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First-principles theory of orbital magnetization

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Within density-functional theory we compute the orbital magnetization for periodic systems evaluating a recently discovered Berry-phase formula. For the ferromagnetic metals Fe, Co, and Ni we explicitly calculate the contribution of the interstitial regions neglected so far in literature. We also use the orbital magnetization to compute the electron paramagnetic resonance *g* tensor in paramagnetic systems. Here the method can also be applied in cases where linear-response theory fails, e.g., radicals and defects with an orbital-degenerate ground state or those containing heavy atoms.

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The electric polarization and the orbital magnetization are well-known textbook topics in electromagnetism and solid-state physics. While it is easy to compute their derivatives in an extended system, the electric polarization and the orbital magnetization themselves are not easy to formulate in the thermodynamic limit due to the unboundedness of the position operator. The problem of the electric polarization has been solved in the 1990s by the modern theory of polarization (MTP),[1,2] which relates the electric polarization to the Berry phase of the electrons. A corresponding formula for the orbital magnetization has been found very recently[3,4] showing that this genuine bulk quantity can be evaluated from the ground-state Bloch wave functions of the periodic system. Since the discovery of the MTP, a wealth of papers have appeared reporting its successful applications to first-principles calculations of dielectric and piezoelectric properties.[2] On the other hand, *ab initio* calculations of the orbital magnetization via the Berry phase formula have not been reported in literature yet, except than for simple tight-binding lattice models.

The origin of the orbital magnetization in molecules and solids is time-reversal breaking caused by e.g., spin-orbit (SO) coupling. In ferromagnetic materials the orbital magnetization is a not negligible contribution to the total magnetization. Several papers in literature[5,6] showed that the orbital magnetic moment of simple ferromagnetic metals (Fe, Co, and Ni) is strongly underestimated within density-functional theory (DFT) if using the local-density approximation (LDA) or generalized gradient approximations (GGA). Empirical corrections such as the orbital polarization (OP) (Ref. 7) have been thus employed to obtain a better agreement with the experimental values. Nevertheless it remains an interesting question if, e.g., functionals beyond LDA or GGA would be able to describe the orbital magnetization correctly.[6] All previous *ab initio* calculations have been however carried out in the muffin-tin (MT) approximation, i.e., computing the orbital magnetization only in a spherical region centered on the atoms, neglecting the contribution of the interstitial region.

In this Rapid Communication, we present first-principles DFT calculations of the orbital magnetization by evaluating the recently discovered Berry phase formula.[3,4] For the ferromagnetic phases of Fe, Co, and Ni we show that the interstitial regions contribute by up to 50% to the orbital magnetic moments. So far neglected in the literature these contributions are thus shown to be one source for underestimated *ab initio* values. Furthermore we make use of a relationship between the orbital magnetization and the electronic *g* tensor that can be measured in electron paramagnetic resonance (EPR) experiments.[8] We propose a nonperturbative method that is highly superior to existing linear-response (LR) approaches[9,10] since it can deal with systems in which spin-orbit coupling cannot be described as a perturbation.

The total (sum of spin and orbital) magnetization can be defined from the derivative energy E_{tot} with respect to the magnetic field $\mathbf{B}$

$$\mathbf{M} \equiv -\left.\frac{\partial E_{\mathrm{tot}}}{\partial \mathbf{B}}\right|_{B=0} = \sum_n f_n \langle \psi_n | -\frac{\partial \mathcal{H}}{\partial \mathbf{B}} | \psi_n \rangle_{B=0}, \qquad (1)$$

where f_n is the occupation of the eigenstate n and in the most general case the expectation value is to be taken on ground-state spinors ψ_n. In the last equality we take advantage of the Hellmann-Feynman theorem. The Hamiltonian in atomic units is

$$\mathcal{H} = \frac{1}{2}[\mathbf{p} + \alpha \mathbf{A}(\mathbf{r})]^2 + V(\mathbf{r}) + \frac{\alpha^2 g'}{8} \boldsymbol{\sigma} \cdot [\nabla V(\mathbf{r}) \times (\mathbf{p} + \alpha \mathbf{A}(\mathbf{r}))], \qquad (2)$$

