

## Alternant Orbitals in Crystals\*

G. DERMIT

*General Telephone and Electronics Laboratories, Incorporated, Bayside, New York*

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Löwdin's alternant orbital method is applied to  $2n$ -electron systems. The total wave function expressed in terms of these orbitals can be changed continuously from a single determinant of doubly occupied orbitals to a linear combination of many determinants consisting of singly occupied orbitals. The energy is an explicit function of  $n$ , and the transition to crystals is obtained for large  $n$ . Electrons of opposite spin are kept apart through ionic interactions depending on the spin coupling of electrons, i.e., the system spin state. Two spin states are of interest: the valence-bond singlet consisting of electron-pair bonds with zero spin, and a "parallel-spin" singlet which splits the system into two groups, each having  $n$  electrons with parallel spins. In covalent crystals consisting of atoms having several valence electrons in an unfilled shell, the valence-bond singlet does not allow for the parallel spin coupling of these electrons. The parallel-spin state does, and correctly permits the system energy to go to its required asymptotic value for infinite lattice parameter. Numerical applications to the binding energy of diamond are carried out by means of an approximate set of orthogonalized atomic orbitals based on the tetrahedral orbitals of carbon. Improved estimates of the correlation error in diamond could be expected with more accurate sets of orbitals and integrals.

## INTRODUCTION

IN solids, the single-determinant wave-function approximation based on doubly occupied molecular orbitals (MO) fails to account for the Coulomb interactions between electrons. Although electrons having parallel spins are kept apart in accordance with the Pauli principle, the assignment of two electrons in one MO allows the electrons to approach each other more closely than Coulomb repulsion would actually permit. This gives rise to the "correlation error": the energy of the single-determinant state is higher than the actual energy of the system. The error becomes apparent for large lattice spacings when the energy approaches an asymptotic value higher than the total energy of the free atoms.

Various approaches for improved approximations utilizing a form of singly-occupied or semilocalized orbitals have been proposed. Singlet wave functions in this case can no longer be represented by one Slater determinant, and consequently, it becomes necessary to construct an appropriate linear combination of many Slater determinants, as well as choose a proper spin state from a large number of possible singlets. A total singlet wave function consisting of individual singlet bond wave functions, has been proposed by Hurley, Lennard-Jones, and Pople.<sup>1</sup> Each bond joining a pair of atoms is assumed to be made up of a two-electron localized function. If the latter is constructed from a pair of semilocalized orbitals, one obtains a total wave function which depends on the degree of semilocalization. This scheme permits the total wave function to be changed continuously from complete localization giving a valence bond function, to complete lack of localization giving a single determinant, and in this manner accounts for the repulsion of electrons.

Schmid<sup>2</sup> has applied this method to the calculation of the cohesive energy of diamond using singlet electron pair bonds corresponding to the covalent structure of this crystal. The semilocalization of the atomic orbitals (AO) for all the bonds could be adjusted with a single parameter. The AO's within any two different bonds were made orthogonal, but the AO's within each bond were made nonorthogonal, which gave rise to desirable ionic interactions within each bond. However, Schmid also showed that this valence bond function runs into a different difficulty. When the orbitals in the bonds are localized to their respective atoms, the spins near an atomic core do not line up as they should, but remain completely arbitrary. This defect causes the infinite lattice spacing energy of a single valence bond function for diamond to be also considerably higher than the energy of the free atoms.

According to Hund's rule, a number of atomic electrons in a shell which is half or more than half empty line up their spins. The forces leading to complete spin alignment in free atoms must be very substantial because the energy required to destroy this spin coupling can be several electrons volts, as we shall see in the next section in the case of carbon. It may be expected that these forces also play a role in solids. Hence, an improvement over a single valence bond function may be sought in an approach that incorporates some degree of spin correlation between bonds. Löwdin<sup>3</sup> constructed a spin state which is a sort of an "antiferromagnetic"-type singlet. The degree of spin alignment between non-bonded electrons is made variable, depending on the semilocalization of the orbitals. In fact, when the orbitals are completely localized the electronic spins about each atom are completely parallel. It has been shown quite generally that this 'parallel-spin' state for infinite lattice parameter does give the proper asymptotic energy of free atoms.

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<sup>1</sup> A. C. Hurley, J. Lennard-Jones, and J. A. Pople, *Proc. Roy. Soc. (London)* **A220**, 446 (1953).

<sup>2</sup> L. A. Schmid, *Phys. Rev.* **92**, 1373 (1953).

<sup>3</sup> P. O. Löwdin, *Phys. Rev.* **97**, 1509 (1955).

Löwdin also introduced semilocalized MO's or alternant orbitals which are particularly suitable in electronic systems consisting of two subsystems with identical symmetry. The MO's in this method are made to alternate from atom to atom, a given MO attaining large amplitudes on the atom sites of one sublattice and small amplitudes at the sites of the other sublattice. If opposite spins are assigned to the two sets of orbitals, the Coulomb interaction between electrons of opposite spin can be accounted for by adjusting a parameter controlling the localization of the MO's which can be changed continuously from doubly-occupied into singly-occupied orbitals. In the next section we shall show that the semilocalized MO's and the semilocalized AO's are formally similar, the same type of a single parameter controlling the degree of semilocalization in both. We shall refer to both types as alternant orbitals, referring to semilocalized MO's as AMO's, and the semilocalized AO's as LAO's. All types of alternant orbitals used in this work will be based on a set of  $N$  orthogonalized AO's (OAO) which may be constructed either by applying Wannier's method<sup>4</sup> to the one-electron MO's obtained by solving the Hartree-Fock equations, or by applying Löwdin's orthogonalization scheme<sup>5,6</sup> to a set of  $N$  atomic orbitals which in the case of diamond belong to an excited state of the free atoms.

The AMO procedure using partly nonorthogonal functions is equivalent to introducing a special configuration interaction (CI) among strictly orthogonal states, with the advantage that its effects can easily be visualized in the study of correlation and spin alignment in solids. It has been applied to the benzene molecule,<sup>7</sup> where the results account for 85% of the correlation energy predicted by the CI treatment,<sup>8</sup> and very recently to the allyl<sup>9</sup> radical where 98.8% of the correlation energy computed by the CI function<sup>10</sup> has been accounted for.

The successful results obtained in molecules such as benzene, where a wave function somewhat superior to the single-determinant function has been obtained without carrying out an extensive CI calculation, make the application of the relatively simple alternant orbital method to crystals of particular interest because CI calculations in crystals are very difficult to carry out. As a first step in this direction it is necessary to calculate the parallel spin state energy formula for an arbitrary degree of localization of the alternant orbitals, and for an arbitrary number of electrons.<sup>11</sup> Such a general energy

expression is applied here to diamond by making use of OAO's and integrals computed by Schmid<sup>2</sup> for his valence-bond spin state. The energies for the two states are compared.

### ALTERNANT ORBITALS

This section introduces the concepts of importance with alternant orbitals, and shows that AMO's based on a linear combination of OAO's lead to a wave function differing only by a unitary transformation from a valence-state wave function based on LAO's.

Let us consider a system of  $N=2n$  electrons represented by two sets of localized OAO's  $\phi_i$  and  $\phi_{i+n}$ , with  $i=1\cdots n$ . Each set of orbitals belongs, respectively, to sublattice  $i$  and sublattice  $i+n$ . The  $2n$  conventional MO's formed as linear combinations of OAO's can be classed into pairs, with orbital energies belonging to symmetric positions in the lower and upper halves of the energy band. The excited orbital is obtained from the lower energy orbital by changing the signs of one set, say the  $\phi_{i+n}$  orbitals.

