end{pmatrix}\langle\theta JM_J|W^{(1,\mathcal{L}')\mathcal{L}}_{\mathcal{M}}|\theta'J'M_J'\rangle\mathbf{Y}^{\mathcal{L}'}_{\mathcal{L}-\mathcal{M}}, \quad (6)$$

where $R_{nl}(r)$ is the radial wave function and the matrix elements $\langle\theta JM_J|W^{(0,\mathcal{L})\mathcal{L}}_{\mathcal{M}}|\theta'J'M_J'\rangle$ and $\langle\theta JM_J|W^{(1,\mathcal{L}')\mathcal{L}}_{\mathcal{M}}|\theta'J'M_J'\rangle$ are given, respectively, by

$$\langle\theta JM_J|\hat{W}^{(0,\mathcal{L})\mathcal{L}}_{\mathcal{M}}|\theta'J'M_J'\rangle=(-1)^{J-M_J}[J,\mathcal{L},J']^{1/2}\begin{pmatrix} J & \mathcal{L} & J'\\ -M_J & \mathcal{M} & M_J'\end{pmatrix}\begin{Bmatrix} S & S' & 0\\ L & L' & \mathcal{L}\\ J & J' & \mathcal{L}\end{Bmatrix}\langle\theta||\hat{W}^{(0,\mathcal{L})}||\theta'\rangle \quad (7)$$

and

$$\langle\theta JM_J|\hat{W}^{(1,\mathcal{L}')\mathcal{L}}_{\mathcal{M}}|\theta'J'M_J'\rangle=(-1)^{J-M_J}[J,\mathcal{L},J']^{1/2}\begin{pmatrix} J & \mathcal{L} & J'\\ -M_J & \mathcal{M} & M_J'\end{pmatrix}\begin{Bmatrix} S & S' & 1\\ L & L' & \mathcal{L}'\\ J & J' & \mathcal{L}\end{Bmatrix}\langle\theta||\hat{W}^{(1,\mathcal{L}')}||\theta'\rangle. \quad (8)$$

Stassis and Deckman[10] have tabulated the values of the reduced matrix elements $\langle\theta\|\hat{W}^{(0,\mathcal{L})}\|\theta'\rangle$ as well as $\langle\theta\|\hat{W}^{(1,\mathcal{L}')}\|\theta'\rangle$ relevant to the ground state of the tripositive rare-earth ions, that is, $\langle\theta\|\hat{W}^{(0,\mathcal{L})}\|\theta'\rangle$ for $\mathcal{L}=1,3$, and 5 and $\langle\theta\|\hat{W}^{(1,\mathcal{L}')}\|\theta'\rangle$ for $\mathcal{L}'=0,2,4$, and 6.

The spin current density being related to the spin magnetization $\mu_B\boldsymbol{\sigma}(\mathbf{r})$ through Eq. (1), the matrix elements of the spin-current density operator are found from Eq. (6) by differentiation

$$\langle\theta JM_J|\hat{\mathbf{j}}^{s(n\text{-electrons})}|\theta'J'M_J'\rangle=i(-1)^{l+\mathcal{M}+1}\frac{\mu_B}{\sqrt{\pi}}(2l+1)\sum_{\mathcal{L}}\sum_{\mathcal{L}'=\mathcal{L}\pm1}\begin{pmatrix} l & \mathcal{L}' & l\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} \mathcal{L}' & 1 & \mathcal{L}\\ 0 & 1 & -1\end{pmatrix}\sqrt{2\mathcal{L}'+1}$$
$$\times\left\{\frac{d}{dr}+\frac{1}{2}[(2\mathcal{L}+1)(\mathcal{L}'-\mathcal{L})+3]\frac{1}{r}\right\}R_{nl}^2\langle\theta JM_J|W_{\mathcal{M}}^{(1,\mathcal{L}')\mathcal{L}}|\theta'J'M_J'\rangle\mathbf{Y}_{\mathcal{L}-\mathcal{M}}^{\mathcal{L}}. \tag{9}$$

Here too, the limitation to a single shell eliminates the vector spherical harmonics with $\mathcal{L}'=\mathcal{L}\pm1$ so that the multipole expansion of the current density operator turns out to be restricted under this condition. Therefore, the orbital, spin and total current density operators can all be cast in the form of a single sum

$$\hat{\mathbf{j}}=\sum_{\mathcal{L}}(-1)^{\mathcal{M}}\hat{j}_{\mathcal{M}}^{(\mathcal{L})}\mathbf{Y}_{\mathcal{L}-\mathcal{M}}^{\mathcal{L}}, \tag{10}$$

containing only the $\mathbf{Y}_{\mathcal{L}\mathcal{M}}^{\mathcal{L}}$ vectors (often denoted as $\mathbf{X}_{\mathcal{L}\mathcal{M}}$ and referred to as the magnetic vectors in the literature).

The presence of the vector spherical harmonics $\mathbf{Y}_{\mathcal{L}-\mathcal{M}}^{\mathcal{L}}$ in Eqs. (5), (9), and (10) is not unexpected there, because $\operatorname{div}[f(r)\mathbf{Y}_{\mathcal{L}-\mathcal{M}}^{\mathcal{L}}]=0$ for any differentiable radial function $f(r)$, so that the obvious condition $\operatorname{div}\mathbf{j}(\mathbf{r})=0$ is automatically satisfied. When calculating the expectation value of the current density in eigenstates of the z component of the total angular momentum from Eqs. (5), (9), and (10), $\mathcal{M}$ will vanish ($M_J'=M_J;\mathcal{M}=0$) and the vector spherical harmonics $\mathbf{Y}_{\mathcal{L}0}^{\mathcal{L}}$ will have the polar components

