Effective single-particle potentials for MnO in light of interatomic magnetic interactions: Existing theories and perspectives

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It is shown that the fundamental gauge-symmetry constraints superimposed on the admissible form of the exchange-correlation energy functional lead to the generalized local force theorem for small nonuniform rotations of the spin magnetic moments near equilibrium. The theorem suggests that the magnetic interactions responsible for the low-energy spin-wave excitations near the ground state can be expressed in terms of the effective single-particle potential designed for the ground-state spin-magnetization density. The theorem allows us to obtain an empirical effective potential for MnO by fitting the experimental low-temperature spin-wave dispersion curve. The theorem is further applied to investigate abilities of several different first-principles techniques: local-(spin)-density approximation, LDA plus ''Hubbard U'' (LDA$+U$) and optimized effective potential (OEP). None of these approaches treats the magnetic interactions in MnO properly. Limitations of the one-electron band picture underlying the failure are elucidated in each case. As one of the perspective techniques to deal with the electronic structure of narrow-band materials, we propose to combine the LDA$+U$ form of the single-particle equations with the variational principles of the OEP approach. Several possible approximations along this line are discussed. [S0163-1829(98)04047-8]

I. INTRODUCTION

Close interplay among magnetic, structural, and transport properties discovered in various perovskite manganese oxides has recently revived an enormous interest in these systems. In some sense, the new wave of intense research activity was facilitated by the fact that many physical mechanisms responsible for these phenomena were known already for many years. However, it is also true that the research has been facing many fundamental problems that are still far from their final solution. Undoubtedly, one such long-standing problem is the description of the narrow-band transition-metal compounds on the level of first-principles band-structure calculations. Despite numerous such studies based on rather different standpoints (see, e.g., Refs. 1 and 2 and references therein), which of the theoretical band pictures lies behind the unique physical properties of manganites is still an open and disputed question.

Although there are several conceptual differences between perovskite and rocksalt materials,[2] we consider that it would be very instructive to address ourselves once more to the classical problem of the electronic structure of the ''simplest manganese oxide''—the monoxide MnO. Certainly, MnO is one of the most well studied compounds, both experimentally and theoretically. Surprisingly, however, after decades of activity, the electronic structure of MnO is still the subject of various controversies, especially in the field of first-principles electronic structure theories. Depending on the approximation employed for treating the exchange and correlation effects, the characteristic electronic properties of MnO can be quite different. (i) A small-band-gap (~ 1 eV) material, the insulating nature of which is directly related to the existence of the particular type-II long-range antiferromagnetic spin ordering, and the energy gap itself may be ascribed to the ''Mott-Hubbard'' type in the sense that both the top of the valence band and the bottom of the conduction band are of predominantly Mn($3d$) character. This is essentially the picture provided by the local-(spin)-density approximation [L(S)DA] to the density-functional theory (DFT).[3,4] (ii) An insulator in the ''charge-transfer'' regime, where the energy band gap of 3.5–4.0 eV is open between O($2p$) and Mn($3d$) states, if the on-site Coulomb correlations at the Mn($3d$) states are included explicitly in the framework of the self-interaction-corrected (SIC) LSDA (Ref. 5) or LDA plus ''Hubbard U'' (LDA$+U$ Ref. 6) approaches. (iii) A moderate-band-gap (~ 3.5–4.0 eV) insulator in the intermediate ''Mott-Hubbard''/''charge-transfer'' regime [the highest occupied states are of mixed Mn($3d$)-O($2p$) character] if the problem is treated within the so-called optimized effective potential (OEP) approach[7,8] or with a model GW method.[9] (iv) A wide-band-gap (~ 13 eV) insulator within the *ab initio* unrestricted Hartree-Fock approach.[10]

The electronic structure of MnO has been intensively investigated by photoemission spectroscopy.[11,12] The results strongly advocate the intermediate Mott-Hubbard/charge-transfer character of the energy gap, as well as the existence of the large (~ 10 eV) splitting between the occupied and unoccupied Mn($3d$) states. It is known, however, that the
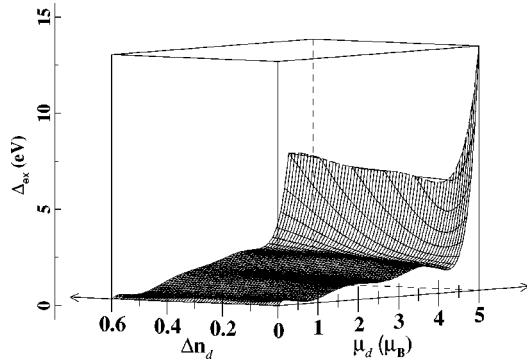
FIG. 1. Results of constraint-LSDA calculations for the AF2 state: the intra-atomic exchange splitting Δ_{ex} between the majority- and minority-spin Mn($3d$) states as the function of the number of Mn($3d$) electrons $n_d = 5 + \Delta n_d$ and the magnetic moment μ_d on the Mn($3d$) states.

photoemission spectroscopy deals mainly with the *excited-state* properties and there is no guarantee that the (generally fictitious) single-particle energies obtained in *ground-state* DFT calculations should coincide with the true single-particle excitations.[13] In this sense one might think that the LSDA, although being inappropriate for treating the electron excitations, does work reasonably well for the ground-state properties of MnO.[14] Indeed, MnO takes a special place among the transition-metal oxides since the Mn^{2+} ion has the half-filled $3d^5$ shell, and the spin subbands are either completely full or completely empty. Thus, the situation is less critical than that in FeO and CoO (and even NiO), where besides the intra-atomic spin splitting, the polarization of $3d$ orbitals within the same spin plays an important role.[3,15] The local magnetic moment μ, being basically of Mn($3d$) character, calculated by integrating the spin-magnetization density in the atomic Mn sphere in the LSDA is typically about $4.5\mu_B$.[4] The value seems to be pretty close to the experimental local magnetic moment reported in the literature: $4.58\mu_B$,[16] or even $4.79\mu_B$.[17] Therefore, one might guess that only a small correction to the LSDA description is needed in the case of MnO (at least, for the ground-state properties). However, such a simple-minded intuition can be very misleading. In Fig. 1, we show results of the constraint-LSDA calculations of $\Delta_{ex} \equiv \Delta_{ex}(\Delta n_d, \mu_d)$ performed in the type-II antiferromagnetic state (AF2), where we fix the number of Mn($3d$) electrons in the atomic sphere[18] as $n_d = 5 + \Delta n_d$ and evaluate the intra-atomic exchange splitting Δ_{ex} between majority- and minority-spin Mn($3d$) states that should be applied in order to obtain the magnetic moment μ_d on the same Mn($3d$) states. One can clearly distinguish two regions in this diagram: (i) ''modest μ_d,'' which corresponds to the unsaturated magnetization produced by partially occupied majority- and minority-spin Mn($3d$) states in the metallic regime. The exchange splitting shows the rigid-split Stoner-like behavior $\Delta_{ex} \simeq I\mu_d$ with the nearly constant parameter $I \sim 1$ eV. Taking into account the Stoner-like form as well as the magnitude of the parameter I, one can expect that this part of the diagram is within the accessibility of the LSDA description, because the latter is generically close to the concept of metallic Stoner magnetism.[19] (ii) μ_d is close to its saturation value $\mu_d \simeq 5 - \Delta n_d$ in the insulating regime, which corresponds to an asymptotic growth of Δ_{ex}. In this

region, the majority- (minority-) spin Mn($3d$) states are nearly filled (empty) and the change of μ_d with Δ_{ex} is caused by the change in the character of the wave-functions related with the hybridization, rather than the direct inter-population of the majority- and minority-spin Mn($3d$) states. ''Unfortunately,'' the experimental data fall into the second region, and in order to increase the local magnetic moment obtained in the LSDA by several tenths of the Bohr magneton (in fact, less than 7% of the LSDA value), the corresponding parameter of the effective single-particle potential responsible for the spin polarization (a generalized Stoner I) should be increased more sensitively by a factor of 2–3. Thus, one should realize that even a small correction to a ground-state property can be conjugated with the need of a large correction for parameters of the LSDA potential.

In this work we will attempt to determine the electronic structure of MnO by using the experimental spin-wave excitations data.[20] The characteristic energy scale of these processes is considerably smaller than those employed in the photoemission measurements [e.g., the typical incident neutron energies are only 30–50 meV (Ref. 20) to be compared with the characteristic photon energies $h\nu \sim 46$–55 eV in the ultraviolet photoemission measurements for MnO].[11] In this sense, the low-temperature spin-wave dispersion is a more direct probe of the ground state of MnO rather than the photoemission spectroscopy. The fact that a small deviation from the ground state can be expressed through the parameters of the ground state has been emphasized by many authors in rather different contexts (see, e.g., Refs. 19 and 21). The case of spin rotational degrees of freedom has several unique aspects that will be discussed in Sec. II. Particularly, we will show how the requirements of the gauge invariance in the DFT (Ref. 22) result in the generalized local force theorem for infinitesimal rotations of the spin magnetic moments, which connects the low-temperature spin-wave dispersion with the parameters of the effective single-particle potential designed for the ground state. The statement itself is not new and is widely used in *ab initio* calculations of magnetic interactions,[4,23] and in the analysis of the finite-temperature spin dynamics in real crystals.[24] We will look at the problem from a different angle and show that, in fact, the theorem is one of the most general results in the DFT, the applicability of which is not limited only by the framework of the LSDA. Thus, the theorem can be applied as the test for already existing DFT schemes, as well as the guideline for possible methodological developments. So, we will show in Sec. III how the parameters of the effective single-particle potential for MnO can be found empirically by fitting the experimental low-temperature spin-wave dispersion curve. In fact, the information provided by the experiment is limited to giving only two inter-atomic exchange integrals.[20] However, we will see that this rather restricted information is sufficient to ''restore'' the one-electron band structure of MnO. In Sec. IV we turn to abilities of existing first-principles techniques to deal with the same problem of magnetic interactions in MnO. Finally, a summary of the work and perspectives will be outlined in Sec. V.

