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The electronic properties of tetrahedral intermetallic compounds

I. Charge distribution

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A discussion is commenced in which the electronic properties of tetrahedral intermetallic compounds are described in terms of localized molecular-orbital bonds. The correct definitions of covalency and polarity of these bonds are linked with the net ionicity of the atoms of the crystal. Detailed non-empirical calculations of boron nitride provide a description of the bonds, and associated formal charges. An alternative simple but partially self-consistent analysis is presented whereby the coefficients in the simple molecular-orbital description may be found semi-empirically. The charges thus predicted agree well with those calculated by the earlier non-empirical method, and also with such experimental values as are available.

1. INTRODUCTION

This is the first of a series of papers concerned with the electronic structure of a large class of solids in which each atom is surrounded by four neighbours, in tetrahedral co-ordination. This class varies from insulators such as diamond to the important group of compound semi-conductors such as InSb or GaAs. The pure monatomic substances are all from group IV of the periodic table (e.g. C, Si, Ge, ...) but the diatomic compounds may be described as IV-IV (e.g. SiC), III-V (e.g. AlP) or II-VI (e.g. ZnS). A limited number of I-VII solids (e.g. CuCl) have this same tetrahedral structure, and it is possible that some of our analysis will apply to them. But in view of the strong ionic character to be expected when the electro-negativity difference is great, less confidence attaches to the application of our methods to the II-VI and I-VII systems.

Previous discussion of these compounds has almost always been in terms of essentially physical concepts, such as that of free electrons, the Fermi surface or the Brillouin zone, but our concern will be to show that in addition to these more physical considerations, further important insight may be obtained by the use of chemical concepts. We do not wish by this to infer that the physical concepts give erroneous results and should be abandoned. We do mean, however, that just as in the field of aromatic chemistry we have profited very greatly from a comparison of results obtained by the 'physicist's' approach (molecular-orbital method) and by the 'chemist's' approach (resonance among covalent and ionic structures), so we may hope to obtain further insight into the properties of this class of intermetallic compounds by approaching them both from the direction of chemistry and of physics. A related situation has already been met in the theory of metals, where Pauling's chemical theory of resonating bond structures provides insight into such

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matters as the interatomic distance in a metal or alloy, which it would be almost impossible to obtain by more conventional physical theories.

This insight has been obtained by methods of quantum chemistry which are usually less precise than those of quantum physics. We must therefore be prepared to find a similar situation in the tetrahedral compounds with which this series of papers is concerned. It is, of course, well known that the concepts with which the chemist works—an electron-pair bond, ionic character, hybridization—are not susceptible of exact definition. But this has not prevented them from giving us an excellent understanding of the polarity and the stereochemistry of a polyatomic molecule. There is, indeed, a very good reason for attempting to bring chemical-bond concepts into a discussion of these present compounds, for the tetrahedral structure is a very open one, and one that would not be expected to be stable unless there were strong directional forces around each of the atoms. Such forces are familiar within the field of chemistry; they are the usual valence forces. We are acquainted with the operation of these forces in the tetrahedral character of the bonding around a saturated neutral carbon atom, or a positively charged nitrogen atom (e.g. NH_4^+). It is a natural step, therefore, to think of diamond as one large saturated molecule, in which the atoms are held together by normal localized chemical bonds. If this can be done, with reasonable success in estimating the bond energy, it is a further natural step to think of a III-V compound, such as BN or AlP as if, again, we were dealing with a large molecule, but in which the bonds were no longer purely covalent but were partly ionic. It has been objected (Cochran 1961) that since at present it is almost impossible to define this polar character in terms of effective ionic charges in such a way that all known properties could be interpreted by their means with one single set of charges, such discussions should therefore be discouraged as being liable to mislead. To maintain this view consistently, however, it would be necessary to show that Pauling's theory of covalent-ionic resonance failed to give us insight into the differences between HF, HCl, HBr and HI. For it is certainly true that no single set of effective charges can be written down which will completely describe these molecules; and it is also true that no such set of formal charges can be measured by any direct experiment. Yet very few chemists would wish to exclude the discussion of this kind of resonance. In so far as our tetrahedral compounds are concerned, the situation would appear to be more satisfactory than for the pure-ionic solids such as NaCl, where the directional effects of the interaction between Na^+ and Cl^- are not associated with bonds, and where the main forces are Coulombic and therefore long-range. In our case the main forces are short-range and of valence character.

The present paper is intended to provide the background for the later papers, by establishing the nature of the bonding in these compounds. We shall show that, provided a suitable definition of ionic character is used, reasonable estimates can be obtained for the ionic character of the bonds in these systems. We also show that, for simple atomic combinations, such as diamond or BN, reasonable calculations of bond energy are not too difficult to make. Our second paper shows, for the particular case of diamond, that a simple and apparently satisfactory account can be given of the conduction band in diamond if an extension of the method of orthogonalized plane waves is made, whereby the conduction orbitals are made orthogonal not only

