

Theoretical study of the surface reactivity of alkaline earth oxides: Local density of states evaluation of the local softness

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The local softness of MgO, CaO, SrO, and BaO (100) surfaces has been studied using a model based on the local density of states. In all the species, the local softness (chemical reactivity) of oxygen atoms at the surface is enhanced as compared to the bulk. The results for the local and the global softness are in agreement with the ionic pattern of the metal-oxygen bond of the series. © 2008 American Institute of Physics. [DOI: 10.1063/1.2819239]

I. INTRODUCTION

Chemical reactivity descriptors of the density functional theory (DFT), such as electronegativity,¹ hardness,² Fukui function,³ and local softness,² are widely applied in the study of chemical reactivity in molecules, especially in organic chemistry.^{4,5} Explorations of these descriptors in extended systems such as large clusters, surfaces, or solids are less usual, however. Reactivity descriptors, as they are defined in DFT, are based on frontier orbital properties,³ namely, the energies and electron densities of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). In an infinitely extended system such as a solid or a surface, the electronic states are not discrete, but they form continuous bands. In these cases, not only will local reactivity be controlled by the HOMO or LUMO but many states close in energy to the HOMO and LUMO will be able to respond to an external perturbation. Nevertheless, it is possible to compute the local softness from the local density of states (LDOS) $g(\mathbf{r}, E)$.^{6,7} The local softness is the derivative of the electron density $\rho(\mathbf{r})$ with respect to the chemical potential μ at constant external potential $v(\mathbf{r})$,

$$s(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial \mu} \right)_v. \quad (1)$$

In the context of this paper, μ is the top of the valence band and is equal to the maximum value of the energy for which the local density goes to zero for any position \mathbf{r} .

Writing the density in terms of the LDOS and changing the derivative of Eq. (1) and using the definition of a derivative as a limit, we have

$$s(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial \mu} \right)_v = \lim_{\delta\mu \rightarrow 0} \frac{1}{\delta\mu} \int_{\mu-\delta\mu}^{\mu} g(\mathbf{r}, E) dE, \quad (2)$$

where $\delta\mu$ can be positive or negative depending on whether the system gains or loses electrons. Equation (2) is a frozen orbital approximation to the exact expression for the softness introduced by Cohen and Ganduglia-Pirovano⁸ where an extra term involving the derivative of LDOS with respect to μ is included. Equation (2) was successfully used to describe local reactivity in metallic nanotubes⁷ and silicon reconstructed surface.⁶ An expression based on similar grounds as Eq. (1) has previously been used to explain local reactivity of alkaline-exchanged zeolites and the adsorption of benzene on Cu and Na-exchanged zeolites,^{9,10} albeit there is a difference in the rigorous way of selecting the smallest possible value of $\delta\mu$ through considering the explicit limit in Eq. (2).

In the present work, we undertake a first attempt to use a LDOS based local softness description to study the surface reactivity of alkaline earth oxides. These oxides form crystals generally assuming cubic symmetry and exposing low

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TABLE I. Bulk and surface structural properties: Bulk cell parameter (a), surface relaxation (ρ), surface rumpling (ε), and surface energy (γ). BaO*: BaO surface modeled as a six slab supercell relaxing the first and second layers of atoms.

Oxide	a (Å)			ρ (%)		ε (%)		γ (J/m ²)			
	Ref. 24	Ref. 23	Expt.	Ref. 23	Ref. 23	Ref. 23	Ref. 24	Ref. 23	Ref. 23		
MgO	4.24	4.25	4.30	4.21	0.0	-0.2	2.2	2.2	0.83	0.9	1.02
CaO	4.84	4.83	4.84	4.81	-1.8	-2.7	-0.3	-0.2	0.68	0.63	0.66
SrO	5.19	5.19	5.19	5.11	-2.0	-3.0	-2.0	-1.3	0.51	0.53	0.61
BaO	5.60	5.6	5.59	5.52	-4.0	-4.0	-3.8	-1.6	0.34	0.33	0.42
BaO*					-5.1		-2.1		0.27		

index (100) faces.¹¹ On the (100) surface, both metal cation and oxygen anion represent the active sites. The electron rich oxygen centers are especially reactive, with a very high proclivity to donate charge¹²⁻¹⁴ that they could be considered as superbasic sites.¹⁵ The purpose of this study is to characterize the local reactivity, particularly toward loss of electrons, through the local softness, of the whole series of alkaline earth oxide (100) surfaces with rocksalt structure, MgO, CaO, SrO, and BaO, permitting also to judge trends in the Periodic Table.

