Simple quantum models of
optical response of condensed matter

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The simplest quantum models based on perturbation theory.

Probability of transitions to excited states and dissipation of energy.

Response functions related to one-electron picture of direct interband transitions of valence electrons in crystals.

Examples: optical functions of doped GaAs.

Quantum transitions in perturbation theory

The light wave is composed by a train of photons, carrying quantized energy. They can be absorbed during the interaction with matter.

In the manybody system of condensed matter, elementary excitations in the form of quasiparticles can be identified (electrons, holes, excitons, phonons etc.).

The photon and quasiparticle fields influence each other via their interactions ("scattering", "collisions"). One of the basic processes is the absorption of a photon, with the transfer of its energy to the quasiparticle system.

Other processes are possible, such as elastic or inelastic scattering of photons, when a photon survives the collision in a modified form (direction of propagation and/or energy). Important processes involve spontaneous or stimulated emission of photons, carrying energy taken from quasiparticles.

In the case of small changes of the studied system, caused by a weak optical field, the prediction of response functions can be based on the standard perturbation theory of quantum mechanics.

A convenient quantity to be calculated is the energy taken from a harmonic electromagnetic wave in a unit volume per unit of time, linked to the imaginary part of the dielectric function,

$$Q = \frac{1}{2}\omega\varepsilon_2\varepsilon_o\left\langle E^2\right\rangle,\tag{4.1}$$

which is proportional to the time average of the power of the wave. Its macroscopic form is usually the (Joule) heat.

The procedure involves a calculation of the increase of the mean energy of the condensed system, and use the above equation for the evaluation of the absorptive part of the dielectric function. The real part can be obtained via Kramers-Kronig transform of the imaginary part calculated for all frequencies.

Matter will be divided into small areas (of the volume V, with their dimensions much smaller than the wavelength of the optical field). In these areas, the electric field intensity of the wave is independent of the position; we retain solely the harmonic time dependence

$$\vec{E}(t) = \vec{E}_o e^{-i\omega t}\tag{4.2}$$

from the time $t_o=0$ of switching the perturbation on. Magnetic component will be neglected.

The perturbative part of hamiltonian can be expressed via the operator of dipole moment (charge times its displacement) as

$$H'(t) = \vec{d}\cdot\mathrm{Re}\left\{\vec{E}_o e^{-i\omega t}\right\} = \frac{\left(\vec{d}\cdot\vec{n}\right)E_o}{2}\left(e^{-i\omega t} + e^{i\omega t}\right),\quad\text{where}\ \ \vec{n} = \vec{E}_o/E_o\tag{4.3}$$

is a unit vector in the direction of force. The force performs work due to the displacement of the charge, equal to the scalar product of the vectors of force and displacement.

Assume the system in a stationary state i (with the energy E_i) at the initial time t_o. The probability of a transition to a stationary final state f (with the energy E_f) at the time T (which is the squared modolus of the probability amplitude) is

$$p_{if}(T,\omega) = \frac{1}{\hbar^2}\left|\left\langle f \left| \int_0^T H'(t)e^{i\frac{E_f-E_i}{\hbar}t}\,dt \right| i \right\rangle\right|^2$$

(4.4)

$$= T\frac{\left|\left\langle f \left| \vec{d}\cdot\vec{n} \right| i \right\rangle\right|^2}{\hbar^2}\left[F(T,\omega_{if}-\omega)+F(T,\omega_{if}+\omega)\right]E_o^2 \ , \ \text{ where}$$

$$\omega_{if} = \frac{E_f-E_i}{\hbar} \ , \quad F(T,x) = \frac{\sin^2\left(\frac{T}{2}x\right)}{\frac{T}{2}x^2} \ .$$

(4.5)

For large T, the probability is negligible except for the fulfillment of the "resonance condition"

$$\omega = \pm\omega_{if} \ .$$

(4.6)

For $T \rightarrow \infty$ the function F can be replaced by the Dirac δ:

$$\int_{-\infty}^{\infty} F(T,x)\mathrm{d}x = \pi \text{ for any } T > 0 ; \quad \lim_{T \to \infty} F(T,x) = \pi\delta(x) . \tag{4.7}$$

Owing to the transition $i \rightarrow f$, the light field performs work, which (per unit volume and time) reads

$$Q_{if}(\omega) = \frac{\hbar\omega p_{if}(T,\omega)}{TV} \rightarrow \frac{\pi\omega}{\hbar V}\left|\left\langle f\left|\vec{d}\cdot\vec{n}\right|i\right\rangle\right|^2 E_o^2\left[\delta(\omega_{if}-\omega)+\delta(\omega_{if}+\omega)\right] . \tag{4.8}$$

The work vanishes whenever the resonance condition is not fulfilled, and diverges otherwise. This is a consequence of the stationary initial and final states. Quasistationary states have finite lifetimes; for the exponential temporal dependence of the probability P_s of the decay of the state of mean energy E_o during the time t (P_n means the probability preserving the state during the time t),

$$P_n(t) = e^{-\frac{2\Gamma}{\hbar}t} , \quad P_s(t) = 1 - e^{-\frac{2\Gamma}{\hbar}t} , \tag{4.9}$$

the probability density of finding the energy E is

$$\rho(E-E_o) = \frac{\Gamma}{\pi}\frac{1}{(E-E_o)^2+\Gamma^2} . \tag{4.10}$$

This is so called Breit-Wigner, or Lorentz, or Cauchy distribution.