If the  $n$  lowest energy MO's are

$$\sum_{i=1}^n (\phi_i + \phi_{i+n}) C_{ij}, \quad (1)$$

where  $j=1\cdots n$ , the corresponding higher energy excited MO's will be

$$\sum_{i=1}^n (\phi_i - \phi_{i+n}) C_{ij}. \quad (2)$$

Let us assume an arbitrary angle  $\theta$ , and form the combinations

$$\psi_j = \sum_{i=1}^n \{(\cos\theta + \sin\theta)\phi_i + (\cos\theta - \sin\theta)\phi_{i+n}\} C_{ij}, \quad (3)$$

$$\psi_{j+n} = \sum_{i=1}^n \{(\cos\theta - \sin\theta)\phi_i + (\cos\theta + \sin\theta)\phi_{i+n}\} C_{ij}, \quad (4)$$

which are Löwdin's AMO's.<sup>12</sup> When  $\theta=0, 45^\circ, 90^\circ$ , respectively, we have: the  $n$  orbitals (1) from the lower half of the energy band, the  $2n$  completely localized MO's with  $n$  orbitals localized in the  $i$  sublattice and  $n$  orbitals in the  $i+n$  sublattice, and finally the  $n$  orbitals (2) from the upper half of the band. Generally, for  $0 < \theta < 90^\circ$  the  $\psi_j$  orbitals are semilocalized on the one sublattice and the  $\psi_{j+n}$  semilocalized on the other sublattice. All the orbitals except the  $\psi_j, \psi_{j+n}$  pairs are orthogonal. The nonorthogonality factor of the latter is

$$\int \psi_j \psi_{j+n} dx = \cos 2\theta \equiv A. \quad (5)$$

We are primarily interested in the modification of the AMO's that is applicable to the valence bond method. Since the orbitals (1) and (2) are orthogonal, the co-

<sup>4</sup> G. Wannier, Phys. Rev. **52**, 191 (1937).

<sup>5</sup> P. O. Löwdin, J. Chem. Phys. **18**, 365 (1950).

<sup>6</sup> P. O. Löwdin, J. Chem. Phys. **19**, 1570 (1951).

<sup>7</sup> T. Itoh and H. Yoshizumi, J. Phys. Soc. Japan **10**, 20 (1955).

<sup>8</sup> R. G. Parr, D. P. Craig, and I. G. Ross, J. Chem. Phys. **18**, 1561 (1950).

<sup>9</sup> H. H. Dearman and R. Lefebvre, J. Chem. Phys. **34**, 72 (1961).

<sup>10</sup> O. Chalvet and R. Daudel, J. Chem. Phys. **49**, 629 (1952).

<sup>11</sup> It has recently come to our attention that a general energy expression has been given in an unpublished report by P. O. Löwdin, J. deHeer, and R. Pauncz, University of Florida Report No. 9, 1960 [J. Chem. Phys. (to be published)].

<sup>12</sup> P. O. Löwdin, Advances in Phys. **5**, 160 (1956).

efficients  $C_{ij}$  form a unitary,  $n$  by  $n$ , matrix  $C$ . We can now write (3) and (4) in the matrix form,

$$\begin{pmatrix} \psi_j \\ \psi_{j+n} \end{pmatrix} = \begin{pmatrix} (\cos\theta + \sin\theta)C & (\cos\theta - \sin\theta)C \\ (\cos\theta - \sin\theta)C & (\cos\theta + \sin\theta)C \end{pmatrix} \begin{pmatrix} \phi_i \\ \phi_{i+n} \end{pmatrix}, \quad (6)$$

where  $\psi_j$ ,  $\psi_{j+n}$  and  $\phi_i$ ,  $\phi_{i+n}$  stand for column matrices that include all the orbitals, i.e.,  $i, j = 1 \cdots n$ . The transformation matrix of (6) is not unitary, but if (6) is transformed by a unitary transformation, the matrix elements of the Hamiltonian operator are not affected by the transformation because the Hamiltonian is a Hermitian operator. If we multiply (6) by the unitary matrix

$$\begin{pmatrix} C^\dagger & 0 \\ 0 & C^\dagger \end{pmatrix}, \quad (7)$$

we obtain

$$\begin{pmatrix} (\cos\theta + \sin\theta)I & (\cos\theta - \sin\theta)I \\ (\cos\theta - \sin\theta)I & (\cos\theta + \sin\theta)I \end{pmatrix} \begin{pmatrix} \phi_i \\ \phi_{i+n} \end{pmatrix}, \quad (8)$$

where  $I$  is a unit matrix of dimension  $n$ . These are the desired localized alternant orbitals (LAO)'s, given explicitly in normalized form by

$$\begin{aligned} \chi_i &= [(\cos\theta + \sin\theta)\phi_i + (\cos\theta - \sin\theta)\phi_{i+n}]/\sqrt{2}, \\ \chi_{i+n} &= [(\cos\theta - \sin\theta)\phi_i + (\cos\theta + \sin\theta)\phi_{i+n}]/\sqrt{2}. \end{aligned} \quad (9)$$

Clearly, Löwdin's AMO's can be transformed without loss of generality into localized functions extending only over pairs of electrons. This viewpoint is particularly of interest in applying Löwdin's approach to crystals with localized bonds such as diamond. In particular it shows that Schmid's semilocalized AO's are equivalent to AMO's if both sets are constructed from the same basic set of orthogonalized atomic orbitals for an alternant system.

### LAO's for Diamond

For both types of semilocalized orbitals, the LAO's and the AMO's, the over-all electronic structure of a system is directly traceable to atomic or localized electrons belonging to certain states of the free atoms. The major requirement is that the AO's should belong to a state of the free atom which has the same electronic orbital symmetry as the lattice.

In diamond the appropriate free-atom state to fulfill the symmetry requirement cannot be the ground state of carbon. This has an electron configuration of  $(1s)^2(2s^2)(2p_x)(2p_y)$ , and is described<sup>13</sup> by the triplet term  $^3P_0$ . It is impossible to form a tetrahedrally bound system with the pair of  $p_x$ ,  $p_y$  orbitals. Thus the ground state of carbon can only give rise to a divalent state,<sup>14</sup>

because it contains only two electrons with unpaired spins.

The experimental facts indicate the occurrence of tetravalent carbon. For instance the  $\text{CH}_4$  molecule, from physical evidence from its rotation-vibration spectrum, has four equivalent valence bonds arranged in tetrahedral symmetry at  $109^\circ 28'$  to each other. To achieve this symmetry the electron-configuration must be an excited one. The first excited-electron configuration of carbon<sup>15</sup> is  $(1s)^2(2s)(2p_x)(2p_y)(2p_z)$  or  $sp^3$ , where the lowest energy term is the quintet state  $^5S_2$  (the subscript is the  $J$  quantum number, i.e., the sum of the orbital angular momentum and the spin vectors). This state has four parallel-spin, unpaired electrons. The energy of its  $2s$  electron is close to the energy of the  $2p$  electrons and the four orbitals can combine linearly to form four tetrahedrally symmetric orbitals. The tetrahedral state of carbon has been calculated<sup>15</sup> and found by experiment<sup>16</sup> to lie  $33735.2 \text{ cm}^{-1}$  or  $96 \text{ kcal/mole}$  above the ground level. Generally, states of tetrahedral symmetry can be obtained only by two types of "hybridization" of electronic configurations,<sup>17</sup> the  $sp^3$  and the  $d^3s$ . An examination of the atomic levels of carbon<sup>18</sup> shows that the  $sp^3$  state mentioned before is the only configuration that can yield tetrahedral valence. Similarly for other tetrahedral crystals such as Si and Ge, the only atomic states with the desired symmetry in their electronic configuration turn out to be also  $sp^3$ s. Si atoms have just one  $sp^3$  state,  $48399.15 \text{ cm}^{-1}$  above their ground state, and Ge atoms have their lowest  $sp^3$  term,  $55473.6 \text{ cm}^{-1}$  above ground.<sup>18</sup> It is interesting to note that, in contrast to carbon, Si and Ge atoms do not have free quintet states at all. Their  $sp^3$  configurations contain triplet states, with two electrons among four having coupled spins. This coupling is apparently destroyed when the atoms approach each other to form the tetravalent crystals of Si and Ge.

