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Core-level shifts in bulk alloys and surface adlayers

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The (initial state) core-level shifts of transition metals in bulk alloys and for bimetallic adlayer systems are calculated and analyzed in terms of extra- and (ℓ-decomposed) intra-atomic contributions. Both the trends and magnitudes of the calculated shifts are consistent with experimental data where they exist. Core-level shifts of the *same* sign for both constituents are common in both alloy and adlayer systems. The commonly used "charge transfer" model for interpreting core-level shifts is shown to be grossly inadequate, especially for describing the adlayer shifts; for bulk alloys, however, there is a correlation between the shifts and the changes in the d electron count. The results support the view that the bonding in bulk alloys and adlayers is fundamentally the same; in particular, there is no evidence for any anomalous charge transfer in adlayer systems. The extra-atomic contributions to the adlayer shifts are found to dominate the total shifts for Cu/Rh(001), Cu/Ta(110), and Pd/Ta(110), with the intra-atomic contributions often having the opposite sign compared to the total shift. For the substrate, however, the intra-atomic contributions are relatively more important, suggesting that substrate core-level shifts may provide a better measure of the local chemical effects than adlayer shifts. The relationship of core-level shifts to other physical properties is also discussed.

I. INTRODUCTION

Core-level photoelectron spectroscopy is a commonly used experimental technique for the characterization of materials. The interpretation and modeling of core-level spectra has a long history.[1,2] Since the core levels are relatively compact and are generally assumed not to take part in the bonding, the hope is that core-level binding energy shifts provide a local probe of the changes in the electronic structure of an atom in different environments in molecules and solids. In the simplest view, charge transfer off (onto) an atomic site leads to a more attractive (replusive) potential, thereby causing a shift in the core-level binding energy. From the earliest days, there has been an adherence to this view because of the simple direct connection between the experimental measurements and interpretation, although there has been frequent evidence that this model of core-level shifts is a gross oversimplification. For example, in a classic paper, Steiner and Hüfner[3] measured the core-level shifts of both atomic constituents for eight binary alloy systems as a function of composition. Of the eight, four had level shifts of the same sign for both atoms. If the charge transfer model were in fact correct, these results would suggest that both constituents gained or lost charge, clearly an impossibility. Of the remaining four systems, not all the inferred directions of charge transfer were compatible with notions of the chemical electronegativities of the constituents. For this set of experiments, the simple charge transfer model was consistent for only about a quarter of the alloys systems.

Clearly, other factors besides interatomic charge transfer are important. A short, nonexhaustive, list follows. (1) Changes in the screening of the final state core hole: The photoemission process leaves the system in an excited state. The energy associated with the relaxation of the electrons around the core hole—the difference between the Koopman energy and the (measured) binding energy—can be quite large in magnitude.[4,5] These final state relaxations will contribute to the core-level shifts only through the difference in relaxation between different environments and these are reasonably small for metallic systems, although not neglible.[6,7] A promising experimental approach[8] for separating out the final state contribution uses a combination of the core-level shifts and core-core-core Auger energies. (2) Changes in the reference level (Fermi energy): While the reference level changing may seem odd at first, changes in bandwidths and shapes due to changes in volumes and/or chemical bonding clearly may change the position of the Fermi level relative to the center of gravity of bands, etc. Such changes in the reference level will contribute to the measured shifts also. (3) Intra-atomic (e.g., $sp \leftrightarrow d$) charge transfer: The intra-atomic charge transfer is important because the d and sp electrons in transition metals have significantly different spatial extent. Changes in the relative occupations resulting from bonding may have a larger effect on the local potential and core-level shifts than the net charge transfer.[9,10] (4) Redistribution of charge due to bonding and hybridization: Significant changes in the spatial distribution of charge can occur even without charge transfer due to bonding effects, an effect that seems to be underappreciated in the literature.[11] For example, for a monoatomic solid, the bonding orbitals will have increased density in the bond region between the atoms and, by charge neutrality, less around the nucleus. Antibonding states, on the other hand, have increased density closer to the nucleus and less in the interstitial region. These charge rearrangements will give rise to increased (decreased) core-

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level binding energies for the bonding (antibonding) case. Therefore, relative changes in the bonding between systems can cause core-level shifts in a completely covalent (no charge transfer) picture.

Although separating out these various (initial state) effects unambiguously is impossible since they are often interrelated, it is still worthwhile to attempt to make such divisions in order to get a simpler picture of the bonding and the core-level shifts themselves. Without such an understanding, it becomes difficult or impossible to interpret the experimental core-level shifts.

Recently there has been increased interest in metal adlayers on transition-metal substrates because of the possibility that these systems will have different chemical and physical properties than bulk alloys. Moreover, it is possible to form stable adlayer systems for which no bulk alloys exist.[12] Recently, Rodriquez and Goodman reported[13] core-level shifts for Cu, Pd, and Ni on various 4*d* and 5*d* substrates. Based on these measured shifts and various observed correlations between the shifts and other properties such as CO binding, they argued that the adlayer bonding is intrinsically different from that in bulk alloys. This assertion is difficult to test experimentally since of the systems considered, only Pd-Ta forms bulk alloys. (The lower surface energies of Pd and Cu compared to those of the substrates make it energetically favorable for these adatoms to wet the surfaces, in apparent contradication to bulk phase diagram behavior.) Theory has the advantage that it is able to deal with systems that are not accessible experimentally. In this paper, calculations of initial state core-level shifts and the charge behavior associated with the bonding in (Cu,Pd)–transition-metal bulk alloys and adlayer systems will be reported. Although the basic bonding behavior of bulk alloys and adlayer systems will be seen to be fundamentally the same, there are subtle and important differences.

The chemistry of the atoms at the surface of an elemental solid differs from that in the bulk primarily because there are fewer neighbors involved in the bonding. For a transition metal, the intrinsic *d* bandwidth of the surface atoms is narrower than that of the bulk due to this lower atomic coordination. Since the Fermi level of the surface must equal that of the bulk, there is an electrostatic shift of the surface *d* bands and a shift of the core levels.[1] If there is approximate layer-by-layer charge neutrality, the apparent core-level binding energy decreases (increases) for transition metals with over (under) half-filled *d* bands.

The situation for a monolayer adlayer is more complicated. In ordered bulk alloys, bonding generally favors *unlike* nearest neighbors. The situation is different for adlayers, particularly if the layer is close packed. In such a case the majority of nearest neighbors to an adlayer atom are of the same type of atom residing in the adlayer. Thus the adlayer involves both the lower coordination typical of a surface and a different balance of like and unlike neighbors involved in the bonding. One point that will prove important when considering core-level shifts will be the choice of whether to compare the core-level binding of an adlayer atom with the binding of an atom in the elemental bulk or at the clean surface. The latter appears to be the better choice.

Core levels do not directly take part in the bonding and, as localized spectators, provide a measure of the environment around an atom. Because of the localized nature and spatial separation of the core and valence electrons, the initial state core-level shifts are dominated by changes in the electrostatic potential near the nucleus. Different core levels will sample these changes differently depending upon the spatial extent of the orbitals and will have different shifts. The general observation, based mainly on calculations, appears to be that the deeper core levels will shift more. In the limit of an infinitely compact core level, the initial state core-level shifts should be given by the shifts in the electrostatic potential at the nucleus. For deep core levels, such as the K and L shells of transition metals, this is an excellent approximation because of their small spatial extent; in fact, the energy separations *between* these deep levels are often nearly independent of local environment and bonding. While the electrostatic potential will be used to make attributions of various contributions to the shifts, our reported core-level shifts were calculated taking into account both the spatial extent of the wave functions and exchange-correlation contributions to the potential.

