

Ab Initio Calculation of Self-Energy Effects on Optical Properties of GaAs(110)

Olivia Pulci, Giovanni Onida, and Rodolfo Del Sole

*Istituto Nazionale per la Fisica della Materia, Dipartimento di Fisica dell' Università di Roma Tor Vergata,
Via della Ricerca Scientifica, I-00133 Roma, Italy*

Lucia Reining

Laboratoire des Solides Irradiés, UMR7642 CNRS-CEA, École Polytechnique, F-91128 Palaiseau, France

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We present a first-principles calculation of self-energy effects on the optical properties of the GaAs(110) surface. Three main results are obtained. (a) The self-energy shifts for the valence bands are larger for surface-localized states, at odds with the commonly assumed “scissor operator” hypothesis. (b) The computed shifts display an almost linear dependence on the surface localization of the wave function; this allows us to realize a well-converged calculation of optical properties based on the *GW*-corrected spectrum. (c) The agreement with experimental data is improved with respect to local-density-approximation calculations. [S0031-9007(98)07843-0]

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The optical properties of surfaces are a developing field of research because of the versatility and nondamaging character of optical spectroscopy [1]. The comparison between measured and calculated spectra has yielded information on the atomic and electronic structure of a number of surfaces [1]. For several years theory has been generally limited to the one-electron approximation and to the tight-binding semiempirical approach. Recently, *ab initio* calculations carried out within the local-density approximation (LDA) to the density functional theory (DFT) [2] have also appeared [3–8].

However, a first-principles calculation of the electronic band structure should be carried out within Green’s function theory. The propagation of independent quasiparticles (electrons or holes) is described by the one-particle Green’s function, involving the self-energy, which can be calculated according to Hedin’s *GW* approximation [9]. The electronic structure and energy gaps determined in this way for semiconductors are in excellent agreement with experiments [10]. In most bulk semiconductors, the corrections are approximately constant, so that the net result is an almost rigid shift of the LDA absorption spectrum to higher frequencies. This justifies the so-called “scissor operator” (SO) approach, in which quasiparticle (QP) energies are obtained by rigidly shifting the LDA empty bands [11,12]. Although a similar rigid shift has also been invoked for some surfaces [4,8], it is not clear whether or not this is a general feature, especially since very few well-converged *GW* calculations on surfaces have been performed up to now [13,14].

One of the goals of the present calculation is to clarify this issue for the GaAs(110) surface. Another goal is to test the capability of the single-quasiparticle approximation to describe surface optical spectra.

In this work we report a well-converged calculation of the reflectance anisotropy (RA) of the GaAs(110) surface within the *GW* approximation. A previous *GW* calculation

on this surface has been performed by Zhu *et al.* [15], using very thin slabs (5 atomic layers) separated by even thinner vacuum regions (2 layers). Their pioneering work gave an electronic structure in good agreement with the experiment, but their RA spectrum was far from being converged. In fact, the reflectance anisotropy is a quantity extremely sensitive to all the details of the calculations.

The RA, defined as the difference of the reflectivity for two different polarization directions of the light, is calculated according to the method described in more detail in Refs. [1,16]. Since the GaAs bulk is optically isotropic, the difference between the reflectivity for light polarized along two different directions is due to the presence of the surface. In our calculation, the semi-infinite solid is replaced by periodically repeated, separated slabs. In order to achieve a good convergence of the results, we have considered a system containing 11 atomic layers, with 7 empty layers separation. Within the slab geometry, the RA can be written as

$$\begin{aligned} \frac{\Delta R}{R} &= \frac{R_{[\bar{1}10]} - R_{[001]}}{\bar{R}} \\ &= \frac{16\pi\omega d}{c} \text{Im} \frac{\alpha_{[\bar{1}10]}(\omega) - \alpha_{[001]}(\omega)}{\epsilon_b(\omega) - 1}, \end{aligned} \quad (1)$$

where \bar{R} is the average of the two reflectivity signals, α the half-slab polarizability, ϵ_b the bulk dielectric function, and d the half-slab thickness. The calculation of α and ϵ_b involves the determination of the matrix elements of the momentum operator between valence and conduction states. Our calculation starts with the DFT-LDA structure, and successively introduces the self-energy corrections using the *GW* scheme [9,10]. In the latter, the self-energy Σ is constructed as the convolution of the one-particle Green’s function G and the screened Coulomb interaction W . QP corrections are evaluated to first order on the DFT-LDA eigenstates [17,18]. The (almost linear) energy

dependence of Σ is taken into account via the calculation of $\langle \partial \Sigma / \partial E \rangle$ at the LDA energy, and the calculations are done in a plane-wave basis.

