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Simple Tight-Binding Calculation of the Transverse Effective Charges in III-V, II-VI, and IV-IV Compound Semiconductors

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A simple tight-binding model is used for a derivation of transverse effective charges in III-V, II-VI, and IV-IV compounds. Introduction of Phillips's spectroscopic parameters into the model provides a very good agreement with experiment. Such a procedure is then justified by detailed comparison with the resonance integrals and the intra-atomic integrals deduced from term values, showing that a very crude tight-binding treatment can yield quantitative values in these systems.

I. INTRODUCTION

An interesting question which arises in the study of III-V and II-VI compounds concerns the validity of the concept of atomic charges and then the evaluation of the charge transfer from one atom to the other. Theoretical studies of the electronic charge distribution in those systems have been done mainly using pseudopotential theory.[1-3] The results are usually expressed as electron density maps which in general show a quite strong accumulation of charge near the more electronegative element. Such an approach is however not suited to an evaluation of atomic charges, a concept which is best defined in the linear-combination-of-atomic-orbitals (LCAO) approximation.

The interest of a definition of atomic charges lies in the fact that it is a physically appealing concept which can lead to very simple models as in the case of the alkali halides for instance. A first evaluation of these charges has been attempted by Coulson, Redei, and Stocker[4] in a very simple tight-binding model. They concluded that there was a transfer of about 0.5 electron towards the more electronegative element. However, they obtained an average energy gap much too small compared to Phillips's spectroscopic one.[5]

Our aim in this work is then to show that a tight-binding model can be at the same time in agreement with Phillips's parameters and lead to charges which are in good agreement with experiment. However, one does not measure static charges directly, but from infrared lattice-reflection spectra one can deduce a transverse effective charge which can be defined theoretically. This one has already been evaluated by Bennett and Maradudin[6] from pseudopotential theory. The agreement with experiment was good for III-V compounds but quite poor for the II-VI compounds, where they concluded that a tight-binding treatment could be more appropriate.

Before evaluating these charges we shall first recall the formalism used by Coulson *et al.* based on the assumption that bonds between nearest neighbors do not interact. In the framework of this simple molecular model we are then able to evaluate quite simply the transverse effective charges and express them as a function of Phillips's ionicity F. To calculate them numerically we first take Phillips's values for F and obtain a very good agreement with experiment in all cases. Finally we show that if one correctly determines the tight-binding parameters from free-atom term values, one obtains results in close agreement with those of Phillips. We believe that this demonstrates the ability of a simple tight-binding model to yield quantitative results and also that it is a strong argument in favor of the static charge transfer we predict which is important, amounting to about 1.2 electron towards the more electronegative element.

II. FORMAL EVALUATION OF THE CHARGES

We consider tetrahedrally coordinated crystals of the $A^N B^{8-N}$ type where N is equal to 4, 5, or 6. In these crystals, each A atom is surrounded by four B atoms and vice versa, and the molecular orbitals for each bond AB are built out of atomic sp^3 hybrid orbitals φ_A and φ_B pointing towards each other (Fig. 1). In the molecular approximation, only the following matrix elements of the Hamiltonian H are taken into account

$$\begin{aligned}\alpha_A &= \langle\varphi_A|H|\varphi_A\rangle ,\\ \alpha_B &= \langle\varphi_B|H|\varphi_B\rangle ,\\ \beta &= \langle\varphi_A|H|\varphi_B\rangle .\end{aligned} \qquad (1)$$

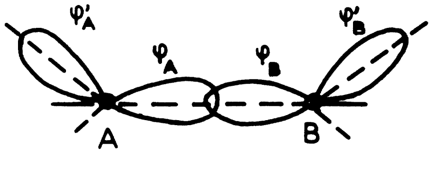

FIG. 1. Atomic sp^3 hybrid orbitals used to define the matrix elements.

α_A and α_B are the intra-atomic terms and β is the resonance integral. We shall neglect $\langle\varphi_A|H|\varphi_A'\rangle$ and $\langle\varphi_B|H|\varphi_B'\rangle$ (Fig. 1).

