

# Interplay of charge-transfer and Mott-Hubbard physics approached by an efficient combination of self-interaction correction and dynamical mean-field theory

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Late-transition-metal oxides with small charge-transfer energy  $\Delta$  raise issues for state-of-the-art correlated electronic structure schemes, such as the combination of density functional theory (DFT) with dynamical mean-field theory (DMFT). The accentuated role of the oxygen valence orbitals in these compounds asks for an enhanced description of ligand-based correlations. Utilizing the rocksaltlike NiO as an example, we present an advancement of charge self-consistent DFT + DMFT by including self-interaction correction (SIC) applied to oxygen. This introduces explicit on-site O correlations as well as an improved treatment of intersite  $p$ - $d$  correlations. Due to the efficient SIC incorporation in a pseudopotential form, the DFT + sicDMFT framework is an advanced but still versatile method to address the interplay of charge-transfer and Mott-Hubbard physics. We revisit the spectral features of stoichiometric NiO and reveal the qualitative sufficiency of local DMFT self-energies in describing spectral peak structures usually associated with explicit nonlocal processes. For  $\text{Li}_x\text{Ni}_{1-x}\text{O}$ , prominent in-gap states are verified by the present theoretical paper.

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## I. INTRODUCTION

An understanding of the electronic structure and phase diagrams of transition-metal (TM) oxides still poses a major challenge. The realistic modeling of strong electronic correlations in this family of compounds has been tremendously improved since establishing the combination of density functional theory (DFT) with dynamical mean-field theory (DMFT). Especially early-TM oxides with a partially filled (empty)  $t_{2g}(e_g)$  submanifold of the TM- $d$  shell, showing dominant Mott-Hubbard physics, often may readily be addressed by such an approach. Late-TM oxides display a more intriguing interplay of hybridization and correlation effects and remain demanding. The reason is that in the latter systems with usually a completely filled  $t_{2g}$  subshell and a partially filled  $e_g$  subshell, the ligand oxygen  $2p$  states are much closer in energy to the TM- $d$  states. The charge-transfer energy  $\Delta$ , required to transfer a ligand electron to a TM- $d$  orbital, eventually becomes smaller than the energy cost for a doubly occupied  $d$  orbital, i.e., the Hubbard  $U$ . In late TMs, the  $d$  states are lower in energy, hence,  $\Delta$  shrinks, but  $U$ , on the other hand, increases due the reduced orbital extension with larger nuclear charge [1]. According to the famous Zaanen-Sawatzky-Allen (ZSA) scheme [2], correlation-induced insulators with  $\Delta < U$  are of the charge-transfer kind.

Although, e.g., Cu oxides are typical charge-transfer compounds, the rocksaltlike NiO, a material of paramount importance for the development of quantum solid-state theory [3], is located in the intermediate regime of the ZSA diagram. This renders NiO particularly interesting and, more generally, marks nickelate compounds as exceedingly affected by various competing instabilities (see, e.g., Ref. [1] for a review).

Stoichiometric nickel oxide is insulating with a sizable charge gap of  $\sim 4.3$  eV [4–7] and becomes antiferromagnetic below  $T_N = 523$  K [8]. Substitutional doping of  $\text{Li}^+$  for  $\text{Ni}^{2+}$  is effective in providing holes to cause conductivity [9–15].

Numerous theoretical studies examined the interacting electronic structure of NiO. Advanced descriptions need to rely on a sophisticated treatment of  $\Delta$ ,  $U$  and further key quantum characteristics of the compound. In addition to cluster calculations [12,16–19], DFT + DMFT [20–27] and variational-cluster-approximation [28] studies provided already a good account of the electronic spectrum, but challenges remain [19]. For instance, to a certain degree, the correct determination and understanding of the specific nature/positioning of peaks within the valence-band spectrum is still a matter of debate. Furthermore, the increased importance of the role of ligand orbitals and their hybridization with TM orbitals in materials, which lack a pure Mott-Hubbard character, renders an investigation of defect properties very demanding.

Therefore, the intention of this paper is twofold. Using NiO as a test case, we first show that an improved description of the intriguing interplay between Mott-Hubbard and charge-transfer physics at stoichiometry is achieved by treating electronic correlations on the TM *as well as* on the ligand sites. This is realized by an efficient combination of the self-interaction correction (SIC) with the charge self-consistent DFT + DMFT framework. Thereby, SIC is applied on O, and Ni marks the DMFT impurity problem. This theory advancement enables us to shed novel light on the intriguing features of the paramagnetic NiO spectrum. Second, the usefulness of this DFT + sicDMFT scheme for advanced correlated materials science is demonstrated by the application to the even

more challenging case of Li-doped NiO. We straightforwardly reproduce the long-standing experimental finding of in-gap states (IGS) at  $\sim 1.2$  eV above the valence-band maximum (VBM).

## II. THEORETICAL APPROACH

### A. Problem and general framework

In the simplest approximation [1], the charge-transfer energy is given by the difference between the TM( $d$ ) and the O( $2p$ ) single-particle levels, i.e.,  $\Delta = \varepsilon_d - \varepsilon_p$ . In early-TM oxides, such as, e.g., certain titanates or vanadates, the respective level separation is rather large with TM( $d$ ) well above O( $2p$ ). Then usually, electronic correlations matter most within the partially filled  $t_{2g}$  subshell of TM( $d$ ) since O( $2p$ ) states are much deeper in energy than the scale of the lower-Hubbard-band formation. The local Hubbard  $U_{dd} := U$  within TM( $d$ ) is the smaller energy and, thus, governs the correlation effects. On the contrary, for late-TM oxides,  $\Delta$  becomes the smaller energy, and O( $2p$ )'s are often located *between* the lower- and the upper-Hubbard-band formation scales.