to the inner-shell electrons but to the valence-band orbitals as calculated in the first paper. This second paper, therefore, depends upon the first, and provides a partial validation for its model. One of the results which we show is that although the top of the valence band lies at wave vector $\mathbf{k} = 0$, the lowest level of the conduction band is not at this value of \mathbf{k} , nor at the edge of the Brillouin zone, but about half-way along the (1, 0, 0) direction. This is in agreement with the forbidden character of the lowest energy transition. It is unlikely that such a situation would be significantly affected by spin-orbit coupling, here neglected. Herman (1955) has shown this to be significant with heavier atoms, but we do not believe it to be important with light ones. In the third paper we consider excitons in diamond (though the method can be extended to other systems) and provide estimates of the structure of the band of exciton levels. The method is essentially 'chemical', since we use not merely the bonding orbitals which dominate the valence band, but also the anti-bonding orbitals, which correspond to a local excitation. In systems such as diamond, where the forbidden energy gap between valence and conduction bands is large, so that the effective dielectric constant is not so high as in germanium, it seems probable that the radius of an exciton orbit is relatively small. Our analysis supposes that it does not exceed two bond lengths. It would, however, be possible to allow a larger orbit by including additional structures, if this seemed to be desirable. There is no reason why the methods of these last two papers should not be applied to other systems of tetrahedral character: some of them are indeed at present being studied in this way. The fourth—and final—paper deals with the width of the valence bands in a very general way. It shows that, provided certain assumptions are acceptable, the methods of molecular structure may be used to estimate these widths. It is probable here that any one individual calculated width may be in error by several electron volts. But this is as good as most previous estimates, and our formulation enables us to see what factors are most important in determining this width. It is a pity that the experimental results with which to compare the theory are so meagre.

It will be seen from this brief summary that all four papers have a close relationship to, and mutual dependence on, each other. Our calculations move on two distinct levels, corresponding to the similar situation that obtains in molecular structure work. Thus, for light atoms we may reasonably hope to make fairly good calculations without recourse to the estimation of parameters by appeal to experiment. This may be called the non-empirical, or *ab initio*, type of calculation; but for heavier atoms, where such computations would be prohibitively complex, we adopt the semi-empirical approach, and are prepared to introduce and use unknown parameters whose numerical values must later be found by appeal to some experimental measurement. It is in these latter calculations that previous experience of molecular approximations is most important.

2. TETRAHEDRAL BONDING

We must now describe the essential points of the model that we are using. This is conveniently done by reference to two relatively simple examples—diamond and boron nitride. Both of these exist as tetrahedrally co-ordinated solids (for BN see

Wentorf 1957), in which each atom lies at the centre of a regular tetrahedron formed by its four neighbours. Diamond is homopolar, but BN is heteropolar, and the B and N atoms alternate, so that each B atom is surrounded by four N atoms, and vice versa. In the case of diamond we are accustomed chemically (see, for example, Coulson 1961) to treat the crystal in its ground state as if it were a huge molecule, where each bond is effectively localized. The wave function for one such bond is approximately to be built out of tetrahedral sp^3 hybrid orbitals, oriented around each atom in such a way that the orbitals which are paired together point directly towards each other. This greatly increases their mutual overlapping, and simultaneously greatly reduces the undesirable overlapping between orbitals on different atoms which are not paired together.

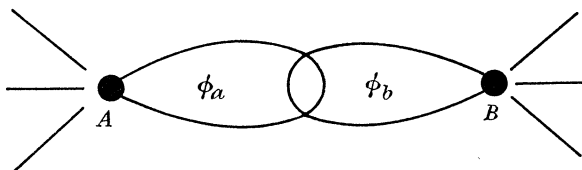


FIGURE 1

To discuss the way in which this pairing takes place, first let us consider the homopolar bond in diamond. Then, if ϕ_a and ϕ_b (figure 1) are the two orbitals to be paired together in this way, we form molecular orbitals ψ and χ , defined by

$$\psi = \phi_a + \phi_b, \quad \chi = \phi_a - \phi_b. \quad (1)$$

The first of these is a bonding orbital, the second anti-bonding. In the simplest form of molecular-orbital (m.o.) treatment we regard the bond $A-B$ as represented by two electrons, with opposed spins, in the orbit ψ . The result is

$$\psi(1)\psi(2)\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}/\sqrt{2}. \quad (2)$$

In a more elaborate calculation we should allow for configuration interaction by writing

$$\{\psi(1)\psi(2) + k\chi(1)\chi(2)\}\{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}/\sqrt{2}. \quad (3)$$

Such a bond, whether described as in (2) or (3), may be called covalent, on account of the symmetry of the m.o.'s in (1).

In the heteropolar case, such as BN, the choice of atomic orbitals is precisely as before. But instead of (1), we write

$$\psi = \phi_a + \lambda\phi_b, \quad \chi = \lambda\phi_a - \phi_b, \quad (4)$$

where λ is a parameter whose value must be obtained variationally, or by some other means. The descriptions (2) and (3) still apply. But this is no longer a pure covalent bond, and its polarity is indicated by the ratio $1:\lambda^2$. A rough description of the bonding orbital ψ is that it corresponds to fractions $1/(1+\lambda^2)$ and $\lambda^2/(1+\lambda^2)$ of an electron on the two atoms A and B , respectively. If there are two electrons in the

orbital ψ , then the charges on A and B associated with this one bond are $2/(1+\lambda^2)$ and $2\lambda^2/(1+\lambda^2)$. Since four bonds end on each atom this implies that the total numbers of valence electrons associated with the atoms are $8/(1+\lambda^2)$ and $8\lambda^2/(1+\lambda^2)$. Now if atom A is the group V atom, it will be more electro-negative than atom B , the group III atom. Electrical neutrality of A would be achieved if it carried 5 valence electrons. Thus the net charge associated with A , measured in electrons, is

$$Q_A = 5 - 8/(1+\lambda^2) = (5\lambda^2 - 3)/(1+\lambda^2). \quad (5)$$

If $Q_A > 0$, the atoms of type A carry a net positive charge; if $Q_A < 0$ it is negative. Similarly

$$Q_B = 3 - 8\lambda^2/(1+\lambda^2) = -Q_A. \quad (6)$$

It is not difficult to generalize (5) and (6) so that they apply to systems of type $A^N B^{8-N}$. This means that for IV-IV compounds $N = 4$, for III-V compounds $N = 5$, and for II-VI compounds $N = 6$. It is readily shown that