A difficulity in any discussion concerning core-level shifts is that quantities such as charge transfer are not uniquely defined. As such, results often depend on the model used to interpret the results. This problem is no less severe for theory than for experiment, even if the exact wave function were known. In this paper, we propose to use a different method to partition the contributions to the core-level shifts based on a spatial decomposition. We separate the contributions to the electrostatic shifts into intra- and extra-atomic pieces defined by the "size" of each atom. There is obviously arbitrariness in the choice of the size of each atom, but as will be seen later, the picture that emerges from such an analysis does not change qualitatively for even quite large changes in size.

To separate the Coulomb potential V_c into intra- and extra-atomic contributions, consider a sphere of radius R centered on the atom. The electrostatic potential at the nucleus can be obtained from the (spherical) charge $n(r)$ inside the sphere and the (averaged) Coulomb potential on the sphere $V_c(R)$ using the Green's function for a sphere.[14,15] (The nonspherical charge density and potential on the sphere boundary do not contribute to the Coulomb potential at the nucleus.) Thus we have

$$V_c(0) = V_c(R) + 4\pi \int_0^R dr\, r^2 \left(\frac{1}{r} - \frac{1}{R}\right) [n(r) - Z\,\delta(0)]\,, \tag{1}$$

where Z is the atomic number. If the atom were not there, then the potential on the sphere boundary would be

$$V_{\rm ext} = V_c(R) - \frac{q-Z}{R}\,, \quad q = \int_0^R d\mathbf{r}\, n(\mathbf{r}), \tag{2}$$

which, by Gauss's law, is also the potential at the origin. Thus the extra-atomic contribution to the electrostatic potential is defined as the potential due to all other charges in the solid except those enclosed in the atomic sphere.

To compare different systems, it is necessary to use the same zero for the Coulomb potential. (For surface core-level shifts of an elemental system, there is no difficulty since the same zero is used by construction.) Two choices suggest themselves: (1) the vacuum zero and (2) the Fermi energy ϵ_F. While the vacuum zero might, at first glance, appear to provide an absolute reference level, in fact it does not. For example, the bulk core levels of an elemental solid measured from different faces would differ by the work function difference between the faces. The choice of the Fermi level, on the other hand, does provide a zero that avoids such problems. However, as mentioned above, even the Fermi level can shift with changes in volume and/or bonding. While neither of these zeros is perfect, the Fermi level does provide a more physically appealing choice and has the advantage that this is the same zero used experimentally to measure core-level binding energies.

The intra-atomic contribution is obtained as $V_c(0)$ V_{ext}:

$$V_{\text{int}} = 4\pi \int_0^R dr\, r^2 \, \frac{1}{r} \, n(r). \tag{3}$$

The contributions of the core electrons to both the intra- and extra-atomic electrostatic potential can be removed since Poisson's equation is linear. Hence the form of the terms will be identical, except the density will be the valence density only. The valence density can be decomposed further into ℓ components. This decomposition into spherical harmonics is uniquely determined by the wave functions, but includes higher ℓ components than one considers in a linear combination of atomic orbitals-type population analysis. Equation (3) can be rewritten in terms of the charge as

$$V_{\text{int}} \equiv q \left\langle \frac{1}{r} \right\rangle = \sum_{\ell} q_\ell \left\langle \frac{1}{r} \right\rangle_{\ell}, \tag{4}$$

where

$$\left\langle \frac{1}{r} \right\rangle = \frac{\displaystyle\int_0^R dr\, r^2 \, \frac{1}{r} \, n(r)}{\displaystyle\int_0^R dr\, r^2 \, n(r)} \tag{5}$$

is a (normalized) measure of the the spatial extent of the density. The intra-atomic contribution to the change in electrostatic potential at the nucleus between two systems is

$$\Delta V_{\text{int}} = \Delta q \left\langle \frac{1}{r} \right\rangle + q \, \Delta \left\langle \frac{1}{r} \right\rangle + \Delta q \, \Delta \left\langle \frac{1}{r} \right\rangle \tag{6}$$

(or its corresponding ℓ decomposition). Thus the changes in the intra-atomic contribution can be split further into the "charge transfer" (Δq) terms and changes in the shape of the valence density ($\Delta \langle 1/r \rangle$). The extra-atomic contributions also depend on both charge transfer and charge redistribution of all the other atoms in the system, but further division of the extra-atomic piece into separate contributions becomes difficult.

Separating intra- and extra-atomic terms by a boundary oversimplifies the issue because the charge at a given site involves charge intrinsic to the site plus charge best understood as being associated with the valence electrons of neighboring atoms.[16] On occasion, this "charge tailing" will be the dominant source of the changing charge count at a site. For example, in calculations[17] for Au-alkali compounds, any reasonable assignment of sphere radii led to the alkali sites being negatively charged because of Au valence charge overlapping ("tailing") onto the alkali sites. Nevertheless, when discussing the alkali atoms in terms of their "own" valence charge, it was chemically meaningful to talk of them as positively charged ions. It is important to note that even if the wave function is separated into orbitals centered on and off site, it is not possible to uniquely apportion the charge density into on-site and tailing contributions because of the cross terms between on- and off-site orbitals resulting from squaring the wave function, a problem associated with all the standard quantum chemical orbital population analyses. However, when sampling the local potential in an experiment, a core photoelectron does not "care" whether or not the contributing electron charge is intrinsic to the site; the issue of attributing charge is important only when arguing the chemistry of the situation. In this paper, we will use Eqs. (1)–(6) as the basis of discussion, although there are distinct indications in the results that part of the modifications in the charge density at a surface site is due to a reduction in charge tailing resulting from the lower atomic coordination at the surface.

Calculations will be reported for the bulk alloy PdM, where M=Ta,W,Re,Ru,Ir are the substrates used by Rodriguez and Goodman.[13] A number of alloys of Cu with 4d and 5d elements will be considered in order to investigate differences between 4d and 5d behavior. Calculations for the Pd/Ta(110), Cu/Ta(110), and Cu/Rh(001) (and their elemental surfaces) will be used to discuss the effects of the core-level shifts in transition-metal adlayer systems. These three systems provide a reasonable test of theory since the core-level shifts were the most extreme, both positive and negative, of the experimentally measured systems.[13] Previously, results were reported[12] for the energetics of Pd-Nb and Ag-Nb multilayers and adlayers; the core-level shifts of some of these systems will also be reported here.

The calculational methods used here are all-electron methods using the local density approximation for exchange and correlation. The core electrons were treated self-consistently and fully relativistically. The bulk alloy calculations used the full-potential linearized augmented Slater-type orbital method.[18] The electronic structure of the surfaces and adlayers were calculated using the full-potential linearized augmented plane wave method[19] for films of 9–15 layers. Details of both methods can be found in the references.

II. HEATS OF FORMATION AND ADHESION

The calculated heats of formation of the ordered alloys and the heats of adhesion of the adlayers are shown in Fig. 1. The latter is the difference between the energy of an adlayer wetting the surface (forming a uniform layer) and the energy of the clean substrate surface plus the energy of a bulk atom of the adlayer metal. A heat of adhesion thus resembles a heat of formation except that there is the additional gain of the substrate surface energy and loss of the surface energy associated with the monolayer covered surface. Note that the heat of adhesion is *not* directly related to an energy deduced, for example, from thermal desorption measurements; the latter is comparable to a cohesive energy, which is significantly larger than a heat of formation. Since surface energies of Cu and Pd are smaller than the substrates considered, the heats of adhesion display greater binding (more negative energies) than do their bulk alloy counterparts. Of the bulk systems, only PdTa is calculated to be binding, consistent with experiment. All the calculated heats of adhesion are binding, consistent with experiment. However, the calculated heat for Cu/Ta(110) is so close to zero that it raises the question of whether the Cu might not form islands on Ta(110) more readily than the other systems considered.

