Charge separation and covalent bonding in metal oxide surfaces: A local density functional study on the MgO(001) surface

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A first principles local density functional investigation on extended, two-dimensional periodic slab models of the MgO(001) surface is performed, using the linear combination of Gaussian-type orbitals (LCGTO) technique as implemented in the FILMS program package. Stimulated by recent theoretical evidence for a reduced charge separation in MgO(001), a detailed analysis of the charge distribution and its influence on the electrical field above the surface is carried out. Two different methods to quantify the charge separation in the ionic substrate are employed, a local one based on the topological atom approach and a global one derived from the Madelung field of the surface near potential adsorbates. Both procedures lead to a charge separation significantly (10%−20%) below the nominal ionic value of ±2 a.u. A variational atomic orbital analysis is utilized to discuss the origin of the Mg 3s and 3p structures discernible in the crystal orbitals of the MgO slab systems. They are identified as covalent magnesium valence orbital admixtures to the oxygen dominated valence bands in consistence with the reduced charge separation. Their influence on the cohesive energy of crystalline MgO, however, is found to be only 5% (~0.5 eV).

I. INTRODUCTION

In recent years the interest in the surface chemistry of metal oxides has rapidly grown. On the one hand, the enhanced attention is related to new types of catalytic reactions on oxide surfaces, on the other hand, it is stimulated by advances in the preparation of well-characterized thin films of these materials.1−5 The increasing experimental efforts are accompanied by numerous theoretical activities. In many of these investigations simple structured metal oxides, like MgO, NiO, ZnO, and related crystals were studied. Especially magnesium oxide, which is assumed to be a perfect ionic crystal (with rock-salt structure), is widely used in surface and adsorption studies.6−19

Since molecular adsorption on a clean MgO(001) surface is governed by electrostatic forces,13−15 an accurate description of the charge distribution in the MgO surface and of the resulting Madelung field is important for a quantitative understanding of the adsorption processes at this surface. Moreover, in molecular modeling investigations of ionic systems (for a review concerning MgO see Ref. 4), the ionic charge is one of the most important empirical parameters defining the force field. Even in “first principles” model cluster studies of molecular chemisorption at the MgO(001) surface,14−16 the ionic charge enters into the calculations via the surrounding point charge arrays required to generate the correct Madelung field near the adsorption site. Usually point charges of ±2.0 a.u. are utilized. However, two recent model cluster studies of CO adsorbed at MgO(001)16,18 have shown that changes in the charge distribution outside the “inner” adsorption cluster may influence the properties of the adsorbate significantly. In one case,16 the point charges around a MgO2 cluster model cluster were reduced from ±2.0 to ±1.5 a.u. As a consequence the induced C−O stretching frequency shift decreased from 54 to 17 cm−1; experimentally this quantity is determined to 14 cm−1.20 In the other study18 the nearest 21 point charges (±2.0 a.u.) surrounding a MgO2 cluster were replaced by real ions, represented in a minimal orbital basis set. This modification yielded a shift of −0.44 eV in the electrostatic potential acting on the adsorbed CO molecule (2.65 Å above the cation). On the other hand, a covalent contribution to the chemical bond in solid MgO would also affect the reactivity of the MgO surface. In the case of a totally ionic bonding, the system consists of closed-shell ions and therefore the chemical reactivity of the MgO surface is essentially restricted to electrostatic interaction and Pauli repulsion. A small covalent contribution, however, opens the possibility for a chemical interaction, including direct covalent bonding and charge transfer either to the incompletely filled 2n shell of the anion or from the partially filled 3n shell of the cation.21 Thus, the charge separation in MgO(001) is important for the characterization the Madelung field around potential adsorbates and for the construction of quantitative models for chemical and catalytic processes at the surface.

Quite a few theoretical and experimental studies have been devoted to the problem of quantifying the amount of ionicity in solid MgO.3,16,19,22−27 Several experimental indications for a charge separation reduced from the nominal ionic value of ±2 a.u. have been found. In a soft x-ray spectroscopy study Fomichev et al. examined the oxygen K emission and the magnesium LIII emission of crystalline...
MgO. With the help of dipole selection rules, they concluded that the MgO valence states, viewed at the cation sites, must exhibit some valence $s$ character, probably due to a Mg $3s$ population. Neutron scattering was applied by Sangster et al. to measure the phonon dispersion in MgO crystals. Several familiar lattice dynamic models which include the ionic charge as a variational parameter were fitted to the experimental data, leading to a charge separation between $\pm 1.89$ and $\pm 1.71$ a.u. ($\pm 1.75$ a.u. for the best fit). Vidal-Valet et al. included Sanger's x-ray diffraction data on MgO in their study of the atomic densities in alkaline-earth metal oxides. Spherical averaged charge densities around each ion were derived from x-ray structural factors, and the ionic radii were fixed at the local minimum of the radial density. The ionic charges (and radii) for MgO determined by this procedure were $+1.36$ a.u. (1.03 Å) for magnesium and $-1.14$ a.u. (1.28 Å) for oxygen. (For comparison, the nearest-neighbor distance in MgO is 2.105 Å.) In an analogous way Sasaki et al. derived a cation charge of $+1.85$ a.u. in MgO from their x-ray diffraction data. However, these experimental results and the conclusions derived from them have generated controversy in the literature (e.g., in Refs. 22 and 29).

Most of the theoretical investigations favor the picture of perfect ionicity for crystalline MgO. In a series of linear combination of Gaussian-type orbitals (LCGTO) calculations performed on point charge embedded MgO(001) cluster models, bulk MgO, and MgO(001) slabs, the ionicity of crystalline MgO was analyzed in the framework of Hartree–Fock (HF) theory. Based on a Mulliken population analysis and supplemented by electron density difference plots, the Mg–O bond was found to be perfectly ionic. Similar results were reported for calculations, based on the local density functional (LDF) theory. Chang and Cohen performed a LDF pseudopotential plane wave calculation to analyze crystalline MgO. They did not find any valence charge around the cation in a density plot along the [100] direction. Redinger and Schwarz used the augmented plane wave method, also based on the LDF formalism, and computed the spherically averaged radial charge density around the ionic centers of MgO. The amount of electronic charge inside the muffin–tin sphere around magnesium (radius 0.885 Å) was found to be 10.04 a.u., and 8.89 a.u. inside the muffin–tin sphere around oxygen (radius 1.219 Å) (the rest is distributed over the interstitial region). Although more than ten electrons were counted inside the Mg muffin–tin sphere, the oxide was classified as perfectly ionic, by a comparison of the crystal charge density and a superposition of the atomic O$^{2-}$ charge densities, restricted to the oxygen muffin–tin sphere. On the other hand, it is known that crystalline charge densities may be built up equally well by superimposing atomic or ionic charge densities. In the present context it is also interesting to note that according to a HF study on the unusual (110) surface of MgO, in contrast to the (001) surface, a reduction of the top layer charge separation by about 0.20 a.u. was found after surface relaxation had been taken into account.

