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Charge transfer, surface charging, and overlayer-induced faceting

J. G. Che* and C. T. Chan

Department of Physics, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, China

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Local density functional calculations are used to analyze the change of surface energy of metallic surfaces upon surface charging. We then studied the systems involving overlayers of fcc metals on Mo(111) and Mo(211). It has been observed experimentally that some fcc overlayers can drive Mo(111) and W(111) surfaces to facet to the {211} orientation, and there is a strong correlation between the electronegativity of the overlayer and the faceting transformation. Only strongly electronegative fcc elements can cause the faceting, and we apply our analysis to see whether surface charging is main driving mechanism in view of such an empirical correlation. Our results show that surface charging is not the dominant force driving the growth-induced faceting phenomena.

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I. INTRODUCTION

There are some situations in which a metal surface is charged. When a metal surface is subjected to an external electric field, say inside a field ion microscope, or near a STM tip, the surface region will have a screening charge. The surface of a metal electrode is also charged inside electrochemical shells. When a surface has absorbates that has a different electronegativity, charge transfer will also take place. In some cases, the surface charging is accompanied by a change of surface morphology and surface properties. For example, it is known that surface charging can cause surface reconstruction in fcc metal surfaces [e.g., Ag(110)(1×1) to (1×2) upon alkali adsorption].[1] It is also known that surface charging can stabilize surface vacancy arrays, leading to a change of surface configuration.[2] Local surface reconstructions and macroscopic faceting have also been observed in metal electrode surfaces.[3] Overlayer adsorption can cause some substrate to become unstable if the overlayer and the substrate have a significant difference in electronegativity.[4] Closely related to surface charging, an external electric field can also cause changes in chemisorption bonds.[5] Some of these changes may be traced to the surface charging effect. However, in the case of absorbate adsorption and overlayer growth on electrode surfaces, the surface atoms are interacting chemically with the absorbates or electrolyte ions. It is not always clear whether the morphology change is mainly driven by surface charging or by a chemical bonding mechanism.

It is always desirable to know which part of the interaction is the main driving force. In particular, we would like to see whether surface charging alone can account for the morphology change and if it is indeed the case, we have a better understanding of the physics of the problem. If surface charging can indeed be identified as the major thermodynamic driving force of certain surface phenomena, it would be a clean and elegant explanation of the observed phenomena since surface charging is rather generic and does not depend on the details of chemistry. A good example is the work of Fu and Ho,[6] in which they considered whether surface charging can cause surface reconstruction in fcc(110) metal surfaces. The experimentally observed reconstruction of Ag(110) is induced by alkali adsorption. The driving force can be surface charging effect or chemical bonding effect. Fu and Ho's LDA calculation had no absorbates and therefore no "chemistry," but considered the change of the surface energy purely as a function of surface charging by imposing an external electric field, and showed that surface charging alone can already drive the (1×1) to (1×2) saw-tooth reconstruction. The main driving force is thereby clarified. The earlier work of Heine and Marks[7] used a simple model, and also traced the reconstruction to increased lateral interaction of surface atoms upon negative charging the surface. Likewise, Che *et al.*[2] found that surface charging can stabilize surface vacancy arrays in bcc(100), leading to a change of surface configuration, which then explained some intriguing phenomena including surface alloying and field-ion observations of the W(100) surface. On the other hand, Bohnen and Kolb[8] considered whether surface charging can account for the lifting of Au(100)-hex reconstruction in an electrochemical environment, and their conclusion is negative. They found that only specific adsorption can explain the voltage-induced morphology change.

It is in the same spirit that we consider whether surface charging is the main cause of some intriguing faceting phenomena induced by the growth of overlayers of fcc metals on top of bcc(111) substrates. It is known that the growth of some ultrathin fcc metal films on Mo and W(111) metal substrate can drive the substrate to facet, exposing macroscopic facets of [211] orientations. It is well documented that only metals with Pauling electronegativity greater than 2 such as Au, Pd, and Pt (2.54, 2.20, and 2.28) on Mo(111) and W(111) substrate can cause faceting. Metals of lower electronegativity such as Cu and Ag (1.90 and 1.93) do not cause faceting.[4] Since different electronegativity will induce different charge transfer, it is natural to ask whether the surface charging is the main driving force for the faceting transformation. It is in fact tempting to think that charging effect is important, as there is indeed an established experimental correlation with electronegativity. We can also argue that faceting increase the total surface area, leading to less electrostatic repulsion. On the other hand, Tao, Rowe, and Madey[9] measured the W $4f_{7/2}$ surface core level shifts from the W(111) interface covered by a monolayer of many metals using high-resolution photoemission and they found a correlation with the heat of adsorption, but no clear correlation with the Pauling electronegativity. If surface charge transfer were playing an important role in the faceting process, one would expect a correlation between electronegativity and the core level shifts. However, the relationship between charge transfer and chemical shift is complicated by many factors.[10] We shall see that the microscopic details are indeed very complex. We note that in the many systems where charge transfer is significant, typically in absorbate systems, we can consider the total energy change of everything and the results usually agree well with experiment. Such an approach has been used successfully[11] for overlayer induced faceting, but in this article we focus on the problem: Is overlayer-induced faceting essentially a surface charging effect? We also note that for metal surfaces, imposing an external field is equivalent to surface charging.

