Band structure of NiO revisited

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The band structure of a strongly correlated semiconductor as NiO has been the object of much debate [PRL 103, 036404 (2009); PRL 102, 226401 (2009)]. Most authors, using computational techniques well beyond the simple density functional theory and the approximations GGA or LDA, claim that the band gap is about 4.0 eV and that the conduction band is of Ni3d nature. Thus they seem to forget the results of electron-energy-loss spectroscopy and inelastic x-ray scattering, both able to determine electronic transitions of only about 1.0 eV to an optically forbidden Ni3d band.

Further, a simple atomic calculation of the Ni++ spin flip energy demonstrates that a Ni3d band at 4.0 eV is impossible. To set the issue straight, we calculated NiO with the very successful technique of PRB 78, 125116 (2008). It turns out that a band at 4.0 eV is optically accessible and made of excited atomic states, not Ni3d. Aside from that, we also found a narrow Ni3d band at about 1.0 eV. To confirm our procedures once again, we also calculated MnO and obtained the standard results of the good calculations as those cited above, and of experiment.

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The band structure of NiO is being the object of many calculations by different techniques. To quote just a few, Physical Review Letters recently published the works of Engel and Schmid [1] on the Exact-Exchange technique, and of Tran and Blaha [2] on a novel semilocal exchange-correlation potential. Physical Review published the work of Rödl et al [3] on a GGA [4] calculation. The Journal of Physics: Condensed Matter published a self-interaction (SIC) calculation [5]. The many authors claim that NiO presents an important challenge for density functional theory because it is a strongly correlated system. The most simple LSDA and GGA calculations are reported to be failures. Thus, along the years NiO is being calculated with many sophisticate techniques. Aside from the works already quoted, we can cite some examples: Deng et al used a variational LDA formulation [6], Fuchs et al [7] with their generalized Kohn-Sham method, Kobayashi et al [8] that used a GW started from LSDA+U, Eder [9] that used a Variational Cluster Approximation, Miura et al [10], Kuneš et al [11], and Ren et al [12] using different LDA+DFMT, Tran et al [13] with a hybrid exchange-correlation, mixing Hartree-Fock, Han et al [14] with LDA+U, Li et al [15] and Kotani and van Schilfgaarde [16] using a self-consistent GW, Korotin et al [17] with a Wannier function method.

Of course it is impossible to review the many papers. We want only to call attention that many of these calculations are wrong when they set the band gap at about 4.3 eV, following the experimental BIS result of Sawatzky and Allen [18], claiming that the conduction band at that energy is a Ni-d band. The location of the conduction Ni-d bands has been determined by Müller and Hüfner [19] using electron energy-loss spectroscopy, and by Huotari et al [20] using inelastic x-ray scattering. The band at 4.3 eV above valence is certainly not Ni-d because these start at a much lower energy, about 1.0 eV. It is simple to show the approximate position of the Ni-d conduction bands by calculating the following atomic energy differences

$$ Ni[4s^2(3d\uparrow)^4(3d\downarrow)^4] - Ni[4s^2(3d\uparrow)^5(3d\downarrow)^3] $$

or the Ni+++ ionic difference

$$ Ni[(3d\uparrow)^4(3d\downarrow)^4] - Ni[(3d\uparrow)^5(3d\downarrow)^3] $$

These differences are the energies required to flip a spin, which correspond to the excitation of an electron to the antiferromagnetic crystal conduction band. Using the PBE exchange-correlation [4], the difference is 0.99 eV for the atom, and 1.03 eV for the ion. Using the LDA exchange-correlation of Ceperley-Alder Perdew-Zunger [21] the differences are only 0.05 eV smaller. In any case, the spin-flip energy is similar to the threshold to the first energy band, as found experimentally [19, 20] and the 4.3 eV BIS band [18] could never be a Ni-d band. Compared with

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NiO, also an antiferromagnetic oxide, NiO is very different. In the case of MnO, the spin-flip energy

\[ M_n[4s^2(3d \uparrow)^4(3d \downarrow)^1] - M_n[4s^2(3d \uparrow)^5] \]

is 3.55 eV, similar to the band gap, so that a Mn-d conduction band is possible.

