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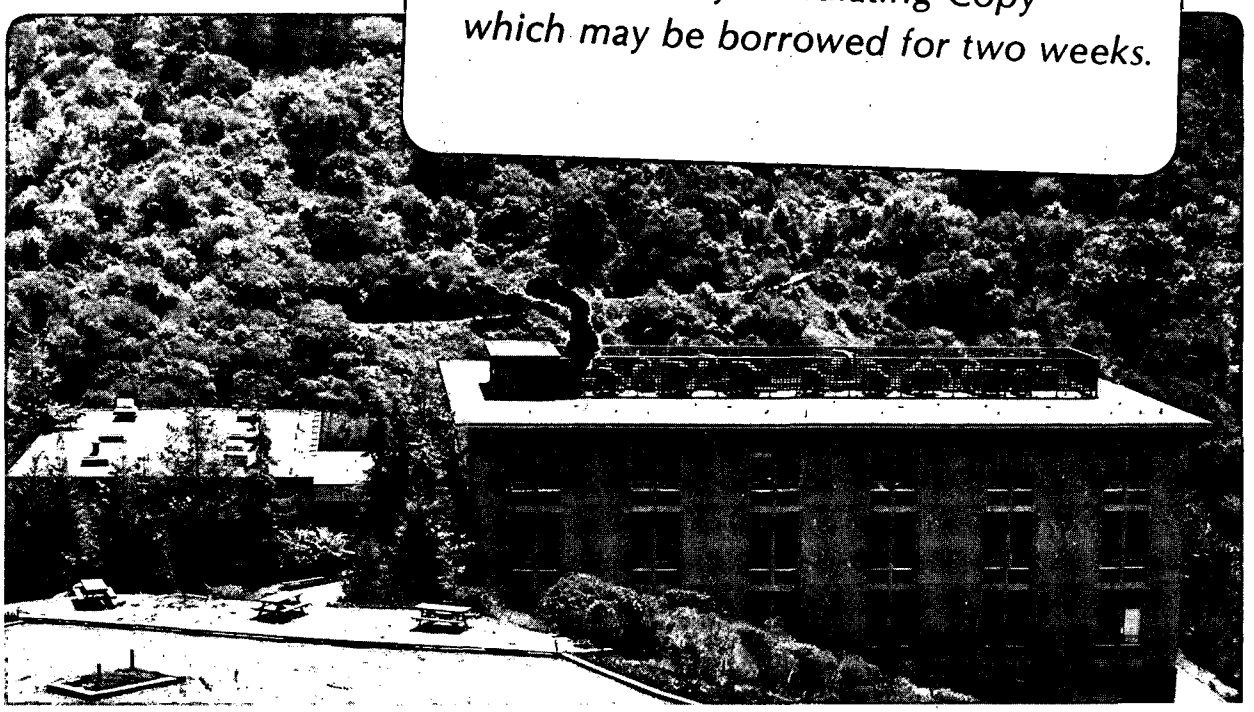

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First-Principles Calculations of Quasiparticle Energies at Surfaces and Interfaces: Semiconductor Surface-State Spectra and Band Offsets

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Abstract

A first-principles theory for calculating surface-state energies and semiconductor band offsets is described. Within a quasiparticle interpretation of excitation spectra, the approach provides well-founded energies which can be compared directly with spectroscopic measurements. Results for the As-capped Si(111) and Ge(111) surfaces and for the GaAs-AlAs(001) heterojunction are discussed and compared with experiment.

1. INTRODUCTION

A detailed description of the electronic excitation spectrum is an essential ingredient in understanding the physical and chemical properties of surfaces and interfaces. Local density functional (LDA) calculations have been quite successful in determining the structure of many surface systems.[1,2] However, since the density functional formalism is a ground-state theory, these calculations do not provide direct information on the excitation spectra. Indeed, as in the case of bulk solids, the common practice of comparing LDA eigenvalues to spectroscopic data has often led to large discrepancies in the surface-state energies. The proper interpretation of the excited-state spectra requires the concept of quasiparticles, the particle-like excitations in an interacting many-electron system.[3,4]