$$[\mathbf{Y}_{\mathcal{L}0}^{\mathcal{L}}]_r=[\mathbf{Y}_{\mathcal{L}0}^{\mathcal{L}}]_\theta=0, \tag{11}$$

$$[\mathbf{Y}_{\mathcal{L}0}^{\mathcal{L}}]_\phi=i\sqrt{\frac{2\mathcal{L}+1}{4\pi\mathcal{L}(\mathcal{L}+1)}}P_1^{\mathcal{L}}, \tag{12}$$

where $P_1^{\mathcal{L}}$ are the associated Legendre functions. Thus, the expectation values of the current density operators have only an azimuthal (ϕ) component and they will be independent of ϕ. This result is in accord with the classical picture of electrons orbiting a central nucleus. The vector spherical harmonics $\mathbf{Y}_{\mathcal{L}-\mathcal{M}}^{\mathcal{L}}$ will have in general only two components, ϕ and θ, since $\mathbf{e}_r\cdot\mathbf{Y}_{\mathcal{L}-\mathcal{M}}^{\mathcal{L}}=0$, irrespective of the value of $\mathcal{M}$. This property is thus common to all linear combinations of such function as for the particular case of linear combinations diagonalizing the crystal-field operator. It is important to note that the statements made above establish general features of current densities, which apply to orbital and spin currents alike. The implication of this generality is that the decomposition of the measured total current density into orbital and spin components is not possible without using additional information or making assumptions.

III. MAGNETIC SCATTERING AMPLITUDE, SMALL-Q AND DIPOLE APPROXIMATIONS

Substituting into the scattering amplitude (2) the matrix elements presented in the previous section,

$$f_{\theta'J'M_{J'}}^{\theta JM_J}(\mathbf{q})=i|\gamma|r_0\frac{1}{2\mu_Bq^2}\times\boldsymbol{\sigma}\cdot\left(\mathbf{q}\times\int e^{i\mathbf{q}\cdot\mathbf{r}}\langle\theta JM_J|\hat{\mathbf{j}}(\mathbf{r})|\theta'J'M_{J'}\rangle dV\right). \tag{13}$$

It is not difficult (see the Appendix) to recover the expressions given by Stassis and Deckman[7] for the contribution of the orbital and spin current density to the above expression

$$f^{o\,\theta JM_J}_{\theta'J'M_{J'}}(\mathbf{e}_q)=(|\gamma|r_0)\boldsymbol{\sigma}\cdot\sum_{\mathcal{L}}i^{\mathcal{L}}\left(\frac{8\pi}{2\mathcal{L}+1}\right)^{1/2}\times[\mathbf{e}_q\times\mathbf{Y}_{\mathcal{L}\mathcal{M}}^{\mathcal{L}}{}^*(\mathbf{e}_q)]R_0(\mathcal{L})\times\langle\theta JM_J|W_{\mathcal{M}}^{(0,\mathcal{L})\mathcal{L}}|\theta'J'M_{J'}\rangle; \tag{14}$$

$$f^{s\,\theta JMJ}_{\theta'J'M_{J'}}(\mathbf{e}_q)=(|\gamma|r_0)\boldsymbol{\sigma}\cdot\sum_{\mathcal{L}}i^{\mathcal{L}}\left(\frac{8\pi}{2\mathcal{L}+1}\right)^{1/2}\times[\mathbf{e}_q\times\mathbf{Y}_{\mathcal{L}\mathcal{M}}^{\mathcal{L}}{}^*(\mathbf{e}_q)]\sum_{\mathcal{L}'=\mathcal{L}\pm1}R_1(\mathcal{L}',\mathcal{L})\times\langle\theta JM_J|W_{\mathcal{M}}^{(1,\mathcal{L}')\mathcal{L}}|\theta'J'M_{J'}\rangle, \tag{15}$$

where the summations over $\mathcal{L}$ run through odd positive integers up to and including $2l+1$,

$$R_0(\mathcal{L})=(-1)^{\mathcal{L}+l}(2l+1)\times\sqrt{\frac{l(l+1)(2l+1)(2\mathcal{L}+3)}{\mathcal{L}}}\begin{pmatrix} l & \mathcal{L}+1 & l\\ 0 & 0 & 0\end{pmatrix}\times\begin{Bmatrix} \mathcal{L}+1 & 1 & \mathcal{L}\\ l & l & l\end{Bmatrix}(\overline{j}_{\mathcal{L}+1}+\overline{j}_{\mathcal{L}-1}) \tag{16}$$

and

$$
\begin{aligned}
R_1(\mathcal{L}',\mathcal{L}) = {} & (-1)^l i^{\mathcal{L}-\mathcal{L}'-1}(2l+1) \\
& \times([\mathcal{L}',\mathcal{L}]/2)^{1/2}\begin{pmatrix} \mathcal{L}' & 1 & \mathcal{L} \\ 0 & 1 & -1 \end{pmatrix} \\
& \times\begin{pmatrix} l & \mathcal{L}' & l \\ 0 & 0 & 0 \end{pmatrix}\overline{j}_{\mathcal{L}'}. \qquad (17)
\end{aligned}
$$

We have used here the recursion relation of the spherical Bessel functions

$$j_l(x) = \frac{x}{2l+1}\{j_{l-1}(x)+j_{l+1}(x)\}, \tag{18}$$

and adopted the notation

$$\overline{j}_{\mathcal{L}} = \int_0^\infty r^2 j_{\mathcal{L}}(qr)R_{nl}^2(r)dr. \tag{19}$$

A. The small-q approximation

In the analysis of elastic-scattering results, the small-q approximation is often invoked. The underlying assumption is that $qr \ll 1$ for all values of r for which $\mathbf{j}(\mathbf{r})$ is not negligible, so that $e^{i\mathbf{q}\cdot\mathbf{r}}$ can be replaced by $1+i\mathbf{q}\cdot\mathbf{r}$ in Eq. (13). There is some justification for this assumption for the scattering of thermal neutrons on rare-earth ions, but not when such neutrons are used to study transition metals or actinides.

