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The absorption spectrum of a heteropolar crystal: 
the rôle of many-particle effects

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Abstract. — We present (a) a local-orbital formulation of the electron-hole interaction in a heteropolar semiconductor which takes into account both the screened electron-hole attraction and its exchange counterpart, giving rise to the excitonic and local-field effects, respectively, and (b) a calculation of the absorption spectrum in GaP, which demonstrates the dominant rôle played by the continuum-exciton effect on the main optical absorption of a compound semiconductor. Our findings on the importance of many-particle effects closely parallel those of previous work on the covalent semiconductor Si.

1. Introduction.

During the last twenty years, the one-electron band theory has provided a quantitative basis for the study of electronic properties of semiconductors and insulators [1-5]. However, many features in the optical absorption spectrum of these solids cannot be explained in the one-particle or the non-interacting electron-hole picture. Examples are the bound exciton lines in the neighbourhood of the fundamental threshold and the continuum-exciton effects [3-6]. Therefore theoretical effort has concentrated on including electron-electron interaction or many-body effects in the optical response formalism in order to explain these observed features. For bound excitons the Wannier exciton model and the Frenkel exciton model deal with completely delocalized or completely localized electron-hole interactions, respectively. Therefore, they are not appropriate for electron-hole excitations with an intermediate extension of electronic wavefunctions like in the continuum of optical excitations in semiconductors and insulators [7, 8].

An alternative approach has recently been developed to extract the optical response of crystals [7, 8]. It takes into account the local-field effects due to the Bragg reflections of the induced charge density on the periodic lattice and also excitonic effects without being limited to the Wannier or Frenkel model. It is based on the Green’s function technique [9-13] with the key quantity being the inverse dielectric function $\varepsilon^{-1}(q + G, q + G'; \omega)$ [14]. The poles of $\varepsilon^{-1}$ determine the elementary excitation spectrum of the solid and, in particular, the linear optical response to a weak electrical field.

In previous work on diamond [7] and on silicon [8], Hanke and Sham have devised a convenient theoretical scheme to calculate the dielectric function $\varepsilon^{-1}$ in the long-wavelength limit for covalent materials. This work has established the basic effects of the many-body interactions. In particular, quantitative agreement with experiment has proven two general features:

- $a)$ to achieve such a quantitative agreement with the experimental optical spectra of covalent crystals, both with respect to peak positions and absorption strength, both electron-hole attraction and its exchange counterpart i.e. the RPA local-field effect...
have to be included in the two-particle Green's function and thus in the optical response;
b) the more the electronic charge distribution is localized (for example in C versus Si), the more important are the many-body interactions.

In this paper, we generalize the optical response treatment of references [7, 8] to the prototype of a heteropolar crystal GaP [15]. Our results stress the importance of both local-field and excitonic many-body effects in the optical response of a two-component semiconductor.

The paper is organized as follows. In section 2 the theoretical framework needed in the following discourse is presented. A local-orbital representation of the Green's function equations similar to references [7, 8] is given in section 3 which facilitates the numerical calculation. Details of the computation of the optical absorption spectrum of GaP are presented in section 4. Section 5 finally contains theoretical results, comparison with experiment and discussions.

2. Theoretical framework.

Here we introduce the theoretical framework needed in the following calculations. Detailed presentations are already contained in references [7] and [8]. Using the standard field-theoretical techniques [16], the inverse dielectric function $\varepsilon^{-1}$ can be related to the density response function $\chi$ by

$$\varepsilon^{-1}(1, 2) = \delta(1, 2) + v(1, 1') \chi(1', 2). \quad (2.1)$$

Here each number represents a set of coordinates (space ($r$), time ($t$), spin ($\sigma$)), and repeated numbers imply integration (or summations) over the corresponding sets of coordinates; $v(1, 1')$ is the Coulomb interaction. The density response function $\chi$ is given by [8]

$$\chi(1, 2) = G(1, 1; 2, 2) \quad (2.2)$$

where $G$ is the two-particle Green's function: $G$ is a solution of the Bethe-Salpeter equation [16, 17] (see Fig. 1):

$$G(1, 1'; 2, 2') = G^0(1, 1'; 2, 2') + G^0(1, 1'; 3, 3') I(3, 3'; 4, 4') G(4, 4'; 2, 2') \quad (2.3)$$