In this paper, we show that a recently developed quasiparticle theory [4] which has been successful in calculating the optical and photoemission spectra of bulk crystals [4-6] extends to surfaces and interfaces. The approach is based on a first-principles evaluation of the electron self-energy operator to first order in the dynamically screened Coulomb interaction and the dressed electron Green's function. The results for the two prototypical systems discussed here illustrate that the theory is accurate and of predictive power. For the As-capped Si(111) and Ge(111) surfaces,[7] the calculated energies are in excellent agreement with data from angle-resolved photoemission experiments and show a substantially larger gap between the empty and occupied surface states in comparison with LDA calculations. The predicted features of the empty surface states have been verified by a recent scanning tunneling microscopy study.[8] Our results for the band offsets of the GaAs-AlAs(001) interface [9] are also in very good agreement with recent experimental values. We find that there is a substantial many-body correction to the value of the valence band offset calculated using the LDA.

2. THEORY OF QUASIPARTICLE ENERGIES

In the Green's function approach, the quasiparticle properties are determined by solving [3]

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

where T is the kinetic energy operator, V_{ext} is the external potential due to the ions, and V_H is the Hartree potential. The exchange and correlation contributions are included in the self-energy operator Σ. Σ, in general, is nonlocal, energy-dependent, and nonHermitian with the imaginary part giving the lifetime of the quasiparticles. Our approach [4] is based on the GW approximation in which a first order expansion for the self-energy operator is taken:

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

where δ is a positive infinitesimal. The major components of the theory are the fully interacting Green's function for which we use a quasiparticle approximation,

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

and the dynamically screened Coulomb interaction,

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

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.

As can be seen from the structure of Eqs. (1)-(4), the quasiparticle energies together with Σ and G must be obtained in a self-consistent fashion. In the calculations, the electron Green's function is constructed initially using the LDA Kohn-Sham eigenfunctions and eigenvalues and is subsequently updated with the quasiparticle spectrum from Eq. (1). The static dielectric matrix $\varepsilon(\vec{r},\vec{r}',\omega=0)$ is obtained as a ground-state quantity from the LDA calculation and extended to finite frequencies using a generalized plasmon pole model together with exact sum rules.[4]

The present approach has been applied successfully to a variety of crystals including semiconductors, ionic insulators, and alkali metals.[4-6] Highly accurate band gaps, optical transition energies, and photoemission spectra have been obtained. It is found that, for semiconductors and insulators, the use of the crystalline Green's function and inclusion of both local fields (the full dielectric matrix) and dynamical screening effects are important factors for quantitative results.[4] For the alkali metals, the quasiparticle bandwidths are shown to be also sensitive to the correct treatment of exchange-correlation effects in the dielectric screening.[6]

3. SEMICONDUCTOR SURFACE-STATE ENERGIES

A survey of the literature shows that, for semiconductor surfaces, even

in cases where the structure is well-determined, there are rather severe discrepancies between the LDA surface-state energies and experimental values. In general, three areas of systematic disagreement exist: (1) the LDA surface-state band dispersion is qualitatively reasonable but is misplaced relative to the valence band maximum; (2) the calculated dispersion of the surface-state band is too small in some cases; and (3) the gap between the empty and occupied surface-state energies is often dramatically underestimated. This last feature is analogous to the "band gap" problem in bulk semiconductors and insulators.

The systems we examined to address the problem of predicting surface-state spectra are the As-chemisorbed Si(111) and Ge(111) surfaces. At saturation coverage, As is found to substitute for the outermost layer atoms. The surface then becomes chemically inactive and is stable against reconstruction showing a 1x1 periodicity. These are ideal prototype systems for the many-body calculation because of their geometric simplicity and the availability of detailed experimental data.[10] Moreover, they are of intrinsic importance as initial stage of GaAs growth on Si and Ge.