The positive parameter Γ has the dimension of energy; it is inversely proportional to the lifetime of quasistationary ($\Gamma \ll E_o$) state,

$$\tau = \frac{\hbar}{2\Gamma} \ . \tag{4.11}$$

For $\quad \Gamma \to 0 \quad (\tau \to \infty) \ , \quad \rho(E - E_o) \to \delta(E - E_o) \ . \tag{4.12}$

Thus, the Fermi golden rule of the perturbation theory can be complemented by the assumption concerning the random values of the energy

$$E_{if} = E_f - E_i = \hbar \omega_{if} \tag{4.13}$$

taken from the wave via the $i \to f$ transition. The width parameters of the Breit-Wigner distribution of the initial and final energies can differ; assuming independent occurrence of both energies, the probability density of the energy difference is the convolution ("Faltung", "svjortka")

$$\rho(E_{if}) = \int_{-\infty}^{\infty} \frac{\Gamma_f / \pi}{(E - E_f^o)^2 + \Gamma_f^2} \frac{\Gamma_i / \pi}{(E_f - E_i - E_i^o - E)^2 + \Gamma_i^2} dE$$

$$= \frac{(\Gamma_i + \Gamma_f) / \pi}{(E_{if} - E_{if}^o)^2 + (\Gamma_i + \Gamma_f)^2} \ . \tag{4.14}$$

This is again the Breit-Wigner distribution; it is centered about the difference of the individual centers.

The width parameters and the corresponding relaxation times are

$$\Gamma_{if} = \Gamma_i + \Gamma_f \ , \quad \frac{1}{\tau_{if}} = \frac{\hbar}{2\Gamma_{if}} = \frac{1}{\tau_i} + \frac{1}{\tau_f} \ .$$

(4.15)

With the interpretation of inverse relaxation time as the frequency of collisions, the result for independent events concerning the initial and final states is the sum of frequencies.

The spectral dependence of the energy absorbed via transitions $i{\to}f$ between quasistationary states is a broadened version of the delta-function singularity for stationary states. Multiplication by the probability density and summation over all possibilities leads to

$$\int_{-\infty}^{\infty} \Big[\delta(\omega_{if} - \omega) + \delta(\omega_{if} + \omega) \Big] \rho(\hbar\omega_{if}) \, \mathrm{d}(\hbar\omega_{if})$$

$$= \int_{-\infty}^{\infty} \Big[\delta(x/\hbar - \omega) + \delta(x/\hbar + \omega) \Big] \rho(x) \, \mathrm{d}(x)$$

$$= \hbar\rho(\hbar\omega) + \hbar\rho(-\hbar\omega)$$

$$= \hbar \frac{\Gamma_{if}}{\pi} \left[\frac{1}{(\hbar\omega - \hbar\omega_{if}^{\mathrm{o}})^2 + \Gamma_{if}^2} + \frac{1}{(\hbar\omega + \hbar\omega_{if}^{\mathrm{o}})^2 + \Gamma_{if}^2} \right] \ .$$

(4.16)

The resonances are of finite magnitude and width, they are centered close to $\omega = \pm\omega_{if}$.

The former result leads to the following approximate expression for the contribution of the $i{\rightarrow}f$ transitions to the imaginary part of the dielectric function,

$$(\Delta\varepsilon_2)_{if} = \frac{2Q_{if}}{\omega\varepsilon_o\langle E^2\rangle} = \frac{4Q_{if}}{\omega\varepsilon_o E_o^2}$$

$$\approx \frac{4}{\varepsilon_o}\frac{\left|\langle f|\vec{d}\cdot\vec{n}|i\rangle\right|^2}{V}\left[\frac{\Gamma_{if}}{(\hbar\omega-\hbar\omega_{if}^o)^2+\Gamma_{if}^2} - \frac{\Gamma_{if}}{(\hbar\omega+\hbar\omega_{if}^o)^2+\Gamma_{if}^2}\right].$$

(4.17)

This formula can be further simplified, and, the need for the Kramers-Kronig transform (to obtain the real part) avoided.

Since

$$\frac{\gamma}{(\omega-\omega_o)^2+\gamma^2}-\frac{\gamma}{(\omega+\omega_o)^2+\gamma^2}$$

$$= \mathrm{Im}\left\{\frac{1}{\omega_o-\omega-i\gamma}+\frac{1}{\omega_o+\omega+i\gamma}\right\}=\mathrm{Im}\left\{\frac{2\omega_o}{\omega_o^2+\gamma^2-\omega^2-i2\omega\gamma}\right\},\tag{4.18}$$

the contribution to the absorptive part of the dielectric function can be expressed in the form

$$(\Delta\varepsilon_2)_{if}=\frac{4}{\varepsilon_o}\frac{\left|\left\langle f\left|\vec{d}\cdot\vec{n}\right|i\right\rangle\right|^2}{V}\frac{2\omega_{if}^o}{\hbar}\mathrm{Im}\left\{\frac{1}{(\omega_{if}^o)^2+\dfrac{\Gamma_{if}^2}{\hbar^2}-\omega^2-i\omega\dfrac{2\Gamma_{if}}{\hbar}}\right\}.\tag{4.19}$$

This is to be compared with the result of classical Lorentz model for the complex dielectric function,

$$\varepsilon=1+\frac{S\omega_o^2}{\omega_o^2-\omega^2-i\dfrac{\omega}{\tau}}.\tag{4.20}$$

The dimensionless "strength" of the $i \to f$ transitions is

$$S_{if} = \frac{8}{\varepsilon_o \hbar \omega_{if}^o} \frac{\left| \left\langle f \left| \vec{d} \cdot \vec{n} \right| i \right\rangle \right|^2}{V} \; ,$$
(4.21)

the eigenfrequency and damping time are

$$\omega_{o,if} = \sqrt{(\omega_{if}^o)^2 + \frac{\Gamma_{if}^2}{\hbar^2}} \; , \quad \tau_{if} = \frac{\hbar}{2\Gamma_{if}} \; .$$
(4.22)

The identical spectral dependencies of the imaginary parts imply identical spectra of the real parts, since they are related by Kramers-Kronig integral transform. Thus, in summing the contributions of (possibly many) independent contributions of transitions from different initial states to different final states, we may include the dispersive (real) part of the dielectric function in the sum:

$$\varepsilon(\omega) = 1 + \sum_{i,f} \frac{S_{if} \omega_{o,if}^2}{\omega_{o,if}^2 - \omega^2 - i \dfrac{\omega}{\tau_{if}}} \; .$$
(4.23)

Each of the terms has poles in the lower plane of complex frequencies.

