Is paramagnetic FeO strongly correlated?

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Paramagnetic FeO is traditionally considered a strongly correlated material, and as such it is commonly studied using dynamical mean field theory, since static mean-field theories are considered not appropriate to describe, for example, the band gap. However we have recently found that the Hartree-Fock method opens a gap in this system [Di Sabatino at al., J. Chem. Theory Comput. 15, 5080 (2019)]. This finding might be interpreted as exchange rather than correlation being responsible for the band-gap opening. We provide an exhaustive study of the band structure and density of states of paramagnetic FeO using various state-of-the art methods, namely, density-functional theory with the standard local density approximation (LDA) as well as with a hybrid functional containing screened exchange (HSE06), Hartree-Fock, various flavours of GW, and our recently derived many-body effective-energy theory (MEET). We show that, with the exception of LDA, all these methods open a gap, although it is overestimated with respect to experiment. However, only the MEET is able to give a correct description of the underlying physics of the band-gap opening, which emerges from a high-spin configuration of the ground-state, which is compatible with experiment, rather than a low-spin configuration as in the other methods.

I. INTRODUCTION

The physics of strongly correlated systems cannot be described by standard band-structure methods and ab initio mean-field theories; correlated methods such as dynamical mean field theory (DMFT)1–3 are hence usually employed to describe them. However, DMFT generally relies on an empirical Mott-Hubbard parameter \( U \). Paramagnetic (PM) FeO is a typical example for which standard density-functional theory (DFT) calculations give a metallic ground state and hence DMFT is often employed to correctly describe its physics.

FeO is a basic oxide component of the Earth’s interior4 and has a rather complex pressure-temperature phase diagram.5–9 Under ambient conditions, it is a paramagnetic Mott insulator with a rock-salt B1 crystal structure and it undergoes a phase transition into rhombohedrally distorted B1 structure above 16 GPa. At high temperature and pressure an insulator-to-metal transition is observed with a collapse of the local magnetic moment. A similar magnetic collapse at high pressure is also observed in other similar transition-metal oxides such as MnO, CoO, and NiO.8,9,10 Various detailed theoretical studies of the electronic structure and phase stability of these transition metal oxides, in particular in the paramagnetic phase, which employ DMFT combined with ab initio band-structure methods, are present in literature, and they can reproduce most of the experimental observations.12–16

However, unlike for MnO, CoO, and NiO, for which even ab initio methods more advanced than DFT, such as GW, cannot capture the insulating behaviour of the PM phase, for FeO Hartree-Fock (HF) is enough to open a gap.17 This raises the question whether or not this system is strongly correlated. We will give the answer in this work.

We propose a detailed study of the band structure and density of states of PM FeO using various levels of theories, namely, DFT within standard Kohn-Sham (KS) and a generalized KS scheme with the nonlocal exchange-correlation functional HSE06,18 Hartree-Fock, self-consistent COHSEX (scCOHSEX)19, quasiparticle self-consistent GW (QPscGW) as proposed in Ref. 20, and our recently derived many-body effective energy theory (MEET).17,21 This paper is organized as follows: in Sec. III we summarize the computational details of the performed calculations. Band structures and density of states (DOS) are presented and discussed in Sec. IV. Summary and conclusions are drawn in Sec. V.

II. THEORETICAL BACKGROUND

In this section we give a few details of the theoretical methods we employed for our calculations.

A. DFT

Density-functional theory is very popular for the calculations of ground-state properties from first-principles. In this work, besides using standard DFT within the local density approximation (LDA) we also use it within the range-separated hybrid functional HSE06 proposed by Heyd et al.,18 in which a screened Coulomb potential is applied to the exchange interaction in order to screen the long-range part of the HF exchange. This relies on the splitting of the Coulomb operator into short-range

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(SR) and long-range (LR) components:
\[
\frac{1}{r} = \frac{1 - \text{erf}(\omega r)}{\sqrt{\pi} SR} + \frac{\text{erf}(\omega r)}{\sqrt{\pi} LR}
\]
where the screening parameter \( \omega \) defines the separation range. Increasing \( \omega \) increases the screening in the system.

**B. \( GW \)**

The \( GW \) approximation\(^{22}\) has become the method of choice for band-structure calculations and photoemission spectra in condensed-matter. Usually Kohn-Sham (KS) DFT band structures are used as starting point for a one-step, perturbative, \( GW \) calculation, the so called \( G_0W_0 \). This procedure, however, suffers from a starting-point dependence, which can bring to unsatisfactory \( GW \) results if the underlying KS band structure is qualitatively incorrect. This is precisely the case for strongly correlated materials. To get rid (at least partially) of this starting-point dependence various level of self-consistency can be introduced. In this work we will use self-consistent COHSEX (Coulomb hole and screened exchange)\(^{19,22}\) and quasiparticle self-consistent \( GW \) according to a variant of the method originally suggested by van Schilfgaarde et al.\(^{24}\) and as implemented in the VASP code.\(^{20}\) Both approaches rely on a static approximation to the \( GW \) self-energy and can, therefore, only treat quasiparticles. The scCOHSEX method also uses a static screening while QPscGW uses a fully dynamical \( W \). In both schemes we update the quasiparticle energies and wave functions with which both the Green’s function \( G \) and screened Coulomb interaction \( W \) are built.