$$Q_A = \frac{N\lambda^2 - (8-N)}{1+\lambda^2} = -Q_B. \quad (7)$$

The simple formulae (5) and (7) help us to elucidate a matter where there appears to be some confusion (Goodman 1960, 1961; Mooser & Pearson 1961 *a, b*). It is usual, chemically, to define a covalent bond by the condition $\lambda = 1$ in (4), but this implies, from (5) and (7), that the atoms as a whole are not neutral. We could therefore say that the crystal was partly ionic. Neutral atoms would require that $\lambda^2 = (8-N)/N$, and only in the case of $N = 4$ does this satisfy the condition for covalence. This means that if we wish to maintain the older usage for covalence and ionicity, we must distinguish between the descriptions that we use for the atom and the bond. Covalence of a bond does not normally imply neutrality of the atoms, and the ionic character of a bond is not to be identified with the ionicity of the atoms. All this is largely a question of semantics, but failure to recognize it has led to confusion. An example will show how it applies. If zinc sulphide is written in the form $Zn^{-2} S^{+2}$ the bonds are purely covalent, although the atoms are far from neutral. If it is written $Zn^{+2} S^{-2}$, the bonds are purely ionic: but if it is written $Zn^0 S^0$, with neutral atoms, the value of λ is $\sqrt{\frac{1}{3}}$ so that the bonding m.o. is $\psi = \phi_S + \sqrt{\frac{1}{3}}\phi_{Zn}$. Such a bond is partly covalent, partly ionic.

The description in (4) is not new. Thus Mooser & Pearson (1960) have referred to it in an attempt to describe the semi-conducting properties of many of these compounds; Gatos & Levine (1960) and Gatos (1961) have used it to discuss the nature of the surface of these crystals, where certain of the bonding tetrahedral hybrids may behave as 'dangling bonds'; Gubanov & Pushkarev (1960) have used a similar idea to discuss the valence bands of diamond and germanium in a tight-binding approximation; and Pauling (1960) has shown that the interatomic distance in AlP is such as corresponds to a covalent bond order of 0.86, and an ionic character just about sufficient to lead to electrical neutrality of the atoms. Similarly, O-hata (1960) has used a Heitler-London function for diamond obtained by putting $k = -1$ in (3) and leading to a bond description $\phi_A(1)\phi_B(2) + \phi_B(1)\phi_A(2)$ to calculate

the bond energy; Schmid (1953) has used (3) itself for the case of diamond;† Kleinman & Phillips (1962) have shown that the assumption of localized chemical bonds leads to a charge distribution in diamond differing slightly from that obtained from purely spherical atoms, and in fair agreement with certain observed X-ray scattering factors. Finally, Morita (1958) has made a similar calculation to Schmid's for InSb and Asano & Tomishima (1956) have considered ZnS. One or two other applications are referred to elsewhere in this series.

3. FULL CALCULATION FOR BORON NITRIDE

We are now in a position to describe some of our new calculations. First, we report a full calculation of the charge distribution in tetrahedral BN. In view of the success with which we had reproduced Schmid's work for diamond by omitting specific reference to the $1s$ electrons (see footnote), we left them out of consideration. For the i th bond we write a localized wave function representing covalent-ionic resonance within the bond

$$\psi_i(2i-1, 2i) \{\alpha\beta - \beta\alpha\} / 2^{\frac{1}{2}}, \quad (8)$$

where the second factor is the spin term, and the first factor is

$$\psi(1, 2) = a\phi_N(1)\phi_N(2) + b\{\phi_N(1)\phi_B(2) + \phi_B(1)\phi_N(2)\}. \quad (9)$$

In (9) a and b are two parameters to be found from the normalization condition, and from the variational principle for the total energy.

It may be objected that (9) does not adequately allow for the presence of both electrons around the boron nucleus. This would need a further term $c_3\phi_B(1)\phi_B(2)$. However, on account of the greater electro-negativity of N as compared with B, we should not expect this term to be important. Also, in view of the inevitable number of approximations in all work of this kind, it seems doubtful whether there would be much validity in the value of a second variational parameter and the calculations would become considerably more complex. We therefore compromised by also using the pure m.o. wave function

$$\psi(1, 2) = \{\lambda_1\phi_N(1) + \lambda_2\phi_B(1)\} \{\lambda_1\phi_N(2) + \lambda_2\phi_B(2)\}, \quad (10)$$

where λ_1 and λ_2 must be found from the normalization and variational conditions.

In terms of the bond function (8) the wave function for the complete crystal may be written

$$\Psi = \mathcal{N} \sum_P (-1)^P P \prod_{i=1}^N \psi_i(2i-1, 2i) \{\alpha\beta - \beta\alpha\} / \sqrt{2}, \quad (11)$$

where N is the number of bonds in the crystal, P represents any of the permutations of the electron co-ordinates (including spin), and \mathcal{N} is a normalizing factor given by

$$\mathcal{N}^{-2} = (2N)! 2^N. \quad (12)$$

† Since these calculations are quite elaborate, we should like to put on record that we have made an independent calculation for diamond, simplifying Schmid's analysis slightly by compressing the $1s$ electrons into the carbon cores, and were able essentially to reproduce his results. Thus, writing the space part of (3) as

$$c_1\{\phi_A(1)\phi_B(2) + \phi_B(1)\phi_A(2)\} + c_2\{\phi_A(1)\phi_A(2) + \phi_B(1)\phi_B(2)\}$$

we found that $c_2/c_1 = 0.78$, to be compared with Schmid's value $c_2/c_1 = 0.82 \pm 0.08$.

