Is Hund's Second Rule Responsible for the Orbital Magnetism in Solids?

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We argue that the key parameter responsible for the exchange-correlation enhancement of the orbital magnetic moments in solids is "Hubbard U" rather than the intra-atomic Hund's second rule coupling, being consistent with a more general concept of the orbital polarization. This leads us to a unified rotationally invariant local density approximation (LDA) + U prescription for the orbital magnetism. Validity of the present theory is demonstrated by numerical calculations, which perfectly account for the orbital magnetism as well as the canted magnetic structure in CoO. [S0031-9007(98)06455-2]

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Novel phenomena caused by strong coupling among spin, orbital, and lattice degrees of freedom are the central issue in the physics of transition-metal compounds for the last few years. One of the modes, when this coupling is mediated by the relativistic spin-orbit interaction (SOI) leads to the orbital magnetism, which is manifested in the magnetocrystalline anisotropy, magneto-optical effects, magnetic x-ray circular dichroism, etc. It may even be a routine work to incorporate the relativistic effects in the modern band structure techniques based on the local-(spin)-density approximation [L(S)DA]. However, the result is rather discouraging: calculated orbital moments are typically too small compared with experiment [1–5]. Besides many limitations of LSDA caused by the homogeneous electron gas picture for exchange and correlation, which is incompatible with the orbital magnetism, the failure may imply an even more fundamental problem in the framework of the density functional theory (DFT). LSDA is the *spin* DFT, where the total energy $E_{\mathrm{LSDA}}[\rho,\mathbf{m}]$ is the explicit functional of the charge $\rho(\mathbf{r})$ and the spin-magnetization $\mathbf{m}(\mathbf{r})$ densities. Even if an exact spin-DFT should be able to include all magnetic orbital effects *implicitly,* there is no guarantee that the orbital-related quantities can be reproduced *explicitly* on the level of fictitious single-particle Kohn-Sham (KS) equations. The explicit formulation for the orbital magnetism gave rise to the concept of orbital polarization (OP) in the band structure calculations. The purpose of this Letter is to clarify the fundamental features, origins, and implications of the OP in the problem of orbital magnetism in solids.

Because of the quenching effects in the crystal field (CF), the orbital moments are expected to be well localized in the spherical potential region near atomic nuclei, and well described in terms of site-diagonal elements of the one-particle density matrix in the basis of atomiclike ($3d$) orbitals $n_{\gamma_1\gamma_2} = \langle\gamma_1|\hat{n}(\mathbf{r},\mathbf{r}')|\gamma_2\rangle$ as $\langle\hat{\mathbf{L}}\rangle = \mathrm{Tr}_{SL}(\hat{\mathbf{L}}\hat{n})$, where $\hat{\mathbf{L}}$ is the orbital angular momentum operator, $\gamma \equiv \{s,m\}$ is the joint index including spin (s) and azimuthal (m) counterparts, and Tr_{SL} denotes the trace over all s and m. The matrix $\hat{n} = \|n_{\gamma_1\gamma_2}\|$ generally consists of both spin-diagonal and spin-nondiagonal elements. The latter can be due to the SOI or a noncollinear magnetic order. This localized nature of the orbital magnetic degrees of freedom has led to formulation of several classes of OP functionals [1,4–7], whose general formula can be written as $E[\rho,\mathbf{m},\hat{n}] = E_{\mathrm{L(S)DA}}[\rho,\mathbf{m}] + \Delta E_{\mathrm{OP}}[\hat{n}]$.

