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Calculating of the Cohesive Energy of Diamond*

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It is well known that a satisfactory value for the binding energy of the hydrogen molecule may be calculated using a wave function which has the form of a Heitler-London (HL) function built on non-orthogonal orbitals. However, Slater has shown that a HL function built on orthogonal orbitals fails to yield any binding for the hydrogen molecule, but binding may be achieved by mixing with the HL function an ionized-molecule function which assigns two electrons to one atom and none to the other. Satisfactory results may also be achieved using a Hund-Mulliken (HM) function which may be built on either orthogonal or non-orthogonal orbitals, since the wave functions resulting in these two cases may be shown to be identical.

The present calculation shows that the situation for diamond is entirely analogous to that for the hydrogen molecule in that the usual formulation of the Slater-Pauling (SP) directional theory of valence, which is a generalization of the HL method using orthogonal orbitals, fails to yield any binding, but satisfactory results are achieved when this theory is reformulated to allow ionization to be introduced into the bonds. It is also shown that for the observed value of the lattice parameter, which is the only value for which the calculations have been performed, satisfactory results are also achieved using a wave function which is built on orthogonal HM orbitals, each of which, like its counterpart in the hydrogen molecule case, is spread out over a pair of bonded atoms.

As a by-product of the main calculation, the total exchange energy of Bloch-type functions belonging to the valence bands of diamond is calculated and found to be essentially equal to the value obtained using free-electron functions.

INTRODUCTION

THE Slater-Pauling (SP) directional theory of valence is essentially a generalization of the Heitler-London (HL) method to the case of an arbitrary molecule or crystal. However, while the HL method as applied to the problem of the hydrogen molecule employs a wave function built on one-electron functions whose space parts are not orthogonal to each other, the wave function used in the general case is built on one-electron functions whose space parts are mutually orthogonal. Until Slater[1] recently applied the general form of the theory based on orthogonal orbitals to the hydrogen molecule, it had never been subjected to a decisive analytical test because all prior applications of it, while using the energy expression appropriate to orthogonal orbitals, in one way or another made unwarranted use of the results of the HL calculation for the hydrogen molecule based on non-orthogonal orbitals. Slater's calculation shows that in the case of hydrogen, the general theory is inadequate in that it not only fails to give any binding, but also indicates that the triplet state has lower energy than the singlet state. This situation may be corrected, in the case of hydrogen, by means of a configuration interaction between a HL function which assigns one electron to each atom and an ionized-molecule wave function which assigns two electrons to one atom and none to the other. But, while the method of configuration interaction is very convenient in the case of the hydrogen molecule, it is unworkable in the case of a large molecule or crystal. A configuration interaction which mixes states of the whole molecule or crystal is also objectionable from the conceptual point of view in that it fails to give expression (or does so only in a very indirect manner) to the fact that the valence bond is a local affair involving only an atom and its immediate neighbors. It will now be shown that the SP theory may be cast into a form which emphasizes the local nature of the valence bond and which allows a generalization that permits the necessary configuration interaction between bonded orbitals to be carried out locally, rather than requiring the mixing of states of the entire molecule or crystal. This will be called the "ionized-bond" formulation of the theory.

1. IONIZED-BOND FORMULATION OF THE SLATER-PAULING THEORY

While the following discussion is in terms of the diamond lattice, it will be apparent that the methods and results may be adapted to the case of any molecule or crystal in which it is valid to assume that the bonds are localized, i.e., no resonance between different bond eigenfunctions occurs. In such a case there is a unique pairing of all the valence orbitals into bonded pairs, the two orbitals of any given pair having opposite spin. In accordance with the intuitive ideas of the SP theory which assert that the bond strength of two bonded orbitals is greater the more they overlap, we regard the orbitals as lobes which point toward their bonded partners. In the case of diamond there are four valence orbitals per atom and every atom has four nearest neighbors located at the vertices of a regular tetrahedron circumscribed about the atom. Since the diamond lattice[2]

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[1] J. C. Slater, J. Chem. Phys. **19**, 220 (1951).

[2] For figures illustrating the diamond lattice see, for example, C. Herring, J. Franklin Inst. **233**, 525 (1942), Fig. 3 on p. 538; or A. F. Wells, *Structural Inorganic Chemistry* (Oxford University Press, London, 1950), second edition, Fig. 166 on p. 511.

consists of two interpenetrating face-centered cubic lattices such that the four nearest neighbors of an atom belonging to one of the two interpenetrating lattices all belong to the other lattice, the lobe-like valence orbitals of atoms belonging to one lattice point toward the vertices of a tetrahedron fixed in space, while the orbitals of atoms belonging to the other lattice point in the opposite directions, i.e., toward the faces of the tetrahedron. Let the space part of a valence orbital of an atom belonging to one lattice be designated u_i and let v_j be the space part of its bonded partner which belongs to an atom of the other lattice and which points in the direction opposite to that in which u_i points so that the overlap of the two lobes is a maximum.

