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Electronic surface states in beryllium

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The $\Gamma-M$ Be surface state found in two recent experiments is confirmed to be highly localized by a study of local density electronic states near the Fermi level of ultrathin Be films (n layers with $n=1$, 2, and 3). For $n=3$, a state at Γ is found 2.0 eV below ε_F (experiment: 2.8 eV) and 1.9 eV above the film level which corresponds to the bulk band edge (experiment: 2.0 eV); good agreement in view of known limitations of local-density-approximation one-electron energies. That state at Γ falls in energy and its intersection with ε_F along both $\Gamma-M$ and $\Gamma-K$ moves out from Γ with increasing n. The n-layer occupied states at M are not uniquely identifiable with either pure bulk or pure surface states, this is again in agreement with experimental indications that they are rather delocalized (as opposed to the one at Γ). The surface core-level 1s shift is estimated from the three-layer film (the thinnest system which can exhibit such a shift) as 0.21 eV (experiment: 0.50 eV). Previous restricted Hartree-Fock calculations on bulk and ultrathin-film Be differ markedly both from these results and from experiment; the discrepancies and their sources are considered.

I. EXPERIMENTAL AND THEORETICAL SETTING

A surface state on Be (0001) at Γ has been identified in two recent angle-resolved photoemission (ARPE hereafter) experiments.[1,2] The essential experimental findings for it are the following: (1) at Γ it lies 2.8 eV below the Fermi level[1,2] and 2.0 eV above the bulk band edge;[2] (2) its one-electron energy crosses ε_F between 55% (Ref. 1) and 67% (Ref. 2) of the way from Γ to M and 56% of the way from Γ to K;[2] (3) its dispersion is quite free-electron-like with effective mass $m^*/m=1.53$ (Ref. 2) or 1.04 (deduced from Ref. 1) along $\Gamma-M$ and $m^*/m=1.45$ along $\Gamma-K$;[2] (4) both its line shape (essentially pure Lorentzian) and its high-energy ($\hbar\omega>40$ eV) photon response are strong indicators of its high localization near the surface [compared, for example, with the (100) surface state of Al].[2]

There is also experimental evidence[2] for two surface states at M, bound by 1.8 and 3.0 eV. The deeper energy lies almost exactly on the edge of the projected bulk bands, while the dispersion of the higher-lying state puts it into coincidence with the projected bulk bands less than 10% away from M toward Γ. Both characteristics indicate that the M surface states extend into and overlap strongly with the bulk states of compatible symmetry.

Published theoretical treatments of Be one-electron states are almost exclusively for the bulk crystal. Karlsson *et al.*[1] analyzed their data in terms of bulk bands calculated non-self-consistently by Inoue and Yamashita[3] some time ago. Bartynski *et al.*[2] used projections of essentially similar non-self-consistent bands by Nilsson *et al.*[4] For our purposes, a newer calculation is more relevant. Chou *et al.*[5] determined both the equilibrium structural parameters and one-electron states of bulk hexagonal-close-packed (hcp) Be in the local-density approximation (LDA) by use of self-consistent *ab initio* pseudopotential techniques and a plane-wave basis. The calculated hcp lattice parameters ($a=4.255$ a.u. vs experiment of 4.32 a.u., c/a reduced about 3% from ideal to 1.586 vs 1.568 from experiment[5]), cohesive energy, bulk modulus, and Poisson ratio all agree well with experimental values.

The older one-electron results[3,4] (used in analysis of the surface ARPE data) are similar, both qualitatively and quantitatively, to the self-consistent, optimum-geometry LDA calculations of Chou *et al.* The LDA occupied levels[5] also agree decently with recent[6] bulk ARPE energies where comparison is available (unfortunately limited to scaling from published figures). For Γ_{1+} the comparison is 11.16 eV calculated (11.1 eV measured), both with respect to ε_F, A_1 (9.0 eV calculated vs 9.1 eV measured), and Γ_{3+} (4.32 eV calculated vs 4.8 eV measured). Given well-known limitations on LDA eigenvalues as approximate quasiparticle excitation energies, the comparison of LDA calculation with experiment is clearly satisfactory for the bulk crystal.