In the latter case, the correlation physics is more subtle. Of course,  $U$  remains a vital player since it triggers strong correlation. However, the charge-transfer energy and, more generally, the Coulomb interactions of the local O( $2p$ ) kind and of the intersite TM( $d$ )-O( $2p$ ) kind gain significant impact. Extended model Hamiltonians, besides  $U_{dd}$  terms, furthermore, including additional on-site  $U_{pp}$  terms on oxygen and intersite  $U_{pd}$  terms, are believed to become relevant for a generic description of the correlated electronic structure [29–31]. But especially in a realistic context, as, e.g., DFT + DMFT, such extensions will raise issues: At least two new Coulomb parameters have to be quantified, and questions concerning the quality of the many-body treatment adequate for the new terms arise. Moreover, the technical/numerical effort increases significantly, particularly, for low-symmetry structures, heterostructure problems, defect properties, etc.

Therefore, we here introduce an efficient extension to the state-of-the-art charge self-consistent DFT + DMFT framework, geared to treat charge-transfer physics with a minimum of additional Coulomb parametrization and essentially without any further increase in technical/numerical effort. First, our DFT and DMFT parts remain structurally unmodified, i.e., a mixed-basis pseudopotential framework [32–34] is utilized for the former, and a continuous-time quantum Monte Carlo technique [35,36] for the latter (see Ref. [37] for further details). Besides these established building blocks, a third one is integrated. A SIC formalism [38,39] is applied to cope with the correlations explicitly originating from the ligand sites. Importantly, the SIC procedure is performed on the pseudopotential level [40,41] and enters the calculational scheme simply as a modified ligand pseudopotential. Hence, during the self-consistency cycle, the SIC effects on the crystal lattice adapt to the system-dependent characteristics. Those effects, without the coupling to DMFT, here, described on the effective single-particle level, capture both, the impact of the ligand-on-site  $U_{pp}$  and of the ligand-TM-intersite  $U_{pd}$ . Yet effectively, only a single additional parameter, namely, the degree of SIC renormalization for O( $2p$ ), may be

sufficient. Last but not least, DFT + sicDMFT allows one to use the identical double-counting approach as for standard DFT + DMFT: The SIC formalism is double-counting free by definition, and the remaining TM-on-site double-counting representation remains unaffected. This is favorable as the issue of double-counting for charge-transfer systems has been a matter of debate [42,43].

### B. Computational details

For the DFT part, the local density approximation (LDA) is utilized. Norm-conserving pseudopotentials according to Vanderbilt [44] are constructed for Ni, O, and Li. The mixed basis consists of localized orbitals for Ni( $3d$ ), O( $2s$ ), and O( $2p$ ), as well as plane waves with an energy cutoff  $E_{\text{cut}}$ . The self-interaction correction for the O pseudopotential employs orbital weight factors  $w(\text{O}) = (w_s, w_p, w_d)$  and a global SIC scaling parameter  $\alpha$  (see Refs. [40,41] for further details). Although, by default, the O( $2s$ ) potential is 100% corrected, and the O( $3d$ ) potential is 0% corrected, key freedom is provided by the correction  $w_p$  of the crucial O( $2p$ ) potential, i.e.,  $w(\text{O}) = (1.0, w_p, 0.0)$ . In the case of an isolated atom,  $\alpha = 1$  (atomic SIC) holds. A detailed study of the variation of  $\alpha$  in different kinds of solids is given by Pemmaraju *et al.* [45]. Throughout the paper, we choose  $\alpha = 0.8$ , shown to be reliable in previous calculations for TM oxides [41,46,47]. If not otherwise stated, we also pick  $w_p = \alpha$ , and thus, effectively, a single additional parameter setting enters here the advanced formalism. Note that no self-interaction correction is applied to Ni since the whole localization/correlation effects originating from the nickel site are here described within DMFT.

Projected local orbitals [48–50] are employed to define the correlated subspace for the DMFT part. The five Ni( $3d$ ) atomiclike orbitals are projected onto eight Kohn-Sham valence states of NiO, namely, onto the dominant Ni( $3d$ ) and O( $2p$ ) dispersions. The remaining states are, of course, included in the complete charge self-consistent framework but do not enter explicitly the correlated subspace. The general Slater-Condon Hamiltonian,

$$\mathcal{H} = \frac{1}{2} \sum_{\substack{m_1 m_2 \\ m_3 m_4}} \sum_{\sigma \sigma'} U_{m_1 m_2 m_3 m_4} c_{m_1 \sigma}^\dagger c_{m_2 \sigma'}^\dagger c_{m_4 \sigma'} c_{m_3 \sigma}, \quad (1)$$

with  $m_i = 1 \cdots 5$  and  $\sigma, \sigma' = \uparrow, \downarrow$ , is used for the electron-electron interaction in the correlated subspace. Coulomb matrix elements for  $l = 2$  are expressed in spherical symmetry via standard Slater integrals  $F^k$  through

$$U_{m_1 m_2 m_3 m_4} = \sum_{k=0}^{2l} a_k(m_1, m_2, m_3, m_4) F^k, \quad (2)$$

with expansion coefficients  $a_k$  given by

$$\begin{aligned} a_k(m_1, m_2, m_3, m_4) &= \sum_{q=-k}^k (2l+1)^2 (-1)^{m_1+q+m_2} \\ &\times \begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} l & k & l \\ -m_1 & q & m_3 \end{pmatrix} \begin{pmatrix} l & k & l \\ -m_2 & -q & m_4 \end{pmatrix}, \end{aligned} \quad (3)$$