In contrast to these direct theoretical analyses of crystalline MgO, recent investigations on chemisorption processes at the MgO(001) surface give, as already mentioned, indirect evidence for a reduced ionicity of the MgO substrate. As the interest in the surface chemistry of metal oxides is growing rapidly, it seems worthwhile to re-examine in detail the electronic charge density near the (001) surface of crystalline MgO and its influence on the electrostatic field above the substrate. For this purpose, LDF calculations on slab models of the MgO(001) surface were performed, based on the LCGTO technique with large and flexible basis sets. On the one hand, the resulting charge distribution is analyzed by partitioning technique based on the topological atom concept. On the other hand, a new method to characterize the Madelung field, similar to a classical multipole expansion, is proposed which directly analyzes the electrostatic potential outside the MgO(001) surface. In the second part of the present study the chemical origin of the reduced charged separation is discussed. After a more qualitative analysis of the crystal orbitals, the variational atomic orbital analysis, a modified variant of the constrained space orbital analysis, is introduced to quantify the energetic influence of the covalent contributions found in the one-particle wave functions.

II. METHOD

A. Computational details

The (001) surface of magnesium oxide was modeled by two-dimensional (2D) periodic slabs of up to five layers, exhibiting either mirror plane or glide plane symmetry. The lattice parameter was fixed to the experimental bulk value of 4.21 Å. No surface deformations were considered since in a previous HF study on MgO(001) only minor surface rumpling and relaxation was found, as confirmed by LEED measurements (rumpling $\leq 0.04$ Å, relaxation $\leq 0.05$ Å) without any noticeable influence on the electronic properties of the surface. The calculations were performed with an improved version of the FILMS program package, which utilizes expansions of Gaussian-type basis functions to represent the wave functions (orbital basis) as well as the charge density and the exchange-correlation potential (fitting bases).

The orbital basis set used throughout this study is very similar to the basis set employed in recent cluster investigations of CO adsorbed on MgO(001). It is derived from the optimized basis sets for Mg$^+$ and O$^-$ [Mg: (1s$^2$,8p$^1$); O: (1s$^2$,7p$^1$)]. However, the contraction scheme was slightly modified (Mg: [7s,4p,1d]; O: [6s,4p,1d]) and $d$-type polarization functions were added on each atom (O: $\alpha=1.154$). For magnesium a single Gaussian $d$-type function ($\alpha=0.293$) was fitted to the STO-$3G$ $d$ function used previously. In addition, the most diffuse $p$ exponent of oxygen (0.035) was only considered for $p$-type orbitals on the outer-layer atoms. To analyze the influence of $d$ polarization functions in the orbital basis set, some of the calculations were also performed without $d$ orbital basis functions.

To generate the fitting basis sets which are used to represent the charge density and the exchange-correlation potential we follow the general concept of even-tempered expansions. However, to get a more balanced basis set the
incremental factors \( \lambda_n = \alpha_n / \lambda_{n-1} \) between successive exponents (which are constant in even-tempered expansions) are allowed to decrease for the more diffuse fitting functions. This was achieved by employing the expression

\[
\alpha_n = \alpha_{\min} (\alpha_{\max}/\alpha_{\min})^{n/N} q^{n(N-n)}/(2N-2), \quad n = 0, 1, \ldots, N,
\]

where the ratio \( q = \lambda_1 / \lambda_N \) between the first and last incremental factor was set to 0.5. The most diffuse and tightest \( s \)-exponents, \( \alpha_{\min} \) and \( \alpha_{\max} \), were obtained by scaling the orbital exponents.41 The exponents of the polarization functions (\( p \)- and \( d \)-type) were chosen to be proportional to the \( s \)-type exponents and fixed such that the radial maximum position of the most diffuse polarization functions are localized at the bond centers. It was found that a \((14s,4p,4d)\) basis set for Mg and a \((12s,4p,4d)\) basis set for O provide a sufficiently flexible representations for the fitted quantities.

To avoid linear dependence of the orbital and of the fitting bases, the basis sets were automatically reduced by eliminating all eigenvectors of the corresponding normalized overlap or self-interaction (charge fit) matrix with eigenvalues less than \( 10^{-7} \). The most diffuse functions are obtained in the exchange-correlation fitting basis; in the case of the five-layer slab, six nearly linear-dependent fitting functions were eliminated by this procedure.

The \( \chi^2 \) form of the local exchange-correlation functional (\( \chi = 0.7 \)) was employed for all calculations for consistency with recent cluster investigations on CO adsorbed at MgO(001).16,17 These studies have shown that no significant changes in the results occur if a different local form of the exchange-correlation potential is used. The \( k \)-space integration was performed using the 2D analog of the tetrahedron method\(^{22} \) with 28 \( k \) points in the irreducible wedge of the 2D Brillouin zone.

The long-range Coulomb interaction lattice sums were computed without introducing cut-off radii or multipole expansions. Instead, a mixed real and reciprocal space technique was developed to evaluate these sums with an accuracy of more than ten digits. The required number of terms in the lattice sums, determined individually for each triple of primitive Gaussian exponents, ranged from zero for the tightest Gaussian orbitals up to almost 200 nearest-neighbor unit cells for the most diffuse exponents.

