Theory of quasiparticle surface states in semiconductor surfaces

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A first-principles theory of the quasiparticle surface-state energies on semiconductor surfaces is developed. The surface properties are calculated using a repeated-slab geometry. Many-body effects due to the electron-electron interaction are represented by the electron self-energy operator including the full surface Green's function and local fields and dynamical screening effects in the Coulomb interaction. Calculated surface-state energies for the prototypical Si(111):As and Ge(111):As surfaces are presented. The calculated energies and dispersions for the occupied surface states (resonances) are in excellent agreement with recent angle-resolved photoemission data. Predictions are made for the position of empty surface states on both surfaces which may be experimentally accessible. The resulting surface state gap at $\bar{\Gamma}$ for Si(111):As agrees with recent scanning-tunneling-spectroscopy measurements. Comparison of the present results to eigenvalues from the local-density-functional calculation reveal substantial corrections for the gaps between empty and occupied surface states. This correction is found to depend on the character of the surface states involved.

I. INTRODUCTION

The local-density-functional approach has been quite successful in explaining the structure of many surfaces, including reconstructions.[1] This rests on the ability to calculate accurately the total energy associated with proposed configurations of atoms. One then proceeds to find that structure which minimizes the total energy. To this stage, a complementary first-principles theory for computing the electronic excitation energies associated with the surface structure has been lacking. This hinders clear comparison of the properties of a proposed surface structure to results from the various spectroscopic probes of surface electronic structure.

In the present paper a theory of the quasiparticle surface-state energies is presented which meets this need.[2] The previously developed theory[3] of the electron self-energy operator in bulk semiconductors and insulators is extended to the case of semiconductor surfaces. In the bulk case the self-energy approach provides a quantitative theory for the band gaps and band dispersions.[3,4] In the surface case, the self-energy operator may be used to deduce the energies of quasiparticle surface states. This allows the atomic coordinates resulting from total-energy calculations to be used directly for a first-principles calculation of the associated surface-state energies. These can then be rigorously compared to spectroscopic data.

The eigenvalues that result from the Kohn-Sham equations in the local-density-functional approach[5] (LDA) often have been interpreted as representing quasiparticle energies. This has well-documented difficulties highlighted by the underestimate of the minimum gap in semiconductors and insulators by 30–100 % in comparison to the

measured value.[6] Similar problems are encountered for surface-state (resonance) energies. Previous comparisons of calculated LDA surface-state energies to experiment[1] reveal three systematic errors: (i) gaps between empty and occupied surface states are too small, (ii) the placement of the occupied surface-state energies relative to the bulk valence band is incorrect (being too high in comparison to measured values), and (iii) the dispersion of the surface-state bands is too small in some cases. In the present work, we address each of these problems by demonstrating a first-principles theory of the quasiparticle surface-state energies that properly includes the exchange interaction and higher-order correlations among the electrons.

To elucidate the basic physical principles involved, it is desirable to consider a surface free of the complication of extensive reconstructions. Recently, this has been realized in practice. Arsenic-terminated Ge (Ref. 7) and Si (Ref. 8 and 9) surfaces have been prepared which exhibit a 1×1 surface periodicity. For the (111) surfaces,[7,9] the As appears to substitute for the final layer of Si or Ge, resulting in a chemically stable surface. The surface states arising from the As lone-pair states have been carefully measured using angle-resolved photoemission. The resulting surface band is consistent with the 1×1 substitutional geometry. This assignment is also consistent with recent standing-wave x-ray studies of the Si(111):As surface.[10] These surfaces have been chosen as a prototype for a first application of our theory because of their geometric simplicity and careful experimental characterization.

In the present theory[2] the self-energy operator Σ is evaluated from first principles and the quasiparticle

surface-state energies are obtained directly. The resulting surface-state energies corresponding to the occupied As lone-pair (p_z) orbital are in excellent agreement with the angle-resolved photoemission data for both Si(111):As and Ge(111):As. Both the placement and the dispersion of the surface band is correct. In comparison to the LDA surface-state energies, there is a substantial (10–20%) correction to the dispersion. The offset of previous calculated LDA band energies from experimental values with respect to the valence-band edge is largely due to one-electron effects in this case. There may be many-body corrections required for other surfaces.

There are also well-defined empty surface states near $\bar{\Gamma}$ in the surface Brillouin zone. These states are split off from the continuum states and have atomic character at the surface similar to the L_{1c} conduction bands which form the conduction-band edge at $\bar{\Gamma}$. For the Si case these are in the gap in the projected bands, but above the bulk conduction-band edge. For the Ge case the surface states are in the minimum gap. The present theory predicts the position of those states relative to the bulk valence-band edge. They should be experimentally accessible using angle-resolved inverse-photoemission measurements and possibly scanning tunneling spectroscopy. The scanning tunneling experiment has recently been done for the Si(111):As surface.[11] Not only is the 1×1 surface observed directly, the surface-state gap in the normalized differential conductivity agrees very well with the value predicted here. Optical transitions from the occupied lone-pair states to the empty surface states near $\bar{\Gamma}$ are dipole allowed for p-polarized light. Therefore surface-derived optical absorption may also be observable with an onset given by the calculation.

The gap between the empty and filled surface states is substantially opened up in comparison to the gap in the LDA eigenvalues analogously to the bulk case. However, the size of the correction depends on the detailed character of the states. As a consequence, it is evident that the shortcomings of the LDA spectrum can not be corrected by a simple rigid shift of the empty states relative to the valence-band edge.

The balance of this paper is organized as follows. In Sec. II the formal aspects of the present theory are briefly reviewed. The technical details of the calculations in the slab geometry and the evaluation of the self-energy operator are contained in Sec. III. The results for the Si(111):As and Ge(111):As surfaces are presented and discussed in Sec. IV. A detailed comparison to available experimental data is made. The quasiparticle energies are compared to the LDA energies and implications for other semiconductor surfaces are discussed. Section V contains some concluding remarks.

II. SELF-ENERGY APPROACH FOR SURFACES

As in the bulk case,[3] the quasiparticle energies are obtained from the electron self-energy operator. In general,[12] these are determined by solution of

$$[T+V_{\rm ext}(\mathbf{r})+V_H(\mathbf{r})]\psi(\mathbf{r})$$
$$+\int d\mathbf{r}'\Sigma(\mathbf{r},\mathbf{r}';E^{\rm qp})\psi(\mathbf{r}')=E^{\rm qp}\psi(\mathbf{r}) , \quad (1)$$

where the terms correspond to the kinetic-energy operator, the external potential due to the ion cores, the average electrostatic (Hartree) potential, and the electron self-energy operator, respectively. The latter contains the effect of exchange and dynamical correlations on the motion of the quasielectrons and holes. The theoretical challenge is to adequately approximate the self-energy operator. As in the bulk case, we use the GW approximation of Hedin:[13]

$$\Sigma(\mathbf{r},\mathbf{r}';E)=\frac{i}{2\pi}\int d\omega\, e^{-i\delta\omega}G(\mathbf{r},\mathbf{r}';E-\omega)W(\mathbf{r},\mathbf{r}';\omega) ,$$

$$(2)$$

where δ is a positive infinitesimal. The full crystalline Green's function G and dynamically screened Coulomb interaction W enter. For the Green's function, a quasiparticle approximation is used. W is defined as

$$W(\mathbf{r},\mathbf{r}';\omega)=\frac{1}{\Omega}\int d\mathbf{r}''\epsilon^{-1}(\mathbf{r},\mathbf{r}'';\omega)V_C(\mathbf{r}''-\mathbf{r}') , \quad (3)$$

where ϵ^{-1} is the time-ordered dielectric matrix and V_C is the bare Coulomb interaction.

