

Review Article

Calculation of reflectance anisotropy for semiconductor surface exploration

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Reflectance anisotropy spectroscopy (RAS) is exquisitely sensitive to probe surfaces, with many potential applications in determining surface geometries or monitoring material growth. Thanks to recent computational and methodological progress it has now become possible to calculate surface optical spectra accurately and with true predictive power. Here I review briefly the simulation of RAS spectra and discuss recent methodological advances, which allow for the modelling of self-energy, excitonic and local-field effects in large and complex systems. Numerical results for semiconductor surfaces in comparison to measured data are used to illustrate the potential and limits of the different levels of theory.

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1 Theory of reflectance anisotropy

Reflection anisotropy spectroscopy (RAS) is a non-destructive optical probe of surfaces that is capable of operation within a wide range of environments [1–3]. For a long time, however, a lack of adequate theoretical treatments presented a substantial barrier to the understanding and full exploitation of RAS spectra. This situation changed at the end of the nineties, when powerful computers allowed for the realistic modelling of the surface optical response from *first principles* [4–6]. This computational progress could build on substantial earlier efforts to understand the light-surface interaction, see, e.g., Refs. [7, 8]. Del Sole obtained an expression for the surface contribution [9] to the reflectance, $\Delta R/R$, where R is the

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reflectance according to the Fresnel equation. For s -light polarized along i and normal incidence it holds

$$\frac{\Delta R_i}{R}(\omega) = \frac{4\omega}{c} \Im \left\{ \frac{\Delta \varepsilon_{ii}(\omega)}{\varepsilon_b(\omega) - 1} \right\}, \quad (1)$$

where ε_b is the bulk dielectric function, and

$$\begin{aligned} \Delta \varepsilon_{ij} = & \int dz dz' [\varepsilon_{ij}(\omega; z, z') - \delta_{ij} \delta(z - z') \varepsilon_0(\omega; z)] \\ & - \int dz dz' dz'' dz''' \varepsilon_{iz}(\omega; z, z') \varepsilon_{zz}^{-1}(\omega; z', z'') \varepsilon_{zj}(\omega; z'', z'''). \end{aligned} \quad (2)$$

Here $\varepsilon_{ij}(\omega; z, z')$ is the non-local *macroscopic* dielectric tensor of the solid-vacuum interface accounting for all many-body and local-field effects [10]. Equation (2) can be evaluated by replacing the semi-infinite crystal by an artificial super-cell, large enough to represent the vacuum as well as the surface and bulk regions of the crystal under investigation. Provided that (i) the material slab is large enough to properly describe the surface region of the crystal, i.e., the surface as well as surface-modified bulk wave-functions and (ii) the off-diagonal terms of the dielectric tensor are small compared to the diagonal ones, a simple expression for the surface contribution to the reflectivity can be derived [11]

$$\frac{\Delta R_i}{R}(\omega) = \frac{4\omega}{c} \Im \left\{ \frac{4\pi \alpha_{ii}^{hs}(\omega)}{\varepsilon_b(\omega) - 1} \right\}. \quad (3)$$

Here $\alpha_{ii}^{hs}(\omega)$ with $i = x, y$ is the diagonal tensor component of the averaged half-slab polarizability. Under the conditions mentioned above, Eq. (3) contains in principle *all* surface contributions to the optical reflectance. Of course, it is not an easy task to include all these contributions in practical calculations of the slab polarizability.

Before discussing the numerical calculation of α , it is in order to mention one point concerning the comparison with experimental data. Optical reflectance or reflectivity is defined as the square of the modulus of the reflection amplitude, $R = |r|^2$, i.e., it gives the ratio of the reflected to incident beam intensity. Care is required here, because the use of R and r is sometimes reversed. Most experimentalists publish spectra of the real part of the reflection amplitude, $\Re(\Delta r/r)$. These are sometimes directly compared with calculations for $\Delta R/R$. This leads to seemingly overestimated anisotropies, since

$$\begin{aligned} \Re \left\{ \frac{\Delta r}{r} \right\} &= 2 \Re \left\{ \frac{r_x - r_y}{r_x + r_y} \right\} = 2 \frac{|r_x|^2 - |r_y|^2}{|r_x|^2 + |r_y|^2 + 2 \Re \{ r_x r_y^* \}} \\ &\approx \frac{|r_x|^2 - |r_y|^2}{|r_x|^2 + |r_y|^2} = \frac{R_x - R_y}{R_x + R_y} = \frac{1}{2} \frac{\Delta R}{R}. \end{aligned} \quad (4)$$

Here I used $r_x r_y^* = |r|^2 - \frac{1}{4} |\Delta r|^2 \approx |r|^2 = R$.