II. ROTATION OF THE SPIN-MAGNETIZATION DENSITY IN THE SPIN-DENSITY-FUNCTIONAL THEORY

Following the Kohn-Sham (KS) formulation of the density-functional theory[25] let us present the energy of an

interacting N-electron system as $E = T_0 + R$, where

$$T_0[\{\psi_i\}] = \sum_{i=1}^{N} \int d\mathbf{r}\, \psi_i^\dagger(\mathbf{r})(-\nabla^2)\psi_i(\mathbf{r}) \qquad (1)$$

is the kinetic energy (in Rydberg units) of a noninteracting system described by a Slater determinant of the one-electron orbitals $\{\psi_i\}$, and R stands for remaining electron-nuclear $E_{\text{ext}}[\rho]$ and electron-electron interactions. The last one is normally partitioned into the Hartree energy $E_{\text{H}}[\rho]$, which is a functional of the charge density $\rho(\mathbf{r})$ only, and the exchange-correlation energy $E_{\text{XC}}[\rho,\{A\}]$, which is an explicit functional of $\rho(\mathbf{r})$ and a certain number of other order parameters $\{A\}$ characterizing the ground state of the many-electron system. It is assumed that the dependence on remaining order parameters enters E_{XC} implicitly through $\rho(\mathbf{r})$ and $\{A\}$. Corrections to the noninteracting kinetic energy are also included in E_{XC}. The KS orbitals ψ_i are the solutions of the fictitious single-particle problem:

$$[-\nabla^2 + \hat{v}_{\text{eff}}(\mathbf{r})]\psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}), \qquad (2)$$

whose order parameters $\{\rho,A\}$ and the total energy are requested to be identical to those of the real interacting-electron system in the ground state. We will further specify the problem and assume that the set of order parameters $\{A\}$ is represented by three Cartesian components of the spin-magnetization density $\mathbf{m}(\mathbf{r})$. Therefore, the effective potential $\hat{v}_{\text{eff}}(\mathbf{r})$ is the 2×2 matrix in the spin space, and $\psi_i(\mathbf{r})$ is the two-component spinor function. Then, the charge $\rho(\mathbf{r})$ and the spin-magnetization $\mathbf{m}(\mathbf{r})$ densities can be expressed as

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} \psi_i^\dagger(\mathbf{r})\psi_i(\mathbf{r}) \qquad (3)$$

and

$$\mathbf{m}(\mathbf{r}) = \sum_{i=1}^{N} \psi_i^\dagger(\mathbf{r})\hat{\boldsymbol{\sigma}}\psi_i(\mathbf{r}), \qquad (4)$$

respectively, where $\hat{\boldsymbol{\sigma}}$ is the vector of Pauli matrices $\hat{\boldsymbol{\sigma}} = (\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z)$. Equations (1)–(4) in combination with the extremum property of the total energy in the ground state $\delta/\delta\psi_i^\dagger(\mathbf{r})\{E - \Sigma_i \varepsilon_i(\int d\mathbf{r}\,\psi_i^\dagger(\mathbf{r})\psi_i(\mathbf{r})-1)\} = 0$ lead to the following expression for the effective KS potential $\hat{v}_{\text{eff}}(\mathbf{r})$:

$$\hat{v}_{\text{eff}}(\mathbf{r}) = v(\mathbf{r})\hat{\mathbf{1}} + \mathbf{b}(\mathbf{r}) \cdot \hat{\boldsymbol{\sigma}}, \qquad (5)$$

where $\hat{\mathbf{1}}$ is the 2×2 unity matrix,

$$v(\mathbf{r}) = \frac{\delta}{\delta\rho(\mathbf{r})}\{E_{\text{ext}}[\rho] + E_{\text{H}}[\rho] + E_{\text{XC}}[\rho,\mathbf{m}]\} \qquad (6)$$

is the scalar part of $\hat{v}_{\text{eff}}(\mathbf{r})$, and

$$\mathbf{b}(\mathbf{r}) = \frac{\delta}{\delta\mathbf{m}(\mathbf{r})} E_{\text{XC}}[\rho,\mathbf{m}] \qquad (7)$$

is the internal spin magnetic field. Equations (2)–(7) should be solved self-consistently. Using Eqs. (1,2,5-7), the kinetic energy can be written as

$$T_0[\{\psi_i\}] = \sum_{i=1}^{N} \varepsilon_i - \int d\mathbf{r}\{v(\mathbf{r})\rho(\mathbf{r}) + \mathbf{b}(\mathbf{r})\cdot\mathbf{m}(\mathbf{r})\}. \qquad (8)$$

Then, the total energy is given by

$$E[\rho,\mathbf{m}] = \sum_{i=1}^{N} \varepsilon_i + E_{\text{dc}}[\rho,\mathbf{m}], \qquad (9)$$

with $E_{\text{dc}}[\rho,\mathbf{m}]$ denoting the double-counting term:

$$E_{\text{dc}}[\rho,\mathbf{m}] = E_{\text{ext}}[\rho] + E_{\text{H}}[\rho] + E_{\text{XC}}[\rho,\mathbf{m}] - \int d\mathbf{r}\{v(\mathbf{r})\rho(\mathbf{r})$$
$$+ \mathbf{b}(\mathbf{r})\cdot\mathbf{m}(\mathbf{r})\}. \qquad (10)$$

These are the basic equations of the KS spin DFT. Our goal is to find the total-energy change caused by small deviations of the spin-magnetization directions $\mathbf{e}'(\mathbf{r}) = \mathbf{m}'(\mathbf{r})/|\mathbf{m}'(\mathbf{r})|$ from the ones in the ground state $\mathbf{e}_{\text{GS}}(\mathbf{r}) = \mathbf{m}_{\text{GS}}(\mathbf{r})/|\mathbf{m}_{\text{GS}}(\mathbf{r})|$. The transformation at each coordinate point $\mathbf{r}$ is given by the standard three-dimensional rotation matrix specified by a small angle $\boldsymbol{\varphi}(\mathbf{r})$: $\mathbf{e}_{\text{GS}}(\mathbf{r}) \to \mathbf{e}'(\mathbf{r}) = \hat{R}[\boldsymbol{\delta\varphi}(\mathbf{r})]\mathbf{e}_{\text{GS}}(\mathbf{r})$. The energy of the excited configuration $\mathbf{e}'(\mathbf{r})$ is given by the constrained functional

$$E_{\boldsymbol{\delta\varphi}}[\rho,\mathbf{m}] = E[\rho,\mathbf{m}] - \int d\mathbf{r}\ \mathbf{h}(\mathbf{r})\cdot\{\mathbf{e}'(\mathbf{r})$$
$$- \hat{R}[\boldsymbol{\delta\varphi}(\mathbf{r})]\mathbf{e}_{\text{GS}}(\mathbf{r})\}, \qquad (11)$$

where only the directions of the spin magnetization at each $\mathbf{r}$ point are fixed along $\hat{R}[\boldsymbol{\delta\varphi}(\mathbf{r})]\mathbf{e}_{\text{GS}}(\mathbf{r})$ by an external field $\mathbf{h}(\mathbf{r})$, whereas $\rho(\mathbf{r})$ and the absolute magnitude of $\mathbf{m}(\mathbf{r})$ are allowed to relax so to minimize $E_{\boldsymbol{\delta\varphi}}$. Let $\rho'(\mathbf{r}) = \rho_{\text{GS}}(\mathbf{r}) + \delta\rho(\mathbf{r})$ and $\mathbf{m}'(\mathbf{r}) = \hat{R}[\boldsymbol{\delta\varphi}(\mathbf{r})]\{\mathbf{m}_{\text{GS}}(\mathbf{r}) + \delta m(\mathbf{r})\mathbf{e}_{\text{GS}}(\mathbf{r})\}$ be the charge and the spin-magnetization densities that minimize $E_{\boldsymbol{\delta\varphi}}$, and, $\rho_{\text{GS}}(\mathbf{r})$ and $\mathbf{m}_{\text{GS}}(\mathbf{r})$ refer to the ground state where $\boldsymbol{\delta\varphi} = 0$. The transformation of $\mathbf{m}(\mathbf{r})$ consists of the longitudinal change of $\mathbf{m}_{\text{GS}}(\mathbf{r})$ by $\delta m(\mathbf{r})$: $\tilde{\mathbf{m}}(\mathbf{r}) = \mathbf{m}_{\text{GS}}(\mathbf{r}) + \delta m(\mathbf{r})\mathbf{e}_{\text{GS}}(\mathbf{r})$, and the subsequent rotation of $\tilde{\mathbf{m}}(\mathbf{r})$ by the angle $\boldsymbol{\delta\varphi}$: $\mathbf{m}'(\mathbf{r}) = \hat{R}[\boldsymbol{\delta\varphi}(\mathbf{r})]\tilde{\mathbf{m}}(\mathbf{r})$. If $\{\tilde{\psi}_i(\mathbf{r})\}$ are the KS orbitals that yield $\rho'(\mathbf{r})$ and $\tilde{\mathbf{m}}(\mathbf{r})$ by the use of Eqs. (3,4), the rotation $\mathbf{m}'(\mathbf{r}) = \hat{R}[\boldsymbol{\delta\varphi}(\mathbf{r})]\tilde{\mathbf{m}}(\mathbf{r})$ is formally equivalent to the unitary transformation of $\{\tilde{\psi}_i(\mathbf{r})\}$:

