

Role of Wave Functions in Electromagnetism: RAS from GaAs (110)

Abstract

We have calculated the reflectance anisotropy for the GaAs (110) surface using the discrete cellular method. This method extends the range of application of standard discrete dipole calculations by incorporating nonlocal polarizabilities. The method adds a second quantum mechanical channel of nonlocality, which turns out to be necessary and yields very good agreement between theory and experiment.

1 Introduction

Photons, electrons and nuclei are the fundamental (quasi)-particles making up the world around us. Maxwell and Schrödinger equations govern their behaviour. To be of any use photons need to interact with matter and that interaction is taken into account classically through the macroscopic Maxwell equations and some kind of dielectric function. It is an intriguing question whether the electrons, which are the most prominent actor in the interaction, have a more exciting role than the linear homogeneous, isotropic one they are forced to play in the classical treatment. Such behaviour seems to be confirmed by the success of the simple macroscopic theory in the classical optical regime.

The reason of that success is cancellation. The simplest possible microscopic model for the dielectric function is Clausius-Mossotti (CM). This model represents a homogeneous continuum by an infinite simple cubic lattice of (independent) discrete dipoles. In this model all short range dipole-dipole interactions cancel on symmetry grounds. So the electromagnetic interaction, apart from some far field Lorentz contribution, has become mute as a source of more interesting behaviour

The electromagnetic *short range* interaction can manifest itself only if CM-like conditions are absent, like in non-cubic materials. The spatial dispersion phenomena found experimentally in cubic materials [1] also violate CM. At surfaces deviation from CM should be found in general, since symmetry gets broken there for geometry reasons. Especially there the short range electromagnetic interaction becomes manifest and can be tested directly. This makes these phenomena so exciting from the more fundamental point of view.

The difficult rigorous treatment of a semi-infinite lattice of dipoles is made tractable by the double cell method [2, 3]. This method improves previous approaches by Ewald and Litzman [4, 5] by taking into account time dependency, retardation effects and existence of the surface. Currently the discrete and continuum treatment of optics have been compared [6, 7], elucidating the nature of boundary conditions. Despite the improved mathematical

treatment, the *local* discrete dipole model has not been particularly successful in the description and interpretation of surface optical experiments [8], apart from trivial physical systems (solid noble gases, alkali-halogenides).

In these systems the assumption of *independently* polarizable entities, commonly made in dipole models, holds sufficiently well. We state that the failure of dipole models for other systems is due to a poor handling of short-range interactions, especially the fact that those short range interactions can be influenced directly by the wavefunction and require as a result explicit use of *nonlocal* polarizabilities.

The study of anisotropic surface optical properties (RAS (Reflectance Anisotropy Spectroscopy), differences in perpendicular reflectance from surfaces of cubic materials for different polarization) offers a unique opportunity to test this hypothesis. Mochán and Barrera [9] were already able to apply the *local* discrete dipole model successfully to the anisotropic reflectance of the Ge (110) surface, but at the expense of assigning two atoms to one dipole. To make the preferred assignment of one atom to one dipole work is only possible by invoking *nonlocal* polarisabilities, as we will show in this paper by focussing primarily on the correct prediction of (measured) intensities. We present the prescription how to calculate these non-local polarisabilities from first principles. We investigated the reflectance anisotropy of the GaAs (110) surface because of its rich spectroscopic structure.

2 Theory

In classical electrodynamics the induced charge and current density are the source terms. The continuity equation allows both to be derived from a single polarization density $\mathbf{P}(\mathbf{r}, t)$ without loss of generality. It can be obtained within first order linear-response theory from

$$\mathbf{P}(\mathbf{r}, \omega) = \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}', \omega) \cdot \mathbf{E}(\mathbf{r}', \omega). \quad (1)$$

