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Density-functional theory and NiO photoemission spectra

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The generalization of the local-density-approximation method for the systems with strong Coulomb correlations is proposed, which restores the discontinuity in the one-electron potential as in the exact density functional. The method is based on the model-Hamiltonian approach and allows us to take into account the nonsphericity of the Coulomb and exchange interactions. The calculation scheme could be regarded as a first-principle method due to the absence of adjustable parameters. The method was applied to the calculation of the photoemission (x-ray photoemission spectroscopy) and bremsstrahlung isochromat spectra of NiO.

What is the main problem in applying the local-density approximation (LDA) to the systems with localized electrons? Perdew *et al.*[1] considered the problem of a free single atom in a reservoir with which it could exchange electrons (open system). They showed that in this case the *exact* density functional (although still unknown) results in a dependence of the total energy on the number of electrons $E(N)$ as a series of straight-line segments:

$$E(N+x)=(1-x)E_N+xE_{N+1}\ , \tag{1}$$

where E_N and E_{N+1} are ground-state energies for the N and $N+1$ electrons. The curve itself is continuous, but its derivative $\partial E/\partial N$ has discontinuities at integral values of N:

$$\partial E/\partial N=\begin{cases}E(M)-E(M-1), & M-1<N<M\\ E(M+1)-E(M), & M<N<M+1\end{cases} \tag{2}$$

(M is an integer value). The same is true for the one-electron potential $V(\mathbf{r})=\delta E/\delta n(\mathbf{r})$, which should jump discontinuously when the number of electrons goes through an integer value.

All actual calculations for real systems are performed in the LDA, where the function E versus N and all its derivatives are continuous. The absence of the potential jump, which appears for the *exact* density functional, is the reason for LDA failure in describing the band gap of Mott insulators such as transition metal and rare-earth compounds. Gunnarsson and Schonhammer[2] showed that the discontinuity in the one-electron potential can give a large contribution to the band gap.

In Ref. 3 we suggested a way to overcome this deficiency of the LDA by adding an orbital-dependent correction to LDA potentials (the so-called LDA+U method). LDA equations themselves are constructed as a mean-field [Hartree-Fock (HF)] theory and they could be modified to take into account an on-site Coulomb interaction U. One can look at the LDA as an analog of a homogeneous solution of the HF equations. This means that the LDA gives the correct solution of the HF equations when variational freedom is restricted by the requirement that the occupancies of all d orbitals are equal (averaged): $n_{m\sigma}=n_0=\sum_{m\sigma}n_{m\sigma}/10$. (The output orbital occupancies can be different in LDA calculations due to the crystal field splitting, but as the potential in the LDA is a functional of the charge density, which is defined by the total or averaged per orbital number of d electrons, and this potential is the same for all d orbitals, then the HF analog of the LDA should have equal orbital occupancies.) Then the variational space can be extended by adding to the LDA functional a correction corresponding to the deviation of the orbital occupancies $n_{m\sigma}$ from the average on n_0:

$$E=E_{\mathrm{LDA}}+\tfrac{1}{2}\sum_{m,m',\sigma}U(n_{m\sigma}-n_0)(n_{m'-\sigma}-n_0)+\tfrac{1}{2}\sum_{m\neq m',\sigma}(U-J)(n_{m\sigma}-n_0)(n_{m'\sigma}-n_0)\ , \tag{3}$$

where J is the exchange parameter. The one-electron potentials $V_{m\sigma}$ are orbital dependent in this approximation:

$$V_{m\sigma}=V_{\mathrm{LDA}}+\sum_{m'}U(n_{m'-\sigma}-n_0)+\sum_{m\neq m'}(U-J)(n_{m'\sigma}-n_0)\ . \tag{4}$$

With this orbital-dependent LDA+U potential orbital polarization becomes possible and the Mott-Hubbard gap appears in the single-particle spectrum. We showed that this method is rather successful in the description of the electronic structure of a variety of $3d$ transition metals compounds, yielding order-of-magnitude improvements on conventional LDA results.[3,4]

