Calculation of surface stress in a linear combination of atomic orbitals representation

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A method is presented for separating "bulk" and "surface" contributions to the strain derivative of the total energy of a two-dimensionally periodic, several-layer slab. The method, involving a layerwise decomposition of the sums and integrals required to calculate the derivative, makes it possible to compute a surface stress via a single, linear combination of atomic orbitals slab calculation. Application to Al(111) yields a predicted tensile surface stress of magnitude 0.090 eV/Å^2.

I. INTRODUCTION

The accumulation of a substantial surface crystallographic data base makes it desirable to systematize our understanding of surface atomic geometry. This means identifying the parameters that determine what adsorption sites are optimal, whether and how surfaces reconstruct under various circumstances, how they relax, and so forth. Since surface stress is an important candidate for such a key parameter, in an earlier paper,[1] I derived a Pulay-type formula[2] that permits the exact evaluation of the strain derivative of the total energy in a first-principles linear combination of atomic orbitals (LCAO), electronic structure calculation. In the present work, for a several-layer, two-dimensionally periodic slab, I show how to evaluate this formula in a way that allows one to compute "bulk" and "surface" contributions separately. This development permits the computation of surface stress via a single slab calculation. The same strategy can also simplify the evaluation of the surface energy.

In what follows, I describe the mathematics of the method (see Sec. II), and then as an example, I calculate the surface stress for Al(111) (in Sec. III). As a test of the present approach, I compare the surface stress that it yields to that of a plane-wave calculation by Needs and Godfrey (NG).[3] Using the same set of approximations as they do, I obtain a surface stress of 0.079 eV/Å^2, compared to their most converged result, 0.078 eV/Å^2.

II. DECOMPOSITION OF THE STRAIN DERIVATIVE OF THE ENERGY

In order to calculate components of the surface stress tensor, one needs to evaluate the surface contribution to the derivative of a sufficiently thick slab's total energy E with respect to a strain ϵ_{ij}. To decompose $dE/d\epsilon_{ij}$ into "bulk" and "surface" parts, I set up "bins" corresponding to the various slab layers. I then assign fractions of each contribution to $dE/d\epsilon_{ij}$ to appropriate bins. If this assignment is made in a consistent manner, and assuming that the contributions to $dE/d\epsilon_{ij}$ are sufficiently "local," then the bins corresponding to the layers near the middle of a thick enough film will contain almost equal contributions; and the average of these central bin contributions will be a good approximation to the "bulk" contribution to $dE/d\epsilon_{ij}$. Knowing the "bulk," per layer contribution to $dE/d\epsilon_{ij}$, and the total $dE/d\epsilon_{ij}$ for the slab, it is straightforward to determine the surface stress.

As shown earlier in great detail,[1] in a first-principles LCAO calculation, $dE/d\epsilon_{ij}$ can be expressed as a sum of two kinds of terms. The first is an integral over space such as

$$2\int_{\mathrm{UC}} d^3r\, \varepsilon^{\mathrm{xc}}(\mathbf{r})\rho(\mathbf{r}) , \tag{1}$$

where $\varepsilon^{\mathrm{xc}}(\mathbf{r})$ and $\rho(\mathbf{r})$ are the exchange-correlation energy density and the electron density, respectively, and where the subscript UC means integration over a surface unit cell. The second is a matrix element sum either of the form

$$\sum_{l,\delta} b_{l,l+\delta} , \tag{2}$$

or of the form

$$\sum_{l,\delta,\gamma} c_{l,l+\delta,l+\gamma} , \tag{3}$$

where $b_{l,l+\delta}$ and $c_{l,l+\delta,l+\gamma}$ represent, for instance, matrix elements of components of the one-electron Hamiltonian times the density matrix. In Eqs. (2) and (3), the subscripts l, $l+\delta$, and $l+\gamma$ refer to orbitals in layers $l, l+\delta$, and $l+\gamma$.

