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Hyperfine magnetic fields of Nd trivalent ions in $NdGaO_3$ tetragonal Perovskite

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Abstract

A new formulation based on fractional parentage method is developed in order to account for orbital and spin current densities of rare earth (RE) *f*-electron shells as well as the consequently resulting magnetic hyperfine field (HMF). We have derived multipole expansions of spin and orbital current densities in terms of vector spherical harmonics. Orbital and spin contributions to HMF were subsequently calculated for ground states of Nd^{3+} free ion and Nd^{3+} ion subjected to hypothetical octahedral crystal fields (CF). The validity of the model was tested through calculating the HMF's of Nd^{3+} atoms in $NdGaO_3$ tetragonal perovskite crystal, where, the results obtained for total HMF therein were in good agreement with result obtained using DFT based ab initio approach.

Key Words: Magnetic hyperfine field, orbital current density, spin current density

1. Introduction

Hyperfine fields represent one of the most important aspects that has been subjected to intensive investigation for many decades, as they provide an effective tool to probe the nuclear environment and obtain important information about the properties of the atom and ion.

Multipole formulation hyperfine electric and magnetic field in terms of spherical tensors has been a powerful method that allows calculations of magnetic properties for different practical case and a subject of theoretical interests for researchers, as an example for studies where this technique is implemented is the investigation carried out by Kusunose [1] where the author could obtain multipole expressions for electric and magnetic field of *f*-electron shells of RE ions in terms of vector spherical harmonics. To calculate matrix elements, the author has employed expansions of fields in terms of stevens' operator equivalents. Starting from multipolar formulation of atomic current densities, Ayuel and Zakaria [2] have proposed a scheme to estimate atomic current densities and their contribution to magnetic fields of transitional metal ions at the nucleus sites. The formulae obtained therein were applied to free Fe^{2+} ion and Fe^{2+} ion in FeF_2 compound. The results obtained for free ion case were in good agreement with the those of FeF_2 and well agreed with pervious experimental findings for effective atomic radius of Fe^{2+} ion ~ 3.0 a. u. Lalić et. al. [3] have used first-principles full potential linearized augmented plane-wave approximation to determine the orbital and spin contributions to HMF of Ce^{3+} in $CeIn_3$ compounds. Calculated values of hyperfine fields in Ce^{3+} and In^- are in good agreement with experimental measurements at low temperature and HMF at Ce site are dominated by *4f*-orbital contribution. The appearance of small HMF at In site is attributed to spin polarization of In *5p*-electron resulting from hybridization with valence electrons of Ce.

In order to understand the magnetic properties of RE ions, extensive experimental and theoretical research effort have been put on the effects of CF on the ground states of *4f*-electronic shell in RE ion, albeit, a systematic formalism to account for CF effect on HMF, in particular, is so far needed.

Since the Hyperfine structure results from interaction between electronic and nuclear magnetic fields, most important magnetic fields are due to electrons in the partially filled $3d$ or $4f$-electron shells. Due to complete or partial quenching of the Russel-Saunders's ground state in addition to electron state hybridization, the $3d$ orbital magnetic moments are negligible so that $3d$ -electrons exhibit mostly spin magnetic moments. On the other hand, $4f$-electrons of RE elements are localized withing the atomic core so that it is important to consider both orbital and spin magnetic fields when studying magnetic hyperfine structures of RE atoms [4]. Neglecting other effect influencing hyperfine structure of RE nuclei such as Fermi contact which is the term due to polarization of core electrons, we can express the magnetic field $\boldsymbol{B}_{4f}$ at the nucleus site as [5]:

$$\boldsymbol{B}_{4f} = \frac{-2\mu_0\mu_B}{4\pi}\langle J\|N\|J\rangle\langle r^{-3}\rangle J \qquad (1)$$

Where J and r is are respectively the total angular momentum and radial coordinate of *f*-electron, μ_0 is the magnetic permeability of free space and μ_B stands for Bohr magneton. The symbol $\boldsymbol{N}$ is defined by the following expression :

$$\boldsymbol{N} = \sum \left(\boldsymbol{l}_i - \boldsymbol{s}_i + 3\frac{(\boldsymbol{r}_i \cdot \boldsymbol{s}_i)\boldsymbol{r}_i}{r_i^2} \right) \qquad (2)$$

where $\boldsymbol{l}_i$, $\boldsymbol{s}_i$ and $\boldsymbol{r}_i$ are the orbital angular momentum, spin angular momentum and position of *4f*-electron, respectively. The case of free RE tri-positive ion was effectively addressed utilizing the aforementioned approach [5], nevertheless, calculation of magnetic fields of $4f$-electron in RE electron subjected to crystalline environment requires a thorough treatment. However, the tensor operator formalism has been successfully used as a powerful tool for calculating magnetic current densities and is therefore expected to render equally successful results for HMF due to atomic electron currents.

In the current study, we aim at employing a tensor operator-based formalism to develop general expressions and conduct calculations for HMF for free RE ion as well as RE ions subjected to a hypothetically octahedral CF. The validity and accuracy of the new approach is tested by finally applying it to practical cases of RE containing tetragonal perovskites.

The remainder of this paper is organized as follows: In Section 2., a complete account of atomic current densities, magnetic fields and HMF's is given, where formulation in terms of vector spherical harmonics is demonstrated. Section 3., contains the results of applications of the developed formalism to estimate HMF's for some particular eigenstates of tripositive RE free ion and ions subjected to octahedral CF's. Section 3. is concluded by application of the method to calculated the current densities and HMF's of Nd^{3+} ions in $NdGaO_3$ tetragonal perovskite. In section 4., the conclusion drawn on the validity and limitation of the suggested model are briefly presented.

2. Method and Formulation:

An appropriate method for representing multipoles mathematically is three-dimensional Cartesian tensors of increasing rank, where monopoles (scalars) are represented by zeroth-rank tensors while dipoles (vectors) are represented by tensors of rank 1 and quadrupoles by tensors of rank 2 e.t.c. [6]. The transformation behavior of each of these quantities is determined by its tensor nature, even though the frame of reference varies depending on the application. The multipole expansion of scalar functions frequently starts with spherical harmonics as a foundation. The Clebsch-Gordan expansion incorporates the spherical harmonics' most valuable characteristic, that is [8].

$$Y_{lm}(\theta,\emptyset)Y_{l`m`}(\theta,\emptyset) = \sum_{kq}\sqrt{\frac{(2l+1)(2l`+1)}{4\pi(2k+1)}}\,C^{k0}_{l0l`0}C^{kq}_{lml`m`}\,Y_{lm}(\theta,\emptyset) \tag{3}$$

Where the $(2l+1)$ spherical harmonics of degree l provide the basis for the representation of the rotation group of order $(2l+1)$. This method also ensures that the derivatives of $Y_{lm}(\theta,\emptyset)$ with respect to the angular variables gives a linear combination of spherical harmonics of the same degree l, so that there is a finite number of terms in the expansion of the product of two spherical harmonics which satisfy some selection rules. The triangle rule is one of the selection rules included in the Clebsch-Gordan coefficients $C^{kq}_{lml`m`}$, This says that, it must be possible to create a triangle with sides of length l , $l`$ and $k$ otherwise $C^{kq}_{lml`m`} = 0$. Utilizing such properties has allowed feasible representation and subsequently easy calculation of scalars such as electronic charge density and resulting potentials. However, similar forms for vector can analogously be obtained in terms of vector spherical harmonics.

Therefore, to examine the atomic currents and magnetic fields we have made extensive use of the concept of vector spherical harmonics, where we follow definitions 's and notations proposed by Varshalovich et. al. [7].

