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Phil. Trans. R. Soc. Lond. A 1984 **313**, 221-227
doi: 10.1098/rsta.1984.0099

Phil. Trans. R. Soc. Lond. A **313**, 221–227 (1984)
Printed in Great Britain

Non-perturbative many-body theory of the optical nonlinearities in semiconductors

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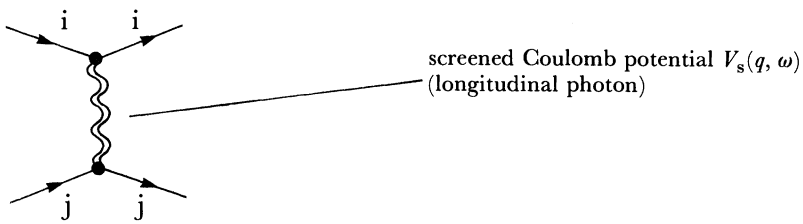
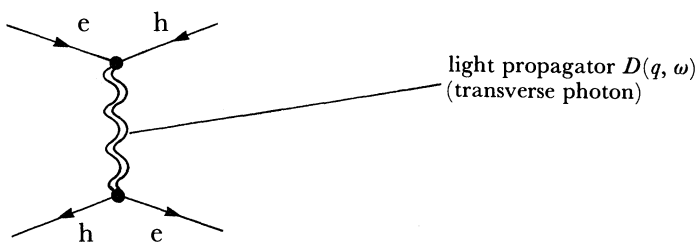
We discuss the various many-body effects that contribute to the large optical nonlinearities of semiconductors close to the band edge. Such effects are: band filling, screening due to the excited electron–hole pairs, band-gap shrinkage, energy broadening and excitonic enhancement. Compared to the Coulomb self-energy corrections, the radiative self-energies are normally small. However, they determine the transition rates in the rate equations of the photons and electrons.

I. Single-particle properties

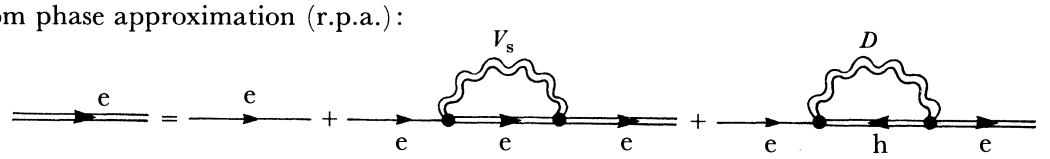
In the region close to but below the band edge, semiconductors show large optical nonlinearities that can be exploited to get optical bistability in transmission or reflection experiments. These nonlinearities are due to the generation of electron–hole pairs in the exciton states and band-tail states. The long-range Coulomb interaction between the mobile electronic excitations requires a genuine non-perturbative many-body treatment. For recent reviews see Klingshirn & Haug (1981), Haug (1982) and Haug & Schmitt-Rink (1984). At low pair concentrations the attractive electron–hole interaction dominates. With increasing excitation the Coulomb forces are increasingly screened until an electron–hole plasma is formed. In the plasma state the band gap is reduced due to exchange and correlation effects below the original exciton energy level. Furthermore, the single-particle energies are smeared out by collision broadening. All these effects of the Coulomb interactions can be described as *intra-band* scattering processes due to the exchange of *longitudinal photons* ($\{i,j\} = \{e,h\}$):



On the other hand, the interaction with the light field causes *inter-band* transitions due to the exchange of *transverse photons*:



With these two types of interactions the Dyson equation of the electron, for example, is in random phase approximation (r.p.a.):



Normally, the Coulomb self-energy is larger than the radiative self-energy correction. Only for extremely intensive laser fields, where a complete bleaching occurs, the radiative self-energy modifies the single-particle spectrum appreciably by causing a gap around the laser frequency (Galitskii *et al.* 1970). Otherwise, the radiative self-energy can be neglected for the calculation of the single-particle spectrum. As shown by Kadanoff & Baym (1962) and systematically developed by Keldysh (1965) in terms of non-equilibrium Green function, one gets the density of particles from the time-dependent Green function (with $\hbar = 1$ throughout the article)

$$G_e(r,t;r,t^+) = -i\langle T\psi_e(r,t)\,\psi_e^\dagger(r,t^+)\rangle = i\langle\psi_e^\dagger(r,t)\,\psi_e(r,t)\rangle = in_e(r,t).$$

The total number of electrons is changed solely by the radiative interaction. Therefore, if one calculates the rate equation for the total number of electrons (in the conduction band) from the electron Dyson equation, only the radiative self-energy contributes and yields the radiative transition rates (Haug & Schmitt-Rink 1984)

$$\partial N_e/\partial t = \alpha(\omega)\,I/\omega - R_{\text{spon}},$$

where $\alpha(\omega)$ is the absorption coefficient, I is the laser intensity and R_{spon} is the rate of spontaneous transitions:

$$R_{\text{spon}} = \int_0^\infty d\omega(\omega n(\omega)/\pi c)^2\alpha(\omega)/[\exp\{\beta(\omega-\mu)\}-1].$$

Here, $n(\omega)$ is the index of refraction and μ the quasi-chemical potential.