The paper is organized as follows. Section II discusses how one may impose an external field to induce surface charging with the local-density formalism, and analyze how the surface energy may change. Section III discusses the effect of Mo(111) and Mo(211) under surface charging. In order to exclude effects of chemical bonding and examine the effects of electron transfer in faceting phenomena, we will model a clean Mo(111) and Mo(211) surface under an electric field. The electric field will induce an extra charge on the clean surface due to screening effects, the magnitude of the electric field is adjusted to reflect the charge transfer between the corresponding adsorb and substrate. Thus, the effect of chemical bonding between adsorbate and substrate can be excluded. Section IV then considers the charging effect due to the specific effect of the overlayer adsorption. Section V is the conclusion.

II. THE IMPOSITION OF ELECTRIC FIELD

We are going to first consider the generic effect of surface charging. For that purpose, the external governing parameter is the surface charge density, or equivalently, the direction and magnitude of an externally imposed field. The imposition of a static external field within the local density (LDA) formalism is not difficult, and various formulations can be found in the literature.[6,8,12] LDA is indeed the method of choice if we want to gain an understanding of the physics at the microscopic level. Empirical and semiempirical methods (e.g., classical force fields, embedded-atom method, tight-binding models) require less resources, but the application of external fields will inevitably lead to induced charge rearrangements that cannot be handled properly by empirical approaches. LDA can take care of these subtle effects self-consistently.

Our surface systems will be modeled by the standard ''slab'' geometry. The slabs are repeated, separated by a vacuum region of 18 Å. To include the effect of an external electric field, the most convenient way is to put two external uniform charge sheets in the vacuum at the distance of a few Å away from the geometrical surfaces, which simulates putting the slab into a capacitor. For metallic systems, the electrons will rearrange themselves to give a surface charge to screen out the field so that the electric field cannot penetrate into the bulk. For good metals, the field can hardly penetrate the top one or two layers, so that slabs of about ten layers should be thick enough for most purposes. The surface electronic charge and the external charge sheet will establish an electric field whose strength is controlled by the surface charge density of the charge sheet. We note that the surface electronic screening charge on both sides of the slab is established automatically during the self-consistency iteration process. Thus the magnitude of the external field and the degree of surface charging can be controlled conveniently simply by varying the charge density of the external charge sheet we impose into the system. The plane-averaged z component of the E field in vacuum would be given by Gauss's Law, and depends on the charge per unit area of the external charge sheet (σ). The profile of the electronic screening charge depends on the properties of the material and the orientation of the surface, and can be determined by finding the difference in charge density between two calculations: one with and the other without the external charge sheets. The atomic positions must be the same in both calculations, and correspond to those that optimize the energy of the system with the external field turned on. The electric field profile can be determined once we know the profile of the induced screening charge. Comparison of the E-field strength in the vacuum region with the Gauss's law result provides a quick and convenient check to see whether the separation between the geometrical surface and the external charge plate is big enough. The induced screening charge profile can also give the penetration depth of the external field.

We choose to use a symmetric configuration for imposing the E field. The external charge sheets outside each side of the slab have the same sign, and we inject or deplete electrons from the slab to maintain overall neutrality. The external charge sheet has the form $\rho_{\text{ext}}(z)=f(z_a)+f(-z_a)$, where z_a and $-z_a$ are the positions of the sheet, with the center of the slab taken to be $z=0$. The function $f(z)$ is taken to be a Guassian which decays fast enough as that we have a ''thin'' charge sheet. We avoid using a delta function since its Fourier transform has strong Gibbs oscillation. Since we are considering metallic systems, the extra (or depleted) electrons will all be localized on the slab surface to screen out the field. The interior of the metal is locally neutral. It is surely possible to impose external sheets of the opposite sign on either side of the slab, as a few authors have done before. There is in fact no difference for the screening charge profile between the two cases. We prefer to use the symmetric configuration because it allows a straightforward consideration for the surface energies of a given field and polarity. Self-consistency of electronic charge and potential is also reached much more easily.

We note that in such a formulation, there is no need to include terms that carry explicitly an external E field (it can be done if we wish to do so). All that enters into the LDA functional are the additional Coulombic potential due to the charge sheets: the field establishes itself automatically as we iterate to self-consistency.

III. GENERAL CONSIDERATIONS

A. Electrostatic energy

We now consider the change in energy when there is an external field imposed on a metal surface, leading to surface charging. We first focus on the electrostatic energy, and we will see that the field-induced energy contains a surface term that depends only on the field strength and a term that depends explicitly on the geometry (the size of the unit cell, the form of the external charge sheet). Thus, specifying the surface charging alone cannot determine the surface formation energy. There is always an additional term that depends on the geometry of the problem, which is indeterminate unless we specify the configuration of the opposing charging. A good example is the case of the metal/electrolyte system. Knowing the surface charge per unit area does not specify the system energy. We also need to know the state of the electrolyte and its spatial distribution before the capacitance energy can be determined.