In order to proceed for the surface case, a choice must be made for representing the surface. The surface breaks the crystalline periodicity so that, in general, new techniques are required to calculate the electronic structure. In order to treat the electronic energy levels associated with the surface, we use the repeated-slab approach.[14] The surface is modeled by a supercell containing several layers of atoms and a vacuum region. In this fashion, three-dimensional periodicity is restored. From a technical point of view, this allows us to carry over the approach developed for bulk semiconductors.

In evaluating the electron self-energy operator, the approach is to make the best possible approximation to G and W separately. These are then combined to form Σ and the quasiparticle energies are obtained directly.[3]

The Green's function is written in terms of the solutions to Eq. (1) analogous to the independent-particle case:

$$G(\mathbf{r},\mathbf{r}';E)=\sum_{n,\mathbf{k}}\frac{\psi_{n\mathbf{k}}(\mathbf{r})\psi^*_{n\mathbf{k}}(\mathbf{r}')}{E-E_{n\mathbf{k}}-i\delta_{n\mathbf{k}}} , \quad (4)$$

where $\delta_{n\mathbf{k}}=0+$ for occupied states and $\delta_{n\mathbf{k}}=0-$ for empty states. The states are indexed by Bloch wave vector $\mathbf{k}$ in the supercell and band number. In the present case, $\mathbf{k}$ is in the surface Brillouin zone (two dimensional). Initially, the wave functions and spectrum are taken from a LDA calculation. Then the spectrum is updated to reflect the true quasiparticle energies. As in the bulk case, the wave functions require no further modification.

The dynamical screening is treated in two steps. Exploiting the periodicity in the supercell approach, the static dielectric matrix $\epsilon^{-1}_{\mathbf{GG}'}(\mathbf{q};\omega=0)$ is obtained as a ground-state property from the LDA calculation.[15] Here the matrices are written in terms of the reciprocal-lattice vectors associated with the supercell and $\mathbf{q}$ is in the surface Brillouin zone. The off-diagonal elements of the dielectric matrices describe the local fields in the material. These are the microscopic variations in the screening

response to a perturbation. In a bulk semiconductor there are important differences in the screening potential around an added point charge, for example, in the bond chain in comparison to the interstitial region.[16] These local fields are crucial in the self-energy operator and, in particular, in opening the band gap. For the present surface systems treated in a supercell, the local fields play a similar role. However, in addition, the off-diagonal elements of the dielectric matrix distinguish the screening response of the bulklike region of the supercell from the response of the vacuum region. This is obviously important as the surface states of interest here are sensitive to the decay of the potential (self-energy operator) into the vacuum region.

The static dielectric matrices are extended to finite frequency using a generalized plasmon-pole model. For each $\mathbf{G},\mathbf{G}',\mathbf{q}$, the weight in the imaginary part of the dielectric matrix is collapsed into a single pole of some amplitude. The amplitude and position of the pole are determined from exact sum rules. The Kramers-Kronig relation gives the inverse ω moment in terms of the static dielectric matrices calculated for the surface:

$$\text{Re}\,\epsilon_{\mathbf{G}\mathbf{G}'}^{-1}(\mathbf{q};\,\omega=0)=\delta_{\mathbf{G}\mathbf{G}'}+\frac{2}{\pi}\text{P}\int_0^\infty d\omega\frac{1}{\omega}\text{Im}\,\epsilon_{\mathbf{G}\mathbf{G}'}^{-1}(\mathbf{q};\omega)\ .$$

$$(5)$$

The generalized f-sum rule relates the first ω moment of the imaginary part of the dielectric matrices to the supercell charge density:

$$\int_0^\infty d\omega\,\omega\,\text{Im}\,\epsilon_{\mathbf{G}\mathbf{G}'}^{-1}(\mathbf{q};\omega)$$

$$=-\frac{\pi}{2}\omega_p^2\frac{(\mathbf{q}+\mathbf{G})\cdot(\mathbf{q}+\mathbf{G}')}{|\mathbf{q}+\mathbf{G}|^2}\frac{\rho(\mathbf{G}-\mathbf{G}')}{\rho(0)}\ .\qquad(6)$$

Here, $\rho(0)$ and ω_p^2 refer to the average density in the supercell. This approach has been quite successful for bulk semiconductors and reproduces the expected behavior for the bulklike states in the repeated-slab geometry.

The self-energy operator for the surface will differ from the bulk case for two reasons. First, there are states localized near the surface. This affects the self-energy operator through the Green's function. It can lead to distinct results when the self-energy operator acts on surface states in comparison to bulk states. Furthermore, some of the states in the energy gap may be built up of both bulk valence- and conduction-band states. This will affect the results obtained when the self-energy operator acts on those states. Second, the plasmon modes are different near the surface. In particular, a distinct surface-plasmon mode appears. Viewing the correlation energy of a quasielectron as arising due to virtual absorption and reemission of plasmons, the modified plasmon energies may introduce novel effects.[17]

III. TECHNICAL DETAILS

The (111) surface is represented by a supercell containing eight, ten, or twelve atoms periodically extended in the lateral direction and a vacuum region corresponding to four or six layers of missing atoms. A 1×1 surface periodicity is assumed in keeping with the observed low-

energy electron-diffraction (LEED) pattern. The outermost layer of atoms on each side of the slab is As in a substitutional position. The resulting unit cell has an inversion center in each case. The final results are largely independent of the thickness of the slab or the vacuum region in the present case. The one exception to this is the splitting of the occupied surface resonances near $\bar{\Gamma}$. As usual, the surface states occur in pairs (one for each surface on the two sides of the slab) which are split by their interaction through the bulk region of the slab. (Splitting due to interaction across the vacuum region is quite small.) At $\bar{\Gamma}$ this splitting is relatively large because of the slow decay of surface resonances into the bulk region. Means for handling this problem are discussed below. In order to minimize this difficulty, the final results reported were calculated with 12-atom unit cells and a vacuum region equivalent to four atomic layers.

The calculations were performed using the *ab initio* pseudopotential approach.[18] The pseudopotentials used for Ge and As include scalar-relativistic effects.[19] The position of the As layer at the surface was relaxed using standard local-density-functional energy-minimization techniques[1,20] with the wave functions in the Kohn-Sham equations expanded in a plane-wave basis.[21] The relaxed position of the As atoms is relatively insensitive to the number of plane waves used in the expansion as well as the number of $\mathbf{k}$ points in the Brillouin summations. However, the final placement of the surface states is more sensitive. In particular, the empty surfaces states found in the gap near $\bar{\Gamma}$ on the Ge(111):As surface were difficult to converge. This reflects the basis-set–convergence difficulties associated with the $\Gamma_{2'c}$ state in bulk Ge. In the LDA band structure this state is the conduction-band edge in the projected bulk band structure. As a function of plane-wave cutoff, it drops precipitously, squeezing the empty surface band down ahead of it. For this reason, large cutoffs have been necessary in the final LDA band calculations reported. We have used plane waves up to a maximum kinetic energy of 10 and 11 Ry for the Ge and Si surfaces, respectively. In the Si case all surface energies are well converged within about 0.1 eV. For the Ge case most energies are similarly converged, although the uncertainty for the empty $\bar{\Gamma}$ surface state just discussed is about 0.2 eV.

The surface states of interest in the present calculation are the occupied As lone-pair (p_z) states (resonances) and the empty states split off the continuum near $\bar{\Gamma}$. The occupied surface states (resonances) can be clearly identified by their weight in the region outside the As atom. The empty states are similarly identified. However, the empty resonances near the zone edges reported below are not very strong and their surface character is less clear. Through most of the Brillouin zone the splitting due to surface-surface interaction through the bulk region is relatively small. This splitting is eliminated by taking a simple average. However, near the zone center the occupied surface resonances are strongly split, reflecting the slow decay of these states into the bulk. This indicates a large overlap between the surface states on opposite faces and a simple average is no longer appropriate (as this assumes near-zero overlap). A simple model (see the Appendix) is

used to estimate the overlap and extract the decoupled position of the surface resonance.

