Covalent Bond in Crystals. III. Anisotropy and Quadrupole Moments

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The form factors of covalent atoms in ansiotropic environments are discussed. As an example of the general theory, the bonding charge in graphite is calculated. Comparison of the planar bonding charge with the tetrahedral one leads to evaluation of the bonding charge in $C=C$ and $C\equiv C$ molecular bonds.

I. INTRODUCTION

IN the two preceding papers of this series we have discussed tetrahedral (sp^3) covalent bonding in elemental and partially ionic[1] crystals. We now wish to extend the discussion to include planar (sp^2) and axial (sp) bonding.

Our *a posteriori* approach to tetrahedral bonding was dictated by considerations of simplicity and the restriction that the theory reduce to linear metallic screening when the bonding charge Z_b approaches zero. This restriction is reasonable since covalent radii are generally even smaller than metallic radii. There is another case when $Z_b=0$, however, and this corresponds to large interatomic separations. In this case binding arises from Van der Waals forces, yet Z_b is also zero. Examples of this kind of binding are furnished by the solid rare gases. In our previous theory, $Z_b \rightarrow 0$ implied that the energy gap $E_g \rightarrow 0$. Yet for the solid rare gases there is a large energy gap caused by the discrete level structure of the free atom. No account was taken of discrete level effects (nor does one appear necessary at covalent distances) for sp^3 bonding, but clearly the effect is important transverse to planar and axial bonds.

A discussion of the microscopic dielectric function $\epsilon(q)$ for a band structure appropriate to the solid rare gases has been given by Hermanson.[2] When the gap parameters are adjusted to give the same value for $\epsilon(0)$, Hermanson's function does not differ greatly from Penn's dielectric function of a model semiconductor.[3] Because covalent binding energies are much greater than Van der Waals energies, we shall continue to use only Penn's function in the discussion of anisotropic binding. The error in this approximation is confined to "open" directions where binding energies are in any case small.

In Sec. II we discuss the generalization of linear screening theory to anisotropic geometries, especially sp^2 and sp bonding. The formulation is guided by the consideration that it reduce to metallic screening along directions of small atomic spacing, and yield "atomic" charge densities along "open" directions. In Sec. III the resulting charge densities are described in terms of multipole moments, and expressions are given for the quadrupole moment in systems possessing uniaxial symmetry. In Sec. IV the planar bonding charge is calculated for graphite and compared with the tetrahedral bonding charge in diamond.

Before proceeding to our formal discussion, we make a remark concerning the tensorial symmetry of the dielectric approach. This symmetry implies that the charge distribution screening the ion core pseudopotential is made up out of s and p wave functions. The part of the charge density made up out of $l \geqslant 2$ states is concentrated in the bonds. This assumption is common in many molecular theories, but in crystal quantum theory it tends to be obscured by the complex geometry of the Brillouin zone. The relation between the two viewpoints can be illustrated by the dielectric properties of cubic zinc-blende and hexagonal wurtzite crystals. In both cases each atomic site has tetrahedral nearest-neighbor symmetry and $\epsilon(\mathbf{q},\omega)$ is almost isotropic for $\mathbf{q}=0=\omega$. This is so even though the over-all wurtzite symmetry is uniaxial. For example, in CdS the difference between $\epsilon_{xx}(0,0)$ and $\epsilon_{zz}(0,0)$ vanishes to within the limits of experimental accuracy.[4] This is what would be expected from sp^3 hybridization. The differences between cubic and hexagonal Brillouin zones become apparent only at energies $\hbar\omega$ of several eV corresponding to interband transition edges.[5] The crystal charge distribution, on the other hand, is determined by the static electronic dielectric function, which characteristically exhibits tensorial (sp^n) symmetry.

II. ATOMIC SCREENING AND ANISOTROPIC SCREENING FUNCTIONS

In I we introduced the prescription for the form factor of the covalent atom,

$$v_s(q) = v_i(q)/\epsilon_s(q), \qquad (2.1)$$

and assumed that for a valence Z the charge

$$Z_a = \frac{Z}{\epsilon_s(0)} = \lim_{q \to 0} \frac{v_i(q)}{\epsilon_s(q)} \frac{q^2}{4\pi e}, \qquad (2.2)$$

not screening the atom should be distributed among the covalent bonds. For atomic screening, $\epsilon_s(0) \neq \infty$, and yet no charge appears in bonds.

