Extended-Hückel study of the (111), (100), and (110) surfaces of copper*

D. G. Dempsey and Leonard Kleinman

Department of Physics, University of Texas, Austin, Texas 78712

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We have found that the energy bands of bulk copper can be fit equally well with a set of Hamiltonian parameters H_{ij} and overlap parameters $S_{ij} = \delta_{ij}$ corresponding to Wannier basis functions or by a set (H'_{ij}, S'_{ij}) corresponding to atomic basis functions or by any of a continuum of sets (H''_{ij}, S''_{ij}) between (H_{ij}, S_{ij}) and (H'_{ij}, S'_{ij}). Using the Wannier parameters in thin-film calculations we previously obtained surface-charge deficits of $-0.198e$, $-0.269e$, and $-0.354e$ for the (111), (100), and (110) films, respectively. Using atomic parameters we obtain a surface-charge surplus of $0.256e$ for a (111) film. Using a set of intermediate parameters we obtain deviations from surface-charge neutrality of $0.0079e$, $-0.0013e$, and $-0.0452e$ for the (111), (100), and (110) films. We give a physical explanation of why one would expect a set of intermediate parameters to yield approximate surface-charge neutrality on all three surfaces. Exact surface-charge neutrality can be obtained by making small surface-parameter shifts. We discuss the effect of the new parameters on the surface states, the most interesting of which is the (111) state in the $L_{2'}$-L_1 gap. It is shifted downward but still lies 0.1 eV above E_F rather than the 0.4 eV below E_F needed if it is to be used to explain the photoemission data of Gartland and Slagsvold.

I. INTRODUCTION

Because one eventually hopes to be able to calculate chemical reactions at transition-metal surfaces, and because it hardly seems possible that this will be done in any representation other than atomic orbitals (AO), it has seemed worthwhile to us to make parametrized tight-binding calculations of the electronic structure of clean transition-metal surfaces. Further justification for parametrized calculations comes from the primitive state of first-principles calculations. There are few *ab initio* (non-step-potential) calculations[1,2] for 3d transition metals and because they are far from self-consistent, the results obtained are only qualitative. There is one self-consistent 4d transition-metal pseudopotential calculation[3] but the accuracy of a transition-metal calculation which is self-consistent in the *pseudo* charge density has yet to be established. Finally, even if one could perform a self-consistent calculation of ultimate numerical accuracy, uncertainties in the exchange and correlation potential are sufficient to make the calculated surface-state structure questionable. Thus we require that our parametrization scheme fit the bulk energy bands, fit whatever is known about the surface-state bands, and yield a surface which is electrically neutral. (A typical self-consistent nearly-free-electron metal result[4] is that the surface-plane charge is $-0.037e$ but this is screened so that the charge on the surface plus first interior plane is $0.0025e$. On the other hand, typical nonself-consistent transition-metal surface charges are[5] of the order of e and are unscreened.)

We have calculated the energy bands and planar densities of states of (100),[6a] (110),[6b] and (111) (Ref.

6c) thin films of ferromagnetic iron. These calculations were performed by fitting the bulk energy bands[7] with Slater-Koster[8] Hamiltonian parameters, which assumes that the AO are all orthogonal; that is, the "atomic" orbitals are actually Wannier functions. The thin-film surface densities of states obtained using these parameters then had of the order of $-0.5e$ too little electronic charge below the Fermi energy. By shifting the "atomic" or zeroth-neighbor Hamiltonian parameter for surface atoms by -0.022 Ry in the (100) and (110) cases we were able to restore surface-charge neutrality. [In the (111) case it required shifting parameters in the surface plus two neighboring planes.] More recently, we have compared the d and sp contributions to the surface charge in both ferromagnetic and paramagnetic iron.[5] For (100) ferromagnetic iron we found a surface deficit of -0.08 d electrons and -0.54 sp electrons. For (100) and (110) paramagnetic iron we found 0.88 and 0.80 d-electron surpluses and -0.53 and -0.35 sp-electron deficits. Desjonqueres and Cyrot-Lackmann[9] (DC-L) who did not use any s or p basis functions found 0.5 and 0.3 d-electron surpluses. Note that all surpulses and deficits are larger for the more open (100) surface than for the close-packed (110) surface of a bcc crystal. The fact that our paramagnetic d-electron surpluses were larger than DC-L's we attribute to hybridized sp-d surface states which DC-L could not obtain, lacking s and p basis functions. The d-electron surpluses in all paramagnetic cases are attributed to the fact that the d-band surface density of states is narrower than the bulk density of states, appearing to be squeezed together from both ends. Because the Fermi level

TABLE I. Net charge (in units of e per atom) on the surface and two next outermost planes of (111), (100), and (110) copper calculated using Wannier, atomic, and intermediate parameters.

	(111)	(100)	(110)
W	−0.198	−0.269	−0.354
	0.004	0.013	−0.052
	0.018	0.020	0.004
A	0.256	...	...
	−0.002	...	...
	−0.022	...	...
I	0.0079	−0.0013	−0.0431
	−0.0180	−0.0130	0.0212
	−0.0036	0.0047	−0.0173

lies on a large peak at the high-energy end of the density of states and this peak is pushed to a lower energy in the surface density of states, there are more states below E_F in the surface density of states than in the bulk. In the ferromagnetic case the Fermi level lies well above this peak in the high-energy tail of the majority-spin density of states. Therefore the squeezing together of the surface density of states adds only 0.19 majority-spin surface d electrons. The Fermi level lies in a minimum in the middle of the minority-spin density of states. The squeezing together plus the formation of a large number of surface states which turn this minimum in the bulk density of states into a maximum in the surface density of states has the net effect of reducing the surface minority-spin d electrons by − 0.27. Thus we thought we understood the d-electron results; however, we shall argue later that understanding the results of Hückel calculations does not necessarily make them correct.

We have performed the same type of calculation for (100),[10a] (110),[10b] and (111) (Ref. 10c) copper, fitting to the bulk bands of Burdick.[11] Because the d bands lie well below the Fermi energy, the surface charge deficits shown in the first row of Table I are almost entirely due to s and p basis functions. Because of the low density of states at the copper Fermi level, it would require surface zeroth-neighbor parameter shifts of the order of − 0.1 Ry to restore surface-charge neutrality. We considered such large shifts unphysical and did not attempt to restore surface-charge neutrality in our copper calculations. Note that the copper surface-charge deficits are similar to the sp surface charge deficits in iron, becoming larger for the more open faces. Unlike the (111) and (100), the first interior plane of a (110) fcc film is missing a nearest neighbor. This causes a small but non-negligible charge deficit on that plane which is also

listed in Table I. A similar effect occured on (111) bcc iron[6c] but we have not discussed it because we did not separate the charge into s, p, and d components for that case.

