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State mixing for quasiparticles at surfaces: Nonperturbative *GW* approximation

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We present *ab initio* calculations for both the wave functions and the energies of single quasiparticles. The conventional quasiparticle approach evaluates energy-level corrections to first order in the difference between the self-energy and the Kohn-Sham exchange-correlation potential. Here, we also recalculate the quasiparticle states. At the example of the GaAs(110) surface we show that this nonperturbative treatment is important for surfaces with electronic states close in energy but different with respect to their localization. As a sensitive observable the reflectance anisotropy is studied. [S0163-1829(99)15947-2]

The state-of-the-art *ab initio* calculations of structural, electronic, and optical properties of solids are based on the density-functional theory (DFT),[1] mainly in the local-density approximation (LDA).[2] However, the electron excitation spectra can be significantly different from those constructed straightforwardly with the solutions of the Kohn-Sham equations of the DFT.[3] They can in principle be described rigorously within a Green's-function approach.[3,4] The quantum-mechanical part of the electron-electron interaction is contained in the exchange-correlation self-energy Σ, which, in Hedin's *GW* approximation,[3] is linearly expanded into the screened Coulomb interaction *W*.

In order to calculate the single-particle excitation energies and optical gaps of solids, usually only the main peak in the spectral function of *G* is considered and satellite structures are neglected.[5,6] The first-principles quasiparticle (QP) method[5,7] yields self-energy effects in form of shifts Δ_λ of the Kohn-Sham (KS) orbital energies ε_λ^{KS}. To be precise, QP excitation energies $\tilde{\varepsilon}_\lambda^{QP}$ are derived from the KS energies in first-order perturbation theory with respect to the difference $\delta\Sigma=\Sigma-V_{XC}$, where V_{XC} denotes the exchange-correlation potential already considered in the KS equations. Off-diagonal elements of the perturbation operator $\delta\Sigma$ are neglected. In fact, it has been shown for states close to the fundamental band edges[5] of bulk semiconductors that the real QP wave function has more than 99.9% overlap with the corresponding KS orbital. The perturbative *GW* approach enables calculations of excitation energies for a variety of different systems including surfaces with an accuracy better than 0.1 eV.[5,7–11]

The perturbative QP method is well established when the quantities of interest are energy levels. Physical properties relying explicitly on the wave functions have been less extensively studied using the QP approach, with the exception of few works on the optical spectra of bulk semiconductors[12] and surfaces[8,13] where, consistently with the first-order perturbative approach, the KS wave functions have been used. The huge amount of excellent results, which has been obtained with the standard procedure for energetic positions does not necessarily imply that those results will be equally excellent for the wave functions. A study concerning this point has been performed on an aluminum surface, where image potential effects have been found using a nonperturbative QP approach.[14]

The perturbative approach is generally valid when the QP shifts Δ_λ do not change the ordering and occupation of the KS states. When the off-diagonal elements of $\delta\Sigma$ are not small in comparison to the differences $|\tilde{\varepsilon}_\lambda^{QP}-\tilde{\varepsilon}_{\lambda'}^{QP}|$, the perturbative QP approach has to be improved. Important systems in this respect can be semiconductor surfaces. States with different localization behave differently under the influence of the perturbation operator $\delta\Sigma$.[11] For some surfaces, it has been shown that occupied surface states shift more rapidly to lower energies than the corresponding bulk states.[13,15] When their energies approach each other, the finite off-diagonal elements may mix them and, hence, change their character, at least partially. The accompanying mixing of the wave functions should influence all quantities containing matrix elements between these states.

In order to investigate this possibility, we calculate quasiparticle wave functions and energies beyond the conventional first-order perturbation treatment of the self-energy effects. The self-energy is constructed using the Kohn-Sham eigenstates of an underlying *ab initio* density-functional calculation, and the resulting operator is diagonalized in the basis of the the KS wave functions. As an example for a sensitive system, the GaAs(110) surface is studied. In fact, a mixing of single-particle states of the same symmetry occurs. The mixing effect is probed by the surface reflectance anisotropy (RA).[16]