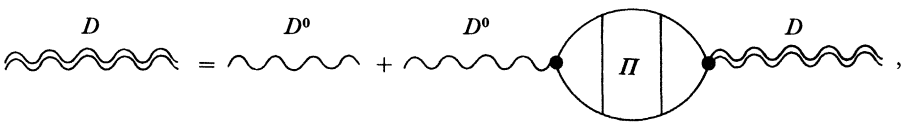
II. Polarization in a dielectric medium

The optical properties of the medium can be determined by calculating the (transverse) photon Green function. Classically, the retarded Green function of the Maxwell wave equation for the transverse vector potential is given by

$$D(q,\omega) = 4\pi c/(\omega^2\epsilon(q,\omega) - q^2c^2),$$

where $\epsilon(q,\omega)$ is the transverse or optical dielectric function. The whole of one-beam spectroscopy is contained in the complex function $\epsilon(q,\omega)$; for example absorption, refraction, reflection and luminescence spectra can be calculated if $\epsilon(q,\omega)$ is known.

Quantum mechanically, the photon Green function is determined by its Dyson equation



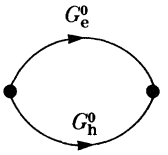
where $\Pi(q,\omega)$ is the irreducible photon self-energy, also called the polarization function. The solution of the Dyson equation is

$$D(q,\omega) = 4\pi c/(\omega^2 - q^2c^2 - 4\pi\Pi(q,\omega)),$$

which yields the relation

$$\epsilon(q,\omega) = 1 - 4\pi\Pi(q,\omega)/\omega^2.$$

The inter-band part of the polarization function $\Pi(q,\omega)$ is in lowest approximation just the electron–hole pair Green function



so that in the long-wavelength limit

$$\epsilon(\omega) = \epsilon_\infty\{1 - \omega_{pl}^2/(\omega + i\delta)^2\} - 4\pi e^2 \sum_k |r_{cv}(k)|^2 (1 - f_{ek} - f_{hk})\, G_{eh}(k,\omega),$$

where ω_{pl} is the plasma frequency

$$\omega_{pl}^2 = \frac{4\pi e^2}{\epsilon_\infty} \sum_k \left(\frac{f_{ek}}{m_{ek}} + \frac{f_{hk}}{m_{hk}} \right)$$

and f_{ek}, f_{hk} and m_{ek}, m_{hk} are the Fermi distribution functions and masses of the electron and holes, respectively; r_{cv} is the dipole matrix element and $G_{eh}(k,\omega)$ is the pair Green function

$$G_{eh}(k,\omega) = 2(\epsilon_{ek} + \epsilon_{hk})/\{(\omega + i\delta)^2 - (\epsilon_{ek} + \epsilon_{hk})^2\}.$$

We illustrate this result by calculating the intensity-dependent changes of the index of refraction for the narrow-gap semiconductor $Pb_{1-x}Sn_xSe$ by using the rate equation of the last section together with the linear response polarization function.

Figure 1 shows the low-frequency, intra-band contributions and the inter-band contributions,