The calculations are carried out using a supercell geometry with a 12-layer thick slab. The surface geometry and the corresponding ground-state charge density are obtained from a LDA calculation using ab initio pseudopotentials. After the structure is determined, the quasiparticle energies for both the bulk states and surfaces states are calculated as described in Section 2. For the Si(111) and Ge(111) surfaces, equilibrium geometry is achieved with an outward displacement of the As atoms by 0.16 Å and 0.17 Å respectively. This structural relaxation is in excellent agreement with the recent experimental result of 0.17 Å from x-ray standing wave measurements on the Si(111):As surface.[11]

The calculated results are depicted in Figs. 1-3. In Fig. 1, the quasiparticle surface-state bands (solid lines) together with the LDA surface-state bands (dashed lines) are plotted against the projected quasiparticle band structure of Si. As expected, the fully occupied surface band corresponds to the dangling bond (lone pair) states of the As adatoms. These lone pair states have been carefully studied using angle-resolved photoemission measurements.[10] The theory also shows an empty surface state band in the gap. These empty states are split off the continuum states and, near $\bar{\Gamma}$, have atomic character at the surface similar to the L_{1c} conduction bands. Very similar results are obtained for the Ge(111):As system.

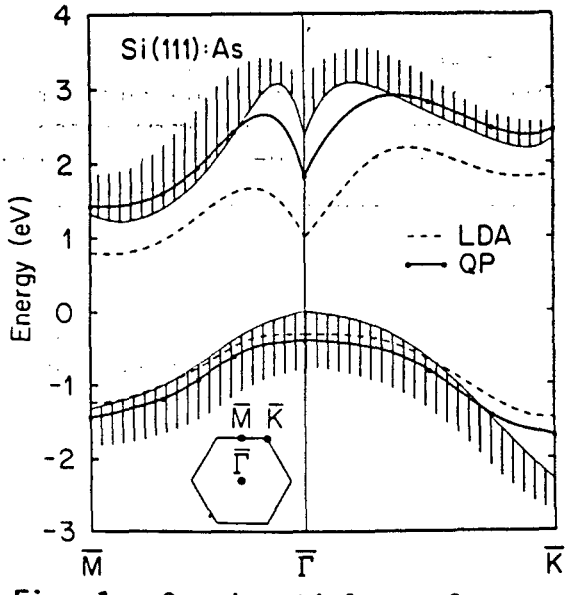

Fig. 1. Quasiparticle surface-state energies compared to LDA surface-state energies for the Si(111):As surface. Also shown is the quasiparticle bulk projected band structure.

In comparison with the LDA results, the occupied quasiparticle surface-state band is lower in energy and has a broader dispersion. Both are needed to bring theory to agreement with experiment. For Ge(111):As, the quasiparticle calculation also

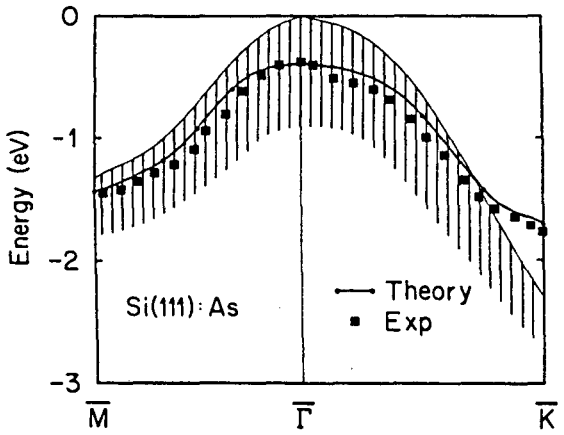

Fig. 2. Calculated filled quasiparticle surface-states energy for Si(111):As compared to data from photoemission (Ref. 10).

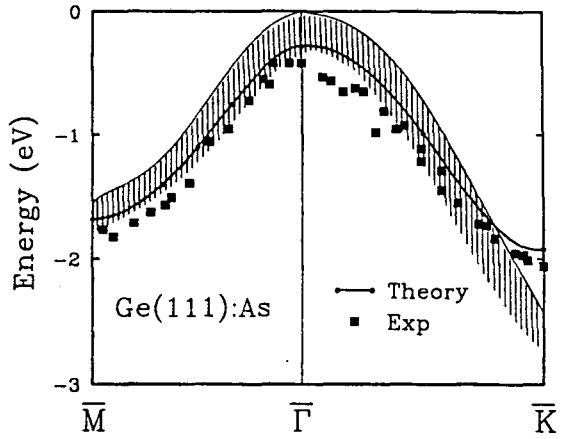

Fig. 3. Same as Fig. 3 except for Ge(111):As.

removes an unusual dispersion in the LDA results near $\bar{\Gamma}$.[7] Figures 2 and 3 compare the calculated lone pair surface-state bands with angle-resolved photoemission data. For both systems, the agreement is excellent in both the placement and the width of the band and is well within the estimated errors of ±0.1 eV with experiment and theory.

