

Dynamical-charge neutrality at a crystal surface

Alice Ruini*

INFM, Scuola Internazionale Superiore di Studi Avanzati, Via Beirut 4, 34014 Trieste, Italy

Raffaele Resta

INFM, Dipartimento di Fisica Teorica, Università di Trieste, Strada Costiera 11, 34014 Trieste, Italy

Stefano Baroni

INFM, Scuola Internazionale Superiore di Studi Avanzati, Via Beirut 4, 34014 Trieste, Italy
and Centre Européen de Calcul Atomique et Moléculaire, 46 Allée d'Italie, 69007 Lyon, France

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For both molecules and periodic solids, ionic dynamical charge tensors—measuring the coupling of electric fields to ionic displacements—are known to obey a *dynamical neutrality* condition. This condition forces their sum to vanish over the whole finite system, or over the crystal cell, respectively. We extend this sum rule to the nontrivial case of the surface of a semi-infinite solid and show that, in the case of a polar surface of an insulator, the surface ions *cannot* have the same dynamical charges as in the bulk. The sum rule is demonstrated through calculations for a couple of SiC surfaces. [S0163-1829(98)02710-6]

The basic quantity addressed in this paper is the *dynamical charge* of a given ion in different environments: within a molecule, in the bulk of a crystalline solid, and at a solid surface. This charge is a Cartesian tensor Z_s^* , whose components $Z_{s,\alpha\beta}^*$, measure the dipole linearly induced in the α direction by a unit displacement of the s th ion in the β direction:¹

$$d_\alpha = \sum_\beta Z_{s,\alpha\beta}^* u_{s,\beta} + \mathcal{O}(u^2). \quad (1)$$

Equivalently, Z_s^* measures the force linearly induced on the given ion by a unit electric field (at zero displacement): the dynamical charges govern therefore the infrared activity of the system and, more generally, the coupling between *macroscopic* electric fields and ionic displacements, such as occurring, e.g., in piezoelectricity, ferroelectricity, and so on.

In a neutral molecule the sum of the dynamical charges of all the ions must vanish, since a rigid translation of the molecule as a whole does not induce any dipole: we will refer to this sum rule as *dynamical neutrality*. More generally, if the molecule carries a net charge Q , the sum of all the Z^* 's must be equal to Q . The analog in a crystalline dielectric goes under the name of *acoustic sum rule* (ASR), and is spelled out in an equally simple manner: the dynamical charges sum to zero over the crystal cell. However, the underlying theory is far less trivial.⁴ The two cases of molecules^{2,3} and bulk solids^{4,5} received previous attention in the literature, both as a matter of principle and as the subject of practical calculations, but the case of a crystal surface was never considered.⁶ We show here that a crystalline surface must be dynamically neutral in order to ensure that a rigid translation of the semi-infinite solid as a whole does not affect the work function. The result is a constraint for the dynamical charges of the surface ions: in the particular case of a polar surface—such as (001) and (111) in the zinc-blende structure—our sum rule

forbids ions of a given chemical species to have the same dynamical charge in the surface region and in the bulk.

Equation (1) is a straightforward definition of Z_s^* (usually called “atomic polar tensor”) for a molecular system.^{2,3} In the crystalline case, this definition can be shown to lead to the *longitudinal* (or Callen) effective charge $Z_s^{*(L)}$, which describes the macroscopic polarization induced by the rigid displacement of two inequivalent sublattices, when the associated depolarizing electric field is allowed to interact with the electron-charge distribution. When this depolarizing field is kept equal to zero by short cutting the surfaces of the dielectric, the macroscopic polarization is instead described by the *transverse* (or Born) charge $Z_s^{*(T)} = \epsilon_\infty Z_s^{*(L)}$, where ϵ_∞ is the electronic dielectric constant. In our work we consistently refer to the *longitudinal* effective charge, as defined by Eq. (1), as *the* effective charge.