where $G^0$ is the propagator of a non-interacting electron-hole pair:

$$G^0(1, 1'; 2, 2') = g(1', 2') g(2, 1). \quad (2.4)$$

Here $g$ denotes the one-particle propagator. The irreducible electron-hole interaction $I$ will be taken, as in references [7] and [8], as the sum of a screened electron-hole attraction $Y$, which gives rise to the excitonic effects, and an unscreened exchange $Z$ between electron-hole pairs which is responsible for the RPA local-field effects [8, 18] (see Fig. 2):

$$I(3, 3'; 4, 4') = \delta(3, 4) \delta(3', 4') Y(3, 3') + \delta(3, 3') \delta(4, 4') Z(3, 4). \quad (2.5)$$

Fig. 2. — The irreducible electron-hole interaction $I$ (a) electron-hole attraction (screened) (b) electron-hole pair exchange (unscreened).

If a static screening is taken in the electron-hole attraction $Y$, then the irreducible interaction $I$ is time-independent, and thus the two-particle Green's function in equation (2.2) depends only on the time difference $t - t'$. Using the Fourier-space representation of the above equations, this time difference will be replaced by a frequency-dependence ($\omega$).

A physical picture can be gained for the content of the Bethe-Salpeter equation by expanding it into a Born's series (Fig. 3):

$$G = G^0 + G^0 I G^0 + G^0 I G^0 I G^0 + \cdots = G^0 + G^0 Y G^0 + G^0 Z G^0 + \cdots \quad (2.6)$$

Fig. 3. — Schematic representation of the interactions between the electron-hole pairs. Only the first two terms of the Born's series are represented.

The external perturbation promotes electrons into the conduction band and creates holes in the valence band and thus gives rise to the non-interacting propagator $G^0$. Electrons and holes within the same pair and of different pairs are then coupled in the process $G^0 I G^0$ via the electron-hole attraction $Y$. Of course there is also the Coulomb repulsion $Z$ between different e-h pairs.
3. Local representation.

3.1 WANNIER REPRESENTATION. — The one-particle Green's function \( g \) in (2.4) can be constructed from quasi-particle states \( \psi_i, E_i \) satisfying the crystal Schrödinger equation:

\[
H \psi_i = E_i \psi_i
\]

where the index \( l \equiv (n, k, \sigma) \) stands for the band index \( n \), the wavevector \( k \) and the spin \( \sigma \). Hence, the one-particle Green’s function reads

\[
g(1, 2; \omega) = \sum_i \frac{\psi_i(1) \psi_i^*(2)}{\omega - E_i}
\]

and the two particle propagator \( G^0 \) which enters the Bethe-Salpeter equation is, as defined in (2.4), the product of two such one-particle Green's functions (3.2).

The Bethe-Salpeter equation (2.3) can be cast into a matrix equation of reasonable dimension by including explicitly one important feature of semiconductor charge densities, namely, their relative localization in space. This leads to the idea of expanding the electronic Bloch states \( \psi_i \) in terms of suitable local orbitals \( \phi_v \) [7, 8, 18] :

\[
\psi_i(1) = N^{-1/2} \sum_v \phi_v(1) T_{di} \phi_v(d),
\]

where

\[
\phi_v(1) = \phi_v(r_1 - R_t)
\]

and

\[
T_{di} = c_n(k) e^{iR_t}.
\]

The index \( v \) identifies the different local orbitals \( \phi_v \) and the vector \( R_t \) denotes their positions in the lattice. \( N \) is the number of lattice vectors.

The input quantities \( G^0 \) and \( I \) of the Bethe-Salpeter equation, can now be replaced by matrices of numerically manageable sizes. The equation can then be solved simply by matrix inversion [7, 8, 18]:

\[
G = G^0[1 - (Y + Z) G^0]^{-1} = [G^0 - (Y + Z)]^{-1}
\]

where the matrix elements of \( G^0 \) are given by:

\[
G^0_{ss'}(q, \omega) = N^{-1} \sum_{n,n',k} c_{n'}^* c_n e^{i(k + q) \cdot R_t} \times \frac{f_s(k + q) - f_s(k)}{E_n(k + q) - E_n(k) - \omega - i\eta}
\]

Here \( f_s(k) \) is the occupation number of the Bloch state \( (n, k) \), \( E_n(k) \) is the eigenvalue corresponding to this state and \( \eta \) is a positive convergence factor \( (\eta \rightarrow 0^+) \). The index \( s \equiv (v, \mu, R_t) \) stands for a set of indices with \( v, \mu \) denoting local orbitals and \( R_t \) giving the distance between these orbitals.