The geometry and one-electron levels of bulk Be have also been treated in the restricted Hartree-Fock (RHF) approximation.[7] While the RHF values for lattice parameters also agree decently with experiment, the RHF one-electron energies differ noticeably and resemble experiment less than do the LDA ones. Quantitatively the occupied RHF levels lie well below the experimental bulk values, a well-known problem. There is also a qualitative problem of incorrect ordering[8] at Γ which may result from a technical artifact. RHF Be n-layer calculations using essentially the same techniques also exist[9] for $n=1,2,3,4$. Performed at ideal bulk geometry, the $n=1$, 2, and 3 RHF systems are perfect semimetals (i.e., the valence and conduction bands touch only at the zone boundaries and the density of states at ε_F is zero), with no occupied state corresponding to any of the experimentally observed surface states. The occupied $n=4$ RHF bands appear to include the surface state at Γ but the same technical artifact found in the bulk RHF bands intrudes. Two RHF $n=4$ states have been identified[9] as prototype surface states at M. A potential difficulty with this identification, along with a brief analysis of the other RHF results, is presented below. The conclusion is that existing RHF bulk and n-layer results are of little avail in understanding Be surface states.

Be n-layer results in LDA have been published for $n=1$ (Refs. 10 and 11) and $n=2$.[12] For $n=1$, the one-electron results are quite consistent[10(b)] for the Hedin-Lundqvist (HL) model.[13] Both differ dramatically with the $n=1$ RHF levels in displaying unequivocally metallic behavior. For $n=2$, only LDA structure-energy relations (not one-electron energies) have been published.[12] We are unaware of any published LDA results for $n=3$ Be.

Here we present LDA one-electron energies for $n=1,2,3$ and use them to interpret the experimental data of Refs. 1 and 2, give a lower bound to the 1s surface core-level shift found experimentally,[14] and interpret the relationship of the prior RHF calculations to the experimental data. The calculations confirm the experimental finding that the Be(0001) surface state at Γ is highly localized, while those at M are not.

II. PROCEDURAL MATTERS

The computational procedures used were those of Ref. 10c with refinements as outlined in Refs. 10(a) and 10(b). The basic scheme is a LCGTO (linear combination of Gaussian-type orbitals) expansion of the Kohn-Sham orbitals plus fitting (variationally) of the electron charge to one auxiliary basis of Gaussian-type orbitals (GTO's) and fitting (weighted least squares) of both the LDA exchange-correlation energy density and potential to another auxiliary GTO basis. An additional refinement since Ref. 10 is the incorporation of the constraint that the fitted exchange-correlation quantities[15] must yield the same contributions to the total energy as the exact ones. While the added constraint does not alter our previous results discernibly, we have recalculated all the energy levels reported here for consistency.

All-electron calculations which can include off-site (bond-centered) fitting functions and treat nearly arbitrary symmetry are quite demanding computationally. Basis size versus quality becomes a critical issue therefore. For $n=1,2$, we used the $6s\,2p$ orbital basis from Ref. 10(c), except that the more diffuse p_x and p_y exponents were 0.1859 (versus 0.118). For $n=3$ we used that same basis for the exterior layers, while for the interior layer the two most diffuse s-type exponents went to 0.26 and 0.13 (from 0.19821 and 0.067376, respectively).

The energies presented below are for the equilibrium geometries (in the HL LDA model) calculated previously[10(a),12] for $n=1,2$. For $n=3$ the geometry was chosen to be midway between our $n=2$ equilibrium LDA values and the LDA bulk equilibrium values from Ref. 5. All three lattice parameter sets are listed in Table I. Only the HL LDA model[13] was used in this work; the $X\alpha(\alpha=\frac{2}{3}$ or Kohn-Sham-Gaspar) model yields such inadequate work functions (see Ref. 12) that comparison with other experimental one-electron properties seems unwarranted.

