



PAPER

Doping induced metal-insulator phase transition in NiO—a reduced density matrix functional theory perspective

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Y Shinohara¹, S Sharma^{1,2}, J K Dewhurst¹, S Shallcross³, N N Lathiotakis^{1,4} and E K U Gross¹¹ Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany² Department of Physics, Indian Institute of Technology, Roorkee, 247667, Uttarakhand, India³ Lehrstuhl für Theoretische Festkörperphysik, Staudstr. 7-B2, D-91058 Erlangen, Germany⁴ Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Vass. Constantinou 48, GR-11635 Athens, GreeceE-mail: sharma@mpi-halle.mpg.de**Keywords:** reduced density matrix functional theory, insulator metal phase transition, Mott insulators**Abstract**

The insulator to metal phase transition in NiO is studied within the framework of reduced density matrix functional theory (RDMFT) and density functional theory (DFT). We find that the spectral density obtained using RDMFT is in good agreement with experiments both for undoped as well as doped NiO. We find that the physical description of the hole-doping induced phase transition *qualitatively differs* depending on whether NiO is calculated within DFT or reduced density matrix functional. In the former case the underlying mechanism of the phase transition is identified to be a rigid shift of chemical potential, while in the latter case a redistribution of the spectral weight drives the transition. These latter results are found to be in good agreement with both experiments and previous many-body calculations.

1. Introduction

Strongly correlated materials possess a wide spectrum physical properties that makes them of both fundamental as well as practical importance. They have been studied as possible candidates for photo-voltaic material [1], field-effect devices [2] and high temperature superconductors [3]. After many decades of research a fully first principles theory capable of treating these materials remains elusive. The anti ferromagnetic (AFM) transition metal oxides (TMOs), which are prototypical strongly correlated materials, present the outstanding ‘test case’ challenge to a first principles treatment of correlated solids. Amongst TMOs NiO, an AFM Mott insulator with a measured gap of 4.1 eV and a magnetic moment of $1.7\mu_B$, is of the most studied systems. The standard local density approximation (LDA) [4] within density functional theory (DFT) predicts a metallic spectrum for NiO, in fundamental disagreement with experimental reality. The inclusion of spin polarization via the local spin density approximation (LSDA) results in a small Kohn–Sham(KS) gap, and a description of NiO as a Slater insulator. However, both the gap and the magnetic moment are severely underestimated suggesting that the Slater AFM state obtained within the LSDA does not describe the true nature of NiO.

In order to overcome this deficiency of the KS spectra obtained using the LSDA, Rödl *et al* proposed the use of two separate fitting parameters: an on-site Coulomb term U and a scissors shift Δ by which the conduction bands are rigidly shifted, with Δ the difference between the experimental gap and the KS gap obtained using LSDA + U functional [5]. With a certain choice of these two parameters the KS spectra of NiO can be made to agree with computationally expensive many-body techniques such as dynamical mean field theory (DMFT) [6–10], reduced density matrix functional theory (RDMFT) [11, 12], and the GW method [5]. This scissors corrected LSDA + U method comes under the heading of the so called correlated band theory method.

What makes NiO even more interesting is its behavior as a function of doping: one finds an insulator to metal phase transition (IMT) on doping the system with Li, which amounts to hole doping [13]. The rich physics of this phase transition entails subtle interplay of charge transfer and Mott localization: despite being a text book Mott insulator, NiO also has a strong charge transfer character due to the large overlap (in energy) of the Ni-d

and O-p states. Any theory attempting to capture this IMT in NiO must be capable of treating Mott correlations and charge transfer effects at an equal footing [9], presenting a significant theoretical challenge.

