

**NiO: Correlated Band Structure of a Charge-Transfer Insulator**J. Kuneš,<sup>1,2,\*</sup> V. I. Anisimov,<sup>3</sup> S. L. Skornyakov,<sup>4</sup> A. V. Lukoyanov,<sup>4</sup> and D. Vollhardt<sup>1</sup><sup>1</sup>*Theoretical Physics III, Center for Electronic Correlations and Magnetism, Institute of Physics, University of Augsburg, Augsburg 86135, Germany*<sup>2</sup>*Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, 162 53 Praha 6, Czech Republic*<sup>3</sup>*Institute of Metal Physics, Russian Academy of Sciences-Ural Division, 620041 Yekaterinburg GSP-170, Russia*<sup>4</sup>*Ural State Technical University-UPI, 620002 Yekaterinburg, Russia*

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The band structure of the prototypical charge-transfer insulator NiO is computed by using a combination of an *ab initio* band structure method and the dynamical mean-field theory with a quantum Monte-Carlo impurity solver. Employing a Hamiltonian which includes both Ni *d* and O *p* orbitals we find excellent agreement with the energy bands determined from angle-resolved photoemission spectroscopy. This brings an important progress in a long-standing problem of solid-state theory. Most notably we obtain the low-energy Zhang-Rice bands with strongly **k**-dependent orbital character discussed previously in the context of low-energy model theories.

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The quantitative explanation of the electronic structure of transition-metal oxides (TMOs) and other materials with correlated electrons has been a long-standing challenge in condensed matter physics. While the basic concept explaining why materials such as NiO are insulators was formulated by Mott a long time ago [1], the development of an appropriate, material-specific computational scheme proved to be a formidable task. The electronic structure of the late TMOs, including the cuprate superconductors, is not only affected by the electronic correlations, it is further complicated by the hybridization between the transition-metal *d* states and O *p* bands located between the lower and upper Hubbard bands formed by the transition-metal *d* orbitals. For such materials Zaanen, Sawatzky, and Allen [2] introduced the term “charge-transfer insulator”, a prototypical example of which is NiO. In principle, the simple crystal structure of NiO allows for a straightforward comparison between theory and experiment. However, a theoretical description of the NiO band structure is made difficult by the competition between the local many-body effects, due to strong Coulomb interaction between Ni *d* electrons, and the band dispersion, due to the lattice periodicity, both observed with the angle-resolved photoemission spectroscopy (ARPES) [3,4].

In this Letter we use a combination of a conventional band structure approach, based on the local density approximation (LDA), and the dynamical mean-field theory (DMFT) [5] to investigate the band structure of NiO. No adjustable parameters enter. While the application of the LDA + DMFT [6] framework has proven successful for the early TMOs, the charge-transfer materials were routinely avoided due to the additional complexity arising from the presence of *p* bands. In the present work the O *p* orbitals and their hybridization with Ni *d* orbitals are explicitly included, thus allowing for a unified description of the full spectrum. Our results reveal a nontrivial effect of

the *p-d* hybridization in strongly correlated systems studied so far only in terms of simple models [7–9].

The application of the standard band structure theory to NiO is marked by the failure of LDA to produce an insulating groundstate [10]. The antiferromagnetic (AFM) solution within LDA [11], despite rendering NiO an insulator, still underestimates the band gap severely, does not reproduce the experimental single-particle spectrum and also many ground state quantities are outside the usual LDA margin (e.g., too low magnetic moment). Theoretical approaches beyond LDA followed several different paths. The LDA + *U* [12] and SIC-LDA theories [13], although different in details and reasoning, enforce energy separation of the occupied and unoccupied Ni-*d* orbitals, which leads to the opening of a gap. This is sufficient to largely improve the ground state properties such as the local moment or the lattice constant [14]. However, the description of photoemission spectra is not satisfactory, in particular, the *d* spectral weight is located mostly in the high-energy satellite (Hubbard band), in striking contrast to a strong *d* contribution at the low excitation energy (top of the valence band) observed experimentally. This failure can be traced to the static character of the theories, which also restricts their success to the insulating stoichiometric NiO (in contrast to doped metallic) and the broken symmetry phase (AFM order). Some improvement in description of the photoemission spectra was achieved by including three-body corrections [15]. A different approach to the electron-electron correlations in NiO is provided by *GW* approximation [16,17]. While the dispersion of *d* bands at the top of the valence band and the band gap compare quite well to the experiment, Aryasetiawan and Gunnarsson [16] have shown and explained why the high-energy satellite, which contains almost 50% of the *d* spectral weight, is completely missing in the *GW* approach. The exact diagonalization study on NiO small

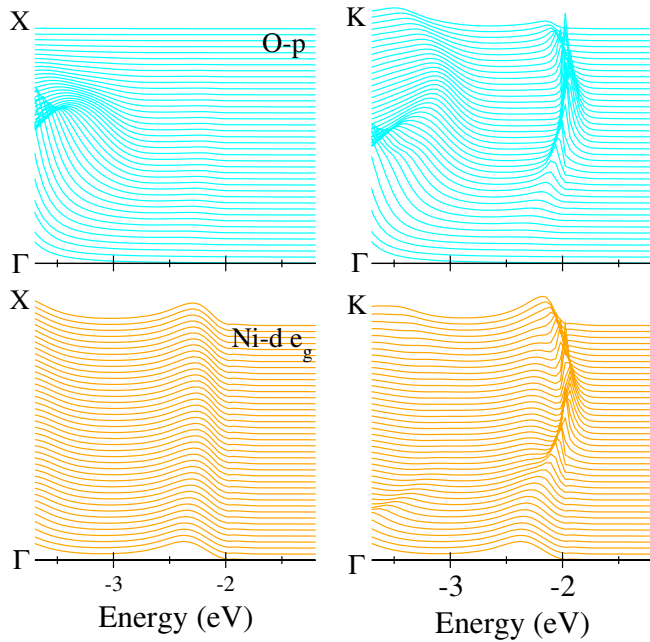


FIG. 3 (color online). Detail of the uppermost valence band along the  $\Gamma$ -K (right) and  $\Gamma$ -X (left) lines. The top panels show the O- $p$  contribution  $A_{pp}(\mathbf{k}, \omega)$ , while Ni- $d$  contribution  $A_{dd}(\mathbf{k}, \omega)$  of the  $e_g$  symmetry is shown in the bottom panels.

we presented an important advance in a long-standing problem—the computation of the full valence band structure of a charge-transfer insulator. We obtained a very good agreement with the ARPES data of Shen *et al.* [3,4] without adjustable parameters. While a detailed comparison to ARPES data is still restricted by the lack of dipolar matrix elements in the theory, the key problem of the NiO spectrum, distribution of  $d$ -spectral weight between the high-energy satellite and the low-energy bands, was resolved. The uppermost valence band is found to have a strongly  $\mathbf{k}$ -dependent orbital composition, which follows the behavior expected of Zhang-Rice bands. Our results clearly demonstrate the capability of DMFT to treat, upon explicit inclusion of  $p$ - $d$  hybridization, the late transition-metal oxides and charge-transfer systems in general.

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\*jan.kunes@physik.uni-augsburg.de

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# Orbital-Occupancy versus Charge Ordering and the Strength of Electron Correlations in Electron-Doped $\text{CaMnO}_3$

Weidong Luo,<sup>1,2</sup> Alberto Franceschetti,<sup>1,2</sup> Maria Varela,<sup>2</sup> Jing Tao,<sup>2</sup> Stephen J. Pennycook,<sup>2</sup> and Sokrates T. Pantelides<sup>1,2</sup>

<sup>1</sup>*Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235, USA*

<sup>2</sup>*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*

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The structural, electronic, and magnetic properties of mixed-valence compounds are believed to be governed by strong electron correlations. Here we report benchmark density-functional calculations in the spin-polarized generalized-gradient approximation (GGA) for the ground-state properties of doped  $\text{CaMnO}_3$ . We find excellent agreement with all available data, while inclusion of strong correlations in the GGA + U scheme impairs this agreement. We demonstrate that formal oxidation states reflect only orbital occupancies, not charge transfer, and resolve outstanding controversies about charge ordering.

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In mixed-valence compounds, a transition-metal (TM) element such as Mn would have a fractional “valence” or “formal oxidation state” unless one distinguishes two species of different integral oxidation states. Examples are the manganites ( $R_xA_{1-x}\text{MnO}_3$ , where  $R$  is a trivalent and  $A$  is a divalent ion, e.g., La and Ca, respectively), where the nominal Mn valence is  $4 - x$ . These materials exhibit complex behavior, including colossal magnetoresistance, phase separation, and spatial ordering of two inequivalent Mn atoms [1–5]. This spatial ordering occurs typically for  $x \leq 0.5$ . It is attributed to  $\text{Mn}^{+3}$  and  $\text{Mn}^{+4}$  oxidation states and is generally interpreted as charge ordering. This phenomenon and accompanying structural distortions and magnetic ordering are widely believed to be manifestations of strong electron correlations. In recent years, however, the presence of physical-charge ordering has been challenged [6–10].

Density-functional theory (DFT) [11,12] is generally viewed as inadequate for transition-metal oxides. Alternative theories such as the local spin-density approximation augmented by a Hubbard U (LSDA + U) [13], GGA + U, and dynamical mean-field theory (DMFT) [14] that include local correlations in the form of a “Hubbard U” are viewed as more suitable alternatives [15–19].

