Linear-combination-of-atomic-orbitals, self-consistent-field method for the determination of the electronic structure of deep levels in semiconductors

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A linear-combination-of-atomic-orbitals (-molecular-orbitals), self-consistent-field method for the treatment of the electronic configuration of deep levels in semiconductors is described. It is applied to clusters of 17 and 47 carbon atoms and to clusters containing a substitutional (boron or nitrogen) impurity. It is shown that self-consistency brings large improvements over a noniterative procedure, such as the extended Hückel theory. We also propose a method to calculate the total energy of the cluster, necessary to take into account the lattice distortion that occurs around the defect. A detailed discussion of all the terms that have to be taken into account in the evaluation of the energy is made. Justifications of the validity of this calculation are given for 17 and 47 carbon atoms clusters, and the Jahn-Teller distortion associated with substitutional nitrogen in a 47 atoms cluster is determined.

I. INTRODUCTION

Various attempts have been made to treat the problem of the electronic states of a defect (or of an impurity) in a semiconductor.[1] Up to now only the effective mass theory and its extensions have been successful and for shallow impurities. For defects associated with deep levels the problem is complicated by the existence of a lattice relaxation and/or of a distortion around these defects. A general method to obtain the electronic states of a defect must therefore be able to provide a determination of the total energy of the system versus the position of the atoms in the lattice in order to treat at the same time electronic and atomic configurations. An approach having potentially the ability to give the total energy of the system is a molecular orbital (MO) technique applied to a cluster of atoms composed of the defect and of several atomic layers which surround it (in such a way that the wave function associated with the defect is confined to this cluster).

This concept of defect molecule has been introduced by Coulson and Kearsley[2] and first used in the extended Hückel theory (EHT) approximation by Moore and Carlson.[3] Applications of EHT on various defect clusters have been made by Messmer and Watkins (MW) and later by others to treat the vacancy in diamond[4] and in silicon,[5] substitutional nitrogen[4] and boron[6] atoms in diamond, the divacancy in silicon,[7] interstitials (carbon,[8] nitrogen[9] and hydrogen[10]) atoms in diamond, and sulfur in silicon.[11]

This EHT approximation applied to a cluster presents some deficiencies which make that the results obtained are only qualitatively valid. The results depend strongly on the cluster size[4,12,13] and on the boundary conditions.[4,12,14] Moreover the EHT approximation is a noniterative procedure which neglects the variations of the electron-electron interactions and therefore is only valid in the case of uniform electron distribution. It cannot handle charge transfers such as those which occur in the vicinity of a defect. Illustration of the limitation of the EHT to uniform electron distributions can be found when it is applied to partially ionic semiconductors (for instance, Birman *et al.*[15,16] must use in their calculation an unrealistic value of the empirical Wolfsberg-Helmholtz's constant K to fit experimental data) or even to some cases in group-IV semiconductors (for instance MW found that a relaxation by a breathing mode around a substitutional nitrogen atom results in a charge build up on this atom, which lowers the energy and therefore makes the cluster unstable).

A self-consistent-field (SCF) procedure should then be used since it will take into account charge transfers which will necessarily occur on a defect site and also because it will allow the treatment of the electronic states of various charge states of a defect, which EHT cannot do. MW consider[4] that a noniterative method is more adapted than a SCF procedure which would give a solution for the cluster *per se* and not for the crystal it is supposed to represent. We argue that, actually, a SCF procedure will be valid, if applied to a cluster large enough so that the atoms at the surface of this cluster are not modified by the presence of the defect in its centre and if the boundary conditions are such that the surface atoms are in the *same* state as in the perfect crystal. The first attempt to use a SCF pro-

cedure has been made by Watkins and Messmer[17] using the X_α scattered wave method. Unfortunately, Messmer and Watkins did not develop the results obtained with this method; they only applied it to the case of a neutral vacancy in diamond in order to evaluate and discuss the many-electron effects.