Here $\mathbf{E}(\mathbf{r}, \omega)$ is the self-consistent perturbing electric field and $\chi(\mathbf{r}, \mathbf{r}', \omega)$ the nonlocal susceptibility. This kernel can be obtained within the scissors-operator approximation to the quasi-particle response theory [10, 11, 12] from LDA-type density-functional calculations. We define the susceptibility $\chi(\mathbf{r}, \mathbf{r}', \omega)$ according to

$$\begin{aligned} \chi(\mathbf{r}, \mathbf{r}', \omega) &= \frac{2e^2}{\omega^2 V_{BZ}^2} \sum_{if} \frac{\mathbf{j}_{if}(\mathbf{r}) \mathbf{j}_{fi}(\mathbf{r}')}{\epsilon_f - \epsilon_i - \hbar\omega^+} \\ \mathbf{j}_{if}(\mathbf{r}) &= -\frac{i}{2} (\psi_i^*(\mathbf{r}) \nabla \psi_f(\mathbf{r}) - \psi_f(\mathbf{r}) \nabla \psi_i^*(\mathbf{r})) \end{aligned} \quad (2)$$

where we corrected properly for the $\omega = 0$ singularity. We assumed adiabatic onset of the perturbation, and retained the conductivity sumrule. This induced polarization acts as source of electromagnetic radiation and contributes to the perturbing electric field,

$$\begin{aligned} \mathbf{E}(\mathbf{r}, \omega) &= \mathbf{E}^{ext}(\mathbf{r}, \omega) + \int d\mathbf{r}' f(\mathbf{r} - \mathbf{r}', \omega) \cdot \mathbf{P}(\mathbf{r}', \omega), \\ f_{\mu\nu}(\mathbf{r}, \omega) &= [k^2 \delta_{\mu\nu} + \nabla_\mu \nabla_\nu] \frac{\exp(ikr)}{4\pi\epsilon_0 r}, \end{aligned} \quad (3)$$

where the transfer kernel $f(\mathbf{r}, \omega)$ describes the retarded electromagnetic interactions ($\mu, \nu = x, y, z$) and $k = \omega/c$ and $r = |\mathbf{r}|$. Direct solution of the microscopic continuum equations is not tractable for surfaces. Discretisation, however, provides an appropriate way to reduce the effort. For the treatment of optical reflection, we model the microscopic polarization as a semi-infinite lattice of point-like dipoles. Each dipole represents the polarization in a particular cell V_i belonging to atom i . It is located at the atomic nucleus \mathbf{r}_i with dipole strength $\mathbf{p}_i(\omega) = \int_{V_i} d\mathbf{r} \mathbf{P}(\mathbf{r}, \omega)$. Assuming a uniform field $\mathbf{E}_i(\omega)$ within each cell V_i , the set of equations (1,3) becomes,

$$\begin{aligned}\mathbf{p}_i(\omega) &= \sum_j \alpha_{ij}(\omega) \cdot \left[\mathbf{E}_j^{\text{ext}}(\omega) + \sum_k f_{jk}(\omega) \cdot \mathbf{p}_k(\omega) \right], \\ \alpha_{ij}(\omega) &= \int_{V_i} d\mathbf{r} \int_{V_j} d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}', \omega)\end{aligned}\quad (4)$$

where the traditional *local* polarizabilities correspond to the case $i = j$ only. With the new *nonlocal* polarizabilities ($i \neq j$), the perturbing field (the quantity between square brackets in eq. (4)), will not only polarize cell i , but also its neighbouring cells. It is the wavefunction itself which has to be set responsible for this quantum mechanical type of nonlocality and results from the requirement that *the wavefunction needs to be continuous and differentiable across the cell boundary*. This quantum induction vanishes if the wavefunction becomes negligible at the cell boundary, as is the case e.g. for alkali-halogenides and solid noble gas systems. This explains in a very transparent way the success of local dipole calculations in such systems and its failure in case of covalent systems and metals.

