

Many-Body Effects on the Electronic and Optical Properties of Bulk GaP

O. PULCI¹ (a), M. PALUMMO (a), V. OLEVANO (b), G. ONIDA (a), L. REINING (b), and R. DEL SOLE (a)

(a) *INFM, Dip. di Fisica, Università di Roma Tor Vergata, Via della Ricerca Scientifica 1, I-00133 Roma, Italy*

(b) *Laboratoire des Solides Irradiés, CNRS-CEA, École Polytechnique, F-91128 Palaiseau, France*

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We present an ab-initio study of GaP bulk as a test case to show the importance of going beyond the single particle Density Functional Theory (DFT) scheme in the calculation of excited state properties. The inclusion of many-body effects within the GW approach for the determination of electronic gaps, and of excitonic effects in the calculations of the dielectric function, is discussed. Comparison with one-particle DFT results and with experimental data are presented.

1. Introduction

Density Functional Theory (DFT) [1] has been shown to be a powerful tool in describing ground state properties of many-particle systems as, for example, equilibrium geometries for different growth conditions, adsorption energies of atoms on surfaces, and so on. However, it is known that the agreement between DFT and experimental band structures is not satisfactory: the calculated electronic band gaps severely underestimate the experimental ones. Moreover, the DFT optical spectra, even if often in *qualitative* agreement with experiment, do not show a *quantitative* agreement: typically, in the dielectric function of a semiconductor, the positions of the optical peaks are redshifted and the intensity of the first peak is underestimated. The problems originating from the use of a single particle ground state theory as DFT can be solved when using an excited state theory approach. In fact, in order to measure the photoemission energy or the optical spectrum, the system must undergo an excitation; this excitation can be realized with photons (as in photoemission and absorption) or with electrons (as in inverse photoemission, to probe the empty states). Hence, excited states are involved. Moreover, a single particle theory does not describe optical absorption experiments: the excited electron can interact with the hole left behind. This two-body interaction is called exciton. In this paper, we study the gallium phosphide bulk as an example for III–V semiconductors. We calculate the quasiparticle energy levels within the GW scheme, and the excitonic effects are included by solving a Bethe-Salpeter equation.

2. Calculation of Quasiparticle Energies within the GW Method

The Kohn-Sham single-particle energies, defined as the eigenvalues of the DFT equation, are not the electron addition or removal energies. This can be seen from Table 1

¹) Corresponding author; Phone: +39 06 72594548; Fax: +39 06 2023507;
e-mail: olivia.pulci@roma2.infn.it

Table 1

Transitions energy (in eV) at the high symmetry points of the Brillouin zone for GaP. a_{lat} is the lattice constant (in Å), E_{gap} the indirect gap. Experimental values are from [5]

	a_{lat}	Γ	X	L	E'_0	E''_0	E_{gap}
LDA	5.41	2.0	4.2	2.8	4.0	8.6	1.5
GW		2.8	5.0	3.6	4.9	9.3	2.3
exp.	5.45	$E_0 : 2.869$ $E_0 + \Delta_0 : 2.949$	$E_2 : 5.21 - 5.36$	$E_1 : 3.785$ $E_1 + \Delta_1 : 3.835$	4.77 $E'_0 + \Delta'_0 : 4.85$	9.38	2.35

comparing the DFT-LDA and the experimental electronic gaps for GaP. The discrepancy is general, as can be seen in Fig. 1 where for different III–V semiconductors the DFT-LDA electronic minimum gap is compared with experiment. Note that the equilibrium lattice constant a_{lat} , being a ground state property, is in reasonably good agreement with experiment.

The proper way to solve the problem of calculating the excitation energies of a system is to solve the so called single quasiparticle Eq. (2)

$$\left(-\frac{1}{2}\nabla^2 + V^{\text{ext}} + V^{\text{H}}\right) \Psi_j(\mathbf{r}) + \int \Sigma(\mathbf{r}, \mathbf{r}', \varepsilon_j^{\text{QP}}) \Psi_j(\mathbf{r}') d\mathbf{r}' = \varepsilon_j^{\text{QP}} \Psi_j(\mathbf{r}), \quad (1)$$

