Influence of donor-triad molecules on the optical properties of semiconductors

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The dielectric constants and the refractive index of *n*-type GaAs are obtained by a second-order many-body-perturbation-theory calculation of the transition energy of the donor-triad molecules. The imaginary part of the dielectric constant, which is associated with the optical conductivity, exhibits a peak at an energy in relatively good agreement with the observed line "X." This result supports the interpretation of this peak as due to the electronic $H_3 \rightarrow H_3^+$ transition from their impurity ground state.

The present calculation aims at investigating the optical properties of *n*-type doped GaAs, which are currently the subject of much technological and academic interest. We have investigated the dielectric constants, derived from the transition $H_3 \rightarrow H_3^+$, which leads to a lower ionization energy than that of the transition between isolated impurities. Such an ionization energy corresponds, in our approximation, to the energy required to promote an electron from the three-donor cluster (or three-impurity molecule) to the bottom of the host conduction band. The investigation of the ionization energy of this triad molecule was also done by Nagasaka and Narita,¹ with a Heitler-London approximation, and by Golka and co-workers,² using a version of the Hartree-Fock (HF) procedure for the semiclosed-shell system. Recently Ferreira da Silva and Canuto³ have calculated the absorption spectra of Si:P and Ge:As and found them to be in relatively good agreement with experiment.^{4,5} In their calculation a spin-unrestricted Hartree-Fock model was used.

In this paper the calculations for the donor-triad molecules involve *ab initio* calculations of H_3 and H_3^+ . Within the Born-Oppenheimer approximation the total energies of H_3 and H_3^+ are calculated assuming a triangular form in D_{3h} symmetry.³ First, the Hartree-Fock self-consistent-field (HF-SCF) equations are solved expanding the atomic orbitals in a basis of Cartesian Gaussian-type functions. This basis consists of 9*s* functions contracted to 4*s*, three sets of uncontracted three-component *p*-type functions, and one set of uncontracted five-component *d*-type functions. This basis is usually referred to as (9*s*3*p*1*d*/4*s*3*p*1*d*) and has been suggested by Siegbahn and Liu.⁶ After the SCF calculations the effects of electron correlation can be included by many-body perturbation theory (MBPT): utilizing the usual Moller-Plesset (MP) partitioning of the Hamiltonian.^{7,8} In this context MP*n* corresponds to the *n*th-order MBPT in the MP partitioning of the Hamiltonian. Figure 1 shows the calculation of the ionization potential of H_3 for increasing uniform separation of H atoms in keeping with D_{3h} symmetry. As seen in Fig. 1, the second-order MP2 gives a better dissociation behavior than MP3 and for that

reason will be adopted throughout. The correlation contribution to second order is given by only one Bradow diagram, which is equivalent to the two second-order Goldstone diagrams. This involves only doubly excited configurations and is the dominant contribution to the total electron correlation energy.⁸ The spin-unrestricted HF configuration is the reference state for the MP2 calculations on H_3 . For H_3^+ the restricted HF configuration is used as reference. For increasing interatomic distance *R*, isolated H_3 dissociates properly into three H atoms. For H_3^+ , proper dissociation is obtained only after the inclusion of the electron-correlation effects.

In a semiconductor system, the only change we have to

FIG. 1. Variation of ionization energy of H_3 for increasing interatomic distance in D_{3h} symmetry. Value shown is $1 - E_I^0$ where $E_I^0 = E^0(H_3^+) - E^0(H_3)$. Different theoretical models are shown.

make is a change of units. The effective Bohr radius a_0^* is calculated from the experimental ionization energies E_I^* via $a_0^* = 1 \times a_0 / E_I^* \epsilon$, where ϵ is the dielectric constant of the host semiconductor. Thus, the donor-triad molecules with separation $R > a_0^*$ have ionization energies smaller than E_I^* of an isolated donor; i.e., $E_I^*(\text{triad}) < E_I^*(1 \text{ Ry})$. This aspect, which is of great interest, should appear in the absorption spectra, dielectric functions, and transport properties. We will use the following atomic units for the n -doped system n -type GaAs: $E_I^* = 5.3 \text{ meV} = 42.75 \text{ cm}^{-1}$, $\epsilon = 13.1$, and $a_0^* = 100 \text{ \AA}$.⁹

The impurity density of states associated with the absorption spectrum of a doped semiconductor with an impurity concentration N of uncompensated donors is obtained as³

$$D(E) = -\frac{1}{\pi} \text{Im} \langle \langle G(E, R) \rangle \rangle, \quad (1)$$

where $\langle \langle \rangle \rangle$ means average in disorder of the Green-function propagator. For the ground-state energies

$$\langle \langle G(E, R) \rangle \rangle = \int P(R) [E - E_I^0(R) + i0^+]^{-1} dR \quad (2)$$

then^{2,10}

$$D(E) \cong \int P(R) \delta[E - E_I^0(R)] dR, \quad (3)$$

where $E_I^0 = E^0(\text{H}_3^+) - E^0(\text{H}_3)$ is the ionization energy of the lowest states of the three-donor molecules and $P(R)$ is the triad distribution function at separation R . We will restrict ourselves to the triangular configuration as the linear case presents the same qualitative behavior.³ $P(R)$ is written as¹

$$P(R) = 4\pi^2 N^2 C_3(R) \exp[-C_3'(R)N], \quad (4)$$

where

$$C_3 = \frac{4}{3}\pi \left[R_0^3 - \frac{3}{4}R_0^2 R + \frac{R^3}{16} \right] \quad (5)$$

and

$$C_3' = \frac{4}{3}\pi \left[R_0^3 + \frac{3}{2}R_0^2 R + \frac{R^3}{8} \right], \quad (6)$$

and $R_0 = 4a_0$ is the radius of the sphere centered at the donor, based on the N dependence of the electron spin resonance.^{1,11}

