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Second-Order Optical Susceptibilities of III-V Semiconductors*†

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An *ab initio* calculation of the low-frequency limit of the second-order optical susceptibility $\chi_{14}^{(2)}$ is presented for eight III-V compounds possessing the zinc-blende symmetry. In the frequency range considered (above the lattice absorption and below the onset of real electronic transitions), the molecular model due to Coulson, Rédei, and Stocker can be used. The susceptibilities $\chi^{(1)}$ and $\chi_{14}^{(2)}$ are expressed in terms of bond polarizabilities. These last quantities are calculated, using a variational perturbation procedure. Effective-field corrections are included in a semiempirical way. Numerical results are given for the following compounds: InSb, InAs, InP, GaSb, GaAs, GaP, AlSb, and BP. They are in good agreement with the available experimental values. For boron phosphide, for which no such data exist, our predicted value is very low, in disagreement with the usual formulation of Miller's rule. This is discussed within the framework of a linear correlation shown by our results to exist between Miller's reduced coefficient and the bond dipole moment p.

INTRODUCTION

The intensity of second-harmonic generation of light is partially determined by the second-order susceptibility tensor $\chi_{ijk}^{(2)}$ which relates the harmonic polarization $\mathbf{P}^{(2)}$ to the applied macroscopic electric field. Formal quantum mechanical expressions for this quantity have been given for localized systems by Armstrong *et al.*[1] and in the formalism of band theory by Butcher and MacLean[2] and by Kelley.[3] The complicated appearance of these expressions prevents any attempt to extract accurate numerical values from them. An empirical rule has been proposed by Miller[4] which permits one to estimate $\chi_{ijk}^{(2)}$ in terms of $\chi_{ij}^{(1)}$. More recently, Robinson[5] has investigated the foundation of this rule and proposed approximate methods of calculation for bound systems.

For crystals with inversion symmetry, $\chi_{ijk}^{(2)}$ vanishes identically. The simplest class of crystals possessing nonzero second-order susceptibility $\chi^{(2)}$ is the $\bar{4}3\,m$ class which includes the members of the important family of III-V semiconducting compounds such as InSb and GaAs. In this paper we attempt to calculate the ground-state second-order susceptibility $\chi^{(2)}$ for III-V compounds with zinc-blende structure in the frequency range above the lattice resonances but below the electronic transitions. This crystal class is cubic and in the long-wavelength limit $\chi^{(1)}$ is a scalar and $\chi^{(2)}$ has only one independent component $\chi_{14}^{(2)}$. Then

$$P(t)=\chi_{14}^{(2)}\mathcal{E}^2(t).$$

For the vexing question of definitions and susceptibility notation, see Robinson.[5] To these susceptibilities the dominant contribution comes from the valence electrons. One possible approach is to use the formalism of band theory, but this is beset with serious computational difficulties. Moreover, in the frequency range considered there is no contribution from real transitions and no particular domain of the Brillouin zone (BZ) is singled out. Thus the detailed band structure has little influence on the value of $\chi^{(2)}$. This point has been emphasized by Leman and Friedel.[6] Furthermore, it should be pointed out that $\chi^{(2)}$ is under generally satisfied conditions determined exclusively by the knowledge of the ground-state electronic density.[7] For a compound with saturated bonds, the total antisymmetrized wave function is not affected by the choice of one-electron wave functions as localized orbitals or suitable linear combinations of these. Hence we start here from a different point of view and use the molecular model proposed by Coulson, Rédei, and Stocker[8] and by Gubanov and others.[9] This model is presented in Sec. I. The susceptibilities are then expressed in terms of bond polarizabilities derived from this model. In using such a microscopic model one is faced with the pertinent question of the effective field. This problem is treated in a semiempirical way in our work. Expressions for $\chi^{(1)}$ and $\chi_{14}^{(2)}$ and discussion of the effective field are given in Sec. II. The primary entities, the bond polarizabilities, are calculated using a variational perturbation procedure. These calculations along with the values for $\chi^{(1)}$, $\chi_{14}^{(2)}$, and the Miller coefficient δ, are given in Sec. III. In Sec. IV we present a discussion of our results as well as a simple but quite general model which accounts for a correlation found between the Miller coefficient δ and the bond dipole moment.

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† Earlier and partial results have been given in previous notes: Compt. Rend. **B266**, 347 (1968); **B266**, 494 (1968); **B266**, 810 (1968); Phys. Letters **26A**, 315 (1968).

[1] J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, Phys. Rev. **127**, 1918 (1962).

[2] P. N. Butcher and T. B. Maclean, Proc. Phys. Soc. (London) **81**, 219 (1962).

[3] P. L. Kelley, J. Phys. Chem. Solids **24**, 607 (1963).

[4] R. C. Miller, Appl. Phys. Letters **5**, 17 (1964).

[5] F. N. H. Robinson, Bell System Tech. J. **46**, 913 (1967).

[6] G. Leman and J. Friedel, J. Appl. Phys. **33S**, 281 (1962).

[7] See, for instance, Appendix E.

[8] C. Coulson, L. Rédei, and D. Stocker, Proc. Roy. Soc. (London) **270A**, 357 (1962); this paper in the following will be denoted by CRS.

[9] (a) I. Gubanov, Fiz. Tverd. Tela **1**, 203 (1959) [English transl.: Soviet Phys.—Solid State **1**, 182 (1959)]; (b) I. Gubanov, and O. Pushkarev, Fiz. Tverd. Tela **2**, 1776 (1960) [English transl.: Soviet Phys.—Solid State **2**, 1607 (1961)].

I. OPTICAL PROPERTIES AND MOLECULAR MODEL

The III-V semiconductors are binary compounds formed by an element of the IIIb column and an element of the Vb column of the periodic table. They possess in the mean four valence electrons of the *s* and *p* type per atom and their lattices are preferentially of tetrahedral symmetry. In the present work we shall restrict ourselves to the compounds with the zinc-blende structure. This is the simplest and commonest structure with point group symmetry $\bar{4}3\,m$ and can be described as two interpenetrated face-centered cubic sublattices parallel to each other, the one being displaced by a vector $\mathbf{R}=(\frac{1}{4},\frac{1}{4},\frac{1}{4})a$ along the diagonal of the other (a is the lattice constant). The sites of these sublattices are occupied by the two atoms III and V, respectively (see Fig. 1).

The linear optical properties of these compounds are described by the wave vector and frequency-dependent complex dielectric tensor $\epsilon(\mathbf{q},\omega)$. In the long-wavelength limit, this quantity behaves as a scalar and the linear macroscopic susceptibility $\chi_0^{(1)}$ is defined then by

$$\epsilon(\omega)=\epsilon_1(\omega)+i\epsilon_2(\omega)=1+4\pi\chi_0^{(1)}(\omega). \tag{1.1}$$

The study of this important quantity has been conducted within the formalism of the band theory and the random-phase approximation (RPA) method. Philipp and Ehrenreich[10] and others,[11] in their extensive experimental and theoretical study of the linear optical properties using sum rules derived from the Kramers-Kronig relations, arrived at the following conclusions:

(1) There is no appreciable difference in the dielectric properties of III-V and IV-IV semiconductors.

(2) The first spectral region extending above the lattice frequency is characterized by a detailed band structure related to the real valence-to-conduction band transitions.

(3) The structure of the absorption curve $\epsilon_2(\omega)$ is almost completely determined by the joint density of states.[11]

(4) The electrons which contribute effectively in this range are the valence electrons, four in the mean per atom, and one can define an energy $\hbar\omega_0$ which "saturates" the sum rule:

$$\int_0^{\hbar\omega_0} \hbar\omega\,\epsilon_2(\hbar\omega)\,d(\hbar\omega)=\tfrac{1}{2}\pi(\hbar\Omega_p)^2, \tag{1.2}$$

where Ω_p is the valence electron plasma frequency and 0 designates an energy or frequency which lies above the lattice frequency but below the first electronic transitions. In view of the previous conclusions $\hbar\omega_0$ can be considered as an averaged energy over the joint density of states. Note that the transitions near the energy gap do not contribute appreciably to this average.

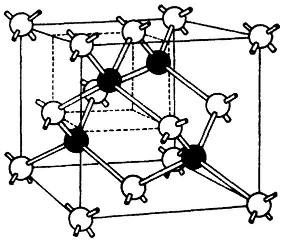

FIG. 1. Zinc-blende structure.

