Orbital Polarization in Itinerant Magnets

I. V. Solovyev
Computational Materials Science Center, National Institute for Materials Science,
1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

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We propose a parameter-free scheme of calculation of the orbital polarization (OP) in metals, which starts with the strong-coupling limit for the screened Coulomb interactions in the random-phase approximation (RPA). For itinerant magnets, RPA can be further improved by restoring the spin polarization of the local-spin-density approximation (LSDA) through the local-field corrections. The OP is then computed in the static GW approach, which systematically improves the orbital magnetization and the magnetic anisotropy energies in transition-metal and actinide compounds.

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An electron in solid can carry spin ($M_S$) and orbital ($M_L$) magnetic moment. For weakly correlated systems, the problem of spin magnetism alone can be formulated in the fully itinerant fashion, meaning that the effect of other electrons onto a given one can be described by an exchange-correlation field (or spin polarization). The field is typically evaluated in the model of homogeneous electron gas, in the basis of plane waves, which is a limiting case of the extended Bloch waves. This constitutes the ground of the Kohn-Sham (KS) formalism within LSDA, which works exceptionally well for the magnetic spin properties of many transition-metal and actinide compounds. They form an extended group of what is currently called the “itinerant electron magnets”.

The orbital magnetism is an atomic phenomenon. In the majority of cases, it is driven by the spin-orbit interaction (SOI), being proportional to the gradient of the one-electron potential, $\nabla V$, which is large only in a small core region close to the atomic nucleus. Furthermore, the angular momentum operator, $L^z$, does not commute with $\hat{V}$. Generally, $\hat{L}^z$ is not an observable quantity, except the same core region, where $\hat{V}$ is spherically symmetrical. Therefore, it is more natural to formulate the problem in the basis of Wannier orbitals $\{\phi_\alpha\}$ ($\alpha$ being a joint spin-orbital index), localized around each atomic site. Then, the orbital moment $M_L=\text{Tr}_{LS}\{\hat{L}^z\hat{n}\}$ is specified by the local density matrix $\hat{n}=\|n_{\alpha\beta}\|$ ($\text{Tr}_{LS}$ being the trace over spin and orbital variables), where $n_{\alpha\beta}=\sum_i n_i d_{\alpha \beta}^\dagger d_{\beta \alpha}$. Then, the orbital moment $M_L=\text{Tr}_{LS}\{\hat{L}^z\hat{n}\}$ is specified by the local density matrix $\hat{n}=\|n_{\alpha\beta}\|$ ($\text{Tr}_{LS}$ being the trace over spin and orbital variables), where $n_{\alpha\beta}=\sum_i n_i d_{\alpha \beta}^\dagger d_{\beta \alpha}$. $\phi_\alpha$ denotes the projection of KS eigenstate $\psi_i$ onto $\phi_\alpha$, $n_i$ is the KS occupation number corresponding to the eigenvalue $\epsilon_i$, and the joint index $i$ stands for the spin, band, as well as the position of the $k$-point in the first Brillouin zone (BZ).

In an analogy with the spin polarization for itinerant magnets, one can think of an OP: an exchange-correlation field in KS equations, which couples with $M_L$. Despite a genuine interest to the problem and wide perspectives of their potential applications, the theories of OP in metals are still in a developing “semi-empirical” stage, as they largely depend on the input parameters, which are typically chosen to fit the experimental data.

Although majority of researches agree that OP is controlled by intra-atomic interactions, which are strongly screened in metals, the details of this screening as well as the form of the OP itself remains to be a largely unresolved and disputed problem.

Therefore, there are two important questions, which we would like to address in this work. (i) How the bare on-site interaction $u_{\alpha\beta\gamma\delta}=\langle \phi_\alpha \phi_\gamma \rangle / |\langle 1/2 \phi_\beta \phi_\delta \rangle|$ between $d$- or $f$-electrons is screened in metals? What is the main mechanism of this screening? (ii) Is there any simple and reliable way to evaluate this screening in ab initio calculations of OP?