[1] J. C. Phillips, Phys. Rev. 166, 832 (1968) (I); 169, (1968) (II).
[2] J. Hermanson, Phys. Rev. 150, 660 (1966).
[3] D. R. Penn, Phys. Rev. 128, 2093 (1962).

[4] S. J. Czyzak, W. M. Baker, R. C. Crane, and J. B. Howe, J. Opt. Soc. Am. 47, 240 (1957).
[5] M. Cardona and G. Harbeke, Phys. Rev. 137, A1467 (1965).

We propose to remedy this situation in cases where the principal axes of the atomic charge distribution can be divided into bonding axes and "atomic" axes by renormalizing the screening charge density. Consider first the case of isotropic "atomic" screening. We write (2.1) as

$$v_s(q) = v_i(q)\{1 - [1 - 1/\epsilon_s(q)]e^*\}, \qquad (2.3)$$

where e^* is a renormalization factor of the valence charge chosen to make the atom neutral. Thus we have in the isotropic case

$$e^* = [1 - 1/\epsilon_s(0)]^{-1}. \qquad (2.4)$$

The mixed case, in which, e.g., two principal axes are covalent and one "atomic" (sp^2 bonding) requires a tensorial generalization of (2.3). Let the subscripts (x,y) refer to covalent axes, and z to an "atomic" axis, and let θ be the angle between $\mathbf{q}$ and the z axis. Define the anisotropic microscopic dielectric function by

$$\frac{1}{\epsilon_s(\mathbf{q})} = \frac{\cos^2\theta}{\epsilon_{zz}(q,E_{gz})} + \frac{\sin^2\theta}{\epsilon_{xx}(q,E_{gx})}. \qquad (2.5)$$

Note that (2.5) differs from the macroscopic anisotropic dielectric function, where $\epsilon_s(q)$ is a tensor. Similarly define the renormalization tensor

$$e^*(\mathbf{q}) = a\cos^2\theta + \sin^2\theta$$
$$= 1 + (a-1)\cos^2\theta, \qquad (2.6)$$

where a represents the renormalization factor e^* along the atomic direction.

Substituting (2.5) and (2.6) into (2.3), we calculate the valence screening charge Z_s and the net atomic charge $Z_a = Z - Z_s$. The result is

$$\frac{Z_a}{Z} = \frac{1}{3}\left(\frac{2}{\epsilon_x} + \frac{1}{\epsilon_z}\right) - \frac{1}{3}(a-1) + C_1, \qquad (2.7)$$

where $\epsilon_x = \epsilon_{xx}(0, E_{gx})$ and where C_1 is a correction term given by

$$C_1 = \frac{1}{9}(a-1)\left(\frac{2}{\epsilon_x} + \frac{1}{\epsilon_z}\right) - \frac{8}{15}\left(\frac{1}{\epsilon_x} - \frac{1}{\epsilon_z}\right)(a-1). \qquad (2.8)$$

If we use for a the value (2.4) with $\epsilon(0) = \epsilon_z$, then in (2.7) the second term cancels the contribution $(\epsilon_z)^{-1}$ to first order. In the covalent limit $a=1$ and (2.7) represents the anisotropic covalent generalization of (2.2).

The terms of second order in $(\epsilon)^{-1}$ arise because both (2.5) and (2.6) are taken as tensors. Thus both screening and renormalization factors are assumed to have quadrupolar symmetry, and it is not clear that the higher-order terms which arise from the product of the two anisotropies are significant. On the other hand, the screening charge is certainly dominated by the $l \leqslant 1$ s-p subspace, so that the higher-order terms may be significant. As they are not small numerically, we discuss a method of evaluating them approximately.

First, suppose $E_{gx} = 0$, i.e., metallic screening in the plane, $\epsilon_x = \infty$. Then $Z_a = 0$ by construction, and this gives a condition on a which is approximately

$$a = 1 + \left(1 - \frac{2}{\epsilon_z}\right)^{-1}\frac{1}{\epsilon_z} \approx 1 + \frac{1}{\epsilon_z} + \frac{2}{\epsilon_z^2}, \qquad (2.9)$$

which differs from (2.4) by the factor of 2 in the third term. This difference measures the uncertainties which arise in the present model from marrying the metallic and tight-binding screening.