Instead of using these one-electron functions to construct the Slater determinants from which the electronic wave function for the crystal is formed in the usual formulation of the SP theory,[3] we shall use them to construct two-electron functions which will in turn be used to build the wave function for the crystal.[‡] Let us assume that the space parts of the valence orbitals are normalized and are mutually orthogonal. Let φ_{ij} be the normalized two-electron function constructed from the two bonded lobes whose space parts are u_i and v_j. Since Slater[1] found that, in the case of the hydrogen molecule, satisfactory results could be obtained using a wave function built on orbitals with orthogonal space parts only if the wave function was taken to be a mixture of the ordinary HL function and the ionized-molecule function, we shall assume φ_{ij} to have the following form:

$$\varphi_{ij}(k,l)=\frac{1}{[2(1+A^2)]^{\frac{1}{2}}}\{[u_i(k)v_j(l)+v_j(k)u_i(l)] +A[u_i(k)u_i(l)+v_j(k)v_j(l)]\} \times\left[\frac{\alpha(k)\beta(l)-\beta(k)\alpha(l)}{\sqrt{2}}\right], \tag{1-1}$$

where α and β are spin functions, and the arguments k and l designate the kth and lth sets of electron coordinates, respectively. The quantity in the first square brackets inside the curly brackets corresponds to the HL function while that in the second square brackets may be called an "ionized-bond" function and corresponds to having two valence electrons on one bonded atom and none on the other. The adjustable parameter A which determines the relative proportions of these two functions in φ_{ij} will ultimately be adjusted so as to minimize the energy. This amounts to carrying out a configuration interaction between the two bonded orbitals having space parts u_i and v_j.

For the sake of simplicity, let us regard the two 1*s* orbitals belonging to any atom of the diamond lattice as constituting a bonded pair. The difference between a bonded pair of 1*s* orbitals and a bonded pair of valence orbitals is that, while the space parts of the bonded valence orbitals are orthogonal, the space parts of the bonded 1*s* orbitals are identical. If we designate the space parts of two bonded 1*s* orbitals by u_i^0 and u_j^0, then $u_i^0=u_j^0$ and the corresponding φ_{ij} is

$$\varphi_{ij}(k,l)=u_i^0(k)u_j^0(l)[\alpha(k)\beta(l)-\beta(k)\alpha(l)]/\sqrt{2}. \tag{1-2}$$

We note that the φ's defined by (1-1) and (1-2) are antisymmetric with respect to interchange of their electron coordinates, that is

$$\varphi_{ij}(k,l)=-\varphi_{ij}(l,k). \tag{1-3}$$

They also constitute an orthonormal system since

$$(\varphi_{ij}(k,l)\,|\,\varphi_{ij}(k,l))_{k,l}=1;\quad (\varphi_{ij}(k,l)\,|\,\varphi_{i'j'}(k,m))_k=0;$$
$$\text{pair } i,\, j\neq\text{pair } i',\, j',\, l\neq k, \text{ and } m\neq k; \tag{1-4}$$

where the subscripts k and l appended to the first inner product indicate that the integration is over the kth and lth sets of electron coordinates and the subscript k on the second inner product means that the integration extends only over the kth set of coordinates.

The electronic wave function of the crystal, ψ, may be written in terms of the φ's as follows:

$$\psi=2^{-N/2}\sum\nolimits_P(-1)^P P\varphi_{1,2}(1,2)\varphi_{3,4}(3,4)\cdots \times\varphi_{N-1,N}(N-1,N), \tag{1-5}$$

where N is the total number of electrons (including 1*s*) in the crystal. The permutation operator P acts only on the electron coordinates and not on the subscripts of the φ's. Because of the antisymmetry of the φ's set forth in (1-3), if the factor $2^{-N/2}$ did not multiply the summation over all permutations, every independent term in ψ would be repeated $2^{N/2}$ times. By multiplying by $2^{-N/2}$, we obtain ψ in the form of the sum of $2^{-N/2}N!$ independent terms. Using the orthonormality conditions (1-4), we see that the norm of ψ is $2^{-N/2}N!$.