To realize this assumption, one should turn to Eq. (A.2) and note that for small values of their arguments the spherical Bessel functions are of the form $j_l(x) \sim x^l/(2l+1)!!$. Therefore, up to second order in $\mathbf{q}\cdot\mathbf{r}$ only the $\mathcal{L}=1$ term remains in the expressions of $f^o(\mathbf{q})$ and $f^s(\mathbf{q})$ [Eqs. (14) and (15)]. However, if this approximation is carried through systematically, the integrals $\overline{j}_0$ and $\overline{j}_2$ appearing in the $\mathcal{L}=1$ terms in the sums in Eqs. (16) and (17) should be replaced by $\int r^2[1-(qr)^2/6]R_{nl}^2 dr$ and $\int r^2(qr)^2 R_{nl}^2 dr$, respectively.

B. The proper dipole approximation

When the terms with $\mathcal{L}>1$ are neglected on the basis of the above argumentation, but the integrals $\overline{j}_0$ and $\overline{j}_2$ are maintained, the proper dipole approximation results. For some reason, the term ''dipole approximation'' is customarily used to denote a truncated dipole term not including the $\mathcal{L}=1$, $\mathcal{L}'=2$ contribution to Eq. (15). Lander and Brun[11] have compared the scattering amplitude in this customary dipole approximation, which they denoted by f_d, to the result of the proper dipole approximation f_p for the tripositive rare-earth ions and found the differences minor, if not negligible.

The definition of the proper dipole approximation is clear cut, as only the dipole component of the current density is maintained. Also, if one insists on defining a magnetization function satisfying Eq. (1), it is clear that the dipole component of $\mathbf{M}$ is related to only the dipole component of $\mathbf{j}$, since $\boldsymbol{\nabla}\times\{f(r)\mathbf{Y}_{\mathcal{L}\mathcal{M}}^{\mathcal{L}}\}$ is a linear combination of terms proportional to $\mathbf{Y}_{\mathcal{L}\mathcal{M}}^{\mathcal{L}-1}$ and $\mathbf{Y}_{\mathcal{L}\mathcal{M}}^{\mathcal{L}+1}$ and the transformation properties (i.e., the multipole nature) of the vector spherical harmonics are determined by the lower indices.

An important feature of the dipole approximation can be deduced from the observation that only the $\mathcal{L}=1$ term contributes to the total magnetic moment, which is given by

$$\int_V \mathbf{M}(\mathbf{r})dV = \frac{1}{2}\int \mathbf{r}\times\mathbf{j}(\mathbf{r})dV = \mathbf{m}. \tag{20}$$

This can be verified using the identity

$$\mathbf{e}_r\times\mathbf{Y}_{\mathcal{L}\mathcal{M}}^{\mathcal{L}}(\mathbf{e}_r) = i[\mathcal{L}]^{-1/2}\{(\mathcal{L}+1)^{1/2}\mathbf{Y}_{\mathcal{L}\mathcal{M}}^{\mathcal{L}-1}(\mathbf{e}_r)+\mathcal{L}^{1/2}\mathbf{Y}_{\mathcal{L}\mathcal{M}}^{\mathcal{L}+1}(\mathbf{e}_r)\} \tag{21}$$

and the fact that the only vector spherical harmonics whose integral over the entire solid angle does not vanish are the three $\mathbf{Y}_{1\mathcal{M}}^{0}$ functions. The implication is that the dipole approximation is exact, when it comes to the determination of the total magnetic moment. In practice, however, the determination of $\mathbf{m}$ involves an extrapolation of $f(q)$ to zero. The reliability of this extrapolation depends on the way $f(q)$ is fitted. As it will be shown in the following section, fitting with a linear combination of $\overline{j}_0(q)$ and $\overline{j}_2(q)$ is not equivalent with the dipole approximation, be it in the customary or proper sense.

IV. THE $\overline{j}_0$ VERSUS $\overline{j}_2$ ANALYSIS

Whenever a sufficient number of low-q values of $f(q)$ is experimentally accessible, an analysis of the scattering amplitude in terms of $\overline{j}_0$ and $\overline{j}_2$ is a reliable way of determining $f(0)$ and hence $\mathbf{m}$. Apart from correctly giving the total magnetic moment, such an analysis is often claimed to enable a distinction of spin and orbital moments.[12] This claim is based on the relation between, on the one hand, some of the Racah double tensors appearing in the dipole component in the scattering amplitude and, on the other hand, the operators of the spin and orbital angular momentum

$$W_m^{(1,0)1} = \left(\frac{2}{2l+1}\right)^{1/2} S_m, \tag{22}$$

$$W_m^{(0,1)1} = \left(\frac{3}{2l(l+1)(2l+1)}\right)^{1/2} L_m. \tag{23}$$

Equations (16) and (17) show that $W_0^{(1,0)1}$ appears in conjunction with $\overline{j}_0$ in the contribution of the spin current density, whereas $W_0^{(0,1)1}$ is multiplied by $\overline{j}_0+\overline{j}_2$ in that of the orbital current density. However, decomposing the measured scattering amplitude into components proportional to $\overline{j}_0$ and $\overline{j}_0+\overline{j}_2$ does not distinguish between the spin and orbital contributions. This is because as pointed out in Sec. III B, spin-current contribution of the former also contains a term proportional to $\overline{j}_2 W_0^{(1,2)1}$ and $W_0^{(1,2)1}$ is not related to S_0 or L_0 in any simple way. Furthermore, if the analysis does not involve an identification of the dipole contribution to the scattering amplitude on the basis of its angular dependence, one has to reckon with contributions proportional with $\overline{j}_2$ from the octupole term. To be more specific, in a systematic $\overline{j}_0$ vs $\overline{j}_2$ analysis one should collect from Eqs. (14) and (15) *all* coefficients of $\overline{j}_0$ and $\overline{j}_2$.