### B. Model convergence

As a first attempt to check the convergence of MgO slabs models towards the real MgO(001) surface, the total energies of the model systems were examined as a function of slab thickness (Table I). The cohesive or binding energy per 2D unit cell of the MgO(001) \( n \)-layer systems, defined as

\[
E_{\text{coh}}(n) = E_{\text{cal}}(\text{Mg}) + E_{\text{cal}}(\text{O}) - E_{\text{cal}}(\text{MgO}(001)),
\]

is calculated with respect to the atomic reference energies \( E_{\text{cal}}(\text{Mg}) = -5414.07 \) eV and \( E_{\text{cal}}(\text{O}) = -2023.04 \) eV which were obtained by spin-polarized LDF calculations using the same orbital basis sets. The layer-by-layer increments \( E_{\text{coh}}(n) = E_{\text{coh}}(n) - E_{\text{coh}}(n-1) \) of the cohesive energies are nearly constant, varying between 10.70 and 10.77 eV. They thus indicate a simple linear dependence:

\[
E_{\text{coh}}(n) = nE_{\text{bulk}} - 2E_{\text{surf}} = nE_{\text{coh}} - 2E_{\text{surf}}.
\]

The second-order energy of the cohesive energy on the number of layers is gained from the deviation \( E_{\text{diff}} = E_{\text{coh}} - E_{\text{surf}} \) of the computed cohesive energies from a linear fit (\( E_{\text{surf}} \)), which are indeed very small, less than 20 meV (see Table I). Similar results have been reported in HF calculations on MgO(001) slabs of up to three layers. The bulk cohesive energy \( E_{\text{bulk}} \) and the surface energy \( E_{\text{surf}} \) obtained via Eq. (3) are 10.73 and 0.64 eV, respectively. They are compared to HF results and to experimental data in Table II. Values for the O 2\( p \) valence bandwidth are also reported. The agreement of the LDF results with the experimental data is remarkably good (note the tendency of slightly overestimating the binding energy) and is generally better than that of the HF results. The influence of \( d \) polarization functions in the orbital basis set on the total energy of crystalline MgO is noticeable, as shown by the corresponding data in Tables I and II. The bulk cohesive energy is 0.13 eV smaller without \( d \) polarization functions in agreement with a recent HF study.43 On the other hand, the surface energy is calculated 14% too large (0.09 eV) without \( d \) polarization functions (Table II).

The linear behavior described by Eq. (3) can be regarded as an indication for the fact that the influence of a (001) surface on a MgO crystal is limited to the first surface layer. A possible local probe to measure the influence of the surface are core level shifts.44 Although LDF one-particle core level energies are not directly related to experimental core

<table>
<thead>
<tr>
<th>Layers</th>
<th>( E_{\text{coh}} )</th>
<th>( E_{\text{surf}} )</th>
<th>( E_{\text{reg}} )</th>
<th>( E_{\text{att}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.43</td>
<td>9.45</td>
<td>-0.02</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>20.20</td>
<td>20.18</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>30.93</td>
<td>30.91</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>41.63</td>
<td>41.64</td>
<td>-0.01</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>52.37</td>
<td>52.38</td>
<td>-0.01</td>
<td></td>
</tr>
</tbody>
</table>

\( E_{\text{coh}}(n) = nE_{\text{bulk}} - 2E_{\text{surf}} \)

### TABLE II. Comparison between theoretical and experimental energies (in eV) for MgO(001). The LDF values are derived from the present results for slabs, the HF energies were obtained in a calculation of the bulk (Ref. 7) except where indicated. The numbers in parentheses are the results from calculations without orbital \( d \) functions.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Exp.</th>
<th>LDF</th>
<th>HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cohesive energy (bulk)</td>
<td>10.27(^a)</td>
<td>10.73 (10.60)</td>
<td>7.25</td>
</tr>
<tr>
<td>Surface energy</td>
<td>0.62 ± 0.04(^b)</td>
<td>0.64 (0.73)</td>
<td>0.78(^c)</td>
</tr>
<tr>
<td>O 2( p ) bandwidth</td>
<td>4.8 ± 0.3(^d)</td>
<td>4.46(^d)</td>
<td>5.1</td>
</tr>
</tbody>
</table>

\(^a\)Reference 52.
\(^b\)Including correlation correction.
\(^c\)Reference 53.
\(^d\)Reference 8.

\( E_{\text{reg}} = E_{\text{att}} = E_{\text{diff}} = E_{\text{surf}} \)
ionization energies, they provide a useful and simple theoretical quantity to discuss different chemical environments. In this sense, the one-particle Mg(1s) and O(1s) core level energies of the various ions in the MgO slab systems are compared to each other in Table III. The values are given relative to the atomic LDF core levels of Mg \( \epsilon_{1s}(\text{Mg}) = -1253.06 \text{ eV} \) and O \( \epsilon_{1s}(\text{O}) = -511.48 \text{ eV} \). The top layer core levels are practically converged for the triple-layer MgO slab with only minor changes relative to the double layer. Furthermore, no significant difference for the subsurface atoms of the five-layer MgO slab can be seen, confirming that only the outermost layer is affected by the presence of the surface. By this criterion, all subsurface layers are essentially bulk-like.

A striking fact, however, is that both the cation and anion core level energies are shifted upward with respect to the free atom core levels. This trend can be rationalized by taking into account three effects, the ionic charges, the crystal field, and Pauli repulsion. A reasonable estimate of the core level shifts in ionic crystals may be obtained by first calculating the shifts of the corresponding free atoms as a function of their ionic charge, and then adding the local Madelung potential produced by the surrounding crystal. We found that for the magnesium ion the computed downward shifts of the free Mg 1s core level due to positive ion charges (up to \(-20 \text{ eV for Mg}^{2+}\)) are always overcompensated by the repulsive Madelung field contribution around the cationic site (up to \(+24 \text{ eV in the case of complete ionicity.} \) Thus the Mg 1s core level energy in MgO is expected to decrease in agreement with the results found for the slab models (Table III). Analogously, the upward shifts of negative oxygen ions are in general overcompensated by the attractive Madelung field around oxygen, at least for anionic charges of more than \(-1.0 \text{ a.u.} \) Hence the O 1s core level energy in MgO is expected to decrease relative to the atomic value. However, the oxygen valence orbitals become very diffuse after taking up additional electrons and therefore a strong Pauli repulsion will act on the oxygen ions in crystalline MgO. This leads to an additional upward shift of the anion core level, more profound in the bulk than at the lower coordinated surface, and obviously strong enough to produce the positive shifts of the O 1s core level energies of the MgO slab models (Table III). That upward shift due to Pauli repulsion was estimated to be in the range of up to \(+10 \text{ eV}\), by comparing the O 1s core levels of free oxygen ions to those inside an octahedron.