where we drop the trivial spin-Zeeman term, reducing the magnetization according Eq. (1) only to its orbital part. We use the symmetric gauge $\mathbf{A}(r) = \frac{1}{2}\mathbf{B} \times \mathbf{r}$. The last term in Eq. (2) is the leading spin-orbit term, describing the on-site SO coupling [with fine structure constant $\alpha = 1/c$ and the abbreviation $g' = 2(g_e - 1)$ (Refs. 9 and 10)] and $\boldsymbol{\sigma}$ are the Pauli matrices. We neglect the spin other orbit (SOO) term, in general a small contribution to the orbital magnetization and to the g tensor.[11]

By inserting Eq. (2) into Eq. (1) we obtain

$$\mathbf{M} = \frac{\alpha}{2} \sum_n f_n \langle \psi_n | \mathbf{r} \times \mathbf{v} | \psi_n \rangle, \qquad (3)$$

where $\mathbf{v} = -i[\mathbf{r}, \mathcal{H}]$, with $\mathcal{H}$ and ψ computed at $\mathbf{B} = 0$. This expression can be directly evaluated in a finite system but not in extended systems because of the unboundedness of the position operator and of the contribution of itinerant surface currents.[3] However, in periodic systems and in the thermodynamic limit, Eq. (3) can rewritten as a bulk property:[3,4]

$$\mathbf{M} = -\frac{\alpha N_{\mathrm{c}}}{2N_k}\mathrm{Im}\sum_{n\mathbf{k}} f_{n\mathbf{k}} \times \langle \partial_{\mathbf{k}} u_{n\mathbf{k}}| \times (\mathcal{H}_{\mathbf{k}} + \epsilon_{n\mathbf{k}} - 2\epsilon_{\mathrm{F}})|\partial_{\mathbf{k}} u_{n\mathbf{k}}\rangle, \tag{4}$$

where $\mathcal{H}_{\mathbf{k}}$ is the crystal Hamiltonian with $\mathbf{B}=0$, $\epsilon_{n\mathbf{k}}$ and $u_{n\mathbf{k}}$ are its eigenvalues and eigenvectors, ϵ_{F} is the Fermi level, N_{c} is the number of cells in the system, and N_k is the number of k points.

Equations (3) and (4) are valid at an all-electron (AE) level. To compute the orbital magnetization within a pseudopotential (PS) approach, we recall that a PS Hamiltonian $(\overline{\mathcal{H}})$ reproduces by construction differences and derivatives of the total energy. Thus we can still obtain $\mathbf{M}$, from Eq. (1), if we replace $\partial\mathcal{H}/\partial\mathbf{B}$ and ψ_n by the corresponding PS quantities $\partial\overline{\mathcal{H}}/\partial\mathbf{B}$ and $\overline{\psi}_n$.

We obtain the PS Hamiltonian in presence of spin-orbit coupling and uniform magnetic field with the gauge including projector augmented waves (GIPAW) method.[12] In particular $\overline{\mathcal{H}}=\mathcal{T}_B^{\dagger}\mathcal{H}\mathcal{T}_B$, where $\mathcal{H}$ is given by Eq. (2) and $\mathcal{T}_B$ is the GIPAW transformation [Eq. (16) of Ref. 12]. If the AE and PS partial waves have the same norm the GIPAW Hamiltonian is given by

$$\overline{\mathcal{H}} = \overline{\mathcal{H}}^{(0)} + \overline{\mathcal{H}}^{(0)}_{\mathrm{SO}} + \overline{\mathcal{H}}^{(1)} + \overline{\mathcal{H}}^{(1)}_{\mathrm{SO}} + O(B^2),$$

where

$$\overline{\mathcal{H}}^{(0)} = \frac{1}{2}\mathbf{p}^2 + V_{\mathrm{ps}}(\mathbf{r}) + V^{\mathrm{NL}}_{\mathbf{R}}, \tag{5}$$

$$\overline{\mathcal{H}}^{(0)}_{\mathrm{SO}} = \frac{g'}{8}\alpha^2\left[\boldsymbol{\sigma}\cdot(\nabla V_{\mathrm{ps}}(\mathbf{r})\times\mathbf{p}) + \sum_{\mathbf{R}} F^{\mathrm{NL}}_{\mathbf{R}}\right], \tag{6}$$