DFT is a ground-state theory. Ground-state properties constitute the real test of the applicability of DFT to mixed-valence compounds. A careful examination of the literature, however, reveals a lack of systematic tests of DFT predictions of ground-state properties to establish benchmarks for discrepancies to be addressed by theories that incorporate additional electron correlations. In this Letter, we report such systematic tests for  $R_x\text{Ca}_{1-x}\text{MnO}_3$  for  $x$  from 0 to 0.5 and establish the following: the predicted structural, electronic, and magnetic ground-state properties are in excellent agreement with all available data for  $R = \text{La}$  and  $R = \text{Bi}$ , obviating strong electron correlations. In addition, inclusion of strong local correlations by the GGA + U scheme impairs the agreement with the data.

The generality of these results is discussed in the context of available data and calculations of ground-state properties for other mixed-valence compounds and in the context of theories for energy gaps.

The  $\text{La}_x\text{Ca}_{1-x}\text{MnO}_3$  (LCMO) system has been widely studied by experiments and theory. Experimental studies of  $\text{Bi}_x\text{Ca}_{1-x}\text{MnO}_3$  (BCMO) were recently reported by some of the present coauthors [20]. Electron-energy loss spectra (EELS) demonstrated that the structural ordering of inequivalent Mn atoms is accompanied by ordering of their “formal oxidation states,” as extracted from  $L_{23}$  ratios (the ratios of the areas under the initial peak of the  $L_2$  and  $L_3$  spectra) [20]. At first glance, this direct evidence of oxidation-state ordering adds further to the controversy as it appears to contradict the data that find no charge ordering [6,7,9]. The theoretical results to be presented here resolve the apparent conflict and elucidate the underlying physics.

Density-functional calculations were performed using spin-polarized generalized-gradient approximation (GGA) and the projector augmented-wave (PAW) method as implemented in the VASP code [21,22]. Convergence tests for  $k$  points and energy cutoff were performed to ensure numerical accuracy. For doped CMO, the calculations were based on “generic doping” by introducing extra electrons compensated by a uniform positive background (the approximation is justified by the experimental fact that the dopants are randomly distributed [20]). Calculations using real dopants should in principle be done in large supercells with different dopant arrangements followed by averaging over such arrangements. Such an undertaking is not practical. However, for 50% doping, we performed calculations for ordered  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ , which confirmed the validity of generic doping. Atomic-orbital occupancies were obtained from the eigenvalues of the on-site density matrix as implemented in the VASP code based on the PAW approach [21,22]. For GGA + U calculations, the results of which are reported at the end of the Letter, we also used the VASP implementation with  $U = 8.0$  eV on the Mn 3d orbitals

from GGA + U have larger bandwidth energies, in disagreement with photoemission data (Fig. 1). The predicted magnetic ordering obtained from GGA + U for CMO at 0, 33%, and 50% doping is shown in Fig. 2 for two different values of U. Clearly, U pushes the crossing point farther away from the experimental value.

The present results call for an assessment of systematic DFT/GGA benchmarks and the extent of discrepancies. For example, viewed by themselves, DFT/GGA results for ordered  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  [blue (or dark gray) circles in Fig. 2] might be interpreted as a failure to predict the observed magnetic ordering (in the data AF prevails up to  $x = 0.52$ ). However, when viewed as a trend with doping, as in Fig. 2, the agreement with experiment is excellent (note the meV scale). It has been believed that one must include double exchange and superexchange explicitly, as a manifestation of strong correlations, to account for the observed magnetic ordering in  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  [29]. Clearly, these effects are included adequately by DFT/GGA. Another example is  $\text{LaMnO}_3$ , for which GGA obtains the correct crystallographic symmetry, but predicts FM ordering instead of the observed AF ordering. The problem can be traced to slightly smaller Jahn-Teller distortions than observed (see, e.g., Refs. [15,30]). However, AF ordering is predicted if the measured distortions are used. Thus, in this case, the magnetic ordering is within the error of DFT/LSDA for atomic positions. GGA + U gets the correct structure (larger Jahn-Teller distortions than GGA) and magnetic ordering.

Overall, we conclude the following. When one examines structural, electronic, and magnetic ground-state properties of the entire LCMO system as opposed to isolated cases, the discrepancies between GGA results and experimental data are small, just as they are in *sp*-bonded materials, obviating the need to invoke strong correlations. Though it is desirable to have theories that go beyond GGA even for ground-state properties, the task is very challenging because such theories would seek improved performance on the scale of 0.1 eV in total energies and 0.1 Å in bond lengths. Our results demonstrate that, as formulated, GGA + U does not meet this challenge in a key mixed-valence system, even though it is often a clear winner over GGA in isolated cases in other systems. It is clear that systematic DFT/GGA benchmarks are needed for ground-state properties of other systems as well before strong correlations are invoked.

GGA + U and DMFT are usually invoked to account for the observed energy gaps of transition-metal oxides, following the suggestion by Mott for NiO [31] and by Hubbard [32]. In *sp*-bonded materials, energy gaps are generally calculated with the *GW* scheme [33], which yield satisfactory agreement with data, even in cases where the LDA gap is zero. In recent years, the *GW* scheme has been shown to yield excellent band gaps for TM oxides as well, in particular, for the benchmark case of NiO [34]. This result, together with the results of the present Letter,

clearly suggest that systematic and accurate benchmarks using DFT/GGA and by *GW* as an extension for energy gaps are needed to establish any discrepancies from experimental data that need to be addressed by theories that include additional correlations.

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# Band gap and Schottky barrier heights of multiferroic BiFeO<sub>3</sub>

S. J. Clark

Physics Department, Durham University, Durham DH1 3LE, United Kingdom

J. Robertson<sup>a)</sup>

Engineering Department, Cambridge University, Cambridge CB2 1PZ, United Kingdom

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BiFeO<sub>3</sub> is an interesting multiferroic oxide and a potentially important Pb-free ferroelectric. However, its applications can be limited by large leakage currents. Its band gap is calculated by the density-functional based screened exchange method to be 2.8 eV, similar to experiment. The Schottky barrier height on Pt or SrRuO<sub>3</sub> is calculated in the metal induced gap state model to be over 0.9 eV. Thus, its leakage is not intrinsic. © 2007 American Institute of Physics.  
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There is increasing interest in materials which display simultaneous ferroelectric and magnetic properties, the multiferroics,<sup>1–5</sup> of which BiFeO<sub>3</sub> is the best known example. It was noted that the remnant polarization of bulk BiFeO<sub>3</sub> of 3.5  $\mu\text{C}/\text{cm}^2$  was low compared to its high Curie temperature.<sup>6</sup> Recently, Wang *et al.*<sup>7</sup> and Eerenstein *et al.*<sup>8</sup> found that thin epitaxial films of BiFeO<sub>3</sub> on SrTiO<sub>3</sub> substrates displayed much higher polarizations of  $\sim 90 \mu\text{C}/\text{cm}^2$  and this is becoming accepted as the bulk value.<sup>5,9</sup> There is also an interest in Pb-free ferroelectrics such as BiFeO<sub>3</sub> for environmental reasons.<sup>10</sup> These observations suggest a number of possible applications of BiFeO<sub>3</sub> thin films in high-density data storage, etc. However, these films often show sizable electrical leakage currents.<sup>11–16</sup> These can mask measurements of the polarization loop and could short-circuit ferroelectric storage devices, so there have been extensive efforts to reduce the leakage currents.<sup>14–16</sup> It is therefore of interest to know the band gap of BiFeO<sub>3</sub> and its conduction mechanisms, in order to know if the leakage is intrinsic or extrinsic.

On the theory side, the atomic structure and multiferroic character of BiFeO<sub>3</sub> and related materials can be partially described by the local spin density approximation (LSDA) of the local density approximation (LDA). However, LDA is known to underestimate the band gap for semiconductors. LSDA is well known to be particularly poor for correlated insulators, of which NiO is the classic case.<sup>17</sup> LDA gives a metal, whereas experimentally it has a 4 eV band gap.<sup>18</sup> For BiFeO<sub>3</sub>, LSDA gives a rather small band gap of 0.3–0.77 eV.<sup>19,20</sup> If this were true, it would lead to a very high leakage current.

This problem can be corrected by using density-functional methods which go beyond LDA. The simplest of these is “LDA+U” in which an empirical on-site potential (U) is added to the atomic (pseudo-) potential.<sup>21</sup> This method was employed by Neaton *et al.*<sup>19</sup> for BiFeO<sub>3</sub>, who found band gaps from 0.3 to 1.9 eV, depending on the value of U. The most accurate but expensive method is the parameter-free GW approximation.<sup>22</sup> Here, we calculate the electronic structure of BiFeO<sub>3</sub> using the screened exchange (sX) method.<sup>23–26</sup> This is a parameter-free, density-functional method of including an improved electronic exchange poten-

tial, but it is less expensive than GW. The sX method has been found to give good band gaps for many insulating oxides and semiconductors.<sup>25,26</sup> We then use this band structure to calculate the Schottky barrier height of various metals on BiFeO<sub>3</sub> and thus find the likely size of any intrinsic leakage currents.

Our calculations use the CASTEP plane-wave pseudopotential code.<sup>27</sup> The sX potential is a density-functional method based on Hartree-Fock, which includes the electron exchange via a Thomas-Fermi screened exchange term.<sup>23</sup> The sX potential is actually a true energy functional which could be used to minimize the total energy. However, for speed reasons, here we calculate the atomic structure by the conventional spin-polarized generalized gradient approximation, and then use sX to calculate the energy bands from this structure. Norm-conserving pseudopotentials are used and the plane-wave cutoff energy is 800 eV.