TABLE I. Lattice parameters utilized for Be n layers, $n=1,2,3$ all in a.u. For $n=1$, see Ref. 10(a); $n=2$, see Ref. 12; $n=3$, see Sec. II. Bulk experimental values as cited in Ref. 5.

n	$a_x=a_y$	$a_z=c/2$	c/a
1	4.00		
2	4.10	3.4645	1.69
3	4.20	3.4230	1.63
Bulk	4.32	3.3869	1.568

III. SURFACE STATES

Valence and low-lying conduction LDA eigenvalues for n-layer Be ($n=1,2,3$) are shown in Figs. 1—3. In spite of well-known deficiencies in LDA eigenvalues used as quasiparticle energies, we treat them as reasonable approximations on the conventional grounds that (a) the calculated bulk bands match the experimental data fairly well, and (b) since the highest occupied eigenvalue is rigorously the LDA Fermi level and would be the exact ε_F if the LDA itself were exact Kohn-Sham theory,[16] the LDA eigenvalues near ε_F should be close to exact. In order to establish correspondences between n-layer states and surface and bulk states we consider the qualitative and quantitative behavior of the n-layer energies at various points in the 2D Brillouin zone.

Note first the behavior of the highest occupied level at Γ as a function of increasing n. For $n=1$, there is an oc-

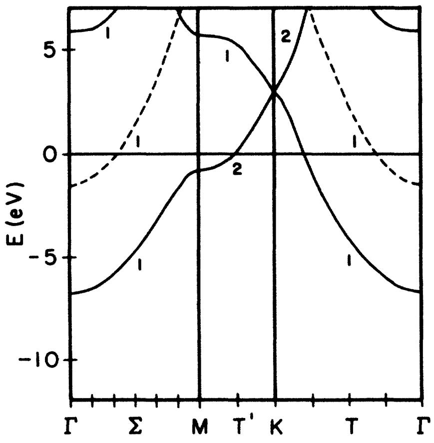

FIG. 1. Energy levels for Be monolayer referenced to ε_F. Symmetries with respect to the film plane are even (odd) for solid (dashed) curves. Symmetries with respect to the mirror plane containing the k-space line indicated are even (odd) for curves labeled 1 (2).

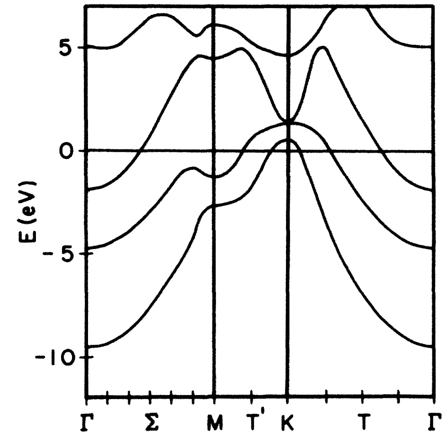

FIG. 2. As in Fig. 1 (except for evident symmetry differences) for Be two-layer. Along the $\Gamma-M$ symmetry line all bands shown are symmetry 1.

cupied p_z-like state bound (with respect to ε_F) by 1.5 eV. It is parabolic and intersects ε_F 36% of the way to M (32% toward K). At $n=2$, that state drops to -1.9 eV and its intersection with ε_F moves out to 43% of the way to M (37% toward K). In the $n=3$ system, the only one with a genuine interior, that occupied p_z-like state is dominated by antibonding contributions from the two exterior planes. Its binding has evolved to -2.0 eV at Γ. It is 1.9 eV above the state first below it (which we show below is a bulk counterpart) and intercepts ε_F 45% of the way to M (39% of the way to K). The effective mass is $m^*/m=1.03$ toward both M and K. For all three values of n, this entire band lies substantially above the projected LDA bulk-band structure[5]

The occupied s-like band, for $n=1$, falls mostly within the projected bulk-band structure except for a region extending about 15% from M toward Γ. For $n=2$, the two deeper states at Γ are at -4.8 and -9.6 eV. Both lie nicely inside the calculated bulk bands[5] (-4.2 and -11.2 eV) and hence correspond about as well with the bulk ARPE data[6] as does the bulk calculation itself. Two of the three low-lying levels at Γ in the three-layer also fall well within the calculated bulk bands (-7.8 and -10.1 eV), while the third one lies only 0.4 eV above the projected bulk bands (at -3.8 eV). The expansion coefficients for the latter state show that it is precisely as expected on physical grounds, namely, a mixture of the bulk state and the (mostly) s-like bonding surface state.

