

Ab initio band-structure studies of beryllium and beryllium-hydrogen ultrathin films

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(Received 7 November 1990; revised manuscript received 26 December 1990)

The electronic properties of hcp beryllium one-, two-, three-, and four-layer films and of a BeH₂ monolayer have been reinvestigated by all-electron Hartree-Fock band-structure calculations with improved basis sets. In agreement with local-density-functional calculations, all Be layers are found to be metallic, in contrast with previous Hartree-Fock calculations, which predicted zero-band-gap semiconductors for the one-layer (1L), 2L, and 3L systems. The metallic character is due to the precursor of the Be(0001) $2p_z$ surface state crossing the Fermi energy. However, this behavior is not observed for the BeH₂ layer, which is still found to be insulating, contrary to local-density calculations, which predicted metallic behavior.

I. INTRODUCTION

Recently, the electronic structure of a BeH₂ monolayer has been investigated in the Hartree-Fock¹ (HF) and in the local-density approximation² (LDA) with contradictory predictions: HF predicted (large gap) insulating behavior; in LDA, the BeH₂ monolayer is found to be metallic. It was conjectured² that this discrepancy is due to the use of a small HF basis set with a "tight" p exponent which is incapable of giving the Be $2p_z$ surface state enough dispersion to push it below the Fermi energy.

This comparison is of more general importance since a similar discrepancy is found for the earlier studies of hexagonal beryllium films: Previous HF calculations^{3,4} predict the one-layer (1L), 2L, and 3L systems to be zero-band-gap semiconductors. Only the four-layer system is found to be metallic. LDA calculations^{5,6} predict all Be layers to be metallic.

The aim of this paper is to investigate this qualitative difference which goes beyond the well-known problem of HF band-gap overestimation and Kohn-Sham LDA band-gap underestimation. As pointed out in Ref. 2, such a calculation is timely not only to end speculations on the outcome of a HF calculation with a rich basis set and on possible technical and/or intrinsic limitations of the HF computational scheme⁷ utilized in the CRYSTAL 88 program,⁸ but also for the following reasons: the BeH₂ planes play a key role in the understanding of hydrides of low- Z metals such as LiBeH₃ as a possible approach to the design of high- T_c superconductors;⁹ thin films are found to be increasingly interesting with physical properties radically different from their bulk counterparts¹⁰ and the appropriateness of theoretical methods has to be established to address fundamental questions in an interplay with angle-resolved photoemission and inverse-photoemission measurements of two-dimensional energy-band structures [see, for example, the recent study of a Li monolayer on Be(0001)¹¹].

The paper is organized as follows: Method and computational details including basis sets are discussed in Sec. II. The results are presented in Sec. III. First, we

discuss, in Sec. III A, the two-dimensional band structure of beryllium 1L, 2L, 3L, and 4L films and the effect of basis sets, especially of the exponent for the Be $2p$ functions. In Sec. III B, the calculations for the BeH₂ monolayer are presented and compared to the LDA results. Finally, in Sec. IV, the conclusions are summarized.

II. METHOD AND COMPUTATIONAL DETAILS

The all-electron linear-combination-of-atomic-orbitals Hartree-Fock (LCAO HF) band-structure calculations are performed employing the CRYSTAL 88 program.⁸ The program and the various truncation criteria for the infinite lattice sums are described in a recent monograph.⁷ This comprehensive review with a large number of applications also demonstrates that the HF approach is adequate for the study not only of insulating and ionic systems, but also of metallic systems if the basis sets are chosen carefully. The results prove that a number of ground-state properties, including binding energy, lattice constant, electron-charge densities, x-ray structure factors, Compton profiles, band structures, and Fermi-surface shapes, can be satisfactorily accounted for within the HF approximation. It is, however, also recognized¹² that the use of atomic-orbital basis sets that are variationally optimized under the constraint of limiting their spatial extent can lead to very unsatisfactory estimates for the virtual states and the corresponding eigenvalues. Since the existence of a gap itself is the fundamental question for the Be and BeH₂ layers, the choice and role of basis sets are investigated very carefully in this paper.

In Table I, different basis sets which have been employed in the Be and BeH₂ layer calculations are summarized. The Be (and H) $1s$ basis is the same as used in a previous study,¹ namely, Huzinaga's $6s$ (Ref. 13) for Be and the hydrogen basis used for lithium hydride.¹⁴ The smallest exponent in the hydrogen set was reduced from 0.2 to 0.15, and the basis was augmented by a p polarization function with exponent 0.5, optimized as reported below.

