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Potential, core-level, and *d* band shifts at transition-metal surfaces

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We have extended the validity of the correlation between the surface $3d$ core-level shift (SCLS) and the surface d band shift (SDBS) to the entire $4d$ transition-metal series and to the neighboring elements Sr and Ag via accurate first-principles calculations. We find that the correlation is quasilinear and robust with respect to the differencies both between initial- and final-state calculations of the SCLS's and two distinct measures of the SDBS's. We show that despite the complex spatial dependence of the surface-potential shift (SPS) and the location of the $3d$ and $4d$ orbitals in different regions of space, the correlation exists because the sampling of the SPS by the $3d$ and $4d$ orbitals remains similar. We show further that the sign change of the SCLS's across the transition series does indeed arise from the d band-narrowing mechanism previously proposed. However, while in the heavier transition metals the predicted increase of d electrons in the surface layer relative to the bulk arises primarily from transfers from s and p states to d states within the surface layer, in the lighter transition metals the predicted decrease of surface d electrons arises primarily from flow out into the vacuum. [S0163-1829(96)01035-1]

I. INTRODUCTION

The surface electronic structure of a metal plays a central role in the surface chemistry that takes place upon it. That is, the surface electronic structure of a metal is central to its chemical reactivity. It has long been understood that, in transition metals in particular, the d electrons dominate their chemistry. More recently, computational studies of chemisorption and dissociation on various metals and alloys have clarified how they do so.[1–6] Thus one can state with confidence that the surface chemical reactivity of a transition metal depends strongly on the response of its surface d electrons to the external perturbations imposed by an atom or molecule with which it interacts. A generic measure of its reactivity should then be provided by their response to a generic perturbation.

One very simple generic perturbation is provided by the difference in environment between surface and bulk. Thus a shift in some suitable feature of the d band structure between surface and bulk could provide a suitable generic measure of the reactivity. The structure of the occupied portion of the d band could be studied experimentally by photoelectron spectroscopy, and the shift in the peaks of the spectrum from surface to bulk could be detected. This measure of the surface d band shift (SDBS) is somewhat ambiguous because of broadening and the role of matrix elements. A sharply defined measure is the shift in the center of gravity of the d band, B_d, or

$$\Delta B_d = -(B_d^{\text{surf}} - B_d^{\text{bulk}}). \tag{1}$$

Another sharply defined measure would be the shift in the relevant matrix element of the Kohn-Sham Hamiltonian; how to model this is discussed in Sec. III.

A recent development which is very interesting is that the differences between the core-electron binding energies of surface atoms of supported metal monolayers on transition-metal substrates and of surface atoms of the clean elemental crystal surface (the latter consisting of the element forming the adlayer) are strongly correlated with the corresponding shift in the center of gravity of the surface d band.[7,8] It has been observed[9] that the core-level shifts tend to correlate with the adlayer's chemical reactivity, and that this can be understood through the correlation with the surface d band shift.[7,4]

The surface core-level shifts (SCLS's) and the SDBS's arise from the surface potential shift (SPS) experienced by the core states and the d states, respectively. Both represent different spatial samplings of the same potential shift; thus the existence of the observed correlation is not surprising. The purpose of this paper is to provide a quantitative test of the correlation and a deeper and more detailed understanding of its origin. In Sec. II, we report the results of SCLS calculations for $4d$ transition metals and for Sr and Ag. We also demonstrate an excellent quasilinear correlation between the computed SCLS values and those of the SDBS's. Indeed, the

SCLS values nearly equal the SDBS values in the initial-state approximation. To demonstrate that this correlation is robust, holding for other measures of the SPS, we extract values of that shift for the xy and x^2-y^2 subbands at the center of the surface Brillouin zone by fitting the computed bands to a simple model in Sec. III. The correlation is found to persist.