We have since come to believe that the large parameter shifts needed to restore surface-charge neutrality in copper are not unphysical because they do not represent a shift in surface potential; rather they result from the surface Wannier functions[12] having much less kinetic energy than the bulk Wannier functions because they have fewer neighbors with which to be orthogonal. Since it does not seem likely that surface Wannier functions can actually be calculated for real crystals, this motivated us to make the extended-Hückel calculations described in this paper. We felt that if the orthogonality effects were explictly included in an overlap matrix, the effect of the surface would be automatically included. We chose to study copper rather than paramagnetic iron because in the latter case the d and sp surface-charge discrepancies had opposite sign and although we suspect that they must individually be very small, all we know for certain is that they must cancel.

In Sec. II we describe our determination of the Hamiltonian and overlap parameters which both fit the bulk energy bands and yield approximate surface charge neutrality. We also discuss the total and planar densities of states (TDS and PDS) for the three films from which the surface charge is calculated. In Sec. III we present the thin-film energy bands and compare the surface states with those previously obtained.[10] Finally, in Sec. IV we attempt to explain why the parameters which yield surface-charge neutrality lie between atomic and Wannier values. We also discuss the implications of these results for other systems such as semiconductors and transition metals with unfilled d bands.

II. PARAMETERS AND CHARGE NEUTRALITY

To obtain parameters corresponding to atomic basis functions we fixed the zeroth-neighbor parameter differences $dd_0 - pp_0$ and $dd_0 - ss_0$ at their free atom values.[13] We then varied dd_0 and the 30 off-diagonal Hamiltonian parameters and 30 off-diagonal overlap parameters to fit Burdick's[11,14] energy bands at 43 points (including some points of no symmetry) in the irreducible $\frac{1}{48}$ Brillouin zone (BZ). After obtaining a partial fit we allowed ss_0 and pp_0 to become free parameters. Because the rms error was close to a local minimum, these parameters did not wander far and eventually ended up very close to their starting values. We fit 250 energy levels[14] below 0.21 Ry with an rms error of 0.0052 Ry and a maximum error of 0.0178 Ry,

TABLE II. First-, second-, and third-neighbor Hamiltonian parameters (in Ry) and overlap parameters corresponding to atomic basis functions. The atomic or zeroth-neighbor Hamiltonian parameters are also listed. The zeroth-neighbor overlap parameters are unity.

	$H1$	$H2$	$H3$	$S1$	$S2$	$S3$
$ss\sigma$	$-0.177\,65$	$-0.047\,33$	$-0.007\,08$	$0.160\,62$	$0.010\,87$	$0.002\,08$
$pp\sigma$	$0.146\,42$	$0.140\,61$	$0.043\,66$	$-0.422\,10$	$-0.146\,75$	$-0.022\,84$
$pp\pi$	$-0.098\,52$	$-0.017\,33$	$0.000\,08$	$0.164\,37$	$0.038\,91$	$0.011\,07$
$dd\sigma$	$-0.026\,69$	$0.000\,08$	$0.000\,00$	$0.000\,00$	$0.000\,00$	$0.000\,00$
$dd\pi$	$0.011\,26$	$0.000\,26$	$0.000\,01$	$0.000\,00$	$0.000\,00$	$0.000\,00$
$dd\delta$	$-0.000\,02$	$-0.000\,03$	$0.000\,00$	$0.000\,00$	$0.000\,00$	$0.000\,00$
$sp\sigma$	$0.229\,00$	$0.092\,26$	$0.019\,94$	$-0.270\,74$	$-0.046\,35$	$-0.010\,39$
$sd\sigma$	$-0.040\,57$	$-0.006\,02$	$0.001\,82$	$0.000\,00$	$0.000\,00$	$0.000\,00$
$pd\sigma$	$-0.069\,80$	$-0.032\,61$	$-0.005\,75$	$0.039\,77$	$0.006\,94$	$0.000\,39$
$pd\pi$	$0.045\,45$	$0.000\,88$	$-0.002\,86$	$-0.020\,03$	$-0.000\,67$	$0.000\,01$

$$ss_0 = -0.440\,13 \qquad pp_0 = -0.181\,19 \qquad dd_0 = -0.558\,09$$

which is slightly better than our previous fit.[10a] The values obtained for the parameters are listed in Table II and may be compared with the Wannier basis parameters listed in Table I of Ref. 10a. Note that all the dd as well as the sd overlaps are zero and that dd_0 is little changed from its Wannier value. This could be a consequence of a theorem of Anderson[15] which states that there exists a pseudopotential which leads to an effective Hamiltonian of the Hückel form, even though the AO are nonorthogonal, and that to first order in the actual overlap of the AO, the diagonal Hamiltonian matrix element takes its Wannier value. However, it is more likely due to the fact that we left dd_0 free to vary from the beginning and the minimization routine found it easier to fit the d bands by centering them around dd_0 and using Wannier parameters than by using atomic parameters.

It is worthwhile to discuss in more detail how we obtained our overlap parameters since we had been warned more than once that it was very difficult to avoid nonpositive definite S matrices. We soon found this to be the case; an S matrix that appeared to be well behaved throughout most of the BZ would over a very small region of $\vec{k}$ space have a negative eigenvalue. To avoid this we initially calculated the overlap matrix from Gaussian orbitals $\psi_{lm} = N_l r^l \exp(-\alpha_l r^2) Y_{lm}(\Omega)$. This guarantees that S will be positive definite so long as all neighbors with nonzero overlap are included in the calculation. Because we eventually wanted the first three neighbor overlaps to be independent parameters and the rest to be zero, we included only three neighbors in the calculation of S. This caused there to be some range of the parameters α_l for which S was not positive definite. We avoided this by forcing our simplex rms minimization algorithm[16] to insert a large rms error (without

actually calculating it)[17] whenever S had an eigenvalue smaller than 0.02. We found that three parameters $(\alpha_0, \alpha_1, \text{ and } \alpha_2)$ were not sufficient for even an approximate fit so we added three more parameters $\alpha_{21}, \alpha_{20}, \text{ and } \alpha_{10}$, where $\alpha_{l'}$ replaces α_l in ψ_{lm} when the overlap of ψ_{lm} with $\psi_{l'm'}$ is being calculated. This gives six independent parameters, two of which, α_2 and α_{20}, are essentially infinite and play no role. With these we were able to get an approximate fit to the bulk energy bands, at which point we discarded the Gaussians and let all 30 first-three-neighbor overlaps be independent parameters.[18] The S_{ij} did not change much when set free; however, small changes in the S_{ij} can lead to large percentage changes in the smaller eigenvalues of S and hence to fairly large changes in the energy eigenvalues. Because the S_{ij} were stuck in a local minimum and could not change much from their Gaussian values, we thought it possible that better results might have been obtained had we used different orbitals to begin with. We then tried orbitals consisting of two Gaussians with three parameters per orbital,
$$\psi_{lm} = N_l r^l [\exp(-\alpha_l r^2) + \gamma_l \exp(-\beta_l r^2)] Y_{lm}(\Omega).$$
This would allow the second-neighbor overlap to get much larger without affecting the first-neighbor overlap appreciably. However the second-neighbor overlap showed no interest in getting much larger and we achieved essentially the same fit as with a single Gaussian. We also tried exponential orbitals, $\psi_{lm} = N_l \exp(-\alpha_l r_l) Y_{lm}(\Omega)$, including 20 neighbors in S and obtained a fit considerably worse than our approximate Gaussian fit.

