Calculating energy loss spectra of NiO: Advantages of the modified Becke-Johnson potential

Walid Hetab,1,* Peter Blaha,2 Fabien Tran,2 and Peter Schattenschneider1,3

1Institute of Solid State Physics, Vienna University of Technology, Wiedner Hauptstraße 8-10/138, A-1040 Vienna, Austria
2Institute of Materials Chemistry, Vienna University of Technology, Getreidemarkt 9/165-TC, A-1060 Vienna, Austria
3University Service Center for Transmission Electron Microscopy, Vienna University of Technology, Wiedner Hauptstraße 8-10/052, A-1040 Vienna, Austria

The density of states and the energy loss near-edge structure of the oxygen K edge in NiO are calculated using different models for the exchange-correlation functional. The results are compared to each other and to experimentally acquired energy loss spectra. It is found that only when using the modified Becke-Johnson potential are the calculated spectra in good agreement with the experimental data. This can be achieved at much less computational costs than with more sophisticated calculation methods but with as good results.

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I. INTRODUCTION

Currently, simulations are often necessary in analytical transmission electron microscopy (TEM) to interpret experimental data. Electron energy loss spectrometry (EELS) is a commonly used method in analytical TEM that measures the kinetic energy of the probe electrons after the interaction with the sample.1,2 The resulting spectra show distinct peaks resulting from core excitations. These peaks exhibit a fine structure in the surrounding of the excited atom. Calculations of the energy loss near-edge structure (ELNES) give acceptable results depends strongly on the investigated material and on the desired property.

Although the local-density approximation (LDA)3 or the generalized gradient approximation (GGA)4 usually are good choices, they fail when calculating strongly correlated electron systems such as that present in transition-metal compounds. In those cases, orbital-dependent methods like LDA + U (Ref. 7) or hybrid functionals are used. A comparison of band gap calculations using these different exchange-correlation functionals and experimental results is given in Ref. 8. There, the calculated density of states (DOS) of NiO is also compared with x-ray photoemission (XPS) and bremsstrahlung isochromat spectroscopy (BIS) measurements reported in Ref. 9.

Recently, a modified Becke-Johnson (TB-mBJ) exchange potential was tested for the calculation of band gaps.10,11 This potential reads

\[ v_{\text{TB-mBJ}}^{x,\sigma}(r) = c \cdot v_{\text{BR}}^{x,\sigma}(r) + (3c^2 - 2) \frac{1}{\pi \sqrt{6}} \frac{t_{\sigma}(r)}{\rho_{\sigma}(r)}, \]  

(1)

where \( \rho_{\sigma} = \sum_{i=1}^{N_{\text{cell}}} |\psi_{i,\sigma}|^2 \) denotes the electron density and \( t_{\sigma} = (1/2) \sum_{i=1}^{N_{\text{cell}}} \nabla \psi_{i,\sigma} \psi_{i,\sigma} \) is the kinetic-energy density.

\[ v_{\text{BR}}^{x,\sigma}(r) = -\frac{1}{\rho_{\sigma}(r)} \left( 1 - e^{-\xi_{\sigma}(r)} - \frac{1}{2} \xi_{\sigma}(r) e^{-\xi_{\sigma}(r)} \right), \]

(2)

is the Becke-Roussel potential,12 which was designed to model the Coulomb potential created by the exchange hole. \( \xi_{\sigma} \) is calculated using a nonlinear equation12 with \( \rho_{\sigma}, \nabla \rho_{\sigma}, \nabla^2 \rho_{\sigma} \), and \( t_{\sigma} \), while \( b_{\sigma} \) is determined using \( b_{\sigma} = [\alpha^2 e^{-\xi}(8\pi \sigma \rho_{\sigma})]^{1/3} \).

