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Bond-Orbital Model and the Properties of Tetrahedrally Coordinated Solids*

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A model electronic structure is explored which attempts to relate a wide range of properties to a few parameters of covalent and polar solids. The model is based upon tight-binding combinations of bonding hybrid orbitals. Of the many overlap matrix elements which enter, only three are retained; the three are associated with covalency, polarity, and metallicity. Many properties may be computed quite simply in terms of the parameters of the model, and measured values of the properties can then be used to determine the parameters. In this study the matrix elements associated with metallicity are obtained directly from the atomic-term values; those associated with covalency and polarity are obtained from the static dielectric constant using essentially the approach of Phillips, but in terms of the formula for the dielectric constant appropriate to this model. Also calculated in terms of the model were the valence energy bands themselves, obtained explicitly for silicon and for gallium arsenide. In treating other properties the unitarity of the final diagonalization was utilized to avoid carrying it out explicitly. The dipole moment of the individual bonds was defined and calculated as was an effective ionic charge and the macroscopic transverse charge. The cohesive energy was also obtained for ionic and metallic structures as well as for the covalent tetrahedral structures. Criteria for the stability of each structure were thereby obtained. The model also explains why some properties scale approximately linearly with the ionicity defined by Phillips.

I. BOND-ORBITAL MODEL

The model which we will use is a slight extension of a model for diamond considered many years ago by Hall.[1] That model has been generalized more recently by Weaire and Thorpe[2] to arbitrary tetrahedrally coordinated solids in order to study the electronic structure of amorphous materials. We will extend it slightly further in allowing more than one atomic species in the system. It is essentially a linear-combination-of-atomic-orbitals (LCAO) model but stripped down to the bare essentials in order to reduce the number of parameters to a few, which can be fit to experiment.

We will follow Hall in discussing only the valence bands and will see in fact that the model is quite inappropriate for the discussion of conduction bands. However, we will go far beyond Hall's treatment of the bands alone in using the model for a direct treatment of a range of properties of semiconductors and insulators. For definiteness we will formulate the model in the context of tetrahedrally coordinated solids, though obviously the same approach can be applied to a much more general class of materials.

We imagine then a structure, such as the zincblende structure, in which each atom is surrounded tetrahedrally by four identical atoms, which may be of a second type. We will denote the anion, the nonmetallic ion, by a superscript a and the cation, the metallic ion, by the superscript c. In the diamond structure the atoms are the same, but a and c distinguish the two atoms in the primitive cell. On each ion, or atom, we construct the usual sp^3 hybrids, oriented towards the four nearest neighbors. Such a hybrid on the anion can be written

$$|h^a\rangle = \tfrac{1}{2}(|s^a\rangle + \sqrt{3}\,|p^a\rangle). \tag{1}$$

The p state in question is positive and maximum in the direction of the bond. We will think of the s and the p states as atomic states and in this particular study will even equate the energy expectation values of these states to the atomic-term values, but this would not be done in general.

Such hybrid orbitals on any given atom are orthogonal to each other if the near neighbors are exactly tetrahedral. It may be convenient to use this definition even when the neighbors are not precisely tetrahedrally arranged and to take explicit account of the nonorthogonality afterwards. The procedure for doing this appears elsewhere.[3]

To the extent that the Hamiltonian is symmetric around each atom, its expectation value with respect to such a hybrid is given by

$$\epsilon^a = \langle h^a|H|h^a\rangle = \tfrac{1}{4}(\epsilon_s^a + 3\epsilon_p^a), \tag{2}$$

where of course $\epsilon_s^a = \langle s^a|H|s^a\rangle$ and $\epsilon_p^a = \langle p^a|H|p^a\rangle$. We may expect the corresponding value for the cation ϵ^c to be different. We write

$$V_3 = \tfrac{1}{2}(\epsilon^c - \epsilon^a), \tag{3}$$

and V_3 will be one of the fundamental parameters of our model. It reflects a tendency towards polar character in the system. In general, we may expect that the electrons will tend to transfer to the anion, corresponding to a positive V_3.

Although two hybrids on any given atom are orthogonal to each other, there will be a nonzero matrix element of the Hamiltonian between any two such hybrids. It may be evaluated, in analogy with

Eq. (2). For the anion, it is given by $\frac{1}{4}(\epsilon_s^a - \epsilon_p^a)$. We define another parameter of the system

$$V_1^a \equiv -\langle h^a | H | h^{a\prime} \rangle = \tfrac{1}{4}(\epsilon_p^a - \epsilon_s^a) . \tag{4}$$

The sign has been chosen so that we may expect V_1^a to be positive. Similarly we define V_1^c.

Within each bond we may form bonding and antibonding combinations of the two hybrids extending into that bond. It turns out that the overlap between two hybrids in the same bond tends to be very large. We will nevertheless proceed formally as if they were orthogonal, as is done in Hückel theory. This is made possible by replacing the true potential by a pseudopotential in evaluating the matrix elements, as shown by Anderson.[4] This change causes no difficulty since we adjust the matrix elements to fit experiment in the end in any case. The procedure will be justified—for the valence bands only—by examining the resulting bands in Sec. II. We define the matrix element of the pseudo-Hamiltonian between two hybrids in the same bond as

$$V_2 = -\langle h^c | H | h^a \rangle , \tag{5}$$

where again the sign is chosen such that V_2 may be expected to be positive. This is the last of the tight binding matrix elements which we will include in the calculation. Others will be discarded.

We first seek within each bond the linear combination of hybrids having lowest energy expectation. Thus we write a bond orbital

$$| b \rangle = u_a | h^a \rangle + u_c | h^c \rangle \tag{6}$$

with, of course, $u_a^2 + u_c^2 = 1$ and minimize the energy using the matrix elements defined above. We obtain

$$u_a = [\tfrac{1}{2}(1 + \alpha_p)]^{1/2} , \quad u_c = [\tfrac{1}{2}(1 - \alpha_p)]^{1/2} , \tag{7}$$

where

$$\alpha_p = V_3 / (V_2^2 + V_3^2)^{1/2} \tag{8}$$

is the parameter which we will call *polarity* for reasons to be discussed in Sec. III. The expectation value of the Hamiltonian with respect to this bond orbital is given by

$$\langle b | H | b \rangle = \tfrac{1}{2}(\epsilon^a + \epsilon^c) - (V_2^2 + V_3^2)^{1/2} . \tag{9}$$

We have constructed one bond orbital for every bond in the crystal; we finally are to construct the valence states as tight-binding combinations of these bond orbitals. The only overlap integrals which we include are between adjacent hybrids. Combining Eqs. (4), (6), and (7), we evaluate the matrix element between two bonds sharing a given anion. In terms of it we define

$$A = -\langle b | H | b' \rangle^a = \tfrac{1}{2}(1 + \alpha_p) V_1^a . \tag{10}$$

In terms of that for the cation, we define

$$C = -\langle b | H | b' \rangle^c = \tfrac{1}{2}(1 - \alpha_p) V_1^c . \tag{11}$$

All other matrix elements, except those given by Eqs. (9)–(11), are neglected. The energy band calculation requires the diagonalization of a 4×4 matrix which can in fact be done analytically. More importantly, we will see that we may compute directly a number of other properties in terms of the parameters of this model system.

