Orbital Polarization in Itinerant Magnets

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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 through the local-field corrections. The OP is then computed as the self-energy correction in the static GW method, 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 local-spin-density approximation (LSDA) [1], 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, $\nabla\hat{V}$, which is large only in a small core region close to the atomic nucleus. Furthermore, the angular momentum operator, $\hat{L}^z$, does not commute with $\hat{V}$, and M_L is not an observable quantity, unless it belongs to the same core region where $\hat{V}$ is spherically symmetrical. Therefore, it is more natural to formulate the problem in the basis of Wannier functions $\{\phi_\alpha\}$ (α being a joint spin-orbital index), constructed for the magnetic d or f electrons and well localized around each atomic site [2]. Then, the orbital moment $M_L = \text{Tr}_{LS}\{\hat{L}^z\hat{n}\}$ is specified by the local density matrix $\hat{n} = \| n_{\alpha\beta} \|$ (Tr_{LS} being the trace over spin and orbital variables), where $n_{\alpha\beta} = \sum_i n_i d_{\alpha i} d^\dagger_{\beta i}$, $d_{\alpha i} = \langle \phi_\alpha | \psi_i \rangle$ is the projection of KS eigenstate ψ_i onto ϕ_α, n_i is the KS occupation number corresponding to the eigenvalue ε_i, and the joint index i stands for the spin, band, as well as the position of the $\mathbf{k}$ point in the first Brillouin zone (BZ).

In an analogy with the spin polarization for itinerant magnets, one can think of an orbital polarization (OP): an exchange-correlation field in KS equations, which couples with M_L. Despite a genuine interest in the problem and wide perspectives of their potential applications, the theories of OP in metals are still in a developing "semiempirical" stage, as they largely depend on the input parameters, which are typically chosen to fit the experimental data. Although the majority of researchers 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 [3–8].

Therefore, there are two important questions that we address in this Letter: (i) How are the bare on-site interactions $u_{\alpha\beta\gamma\delta} = \langle \phi_\alpha \phi_\gamma | 1/r_{12} | \phi_\beta \phi_\delta \rangle$ 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 $\hat{u} = \| u_{\alpha\beta\gamma\delta} \|$ for the d or f shell is controlled by a small number of Slater integrals $\{F^k\}$. Then, an old empirical rule states that in metals, the screening affects mainly F^0, which contributes to the Coulomb matrix elements $u_{\alpha\alpha\gamma\gamma}$. Other Slater integrals, which control the exchange and nonsphericity of Coulomb interactions, do not change so much [9].

First, we argue that the same type of screening can be naturally obtained in random-phase approximation (RPA), in the fully deterministic fashion. The screened interaction in RPA [10,11],

$$\hat{U}(\omega) = [1 - \hat{u}\hat{P}(\omega)]^{-1}\hat{u}, \tag{1}$$

depends on the polarization $\hat{P} = \| P_{\alpha\beta\gamma\delta} \|$, which is treated in the approximation of noninteracting KS quasiparticles:

$$P^{\text{RPA}}_{\alpha\beta\gamma\delta}(\omega) = \sum_{ij} \frac{(n_i - n_j) d^\dagger_{\alpha j} d_{\beta i} d^\dagger_{\gamma i} d_{\delta j}}{\omega - \varepsilon_j + \varepsilon_i + i\delta(n_i - n_j)}. \tag{2}$$

The ω dependence of $\hat{P}$ contributes mainly to the redistribution of the spectral density, whereas the ω-integrated ground-state properties are controlled by $\hat{U} \equiv \hat{U}(0)$. Therefore, we consider only the static case, which 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 [12].

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 $\langle 001 \rangle$ 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

$$\hat{u} = \begin{pmatrix} u & u' & 0 & 0 \\ u' & u & 0 & 0 \\ 0 & 0 & 0 & j \\ 0 & 0 & j & 0 \end{pmatrix}, \tag{3}$$

where $u = F^0 + \frac{4}{49}F^2 + \frac{36}{441}F^4$, $j = \frac{3}{49}F^2 + \frac{20}{441}F^4$, and $u' = u - 2j$. Because of the orthogonality of the yz and zx orbitals, the Coulomb ($\alpha\beta = 11, 22$) and exchange ($\alpha\beta = 12, 21$) matrix elements are fully decoupled from each other. In order to illustrate the main idea of RPA screening, $\hat{P}$ can be taken in the form $P_{\alpha\beta\gamma\delta} = P\delta_{\alpha\delta}\delta_{\beta\gamma}$ [2], which yields $U = [u - (u^2 - u'^2)P]/[(1 - uP)^2 - (u'P)^2]$, $U' = u'/[(1 - uP)^2 - (u'P)^2]$, 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 regimes, respectively, so that $u|P| \gg 1$ while $j|P| \ll 1$ [12]. This yields $U \simeq -1/(2P) + 2J$, $U' \simeq -1/(2P)$, and $J \simeq j$. Thus, this is 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 easily be generalized for an arbitrary number of orbitals M ($M = 5$ and 7 for d and f electrons, respectively), which yields $U' \simeq -1/(MP)$ [2]. Then, in order to justify the validity of the strong-coupling limit, it is sufficient to have a milder condition: $uM|P| \gg 1$.

