

MAGNETISM WITHIN THE LIMITATIONS OF THE LDA BAND STRUCTURE CALCULATIONS

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We discuss the limitations of the local density approximation for high-temperature superconductors and related to them parent antiferromagnetic insulators. The calculated band-gap accuracy is pointed out for two cases: C_{60} -FCC and $YBa_2Cu_3O_6$. We also compare the results for parent $CaCuO_2$ and NiO systems, as well as discuss the role of gradient and self-energy (GW) corrections for the Mott insulators.

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1. Introduction

The discovery of high- T_c superconductors [1] has generated research interest on an unprecedented scale. Thousands of papers have been published with many of them contradicting each other. After several years of intensive research we still do not know what is the mechanism leading to transition temperature far above those previously considered possible for superconductivity. Ironically, this new materials are so complex that even electronic structure of the normal state is not fully understood. The spin polarized version of band theory is not sufficiently accurate to predict the observed antiferromagnetic insulating state for undoped phases which are insulators (and not superconductors). There are several review articles [2] now available which discuss progress in electronic structure calculations. We will not discuss all those contributions but would like to focus on what are the major difficulties in this field.

In the present work we will focus on the limitations of the LDA (local density approximation) band structure calculations. One fundamental difficulty is that all electronic structure calculations are based on the one-electron approximation. This approximation works very well for metals but for nonmetals, where the screening is poor, one-electron excitation energies may be different than the spectrum obtained from one-electron calculations. In the calculations of the screening effect a plane-wave basis set is used (due to simple form of Coulomb's potential in this representation), which for d electrons of transition metals leads to large matrices and makes accurate calculations almost impossible. At present we believe that at

least for phases which are insulating some corrections beyond standard electronic calculations are necessary. The self-interaction corrections (SIC) have been applied to La_2CuO_4 and transition metal oxides and stable antiferromagnetic solution has been found with the band gap in agreement with experimental results [3]. The SIC are however not well defined in solids and therefore in the present work we will focus on another possible corrections to LDA, i.e. GW and gradient corrections.

2. The LMTO-ASA method

The linear muffin-tin orbital atomic-spheres approximation method [4] (LMTO-ASA) which is used widely for electronic structure calculations is in fact a first-principles tight-binding method. The assumption is that the whole space can be filled with overlapping Wigner-Seitz atomic spheres (ASA), so that the total unit cell volume is conserved. This leads to enormous simplifications, but for open structures, empty spheres are often used to improve the shape of the potential. Also, the so-called combined corrections are used to reduce the error of shape approximation [4]. Since we assume spherical shape of the potential, a minimal basis set can be used which means one orbital per lm quantum numbers. The Taylor expansion can be used for energy dependence and our basis functions have a simple form

$$\Phi(E, r) = \Phi(E_\nu, r) + (E - E_\nu)\Phi'(E_\nu, r). \quad (2.1)$$

By assuming that kinetic energy is zero at the atomic spheres boundaries, we can perform transformation to the basis sets in which our Hamiltonian factorizes into energy dependent part and structure part, energy independent. This structure dependent part, called structure constants, can be calculated only once in the iterative process shown in Fig. 1 and speeds up calculations enormously.

To initiate our calculations for solids, we use the atomic charge density as a starting point from which we calculate Hartree's part (V_c) of the potential using Poisson's equation. For the nonlocal part of the potential, also so-called exchange correlation potential (V_{xc}), we use local spin density functional (LSDF) description. According to LSDF approximation, V_{xc} is only dependent on the local density and can be calculated from the exchange correlation energy density of the homogeneous gas [5]. This approximation is formally justified if the electron density is slowly varying on the relevant length scale (the Fermi wavelength or the Thomas-Fermi screening length). Then we can write the Schrödinger equation in a matrix form using our basis set representation and the problem reduces to finding eigenvalues and eigenvectors as it is shown in Fig. 1. This is the part of the calculations where access to sufficient memory is essential. The required memory is proportional to the square of the number of atoms per unit cell multiplied by the number of basis functions. We reduce further requirements for memory by freezing the core and semicore electrons and relaxing only valence electrons (minimal basis set) with wave functions expanded up to $l = 2$ (d electrons). Then we can calculate the new charge density and perform iterations until self-consistency is obtained (Fig. 1). Calculations sometimes are slow to converge and the low mixing parameter (e.g. 1% of new charge density added to the old one as an

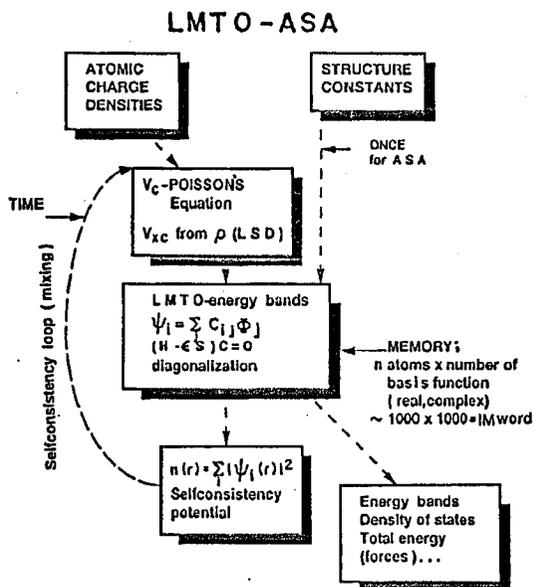


Fig. 1. The flow chart for the LMTO-ASA method.

input to new iteration) is necessary to use. The more sophisticated methods of mixing charge densities might be helpful and are called convergence accelerators [6]. Our calculations are self-consistent and include all quasi-relativistic effects except spin-orbit coupling [4]. The exchange-correlation energy is derived from the Von Barth-Hedin or the Vosko-Wilk-Nusair approximation [5].

The LMTO-ASA (linear muffin-tin orbital atomic-spheres approximation) method has been used successfully in explaining electronic and magnetic properties of metals and their alloys [4]. For example, the calculated moment in metallic nickel [7] was in agreement with experiment to within $0.01\mu_B$. It was also predicted that nickel loses magnetic moment during hydrogenation. For the new high- T_c oxides less approximate methods such as the high precision full-potential linearized augmented plane wave (FLAPW) method [8] should better reveal the details of the electronic and magnetic structure, but the important features in these compounds can be obtained by LMTO-ASA and similar methods with much less computer time required for the computations. The LMTO-ASA method is much faster than most other methods and thus permits the use of a larger number of “ k ” points in the Brillouin zone which is essential [9] for magnetic studies in these compounds.

3. LDA electronic structure calculations for C_{60} -FCC (Rb)

The discovery of the truncated-icosahedron structure of the C_{60} molecule [10] initialized a new area of research on these football-like molecules. Recently it has been found that this interesting molecule can form crystals and when doped these crystals become high-temperature superconductors [11].