BiFeO<sub>3</sub> is a perovskite whose most stable phase is the *R3c* rhombohedral structure.<sup>28</sup> This is a distortion of the basic cubic perovskite structure in which the oxygen octahedra are rotated in alternate senses about the (111) axis, as seen in two projections in Fig. 1. The Bi<sup>3+</sup> ions are displaced along (111) and this leaves the oxygens effectively fourfold coordinated to two Bi<sup>3+</sup> ions and two Fe<sup>3+</sup> ions. BiFeO<sub>3</sub> has an antiferromagnetic ordering, with the spins on the Fe<sup>3+</sup> ions being aligned in opposite senses along the (111) axis.

Our calculated structural parameters are similar to those of Neaton *et al.*<sup>19</sup> The resulting bands in sX are shown in

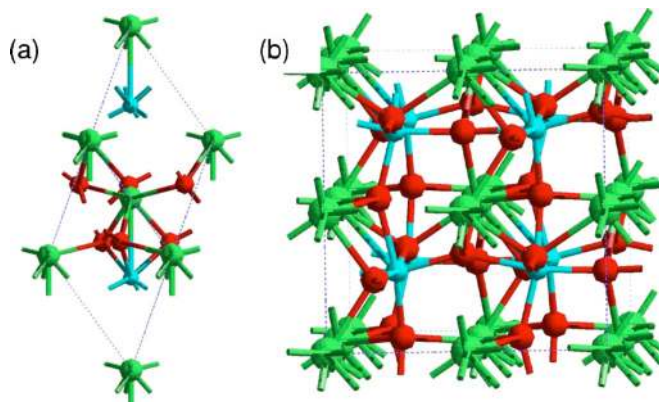


FIG. 1. (Color online) Structure of the *R3c* phase (a) rhombohedral cell and (b) pseudocubic cell. Oxygen=red, Bi=green, and Fe=blue.

<sup>a)</sup>Electronic mail: jr@eng.cam.ac.uk

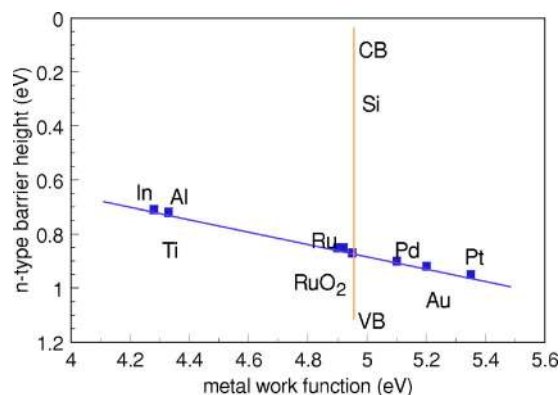


FIG. 4. (Color online) Schottky barrier heights vs metal work functions.

in Fig. 4. This shows that the barrier of Pt will be 0.95 eV. The barrier to a typical conducting oxide  $\text{RuO}_2$  or  $\text{SrRuO}_3$  would be 0.9 eV. These are sizable energy barriers. Thus overall, the band gap of  $\text{BiFeO}_3$  is not as large but approaches that of  $\text{SrTiO}_3$ . The barrier heights are sufficiently large to inhibit Schottky emission from the metal into the oxide conduction band, the most likely intrinsic form of conduction.

Experimentally,  $\text{BiFeO}_3$  films can show considerable electrical conductivity.<sup>11–16</sup> It was found that the conductivity could be reduced by optimizing the growth procedures.<sup>12–16</sup> The conductivity could be greatly reduced by doping the  $\text{BiFeO}_3$  with  $\text{Ti}^{4+}$  ions<sup>13</sup> or Mn,<sup>16</sup> but increased by doping with NiO.<sup>13</sup> This suggests that the conductivity originates from oxygen vacancy levels in the oxide band gap. They form rather shallow states in many perovskites. O vacancies occur to allow mixed Fe valence.

Overall, our calculated band gap and Schottky barrier heights for  $\text{BiFeO}_3$  are large enough to suggest that electronic leakage can be small. The gap is much larger than found in earlier LSDA calculations and similar to experiment. It suggests that the screened exchange method works well for correlated oxides as well as simple oxides. It suggests that leakage current can be reduced by better processing conditions of the oxide films.

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# Self-interaction in Green's-function theory of the hydrogen atom

W. Nelson,<sup>1,\*</sup> P. Bokes,<sup>2,3</sup> Patrick Rinke,<sup>3,4</sup> and R. W. Godby<sup>1,3,†</sup>

<sup>1</sup>*Department of Physics, University of York, Heslington, York YO10 5DD, United Kingdom*

<sup>2</sup>*Department of Physics, Faculty of Electrical Engineering and Information Technology, Slovak University of Technology, Ilkovičova 3, 841 04 Bratislava, Slovak Republic*

<sup>3</sup>*European Theoretical Spectroscopy Facility (ETSF)*

<sup>4</sup>*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany*

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Atomic hydrogen provides a unique test case for computational electronic structure methods, since its electronic excitation energies are known analytically. With only one electron, hydrogen contains no electronic correlation and is therefore particularly susceptible to spurious self-interaction errors introduced by certain computational methods. In this paper we focus on many-body perturbation theory (MBPT) in Hedin's *GW* approximation. While the Hartree-Fock and the exact MBPT self-energy are free of self-interaction, the correlation part of the *GW* self-energy does not have this property. Here we use atomic hydrogen as a benchmark system for *GW* and show that the self-interaction part of the *GW* self-energy, while nonzero, is small. The effect of calculating the *GW* self-energy from exact wave functions and eigenvalues, as distinct from those from the local-density approximation, is also illuminating.

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## I. INTRODUCTION

*Ab initio* many-body quantum mechanical calculations are crucially important to our understanding of the behavior of atomic, molecular, and condensed matter systems. It is well-known that predicting the behavior of these systems requires the description of electronic correlation. While density-functional theory (DFT) in the local-density approximation (LDA) does this with startling success in many cases, it does so at the expense of a nonphysical electron self-interaction. For delocalized electron systems this self-interaction becomes negligible, but in atomic or strongly localized electronic systems it plays an important role. If one is interested in the calculation of quasiparticle excitation spectra, many-body perturbation theory (MBPT) is formally a correct way to proceed. For solids, MBPT in Hedin's *GW* approximation [1] has become the method of choice, but it is also increasingly being applied to molecular systems and clusters. The *GW* self-energy can be decomposed into correlation and exchange parts, where the latter is the same as the Fock operator encountered in Hartree-Fock theory and thus self-interaction free. While the exact self-energy must also be free of self-interaction, the correlation part of the *GW* self-energy does not have this property. To investigate the influence of self-interaction in the *GW* approach the hydrogen atom provides an ideal case because the exact solution is known analytically.

Hydrogen in its solid phase has previously been studied within the *GW* approximation by Li *et al.* [2], who analyzed the transition between the high-pressure solid phase and the low density, atomiclike limit. For individual atoms, *GW* electron removal and addition energies (we use the term "quasiparticle" energies by analogy with the solid-state situation)

have been investigated by Shirley and Martin [3], Dahlen *et al.* [4,5], Stan *et al.* [6], and Delaney *et al.* [7], although hydrogen was not considered. These studies have shown that *GW*, in general, gives quasiparticle properties which are much improved over DFT and Hartree-Fock methods, even for atoms.

In this paper we use the hydrogen atom as a benchmark system to quantify the self-interaction error in the *GW* approach. Since the self-energy diagrams *beyond GW*, known as the vertex correction, must by definition correct this self-interaction error, our findings are relevant for research into vertex functions for the many-electron problem.

Attention has recently focused on the prospects for improving the usual non-self-consistent *GW* calculations by choosing an initial Green's function,  $G_0$ , that is physically more reasonable than the LDA (e.g., [2,8,9]). We explore this here by determining the sensitivity of the self-interaction error to the use of the exact hydrogenic orbitals and energies in place of those from the local-density approximation (LDA). We also assess the error introduced into *GW* calculations by employing first-order perturbation theory in solving the quasiparticle equation (as opposed to the full numerical solution), and we analyze the quasiparticle wave functions that emerge from a full solution.

## II. HARTREE-FOCK VERSUS DFT-LDA

In many-body perturbation theory the quasiparticle excitation energies  $\epsilon_{i\sigma}$  and wave functions  $\psi_{i\sigma}$  are the solutions of the quasiparticle equation

$$H_0(\mathbf{r})\psi_{i\sigma}(\mathbf{r}) + \sum_{\sigma'} \int d\mathbf{r}' M_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}'; \epsilon_{i\sigma}^{\text{qp}}) \psi_{i\sigma'}(\mathbf{r}') = \epsilon_{i\sigma}^{\text{qp}} \psi_{i\sigma}(\mathbf{r}), \quad (1)$$

where, in Hartree atomic units,  $H_0(\mathbf{r}) = -\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r})$  and  $v_{\text{ext}}(\mathbf{r})$  is the external potential. It is customary to divide the

\*Present address: Department of Physics, King's College London, Strand, London WC2R 2LS, United Kingdom.

†Electronic address: rwg3@york.ac.uk

the correct physics in this extreme system (owing to the large self-interaction present in the LDA calculation itself, as reflected in the large error in the LDA Kohn-Sham eigenvalue) that it forms a very unsuitable starting point for *GW*. However, a physically reasonable starting point reduces the *GW* self-interaction error to a small size.

Since  $\Sigma_c$  gives a nonvanishing contribution to the hydrogen *1s* state, even if the analytic solution is used as a starting point, the quasiparticle wave function will differ from the exact one. Figure 1 shows that the *GW* correlation gives rise to a slight delocalization of the quasiparticle wave function in this case. This relaxation, however, now makes the quasiparticle wave function an eigenfunction of the quasiparticle Hamiltonian. In the LDA the self-interaction error is much more pronounced and the wave function becomes significantly more delocalized. The *GW* self-energy corrects this to a small extent (as reflected in the quasiparticle wave function), but the remaining discrepancy reiterates the unsuitability of the LDA as a starting point for *GW* in this self-interaction-dominated atom.