Another problem must be considered, the determination of the distortions which occur around the defect. As demonstrated by Watkins and Messmer,[6] the use of a linear-combination-of-atomic-orbitals (LCAO)-MO technique applied on a cluster of atoms surrounding the defect is a way of getting the atomic configuration since this technique allows relatively easily, through the calculation of the total energy of the system versus atomic position, the determination of the lattice distortion. Messmer and Watkins and subsequently others[4-13] applied this technique, in the extended Hückel approximation, on several kinds of defects in diamond and silicon. In the EHT approximation the total energy E_T of the system is taken to be the sum of the one-electron energies, i.e., the interactions between electrons are assumed to compensate *exactly* the interactions between nuclei. This assumption which, again, requires a perfectly uniform electronic distribution can lead to situations in which the cluster considered, even a "perfect" cluster, is unstable.

In this paper, we shall describe a LCAO-MO-SCF procedure based on a method proposed by Berthier, Millie and Veillard (BMV),[18] which takes into account interelectronic repulsions. The calculation is self-consistent and allows to treat the charge redistributions due to the presence of the defect.[19] The method is described in Sec. II. It is then applied to clusters of 17 and 47 carbon atoms. Energy levels and charge distributions obtained for the $17C$ and $47C$ clusters and for clusters containing substitutional boron or nitrogen atoms are given in order to justify the method and to show the improvements it provides compared to the non-iterative EHT method. In Sec. III, we consider the problem of the determination of the atomic configuration, i.e., of the lattice distortion and relaxation which occur around the defect. We calculate the Roothaan-Hartree-Fock energy of the system, i.e., we include in the expression of the energy the interactions between electrons and between nuclei. Verification of the validity of the calculation is made in the case of 17 and 47 carbon atoms clusters and results concerning the determination of the Jahn-Teller distortion which occurs around substitutional nitrogen in diamond are presented.

II. ELECTRONIC STRUCTURE

A. Description of the LCAO-MO-SCF method

1. Matrix elements of the Fock's operator

In the BMV method the Hartree-Fock equations, simplified by the use of the Mulliken approximation,[20] are applied to a set of valency atomic orbitals (AO). The diagonal elements of the Fock's operator can then be written

$$F_{pp} = W_p + \sum_{r \in P} q_r (J_{pr} - \tfrac{1}{2}K_{pr})$$
$$+ \sum_{r \in R \neq P} q_r (J_{pr} - \tfrac{1}{2}K_{pr}) - \sum_{R \neq P} \left\langle \chi_p \left| \frac{Z_R^* e^2}{\rho} \right| \chi_p \right\rangle. \tag{1}$$

Indices p and r correspond to AO's χ_p and χ_r; χ_p belongs to atom P, χ_r to atoms P or R. The quantities J_{pr} and K_{pr} are, respectively, the Coulomb and exchange integrals between χ_p and χ_r. Z_R^* is the effective charge of the core of atom R. q_r is the charge, in the Mulliken definition, of the χ_r AO.

The first term of expression (1), W_p, is the diagonal element of the sum of two operators: kinetic and Coulomb energy of the core of atom P. The second term $\sum_{r \in P} q_r (J_{pr} - \tfrac{1}{2}K_{pr})$ is an intra-atomic electronic contribution. The third term $\sum_{r \in R \neq P} q_r (J_{pr} - \tfrac{1}{2}K_{pr})$ is an inter-atomic electronic contribution. The fourth term $\sum_{R \neq P} \langle \chi_p | Z_R^* e^2 / \rho | \chi_p \rangle$ is the inter-atomic core contribution.

In the BMV method, expression (1) is written in terms of the net charge associated with each atomic orbital and of the interaction between the atomic orbital χ_p and the neutral atom R. Let n_r be the charge (or occupation number) associated with the AO χ_r in the neutral atom; the third and fourth terms of Eq. (1) become

$$\sum_{r \in P \neq R} (q_r - n_r)(J_{pr} - \tfrac{1}{2}K_{pr})$$

$$+ \sum_{R \neq P} \left[\left\langle \chi_p \left| \frac{-Z_R^* e^2}{\rho} \right| \chi_p \right\rangle + \sum_{r \in R} n_r (J_{pr} - \tfrac{1}{2}K_{pr}) \right] \tag{2}$$

BMV suggested that the above two terms can be neglected in formula (1). Indeed, the first of these two terms is small for covalent materials. The second one (a matrix element of a multipolar potential of neutral atoms, which will be later on called "penetration integral") is small and depends only slightly of the AO's under consideration.

