RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 52, NUMBER 8 15 AUGUST 1995-II

Density-functional theory and strong interactions: Orbital ordering in Mott-Hubbard insulators

A. I. Liechtenstein
Max-Planck-Institut für Festkörperforschung, D-70506 Stuttgart, Germany

V. I. Anisimov
Institute of Metal Physics, GSP-170 Ekaterinburg, Russia

J. Zaanen
Lorentz Institute for the Theoretical Physics, Leiden University, Leiden, The Netherlands

(Received 15 May 1995)

Evidence is presented that within the density-functional theory orbital polarization has to be treated on an equal footing with spin polarization and charge density for strongly interacting electron systems. Using a basis-set independent generalization of the LDA+U functional, we show that electronic orbital ordering is a necessary condition to obtain the correct crystal structure and parameters of the exchange interaction for the Mott-Hubbard insulator $KCuF_3$.

According to the Hohenberg-Kohn theorem and its extensions, the ground state of an electron system should be uniquely determined by the charge density as well as all other quantities with nonzero macroscopic expectation values, like magnetic order parameters (spin density). Here we propose that the failure of the local approximation to (spin-) density-functional theory [L(S)DA] in the description of Mott-Hubbard insulators (MHI) is fundamentally related to the neglect of one of these averaged quantities, the polarization of the remnants of atomic angular momentum.

LDA itself is structured after standard semiclassical mean-field theory (MFT). Although alternatives exist,[1] one would like to see if functionals can be constructed within the limitations of this general framework that are free of the large-scale problems of LDA. As realized long ago,[2] MFT yields essentially correct physics if applied to Hubbard models describing MHI. The reason is that MFT is controlled by large S and not by coupling constants originating in the interaction strength.[3] However, in addition, it appears necessary to treat atomic orbital degeneracies on the same footing as the spin degeneracies. According to MFT, all (non-s) Mott-Hubbard insulators are characterized by orbital order parameters, although these are less obvious than, e.g., spin order parameters because the ionic lattice breaks the rotational invariance as well. On the other hand, the explicit symmetry breaking by the lattice can only cause small (crystalline-field) gaps in the excitation spectrum that are independent of particle number. In order to obtain the Mott-Hubbard gaps away from the half-filled shell one has to invoke orbital polarization.

Based on these observations, we constructed some time ago a minimal generalization of LDA (LDA+U), incorporating orbital ordering as well as the notion that both spin and orbital polarization are driven by the screened on-site Coulomb interactions instead of the exchange interactions of the homogeneous electron gas.[4] We showed that this functional is rather successful in the description of a variety of insulating $3d$ oxides,[4] while it also proved to be of use in the more complicated context of doped MHI.[5] Nevertheless, we found this functional theoretically unsatisfactory because it invoked the choice of a particular choice of basis [linear-muffin-tin orbital (LMTO) tight-binding orbitals], while results should be invariant under change of basis. Here we will present a generalization of this LDA+U functional that is *basis set independent.* The only ambiguity left is the much more stringent physical requirement to choose the "atomic spheres" to identify both the remnants of atomic angular momentum and the screened atomic Coulomb and exchange interactions.

A suitable testing ground for these ideas is the Mott-Hubbard insulators where orbital degeneracy is only partly lifted by the lattice structure. In these cases, orbital polarization becomes manifest already in the ground state and the basis-set independence becomes a necessary condition because the shape of the charge distribution has to be generated by the electronic theory itself.