$$\tilde{\psi}_i(\mathbf{r}) \to \psi_i'(\mathbf{r}) = \hat{U}_S[\boldsymbol{\delta\varphi}(\mathbf{r})]\tilde{\psi}_i(\mathbf{r}), \qquad (12)$$

where $\hat{U}_S[\boldsymbol{\delta\varphi}(\mathbf{r})] = \exp[i\boldsymbol{\delta\varphi}(\mathbf{r})\cdot\boldsymbol{\sigma}/2]$ is the 2×2 rotation matrix in the spin space. The fundamental theorem by Vignale and Rasolt[22] states in this context: the unitary transformations of the KS orbitals (12) with a coordinate-dependent phase factor does not change the exchange-correlation energy functional E_{XC} (the so-called gauge-symmetry constraint on the admissible form of E_{XC}). Thus, we have $E_{\text{XC}}[\rho',\mathbf{m}'] = E_{\text{XC}}[\rho',\tilde{\mathbf{m}}]$, which further leads to the following property for the internal spin magnetic field:

$$\mathbf{b}'(\mathbf{r}) = \frac{\delta}{\delta \mathbf{m}'(\mathbf{r})} E_{\mathrm{XC}}[\rho', \mathbf{m}'] = \hat{R}[\,\boldsymbol{\delta\varphi}(\mathbf{r})]$$

$$\times \left(\frac{\delta}{\delta \tilde{\mathbf{m}}(\mathbf{r})} E_{\mathrm{XC}}[\rho', \tilde{\mathbf{m}}] \right) = \hat{R}[\,\boldsymbol{\delta\varphi}(\mathbf{r})]\tilde{\mathbf{b}}(\mathbf{r}),$$

and therefore $\mathbf{b}'(\mathbf{r}) \cdot \mathbf{m}'(\mathbf{r}) = \tilde{\mathbf{b}}(\mathbf{r}) \cdot \tilde{\mathbf{m}}(\mathbf{r})$. The transformation (12) does not affect $\rho'(\mathbf{r})$ and therefore the scalar part of the KS potential. Then, using Eqs. (9,11) and expanding $E_{\mathrm{dc}}[\rho', \mathbf{m}'] - E_{\mathrm{dc}}[\rho_{\mathrm{GS}}, \mathbf{m}_{\mathrm{GS}}]$ explicitly up to the first order of $\delta\rho(\mathbf{r})$ and $\delta m(\mathbf{r})$, it is rather straightforward to show that the total-energy change $\delta E_{\boldsymbol{\delta\varphi}} = E_{\boldsymbol{\delta\varphi}}[\rho', \mathbf{m}'] - E[\rho_{\mathrm{GS}}, \mathbf{m}_{\mathrm{GS}}]$ is given by

$$\delta E_{\boldsymbol{\delta\varphi}} = \delta \left(\sum_{i=1}^{N} \varepsilon_i \right) - \int d\mathbf{r} \{\delta v(\mathbf{r})\rho_{\mathrm{GS}}(\mathbf{r}) + \delta \tilde{\mathbf{b}}(\mathbf{r}) \cdot \mathbf{m}_{\mathrm{GS}}(\mathbf{r})\}$$
$$+ O[(\delta\rho)^2, (\delta m)^2], \qquad (13)$$

where the first term is the change of the KS single-particle energies, $\delta v(\mathbf{r}) = v'(\mathbf{r}) - v_{\mathrm{GS}}(\mathbf{r})$ and $\delta \tilde{\mathbf{b}}(\mathbf{r}) = \tilde{\mathbf{b}}(\mathbf{r}) - \mathbf{b}_{\mathrm{GS}}(\mathbf{r})$, with $(v_{\mathrm{GS}}, \mathbf{b}_{\mathrm{GS}})$ and $(v', \tilde{\mathbf{b}})$ corresponding to $(\rho_{\mathrm{GS}}, \mathbf{m}_{\mathrm{GS}})$ and $(\rho', \tilde{\mathbf{m}})$, respectively.

An explicit expression for the first term in Eq. (13) is

$$\delta \left(\sum_{i=1}^{N} \varepsilon_i \right) = \sum_{i=1}^{N} \varepsilon_i(\rho', v', \mathbf{m}', \mathbf{b}')$$
$$- \sum_{i=1}^{N} \varepsilon_i(\rho_{\mathrm{GS}}, v_{\mathrm{GS}}, \mathbf{m}_{\mathrm{GS}}, \mathbf{b}_{\mathrm{GS}}). \qquad (14)$$

Noting that

$$\rho' = \rho_{\mathrm{GS}} + \delta\rho,$$

$$v' = v_{\mathrm{GS}} + \delta v,$$

$$\mathbf{m}' = \hat{R}[\,\boldsymbol{\delta\varphi}]\mathbf{m}_{\mathrm{GS}} + \delta m \hat{R}[\,\boldsymbol{\delta\varphi}]\mathbf{e}_{\mathrm{GS}},$$

$$\mathbf{b}' = \hat{R}[\,\boldsymbol{\delta\varphi}]\mathbf{b}_{\mathrm{GS}} + \hat{R}[\,\boldsymbol{\delta\varphi}]\delta\tilde{\mathbf{b}},$$

and expanding the first term of Eq. (14), we obtain in the first order of $\delta\rho$ and δm

$$\sum_{i=1}^{N} \varepsilon_i(\rho', v', \mathbf{m}', \mathbf{b}')$$

$$= \sum_{i=1}^{N} \varepsilon_i(\rho_{\mathrm{GS}}, v_{\mathrm{GS}}, \hat{R}[\,\boldsymbol{\delta\varphi}]\mathbf{m}_{\mathrm{GS}}, \hat{R}[\,\boldsymbol{\delta\varphi}]\mathbf{b}_{\mathrm{GS}})$$

$$+ \int d\mathbf{r} \{\delta v(\mathbf{r})\rho_{\mathrm{GS}}(\mathbf{r}) + \hat{R}[\,\boldsymbol{\delta\varphi}(\mathbf{r})]$$

$$\times \delta\tilde{\mathbf{b}}(\mathbf{r}) \cdot \hat{R}[\,\boldsymbol{\delta\varphi}(\mathbf{r})]\mathbf{m}_{\mathrm{GS}}(\mathbf{r})\}. \qquad (15)$$

As $\hat{R}[\,\boldsymbol{\delta\varphi}]\delta\tilde{\mathbf{b}} \cdot \hat{R}[\,\boldsymbol{\delta\varphi}]\mathbf{m}_{\mathrm{GS}} = \delta\tilde{\mathbf{b}} \cdot \mathbf{m}_{\mathrm{GS}}$, the second term of Eq. (15) cancels with the second term of Eq. (13). Therefore, we arrive at the well-known local force theorem for small non-uniform rotations of the spin magnetization as expressed by

$$\delta E_{\boldsymbol{\delta\varphi}} = \delta^* \left(\sum_{i=1}^{N} \varepsilon_i \right) + O[(\delta\rho)^2, (\delta m)^2], \qquad (16)$$

with

$$\delta^* \left(\sum_{i=1}^{N} \varepsilon_i \right) = \sum_{i=1}^{N} \varepsilon_i(\rho_{\mathrm{GS}}, v_{\mathrm{GS}}, \hat{R}[\,\boldsymbol{\delta\varphi}]\mathbf{m}_{\mathrm{GS}}, \hat{R}[\,\boldsymbol{\delta\varphi}]\mathbf{b}_{\mathrm{GS}})$$

$$- \sum_{i=1}^{N} \varepsilon_i(\rho_{\mathrm{GS}}, v_{\mathrm{GS}}, \mathbf{m}_{\mathrm{GS}}, \mathbf{b}_{\mathrm{GS}}). \qquad (17)$$

Thus, in order to calculate the total-energy change $\delta E_{\boldsymbol{\delta\varphi}}$, we only have to calculate the KS single-particle energies of the excited configuration $\mathbf{e}'(\mathbf{r})$ for the potential given by $(v_{\mathrm{GS}}, \hat{R}[\,\boldsymbol{\delta\varphi}(\mathbf{r})]\mathbf{b}_{\mathrm{GS}})$.