II. ENERGY BANDS

The Hamiltonian matrix for the valence bands which arises in the bond-orbital model may be written down for any given system. In particular we consider the zinc-blende (or diamond) structure. There are four distinct bond orientations which we number 1 through 4. The expectation value of the Hamiltonian with respect to each is identical and given by Eq. (9). For the αth orientation we construct the Bloch tight-binding sum corresponding to wave number $\vec{k}$ in the usual form;

$$| \alpha, \vec{k} \rangle = \frac{1}{\sqrt{N}} \sum_j e^{i\vec{k}\cdot\vec{r}_j} | b_\alpha(\vec{r} - \vec{r}_j) \rangle , \tag{12}$$

where the sum is over the N positions $\vec{r}_j$ of the midpoints of bonds of the αth orientation. Each state of wave number $\vec{k}$ is written as a linear combination of the four Bloch sums given by Eq. (12) for that wave number. The matrix elements of the corresponding 4×4 Hamiltonian matrix may be evaluated directly and the secular equation solved. This can be done analytically, and in fact was done by Hall[1] for the case of diamond, $V_3 = 0$ and $V_1^a = V_1^c$. For our purposes the solution along a [110] direction will suffice. The corresponding bands [measured from the energy of Eq. (9)] are given by

$$\begin{aligned} E_1 &= -(A + C) - 2[4AC\cos^4\theta + (A - C)^2]^{1/2} , \\ E_2 &= -(A + C) + 2[4AC\cos^4\theta + (A - C)^2]^{1/2} , \\ E_3 &= A + C , \quad E_4 = A + C , \end{aligned} \tag{13}$$

With $\theta = ka\frac{1}{8}\sqrt{2}$. The point $\theta = 0$ corresponds to Γ in the Brillouin zone, $\theta = \frac{3}{8}\pi$ corresponds to the point K, and $\theta = \frac{1}{2}\pi$ corresponds to the point X. This agrees with Hall's results for $A = C$.

Note that the two upper bands are independent of wave number, and this is true throughout the zone. Note also that the total bandwidth is given by $4(A + C)$. It is convenient to define a parameter V_1 which represents this spreading of the valence band;

$$V_1 = A + C = \tfrac{1}{2}(V_1^a + V_1^c) + \tfrac{1}{2}(V_1^a - V_1^c)\,\alpha_p . \tag{14}$$

We look first at silicon, for which $A = C = \frac{1}{2} V_1$. Then the energy bands are given by

$$E_{1,2} = -V_1 \pm 2V_1\cos^2\theta , \quad E_{3,4} = V_1 . \tag{15}$$

We could regard V_1 as an adjustable parameter and

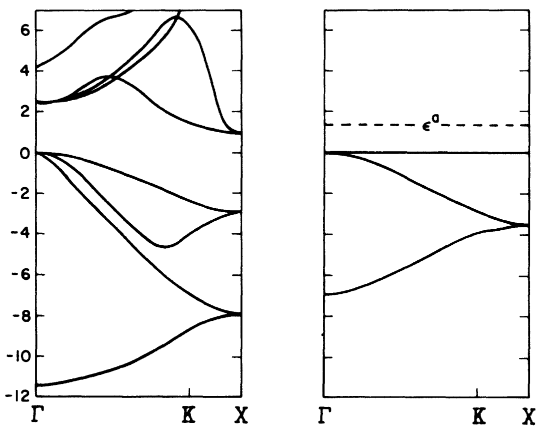

FIG. 1. The energy band structure of silicon along a [110] direction in electron volts. On the left are the bands calculated by Herman, Kortum, and Kuglin (Ref. 6). On the right are valence bands obtained with the bond-orbital model with $V_1 = 1.75$ and $V_2 = 3.02$ eV, corresponding to a metallicity of 0.58. The zero of energy has been taken at the top of the valence band in both cases.

fit the bandwidth. However, this is probably not the best standard for selecting V_1 for our model system. Of course when a model predicts many properties, any one of those properties can be used as a standard. For the purposes of this paper we will use Eq. (4) to relate V_1^a and V_1^c to the atomic-term values as given by Herman and Skillman,[5] and will compute other properties in terms of that choice. Consideration of the cohesive energies in Sec. V would suggest that this may not be the best standard for choosing V_1. However, those considerations also make clear that the total bandwidth is a worse choice. Very possibly the cohesive energy of each element (even if as an element it is metallic) may be the best standard. Then of course the model *predicts* the difference in atomic term values, though not very accurately.

Substituting for A and C in Eq. (15) gives directly the energy bands, which are shown in Fig. 1, along with those calculated by Herman, Kortum, and Kuglin[6] along the same line. We will see in Sec. IV how to obtain V_2 and can therefore determine the energy of the unbonded hybrids, ϵ_a, which is also indicated in the figure. In Sec. III we will relate the concept of metallicity to the proximity of the valence band edge to this value ϵ_a. As we expected, this is a crude representation of the bands, but nevertheless is sufficiently close to give us some hope of calculating other properties. In particular, we note that our calculated bandwidth is considerably too small. A calculation of the antibonding bands with the same model gives bands of the same shape, though possibly scaled or inverted. These clearly have little relation to the true bands and will not be considered further.

We consider second a partly ionic crystal, gallium arsenide. V_2 was obtained from Eq. (26). V_3 was obtained from V_2 using Eqs. (8) and Eq. (29). It is interesting that the value we would have obtained by using Eq. (3) ($V_3 = 1.7$ eV as opposed to 1.5 eV) is quite similar. V_1^a and V_1^c were obtained from Eq. (4). Energy bands from Eq. (13) for gallium arsenide are plotted in Fig. 2, along with those calculated by Herman, Kortum, Kuglin, and Van Dyke.[7]

The bandwidth is again $4V_1$, as it was in the nonpolar crystal. However, in addition a band gap has been opened up at X. That band gap is given by $4|A - C|$. Figure 2 would suggest that we have overestimated that gap, and this turns out generally to be the case with the choice of parameters used here. Grobman, Eastman, and Cohen[8] have recently compiled experimental values for this gap, obtained from photoemission experiments. These are plotted in Fig. 3 against the predictions of the bond-orbital model. The s-p splittings for the divalent metals were obtained by extrapolating the splittings from the same row in the Periodic Table since the tables have no ϵ_p for these cases. Sodium chloride and rubidium chloride (both rocksalt structure) were included by taking (see Sec. VI) α_p equal to 1 in this structure, and thus $4(A - C)$ is $\epsilon_p - \epsilon_s$ for chlorine.