We use a Fourier space expression since we are using periodic boundary conditions in our LDA calculations. We note that the system is always neutral overall. The external field is imposed by external charge sheets, which is presented by ρ_{ext}, which will be balanced by the extra charge of opposite sign in the surface of the slab. For example, if ρ_{ext} is positive, extra electron states will be occupied and if ρ_{ext} is negative, there will be less electron occupancy in the system.

We write the total electrostatic energy per unit cell ξ as

$$\xi_{\mathrm{Coul}}=\frac{\Omega}{2}\sum_{\mathbf{G}\neq 0}\frac{8\pi}{G^2}\{\rho_{\mathrm{slab}}(\mathbf{G})+\rho_{\mathrm{ext}}(\mathbf{G})\}^2, \tag{1}$$

where $\rho_{\mathrm{ext}}(\mathbf{G})$ and $\rho_{\mathrm{slab}}(\mathbf{G})$ are the Fourier components of the external charge sheet and the slab, respectively. ρ_{slab} here includes charge from electrons and ionic cores. Ω is the unit cell volume. It is convenient to write

$$\rho_{\mathrm{slab}}(\mathbf{G})=\rho_0(\mathbf{G})+\Delta\rho(\mathbf{G}), \tag{2}$$

where $\rho_0(\mathbf{G})$ is the total charge of the slab when we turn off ρ_{ext} (i.e., no external field), but the atomic positions are fixed at those that minimize the total energy of the system in the presence of an external field. $\rho_0(\mathbf{G})$ contains both the charge of the ionic core and the electrons. $\Delta\rho$ is then the screening charge and it is localized near the metal surface to screen the bulk of the metal from the external field. We shall see the form of $\Delta\rho$ for Mo(211) in Fig. 1 below. We note that $\Delta\rho(\mathbf{G}=0)=\rho_{\mathrm{ext}}(\mathbf{G}=0)$ a nd the Fourier components $\Delta\rho$ is dictated by the response of the system. For metals, the $\Delta\rho(\mathbf{r})$ in real space will be localized in the surface region to screen out the external field so that it cannot penetrate into the bulk of the metal (except for the Friedel oscillations). The surface charge density given by $\sigma=(1/A)\int dz\int\int_A\Delta\rho(\mathrm{r})dxdy$, where A is the area of the surface unit cell (in the LDA calculations, the $\int dz$ is performed from the middle of the slab to the middle of the vacuum region). We can write Eq. (1) as

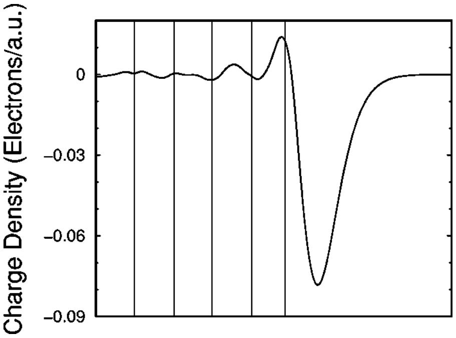

FIG. 1. The screening charge for Mo(211), under an external field of 3 V/Å. The vertical solid lines indicate the position of the atomic layers. Only half of the slab is shown.

$$\xi_{\mathrm{Coul}}=\frac{\Omega}{2}\sum_{\mathbf{G}\neq 0}\frac{8\pi}{G^2}\{\rho_0^2+\rho_0^*[\Delta\rho(\mathbf{G})+\rho_{\mathrm{ext}}(\mathbf{G})]+[\Delta\rho(\mathbf{G})+\rho_{\mathrm{ext}}(\mathbf{G})]^2\} \tag{3}$$

The charge distribution $\Delta\rho+\rho_{\mathrm{ext}}$ will lead to an electric field in the vacuum. [See Fig. 2 for Mo(211)]. According to the Poisson equation, the $\Delta\rho+\rho_{\mathrm{ext}}$ will have a corresponding electrostatic potential with Fourier components

$$V(\mathbf{G})=8\pi\frac{\Delta\rho(\mathbf{G})+\rho_{\mathrm{ext}}(\mathbf{G})}{G^2} \tag{4}$$

and a corresponding electric field with Fourier components

$$\mathbf{E}(\mathbf{G})=-i\mathbf{G}V(\mathbf{G}). \tag{5}$$

If the external charge sheet ρ_{ext} is placed far away from the surface, this electric field will be nearly uniform, pointing