and parametrized using the Hubbard  $U$  and Hund's exchange  $J_H$  via

$$F^0 = U, \quad F^2 = \frac{14}{1+r} J_H, \quad F^4 = r F^2. \quad (4)$$

The  $F^4/F^2$  Slater-integral ratio is chosen as  $r = 0.625$ , which is adequate for transition-metal atoms. For the present NiO study,  $U = 10$  and  $J_H = 1.0$  eV are employed. Although the latter value is standard for this compound, the Hubbard interaction is somewhat larger than the usual value of  $\sim 8$  eV [20,21]. But charge self-consistent DFT + DMFT often enforces an enhanced local Coulomb interaction compared to one-shot calculations [51] because of the increased number of screening channels. A recent computation [31] of NiO Coulomb parameters for a  $dp$  Hamiltonian within the constrained random-phase approximation yields also a Hubbard  $U \sim 10$  eV. The DMFT problem is solved by hybridization-expansion continuous-time quantum Monte Carlo [36] as implemented in the TRIQS package [52,53]. A double-counting correction of fully localized-limit (FLL) type [54] is applied. All calculations are performed in the paramagnetic regime at a system temperature of  $T = 580$  K. In order to obtain the spectral function  $A(\omega) = -1/\pi \text{Im} G(\omega)$ , analytical continuation of the Green's function  $G$  from the Matsubara axis to the real-frequency axis is performed by the maximum-entropy method. To reveal  $\mathbf{k}$ -resolved spectra, we use the Padé method applied to the Ni self-energy for the analytical continuation. If not otherwise stated, the shown spectra are based on the maximum-entropy method.

The NiO lattice constant is set to the experimental value [55] of  $a = 4.17$  Å. Doping with lithium is realized by means of a supercell approach. Each symmetry-inequivalent Ni site poses a different single-site DMFT problem; all are coupled within the general multisite many-body scheme [56]. As DFT convergence parameters, we used  $E_{\text{cut}} = 16(13)$  Ryd and a  $k$ -point mesh of  $13(5) \times 13(5) \times 13(5)$  for the pristine (Li-doped) case.

### III. RESULTS

#### A. Self-interaction corrected oxygen in NiO

Before delving into the results of the new DFT + sicDMFT scheme, it is illustrative to inspect the impact of the self-interaction correction to oxygen in nonmagnetic NiO from the effective single-particle LDA + SIC viewpoint.

Figure 1 displays the site- and orbital-projected DOS within LDA and for two different SIC parameters  $w_p = 0.7, 0.8$ . The Ni- $t_{2g}$  states are completely filled, and the strongly hybridized {Ni- $e_g$ , O(2p)} states are partially filled. Hence, holes are located on the TM site as well as on the ligand sites. Not surprisingly, each scheme renders the system metallic. It is well known that, for gap opening on the static DFT(+ $U$ ) level, symmetry breaking in the form of magnetic ordering is indispensable and the same applies here. Note that we could apply SIC also on the TM site [41,47] and allow for antiferromagnetic order to investigate the insulating state in that effective-single-particle approximation. The result would be qualitatively similar to the one obtained from a DFT(+ $U$ ) treatment [57], but we do not want to follow this route in the present paper.

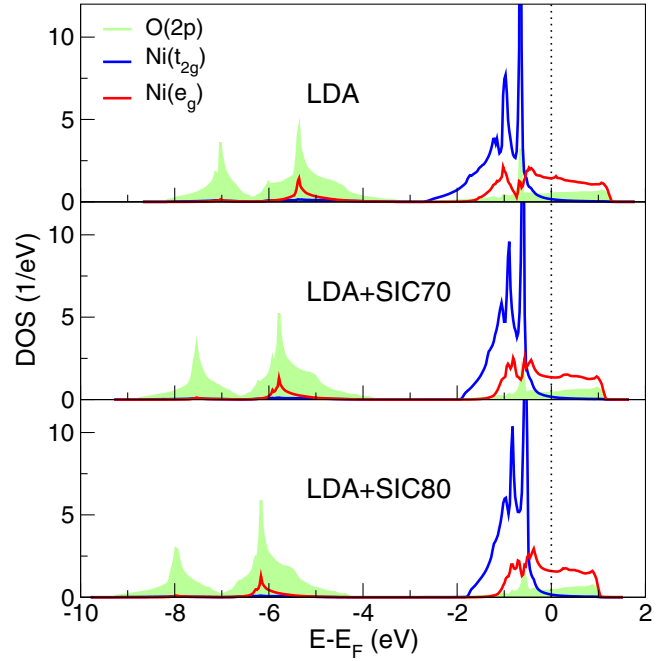


FIG. 1. Site- and orbital-projected density of states (DOS) of NiO within LDA (top), LDA + SIC for  $w_p = 0.7$  (middle), and for  $w_p = 0.8$  (bottom).

Instead, let us concentrate on the principal effects of SIC applied on the oxygen site. There are, in essence, two main effects. First, the  $pd$  splitting and hence, the charge-transfer energy is increased by SIC. Using  $\Delta = \varepsilon_d - \varepsilon_p$ , the value reads, respectively,  $\Delta_{\text{LDA}} = 3.13$ ,  $\Delta_{w_p=0.7} = 3.98$ , and  $\Delta_{w_p=0.8} = 4.50$  eV. Fits to experimental data yield  $\Delta$  values in the range of  $\sim [4, 5]$  eV [16,19,58]. Thus, LDA severely underestimates  $\Delta$ , and the effect of SIC on oxygen brings the charge-transfer energy in line with experimental estimates. Second, band narrowing takes place with SIC, roughly on the order of  $Z \sim 0.8$  for  $w_p = 0.8$  as also visible from Fig. 1. Importantly, the band-narrowing effects are not only encountered for the O(2p) contribution, but also for the dominant Ni(3d) bands. Hence, a nonlocal ligand-TM correlation effect occurs as a result of self-interaction correction applied to the oxygen pseudopotential. Those two key effects originate from the effective inclusion of  $U_{pp}$  and  $U_{pd}$  terms within the present LDA + SIC treatment.