The two most prominent features of the results in Secs. II and III are (i) the quasilinear correlation between the SCLS's and the SDBS's, and (ii) the sign change which occurs across the 4d series. Understanding (i) requires less depth of analysis than understanding (ii). Accordingly, in Sec. IV we present plots of the 3d core-orbital density and the 4d valence-orbital density overlaid upon the SPS, which make clear that the sampling argument referred to above is valid. On the other hand, to understand (ii) fully requires probing more deeply into the origin of the SPS than is done in the usual surface d-band-narrowing argument. In Sec. V we provide such an analysis of the origin of the SPS via a decomposition of the SPS into its component parts together with a decomposition of the electron-density changes $\Delta\rho(r)$ responsible for it. In the process, we confirm the essential correctness of the band-narrowing argument. The resulting improved understanding of the SPS and $\Delta\rho(r)$ is our most significant contribution. We discuss our results briefly in Sec. VI.

II. CORRELATION BETWEEN SCLS'S AND SDBS

We have considered fcc(001) surfaces of the 4d transition metals and of Sr and Ag, and have calculated the SCLS's, Δ_c, for the 3d levels. All calculations have been done for the fcc(001) structure to facilitate intercomparison and the establishment of trends, irrespective of whether fcc is the equilibrium structure.

Using Slater's transition-state concept[10] to evaluate total-energy differences, Δ_c can be estimated from

$$\Delta_c \approx -[\epsilon_c^{\mathrm{surf}}(n_c=1.5)-\epsilon_c^{\mathrm{bulk}}(n_c=1.5)], \qquad (2)$$

where $\epsilon_c^{\mathrm{surf}}$ and $\epsilon_c^{\mathrm{bulk}}$ denote the Kohn-Sham eigenvalues of a particular core state of a surface or bulk atom, and n_c is the occupation number of the core orbital. In the initial-state approximation, the SCLS's are given by Eq. (2) with $n_c=2$.

The electron density, core-electron eigenvalues, and densities of states are calculated by means of an efficient surface-Green's-function technique based on the tight-binding, all-electron linear muffin-tin orbital theory within the local-density approximation (LDA) of the exchange-correlation functional in the Ceperley and Alder form[11] as parametrized by Perdew and Zunger.[12] The details of the method have been described elsewhere.[13,14] The potentials are calculated self-consistently within the atomic-sphere approximation (ASA) in an intermediate region consisting of the surface layer, three substrate layers, and two layers of empty spheres simulating the vacuum-sample interface. This intermediate region is coupled to the semi-infinite vacuum on one side and to the semi-infinite crystal on the other, with frozen potentials. Calculations are performed for sphere radii chosen so as to minimize the total energy of the bulk in the fcc structure. No relaxation of the topmost layers has been assumed; all interatomic distances in the surface layer, as well as between surface and substrate layers, are assumed to be the same and equal to those in the substrate. To describe the transition-state [see Eq. (2)], self-consistent electronic structure calculations are performed under the constraint of charge neutrality. The single-impurity problem of the localized core hole with half an electron missing in the 3d shell can be easily treated within the surface-Green's-function formalism. The charge neutrality constraint within this scheme results in a nearly fully relaxed final state, i.e., that the valence charge of the excited single impurity nearly equals that of the unperturbed atom plus 0.5e. In Table I we compare three of our calculated shifts with independent first-principles calculations, which include final-state effects to some approximation, and with available experimental data. A number of other calculations for the most close-packed surfaces[19] have achieved a similar degree of agreement between experiment and theory using similar but not identical computational methods.

TABLE I. Comparison between independent first-principles calculations of surface core-level shifts with available experimental data.

	SCLS (eV)	
	Calculated	Experiment
Rh(001)	$-0.83^{a}, -0.62^{b}$	-0.62^{c}
Pd(001)	$-0.34^{a}, -0.33^{b}$	-0.44^{d}
Ag(001)	$-0.11^{a}, -0.10^{b}$	-0.0 ± 0.1^{e} [fcc(111)]

[a] Present work.

[b] Methfessel, Hennig, and Scheffler (Ref. 15).

[c] Borg *et al.* (Ref. 17).

[d] Nyholm *et al.* (Ref. 16).

[e] Andersen *et al.* (Ref. 18).

We have also calculated the linear muffin-tin orbital (LMTO) potential parameters C_d,[20] which correlate closely with the center of gravity of the d band, B_d, for both bulk and surface, and have constructed SDBS's from them according to Eq. (1) ($\Delta B_d \approx \Delta C_d$). The calculated initial- and final-state core-level shifts for the fcc(001) surfaces of the 4d transition metals plotted vs these calculated SDBS's are presented in Fig. 1. Note the near linearity of the correlation between the initial SCLS's and the SDBS's. The smaller screening contributions to the shifts, which are related to the downward shifts of the core levels when deoccupied, leave the overall linear correlation largely unaffected.