If (1-5) is to be a valid wave function for the diamond lattice, it must be an eigenfunction of total spin (assuming a spin-independent Hamiltonian for the crystal) belonging to the eigenvalue $S^2=0$, because diamond is diagmagnetic. This is obviously the case since each of the φ's as defined by (1-1) and (1-2) belongs to the eigenvalue $S^2=0$. ψ must also belong to an irreducible representation of the space group O_h^7 which describes the symmetry of the diamond lattice. ψ does, in fact, belong to the identity representation. This may easily be seen from the following argument: Any symmetry operation will result in a relabelling of the orbitals of

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[3] See, for example, Eyring, Walter, and Kimball, *Quantum Chemistry* (John Wiley and Sons, New York, 1944), Chap. XIII.

[‡] Note added in proof: The author's attention has been called to the brief discussion of the possibility of formulating the wave function of a crystal in terms of two-electron functions which has been given by L. Pauling, Proc. Roy. Soc. (London) **196**, 343 (1949). See p. 361 of this article.

the lattice, but a bonded pair of orbitals before the symmetry operation will be a bonded pair afterward, so the net effect on ψ will be a reordering of the factors in the terms of (1-5). But since the order of the factors in any term is completely irrelevant, ψ is unchanged. Hence it belongs to the identity representation.

It can be shown[4] that ψ as defined by (1-5) reduces for the case $A=0$ to the wave function employed in the usual formulation of the SP theory.[3] It can also be shown[4] that for the case $A\neq 0$, (1-5) is equal to a linear combination of the usual SP wave functions corresponding to all possible configurations which may be generated in the diamond lattice by shifting electrons into the orbitals of their bonded partners, that is by ionizing the bonds. Thus, if we evaluate the energy of the diamond lattice using ψ as defined in (1-5) for the case of arbitrary A, and then adjust A to minimize the energy, we are, from the point of view of the usual form of the SP theory, carrying out an immensely complicated configuration interaction, but doing it in a way which is not only computationally much more tractable, but is also intuitively more appealing because it stresses the local nature of the valence bond.

Finally, we note that for $A=1$, (1-1) may be written in the form

$$\varphi_{ij}(k,l)=\tfrac{1}{2}[u_i(k)+v_j(k)][u_i(l)+v_j(l)] \times[\alpha(k)\beta(l)-\beta(k)\alpha(l)]/\sqrt{2}, \quad (1.6)$$

which has the form of the simple Hund-Mulliken wave function for the two bonded orbitals of the hydrogen molecule. Writing all the φ's in (1-5) in this way and expanding all the products of spin functions, we obtain a sum of products of one-electron orbitals which is antisymmetric for the interchange of any pair of electron coordinates. The number of terms in this sum is $2^{N/6}2^{N/3}2^{-N/2}N!=N!$, where $N/6$ and $N/3$ are the number of pairs of $1s$ orbitals and valence orbitals, respectively, and $2^{-N/2}N!$ is the number of terms in (1-5). A typical one-electron function in this expression would have the form

$$2^{-3/4}[u_i(k)+v_j(k)]\alpha(k).$$

Thus, for $A=1$, (1-5) is identical, except for normalization, to a single Slater determinant constructed from Hund-Mulliken type orbitals, each of which is the sum of two bonded localized orbitals. This could be called a "semi-generalization" of the Hund-Mulliken method to distinguish it from the "complete generalization" represented by a wave function which is a Slater determinant of Bloch waves, which are spread out over all the atoms of the lattice, instead of just the two atoms of a bonded pair. However, it should be noted that the determinant of the semi-generalization differs only by a unitary transformation from a determinant of Bloch-type functions which are similar to Bloch waves in that they are spread out over all atoms of the lattice, but are more restricted than Bloch waves because they are prescribed linear combinations of atomic orbitals.

2. ENERGY EXPRESSION FOR DIAMOND LATTICE

We must next find an expression for $(\psi|H|\psi)/(\psi|\psi)$ where ψ is given by (1-5) and the spin-independent Hamiltonian H for the diamond lattice has the form

$$H=\sum_{k=1}^{N}O_1(k)+\sum_{k=1}^{N}\sum_{l<k}^{N}O_2(k,l), \quad (2\text{-}1)$$

where, in atomic units,

$$O_1(k)=-\tfrac{1}{2}\nabla_k^2-6\sum_{L}^{N/6}\frac{1}{|\mathbf{r}_k-\mathbf{R}_L|}, \quad (2\text{-}2)$$

where $\mathbf{r}_k$ and $\mathbf{R}_L$ are the vectors specifying the kth set of electron coordinates and the Lth lattice point, respectively, and ∇_k^2 is the Laplacian operating on the kth set of electron coordinates.