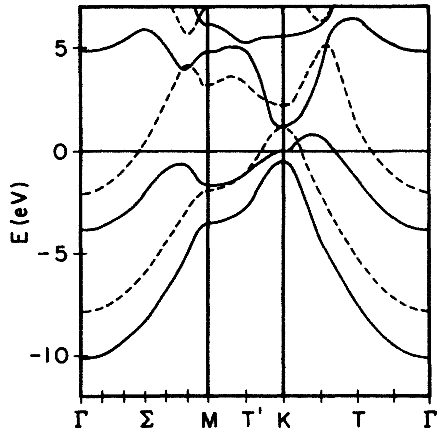

FIG. 3. As in Fig. 2 for Be three layer.

Along $\Gamma-M$ in the two layer the higher fully occupied band has a rounded local maximum 0.8 eV below ε_F about 80% of the way to M, with a local minimum directly overhead in the second unoccupied band. The local maximum near M becomes more pronounced and less bound (-0.6 eV) for $n=3$, while the local minimum directly overhead (in the unoccupied band of even symmetry) moves down more than 1.5 eV from $n=2$ to $n=3$. This pair of extrema are evidently the forerunners of the intersection which occurs in the bulk energies between the Γ_4^- to M_2^- and the Γ_3^+ to M_4^- valence bands just at ε_F.

Along $\Gamma-K$ the occupied even-symmetry band for $n=1$ is well inside the projected bulk bands and the same is true for the lowest two states of the two layer. For $n=3$, the highest even symmetry state crosses ε_F 65% of the way to Γ while the projected bulk value for the crossing nearest Γ is 57%. In the projected bands, there is a sliver of unoccupied energies about 1-eV deep very close to K. The behavior of the $n=3$ states near K is certainly compatible with the properties of that sliver. Note particularly the odd-symmetry state crossing of ε_F 87% of the way from Γ to K and the 0.5-eV gap at K between the occupied and lowest empty even-symmetry states.

Matters at M are less distinct. As noted, the fully occupied one-layer band at -0.8 eV is 2.3 eV above the calculated bulk band edge at M (-3.1 eV). The upper of the two occupied states of the two layer lies about 1.8 eV above the band edge while the lower one is barely within the projected bulk states. For $n=3$, the two occupied states of even symmetry (-3.5 and -1.7 eV) are about evenly divided between inner- and outer-plane contributions while the occupied odd-symmetry state (-1.8 eV) is dominated by outer-plane orbitals. Even the deepest one is only 0.4 eV below the bulk-band edge.

These considerations make clear the identification of the deepest states at and substantially out from Γ for $n=1$, 2, and 3 as primarily bulklike and the shallow, p_z-like state as the surface state at Γ found experimentally. The appearance of that Γ surface state in an ultrathin system is dramatic confirmation of the correctness of the experimental interpretation that the state is highly localized. Its calculated ($n=3$) and experimental parameters are compared in Table II.

Though the calculated Γ surface state becomes more bound with increasing n its binding energy is still too high, by 0.8 eV, relative to experiment for $n=3$. Two significant sources for this discrepancy exist, finite thickness effects and spurious self-interaction in LDA. It is difficult to provide more than the rough estimates that follow for these effects. To estimate the finite thickness contribution to the Γ surface state, observe that the calculated one-electron energy is shifted by -0.4 eV on going from $n=1$ to $n=2$ and another -0.1 eV from $n=2$ to $n=3$. This behavior suggests that a plausible estimate of finite thickness effects beyond $n=3$ is -0.1 to -0.2 eV.

TABLE II. Experimental and calculated ($n=3$) parameters for the Be (0001) surface state at Γ. Experimental intersection fractional distances for Ref. 2 calculated from effective masses quoted there. Effective mass for Ref. 1 calculated from binding at Γ and intersection distance toward M quoted there. See text.