II. COMPUTATIONAL DETAILS

A. Bulk and surface *ab initio* calculations

Density functional theory with periodic boundary conditions and plane wave basis set was used for computing the ground state of bulk and surface models. In order to represent the core electrons, the projector-augmented wave method¹⁶ has been employed as implemented in the Vienna

ab initio package.¹⁷⁻²⁰ The general gradient approximation (GGA) for the exchange and correlation functional as proposed by Perdew *et al.*²¹ was applied. The plane wave basis set was truncated at 520 eV, which practically represents the complete basis set limit. In both (bulk and surfaces) models, changing the energy cutoff above 400 eV results in energy and structure changes smaller than 0.01 eV/atom and 0.01 Å, respectively. For sampling the reciprocal space, the Monkhorst-Pack method²² scheme was chosen, using $15 \times 15 \times 15$ and $9 \times 9 \times 1$ k meshes for bulk and surface supercells, respectively.

Since the charge density and the effective potential converge rapidly with increasing the number of k points, one can compute more precisely the DOS using the converged density and solving the Kohn-Sham equation for more k points at fixed density, i.e., without self-consistency. We have used this procedure to evaluate the local softness using a $15 \times 15 \times 1$ k mesh.

The (100) surfaces were modeled using periodically reproduced slab supercells, consisting of four oxide layers. The vacuum space between the surfaces was set to 4.5 times the primitive cubic cell parameter computed for the bulk, i.e., nine bulk interslab spaces. Starting from bulk interatomic distances, the surface layer was allowed to relax in the vertical (z) direction. In the BaO case, it was necessary to model the surface at least with six slabs and to relax both the

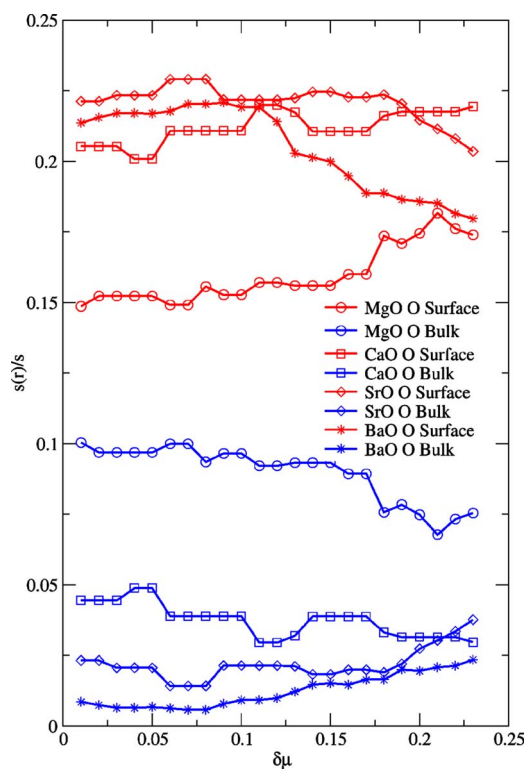


FIG. 1. (Color online) Dependence of the normalized local softness on the value selected for the parameter $\delta\mu$ (see text).

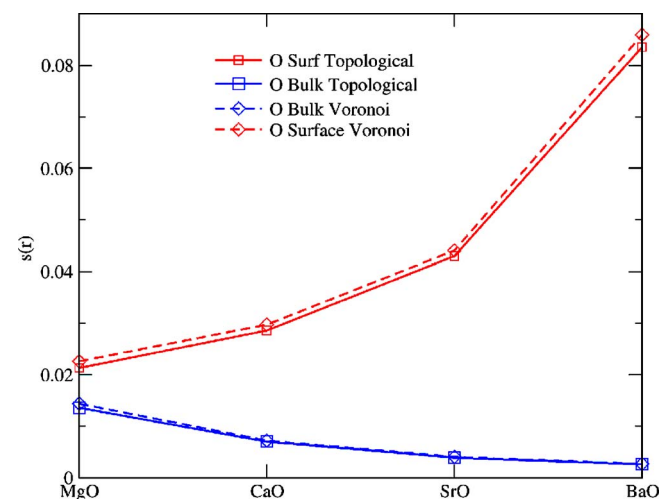


FIG. 2. (Color online) Local softness condensed to oxygen atoms at the surface and in the bulk. Voronoi and topological schemes of condensation.