2.1 Multiple Expansion of The Orbital Current Density

we'll use the more elegant formalism proposed by Ayuel [8], which is based on tensor operator formalism and Racah algebra, since this formalism allows for a more powerful analytical tool when dealing with tensor operators of order 1 (vectors such as current densities and magnetic field) which are frequently encountered when magnetic vector potential, atomic magnetization, and other aspects of atomic magnetism are studied. The procedure ensues breaking down the current density into components with different transformation properties. We begin by defining the atomic orbital current density $\hat{\mathbf{J}}^{o}(\mathbf{r})$, which is defined in the non-relativistic limit of the Dirac equation in the absence of an external field as [5].

$$\hat{\boldsymbol{J}}^{o}(\boldsymbol{r}) = \frac{-e}{2m_e}[\delta(\boldsymbol{r}´-\boldsymbol{r})\hat{P} + \hat{P}\,\delta(\hat{\boldsymbol{r}}-\boldsymbol{r})] \tag{4}$$

Expanding the Dirac δ function $\delta(\boldsymbol{r}´-\boldsymbol{r})$ in terms of spherical harmonics we have [9]

$$\delta(\hat{\boldsymbol{r}} - \boldsymbol{r}) = \frac{1}{\acute{r}^2}\ \delta(\acute{r} - r)\sum_{l\,m} Y_m^l(\theta,\phi)Y_m^l(\acute{\theta},\acute{\phi}) \tag{5}$$

we get

$$\hat{\boldsymbol{j}}^o(\boldsymbol{r}) = \frac{-e}{2m_e\,r^2}\sum_{kq}[\,\delta(r'- r)\hat{Y}_q^k(\hat{e}_{\acute{r}})\widehat{\boldsymbol{P}} + \widehat{\boldsymbol{P}}\delta(\acute{r} - r)\ \hat{Y}_q^k(\hat{e}_{\acute{r}})]Y_q^{k^*}(\hat{e}_r) \tag{6}$$

where the operator $\hat{P}$ is defined by:

$$\widehat{\boldsymbol{P}} = -i\hbar[\hat{\boldsymbol{e}}_{\acute{r}}\frac{\partial}{\partial\dot{r}} + \frac{1}{\acute{r}}\widehat{\boldsymbol{\nabla}}_{\acute{\Omega}}] \tag{7}$$

And $\widehat{\boldsymbol{\nabla}}_{\acute{\Omega}}$ is the angular part of the $\widehat{\boldsymbol{\nabla}}_{\Omega}$ operator defined as follows

$$\widehat{\boldsymbol{\nabla}}_{\acute{\Omega}} = \frac{\partial}{\partial\acute{\theta}}\hat{\boldsymbol{e}}_{\acute{\theta}} + \frac{1}{sin\,\acute{}}\frac{\partial}{\partial\acute{\phi}}\hat{\boldsymbol{e}}_{\acute{\phi}} \tag{8}$$

The angular components of $\hat{\mathbf{J}}^{\mathrm{o}}$ will therefore be represented by rank k tensors $\hat{Y}^{(k)}$ and vectors $\hat{\mathrm{e}}_{\mathrm{r}}$ and $\widehat{\boldsymbol{\nabla}}_{\acute{\Omega}}$, which are actually rank 1 tensors. Recognizing the fact that $\hat{\mathbf{J}}^{\mathrm{o}}$ operator is independent of spin (ie it doesn't act on the spin space), then its matrix element between single electron eigenstates $|nlsm_lm_s\rangle$ and $|\acute{n}\acute{l}\acute{s}\acute{m}_l\acute{m}_s\rangle$ can be written [7]

$$\langle nlsm_lm_s|\hat{\boldsymbol{j}}^o(r)|\acute{n}\acute{l}\acute{s}\acute{m}_l\acute{m}_s\rangle = \frac{i\hbar e}{2m_e}\sum_{Kq}\left\{\left(R_{nl}\frac{dR_{\acute{n}\,\acute{l}}}{dr} - \frac{dR_{n\,l}}{dr}\ R_{\acute{n}\,\acute{l}}\right)\times\langle lm_l|\hat{e}_{\acute{r}}Y_q^k|\acute{l}\acute{m}_l\rangle + \right.$$
$$\left.\frac{R_{n\,l}R_{\acute{n}\,\acute{l}}}{r}\langle lm_l|\left(2\hat{e} + \hat{\nabla}_{\acute{\Omega}}\right)Y_q^k + Y_q^k\nabla_{\acute{\Omega}}|\acute{l}\acute{m}_l\rangle\right\}Y_q^{k^*} \tag{9}$$

In equation (8), the single electron eigen states are approximated by a Hydrogen-like wave function $|nlsm_lm_s\rangle = R_{nl}(r)Y_m^l(\theta,\phi)\left|\frac{1}{2}\ m_s\right\rangle$ where separation of radial, angular and spin part of the electron wave function is guaranteed and $R_{nl}(r)$ is radial part of the wave function.

The direct product of two tensor operators is defined as the spherical tensor $\hat{X}^k$ with $(2k_1 + 1)(2k_2 + 1)$ components$\hat{X}_Q^{(K)}$. So that, with $k_2 = 1$ and hence $\mu = 0, \pm 1$, $\hat{X}_Q^K$ is defined according to the relation:

$$T_q^kT_\mu^1 = \sum_{k=k-1}^{k+1}\langle q\mu|k1KQ\rangle\hat{X}_Q^K \tag{10}$$

The general formula (10) is used to extend the tensor products of tensors encountered in equation (9), while the products of opposite order are pulled together using the symmetry features of the Clebsch-Gordan coefficients depicted in the corresponding 3-j symbols [7]. Making appropriate substitution of the components of vector spherical harmonics as defined in terms of spherical harmonics and the Clebsch-Gordan coefficients [10] and using the Wigner-Eckart theorem [11], the matrix elements of the μ-th component orbital current density between two single electron eigenstates may then be written in the multipole form

$$\langle nlsm_l m_s|\hat{\boldsymbol{j}}^o(r)_\mu|\acute{n}\acute{l}\acute{s}\acute{m}_l\acute{m}_s\rangle = (-1)^{m_l-\acute{m}_l}\, i\mu_B \sum_{k\acute{k}}\Big\{\Big(R_{nl}\frac{dR_{\acute{n}\,\acute{l}}}{dr}-\frac{dR_{n\,l}}{dr}\,R_{\acute{n}\,\acute{l}}\Big)\times \langle l||[\,(\hat{e}_{\acute{r}})^{(1)}\otimes\hat{Y}^{(k)}\,]^{(\acute{k})}||\acute{l}\rangle + \frac{R_{n\,l}R_{\acute{n}\,\acute{l}}}{r}\Big[\langle l||[\,(-2\hat{e}_{\acute{r}}+\hat{\nabla}_{\acute{\Omega}})^{(1)}\otimes\hat{Y}^{(k)}]^{(\acute{k})}||\acute{l}\rangle + (-1)^{\acute{k}-k-1}\Big\langle l\Big|\Big|\hat{Y}^{(k)}\otimes\big(\hat{\nabla}_{\acute{\Omega}}\big)^{(1)}\,]^{(\acute{k})}\Big|\Big|\acute{l}\Big\rangle\,\Big]\Big\}\frac{\langle\acute{l}\acute{k}\acute{m}_l m_l-\acute{m}_l\,|\acute{l}\acute{k}lm_l\rangle}{\sqrt{2l+1}}[Y^{k}_{\acute{k}\,\acute{m}_l-m_l}]_\mu \tag{11}$$

The orbital current density is then expressed in terms of these multipolar components as follows

$$\hat{\boldsymbol{J}}^o(\boldsymbol{r}) = \mu_B\sum_{k\acute{k}\acute{q}}(-1)^{\acute{q}}(\hat{j}^o)^{(\acute{k})}_{\acute{q}}(k)Y^k_{k-\acute{q}}(\hat{e}_r) \tag{12}$$

where $(\hat{\boldsymbol{j}}^o)^{(\acute{k})}_{\acute{q}}(k)$ are the multipolar components of the orbital current density. The problem then reduces to obtaining an expression for the matrix elements of these components between two eigenstates of a single electors and then to obtain a generalized expression for the case of *n*-electron shell.

