

NON-DISPERSIVE PART OF BILINEAR OPTICAL SUSCEPTIBILITY IN JHA-BLOEMBERGEN APPROACH

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ABSTRACT

Within the bonding-antibonding orbital approach of Jha and Bloembergen, it is shown that the bilinear optical susceptibility $\chi^{(2)}$ for II-VI and III-V semiconductors satisfies a very simple relation in terms of other measurable physical quantities.

INTRODUCTION

SEVERAL phenomenological and empirical models¹⁻⁷ have been proposed to describe the contributions of bound electrons to the bilinear optical susceptibility $\chi_{ijk}^{(2)}$ defined by

$$P_i = \sum_j \chi_{ij}^{(1)} E_j + \sum_{j,k} \chi_{ijk}^{(2)} E_j E_k + \dots \quad (1)$$

where P is the optical polarization induced in the medium by an electric field E and $\chi_i^{(1)}$ is the linear susceptibility. Although the dispersive part of $\chi^{(2)}$ may be calculated by using a detailed knowledge of the band structure for the material in a limited range of energy, e.g., using the procedure of Jha and Wynne⁷, the non-dispersive part of $\chi^{(2)}$ is difficult to obtain theoretically in such an approach. A simple approximation scheme, using tetrahedral bonding orbitals for the ground state of III-V semiconductors, has been considered by Jha and Bloembergen² to obtain $\chi^{(2)}$ in these materials. Flytzanis and Ducuing³ did a more detailed calculation along these lines, using a sophisticated variational procedure. Phillips and Van Vechten⁴ and Kleinman⁵ have based their calculations on the dielectric theory developed earlier by Phillips. On similar lines, Tang and Flytzanis³ have developed the so-called charge-transfer model. Apparently the most successful approach at present seems to be that of Levine⁶, which is based on a semiclassical phenomenological bond-charge model.

In a two-band model involving bonding and antibonding orbital states, we show here that within the Jha-Bloembergen approach, $\chi^{(2)}$ can be exactly related to $\chi^{(1)}$ and the effective charge on the adjacent sites in II-VI or III-V compounds, apart from certain overlap terms. Thus, any honest calculation neglecting the overlap must lead to the results described in this paper.

EXACT RESULTS IN TWO-BAND MODEL

For definiteness, let us consider semiconductors involving two types of atoms A and B, with a

zincblende structure. The unperturbed valence and conduction band wave-functions $\psi_{\tilde{t}}^v$ and $\psi_{\tilde{t}}^c$ for the bond in the direction $\tilde{t} = a/4 \{1, 1, 1\}$ are

$$\psi_{\tilde{t}}^v = (1 + \lambda^2 + 2\lambda S_{AB})^{-1/2} (\lambda \phi_{\tilde{t}}^A + \phi_{\tilde{t}}^B) \quad (2)$$

$$\psi_{\tilde{t}}^c = (1 + \lambda^2 - 2\lambda S_{AB})^{-1/2} (-\phi_{\tilde{t}}^A + \lambda \phi_{\tilde{t}}^B) \quad (3)$$

where $\phi_{\tilde{t}}^A$ and $\phi_{\tilde{t}}^B$ are normalized sp^3 hybridized orbitals centered on atoms A and B, S_{AB} is the overlap between these two orbitals and λ is a parameter which is directly related to the effective charge at each site. Within a two-band model, one has²

$$\chi_{xx}^{(1)} = (2e^2 n/Eg) |\langle x \rangle_{vc}|^2 \quad (4)$$

$$\chi_{xyz}^{(2)} = - (3e^3 n/Eg^2) |\langle x \rangle_{vc}|^2 (\langle x \rangle_{cc} - \langle x \rangle_{vv}) \quad (5)$$

where n is the valence electron density and Eg is the energy gap between the valence and conduction band states. With our wave-functions, the dipole matrix elements are

$$\langle x \rangle_{vc} = \{ (1 + \lambda^2)^2 - 4\lambda^2 S_{AB}^2 \}^{-1/2} \times \{ \lambda (x_{BB} - x_{AA}) + (\lambda^2 - 1) x_{AB} \} \quad (6)$$

