

Computing the Fukui Function in Solid-State Chemistry: Application to Alkaline Earth Oxides Bulk and Surfaces

Published as part of *The Journal of Physical Chemistry virtual special issue "Paul Geerlings Festschrift"*.

M. L. Cerón, T. Gomez, M. Calatayud,* and C. Cárdenas*

Cite This: *J. Phys. Chem. A* 2020, 124, 2826–2833

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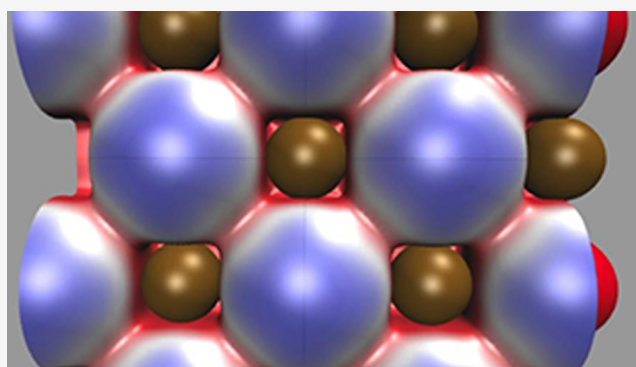
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ABSTRACT: Fukui functions (FFs) are chemical descriptors that are useful to explain the reactivity of systems toward electron transfer. Whereas they have been widely employed for molecules, their application to extended systems is scarce. One of the reasons for the limited development of such analysis in solids is the improper evaluation of FFs in the usual computational approaches based on density functional theory and periodic boundary conditions. In this work we compare the available approaches and propose a new method based on the interpolation of partially charged systems that mitigates some of the problems encountered. We discuss the reactivity of alkaline earth oxides (MgO, CaO, SrO, and BaO) in terms of the FF analysis, providing a robust way to account for the higher reactivity of surface oxygen sites compared with bulk sites.



INTRODUCTION

In both organic and inorganic chemistry it is customary to classify reactions as being controlled by either electron transfer or electrostatic effects. These are two limiting cases, however, as in actual reactions both effects are always present. This was first pointed out in the context of molecular orbital theory in seminal works by Klopman¹ and Salem.² Nevertheless, reactions mostly controlled by electron transfer are of utmost importance to chemistry because most reactions in which covalent bonds are broken and created fall within this category. It was Fukui who first realized that the reactivity of a molecule participating in an electron-transfer reaction is dictated by the density of the HOMO or LUMO, depending on whether the molecule donates or accepts electrons. That simple idea is the basis of the frontier molecular orbital (FMO) theory.³ The above-mentioned works by Klopman and Salem provided the theoretical basis for the FMO theory by using molecular orbital perturbation theory with single-determinant wave functions. That is, FMO theory seems to be linked to a coarse approximation of the wave function. However, a strict generalization of Fukui's ideas is possible within the mathematical framework of density functional theory (DFT). In 1978, Parr realized that the Lagrange multiplier of the Euler–Lagrange equation of DFT is nothing but the electronic chemical potential of the molecule, μ , and that its negative provides a nonempirical scale of electronegativity.⁴ This pioneering work was the first step to construct a unified corpus of chemical reactivity using DFT. Nowadays, this area

of research is known by the name given by Geerlings: conceptual DFT. Among the several reviews in the literature,^{5–9} the one by P. Geerlings et al. in 2003 is still the most comprehensive one.¹⁰

The chemical potential of a molecule is unique in the sense that it is the same for all parts of the molecule. Therefore, if a reaction is to happen, the chemical potential has to change. Such change comes either from the flow of electrons or from a change in the external potential of the nuclei on the electrons. If a molecule is perturbed in its number of electrons, N , and its external potential, $v(\mathbf{r})$, the first-order change in the chemical potential is

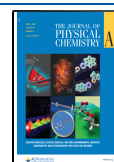
$$d\mu = \left(\frac{\partial \mu}{\partial N} \right)_{v(\mathbf{r})} dN + \int \left(\frac{\delta \mu}{\delta v(\mathbf{r})} \right)_N \delta v(\mathbf{r}) d\mathbf{r} \quad (1)$$

Hence, a molecule can be considered reactive when its chemical potential changes easily. Parr called this the “ $\Delta\mu$ big is good” rule, for which a recent proof is available.^{11–13} Therefore, for a nondegenerate ground state,^{14–17} a perturbation will be more effective in changing the chemical