III. CORRELATION OF THE SCLS'S WITH SURFACE POTENTIAL PERTURBATIONS

We have somewhat arbitrarily selected the SDBS as defined by Eq. (1) as the generic measure of the response of the d electrons to a generic perturbation, and have shown that it has a beautiful quasilinear correlation with the SCLS's. However, the d band structure is complex, with changes in width, shape, and centroid position at the surfaces. We now examine the relationship between the SCLS's and the values of a quite different measure of the SDBS to test whether the above correlation is relevant despite the complexity of the d band.

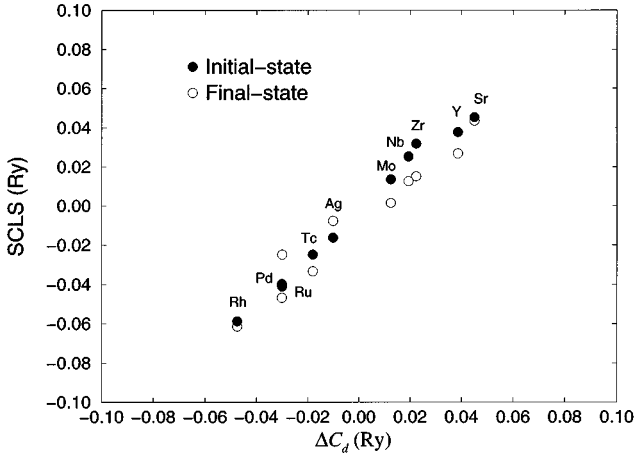

FIG. 1. The calculated initial- and final-state core-level shifts and the shift of the d band center between the bulk and surface d bands.

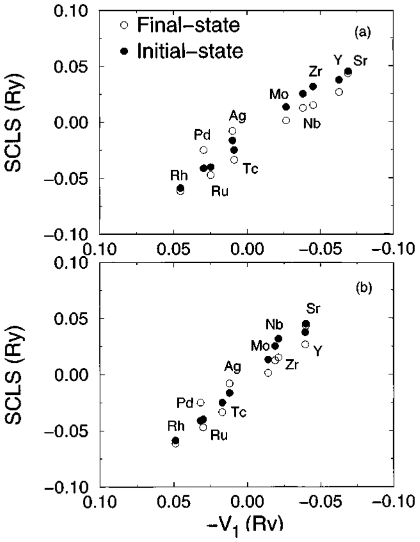

FIG. 2. The calculated initial- and final-state core-level shifts, and the fitted surface potential shifts, V_1, for the (a) x^2-y^2 and (b) xy subbands.

In earlier papers we have shown how to extract and display the individual physical effects of the presence of the surface on the electronic structure by examining the $\mathbf{k}_\parallel$-, symmetry-, and layer-resolved density of states (DOS) at $\mathbf{k}_\parallel = \mathbf{0}$ for both clean surfaces[21] and overlayers.[22] For the fcc(001) surface, the xy and x^2-y^2 subbands do not couple with any other low-lying bands. The bulk xy and x^2-y^2 contributions to the DOS are accurately fitted by a simple cosine band, and are thus represented by the band structure of an infinite one-dimensional chain of sites having only nearest-neighbor coupling t of a nondegenerate level. For the surface layer and substrate layers underneath, the xy and x^2-y^2 subbands DOS at $\mathbf{k}_\parallel = \mathbf{0}$, are accurately represented by that of a semi-infinite chain perturbed by potential shifts V_1 and V_2 at terminal and penultimate sites. The quantity V_1 can be interpreted as a model of the surface shift of the diagonal matrix element of the true Hamiltonian in a generalized Wannier representation. We take its negative as an alternative measure of the SDBS which reflects in quantitative detail the shift in the surface d band structure caused by the surface potential shift. The bandwidths $4t$ were fixed by fitting to the bulk subbands, and the values of V_1 and V_2 were fixed by fitting the zeroes in the DOS in the third layer. The resulting fits for the full energy and layer dependence were in general extraordinary, as shown in Fig. 3 for the Rh xy subband, for which the fitted and calculated DOS's are nearly undistinguishable. In Ref. 21, the DOS was fitted with V_1 only. The fits with two parameters are slightly better, but the V_1 values are robust, i.e., they change little between the one- and two-parameter fits. The calculated initial- and final-state core-level shifts for the fcc(001) surface of the $4d$ transition metals plotted vs the fitted surface-potential shifts V_1 for the x^2-y^2 and xy subbands, are presented in Figs. 2(a) and 2(b), respectively. Once again we find a quasilinear correlation between the initial-state shifts and an independent measure of the SDBS's which is relatively slightly affected by final-state contributions to the core-level shifts, demonstrating that the correlation is indeed robust.