The electron-hole attraction \( Y \) has the matrix elements:

\[
Y_{ss'}(q) = -\frac{1}{Z} \sum_m e^{-i \mathbf{R}_m} \int d^3r \times \int d^3r' \phi^*_s(r - R_t - R_m) \phi_s(r' - R_m) \times v_\mu(r - r') \phi^*_\mu(r') \phi_\mu(r - R_t)\]

(3.7)

where \( v_\mu(r - r') \) is the screened Coulomb potential [8]. For the electron-hole exchange one has:

\[
Z_{ss'}(q) = \sum_G A^*_{ss'}(q + G) v(q + G) A_{ss'}(q + G)
\]

(3.8)

\[
= \sum_m e^{-i \mathbf{R}_m} \int d^3r \int d^3r' \phi^*_s(r - R_t - R_m) \phi_s(r - R_m) \times v(r - r') \phi^*_\mu(r') \phi_\mu(r - R_t),
\]

(3.9)

where

\[
A_{ss'}(q + G) = \int d^3r \phi^*_s(r) e^{-i(q + G)r} \phi_s(r - R_t)
\]

(3.10)

are density form-factors.

With this the inverse dielectric function, defined in (2.1), takes the form [7, 8, 18]:

\[
\epsilon^{-1}(q + G, q + G'; \omega) = \delta_{G'G} + v(q + G) \sum A_{ss'}(q + G) G_{ss'}(q; \omega)
\]

(3.11)

where \( v(q + G) \) is the Coulomb potential in wave-vector representation and \( G_{ss'}(q; \omega) \) is the full electron-hole propagator.

Aiming at the absorption spectrum we have to consider the long-wavelength limit of the dielectric function. Particular care is needed in taking this limit in order to include the local-field effects. This leads to the formula [19-21]

\[
e(\omega) = \lim_{q \rightarrow 0} \frac{1}{\epsilon(q + G, q + G'; \omega)}
\]

(3.12)

which, in the local-orbital representation, reduces to [7]

\[
e(\omega) = \epsilon_z(\omega) + i\epsilon_2(\omega) = 1 - \frac{4\pi e^2}{\Omega_0} \sum s \epsilon_s G_{ss'}(\omega) f_s^*.
\]

(3.13)

Here \( G(\omega) = G(q = 0; \omega) \), and

\[
f_s^* = \int d^3r \phi^*_s(r) r_s \phi_s(r - R_t)
\]

(3.14)

are again density form factors, \( \alpha \) denotes a principal axis of the cubic crystal and \( \Omega_0 \) is the volume of the unit cell.
At this point it is worth noting that three approximations will be met in the following discourse [15],
a) $\varepsilon_0(\omega)$ is the dielectric function calculated by neglecting both local-field and exchange effects (matrices $Y$ and $Z$ in Eq. (3.5) set equal to zero).
b) $\varepsilon_{\text{BRPA}}(\omega)$ is the result of the calculation which includes only local-field effects (matrix $Z \neq 0$ and matrix $Y = 0$).
c) $\varepsilon_{\text{exc}}(\omega)$ is the result of the calculation which includes both local-field and excitonic effects (matrices $Y$ and $Z \neq 0$).

3.2 GAUSSIAN REPRESENTATION. — In order to extract numerical values for $\varepsilon(\omega)$ from equation (3.13), explicit expressions for the local orbitals $\phi_i$ are needed. In our application to GaP, we construct these local orbitals following a method originally proposed by Hall [22] and later by Stocker [23]. On each atom $\text{sp}^3$-hybrids are formed from s- ($R_s(1 \ r 1 \ D)$ and p-like ($R_p(1 \ r 1)$) orbitals in such a way that they point in the four tetrahedral directions connecting each atom to its nearest neighbours [24].

$$\chi^{(0)}_t(t) = \frac{(4\sqrt{\pi})^{-1}}{N_+} \times \left\{ R^{(0)}_t(1 \ r 1) + \sqrt{2} \frac{v \cdot r}{|r|} R^{(0)}_p(1 \ r 1) \right\}. \quad (3.15)$$