The theoretical equilibrium geometry is calculated in the DFT LDA [19]; we use norm-conserving, fully separable pseudopotentials with nonlinear core corrections for the Ga atom [20]. We use a cutoff of 18 Ry and four special k points [21] in the irreducible part of the surface Brillouin zone. DFT-LDA results are then used as ingredients for the calculation of the self-energy corrections to the Kohn-Sham eigenvalues at four high-symmetry k points (Γ , X , M , X').

First, in order to obtain W , we compute each matrix element of the RPA inverse dielectric function $\epsilon_{\mathbf{G},\mathbf{G}'}^{-1}(\omega, q)$ at two imaginary energies, and the energy dependence is fitted to a plasmon-pole model [17]. Subsequently, we evaluate the expectation value of $\Sigma - V_{xc}$ between LDA eigenstates for the 9 highest occupied bands and for the 12 lowest conduction bands, corresponding to an energy range of about 6 eV around the Fermi level.

A technical point that must be addressed with care is the set of k' points used in the calculation of the screening function [sum over k' in Eq. (1) of Ref. [22]], and in the calculation of the Brillouin zone integrals appearing in both the exchange and correlation part of $\langle \Sigma \rangle$. This point is more complicated here than in the bulk case, due to the anisotropy of the system. In fact, $\epsilon^{-1}(\vec{q})_{G=G'=0}$ (where $\vec{q} = \vec{k} - \vec{k}'$) is nonanalytic for $q \rightarrow 0$, since the value of its limit (i.e., the static dielectric constant) depends on the direction of \vec{q} . This point is not a minor one, since for $G = G' = 0$ the “small q ” region contributes strongly to the integrals, having q^2 in the denominator [see Eq. (4) of Ref. [22]]. The simplest approach, i.e., introducing a shift of the k' mesh in order to avoid the $k = k'$ case in the latter equation, has proved to yield large underestimations of $|\langle \Sigma_x \rangle|$ and $|\langle \Sigma_c \rangle|$.

In order to improve the convergence, keeping the number of k' (and hence q) points within the computationally accessible range (which is of the order of 10), we have replaced the value of the $q \rightarrow 0$ term in Eq. (4) of Ref. [22] with the value of the integral performed over the appropriate region of reciprocal space surrounding the $q = 0$ point, the shape of this region depending on the geometry of the remaining, nonzero q points. In this integral, $\epsilon^{-1}(q \approx 0)/q^2$ is approximated with the analytic expression

$$\frac{\epsilon^{-1}(q)}{q^2} \approx \sum_i \frac{\epsilon^{-1}(q_{0i})}{q^2} \left(\frac{q_i}{q} \right)^2, \quad (2)$$

where $\epsilon^{-1}(q_{0i})$ is the limit of $\epsilon^{-1}(q)$ for $q \rightarrow 0$ along the i direction (with $i = x, y, z$). A similar procedure (which we call in the following “improved integration”) has to be used in the calculation of $\langle \Sigma - V_{xc} \rangle$ for the evaluation of every $\int d^3 q [f(q)/|q + G|^2]$ appearing in the expression of $\langle \Sigma \rangle$: the Coulomb interaction is integrated around each q over a small volume centered at $\vec{q} + \vec{G}$, while the rest of the integrand $f(q)$ is supposed to be constant over that

volume. This improved treatment of the Coulomb interaction turns out to be essential, as illustrated in the inset of Fig. 1, where the convergence of the exchange part of the self-energy, with and without the improved integration (black and gray columns, respectively), is shown.

We have found that in this way a good convergence is reached using in the irreducible part of the Brillouin zone (IBZ) the four high-symmetry points Γ , X , M , and X' , plus the Baldereschi point [23,24]. In particular, this choice yields $\langle \Sigma_x - V_{xc} \rangle$ values converged within 100 meV. In order to obtain this level of convergency, 1667 plane waves per electronic state are included [997 in $\epsilon^{-1}(q)$] and 650 conduction states in the calculation of $\epsilon^{-1}(q)$ and $\langle \Sigma_c \rangle$, corresponding to an energy of about 46 eV above the Fermi level.

Our results for the dispersion and the energy gaps between surface states are compared in Table I with experimental data measured by direct and inverse photoemission on the same sample by Carstensen *et al.* [25]. The agreement is good, as in [15], and the improvement with respect to the LDA level is important.