The value of parameter \( c \) in Eq. (1) is calculated using

\[ c = \alpha + \beta \left( \frac{1}{V_{\text{cell}}} \frac{1}{\rho_{\sigma}(r)} \right)^{1/2}, \]

(3)

where \( V_{\text{cell}} \) is the unit cell volume and \( \alpha = -0.012 \) and \( \beta = 1.023 \) bohr\(^{-1/2} \) are parameters determined according to a fit to experimental values.11 The original Becke-Johnson potential is recovered by setting \( c = 1 \). It is notable that the TB-mBJ potential cannot be obtained as a functional derivative of an exchange functional (there is no \( E_x \), such that \( v_{\text{TB-mBJ}}^{x,\sigma} = \delta E_x / \delta \rho_{\sigma} \)). Therefore, this potential should not be used for the calculation of forces, the comparison of total energies, or the optimization of the geometry.10,11,13,14

The Becke-Johnson potential and modified versions of it (including the TB-mBJ potential used in the present work) have been utilized by several groups so far. For example, Singh tested the prediction of the TB-mBJ potential for the electronic structure and magnetic properties of condensed systems.15 Kim et al.16 applied the TB-mBJ potential on III-V semiconductors, while Pittalas et al.17 extended the Becke-Johnson potential for use on two-dimensional systems. Rässänen et al.18 provided a different correction of the Becke-Johnson potential, which Oliveira et al.19 compared to experiments for atoms, molecules, and atomic chains.

When investigating the effects of a modified Becke-Johnson potential, the focus usually lies on comparing the band structure, density of states, and band gaps, but magnetic moments have also been analyzed successfully.10,11,14 In comparison to Perdew-Burke-Ernzerhof (PBE) calculations, the TB-mBJ potential gives much better values compared to experimental magnetic moments.11,14 The experimental values for NiO are 1.64–1.9 \( \mu_B \) (Ref. 8) compared to 1.39 \( \mu_B \) for PBE and 1.76 \( \mu_B \) for TB-mBJ.

In Ref. 11, the resulting DOS, obtained with calculations using the TB-mBJ potential, is compared to XPS/BIS measurements from Ref. 9. In Fig. 2 of Ref. 11, the calculated valence band DOS is compared with O K and Ni L x-ray emission spectroscopy. From there, it can be seen that the
TB-mBJ calculation gives the correct positions of Ni \( d \) and O \( p \) bands with respect to each other. The TB-mBJ potential gives results in good agreement with experimental values that are similar to those produced by more sophisticated methods but at much lower computational costs.\(^1\)

As NiO is a 3\( d \) transition-metal oxide, it is an ideal example to demonstrate the effects of different exchange-correlation potentials. In this work we calculate the oxygen \( K \) edge ELNES of NiO using different models for the exchange-correlation functional and compare it to experimental measurements. The focus lies on the oxygen \( K \) edge, as DFT is not sufficient for the calculation of the Ni \( L_{2,3} \) edge and one would need to solve the Bethe-Salpeter equation instead.\(^2\)

II. DENSITY OF STATES

The simulations were performed using the full-potential augmented-plane-wave code WIEN2K,\(^2\) version 10.1. The in-

![Graph showing total DOS calculated using different models for the exchange-correlation potential. The energy is plotted with respect to the Fermi energy \( E_F \). The total atomic DOS is marked in different colors. The labels Ni\(_1\) and Ni\(_2\) refer to majority and minority spin of Ni atoms in the spin-polarized calculation. (a) PBE. (b) LDA + U. (c) Hybrid potential B3PW91. (d) Hybrid potential PBE0. (e) Modified Becke-Johnson potential TB-mBJ.](image-url)
put for structure type, lattice parameters, and atomic positions to calculate antiferromagnetic NiO is shown in Table I. All calculations were performed using 2000 k points, similar to the simulations reported in Ref. 23. A plane-wave cutoff parameter $R_{MT}K_{\text{max}}$ of 7 was used. The atomic sphere radii of both Ni atoms were 2.09 and 1.85 a.u. for the O atom, which corresponds to 0.111 and 0.098 nm, respectively. All calculations were performed using spin polarisation. Simulations were done systematically with the generalized gradient approximation reported by Perdew, Burke and Ernzerhof,6 LDA + U (Ref. 7), two different local8,24 hybrid potential methods [PBE0 (Refs. 25 and 26) and B3PW91 (Ref. 27)], and TB-mBJ11 as implemented self-consistently in the WIEN2k package. After convergence of the self-consistent field (SCF) cycle the DOS and ELNES spectra were calculated in order to compare them with experimental values.

The total DOS calculated using the PBE method is shown in Fig. 1(a). It can be seen that the PBE method gives a band gap of about 1 eV. Thus, it severely underestimates the experimental band gap of 4.0–4.3 eV (see Ref. 8, references therein and Ref. 9).