In the following we shall also neglect the penetration integrals in expression (2). However we shall take into account their variations when we shall treat geometrical configuration problems.

We do keep the first term of expression (2) which plays a role in charge transfers between the defect and the surrounding atoms. Such a term is small (since $n_r \simeq q_r$) and we can neglect the exchange dicentre integral K_{pr}.

Finally Eq. (1) can be written

$$F_{pp} = W_p + \sum_{r \in P} q_r (J_{pr} - \tfrac{1}{2} K_{pr}) + \sum_{r \in R \neq P} (q_r - n_r) J_{pr} . \qquad (3a)$$

Equivalently, one can write F_{pp} as

$$F_{pp} = F_{pp}^0 + \sum_{r \in R} (q_r - n_r)(J_{pr} - \tfrac{1}{2} K_{pr}) , \qquad (3b)$$

the summation running over all the AO's. The quantity F_{pp}^0 is the value of the diagonal element of the Fock's operator in the EHT approximation. This form of F_{pp} explicits the variation of this matrix element with the charge redistributions. Expressions (3a) and (3b) are valid for closed shells systems. Actually we shall use them also for open shells (taking fractional MO's occupation numbers).

The off-diagonal elements of the Fock's operator are calculated using the Wolfsberg-Helmholtz approximation

$$F_{pr} = \frac{K}{2} S_{pr} (F_{pp} + F_{rr}) , \qquad (4)$$

where S_{pr} is the overlap integral $\langle \chi_p | \chi_r \rangle$. The empirical constant K is taken to be 1.75. This value,[21] also used by MW[4] will allow the comparison between the results obtained by the method described here and the results obtained by EHT.

2. Numerical values

The numerical values considered for the intra-atomic interelectronic integrals $J_{pr} - \tfrac{1}{2} K_{pr}$ are deduced from atomic spectra; we take the values given by Oleari *et al.*,[22] who calculated these quantities for the elements belonging to the second and third lines of the periodic chart. They used valence states of atoms in three consecutive charge states, such as C^-, C and C^+, or C, C^+ and C^{++}. For the matrix element W_p we have considered two types of values: in calculations noted "0", W_p—given by Oleari[22]—is calculated in order that the quantity $W_p + \sum_{r \in P} n_r (J_{pr} - \tfrac{1}{2} K_{pr})$ is equal to the electronegativity deduced from C, C^- and C^+; in calculations noted "MW" we have taken for W_p values deduced from the ionization potentials I_p (provided by Pople and Segal[23] and also used by MW) through

$$W_p = I_p - \sum_{r \in P} n_r (J_{pr} - \tfrac{1}{2} K_{pr}) . \qquad (5)$$

TABLE I. The two types ("MW" and "0") of W_p values (eV) used in the calculation.

	MW		0	
	2s	2p	2s	2p
C	−56.33	−45.53	−52.14	−40.88
B	−36.66	−30.06	−33.71	−25.21
N	−76.73	−62.91	−71.86	−58.50

This last choice allows the comparison of the results obtained at the first step in the iterative procedure ($q_r = n_r$ for all r), with those of MW. All the W_p values considered are given in Table I.

BMV have shown that the electronic structure obtained using MO calculations are correct only when the intra-atomic parameters W, J, and K are deduced from atomic configurations similar to the atomic configuration of the molecule (or cluster) considered. Consequently, we must take spectroscopic data corresponding to ionization states as close as possible to the charge states the atoms will have in the cluster. Therefore, for the study of covalent materials, in which small charge transfers (lower than about $0.5e$) occur, the more reasonable choice consists in taking the spectroscopic data related to neutral atoms. This choice is done by considering intra-atomic integrals W_p relative to the electronegativity.

The Coulomb integrals J_{pr} between AO's belonging to different atoms (separated by a distance ρ) are evaluated following Mataga[24,25]:

$$J_{pr} = e^2 / (\rho + r_0) , \qquad (6)$$

with

$$r_0 = \alpha e^2 / (J_{pp} + J_{rr}) \qquad (7)$$

and $\alpha = 2$.