The calculations for the ordered alloys were done in the cubic CuAu-I structure (undistorted fcc lattice). This structure appears to be the most reasonable choice for the set of systems of concern here; calculations in the CsCl structure, for example, yield heats that are less bound. PdTa is variously reported as being in a disordered fcc lattice and in the ordered CuTi structure. The latter structure is a "multilayer" in the sense that there is an *aabb* stacking of atomic layers. A calculation for the heat of formation for PdTa in this structure yields a result 0.01 eV/atom more bound than the CuAu-I heat of Fig. 1. The fact that PdTa is calculated to be only slightly more stable in the CuTi structure is plausible since PdTa is the only transition-metal–transition-metal system that is reported to form in this phase.

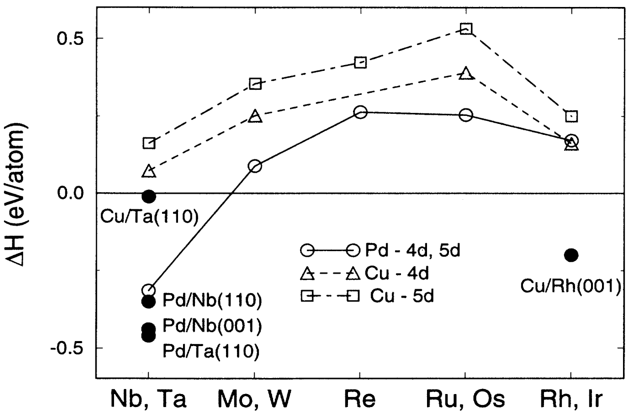

FIG. 1. Calculated heats of formation per atom for bulk alloys of Cu or Pd with various 4*d* and 5*d* metals in the cubic CuAu-I structure (1:1 alloys) and calculated heats of adhesion for various adlayer systems. $\Delta H < 0$ indicates binding; heats of adhesion per adlayer-substrate interface are twice the values shown.

III. CORE-LEVEL SHIFTS

A number of the computed and the experimentally measured core-level shifts are summarized in Fig. 2. For both theory and experiment, the core-level shifts of the bulk alloys and the substrate atoms have been measured relative to the bulk elemental metal, while the adlayer shifts have been measured relative to the clean (001) surface of the adlayer metal. As was the case for the results of Steiner and Hüfner,[3] the core-level shifts of both sites in the bulk alloy and the adlayer systems may be of the same sign, both theoretically and experimentally.[20] There is a distinct suggestion that the substrate shifts in the adlayer systems are smaller in magnitude than the bulk alloy shifts. Theory is in reasonable accord with the experimental adlayer shifts.[13] In the one case (PdTa) where both a measured adlayer shift[13] and a measured Pd shift[21] for the bulk alloy exist, these shifts agree with the calculations. In Fig. 2, there are noticeable breaks in the curves of the calculated core-level shifts for the 4*d* and 5*d* metal sites occurring around Mo and W. These dips can be understood by noting that Nb, Mo, Ta, and W are bcc metals, while those to the right are close-packed metals. The open squares in Fig. 2 are the result of measuring the calculated W shifts with respect to fcc, rather

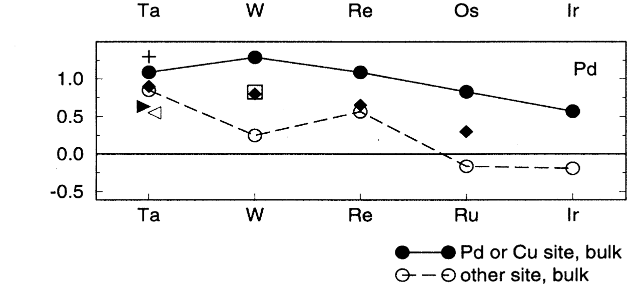

FIG. 2. Calculated initial state core-level shifts for the bulk alloys given in Fig. 1 (circles) and the adlayer systems (triangles). Positive values indicate increased binding energy. Also shown are the experimental values for bulk PdTa (+; Ref. 21) and adlayers (filled diamonds, Ref. 13) and the calculated shifts for W relative to fcc W (open squares).

TABLE I. Calculated initial state shifts for the Nb $3d_{5/2}$ and Pd $3d_{5/2}$ core level for bulk, multilayer, and adlayer systems in different structures.

Structure	Nb $3d_{5/2}$ (eV)	Pd $3d_{5/2}$ (eV)
Bulk		
NbPd (CsCl)	1.5	1.3
NbPd (CuAu-I)	1.1	1.2
$NbPd_2$ ($MoPt_2$)	1.6	1.0
Pd_4Nb_4(110) "bulk"	0.4	0.4
interface	1.2	0.9
Adlayers		
Pd/Nb(001)	1.1	0.7
Pd/Nb(110)	0.5	0.6
Pd/Nb/Pd(001)	1.0	0.4

than bcc, W. The break in the curves thus appear to be an artifact of the changing ground state structures of the reference metals. The differences between the bcc and the fcc reference result, in part, from changes in charge tailing due to changes in the coordination and also to the difference of the long-range electrostatic interactions due to the different structures, i.e., the different Madlung constants.

The calculated level shifts for a number of Pd-Nb systems[12] are listed in Table I. The Pd_4Nb_4 system is an *aaaabbbb* multilayer stacking. Not surprisingly, the "bulk" atoms show small level shifts. Included among the adlayers is a Pd(001) substrate covered with a monolayer of Nb and then another layer of Pd. The set of bulk and adlayer level shifts shows semiquantitative agreement; as before, the surface adlayers display somewhat smaller shifts than the bulk. A shift as substantial as any is found for the substrate on going from Pd/Nb(001) to Pd/Nb(110); this shift results in a large part from the different ratio of like to unlike neighbors for the Nb site.

TABLE II. Calculated initial state and experimental core-level shifts $\Delta(\epsilon_F - \epsilon_c)$ for adlayers (S) and interface substrate ($S-1$) atoms for the Ta $4f_{7/2}$, Pd $3d_{5/2}$, Rh $3d_{5/2}$, or Cu $2p_{3/2}$ levels. The shifts for adatoms (interfaces) are measured relative to the clean (001) surface (bulk). The calculated work function changes $\Delta\phi$ are also given. All energies are in eV.

	Calculated	Experiment	$\Delta\phi$
Pd/Ta(110)			-0.43
Ta ($S-1$)	0.55	~0.5[a]	
Pd (S)	0.63	0.9[b]	
Cu/Ta(110)			-0.95
Ta ($S-1$)	0.45		
Cu (S)	0.56	0.25[b]	
Cu/Rh(001)			-0.65
Rh ($S-1$)	-0.34		
Cu (S)	-0.31	-0.42[b]	

[a] Reference 20.

[b] Reference 13.

TABLE III. Calculated initial and final state $4f_{7/2}$ core-level shifts for Ta(001) (with a 14% contraction of the surface layer) for surface (S) and subsurface ($S-1$) atoms. Calculated values for the bulk binding energy ϵ_{bulk} and experiment are also given. All energies are in eV.

	Initial state	Final state	Experiment[a]
$\Delta\epsilon_c$ ($S-1$)	0.05	0.10	
$\Delta\epsilon_c$ (S)	0.99	0.86	0.74
ϵ_{bulk}	17.78	21.88	21.74

[a] Reference 1.