$$O_2(k,l)=1/r_{k,l}=1/|\mathbf{r}_k-\mathbf{r}_l|. \quad (2\text{-}3)$$

(The subscripts on the operators O_1 and O_2 indicate that they involve coordinates of one and two electrons, respectively.) The derivation of an expression for $(\psi|H|\psi)/(\psi|\psi)$ in terms of matrix elements between the one-electron orbitals is a strightforward matter and has been given elsewhere,[4] so it will be omitted here. The expression itself is made somewhat more manageable by a condensation of notation. Since the integral $(u_iu_j|O_2|u_ku_l)$ may be thought of as the Coulomb interaction between the "charge densities" u_iu_k and u_ju_l we shall denote it by $C(ik;jl)$. This notation does not indicate whether the orbitals involved are u's or v's, but no ambiguity results since the u's and v's always have different subscripts. In the expression (2-4) given below the indices i and j, when they appear in the same summation, will designate a bonded pair, and similarly for the indices k and l. If an index j appears in the summand of a summation over i this means that j is not a fixed index but is always the bonded partner of the index i which is being summed. The symbol (ij) under a summation sign means the orbitals i and j are bonded. i/k means the orbitals i and k are not bonded. An upper limit of N for a summation means that the summation is taken over all orbitals of the crystal, including the $1s$ orbitals, even if the summand is written in terms of only u_i and not both u_i and v_j, as in the first summation. An upper limit of $2N/3$ means that the summation is taken over all valence orbitals (but not $1s$ orbitals), and a limit of $N/3$ means that it is taken over all bonded *pairs* of valence orbitals.

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[4] L. A. Schmid, Thesis, Princeton University, 1953 (unpublished).

$$
\begin{aligned}
(\psi|H|\psi)/(\psi|\psi) \\
=\sum_{i=1}^{N}(u_i|\overset{\textcircled{1}}{O_1}|u_i)+\sum_{i=1}^{N}\sum_{k<i}^{N} C(\overset{\textcircled{2}}{ii};kk)+\sum_{\substack{i\\(ij)}}^{N/3} C(\overset{\textcircled{3}}{ij};ij) \\
-\tfrac{1}{2}\sum_{\substack{i=1\\i/k}}^{N}\sum_{k<i}^{N} C(\overset{\textcircled{4}}{ik};ik)+\frac{4A}{1+A^2}\sum_{\substack{i\\(ij)}}^{N/3}(u_i|\overset{\textcircled{5}}{O_1}|v_j) \\
+\frac{4A}{1+A^2}\sum_{\substack{i\\(ij)}}^{N/3}\Big[\sum_{k=1}^{N} C(\overset{\textcircled{6}}{ij};kk) \\
-\tfrac{1}{2}C(ij;ii)-\tfrac{1}{2}C(ij;jj)\Big] \\
+\frac{A^2}{2(1+A^2)}\sum_{\substack{i\\(ij)}}^{2N/3}\big[C(ii;ii)\overset{\textcircled{7}}{-}C(ii;jj)\big] \\
+\frac{16A^2}{(1+A^2)^2}\sum_{\substack{i\\(ij)}}^{N/3}\sum_{\substack{k<i\\(kl)}}^{N/3} C(\overset{\textcircled{8}}{ij};kl) \\
-\frac{2A}{1+A^2}\sum_{\substack{i\\(ij)}}^{N/3}\sum_{k=1}^{N} C(\overset{\textcircled{9}}{ik};jk) \\
-\frac{4A^2}{(1+A^2)^2}\sum_{\substack{i\\(ij)}}^{N/3}\sum_{\substack{k<i\\(kl)}}^{N/3}\big[C(ik;jl)\overset{\textcircled{10}}{+}C(il;jk)\big]. \quad (2\text{-}4)
\end{aligned}
$$

It will be noted that the first four terms give the energy for the case $A=0$. This constitutes a slight generalization of the energy expression for the case of localized bonds usually cited[5] as resulting from the SP theory in that the 1s orbitals, as well as the valence orbitals, have been taken into account.

In the case of the terms involving A, we take the point of view that when A assumes a non-zero value, that is when ionization is introduced into the bonds, a new charge density

$$\rho_A=\sum_{\substack{i\\(ij)}}^{N/3}\rho_{ij},$$

where $\rho_{ij}=[4A/(1+A^2)]u_iv_j$, is superimposed on the charge density for $A=0$, and the terms in (2-4) involving A give the energy associated with this new charge density. Since u_i and v_j are orthogonal, the net charge of ρ_{ij}, and consequently of ρ_A, is zero.

The origin of this charge density is most easily seen for the case $A=1$. In this case we are effectively dealing with Hund-Mulliken type orbitals having space parts $(1/\sqrt{2})(u_i+v_j)$. Squaring these orbitals gives rise to the sum of the squares of the localized orbitals plus cross-product terms. These cross-product terms constitute the new charge density.