$$\overline{\mathcal{H}}^{(1)} = \frac{\alpha}{2}\mathbf{B}\cdot\left(\mathbf{L} + \sum_{\mathbf{R}}\mathbf{R}\times\frac{1}{i}[\mathbf{r},V^{\mathrm{NL}}_{\mathbf{R}}]\right), \tag{7}$$

$$\overline{\mathcal{H}}^{(1)}_{\mathrm{SO}} = \frac{g'}{16}\alpha^3\mathbf{B}\cdot\left(\mathbf{r}\times(\boldsymbol{\sigma}\times\nabla V_{\mathrm{ps}}) + \sum_{\mathbf{R}}\mathbf{E}^{\mathrm{NL}}_{\mathbf{R}} + \sum_{\mathbf{R}}\mathbf{R}\times\frac{1}{i}[\mathbf{r},F^{\mathrm{NL}}_{\mathbf{R}}]\right). \tag{8}$$

Here V_{ps} and $V^{\mathrm{NL}}_{\mathbf{R}}$ are the local part and the nonlocal part in separable form of the norm-conserving PS. $F^{\mathrm{NL}}_{\mathbf{R}}$ and $\mathbf{E}^{\mathrm{NL}}_{\mathbf{R}}$ are the separable nonlocal GIPAW projectors, accounting, respectively, for the so-called paramagnetic and diamagnetic contributions[13] of the atomic site $\mathbf{R}$.

Inserting $\overline{\mathcal{H}}^{(1)}+\overline{\mathcal{H}}^{(1)}_{\mathrm{SO}}$ in Eq. (1) we obtain

$$\mathbf{M} = \mathbf{M}_{\mathrm{bare}} + \Delta\mathbf{M}_{\mathrm{bare}} + \Delta\mathbf{M}_{\mathrm{para}} + \Delta\mathbf{M}_{\mathrm{dia}}, \tag{9}$$

$$\mathbf{M}_{\mathrm{bare}} = \frac{\alpha}{2}\sum_{\mathbf{R}}\left\langle \mathbf{r}\times\frac{1}{i}[\mathbf{r},\overline{\mathcal{H}}^{(0)} + \overline{\mathcal{H}}^{(0)}_{\mathrm{SO}}]\right\rangle, \tag{10}$$

$$\Delta\mathbf{M}_{\mathrm{bare}} = \frac{\alpha}{2}\sum_{\mathbf{R}}\left\langle(\mathbf{R}-\mathbf{r})\times\frac{1}{i}[\mathbf{r}-\mathbf{R},V^{\mathrm{NL}}_{\mathbf{R}}]\right\rangle, \tag{11}$$

$$\Delta\mathbf{M}_{\mathrm{para}} = \frac{g'\alpha^3}{16}\sum_{\mathbf{R}}\left\langle(\mathbf{R}-\mathbf{r})\times\frac{1}{i}[\mathbf{r}-\mathbf{R},F^{\mathrm{NL}}_{\mathbf{R}}]\right\rangle, \tag{12}$$

$$\Delta\mathbf{M}_{\mathrm{dia}} = \frac{g'\alpha^3}{16}\sum_{\mathbf{R}}\langle\mathbf{E}^{\mathrm{NL}}_{\mathbf{R}}\rangle, \tag{13}$$

where $\langle\ldots\rangle$ stands for $\Sigma_{n\mathbf{k}}f_{n\mathbf{k}}\langle\bar{u}_{n\mathbf{k}}|\ldots|\bar{u}_{n\mathbf{k}}\rangle$.

In a periodic system $\mathbf{M}_{\mathrm{bare}}$ can be nicely calculated by evaluating Eq. (4) for the GIPAW Hamiltonian $\overline{\mathcal{H}}$ and corresponding PS eigenvectors $\bar{u}_{n\mathbf{k}}$ and eigenvalues $\bar{\epsilon}_{n\mathbf{k}}$. All the reconstruction terms [Eqs. (11)–(13)] can be easily evaluated in extended systems since the nonlocal operators $V^{\mathrm{NL}}_{\mathbf{R}}$, $F^{\mathrm{NL}}_{\mathbf{R}}$ and $\mathbf{E}^{\mathrm{NL}}_{\mathbf{R}}$ act only inside finite spherical regions, centered around each atom.