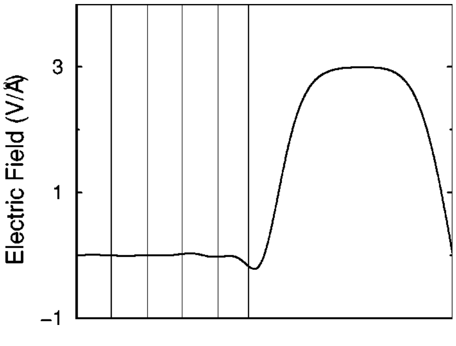

FIG. 2. The xy-averaged electric field as a function of z, as calculated from Eq. (5) for Mo(211) when an external charge sheet is placed in the vacuum to impose an field of 3 V/Å. The vertical solid lines indicate the position of the atomic layers. Only half of the slab is shown. The field inside the slab is zero, as the external field is screened by the screening charge shown in Fig. 1. The field rises smoothly from the surface to the value of 3 V/Å in the vacuum, as the screening charge resides outside the geometrical plane of the top surface layer. The smooth change of the potential in the middle of vacuum is because we have a Gaussian-like charge sheet.

in the z direction in the vacuum region, and has a value given by σ according to the Gauss's Law. Close to the surface, the electric field will be inhomogeneous and deviates from the Gauss's law value and eventually becomes zero in the bulk of the metal.

The three terms in Eq. (3) can be interpreted as follows. The first term is the electrostatic energy of the ions and the electrons in the slab when the external charge sheet is not there. The second term is the interaction of the external field with the slab. Since the field is zero deep inside the slab while the charge density of the slab is zero deep inside the vacuum, this is a surface term. For a small and moderate amount of surface charging, this term is expected to be proportional to the surface charge density σ (or the electric field). This term can also be interpreted as the interaction of the external field with the surface dipole of the metal surface. If the metal slab is approximated by a jellium slab, the change in the surface energy to the first order is proportional to $\rho_0\sigma/\alpha^2$, where α is an inverse length that measures the penetration of the electric field into the jellium slab.[13] Our work here basically calculates this term faithfully within the local density formulation. We note that if the external field points outward from the surface, the external electric field and the intrinsic surface dipole would point to opposite directions, causing an increase in energy. Likewise, a decrease of surface energy is expected if the external field points towards the surface. This will be shown to be indeed the case in our calculations. If the induced surface charge is big, it is possible that the surface atomic structures are modified, and this will make the second term slightly nonlinear. The third (last) term can be rewritten as $(1/8\pi)\int \mathbf{E}^2 dV$, where the electric field E is given by Eqs. (5) and (4). Most of the energy of this term is stored in the vacuum region sandwiched between the external charge sheet ρ_{ext} and the electronic screening charge $\Delta\rho$, which literally forms a capacitor. Since the value of this term is dependent on the distance between the charge sheet and the metal surface ($\Delta\rho$ is always near the metal surface), this "capacitance energy" term is always geometric dependent. We subtract away the bulk energy from the total energy of the system, and we will have the surface energy in the presence of surface charging in the form $\gamma(\sigma)=\lambda(\sigma)+C(\sigma,\mathbf{G})$, where σ is the surface charge density, $\lambda(\sigma)$ is the term linear in σ. $C(\sigma,\mathbf{G})$ is a "capacitance" energy due to the existence of an electric field outside the surface charges. This term is geometry dependent, and should be second order in σ. In our LDA supercell calculations, this term depends on the choice of the unit cell, and is proportional to the square of the electric field in the vacuum (or σ) region and the size of the vacuum. It is interesting to note that some of the surface energy curves in the presence of E field of some previous work[6,8] have a quadratic appearance because of this term.[14] In electrochemical cells, this term manifests itself as the electrostatic energy in the dipole layer, and will depend on the spatial distribution of the ions and electrolytes. In the overlayer induced faceting problem that we shall consider in the next section, this "capacitance energy" term depends on the distance between the overlayer and the substrate as well as the amount of charge transferred.

In our LDA calculations, we can calculate $\lambda(\sigma)$ according to

$$\lambda(\sigma)=\frac{1}{A}\left\{\xi_{\mathrm{total}}(\sigma)-n\xi_{\mathrm{bulk}}-\frac{1}{8\pi}\int \mathbf{E}^2 dV\right\}, \tag{6}$$

where $\xi_{\mathrm{total}}(\sigma)$ is the total energy of the whole surface unit with the external charge sheet in place, and ξ_{bulk} is the total energy of the atom in the bulk. We note that the term $\lambda(\sigma)$ defined here includes not only the field-dipole energy as a contribution to the surface energy change due to the external electric field. It actually contains *everything* LDA gives for the field-induced change that is specifically a surface term, including the change in exchange-correlation energy. The field induced atomic relaxation, as well as the field induced change in the surface dipole, are all taken into account automatically and self-consistently. Both are small effects in small fields, but will make $\lambda(\sigma)$ vs σ deviates slightly from linearity at higher fields. The electric field $\mathbf{E}$ is calculated according to Eq. (5). The $\lambda(\sigma)$ term is well defined, in the sense that for a given substrate and a given amount of surface charging (so many electrons per surface unit cell), this quantity has a unique value, independent of the choice of the unit cell.