In the atomic limit, the full matrix $\hat{u}=u_{\alpha\beta\gamma\delta}$ is controlled by a small number of Slater integrals $\{F^k\}$. Then, there is an old empirical rule $F$, which states that in metals, the screening affects mainly $F^0$, which contribute to the Coulomb matrix elements $u_{0\alpha\gamma\gamma}$. Other Slater integrals, which control the exchange and nonsphericity of Coulomb interactions do not change so much.

First, we argue that the same type of screening can be naturally obtained in RPA, in the fully deterministic fashion. The screened interaction in RPA $\tilde{U}\omega$ depends on the polarization $\hat{P}=\|P_{\alpha\beta\gamma\delta}\|$, which is treated in the approximation of noninteracting KS quasiparticles:

$$ \tilde{U}\omega = \left[1 - \hat{\mu}(\omega)\right]^{-1}\tilde{u}, $$

(1)

The $\omega$-dependence of $\hat{\mu}$ contributes mainly to the redistribution of the spectral density, whereas the $\omega$-integrated ground-state properties are controlled by $\hat{U}\equiv\hat{U}(0)$. Therefore, we consider only the static limit, in which RPA describes the screening of $\hat{u}$ caused by the relaxation of $\{\psi_i\}$ upon removal or addition of an electron in terms of the perturbation-theory expansion.

The simplest toy model, which illustrates the physics, may consist of two spin-polarized bands, formed by $yz$ (1) and $zx$ (2) orbitals. The model is compatible with the...
orbital magnetization in the (001) direction. Adopting
the following order of orbitals (within one spin channel):
\( \alpha_\beta (\gamma \delta) = 11, 22, 12, \) and 21, it is easy to show that
\[
\hat{u} = \begin{pmatrix}
  u & u' & 0 & 0 \\
  u' & u & 0 & 0 \\
  0 & 0 & u & 0 \\
  0 & 0 & 0 & u \\
\end{pmatrix},
\]
(3)
where \( u = F_0 + \frac{4}{9} F_2 + \frac{36}{441} F_4, \)
and \( u' = u - 2j. \) Due to the orthogonal
ty of the \( yz \) and \( xz \) orbitals, the Coulomb
\((\alpha_\beta = 11, 22, \) and 21) matrix elements are fully decoupled from each other.
In order to illustrate the main idea of RPA-screening,
\( P \) can be taken in the form
\( P_{\alpha_\beta \gamma \delta} = \delta_{\alpha \gamma} \delta_{\beta \delta} \) [13], which yields:
\( U = [u - (u^2 - u^2)P] / (1 - uP)^2 - (u^2P)^2, \)
\( U' = u' / (1 - uP)^2 - (u^2P)^2, \) and \( J = j / (1 - jP). \) There is
a certain hierarchy of bare interactions, and for many
metals the screening of \( u \) and \( j \) falls in the
strong- and weak-coupling regime, respectively, so that \( u|\mathcal{P}| \geq 1 \)
while \( j|\mathcal{P}| \ll 1[13]. \) This yields:
\( U \approx -1/(2P) + 2J, \)
\( U' \approx -1/(2P), \) and \( J \approx j. \) Thus, the inverse
polarization, which plays a role of effective Coulomb
interaction in metals [12]. \( U \) is strongly screened and
does not depend on the value of bare interaction. On
the other hand, \( J \) is insensitive to the screening. The
multiplier \( 1/2 \) in the expressions for \( U \) and \( U' \) stands for
the orbital degeneracy. The result can be easily
generalized for an arbitrary number of orbitals \( M \) (\( M = 5 \) \)
and 7 for \( d^\text{-} \) and \( f^\text{-} \)electrons, respectively),
which yields \( U' \approx -1/(MP) \) [2]. In this case, in order to justify
the strong-coupling regime, it is sufficient to have a
milder condition, \( u|\mathcal{P}| \geq 1, \) which naturally explains
the empirical rule [3].

