Bilinear optical susceptibilities of potassium dihydrogen phosphate and of III–V, II–VI and I–VII semiconductors

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Abstract. The approximate orbital-approach of Jha and Bloembergen is used to calculate the non-dispersive part of the bilinear optical susceptibility, $\chi^{(2)}$, for various compounds. Using bonding and antibonding states of the molecular orbital theory it is shown that $\chi^{(2)}$ satisfies a simple relation in terms of other measurable physical quantities. This relation is used to calculate $\chi^{(2)}$ for various III–V, II–VI and I–VII semiconductors, both with cubic zinc blende structure and with hexagonal wurtzite structure. The same procedure is used to obtain $\chi^{(2)}$ for potassium dihydrogen phosphate (KDP). The calculated values are compared with the experimentally observed values and it is found that the present model gives excellent results for II–VI compounds and for KDP.

Keywords. Bilinear susceptibility, KDP.

1. Introduction

Several phenomenological and empirical models (Robinson 1967, Jha and Bloembergen 1968, Flytzanis and Ducuing 1969, Phillips and Van Vechten 1969, Kleinman 1970, Tang and Flytzanis 1971, Tang 1973, Jha and Wynne 1972, Levine 1973) have been proposed to describe the contributions of bound valence electrons to the bilinear susceptibility χ^2 defined by

$$P_i = \sum_j \chi^{(1)}_{ij} E_j + \sum_{j,k} \chi^{(2)}_{ijk} E_j E_k + \cdots \tag{1}$$

where P is the optical polarization induced in the medium by an electric field E and $\chi^{(1)}_{ij}$ is the linear susceptibility. The formal quantum mechanical expressions for these susceptibilities for a crystal can be written down in terms of the unperturbed electronic states of the band theory. However, because of the difficulty in obtaining accurate unperturbed states, it becomes very difficult to calculate these susceptibilities to yield any quantitative result for the non-dispersive part of $\chi^{(2)}$. The dispersive parts of $\chi^{(1)}$ and $\chi^{(2)}$, on the other hand, may be calculated fairly accurately, since these require a detailed knowledge of the band structure, only in a limited region of energy. A simple approach to such a calculation for $\chi^{(2)}$ has been proposed by Jha and Wynne (1972) and was applied to the case of InSb. For the nondispersive part of $\chi^{(2)}$, Robinson (1967) has given an approximation, in which the bilinear susceptibility is written in terms of the

octupole moment of the ground state charge distribution. Using the molecular orbital approach, Jha and Bloembergen (1968) used tetrahedral bonding states for the ground state wave-functions of III–V semiconductors, to calculate $X^{(2)}$ in these materials. Flytzanis and Ducuing (1969) did a more detailed calculation along these lines using a sophisticated variational procedure. Phillips and Van Vechten (1969) and Kleinman (1970) based their calculations on the dielectric theory, developed earlier by Phillips. On similar lines, Tang and Flytzanis (1971) and Tang (1973) have developed the so-called charge transfer model. Apparently, the most successful approach at present seems to be that of Levine (1973), which is, however, based on a semiclassical-phenomenological bond-charge model.

In this paper, we consider compounds with two types of atoms A and B. Using the molecular orbital approach of Jha and Bloembergen, we show that $X^{(2)}$ can be written exactly in terms of other measurable physical quantities. In section 2, we derive this exact relation for $X^{(2)}$, in terms of $X^{(1)}$ and the effective charge on the adjacent sites A and B, apart from certain overlap terms (Arya and Tankhiwale 1974). This relation is independent of the explicit form of the orbital wave functions. In section 3, we use this result to calculate $X^{(2)}$ for AB compounds with tetrahedral symmetry. We give numerical values for various III–V, II–VI and I–VII semiconductors both with cubic zinc blende and with hexagonal wurtzite structure. Values thus obtained for II–VI semiconductors are found to be in excellent agreement with the experimentally observed values.

In potassium ·dihydrogen phosphate (KDP), the P-atom is tetrahedrally surrounded by four O-atoms and forms four tetrahedral P–O bonds. In the paraelectric phase, the main contribution to the bilinear susceptibility comes from these P–O bonds (Levine 1973). In section 4, we calculate $X^{(2)}$ due to these bonds in this compound. The numerically calculated value agrees fairly well with the experimentally observed value. We discuss our results in section 5.