The calculated adlayer and substrate core-level shifts are compared to the available experimental data in Table II. The calculated initial state shifts are in reasonable agreement with experiment; in all cases the sign is correctly predicted. Most importantly, the trends seen experimentally are reproduced by the calculations, implying that the major features of the core-level shifts can be understood in terms of initial state effects. One example of final state screening effects at surfaces is presented in Table III. The core-level binding energies, including final state relaxation, are obtained as the difference in total energies between the ground state of the Ta(001) surface (including surface relaxation[22]) and the fully relaxed excited state calculated by placing a single core hole in a bulk, surface, or subsurface layer in a (2×2) surface supercell. Inclusion of final state screening measurably improves the agreement with experiment.[23] The results indicate a differential final state relaxation of 0.1 – 0.2 eV for the surface atom, but approximately zero for the subsurface layer. This range of values is consistent with the discrepancies given in Table II. Thus final state effects, while not insignificant, do not appear to be the dominant factor in the core-level shifts considered in this paper.

Two measures of the change in the d electron count Δq_d for the bulk alloys are shown in Fig. 3: (i) the change of the total d-like charge within the atomic spheres and (ii) the change in the on-site-only[16] d count within the Wigner-Seitz spheres. The two samplings yield similar results and both values of Δq_d are small in magnitude. There is an almost perfect correlation between the signs of Δq_d and the level shifts of Fig. 2: A decreased d count (negative Δq_d) results in a more attractive potential and hence increased binding energy. (The scale in Fig. 2 is inverted to highlight this correlation.) This correlation between core-level shifts and the d count changes was previously deduced[9] for Au sites in Au alloys. It is important, however, to emphasize that this semiquantitative correlation does not imply that other contributions are unimportant to the level shifts.

For the adlayer systems, this correlation does not hold as well. For those substrates where the calculated Δq_d values are greater in magnitude than ~0.01, there is a correlation in sign and, within a factor of ~2, magnitude between these Δq_d and the shifts. Dividing the shifts by the Δq_d yields *effective* Coulomb interaction energies ranging from 6 to 18 eV and averaging about 12 eV. These values are rather large, implying that terms in addition to a d contribution contribute to the level shifts. Although the substrate Δq_{tot} tends to reflect the d electron count changes, the correlation with the level shifts is

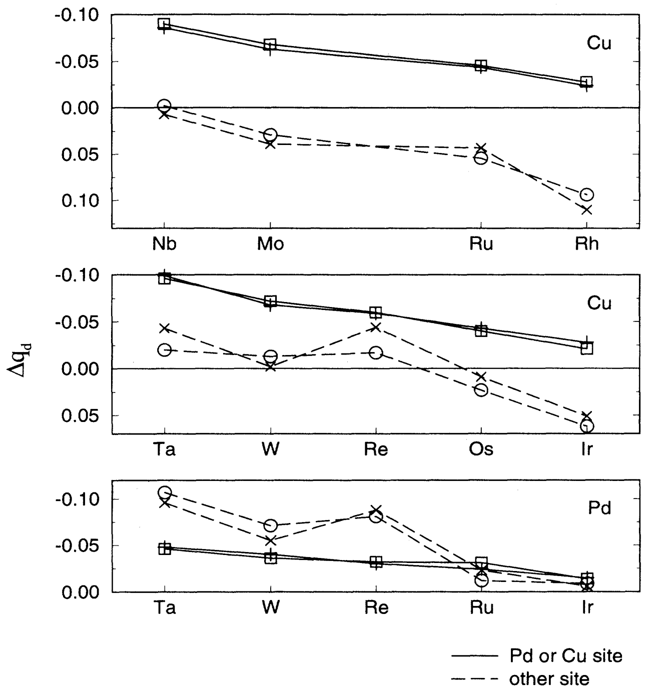

FIG. 3. Calculated changes in the on-site d electron count Δq_d for the bulk alloys in Figs. 1 and 2. Positive values indicate an increased number of d electrons at a site. Note the inverted scale, which allows a direct comparison with Fig. 2. Circles and squares (pluses and crosses) correspond to the atomic sphere (on-site-only) sampling of the density. See the text for a discussion of the two measures of Δq_d shown.

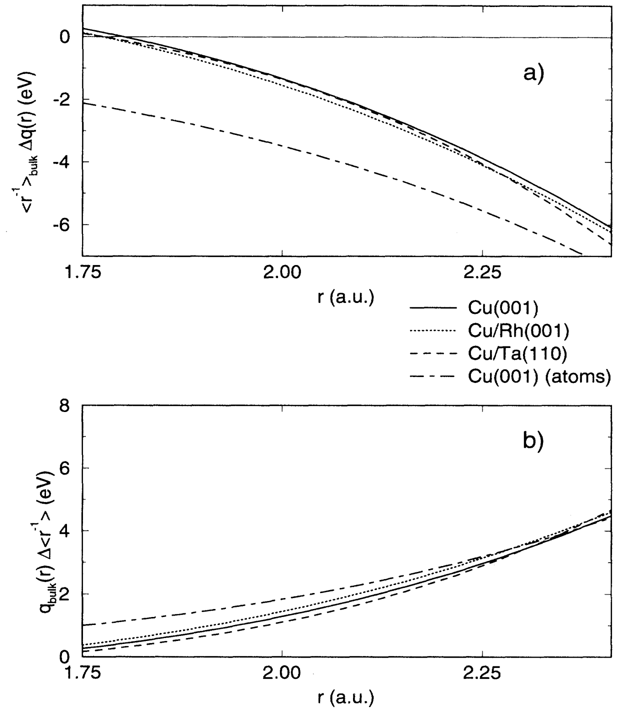

FIG. 4. Calculated intra-atomic contributions [cf. Eq. (6)] to the core-level shifts for Cu adlayers relative to bulk Cu for a range of radii. Also shown are the contributions for Cu(001) determined from overlapped spherical atoms [dash-dotted line labeled "Cu(001) (atoms)"] relative to the "bulk" atoms in this model density.

poorer than the correlation between Δq_d and the shifts. The situation is worse for the adlayers where both Δq_d and Δq_{tot} correlate badly in sign and magnitude with the level shifts. As will be seen in the next section, factors other than on-site charge count changes are important to the chemcial shifts in the adlayers.

IV. INTRA- AND EXTRA-ATOMIC CONTRIBUTIONS

The first two terms of Eq. (6) for Cu surface or adsorbate atoms relative to bulk Cu are plotted in Fig. 4 for a range of cutoff radii. The range of radii plotted in this and the other figures include both the ionic radii normally assigned to the elements and radii more representative of the metallic radius. Presenting a range of values allows one to judge the sensitivity of the conclusions to the choice of atomic "size." The three sets of curves for Cu(001), Cu/Rh(001), and Cu/Ta(110) are essentially alike, implying that the large effects in both Δq and $\Delta\langle r^{-1}\rangle$ are mainly associated with the reduced coordination at the surface and that the effects due to the chemistry of bimetallic bonding are significantly smaller. Further evidence for this view is provided by comparing the behavior of these two terms for a density constructed by simply overlapping spherical charge densities [the curve labeled "Cu(001) (atoms)" in Fig. 4]: Both the Δq and $\Delta\langle r^{-1}\rangle$ terms for this simple case show the same general trends and magnitudes as do the self-consistent results. The decrease in charge at the surface compared to the bulk for "Cu(001) (atoms)" is simply due to the lack of tailing charge from neighbors at the surface. That $\Delta\langle r^{-1}\rangle > 0$ is also related to this change in tailing charge since the outer regions of the atomic site will have a proportionally larger decrease in density than the interior regions and $\langle r^{-1}\rangle$ weighs the interior regions more heavily in a normalized sense. Based on these observations, as well as experimental convention, the surface of the clean metal is the most appropiate reference state to use to measure changes due to chemical effects for adlayer systems.