The above scheme is based on the suggestion that the LDA corresponds to the homogeneous solution of the HF equations with equal (averaged) occupancy of all d orbitals. But is it the best way to set the relationship between the LDA and a model Hamiltonian approach? If one follows the arguments of Perdew *et al.*[1] then one can see that the main difference between the LDA and the *ex-*

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act density functional is that in the latter the potential must jump discontinuously as N increases through integer values and in the former the potential is a continuous function of the number of electrons N. The second important fact is that while LDA orbital energies [which are derivatives of the total energy on orbital occupation numbers n_i ($\epsilon_i=\partial E/\partial n_i$)] are often in rather bad agreement with experiment or more rigorous calculations, the LDA total energy is usually quite good (this is demonstrated by the LDA success to give correct crystal structure and equilibrium volume and even the properties defined by the second derivative of total energy such as phonon frequency[5]). A good example is a hydrogen atom where the LDA orbital energy is -0.54 Ry (instead of -1.0 Ry) but the total energy (-0.96 Ry) is quite close to -1.0 Ry.[6] The main idea of our LDA+U method is the same as the Anderson impurity model:[7] to separate electrons into two subsystems—localized d or f electrons for which the Coulomb d-d interaction should be taken into account by a term $\frac{1}{2}U\sum_{i\neq j}n_in_j$ in a model Hamiltonian and delocalized s and p electrons which could be described by using an orbital-independent one-electron potential (LDA). Let us consider a d ion as an open system with a fluctuating number of d electrons. The above arguments allow us to suggest that the Coulomb energy of d-d interactions as a function of the number of d electrons N given by the LDA is a good approximation [but not the orbital energies (eigenvalues)]. The correct formula for this energy should be $E=UN(N-1)/2$. If we subtract this expression from the LDA total energy functional and add a Hubbard-like term (neglecting for a while exchange and nonsphericity) we will have the following functional:

$$E=E_{\mathrm{LDA}}-UN(N-1)/2+\frac{1}{2}U\sum_{i\neq j}n_in_j \; . \tag{5}$$

The orbital energies ϵ_i are derivatives of (5) on orbital occupations n_i:

$$\epsilon_i=\partial E/\partial n_i=\epsilon_{\mathrm{LDA}}+U(\tfrac{1}{2}-n_i) \; . \tag{6}$$

This simple formula gives the shift of the LDA orbital energy $-U/2$ for occupied orbitals ($n_i=1$) and $+U/2$ for unoccupied orbitals ($n_i=0$). A similar formula is found for the orbital-dependent potential [$V_i(\mathbf{r})=\delta E/\delta n_i(\mathbf{r})$ where variation is taken not on the total charge density $n(\mathbf{r})$ but on the charge density of a particular ith orbital $n_i(\mathbf{r})$]:

$$V_i(\mathbf{r})=V_{\mathrm{LDA}}(\mathbf{r})+U(\tfrac{1}{2}-n_i) \; . \tag{7}$$

Expression (7) restores the discontinuous behavior of the one-electron potential of the *exact* density-functional theory. In Ref. 1 it was shown that the maximum occupied Kohn-Sham orbital energy $\epsilon_{\max}$ jumps by $[E(N+1)-E(N)]-[E(N)-E(N-1)]$ (which is equal to the Coulomb parameter U by definition, if one neglects the hybridization[8,9]) when the number of electrons changes from $N-\delta$ to $N+\delta$. From (6) one can see that if for N electrons the ith orbital is occupied and the jth orbital is empty, then $\epsilon_{\max}=\epsilon_i$ for the $N-\delta$ case and $\epsilon_{\max}=\epsilon_j$ for $N+\delta$. As $(\epsilon_j-\epsilon_i)=U$ expression (6) reproduces this jump. Again we could look at a hydrogen atom H. In this case $U=0.945$ Ry and $\epsilon_{\mathrm{LDA}}=-0.54$ Ry.[6] If we consider the "spin-up" orbital to be occupied ($n_\uparrow=1$) and the "spin-down" orbital to be empty ($n_\downarrow=0$), then $\epsilon_\uparrow=-1.0125$ Ry and $\epsilon_\downarrow-0.0675$ Ry. It looks quite reasonable. The ionization potential for H is exactly 1 Ry and the electron affinity is -0.055 Ry.