2. Exact results for $X^{(2)}$

In the molecular orbital theory of Coulson, Redei and Stocker (1962) the bonding orbital corresponds to the ground state wave-function for the bound electron whereas the anti-bonding orbital corresponds to the excited state. These bonding and antibonding states Ψ_t^b and Ψ_t^a, respectively, for a bond in the direction t are

$$\Psi_t^b = (1 + \lambda^2 + 2\lambda S_{AB})^{-\frac{1}{2}} (\lambda\phi_t^A + \phi_t^B) \tag{2}$$

$$\Psi_t^a = (1 + \lambda^2 - 2\lambda S_{AB})^{-\frac{1}{2}} (-\phi_t^A + \lambda\phi_t^B) \tag{3}$$

where ϕ_t^A and ϕ_t^B are the normalized atomic orbitals centered on atoms A and B, respectively, S_{AB} is the overlap between these two orbitals, and λ a parameter which is directly related to the effective charge at each site. Considering only these bonding and antibonding states, one can easily write the expressions for $X^{(1)}$ and $X^{(2)}$ (Jha and Bloembergen 1968). The contributions to linear and bilinear suscepti-bilities $\beta^{(1)}$ and $\beta^{(2)}$, respectively, from a single bond having two electons, are given as

$$\beta^{(1)}_{\xi\xi} = (4e^2/E_g) \, | \langle \, \xi \, \rangle_{ab} \, |^2 \tag{4}$$

$$\beta^{(2)}_{\xi\xi\xi} = - (6e^3/E_g{}^2) \, | \langle \, \xi \, \rangle_{ab} \, |^2 \, (\langle \, \xi \, \rangle_{aa} - \langle \, \xi \, \rangle_{bb}) \tag{5}$$

where the subscript ξ refers to the component parallel to the bond direction and E_g is the energy gap between the bonding and antibonding states. The dipole moment matrix elements are

$$\langle \, \xi \, \rangle_{ab} = \{(1 + \lambda^2)^2 - 4\lambda^2 \, S^2_{AB}\}^{-\frac{1}{2}} \{\lambda \, (\xi_{BB} - \xi_{AA}) + (\lambda^2 - 1) \, \xi_{AB}\} \tag{6}$$

$$\langle \, \xi \, \rangle_{bb} = (1 + \lambda^2 + 2\lambda S_{AB})^{-1} \, (\lambda^2 \, \xi_{AA} + \xi_{BB} + 2\lambda\xi_{AB}) \tag{7}$$

$$\langle \, \xi \, \rangle_{aa} = (1 + \lambda^2 - 2\lambda S_{AB})^{-1} \, (\lambda^2\xi_{BB} + \xi_{AA} - 2\lambda\xi_{AB}) \tag{8}$$

where ξ_{IJ} is the matrix element of ξ between the atomic orbitals centered at sites I and J.

Equations (4) and (5) give the longitudinal part of the susceptibilities due to a single bond. Transverse parts of $\beta^{(1)}$ and $\beta^{(2)}$ can be shown to be zero with in our model (Levine 1973). Thus we can write for the susceptibilities $\chi^{(1)}$ and $\chi^{(2)}$ due to all the bonds in a crystal as

$$\chi^{(1)}_{ij} = G^{(1)}_{ij} \, N_b \, \beta^{(1)}_{\xi\xi} \tag{9}$$

$$\chi^{(2)}_{ijk} = G^{(2)}_{ijk} \, N_b \, \beta^{(2)}_{\xi\xi\xi} \tag{10}$$

Here N_b is the number of bonds per unit volume, each bond having two electrons. The geometrical factors $G^{(1)}_{ij}$ and $G^{(2)}_{ijk}$ can be calculated by taking into account the orientations of the bonds in each unit cell as

$$G^{(1)}_{ij} = (1/n_b) \sum_\lambda a_i \, (\lambda) \, a_j \, (\lambda) \tag{11}$$

$$G^{(2)}_{ijk} = (1/n_b) \sum_\lambda a_i \, (\lambda) \, a_j \, (\lambda) \, a_k \, (\lambda) \tag{12}$$

where the sum on λ is over all the n_b bonds in the unit cell and $a_i(\lambda)$ is the direction cosine of the λ-th bond in the unit cell with respect to the i-th coordinate axis. Equations (4) to (10) then immediately lead to the following result

$$\chi^{(2)}_{ijk} = G_{ijk} \, \frac{3e}{2E_g} \, \frac{\chi^{(1)}_{ij}}{G^{(1)}_{ij}} \left[\frac{(1 + \lambda^2)}{(1 + \lambda^2)^2 - 4\lambda^2 S^2_{AB}} \left\{ ((1 + \lambda^2)^2 - 4\lambda^2 \, S^2_{AB})^{\frac{1}{2}} \right. \right.$$

$$\left. \left. \times \left(\frac{1 - \lambda^2}{\lambda} \right) \langle \, \xi \, \rangle_{ab} + \frac{(1 + {}^2)^2}{\lambda} \, \xi_{AB} - 2\lambda S_{AB} \, (\xi_{AA} + \xi_{BB}) \right\} \right] \tag{13}$$