It is very well known that the dielectric function $\epsilon(\omega)$ describes the optical response of the host semiconductor and is generally written as composed of a real and an imaginary part $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$. We will calculate $\epsilon(\omega)$ via the refractive index at very low frequency; $\epsilon(\omega) \rightarrow \epsilon(0) = n(0)^2$.

Once we get $D(E)$ for a certain impurity concentration N of n -type GaAs we obtain the refractive index $n(\omega)$ through the Kramers-Krönig relations¹²

$$\text{Re}[n(\omega)] = n + \frac{2}{\pi} \text{P} \int_0^\infty \frac{\omega' \text{Im}[n(\omega')]}{\omega'^2 - \omega^2} d\omega', \quad (7)$$

$$\text{Im}[n(\omega)] = -\frac{2\omega}{\pi} \text{P} \int_0^\infty \frac{\text{Re}[n(\omega') - n]}{\omega'^2 - \omega^2} d\omega', \quad (8)$$

FIG. 2. Real $\epsilon_1(\omega)$ and imaginary $\epsilon_2(\omega)$ parts of the dielectric constant in n -type doped GaAs for $N = 2.2 \times 10^{15} \text{ cm}^{-3}$.

where $n = n_{\text{GaAs}} = \epsilon_{\text{GaAs}}^{1/2} = 3.619$ and P stands for principal value. As

$$\text{Im}[n(\omega)] \sim \alpha(\omega)/2\omega, \quad (9)$$

where $\alpha(\omega)$ is identified as $D(E)$, we can write

$$n(\omega) = n + \frac{1}{\pi} \text{P} \int_0^\infty \frac{\alpha(\omega')}{\omega'^2 - \omega^2} d\omega' \quad (10)$$

with $\omega = 0$ and $\omega' = E$; we obtain

$$n(0) = n + \frac{1}{\pi} \int_0^\infty \frac{\alpha(E)}{E^2} dE \quad (11)$$

for the semiconductor system. The dielectric constant is readily obtained from the above equation and $\epsilon(0) = n(0)^2$.¹³ Following the interdependent Kramers-Krönig relations to refractive index we obtain similar expressions for ϵ_1 and ϵ_2 (Ref. 12) as

$$\epsilon_1(\omega) = \epsilon_{\text{GaAs}} + \frac{2}{\pi} \text{P} \int_0^\infty \frac{\omega' \epsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega' \quad (12)$$

and

$$\epsilon_2(\omega) = \frac{2\omega}{\pi} \text{P} \int_0^\infty \frac{\epsilon_1(\omega')}{\omega'^2 - \omega^2} d\omega'. \quad (13)$$

FIG. 3. Total dielectric constant $\epsilon(0)$ of n -type doped GaAs as a function of the impurity concentration. Inset shows, for comparison, results from Refs. 15 and 16 for Si:P.

These equations can be easily solved making use of the relation¹²

$$\epsilon_2(\omega) \cong 2\{\text{Re}[n(\omega)]\text{Im}[n(\omega)]\} . \quad (14)$$

It is worthwhile to point out that we may also obtain the optical conductivity from the previous relation through $\sigma(\omega) \sim \omega \epsilon_2(\omega)$. In Fig. 2 we show the results of the real and imaginary parts of the dielectric constant, ϵ_1 and ϵ_2 , for the impurity concentration $N = 2.2 \times 10^{15} \text{ cm}^{-3}$, as obtained from the Kramers-Krönig relation. Note that ϵ_2 has a peak slightly below 24 cm^{-1} , which is about 56% of E_I^* in good agreement with the position of the line at 27.5 cm^{-1} (60% of E_I^*) of the n -type GaAs observed by Bajaj *et al.*¹⁴ in their spectroscopic studies of the n donors in III-V and II-VI compounds in the region of the $1s$ - $2p$ transition. This distinct peak can now be explained in

terms of the existence of donor assemblies composed of three impurity atoms, as corroborated by the good numerical agreement between theory and experiment.

In Fig. 3 we thus show the total dielectric constant as a function of N for our donor-triad impurity molecule. For very low N , the system behaves as a pure system and $\epsilon_{\text{GaAs}} = 13.1$, as expected. For increasing N the dielectric constant increases, and around 10^{15} cm^{-3} , $\epsilon(0)$ increases rapidly. This behavior is indeed observed in doped-semiconductor systems where the dielectric constant blows up around the critical concentration $N_c \cong 1.6 \times 10^{16} \text{ cm}^{-3}$ for metal-nonmetal transition.¹⁵ In our calculations the donor-triad molecules have been found to play a dominant role around $N = 6 \times 10^{15} \text{ cm}^{-3}$ where we observed a saturation of $\epsilon(0)$.

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