The transfer tensors can be derived accordingly from eq. (3),

$$f_{ij}(\omega) = \begin{cases} f(\mathbf{r}_i, \mathbf{r}_j, \omega) & \text{for } i \neq j \\ \frac{V}{|V_i|} \alpha^{-1}(\omega) - \frac{1}{3\epsilon_0|V_i|} \left(\frac{\epsilon_r(\omega) + 2}{\epsilon_r(\omega) - 1} \right) - \frac{ik^3}{6\pi\epsilon_0} & \text{for } i = j. \end{cases} \quad (5)$$

For $\mathbf{r}_i = \mathbf{r}_j$ the point-dipole interaction becomes singular and we have to take the finite extent of the cells into account. We make use of the Lorentz field for a uniformly polarised medium with the same polarization density. This field is modified by the first two terms in the expression for f_{ii} , accounting for the deviation from the homogeneous system. The third term in the f_{ii} tensors accounts for the radiation losses and is called the Lorentz' damping term. Further $V = \sum_i V_i$ is the volume of the primitive cell, $\epsilon_r(\omega)$ is the experimentally observed relative dielectric function, and the mean polarizability $\alpha(\omega)$ of the primitive cell is obtained from $\alpha(\omega) = \sum_{i \in V_j} \alpha_{ij}(\omega)$

The technical advantage of using this discretization scheme is that we can use the double cell method [2, 3], which obtains the response of a semi-infinite crystalline system of interacting dipoles to a given incident field, $\mathbf{E}_i^{\text{ext}}(\omega) = \mathbf{E}_0 \exp(ik \cdot \mathbf{r}_i)$. The essence of the method is a decomposition of the system into a semi-infinite stack of dipole layers, each obeying parallel translational symmetry. To describe the response of the i^{th} layer, it suffices to consider a single characteristic dipole \mathbf{p}_i . For the first N_S layers of the surface the interaction between these characteristic dipoles is taken into account explicitly. All further layers can be treated by making use of just a few normal modes, because of bulklike symmetry. Normal modes

have been introduced by Litzman and Dub [4, 5], starting from the regular arrangement of bulk sites as $\mathbf{r}_{wW} = \mathbf{r}_w^B + W\mathbf{s}_3$, where \mathbf{s}_3 is a lattice vector controlling the stack sequence and \mathbf{r}_w^B locates a dipole within the bulk unit cell. The normal mode expansion is postulated as:

$$\mathbf{p}_{wW} = \sum_{m=1}^M \nu_m \mathbf{u}_{mw} e^{iW\mathbf{k}_m \cdot \mathbf{s}_3} \quad (6)$$

As for the local case the normal mode propagation vector given by $\mathbf{k}_m = \mathbf{k}_{\parallel} + q_m \mathbf{n}$ with \mathbf{n} the inward surface normal, and normal mode polarization vector \mathbf{u}_{mv} follow from the condition that

$$\| \mathbf{1} - \alpha_0^{-1} \mathbf{A}(\mathbf{k}_m) \mathbf{F}(\mathbf{k}_m) \| |\mathbf{u}| = 0 \quad (7)$$

This is the (square) bulk secular matrix. \mathbf{F} is the matrix of phase corrected sums of transfer tensors and $\mathbf{A}(\mathbf{k}_m)$ is a matrix, having sums of nonlocal polarizabilities (4) as its matrix elements. Both matrices are not square, different from the local case. Since these sums also contain \mathbf{k}_m dependent phase factors, the matrix $\mathbf{A}(\mathbf{k}_m)$ is an explicit function of \mathbf{k}_m , again different from the local case. Once the normal mode parameters are known, the free variables of the system, the normal mode strenght ν_m and the dipole strength's \mathbf{p}_i for the surface layer follow from the double cell interaction matrix,

$$\left\| \begin{array}{cc} \mathcal{M}_{SS} & \mathcal{M}_{SB} \\ \mathcal{M}_{BS} & \mathcal{M}_{BB} \end{array} \right\| \left\| \begin{array}{c} \mathbf{p}_i \\ \nu_m \end{array} \right\| = \left\| \begin{array}{c} \mathbf{A}(\mathbf{k}) \mathbf{E}_{Ext,i} \\ \mathbf{t}_n^T \mathbf{E}_{Ext}^B \end{array} \right\| \quad (8)$$

The components of this matrix are either the same as for the local case (BS and BB part) or constructed in a manner closely resembling the construction of (7). The S -part of the inhomogeneous vector now contains however an additional polarizability matrix $\mathbf{A}(\mathbf{k})$, due to a rearrangement of components, necessary because of nonlocality [2, 3]. Once the microscopic sources ν_m and \mathbf{p}_i are found, the remote fields and connected observables, such as reflection coefficients, can be found in exactly the same way as for the local case.