The experimental results scale with the prediction but are some 33% smaller (though the discrepancy in Fig. 2 is only 10%). In these terms we overestimate the s-p splitting in this calculation. On the other hand, the narrowness of the model

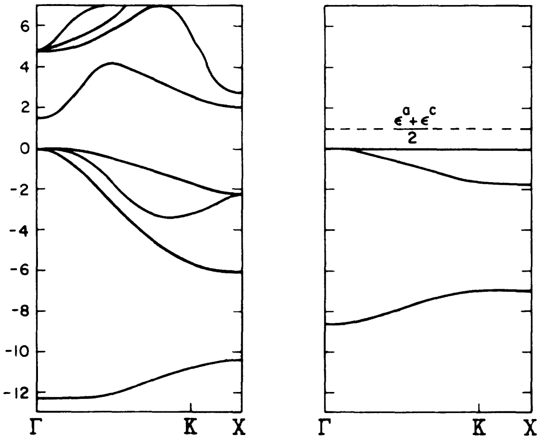

FIG. 2. Energy bands of gallium arsenide along a [110] direction in electron volts. On the left are the bands calculated by Herman, Kortum, Kuglin, and Van Dyke (Ref. 7). On the right are the energy bands from the bond-orbital model with $V_1^c = 1.62$, $V_1^a = 2.36$, $V_2 = 2.67$, and $V_3 = 1.51$ eV. These correspond to a polarity of 0.49 and a metallicity of 0.71.

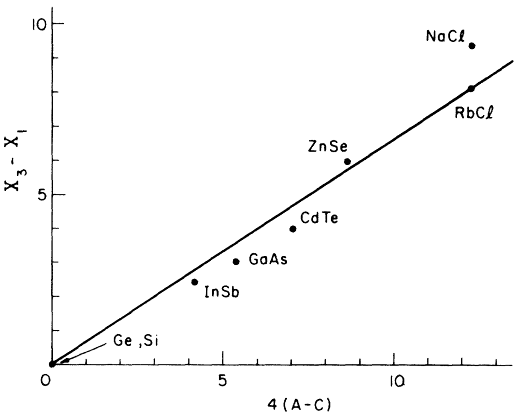

FIG. 3. Experimental (Ref. 8) splitting of the first two bands at X plotted against the predicted values, both in electron volts. The line represents $\frac{2}{3}$ of the predicted value.

valence bands shown in Figs. 1 and 2 indicates that we underestimate the *s-p* splitting in that regard. Again, it is interesting to see the predictions from the simplest choice of parameters, and it appears that other choices could be better.

Grobman *et al.*, noted that these gaps were approximately equal to the parameter C of the Phillips[9]-Van Vechten[10] model (see Sec. IV) though there is no *a priori* reason to expect that particular result. From the point of view of our model the gap approaches the anion *s-p* splitting in highly polar materials and is of course zero in nonpolar materials. If the *s-p* splittings in the anion and cation were the same, $4|A-C|$ would equal α_p times the total bandwidth, or $\alpha_p(4V_1)$; however, there are significant contributions from the differences in splitting also. In general, the effect of asymmetry between the two atoms in the primitive cell is to separate the *p* bands from the *s* bands. As the effect becomes larger the valence band states correspond more closely to atomic *s* and *p* states on the anion. The fact that the bond-orbital model correctly portrays these states in the ionic limit will prove to be essential to the utility of the method in describing the properties of polar materials.

III. POLARITY AND METALLICITY

In a solid the charge to be associated with an atom is an ill-defined quantity since there is arbitrariness in associating each contribution of the charge density to a particular atom or a particular bond. However, the choice becomes quite natural within the context of our model. The bond wave function is written as in Eq. (6), and that state may be thought of as being a fraction $u_a^2/(u_a^2+u_c^2)$ on the anion and a fraction $u_c^2/(u_a^2+u_c^2)$ on the cation. We imagine the bonds to be doubly occupied. Thus each bond contributes to the anion a charge $-2eu_a^2/(u_a^2+u_c^2)$, seen from Eq. (7) to be $-e(1+\alpha_p)$. Similarly, it contributes a charge $-e(1-\alpha_p)$ to the cation. In this context the term "polarity" for α_p is most natural. The anion also has a nuclear charge of $(4+\Delta Z)e$, where $4+\Delta Z$ is the column number in the Periodic Table. $\Delta Z = 0$ for carbon, 1 for nitrogen, 2 for oxygen, and 3 for fluorine. Thus the net charge on the anion (in units of $-e$) is

$$Z^* = 4\alpha_p - \Delta Z\,. \qquad (16)$$

Of course the charge on the cation is equal and opposite. Note that as the polarity approaches 1, the magnitude of the effective charge approaches the chemical valence, 1 for sodium, 2 for magnesium, and 3 for aluminum and 1 for chlorine, 2 for sulphur, and 3 for phosphorous. When we determine the polarity of gallium arsenide we will see that it is near 0.5, leading to an effective charge of 1, with the arsenic negative. We will in fact find in general that the electronic transfer is larger than the proton transfer and therefore that the nonmetallic ion is negative, as we might have anticipated. We may note, however, that the description of the system in terms of screening might have suggested that the proton transfer would be only partially screened and for small valence differences that the charges might have been reversed from what we find here.

It is convenient to associate a dipole moment with each bond in a similar way. That dipole moment is equal to the asymmetrical charge, $-e\alpha_p$, times a length which we write γd, where d is the internuclear distance and γ is a parameter which would be unity if the hybrids were nonoverlapping and spherically symmetric and if there were no local field effects. We tentatively take it the same for all systems. Because of the way γ will enter the dielectric constant [Eq. (23)] and because we are determining V_2 and V_3 from that dielectric constant, γ will scale the values of V_2 and V_3 we obtain. A value $\gamma^2 = 2$ seems to give an appropriate scale, and we will use that in our numerical examples. The fact that it is larger than 1 suggests that as a bond becomes polar the principal charge transfer is between the far sides of the corresponding ions. In any case, the dipole moment becomes

$$\vec{P} = -\gamma e \vec{d} \alpha_p\,, \qquad (17)$$

where $\vec{d}$ is the vector distance from cation to anion.

The effective charge given in Eq. (16) is appropriate for the evaluation of Madelung potentials, but in many properties there are other contributions. For example, the dipole moments arising from the displacement of the anions with respect to the cations contain a "dynamic" contribution.[11] In the context of Eq. (17) this contribution arises directly from the change in α_p with the displacement. V_3 is not expected to have any variation linear in this displacement but V_2 is found [Eq. (26)] to vary as d^{-3}. This leads immediately to a change in α_p of $-3\alpha_p(1-\alpha_p^2)/d$ times the change in d. When an anion is moved with respect to its neighbors there are contributions from four neighboring bonds, but angular factors reduce the effect by a factor of three. In all cases the electron transfer is in the direction of the motion of the anion. Thus the dynamic charge adds to the effective charge in Eq. (16) to give a macroscopic transverse effective charge of

$$e_T^* = 4\alpha_p - \Delta Z + 4\gamma\alpha_p(1-\alpha_p^2) . \tag{18}$$

This is compared with the experimental values given by Lucovsky, Martin, and Burstein[11] in Table I. The values of α_p used are obtained from the ionicities also given in Ref. 11 using Eq. (29). We have overestimated e_T^* somewhat, but have reproduced the remarkable feature that it tends not to increase appreciably with increasing polarity for a given structure. This arises from the reduction in the dynamic charge as the electrons become more tightly bound to the anion.