Expression (6) could remind us of the "transition state" approximation of Slater.[10] Slater showed that the excitation energy defined as a difference of total energies in the final and initial states [for example, the removal energy $E(N-1)-E(N)$] could be approximated with good accuracy by LDA orbital energies (one-electron eigenvalues), calculated not in the ground state but in the so-called transition state with occupancies halfway between the final and initial states. For the removal energy it means $\epsilon(N-\frac{1}{2})$ and for additional energy $\epsilon(N+\frac{1}{2})$. If we suggested that the LDA gives the d-d interaction energy in a form $UN(N-1)/2$, then the derivative of ϵ over N is equal to U and $\epsilon(N-\frac{1}{2})=\epsilon(N)-U/2, \epsilon(N+\frac{1}{2})=\epsilon(N)+U/2$. Comparing this with expression (6) one can see that our corrected orbital energies for occupied orbitals correspond to the removal energies in the transition state approximation and orbital energies for unoccupied orbitals correspond to the addition energies.

The functional (5) neglects exchange and nonsphericity of the Coulomb d-d interaction. If we take into account exchange, then for electrons with the same spin projection σ, the interaction energy will be $(U-J)$, and with different spin it is still U:

$$E=\tfrac{1}{2}U\sum_{m,m',\sigma}n_{m\sigma}n_{m'-\sigma}+\tfrac{1}{2}(U-J)\sum_{m\neq m',m',\sigma}n_{m\sigma}n_{m'\sigma} \; . \tag{8}$$

In the LDA exchange is partially taken into account in such a way that the number of electrons with different spin projection are equal ($N_\uparrow=N_\downarrow, N=N_\uparrow+N_\downarrow$). That leads to the following expression for the LDA Coulomb energy of d-d interactions as a function of total number of d electrons N:

$$UN(N-1)/2-JN(N-2)/4 \; .$$

Finally we could taken into account nonsphericity of the Coulomb and exchange interactions, i.e., dependence on what particular d orbitals m and m' are occupied by introducing matrices $U_{mm'}$ and $J_{mm'}$:

$$U_{mm'}=\sum_k a_kF^k \; , \tag{9}$$

$$J_{mm'}=\sum_k b_kF^k \; , \tag{10}$$

$$a_k=\frac{4\pi}{2k+1}\sum_{q=-k}^{k}\langle lm|Y_{kq}|lm\rangle\langle lm'|Y_{kq}^*|lm'\rangle \; , \tag{11}$$

$$b_k=\frac{4\pi}{2k+1}\sum_{q=-k}^{k}|\langle lm|Y_{kq}|lm'\rangle|^2 \; . \tag{12}$$

(F^k are Slater integrals and $\langle lm|Y_{kq}|lm'\rangle$ are integrals over products of three spherical harmonics Y_{lm}.) Note that the off-diagonal Coulomb and exchange matrix elements cannot be treated in this way, i.e., $\langle mm'|1/r_{12}|m''m'''\rangle$. These types of terms, which are very important in atomic multiplet theory, are still neglected. To take this into account we would have to abandon the concept of an orbital energy and also the use of a single Slater determinant to describe the states of the system. The same type of problem occurs in treating only the z component of the spin and thereby neglecting terms such as $JS_1^+S_2^-$, which again are so important in multiplet theory. We remind the reader that two electrons in different orbitals with an exchange interaction JS_1S_2 form a triplet and a singlet with an energy splitting of J whereas if we consider only the z component of this spin $JS_{1z}S_{2z}$ the splitting between ferromagnetic and antiferromagnetic configurations is $J/2$. This stresses the importance of the spin-flip terms which cannot be incorporated into a single-particle potential.