In the present work we study the IMT in NiO using three different approaches: the LSDA within DFT, correlated band theory method [14, 15], LSDA + U , and a many-body technique, RDMFT. In doing so we demonstrate that even though at zero doping all these methods give similar spectra, the physics of hole doping induced phase transition is *qualitatively different* for the different theoretical methods: within band and correlated band theory methods the metalization occurs due to a rigid shift of the chemical potential into the valence band, with the separation between the Hubbard bands remaining approximately constant. In total contrast to this, within RDMFT one finds that the phase transition is driven by a transfer in spectral weight from the upper and lower Hubbard bands to a low energy peak, known as the correlated peak. These latter results we find to be in good agreement with previous many-body results obtained using DMFT [9].

2. Theory

Recently, RDMFT has shown potential for correctly treating band as well as Mott insulators [11, 12, 16], or in other words, treating both Mott correlation and charge transfer effects equally well. Within RDMFT, the one-body reduced density matrix (one-RDM) is the basic variable [17, 18]

$$\gamma(\mathbf{x}, \mathbf{x}') \equiv N \int d\mathbf{x}_2 \dots d\mathbf{x}_N \Psi(\mathbf{x}, \mathbf{x}_2 \dots \mathbf{x}_N) \Psi^*(\mathbf{x}', \mathbf{x}_2 \dots \mathbf{x}_N), \quad (1)$$

where Ψ denotes the many-body wave function and N is the total number of electrons and $\mathbf{x} \equiv (\sigma, \mathbf{r})$. Diagonalization of γ produces a set of orthonormal Bloch functions, the so called natural orbitals [17], $\varphi_{i\mathbf{k}}$, and occupation numbers, $n_{i\mathbf{k}}$. Extending RDMFT to the truly non-collinear magnetic case [12], by treating the natural orbitals as two component Pauli-spinors, leads to the spectral representation

$$\gamma(\mathbf{x}, \mathbf{x}') = \sum_{i\mathbf{k}} n_{i\mathbf{k}} \varphi_{i\mathbf{k}}(\mathbf{x}) \varphi_{i\mathbf{k}}^*(\mathbf{x}'). \quad (2)$$

The necessary and sufficient conditions for ensemble N -representability of γ were provided, in a classic work, by Coleman [19]. These conditions require

$$\begin{aligned} 0 &\leq n_{i\mathbf{k}} \leq 1 \\ \sum_{i\mathbf{k}} n_{i\mathbf{k}} &= N. \end{aligned} \quad (3)$$

In terms of γ , the total ground-state energy [18] of the interacting system is (atomic units are used throughout)

$$\begin{aligned} E[\gamma] &= -\frac{1}{2} \text{tr}_\sigma \int \lim_{\mathbf{r} \rightarrow \mathbf{r}'} \nabla_{\mathbf{r}}^2 \gamma(\mathbf{x}, \mathbf{x}') d^3 r' + \int \rho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d^3 r \\ &+ \frac{1}{2} \int \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r d^3 r' + E_{\text{xc}}[\gamma], \end{aligned} \quad (4)$$

where $\rho(\mathbf{r}) = \text{tr}_\sigma \gamma(\mathbf{x}, \mathbf{x})$, V_{ext} is a given external potential, and E_{xc} we call the exchange-correlation (xc) energy functional. In principle, Gilbert's [18] generalization of the Hohenberg–Kohn theorem to the one-RDM guarantees the existence of a functional $E[\gamma]$ whose minimum, for fixed a V_{ext} , yields the exact γ and the exact ground-state energy. In practice, however, the xc energy is an unknown functional of γ and needs to be approximated. Several approximations for the xc energy functionals are known [20–30]. For finite systems spectral properties [31–35] as well as molecular dissociation [21–23, 36, 37] can be accurately described using these xc functionals. For extended systems, the most promising approximation is the power functional [11, 38, 39] where the xc energy is given by

$$E_{\text{xc}}[\gamma] = -\frac{1}{2} \int \int d\mathbf{x}' d\mathbf{x} \frac{|\gamma^\alpha(\mathbf{x}, \mathbf{x}')|^2}{|\mathbf{r} - \mathbf{r}'|} \quad (5)$$

with α indicating the power in the operator sense. In view of the universality of the functional $E_{\text{xc}}[\gamma]$, the value of α should, in principle, be system-independent. A few 'optimum values' of α have been suggested in the literature [11, 39, 40]; in the present work α is fixed to 0.56.