Placement of the surface states relative to the bulk projected band structure is important for comparison to experiment. Identifying the bulk valence-band edge with the energy of the highest occupied bulklike state in the slab is not adequate. There are simply not enough bulklike states in a 12-layer slab. One can envision two ways to get around this problem. First, the major peaks in the occupied density of states should be reproduced by the slab calculation. Therefore, the s-p peak, for example, can be aligned between the bulk density of states and the slab density of states. This places the bulk valence-band edge on the energy scale of the slab calculation. Second, the local potential near the center of the slab should conform to the local potential in the bulk semiconductor except for an overall shift. Therefore, the valence-band edge in the bulk relative to the average potential can be aligned to the average potential in the central region of the slab. These two methods yield the same result for Ge(111):As within less than 0.1 eV. For simplicity, we employ the average potential approach throughout. It should be noted that in the present cases the energy of the highest occupied bulklike states in the slab calculation deviates from the valence-band edge determined from the average potential by as much as 0.2–0.3 eV.

In the self-energy calculations several numerical cutoffs enter. Because of the magnitude of the surface problem, these must be reduced from the values used in bulk Si and Ge which assured full convergence. In reducing the cutoffs, it is essential to verify that the calculated gaps and band dispersions are only minimally affected.

The dielectric matrices employed were cut off at $|q+G| \leq 2.1$ a.u., yielding matrices of order 400×400 for each q. In the calculation of $\epsilon_{GG'}^{-1}(q; \omega=0)$, LDA bands were used with plane waves up to a kinetic energy of 7 Ry. The sum over empty states included about 600 bands. Dielectric matrices were generated for q evenly spaced in the surface Brillouin zone and including $q=0$. Sets of four and seven points in the irreducible wedge were used. The latter includes $\bar{\Gamma}$, $\bar{M}$, and $\bar{K}$ as well as intermediate q corresponding to division of $\bar{\Gamma}$-$\bar{M}$ into thirds. This sampling of q in the surface Brillouin zone for the q summation required for Σ yields quasiparticle energies converged to better than 0.1 eV. In the calculation of Σ, the sum over empty states includes about 200 bands. This includes empty states within about 45 eV of the bottom of the valence band. The wave functions and spectrum were taken from well-converged LDA calculations (cutoffs of 10 and 11 Ry for Ge and Si, respectively). Also, the spectrum in the Green's function was not updated in these calculations. The effect of this is quite small for the occupied surface-state energies and is about 0.1 eV for the empty surface-state energies. Finally, the effect of the self-energy on the bulk valence-band edge must be taken into account. This was done by shifting the calculated LDA valence-band edge by $E^{qP}-\epsilon^{LDA}$ calculated in the bulk using precisely the same cutoffs. In particular, the sum over empty states was cut off in energy (instead of band index) to assure that the bulk calculation completely mirrored the slab calculation.

Equation (1) is not solved directly for E^{qP}. Instead, the first-order corrections

$$\Delta_{n\mathbf{k}} = \langle n\mathbf{k} \mid \Sigma(E^{qP}) - V_{xc} \mid n\mathbf{k} \rangle \tag{7}$$

are calculated. The quasiparticle energies follow when the $\Delta_{n\mathbf{k}}$ are combined with the LDA bands. The second-order corrections have been checked and are found to change the results by a few hundredths of an eV in the worst case. For bulk materials[3] the LDA wave functions were found to be an excellent approximation to the solutions of Eq. (1). Evidently, a similar situation holds in the present case.[22]

The reduced cutoffs were tested by performing self-energy calculations for bulk Si and Ge. The results for the near-band-edge states (of primary concern here) are shown in Table I. The difference $E^{qP}-\epsilon^{LDA}$ is displayed in comparison to fully converged results obtained previously. Values relative to the valence-band edge are shown. These enter the quasiparticle band dispersions and band gaps. For states within 2.0 eV of the gap region, the differences are less than 0.1 eV. (The X_{4v} state is about 3 eV below the valence-band edge.) This provides confidence that the present calculation will yield relative quasiparticle energies reliable to about 0.1 eV.

IV. RESULTS FOR Si(111):As AND Ge(111):As SURFACES

The minimum-energy geometry for the surface atoms is presented in Sec. IV A. Results for the quasiparticle energies are given in Sec. IV B and compared to available experimental data. In Sec. IV C the quasiparticle energies are compared to the LDA energies and implications for other semiconductor surfaces are discussed.

A. Relaxed As position

The first step in determining the surface-state energies is to establish the positions of the atoms near the surface. For the present case we have used total-energy–minimization techniques relying on the local-density-functional approach.[1] Just as in the previous work for these surfaces,[7,9] the surface periodicity is as-

TABLE I. The accuracy of the self-energy corrections to the LDA eigenvalues for the surface calculation performed with reduced cutoffs is assessed. The correction relative to that of the valence-band edge is compared to fully converged results for bulk Si and Ge.

$E^{qP}-\epsilon_{LDA}$	Si		Ge	
	Reduced	Full	Reduced	Full
$\Gamma_{25'v}$	0.00	0.00	0.00	0.00
Γ_{15c}	0.74	0.74	0.62	0.62
$\Gamma_{2'c}$	0.90	0.76	0.89	0.71
X_{4v}	−0.22	−0.08	−0.20	−0.06
X_{1c}	0.59	0.72	0.47	0.55
$L_{3'v}$	−0.10	−0.06	−0.09	−0.03
L_{1c}	0.72	0.67	0.64	0.61
L_{3c}	0.78	0.76	0.62	0.63

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sumed to be 1×1 and the position of the As atom above the perfectly terminated Si(111) or Ge(111) surface is considered. The substitutional geometry is assumed. Then the energy as a function of position is calculated. These results are summarized in Fig. 1. The relaxation energy per two surfaces (slab unit cell) is plotted as a function of the relaxation of the position of the As atom from the ideal termination of the (111) surface. The minimum energy occurs for about 20% outward relaxation.

The present results are in good agreement with the previous calculation of the equilibrium position. For the Ge case, Bringans et al.[7] report 0.20 Å outward relaxation, while we find 0.17 Å. For the Si case, Uhrberg et al.[9] give 0.19 Å outward relaxation in comparison to 0.16 Å in the present calculation. These values agree within the established precision of the present technique. Furthermore, the position of the As atom on the Si surface has been determined by x-ray standing-wave techniques.[10] The result is 0.17±0.03 Å outward relaxation, in excellent agreement with the theoretical values. In addition, this technique unambiguosly confirms the substitutional geometry. The recent scanning tunneling images obtained for the Si(111):As surface clearly show the 1×1 periodicity of this surface.[11]

B. Quasiparticle surface-state energies

The results of the quasiparticle calculation are summarized in Figs. 2 and 3. The calculated quasiparticle surface-state (resonance) energies are plotted along symmetry lines in the surface Brillouin zone for Ge(111):As and Si(111):As. The projected bulk quasiparticle bands are shown as the shaded region. The dashed lines are the corresponding LDA surface-state (resonance) energies. The k points for which the quasiparticle energies are actually calculated are indicated by the solid dots. The solid line is an interpolation.

The overall features are quite similar for the Ge and Si cases. The character of the states has been mentioned previously: the occupied surface states (resonances) are the As lone-pair state, while the empty surface states derive their character from the bulk band-edge states. The lone-pair state is resonant through much of the Brillouin zone, being outside the bulk-projected bands only near the zone edge (especially near $\overline{K}$). These states have been illustrated in Ref. 7 and are discussed further below. The empty surface resonances near the zone edge are quite weakly localized at the surface and their identification as surface features is somewhat ambiguous. However, the empty surface state in the gap near $\overline{\Gamma}$ (in the projected gap for the Si case) is strongly localized at the surface.