In Fig. 1(b) the total DOS calculated using the LDA + U method is shown. As in Ref. 8 the value for $U_{\text{eff}}$ was 7.05 eV = 0.52 Ry. With a calculated band gap width of 3.2 eV a significant improvement is evident. Also the general shape of the valence band states is different compared to the PBE calculation and to experimental data.8,9

The total DOS calculated with two different hybrid potential methods, namely, the B3PW91 and PBE0 functionals, is shown in Figs. 1(c) and 1(d). It can be seen that in both cases the band gap width of 2.8 eV still underestimates the experimental values. Both plots are very similar, with only slight differences in the valence band and the unoccupied Ni 3d states between Fermi level $E_F$ and $E_F + 5$ eV.

Figure 1(e) shows the calculated total DOS using the modified Becke-Johnson potential which is used together with LDA (mBJLDA) for the correlation. It can be seen that this simulation method results in a band gap of 4.16 eV.

Thus, from all the potentials applied in this work, the modified Becke-Johnson potential is the only one which gives a band gap width similar to the experimentally acquired one. The DOS of the valence band is very similar to the PBE and the hybrid potential simulations and also in agreement with XPS/BIS measurements.9 Compared to the LDA + U simulation the structure of the valence band is clearly different, which is mainly due to differences in the Ni 3d DOS. The unoccupied Ni 3d states are shifted to higher energies in the mBJLDA calculation, causing a more realistic value of the band gap.

As the electron energy loss spectra depend on the occupancy of states (for calculation methods see, e.g., Ref. 28), attention has to be directed to the structures above the Fermi level. In all calculation methods the shapes of these structures are similar, but peak positions and relative intensities are different. This gives rise to different near-edge structures in the energy loss spectra, which will be discussed in the next section.

### III. ENERGY LOSS NEAR-EDGE STRUCTURE

ELNES spectra were calculated using the program TELNES.8,29,30 All the following calculations were done using 200 keV primary beam energy, a collection semiangle of 10.0 mrad, and a convergence semiangle of 0.01 mrad. An energy window of 50 eV and a step size of 0.05 eV were used. A value of 1.4 eV was taken for the spectrometer broadening according to the full width at half maximum (FWHM) of the experimentally measured zero-loss peak (ZLP). A Lorentzian broadening for core and valence lifetimes was also applied.

In Fig. 2 a comparison of the oxygen K edge ELNES calculated with different exchange-correlation functionals is shown. As the oxygen K edge EELS probes the excitation of ls electrons, dipole-allowed transitions are those into $p$ states. Therefore the shape of the ELNES should resemble the $p$-projected DOS above the Fermi level, except for effects like broadening. Other contributions like monopole or quadrupole transitions can be neglected as they are much smaller than the dipole-allowed contributions.31,32

The hole left by the excited core electron changes the electronic structure of the crystal. However, the effect of this core-hole is not always visible.33 Usually a core-hole calculation with supercells has to be performed to take these changes into account and to see wether it has any effect on the calculated spectra. For the oxygen K edge of NiO considering the core-hole does not modify the resulting spectra significantly.34 However, we still investigated its effect in the mBJLDA calculation using 48-atom supercells and taking either a full or half a core-hole into account. The excited electron was not added to the valence states since this would

TABLE I. Input data for the calculation of antiferromagnetic NiO using WIEN2K according to Ref. 22. Atom positions are given in local coordinates of the rhombohedral unit cell.

<table>
<thead>
<tr>
<th>Lattice</th>
<th>Lattice parameters</th>
<th>Atom positions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R$</td>
<td>$a = b = 2.966163$ Å</td>
<td>Ni$_1$: $x = 0$, $y = 0$, $z = 0$</td>
</tr>
<tr>
<td></td>
<td>$c = 14.531171$ Å</td>
<td>Ni$_2$: $x = \frac{1}{2}$, $y = \frac{1}{2}$, $z = \frac{1}{2}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O: $x = \pm \frac{1}{2}$, $y = \pm \frac{1}{2}$, $z = \pm \frac{1}{2}$</td>
</tr>
</tbody>
</table>
(unphysically) occupy a Ni d state, but it was added as uniform charge in the unit cell (these high O p states are expected to be very diffuse states).

