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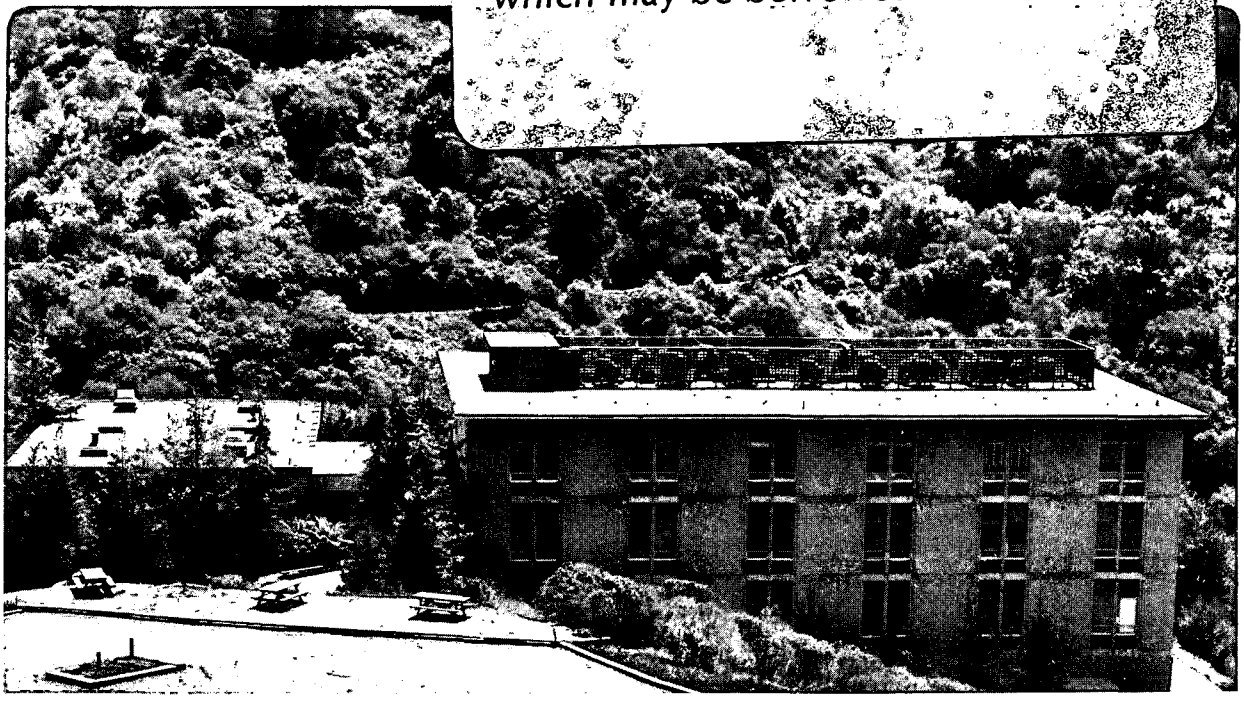

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ABSTRACT

A new approach for surface studies using the density functional formalism for structural determination and a first principles many-body theory for the quasiparticle surface state energies is discussed. The many-body calculation involves the evaluation of the electron self-energy operator including both local fields and dynamical screening effects. Results for the Ge(111):As and Si(111):As surface are in excellent agreement with recent angle-resolved photoemission data and show a substantially larger gap between the empty and occupied surface states in comparison to local density functional calculations.

1. INTRODUCTION

A full understanding of the properties of a surface requires knowledge of both it geometric and electronic structure. Thus it has been a long-sought goal to develop theoretical methods which are capable of predicting both the structure and the electronic excitation spectra of surfaces from first principles. For structural determination, local density functional (LDA) total energy calculations[1,2] have had considerable successes in the past few years. Unfortunately, the eigenvalues from the associated one-particle equations in these calculations are not interpretable as quasiparticle energies. Thus the calculated LDA spectra cannot be justifiably compared to excitation spectra measured in experiment. Because of lack of other alternatives, the LDA results nevertheless have been widely used to interpret spectroscopic data often leading to large discrepancies in the surface state energies.