TABLE I. Polarity, effective charge [Eq. (16)], transverse effective charge [Eq. (18)], and experimental transverse effective charge. Polarity was obtained from Ref. 11 using Eq. (29). Experimental values of e_T^* were also taken from Ref. 11.

Crystal	α_P	Z^*	e_T^*	e_T^*(expt)
		Zinc-blende structure		
CuCl	0.78	0.11	1.85	1.12
CuBr	0.77	0.08	1.85	1.49
CuI	0.74	−0.06	1.85	2.40
AgI	0.79	0.16	1.84	1.40
ZnS	0.69	0.76	2.80	2.15
ZnSe	0.70	0.78	2.81	2.03
ZnTe	0.68	0.73	2.79	2.00
CuTe	0.76	1.02	2.86	2.35
HgTe	0.78	1.11	2.85	2.96
BN	0.43	0.71	2.68	2.47
AlP	0.47	0.87	2.94	2.28
AlAs	0.44	0.74	2.74	2.30
AlSb	0.56	1.24	3.41	1.93
GaP	0.48	0.94	3.03	2.04
GaAs	0.47	0.87	2.94	2.16
GaSb	0.43	0.71	2.68	2.15
InP	0.55	1.21	3.38	2.55
InAs	0.51	1.03	3.16	2.53
InSb	0.48	0.90	2.99	2.42
SiC	0.35	1.41	3.15	2.57
		Wurtzite structure		
BeO	0.68	0.70	2.78	1.83
ZnO	0.69	0.76	2.80	2.09
CdS	0.74	0.95	2.85	2.27
CdSe	0.74	0.97	2.85	2.25
GaN	0.61	1.43	3.60	3.20
AlN	0.57	1.29	3.47	2.75

TABLE II. Dependence of cohesion on metallicity.

	Material parameters			Cohesive energy (eV/atom)	
	V_2(eV)	V_1(eV)	α_m	$4V_2(1-\alpha_m)$	Expt[a]
C	10.8	2.14	0.20	34.5	7.4
Si	3.0	1.76	0.58	5.7	4.6
Ge	2.7	2.00	0.74	2.8	3.9
Sn	1.8	1.64	0.92	0.6	3.1

[a] C. Kittel, *Introduction to Solid State Physics*, 3rd ed. (Wiley, New York, 1967), p. 78.

We see that in each of Eqs. (16)–(18) the polarity α_p gives a very reasonable measure of the polar character of the electronic states. The definition of α_p in Eq. (8) is clearly analogous to the definition of ionicity made by Phillips[9] on the basis of an approach we will discuss later. A central feature of Phillips's work was the determination of ionicity from the dielectric constant, and we use the operational definition of ionicity as the quantity obtained from the dielectric constant following the prescription given by Phillips. Within our model we may calculate the dielectric constant, which will depend on polarity, and can therefore obtain Phillips's ionicity in terms of our polarity.

We have noted that the total bandwidth is given by $4V_1$ for any system. We will see that this broadening of the valence bands is closely related physically to the concept of metalization introduced by Mooser and Pearson,[12] and it will be convenient to make a quantitative definition of *metallicity*,

$$\alpha_m = V_1/(V_2^2 + V_3^2)^{1/2} , \tag{19}$$

in analogy with the polarity defined in Eq. (8). We will see that the metallicity increases with the principal quantum number of the valence states, as indicated by Mooser and Pearson, but because the denominator becomes small rather than because the numerator V_1 becomes large. The interpretation of this quantity in terms of electronic structure may be seen from Eqs. (9) and (13). The average hybrid energy is given by $\frac{1}{2}(\epsilon^a + \epsilon^c)$. The energy of the bond is lowered through the covalent bonding, represented by V_2, and ionic transfer represented by V_3. These bond orbitals are then broadened into a band by metallicity, arising from V_1. A metallicity of *one* corresponds to a sufficient broadening to bring the top of the band up to the initial hybrid energy. Figures 1 and 2, and the values of α_m we give for the elemental semiconductors in Table II, would suggest that this may be associated with a vanishing band gap. We will see that when the metallicity is of the order of or greater than 1, a metallic structure tends to be favored over the tetrahedral structure postulated in this paper.

We could also of course defined a third parameter, *covalency*,

$$\alpha_c = V_2/(V_2^2+V_3^2)^{1/2}, \tag{20}$$

though for the purposes of this paper it has not proven very useful. Obviously, the covalency and the polarity are related by $\alpha_c = (1-\alpha_p^2)^{1/2}$.

We will see that metallicity, and the matrix element V_1, play a smaller role in the properties than one might first guess. The reason is related to the fact that in our band calculation V_1 first entered in the final diagonalization which led to Eq. (13). That diagonalization corresponds to a unitary transformation and therefore left the sum of diagonal elements unchanged. It follows that for computing the total energy, since all valence band states are occupied, we may simply use four times the diagonal element, Eq. (9); the total energy is independent of V_1. Thus within the model the total valence band energy is exactly a sum of identical bond energies. In addition, because the transformation is unitary, the total charge density may be computed from the bond states of Eq. (6). That charge density also is not changed in the final diagonalization and is independent of V_1. These two features will tremendously simplify the calculation of a number of the properties of the systems in question.

IV. DIELECTRIC CONSTANT AND THE DETERMINATION OF V_2 AND V_3

The calculation of the dielectric constant is very central to this approach since we will follow Phillips[9] in using it as the standard for determining two of the parameters of the theory, V_2 and V_3. V_1 will be obtained in this study from the atomic term values using Eq. (4) as indicated earlier.

Our approach to calculating the dielectric constant will be to compute the change in dipole in each bond due to the presence of a field, to sum this over bonds to obtain the susceptibility, and finally to write the dielectric constant. This is quite distinct from the usual approach of obtaining the dielectric constant in terms of oscillator strengths between the ground and excited states. That approach is not immediately accessible to us; we have seen that though our model gives a reasonable description of the ground states it does not represent the excited states at all well. Such a calculation of the dielectric constants based upon our valence states could be carried out using the orbital correction method[3] as further developed by Meserve for calculating the polarizability of the inert gases.[13] In this method, the correction to the wave function induced by the electric field could be expanded in plane waves, orthogonalized to the ground state. However, at this stage, and in view of the crudeness of our model, it seems preferable to calculate the polarizability by computing directly the ground state in the presence of a field. Such an approach is reminiscent of the rigorous relation found by Hopfield[14] between the dielectric function and the properties of the ground state.