All these trends are clearly seen in the first-principles calculations for realistic materials shown in Fig. 1 [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 $F^0 \to \infty$, 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 can be different for different types of Wannier orbitals (e.g., e_g and t_{2g} for d electrons in the cubic environment).

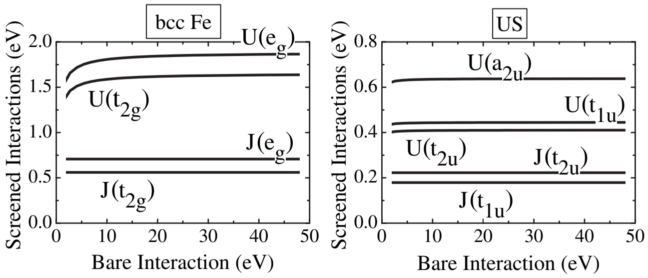

FIG. 1. Effective Coulomb and exchange interactions in RPA versus bare Slater integral F^0 for $3d$ states in bcc Fe and $5f$ states in uranium sulfide. The symbols denote the matrix elements corresponding to different representations of the point group O_h. The calculations have been performed in the ferromagnetic state without spin-orbit coupling.

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 exchange-correlation self-energy, incorporating the effects of OP, can be calculated within static approximation in the GW method [10], obtained after replacing $\hat{U}(\omega)$ by $\hat{U}(0)$:

$$\Sigma_{\alpha\beta} = -\sum_{\gamma\delta} U_{\alpha\delta\gamma\beta} n_{\gamma\delta}. \tag{4}$$

The proper correction to the KS Hamiltonian in LSDA is controlled by $\Delta\hat{n} = \hat{n} - \frac{1}{2M}\sum_{r=0}^{3} \mathrm{Tr}_{LS}\{\hat{\sigma}_r \hat{n}\}\hat{\sigma}_r$. It is obtained after subtracting the charge ($r = 0$) and spin ($r = 1$, 2, and 3) density elements of $\hat{n}$, which are already included in the LSDA part ($\hat{\sigma}_0$ being the unity matrix, and $\hat{\sigma}_1$, $\hat{\sigma}_2$, and $\hat{\sigma}_3$ being the Pauli matrices of the dimension $2M$). Thus, in the actual calculations we use the change of the self-energy $\Delta\hat{\Sigma}$, obtained after replacing $\hat{n}$ by $\Delta\hat{n}$ in Eq. (4). It was incorporated into KS equations via projector operators, $\sum_{\alpha\beta}|\phi_\alpha\rangle\Delta\Sigma_{\alpha\beta}\langle\phi_\beta|$, and 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 the atomic sphere), and 4.5 eV (the value obtained in the constraint LSDA, which includes the screening by the sp electrons [12]), respectively. Thus, even if one takes the lowest estimate $F^0 = 4.5$ eV, the additional approximation $F^0 \to \infty$ within RPA would *overestimate* U by less than 10%. For f 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 to the RPA itself, which typically underestimates the spin polarization $\Delta^{\mathrm{RPA}} = \mathrm{Tr}_{LS}\{\hat{\Sigma}\hat{\sigma}_3\}$, meaning that even for the upper limit in RPA, corresponding to $F^0 \to \infty$, 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 the exchange-correlation hole for the polarization matrix: $(\hat{P})^{-1} = (\hat{P}^{\mathrm{RPA}})^{-1} - \hat{g}$. 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 ($\Delta^{\rm LSDA}$). In order to do so, we search $\hat{g}$ in the form of the local diagonal matrix: $g_{\alpha\beta\gamma\delta} = g\delta_{\alpha\beta}\delta_{\gamma\delta}$. Then, the asymptotic part of the effective Coulomb interaction and the self-energy can be easily recalculated using Eqs. (1) and (4), respectively, and the unknown parameter g is obtained from the condition ${\rm Tr}_{LS}\{\hat{\Sigma}\hat{\sigma}_3\} = \Delta^{\rm LSDA}$, which is solved self-consistently together with the KS equations. In the following, this method is referred to as corrected RPA (c-RPA).

In ferromagnetic transition metals, 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 gyromagnetic ratios, the neutron scattering, and the x-ray magnetic circular dichroism (XMCD) [15] (Fig. 2). Despite an apparent simplicity, LSDA encounters a wide spectrum of problems for bcc Fe, hcp Co, and fcc Ni. We argue that many of them can be systematically corrected by applying consequently RPA and c-RPA techniques. LSDA has a 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) μ_B, respectively, to be compared with the experimental moments of 2.13 (0.08) μ_B [5]. The 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 situation is substantially improved in RPA ($M_L = 0.10\mu_B$) and c-RPA ($M_L = 0.11\mu_B$). The 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 the 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 to the second pocket of the FS around the X point of the BZ, which is not seen in the experiment [7]. The experimental FS can be reproduced in the LSDA + U approach by treating U as an adjustable parameter [7]. Therefore, it is important that the same problem can be successfully resolved in both 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.