Suppose we have a semi-infinite crystalline insulator, and let us assume that the macroscopic electric field vanishes both in the bulk of the solid and outside in the vacuum region: this amounts to requiring that no static charge is present at the surface. In these hypotheses, the average of the electrostatic potential in the bulk of the solid with respect to the vacuum level is a well-defined quantity, which in fact determines the work function of the given surface and is obviously unaffected by a rigid translation of the semi-infinite solid as a whole. A necessary condition for this to occur is our sum rule for the dynamical charges. If the z axis is assumed to be oriented along the normal to the surface, then the system has a two-dimensional periodicity in the xy plane. We consider a rigid displacement of an ionic layer, i.e., we displace a given ion and all its periodic images by the same amount \mathbf{u}_s : this rigid displacement induces a dipole (along z) per unit area, and hence a potential lineup across the layer. The latter is expressed in terms of the $\alpha=3$ components of the dynamical charge tensor as

$$\Delta\phi = \frac{4\pi}{A} \sum_\beta Z_{s,3\beta}^* u_{s,\beta}, \quad (2)$$

where A is the area of the surface unit cell.

A rigid translation of the semi-infinite crystal by an amount \mathbf{u} induces a total lineup which is, by linearity, the sum over s of the expressions in Eq. (2). As anticipated above, we explicitly require this lineup to vanish; hence a naïve expression for our sought sum rule appears to be

$$\sum_s Z_{s,3\beta}^* = 0 \quad (\text{any } \beta). \quad (3)$$

This formal expression for the surface dynamical charge neutrality cannot be used as such, given that the infinite sum in general does not converge: in the bulk region it oscillates periodically, owing to bulk dynamical-charge neutrality. Therefore, the problem is to regularize the indeterminate sum in Eq. (3) by using an appropriate physical criterion. The standard technique to tackle this kind of problem is the *macroscopic average* introduced in Ref. 7 and widely used by several authors: by construction, the macroscopic average yields the correct electrostatic-potential average in the bulk region. Application to the present case is straightforward. One first maps the problem onto a simple electrostatic one by assigning a point charge of magnitude $Z_{s,3\beta}^*$ to each ion. Second, one evaluates the planar average of this charge distribution, which takes the general form

$$\bar{\rho}(z) = \frac{1}{A} \sum_s Z_{s,3\beta}^* \delta(z - z_s), \quad (4)$$

where z_s are the positions of the ionic planes along the z axis. Finally, one filters $\bar{\rho}(z)$ through the convolution

$$\bar{\bar{\rho}}(z) = \frac{1}{b} \int_{z-b/2}^{z+b/2} dz' \bar{\rho}(z'), \quad (5)$$

where b is the one-dimensional periodicity of the bulk region. The result is a piecewise constant function, vanishing both in the vacuum and in the bulk, and whose integral in the surface region is trivial. We state the sum rule by requiring this integral to vanish. It is important to realize that—at variance with the naïve expression of Eq. (3)—the surface sum rule involves *both* the values of the dynamical charges *and* the plane coordinates z_s .

The nontrivial content of the sum rule will be made clear by a few examples. We consider simple polar surfaces of a cubic binary crystal, whose bulk dynamical charges have the form $Z_{s,\alpha\beta}^{*(\text{bulk})} = (-1)^s |Z^*| \delta_{\alpha\beta}$. The $\beta \neq 3$ components of the sum rule expressed by Eq. (3) are correct, because of periodicity, for the same reason that this equation is correct in the bulk. We then focus on the $\beta=3$ component, and we further limit ourselves to the cases where the ionic planes parallel to z contain either cations only, or anions only, alternately. This is the case for the (001) and (111) surfaces in the zinc-blende structure, which we are going to illustrate separately, assuming an ideal (truncated-bulk) geometry.