There are detailed angle-resolved photoemission results for these surfaces.[7,9] The results of the present quasiparticle calculations are compared to experiment in Figs. 4 and 5. There is excellent agreement both in the dispersion and the placement of the lone-pair band with respect to the photoemission data. The data at the symmetry points is summarized in Table II. One can see that the
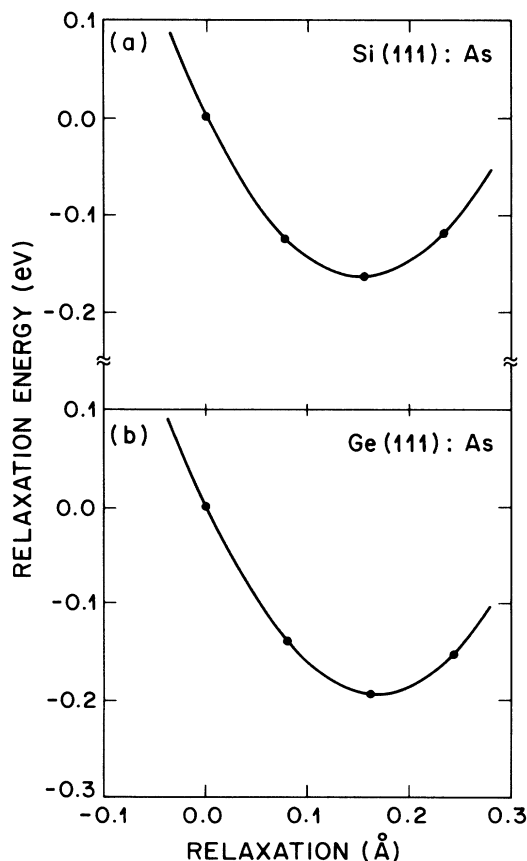

FIG. 1. Relaxation energy per two surface atoms plotted as a function of the relaxation of the As atom from the ideal termination of the (111) surface in the case of (a) Si and (b) Ge.
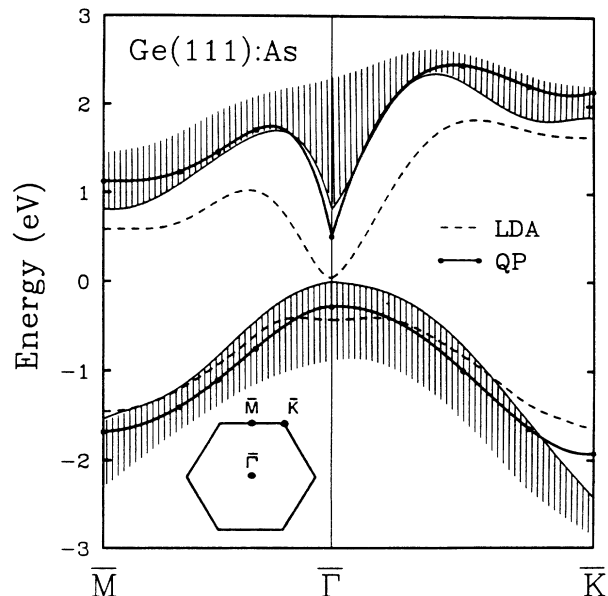

FIG. 2. For the As-capped Ge(111) surface, the calculated quasiparticle surface bands along the indicated directions in the surface Brillouin zone are plotted against the bulk-projected bands. For comparison, the LDA surface band energies are also shown (dashed lines).
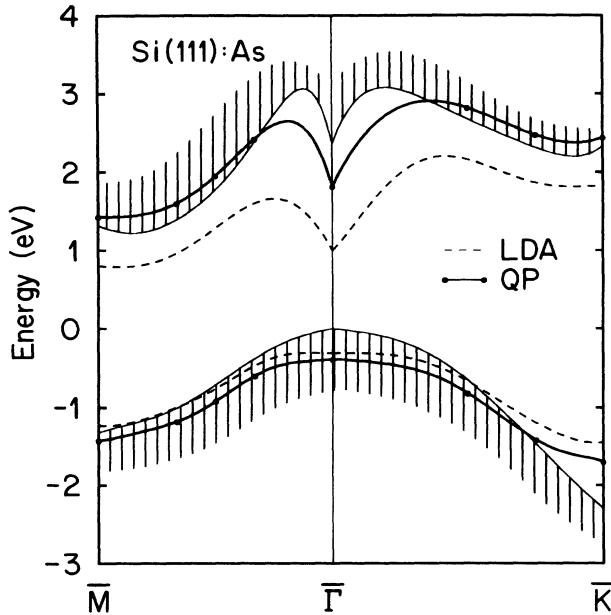
FIG. 3. Same as Fig. 2 for the As-capped Si(111) surface.

FIG. 5. Same as Fig. 4 for the As-capped Si(111) surface in comparison to the photoemission data from Ref. 9.

LDA energies for the lone-pair band exhibit significant discrepancies with experiment. However, the results of the present self-energy calculation agree with the photoemission data to within about 0.1 eV in the overall placement and rather better for the dispersion.

The position of the empty surface states in Figs. 2 and 3 are predictions. The present theory gives quantitatively reliable band gaps and dispersions. These states may well be observable in either angle-resolved inverse-photoemission or scanning tunneling spectroscopy measurements. The obvious difficulty is associated with the rather low density of states in the surface band near $\overline{\Gamma}$. The bands disperse upwards, sharply following the edge of the bulk-projected bands. Dipole matrix elements have been calculated in the slab geometry. Transitions

between the occupied and empty surface states at $\overline{\Gamma}$ are dipole allowed for p polarization of the light. Thus, the onset of surface-derived absorption may be observable for these surfaces starting at energies indicated in Figs. 2 and 3. The differential reflectivity for the Si(111)-(2×1) surface shows broad features above bulk band edge which are interpreted in terms of surface band transitions.[23] Such surface transitions might also be seen in electron-energy-loss spectroscopy.[24]

Quite recently, the Si(111):As surface has been studied with the scanning tunneling microscope.[11] The normalized differential conductivity measurements definitely show a large surface gap of 1.9–2.2 eV. Generally, these measurements exhibit features associated with the surface density of states near the $\overline{\Gamma}$ point. Therefore the measured gap should be compared to the calculated surface-state gap between the empty surface states and the As lone-pair resonance near Γ. The theoretical result of 2.2
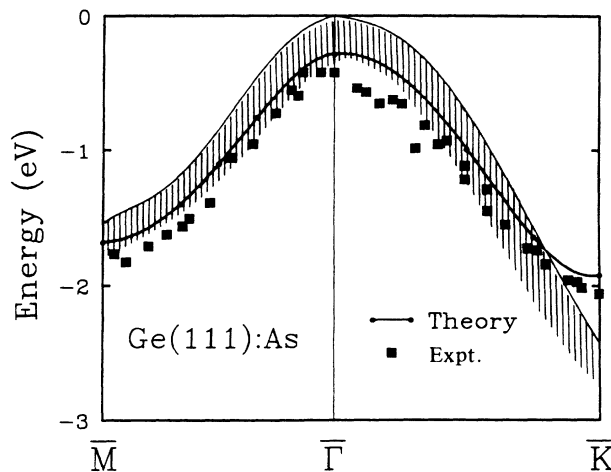