We can now write the total energy functional in the form

$$E=E_{\text{LDA}}-[UN(N-1)/2-JN(N-2)/4] +\tfrac{1}{2}\sum_{m,m',\sigma} U_{mm'}n_{m\sigma}n_{m'-\sigma} +\tfrac{1}{2}\sum_{m\neq m',m',\sigma}(U_{mm'}-J_{mm'})n_{m\sigma}n_{m'\sigma}\ . \tag{13}$$

The derivative of (13) over orbital occupancy $n_{m\sigma}$ gives us the expression for the orbital-dependent one-electron potential:

$$V_{m\sigma}(\mathbf{r})=V_{\text{LDA}}(\mathbf{r})+\sum_{m'}(U_{mm'}-U_{\text{eff}})n_{m-\sigma} +\sum_{m'\neq m}(U_{mm'}-J_{mm'}-U_{\text{eff}})n_{m\sigma} +U_{\text{eff}}(\tfrac{1}{2}-n_{m\sigma})-\tfrac{1}{4}J\ , \tag{14}$$

where $U_{\text{eff}}=U-\frac{1}{2}J$.

In order to calculate the matrices $U_{mm'}$ and $J_{mm'}$ one should know the Slater integrals F^k (F^0,F^2,F^4 for d electrons). In Ref. 9 we showed that the Coulomb parameter U, which we calculate in the supercell approximation, could be identified with the Slater integral F^0. What is the relationship between exchange parameter J and F^2,F^4 integrals? If we average matrices $U_{mm'}$ and $(U_{mm'}-J_{mm'})$ over all possible pairs of mm' we should obtain U and $U-J$ as in expression (8). Using properties of the Clebsch-Gordan coefficients one can prove that this averaging gives

$$U=\frac{1}{(2l+1)^2}\sum_{mm'}U_{mm'}=F^0\ , \tag{15}$$

$$U-J=\frac{1}{2l(2l+1)}\sum_{mm'}(U_{mm'}-J_{mm'}) =F^0-(F^2+F^4)\ , \tag{16}$$

$$J=(F^2+F^4)/14\ . \tag{17}$$

To define all three Slater integrals from U and J one needs to know only the ratio F^4/F^2. In Ref. 11 F^2 and F^4 are tabulated for all $3d$. The ratio F^4/F^2 for all ions is between 0.62 and 0.63. So we fixed the value of this ratio at 0.625. Then the expressions for the Slater integrals are

$$F^2=\frac{14}{1.625}J\ , \tag{18}$$

$$F^4=0.625F^2\ . \tag{19}$$

The screened Coulomb and exchange parameters U and J are calculated self-consistently in the supercell approximation as described in Ref. 9. Expressions (9)–(19) define the version of our LDA $+U$ method. One could consider it as one step further from local-density approximation to *exact* density functional. The first step was the so-called local *spin* density approximation (LSDA) where, instead of a functional of total charge density $E[n(\mathbf{r})]$, the functional of two *spin* densities $E[n_\uparrow(\mathbf{r}),n_\downarrow(\mathbf{r})]$ was introduced. Quite naturally the next step is to define a functional of *spin-orbital* densities $E[\{n_{m\sigma}(\mathbf{r})\}]$ and expressions (13) and (14) give this type of functional. The most important property of this functional is the discontinuity of the potential and the maximum occupied orbital energy $\epsilon_{\max}$ as the number of electrons increases through an integer value, the absence of which is the main deficiency of the *local*-density approximation comparing with the *exact* density functional[1] as far as band gaps are concerned.

We applied this scheme to the linear muffin-tin orbital (LMTO) method in two versions: atomic sphere approximations (ASA's) in orthogonal representation[12] and the more rigorous full-potential (FP-LMTO) version of Methfessel.[13] The earlier variant of our scheme[3] [Eqs. (3) and (4)] was used in the ASA-LMTO method. We chose NiO as the object of the investigation because a lot of the experimental and theoretical work was performed for this compound. The results for the magnetic moments value are rather close in both methods: 1.6–1.7μ_B per Ni atom. The energy gap value is more sensitive to the choice of the method and to the details of the calculation. The most accurate calculations (with a filling of the interstitial sites with the empty spheres and with the maximum basis-orbital set on every sphere) results in an energy gap of 3.4 eV in the ASA-LMTO calculation and 3.7 eV in the FP-LMTO calculation [the experimental value is 4.3 eV (Ref. 14)]. It is worth mentioning that in less accurate calculations, for example, without empty spheres or with the smaller basis-orbital set, the results could vary significantly: in the range 3.0–3.4 eV in ASA-LMTO and 3.7–4.2 eV in FP-LMTO. We used the FP-LMTO method for further calculations.