2 Numerical implementation and examples

2.1 Three-step approach to calculate the optical response

The state-of-the-art approach to the microscopic calculation of the slab polarizability consists of three steps. (i) At first the structurally relaxed ground state of the system is calculated, most often within density functional theory (DFT) employing either the local density approximation (LDA) or the generalised gradient approximation (GGA) for the description of the electron exchange and correlation interaction. These calculations yield the eigenenergies and eigenfunctions used to represent the one- and two-body Green's functions. At this stage optical properties can be calculated within the so-called independent-particle approximation (IPA) (see, e.g., Ref. [12]). Quantitatively, however, the description of the reflectance anisotropy based on IPA calculations is not reliable. Often a red-shift of the calculated RAS spectra

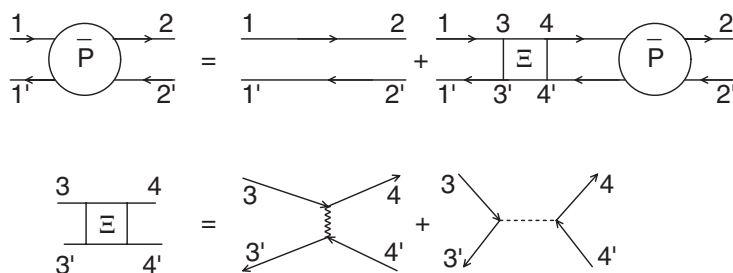


Fig. 1 Diagrammatic representation of the Bethe–Salpeter equation. The macroscopic polarization is related to the polarization of independent particles (lines $1 \rightarrow 2$ and $1' \rightarrow 2'$) and an interaction kernel Ξ containing the screened electron–hole attraction (wiggled line) and the unscreened electron–hole exchange (dashed line).

in comparison to experiment is observed that results from the band gap problem in DFT calculations [13]. Also the line shape is often not correctly described. (ii) To correct for this, in the second step the quasiparticle character of the electrons is taken into account. Thereby the electronic self-energy is usually obtained within the GW approximation (GWA), which accounts for the discontinuity of the electron–electron exchange and correlation energy on addition of an electron, and allows for calculating accurate single-quasiparticle spectra. RAS spectra obtained in this so-called independent quasiparticle approximation (IQA) often agree much better with experiment than the IPA results. This has been shown, e.g., for GaAs(110) [14], InP(001) [15] and GaP(001) surfaces [16]. In other instances, however, the IQA results are less satisfactory. Sometimes the excitation energies are noticeable overestimated and the calculated line shapes deviate considerably from experiment. One reason for this is the complete neglect of electron–hole interaction. For Si(111), Ge(111) and diamond(001) surfaces, surface excitons with binding energies of up to 0.9 eV exist [17–19]. In these cases the existence of bound surface states energetically well separated from the edges of the bulk band structure leads to an enhancement of the electron–hole interaction, simply because of the spatial confinement. There are also cases in which strong excitonic effects in the bulk optical properties show up in the surface optical response. Examples are the Si(001):H surface [20, 21], and the passivated Si(110) surface [22]. In such cases it is inevitable to go beyond the approximation of independent (quasi) particles and to account for the electron–hole attraction. (iii) This leads to the third step of the calculation of the slab polarizability, where the screened electron–hole attraction and the unscreened electron–hole exchange are obtained from the solution of the Bethe–Salpeter equation (BSE) for the macroscopic polarization. From the BSE (shown schematically in Fig. 1) the linear optical spectrum including the effects of many-body electron–electron and electron–hole interaction is obtained.

The three-step approach described above allows for an accurate *ab initio* description of surface optical properties. No assumption about the atomic configuration or the electronic properties of the system needs to be made; they are calculated self-consistently and without any input from experiment. However, the numerical effort is considerable. Even with today's powerful supercomputers it may take weeks or months to perform GW calculations or solve the BSE for medium-size surface unit cells. For very large surface reconstructions it will be impossible for the mid-term future. IPA calculations will remain state-of-the-art for many systems. Below I sketch the methodology that has been developed in the solid-state theory groups in Raleigh (North Carolina) [23] and Jena (Germany) [24] to calculate linear optical properties. Examples for numerical results obtained on the IPA, IQA and BSE levels of theory for semiconductor surface optical anisotropies are discussed in order to illustrate the potential and limits of the respective approaches.

2.2 Independent-particle approximation

We start from *first-principles* pseudopotential calculations based on a massively parallel real-space finite-difference DFT implementation [25]. A multigrid technique is used for convergence acceleration.

From the DFT calculations Bloch band eigenfunctions $|n\mathbf{k}\rangle$ are obtained, characterized by band index n and wave vector $\mathbf{k}$ in the first Brillouin zone (BZ), with energy eigenvalues $\varepsilon_n(\mathbf{k})$. For semiconducting systems where the Bloch states have either the occupancy 0 for conduction bands, $n = c$, or 1 for valence bands, $n = v$ one obtains in the optical limit of vanishing wave vector $\mathbf{q} \rightarrow 0$ the IPA microscopic dielectric tensor [12, 26–28]

$$\begin{aligned}\varepsilon_{ij}(\omega) &= \delta_{ij} + 4\pi\alpha_{ij}(\omega) \\ &= \delta_{ij} + \frac{16\pi e^2 \hbar^2}{\Omega} \sum_{\mathbf{k}} \sum_{c,v} \frac{\langle c\mathbf{k} | v_i | v\mathbf{k} \rangle \langle v\mathbf{k} | v_j | c\mathbf{k} \rangle}{[\varepsilon_c(\mathbf{k}) - \varepsilon_v(\mathbf{k})][\varepsilon_c(\mathbf{k}) - \varepsilon_v(\mathbf{k}) - \hbar^2[\omega + i\eta]^2]}.\end{aligned}\quad (5)$$