The vector $v$ denotes the tetrahedral directions $(1,1,1); (1,-1,-1); (-1,1,-1)$ and $(-1,-1,1)$ which will be referred to by the numbers $v=1, 2, 3, 4$, respectively. $i = 1$ or 2 refers to the type of atom considered. The bonding orbitals, which give rise to the valence bands, are formed by adding two hybrids from neighbouring atoms pointing towards each other:

$$\psi_i(\phi_i + \phi_i +) = \frac{1}{N_+} \left( \chi^{(0)}_t(t) + \lambda \chi^{(2)}_t(t - b v) \right). \quad (3.16)$$

The factor $\lambda$ takes account of the asymmetry of the bond; $b = \frac{a_0}{4}$ with $a_0$ being the lattice constant and $N_+$ is a normalization factor.

The antibonding orbitals, spanning the conduction bands of the crystal, are orthogonalized [18] to the bonding orbitals by Schmid’s orthogonalization procedure [25]:

$$\tilde{\phi}_i(\phi_i -) = \frac{1}{K(1, -)} \left\{ \phi_i(\phi_i -) - \frac{1}{N_+} \left( \phi_1(1) \phi_2(1) \right) \times \sum_{\nu \neq \mu} \left( \phi_\nu(\phi_i -) - \phi_\nu(\phi_i - R_{\mu}) \right) \right\}. \quad (3.17)$$

Here $K(1, -)$ is a normalization constant, $R_{\nu} = \frac{a_0}{4} (\mu - v)$ with $\mu$ and $v$ being one of the tetrahedral directions and

$$\phi_i(\phi_i -) = \frac{1}{N_+} \left( \chi^{(1)}_t(t) - \lambda \chi^{(2)}_t(t - (b + a_0) v) \right). \quad (3.18)$$

The scalar product $\langle \phi_1(1) | \phi_2(1) \rangle$ denotes the overlap between bonding and antibonding (non-orthogonalized) orbitals pointing in different directions.

As in our previous work on one-component insulators (C) and semiconductors (Si) the local-orbitals are expanded in a Gaussian basis

$$R_\alpha(r) = \sum_i a_i e^{-a_i r^2}. \quad (3.19)$$

$$R_\alpha(r) = r \sum_j b_j e^{-b_j r^2}. \quad (3.20)$$

This Gaussian basis is convenient in that all multicenter integrals in $\varepsilon(\omega)$ due to the many-body effects (the matrices $Z$ and $Y$) of the form

$$\int d^3r \int d^3r' e^{-a(r - A)^2} e^{-b(r - B)^2} e^{-c(r - c)^2} \times \frac{1}{|r - r'|} \times e^{-d(r - D)^2}. \quad (3.21)$$

where $a, b, c, d, \alpha$ are coefficients and $A, B, C, D$ vectors, can be integrated analytically (see appendix of Ref. [8]).

4. Numerical calculation for a heteropolar crystal.

4.1 ENERGY BANDS AND WAVE FUNCTIONS. — The computation of the free electron-hole propagator $G^0$ (see Eq. (3.6)) needs the energy-band structure $E_n(k)$ of the crystal as well as the expansion coefficients $c_n(k)$. We use a Slater-Koster LCAO interpolation [26] of the band structure of GaP. Of course, we should ideally use a quasiparticle band structure and not a pseudopotential band structure which is adjusted to optical gaps [7, 18]. Such a band structure calculated from first principles is now available for diamond [27]. However, in lack of such a calculation for GaP, the energy spectrum of the non-local pseudopotential calculation of Chelikowsky and Cohen [28] has been used as an empirically adjusted approximation to a quasiparticle band structure. We expand the Bloch wavefunctions $\psi_{\alpha}(r)$ in terms of local orbitals:

$$\psi_{\alpha}(r) = \sum_{\nu \in \mu} c_{\nu \alpha}(k) e^{iR_{\nu} \phi_i(r - R_{\nu})} = \sum_{\nu \in \mu} c_{\nu \alpha}(k) \sum_{\nu \in \lambda} e^{iR_{\nu} \phi_i(r - R_{\nu})} \quad (4.1)$$

The matrix elements of the Hamiltonian $H$ are

$$H_{\mu \nu}(k) = \sum_{\nu \in \mu} c_{\mu \nu}(k) h_{\mu \nu}(k) c_{\mu \nu}(k) \quad (4.2)$$

where

$$h_{\mu}(k) = \sum_{\nu \in \mu} \langle \phi_i(\phi_i -) | H | \phi_i(\phi_i -) \rangle \quad (4.3)$$

is the transformed Hamiltonian in the local basis. Hence the diagonalization of $H$ is reduced to that of $h$ at each point $k$ of the Brillouin zone. In the zincblende structure of GaP (Fig. 4), the sum over the f.c.c. lattice vector $R_m$ in equation (4.3) is carried up to the third-nearest neighbours. The lengthy expres-
sions for matrix elements of $h$ are listed in the appendix.