3 Results

The GaAs bulk and surface polarizabilities have been obtained from the single particle energies and wavefunctions using accurate periodic DFT-LDA calculations [13, 14]. In the bulk calculation we used a lattice constant $a = 5.613\text{\AA}$. The surface was modelled using a slab having 4 *Ga* and 4 *As*-layers, with the 1 *As* and 2 *Ga*-layers on top at surface reconstructed positions [15]. This slab has been made bulk terminated at the bottom by adding 2 *H*-layers and 2 *Ga* and 2 *As*-layers of frozen ion type to model the bulk Madelung potential. We used the scissors operator to fix the bulk(-like) band-gap to 1.52 eV. The cut-off range for the nonlocal polarizability was set to 7.93\AA , resulting in eight shells of neighbouring atoms. The self correction given in (5) deviates only slightly from the Lorentz field contribution, indicating that the bulk dielectric function is reproduced accurately. Due to the limited slab thickness, we used bulk values for $\alpha_{ij}(\omega)$ throughout the system except for i, j both top-layer atoms.

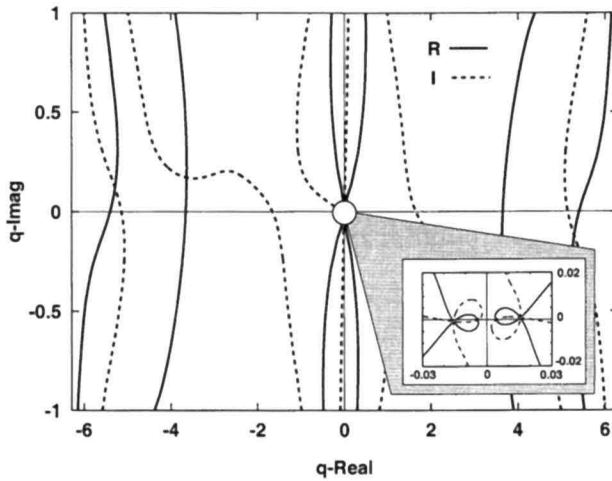


Figure 1: Zero-contours of real and imaginary part of the secular determinant at $\hbar\omega = 2.0\text{eV}$.

The first step in the dipole calculation is to obtain the normal modes. Fig. (1) shows the roots q_m of the secular determinant (7), at the intersections of the zero-contours of its real and imaginary parts. The figure has inversion symmetry and is periodic along the real axis, with period $2\pi/s_3 \cdot n$. The search can be restricted along the imaginary axis to some suitably chosen cutoff value for the damping. Very close to the origin (see inset) 4 solutions are found almost coinciding with the Fresnel values in addition to the two poles at $\pm k_z$. But there are also 4 other solutions for which damping is too small to be ignored. Since for surface calculations only modes with positive imaginary part are physically acceptable, we included 4 normal modes in the calculation.

We have examined in some detail the behaviour of the extra (non-Fresnel) normal modes. For very low frequencies the extra normal modes are exactly at the boundary of the Brillouin zone, but have enough damping to be ignored. Starting from 1.1 eV two definitely different extra normal modes move from the zone boundary towards the imaginary axis. They start as being perfectly transparent, one being purely transverse ($\mathbf{u} \cdot \mathbf{k}_m = 0$), the other having also a strong longitudinal component ($\mathbf{u} \cdot \mathbf{k}_m \neq 0$). So this mode has to affect also the bulk behaviour. All modes start to show a nonzero imaginary component starting from the bandgap at 1.5 eV. The extra modes preserve their transverse/longitudinal character, but they continue to move towards the imaginary axis, meanwhile getting more and more absorbing. Their influence can be discarded above 2.6 eV.