Practical calculations are carried out using the simple replacement $\mathbf{v} = \mathbf{p}/m = \frac{\hbar}{im}\nabla$ for the calculation of the matrix elements. This neglects the influence of the non-locality of the pseudopotentials on the dielectric function. However, it turns out that the non-local effects, although appreciable in size (5–10%) if single matrix elements are considered, do not affect much the spectral shape of the dielectric function. Their influence can be completely neglected in the calculation of the surface optical anisotropy [29], because RAS spectra are difference spectra, normalised furthermore to the bulk dielectric function. The calculation of the gradient, however, needs to be performed with care, since the numerical differentiation easily leads to an artificial roughening of the function and thus to numerical noise. In order to obtain numerically converged results for the derivative of the wave functions, a high-order scheme was implemented. Specifically, given the mesh spacing $h = x_{i+1} - x_i$ in x direction,

$$\begin{aligned}\frac{\partial}{\partial x} f(x_i, y_j, z_k) &= \frac{1}{60h} \{45[f(x_{i+1}, y_j, z_k) - f(x_{i-1}, y_j, z_k)] \\ &\quad - f[f(x_{i+2}, y_j, z_k) - f(x_{i-2}, y_j, z_k)] + f(x_{i+3}, y_j, z_k) - f(x_{i-3}, y_j, z_k)\} + O(h^6)\end{aligned}\quad (6)$$

and equivalent formulations for the partial derivatives with respect to y and z are used.

RAS calculations on the IPA level of theory have contributed substantially to the present detailed understanding of many semiconductor surface structures. Thereby the identification of the surface geometry rests on the comparison of measured RAS data with simulations for candidate structures. The long-standing problem of determining the geometry of the (3×2) reconstructed (001) surface of β -SiC is one impressive example in this context. While total-energy calculations, electron diffraction experiments and scanning tunnelling microscopy failed to give a clear answer concerning the structure of this surface, the comparison of measured and simulated RAS spectra (cf. Fig. 2) gave a strong indication for the formation of the two-adlayer asymmetric-dimer model (TAADM) reconstruction [31]. This model was subsequently confirmed by grazing-incidence X-ray diffraction [32] and is now well accepted in the community. Similarly successful examples for the application of RAS to the surface structure determination include the (001) surfaces of InP [33], GaP [34] and GaAs [35–37]. RAS calculations on the IPA level of theory gave indications for the atomic structures of steps on Si(111) [38] and Si(001) surfaces [39] and allowed for the verification of structural models proposed for In nano-wires on Si(111) [40]. More recently, they were used to explore the adsorption of organic molecules [41–43] or water on semiconductor surfaces [44], the long-standing problem of Si(001) surface oxidation [6, 45, 46] as well as compound semiconductor surfaces in gas-phase epitaxy conditions [47, 48].

The physical origin of optical anisotropies has been controversially discussed for a long time, see, e.g., Refs. [49–54]. IPA calculations were very helpful to resolve this issue by using a layer-by-layer analysis of the reflectance anisotropy [33, 34, 55, 56] and by singling out contributions from specific (surface) states to the RAS signal [4, 15]. These investigations have confirmed Aspnes and Studna, who discriminated in their pioneering work on reflectance anisotropy [57] between two components: “intrinsic” contributions from surface effects on bulk wave functions and “extrinsic” contributions related directly to the surface electronic states.

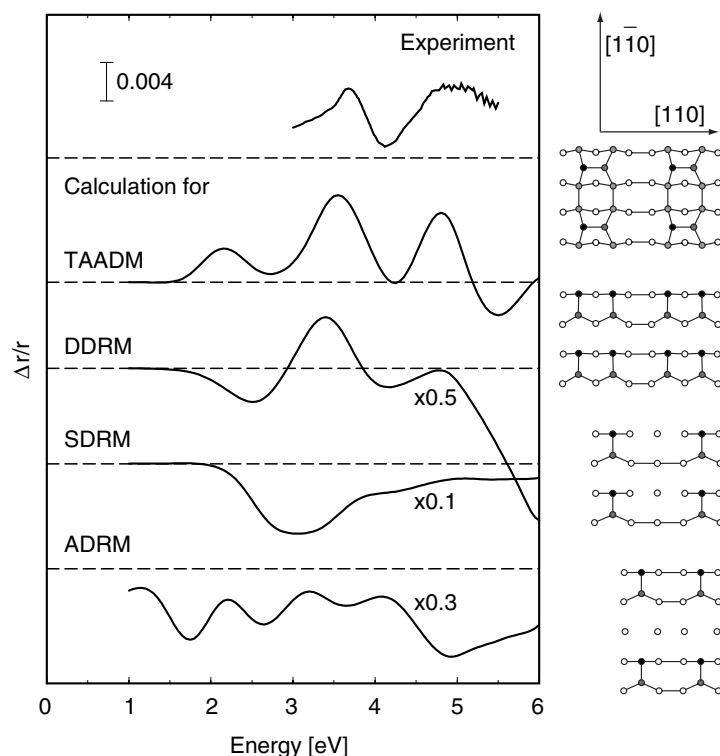


Fig. 2 RAS [$\Re\{(r_{[110]} - r_{[1\bar{1}0]})/\langle r \rangle\}$] calculated for different structural models of the Si-rich (001) surface of β -SiC (shown in the right panel) are compared with the measured data from Ref. [30]. The zero line in each spectrum is indicated by a horizontal dashed line. Data from Ref. [31].