The result is well know in the LSDA,[23] where it is in a rather direct consequence of the peculiar functional dependence of the exchange-correlation energy:

$$E_{\mathrm{XC}}[\rho, \mathbf{m}] = \int d\mathbf{r}\rho(\mathbf{r})\varepsilon_{\mathrm{XC}}[\rho(\mathbf{r}), |\mathbf{m}(\mathbf{r})|].$$

As we have seen, however, the conclusion is more general and is one of the fundamental properties in DFT. In principle, the gauge-symmetry constraint on the form of the exchange-correlation energy functional[22] leads in this context to a simple but nevertheless very important conclusion: the error $O[(\delta\rho)^2, (\delta m)^2]$ is determined by the *scalar* longitudinal change of the spin magnetization. The central question, however, is how $\delta\rho$ and δm depend on $\boldsymbol{\delta\varphi}$. From the equilibrium condition in the ground state we have in the first order of $\boldsymbol{\delta\varphi}$: $\delta^{(1)}E_{\boldsymbol{\delta\varphi}} = 0$, and therefore $\delta E_{\boldsymbol{\delta\varphi}} = O[(\boldsymbol{\delta\varphi})^2]$. Then, the total-energy change $\delta E_{\boldsymbol{\delta\varphi}}$ can be described entirely by the change of the KS single-particle energies [first term in Eq. (16)] only if $\delta^{(1)}\rho = \delta^{(1)}m = 0$. The latter requirement is equivalent to the collinearity condition $[\mathbf{m}_{\mathrm{GS}}(\mathbf{r}) \times \mathbf{f}(\mathbf{r})] = 0$ between the spin magnetization $\mathbf{m}_{\mathrm{GS}}(\mathbf{r})$ and the force $\mathbf{f}(\mathbf{r})$ acting on this magnetization in the ground state. Indeed, the total change of $\mathbf{m}(\mathbf{r})$ in the first order of $\delta\varphi$ is given by $\delta^{(1)}\mathbf{m}(\mathbf{r}) = \delta^{(1)}m(\mathbf{r})\mathbf{e}_{\mathrm{GS}}(\mathbf{r}) + [\,\boldsymbol{\delta\varphi}(\mathbf{r}) \times \mathbf{m}_{\mathrm{GS}}(\mathbf{r})]$, where the first term is the longitudinal change and the second term is the transversal change caused by the rotation. Then, the equilibrium condition in the ground state $\delta^{(1)}E_{\boldsymbol{\delta\varphi}} = 0$ leads to

$$\int d\mathbf{r} \left\{ \frac{\delta E[\rho, \mathbf{m}]}{\delta\rho(\mathbf{r})}\delta^{(1)}\rho(\mathbf{r}) + \frac{\delta E[\rho, \mathbf{m}]}{\delta\mathbf{m}(\mathbf{r})} \cdot \mathbf{e}_{\mathrm{GS}}(\mathbf{r})\delta^{(1)}m(\mathbf{r}) \right.$$

$$\left. - \left[\frac{\delta E[\rho, \mathbf{m}]}{\delta\mathbf{m}(\mathbf{r})} \times \mathbf{m}_{\mathrm{GS}}(\mathbf{r}) \right] \cdot \boldsymbol{\delta\varphi}(\mathbf{r}) \right\} = 0. \qquad (18)$$

Since by the definition $\mathbf{f}(\mathbf{r}) = -\delta E[\rho, \mathbf{m}]/\delta\mathbf{m}(\mathbf{r})$, the condition $\delta^{(1)}\rho = \delta^{(1)}m = 0$ is equivalent to the natural requirement of the lack of the rotational forces acting on the spin magnetization in the ground state $[\mathbf{m}_{\mathrm{GS}}(\mathbf{r}) \times \mathbf{f}(\mathbf{r})] = 0$.

III. EMPIRICAL EFFECTIVE POTENTIAL FOR MANGANESE OXIDE

The practical consequence of the analysis presented in the previous section is that the ground-state spin-magnetization density and the low-energy excitations caused by rotations of the spin magnetic moments near the ground state can be

expressed in terms of the same effective single-particle potential. We will exploit this fact and attempt to obtain such potential and therefore to restore the one-electron band picture of MnO empirically on the basis of available experimental spin-wave dispersion data.[20] First, we shall specify the form of the effective potential. Our ''guess'' is the following. (i) LDA is sufficient for the nonmagnetic part of the potential. (ii) The magnetic part of the effective potential is given by its site-diagonal matrix elements in an appropriate atomiclike basis. In fact, such a view on the one-electron band structure of the transition-metal oxides was suggested by Brandow[15] and later on employed in LDA+U approach.[6] MnO is certainly the simplest example among the transition-metal oxides due to unimportance of the orbital polarization effects.[26] In practice, we use the nearly orthogonal ASA-LMTO (where ASA is atomic-sphere apprximation) method[18,27] and assume that the magnetic potential affects only the site-diagonal block of Mn($3d$) states in the LMTO Hamiltonian. Then, the magnetic part of our empirical effective potential is represented by only two parameters $\Delta_{\uparrow,\downarrow}$: the shift of the LMTO band-center[27,28] for the majority-spin and minority-spin Mn($3d$) states $C_{\uparrow,\downarrow}=C_{3d}+\Delta_{\uparrow,\downarrow}$.

The shift of the diagonal matrix elements on $\Delta_{\uparrow,\downarrow}$ is equivalent to the following correction to the LDA potential: $\Delta v^{\uparrow,\downarrow}(\mathbf{r},\mathbf{r}')=\Sigma_{mm'}\chi_{nlm}(\mathbf{r})[\Delta_{\uparrow,\downarrow}\delta_{mm'}]\chi^*_{nlm'}(\mathbf{r}')$, where $\chi_{nlm}(\mathbf{r})=R_{nl}(r)Y_{lm}(\hat{\mathbf{r}})$ is the $3d$ basis orbital [$R_{nl}(r)$ being the radial part, $Y_{lm}(\hat{\mathbf{r}})$ being the angular part]. Thus, the selectivity of the LDA+U type correction, in the sense that it acts only on the states with a particular combination of the principal (n) and angular (l) quantum numbers at each site of the periodic lattice, is equivalent to the nonlocality of the effective potential on the intra-atomic scale, which appears through the nonlocality of the projectors $\chi_{nlm}(\mathbf{r})\chi^*_{nlm'}(\mathbf{r}')$. However, such an effective potential of LDA+U type remains to be site diagonal, unlike the non-local potential in the full-length Hartree-Fock approach. This is also different from the conventional KS spin DFT discussed in the preceding section, because the present formulation implies[6] that instead of the KS variables ($\rho,\mathbf{m}$), the total energy should be treated as the functional of the charge density $\rho(\mathbf{r})$, the local Mn($3d$) population n_d and the local magnetic moment μ_d on the Mn($3d$) states: $E[\rho,n_d,\mu_d]$. Importantly, however, if the class of possible spin rotations is restricted to the ones, which preserve the collinear alignment within each atomic sphere (i.e., we use the classical picture where there is only one spin vector associated with each magnetic site in the lattice, and these vectors are allowed to rotate relative to each other), the arguments of the preceding section can be repeated and the potential parameters $\Delta_{\uparrow,\downarrow}$ designed for the set of the ground-state variables (ρ,n_d,μ_d) should be able to reproduce the small spin-wave excitations near the ground state and vice versa.

The experimental spin-wave dispersion of MnO measured at 4.2 K by inelastic neutron scattering[20] can be described in terms of the following Heisenberg spin Hamiltonian:

$$\mathcal{H}=-\frac{1}{2}\sum_{j,k}J_k\mathbf{e}_j\cdot\mathbf{e}_{j+k}, \qquad (19)$$

where only two non-negligible interactions between Mn atoms are the nearest-neighbor (nn) exchange J_1 and the next-nearest-neighbor (nnn) exchange J_2. $\mathbf{e}_j$ is the direction of the spin magnetic moment at the site j. Strictly speaking, the monoxide MnO reveals a small trigonal distortion below the Néel temperature caused by the exchange striction effects and resulting in somewhat different exchange constants $J_1^{\pm}$ for the nn interactions with parallel and antiparallel spins.[20,29] However, we will consider the ideal rocksalt structure where all nn distances are equal and assume that all nn exchange interactions can be described by only one parameter J_1. Importantly, the nature of the nn and nnn interactions in the rocksalt MnO is different. J_2 is the typical 180° superexchange interaction which depends on the intra-atomic exchange splitting $\Delta_{\text{ex}}=C_\downarrow-C_\uparrow$ and the relative position of Mn($3d$) and O($2p$) states (the so-called charge-transfer energy $\Delta_{\text{ct}}=C_\downarrow-C_{2p}$),[4,30] whereas both the 90° superexchange and the direct dd interactions contribute to the nn exchange integral J_1. Thus, one can expect that the shift of the Mn($3d$) states by $\Delta_{\uparrow,\downarrow}$ will have a different effect on J_1 and J_2.[31] As we shall see below, this leads to an unambiguous choice for $\Delta_{\uparrow,\downarrow}$ in the case of MnO.[32]

In our numerical procedure we start with the nonmagnetic LDA band structure and shift the Mn($3d$) states by $\Delta_{\uparrow,\downarrow}$ interchanging $\Delta_\uparrow$ and $\Delta_\downarrow$ in two different magnetic sublattices of the AF2 ordered structure. Then, the total-energy change associated with the small rotations of the spin magnetic moments [Eq. (16)] can be exactly mapped onto the Heisenberg model [Eq. (19)] with the parameters given by[23]

$$J_k=\frac{\Delta_{\text{ex}}^2}{2\pi}\text{Im}\int_{-\infty}^{\varepsilon_F}d\varepsilon\,\text{Tr}_L\{G^\uparrow_{0k}(\varepsilon)G^\downarrow_{k0}(\varepsilon)\}, \qquad (20)$$

where $G^{\uparrow,\downarrow}_{0k}$ is the intersite block of LMTO Green's function and Tr_L denotes the trace over the orbital indices. As expected,[31] the splitting Δ_{ex} controls mainly the absolute magnitude of both J_1 and J_2, whereas the spin-independent shift $(\Delta_\uparrow+\Delta_\downarrow)/2$ strongly affects the ratio J_2/J_1. Thus, there is a direct correspondence between two parameters of the effective potential ($\Delta_\uparrow,\Delta_\downarrow$) and two interatomic exchange integrals (J_1,J_2). The experimental values $J_1=-4.8$ and $J_2=-5.6$ meV (Table I) suggest $\Delta_\uparrow=-3.8$ and $\Delta_\downarrow=6.8$ eV.