We performed self-consistent first-principles electronic structure calculations using linear muffin-tin orbitals (LMTO's) in a tight-binding representation (TB) [12]. Since C_{60} -FCC has a very open structure (lattice constant equals 26.778 a.u. [11] while C-C bond lengths are: 2.702 a.u. for 5/6 edges and 2.646 a.u. for 6/6 edges [13]), it is very important to choose empty spheres properly. In our calculations [14] we chose a minimal number of spheres (76 atomic spheres). We chose one sphere ($r = 5.855$ a.u.) in the octahedral position where Rb is located in C_{60} Rb-FCC and two empty spheres ($r = 5.1$ a.u.) in tetrahedral position as well as one inside the C_{60} molecule ($r = 5.586$ a.u.). Additionally outside C_{60} molecules twelve empty spheres ($r = 2.6$ a.u.) were located in the middle between the pentagon and hexagon faces of nearest neighbor C_{60} molecules. The atomic sphere radii of carbon site were equal to 1.7 a.u. and we assumed that all carbon sites are equivalent. We included in our calculations s , p , and d electrons with downfolded [15] p and d electrons on empty spheres. The values of E_ν were chosen at the center of gravity of the respective occupied band. On carbon and rubidium atoms (an empty sphere in the octahedral site in C_{60} -FCC) only d electrons were downfolded. On the large sphere inside the C_{60} we downfolded all electrons. In Fig. 2

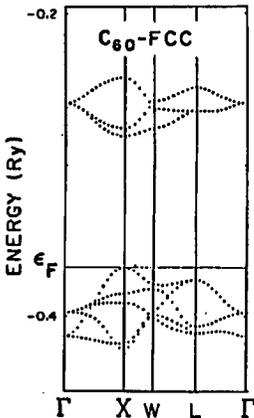


Fig. 2

Fig. 2. The band structure of C_{60} -FCC.

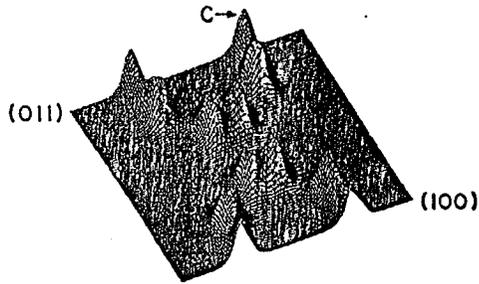


Fig. 3

Fig. 3. The charge density of pure C_{60} -FCC.

the LMTO-ASA band structure of C_{60} -FCC is presented for the region close to the Fermi energy. The degeneracy of h_u energy level is lifted and we have splitting of h_u band at Γ point. The unoccupied state t_{1u} is not split at Γ point. Our calculated energy gap [14] is smaller than obtained in earlier calculations [16] (1.5 eV) and is equal to 1.17 eV. This is due to the inclusion of d electrons hybridization which reduces the energy gap. If we do not include d orbitals contribution, the energy gap widens to 2 eV. It is worth to notice that in this case less accurate calculations are giving a better agreement with experimental value of band gap 3.5 eV [17] and therefore we cannot judge quality of calculations by their agree-

ment with experiment! More recent calculations [18] show a direct gap of 1.23 eV and, as it has been discussed earlier, these results are within 0.1 eV agreement with other more recent LCAO calculations and recent plane-wave pseudopotential calculations [18]. In Fig. 3 we show the charge densities for undoped C_{60} -FCC. The electron charge density is very inhomogeneous and localized on the surface of the sphere. We suggest that the sensitiveness to approximation is due to the inhomogeneity of electron charge density.

4. Electronic structure and magnetism of $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$

It is obvious that one-electron theory cannot tell so directly about possible mechanism of superconductivity, but it might answer to important questions such as what is the nature of carriers in this new material. Our first calculations [19] for $YBa_2Cu_3O_{6+x}$ were intended to solve this problem. It is interesting that as the oxygen content is varied from $YBa_2Cu_3O_{6.9}$ to $YBa_2Cu_3O_{6.24}$, the material changes from an orthorhombic superconductor to a tetragonal antiferromagnetic semiconductor [20]. In order to aid in our understanding of the new 90-K superconductors, we performed band structure calculations for both related compounds in order to identify the structural and electronic features responsible for the superconductivity. Since we cannot perform proper band structure calculations for these compounds without using supercells with hundreds of atoms, we made calculations in each case for the unit cell with the closest total number of oxygens to the actual concentration, i.e., $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$. An interesting comparison can be made by examining separately the d and p electrons contributions to the density of states as shown in Fig. 4. It is important that for $YBa_2Cu_3O_7$ there is a large contribution due to p electrons (top Fig. 4) around the Fermi energy in contrast to $YBa_2Cu_3O_6$ (bottom Fig. 4) where the d character of the electrons dominates Fig. 4. These results were the first theoretical calculations indicating that p character of the electrons around Fermi energy in superconducting phase is important.

We note that many of the models for high- T_c superconductivity which have appeared [21], involve a new mechanism for superconductivity based on magnetic interactions between the copper atoms.

Investigation of possible magnetic phenomena is complicated as it is now known that the local spin density functional approach does not account for spontaneous magnetic ordering in these compounds and spin-non-polarized calculations predict metallic properties for the related insulators [22]. It is important to mention that for these materials which have very nonuniform charge densities [2] (like FCC- C_{60}) the details of structure around the Fermi energy might be sensitive to approximations, such as the values of the atomic sphere radii (influences the Madelung energy contribution), E_ν value (changes the initial hybridization), etc. We find that, in the LMTO-ASA approximation, the initially chosen E_ν values for π electrons of yttrium can change the unoccupied band position by several eV. This is probably the reason why the position of the unoccupied bands in an earlier LMTO-ASA calculation [23] is much lower than in our LMTO-ASA and in highly precise FLAPW calculations [24]. In later work by these authors [25], the position

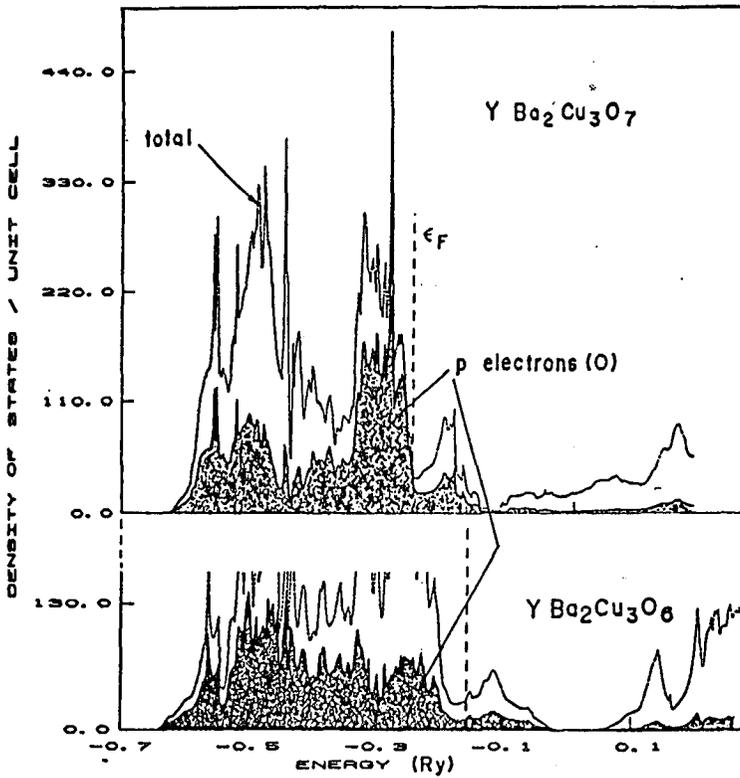


Fig. 4. The total and projected p electron density of states correspondingly in $\text{YBa}_2\text{Cu}_3\text{O}_7$ (top) and $\text{YBa}_2\text{Cu}_3\text{O}_6$ (bottom).