The first idea in this direction belongs to Brandow [8], who realized that parameters of the nonmagnetic LDA band structure in combination with the on-site interactions among $3d$ electrons taken in a renormalized Hartree-Fock (HF) form provide a very realistic electronic picture behind various Mott-Hubbard phenomena. This leads to the LDA + U functional, which in the most recent rotationally invariant form has the following OP term [6,7]:

$$\Delta E_{\mathrm{OP}}^{\mathrm{LDA}+U} = E_{\mathrm{HF}}[\hat{n}] - E_{\mathrm{dc}}[\mathrm{Tr}_L(\hat{n})], \qquad (1)$$

where

$$E_{\mathrm{HF}}[\hat{n}] = \frac{1}{2}\sum_{\{\gamma\}}(U_{\gamma_1\gamma_3\gamma_2\gamma_4} - U_{\gamma_1\gamma_3\gamma_4\gamma_2})n_{\gamma_1\gamma_2}n_{\gamma_3\gamma_4} \qquad (2)$$

is the renormalized HF energy of the on-site $3d$ interactions, whose first term is the direct Coulomb interaction $E_{\mathrm{H}}[\hat{n}]$ and the second term is the exchange interaction $E_{\mathrm{X}}[\hat{n}]$. $E_{\mathrm{dc}}[\mathrm{Tr}_L(\hat{n})]$ is a double-counting term, which does not depend on the orbital degrees of freedom [6]. It is assumed that the renormalization can be described by retaining the (unrenormalized) HF form for the electron-electron (e-e) interactions $U_{\gamma_1\gamma_3\gamma_2\gamma_4} = \langle m_1m_3|\frac{1}{r_{12}}|m_2m_4\rangle\delta_{s_1s_2}\delta_{s_3s_4}$ and tuning three (in the case of d electrons) Slater integrals F^0, F^2, and F^4 [7]. The latter is equivalent to the definition of three physical parameters: the on-site Coulomb repulsion $U = F^0$, $J = \frac{1}{14}(F^2 + F^4)$, and $B = \frac{1}{441}(9F^2 - 5F^4)$. Typically, the behavior of F^2 and F^4 in solids does not differ significantly from the one in atoms and it holds $F^4/F^2 \sim 0.6$ (e.g., [6]), which further leads to the estimate $B \sim 0.1J$. If the orbital populations are integer (0 or 1), it holds $\hat{n}^2 = \hat{n}$. Then, an analog of two Hund's rules can be derived from $E_{\mathrm{HF}}[\hat{n}]$: first, the s-dependent occupation is

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driven by J; second, the m-dependent occupation is driven by B. This is the atomic picture. In solids, however, the local orbital populations are fractional and shall be treated as independent variational degrees of freedom, which is the essence of U dependence of the OP in LDA + U: if B is neglected, OP is determined by $U_{\text{eff}} = U - J$ [8]. As we will explicitly show below, the same is true for the orbital *magnetic* degrees of freedom. Naturally, the spontaneous formation of the orbital moments in LDA + U is closely related with opening a Hubbard gap. Another theory of the orbital magnetism in solids which is based on the similar "Hubbard U" idea is the self-interaction-corrected LSDA [5].

The role of the Hubbard U terms in OP functionals is less clear in the theories designed for another category of magnetic materials, which exhibit clear tendencies to the itinerary and whose spin magnetic properties can be reasonably well described within LSDA. Brooks and collaborators put forward an idea to connect the OP entirely with atomic Hund's 2nd rule coupling, and proposed an *ansatz* for the OP functional (called OPB hereafter), which is based on two assumptions [1]: (i) OP is driven by B; (ii) the functional form itself is given by $\Delta E_{\text{OP}}^{\text{OPB}} = -\frac{1}{2} B \langle \hat{\mathbf{L}} \rangle^2$ with the atomic B value and the expectation value of $\hat{\mathbf{L}}$ taken by use of the KS orbitals including the effects of the OPB functional self-consistently. OPB has attracted considerable attention in the computational electronic-structure community (e.g., Refs. [1–3]) because of its simplicity and relatively encouraging results obtained along this line for several classes of metallic compounds. Norman [4] applied similar ideas to the series of Mott-Hubbard insulators, claiming that only a part of interactions in $E_{\text{H}}[\hat{n}]$ and $E_{\text{X}}[\hat{n}]$, which does not depend on U should be able to open a band gap (no matter how small it is) on the level of ground-state DFT calculations, whereas the actual magnitude of the gap is determined by U and is an excited-state effect. Despite such apparent success, we consider that there are serious confusions in the basic physics of OPB. We will show that (i) the claim that the OPB functional $\Delta E_{\text{OP}}^{\text{OPB}}$ directly follows from the open-shell HF analysis [i.e., Eq. (2)] is *incorrect*, (ii) the actual form of the orbital magnetic enhancement driven by the parameter B in Eq. (2) is different from $\Delta E_{\text{OP}}^{\text{OPB}}$, and (iii) the form of OPB correction can be mimicked by taking into account remaining terms of Eq. (2) and considering the limit of a relatively small, but still finite parameter U. Thus, if the OPB picture is practically meaningful, as is apparently true for many metallic magnets, the "hidden parameter" responsible for the orbital enhancement is again U_{eff}, and OPB is one of the limiting cases of the more general LDA + U concept.