The valence state of carbon comes about by the overlap of the tetrahedral orbitals of neighboring atoms. When two nearest-neighbor orbitals overlap strongly enough to form "perfectly-paired" bonds with anti-parallel spins, the spin coupling of the  $^5S$ -state orbitals is destroyed completely. This valence state of carbon is  $3.46 \text{ eV}$  above the  $^5S$  state<sup>19,20</sup> (and about  $7.64 \text{ eV}$  above the  $^3P$  ground state), solely because it lacks spin coupling. The valence state is not a spectroscopically observable state and could not exist in the free carbon atom because the spins of its four electrons must be random with respect to each other. Thus, random spins in this case violate Hund's rule completely.

<sup>15</sup> R. F. Bacher and S. Goudsmit, Phys. Rev. **46**, 948 (1934).

<sup>16</sup> A. G. Shenstone, Phys. Rev. **72**, 411 (1947).

<sup>17</sup> See reference 14, p. 230.

<sup>18</sup> See reference 13, p. 144 V.I., and p. 135 V.II.

<sup>19</sup> H. H. Voge, J. Chem. Phys. **16**, 984 (1948).

<sup>20</sup> L. A. Schmid "Calculation of Cohesive Energy of Diamond" (Dissertation Series Publication 8088, Ann Arbor, Michigan), p. 43.

<sup>13</sup> C. E. Moore, *Atomic Energy Levels*, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1949), Vol. 1, p. 21.

<sup>14</sup> H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1944), p. 220.

So far we have considered only the natural AO's of the  $^5S$  state of carbon. Since these orbitals are non-orthogonal between neighboring atoms, they lead to well-known serious computational difficulties<sup>21</sup> when a valence-bond-type total wave function is constructed with them. By introducing orthogonalized AO's<sup>5</sup> the computational difficulties are circumvented. However, electrons in OAO's do not give bound states when paired with antiparallel spins,<sup>21</sup> because OAO's in a bond tend to accumulate the charge in the vicinity of the nuclei and deplete the bond centers causing the repulsion of the nuclei. On the other hand, LAO's restore the charge in the bond centers by introducing ionic or polar structures which cause electronic transitions from one atom to the other.<sup>22,23</sup> Thus, electrons in LAO's do in fact give bound states.

In diamond, the valence bond approach can now be described as follows: a singlet wave function is constructed by forming singlet bonds between neighboring-atom LAO's based on a set of OAO's which are constructed from the tetrahedral orbitals of carbon. This singlet state was used in the calculation of the cohesive energy of diamond.<sup>20</sup> Starting with the same set of OAO's, it is our purpose to introduce another singlet state offering the possibility of some spin alignment among electrons near the same atom, of course at the expense of modifying the singlet character of each bond. Since such spin alignment, if complete, corresponds to the proper state of a system of free  $^5S$  carbon atoms, it has the correct limit for large lattice separation and it is very likely that a certain amount of spin alignment may contribute to the over-all binding of the crystal.

### SPIN STATES

The problem of constructing the various spin states for molecules can be approached in a general way from the theory of groups.<sup>24</sup> Starting with a given set of singly occupied spin-orbitals  $u_1, u_2, \dots, u_N$ , product functions may be formed from  $U_0 = u_1(x_1)u_2(x_2) \dots u_N(x_N)$  by permutation of the electrons. There are altogether  $N!$  permutations which form a group whose regular representation is  $G$ . By a similarity transformation,  $G$  can be reduced completely to  $g_i$ -dimensional irreducible representations  $G_i$ , each appearing  $g_i$  times. When the spin is taken into account, the spin function of each electron being  $\alpha$  or  $\beta$ , the only  $G_i$ 's to be considered are the irreducible representations of  $G$  in a basis constructed from the  $2^N$  linearly independent spin functions. If  $G_i^s$  is a  $g_i$ -dimensional irreducible representation of  $G$  in a basis of the  $2^N$  spin-product functions  $\alpha_1\alpha_2 \dots \alpha_N, \alpha_1\beta_2 \dots \beta_N, \dots$ , etc., the spin-orbitals  $U_0$  provide a basis for the irreducible representation  $G_i \times G_i^s$ . Unfortunately, the construction of

such representations is very tedious. Explicit forms of matrices of irreducible representations were given by Serber<sup>25</sup> up to eight-electron singlet states, and by Yamanouchi,<sup>26</sup> who constructed representation matrices by making use of the branching diagram,<sup>27</sup> a pictorial display of adding the spins of electrons one by one. Complete representation matrices by both methods have been compared for systems for which  $N+2S \leq 8$ , by Kotani.<sup>28</sup>

A more direct method than group theory for constructing singlet states is by allocating "bonds" between pairs of electrons. This valence bond method leads to the correct number of  $N! / (\frac{1}{2}N)! (\frac{1}{2}N+1)!$  linearly independent singlets, but the states or canonical structures obtained in this way are not orthogonal.<sup>29</sup> Another method of constructing the singlets is by using Pratt's spin operator<sup>30</sup> for setting up all the orthogonal singlets represented in the branching diagram. This scheme shows, for an arbitrary number of electrons, how many states of a given multiplicity there are and what the parentage of each state is. The spin operator is a function of step-up and step-down operators which will be discussed in the next section.

### Projection Operators

The problem of constructing spin states by projection depends on the use of operators which are special functions of the electron spins and of  $S^2$ . A state of given multiplicity is generated by applying these operators on a single Slater determinant made up of  $N$  singly occupied orbitals. The projection of a spin state is accomplished with the aid of  $S^2$ , which is used to classify the eigenstates of the Hamiltonian and remove their spin degeneracy. The eigenvalues of the spin operator  $S^2$ , for a  $N=2n$  electron system, are  $l(l+1)$ , where  $l=n, n-1, n-2, \dots, 0$ . If  $\psi_l$  are the eigenfunctions of the spin operators  $S^2$  corresponding to the eigenvalues  $l(l+1)$ , then an arbitrary wave function, associated with the space of spin degeneracy, can be expanded as a linear combination of the complete set of  $\psi_l$ 's. An operator such as  $S^2 - k(k+1)$ , if applied on  $\psi$ , will have the effect of removing from the expansion of  $\psi$  the eigenfunction  $\psi_k$ . The singlet operator for  $l=0$  is

$$^1O = 1 + \sum_{m=1}^n (-1)^m S^{2m} / f(m) \quad (10)$$

where  $f(m)$  is a product of integers that depends on  $m$ .

### Projection of Slater Determinants

In order to make use of the operator (10) it is necessary to consider it in relation to the initial Slater deter-

<sup>21</sup> J. C. Slater, *Revs. Modern Phys.* **25**, 199 (1953).

<sup>22</sup> R. McWeeny, *Proc. Roy. Soc. (London)* **A223**, 63 (1954).

<sup>23</sup> R. McWeeny, *Revs. Modern Phys.* **32**, 335 (1960).

<sup>24</sup> R. Serber, *J. Chem. Phys.* **2**, 697 (1934).

<sup>25</sup> R. Serber, *Phys. Rev.* **45**, 461 (1934).

<sup>26</sup> T. Yamanouchi, *Proc. Phys.-Math. Soc. Japan* **18**, 623 (1936).

<sup>27</sup> E. Corson, *Perturbation Methods in Quantum Mechanics* (Hafner Publishing Company, New York, 1950), p. 189.

<sup>28</sup> M. Kotani, *Table of Molecular Integrals* (Maruzen Company, Ltd. Tokyo, 1955), p. 28.

<sup>29</sup> See reference 14, Chap. XIII.