Major attention was given to the selection of a basis for

TABLE I. Exponents (in a.u.) and contraction coefficients of the s and p Gaussian functions used in various basis sets.

Atom	Type	Exponent	s coefficient	p coefficient
Be Core	s	1154.764 5	0.002 180 2	
		172.767 87	0.016 707 2	
		39.150 318	0.080 427 7	
		11.023 330	0.254 978 7	
		3.493 437 6	0.479 935 6	
		1.169 072 6	0.320 053 2	
Valence 1	sp	0.85	-0.3060	0.1747
		0.2688	1.2239	0.8737
Valence 2	sp	0.85	1.0	1.0
	s	0.25	1.0	
	p	0.20		1.0
Valence 3	sp	0.85	1.0	1.0
	sp	0.16	1.0	1.0
Valence 4	s	0.85	1.0	
	sp	0.326	1.0	1.0
Valence 5	sp	0.85	1.0	1.0
	sp	0.27	1.0	1.0
	p	0.08		1.0
H	s	120.0	0.000 267	
	s	40.0	0.002 249	
	s	12.0	0.006 389	
	s	4.0	0.032 906	
	s	1.2	0.09	
	sp	0.5	1.0	1.0
	s	0.15	1.0	

the Be $2p$ orbital. A "tight" p exponent of 0.32 was identified in Ref. 2 as the source of discrepancy between the HF and LDA results for the BeH_2 layer: It could be shown² that LDA reproduces a band structure which is qualitatively the same as the HF band structure if the HF basis is used. That is, the LDA Be $2p$ band is reduced in width from 4 to 1 eV and shifted up in energy, above the Fermi energy E_F , thus opening up a gap.

This Be $2p$ band was also identified with the Be surface-state band of the Be(0001) surface.² A precursor to this state crosses the Fermi energy in the LDA results for the 1L, 2L, and 3L beryllium films and is responsible for the strong metallic character. In these calculations,^{5,15,16} p exponent sets varying from (0.509, 0.118)¹⁵ to (4.0, 1.2, 0.4, 0.17, plus 0.07 for p_z)¹⁶ were used. On the other hand, in HF calculations for the Be layers^{3,4} the comparatively "tight" valence basis 1 in Table I (contracted from the sp basis used in the Be bulk study¹⁷) was employed; metallic behavior was not found except for the four-layer film. Therefore, the first calculations presented below are aimed at resolving the discrepancy for the Be layers. The next set of calculations then address the electronic structure of the BeH_2 plane.

Other computational parameters entering the calculations were chosen as follows:

The five threshold parameters^{7,8} that control the accuracy of the calculation of the bielectronic Coulomb and exchange series were 10^{-5} (overlap threshold for Coulomb integrals), 10^{-5} (penetration threshold for Coulomb integrals), 10^{-5} (overlap threshold for exchange

integrals), and 10^{-5} and 10^{-11} (pseudo-overlap thresholds for the exchange series). A second, more stringent set (10^{-6} , 10^{-8} , 10^{-6} , 10^{-6} , and 10^{-13}) was employed for the potential curve (total energy versus lattice parameter) calculation for BeH_2 and for calculations with small exponents which required higher precision.

Multipole terms up to $l=4$ (hexadecapole) have been used in the evaluation of the Coulomb interaction between separate charge distributions. For higher-precision calculations, terms up to $l=6$ have been included.

Between 10 (Be layers) and 28 (bulk Be) \mathbf{k} points in an irreducible wedge of the Brillouin zone have been utilized. To calculate the Fermi energy and charge-density matrix, five symmetrized plane waves are used to expand $E(k)$ and 28 (133) \mathbf{k} points were sampled in the Gilat net for the layers (bulk Be).

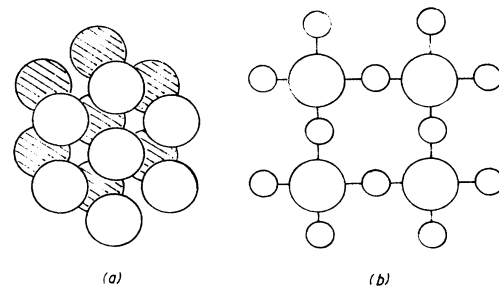


FIG. 1. (a) A hexagonal Be dilayer as viewed normal to the film. The second-layer Be atoms are cross hatched. (b) The square BeH_2 monolayer with small circles denoting H atoms.