The fifth term of (2-4) gives the change in kinetic energy resulting from the ionization correction, and the energy of Coulomb interaction between the nuclear charges and the charge density ρ_A. The sixth term gives the energy of Coulomb interaction of ρ_A with the electronic charge density of the crystal. This interaction may be interpreted in the following way: The charge density ρ_{ij} interacts with the entire electronic charge density of the crystal for the case $A=0$ from which, however, is subtracted half the charge density of the orbitals u_i and v_j. Thus, if we combine the sixth term with the Coulomb part of the fifth term, we may regard the charge density ρ_{ij} as interacting with the neutral atoms of the crystal, except that the two atoms adjoining ρ_{ij} have holes cut into their electronic charge densities through which ρ_{ij} can "see" some of the nuclear charge of these two atoms which would otherwise be shielded. (Calculation[4] shows that, as far as its interaction with the nuclear charges of the two adjoining atoms is concerned, ρ_{ij} behaves like an ordinary electronic charge density; that is, the interaction is attractive.) In this way ρ_{ij} tends to bind together the two atoms adjoining it. The seventh term of (2-4) is just the increase in Coulomb energy associated with ionizing a bond, that is crowding two electrons (with opposite spins) into a single orbital. The eighth term involves the Coulomb interaction between two different charge densities of the type ρ_{ij}. Because each of these has zero net charge, the Coulomb interaction between them is negligible. The ninth and tenth terms involve exchange-type integrals which are of the same order of magnitude, or smaller than the exchange integrals between non-bonded orbitals belonging to neighboring atoms which occur in the fourth term. The approximate value of the latter integrals has been evaluated[4] and found to be completely negligible. Thus the ninth and tenth terms may also be neglected.

The expectation value of the energy of the diamond lattice as given by (2-4) has been calculated for the observed lattice parameter (1.542A) using orbitals derived from the free atom orbitals for carbon given by Torrance.[6] The details of this calculation are given elsewhere,[4] but the essential results will be presented in the following sections. First, the result given by only the first four terms of (2-4) will be discussed. This corresponds to the application of the usual form of the SP theory.[3] The effect of the ionization correction associated with the terms of (2-4) which involve the parameter A will then be discussed.

3. ENERGY OF LATTICE FOR $A=0$

For the case of infinite lattice parameter, the lobe-like u's or v's of a particular atom may be expressed as linear combinations of the single 2s orbital and the three 2p orbitals occuring in the ^5S state of the free carbon atom. If we designate the space parts of the free atom orbitals by f^s, f_x^p, f_y^p, and f_z^p then the u's belonging to some particular atom may be written

$$
\begin{aligned}
u_1&=\tfrac{1}{2}[f^s+f_x^p-f_y^p-f_z^p],\\
u_2&=\tfrac{1}{2}[f^s+f_x^p+f_y^p+f_z^p],\\
u_3&=\tfrac{1}{2}[f^s-f_x^p-f_y^p+f_z^p],\\
u_4&=\tfrac{1}{2}[f^s-f_x^p+f_y^p-f_z^p].
\end{aligned}
\qquad (3\text{-}1)
$$

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[5] See, for example, reference 3, p. 248.

[6] C. C. Torrance, Phys. Rev. **46**, 388 (1934).

The v orbitals which point in the opposite directions from the u's would be defined in a similar way except that the signs in front of f_x^p, f_y^p, and f_z^p would be changed.

If the spins of the four lobes associated with an atom were all aligned then, in the case of infinite lattice parameter, the atoms of the lattice would all be in the ^5S state because a Slater determinant written in terms of the u's of (3-1) differs only by a unitary transformation from the Slater determinant written in terms of the f's. However, for the wave function defined in (1-5), there is no correlation whatever between the spins of two lobes of an atom. For this reason the energy of the wave function (1-5) for infinite lattice parameter is not the same as the energy of an aggregate of non-interacting carbon atoms in the ^5S state. The energy difference of these two situations has been calculated[4] with the help of the Coulomb and exchange integrals for carbon in the ^5S state given by Ufford[7] and is found to be 0.127 atomic unit per atom where (1-5) is the higher energy state. (1 atomic unit of energy equals 2 Rydbergs or 27.07 ev.) Using the observed value [8] for the energy difference between the ^5S state and the ^3P ground state of the free carbon atom, which is 0.154 atomic unit, we find that the wave function (1-5) for infinite lattice parameter has an energy 0.281 atomic unit per atom above the ground state of the free carbon atom. Let us call (1-5) for infinite lattice parameter the "reference level." The energy of (1-5) for the case of finite lattice parameter must be at least 0.281 atomic unit per atom below the reference level if binding is to be achieved.