**FIG. 1.** Valence electron density of a MgO(001) triple layer shown in the (100) plane perpendicular to the surface. Large circles enclose the oxygen, small circles the magnesium sites. The values of the contours (solid lines) are 0.32, 0.10, 0.032, and 0.010 a.u., the dotted lines indicate the zero-flux boundaries of the topological atom regions.

Ne atoms (at MgO bulk distance) carrying the occupied frozen Mg\(^{2+}\) orbitals.

The linear behavior of the cohesive energies together with the convergence of the various core level energies provide evidence that a triple-layer MgO slab, containing one completely coordinated, bulk-like MgO layer is sufficient to model the MgO(001) surface. Indeed, most recent theoretical studies of the adsorption on MgO based on 2D periodically extended slab models were carried out with a triple-layer substrate. However, since the changes of the core levels are not very profound, an acceptable qualitative description of the surface may even be obtained from a monolayer model, as used previously to limit the necessary computational effort.

**III. CHARGE DISTRIBUTION**

The main purpose of this investigation is to characterize the charge separation in the (001) surface of a MgO crystal and to analyze its influence on the Madelung field around possible adsorption sites. In quantum chemical investigations it is common to characterize a charge distribution via an orbital population analysis (for an overview see Ref. 47). Since these methods tend to yield unrealistic results when applied to extended basis sets as used in the present investigation, we preferred to base our analysis of the charge separation directly on the charge density.

**A. Topological atoms**

The topological atom approach to define reasonably shaped, disjoint, and space-filling atomic regions for any accumulation of atoms, like molecules, clusters, crystals, etc., is based on the electron density of those systems. The atomic boundaries are defined as zero-flux surfaces in the gradient field of the total electron density. The typical size and shape of these topological atoms in a MgO(001) surface are illustrated in Fig. 1 for a triple-layer slab. The two types of ions are clearly discernible and the Mg cations are, as expected, smaller than the O anions. While the bulk cations, whose shape is approximately cubic, are only coordinated to their six nearest-neighbor counterions, the shape of the an-
ions indicates that in addition to the sixfold coordination there is a direct next-nearest-neighbor oxygen—oxygen interaction.

Once the topological atoms are determined, the corresponding atomic charges can be evaluated. To avoid problems during the numerical integration due to the extremely localized core densities, only the valence electron density, including the O 2s band, was integrated. The remaining core levels describe the well localized atom-like states of the ions, in particular the 1s state of O\(^{2-}\) and all five occupied states of Mg\(^{2+}\). The valence electron density displayed in Fig. 1 for the triple-layer slab is typical for all systems investigated. The most important feature in the present context is the charge accumulation around the cation sites. It clearly shows that some of the valence charge, nominally attributed to the anionic O 2s and 2p states, is localized near the cations. Thus the MgO slab systems cannot exhibit perfect ionicity as is corroborated by the charges of the topological atoms (Table IV).

The topological atom charges exhibit a similar convergence behavior as was found for the core level shifts. The top layer charges are completely stable from the triple-layer slab on, and practically identical values are obtained for all suburface atoms in the five-layer slab. The charge separation found for the ion pairs in each MgO layer varies from \(\pm 1.615\) up to \(\pm 1.700\) a.u., and thus is remarkably lower than the nominal value of \(\pm 2.0\) a.u. for perfect ionicity. In the surface layer the charge separation is somewhat larger (by 0.039 a.u.) than in the bulk-like inner layers. A further increase of the charge separation (by 0.042 a.u.) is found for the monolayer. This is probably connected to the unique boundary conditions of this system. Below, both trends will be discussed further. The total atomic charge in each MgO layer is negligibly small, \(+0.002\) a.u. for the surface layer, and \(-0.002\) a.u. for the second layer. Thus practically no interlayer charge redistribution occurs in the MgO(001) surface, confirming the findings of a previous HF study.\(^a\)

### B. Madelung field

The direct analysis of the Madelung field generated by a MgO(001) surface has as its ultimate goal the definition of effective point charges to be used in point charge arrays surrounding finite cluster models of the MgO(001) surface as they are utilized in many adsorption studies.\(^a\)\(^\text{-}^\text{10}\) If this analysis were based on an indented, extended surface with the finite cluster removed, significant contributions to the electric field would be due to the boundary region and the results would depend crucially on the choice of the boundary. Therefore, the well-defined Madelung field of a complete substrate slab will be analyzed.

As shown in detail in the Appendix, the electrostatic potential above a surface which, like MgO(001), does not exhibit a total dipole moment, can be expressed as

\[
\varphi(s,z) = \frac{2\pi}{A} \sum_{|K|} M_K e^{-|K|z},
\]

where

\[
M_K = \int_{-\infty}^{\infty} dz \int |V| d^2s \rho(s,z) e^{-iKs} e^{+|K|z}.
\]

Because of the analogy to classical (3D) multipoles, the coefficients \(M_K\) will be denoted as “2D multipoles.” It should be pointed out that in contrast to any finite substrate model clusters, whose electrical field decreases into the vacuum as \(1/R^{1/2}\) (where \(l\) is the order of the first nonvanishing multipole moment of the cluster) the Madelung field above an infinitely extended surface decreases exponentially. The main contribution to this field arises from the 2D multipoles of the shortest nonzero reciprocal lattice vectors \(K = (\pm 2\pi/\alpha,0)\) and \((0,\pm 2\pi/a_0)\). Due to the alternating phase factor \(e^{-iKs}\) they provide a suitable measure for the effective charge separation in the MgO(001) surface. In addition, as a consequence of the exponentially increasing weight factor \(e^{+|K|z}\), these 2D multipoles are highly surface sensitive, since the subsurface layers \((z<0)\) contribute very little to the surface Madelung field.