B. The term $\lambda(\rho)$

After the general consideration, we will consider the specific case of overlayer induced faceting of the substrate in (111) surface of Mo and W, and see if surface charging (due to charge transfer between substrate and overlayer) can account for the experimentally observed phenomena.

Some details of the calculation is now in order. We will consider Mo and the substrate is modeled by a slab of 11 layers of Mo for both (111) and (211).[15] One physical monolayer of adsorbates [which corresponds to three geometric layers for (111) orientation and two geometric layers for (211) orientation][16] are added as additional pseudomorphic layers on the both side of the slab. The slabs are separated by a vacuum distance of 18 Å. More vacuum is used than usual because of the need to include the E field. The calculations are done in the framework of the local density functional approximation,[17] norm conserving pseudopotential[18] and the Ceperly-Alder form of local exchange-correlation potential.[19] We employed a "mixed basis set"[20] which consists of both local orbitals centered on atomic sites and plane waves with a kinetic energy up to 11.5 Ry. The numerical local orbitals are varied to minimize the plane wave cutoff to obtain convergence. The method has been applied successfully to many transition metal systems.[20] The $\mathbf{k}$ points are sampled on an $8\times8\times1$ grid in the surface Brillouin zone.

Figure 1 shows the plane-averaged screening charge $\Delta\rho$ [see Eq. (2)] on a Mo(211) slab due to the electric field of 3 V/Å. This is the upper bound of the field we used in the following calculations. Since the external charge plate is negative, the screening charge corresponds to a depletion of electrons. We note that the screening charge is induced by charge plates outside the slab. The external charge plate and the screening charge of the metal surface together give rise to a Coulombic potential, which gives an electric field. We note

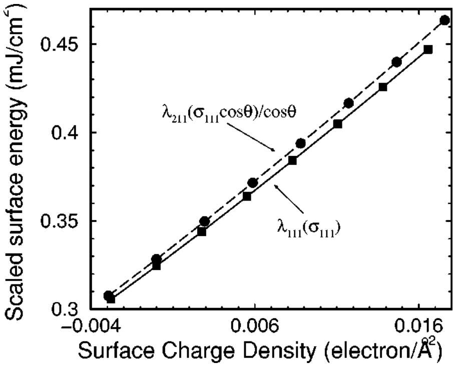

FIG. 3. The squares and solid dots show, respectively, the scaled surface energies $\lambda_{111}(\sigma_{111})$ and $\lambda_{211}(\sigma_{111}\cos\theta)/\cos\theta$ (see text for definition) as a function surface charge density. The highest surface charge density calculated corresponds to a very high field of 3 V/Å.

that the screening charge $\Delta\rho$ screens the external field, and therefore the interior of the slab has essentially zero field. The field does not rise abruptly at top layer, but rises smooth to its vacuum value of 3 V/Å when the $\Delta\rho$ is nearly zero. The charge profile (and hence the surface charge density) in Fig. 1 is an unique property of the Mo(211) and the strength of the external field which determines $\lambda(\rho)$. However, the electric field energy in the vacuum depends on the size of the vacuum region. This leads to a geometry dependent $C(\sigma,\mathbf{G})$ that we will consider later.

In Fig. 3, we plot the value of $\lambda(\sigma)$, defined by Eq. (6) as a function of surface charge density for Mo(111) and Mo(211). As predicted by the theory, it is almost linear.

In order to determine whether surface faceting is possible or not, we should consider the inequality, according to the theory of Herring:[21]

$$\frac{\gamma_{211}}{\cos\theta}<\gamma_{111}. \tag{7}$$

If this inequality is satisfied, there is a thermodynamic driving force for faceting. The cosine term takes into account of the increase in area of the facets.

Let us now consider the contribution of the surface specific (field-dipole interaction) term λ to the surface energy in Eq. (7) to see if the λ term satisfies this condition. When the surface is charged (due to the charge transfer to the overlayer), we have to know the charge transferred on different orientations before we can compare them. It is known that exactly the same number of overlayer atoms that covers a (111) surface will cover the (211) facets after the faceting transformation.[4] If we assume that the amount of charge transferred per unit area is proportional to the number of overlayer atoms per unit area (we will see that this assumption is better for some elements than others in the following sections), then the surface charging on the (211) facets are smaller than the surface charging on (111) by a factor of $\cos\theta$. That is because we have exactly the same number of atoms on (211) as on the (111) orientation, but the (211) facets have an area increased by the geometrical factor of $\cos\theta$. This being the case, $\sigma_{211}=\sigma_{111}\cos\theta$, where σ_{211} and σ_{111} are the surface charges per unit area on the (211) and (111) orientations, respectively, so that when we are considering the Herring faceting condition, we should consider

$$\frac{\lambda_{211}(\sigma_{111}\cos\theta)}{\cos\theta}<\lambda_{111}(\sigma_{111}). \tag{8}$$

This is plotted in Fig. 3, where we compare $\lambda_{211}(\sigma_{111}\cos\theta)/\cos\theta$ with $\lambda_{111}(\sigma_{111})$ as a function of σ_{111}. We note that the $\cos\theta$ term in the denominator penalizes the (211) orientation because the area increases after faceting leading to an increase in the total energy for a fixed value of the surface energy. However, the $\cos\theta$ term in the bracket of the numerator favors the (211) orientation because the area increases, the transferred charge is spread out over a bigger area, leading to a smaller surface charge density. Figure 3 shows that when both effects are considered, the inequality is not satisfied, and thus if we ignore the "capacitance energy" term, the surface charging will not lead to faceting of Mo(111), as the inequality is never satisfied for any reasonable values of charge transfer.

