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Effect of exchange and correlation on bulk properties of MgO, NiO, and CoO

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Bulk properties of the isostructural oxides MgO, NiO, and CoO have been calculated quantum chemically with periodic models and compared with experimental data from the literature. *Ab initio* Hartree-Fock, gradient-corrected density-functional methods, and hybrid approaches have been used for the calculation of the lattice constants, heats of atomization, and electronic structures. General trends of the effects of electron correlation and the treatment of exchange on the calculated properties are observed. None of the standard methods considered provided results in agreement with experimental data for all properties. A combination of Becke's three-parameter exchange functional and the Lee-Yang-Parr correlation functional (B3LYP) leads to a consistent description of the electronic and structural properties in comparative studies of the three compounds. Other methods are more accurate than B3LYP if certain properties or compounds are considered. The combination of the Hartree-Fock exchange functional with the Lee-Yang-Parr density-functional correlation is the best method for the open-shell transition-metal oxides NiO and CoO in terms of relative stability and geometry and the electronic structure of the valence band. The absolute values of calculated heats of atomization, however, are generally too small. The density-functional method based on the Perdew-Wang generalized gradient approximation (PWGGA) is preferable for the calculation of thermodynamic properties for all compounds but is less reliable in the prediction of structural and electronic properties. A hybrid approach based on the PWGGA method is proposed that improves the results for bulk geometries and electronic properties while maintaining the high quality of calculated energetic results.

I. INTRODUCTION

In the present study first-principles methods are applied to quantum-chemical calculations of bulk properties for the isostructural oxides MgO, NiO, and CoO. The effect of electron correlation and exchange is studied by comparing results obtained with the Hartree-Fock (HF) method and approaches based on the density-functional theory (DFT). The accuracy of the various standard methods is investigated by a comparison of the calculated geometric, energetic, and electronic properties with experimental data from the literature.

The motivation for the present work is to find a reliable theoretical framework for a comparative study of the three oxides focused on their surface structures, energetics, and reactivities. Despite their similar crystal structures and lattice energies, they exhibit differences in their chemical behavior, for example, in surface-adsorption reactions[1–3] and their dissolution mechanisms.[4] An accurate description of the bond strength, the geometry, and the electronic structure of the bulk oxides is a necessary prerequisite for further investigations of surface processes.

The purpose of these surface studies will be to resolve existing discrepancies between theory and experiment that still exist despite the large number of studies reported in the literature.[1] An example is the adsorption of carbon monoxide on the (100) surfaces of magnesium oxide and nickel oxide, where different theoretical approaches lead to strongly disagreeing descriptions for the nature of the CO-surface interaction. This has only recently been clarified experimentally by studies of high-quality surfaces.[2] Another topic where theoretical studies do not give a coherent picture is the surface structure of MgO. Although most theoretical investigations agree in that there is only a small deviation from the ideally truncated (100) plane geometry, the exact degree of relaxation and rumpling varies considerably from method to method, and the agreement with accurate experimental results[5] is still not satisfying.

The structural and thermodynamical data for bulk MgO, NiO, and CoO are well established in the literature.[6] This is also the case for the electronic structure of the large-band-gap insulator MgO;[7,8] however, there has been considerable uncertainty for the ground states of the magnetic insulators NiO (Ref. 9) and CoO (Ref. 10). One reason for the discrepancies, especially for the role of 3d orbitals of Ni and Co in the upper part of the valence band and thus the nature of optical transitions, was the use of DFT calculations within the local density approximation (LDA) for the interpretation of experimental spectra. It is now well understood[11] why this approximation fails to give the correct ground state for highly correlated systems, and several *a posteriori* schemes have been developed to improve the LDA.[12–15] The DFT methods employed in the present investigation are based on the generalized gradient approximation (GGA), which is a more general improvement over the LDA scheme.

II. COMPUTATIONAL METHOD

The oxides were modeled with three-dimensional periodic structures using the crystalline-orbital program CRYSTAL98.[16] Six standard first-principles methods have been employed for the quantum-chemical calculations: (1) the HF method, which has been used in previous CRYSTAL studies,[17–21] (2) HF and electron correlation described by the correlation functional of Lee, Yang, and Parr[22] (LYP) (HF+LYP), (3) a combination of Becke's three-parameter exchange functional[23] with the LYP correlation functional (B3LYP), (4) the Becke-LYP[24] (BLYP) DFT method, (5) the Perdew-Burke-Ernzerhof[25] (PBE) DFT method, and (6) the

Perdew-Wang[26] PWGGA DFT method, all based on the GGA. The comparison of the first two methods, HF and HF+LYP, allows for an investigation of correlation effects. The LYP functional was chosen since it is also part of the hybrid method B3LYP and the pure DFT method BLYP, and it is possible in this way to study different theoretical descriptions of exchange with the same correlation formalism. The two other DFT methods, PBE and PWGGA, are examples of recent developments in DF theory and have been taken into account for further comparison.