	Experiment	Calculation
Binding (eV)	$-2.8^{a,b}$	-2.0
Interval to nearest bulk state	-2.0^{b}	-1.9
Intersection fraction Γ—M	0.55,[a] 0.668^{b}	0.45
Intersection fraction Γ—K	0.564^{b}	0.39
m^*/m (toward M)	1.04,[a] 1.53^{b}	1.03
m^*/m (toward K)	1.45^{b}	1.03
$m^*(\rightarrow M)/m^*(\rightarrow K)$	1.06^{b}	1.00

[a] Reference 1.

[b] Reference 2.

Such values are consistent with results beyond $n=3$ in several other calculations, e.g., Krakauer *et al.*[17] and Arlinghaus *et al.*[18] In principle, this estimate could be checked by comparison of the splitting of the bonding and antibonding surface states for $n \geq 2$. That check cannot be performed here because the bonding surface state cannot be distinguished unequivocally from a bulklike state at low n (recall above).

The remaining discrepancy between $n=3$ LDA and ARPE values at Γ (-0.6 to -0.7 eV) is attributable primarily to the spurious self-interaction characteristic of LDA.[19] A small amount is attributable to lattice relaxation effects (because the $n=3$ lattice parameters were prescribed, not calculated). Experience suggests -0.1 eV at most. Therefore, the estimated self-interaction correction (SIC) is -0.5 to -0.6 eV or 25—30% of the LDA eigenvalue at Γ (-2.0 eV).

To check this estimate, observe that the SIC for the highest occupied state at Γ of crystalline Be can be estimated, by comparison of the ARPE value (-4.8 eV) with the LDA eigenvalue (-4.32 eV),[6] as 11% of the latter. The SIC for the highest occupied atomic Be eigenvalue is approximately 52% of the bare LDA eigenvalue (from the *post hoc* correction, the only available value[20]). The $n=3$ version of the Γ surface state will be intermediate in localization between the atomic and crystalline states and the SIC for it should there be intermediate as well. A simple estimate is the mean of the atomic and bulk percentage SIC or 32% of the bare eigenvalue. This independent estimate falls at the upper end of the range (25—30% of the bare LDA eigenvalue) deduced in the preceding paragraph, in confirmation of the reasonableness of that result.

The estimated contributions to the discrepancy between the ARPE and the $n=3$ LDA surface-state binding energy at Γ therefore are the following: finite thickness effects, 0.1—0.2 eV; lattice relaxation effects, ≤ 0.1 eV, SIC 0.6—0.5 eV. It is significant that even if the finite thickness correction is substantially bigger than we have any reason to expect (e.g., 50% higher than our largest estimate), the SIC will still be of comparable magnitude. In the large-n limit, however, the finite thickness correction will vanish, while the SIC will not, precisely because of the localized nature of the Γ surface state. In LDA treatments of metals a substantial SIC for an occupied state near ε_F is not usually encountered, so the Be Γ surface state provides something of a novel test for LDA or beyond.

While the experimental fractional intersections of the surface state with ε_F along Γ to M and K are larger than those calculated for $n=3$, their evolution with n is qualitatively proper in that the calculated intersections move substantially outward with increasing n. However, there is a puzzle in the experimental data. Along Γ—M the fractional intersection is reported in Ref. 1 as 0.55, while Ref. 2 reports 0.668 (from effective mass; measurement of Fig. 6 of Ref. 2 gives 0.63 at the smallest). The discrepancy is larger than the expected experimental imprecision.[21] Since the two experimental values of the Γ surface-state binding energy are identical, the intersection fraction discrepancy introduces a substantial discrepancy into the experimental Γ—M effective masses as well. Reference 2 gives $m^*/m=1.53$ for that direction while the published data of Ref. 1 (binding at Γ plus crossing distance toward M) gives $m^*/m=1.04$. The $n=3$ calculated value is 1.03. The only experimental determination[2] of m^*/m along Γ—K gives 1.45, while the three-layer calculated value is 1.03. The effective mass ratio for the two directions (see Table II) is 1.06 measured versus 1.00 for the $n=3$ calculation.