The extra normal modes are indispensable for the optical properties, both of surface and bulk. Good surface optical results require close to perfect matching of dipole strength's between surface and normal mode region. For $\hbar\omega = 1.9\text{eV}$ we show in fig. (2) the individual dipole strength's for polarization parallel to the $(1\bar{1}0)$ direction. The dipole strength varies clearly from a *Ga* to an *As* site, a variation controlled already by the Fresnel-type of normal mode. But there is also a weak modulation in dipole strength of both the *Ga* and *As* sites. This modulation extends further than the depth of the surface layer (indicated by the arrow),

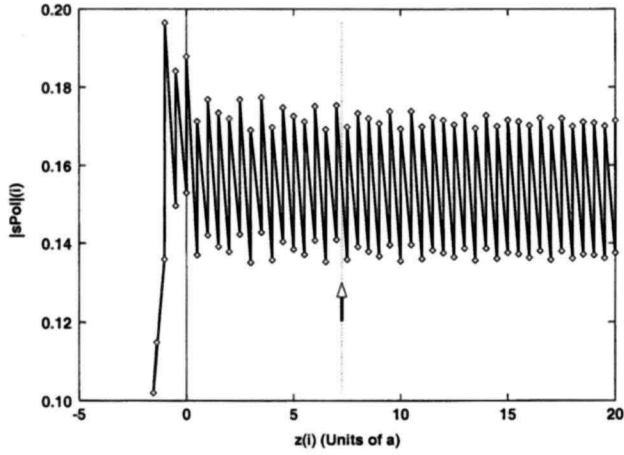


Figure 2: Modulus $|p_i|$ for $\phi = 0^\circ$ at $\hbar\omega = 1.9\text{ eV}$.

	Expt	LDA	f_{LDA}	GW	f_{GW}	DsC	f_{DsC}
P_1 (max)	0.00142	—	—	0.0019	1.34	0.00100	0.70
S (max)	0.00522	0.0045	0.86	0.0044	0.84	0.00525	1.01
P_2 (max)	0.00656	0.0103	1.57	0.0141	2.15	0.00561	0.86
E'_0 (max)	0.00569	0.0117	2.05	0.0144	2.53	0.00502	0.88
E_1 (min)	0.00131	-0.004	-3.05	-0.0022	-1.68	0.00314	2.40
E'_2 (min)	0.00067	0.0013	1.94	0.0044	6.57	0.00269	4.01

Table 1: Anisotropic reflectances $\Delta R/R$. LDA- and GW-type results from [16], DsC-type present results. Experimental data from [17]. f -factor = Theory/Experiment

into the bulk normal mode region, but almost vanishes at the right of the figure. This is the influence of the extra normal modes. Artificial removal of these modes strongly affects the anisotropic reflectance.

Reflectance anisotropy spectra have been measured recently very accurately by Esser et al. [17]. We have calculated the theoretical reflectance anisotropy for GaAs (110), using the previously outlined discrete cellular (DsC) method and used the convention

$$\Delta R/R = (\Delta R/R)_{[\bar{1}\bar{1}0]} - (\Delta R/R)_{[001]}. \quad (9)$$

Results of experiment and calculation are shown in table 1, comparing our results and the ones obtained by Pulci et al. [16]. We have used a background subtraction (bulk terminated GaAs) to account for the calibration of the experimental setup. The selected peak heights and minima have been labelled as in [16], but two prominent maxima have been labelled by us (P_1 at 1.7 eV and P_2 at 3.4 eV). The intensities of the three main maxima (S , P_2 and E'_0) are much better replicated by the DsC method, than by the continuum method used

in [16]. Also the negative value for the minimum at E_1 is positive in the DsC approach in agreement with experiment. The other features are too weak to be conclusive. Although the DsC calculations use a conventional energy shift of 0.40 eV for the *bulk*, the comparison with experiment suggests an additional shift of -0.3 eV for the *surface*. This means that the surface contribution is almost LDA-like. Pulci et al. found an additional surface shift of +0.3 eV. We emphasize that our results are ab-initio, except for the scissors energy shift and the self term f_{ii} in (5), which have been tuned using bulk optical data.

The calculated DsC spectra have the right sign and magnitude and reproduce remarkably well the spectral structure. In that aspect DsC-type of calculations are superior to LDA/GW schemes of calculation. It is our conclusion that the good agreement of the present calculations with experiment is sufficiently demonstrated. As such the main statement of this paper, that inclusion of (real space) local field effects in surface optics requires explicit inclusion of nonlocality in the polarizabilities. This conclusion should hold in general for the optics of inhomogeneous systems.

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