Qualitative trends, for example with respect to the influence of surface electric fields [61] or the surface chemistry – such as the density of cation–cation bonds – are most often correctly described by RAS calculations [34, 33] on the IPA level of theory. As an example we show in Fig. 3 RAS spectra measured and calculated (within IPA) for InP(001) (2×4) surface reconstructions [33]. The spectra measured by Ozanyan and co-workers [58] for temperatures between 470 and 590 °C show a distinct temperature dependence: The 590 °C spectrum shows a pronounced negative anisotropy around 1.7 eV, which gradually disappears with decreasing temperature. At the same time the positive anisotropy at 2.6 gains strength and the “three-buckle” shape flattens between 3.5 and 4.5 eV, resulting in a “camel-back” overall spectrum shape. Ref. [58] explains these spectral changes as due to the transition from a In-rich surface to a less In-rich stoichiometry. The assumption of a stoichiometry-related RAS is backed by the works of Zorn et al. [62] and Postigo and co-workers [63], who observe similar modifications in their RAS spectra measured at varying phosphorus partial pressure. For comparison, we also show a room temperature (RT) spectrum measured by Kinsky and co-workers [59] at an In-rich InP(001) surface. While the overall line shape is very similar to the corresponding high-temperature spectrum of the In-rich surface, a small blue-shift of about 0.1–0.2 eV, together with sharpened and increased anisotropies occurs. In the lower panel of Fig. 3 the RAS spectra calculated for four structural models of InP(001) (2×4) [60] are shown. A strong negative anisotropy around 1.7 eV occurs for the mixed-dimer model, which contains six In–In bonds along the [110] direction in the surface atomic layer. The strength of this anisotropy is strongly reduced for the top-P-dimer model with four In–In bonds and even weaker in case of the α structure with two In–In bonds. The $\beta 2$ structure, which does not contain any In–In bonds shows no negative anisotropy at all. Thus the negative anisotropy below 2 eV seems to be related to the existence of cation–cation bonds. This supports the interpretation of the experimental spectra discussed above and is similar to earlier theoretical findings for the GaAs(001) surface [64, 65].

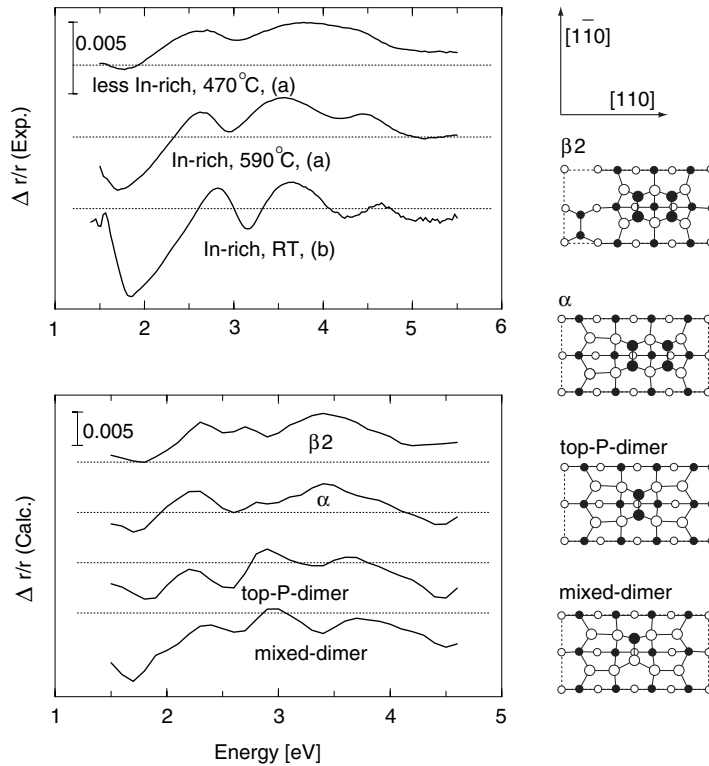


Fig. 3 RAS [$\Re\{(r_{\bar{1}10} - r_{110})/\langle r \rangle\}$] for InP(001) (2×4) surfaces. Upper left panel: Measured data from Refs. [58] (a) and [59] (b). Lower left panel: Data calculated for structural models of the InP(001) (2×4) surface shown in the right panel [60]. The zero line in each spectrum is indicated by a horizontal dotted line. Data from Ref. [33].

Note the different energy scale for calculated and measured spectra in Fig. 3. The red shift of the calculated spectra in comparison to experiment is an expression of the well-known band gap problem in DFT calculations [13]. To correct for this, one needs to go beyond the IPA and to take the quasiparticle character of the electrons into account. This leads to the second step of the approach of calculating the slab polarizability.

2.3 Independent-quasiparticle approximation

On the IQA level of theory electronic self-energy effects are included by post-processing the DFT results. The local exchange and correlation potential $V^{\text{xc}}(\mathbf{r})$ is replaced by the nonlocal and energy-dependent self-energy operator $\Sigma(\mathbf{r}, \mathbf{r}'; E)$ [66]. For the calculation of Σ the GW approximation [67, 68] is used, where the self-energy operator is expressed as convolution $\Sigma = iGW$ of the dynamically screened Coulomb potential W and the single-particle propagator G . The calculation of surface optical spectra usually involves a very large number of electronic states. Therefore we introduced further approximations: The GW quasiparticle energies are obtained from the DFT eigenvalues in a perturbative manner by

$$\varepsilon_n(\mathbf{k})^{\text{QP}} = \varepsilon_n(\mathbf{k}) + \frac{1}{1 + \beta_{n,\mathbf{k}}} [\Sigma_{n,\mathbf{k}}^{\text{st}} + \Sigma_{n,\mathbf{k}}^{\text{dyn}}(\varepsilon_n(\mathbf{k})) - V_{n,\mathbf{k}}^{\text{xc}}], \quad (7)$$