Received: February 3, 2020

Revised: March 11, 2020

Published: March 12, 2020



potential if such a perturbation (a reagent) occurs in places where $\left(\frac{\delta\mu}{\delta v(\mathbf{r})}\right)_N$ is large. A Maxwell relation shows that this functional derivative is also equal to the response of the electron density to changes in the number of electrons,

$$f(\mathbf{r}) \equiv \left(\frac{\delta\mu}{\delta v(\mathbf{r})}\right)_N = \left(\frac{\partial\rho(\mathbf{r})}{\partial N}\right)_{v(\mathbf{r})} \quad (2)$$

The function $f(\mathbf{r})$ is called the Fukui function (FF) because it generalizes the FMO theory. That is better seen when the Fukui functions are written in terms of the Kohn–Sham (KS) orbitals:

$$f^{-/+}(\mathbf{r}) \equiv |\phi_{\text{HOMO/LUMO}}(\mathbf{r})|^2 + \sum_{i=1}^N \left(\frac{\partial\phi_i(\mathbf{r})}{\partial N}\right) \quad (3)$$

The Fukui function comprises two terms: the density of the HOMO or LUMO and a relaxation term. It should be noted that there are two Fukui functions, one for donation of electrons ($-$, oxidation) and one for accepting electrons ($+$, reduction). This is so because of the discontinuity of the density as a function of the number of electrons.¹⁸ In molecules, the relaxation term is usually very small because of the discrete nature of the KS orbitals' spectra.¹⁹ Summarizing, if electrostatic effects are ignored, a molecule is prone to donate/accept electrons in those sites where the Fukui function is large.

The Fukui function is extremely useful in characterizing the reactivity of molecules.²⁰ Its use is so broadly accepted that it is discussed in modern organic chemistry books. However, its use in solid-state chemistry is scarce because its calculation brings theoretical and computational challenges. Briefly, in molecules the density of the frontier orbitals is unambiguously defined, while in extended system the continuous character of the Bloch states makes it difficult to identify just one frontier state, and the relaxation term could be large. In this work, we will discuss the advantages and problems of the methods available to compute the Fukui function in solid-state chemistry and present a new method that alleviates some of those difficulties. We compare three different ways of computing the Fukui function and analyze the family of alkaline earth metal oxide (MO, M = Mg, Ca, Sr, Ba) rock salt structures using both bulk and surface slab models.

■ COMPUTATIONAL DETAILS

All the calculations were done with the Vienna Ab Initio Simulation Package (VASP).^{21–23} DFT with periodic boundary conditions and a plane-wave basis set was used to compute the ground states of bulk and surface models. Core electrons were replaced by augmentation charges according to the projector-augmented wave (PAW) method.²⁴ The generalized gradient approximation (GGA) PBE exchange–correlation functional proposed by Perdew et al. was used.²⁵ The plane-wave basis set was truncated at 500 eV (which practically represents the complete basis set limit) for the bulk systems and 400 eV for the slabs. For sampling of the reciprocal space, the Monkhorst–Pack scheme²⁶ was chosen, using $25 \times 25 \times 25$ and $15 \times 15 \times 1$ k-point meshes for the bulk and surface slabs, respectively. Integrals in the reciprocal space were done with the tetrahedron method with Blöchl corrections.

Bulk systems were computed using a conventional unit cell with four formula units. The optimized cell parameters, numbers of valence electrons, and band gaps are reported in Table S1 in the Supporting Information. They agree with experimental and previous theoretical data obtained for similar computational settings.^{27–29} The (100) surfaces were cut from the optimized bulk structure; they were six oxide layers thick and contained 12 formula units. The vacuum space between the surfaces was set to a minimum of 15 Å. Two sets of slabs were investigated: asymmetric slabs (in which the two top layers were allowed to relax) and symmetric slabs (in which the two top and two bottom layers were allowed to relax and the two central layers were kept fixed at the bulk positions). The conjugate-gradient algorithm was used in the geometry optimizations with a convergence threshold of 0.01 eV/Å for the forces. The effect of geometrical relaxation on the interlayer distance for the two slab models is reported in Table S2. A similar protocol was found to be able to describe properly the surface structure in alkaline earth oxides.²⁸

The Fukui Function f^- condensed to atoms was computed by integrating the charge (CHGCAR file) into Voronoi volumes using Henkelman's program.³⁰ Only the oxygen values are reported.

■ RESULTS AND DISCUSSION

In this section we present the computational schemes to compute the Fukui Function f^- , as well as the application to MO surfaces.