The strategy I use to evaluate terms of the form of Eqs. (2) and (3) is to define B_l and C_l by

$$B_l \equiv \tfrac{1}{2}\sum_{\delta} [b_{l,l+\delta}+b_{l-\delta,l}] , \tag{4}$$

and

$$C_l \equiv \tfrac{1}{3}\sum_{\delta,\gamma} [c_{l,l+\delta,l+\gamma}+c_{l-\delta,l,l+\gamma-\delta}+c_{l-\gamma,l+\delta-\gamma,l}] . \tag{5}$$

According to these definitions,

$$\sum_{l,\delta} b_{l,l+\delta} = \sum_{l} B_l \tag{6}$$

and

$$\sum_{l,\delta,\gamma} c_{l,l+\delta,l+\gamma}=\sum_{l} C_l \ , \tag{7}$$

since all the terms that result from substituting Eq. (4) into Eq. (6), and Eq. (5) into Eq. (7), are summed over the same set of layer indices. At the same time, in the middle of a sufficiently thick slab, *or in bulk*, B_l and C_l are independent of l, since layers $l-\delta$, and $l-\gamma$ are physically indistinguishable from l. Thus for l near the middle of a slab, B_l and C_l represent contributions to the matrix element portion of $dE/d\epsilon_{ij}$ that are attributable to a single "bulk" layer. The l independence of B_l and C_l, for l near the middle of a slab that need not be "too" thick, clearly depends on choosing an atomic orbital basis such that $b_{l,l+\delta}$ and $c_{l,l+\delta,l+\gamma}$ are small if the magnitude of either δ or γ is larger than a small number, i.e., 2 or 3. That this is possible is demonstrated explicitly in the next section, via a calculation for Al(111).

Decomposing an integral like that of Eq. (1) is also straightforward. For slab layers $l=1,\ldots,N$, one defines a set of functions $f_l(z)$ such that

$$\sum_{l} f_l(z)=1 \ , \tag{8}$$

and such that

$$f_{l+1}(z)=f_l(z-s), \quad l=2,\ldots,N-1 \ , \tag{9}$$

where z is the coordinate along the slab normal, s is the distance between physically equivalent atomic layers in the bulk region,[4] and $l=1$ and $l=N$ represent the slab's outermost layers.

Equation (8) guarantees that for any function $g(\mathbf{r})$ [e.g., for $g(\mathbf{r})=2\varepsilon^{xc}(\mathbf{r})\rho(\mathbf{r})$],

$$\int_{UC} d^3r\, g(\mathbf{r})=\sum_{l} G_l \ , \tag{10}$$

where

$$G_l \equiv \int_{UC} d^3r\, f_l(z) g(\mathbf{r}) \ . \tag{11}$$

Equation (9) implies that in the interior of a thick enough slab, G_l will be l independent and equal to the "bulk" per layer contribution of the integral of $g(\mathbf{r})$ to the desired component of the stress tensor.

The precise form of the $f_l(z)$ is not important, as long as Eqs. (8) and (9) are satisfied. For example, for an N-layer slab one might define the f's in terms of step functions, $\theta(z)$, via

$$f_1(z)\equiv 1-\theta[z-(z_1+z_2)/2] \ , \tag{12}$$

$$f_l(z)\equiv \theta[z-(z_{l-1}+z_l)/2] - \theta[z-(z_l+z_{l+1})/2], \quad l=2,\ldots,N-1 \ , \tag{13}$$

$$f_N(z)\equiv \theta[z-(z_{N-1}+z_N)/2] \ , \tag{14}$$

where z_l is the position of the lth layer, and $z_l<z_{l+1}$, for all l.

III. A NUMERICAL EXAMPLE: THE SURFACE STRESS OF Al(111)

To demonstrate the effectiveness of the bin-decomposition approach outlined in the previous section, I have used it to compute the surface stress of Al(111). Obtaining an adequately converged value of this quantity has been the subject of several papers by Needs and coworkers.[3,5–7] In the most recent of these (NG),[3] the result of a "new and exhaustive study" is reported to be 0.078 eV/Å^2. At the same level of approximation as NG used (detailed below), but with a LCAO basis set instead of plane waves, and using the bin approach developed here, I find 0.079 eV/Å^2. This excellent agreement gives confidence in the bin method.