The matrix element involving the charge and position,

$$D_{if} = \left\langle f \left| \vec{d} \cdot \vec{n} \right| i \right\rangle = e \left\langle f \left| \vec{r} \cdot \vec{n} \right| i \right\rangle \ , \tag{4.24}$$

can be expressed in terms of the momentum operator, using the commutator of the unperturbed hamiltonian H_o with the position:

$$\left\langle f \left| H_o \vec{r} \right| i \right\rangle = E_f \left\langle f \left| \vec{r} \right| i \right\rangle \ , \ \left\langle f \left| \vec{r} H_o \right| i \right\rangle = E_i \left\langle f \left| \vec{r} \right| i \right\rangle \ ,$$

$$\left\langle f \left| \left[H_o, \vec{r} \right] \right| i \right\rangle = (E_f - E_i) \left\langle f \left| \vec{r} \right| i \right\rangle \ , \tag{4.25}$$

$$\left\langle f \left| \vec{r} \right| i \right\rangle = \frac{\left\langle f \left| \left[H_o, \vec{r} \right] \right| i \right\rangle}{E_f - E_i} \ .$$

Since

$$\left[H_o, \vec{r} \right] = -i\hbar \frac{d\vec{r}}{dt} = -i\hbar \frac{\vec{p}}{m} \ , \tag{4.26}$$

we arrive at

$$D_{if} = -i \frac{e\hbar}{m(E_f - E_i)} \left\langle f \left| \vec{p} \cdot \vec{n} \right| i \right\rangle \ . \tag{4.27}$$

The transition probability is proportional to

$$\left| D_{if} \right|^2 = \left| \frac{e\hbar}{m(E_f - E_i)} \right|^2 \left| \left\langle f \left| \vec{p} \cdot \vec{n} \right| i \right\rangle \right|^2 . \tag{4.28}$$

This form is usually used for the one-electron transitions in crystals, which do not involve other excitations (such as phonons). As the momentum is proportional to the k–vector of the Bloch states, the matrix element is zero for states of different k (the state vectors are orthogonal). The allowed transitions are called "direct" (in k-space). This selection rule can also be interpreted as the requirement of momentum conservation, since the momentum of the involved photon is negligible.

Adding independent contributions from all available pairs of initial and final states provides the total response. In the picture of transitions between different electronic bands, occupied l and unoccupied l', the Fermi golden rule and conservation of momentum implies the dielectric function (4.23) in the form

$$\varepsilon(\omega) = 1 + \sum_{\vec{k} \in BZ} \sum_{l,l'} \frac{S_{ll'}(\vec{k}) \left[\omega_{l'}(\vec{k}) - \omega_l(\vec{k}) \right]^2}{\left[\omega_{l'}(\vec{k}) - \omega_l(\vec{k}) \right]^2 - \omega^2 - i \dfrac{\omega}{\tau_{if}(\vec{k})}} . \tag{4.29}$$

The energy differences between different bands ("interband energies") resonate with the energy of incoming photons.

Joint density of states (JDOS) is usually very instrumental in dealing with most of the crystalline matter. In fact, neglecting the k-dependence of the matrix elements in (4.29), the frequency dependence of the probability of a photon being absorbed is proportional to the number of available energy differences between the occupied initial and free final electron states.

JDOS changes strongly with frequency in the neighborhood of the critical points (minima, saddle points, maxima) of the interband energy.

The transitions produced by the light waves can be illustrated conveniently in the case of GaAs (a prototype polar material):