In order to find an explicit expression for the orbital enhancement, we take the following procedure: (i) solve an inverse problem so as to express $\hat{n}$ in terms of the expectation values of the orbital angular momentum operators; (ii) single out all interactions involving these variables in $E_{\text{H}}[\hat{n}]$ and $E_{\text{X}}[\hat{n}]$. First, we extract the spin dependence of the density matrix $\hat{n}$ by a standard decomposition $\hat{n} = \frac{1}{2}\sum_{\nu=0}^{3} \hat{n}^{\nu} \otimes \hat{\sigma}_{\nu}$, where $\hat{\sigma}_0$ is the 2×2 unity matrix and the rest of $\hat{\sigma}_{\nu}$ ($\nu = 1,2,3$) are Pauli matrices ($\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z$). The spinless matrices $\hat{n}^{\nu}$ are given by $\hat{n}^{\nu} = \text{Tr}_S(\hat{\sigma}_{\nu}\hat{n})$. It is rather straightforward to show that $E_{\text{X}}[\hat{n}] = \frac{1}{2}\sum_{\nu=0}^{3} E_{\text{X}}[\hat{n}^{\nu}]$. Taking into consideration the time-inversion $\hat{R}$, each matrix $\hat{n}^{\nu}$ can be further decomposed as $\hat{n}^{\nu} = \hat{n}^{\nu +} + \hat{n}^{\nu -}$, where $\hat{R}\hat{n}^{\nu \pm} = \pm \hat{n}^{\nu \pm}$ [9]. Using the basic property $\hat{R}\hat{\mathbf{L}} = -\hat{\mathbf{L}}$, we get

$$\text{Tr}_L(\hat{\mathbf{L}}\hat{n}^{\nu +}) = 0, \qquad \text{Tr}_L(\hat{n}^{\nu +}) = \langle \hat{\sigma}_{\nu} \rangle,$$
$$\text{Tr}_L(\hat{\mathbf{L}}\hat{n}^{\nu -}) = \langle \hat{\mathbf{L}} \rangle_{\nu}, \qquad \text{Tr}_L(\hat{n}^{\nu -}) = 0,$$

where $\langle \hat{\mathbf{L}} \rangle_{\nu}$ are the orbital momenta in the spin subspace ν. Thus, all spin-density variables $\langle \hat{\sigma}_{\nu} \rangle$ are given by $\hat{n}^{\nu +}$, whereas the orbital part is represented solely by $\hat{n}^{\nu -}$. The contribution of $\hat{n}^{\nu -}$ to $E_{\text{H}}[\hat{n}]$ is vanishing. Since $E_{\text{X}}[\hat{R}\hat{n}^{\nu}] = E_{\text{X}}[\hat{n}^{\nu}]$, one can write $E_{\text{X}}[\hat{n}^{\nu}] = E_{\text{X}}[\hat{n}^{\nu +}] + E_{\text{X}}[\hat{n}^{\nu -}]$. Therefore the e-e interactions responsible for the magnetic part of OP are included only in $E_{\text{X}}[\hat{n}^{\nu -}]$. This is a general property of the exchange energy.