The LDA calculated results can be understood as follows. Consider the difference

$$D(\sigma)=\lambda_{211}(\sigma\cos\theta)-\lambda_{111}(\sigma)\cos\theta, \tag{9}$$

where $\sigma=\sigma_{111}$, since $\lambda(\sigma)$ is nearly linear with respect to σ, we have upon expansion to first order

$$\begin{aligned} D(\sigma)&=\{\lambda_{211}^{0}+\chi_{211}\sigma\cos\theta+\cdots\}\\ &\quad-\{\lambda_{111}^{0}\cos\theta+\chi_{111}\sigma\cos\theta+\cdots\}\\ &=\{\lambda_{211}^{0}-\lambda_{111}^{0}\cos\theta\}+\{\chi_{211}-\chi_{111}\}\sigma\cos\theta\\ &\quad(\text{with}\quad\sigma>0), \end{aligned} \tag{10}$$

where λ_{211}^{0} is the energy of the (211) orientation without surface charging, and the χ's are the derivative of the surface energy [as defined by Eq. (6)] with respect to the surface charge (or external field). As such, the χ's are proportional to the surface dipole potential. The first term $(\lambda_{211}^{0}-\lambda_{111}^{0}\cos\theta)$ is just the Herring faceting condition.[21] We see from Fig. 3 (at $\sigma=0$) that $\lambda_{211}^{0}-\lambda_{111}^{0}\cos\theta>0$ so that the clean Mo(111) should not facet to Mo(211) even though (211) has a lower surface energy per area, but not low enough to compensate for the penalty of area increase. This is consistent with experimental observations that clean Mo(111) is a stable surface. For the same metal, the orientation with a higher surface dipole has a higher work function. Since the (211) orientation is a more compact surface, it should have a higher work function than (111). Our calculations found that the work function for (211) is 4.8 eV, higher than the calculated result of 4.4 eV for (111), and this implies that $\chi_{211}>\chi_{111}$. This is indeed the case as the slope for the (211) curve in Fig. 3 is indeed higher than that of the (111). This also means that the second term in Eq. (9) will only make (211) less favorable if $\sigma>0$, which is the case when the overlayer is more electronegative.

Our result shows that a negative electric field (pointing out from surface) does not promote faceting. This is as far as

TABLE I. LDA calculated charge transfer (in 10^{-3} electrons/Å^2) for Ag, Cu, Au, Pd, and Pt on Mo(111) and Mo(211). θ is the angle between [111] and [211], and cos θ=0.9428.

	more electronegative →				
	Ag	Cu	Au	Pd	Pt
σ_{111}	1.54	1.91	3.84	6.32	6.26
σ_{211}	0.97	1.08	3.64	6.22	7.39
$\sigma_{111}\cos\theta$	1.45	0.94	3.62	5.95	5.90

we can go to discuss the phenomena as a generic effect of surface charging. Beyond this point, we need specific information about the interaction with overlayers, and we shall derive the information from further LDA calculations. We first try to determine the charge transfer. We consider the adsorption of Cu, Ag, Au, Pd, Pt on Mo(100) and (112). We note that Cu and Ag are less electronegative than Au, Pd, Pt. Experimentally, it is observed that the former group does not cause Mo(111) to facet. The second group does.

C. LDA calculated charge transfer and electrostatic energy term that is second order in σ

It is possible to determine the effect of surface charging as a ‘‘generic’’ effect up to the lowest order (linear in σ). As shown above, the electrostatic energy term that is second order in σ cannot have a generic description. We must consider the specific properties of the overlayer (at least we need to know how far is the overlayer away from the substrate).