It is fairly clear that the energy associated with Ψ can be divided up into the following four parts:

energy per bond = energy within one bond + Coulomb repulsions and exchanges between adjacent bonds + Madelung energy + some correction terms to avoid counting certain Coulomb interactions twice.

To proceed further we need the full Hamiltonian. We write this (with absorption of the 1s electrons into the nuclei) in atomic units

$$H = \sum_{\alpha < \beta} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} - \frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i,\alpha} \frac{Z_\alpha}{r_{\alpha i}} + \sum_{i < j} \frac{1}{r_{ij}}, \quad (13)$$

where Z_α, Z_β are the effective atomic numbers (here 5 and 3 for N and B atoms respectively), $R_{\alpha\beta}$ is the distance between nuclei α and β , $r_{\alpha i}$ is the distance of electron i from nucleus α , and r_{ij} is the interelectronic separation of i and j . We now adopt the separability condition (Löwdin 1961) in the form†

$$\int \psi_i(1, 2) \psi_j(1, 3) d\tau_1 = 0 \quad \text{for } i \neq j, \quad (14)$$

and define the bond density matrix

$$\gamma_i(1, 1') = 2 \int \psi_i(1, 2) \psi_i(1', 2) d\tau_2. \quad (15)$$

The diagonal element of this matrix is just the bond density

$$\gamma_i(1) = \gamma_i(1, 1).$$

Combining (11), (13), (14) and (15) we can evaluate the energy from the usual relation

$$E = \int \Psi^* H \Psi d\tau.$$

After some considerable, but straightforward, algebra this can be expressed in the following manner

$$E = \sum_{\alpha < \beta} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} - \frac{1}{2} \sum_i \int [\nabla^2 \gamma_i(1, 1')]_{1=1'} d\tau_1 + \sum_i \int \frac{\psi_i^2(1, 2)}{r_{12}} d\tau_1 d\tau_2 - \sum_i \sum_\alpha \int \frac{Z_\alpha}{r_{\alpha i}} \gamma_i(1) d\tau_1 + \sum_{i < j} \int \frac{\gamma_i(1) \gamma_j(2) - \frac{1}{2} \gamma_i(1, 2) \gamma_j(1, 2)}{r_{12}} d\tau_1 d\tau_2, \quad (16)$$

This may be simplified by writing

b.e. = intrinsic bond energy

$$= \int \left\{ \left[-\frac{1}{2} \nabla^2 \gamma(1, 1') \right]_{1=1'} + \left[\frac{Z_\alpha}{r_{\alpha 1}} + \frac{Z_\beta}{r_{\beta 1}} \right] \gamma(1) \right\} d\tau_1 + \int \frac{\psi_1^2(1, 2)}{r_{12}} d\tau_1 d\tau_2. \quad (17)$$

Let us number the atoms and bonds as in figure 2.

† This condition is implied in the normalization relation (12). It can be seen to be plausible from the fact that unless ψ_i and ψ_j have one atom in common, the product $\psi_i \psi_j$ will be very small everywhere; and if they do have an atom in common, the two sp^3 hybrids involved around this atom are themselves mutually orthogonal.

Then after combination of (16) and (17) we can write down the energy per bond. It is convenient here to introduce the point-charge approximation for second and higher neighbour Coulomb interactions, and to neglect distant exchange effects. The final result† is that the

$$\begin{aligned} & \text{total energy per bond} = \text{b.e.} \\ & + \frac{3}{2} \left[\int \frac{\gamma_1(1)\gamma_2(2) - \frac{1}{2}\gamma_1(1,2)\gamma_2(1,2)}{r_{12}} d\tau_1 d\tau_2 + \int \frac{\gamma_1(1)\gamma_3(2) - \frac{1}{2}\gamma_1(1,2)\gamma_3(1,2)}{r_{12}} d\tau_1 d\tau_2 \right] \\ & - \frac{\alpha Q^2}{4R} + \left[\frac{Q^2}{R} + \frac{(Z_N - 3q_N)(Z_B - 3q_B)}{R} - \frac{3q_N^2}{2R'} - \frac{3q_B^2}{2R'} \right]. \end{aligned} \quad (18)$$

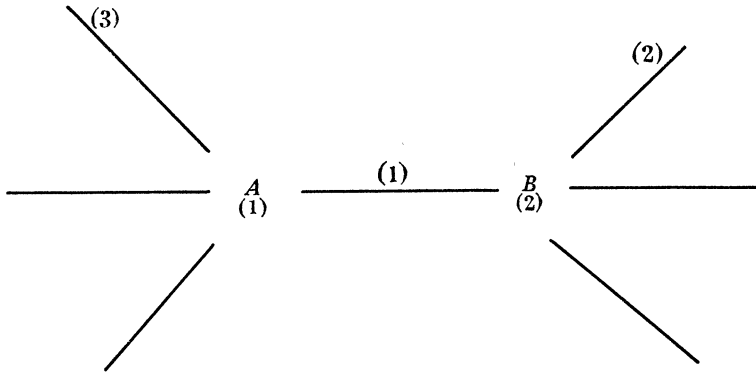


FIGURE 2

In this expression the undefined quantities are

- Z_N, Z_B effective nuclear charges (5, 3) of N and B,
- α Madelung constant,
- Q net charge on atoms of N and B, as in (5) and (6),
- q_N, q_B effective charges *per bond* to yield same bond dipole moment as $\psi(1, 2)$,
- R bond length for first neighbours,
- R' distance between second neighbours $\{R' = (2/\sqrt{3})R\}$.