In order to demonstrate that the empirical effective potential does account well for the magnetic interatomic interactions problem and the interactions different from J_1 and J_2 are indeed negligible in the obtained one-electron picture for MnO, we directly calculate the spin-wave spectrum by using the spin-spiral idea in the band-structure calculations.[34] The main advantage of this approach is that it allows us to avoid the real-space summations and to obtain directly the Fourier images of the pairwise exchange interactions.[35] Then, the spin-wave energies of an antiferromagnet can be expressed through the Fourier images of the intra-sublattice $J_{++}(\mathbf{q})$ and intersublattice $J_{+-}(\mathbf{q})$ interactions as[36]

$$\omega(\mathbf{q})=\frac{2}{\mu}[(J_{++}(\mathbf{q})-H_0)^2-J_{+-}^2(\mathbf{q})]^{1/2}, \qquad (21)$$

where $H_0=J_{++}(0)-J_{+-}(0)$. The results of these calculations with the above-mentioned parameters $\Delta_{\uparrow,\downarrow}$ are summarized in Fig. 2. The calculated spin-wave energies do fit well with the experimental curve, suggesting that the underlying

TABLE I. Magnetic moment inside the atomic Mn sphere μ and the interatomic exchange integrals J_k calculated in various magnetically ordered states (F, AF1, and AF2) by using the empirical effective potential as well as the different first-principles techniques: LSDA, LDA$+U$, and OEP. Note that in accordane with the definition of Eq. (19), the experimental parameters J_1 and J_2 have been multiplied by $S^2 = (5/2)^2$.

	μ (μ_B)	J_1 (meV)	J_2 (meV)
Empirical (F)	4.89	-4.9	-6.0
Empirical (AF1)	4.89	-4.7	-5.9
Empirical (AF2)	4.84	-4.8	-5.6
LSDA-x [a] (AF2)	4.66	-8.8	-15.5
LSDA-xc [b] (AF2)	4.50	-13.2	-23.5
LDA$+U$ (AF2)	4.68	-5.0	-13.2
OEP-x [c] (AF2)	4.85	-5.7	-11.0
OEP-xc [d] (AF2)	4.80	-8.9	-12.0
Expt.	4.79, [e] 4.58 [f]	-4.8, [g] -5.4 [h]	-5.6, [g] -5.9 [h]

[a]LSDA exchange potential only.
[b]LSDA exchange-correlation potential by Vosko, Wilk, and Nusair (Ref. 33).
[c]LMTO exact exchange potential by Kotani and Akai (Ref. 7).
[d]LMTO exact exchange plus static RPA correlation potential by Kotani (Ref. 8).
[e]Fender *et al.* (Ref. 17).
[f]Cheetham *et al.* (Ref. 16).
[g]Inelastic neutron scattering by Kohgi *et al.* (Ref. 20).
[h]Analysis of thermodynamic data by Lines and Jones (Ref. 29).

one-electron band picture of MnO may indeed be very realistic. Note, that by adjusting J_1 and J_2 to their experimental values we did not treat the magnetic moment μ as an independent fitting parameter. Nevertheless, the moment obtained inside the atomic Mn sphere is in fairly good agreement with the experimental local magnetic moments reported in the literature (Table I). Comparison of the obtained density of states with the combined x-ray photoemission and bremsstrahlung-isochromat spectroscopy data[12] is also rather remarkable in three respects: the mixed Mn($e_{g\uparrow}$)-O($2p$)

FIG. 2. Electronic structure of MnO: total and partial Mn($3d$) densities of states of t_{2g} and e_g symmetry and energy bands, which gives the experimental low-temperature spin-wave dispersion. Results of the fitting of the spin-wave dispersion are shown in the right inset: calculated energies (squares) and experimental curve (solid line). Left inset shows the first Brillouin zone of the AF2 unit cell.

character of the top valence band; the energy splitting between occupied and empty Mn($3d$) states; the relative position of the occupied O($2p$), Mn($t_{2g\uparrow}$), and Mn($e_{g\uparrow}$) states. In all these features, the calculated density of states agrees well with the picture suggested by the photoemission spectroscopy.[37]

Another important feature of the magnetic interactions in MnO is that the simple two-parameter Heisenberg model (19) appears to be more universal in the sense that not only the low-temperature magnon spectrum[20] but also the behavior of various thermodynamic quantities in a wide temperature range below and above the Néel temperature[29] can be successfully described by the same Heisenberg model with practically the same parameters J_1 and J_2. It means that the Heisenberg exchange interactions, being originally derived only for infinitesimal rotations of the spin magnetic moments near an equilibrium (AF2) state [Eq. (20)], should depend only weakly on the type of spin ordering realized in this equilibrium state. The latter appears to be possible if Δ_{ex} (and Δ_{ct}) are the largest parameters in the problem and the series of perturbation theory with respect to the hopping integrals rapidly converge.[36] Then, the magnetic interactions will be entirely represented only by the leading terms in this series[31] and the simplest Heisenberg form of the spin-Hamiltonian [Eq. (19)] becomes exact. The one-electron picture of MnO obtained by fitting the experimental spin-wave dispersion satisfies these requirements. First, we fix the parameters of the KS potential $\Delta_{\uparrow,\downarrow}$ and evaluate the exchange integrals J_1 and J_2 for three different magnetic equilibrium states: ferromagnetic, F; antiferromagnetic of the first type, AF1; and antiferromagnetic of the second type, AF2. All three magnetically ordered states were found to be insulating (the energy band gap is 4.9, 5.5, and 6.9 eV for F, AF1, and AF2, respectively) and the exchange integrals themselves only weakly depend on the type of the long-range magnetic ordering (Table I). Then, on the basis of the obtained parameters $\Delta_{ex} = 10.6$ eV, $\Delta_{ct} = 10.7$ eV, and $J_2 = -5.6$ meV, the effective pd hopping can be evaluated using the formula for the superexchange interaction as[31] $t_{pd} = 1.36$ eV, being almost one order of magnitude smaller than Δ_{ex} and Δ_{ct}.

Finally, t_{pd} can be also expressed in terms of the Slater-Koster transfer integrals as[4] $t_{pd}^4 = (pd\sigma)^4 + 2(pd\pi)^4$. Since $(pd\pi) \simeq -0.45(pd\sigma)$, one can find that $(pd\sigma) \simeq 1.33$ eV, which is again in a remarkable agreement with the value $(pd\sigma) \simeq 1.3$ eV suggested by the analysis of the photoemission spectra in terms of the configuration-interaction cluster model.[12]

IV. FIRST-PRINCIPLES TECHNIQUES

Being based on the one-electron picture adjusted to reproduce the experimental magnetic data, let us turn to the analysis of various first-principles approaches that have been applied hitherto to MnO. In Fig. 3 we show the theoretical spin-wave dispersion curves calculated within different band structure schemes (LSDA, OEP, LDA$+U$) on the basis of the local force theorem by using Eq. (21) and the spin-spiral technique[35] in order to obtain $J_{++}(\mathbf{q}) - H_0$ and $J_{+-}(\mathbf{q})$. Following the arguments of Sec. II, the spin-wave dispersion can be considered as a probe of the effective single-particle potentials that were used in these calculations. Obtained pa-
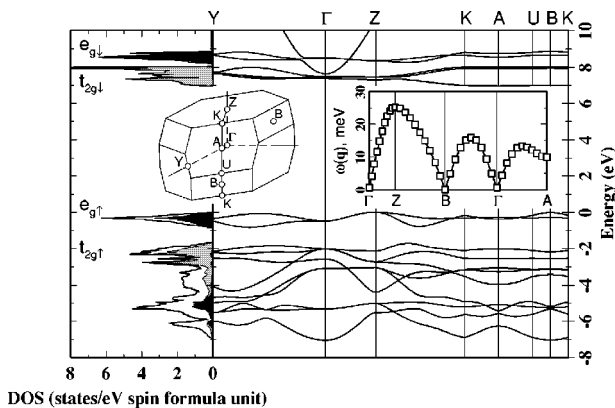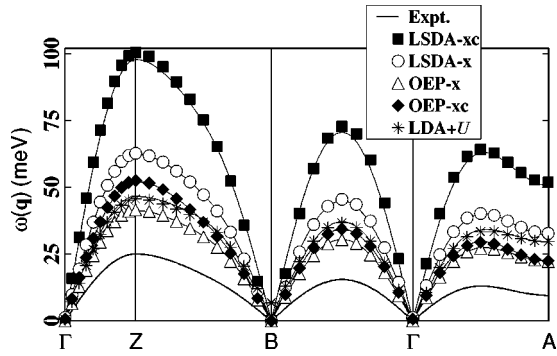
FIG. 3. Theoretical spin-wave dispersion calculated by using several first-principles electronic structure techniques in comparison with the experiment. Symbols show the calculated spin-wave energies; the solid line is the result of interpolation with the parameters listed in Table I. The notations are the same as in Table I.

rameters J_1 and J_2 are listed in Table I. One can see, that none of the considered approaches treats the interatomic magnetic interactions properly.