In order to study the doping dependent metalization of NiO one crucially needs spectral information. To obtain this information from RDMFT, which by its very nature is a ground-state theory, is a difficult task. In this work we extract spectral density from RDMFT using the method recently proposed in [12]. Within this method the diagonal of the spectral density, i.e. the density of states, is determined using the following relation:

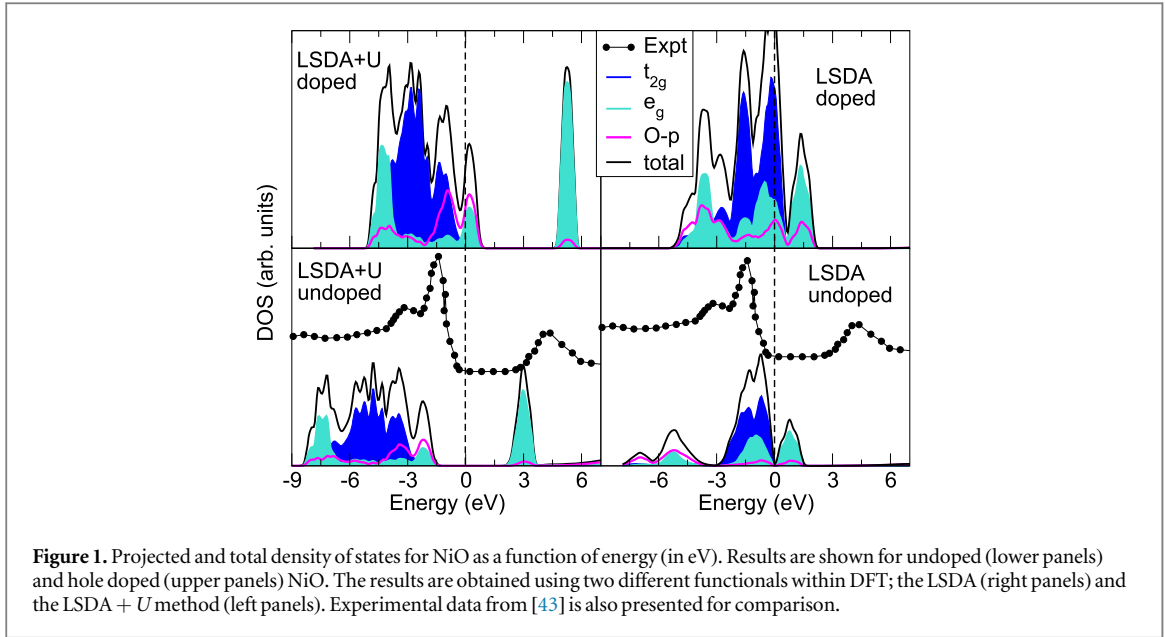


Figure 1. Projected and total density of states for NiO as a function of energy (in eV). Results are shown for undoped (lower panels) and hole doped (upper panels) NiO. The results are obtained using two different functionals within DFT; the LSDA (right panels) and the LSDA + U method (left panels). Experimental data from [43] is also presented for comparison.

$$\text{DOS} = 2\pi \sum_{i,\mathbf{k}} \left[n_{i\mathbf{k}} \delta(\omega - \epsilon_{i\mathbf{k}}^-) + (1 - n_{i\mathbf{k}}) \delta(\omega + \epsilon_{i\mathbf{k}}^+) \right], \quad (6)$$

where

$$\epsilon_{i\mathbf{k}}^\pm = \left. \frac{\partial E[\{\phi\}, \{n\}]}{\partial n_{i\mathbf{k}}} \right|_{n_{i\mathbf{k}}=1/2} - \mu, \quad (7)$$

where, μ is the chemical potential. This method is known to produce accurate spectra for finite systems [38] as well as solids [12]. Following the above procedure the spectral density for doped and undoped NiO is calculated using the full-potential linearized augmented plane wave [41] code Elk [42].