An 8-411/1G basis set of triple-ζ plus polarization quality was used for oxygen as optimized for NiO in a previous study.[19] The same oxygen basis set was used for the comparison of MgO, NiO, and CoO. Magnesium was described with an 8-511/1G basis set taken from Ref. 20 and augmented with a single *d* function with an exponent of 0.65. The 86-411/41G basis sets used for Ni and Co have been taken from Refs. 19 and 21, respectively. All metal basis sets have been optimized for the M^{2+} ions with the HF method. Test calculations on the oxide systems with DFT methods showed that changes of the outer valence exponents did not considerably lower the total energies.

The thresholds for Coulomb and exchange integral evaluations were set to strict values (7 7 7 7 14). For the DFT calculations, the accuracy of the radial and angular numerical integration during the self-consistent procedure was increased to that of the post–self-consistent field (SCF) exchange-correlation energy estimation. The following even-tempered auxiliary basis sets for fitting the exchange-correlation potential were used—oxygen: 14 *s*-type Gaussian functions with exponents between 0.07 and 4000.0; magnesium, nickel, and cobalt: 12 *s*-type functions with exponents between 0.1 and 6000.0 and 3 *g*-type functions with exponents between 0.45 and 3.3. These auxiliary basis sets are slight modifications of those recommended for O and Ni in the CRYSTAL98 database. Our experience is that the increased accuracy of the numerical integration only slightly changes the total energy in DFT calculations, by less than 10^{-3} a.u./cell, but improves the convergence behavior and also leads to smoother potential curves. The shrinking factors defining the *k*-point net in reciprocal space were set to 8 throughout. The SCF thresholds were set to 10^{-7} a.u. for the eigenvalues and to 10^{-5} a.u. for the total energy. By using these enhanced accuracies as compared to the standard settings, problems connected with the numerical accuracy of integral evaluation were believed to play only a minor role in our calculations.

For calculations of diamagnetic magnesium oxide, the primitive cell contained only one MgO unit and the spin-restricted HF and DFT methods were used. Two formula units were included in the primitive cells for NiO and CoO calculations of the antiferro- and ferromagnetic states using spin-unrestricted theory. For both oxides, only one antiferromagnetic state, AF_2 with parallel spins in the (111) planes, was considered. This has been proven to be the ground state for NiO,[19] while for CoO other spin configurations have also previously been considered.[10]

For all three oxides, HF wave functions were used as an initial starting guess for the DFT calculations. The numerical stability of the final solutions was tested by repeating the self-consistent procedure, taking the previous wave function as the starting point. In the case of CoO, this procedure had to be repeated a second time for all methods in order to reach the electronic configuration with the lowest energy. For this system special difficulties arise due to the partial degeneracy of the Co^{2+} high-spin $t_{2g}^5e_g^2$ ground state in an octahedral ligand field.

The atomic reference energies for calculations of the heats of atomization were obtained in the following way: Starting with the basis sets used for the periodic calculations, single Gaussian *sp* and *d* shells were added until the total energy converged, using a fixed ratio of 1:3 for the exponents. This was done at the HF level and the same basis sets, 8-41111/11G (O), 8–511111/11G (Mg), 86-411111/411G (Ni and Co), were then used for the atomic references for the other methods. Test calculations showed that further addition of diffuse functions did not significantly lower the atomic energies for the DFT methods. No reoptimizations of the exponents or the contraction coefficients of the more contracted orbitals were performed. The atomic energies for oxygen and magnesium obtained in this way were lower than those used in previous CRYSTAL studies[16] by 0.20 and 0.23 eV, respectively. This extension of the basis is necessary to obtain an appropriate atomic reference because in the periodic wave-function calculation, the atom-centered functions are transformed to Bloch functions, which are much closer to the variational limit than the localized atomic basis functions in molecular wave-function calculations. Any attempt to introduce in a similar way more diffuse functions in the periodic calculations lead to linear basis-set dependencies.

The optimized lattice parameters *a* were obtained numerically by fitting a fourth-order polynomial to the total energies of five single-point calculations varying *a* in steps of 0.04 Å around the experimental bulk value. Properties were then determined for the optimized structures of each state and method, except for the ferromagnetic states of CoO with the pure DFT approaches due to severe convergence problems in the self-consistent procedure. In these cases the geometries of the corresponding antiferromagnetic states have been taken for the calculation of thermodynamic and electronic properties. The heats of atomization ΔH_a were approximated as binding energies, neglecting contributions from zero-point energies and thermal corrections that are contained in the experimental values, and have been normalized to one formula unit. The band gaps were estimated as the difference of the Fermi level E_F and the energy of the lowest virtual level. Atomic charges q and spin moments m_s were obtained from a Mulliken analysis of the crystalline orbitals.