**C. Many-body Effective Energy Theory**

The Many-body Effective Energy Theory expresses the spectral function in terms of \( n \)-body reduced density matrices. Truncation to one- and two-body density matrices, \( \gamma \) and \( \Gamma \), respectively, gives qualitative good spectra for strongly correlated materials. More details can be found in Refs \([17,21]\). In particular we calculate the one- and two-body density matrices within reduced-density matrix functional theory (RDMFT),\(^{24}\) and we use the so-called power functional\(^{25}\) (including the Goedecker and Umrigar (GU) self-interaction correction\(^{26}\)) to approximate the two-body density matrix as
\[
\Gamma(x, x'; x, x') = \gamma(x, x') \gamma(x', x') - \gamma^0(x, x') \gamma^0(x', x),
\]
where \( \gamma^0(x, x') = \sum_j n_j^0 \phi_j(x) \phi_j(x') \) with \( n_j \) and \( \phi_j \) the occupations numbers and natural orbitals, respectively, and \( 0.5 \leq \alpha \leq 1 \). The fractionality of the natural occupation number, \( n_j \), can be related to the amount of electron correlation in a system.\(^{27,28}\) Therefore, the parameter \( \alpha \) controls the degree of correlation: the optimal value suggested in literature is in the range \( \alpha = 0.65 - 0.70.\(^{25,29}\)\)

**III. COMPUTATIONAL DETAILS**

DFT, HF and \( GW \) calculations have been performed using the Vienna Ab-initio Simulation Package (VASP)\(^{30,31}\) with the projector-augmented wave (PAW) method.\(^{32,33}\) The MEET calculations have been performed using a modified version of the open-source full-potential linearized augmented plane wave (FP-LAPW) code ELK,\(^{34}\) with practical details of the calculations following the scheme described in Ref. \(^{25}\). We described the PM phase of FeO as nonmagnetic and we used a rocksalt structure with half of the experimental lattice constant of the corresponding AF phase, i.e. \( 8.666 \) Å.\(^{35}\)

For LDA, HF and HSE06 we used a \( \Gamma \)-centered \( 14 \times 14 \times 14 \) \( k \) point mesh. The electronic wave functions are expanded in plane waves up to a cutoff of 500 eV.

For the \( GW \) calculations we treat the dielectric screening at the level of the random-phase approximation (RPA). We include 200 bands for screening and self-energy, and expand the pseudowavefunctions and dielectric matrices in the basis of plane waves up to 700 eV and 800 eV, respectively. We use \( \Gamma \)-centered \( 8 \times 8 \times 8 \) \( k \)-point grid. We include Fe 3s, 3p, 3d, and 4s and O-2s and 2p as valence states. For HF, HSE06 and \( GW \), we obtain the band structures using Wannier interpolation as implemented in the Wannier90 computer program.\(^{37}\)

For the ELK calculations we used a \( \Gamma \)-centered \( 8 \times 8 \times 8 \) \( k \)-point grid. The muffin-tin radius for Fe and O atoms are 2.31 and 1.73 a.u., respectively. The muffin-tin (MT) radius times maximum \( |G + k| \) vectors, \( R_{\text{MT}} \times \max|G + k| \), is 7.0, while the maximum length of \( |G| \) for expanding the interstitial density and potential is 12.0 a.u.\(^{-1}\). We use 8 empty bands.

**IV. RESULTS: BAND STRUCTURE AND DENSITY OF STATES**

**A. LDA, HF, and HSE06**

In Fig. 1 we show the band structure and DOS of PM FeO calculated using LDA, HF, and HSE06. The experimental photoemission spectrum from Ref. \(^{36}\) is also reported for comparison. We see that within the LDA we obtain a metallic ground state which is qualitatively wrong. We also observe that the Fe \( t_{2g} \) and \( e_g \) states are nearly degenerate and located around the Fermi level with the six \( d \) electrons of Fe distributed predominantly in the \( t_{2g} \) orbitals. We note that we have verified that a semilocal functional (PBE)\(^{38}\) gives very similar results.