The extent and comprehensiveness of the Ref. 2 data compared with Ref. 1 lend support to the view that the higher m^* values reported in Ref. 2 are the more nearly correct ones. Again because of spurious self-interaction in the simple LDA, the calculated m^*/m for an n-layer will be below that for a bulk-crystal surface. It is a simple case of self-repulsion causing artificial delocalization; hence reduced effective mass of surface states. The extreme thinness of the three-layer would tend to exacerbate this problem, since the two surfaces are not completely decoupled. Checking the SIC contribution to the effective mass would require computational implementation of that theory, a task made difficult by its representation-dependent nature.[19] We have checked for possible basis set limitations (i.e., that the p_z basis might make the p_z-like states too diffuse) by utilizing a $9s\,5p$ basis in the monolayer. The result is $m^*/m=1.00$ along Γ—M so that basis set effects are small.

Though perhaps less obvious than for the state at Γ, the three-layer LDA states at M are also in reasonable accord with experiment. That is, two of those states are roughly equally interior and exterior in character, while the third (which is mostly exterior in character) has an energy in reasonable agreement with the more localized of the two M surface states seen experimentally. Thus the three-layer mimics about as closely as it can the qualitative behavior of the semi-infinite solid.

IV. CORE 1S SHIFT

Nyholm *et al.*[14] have reported photoelectron spectroscopy measurements of the difference in Be 1s levels for bulk atoms and atoms in the first layer of a clean Be (0001) crystalline surface. They find a surface core-level shift

$$E_{\mathrm{scs}} = \varepsilon_{1s,\mathrm{bulk}} - \varepsilon_{1s,\mathrm{surf}} = -0.50 \text{ eV} .$$

On the basis of physical arguments (to provide bounds and interpretations of the relevant cohesive energies) they calculate -0.53 eV while Miedema's estimate procedure[22] gives -0.15 eV.

The thinnest n-layer that can exhibit such a shift is $n=3$. Clearly the difference between the interior and exterior 1s levels will be a lower bound to the magnitude of E_{scs} since the interior level will be increasingly decoupled from the exterior one with increasing n. We find $E_{\mathrm{scs},n=3} = -0.21$ eV from 1s levels which are sensibly flat (total bandwidth = 0.02 eV). Thus 40% of the experimental splitting is found at only three layers. More significantly, the ordering of the splitting deduced experimentally is given microscopic confirmation even at $n=3$.

This simple calculation does not, of course, take account of core-hole screening relaxation effects which must, on principle, differ between bulk and surface states. Feibelman and Hamann[23] have summarized the evidence for assuming that those effects are small relative to one-electron eigenvalue differences such as used above. There is no apparent reason to expect the present situation to differ markedly.

V. COMPARISON WITH OTHER RESULTS

As mentioned, the only LDA one-electron n-layer results other than those here (and the related work of Refs. 10) are Wimmer's for $n=1$.[11] Both are all-electron calculations but with differing numerical techniques [LCGTO here versus full-potential linearized augmented plane wave (FLAPW) for Wimmer]. Wimmer also used $a=4.20$ a.u., while our results are for LDA equilibrium ($a=4.00$ a.u. for $n=1$). The results are mutually consistent with only small differences of detail. Nothing in the comparison suggests any need to alter the interpretation of the p_z-like state at Γ as the experimentally found surface state.

Turning to the RHF comparison, the $n=1$, 2, and 3 results[9] describe the system as a perfect semimetal, so they are poor candidates for modeling the manifestly metallic Be surface (an observation first due to Wimmer[11]). Moreover, none of the RHF occupied states for these three systems can be identified cleanly with experimentally observed surface states at Γ and, in fact, the $n=3$ odd-symmetry p_z-like state that is predominately from the exterior layers is unbound by about 1 eV.

The $n=4$ RHF system is metallic, with occupied bands which include, at Γ, a p_z-like state bound by -1.9 eV that crosses ε_F about 33% of the way to M. In Ref. 7 it is argued that this state is the counterpart of the Γ_3^+ bulk state. From the published results it seems at least possible that it is the first sign, in the RHF n-layer sequence, of the surface state at Γ but that its location is accidental. The difficulty is that the $n=4$ occupied RHF manifold includes not only the p_z-like state but also the counterpart of an unphysical occupied RHF state found in the bulk.