(5) Along with $\hbar\omega_0$ one can define an effective dielectric constant

$$\bar{\epsilon}(0)=1+\frac{2}{\pi}\int_0^{\hbar\omega_0}\frac{\epsilon_2(\hbar\omega)}{\hbar\omega}d(\hbar\omega). \tag{1.3}$$

The difference $\epsilon(0)-\bar{\epsilon}(0)$ is attributed to the contributions of the inner *d* shells and is of the order of 5% of $\epsilon(0)$. This shows that the virtual transitions below $\hbar\omega_0$ are mainly responsible for the magnitude of $\epsilon(0)$.

The first-order nonlinear response is described by the second-order susceptibility $\chi_{ijk}^{(2)}$. In the long-wavelength limit, this third-rank tensor quantity possesses only one independent component denoted by $\chi_{14}^{(2)}$ in Voigt notation.

The previous conclusions show that in the frequency range of interest it is mainly the valence electrons which are responsible for the linear dielectric properties and the nuclei and core electrons can be discarded in the calculation of the first-order susceptibility $\chi^{(1)}$. This can be seen to be even more legitimate for $\chi^{(2)}$. The same arguments as before apply also for this quantity and the role played by the joint density of states has been stressed particularly by Chang, Ducuing, and Bloembergen.[12] Moreover, the second-order susceptibility is zero for a free atom possessing the inversion symmetry; in a solid this symmetry can be removed because of the mutual interactions with the neighbor atoms. Clearly, the valence electrons are the ones most perturbed, and the mechanism of the optical nonlinearities must be sought in the dynamics of this system in interaction with the incident radiation.

For this kind of calculation the molecular model seems to be quite adequate. In this frequency range no real transitions occur and the joint density of states is irrelevant for the calculation of the dielectric constant. This point has been stressed by Leman and Friedel[6] for the pure elemental IV-IV semiconductors. For these semiconductors the bond picture seems to be quite well established. Owing to the similarity of the IV-IV and III-V materials as far as the linear optical properties is concerned we can assume that the validity of the bond picture persists in the case of III-V compounds as well.

The molecular model of these compounds has been proposed and discussed by many authors, in particular, by Gubanov,[9a] Gubanov and Pushkarev,[9b] and by Coulson, Rédei, and Stocker (CRS).[8] According to this

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[10] H. R. Philipp and H. Ehrenreich, Phys. Rev. **129**, 1550 (1963).

[11] D. Brust, Phys. Rev. **134**, A1337 (1964).

[12] R. K. Chang, J. Ducuing, and N. Bloembergen, Phys. Rev. Letters **15**, 415 (1965).

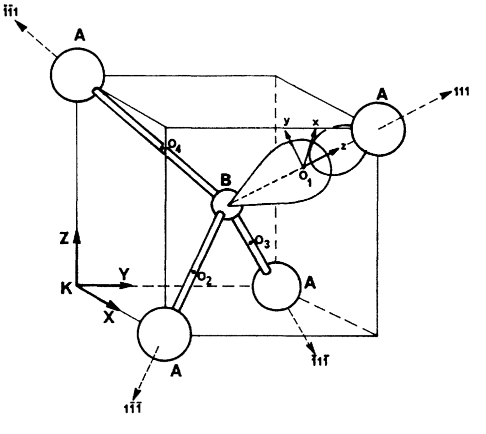

FIG. 2. Four equivalent tetrahedral bonds in a unit cell: B is the III atom and A is the V atom. The crystalline axis 111 and the corresponding bond axis O_1z are pointing from the III atom to the V atom of the BA_1 bond and similarly for the other three bond directions. This convention is the one adopted by H. C. Gatos and M. C. Lavine, J. Electrochem. Soc. **107**, 427 (1960).

model, the valence electrons, eight per unit cell, are considered as a system of separated electron pairs accommodated in effectively localized bonds between adjacent atoms. The core electrons are assumed unaffected by the bonding and not coupled to the valence electrons. There are four equivalent tetrahedral bonds per unit cell and following CRS we will use the simple linear-combination-of-atomic-orbitals–molecular-orbital (LCAO–MO) treatment and regard each bond A-B as represented in its ground state by two uncorrelated electrons with opposite spins in the orbital $\psi^{(0)}$. Then the two-electron-bond wave function of the i bond is

$$\Psi_i(1,2)=\psi^{(0)}(1)\psi^{(0)}(2)\left\{\frac{\alpha(1)\beta(2)-\alpha(2)\beta(1)}{\sqrt{2}}\right\}, \quad (1.4)$$

where α and β are the two spin states, and the numbers 1 and 2 refer to the two electrons. By analogy with the situation for IV–IV semiconductors, the LCAO–MO are of the bonding type

$$\psi^{(0)}=N^{-1/2}(\varphi_A+\lambda\varphi_B), \quad (1.5)$$

where N is the normalization constant; A and B stand for the group-V and -III atoms, respectively; φ_A and φ_B are tetrahedral sp^3 hybrid orbitals, oriented around each atom in such a way that the orbitals which are paired together to form (1.5) point directly towards each other; and λ, a parameter to be determined variationally or by some other means, is a measure of the polarity of the III-V bond: it is equal to unity in the case of homopolar IV-IV bonds.

In the model of CRS the atomic orbitals φ_A and φ_B are nodeless Slater-type orbitals (see Appendix A) whose ζ coefficients are determined by assuming the electronic configuration A^+B^- for the bond, and the parameter λ is then determined by the usual LCAO method. In the model of Gubanov and others, the choice of φ is quite different, as described in Appendix B, and the value of λ is determined by assuming neutrality of the bonds. Discussion of the above orbitals in terms of ionic and covalent parts is quite difficult and will not be attempted here.

In the above descriptions, the bonds are assumed to possess axial symmetry, since we have assumed only s-p mixing. Actually the $\bar{4}3\,m$ symmetry allows an admixture of sp^3, d, and f orbitals, and this would introduce a rotational asymmetry in the bonds. Inclusion of such effects has not been undertaken, although the formulas given below can be extended to allow for such corrections.

In terms of the two-electron-bond function (1.4), the total ground-state electronic distribution of the crystal is given by the antisymmetrized function

$$\Psi_{\text{val}}=C^{-1/2}\sum_P(-1)^P P\prod_{i=1}^{M}\Psi_i(2i-1,2i), \quad (1.6)$$

where M is the number of bonds and P represents any of the permutations of the electron coordinates; the normalizing factor C is equal to $(2M!)2^M$. We assume throughout that[13]

$$\int\Psi_i(1,2)\Psi_j(1,3)d\tau_1=0 \quad \text{for} \quad i\neq j. \quad (1.7)$$

With this picture, and regarding the bonds as the primary entities, we can express the susceptibilities of our system in terms of bond polarizabilities.

II. OPTICAL SUSCEPTIBILITIES AND EFFECTIVE FIELD

We now proceed to obtain expressions of $\chi^{(1)}$ and $\chi_{14}^{(2)}$ in terms of the bond polarizabilities. First we use these quantities to derive expressions for the microscopic susceptibilities relating the medium polarization to the effective field. Then we consider the relation between effective and applied macroscopic field.

Owing to the $\bar{4}3\,m$ symmetry, all bonds are equivalent to each other and can be obtained from one another by successive application of the group operations. In Fig. 2 we show a group of four bonds centered around a group-III atom and the crystalline axes $KXYZ$. In this reference frame, the bonds point along the principal diagonals 111, $\bar{1}\bar{1}1$, $\bar{1}1\bar{1}$, and $1\bar{1}\bar{1}$. We also introduce the bond axes $O_\kappa xyz$, where $\kappa=1$, 2, 3, and 4. The bond axes are oriented so that they are equivalent with respect to the $\bar{4}3\,m$ point group operations. The z axis is oriented along the bond axis towards the group-V atom, and O is the geometric midpoint of the bond. We single out one bond and call W the energy of such a bond in the presence of an electric field $\mathcal{E}$ of arbitrary direction. The polarizabilities of different orders are then defined by the following expression:

$$W=W_0-\mathbf{p}\cdot\mathcal{E}-\tfrac{1}{2}\alpha:\mathcal{E}\mathcal{E}-\tfrac{1}{3}\beta\vdots\mathcal{E}\mathcal{E}\mathcal{E}, \quad (2.1)$$

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[13] J. Parks and R. Parr, J. Chem. Phys. **28**, 335 (1958).

where W_0 is the bond ground energy, $\mathbf{p}$ is the permanent bond dipole moment, α_{ij} is the first-order bond polarizability tensor, and β_{ijk} is the second-order bond polarizability tensor.