III. RESULTS AND DISCUSSION

A. MgO

The calculated MgO bulk properties as obtained with the different approaches are presented in Table I and compared with available experimental data. The restricted HF (RHF) method gives an excellent value for the lattice parameter *a* of 4.20 Å, while the heat of atomization ΔH_a, 7.28 eV, is too small by about 3 eV. The band gap, 16.5 eV, is too large by almost 9 eV. The overestimation of the band gap with HF theory is a consequence of the single-particle approximation that has been used here. More accurate estimates can be obtained with the configuration-interaction method (see the

TABLE I. Calculated bulk properties for MgO: lattice constant a (Å), heat of atomization per MgO unit ΔH_a, band gap, Fermi level E_F (eV), and Mulliken charges q (a.u.).

Method	RHF	RHF+LYP	B3LYP	BLYP	PBE	PWGGA	Expt.
a	4.20	4.09	4.23	4.28	4.25	4.25	4.212[a]
ΔH_a	7.28	9.51	9.59	9.56	10.09	10.22	10.26[a]
Band gap	16.5	17.5	7.6	5.3	5.3	5.2	7.8[b]
E_F	−8.2	−8.9	−4.4	−3.2	−3.2	−3.6	
q	1.87	1.85	1.78	1.78	1.78	1.79	

[a] Reference 6.

[b] Reference 7.

quoted work in Ref. 12), which is, however, currently not applicable for the periodic approach used here. The calculated atomic charge for Mg, +1.87, is close to the formal charge +2, and is consistent with the fact that the MgO valence band (Fig. 1) has only minor contributions from Mg orbitals and is dominated by O($2p$) orbitals. This highly ionic picture for MgO is in line with most previous studies.[12,20]

The effect of electron correlation introduced by the LYP functional in the RHF+LYP approach is an increased bonding interaction, as can be seen by the decrease of a and the increase of ΔH_a compared to the RHF results, Table I. The decrease of a due to electron correlation is in quantitative agreement with that found in a previous study,[18] where different DFT correlation functionals were utilized. The RHF+LYP lattice parameter, 4.09 Å, is considerably smaller than the experimental value, whereas the binding energy, 9.51 eV, is in much better agreement with experiment than the RHF value. Electron correlation slightly lowers the occupied orbitals (E_F decreases from −8.2 to −8.9 eV), while there is little effect on the virtual levels, as can be seen by the increased band gap and from the density of states (DOS) in Fig. 1. The Mulliken charges and the calculated DOS indicate that the electronic structure of MgO is not altered significantly by electron correlation.

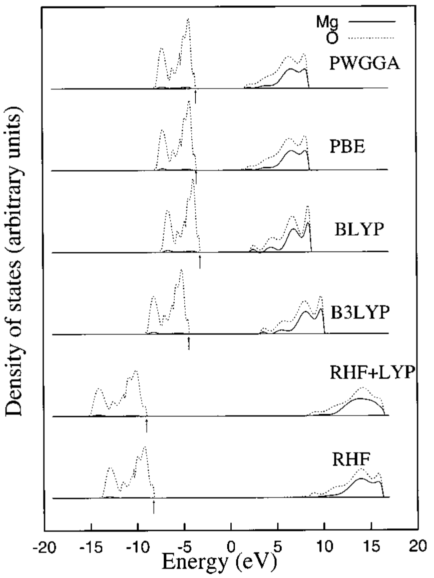

FIG. 1. Density of states for MgO as calculated with different methods: solid lines, Mg; dashed lines, O. Only the valence band and the lower part of the conduction band are shown. Fermi levels are indicated by small arrows.

If the B3LYP method is used, the calculated lattice parameter increases to 4.23 Å, only 0.5% larger than the experimental lattice parameter. The calculated heat of atomization, 9.59 eV, is similar to that obtained with the RHF+LYP method. The calculated band gap decreases drastically from 17.5 eV with RHF+LYP to 7.6 eV with B3LYP, the latter being in almost perfect agreement with the experimentally observed band gap, 7.8 eV.[7] Two effects are responsible for the reduction of the band gap compared to the HF-based approaches: In DFT, virtual orbitals experience the correct $(n-1)$-particle potential and their energies therefore better describe electron affinities as those in HF theory. Due to the different descriptions of Coulomb and exchange potentials in DFT, one-center electron repulsion integrals do not vanish and an artificial ''self-interaction'' is created, which destabilizes the occupied levels. The GGA, especially in the B3LYP formalism, where 20% exact HF exchange is mixed with 80% Becke exchange, strongly reduces the self-interaction, but the effect on the valence band can still be seen from the less negative E_F, −4.4 eV, and in the DOS, Fig. 1. The Mg Mulliken charge is +1.78. Thus, the ionicity of MgO is slightly reduced with B3LYP compared to the RHF and RHF+LYP methods.

The trend of increasing Mg-O distance from RHF+LYP to B3LYP is continued with the pure DFT method BLYP. The resulting value for a, 4.28 Å, is noticeably larger than the experimental value, Table I, while the binding energy is essentially not affected by the change of the exchange formulation. The self-interaction has increased as can be seen from the further increase of the Fermi level, Fig. 1. The band gap, 5.3 eV, is more than 2 eV smaller than that for B3LYP and underestimates the experimental gap considerably.