The main peaks in the spectral function of the single-electron Green function define quasiparticles.[3] For energies *E* close to these peak positions they can be characterized by quasiparticle energies $\varepsilon_\lambda(E)$ and wave functions $\Psi_\lambda(E,\mathbf{x})$, obtained by solving[3]

$$\{T(\mathbf{x})+V_{ext}(\mathbf{x})+V_h(\mathbf{x})\}\Psi_\lambda(E,\mathbf{x}) + \int d^3\mathbf{x}'\Sigma(\mathbf{x},\mathbf{x}';E)\Psi_\lambda(E,\mathbf{x}')=\varepsilon_\lambda(E)\Psi_\lambda(E,\mathbf{x}), \tag{1}$$

where T is the kinetic energy operator, V_{ext} is the external potential due to the ions, and V_h is the Hartree potential of the electrons. In the following, we neglect the lifetime of the quasiparticles and take only the Hermitian part of Σ into account. Then the quasiparticle is represented by a δ-like peak in the spectral function at the solution ε_λ^{QP} of the equation $\varepsilon_\lambda(E)=E$ and by a wave function $\Psi_\lambda(\varepsilon_\lambda^{QP},\mathbf{x})$. The QP Eq. (1) and the KS equation[2] only differ by the respective exchange-correlation potential. We, therefore, expand the QP wave functions into the complete set of orthonormalized KS orbitals $\phi_m(\mathbf{x})$ according to $\Psi_\lambda(E,\mathbf{x})=\Sigma_m c_{\lambda m}(E)\phi_m(\mathbf{x})$. The QP equation is transformed into a system of algebraic equations

$$\sum_{m'}\{[\varepsilon_{m'}^{KS}-\varepsilon_\lambda(E)]\delta_{mm'}+\delta\Sigma_{mm'}(E)\}c_{\lambda m'}(E)=0, \tag{2}$$

where $\delta\Sigma_{mm'}(E)$ is the matrix element of the difference between the self-energy operator and the LDA exchange correlation potential. Equation (2) has to be solved for E in the interval we are interested in. For a given E the matrix elements $\delta\Sigma_{mm'}(E)$ form a Hermitian matrix after the neglect of the lifetime effects due to Σ. It guarantees that also the QP states $\Psi_\lambda(E,\mathbf{x})$ at the same energy E form a complete system of orthonormalized wave functions. In general, we apply a linear approach to the energy dependence of the perturbation. In the diagonal case, $\delta\Sigma_{mm}(E)=\alpha_{mm}-(E-\varepsilon_m^{KS})\beta_{mm}$, the reliability of such an approach has been shown.[5,7] In first-order perturbation theory it gives QP eigenvalues $\tilde{\varepsilon}_m^{QP}=\varepsilon_m^{KS}+\alpha_{mm}/(1+\beta_{mm})$ as shifted KS energies. Since the off-diagonal elements of the perturbation, $\delta\Sigma_{mm'}$, are small in comparison to the diagonal ones, the resulting QP energies ε_λ^{QP} are rather close to the perturbation-theory values $\tilde{\varepsilon}_\lambda^{QP}$. For that reason only the correct energy dependence of $\delta\Sigma_{mm'}(E)$ close to $E=\tilde{\varepsilon}_m^{QP}$ and $E=\tilde{\varepsilon}_{m'}^{QP}$ is needed. We have checked that in their surrounding intervals (about 4 eV wide) the linear interpolation around $(\tilde{\varepsilon}_m^{QP}+\tilde{\varepsilon}_{m'}^{QP})/2$, $\delta\Sigma_{mm'}(E)=\alpha_{mm'}-[E-(\tilde{\varepsilon}_m^{QP}+\tilde{\varepsilon}_{m'}^{QP})/2]\beta_{mm'}$ $(m\neq m')$, is still valid. Neglecting the energy dependence of $\delta\Sigma_{mm'}(E)$ for $(m\neq m')$, i.e., keeping only the first-right hand term in the equation above, can change significantly the off-diagonal matrix elements. Hence, in our calculation the energy dependence of all matrix elements of $\delta\Sigma(E)$ is accounted for.

We perform the QP calculations in three steps: the output ε_m^{KS} and ϕ_m of the first step based on the DFT-LDA is used to calculate the QP energies $\tilde{\varepsilon}_m^{QP}$ in first-order perturbation theory in the second step. In the third step, not only the energies but also the wave functions are updated nonperturbatively under inclusion of the off-diagonal elements of the perturbation operator. As a consequence of the energy dependence of the self-energy, QP wave functions with different QP eigenvalues are not orthogonal to each other.