All these trends are clearly seen in the first-principles
calculations for realistic materials shown in Fig. [11][13],
where all Slater integrals except \( F_0 \) were calculated
inside atomic spheres, and \( F_0 \) was treated as a parameter.
When \( F_0 \) increases, the effective interactions quickly
reach the asymptotic limit \( F_0 \rightarrow \infty, \) where \( \hat{U} \) is fully
determined by details of the electronic structure, through
the polarization \( \hat{P}, \) and do not depend on \( F_0. \) This
removes the main ambiguity with the choice of interaction
parameters for metallic compounds. Since \( \hat{P} \) depends on
the local environment in solid, the screened interactions
are different for different types of Wannier orbitals
\((e.g., e_g \) and \( t_{2g} \) for \( d^\text{-} \)electrons in the cubic environment).

Thus, OP in the itinerant magnets can be naturally
evaluated in the framework of a universal parameter-
free scheme based on the strong coupling limit for the
matrix of effective Coulomb interactions \( \hat{U}. \) The self-
energy, incorporating the effects of OP, can be calculated
within static approximation in the GW method [11]:
\[
\Sigma_{\alpha_\beta} = - \sum_{\gamma \delta} U_{\alpha_\beta \gamma \delta} n_{\gamma \delta}.
\]
(4)
The proper correction to the KS Hamiltonian in LSDA
is controlled by \( \Delta n = - \sum_{\gamma \delta} \sum_{r \in \{g, s\}} \text{Tr}_{LS} (\sigma_{\gamma \delta} n_{\gamma \delta}). \) It is obtained
after subtracting the charge \((r=0) \) and spin \((r=1, \)
2, and 3) density elements of \( \hat{n} \), which are already taken
into account in LSDA (\( \sigma_0 \) being the unity matrix, and
\( \sigma_1, \sigma_2, \) and \( \sigma_3 \) being the Pauli matrices of the dimension
2). Therefore, in the actual calculations we use the
change of the self-energy \( \Delta \Sigma, \) which was obtained after
replacing \( \hat{n} \) by \( \Delta \hat{n} \) in Eq. (4). The problem was solved
self-consistently with respect to \( \Delta \hat{n}. \)

The validity of the strong-coupling approach is well
justified. So, the effective Coulomb interaction between
\( t_{2g} \) electrons in bcc Fe can be estimated in RPA as 1.50,
1.47, and 1.37 eV for \( F_0 = \infty, \) 21 eV (the bare Slater
integral inside atomic sphere), and 4.5 eV (the value
obtained in the constraint-LSDA, which includes the
screening by the \( sp^\text{-} \)electrons [12]), respectively. Thus, even
if one takes the lowest estimate \( F_0 \approx 4.5 \) eV, the additional
approximation \( F_0 \rightarrow \infty \) within RPA would overestimate
\( U \) by less than 10%. For \( f^\text{-} \)electrons, this error is even
smaller due to the higher orbital degeneracy.

However, this is not the main source of the error. A
more fundamental problem is related with the RPA itself,
which typically underestimates the spin polarization
\( \Delta \Sigma_{\text{RPA}} = \text{Tr}_{LS} (\Sigma_{\text{RPA}}), \) meaning that even for the upper
limit in RPA, corresponding to \( F_0 \rightarrow \infty, \) the effective
Coulomb interaction is overscreened and underestimated.
For example, had we replaced the spin part of LSDA
by the one of RPA, the spin moment would be underestimated.
Obviously, this would destroy the most attractive
point of LSDA for itinerant electron magnets. Therefore,
there is certain inconsistency in the RPA approach.