Using the parameters of Table II we calculated the energy bands for a 30 layer copper (111) thin film at 61 points in the $\frac{1}{12}$ hexagonal irreducible two-dimensional BZ (2D BZ) corresponding to 576 points in the full 2D BZ. The planar density of

states (PDS) for the jth plane is

$$\mathfrak{N}_j(E) = \frac{2}{K} \sum_{i\alpha\beta n\bar{k}} W(\bar{k}) C^{n\bar{k}}_{\alpha i} C^{n\bar{k}}_{\beta j} S^{\alpha\beta}_{ij}(\bar{k}) \delta(E - E_{n\bar{k}})$$

in electrons per atom Ry where K is the number of points in the full 2D BZ, $\bar{k}$ is one of the 61 points in the $\frac{1}{12}$ 2D BZ, $W(\bar{k})$ is the number of points in the star of $\bar{k}$, $C^{n\bar{k}}_{\alpha i}$ is the coefficient of the αth orbital on the ith plane in the nth eigenfunction at $\bar{k}$, and $S^{\alpha\beta}_{ij}(\bar{k})$ is the overlap of the 2D Bloch basis functions $\Phi_{i\alpha}(\bar{k})$ and $\Phi_{j\beta}(\bar{k})$, where

$$\Phi_{i\alpha}(\bar{k}) = N^{-1/2} \sum_m \exp(i\bar{k} \cdot \vec{R}_{im}) \phi_\alpha(\vec{r} - \vec{R}_{im}),$$

$\vec{R}_{im}$ is a vector to the mth atom on the ith plane and there are nine α's (one s, three p's, and five d's). The total density of states (TDS) is $\mathfrak{N}(E)$ $= P^{-1}\sum_j \mathfrak{N}_j(E)$, whence we obtained E_F, that energy below which the integral of $\mathfrak{N}(E)$ contains eleven electrons per atom (where P is the number of planes in the film).

To our great surprise we discovered that the integral of the surface PDS contained 11.256 electrons per atom below E_F and the surplus has been entered in the second row of Table I. At this point we abandoned the parameters of Table II and generated the parameters of Table III as follows. We essentially[19] took an average consisting of 49% of the Wannier parameters[10a] and 51% of the atomic parameters of Table II as initial values for our simplex minimization routine and with all parameters free from the start, fit the bulk bands with a 0.005 58-Ry rms error and a 0.0174-Ry maximum error. Comparing Table III with the average of Table II and Table I of Ref. 10a, we see that ss_0 did not stray from its starting value, whereas pp_0 increased by 0.06 Ry, still staying well below its Wannier value. Because the starting values of the overlap parameters were small (51% of their value in Table II), none of the $S^{\alpha\beta}_{ij}(\bar{k})$ had extremely

small eigenvalues; this allowed the overlap parameters considerable freedom to vary and one notes for example that the final $pp\sigma$ first- and second-neighbor overlap parameters are 59% and 27%, respectively, of their values in Table II.

Using the parameters of Table III we calculated the energy bands of a 30-layer (111) film, a 33-layer (100) film, and a 47-layer (110) film.[20] The calculations were performed at 61, 91, and 88 points in the irreducible $\frac{1}{12}$, $\frac{1}{8}$, and $\frac{1}{4}$ 2D BZ's, respectively. The Fermi energies obtained from the TDS's are -0.3220, -0.3243, and -0.3240 Ry, respectively. In Fig. 1 we display the TDS and the PDS for the central plane and the surface plane and the three planes next to the surface for all three films. We have shifted[21] the (111) energies by -0.038 Ry and the (100) and (110) by -0.018 Ry to obtain agreement with the experimentally determined[22] work functions, $\phi_{111} = 0.360$ Ry and $\phi_{100} = 0.342$ Ry. The amount of noise in these plots may be estimated by comparing the central plane PDS's which should be bulklike and hence independent of surface. The number of independent states included is proportional to the number of points sampled in the irreducible 2D BZ times the number of planes in the film. Thus we expect the (110) PDS's to be the least noisy and indeed we note that the main difference between the (110) and (100) and (111) central-plane PDS's is a smoothing of the structure between the two highest peaks. We note that there are much larger real differences between the different films in the PDS's for the surface and first one or two interior planes. We also note, as usual,[6,10] that the d-band surface PDS is narrower than the interior PDS's and that the (110) surface PDS is the narrowest because a (110) surface atom has fewer neighbors than a (111) or a (100).

We integrated the PDS's up to E_F and list the net charge (electronic charge minus eleven) on the

TABLE III. Same as Table II except that parameters correspond to basis functions intermediate to Wannier and atomic functions.

	H1	H2	H3	S1	S2	S3
$ss\sigma$	−0.131 61	−0.024 91	−0.001 37	0.082 56	0.005 66	0.000 82
$pp\sigma$	0.164 65	0.080 85	0.012 80	−0.249 70	−0.039 45	−0.004 46
$pp\pi$	−0.061 40	−0.014 60	−0.000 18	0.054 63	0.036 66	0.006 82
$dd\sigma$	−0.026 66	−0.004 35	0.000 01	0.000 00	0.000 00	0.000 00
$dd\pi$	0.016 23	0.001 50	0.000 03	0.000 00	0.000 00	0.000 00
$dd\delta$	−0.003 89	0.000 09	0.000 00	0.000 00	0.000 00	0.000 00
$sp\sigma$	0.167 49	0.041 26	0.007 06	−0.136 00	−0.032 55	−0.001 76
$sd\sigma$	−0.031 60	−0.005 75	0.000 06	0.000 00	0.000 00	0.000 00
$pd\sigma$	−0.024 66	−0.022 03	−0.000 24	−0.013 85	0.006 97	0.000 00
$pd\pi$	0.040 13	0.000 32	−0.000 31	−0.010 25	−0.000 36	0.000 00