Beyond reproducing the stress value obtained by NG,[3] I have investigated the degree to which it is changed if one were to redo the calculation using the Al lattice parameter that minimizes the local-density approximation[8] (LDA) total energy, rather than the experimental lattice parameter, and if one relaxes the spacings between the outer crystal layers, instead of fixing them at the "ideal" bulk value. I have also determined the systematic difference occasioned by the use of Hamann's generalized norm-conserving pseudopotential[9] (GNCPP) instead of the Kerker potential[10] employed by NG.[3] The overall result is that using the GNCPP together with the LDA lattice parameter and a relaxed surface produces a calculated stress 15% higher than NG's value, namely, 0.090 instead of 0.078 eV/Å^2.

A. Comparison with Needs and Godfrey

In NG,[3] the bulk Al lattice parameter was set to a low-temperature experimentally determined value, 4.02 Å. The Al(111) surface was modeled as a nine-layer slab. The spacings between neighboring layers were fixed at the ideal bulk value. The surface Brillouin zone was sampled with 37 equally spaced Bloch vectors. Exchange and correlation were represented by the Ceperley-Alder local exchange-correlation potential.[11] Finally, as mentioned above, the electron-ion-core interaction was represented via a Kerker pseudopotential.[10]

To perform a first-principles LCAO calculation of Al(111) with the same specifications, one must also choose an adequate orbital basis set. I use the set reported in Ref. 12, with a slightly modified s pseudofunction on each Al center to account for the small difference between s pseudofunctions of a Kerker and a Hamann pseudo-Al.[13] The fact that the basis set includes "floating" orbitals, i.e., orbitals not centered at the positions of Al nuclei requires additional care in defining "bins" and determining the bulk contribution to the stress of the nine-layer slab, as explained below.

In what follows, I describe the evaluation of the trace of the stress tensor,

$$S\equiv dE/d\epsilon_{xx}+dE/d\epsilon_{yy} \ , \tag{15}$$

using Eq. (43) of Ref. 1. To compute spatial integrals, I define nine bins as explained in the previous section, corresponding to the slab's nine layers of nuclei. To com-

pute the terms in the formula for S involving matrix sums, I assign a bin to each of the 23 sites in the slab unit-cell where an orbital is centered (9 nuclei + 8 octahedral sites + 2 atop sites + 4 hollow sites). Since the Al layers other than the outermost (i.e., layers 2 through 8 of the nine-layer slab) have layers of octahedral-site orbitals immediately above and below them, I reassign to the bin for each of these interior Al layers the average of the contributions from the nearest octahedral-site bins. Similarly, I reassign half the contributions for the octahedral site immediately below the surface and all the contents of the bins corresponding to atop and hollow sites to the bins of the adjacent surface layer Al's. I thereby arrive at the decomposition of S reported in Table I. The numbers in the table include both the matrix sum and the spatial integral contributions to S.

Note that the contributions to S attributable to the central layer of the film is 0.62 eV/atom. From the next layer it is 0.66 eV/atom and from the third layer starting from the center, it is 0.65 eV/atom. The fact that these values agree to within a few hundredths of an eV/atom implies that although the middle of the nine-layer film is not exactly like the bulk, quantum size effects on S in that region are relatively minor. Averaging the contributions of the central three layers, one obtains a value of 0.65 eV/atom for the contribution to S of a bulk layer. Averaging the central five layers evidently gives the same answer.

Knowing the "bulk" component of S, it is easy to determine that attributable to each surface atom. It is

$$\tfrac{1}{2}(S_{\text{total}} - 9S_{\text{bulk}}) , \tag{16}$$

where the factor $\frac{1}{2}$ reflects the fact that the slab has two surfaces. Using the fact that $S_{\text{bulk}} = 0.65$ eV/surface atom, and that the sum of all the bin contributions, $S_{\text{total}} = 8.05$ eV/surface atom, Eq. (16) implies that $S_{\text{surface}} = 1.1$ eV/surface atom. To compare this result with that of NG, one must divide it by twice the area of the surface unit cell, 14.0 Å^2. The factor of 2 is necessary because S is the trace of the stress tensor, while "the surface stress" for the isotropic (111) surface is defined as a single diagonal component of the tensor. Thus the bin calculation yields a surface stress of 0.079 eV/Å^2 in excellent agreement with the results of NG's plane-wave pseudopotential (PWPP) calculation, 0.078 eV/Å^2.