The intra- and extra-atomic contributions to $\Delta V_c(0)$ for the different adatoms, relative to the elemental surfaces, are shown in Fig. 5. In all cases, regardless of the radius of the atom chosen, the extra-atomic contributions dominate and determine the sign of the shift; only in the case of Cu/Ta(110) does the intra-atomic contribution even have the same sign as the overall shift. The changes with the choice of atomic radius are rather small for the Cu adlayers, whereas for Pd/Ta(110) there is a larger variation. This difference in behavior is a result of the increased chemical bonding—and resulting redistribution of charge density—that occurs for systems such

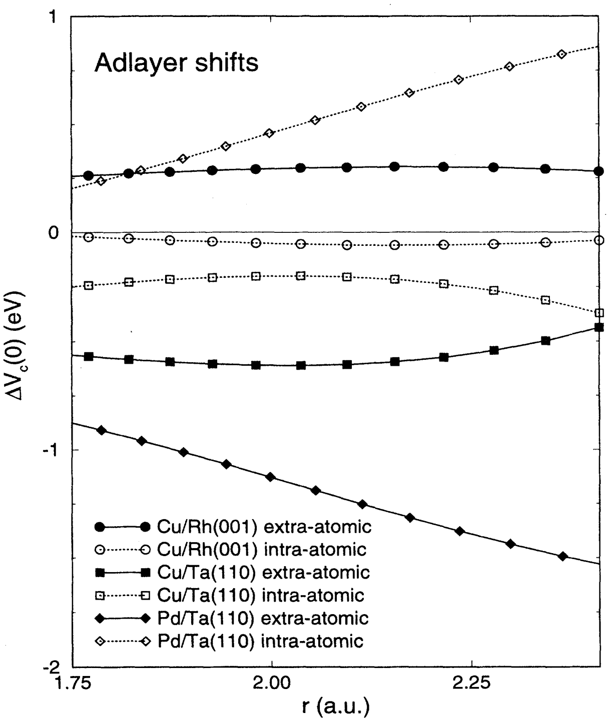

FIG. 5. Calculated intra- and extra-atomic contributions to $\Delta V_c(0)$ for adatoms relative to the surface atoms at the (001) surfaces. $\Delta V_c(0) < 0$ indicate increased core electron binding, i.e., positive core-level shifts.

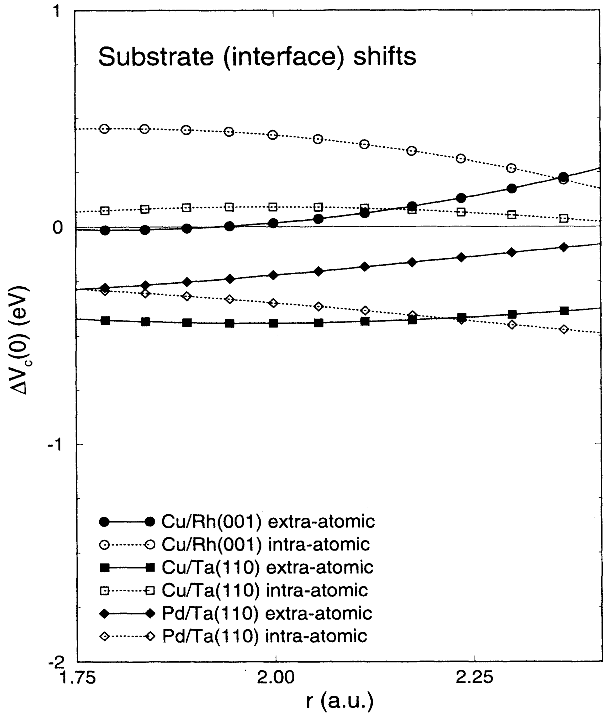

FIG. 6. Calculated intra- and extra-atomic contributions to $\Delta V_c(0)$ for substrate atoms relative to substrate atoms in the clean metal.

as Pd-Ta that form compounds. A somewhat different situation occurs for the substrate contributions shown in Fig. 6. Here the intra-atomic contributions are a far better measure of the shifts, although for Cu/Ta(110) the small intra-atomic shift again has the wrong sign.

Although the intra-atomic contributions do not dominate the adlayer core-level shifts, it is worthwhile to investigate the various contributions in more detail. The intra-atomic contributions for both adatoms and substrate decomposed by ℓ are shown in Fig. 7. The contributions with $\ell > 2$ are due to the tailing charge discussed earlier and these terms are generally small. In all cases, however, these higher ℓ terms for the substrate are of opposite sign compared to the adlayer, as one might naively expect based on charge tailing arguments. The most striking feature in Fig. 7(a) is that the largest contribution does not come from the d electrons, but rather the s electrons. This behavior is in sharp contrast to the case of the bulk alloys considered earlier and the observed correlation between core-level shifts and Δq_d. Since most (if not all) simple models of core-levels shifts for transition metals concentrate on the d electrons, these models obviously will not be able to explain the observed shifts. If one were to remove the s contribution, then the intra-atomic contribution would be of the correct sign for Cu/Rh(001) and Cu/Ta(110) and, depending on the radius chosen, approximately zero or of the correct sign for Pd/Ta(110). Thus the major difference in the intra-atomic contributions to the core-level shifts between bulk alloys and adlayers is due to the different behavior of the s electrons. While this may be somewhat surprising since there are simply fewer s than d electrons in a transition metal, proportionally larger changes in s character due to changes in hybridization are commonly found in surface calculations.

The contributions to the substrate $\Delta V_c(0)$, on the other hand, are more similiar to the bulk. The d contribution is significant and is generally the dominant term [cf. Fig. 7(b)]. The other important term is the p term. In the case of bulk transition-metal alloys, the changes in the p count mainly reflect charge tailing effects rather than intrinisc p changes.[16] The difference in bonding between Cu and Pd is more clearly seen in the substrate core-level shifts than the adlayer shifts: For Cu, the p and d contributions are of opposite sign, with the d term shifting the core level to smaller binding energy, while for Pd the two terms are of the same sign.

The calculated "charge transfer" for the adlayers and substrates are given in Fig. 8. The most obvious point is that the values of Δq_ℓ are small in magnitude regardless of the choice of radius. It is precisely because the charge transfers are small that the core-level shifts cannot be explained within a simple charge transfer picture; conversely, if the charge transfers were actually on the order of an electron, then such a model would be appropiate and the core-level shifts would also be significantly larger. The Δq_ℓ for $\ell > 2$ are a direct measure of the changes