Finite Difference with $\Delta N = \pm q$. Computing the Fukui function in finite systems is straightforward from the “finite difference” expression

$$f^-(\mathbf{r}) = \rho^N(\mathbf{r}) - \rho^{N-1}(\mathbf{r}) \quad (4)$$

where N stands for the system of interest and $N - 1$ for its vertical cation. A similar expression exists for f^+ . It should be noted that although eq 4 seems to be an approximation to the derivative in eq 2, the difference in eq 4 is exact in principle. This exactness comes from the derivative discontinuity of the energy and the density as functions of the number of electrons. For finite systems, Perdew et al.¹⁸ proved that the density of an open system with $N_0 \pm \delta q$ electrons, where N_0 is an integer, is a linear combination of the densities of the systems with the closest integer numbers of electrons. Therefore, any departure from exactness for eq 4 comes from the approximations used to compute the density. In the special case of DFT, approximations to the exchange–correlation functional are designed to give good densities for integer numbers of electrons but not for noninteger numbers.³¹

The discussion of how to compute the Fukui function has so far been given mostly for finite systems.^{32,33} We will now focus on alternatives for computing the Fukui function in extended systems with periodic boundary conditions (PBCs). We will focus only on the Fukui function for removal of electrons, f^- , because in PBC calculations with GGA functionals the conduction band is normally not as accurate as the valence band. However, similar results hold for f^+ .

A natural extension of eq 4 to extended systems suggests that the Fukui function be computed by removing/adding electrons from/to the neutral system. However, this procedure leaves a charged cell or supercell, the images of which will interact electrostatically. Hence, adding or removing a whole electron can add a non-negligible unphysical external potential

to the unit cell. Naively, one may think that increasing the size of the unit cell will fix this problem. However, the Coulomb interaction is a long-range one, and regardless of how large the unit cell is, it never converges to zero. The magnitude of the effect of this electrostatic “noise” is not easy to determine a priori, but it is expected to be more significant in soft systems, such as metals with a large density of states (DOS) at the Fermi level. Approximations for canceling the electrostatic fields of charged images on the total energy are available, but these methods are usually limited to cubic unit cells. Some of us used this approach to identify the regions that maximize the Fukui function in V_2O_5 systems, allowing a qualitative visual inspection of the different oxygen surface sites³⁴ as well as a comparison of different vanadium-based systems.

In the present work, we obtained the difference between the charge files for neutral and charged systems by adjusting the total number of electrons per cell with the keyword NELECT in VASP. Table 1 displays the f^- values obtained for the four

Table 1. Values of f^- Obtained with Finite Differences (Equation 4) for the Four Bulk Systems of the Alkaline Earth Metal Oxide Series

δq	MgO	CaO	SrO	BaO
-0.05	0.168	0.167	0.171	0.157
-0.10	0.168	0.169	0.172	0.157
-0.15	0.168	0.171	0.172	0.157
-0.20	0.168	0.172	0.172	0.157
-0.25	0.168	0.171	0.172	0.157
-0.30	0.168	0.172	0.171	0.157
-1.00	0.168	0.169	0.171	0.160

bulk systems with the finite differences procedure for different values of the charge, δq . It can be observed that the values are almost constant within each series: MgO (0.168), CaO (0.167–0.172), SrO (0.171–0.172), and BaO (0.157–0.160). There are no significant differences between the fractional charges and the integer (charge -1) one. The BaO system always exhibits lower values of f^- , around 0.160, compared with MgO, CaO, and SrO, for which f^- oscillates around 0.169. The slightly lower value of f^- for BaO can be understood as a consequence of its larger softness and the condensation scheme. As Ba is the softest metal in the series, the frontier density is expected to be less localized around the oxygen atom. Hence, the Voronoi polyhedra may be not an accurate representation of the space belonging to atoms.

Fukui Functions from the Local Density of States. An alternative to evaluate the Fukui function that avoids calculations of charged cells is to compute the local softness from the local density of states (LDOS), $g(\mathbf{r}, E)$,^{6,7} and from it to compute the Fukui function. The local softness is the derivative of the electron density with respect to the chemical potential at constant external potential:

$$s(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial \mu} \right)_{v(\mathbf{r})} = \left(\frac{\partial \rho(\mathbf{r})}{\partial N} \right)_{v(\mathbf{r})} \left(\frac{\partial N}{\partial \mu} \right)_{v(\mathbf{r})} = f(\mathbf{r})S \quad (5)$$

That is, the Fukui function is equal to the local softness divided by the global softness, S . In systems with a fundamental gap, S is the inverse of the gap, while in gapless systems S is the DOS at the Fermi level. The link between the local softness and the LDOS is easily deduced from the definition of the density in terms of the LDOS,

$$\rho(\mathbf{r}) = \int^{\mu} g(\mathbf{r}, E) dE \quad (6)$$

by taking the derivative with respect to the chemical potential (Fermi level):

$$s(\mathbf{r}) = g(\mathbf{r}, \mu) + \int^{\mu} \frac{\partial g(\mathbf{r}, E)}{\partial \mu} dE \quad (7)$$