In order to evaluate $E_{\text{X}}[\hat{n}^{\nu -}]$ let us consider first the p-electron shell, the simple example of the system which can carry the orbital moment. Then, the antisymmetric 3×3 matrix $\hat{n}^{\nu -}$ is represented by three nonequivalent elements (in the real harmonics basis): $n_{xy}^{\nu -}$, $n_{yz}^{\nu -}$, and $n_{zx}^{\nu -}$ [9], which can be expressed through the expectation values of three antisymmetric operators $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$ as $n_{m_1 m_2}^{\nu -} = -\frac{i}{2}\langle \hat{L}_{m_3} \rangle_{\nu}$, where $(m_1 m_2 m_3)$ is an even permutation of (xyz). Taking into account the matrix elements of the Coulomb interaction, one can find $E_{\text{X}}[\hat{n}^{\nu -}] = -\frac{1}{4} U_{\text{eff}} \langle \hat{\mathbf{L}} \rangle_{\nu}^2$ (for p electrons $J = \frac{1}{5} F^2$). The Stoner-like form of this expression coincides with the one of OPB. However, the OP is driven entirely by U_{eff}. The result is very natural, because the p-electron exchange is purely spherical: due to the rotational invariance, there is no preferential orbital configuration of the exchange origin for a single electron; the same is also true for two p electrons due to the electron-hole symmetry between states with the same spin.

Generalization for d (and higher ℓ) electrons is cumbersome, but still feasible. The maximal number of nonequivalent matrix elements of $\hat{n}^{\nu -}$ for d electrons is ten. The same number of irreducible antisymmetric operators being odd order products of $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$ are required in order to represent this matrix. Let us consider an isotropic case, when the CF is small, and the spin and orbital moments have the same quantization axis (z). Then, we shall retain only two operators, $\hat{L}_z$ and $\hat{L}_z^3$, which simplifies the problem significantly and leads to the following expression:

$$E_{\mathrm{X}}[\hat{n}^{\nu-}] = -c_1\langle \hat{L}_z\rangle_\nu^2 + c_2\left(\langle \hat{L}_z\rangle_\nu \langle \hat{L}_z^3\rangle_\nu - \frac{5}{34}\langle \hat{L}_z^3\rangle_\nu^2\right),$$

where $c_1 = \frac{1}{288}(130U_{\mathrm{eff}} - 369B)$ and $c_2 = \frac{17}{144} \times (2U_{\mathrm{eff}} - 9B)$. The result clearly shows that not only B but also U_{eff} is responsible for the OP. Besides the Stoner-like exchange, OP for d electrons is determined by the higher order effects with respect to the orbital angular momentum operators. c_2 vanishes if $U = J + \frac{9}{2}B \sim 1.5J$. Then, the strength of Stoner's orbital exchange is $c_1 = \frac{3}{4}B$. Thus, both the form and the magnitude of $E_{\mathrm{X}}[\hat{n}^{\nu-}]$ in this limit is close to the assumption made in OPB. The central question is whether the limit $U \sim 1.5J$ is consistent with other features of metallic magnetic materials where LSDA does a good job for the spin magnetism, like ferromagnetic 3d metals. The spin polarization in LSDA is also generically close to the Stoner concept $\Delta E_{\mathrm{SP}}^{\mathrm{LSDA}}[\mathbf{m}] \simeq -\frac{1}{2}I\mathbf{m}^2$, with the characteristic parameter I being of the order of 0.6–1.0 eV [10]. The averaged spin splitting for d electrons in LDA + U is driven by $I = \frac{1}{5}(U + 4J)$ [8]. Then, $U \sim 1.5J$ leads to the estimate $I \sim 1.1J$. If J varies from 0.7 to 1.0 eV [8], I varies from 0.8 to 1.1 eV, being well consistent with the LSDA picture. Although some attempts have been made [11], the concrete scenario of how the on-site U is renormalized up to $U \sim 1.5J$ for many metallic compounds is still an open question.