If one neglects the overlaps S_{AB} and ξ_{AB} and makes use of the f-sum rule,

$$(2mE_g/\hbar^2) \, | \langle \, \xi \, \rangle_{ab} \, |^2 = 1 \tag{14}$$

one obtains

$$\chi^{(2)}_{ijk} = G^{(2)}_{ijk} \, (3/\sqrt{8}) \, (m/8e^2\hbar^2N^3_b)^{\frac{1}{4}} \, (\chi^{(1)}_{pq}/G^{(1)}_{pq})^{7/4} \, (1 - \lambda^2)/\lambda \tag{15}$$

relating $\chi^{(2)}_{ijk}$ to the known physical quantities.

It is to be noted that in eq. (4) and in eq. (5), for $\beta^{(1)}$ and $\beta^{(2)}$, respectively, no local field correction has been included explicitly. However, in our final calculations of $\chi^{(2)}$, from eq. (15), we would use experimental values of $\chi^{(1)}$ and these

include the local field effects. Thus, $\chi^{(2)}$ calculated in this manner, would have taken into account the local field correction to that extent.

3. Tetrahedral compounds: Semiconductors with cubic zinc blende and hexagonal wurtzite structures

The simplest AB compounds with tetrahedral symmetry are III–V, II–VI and I–VII semiconductors, with cubic zinc blende or hexagonal wurtzite structure. There are four tetrahedral bonds formed by an atom A sitting at the center of the tetrahedron with the four B-atoms situated at the four corners of the tetrahedron. Thus eq. (15), derived in the previous section, can directly be used to calculate $\chi^{(2)}$ in these compounds. This requires the value of the parameter λ. For compounds of the type $A^N B^{8-N}$, it is related to the effective charge Q at the atomic sites A and B through a relationship

$$Q_A = \frac{N - (8 - N)\lambda^2}{1 + \lambda^2} = -Q_B \tag{16}$$

We find effective charges from experimental results on phonon frequencies by using Szigeti formula with the local field correction factor, and therefrom determine λ for various semiconductors. These values of λ are found to be in close agreement with those given by Coulson *et al* (1962).

In zinc blende compounds, the four bonds point along the four {111} directions. From crystal symmetry considerations, it can be shown that $\chi^{(1)}_{xx} = \chi^{(1)}_{yy} = \chi^{(1)}_{zz}$ and $\chi^{(2)}_{xyz} = \chi^{(2)}_{xzy} = \chi^{(2)}_{yzx} = \chi^{(2)}_{yxz} = \chi^{(2)}_{zxy} = \chi^{(2)}_{zyx}$, the remaining compounds being zero. The geometrical factors $G^{(1)}_{xx}$ and $G^{(2)}_{xyz}$ corresponding to $\chi^{(1)}_{xx}$ and $\chi^{(2)}_{xyz}$ are 1 and $+ (1/3\sqrt{3})$ respectively. Using the values of λ calculated above and the experimental values of $\chi^{(1)}$, we obtain $\chi^{(2)}$ for various III–V, II–VI and I–VII semiconductors with zinc blende structure (see table 1).

Compounds with hexagonal wurtzite structure have the same structural unit as that of cubic zinc blende structure, *i.e.*, a regular tetrahedron of one kind of atoms about a single atom of the other kind. For a given compound, the size of this tetrahedron and the density of atoms are the same for both cases. In cubic crystals, the tetrahedral corners lie along the {111} directions of the crystal whereas in hexagonal crystals there are two inequivalent tetrahedra. These are obtained from the orientation corresponding to the cubic axes by rotation with the matrices (Robinson 1968)

$$\mathbf{R} = \begin{pmatrix} \dfrac{1}{\sqrt{2}} & 0 & \dfrac{1}{\sqrt{2}} \\ -\dfrac{1}{\sqrt{6}} & \dfrac{2}{\sqrt{6}} & \dfrac{1}{\sqrt{6}} \\ -\dfrac{1}{\sqrt{3}} & -\dfrac{1}{\sqrt{3}} & \dfrac{1}{\sqrt{3}} \end{pmatrix} \quad \text{and} \quad \mathbf{S} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{17}$$