Let us remark again that the parameter setting  $\alpha = 0.8$  is not specifically adjusted to NiO, but this  $\alpha$  value turns out to be a proper choice for various TM oxides [41,46,47]. In other words, a present SIC parametrization with  $w_p = \alpha$  is much less case sensitive as the usual choice/calculation of the Hubbard interaction(s).

#### B. NiO many-body spectrum

##### 1. DFT + sicDMFT examination

We now discuss the spectral results from the complete DFT + sicDMFT approach, employing  $w_p = 0.8$ . Figure 2 shows the main outcome for stoichiometric NiO together with the combined experimental data [6] from photoemission and inverse photoemission.

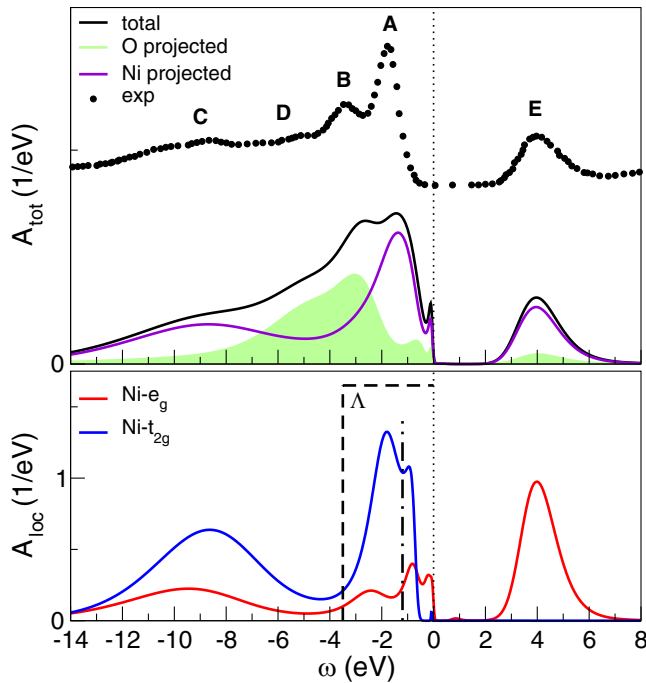


FIG. 2. NiO  $k$ -integrated spectral function from DFT + sicDMFT. Top: total spectrum with site and orbital projection as well as comparison to photoemission and inverse photoemission data [6] at a photon energy of 1486.6 eV. Points A–E mark specific spectral features (see the text). Bottom: local Ni(3d) spectrum with  $e_g$  and  $t_{2g}$  characters. The dashed-line rectangle represents energy window  $\Lambda$  with competing  $\{d^8\bar{Z}, d^8\bar{L}\}$  states (see the text). The dot-dashed line denotes the  $d^8\bar{Z}$ -dominated region.

Let us first briefly recall the state-of-the-art interpretation [6,16,17] of the experimental spectrum. NiO is a correlation-induced insulator subject to the interplay of Mott-Hubbard and charge-transfer physics. The Ni ground state in the 3d shell amounts to  $d^8$ , and  $\bar{L}$  describes a hole in the ligand O(2p) states. The crucial charge-transfer process, associated with the energy  $\Delta$ , is described by the transition  $d^8 \rightarrow d^9\bar{L}$ , i.e., electron transfer from O(2p) to Ni(3d). This energy scale sets the NiO charge gap of  $\sim 4.3$  eV. An added electron conclusively enters the  $d^9$  state associated with peak E. On the other hand, adding a hole to the system either results in the high-energy  $d^7$  state (i.e., lower Hubbard band) associated with peak C, or gives rise to  $d^8\bar{L}$  at a much lower energy of peak A. The shoulder D is usually [6] interpreted as originating from the nonbonding part of O(2p). The most-controversially discussed peak B is built from a substructure of the  $d^8\bar{L}$  state and often associated with nonlocal excitations [17] (see Ref. [19] for a detailed discussion).

Let us note that Taguchi *et al.* [18] suggested an alternative scenario for the lower-energy peaks A and B. Namely, peak A should originate from a  $d^8\bar{Z}$  state, and only peak B builds up from  $d^8\bar{L}$  without the need for invoking explicit nonlocal processes. Here,  $d^8\bar{Z}$  refers to a Zhang-Rice (ZR) bound state, a strongly correlated TM-O-hybridized low-energy entity, presumably most relevant for low-energy cuprate physics [59]. In NiO, the ZR (doublet) bound state is based on the interaction

of the O(2p) hole with both Ni(3d) holes. Loosely speaking,  $d^8\bar{Z}$  is the tightly bound “collective” counterpart of the weakly bound  $d^8\bar{L}$  excitation.