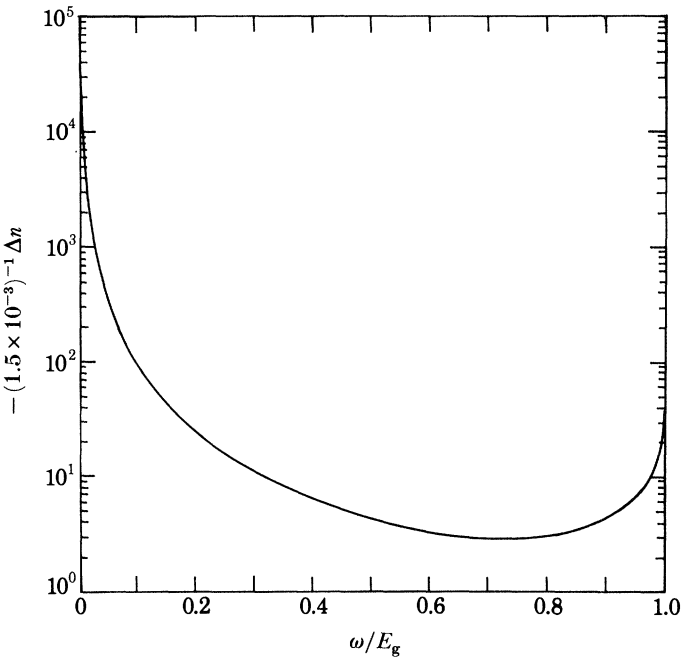


FIGURE 1. Changes of the index of refraction of $Pb_{1-x}Sn_xSe$ at 77 K under laser excitation at $\omega_0 = 0.96\ E_g$ with an intensity $I = 1.5\times10^3$ W cm^{-2}; $x = 0.051$, $E_g = 0.117$ eV.

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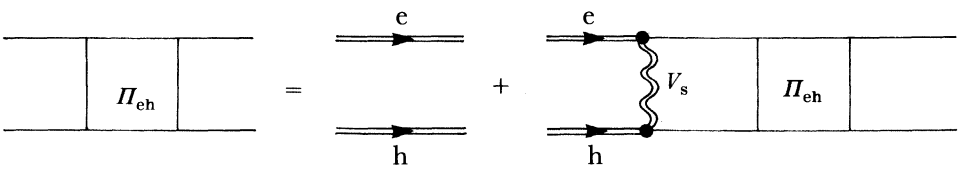
which become resonant at the band gap. Often, this simple free-particle approximation is not sufficient. The Coulomb interaction has to be taken into account by replacing the free electron–hole pair Green function by



Radiative vertex corrections are completely non-resonant and can be neglected. The integral equation for Π_{eh} is the Bethe–Salpeter equation in the screened ladder approximation. In the low-density limit, where screening and single-particle renormalization are unimportant, one obtains analytically the exciton spectrum with an infinite number of bound states and an ionization continuum (i.e. the so-called Elliot spectrum). For arbitrary densities the integral equation for the polarization function has to be solved numerically. For static free-carrier

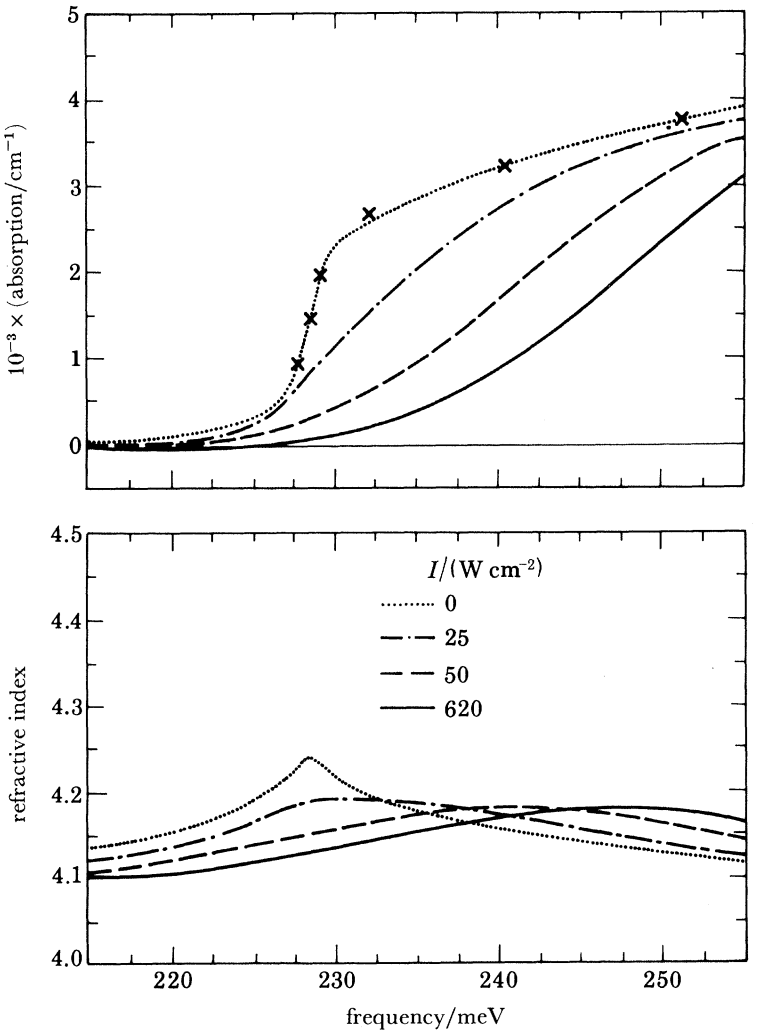


FIGURE 2. Absorption and refraction spectra of InSb at 77 K for various excitation intensities (from Löwenau *et al.* 1982). The frequency of the exciting laser beam is $\omega_0 = 0.225$ eV. The experimental points of the low-intensity absorption spectrum are taken from Gobeli *et al.* (1960).