It was pointed out above that in our method the orbital one-electron energies of occupied states have a meaning of removal energies and those of the empty states correspond to the addition energies. If it is so, is it possible to reproduce photoemission spectra and bremsstrahlung isochromat spectroscopy (BIS) of NiO by the results of our LDA $+U$ calculations?

Figure 1 shows the total and partial densities of states (DOS) for the valence band of NiO. One can see a rather broad ($\approx$7.5 eV width) band with strongly mixed Ni $3d$ and O $2p$ states. That is in striking contrast with the standard LSDA calculations[15] where Ni $3d$ bands are above the oxygen bands and those two groups of bands

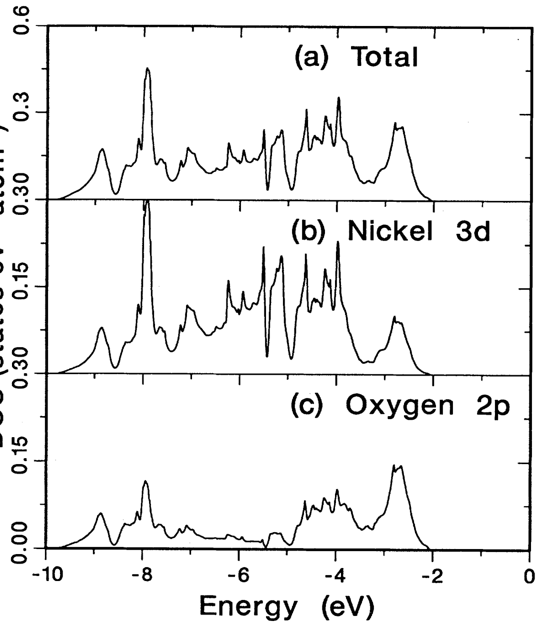

FIG. 1. The density of states (DOS) for the NiO valence band in the LDA + U calculation ("unmodified"). (a) The total DOS, (b) the Ni 3d partial DOS, and (c) the O 2p partial DOS.

are well separated. The reason for this is the shift down in energy for occupied d orbitals due to the LDA + U correction. The energy of unhybridized occupied d orbitals is now even lower than the O 2p orbitals and in the result the top of the valence band of NiO has predominantly O 2p character with a strong admixture of Ni 3d states. If we compare this result with the experimental photoemission spectrum of NiO (upper curve on Fig. 3) one can see that the experimental band is broader and that there is the strong peak at the lowest binding energy of the experimental spectrum which is absent in calculated DOS.

It is known that configuration interaction calculations based on the model Hamiltonian approach were quite successful in describing photoemission spectra of strongly correlated systems.[16,17] What is the possible relationship between LDA + U and those models? We showed above that in our method one-electron energies of occupied d orbitals correspond to the removal energy of the d shell and in the configuration interaction calculation it is the energy of the configuration $|d^7\rangle$ for NiO. LDA + U can even *partially* imitate multiplet splitting for this configuration by different one-electron energies for different d orbitals due to the nonspherical Coulomb and exchange interactions [$U_{mm'}$,$J_{mm'}$ matrices in (14)]. In a model Hamiltonian approach the photoemission spectrum is calculated as a distribution of the final states which are linear combination of configurations $|d^7\rangle$ and $|d^8\underline{L}\rangle$.[14,17] Both of these configurations have multiplet structure and the resulting Hamiltonian matrix and many-electron wave functions are rather complicated. This complex picture can be crudely approximated in the following way.