A. LSDA

LSDA provides quite a reasonable description for the valence band of MnO. The discrepancies that are directly re-
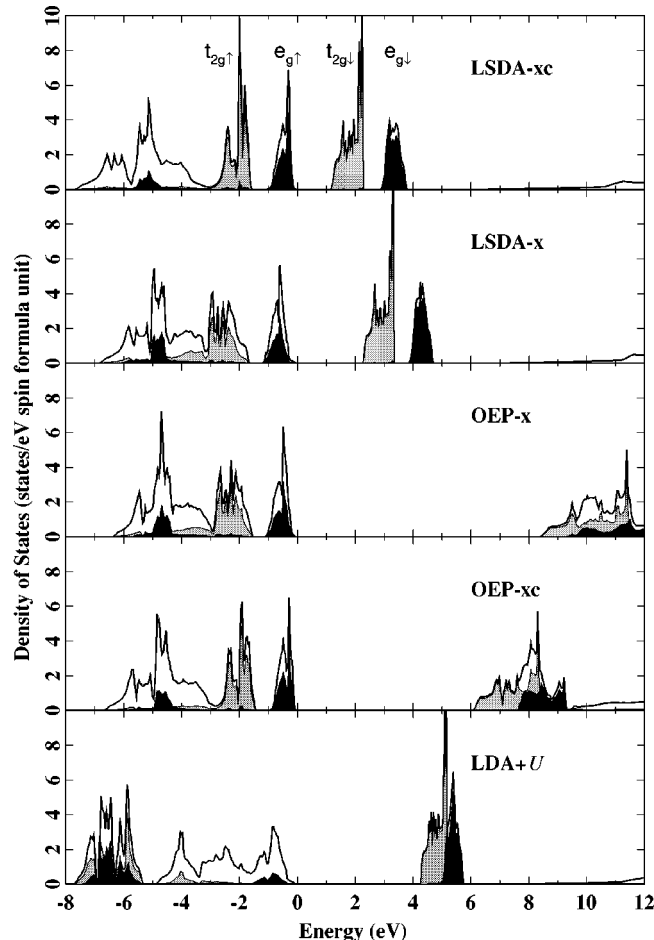
FIG. 4. Total and partial Mn($3d$) densities of states of t_{2g} and e_g symmetry in LSDA, OEP, and LDA+U. The notations are the same as in Table I.

lated with the band-gap problem are more evident: the intra-atomic exchange splitting and the charge-transfer energy are seriously underestimated (Fig. 4). The nonlocal corrections in the form of the generalized gradient approximations (GGA) improve the situation only partially.[38] This has several negative consequences on the interatomic magnetic interactions: (i) Both $|J_1|$ and $|J_2|$ are significantly overestimated (previous calculations by Oguchi, Terakura, and Williams[4] and Table I); (ii) Δ_{ex} and Δ_{ct} are no longer the largest parameters in the problem: the band gap can be closed by a finite rotation of the spin magnetic moments away from the AF2 ground state.[3,4] Then, the exchange integrals themselves strongly depend on the type of the magnetically ordered state in which they are calculated (for example, the estimations based on the finite rotations in the medium of randomly oriented magnetic moments yields[4] $J_2 = -12.7$ meV, being quite different from the value $J_2 = -23.5$ meV listed in Table I and corresponding to the infinitesimal rotations near the AF2 state); (iii) the problem, which is typically less realized. Both LSDA and GGA overestimate the magnitude of the trigonal contraction along the [111] direction of the cube.[39] The contraction is known to be caused by the exchange striction effects in the AF2 state.[29] If the distorted cube corner angles are $\pi/2 \pm \beta$, the equilibrium distortion β is proportional to $[\partial J_1/\partial r]/C_{44}$, where r is the nn Mn-Mn distance in the rocksalt structure and C_{44} is the shear elastic constant.[29] At the equilibrium volume, GGA yields[39] $\beta \simeq 2.2 \times 10^{-2}$, which is two times larger than the experimental value[20,29] $\beta \simeq 1.1 \times 10^{-2}$. Thus, the same factor 2 can be viewed as the error of GGA (LSDA) for the derivative $\partial J_1/\partial r$, provided that C_{44} is correct.

It is well known that the electron correlation can reduce Δ_{ex} substantially.[19] The use of the LSDA exchange potential alone without the correlation counterpart does increases the band gap (Fig. 4) and brings the inter-atomic exchange integrals in a better agreement with the experimental data (Table I). However, the improvement is only partial, indicating that the limitations of the LSDA description for MnO start already on the level of approximations made for the exchange energy functional, and correlations added afterwards only aggravate the problem.

B. OEP

OEP is the potentially promising approach. The idea of this method[40] is to find numerically the local KS potential that minimizes the total-energy functional based on the exact Fock expression for the exchange energy and an approximate form for the correlation energy (e.g., in the random-phase approximation, RPA). The latter can be beyond the homogeneous electron gas limit.[8] In the present work we used the self-consistent LMTO potentials obtained by Kotani.[7,8] When the static correlation in the inhomogeneous RPA form is taken into account, both the occupied density of states and the intra-atomic exchange splitting (Fig. 4) are in accord with the expectations based on the analysis of the experimental spin-wave dispersion (Fig. 2). The puzzling aspect of the OEP-LMTO approach developed by Kotani is that it seems to exaggerate the radial dependence of the intra-atomic exchange splitting, resulting in rather discouraging inter-atomic magnetic interactions (Table I). The result can be understood

as follows. The canonical OEP-LMTO bandwidth[27] W_l for Mn($3d_\uparrow$), Mn($3d_\downarrow$), and O($2p$) states is 2.6, 6.6, and 14.3 eV, respectively (to be compared with 3.3, 4.6, and 13.8 eV, obtained within LSDA). Therefore, the pd hybridization, being proportional to[27] $t_{pd\uparrow,\downarrow} \propto (W_p W_{d\uparrow,\downarrow})^{1/2}$, differs significantly for the majority-spin and minority-spin pd channels. One of the consequences of this difference is clearly seen in Fig. 4: despite larger energy separation from the center of O($2p$) band, the unoccupied part of the Mn($3d$) states is significantly wider than the occupied one. The fact that the pd hoppings strongly depend on the spin indices also plays a negative role in the problem of superexchange interactions: starting from the ground-state antiferromagnetic alignment, the downward energy shift of the O($2p$) states due to the interaction with the unoccupied Mn($3d$) states in the Mn-O-Mn bond[4] is given in the first order of $t_{pd\uparrow,\downarrow}/\Delta_{ct}$ by $\delta C_{2p} = -\{(t^2_{pd\downarrow} + t^2_{pd\uparrow}) + (t^2_{pd\downarrow} - t^2_{pd\uparrow})|\sin(\vartheta/2)|\}/\Delta_{ct}$, where ϑ is the angle between magnetic moments of two Mn atoms in the Mn-O-Mn bond. Since $t_{pd\downarrow} > t_{pd\uparrow}$, $|\delta C_{2p}|$ is maximal in the antiferromagnetic ground-state corresponding to $\vartheta = \pm\pi$. This will additionally stabilize the ground-state AF2 order and overestimate the inter-atomic exchange coupling even without the RPA correlation (Table I). The problem exists already on the level of LSDA, which also result in two different parameters for the canonical Mn($3d_\uparrow$) and Mn($3d_\downarrow$) bandwidths, although the difference is considerably smaller than in the case of OEP approach. The reason of such unphysical behavior is not entirely clear. We would like to mention three possibilities. (i) Shape approximation superimposed on the OEP in the LMTO approach. Especially, the internal spin magnetic fields [Eq. (7)] are totally suppressed within oxygen atomic spheres when the AF2 ordering is treated in the framework of the LMTO method. (ii) The uniform rotations of the spin magnetization within atomic spheres may not correspond to the lowest-energy spin-wave excitations. A more advanced treatment of the spin waves should allow the possibility of a noncollinear distribution of the spin-magnetization density on the intra-atomic scale in the excited state. The theories in this context have been developed very recently in the series of publications.[41] These two scenarios, however, seem to contradict the widespread concept of the localized magnetism in MnO. (iii) As was shown by Vignale and Rasolt,[22] the gauge-invariant form of the KS equations with respect to the spin rotations, on which the local force theorem is based, can be preserved only if both the spin-magnetization density $\mathbf{m}(\mathbf{r})$ and the fictitious spin-current densities

$$\mathbf{j}_\alpha(\mathbf{r}) = -i\sum_{i=1}^{N}\{\psi_i^\dagger(\mathbf{r})\hat{\sigma}_\alpha[\nabla\psi_i(\mathbf{r})] - [\nabla\psi_i^\dagger(\mathbf{r})]\hat{\sigma}_\alpha\psi_i(\mathbf{r})\},$$

where $\hat{\sigma}_\alpha$ is one of the Pauli matrices ($\alpha = x$, y or z), are treated as the basic variables in the framework of current-DFT formalism. The spin-current densities themselves have no physical meaning and therefore should be determined by other real physical observables $\mathbf{j}_\alpha(\mathbf{r}) = \mathbf{j}_\alpha[\rho(\mathbf{r}), \mathbf{m}(\mathbf{r})]$. Then, the problem can be formally reformulated as a spin DFT,[42] where the magnetic part of the KS potential is given by the chain derivation:

$$\mathbf{b}(\mathbf{r}) = \left.\frac{\delta E_{XC}}{\delta\mathbf{m}(\mathbf{r})}\right|_{\mathbf{j}_\alpha} + \sum_\alpha \int d\mathbf{r}' \left.\frac{\delta E_{XC}}{\delta\mathbf{j}_\alpha(\mathbf{r}')}\right|_{\mathbf{m}} \frac{\delta\mathbf{j}_\alpha(\mathbf{r}')}{\delta\mathbf{m}(\mathbf{r})}.$$

However, there is no guarantee that the second part of this expression can be described by a simple multiplicative potential, as it is implied in the OEP theory.