Bonding in the (x,y) plane alters ϵ_z by increasing E_{gz} above the atomic value, but bonding in the (x,y) directions has little effect on oscillator strengths for $\mathbf{E} \| z$. Using Penn's basic relation,[3]

$$\epsilon_s(0) = 1 + \left(\frac{\hbar\omega_p}{E_g}\right)^2 C, \qquad (2.10)$$

where $C = C(E_g/E_F)$ can be evaluated in terms of the isotropically averaged E_g, we can estimate the effect of (x,y) bonding on ϵ_z. Denote the atomic energy gap by E_{gz}^0, the actual gap by E_{gz}, the atomic value of the static dielectric constant by ϵ_z^0, and the actual value by ϵ_z. Then we have

$$\epsilon_z^0 = 1 + (\hbar\omega_p/E_{gz}^0)^2 C, \qquad (2.11)$$

$$\epsilon_z = 1 + (\hbar\omega_p/E_{gz})^2 C, \qquad (2.12)$$

with the relation between E_{gz} and E_{gz}^0 being approximately

$$E_{gz} = E_{gz}^0 + E_{gx}. \qquad (2.13)$$

This relation assumes that the average energy-gap increase due to (x,y) bonding for $\mathbf{E} \| z$ is the same as the bonding gap in the (x,y) plane, i.e., E_{gx}. This assumption is only approximately correct, but it simplifies the calculation considerably. It has two immediate consequences:

(1) In addition to the bonding charge Z_σ in the (x,y) plane, because $\epsilon_z < \epsilon_z^0$, and $E_{gz} > E_{gz}^0$, there is a bonding charge Z_π associated with the π orbitals along the z axis.

(2) In determining the renormalization factor a, one must use ϵ_z^0 in (2.7) or (2.9), rather than the observed value ϵ_z. The value of ϵ_z^0 can be obtained from ϵ_x and ϵ_z through (2.11)–(2.13) and the relation

$$\epsilon_x = 1 + (\hbar\omega_p/E_{gx})^2 C. \qquad (2.14)$$

The use of these relations will be illustrated in Sec. IV by the calculation of Z_σ and Z_π in graphite.

Having proposed a set of relations for handling metallic, covalent and tight-binding screening charges, we discuss the considerations which guided the selection of these relations. In principle, of course, one can calculate screening charges for any given system by solving the Schrödinger equation as accurately as one desires, in

accordance with the variational principle. In practice, such solutions are extremely difficult to obtain, and (apart from the energy levels themselves), the physical content of the results is not always apparent. Here we have focused our attention primarily on charge densities, which we hope to make self-consistent to high accuracy with relatively little effort by appealing to observed dielectric properties. If we further require an algebraically simple formulation, then the separation of deformations of the atomic charge density into metallic and covalent parts is a natural part of the relations proposed. Note, moreover, that specific basis functions (e.g., atomic orbitals) nowhere make their appearance. If one is concerned primarily with *intra*-atomic effects, then this is a handicap, because Eq. (2.3) certainly does not give as accurate a representation of the free-atom charge density as free-atom wave functions would. On the other hand, if one's primary interest is *inter*-atomic effects, then the present dielectric formalism offers a promising (although still likely to undergo considerable refinement) approach. Note that specific atomic orbitals contain no information whatsoever on interatomic effects, and that the expansion of such effects in terms of atomic orbitals converges quite slowly, if at all.

We mentioned at the outset that we are able to factorize metallic-covalent effects from atomic ones only when the principal axes of the screening charge distribution can be classified into one category or the other. This condition is far less restrictive than it may appear to be. In crystals rhombohedral distortions almost always arise because of covalent effects, as one can verify from the interatomic distances involved. (Good examples are the group V semimetal and the IV-VI semiconductors.[6]) Planar and axial bonding dominate most molecular structures, with the exception of boranes, where the structures are distorted by partial covalent effects just as the semimetals are. Taken altogether these facts suggest that factorization along principal axes is a satisfactory method of separating atomic and covalent interactions in most systems.

III. MULTIPOLE MOMENTS OF THE COVALENT ATOM

In the preceding section we have indicated how to calculate $v_s(q)$ for an atom in an elemental structure. Within the Hartree approximation (which is adequate for our present purposes) the covalent atomic charge density is given by

$$\rho_s(\mathbf{q}) = \frac{q^2}{4\pi}\left[1 - \frac{1}{\epsilon_s(\mathbf{q})}e^*(\mathbf{q})\right]v_i(q), \qquad (3.1)$$

where $\epsilon_s(\mathbf{q})$ and $e^*(\mathbf{q})$ are given by (2.5) and (2.6) ,and

$v_i(q)$ can be obtained either semiempirically[7] or from tables[8] based on atomic spectra.

