Fermi surface nesting and possibility of orbital ordering in FeO

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We study FeO, a Mott insulator in GGA and GGA+U approximations. In the GGA we find a multi-band metallic state with remarkable inter-band nesting between two $t_{2g}$ bands of Fermi surface, which signals possible instability towards an orbital ordered insulating phase. Such broken symmetry state, although has lower energy than the underlying homogeneous metallic state, but the gap magnitude is less than the experimentally observed optical gap. Therefore we incorporate the calculated value of on-site Coulomb repulsion $U$ on orbital ordered state. We find that symmetry breaking and Coulomb correlations cooperate together to stabilize the system and give an insulating orbital ordered state, with the gap magnitude very close to the experimental value. We propose this method as a possible indication of orbital ordering in LDA and GGA calculations. We check our method with known examples of LiVO$_2$ and LaMnO$_3$.

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INTRODUCTION

Charge and spin are two fundamental characteristics of electrons. Pauling invented the concept of "orbital" as another important attribute of electrons. This theoretical tool which intuitively refers to the shape of electronic clouds, was so powerful that enabled a qualitative understanding of the electronic properties of elements in the periodic table, as well as binding in many molecules and solids in very early days of quantum mechanics, when no computers existed. Unlike charge and spin which directly couple to many experimental probes, the question of the experimental observation of orbital degrees of freedom remained untouched until recently [1]. Resonance x-ray scattering has been successfully employed for direct observation of the ordering of orbitals in manganites, $A_1-xB_2$MnO$_3$ [2], as well as some other systems such as transition metal oxides (See table 1 of Ref. [1]).

Observation of orbital ordering has established that orbitals are not just theoretical hypotheses. They are another degree of freedom, just like charge and spin which at low temperatures can form various types of ordered states. For materials such as KCuF$_3$ and LaMnO$_3$, which are a priori known to be orbital ordered, people have employed LDA+U approximation with the assumption of orbital ordering to justify the ground state properties [3, 4]. However, an important theoretical question is, given the Fermi surface topology and the electronic structure of an unknown material, under what conditions the strong correlation effects are anticipated to stabilize an orbital ordered state at low temperatures. In this paper we show that one can study the possibility of orbital ordering within ab initio spin-density-functional scheme by appropriate Fermi surface analysis. We employ our method to predict the possibility of orbital ordered phase for FeO at ambient pressure.

Despite the stoichiometric simplicity, the iron-monoxide, FeO, presents a challenge in terms of the theoretical understanding of its electronic and magnetic properties [5, 6, 7]. In series of transition metal mono-oxides the cubic crystal field splits the $d$ orbitals into two-fold $e_g$ and three-fold degenerate $t_{2g}$ states. As one moves from MnO to NiO along the periodic table of elements, the minority spins are being filled. In these systems, each (111) plane has majority spins aligned ferromagnetically within the plane (and so are the minority spins), while in the next (111) plane the ferromagnetic alignment is in opposite direction. When we consider the filling of minority spins, the degeneracy left behind in $t_{2g}$ gives rise to a metallic state with partially filled $t_{2g}$ band for FeO and CoO in Density functional Theory (DFT) within generalized gradient approximation (GGA). However, this prediction is in contradiction to experiment, where it is found to be a Mott insulator with an optical band gap of 2.4 eV [8]. Ref. [9] summarizes the various theoretical values obtained for the optical gap. The Hartree-Fock approximation largely overestimates the gap [9]. The diffusion Monte Carlo method give the gap value of $2.8 \pm 0.3$ eV [10]. In this paper, we show that this insulating behavior can be accounted for by an orbital ordering, on top of which a Hubbard type of correlation further stabilizes the insulating state. The gap value we obtain is $2.2$ eV.

In this research we use QUANTUM-ESPRESSO [11] as DFT code to apply GGA and GGA+U to FeO and GGA to LiVO$_2$ and LaMnO$_3$. For core-electron interaction ultra-soft pseudopotentials have been used. Wavefunction and charge density are expanded in plane-wave with 40 Ry and 400 Ry cutoff respectively. The Hubbard $U$ is set to 4.3 eV for GGA+U calculation for FeO [7].