At the present stage we do not know whether there is a connection between the local KS current-DFT formulation and our empirical procedure discussed in Sec. III which implies a nonlocality of the effective single-particle potential within atomic Mn spheres. Presumably, such nonlocality is an alternative standpoint, which, however, allows us to resolve rather easily the main drawback of the OEP picture related with the very different strength of the pd hybridization in different spin channels. To conclude this part we would like to note that our empirical electronic band structure of MnO (Fig. 2) agrees reasonably well with the model GW calculations by Massidda et al.[9], which are based on a nonlocal energy-independent expression for the electron self-energy.

C. LDA+U

LDA+U, being based on ideas learned from the periodic Anderson model with the orbital degeneracy, is another potentially promising approach for the transition metal oxides.[6,15] In this picture, the intra-atomic exchange splitting of the Mn($3d$) states is given by $\Delta_{ex} = I\mu_d$, where for the half-band-filling the Stoner parameter I is related with the on-site Coulomb repulsion U and the Hund's first rule coupling J_H as $I = (U + 4J_H)/5$.[43] With the parameters obtained from the fit to the magnon spectrum we would expect $I = \Delta_{ex}/\mu_d = 10.6/4.84 \simeq 2.2$ eV, which is more than two times larger than the LSDA value $4.0/4.50 \simeq 0.9$ eV. Typically, the Hund's first rule coupling for $3d$ compounds is $J_H \simeq 0.7$–0.8 eV and only weakly depends on the environment of $3d$ ions in solids (e.g., Ref. 6, and references therein). Then, the on-site Coulomb repulsion U can be evaluated from I as $U \simeq 8$ eV, being in fairly good agreement with the results of the constraint-LSDA calculations ($U = 6.9$ eV, reported in Ref. 6).

Results of the LDA+U calculations with the above-mentioned parameters are shown in Fig. 4 and in Table I. Obvious drawback of this picture is the underestimate of the charge-transfer energy Δ_{ct}. Formally, the situation can be improved by introducing a more sophisticated approximation for the so-called double-counting energy (E_{dc}^U) in LDA+U. This term is aimed to subtract the part of the LDA energy, which has the same origin as the energy of added on-site Hartree-Fock interactions.[6] At present, there are two *anzatzs* for E_{dc}^U: the original one, where E_{dc}^U is chosen as the on-site Hartree-Fock energy with averaged single-particle populations;[6] and an alternative, where E_{dc}^U is interpolated between the on-site Hartree-Fock energies taken at the points of integer single-particle populations. Merits of the latter approach have been discussed in Ref. 44. However, MnO presents an exceptional case, because for the half-band-filling these two schemes yield the same correction to the LDA potential: $\Delta_{\uparrow,\downarrow} = \pm I\mu_d/2$ [the symmetric spin splitting of the Mn($3d$) states]. Thus, both LDA+U schemes do not handle

the situation properly. The problem cannot be solved by treating the Hubbard U as an adjustable parameter in the present formulation of the LDA$+U$ approach: the procedure fails to reproduce two exchange integrals J_1 and J_2 simultaneously. Phenomenologically, it is clear that the corrected LDA$+U$ potential for MnO should include an additional upward shift of *all* Mn($3d$) states relative to the O($2p$) band, although it is not clear now whether there is a simple prescription for such correction. We will return to this problem in Sec. V. The same problem is anticipated for LaMnO$_3$, where the straightforward application of LDA$+U$ even worsens the LSDA picture and leads to the incorrect magnetic ground state (ferromagnetic, instead of A-type antiferromagnetic—see discussions by Solovyev, Hamada, and Terakura and Sawada *et al.* in Ref. 1).

The standard SIC-LSDA technique affects only the occupied Mn($3d$) states and results in even smaller charge-transfer energy parameter Δ_{ct} than in LDA$+U$.[5] Thus, the overall picture for the magnetic interactions is expected to be even worse. The situation may be improved if we apply the self-interaction correction not only to Mn($3d$) orbitals, but also to O($2p$) orbitals, although the procedure has no rigorous justification (see arguments of Arai and Fujiwara in Ref. 5).

D. *Ab initio* Hartree-Fock approach

The *ab initio* Hartree-Fock (HF) approach does not take into account the electron correlation, and underestimate the interatomic exchange coupling as well as the exchange striction in MnO.[10] The discrepancies are commonly attributed to the band gap, which is severely overestimated in the *ab initio* HF calculations. This is true only partially, because the interpretation of the HF band structure requires some caution related with the fact that the *ab initio* HF is essentially nonlocal approach.

In order to illustrate the characteristic features of the full-length HF approach let us focus on interactions between the minority-spin Mn($3d$) states and the O($2p$) states in one of the Mn-O bonds by taking the simple tight-binding picture, where we disregard for a while the orbital degeneracy of the atomic $3d$ and $2p$ levels and model them by fictitious s states. Then, the Fock exchange energy associated with the Mn-O bond is given by $E_x^{pd} = -Vn_{dp}n_{pd}$, where V is the inter-site Mn-O Coulomb interaction $V = \langle pd|1/r_{12}|pd \rangle$. In these notations, the $3d$ orbital is centered at the Mn site and $2p$ orbital is centered at the O site. We assume that the weight of the atomic O($2p$) states at the Mn site (and vice versa) is small and all other integrals relevant to the Mn-O exchange interaction ($\langle dd|1/r_{12}|pd \rangle$, $\langle pp|1/r_{12}|pd \rangle$, and $\langle pd|1/r_{12}|dp \rangle$) are negligible. $n_{pd} = n_{dp}$ are the site-off-diagonal elements of the single-particle density matrix: $n_{pd} = \langle G|\hat{c}_p^\dagger \hat{c}_d|G \rangle$, where $\hat{c}_p^\dagger(\hat{c}_d)$ creates an electron (hole) in the atomic $2p$($3d$) state and $|G\rangle$ is the ground-state wave function of the many-electron system that in the HF approach is given by a single Slater determinant of single-particle orbitals $\{\psi_i\}$. Then, in the regular HF approach, the nonlocal pd-exchange potential is given by

$$\frac{1}{\psi_i} \left(\frac{\partial E_x^{pd}}{\partial n_{pd}} \frac{\delta n_{pd}}{\delta \psi_i^\dagger} + \frac{\partial E_x^{pd}}{\partial n_{dp}} \frac{\delta n_{dp}}{\delta \psi_i^\dagger} \right) = -Vn_{pd}(\hat{c}_p^\dagger \hat{c}_d + \hat{c}_d^\dagger \hat{c}_p).$$

Since corresponding kinetic term of the tight-binding Hamiltonian is $-t_{pd}(\hat{c}_p^\dagger \hat{c}_d + \hat{c}_d^\dagger \hat{c}_p)$, where $t_{pd} > 0$, the nonlocal pd exchange enters the site-off-diagonal part of this Hamiltonian as the renormalization of the kinetic hopping parameters $\tilde{t}_{pd} = t_{pd}[1 + (V/t_{pd})n_{pd}]$, and determines the strength of the effective Mn-O hybridization. For the occupied bonding states it holds $n_{pd} > 0$, and therefore $\tilde{t}_{pd} > t_{pd}$. The site-diagonal elements of the Hamiltonian are determined by the unrenormalized on-site Coulomb interactions. This results in the characteristic wide-band-gap picture for MnO in the *ab initio* HF approach.[10]

Nevertheless, the same problem can be reformulated in terms of site-diagonal ("local") variables. This fact follows from the idempotency property of the whole density matrix $\hat{n}^2 = \hat{n}$ (note, that $\hat{n}$ is the projector onto the occupied states), which leads to the series of constraints like $n_d^2 + zn_{dp}n_{pd} \simeq n_d$, where z is the number of Mn-O bonds in which the atomic $3d$ orbital participates, and $n_d = \langle G|\hat{c}_d^\dagger \hat{c}_d|G \rangle$ is the site-diagonal element of the density matrix (local population). The condition $n_d^2 + zn_{dp}n_{pd} \simeq n_d$ becomes exact if the density-matrix is sufficiently short range in the real space and the site-off diagonal elements except n_{pd} for the nearest Mn-O neighbors are vanishing. Thus, n_{pd} and n_d are not independent variational parameters. The pd-exchange energy per one Mn-O bond can be expressed as $E_x^{pd} \simeq -V/z(n_d - n_d^2)$, whose derivative with respect to n_d results in the site-diagonal potential shift of the minority-spin Mn($3d$) states by $-(V/z)(1 - 2n_d) \simeq -(V/z)$, whereas the site-off-diagonal part of the new Hamiltonian is given by the standard kinetic hopping parameters t_{pd}. Thus, the effect of the intersite pd-exchange interaction in this picture is similar to a renormalization of the on-site Coulomb interaction, and therefore "cures" the band-gap problem. If the condition $n_d^2 + zn_{dp}n_{pd} \simeq n_d$ were exact, the transformation between the site-off-diagonal and the site-diagonal representations for the exchange energy in the considered model would be also exact. Thus, both pictures would yield the same ground-state properties, although the single-particle spectra underlying these two approaches may differ significantly.