Our approach is to first treat the deformation of each individual bond by the electric field. This leads us to modified bond states but nevertheless to a Hamiltonian containing the various matrix elements V_1^a and V_1^c coupling bonds, which could be diagonalized to obtain the eigenstates and their energies. However, we have noted that the unitary transformation which diagonalizes this last matrix does not modify the charge distribution. Therefore in our calculation of the polarizability we may simply add the contributions of the individual bond.

We gave in Eq. (17) the dipole moment which we associate with an individual bond. The interaction of an electric field with this dipole will give a change in energy as a function of a u_a and u_c;

$$-\vec{\mathcal{E}}\cdot\vec{\mathrm{P}} = +\gamma e\vec{\mathrm{d}}\cdot\vec{\mathcal{E}}(u_a^2-u_c^2)/(u_a^2+u_c^2). \tag{21}$$

The corresponding approximation in the Hamiltonian matrix is to replace the field seen by each electron in the bond by a change in V_3 of $-\gamma e\vec{\mathrm{d}}\cdot\vec{\mathcal{E}}/2$. Thus we may compute the change in polarization of the bond by taking the derivative of the dipole moment with respect to V_3 and multiplying by $-\gamma e\vec{\mathrm{d}}\cdot\vec{\mathcal{E}}/2$. The contribution of the bond in question to the induced polarization is given by

$$\delta P = \frac{\gamma^2 e^2 d^2}{2}\cos^2\theta\,\mathcal{E}\,\frac{\partial\alpha_p}{\partial V_3}, \tag{22}$$

where θ is the angle between the field and the bond. This is to be averaged over angle and multiplied by the density of bonds $\frac{1}{2}N$ (where N is equal to the density of electrons) to obtain the susceptibility, leading finally to a static dielectric constant

$$\epsilon_0 = 1+\gamma^2\pi N e^2 d^2 V_2^2/3(V_2^2+V_3^2)^{3/2}. \tag{23}$$

Again, d is the interatomic distance, and again we take $\gamma^2=2$.

This is a surprising formula in the context of the familiar formula[15]

$$\epsilon_0 = 1+4\pi N e^2\hbar^2/mE_g^2. \tag{24}$$

Here E_g is the energy difference between ground and typical excited states. One factor of $1/E_g$ came from the usual energy denominator, the other from variations in the oscillator strength. The matrix element $(V_2^2+V_3^2)^{1/2}$ of Eq. (23) has some relation to an energy gap but we see that the dependence is very much different depending upon whether the variation is a covalent or an ionic one. We have seen that the tetrahedral solid does not have a simple two-level electronic structure, and it is perhaps not surprising that the formula differs appreciably from that derived for the simple two-level system.

We will follow the method used by Phillips[9] to relate the parameters of our theory to the measured dielectric constant. In particular we will determine V_2 for diamond and silicon from the measured ϵ_0 using Eq. (23). We then assume, as did Phillips, that the V_2 for all other systems depends only upon the bond length, using the formula

$$V_2 = C_0 d^s , \tag{25}$$

where C_0 and s are adjusted to fit diamond and silicon. This approach was motivated by the fact that the measured ϵ_0 of heavier elements has contributions from core polarization and relativistic effects which have little relevance to the valence bands. We see from Eq. (23) that $\epsilon_0 - 1$ (for $V_3 = 0$) varies as $V_2^{-1} d^{-1}$. The variation from Eq. (24) is as $E_g^{-2} d^{-3}$. Equation (24) is essentially the Penn[16] formula used by Phillips. Thus where Phillips found that E_g varied as $d^{-2.5}$, we find V_2 varies as d^{-3}, a result noted first by Ciraci.[17]

This seems a very natural result; V_2 is inversely proportional to the volume. This finding, combined with the expression in Eq. (23) for the dielectric constant, explains why the use of the Penn dielectric constant [Eq. (24) except for a small correction] leads to the rather peculiar dependence of $d^{-2.5}$. We obtain V_2 for a material from the bond length d,

$$V_2 = 10.8 (d_{\text{dia}}/d)^3 . \tag{26}$$

10.8 eV is the value of V_2 for diamond and $d_{\text{dia}} = 1.54$ Å.

Given V_2 from Eq. (26) we wish to use Eq. (23) to obtain V_3 from the measured dielectric constant for any material. Of course the measured dielectric constant for the nonelemental semiconductors also has contributions from core polarization, etc., and corrections must be made for these before V_3 can be evaluated. These corrections should be made with our model in mind, presumably by generalization of the corrections found for elemental semiconductors, in analogy with the corrections made by Van Vechten.[10] However, for the purposes of this preliminary study we may take the short cut of adopting precisely the corrections which Van Vechten used. Thus we could work backwards from the Phillips–Van Vechten ionicities to obtain the corrected dielectric constant, and then use it to compute the polarity. In fact, if we neglect the small difference (of the order of 10%) between Eq. (24) and the Penn formula, we can do this formally and obtain a direct relation between polarity and ionicity.

We first relate ionicity to the dielectric constant. The gap is written in terms of homopolar (E_h) and ionic (C) contributions with Phillips's formula,

$$E_g^2 = E_h^2 + C^2 . \tag{27}$$

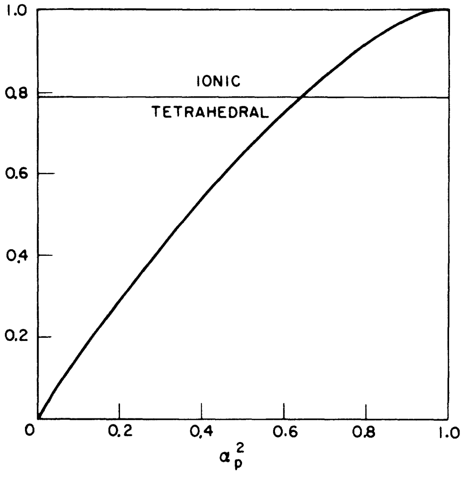

FIG. 4. Ionicity of Phillips and Van Vechten as a function of the square of polarity.