Nested Fermi surfaces can potentially lower the symmetry of the ground state by either developing some sort of long-range order [12], or appropriate distortion of the lattice structure [13]. Efremov and Khomskii [14] developed a theory of orbital ordering in terms of inter-band nesting between the two $e_g$ bands in manganites. According to their work, the underlying inter-band nesting can lead to instability towards a symmetry broken phase with ordering in $e_g$ orbitals. In this work we analyze the GGA Fermi surface of FeO. We observe a remarkable nesting pattern between two of the three ($t_{2g}$) bands crossing the Fermi level. This qualitative observation can be made quantitative by calculating appropriate inter-band susceptibiliy which peaks around $q = 1/3G$, where $G$ is the reciprocal lattice vector in (111) plane. The evidence for
instability towards orbital ordered phase from GGA metallic ground state of FeO is substantiated with another independent GGA calculation for the broken symmetry phase. We also perform a GGA+U calculation to compare states with broken symmetry and those without broken symmetry. Thus, orbital ordering (OO), and Hubbard correlations work together to give a Mott insulator with orbital ordering pattern, in agreement with a similar scenario proposed for LiVO$_2$ [15].

To verify our approach, we apply this analysis to the well known orbital ordered materials, such as, LiVO$_2$ and LaMnO$_3$. The former example is closer to FeO in two respects: (i) The ordering pattern occurs in a triangular lattice of (111) plane. (ii) Both LiVO$_2$ and FeO have degenerate $t_{2g}$ bands; however, the difference is that in LiVO$_2$ we have a $d^2$ class [15], while the minority spin electrons of FeO belong to $d^1$ class. Note that the majority spin states are well separated from those of minority spins [7]. In case of FeO we are dealing with Fe$^{2+}$ cations with $3d^6$ configuration. By Hund’s rule, such $d^6$ configuration is equivalent to $d^3$ class in the minority spin sector. We first calculate the GGA bands and Fermi surface for the trigonal structure. This gives us a metallic state with remarkable inter-band nesting shown in Fig. 1(a). In this figure, the nesting is only between two of the $t_{2g}$ Fermi surfaces. The third $t_{2g}$ band does not contribute substantially to the Fermi surface. We have checked that this band is further pushed away from the Fermi level by small amounts of on-site Coulomb interaction $U$. Hence despite the threefold degeneracy of $t_{2g}$ bands, here we are dealing with a two-band situation to which the picture proposed by Efremov and Khomskii in the context of orbital ordering instability of $e_g$ bands [L4] can be applied. The same type of inter-band nesting can be observed in the GGA Fermi surfaces of LiVO$_2$ (Fig. 1b), which is known to exhibit orbital ordering at low temperatures [15, 16, 17]. The example of LiVO$_2$ is very similar to FeO, in terms of underlying triangular lattice structure in (111) plane. This is also reflected in their Fermi surface topologies in Fig. 1. In Fig. 1(c) we plot the GGA Fermi surface of LaMnO$_3$. As shown by Efremov and Khomskii [14], such a nesting leads to an instability towards orbital ordered state at low enough temperatures. In the following we are going to argue that the same argument predicts orbital ordering for LiVO$_2$ and FeO.

To quantify the above discussion, we calculate the contribution of inter-band processes to generalized susceptibility defined by,

$$
\chi_{\text{inter}}(q) = \sum_k \frac{f(\epsilon^a_k) [1 - f(\epsilon^b_{k+q})]}{\epsilon^a_{k+q} - \epsilon^b_k},
$$

where $a$ and $b$ denotes the two nested bands, $f(\epsilon)$ is the occupation number and $\epsilon^{a,b}$ denotes the band energy. To identify the exact value of nesting vector we calculated generalized susceptibility in direction of $G_1 \pm G_2$, where $G_1$ and $G_2$ are two basis vectors in the reciprocal space.