To derive effective charges from the Madelung field, the first nonvanishing and symmetry equivalent 2D multipoles, determined from the charge distribution of the MgO slab systems, can be simulated by an array of alternating point charges. Alternatively the \(z\) dependence of the electrostatic potential above the surface could have been evaluated directly, as done for a triple MgO(001) layer in a recent HF study,\(^\text{13}\) and fitted to the analytical form (4). Unfortunately the data reported there are not given explicitly.

In this study, the first approach is used; the resulting effective charges are also listed in Table IV. A charge separation characterized by values between \(\pm 1.603\) and \(\pm 1.816\) a.u. was found for the various model systems. Again, con-
vergence of the effective charges is reached with the triple-layer slab with only minor changes relative to the double-layer system. Hence a significant reduction in the charge separation, as compared to a fully ionic compound, may also be deduced from the Madelung analysis of the MgO(001) surface. In this context it is interesting to note that the neglect of \( d \) polarization functions in the orbital basis set leads to a substantial increase of the effective charge separation by about 0.25 a.u. Except for the monolayer, the nominal ionicity of \( \pm 2.0 \) a.u. is reached, similar to the findings of several HF studies \(^{7,8,13,19,90}\) which also employed orbital basis sets without \( d \) polarization functions (see Sec. V).

It is most striking to note the discrepancy between the values of the atomic charges derived by the two procedures, the Madelung analysis and the topological atom method. However, these differences may easily be rationalized by higher multipoles of the charge distribution and their influence on the 2D multipoles. Let us imagine the charge density of the slab to be constructed as a periodic superposition of localized cationic and anionic contributions, e.g., of topological atoms. If such an individual atomic contribution \( \rho^{(\pm)} \) is centered at \((s_0, z_0)\), one derives the following general relation between its classical 3D multipoles \( \sum m \rho^{(\pm)} \) and the 2D multipoles \( M_k^{(\pm)} \) of its periodic superposition (see the Appendix):

\[
M_k^{(\pm)} = e^{-iK_0K_0} \sum_{m} 4\pi \left(2l + 1\right)! \times \left(-iK_0K_0\right)^m \rho^{(\pm)} \rho^{(\mp)}.
\]

This relationship holds separately for the cations and anions, and one finally arrives at

\[
M_k = M_k^{(\pm)} + M_k^{(-)}.
\]

Not only the monopoles (total charges), but all 3D multipoles contribute via the 2D multipoles to the value of the effective Madelung charges of the MgO surface. Since there is no factor which significantly suppresses contributions of higher-order terms, the effective Madelung charges must be regarded as a global measure including higher-order multipole effects. That these higher multipole contributions to the Madelung field above the MgO(001) surface are important, can be derived from the results reported in a recent cluster investigation on CO adsorption on MgO(001).\(^{18}\) It was found that the CO adsorption characteristics depend on the explicit treatment of the ions surrounding the "inner" MgO\(_x\) cluster (for the cationic adsorption site). A poor description of the outer ions, not allowing for any polarization, or even their simulation by simple point charges led to an incorrect electric field acting on the CO adsorbate.

In addition Eq. (6) may help to rationalize the distinct decrease of the effective Madelung charges observed for the MgO monolayer. Charge displacements from the top-layer anions into the vacuum, probably the most important polarization effects, increase the oxygen contribution to the 2D multipoles, as may easily be verified, thus enhancing the effective charge separation. However, in a monolayer slab the polarization into the vacuum occurs on both sides of the layer. Hence the upward polarization which contributes most to the 2D multipole moments is weaker than for the multilayer slabs where only one vacuum side is accessible for the top-layer atoms.

Despite the discrepancy in the absolute value, it is important to note that both procedures yield effective charges which are significantly reduced from the nominal ionic value of \( \pm 2 \) a.u. While the charges from the topological atoms may be regarded as a local characterization of the charge separation, the effective Madelung charges of \( \sim \pm 1.8 \) a.u. yield a global description of the electric field experienced by an adsorbate above the surface. Hence in model cluster investigations, where the Madelung field near the adsorbate is generated with the help of extended point charge arrays around the substrate cluster, it is appropriate to use these effective Madelung charges.

IV. BONDING CHARACTER

A. One-electron wave functions

An inspection of the charge density (Fig. 1) reveals that the additional valence charge of Mg is not due to a distribution that just enters across the atomic boundaries into the cation region, but instead exhibits a well-localized feature at the sites of the cations. This finding is at variance with the well-known picture of perfect, closed-shell ions, interacting via Coulomb attraction and Pauli repulsion (see, e.g., Ref. 4), which is also invoked in recent HF calculations.\(^{7,8,13}\)

To examine the binding mechanism in MgO the one-electron Bloch wave functions (the crystal orbitals) will be analyzed in some detail. Two characteristic examples of valence one-electron wave functions of the MgO(001) monolayer are shown in Fig. 2. The first one depicts the low-lying O 2s dominated valence band at the \( \Gamma \) point (20.1 eV), the second one is from the high-lying O 2p dominated valence band complex at the \( M \) point (7.1 eV). The translational symmetry of the wave functions as determined by the \( k \) points is easily recognized. The dominating atomic orbital contributions around the oxygen atom are also clearly discernible. Furthermore, one is able to discriminate a significant overlap between neighboring O 2p orbitals, confirming the existence of a direct oxygen–oxygen interaction as already indicated by the shape of the topological anions. However, in the present context, the most important features are the nonvanishing \( s \)– or \( p \)-type contributions at the cation sites which lead to the valence charge density localized on Mg. Their nodal patterns match in shape and size the nodes of the unoccupied Mg 3s and Mg 3p states of the free Mg\(_2^+\) ion. It seems as if the \( O^2- \) valence electrons, despite the Pauli repulsion of the closed-shell Mg\(_2^+\) cation, are sharing some of the virtual cation orbitals. However, whether this behavior represents a covalent contribution to the Mg–O bond or whether it is simply a consequence of the orthogonalization of the rather extended oxygen orbitals with respect to the magnesium core orbitals will be the subject of further analysis.