We may then write the bonding orbital

$$\Psi=[1/(1+\lambda^2)^{1/2}](\varphi_A+\lambda\varphi_B)\ , \tag{2}$$

and the antibonding one

$$\chi=[1/(1+\lambda^2)^{1/2}](\lambda\varphi_A-\varphi_B)\ , \tag{3}$$

neglecting the overlap between φ_A and φ_B. A fraction $1/(1+\lambda^2)$ of an electron described by Ψ belongs to atom A, and a fraction $\lambda^2/(1+\lambda^2)$ to atom B. As there are two electrons per bond and four bonds per atom, the net charges associated with A and B are, respectively,

$$q_A=N-8/(1+\lambda^2),\quad q_B=-q_A\ . \tag{4}$$

The secular equation leads to bonding and antibonding levels E_v and E_c, the values of which are given by

$$E_{\substack{v\\c}}=\tfrac{1}{2}(\alpha_A+\alpha_B)\mp[\tfrac{1}{2}(\alpha_A-\alpha_B)^2+\beta^2]^{1/2}\ . \tag{5}$$

Defining the ionicity parameter by

$$f=(1-\lambda^2)/(1+\lambda^2)\ , \tag{6}$$

we obtain

$$f=(\alpha_B-\alpha_A)/[(\alpha_B-\alpha_A)^2+4\beta^2]^{1/2}\ , \tag{7}$$

and we may write

$$q_A=N-4(1+f)\ . \tag{8}$$

One can formally compare this model with Phillips's spectroscopic one.[5] In the latter, the electronic dielectric constant is determined in a simple one-gap approximation for the electronic band structure. The average gap E_g may be separated into homopolar and heteropolar parts, E_h and C, these three parameters following the relation

$$E_g^2=E_h^2+C^2\ . \tag{9}$$

Assuming that E_g represents the distance between the bonding and antibonding levels E_v and E_c, one obtains

$$E_g^2=4\beta^2+(\alpha_B-\alpha_A)^2\ . \tag{10}$$

So, the molecular model also leads to a homopolar term

$$E_h=2|\beta| \tag{11}$$

and a heteropolar one

$$C=|\alpha_B-\alpha_A|\ . \tag{12}$$

Let us now derive the expression for the transverse effective charge e_T^*. Denoting the μth component of the dipole moment of the crystal by M_μ, and by $u_\alpha(l,k)$ the αth component of the displacement of the kth ion in the lth cell, the elements of the transverse effective charge tensor are given by[6,7]

$$M_{\mu,\alpha}(l,k)=\left(\frac{\partial M_\mu}{\partial u_\alpha(l,k)}\right)\ , \tag{13}$$

the derivative being evaluated in the absence of the macroscopic electric field and for zero atomic displacements.

In the zinc-blende structure, one can show[6] that

$$M_{\mu,\alpha}(l,k)=\delta_{\mu,\alpha}\epsilon(k)\ , \tag{14}$$

where $\epsilon(k)$ reduces to $\pm e_T^*$, respectively, for A and B atoms, and e_T^* is the transverse effective charge.

From Eq. (13), in the absence of a macroscopic electric field, one can write the crystal dipole moment to first order in the atomic displacements as

$$M_\mu=\sum_{l,k\alpha}M_{\mu,\alpha}(k)u_\alpha(l,k)\ . \tag{15}$$

We shall assume for simplicity a displacement pattern such that only the A atoms move in a [111] direction by the same quantity u_A independent of the cell index l.

Denoting the component of the dipole moment along this direction by M_0, one easily finds from Eq. (14) that

$$M_0=Ne_T^*u_A\ , \tag{16}$$

where N is the number of unit cells in the crystal. From this e_T^* can be determined as

$$e_T^*=\frac{1}{N}\frac{\partial M_0}{\partial u_A}\ . \tag{17}$$

The advantage of Eqs. (16) and (17) is that the system retains its translational symmetry. This fact allows for a great simplification in the calculation of e_T^*. In the molecular approximation described above one has only four different types of bonds. One of them, AB, (Fig. 2) is along the displacement u_A while the others AB_1, AB_2, and AB_3 are equivalent with respect to u_A. It is then clear that the total dipole moment M_0 will be N times the dipole moment m_0 of the unit shown in Fig. 2 built from these four bonds. This one is given by

$$m_0=\sum_j q_jR_{j\alpha}\ , \tag{18}$$

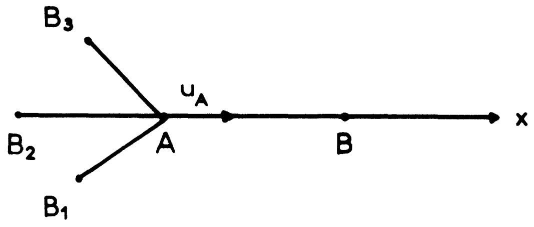

FIG. 2. Schematic representation of the chosen displacement u_A.

where $R_{j\alpha}$ is the αth component of $\vec{R}_j$, the vector joining the origin to the jth atom (A, B, B_1, B_2, B_3 or Fig. 2) and q_j is the contribution of the four bonds of Fig. 2 to the charge of atom j.