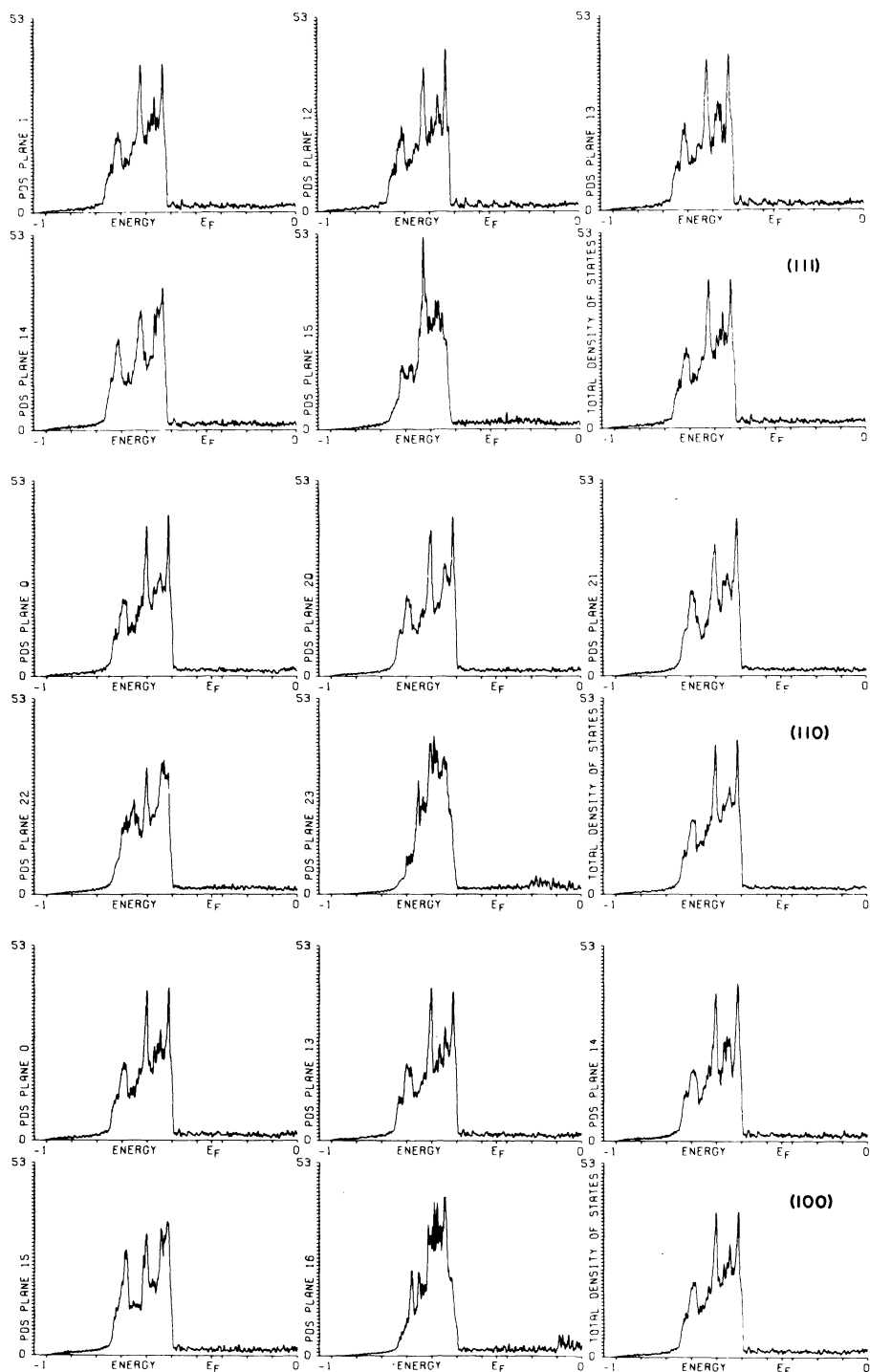$$ss_0 = -0.260\,70 \qquad pp_0 = 0.183\,17 \qquad dd_0 = -0.568\,33$$

FIG. 1. Planar densities of states [in units of $2e/$(atom Ry)] for central plane and surface and three next outermost planes and total density of states of (111), (110), and (100) copper films.

surface and first two interior planes in Table I. We note that the net planar charge is an order of magnitude smaller than that obtained using atomic or Wannier parameters. The largest net charge

on a more interior plane is $0.0047e$ [the eighth (111) plane] of which $0.0035e$ we estimate to be noise.[23] For the other faces, we estimate the maximum noise to be $0.002e$. Had we chosen our intermedi-

ate parameters to be very slightly more atomic-like, we could have made the total net charge of the three outermost (111) and (100) planes essentially zero and reduced the total net (110) charge to about − 0.025e but we would not have reduced the differences between the surface and first interior planes appreciably. Note that when Wannier or atomic parameters are used, the first interior plane has a net charge close to the bulk value[23] in the (111) and (100) cases, but in the (110) case the first interior plane has a small but non-negligible net charge of the same sign as the surface plane. This is because each first interior (110) plane atom is missing a nearest neighbor and this causes the zeroth-neighbor parameter to be shifted away from the bulk value by about $\frac{1}{5}$ the amount that the zeroth-neighbor surface-plane parameters are shifted. (The surface-plane atoms are missing five nearest neighbors.) It is, of course, our failure to include these shifts which causes the large charge discrepancies. On the other hand, when the intermediate parameters are used, the surface zeroth-neighbor parameters are essentially unchanged from the bulk, except for self-consistency effects which are not included. The difference in net charge between the surface, first interior and further interior planes in this case is due to small remaining zeroth-neighbor corrections together with off-diagonal effects which are probably larger than the remaining zeroth-neighbor corrections but have an order of magnitude smaller effect on the net charge than the large zeroth-neighbor corrections in the Wannier and atomic cases.

III. SURFACE STATES

Here we list all the surface states found in this calculation and note differences from those found before using the Wannier parameters. To save space we show only the composite energy bands in Figs. 2–4. For the surface states in subband gaps, i.e., gaps in bands of one symmetry which are overlapped by bands of another symmetry, we will refer to figures in Ref. 10. The casual reader who is not interested in a detailed listing of the surface states may wish to inspect Figs. 2–4 and then skip to the end of this section where we discuss a surface state of some experimental interest.