The use of such an evaluation for these integrals provides a supplementary justification of the approximation expressed by relations (3a) and (3b), that is to say, the neglect of penetration integrals in Eq. (2).

Indeed, the evaluation of the penetration integrals given by (2) using semiempirical values for the J_{pr} terms and exact values for the nuclear terms $\langle \chi_p | Z^* e^2 / \rho | \chi_p \rangle$ provides too large numbers, thus inducing an important shift of the energies. Since the Wolfsberg-Helmholtz approximation is not invariant under a shift of the zero of energy, this would not lead to meaningful results. The AO's chosen are Slater-type orbitals[26] with an exponent deduced from Slater's rules.

3. Computational method

The self-consistency of the Fock's operator is realized through AO's charges. These charges

are calculated from eigenvectors after diagonalization, by Mulliken's analysis. Different procedures are used in order to obtain the convergence.

Some of the MO's are built on AO's belonging to atoms situated at the surface of the cluster. Some of these AO's give rise to dangling bonds and contain only one electron. Since the MO's are not localized, there is no MO built with only such dangling bonds. We therefore populated all bonds with two electrons and the corresponding value of n_r is corrected in order to insure the cluster neutrality.

Finally, in order to speed up matricial computation, we use symmetry orbitals built on the AO's. The change of basis is made through a program designed for C_{3v} and D_2 symmetry groups.

B. Results and discussion

We have treated clusters containing only carbon atoms in order to examine to what extent the method is able to give a good representation of the perfect crystal, and then clusters containing substitutional boron or nitrogen. These impurities are chosen because it is possible to compare the electronic structures obtained with available experimental data.

The substitutional impurity is at the centre of the cluster, i.e., all the atoms of the cluster are within a sphere centered on the substitutional site of the impurity (the central atom). A 17 atoms cluster is made of the central atom (first layer), the four nearest neighbors (second layer) and all the twelve second neighbors (third layer). A larger cluster including all the third neighbors should also include a few of the fourth neighbors (those which are inside the sphere containing all these third neighbors). The number of atoms in the cluster is then 47. We call fourth layer the set of these third and fourth neighbors. In order to have a cluster with all the fourth neighbors it should have been necessary to consider 99 atoms.

In the 17 atoms cluster the atoms of the third layer have three dangling bonds. In the 47 atoms cluster, the atoms of the fourth layer have one, two or three dangling bonds (for this reason the fourth layer will be divided in subsets noted 4', 4'', and 4'''). We shall first describe the results obtained with clusters containing 17 atoms and then the results obtained with clusters containing 47 atoms.

1. Clusters of 17 atoms

Table II gives the bottom of the conduction band (E_c), the top of the valence band (E_v), the valence band width (ΔE) and the position (E_T) of

TABLE II. Conduction (E_c), valence (E_v) bands, width of the valence band (ΔE), position of the impurity level (E_T) in a 17 atoms cluster. The energies are given in electron volts. The type of values ("MW" or "0", see text) taken for the W_p are indicated.

Cluster	E_c	E_v	ΔE	E_T	
$17C^a$	2.73	−8.57	18.18	$\cdots$	MW
$17C^b$	2.73	−8.84	20.25	$\cdots$	MW
$17C^a$	2.26	−3.86	14.98	$\cdots$	0
$17C^b$	1.98	−4.94	16.23	$\cdots$	0
$16C+B^a$	4.97	−8.85	18.0	−8.01	MW
$16C+B^b$	4.89	−9.08	18.4	−8.32	MW
$16C+N^a$	6.57	−8.62	20.84	−0.17	MW
$16C+N^b$	6.42	−8.66	22.39	−0.13	MW

[a] First step $(q_r = n_r)$.
[b] At the convergence.

the level associated with the substitutional impurity considered in the forbidden gap. Table III gives the charge distribution over the three different layers of atoms. In order to investigate the effect of self-consistency these results are given at the first step of the iterative procedure, for which $q_r = n_r$ (a) and after the convergence has been reached (b).