The two DFT methods PBE and PWGGA give a very similar description of MgO bulk properties. The calculated lattice parameters are essentially the same, 4.25 Å, 1% larger than the experimental length. From all methods considered here, they yield the best estimation of the heat of atomization, 10.09 and 10.22 eV, respectively. The position of the Fermi level, the band gap, and the electronic structure are very similar for all DFT methods.

B. NiO

For all methods considered in this study, the AF_2 antiferromagnetic state with Ni atoms having parallel spins along the (111) planes is more stable than the ferromagnetic state

TABLE II. Calculated bulk properties for AF_2 antiferromagnetic NiO: lattice constant a, difference Δa to ferromagnetic state (Å), heat of atomization per NiO unit ΔH_a, difference to ferromagnetic state $\Delta\Delta H_a$, band gap, Fermi level E_F (eV), Mulliken charges q (a.u.), and atomic spin moment m_s (μ_B).

Method	UHF	UHF+LYP	B3LYP	BLYP	PBE	PWGGA	Expt.
a	4.26	4.16	4.23	4.23	4.18	4.18	4.177[a]
Δa	-0.005	-0.009	-0.006	-0.034	-0.078	-0.013	
ΔH_a	5.93	8.43	8.11	8.17	8.90	9.00	9.5[a]
$\Delta\Delta H_a$	$+0.018$	$+0.028$	$+0.103$	$+0.272$	$+0.323$	$+0.288$	
Band gap	14.7	15.2	4.2	0.4	0.5	0.4	3.8[b]
E_F	-8.2	-8.9	-4.2	-2.2	-2.3	-2.4	-4.4[c]
q	1.88	1.86	1.67	1.53	1.55	1.54	
m_s	1.92	1.91	1.68	1.34	1.33	1.33	1.64–1.90[d]

[a] Reference 6.
[b] Reference 27.
[c] Reference 28.
[d] References 29–31.

as can be seen from the positive $\Delta\Delta H_a$ in Table II. Therefore the following discussion of calculated NiO properties concentrates on the antiferromagnetic state.

In contrast to MgO, the NiO lattice constant computed with the unrestricted HF (UHF) method, 4.26 Å, is considerably overestimated compared to experiment, Table II. The binding energy per NiO unit, 5.93 eV, is too small by approximately 3.6 eV, and the band gap, 14.7 eV, is almost 11 eV larger than the experimental value. The two latter findings are similar to the observations for MgO. The UHF method describes nickel oxide as highly ionic with a charge of +1.88, essentially the same as for Mg in magnesium oxide. This closely resembles the formal situation of a ^3F Ni^{2+} ion with a high-spin s^0d^8 configuration, consistent with the atomic spin moment m_s of 1.92, Table II. The UHF spin moment is close to the upper range of experimental values for m_s, 1.64–1.90.[29–31] A very important aspect of the electronic structure of NiO is the nature of the upper part of the valence band. Whereas early interpretations of ultraviolet (UPS) and x-ray (XPS) photoelectron spectroscopy data came to the conclusion that Ni $3d$ orbitals dominate the valence-band edge, classifying NiO as a Mott-Hubbard magnetic insulator, the situation[9] accepted now is that O $2p$ orbitals form the upper part of the valence band and the optical band gap in NiO is due to a charge-transfer transition. The UHF approach confirms the latter interpretation as can be seen from the DOS in Fig. 2. The valence-band region up to 3 eV below E_F is dominated by oxygen orbitals with only small contributions from nickel. It has to be mentioned that most of the NiO features presented above are essentially identical to those reported in a previous UHF study[17] on NiO. The exception is the binding energy, which is slightly larger, 6.2 eV, in Ref. 17. Since the same methodology and basis sets were used in both of these studies of the periodic system, the discrepancy is most probably due to the lower atomic reference energies used here.

The effect of electron correlation on NiO is very similar to the previously described effect on MgO. The lattice constant obtained with UHF+LYP, 4.16 Å, is 0.10 Å shorter compared to UHF, and the heat of atomization, 8.43 eV, is 2.5 eV larger. Both geometry and energy are in much better agreement with experiment than the UHF results. There are only minor changes in the electronic structure compared to the UHF approach; the band gap, E_F, the atomic charge and spin moment, and the nature of the valence band remain essentially the same.