From Eqs. (17) and (18) one obtains

$$e_T^* = q_A + X_A \frac{\partial q_A}{\partial u_A} + X_B \frac{\partial q_B}{\partial u_A} + \sum_{i=1} X_{B_i} \frac{\partial q_{B_i}}{\partial u_A} , \tag{19}$$

where X_j is the component of $\vec{R}_j$ along the [111] direction defined by u_A. All the quantities in Eq. (19) are taken at zero displacement.

Charge conservation implies

$$\frac{\partial q_A}{\partial u_A} = - \frac{\partial q_B}{\partial u_A} - \sum_{i=1}^{3} \frac{\partial q_{B_i}}{\partial u_A} . \tag{20}$$

Furthermore as the three bonds AB_i of Fig. 2 are equivalent,

$$\frac{\partial q_{B_i}}{\partial u_A} = \frac{\partial q_{B_1}}{\partial u_A} , \qquad X_{B_i} - X_A = X_{B_1} - X_A , \tag{21}$$

for every i.

Denoting as R the distance between nearest neighbors, we have

$$X_B - X_A = R, \quad X_{B_1} - X_A = -\tfrac{1}{3}R , \tag{22}$$

and

$$e_T^* = q_A + R\left(\frac{\partial q_B}{\partial u_A} - \frac{\partial q_{B_1}}{\partial u_A}\right) .$$

Relations similar to Eqs. (4) and (8) give us

$$q_B = (1 + f_{AB}) - \tfrac{1}{4}N , \qquad q_{B_1} = (1 + f_{AB_1}) - \tfrac{1}{4}N , \tag{23}$$

where f_{AB} and f_{AB_1} are the ionicity parameters defined by Eq. (6) for the corresponding bonds. With these notations

$$\frac{\partial q_B}{\partial u_A} = \frac{\partial f_{AB}}{\partial u_A} , \quad \frac{\partial q_{B_1}}{\partial u_A} = \frac{\partial f_{AB_1}}{\partial u_A} . \tag{24}$$

For both terms one can write

$$\frac{\partial f}{\partial u_A} = \frac{\partial f}{\partial \beta}\frac{\partial \beta}{\partial u_A} + \frac{\partial f}{\partial(\alpha_B - \alpha_A)} \frac{\partial(\alpha_B - \alpha_A)}{\partial u_A} . \tag{25}$$

We shall in the following assume that the second term is negligible. This procedure will be justified at the end of Sec. III.

Then if we define

$$\theta = -\frac{R}{\beta}\frac{\partial \beta}{\partial R} , \tag{26}$$

we obtain

$$\frac{\partial \beta}{\partial u_A} = \frac{\theta\beta}{R} \tag{27}$$

for the AB bond, and

$$\frac{\partial \beta}{\partial u_A} = -\frac{1}{3}\frac{\theta\beta}{R}$$

for the AB_1 bond.

Now from Eq. (7) one can show that

$$\beta \frac{\partial f}{\partial \beta} = -f(1 - f^2) .$$

This combined with Eqs. (22), (24), and (27) leads to the final result

$$e_T^* = N - 4 - 4f[1 + \tfrac{1}{3}\theta(1 - f^2)] . \tag{28}$$

This charge can be determined experimentally from the long-wavelength longitudinal and transverse optical frequencies ω_L and ω_T, using the relation

$$\omega_L^2 - \omega_T^2 = 4\pi(e_T^*)^2/\epsilon_\infty \mu v , \tag{29}$$

where ϵ_∞ is the optical-frequency dielectric constant, μ the reduced mass of the two atoms, and v the volume of a primitive unit cell. In Sec. III we shall compare these values with those derived from the molecular model by Eq. (28).