In order to determine of the charge transfer Q between the substrate and the overlayer, the metal overlayers are put on both sides of the Mo substrate slab and the atomic positions are fully relaxed and the total electronic charge density ρ_{slab} is recorded. The charge density of the clean substrate $\rho_{\text{substrate}}$ and that of the freely suspended overlayer $\rho_{\text{overlayer}}$ are calculated separately and we the calculate the difference

$$\delta\rho=\rho_{\text{slab}}(\mathbf{r})-\{\rho_{\text{substrate}}(\mathbf{r})+\rho_{\text{overlayer}}(\mathbf{r})\}.$$

We note that this $\delta\rho(\mathbf{r})$ is not the same as the screening charge density $\Delta\rho(\mathbf{r})$ in the previous section. The screening charge density $\Delta\rho(\mathbf{r})$ is the screening charge of the metal substrate in response to a uniform externally imposed field. As such, $\Delta\rho(\mathbf{r})$ is strictly the property of the metal substrate (Mo in this case) only, while the $\delta\rho(z)$ defined here depends on both the properties of the substrate and the overlayer. By averaging $\delta\rho(\mathbf{r})$ over the x-y plane, we obtain $\delta\rho(z)$ from which we see that there is a depletion of electrons on the Mo substrate and an excess of electrons of the fcc metals. The charge transfer Q from the Mo substrate to the overlayer is determined by integrating $\delta\rho(z)$ from the middle of the slab to a dividing that half way between the last Mo plane and the first overlayer atomic plane.[22] The surface charge density σ is just Q per unit area. The values are shown in Table I. We see from the LDA calculations that electrons always move from the Mo substrate to the fcc metal overlayer, consistent with the fact that the fcc metals are more electronegative. This is true for both (111) and (211). We also see that the more electronegative is the fcc element on the Pauling scale, the larger is the magnitude of the calculated charge transfer. We found that for the case of Au, $\sigma_{211}\approx\sigma_{111}\cos\theta$, so that the assumption we have used in the previous section (charge transfer per absorbate atom is independent of the orientation) is good for Au. In addition, we see a systematic trend. For the elements Cu and Ag that are less electronegative than Au, we found that $\sigma_{211}<\sigma_{111}\cos\theta$, while for the elements Pd and Pt that are more electronegative than Au, we found that $\sigma_{211}>\sigma_{111}\cos\theta$. This trend has the following implication. We note that if $\sigma_{211}>\sigma_{111}\cos\theta$, which is the case for the electronegative elements that cause faceting

$$\begin{aligned}&\lambda_{211}(\sigma_{211})-\lambda_{111}(\sigma_{111})\cos\theta\\&\quad>\lambda_{211}(\sigma_{111}\cos\theta)-\lambda_{111}(\sigma_{111})\cos\theta.\end{aligned}\tag{11}$$

This means that if we take the LDA calculated charge transfer, instead of using the simplified assumption of $\sigma_{211}=\sigma_{111}\cos\theta$, the surface energy contribution due to the field-dipole interaction is even more unfavorable for faceting since it makes the $\lambda_{211}(\sigma_{211})$ even higher compared with $\lambda_{111}(\sigma_{111})$. In short, the surface specific term (λ) induced by surface charging should suppress rather than contribute to the faceting transformation, and the conclusion is the same whether we determine the charge transfer approximately from simple geometric arguments, or more elaborately with LDA calculations.

We now consider $C(\sigma,\mathbf{G})$, which depends on geometry. On simple terms, one may argue that this term should favor the facetted surface. The argument usually goes as follows. If we put (say) Au on Mo, there is a certain amount of charge transferred from the Mo substrate to the Au overlayer, due to a difference in electronegativity. If the Au covered Mo(111) system facets to the [211] orientation, the surface area increases by a factor of 1/cos θ, where θ is the angle between the two orientations. The surface charge density should decrease, leading to a lower electrostatic energy of the order of $\cos^2\theta$. Such an argument is very reasonable from a macroscopic phenomenological point of view, but the reality in the atomic scale is much more complicated. Such argument implicitly assumed that the charge transferred per atom is the same, independent of orientation. We already found through direct LDA calculation that it is not quite true (see Table I). In addition, there are always ‘‘counter charges’’ in the system, and their position and configuration changes with orientation. In the system we are calculating, the charge is transferred from the substrate to the overlayer. If we want to consider the electrostatic energy, that of the whole system should be considered. It turns out that the charge transfer distribution $\delta\rho(z)$, as calculated from LDA, is a fairly complex function. It has envelopes that show charge transfer from the substrate to the overlayer, but there are oscillations within the envelope, indicating that there are charge rearrangement within the substrate and the overlayers as a result of the overlayer-substrate chemical interaction and rehybridization. To make things more complicated, the distance between the overlayer and the substrate varies, depending on the orientation and the overlayer. For the same orientation, the distance of the overlayer depends on the intrinsic size of the overlayer atoms and the cohesive energy between the

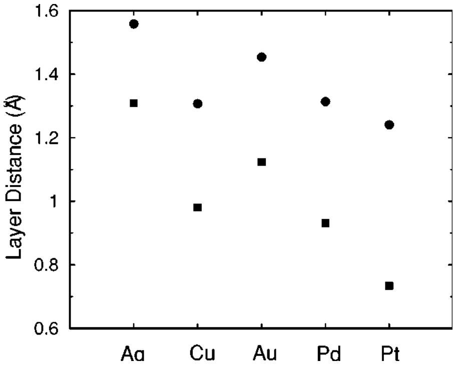

FIG. 4. The distance of the bottom atomic layer of the overlayer from the top atomic layer of substrate. The squares are for (111) and circles for (211).

overlayer and the substrate. This can be seen in Fig. 4, where we show the distance of the bottom atomic layer of the overlayer from the top atomic layer of substrate. The heat of formation[11] is larger in magnitude for faceting agents such as Au, Pd, Pt, and the overlayer is found to be closer to the substrate. We found the higher the heat of the formation of the overlayer, the closer is the distance between the overlayer and the substrate. Cu is an exception because of its small atomic radius. We also see that (111) is closer to the substrate.