FIG. 4. For the As-capped Ge(111) surface, the calculated occupied surface band is compared to the photoemission results from Ref. 7. Both are plotted against the bulk-projected bands.
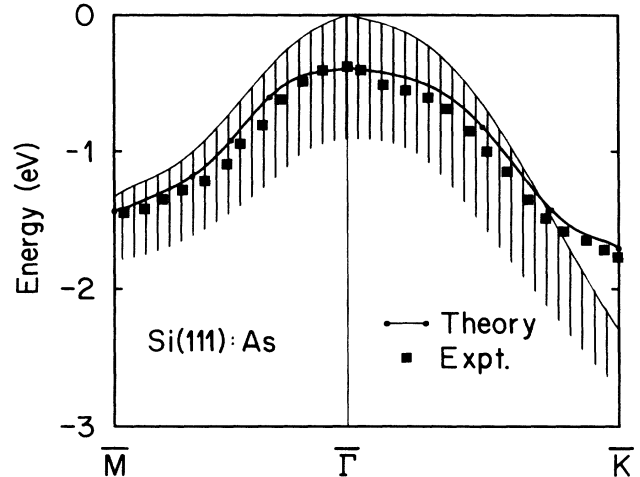
TABLE II. The results of the present quasiparticle calculation (qp) for the occupied surface band energies at symmetry points in the surface Brillouin zone are compared to the LDA eigenvalues and the angle-resolved photoemission data. The overall dispersion of the surface band is also compared.

	LDA	qp	Expt.[a]
	Si		
$\overline{\Gamma}$	−0.31	−0.39	−0.39
$\overline{M}$	−1.23	−1.44	−1.44
$\overline{K}$	−1.45	−1.71	−1.75
$\overline{\Gamma} \rightarrow \overline{K}$	1.14	1.31	1.36
	Ge		
$\overline{\Gamma}$	−0.43	−0.28	−0.44
$\overline{M}$	−1.45	−1.68	−1.81
$\overline{K}$	−1.61	−1.92	−2.06
$\overline{\Gamma} \rightarrow \overline{K}$	1.18	1.64	1.62

[a]Si results from Ref. 9; Ge results from Ref. 7.

eV for the Si(111):As surface is in excellent agreement with the measurement.

C. Comparison to LDA

In Sec. I we pointed out that the common interpretation of the LDA surface band energies as quasiparticle energies has three systematic difficulties: (i) surface-state gaps are too small, (ii) occupied surface states are placed too high relative to the bulk valence-band edge, and (iii) the surface band dispersion may be too small. The present theory addresses each of them. Comparing the LDA energies to the quasiparticle bands in Figs. 2 and 3 shows that the quasiparticle surface bands have a substantially larger gap. This illustrates that the self-energy approach leads to larger surface-state gaps just as it gives larger bulk gaps. The question of how this difference might scale in different cases is discussed below. Referring to Figs. 2 and 3, the quasiparticle long-pair band is broader than the LDA band. The dispersion of the surface states (resonances) is in considerably better agreement with experiment.

The other difficulty does not play a large role for the surfaces studied. The LDA occupied surface band is already approximately in the correct position relative to the bulk valence-band edge (at least near $\bar{\Gamma}$). The general problem may depend on two factors in the one-particle part of the band problem which are cleanly treated here. First, the present calculation is quite well converged with respect to the basis set. As the number of plane waves included was increased, the surface band has tended to drop lower relative to the bulk valence-band edge. Second, considerable care was taken to properly place the true bulk valence-band edge on the energy scale of the slab calculation. Due to the small number of bulklike layers in the slab calculation, relying on the highest occupied bulklike state in the slab structure to represent the valence-band edge introduces noticeable errors. For the present surfaces the discrepancy is about 0.2–0.3 eV. We feel the potential alignment method used here (Sec. III) is soundly based. It also leads to the occupied surface states being lower with reference to the bulk valence-band edge for the present surfaces.

Having emphasized the one-electron aspect of the placement problem, we point out that the many-body corrections may be important for other surfaces. In particular, this may be true for surface states that are closer to midgap, where the character of the states may no longer be strongly derived from the occupied bulk bands. An important example of this case would be the Si(111)-(2×1) surface where the π-bonded chain model[25] leads to both empty and occupied surface bands near midgap. This issue is amplified below.

There appears to be anomalous dispersion associated with the LDA lone-pair band (occupied resonances) near $\bar{\Gamma}$ for the Ge case (Fig. 2). This may be partly associated with the strong resonant character of these states and the corresponding coupling of the two surfaces through the slab in the present calculation. However, we point out that the quasiparticle calculation appears to correct this situation. Further note that the empty surface state as calculated in the LDA is quite close to the valence-band edge. This is due to the fact that the direct gap in a bulk LDA calculation is quite close to zero. Thus the empty surface state is "pinched" down between the bulk bands and tends to couple to the occupied resonance. This then drives the lone-pair states down in energy near the $\bar{\Gamma}$ point. As the gap problem is relieved in the quasiparticle calculation, this coupling is less.

It turns out that the magnitude of the self-energy for the surface states is quite distinct from that for the bulk like states. This is illustrated in Table III for near-gap states at $\bar{\Gamma}$ for Si(111):As. The quasiparticle energies relative to the bulk valence-band edge are shown together with the matrix elements of the LDA potential and the self-energy operator. The self-energy for the occupied surface resonance at $\bar{\Gamma}$ is more than 0.6 eV smaller in magnitude than the self-energy for a nearby bulklike state. A similar effect pertains, with opposite sign, for the empty surface state. It is interesting to note that much of this effect is reproduced by the LDA potential. In that case, the magnitude of the potential is decreasing with the charge density through the surface region and into the vacuum region. The surface states have more weight there and hence the reduction. For the nonlocal self-energy operator the situation is more complex. The intermediate states may be either surface or bulk derived. This is illustrated by the matrix element of the bare-exchange operator:

$$\langle n\mathbf{k}\,|\,\Sigma_X(\mathbf{r},\mathbf{r}')\,|\,n\mathbf{k}\rangle = -\sum_{n_1}^{\text{occ}}\sum_{q,\mathbf{G}}\langle n\mathbf{k}\,|\,e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}\,|\,n_1\mathbf{k}-\mathbf{q}\rangle\langle n_1\mathbf{k}-\mathbf{q}\,|\,e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}'}\,|\,n\mathbf{k}\rangle v(\mathbf{q}+\mathbf{G})\,, \tag{8}$$

where $v(\mathbf{q})$ is the usual Coulomb kernel. The sum over intermediate states (n_1) includes both bulk- and surface-derived states in the slab. One can imagine dividing these contributions so that the self-energy derives from exchange with states from the bulk manifold and the surface manifold. For surface states one would expect the surface-surface exchange to be more important and the surface-bulk exchange to be less so.

In order to probe this more quantitatively, we have partitioned the slab into bulk and surface (vacuum) regions. Rather than arbitrarily assigning bulk or surface character, the self-energy has been divided into two pieces according to the weight of the intermediate state in the surface region:

$$w_{n_1\mathbf{k}-\mathbf{q}} = \frac{1}{\Omega_c}\int_{z_1}^{z_2}dz\int\int dx\,dy\,|\,\psi_{n_1\mathbf{k}-\mathbf{q}}(\mathbf{r})\,|^2\,. \tag{9}$$

Here, Ω_c is the slab unit-cell volume to which all wave

TABLE III. For the Si(111):As case the magnitudes of the matrix elements of Σ and V_{xc} are compared for bulk and surface states from the slab calculation with the indicated quasiparticle energy relative to the bulk valence-band edge. Occupied (occ) and empty (emp) states near the band edge at $\bar{\Gamma}$ are considered. The self-energy is evaluated at the corresponding LDA energy and hence does not include some of the renormalization that enters the final quasiparticle energy. The self-energies are further broken down into screened exchange (SX) and Coulomb-hole (COH) terms with contributions from the bulk region (Bulk) and surface-vacuum region (Surf.) of the slab as described in the text.