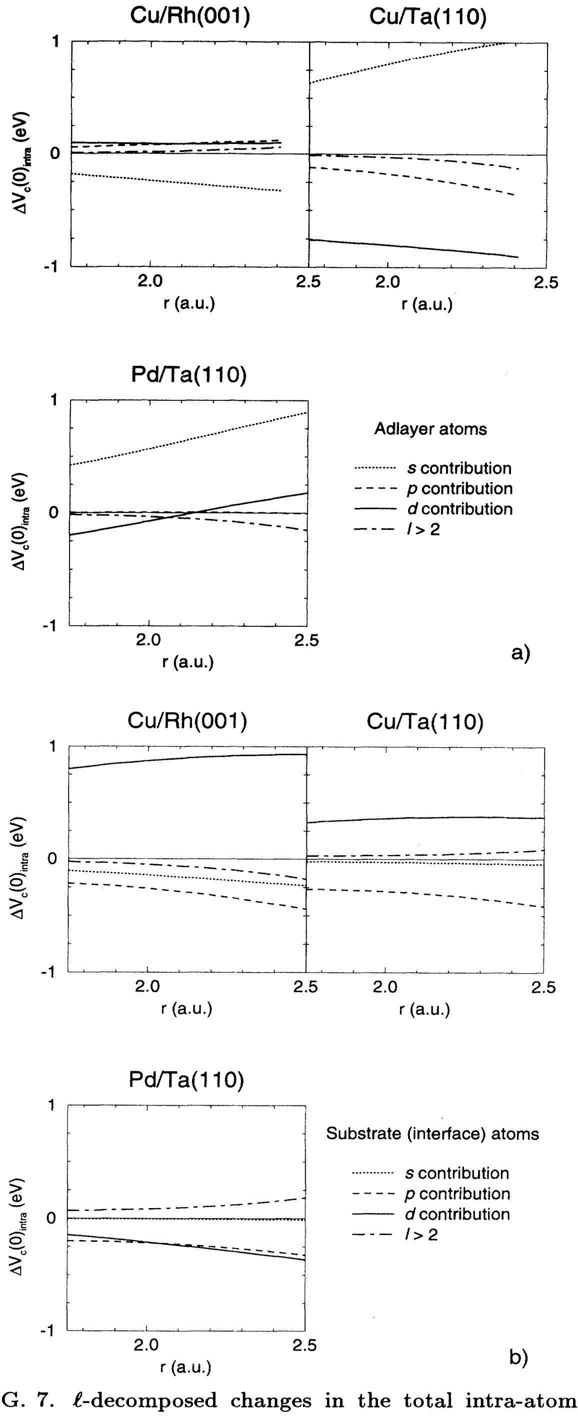

FIG. 7. ℓ-decomposed changes in the total intra-atomic contribution $\Delta V_c(0)$ for (a) adatoms relative to the clean (001) surfaces and (b) the substrate interface atoms relative to the substrate atoms of the clean material.

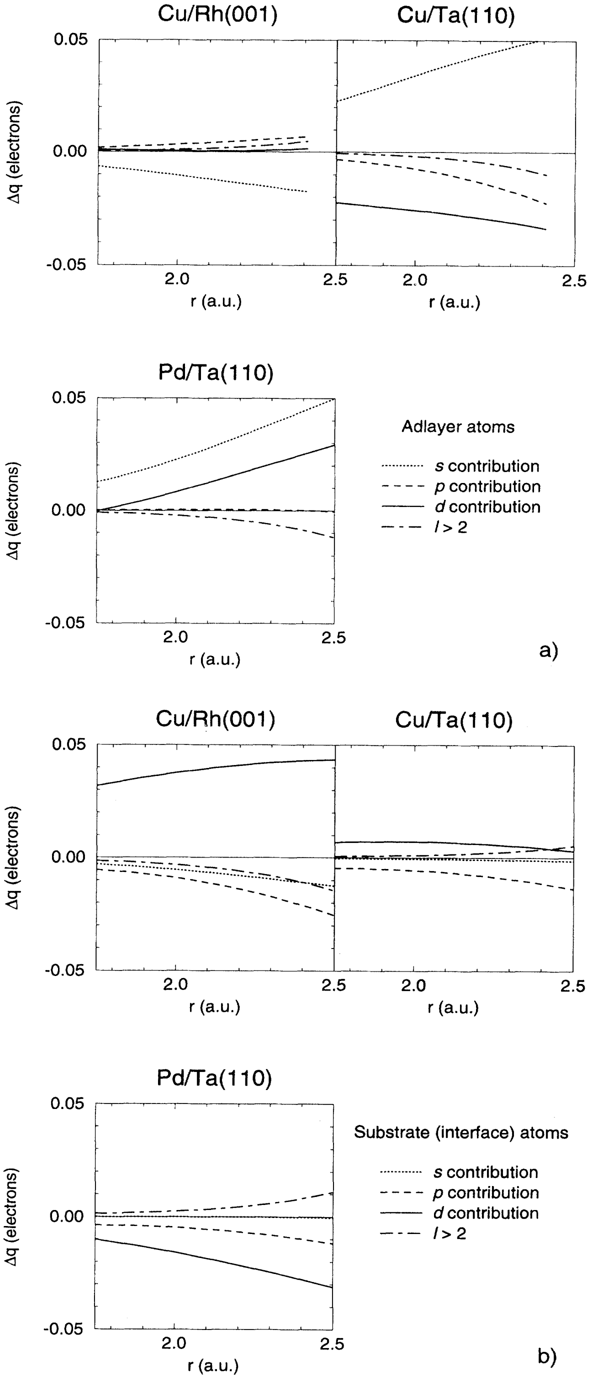

FIG. 8. ℓ-decomposed changes in electron count Δq_ℓ for (a) adatoms and (b) the substrate interface atoms as in Fig. 7.

in tailing of valence charge of neighboring atoms onto a site. In the three cases considered, these higher ℓ contributions for the adlayer and substrate are of comparable magnitude but opposite sign, reflecting the charge redistribution resulting from the bimetallic bonding.

The similarity between Figs. 7 and 8 is striking at first glance, suggesting that the Δq terms of Eq. (6) are the main contributions to the intra-atomic shifts. On closer examination, however, significant differences can be seen. (1) For Pd/Ta(110), the Pd Δq_d is postive for all choices of radii, whereas $\Delta V_{\rm intra}(0)$ changes sign. (2) The ratio of $\Delta V_{\rm intra}(0)/\Delta q_s$ for Cu differs by approximately a factor of 2 between Cu/Rh(001) and Cu/Ta(110), as do the substrate d ratios for Ta in Pd/Ta(110) and Cu/Ta(110).

These differences point out that even for the intra-atomic contributions alone, other terms besides Δq_ℓ are important.

The other terms contributing to the intra-atomic shifts depend on $\Delta\langle r^{-1}\rangle_\ell$, which are shown in Fig. 9. The $\langle r^{-1}\rangle_\ell$ are Coulomb integrals and thus clearly will have an effect on the core-level shifts. Changes in the values of these integrals are a measure of the changes in wave function shape due to chemical interactions: If the wave functions did not relax in response to the different interactions, these terms would be identically zero. A negative value of $\Delta\langle r^{-1}\rangle_\ell$ for an atom implies that the normalized ℓ wave function has moved radially outward. Interpreting changes in $\langle r^{-1}\rangle_\ell$ for a solid is, however, more difficult since $\Delta\langle r^{-1}\rangle$ also reflects the changes in charge tailing (cf. discussion of Fig. 4 above) and differences in intrinsic atomic size. For example, it is quite possible for a bonding state to have $\Delta\langle r^{-1}\rangle_\ell > 0$ even though such a value is indicative of a more antibonding state for equal sized atoms. Even with these caveats, certain statements can be made. There are reasonably large changes with radius for both the adlayer and the substrate, reflecting the redistribution of density due to the bimetallic bonding. As might be expected from the previous discussion, the substrate p and $\ell > 2$ contributions are largest since these are the components of the density that are most sensitive to charge tailing effects. For the adlayers, the $\ell > 2$ term is again large, as are also the terms for the extended s and p orbitals. The more compact d orbitals show far less variation in $\Delta\langle r^{-1}\rangle$ with radius for both the adlayers and the substrate sites.