IV. SURFACE-POTENTIAL SHIFT AND ORIGIN OF THE CORRELATION

It is very interesting that the numerical values of the SCLS's are not merely correlated with, but are nearly equal to those of the potential shifts $-V_1(xy)$, $-V_1(x^2-y^2)$, and ΔC_d, and particularly so for the initial-state contributions to the shifts and ΔC_d. To understand this near equality better we have examined the spherically symmetric part of the surface potential shift $\Delta V(r)$,

$$\Delta V(r) = V^{\mathrm{surf}}(r) - V^{\mathrm{bulk}}(r) \tag{3}$$

together with $r^2|R_{3d}(r)|^2$ and $r^2|R_{4d}(r)|^2$, where $R_{3d}(r)$ and $R_{4d}(r)$ are the radial solutions of the Schrödinger equation within the corresponding atomic sphere in the bulk. To first order,

$$\Delta_{3d}^{\mathrm{initial}} \approx -\int dr\, \Delta V(r) r^2 |R_{3d}(r)|^2, \tag{4}$$

$$\Delta C_d \approx -\int dr\, \Delta V(r) r^2 |R_{4d}(r)|^2, \tag{5}$$

hold, with appropriate normalization. Equation (4) is expected to be more accurate than Eq. (5) since the $3d$ core level is much more tightly bound, and the LMTO orbital by itself cannot represent the full complexity of the $4d$ band.

We show our results in Fig. 4(a) for Y, representative of the lighter $4d$ transition metals with a positive shift, in Fig. 4(b) for Mo, representative of the midseries elements with small shifts, and in Fig. 4(c) for Pd, representative of the heavier $4d$ transition metals with a nearly filled d band and a

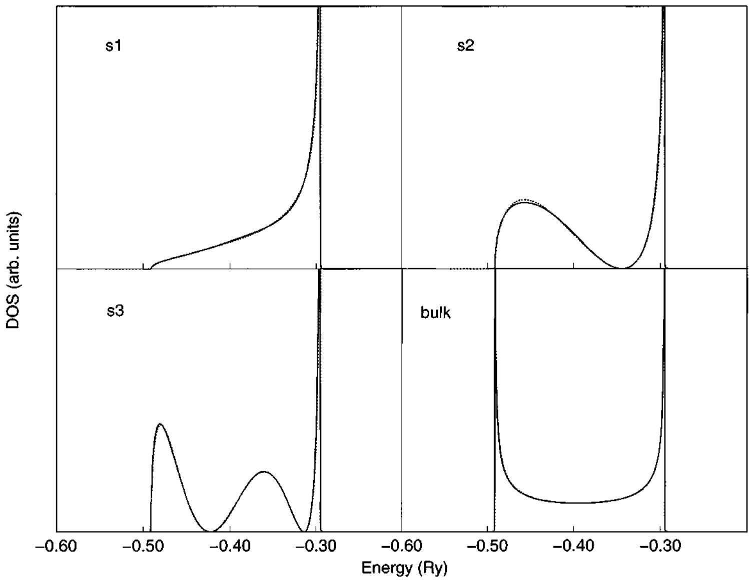

FIG. 3. The solid lines are the calculated xy contributions to the $\mathbf{k}_{\parallel}$, and layer-resolved DOS at $\mathbf{k}_{\parallel}=\mathbf{0}$ for a Rh(001) surface. The topmost three sample layers are denoted $s1$, $s2$, and $s3$. The dotted lines are the local density of states of the terminal, and first two interior neighbors of a perturbed semi-infinite chain with nearest-neighbor coupling $2t=0.0980$ Ry, and potential shifts $V_1/2t=0.4984$ and $V_2/2t=0.0010$ on the terminal and penultimate sites. The position of the bulk substrate Fermi level is at -0.0765 Ry.