For an analysis of the contributions to the self-energy we turn to the perturbative solution of the quasiparticle equation using Eq. (17), shown in Table II. When the exact Kohn-Sham wave function and eigenvalues are used, as in the Hartree-Fock case the exchange part of the self-energy is seen to cancel the self-interaction contribution from the Hartree potential exactly. The correlation part, on the other hand, is not zero, but amounts to a self-polarization of 0.25 eV. When the LDA is used as the starting point the influence of the LDA wave function on the exchange operator becomes apparent and it reduces from  $-17.00$  eV in the exact case to  $-15.38$  eV. This corrects the highly overestimated LDA eigenvalue for the *1s* state of  $-6.36$  eV (see Table I) to  $-13.49$  eV. However, in this case the contribution from the correlation part of the *GW* self-energy is even larger than when starting from the exact case and increases the quasiparticle energy to  $-12.93$  eV.

TABLE II. Quasiparticle energies (eV) for the *1s* state of hydrogen obtained by solving Eq. (17). The contributions from the exchange  $\langle \Sigma_x \rangle$  and correlation  $\langle \Sigma_c \rangle$  part of the self-energy are compared to that of the exchange-correlation potential  $\langle v_{xc} \rangle$  for the LDA and the exact case ( $v_{xc} = -v_H$ ) as a starting point. Exact value for  $\epsilon_{1s}$  is  $-13.61$  eV.

Kohn-Sham $G_0$	$\epsilon_{1s}^{GW}$	$\langle \Sigma_x \rangle$	$\langle v_{xc} \rangle$	$\langle \Sigma_c \rangle$
LDA	$-12.93$	$-15.38$	$-8.25$	$0.56$
Exact	$-13.35$	$-17.00$	$-17.00$	$0.25$

## VI. CONCLUSION

We have performed spin-resolved benchmark calculations for the *GW* formalism using the analytically known solutions of the hydrogen atom as a reference, making the self-interaction error introduced by the correlation part of the *GW* self-energy directly assessable. When the exact Kohn-Sham Green's function is used as the input to *GW*, the self-interaction error is small (0.21 eV, 1/30 the size of that in the LDA), but not negligible. If the LDA Kohn-Sham Green's function is used, as done in many *GW* calculations for more complex systems, a larger self-interaction error remains, inherited from the LDA starting point.

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# Effect of Surrounding Point Charges on the Density Functional Calculations of $\text{Ni}_x\text{O}_x$ Clusters ( $x = 4\text{--}12$ )

EVGUENI B. KADOSSOV, KAREN J. GASKELL, MARJORIE A. LANGELL  
 Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588-0304

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**Abstract:** Embedded  $\text{Ni}_x\text{O}_x$  clusters ( $x = 4\text{--}12$ ) have been studied by the density-functional method using compensating point charges of variable magnitude to calculate the ionic charge, bulk modulus, and lattice binding energy. The computations were found to be strongly dependent on the value of the surrounding point charge array and an optimum value could be found by choosing the point charge to reproduce the experimentally observed Ni—O lattice parameter. This simple, empirical method yields a good match between computed and experimental data, and even small variation from the optimum point charge value produces significant deviation between computed and measured bulk physical parameters. The optimum point charge value depends on the cluster size, but in all cases is significantly less than  $\pm 2.0$ , the formal oxidation state typically employed in cluster modeling of NiO bulk and surface properties. The electronic structure calculated with the optimized point charge magnitude is in general agreement with literature photoemission and XPS data and agrees with the presently accepted picture of the valence band as containing charge-transfer insulator characteristics. The orbital population near the Fermi level does not depend on the cluster size and is characterized by hybridized Ni 3d and O 2p orbitals with relative oxygen contribution of about 70%.

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**Key words:** nickel oxide clusters; point charge embedding; density-functional methods; electronic structure ab initio calculations

## Introduction

The electronic structure of NiO has been under active investigation for almost 6 decades, dating from the historic studies of Neville Mott,<sup>1–3</sup> which explained the insulating nature of the partially filled  $\text{Ni}^{2+}$  3d level with a localized, antiferromagnetically ordered conduction band. Subsequent refinements produced the Mott-Hubbard model,<sup>4,5</sup> in which an insulating gap of energy  $U$  forms within the 3d level due to the strong Coulomb repulsion among the highly correlated 3d electrons. NiO was considered a prototypical Mott-Hubbard insulator for quite some time until the model was challenged by a series of photoemission experiments,<sup>6,7</sup> supported by ab initio cluster calculations,<sup>8</sup> which proposed the insulating nature originated from hybridization between localized nickel 3d and oxygen 2p levels. The band structure in this charge-transfer model is described by inclusion of configurations that transfer electron density between the filled O 2p<sup>6</sup> band into the empty Ni 3d:

$$\Psi_{\text{band}} = \alpha 3d^8 + \beta 3d^9 L + \gamma 3d^{10} L^2 \quad (1)$$

where,  $L$  represents a hole in the oxygen 2p band. The charge-transfer model explains satellite structure in photoemission quite well, but is less satisfactory in describing the composition of the

top of the valence band and bottom of the conduction band, and thus the nature of the band gap. These problems occasionally give rise to a new round of controversy,<sup>9–13</sup> and the presently adopted picture of the NiO band structure often includes both Mott-Hubbard and charge-transfer nature.

As a theoretical understanding of the electronic nature of nickel oxide and other rocksalt 3d monoxides has developed, it has become apparent that in many cases computational methods have proven inadequate to describe key features of the band structure. In particular, ab initio studies of nickel oxide, especially those employing DFT methods, often fail to correctly describe the band gap, found experimentally to be in the range of 3.5–4.3 eV.<sup>14–18</sup> Many calculations either significantly underestimate the value at less than 1 eV,<sup>19,20</sup> or strongly overestimate it at greater than 4.5 eV.<sup>21–25</sup>

While the controversy over the nature of the band gap is fundamental, there is reason to believe that some inaccuracies in

**Correspondence to:** M. A. Langell; e-mail: mlangell@unlserve.unl.edu

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# Electrochromics for smart windows: thin films of tungsten oxide and nickel oxide, and devices based on these

Gunnar A. Niklasson and Claes G. Granqvist

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Electrochromic (EC) materials are able to change their optical properties, reversibly and persistently, by the application of an electrical voltage. These materials can be integrated in multilayer devices capable of modulating the optical transmittance between widely separated extrema. We first review the recent literature on inorganic EC materials and point out that today's research is focused on tungsten oxide (colouring under charge insertion) and nickel oxide (colouring under charge extraction). The properties of thin films of these materials are then discussed in detail with foci on recent results from two comprehensive investigations in the authors' laboratory. A logical exposition is obtained by covering, in sequence, structural features, thin film deposition (by sputtering), electronic band structure, and ion diffusion. A novel conceptual model is given for structural characteristics of amorphous W oxide films, based on notions of defects in the ideal amorphous state. It is also shown that the conduction band density of states is obtainable from simple electrochemical chronopotentiometry. Ion intercalation causes the charge-compensating electrons to enter localized states, implying that the optical absorption underlying the electrochromism can be described as ensuing from transitions between occupied and empty localized conduction band states. A fully quantitative theory of such transitions is not available, but the optical absorption can be modeled more phenomenologically as due to a superposition of transitions between different charge states of the W ions (6+, 5+, and 4+). The Ni oxide films were found to have a porous structure comprised of small grains. The data are consistent with EC coloration being a surface phenomenon, most likely confined to the outer parts of the grains. Initial electrochemical cycling was found to transform hydrated Ni oxide into hydroxide and oxy-hydroxide phases on the grain surfaces. Electrochromism in thus stabilized films is consistent with reversible changes between Ni hydroxide and oxy-hydroxide, in accordance with the Bode reaction scheme. An extension of this model is put forward to account for changes of NiO to Ni<sub>2</sub>O<sub>3</sub>. It was demonstrated that electrochromism is associated solely with proton transfer. Data on chemical diffusion coefficients are interpreted for polycrystalline W oxide and Ni oxide in terms of the lattice gas model with interaction. The later part of this review is of a more technological and applications oriented character and is based on the fact that EC devices with large optical modulation can be accomplished essentially by connecting W-oxide-based and Ni-oxide-based films through a layer serving as a pure ion conductor. Specifically, we treat methods to enhance the bleached-state transmittance by mixing the Ni oxide with other oxides characterized by wide band gaps, and we also discuss pre-assembly charge insertion and extraction by facile gas treatments of the films, as well as practical device manufacturing and device testing. Here the emphasis is on novel flexible polyester-foil-based devices. The final part deals with applications with emphasis on architectural "smart" windows capable of achieving improved indoor comfort jointly with significant energy savings due to lowered demands for space cooling. Eyewear applications are touched upon as well.

## I. Introduction

Chromogenic materials are able to change their optical properties as a response to an external stimulus,<sup>1</sup> such as irradiation by light (photochromic materials), change in temperature (thermochromic materials), the application of an electrical voltage (electrochromic materials), to

mention the most common types. Electrochromic (EC) materials, which this Feature Article is about, were brought to public attention some 35 years ago thanks to the seminal work on tungsten oxide films by Deb.<sup>2,3</sup> In essence, the optical absorption in the visible range changes widely as charge is inserted or extracted. Not surprisingly, these materials were immediately considered for application in information displays, but they did not stand up to the competition from the then rapidly developing liquid-crystal-based technology.