Equation 7 is very similar to eq 3 in the sense that it has a frontier contribution (the LDOS at the Fermi level) and a relaxation term (given by the integral). Contrary to molecules, the relaxation term could be not small because the density of states around the Fermi level is finite. That is, the states close to the Fermi level contribute to the Fukui function. However, there is no known analytical expression or method that allows the relaxation term in eq 7 to be computed. A decade ago, Geerlings and one of us proposed an alternative expression to include the contribution of inner states to the local softness:²⁸

$$s(\mathbf{r}) = \left(\frac{\partial \rho(\mathbf{r})}{\partial \mu} \right)_{v(\mathbf{r})} = \lim_{\delta \mu \rightarrow 0} \frac{1}{\delta \mu} \int_{\mu - \delta \mu}^{\mu} g(\mathbf{r}, E) dE \quad (8)$$

The reasoning behind this equation is that a derivative is nothing but a limit. Equation 8 has the advantage that the integral is very easy to evaluate and is available in almost any solid-state code. However, it has two disadvantages: (i) as the limit cannot be taken to zero, $s(\mathbf{r})$ depends on the value chosen for $\delta \mu$, and (ii) it assumes that states below the Fermi level contribute as much as to $s(\mathbf{r})$ as the Fermi level does, whereas it is known from perturbation theory that deeper states make smaller contributions. Possible ways to weight the contributions of inner states have been discussed elsewhere.^{35–37}

The Fukui function can be evaluated from eq 8 by normalizing it:

$$f^-(\mathbf{r}) = \frac{\lim_{\delta \mu \rightarrow 0} \int_{\mu - \delta \mu}^{\mu} g(\mathbf{r}, E) dE}{\lim_{\delta \mu \rightarrow 0} \int_{\mu - \delta \mu}^{\mu} g(\mathbf{r}, E) d\mathbf{r}} \quad (9)$$

We applied this method to evaluate f^- for the bulk systems. The partial DOS between $\delta \mu$ and the Fermi level (obtained from PARCHG files) was integrated in the Voronoi polyhedron. Table 2 shows the f^- values obtained by

Table 2. Values of f^- Obtained with the DOS for the Four Bulk Systems of the Alkaline Earth Metal Oxide Series

$\delta \mu$	MgO	CaO	SrO	BaO
-0.05	0.236	0.241	0.239	0.219
-0.10	0.235	0.240	0.239	0.219
-0.15	0.235	0.239	0.236	0.220
-0.20	0.235	0.238	0.234	0.221
-0.25	0.234	0.236	0.232	0.222
-0.30	0.234	0.236	0.232	0.222
-1.00	0.228	0.225	0.224	0.222

normalization as in eq 9 for different values of $\delta \mu$. It can be observed that for a given oxide there is little dependence on $\delta \mu$. While MgO, CaO, and SrO show similar values of around 0.23, BaO exhibits slightly smaller values of around 0.22. It is remarkable that the f^- computed with the LDOS has the same trend as f^- obtained by finite differences (Table 1). The fact that the values of f^- are smaller for finite differences than for LDOS can be attributed to fact that eq 9 misses a part of the

relaxation term in the exact expression for the softness (eq 7). It should be noted that $\delta\mu$ and δq do not represent the same quantity.

Fukui Functions from Interpolated Noninteger Number of Electrons. Using calculations with different numbers of electrons easily allows relaxation effects to be incorporated but has the trouble of creating a fictitious electric field in systems with PBCs. The approach based on the LDOS solves that problem, but relaxation effects are not strictly incorporated. Another alternative is to use finite differences with a fractional number of electrons. Importantly, reducing the step in the number of electrons in eq 4 does not fix the problem of the electric field of charged images unless δN is taken at the zero limit. A way to take that limit is to compute the densities of the neutral system, $\rho(\mathbf{r}, N_0)$, and several slightly charged systems, $\rho(\mathbf{r}, N_0 + \delta)$, $\rho(\mathbf{r}, N_0 + 2\delta)$, \dots . Then for every point in the space, a linear interpolation of the density as a function of the number of electrons can be made. The slope of such an interpolation is the Fukui function because

$$\rho(\mathbf{r}, N) = \rho(\mathbf{r}, N_0) + \frac{\partial \rho(\mathbf{r}, N)}{\partial N} (N - N_0) + \dots \quad (10)$$

Of course, this approximation will be valid only if the charge of the charged systems is small enough to fall within the linear regime of ρ versus N . This interpolation approach fixes the charged images problem and takes into account the relaxation of inner states. However, it introduces a new difficulty, which is the lack of accuracy of approximate functionals to describe the electron density of systems with a fractional number of electrons. It is well-known that local density approximation (LDA) functionals, all GGA functionals, and most hybrid and long-range-corrected functionals fail to predict the piecewise E versus N function.³¹ All of those functionals follow the same trend, which is a convex underestimation of E versus N . This underestimation results in a delocalization error in the density. That is, the density of a system with a fractional number of electrons computed with approximate functionals is less compact than the exact one.