<sup>30</sup> G. Pratt, *Phys. Rev.* **92**, 278 (1953).

minant upon which it operates. We shall only be interested in states that have an equal number of  $\alpha$  or  $\beta$  spins, that is, the starting function  $\psi$ , as well as its projections, will be states with  $S_z=0$ . Starting with  $2n$  spatial orbitals  $u_1(r_1), u_2(r_2) \cdots u_n(r_n), u_{n+1}(r_{n+1}) \cdots u_{2n}(r_{2n})$ , and the  $2n$  spin functions  $\alpha_1(s_1), \alpha_2(s_2), \cdots \alpha_n(s_n), \beta_{n+1}(s_{n+1}), \cdots, \beta_{2n}(s_{2n})$ , where  $r_1$  and  $s_1$  are the spatial and spin coordinates of electron 1, respectively, the initial Slater determinant can be expanded into a sum of products of two  $n$  by  $n$  determinants, one having spins  $\alpha$  and the other spins  $\beta$ . The total spin of both the  $\alpha$  and the  $\beta$  determinants is  $n/2$ , and the  $z$  component  $n/2$  and  $-n/2$ , respectively. Any spin operator

$$S = \sum_{i=1}^n (\mathbf{s}_i + \mathbf{s}_{n+i})$$

operating on  $\psi$  consists of two parts which are designated

$$\sum_{i=1}^n \mathbf{s}_i = S_A, \quad \sum_{i=1}^n \mathbf{s}_{n+i} = S_B.$$

$S_A$  always operates on the spins of the 1 to  $n$  spin-orbitals, giving identical results for each  $n$  by  $n$  determinant formed from the  $2n$  by  $n$  matrix. Similarly,  $S_B$  operates on the  $n+1$  to  $2n$  orbitals, giving identical results for each determinant. In view of these properties,  $\psi$  can be written as a special matrix product of  $n$  by  $2n$  matrices,

$$\begin{aligned} \psi &= \frac{1}{[(2n)!]^{1/2}} \begin{vmatrix} \phi_A \\ \phi_B \end{vmatrix} \\ &= \frac{1}{[(2n)!]^{1/2}} \phi_A(S_A = \tfrac{1}{2}n, M_A = \tfrac{1}{2}n) \\ &\quad \times \phi_B(S_B = \tfrac{1}{2}n, M_B = -\tfrac{1}{2}n), \end{aligned} \quad (11)$$

where  $M_A$  is the eigenvalue of  $(S_A)_z$ . The initial Slater determinant in this product form is easier to follow with respect to the spin operations of interest in this work.

The study of the effects of the projection operator (10) on the initial Slater determinant requires establishing the effect of  $S^2$  and its powers operating on  $\phi_A \cdot \phi_B$ . Since  $S_z$  operating on determinants with equal number of  $\alpha$  and  $\beta$  spins gives zero, the expression for  $S^2$  is simplified to<sup>31</sup>

$$\begin{aligned} S^2 &= S^- S^+ \\ &= (S_A^- + S_B^-)(S_A^+ + S_B^+). \end{aligned} \quad (12)$$

We now introduce the various matrix elements of  $S_A^-, S_A^+, S_B^-,$  and  $S_B^+$ . Designating an eigenfunction of  $S$  as  $\theta(S, M)$ , where the symbols within the parenthesis indicate the eigenvalues of the spin and its  $z$  component, the matrix elements of the operators  $S^+$  and  $S^-$  are<sup>31</sup>

given by

$$S^+ \theta(S, M) = [(S-M)(S+M+1)]^{1/2} \times \theta(S, M+1), \quad (13)$$

$$S^- \theta(S, M+1) = [(S-M)(S+M+1)]^{1/2} \theta(S, M).$$

Making use of these expressions, the wave function that is generated by the operation of  $S^2$  on (11) is

$$\begin{aligned} S^2 \phi_A(S = \tfrac{1}{2}n, M = \tfrac{1}{2}n) \phi_B(S = \tfrac{1}{2}n, M = -\tfrac{1}{2}n) \\ = n \phi_A(S = \tfrac{1}{2}n, M = \tfrac{1}{2}n) \phi_B(S = \tfrac{1}{2}n, M = -\tfrac{1}{2}n) \\ + n \phi_A(S = \tfrac{1}{2}n, M = \tfrac{1}{2}n-1) \\ \times \phi_B(S = \tfrac{1}{2}n, M = -\tfrac{1}{2}n+1), \end{aligned} \quad (14)$$

which is  $n$  times (11) plus  $n$  times another wave function whose  $A$  and  $B$  matrices have the same spin  $S_A = S_B = \tfrac{1}{2}n$  but the  $z$  components of its spins,  $M_A = \tfrac{1}{2}n-1$  and  $M_B = \tfrac{1}{2}n+1$ , are changed by one. Because of the single-spin permutation, this wave function consists of the sum of  $n^2$  determinants which are discussed in more detail later. The symbolic notation for  $S^2$  operating on the state (11) is

$$S^2 = n + S_A^- S_B^+. \quad (15)$$

By applying  $S^2$  successively it is found that the projection operator can be expanded as a series<sup>30</sup> of the powers of  $S_A^- S_B^+$ , with respect to the chosen initial state (11).

### Generation of Spin States and Singlets by Projection

The general term in the series expansion of the projection operator (10) operating on the initial Slater determinant  $\phi_A \phi_B$  gives

$$\begin{aligned} [S_A^- S_B^+]^k \phi_A(S = \tfrac{1}{2}n, M = \tfrac{1}{2}n) \phi_B(S = \tfrac{1}{2}n, M = -\tfrac{1}{2}n) \\ = k! \frac{n!}{(n-k)!} \phi_A(S = \tfrac{1}{2}n, M = \tfrac{1}{2}n-k) \\ \times \phi_B(S = \tfrac{1}{2}n, M = -\tfrac{1}{2}n+k). \end{aligned} \quad (16)$$

Thus, a state of desired spin multiplicity is a linear combination of all the functions

$$\begin{aligned} \phi_A(S = \tfrac{1}{2}n, M = \tfrac{1}{2}n-k) \phi_B(S = \tfrac{1}{2}n, M = -\tfrac{1}{2}n+k) \\ = [(2n)!]^{1/2} T_k \end{aligned} \quad (17)$$

designated by  $T_k$ , where  $k=0, 1, \cdots, n$ , and the coefficient of each function depends on  $k$  as well as the spin multiplicity of the state  $l$ . The index  $k$  represents the number of spin permutations from matrix  $A$  to  $B$  in the initial Slater determinant. In fact,  $T_k$  consists of the sum of  $\binom{n}{k}^2$  determinants resulting from all the possible permutations of  $k$  spins.

The singlet state generated from a simple Slater determinant  $T_0$  is<sup>3</sup>

$$^1OT_0 = C_0 \sum_{k=0}^n (-1)^k \binom{n}{k}^{-1} T_k. \quad (18)$$

<sup>31</sup> E. Feenberg and G. Pake, *Notes on the Quantum Theory of Angular Momentum* (Stanford University Press, Stanford, California, 1953), p. 11.

This state forms the basis for our energy computations. It represents a special type of a singlet state consisting of two subsystems  $A$  and  $B$  of  $n$  electrons each. The electron spins within each subsystem are parallel, but the  $z$  components of the total spin of each subsystem are equal and opposite. In each  $T_k$  the  $z$  components of the spins of each subsystem satisfy the relation  $(S_A)_z = -(S_B)_z = \frac{1}{2}n - k$ , where  $k=0, \dots, n$ , with the total spin quantum numbers satisfying the relation  $S_A = S_B = \frac{1}{2}n$  for all  $k$ 's. The total singlet state (18) is a linear combination of functions having subsystem spin  $z$  components ranging from zero to  $\pm \frac{1}{2}n$ , each subsystem being in an average state of zero magnetization and having a total spin  $\frac{1}{2}n$ .