Combined with Eq. (24) it follows that E_g^{-2} is equal to $(\epsilon_0 - 1)d^3$ times a universal constant. Furthermore with the definition of ionicity

$$f_i = C^2 / E_g^2 , \tag{28}$$

we see that $1 - f_i = E_h^2 / E_g^2$ is proportional to $(\epsilon_0 - 1)d^{-2}$, where we have used $E_h \propto d^{-2.5}$. In a similar way we relate α_p to $\epsilon_0 - 1$ using Eq. (23). We see that $\epsilon_0 - 1$ is proportional to $(1 - \alpha_p^2)^{3/2} d^2$. Equating the two expressions for $\epsilon_0 - 1$, the d^2 factors cancel. We note that both α_p and f_i vanish for an elemental semiconductor and find

$$f_i = 1 - (1 - \alpha_p^2)^{3/2} . \tag{29}$$

This is an approximate relation (because of small corrections which Phillips and Van Vechten included), but this provides us with a simple way of obtaining polarities and covalencies directly from the ionicities listed by Phillips. Equation (29) is plotted in Fig. 4. In our model calculations we may expect some properties to scale with α_p^2. From Fig. 3 we see that ionicity is very nearly proportional to α_p^2 over the range of ionicities less than 0.785, over which tetrahedrally coordinated structures are found. Thus it is not surprising, in the context of our model, that Phillips found a number of properties to scale approximately with his ionicity. However, from the point of view of our model, ionicity is not a very natural, nor a linear, scale.

V. COHESIVE ENERGY

Though calculating the cohesive energy is clearly pushing the model very far we may hope for correct orders of magnitude and for meaningful trends. To do this calculation we begin with two isolated atoms which are to make up a primitive cell, each atom initially neutral. We then move step by step to form the crystal keeping track of the change in energy at each step. The most usual procedure for doing this for polar crystals is to imagine forming ions at large separations, requiring an energy equal to the difference between cation ionization energy and the anion electron affinity. The ions are then brought to the equilibrium separation gaining an electrostatic energy equal to the Madelung energy. In order to make contact with the parameters of our model and to be able to include also covalent materials we instead imagine bringing the neutral atoms to their equilibrium positions before transforming the electrons. Then both of the contributions described above in the ionic crystal are incorporated in a term, $2V_3$ times the number of electrons transferred. This makes clear the point that V_3 represents a difference in energy for electrons on different atoms *within the crystal* and explains also why the Madelung energy does not appear explicitly in our result.

The first step in constructing the states in the crystal is to promote every electron from its atomic orbital to a hybrid orbital. This requires an energy $3V_1^a$ or $3V_1^c$ for every s state, and provides an energy V_1^a or V_1^c for every p state. We may readily compute the promotion energy (which reduces the cohesive energy) by considering the starting configuration in each case. We obtain a promotion energy per atom pair of

$$E_{\text{pro}} = (4+\Delta Z)V_1^c + (4-\Delta Z)V_1^a \qquad (30)$$

for ΔZ equal to 0, 1, and 2. For $\Delta Z = 3$, as in sodium chloride, this value is to be reduced by $4V_1^c$; there is only a single s electron on the cation to be promoted.

The next step is to transfer ΔZ electrons from the anion (the nonmetallic ion) to the cation (the metallic ion) in order to occupy equal numbers of hybrid orbitals on the two atom types. This required an additional energy $2\Delta Z V_3$. Next we form bond orbitals, gaining an energy $8(V_2^2+V_3^2)^{1/2}$ per atom pair. In ionic crystals this will of course involve transferring the electrons back to the anion. Finally we broaden these levels into bands without altering the total energy. Thus the cohesive energy per atom pair becomes

$$E_{\text{coh}} = 8(V_2^2+V_3^2)^{1/2} - 2\Delta Z V_3 - E_{\text{pro}} . \qquad (31)$$

We first consider purely covalent systems, in which V_3 and ΔZ are both zero. The cohesive energy per atom becomes

$$E_{\text{coh}}/\text{atom} = 4(V_2 - V_1) = 4V_2(1-\alpha_m) . \qquad (32)$$

Thus V_2 may be interpreted directly as a covalent bonding energy per electron which is then reduced by metallicity. It is remarkable that metallicity as we have defined it provides such a direct degradation of covalency in our model. This did not occur as an effect of the band broadening in the crystal, but as a result of the associated promotion energy in the atom required in the formation of the hybrids.

This is an appealing picture and one which is crudely in accord with experiment as indicated in Table II. The computed cohesive energies are of the correct order of magnitude and do in fact drop off with increasing metallicity, though the decrease in cohesion with increasing row is much too great. This is a result, at least for high metallicity, of sensitivity to α_m, and suggests that the cohesive energy itself might provide a good standard for determining V_1.

We next consider the cohesive energy of a strongly ionic material. As the polarity approaches one, V_2 becomes negligible compared to V_3, and the cohesive energy per atom pair approaches

$$E_{\text{coh}} = 2V_3(4-\Delta Z) - E_{\text{pro}} . \qquad (33)$$

The first term is simply $2V_3$ times the number of electrons transferred from the metallic to the nonmetallic ion. The cohesive energy is this transfer energy, reduced by the energy required to promote the electrons to a full shell configuration in the nonmetallic ion.

In the intermediate case it could be useful to rewrite Eq. (31) by writing V_3 in terms of the polarity. We obtain

$$E_{\text{coh}} = \frac{8V_2(1-\frac{1}{4}\alpha_p\Delta Z)}{(1-\alpha_p^2)^{1/2}} - E_{\text{pro}} . \qquad (34)$$

We see that as we move from a covalent to a polar material there are two competing factors in the cohesive energy. By expanding all factors in α_p we see that the cohesive energy will drop with increasing polarity if α_p is less than $\frac{1}{2}\Delta Z$ but will increase with α_p if it is greater. We have indicated in fact that α_p is almost always greater than $\frac{1}{4}\Delta Z$, the metallic ion having net negative effective charge if this is not the case. However, a survey of the polarities listed in Table I indicates that they are almost always less than $\frac{1}{2}\Delta Z$, and therefore our model predicts that the cohesive energy will decrease with polarity as is observed. It will in fact tend to decrease with the square of polarity, or with ionicity as indicated by Phillips.[9] This is a rather small effect, superimposed upon the much larger effect of metallicity, which we have seen is overestimated in our model, at least with the choice of V_1 evaluated in terms of the atomic term values.

VI. STABILITY OF STRUCTURES

Of course when a material becomes sufficiently polar, we expect that a closely packed structure, such as the sodium chloride or cesium chloride structure, will be favored. Phillips has in fact found that all materials with an ionicity greater than 0.785 form such structures. Since we have found a monotonic relation between ionicity and polarity, Eq. (29), that empirical result carries over automatically to our model; the dividing line occurs at a polarity of 0.80. However it is worth considering the relative stability of structures more carefully in terms of our model. This study is somewhat more intuitive than were the other derivations.

In order to do this we must consider again the origin of the matrix element V_3. We indicated that there were ultimately two contributions to V_3, one related to the energy required to transfer electrons between the isolated metallic and nonmetallic atoms. The second was an electrostatic energy difference for an electron on each of the ions in the crystal. Thus V_3 will differ for different structures and the difference, δV_3, may be evaluated directly in terms of the Madelung constant α.[18] The contribution to V_3 arising from this contribution to the energy may be estimated from

$$V_3^{es} = \frac{Z^* e^2}{\epsilon_0 d} \sum_i \mp \frac{d}{r_i} = \frac{Z^* e^2 \alpha}{\epsilon_0 d}, \tag{35}$$

where Z^* is the effective ionic charge given in Eq. (16). The electrostatic potential is reduced by the dielectric constant. The sum is over all neighbors to an ion; r_i is the distance. The minus obtains if the neighbors are of a different type, the plus if they are the same.