In order to describe the relaxed GaAs(110) surface, the repeated-slab method is used. Each slab consists of 11 atomic layers and 7 layers of vacuum. The total energy optimization and the electronic structure calculations are performed using a pseudopotential-plane wave code. The KS orbitals are expanded in a set of plane waves up to an energy cutoff of 15 Ry. Further details for the calculations of $\tilde{\varepsilon}_m^{QP}$ are given in Ref. 13.

For the nonperturbative calculation, we expand the QP wave function in a set of 26 valence and 26 conduction KS states, neglecting the mixing between valence and conduction states. The 52 bands considered cover the energy interval of 9 eV around the Fermi level, which allows for a correct description of the RA spectrum for photon energies below 5 eV. For the screened Coulomb interaction W in the self-energy $\Sigma=iGW$, we use a plasmon-pole model described in Ref. 17.

The solutions of the KS equations and the results of the perturbative self-energy calculation have been used to calculate QP wave functions and energies at the four high-symmetry points Γ, X, M, and X' as well as at the Baldereschi point in the surface Brillouin zone (BZ). We find that in general the coupling matrix elements $\delta\Sigma_{mm'}(E)$ are small. The most important changes happen for the lowest conduction slab bands $c1$, $c2$, and $c3$ at the BZ center. Already in the DFT-LDA treatment the cation-related surface band C_3 merges near Γ into the projected bulk bands, and crosses with the bands cn. This leads to a remarkable coupling of the two lowest empty KS states as represented in the inset of Fig. 1. The eigenvalues of the three lowest empty states are shifted towards higher energies within the perturbative GW approximation. After the application of the nonperturbative procedure the two coupled lowest bands show an anticrossing behavior. The lowest one moves down in energy, whereas the other one is further shifted to higher energies.

The consequences for the wave functions are shown in Fig. 1 for the lowest empty band at Γ. In this figure, the square modulus of the wave function, integrated over the surface plane, is plotted versus the coordinate perpendicular to the surface. In the case of DFT-LDA, this state exhibits a clear bulk character: the probability to find an electron at the first atomic layer is the same as in the bulk, at the third and fifth layer. The inclusion of the off-diagonal elements, instead, gives rise to a clear change in the localization. The probability to find the quasiparticle in the surface region is considerably increased, whereas it is decreased in the region of the bulklike atomic layers.

In the case of the X point, one expects smaller effects of the intermixing of KS wave functions at the band edges of the fundamental gap because of the energy separation of bulk and surface states. The empty cation-related C_3 states are clearly below the bulk conduction bands.[18,19] In fact, as can be seen in Fig. 2 no mixing occurs for the lowest empty state, which is clearly a surface state. In all other cases shown in Fig. 2 a hybridization of surfacelike and bulklike states is observed. The changes in the localization behavior of the electronic states are smaller than in Fig. 1. Nevertheless, they are of the order of 10%, hence much larger than