	E^{qp}	V_{xc}	Σ	Σ_{SX} Bulk	Surf.	Σ_{COH} Bulk	Surf.
			$\bar{\Gamma}$(occ)				
Bulk	−0.57	−11.08	−11.31	−3.61	−0.24	−6.75	−0.71
Surf.	−0.39	−10.47	−10.71	−3.09	−0.60	−5.67	−1.35
Bulk	−0.22	−11.16	−11.37	−3.64	−0.21	−6.83	−0.69
			$\bar{\Gamma}$(emp)				
Surf.	1.82	−10.53	−9.62	−1.66	−0.28	−6.37	−1.30
Bulk	2.48	−10.14	−9.38	−1.73	−0.14	−6.80	−0.71

functions are normalized and z_1 to z_2 define the surface-plus-vacuum region of the slab. Here we have taken this to extend from one plane of As atoms through the vacuum to the other plane of As atoms, which is somewhat arbitrary. The sum in Eq. (8) is partitioned into two pieces, one weighted by $w_{n_1 \mathbf{k}-\mathbf{q}}$ and one weighted by $1 - w_{n_1 \mathbf{k}-\mathbf{q}}$. Clearly, these sum to give the same result as before. Also, the partitioning straightforwardly extends to the full dynamical self-energy operator [Eq. (34) in Ref. 3].

The results of this exercise are shown in Table III, broken down further according to $\Sigma = \Sigma_{SX} + \Sigma_{COH}$, the screened-exchange and Coulomb-hole contributions to Σ. The bare exchange is contained in Σ_{SX}. The general idea concerning the relative importance of surface-surface and surface-bulk exchange is supported. The surface states have an enhanced contribution from surface-surface exchange and a reduced contribution from surface-bulk exchange in comparison to the bulklike states (where it is bulk-surface and bulk-bulk exchange). These effects compensate for one another, leaving a small net reduction in the magnitude of Σ_{SX}. A somewhat larger effect is seen for Σ_{COH}. Here the changes also more strongly reflect the modified screening response near the surface region. In the static limit, Σ_{COH} reduces to a local potential which is the screening potential at $\mathbf{r}$ due to the added electron at $\mathbf{r}$. This behaves very much like the LDA potential in that it tends to follow the magnitude of the local density.[3] Examination of Table III shows that much of the reduction in the magnitude of Σ for occupied surface states comes from the Coulomb-hole term (treated dynamically here). Therefore it is somewhat less surprising that the general behavior of Σ is reproduced by V_{xc} in the LDA. The differences between Σ and V_{xc} are smaller and somewhat subtler.

The trends in the difference between LDA and quasiparticle energies through the calculations are illustrated in Fig. 6. Here the difference between the quasiparticle and LDA band energies are plotted as a function of energy for selected bands and $\mathbf{k}$ points in the surface Brillouin zone near the gap region.[26] Figure 6 can be loosely inter-

preted as the correction required to "fix" the LDA bands in the present surface systems. The first feature to note in Fig. 6 is that the bulklike states for both the Si and Ge cases approximately follow two smooth lines with a sharp jump at the gap. The bulk states reproduce the behavior observed in the full bulk calculations.[3] Secondly, the surface states in the Si(111):As case follow a similar trend. However, the correction to the occupied band dispersions (the correction as compared to that at the valence-band
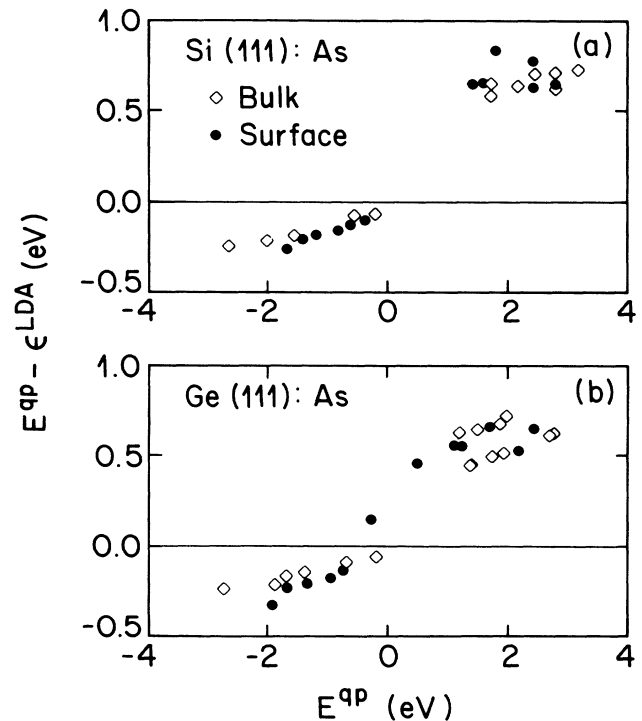

FIG. 6. Calculated difference between the quasiparticle energy (E^{qp}) and the LDA eigenvalue (ε^{LDA}) plotted as a function of energy for states near the gap region for the (a) As-capped Si(111) and (b) As-capped Ge(111) surfaces. Bulklike states and surface states (resonances) are distinguished.

edge) is distinct for the surface-derived states. This is a rather small effect here, but leads to more broadening of the surface bands in comparison to the bulk bands. The correction for the surface band gap is essentially the same as for the bulk in the Si case.

The Ge case exhibits two exceptional points in Fig. 6(b). Otherwise, the features are the same as for Si, with the occupied surface dispersions showing a distinct correction and a large increase in the surface band gap. The exceptional points tend to bridge over the jump between occupied and empty states. They correspond to the occupied and empty surface states at $\bar{\Gamma}$. For the occupied states, this distinctive placement shows that the self-energy calculation corrects for the anomalous dispersion in the LDA lone-pair band near $\bar{\Gamma}$. The empty states near midgap display a correction that is intermediate between bulk valence- and conduction-band states.

This interesting result can be qualitatively understood by examining the character of the states involved. In Fig. 7 the occupied and empty surface states at $\bar{\Gamma}$ are shown for the Si case (S_+ bonding combination in the slab[27]). From Fig. 6(a) there is nothing anomalous in the self-energy for these states, so they can serve as a reference. The occupied state is a p_z state near the As atom, but clearly extends well into the bulk as it is a resonance. The empty state has a combination of atomic s and p_z character deriving from the projected conduction-band edge (L_{1c} states). The state has weight directly above the subsurface Si and directly below the As at the surface. Figure 8 shows the same states for the Ge surface. With reference to Fig. 7, these states are of mixed character, having features from both the lone-pair state and the antibonding backbond state. Alternatively, these states result from strong coupling between states of that character. We believe it is precisely the mixed character exhibited in Fig. 8 which leads to the anomalous corrections in Fig. 6(b). If a state derives character both from bulk valence- and conduction-band states, then the correction to the LDA energies should be intermediate in magnitude.

It was not *a priori* clear that this would be the case. That the character of the surface wave function should
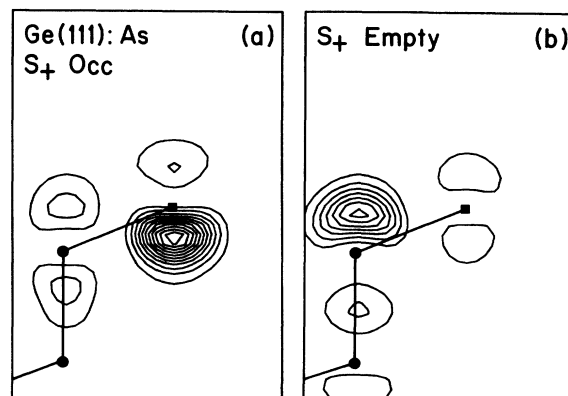
FIG. 8. Same as Fig. 7 for the As-capped Ge(111) surface.

determine the correction to the LDA surface band energies is certainly an appealing result. It suggests that the crucial change in the self-energy operator at the surface may be largely contained in the Green's function. The screened Coulomb interaction may more closely follow the variation in the local density at the surface. However, this is certainly not a rigorous conclusion. It will require further examples in order to substantiate it as well as a critical evaluation of the slab approach for the surface self-energy operator. It also does not follow that the same result will hold in other situations, e.g., point defects. In that context, the "scissors operator" has been used to correct the LDA bands for use in the Green's function and for evaluating defect levels.[28] There, the correction is based on the relative weight of bulk conduction- and valence-band character in a particular state. This is similar to our observation in the Ge(111):As case. However, the correct treatment of the self-energy for the defect case remains to be done.