We should also note that when we form an ionic structure, with six to eight nearest neighbors, we can no longer form orthogonal hybrid orbitals and we may expect the covalent contribution V_2 to the energy to disappear. The promotion energy, Eq. (30), is present in either case. Thus we may directly compare the energies in the tetrahedral and ionic structures. The cohesive energy in the zinc-blende structure minus that in the sodium chloride structure is found to be

$$E_{\mathrm{coh}}^{\mathrm{ZnS}} - E_{\mathrm{coh}}^{\mathrm{NaCl}} = 8(V_2^2 + V_3^2)^{1/2} - 8(V_3 + \delta V_3) + 2\Delta Z \delta V_3. \tag{36}$$

We expect the dividing line between structures to occur when this is zero.

We may rewrite this criterion in approximate form by estimating δV_3. The Madelung constant α is approximately the same in the cesium chloride and sodium chloride structures, 1.763 and 1.748, respectively, and somewhat smaller in the zinc-blende structure, 1.638.[18] We take the difference to be 0.11 and neglect changes in d, Z^*, and ϵ_0. Thus the difference in V_3 is $\delta V_3 = 0.11 Z^* e^2/\epsilon_0 d$. Thus ionic structures are favored when

$$\alpha_p > 1 - 0.028 Z^*(4 - \Delta Z) e^2/\epsilon_0 d (V_2^2 + V_3^2)^{1/2} \tag{37}$$

which provides a crude criterion for predicting the structure, the biggest error in going from Eq. (36) to Eq. (37) being the neglect of the change in d.

We may estimate the right side approximately by noting that the dividing line will occur at rather high polarity where $4 - \Delta Z$ and Z^* are approximately equal to the valence Z and ϵ_0 is near 1. Then the right-hand side becomes $1 - 0.028 Z^2 e^2/d(V_2^2 + V_3^2)^{1/2}$. Taking $Z = 1$ and typical values of $d = 2$ Å and $(V_2^2 + V_3^2)^{1/2} = 4$ eV, we obtain a polarity 0.95, of the same order as the experimental 0.8. This criterion is qualitatively correct and can provide a guide to the influence of factors other than the polarity in determining structures. We have not yet explored the reliability of Eq. (36) for a range of materials.

We may make a similar analysis with respect to metallicity. Note in Eq. (32), for elemental semiconductors, that the promotion energy tended to cancel the energy gain in forming the bond and that at a metallicity of one they exactly canceled; no net energy was gained in promoting the electrons and forming the bonds. Thus we may regard the energy of the covalent structure with $\alpha_m = 1$ as being comparable to that of a metal with the tetrahedral structure. In a metal no promotion occurs and the electrons are broadened into bands with no energy gap. In such a state the ions may be expected to rearrange themselves to minimize their electrostatic energy of interaction; the energy is lower in the close-packed metallic structure than in the zinc-blende or diamond structure. The electrostatic energy per atom in the case of the metal is written[19]

$$E^{es} = -(Z^2 e^2/2r_0)\alpha, \tag{38}$$

where r_0 is the radius of the sphere with volume equal to the atomic volume. This is approximately equal to the energy of an ionic charge in a uniform compensating charge distribution of radius r_0. Thus it contains an estimate of the binding energy of the electrons to the atom and is more appropriately compared at constant volume than at constant d. α takes the value 1.79 for the three common metallic structures and the value 1.67 for the diamond structure.[19] The difference may be written $0.45 Z^2 e^2/\epsilon_0 d$, where this rearrangement energy, as in the polar case, has been reduced by the dielectric constant for the tetravalent structure. d is again the separation in the tetrahedral structure. Thus the energy in the diamond structure minus that in the metallic structure is given by

$$E_{\mathrm{coh}}^{\mathrm{dia}} - E_{\mathrm{coh}}^{\mathrm{met}} = 4V_2(1 - \alpha_m) - 0.45 Z^2 e^2/\epsilon_0 d. \tag{39}$$

We conclude that a metallic structure is favored when

$$\alpha_m > 1 - 0.11 Z^2 e^2/V_2 \epsilon_0. \tag{40}$$

In the elemental semiconductors $Z = 4$ and taking

V_2, d, and ϵ_0 from tin we obtain a critical metallicity of 0.79. This is a reasonable figure, particularly when we note that the metallicity, in contrast to the polarity, is not restricted to the range 0 to 1. We noted in Table I that the metallicity of tin was 0.92 putting it on the metallic side of the critical value.

Note that both in the formulas (37) and (40) one should evaluate both sides of the equation for the material in question in order to see which structure has lower energy. In our model there does not exist a true critical polarity or critical metallicity because other variables have been included. Note in particular the sensitivity of the right-hand side of Eqs. (37) and (40) to the dielectric constant, which varies from 6.7 to 24 from diamond to tin.

The criterion for the formation of a metallic structure can be directly generalized to nonelemental materials simply by using the appropriate electrostatic energy. Of course the degree of reliability of these criteria will only be learned by a rather extensive comparison of a wide variety of materials. Such a study has been undertaken by Ciraci.[17]

VII. COMPARISON WITH OTHER APPROACHES

It is apparent that we have drawn heavily on the work of Pauling[20] who postulated an ionicity scale to classify the properties of partially covalent materials. We have drawn also heavily on the work of Phillips[9] and Van Vechten[10] who redefined and evaluated ionicity on the basis of the dielectric constant. It may be helpful to comment specifically also on some of the differences in these approaches.

The distinction between our model and the work of Pauling is perhaps the sharpest. The conception of ionicity, a number to be associated with each material, and, the finding that a wide range of properties depended principally on that number, provided a great conceptual simplification and a codifying of a wide range of experimental data. It allowed also a prediction of those properties for materials for which they have not been measured, this prediction being ultimately based on the measurements on other materials. For many purposes one need ask no more of a theory. It is however an *interpretive* theory; without looking at experiment we do not know for example if cohesion should scale with ionicity or with the square root of ionicity or in some other way. In contrast, our model is an attempt at a *predictive* theory. Knowing only the definition of the model, given in Sec. I, we may predict the cohesive energy. That prediction does not depend upon the measurement of other cohesive energies, only upon the atomic term values, the dielectric constant, or other properties with no immediate relation to cohesion. Some might regard this as a step backward since the predicted cohesive energy is very inaccurate in comparison to that obtained from the ionicity and an empirical cohesive-energy curve; to others, a predictive theory is the essence of understanding. In addition, it is always possible that a predictive theory will provide a more complete and accurate interpretive theory. Much of the difference is in what we seek to accomplish. The same contrast between the bond-orbital model and the discussions of metalization by Mooser and Pearson[12] reflects the contrast between predictive and interpretive approaches.