We start with the (001) surface, where b is one-half of the cubic lattice constant and the ionic planes are equally spaced by an amount $b/2$. We assume that the crystal lies in the positive- z half-space, so that the coordinate of the s th plane can be assumed to be $(s-1)b/2$. The function $\bar{\rho}(z)$ is schematically shown in Fig. 1, left panel, for the special case

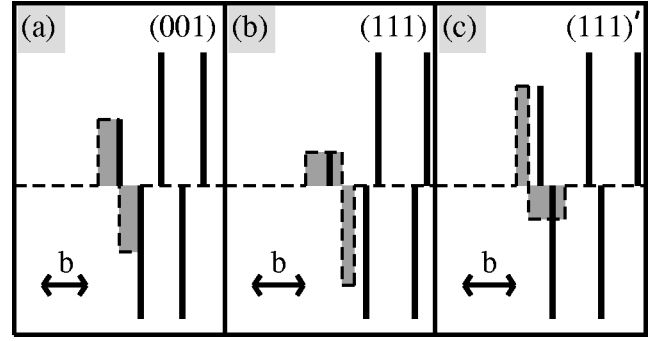


FIG. 1. Macroscopic averages (shaded thick lines) of δ -like planar charge distributions (displayed by thick vertical lines whose height indicates the value of the planar density). The three panels refer to three different cation-terminated polar surfaces. (111) indicates the termination in which the distance between the two outermost atomic layers is one bond length, whereas in the (111)' geometry such a distance is three times shorter.

where the surface is cation terminated, and only the outermost cation has a dynamical charge different from the bulk one: the corresponding macroscopic average $\bar{\bar{\rho}}(z)$ is also shown, and integrates to zero. For the most general (001) surface—where several Z_s^* in the surface region may deviate from their bulk value—the piecewise constant function $\bar{\bar{\rho}}(z)$ vanishes from $-\infty$ to $-b/2$; it assumes the value $Z_{1,33}^*$ (apart for a constant factor) up to $z=0$; then $\bar{\bar{\rho}}(z) = Z_{1,33}^* + Z_{2,33}^*$ up to $b/2$, and in general $Z_{s,33}^* + Z_{s+1,33}^*$ in the following intervals, until it vanishes again in the bulk region, say for $s > N$. Since the intervals are of equal length, the sum rule for the integral of $\bar{\bar{\rho}}(z)$ requires that

$$2 \sum_{s=1}^N Z_{s,33}^* + Z_{N+1,33}^* = 0. \quad (6)$$

We thus arrive at the unexpected conclusion that the dynamical charges of the ions in the surface region sum up to *one-half* of the bulk dynamical charge (with the appropriate sign), as indeed it occurs in the simple realization depicted in Fig. 1(a). The neutrality relationship is precisely the same as would be obtained by replacing the dynamical charges with static pointlike charges, and requiring the surface to be neutral.

Switching now to the (111) geometry, the linear period b is $1/\sqrt{3}$ times the lattice constant, and the ionic planes are no longer equally spaced. The function $\bar{\rho}(z)$ is schematically shown in Figs. 1(b) and 1(c) for two nonequivalent cation-terminated surfaces, where again we depict the special case where only the outermost cation has a dynamical charge different from the bulk one. In the center (right) panel the dynamical charge of the surface cation is $1/4$ ($3/4$) of the bulk value, and the macroscopic average $\bar{\bar{\rho}}(z)$ integrates to zero in each case. The reasoning detailed above for the (001) case can be repeated here: for the most general (111) surface the sum of the dynamical charges in the surface region is equal to $\pm 1/4$ or $\pm 3/4$ times the bulk dynamical charge.

The above arguments show that for any polar surface we have a constraint which forbids the surface ions to have the same dynamical charges as in the bulk: instead, the sum of

the dynamical charges in the surface region must be equal to a well-defined fraction of the bulk dynamical charge. The actual value of the fraction depends on geometry, as shown from the examples previously considered. One can easily recognize that this value ($\pm\frac{1}{2}$, $\pm\frac{1}{4}$, or $\pm\frac{3}{4}$ for the above-mentioned surfaces) is solely determined by the stacking of the bulk planes along the direction normal to the surface, and is independent of anything occurring in the surface region (provided the surface remains *statically* neutral). Therefore the sum rule applies—with the same fraction value as for the truncated–bulk case—to surfaces undergoing relaxation, reconstruction, and even impurity adsorption.