III. NUMERICAL RESULTS AND DISCUSSION

The calculation of e_T^* requires the knowledge of f and θ. The first term can be readily evaluated by noticing that f must be equal to $\sqrt{F}$ where F corresponds to the ionicity defined by Phillips[5] as

$$F = C^2/(E_h^2 + C^2) . \tag{30}$$

If one assumes that the molecular model reproduces exactly Phillips's spectroscopic model, one evidently obtains from Eqs. (7), (11), and (12)

$$f = \sqrt{F} . \tag{31}$$

We shall come back to this transposition later to show that in fact the intra-atomic terms α_A and α_B give values of C in Eq. (12) in reasonable agreement with those of Phillips, thereby justifying the present procedure. For the moment we then take for F in Eq. (28) values tabulated in the work of Phillips[5] and Van Vechten.[8]

The only parameter which remains to be determined is θ equal to $-(R/\beta)(d\beta/dR)$. We shall estimate it to be of order 2 on the basis of different arguments.

The first one is related to the fact that 2β should be equal to E_h, the homopolar part of the average gap in Phillips's model. From pseudopotential theory this one should be roughly proportional to R^{-2} giving a value of 2 for θ. This argument is in line with the scaling law $R^{-2.5}$ adopted by Phillips for E_h when going from C to Sn via Si and Ge.

The second way of estimating θ proceeds from standard tight-binding theory. If one estimates β from Slater-type orbitals the result should be roughly proportional to $e^{-\alpha R}$ multiplied by a polynomial in R. If one only takes into account the derivative of the exponential, one obtains $\theta = \alpha R = 4.75$ for C, for instance, and similar values for Si, Ge, and Sn. The polynomial will act to reduce this value to about 2 as is the case in diamond, where one finds $\theta \simeq 1.5$ (β being deduced from the extended Hückel theory[9]). (It must be realized that the extended Hückel theory which assumes the Hamiltonian matrix elements H_{ij} to be proportional to the overlap terms S_{ij}, probably underestimates the value of θ, because the kinetic energy terms vary more rapidly than do the S_{ij}. This explains why we have chosen $\theta = 2$ to take some account of this effect.)

The results for e_T^* determined in this way for $\theta = 2$ are presented in Table I where they are compared to experimental data and to the values derived by Bennett and Maradudin[6] from pseudopotential theory. We obtain the same sort of agreement for the III-V compounds, but a much better one for the II-VI and IV-IV systems. One can then definitely conclude, as they suggested, that a tight-binding treatment is more appropriate in those cases.

At this stage it is important to see if the inclusion of f values directly deduced from Phillips's model can be justified in our tight-binding scheme. To demonstrate this it is necessary to show that values for 2β are consistent with those of E_h and that $\alpha_B - \alpha_A$ is of the order of C.

For this we shall recall the method used by Coulson *et al.*[4] who have done the first calculation of the charge distribution in III-V and II-VI compounds. To determine the intra-atomic terms α_A and α_B, they used the following linear expansions (see Moffitt[10]):

$$\alpha_A = \alpha_A^0 + \alpha_A' q_A, \quad \alpha_B = \alpha_B^0 + \alpha_B' q_B , \qquad (32)$$

where q_A and q_B are the net atomic charges. The parameters α^0 and α' can be evaluated semiempirically from free-atom values. Using the particular values 0 and -1 for q_A and 0 and $+1$ for q_B, it is quite easy to show that

$$\alpha_A' = \alpha_A^0 - E_A , \quad \alpha_B' = \alpha_B^1 - \alpha_B^0 , \qquad (33)$$

where α^0 and α^1 are the first and second ionization potentials and E is the electron affinity.

TABLE I.

Nature	f[a]	$\lvert e_T^* \rvert$ BM[b]	$\lvert e_T^* \rvert$ Expt[c]	$\lvert e_T^* \rvert$[d]
GaP	0.61	2.37	2	2.4
GaAs	0.56	2.39	2.2	2.3
GaSb	0.51	2.51	2	2.0
InP	0.65	2.44	2.7	2.6
InAs	0.60	2.52	2.7	2.4
InSb	0.57	2.58	2.5	2.2
ZnS	0.79	3.68	2	2.0
ZnSe	0.82	3.75	1.8	2.0
ZnTe	0.74	3.84	2	1.8
AlSb	0.65	2.28	2.2	2.7
CdTe	0.82	3.92	2.35	2.0
SiC	0.42	1.4	2.7	2.5

[a] Ionicity parameter.