We shall formulate the above criticism of the customary $\overline{j_0}$ vs $\overline{j_2}$ analysis in terms of the expressions for the scattering amplitude, which are limited to $\overline{j_0}$ vs $\overline{j_2}$ but otherwise are exact. We choose for this calculation the most common experimental configuration, in which the scattering vector is constrained in the plane perpendicular to the magnetic field. We assume that the atomic magnetic moments and the neutron spin are fully aligned by this field. The vector spherical harmonics $\mathbf{Y}^1_{1\,0}$ and $\mathbf{Y}^3_{3\,0}$ are then only needed in the ''equatorial plane,'' i.e., for $\theta_q=\pi/2$, in which case they only have a ϕ component and are independent of ϕ. Their vector product with $\mathbf{e}_q$ is then pointing in the $\mathbf{e}_\theta$ direction, which, in the equatorial plane, coincides with $-\mathbf{e}_z$, making the scalar product with $\boldsymbol{\sigma}$, occurring in Eqs. (15) and (16), trivial and leading to

$$\boldsymbol{\sigma}\cdot\mathbf{e}_q\times\mathbf{Y}^1_{1\,0}(\mathbf{e}_q)=-i\frac{1}{2}\sqrt{\frac{3}{2\pi}} \tag{24}$$

and

$$\boldsymbol{\sigma}\cdot\mathbf{e}_q\times\mathbf{Y}^3_{3\,0}(\mathbf{e}_q)=i\frac{1}{8}\sqrt{\frac{21}{\pi}}. \tag{25}$$

Substituting these values into Eq. (14) and rearranging the terms as described above, we find

$$f^{o\,\theta JJ}_{\;\theta JJ}(\mathbf{e}_q)=(a_{1\,0})\overline{j_0}+(a_{1\,2}+a_{3\,2})\overline{j_2}, \tag{26}$$

with

$$a_{1\,0}=a_{1\,2}=(|\gamma|r_0)(-1)^{l+1}\sqrt{5}\{[l]^3l(l+1)\}^{1/2}\begin{pmatrix} l & 2 & l\\ 0 & 0 & 0\end{pmatrix}\times\begin{Bmatrix} 2 & 1 & 1\\ l & l & l\end{Bmatrix}\langle\theta JJ|W_0^{(0,1)1}|\theta JJ\rangle \tag{27}$$

and

$$a_{3\,2}=(|\gamma|r_0)(-1)^{l+1}\frac{3}{\sqrt{8}}\{[l]^3l(l+1)\}^{1/2}\begin{pmatrix} l & 4 & l\\ 0 & 0 & 0\end{pmatrix}\times\begin{Bmatrix} 4 & 1 & 3\\ l & l & l\end{Bmatrix}\langle\theta JJ|W_0^{(0,3)3}|\theta JJ\rangle. \tag{28}$$

A similar rearrangement of terms in Eq. (15) gives

$$f^{s\,\theta JJ}_{\;\theta JJ}(\mathbf{e}_q)=(b_{1\,0})\overline{j_0}+(b_{1\,2}+b_{3\,2})\overline{j_2}, \tag{29}$$

with

$$b_{1\,0}=(|\gamma|r_0)(-1)^{l}\sqrt{\frac{3}{2}}[l]\begin{pmatrix} 0 & 1 & 1\\ 0 & 1 & -1\end{pmatrix}\begin{pmatrix} l & 0 & l\\ 0 & 0 & 0\end{pmatrix}\times\langle\theta JJ|W_0^{(1,0)1}|\theta JJ\rangle, \tag{30}$$

$$b_{1\,2}=(|\gamma|r_0)(-1)^{l+1}\sqrt{\frac{15}{2}}[l]\begin{pmatrix} 2 & 1 & 1\\ 0 & 1 & -1\end{pmatrix}\begin{pmatrix} l & 2 & l\\ 0 & 0 & 0\end{pmatrix}\times\langle\theta JJ|W_0^{(1,2)1}|\theta JJ\rangle, \tag{31}$$

and

$$b_{3\,2}=(|\gamma|r_0)(-1)^{l+1}\frac{\sqrt{105}}{2}[l]\begin{pmatrix} 2 & 1 & 3\\ 0 & 1 & -1\end{pmatrix}\begin{pmatrix} l & 2 & l\\ 0 & 0 & 0\end{pmatrix}\times\langle\theta JJ|W_0^{(1,2)3}|\theta JJ\rangle. \tag{32}$$

It is seen that the first label of the coefficients a_{ij} and b_{ij} refers to the order of the multipole component ($i=1$ dipole, $i=3$ octupole) while the second label gives the order of the spherical Bessel function involved.

In terms of the coefficients defined in Eqs. (26) and (29), the customary dipole approximation is based on the assumptions $a_{3\,2}=b_{1\,2}=b_{3\,2}=0$. On the other hand, in a proper dipole approximation only $a_{3\,2}$ and $b_{3\,2}$ are set equal to zero, as these originate from the octupole component of the current density. In the analysis of form factors, one decomposes the measured scattering amplitude as

$$f^o+f^s=f(\overline{j_0}+C_2\overline{j_2}) \tag{33}$$

and uses the resulting value of C_2 to determine μ_L/μ_S, the ratio of orbital and spin moments. The moments being fully determined by the extrapolated values of f^o and f^s at $q=0$,[12] the ratio we are looking for is $a_{1\,0}/b_{1\,0}$ [note that $\overline{j_2}(0)=0$]. However, this does not justify the application of the dipole approximation in the $\overline{j_0}$ vs $\overline{j_2}$ analysis, because it is not possible to isolate the dipole contributions to Eq. (33). In fact, adding up f^o and f^s as given by Eqs. (26) and (29), normalizing the results as in Eq. (33) we find