With B3LYP, the Ni-O bonding interaction is weaker compared to UHF+LYP, the lattice parameter increases to 4.23 Å and the binding energy is slightly smaller, 8.11 eV. The agreement with experiment is extremely good for the band gap, 4.2 eV, the position of the Fermi level, −4.2 eV, and the spin moment, $1.68\mu_B$. The ionicity of NiO obtained with B3LYP is smaller than that at the UHF and UHF+LYP level, as can be seen by the smaller atomic charge on nickel, +1.67, Table II. But the most important difference between the methods of pure HF exchange and the hybrid approach is the increased contribution of nickel $3d$ orbitals in the upper part of the valence band, Fig. 2, which is slightly larger than the contribution of O $2p$ orbitals. It is apparent that the DFT

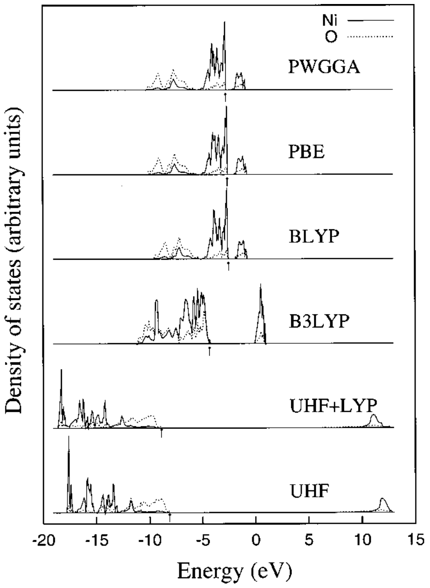

FIG. 2. Density of states for NiO in the AF_2 states as calculated with different methods: solid lines, Ni; dashed lines, O. Only the valence band and the lower part of the conduction band are shown. Fermi levels are indicated by small arrows.

TABLE III. Calculated bulk properties for AF_2 antiferromagnetic CoO: lattice constant a, difference Δa to ferromagnetic state (Å), heat of atomization per CoO unit ΔH_a, difference to ferromagnetic state $\Delta\Delta H_a$, band gap, Fermi level E_F (eV), Mulliken charges q (a.u.), and atomic spin moment m_s (μ_B).

Method	UHF	UHF+LYP	B3LYP	BLYP	PBE	PWGGA	Expt.
a	4.35	4.24	4.29	4.26	4.22	4.22	4.260[a]
Δa	−0.003	−0.003	−0.010				
ΔH_a	5.84	8.29	8.48	8.86	9.74	9.86	9.45[a]
$\Delta\Delta H_a$	+0.008	+0.016	+0.074	+0.171	+0.182	+0.274	
Band gap	14.2	14.4	3.5	0.8	0.8	0.8	2.6[b]
E_F	−8.1	−8.9	−3.4	−1.7	−1.9	−2.0	−4.9[c]
q	1.88	1.86	1.68	1.54	1.56	1.55	
m_s	2.91	2.88	2.69	2.42	2.42	2.32	3.35–3.8[d]

[a] Reference 6.
[b] References 27 and 34.
[c] Reference 28.
[d] References 35 and 36.

exchange formulation is responsible for the appearance of Ni $3d$ orbitals near the Fermi level. This can be seen from the valence-band structure for the pure DFT methods in Fig. 2. Irrespective of the different form of the exchange potential in BLYP, PBE, and PWGGA, all three DFT methods give essentially the same description of the electronic structure of NiO. The calculated band gaps of about 2 eV are only half the experimental value, and the atomic spin moments on Ni, $(1.33-1.34)\mu_B$, are also smaller than all experimental estimates. The ionicity is reduced compared to UHF, UHF+LYP, and B3LYP, with an atomic charge of only +1.53 to +1.55 on Ni. This is also smaller than the charges on MgO calculated with the same methods and would indicate that NiO has a less ionic nature than MgO. However, the most striking difference in the HF-based methods and also in the intermediate B3LYP method is the strong predominance of Ni $3d$ orbitals in the upper valence band (Fig. 2), which is in disagreement with the actual interpretation of the NiO electronic structure.[9] In this respect, the deficiency of the LDA for the description of the ligand-field splitting of the $3d$ orbitals has not fully been overcome by the use of GGA, although the latter methods give the correct antiferromagnetic ground state for NiO, which was not the case with LDA.[13,15] The large contribution of Ni orbitals close to the Fermi level is expected to have considerable effect on their role in bonding interactions with molecules at the NiO surface. A similar effect has been found for the CO adsorption at the $Cu_2O(111)$ surface,[32] where both B3LYP and BLYP methods lead to an enhanced Cu $3d\rightarrow$CO back donation compared to the HF or HF+DFT correlation approaches,[33] which in turn strongly affects the calculated C-O stretching frequency of the adsorbed molecule.

All DFT methods give a strong antiferromagnetic coupling. The calculated energy differences $\Delta\Delta H_a$ between the antiferromagnetic and the ferromagnetic state of NiO, 0.272–0.323 eV (Table II), are one order of magnitude larger than that for the UHF and UHF+LYP methods and appear to be overestimated since the thermal energy at 523 K, the Néel temperature of NiO,[27] is sufficient to destroy the antiferromagnetic ordering.