The (100) bands are displayed in Fig. 2. At − 0.174 Ry there is a new $\overline{\Gamma}_1$ surface state (ss) which is part of a new $\overline{\Sigma}_1$-$\overline{\Gamma}_1$-$\overline{\Delta}_1$ surface band running up to positive energies. There is a new isolated $\overline{\Gamma}_1$ ss at − 0.587 Ry and an $\overline{\Gamma}_1$ ss at − 0.735 Ry which is part of an old $\overline{\Sigma}_1$-$\overline{\Gamma}_1$-$\overline{\Delta}_1$ surface band. The $\overline{\Sigma}_1$ ss lies near the bottom of a wide subband gap of which the absolute gap forms only a small piece. The only other $\overline{\Sigma}$ ss lies in a $\overline{\Sigma}_2$ subband gap and runs almost the entire length of $\overline{\Sigma}$ as seen in Fig. 3 of Ref. 10a. A small piece of this ss may be seen in an absolute gap at − 0.614 Ry, one-sixth of the distance away from $\overline{\Gamma}$ toward $\overline{M}$. The lowest $\overline{\Delta}$ gap whose surface state we have already mentioned, appears quite different than in Ref. 10a. This is due to the discrepancies in fitting the bulk bands in the two cases conspiring to have opposite effects on this particular gap. Since these discrepancies are of the same magnitude as uncertainties in the bulk bands, one gets an estimate of how un-
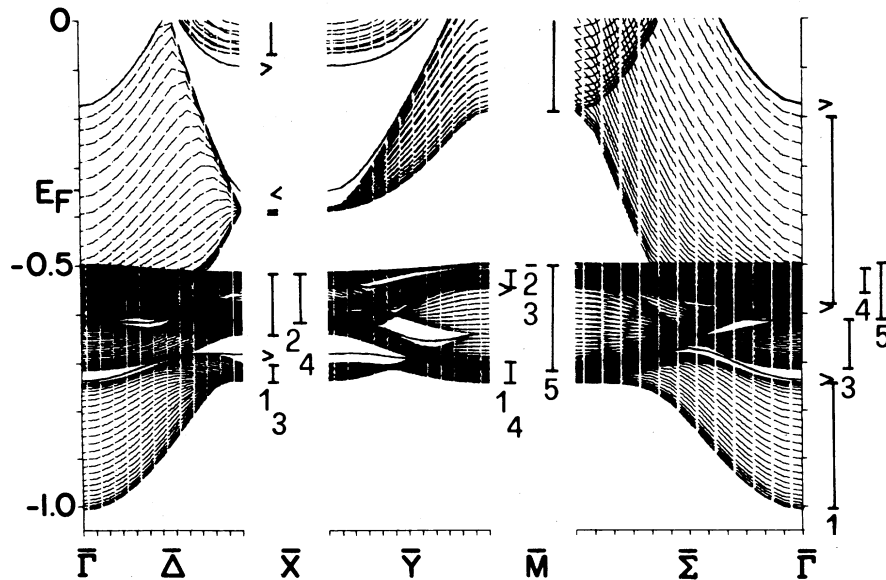

FIG. 2. Composite two-dimensional energy bands of a (100) copper film. At symmetry points the surface states are indicated by > or <. The continua for symmetries which are degenerate in the bulk are shown only once.

certainties in the bulk bands can effect narrow gaps in the two-dimensional energy bands. This gap appears to pinch off but a projection[24] of the bulk bands shows that it never gets any narrower than 0.001 Ry. The $\overline{\Delta}_1$ ss disappears in the very narrow region of the gap but reappears on the other side where it runs to $\overline{X}_1$ at -0.681 Ry and then through the lowest $\overline{Y}$ gap with $\overline{Y}_1$ symmetry just as it did previously.[10a] This $\overline{Y}$ gap also contains a new $\overline{Y}_2$ ss band at the bottom of the gap which extends only between the third and fifth mesh points on the $\overline{Y}$ axis. The next highest $\overline{\Delta}$ gap (at -0.62 Ry), previously empty, now contains a $\overline{\Delta}_1$ ss band. The $\overline{X}_1$ ss at -0.094 Ry and the X_3 ss at -0.348 Ry are part of $\overline{\Delta}_1$-$\overline{X}_1$-$\overline{Y}_1$ and $\overline{\Delta}_1$-$\overline{X}_3$-$\overline{Y}_2$ surface bands which were previously at higher energies. This lowering of sp surface states occurs for (110) and (111) films also, and is due to the fact that the pp_0 parameter has dropped 0.072 Ry more than the ss_0 from its Wannier value. This has the effect of making the hybridized ss more p-like and since the three-dimensional (3D) BZ boundary gaps at X and L have the p states lying below the s, this pulls the ss toward lower energy. The last two $\overline{\Delta}$ ss lie in the triangularly shaped $\overline{\Delta}_1$ subband gap at -0.58 Ry. The ss band seen near the bottom of the gap in Fig. 3 of Ref. 10a is now even lower in energy and a new ss band runs along the top of the gap. There are three $\overline{Y}$ gaps which do not reach $\overline{X}$. The lowest of these contains a $\overline{Y}_2$ ss band which now extends the length of the gap whereas previously it ran along only the lower left-hand side. It also contains a new very short $\overline{Y}_2$ ss band which exists only at the bottom center of the gap. A tiny gap at -0.58 Ry (just above the gap just discussed) contains a $\overline{Y}_1$ ss band unchanged from before, however previously, after pinching off, this gap reopened and ran all the way to $\overline{X}$ containing a $\overline{Y}_2$ ss band. That part of the gap is now either extremely narrow or nonexistent and there is no $\overline{Y}_2$ ss or resonance in

that region. The very long narrow gap at -0.052 Ry contains a $\overline{Y}_2$ ss band running about half the length of the gap and a $\overline{Y}_1$ ss band below it running only one-third the length of the gap. Previously, both ran the entire length of the gap.

Thus we see that the new parameters have caused considerable change in the (100) surface state structure. For the high energy ss which consist mainly of s and p basis functions this was to be expected but for the mainly d-like ss at lower energies it is somewhat surprising. For example, the new[25] Γ_1^- ss at -0.587 Ry consists of $0.624d_{3z^2-r^2}+0.026p_z+0.148s$ in the surface plane and $0.331d_{3z^2-r^2}+0.029p_z+0.043s$ in the first interior plane and the new Δ_1^+ ss at -0.616 Ry and $\overline{k}=(\pi/a)(\frac{5}{12},0)$ consists of

$$0.291d_{3z^2-r^2}+0.578d_{x^2-y^2}+0.449d_{xy}$$
$$+0.021p_z+0.051p_x+0.106s$$

in the surface plane and

$$0.108d_{3z^2-r^2}+0.340d_{x^2-y^2}+0.430d_{xz}$$
$$+0.018p_z+0.019p_x+0.030s$$

in the first interior plane. Thus again we see the importance of even a fairly small amount of sp-d hybridization in inducing surface states in the d bands.