$$C_2=\frac{(a_{1\,2}+a_{3\,2}+b_{1\,2}+b_{3\,2})}{(a_{1\,0}+b_{1\,0})}, \tag{34}$$

whence

$$\frac{\mu_L}{\mu_S}=\frac{2-g}{2(g-1)}=\frac{a_{1\,0}}{b_{1\,0}}=\frac{C_2-(b_{1\,2}+b_{3\,2})/b_{1\,0}}{(a_{1\,2}+a_{3\,2})/a_{1\,0}-C_2}, \tag{35}$$

which, in its final form, contains the experimentally accessible parameter C_2, and evidently involves coefficients related to the octupole components of both current densities. Here g is the Landé g factor. If we omit from Eq. (35) $a_{3\,2}$, $b_{1\,2}$, and $b_{3\,2}$ and take into account that $a_{1\,2}=a_{1\,0}$ [cf. Eq. (27)], we get the formula used in the customary dipole approximation:[2]

$$\left(\frac{\mu_L}{\mu_S}\right)_d=\frac{C_2}{1-C_2}. \tag{36}$$

Comparing Eqs. (35) and (36), we see that the validity of the latter is doubtful, if $b_{1\,2}+b_{3\,2}$ is not negligible compared to $b_{1\,0}$ or $a_{3\,2}$ is not negligible compared to $a_{1\,0}$. These coefficients are tabulated in Table I for the Russell-Saunders ground states of tripositive rare-earth ions, except Eu^{3+} ($J=0$) and Gd^{3+} ($L=0$). The general impression of these tabulated numbers is not very reassuring concerning the customary procedure: there does not seem to be an order of magnitude difference between the neglected and retained coefficients. We have also listed the coefficients obtained in the customary dipole approximation

$$(C_2)_d=\frac{a_{12}}{a_{10}+b_{10}} \tag{37}$$

TABLE I. The coefficients $a_{1\,0}, a_{1\,2}, \ldots, b_{3\,2}$ of Eqs. (27), (28), and (30)–(32). The common factor $(|\gamma| r_0)$ is omitted. The ratios $(C_2)_d$, $(C_2)_p$, and C_2 are defined by Eqs. (37), (38), and (34), respectively.

Ion	$a_{1\,0}$	$a_{1\,2}$	$a_{3\,2}$	$b_{1\,0}$	$b_{1\,2}$	$b_{3\,2}$	$(C_2)_d$	$(C_2)_p$	C_2
Ce^{3+}	$\frac{10}{7}$	$\frac{10}{7}$	$-\frac{5}{28}$	$-\frac{5}{14}$	$\frac{2}{7}$	$\frac{1}{14}$	$\frac{4}{3}$	$\frac{8}{5}$	$\frac{3}{2}$
Pr^{3+}	$\frac{12}{5}$	$\frac{12}{5}$	0	$-\frac{4}{5}$	$\frac{52}{225}$	$\frac{91}{825}$	$\frac{3}{2}$	$\frac{74}{45}$	$\frac{1357}{792}$
Nd^{3+}	$\frac{63}{22}$	$\frac{63}{22}$	$\frac{294}{1573}$	$-\frac{27}{22}$	$\frac{21}{242}$	$\frac{147}{3146}$	$\frac{7}{4}$	$\frac{119}{66}$	$\frac{1113}{572}$
Pm^{3+}	$\frac{14}{5}$	$\frac{14}{5}$	$\frac{98}{605}$	$-\frac{8}{5}$	$-\frac{14}{165}$	$-\frac{49}{1210}$	$\frac{7}{3}$	$\frac{224}{99}$	$\frac{10297}{4356}$
Sm^{3+}	$\frac{15}{7}$	$\frac{15}{7}$	0	$-\frac{25}{14}$	$-\frac{13}{63}$	$-\frac{13}{252}$	6	$\frac{244}{45}$	$\frac{95}{18}$
Tb^{3+}	$\frac{3}{2}$	$\frac{3}{2}$	$-\frac{1}{4}$	3	$\frac{1}{6}$	$\frac{1}{4}$	$\frac{1}{3}$	$\frac{10}{27}$	$\frac{10}{27}$
Dy^{3+}	$\frac{5}{2}$	$\frac{5}{2}$	0	$\frac{5}{2}$	$\frac{1}{6}$	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{8}{15}$	$\frac{7}{12}$
Ho^{3+}	3	3	$\frac{1}{4}$	2	$\frac{1}{15}$	$\frac{1}{10}$	$\frac{3}{5}$	$\frac{46}{75}$	$\frac{41}{60}$
Er^{3+}	3	3	$\frac{1}{4}$	$\frac{3}{2}$	$-\frac{1}{15}$	$-\frac{1}{10}$	$\frac{2}{3}$	$\frac{88}{135}$	$\frac{37}{54}$
Tm^{3+}	$\frac{5}{2}$	$\frac{5}{2}$	0	1	$-\frac{1}{6}$	$-\frac{1}{4}$	$\frac{5}{7}$	$\frac{2}{3}$	$\frac{25}{42}$
Yb^{3+}	$\frac{3}{2}$	$\frac{3}{2}$	$-\frac{1}{4}$	$\frac{1}{2}$	$-\frac{1}{6}$	$-\frac{1}{4}$	$\frac{3}{4}$	$\frac{2}{3}$	$\frac{5}{12}$