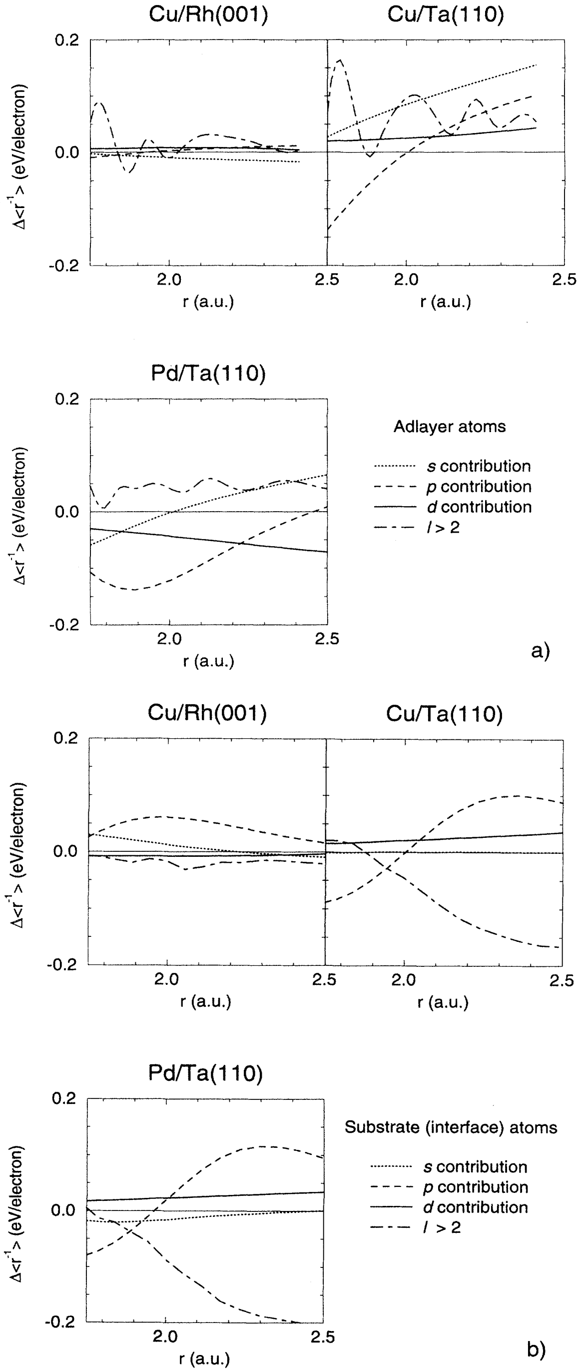

FIG. 9. ℓ-decomposed changes in $\langle r^{-1}\rangle$ for (a) adatoms and (b) substrate interface atoms as in Fig. 7.

Although a unique decomposition of the extra-atomic terms is difficult, several further observations can be made. For the adlayers sites, these terms are clearly the dominant contributions to the core-level shifts for the systems considered here. The changes in the extra-atomic terms reflect the changed environment of the adlayer compared to the clean surface. Broadly speaking, these changes take two forms: (i) structural changes and (ii) different chemical species.

The first includes changes both in crystal structure (e.g., both Cu and Pd are fcc metals, but are adsorbed on Ta, a bcc metal) and in lattice constant. The effect of changing the crystal structure was already seen in Fig. 2, where the core-level shifts relative to both bcc and fcc W were given. This shift of ~0.5 eV, which is strictly due to changes in crystal structure, is significant on the scale of transition-metal core-level shifts. Even if the crystal structure is the same, the changed environment due to different crystal orientations will cause core-level shifts; for example, the surface core-level shifts for different crystal faces may differ on the order of several tenths of an eV.[24] Since the atomic size of the substrate and the adlayer atoms differ, the pseudomorphic adlayer is at a different effective lattice constant than the reference system. Depending on the system and the amount of distortion, this effect again can be of the same order of magnitude as the core-level shifts for the bimetallic systems. To clarify this point, we give a few examples. For Pd(001) expanded to the same in-plane lattice constant as Nb(001), there is an additional calculated shift of ~ 0.4 eV; for Rh(001), a decrease of the lattice constant by 1.5% will shift the bulk core level by ~ 0.1 eV, but the surface shift measured relative to the corresponding bulk position differs by only ~ 0.01 eV. Likewise, for Cu in the Cu/Rh(001) structure (~16% increase in volume), there are shifts in both the bulk and the surface levels to smaller binding, with the surface shift being smaller than the bulk. The case of Cu in the Cu/Ta(110) structure is more complicated because there are changes in both structure and volume. First, there is a core shift of 0.1 eV to greater binding for the (110) surface of bcc Cu (at the same volume as fcc Cu) relative to the (001) face of fcc Cu, but almost no change for the bulk level. Expanding the bcc Cu lattice constant to that of Ta (a volume increase of ~54%), the calculated bulk core level decreases in binding by almost 1 eV. For an unrelaxed surface layer of Cu, there is a surface core-level shift of ~−0.3 eV (relative to the expanded bulk), which decreases to less that 0.1 eV when relaxation of the surface layer corresponding to the Cu/Ta(110) structure (~15% contraction) is included. Both surface shifts are smaller than the corresponding fcc (001) shift. The small surface shift is due to the fact that the Cu atoms at this expanded volume are interacting much less strongly and hence are more atomiclike. Thus changes in crystal structure, orientation, and lattice constants of pure metals can easily cause core-level shifts of order ~0.5 eV and are a major part of $\Delta V_{\rm ext}$. Since these types of changes in coordination and structure in bimetallic systems are more pronounced for the adlayer than the substrate, the extra-atomic contributions to the core-level shifts play a greater role in determining the adlayer shifts.

The other class of contributions to the extra-atomic terms arise from having different atom species near each other. Because of the changes in charge counts resulting from the chemical bonding (cf. Fig. 8), the Madelung potentials at both the adlayer and the substrate interface sites will be changed, resulting in an additional extraatomic shift beyond the purely structural ones discussed above. The values of Δq do give some measure of these shifts, but only crudely. Most of the important redistribution of charge density occurs in the interface between the adlayer and the substrate with the result that the (spherical) potential at the interface sites has large and important contributions from the higher multipoles on neigboring sites. The relative importance of these types of terms was already seen in the high ℓ contributions to the intra-atomic terms (cf. Figs. 8 and 9), in particular with respect to $\Delta\langle r^{-1}\rangle$.

V. DISCUSSION AND CONCLUSIONS

The results presented here, as well as a number of experimental results, strongly argue that the core-level shifts of adlayer systems cannot be described in a simple charge transfer model. This conclusion is consistent with a large body of previous work and, regardless of claims[13] to the contrary, should not be surprising. The calculated initial state shifts are in reasonable agreement with the available experimental data, suggesting that the shifts can be understood without invoking final state effects. Comparsions of calculated initial state core level of bulk alloys and adlayers show that the shifts in both cases are similiar, with an indication that the adlayer shifts are in fact smaller in magnitude. Such a comparison is not unambiguous, of course, since there is always a question of the reference level. Results presented here suggest that the commonly used reference of the clean surface core-level binding energy for adlayer systems is, in fact, the most appropiate one. The similarity of adlayer and bulk alloy shifts strongly argue that the basic chemistry and physics, as measured by electronegativity scales, for example, are similarly independent of any particular model of the core-level shifts. New conceptual frameworks for understanding bimetallic adlayer bonding are not necessary, although obviously the lower coordination (and related differences) of a surface systems must be accounted for if one hopes to get quantitative answers.

The relationship between other physical properties and core-level shifts is important in determining how useful core-level spectroscopy is as an analytic technique. One such commonly measured property is the change in work function $\Delta\phi$. In fact, a correlation between core-level shifts and work function changes has been invoked[13] to support the simple charge transfer picture in bimetallic systems. While the results presented in this paper have demonstrated that the simple picture is incorrect, it is still worthwhile to consider whether a correlation between core-level shifts and $\Delta\phi$ exists and if so, why. The calculated values of $\Delta\phi$ for the three adlayer systems considered in detail here are given in Table II. For monolayer coverage, there is no correlation with both relative signs occurring. The experimental situation is similiar. For Pd, Ni, Ag, and Cu on W(110), $\Delta\phi$ decreases[25] for monolayer coverage, consistent with a charge transfer picture of the core-level shifts. For Au/W(110), however, the work function increases[25] for all coverages. For Pd/Ru(0001), the work-function first decreases at low coverage and then increases so that $\Delta\phi \approx 0$ at monolayer coverage,[26] a result that is at best inconsistent with the core-level shift[13] of 0.3 eV. Finally, a counterexample is provided by measurements[27] of $\Delta\phi$ and the core-level shifts for Pt/Re(0001): $\Delta\phi \sim 0.6$ eV and $\Delta\epsilon_c = 0.4$ eV (at ~0.1 monolayers, $\Delta\phi \approx -0.2$ eV). The simple charge transfer model applied to both $\Delta\phi$ and $\Delta\epsilon_c$ for Pt/Re(0001) would imply different directions of charge transfer.