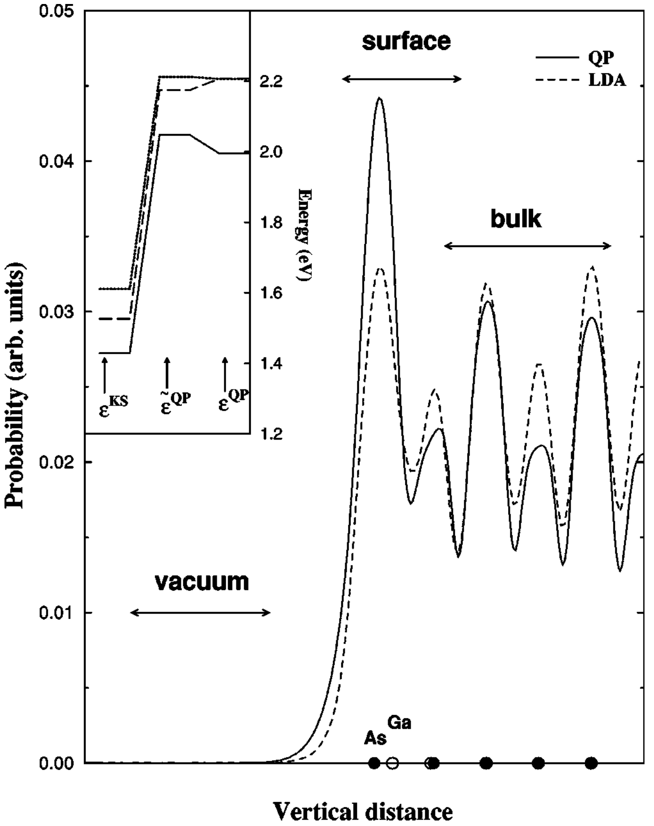

FIG. 1. Quasiparticle and DFT-LDA wave function (square modulus integrated over the surface plane) for the lowest empty state at the Γ point. The positions of the As atoms (full circles) and Ga atoms (open circles) are indicated along the coordinate normal to the surface. The solid line indicates the probability to find an electron as calculated in the present non-perturbative QP approach; the standard KS result (DFT-LDA wave function) is shown by the dashed line. Inset: Energy of the three lowest conduction bands of GaAs(110) at the Γ point, calculated according to LDA (KS), standard perturbative *GW* ($\tilde{\varepsilon}^{QP}$), and the present approach (ε^{QP}).

those occuring in the bulk. They could contribute to a modification of surface optical properties.

In order to demonstrate the effect of intermixing of single-particle states of the DFT-LDA into QP states we have calculated the reflectance anisotropy of the relaxed GaAs(110) surface within the different approximations considered for the electronic structure. The RA is defined as $\Delta R/R=2(R_y-R_x)/(R_x+R_y)$,[16] where R_y is the reflectivity for light polarized along $[\bar{1}10]$, the direction of the zig-zag chains at the surface,[19] and R_x is for light polarized along [001]. There are two main reasons for an influence of the mixing effect: (i) Since the bulk of zinc-blende GaAs is optically isotropic, the only source of the RA is the surface region. (ii) The signal is proportional to the difference $[|\mathbf{v}^y_{cv}(\mathbf{k})|^2-|\mathbf{v}^x_{cv}(\mathbf{k})|^2]$ of the matrix elements of components of the velocity operator $\mathbf{v}$ between conduction ($\lambda=c$) and valence ($\lambda=v$) states $\Psi_\lambda(\varepsilon^{QP}_\lambda,\mathbf{x})$, at the same $\mathbf{k}$ point in the surface BZ. Small changes of the wave functions in the surface region may induce huge changes of the above difference and, hence, of the resulting RA.

In order to evaluate the optical response using the QP states, we use the random-phase approximation form of the

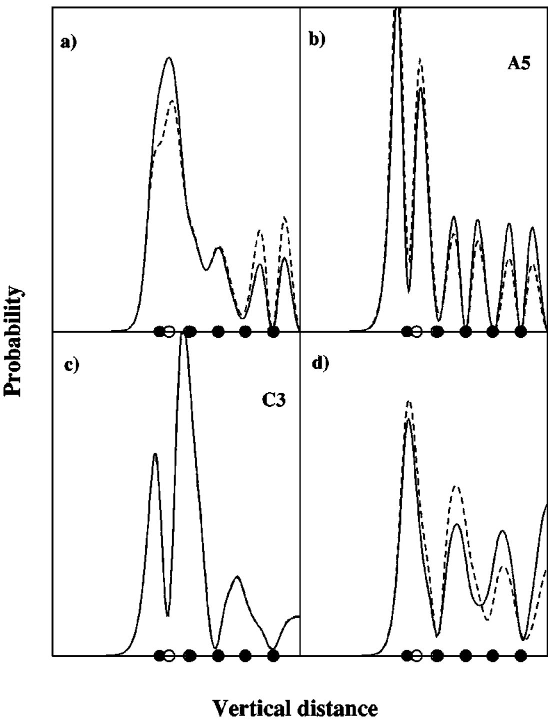

FIG. 2. Squared moduli of the wave functions integrated over the surface plane for valence and conduction states near the fundamental gap at *X*. The atomic positions are indicated as in Fig. 1. Solid line: present QP, dashed line: standard KS. (a) Valence state at −2.19 eV; (b) uppermost valence state, related to the anion filled dangling bond; (c) lowest empty state, related to the cation empty dangling bond; (d) conduction state at 2.88 eV. Energies are given relatively to the top of the valence band at Γ.