In this paper, we show that the recently developed many-body theory for the quasiparticle energies and band gaps in bulk crystals[3] extends to the case of surfaces. This provides, for the first time, a procedure using the atomic coordinates given by total energy minimization calculations to predict the surface state energies allowing well founded comparison to spectroscopic measurements. The optical and photoemission spectra are properly interpreted as transitions between quasiparticle states of the many-electron system.

2. LOCAL DENSITY FUNCTIONAL CALCULATIONS

The successes of LDA calculations in determining the structure and related ground-state properties of solids and solid surfaces are by now well documented.[1,2] A good example of a surface calculation of this kind is a recent *ab initio* study of the structural properties of hydrogen chemisorption on the Pd(001) surface.[4] The calculation is carried out using *ab initio* pseudopotentials in a gaussian orbital basis with a repeat slab geometry. The preferential adsorption sites, bond lengths, and vibrational frequencies were determined with the atomic number and mass of Pd and H as the only input. Figure 1 illustrates the calculated adsorption bond energy E_{ad} as a function of the hydrogen distance h from the surface for three high symmetry adsorption sites. These results establish that at low coverage H occupies four-fold hollow sites. The calculated adsorption energy, equilibrium bond length, and vibrational frequencies are all in good agreement with available experimental data.[4]

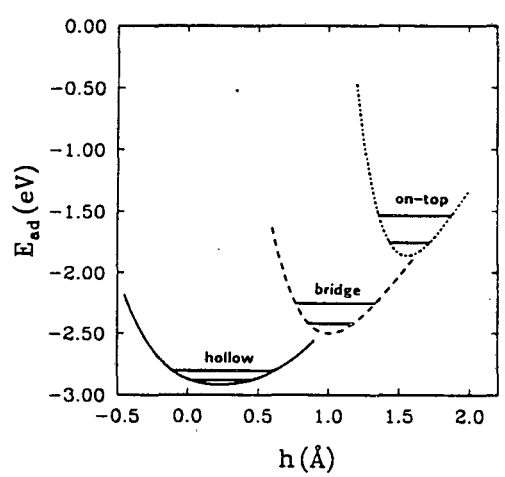

Fig. 1. H adsorption bond energy E_{ad} as a function of the adsorption height h above the Pd(001) surface for the fourfold hollow, bridge, and on-top sites. The lowest two vibrational levels are shown in the potential wells.

However, the density functional formalism, being a ground-state theory, does not in principle provide information on the electronic excitation spectra such as those measured in optical and photoemission experiments.[5] The band structure resulting from the LDA calculations has well known defects in comparison to these experiments, the most prominent being the underestimation of the minimum band gap in semiconductors and insulators by 30-100%, giving rise to the so-called "band-gap" problem. This is illustrated in Table I. Similarly large discrepancies in the band gaps and band widths have been observed for the metals.[8]

Table I. Comparison of calculated band gap E_g (in eV) with experiment. The results for Ge include relativistic effects.

	LDA	Present Theory	Expt.
Diamond	3.9	5.6	5.48[a]
Silicon	0.52	1.29	1.17[a]
Germanium	<0	0.75	0.744[a]
LiCl	6.0	9.1	9.4[b]

[a]Ref. 6 [b]Ref. 7

The difficulties associated with the LDA band energies extend to the interpretation of surface states and resonances.[2] For semiconductor surfaces, there are three areas of systematic disagreement for the surface state bands: (1) the dispersion is qualitatively reasonable for the minimum energy structure but the placement relative to the bulk valence band maximum differs from experiment by a nearly rigid shift which can be as large as one eV; (2) the calculated dispersion of the surface states is too small in some cases; and (3) the LDA gap between the empty and occupied surface states is quite often dramatically underestimated. This is analogous to the band-gap problem in the bulk case.