That work function data cannot be used to support simple notions of charge transfer should not be surprising since ϕ is a delicate quantity that depends on the details of the charge distribution at the surface (dipole barrier) and the bulk chemical potential. For example, even small changes in the $sp \leftrightarrow d$ electron counts can cause large changes since ϕ depends on the $\langle r^2\rangle$ moment of the atomic density.[28] Likewise, it is important to note that simply adding a noninteracting layer of atoms to a substrate will not cause a change in the work function; a polarization of the density is necessary.

If adlayer core-level shifts cannot be used as a reliable measure of charge transfer of metallic overlayers, how can or should they be used? A possibility is to use them in the determination of the thermodynamics, e.g., adhesion energies. One successful method[29,30] relates the core-level shifts to thermodynamical quantities through Born-Haber cycles and the so-called Z^* approximation in which a core-hole excited atom of atomic number Z is treated as a $Z+1$ impurity. This method does not give absolute numbers, but rather differences between the Z and $Z+1$ materials. The agreement[31] between the directly calculated and Z^* surface and adhesion energies for transition metals is reasonable, within a few tenths of an eV, but there is an inherent uncertainty related to the choice of reference system. The results—and underlying assumptions—are best for systems that are lattice matched.

In a one-electron picture, one can relate the heat of formation to changes in the valence-band density of states (as measured by photoemission, for example) and core-level binding energies between the elements and the compounds.[31,32] There is semiquantitative agreement between the estimated and calculated heats of adsorption,[31] although the actual values can be off considerably. The difficulty with this approach is again related to questions of reference levels (e.g., bulk or surface core level) and separating the valence bands into contributions from each atomic type. For systems not in the split band limit, experimentally obtaining the local density of states is very difficult.

Although this last approach is not particularly accurate, it does suggest a qualitative use for core-level shifts of providing an alternate reference level. The effects of the chemical bonding for bulk alloys and adlayers are reflected in the valence-band density of states. As an example, the valence-band photoemission data[33] for Pd/Nb(110) show the Pd "d bands" below the Fermi energy, a significant increase in the core-level binding energy, and a reduced density of states at the Fermi level. One measure of the changes is the shift of the center of gravity of the (local) occupied density of states. Generally this is measured relative to the Fermi level. However, another possible zero is to measure changes relative to the position of the core levels:

$$\bar{\epsilon} \equiv \langle \epsilon_d \rangle - \epsilon_c, \tag{7}$$

$$\Delta\bar{\epsilon} = \bar{\epsilon}_{\text{surface}} - \bar{\epsilon}_{\text{bulk}}, \tag{8}$$

where $\langle \epsilon_d \rangle$ is the center of gravity of the occupied local d-like density of states, ϵ_c is the position of the core level, and $\Delta\bar{\epsilon}$ is the difference between the surface and the bulk values. Defined in this way, there is almost no shift (0.03 eV) between the Pd(001) surface and Pd/Nb(110), whereas there is a ~0.6 eV core-level shift. Thus, to a first approximation, the core levels are simply following the behavior of the occupied valence-band states, in particular the d states. This case is not unique; in Table IV values of $\Delta\bar{\epsilon}$ for various clean and adlayer systems are given. For elements at the right-hand side of the transition-metal rows, the shifts are small in magnitude and much smaller than the corresponding core-level shifts. For elements close to the beginning of the row, there are larger deviations since the d orbitals themselves are significantly larger and sample different regions of space than do the core levels. Hence for elements with almost filled d bands, the core-level shifts are a good indicator of shifts in the center of gravity of the occupied states. Note that the small changes in $\Delta\bar{\epsilon}$ are consistent with the standard picture[1] for surface core-level shifts of the pure elements. Experimentally, similiarly small values of $\Delta\bar{\epsilon}$ have been observed in bulk CuPd alloys,[34] even though there are large (>1 eV) shifts in the Cu core levels.

TABLE IV. Calculated shifts of the center of gravity of the surface occupied local d density of states $\Delta\bar{\epsilon}$ [relative to the bulk; see Eq. (8)], for various adlayer systems. The two systems labeled "Cu[Rh(001)]" and "Cu[Ta(110)]" are identical in structure to the Cu/Rh(001) and Cu/Ta(110) systems, respectively, except the Rh and Ta atoms have been replaced by Cu. All energies are in eV.

	$\Delta\bar{\epsilon}$		$\Delta\bar{\epsilon}$
Cu		Ag	
Cu(001)	-0.04	Ag(001)	-0.10
Cu/Rh(001)	-0.05	Ag(110)	-0.06
Cu[Rh(001)]	-0.03	Ag/Nb(001)	-0.05
Cu/Ta(110)	0.02	Ag/Nb(110)	-0.08
Cu[Ta(110)]	-0.04	Ag/Nb/Ag(001)	-0.02
Cu(110) (bcc)	0.00		
Pd		Nb	
Pd(001)	-0.06	Nb(001)	1.20
Pd(110)	-0.04	Nb(110)	0.64
Pd/Ta(110)	-0.12	Nb/Pd(001)	0.69
Pd/Nb(001)	0.09	Nb/Ag(001)	1.14
Pd/Nb(100)	-0.03		
Pd/Nb/Pd(001)	-0.04		
Rh		Ta	
Rh(001)	0.12	Ta(001)	0.86
Rh(110)	0.15	Ta(110)	0.69

Thus adlayer core-level shifts do provide a measure of the changes in the valence band. As discussed above, the interface substrate atoms more closely obey the simple charge transfer interpretation of core-level shifts, suggesting that trends in the substrate core-level shifts will give a better measure of the bonding of transition-metal adlayer systems. While it is more difficult to resolve the substrate shifts, these shifts may provide more information than the adlayer shifts. Recent experiments[35] that measure the substrate core-level shifts for transition-metal adlayers on W(110) likewise support the conclusions that bulk and surface bonding are essentially similiar, contrary to previous claims.[13] Further experimental work on bimetallic adlayer systems would greatly benefit from simultaneous measurements of both the adlayer and the substrate core-level shifts.

One important conclusion that can be drawn from the results presented here is that the interpretation of core-level shifts is more complicated than is generally acknowledged. A number of competing effects all contribute to an experimentally observed shift. A more positive conclusion is that theory can help to disentangle these terms. Likewise, the ability of theory to calculate the electronic structure of systems that do not exist in nature (e.g., most of the bulk alloys considered in this paper) allows the study of trends and gedanken experiments that would not be possible otherwise. The decomposition into intra- and extra-atomic contributions that we have used differs from previous ones, but has the advantage that the interpretation of the shifts is independent of the details of the underlying electronic structure calculations. This decomposition provides a reasonably unbiased, although not unique, separation of terms that can be applied in different situations and allows a consistent interpretation of the core-level shifts; in particular, our general conclusions regarding charge transfer are independent of the choice of atomic radius used to define the atomic size. The results presented here demonstrate that while the same basic bonding effects occur in alloys and adlayers, the adlayers shifts have a different balance of intra- to extra-atomic contributions than either the bulk alloys or the substrate shifts.

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[24] The calculated initial state surface core-level shifts for the (001) and (110) faces for various fcc and bcc metals differ in magnitude by (in eV): Al, 0.02; Ag, 0.2; Pd, 0.2; Rh, 0.1; Nb, 0.6; Ta, 0.4. Experimental shifts for different surfaces are comparable in magnitude.

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