In fitting, we consider the overlap matrix elements \( \langle \phi_\mu(r) \mid H \mid \phi_\nu(r - R_m) \rangle \) as parameters. Hence we get two \((4 \times 4)\) matrices at each \(k\)-point, one for the valence bands and the other for the conduction bands. The least-square fit of the non-local pseudopotential [28] band structure of GaP results in the two sets of parameters which are given in table I. The Slater-Koster band structure is displayed in figure 5. The eigenvalues and eigenvectors resulting from the diagonalization of the above matrices at each \(k\) point are combined to calculate the free electron-hole propagator using the tetrahedron Brillouin zone integration method [29, 30].

Table I. — Parameter \( \langle \phi_\mu(r) \mid H \mid \phi_\nu(r - R_m) \rangle = \xi_i \)
of the Slater-Koster representation of the non-local pseudopotential band structure of gallium phosphide [28]. The origin is taken at a gallium atom. The indices Ga and P in \(\xi_i\) are added, when needed, to take account of the asymmetry of the bonds. The indices 1 and 2 for \(\nu\) or \(\mu\) refer to the tetrahedral vectors \([1, 1, 1]\) and \([1, -1, -1]\) respectively. The f.c.c. lattice \(R_m\) are in units of \(a_0/2\), \(a_0 = 5.45\) Å being the lattice constant.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>(v)</th>
<th>(\mu)</th>
<th>(R_m \left( a_0/2 \right))</th>
<th>Valence bands (eV)</th>
<th>Conduction bands (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\xi_0)</td>
<td>1</td>
<td>1</td>
<td>((0, 0, 0))</td>
<td>−4.9374</td>
<td>+7.6737</td>
</tr>
<tr>
<td>(\xi_{1P})</td>
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<td>2</td>
<td>((0, 0, 0))</td>
<td>−0.1991</td>
<td>−0.0469</td>
</tr>
<tr>
<td>(\xi_{1Ga})</td>
<td>1</td>
<td>2</td>
<td>((0, 1, 1))</td>
<td>−1.6858</td>
<td>−0.8022</td>
</tr>
<tr>
<td>(\xi_{2})</td>
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<td>1</td>
<td>((0, 1, 1))</td>
<td>0.53475</td>
<td>−1.07315</td>
</tr>
<tr>
<td>(\xi_{3})</td>
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<td>2</td>
<td>((1, 1, 0))</td>
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<td>0.1920</td>
</tr>
<tr>
<td>(\xi_{4})</td>
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<td>1</td>
<td>((1, −1, 0))</td>
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<td>0.86825</td>
</tr>
<tr>
<td>(\xi_{5P})</td>
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<td>((0, 1, −1))</td>
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<td>0.2474</td>
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<tr>
<td>(\xi_{5Ga})</td>
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<td>2</td>
<td>((0, 0, 2))</td>
<td>−0.1379</td>
<td>−0.7436</td>
</tr>
<tr>
<td>(\xi_{6})</td>
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<td>((0, 0, 2))</td>
<td>0.0004</td>
<td>−0.29905</td>
</tr>
<tr>
<td>(\xi_{7P})</td>
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<td>((1, −1, 0))</td>
<td>0.0183</td>
<td>0.1844</td>
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<tr>
<td>(\xi_{7Ga})</td>
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<td>((1, 1, 2))</td>
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<td>0.0110</td>
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<tr>
<td>(\xi_{8P})</td>
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<td>((0, −1, −1))</td>
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<tr>
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<td>2</td>
<td>((0, 2, 2))</td>
<td>0.07301</td>
<td>0.04368</td>
</tr>
</tbody>
</table>

Having found higher-order overlap to introduce about 5% corrections, only nearest-neighbour f.c.c. overlaps (in bonding and antibonding orbitals) are used in equation (3.13). Thus, the matrices \(G^0, Y\) and \(Z\) are of dimensions \((28 \times 28)\). Group symmetry arguments then lead for \(G^0\) to 26, and for \(Y = Y(q = 0)\) and \(Z = Z(q = 0)\) to 27 independent elements.