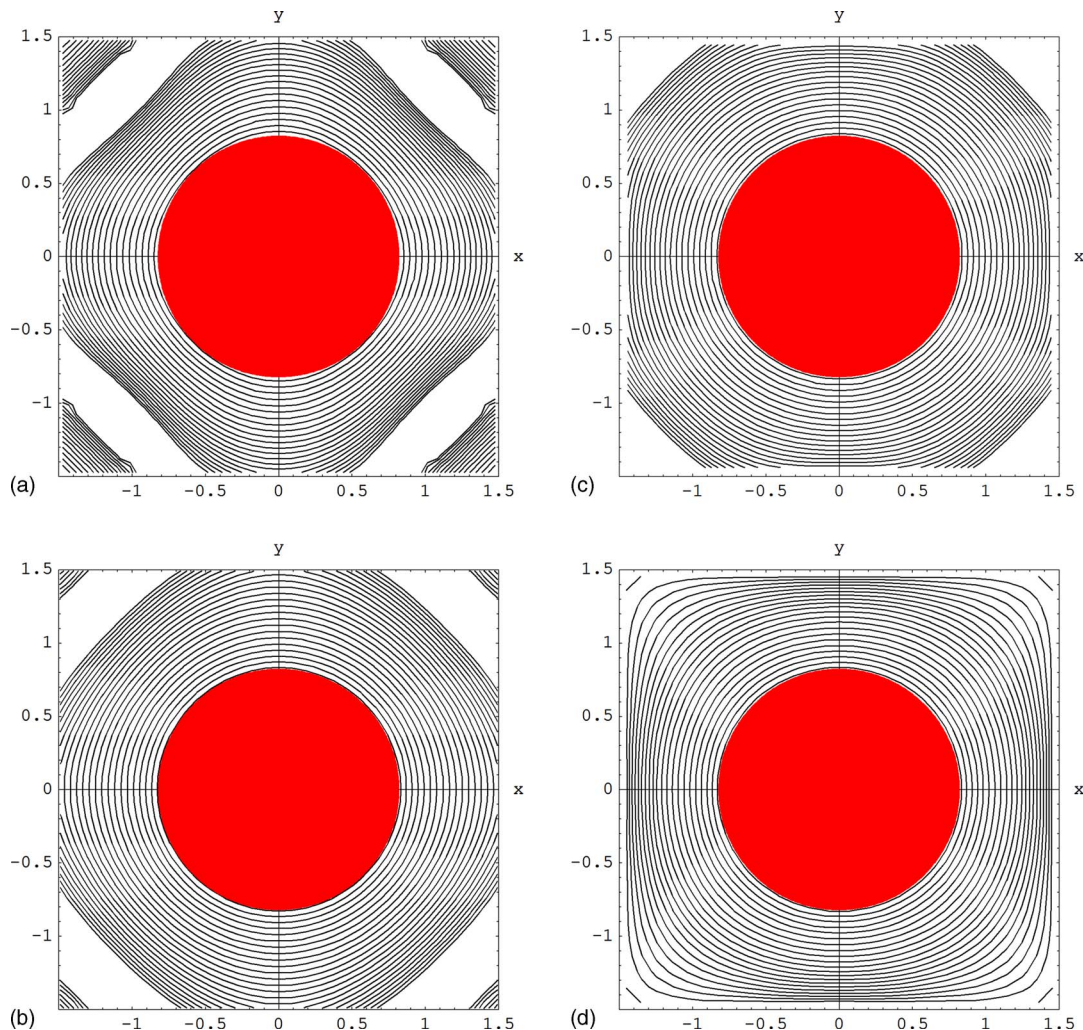


FIG. 3. (Color online) Contour plots of the local softness in the surface plane of the oxygen atoms. The contours are distributed according to $0.0001e^{i/6.27}$ with $i=1, 2, \dots, 30$. The units of $s(\mathbf{r})$ are $1/(\text{eV} \cdot \text{\AA})$. The oxygen atom is in the origin. The red disks indicate the region where the wave function is represented by the pseudofunction, the core. (a) MgO, (b) CaO, (c) SrO, and (d) BaO.