where the self-energy operator Σ has been divided into static (st) and dynamic (dyn) contributions. Indices at Σ and V^{xc} indicate diagonal matrix elements with the respective wave functions. $\beta_{n,\mathbf{k}}$ is the

linear coefficient in the expansion of Σ^{dyn} around the DFT eigenvalue $\varepsilon_n(\mathbf{k})$. The static part is split into two parts

$$\begin{aligned}\Sigma^{\text{st}}(\mathbf{r}, \mathbf{r}') = & \frac{1}{2} \sum_{n, \mathbf{k}} \psi_{n, \mathbf{k}}(\mathbf{r}) \psi_{n, \mathbf{k}}^*(\mathbf{r}') [W(\mathbf{r}, \mathbf{r}'; 0) - v(\mathbf{r} - \mathbf{r}')] \\ & - \sum_{v, \mathbf{k}} \psi_{v, \mathbf{k}}(\mathbf{r}) \psi_{v, \mathbf{k}}^*(\mathbf{r}') W(\mathbf{r}, \mathbf{r}'; 0),\end{aligned}\quad (8)$$

representing the Coulomb hole Σ^{COH} and the screened exchange Σ^{SEX} . The $\psi_{n, \mathbf{k}}$ are the DFT-LDA wave functions. Σ^{SEX} contains a sum over the occupied valence states v only. The major bottleneck in the GW calculation is the computation of the screened interaction W . An extreme speedup can be achieved by using a model dielectric function. We use the version suggested by Bechstedt et al. [69]

$$\varepsilon(\mathbf{q}, \rho) = 1 + \left[(\varepsilon_\infty - 1)^{-1} + \left(\frac{q}{q_{\text{TF}}(\rho)} \right)^2 + \frac{3q^4}{4k_F^2(\rho)q_{\text{TF}}^2(\rho)} \right]^{-1}, \quad (9)$$

where k_F and q_{TF} represent the Fermi and Thomas-Fermi wave-vectors, respectively, which depend on the electron density ρ . Together with the LDA-like ansatz of Hybertsen and Louie [70] for approximating the spatial dependence of the screening of the inhomogeneous system

$$W(\mathbf{r}, \mathbf{r}'; 0) = \frac{1}{2} [W^h(\mathbf{r} - \mathbf{r}, \rho(\mathbf{r})) + W^h(\mathbf{r} - \mathbf{r}, \rho(\mathbf{r}'))] \quad (10)$$

by that of a homogeneous electron gas W^h , Eq. (9) allows for an analytic solution for Σ_{COH} . The static Coulomb hole contribution to the self-energy takes the form of a local potential

$$\Sigma^{\text{COH}}(\mathbf{r}) = -\frac{q_{\text{TF}}(\mathbf{r})}{2} \sqrt{1 - \frac{1}{\varepsilon_\infty}} \left[1 + \frac{q_{\text{TF}}(\mathbf{r})}{k_F(\mathbf{r})} \sqrt{\frac{3\varepsilon_\infty}{\varepsilon_\infty - 1}} \right]^{-\frac{1}{2}}, \quad (11)$$

where k_F and q_{TF} are computed at the local density $\rho(\mathbf{r})$.

The matrix elements $\Sigma_{n, \mathbf{k}}^{\text{SEX}}$ are calculated in reciprocal space. However, only the diagonal elements in the Fourier transform of W are retained and its nonlocality is approximated by using state-averaged electron densities

$$\rho_{n, \mathbf{k}} = \int d\mathbf{r}^3 \rho(\mathbf{r}) |\psi_{n, \mathbf{k}}(\mathbf{r})|^2, \quad (12)$$

in the calculation of k_F and q_{TF} [69]. Finally, the dynamic terms $\beta_{n, \mathbf{k}}$ and Σ^{dyn} in (7), are approximated by integrals of the dielectric function (9) assuming a single plasmon-pole to describe the frequency dependence. Local-field effects are again included using the mean-density approximation (12). The integrals are numerically evaluated for a dense sampling of ρ and the results for $\beta_{n, \mathbf{k}}(\rho)$ and $\Sigma^{\text{dyn}}(\rho)$ are fitted to polynomials. These are then used for a fast computation of the dynamic contributions to the self-energy during the actual GW calculations. For several III–V compounds and their surfaces this approximate treatment of self-energy corrections has been shown to result in excitation energies which are within about 0.1 eV of the experimental values [15, 16, 71].

The effect of quasiparticle corrections on RAS spectra is demonstrated here for the case of the GaP(001)(2 × 4) mixed-dimer reconstruction [16]. Figure 4 shows a comparison between experiment and IPA (DFT-LDA) as well IQA (GW) theory. The calculated contributions to the RAS have been classified with respect to their spatial origin. The dashed curves in Fig. 4 show the anisotropy due to transitions between the electronic states localised below the top four atomic layers. They give rise to strong anisotropies for high photon energies. In particular, a feature occurs near the calculated E'_0 energy of the GaP bulk band structure. This bulk related feature depends only weakly on the actual surface structure. Ex-