All processes considered so far have been related with the enhancement of the orbital magnetic moments. However, the problem has a counterpart, i.e., their quenching. The basic mechanism of this phenomenon is the CF effects, whose consequences are twofold: (i) Quenching of the orbital moments due to the CF is also enhanced by the e-e interaction through $E_{\mathrm{X}}[\hat{n}^{\nu+}]$, which should be treated on an equal footing with $E_{\mathrm{X}}[\hat{n}^{\nu-}]$ [4]. Such a unified treatment of magnetic and nonmagnetic orbital interactions also guarantees that in the absence of SOI and CF, the total energy displays a high degeneracy with respect to the real orbitals and the complex orbitals occupation. (ii) CF leads to the anisotropy of the orbital moments. Generally, the problem cannot be formulated through the expectation values of only $\hat{L}_z$ and $\hat{L}_z^3$, and involves all elements of $\hat{n}^{\nu-}$. Thus, the correct OP functional should satisfy the requirement of the rotational basis invariance: any unitary transformation of $\hat{n}$ does not change $\Delta E_{\mathrm{OP}}[\hat{n}]$.

The intersite part of the density matrix relevant to the orbital magnetic phenomena can be evaluated using the criterion

$$\varepsilon = |\hat{n}^+\hat{n}^- + \hat{n}^-\hat{n}^+ - \hat{n}^-|/|\hat{n}^-|, \tag{3}$$

where $\hat{n}^\pm = \frac{1}{2}\sum_{\nu=0}^{3}\hat{n}^{\nu\pm} \otimes \hat{\sigma}_\nu$, and $|\hat{A}|$ means the matrix norm [12]. If $\hat{n}(\mathbf{r},\mathbf{r}')$ is totally localized at lattice points (i.e., site diagonal in the basis of atomiclike orbitals), we have $\varepsilon = 0$ as the result of idempotency of the density matrix $\hat{n}^2 = \hat{n}$.

It is very demanding to derive an explicit general expression for OP in terms of expectation values of the angular momenta. We have demonstrated some examples and discussed general ideas of how it can be done. In practice, however, the problem can be solved numerically by working directly with the site-diagonal elements of the density matrix $\hat{n}$ in the rotationally invariant LDA + U approach.

Let us illustrate this scheme for the rock-salt oxide CoO, where the orbital moment is not necessarily quenched in the $\frac{2}{3}$ filled t_{2g} manifold [13]. The antiferromagnetic spin order additionally lowers the cubic symmetry of CoO to the trigonal one, resulting in complicated anisotropy effects. Since the orbital moments are least quenched along the magnetic easy axis [14], the maximum of the orbital angular momentum directly corresponds to the minimum of the magnetic anisotropy energy (E_{MA}). The general tendencies of E_{MA} can be well understood as a competition of cubic (K) and trigonal (T) terms [13]: $E_{\mathrm{MA}} = K(e_x^2e_y^2 + e_y^2e_z^2 + e_z^2e_x^2) + T(e_xe_y + e_ye_z + e_ze_x)$, where $\{e_i\}$ are the direction cosines of the spin magnetization. If both K and T are positive as in the case of CoO [13], the model allows only one class of equilibrium solutions, where the moments are confined in the plane $(1\bar{1}0)$ and canted off the [001] axis by the angle θ varying from 0° (the [001] axis) to $-35°$ [the $[\bar{1}\bar{1}2]$ direction in the plane (111)] depending on the relative strength of K and T (Fig. 1). Existence of such canted magnetic structure in CoO is well established. In fact, it has been predicted in the pioneering work of Kanamori [13] and supported by subsequent