surface and subsurface layers to describe correctly the local reactivity. This procedure has been shown to be enough to mimic the principal aspect of the surface structure in alkaline earth oxides.^{23,24}

B. Computation of local softness

To take into account the states around the Fermi level, a small finite value of $\delta\mu$ has been used. To avoid working with the arbitrary virtual manifold of the Kohn-Sham spectrum and because our interest is the response of the surfaces to electrophiles, only negative values have been used. Taking the limit in Eq. (2), the expression for the softness is just the LDOS evaluated at the Fermi level, which is the previous result reported by Parr and Yang²⁵ for metallic systems. However, the participation in the reactivity of the states around the Fermi level is not negligible and it should be included in some practical way. Consequently, we can consider small finite values of $\delta\mu$.

At the same value of $\delta\mu$, the number of states counted in the integral of Eq. (2) depends on the characteristics of the band structure of each oxide. Although the global softness can be computed by integrating Eq. (2), its value will be

different from the global softness computed as the inverse of the energy gap S because Eq. (2) is not exact. In order to allow better comparisons among the series, we prefer a normalized version of Eq. (2) as working expression,

$$s(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial \mu} \right)_v = \frac{\lim_{\delta\mu \rightarrow 0} (1/\delta\mu) \int_{\mu}^{\mu+\delta\mu} g(\mathbf{r}, E) dE}{\lim_{\delta\mu \rightarrow 0} (1/\delta\mu) \int_{\mu}^{\mu+\delta\mu} g(E) dE} S. \quad (3)$$

This expression looks similar to the one reported by Santos *et al.*⁹ The difference is that in the present procedure, the limit for $\delta\mu$ was taken in order to use the smallest possible value, whereas they used a value for $\delta\mu$ as big as 10 eV in order to include all the valence states.

To condense the local softness to atoms, two completely different methodologies have been used: the Voronoi partitioning of the crystal space and the topological analysis of the local softness itself.^{26,27} In the Voronoi procedure, the local function is integrated in the Voronoi polyhedra around atoms. In the topological approach, the space is divided into basins defined by the zero flux surface of the gradient field $\nabla s(\mathbf{r})$. These regions are then assigned to atoms using as criteria the distance between the attractor enclosed for every basin and the atomic positions. It is worth stressing that the