We have written a Python script to evaluate the Fukui function from the interpolation scheme of eq 10. A copy of it is provided in the Supporting Information and can be obtained upon request.

Table 3 displays the values of f^- computed with the interpolation method for selected systems with different

Table 3. Values of f^- Condensed to O Atoms Obtained with the Interpolation Method for the Four Bulk Systems of the Alkaline Earth Metal Oxide Series

interpolation scheme	MgO	CaO	SrO	BaO
-0.15/-0.10/-0.05/0.00	0.168	0.170	0.172	0.157
-0.30/-0.20/-0.10/0.00	0.168	0.172	0.171	0.157
-0.15/-0.10/-0.05	0.168	0.172	0.172	0.157
-0.30/-0.20/-0.10	0.168	0.173	0.171	0.158

fractional numbers of electrons. The δq values were chosen to be small enough to fall within the linear behavior of the electron density, i.e., close to the neutral system. Three different charges were computed for each system, with δq ranging between $-0.30e$ and $-0.05e$, as represented by the "interpolation scheme" column in the table. In some cases the neutral system was included in the interpolation. A linear interpolation point-by-point is carried out, and a grid file

containing the interpolated values of f^- is obtained. Condensation is done within the Voronoi polyhedra. The results show that the values of condensed f^- on the oxygen sites are robust and do not exhibit significant deviations for a given composition: MgO always shows 0.168, CaO and SrO oscillate between 0.170 and 0.173, and BaO oscillates between 0.157 and 0.158. No significant change is observed upon inclusion of the neutral density in the interpolation. The results are consistent with the values obtained with finite differences of charged systems (Table 1). Although the numbers are smaller than those obtained for the DOS approach, the trend that the BaO values are smaller than those for MgO, CaO, and SrO is conserved.

To summarize, the results obtained for the bulk systems show that the different approaches lead to qualitative agreement, i.e., bulk BaO shows smaller f^- values than MgO, CaO, or SrO irrespective of the scheme used. The values obtained are robust with regard to the numerical settings within the approaches followed, although the numbers are found to be smaller when considering charged systems (finite differences and interpolation schemes) than with DOS. A remark here is that the values of condensed FF are all normalized to 1. This means that if the size of the unit cell is doubled, the values obtained will be halved, since there will be twice as many oxygen sites. A convenient way to express the values could thus be to give the FF value per formula unit, which would apply to systems with the same stoichiometry and allow comparison among them.

Application to Surfaces. The analysis of the different computational schemes to calculate f^- can be used to illustrate the different reactivities of oxygen sites located at the surface and in bulk positions. It is expected that surface sites are more reactive than bulk sites because of the low coordination of the former that raises the electronic levels. In this section we analyze whether such behavior is captured by the Fukui Function f^- , together with the effect of relaxing the slab symmetrically or not. Figure 1 shows the two sets of slab models used. In the asymmetric slab, the two uppermost layers (labeled 1 and 2) have been relaxed and the rest are frozen at the bulk positions, whereas in the symmetric slab the two top

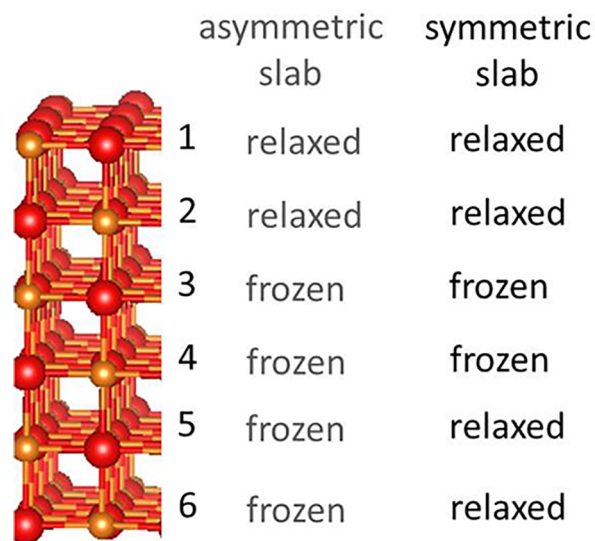


Figure 1. Slab models used in this work to study the surfaces. Layers are labeled with numbers 1–6.

and two bottom layers (labeled 1, 2, 5, and 6) have been relaxed, keeping the inner layers (3 and 4) frozen at the bulk positions. We chose to analyze the interpolation scheme that we have defined in this work for the first time and the DOS scheme for comparison purposes.