3. QUASIPARTICLE THEORY OF EXCITATION SPECTRA

The energy and wavefunction of the quasiparticles, the particle-like excitations in an interacting many-electron system, are given by [9]

$$(T + V_{ext} + V_H)\psi_{n\mathbf{k}}(\mathbf{r}) + \int d\mathbf{r}'\, \Sigma(\mathbf{r},\mathbf{r}';E_{n\mathbf{k}})\psi_{n\mathbf{k}}(\mathbf{r}') = E_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r}) \,. \quad (1)$$

Here, T is the kinetic energy operator, V_{ext} is the external potential due to the ions, V_H is the Hartree potential, and the exchange-correlation contributions are

included in the self-energy operator Σ which, in general, is non-local, energy-dependent, and non-Hermitian, with the imaginary part giving the lifetime of the quasiparticles. Our approach is based on a first order expansion[9] for the self-energy operator (the GW approximation):

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

where δ is a positive infitesimal. The required inputs to evaluate Σ are the full interacting Green's function for which we use a quasiparticle approximation,

$$G(\mathbf{r},\mathbf{r}';E) \;=\; \sum_{n\mathbf{k}} \frac{\psi_{n\mathbf{k}}(\mathbf{r})\psi^*_{n\mathbf{k}}(\mathbf{r}')}{E - E_{n\mathbf{k}} - i\delta_{n\mathbf{k}}}\ , \tag{3}$$

and the dynamically screened Coulomb interaction,

$$W(\mathbf{r},\mathbf{r}';\omega) \;=\; \Omega^{-1}\int d\mathbf{r}''\epsilon^{-1}(\mathbf{r},\mathbf{r}'';\omega)V_C(\mathbf{r}''-\mathbf{r})\ , \tag{4}$$

where ϵ is the time-ordered dielectric matrix whose off-diagonal elements in Fourier space describe the local fields (variations in the screening through the unit cell) and V_C is the bare Coulomb interaction. We note that the self-energy operator must be obtained with G in a self-consistent fashion.

In the calculations, the electron Green's function is constructed initially with the use of the LDA eigenfunctions and eigenvalues and is subsequently updated with the quasiparticle spectrum from Eq. (1). The static dielectric matrix $\epsilon(\mathbf{r},\mathbf{r}';\omega = 0)$ is obtained as a ground-state property from the LDA calculation and extended to finite frequency using a generalized plasmon pole model.[3]

Successful application of the present theory has been made to the quasiparticle band structure of the semiconductors, ionic insulators, and alkali metals.[3,10] In all cases, the theoretical results are in excellent agreement with available optical, photoemission, and inverse photoemission data. Table I presents the calculated minimum gap for four materials together with the experimental values. The gaps open up quite dramatically as compared to the LDA values. Local field effects in

the screening play an important role in this result. This screening deepens the Coulomb-hole contribution to the electron self-energy for states with wavefunctions at regions of concentrated charge density, leading to a larger band gap for insulators.[3)]

4. Ge(111):As AND Si(111):As SURFACES

The Ge(111):As and Si(111):As surface are chosen as prototype systems for the many-body calculation[11)] because of their geometric simplicity and availability of detailed experimental data.[12,13)] At saturated coverage, the As atoms are found to substitute for the outermost layer surface atoms of the host. The resulting surface is chemically passive and stable against reconstruction, exhibiting a 1x1 surface periodicity.

The calculations are carried out using a repeated slab geometry with 12 layers of atoms. The structural relaxation of the As layer and the corresponding ground-state charge density are obtained from the LDA calculation using *ab initio* pseudopotentials. The equilibrium structure is determined to be an outward relaxation of the As layer by approximately 0.16 Å for both the Si(111) and Ge(111) surfaces. The value of 0.16 Å for the Si case is in good agreement with the value of 0.17 Å from recent X-ray standing wave measurements.[14)]

Once the structure is determined, the quasiparticle energies, including those associated with the surface states, are calculated using the theoretical method discussed in Sec. 3. The results are summarized in Figs. 2–4. In Fig. 2, the LDA surface states bands (dashed lines) together with the quasiparticle surface state bands

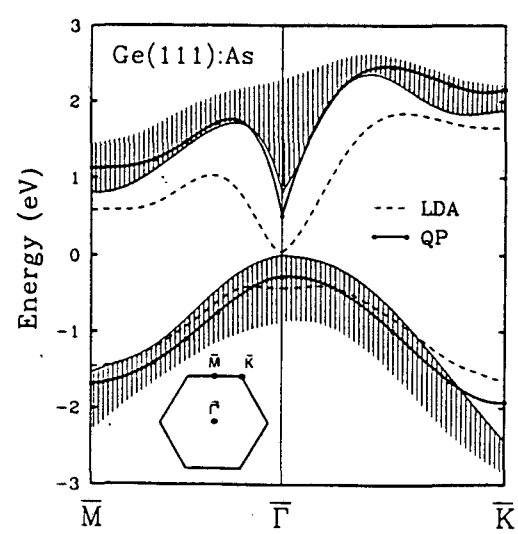

Fig. 2. LDA surface state energies compared to the quasiparticle surface state energies of Ge(111):As along symmetry directions indicated. The quasiparticle bulk projected band structure is shown.