Simple examples are the perovskites $KCuF_3$ and K_2CuF_4. These compounds are subject to a collective Jahn-Teller–like distortion, which is more complicated than the simple tetragonal distortion of the cuprates, involving a staggering of quadrupolar distorted CuF_4 units (two short and two long Cu-F bonds) in the a-b planes. In a seminal work, Kugel and Khomskii[6] pointed out that this distortion is in the first instance electronically driven. They showed that the e_g (x^2-y^2, $3z^2-1$) orbital degrees of freedom, just as the spins, are subject to kinetic exchange interactions, while, in addition, the spin and orbital degrees of freedom are mutually coupled as well. Orbital ordering is found in their model Hamiltonians involving a staggering of the orbitals in a-b directions ($\sim x^2-z^2$, y^2-z^2) and a ferromagnetic ordering of the spins. Because of this "preexisting" electronically driven orbital polarization, any nonzero electron-phonon interaction then leads automatically to the observed lattice distortion.[6] We will show (for $KCuF_3$) the following: (i) LDA fails to reproduce this lattice deformation. The crystal remains cubic (Fig. 1), thereby establishing that LDA can fail even with regard to the symmetry of the crystal structure. (ii) On suppression of the terms driving the electronic orbital

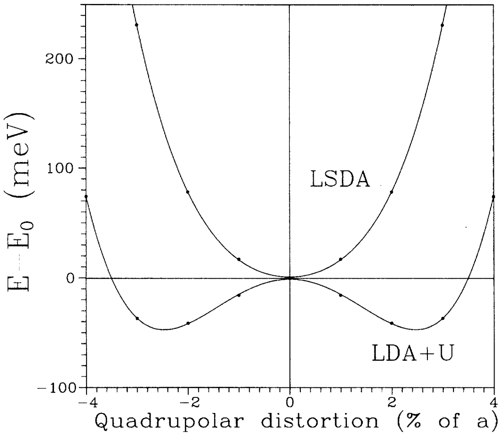

FIG. 1. The dependence of the total energy of $KCuF_3$ on the quadrupolar lattice distortion obtained in calculations with LSDA and LDA+U functionals.

polarization in our new functional, while allowing for spin polarization, the cubic lattice remains stable. (iii) Keeping the (cubic) lattice fixed, we find a practically saturated orbital polarization of the right type if the orbitals are allowed to polarize. (iv) If, and only if, orbital polarization is allowed, the electron-phonon coupling yields the correct order of magnitude for this distortion as well as for the spin-spin superexchange interactions.

The basis-set dependence of the original LDA+U functional was introduced on artificial grounds. All one needs is the identification of regions in space where the atomic characteristics of the electronic states have largely survived. This is not a problem for d or f electrons. Within atomic spheres one can expand wave functions in a localized orthonormal basis[7] $|inlm\sigma\rangle$ (i denotes the site, n the main quantum number, l the orbital quantum number, m the magnetic number, and σ the spin index). Although not strictly necessary, let us restrict ourselves to the usual situation where only a particular nl shell is partly filled. We define the density matrix for correlated electrons in this shell,

$$n^{\sigma}_{mm'} = -\frac{1}{\pi}\int^{E_F} \mathrm{Im}G^{\sigma}_{ilm,ilm'}(E)dE, \tag{1}$$

where $G^{\sigma}_{ilm,ilm'}(E)=\langle ilm\sigma|(E-H)^{-1}|ilm'\sigma\rangle$ are the elements of the Green-function matrix in this localized representation, and H is the effective single-electron Hamiltonian. In terms of the elements of this density matrix $\{n\}$, we define the generalized LDA+U functional as follows:

$$E^{\mathrm{LDA}+U}[\rho^{\sigma}(\mathbf{r}),\{n^{\sigma}\}] = E^{\mathrm{LSDA}}[\rho^{\sigma}(\mathbf{r})] + E^{U}[\{n^{\sigma}\}] - E_{\mathrm{dc}}[\{n^{\sigma}\}], \tag{2}$$

where $\rho^{\sigma}(\mathbf{r})$ is the charge density for spin-σ electrons and $E^{\mathrm{LSDA}}[\rho^{\sigma}(\mathbf{r})]$ is the standard LSDA functional. This follows the same spirit as the original LDA+U functional. Equation (2) asserts that LSDA suffices in the absence of orbital polarizations, while the latter are described by the mean-field (Hartree-Fock) type of theory:

$$\begin{aligned} E^{U}[\{n\}] = \tfrac{1}{2}\sum_{\{m\},\sigma} \{&\langle m,m''|V_{ee}|m',m'''\rangle n^{\sigma}_{mm'} n^{-\sigma}_{m''m'''} \\ &+ (\langle m,m''|V_{ee}|m',m'''\rangle \\ &- \langle m,m''|V_{ee}|m''',m'\rangle) n^{\sigma}_{mm'} n^{\sigma}_{m''m'''}\}, \end{aligned} \tag{3}$$

where V_{ee} are the screened Coulomb interactions among the nl electrons. Finally, the last term in Eq. (2) corrects for double counting [in the absence of orbital polarizations, Eq. (2) should reduce to E^{LSDA}] and is given by

$$E_{\mathrm{dc}}[\{n^{\sigma}\}] = \tfrac{1}{2}Un(n-1) - \tfrac{1}{2}J[n^{\uparrow}(n^{\uparrow}-1) + n^{\downarrow}(n^{\downarrow}-1)], \tag{4}$$

where $n^{\sigma}=\mathrm{Tr}(n^{\sigma}_{mm'})$ and $n=n^{\uparrow}+n^{\downarrow}$. U and J are screened Coulomb and exchange parameters.[8] If the density matrix becomes diagonal, $n^{\sigma}_{mm'}=n^{\sigma}_{m}\delta_{mm'}$, the present rotationally invariant method is equivalent to the ordinary LDA+U approach.[4,8,9]

In addition to the usual LDA potential, we find for the effective single-particle potentials to be used in the effective single-particle Hamiltonian H,

$$\begin{aligned} V^{\sigma}_{mm'} = \sum_{m''m'''} \{&\langle m,m''|V_{ee}|m',m'''\rangle n^{-\sigma}_{m''m'''} \\ &+ (\langle m,m''|V_{ee}|m',m'''\rangle \\ &- \langle m,m''|V_{ee}|m''',m'\rangle) n^{\sigma}_{m''m'''}\} \\ &- U(n-\tfrac{1}{2}) + J(n^{\sigma}-\tfrac{1}{2}). \end{aligned} \tag{5}$$

The V_{ee}'s remain to be determined. We again follow the spirit of LDA+U by claiming that within the atomic spheres these interactions largely retain their atomic nature. Moreover, it is claimed that LSDA itself suffices to determine their values, following the well-tested procedure of the supercell LSDA approach:[8] the elements of the density matrix $n^{\sigma}_{mm'}$ have to be constrained locally and the second derivative of the LSDA energy with respect to the variation of the density matrix yields the wanted interactions. In more detail, the matrix elements can be expressed in terms of complex spherical harmonics and effective Slater integrals F^{k} (Ref. 10) as

$$\langle m,m''|V_{ee}|m',m'''\rangle = \sum_{k} a_{k}(m,m',m'',m''')F^{k}, \tag{6}$$

where $0 \leqslant k \leqslant 2l$ and

$$a_{k}(m,m',m'',m''') = \frac{4\pi}{2k+1}\sum_{q=-k}^{k} \langle lm|Y_{kq}|lm'\rangle \times \langle lm''|Y^{*}_{kq}|lm'''\rangle.$$

If the $|lm'\rangle$ basis consists of complex spherical harmonics, then

$$a_k(m,m',m'',m''')=\sum_{q=-k}^{k}(2l+1)^2(-1)^{m+q+m'}\times\begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}^2\begin{pmatrix} l & k & l \\ -m & q & m' \end{pmatrix}\times\begin{pmatrix} l & k & l \\ -m'' & -q & m''' \end{pmatrix}. \tag{7}$$

For d electrons one needs F^0, F^2, and F^4, and these can be linked to the Coulomb and Stoner parameters obtained from the LSDA-supercell procedures via $U=F^0$ and $J=(F^2+F^4)/14$, while the ratio F^4/F^2 is constant (~ 0.625) to a good accuracy for $3d$ elements.[11,9] For $KCuF_3$ we find $U=7.5$ eV, $J=0.9$ eV. Note that the orbital polarization correction[12] is automatically included in the present approach as the orbital-dependent effects coming from the parameters F^2 and F^4.