negative shift. We compare the computed values for the initial-state contributions to the shifts and ΔC_d with those estimated via Eqs. (4) and (5) in Table II. We see that the agreement is better for the initial-state SCLS than for the ΔC_d's, as anticipated, but Figs. 4 and Table II clearly imply that the sampling argument for explaining the correlation is correct. It could not be anticipated in advance of these plots, however, that the sampling argument must be correct, considering the complexity of the spatial dependence of $\Delta V(r)$ and the fact that the $3d$ and $4d$ orbitals are localized in quite different regions of space. However, the spread of the $4d$ orbitals effectively averages over the spatial fluctuations of $\Delta V(r)$.

It should be noted that for radii r larger than half the nearest-neighbor separation, indicated by a vertical line in both Figs. 4 and 5, the computed quantities become unreliable because of the use of the ASA. The resulting uncertainties do not weaken any of the conclusions drawn above from Figs. 4 and below from Figs. 5.

V. ORIGIN OF THE SURFACE-POTENTIAL SHIFT

Figures 1, 2(a), and 2(b) show the well-known change of sign that was observed to occur in the middle of the $5d$ transition series,[23] and predicted the most close-packed surface of the observed crystal structure of the $4d$ series.[19] This fact has usually been qualitatively explained by using the decrease in width of the d band at the surface compared to the bulk, and assuming an approximate conservation of d charge in each layer. Thus the self-consistent potential at the surface changes so as to mantain the d band filling approximately constant, and consequently the surface d band shifts relative to the bulk band. This perturbing potential acts on the core electrons as well and is repulsive for late transition

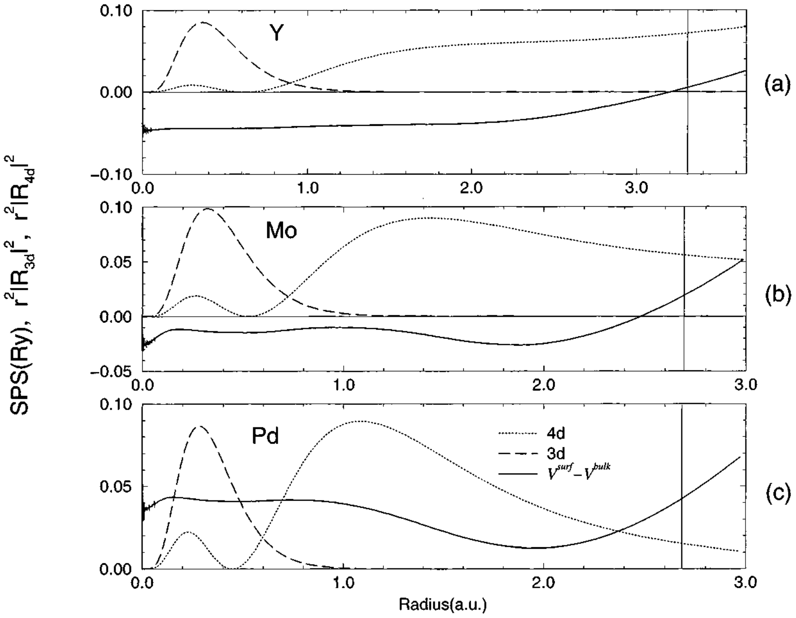

FIG. 4. Spherically symmetric part of the surface-potential shift and the radial solutions of the Schrödinger equation within the corresponding atomic sphere in the bulk, $r^2|R_{nl}(r)|^2$, $nl=3d$ and $4d$ for (a) Y, (b) Mo, and (c) Pd. The vertical lines correspond to a radius of half the nearest-neighbor separation.

TABLE II. Comparison of the first-order estimates for the 3d core-level and d band shifts with computed initial-state shifts and d band shifts, in Ry.