The composite (110) energy bands are shown in Fig. 3. There are three new isolated $\overline{S}$ surface states: $\overline{S}_1$ at -0.514 Ry, $\overline{S}_2$ at -0.522 Ry, and $\overline{S}_1$ at -0.640 Ry. There are $\overline{Y}_3$ and $\overline{Y}_1$ ss at -0.206 and -0.360 Ry, respectively, in $\overline{C}_2$-$\overline{Y}_3$-$\overline{\Delta}_1$ and $\overline{C}_1$-$\overline{Y}_1$-$\overline{\Delta}_1$ ss bands. These mainly sp bands have been lowered drastically from their previous positions. The $\overline{Y}_2$ ss at -0.538 Ry extends farther along the top of the $\overline{\Delta}_2$ subband gap (shown in Fig. 1 of Ref. 10b) than it did previously but the $\overline{Y}_1$ ss which previously existed at the bottom of that gap, is no longer present. The $\overline{Y}_3$ ss at -0.702 Ry and its
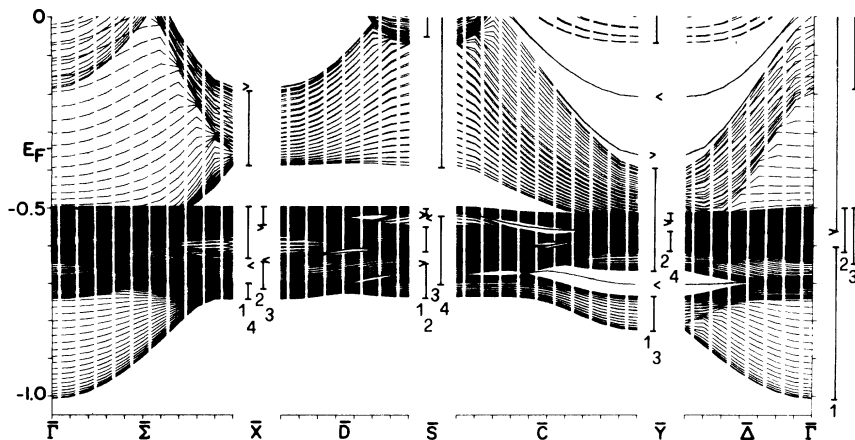

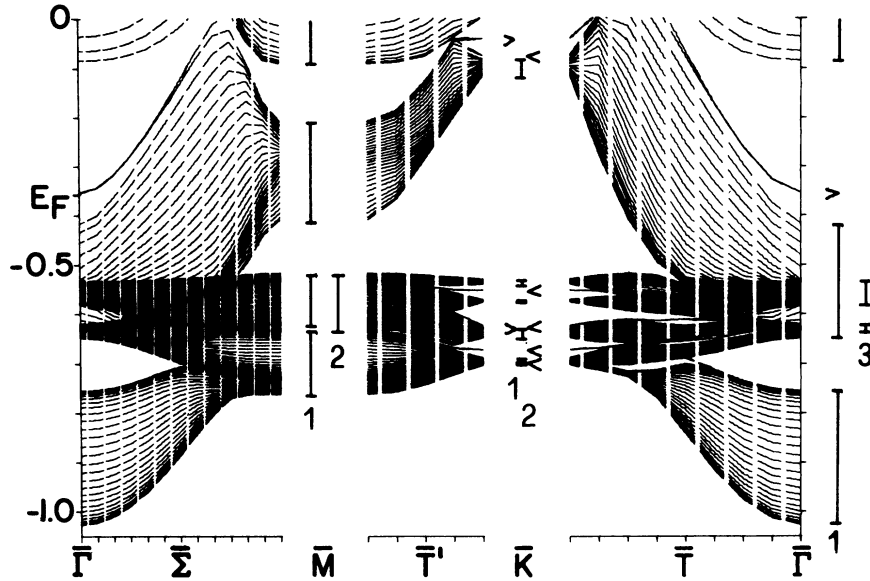FIG. 3. Composite two-dimensional energy bands of a (110) copper film.

FIG. 4. Composite two-dimensional energy bands of a (111) copper film.

$\overline{C}_2$-$\overline{Y}_3$-$\overline{\Delta}_1$ ss band are unchanged from before. There is a $\overline{\Gamma}_1$ ss at -0.560 Ry which extends about 60% of the way along the top of a $\overline{\Sigma}_1$ subband gap[10b]; previously it extended about 90% of the way along the bottom and a second $\overline{\Sigma}_1$ ss band existed in the top of the half of the gap away from $\overline{\Gamma}$. The $\overline{X}_1$ ss at -0.182 Ry has been pushed so close to the bottom of the gap that what used to be a very extensive $\overline{\Sigma}_1$-$\overline{X}_1$-$\overline{D}_1$ ss band now runs into the continuum before the first $\overline{\Sigma}$ mesh point and just beyond the first $\overline{D}$ mesh point. The $\overline{X}_2$ and $\overline{X}_3$ ss at -0.552 and -0.637 Ry now extend only one mesh point into the wide $\overline{\Sigma}_2$ subband gap.[10b] There is a very long narrow absolute $\overline{D}$ gap at -0.61 Ry. The $\overline{X}_3$ ss now extends as a $\overline{D}_1$ ss less than the one mesh point into that gap that it did before. The $\overline{X}_4$ ss at -0.653 Ry extends into the $\overline{\Sigma}_1$ subband gap exactly as it did before but cannot extend into the $\overline{D}$ gap as it did before, because it lies 0.010 Ry below the bottom of the $\overline{D}$ gap at $\overline{X}$. In the interior of that gap are two $\overline{D}_2$ ss, one of which previously extended all the way to the $\overline{X}_4$ ss. The lowest $\overline{D}$ gap contains a very short $\overline{D}_2$ ss band at about -0.68 Ry. This band together with a $\overline{D}_1$ ss band previously ran almost the entire length of the gap. The $\overline{D}$ gap at -0.52 Ry contains three very short ss bands, $\overline{D}_2$'s at the top and bottom of the gap and a $\overline{D}_1$ just above the lower $\overline{D}_2$. These three bands previously ran almost the entire length of the gap. There is a long $\overline{C}$ gap at -0.55 Ry which contains a $\overline{C}_1$ ss band running its entire length. Previously this gap contained two $\overline{C}_1$ ss bands and a $\overline{C}_2$ ss band. However, below this gap at -0.59 Ry, is a short gap which was previously nonexistent. This gap contains a $\overline{C}_1$ ss band running through its cen-

ter with a $\overline{C}_2$ ss band running the length of the gap along its bottom and another $\overline{C}_2$ ss band running along the top of the right-hand side of the gap.

The composite (111) energy bands[26] are shown in Fig. 4. The highest $\overline{K}$ gap contains a $\overline{K}_1$ ss at -0.041 Ry and a $\overline{K}_2$ ss at -0.075 Ry. As before the $\overline{K}_1$ ss continues into the $\overline{T}$ and $\overline{T}'$ gaps, whereas the $\overline{K}_2$ ss band runs into the bottom of the gap almost immediately upon leaving $\overline{K}$. A $\overline{K}_2$ ss at -0.551 Ry forms a $\overline{T}'$-$\overline{K}_2$-$\overline{T}$ band as before but another $\overline{K}_1$ ss previously at the bottom of the same gap no longer occurs. The next gap contains a $\overline{K}_2$ ss at -0.623 Ry in a $\overline{T}'$-$\overline{K}_2$-$\overline{T}$ ss band. Along $\overline{T}$ this disappears into the bottom of the gap and then reappears, running to the end of the gap. A $\overline{K}_1$ ss at -0.627 Ry runs into the bottom of the $\overline{T}$ and $\overline{T}'$ gaps immediately after leaving $\overline{K}$. Previously these two ss were further from the bottom of the gap allowing the $\overline{K}_1$ ss to extend much further into the $\overline{T}$ and $\overline{T}'$ gaps. A $\overline{K}_2$ ss in the $\overline{K}$ gap at -0.672 Ry is in a $\overline{T}'$-$\overline{K}_2$-$\overline{T}$ ss band. The $\overline{T}$ gap pinches off and then reopens into a very narrow gap which contains two $\overline{T}$ ss bands, one of which is new. There is an extremely sharp surface resonance band which runs along $\overline{T}'$ from a new $\overline{K}_2$ ss at -0.699 Ry (lying in a gap only 0.001 Ry wide) to an $\overline{M}_1$ resonance at -0.719 Ry. Neither this nor any other well-defined resonance band existed in any of our previous copper calculations[10] although they were common for iron.[6] Previously there was a $\overline{\Sigma}_1$-$\overline{\Gamma}_1$-$\overline{T}$ ss band which ran the entire length of the bottom of the lowest gap centered at $\overline{\Gamma}$, a small remnant of which exists in the right-hand bottom of the $\overline{\Sigma}$ gap. This gap pinches off in the middle of $\overline{T}$ and then reopens. Because of the