As pointed out in the Introduction, we are interested in the response of the valence electrons to a field the frequency of which is well below the electronic transitions but above the lattice resonance frequency and can be taken equal to zero. Thus time-independent perturbation theory involving only electronic wave functions can be used to calculate the above quantities.

The tensor indices of these quantities refer to the bond axes. It can be shown that the components of these tensors satisfy the following relations:

$$\alpha_{ij}=\alpha_{ji}$$

and

$$\beta_{ijk}=\beta_{jki}=\beta_{kij}=\beta_{ikj}=\beta_{jik}=\beta_{kji},$$

so that finally there exist six independent α components and 10 independent β components. They are given in Appendix C, where it is shown that the first-order microscopic susceptibility of the crystal is given by

$$\chi^{(1)}=(4/a^3)\tfrac{4}{3}(\alpha_{xx}+\alpha_{yy}+\alpha_{zz}) \tag{2.2}$$

and the second-order microscopic susceptibility by

$$\chi_{14}{}^{(2)}=\frac{4}{a^3}\times\frac{8}{3\sqrt{3}}\left[\beta_{zzz}-\tfrac{3}{2}(\beta_{xzx}+\beta_{yzy})-\frac{1}{\sqrt{2}}(\beta_{yyy}-3\beta_{xyx})\right]. \tag{2.3}$$

In the present work we assume from now on that the bonds possess axial symmetry. Then $\alpha_{xx}=\alpha_{yy}=\alpha_\perp$, $\beta_{xzx}=\beta_{yzy}=\beta_\perp$, and $\beta_{xyx}=\beta_{yyy}=0$. We also put $\alpha_{zz}=\alpha_{\|}$ and $\beta_{zzz}=\beta_{\|}$. The above expressions reduce then to

$$\chi^{(1)}=(16/3)a^{-3}(\alpha_{\|}+2\alpha_\perp), \tag{2.4}$$

$$\chi_{14}{}^{(2)}=(32/3\sqrt{3})a^{-3}(\beta_{\|}-3\beta_\perp), \tag{2.5}$$

respectively; $\alpha_{\|}$ and $\beta_{\|}$ are the longitudinal bond polarizabilities, $\alpha_\perp$ and $\beta_\perp$ are the transverse bond polarizabilities.

The polarizable units in a crystal, the bonding electrons in our case, do not respond to the externally applied electric field but rather to the effective field. This field includes also the contributions of the induced dipoles and is different from the macroscopic field. Lorentz considered the case of a fictitious cubic crystal with well-localized and tightly bound electrons and calculated the effective field at a cubic site emanating from the induced parallel dipoles on the other sites. Darwin[14] in his careful discussion of the local field shows that this model applies at least qualitatively to ionic crystals. But for metals where the electrons are free to move around and feel a spatial average of the field over the crystal one must take $\mathcal{E}_{\text{eff}}=\mathcal{E}$. Neither model is applicable in our case. The electrons are not confined to cubic sites, and neither are they free to move around; rather, because of the strong overlap of the atomic functions paired together to form the bond orbitals, they are localized in the regions between adjacent atoms. $\mathcal{E}_{\text{eff}}$ varies strongly over this region. The complexity of its functional dependence field prevents any *a priori* calculation and compels us to resort to very drastic simplifications and approximations. The first one is that for a cubic lattice we can write

$$\boldsymbol{\mathcal{E}}_{\text{eff}}=\boldsymbol{\mathcal{E}}+\tfrac{4}{3}\pi\Gamma\mathbf{p}=f\boldsymbol{\mathcal{E}}, \tag{2.6}$$

where Γ and f are scalars. The second is that $\mathcal{E}_{\text{eff}}$ is constant over the polarizable unit, in our case the bond. Then it can be shown[15] that the experimentally measured macroscopic susceptibilities are

$$\chi^{(1)}=\frac{16}{3}\times\frac{f}{a^3}(\alpha_{\|}+2\alpha_\perp), \tag{2.7}$$

$$\chi_{14}{}^{(2)}=\frac{32}{3\sqrt{3}}\times\frac{f^3}{a^3}(\beta_{\|}-3\beta_\perp). \tag{2.8}$$

In the case considered by Lorentz $f_L=\frac{1}{3}[\epsilon(0)+2]$ and in the case of metals $f=1$. A theoretical framework to compute the effective field has been proposed by Adler,[16] but no attempt has been made until now to apply his treatment to actual crystals. Lacking any other evidence about the effective-field value in a III-V compound, we determine the factor f by requiring that the effective-field factor is such that the value of $\chi^{(1)}$ calculated by (2.7) is equal to the experimental one $\chi_0{}^{(1)}=[\epsilon(0)-1]/4\pi$. Actually, in addition to the inductive interactions between bonds in the presence of the external electric field, the factor f includes the interactions of the bonds in their ground state as well. These last interference effects between bonds cannot be taken into account explicitly in our treatment owing to the assumption of strong orthogonality (1.7) between different bond orbitals.

Following Miller,[4] we also define a parameter:

$$\delta=\chi_{14}{}^{(2)}/(\chi^{(1)})^3. \tag{2.9}$$

This parameter is actually independent of effective-field factors[5] and depends only on the microscopic susceptibilities.

III. BOND POLARIZABILITIES AND RESULTS

We proceed now to the calculation of bond polarizabilities. These quantities describe the response of the bond to an applied uniform electric field $\mathcal{E}$ of arbitrary orientation with respect to the bond axis, and can be calculated using conventional quantum-mechanical perturbation theory. According to the usual LCAO–MO

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[14] G. Darwin, Proc. Roy. Soc. (London) **A146**, 17 (1934).

[15] N. Bloembergen, *Non-linear Optics* (W. A. Benjamin, Inc., New York, 1965).

[16] S. L. Adler, Phys. Rev. **126**, 413 (1962).

method we suppose that the two electrons in any given bond are uncorrelated and equivalent. In the absence of external fields each electron is described by an effective one-electron Hamiltonian H_0 and by a wave function $\psi^{(0)}$ of type (1.5). In the presence of a uniform electric field the perturbation part of the one electron Hamiltonian is

$$H' = -e\mathbf{r}\cdot\boldsymbol{\mathcal{E}}, \quad r = (x,y,z). \tag{3.1}$$

Because of the assumed rotational symmetry of the bonds, the direction of the Ox axis is immaterial and can be chosen for convenience such that the electric field has the components $(\mathcal{E}_\perp, O, \mathcal{E}_\parallel)$. Then the wave function ψ perturbed to the first order in H' is

$$\psi = \psi^{(0)} + \psi^{(1)} \tag{3.2}$$

and the energy perturbed to the third order in H' is

$$W = W_0 + W_1 + W_2 + W_3, \tag{3.3}$$

where

$$W_0 = \langle\psi^{(0)}|H_0|\psi^{(0)}\rangle, \tag{3.4a}$$

$$W_1 = \langle\psi^{(0)}|H'|\psi^{(0)}\rangle, \tag{3.4b}$$

$$W_2 = \langle\psi^{(0)}|H'|\psi^{(1)}\rangle, \tag{3.4c}$$

$$W_3 = \langle\psi^{(1)}|(H' - \langle\psi^{(0)}|H'|\psi^{(0)}\rangle)|\psi^{(1)}\rangle. \tag{3.4d}$$