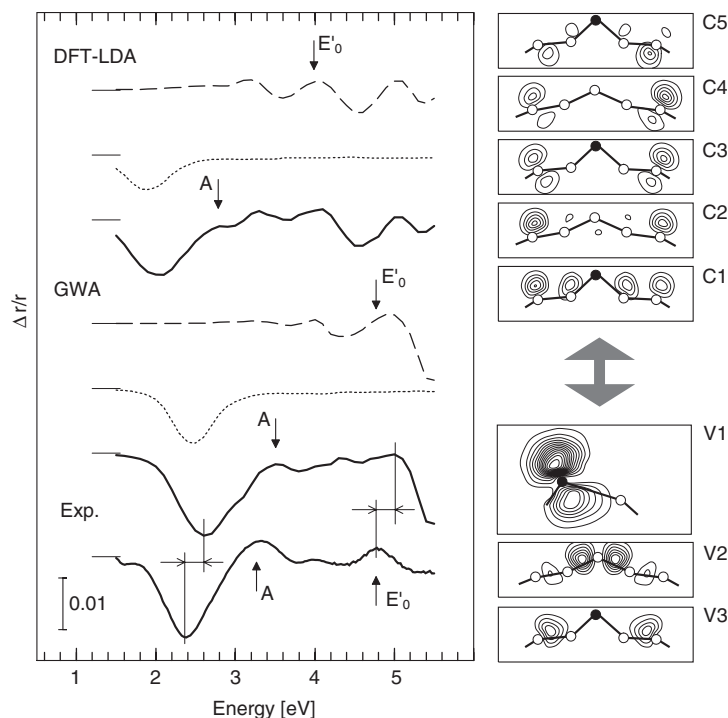


Fig. 4 RAS [$\Re\{(r_{\perp 101} - r_{\parallel 101})/\langle r \rangle\}$] calculated within IPA/IQA (DFT-LDA/GWA) for the mixed-dimer structure of the GaP(001) (2×4) surface are compared with the measured data [34]. The calculated/measured positions of E'_0 are indicated. Dashed and dotted lines show RAS contributions from transitions between bulk states and the surface electronic states shown in the right panel, respectively. Solid lines represent the calculations for the complete slab. Data from Ref. [16].

perimentally, the maximum at the E'_0 CP was found irrespective of the surface preparation conditions [34, 72].

On the other hand, strong anisotropies in the low-energy part of the spectrum arise from transitions between surface localised states (dotted lines, right panel in Fig. 4). In particular transitions between Ga-Ga bond-related states and empty Ga dangling bonds cause a strong negative anisotropy around 2 eV. The optical anisotropy calculated for the complete slab (solid lines in Fig. 4) corresponds roughly to a superposition of the bulk- and surface-related features.

If the two sets of theory data in Fig. 4 – DFT-LDA and GWA – are compared, a distinct blue-shift of the spectrum upon inclusion of self-energy effects is observed. However, the shift is non-uniform: it amounts to about 0.6 eV for the surface-state related features (dotted lines) and 0.8–1.0 eV for the bulk-related ones (dashed lines). This agrees with a study by Hybertsen and Louie [73] who found that, depending on their orbital character, surface states may actually be less affected by self-energy effects than bulk states. The non-uniformity of the calculated quasiparticle shifts agrees with experiment: As indicated by the arrows in the lower part of Fig. 4, the energy shift between the measured data and the spectrum calculated in GWA is nearly constant and amounts to about 0.3 eV. The inclusion of self-energy effects in the calculations does not only lead to energy shifts, but also to pronounced changes in the line shape. The weak shoulder *A* at 2.8 eV in the DFT-LDA spectrum develops into a maximum at 3.5 eV, in good agreement with experiment.

While the agreement between the measured and the calculated spectra improves much upon inclusion of GW corrections, the agreement is certainly not perfect on the IQA level of theory. In particular a blue-shift of the calculated data in comparison to experiment is noted. One reason for this is the still missing contribution from excitonic effects.

2.4 Local fields and electron–hole attraction

Excitation energies obtained within the quasiparticle formalism describe one-particle excitations, such as involved in direct or inverse photoemission experiments. For the description of the optical absorption process, however, one needs to go beyond this single-quasiparticle level. The polarization function $\bar{P}$ including electron–hole attraction and local-field effects (or electron–hole exchange) can be obtained from the solution of the Bethe–Salpeter equation (shown schematically in Fig. 1) [74–77]),

$$\bar{P} = P_0 + P_0(\bar{v} - W)\bar{P}, \quad (13)$$

where $\bar{v}$ is the bare Coulomb potential without its long-range part and P_0 represents the polarization function in IQA. The macroscopic polarizability is obtained from the diagonal part of $\bar{P}$. For practical calculations, the BSE is transformed into a two-particle Schrödinger equation. Neglecting non-resonant contributions [78], dynamical screening and umklapp processes, the exciton Hamiltonian for direct transitions and spin-singlets can be calculated in reciprocal space according to

$$\begin{aligned} \hat{H}_{vck,v'c'k'}^{\text{res}} = & (\varepsilon_c^{\text{OP}}(\mathbf{k}) - \varepsilon_v^{\text{OP}}(\mathbf{k})) \delta_{vv'} \delta_{cc'} \delta_{kk'} \\ & + \frac{4\pi}{\Omega} \sum_{\mathbf{G}, \mathbf{G}'} \left\{ 2 \frac{\delta_{\mathbf{GG}'}(1 - \delta_{\mathbf{G}0})}{|\mathbf{G}|^2} B_{cv}^{kk}(\mathbf{G}) B_{c'v'}^{k'k'*}(\mathbf{G}) \right. \\ & \left. - \frac{\varepsilon^{-1}(\mathbf{k} - \mathbf{k}' + \mathbf{G}, \mathbf{k} - \mathbf{k}' + \mathbf{G}', 0)}{|\mathbf{k} - \mathbf{k}' + \mathbf{G}|^2} B_{cc'}^{kk}(\mathbf{G}) B_{vv'}^{k'k'*}(\mathbf{G}') \right\}, \end{aligned} \quad (14)$$