The approach presented so far allows the calculation of the orbital magnetization in a general PS scheme including noncollinear spin polarization. In this work for the sake of simplicity we use a collinear implementation. All expectation values are evaluated by assuming decoupled spin channels along the spin direction $\mathbf{e}$. In particular all the spinors are eigenvectors of $\boldsymbol{\sigma}\cdot\mathbf{e}$ and the local and total spin $(\mathbf{S}=S\mathbf{e})$ are aligned along $\mathbf{e}$. Since the choice of $\mathbf{e}$ changes the spin-orbit coupling, the orbital magnetization is a function of $\mathbf{e}$. In ferromagnets, each spin direction $\mathbf{e}$ is characterized by a corresponding total energy, whereby the minimum of the total energy with respect to $\mathbf{e}$ defines the preferred direction of the spin alignment, the so-called *easy axis* of the ferromagnet.

We implemented our method in the QUANTUM-ESPRESSO plane-wave code.[14] We use standard norm-conserving pseudopotentials[15] with two GIPAW projectors per angular momentum channel. Using spin-polarized LDA (Ref. 16) and PBE (Ref. 17) functionals, we perform standard self-consistent-field (SCF) calculations including the SO term of Eq. (6) in the collinear approximation within the Hamiltonian. Then we evaluate the orbital magnetization, according to the Eqs. (4), (9), and (11)–(13) for $\mathbf{M}_{\mathrm{bare}}$. We neglect any explicit dependence of the exchange-correlation functional on the current density. In practice, spin-current density-functional theory (SCDFT) calculations have shown to produce negligible corrections to the orbital magnetization.[6] We compute $\mathbf{M}(\mathbf{e})$ with $\mathbf{e}$ along easy axis and along other selected directions. The $\mathbf{k}$ derivative of the Bloch wave functions can be accurately evaluated by either a covariant finite difference formula[18] or by the $k\cdot p$ method.[19] For insulating systems both methods provide exactly the same results; for metallic systems the covariant derivative is more involved and we apply just the $k\cdot p$ method. For the ferromagnetic Fe, Co, and Ni, calculations are carried out at the experimental lattice constants. We consider 4s and 4d states in the valence with nonlinear core correction. use a relatively low cutoff of 90 Ry. In the case of Fe, the results do not change by more than 1% by including 3s and 3p in valence and working at 120 Ry. We use a Marzari-Vanderbilt cold smearing of 0.01 Ry. We carefully test our calculations

TABLE I. Orbital magnetic moments $\mathbf{M}(\mathbf{e})\cdot\mathbf{e}$ in μ_B per atom of ferromagnetic metals parallel to the spin, for different spin orientations $\boldsymbol{e}$. $*$ denotes the experimental easy axis. The interstitial contribution is defined by the difference between $\mathbf{M}(\mathbf{e})$ and $\mathbf{M}^{MT}_{\text{orb}}=\Sigma_{n\mathbf{k}}\int_{\Omega_s}u^{\star}_{n\mathbf{k}}(\mathbf{r})\mathbf{r}\times(-i\nabla+\mathbf{k})u_{n\mathbf{k}}(\mathbf{r})d\mathbf{r}$, where Ω_s is a atom-centered sphere of radius $R_{\text{MT}}=2.0$ r_{bohr}. All theoretical values are based on the gradient corrected PBE functional. The decomposition of $\mathbf{M}$ according to Eq. (9) is shown Table II of the auxiliary material.