The values of f^- condensed to oxygen atoms were obtained for the asymmetric slabs of the four oxides. Table 4

Table 4. Values of f^- Condensed to O Atoms Obtained with the Interpolation Method for the Asymmetric Slabs

layer	MgO	CaO	SrO	BaO
	−0.30/−0.20/−0.10/0.00			
1	0.099	0.116	0.128	0.112
2	0.038	0.027	0.023	0.025
3	0.035	0.036	0.046	0.023
4	0.036	0.022	0.017	0.016
5	0.046	0.025	0.012	0.008
6	0.084	0.115	0.140	0.129
bulk	0.168	0.172	0.171	0.157
	−0.30/−0.20/−0.10			
1	0.101	0.112	0.122	0.108
2	0.038	0.027	0.028	0.030
3	0.034	0.023	0.024	0.027
4	0.036	0.022	0.020	0.018
5	0.046	0.025	0.013	0.008
6	0.085	0.110	0.134	0.122
bulk	0.168	0.173	0.171	0.158

summarizes the results for two schemes of interpolation of charged systems, $\delta q = -0.30/-0.20/-0.10$ with and without the neutral system. The results are very similar to those for the interpolation scheme with $\delta q = -0.15/-0.10/-0.05(/0.00)$, which are compiled in the Supporting Information. It can be observed that in all of the systems and interpolation schemes used, the surface oxygen sites display the highest values of the condensed Fukui function, ranging from 0.084–0.099 for MgO to 0.128–0.140 for SrO in the first interpolation scheme (the second, not considering the neutral system, leads to similar results). The inner layers show lower values, from 0.008 for BaO to 0.046 for MgO and SrO. This is a clear indication of the increase in the reactivity of surface sites compared with inner positions. The comparison with the bulk is not straightforward because the condensed f^- values are extensive, i.e., f^- always integrates to 1 independent of the number of atoms. In the case of surfaces, a distribution of the Fukui function among all of the positions is observed. The same behavior occurs for the four oxides, although different numbers are obtained.

It is interesting to note that structural relaxation of the surfaces leads to a variation in the value of f^- for all of the oxides, but for CaO, oxygens in layer 1 and in layer 6 seem to react in a different manner to the removal of electrons, which is reasonable considering that the electronic states around the Fermi level are affected by the geometrical relaxation. There is not a clear trend within in the oxides: in MgO, the relaxed O shows higher values (0.099 relaxed vs 0.084 unrelaxed); in CaO, relaxed and unrelaxed O show similar values (0.116 vs 0.115); and higher values for the unrelaxed O are found for SrO (0.128 relaxed vs 0.140 unrelaxed) and BaO (0.113 relaxed vs 0.130 unrelaxed). The value of δq does not influence the outcome much, although in the case of BaO the $-0.15/-0.10/-0.05$ scheme leads to similar values of relaxed and

unrelaxed sites (see the Supporting Information). What is clear is that an accurate relaxation of a surface is of uttermost importance to assess its reactivity. Small changes in geometry may not change the energy significantly, but they change the position (relative to the Fermi level) of surface states.

In order to analyze the role of the computational method in the description of the surface oxygen f^- , we also computed the descriptor with the DOS approach for different $\delta\mu$. Table 5

Table 5. Comparison of f^- Values Obtained by Integration of the DOS ($\delta\mu = -0.20$ eV) and the Interpolation of $\delta q -0.30/-0.20/-0.10$ for Asymmetric and Symmetric Slabs of MgO and BaO

MgO				
layer	asymmetric		symmetric	
	DOS	interpolation	DOS	interpolation
1	0.101	0.101	0.113	0.103
2	0.069	0.038	0.065	0.036
3	0.071	0.034	0.056	0.031
4	0.079	0.036	0.056	0.032
5	0.084	0.046	0.065	0.045
6	0.067	0.085	0.116	0.090

BaO				
layer	asymmetric		symmetric	
	DOS	interpolation	DOS	interpolation
1	0.161	0.108	0.183	0.113
2	0.012	0.030	0.026	0.023
3	0.008	0.027	0.017	0.020
4	0.003	0.018	0.017	0.020
5	0.002	0.008	0.025	0.022
6	0.267	0.122	0.182	0.113

shows the data obtained for MgO and BaO asymmetric and symmetric slabs with selected values of $\delta\mu$ and interpolation scheme. It can be observed that the two approaches account for the increase in reactivity of the surface sites compared with inner positions. Also, the symmetric slabs reflect the same value for layers 1 and 6, as expected from the relaxation, whereas the unrelaxed sites of layer 6 show lower values than those in layer 1 in MgO and higher in BaO, following the trend discussed above.