From (3.1) one can calculate the multipole moments of the atom in an anisotropic environment. As an illustration we carry out this calculation for the quadrupole moment assuming only covalent screening, i.e., $e^*(\mathbf{q}) = 1$. The quadrupole moment is defined in terms of traceless components $Q_x = Q_y$ and Q_z given by

$$Q_{x,z} = Q_{x,z}' - Q', \qquad (3.2)$$

$$Q' = \tfrac{1}{3}(2Q_x' + Q_z'), \qquad (3.3)$$

$$Q_x' = \frac{1}{2}\int d^3r\, \rho(\mathbf{r})(x^2 + y^2), \qquad (3.4)$$

$$Q_z' = \int d^3r\, \rho(\mathbf{r})z^2. \qquad (3.5)$$

Now using the energy gaps defined by

$$E_{g(x,z)} = \hbar\omega_p[(\epsilon_{x,z} - 1)/C]^{-1/2}, \qquad (3.6)$$

we can rewrite (2.5) as

$$\frac{1}{\epsilon_s(\mathbf{q})} = \frac{1}{\epsilon_0(q)} + \frac{1}{\epsilon_2(q)}(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2}), \qquad (3.7)$$

where the functions $\epsilon_0(q)$ and $\epsilon_2(q)$ are given by

$$\frac{1}{\epsilon_0(q)} = \frac{1}{3}\left[\frac{2}{\epsilon_s(q, E_{gx})} + \frac{1}{\epsilon_s(q, E_{gz})}\right], \qquad (3.8)$$

$$\frac{1}{\epsilon_2(q)} = \frac{2}{3}\left[\frac{1}{\epsilon_s(q, E_{gz})} - \frac{1}{\epsilon_s(q, E_{gx})}\right]. \qquad (3.9)$$

The relation (3.7) implies that $\rho(\mathbf{r})$ can be written as

$$\rho(r, \cos\theta') = \rho_0(r) + \rho_2(r)P_2(\cos\theta'), \qquad (3.10)$$

where θ' is the angle between $\mathbf{r}$ and the z axis. Of course $\rho(\mathbf{r})$ is given by

$$\frac{1}{(2\pi)^3}\int e^{i\mathbf{q}\cdot\mathbf{r}}\rho_s(\mathbf{q})\,\sin\theta\,d\theta\,d\phi\,q^2 dq. \qquad (3.11)$$

Substituting the addition theorem

$$e^{i\mathbf{q}\cdot\mathbf{r}} = \sum_l j_l(qr)P_l(\cos\theta)P_l(\cos\theta') + \cdots \qquad (3.12)$$

in (3.11), noting that the integral over ϕ causes the remaining contributions in (3.12) to vanish, and using for $v_i(q)$ the empty-core model,

$$v_i(q) = (4\pi Ze/q^2)\cos qr_c, \qquad (3.13)$$

[6] M. H. Cohen, L. M. Falicov, and S. Golin, IBM J. Res. Develop. **8**, 215 (1964).

[7] M. L. Cohen and T. K. Bergstresser, Phys. Rev. **141**, 789 (1966); **164**, 1069 (1967).
[8] A. O. E. Animalu and V. Heine, Phil. Mag. **12**, 1249 (1965).

we obtain a closed expression for $\rho_2(r)$ which is

$$\rho_2(r) = -\frac{Ze}{10\pi^2}\int_0^\infty \cos qr_c \frac{j_2(qr)}{\epsilon_2(q)}q^2 dq. \quad (3.14)$$

The quadrupole moments Q_x' and Q_z' may be calculated by substituting (3.14) in (3.4) and (3.5). Expressions of this kind may be useful in analyzing nuclear-resonance data in covalent crystals, or in estimating the quadrupole moments of molecules.

IV. GRAPHITE

Although simple in principle, the formulas discussed in Sec. II may not always be easy to implement. Taft and Philipp have studied[9] the optical spectrum of graphite, but they measured only $\epsilon_{xx}(\mathbf{q}=0,\omega)$. Recently Greenaway and Harbeke[10,11] have measured ϵ_{zz} at low frequencies; their value for ϵ_z can be combined with that of Taft and Philipp for ϵ_x to estimate bonding charges in graphite.