This raises the issue of whether LDA calculations for surface-state energies can be simply corrected in a reliable way. In the bulk case the plots analogous to Fig. 6 are dominated by a large jump at the gap region. This is consistent with the formal result that there is correction Δ which must be added to the *exact* gap in the Kohn-Sham spectrum in a semiconductor or insulator in order to obtain the correct minimum gap.[29] In the bulk case the necessary correction required to obtain quasiparticle energies away from the gap is more complex.[3] *A priori*, there is no reason to expect the correction required for surface-state gaps to be the same as the bulk. In particular, Δ might be rather different. The results for Ge(111):As illustrate this point. The region of Fig. 6(b) which would exhibit a jump in the bulk case is bridged by the midgap states.

Since the bulk correction cannot be carried over to the surface states, one may ask whether the correction may be obtained by some reasonable scaling. On this point, our results can only be suggestive. We observe a qualitative dependence on the character of the surface states involved. The qualitative picture can be supported indirectly. Surface states which fall near midgap may be expected to have both valence- and conduction-band character on general grounds.[30] An example of this cited
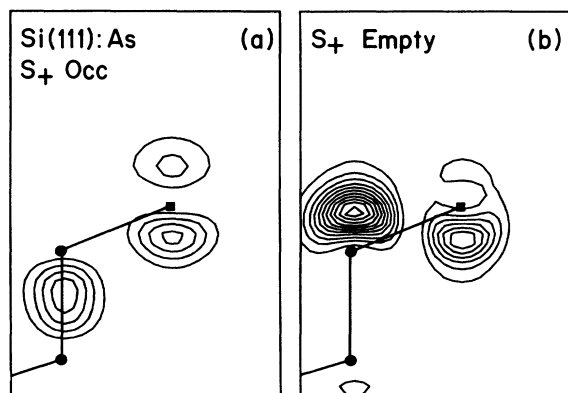

FIG. 7. Density $|\psi(\mathbf{r})|^2$ associated with the even occupied and empty surface states (resonances) at $\bar{\Gamma}$ drawn for the As-capped Si(111) surface.

above is Si(111)-(2×1) for which the π bonded chain model[25] seems to be the correct reconstruction.[31] This surface exhibits a "band-gap problem" as discussed previously.[2] The measured surface gap[32] of 0.45 eV is about twice as large as the calculated LDA gap.[1] The required correction is therefore considerably smaller than the 0.7 eV found for bulk Si.[3] However, the dependence of the correction on the character of the states explains this qualitatively. The surface gap will open less than the bulk gap since the relevant states are of mixed character. The correction will fall in an interpolation region in Fig. 6(b).

At present our results suggests that a self-energy calculation is required to get the correct surface gap for a given case. The bulk correction does not carry over simply to the surface. It may be possible with further data to support a relatively simple scaling rule for correcting LDA surface states based on bulk data and a scheme for projecting bulk conduction- and valence-band character of the surface states.

V. SUMMARY

We have developed a first-principles theory for the surface quasiparticle energies in semiconductor surfaces. In the investigation of physical properties of surfaces, this is a natural complement to the total-energy–minimization techniques based on the local-density-functional approach. The total-energy approach can be used to find the atomic configuration at the surface with the lowest total energy. With the atomic positions thus determined, the present theory may be applied to derive the energies, dispersions, and gaps associated with the electronic states localized at the surface. This allows the results of first-principles calculations to be directly compared to measurements based on the various spectroscopic surface probes. Because this unified approach provides quantitatively reliable information on the surface electronic structure, it should prove to be a powerful technique.

We have applied this program to the interesting test cases of the As-capped Si(111) and Ge(111) surfaces. These have been shown to be geometrically simple and have been well characterized both structurally and electronically. The total-energy calculation yields the position of the As atoms at the surface, in good agreement with the results of x-ray standing-wave measurements. The self-energy approach for the electronic structure gives the As lone-pair surface band in excellent agreement with angle-resolved photoemission data. The position of an empty surface state is predicted for both surfaces. The recently measured surface gap on the Si(111):As surface agrees quite well with the present calculation. The present results do not yield a simple prescription for correcting LDA surface band energies. Further work is required in this area.

Extension of the self-energy approach to the surface case involves heavy computations. The geometric simplicity of the present surfaces (1×1 surface periodicity) has certainly been helpful. Application to surfaces with more atoms in the surface unit cell would be more demanding. However, the present results have already provided some insight for other semiconductor surfaces.

APPENDIX: MODEL FOR DECOUPLED SURFACE-RESONANCE ENERGIES

When using the slab geometry to represent a surface, one always has two surfaces and therefore a doublet in energy for each surface state. In the limit of a very thick slab, these would be degenerate and equal to the surface-state energy. In practice, the finite thickness of the slab used means that there is always some coupling which derives from the slight overlap of the surface states on the two sides of the slab. These form bonding and antibonding combinations and the associated doublet is split. If the coupling is relatively small, the decoupled surface-state energy can be taken to be the simple average over the doublet. However, for surface resonances, especially near $\bar{\Gamma}$ in the surface Brillouin zone, the states may extend well into the bulk region, leading to significant overlap and a relatively large splitting of the doublet. This is the case in the present calculation for the occupied lone-pair resonance near $\bar{\Gamma}$. In order to place more accurately the decoupled surface-resonance energy, we use a simple model to estimate the overlap matrix.

We use a simple 2×2 model with E_0 being the decoupled surface-state energy, V being the coupling, and S the overlap in the finite slab geometry. Then the energies of the split doublet are simply given by

$$E_{\pm} = (E_0 \pm V)/(1 \pm S) . \tag{A1}$$

Here, $E_{\pm}$ are the energies of the split doublet which are actually calculated in the slab band structure. Clearly, if S is not negligible, the decoupled surface-state energy can be significantly different than the simple average of E_+ and E_-. However, there are only two energies and three parameters to be determined. Here we use a simple model to extract S separately from the wave functions associated with $E_{\pm}$ in the slab calculation.

In this simple model the slab wave functions are linear combinations of the decoupled surface wave functions:

$$\psi_{\pm} = (\phi_1 \pm \phi_2)/(2 \pm 2S)^{1/2} . \tag{A2}$$

Here the slab wave functions are denoted by $\psi_{\pm}$ and ϕ_1

and ϕ_2 refer to the surface wave function on the left- and right-hand sides of the slab, respectively. The idea is to exploit the fact that ϕ_1 is largely localized on the left-hand side and similarly for ϕ_2 on the right. Split the slab into two halves, left (R_1) and right (R_2). Then integrate the product of the bonding and antibonding slab wave functions over half the slab:

$$I = \int_{R_1} \psi_+^* \psi_- = \frac{1}{2(1-S^2)^{1/2}} \left[\int_{R_1} |\phi_1|^2 - \int_{R_1} |\phi_2|^2 \right] .$$

(A3)

This follows since $\phi_{1,2}$ may be chosen with the same overall phase.