[b] Transverse effective charge: Bennett and Maradudin (Ref. 6).

[c] Transverse effective charge: experimental.

[d] Transverse effective charge: this model.

The difference $\alpha_B - \alpha_A$ can then be written

$$\alpha_B - \alpha_A = \alpha_B^0 - \alpha_A^0 - (\alpha_A' + \alpha_B') q_A . \qquad (34)$$

This term depends on q_A which itself depends on $\alpha_B - \alpha_A$ through Eqs. (7) and (8). Such a self-consistent determination of $\alpha_B - \alpha_A$ was done by Coulson *et al.*[4] for all the III-V and II-VI compounds. For this they used β values deduced from the experimental cohesive energies ($\beta \simeq 1.6$ eV for C). They also obtained for $\alpha_B^0 - \alpha_A^0$ typical values of 20 eV while $\alpha_A' + \alpha_B'$ was of order -30 eV.

With such parameters they obtained a reasonable charge transfer of about 0.5 electron from the electropositive towards the electronegative atom ($B \rightarrow A$). However the main deficiency in their results is that the bonding-antibonding gap which they obtained is always 4 to 5 times smaller than the spectroscopic value E_g.[8] This is quite easy to understand in view of the small values of β and the strong reaction term $(\alpha_A' + \alpha_B') q_A$ which almost exactly cancels $\alpha_B^0 - \alpha_A^0$.

Such a discrepancy has led us to modify their parameters quite substantially. The first important modification comes from the Madelung terms due to the excess or the lack of charge on the various sites which add electrostatic contributions to α_A and α_B. In a point-charge approximation these simply add a quantity 2ρ to the reaction term $\alpha_A' + \alpha_B'$ in Eq. (34) where ρ is equal to the Madelung constant divided by the interatomic distance R. Such a term has an important value ($2\rho \sim 20$–30 eV) and obviously cannot be neglected.

A second important modification comes from the fact that Coulson *et al.* have used s-state ionization potentials E_s for the more electronegative atom and p-state potentials E_p for the more electropositive, instead of using the appropriate sp^3 average. We have corrected for this by taking $\frac{1}{4}(E_s + 3E_p)$ for both atoms. This considerably reduces $\alpha_B^0 - \alpha_A^0$, the sum $\alpha_A' + \alpha_B'$ remaining almost constant.

The last important effect comes from the value of β. If one wants to obtain agreement with the spectroscopic results, β cannot be chosen from the cohesive energies. As was shown[11] it has a

TABLE II. All energies are in eV.

Nature	α'_B [a]	α'_A [a]	ρ [b]	$\alpha'_B+\alpha'_A+2\rho$ [c]	$\alpha'_B+\alpha'_A+2\rho_-$ [d]	C_s [e]
GaP	−7.9	−8.4	10	3.7	0.7	3.3
GaAs	−7.9	−7.8	9.6	3.5	0.6	2.9
GaSb	−7.9	−7	8.9	2.9	0.2	2.1
AlSb	−7.5	−7	8.9	3.4	0.7	3.1
InP	−6.9	−8.4	9.3	3.7	0.9	3.4
InAs	−6.9	−7.8	9	3.3	0.6	2.7
InSb	−6.9	−7	8.4	2.9	0.4	2.1
SiC	−8.6	−9.6	12.5	6.75	3	3.9
ZnS	−7.4	−8.5	10	4.1	1.1	6.2
ZnSe	−7.4	−8.3	9.6	3.5	0.6	5.6
ZnTe	−7.4	−8.2	7.9	2.9	0.5	4.5
CdTe	−6.9	−7.2	8.3	2.5	0	4.4

[a] α'_B and α'_A are reaction terms of the purely intra-atomic potentials.

[b] ρ is the Madelung terms.

[c] $\alpha'_B+\alpha'_A+2\rho$ are the reaction terms in C.

[d] $\alpha'_B+\alpha'_A+2\rho_-$ are the reaction terms in C taking account of the 15% reduction (see text).

[e] C_s is the spectroscopic heteropolar term.

great influence on the charge transfer and a good method is to deduce it from the value it takes for the purely covalent systems.