Finally, the lattice parameters for the hexagonal Be layers [see Fig. 1(a)] were kept at their experimental values for bulk Be, i.e., $a = 2.29 \text{ \AA}$ and $c = 3.59 \text{ \AA}$.¹⁸ The interplane distance $c/2$ was varied only for the Be dilayer. For the BeH_2 plane [see Fig. 1(b)], the lattice constant was optimized.

III. RESULTS AND DISCUSSION

A. Be Layers

The band structure of Be monolayer, obtained with the valence basis 1, is shown in Fig. 2(a). The important qualitative feature is that the pure p_z band, shown as a heavy solid line, lies completely above the Fermi energy E_F . The monolayer is a zero-band-gap semiconductor since the lowest eigenvalue at K is a degenerate state, analogous to the K_1 state in the bulk.³ The total energy per atom (E/atom) is -14.5560 hartrees.

By monitoring the p_z band as a function of decreasing p exponent, it is found that the transition to a metallic state occurs between 0.23 and 0.20 for the p exponent, while the total energy is constantly decreasing.

The band structure, obtained with set 2, is shown in Fig. 2(b). The corresponding total energy per atom is -14.5867 hartrees. Further energy optimization leads to basis 3 in Table I and $E/\text{atom} = -14.6128$ hartrees [the band structure of the metal is shown in Fig. 2(c)].¹⁹ Comparison with the HF limit for a Be atom (-14.5730 hartrees²⁰) yields a HF binding energy of 1.08 eV. The missing correlation energy for metallic Be was estimated¹⁷ to be between 1.4 eV (Nozières-Pines) and 1.9 eV (Gunnarsson-Lundqvist) which gives a cohesive energy between 2.5 and 3 eV in surprisingly good agreement with LDA values⁶ of 2.41 ($X\alpha$) and 2.87 eV (Hedin-Lundqvist).

The results for the Be monolayer can be summarized as follows:

The beryllium monolayer is metallic. The discrepancy between LDA and earlier HF calculations is indeed due

to a rather tight p exponent in the HF basis. However, the HF approach^{7,8} has no difficulty in converging to the "right" solution (an accuracy of 10^{-4} hartrees is reached in six iterations). The metallic solution is obtained long before numerical instabilities due to small exponents are encountered (0.15 for the Be 1L, if the first set of truncation criteria discussed in Sec. II is employed).

The band structure of the 2L Be film has first been calculated with basis set 2 using the bulk value of $d = c/2 = 1.795 \text{ \AA}$ for the interlayer distance. Surprisingly, a semiconducting solution is obtained [see Fig. 2(a)] with $E/\text{atom} = -14.6146$ hartrees. If, however, the interplane distance is relaxed, the transition to the metallic state occurs between 1.825 and 1.850 \AA . The band structure for the metallic dilayer, in which the $2p_z$ state crosses again the Fermi energy, is shown in Fig. 2(b) for $d = 2 \text{ \AA}$, the energy minimum for the metallic state with basis set 2. E/atom is found to be -14.6096 hartrees, above the semiconducting solution. Utilizing basis set 3—and the more stringent second set of truncation criteria as well as summing multipole contributions up to $l = 6$ —the insulator-metal transition is observed if d relaxes from 1.75 to 1.76 \AA . The minimum for the metallic state is found for an interplanar separation between 2 and 2.1 \AA . The band structure is shown for $d = 2.1 \text{ \AA}$ in Fig. 3(c). With this basis the metallic state is below the semiconducting state, and E/atom is -14.6260 hartrees. Subtracting the equivalent energy for the Be monolayer gives an interplanar binding of the Be dilayer relative to the monolayer of 0.0132 hartree or 0.36 eV. For comparison, the LDA Hedin-Lundqvist value is 0.35 and the $X\alpha$ value is 0.29 eV/atom for an interplanar separation of 1.88 and 1.83 \AA , respectively.⁶

These results for the Be dilayer show again that the discrepancy to earlier HF calculations is due to the limited p basis. The HF approach has no intrinsic problems with converging to a metallic solution. The limited potential-surface search revealed an interesting possibility: a metal-insulator transition for the Be dilayer upon compression beyond the bulk interplanar distance. Since