Substituting the reduced matrix elements of vectors $\hat{e}_r$, $\hat{\boldsymbol{\nabla}}_\Omega$ and $\hat{Y}^k$ as given respectively by equations (A. 46), (A.47) and (A.48) of reference [16], the reduced matrix element $\Big\langle nl\Big|\Big|(\hat{\boldsymbol{j}}^o)^{(\acute{k})}_{\acute{q}}(k)\Big|\Big|\acute{n}\acute{l}\Big\rangle$ can be expressed as

$$\Big\langle nl\Big|\Big|(\hat{\boldsymbol{j}}^o)^{(\acute{k})}_{\acute{q}}(k)\Big|\Big|\acute{n}\acute{l}\Big\rangle = (-1)^{l+1+\acute{k}-k}\frac{i}{\sqrt{4\pi}}\Big[[\acute{k},k,\acute{l}]^{\frac{1}{2}}[D^{+}_{l,\acute{l};k,\acute{k}}-D^{-}_{l,\acute{l};k,\acute{k}}]\times\Big(R_{nl}\frac{dR_{\acute{n}\acute{l}}}{dr}-\frac{dR_{nl}}{dr}R_{\acute{n}\acute{l}}\Big)+\frac{R_{nl}R_{\acute{n}\acute{l}}}{r}\Big\{[\acute{k},k,\acute{l}]^{\frac{1}{2}}[lD^{+}_{l,\acute{l};k,\acute{k}}+(l+1)D^{-}_{l,\acute{l};k,\acute{k}}]+(-1)^{\acute{l}-l-\acute{k}-1}[\acute{k},k,l]^{\frac{1}{2}}[\acute{l}D^{+}_{l,\acute{l};k,\acute{k}}+(\acute{l}+1)D^{-}_{l,\acute{l};k,\acute{k}}]\Big\}\Big] \tag{13}$$

Where

$$D^{\pm}_{l,\acute{l};k,\acute{k}} = \sqrt{\tfrac{1}{2}(2l+1\pm1)(2l+1\pm2)}\begin{Bmatrix} k & \acute{k} & 1\\ l & l\pm1 & \acute{l}\end{Bmatrix}\begin{pmatrix}\acute{l} & k & l\pm1\\ 0 & 0 & 0\end{pmatrix} \tag{14}$$

Substituting the explicit expression for the 6-j symbol and making use of the recursion relation (2.23) of reference [12] for the 3-j symbols in equation (14) we have for the case $k = \acute{k}$

$$\langle nl||(\boldsymbol{j}^o)^{(\acute{k})}(k)||\acute{n}\acute{l}\rangle = (-1)^{\acute{l}}\frac{i}{2\sqrt{4\pi}}\frac{R_{nl}R_{\acute{n}\acute{l}}}{r}\times\Big[\frac{(2\acute{k}+1)(2l+1)(2\acute{l}+1)(\acute{l}+l+\acute{k}+1)(\acute{l}+l-1)}{\acute{k}(\acute{k}+1)}\Big]^{\frac{1}{2}}\times\Big\{[(\acute{l}-l+\acute{k}+1)(l-\acute{l}+\acute{k})]^{\frac{1}{2}}\begin{pmatrix}\acute{l} & \acute{k} & l-1\\ 0 & 0 & 0\end{pmatrix}+[(l-\acute{l}+\acute{k}+1)(\acute{l}-l+\acute{k})]^{\frac{1}{2}}\begin{pmatrix}l & \acute{k} & \acute{l}-1\\ 0 & 0 & 0\end{pmatrix}\Big\} \tag{15}$$

It is straight forward to obtain similar for the two important cases $k = \acute{k} + 1$ and $k = \acute{k} - 1$

In the case of diagonal matrix elements (i.e. $\acute{n} = n$ and $\acute{l} = l$ the none diagonal matrix elements of equations. (13) and (15) will vanish, so that within an (*n, l*) manifold, the multipole expansion of orbital current density involves only the $\acute{k} = k$ term i. e.

$$\hat{\boldsymbol{J}}^{o}(\boldsymbol{r}) = \mu_B \sum_{k=1,3,..} \sum_{q} (-1)^{q} \, (\hat{J}^{o})_{q}^{(k)} Y_{k-q}^{k} \tag{16}$$

The reduced matrix element $\langle nl \| (\hat{J}^{0})^{k} \| \acute{n}\acute{l} \rangle$ is given by [13]

$$\langle nl \| (\hat{\boldsymbol{J}}^{0})^{k} \| \acute{n}\acute{l} \rangle = (-1)^{l} \imath (2l+1) [k]^{\frac{1}{2}} \sqrt{\frac{(2l+k+1)(2l-k)}{4\pi}} \times \frac{R_{nl}^{2}}{r} \begin{pmatrix} l & k & l-1 \\ 0 & 0 & 0 \end{pmatrix} \tag{17}$$

The above form for orbital current density can be generalized to the case of n-electrons by summing the over electron using Racah single particle fractional parentage method [12], For a system n-electrons we can sum up such a single particle operator $\hat{\mathbf{f}}$ to form the *N*-particle operator $\hat{\boldsymbol{F}}^{N-electron} = \sum_{i}^{n} \hat{\boldsymbol{f}}(i)$

So that, by using the expression for the reduced matrix element of the Racah unit double tensor operator $W^{(k_1,k_2)K}$ for the outer product of two tensor of orders k_1 and k_2 as defined by equation (47) of reference [12]. The orbital current density for ground state of n-electron system can now be evaluated according to the formula

$$\hat{\boldsymbol{J}}^{o\,n-electron} = \sqrt{2}\mu_B \sum_{k\acute{k}\acute{q}} (-1)^{\acute{q}} [K]^{\frac{1}{2}} \langle nl \| (\hat{J}^{0})^{k} \| \acute{n}\acute{l} \rangle \langle \theta J \| W^{(0,k)k} \| \acute{\theta}\acute{J} \rangle \, Y_{\acute{k}\,-\acute{q}}^{k}(\hat{e}_{r}) \tag{18}$$

In equation (18) the definition of a single electron reduced matrix element of a tensor operator of rank 0 in the spin space is recognized as $\langle s \| \hat{\mathbf{1}}^{(0)} \| s \rangle = \sqrt{2s+1}$ [14].

2.2 Multipole expansion of spin current density

The relation between the spin current density operator $(\hat{\boldsymbol{J}}^{s})$and the spin density operator $\hat{\mathbf{s}}(\mathbf{r})$ is [10]

$$\langle \Psi | \hat{\boldsymbol{J}}^{s} | \acute{\Psi} \rangle = -\mu_B \nabla \times \langle \Psi | \delta(\hat{\boldsymbol{r}} - \boldsymbol{r}) | \acute{\Psi} \rangle = \nabla \times \langle \Psi | \hat{\boldsymbol{s}}(\boldsymbol{r}) | \acute{\Psi} \rangle \tag{19}$$

where $\hat{\mathbf{s}}(\boldsymbol{r})$ is the single electron spin density operator. We start by witting the spin density operator in terms of multipole expansion in order to generate a multipole form for the spin current density operator. For a single electron, we can express the spin density operator in terms of the Pauli spin matrices $\hat{\boldsymbol{\sigma}}$ as follows [14]

$$\hat{\boldsymbol{s}}(\boldsymbol{r}) = \mu_B \, \delta(\acute{\boldsymbol{r}} - \boldsymbol{r}) \hat{\sigma} \tag{20}$$