For finite lattice parameter the u's and v's may still be written in the form (3-1) except that instead of the f's which are free atom orbitals, we must use functions which belong to certain irreducible representations of the point group T_d which describes the symmetry of the diamond lattice with respect to rotations and reflections. Which of the representations of T_d are involved is determined by the condition that the functions belonging to the representations go over smoothly into free atom functions as the lattice parameter is increased to infinity. These functions may be regarded as distorted versions of the free atom functions and as such may be designated g^s, g_x^p, g_y^p, and g_z^p.

In deriving (2-4) it was assumed that the u's and v's are all mutually orthogonal. The u's or v's belonging to a given atom are mutually orthogonal because the g's belong to different rows of irreducible representations and are consequently orthogonal. (It may be seen from (3-1) that if the f's or g's constitute an orthonormal system, the u's do also.) If the g's on neighboring atoms are mutually orthogonal, then the u's and v's on neighboring atoms are also orthogonal, thus fulfilling the condition assumed in deriving (2-4). We may construct a set of mutually orthogonal g's from the non-orthogonal f's by applying the orthogonality correction which was first given by Landshoff[9] and later generalized by Löwdin.[10] In Löwdin's notation this is, for the case of real orbitals

$$\varphi_\mu = \phi_\mu - \tfrac{1}{2}\sum_\alpha \phi_\alpha S_{\alpha\mu} + \tfrac{3}{8}\sum_{\alpha,\beta} \phi_\alpha S_{\alpha\beta} S_{\beta\mu} - \cdots, \qquad (3\text{-}2)$$

where the φ's are mutually orthogonal orbitals constructed from the ϕ's which are not, and

$$S_{\mu\nu} = (\phi_\mu | \phi_\nu) - \delta_{\mu\nu}; \quad \delta_{\mu\nu} = \begin{matrix} 1 & \mu = \nu \\ 0 & \mu \neq \nu \end{matrix}. \qquad (3\text{-}3)$$

If we neglect ϕ's in (3-2) which are multiplied by factors of order $(S_{\mu\nu})^2$ except for terms involving ϕ_μ (the leading orbital in the expansion), we obtain the form of the orthogonality correction used by Landshoff.

$$\varphi_\mu = \phi_\mu[1 + \tfrac{3}{8}\sum_\alpha (S_{\mu\alpha})^2] - \tfrac{1}{2}\sum_\alpha \phi_\alpha S_{\alpha\mu}. \qquad (3\text{-}4)$$

Landshoff showed that the φ's are normalized (if the ϕ's are) to terms of order $(S_{\mu\nu})^3$ and are mutually orthogonal to the extent that $\frac{3}{4}\sum_\alpha S_{\mu\alpha}S_{\alpha\nu}$ and higher order terms are negligible. In our case the φ's are to be identified with the g's and the ϕ's with the f's.

In applying (3-4), only first-nearest neighbors have been taken into account. By concentrating on a g function belonging to some particular atom, which may be called the "central atom," with the help of group theory, the orbitals entering into the orthogonality correction which belong to atoms that are first-nearest neighbors of the central atom may be expressed as a sum of products of radial and angular functions expressed in terms of coordinates centered on the central atom. Using Torrance's free atom functions for carbon,[6] the radial functions in these expansions may be plotted graphically. Thus we obtain the g's in terms of such expansions. The matrix elements of the first term of (2-4) may be expressed in terms of matrix elements involving the g's. Using the expansions for the g's, these matrix elements may then be reduced to sums of one-dimensional radial integrals which may be evaluated graphically. The details of this calculation are given in reference 4. The results show that because the orthogonality correction makes the orbitals bumpier, the kinetic energy is greatly increased. This works against binding. In partial compensation for this increase in energy, there is an increase in the magnitude of the negative energy of the Coulomb interaction of the orbitals of an atom with the nuclear charge of that atom. This comes about because the effect of the orthogonality correction on an orbital is to increase its absolute value (and consequently its charge density) in the neighborhood of the nucleus of the atom to which it belongs and in the vicinity of neighboring atoms, but to decrease it in the region in between. Because of the weighting factor $1/r$ where r is the distance from the nucleus, the net effect as far as interaction of an orbital with the nuclear charge of its own atom is concerned is that of a net shift of charge toward the nucleus.

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[7] C. W. Ufford, Phys. Rev. **53**, 568 (1938).

[8] A. G. Shenstone, Phys. Rev. **72**, 411 (1947).

[9] R. Landshoff, Z. Physik **102**, 201 (1936).

[10] P. O. Löwdin, J. Chem. Phys. **18**, 365 (1950).