and in the proper dipole approximation

$$(C_2)_p = \frac{a_{12}+b_{12}}{a_{10}+b_{10}}. \tag{38}$$

These data are tabulated by Lander and Brun[11] under ‘‘dipole approx.’’ and c_2/c_1, respectively. Comparison of the last three columns of Table I shows that the terms originating from the octupole component, which are included in C_2 [Eq. (34)], are by no means negligible. In fact, $|C_2-(C_2)_p|$ mostly exceeds $|(C_2)_p-(C_2)_d|$ and sometimes the sign of the two corrections are opposite. Table II enables a more explicit assessment of the approximate method. Here, we tabulated the actual values of μ_L/μ_S and $(\mu_L/\mu_S)_d$ in which the coefficients C_2 of the last column of Table I are used as input parameters into Eq. (36). In other words, the forth column contains the μ_L/μ_S values one would find by applying the customary dipole approximation to C_2 measured on isolated ions with moments given by μ_L/μ_S values of the second column. The difference between the approximate and actual ratios is given in percents of the latter in the last column. It is difficult to find any systematic trend in these errors, but, except for Pm^{3+} and Sm^{3+}, they all fall outside the likely experimental inaccuracy.

Admittedly, the test of Eq. (36) described above is not very realistic, since it is based on a situation, where only a single J manifold is involved. Within such a manifold, the Winger-Eckart theorem ensures that the vectors **J**, **L**, and **S** are proportional and therefore only μ_L/μ_S ratios listed in the third column of Table II can occur. Quenching of the orbital moment, leading to a smaller value of μ_L/μ_S, is only possible, if other states are involved. If these belong to the same L, S manifold, Eqs. (22) and (23) remain valid. A systematic analysis within the proper dipole approximation can be carried out, using the appropriate operator equivalent to calculate the matrix elements appearing in b_{12}.

TABLE II. The actual and approximate values μ_L/μ_S which are calculated using Eqs. (35) and (36), respectively.

Ion	g	$\frac{\mu_L}{\mu_S} = \frac{2-g}{2(g-1)}$	$\left(\frac{\mu_L}{\mu_S}\right)_d$	Error
Ce^{3+}	$\frac{6}{7}$	-4	-3	-25%
Pr^{3+}	$\frac{4}{5}$	-3	$-\frac{1357}{565}$	-20%
Nd^{3+}	$\frac{8}{11}$	$-\frac{7}{3}$	$-\frac{1113}{541}$	-11.8%
Pm^{3+}	$\frac{3}{5}$	$-\frac{7}{4}$	$-\frac{10297}{5941}$	-1%
Sm^{3+}	$\frac{2}{7}$	$-\frac{6}{5}$	$-\frac{95}{77}$	2.8%
Tb^{3+}	$\frac{3}{2}$	$\frac{1}{2}$	$\frac{10}{17}$	17.6%
Dy^{3+}	$\frac{4}{3}$	1	$\frac{7}{5}$	40%
Ho^{3+}	$\frac{5}{4}$	$\frac{3}{2}$	$\frac{41}{19}$	43.9%
Er^{3+}	$\frac{6}{5}$	2	$\frac{37}{17}$	8.8%
Tm^{3+}	$\frac{7}{6}$	$\frac{5}{2}$	$\frac{25}{17}$	-41.2%
Yb^{3+}	$\frac{8}{7}$	3	$\frac{5}{7}$	-76.2%

The operator involved in b_{12} is $W^{(1,2)1}$, the irreducible vector product of a vector operator acting on the spin coordinates and a rank 2 tensor acting on the orbital coordinates. The operator equivalent constructed from the spin and position vectors

$$\mathbf{T}^{(1)} = \sqrt{15}\left[\mathbf{S}^{(1)} \otimes [\mathbf{e}_r^{(1)} \otimes \mathbf{e}_r^{(1)}]^{(2)}\right]^{(1)} \tag{39}$$

is known as the dipolar vector, owing to its form reminiscent of a dipole field

$$\mathbf{T} = \mathbf{S} - 3\mathbf{e}_r(\mathbf{e}_r \cdot \mathbf{S}). \tag{40}$$

Noting that in Cartesian coordinates the quadrupole tensor has the form $Q_{\alpha\beta} = \delta_{\alpha\beta} - 3r_\alpha r_\beta / r^2$, we can write a component of **T** in the transparent form $T_\alpha = \Sigma_\beta Q_{\alpha\beta} S_\beta$. The operator $W^{(1,2)1}$ is thus seen to represent the coupling of the quadrupole moment of the charge distribution to the spin moment. The emergence of the spin-orbit coupling is clearly reflected in another operator equivalent[13] of $W^{(1,2)1}$,

$$[\mathbf{S}^{(1)} \otimes [\mathbf{L}^{(1)} \otimes \mathbf{L}^{(1)}]^{(2)}]^{(1)} = \frac{1}{\sqrt{15}}\left\{ L(L+1)\mathbf{S} - \frac{3}{2}[\mathbf{L}(\mathbf{S}\cdot\mathbf{L}) + (\mathbf{S}\cdot\mathbf{L})\mathbf{L}] \right\}. \tag{41}$$

In general, $W^{(1,\mathcal{L}')\mathcal{L}}$ involves the rank $\mathcal{L}'$ pole of the charge distribution, which immediately explains why the form factor of Gd^{3+} (an S-state ion with a spherical charge distribution) is strictly proportional to $\overline{j_0}$.[14] The very successful analysis of the Gd data[15] in these terms may have given some credence to the customary dipole approximation, which implies that the spin contribution to $f(\mathbf{q})$ is *always* proportional to $\overline{j_0}$. However, this is not the case, not even if the orbital moment is fully quenched. To realize this, consider a strong crystal field, which breaks up the spin-orbit coupling, but does not lead to significant admixture of states outside a given L,S manifold. Clearly, all superpositions of states within this manifold will be eigenstates of $\mathbf{L}^2$, with the same eigenvalue $\hbar^2 L(L+1)$, whereas in some states, including perhaps the crystal-field ground state, the orbital moment may be completely quenched, i.e., $\langle \mathbf{L} \rangle = 0$. The charge density in such a state is of course not spherically symmetric. On the contrary, it is well adjusted to the symmetry of the crystal field, so that the crystal-field energy is minimized.