coarseness of our mesh, the gap appears to exist everywhere. However, one can see a single $\overline{T}_2$ bulk state running from the continuum below the right-hand gap to the continuum above the left-hand gap through a region in which the gap does not actually exist. As before there is a very short $\overline{T}$ ss band at the bottom of the left-hand gap. The $\overline{\Sigma}_2$ subband gap in Fig. 2 of Ref. 10c now does not re-open after it pinches off and hence the ss band that previously ran through its extremely narrow middle third cannot now exist. A previous $\overline{M}_1$ ss at the bottom of the highest $\overline{M}$ gap, being sp-like, has been pulled down into the continuum and now does not exist.

The $\overline{\Gamma}_1$ ss at -0.354 Ry is at the center of a very extended $\overline{\Sigma}_1$-$\overline{\Gamma}_1$-$\overline{T}$ ss band. This ss band has been considerably lowered in energy from our previous calculation[10c] but is still 0.1 eV above the Fermi level at $\overline{\Gamma}$. It remains 0.5 eV above the position at which Gartland and Slagsvold[27] place it in order to explain a peak in their angle resolved photoemission data. We have previously[10c] given our reasons for having some doubt that the experimental peak is due to a surface state and will here only discuss the theoretical calculations. The first question to ask is: Could we change our parameters to lower this $\overline{\Gamma}_1$ ss by 0.5 eV without destroying our surface-charge neutrality? The answer is that we believe our parametrization scheme has that flexibility. The $\overline{\Gamma}_1^+$ ss has $0.323s + 0.473p_z$ $+ 0.104d_{3z^2-r^2}$ in the surface plane and $-0.174s$ $-0.289p_z - 0.127d_{3z^2-r^2}$ in the first interior plane. Thus raising the ss_0 parameter and lowering the pp_0 by an equal or greater amount will lower the $\overline{\Gamma}_1$ surface state. On the other hand, many of the states around the Fermi level are more s-like than p-like so that an upward ss_0 shift combined with a larger downward pp_0 shift would keep the surface charge neutral. These zeroth-neighbor parameter shifts could be made either for just the surface atoms or for all the atoms. In the latter case one would have to vary all the parameters to refit the bulk energy bands.

Gurman[28] has calculated this surface state using the layer-scattering method which required him to use a muffin-tin potential that maintained its constant interstitial value out to a plane midway between the surface and first missing planes of atoms. He used three different surface potentials. One jumped discontinuously to the vacuum level at the midplane and yielded the $\overline{\Gamma}_1$ ss at 0.63 eV above E_F. The other two potentials were parametrized to yield the ss at 0.4 eV below E_F. These potentials rose smoothly from the muffin-tin zero at the midplane outward toward the vacuum level without any planar variation. Gurman's Fig. 1 compares these potentials with Inkson's calculated

potential which starts rising well before the midplane and has risen $\frac{3}{8}$ of the distance to the vacuum level when it has reached the midplane. One of Gurman's potentials is everywhere below the calculated potential whereas the other one crosses it, but at a point sufficiently far from the surface so as to have little effect on the surface state. It appears that the discontinuous potential is a better approximation to the calculated potential than either of the smooth parameterized potentials. It is to be regretted that Gurman did not calculate the net surface charge induced by his three potentials. It is very likely that his two smooth potentials would have induced a large excess electronic charge so that the ss energy obtained from them would have to be presumed to be incorrect. Thus we conclude that both Gurman's calculation and our calculation favor the location of the $\overline{\Gamma}_1$ ss to be above the Fermi level but if experimental evidence to the contrary became convincing, our parametrization scheme could fit it. Whether Gurman's parametrization scheme is too restricted by the requirement of a flat potential out to the midplane to both yield surface charge neutrality and to still have the freedom to fit the surface state, wherever it might be, is uncertain.

IV. COMMENTS ON ATOMIC ORBITALS

We have already explained how the large orthogonalization kinetic energy of the Wannier atomic orbitals (WAO) makes the bulk WAO parameters unsuitable for surface atoms and results in a large electronic surface charge deficit. Similarly, when one uses free-atom atomic orbitals (FAAO), one finds that the s and p FAAO are lowered in energy relative to the d because of their larger overlap with the attractive potential of neighboring atoms in the crystal. Therefore the bulk FAAO s and p zeroth-neighbor parameters are lower than the same surface parameters, and if used at the surface result in a large electronic charge surplus. The perspicacious reader will object that although the surface parameters should be higher than the bulk, both should lie below the corresponding free-atom energy levels. To this we respond that the correct AO to use in a bulk calculation, which we will call crystal AO (CAO), are atomiclike but are definitely not the FAAO. For example, if the crystal wave function is to look like a free-atom wave function near an atomic nucleus and if the crystal wave function consists of a sum of overlapping CAO, no individual CAO can look like a free-atom wave function. In principle one could construct the CAO from the WAO by simply writing

$$f_\alpha(r) = \sum_{n=0}^{\infty} \sum_{\beta=1}^{9} C_{\alpha\beta}(\vec{n}) a_\beta(\vec{r} - \vec{n}),$$

where $a_\beta(\vec{r} - \vec{n})$ is the WAO centered at $\vec{R}_n$ and originating from the βth energy band and

$$C_{\alpha\beta}(\vec{n}) = \int f_\alpha^{\,0}(\vec{r}) a_\beta(\vec{r} - \vec{n}) d^3r ,$$

with $f_\alpha^0(\vec{r})$ a somewhat arbitrary atomiclike orbital tranforming like the αth cubic harmonic. If the nine a_β formed a complete set, $f_\alpha(\vec{r})$ would be identical to $f_\alpha^0(\vec{r})$, but since they do not, $f_\alpha(\vec{r})$ is only similar to $f_\alpha^0(\vec{r})$. The zeroth-neighbor parameter for the αth CAO is given by

$$\langle f_\alpha(\vec{r}) | H | f_\alpha(\vec{r}) \rangle = \sum_{\beta nm} C_{\alpha\beta}(\vec{n} - \vec{m}) C_{\alpha\beta}(\vec{n}) E_\beta(\vec{m}) ,$$

where $E_\beta(\vec{m})$ is the $\vec{R}_m$th Fourier transform of the βth energy band. The diagonal energy (i.e., zeroth-neighbor parameter) for a CAO must be higher than for a FAAO because a single FAAO looks more like a crystal eigenfunction near an atomic nucleus than does a single CAO. Whether it is higher or lower than the corresponding free-atom energy level probably depends on the exact choice of $f_\alpha^0(\vec{r})$.