*Department of Engineering Sciences, The Ångström Laboratory, Uppsala University, P. O. Box 534, SE-75121 Uppsala, Sweden*

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C.G. GRANQVIST<sup>1,✉</sup>  
G.A. NIKLASSON<sup>1</sup>  
A. AZENS<sup>2</sup>

# Electrochromics: Fundamentals and energy-related applications of oxide-based devices

<sup>1</sup> Department of Engineering Sciences, The Ångström Laboratory, Box 534, 75121 Uppsala, Sweden

<sup>2</sup> ChromoGenics Sweden AB, Märstagan 4, 75323 Uppsala, Sweden

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**ABSTRACT** We first introduce electrochromic (EC) device technology, which uses transparent conducting oxides as one of its critical components, and consider how this technology can be employed to obtain urgently needed energy savings for modern buildings. The discussion then focuses on two of the most suitable EC materials,  $\text{WO}_3$  and  $\text{NiO}$ ; we cover recent advances in basic physics and chemistry as well as the properties of flexible foil-type devices combining the two oxides. The final part of the paper provides a broader, more general overview of chromogenic materials.

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## 1 Introduction

Electrochromic (EC) devices incorporate transparent conducting oxides (TCOs) and a three-layer stack comprising a “battery-like” structure with thin films serving as “cathode”, “anode”, and electrolyte. Figure 1 illustrates a typical EC device wherein the TCOs are of  $\text{In}_2\text{O}_3:\text{Sn}$  (indium tin oxide, or ITO), the “cathode” is  $\text{WO}_3$ , and the “anode” is  $\text{NiO}$ . Charging and discharging this “battery” leads to varying optical absorption, a phenomenon that can be used in a multitude of applications.

This paper highlights applications to solar energy and energy savings with a focus on modern building construction. In this context it is customary to speak of EC “smart windows”. Section 2 below is devoted to energy-related applications and their urgency, and where electrochromics – and hence TCOs – come into play. Section 3 outlines EC device technology in general, and then focuses on  $\text{WO}_3$ ,  $\text{NiO}$ , and foil-type devices made from them. Section 4 broadens the scope and gives a more general survey of chromogenic devices including ECs, photochromics, thermochromics, and other “chromics”.

## 2 TCOs, electrochromics, and the need for chromogenic building skins

There can be no doubt that future energy supplies and energy security will demand revolutionary advances in technology in order to maintain or forward today’s (2006) general standard of living and level of economic prosper-

ity [1]. Indeed, the magnitude of the problems surrounding these issues may seem daunting. For example, it has been stated that the warming and precipitation trends due to anthropogenic, energy-related climate change during the past thirty years already claim over 150 000 human lives annually [2, 3]. Furthermore, the advances in energy technology must take place for a growing population whose increasing concentration in mega-cities leads to “heat islands”, thereby accelerating the warming [4]. By 2050 there will be some 10 billion people in the world. Energy must be available to them all, and it has to be clean. New technologies are urgently needed to accomplish this.

Where do the TCOs, and devices using them, enter into this scenario? A basic reason why they are relevant in this context is that they can show transparency in a limited and well-defined range, normally encompassing visible light in the  $0.4 < \lambda < 0.7 \mu\text{m}$  wavelength interval. This has led to a range of applications in fenestration technology with doped  $\text{SnO}_2$  being extensively used for providing low thermal emittance and thus good thermal insulation [5]. Other windows-related applications employ antireflected noble-metal-based films for admitting visible light and rejecting infrared solar irradiation, and/or for providing low thermal emittance [5]. In some markets, the penetration of coated glass for new buildings is currently almost total, whereas the market share is smaller elsewhere. Given the obvious need to diminish energy use on a global scale, these technologies can only be expected to grow. The enormity of the market is apparent; the production of float glass – used almost without exception in modern fenestration – exceeds 4 billion  $\text{m}^2$  per year [6]. Coating even a small portion of this with TCOs makes architectural (and automotive) windows by far the largest field of applications for transparent conductors, completely outstripping other applications such as displays and transparent electronics.

Modern people normally spend some 90% of their time inside buildings and vehicles, hence the quality of the indoor environment is of great importance. More and more energy is used to maintain the indoor environment at a level that is both comfortable and healthy. Within the EU, some 40% of the energy supply is used for heating, cooling, ventilation and lighting of buildings, as well as for appliances; this corresponds to  $\sim 4\%$  of the Gross National Product [4, 7]. As indicated recently [8, 9], air conditioning and refrigeration is becoming increasingly important to peak electricity demand. It has risen by an average of 17% per year in the EU between 1995 and 2003 [10]. A further indication of the pressing de-

✉ Fax: +46 18 500131,  
E-mail: Claes-Goran.Granqvist@Angstrom.uu.se

ate light-weight buildings with little embedded energy inside huge membranes. These membranes could allow the flow of visible light and solar energy to be controlled and optimized. The possibilities offered by such membranes were in fact pointed out more than 50 years ago by the great visionary Buckminster Fuller [83], although based on conventional glass technology. Perhaps this grand vision will one day come true – thanks to electrochromics.

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# Exact-exchange-based quasiparticle energy calculations for the band gap, effective masses, and deformation potentials of ScN

Abdallah Qteish

*Department of Physics, Yarmouk University, 21163-Irbid, Jordan*

Patrick Rinke and Matthias Scheffler

*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany*

Jörg Neugebauer

*MPI für Eisenforschung, Max-Planck Straße 1, D-40237 Düsseldorf, Germany*

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The band gaps, longitudinal and transverse effective masses, and deformation potentials of ScN in the rock-salt structure have been calculated employing  $G_0W_0$ -quasiparticle calculations using exact-exchange Kohn-Sham density-functional theory one-particle wave functions and energies as input. Our quasiparticle gaps support recent experimental observations that ScN has a much lower indirect band gap than previously thought. The results are analyzed in terms of the influence of different approximations for exchange and correlation taken in the computational approach on the electronic structure of ScN.

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## I. INTRODUCTION

Scandium nitride (ScN) is emerging as a versatile material for promising technological applications. As part of the transition-metal nitride family it initially generated interest for potential applications as wear-resistant and optical coatings due to its mechanical strength, high melting point of 2600 °C,<sup>1</sup> and high hardness ( $H=21$  GPa) with respect to load deformations.<sup>2</sup> ScN crystallizes in the rock-salt phase with a lattice parameter of 4.50 Å.<sup>3</sup> The octahedral bonding arrangement provides a much more favorable environment for the incorporation of transition-metal atoms like Mn or Cr than the tetrahedrally coordinated III-V semiconductors, which have up until now been popular candidates for spintronic materials. Successful incorporation of Mn into ScN has been demonstrated<sup>4</sup> and *ab initio* calculations predict Mn-doped ScN to be a dilute ferromagnetic semiconductor.<sup>5</sup> Moreover, ScN has a lattice mismatch of less than 2% to cubic gallium nitride (GaN). This makes ScN structurally compatible with the group-IIIA nitrides<sup>6–13</sup>—an important technological material class, in particular, for applications in optoelectronic devices. Alloying ScN with GaN (Refs. 9–12) might provide a viable alternative to InGaN alloys for use in light-emitting devices or solar cells. In addition, multifunctional devices are conceivable if the strong electromechanical response predicted for hexagonal ScN (Ref. 14) can be utilized.

The electronic band structure of ScN—a key quantity for the design of optoelectronic devices—has been difficult to access both experimentally and theoretically. Early experiments were hampered by various complications in growing films with well-defined crystalline orientation, stoichiometry, low background carrier concentration, and surface roughness. For a detailed discussion we refer to, e.g., Ref. 15. Recent advances in growth techniques have led to a systematic improvement of the material's quality.<sup>16</sup> Employing optical spectroscopy and photoemission, Gall *et al.*<sup>15</sup> concluded

that ScN is a semiconductor with an indirect  $\Gamma$ – $X$  band gap ( $E_g^{\Gamma-X}$ ) of  $1.3\pm 0.3$  eV. The sizable error bar of 0.3 eV has been mainly attributed to the large background carrier concentration of  $\sim 5 \times 10^{20} \text{ cm}^{-3}$  causing an apparent increase of the band gap due to the Burnstein-Moss shift.<sup>17</sup> Reducing the electron carrier concentration to  $4.8 \times 10^{18} \text{ cm}^{-3}$  and combining tunneling spectroscopy and optical-absorption measurements, Al-Britthen *et al.*<sup>18</sup> were able to reduce the error bar and found a value for  $E_g^{\Gamma-X}$  of  $0.9\pm 0.1$  eV.