From the definitions of q_N and q_B it follows that

$$\left. \begin{aligned} Q_N &= 5 - 4q_N, \\ Q_B &= 3 - 4q_B, \\ q_N + q_B &= 2, \\ Rq_B &= \int \gamma(1) x_N(1) d\tau_1, \end{aligned} \right\} \quad (19)$$

where x_N is distance measured from N in the direction of B. A word needs to be said about the introduction of q_N, q_B and the calculation of the Madelung energy in (18). One policy would be to use the charges as defined by (5) and (6), where λ was obtained from the polarity of the wave function $\psi(1, 2)$. But since our wave function (9) is not

† The argument is given in full in L. Rèdei, D.Phil. Thesis, Oxford 1961.

quite of pure m.o. form, we decided instead to choose effective charges q_N, q_B per bond such that these charges reproduced the same dipole moment as the bond charge $\gamma(1)$. Fortunately the Madelung energy is not of major importance in these systems, and so the precise mode of its calculation does not greatly matter.

For the numerical calculations we constructed ϕ_N and ϕ_B as tetrahedral hybrids of Slater atomic orbitals. The orbital exponents adopted were

$$\eta_N = 2.125, \quad \eta_B = 1.125. \quad (20)$$

These would correspond to tetrahedral atoms N^+ and B^- . It was realized too late that since, as the calculations show, the net charge on the atoms is small, it might have been better to decrease η_N and increase η_B slightly. But for the purposes of our charge distribution this would not be expected to change our results very seriously.

The total energy per bond (18) is now minimized with respect to the parameters a and b (see equation (9)). As these are lengthy calculations we made no attempt to vary the internuclear distance, and used the observed value $R = 2.958a_0$. There are many types of integral to evaluate. The one-centre integrals and the one- and two-centre one-electron integrals presented no serious difficulty (Preuss 1957). Root-haan's tables (1955) of two-centre Coulomb integrals provided many of the values of this particular class of integral. The three- and four-centre integrals were estimated by point-charge approximations in all this work on BN. The two-centre penetration integrals were evaluated by the zeta-function method of Barnett & Coulson (1951).

The result of the minimization was that

$$a = 0.300, \quad b = 0.428. \quad (21)$$

These led to

$$Q_N = -0.38, \quad Q_B = 0.38, \quad (22)$$

where the signs imply that the nitrogen atom is slightly negative. Thus we concluded from these calculations that in BN the atoms are not far from neutral, and the more electro-negative atom carries a small negative charge of the order of 0.4 electron.

As a further check on this value we next repeated the calculations, using wave function (10) instead of (9). The minimum value of the energy was associated with

$$\lambda_1 = 0.709, \quad \lambda_2 = 0.420, \quad (23)$$

which lead to net atomic charges

$$Q_N = -0.26, \quad Q_B = 0.26. \quad (24)$$

These charges are very similar to those in (22).

From a comparison of (9), (10), (21) and (23) we see that $\lambda_1 \lambda_2 < b$, $\lambda_1^2 > a$ and so in the m.o. bond function the weight of the covalent part is diminished, whereas the coefficients of both ionic terms $\phi_N(1)\phi_N(2)$ and $\phi_B(1)\phi_B(2)$ have been increased, leaving the net charge on the nitrogen atom approximately unchanged.

In view of the difficulty of interpreting our wave function in terms of Q_N and Q_B , we have made a few additional calculations with the wave function (9). For example, we superposed the charge densities of all four bonds around a nitrogen and a boron atom, and then made suitable volume integrations to enable us to assign formal charges to these nuclei. We are aware of the difficulties here stressed by Cochran

(1961), but believe that even if no completely satisfying definitions of Q_N and Q_B can be given, there is significance in comparing different measures of these quantities. We shall find that no less than four such measures (two of which have already been given) agree surprisingly well.

Our integrations are achieved by drawing two spheres of radii r_N and r_B around the nuclei, where $r_N + r_B = R$ and r_N/r_B is equal to the ratio of the two covalent radii of these atoms. We then compute the total charge lying inside each such sphere. Some charge (approximately 25%) lies outside these spheres. We therefore scale our integrals to make the total charge correct. This gives

$$Q_N = -0.50, \quad Q_B = 0.50. \quad (25)$$

A final measure of charge follows the proposals made by Mulliken (1949*b*). If we consider a normalized m.o. wave function

$$\lambda_1 \phi_N + \lambda_2 \phi_B,$$

we assign a charge $\lambda_1^2 + \lambda_1 \lambda_2 S$ to the N atom, and $\lambda_2^2 + \lambda_1 \lambda_2 S$ to the B atom, where S is the overlap integral $\int \phi_N(1) \phi_B(1) d\tau_1$. This leads to a final value

$$Q_N = -0.31, \quad Q_B = 0.31. \quad (26)$$

In table I we list the values given in (22) to (26).

TABLE I. NET ATOMIC CHARGES IN BORON NITRIDE

	Q_N	Q_B
valence-bond method (22)	-0.38	0.38
molecular-orbital method (24)	-0.26	0.26
formal charges (26)	-0.31	0.31
integration over spheres (25)	-0.50	0.50

The set of values for Q_N recorded in this table all agree as to order of magnitude. All suggest that the nitrogen atom is negative and the boron atom positive. If we discount the last entry (which is less satisfactory than the others) it would seem that the ionicity of the crystal is that due to a charge transfer of approximately 0.3 electron.

After this work was completed Kleinman & Phillips (1960) published the results of an elaborate partially self-consistent potential for BN. They concluded that the charge-cloud may be regarded as responsible for a 'valence screening charge' of about 0.3 e. This would imply that the net charges on the atoms are approximately ± 0.3 e, in excellent agreement with table I.