where V^{H} is the Hartree potential and Σ is a non local, energy dependent, non-hermitian potential that describes the exchange and correlation effects of the many-electron system. It is called “quasiparticle equation” because it describes the extra hole created when an electron is extracted from the system (for example in a photoemission experiment; or, in an inverse photoemission experiment, the extra electron added to the system) and the polarization cloud that the other electrons create in order to screen it. Due to the non-hermiticity of Σ , the energies ε^{QP} are in general not real: the imaginary part gives the life time of the excited particle. The self-energy Σ is defined by a set of coupled equations [2] involving Green’s functions, screened Coulomb interaction and polarizability. They are very difficult to solve even for simple systems. A successful way to deal with this problem is to approximate the self-energy with an expression that corresponds to solve the set of coupled equations in an iterative way, starting from $\Sigma = 0$ (Hartree) and ending with the first iteration: $\Sigma = iGW$, where G is the single particle Green’s function and W is the screened Coulomb interaction ($W = \epsilon^{-1}v$). The common way [3] to calculate Σ is to use the DFT independent single particle G and, for ϵ^{-1} , the inverse of the dielectric function ϵ computed in DFT within the independent single particle approach (also called Random Phase Approximation: RPA) [4].

The results for GaP and other III–V semiconductors, using a set of 256 k -points

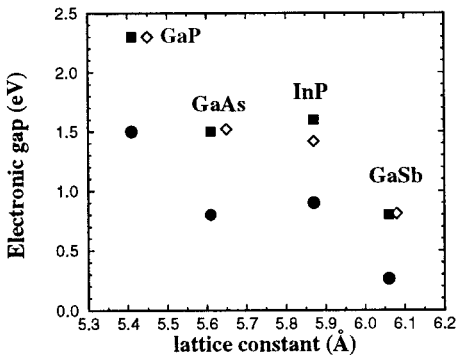


Fig. 1. Lattice constant and minimum gap for several bulk III–V semiconductors. ● DFT-LDA, ■ GW, ◇ experiment

in the BZ and 18 Ry energy cutoff in the LDA calculation (12 Ry in the *GW*), are shown in Table 1 and in Fig. 1. The agreement between *GW* and experimental energy gaps is improved compared with DFT-LDA results, but still discrepancies larger than 0.2 eV are present.

3. Dielectric Function: Inclusion of Excitonic Effects

In this section we discuss the theory and the computational method used to calculate the dielectric function including the electron–hole interaction. In fact it is well known that a correct description of the optical absorption spectra in semiconductors and insulators requires the inclusion of the excitonic effects. Due to the fact that this kind of computation can be very cumbersome, because a two particle Bethe-Salpeter equation must be solved, first-principle calculations of the optical properties of different materials, including excitonic effects, have appeared only in the last years [6].

The absorption spectrum is given by the imaginary part of the macroscopic dielectric function ϵ_M

$$\epsilon_M(\omega) = 1 - \lim_{\mathbf{q} \rightarrow 0} v(\mathbf{q}) \hat{\chi}_{\mathbf{G}=0, \mathbf{G}'=0}(\mathbf{q}; \omega), \quad (2)$$

where $\hat{\chi}(\mathbf{r}, \mathbf{r}'; \omega) = -iS(\mathbf{r}, \mathbf{r}, \mathbf{r}', \mathbf{r}'; \omega)$. The four-point function S obeys the Bethe-Salpeter equation,

$$S(1, 1'; 2, 2') = S_0(1, 1'; 2, 2') + S_0(1, 1'; 3, 3') \Xi(3, 3'; 4, 4') S(4, 4'; 2, 2'). \quad (3)$$

The notation (1,2) stands for two pairs of space and time coordinates, $(\mathbf{r}_1, t_1; \mathbf{r}_2, t_2)$. Repeated arguments are integrated over. The term $S_0(1, 1'; 2, 2') = G(1', 2')G(2, 1)$ yields the independent-particle polarizability χ_0 from which ϵ_M without excitonic effects is obtained ($G(1, 1')$ is the one-particle Green's function [7]). The kernel Ξ contains two contributions:

$$\Xi(1, 1', 2, 2') = -i\delta(1, 1')\delta(2, 2') v(1, 2) + i\delta(1, 2) \delta(1', 2') W(1, 1'). \quad (4)$$