Interestingly, the calculation of f^- with the DOS approach is found to be very sensitive to the value of $\delta\mu$ used for the integration in eq 9. Figure 2 shows the profile of the condensed FF for the different layers from the data in Table 5. MgO shows a very asymmetric profile for the DOS approach of the asymmetric slab. BaO shows a large difference between layers 1 and 6 with the same approach. The results for symmetric slabs are more homogeneous. In the Supporting Information three different ranges are studied, and it can be observed that the profile of the Fukui function condensed in the different layers depends on $\delta\mu$. It seems that small integration ranges lead to large variations in the profiles, maybe because of numerical instability in such tiny ranges. Values of $\delta\mu$ of -0.20 and -0.30 led to results similar to the interpolation approach for the scheme $-0.30/-0.20/-0.10$ and could be a good starting point.

In summary, the Fukui function f^- condensed to oxygen atoms appears to be a good descriptor for the surface reactivity within a given material. The different approaches tested give the same qualitative results: the surface O atoms are more

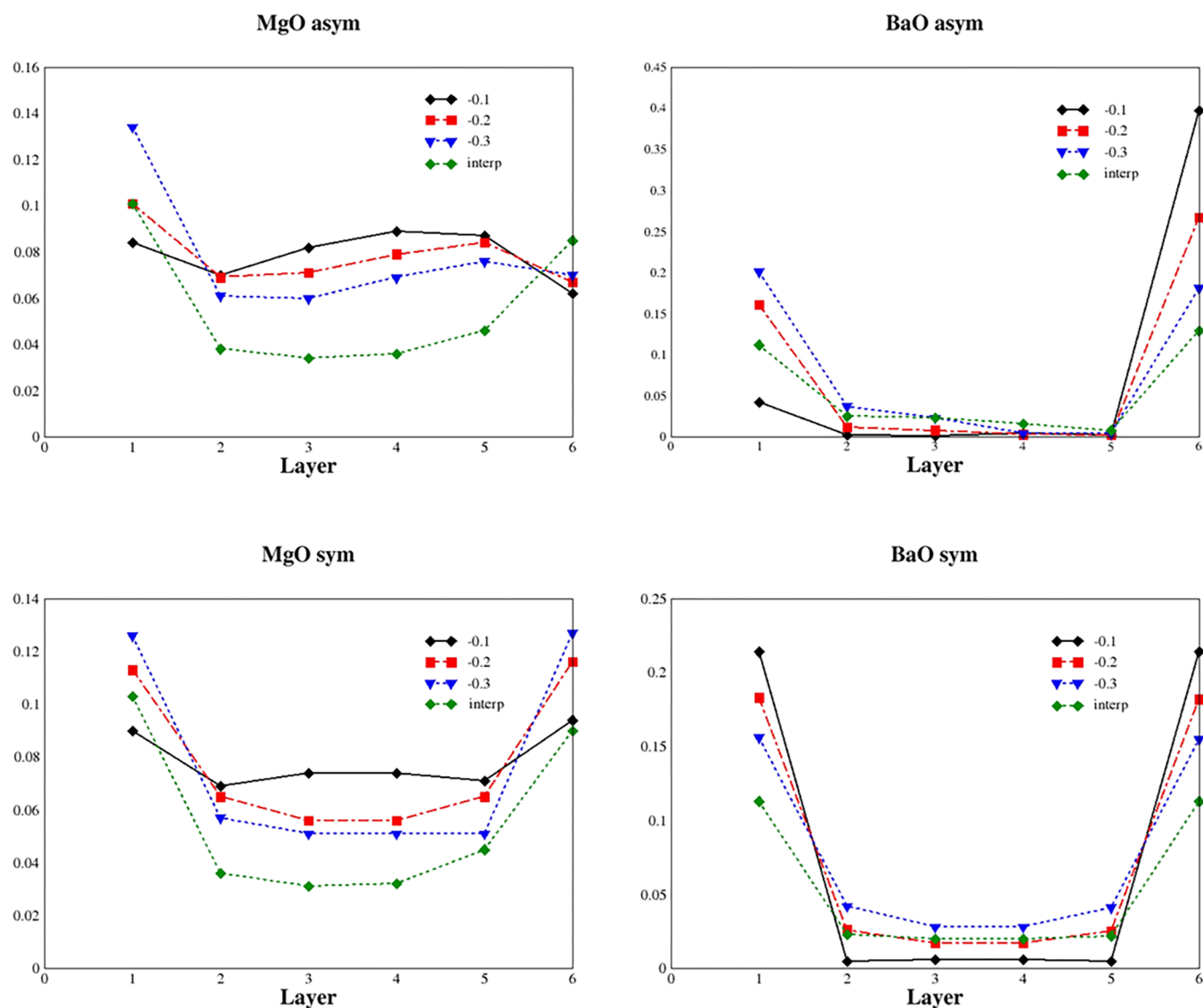


Figure 2. Values of f^- for the O sites of the slab layers for the MgO and BaO systems using asymmetric and symmetric slabs. The following settings are represented: integration of DOS within -0.10 , -0.20 , and -0.30 eV and the Fermi level, and the interpolation of charged systems for $-0.30/-0.20/-0.10e$.

reactive (the value of f^- is larger) than the inner-layer atoms. The interpolation of eq 10 is a robust way to obtain f^- in noncharged systems and is found to be sensitive to the relaxation state of the atom. Attention must be paid to the parameters used to obtain f^- , i.e., the partial charges δq in the charged systems (finite differences and interpolation schemes) or the $\delta\mu$ range to integrate the DOS, which should not take too much small values. Comparison between surface and bulk or between MgO/CaO/SrO/BaO is not straightforward because the computed f^- always normalizes to 1 independent of the nature of the system and the number of atoms in the simulation cell. Comparison of reactivity between systems of the same size could be achieved by using the local softness instead of the Fukui function. As for the matter of extensivity of the condensed Fukui function, an alternative is to standardize that, whenever possible, by reporting the value multiplied by the number of formula units in the cell. For instance, the values of the Fukui function of the O in the bulks of MgO and BaO in Table 3 and the central layers (3 and 4) in Table 4 become comparable if they are multiplied by 2 and 12,

respectively. This means that it does not take into account the total number of electrons in the system, nor the size or the nature of the elements. Providing the FF per formula unit and considering the global softness may improve the description and expand the limits of use of Fukui functions.