For the lattice constant and the heat of atomization, the BLYP method gives different results from PBE and PWGGA, Table II. BLYP overestimates a and underestimates ΔH_a in a way similar to B3LYP. The two latter methods give an excellent lattice parameter, 4.18 Å compared to the experimental value, 4.177 Å, and the closest estimate to the experimental heat of atomization, 8.9 and 9.0 eV, respectively. If only geometrical and thermodynamical properties were considered, the use of the DFT methods PBE and PWGGA would be strongly recommended by the present results. There remains, however, a strong concern as to the electronic structure, which could introduce artificial effects upon the description of chemical reactions at the NiO surface.

C. CoO

The results for bulk properties of CoO are summarized in Table III. All methods result in lower energies for the AF_2 antiferromagnetic state as compared to the ferromagnetic state. A comparison has been made between the optimized structures of both states for UHF, UHF+LYP, and B3LYP. The same geometry, the optimal structure of the AF_2 state, has been considered in the case of the pure DFT methods due to SCF convergence problems in the ferromagnetic state. Since the energy differences between the ferromagnetic and the antiferromagnetic states are comparably large for BLYP, PBE, and PWGGA (one order of magnitude larger than for UHF and UHF+LYP) it is expected that the numerical inaccuracy for the ferromagnetic state will not reverse the order of stability. As for NiO, the UHF method gives a too large lattice constant for cobalt oxide, 4.35 Å instead of 4.26 Å from experiment, Table III. The calculated heat of atomization, 5.84 eV, is too small by 3.6 eV, a similar observation as for MgO and NiO. The band gap, 14.2 eV, is too large compared to the experimental value by 11.6 eV, which is in line with the observations for the other oxides and has been explained above. If, however, the relative values of the band gaps are considered, the qualitatively correct trend MgO$\gg$NiO$>$CoO is obtained with the HF method. The ionicity of CoO as measured by the Mulliken charges of ±1.88 is indistinguishable from NiO and MgO with the HF method. The calculated atomic spin moment, $2.91\mu_B$, corresponds to almost three unpaired electrons, which is consistent with a

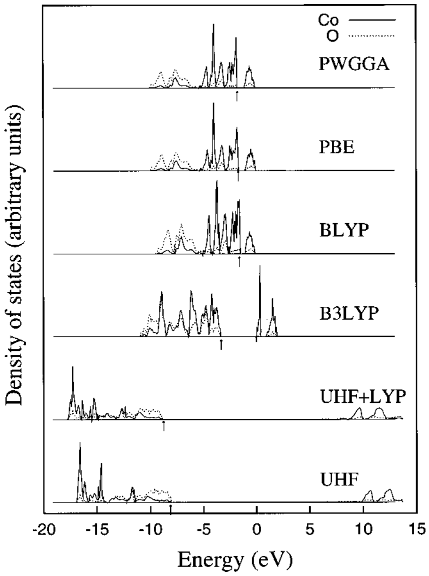

FIG. 3. Density of states for CoO in the AF_2 state as calculated with different methods: solid lines, Co; dashed lines, O. Only the valence band and the lower part of the conduction band are shown. Fermi levels are indicated by small arrows.

formal Co^{2+} in a high-spin $t_{2g}^5 e_g^2$ configuration. Following the considerations in Ref. 13, the experimental spin moments, $(3.38–3.8)\mu_B$,[35,36] contain an orbital moment of about 1 μ_B. Since the theoretical calculations of the present work do not include spin-orbit interactions, the correct experimental reference for m_s would therefore be $(2.38–2.8)\mu_B$. This would also be in line with the UHF results for m_s(Ni) in NiO, which were slightly larger than the experimental values. From the DOS in Fig. 3 it can be seen that the UHF method gives qualitatively the same valence-band structure for CoO as for NiO.

As for MgO and NiO, the inclusion of electron correlation by the UHF+LYP method shortens a by 0.11 to 4.24 Å (Table III) and increases ΔH_a by 2.45 to 8.29 eV. For both transition-metal oxides CoO and NiO, this effect leads to an improved agreement with the experimental results for both properties, while the effect on MgO improves the binding energy but deteriorates the lattice parameter. The stabilization of the oxides by inclusion of electron correlation is mainly due to the strengthening of interatomic forces and not to intra-atomic contributions. This has been evaluated by comparison of the LYP correlation energies ΔE^{corr} for the isolated neutral atoms and M^{2+} and O^{2-} species, which represent the idealized valence states of the oxide ions.

$$\Delta E^{\text{intra}} \approx \Delta E^{\text{corr}}(M^{2+}) + \Delta E^{\text{corr}}(O^{2-}) - \Delta E^{\text{corr}}(M) - \Delta E^{\text{corr}}(O). \quad (1)$$

The ionic species are stabilized by 0.35 eV ($M=$Mg) and 0.22 eV ($M=$Ni, Co), respectively, which is one order of magnitude smaller than the stabilization of the oxides. Other properties such as the band gap, 14.4 eV, the ionicity, and the valence-band structure, Fig. 3, are similar for UHF+LYP and UHF.