The parameters of the Gaussian representation of local orbitals are obtained from a least-square fit to the charge density [28]. They are given in table II. The parameter \(\lambda\) could, in principle, be determined by minimizing the ground state energy of the crystal. We have determined it by minimizing the remaining (after the Schmid process in (3.17)) overlap between

Table II. — Parameters of the Gaussian representation of the local orbitals in GaP. The indices 1 and 2 refer to gallium and phosphorus atom, respectively.

| Parameter | \(R_s^{(1)}\) | \(a_1\) | \(\alpha_1\) | \(a_2\) | \(\alpha_2\) | \(b_1\) | \(\beta_1\) | \(b_2\) | \(\beta_2\) | \(a_1\) | \(\alpha_1\) | \(a_2\) | \(\alpha_2\) | \(b_1\) | \(\beta_1\) | \(b_2\) | \(\beta_2\) |
|-----------|-------------|--------|-------------|--------|-------------|--------|-------------|--------|-------------|--------|-------------|--------|-------------|--------|-------------|--------|-------------|--------|-------------|
| \(R_s\)  | 3.08960     | −2.75720 | 0.25000     | 0.32000 | 0.17380     | 0.03710 | 0.11000     | 0.25000 | 2.37860     | −2.12270 | 0.20000     | 0.26670 | 0.09820     | 0.02100 | 0.07000     | 0.15000 |
bonding and orthogonalized antibonding orbitals. In this way a value $\lambda = 0.2$ was found, resulting in the overlap $\langle \phi_1^+ | \phi_2^- \rangle = 0.040$, with the phosphorus atom as origin.

4.2 Electron-hole interactions. — The independent matrix-elements of the electron-hole exchange matrix $\tilde{Z} = Z(\mathbf{q} = 0)$ are evaluated through the density-form factors $A(\mathbf{q} + \mathbf{G})$ (see (3.8)) which can be calculated analytically in the Gaussian representation. The indices $v$ and $\mu$ in the matrix $\tilde{Z}$, as well as in $\tilde{Y} = Y(\mathbf{q} = 0)$, are restricted, so that $v$ refers to bonding and $\mu$ to antibonding orbitals $[18]$. The orthogonalized antibonding orbitals $\tilde{\phi}_\mu$ in (3.17) which replace $\phi_\mu$ in all formulae, lead to additional correction terms in the density form factors $A$, as well as in the exchange matrix $\tilde{Z}$. We considered the most important of these terms and we summed over the reciprocal lattice vectors $\mathbf{G}$ until convergence is reached.

For the static screening entering the electron-hole attraction $\tilde{Y} = Y(\mathbf{q} = 0)$, we took that of silicon $[18]$ assuming that the variation of the dielectric function, at least in the middle of the bond-region, where electron-hole pairs are most likely created, is approximately the same for these two crystals of nearly equal lattice constants $[31]$. In the electron-hole attraction $\tilde{Y}$ the orthogonalized antibonding orbitals $\tilde{\phi}_\mu$ (Eq. (3.17)) when used instead of $\phi_\mu$ lead to an enormous number of correction terms, the most important of which we consider. The sum over the lattice vectors $\mathbf{R}_m$ in $\tilde{Y}$ is carried out up to third-nearest neighbours.

5. Results and discussion.

This section contains our results for the absorption spectrum of gallium phosphide in comparison with the recent ellipsometric measurements of Aspnes and Studna $[32]$. Figures 6(a) and (b) display the theoretical absorption spectra ($\tilde{\epsilon}$, $\epsilon_{\text{RPA}}$, $\epsilon_{\text{xc}}$) corresponding to the already mentioned three steps in the many-body approximations.