Early Kohn-Sham density-functional theory (KS-DFT) calculations employing the local-density (LDA) or  $X\alpha$  approximations predicted ScN to be a semimetal with a small negative band gap between  $-0.01$  and  $-0.21$  eV.<sup>19–21</sup> In order to overcome the well-known underestimation of the LDA band gap, more advanced exact-exchange [OEPx(cLDA)] (Ref. 15) and screened-exchange<sup>22</sup> calculations have been performed, and showed that ScN is a semiconductor with an indirect  $\Gamma$  to  $X$  band gap, in accord with experimental evidence.<sup>15,18</sup> However, the calculated band gap of 1.60 eV found in both studies is significantly larger than the most recent experimental value of  $0.9\pm 0.1$  eV.<sup>18</sup>

In order to shed light on this discrepancy we have performed quasiparticle energy calculations in Hedin's  $GW$  approximation,<sup>23</sup> which is a well-established technique to calculate accurate band-structure energies and currently the choice for computing quasiparticle band structures of solids.<sup>24–26</sup> The quasiparticle calculations predict ScN in the rock-salt phase to have an indirect band gap between the  $\Gamma$  and  $X$  point of  $0.99\pm 0.15$  eV, strongly supporting recent experimental findings. In addition, we have also determined the direct band gaps and other electronic structure parameters relevant for device simulations: the volume deformation potentials of the main band gaps and the longitudinal and transverse effective masses of the conduction band at the  $X$  point. The effective mass has previously been calculated at the level of the LDA,<sup>27</sup> but to the best of our knowledge, only one experimental study has reported a conduction-band ef-



## IV. CONCLUSIONS

Pseudopotential  $G_0W_0$  calculations based on Kohn-Sham density-functional theory calculations in both the LDA and OEPx(cLDA) have been performed for the electronic structure of ScN in the thermodynamically stable rock-salt phase. To analyze the effects of exchange and correlation the atomic and electronic structures have been studied within DFT for several levels of approximations for the exchange-correlation functional [LDA, GGA and OEPx(cLDA)]. In agreement with previous calculations for ScN, our LDA [OEPx(cLDA)] band gaps are underestimated (overestimated) by about 100%. Despite this large difference, OEPx(cLDA)- $G_0W_0$  and LDA- $G_0W_0$  calculations for the quasiparticle band structure agree to within 0.3 eV. Our quasiparticle gap of  $0.99 \pm 0.15$  eV supports the recent observation that ScN has a

much lower indirect band gap than previously thought. The main advantage of the OEPx(cLDA)- $G_0W_0$  approach lies in the fact that it facilitates a direct calculation of the electronic structure of ScN at the experimental equilibrium volume, whereas for the LDA- $G_0W_0$  calculation an indirect approach has to be taken due to the negative LDA band gap.

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# Optical properties and magnetic-field-induced phase transitions in the ferroelectric state of $\text{Ni}_3\text{V}_2\text{O}_8$ : Experiments and first-principles calculations

R. C. Rai,<sup>1</sup> J. Cao,<sup>1</sup> S. Brown,<sup>1</sup> J. L. Musfeldt,<sup>1,\*</sup> D. Kasinathan,<sup>2</sup> D. J. Singh,<sup>3</sup> G. Lawes,<sup>4</sup> N. Rogado,<sup>5</sup> R. J. Cava,<sup>6</sup> and X. Wei<sup>7</sup>

<sup>1</sup>*Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, USA*

<sup>2</sup>*Department of Physics, University of California–Davis, Davis, California 95616, USA*

<sup>3</sup>*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6032, USA*

<sup>4</sup>*Department of Physics, Wayne State University, Detroit, Michigan 48201, USA*

<sup>5</sup>*DuPont Central Research and Development, Experimental Station, Wilmington, Delaware 19880-0328, USA*

<sup>6</sup>*Department of Chemistry and Princeton Materials Institute, Princeton University, Princeton, New Jersey 08544, USA*

<sup>7</sup>*National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32310, USA*

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We use a combination of optical spectra, first-principles calculations, and energy-dependent magneto-optical measurements to elucidate the electronic structure and to study the phase diagram of  $\text{Ni}_3\text{V}_2\text{O}_8$ . We find a remarkable interplay of magnetic field and optical properties that reveals additional high magnetic-field phases and an unexpected electronic structure, which we associate with the strong magnetodielectric couplings in this material over a wide energy range. Specifically, we observed several prominent magnetodielectric effects that derive from changes in the crystal-field environment around Ni spine and cross tie centers. This effect is consistent with a field-induced modification of local structure. Symmetry-breaking effects are also evident with temperature. We find  $\text{Ni}_3\text{V}_2\text{O}_8$  to be an intermediate-gap, local-moment band insulator. This electronic structure is particularly favorable for magnetodielectric couplings, because the material is not subject to the spin-charge separation characteristic of strongly correlated large-gap Mott insulators, while at the same time remaining a magnetic insulator independent of the particular spin order and temperature.

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## I. INTRODUCTION

$\text{Ni}_3\text{V}_2\text{O}_8$  is a particularly interesting magnetic material,<sup>1–5</sup> both because of its unusual structure, which provides an example of a spin-1 system on a Kagomé staircase lattice, and because of the rich variety of magnetic and structural phases that are stabilized under different conditions. One especially interesting feature is the occurrence of a magnetic, ferroelectric phase as a function of temperature and magnetic field. More generally, coupled magnetic and electric degrees of freedom, flexible lattices, and magnetic frustration in multiferroics can result in cascades of coupled magnetic and dielectric transitions.<sup>6–13</sup> The recent report<sup>10</sup> of colossal low-frequency (1 kHz) magnetodielectric effects in inhomogeneously mixed-valent  $\text{DyMn}_2\text{O}_5$  is especially important, because it illustrates that a sizable dielectric contrast can be achieved by physical tuning through an unusual commensurate-incommensurate magnetic transition and is facilitated by a soft lattice. The 300 K low-frequency magnetodielectric effect in mixed-valent  $\text{LuFe}_2\text{O}_4$  has also attracted attention due to the very low magnetic fields needed to achieve dielectric contrast.<sup>14</sup>  $\text{Ni}_3\text{V}_2\text{O}_8$  is another system where the temperature and field dependence of the spontaneous polarization shows a strong coupling between magnetic and ferroelectric order.<sup>3–5</sup> This coexistence is unusual and appears only when certain symmetry conditions are fulfilled.<sup>3</sup> That the effect can be controlled with an external magnetic field makes it attractive for device applications. Based upon our previous work with inhomogeneously mixed-valent  $\text{K}_2\text{V}_3\text{O}_8$ ,<sup>15</sup> the significant coupling between spin, lattice, and charge degrees of freedom make  $\text{Ni}_3\text{V}_2\text{O}_8$  an excellent can-

didate for the discovery of higher-energy magnetodielectric effects.

Figure 1(a) shows the orthorhombic ( $Cmca$ ) crystal structure of  $\text{Ni}_3\text{V}_2\text{O}_8$ . It consists of Kagomé layers of edge sharing  $\text{NiO}_6$  octahedra separated by nonmagnetic  $\text{VO}_4$  tetrahedra.  $\text{Ni}_3\text{V}_2\text{O}_8$  is considered to be a Kagomé staircase compound due to buckling of the lattice perpendicular to the  $a$  axis. There are two distinct types of  $\text{Ni}^{2+}$  ( $S=1$ ) centers, which we refer to as “spine” and “cross tie” sites. The spine sites run along the  $a$  axis. A view of the Kagomé staircase showing only the Ni atoms is displayed in Fig. 1(b). Note that the spine and cross tie sites have very different local symmetries. The spin-ordering arrangements in  $\text{Ni}_3\text{V}_2\text{O}_8$  have been extensively investigated by neutron scattering and

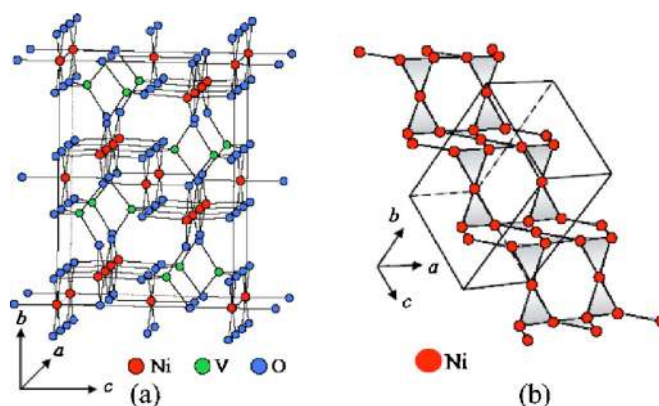


FIG. 1. (Color online) (a) Crystal structure of  $\text{Ni}_3\text{V}_2\text{O}_8$ . (b) View of the Kagomé staircase showing only the Ni atoms.

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**LDA+DMFT computation of the electronic spectrum of NiO**X. Ren,<sup>1,\*</sup> I. Leonov,<sup>1</sup> G. Keller,<sup>1</sup> M. Kollar,<sup>1</sup> I. Nekrasov,<sup>2</sup> and D. Vollhardt<sup>1</sup><sup>1</sup>*Theoretical Physics III, Center for Electronic Correlations and Magnetism, University of Augsburg, 86135 Augsburg, Germany*<sup>2</sup>*Institute of Electrophysics, Ural Branch of Russian Academy of Science, 620016, Ekaterinburg, Russia*

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The electronic spectrum, energy gap and local magnetic moment of paramagnetic NiO are computed using the local density approximation plus dynamical mean-field theory (LDA + DMFT). To this end the noninteracting Hamiltonian obtained within the LDA is expressed in Wannier function basis, with only the five antibonding bands with mainly Ni 3d character taken into account. Complementing it by local Coulomb interactions one arrives at a material-specific many-body Hamiltonian which is solved by DMFT together with quantum Monte Carlo (QMC) simulations. The large insulating gap in NiO is found to be a result of the strong electronic correlations in the paramagnetic state. In the vicinity of the gap region, the shape of the electronic spectrum calculated in this way is in good agreement with the experimental x-ray-photoemission and bremsstrahlung-isochromat-spectroscopy results of Sawatzky and Allen. The value of the local magnetic moment computed in the paramagnetic phase (PM) agrees well with that measured in the antiferromagnetic (AFM) phase. Our results for the electronic spectrum and the local magnetic moment in the PM phase are in accordance with the experimental finding that AFM long-range order has no significant influence on the electronic structure of NiO.