The different treatment of exchange in the B3LYP method leads to an increase of the CoO lattice constant to 4.29 Å but at the same time to a slight increase of the binding energy, to 8.48 eV, compared to the UHF+LYP approach. The band gap, 3.5 eV, is in good agreement with the experimental value, 2.6 eV.[27,34] The same improved agreement with experiment is achieved for m_s(Co), which is calculated to $2.69\mu_B$. The ionicity of CoO is slightly smaller for B3LYP than for UHF and UHF+LYP. An increase of metal $3d$ contributions in the upper valence band similar to NiO is observed, Fig. 3.

Among the three DFT methods, the BLYP approach gives slightly different results from PBE and PWGGA, which are again similar in their calculated properties to MgO and NiO. The lattice constant calculated with BLYP, 4.26 Å, is identical to the experimental value, while the obtained binding energy, 8.86 eV, is too small by 0.59 eV. The Co-O interaction represented by PBE and PWGGA is stronger than that with BLYP, with a smaller a, 4.22 Å, and heats of atomization, 9.74 and 9.86 eV, respectively, which are slightly larger than the experimental reference, 9.45 eV.[6] All three DFT methods underestimate the band gap, which is 0.8 eV in all cases mainly due to the Fermi energies, -1.7 to -2.0 eV, which are considerably higher than those for the other methods, and also the experimental value, -4.9 eV.[28] The calculated spin moments, $(2.32–2.42)\mu_B$, are in the lower range of the experimental estimates. As for NiO, metal $3d$ orbitals are predominant in the upper valence band, which would lead to a classification of CoO as a Mott-Hubbard insulator, whereas the most recent interpretation of experimental results places CoO in an intermediate situation between a charge-transfer insulator and a Mott-Hubbard insulator.[34] This gradual difference between NiO and CoO is not clearly represented in the valence-band structure of any of the considered methods, although UHF and UHF+LYP show a slight increase of metal $3d$ contributions from NiO to CoO. An analysis based on the B3LYP results would classify both NiO and CoO as intermediate cases with non-negligible contributions from both the metal and the oxygen near the Fermi energy. The results obtained with the pure DFT methods place both NiO and CoO as Mott-Hubbard insulators, which must be considered as an artifact due to the approximate nature of the exchange formalism.

D. Hybrid approach based on the PWGGA method

The results obtained with the present standard methods are not perfectly satisfying since no approach reproduces experimental data for all compounds with equally high accuracy. It would be desirable to combine the high quality of thermodynamic properties obtained with the PWGGA method and the more reliable electronic structure data from the B3LYP method. Since the calculated electronic structure of the oxides was mainly influenced by the theoretical description of the exchange potential, it was expected that a combination of the exact HF expression with the PWGGA functional would give better results for the electronic structure than the PWGGA method itself while maintaining the good description of energetics. In an approach similar to the B3LYP hybrid method, we therefore combined the HF and PWGGA exchange potentials and the PWGGA correlation functional and varied the relative contributions of the two exchange expressions as an empirical parameter. A crude

TABLE IV. Calculated bulk properties for MgO, NiO, and CoO, as obtained with the HF+PWGGA hybrid approach; lattice constant a (Å), heat of atomization per unit ΔH_a, and band gap (eV).

	HF+PWGGA	Expt.
	MgO	
a	4.21	4.212[a]
ΔH_a	10.03	10.26[a]
Band gap	7.4	7.8[b]
	NiO	
a	4.17	4.177[a]
ΔH_a	8.71	9.5[d]
Band gap	4.1	3.8[c]
	CoO	
a	4.25	4.260[a]
ΔH_a	9.20	9.45[a]
Band gap	3.3	2.6[d]

[a] Reference 6.
[b] Reference 7.
[c] Reference 27.
[d] References 27 and 34.

optimization on the energetic and geometric properties of the three oxides yielded exactly the same relation as realized in the B3LYP method,[23] 20% HF exchange and 80% DFT exchange. As can be seen from the results presented in Table IV, this special hybrid approach gives almost perfect agreement with the experimental lattice parameters and heats of atomization for MgO, NiO, and CoO and describes the electronic structure, represented by the band gap, in a way similar to the B3LYP method. The deviations from experiment for a are not larger than 0.01 Å, which is a considerable improvement with respect to all standard methods used in the present study. The calculated binding energies for MgO and CoO, 10.03 and 9.20 eV, are only 0.2–0.3 eV smaller than the experimental values. Only the deviation for NiO, 8.71 eV instead of 9.5 eV, is somewhat larger, reflecting the larger error of the PWGGA method for this particular compound. The calculated band gaps, 7.4 eV (MgO), 4.1 eV (NiO), and 3.3 eV (CoO), are in similar or even better agreement with experiment than those obtained with the B3LYP method. A possible disadvantage of the HF+PWGGA hybrid approach is the contribution of metal $3d$ orbitals in the upper valence band of NiO and CoO, which is comparably high as in the B3LYP results, Fig. 4.