The first step is to expand the Dirac δ-function in terms of spherical harmonics according to equation (5), the spin density operator may hence be rewritten in the form

$$\hat{\boldsymbol{s}}(\boldsymbol{r}) = \frac{-\mu_B}{r^2}\delta(\acute{r}-r)\sum_{kq}[\hat{Y}_q^k(\hat{e}_{\acute{r}})\hat{\boldsymbol{\sigma}}]Y_q^{k^*}(\hat{e}_r) \tag{21}$$

Being a spherical tensor of rank 1, $\hat{\boldsymbol{s}}(\boldsymbol{r})$ can hence be repressed in component form

$$\hat{\boldsymbol{s}}_\mu^{(1)}(\boldsymbol{r}) = \frac{-\mu_B}{r^2}\delta(\acute{r}-r)\sum_{kq}[\hat{Y}_q^k(\hat{e}_{\acute{r}})\hat{\boldsymbol{\sigma}}_\mu]Y_q^{k^*}(\hat{e}_r) \tag{22}$$

Once again, we make use of component form (5) of the vector spherical harmonics $\mathrm{Y}_{\acute{k}-\acute{q}}^{k}$ so that, for the particle designated by $(\imath)$, equation (22) can be reformed as follows:

$$\hat{\boldsymbol{s}}(\imath) = \frac{\mu_B}{r^2}\delta(r_\imath - r)\sum_{k\acute{k}\acute{q}}(-1)^{k-\acute{k}+\acute{q}}[\hat{Y}^{(k)}(\imath)\otimes\hat{\sigma}^{(1)}(\imath)]_{\acute{q}}^{(\acute{k})}Y_{\acute{k}-\acute{q}}^{k} \tag{23}$$

The reduced matrix element of the spin density operator $\hat{\mathbf{s}}$ between tow spin-orbit coupled eigenstates can now be deduced using reduced matrix elements already described for $\hat{e}_r$, $\hat{\boldsymbol{\nabla}}_\Omega$ and $\hat{Y}^k$ together with the fact that for a single electron, $\acute{s} = s = \frac{1}{2}$. Therefore, $\left\langle\frac{1}{2}\middle\|\left|(\hat{s})^1\right|\middle\|\frac{1}{2}\right\rangle = \sqrt{6}$, hence, the reduced matrix element of the spin density operator between two single electron eigenstates is given by

$$\left\langle nl\tfrac{1}{2}j\middle\|\hat{\mathbf{s}}^{(\acute{k})}(k)\middle\|\acute{n}\acute{l}\tfrac{1}{2}\acute{j}\right\rangle = (-1)^{\acute{l}-k}\left(\frac{3}{\sqrt{2\pi}}\right)\{[j][\acute{j}][k][\acute{k}][l][\acute{l}]\}^{\frac{1}{2}}\begin{pmatrix} l & k & \acute{l} \\ 0 & 0 & 0 \end{pmatrix}\begin{Bmatrix} l & \acute{l} & k \\ \frac{1}{2} & \frac{1}{2} & 1 \\ J & \acute{J} & \acute{k} \end{Bmatrix}\delta_{\acute{n}n} \tag{24}$$

where n is the principal quantum number. The matrix elements of the spin current density can be derived from the spin density operator by applying equation (19) to get:

$$\left\langle nl\tfrac{1}{2}jm_j\middle|\hat{\boldsymbol{J}}^s(\boldsymbol{r})\middle|\acute{n}\acute{l}\tfrac{1}{2}\acute{J}\acute{m}_J\right\rangle =$$

$$(-1)^{j-m_j}\sum_{\acute{k}\,k}(-1)^{\acute{l}}\begin{pmatrix} j & \acute{k} & \acute{j} \\ -m_j & m-m_j & \acute{m}_J \end{pmatrix}\left\langle nl\tfrac{1}{2}j\middle\|\hat{\mathbf{s}}^{(\acute{k})}(k)\middle\|\acute{n}\acute{l}\tfrac{1}{2}\acute{j}\right\rangle \boldsymbol{\nabla}\times \mathrm{R}_{n\,l}\mathrm{R}_{\acute{n}\,\acute{l}}\mathbf{Y}_{k\,m_j-m_j}^{\acute{k}} \tag{25}$$

To find the curl in equation (25) above, we make use of equation (55) of reference [7].

To generalize to the case of *N*-electron, we start by summing the single electron spin density operator defined in equation (23) over all electrons in the shell [14]. The matrix element$\langle\theta\, J\, M_J|\hat{\mathbf{S}}|\acute{\theta}\, \acute{J}\, \acute{M}_J\rangle$ of the spin density operator $\hat{\mathbf{S}}$ between tow spin-orbit coupled eigenstates of *N*-electron can now be determined substituting reduced matrix element of the spherical harmonic by equations (A. 46), (A.47) and (A.48) of reference [12].

$$\left\langle \theta\, J\, M_J \middle| \hat{\mathbf{S}} \middle| \acute{\theta}\, \acute{J}\, \acute{M}_J \right\rangle = (-1)^{l+M+1} \frac{\mu_B}{\sqrt{2\pi}} (2l+1) R_{nl}^2 \times$$

$$\sum_k \sum_{\acute{k}=k\pm 1} \begin{pmatrix} l & \acute{k} & l \\ 0 & 0 & 0 \end{pmatrix} \left\langle \theta\, J\, M_J \middle| W_q^{(1,\acute{k})k} \middle| \acute{\theta}\, \acute{J}\, \acute{M}_J \right\rangle \mathrm{Y}_{k-q}^{\acute{k}} \tag{26}$$

Where $q = M_J - \acute{M}_J$. The matrix element $\left\langle \theta\, J\, M_J \middle| W_q^{(1,\acute{k})k} \middle| \acute{\theta}\, \acute{J}\, \acute{M}_J \right\rangle$ can be evaluated using the Wigner-Eckart theorem, so that we get:

$$\left\langle \theta\, J\, M_J \middle| W_q^{(1,\acute{k})k} \middle| \acute{\theta}\, \acute{J}\, \acute{M}_J \right\rangle = (-1)^{J-M_J} \{[J][k][\acute{J}]\}^{\frac{1}{2}} \begin{pmatrix} J & k & \acute{J} \\ -M_J & q & \acute{M}_J \end{pmatrix} \times$$

$$\begin{Bmatrix} S & \acute{S} & 1 \\ L & \acute{L} & \acute{k} \\ J & \acute{J} & k \end{Bmatrix} \langle \theta || \widehat{W}^{(1,\acute{k})} || \acute{\theta} \rangle \tag{27}$$

For the case of $4f^N$ – electrons we should consider only the terms in equation (27) corresponding to $k = 1, 3$ and 5 and $\acute{k} = 0, 2, 4$ and 6 which is imposed by symmetry properties of the 3-j and the 9-j symbols found therein. The problem has now reduced to calculating the reduced matrix element of the unit double tensor operator $\langle \theta || \widehat{W}^{(1,\acute{k})} || \acute{\theta} \rangle$, here we resort to fractional method described by Statsis and Deckman [15] .