There are two features of the Phillips-Van Vechten work on ionicity which we should mention and compare with: First, was the modified choice of the standard for determining ionicity. We have discussed at various stages in this article the selection of standards for the evaluation of the parameters of the bond orbital model. With respect to the choice of covalent energy V_2 and polar energy V_3, we have adopted precisely the standards used by Phillips and Van Vechten to obtain the corresponding parameters in their approach. We are uncertain of the standard which might best be chosen for the metallic energy V_1. For the purpose of this article, we have used the atomic term values, though our preliminary results would suggest that the cohesive energy itself would provide a better choice. Perhaps some other property would do even better; it does not affect the main features nor the importance of the model.

The second aspect of the Phillips–Van Vechten approach, which was based upon pseudopotentials, is a closer identification of the parameters of the model with the fundamental parameters of the electronic structure than that provided by the Pauling theory. However, even in the Phillips-Van Vechten approach the connection with the electronic structure is quite tenuous. It is based upon the Penn formula[16] which relates the dielectric constant to the average band gap on the Jones zone face. However, Heine and Jones[21] pointed out that the band gap is not expected to be related to the even and odd parts of the pseudopotential through Eq. (27) as assumed by Phillips and Van Vechten. On the other hand, the use of the formulas expected on the basis of our knowledge of the electronic structure did not lead to an ionicity which suitably scales the experiments. Thus experiment required the use of Eq. (27) but the clear connection with the electronic structure was lost.

One might ask why the very plausible formulation of the dielectric constant by Penn, combined with our knowledge of electronic structure, failed to produce a suitable scale of ionicity. The answer may be that it *does* when the ionicity and the band gaps are sufficiently small. Then in almost any model the dielectric constant will vary as the square of the asymmetry in the potential (V_3 or C) and, except for a scale factor, all scales are the same. If, however, the band gap and the ionicity become large, it may be necessary to use a model, such as the bond-orbital model, which provides a good description even in the extreme ionic limit; in that limit we expect a full rare-gas configuration on the anion. The Penn model does not do that. Thus it may have been necessary to use a formula such as Eq. (27), which we have seen provides an ionicity very nearly linear in α_p^2 over the range of interest.

Another difficulty in the pseudopotential-based model, which arises from the absence of a clear relation with electronic structure, is that we cannot calculate properties directly in terms of the ionicity parameter. Thus it becomes difficult to use it as a predictive theory.

A very important feature of the bond-orbital model is the use of two parameters to characterize a material. We could of course use as many parameters as we wish to distinguish materials; it is a tradeoff between simplicity and accuracy. However, the two parameters, polarity and metallicity, which are basically the same two characteristics used by Mooser and Pearson,[12] provide the criteria for choosing among the three natural classes of bonding: covalent, ionic, and metallic. They also seem, as we have found in our discussion here, to describe the two major trends which are apparent in the properties of partially covalent materials.

VIII. EXTENSIONS OF THE METHOD

Starting with the bond-orbital model, as described here, there are four natural directions to go: The first is in the application of the model to the complete range of tetrahedrally bonded materials. In doing this we would hope to learn the best criteria to the use in the selection of the parameters, particularly the V_1^a and the V_1^c. In addition, we should learn the extent of the reliability of the method for the particular properties we have discussed.

A second activity would be the application to systems other than tetrahedral solids; in a number of cases the extension is most natural. In the trigonally bonded graphite, for example, sp^2 hybrids may be constructed directly and are known to provide a meaningful description of the σ bands. The definition of V_1 and V_2 is immediate as well as a choice of V_3 for a partially polar counterpart. The π states are quite separate. Though they do not fit in the same category, in the spirit of the bond-orbital method we would characterize them by the smallest number of parameters possible, presumably the position of the band in comparison to the σ bands, and a single overlap integral. Similarly, the extension to transition metal compounds, in which hybrids are constructed with d states, as well as s-p states, is quite natural. It does not appear at this stage fruitful to carry over this tight-binding approach to the simple metals. When a system has formed the metallic structure covalency, in the sense we have used it in this paper, becomes a small correction. The system is in essence a free-electron gas, and corrections should be made on that description, presumably using pseudopotentials. Similarly, in an ionic structure it appears appropriate to use the fully ionized state as the starting description.

A third extension of the system is the study of properties other than those considered here. One class of properties which may be considered are those which involve the deviation of the system from tetrahedral arrangement; the elastic shear constants are such a property. It is not clear that these can be meaningfully treated without the introduction of an additional parameter. Certainly an understanding of the equilibrium spacing will require terms in the energy which were not included in the model described in Sec. I. The properties for which the extension seems the least appropriate, are those which involve the conduction bands, such as transport properties in n-type semiconductors.

A fourth activity in relation to this model might be the refinement of the model. This could be done by the introduction of additional parameters, though we indicated in Sec. VII we feel that in some sense the number introduced here is optimum. Another refinement could be the addition of corrections to the model in a perturbative scheme. The traditional method for doing this is based upon the configuration interaction in which excited configurations are added to the starting ground state. Such an approach seems quite inappropriate in the context of the bond-orbital model, which does not provide a meaningful description of those excited configurations. A much more natural refinement of the bond-orbital model is provided by the orbital correction method.[3] In this method starting orbitals are defined, and the difference between the true eigenstate and the starting states is called the orbital correction. The energy is computed systematically in an expansion in that correction. It is frequently useful, though not necessary, to expand the orbital correction in a complete set, such as plane waves or plane waves orthogonalized to the starting state. Thus the method does not require any detailed knowledge of the excited states, it requires only a reasonable description of the ground state. An extremely important feature of the method is that it is possible to calculate the energy to second order in the orbital correction without ever performing the diagonalization which specifies the particular linear combination of orbitals which makes up the true eigenstate. It was the corresponding feature of the bond-orbital method which enabled us to obtain the total energy and the charge distributions without ever diagonalizing with respect to the matrix elements V_1; that is, without ever performing a band calculation. In the bond-orbital model this feature arose from the unitarity of the transformation. In the orbital correction method the transformation is not necessarily unitary since the starting orbitals may not be orthogonal. (In particular if the bond orientations are not exactly tetrahedral, the bond orbitals will not be orthogonal.) In addition, there is an energy dependence which spoils this feature even if the orbitals are orthogonal. However, we succeeded in overcoming that problem formally. This leads to extra terms in the result [Eq. (33) of Ref. 3] but ones which can be evaluated without the diagonalization.

Our experience with the orbital correction method, and related methods, would suggest that the rewards are not so great in seeking small corrections where the zero-order theory is meaningful but that the orbital correction method is an appropriate vehicle when the essential features are not contained in the zero-order theory. It appears at present that the elastic shear constants may be such a case.

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