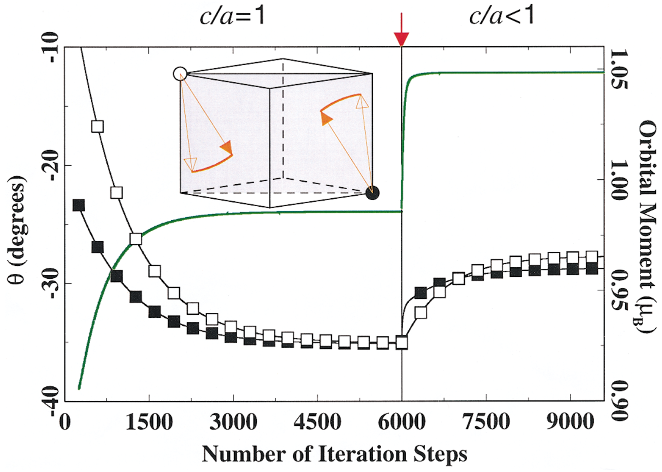

FIG. 1(color). Relaxation to the new magnetic equilibrium after turning on the SOI in CoO: orbital moment (green line) and deviations of spin (white squares) and orbital (black squares) magnetic moments from the [001] axis. The inset shows trajectories of the spins attached to magnetically different Co sites in the plane $(1\bar{1}0)$. Open and filled arrows correspond to the initial and final states. After reaching the equilibrium, a small tetragonal distortion $c/a = 0.988$ has been turned on at the point shown by the red arrow. $U = 8$ eV, $J = 1$ eV, and $B = 0.1J$ are used.

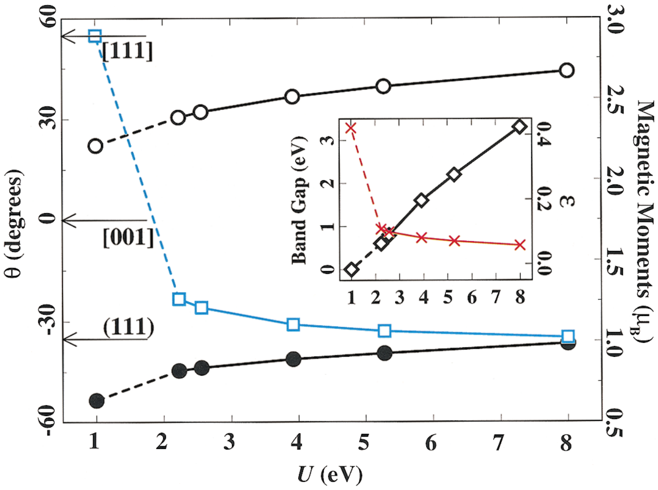

FIG. 2(color). Spin magnetic moments (open circles), orbital magnetic moments (filled circles), and the angles between the [001] axis and the easy magnetization directions (open squares) obtained for different values of U, $J = 1$ eV, and $B = 0.1J$. Arrows correspond to the high symmetry directions in the cube. The inset shows the band gap (open diamonds) and degree of orbital localization ε given by Eq. (3) (crosses). Parts corresponding to the metallic behavior ($U < 2.2$ eV) are shown by broken lines.

experiments, although different authors report different values of θ [15]. Our numerical calculations [16] are in excellent agreement with this picture. We start with a self-consistent LDA + U solution without SOI where spins can take an arbitrary direction and there is no orbital moment. With turning on the SOI, a typical relaxation process to the new equilibrium state as a function of iteration steps is shown in Fig. 1, where we used $U = 8$ eV, $J = 1$ eV, and $B = 0.1J$, suggested by the constraint-LSDA calculations (e.g., [6]). As approaching the equilibrium, the orbital moment grows at the Co site and is stabilized between two high-symmetry directions [001] and [$\overline{1}\overline{1}2$], causing a similar reorientation of the spin counterpart. The orbital instability is directly related with appearance of the band gap in CoO. Once the band gap opens when U varies in the wide range from 2.2 to 8 eV (Fig. 2), the orbital moment becomes well localized [17] and the angle θ is stabilized between $-29°$ and $-35°$. On the contrary, $U_{\mathrm{eff}} = 0$ closes the band gap, increases ε, and aligns magnetic moments parallel to the cube diagonal. Finally, the magnetostriction is responsible for the tetragonal deformation in CoO in the direction $c/a < 1$ which further enhances the orbital magnetic moment (Fig. 1).

In conclusion, we have shown how the magnetic OP can be systematically included in band structure calculations. A remaining question is the *ab initio* renormalization of the effective on-site e-e interactions. The solution should be found along the following line. The first step is to map a real many-electron problem to the fictitious one described by the single-particle KS equations in the LDA + U form. The most advanced way is to use the optimized effective potential scheme [18] and to treat the on-site e-e interactions in LDA + U as variational degrees of freedom, which minimize the true total energy functional based on a rigorous static expression for the exchange-correlation energy. The dynamic fluctuations near the static mean-field solution then might be included in the local form [19].

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