	First-order perturbation theory		Computations	
	SDBS	$\Delta_{3d}^{\text{initial}}$	SDBS	$\Delta_{3d}^{\text{initial}}$
Pd	−0.031	−0.042	−0.042	−0.046
Mo	+0.010	+0.013	+0.011	+0.018
Y	+0.021	+0.044	+0.038	+0.038

TABLE III. Potential shifts in Ry at the center and surface of the muffin-tin sphere.

	$r=0$			$r=r_s$		
	ΔV_M	ΔV_c	$\Delta V_M+\Delta V_c$	ΔV_M	ΔV_c	$\Delta V_M+\Delta V_c$
Pd	+0.18	−0.16	+0.02	+0.18	−0.14	+0.04
Mo	+0.26	−0.26	+0.00	+0.26	−0.28	−0.02
Y	+0.16	−0.18	−0.02	+0.16	−0.21	−0.05

metals, and attractive for early transition metals. These arguments apply as well to the nominally empty or filled d bands of Sr and Ag.[24] For Ag, the sp states below and above the Fermi level E_F are hybridized with the d states below E_F. The d band narrows at the surface, as above. Were the d band center to remain unchanged, the sp-d hybridization of the empty states above E_F would decrease, and the net d character f_d of the occupied states would increase. Here f_d is defined as $f_d=\int^{E_F}dE\,n_d(E)$, where $n_d(E)$ is the density of states per atom projected on to the LMTO d basis functions, either for a bulk or a surface site. A repulsive potential shift moves the d band center upward and conserves the d character. For Sr, the sp states are hybridized with states from the empty d band above E_F. When the empty d band narrows, f_d would decrease if the center of the d band were to remain fixed. An attractive potential shift moves the d band center downward, and approximately conserves f_d.

It is important to recognize that in this argument the potential shifts are assumed to occur primarily to conserve d character and not strictly to preserve electrical neutrality. For the heavier transition metals, it is known[25] that the outflow of electrons from the surface layer to the vacuum, which generates the surface dipole layer, indeed originates predominantly from states of s and p character. Despite the qualitative consistency of the d-band-narrowing argument, we regard it as incomplete, and now present a complementary but deeper analysis. This analysis yields a considerably more detailed understanding of the surface-potential shift and in the process confirms the essential features of the band-narrowing argument.

The Kohn-Sham potential V_{TOT} is conveniently decomposed into three components in our computational methods; the Coulomb term V_c, which is the Coulomb potential within a muffin-tin sphere arising from all charge within that sphere; the Madelung term V_M, which is the Coulomb potential arising from all charge external to that sphere and which is constant within the sphere; and the exchange-correlation term V_{xc}, which is evaluated in the LDA. Thus the change in the total potential is

$$\Delta V_{\text{TOT}}=\Delta V_M+\Delta V_c+\Delta V_{\text{xc}}, \tag{6}$$

where Δ indicates the difference between surface and bulk quantities. ΔV_M are constants, and are listed in Table III for Y, Mo, and Pd. The spherical averages of $\Delta V_M+\Delta V_c$, ΔV_{xc}, and ΔV_{TOT} are shown in the upper panel of Figs. 5(a)–5(c). One sees inmediately that ΔV_{xc} is of significance