lattice dynamics, electronic bandstructure: quasiparticles are

bosons   fermions
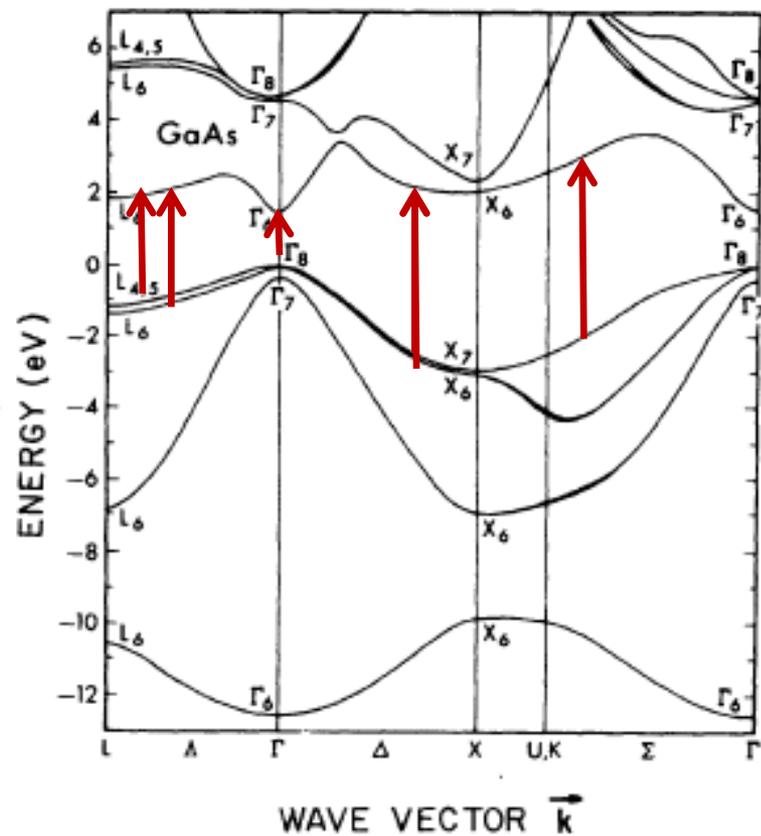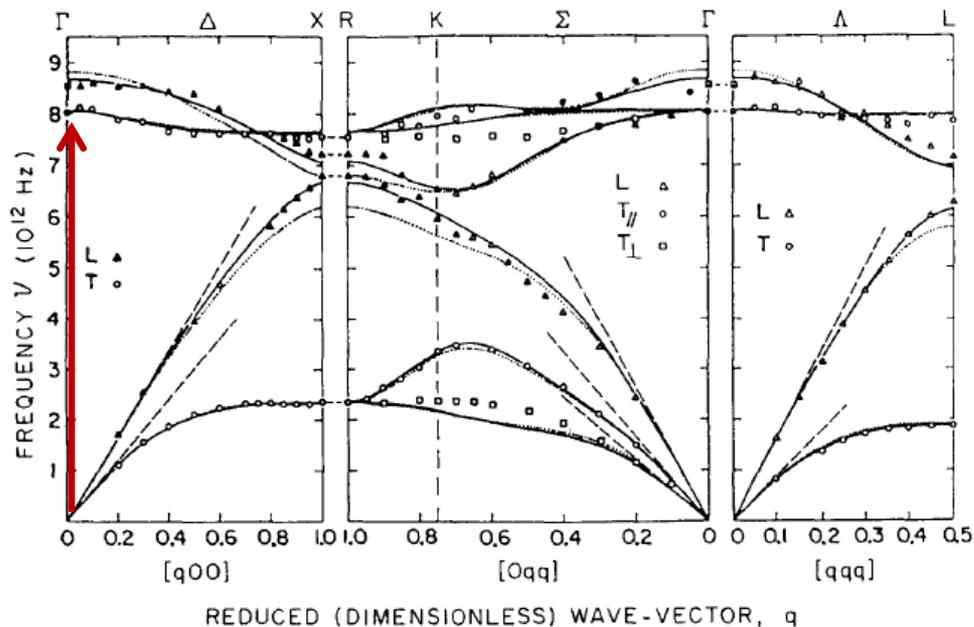
Electron density in the ground state

(Cohen and Chellikowsky, Electronic Structure and Optical Properties of Semiconductors, nonlocal pseudopotential)

suggests a difference in the IR response between Si and GaAs due to lattice vibrations

Si
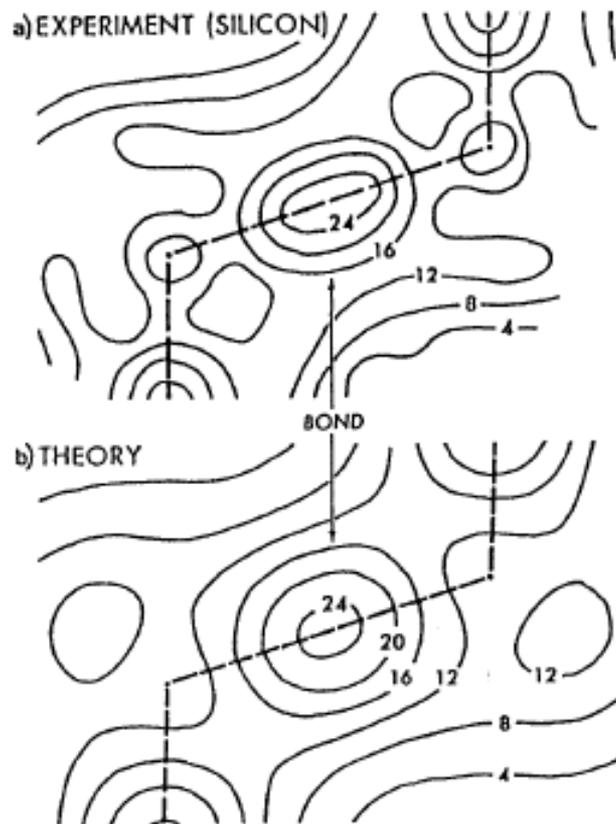
GaAs
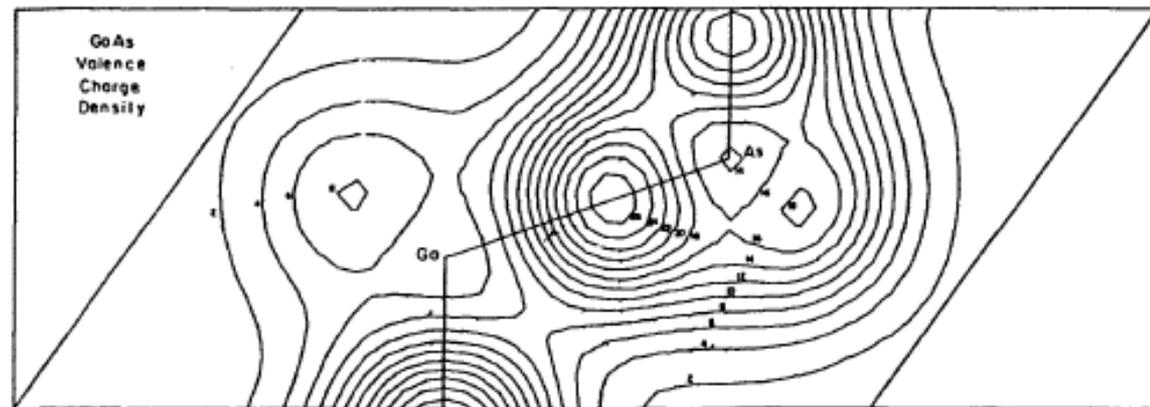
Fig. 8.29. Valence band charge density for gallium arsenide. The charge density contours are in units of electrons per unit cell volume

Spectral structure due to critical points (CP) of JDOS

Differentiation of high-quality optical spectra, enhancement of critical points of JDOS

PrehledCP_eps

PrehledCP_D1

PrehledCP_D2

ε

ε' (a.u.)