All these arguments concerning the various spin eigenvalues of the subsystems for the singlet (18) hold only when the orbitals are strictly singly occupied. In the case of doubly occupied orbitals, a spin permutation from two different orbitals gives identical rows and therefore the determinant becomes zero. Thus for doubly occupied orbitals, (18) gives  ${}^1OT_0 = C_0(n+1)T_0$ , and a single Slater determinant as expected with no spin alignment.

With singly occupied orbitals, the complete spin alignment in each subsystem gives (18) an antiferromagnetic character which, however, is different from a real antiferromagnetic system since (18) is invariant with respect to interchanges of spins between subsystems. We refer to (18) as the parallel-spin singlet, or the singlet state of maximum-spin alignment, in contrast to the valence bond singlet which is at the other extreme displaying no spin alignment.

In computing the energy of the system, it is necessary to select an appropriate singlet state. The total number of independent singlet states is  $N!/n!(n+1)!$ . Since there are  $\binom{N}{n}$  different ways of distributing the equal number of  $\alpha$  and  $\beta$  electrons over the  $N$  orbitals, it is possible to start with the  $T_0$ 's that correspond to each distribution, and generate  $\binom{N}{n}$  different spin states, a fraction  $1/(n+1)$  of which are linearly independent. Generally, this spin degeneracy could be treated by taking a linear combination of the various singlets and carrying out configuration interaction. In the approach used here, the correlation effects are accounted for by the use of alternant orbitals. The method is essentially equivalent to a form of configuration interaction involving various spin states in a special way. The configurations in the case of alternant orbitals are introduced by allowing the state to vary continuously from a single determinant of doubly occupied orbitals to the parallel-spin singlet state involving the full set of  $N$  orthogonal orbitals.

This special configuration interaction of the alternant orbitals can be carried out with various types of spin-states. We shall be interested in the valence bond singlet, primarily for the purpose of comparing the results ob-

tained from it<sup>20</sup> with our energy computations using the parallel-spin singlet.

#### PARALLEL-SPIN SINGLET STATE ENERGY

To derive a general formula for the energy of the parallel-spin singlet state for an  $N$ -electron system, and then compute the limiting energy as  $N$  becomes very large, it is necessary to find the transition matrices of the Hamiltonian between  $T_0$  and the  $T_k$ 's expressed in terms of alternant orbitals, as well as the scalar products of the  $T$ 's. The energy is<sup>3</sup>

$$E = \frac{\sum_{k=0}^n (-1)^k \binom{n}{k}^{-1} \int T_0^* H_{op} T_k(dx)}{\sum_{k=0}^n (-1)^k \binom{n}{k}^{-1} \int T_0^* T_k(dx)}, \quad (19)$$

where the Hamiltonian operator for an  $N$ -particle system consisting of a constant term and one-particle and two-particle operators is

$$H_{op} = H_{(0)} + \sum_{i=1}^N H_i + \sum_{i<j}^N H_{ij}. \quad (20)$$

The integral  $\int T_0^* T_k$  consists of a sum of  $\binom{n}{k}^2$  scalar products of Slater determinants. Similarly, the one-particle integral between  $T_0$  and any  $T_k$  is the sum of the  $\binom{n}{k}^2$  one-particle transition matrix elements. The same holds for the two-particle integrals between  $T_0$  and  $T_k$ . It is clear that once the orbitals are known, the energy can be calculated provided  $N$  is not very large. The calculation of the energy for a system with large  $N$ , or a crystal, can still be carried out if a substantial number of the orbitals are made orthogonal.

So far, all the singly-occupied orbitals  $u_i$  have been assumed to be nonorthogonal. In certain systems, such as the diamond lattice, there is a natural splitting of the crystal into two equivalent sublattices, dictating the choice of orbital types in the system. From the standpoint of the valence bond or AO approach, nonorthogonal orbitals forming covalent bonds between sublattices give rise to sufficient binding to account for the binding of the system, the degree to which the bond-orbitals overlap determining the energy of the system. However, if the orbitals are made to overlap completely, such as when two opposite-spin electrons occupy one MO consisting of the sum of two AO's, the Coulomb repulsion between the two electrons increases to the point where the binding of the system is affected adversely. These two competing tendencies of higher internuclear attraction and stronger electronic repulsion, which are present with strong overlaps, can be reconciled by the use of alternant orbitals. Such orbitals introduce a device of orbital adjustment to allow for Coulomb interactions by making bond-forming pairs of orbitals "alternate," such that each



which has  $2k$  nondiagonal  $A$ 's and  $2k$  zeros along the main diagonal. Since, by  $k$  interchanges of rows, (25) can be thrown into diagonal form the  $(n-1)$ -order diagonal minors are  $(-1)^k A^{2k}$ , and because of the  $\binom{n}{k}$  symmetrical determinants and  $2n-2k$  diagonal minors in each determinant, the sum of the diagonal integrals occur  $\binom{n}{k} (2n-2k)/2n$  times. Similarly, in (25) there are  $2k$  off-diagonal minors  $(-1)^k A^{2k-1}$ , which occur  $\binom{n}{k} 2k/2n$  times.

Combining these results, the one-particle Hamiltonian value is

$$\langle H_1 \rangle = \sum_{k=0}^n \frac{k A^{2k+1}}{n} \sum_{j=1}^n \int [\chi_j^* H_1 \chi_{j+n} + \chi_{j+n}^* H_1 \chi_j] + \sum_{k=0}^n \frac{(n-k) A^{2k}}{n} \sum_{j=1}^n \int [\chi_{j+n}^* H_1 \chi_{j+n} + \chi_j^* H_1 \chi_j]. \quad (26)$$

So far we have retained the alternant orbitals  $\chi$  that still contain  $A$ . To exhibit the  $A$  dependence explicitly, the alternant orbital integrals of  $H_1$  must be expressed in terms of the initial OAO's, i.e., the orbitals in (9). The one-particle energy,  $E_1 = \langle H_1 \rangle / D$ , becomes

$$E_1 = \sum_{j=1}^n \left\{ \int (\phi_j^* H_1 \phi_j + \phi_{j+n}^* H_1 \phi_{j+n}) + A \frac{n+1}{n} \frac{1-A^{2n}}{1-A^{2(n+1)}} \times \int (\phi_j^* H_1 \phi_{j+n} + \phi_{j+n}^* H_1 \phi_j) \right\}. \quad (27)$$

Note that for  $A=1$ , the case of doubly occupied orbitals with two electrons occupying the orbitals  $(\phi_j + \phi_{j+n})/\sqrt{2}$ , the coefficient of the off-diagonal integrals becomes unity.

### Two-Particle Energy

The general two-particle operator term for any  $k$  value has two types of integral factors. When the spin-orbitals have the same spin parts, the integral has a Coulomb term as well as an exchange term:

$$\int \chi_i^*(x_1) \chi_k(x_2) H_{12} [\chi_{i'}(x_1) \chi_{k'}(x_2) - \chi_{i'}(x_2) \chi_{k'}(x_1)] \times dx_1 dx_2 = (lk | E l' k'),$$

but if the spins are different, the integral factor consists of one term only:  $(lk | l' k')$ . The abbreviation for the Coulomb-exchange integral has been shown with the letter  $E$ .

### A. Diagonal Elements

The integrals associated with the unity elements in the first quadrant [see (25)] are Coulomb-exchange types  $(ij | E kj)$ , and  $(i+n, j+n | E i+n, j+n)$  for the

second quadrant diagonals. There are  $(n-k)$  identical-spin elements, which, taken two at a time, give  $\binom{n-k}{2}$  minors. Since there are  $\binom{n}{k}$  possible minors, the multiplicity of these integrals, as well as the  $(i, j+n | i, j+n)$ , is  $\binom{n-2}{k}$ . The multiplicity of  $(i, i+n | i, i+n)$  is  $\binom{n-1}{k}$ , and a coefficient  $(-1)^k A^{2k}$  comes about by the  $k$  row interchanges that diagonalize the minors.

