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$sp \leftrightarrow d$ charge transfer at transition- and noble-metal surfaces

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Tersoff and Falicov have calculated that there is a transfer of electronic charge from the *sp* bands into the *d* bands at the surface of nickel and copper. They have used this charge transfer to account for the enhanced catalytic activity of stepped surfaces. I point out that self-consistent calculations for Cu yield the opposite direction of charge transfer and also yield atomic-orbital surface-matrix-element shifts of opposite sign to those obtained by Tersoff and Falicov. It is argued that Tersoff and Falicov's error consists of considering only on-site charge-transfer contributions to these matrix-element shifts even though the off-site (missing neighbor) effects are an order of magnitude larger for the *sp* matrix elements. A qualitative argument is given which indicates that in nickel, also, the surface charge transfer is from *d* bands into *sp* bands.

Recently Tersoff and Falicov[1] (TF) made "self-consistent" parametrized linear combination of atomic orbitals calculations of ideal and stepped (111) surfaces of Ni and Cu. They found an increase of local *d*-state occupancy at the surface (i.e., a flow of charge from *sp* states into the *d* states) and concluded that the enhanced catalytic activity of stepped Ni surfaces was due to the exposure of second-layer atoms which had a higher concentration of *d* holes than the surface-layer atoms. They also find that the self-consistent surface shift in the diagonal matrix elements for copper *d* and *sp* orbitals is negative. It is the purpose of this Comment to point out that truly self-consistent calculations for Cu show that they have obtained the wrong sign for the $sp \leftrightarrow d$ surface charge flow as well as for atomic-surface-orbital diagonal-matrix-element shifts, and to explain why TF obtained the wrong signs for these quantities. I then give a qualitative argument showing that the Ni surface charge flow is also from *d* into *sp* states.

In Table I we show the *d* and total valence charge on each plane of a seven-layer Cu(001) film. In this recently completed calculation we[2] used a basis set consisting of all atomic orbitals through $4p$, one (two) extra sets of *s*, *p*, and *d* Gaussians on the interior (surface) planes and a set of *s* and *p* Gaussians floating above the surface plane. These floating Gaussians contributed 0.122 electrons to the surface total charge. Although projections onto nonorthogonal basis sets are not unique, past experience[3] convinces us that the Löwdin[4] projection used here gives meaningful results. These charges are to be compared with the change in surface occupation for[5] Cu(111) obtained by TF, $\Delta n_d = 0.09$, and $\Delta n_{sp} = -0.19$.

In Table II we display the energy difference between *atomic* orbitals at the surface and center of the seven layer Cu(001) film. The surface shift relative to the plane below the surface is about 0.1 eV larger. Our $3s$ and $3p$ shifts are slightly larger than the corresponding eigenvalue shifts calculated by Arlinghaus, Gay, and Smith.[6] They are larger (as they should be[5]) than the $3s,p$ core shifts of 0.4 eV calculated by Appelbaum and Hammann[7] for Cu(111) surfaces. Note that the potential shift is large in the inner core, smaller in the outer core, and then very large for valence orbitals which extend well beyond the surface.

Our $3d$ shifts are to be compared with TF's $\Delta \mathcal{E}_d = -0.23$ eV and our $4s$ and $4p$ shifts with their

TABLE I. *d* and total valence charge for each layer of a seven-layer Cu(001) film.

	d	Total
Center	9.942	10.990
$C+1$	9.942	10.988
$C+2$	9.920	10.969
Surface	9.871	11.048

TABLE II. Surface energy shift (relative to center layer) of Cu *atomic* orbitals in (001) film (in eV).

$\Delta 1s = 1.52$
$\Delta 2s = 1.58$
$\Delta 2p = 1.59$
$\Delta 3s = 0.77$
$\Delta 3p_{x,y} = 0.73$
$\Delta 3p_z = 0.74$
$\Delta 4s = 3.49$
$\Delta 4p_{x,y} = 5.22$
$\Delta 4p_z = 10.41$
$\Delta 3d_{x^2-y^2} = 0.82$
$\Delta 3d_{3z^2-r^2} = 0.78$
$\Delta 3d_{xy} = 0.66$
$\Delta 3d_{yz,xz} = 0.99$