B. Al(111) stress using the LDA lattice parameter and a relaxed surface

By specifying the bulk lattice parameter according to experiment, and by setting the layer spacing of a slab to its ideal value for all layers, one saves the labor of determining the optimal LDA lattice parameter and the surface relaxation. In the case of Al, the LDA lattice spacing, using the Ceperley-Alder exchange-correlation potential,[11] is roughly 1.4% smaller than the experimental value. The outermost layer spacing, both theoretically[14] and experimentally,[15] is expanded by roughly 1% relative to "ideal." In this section I show that the surface stress computed with these optimized parameters is significantly larger than NG's result.

Nelson has carried out an optimization of the LDA lattice parameter via a highly converged plane-wave pseudopotential calculation.[16] The result is a value of 3.965 Å, rather than the experimental value of 4.02 Å. Using the LDA lattice parameter, and the basis set appropriate to the GNCPP (Table II), for a nine-layer slab, a Bloch vector sample of 37 equally spaced points and the Ceperley-Alder exchange correlation potential,[10] I find that the outer layer spacing of the Al(111) surface is expanded by 1.1% relative to ideal, while the second layer spacing is contracted by 0.7%.

For this relaxed geometry, I compute stress contributions in bins defined just as in the previous subsection. The results are given in Table II. Following the same procedure as in the case of the NG-like film, I now find that the contribution to S from the central film layer is -0.080 eV/atom, for the adjacent layer it is -0.027 eV/atom, and for the third layer from the center it is -0.159 eV/atom. The fact that the contributions of S from the innermost layers of the film are of the order of tens of meV/atom demonstrates that the LCAO calculation faithfully represents Nelson's PWPP result that the LDA lattice parameter is 3.965 Å. If the LCAO basis, or some other aspect of the LCAO calculation, resulted in a poor approximation to the plane-wave result, I would expect a substantial stress contribution from the "bulk" region of the slab.

The reason that the stress contribution from the third layer of the film is considerably larger than that of the central three slab-layers is that the slab's second interlayer spacing is contracted. Thus, the third layer Al's are not in the periodic, "bulk region" of the slab.

TABLE I. Layerwise decomposition of contributions to the trace of the stress tensor for a nine-layer Al(111) slab. The Al lattice parameter, here, has the experimentally derived value of 4.02 Å, and the surface layers are unrelaxed.

Layer	Contribution to S
1,9 (Surface)	2.580 eV/atom
2,8 (Subsurface)	−0.178 eV/atom
3,7	0.647 eV/atom
4,6	0.662 eV/atom
5 (Central)	0.623 eV/atom

TABLE II. Layerwise decomposition of contributions to the trace of the stress tensor for a nine-layer Al(111) slab. The Al lattice parameter, here, has the LDA optimum value of 3.965 Å, and the surface layers are in relaxed positions.

Layer	Contribution to S
1,9 (Surface)	2.168 eV/atom
2,8 (Subsurface)	−0.914 eV/atom
3,7	−0.159 eV/atom
4,6	−0.027 eV/atom
5 (Central)	−0.080 eV/atom

Following the same procedure as in the previous subsection, I find from the results in Table II that the surface component of the trace of the stress tensor is 1.23 eV/surface atom, for the relaxed Al(111) film. In units of energy per area, this amounts to a tensile surface stress of 0.090 eV/Å^2, i.e., 15% higher in the value than the result quoted by NG. Of this 15% difference, about 3% is attributable to the fact that the LDA lattice parameter is 1.4% smaller than the experimental one, 4% is the result of using Hamann's GNCPP instead of the Kerker potential,[17] and the remaining 7% follows from the change in electronic structure associated with the smaller lattice parameter and relaxed surface. NG assert that the effects of using the experimental lattice parameter and an ideal surface are "small." The present results help to quantify what "small" means.

III. DISCUSSION

LCAO calculations offer substantial advantages for systems involving atoms with strong pseudopotentials. For such systems, plane-wave basis sets need to be rather large,[18] while LCAO basis sets are much more modest in size. The difficulties encountered by Needs and coworkers[3,5–7] in obtaining a converged value of the stress for Al, a very weak pseudopotential atom, emphasize the convergence requirements for strong pseudopotential species. The LCAO-based "bin" method for evaluating surface stress should be particularly valuable in these cases.

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