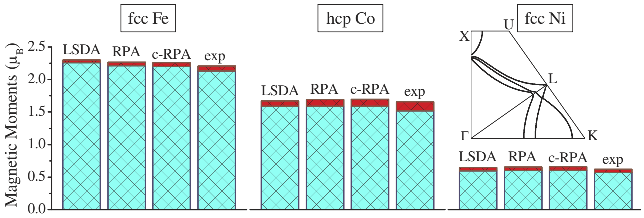

FIG. 2 (color online). Spin (light blue area), orbital (dark red area), and total (full hatched area) magnetic moments in ferromagnetic transition metals. The experimental data are taken from Ref. [5]. The inset shows the Fermi surface of fcc Ni in the c-RPA approach.

The uranium pnictides (UX, where X = N, P, As, Sb, and Bi) and chalcogenides (X = S, Se, and Te) are some of the most studied actinide compounds. They crystallize in the rock-salt structure. All chalcogenides are ferromagnets, whereas the pnictides have a type-I antiferromagnetic structure, which can also transform into a multi-$\mathbf{k}$ 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 [4,16], 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 materials with different characters 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

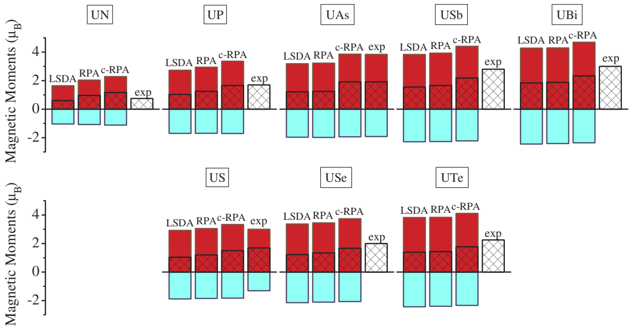

FIG. 3 (color online). Magnetic moments in uranium pnictides (top) and chalcogenides (bottom). The pnictides (chalcogenides) have been computed in the type-I antiferromagnetic (ferromagnetic) structure with $\langle 001\rangle$ ($\langle 111\rangle$) direction of the magnetization. The symbol "exp" shows the results of neutron diffraction, which were separated into spin and orbital contributions for US (Ref. [4]) and UAs (Ref. [16]). Other notations are the same as in Fig. 2.

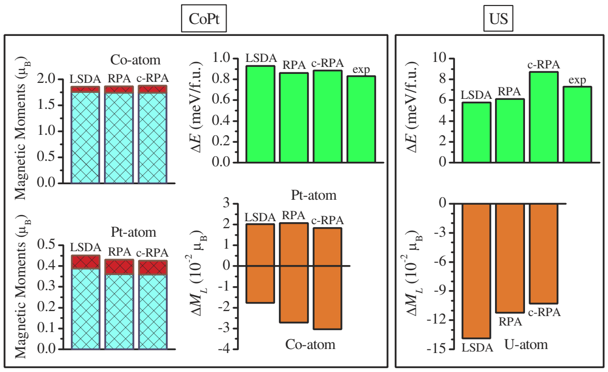

FIG. 4 (color online). Magnetocrystalline anisotropy energy (ΔE) and the anisotropy of orbital magnetization (ΔM_L). For each quantity, the anisotropy is defined as the difference between values corresponding to the ⟨100⟩ and ⟨001⟩ (CoPt), and ⟨100⟩ and ⟨111⟩ (US) directions of the magnetization. The experimental values are taken from Ref. [8] (CoPt, at 293 K) and Ref. [18] (US). For CoPt, the values of M_S and M_L in the ⟨001⟩ direction are shown in the left part of the figure. Other notations are the same as in Fig. 2.

experimental data for $X = \text{S}$, P, and As. For the end-series compounds ($X = \text{Te}$, Sb, and Bi) the agreement is not so good, signaling 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 are promising candidates for magnetic recording applications. An intriguing point is that, although LSDA underestimates M_L, MAE is reproduced surprisingly well (Fig. 4) [8]. Therefore, the "correct" OP in CoPt should affect only M_L. This requirement is well satisfied in both RPA and c-RPA. The orbital moments systematically increase in the direction LSDA → RPA → c-RPA to reach $M_L^{\text{Co}} = 0.14\mu_B$ and $M_L^{\text{Pt}} = 0.07\mu_B$ [17]. The anisotropy of M_L also increases (mainly at Co sites). However, the MAE does not change so much because of the large cancellation of the exchange-correlation energies associated with Co and Pt sites [8].

US has the largest MAE among cubic compounds [18], which is underestimated in LSDA. The situation is corrected in c-RPA, at least qualitatively, due to the change of the exchange-correlation energy. It is curious that MAE "anticorrelate" with the anisotropy of M_L, which *decreases* in the direction LSDA → RPA → c-RPA.

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 $\hat{U}$ was computed only once: in LSDA and without SOI. An important extension would be the self-consistent calculation of $\hat{U}$, 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 the SOI. (ii) Since the OP removes the d and f states from the Fermi level, 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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