of the unoccupied bands above the $pd\sigma$ antibonding band agrees with our calculations. It is possible that too low position of the unoccupied bands might suppress the gap at the Fermi energy. Expansion about the center of the band (not as in the conventional way around the center of gravity of the band) should give for a half-filled band a better description around the Fermi energy than the expansion around the center of the occupied portion. In our unconventional LMTO-ASA band structure calculations [9] (with E_ν being at the center of the band) we had to assume a large value for E_ν for p electrons of Y($5p$) and Ba($6p$), and s electrons of O($3s$) to avoid ghost bands [4] in the minimal basis set approximation [4]. We also demonstrated that by performing forced antiferromagnetic ordering calculations for a half-filled band, an antiferromagnetic “Peierls-type gap” or as more commonly called the Slater gap [26] opens up at the Fermi energy due to the doubling of the unit cell. We called the gap a “Peierls gap” as the effect of meta-antiferromagnetic ordering on the electronic structure is analogous to the Peierls lattice distortion effect. As soon as the gap opens in the iterative process,

the density of states close to the gap boundary rises due to flattening of the bands, and the energy lowers. As a result the external splitting can be removed and the antiferromagnetic ordering becomes stable. Thus in this case the insulating state can be obtained in the LSD approximation provided an antiferromagnetic phase can be created.

The consequences of the sharpening of the density of states around the gap for superconductivity should be noted. The gap produced at the Fermi energy is small (≈ 0.1 eV) due to a low value of the local moment on the Cu₂ sites (in Cu-O₂ plane) ($\approx 0.3\mu_B$). Since we neglected spin-orbit interaction in our calculations, the absolute direction of the moment is not defined. We predict that as long as there is antiferromagnetic coupling between spins of copper atoms, the material stays insulating. By variation of the band filling due to doping, the Fermi energy is lowered and so, as soon as the metallic state is approached, the local magnetic moment disappears. This stabilization of the magnetic ordering due to the existence of the gap at the Fermi energy explains the strong sensitivity of the magnetic moment to doping which would not be true for spontaneous antiferromagnetism. In a way we are lucky that LSD approximation predicts metallic state in those compounds, since otherwise we would have to perform calculations for a large supercells (due to small doping in high- T_c superconductors) to destroy the magnetic ordering and to obtain the metallic state.

The electronic structure around the Fermi energy for high- T_c superconductors can be well described in the tight binding scheme with consideration of only p electrons of oxygen and d of copper. It has been demonstrated [27] in this model that the (110) nesting (required for stability of antiferromagnetic ordering) is only present when we neglect second neighbors interaction and when it is included, we have (100) and (010) nesting which is once obtained in band structure calculation for most high- T_c superconductors. Thus observed antiferromagnetic ordering cannot be obtained in tight binding scheme (*nota bene* equivalent to LMTO-ASA approximation) when parameterization from self-consistent LSDF calculation is used due to overestimation of overlapping parameters in this method. This indicates that the spontaneous antiferromagnetic ordering cannot be created by only increasing artificially the exchange correlation potential, but the corrections leading to the reduction of overlapping integrals are necessary as well.

The only way of creating antiferromagnetic ordering with the present parameterization of band is to create it by applying a large external antiferromagnetic fields. In our calculations we apply this field (0.05 Ry-0.1 Ry) to all atoms with the restriction that the sign of the field was opposite on nearest neighbor copper atoms. Hundreds of iterations (initially with small number of k points) were performed until gap opened up around the Fermi energy. Then external field was switched to zero and further iterations were performed with a large number of k points and low mixing of new (5%) and old charge density. In contrary to our earlier calculations [19], in spin polarized calculations we use empty spheres at oxygen vacancies (no orbitals were assumed in the empty spheres except from overlapping spheres). There is also evident analogy between our calculations and those previously performed for the metamagnetic [28] state in Pd. In both cases a large number of k points were needed in order to eliminate artificial fluctuations

at the Fermi energy. We used 108 k points in the irreducible wedge of the Brillouin zone.

At this point we would like to comment about the sensitivity of antiferromagnetic solutions to the number of k points employed. According to Guo and Temmerman [29] the moment for the antiferromagnetic solution in La_2CuO_4 decreases smoothly for increasing number of k points and the opposite behavior is found for La_2NiO_4 where the moment is present only for more than 105 k points [29]. We do not find for $\text{YBa}_2\text{Cu}_3\text{O}_6$ a smooth dependence of the value of the moment on the number of k points. The value varies quite randomly from higher to lower values for small numbers of k points and becomes relatively stable for 108 k points where for example there is essentially no difference ($< 0.01\mu_B$) between our calculations obtained with 108 and 135 k points. The magnetic moment for the antiferromagnetic solution is more sensitive to the number of k points than for the ferromagnetic solution. This is mainly due to interpolation errors for spin up and down electrons which in the antiferromagnetic case do not subtract as in the ferromagnetic case where the spin up and down electrons density of states are almost rigidly shifted and the detailed features of the density of states are not important.

5. Gradient corrections for the LSD exchange potential

In this section we will review our work [30] on gradient corrections. The local spin density functional (LSDF) method has been remarkably successful in describing fundamental properties of solids and molecules [31]. However, very early on it was pointed out [32] that for systems with inhomogeneous charge density some modifications might be necessary. Many different modifications have been proposed and tested on various systems [31]. We would like to focus on a relatively simple generalization of the LSDF method, namely the so-called gradient corrections [32–34] to the exchange or exchange–correlation energy. A number of gradient corrected energy have been proposed [35–38] in recent years; many of these for the exchange energy (E_{xg}) have been in polynomial form in order to have a relatively simple form for the gradient corrections to the exchange potential (V_{xg}) which is calculated as a functional derivative of E_{xg} :

$$V_{\text{xg}} = \frac{\delta E_{\text{xg}}}{\delta n}, \quad (5.1)$$

where n is the electron density.

The cost of this simplicity was the need for several fitting parameters [36, 37]. In the present work we calculate gradient corrections to V_{xg} from Becke's recently proposed formula [39]. His latest expression has been found to fit well the Hartree–Fock exchange energies of a number of atoms and to fulfil the exact asymptotic behavior of the exchange-energy density. However, as we will show later this proposed expression leads to a complicated formula for V_{xg} but has the advantage that it contains only one fitting parameter which seems to be independent of the atomic number Z [38]. On the other hand, it has the disadvantage that for large r , V_{xg} behaves as r^{-2} instead of the desired r^{-1} .