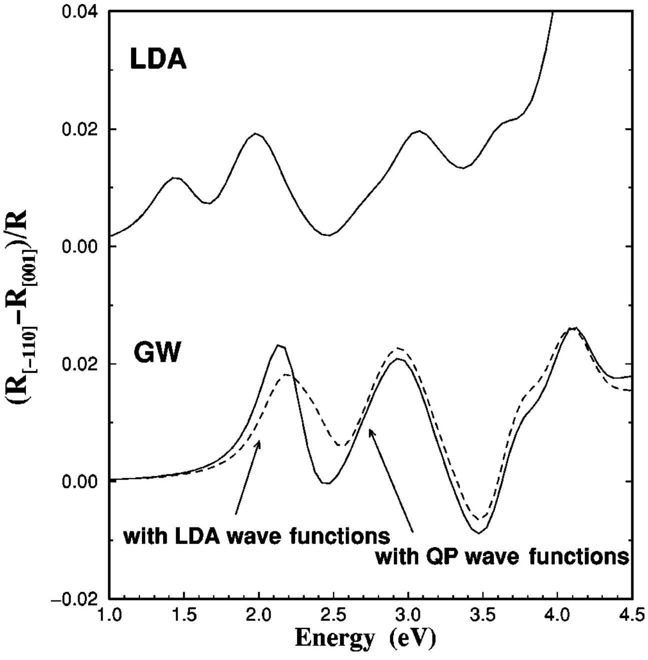

FIG. 3. Reflectance anisotropy of GaAs(110), calculated with a five **k**-points set: Top full line: DFT-LDA; dashed line: perturbative *GW* approximation; bottom full line: non-perturbative *GW* approximation (see text).

polarizability propagator within the length gauge.[20] QP wave functions are in general not orthogonal to each other. However, since the valence (conduction) QP wave functions do not contain contributions from LDA conduction (valence) states, the mutual orthogonality between filled and empty bands, which is important in the calculation of the optical properties, is preserved.[21] The results of the calculations within three different approaches to the electronic structure are shown in Fig. 3. The spectra have been calculated with just five **k** points in the irreducible part of the BZ. This restriction arises from the necessity to calculate 1404 self-energy matrix elements per **k** point, and to handle the corresponding energy dependence. Convergence is expected for a larger number of **k** points, even if the triangle method is applied.[22] So we do not expect a reasonable resemblance with experimental RA data.[23] Nevertheless, the RA spectra in Fig. 3 allow to demonstrate the effect of the nonperturbative treatment of the quasiparticle corrections, in particular the mixing of KS states of different localization into new QP wave functions. The main effect of the perturbative *GW* approximation is the shift of the RA spectrum towards higher energies. Since the QP shifts of the KS states are not rigid, also the line shape is changed, with some transfer of oscillator strength to the low-energy peak. When also the changes of the QP wave functions with respect to the KS orbitals are taken into account, there is a further transfer. This effect is mainly restricted to the low photon energy region, from 2.0 to 2.5 eV. This is related to the fact that the RA in this region is governed by transitions at the Γ point, which are strongly influenced by hybridization effects as discussed in Fig. 1. The higher energy region is dominated by optical transitions between modified bulklike states.[13] Mixing of such states is weaker and, moreover, does not significantly influence the RA.

In conclusion, we have presented an *ab initio* treatment of quasiparticle effects within the *GW* approximation that is not restricted to pure energy shifts. Rather, changes of the wave functions with respect to the solutions of the Kohn-Sham equation have been taken into account. As a model system the GaAs(110) surface is considered. Differently from the case of bulk semiconductors, sometimes, the identification of DFT-LDA wave functions as the quasiparticle ones may not be correct. Significant hybridization between surface and bulklike states may occur. Physical properties that are dominated by matrix elements may be affected by the small changes in the wave functions. This is demonstrated at the example of the surface reflectance anisotropy. Nevertheless, the spectrum does not change *qualitatively*. We believe that other surfaces, like $C(111)2\times1$, where perturbative *GW* results for the gap do not agree with experiments,[24] are also candidates for the application of the nonperturbative QP approach.

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