Thus, any component of $\chi^{(1)}$ and $\chi^{(2)}$ for compounds with wurtzite structure can be expressed in terms of the corresponding components of cubic compounds as

$$\chi^{(1)W}_{ij} = \tfrac{1}{2} \sum_{p,q} (R_{ip}R_{jq} + S_{ip}S_{jq}) \chi^{(1)Z}_{pq} \tag{18}$$

Table 1. $\chi^{(1)}$ and $\chi^{(2)}$ of semiconductor with zinc blende structure

Crystal	$\chi^{(1)}_{ss}$	23^{N_b} (10 cm^{-3})	λ	$\chi^{(2)}_{sys}$ (10^{-6} esu) (theor.)	$\chi^{(2)}_{sys}$ (10^{-6} esu) (expt.)
GaAs	0·79	0·89	0·66	0·53	1·80±0·6[a]; 0·90±0·30[b]
GaSb	1·07	0·71	0·69	1·27	3·10[a]; 2·50[b]
GaP	0·59	0·99	0·65	0·31	0·50 ± 0·1[a]; 0·40 ± 0·1[b]
InAs	0·86	0·72	0·66	0·73	2·00 ± 0·60[a]; 2·40[b]
InSb	1·17	0·59	0·69	1·27	3·30 ± 0·70[a]
InP	0·69	0·79	0·64	0·50	
Al As	0·74	0·88	0·64	0·52	
AlSb	0·71	0·69	0·61	0·64	
BN	0·28	3·38	0·59	0·05	
ZnS	0·33	1·01	0·41	0·25	0·15 ± 0·04[a]
ZnSe	0·39	0·88	0·44	0·34	0·37 ± 0·14[a]
ZnTe	0·50	0·71	0·46	0·57	0·44 ± 0·16[a]
CdTe	0·49	0·59	0·46	0·63	0·80 ± 0·30[a]
CuCl	0·22	1·01	0·28	0·20	
CuI	0·36	0·72	0·30	0·20	
AgI	0·39	0·59	0·30	0·75	

[a] Bechmann R and Kurtz S K, in Landolt Bornstein: *Numerical Data and Functional Relationships, Group III. Crystal and Solid State Physics,* Hellwege K H (Springer, Berlin, 1970), Vol. 1.

[b] Wynne J J and Bloembergen N 1969 *Phys. Rev.* **188** 1211.

$$\chi^{(2)\,W}_{iik} = \tfrac{1}{2} \sum_{p,\,q,\,r} (R_{ip}R_{jq}R_{kr} + S_{ip}S_{jq}S_{kr})\, \chi^{(2)\,Z}_{pqr} \tag{19}$$

which gives

$$\chi^{(1)\,W}_{ss} = \chi^{(1)\,W}_{yy} = \chi^{(1)W}_{ss} = \chi^{(1)\,Z}_{ss} \tag{20}$$

$$\chi^{(2)\,W}_{sss} = \chi^{(2)\,W}_{sss} = \chi^{(2)\,W}_{sss} = \chi^{(2)\,W}_{yys} = \chi^{(2)\,W}_{syy} = \chi^{(2)\,W}_{ysy} = -\frac{1}{\sqrt{3}}\,\chi^{(2)\,Z}_{sys} \tag{21}$$

$$\chi^{(2)\,W}_{sss} = \frac{2}{\sqrt{3}}\,\chi^{(2)\,Z}_{sys} \tag{22}$$

and the remaining components being zero. In the above expressions, superscripts W and Z stand for wurtzite and zinc blende structures, respectively. We calculate these components for various compounds within our model (table 2). From the experimental data on $\chi^{(2)\,w}$, we find that $|\chi^{(2)\,W}_{sss}/\chi^{(2)\,Z}_{sys}| \approx 2$ in agreement with eqs (21) and (22).