(solid lines) are plotted against the projected quasiparticle band structure of Ge. As seen from the figure, there is a fully occupied surface band corresponding to the dangling bond (lone pair) states of the As adatoms. These states have been observed by angle-resolved photoemission experiments.[12,13] In addition to the lone pair states, we note that there is also an empty surface state band in the gap which corresponds to anti-bonding back bond states. These have not been observed experimentally. Very similar results are obtained for the Si(111):As system.

The primary effects of the many-body correction on the occupied states are to lower the band relative to the valence band maximum, broaden the band, and, in the case of the Ge(111) surface, correct the unusual dispersion near $\bar{\Gamma}$. All three are required for better agreement with experiment. The effect on the empty surface states is more dramatic. These states are substantially shifted upwards, opening the gap between empty and occupied surface states by nearly 1 eV at some k-points. The position of the empty surface states is thus a prediction of the present theory which is verifiable by experiment. Figures 3 and 4 compare the calculated quasiparticle surface state bands with angle-resolved photoemission data. For both systems, the agreement is excellent and well within the estimated errors with experiment (±0.1 eV) and theory (±0.1 eV).

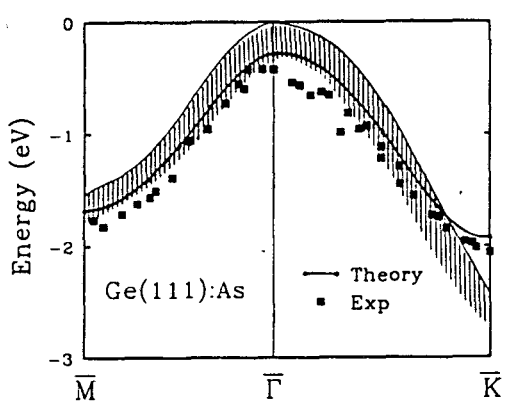

Fig. 3. Calculated occupied quasiparticle surface state energies for Ge(111):As compared to data from angle-resolved photoemission (Ref. 12).

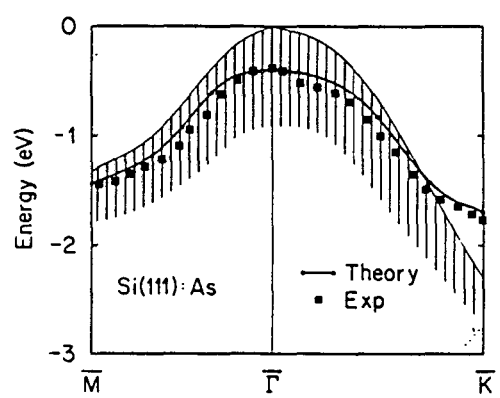

Fig. 4. Same as Fig. 3 except for Si(111):As. Experimental data are from Ref. 13.

Thus the many-body results here address the difficulties with the LDA surface bands described in Sec. 2. This should have implications for LDA calculation of surface bands on other semiconductor surfaces. In particular, the many-body approach yields a larger gap between empty and occupied surface states than that found in the LDA calculation. However, we note that it is not possible to deduce this difference from the known correction to the bulk gap. A survey of the experimental data shows that the errors in the surface state band gaps are, in general, smaller than those for the corresponding bulk gaps.

5. SUMMARY AND CONCLUSIONS

A first principles quasiparticle theory for calculating surface state energies is reviewed. Together with total-energy methods, this development allows, for the first time, *ab initio* calculation of surface state spectra which can be directly compared with spectroscopic measurements. For the prototype systems Ge(111):As and Si(111):As, the many-body results are found to be in excellent agreement with experiment.

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