In view of the approximations made in estimating the various integrals occurring in this calculation for BN it is not reasonable to expect perfect agreement with experiment for the cohesive energy. Our calculations give for the energy of the valence electrons the values -3.721 a.u. per bond with the m.o. wave function (10), and -3.730 a.u. per bond with the valence-bond function (9). If we now subtract the appropriate share of the valence-shell energies in isolated N(4S) and B(2P) states, the cohesive energy per bond turns out to be about 125 kcal/mole. This is about twice the latest recorded value (60 to 62 kcal/mole due to Galchenko *et al.*, reported

by Berl & Wilson 1961). To improve significantly on this value would require a complete evaluation of all the many-centre integrals, and a better allowance for exchange and other correlation effects. Errors of the order of 60 kcal/mole are not at all unusual in calculations of molecular energies with approximate wave functions of this general kind.

4. APPROXIMATE L.C.A.O. CALCULATIONS

Our previous section dealt very carefully with one particular system, and in it we tried to avoid any unnecessary approximations. Such calculations are very heavy, and quite unsuited to a general survey of these solids, or to heavy atoms. In this section therefore we discuss a much simpler and more naïve method, which is sufficiently simple to be used very widely. This is the simple m.o. method of linear combinations of atomic orbitals (l.c.a.o.), in which we consider that the two electrons in any given bond are defined by an effective one-electron Hamiltonian H , and are represented by a wave function ψ of type (4). Let us choose the example of BN (figure 3) to illustrate the method.

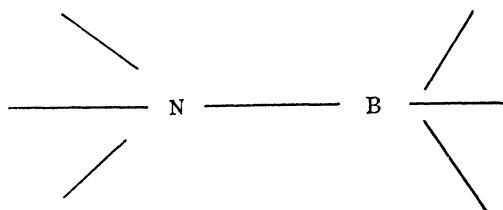


FIGURE 3

If, as before, ϕ_N and ϕ_B denote the atomic orbitals (figure 1) to be used in constructing the bond N—B, and if we put

$$\psi = \mathcal{N}^{-\frac{1}{2}}(\phi_N + \lambda\phi_B), \quad (27)$$

then with neglect of overlap integrals, normalization requires that

$$\mathcal{N} = 1 + \lambda^2. \quad (28)$$

The value of λ , and the energy ϵ of the orbital, are given (see e.g. Coulson 1961, p. 75) by the secular equations

$$\left. \begin{aligned} \alpha_N - \epsilon + \lambda\beta &= 0, \\ \beta + \lambda(\alpha_B - \epsilon) &= 0. \end{aligned} \right\} \quad (29)$$

In these equations β is the resonance integral, defined by

$$\beta = \int \phi_B^* H \phi_N d\tau, \quad (30)$$

and α_N , α_B are the Coulomb terms defined by

$$\alpha_N = \int \phi_N^* H \phi_N d\tau, \quad \text{etc.} \quad (31)$$

At this stage it is necessary to show how α_N and α_B depend upon the net charges Q_N and Q_B . We follow Mulliken (1949*a*) in noting that since α_N measures the energy

needed to remove the electron from the N atom, it will have a larger numerical value if N is positively charged than if it is neutral or negatively charged. We shall therefore adopt the expansion originally used in somewhat similar connexions by Moffitt (1949), and express the dependence of α on Q by writing

$$\left. \begin{aligned} \alpha_{Q,N} &= \alpha_0^N + Q_N(\alpha_0^N + E^N), \\ \alpha_{Q,B} &= \alpha_0^B + Q_B(\alpha_1^B - \alpha_0^B). \end{aligned} \right\} \quad (32)$$

Here α_0 and α_1 represent the ionization potentials of neutral and positively charged atoms, and E is the electron affinity. We use the different expressions (32) for N and B because it will appear (as in § 3) that N carries a net negative charge so that α_0 and E are the significant experimental values between which we are interpolating. But B carries a net positive charge, and so α_1 and α_0 are now the significant magnitudes. Ionization potentials are given by Moore (1949, 1952), and electron affinities by Pritchard & Skinner (1955). In the case of BN the values are

$$\begin{aligned} \alpha_{Q,N} &= \alpha_0^N + Q_N \alpha'_N, \\ \alpha_{Q,B} &= \alpha_0^B + Q_B \alpha'_B, \end{aligned}$$

where

$$\alpha_0^N = -24.99, \quad \alpha'_N = -24.12, \quad \alpha_0^B = -8.53, \quad \alpha'_B = -10.87, \quad \text{all in eV.} \quad (33)$$

The resonance integral β_{NB} was assumed to have the same value as in diamond (β_{CC}). The bond energy 85.6 kcal/mole leads to a value $\beta = -42.8$ kcal/mole = -1.86 eV, when overlap integrals are neglected. Fortunately we found that our final results are very insensitive to the value of β , and concluded that it was not necessary to consider any variation of β with Q_N, Q_B .

The assumptions above allow us to set up an equation for the polarity coefficient λ of (27). For this parameter determines Q_N and Q_B ; these determine $\alpha_{Q,N}$ and $\alpha_{Q,B}$; these from (29) determine ϵ and λ . If we equate the final λ to the original one, we obtain what may be called a self-consistent value of λ . It satisfies the quartic equation

$$\lambda^4 + \lambda^3 \left[\frac{\alpha_0 + 5\alpha'}{\beta} \right] - \lambda \left[\frac{3\alpha' - \alpha_0}{\beta} \right] - 1 = 0, \quad (34)$$

where

$$\alpha_0 = \alpha_0^N - \alpha_0^B, \quad \alpha' = \alpha'_N + \alpha'_B. \quad (35)$$

There is only one real positive root of this equation. It gives

$$\lambda = 0.69, \quad Q_N = -0.43, \quad Q_B = 0.43. \quad (36)$$

It is very interesting that this value for BN fits so well with the more elaborate values in table 1. Indeed, this agreement encourages us to make the analysis more general.