In the final state of the photoemission removal process (before hybridization with oxygen states is taken into account) there are three holes in the d shell which can be in three configurations: $|e_{g\downarrow}^2 e_{g\uparrow}^1\rangle$, $|e_{g\downarrow}^2 t_{2g\downarrow}^1\rangle$, and $|e_{g\downarrow}^2 t_{2g\uparrow}^1\rangle$ neglecting off-diagonal Coulomb interactions as discussed above. The first configuration (e^3) hybridizes with oxygen 2p states with σ-bond hopping parameter. In this simplified scheme in order to take into account three possible ways of hybridization corresponding to three holes this hopping parameter is multiplied by $\sqrt{3}$ (Ref. 16) in the spirit of the $1/L$ approximation by Gunnarsson and Schonhammer[18] where L is the orbital degeneracy. In this way we collected the hybridization of each of the one electron orbitals in the configuration in an effectively larger one for the complete configuration. The other two configurations (e^2t^1) can hybridize with oxygen 2p states by two possible ways: through the e_g channel, with a σ-bond hopping parameter multiplied by $\sqrt{2}$, and through the t_{2g} channel, with a π-bond hopping parameter. This scheme could be easily simulated in the LDA + U calculations. The energy of the $|e_{g\downarrow}^2 e_{g\uparrow}^1\rangle$ configuration is the removal energy of $e_{g\uparrow}$ states and in our method it is the one-electron energy of occupied $e_{g\uparrow}$ orbitals. For configurations $|e_{g\downarrow}^2 t_{2g\downarrow}^1\rangle$ and $|e_{g\downarrow}^2 t_{2g\uparrow}^1\rangle$ it will be the one-electron energies of $t_{2g\downarrow}$ and $t_{2g\uparrow}$ orbitals, respectively. For every configuration we performed calculations where only corresponding d orbitals were taken into account with the proper factor increasing hopping parameters. The partial density of Ni 3d states obtained in this calculation is presented in Fig. 2. Figure 2(a) is for the configuration $|e_g^3\rangle$($e_{g\uparrow}$ orbital energy with e_g − O 2p off-diagonal matrix elements increased by a factor $\sqrt{3}$), and Fig. 2(b) is for the configuration $|e^2t^1\rangle$ hybridizing with

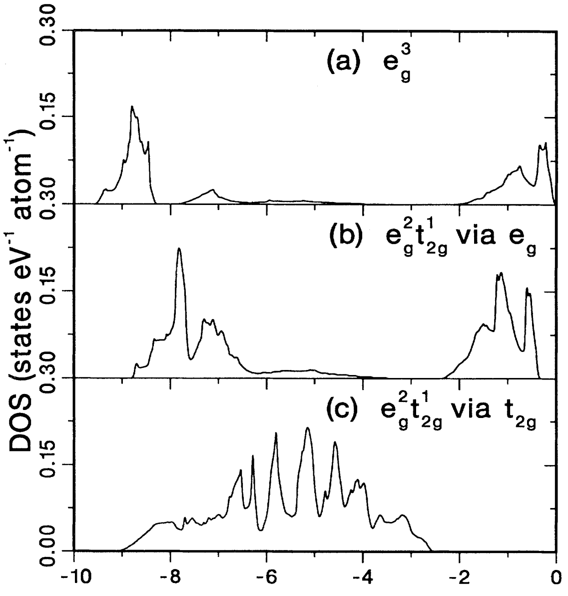

FIG. 2. The partial Ni 3d DOS from the LDA + U calculation with "modified" hopping parameters for (a) the configuration e_g^3; (b) the configuration $e_g^2t_{2g}^1$, hybridization via the e_g channel; and (c) the configuration $e_g^2t_{2g}^1$, hybridization via the t_{2g} channel.

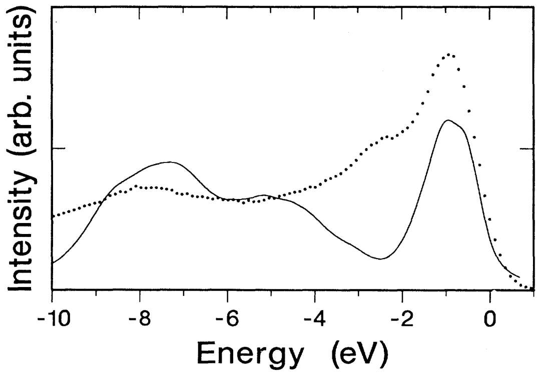

FIG. 3. The experimental (dots) and the calculated (solid line) photoemission spectra for NiO.