These findings are illustrated by first-principles calculations of the surface dynamical charges for some paradigmatic test cases: to keep matters simple, we deal with insulating surfaces. Our first choice is the (001) Si-terminated surface of the zinc-blende semiconductor SiC, which was the subject of recent theoretical work.^{8,9} The actual structure is 2×1 reconstructed, but even the ideal (truncated bulk) one is insulating, and fits well our purpose of dealing with a test case as simple as possible: the sum rule for this case takes precisely the form of Eq. (6). Our second test case, again for SiC, concerns two nonequivalent (111) surfaces: in order to get them insulating, we saturated the dangling bonds with hydrogen. The surface sum rule includes then contributions from the H dynamical charge.

All calculations are performed using density-functional theory in the local-density approximation.¹⁰ Most technical ingredients are fairly standard: plane-wave basis sets and norm-conserving pseudopotentials,¹¹ Ceperley-Alder exchange-correlation potential,¹² and special-point Brillouin-zone sampling. We use plane waves up to a kinetic-energy cutoff of 18 Ry. This basis set is too small if one aims at a precise prediction of the physical properties of any carbon-based materials, but it is enough to demonstrate the points of principle addressed here, because the ASR in the bulk is well satisfied. We use a set of 28 irreducible special points in the bulk calculations, and a consistent set in the supercell ones. This large number of special points is needed to satisfy the ASR.¹³

Our calculations provide a theoretical lattice constant of 8.24 a.u. (expt. 8.25). Density-functional perturbation theory (DFPT),¹³ implemented as in Ref. 14, provides for the bulk solid $|Z^*| = 0.34$, in very good agreement with the experimental estimate.¹⁵

The surface calculations were performed in a supercell geometry, where the SiC slab has a double Si termination. In Fig. 2 we plot the pseudopotential valence-electron density for the nine-atom supercell; we also plot the macroscopic average [Eq. (5)] of the same density. Figure 2 clearly shows that the two surfaces are well separated, and that the central region of the slab is bulklike, with eight electrons per cell in average. We also accurately checked that each of the two Si-terminated surfaces is statically neutral.

Starting from the reference equilibrium ground state of Fig. 2, we calculate the longitudinal dynamical charges of all the ions in the supercell using again DFPT for our composite structure of periodically repeated slabs: they are anisotropic tensors in the surface region, and they must converge to their (isotropic) value $\pm 0.34\delta_{\alpha\beta}$ in the bulk region. The convergence proves to be rather slow: insofar as the dynamical

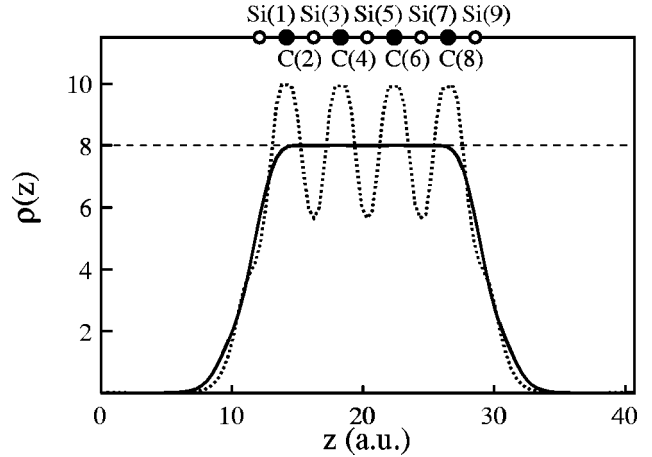


FIG. 2. Self-consistent valence-electron density in the nine-atom computational supercell, in units of electrons per bulk cell. The solid line shows the average over planes parallel to the surface, as a function of the normal coordinate z . The dashed line shows the same function after the macroscopic-average filtering.