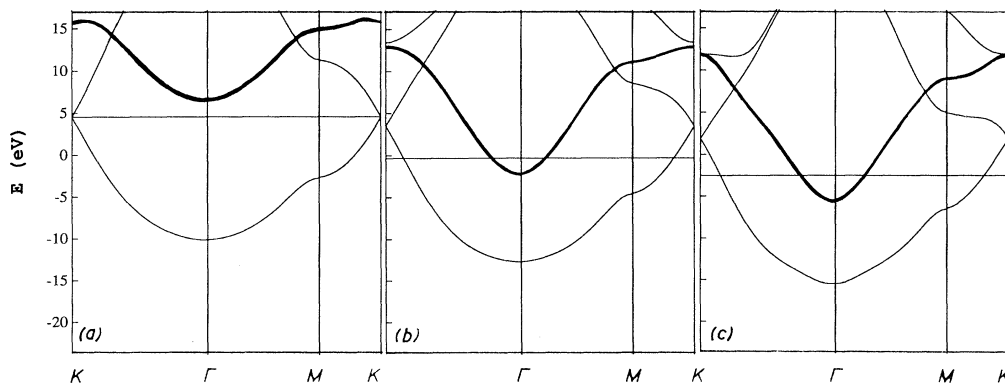


FIG. 2. Band structure of a Be monolayer for (a) basis set 1, (b) set 2, and (c) set 3. The heavy solid line is the Be p_z band, the precursor of the $\text{Be}(0001)$ surface-state band.

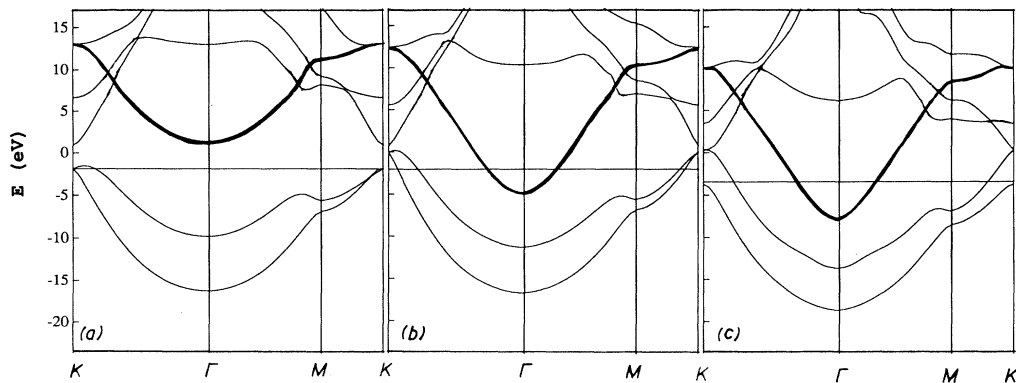


FIG. 3. Band structure of a Be bilayer for basis set 2 with an interplane distance (a) $d = c/2 = 1.795 \text{ \AA}$, (b) 2.0 \AA , and (c) for basis set 3 and $d = 2.1 \text{ \AA}$. The heavy solid line is the "surface"-state band.

the interplanar binding is rather weak and the dilayer interplanar vibration is expected to be rather soft (also concluded from the LDA results⁶), this transition would not require high pressure. A more detailed potential-surface search, i.e., variation of both the a and c lattice parameters, is under way to see whether the metal-insulator transition persists or disappears upon relaxation of a and to determine a more precise HF value for the interplanar-energy minimum separation.

No more surprises were found in the Be three- and four-layer calculations. Using basis set 2, the predominantly p_z -like state crosses E_F [see Figs. 4(a) and (b)] and is responsible for the metallic property of these films. It is clearly the precursor to the experimentally observed^{21,22,11} state on Be(0001). The lower-lying states are bulklike, as the comparison with the projected bulk band structure, given in Fig. 4(c), shows.

For the Be three-layer system, the precursor to the Be surface state [heavy solid line in Fig. 4(a)] lies, at Γ , 3.4 eV below the Fermi energy and crosses ϵ_F at 36% of the way from Γ to M . This gives an effective mass m^* of

$0.36m_0$. A similar value is obtained if, in the parabolic fit and calculation of the second derivative, only points in the vicinity of Γ are included. The corresponding Be four-layer results [see also Fig. 4(b)] are 3.8 eV, 39%, and $m^* = 0.38m_0$. The Be three-layer LDA values in Ref. 5 are 2 eV, 45%, and $m^* = 1.03m_0$. The latest experimental number for the effective mass of the Be surface state, quoted in Ref. 11, is 1.27. Thus, it is quite clear that the Hartree-Fock value for m^*/m_0 is much too small. This goes beyond the expected self-repulsion in thin layers and, therefore, reduced effective mass of layer surface states compared with bulk surface states (see discussion in Ref. 5). A possible explanation could be that HF calculations exaggerate, as a rule (see Ref. 14), the separation between levels in the vicinity of the Fermi energy and, therefore, yield higher dispersion and, consequently, a parabolic band with a higher curvature. This effect is illustrated in Figs. 2 and 3: The curvature increases when the band is pulled below the Fermi energy. Overall, the inadequate computation of m^*/m_0 at the HF level needs further study.