We may now substitute all expression involved into equation (19). Recognizing that the dependence of $R_{nl}(r)$ and hence its derivatives on r will not differ from the case of a single electron, it follows that the matrix element of the spin current density may appropriately be expanded in term of vector spherical harmonics, so that we finally get:

$$\left\langle \theta\, J\, M_J \middle| \hat{\boldsymbol{j}}^{s(N)} \middle| \acute{\theta}\, \acute{J}\, \acute{M}_J \right\rangle = i(-1)^{l+q+1} \frac{\mu_B}{\sqrt{\pi}} (2l+1) \times \sum_{k,\acute{k}=k\pm 1} \begin{pmatrix} l & \acute{k} & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \acute{k} & 1 & k \\ 0 & 1 & -1 \end{pmatrix} [\acute{k}] \times$$

$$\left\{ \frac{d}{dr} + \frac{1}{2} [(2k+1)(\acute{k}-k)+3] \frac{1}{r} \right\} R_{nl}^2 \left\langle \theta\, J\, M_J \middle| W_q^{(1,\acute{k})k} \middle| \acute{\theta}\, \acute{J}\, \acute{M}_J \right\rangle \mathrm{Y}_{k-q}^{\acute{k}} \tag{28}$$

2.3 Formulation of magnetic hyperfine fields

The current density at any point surrounding the nucleus is of relevance when dealing with the magnetism of atoms, since the magnetic field at atomic sites strongly depend on these currents according to the classical Biot-Savart's law

$$\boldsymbol{B}(\boldsymbol{r}) = \frac{\mu_0}{4\pi} \int \boldsymbol{J}(\boldsymbol{r}) \times \frac{\boldsymbol{r}-\acute{\boldsymbol{r}}}{|\boldsymbol{r}-\acute{\boldsymbol{r}}|^3} d\boldsymbol{r} \tag{29}$$

The magnetic field $\boldsymbol{B}(\boldsymbol{r})$ in equation (29) can easily be calculated by expanding the part $\frac{\boldsymbol{r}-\acute{\boldsymbol{r}}}{|\boldsymbol{r}-\acute{\boldsymbol{r}}|^3}$ of the integrand in terms spherical harmonics and substituting total atomic current density Considering $\boldsymbol{J}(\boldsymbol{r})$ as the total atomic current density composed of orbital and spin current densities. The total hyperfine field can be separated into magnetic fields $\boldsymbol{B^o}(\boldsymbol{r})$ due to orbital currents and $\boldsymbol{B^s}(\boldsymbol{r})$ due to spin current**.**

With the absence of external fields, the Hamiltonian representing the electrons exhibits rotational invariance at the position of the nucleus $r = 0$, hence the magnetic field at the nucleus sites can be attributed to atomic current densities.

We consider the 4f-electron ground state $|\Psi\rangle$ to be a linear combination of the spin coupled eigenstates $|\theta \, \mathrm{J} \, M_J \rangle$ (i.e. $|\Psi\rangle = \sum_{M_J} C_{M_J} |\theta \, J \, M_J \rangle$) , The orbital current density can then be expressed in the parametric form

$$\boldsymbol{J}^o(\boldsymbol{r}) = \frac{i\mu_B}{\sqrt{\pi}} \frac{R_{32}^2(r)}{r} \sum_{k(odd)=1}^{5} \alpha_i \, R_{4f}^2 Y_{k0}^k(\theta, \emptyset) \tag{30}$$

A similar form can be obtained for the spin current density $\boldsymbol{J}^s$, that is:

$$\boldsymbol{J}^S(\boldsymbol{r}) = \frac{i\mu_B}{\sqrt{\pi}} \sum_{\mathcal{L}(odd)=1}^{7} a_i \left(b_i \frac{d}{dr} + \frac{c_i}{r} \right) R_{4f}^2(r) Y_{\mathcal{L}0}^{\mathcal{L}}(\theta, \emptyset) \tag{31}$$

Where $R_{4f}(r)$ is the radial part of the eigenfunction $|\theta \, J \, M_J \rangle$. Calculated values of the coefficients α_i of equation (30) as well as the set of coefficients a_i ,b_i and c_i of (31) are presented in Tables 3 and 4 respectively.

Each of $\boldsymbol{B^o}(\boldsymbol{r})$ and $\boldsymbol{B^s}(\boldsymbol{r})$ can be determined in view of the following definition for spherical waves [7].

$$Y_{klm}^{\acute{l}} = k \left(\frac{2}{\pi}\right)^{\frac{1}{2}} b_{\acute{l}}(kr) Y_{lm}^{\acute{l}} (\theta, \phi) \tag{32}$$

Where $b_{\acute{l}}(kr)$ is the spherical Bessel function, whereof, the series expansion starts at the term with power *l* for the function argument, hence

$$\lim_{kr \to 0} b_{\acute{l}}(kr) = \frac{(kr)^{\acute{l}}}{(2l+1)!!} \tag{33}$$

It follow from (33) that, the multipole term in the expansion of the current density operator which does not vanish is that which contains $Y_{1\,q}^{0}$, as multipole component with higher rank should tend to vanish at this limit [9]. Besides, we have $k = 1, q = 0$ is the only term contributing to dipole term, hence $M_j - \acute{M}_j = 0$, so that

$$B_{1\,0}^{M_jM_j}(r) = i\mu_0\sqrt{\frac{2}{3}} \int_{\acute{r}=0}^{\infty} j_{1\,0}^{M_jM_j}(\acute{r})\, d\acute{r}\, Y_{1\,0}^{0}(\theta,\phi) \tag{34}$$

The remaining components $J_{1\,0}^{M_jM_j}$ of the orbital current density orbital are then given by

$$J_{1\,0}^{M_jM_j}(\acute{r}) = \frac{i\mu_B}{\sqrt{\pi}} \frac{R_{4f}^2(\acute{r})}{\acute{r}} C_{M_J}^2 \alpha_1^{M_JM_J} \tag{35}$$

Similarly, the spin current density will maintain the components

$$J_{1\,0}^{M_jM_j}(\acute{r}) = \frac{i\mu_B}{\sqrt{\pi}} C_{M_J}^2 a_1^{M_JM_J} \left(b_1^{M_JM_J} \frac{d}{d\acute{r}} + \frac{c_1^{M_JM_J}}{\acute{r}} \right) R_{4f}^2(\acute{r}) \tag{36}$$

Substituting $J_{1\,0}^{M_jM_j}(\acute{r})$ from equations (35) and (36) into equation (34) and considering values of $\mu_0 = 4\pi \times 10^{-7}\ Tm/A$ and $\mu_B = 9.274 \times 10^{-24}\ A\,m^{-1}$ we get respectively, the orbital and spin contributions to the total hyperfine magnetic field as

$$B_o^{M_JM_J} = 12.515\sqrt{\frac{2}{3}} C_{M_J}^2 \alpha_1^{M_JM_J} \int_r^{\infty} \frac{R_{4f}^2(\acute{r})}{\acute{r}}\, d\acute{r}\, \hat{\boldsymbol{e}}_z \tag{37}$$

$$B_s^{M_JM_J} = 12.515\sqrt{\frac{2}{3}} C_{M_J}^2 \alpha_1^{M_JM_J} \int_r^{\infty} \left(b_1^{M_JM_J} \frac{d}{d\acute{r}} + \frac{c_1^{M_JM_J}}{\acute{r}} \right) R_{4f}^2(\acute{r}) d\acute{r}\ \hat{\boldsymbol{e}}_z \tag{38}$$

The integrals in equations (37) and (38) can be evaluating making use of the approximation described in reference [16] as $\int_r^{\infty} \frac{R_{4f}^2(\acute{r})}{\acute{r}}\, d\acute{r} = \langle r^{-3} \rangle$, hence

$$B_o^{M_JM_J} = 12.515\sqrt{\frac{2}{3}} C_{M_J}^2 \alpha_1^{M_JM_J} \langle r^{-3} \rangle\, \hat{\boldsymbol{e}}_z \tag{39}$$

and

$$B_S^{M_JM_J} = 12.515\sqrt{\frac{2}{3}} C_{M_J}^2 a_1^{M_JM_J} C_1^{M_JM_J} \langle r^{-3} \rangle\, \hat{\boldsymbol{e}}_z \tag{40}$$

Values of $\langle r^{-3} \rangle$ for some rare earth element are tabulated by Freeman, A. J., and Watson [16].