These tendencies are clearly seen in realistic calculations of the one-electron band structure of MnO obtained in the *ab initio* HF (Ref. 10) and the OEP (Ref. 7) approaches. Both techniques are based on the minimization of the HF total energy. The *ab initio* HF method treats the nonlocality of the exchange interaction directly, whereas the basic idea of the OEP approach is to work with a fictitious local KS potential, which can be obtained numerically.[40] As expected, the intra-atomic exchange splitting Δ_{ex}, as well as the band gap are considerably reduced in the OEP approach [e.g., Δ_{ex} is about 27 eV in HF,[10] and only 13 eV in OEP (Ref. 7)]. The comparison stresses the importance of the intersite Mn-O Coulomb interactions (V) and raises several important questions: (i) whether the effect of the intersite Coulomb interactions can be entirely described as a renormalization of parameters of the on-site Hartree-Fock interactions, as frequently assumed in the model tight binding or LDA$+U$ calculations for the transition-metal oxides; (ii) whether the same renormalization is justified on the level of model HF calculations, and when the electron correlations are taken into account

starting from the model HF solution. These issues should be seriously reconsidered in the future.

V. SUMMARY AND PERSPECTIVES

We have shown that the requirement of gauge invariance in the density-functional theory automatically leads to the generalized local force theorem for spin rotational degrees of freedom. The theorem suggests that the magnetic interatomic exchange interactions relevant to the low-energy spin-wave excitations near the ground state can be expressed in terms of the effective single-particle potential, which yields the correct ground-state spin-magnetization density. Thus, the theorem poses a severe test for the modern first-principles electronic structure techniques designed to deal with the ground-state properties of narrow-band materials.

The problem has been analyzed in detail for MnO. On the one hand, the result of our work is rather discouraging: the spin-wave dispersion calculated by using LSDA, LDA+U, and OEP methods on the basis of the local force theorem is far from the experimental one. Although both LDA+U and OEP methods improve the LSDA description for MnO, the improvement is only partial. On the other hand, results of our work strongly suggest that at least one effective single-particle potential which is compatible with the observed magnetic inter-atomic interactions in MnO does exist and can be found phenomenologically by fitting the experimental low-temperature magnon spectrum.

The phenomenological view on this problem appears to be even more universal in two respects: (i) the obtained one-electron band structure of MnO is also in fairly good agreement with the photoemission spectra; (ii) the empirical effective potential, which was initially constructed in the limit of infinitesimal rotations of the spin magnetic moments near the AF2 ground state, is also applicable to the finite angle rotations. The interatomic exchange integrals only weakly depend on the type of the magnetically ordered state, being consistent with the observed thermodynamic properties of MnO in a wide temperature range, and in a drastic contrast with the picture provided by LSDA. Such a universal behavior is related with the fact that two characteristic parameters of the one-electron Hamiltonian, i.e., the intra-atomic exchange splitting Δ_{ex} and the charge-transfer energy Δ_{ct}, are substantially larger than the interatomic hopping elements.

A challenge for the future research is to obtain the same picture on the level of *ab initio* electronic structure calculations. The perspectives in this direction seem to be rather promising. The central question is the form of the effective single-particle potential. In this respect, the physical idea proposed by Brandow[15] to construct the one-electron Hamiltonian for the transition-metal oxides as the nonmagnetic LDA part plus a site-diagonal correction for the 3d electrons in the model Hartree-Fock form is very fruitful and certainly puts the LDA+U form of the single-particle equations in perspective. One should also note that LDA+U is a very convenient physical approach to deal with the orbital polarization and orbital magnetism in the band-structure calculations.[45] The basic problem of the LDA+U method, as it is currently formulated, is the lack of the well justified prescription of how to choose the parameters of the LDA +U potential. In addition to this, the method designed to

deal with the ground-state properties should be based on variational principles which minimize the *true* total energy. Unfortunately, this is not the case for the currently used LDA+U functionals,[6,44] in which the total-energy is given by an *ad hoc* constraint-LSDA expression. These merits and demerits of the LDA+U description for the narrow-band transition-metal compounds are reversed in the OEP approach.[7,8,40] The OEP technique is based on a rigorous expression for the total energy functional, which is accompanied by a rather cumbersome procedure of how to construct the KS potential, the form of which is, however, restricted to the local multiplicative one. Any extension of this approach to go beyond the conventional spin-density-functional formulation and to take into account, for instance, the orbital polarization effects on the level of one-electron band-structure calculations is already hardly feasible. Thus, as the next step in this direction, it would be highly desirable to combine the LDA+U form of the single-particle equations with the ideas of the OEP approach and to treat the parameters of the LDA+U potential as variational degrees of freedom that minimize the true total-energy functional. Several levels of approximations can be then introduced for the nonlocal spin-dependent part of the LDA+U potential:

$$\Delta v^{\sigma}(\mathbf{r},\mathbf{r}') = \sum_{mm'} \chi_{nlm}(\mathbf{r}) \Delta v^{\sigma}_{mm'} \chi^{*}_{nlm'}(\mathbf{r}'), \qquad (22)$$

with σ denoting a particular spin state (the extension to the spin-off diagonal case associated with the spin-orbit interaction or the noncollinear arrangement of the spin magnetic moments is straightforward).

(i) The standard LDA+U formulation, where the matrix elements $\Delta v^{\sigma}_{mm'}$ are given by the model Hartree-Fock expression for the Coulomb and exchange interactions between the 3d electrons at the same site:

$$\Delta v^{\sigma}_{mm'} = \sum_{m''m'''} \left\{ \left\langle mm'' \left| \frac{1}{r_{12}} \right| m'm''' \right\rangle (n^{\sigma}_{m''m'''} + n^{-\sigma}_{m''m'''}) \right.$$
$$\left. - \left\langle mm'' \left| \frac{1}{r_{12}} \right| m'''m' \right\rangle n^{\sigma}_{m''m'''} \right\} - \Delta v_{ct} \delta_{mm'},$$

$$(23)$$

where $n^{\sigma}_{m''m'''}$ are the site-diagonal elements of the single-particle density matrix in the basis of atomiclike 3d orbitals $\{\chi_{nlm}(\mathbf{r})\}$. Δv_{ct} has the same purpose as the charge-transfer energy parameter in the model Hamiltonians[11,12,30] and controls the position of the 3d-band center relative to the other states. All Coulomb matrix elements $\langle mm''|1/r_{12}|m'm'''\rangle$ are expressed in terms of the Clebsch-Gordon coefficients and $(l+1)$ effective Slater integrals $\{F^{\alpha}\}$, $\alpha=0,2,\ldots,2l$ (e.g., Ref. 46). Therefore, the method comes to the variational determination of only $(l+2)$ potential parameters: $(l+1)$ effective Slater integrals $\{F^{\alpha}\}$ plus the 3d-band center shift Δv_{ct}, provided that the elements of the density matrix in Eq. (23) $n^{\sigma}_{m''m'''} \equiv n^{\sigma}_{m''m'''}[F^{\alpha}, \Delta v_{ct}]$ are obtained in the process of self-consistent solution of the LDA+U equations for each set of parameters $\{F^{\alpha}, \Delta v_{ct}\}$. Thus, the numerical solution of the problem in the spirit of the OEP method seems to be

feasible and would require only small modification of the OEP-LMTO algorithm developed by Kotani.[7,8]

(ii) All $(2l+1)^2$ parameters characterizing the Hermitian matrix $\|\Delta v^{\sigma}_{mm'}\|$ are treated as independent variational degrees of freedom in the OEP-type approach. This technique is expected to be more advanced than the previous one, because it allows the deviation of the LDA$+U$ potential from the traditional atomic Hartree-Fock form. The deviation can be viewed as a different renormalization of the effective on-site Coulomb interactions for the $3d$ states of different symmetry caused by correlation effects[47] or a more complex structure of the interatomic exchange interactions, which does not necessarily lead to the simplest renormalization scenario considered in Sec. IV D for the nondegenerate s orbitals. We expect that this strategy is essentially important to account for the different nature of t_{2g} and e_g $3d$ states in perovskite transition-metal oxides, as was originally suggested by Solovyev $et\ al.$ in Ref. 1. If there is one-by-one correspondence between the potential matrix $\|\Delta v^{\sigma}_{mm'}\|$ and the on-site $(3d)$ part of the density matrix $\|\Delta n^{\sigma}_{mm'}\|$, the scheme should be equivalent to a generalized DFT approach in which $\rho(\mathbf{r})$ and $\|\Delta n^{\sigma}_{mm'}\|$ participate as the basic variables of the total-energy functional $E[\rho, n^{\sigma}_{mm'}]$.

(iii) Typically, there is some flexibility in the choice of the atomiclike orbitals $\{\chi_{nlm}(\mathbf{r})\}$ in LDA$+U$, because the second boundary condition at the atomic sphere is not rigidly fixed for the atomic wave functions in solids. Thus, the shape of the basis orbitals themselves can be treated as another variational degree of freedom. Such a variational procedure would resolve one of the ambiguities of the LDA$+U$ approach related to the choice of the appropriate atomic orbitals $\{\chi_{nlm}(\mathbf{r})\}$.

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