The functional derivative of E_{xg} can be rewritten as follows [39]:

$$\frac{\delta E_{\text{xg}}}{\delta n} = \frac{\partial E_{\text{xg}}}{\partial n} - \frac{\partial}{\partial x} \left(\frac{\partial E_{\text{xg}}}{\partial n_x} \right) - \frac{\partial}{\partial y} \left(\frac{\partial E_{\text{xg}}}{\partial n_y} \right) - \frac{\partial}{\partial z} \left(\frac{\partial E_{\text{xg}}}{\partial n_z} \right), \quad (5.2)$$

where $\partial n_x = \partial n / \partial x$, etc. For simplicity we shall either treat systems which are spherically symmetric (e.g. atoms with filled subshells so that the ground state is spherically symmetric) or make this approximation around atomic sites (atomic sphere approximation, ASA) and angularly average the electron densities in a similar manner. Many methods for electronic structure calculations in solids use the spherical, central field approximation (only r dependence) for the potential as for example in discussed in Sec. 2 the LMTO-ASA method [4]. Due to the r dependence of the spherically-averaged electron density, expression (5.2) for the functional derivative simplifies to

$$\frac{\delta E_{\text{xg}}}{\delta n} = \frac{\partial E_{\text{xg}}}{\partial n} - r^{-2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial E_{\text{xg}}}{\partial n_r} \right), \quad (5.3)$$

where $n_r = \partial n / \partial r$.

We assume that E_{xg} is only dependent on n_σ and x_σ where σ is a spin index and

$$x_\sigma = \text{abs}(g_\sigma) / n_\sigma^{4/3} \quad (5.4)$$

is a dimensionless variable and $g_\sigma = \partial n_\sigma / \partial r$. Then we obtain the following expression for the functional derivative:

$$V_{\text{xg}}^\sigma = \frac{\partial E_{\text{xg}}}{\partial n_\sigma} - x_\sigma \frac{\partial}{\partial n_\sigma} \left(\frac{\partial E_{\text{xg}}}{\partial x_\sigma} \right) + x_\sigma^2 \left(\frac{4}{3n_\sigma} - \frac{s_\sigma}{g_\sigma^2} \right) \frac{\partial^2 E_{\text{xg}}}{\partial x_\sigma^2} - \frac{2x_\sigma}{rg_\sigma} \frac{\partial E_{\text{xg}}}{\partial x_\sigma}, \quad (5.5)$$

where $s_\sigma = \partial g_\sigma / \partial r$. Then by substituting Becke's expression for E_{xg} [38]:

$$E_{\text{xg}} = -\beta \sum_\sigma \int d^3r n_\sigma^{4/3} \frac{x_\sigma^2}{1 + 6\beta x_\sigma \text{arcsinh}(x_\sigma)} \quad (5.6)$$

and performing the differentiation, we obtain an explicit expression for the gradient-corrected exchange potential corresponding to (5.6):

$$\begin{aligned} V_{\text{xg}}^\sigma = & (2/3)\beta x_\sigma^2 n_\sigma^{1/3} [-2g_\sigma^2(1+x_\sigma^2)^{3/2} + 12g_\sigma^2\beta x_\sigma \text{arcsinh}(x_\sigma)(1+x_\sigma^2)^{3/2} \\ & + 60g_\sigma^2\beta x_\sigma^2 + 48g_\sigma^2\beta x_\sigma^4 + 72g_\sigma^2\beta^2 x_\sigma^3 \text{arcsinh}(x_\sigma) - 144g_\sigma^2\beta^2 x_\sigma^4(1+x_\sigma^2)^{1/2} \\ & + 3s_\sigma n_\sigma(1+x_\sigma^2)^{3/2} - 54s_\sigma n_\sigma \beta x_\sigma^2 - 45s_\sigma n_\sigma \beta x_\sigma^4 \\ & - 108s_\sigma n_\sigma \beta^2 x_\sigma^3 \text{arcsinh}(x_\sigma) - 54s_\sigma n_\sigma \beta^2 x_\sigma^5 \text{arcsinh}(x_\sigma) \\ & + 108s_\sigma n_\sigma \beta^2 x_\sigma^4(1+x_\sigma^2)^{1/2}] / [g_\sigma^2(1+6\beta x_\sigma \text{arcsinh}(x_\sigma))^3(1+x_\sigma^2)^{3/2}] \\ & + 4\beta x_\sigma^2 r^{-1} n_\sigma^{4/3} [(1+x_\sigma^2)^{1/2} + 3\beta x_\sigma \text{arcsinh}(x_\sigma)(1+x_\sigma^2)^{1/2} \\ & - 3\beta x_\sigma^2] / [g_\sigma(1+6\beta x_\sigma \text{arcsinh}(x_\sigma))^2(1+x_\sigma^2)^{1/2}]. \end{aligned} \quad (5.7)$$

As one can see, the expression (5.7) is quite complicated, but has the advantage that the only unknown parameter is β and for many atoms $\beta = 0.0042$ a.u. [38] has been found to work well. This implies that β can be kept constant for all

atoms. In contrast to the energy density (5.6), this V_{xg} has a very complicated form and contains the second derivative of charge density (s_σ). The latter leads to inaccuracies at the boundary of atomic spheres. In addition, the formula (5.7) does not have the correct asymptotic inverse dependence on r as does the energy density (5.6) but rather r^{-2} .

Since in one-electron band structure calculations the primary quantity is the potential and not the energy density, we propose that the gradient correction of the potential should have a functional form similar to the energy density expression proposed by Becke while the energy contribution due to V_{xg}^σ is expressed in the following form:

$$\varepsilon_{\text{xg}}^\sigma = \int d^3r n_\sigma V_{\text{xg}}^\sigma. \quad (5.8)$$

Next, by comparing the asymptotic limits of the energy density (5.6) and the expression (5.7) for small x_σ and large r we introduce $2/3$ as the coefficient of proportionality in the expression for V_{xg}^σ :

$$V_{\text{xg}}^\sigma = -\frac{2}{3\gamma} \frac{n_\sigma^{1/3} x_\sigma^2}{1 + 6\gamma x_\sigma \operatorname{arcsinh}(x_\sigma)}. \quad (5.9)$$

The above potential has the same limit for slowly varying electron density as expression (5.7) and has the proper $1/r$ dependence at infinity.

The value of the constant γ in this expression may not be the same as Becke's β ($\beta = 0.0042$ a.u. [38]) and would need to be determined. In the numerical work below, we make the preliminary assumption that they are the same.

The value for β for infinite systems such as solids is an open question and could be determined by means of numerical calculations for a number of systems. However, the fitting of the gradient corrections for finite systems was performed in a semiempirical manner by adjusting β to the known Hartree–Fock solutions [38]. For solids the Hartree–Fock approximation does not work well, thus in practice gradient corrections must be introduced empirically. However, the use of the atomic values has the advantage in the calculations of dissociation and binding.