![FIG. 1: (Color online) Fermi surface for (a) FeO, (b) LiVO$_2$ and (c) LaMnO$_3$. The Fermi surfaces are plotted in the reciprocal lattice (not in the first Brillouin zone). For FeO and LiVO$_2$ the lattice is trigonal and for LaMnO$_3$ is tetragonal.](image1)

![FIG. 2: (Color online) Generalized susceptibility for FeO, LiVO$_2$ and LaMnO$_3$. For FeO and LiVO$_2$ the direction of $q$ is parallel to $G_1 - G_2$ where $G_1$ and $G_2$ are vectors in reciprocal space of the trigonal lattice. For LaMnO$_3$ we chose $q$ in the direction of $G_1 + G_2$ where $G_1$ and $G_2$ are reciprocal lattice vectors of the tetragonal lattice ($|G_1| = |G_2|$). The vertical line indicates the maximum of generalized susceptibility at $q = \frac{1}{3}(G_1 - G_2)$ for FeO and LiVO$_2$.](image2)
panels (a)-(c) of Fig. 1 respectively [18]. As can be seen in Fig. 2 for the case of LaMnO$_3$, the inter-band susceptibility peaks around the ordering vector, $q = \frac{1}{2}(G_1 + G_2)$ in (001) plane [14]. This implies an ordering in the $xy$ plane with $2a \times 2a$ unit cell. Now let us focus on the case of $t_{2g}$ systems, FeO and LiVO$_2$. As can be seen in Fig. 2 for the case of FeO and LiVO$_2$, the susceptibility peaks around $q = \frac{1}{2}(G_1 - G_2)$. Based on the theory of Ref. [14], we speculate this implies a possible instability towards ordering of $t_{2g}$ bands on a triangular lattice of (111) plane.

Feeding these information back into the DFT machinery, we examine the total energy, gap magnitude and charge distribution profile assuming an ordering pattern suggested from our Fermi surface analysis. Hence we are left to examine a broken symmetry phase with a $\sqrt{3}a \times \sqrt{3}a$ supercell in (111) plane [2,15]. The structure contains three Fe atom per (111) plane. With the new supercell, we allow for a small displacement of Fe atoms (according to Ref. 7) to check for the possibility of relaxation towards a new minimum in the GGA approximation. This new state is orbital ordered insulating state, as can be seen in the charge density profile shown in Fig. 4. The insulating behavior of this state is due to broken symmetry accompanying the orbital ordering. The gap magnitude at $\Gamma$ point for this state is $E_g^{\text{GGA}} \approx 0.54$ eV. The energy of this new minimum per supercell is about 0.47 eV lower than the corresponding non-ordered metallic state.

Although in the GGA approximation when we allow for the possibility of a broken symmetry state, we find an insulating state with lower energy than the original metallic one, but the energy gap is still far less than the experimentally observed value of $E_g = 2.4$ eV [8]. The GGA energy level of FeO suggests the following picture: Five majority spins are well below the Fermi level, leaving one minority spin in the relevant $t_{2g}$ band [7]. To this extent, we consider FeO to belong to $d^1$ class. Therefore we are dealing with one minority spin per site Mott insulating situation. Hence, we have to take into account the role of on-site Coulomb interaction, $U$. We incorporate the effect of $U \sim 4.3$ eV within the GGA+U approximation. With this value of $U$, we obtain the energy gap $E_g^{\text{GGA}+U} \sim 2.2$ eV at the $\Gamma$ point. Note that we did not adjust the value of $U$. The above value for $U$ was calculated in Ref. [7]. Compared to sophisticated quantum Monte Carlo calculations [10], our result is in remarkable agreement with the experimental value [9]. Therefore both orbital ordering, as well as Coulomb correlations are important to understand the electronic structure of FeO Mott insulator.