screening accurate solutions can be obtained by matrix inversion (Löwenau *et al.* 1982). A finite single-particle energy broadening γ is incorporated in the treatment. For InSb this broadening is larger than the exciton Rydberg E_0, so that no well-resolved bound state exists. The absorption and refraction spectra for InSb are shown in figure 2 for various light intensities. The curve for vanishing light intensity shows that the exciton effects tend to produce a 'squared' absorption continuum. For increasing light intensity there is a pronounced compensation between the effects of the band-gap shrinkage and the reduction of excitonic enhancement, so that the dominating effect is band filling. The decrease of the index of refraction has been exploited (Miller *et al.* 1979) to obtain optical bistability. In bulk GaAs the broadening γ is smaller than the exciton Rydberg, at least at low temperatures ($T \lesssim 77$ K), in superlattice structures even at room temperature. Therefore, the calculated spectra (figure 3) exhibit in the low-density limit sharp exciton lines. For higher light intensities, and therefore higher free-carrier concentrations, the exciton vanishes due to the increased screening. This bleaching of the exciton resonance causes again a decrease of the index of refraction for $\omega < E_g - E_0$, which is large enough to allow the realization of optical bistability (Gibbs *et al.* 1979). In wide-gap semiconductors, where the (longitudinal) dielectric functions are smaller, large band-gap

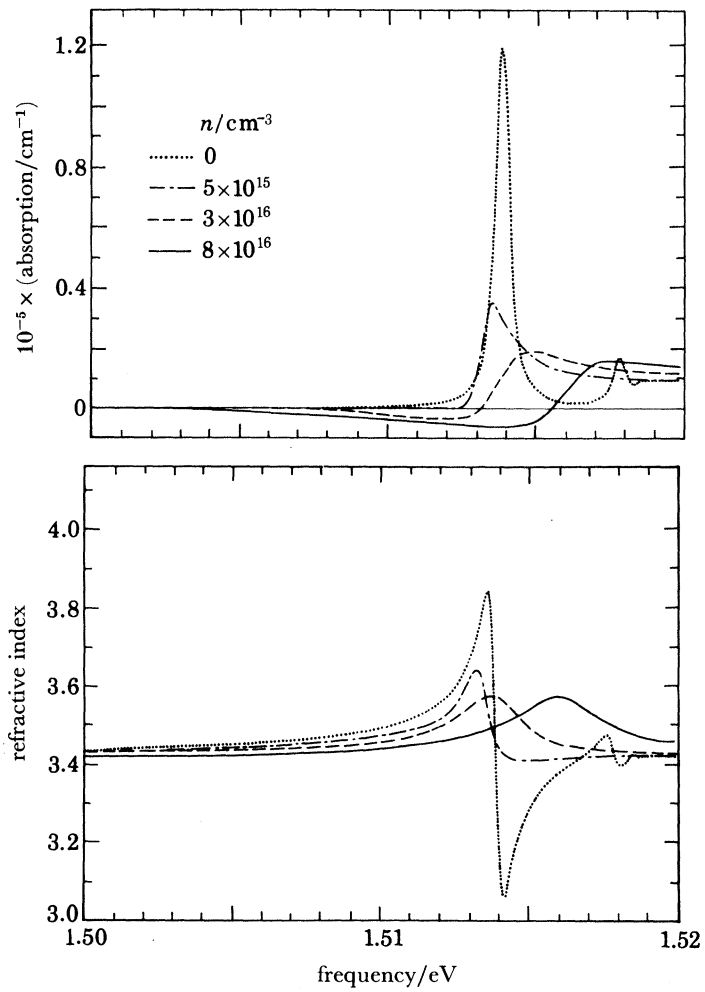


FIGURE 3. Absorption and refraction spectrum for GaAs at 10 K for various free-carrier densities n (from Löwenau *et al.* 1982).

reductions are measured with increasing concentration of electronic excitations (Bohnert *et al.* 1981), as shown in figure 4. The calculated exchange and correlation energy shifts are in good agreement with the measured ones. For laser frequencies below the lowest exciton resonance the absorption is initially weak, but increases strongly at higher intensities when the band gap passes the laser frequency.