$$\langle x \rangle_{vv} = \{ (1 + \lambda^2 + 2\lambda S_{AB})^{-1} \times (\lambda^2 x_{AA} + x_{BB} + 2\lambda x_{AB}) \} \quad (7)$$

$$\langle x \rangle_{cc} = \{ (1 + \lambda^2 - 2\lambda S_{AB})^{-1} \times (\lambda^2 x_{BB} + x_{AA} - 2\lambda x_{AB}) \} \quad (8)$$

where x_{ij} is the matrix element of x between the sp^3 orbitals centered at sites I and J. Eqs. (4-8) immediately lead to our main result

$$\chi_{xyz}^{(2)} = \frac{3e}{2E_g} \chi^{(1)} \left[\frac{(1 + \lambda^2)}{(1 + \lambda^2)^2 - 4\lambda^2 S_{AB}^2} \times \left\{ ((1 + \lambda^2)^2 - 4\lambda^2 S_{AB}^2)^{1/2} \times \frac{(1 - \lambda^2)}{\lambda} \langle x \rangle_{vc} + \frac{(1 + \lambda^2)^2}{\lambda} x_{AB} - 2\lambda S_{AB} (x_{AA} + x_{BB}) \right\} \right] \quad (9)$$

Note that if one neglects overlaps S_{AB} and x_{AB} , and uses the f -sum rule

$$(2mE_p/\hbar^2) |\langle x \rangle_{vc}|^2 = 1 \quad (10)$$

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TABLE I

Crystal	$\chi^{(1)}$	$n (10^{23} \text{ cm}^{-3})$	λ	$\chi_{xyx}^{(2)}$ (10^{-6} esu) (Theor.)	$\chi_{xyx}^{(2)}$ (10^{-6} esu) (expt.)	
ZnS	..	0.33	2.02	0.41	0.25	0.15 ± 0.04 [9]
ZnSe	.	0.39	1.76	0.44	0.34	0.37 ± 0.14 [9]
ZnTe	..	0.50	1.42	0.46	0.57	0.44 ± 0.16 [9]
CdTe	..	0.49	1.18	0.46	0.63	0.80 ± 0.30 [9]
GaAs	..	0.79	1.78	0.66	0.53	1.80 ± 0.6 [9]; 0.90 ± 0.3 [10]
InAs	..	0.90	1.44	0.66	0.73	2.00 ± 0.6 [9]
InSb	..	1.17	1.18	0.69	1.27	3.30 ± 0.7 [9]
GaP	..	0.65	1.97	0.65	0.31	0.50 ± 0.1 [9]

one obtains a very important expression for $\chi^{(2)}$

$$\chi_{xyx}^{(2)} = (3/\sqrt{8}) (m/e^2 \hbar^2 n^3)^{1/4} \times (\chi^{(1)})^{7/4} (1 - \lambda^2)/\lambda \quad (11)$$

relating $\chi_{xyx}^{(2)}$ to known physical quantities. Similar relations may be obtained for other materials with different structures.

Using known values of $\chi^{(1)}$ and the values of λ determined from experimental results on phonon frequencies and the Szigeti formula with the local field correction factor (these are also in close agreement with Coulson, Redei and Stocker⁸), we give values of $\chi^{(2)}$ for II-VI and III-V compounds, in Table I. A comparison of our theoretical values with known experimental results shows that there is an excellent agreement for II-VI compounds. However, except for GaP, the agreement is poor for III-V compounds. We would like to stress again that our conclusion is independent of the explicit forms of the orbital wave-functions, and any calculation which neglects overlaps and considers only two bands must lead to these results. Since the role played by overlap integrals, if any, must be similar in both II-VI and III-V compounds, for explaining the discrepancy in the microscopic calculations for III-V compounds, it is perhaps necessary either to modify the effective values of λ in order to avoid overestimating the local field correction factors, or to consider more than two bands.

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