The main absorption (2.5 eV-6 eV) in the measured spectrum comes predominantly from transitions between the upper valence and the lower conduction bands. The two main peaks denoted by $E_1$ and $E_2$ in figure 6, were attributed by Chelikowsky and Cohen $[28]$ to the transitions $L_3^-\Gamma_1^-$ and $\Gamma_{15}^-\Gamma_5^-$. The curve $\tilde{\epsilon}(\omega)$, calculated in the approximation of non-interacting electron-hole pairs ($G = G^0$), places these two peaks at essentially the same positions as in the pseudopotential calculation of Chelikowsky and Cohen, namely at 4.0 eV and 5.2 eV. These values agree fairly well with the old experimental results of H. R. Philipp and H. Ehrenreich $[33]$. However, the oscillator strength of the peak $E_1$ is about half the recently measured value $[32]$. This feature has also been observed within the non-interacting approximation in the calculation of the optical spectra of diamond and silicon $[7, 8]$ and it turns out to be the same for all III-V and II-VI semiconductors $[28]$. In the next step, we include the RPA Coulomb repulsion between electron-hole pairs (interaction $Z$) which is responsible for the local-field effects. The curve $\epsilon_{\text{RPA}}$ displays a further discrepancy with experiment: the two main peaks are simultaneously reduced in strength and shifted to higher energies. This trend of the repulsive RPA Coulomb interaction has also been noted in covalent crystals $[7, 8, 14, 34]$. The shift of the absorption strength to higher energies is also reflected in a decrease of the calculated static dielectric constant $\epsilon_{\text{RPA}}(\omega = 0) = 7.66$ extracted from Kramers-Kronig analysis: The value obtained in the single-particle approximation is $\tilde{\epsilon}(\omega = 0) = 13.01$ compared to the experimental value 11.1 $[35]$. However, the calculated values of the static dielectric constant are to be taken with caution because of the bad reproduction of the higher conduction bands in the Slater-Koster interpolation. In the least-square fit emphasis has been placed on the valence and the lower conduction bands which contribute to the region of main absorption (2.5 eV-6 eV). On the other hand, the integration in the Kramers-Kronig relations is over the entire spectrum. However, for the higher conduction bands, we also believe that the empirical pseudopotential bands are probably fairly inaccurate: they suffer from similar restrictions, in that they are adjusted only for the lower-energy optical transitions.

A significant improvement arises in the calculated
absorption spectrum when we additionally include the electron-hole attraction (interaction Y) which is responsible for the excitonic effect (the curve $\varepsilon_{ex}(\omega)$ in Fig. 6a). The peak $E_1$ is significantly enhanced and agrees with the experimental magnitude of 25.52 [32]. Due to the combined excitonic and local-field effects it is shifted by 0.2 eV to lower energies. Similar to previous work on the covalent crystals [7, 8], the absorption strength around the peak $E_2$ is severely lowered on the high energy side. But although improvement in the oscillator strength results, further improvement in the absorption lineshape of $\varepsilon_{ex}(\omega)$ around $E_1$ is still required. Our experience in C and Si is that such an improvement is only possible on the basis of an accurate calculation of quasiparticle conduction bands, in particular, also for higher energies [18, 27, 36]. As was already noted in the previous work on silicon [8, 27], a more precise description of conduction-band states renders our present assumption of nearest-neighbour f.c.c. overlap between bonding and antibonding orbitals as insufficient. This assumption reduced the propagator $G^0$ and the interactions $Z$ and $Y$ to matrices of the size $(28 \times 28)$. Extension to second-nearest neighbour overlaps between bonding and antibonding orbitals increased the matrix sizes to $(52 \times 52)$ and resulted in significantly improved absorption lineshapes also around the $E_2$-peak in silicon [18]. Similar improvement in the case of GaP is expected and is under consideration. The calculated value of the dielectric constant in the time-dependent screened Hartree-Fock approximation is $\varepsilon_{xc}(\omega = 0) = 12.8$, value which is significantly closer than $\varepsilon_{RPA}$ or $\varepsilon$ to experiment.

Summarizing, our investigation demonstrates the importance of both the electron-hole attraction and the electron-hole exchange which is responsible for the local fluctuating fields, in the calculation of the optical response of a III-V compound. The main features of these many-body effects, already stressed in previous studies of single-element covalent crystals [7, 8, 18] are again observed in gallium phosphide: The still commonly used approximation of a non-interacting electron-hole polarization significantly underestimates the optical absorption strength on the low-energy side and, because of the f-sum rule, overestimates the absorption on the high energy-side. The RPA local-field effect, as a repulsive interaction between e-h pairs, further enhances the discrepancy with experiment, by shifting the absorption structures to higher energies. The excitonic effect in the low- and main-absorption region overwhelms the RPA Coulomb repulsion and the combined effects result in a factor of two (« excitonic » enhancement) of the $E_1$ absorption strength, also shifting the non-interacting peak position by about 0.2 eV for Si : 0.3 eV] to lower energies. Even if further work has clearly to be directed towards a better description of the underlying single-particle (both energies and wavefunctions) properties, the present work establishes the need for a careful implementation of many-body effects in the electronic response of compound semiconductors.