3. Results and discussion

3.1 Racah parameters and current densities for free Nd^{3+} ion

Calculation of matrix element of the Racah unit double tensor operators W_q^k for fully colinear ground states $|L, S, J, M_J = J\rangle$ of free rare earth ions was conducted using equation (17). To account for orbital current density (J^o), only W_0^k within the range $1 \leq k \leq 2l - 1$ is used where the *3j*-symbol in equation (28) imposes the condition that k should be odd. Upon applying the Wigner – Eckart theorem, the problem reduces to calculating the reduced matrix elements $\langle \theta || \mathrm{W}^{(0,\mathrm{k})} || \theta \rangle$ which was done using a special procedure according to the general formula (55) described in reference [15]. The values of $\langle \theta || \mathrm{W}^{(0,\mathrm{k})} || \theta \rangle$ for all for Nd^{3+} elements are presented in Table 1. On the other hand calculation of the spin current density should necessarily require the calculation of $W_q^{(1,\acute{k})k}$ in the range $1 \leq k \leq 2l - 1$ where $k' = k + 1,\ k - 1$, this is imposed by condition of equation (28) as dictated by the nature of spin current density which is a double tenor operator defined in spin space of dimension 1 and orbital space of dimension *k*. It once again important to account for the reduced matrix elements. The values of $\langle \theta || \mathrm{W}^{(1,\mathrm{k})} || \theta \rangle$ for all tri-positive free RE ions are tabulated in Table 2.

Table 1: The reduced matrix elements $\langle \theta || \mathrm{W}^{(0,\mathrm{L})} || \theta \rangle$ of the Racah double tensor $W_0^{(0,l)}$ for Nd^{3+}

Ion	***state***	$\boldsymbol{W^{(0,0)}}$	$\boldsymbol{W^{(0,1)}}$	$\boldsymbol{W^{(0,2)}}$	$\boldsymbol{W^{(0,3)}}$	$\boldsymbol{W^{(0,4)}}$	$\boldsymbol{W^{(0,5)}}$	$\boldsymbol{W^{(0,6)}}$
$\boldsymbol{Nd^{3+}}$	$4f^3$	$\frac{3}{7}\sqrt{182}$	$\sqrt{39}$	$\frac{1}{33}\sqrt{2145}$	$-\frac{2}{33}\sqrt{3003}$	$-\frac{2}{11}\sqrt{221}$	$\frac{1}{33}\sqrt{14586}$	$\frac{5}{231}\sqrt{176358}$

Table 2: The reduced matrix elements $\langle \theta || \mathrm{W}^{(1,\mathrm{k})} || \theta \rangle$ of the Racah double tensor $W_0^{(1,k)}$ for Nd^{3+}

Ion	***State***	$\boldsymbol{W^{(1,0)}}$	$\boldsymbol{W^{(1.2)}}$	$\boldsymbol{W^{(1,4)}}$	$\boldsymbol{W^{(1,6)}}$
$\boldsymbol{Nd^{3+}}$	$4f^3$	$\frac{1}{7}\sqrt{2730}$	$\frac{5}{33}\sqrt{143}$	$-\frac{2}{33}\sqrt{3315}$	$\frac{5}{231}\sqrt{293930}$

As for current densities, a parameterized form is given by equation (30) for orbital part of the current density in terms of the vector spherical harmonics Y_{k0}^k. It is sufficient to calculate the expansion parameter (α_i), for odd indices k = 1,3, and 5. Although exact forms of vector spherical harmonics are readily available [17], the use of a special procedure based on their definition in terms of Clebsch-Gordan coefficients is more profitable as far as complete calculation is required. The transformation relation from covariant spherical to polar components of a vector is given below

$$\begin{pmatrix} A_r \\ A_\theta \\ A_\emptyset \end{pmatrix} = \begin{pmatrix} \frac{-sin(\theta)e^{i\emptyset}}{\sqrt{2}} & cos(\theta) & \frac{sin(\theta)e^{-i\emptyset}}{\sqrt{2}} \\ \frac{-cos(\theta)e^{i\emptyset}}{\sqrt{2}} & -sin(\theta) & \frac{cos(\theta)e^{-i\emptyset}}{\sqrt{2}} \\ \frac{-ie^{i\emptyset}}{\sqrt{2}} & 0 & \frac{-ie^{-i\emptyset}}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} A^{+1} \\ A^{0} \\ A^{-1} \end{pmatrix} \tag{41}$$

then we can determine the exact value of $(\hat{J}^o)$ for spherical space and consequently for Cartesian space $(r, \theta, \emptyset)$, by appropriate transformation (30). Values of (α_i), for all RE elements are given in Table 3.

Similarly, the spin current density $(\hat{J}^s)$ are expanded in terms of the vector spherical harmonics Y_{k0}^{k} according to equation (31) where we need the three parameters , $\acute{b}_i$ and $\acute{c}_i$ corresponding to each spherical component $\hat{J}^s$. Here we have $\acute{b}_i = a_i b_i$ and $\acute{c}_i = a_i c_i$. These parameters are presented in Table 4.

Table 3: expansion parameters α_i of Orbital current density of equation (30) for fully colinear ground states of Nd^{3+} ions:

Element	$\boldsymbol{\alpha_1}$	$\boldsymbol{\alpha_3}$	$\boldsymbol{\alpha_5}$
Nd	3.957478436	0.6443058217	**0.1409735325**

Table 4: expansion parameters b_i and C_i of spin current density of equation (31) for fully colinear ground states of Nd^{3+} ions

Element	$\boldsymbol{C_1}$	$\boldsymbol{b_1}$	$\boldsymbol{C_3}$	$\boldsymbol{b_3}$
Nd	−1.072916995	−0.2125590273	−0.04325766424	**−0.017889051**

Element	$\mathbf{C_5}$	$\mathbf{b_5}$	$\mathbf{C_7}$	$\mathbf{b_7}$
Nd	−0.1034256635	−0.8905590321	0.006120240559	**−0.03672144335**

3.2 Hyperfine magnetic fields for Nd^{3+} free ion

Since they are vector (tensors of rank 1), The HMF's B^o due to orbital currents and B^s due to spin currents were formulated in terms of vector spherical harmonics according to equation (39) and (40) and afterwards transformed into their cartesian counterparts. The approximate value $\langle r^{-3} \rangle = 5.127\ a_0^{-3}$ for *4f*-electron Nd^{3+} where a_0 stands for Bohr radius is extracted from Table 4 of reference [16]. However, we have observed that, it is only the z- component of each of B^o and B^s that doesn't vanish.

Table 5: The orbital and spin contribution to HMF's B^o, B^s in units of Tesla for Nd^{3+} free ions.

Ion	$\boldsymbol{B^o}$	$\boldsymbol{B^s}$	$\mathbf{B_T}$
Nd	243.8490646	−13.09730951	230.7517551