charges are concerned, the surface region is much larger than the equilibrium charge density of Fig. 2 would suggest. Despite this fact, our slab is large enough to recover the bulk Z_{33}^* value for the center Si ion (0.33 vs 0.34 from the bulk calculation). The calculated relevant effective charges are $Z_{\text{Si}(1),33}^* = +0.13$, $Z_{\text{C}(2),33}^* = -0.27$, $Z_{\text{Si}(3),33}^* = +0.29$, $Z_{\text{C}(4),33}^* = -0.31$, and $Z_{\text{Si}(5),33}^* = +0.33$. The robustness of these figures was then checked in two different ways. First, we performed similar calculations on a fully relaxed (though unreconstructed) structure: the outermost SiC bond length increased by 4%. The picture is unchanged, but the bulklike limit is recovered faster, with $Z_{33}^* = 0.34$ for the center Si ion. Second, the adequacy of our nine-atom supercell was checked against a few test calculations performed with a slab of 13 atoms. Using the data reported above, the sum of the dynamical charges $Z_{s,33}^*$ over five layers in the surface region, up to the central Si, is 0.17, thus demonstrating our main finding of Eq. (6).

In this particular example the surface sum rule seems equivalent to the previously known (molecular) sum rule for the finite slab. But one has to bear in mind that our sum rule is indeed a property of each surface individually: as such, it applies to a semi-infinite solid with only one surface. This is even more clear from the following example, where a (111) SiC slab is used: in this case four different truncations are possible, and the two surfaces are necessarily inequivalent. Our case-study slab is built of four SiC bilayers, and furthermore one H per surface atom is added on each side in order to saturate the dangling bonds. The sum rule constrains the sum of all the dynamical charges (including the H one) in the two surface regions to be in modulus equal to $\frac{1}{4}$ and $\frac{3}{4}$ of the bulk value, respectively.

Slabs having nonequivalent surfaces may lead to unpleasant technical problems when a supercell geometry is adopted for simulation. The reason is that the work functions of the two surfaces are generally different. The supercell is an artificial periodic structure of repeated slabs and vacuum layers, where the electrostatic potential is enforced to be periodical.

This periodicity, combined with the vacuum-level difference (due to the different work functions), necessarily originates fictitious electric fields and *static* surface charges. Such unphysical charges can in principle be made arbitrarily small by increasing the thickness of the vacuum layers, but in practice a large enough supercell may be computationally unaffordable. We recall at this point that the static neutrality of the surface is an essential hypothesis of our sum rule, and therefore the $Z_{s,33}^*$ calculated for the ten-atom slab cannot obey our dynamical neutrality condition as such. As it is the case for molecules, the latter can be generalized to statically charged surfaces, so that effective charges would sum to the surface static charge. Our calculated effective charges are: $Z_{\text{H}(1),33}^* = -0.06$, $Z_{\text{Si}(2),33}^* = +0.25$, $Z_{\text{C}(3),33}^* = -0.33$, $Z_{\text{Si}(4),33}^* = +0.35$, $Z_{\text{C}(5),33}^* = -0.34$, $Z_{\text{Si}(6),33}^* = +0.34$, $Z_{\text{C}(7),33}^* = -0.33$, $Z_{\text{Si}(8),33}^* = +0.37$, $Z_{\text{C}(9),33}^* = -0.18$, and $Z_{\text{H}(10),33}^* = -0.04$. The bulk effective charge is recovered for the innermost SiC pair. However, we find that the integral of the macroscopic average of the effective charges on the two sides of the central bond does not vanish, but is $Q^* = \pm 0.06$, with the plus sign appropriate to the Si-terminated surface. The net surface static charges were evaluated by integrating

of the ionic plus electronic charge in the appropriate supercell region: we obtained $Q = \pm 0.03$. The small absolute difference is due to numerical difficulties in achieving well-converged supercell calculations: we estimate that the above value of the (fictitious) surface static charge is consistent with Q^* .

In this paper we showed how a proper generalization of dynamical charge neutrality from finite to infinite systems based on concepts of *local* charge neutrality may lead to nontrivial sum rules. We formulated such a sum rule for the specific case of a (statically) neutral surface. We believe that this generalization, which is technically made possible by a clever use of the *macroscopic average* technique, is also feasible and fruitful for disordered systems,¹⁶ possibly in the presence of localized charged states. Further work is needed and planned in this direction.

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*Present address: Dipartimento di Fisica, Università di Modena, v. Campi 213/A, 41100 Modena, Italy.

¹Atomic units of charge are used throughout.

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