Considering the first term in the calculation of S is equivalent to the inclusion of local field effects in the matrix inversion of a standard RPA calculation. In order to obtain the macroscopic dielectric constant, the bare Coulomb interaction v contained in this term must, however, be used without the long range term of vanishing wave vector [8]. When spin is not explicitly treated, v gets a factor of two for singlet excitons. In the second term, W is the screened Coulomb attraction between electron and hole. It is obtained as a functional derivative of the self-energy in the *GW* approximation, neglecting a term $G \delta W / \delta G$. This latter term contains information about the change in screening due to the excitation, and is expected to be small [9]. We limit ourselves to static screening, since dynamical effects in the electron–hole screening and in the one particle Green's function tend to cancel each other [10], which suggests to neglect both of them. The set of Eqs. (2)–(4) are at the basis of all the ab initio exciton calculations which have appeared in the literature recently (see for example Ref. [6] and references therein).

In order to solve Eq. (3), we rewrite it as an effective eigenvalue problem,

$$\sum_{(n_3, n_4)} H_{\text{exc}}^{(n_1, n_2), (n_3, n_4)} A_{\lambda}^{(n_3, n_4)} = E_{\lambda} A_{\lambda}^{(n_1, n_2)}, \quad (5)$$

with

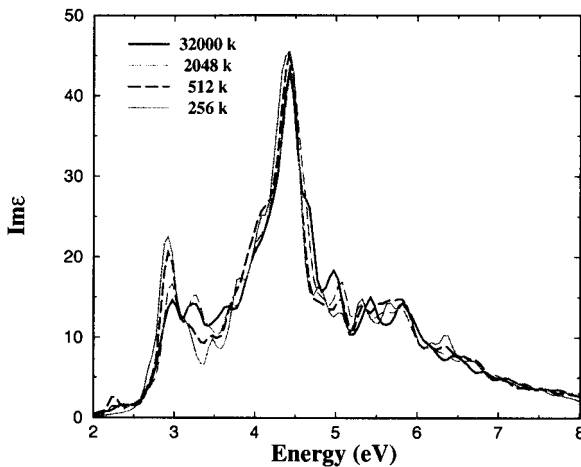
$$H_{\text{exc}}^{(n_1, n_2), (n_3, n_4)} = (E_{n_2} - E_{n_1}) \delta_{n_1, n_3} \delta_{n_2, n_4} - i(f_{n_2} - f_{n_1}) \times \int d\mathbf{r}_1 d\mathbf{r}'_1 d\mathbf{r}_2 d\mathbf{r}'_2 \psi_{n_1}(\mathbf{r}_1) \psi_{n_2}^*(\mathbf{r}'_1) \Xi(\mathbf{r}_1, \mathbf{r}'_1, \mathbf{r}_2, \mathbf{r}'_2) \psi_{n_3}^*(\mathbf{r}_2) \psi_{n_4}(\mathbf{r}'_2). \quad (6)$$

The $\psi_n(\mathbf{r})$ are LDA Bloch functions, with n denoting a band index and a Bloch vector \mathbf{k} . For the calculation of absorption spectra, we can limit ourselves to transitions with positive frequency, i.e. (n_1, n_2) and (n_3, n_4) are pairs of one valence and one conduction band, respectively (in other words, we consider only the resonant part). Moreover, we build up the spectra of optical properties by considering only negligible momentum transfer, hence the same \mathbf{k} for the valence and the conduction state. Equation (2) reads then:

$$\epsilon_{\text{M}}(\omega) = 1 + \lim_{\mathbf{q} \rightarrow 0} v(\mathbf{q}) \sum_{\lambda} \frac{\left| \sum_{v, c, \mathbf{k}} \langle v, \mathbf{k} - \mathbf{q} | e^{-i\mathbf{q}\mathbf{r}} | c, \mathbf{k} \rangle A_{\lambda}^{(v, c; \mathbf{k})} \right|^2}{(E_{\lambda} - \omega)}. \quad (7)$$

This calculation is generally very demanding because the matrix to diagonalize can be very large. In fact the relevant parameters which determine its size are the number of k -points in the BZ, the number of the valence bands N_v , the number of conduction bands N_c which build the basis set of pairs of states. In this work we used a recent perturbative approach [11, 12], to the solution of the Bethe-Salpeter equation which greatly reduces the use of memory. It consists in a separate diagonalization of subblocks of the excitonic Hamiltonian including the contribution of the missing terms in a perturbative way.