If, as in (7) we consider a tetrahedral compound $A^N B^{8-N}$, where A is the electro-negative atom, and $N = 4, 5, 6$ or 7 , then the equation which generalizes (34) is

$$\lambda^4 + \lambda^3 \left[\frac{\alpha_0 + N\alpha'}{\beta} \right] - \lambda \left[\frac{(8-N)\alpha' - \alpha_0}{\beta} \right] - 1 = 0 \quad (37)$$

with

$$\alpha_0 = \alpha_0^A - \alpha_0^B, \quad \alpha' = \alpha'_A + \alpha'_B.$$

When $N = 5$, as in V-III compounds, (37) reduces to (34). In all cases that we studied, this equation only had one real positive root. This is the final self-consistent value of λ .

The values of α_Q for the atoms which we have considered are shown in table 2.

TABLE 2. VARIATION OF COULOMB TERMS α WITH EFFECTIVE CHARGE Q

$\alpha_Q^{\text{Cu}} = -7.72 - 12.57Q$	$\alpha_Q^{\text{Cl}} = -25.26 - 21.44Q$
$\alpha_Q^{\text{Ag}} = -7.57 - 13.91Q$	$\alpha_Q^{\text{Br}} = -24.09 - 21.40Q$
—	$\alpha_Q^{\text{I}} = -20.34 - 16.79Q$
$\alpha_Q^{\text{Be}} = -5.96 - 12.25Q$	$\alpha_Q^{\text{O}} = -32.28 - 29.58Q$
$\alpha_Q^{\text{Zn}} = -4.90 - 13.06Q$	$\alpha_Q^{\text{S}} = -21.06 - 18.36Q$
$\alpha_Q^{\text{Cd}} = -4.73 - 12.17Q$	$\alpha_Q^{\text{Se}} = -20.87 - 18.59Q$
$\alpha_Q^{\text{Hg}} = -4.87 - 13.88Q$	$\alpha_Q^{\text{Te}} = -19.69 - 17.27Q$
$\alpha_Q^{\text{B}} = -8.53 - 10.87Q$	$\alpha_Q^{\text{N}} = -24.99 - 24.12Q$
$\alpha_Q^{\text{Al}} = -6.67 - 6.81Q$	$\alpha_Q^{\text{P}} = -18.54 - 17.25Q$
$\alpha_Q^{\text{Ga}} = -6.93 - 6.90Q$	$\alpha_Q^{\text{As}} = -18.54 - 17.17Q$
$\alpha_Q^{\text{In}} = -6.39 - 6.37Q$	$\alpha_Q^{\text{Sb}} = -17.07 - 15.54Q$
$\alpha_Q^{\text{S}} = -8.99 - 7.77Q$	$\alpha_Q^{\text{C}} = -11.42 - 2.16Q$

TABLE 3. RESONANCE INTEGRALS β FOR COMPOUNDS $A^{\text{III}}B^{\text{V}}$.

compound	β (eV)	compound	β (eV)	compound	β (eV)	compound	β (eV)
BN	-1.86	BP	-1.35	BA _s	-1.17	BS _b	-1.19
AlN	-1.35	AlP	-0.98	AlA _s	-0.85	AlS _b	-0.86
GaN	-1.17	GaP	-0.85	GaA _s	-0.74	GaS _b	-0.75
InN	-1.19	InP	-0.86	InA _s	-0.75	InS _b	-0.76
TiN	-1.10	TiP	-0.80	TiA _s	-0.69	TiS _b	-0.70

The corresponding sets of values for the resonance integrals β are shown in table 3. These values were obtained by the following assumptions:

- (1) $\beta_{XX} = \frac{1}{2}$ bond energy when X is a group IV atom;
- (2) $\beta_{XX'} = \{\beta_{XX}\beta_{X'X'}\}^{\frac{1}{2}}$ (X, X' both group IV atoms) as proposed by Pearson (1949);
- (3) $\beta_{\text{IV-IV}'} = \beta_{\text{III-V}'} = \beta_{\text{II-VI}'} = \beta_{\text{I-VII}'}$, where atoms I...IV and also IV'...VII' are adjacent in the periodic table.

With the numerical values in tables 2 and 3 it is easy to solve the equations (37) and hence to calculate λ and the net charges Q . It was found that the more electro-negative atom was always negatively charged (as, for example, N in BN). Table 4 shows the charges thus obtained for a wide variety of compounds. As we move across any row of this table from left to right, we are keeping the same electro-positive element, and are moving down the appropriate column of the periodic table for the electro-negative element. The charges Q almost always decrease in such a sequence. On the other hand, if we keep the electro-negative element fixed and move down the column for the electro-positive element, the Q values hardly change. It is surprising that the range of Q values appears to be so small.

Before attempting to compare the values in table 4 with the limited available experimental results, it is tempting to consider some possible refinements of the method used. There are three that we have investigated. They are

- (1) inclusion of Madelung energy $\alpha Q^2/R$,
- (2) inclusion of overlap integral $\int \phi_A \phi_B d\tau$,
- (3) consideration of appropriate valence states of A and B .

In the case of BN inclusion of (1) makes very little difference to the charges. Some little care is needed because certain electronic Coulomb interactions are already involved implicitly (but not explicitly) in our definition of the one-electron Hamiltonian H and the Coulomb terms α of (31) and (32). Our result was that now $\lambda = 0.71$ and $Q = 0.33$. It seems, therefore, that the inclusion of Madelung energy does not materially affect the charge distribution.