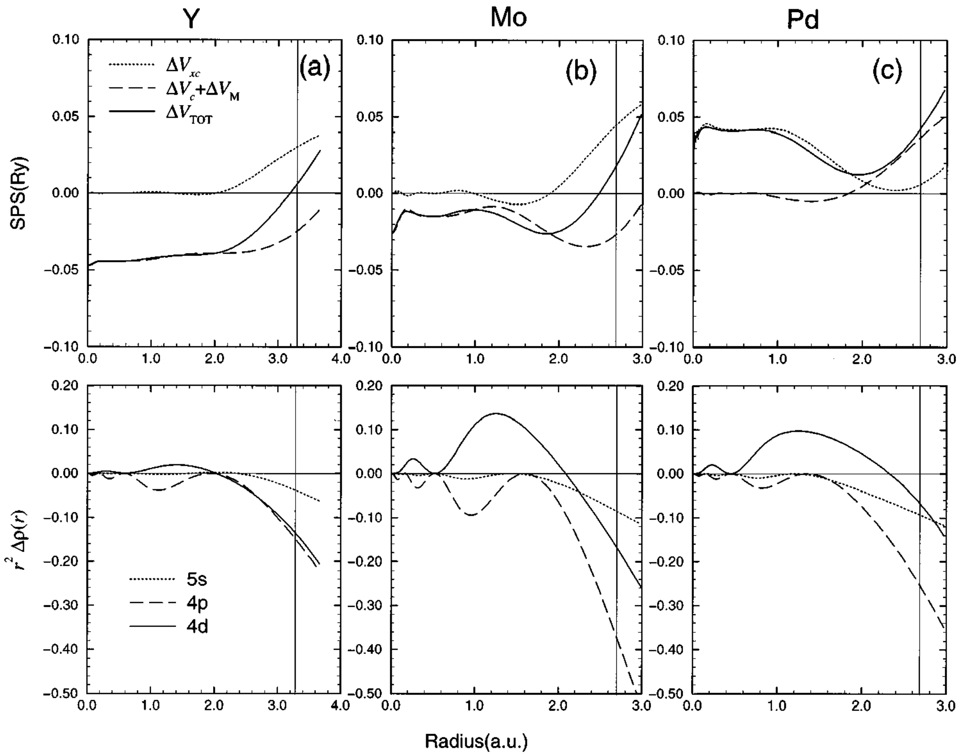

FIG. 5. Spherically symmetric part of the contributions to the surface-potential shift and the $r^2\Delta\rho_l(r)$, $l=s$, p, and d of the surface atoms for (a) Y, (b) Mo, and (c) Pd. The vertical lines correspond to a radius of half the nearest-neighbor separation.

TABLE IV. Shifts in the number of electrons per atom at the surface and vacuum layers.

	Surface				Vacuum
		ΔQ_l		ΔQ	ΔQ
	s	p	d		
Pd	-0.090	-0.227	$+0.077$	-0.240	$+0.248$
Mo	-0.075	-0.330	$+0.022$	-0.382	$+0.385$
Y	-0.035	-0.170	-0.117	-0.322	$+0.300$

only in the outer region of the atomic sphere, where it is repulsive. This occurs because to lowest order the derivative

$$\Delta V_{\mathrm{xc}}(r)=\left.\frac{\partial V_{\mathrm{xc}}}{\partial\rho}\right|_r \Delta\rho(r) \tag{7}$$

diverges as the density goes to zero, and the density is lowest in the outer regions of the sphere. However, comparing $\Delta V_{\mathrm{xc}}(r)$ in Figs. 5 with the $3d$ and $4d$ orbital densities in Figs. 4, one sees that $\Delta V_{\mathrm{xc}}(r)$ makes little contribution to the SCLS's, and makes a comparable negative contribution to the SDBS's in all cases. ΔV_M is positive and ΔV_c is negative in all three cases. Moreover, both ΔV_M and ΔV_c vary monotonically in the series Y, Mo, and Pd, as illustrated by the values of $\Delta V_M(r)$ and of $\Delta V_{\mathrm{xc}}(r)$ at $r=0$ and $r=r_s$ (r_s is the atomic sphere radii within the ASA) listed in Table III and by the curves in Figs. 5. It is only the sum of the Coulomb and Madelung potential shifts which establishes the trend in the SPS's, SCLS's, and SDBS's.

This behavior of the potential shifts is associated with a corresponding self-consistent behavior of the spherically averaged electron density $\rho(r)$. The shifts $\Delta\rho(r)$ are plotted in the lower panels of Figs. 5 for Y, Mo, and Pd, respectively, together with their decomposition $\Delta\rho_l(r)$ into contributions from states of given angular momentum, $l=s$, p, and d. One sees that the s and p contributions to $\Delta\rho(r)$ are negative everywhere. Table IV lists the electron number shifts

$$\Delta Q_l=8\pi\int_0^{r_s} r^2\Delta\rho_l(r)\,dr, \tag{8}$$

and the total shift per sphere

$$\Delta Q=\sum_l \Delta Q_l \tag{9}$$

for the surface layer together with ΔQ for the first vacuum layer. One sees first that the ΔQ's are essentially equal and of the opposite sign for the vacuum and surface layers. That is, the net electron transfer occurs primarily between the surface and the vacuum, with little transfer occurring between the surface and the interior. Next, one sees that, for Pd,