3. Results

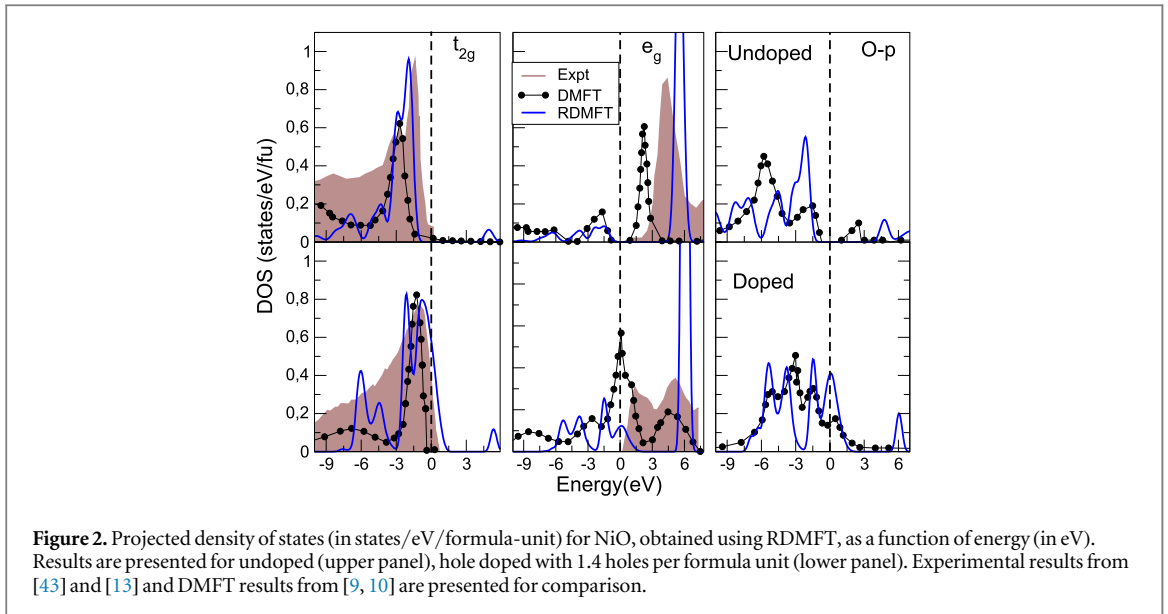
3.1. Correlated band theory

We first examine the behavior of undoped NiO within band and correlated band theory by using LSDA [4] and LSDA + U methods [14, 15]; results for total DOS and the site and symmetry projected spectral density are presented in figure 1. One can observe that while the LSDA band gap is grossly underestimated as compared to experiment, a *rigid shift* of the valence band to lower energies would result in a spectrum with an overall shape in good agreement with experiment. Indeed, despite severely underestimating the gap, the correct ordering of the t_{2g} and e_g states is obtained within LSDA, i.e., the band gap separates a t_{2g} valence and a e_g conduction band, with a substantial overlap of e_g and t_{2g} states seen in the valence band.

On applying an on-site Coulomb repulsion the gap opens, but at the cost of a deterioration in the agreement of the overall spectral weight with experiment. In particular, the band ordering is now found to be incorrect at precisely the value of U that leads to the correct magnitude of the gap, which occurs between purely e_g states. This striking defect of the LSDA + U treatment of NiO was also noticed in [5], and the use of a smaller U with an additional external parameter, the so called scissors correction Δ , was suggested as a remedy. However, while the spectrum of the equilibrium ground state is improved by this procedure, albeit with the use of an additional fitting parameter, such an approach cannot be used to study the insulator to metal transition in NiO: the very meaning of the parameter Δ is lost once the material enters the metallic phase. Upon doping the KS spectrum shows a rather simple behavior for both LSDA and LSDA + U methods; the chemical potential rigidly moves into the valence band leading in consequence to metalization. In the case of LSDA + U method this implies same value of U across the phase transition.