The low-frequency limit of ϵ_x, neglecting the Drude contribution, can be estimated from Taft and Philipp's data as

$$\epsilon_x = 4.7, \quad (4.1)$$

while Greenaway and Harbeke obtain

$$\epsilon_z = 2.4. \quad (4.2)$$

From (4.1), (4.2), and (2.11)–(2.14), we obtain

$$\epsilon_z^0 = 10.5, \quad (4.3)$$

which gives from (2.9) the renormalization factor

$$a = 1.11. \quad (4.4)$$

Then from (2.7), with $\epsilon_z = \epsilon_z^0$ (neglecting π bonding, i.e., setting $E_{gz} = E_{gz}^0$),

$$\frac{Z_a}{Z} = \frac{2}{3\epsilon_x} + \frac{2}{(\epsilon_z^0)^2} + C_1, \quad (4.5)$$

where $|C_1| < 0.003$. From (4.1) and (4.3),

$$Z_a^0/Z = 0.16. \quad (4.6)$$

The charge $0.64e$ is to be divided among three σ bonds, giving

$$Z_\sigma = -0.21e. \quad (4.7)$$

We now repeat the calculation using ϵ_z and E_{gz} instead of ϵ_z^0 and E_{gz}^0. The increased value of Z_a will clearly be associated with π bonding. Substituting (4.4) (4.1) and (4.2) into (2.7) and (2.8) gives $C_1 \approx 0.02$,

$$\frac{Z_a}{Z} = \frac{2}{3\epsilon_x} + \frac{1}{3}\left(\frac{1}{\epsilon_z} - a + 1\right) + C_1$$

$$= 0.14 + 0.11 + 0.02 = 0.27. \quad (4.8)$$

[9] E. A. Taft and H. R. Philipp, Phys. Rev. **138**, A197 (1965).
[10] D. Greenaway and G. Harbeke, (to be published). See also Ref. 11.
[11] S. Ergun, Nature **213**, 135 (1967).

TABLE I. Bond charge versus bond length. The values in parentheses are theoretical values derived by the method described in the text. Bond lengths are taken from Ref. 12.

Bond	$-$Charge/$|e|$	Length (Å)
Z_t	0.17	1.54
Z_p	0.36	1.42
Z_1	(0.17)	1.54
Z_2	(0.52)	1.33
Z_3	(0.71)	1.20

The second term in (4.8) is associated with π bonding. It leads to a bonding charge

$$Z_\pi = -0.15e, \quad (4.9)$$

in addition to the bonding charge Z_σ.

If we lump the bonding charges together, we can define a planar bonding charge Z_p by

$$Z_p = Z_\sigma + Z_\pi. \quad (4.10)$$

We remark that our estimate of Z_σ is much more reliable than the estimate of Z_π. This is because Z_σ is determined from ϵ_x alone. To obtain Z_π one must use the factorization and renormalization procedure on ϵ_x and ϵ_z from which an artificial parameter (ϵ_z^0) emerges. We regard the value of Z_π obtained in (4.9) as plausible, but by no means firm.

V. COMPARISON OF PLANAR, TETRAHEDRAL, AND MOLECULAR BONDS

The well-separated layers of graphite are presumably bound primarily by Van der Waals forces. This leaves the charge (4.8) to be distributed equally among the trigonal planar bonds, each with charge $2Z_p$ given by

$$Z_p = -0.36e. \quad (5.1)$$

This should be compared with the result (3.4) of I for the tetrahedral bonding charge

$$Z_t = -0.17e, \quad (5.2)$$

which yields

$$Z_p \approx 2Z_t. \quad (5.3)$$

It is interesting to correlate (Table I) bond charge Z_b with bond length l for equilibrium configurations (no external pressure). Consider the crystal sequence Z_t: C—C (diamond); Z_p: C—C (graphite); and compare it with the molecular sequence Z_1: H_3C—CH_3; Z_2: $H_2C = CH_2$ and Z_3: $HC \equiv CH$. In the crystalline sequence with $Z_c = Z_t$ and Z_p,

$$dZ_c/dl = -1.5 \ e/\text{Å}. \quad (5.4)$$

On the other hand, the bonding charges in the molecular sequence Z_1, Z_2, Z_3 are not obtainable from macroscopic dielectric properties. The fact that $l(Z_1) = 1.54 \pm 0.02$ Å in seventeen molecules suggests that[12]

$$Z_1 = -0.17|e|, \quad (5.5)$$

[12] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1940).