### B. Off-Diagonal Elements

Off-diagonal integrals  $(ij | E i+n, j+n)$  and  $(i+n, j+n | E ij)$  associated with the right and left off-diagonal quadrants, respectively, are of the Coulomb-exchange type, since the spins of the electron pairs are the same. The multiplicity of these integrals is  $\binom{n-2}{k-2}$  and the associated minors  $(-1)^k A^{2k-2}$ .

The remaining off-diagonal integrals are of the exchange type. The multiplicity of  $-(i, i+n | i+n, i)$  and  $-(i, j+n | i+n, j)$  are  $\binom{n-1}{k-1}$  and  $\binom{n-2}{k-2}$ , respectively, and have the common minor  $(-1)^{k-1} A^{2k-2}$ .

### C. One-Diagonal and One-Off-Diagonal Elements

The integrals  $(ij | E i, j+n)$ ,  $(i+n, j+n | E i, j+n)$  and the integrals  $(ij | E j, i+n)$ ,  $(i+n, j+n | E j, i+n)$  both have multiplicities  $\binom{n-2}{k-1}$ , and minors  $(-1)^k A^{2k-1}$ ,  $(-1)^{k-1} A^{2k-1}$ , respectively.

The rest of the integrals  $(i, j+n | i+n, j+n)$  and  $(i, j+n | i, j)$  have the same multiplicities as the former minors.

### D. Integrals of Nonsymmetrical Determinants

There are  $\binom{n}{k}^2 - \binom{n}{k}$  nonsymmetrical permutation determinants in each  $T_k$ . A typical scalar determinant with one nonsymmetrical spin has two rows of all-zero elements limiting the possible nonzero minors to only six. Similarly, determinants with two pairs of nonsymmetrical spins will have four zero rows, and no minors at all. Thus nonsymmetrical permutation determinants of interest have asymmetry with respect to one pair of spins only.

To calculate the minors and the integral multiplicities, note that there are  $k(n-k)$  determinants deviating from symmetry by only one permutation. In each, there are three types of minors  $A^{2k}$ ,  $A^{2k-1}$ ,  $A^{2k-2}$  with the multiplicity  $\binom{n-2}{k-1}$ .

### E. Total Energy

The average value of the two-particle energy  $E_{12}$  is obtained by adding the various contributions and



summing over  $k$ :

$$\begin{aligned}
 E_{12} &= \sum_{k=0}^n (-1)^k \binom{n}{k}^{-1} \int T_0 \sum_{i < j} H_{ij} T_k(dx) / \sum_{k=0}^n A^{2k} \\
 &= Q \{ L_1 \sum_{i < j} (\chi_i^* \chi_j^* | EX_i \chi_j + \chi_{i+n}^* \chi_{j+n}^* | EX_{i+n} \chi_{j+n}) + L_1 \sum_{i \neq j} (\chi_i^* \chi_{j+n}^* | \chi_i \chi_{j+n}) + L_2 \sum_i (\chi_i^* \chi_{i+n}^* | \chi_i \chi_{i+n}) \\
 &\quad + L_3 \sum_i (\chi_i^* \chi_{i+n}^* | \chi_{i+n} \chi_i) + L_4 \sum_{i \neq j} (\chi_i^* \chi_{j+n}^* | \chi_{i+n} \chi_j) + L_4 \sum_{i < j} [(\chi_i^* \chi_j^* | EX_{i+n} \chi_{j+n}) + (\chi_{i+n}^* \chi_{j+n}^* | EX_i \chi_j)] \\
 &\quad + AL_5 \sum_{i < j} [(\chi_i^* \chi_j^* | EX_{i+n} \chi_j) + (\chi_{i+n}^* \chi_{j+n}^* | EX_i \chi_{j+n}) + (\chi_i^* \chi_j^* | EX_i \chi_{j+n}) + (\chi_{i+n}^* \chi_{j+n}^* | EX_{i+n} \chi_j)] \\
 &\quad + AL_5 \sum_{i \neq j} [(\chi_i^* \chi_{j+n}^* | \chi_{i+n} \chi_{j+n}) + (\chi_i^* \chi_{j+n}^* | \chi_i \chi_j) - (\chi_i^* \chi_{j+n}^* | \chi_j \chi_i) - (\chi_i^* \chi_{j+n}^* | \chi_{j+n} \chi_{i+n})] \\
 &\quad + L_5 \sum_{i \neq j} (\chi_i^* \chi_{j+n}^* | \chi_{j+n} \chi_i) + L_5 A^2 \sum_{i \neq j} (\chi_i^* \chi_{j+n}^* | \chi_j \chi_{i+n}) \}, \quad (28)
 \end{aligned}$$

where the constants  $Q$  and  $L$  are the following functions<sup>32</sup> of  $A$ :

$$\begin{aligned}
 Q &= 1/(A^{2n+2}-1)(A^2-1)n, \\
 L_1 &= \frac{2A^{2n+2}-A^4(n+1)n+2A^2(n^2-1)-(n-1)n}{(n-1)(A^2-1)}, \\
 L_2 &= nA^{2n+2}-A^2(n+1)+n, \\
 L_3 &= nA^{2n+2}-(n+1)A^{2n}+1, \\
 L_4 &= \frac{n(n-1)A^{2n+4}-2(n^2-1)A^{2n+2}+(n+1)nA^{2n}-2A^2}{(n-1)(A^2-1)}, \\
 L_5 &= \frac{(n-1)(A^{2n+2}-1)+(n+1)(A^2-A^{2n})}{(n-1)(A^2-1)}.
 \end{aligned} \quad (29)$$

If the alternant orbitals are taken to be of the LAO type, the functions can be expressed in terms of the OAO's given in (9). Introducing the abbreviations

$$\begin{aligned}
 (\phi_i^* \phi_j^* | \phi_k \phi_l) &= (ij|kl), \\
 \{(ij|kl)\} &= (ij|kl) + (ij|kl)^*, \\
 \{(i|i+n)\} &= (i|i+n) + (i|i+n)^*,
 \end{aligned}$$

the average energy expression for the system in the parallel-spin singlet state  $\psi$ , and for an arbitrary number of  $2n$  electrons, is given in the author's thesis.

The extension to crystals is straightforward. Calculating the limiting values of the various coefficients of the integral expressions, the crystal energy for  $n = \infty$  is

$$\begin{aligned}
 E_{\text{crystal}} &= \sum_i^n [(i|i) + (i+n|i+n) + A((i|i+n) + (i+n|i))] \\
 &\quad + \sum_i^n \left( [(ii|ii) + (i+n, i+n|i+n, i+n) + \{(ii|i+n, i+n)\}] \frac{A^2}{4} + 2\{ \{(ii|i, i+n) + (i, i+n|i+n, i+n)\} \frac{A}{4} \right. \\
 &\quad + (i, i+n|i+n, i) \frac{A^2}{2} + (i, i+n|i, i+n) \frac{2-A^2}{2} \Big) + \sum_{i < j}^n \left( (ij|ij) + (i+n, j|i+n, j) + (i, j+n|i, j+n) \right. \\
 &\quad + (i+n, j+n|i+n, j+n) + \{ \{(ij|i+n, j) + (ij|i, j+n) + (i, j+n|i+n, j+n) + (i+n, j|i+n, j+n)\} A \\
 &\quad + \{ \{(ij|i+n, j+n) + (i, j+n|i+n, j)\} A^2 - [(ij|ji) + (i+n, j+n|j+n, i+n)] \frac{2-A^2}{2} \\
 &\quad - \{ \{(i, j+n|j, i+n)\} \frac{A^2}{2} - \{ \{(ij|j+n, i) + (ij|j, i+n) + (i, j+n|j+n, i+n) + (i+n, j|j+n, i+n)\} \frac{A}{2} \\
 &\quad \left. - [(i, j+n|j+n, i) + (i+n, j|j, i+n) + \{ \{(ij|j+n, i+n)\} \frac{A^2}{2} \} \right]. \quad (30)
 \end{aligned}$$