where the Bloch integral

$$B_{mv'}^{kk'}(\mathbf{G}) = \frac{1}{\Omega} \int d\mathbf{r} u_{nk}^*(\mathbf{r}) e^{i\mathbf{G}\mathbf{r}} u_{n'k'}(\mathbf{r}) \quad (15)$$

over the periodic parts u of the Bloch wave functions has been introduced and Ω denotes the volume of the unit cell [79, 80]. We replace the inverse dielectric matrix ε^{-1} by the same diagonal model dielectric function (9) that has been used in the calculation of the self-energy operator. The influence of the off-diagonal elements is again approximated by using state-dependent electron densities in (9), which were calculated using the mean-density approximation (12). From the eigenvectors $|A^\lambda\rangle$ and eigenvalues E_λ of the exciton Hamiltonian

$$\hat{H} |A^\lambda\rangle = E_\lambda |A^\lambda\rangle, \quad (16)$$

the diagonal components of the macroscopic polarizability are given by

$$\begin{aligned} \alpha_{jj}^M(\omega) = & \frac{4e^2\hbar^2}{\Omega} \sum_{\lambda} \left| \sum_{\mathbf{k}} \sum_{c,v} \frac{\langle c\mathbf{k} | v_j | v\mathbf{k} \rangle}{\varepsilon_c(\mathbf{k}) - \varepsilon_v(\mathbf{k})} A_{vck}^\lambda \right|^2 \\ & \times \left\{ \frac{1}{E_\lambda - \hbar(\omega + i\gamma)} + \frac{1}{E_\lambda + \hbar(\omega + i\gamma)} \right\}, \end{aligned} \quad (17)$$

where v_j is the corresponding Cartesian component of the single-particle velocity operator and γ the damping constant. Here, the contributions of the anti-resonant part of the exciton Hamiltonian have been formally included, while the coupling parts are neglected.

The dimension of the exciton Hamiltonian $N = N_v \cdot N_c \cdot N_k$ is about $10^5 \dots 10^6$ already for the relatively small unit cell of an unreconstructed surface. Even with today's powerful supercomputers, the diagonalization of matrices of this size, which scales as $\mathcal{O}(N^3)$, is prohibitively slow.

Therefore, we formulate the calculation of the ω -dependent polarizability as an initial-value problem. If a vector $|\mu^j\rangle$ of dipole moments with elements

$$\mu_{vck}^j = \frac{\langle c\mathbf{k} | v_j | v\mathbf{k} \rangle}{\varepsilon_c(\mathbf{k}) - \varepsilon_v(\mathbf{k})} \quad (18)$$

is introduced, Eq. (17) takes the form

$$\alpha_{ij}^M(\omega) = \frac{4e^2\hbar^2}{\Omega} \sum_{\lambda} |\langle \mu^j | A^{\lambda} \rangle|^2 \left\{ \frac{1}{E_{\lambda} - \hbar(\omega + i\gamma)} + \frac{1}{E_{\lambda} + \hbar(\omega + i\gamma)} \right\}. \quad (19)$$

This is equivalent to the Fourier representation

$$\alpha_{ij}^M(\omega) = \frac{4e^2\hbar^2}{\Omega} i \int_0^{\infty} dt e^{i(\omega + i\gamma)t} \{ \langle \mu^j | \xi^j(t) \rangle - \langle \mu^j | \xi^j(t) \rangle^* \}, \quad (20)$$

where the time evolution of the vector $|\xi^j(t)\rangle$ is driven by the pair Hamiltonian

$$i\hbar \frac{d}{dt} |\xi^j(t)\rangle = \hat{H} |\xi^j(t)\rangle \quad (21)$$

and the initial vector elements are given by

$$|\xi^j(0)\rangle = |\mu^j\rangle. \quad (22)$$

We solve the initial-value problem defined by (21) and (22) using the central-difference method which obtains $|\xi(t_{i+2})\rangle$ from $|\xi(t_i)\rangle$ and $|\xi(t_{i+1})\rangle$ by an explicit scheme

$$\hat{H} |\xi(t_{i+1})\rangle = i\hbar \frac{|\xi(t_{i+2})\rangle - |\xi(t_i)\rangle}{2\Delta t}. \quad (23)$$

This procedure only requires one matrix-vector multiplication per time step. The stability of the difference scheme (23) requires that $\Delta t < \hbar / \|\hat{H}\|$. The upper limit of the Fourier integral (20) can be truncated, due to the exponential $e^{-\gamma t}$. Therefore, the number of time steps, i.e., matrix-vector multiplications, is nearly independent of the dimension of the system and governed by γ . Of the order of 10^3 time steps are typically required using a broadening parameter $\gamma = 0.1$ eV. The operation count for this method scales thus as $\mathcal{O}(N^2)$, compared to the $\mathcal{O}(N^3)$ for the matrix diagonalization. The cross-over point for the CPU time usage of both methods in our implementation is reached for a number of electron-hole pair states as low as about 2000. Moreover, the matrix-vector multiplications can be easily distributed on several processors of a parallel computer. Hence it is possible to include all relevant many-body effects from *first-principles* in numerical calculations of the surface optical response [22, 20].