in agreement with Z_t. If we assume that the bond charge-bond length relationship is linear (as seems appropriate from the fact that $Z_b \ll 4$) with coefficient given by (5.4), then (5.4) and (5.5) give

$$Z_2 = 3.0 Z_1, \quad Z_3 = 4.2 Z_1. \tag{5.6}$$

The results[13] for double and triple bonds in (5.6) suggest that the lumped bonding charge (4.10) may not be a useful construct. Note that Z_σ in graphite is greater than Z_t (diamond), but that most of the excess in Z_p then comes from the less meaningful Z_π. Presumably the σ bonding charge is concentrated in the neighborhood of the C-C midopint (as Z_t is in diamond), but the π bonding charge is spread out approximately an atomic radius above and below the atomic plane. It is, therefore, less effective than the σ charge in binding, and should not be given equal weight in (4.10). If its weight were reduced (e.g., by a factor of 2) then more plausible results for Z_2 and Z_3 would obtain (e.g., approximately $2Z_1$ and $3Z_1$, respectively).

Several attempts have been made to derive bond lengths from the concept of bond order.[14] The results are useful for correlating and predicting molecular structure.[15] One may hope to extend this analysis by studying the bonding charge $Z_b = Z_\sigma$ or Z_π, as a function of bond length, by minimizing the total valence energy E_v as a function of N, E_{gx} and E_{gz}.

A promising alternative approach in the *a posteriori* spirit is the following. For each system of A-B bonds one studies the bonding charge $2Z_b$ as a function of bond length l. [Thus (5.4) describes $Z_b(l)$ in C—C bonds.] As in II, Sec. IV, one may then be able to effect the additive separation of the bonding charge

$$2Z_b = Z_b{}^A + Z_b{}^B, \tag{5.7}$$

as well as divide the bond length into covalent radii[6]

$$l = r_A + r_B, \tag{5.8}$$

from which we obtain the functions $Z_b{}^A(r_A)$ and $Z_b{}^B(r_B)$. Now the charge $Z_a(m)$ on atom m is given by the covalent sum rule

$$Z_a(m) = -\sum_b Z_b{}^m, \tag{5.9}$$

where the sum extends over all bonds attached to atom m. Knowing $Z_b{}^m$ and $Z_a(m)$ we can determine $\mathbf{E}_g{}^m$ by a suitable averaging procedure [as in Eqs. (4.6) and (4.7)]. Thus from the observed bond lengths, it should be possible to derive (in an *a posteriori* spirit) a complete microscopic model for the charge distribution in the molecule.

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[13] These results replace those quoted earlier [J. C. Phillips, Phys. Rev. Letters **19**, 415 (1967)] on the basis of an incorrect separation of Z_σ and Z_π.

[14] C. A. Coulson, Proc. Roy. Soc. (London) **A169**, 413 (Z939).

[15] A. Streitweiser, Jr., *Molecular Orbital Theory for Orgainc Chemists* (John Wiley & Sons, Inc., New York, 1961), p. 165 ff.

Such a model would have numerous applications, particularly to the study of oscillator strengths of infrared spectra (which depend on induced dipole moments), molecular vibrations, and hindered rotation in molecules.

VI. ABSOLUTE BINDING ENERGIES

We have described in Sec. VI of I a procedure for the calculation of ground-state energy E_v in our microscopic model. The structural parameters N and E_g are determined by minimizing E_v. For most purposes this prescription is sufficient. In this section we discuss the significance of the minimum value $E_v{}^0$.

In contrast to theories based on atomic orbitals, in our theory attention is focussed not on intra-atomic self-energies, but rather on interatomic interaction energies. When the system is resolved into separated neutral atoms, our continuum method will not yield an accurate expression for the energy of a neutral atom. For structural purposes (where we are primarily in energy differences of structures close to the equilibrium value of N), this is of little importance. However, if we wish to calculate absolute binding energies of crystals or molecules, an interpretation of the meaning of the absolute value of $E_v{}^0$ is required.