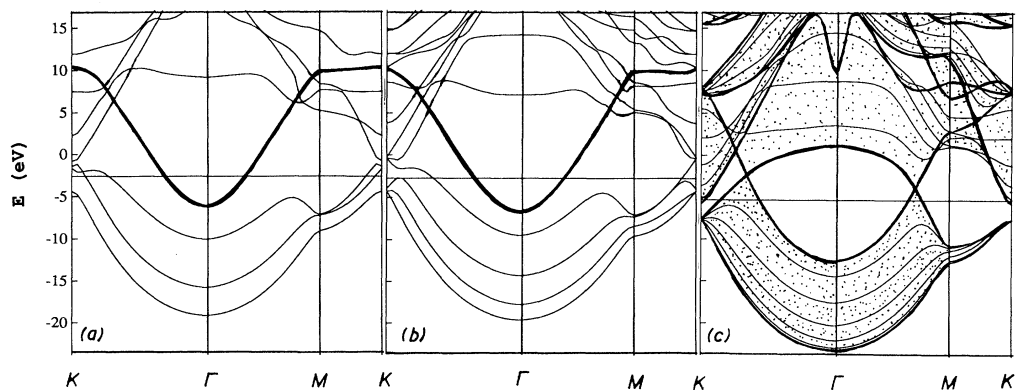


FIG. 4. Band structure for the (a) 3L and (b) 4L film of Be with basis set 2 and $d = c/2 = 1.795 \text{ \AA}$. The heavy solid line is the precursor of the Be(0001) surface-state band. In (c), the projected band structure of bulk Be is shown. Heavy solid lines indicate the bands with $k_z = 0$.

B. BeH₂ monolayer

The Hartree-Fock band structure for the BeH₂ monolayer along the high-symmetry lines of the two-dimensional Brillouin zone is shown in Fig. 5(a) for the basis set used in Ref. 1, i.e., with a p exponent of 0.326 (basis 4 in Table I), and using the equilibrium value of 3.1 Å for the lattice constant. The p_z band which was identified as the source of discrepancy between the HF and LDA results is shown as the heavy solid line. The total energy per unit cell for this case is -15.7252 hartrees.

The basis-set valence 5 in Table I was the outcome of a large series of calculations. All these calculations have been performed at a reduced value of $a = 2.92$ Å for the lattice constant, the equilibrium value found in the LDA calculations.² Using valence set 2 lowers the total energy to -15.7397 hartrees; set 3 yields -15.7424 hartrees (the more stringent set of truncation criteria has to be employed). With basis set 5, a total energy per unit cell of -15.7463 hartrees is obtained. Enriching the p basis and adding more diffuse p functions have the predicted effect of broadening the p band and lowering it in energy, but does not make the system metallic. Figure 5(b) shows the band structure at the HF equilibrium lattice constant of 3.04 Å, obtained from the total-energy potential curve shown in Fig. 6. The band structure is qualitatively the same as that obtained in Ref. 2 with the important difference that all conduction bands are shifted up in energy by about 6 eV, opening up a gap. The direct band gap at Γ is 4.6 eV, the dispersion of the unoccupied p band is 5 eV, and the total energy per cell is -15.7484 hartrees. This gives a HF cohesive energy (with respect to the free Be and H atoms) of 4.8 eV for the BeH₂ monolayer. The calculated equilibrium intraplanar force constant $\partial^2 E / \partial a^2$ is 0.075 hartree/a.u.² [0.089 in LDA (Ref. 2)]. The lowest-energy configuration is characterized by a significant charge transfer from Be to H: A Mulliken population as a qualitative measure gives 3.0 for Be and 1.5 for H.