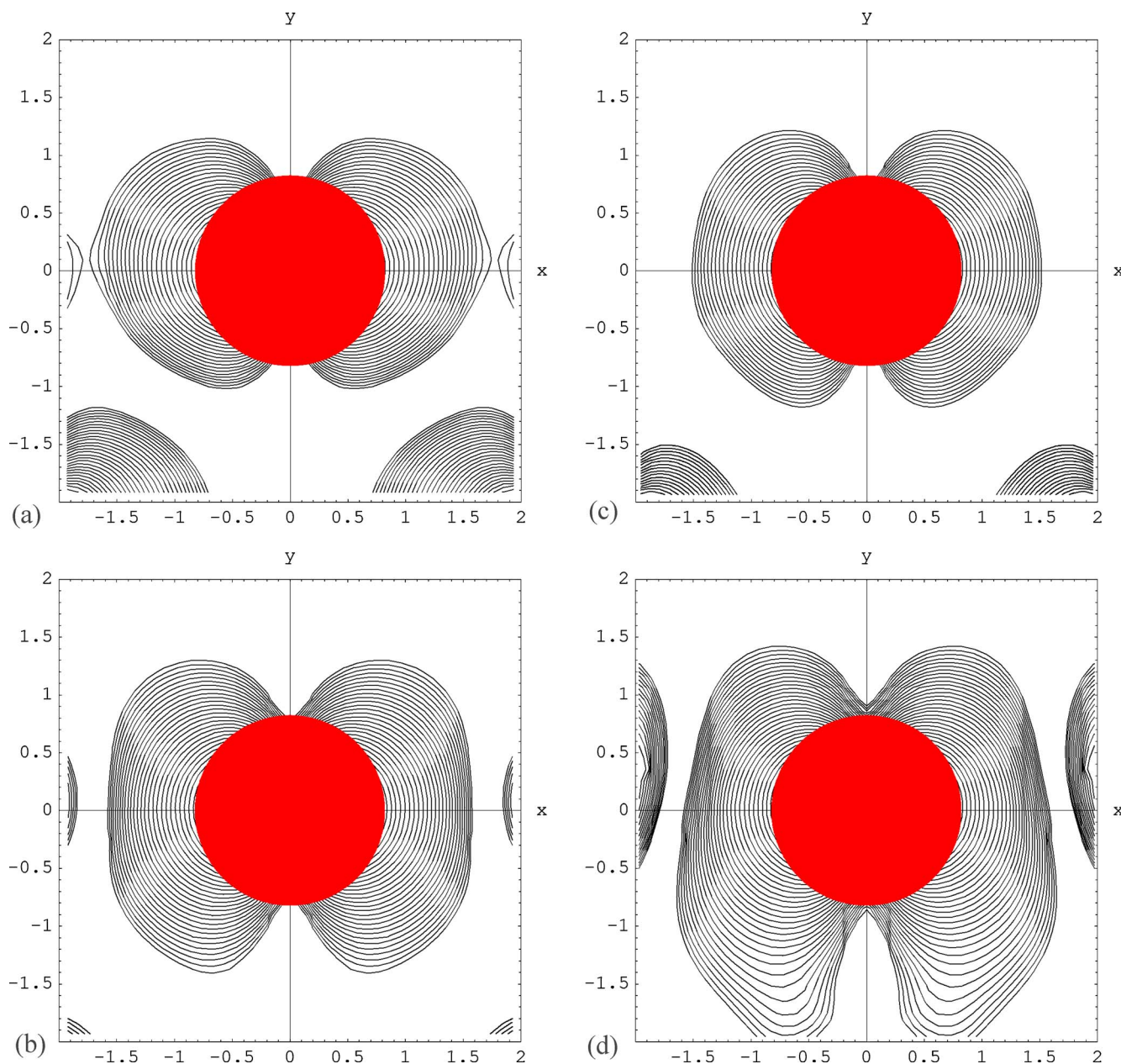


FIG. 4. (Color online) Contour plots of the local softness in the (002) plane, perpendicular to the surface. The contours are distributed according to $0.0001e^{i/6.27}$ with $i=1, 2, \dots, 30$. The units of $s(\mathbf{r})$ are $1/(\text{eV} \cdot \text{\AA})$. The oxygen atom is in the origin. The red disks indicate the region where the wave function is represented by the pseudofunction, the core. (a) MgO, (b) CaO, (c) SrO, and (d) BaO.

basins computed from the local softness are not the same as the basins of the atoms in molecules (AIM) theory. However, through the highly ionic character of alkaline earth oxides, the valence states are well localized around atoms and have an approximately spherical distribution. In these conditions, most of the basins of the gradient field of the local softness enclose atoms leading to a clear cut assignment. Nevertheless, in systems with high electron delocalization, e.g., metals, the reactivity sites will not necessarily coincide with the atom sites. In these cases, the condensation of the local softness to its own basins could be more suitable than the Voronoi scheme. We present the method of condensation based on the basins of the local softness in order to keep the presented methodology as general as possible.

III. RESULTS AND DISCUSSION

A. Bulk and surface properties

Although a full characterization of the structural and energetic aspects of the alkaline earth oxide (100) surfaces and bulk is outside the scope of this work, Table I shows the more relevant properties so as to validate our surface models against other theoretical studies.^{23,24} Alkaline earth oxides from MgO to BaO have a rocksalt structure and the primitive cubic cell parameter increases with the size of the cation. Our results for the bulk cell parameters are in perfect agreement with previously reported theoretical values and with the experimental ones, taking into account the well known overestimation of bond lengths associated with the GGA.²⁸ The relaxation ρ (which is a measure of the average change in