ε'' (a.u.)

PHOTON ENERGY

PHOTON ENERGY

PHOTON ENERGY

removes any constant background

removes any linear background

Low—noise data: even triple differentiation might be possible (not very often, though)

PrehledCP_D3

PrehledCP_eps
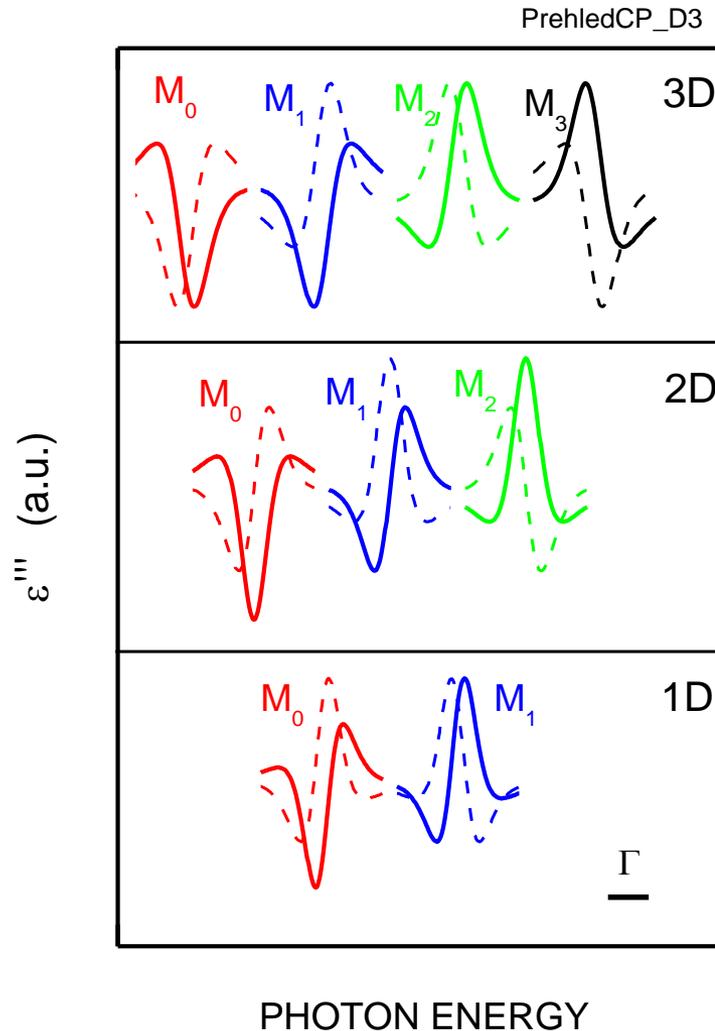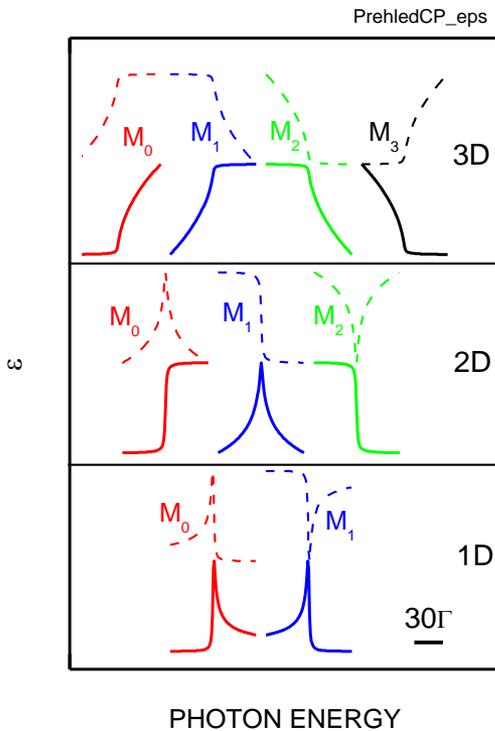
removes any quadratic background,

spans a narrow ($\sim\Gamma$) spectral range centered at the critical-point energy