The energy formulas (28) and (30) apply to the parallel-spin singlet state. (28) is general with respect

to either type of alternant orbitals, and (30) has been specialized to LAO's only. As it was noted in Sec. 4, it is possible to construct spin state configurations other than the parallel-spin singlet. This suggests the possibility of taking a linear combination of the various

<sup>32</sup> This formula is given in the report by Löwdin, deHeer, and Paunz referred to in the Introduction. Details of the derivation have been given in this author's thesis.

singlet states to achieve a better approximation to the wave function of the system. With alternant orbitals this is possible only if  $A=0$ , in which case the advantage of having an arbitrary parameter to adjust the orbitals for electronic correlation effects is lost. For  $A=0$ , and using a linear combination of various singlets, the spin-degeneracy of the system is removed in a usual configuration interaction approach utilizing a set of  $2n$  orthogonal orbitals. However, with  $2n$  alternant orbitals, configuration interaction with several singlet states cannot be carried out systematically when  $0 < A \leq 1$ , because in this case the various singlet states are no longer linearly independent. This situation becomes obvious for  $A=1$  when all the singlets become identical, reverting to the doubly occupied single Slater determinant state.

#### PARALLEL-SPIN AND VALENCE BOND STATES FOR DIAMOND

The known applications of alternant orbitals to molecules have been carried out with the aid of integrals taken from accurate CI calculations. Since such calculations for crystals do not exist, we shall use Schmid's valence-bond integrals. These are in the proper form applying to the parallel-spin state, but not being very accurate, the comparison is at best crude. In particular, the numerical improvement over the single-determinant, doubly-occupied orbital calculation that the alternant scheme is intended to achieve, may well be lost with the use of these integrals and the OAO's upon which they are based.

#### Valence Bond State

It must be noted that the designation of the valence bond function as a "two-electron" function is somewhat misleading. These localized orbitals are actually built from products of one-electron functions and they are in no way different from the determinantal products of one-electron orbitals. A two-electron function usually contains the quantity  $r_{12}$ , and cannot be factored out into one-coordinate orbitals.

The valence bond function can be written in very simple form in terms of the LAO's, see (9):

$$\psi_{VB} = \sum_P (-1)^P P X_1(1) X_{n+1}(n+1) \cdots X_n(n) X_{2n}(2n) \times (\alpha_1 \beta_{n+1} - \beta_1 \alpha_{n+1}) \cdots (\alpha_n \beta_{2n} - \beta_n \alpha_{2n}), \quad (31)$$

where the permutations apply simultaneously to the coordinates of the  $\chi$ 's and the indices of the spins. For purposes of comparison with the parallel-spin state, the system<sup>20</sup> energy can be expressed in our notation.

In both the parallel-spin and valence bond energy formulas the integrals are the same but the coefficients different. The values of the integrals determined by Schmid for the valence bond energy are used in the next section to examine the energy of the parallel-spin state in diamond.

#### Comparison of Binding Energies for Parallel-Spin and Valence Bond States

For infinite lattice parameter, the real system consists of free carbon atoms in their  $^5S$  state. The OAO's for both the valence bond and the parallel-spin function go over to the OAO's of tetrahedral carbon, but the spin couplings differ. Although the free-atom electrons in the parallel-spin state line up their spins, as they should since the OAO's are spectroscopically possible only in the  $^5S$  state, the electron spin couplings for the valence bond singlet go over to a higher energy and nonspectroscopic state having arbitrary spin coupling. Because of this difference, the two energy equations have different reference levels.

To compare the reference levels of the two states, i.e.  $A=0$  and infinite lattice parameter, it is noted that the kinetic energy and Coulomb interactions of orbitals with their own nuclei

$$\sum_{i=1}^n [(i|i) + (i+n|i+n)], \quad (32)$$

are the same in the solid as in the free atoms.<sup>33</sup> The OAO's or lobes in the free-atom case differ from the lobes in the solid in that they are distorted in the vicinity of neighboring nuclei. The total exchange interactions between lobes and  $1s$  orbitals

$$-\sum_{i < j}^n [(ij|ji) + (i+n, j+n|j+n, i+n) + (i, j+n|j+n, i) + (i+n, j|j, i+n)], \quad (33)$$

are also the same in the solid as in the free atom<sup>34</sup> and, therefore, we only need concern ourselves with the Coulomb and exchange interaction between valence orbitals. The total Coulomb interaction between lobes,

$$\sum_{i < j}^n [(ij|ij) + (i+n, j|i+n, j) + (i, j+n|i, j+n) + (i+n, j+n|i+n, j+n)] = 2.8512 \quad (34)$$

in atomic units (au),<sup>34</sup> is the same for both the valence bond energy and the parallel-spin state energy (30). The total exchange interaction between lobes for the valence bond state<sup>34</sup> is

$$-\sum_{i < j}^n (ij|ji) \frac{1}{2} = -0.1274, \quad (35)$$

and for the parallel-spin state is

$$-\sum_{i < j}^n (ij|ji) \frac{2-A^2}{2} = -0.1274(2-A^2),$$

which for  $A=0$  is twice (35). The sum of Coulomb and exchange interactions involving  $2s$  and  $2p$  orbitals of free carbon atoms in the  $^5S$  state is given by Ufford<sup>34</sup> as 2.5964 au. Consequently, the energy difference between

<sup>33</sup> Reference 20, p. 37.

<sup>34</sup> Reference 20, p. 42.

the valence bond function for infinite lattice parameter and an equal number of noninteracting atoms is

$$(2.8512 - 0.1274) - 2.5964 = 0.1274$$

and the difference for the parallel-spin function for  $A=0$ , is

$$(2.8512 - 0.1274 \times 2) - 2.5964 = 0,$$

which shows the parallel-spin state energy to go over to the energy of noninteracting atoms, and the valence bond state going over to the nonspectroscopic valence state of carbon.

To discuss binding, we need the energy of carbon atoms in the ground state. The observed difference between the  $^5S$  and  $^3P$  states of free carbon<sup>20</sup> is 0.154 au. Therefore, the reference level for the valence bond function is

$$0.154 + 0.127 = 0.28,$$

and for the parallel-spin function ( $A=0$ ) it is

$$0.154 + 0.127A^2.$$

We shall now determine the energy of the crystal. The changes in the kinetic energy and Coulomb interaction of orbitals with the nuclei, when the atoms are brought from their free state into the solid, are given by (32) provided the distorted orbitals in the solid are used. These energy contributions are the same for the valence bond and parallel-spin states. Similarly, the Coulomb interactions (34) for the lobes in the solid are the same for both states. Consider now the various exchange interactions in the solid. The exchange between bonded orbital pairs for the valence bond state are independent of  $A$  and for the parallel-spin state depend on  $A^2$ . The exchange interactions between central atom lobes and 1s orbitals are the same for both states. This is due to the fact that the 1s orbitals occur in bonded pairs and, consequently, their interactions with external electrons do not depend on the spin coupling of the external electrons. The exchange interactions between central atom lobes given by (35) and between nonbonded pairs of neighbors are, for the valence bond state, both independent of  $A$ , and for the parallel-spin state  $A^2$  dependent.

So far we have considered the un-ionized valence bond function with  $A=0$ . The energy in terms of OAO's is repulsive for both the valence bond and the parallel-spin states, although the latter is less repulsive. It will be possible to obtain binding as  $A$  is made different from zero or excitation of orbitals is introduced into the system. The exchange type integrals of orbitals on neighboring atoms should be of the order of the exchange integrals between nonbonded orbitals on neighboring atoms, and negligible. Similarly, the integrals that can be regarded as Coulomb interactions between charge densities  $\phi_i\phi_{i+n}$  and  $\phi_j\phi_{j+n}$ , being due to orbital pairs that are orthogonal, have zero charges, and as a result these integrals are assumed to be negligible.