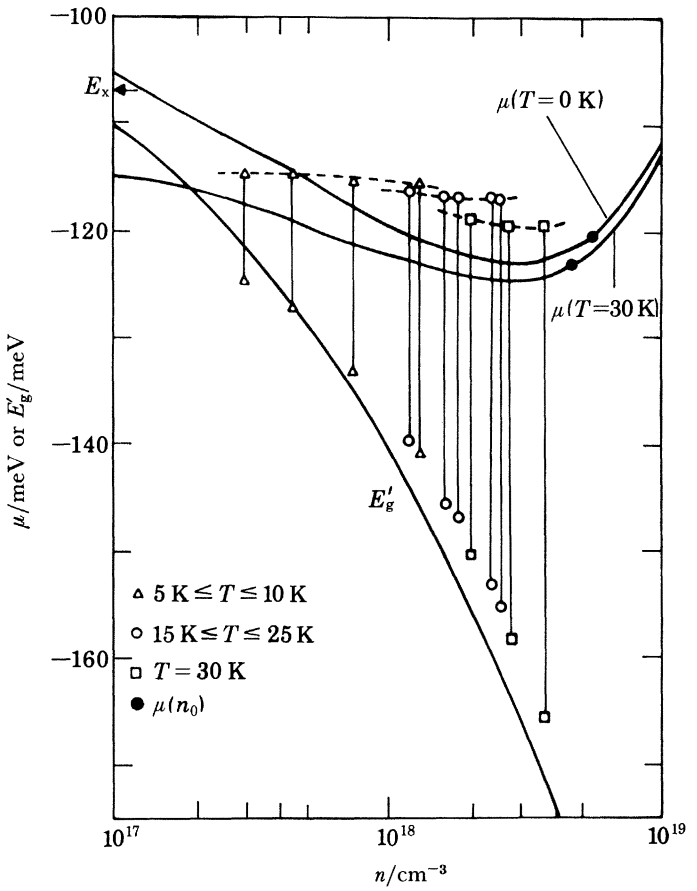
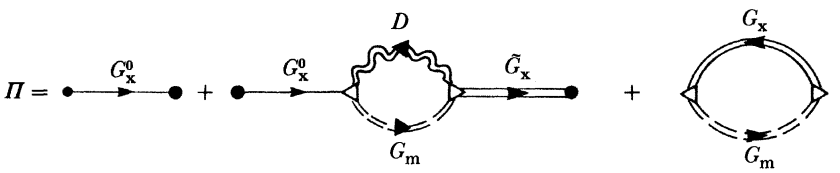


FIGURE 4. Renormalized energy-gap E_g' and quasi-chemical potential μ for CdS (from Bohnert *et al.* 1981). The solid line is for theory and the broken line is for experiment.

This induced absorption can be used to obtain an absorptive optical bistability in CdS (for the experiment see Bohnert *et al.* (1984): for the theory, see Schmidt *et al.* (1984)) with a clockwise hysteresis loop. Owing to the nonlinear absorption, density kinks develop in the medium, which give rise to interesting time dependences of the transmitted light. These effects can be studied by solving the coupled transport equations for photons and free carriers (Koch *et al.* 1984).

Finally, in CuCl, which has a gap of about 3.5 eV, the biexcitons determine the nonlinear optical properties of the medium. The polarization function Π is now explicitly nonlinear. The two-photon absorption is described by the following irreducible diagrams:



G_x and G_m are the exciton and biexciton Green functions, $\tilde{G}_x$ is the exciton Green function without polariton renormalization. An evaluation of these diagrams yields, if damping is neglected (Schmitt-Rink, unpublished work)

$$\epsilon(\omega) = \epsilon_\infty - 4\pi\mu_{gx}^2 \tilde{G}_x^2 / G_x^0,$$

where

$$\tilde{G}_x = (G_x^{0-1} - \tilde{\Pi}_x)^{-1},$$

and $\tilde{\Pi}_x$ is the exciton self-energy contained in the second polarization diagram. This result was first derived by Abram & Maruani (1982). In earlier treatments we omitted the third polarization diagram, which is, however, also important close to the biexciton resonance. Optical bistability due to the nonlinearity calculated here has been observed recently (Levy *et al.* 1983; Peyghambarian *et al.* 1983).

This work has been supported by the Commission of the European Communities (under the experimental phase of the European Stimulation Action).

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