An instructive case study: doped crystalline GaAs

Doped GaAs – dielectric function (Drude, Lorentz, ε_∞, interband transitions)
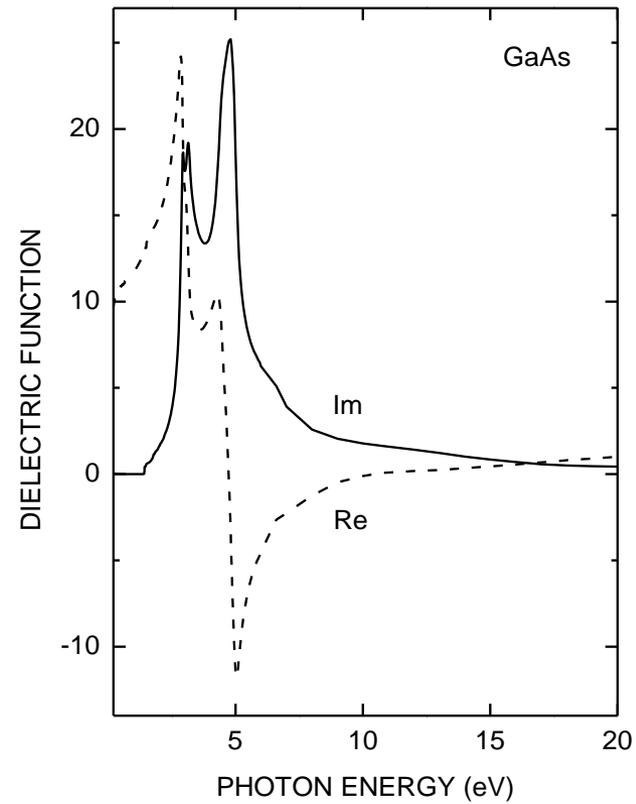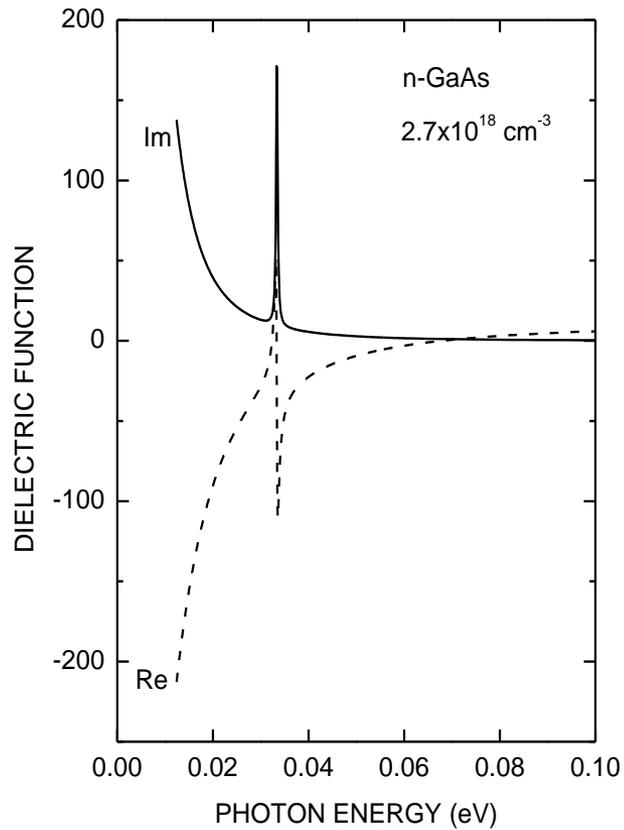
Doped GaAs - conductivity