Next we present the results of our calculation for NiO. Our calculation was all-electron with wavefunctions expanded in LAPW+lo \[22\]. We avoided the pseudopotential calculations for two reasons. First, in the case of NiO, the Ni-d functions are not easily expanded with plane waves. Second, for magnetic systems, the exchange-correlation potential may depend much on the way the core density is treated \[23\], because linearization is unacceptable. So it is not just a problem of finding the good pseudopotential, but the good core density must also be found. NiO is an antiferromagnet with the rock salt structure. The Ni sublattice is antiferromagnetically ordered as an \( L1_1 \) (CuPt) alloy. It has a very small trigonal distortion along the body diagonal. Along this direction, the planes alternate spins, up and down. We used the experimental lattice parameters and did not optimize geometry, which is the best procedure to calculate the elementary excitation spectrum.

In Fig. 1(a) we show the valence and conduction bands of the Kohn-Sham eigenvalues calculated with the PBE exchange-correlation \[4\]. Contrary to the opinion of many authors, we do not see anything wrong with those bands. The Kohn-Sham eigenvalues should not compare well with the excitation spectrum, the band gaps being notoriously smaller. Unfortunately there seems to be no procedure to simultaneously calculate the total energy, which is the object of Density Functional Theory, and the excitation spectrum. The spectrum calculation should be made following a very good GW \[24\] that uses the self-energy operator instead of the exchange-correlation potential. Though not correct, the Kohn-Sham energy spectrum usually gives an indication of how the correct spectrum will be. As it stands in Fig. 1(a) NiO is an insulator, the first conduction bands are about 1 eV above the valence band and is made of minority Ni d wavefunctions. The identification of the many valence states as Ni d majority and minority spins follows in Fig. 1(a) NiO is an insulator, the first conduction bands are about 1 eV above the valence band and is made of minority Ni d wavefunctions. The identification of the many valence states as Ni d majority and minority spins follows in Fig. 1(a) NiO is an insulator, the first conduction bands are about 1 eV above the valence band and is made of minority Ni d wavefunctions. The identification of the many valence states as Ni d majority and minority spins follows in Fig. 1(a) NiO is an insulator, the first conduction bands are about 1 eV above the valence band and is made of minority Ni d wavefunctions. The identification of the many valence states as Ni d majority and minority spins follows in Fig. 1(a) NiO is an insulator, the first conduction bands are about 1 eV above the valence band and is made of minority Ni d wavefunctions.
case of NiO we used $CUT(Ni3d) = 1.97\,a.u.$ and $CUT(O2p) = 2.41\,a.u.$ to make the “4.3 band gap” maximum. The maxima are not sharp and neighboring values of $CUT$ could be used as well.

The energy spectrum calculated with the inclusion of self-energies is represented in Fig. 1(b). The results obtained with GGA does differ from those from LDA. Aside from the relative upwards motion of the “4.3 band”, there is not much difference from the results of a standard all-electron calculation (Fig. 1(a)). It is clear why the “acceptor band” at $\sim 1\,eV$ does not move with respect to the valence bands: Both are Ni3d bands and have the same self-energy. On the other hand, these acceptor bands do not exist in the case of MnO. In this latter case, using our technique, we obtained a gap of 4.18 eV (GGA) and 3.98 eV (LDA), matching the results of other calculations and experiment, and no surprises were obtained [27].

To conclude we want to say that standard LDA or GGA calculations seem reliable even for a strongly correlated material as NiO. But it is important to remember that DF will never give the excitation spectrum. An attempt to force the obtaining of such spectrum may generate errors and misinterpretation of the calculated results, as the impossible 4.3 eV Ni d band.

![Energy Spectra](image)

**FIG. 1:** (a) NiO energy bands calculated with GGA. (b) NiO energy bands calculated with GGA-1/2, and in parenthesis, calculated with LDA-1/2.

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