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Appendix.

MATRIX ELEMENTS OF THE HAMILTONIAN $h$ (SEE EQ. (4.3)). — The vectors $t_1$, $t_2$, $t_3$ in the following equations are the primitive translations of the cubic lattice

$$t_1 = \frac{a_0}{2} (1, 1, 0); \quad t_2 = \frac{a_0}{2} (0, 1, 1); \quad t_3 = \frac{a_0}{2} (1, 0, 1)$$

and $k = (k_x, k_y, k_z)$ is a vector in the first Brillouin zone. The matrix elements of the Hamiltonian $h$ are given by equation (4.3) considering the overlap quantities $\langle \phi_p(r) | H | \phi_q(r - R_m) \rangle$ as parameters (see table 1):

$$h_{11} = \xi_0 + 2 \xi_2 [\cos k(t_1 - t_2) + \cos k(t_1 - t_3) + \cos k(t_2 - t_3)] +$$

$$+ \frac{2 \xi_3}{\cos k(t_1 - t_2 + t_3) + \cos k(t_1 + t_2 - t_3) + \cos k(-t_1 + t_2 + t_3)}.$$  

$$h_{22} = \xi_0 + 2 \xi_2 [\cos k(t_2 - t_3) + \cos k(t_1 - t_2) + \cos k(t_1 - t_3)] +$$

$$+ \frac{2 \xi_3}{\cos k(t_1 - t_2 + t_3) + \cos k(t_1 + t_2 - t_3) + \cos k(-t_1 + t_2 + t_3)}.$$  

$$h_{33} = \xi_0 + 2 \xi_2 [\cos k(t_3 - t_2) + \cos k(t_1 - t_3) + \cos k(t_1 - t_2)] +$$

$$+ \frac{2 \xi_3}{\cos k(t_1 - t_2 + t_3) + \cos k(t_1 + t_2 - t_3) + \cos k(-t_1 + t_2 + t_3)}.$$  

$$h_{12} = h_{21} = h_{13} = h_{31} = h_{23} = h_{32} = 0.$$  

$$h_{1i} = h_{2i} = h_{3i} = 0.$$
\[ h_{44} = \xi_0 + 2 \xi_2 [\cos k \cdot t_1 + \cos k \cdot (t_1 - t_2) + \cos k \cdot (t_1 - t_3)] + \\
+ 2 \xi_4 [\cos k \cdot t_2 + \cos k \cdot t_3 + \cos k \cdot (t_2 - t_3)] + \\
+ 2 \xi_6 [\cos k \cdot (t_1 - t_2 + t_3) + \cos k \cdot (t_1 + t_2 - t_3) + \cos k \cdot (-t_1 + t_2 + t_3)]. \]

\[ h_{12} = \xi_{1P} + \xi_{1Ga} e^{i k \cdot t_2} + \xi_{5Ga} \left[ e^{i k \cdot t_1} + e^{i k \cdot (t_1 - t_2)} + e^{i k \cdot (t_1 - t_3)} + e^{i k \cdot (t_2 - t_3)} \right] + \\
+ \xi_{7Ga} \left[ e^{i k \cdot t_1} + e^{i k \cdot (t_1 - t_2)} + e^{i k \cdot (t_1 - t_3)} + 2 \xi_{SP} \cos k \cdot (t_1 - t_2) + \\
+ \xi_{7SP} e^{i k \cdot t_1} + \xi_{5Ga} \left[ e^{i k \cdot (t_1 - t_2)} + e^{i k \cdot (t_1 - t_3)} + \xi_{BGa} e^{i k \cdot t_1} + \xi_{7Ga} \left[ e^{i k \cdot (t_1 - t_2)} + e^{i k \cdot (t_1 - t_3)} + e^{i k \cdot (t_2 - t_3)} + e^{i k \cdot (t_2 - t_3)} \right] \right]. \]

References