			This method			
Metal	$\boldsymbol{e}$	Expt. [20]	Total	Interstitial	MT	FLAPW[5]
bcc-Fe	[001]*	0.081	0.0658	0.0225	0.0433	0.045
bcc-Fe	[111]		0.0660	0.0216	0.0444	
fcc-Co	[111]*	0.120	0.0756	0.0122	0.0634	0.073
fcc-Co	[001]		0.0660	0.0064	0.0596	
hcp-Co	[001]*	0.133	0.0957	0.0089	0.0868	
hcp-Co	[100]		0.0867	0.0068	0.0799	
fcc-Ni	[111]*	0.053	0.0519	0.0008	0.0511	0.050
fcc-Ni	[001]		0.0556	0.0047	0.0509	

for k-point convergence. In all cases a $28\times28\times28$ mesh yields converged results within $\pm0.0001\mu_B$.

Table I reports our results for the orbital magnetization of the three metals Fe, Co, and Ni, together with experimental values and a recent calculation performed by full potential linearized augmented plane wave (FLAPW).[5] All theoretical data were obtained using the PBE functional. LDA gives within $\pm0.003\mu_B$ the same values (see Table II in the additional material[21]). In order to evaluate the contribution of the interstitial regions neglected so far in the literature (as in Refs. 5 and 6), we have equally computed $(\alpha/2)\langle\mathbf{L}\rangle$ only inside atomic spheres. Except for fcc-Co our results agree very well with FLAPW calculations. For Ni the influence of contributions is indeed negligible, explaining the agreement of early DFT calculations in this case. For the other ferromagnets however it becomes evident from Table I that these contributions can by no means be neglected. For Fe, e.g., the interstitial contribution is about 50% of that inside a MT sphere and thus leads to considerably improved *ab initio* values. This result indicates the importance of the contributions from the interstitial regions when benchmarking and/or developing improved DFT functionals for orbital magnetism.

TABLE II. Principal values Δg in ppm for the diatomic molecules of the RnF-family calculated by LR (Ref. 10) and with the current method. $\parallel$ is symmetry axis of the dimer. $\Delta g(\Delta M)$ gives the contributions of $\Delta\mathbf{M}_{\text{bare}}$, $\Delta\mathbf{M}_{\text{para}}$, and $\Delta\mathbf{M}_{\text{dia}}$ to the g tensor. A (small) relativistic mass correction term Δg_{RMC} (Ref. 10) is included in both sets of data.

		Linear response	This method	$\Delta g(\Delta M)$
NeF	$\Delta g_{\parallel}$	−336	−328	−414
	$\Delta g_{\perp}$	52633	52778	2935
ArF	$\Delta g_{\parallel}$	−349	−343	−4450
	$\Delta g_{\perp}$	42439	42519	2914
KrF	$\Delta g_{\parallel}$	−360	−353	−968
	$\Delta g_{\perp}$	59920	59674	−1918
XeF	$\Delta g_{\parallel}$	−358	−354	−3733
	$\Delta g_{\perp}$	163369	158190	−55099
RnF	$\Delta g_{\parallel}$	−356	−299	−13670
	$\Delta g_{\perp}$	603082	488594	−255079

In the following we will show that the anisotropies in the orbital magnetizations are well described to allow us to calculate the electronic g tensor of paramagnetic systems, in order to understand the microscopic structure of radicals or paramagnetic defects in solids. From the orbital magnetization we can obtain the deviation of the g tensor, $\Delta g_{\mu\nu}$ from the free-electron value $g_e=2.002\,319$ by the variation in $\mathbf{M}$ with a spin flip:

$$\Delta g_{\mu\nu}=-\frac{2}{\alpha}\mathbf{e}_{\mu}\cdot\frac{\mathbf{M}(\mathbf{e}_{\nu})-\mathbf{M}(-\mathbf{e}_{\nu})}{S-(-S)}=-\frac{2}{\alpha S}\mathbf{e}_{\mu}\cdot\mathbf{M}(\mathbf{e}_{\nu}), \tag{14}$$

where ν, μ are Cartesian directions of the magnetic field, and the total spin S, respectively. To get the full tensor $\Delta g_{\mu\nu}$, for every paramagnetic systems we carry out three calculations by aligning the spin-quantization axis along the three Cartesian directions.