Nevertheless a consistent explanation of the trends observed for the atomic charges of the topological atoms is feasible based on such valence contributions (Table IV). As will be confirmed in Sec. IV B, the valence electrons of the
B. Variational atomic orbital analysis

To address the question of possible covalent contribution to the Mg–O bond, the valence bands of MgO were analyzed within the linear combination of atomic orbital (LCAO) picture. For the sake of simplicity, this analysis was carried out for the MgO(001) monolayer. However, since the monolayer already exhibits all typical features of the MgO surface, the qualitative results will also hold for the real surface.

The central concept of our analysis is to reexpress the GTO orbital basis sets used for Mg and O by the atomic orbitals of the Mg$^{2+}$ and O$^{2-}$ ions. This transformation to an alternative, but equivalent basis set will allow us to explicitly remove specific atomic orbitals from the variational space. In this way, we are able to probe their relevance for the different bonding mechanisms, like polarization, charge transfer, and covalent bonding, and to examine the energetic consequences of these reductions in the variational freedom. This variational atomic orbital (VAO) analysis bears some similarities to the constrained space orbital variation analysis. However, no mutual orthogonalization of orbital subsets is required in the present scheme. Another useful feature of the alternative VAO basis set is the possibility to perform a population analysis in terms of rather localized atomic orbitals.

The Mg$^{2+}$ orbitals were taken from a LDF atomic calculation using the original Mg orbital basis set. To arrive at realistic orbitals for O$^{2-}$, a more complicated procedure had to be performed. The O$^{2-}$ ion, which is unstable in the gas phase, is stabilized in crystalline MgO by the surrounding cations. Thus, to generate the O$^{2-}$ orbitals, we surrounded the O$^{2-}$ ion octahedrally by Mg$^{2+}$ ions, like in MgO, described by a minimal basis of fully contracted atomic orbitals determined previously. Finally the Mg contributions, required for the orthogonality of the O$^{2-}$ orbitals on those of the frozen cations, were removed from the eigenstates and the resulting pure O$^{2-}$ wave functions were reorthogonalized. For the following, it is important to note that, as a consequence of the special O$^{2-}$ reference, important polarization effects are already built into the O$^{2-}$ basis set. The only chemical effects that may be investigated with the chosen VAO basis set are covalent contributions, Mg polarization, and O “repolarization” due to the difference in the chemical environment produced by an Mg$^{2+}$ octahedron and a MgO monolayer.

Three different VAO basis subsets have been used for the two ions. A minimal basis ($m$) containing only the occupied 1s, 2s, and 2p orbitals, a so-called valence basis ($v$), which is derived from the minimal basis by adding the unoccupied 3s and 3p orbitals, and the full VAO basis set ($f$) of each ion. Various combinations of these VAO basis subsets have been taken into account, which will be denoted in the following by ($x,y$) with $x$ and $y$ indicating the atomic basis set used for the Mg$^{2+}$ cation and O$^{2-}$ anion, respectively. However, the valence basis ($v$) was only employed for Mg$^{2+}$.
TABLE V. Population analysis of the valence bands of a MgO(001) monolayer in terms of atomic orbitals of Mg$^{2+}$ and O$^{2-}$. For details on the O$^{2-}$ orbitals see the text. Contributions less than 1% are omitted for clarity.

<table>
<thead>
<tr>
<th>Band complex</th>
<th>Cation orbitals</th>
<th>Anion orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2s  3s  2p  3p</td>
<td>2s  3s  2p  3p</td>
</tr>
<tr>
<td>O 2s</td>
<td>0.02 0.24 1.76 0.03 0.01</td>
<td>0.02 0.24 1.76 0.03 0.01</td>
</tr>
<tr>
<td>O 2p$<em>{z}$, 2p$</em>{y}$</td>
<td>0.47 0.88 0.01 0.05 0.20</td>
<td>0.47 0.88 0.01 0.05 0.20</td>
</tr>
<tr>
<td>O 2p$_{z}$</td>
<td>0.13</td>
<td>0.13</td>
</tr>
</tbody>
</table>

The results of the variational atomic orbital analysis for the MgO(001) monolayer are summarized in the Tables V and VI. Table V shows results from a population analysis of the O 2s and 2p dominated bands in terms of the Mg$^{2+}$ and O$^{2-}$ orbitals of the 2σ and 3σ shell. On the one hand, no Mg 2s and 2p contributions were found in any of the valence bands, on the other hand, a significant Mg 3s and 3p population together with a reduced O 2s and 2p population is clearly discernible. Thus the features around the cation sites in the one-electron wave functions of MgO cannot be interpreted by core orthogonalization, but have to be regarded as covalent Mg 3s and 3p admixtures to the valence bands in crystalline MgO.

Although this covalent contribution to the Mg--O bond in solid MgO is of significant importance for the charge separation, its influence on the cohesive energy is not as profound, as can be deduced from the results displayed in Table VI. Concerning the energetics, electrostatic attraction, Pauli repulsion, and oxygen polarization seem to be the major mechanisms, as can be seen from the minimal basis calculation (m,m) in which only the occupied ion orbitals are used. This calculation may also be regarded as an approximate frozen ion calculation (with polarized oxygen ions). It leads to a cohesive energy of 7.88 eV which is 84% of the total cohesive energy of 9.43 eV. The remaining amount of 1.55 eV is distributed among the different bonding mechanisms as follows: 0.67 eV covalent contribution (m,m)→(v,m), 0.27 eV Mg polarization (v,m)→(f,m), and 0.61 eV final O repolarization (f,m)→(f,f). Since some of the more diffuse ionic Mg orbitals can also contribute to the O repolarization (and vice versa), the energy partitioning according to the various mechanisms cannot be taken in quantitative sense. Thus the energetic contributions are modified to some extent when the basis set is released in a different order (Table VI): 0.87 eV O repolarization on the

frozen cation (m,m)→(m,m), 0.37 eV covalent contribution (m,f)→(v,f), and 0.31 eV Mg polarization including the O relaxation on the modified cation (v,f)→(f,f). Furthermore, the basis set superposition error (BSSE)\textsuperscript{43} may affect the individual cohesive energies. As the standard counterpoise correction\textsuperscript{48} cannot be applied easily to an extended system, the possible errors have been estimated by calculations of single atoms using augmented basis sets which correspond to the nearest-neighbor coordination in the crystal. The calculated corrections are 0.01 eV for O and 0.04 eV for Mg. Thus for the present analysis the BSSE is only of minor importance.