The upper part of Fig. 2 displays the total  $k$ -integrated spectral function  $A_{\text{tot}}(\omega) = \sum_{\nu} A_{\nu}(\omega)$  with  $\nu$  as the Bloch (band) index from DFT + sicDMFT compared to the experimental data. Additionally, the projection of  $A_{\text{tot}}(\omega)$  onto Ni(3d) and O(2p) is depicted. Note that this site- and orbital-resolved spectrum is strictly not identical to the true local spectral function in a many-body sense. Since the projection is performed from the Bloch-resolved  $A_{\nu}(\omega)$ , it carries the complete hybridization on the lattice, and moreover, results from an analytical continuation of the Bloch-Green’s function  $G_{\nu}$ . Overall, the agreement with experiment is quite remarkable: The theoretical charge gap of  $\sim 4$  eV matches perfectly, and the further features A–D are well reproduced. The principal charge-transfer character is obvious from the fact that the dominant part of O(2p) is located between the lower Hubbard band at  $\sim -9$  eV and the upper Hubbard band at  $\sim 4$  eV. As already expected from the previous discussion, the lower-energy region  $\Lambda = [-3.5, 0]$  eV, indeed, asks for a deeper analysis.

Therefore, the lower part of Fig. 2 shows the Ni(3d) local spectral function  $A_{\text{loc}}(\omega)$  as obtained from analytical continuation of the local Green’s function  $G_m$ . Locally, the  $t_{2g}$  manifold is completely filled, and the upper Hubbard band is exclusively of  $e_g$  character. Within  $\Lambda$ , the  $e_g$  part displays a three-peak structure, whereas the  $t_{2g}$  part displays a two-peak structure. The first sharp resonance closest to the VBM at  $\sim -0.1$  eV is of exclusive  $e_g$  kind, in line with previous studies [12,19,21,22]. A second sharp peak resonates in both cubic 3d sectors roughly at the same energy  $\sim -0.85$  eV, whereas a slightly broader peak occurs at  $\sim -1.8$  (–2.5) eV for  $t_{2g}(e_g)$ . Albeit a bit speculatively, we interpret this intriguing structure as follows: The first sharp substructure at  $\geq -1.2$  eV belongs to  $d^8\bar{Z}$ , whereas, the higher-energy substructure in  $\Lambda$  belongs to  $d^8\bar{L}$ . Then, the experimental peak A is a  $\{d^8\bar{Z}, d^8\bar{L}\}$  superposition (with larger  $d^8\bar{Z}$  content), and peak B results from a superposition of  $d^8\bar{L}$  with part of the nonbonding O(2p) spectrum. Explicit nonlocal correlations, e.g., through an intersite Ni-Ni self-energy, appear not necessary to qualitatively account for a sizable Ni spectral weight within peak B. As our many-body method is (charge) self-consistent on the lattice, *implicit* features of nonlocality are included. It still may be that *explicit* nonlocal self-energies beyond DMFT enhance the Ni weight in peak B. Thus, in essence, the present paper highlights the intricate entanglement between the more basic aspects of charge-transfer physics and its highly correlated ZR ramifications.

Finally, we display, in Fig. 3(a), the  $\mathbf{k}$ -resolved spectral function  $A(\mathbf{k}, \omega)$  obtained by analytical continuation of the Matsubara self-energy via the Padé method. It can be seen that the upper Hubbard band still displays some dispersion. Note that we did not include higher-energy states above the Ni- $e_g$ -based bands in our construction of the spectral function. Additionally, Fig. 3 provides a comparison between spectral data obtained via the Padé and the maximum-entropy methods. Naturally, the former method produces sharper details. Concerning the total spectrum, all peaks A–E are also visible with Padé, albeit the peaks A and B are slightly



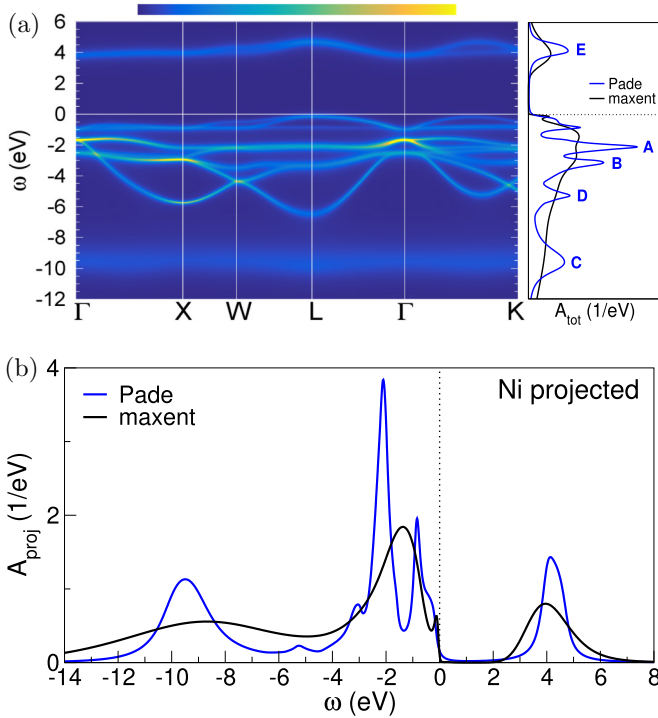


FIG. 3. DFT + sicDMFT  $k$ -resolved data and comparison of different analytical-continuation schemes. (a) NiO  $k$ -resolved spectral function along high-symmetry lines (left) and comparing the total spectral function obtained from the maximum-entropy method and Padé method. (b) Projected Ni(3d) spectral function from the Padé method and maximum-entropy method. Note that the Padé data are obtained from analytical continuation of the Ni self-energy, whereas the maximum-entropy data are obtained from an analytical continuation of the Bloch-Green's function.

shifted to higher energies. Very close to the VBM, both analytical-continuation methods display spectral features in the  $k$ -integrated spectrum. Those features are supported by the still visible dispersion, e.g., around the  $L$  point, up to the VBM in Fig. 3(a). However, this structure is not observed in the experimental spectrum [6]. This might be due to different reasons, e.g., to the suppression of spectral weight close to the VBM/Fermi level because of Fermi-function effects at the boundary of the occupied part and/or resolution issues in experiment. Novel experimental examinations with the focus on the Ni-O hybridization in bulk NiO close to the VBM region would be helpful to clarify this matter. Last but not least, Fig. 3(b) shows a clearer projected-Ni(3d) contribution to peak B at  $\sim 3$  eV within the Padé-based spectrum compared to the more-smeared maximum-entropy spectrum.