CONCLUSIONS

In this work, we have presented methods to compute the Fukui function f^- in periodic boundary conditions within the density functional theory framework and applied them to bulk and surface models of alkaline earth metal oxides. The approaches to calculate f^- are based on (i) finite differences of charge density for integer and noninteger δq partially charged cells, (ii) integration of the local density of states for a $\delta\mu$ interval, and (iii) interpolation of the charge density obtained for partially charged systems. All of the methods provide robust qualitative results; however, special attention must be given to the choice of δq and $\delta\mu$ to obtain a stable description. The interpolation method appears to be an appropriate way to account for the relaxation of inner states and to improve the

finite differences description for charged systems. It is particularly sensitive to the effect of geometry relaxation in slab models and thus seems to be well-suited to study solid-state reactivity.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpca.0c00950>.

Computed properties of bulk systems, geometrical parameters of surfaces, FFs computed using different approaches and MO systems, geometrical structures of asymmetric slab models (POSCAR format), python script to interpolate charge density files, and examples of application (PDF)

Fukui interpolation script (ZIP)

■ AUTHOR INFORMATION

Corresponding Authors

M. Calatayud – Sorbonne Université, CNRS, Laboratoire de Chimie Théorique, LCT, F. 75005 Paris, France; orcid.org/0000-0003-0555-8938; Phone: +33 (0)1 44272505; Email: calatayu@lct.jussieu.fr; Fax: +33 (0)1 44274117

C. Cárdenas – Departamento de Física, Facultad de Ciencias, Universidad de Chile, Santiago, Chile; Centro para el Desarrollo de la Nanociencia y la Nanotecnología (CEDENNA), Santiago 9170124, Chile; orcid.org/0000-0002-0648-6502; Phone: +56 (2) 229787161; Email: cardena@uchile.cl

Authors

M. L. Cerón – Facultad de Ingeniería, Universidad Finis Terrae, Santiago, Chile

T. Gomez – Theoretical and Computational Chemistry Center, Institute of Applied Chemical Sciences, Faculty of Engineering, Universidad Autónoma de Chile, Santiago, Chile

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acs.jpca.0c00950>

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financed by (i) FONDECYT through Project 1181121, (ii) CONICYT, REDES 190102, and (iii) Centers of Excellence with Basal-Conicyt Financing, Grant FB0807. Powered@NLHPC: This research was partially supported by the supercomputing infrastructure of the NLHPC (ECM-02). M.L.C. thanks the Internal Research Project of Universidad Finis Terrae (2018). This work was performed using HPC resources from GENCI-CINES/IDRIS (Grant 2019-x2019082131) and the LCT cluster. Dr. B. Diawara is warmly acknowledged for the Modelview visualization program.

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