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**I. INTRODUCTION**

NiO is a strongly correlated electron material with a large insulating gap of 4.3 eV and an antiferromagnetic (AFM) ordering temperature of  $T_N=523$  K. Conventional band theories which stress the delocalized nature of electrons cannot explain this large gap and predict NiO to be metallic.<sup>1</sup> On the other hand, spin-polarized band calculations—e.g., density functional calculations based on the local spin-density approximation<sup>2</sup> (LSDA)—which do find an AFM insulating ground state in NiO, produce a band gap and local magnetic moment which are considerably smaller than the experimental values. These facts are often taken as evidence for the inapplicability of conventional band theories to strongly correlated systems like NiO. Indeed, already a long time ago Mott<sup>3</sup> showed that NiO and similar insulators may be better understood within a real-space picture of the solid, where localized electrons are bound to atoms with incompletely filled shells. This leads to the formation of incoherent bands, the lower and upper Hubbard bands, which are separated by a correlation gap of the order of the local Coulomb repulsion  $U$ . For this reason NiO has long been viewed as a prototype “Mott insulator.”<sup>3,4</sup>

This view of NiO was later replaced by that of a “charge transfer insulator,”<sup>5</sup> after Fujimori and Minami had successfully explained the photoemission data in terms of a cluster model treated within the configuration-interaction method.<sup>6</sup> In particular, this interpretation was supported by the combined x-ray-photoemission (XPS) and bremsstrahlung-isochromat-spectroscopy (BIS) measurements of Sawatzky and Allen.<sup>7</sup> Within this new picture an additional ligand  $p$  band appears between the lower and upper Hubbard bands, and the insulating gap is formed between the ligand  $p$  band and the upper Hubbard  $d$  band. However, unless the  $p$ - $d$  hybridization is taken into account, this picture is still an oversimplification. Namely, the hybridization between

transition-metal  $d$  and ligand  $p$  states will lead to some  $d$ -electron features also in the upper valence bands. Indeed, subsequent studies suggested that the first valence peak is actually a bound state arising from the strong hybridization of Ni 3d and O 2p states,<sup>8,9</sup> such that NiO is close to the intermediate regime of the Zaanen-Sawatzky-Allen scheme.<sup>5</sup> Despite the success of the cluster approach it has apparent drawbacks since it neglects the band aspects of O 2p states completely which are known to play an important role in NiO.<sup>8,10</sup> The translational symmetry has been taken into account to some extent within the cluster perturbation theory recently.<sup>11</sup> Another extension is the treatment of a larger cluster (Ni<sub>6</sub>O<sub>19</sub>) so that nonlocal charge transfer excitations can be identified.<sup>12</sup>

Since the cluster approach relies on adjustable parameters to fit the experimental spectrum, it is highly desirable to obtain a description of the electronic structure of NiO from first principles. Already within L(S)DA the O 2p bands can be accounted for quite well.<sup>8</sup> Attempts to go beyond L(S)DA are based on the self-interaction-corrected density functional theory (SIC-DFT),<sup>13</sup> the LDA+U method,<sup>14</sup> and the GW approximation.<sup>15,16</sup> These methods represent corrections of the single-particle Kohn-Sham potential in one way or another and lead to substantial improvements over the L(S)DA results for the values of the energy gap and local moment. Within the SIC-DFT and LDA+U methods the occupied and unoccupied states are split by the Coulomb interaction  $U$ , whereas within the LSDA this splitting is caused by the Stoner parameter  $I$ , which is typically one order of magnitude smaller than  $U$ . Therefore, compared with the LSDA, the SIC-DFT and LDA+U methods capture more correctly the physics of transition-metal (TM) oxides and improve the results for the energy gap and local moment significantly. The GW method goes one step further by calculating the self-energy to lowest order in the screened Coulomb interaction  $W$ , and the obtained band structure shows better agree-

NiO is due to strong electronic correlations in the paramagnetic phase. The magnetic order in NiO is therefore only a secondary effect—i.e., a consequence rather than the origin of the gap. Hence we expect the conduction band photoemission spectra to remain almost unchanged by the AFM long-range order.

In the construction of the *ab initio* Hamiltonian (4), only the five “antibonding” bands (which have mainly Ni 3*d* characters in the LDA calculation) were included, while the three “bonding” bands (which are the mixture of the Ni 3*d* and O 2*p* states, but have more O contributions) below them were neglected. Therefore in the present work the contributions to the Wannier functions from Ni 3*d* and O 2*p* states depend on the LDA results. This means that the valence bands close to the Fermi level have mainly Ni 3*d* character. The insulating gap we obtained is therefore an effective Mott-Hubbard gap between Wannier states. In other words, we used an effective Mott-Hubbard gap to mimic a charge-transfer gap<sup>6,7</sup> or a gap with mixed character.<sup>21,68</sup> Strictly speaking, the gap here is also of mixed character since some amount of oxygen contribution is contained in the Wannier functions. The results obtained by such a treatment are surprisingly good. This may be due to the fact that correlation effects are treated better within DMFT than within any other theoretical approach

available so far, and also because features due to oxygen are rather suppressed in XPS.<sup>60</sup>

In spite of the limitations of the current implementation, we showed that the LDA+DMFT approach which combines first-principles, material-specific information with strong correlation effects is able to deal with late transition-metal monoxides like NiO. A more complete treatment of NiO within the LDA+DMFT approach will require the inclusion of oxygen bands and the *p-d* hybridization. Only in this way can one produce a full spectrum of NiO and identify the satellite structure at high binding energies.

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\*Current address: Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, 14195 Berlin, Germany.

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# Phononic effects and nonlocality contributions to second harmonic generation in NiO

G. Lefkidis\* and W. Hübner

Department of Physics, Kaiserslautern University of Technology, PO Box 3049, 67653, Kaiserslautern, Germany

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We present a method for calculating second harmonic generation on a purely *ab initio* basis in NiO, both for the (001) surface and for the bulk. We go beyond the electric dipole approximation and we incorporate magnetic dipoles and electric quadrupoles in our results. A full detailed symmetry analysis of these contributions is given. Then we calculate phononic contributions to the second order susceptibility tensor for the bulk within the frozen phonon approximation. It is shown that transient lattice distortions can lead to a second harmonic signal, even in centrosymmetric materials like NiO. The second order susceptibility tensor is calculated from first principles, including nonlocalities in two different ways: (i) with phononic contributions on a time averaged way and (ii) with a time resolved single optical phonon at the  $\Gamma$  point. Furthermore the effects of electronic redistribution prior to the probe pulse are given.

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## I. INTRODUCTION

In recent years there has been a continuous strive to understand nonlinear (magneto-) optics in antiferromagnetic materials, in order to employ a possible ultrafast magnetic switching scenario. Nonlinear optics is more selective than nonlocal linear optics, and while less sensitive it falls within the frame of modern detecting apparatus, thus making it an ideal tool for investigating antiferromagnets. Several experimental and theoretical works have been published on a number of such materials, nickel oxide among others, which is a good candidate for such a scenario due to its large spin density, antiferromagnetic order, and clearly separated intragap states. It has a rocksalt structure above the Néel temperature ( $T_N=523$  K) and exhibits a small distortion along the  $\langle 111 \rangle$  axis below  $T_N$ . Although NiO possesses a center of inversion, it generates a second harmonic signal.<sup>1</sup> In the literature there are to date four main explanations for its origin (i) lowering of the crystallographic symmetry due to local distortions or phonons, (ii) spin-orbit coupling (SOC), (iii) a signal that mainly results from the surface, and (iv) inclusion of higher order transitions. Recent works<sup>2,3</sup> from our group showed that explanations (ii) and (iv) are the most probable candidates for the physics behind the work. In this paper we elaborate further on the inclusion of higher order transitions and give the symmetry analysis of the second order susceptibility tensor for them. Then we include the phononic effects, both with and without higher order transitions, and we discuss how the transient lowering of the local symmetry affects the second harmonic generation (SHG) signal.

## II. QUANTUM CHEMISTRY

### A. Computational model

In order to model both the surface and the bulk of NiO one can use either the real or the momentum space approach. Their major difference manifests itself in the ability of only the first one to find the localized intragap  $d$  states of the Ni ion. These dispersionless states are experimentally confirmed for the surface<sup>4,5</sup> and for the bulk.<sup>6</sup> Although some recent calculations with extended local density approximation

(LDA++) within the Hubbard-I approach<sup>7</sup> (a gap of 4.3 eV and an absorption edge of 3.1 eV) and within the *GW* approximation<sup>8-10</sup> give better results for the gap than the real space approach (2.9 to 5.5 eV), they persistently miss the intragap states. In the energy window we are interested in (up to 4 eV), these states are the most relevant ones for optics. Furthermore NiO is a compound in which correlations play an important role, and the real space approach is therefore more suitable to describe its complex electronic structure. Last but not least we wish not only to calculate the energy levels but the transition matrix elements between them as well, in order to compute the second order susceptibility tensor. For the calculation of the transition moment elements we use wave functions in the real space. If however, one had a reciprocal space approach (density functional methods) then one would get from the wave functions the  $\langle \alpha | \mathbf{p} | \beta \rangle$  elements, which then have to be transformed using

$$\langle \alpha | \mathbf{p} | \beta \rangle = -\frac{im_e}{\hbar} \langle \alpha | [\mathbf{r}, \hat{H}_0] | \beta \rangle = im_e \omega_{\alpha\beta} \langle \alpha | \mathbf{r} | \beta \rangle. \quad (1)$$

Equation (1) works fine as long as the transition does not take place between two states with the same (or almost the same) energy, otherwise  $\langle \alpha | \mathbf{r} | \beta \rangle$  becomes infinite; the matrix elements of the operator  $\mathbf{r}$  are ill defined when the wave functions, which include local pseudopotentials, obey Born-von Kármán boundary conditions.<sup>11</sup> One way to overcome the problem is to introduce a factor  $\lambda$  and then Eq. (1) becomes

$$\langle \alpha | \mathbf{r} | \beta \rangle = -\frac{i}{m_e \omega_{\alpha\beta} + i\lambda} \langle \alpha | \mathbf{p} | \beta \rangle \quad (2)$$

which, however, leads to the problem of introducing one additional arbitrary constant, the value of which cannot be evaluated from first principles. Furthermore,  $\lambda$  smears out the transition elements, and can thus lead to very different spectra, especially around energy regions with a high density of states. The real space approach used here does not present these problems, since the calculation of the transition moments does not rely on any energy differences.

spatial extension of the intragap  $d$  states. However, a simple model Hamiltonian can be used to describe the  $d$  bands at various interaction levels within a tight-binding approximation, and to give qualitative insight in the effects of the inclusion of intersite two-center integrals in the Fock matrix.