The following characteristic features were observed

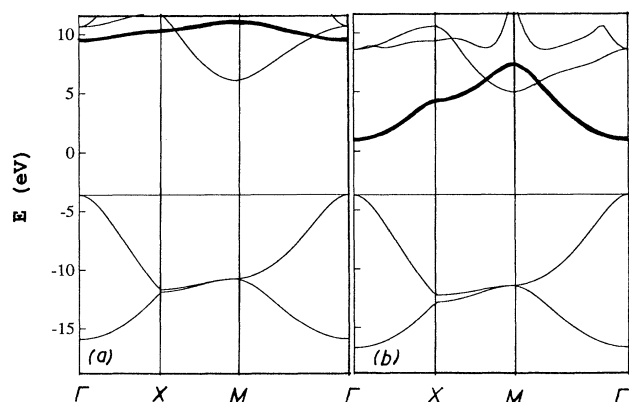


FIG. 5. Band structure for the BeH₂ monolayer (a) with basis set 4 and a lattice constant $a = 3.1$ Å and (b) with set 5 and $a = 3.04$ Å. The heavy solid line is a pure Be $2p_z$ band.

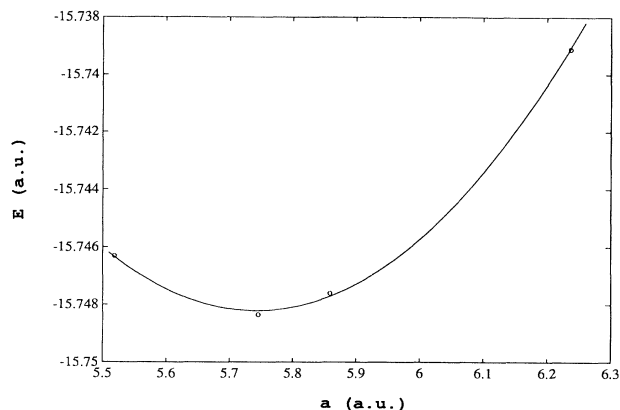


FIG. 6. Total energy E (in a.u.) as a function of lattice constant a (in a.u.) for the BeH₂ monolayer obtained with basis set 5.

during the basis-set optimization: Adding a p polarization function to hydrogen has a minor effect on the total energy: 0.001 a.u. for an exponent of 1.0 and 0.002 a.u. for an exponent of 0.5. Decreasing the s exponent on H from 0.2 to 0.15 decreases the energy further by 0.001 a.u., but increases the band gap. The increase in the band gap is understandable because a decrease in the H exponent allows for more charge transfer to the hydrogen atom, i.e., for more ionicity in the system. The conjecture of Ref. 2 that it is energetically favorable to transfer some of the electron charge from the in-plane Be—H bond into the vacuum region by occupying the Be $2p_z$ “surface” state was tested by constricting the H basis set (exponent of 0.25) and making the Be set more diffuse (with a p exponent of 0.07, the same as employed in the LDA calculation). This calculation was performed for $a = 2.92$ Å; it yields a higher total energy ($E_{\text{tot}} = -15.7459$ hartrees) and still a band gap of 3.95 eV (the truncation criteria were 10^{-8} , 10^{-10} , 10^{-8} , 10^{-8} , and 10^{-16} to avoid catastrophic numerical behavior; the computer time went from 220 s for basis 4 to 6700 s). Increasing the number of k points to 28 has no effect. The self-consistent-field (SCF) iterations started from atomic charge populations with a vanishing energy gap. The gap widens during the convergence to the lower-energy solution.

IV. CONCLUSIONS

These Hartree-Fock calculations with improved basis sets resolve the discrepancy between Hartree-Fock and local-density results for Be layers. They confirm the metallic nature of the 1L, 2L, 3L, and 4L beryllium films. There is no technical or intrinsic limitation in the HF computational scheme. The key Be surface state is represented correctly.

On the other hand, the difference in the results for the BeH₂ monolayer persists. Use of exponents as diffuse as those used in the LDA calculations still produces a nonmetallic lowest-energy solution with a HF band gap of 4.6 eV. Correlation corrections are expected to reduce

this band gap to around 2 eV, but it is highly unlikely that a metallic solution such as that found in the local-density study will arise. The results clearly underline the difference between a beryllium layer and a beryllium hydride layer: The metallic nature of the first one arises because it is energetically favorable to transfer the charge away from the Be plane into the "vacuum" region by occupying the Be $2p_z$ orbital perpendicular to the plane, the precursor of the Be surface state, as discussed in Ref. 2. Beryllium hydride, on the other hand, is largely ionic in

character. It is energetically more favorable to transfer the charge to the hydrogen atoms rather than into the p_z orbital.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge stimulating discussions with S. B. Trickey about the intricacies of the Be surface state prior to publication of the local-density results.

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