## 2. Comparing with standard DFT + DMFT

Let us now comment on the methodological aspect of our approach. In order to compare the present scheme with the traditional DFT + DMFT method for NiO, Fig. 4 shows the total spectral function as well as the Ni- $e_g$ ,  $t_{2g}$  local spectral function with and without SIC for oxygen. The most obvious and striking difference concerns the gap size: Without SIC, the charge gap turns out only of order  $\sim 1.5$  eV. A similar

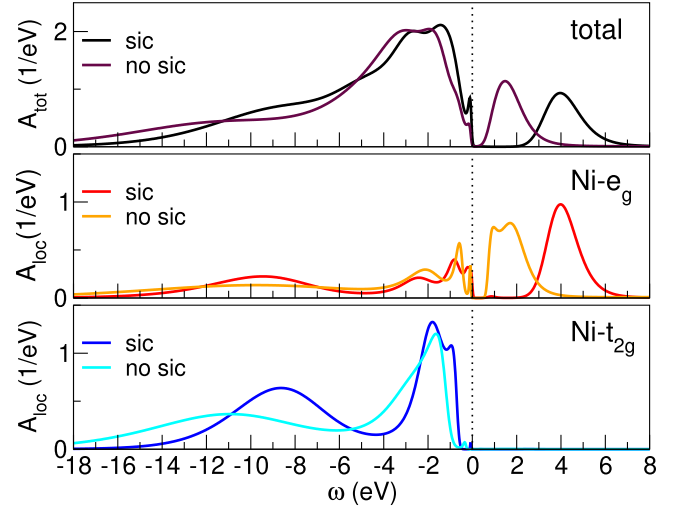


FIG. 4. Comparison of NiO spectral information from DFT + sicDMFT and DFT + DMFT. Top: total spectrum, middle: local Ni  $e_g$ , and bottom: local Ni  $t_{2g}$ .

qualitative observation has been made by Panda *et al.* [27], who noted that they reached only a small NiO charge gap with the FLL double-counting in charge self-consistent DFT + DMFT. On the occupied high-energy side, the lower Hubbard band is shifted to more negative energies without SIC. On the other hand, the structure in the  $\Lambda$  region is not dramatically altered, albeit the fine-structure appears less detailed without SIC. For instance, the local Ni- $t_{2g}$  spectrum exhibits only a single peak in standard DFT + DMFT. Altogether, even if focusing only on the occupied spectrum, the agreement with experiment concerning peak signature and position is less satisfactory than with SIC. We also performed DFT + DMFT calculations for smaller  $U = 8$  eV, but the gap size did not change.

The very fact that charge self-consistent DFT + DMFT with standard double-counting fails in reproducing the correct paramagnetic gap size for a charge-transfer(like) compound, is not that surprising. As observed, the main Mott-Hubbard physics, i.e., the formation of Hubbard bands and their splitting in energy, is rather similar with and without SIC. However, without SIC, the O(2p) level is too strongly shifted in the direction of the upper Hubbard band, rendering the final charge gap small. Because energy-beneficial charge fluctuations are suppressed on the Ni site, the formalism tries to shift O(2p) towards the upper Hubbard band to enable as much as possible the (virtual) charge fluctuations between O(2p) and Ni  $e_g$ . Since there is no Coulomb penalty from SIC, the charge-transfer energy shrinks. Note that there is a recent charge self-consistent NiO calculation by Leonov *et al.* [26], providing a reasonable spectrum with only minor gap-size reduction. But in that calculation, only density-density interactions in the local interacting Hubbard Hamiltonian have been taken into account.

Generally, one-shot DFT + DMFT calculations [20,21] obtain a charge gap somewhat smaller than in experiment but still of sensible size. This is understandable as the O(2p) level remains essentially fixed in those calculations, and the DFT charge-transfer energy of  $\sim 3.2$  eV is nearly

unaltered. Hence, when promoting the method to charge self-consistency, it is essential to include also the ligand-based Coulomb interactions. Of course, it may be that some other double-counting protocol can fix the problem. But the present approach is more physical, it is applicable to general charge-transfer problems, and allows one the use of the identical standard double-counting form for Mott-Hubbard and charge-transfer systems without any further adjustments. Last but not least, we are confident that the correct interplay of Mott-Hubbard, charge-transfer, and charge self-consistent processes is very well captured by our DFT + sicDMFT framework.

### C. Li-doped NiO

Lithium doping of NiO has first been studied in detail in the 1950s [9,10] and remained of research significance ever since [11–15,21]. Recently, it, furthermore, gained interest in the context of hybrid organic-inorganic perovskite solar cells [60,61].

The alkali element enters as a substitutional  $\text{Li}^+$  defect replacing  $\text{Ni}^{2+}$  and, thus, providing holes to the compound. The  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  system is stable for a wide  $x$  range up to  $\text{LiNiO}_2$  [10]. Importantly, Li doping does not render NiO metallic but semiconducting with in-gap states appearing at  $\sim 1.2$  eV above the valence-band maximum [12,15]. In the following,  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  is studied for  $x = 0.125$  by our DFT + sicDMFT method within a supercell approach. We reduced the stoichiometric lattice constant for the 16-atom cell to  $a_{\text{dop}} = 4.15$  Å in the doped case [10] and relaxed the atomic positions in antiferromagnetic LDA +  $U$  (see Fig. 5). There are three symmetry-inequivalent Ni classes in the supercell. Note that structural relaxation including local Coulomb interactions is important since a LDA-based relaxation leads to a too strong shift of the O sites next to Li towards Ni. This results in artificial resonances in the low-energy part of the spectral function. Identical local Coulomb parameters as chosen for stoichiometric NiO are used for the defect problem. The number of Kohn-Sham projection states of it is properly scaled from 8 at  $x = 0$  to 59 ( $= 7 \text{ Ni} \times 5 d \text{ orbitals} + 8 \text{ O} \times 3 p \text{ orbitals}$ ) at  $x = 0.125$ .