RPA can be improved by introducing the local-field
factor \( g, \) which incorporates the effects of
exchange-correlation hole for the polarization matrix:
\( (P)^{-1} = (P_{\text{RPA}})^{-1} - \hat{g}. \) Other corrections can be formally
reduced to \( \hat{g} [14]. \) Our goal is to find such a correction
to the matrix of effective Coulomb interactions, which after
substitution in Eq. (4) would yield the same spin
polarization as LSDA (\( \Delta \Sigma_{\text{LSDA}} \)). In order to do so, we search
\( \hat{g} \) in the form of local diagonal matrix: \( g_{\alpha\beta\gamma\delta} = g_{\delta\alpha\beta\gamma} \).

Then, the asymptotic part of the effective Coulomb interaction and the self-energy can be easily recalculated using Eqs. (1) and (2), respectively, and the unknown parameter \( g \) is obtained from the condition \( \text{Tr}_{LS} \{ \hat{\Sigma} \} = \Delta^{LS\text{DA}} \), which is solved self-consistently together with the KS equations. In the following, this method will be referred to as corrected-RPA (c-RPA).

Let us consider first the canonical example of ferromagnetic transition metals (Fig. 2), where \( M_L \) is small and typically regarded as a small perturbation to the spin-dependent properties. \( M_S \) and \( M_L \) can be measured separately using the x-ray magnetic circular dichroism combined with the spin and orbital sum rules (17). Despite an apparent simplicity, LSDA encounters a wide spectrum of problems for bcc Fe, hcp Co, and fcc Ni. We will argue that many of them can be systematically corrected by applying consequently RPA and c-RPA techniques.

LSDA has certain tendency to overestimate \( M_S \) in bcc Fe and underestimate \( M_L \), while RPA and especially c-RPA substantially improve the LSDA description and yield a good agreement with the experimental data. The values of \( M_S \) (\( M_L \)) obtained in LSDA, RPA, and c-RPA are 2.26 (0.04), 2.21 (0.05), and 2.20 (0.06) \( \mu_B \), respectively, to be compared with the experimental moments of 2.13 (0.08) \( \mu_B \) (3). Hcp Co has the largest orbital moment among pure transition metals (\( M_L = 0.14 \mu_B \)), which is strongly underestimated in LSDA (\( M_L = 0.08 \mu_B \)). The situations is substantially improved in RPA (\( M_L = 0.10 \mu_B \)) and c-RPA (\( M_L = 0.11 \mu_B \)). Fcc Ni is a rare example of ferromagnetic systems for which \( M_L = 0.05 \mu_B \) is well reproduced already in LSDA. Both RPA and c-RPA preserve this good feature of LSDA and do not substantially change \( M_L \). However they do change the electronic structure of fcc Ni. Namely, the form of Fermi surface (FS) of fcc Ni has been intensively discussed in the context of the magnetocrystalline anisotropy energy (MAE). It was argued that the reason why LSDA fails to reproduce the correct \( \langle 111 \rangle \) direction of the magnetization is related with the second pocket of the FS around the X-point of BZ, which is not seen in the experiment (3). The experimental FS can be reproduced in the LSDA+U approach, by treating \( U \) as an adjustable parameter (3). Therefore, it is important that the same problem can be successfully resolved both in RPA and c-RPA, without any adjustable parameters. The calculated FS, which reveals only one pocket around the X-point, is shown in the inset of Fig. 2.