As seen in Fig. 1, the effect of the many-body correction on the empty surface states is quite dramatic. These states are substantially shifted upwards, opening up the gap between the empty and filled surface states by nearly 1 eV at some k-points. The position of the empty surface states is a prediction of the present theory. They should be experimentally accessible using angle-resolved inverse photoemission measurements, surface optical transition measurements, or scanning tunneling spectroscopy. The scanning tunneling experiment has recently been done for the Si(111):As surface.[8] Not only is the 1x1 surface structure observed directly, the observed surface-state gap of 1.9 - 2.3 eV in the normalized differential conductivity agrees very well with the predicted value of 2.2 eV.

The many-body results here, thus, address the many difficulties associated with the LDA surface-state bands. In particular, the gap between the empty and filled surface states is substantially opened in comparison with the LDA gap. Analysis of the calculated results, however, shows that the size of the correction depends on the detailed character of the surface states.[7] Hence, the shortcomings of the LDA surface-state spectrum cannot be corrected by a simple rigid shift.

4. SEMICONDUCTOR BAND OFFSETS

The present approach has also been applied to compute the band offsets of the GaAs-AlAs(001) interface.[9] The band discontinuities at a semiconductor interface are simply the differences in the quasiparticle energy E_{qp} across the junction for the band edge states. Since previous bulk and surface calculations showed that the quasiparticle wavefunctions are virtually identical to the LDA wavefunctions, we may write E_{qp} near an interface as

$$E^{qp}_{n\vec{k}} = \varepsilon^{LDA}_{n\vec{k}} + \Sigma_{n\vec{k}} - V^{n\vec{k}}_{xc} \tag{5}$$

where $\Sigma_{n\vec{k}}$ and $V^{n\vec{k}}_{xc}$ are respectively the expectation value of the self-energy operator and the LDA exchange-correlation potential for a given state. Then, the valence band offset ΔE_v becomes [12]

$$\Delta E_v = E^{LDA}_v + \delta_{vbm} \tag{6}$$

where ΔE^{LDA}_v is the LDA calculated valence band offset and δ_{vbm} is a many-body correction given by

$$\delta_{vbm} = \left(\Sigma - V_{xc}\right)^{vbm}_{GaAs} - \left(\Sigma - V_{xc}\right)^{vbm}_{AlAs} \tag{7}$$

Since E_{qp} in Eq. (5) should be evaluated at a distance away from the interface in determining the band offset and both Σ and V_{xc} are short range interactions, $(\Sigma - V_{xc})^{vbm}$ can be replaced by bulk values. To calculate the LDA band offset, we perform a fully converged 12-layer superlattice calculation using an approach similar to that of Van de Walle and Martin.[13]

For the GaAs-AlAs(001) interface, we find that the many-body correction is quite significant; that is, $\delta_{vbm} = 0.12$ eV. It is more than 29% of the LDA result for the valence band offset which is $\Delta E^{LDA}_v = 0.41$ eV. Combining the two gives a calculated value for the valence band offset of $\Delta E_v = 0.53$ eV. This result is in excellent agreement with the most recent experimental values of 0.53 - 0.56 eV.[14] The many-body correction can be understood in terms of a more localized valence band wavefunction for AlAs which leads to a more negative self-energy for AlAs as compared to GaAs and, thus, a positive δ_{vbm}. We expect the many-body correction to play an even more important role for cases where the junctions are made of materials with lesser chemical similarities than GaAs and AlAs.

5. SUMMARY AND CONCLUSIONS

A self-energy approach for calculating quasiparticle surface-state energies and band offsets from first principles is described. This development allows, for the first time, ab initio calculation of electronic excitation energies at surfaces and interfaces which can be directly compared with spectroscopic measurements. Results for the Si(111):As and Ge(111):As surfaces and the GaAs-AlAs(001) heterojunction show that the theory is accurate and of predictive power.

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