A very interesting feature of the obtained QP corrections is their dependence on the localization of a state at the surface. The main panels of Fig. 1 show the relation between the GW corrections (defined as the GW quasiparticle energies minus the LDA eigenvalues) and the degree of “surface localization” of the eigenstate. The localization is computed as the integral of $|\Psi|^2$ over the two outermost atomic layers and the first “empty layer” of both surfaces (corresponding to a region limited by the planes $|z| = 6.88 \text{ \AA}$ and $|z| = 12.77 \text{ \AA}$, having $z = 0$ at the center of the slab; a state uniformly distributed over the 11 layers of the slab should yield a value of about $4/11 = 0.36$).

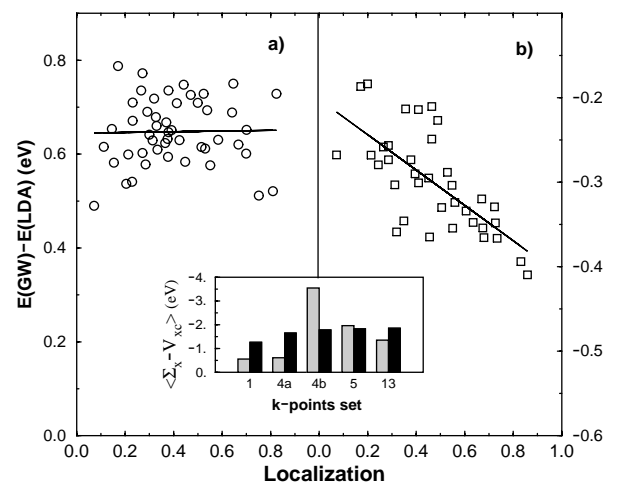


FIG. 1. Calculated self-energy GW corrections to the LDA eigenvalues at Γ , X , X' , and M plotted against the surface localization of the states. (a) Conduction bands. (b) Valence bands. In the inset, we show the convergence, with respect to the IBZ sampling, for $\langle \Sigma_x - V_{xc} \rangle$ evaluated for the highest valence state at M (see text and [24]).

TABLE I. Results for the surface energy gaps: LDA and *GW*, compared to experiment (eV).

	$E_{s-s}^{\text{gap}}(\Gamma)$	$E_{s-s}^{\text{gap}}(X)$	$E_{s-s}^{\text{gap}}(M)$	$E_{s-s}^{\text{gap}}(X')$
LDA	1.8	1.9	2.2	2.0
<i>GW</i>	2.7	2.9	3.2	2.9
Exp. [25]	2.4	3.1	3.3	3.0

The least-squares linear fit to the data is also shown. A clear correlation is visible for the holes (valence states), while conduction bands appear to undergo *GW* corrections which are almost independent from the surface localization. In particular, filled surface states correct 0.2–0.3 eV more than bulk ones. The bulk gap correction of about 0.8 eV agrees with previous calculations [10], and the surface corrections tend to increase up to 1.1 eV.

A deviation from the scissor operator scheme has also been found by Blase *et al.* [13] on the Si(111):H surface and predicted by Bechstedt and Del Sole [26] for the (110) surfaces of the III-V compounds. A qualitative argument that explains the larger *GW* shift of the surface states with respect to bulk states is the following: Self-energy corrections with respect to DFT-LDA eigenvalues are approximately proportional to the inverse of the dielectric function, ϵ . Since passing from a bulk semiconductor to its surface ϵ is predicted to undergo a reduction of about a factor of 2, one could expect a doubling of the “gap correction” [26]. Of course, this picture is oversimplified, since it neglects any kind of surface effect except the crystal termination.

Our results indicate that a scissor operator approximation for surfaces is less appropriate than in bulk, although the effect is less dramatic than predicted by [26]. In fact, filled surface states exhibit an increased downwards shift due to an increased self-interaction correction (which does not exist for empty states) arising from their greater localization. Our calculations show that at this surface the localization is not too strong, which explains the reduced effect, also when compared to the findings of Ref. [13].

The obtained linear relation between surface localization and *GW* corrections can be used to deduce the QP shifts for all of the many bands and k points required in a calculation of optical properties. Using this scheme we compute the RA of this surface [Eq. (1)]. The calculation requires the knowledge of the momentum matrix elements and transition energies between all the valences and an approximately equivalent number of conduction states for a large number of k points in the IBZ. The direct calculation of QP shifts for all those states is clearly unaffordable; however, their degree of surface localization is obtained very easily. Starting from our *GW* results for the 21 states around the Fermi level at the 4 high-symmetry k points, we have then extrapolated the corrections to all of the required states at 64 k points in the IBZ.