Let us now discuss our results for $KCuF_3$, using this new functional, in more detail. We used the full-potential scalar-relativistic LMTO method[13] to calculate the self-consistent LDA+U band structure, using the tetrahedron method with 64 **k** points for the integration over the Brillouin zone. $KCuF_3$ has the perovskite crystal structure with a slight tetragonal distortion ($c/a<1$) while the planes show quadrupolar distortion. The spins are ferromagnetically ordered in the planes while the unit cell is doubled in the c direction by antiferromagnetic spin ordering, so that the resulting unit cell contains four formula units.

The prime subject of our investigation was the quadrupolar distortion in planes, which is directly connected with the peculiar orbital ordering. The total energy as a function of the shifts of the fluorine ions in the CuF_2 plane was calculated with the standard LSDA and LDA+U functionals (Fig. 1). The striking difference between the two calculations is that the LSDA solution has no instability against quadrupolar distortion while the LDA+U curve has a minimum at $Q=2.5\%$ of a compared with the experimental value of 4.4%. It means that exchange-only and lattice-electron ("electron-phonon") interactions in LSDA are not enough to drive the collective Jahn-Teller distortion: the orbital-dependent interaction terms must be included in the functional as is the case with LDA+U. It is possible to observe directly the orbital ordering in $KCuF_3$ by plotting the three-dimensional spin density obtained in our LDA+U calculation (Fig. 2). Since the spins are concentrated in the d orbitals, the three-dimensional (3D) spin density also gives away the orbital ordering (Fig. 2), showing the alternating x^2-z^2 and y^2-z^2 Cu $3d$ orbitals. We notice that the charge distribution changes only very little under the influence of the lattice distortion, emphasizing that this ordering is in this instance of electronic origin.

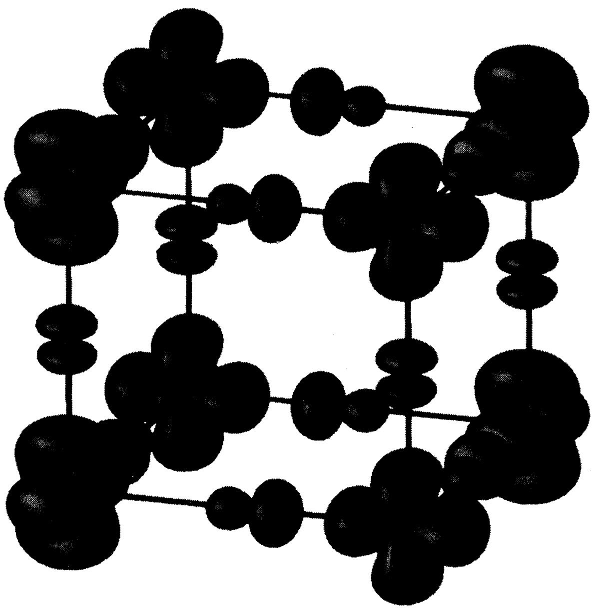

FIG. 2. The three-dimensional plot of the electron-spin-density distribution in $KCuF_3$ from the result of LDA+U calculation. Note that x^2-z^2- and y^2-z^2-like "d orbitals" correspond to spin density located at the copper atoms, while p-like density corresponds to fluorine ions.

As expected, the electronic properties come out essentially correct. The "Koopman theorem" gap in the LDA+U band structure should give an order of magnitude estimate for the single-particle gap,[5] and we find it to be similar to that in the cuprates (2 eV). Furthermore, the magnetic ordering is reproduced, and to test the method more rigorously we calculated the magnetic exchange interactions as well. Using the Green-function method to calculate effective exchange interaction parameters as second derivatives of the ground-state energy with respect to the magnetic-moment rotation angle[14] in combination with Eqs. (1–4), we obtain

$$J_{ij}=\sum_{\{m\}} I^i_{mm'}\chi^{ij}_{mm'm''m'''}I^j_{m''m'''}, \tag{8}$$

where the spin-dependent potentials I^i are expressed in terms of the LDA+U potentials [Eq. (5)] for the ith atom in the unit cell,