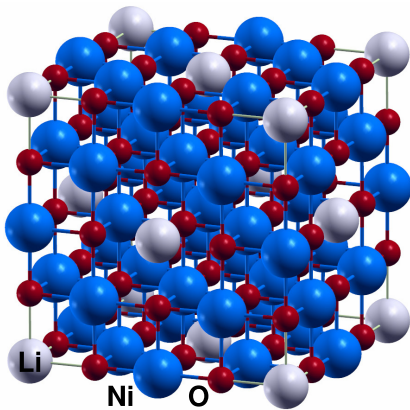


FIG. 5. Supercell of  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  for  $x = 0.125$ , consisting of 16 lattice sites in the primitive fcc cell. Ni: large blue, O: small red, and Li: large gray.

### 1. Many-body spectrum with in-gap states

Figure 6 depicts the collected spectral results together with inverse-photoemission data from van Elp *et al.* [12]. The total spectrum in the upper part of Fig. 6(a) shows minor shifts and changes in intensity for the occupied states compared to the stoichiometric case. A shift of the spectrum to smaller binding energies with Li doping is also observed in experimental data [12,13,15]. Peak E in the conduction states is shifted to higher energy, which qualitatively coincides with available experimental data from Reinert *et al.* [13], yet the present theoretical shift appears somewhat too strong. Note, in addition, that the inverse-photoemission data in Ref. [12] were aligned at 5 eV. There is some minor occupation just above the VBM, i.e., the spectrum is not of a perfectly strict insulating kind. Without disorder mechanisms and/or without a local structural/electronic mechanism [51], avoiding

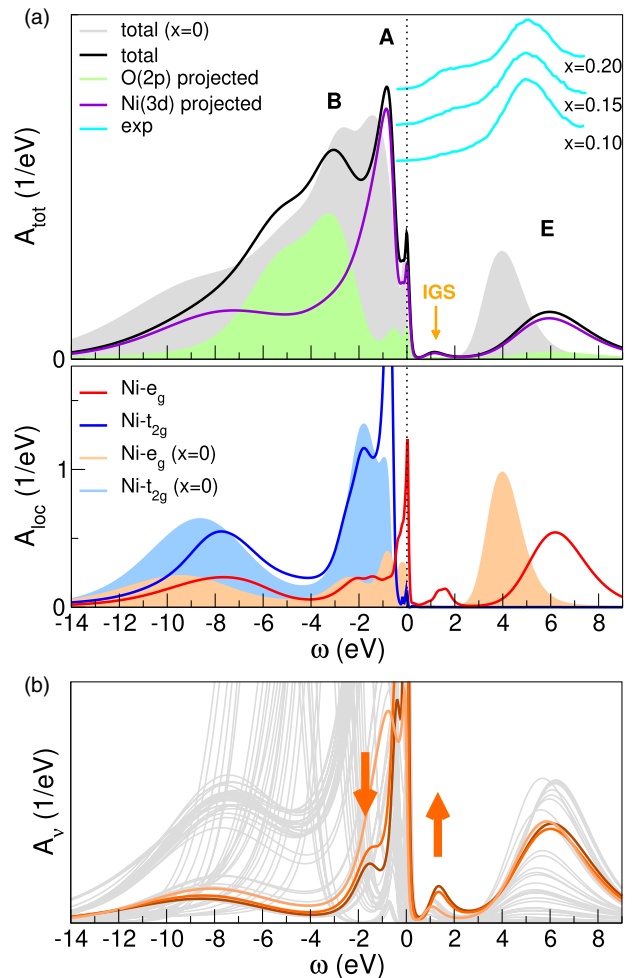


FIG. 6.  $\text{Li}_{0.125}\text{Ni}_{0.875}\text{O}$  spectral function from DFT + sicDMFT. Top: total spectrum with site and orbital projections as well as comparison to the stoichiometric case ( $x = 0$ ) and to inverse photoemission data [12] at a photon energy of 1486.6 eV. IGS are marked with the orange arrow. Bottom: local Ni(3d) spectrum with  $e_g$  and  $t_{2g}$  characters with comparison to the stoichiometric case. (b) Bloch-resolved spectrum  $A_v$  with  $v = 1 \dots 59$ . The orange lines ordered by intensity mark four  $v$ 's with decreasing contribution strength to the IGS. The arrows mark growth (reduction) of spectral weight.

residual metallicity in a doped correlated insulator is very challenging in theoretical electronic structure methods. We still believe that our spectrum provides a reasonable account of experimentally semiconducting  $\text{Li}_{0.125}\text{Ni}_{0.875}\text{O}$ .