If we want to push further to see if the electrostatic energy stored between the charged layer can account for faceting, we can define

$$C(\sigma)=\sum_{\mathbf{G}} \frac{8\pi}{G^2}(\delta\rho)^2(\mathbf{G}).$$

Since $\delta\rho$ is overall neutral, this electrostatic energy is well defined. If we do so, we can consider the contribution of $C(\sigma)$ to the surface energy in Eq. (6). We thus consider $\Delta C = C_{211}/\cos\theta - C_{111}$, to see if this term can contribute to help the faceting and we note that $\Delta C<0$ favors faceting. The results are shown in Table II. We found numerically that the two terms in ΔC are small and nearly cancel each other so that the ΔC term is quite small compared with the surface specific term λ, and thus would not have changed the conclusion we have reached in the previous sections. In addition, the numerical results shows that $\Delta C>0$ for the more electronegative elements Au, Pd and Pt; just the opposite that is required for the driving the faceting transformation. There are two reasons that ΔC does not help the faceting. First, the overlayer is closer to the substrate in the (111) orientation. Second, for the more electronegative elements such as Pd and Pt, the interaction between the substrate is stronger for the (211) and the (111) orientation, leading to a larger charge transfer in (211) than the simple geometric relationship. In fact, the surface charge density in facetted (211) is larger than that on (111) for Pt, even though the Pt is more spread out on the (211). This causes $\Delta C>0$ for the more electronegative elements (Au, Pd, Pt). Thus, whether we consider the field and surface dipole interaction λ, or including the electrostatic energy between of the charge transfer, surface charging cannot be attributed as the mechanism that promotes faceting.

TABLE II. The value of ΔC (in 10^{-3} J m^{-2}, see text) calculated by LDA charge densities for five different elements on Mo substrate.

	more electronegative →				
	Ag	Cu	Au	Pd	Pt
ΔC	−0.4	−1.4	0.3	7.8	16.2

IV. CONCLUSION

We have analyzed the change of surface energy as consequence of surface charging. We found that a surface specific term, interpreted as field and surface-dipole interaction, can be well defined as long as the extent of surface charging is given. Other contributions depend on the detail geometry of the system. We believe that such analysis is useful in a variety of physics and chemistry problems, and can help to delineate the contribution between charge transfer effects and chemical bonding effects. We then applied the analysis to consider the overlayer induced faceting of Mo(111) surface. Experimentally, there is an empirical relationship that the overlayer must have an Pauling electronegativity of at least 2 in order that the faceting be possible. This empirical observation may suggest that that the faceting is a consequence of charge transfer and surface charging of the substrate, and indeed such notion is consistent with a macroscopic picture that the faceted surface has more area to accommodate the transferred charge. However, we found that neither the surface specific term due to field-surface-dipole interaction, nor the electrostatic energy of the geometry dependent term can account for the phenomena. In fact, complex surface phenomena such as overlayer growth induced instability (faceting) and surface morphology changes in electrochemical cells always have different species interacting strongly with each other. The interaction leads to charge transfer as well as chemical bonding and hybridization. All factors contribute to the energetics, and it is not obvious which factor is the most important. For the case of overlayer induced faceting, the present analysis shows that surface charging is not the governing factor despite the strong correlation with electronegativity. The governing factor is thus the specific chemical bonding between the substrate and the overlayer. This is consistent with previous calculations[11] which found that faceting agents such as Pd and Pt has stronger heat of adsorption than the nonfaceting overlayer elements. We note that a previous calculation[8] also concluded that surface charging is not the driving force for Au(100) surface reconstruction inside an electrochemical cell. Lastly, we note that all numerical calculations are performed with LDA. The qualitative features of the results will not be changed if we use the generalized gradient approximation (GGA) since the results can be interpreted semianalytically [see Eq. (10)], and thus will not depend on the details of the exchange-correlation functional.

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[*] Permanent Address: Department of Physics, Fudan University, Shanghai, China.

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[15] Results has been checked with 13 layer slabs, and are essentially the same.

[16] The term ‘‘physical monolayer’’ has been used in the experimental literature (see Ref. 4) to refer to an overlayer coverage that shadows all the substrate atoms in a ball-and-stick model. The number of geometric layers corresponding to a ‘‘physical monolayer’’ varies with orientation, and is typically one for closed packed surface such as (110) for a bcc substrate. A physical monolayer contains more than one geometric monolayer for higher index orientations.

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