$$I^i_{mm'}=V^{i\uparrow}_{mm'}-V^{i\downarrow}_{mm'}, \tag{9}$$

while the susceptibilities are given in terms of the LDA+U eigenfunctions ψ and energies $\epsilon_{n\mathbf{k}\sigma}$ as

$$\chi^{ij}_{mm'm''m'''}=\sum_{\mathbf{k}nn'}\frac{n_{n\mathbf{k}\downarrow}-n_{n'\mathbf{k}\uparrow}}{\epsilon_{n\mathbf{k}\uparrow}-\epsilon_{n'\mathbf{k}\downarrow}}\psi^{ilm*}_{n\mathbf{k}\uparrow}\psi^{jlm''*}_{n\mathbf{k}\uparrow}\psi^{ilm'}_{n'\mathbf{k}\downarrow}\psi^{jlm'''}_{n'\mathbf{k}\downarrow}. \tag{10}$$

We find that the antiferromagnetic exchange in the CuF "chains" amounts to $J_c=20.7$ meV while the ferromagnetic exchange in the a-b planes is much smaller ($J_{ab}=-0.5$ meV), emphasizing the quasi-1D character of this $S=\frac{1}{2}$ spin system. This compares quite well with the neutron-scattering measurements, showing the Luttinger liquid nature of the spin system, with the 1D exchange estimated to be $J_c=17.5$ meV and $J_{ab}=-0.2$ meV.[15,16]

To appreciate the rather nontrivial nature of these results, it is instructive to consider what happens using other functionals focusing on the conditions under which the lattice distortion can occur. In order to find this instability, one needs a criterion like $1-g\chi_{\mathrm{JT}}(\mathbf{Q})<0$, where g is the electron-phonon interaction and χ_{JT} is the relevant electronic susceptibility evaluated at the ordering wave vector $\mathbf{Q}=(\pi,\pi,0)$ in the cubic zone. There is nothing special to the quadrupolar phonons, and in order to find a band Jahn-Teller instability a large enhancement of χ_{JT} is needed. It is not surprising that LSDA fails to reproduce the instability (Fig. 1), since there is no anomalous feautre in the LSDA band structure in this regard: $KCuF_3$ would be a paramagnetic metal and two bands $(\sim x^2-y^2,3z^2-1)$ cross the Fermi surface, which consists therefore of two sheets. Both bands are three-quarter filled and therefore nothing special is expected to happen at wave vector **Q**. Subsequently, one could argue that the problem of LSDA lies in the treatment of spin polarization; one can imagine that an effective Stoner theory still makes sense, although LSDA underestimates the magnitude of the Stoner splitting. This can be mimicked by neglecting the terms in Eqs. (2–4) driving the orbital polarization, and by taking F^0 as an adjustable parameter. One notices that if F^0 is taken large enough, both bands are approximately half filled in the ferromagnetic state, and at least a motive is present for finding ordering at **Q**. We checked this possibility and we find the electron-phonon coupling still too weak to destabilize the cubic structure.

The situation changes drastically if we allow for orbital polarization. Because U exceeds the bandwidth, the orbital sector is already strongly polarized (as are the spins) before the lattice is allowed to react. Overlooking some unimportant details concerning the coherence of the intermediate states, the well-known rule that electronic MFT in strong coupling maps onto the classical "spin" problem holds also in this case. In other words, we find the quadrupolar orbital-ferromagnetic spin phase to be most stable (for the same reasons as Kugel and Khomskii[6]). Obviously the cubic lattice is unstable in the presence of this orbital order parameter. In fact, despite large-scale changes in the electronic system the deformation is modest, indicating a rather weak electron-phonon coupling.

In summary, a basis-set independent generalization of the LDA+U method is developed and used to investigate the Jahn-Teller distortion and exchange interactions in the Mott-Hubbard insulator $KCuF_3$. We find that orbital ordering is a necessary condition to obtain the quadrupolar lattice distortion and 1D antiferromagnetism of this compound.

We thank S. Savrasov for providing full-potential LMTO code. J.Z. acknowledges financial support by the Royal Dutch Academy of Sciences (KNAW).