To illustrate this point, we have carried out a calculation for a hypothetical crystal-field state of an f^2 shell (appropriate to Pr^{3+} or U^{4+}). Assuming that a cubic crystal field dominates the spin-orbit coupling, we neglected the latter entirely and considered one of the Γ_3 states of the $L=5$ multiplet,[16] $|\Gamma_{3,1}\rangle = (|+4\rangle - |-4\rangle)/\sqrt{2}$. The Γ_3 state is a nonmagnetic doublet, in which the orbital angular momentum is fully quenched; $|\Gamma_{3,2}\rangle = (|+2\rangle - |-2\rangle)/\sqrt{2}$, so that $\langle \mathbf{L} \rangle = 0$ and $\mu_L = 0$ for any linear combination of $|\Gamma_{3,1}\rangle$ and $|\Gamma_{3,2}\rangle$. It is also evident that $f^{o\Gamma_{3,1}}_{\Gamma_{3,1}} = 0$, because $\langle +4 | W_0^{(0,\mathcal{L})\mathcal{L}} | +4 \rangle = -\langle -4 | W^{(0,\mathcal{L})\mathcal{L}} | -4 \rangle$ ($\mathcal{L}$ is odd) and $\langle +4 | W_{\mathcal{M}}^{(0,\mathcal{L})\mathcal{L}} | -4 \rangle = 0$, as $\mathcal{M}$ cannot exceed 5 [$\mathcal{L} \leqslant 2l-1$, cf. Eq. (16)]. We have calculated the scattering amplitude $f^s(\mathbf{q})$ for $\mathbf{q}$ in the plane perpendicular to the direction in which the $S=1$ spin moment and a fourfold axis of the crystal are aligned. The outcome is that the $\overline{j_2}$ term is not negligible, $C_2 = 0.112$. Applying Eq. (36) to this result gives $\mu_L/\mu_S = 0.126$, meaning that if such an ion existed and a careful form-factor measurement would be analyzed in the customary way, one would conclude that the orbital moment exceeds 10% of the spin moment and the coupling between them is contrary to Hund's third rule, which would require $\mu_L/\mu_S < 0$ for f^2. In view of what was said in connection with Eqs. (40) and (41), it may seem odd that we found $C_2 \neq 0$, even though the spin-orbit coupling was neglected. The correlation between the orientation of the spin magnetic moment and the electric quadrupole moment is not a consequence of a direct coupling in this case. Instead, both are oriented by external agents: the magnetic moment by the magnetic field and the quadrupole moment by the crystal lattice, which is supposed to be clamped in a sample holder.

A strong crystal field, which breaks the spin-orbit coupling and totally quenches the orbital moment can thus lead to a scattering amplitude with the signature taken to be characteristic of orbital scattering in the customary dipole approximation. This mechanism of quenching offers itself to the description in terms of localized states used in the present paper, but it is not likely to be of importance in rare earths (except samarium[17]) or in actinides.

The orbital moment of the $5f$ shell in the latter case is reduced by hybridization, that is, a superposition of $5f^n$ and $5f^{n-1}6d$ configurations. However, as mentioned in the Introduction, the delocalized nature of the $6d$ states makes the relevance of free-atom models doubtful. An approach[18] that treats the delocalized states properly within the density-functional formalism and introduces intra-atomic correlations separately seems the only way out.

ACKNOWLEDGMENTS

We are thankful to J. E. Hansen, B. R. Judd, E. Frikkee, and T. J. Hicks for valuable discussions. K.A. gratefully acknowledges the full financial support of the ''Steunfonds Soedanese Studenten,'' Leiden, which enabled him to work at the Van der Waal–Zeeman Institute.

APPENDIX

The contribution of the orbital current density (5) to the scattering amplitude (14) can be found by rewriting the spherical harmonics $\mathbf{Y}^{\mathcal{L}}_{\mathcal{L}-\mathcal{M}}$ of Eq. (5) in terms of their complex conjugates with the aid of the identity

$$\mathbf{Y}^{L}_{JM}{}^{*} = (-1)^{J+L+M+1}\mathbf{Y}^{L}_{J-M} \tag{A1}$$

substituting the matrix elements (5) in Eq. (14), expanding $e^{i\mathbf{q}\cdot\mathbf{r}}$ with the identity

$$\mathbb{1}e^{i\mathbf{q}\cdot\mathbf{r}} = 4\pi \sum_{JLM} i^L j_L(qr)\mathbf{Y}^{L}_{JM}{}^{*}(\mathbf{e}_q) \otimes \mathbf{Y}^{L}_{JM}(\mathbf{e}_r), \tag{A2}$$

where $j_L(qr)$ is a spherical Bessel function, and using the orthogonality of the vector spherical harmonics

$$\int \mathbf{Y}^{L'}_{J'M'}{}^{*}(\mathbf{e}_r) \cdot \mathbf{Y}^{L}_{JM}(\mathbf{e}_r) d\Omega = \delta_{J'J}\delta_{L'L}\delta_{M'M}. \tag{A3}$$

We find

$$\begin{aligned} f^{o\,\theta J M_J}_{\;\theta' J' M_{J'}}(\mathbf{q}) = 2\sqrt{2}|\gamma| r_0 \boldsymbol{\sigma} \cdot \sum_{\mathcal{L}} i^{\mathcal{L}} \Bigg\{ & (-1)^{l+\mathcal{L}}(2l+1) \\ & \times \sqrt{\frac{(2l+\mathcal{L}+2)(2l-\mathcal{L}+1)}{4\pi}} \\ & \times \begin{pmatrix} l & \mathcal{L} & l+1 \\ 0 & 0 & 0 \end{pmatrix} \Bigg\} \langle \theta J M_J | W^{(0,\mathcal{L})\mathcal{L}}_{\mathcal{M}} | \theta' J' M_{J'} \rangle \\ & \times [\mathbf{e}_q \times \mathbf{Y}^{\mathcal{L}}_{\mathcal{L}\mathcal{M}}{}^{*}(\mathbf{e}_q)] \int \left(\frac{1}{qr}\right) j_{\mathcal{L}}(qr) R^2_{nl} r^2 dr. \end{aligned} \tag{A4}$$