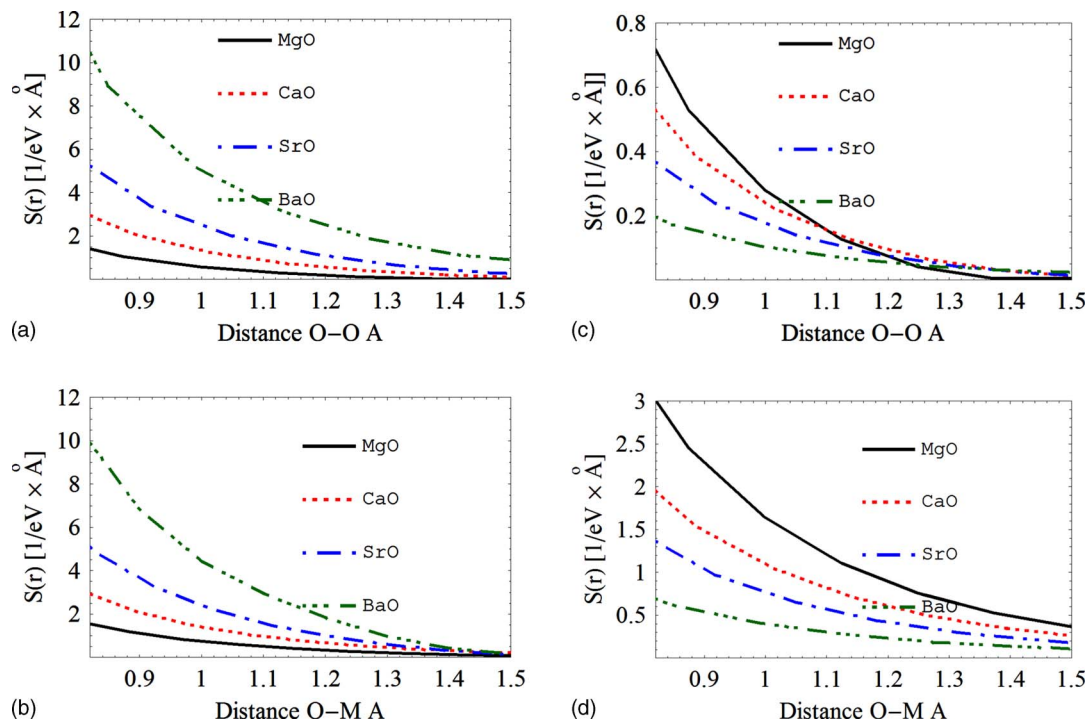


FIG. 5. (Color online) Local softness profiles along nearest neighbors. (a) along adjacent oxygen atoms at the surface. (b) along adjacent oxygen and cation at the surface. (c) along adjacent oxygen atoms in bulk. (d) along adjacent oxygen and cation in bulk.

spacing between surface and subsurface planes relative to the bulk) and rumpling (which refers to the displacement normal to the surface of the cation relative to the anion) were calculated using the definitions of Ref. 23. Except for MgO, the interplanar distance at the surface is smaller than in the bulk, and this structural change is more pronounced for big cations. For CaO, SrO, and BaO, the cations at the surface are placed above the plane of the oxygen atoms, whereas in the MgO oxide, the contrary behavior was found. These results are in agreement with previous theoretical works.^{23,24,29}

However, to date, there are no conclusive experimental results about the sign of the rumpling for these systems.^{30–33}

Our values of surface energy are in the interval of the previously reported ones for the whole series.^{23,24,29} The calculations have been also done using a seven layer slab and relaxing the atomic positions in the first layer. The results are very similar (i.e., 0.91, 0.68, 0.57, and 0.34 J/m² for MgO, CaO, SrO, and BaO, respectively). Therefore, it seems that for this type of calculations, four layers are sufficient.

B. Local softness

In order to get insight about the dependence of the local softness on the width of the band used to integrate Eq. (3), the local softness has been computed by changing $\delta\mu$ from 0.23 to 0.01 eV. Figure 1 shows the behavior of the normalized local softness (Fukui function) condensed to the oxygen atom on the surface and in the bulk. It can be seen that for all the systems, the local softness is converged for $\delta\mu$ around 0.05 eV. Hence, as long as $\delta\mu$ is selected in the region of convergence, the local softness is almost independent of $\delta\mu$. A value of $\delta\mu=0.05$ has been selected here for all the systems.