In summary, the covalent contribution to the Mg--O bond is estimated to be about 0.5 eV, although the cohesive energy increases by 0.67 eV in the “frozen ion” step (m,m)→(v,m). This difference is related to the fact that the Mg$^{2+}$ 3s and 3p orbitals, which in MgO exhibit some overlap with the O valence region, are also involved in some O repolarization of the frozen ion. The small energetic effect of the partial covalent bond in MgO is indirectly confirmed by the large variety of very successful force field simulations on the structure and energetics of various MgO surfaces which do not directly take into account any covalent bonding effect.\textsuperscript{4}

V. DISCUSSION

The reduced charge separation found in the present work agrees quite well, at least qualitatively, with the various previous analyses of the experiments,\textsuperscript{2,27} but is at variance with the results of previous HF studies on bulk MgO\textsuperscript{7} and MgO(001) slabs.\textsuperscript{8,13} In those calculations a minimal basis for the ions has been extended by a single shell of 3s 3p “polarization” functions (equal exponents for s- and p-type functions). This choice of the basis set influences the Mg valence population; increases from −0.069 to −0.163 a.u. for the monolayer and from −0.056 to −0.133 a.u. for the double layer are reported, when the Gaussian exponent of the polarization functions (the most diffuse exponent in these basis sets) is lowered from 0.40 to 0.25.\textsuperscript{8} This observed cationic charge was attributed to artifacts of the Mulliken partitioning scheme.\textsuperscript{8} We would like to mention that the most diffuse exponent in the present LDF study is 0.035.

The effect of additional d polarization functions in HF studies of crystalline MgO has been analyzed recently.\textsuperscript{43} Only a small effect on the total energy (0.1 eV) and minor d population (0.02) due to the inclusion of a d polarization function on Mg (exponent not given) were found in this study. The influence of d polarization function on O was even smaller. In another recent HF study on alkaline-earth oxides\textsuperscript{19} the ionicity of these compounds were investigated in the framework of the constrained space orbital variation method.\textsuperscript{36} On adding d polarization functions to the magnesium orbital basis set, the total energy of the analyzed [MgO$_{22}$]\textsuperscript{10−} model cluster decreases by 0.06 eV. This energetic shift was totally attributed\textsuperscript{19} to a change in the covalent contributions of 0.11 (without d functions) and 0.17 eV (with d functions) to the Mg--O bond. On the other hand, the present study has shown that in LDF calculations the inclusion of d polarization functions has significant consequences.

TABLE VI. Variational atomic orbital analysis of the MgO(001) monolayer. Cohesive energies (in eV) as a function of the atomic orbitals of Mg$^{2+}$ and O$^{2-}$ included in the basis sets used for Mg and O: m—minimal, v—valence, f—full basis set for Mg (see text). The individual energy increases (ΔEcoh) due to the basis set changes are also given.

<table>
<thead>
<tr>
<th>Basis set</th>
<th>E$_{coh}$</th>
<th>ΔE$_{coh}$</th>
<th>Basis set</th>
<th>E$_{coh}$</th>
<th>ΔE$_{coh}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(m,m)</td>
<td>7.88</td>
<td>7.88</td>
<td>(m,m)</td>
<td>7.88</td>
<td>7.88</td>
</tr>
<tr>
<td>(v,m)</td>
<td>8.55 0.67</td>
<td>8.75 0.87</td>
<td>(f,m)</td>
<td>9.12 0.37</td>
<td>9.43 0.31</td>
</tr>
<tr>
<td>(f,f)</td>
<td>9.43 0.61</td>
<td>9.43 0.31</td>
<td>(f,f)</td>
<td>9.43 0.61</td>
<td>9.43 0.31</td>
</tr>
</tbody>
</table>

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The cohesive energy is reduced by 0.29 eV for the MgO(001) monolayer, by 0.46 eV for the double-layer, and by 0.59 eV for the triple-layer slab, when the \( d \) polarization functions are removed from the basis set (Table I). The effect on the charge distribution is even more profound, as the absolute value of the effective charges characterizing the Madelung field increases by about 0.25 a.u. upon the removal of the \( d \) functions, reaching the value \( \pm 2.0 \) a.u. of nominal ionicity in the case of the double- and triple-layer slab. Further investigations are desirable to establish the extent to which fundamental differences between LDF and HF theory, implementational details, or different basis sets are responsible for these differences.

In this context a recent cluster study of CO adsorbed on MgO(001) is of importance, where the HF and the LDF method are compared using identical orbital basis sets and cluster geometries. It was found that HF theory in comparison to LDF theory tends to overestimate the ionicity of the chemical bond in MgO. This is in perfect agreement with the discrepancy between the present results for the charge separation in MgO(001) and those of previous HF calculations. One may speculate that the inclusion of correlation effects into the HF method as well as the use of nonlocal exchange-correlation functionals in the LDF method would reduce these discrepancies.

VI. CONCLUSIONS

The charge distribution in the MgO(001) surface has been analyzed in detail by means of 2D periodically extended model systems. The LDF cohesive energy of the MgO(001) model slabs (up to five layers) show a perfect linear dependence on the number of layers. Moreover, model convergence is reached by the triple-layer system, containing just one completely coordinated, bulk-like layer. Thus the influence of the (001) surface on the MgO crystal is essentially limited to the top surface layer.

The local characterization of the charge distribution in the MgO surface as given by the atomic charges of the topological atoms leads to a charge separation of \( \pm 1.66 \) a.u. in the top layer and \( \pm 1.62 \) a.u. in all subsurface layers, values that are significantly below the nominal ionic value of \( \pm 2.0 \) a.u. The electric field acting on potential adsorbates above the MgO(001) surfaces, however, is characterized by effective Madelung charges of \( \pm 1.81 \) a.u. This value is appropriate for the description of the surface Madelung field, e.g., when point charge arrays are used in adsorption cluster models of MgO(001).