The recent calculations [40] of gradient corrections to the total energy of K, Ca, V, Fe, Cu show a promising improvement and in particular solved the problem of stability of bcc structure versus fcc structure where the LSD approximation had difficulties. However, the differences between energies for different crystal structures are very small and gradient corrections of the order of 10 meV might play a crucial role for stabilization. Unfortunately, they are not large enough [30] to influence the value of the magnetic moment on Ni in NiO (Fig. 5) or solve the problem of stabilization of the magnetic ordering in the semiconducting phases related to high- T_c superconductors, e.g. $\text{YBa}_2\text{Cu}_3\text{O}_6$ (Fig. 6) where the local charge density has been calculated using the LMT0-ASA method [4]. The calculated moment on nickel in NiO is one-half experimental value and in the first approximation an exchange potential twice as large would be needed to describe the moment correctly. After we completed our calculations we learned that the magnetic moment on iron has been calculated with several gradient correction schemes and in agreement with our conclusion the change in the moment was very small [41].

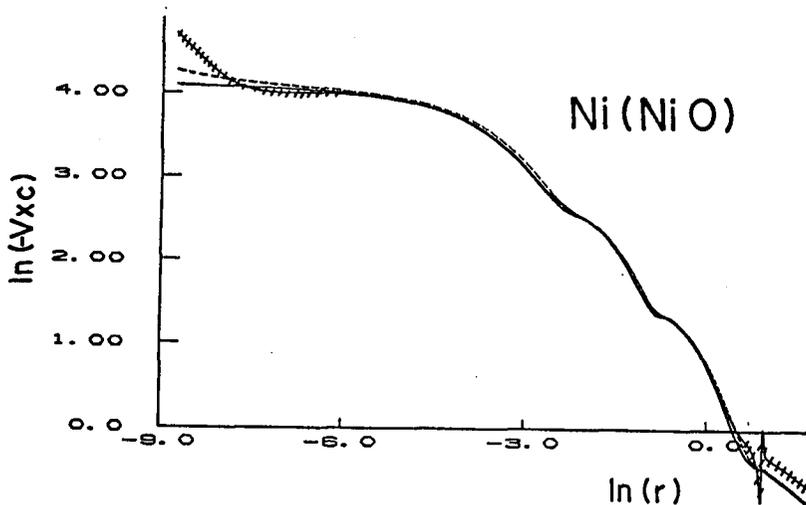


Fig. 5. The full line represents $\ln(-V_{xc})$ for Ni atoms in NiO. The broken line is the above corrected according to formula (5.9) and the hashed line represents the same with exchange correction according to formula (5.7).

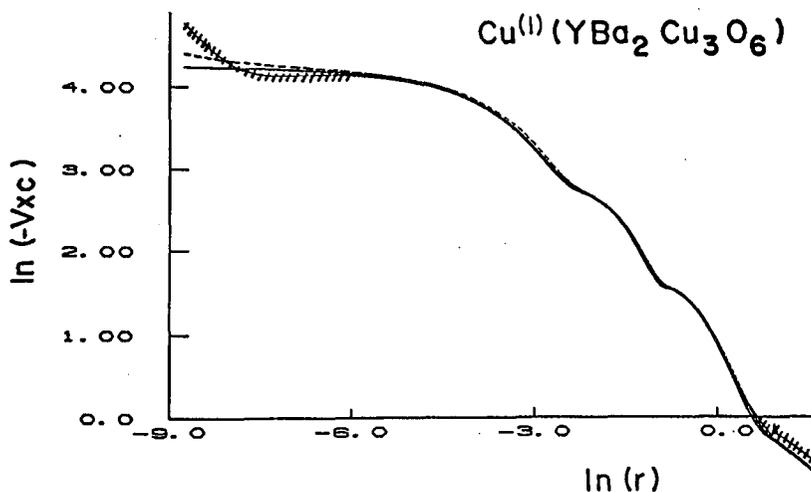


Fig. 6. The full line represents $\ln(-V_{xc})$ for the Cu(1) atoms (which are not in the Cu-O planes) in $\text{YBa}_2\text{Cu}_3\text{O}_6$. The broken line is the above corrected according to formula (5.9) and the hashed line represents the same with exchange correction according to formula (5.7).

In the present work we are mostly interested in magnetism and therefore we discussed only exchange gradient correction.

6. The Slater versus the Mott insulators

The discovery of new high- T_c superconductors has redirected attention to the class of materials called the Mott insulators [42], i.e. “magnetic insulators” in which (in contrary to the Slater insulators) local magnetic moments and the insulating nature of the state persist above the magnetic transition temperature [42]. Mott [42] argued that band structure calculations might not be applicable in systems where the on-site Coulomb energy is large in comparison to the bandwidth, i.e. unusually strong localization effects would favor a localized (cluster) description over an itinerant (band) description. One class of such materials are oxides of transition metals, known for 50 years as difficult to describe by band structure calculations, due to unusually strong correlation effects [42]. The methods used to calculate electronic structure have improved in recent years and band structure calculations have successfully shown that NiO and MnO are antiferromagnetic Slater insulators [43], albeit with too small band gaps.

In this work we discuss the difficulties of obtaining magnetic ordering within the one-electron approximation for copper and nickel perovskites [9, 22, 29]. We find that it is much easier to obtain magnetic ordering in compounds where copper is replaced by nickel, because d electrons of nickel have higher energy than d electrons of copper and p electrons of oxygen. La_2CuO_4 appears to be unstable in the antiferromagnetic phase unless a gap is forced around the Fermi energy [22, 29]. The calculated moment on copper sites is very low in this case ($0.136\mu_B$ [22b] or $0.16\mu_B$ [29]). The calculations [22a] for K_2CuF_4 show that magnetic ordering on copper-fluorine planes is possible but the calculated moment on copper is lower than that experimentally measured by a factor of two. At low temperatures La_2CuO_4 and La_2NiO_4 are similar with respect to both their crystal structure (tetragonal/orthorhombic) and their magnetic properties (antiferromagnetism). However, in high temperature paramagnetic state La_2NiO_4 becomes metallic [44] in contrast to La_2CuO_4 and indicates that these compounds are Slater’s and Mott’s insulators respectively, because the first becomes metallic at high temperature while the second stays insulating. As we demonstrated in our previous paper [45], antiferromagnetic ordering can be obtained easily in nickel perovskites. Two independent studies [29, 46] support our results while another one [47] claims that a scaling factor (1.5) in the potential is necessary in order to obtain stable antiferromagnetic ordering. Thus even for the Slater insulators there are discrepancies in the results due to the approximations used.

Another intriguing question is why NiO (a Mott insulator) should be so much different from La_2NiO_4 (a Slater insulator). The formal ionicity on Ni is the same in both compounds. One possible difference is the presence of the d band of La in La_2NiO_4 . The La d band is closer to the d -electron band of the weakly bound electrons of Ni [45] than to those of Cu, where the analogy between La_2CuO_4 and CuO is commonly accepted.

Although it was thought originally that the local spin density (LSD) functional method should be used only for materials with slowly varying electron densities [48], there is evidence that it is successful for many systems which do not obey this constraint. The new high- T_c materials are an example of inhomogeneous

TABLE

The Stoner parameter I and spin moment for d electrons on the transition metal in various compounds calculated with the LMTO-ASA method.