The bond polarizabilities are defined by

$$W = W_0 - p\mathcal{E}_\parallel - \tfrac{1}{2}(\alpha_\perp \mathcal{E}_\perp^2 + \alpha_\parallel \mathcal{E}_\parallel^2) - \tfrac{1}{3}(3\beta_\perp \mathcal{E}_\perp^2 \mathcal{E}_\parallel + \beta_\parallel \mathcal{E}_\parallel^3), \tag{3.5}$$

which is the simplified form of (2.1) for the case of axial bonds. By identification of the corresponding terms in the two expansions (3.3) and (3.5) we obtain

$$\alpha_\parallel = 4e(\partial/\partial\mathcal{E}_\parallel)\langle\psi^{(0)}|\hat{z}|\psi^{(1)}\rangle, \tag{3.6a}$$

$$\alpha_\perp = 4e(\partial/\partial\mathcal{E}_\perp)\langle\psi^{(0)}|x|\psi^{(1)}\rangle, \tag{3.6b}$$

$$\beta_\parallel = 3e(\partial^2/\partial\mathcal{E}_\parallel^2)\langle\psi^{(1)}|\hat{z}|\psi^{(1)}\rangle, \tag{3.7a}$$

$$\beta_\perp = 2e(\partial^2/\partial\mathcal{E}_\parallel\partial\mathcal{E}_\perp)\langle\psi^{(1)}|x|\psi^{(1)}\rangle + e(\partial^2/\partial\mathcal{E}_\perp^2)\langle\psi^{(1)}|\hat{z}|\psi^{(1)}\rangle, \tag{3.7b}$$

where $\hat{z} = z - \langle\psi^{(0)}|z|\psi^{(0)}\rangle$ and account was taken of the fact that there are two equivalent electrons per bond. These expressions give a concise formulation of the usual expressions using summation expansions. In this formulation the polarizabilities are written

$$\alpha_\parallel = 4e^2 \sum_i{}' \frac{\langle 0|z|i\rangle\langle i|z|0\rangle}{E_i - E_0}, \tag{3.8a}$$

$$\alpha_\perp = 4e^2 \sum_i{}' \frac{\langle 0|x|i\rangle\langle i|x|0\rangle}{E_i - E_0}, \tag{3.8b}$$

$$\beta_\parallel = 6e^3 \left[\sum_{i,j}{}'' \frac{\langle 0|z|i\rangle\langle i|z|j\rangle\langle j|z|0\rangle}{(E_i - E_0)(E_j - E_0)} - \langle 0|z|0\rangle \sum_i{}' \frac{|\langle 0|z|i\rangle|^2}{(E_i - E_0)^2} \right], \tag{3.9a}$$

$$\beta_\perp = 2e^3 \left[\sum_{i,j}{}'' \frac{2\langle 0|x|i\rangle\langle i|x|j\rangle\langle j|z|0\rangle + \langle 0|x|i\rangle\langle i|3|j\rangle\langle j|x|0\rangle}{(E_i - E_0)(E_j - E_0)} - \langle 0|z|0\rangle \sum_i{}' \frac{|\langle 0|x|i\rangle|^2}{(E_i - E_0)^2} \right]. \tag{3.9b}$$

The above expressions suppose that the eigenvalue problem,

$$H_0\psi_i^{(0)} = E_i^{(0)}\psi_i^{(0)},$$

is resolved. This is seldom the case in practice and even then the summation is a hopeless task. In the present work we have used the variational perturbation method in the form proposed by Dalgarno and Lewis[17] and Schwartz[18] and applied by Karplus and Kolker[19] and O'Hare and Hurst[20] in the calculation of bond polarizabilities of diatomic molecules. A brief account of this method is given in Appendix E. Its crucial point is that it permits the calculation of both α and β from a knowledge of the exact ground-state wave function $\psi^{(0)}$ only. Actually, as is stressed in Appendix E, one needs to know only the ground-state electronic distribution if spin-orbit coupling is neglected. Lacking the exact $\psi^{(0)}$ in our case, we have to formulate the method for the available approximate molecular orbitals of the type (1.5). Since the orientation of the electric field is arbitrary we can consider the two parts $H_\perp' = -e\mathcal{E}_\perp x$ and $H_\parallel' = -e\mathcal{E}_\parallel z$ of $H' = H_\parallel' + H_\perp'$ as independent and use double-variational perturbation theory. Accordingly we have to use two trial variation functions $F_\parallel$ and $F_\perp$, respectively. This can be cast in matrix form as follows. Formally in our case we can write

$$H' = \mathrm{Tr}\,\mathbf{H}', \tag{3.10}$$

where $\mathbf{H}'$ is the 2×2 diagonal matrix

$$\mathbf{H}' = \begin{vmatrix} H_\parallel' & 0 \\ 0 & H_\perp' \end{vmatrix}. \tag{3.11}$$

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[17] A. Dalgarno and J. Lewis, Proc. Roy. Soc. (London) **A233**, 70 (1956).

[18] C. Schwartz, Ann. Phys. (N. Y.) **6**, 156 (1959).

[19] M. Karplus and J. Kolker, J. Chem. Phys. **38**, 1263 (1963); **39**, 2011 (1963).

[20] J. M. O'Hare and R. P. Hurst, J. Chem. Phys. **46**, 2356 (1967).

We also construct the matrix functional

$$\mathbf{J}(\mathbf{F})=\langle 0|[\mathbf{F}(\mathbf{H}'-\langle\mathbf{H}'\rangle)+(\mathbf{H}'-\langle\mathbf{H}'\rangle)\mathbf{F}-\tfrac{1}{2}[\mathbf{F},[\mathbf{F},\mathbf{H}_0]]]|0\rangle, \tag{3.12}$$

where unspecified expectations $\langle\ \rangle$ hereafter refer to the initial ground state $\psi^{(0)}$. Here $\mathbf{F}$ is the class of 2×2 diagonal matrices of the form

$$\mathbf{F}(l,m)=\begin{vmatrix} F_{\parallel}(l) & 0 \\ 0 & F_{\perp}(m)\end{vmatrix}, \tag{3.13}$$

where $F_{\parallel}(l)$ and $F_{\perp}(m)$ are the trial polynomial functions with l and m parameters, respectively. In our case we have used three pairs $\{F_{\parallel},F_{\perp}\}$ with $\{1,1\}$, $\{3,2\}$ and (4,4) parameters as follows:

$\{1,1\}$ parameters:

$$\begin{aligned} F_{\parallel}(1)&=\lambda_1 H_{\parallel}', \\ F_{\perp}(1)&=\mu_1 H_{\perp}'; \end{aligned} \tag{3.14a}$$

$\{3,2\}$ parameters:

$$\begin{aligned} F_{\parallel}(3)&=H_{\parallel}'(\lambda_1+\lambda_2 r_A+\lambda_3 r_B), \\ F_{\perp}(2)&=H_{\perp}'(\mu_1+\mu_2 z); \end{aligned} \tag{3.14b}$$

$\{4,4\}$ parameters:

$$\begin{aligned} F_{\parallel}(4)&=H_{\parallel}'(\lambda_1+\lambda_2 r_A+\lambda_3 r_B+\lambda_4 z), \\ F_{\perp}(4)&=H_{\perp}'(\mu_1+\mu_2 r_A+\mu_3 r_B+\mu_4 z); \end{aligned} \tag{3.14c}$$

or in matrix form (superscript T indicates the transposed matrix):

$$F_{\parallel}=\boldsymbol{\lambda}^T\cdot\mathbf{f}_{\parallel},\quad F_{\perp}=\boldsymbol{\mu}^T\cdot\mathbf{f}_{\perp}.$$

$\boldsymbol{\lambda}$ and $\mathbf{f}_{\parallel}$ are the $l\times1$ column matrices $\{\lambda_i\}$ and $\{f_i'\}\equiv\{H_{\parallel}',H_{\parallel}'r_A,H_{\parallel}'r_B,\cdots\}$, respectively; $\boldsymbol{\mu}$ and $\mathbf{f}_{\perp}$ are the $m\times1$ column matrices $\{\mu_i\}$ and $\{f_i''\}\equiv\{H_{\perp}',H_{\perp}'z,H_{\perp}'r_A\cdots\}$, respectively; r_A and r_B are the distances of the bonding electron from the V- and III-atom, respectively (see Appendix D).