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$\Delta\mathscr{E}_s=-0.53$ eV. The reason TF's results are incorrect is that they obtained "self-consistency" by assuming

$$\Delta\mathscr{E}_s=\alpha\Delta n_s+\beta\Delta n_d \ , \quad \Delta\mathscr{E}_d=\beta\Delta n_s+\gamma\Delta n_d \ ,$$

i.e., that the shift in the surface diagonal-matrix elements depends only on the on-site charge shift. While this is essentially true for core states, it is obviously not true for valence orbitals which extend beyond the edge of the film. Furthermore, TF's orbitals are assumed to be orthogonal and therefore their surface orbitals are different from their bulk orbitals. Because they have fewer neighbors to which they are orthogonalized, the surface *sp* orbitals have much less kinetic energy than the bulk orbitals. This actually overwhelms the large surface potential shifts shown in Table II, and TF's $\Delta\mathscr{E}_s$ should be large and negative. Anderson[8] has shown that if the overlap between orbitals is small, then to first order in the overlap the diagonal energy of an orbital is independent of its neighbors, i.e., the attractive potential energy and kinetic energy of orthogonalization due to the neighbors cancel. Therefore $\Delta\mathscr{E}_d$ should depend only on the on-site charge shift, but only because two effects that TF ignored happen to cancel. The large negative $\Delta\mathscr{E}_s$ will induce a positive Δn_s which will induce a small positive $\Delta\mathscr{E}_d$ (and also somewhat reduce $\Delta\mathscr{E}_s$). The positive $\Delta\mathscr{E}_d$ will in turn induce a negative Δn_d. Thus we see that the sign of $\Delta\mathscr{E}_s$ depends upon whether one uses atomic orbitals or orthogonalized orbitals (such as Wannier functions) but that the flow of charge in the Cu surface, however calculated, is out of the *d* orbitals and into the *sp*. (These effects have been discussed in regard to our own[9,10] parameterized calculations. There we found that if the surface parameters are not shifted, the change in surface charge for Cu(111) is -0.198 or $+0.256$ electrons per atom, depending upon whether Wannier or atomic basis functions are used. Thus very large negative or positive values of $\Delta\mathscr{E}_s$ would be required to obtain the approximate surface charge neutrality which occurs at self-consistency.)

The situation in Ni is quite different than in Cu although the end result appears to be the same. Before considering the "self-consistent" response to the on-site charge we again find a large *sp* surface charge excess due to reduced kinetic energy of orthogonalization of the surface *sp* orbitals. But for Ni we also find an even larger surface *d* charge excess. This is due to the fact that the Fermi surface cuts through the top of the minority spin *d* bands and that the surface *d* (density of states) DOS is narrower than the bulk which causes more *d* states to lie below E_F at the surface than in the bulk.[10] Because the Fermi surface cuts through the *d* bands, the *d* DOS is an order of magnitude greater than the *sp* at E_F. Thus the *d* electrons respond much more strongly to the self-consistent potential induced by what was originally a large excess of both *d* and *sp* surface charge so that the self-consistent surface charge again should end up with a small *sp* excess and *d* deficit. One would again expect positive surface shifts for diagonal atomic-orbital-matrix elements but a large negative shift for $\Delta\mathscr{E}_s$ if it were calculated for a surface Wannier function.

I know of no accurate self-consistent Ni calculation in which these potential and charge shifts are reported. Wang and Freeman[11] obtain a surface flow from 4*p* into both 4*s* and 3*d*. They expanded in occupied valence atomic orbitals only; these do not have sufficient variational freedom to yield a very accurate surface charge density. Furthermore, they use a charge fitting procedure to obtain the potential for each iteration in which the charge is forced to be a superposition of spherical atomic 4*s*, 4*p*, and 3*d* charges whose amplitude, but not shape, is varied. It is this spherical fitted charge, and not a projection against spherical harmonics, which shows the increase in surface *d*-charge density. On the other hand, Gallagher and Haydock,[12] using a scheme in which *d* orbitals are chosen so as to maximally decouple the *d* bands from the *sp*, calculated the *d* bands only in a self-consistent manner. They found surface *d* atomic-orbital energy shifts and a surface *d* deficit for Ni approximately half as large as those reported for Cu in Tables I and II. Their calculated result, that *d* electrons taken in the absence of *sp* want to flow from the surface into the interior, may seem to be of little utility. However, when one couples their result with the fact that off-site kinetic effects, acting on *sp* electrons alone, force charge to flow from the interior to the surface, one is reinforced in his belief that the net surface charge flow is from *d* into *sp*.

TF proposed that enhancing the number of holes on a Ni atom would increase its catalytic activity. They also noted that the amount of *sp* ↔ *d* charge flow is roughly proportional to the deviation of the site coordination number from its bulk value of 12. Because they (presumably) had the wrong sign for the *sp* ↔ *d* charge transfer, they concluded that the enhanced catalytic activity of Ni steps was due to the exposure of atoms at the bottom of the steps which have a higher coordination number than surface atoms. We do not consider it unlikely that their basic premise is correct but that the enhanced activity is due to atoms at the step tops which have a lower coordination number than ordinary surface atoms.

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