Compound	Stoner parameter I [Ry]	Spin moment/atom [μ_B]
(CuO ₂) ²⁻	0.076	0.61
YBa ₂ Cu ₃ O ₆	0.078	0.31 (meta-antiferro)
La ₂ NiO ₄	0.074	0.54
NiO	0.070	1.03

systems where a high charge density is found around the copper oxide planes which decrease rapidly with increasing distance from the planes.

In Table we summarize results of our LMTO-ASA calculations [49] for several cuprates and nickelates. There is no significant difference between the values of the Stoner parameter I for the Mott and the Slater insulators. The calculated gap is of the order of a tenth of an eV which is one order of magnitude too small for the Mott insulators and about right for the Slater insulators. Since the calculated gaps for semiconductors do not agree with experimental data unless self-energy corrections (e.g. in the GW approximation) are introduced [50], the possible role of such corrections for the Mott insulators requires investigation [50] and will be discussed in Sec. 7.

7. LDA versus HF electronic structure calculations

Recently suggestions have been made that self-interaction corrections (SIC) in the local density approximation (LDA) may significantly influence the computed electronic structure for high- T_c superconductors as well as other transition metal oxides [3]. Since SIC are naturally included in the Hartree-Fock (HF) method, studies have been carried out by comparing HF and LDA computations for NiO and CaCuO₂ (so-called parent of high-temperature superconductors) due to their relatively simple crystal structure [51]. We employed, described in Sec. 2, LMTO-ASA method in our LDA calculations [4]. In our HF calculations we used *ab initio* HF method with the Gaussian-type orbitals [52]. In HF approximation correlation is not included at all, while for the LDA, correlations effect for homogeneous electron gas is included exactly. However, very inhomogeneous charge distribution in principle invalidates the approximations which are made.

In Fig. 7 we present the electron charge density for NiO calculated within the LDA LMTO-ASA approximation. High charge density of d electrons on nickel atoms is visible. These are also electrons which contribute mostly to the magnetic moment on nickel. There is no problem to obtain stable antiferromagnetic ordering in NiO within LSDF method, but as mentioned already the moment is too small ($1\mu_B$). When we reduced lattice constant as shown in Fig. 8, the moment was reduced even further due to the delocalization of d electrons. In practice, this

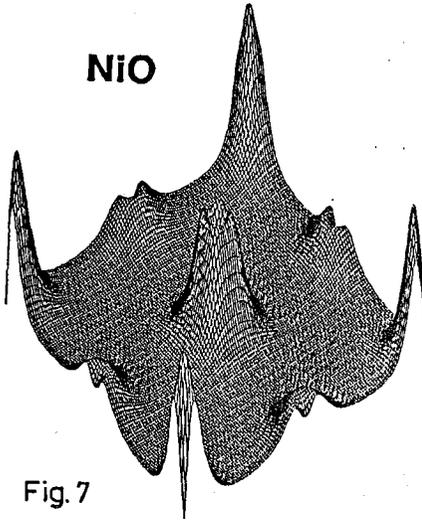


Fig. 7

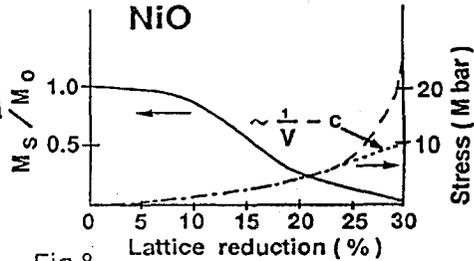


Fig.8

Fig. 7. The charge density of NiO.

Fig. 8. The stress dependence of the magnetic moment of nickel and the lattice constant in NiO compound.

effect can be observed by applying large pressure as indicated in Fig. 8. It would be interesting to compare those results with spin polarized IIF but at the moment we can only compare spin-non-polarized IIF and LDA calculations.

In Figs. 9 and 10 we present spin-non-polarized band structure calculations for NiO and CaCuO_2 . The overall shape of bands is similar in both methods of calculations but the bandwidths are different by a factor of two and for example the bandwidths of antibonding bands crossing the Fermi energy are correspondingly for NiO 6.8/2.7 eV and for CaCuO_2 10.8/4.1 eV. It is well known that using the HF method (due to the non-local exchange term), the calculated band structure for metals, where screening is very important, is about twice as wide as that determined from experiment. On the other hand, in LDA, SIC are not properly included and might lead to the relative shift of bands with different localization. The most significant difference between the HF results and the LDA results is that it gives a larger splitting between bands which have different localization levels as for example the $d-t_{2g}$ and $d-e_g$ bands in NiO. As a result of it the lowest energy band in NiO using HF calculations is $d-t_{2g}$ while from LDA calculations it is a p band.

It was suggested [43] that the use of the spherical potential approximation might be a cause of the underestimation of the magnetic moment but full potential linearized augmented plane wave (FLAPW) method calculations [53] discussed herein indicate that the moment on nickel is about the same ($1.03\mu_B$) as in previous calculations [43] and the band gap (0.02 Ry) is one order of magnitude smaller than obtained in experiment.

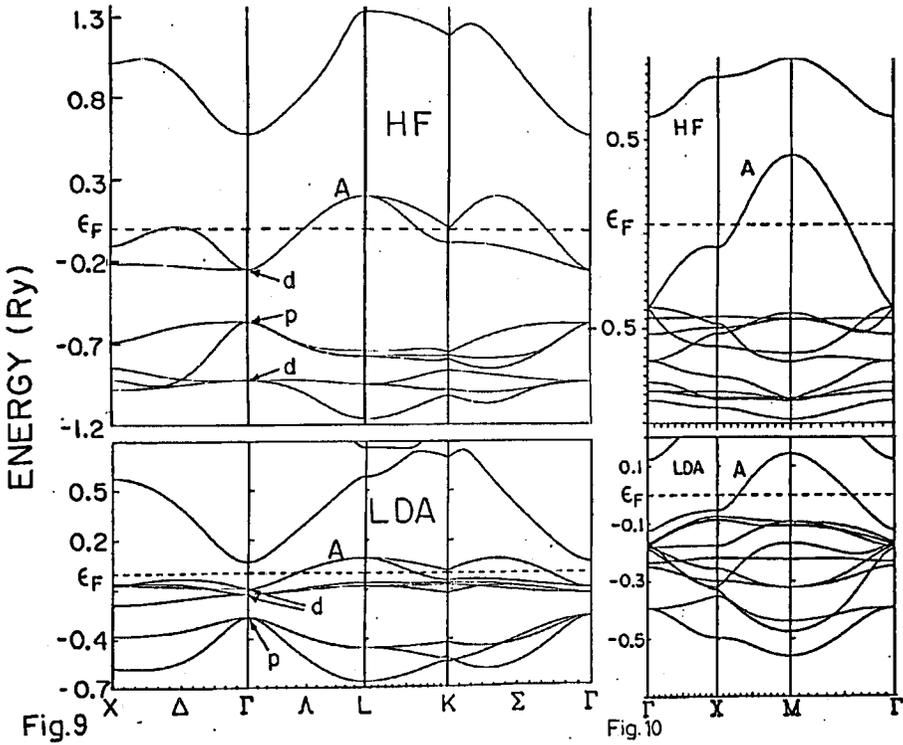


Fig. 9. Band structures of NiO in paramagnetic state calculated with both HF and LDA methods.