This choice was guided by the requirement of symmetry, boundary conditions, and simplicity of calculation (see Appendix E). The parameters μ_i and λ_i were then fixed by the requirement that the first variation of the functional $\mathbf{J}$ should vanish: $\delta\mathbf{J}=0$. This is equivalent to

$$\partial\mathbf{J}/\partial\boldsymbol{\lambda}=0 \quad\text{and}\quad \partial\mathbf{J}/\partial\boldsymbol{\mu}=0, \tag{3.15}$$

or to the two systems of linear homogeneous equations:

$$A_{ij}\lambda_j=a_i \quad\text{and}\quad B_{ij}\mu_j=b_i, \tag{3.16}$$

respectively, where

$$A_{ij}=\langle\nabla f_i'\cdot\nabla f_j'\rangle$$

and

$$a_i=(2/e^2a_0)[\langle f_i'\cdot H_{\parallel}\rangle-\langle f_i'\rangle\langle H_{\parallel}'\rangle],$$

$$B_{ij}=\langle\nabla f_i''\cdot\nabla f_j''\rangle,\quad\text{and}\quad b_i=(2/e^2a_0)\langle f_i''H_{\perp}'\rangle.$$

Once these parameters were determined the polarizabilities were calculated by the expressions

$$\alpha_{\parallel}=-(\partial^2/\partial\mathcal{E}_{\parallel}^2)\langle\mathrm{Tr}\Delta\mathbf{H}'\cdot\mathrm{Tr}\Delta\mathbf{F}\rangle, \tag{3.17a}$$

TABLE I. Data concerning the III-V compounds. The values of $\chi_0^{(1)}$, the linear macroscopic susceptibility, were calculated using the value of $\epsilon(0)$ given by Hass and Henvis,[a] and the values of the lattice constants were taken from Gieseche.[b]

Compound	Lattice constant a (Å)	Linear macroscopic susceptibility $\chi_0^{(1)}$	Mean gap energy[c] $\hbar\omega_0$ (eV)
InSb	6.479	1.17	4.7
InAs	6.058	0.86	
InP	5.869	0.69	
GaSb	6.095	1.07	
GaAs	5.653	0.81	5.9
GaP	5.451	0.59	6.5
AlSb	6.135	0.71	
BP	4.538		

[a] M. Hass and B. W. Henvis, J. Phys. Chem. Solids **23**, 1099 (1962).
[b] G. Gieseche, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic Press Inc., New York, 1966), Vol. 2, p. 63.
[c] Reference 10.

$$\alpha_{\perp}=-(\partial^2/\partial\mathcal{E}_{\perp}^2)\langle\mathrm{Tr}\Delta\mathbf{H}'\cdot\mathrm{Tr}\Delta\mathbf{F}\rangle, \tag{3.17b}$$

$$\beta_{\parallel}=-(\partial^3/\partial\mathcal{E}_{\parallel}^3)\langle\mathrm{Tr}\Delta\mathbf{F}\cdot\mathrm{Tr}\Delta\mathbf{H}'\cdot\mathrm{Tr}\Delta\mathbf{F}\rangle, \tag{3.18a}$$

$$\beta_{\perp}=-(\partial^3/\partial\mathcal{E}_{\parallel}^2\partial\mathcal{E}_{\perp})\langle\mathrm{Tr}\Delta\mathbf{F}\cdot\mathrm{Tr}\Delta\mathbf{H}'\cdot\mathrm{Tr}\Delta\mathbf{F}\rangle, \tag{3.18b}$$

where

$$\Delta\mathbf{H}'=\mathbf{H}'-\langle\mathbf{H}'\rangle$$

and

$$\Delta\mathbf{F}=\mathbf{F}-\langle\mathbf{F}\rangle.$$

The effective-field factor f was calculated according to the prescription given in Sec. II. Finally, the second-order susceptibility $\chi_{14}^{(2)}$ and the Miller coefficient δ were calculated through the formulas (2.8) and (2.9).

The results for the $\{1,1\}$ parameter choice are given in Tables I and II, while those for the $\{3,2\}$ and $\{4,4\}$ parameters are given in Table III. For comparison, we have included in both tables the experimental results. The values of $\chi_{14}^{(2)}$ and δ as calculated by the $\{3,2\}$- and $\{4,4\}$-parameter choices are almost equal to each other but differ appreciably from the values obtained with the $\{1,1\}$-parameter choice. All the calculations were

TABLE II. Values of $\chi^{(2)}$ and δ calculated using the $\{1,1\}$-parameter trial function (Unsöld approximation). With the convention of the crystalline and bond axes given in Fig. 2 the calculated values of $\chi_{14}^{(2)}$ and δ are positive.

	Calculated					Experimental	
Compound	$\hbar\Omega_{\parallel}$ (eV)	$\hbar\Omega_{\perp}$ (eV)	f	$10^7\chi_{14}^{(2)}$ (e.s.u.)	$\frac{10^9}{(4\pi)^3}\delta$ (e.s.u.)	$10^7\chi_{14}^{(2)}$ (e.s.u.)	Wavelength[a] λ (μ)
InSb	4.8	5.2	2.35	9.8	0.30	30±15[b]	extrapolated
InAs	5.6	6.1	1.90	6.9	0.55	20±8[c]	10.6
InP	5.9	6.8	1.60	5.3	0.80		
GaSb	5.3	5.9	2.24	1.9	0.09	(18)[d]	
GaAs	6.3	7.0	1.87	2.9	0.27	18±8[c]	10.6
GaP	6.9	7.9	1.52	2.1	0.51	(5)[e]	1.06
AlSb	5.3	5.9	1.48	1.0	0.13		
BP	9.2	10.7		0.0	0.0		

[a] See Sec. IV A.
[b] Reference 12.
[c] Reference 22.
[d] Reference 23.
[e] Reference 4.

TABLE III. Values of $\chi^{(2)}$ and δ calculated using the {3,2} and {4,4} trial functions. With the convention of the crystalline and bond axes given in Fig. 2 the calculated values of $\chi_{14}^{(2)}$ and δ are positive.

	Calculated (variational)						Experimental	
	{3,2} term			{4,4} term				
Compound	f	$10^7\chi_{14}^{(2)}$ (e.s.u.)	$[10^9/(4\pi)^3]\delta$ (e.s.u.)	f	$10^7\chi_{14}^{(2)}$ (e.s.u.)	$[10^9/(4\pi)^3]\delta$ (e.s.u.)	$10^7\chi_{14}^{(2)}$ (e.s.u.)	Wavelength[a] λ (μ)
InSb	1.95	63	2.0	1.95	65	2.0	30 ± 15[b]	extrapolated
InAs	1.41	40	3.3	1.41	41	3.3	20 ± 8[c]	10.6
InP	1.23	26	3.7	1.20	28	3.8		
GaSb	1.93	15	0.7	1.93	16	0.7	(18)[d]	
GaAs	1.55	18	1.7	1.50	19	1.8	18 ± 8[c]	10.6
GaP	1.26	13	2.7	1.24	14	2.8	(5)[e]	1.06
AlSb	1.30	6	0.9	1.30	7	1.0		
BP		~0.0	~0.0		~0.0	~0.0		

[a] See Sec. IV A. [b] Reference 12. [c] Reference 22. [d] Reference 23. [e] Reference 4.

performed after transformation to prolate spheroidal coordinates (see Appendix D).

To gain physical insight into the above calculation we consider more closely the {1,1}-parameter choice, and show that this is a special case of the Unsöld approximation.[21] According to this method, one replaces all energy denominators (E_i-E_0) in (3.8a) and (3.8b) by common energies $\hbar\Omega_{\parallel}$ and $\hbar\Omega_{\perp}$, respectively, which must be determined by other means. Now if we perform the same substitution into the Thomas-Khun sum rules

$$\sum_i \frac{2m}{\hbar^2}(E_i-E_0)|\langle 0|z|j\rangle|^2=1\,, \tag{3.19a}$$

$$\sum_i \frac{2m}{\hbar^2}(E_i-E_0)|\langle 0|x|j\rangle|^2=1\,, \tag{3.19b}$$

we obtain

$$\hbar\Omega_{\parallel}=(\hbar^2/2m)\langle\langle z^2\rangle\rangle^{-1} \quad\text{and}\quad \hbar\Omega_{\perp}=(\hbar^2/2m)\langle\langle x^2\rangle\rangle^{-1},$$

respectively, where $\langle\langle z^2\rangle\rangle=\langle(z-\langle z\rangle)^2\rangle$ and $\langle\langle x^2\rangle\rangle=\langle x^2\rangle$.