In the RHF crystal,[7] an occupied Γ_{4-} state is found at -1.4 eV for which there is no experimental evidence.[6,8] Since RHF levels are known to be too deeply bound, the fact that this one lies *above* the ARPE Γ surface state energy is an unequivocal prediction positioning that surface state in the bulk manifold, in contradiction with experiment.[1,2] Dovesi *et al.*[7] suggested that this spurious state is a technical artifact (strong sensitivity to the diffuse p-basis). Basis set restrictions apparently removed it in the bulk RHF calculation of Ref. 9 which used the same methods. In any case, the $n=4$ counterpart of that spurious RHF Γ_4^- occupied level occurs *below* the p_z-like level. The effect of that ordering is to push the p_z upward in energy artificially close to ε_F, hence in rough but spurious coincidence with the surface state at Γ.

The RHF four-layer also has two states at M which lie about 5.8 eV below ε_F and in the projected RHF bulk gap. This fact, plus a sharp peak in the surface local density of states, led Angonona *et al.* to identify them as prototype surface states in the bulk. The difficulty with the identification is that it leads to the conclusion that both surface states at M are strongly localized (since they appear in the four-layer) whereas the experimental data show the lower of the two to be rather well overlapped with the bulk states at M. Furthermore, the upper one is part of the band that includes the counterpart of the spurious Γ_4^- bulk level, so that the extent to which its RHF behavior is even qualitatively physical is hard to determine.

In sum, existing RHF n-layer and bulk Be calculations differ noticeably from both LDA calculations and experiment. The LDA calculations resemble experiment more closely than the RHF ones. The latter seem to have enough technical and intrinsic limitations that they cannot be used for reliable interpretation of experimental ARPE data.

VI. CONCLUSIONS

Several conclusions are evident from this study. First, comparison of ultrathin film LDA results with bulk LDA results can be of a significant utility in interpreting experimental data on well-localized surface states. In particular, the three-layer can display both bulk and surface features to a significant extent, in spite of its minimalist interior (one atomic plane). This result is encouraging in that it suggests that it will not always be necessary to find the LDA equilibrium geometry of an 11 or 13 layer (an extremely demanding task) to get a useful calculation of well-localized surface states at calculated equilibrium. Second, the experimental characterization of the Γ surface state in Be as extremely localized is confirmed by density-functional theory (in the LDA). The state appears unequivocally even in the monolayer and its quantitative features are reproduced reasonably well by the three layer. Third, the LDA states at M in the n layers exhibit behavior which is compatible with their experimental description as strongly overlapped with bulk states.

The fourth conclusion deserves separate comment. Spurious self-interaction in LDA has a strong effect on surface-state effective masses which has apparently gone unremarked heretofor. The effective masses are reduced substantially by artificial delocalization from Coulomb self-repulsion. A common computational trick to estimate the SIC for an insulator band gap is to use $X\alpha$ LDA with $\alpha=1$. Perdew and Zunger[19] have analyzed that ploy in terms of density functional theory including SIC. However, it does not work even as a rough estimate in this context because it only widens gaps without substantially altering m^*. Improved values of m^* probably will not arise from correcting the LDA image potential problem (i.e., patching the long-ranged effect of self-interaction by altering the Kohn-Sham potential with a Latter tail correction[24] for the z direction).[25]

This LDA self-interaction misbehavior of a well-localized surface state will also cause a subtle modification of the LDA desorption problem analyzed by Perdew and Smith.[26] The essence of their argument is that in LDA an atom which desorbs from a dissimilar surface exhibits a common Fermi energy with that surface even at arbitrarily large distances. The atom then is unphysically fractionally charged, the desorption energy curves therefore are qualitatively incorrect, etc. Clearly the LDA description of desorption from a system with surface states would be more flawed, since self-interaction makes such surface states too diffuse (i.e., have m^* too small), hence strongly interacting with the fractionally charged desorbing atom even at large z.

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