Within the non-local Hartree-Fock theory we obtain a very different picture. Compared to the LDA results, the \( t_{2g} \)-\( e_g \) degeneracy is lifted. HF favors a completely filled \( t_{2g} \) shell and a gap appears between \( t_{2g} \) and \( e_g \) states. The band gap is, however, overestimated with respect to the experimental value, as one can see from Table I. We note that Zimmermann \textit{et al.}\(^{36}\) did not derive a value for the fundamental gap from their experimental data.
Figure 1: (Color online) Band structure and DOS calculated using LDA (left panel), HF (middle panel), and HSE06 (right panel). The experimental photoemission spectrum is taken from Ref. [36]. In the calculated spectra the contributions of the Fe $t_{2g}$ and $e_g$ states and of the O-$2p$ states to the total DOS are also reported.

Only the gap derived from optical absorption (2.4 eV) of the nonstoichiometric FeO phase is available, which is much larger than the gap one would estimate from the alignment of the XPS and BIS spectra in Ref. [36].

One might be tempted to conclude that HF at least gives the correct qualitative picture since it yields an insulating ground state. However, the projected DOS (PDOS) in HF is compatible with a low-spin configuration, in which all six $d$ electrons of Fe occupy the $t_{2g}$ states. This is in contradiction with DMFT studies, which found FeO to be in a high-spin (HS) configuration at room temperature and atmospheric pressure and undergoing a transition to a low-spin configuration by applying pressure (see Fig. 2). This is also in agreement with the experimental observation that the local magnetic moment collapses when pressure is applied. Therefore it seems that exchange produces a gap for the wrong reason. In fact the appearance of the gap is simply fortuitous: exchange tends to separate $t_{2g}$ and $e_g$ and since Fe has six $d$ electrons, they fully occupy the $t_{2g}$, opening a gap. In other similar transition-metal oxides such as MnO, CoO, and NiO, this does not happen since the transition metal has less or more than six electrons, and therefore they partially occupy the $t_{2g}$ or $e_g$ bands, leading to a metal.

Finally, we introduce correlation by applying the HSE06 functional, a non-local screened hybrid (see rightmost panel of Fig. 1). Compared to HF the HSE06 band gap is smaller and, although still too large, much closer to the experimental value. However, like HF, the origin of the gap is qualitatively wrong since also HSE06 favors the low-spin configuration. One can also observe that screening drastically changes the character of the valence bands, with the topmost occupied bands becoming predominantly $t_{2g}$-like and the lower occupied bands mainly $O-2p$ like, thus strongly decreasing the hybridization between $O-2p$ and Fe-$d$ states with respect to HF.

We checked that increasing screening, i.e., by increasing the value of the screening parameter $\omega$ in Eq. (1), tends to close the gap towards the experimental value of ~2.4 eV.

One might hope that using a HSE06 band structure as starting point for a one-step, perturbative, but fully dynamical $GW$ ($G_0W_0$) calculation could correctly reproduce the band gap width of PM FeO, although this would be opposite to the trend found for the antiferromagnetic (AF) phase, for which $G_0W_0$ on top of HSE03 slightly opens the gap.

Figure 2: High-spin to low-spin transition induced by increasing pressure.
Can a self-consistent GW calculation change the projected DOS of PM FeO with respect to HF/HSE06? By introducing self-consistency the final result should, in principle, be independent of the starting point. Starting from LDA results as input, GW calculations are hard to converge, therefore we started from HSE06 as well as LDA+U (with various values of U) and checked that we converge to the same result using self-consistent COHSEX. Note that this procedure in general yields results close to quasiparticle self-consistent GW, but at a lower computational cost. With HSE06 and LDA+U as starting points the initial band gap has already the incorrect nature, since it is between completely full and completely empty states. Self-consistent COHSEX does not change this picture, but it does alter the band gap width, which departs even more from experiment (see Table I). One-step GW on top of COHSEX slightly closes the direct band gap while the indirect band gap remains practically unaffected. The modifications that the \( G_0 W_0 \) induces are clearly not uniform, as one can see from Fig. 3. Bands with different atomic orbital character have different shifts in energy upon application of \( G_0 W_0 \). To complete our analysis we calculated the band structure and DOS using QPscGW. The results are depicted in Fig. 4. The \( t_{2g} \) and \( e_g \) states are split at the band gap, as they are in HF and HSE06. We observe that the QPscGW and scCOHSEX+\( G_0 W_0 \) band structures are quite similar for the valence Fe-\( d \) states, but they differ by \( \sim 0.5 \) eV for the valence O-2\( p \) as well as the conduction states.