The polarizabilities take then the following simple form:

$$\alpha_{\parallel}=8\langle\langle z^2\rangle\rangle^2/a_0\,, \tag{3.20a}$$

$$\alpha_{\perp}=8\langle\langle x^2\rangle\rangle^2/a_0\,, \tag{3.20b}$$

$$\beta_{\parallel}=\frac{24\langle\langle z^3\rangle\rangle}{ea_0^2}\langle\langle z^2\rangle\rangle^2\,, \tag{3.21a}$$

$$\beta_{\perp}=\frac{8\langle\langle z^2x\rangle\rangle}{ea_0^2}\langle\langle x^2\rangle\rangle(2\langle\langle z^2\rangle\rangle+\langle\langle x^2\rangle\rangle)\,, \tag{3.21b}$$

where $\langle\langle z^3\rangle\rangle=\langle(z-\langle z\rangle)^3\rangle$ and $\langle\langle x^2z\rangle\rangle=\langle x^2(z-\langle z\rangle)\rangle$. These expressions are identical with the ones obtained using {1,1}-parameter trial functions. Similar results were obtained by Robinson.[5] The results were given in Table II where also the values of $\hbar\Omega_{\parallel}$ and $\hbar\Omega_{\perp}$ are included. These two energies are almost equal, which amounts to saying that the bonds as far as linear properties are concerned behave almost as isotropic bonds; also $\beta_{\parallel}$ is always greater that $\beta_{\perp}$. If we put then $\hbar\Omega_{\parallel}=\hbar\Omega_{\perp}=\hbar\Omega_0$, we obtain

$$\epsilon(0)=1+f(\hbar\Omega_p/\hbar\Omega_0)^2\,, \tag{3.22}$$

$$\chi_{14}^{(2)}=\frac{f^3}{2\pi\sqrt{3}}\left(\frac{\hbar\Omega_p}{\hbar\Omega_0}\right)^2\frac{\langle\langle z^3\rangle\rangle-3\langle\langle z^2x\rangle\rangle}{ea_0}\,, \tag{3.23}$$

where $\Omega_p=(4\pi ne^2/m)^{1/2}$ is the valence electron plasma frequency and $n=8(4/a^3)$ is the valence electron density. Furthermore the energy $\hbar\Omega_0$ is almost equal to $\hbar\omega_0$, the energy defined by Philipp and Ehrenreich,[10] and which plays the role of a mean energy gap.

No such simple interpretation can be given to the higher-order trial functions. Yet the qualitative conclusions are the same: The bonds behave as isotropic as far as the linear response to an electric field is concerned, but in the nonlinear case $\beta_{\parallel}$ is the dominant part, showing that the bonds in this regime behave as longitudinal unidimensional bonds.

We have attempted a calculation using the Gubanov and Gubanov-Pushkarev wave functions (see Appendix B). No satisfactory agreement was obtained. Perhaps some improvement could be achieved by reconsidering carefully the choice of parameters in these wave functions. In particular the calculation showed that the transversal polarizabilities calculated with the Gubanov wave functions were greater by a factor of 2 than the longitudinal polarizabilities. These latter ones were in good agreement with those obtained by CRS wave functions. The difference between transverse and longitudinal polarizabilities was much less pronounced for the values obtained with the Gubanov-Pushkarev wave functions and shows that the r factors in front of the exponentials play an important role.

In general $\chi_{14}^{(2)}$ seems to be more sensitive than $\chi^{(1)}$ to the choice of the ground-state wave functions.

The convergence of the variational perturbation technique, though not completely conclusive from our calculations, seems to be satisfactory. A calculation with (5,6)-parameter trial functions gave only slight changes from the (4,4)-parameter choice, and left unchanged the trend of the results. The convergence is more satisfactory for $\chi^{(1)}$ than for $\chi_{14}^{(2)}$.

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[21] A. Unsöld, 43, 388 (1927).

IV. DISCUSSION

A. Results Compared with Experimental Data

Our results must be compared to experimental data obtained when the fundamental and harmonic frequencies fall within the transparency range between the lattice and electronic absorption bands. This is the case for Patel's measurements[22] at 10.6 μ on GaAs and InAs. As shown by Table III, the agreement there is good, though that obtained for GaAs must be considered as an accident rather than really indicative of the accuracy of the method. For other compounds no experimental results are now available in this range. Chang *et al.*[12] have studied the dispersion of $\chi_{14}^{(2)}$ in InSb in the range between 1 and 2 eV. A rough estimate of the low-frequency value of this quantity can be obtained from an extrapolation of their results, the uncertainty being of order $\pm 50\%$. Here also theoretical and experimental results seem to be within a factor of 2. The agreement for GaSb is good, but it must be noted that the experimental values[23] are made very uncertain by the lack of precise knowledge of the linear constants for this compound. For GaP the experimental data of Miller[4] at 1.06 μ indicate a value substantially lower than ours.[24] In the absence of either a measurement in the low-frequency range or a systematic study of dispersion, it is difficult to draw any conclusion. For other compounds no experimental data have been published at the time of this writing.

B. Miller's Rule

According to Miller's rule,[4] the coefficient δ defined by Eq. (2.9) should be roughly the same for the eight compounds considered here. In fact our values of δ show a remarkable correlation with the values of the bond dipole moment p calculated with the CRS orbitals (1.5). The values of δ versus p are plotted in Fig. 3. It is seen that for the seven first compounds the range of variation of the calculated δ is about 4. For the last compound BP, δ is smaller by nearly two orders of magnitude. A study of the CRS functions for BP shows that although the centroid of the electronic charge is slightly displaced towards the P atom the electronic distribution is symmetrical around this point.

We can understand at least qualitatively this linear dependence of δ by using a simple classical point model for the electronic distribution of the bonds. As it has stated $\beta_{\parallel} > \beta_{\perp}$ and thus we can to a good approximation assume that the bonds are unidimensional. Then, within the Unsöld approximation,

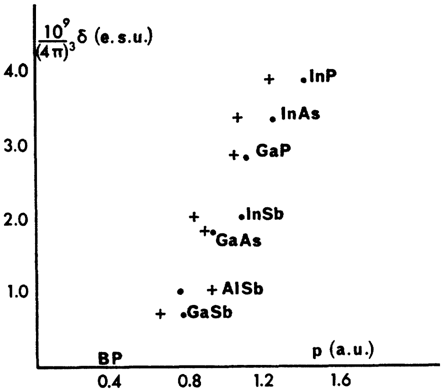


FIG. 3. Plot of Miller's reduced coefficient δ versus the bond dipole moment, as calculated with CRS orbitals (black circles) and Callen's effective charges (crosses), respectively. The values of Callen's effective charges for the III-V compounds were taken from M. Hass and B. W. Henvis, J. Phys. Chem. Solids **23**, 1099 (1962).

$$\chi^{(1)} = C_1 f \frac{e^2}{d^3} \frac{\langle\langle z^2 \rangle\rangle}{\hbar\Omega}, \tag{4.1}$$

$$\chi^{(2)} = C_2 f^3 \frac{e^3}{d^3} \frac{\langle\langle z^3 \rangle\rangle}{\hbar^2\Omega^2}, \tag{4.2}$$

where C_1 and C_2 are numerical coefficients containing crystal-structure factors, f is the effective-field factor and

$$\hbar\Omega = (\hbar^2/2m)\langle\langle z^2 \rangle\rangle^{-1}.$$

To estimate $\langle\langle z^2 \rangle\rangle$ and $\langle\langle z^3 \rangle\rangle$ we assume that the bonding electron charges are located at the atoms as shown in Fig. 4. We obtain then

$$p = 2\epsilon e d, \tag{4.3}$$

$$\langle\langle z^2 \rangle\rangle = 2d^3(1-\epsilon^2) \simeq 2d^2, \tag{4.4}$$

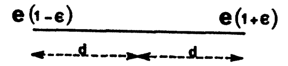
$$\langle\langle z^3 \rangle\rangle = -4\epsilon(1-\epsilon^2)d^3 \simeq -4\epsilon d^2, \tag{4.5}$$

and finally

$$\delta = [D/(1\ \mathrm{Ry})]p, \tag{4.6}$$

where D is a numerical dimensionless coefficient depending only on the crystal structure. The above discussion is valid only for small values of ϵ ($\epsilon < 1$). This is the case for the III-V compounds. For higher values of the dipole moment the ionicity of the bond increases, $\epsilon \to 1$, and as the electronic distribution becomes more spherical around the atoms δ increases. In this picture the small variation of δ for various materials is consequence of the small variation of p. Although this simple model reproduces the linear variation of δ with p it does not give rise to a p-independent term. This can only be obtained by giving up the point distribution. In Fig. 3

FIG. 4. Point-charge distribution for an A-B bond.



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[22] C. K. Patel, Phys. Rev. Letters **16**, 613 (1966).

[23] N. Bloembergen, R. Chang, J. Ducuing, and P. Lallemand, *Physics of Semiconductors* (Dunod Cie., Paris, 1964), p. 121.