IV. CONCLUSIONS

Bulk properties of the oxides MgO, NiO, and CoO have been calculated with periodic models using different standard first-principles methods, HF, HF+LYP, B3LYP, PBE, and PWGGA. A comparison of the calculated results with available experimental data reveals that none of the utilized methods gives a perfect agreement for all three compounds.

The HF method drastically underestimates all three binding energies, which indicates that important contributions of the metal-oxygen interaction are missing. A good agreement of the HF lattice parameter with the experimental geometry is given only for the non-transition-metal oxide MgO while the lattice constants of NiO and CoO are overestimated by 0.08 and 0.09 Å, respectively. Band gaps as obtained within the simple one-particle approximation are too large in all cases, but the relative contributions of metal and oxygen orbitals in the valence band are in qualitative agreement with experiment.

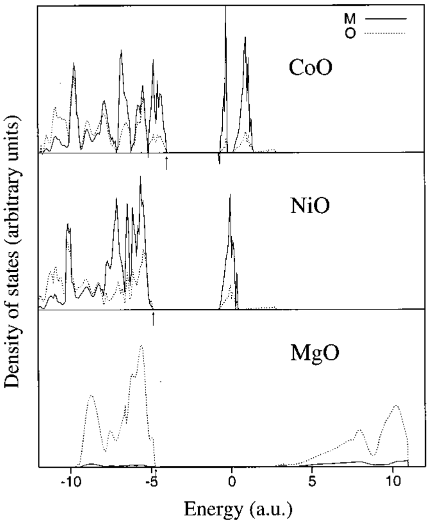

FIG. 4. Density of states for MgO, NiO, and CoO with the HF+PWGGA hybrid approach: solid lines, metal; dashed lines, O. Only the valence band and the lower part of the conduction band are shown. Fermi levels are indicated by small arrows.

The general effect of electron correlation, introduced in the present case with the HF+LYP method, is to contract the crystal lattices and to increase their binding energy with respect to the noncorrelated approach. The effects are almost quantitatively the same for the three oxides, a decrease of 0.10–0.11 Å for the lattice parameter and an increase of 2.2–2.5 eV for the heat of atomization. These changes worsen the lattice parameter for MgO compared with HF theory but improve the geometries for NiO and CoO and all binding energies, especially the relative stabilities of the different systems. The calculated electronic structure data are similar to the noncorrelated Hartree-Fock approach.

The hybrid method B3LYP slightly overestimates all three lattice parameters by less than 1.5% and yields binding energies that are comparable to the HF+LYP method, generally 85–95 % of the experimental value. It gives the best description of the electronic structure data for all three compounds within the methods tested here. The relative contributions of metal and oxygen orbitals in the valence band are between the two extremes represented by the HF-based and the DFT methods.

Pure DFT methods such as PBE and PWGGA give lattice parameters that are slightly too large for MgO, in good agreement with experiment for NiO and too small for CoO. The BLYP method generally underestimates binding energies, while the heats of atomization obtained with PBE and PWGGA are closest to experiment for all methods considered here. However, all three DFT methods strongly underestimate the band gaps of all three compounds and give a valence-band structure for NiO and CoO, which is contrary to recent experimental considerations. This has been attributed to the theoretical description of exchange by the various density functionals, which is an approximation to the exact exchange potential.

The present observations lead to a differentiated suggestion for the best use of the standard methods in investigations of the different oxides. The B3LYP method is the only approach among those investigated that gives reasonable to good agreement with experiment for all properties that were taken into account in the present study. It is therefore the best choice for comparative investigations on different oxides of main-group elements and transition metals. Other methods, however, give better performance than B3LYP in particular cases. If only the transition-metal oxides NiO and CoO are considered, the HF+LYP approach is better suited for the representation of relative stabilities and the geometries. The contribution of metal $3d$ orbitals in the upper valence band is in better accordance with experimental consideration than that for B3LYP. This is of importance for adsorption reactions at oxide surfaces that involve the interaction with the metal atoms. The DFT method PWGGA is superior for the calculation of thermodynamic properties of pure oxides. It would therefore be the method of choice for studies of the energetics of defect formation.

Based on the results for the previously used standard methods, a hybrid approach combining the exchange potentials of the HF and the PWGGA method together with the PWGGA correlation functional has been invented. The relative contribution of the two exchange descriptions was treated as an adjustable parameter and was optimized on the bulk properties of MgO, NiO, and CoO. The results obtained with this hybrid approach are in better agreement with experimental data for all three compounds than those from all standard methods used before in this study. Further investigations have to show if the proposed new approach gives the same quality for structures and energetics of other main-group and transition-metal oxides or other classes of ionic compounds. But since the technical parameters used in the present study, such as atomic basis functions, auxiliary basis sets, and numerical accuracy, are of relatively high quality, a transferability of the present results to other substances can be expected. Studies on surface properties and adsorption reactions will be undertaken in future studies for the three oxides using the new hybrid approach.

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