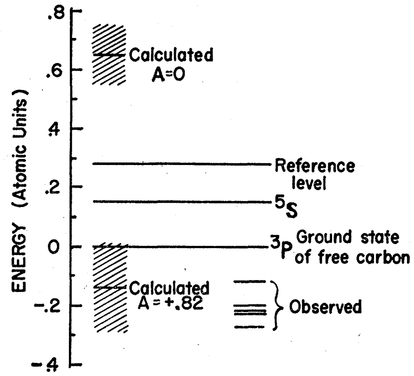

FIG. 1. Energy level diagram for diamond and free carbon. Uncertainty in calculations is indicated by cross-hatching.

The second, third, and fourth terms of (2-4) have also been evaluated by graphical means.[4] Restricting ourselves to only the most important energy contributions, we may give the following description of the situation for the case $A=0$. The orthogonality correction causes a large increase in the kinetic energy. This increase is only partially compensated for by an increase in the magnitude of the negative energy of Coulomb interaction of the orbitals with the nuclear charges of the atoms to which they belong. The Coulomb interaction between neighboring atoms contributes an appreciable negative energy which, however, is not large enough to overcome the effect of the increase in kinetic energy. The exchange integrals between bonded orbitals [third term in (2-4)] contribute a relatively small positive energy and the exchange integrals between non-bonded orbitals on neighboring atoms are found to be completely negligible. The resulting energy of the lattice for the case $A=0$ is $+0.37\pm0.1$ atomic unit per atom with respect to the reference level or $+0.65\pm0.1$ atomic unit per atom with respect to the ground state of free carbon. The uncertainty in this result arises both because of analytical approximations made in the course of the calculations, as well as from the fact that the calculations involve small differences of large numbers, particularly in the case of the Coulomb interaction between neighboring atoms.

The exact value of the observed cohesive energy with which this result is to be compared is still an open question.[11] In all, five values are defended by different workers in the field. They are 73, 125, 136, 141, and 170 kcal/mole or 0.117, 0.200, 0.218, 0.226, and 0.273 atomic unit per atom. The calculated result for $A=0$ is compared with the observed values in the energy level diagram of Fig. 1, which also shows the calculated result when allowance is made for the ionization correction ($A=0.82$).

It should be emphasized that the calculations have been carried out only for the observed lattice parameter and that, while in principle the methods used allow for a variation in the functional forms of the orbitals to minimize the energy, no such variation has actually been carried out. Rather the orthogonalized versions of Torrance's free atom orbitals[6] have been used directly in evaluating the matrix elements. However, varying the functional forms of the orbitals would have only a small effect and would do little to reduce the very large positive value for the energy of the lattice. It will now be shown, however, that the ionization correction ($A\neq0$) decreases this energy by the right amount to give agreement (within the accuracy of the calculation) with experiment.

4. IONIZATION CORRECTION

In order to apply the ionization correction, we must evaluate the matrix elements of the fifth, sixth, and seventh terms of (2-4). It has been mentioned previously that the eighth, ninth, and tenth terms are negligible. Once these matrix elements have been evaluated, we may minimize the energy with respect to A. The calculations show[4] that the energy is minimum for

$$A=+0.82\pm0.06, \tag{4-1}$$

and that the contribution to the lattice energy of the kinetic energy part of the fifth term is -0.69 atomic unit per atom while the contribution of the Coulomb part of the fifth term together with the sixth term is -0.25 and the contribution of the seventh term is $+0.15$. The total contribution of the ionization correction is thus -0.79 atomic unit per atom yielding for the energy of diamond -0.14 atomic unit per atom with respect to the ground state of the free carbon atom. Because it turns out that the calculations for the ionization correction are more sensitive to errors in the orthogonality correction than the calculations for the case $A=0$, the uncertainty in the result is correspondingly greater. However, because the various errors involved arise from independent sources, they may be combined in the manner for random errors which allows for some cancellation. The estimated uncertainty in the final result for the energy of diamond is ±0.15 atomic unit per atom. The calculated energy of diamond for the case $A=+0.82$, together with the uncertainty, is shown in the energy level diagram of Fig. 1.