We show in Fig. 2 the resulting RA spectrum, compared with the corresponding LDA result. The *GW* curve

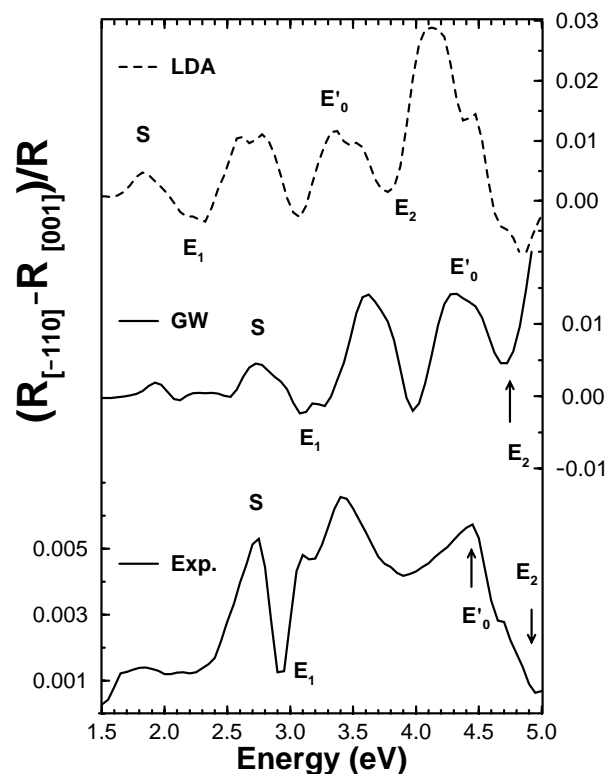


FIG. 2. Reflectance anisotropy spectrum of GaAs(110) computed according to Eq. (10) of Ref. [16], at the LDA level (top) and including *GW* corrections (middle). Bottom: experimental data from Ref. [28].

is shifted toward the high-energy side, because QP corrections increase the gaps and therefore the transition energies. A similar effect is obtained in bulk GaAs as well as in other semiconductors [27]. In our case, the shift is not rigid because of the localization dependence of QP corrections. The line shapes in the LDA and *GW* spectra turn out, however, to be qualitatively similar. The experimental curve measured by Esser *et al.* [28] at room temperature is also shown. The low-frequency peak S has a substantial contribution due to the transitions between near-gap surface states, while all other structures originate from transitions between surface-perturbed bulk states. Hence the dip at about 3.2 eV in the *GW* RA (at about 2.4 eV in the LDA spectrum) and the subsequent peak corresponds to the E_1 bulk structure, and the next peak at about 4.3 eV (at about 3.5 eV in the LDA case) corresponds to the E'_0 structure. The E_2 bulk absorption peak, occurring in experiments at about 5 eV, corresponds in the *GW* RA spectrum to a dip at about 4.7 eV (the one in the LDA spectrum is located at 3.9 eV).

The agreement between theory and experiment is clearly improved; however, some discrepancies remain both in energy position and line shape. They may be ascribed to effects which have been neglected in the calculation, as dynamical self-energy effects on the dielectric function [29,30], the difference between QP and DFT-LDA wave

functions, and, more importantly, to electron-hole interaction and local-field effects. These effects strongly distort the absorption spectra of clusters and bulk semiconductors and are expected to do so also at surfaces [31,32].

In conclusion, we have carried out a well-converged calculation of the electronic structure and of the reflectance anisotropy of GaAs(110) within the *GW* approximation. We have shown that filled bands undergo downward self-energy corrections which depend on their localization at the surface, and empty bands undergo an almost constant upward shift. We find very good agreement with direct and inverse photoemission measurements and a (almost linear) relation between surface localization and quasiparticle shifts. This last feature has allowed us to calculate a well-converged RA spectrum.

The calculated reflection anisotropy line shape turns out to be quantitatively different from the DFT-LDA line shape, as a consequence of the deviation of actual QP corrections from the SO scheme. The positions of the main features in the experimental spectrum are underestimated by more than 0.5 eV by LDA, but correctly reproduced by the *GW* calculation. The remaining discrepancies may probably be eliminated by the inclusion of excitonic and local-field effects. If this situation will also be confirmed for other surfaces, *ab initio* calculations will soon replace semiempirical ones as state of the art in the theory of surface optical properties.

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