[24] After the present paper was sent in for publication our attention was called to the work of D. F. Nelson and E. M. Turner [J. Appl. Phys. **39**, 3337 (1968)], where an indirect measurement of $\chi_{14}^{(2)}$ for GaP is given. This value is also still lower than Miller's value. We thank Dr. D. F. Nelson for communicating his results prior to publication.

we show also the points obtained when p is calculated with the Callen's effective charges.[25]

It is worth noticing that a similar result can be derived from the anharmonic-oscillator model used by Garrett and Robinson.[26] Writing the equation of motion for the oscillator as

$$\ddot{z}+\Omega^2 z-vz^2=(e/m)\mathcal{E}(t)\,, \tag{4.7}$$

they show that

$$\delta=mv/N^2e^3\,, \tag{4.8}$$

where N is the number of oscillators per unit volume. Such an oscillator possesses a permanent dipole moment given by

$$p=ev\hbar/2m\Omega^3\,. \tag{4.9}$$

From this equation one deduces easily a relation similar to Eq. (4.6). In view of this it seems to us more reasonable to interpret δ not as a constant, but as proportional to an asymmetry parameter of the ground-state electronic distribution. The components of the octupole moment of the charge distribution[5] are certainly the best choice for this parameter. Nevertheless, it is seen here that consideration of a more accessible quantity, namely the bond dipole moment, will probably suffice in most cases to interpret the variation of δ.

The considerations developed here for the III-V compounds may be generalized. Thus assuming that the valence charge distribution can be decomposed in independent polarizable bonds

$$\chi^{(1)}=\sum_i \chi_i^{(1)}\,, \tag{4.10}$$

$$\chi^{(2)}=\sum_i \chi_i^{(2)}\,, \tag{4.11}$$

where a Miller-type relation connects the components of $\chi^{(2)}$ and $\chi^{(1)}$. If a given type of bonds dominates the linear properties, it is likely to dominate the nonlinear ones.[27] Then δ can be expressed as in Eq. (4.6), where p must now be interpreted as the dipole moment for the most polarizable bond.

C. Final Remarks

Jha and Bloembergen[28] have independently performed a calculation of the second-order susceptibilities. They use a method which is similar to our Unsöld approximation. The difference between their results and ours can be attributed to a different choice of ground-state wave functions and of energy denominators. They also take the microscopic and macroscopic susceptibilities identical.

In our work assuming effectively localized bonds, we have used the fact that one can calculate $\chi_{14}^{(2)}$ from a knowledge of the bond-charge density of a filled valence band. Lacking the exact ground-state wave functions we used the only available sets of approximate molecular orbitals proposed by CRS to describe the valence electron pairs. There are good reasons to believe[29] that at least qualitatively the bond picture adequately describes the optical properties of the III-V compounds. On the other hand we cannot claim that an electron pair is well described by a simple MO of the type (1.5) where interpair and intrapair electron correlations are completely neglected. Quantitative estimation of the relative magnitude of these two contributions even for simple models is scarce.[30] The effective-field factor f has usually been assumed equal to unity. In some others cases, as for the calculation of the Szigetti[31] effective ionic charges, it is taken equal to the complete Lorentz factor $f_L=\frac{1}{3}[\epsilon(0)+2]$. Qualitative arguments against these two extreme cases have been given before.[32] Our model gives a value for f which is substantially smaller than the Lorentz correction but still larger than unity showing that the localization of the bonding electron pairs cannot be completely neglected. The influence of electron correlation and bond interference on our results can be considered as incorporated in the value of f. Explicit consideration of these effects, a better choice of ground-state wave functions, and an explicit calculation of the F operator are among the possible improvements.

APPENDIX A: CRS ORBITALS

The CRS orbitals φ_A and φ_B paired together to form a molecular orbital (1.5) are tetrahedral sp^3 hybrids constructed with Slater-type nodeless atomic orbitals. The radial part of these orbitals, the same for s and p states, is defined by the formula

$$R(r_i)=(4\pi)^{-1/2}\frac{(2\zeta_i)^{n_i^*+0.5}}{\Gamma(2n_i^*+1)^{1/2}}r_i^{n_i^*-1}e^{-\zeta_i r_i}\,, \tag{A1}$$

where i stands for A or B. In each bond the φ_A and φ_B are directed along the bond axis towards each other and they overlap strongly. On the other hand the overlap between atomic sp^3 orbitals not paired together to form a molecular orbital (1.5) is very small. Including the radial part and using the notations of Appendix D below the φ_A is written

$$\varphi_A=\tfrac{1}{2}(4\pi)^{-1/2}\frac{(2\zeta_A)^{n_A^*+0.5}}{\Gamma(2n_A^*+1)^{1/2}}r_A^{n_A^*-1} \times e^{-\zeta_A r_A}(1+3\cos\theta_A) \tag{A2}$$

and a similar form for φ_B.

The parameters ζ_i, the orbital exponent, and n_i^*, the effective total quantum number, were determined ac-

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[25] H. Callen, Phys. Rev. **76**, 1394 (1949).

[26] C. B. G. Garrett and F. N. H. Robinson, J. Quant. Electron. QE-2, 328 (1966).

[27] Note that if this is not true $\chi^{(2)}$ will necessarily be small.

[28] S. Jha and N. Bloembergen, Phys. Rev. **171**, 891 (1968).

[29] L. Rédei, Proc. Roy. Soc. (London) **270A**, 383 (1962); **270A**, 405 (1962); D. Stocker, *ibid.* **270A**, 420 (1962).

[30] O. Sinanoglou, Proc. Natl. Acad. Sci. U. S. **47**, 1217 (1961).

[31] B. Szigetti, Trans. Faraday Soc. **45**, 155 (1949).

[32] M. H. Brodsky and E. Burstein, Bull. Am. Phys. Soc. **7**, 214 (1962); R. Quertin and F. Stern, Phys. Rev. **134**, A427 (1964).

cording to the usual rules[33] and correspond, following CRS, to tetrahedral atoms A^+ and B^-. In other words only the configuration A^+B^- is kept. The parameter λ was then determined by CRS by applying the usual methods of LCAO–MO. Its value was found equal to 0.68 for almost all III-V compounds with the zinc-blende structure. CRS extended this picture to the II-VI and I-VII compounds as well, but we believe that the omission of other electronic configurations than the one considered by these authors is too crude an approximation. As a matter of fact $\chi_{14}^{(2)}$ seems to be very sensitive to the choice of the values of ζ_A and ζ_B or more precisely to the value of $(\zeta_A-\zeta_B)d$. No attempt was made to calculate this value variationally by minimizing the energy; instead, we used the values prescribed by CRS.

APPENDIX B: GUBANOV AND GUBANOV-PUSHKAREV ORBITALS

The Gubanov and Gubanov-Pushkarev orbitals φ_A and φ_B are also tetrahedral hybrids (sp^3) with the same angular dependence as the CRS orbitals but their radial parts for each kind of atom are given by

$$R(r)=a(e^{-r/cr_c}-be^{-r/r_i}), \tag{B1}$$

$$R(r)=ar(e^{-2r/r_c}-be^{-4r/r_i}), \tag{B2}$$

respectively. r_c and r_i are the tetrahedral covalent and ionic radii, respectively, for the corresponding atom. These orbitals have a node. The constants a and b are determined in both cases as follows: b is determined by requiring that

$$\int_0^{r_i} r^2R(r)dr=0, \tag{B3}$$

which is equivalent to saying that the wave function $R(r)$ is orthogonal to a wave function describing a uniform electronic distribution inside a sphere of radius r_i. The a is determined by the normalization condition

$$\int_0^{\infty} r^2R^2(r)dr=1. \tag{B4}$$

Finally, c is taken quite arbitrarily equal to $\frac{3}{4}$ in the case of the Gubanov orbitals.

APPENDIX C: SUSCEPTIBILITIES

The independent components of the tensors α_{ij} and β_{ijk} are

α components: $\alpha_{xx},\alpha_{yy},\alpha_{zz},\alpha_{xy},\alpha_{yz},\alpha_{zx}$.

β components: $\beta_{xxx},\beta_{yyy},\beta_{zzz},\beta_{xyz},\beta_{xyx},\beta_{yxy},\beta_{yzy},\beta_{zyz}$, β_{zxz},β_{xzx}.