Their influence on RAS spectra is demonstrated in Fig. 5 for the hydrogen-passivated Si(110) surface [22]. It is one of the first systems studied by RAS [57] and has become a calibration standard for RAS apparatus and a textbook example for surface optical properties [81]. Figure 5 contains the calculated RAS spectra [22] for the Si(110):H surface represented by a 12-layer slab. The DFT-LDA spectrum shows two strong positive RAS features near the E_1 and E_2 bulk critical point energies. However, the features are far too broad. Inclusion of quasiparticle effects in GW approximation leads to a blue-shift of the spectrum by about 0.6–0.7 eV and changes the line shape. In particular the anisotropy at the E_1 energy is enhanced compared to the DFT-LDA spectrum. The E_1 peak height relative to the E_2 anisotropy is still much smaller than measured, however. Local-field (LF) effects lead to surprisingly small changes of the spectrum. Rather than increasing the ratio of the E_1/E_2 peak heights, LF effects even lead to a small decrease. A drastic enhancement of the optical anisotropy at the E_1 energy and a red-shift of the entire spectrum by about 0.1–0.2 eV result, however, from the inclusion of the attractive electron-hole interaction. This is shown by the uppermost spectrum in Fig. 5. Also the characteristic negative anisotropy below the E_1 energy is enhanced by excitonic effects.

Although a substantial and systematic improvement of the calculated spectrum occurs upon inclusion of many-body effects, still no complete reproduction of the experiment [57] is possible. From numerical tests on the IPA level of theory [38], the remaining discrepancies can be traced to the insufficient k -point sampling and a slab which is too thin to allow for the complete description of the surface-perturbed bulk

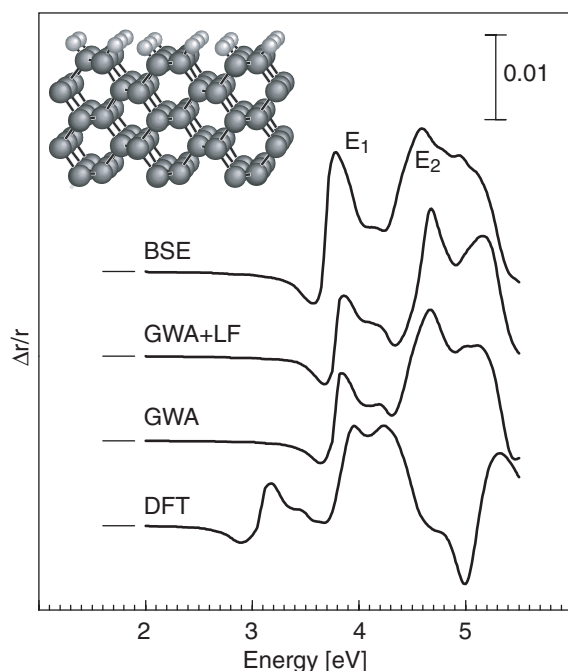


Fig. 5 RAS $[\Re\{(r_{[1\bar{1}0]} - r_{[001]})/\langle r \rangle\}]$ calculated for Si(110):H (shown schematically in inset) within IPA (DFT-LDA), in IQA (GWA), in IQA with the effects of local fields included (GW + LF), and from the solution of the BSE. Data from Ref. [22].

wave functions responsible for the observed optical anisotropies. This points to one major problem of the approach outlined above: It is still computationally very demanding. After the diagonalization of the exciton Hamiltonian has been bypassed, its calculation, although extremely sped up by using a model dielectric function, has become the numerical bottleneck. Possibly the formulation of the BSE as a boundary-value problem [82, 83] allows for computationally more efficient implementations.

3 Outlook

As shown above, the calculation of RAS spectra has made substantial progress in the last couple of years. The accuracy of the calculations allows now for a detailed understanding of the origin of surface optical anisotropies for many semiconductor surfaces. This includes contributions due to surface electronic states, atomic relaxations, the influence of the surface potential on the bulk wave-functions as well as surface LF effects and many-body effects such as the electronic self-energy and the electron-hole attraction. RAS calculation can now be used not only to explain *a posteriori* the origin of specific measured features, but are often very helpful in predicting surface geometries.

However, there remain challenging tasks. The methodology described above for calculating LF and many-body effects relies on a model dielectric function to describe screening effects. While this works well for systems with relatively small charge inhomogeneities, it seems to be questionable for systems with largely inhomogeneous screening, such as surfaces. While an *ab-initio* calculation of the screening for such cases is possible in principle, see, e.g. Refs. [19, 21], it is computationally very expensive and presents a series bottleneck for that kind of calculations. Time-dependent density-functional theory with new exchange-correlation kernels [84–86] may represent a promising alternative.

In the last few years the characterisation of metal surfaces by means of RAS has become immensely popular [3]. The theoretical modelling and interpretation of these results, however, is lagging behind. The few existing computational studies (see, e.g., Ref. [87]) are just beginning to achieve the level of accuracy that is established for semiconductor surfaces. More powerful computers enabling the careful evaluation of the intra-band (Drude tail) contribution to the dielectric functions may help to improve our understanding of metal surface optics.

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