Fig. 10. Band structures of CaCuO₂ in paramagnetic state calculated with both HF and LDA methods.

In Fig. 11 we compare spin-non-polarized LDA and Hartree-Fock (HF) results [52, 53] for NiO, with spin-polarized LDA calculations with and without aspherical effect. In the Γ -Z direction for NiO we present at the left, paramagnetic Hartree-Fock and LDA — linear muffin-tin orbital atomic-spheres approximation (LMTO-ASA) results and on the right, spin-polarized TB-LMTO-ASA and FLAPW spin-polarized calculations are shown where the opening of the gap due to antiferromagnetic ordering is observed. In the paramagnetic plots, we represented with broken lines the image of the bands in the reduced Brillouin zone scheme for the antiferromagnetic state so as to make easier the comparison between the spin-polarized and the spin-non-polarized calculations. It is worth noting that the LSD approximation provides an insulating state for systems such as NiO, which in this case is an antiferromagnetic band insulator [43]. However, the calculated moment is about twice smaller and the band gap is an order of magnitude smaller than the corresponding experimental values.

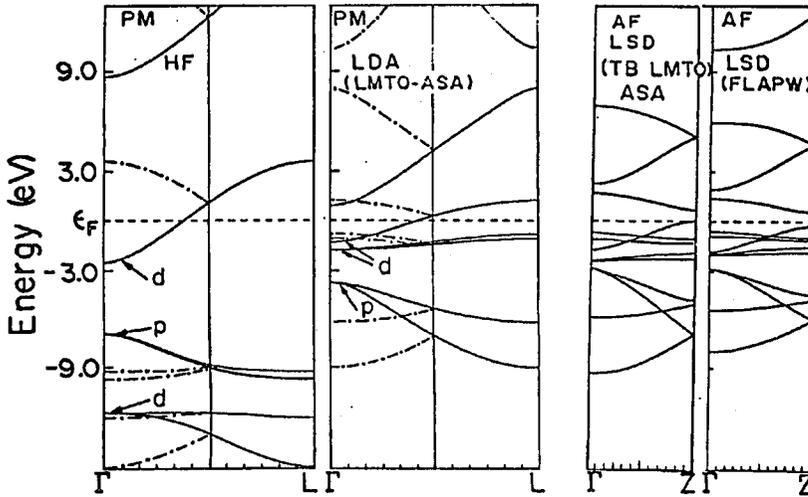


Fig. 11. The band structure for NiO in the z direction starting from the left as indicated: paramagnetic HF, paramagnetic LMTO-ASA LSDF, spin-polarized TB-LMTO-ASA and spin-polarized FLAPW LSDF calculations.

We conclude that the correlation effect included in the LDA approximation leads to substantial narrowing of the bandwidth (factor of two) but there are other corrections as for example SIC or GW which might be significant for understanding electronic structure of transition metals oxides and high-temperature superconductors.

8. Self-energy corrections within GW approximation

It is well known that for insulators and semiconductors the LSD functional method underestimates the insulating gap [54]. It is believed that the LSD approximation describes ground state properties well but fails to describe properly experimental gaps where quasiparticle excitations should be taken into account [54]. One of the differences between metals and insulators [55] is that for metals the electron affinity and the ionization potential are the same and equal to the chemical potential $\mu = \partial E / \partial N$, where E is the total system energy and N is the total number of electrons. For nonmetals the energy difference between the electron affinity and the ionization potential is nonzero [56]. The density functional theory (DFT) band gap (the difference between the lowest unoccupied and the highest occupied orbital energies of the N electron system) is not necessarily the same as a quasiparticle gap between an excited state of $N + 1$ electrons and the ground state of N electrons. In fact, it differs by the discontinuity in the exchange-correlation potential when one electron is added. We consider this point further in our report on the so-called GW corrections within the LSD approximation [56]. Although the GW formalism [56] has been known for a long time, it has not been used previously for transition metal oxides due to large-scale computer requirements [53].

Since the present GW correction calculations are based on the formalism described previously for paramagnetic materials [57], only the most important features and approximations will be noted here [53].

8.1. Dielectric matrix

The microscopic screening effect which results in a reduced effective Coulomb interaction between electrons is fully described by the dielectric matrix. To calculate this matrix, it is convenient to use plane waves due to the simplicity of the Coulomb potential in this representation

$$v_{G,G'}(q+G) = 4\pi|q+G|^{-2}\delta_{G,G'}, \quad (8.1)$$

where G and G' are vectors in reciprocal space, q is a vector in the first Brillouin zone and $\delta_{G,G'}$ is the Kronecker delta. The number of vectors needed in reciprocal space is dependent on the degree of localization of the electron wave functions, e.g. more points are required for the more localized d electrons than for the more extended p electrons. An alternative procedure has been proposed recently for localized basis sets [58].

The dielectric function is calculated in the random phase approximation: $\xi = 1 - vP$, where P is the bare polarizability to be calculated with the use of the eigenstates and eigenenergies generated by the band structure calculations with the FLAPW method [8] within the LDA. For convenience in numerical calculations, the quantity $u(q+G) = [v(q+G)]^{1/2}$ is introduced. Then, the dielectric function is represented by the Hermitian matrix

$$\begin{aligned} \varepsilon_{GG'}(q, \omega) = & \delta_{GG'} + u(q+G) \sum_{v,c,k,\sigma} \langle v, k, \sigma | e^{-i(q+G)r} | c, k+q, \sigma \rangle \\ & \times \langle c, k+q, \sigma | e^{-i(q+G')r} | v, k, \sigma \rangle \frac{u(q+G')}{E_{c,k+q,\sigma} - E_{v,k,\sigma} - \omega - i0^+}, \end{aligned} \quad (8.2)$$

where the c and v indices correspond to the conduction band (zero occupation) and valence band (full occupation) respectively, σ is a spin index and E represents the corresponding eigenvalues calculated within the FLAPW method ($\hbar \equiv 1$). The number of eigenvalues used was limited to forty, since it has been shown [57] that the error introduced should not exceed a few percent. Since these calculations are very extensive, further approximations are needed. First, the above formula is used only to calculate the static dielectric matrix $\varepsilon_{GG'}(q, \omega = 0)$.