3.2 Hyperfine magnetic fields for Nd^{3+} ion subjected to cubic crystal field

It is well known that *4f* electrons of a RE elements are deeply located withing the core of the RE atom and therefore electrostatically shielded from crystalline environment by *5s* valence electrons this gives rise to weak CF interaction, that means CF Hamiltonian is considered as perturbation on the Hamiltonian containing the spin-orbit coupling contribution H_{so} making a good quantum number of total angular momentum (J). The CF Hamiltonian for octahedral ligand configuration is given by [18]:

$$H_{Cf} = \sum_{kq} B_{kq} O_{kq} \tag{42}$$

Where B_{kq} are the crystal field parameters (CFP's) and O_{kq} are the so called stevens operator equivalents. The CFP's are approximated by stevens [19] according to the following scheme [17]: The $(2J + 1) \times (2J + 1)$ matrix is written down for each J-manifold using the operator equivalent matrix elements listed in Tables 2-4 of reference [19]. These tables include factors that are present in all matrix elements, $F(6)$ and $F(4)$, these factors are segregated in the current computation to preserve the eigenvalues to within the same numerical range for all fourth and sixth degree term ratios [18]. The CF Hamiltonian is then given by:

$$H = B_4 F(4) \frac{0_4}{F(4)} + B_6 F(6) \frac{0_6}{F(6)} \tag{43}$$

Where

$$0_4 = [0_4^0 + 5.0_4^4] \text{ and } 0_6 = [0_6^0 - 21.0_6^4] \tag{44}$$

And B_4 , B_6 are weighted CFP's. To account for all possible ratio, between the terms of the fourth and sixth degrees, a weight function W is used such that

$$B_4 F(4) = W_x \tag{45}$$

$$B_6 F(6) = W_{(1-|x|)} \tag{46}$$

Where x is a scaling factor so that x $-1 < x < +1$

Consequently,

$$\frac{B_4}{B_6} = \frac{x}{1-|x|} \cdot \frac{F(6)}{F(4)} \tag{47}$$

So that $\frac{B_4}{B_6} = 0$ for $x = 0$ while $\frac{B_4}{B_6} = \pm\infty$ for $x = \pm 1$

Equation (42) can now be rewritten in the following form:

$$H = W[x\left(\frac{O_4}{F(4)}\right) + (1 - |x|)\left(\frac{O_6}{F(6)}\right)] \tag{48}$$

The eigenvalues are connected to the CF energy levels. And the term in square brackets denotes a matrix whose eigenvectors correspond to the most common combination of fourth and sixth-degree CF terms [19]. Based on the scheme described above, the ground state of RE ions in Octahedral symmetry is given as linear combination of the degenerate eigenstates ($|j\ m_j\rangle$) of free ion so that:

$$\psi^{(O_h)} = \sum_i C_i\ |J\ m_i\rangle \tag{49}$$

Where C_i is a cross term coffiecient resulting from CF splitting.

Diagonalization of the CF term of the effective Hamiltonian have rendered the ground states for Nd^{3+} ions in Octahedral CF as given below:

$$\psi^{(O_h)}(Nd) = 0.9531\left|\frac{9}{2}\frac{7}{2}\right\rangle - 0.298\left|\frac{9}{2} - \frac{1}{2}\right\rangle + 0.054\left|\frac{9}{2} - \frac{9}{2}\right\rangle \tag{50}$$

The ground state function $\psi^{(O_h)}$ as described by equation (50) was substituted in equations (30) and (31) to determine the orbital and spin parts of the atomic current densities for Nd in octahedral CF's for a fixed approximate *4f*-electron radial coordinate *r* and various angular coordinates $((\theta, \emptyset)$. The angular variations thus accounted for is illustrated in Figures (1) and (2). It is to be noted here that the only none-vanishing component of both current densities is that in the ϕ-direction as $J_r = J_\theta = 0\ , J_\emptyset \neq 0$ for all value of (θ, ϕ). because if $J_r\ or\ J_\theta \neq 0$ this will contradict the physical reality, That the electron should not fall into nucleus.

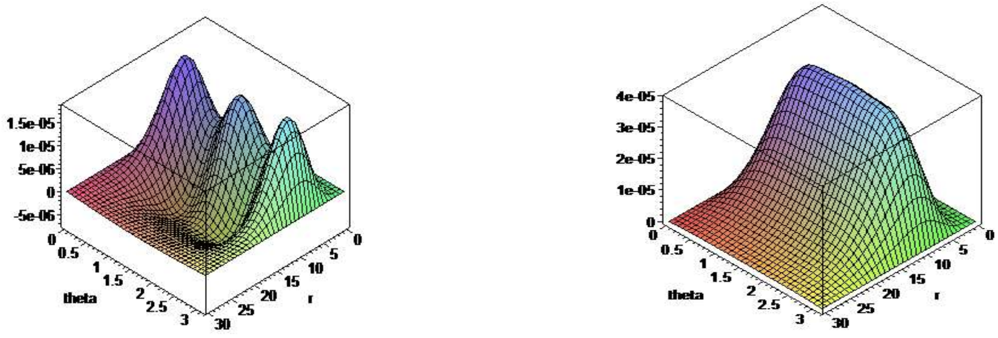

Figure 1: (a) Orbital and (b) spin current densities for free Nd^{3+}

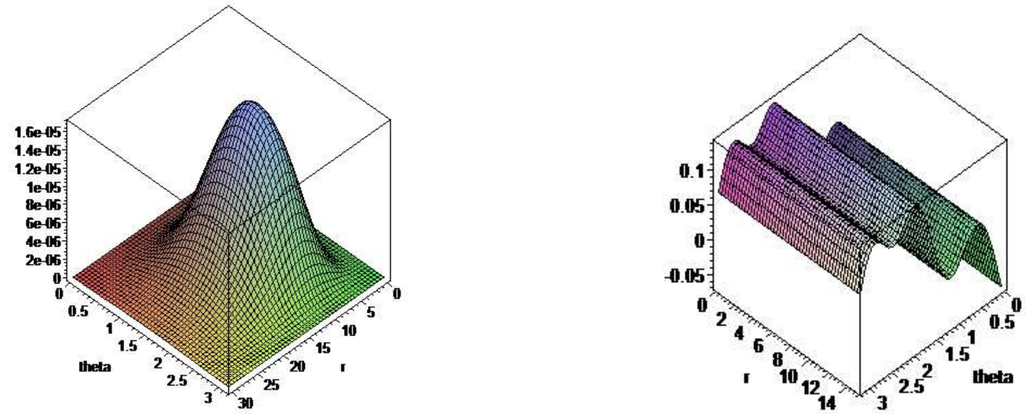

Figure 2: (a) Orbital and (b) spin current densities for Nd^{3+} in cubic CF.

Values of orbital, spin and total HMF's calculated according to equation (39) and (40) are enlisted in Table (7). As compared with those obtained for the case of free ions, it is observed that the advent of octahedral CF tends to increase the magnitude of both orbital and the spin contributions and changes the direction of the last changed and thus gives rise to increase in total hyperfine field.

3.3 Hyperfine magnetic fields for Nd^{3+} ion in $NdGaO_3$ tetragonal perovskites

It is well known that $NdGaO_3$ crystallizes in orthorhombic structure within crystallographic space group *Pnma* and the local symmetry point group for RE constituents (Nd) here is C1a[20]. For this point group we need incorporate a total of nine nonzero CFP's instead of only two parameters identified for the case of octahedral CF potential.

To obtain appropriate crystallographic structural, we have carried out structure optimization using the DFT based full potential linearized augmented plane wave (FP-LAPW) as implemented in WIEN2k software package [21] where the variation of energy per unit volume was fitted according to Birch-Murnaghan equation of the state [22]. Structure optimization have retained tetragonal structure with lattice parameter $a = 5.4323$ Å, $b = 5.4966$Å and $c = 7.7064$ Å

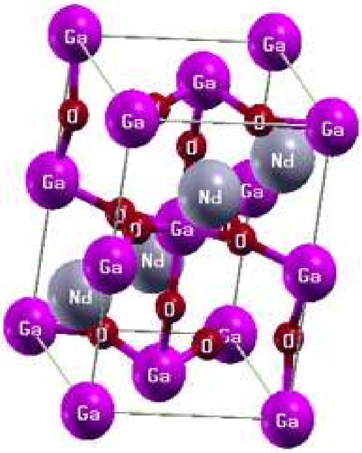

Figure 3: Tetragonal unit cell of $NdGaO_3$.

The set of nine CFP's calculated using maximally localized Wannier functions method are tabulated in Table 6: below. The effective CF Hamiltonian is constructed through stevens operator equivalents [13] and can hence be written as in equation (42).