Concerning the joint appearance of the  $d^8\bar{Z}$  and  $d^8\bar{L}$  states, the inspection of the local spectral function again turns out to be useful [see the lower part of Fig. 6(a)]. In the energy window  $\Lambda = [-3.5, 0]$  eV, the lowest-energy peak of the  $t_{2g}$  spectral weight is increased, and the other one of the two-peak substructure is weakened compared to the stoichiometric case. The changes in the  $e_g$  spectrum within this region have an even larger bearing: The stoichiometric peak at  $\sim 2.6$  eV is nearly smeared out for  $x = 0.125$ . This means that the vital  $\text{Ni}(3d)$  peak contribution to peak *B* in the total spectrum is weakened. Thus, the subtle balance between  $d^8\bar{Z}$  and  $d^8\bar{L}$  as observed in the stoichiometric case becomes qualitatively disturbed with Li doping. The spectral weight of  $d^8\bar{Z}$  states close to the VBM is increased.

Finally, let us focus on the IGS visible in the range of [0.7, 1.7] eV of the total spectrum. The energy location of the IGS is in excellent agreement with inverse-photoemission data [12,13,15]. In the local Ni spectrum, as already seen for the upper Hubbard band, there is no  $t_{2g}$  contribution to the IGS. The question arises at the expense of which spectral weight do the IGS appear? Inspection of the weight transfers among the Bloch-resolved spectral functions  $A_\nu(\omega)$  may help to answer this question. Figure 6(b) displays all 59  $A_\nu$  functions and highlights the four ones with a major contribution to the IGS. From these, one observes that the “spectral growth” of the IGS corresponds with spectral weight at the VBM and a “spectral shrinkage” of weight that is just somewhat deeper than peak *A* in the occupied spectrum. It is, therefore, tempting to directly associate the IGS with the weakening of the original  $d^8\bar{L}$  subpeak in the local  $\text{Ni-}e_g$  spectrum as noted above.

## 2. Where are the holes?

The rigorous real-space location of the holes introduced by Li doping of NiO is a tenacious matter of debate [9,11–13,15]. Originally, data have been interpreted via the formation of  $\text{Ni}^{3+}$ , yet more recent studies favor the picture of the holes being located in the  $\text{O}(2p)$  shell. From a theoretical point of view, it is, indeed, notoriously difficult to uniquely associate valence charges in a condensed-matter system with a specific lattice site. Depending on the choice of local orbitals and the kind of charge analysis, often rather different results are obtained.

From a general point of view, underlined by the previous discussions of spectra, the relevant charge-transfer physics in NiO renders the tight entanglement of  $\text{Ni}(3d)$  and  $\text{O}(2p)$  in the immediate neighborhood of the VBM obvious. The Zhang-Rice doublet state is a direct consequence thereof. Quantitatively, doping of  $x$ -Li ions introduces a hole doping of  $\delta = x/(1-x)$  on the remaining Ni sites. Thus, in the present case of  $x = 0.125$ , this amounts to  $\delta = 0.143$ . The  $\text{Ni}(3d)$  occupation from the local Green’s function reads  $n_d = 8.175$  at stoichiometry and  $n_d = 8.064$  with Li doping. Hence, numbers  $\delta_d = 0.111$  of effective nickel holes and  $\delta_p = \delta - \delta_d = 0.032$  of effective oxygen holes results here.

The mixed character of hole formation is in line with doping into the entangled  $\text{Ni}(3d)\text{-O}(2p)$  VBM states. Note that the real-space hole distribution is, of course, also subject to the actual choice of the supercell.

## IV. SUMMARY

A methodological advancement of the combination of density functional theory and dynamical mean-field theory, geared to especially address materials problems with substantial charge-transfer character, has been presented. The combination of the self-interaction correction on the ligand sites within the state-of-the-art charge self-consistent DFT + DMFT framework proves to be a powerful tool. Not only to approach long-standing basic problems of late-TM oxides, but also due to its efficient and easily scalable structure for application to novel problems, e.g., occurring from nanoscale structuring. There are also other theoretical approaches that may deal with electronic correlations originating directly from ligand states. Most notably, the GW + DMFT scheme [27,62,63] has the potential to tackle such physical issues. But that framework is computationally much heavier than the DFT + sicDMFT scheme and has not yet been applied to materials with defects or dopants.

We exemplified our method for the case of stoichiometric and Li-doped NiO, two persistently problematic correlated materials. A faithful description of the NiO spectrum at stoichiometry with good accordance to experimental findings was given. The interplay of different forms of  $\text{Ni}(3d)$ - and  $\text{O}(2p)$ -hole states, in the form of  $d^8\bar{Z}$  and  $d^8\bar{L}$ , (re)emerged [18] from this analysis. Importantly, the present scheme based on still local DMFT self-energies is sufficient to account for the experimentally derived hypotheses of  $\text{Ni}(3d)$  contributions to the double-peak structure (i.e., peaks *A* and *B*) below the valence-band maximum. The introduction of *explicit* nonlocal Ni-Ni self-energies (e.g., via cluster-DMFT) is not needed for a *qualitative* appearance of such contributions. In the case of  $\text{Li}_x\text{Ni}_{1-x}\text{O}$ , we theoretically verified the long-standing experimental observation of in-gap states at  $\sim 1.2$  eV above the VBM. Our examination suggests that spectral-weight transfer from  $d^8\bar{Z}$ ,  $d^8\bar{L}$  into the gap region plays a relevant role in the formation of the IGS.

Our extended DFT + DMFT treatment of NiO does, however, not provide an end to the enduring theoretical investigation of this challenging material. For instance, in order to improve on the classification of the competing states, interacting many-body and multiplet resolution on Ni, on O and in between, within a translational-invariant DMFT construction is needed. Still, the successful state-of-the-art DFT + DMFT approach for early-/middle-row transition-metal oxides is, thus, complemented with the DFT + sicDMFT framework for late-row TM oxides. Various problems of materials with interacting electrons, such as e.g., rare-earth nickelates or high- $T_c$  cuprates, await (renewed) investigation.

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