If one corrects for these three points, the results turn out to be quite different. We first give corrected values for α'_A, α'_B (Table II) and $\alpha^0_B-\alpha^0_A$ (Fig. 3) by taking the appropriate sp^3 average $\frac{1}{4}(E_s+3E_p)$ over s and p ionization energies. The most important thing to notice is that $\alpha^0_B-\alpha^0_A$ (Fig. 3) is drastically reduced with respect to Coulson's values (~20 eV) and compares quite well with the heteropolar part C_s of Phillips's spectroscopic energy gap. However as it is $\alpha_B-\alpha_A$ must be compared to C_s and one has still to analyze the effect of the reaction term $(\alpha'_A+\alpha'_B+2\rho)q_A$.

From Table II one can see that this term is the sum of two important quantities (~20 eV) with opposite sign which nearly cancel. This cancellation increases when ρ is reduced by 15%. Such a reduction in ρ is in fact quite reasonable when one takes into account charge delocalization (we have estimated this reduction to be 15% when using Slater orbitals with carbon parameters). One can also expect further reduction due to the compression of the atomic wavefunction in the crystal which in fact would tend to increase $\alpha'_A+\alpha'_B$ with respect to the free-atom value. It is then a quite reasonable assumption to assume that $\alpha'_A+\alpha'_B+2\rho$ is negligible (in fact it could perhaps become slightly negative in most cases which would increase the agreement between $\alpha_B-\alpha_A$ and C_s). It is worth noticing that only BN and SiC deviate from the linear law in Fig. 3 and only these cases give a more important reaction term which tends to readjust the value of $\alpha_B-\alpha_A$ with respect to C_s.

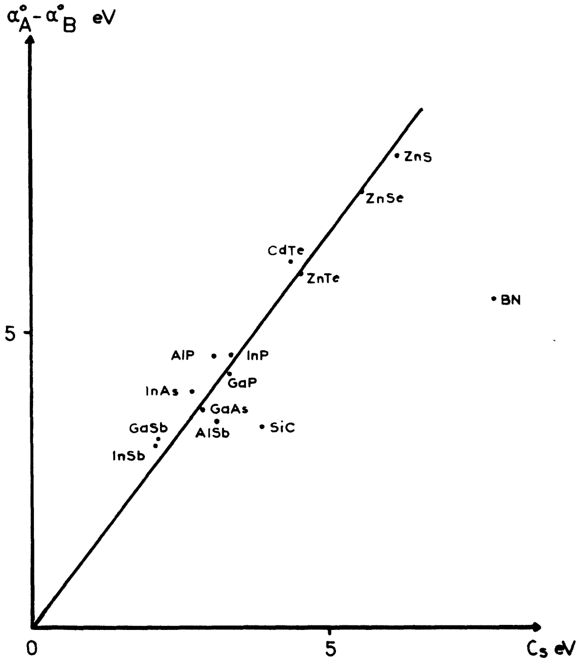

FIG. 3. $\alpha^0_B-\alpha^0_A$ vs C_s heteropolar part of the spectroscopic average gap.

Having shown that a tight-binding determination of C is in good agreement with Phillips's value C_s we must now try to see if 2β can correctly simulate the homopolar part E_h of Phillips's gap. This requires a computation which has been done for carbon, for instance,[12] where 2β is found to be of order 14 eV in quite good agreement with the spectroscopic value 13.6 eV. The reported value of 8.7 eV for Si is somewhat higher than Phillips's E_h of about 5 eV, but associated with $\alpha_B - \alpha_A$ for AlP, for instance, would lead to almost the same value of F than in Phillips's work.

From this we can now conclude that our tight-binding parameters are in good agreement with Phillips's values and this justifies the use of Phillips's ionicity to derive e_T^*. There is now one important approximation which must still be justified, i.e., the neglect of $(\partial/\partial u_A)(\alpha_B - \alpha_A)$ in Eq. (25). For this we shall detail α_A and α_B:

$$\begin{aligned} \alpha_A &= \alpha_A^0 + \alpha_A' q_A - q_A \sum_{A'} \frac{1}{R_{AA'}} - q_B \sum_{B'} \frac{1}{R_{AB'}} , \\ \alpha_B &= \alpha_B^0 + \alpha_B' q_B - q_B \sum_{B'} \frac{1}{R_{BB'}} - q_A \sum_{A'} \frac{1}{R_{BA'}} , \end{aligned} \tag{35}$$

where the last two terms in α_A or α_B correspond to the electrostatic energy experienced by one electron at site A or B. $R_{AA'}$, $R_{AB'}$, and $R_{BB'}$ are the interatomic distances and use has been made of atomic units.