To calculate the dynamical dielectric matrix ($\omega \neq 0$ and real) a generalized plasmon-pole model is used [57]:

$$1/\varepsilon_i(q, \omega) = 1 + C_i(q)/(\omega - \omega_i(q) + i0^+) - C_i(q)/(\omega + \omega_i(q) + i0^+), \quad (8.3)$$

where $\varepsilon(q, \omega)$ is the i -th eigenvalue of the dynamical dielectric matrix, and $\omega_i(q)$ is found from the required static limit, i.e. $\varepsilon_i(q, \omega) \rightarrow \varepsilon_i(q, 0)$ when $\omega \rightarrow 0$. The requirement of the proper high frequency limit leads to the expression [8] $\omega_p^2/2\text{Re}\omega_i(q)$ for $C_i(q)$ where the plasma frequency $\omega_p^2 = 4\pi n$ for the uniform valence electron density (n). Since electrons in NiO behave quite differently from a free-electron gas, the calculations were tested by assuming two different plasma frequencies, one with all-valence electron contributions and one with only d electron contributions taken into account. There was no much effect on the final value

of GW corrections due to the choice of the plasma frequency and in the following we present results with the plasma frequency corresponding to the all-valence electron contributions.

The next approximation is to calculate the full dynamical dielectric matrix from the above eigenvalues using eigenvectors ($U_{Gi}(q)$) of the static dielectric matrix. This means that the off-diagonal elements will not be correct for higher frequencies but for calculations of the self-energy the most important contribution comes from $\omega < \omega_p$ [57].

We applied at this stage a correction where all conduction bands are shifted by a constant amount in order to correct the LSD gap. Without doing this the calculated dielectric constant would be much too large (40). The experimental dielectric constant is 5.4 [59]. When using a gap shift (0.24 Ry) corresponding to the experimental value of the gap the dielectric constant equals 12. A larger gap shift (0.40 Ry) results in a better value of the dielectric constant: 8.7.

8.2. GW approximation

The next task is to calculate the corrections to the LSD gap. To do this, the self-energy, calculated by including the first diagram of the expansion in terms of the screened Coulomb operator (W), is of the following form ($\delta \equiv 0^+$):

$$\Sigma(r, r'; \omega) = (i/4\pi) \int_{-\infty}^{\infty} d\omega' e^{i\omega'\delta} G(r, r'; \omega - \omega') W(r, r'; \omega'), \quad (8.4)$$

where the Green function is calculated using the FLAPW eigenvalues and eigenvectors;

$$G(r, r'; \omega) = \sum_{n, k\sigma} \frac{\phi_{nk\sigma}(r) \phi_{nk\sigma}^*(r')}{\omega - E_{nk\sigma} + i\delta_{nk\sigma}}. \quad (8.5)$$

$\delta_{nk\sigma}$ is 0^- for valence band energies and 0^+ for conduction band energies. The screened Coulomb interaction W is

$$W(r, r'; \omega') = \sum_{q, G, G'} e^{i(q+G)r} \varepsilon_{GG'}^{-1}(q, \omega') v(q+G) e^{-i(q+G')r'}. \quad (8.6)$$

After substituting (8.5) and (8.6) into (8.4) the real part of the self-energy can be written as

$$\text{Re}\Sigma = \Sigma_{\text{SEX}} + \Sigma_{\text{COH}}, \quad (8.7)$$

where the notation due to Hedin [56] is used. The first part comes from the poles of the Green function and the second part, the so-called Coulomb hole part, arises from the poles of the screened interaction.

If enough G points are used and the same approximations are made in the calculation of the LSD exchange-correlation potential and the self-energy, the self-energy corrections (SEC) should be calculated as

$$\Delta_{nk\sigma} = \Sigma_{nk\sigma}(E_{nk\sigma}) - V_{nk\sigma}^{\text{xc}}, \quad (8.8)$$

where $\Sigma_{nk\sigma}(E_{nk\sigma}) \equiv \langle nk\sigma | \Sigma(E_{nk\sigma}) | nk\sigma \rangle$ and $V_{nk\sigma}^{\text{xc}} \equiv \langle nk\sigma | V^{\text{xc}}(\rho(r)) | nk\sigma \rangle$. Since we use only 111 G points and a very crude approximation for the self-energy, we will make use of the fact that the exchange-correlation energy within the LSD

approximation is equal to the self-energy calculated at the Fermi energy [60]. In this way, the corrections can be calculated more accurately [61] as

$$\Delta_{nk\sigma} = \Sigma_{nk\sigma}(E_{nk\sigma}) - \Sigma_{nk\sigma}(E_{n_F k_F \sigma}). \quad (8.9)$$

To simplify the calculations, we used for the second term in expression (8.9) the self-energy of the valence band which lies closest to the Fermi energy. This approximation is probably not bad for d electrons which have energies close to the Fermi energy. For p electrons it means just adding (renormalized by a constant value) the self-energy onto the LSD exchange–correlation energy. In Fig. 12, the d bands calculated with and without corrections are presented. A significant gap increase can be seen in Fig. 12b.

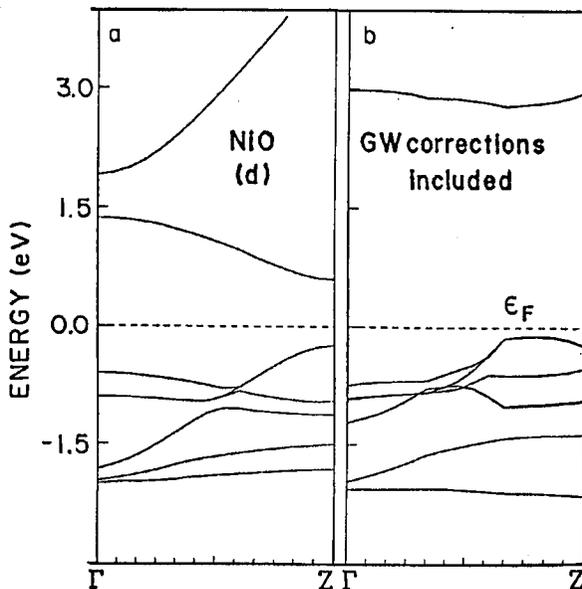


Fig. 12. d -electron FLAPW bands for antiferromagnetic NiO in z direction; (a) without and (b) with GW corrections.

Due to the extensive computer requirements of this method for d electrons, the calculations of SEC were restricted to only four k points for each band, 40 eigenstates and eigenvalues generated by the FLAPW method and 111 points in reciprocal space. The SEC corrections are not very sensitive to the plasma frequency values used in the plasmon-pole model. It is important to use the same model for both the self-energy and exchange–correlation potential so that the accumulated error cancels in the calculation of SEC.

These preliminary results are very encouraging. The next question is how to explain that the LSDF calculations underestimate the value of the magnetic moment on the transition metal in oxides which is obviously ground state property. The answer to this problem was proposed recently [62] by the introduction of the so-called unoccupied states potential correction (USPC). It has been shown that by

shifting unoccupied states to higher energies (the effect similar to GW corrections) hybridization is changed and as a result of it the significant increase in the value of the calculated magnetic moment has been found.

9. Summary

We were trying to demonstrate that the new, high- T_c superconductors and related materials challenged the researchers working on LDA electronic structure calculations. Even though LSDF method showed the important features of these materials like the anisotropic two-dimensional character, the importance of p electrons of oxygen and d electrons of copper, more sophisticated calculations are necessary. There is an indication that SIC, USPC and self-energy corrections might be a possible improvement but this requires elaborated computer calculations. Also, the problem of calculations beyond idealized crystal structure remains to be addressed.

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