For $A=1$ we find that the contribution of the ionization correction is -0.77 atomic unit per atom which differs by only a negligible amount from the minimum value of -0.79. This means that a calculation of the cohesive energy for the observed lattice parameter using the single-determinant wave function of the "semi-generalization" of the Hund-Mulliken (HM) method yields substantially the same result as a calculation based on the more general wave function (1-5). While this is true for the observed lattice parameter and probably also for smaller parameters, it is not true for

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[11] The experimental situation with regard to the cohesive energy of diamond is reviewed very briefly, with references to the literature, in Appendix B of reference 4. The work prior to 1947 has also been reviewed by H. D. Hagstrum, Phys. Rev. **72**, 947 (1947).

large lattice parameters. The reason for this is well known.[12] It is simply that when we use orbitals which are spread over several atoms, we are automatically introducing into the wave function ionized states, i.e., states in which some atoms have too many, and others too few electrons, but the crystal as a whole stays electrically neutral. These ionized states remain in the wave function even when the lattice parameter is increased to infinity with the result that we calculate too large an energy for the case of infinite lattice parameter. This would not happen if we were to use the more general wave function (1-5) because in this case we could remove the ionized states by setting $A=0$.

The negative sign of the kinetic energy contribution of the fifth term of (2-4) may be understood most easily in terms of the HM-type orbitals. When we go over from orbitals localized about single atoms to HM-type orbitals spread over two atoms, the orbitals necessarily become smoother with a resultant decrease in kinetic energy. The signs of the two Coulomb contributions of the ionization correction are apparent from the discussion in Sec. 2.

5. CONCLUSIONS

Since the energy for the case $A=1$ differs only by a negligible amount from that for $A=0.82$ and since it has been shown that the general wave function (1-5) reduces in the case $A=1$ to a single Slater determinant of one-electron functions similar to those employed in the HM approach to the hydrogen molecule in that each of the functions is spread over the two orbitals of a bonded pair, the following rough explanation of the nature of the binding in diamond may be given: When the free carbon atoms are brought together to form the diamond lattice, the localized orbitals become distorted in order that they might be orthogonal to orbitals on neighboring atoms. This distortion causes an increase in kinetic energy which outweighs the negative energy associated with the Coulomb interaction between neighboring atoms and the negative energy which results because the orthogonality correction brings about a net displacement of the charge of the orbitals of an atom closer to the nuclear charge of that atom. By going over from orbitals localized about single atoms to HM-type orbitals spread over two atoms a decrease in kinetic energy is brought about as well as a change in the Coulomb energy which favors binding. The two effects are of just the right magnitude to achieve the desired binding. The change in Coulomb energy may be interpreted as resulting from the redistribution of charge density associated with the transition to HM-type orbitals. In the case of HM-type orbitals the charge density tends to concentrate more between bonded atoms and, by its interaction with the nuclear charges of the atoms, hold them together. This explanation of the binding is very rough and omits many smaller contributions to the energy which are of both signs and thus tend to cancel. These contributions, however, have been taken into account in the calculations.

The most striking aspect of the calculation is its direct analogy with the corresponding calculation[1] for the hydrogen molecule which, for a HL wave function built on orthogonal orbitals, shows that an energy per atom greater than the energy of a free hydrogen atom in its ground state results. The present calculation shows that for a wave function which is the generalization of the HL function using orthogonal orbitals [(1-5) with $A=0$], the same thing happens in diamond. The calculation for hydrogen shows that satisfactory results can be obtained by mixing some of the ionized-molecule state with the HL function built on orthogonal orbitals, and it turns out that satisfactory results are also achieved when the corresponding thing is done for diamond. Finally, in the case of the hydrogen molecule, it is evident that a HM function built on orthogonal orbitals gives satisfactory results because this wave function may easily be shown to be identical with a HM function built on non-orthogonal orbitals, and the results obtained with such a function are about as satisfactory as the results obtained using a HL function built on non-orthogonal orbitals. The present calculation shows that a generalization of the HM function for hydrogen built on orthogonal orbitals also gives satisfactory results in the case of diamond.

As a by-product of the calculation, the total exchange energy per atom of the valence orbitals has been calculated for a wave function of the form of a single Slater determinant of localized HM-type orbitals. It may be shown[4] that this is equal to the exchange energy of valence orbitals for a Slater determinant of Bloch-type functions which are constructed from linear combinations of the localized HM orbitals, the valence orbitals in this case being the Bloch-type functions in the valence bands. It is found when this is compared with the exchange energy for free electrons that, to within the accuracy of the calculation, the two are equal. The exchange energy per atom for the Bloch-type functions is -1.43 ± 0.1 atomic units as against -1.39 atomic units for free electrons. Herring and Hill have shown[13] that an approximate equality of the exchange energy of Bloch waves with that of free-electron functions is to be expected in the case of monovalent metals. The present results indicate that this approximate equality is valid in much more general cases.

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[12] See, for example, J. C. Slater, Quarterly Progress Report, Solid State and Molecular Theory Group, Massachusetts Institute of Technology, July 15, 1952 (unpublished), p. 27.

[13] C. Herring and A. G. Hill, Phys. Rev. **58**, 132 (1940).