The quantity in the curly bracket has to be transformed with the aid of

$$\begin{pmatrix} l & \mathcal{L} & l+1 \\ 0 & 0 & 0 \end{pmatrix} = (-1)^{\mathcal{L}+1} \begin{pmatrix} l & \mathcal{L}+1 & l \\ 0 & 0 & 0 \end{pmatrix} \times \sqrt{\frac{(\mathcal{L}+1)(2l-\mathcal{L})}{\mathcal{L}(2l-\mathcal{L}+1)}} \tag{A5}$$

and

$$\begin{Bmatrix} \mathcal{L}+1 & 1 & \mathcal{L} \\ l & l & l \end{Bmatrix} = (-1)^{\mathcal{L}} \times \frac{1}{2} \sqrt{\frac{(2l+\mathcal{L}+2)(2l-\mathcal{L})(\mathcal{L}+1)}{l(2l+1)(l+1)(2\mathcal{L}+1)(2\mathcal{L}+3)}} \tag{A6}$$

to recover the expression given by Stassis and Deckman [cf. Eq. (59) of Ref. 7].

To find the contribution of the spin current density (9) to the scattering amplitude (13), it is convenient to deal directly with the spin density (6), using

$$\begin{aligned}\int e^{i\mathbf{q}\cdot\mathbf{r}}\langle\theta JMJ|\hat{\mathbf{j}}^{s}(\mathbf{r})|\theta' J' M_{J'}\rangle dV &= \int e^{i\mathbf{q}\cdot\mathbf{r}}\boldsymbol{\nabla}\times\langle\theta JM_{J}|\hat{\boldsymbol{\sigma}}(\mathbf{r})|\theta' J' M_{J}'\rangle dV\\ &= -i\mathbf{q}\times\int e^{i\mathbf{q}\cdot\mathbf{r}}\langle\theta JM_{J}|\hat{\boldsymbol{\sigma}}(\mathbf{r})|\theta' J' M_{J'}\rangle dV, \qquad \text{(A7)}\end{aligned}$$

which relates the Fourier transform of the spin current density with that of the spin density. The Fourier transform $\int e^{i\mathbf{q}\cdot\mathbf{r}}\langle\theta JM_{J}|\hat{\boldsymbol{\sigma}}(\mathbf{r})|\theta' J' M_{J'}\rangle dV$ of the spin density (6) can be easily evaluated, if one makes use of Eqs. (A2) and (A3). Equation (A7) then requires the vector products $\mathbf{e}_{q}\times\mathbf{Y}^{\mathcal{L}'\pm 1}_{\mathcal{L}'0}$, for which we use

$$\mathbf{e}_{q}\times\mathbf{Y}^{\mathcal{L}}_{\mathcal{L}'\mathcal{M}}(\mathbf{e}_{q}) = i(-1)^{\mathcal{L}}(2[\mathcal{L}])^{1/2}\begin{pmatrix}\mathcal{L} & 1 & \mathcal{L}'\\ 0 & 1 & -1\end{pmatrix}\mathbf{Y}^{\mathcal{L}'}_{\mathcal{L}'\mathcal{M}},$$

which can be easily verified for $\mathcal{L}\neq\mathcal{L}'$. Collecting terms and substituting into Eq. (13) we again recover the result of Stassis and Deckman.[7]

---

[1] S. Legvold, in *Ferromagnetic Materials*, edited by E. P. Wohlfarth (North-Holland, Amsterdam, 1980), Vol. 1, pp. 185–190.

[2] G. H. Lander, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, L. Eyring, G. H. Lander, and G. R. Choppin, (North-Holland, Amsterdam, 1993), Vol. 17 p. 662.

[3] E. Balcar, J. Phys. C **8**, 1581 (1975).

[4] L. L. Hirst, Rev. Mod. Phys. **69**, 607 (1997).

[5] P. F. de Châtel and K. Ayuel, Physica B **266**, 256 (1999).

[6] G. T. Trammell, Phys. Rev. **92**, 1387 (1953).

[7] C. Stassis and H. W. Deckman, Phys. Rev. B **12**, 1885 (1975).

[8] D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskii, *Quantum Theory of Angular Momentum* (World Scientific, Singapore, 1988), pp. 208–234.

[9] Karlo Ayuel Kuacgor, Ph.D. thesis, University of Amsterdam, 2000.

[10] C. Stassis and H. W. Deckman, J. Phys. C **9**, 2241 (1976).

[11] G. H. Lander and T. O. Brun, J. Chem. Phys. **53**, 1387 (1970).

[12] G. H. Lander and M. S. S. Brooks, Phys. Rev. B **43**, 13 672 (1991).

[13] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970), pp. 692–693.

[14] R. M. Moon, W. C. Koehler, J. Cable, and H. R. Child, Phys. Rev. B **5**, 997 (1972).

[15] R. M. Moon and W. C. Koehler, Phys. Rev. B **11**, 1609 (1975).

[16] K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids **23**, 1381 (1962).

[17] H. W. de Wijn, A. M. van Diepen, and K. H. J. Buschow, Phys. Status Solidi B **76**, 11 (1976).

[18] O. Eriksson, M. S. S. Brooks, and B. Johansson, Phys. Rev. B **41**, 9087 (1990).