Such an interpretation can be derived naturally from our discussion of the anisotropy of $\mathbf{E}_g$ in graphite. Along the c axis the binding is very weak (negligible for our purposes). Along this same axis E_{gz} is small. This means that in the limit of well-separated atoms, $E_{gz} = E_{gz}{}^0$.

This suggests that we separate the absolute binding energy from $E_v{}^0$ by calculating the self-energy E_a of the free atoms in the continuum approximation, with an isotropic E_g equal (in the case of carbon atoms) to $E_{gz}{}^0$. The binding energy is then

$$E_B = E_a - E_v{}^0, \tag{6.1}$$

where the errors contained in the continuum approximation itself can be expected largely to cancel on the rhs of (6.1).

VII. CONCLUSIONS

In this note we have attempted to generalize the approach of I to include atomic as well as metallic and covalent screening. An application of the theory has been made to graphite, and we have estimated the bonding charges Z_σ and Z_π for this material. A critical test of the theory would be obtained from comparison of our estimated charge distributions with those measured by x-ray scattering. Unfortunately graphite single crystals of sufficiently high quality are not obtainable to make possible highly accurate x-ray measurements.

In the following paper we show that it is possible, at least in principle, to calculate the lattice dynamics of diamond-type crystals from the present approach. Should numerical calculations prove successful and sen-

sitive to the magnitude of Z_t in diamond, similar calculations of the normal modes of vibration for planar molecules (such as benzene) should test the validity of the present $Z_\sigma - Z_\pi$ model of sp^2 bonding. We also remark that the two-phonon induced infrared absorption in diamond[16] and benzene measures the magnitude and displacement of the bonding charges directly.

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[16] R. Wehner, H. Borik, and W. Kress, Solid State Commun. 5, 307 (1967).

Covalent Bond in Crystals. IV. Lattice Deformation Energies

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A general method is described for calculating lattice deformation energies in covalent structures. The formulas are presented explicitly for harmonic energies in diamond-type crystals. The theory differs intrinsically from linear screening theories because of the inclusion of bond-stretching terms. These are calculated using a dynamical covalent sum rule. The results show that bond stretching leads to large bond-bond interaction energies that are similar to those in a nearest-neighbor classical shell model. The theory can be used to infer the covalent screening function from lattice vibration spectra measured by inelastic neutron scattering.

I. INTRODUCTION

IN the preceding papers of this series[1-3] we have developed the elements of a microscopic theory of covalent bonding with special reference to crystalline structures. At present the theory is axiomatic in character, but it is straightforward to calculate the total energy of the system as a functional of the structural parameters. Minimization of this energy with regard to these parameters yields a self-consistent theory. Several preliminary numerical estimates based on optical data suggested that the self-consistent theory will differ little from the *a posteriori* one with parameters determined from macroscopic dielectric properties.

The purpose of the present paper is to carry the axiomatic theory one step further and to present a simple prescription for lattice deformation energies. According to the usual theory of lattice dynamics[4] (based on the adiabatic approximation), nuclear motion can be described in terms of an effective potential energy function Φ. This function describes the change in electronic energy induced by the displacements $\mathbf{u}(l)$ and $\mathbf{u}(l')$ of the atoms with equilibrium sites at $\mathbf{r} = \mathbf{R}_l$ and $\mathbf{R}_{l'}$, respectively. If we know the lattice deformation

energies, $[\partial^2\Phi/\partial\mathbf{u}(l)\partial\mathbf{u}(l')]:\mathbf{u}(l)\mathbf{u}(l')$, then the lattice vibration frequencies can be obtained by a transformation to normal modes.

The method adopted in this paper follows closely the procedure which has proved successful in metals.[4-6] Briefly that method calculates lattice deformation energies using linear screening of the ion core potential $\tilde{v}_i(r)$. Such screening can easily be described[7] in terms of plane-wave screening of ion-core pseudopotential form factors $v_i(q)$. Our treatment reduces to the metallic one when $E_g = 0$.

In Sec. II we review the metallic theory.[8-11] In Sec. III the modifications of the metallic theory required when $E_g \neq 0$ are presented. It turns out that these can be described in terms of one additional axiom which expresses the effect of bond stretching on E_g. This is described in Sec. IV, and the contribution of a normal mode is derived in Sec. V. Electron-phonon interaction is discussed in Sec. VI and the relation to linear response theory is discussed in Sec. VII.

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