The uranium pnictides (\( UX \), where \( X = \text{N, P, As, Sb, and Bi} \)) and chalcogenides (\( X = \text{S, Se, and Te} \)) are ones of the most studied actinide compounds. They crystallize in the rock-salt structure. All chalcogenides are ferromagnets, whereas the pnictides have type-I antiferromagnetic structure, which may also transform into a multi-\( k \)-structure. The basic difference from the transition metals is that \( M_L \) in actinides, which can be extracted from the analysis of magnetic form factors (18), is very large and typically dominates over \( M_S \). According to the third Hund rule, \( M_S \) and \( M_L \) in \( UX \) are coupled antiferromagnetically. As the U-U distance increases, the \( U(5f) \) states become more localized, and all magnetic moments increase monotonously from UN to UBi and from US to UTe (Fig. 3). UN and US are usually classified as itinerant magnets. However, the role of intra-atomic correlations is expected to increase for the end-series compounds. Obviously, the real ab initio scheme does not know whether the system is itinerant or not. Therefore, it is important to test both RPA and c-RPA methods for all considered compounds in order to see how they will work for the materials with the different character of the 5f-electrons. The orbital moments are systematically underestimated in LSDA. The error is really large so that the total magnetic moments are typically off the experimental values by 20-50%. RPA systematically improves the LSDA description. However, it is not enough, and for many uranium compounds it is essential to go beyond RPA. For these purposes, c-RPA works exceptionally well and further improves the RPA description. Particularly, we note an excellent agreement with the ex-
perimental data for $X = S$, P, and As. For the end-series compounds ($X= Te$, Sb, and Bi) the agreement is not so good, signalling at the necessity of more radical improvements, involving both orbital and spin polarization of LSDA. However, even for these complicated systems, c-RPA is a big step forward over conventional LSDA.

Finally, let us discuss applications for the MAE. We consider two characteristic examples: CoPt and US. The ordered tetragonal CoPt alloys is a promising candidate for magnetic recording applications. An intriguing point is that although LSDA underestimates $M_L$, MAE is reproduced surprisingly well (Fig. 4). Therefore, the “correct” OP in CoPt should affect only $M_L$. This requirement is well satisfied both for RPA and c-RPA. The orbital moments systematically increase in the direction LSDA→RPA→c-RPA to reach $M_L^{\text{c-RPA}}=0.14\mu_B$ and $M_L^{\text{RPA}}=0.07\mu_B$. The anisotropy of $M_L$ also increases (mainly at Co-sites). However, the MAE does not change so much because of large cancellation of on-site interaction energies associated with Co and Pt sites.

**FIG. 4:** (Color online) Magnetocrystalline anisotropy energy ($\Delta E$) and the anisotropy of orbital magnetization ($\Delta M_L$). For each quantity, the anisotropy is defined as the difference between values corresponding to the $\langle 100 \rangle$ and $\langle 001 \rangle$ (CoPt), and $\langle 100 \rangle$ and $\langle 111 \rangle$ (US) directions of the magnetization. The experimental values are taken from Ref. 8 (CoPt, at 293 K) and Ref. 11 (US). For CoPt, the values of $M_S$ and $M_L$ in the $\langle 001 \rangle$ direction are shown in the left part of the figure. Other notations are the same as in Fig. 2.

US has the largest MAE among cubic compounds 19, which is underestimated in LSDA. The situation is corrected in c-RPA, at least qualitatively. It is curious that MAE “anticorrelate” with the anisotropy of orbital magnetization, which decreases in the direction LSDA→RPA→c-RPA. However, this is not surprising, because in cubic compounds, MAE is the forth order effect with respect to SOI. Therefore, there is no simple relation between $\Delta E$ and $\Delta M_L$ and the main correction to MAE in c-RPA comes from the change of the on-site interaction energy.

In summary, we have argued that the problem of OP in metals can be naturally formulated “from the first principles”, by considering the strong-coupling limit for the screened Coulomb interactions. In the present work, the screened $U$ was computed only once: in LSDA and without SOI. An important extension would be a self-consistent determination of $U$, which would incorporate the effects of OP into the screening. (i) It could improve the description of some itinerant actinide compounds (e.g., UN) for which the spin polarization is small, and the screening is strongly influenced by SOI. (ii) Since the OP affects the KS eigenvalues $\{\varepsilon_i\}$, which stand in the denominator of the polarization matrix 2, the screening is expected to decrease. This could extend the applicability of the proposed method for materials with more localized $5f$- and $4f$-electrons.

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