---

[1] A. Svane and O. Gunnarsson, Phys. Rev. Lett. **65**, 1148 (1990).

[2] B. Brandow, Adv. Phys. **26**, 651 (1997).

[3] E. Fradkin, *Field Theories of Condensed Matter Physics* (Addison-Wesley, Redwood City, CA, 1991).

[4] V.I. Anisimov, J. Zaanen, and O.K. Andersen, Phys. Rev. B **44**, 943 (1991).

[5] V.I. Anisimov, M.A. Korotin, J. Zaanen, and O.K. Andersen, Phys. Rev. Lett. **68**, 345 (1992).

[6] K.I. Kugel and D.I. Khomskii, Usp. Fiz. Nauk. **136**, 621 (1982) [Sov. Phys. Usp. **25**, 231 (1982)].

[7] Nonorthogonality is in principle not a problem since one can use $S^{-1/2}(\mathbf{k})H(\mathbf{k})S^{-1/2}(\mathbf{k})$ instead of $H(\mathbf{k})$ in the construction of the functional [$S(\mathbf{k})$ is the overlap matrix].

[8] V.I. Anisimov and G. Gunnarsson, Phys. Rev. B **43**, 7570 (1991).

[9] V.I. Anisimov, I.V. Solovyev, M.A. Korotin, M.T. Czyzyk, and G.A. Sawatzky, Phys. Rev. B **48**, 16 929 (1993).

[10] B.R. Judd *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill, New York, 1963).

[11] F.M.F. de Groot, J.C. Fuggle, B.T. Thole, and G.A. Sawatzky, Phys. Rev. B **42**, 5459 (1990).

[12] O. Erikson, M.S.S. Brooks, and B. Johanson, Phys. Rev. B **41**, 7311 (1990); L. Severin, M.S.S. Brooks, and B. Johanson, Phys. Rev. Lett. **71**, 3214 (1993).

[13] S. Savrasov and D. Savrasov, Phys. Rev. B **46**, 12 181 (1992).

[14] A.I. Liechtenstein, M.I. Katsnelson, V.P. Antropov, and V.A. Gubanov, J. Magn. Magn. Mater. **67**, 65 (1987).

[15] S.K. Satija, J.D. Axe, G. Shirane, H. Yoshizawa, and K. Hirokawa, Phys. Rev. B **21**, 2001 (1980).

[16] M.T. Hutchings, H. Ikeda, and J.M. Milne, J. Phys. C **12**, L739 (1979).

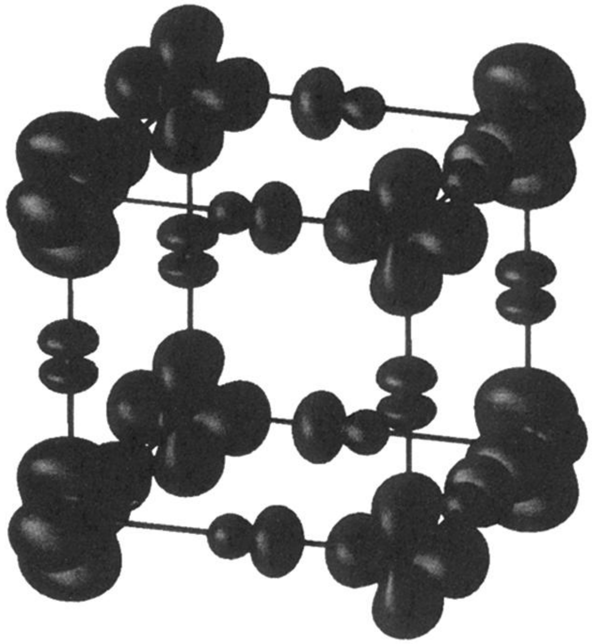

FIG. 2. The three-dimensional plot of the electron-spin-density distribution in $KCuF_3$ from the result of LDA+U calculation. Note that x^2-z^2- and y^2-z^2-like "d orbitals" correspond to spin density located at the copper atoms, while p-like density corresponds to fluorine ions.