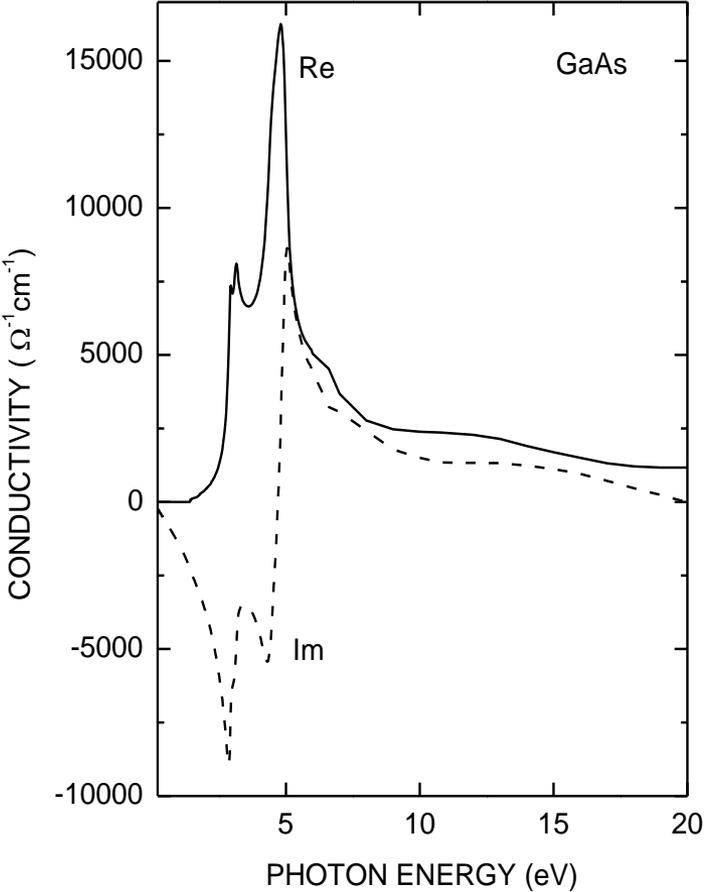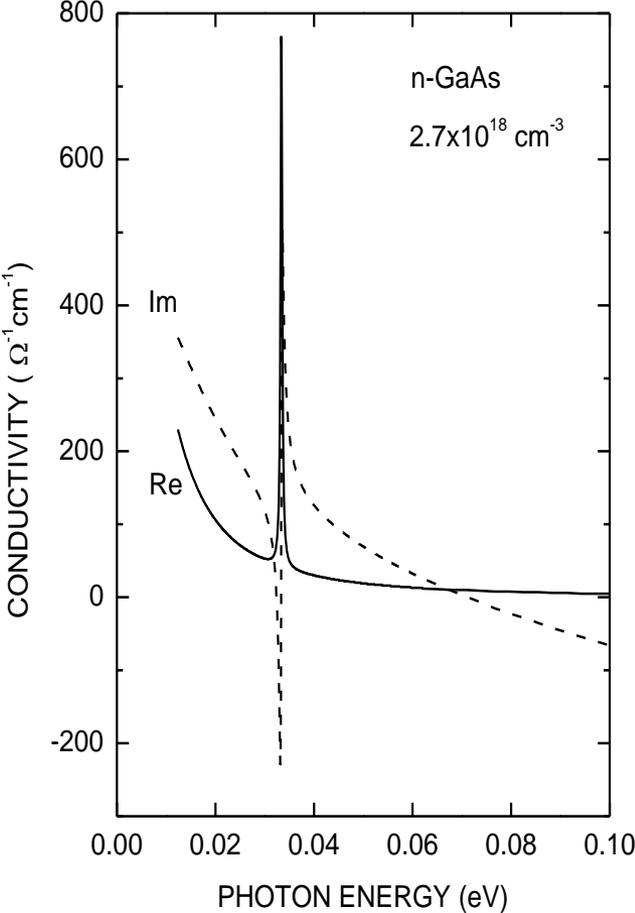
Doped GaAs – refractive index
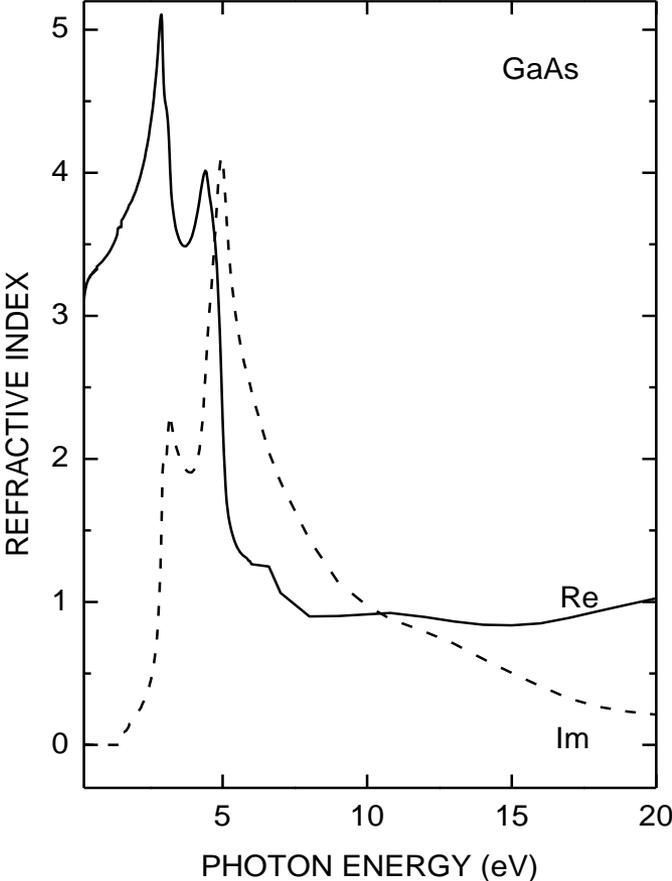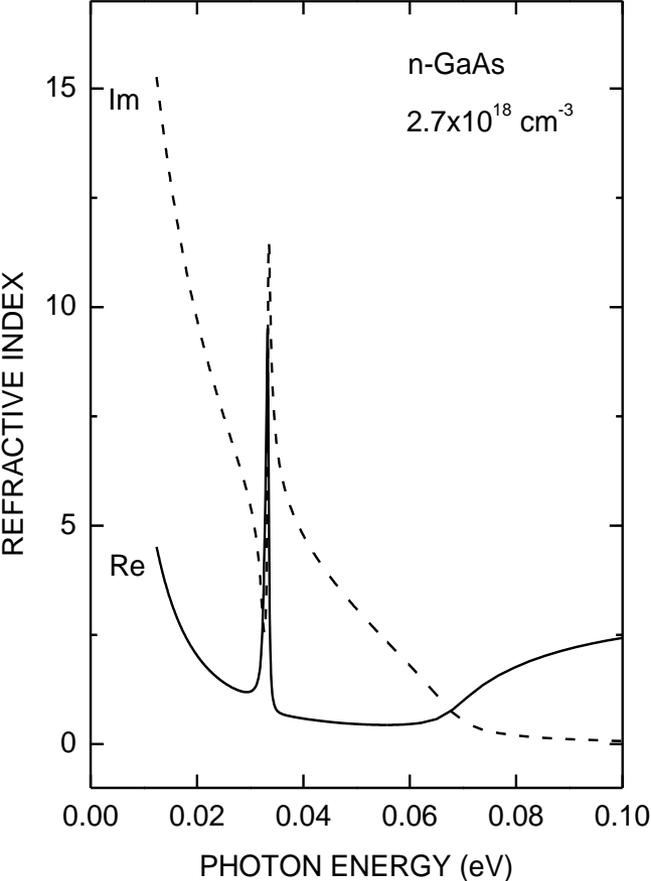
Doped GaAs – inverse dielectric function