In all the species, the oxygen atom on the surface is significantly softer than the oxygen in the bulk (see Fig. 2). Because of the dominant ionic character of the oxygen-metal bond, the softness of the cations in bulk and at surface is practically zero. This is in agreement with the AIM charges on the cations, +1.73, +1.52, +1.48, and +1.44 a.u. for MgO, CaO, SrO, and BaO, respectively. The values of condensed softness are practically independent of which scheme of condensation is used, the Voronoi scheme or the topological one. From the differences between the softness in bulk and at the surface, we can conclude that the reactivity of oxygen at the surface is enhanced as compared to the oxygen in the bulk. The global softness increases with the size of the cation: 0.28, 0.36, 0.41, and 0.48 eV⁻¹ for MgO, CaO, SrO, and BaO, respectively. This tendency can be accounted for by the increasing cation polarizability with cation size because the global softness should be proportional to the polarizability.^{34,35}

The differences in softness between bulk and surface can be more clearly seen by exploring the local behavior of the softness. Figures 3 and 4 show contour plots of $s(\mathbf{r})$ in the surface plane of the oxygen atoms and the plane (002) perpendicular to the surface, respectively. One can clearly notice a striking increase of the softness of the oxygen from MgO to BaO. Note that the contour lines are expanding much more in BaO than in SrO, CaO, and MgO. Profiles along specific directions can elucidate the differences among the series clearer than contour plots. Figure 5 shows profiles of the local softness along lines that connect two nearest neighbor oxygen atoms and an oxygen atom and its neighbor cation, both at the surface and in the bulk. At the surface, in both directions, the local softness increases from MgO to BaO. The same behavior is found for the O-cation profile. In

the bulk (inner slab), the local softness is one order of magnitude smaller than at the surface and, opposed to the surface, increases from BaO to MgO. It is worth noting that the oxygen softness in BaO is practically zero in the bulk, i.e., the states below the Fermi level in this system are completely localized on the surface. This general tendency can be again rationalized from the relationship between softness and polarizability: soft systems can more easily rearrange their electronic density when they are perturbed by electric fields. The surface can be looked upon as a defect which introduces a loss of symmetry in the perfect translational symmetry. The abrupt change in the translational symmetry induces a polarization of the charge in the surface and an associated local electric field. Electrons at the surface undergo a different external field than electrons in the bulk because of the missing atoms just above the surface. In this sense, soft systems can screen efficiently the surface defect introducing small perturbations in the electronic structure of bulk states near the top of the valence band.

Since soft systems have a proclivity for covalent bonding, the ionicity of the metal-oxygen bond should decrease

from MgO to BaO. It is expected that the ionicity in these systems increases with increasing cation sizes as in isoelectronic and isostructural alkali halides.³⁶ However, the reverse trend predicted from local softness values has been previously discussed by Mankefors³⁷ in terms of the *p-d* hybridization between oxygen and metal. The decreasing ionicity is also supported by the decreasing charge of the cation. It is important to stress that the local softness does not enclose the whole reactivity of the surface but only the onset of the response of the systems to external perturbations in the chemical potential. The true reactive behavior will be also modulated by steric effects introduced by negative rumpling present in CaO, SrO, and BaO, where the big size of the cations can create a screening effect over the surface oxygen atoms.

We have also found that the local softness could depend on the model used for representing the surface, namely, on the number of relaxed layers.^{23,24} The surface induces a band bending (i.e., a dependence of LDOS condensed to atoms on the position of the atoms) in such a way that the oxygen's states on the surface are shifted up in energy with respect to