With GGA+U there is a freedom on choosing the appropriate state in the $t_{2g}$ subspace to be occupied by minority spin. The most general state in this subspace is of the form, $\alpha|xy\rangle + \beta|yz\rangle + \gamma|zx\rangle$. The underlying triangular lattice structure with $C_3$ symmetry requires invariance under $120^\circ$ rotations. Therefore the two other states are required to be, $\alpha|yz\rangle + \beta|zx\rangle + \gamma|xy\rangle$, $\alpha|zx\rangle + \beta|xy\rangle + \gamma|yz\rangle$. Each set of values for $(\alpha, \beta, \gamma)$ corresponds to a new orbital ordered configuration. The only choice which leads to state without orbital ordering is the homogeneous one with $|\alpha| = |\beta| = |\gamma| = 1/\sqrt{3}$ (the so called $a_{1g}$ state). In GGA+U it is not feasible to check the energy of all possible states. In Table I we compare the energy of the non-ordered $a_{1g}$ state with two states corresponding to $(\alpha, \beta, \gamma) = (1, 0, 0)$, and $(\alpha, \beta, \gamma) = (1, 1, 0)/\sqrt{2}$. Second column of table I indicates that, in presence of electron-electron interaction $U$, orbital ordering still reduces the total energy by tens of meV per unit cell.
cell. The state $(1, 0, 0)$ has lower energy for which we have plotted the charge density in Fig. 4. This state is the negation of the state proposed in Ref. [15] for the LiVO$_3$. Such a negation image is reasonable given the fact that $d^1$ and $d^2$ classes in $t_{2g}$ subspace are connected with a particle-hole symmetry transformation.

So far we have checked that electronic interactions can take advantage of the instability suggested by the nested Fermi surface, to stabilize an orbital ordered pattern. Next we ask the question, can electron-lattice interactions take advantage of this instability to give rise to appropriate form of Jahn-Teller distortion? To verify this for the case of FeO, we start with orbital ordered states $(\alpha, \beta, \gamma)$, then we allow the atomic positions to relax. In the third column of table [1] we report the calculated total energy per unit cell when the relaxation is allowed. As it can be seen, the relaxed structure has lower energy than the corresponding non-relaxed state. Note that to verify whether the orbital ordered state is more stable than the non-ordered state, we first distorted the atomic positions which resulted in orbital ordering pattern of Fig. 3. But here we check the reverse sequence, i.e. we start off with an orbital ordered state, then we check whether the atomic displacements can further stabilize orbital ordered state or not. Therefore for both orbital ordered states considered here, the ordering is always accompanied with cooperative Jahn-Teller distortion.

To summarize, we started with a GGA metallic band picture. The inter-band nesting pointed us to examine the energy of orbitally ordered state within the same approximation. However, since in the case of transition metal oxides the Coulomb correlation U is also important, we also compared the energy of orbital ordered states in presence of on-site Coulomb interaction U, in the GGA+U approximation. In FeO, orbital ordering significantly stabilizes both GGA as well as GGA+U states with respect to corresponding non-ordered phases. We also allowed for relaxation of the atomic positions on top of orbitally ordered GGA+U state. We found that the Jahn-Teller distortion accompanying the orbital ordering is automatically realized in our approach. As a check of this method, we also studied the cases of LiVO$_3$ and LaMnO$_3$ which are known to exhibit orbital ordering at low temperature. Therefore we propose this Fermi surface analysis as a rout to explore the possibility of orbital ordering and/or reduction in the lattice symmetry, within the DFT (LDA/GGA) electronic structure calculations.

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[18] To calculate the generalized susceptibility we used $120 \times 120 \times 120$ k-point mesh for FeO. For LiVO$_3$ and LaMnO$_3$ we used $100 \times 100 \times 100$ and $100 \times 100 \times 50$ mesh respectively. Since the LiVO$_3$ is spin singlet, we assume a nonmagnetic solution, while in FeO with the same lattice structure (trigonal) we assume magnetic solution. For LaMnO$_3$ we use a tetragonal structure for the A-type phase.