For this purpose we employ a  $8 \times 8$  Hamiltonian matrix for an fcc lattice, with Bloch functions basis set of the type  $|G(\mathbf{k})\rangle = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} |e^{-a\mathbf{r}}|\psi\rangle$ , where  $|\psi\rangle$  is the angular part of the localized atomic Gaussian functions,  $\mathbf{k}$  the wave vector, and  $\mathbf{R}$  the position of the atoms. We restrict ourselves to the nearest neighbors, and use the five pure  $d$  functions and a set of three high energy  $p$  functions which describe the charge transfer states, needed as intermediate levels for the second harmonic signal. The matrix elements are computed from the resonance integrals and the geometric considerations as described by Slater and Koster.<sup>19</sup> The resonance integrals scale as  $e^{-aR^{2/2}}$  like the two center overlap integrals  $S_{ij}$  and can be

calculated for each coefficient  $a$ . In the extreme case of  $S_{ij} = 0$  there is no interaction at all, and the  $d$  bands are completely flat. Giving a value of 0.0 eV for the  $t_g$  orbitals and 0.94 for the  $e_g$  ones, as calculated in our previous paper, and taking  $a=0.0134$  so that the system barely stays an insulator one gets after integration over the whole Brillouin zone the second order susceptibility tensor depicted in Fig. 15. This value for  $a$  is much smaller than the diffuse primitive Gaussian in both the LANL2DZ and the very large Roos<sup>20</sup> basis sets (0.836 and 0.0728 51, respectively). One notes that even in the case of an almost metallic system, the calculated tensor elements do not present any new features except a broadening of the peaks. Using the integrals from our LANL2DZ (Ref. 21) basis set, both the  $t_g$  and  $e_g$  bands undergo a broadening of less than  $5 \times 10^{-3}$  eV, which practically does not affect the tensor elements at all.

\*Electronic address: lefkidis@physik.uni-kl.de

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# Comparison of Hybrid Density Functional, Hartree–Fock, and GW Calculations on NiO

C. H. PATTERSON

*University of Florida, Quantum Theory Project, P. O. Box 118435, Gainesville, Florida 32611-8435*

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**ABSTRACT:** The electronic band structure of NiO in the ferromagnetic state is calculated using the B3LYP hybrid density functional, the Hartree–Fock (HF) method, and the GW approximation (GWA) with dielectric functions constructed using either B3LYP or HF wave functions and energy eigenvalues. The band structure from the GWA calculation based on B3LYP wave functions is quite similar to the parent B3LYP band structure; the main differences are in valence bandwidth and in the upward shift of the empty minority spin Ni 3d bands relative to the same bands in the B3LYP calculation. The band structure from the GWA calculation based on HF wave functions differs in that there are large upward shifts in valence band positions in the GWA calculation relative to the HF calculation, which result from screening of the bare exchange term in the Fock operator. Matrix elements of the HF exchange operator are obtained using wave functions from self-consistent HF or B3LYP calculations. Magnitudes of these matrix elements for several states at the  $\Gamma$  point of the Brillouin zone are compared, and it is found that the only major difference occurs in the empty minority spin bands derived from Ni 3d states of *e* symmetry. © 2006 Wiley Periodicals, Inc. *Int J Quantum Chem* 106: 3383–3386, 2006

**Key words:** B3LYP functional; GW approximation; nickel oxide; perturbation theory

## Introduction

Nickel oxide (NiO) is an anti-ferromagnetic transition metal oxide whose electronic structure has been studied using a wide range of theo-

retical techniques [1–9]. There have been a number of ab initio Hartree–Fock (HF) and density functional theory (DFT) studies of NiO. It is well known that these approaches over- or underestimate the bandgap to a large extent. In fact, the local spin density approximation (LSDA) to DFT predicts that NiO in a ferromagnetic (FM) state is metallic [3], while in the anti-ferromagnetic-II (AF-II) state it is predicted to have a small bandgap of 0.3 eV [8]; the bandgap for the AF-II state is observed to be  $\sim 4.3$

Correspondence to: C. H. Patterson; e-mail: Charles.Patterson@tcd.ie

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**TABLE I**  
**Matrix elements of the exchange operator for bands in NiO.**

$\alpha$ spin	B3LYP ( $x = 0.07$ )	B3LYP ( $x = 0.2$ )	HF ( $x = 1.0$ )
Ni e	47.1	47.6	49.1
Ni t	44.7	45.3	47.1
O 2p	27.8	27.6	27.1
CBM	11.7	11.5	10.4
$\beta$ spin			
Ni	42.3	42.8	44.1
O 2p	24.4	25.0	26.1
Ni	22.0	20.4	15.6
CBM	10.8	10.7	10.0

upward shift of the valence bands by  $\sim 4$  eV and some band narrowing.

To attempt to understand the differences in electronic structures predicted by B3LYP and HF calculations, matrix elements of the exchange contribution to the Fock operator were computed for the three principal types of state in the valence band at the  $\Gamma$  point and the strongly dispersive state at or near the conduction band minimum (CBM) (Table I).

When  $x = 0$ , NiO in the FM state is metallic, and the correct electronic configuration is not converged. Values of  $x = 0.07, 0.20$ , and  $1.00$  were used. For  $x = 0.07$ , the smallest difference between occupied and vacant levels is just  $0.4$  eV; for  $x = 1.00$ , a direct bandgap of  $15.0$  eV is obtained. There are only relatively small changes in magnitude of the matrix elements for occupied states (Table I), especially for the state with O  $2p$  character. The largest change is for the vacant Ni  $3d$  state with  $e$  symmetry where the magnitude changes from  $22.0$  to  $15.6$  eV on going from  $x = 0.07$  to  $1.0$ . The decrease in magnitude for empty states and increase for occupied states on going from  $x = 0.07$  to  $1.0$  suggest that occupied  $3d$  orbitals are somewhat more compact in HF, while empty  $3d$  orbitals are significantly more diffuse.

In summary, a B3LYP calculation on FM NiO results in an indirect bandgap of  $3.7$  eV, in reasonable agreement with the experimental value of  $4.3$

eV [10]. When a perturbative GWA calculation is performed using a B3LYP wave functions and energy eigenvalues the indirect bandgap increases to  $4.7$  eV. There is little shift in the positions of most bands, with the exception of the empty Ni  $3d$  minority spin bands, in contrast to GWA calculations using DFT [5] or HF wave functions. This is most likely because the exchange operator in the B3LYP calculation contains only a fraction ( $0.2$ ) of the full HF value, and this may be approximately the fraction that is unscreened in the GWA calculation. B3LYP wave functions may therefore present a superior starting point for perturbation theories in solids, especially when DFT or HF approaches fail.

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Review

# Transparent conductors as solar energy materials: A panoramic review

Claes G. Granqvist\*

*Department of Engineering Sciences, The Ångström Laboratory, Uppsala University, P.O. Box 534, SE-75121 Uppsala, Sweden*

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This Review is dedicated to the memory of Godfrey W. Mbise, whose research was instrumental for the development of angular selective transparent conductors discussed in Section 4.

## Abstract

Transparent conductors (TCs) have a multitude of applications for solar energy utilization and for energy savings, especially in buildings. The largest of these applications, in terms of area, make use of the fact that the TCs have low infrared emittance and hence can be used to improve the thermal properties of modern fenestration. Depending on whether the TCs are reflecting or not in the near infrared pertinent to solar irradiation, the TCs can serve in “solar control” or “low-emittance” windows. Other applications rely on the electrical conductivity of the TCs, which make them useful as current collectors in solar cells and for inserting and extracting electrical charge in electrochromic “smart windows” capable of combining energy efficiency and indoor comfort in buildings. This Review takes a “panoramic” view on TCs and discusses their properties from the perspective of the radiative properties in our ambience. This approach leads naturally to considerations of *spectral selectivity*, *angular selectivity*, and *temporal variability* of TCs, as covered in three subsequent sections. The spectrally selective materials are thin films based on metals (normally gold or titanium nitride) or wide band gap semiconductors with heavy doping (normally based on indium, tin, or zinc). Their applications to energy-efficient windows are covered in detail, experimentally as well as theoretically, and briefer discussions are given applications to solar cells and solar collectors. Photocatalytic properties and super-hydrophilicity are touched upon. Angular selective TCs, for which the angular properties are caused by inclined columnar nanostructures, are then covered. A discussion of TC-like materials with *thermochromic* and *electrochromic* properties follows in the final part. Detailed treatments are given for thermochromic materials based on vanadium dioxide and for electrochromic multi-layer structures (incorporating TCs as essential components). The reference list is extensive and aims at giving an easy entrance to the many varied aspects of TCs.

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**Keywords:** Transparent conductor; Thin film; Solar energy; Energy efficiency

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\*Tel.: +46 18 471 3067; fax: +46 18 500 131.

E-mail address: [claes-goran.granqvist@angstrom.uu.se](mailto:claes-goran.granqvist@angstrom.uu.se)

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