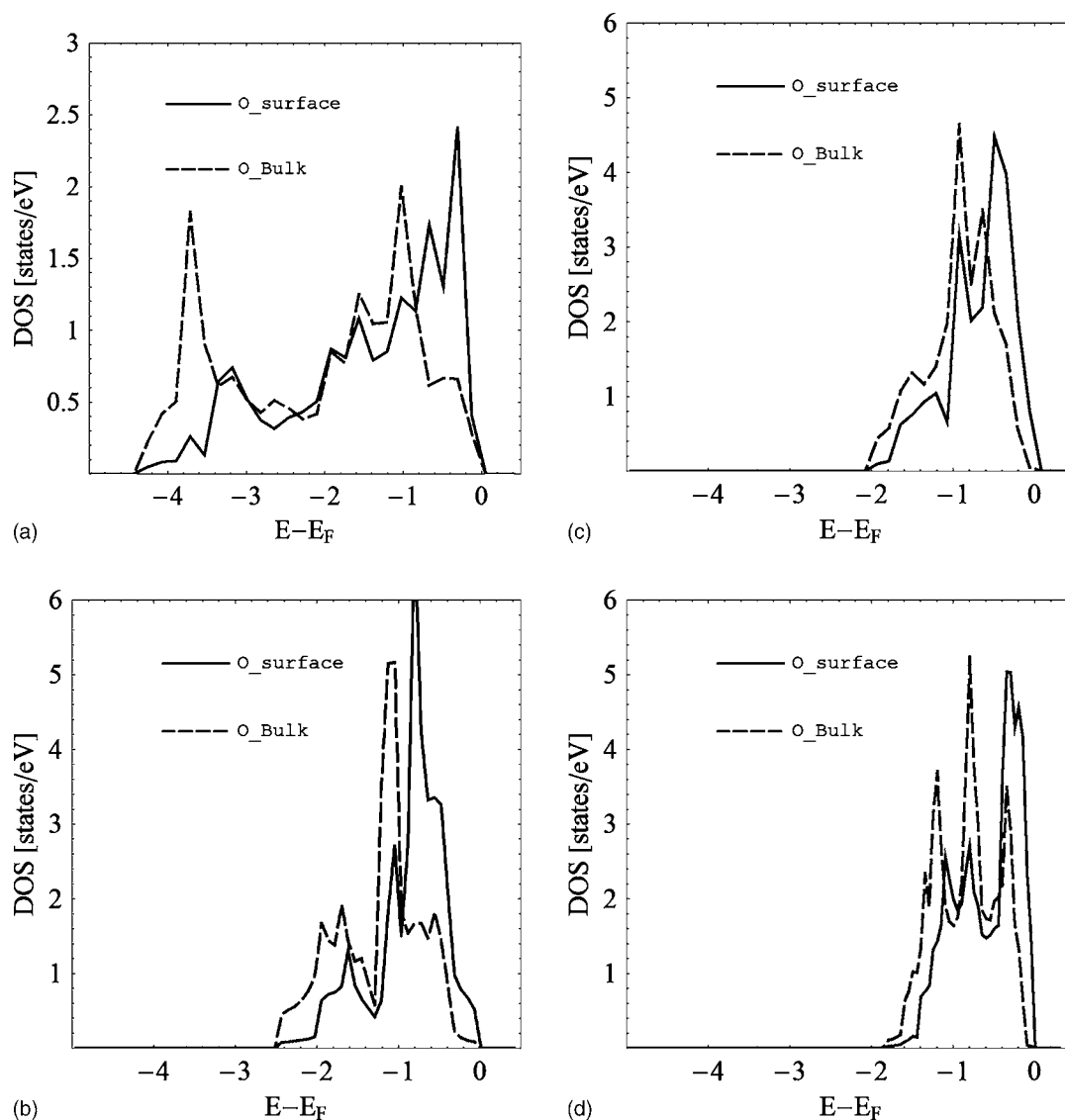


FIG. 6. Local density of states of the oxygen atom at the surface and in the bulk: (a) MgO, (b) CaO, (c) SrO, and (d) BaO.

the oxygen in the center of the slab (see Fig. 6). The relaxation of the atoms in the first slab of the MgO, CaO, and SrO surfaces decreases the intensity of the band bending, although the states in the surface's oxygen are still higher in energy and represent almost all DOS below the top of the valence band. In BaO, however, to relax only the first atomic slab is not enough to reproduce that behavior. The correct behavior in BaO is recovered when the first and second layers are allowed to relax. Although the surface energies computed from a first layer relaxed model (0.34 J/m^2) and from a two layer relaxed model (0.27 J/m^2) are similar, local properties such as local softness could be different.

IV. CONCLUSIONS

The local softness $s(\mathbf{r})$, the functional derivative of the density with respect to the chemical potential, has been evaluated numerically for the (100) surface of the earth alkaline oxides by taking the limit for small $d\mu$ of the normalized form of the local density of states. The global softness increases with the size of the cation (Mg, Ca, Sr, Ba). At the local level, the difference between bulk and surface softness is retrieved from $s(\mathbf{r})$ plots showing a considerable enhancement of reactivity of oxygen at the surface. The local softness of the oxygen atoms at the surface increases from MgO to BaO.

All in the methodology exposed in this paper can be routinely used to study the electronic properties of surfaces in terms of conceptual DFT.

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