Particular care has to be taken for the convergence of the optical spectra with the number of k -points used to sample the BZ. In Fig. 2 we plot the RPA imaginary parts of the dielectric function of GaP obtained using different sets of k -points in the calculation. DFT-LDA energies, obtained using 18 Ry energy cutoff and including non-linear core corrections for Ga pseudopotential, have been used. Even for a very large number of k -points (32000 in BZ), small spurious structures due to the k -points sampling do appear. Because of the big computational effort, we could use, in the excitonic calculation, a maximum of 2048 k -points in the BZ, which give anyway a convergence comparable with using 32000 k -points.



The experimental imaginary part of the dielectric function of GaP is shown in Fig. 3 together with the theoretical results obtained with different level of approximations in the calculation.

Fig. 2. Convergence test of the RPA dielectric function for GaP (excitons not included) using different sets of k -points in the Brillouin zone. 2048 k -points give a satisfactory convergence. DFT-LDA energies have been used

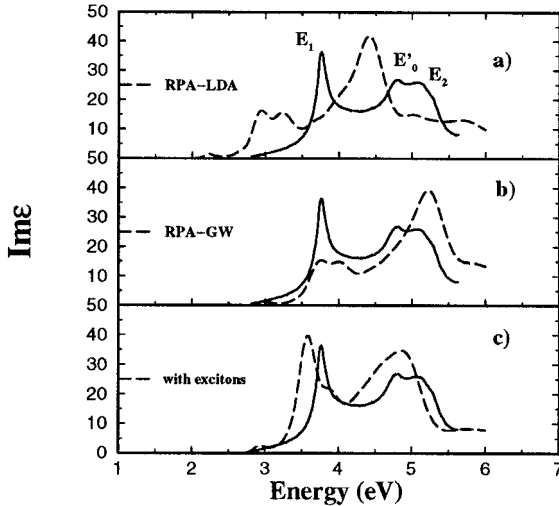


Fig. 3. Solid line: experimental dielectric function for GaP at $T = 15$ K, after [13]; dashed lines: a) RPA dielectric function (excitons not included) obtained with DFT-LDA energies, b) RPA dielectric function (excitons not included) obtained with GW energies, c) dielectric function obtained with GW energies and including excitonic effects. All the spectra have been calculated using 2048 k in BZ and an artificial broadening of 0.1 eV

We have used here a broadening of 0.1 eV (about a factor 2 larger than the the experimentally determined broadening at E_1 [13]) to take into account numerical noise due to a fi-

nite k -point sampling. In Fig. 3a, b we plot the RPA dielectric function (hence without excitonic effects) calculated respectively using DFT-LDA (Fig. 3a) and GW (Fig. 3b) energy bands. The agreement with experiment is in both cases only qualitative. In Fig. 3c, finally, excitonic effects are included (together with GW energy bands). It is evident that the curve obtained including the excitonic effects is in better agreement with the experimental result from Ref. [13] but still discrepancies appear. Our theoretical spectrum is, in fact, redshifted respect to the experimental one. Inclusion of electron-phonon interaction would further redshift the theoretical spectrum of about 0.07 eV [13].

Recently, a calculation of dielectric function of GaP within Time-Dependent Density Functional Theory has appeared [14]. The result from de Boeij et al. [14] shows a pronounced underestimation of E_1 (when compared with the low temperature experiment) and, as pointed out by the authors themselves, a quite large overestimation of the E'_0 and E_2 peaks. The energetic position of the peaks, being determined with an *ad hoc* scissor operator shift, is in good agreement with the experimental one.

4. Conclusions

We have presented a calculation of transitions energies and optical spectra of GaP bulk. The electronic gaps, underestimated in DFT-LDA, are in better agreement with experiment when calculated within the GW approach. The absorption spectrum constructed as a sum of independent transitions between quasiparticle states shows large deviations from experiment. The inclusion of excitonic effects in the calculations strongly improves the spectrum, yielding reasonable agreement with the measured one. Remaining discrepancies might be attributed to the pseudopotential approach, approximations in the calculation of the quasiparticle energies and/or limitations of the Bethe-Salpeter approach in its present forms.

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