oxygen $2p$ states through the e_g channel ($t_{2g\downarrow}$ and $t_{2g\uparrow}$ orbital energies with $e_g-\mathrm{O}\ 2p$ off-diagonal matrix elements increased by a factor $\sqrt{2}$), and Fig. 2(c) is for the configuration $|e^2t^1\rangle$ hybridizing with oxygen $2p$ states through the t_{2g} channel ($t_{2d\downarrow}$ and $t_{2g\uparrow}$ orbital energies with $t_{2g}-\mathrm{O}\ 2p$ off-diagonal matrix elements).

Comparing with Fig. 1 one can see that the result of stronger hybridization is that peaks appear 2 eV higher than in the "nonmodified" calculation and also the "satellite" peaks around 8–9 eV become more pronounced. This result is very similar to the one obtained from the model Hamiltonian calculations where the first ionization states are of $3d^7$ symmetry pushed out of the top of the O $2p$ band because of strong hybridization.[8] In the case of the high-T_c compounds or CuO these are the Zhang-Rice singlets.[19] We summed the curves of Fig. 2 with the proper weights and broadened them corresponding to experimental resolution. [We note that in x-ray photoemission spectroscopy (XPS) it is mainly the Ni $3d$ density of states which is probed.] The result, together with the experimental XPS for NiO, is shown in Fig. 3. Two main features of the experimental curve—"the main line" on the top and the "satellite" around 8 eV—are reproduced in the calculated spectrum.

In the final state of the BIS for NiO there is only one hole in the d shell in configuration $|e^1_{q\downarrow}\rangle$. In our approximated scheme it means that we can use the density of unoccupied states obtained in the calculation without any renormalization of the hopping parameters for the comparison with the experimental BIS (Ref. 14) or NiO (Fig. 4). The first peak in Fig. 4 corresponds to Ni $3d$ states and the rest of the spectrum corresponds to Ni $4s$ and $4p$-derived bands. The $4s$ and $4p$ bands start immediately above the Ni $3d$ empty band, but their intensity is very low and becomes significant only 5 eV higher than the Ni $3d$ peak. It is worth mentioning that the good agreement in the relative position of the Ni $3d$ peak and the $4s$ and $4p$ bands is due to the LDA+U potential correction which pushes up the energy of the unoccupied Ni $3d$ states. Without such a correction (in standard LDA) the Ni $3d$ peak is significantly lower in energy (≈ 3 eV).

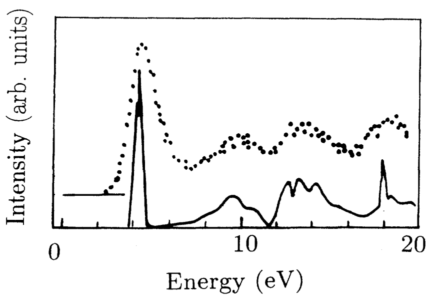

FIG. 4. The experimental (dots) and the calculated (solid line) BIS for NiO.

Naturally our scheme is too oversimplified to reproduce all details of experimental spectra. The remarkable lack of intensity in the calculated photoemission spectra around 2 eV compared with the shoulder in this energy region for experimental spectra is, in our opinion, due to the fact that in the full configuration interaction calculation there are also states which do not hybridize as strongly as the factor of $\sqrt{3}$ suggests.

In summary, we propose the generalization of the local-density approximation based on the model Hamiltonian approach which restores the discontinuity in the one-electron potential as in the exact density-functional theory. In order to calculate photoemission spectra of the strongly correlated systems, such as NiO, it is necessary to renormalize the Ni $3d$–O $2p$ hopping parameters in the spirit of the $1/L$ approximation. Although the method presented here can yield quite accurate results for magnetic moments and band gaps, we note that it is still a mean field method in which electron removal and addition states are represented by single Slater determinants. Because of this, multiplet structures cannot be properly described and phenomena such as spectral weight transfers, which are so characteristic of correlated systems,[20] are absent.

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