An experimental spectrum is also shown in Fig. 2. It was acquired using a FEI TECNAI G2 20 microscope with a LaB6 cathode, operated at 200 kV and equipped with a GATAN GIF 200i energy filter. All the spectra were aligned at the first peak. This was done because a WIEN2K and TELNES calculation does not give absolute energy values. The energies are rather given with respect to the Fermi level, which is set to the valence band maximum. It is evident that by using different functionals a change in peak positions and relative intensities can be seen. This results from differences in the oxygen p DOS above the Fermi energy, which is shown in Fig. 3.

It is clear from Fig. 2 that although the shape of the spectra is reproduced well, the peak positions do not match the experiment very well when using PBE, LDA + U, or the hybrid potentials. Furthermore, using LDA + U and the hybrid functional PBE0, the relative intensity of the first peak is underestimated; using the hybrid exchange-correlation functional B3PW91, it is minimally overestimated, whereas using the GGA functional, the peak intensity is far overestimated.

All parameters in a WIEN2K calculation which can affect the results (k mesh, plane-wave cutoff) have been converged, but in agreement with what is reported in Ref. 34, neither changes in those parameters nor performing simulations including spin-orbit interaction improves the agreement with experiment.

The calculation of the actual values of $U_{\text{eff}} = U - J$ (with $U$ and $J$ being the Coulomb and exchange interaction) is discussed in Ref. 23. Following this discussion, in Fig. 4 oxygen K edge ELNES calculations for different values of $U_{\text{eff}}$, ranging from 0.25 to 0.55 Ry, are compared.

With increasing $U_{\text{eff}}$ the relative intensity of the first peak decreases, leading to a better agreement with the experiment. However, at the same time the peak positions are changed, and therefore the agreement with experimental spectra is getting worse.

In Fig. 2, the experimentally measured oxygen K edge ELNES is compared to the simulation using the TB-mBJ potential. It can be seen that the peak positions and the relative intensities are reproduced very well. The differences to the experimental spectrum at the peaks at 534 and 543 eV lead to the assumption that these parts in the unoccupied DOS are still underestimated. This gives rise to the fact that these peaks are not emphasized enough when calculating the broadening. This can be seen in Fig. 5, where a comparison of the oxygen p DOS calculated using the modified Becke-Johnson potential and the broadened and the unbroadened spectra are shown. For more details on calculating the broadening see for example Refs. 35 and 36.

In Fig. 6 mBILDA calculations using half a core-hole and a full core-hole are compared to the calculation without a core-hole and to the experimental spectrum. When using half
a core-hole the peaks at 537.5 and 558 eV are shifted to lower values of the energy loss, while the peak at 543 eV is shifted to higher values. These shifts are increased when using a full core-hole. In both core-hole calculations the peak at 543 eV is more pronounced than in the one without a core-hole. The relative intensity of the first peak is minimally overestimated with the partial core-hole, while it is underestimated when using a full core-hole. Compared to the main peak, the relative intensity of the peak at 534 eV fits best to the experimental spectrum when using half a core-hole. Considering all these details, the calculation using a partial core-hole fits best to the experimentally acquired spectrum. This is in agreement with what is reported in Ref. 37 and the concept of Slater’s transition state.$^3$

As the calculations using the modified Becke-Johnson potential show the best agreement with the experimental spectra, it is of interest to mention which part of this potential is responsible for the improvement compared to other exchange-correlation functionals. In addition to a term which models the Coulomb potential of the exchange hole [Eq. (2)], the Becke-Johnson potential includes a term with the kinetic-energy density [second term in Eq. (1)].$^4$ It is determined from the electron density $c$ [Eq. (3)], on the other hand, the modified Becke-Johnson potential gives good results for a wide variety of different materials.

### IV. CONCLUSION

Simulations of the DOS and oxygen $K$ edge energy loss spectra of NiO were conducted using different models of the exchange-correlation potential. Whereas the PBE and hybrid potential methods give unsatisfactory results for the band gap as well as the ELNES spectra, the modified Becke-Johnson potential is in good agreement with experimental results. LDA $+U$ improves the value of the calculated band gap, but the shape of the occupied DOS does not fit the experimental data. The modified Becke-Johnson potential renders a more realistic density of states due to a kinetic-energy density term and a weighting parameter which is determined for each material during the calculation. Furthermore, there is no need to tune calculation parameters. Another advantage of this exchange-correlation potential is that it is as cheap in the sense of computational costs as LDA or GGA methods.

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