The result in (A3) is quite general at this point. In order to exploit it, a simple relation between the integrals in (A3) and S must be obtained. Here we use a simple model. The decoupled surface wave functions at large distance are modeled by simple Slater orbitals centered at opposite surfaces of the slab:

$$\phi_{1,2}(\mathbf{r}) = \left[\frac{\alpha^3}{\pi} \right]^{1/2} e^{-\alpha|\mathbf{r} \pm a\hat{z}|} ,$$

(A4)

where $2a$ is the thickness of the slab. With the simple cylindrical symmetry, the integrals appearing in Eq. (A3)

can be done analytically. The integral for S can be approximated using these model wave functions and one can show that roughly

$$1 - S \approx \int_{R_1} |\phi_1|^2 - \int_{R_1} |\phi_2|^2 .$$

(A5)

From this and Eq. (A3), it follows that

$$S \approx (1 - 4I^2)/(1 + 4I^2) .$$

(A6)

Thus from a simple integral over half the slab, the relevant overlap matrix is estimated. The only remaining point is to assign the bonding and antibonding wave functions to the proper elements of the doublet. This gives the sign of V and may be done by a cursory examination of the slab wave functions.

In application to the lone-pair resonance at $\bar{\Gamma}$ in the present calculation, we find $S \approx 0.63$ and 0.22 for the Ge and Si cases, respectively. This alters the position of the decoupled surface-resonance energy from that found by a simple average by 0.27 and 0.06 eV, respectively. In both cases the decoupled resonance energy lies higher than would be found for a simple average. Numerical evaluation of S in the present model yields somewhat smaller values for S, e.g., 0.4 in the Ge case, but this alters the surface-resonance energy by less than 0.1 eV.

[1]This is illustrated in S. G. Louie, in *Electronic Structure, Dynamics and Quantum Structural Properties of Condensed Matter,* edited by J. Devreese and P. van Camp (Plenum, New York, 1985), p. 335.

[2]Preliminary results for the Ge(111):As surface have appeared in M. S. Hybertsen and S. G. Louie, Phys. Rev. Lett. **58**, 1551 (1987).

[3]M. S. Hybertsen and S. G. Louie, Phys. Rev. Lett. **55**, 1418 (1985); Phys. Rev. B **34**, 5390 (1986).

[4]R. W. Godby, M. Schlüter, and L. J. Sham, Phys. Rev. Lett. **56**, 2415 (1986); Phys. Rev. B **35**, 4170 (1987), and unpublished.

[5]P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

[6]These data are scattered in the literature. For Si, in particular, see D. R. Hamann, Phys. Rev. Lett. **42**, 662 (1979). A broader discussion may be found in Ref. 1.

[7]For the Ge(111) surface, see R. D. Bringans, R. I. G. Uhrberg, R. Z. Bachrach, and J. E. Northrup, Phys. Rev. Lett. **55**, 533 (1985); R. D. Bringans, R. I. G. Uhrberg, and R. Z. Bachrach, and J. E. Northrup, J. Vac. Sci. Technol. A **4**, 1380 (1986); R. D. Bringans, R. I. G. Uhrberg, and R. Z. Bachrach, Phys. Rev. B **34**, 2373 (1986).

[8]For the Si(001) surface, see R. I. Uhrberg, R. D. Bringans, R. Z. Bachrach, and J. E. Northrup, Phys. Rev. Lett. **56**, 520 (1986); J. Vac. Sci. Technol. A **4**, 1259 (1986); R. D. Bringans, R. I. G. Uhrberg, M. A. Olmstead, and R. Z. Bachrach, Phys. Rev. B **34**, 7447 (1986).

[9]For the Si(111) surface, see M. A. Olmstead, R. D. Bringans, R. I. G. Uhrberg, and R. Z. Bachrach, Phys. Rev. B **34**, 6041 (1986); R. I. G. Uhrberg, R. D. Bringans, M. A. Olmstead, R. Z. Bachrach, and J. E. Northrup, *ibid.* **35**, 3945 (1987).

[10]J. R. Patel, J. A. Golovchenko, P. E. Freeland, and H.-J.

Grossmann, Phys. Rev. B **36**, 7715 (1987).

[11]R. S. Becker, B. S. Swartzentruber, J. S. Vickers, M. S. Hybertsen, and S. G. Louie Phys. Rev. Lett. **60**, 116 (1988).

[12]L. Hedin and S. Lundqvist, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1969), Vol. 23, p. 1.

[13]L. Hedin, Phys. Rev. **139**, A796 (1965).

[14]M. Schlüter, J. R. Chelikowsky, S. G. Louie, and M. L. Cohen, Phys. Rev. B **12**, 4200 (1975).

[15]M. S. Hybertsen and S. G. Louie, Phys. Rev. B **35**, 5585 (1987).

[16]M. S. Hybertsen and S. G. Louie, Phys. Rev. B **35**, 5602 (1987).

[17]Examination of the surface-plasmon modes in a semiclassical picture for the present repeated-slab geometry suggests that the energies disperse considerably as a function of q in the long-wavelength limit due to interaction through the slab and across the vacuum region. It is also somewhat unclear precisely what corresponds to the surface plasmons in the present generalized plasmon-pole model. Certainly, the corresponding spectral weight will be distinctly different in the bulk and surface regions.

[18]D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979). The algorithm used is from G. P. Kerker, J. Phys. C **13**, L189 (1980).

[19]G. B. Bachelet and M. Schlüter, Phys. Rev. B **25**, 2103 (1982).

[20]The correlation data used are from D. M. Ceperley and B. I. Alder, Phys. Rev. Lett. **45**, 566 (1980), as parametrized in J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[21]J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4409 (1979).

[22]One exception might be a case where a surface resonance in the LDA calculation was pushed into the projected gap by

the self-energy corrections. In that case, the wave function should be more localized at the surface, being no longer in resonance with the bulk states. This situation has not been encountered for the **k** points examined in the present systems.

[23]S. Selci, P. Chiaradia, F. Ciccacci, A. Cricenti, N. Sparvieri, and G. Chiarotti, Phys. Rev. B **31**, 4096 (1985); A. Selloni, P. Marsella, and R. Del Sole, *ibid.* **33**, 8885 (1986).

[24]In this way, transitions to the empty surface states on C(111)-(2×1) have been observed: S. V. Pepper, Surf. Sci. **123**, 47 (1982).

[25]K. C. Pandey, Phys. Rev. Lett. **47**, 1913 (1981).

[26]The difference $E^{qp}-\varepsilon^{LDA}$ is plotted relative to the value at the valence-band edge. This eliminates the absolute value of this difference from consideration as it cannot be as well converged as the relative values due to the numerical cutoffs used in the surface calculation.

[27]The bonding and antibonding combinations arise due to cou-pling through the slab and are the wave functions directly available from the slab calculation. The bonding combination shown here shows the largest effect. The states plotted in Ref. 11 are a proper weighted average of the bonding and antibonding combinations.

[28]G. A. Baraff and M. Schlüter, in *Defects and Radiation Effects in Semiconductors, 1980,* edited by R. R. Hasigati (IOP, London, 1981), p. 287, and private communication.

[29]L. J. Sham and M. Schlüter, Phys. Rev. Lett. **51**, 1888 (1983).

[30]This is certainly true for a pure surface. One may imagine states (e.g., some adsorbate levels) near midgap which would not have a wave function of mixed character.

[31]For example, R. M. Tromp, L. Smit, and J. F. van der Veen, Phys. Rev. Lett. **51**, 1672 (1983).

[32]P. Chiaradia, A. Cricenti, S. Selci, and G. Chiarotti, Phys. Rev. Lett. **52**, 1145 (1984); M. A. Olmstead and N. M. Amer, *ibid.* **52**, 1148 (1984); Phys. Rev. B **29**, 7048 (1984).