TABLE 4. EFFECTIVE CHARGES Q AND IONICITY PARAMETERS λ FOR $A^N B^{8-N}$ COMPOUNDS

com- pound	Q	λ	com- pound	Q	λ	com- pound	Q	λ	com- pound	Q	λ
			CuCl ^b	0.43	0.28	CuBr ^b	0.41	0.28	CuI ^b	0.35	0.30
									AgI ^{b,w}	0.34	0.30
BeO ^w	0.56	0.47	BeS ^b	0.43	0.50	BeSe ^b	0.42	0.50	BeTe ^b	0.40	0.50
ZnO ^w	0.60	0.46	ZnS ^{b,w}	0.47	0.49	ZnSe ^b	0.47	0.49	ZnTe ^b	0.45	0.49
			CdS ^{b,w}	0.49	0.48	CdSe ^{b,w}	0.49	0.48	CdTe ^b	0.47	0.49
			HgS ^b	0.46	0.49	HgSe ^b	0.46	0.49	HgTe ^b	0.44	0.49
BN ^b	0.43	0.69	BP ^b	0.32	0.71						
AlN ^w	0.56	0.66	AlP ^b	0.46	0.68	AlAs ^b	0.47	0.68	AlSb ^b	0.44	0.69
GaN ^w	0.55	0.66	GaP ^b	0.45	0.68	GaAs ^b	0.46	0.68	GaSb ^b	0.43	0.69
InN ^w	0.58	0.66	InP ^b	0.49	0.68	InAs ^b	0.49	0.68	InSb ^b	0.46	0.68
SiC ^b	0.23	0.94									

^b denotes that the crystal has zinc-blende structure.

^w denotes that the crystal has wurtzite structure.

Similarly we dealt with (2), by adapting the self-consistency equation (34) to include overlap integrals. The result was that $Q = 0.41$. Our conclusion therefore is that neglect of overlap integrals is not serious.

The question (3) concerning valence states is more difficult to deal with. What we require, in the case of boron nitride, for example, are the ionization potentials of a tetrahedral hybrid orbital, when there are three other tetrahedral hybrids around the same atom, and these each contain $2/(1 + \lambda^2)$ or $2\lambda^2/(1 + \lambda^2)$ electrons around the N and B atoms, respectively, and all these electrons have random mutual spin alignments. For BN it was possible to estimate such ionization potentials and so obtain a modified form of the Coulomb-term equations (32). We shall not describe the work in detail, but merely mention that self-consistency was now obtained with $\lambda = 0.70$, $Q = 0.38$.

It seems, therefore, that none of these three refinements makes any significant difference in the case of BN. It is reasonable to suppose that much the same is true for the other compounds in table 4.

We are now ready to compare our calculated Q values with experimentally determined values. However, as Cochran (1961) has shown, the difficulties, both in measurement and in the interpretation of the measurements, make this a delicate matter. The most complete set of Q values published for III-V compounds is that of Picus, Burstein, Henvis & Haas (1959), which are shown in table 5. A comparison of these values with our calculated values in table 4 shows that the variation as we go down a column of the periodic table is in the same direction as calculated. Further, the order of magnitude is much the same, but Picus *et al.* were not able to decide whether the group V atoms were positive or negative. Our calculations do decide this, as we have already shown.

There are even fewer results available for II-VI and I-VII solids. Some infra-red lattice vibration studies led Szigeti (1949) to propose the following values:

$$\text{CuCl}, Q = 1.10; \quad \text{CuBr}, Q = 1.00; \quad \text{ZnS}, Q = 0.96.$$

TABLE 5. EFFECTIVE CHARGES IN III-V COMPOUNDS AS DETERMINED BY PICUS *ET AL.* (1959)

compound	Q	compound	Q	compound	Q
				AlSb	0.48
		GaAs	0.43	GaSb	0.30
InP	0.60	InAs	0.56	InSb	0.34

The values for CuCl and CuBr suggest pure ions Cu^+Cl^- , but if this is indeed the case, it is hard to see why these crystals adopt the open tetrahedral structure. In view of the extreme difficulty of interpreting the experimental measurements we are inclined to believe that these Q values are not directly comparable with our own. Another II-VI compound recently studied is CdS, where Keffer (1960) has shown that the group VI atom carries a resultant negative charge. Three distinct estimates from elastic and piezoelectric constants give net charges 0.73, 0.71 and 0.91 e . These are in the same direction as our values in table 4, but are rather bigger in absolute magnitude.

5. CONCLUSION

The conclusions that we draw from the studies reported in this paper may be summarized as follows:

(1) If it is desired to adopt a chemical-bond formulation for the ground state of a tetrahedral compound, it is important to distinguish carefully the ionic character of each bond and the net ionic character of each atom.

(2) With a simple molecular-orbital approach, formal charges may be associated with the atoms. Such charges are found from a self-consistency equation in which the effective electro-negativity of each atom is made to depend on its net formal charge. Values so obtained are in reasonably good agreement with such limited experimental measurements as are available. In all cases the more electro-negative atom carries a net negative formal charge.

(3) More sophisticated calculations are possible for small molecules. In the cases of diamond and boron nitride reasonable values are obtained for the bond strength

and atomic charge respectively. The molecular orbitals thus obtained for these localized bonds are in a form which is suitable for immediate use in the papers which follow this one. Even if the absolute accuracy of some of these calculations, particularly in (2), is not great, it is reasonable to suppose that relative values are more correctly predicted by these methods.

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