### Table I: Indirect and direct band gaps from different electronic-structure methods.

| method               | \( E_g^{\text{ind}} [\text{eV}] \) | \( E_g^{\text{dir}} [\text{eV}] \) |
|----------------------|----------------------------------|----------------------------------|
| LDA                  | 0.0                              | 0.0                              |
| HF                   | 14.7                             | 14.9                             |
| HSE06                | 2.9                              | 3.4                              |
| HSE06+\( G_0 W_0 \)  | 3.5                              | 3.9                              |
| scCOHSEX             | 4.1                              | 4.6                              |
| scCOHSEX+\( G_0 W_0 \)| 4.1                             | 4.6                              |
| QPscGW               | 3.6                              | 4.2                              |
| MEET \( (\alpha = 0.65) \) | 16.2                          | 16.5                             |
| Exp (opt. abs.)      | 2.4\(^{39}\)                    |                                   |

Figure 3: Band structure calculated using self-consistent COHSEX (scCOHSEX, red dotted line), self-consistent COHSEX+\( G_0 W_0 \) (scCOHSEX+\( G_0 W_0 \), blue dashed line), and quasiparticle self-consistent GW (QPscGW, black solid line).

### B. GW

In Table I we report the band gap obtained with \( G_0 W_0 \) on top of HSE06 (HSE06+\( G_0 W_0 \)), scCOHSEX, \( G_0 W_0 \) on top of scCOHSEX (scCOHSEX+\( G_0 W_0 \)), and QPscGW. It becomes clear that a simple \( G_0 W_0 \) calculation on top of HF/HSE06 results will not correct the nature of the band gap, but will only change its width. For example, \( G_0 W_0 \) on top of HSE06 leads to a band gap (both direct and indirect) of \( \sim 0.5 \) eV larger than the HSE06 band gap. This trend is qualitatively similar to what is observed for the antiferromagnetic FeO, where \( G_0 W_0 \) induces a slight opening (\( \sim 0.1 \) eV) of the gap on top of HSE06\(^{42,49}\). However, in the case of antiferromagnetic FeO\(^{40}\) the opening induced by \( G_0 W_0 \) improves the agreement with the experimental band gap; in the present paramagnetic case, instead, the \( G_0 W_0 \) increases the discrepancy with experiment. We checked that the static macroscopic dielectric function used to build \( W \) is similar for the AF and the PM phases: the macroscopic static dielectric constant in AFM phase is 4.4\(^{40}\), while in our PM phase is 4.5. Therefore the quantitative difference of the HSE06/HSE06+\( G_0 W_0 \) band gap between the two phases is most likely due to the different nature of the states involved in the calculations: in the PM phases the band gap occurs between \( t_{2g} \) and \( e_g \) states, whereas in the AF phase it should occur within the minority-channel \( t_{2g} \) states\(^{40}\).

### C. Many-body Effective Energy Theory

To conclude our analysis we calculated the spectral function of PM FeO using our recently derived Many-body Effective Energy Theory\(^{17,21}\). In the third panel of Fig. 5 we report the spectral function of PM FeO calculated using the MEET with \( \alpha = 0.65 \), which, as mentioned before (see Sec. II C), is considered to be in the range of optimal values and is the value we used in previous studies\(^{17,21}\). We observe that the MEET is the only approach that yields a qualitatively correct band gap because the composition of the spectral function in terms of \( t_{2g} \) and \( e_g \) is compatible with a high-spin configuration.
Figure 4: Band structure and quasiparticle density of states (DOS) from quasiparticle self-consistent GW (QPscGW). The experimental photoemission spectrum is taken from Ref. [36]. In the calculated spectra the contributions of the Fe $t_{2g}$ and $e_g$ states and of the O-2p states to the total DOS are also reported.

Figure 5: Photoemission spectrum calculated using MEET for various values of $\alpha$. The contributions of the Fe $t_{2g}$ and $e_g$ states and of the O-2p states to the total DOS are also reported.

V. SUMMARY AND CONCLUSIONS

We presented a detailed study of the band-gap opening nature of bulk FeO in the paramagnetic phase. Using various first-principle mean-field methods we showed that it is enough to introduce exchange to open a gap. Screening is however necessary to reduce the band gap towards the experimental value, although discrepancies of more than 0.5 eV still remain. The nature of the band-gap opening, however, is incorrect, since it emerges from an upward shift of the $e_g$ bands, which favors the full filling of the lower-lying $t_{2g}$ bands with the six $d$ electrons of Fe, which is compatible with a low-spin configuration. This scenario is quite different from previous DMFT calculations which shows the FeO to be in a high-spin configuration at ambient temperature and pressure, and undergoing a transition to a low-spin configuration at high pressure. We show that only using a method which can treat strong correlation, such as the MEET, gives a qualitatively good description of the band-gap opening. This confirms that paramagnetic FeO is a strongly correlated material.

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We note that we have also calculated the band structure and DOS of the paramagnetic phase using HSE03 and we find similar results and trends as for the HSE06.

We have verified that $G_0W_0$ on top of HSE03 shows the same trend as $G_0W_0$ on top of HSE06.