Table 6: CFP's B_q^k for $NdGaO_3$ calculated by Novak et. al. [20] (All CFPs are in units of meV),

k	q	B_q^k
2	0	-29.19
2	2	18.75 +76.02i
4	0	-52.61
4	2	-20.63 +83.55i
4	4	20.76 - 75.35i
6	0	-74.44
6	2	11.97 +34.56i
6	4	-164.72+0.52i
6	6	15.46 - 1.95i

To construct the ground state of Nd^{3+} ion in $NdGaO_3$, we have substituted the set of CFP's of Novak et al [20] in the CF Hamiltonian and carried out diagonalization of the effective Hamiltonian matrix in order to obtain all energy eigenvalues and corresponding eigenvectors including ground state. The ground state wave function thus obtained is then substituted in equations (30) and (31) as was done for the case of octahedral CF described in section 3.2.

$$\psi = (.33 - .18i)\left|\frac{9}{2}\frac{9}{2}\right\rangle + (.01 - .01i)\left|\frac{9}{2}\frac{7}{2}\right\rangle + (0.62 - 0.04i)\left|\frac{9}{2}\frac{5}{2}\right\rangle + (-.095 - .13i)\left|\frac{9}{2}\frac{3}{2}\right\rangle + (.28 - .07i)\left|\frac{9}{2}\frac{1}{2}\right\rangle + (.06 + .05i)\left|\frac{9}{2}\frac{-1}{2}\right\rangle + (-.58 + .01i)\left|\frac{9}{2}\frac{-3}{2}\right\rangle + (\,.11 + .13i)\left|\frac{9}{2}\frac{-5}{2}\right\rangle + (-.01 - .05i)\left|\frac{9}{2}\frac{-7}{2}\right\rangle + (.091 + .04i)\left|\frac{9}{2}\frac{-9}{2}\right\rangle$$

Table 7: The orbital, spin contributions and total HMF's, for Nd^{3+} *4f*-electrons in units of Tesla

Case	B^o	B^s	**B_T**
Free Ion	243.8490646	−13.09730951	230.7517551
Cubic CF	311.3361444	299.7824181	611.1185625
$NdGaO_3$ (Current)	9.745	−0.2952	9.4498
$NdGaO_3$ (DFT)	10.028 ∗	—0.327	9.701

*Ahmed Elhag private communication

Values of HMF's for the case of free Nd^{3+} presented in Table 7 fully agree with results obtained by Netz [4], mean while, those obtained for Nd^{3+} ion subjected to hypothetical cubic CF's are in good agreement with experimental results despite the use of relatively inaccurate point charge model of CF to determine ground state wavefunction. As for the sample of tetragonal crystal of $NdGaO_3$, the results agree well with those obtained using DFT approach.

Conclusion:

We have developed multipole expressions for atomic orbital and spin current densities for RE ions and performed calculations of HMF's for those ions resulting from their atomic current densities. Though fairly involved in tensor operator algebra, the model proposed in this paper is straight forward to computer coding. For the case of cubic CF, the accuracy of the model might have been limited by non-relativistic Hartree-Fock approximation for the radial part of the wave function. For the case of octahedral CF, the use of relatively inaccurate and naïve point charge model could end up in poor estimation of CFP’s that could generally affect the accuracy of our results. As for calculations involving $NdGaO_3$, incorporation of the Nd(*4f*)-O(*2p*) exchange interaction within the framework of the exchange charge model of the CF is expected to enhance the accuracy of ground state eigenfunction and consequently yield more accurate results for current densities and HMF's.

However, the model proposed conclusively renders fairly accurate results for different CF environments so far investigated thereby. The model is also made flexible to incorporate ab initio as well as semi-empirically and experimentally determined sets of CFP's. in calculation procedure.

References:

1. K. Hiroaki, Description of Multipole in f-Electron Systems, J. Phys. Soc. Jpn, 77-064710, 2008.

2. K. Ayuel, A. Zakaria, Orbital and spin contributions to magnetic hyperfine fields of the 3d transition metal ions, JMMM, 457, 142-147, 2019.

3. M. V. Lalić, J. Mestnik-Filho, A. W. Carbonari, R. N. Saxena, and H. Haas, First-principles calculations of hyperfine fields in the CeIn$_3$ intermetallic compound, Phys. Rev. B 65, 054405, 2001.

4. G. Netz, The magnetic hyperfine fields of rare earth ions in metals, Zeitschrift for Physik B Condensed Matter, 63(3), 343–349, 1986.

5. A. Abragam, B. Bleaney, Electron paramagnetic resonance of transition ions 5th edition, Oxford University Press, 2013.

6. K. Ayuel, P. F. de. Châtel, and A. El Hag, Orbital and spin contributions to magnetic hyperfine fields of tri-positive rare earth ions. Physica B: Condensed Matter, 457, 245–250, 2015

7. D. A. Varshalovich, A. N. Moskalev and V. K. Khersonskiĭ, Quantum theory of angular momentum: Irreducible tensors, spherical harmonics, vector coupling coefficients, 3NJ symbols, World Scientific Pub, 1988.

8. K. Ayuel, P. F. De Châtel, Multipole expansions: Magnetic and electric fields generated by electrons bound in spin–orbit eigenstates, Physica B: Condensed Matter, 404(8-11), 1209-1217, 2009.

9. G. B. Arfken, H.-J. Weber, Instructor's manual: Mathematical methods for physicists, 5th edition , Academic Press London, 2006

10. A. Elhag, The Effect of Cubic Crystal Fields on Charge, Spin and Current Densities in Rare Earth Elements, Ph.D thesis , Sudan University of Science and Technology, 2008.

11. W. J. Thompson, Angular Momentum: An Illustrated Guide to Rotational Symmetries for Physical Systems , 1st edition, Wiley-VCH, 1994.

12. C. Stassis and H. W. Deckman, Magnetic scattering of neutrons,Phys. Rev. B. 12, 5. 1885, 1975.

13. I. I. Sobel'man, Introduction to the theory of Atomic Spectra, 1st edition, Pergamon Press Oxford,1972.

14. K. A. Kuacgor, Atomic current densities and magnetism, Ph. D thesis, Universiteit van Amsterdam, 2000.

15. C. Stassis, H. W. Deckman, Magnetic scattering of neutrons by a relativistic atom, Phys. Rev. B. 13, 11. 4934, 1976.

16. A. J. Freeman, R. E. Watson, Theoretical investigation of some magnetic and spectroscopic properties of rare-earth ions, Physical Review, 127(6), 2058–2075, 1962.

17. R. G. Barrera, G. A. Estevez and J. Giraldo, Vector spherical harmonics and their application to magnetostatics, Eur J. Phys 6, 287-294, 1985.

18. K. R. Lea, M. J. M. Leask and W. P. Wolf, The raising of angular momentum degeneracy of F-electron terms by cubic crystal fields, Journal of Physics and Chemistry of Solids, 23(10), 1381–1405,1962.

19. K. W. Stevens, Matrix elements and operator equivalents connected with the magnetic properties of rare earth ions, Proceedings of the Physical Society, Section A, 65(3), 209–21,1952.

20. P. Novák, K. Knížek, M. Maryško, Z. Jirák and J. Kuneš, Crystal Field and magnetism of PR3+and nd3+ions in orthorhombic perovskites, Journal of Physics: Condensed Matter,25(44), 446001, 2013.

21. P. Blaha, K. Schwarz, F. Tran, R. Laskowski, G.K.H. Madsen and L.D. Marks, WIEN2k: An APW+lo program for calculating the properties of solids, J. Chem. Phys. 152, 074101, 2020.

22. M. Musa, H.-E Saad and A. Elhag, DFT study on the crystal, electronic and magnetic structures of tantalum based double perovskite oxides Ba_2MTaO_6 (M = Cr, Mn, Fe) via GGA and GGA + U", Results in Physics 9, 793-805, 2018.