The susceptibilities $\chi_{ij}^{(1)}$ and $\chi_{ijk}^{(2)}$ in terms of bond polarizabilities are given by the formulas

$$\chi_{ij}^{(1)}=\frac{4}{a^3}\sum_{\kappa} a_{ik}^{\kappa}a_{jl}^{\kappa}\alpha_{kl}, \tag{C1}$$

$$\chi_{ijk}^{(2)}=\frac{4}{a^3}\sum_{\kappa} a_{il}^{\kappa}a_{jm}^{\kappa}a_{kn}^{\kappa}\beta_{lmn}, \tag{C2}$$

where κ runs over the four bonds of Fig. 2 and a_{ij}^{κ} are the direction cosines of the κ-bond axes $O_{\kappa}xyz$ with respect to the crystalline axes K,X,Y,Z. After substituting their values in the above expressions, (C1) and (C2), one obtains

$$\chi_{ij}^{(1)}=\chi^{(1)}\delta_{ij}, \tag{C3}$$

$$\chi_{ijk}^{(2)}=\chi_{14}^{(2)}|\epsilon_{ijk}|, \tag{C4}$$

where

$$\chi^{(1)}=(4/a^3)\tfrac{4}{3}[\alpha_{xx}+\alpha_{yy}+\alpha_{zz}],$$

$$\chi_{14}^{(2)}=\frac{4}{a^3}\times\frac{8}{3\sqrt{3}}\left[\beta_{zzz}-\tfrac{3}{2}(\beta_{xzx}+\beta_{yzy})-\frac{1}{\sqrt{2}}(\beta_{yyy}-3\beta_{xyx})\right],$$

and δ_{ij} and ϵ_{ijk} are the Kronecker and Levi-Civita tensors.

APPENDIX D: PROLATE SPHEROIDAL COORDINATES

For our calculations it was found convenient to use the prolate spheroidal coordinate system with foci at the positions of the nuclei A and B. We refer to Fig. 5 for notations where we show also the three Cartesian coordinates $Ax_ay_az_a$, $Oxyz$ and $Bx_by_bz_b$ centered at A, the bond midpoint and B, respectively. The coordinates of a bonding electron in this system are then

$$\xi=(r_A+r_B)/2d, \quad 1\leqslant\xi\leqslant\infty$$
$$\eta=(r_A-r_B)/2d, \quad -1\leqslant\eta\leqslant 1$$

and the azimuthal angle φ. It can be shown that[34]

$$x=d(\xi^2-1)^{1/2}(1-\eta^2)^{1/2}\cos\varphi,$$
$$y=d(\xi^2-1)^{1/2}(1-\eta^2)^{1/2}\sin\varphi,$$
$$z=-d\xi\eta,$$
$$d\tau=d^3(\xi^2-\eta^2)d\xi d\eta d\varphi,$$

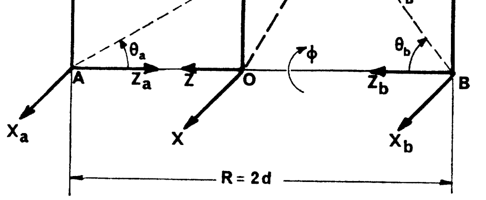

FIG. 5. Bond coordinates.

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[33] See, for instance, W. Bingel, Z. Naturforsch. 9A, 675 (1954).

[34] See, for instance, H. Preuss, *Integraltaffeln zur Quantenchemie* (Julius Springer-Verlag, Berlin, 1956).

$$\nabla^2 f=\frac{d^2}{(\xi^2-\eta^2)}\left[\frac{\partial}{\partial\xi}\left\{(\xi^2-1)\frac{\partial f}{\partial\xi}\right\}\right.$$

$$\left.+\frac{\partial}{\partial\eta}\left\{(1-\eta^2)\frac{\partial f}{\partial\eta}\right\}+\frac{(\xi^2-\eta^2)}{(\xi^2-1)(1-\eta^2)}\frac{\partial^2 f}{\partial\varphi^2}\right],$$

$$\nabla f\cdot\nabla g=\frac{d^2}{(\xi^2-\eta^2)}\left[(\xi^2-1)\frac{\partial f}{\partial\xi}\frac{\partial g}{\partial\xi}+(1-\eta^2)\frac{\partial f}{\partial\eta}\frac{\partial g}{\partial\eta}\right.$$

$$\left.+\frac{(\xi^2-\eta^2)}{(\xi^2-1)(1-\eta^2)}\frac{\partial f}{\partial\varphi}\frac{\partial g}{\partial\varphi}\right].$$

APPENDIX E: VARIATION-PERTURBATION PROCEDURE (*F* OPERATOR)

In the Rayleigh-Schrödinger perturbation theory the higher-order corrections are expressed in terms of infinite sums over intermediate states. The variation-perturbation procedure circumvents these infinite summations by reducing the problem of summation to that of solving an inhomogeneous differential equation; conveniently, this method can be presented as a consequence of the conditional identity

$$\langle i|H'|0\rangle/(E_i-E_0)=\langle i|F|0\rangle \tag{E1}$$

for any operator F satisfying the equation

$$[F,H_0]|0\rangle=(H'-\langle 0|H'|0\rangle)|0\rangle \tag{E2}$$

and its adjoint; H_0 is the unperturbed Hamiltonian with eigenvectors $|i\rangle$ and H' the perturbation. The first-order correction $|0_1\rangle$ to the wave function $|0\rangle$ is given by

$$|0_1\rangle=(F-\langle 0|F|0\rangle)|0\rangle \tag{E3}$$

and the second- and third-order corrections to the energy by

$$W_2=\langle 0|H'F|0\rangle-\langle 0|H'|0\rangle\langle 0|F|0\rangle \tag{E4}$$

and

$$W_3=\langle 0|(F-\langle 0|F|0\rangle)(H'-\langle 0|H'|0\rangle)\times(F-\langle 0|F|0\rangle)|0\rangle, \tag{E5}$$

respectively.

Schwartz[18] showed that one can construct a variational principle for F. The quantity

$$J=\langle 0|\{\bar{F}(H'-\langle 0|H'|0\rangle)+(H'-\langle 0|H'|0\rangle)\bar{F}-\tfrac{1}{2}[\bar{F},[\bar{F},H_0]]\}|0\rangle \tag{E6}$$

is stationary for arbitrary variations of the operator $\bar{F}$, provided that $\bar{F}$ satisfies an equation like (E2) and its adjoint. Further, the extremum value of J is W_2.

We assume an unperturbed one-electron Hamiltonian

$$H_0=-(\hbar^2/2m)\nabla^2+V(r), \tag{E7}$$

where $V(r)$ is a scalar, and we restrict ourselves to the ground-state state described by the wave function $\psi^{(0)}=\langle r|0\rangle$. Then the equation (E2) reduces to

$$(\hbar^2/2m)[\psi^{(0)}\nabla^2 F+2\nabla F\cdot\nabla\psi^{(0)}]=(H'-\langle 0|H'|0\rangle)\psi^{(0)} \tag{E8}$$

and the functional (E6) to

$$(\hbar^2/2m)\langle 0|(\nabla F)^2|0\rangle+2\langle 0|F(H'-\langle 0|H'|0\rangle)|0\rangle. \tag{E9}$$

The equation (E8) was derived initially by Dalgarno and Lewis.[17] It can be written also in the form[35,36]

$$\nabla[\rho(r)\nabla F]=(2m/\hbar^2)(H'-\langle 0|H'|0\rangle)\rho(r), \tag{E10}$$

where $\rho(r)=\psi^{(0)}(r)\psi^{(0)}(r)$ is the ground-state electronic density. This last equation shows that F is uniquely determined by the ground-state electronic density when $V(r)$ is a scalar. To solve equation (E8) one must require $\psi=\psi^{(0)}+F\psi^{(0)}$ to be a wave function normalized in first order with respect to H'.

The explicit solution of (E8) is possible only for some simple cases. For more complicated cases one must resort to computer solutions or use the variational formulation of the method and apply the Ritz-Rayleigh procedure as suggested by Karplus and Kolker.[19] According to this method one chooses a suitable class of trial functions $f(a_i)$ containing a certain number of parameters a_i which are determined by minimizing the functional (E9). The choice of the trial functions $f(r;\,a_i)$ is restricted by symmetry conditions (the same as for the perturbation H'), boundary conditions ($\psi=\psi^{(0)}+\psi^{(1)}$ must be a normalizable wave function), and simplicity of calculations which makes the polynomial forms most suitable. Actually this last choice is suggested by the exact solutions of the simple cases.

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[35] S. Prager and J. Hirschfelder, J. Chem. Phys. **39**, 3289 (1963).

[36] J. Pople and P. Schofield, Phil. Mag. **2**, 591 (1957).