Thus in calculating the diagonal energy the neighboring atoms appear highly attractive to CAO and highly repulsive to WAO. What is needed is a set of orbitals intermediate to the CAO and WAO (called IAO) for which the neighboring atoms appear neither attractive nor repulsive. That is not to say that the surface IAO are identical to the bulk IAO but rather that because the neighboring atoms have no effect on their diagonal energy, the surface IAO zeroth-neighbor parameters are identical to the bulk.

We now discuss the implications of these results for other systems. We begin with semiconductors where Pandey and Phillips[29] have made a remarkable fit to the silicon electronic surface structure using only simple Hückel theory. It has been proven[30] that the bulk band of a semiconductor is electrically neutral (and hence so is the surface) and that the dangling bond surface band is half filled (containing exactly one electron per surface atom), providing only that the middle of the surface band lies within the absolute energy gap. Otherwise charge will flow from the bulk to surface bands (or vice versa) resulting in long-range band bending. Thus surface-charge neutrality is not an independent constraint on a semiconductor calculation; it automatically occurs whenever the middle of the surface band lies in the absolute gap, and should not occur otherwise. We believe that there are two reasons that the simple Hückel theory placed the dangling bond surface state so ac-

curately in the energy gap. The (111) surface atoms are missing only one neighbor and they are relaxed inward toward their remaining neighbors which tends to cancel the effect of losing a neighbor on their diagonal energy. Secondly, the surface state is in a bonding-antibonding gap rather than an s-p gap. Thus relative errors between the s and p surface zeroth-neighbor parameters do not strongly favor pulling the ss to one band edge or the other.

Hückel calculations of unfilled transition metal d bands usually lead to large net surface charges[5,9] which we previously explained as being due to a narrowing of the surface density of states. Presumably one would correctly restore surface charge neutrality by replacing the bulk WAO zeroth-neighbor parameters by parameters appropriate to surface Wannier functions. These parameters would differ amongst orbitals which had been degenerate in the bulk, i.e., for a (001) surface the d_{xz} orbital is not degenerate with the d_{xy}. Hence the standard method of shifting all the zeroth-neighbor parameters by the same amount to restore surface-charge neutrality is not correct. On the other hand if one had used the IAO parameters, chosen to make the surface charge neutral, this error would not be present because the surface IAO parameters are all identical to the bulk. There would still be self-consistency errors present, i.e., the calculated occupancy of the various surface d orbitals would vary from the bulk values[31] (although by much less than for the Hückel calculation) indicating differences in the Coulomb and exchange contributions to the various surface parameters. There seems to be no way to get the d surface charge correct vis à vis the sp. One could, and probably as a reasonable guess should, choose the IAO parameters so that the d and sp surface charges are independently equal to their bulk values. But without any prescription for choosing the IAO so that the neighboring atoms have no effect on the diagonal energies, one has no way to calculate whatever transfer of charge does occur between surface d and sp IAO, unless, of course, one has enough experimental data on surface states to uniquely fix the IAO parameters.

Note added in proof. We recently completed a Ni(100) thin film calculation in which we used IAO sp parameters. Because for very tightly bound d electrons the Wannier energy is essentially the same as the free-atom energy (Ref. 15), we were unable to obtain IAO d parameters and were therefore forced to make surface shifts in our WAO d parameters to obtain surface charge neutrality.

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[13] Because $dd_{(xy)0}$ and $dd_{(x^2-y^2)0}$ were almost identical in Ref. 10a, we used only a single dd_0 parameter in this calculation.

[14] We include the same 0.05-Ry shift in Burdick's bands that we used in Ref. 10a so that we may directly compare the parameters obtained there with those obtained here. The signs of the $pd\sigma$ and $pd\pi$ parameters in Table I of Ref. 10a are reversed; the correct signs were used in all calculations.

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[17] If S had a negative eigenvalue the computer calculation would otherwise halt because the energy eigenvalues depend on square roots of the overlap matrix eigenvalues.

[18] Because our minimization algorithm varies the parameters by a percentage of their values, once a parameter becomes zero, it is stuck there. We therefore occasionally would reset our dd and sd overlap parameters to small finite values and they would always head straight back to zero.

[19] We actually took a 50-50 average for initial values,
varied the parameters to fit the bulk bands with somewhat less than our usual accuracy, and calculated the (111) surface charge density using a reduced number of points in the 2D BZ, finding a slight deficit. We then took an average consisting of 98% of our new parameters with 2% of the atomic parameters and continued the fit of the bulk bands.

[20] In units of the lattice constant a these films have a thickness of $17.32a$, $16.50a$, and $16.62a$, respectively.

[21] We merely shifted the calculated energy bands rigidly by the amounts stated. To calculate these bands directly one would have to change the Hamiltonian parameters by $\Delta H_{ij} = \Delta ES_{ij}$.

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[23] The interior planes should have a constant net charge which for a finite film must be nonzero in order to cancel the net charge on the exterior planes.

[24] This gap at its narrowest point is due to an indirect gap in the 3D energy bands. Therefore, with a slight change of parameters the gap could be made to pinch off.

[25] The Γ_1^+ coefficients differ by less than 1% from the Γ_1^-. As the film becomes thicker the two members of the ss pair become identical except for their opposite parity under reflection in the central plane.

[26] Because the (111) film has inversion rather than reflection symmetry, the ss pairing is somewhat peculiar. At $\bar{\Gamma}$ and $\bar{M}$ where inversion is a member of the group of the wave vector, the pair is even and odd under inversion, i.e., $\bar{\Gamma}_3^+$ and $\bar{\Gamma}_3^-$. At $\bar{T}$ and $\bar{T}'$ there are only two representations which are always paired, i.e., $\bar{T}_1$ and $\bar{T}_2$. At $\bar{K}$, $\bar{K}_2$ is a twofold degenerate representation which forms its own pair and $\bar{K}_1^+$ and $\bar{K}_1^-$ which are even and odd under a twofold rotation form ss pairs. At $\bar{\Sigma}$ there is no operation in the group of the wave vector which interchanges the two faces of the film; thus a $\bar{\Sigma}$ ss pair contains two states of the same symmetry.

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