From this one obtains

$$\begin{aligned} \frac{\partial(\alpha_B - \alpha_A)}{\partial u_A} &= -(\alpha_A' + \alpha_B' + 2\rho)\frac{\partial q_A}{\partial u_A} \\ &\quad - q_A \frac{\partial}{\partial u_A}\left(\sum_{A'} \frac{1}{R_{AA'}} + \sum_{B'} \frac{1}{R_{BB'}} - \sum_{B'} \frac{1}{R_{AB'}} - \sum_{A'} \frac{1}{R_{BA}}\right) . \end{aligned} \tag{36}$$

ρ is the Madelung constant and Eq. (36) has been obtained from the fact that

$$q_B = -q_A, \quad \frac{\partial q_B}{\partial u_A} = -\frac{\partial q_A}{\partial u_A} . \tag{37}$$

We have already shown that $\alpha_A' + \alpha_B' + 2\rho$ is negligible.

If now one looks at $\sum_{A'}(1/R_{AA'})$ and $\sum_{B'}(1/R_{BB'})$, it is clear that a translation u_A of all the A atoms does not change these terms so that their derivative with respect to u_A vanishes.

For the two remaining terms, one can expand $1/R_{AB'}$ and $1/R_{BA'}$ to first order in u_A. From this it is easy to obtain

$$\left(\frac{\partial}{\partial u_A} \sum_{B'} \frac{1}{R_{AB'}}\right)_0 = \sum_{B'} \left(\frac{1}{R_{AB'}}\right)^3 \vec{R}_{AB'} \cdot \vec{n} ,$$

$$\left(\frac{\partial}{\partial u_A} \sum_{A'} \frac{1}{R_{BA'}}\right)_0 = \sum_{A'} \left(\frac{1}{R_{A'B}}\right)^3 \vec{R}_{A'B} \cdot \vec{n} , \tag{38}$$

where $\vec{n}$ is the unit vector of the (111) direction.

Now one can take the sums in Eq. (38) on spheres of equivalent atoms, and from symmetry these vanish in the zinc-blende structure. We then come to the conclusion that $\partial(\alpha_B - \alpha_A)/\partial u_A$ is negligible. This shows that one can neglect the second term in Eq. (25) for which the only important contribution is due to $\partial\beta/\partial u_A$.

To summarize this section, we have calculated the effective charge e_T^* from our tight-binding model using Phillips's value for the ionicity and we have then justified this procedure. We find a negative effective charge of about two to three electrons on the more electronegative atom. The results are in quite good agreement with the experimental values which however cannot conclude about the sign. It is finally worthwhile noticing that our results exhibit the same sort of agreement with experiment as the empirical law found by Lawaetz[13] between the Szigeti charge and the ratio $C_s/\hbar\omega_p$, where ω_p is the plasma frequency (this one has, however, been applied to a larger number of systems while our work is concerned only with zinc-blende and wurtzite systems).

IV. CONCLUSION

We have applied a simple tight-binding method to the determination of transverse effective charges in III-V, II-VI, and IV-IV compound semiconductors. This molecular model leads to a very simple definition of static and dynamic charges.

Introduction of Phillips's spectroscopic parameters into this simple tight-binding model has allowed us to obtain transverse effective charges in quite good agreement with experimental data for all systems where they were available. Such a simple method then seems best adapted to this type of problem than Bennett and Maradudin's calculation based on pseudopotential theory which gave poor results for II-VI and IV-IV compounds.

We have finally justified the use of Phillips's parameters, showing that intra-atomic matrix elements deduced from free-atom term values give an heteropolar part of the energy gap close to Phillips's one, and that resonance integrals can account satisfactorily for the corresponding homopolar part.

We then believe from this work that a simple tight-binding approximation provides a useful tool for studying these systems. It can lead to quantitative results for the perfect crystal. It defines unambiguously charge transfers and then seems particularly well adapted to the study of defects in all of this family of compounds where it will lead to fairly simple and tractable models.

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