To evaluate the approach, we compute the g tensors of selected diatomic radicals. An energy cutoff of 100 Ry is used in all molecular calculations. They are performed in a cubic repeated cell with a large volume of 8000 Å^3 and the Brillouin zone is sampled only at the Γ point. For comparison, we also compute the g-tensor via the LR method,[10] which we recently implemented in the QUANTUM-ESPRESSO package. For a wide range of molecular radicals including almost all of the examples discussed in Ref. 10, the approach reproduces the values obtained via LR within a few ppm (see also auxiliary Table I in Ref. 21). In Tables II and III we report the calculated principal components of the computed g tensors for the RnF and PbF families. For the members of the RnF family qualitative deviations are only observed if heavy elements like Xe and Rn are involved, showing in LR large deviations $\Delta g_{\perp}$ of up to 10^5 ppm from g_e for the corresponding fluorides. The treatment of SO-coupling beyond

TABLE III. Calculated principal values Δg in ppm for the diatomic molecules of the PbF-family. See Table II for details.

		Linear response	This method	$\Delta g(\Delta M)$
CF	$\Delta g_{\parallel}$	$-\infty$	−1999719	−119746
	$\Delta g_{\perp}$	1920	−553	−240
SiF	$\Delta g_{\parallel}$	$-\infty$	−1995202	−100021
	$\Delta g_{\perp}$	−480	−2470	−535
GeF	$\Delta g_{\parallel}$	$-\infty$	−1998078	−40609
	$\Delta g_{\perp}$	−15505	−39101	−388
SnF	$\Delta g_{\parallel}$	$-\infty$	−1996561	−72464
	$\Delta g_{\perp}$	−64997	−142687	−5339
PbF	$\Delta g_{\parallel}$	$-\infty$	−1999244	−90214
	$\Delta g_{\perp}$	−288383	−556326	−22476

LR leads to considerably smaller values of $\Delta g_{\perp}$, reduced by 3% (XeF) and 19% (RnF), respectively. Note that the reconstruction terms, Eqs. (11)–(13), significantly contribute to the g tensor. For the RnF family (see Table II) this is essential to obtain a value of $\Delta g_{\parallel} \approx 0$ (Ref. 22) as also expected analytically.[23]

In contrast to the RnF family (five electrons in the p shell, $e^4 a_1^1$ electronic configuration), the PbF family has only one electron within the p shell. Without SO-coupling the unpaired electron occupies a degenerate e level. Consequently, without SO, the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap between the unpaired electron and the empty levels is zero, leading within LR to diverging values $g_{\parallel}$. This failure of LR is observed for all members of the PbF family, already for CF containing light elements exclusively. In contrast, our method circumvents perturbation theory, and predicts a nearly vanishing g value $g_{\parallel} = g_e + \Delta g_{\parallel} \approx 0$ along the bond direction of the diatomic molecules as expected analytically.[23]

In conclusion, we have shown how a recently developed formula for the orbital magnetization can be applied in an *ab initio* pseudopotential scheme whereby the spin-orbit coupling enters explicitly the self-consistent cycle. In comparison with linear response methods, our approach allows an improved calculation of the electronic g tensor of paramagnetic systems containing heavy elements or with large deviations of the g tensor from the free-electron value. The latter situation is encountered in many paramagnetic centers in solids, such as those exhibiting a Jahn-Teller distortion[24] and/or containing transition metal impurities. In addition, our method provides improved orbital magnetizations with respect to the pre-existing approaches that neglect the contributions of the interstitial regions. This has been shown for the highly ordered ferromagnets where the orbital contribution is partially quenched by the crystal field. The presented approach is perfectly suited to describe also the ferromagnetism of nanostructures where the orbital quench is weaker and the orbital part of the magnetic moments becomes more dominant.

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[23] Along the bond direction (in absence of SO) the angular momentum is a good quantum number leading to $g_{\parallel} \approx g_e + 2m_l$: for the PbF family $g_{\parallel} \approx 0$ (the unpaired electron occupies the $m_l = -1$ p-like orbital); for the RnF family $m_l = 0$ and, thus, $g_{\parallel} \approx g_e$.

[24] The method is, e.g., applicable in case of some intrinsic defects (silicon antisites) in the compound semiconductor SiC where LR fails to achieve convergence with respect to k points; U. Gerstmann *et al.* (unpublished).