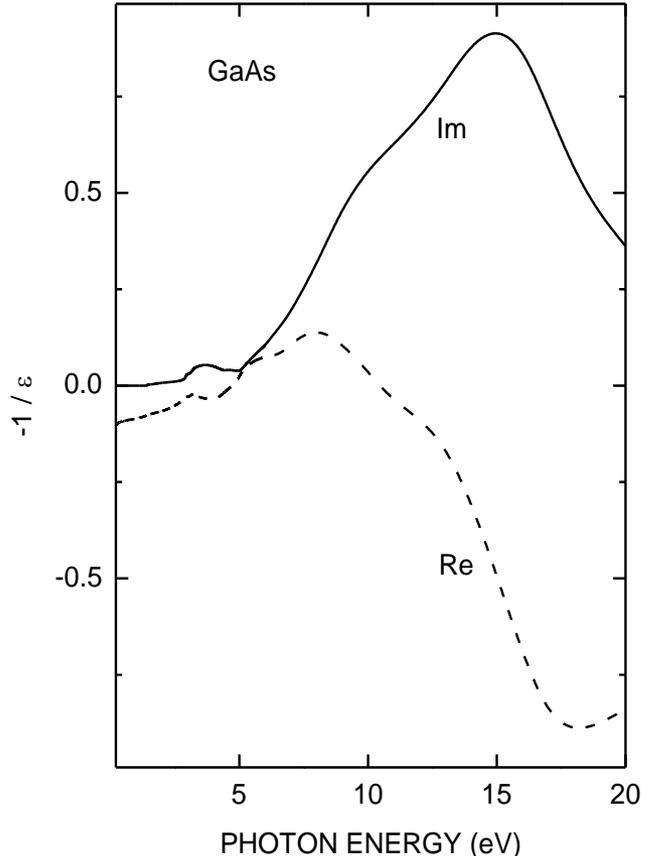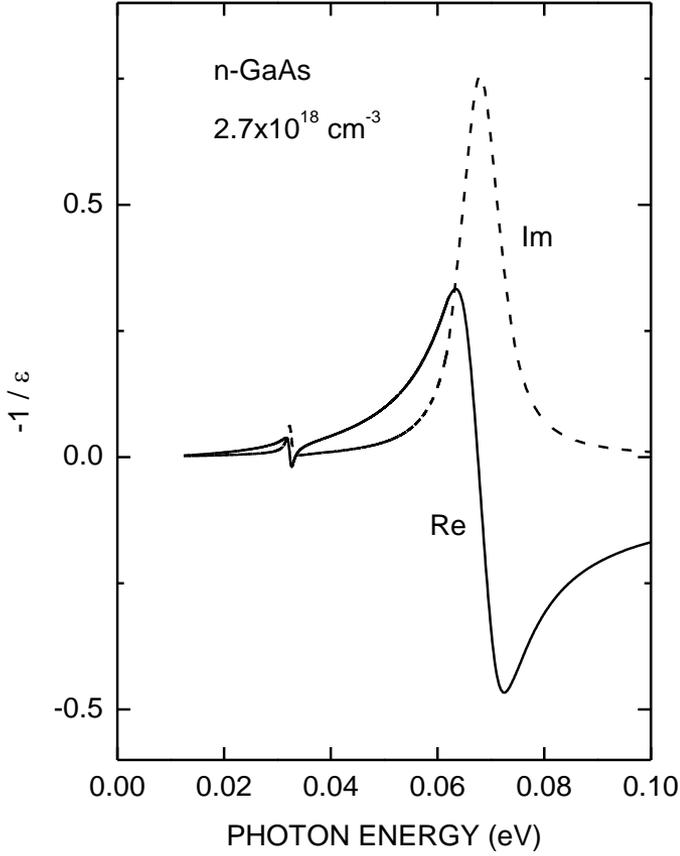
Doped GaAs – penetration depth
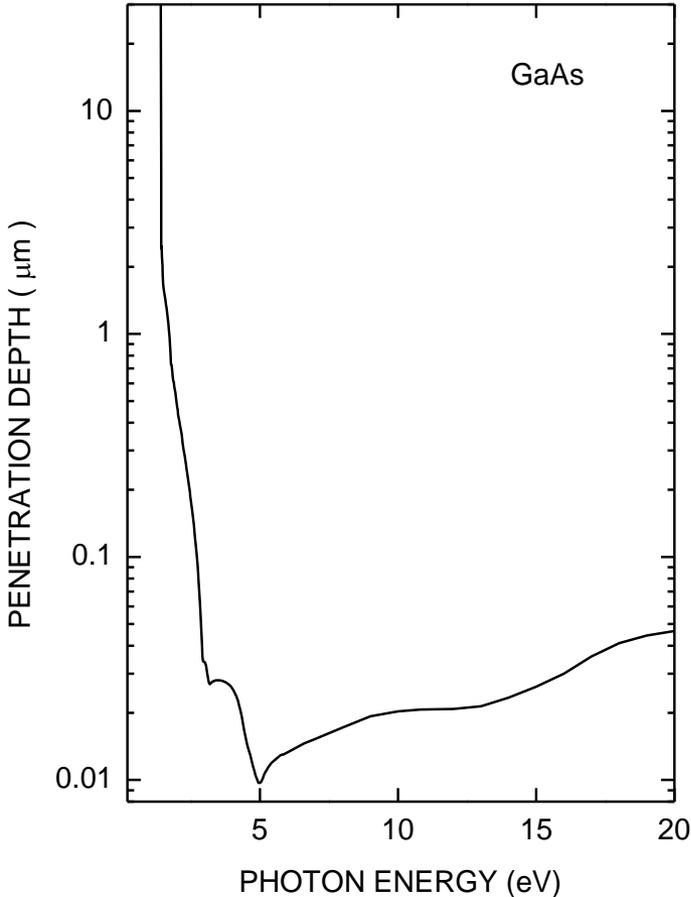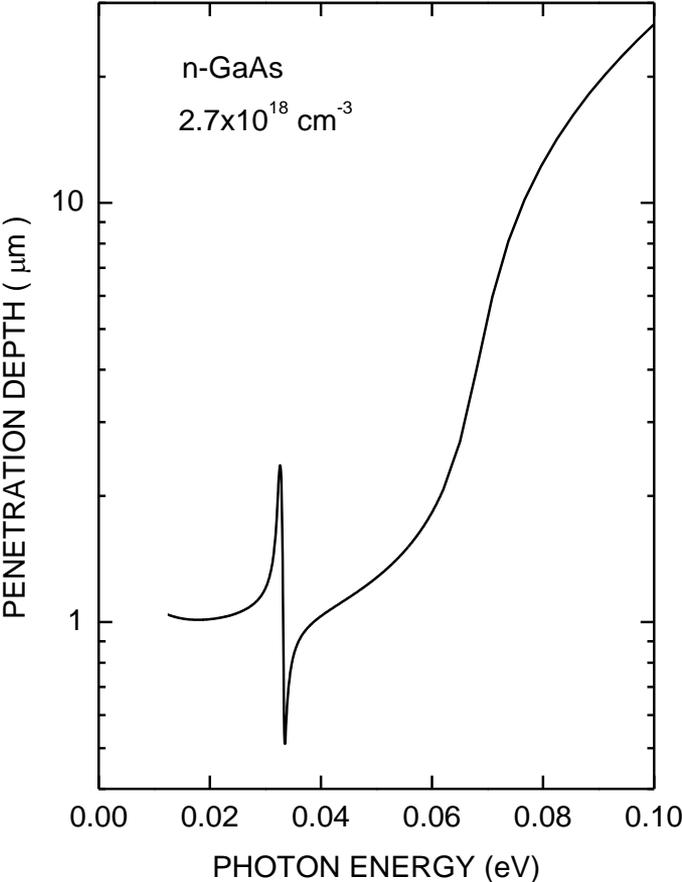
Doped GaAs – normal-incidence reflectivity