Next, consider the integrals representing the Coulomb interaction of bonded pairs and the self-Coulomb energy of orbitals. The difference between these two interactions for the valence bond function gives  $0.38A^2/(1+A^2)$ , and for the parallel-spin state  $0.19A^2$ .

Finally, consider the last and very important integrals in (30) where the charge densities  $\phi_i\phi_{i+n}$  appear, and it is necessary to find their kinetic energies and their Coulomb interactions with all the normal charges  $\phi_i\phi_i$ . The assumption of the exchange hole is made in order to compute the Coulomb interaction of the charge density  $\phi_i\phi_{i+n}$  with the charge density

$$\sum_{j=1}^n [\phi_j\phi_j + \phi_{j+n}\phi_{j+n} - \frac{1}{2}(\phi_i\phi_i + \phi_{i+n}\phi_{i+n})],$$

which is the entire electronic charge density of the lattice diminished by one-half the charge density of  $\phi_i$  and  $\phi_{i+n}$ . Thus, the electronic charge clouds of the atoms  $i$  and  $i+n$  are diminished by  $\frac{1}{2}\phi_i\phi_i$  and  $\frac{1}{2}\phi_{i+n}\phi_{i+n}$ , respectively, which allows the charge density  $\phi_i\phi_{i+n}$  to see positive nuclear charges. The formation of this hole in the electronic clouds of the atoms leads to attractive Coulomb forces between the nuclei and  $\phi_i\phi_{i+n}$ , which gives a considerable amount of the binding of the atoms. In calculating the Coulomb attraction the simplifying assumption is made that the charge  $\phi_i\phi_{i+n}$  sees two nuclear point charges of  $+1/2$ , located at the atomic sites  $i$  and  $i+n$ . The total energy of the parallel-spin state is

$$E = 0.47 + 0.37A^2 - 0.96A.$$

Varying  $E$  with respect to  $A$  gives a minimum at  $A=1.2$ , which means the minimum energy of the system occurs for  $A=1$ , or for the single Slater determinant wave function. The nature of the approximations made in calculating the integrals and in constructing the OAO's make this computation only approximate. It is noted that for  $A=1$ , the doubly occupied orbital case, the parallel-spin state energy and the valence bond energy give identical energy.

The energy for the valence bond state is given by

$$E = 0.65 + 0.38A^2/(1+A^2) - 1.93A/(1+A^2),$$

and, as shown by Schmid, this has a minimum for  $A=0.82$ . Thus, Schmid's state leads to a somewhat lower energy. However, it must be pointed out that the over-all numerical reliability of  $\pm 0.15$  eV causes the final figure for the binding energy to range even into positive or repulsive values at its upper limit.

## CONCLUSION

To examine the results of the last section showing that the parallel-spin state has lowest energy for  $A=1$ , and also that its energy lies for some of the range of  $A$  above that of the valence bond state, we note, first of all, the outcome that the energy is monotonically decreasing as  $A$  approaches unity is surprising. The ex-

perience with molecular systems has been that whenever the alternant orbitals procedure is used, the wave function always improves and leads to a reduction in energy. However, the successful results achieved in applying alternant orbitals to certain molecules have only been possible where accurate estimates for the Coulomb and exchange integrals have been available. Precise integrals, originally computed in connection with CI calculations, have been used directly in AMO applications. In order to achieve comparable results in solids where CI calculations are nonexistent, it is necessary to construct an accurate set of OAO's starting with the basic atomic orbitals of the free atoms and to evaluate the various integrals with precision. The purpose of the alternant method is to achieve improvement in the wave function of the system and in its energy over that obtained with the simpler function of doubly occupied orbitals. The improvement is indeed obtained without going into extensive wave-function expansions of the type required with the CI method, but the need for accurate orbitals and integrals is still present.

There is no question that the values of the integrals, as shown by Schmid's own estimate of error in the final result, are only approximate. Concentrating on the two largest contributions alone,  $(0.37A^2)$  and  $(0.96A)$ , we find that the former would have to be increased by 0.11 unit or the latter to be decreased by 0.22 unit. Since Schmid's estimate of total reliability is  $\pm 0.15$  unit, the required integral changes which will introduce some degree of spin alignment into the system are not outside the realm of possibility.

If we concentrate on values of  $A$  near unity, we can study whether or not the trend of the parallel-spin state is in the direction which physical arguments, together with the evidence for Hund's rule, led us to expect. The main differences occur in the terms  $(0.37A^2)$  and  $(0.96A)$  in the equation for the energy. The first describes the Coulomb repulsion between orbitals on the same atom, and the second linear equation describes energies, Coulomb and exchange, within the bond. This term is, as it ought to be, the main source of binding, since it describes the sharing of electrons between two atoms, such that the electrons are in the field of both nuclei. As the double occupancy is described, two opposing effects ought to occur: less overlap with the neighboring nucleus decreases the attraction, less overlap with the neighboring valence electron decreases the correlation repulsion. The net effect initially should be more attraction because of the separation of the electrons and consequent reduction in the correlation error. Actually neither spin-state shows any significant improvement in this respect, probably because of the uncertainty in the numerical values.

Although for  $A=1$  the valence bond and the parallel-spin states both become the same single-determinant, doubly occupied orbital state, at the other extreme, for the dissociated atoms when  $A=0$ , the valence-bond function goes over to nonspectroscopic, high-energy

states of free atoms with  $^1S$  state orbitals but no spin coupling, whereas the parallel-spin function goes over to lower energy spectroscopic states of  $^3S$  carbon atoms having the appropriate spin coupling. In this respect the parallel-spin function gives a more accurate physical model.

The behavior of the spin functions is closely related to the balance of energy between electronic Coulomb repulsion that raises the energy of the system, and spin alignment that lowers it. Both effects come into play for  $A$  values less than one that split the doubly occupied orbitals into emerging pairs of "semi-singly occupied" orbitals. In the valence-bond case these semiseparated orbitals in the vicinity of each atom see only other electrons having completely arbitrary spins. This has the effect of leading to higher energy for the nonbonded electrons. In the parallel-spin function, the same emerging orbitals in the vicinity of each atom see only electrons with parallel spin which should lead to lower energy for these nonbonded electrons.

It must be noted here that it is not possible to take a linear combination of various spin states in the alternant scheme, because these states are not linearly independent when  $0 < A \leq 1$ . This is due to the semilocalized nature of the alternant orbitals. In a sense, the orbitals are only part of the time singly occupied, changing from double occupancy for  $A=1$  to single occupancy for  $A=0$ . Thus no matter what spin state we use, for  $A=1$  all of them revert to the single-determinant state.

We have been concerned with covalent bonds in systems containing more than one electron per atom. Since a pair of electrons in a bond repel each other by virtue of the Coulomb forces, the bond can no longer be regarded as neutral, and the spins of the electrons in the bond must interact with the spins of neighboring electrons. In the case of the unsaturated bond, where a single electron per atom may share a bond with many other electrons belonging to neighboring atoms, the same question of spin coupling may arise. Quite generally, if there are several equal-energy orbitals available in the system, the electrons prefer to occupy different orbitals and line up their spins. Since it takes a considerable amount of energy to destroy the spin coupling (several electron volts in carbon), the Coulomb interaction and the spin-coupling forces operating independently of each other should affect the structure of electrons in crystals.

In conclusion, it is noted that in alternant orbitals, the limited interactions with configurations accounting for Coulomb repulsions and spin couplings which are inherently built into the wave function, could lead to improved functions for crystals. Basic to this approach, however, is the need for an accurate set of OAO's and integrals for the system.

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