$$|\Delta Q_s+\Delta Q_p|>|\Delta Q| \tag{10}$$

in the surface layer. Thus, for Pd, s and p electrons both flow out of the surface layer and are transferred into the surface d bands, giving rise to a positive ΔQ_d. For Mo, there is less than one-third as much internal transfer from s and p to d, leading to a small ΔQ_d. Finally, for Y, d electrons flow out of the surface into the vacuum, giving rise to a negative ΔQ_d.

This trend in ΔQ_d is precisely what is expected from the d-band-narrowing argument. Because for Pd the band centroid is below E_F, the narrowing of the surface d band initiates a transfer of s and p electrons into d electrons states at the surface which tends to increase the Coulomb repulsion V_c and shift the d band centroid upward, thus moderating but not eliminating the transfer. For Mo, with E_F near the centroid, the effect is much smaller. For Y, with the centroid above E_F, the narrowing causes a decrease of the d electrons, reducing V_c and shifting the centroid downwards. One cannot at this point distinguish between a transfer of d to s and p electrons, which then flow outward, and a direct outflow of d electrons; the effect is the same. However, the large value of $r^2R_{4d}^2(r)$ in the outer region of the atomic sphere evident in Fig. 4(a) for Y suggests at least some direct d outflow.

Examination of $\Delta\rho_d(r)$ in the density-shift plots in the lower panels of Figs. 5 reveals more interesting results. One sees clearly that both transfer from sp to d states into the inner region of the atomic spheres and d flow out of the outer region into the vacuum occur in all three cases. In Pd, transfer within the interior dominates, in Mo the two effects nearly balance, and in Y the outflow dominates.

VI. SUMMARY AND DISCUSSION

In Secs. II and III we have established a robust quasilinear correlation between the surface core-level shifts and two different measures of the surface-potential shift of the entire $4d$ transition series plus Sr and Ag. We then demonstrated in Sec. IV for the representative elements Y, Mo, and Pd that the initial-state contributions to the SCLS's are accurately given by the average of the SPS over the $3d$ LMTO orbital, and that the SDBS is given approximately by the corresponding average over the $4d$ orbital. The latter, being quite broad, averages over the spatial fluctuations in the SPS, and so, in effect, samples a potential shift little different from that sampled by the $3d$ orbital. This provides a detailed explanation of the correlation between the SCLS's and SDBS's, and does not assume an approximate spatial constancy of $\Delta V(r)$ throughout the region sampled by both orbitals. Finally, we show in Sec. V that the sign change in the shifts across the $4d$ series is indeed correctly given by the standard band-narrowing argument, but that the situation is considerably more complex than envisaged in the argument in its original form. In the heavier elements, the s and p character of the surface-electron density is reduced both by flow into the vacuum and local transfer into surface d states. That is, transfer from s and p states provides the increase in the d electrons predicted by the band-narrowing argument. In the lighter elements, it is the outflow of d electrons into the vacuum which provides the decrease in d electrons predicted by the band-narrowing argument. In the middle of the series, there is little net change in the number of d electrons because the transfer from s and p electrons into d states at the surface is balanced by the outflow into the vacuum. It is this systematic variation in the d-electron-density shift and the shift in the total number of d electrons which is responsible for the sign change in the SCLS's and SDBS's through its contribution to the shift in the total Hartree potential $\Delta V_M + \Delta V_c$.

In Sec. I, we pointed out that the SDBS could be regarded as a response of the d band to a surface perturbation $\Delta V_{\mathrm{TOT}}(r)$, and as such could be used as a measure of surface chemical reactivity. However, it is a very crude measure, indicating intensity of response but giving no indication of the spatial variation or the geometry of the response. Recently, some progress has been made in understanding the geometry of response as well as its intensity through the introduction of the concepts of chemical reactivity theory into the discussion of the surface chemistry of metals.[25–28] The success of the present study of trends in SCLS's and SDBS's suggests that studies of trends in these more sophisticated measures of chemical reactivity could be both feasible and fruitful.

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