3.2. Reduced density matrix functional theory

RDMFT has already shown its effectiveness in capturing the pressure induced phase transition in Mott insulators [12], in the present work we look at the doping induced phase transition, see figure 2. In good agreement with previous many-body studies [44, 45], we find that the conduction band is almost entirely e_g in



character. A substantial overlap of Ni-d and O-p states may be seen in the valence spectrum, highlighting the presence of charge transfer effects in NiO.

For the undoped case, the spectral density is in good agreement with experiments [43]. The RDMFT results also agree very well with previous DMFT calculations [9, 10, 44, 45] with one important difference between the two; the experimental data shows a shoulder at -3 eV, which is well captured by t_{2g} like states within RDMFT but is missing in DMFT results. The value of the band-gap obtained using RDMFT (4.9 eV) is larger than experiments (4.1 eV), and the magnetic moment ($1.52\mu_B$) smaller than the experimental value of $1.7\mu_B$. There are two reasons for the smaller value of the magnetic moment within RDMFT as compared to experiment. Firstly, the calculations are performed with the FP-LAPW method in which space is divided into spheres around the atoms, the so called muffin-tins, and an interstitial region. In the case of fully non-collinear magnetic calculations the magnetic moment per site is calculated by integrating the magnetization vector field inside the muffin-tin. This implies the loss of a small part of the moment to the interstitial region. Secondly, the power functional induces a slight non-collinearity in the magnetization leading to yet more loss in the integrated z -projected moment.

Turning to the hole doping of NiO, we find that the effect on the spectral density is strikingly different within RDMFT, as compared to both the LSDA and LSDA + U methods. Hole doping is found to lead to a redistribution of spectral weight of the Ni e_g states from the upper and the lower Hubbard bands towards the chemical potential, which in turn leads to an IMT. The Ni t_{2g} like states remain almost the same as in undoped case. If one uses the correlated band theory definition of U as being roughly equal to the distance between the upper Hubbard band and the correlated peak, then it is evident that the value of U changes as a function of doping. These results are in good agreement with experiments as well as a previous DMFT calculation, but are evidently in profound disagreement with both the LSDA and LSDA + U pictures of the transition. These strikingly different pictures highlight the importance of a physically correct treatment of correlation in these materials.

Turning to the quantitative description of the phase transition afforded by RDMFT, we find that, as in DMFT, significant metalization occurs at a much higher value of hole doping (1.2 holes per formula-unit for RDMFT) than observed in experiments (0.5 holes). There are two principle reasons for this. Firstly, the undoped gap for NiO (4.88 eV) is larger than the experimental value, and hence additional hole doping will be required to drive the material to the metallic state. Secondly, we do not study the effect of an actual impurity added to the system, but rather the hole doping is simulated by the removal of electronic charge from the unit cell while adding a constant compensating background to ensure charge neutrality. This method is commonly known as the virtual crystal approximation.

4. Summary

To summarize we have presented the physics behind the doping IMT in NiO and have found that the physics of phase transition is brought out in strikingly different ways by different theoretical methods: within DFT based studies metalization occurs due to a rigid shifting of the chemical potential into the valence band, with the

separation between the Hubbard bands remaining approximately constant. In contrast, within RDMFT the phase transition is driven by a transfer in spectral weight from the upper and lower Hubbard bands to what is known as the correlated peak. We thus find that RDMFT treatment of NiO is much close to many-body theories such as the DMFT, than to the LSDA or correlated band approaches.

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