The valence electron density of MgO exhibits a noticeable charge accumulation around the cations. In addition, the O 2\( s \) and O 2\( p \) dominated one-electron valence wave functions are rather delocalized and, despite the Pauli repulsion of the closed-shell cations, are able to use some extent atomic orbitals of Mg. Typical Mg 3\( s \) and 3\( p \) structures are clearly discernible in these wave functions. With the help of a variational atomic orbital analysis these features were identified as covalent contributions to the Mg–O bond. Although their influence on the charge separation of solid MgO is quite significant, they affect the cohesive energy by only 5% (~0.5 eV). Concerning the bonding mechanism, one may speculate that electrophilic adsorbates (Lewis acids) may directly interact with the rather extended valence states of the oxygen anions. One of the driving forces for such a process would be the Pauli repulsion between the surface anions and the surrounding closed-shell cation which could be significantly reduced by this type of interaction.

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APPENDIX: 2D MULTipoLES

An expression for the electrostatic potential generated by an extended, 2D periodic charge distribution \( \rho \) will be derived, using Green’s functions. In the special case of a charge density restricted to the half-space \( z<z_0 \) it will lead directly to the 2D multipoles. Finally a relation between 2D multipoles and classical 3D multipoles will be derived.

In the following we will use Cartesian coordinates \((s,z)\) where \( s \) is a 2D vector parallel to the surface and \( z \) is the coordinate perpendicular to the surface. The periodic charge density \( \rho \) can be expressed by a Fourier expansion:

\[
\rho(s,z) = \sum_k \rho_k(z) e^{ik_s}.
\]

where

\[
\rho_k(z) = \frac{1}{A} \int_{UC} \rho(s,z) e^{-iks} d^2s.
\]

Here, UC is any unit cell of the underlying 2D periodic lattice, \( A \) its area, and \( K \) denotes the 2D vectors of the corresponding reciprocal lattice. A similar expression holds for the periodic electrostatic potential

\[
\varphi(s,z) = \sum_k \varphi_k(z) e^{iks}.
\]

The Poisson equation applied to these representations reduces to a differential equation for the Fourier coefficients:

\[
(\partial^2_z - K^2) \varphi_k(z) = -4 \pi \rho_k(z).
\]

The physical boundary conditions

\[
K \neq 0: \quad \lim_{z \to \pm \infty} \varphi_k(z) = 0,
\]

\[
K = 0: \quad \lim_{z \to \pm \infty} \varphi_0(z) = \pm (p - qz)
\]

with suitable, but identical coefficients \( p \) and \( q \) in both limits together with the cusp condition

\[
\lim_{\epsilon \to 0^+} [\partial_z G_k(z + \epsilon, z') - \partial_z G_k(z - \epsilon, z')]|_{z'=z} = -4 \pi e^{-q}\epsilon
\]

leads to the symmetric Green’s function.
\[ K \neq 0: \quad G_k(z, z') = \frac{2 \pi}{|k|} e^{-|k||z - z'|}, \quad (A7) \]
\[ K = 0: \quad G_0(z, z') = -2 \pi |z - z'|. \]

The general solution of the differential equation (A4) is then given by
\[ \varphi_k(z) = \int_{-\infty}^{\infty} G_k(z, z') \rho_k(z') dz'. \quad (A8) \]

To obtain the 2D multipoles, we assume that the charge density vanishes (or at least decreases sufficiently rapidly) for all \( z \) greater than an upper boundary \( z_0 \). In this case the expression for the electric potential (A8), restricted to arguments \( z > z_0 \), reduces to
\[ K \neq 0: \quad \varphi_k(z) = \frac{2 \pi}{A} e^{-|k||z_0|} M_k, \]
\[ K = 0: \quad \varphi_0(z) = \frac{2 \pi}{A} (P - Qz), \quad (A9) \]

where the quantities \( M_k, P, \) and \( Q \), denoted as 2D multipoles, are defined as
\[ M_k = \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} d^2 s \ e^{-ik\xi} \rho(s, z), \]
\[ P = \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} d^2 s \ \rho(s, z), \]
\[ Q = \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} d^2 s \ \rho(s, z). \quad (A10) \]

The 2D multipoles \( Q \) and \( P \) for the zero reciprocal lattice vector are the total charge and \( z \) dipole moment per unit cell.

The 2D multipoles of a periodic superposition of a given finite charge distribution \( \rho_0 \) are uniquely determined by the classical 3D multipoles of \( \rho_0 \). Let \( \rho(s, z) \) be the periodic superposition (at 2D lattice vectors \( R \)) of the finite charge distribution \( \rho_0 \) centered at \( (s_0, z_0) \). Then one obtains
\[ M_k = \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} d^2 s \ e^{-ik\xi} \rho_0(s - s_0 - R, z - z_0), \]
\[ = e^{-ik\xi_0} e^{-|k||z_0|} \tilde{\rho}_0(k, |K|), \quad (A11) \]

where \( \tilde{\rho}_0 \) denotes the Fourier transform of \( \rho_0 \). Using the expansion
\[ e^{-ik\xi} = \sum_{lm} 4 \pi (-i)^l j_l(|k||r|) Y_{lm}(|\hat{r}|) Y_{lm}(|\hat{r}|), \quad (A12) \]

the Fourier transform \( \tilde{\rho}_0 \) may be written as
\[ \tilde{\rho}_0(k) = 4 \pi \sum_{lm} (-i)^l Y_{lm}(|k|) \int_{R^3} \rho_0(r) Y_{lm}^* (\hat{r}|k|) |r| d^3 r. \quad (A13) \]

The absolute value \( |k| \) of the special argument \( k = (K, |K|) \) required in Eq. (A11) is zero. Hence, together with the expansion valid for small arguments \( x, \)
\[ j_l(x) = \frac{x^l}{(2l + 1)!!} + O(x^{l+1}), \quad (A14) \]

Eq. (A13) substituted into Eq. (A11) finally yields
\[ M_k = e^{-ik\xi_0} e^{-|k||z_0|} \sum_{lm} \frac{4 \pi}{(2l + 1)!!} Q_{lm} Y_{lm}(-iK, |k|). \quad (A15) \]

Here the quantities \( Q_{lm} \) represent the classical multipoles of the charge distribution \( \rho_0 \) and \( Y_{lm} (\hat{k}) \) the corresponding harmonic polynomials.51

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