Table 2. Components of $\chi^{(2)}$ for various compounds *with wurtzite structure* calculated from the present model

Crystal	$\chi^{(1)}_{zz}$	$23N_b$ (10 cm^{-5})	λ	$\chi^{(2)}_{zzz}$ (10^{-6} esu) (theor.)	$\chi^{(2)}_{zxx}$ (10^{-6} esu) (theor.)	$\chi^{(2)}_{zxx}$ (10^{-6} esu) (expt.)	$\chi^{(2)}_{zzz}$ (10^{-6} esu) (expt.)
CdS	0·33	0·80	0·40	0·36	0·18	0·21±0·06[a]	0·13±0·03[a]
CdSe	0·38	0·71	0·40	0·50	0·25	0·26±0·06[a]	0·14±0·03[a]
ZnS	0·33	1·01	0·41	0·29	0·15	0·18±0·06[a]	0·09±0·03[a]
ZnO	0·24	1·68	0·38	0·12	0·06		
AlN	0·31	1·89	0·54	0·11	0·06		
CuBr	0·27	0·84	0·28	0·38	0·19		
BeO	0·16	2·87	0·47	0·03	0·015		
GaN	0·37	1·76	0·66	0·10	0·05		

[a] Bechmann R and Kurtz S. K, in Landolt Bornsten: *Numerical Data and Functional Relationships, Group III: Crystal and Solid State Physics*, ed Hellwege K H (Springer, Berlin, 1970), Vol. 1.

4. $\chi^{(2)}$ for potassium dihydrogen phosphate

In KDP, in the paraelectic phase, the main contribution to bilinear susceptibility comes from the P–O bonds (Levine 1973). Our results can therefore be directly used to calculate $\chi^{(2)}$ arising from these bonds. But in so doing, we note that for $\chi^{(1)}$ appearing in eq. (15) we cannot use the experimentally observed value, but instead should use the contribution to $\chi^{(1)}$ from the P–O bonds only. This is because, the O–H bonds in KDP, which are centro-symmetric on the average, even though do not make a contribution to the bilinear susceptibility, do contribute to $\chi^{(1)}$. Thus experimentally observed value of $\chi^{(1)}$ (KDP) $\neq \chi^{(2)}$ (P–O), But $\chi^{(1)}$ (P–O) can be calculated, within our model by using a simple relation, *viz.*, $\chi^{(1)}$ (P–O) $= 2N_b e^2\hbar^2/mE_g$ where N_b is the number of P–O bonds per unit volume, each bond having two electrons and E_g is the energy gap between the bonding and antibonding states for a P–O bond. Using the value of $E_g = 18\cdot2$ eV as given by Levine (1974) and $N_b = 4\cdot14 \times 10^{22}$ we find $\chi^{(1)}_{P-O} = 0\cdot0274$. With $\lambda = 0\cdot59$ and $G^{(2)}_{xyz} = 0\cdot168$ where x, y, z refer to the KDP crystallographic axes, eq. (15) gives $\chi^{(2)}_{xyz}$ to be $2\cdot878 \times 10^{-9}$ esu. This is quite in agreement with the experimental value, *viz.*, $(4\cdot1 \pm 1\cdot4) \times 10^{-9}$ esu.

5. Discussion

Using a simple molecular orbital model for the bond, we have derived an expression for $\chi^{(2)}$ for AB compounds, in terms of the linear susceptibility, the effective charges on the sites A and B and other known quantities. We have used this relationship to calculate $\chi^{(2)}$ for various III–V, II–VI and I–VII semiconductors,

which possess tetrahedral symmetry. A comparison of our calculated values with the known experimental numbers shows that the agreement is, in general, good, considering the simplicity of the model and the uncertainties involved in the experimental results and in the parameters used. For II–VI compounds, both with zinc blende structure and with wurtzite structure, our theoretical values agree quite well with the experimental values. However, except for GaP, the agreement is poor for III–V compounds. For I–VII compounds, sufficient experimental data is not available. We have used our scheme for KDP as well, which, in fact, is a multibond compound. This is made possible because, in its paraelectric phase, the main contribution to $X^{(2)}$ is from the P–O bonds only. $X^{(2)}$ calculated in this way, is in good agreement with the experimental value.

It is to be emphasized again that within the molecular orbital theory, our result for $X^{(2)}$ is independent of the explicit form of the orbital states. It follows, therefore, that any calculation for $X^{(2)}$, which considers only two states and neglects the overlap integrals, must lead to the same results as ours. The discrepancy in the results for the case of III–V compounds cannot be entirely due to the neglect of our overlap integrals because these overlap integrals play a similar role in II–VI compounds also, where the agreement is quite good. For a better agreement the case of III–V compounds, it is, perhaps, necessary to avoid the possible over-estimation of the local field correction in the calculation of the effective charges, through the Szigeti formula. Also, one may have to consider more than two states.

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