As shown in Table II, using MW values of W_p, we obtain a forbidden gap of ~11 eV and a valence band width of $\simeq 20$ eV. The electronic structure obtained is strongly dependent upon the W_p values considered since, with "0" values of W_p, we have $E_c - E_v \simeq 6$ eV and $\Delta E \simeq 16$ eV. These values have to be compared to the gap (8.7 eV direct, 5.5 eV indirect) and to the valence band width (21 eV) given by band structure calculations. The nitrogen level and the boron level are found respectively at $E_c - E_T \simeq 6$ eV and $E_T - E_v \simeq 0.6$ eV. The value found for the boron level has to be compared to the experimental value $E_v + 0.37$ eV. The value found for nitrogen is also in qualitative agreement with experiment since luminescence

TABLE III. Charge per atom (electron) for each of the three layers in a 17 atoms cluster. The types of value ("MW" or "0," see text), used for the W_p are indicated.

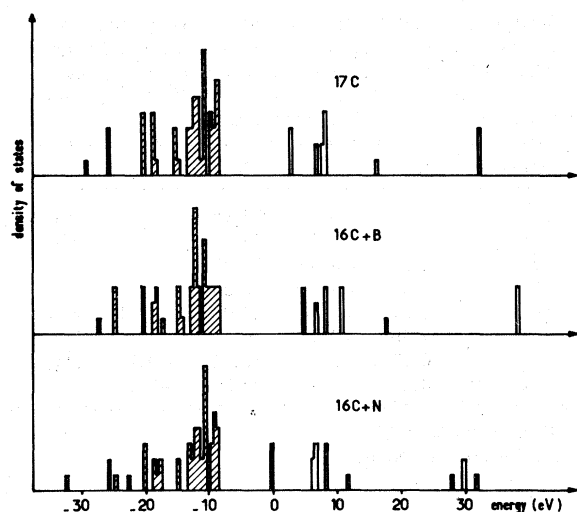| Cluster	1	2	3	
$17C^a$	4.20	3.67	4.09	MW
$17C^b$	4.10	3.82	4.05	MW
$17C^a$	2.40	3.62	4.26	0
$17C^b$	4.10	3.73	4.08	0
$16C+B^a$	2.45	4.01	4.04	MW
$16C+B^b$	2.75	3.99	4.02	MW
$16C+N^a$	5.82	3.55	4.08	MW
$16C+N^b$	5.41	3.76	4.04	MW

[a] First step.
[b] After convergence.

FIG. 1. Energy diagrams obtained for the 17C, 16C +B, and 16C+N clusters after the convergence has been reached (using "MW" values of W_p).

studies have shown this level to be deep in the gap ($\sim E_c - 4$ eV). Actually this (donor) level being triply degenerate should undergo a Jahn-Teller distortion which, as shown by MW,[4] will strongly modify its position in the gap. As mentioned earlier we shall treat distortions, including this case, in the third Section of this paper.

The results obtained for the 17C cluster at the first step are those reported by MW.[4] The results obtained for the 16C +N and 16C +B clusters cannot be directly compared since MW performed the corresponding calculations on 35 atoms clusters.

Self-consistency does not affect strongly the energy levels (the energy level diagrams are given in Fig. 1); it increases the valence band width by 10%. But Table III shows that self-consistency modifies in a non-negligible fashion (by $\sim 0.1e$) the charge distribution found at the first step. The atomic charges on the layers tend towards the value of 4e, which is the value they should have in the perfect crystal. The charge (4e within 2%) found on the atoms of the third layer, which are the surface atoms, indicate that the boundary conditions we have chosen are satisfactory.

The introduction of an impurity in the 17C cluster illustrates another advantage of the use of a SCF procedure. For both impurities a large charge redistribution is induced by the self-consistency: the charge differences found between the first step of the iteration procedure and the last one at which the convergence has been reached are 0.3 and 0.4e for boron and nitrogen,

respectively. In case of nitrogen the level E_T is initially triply degenerate (symmetry T_2 of the T_d group). There is one electron on this level: we choose to populate the MO having the symmetry A_1 in the C_{3v} subgroup. As a result the charges on the four nearest neighbors are not the same: three atoms are charged with 3.71e and the fourth is charged with 3.91e. Only the averaged charge is given in Table III. This choice has been made because a trigonal distortion will have to be considered in the study of the Jahn-Teller effect.

The charges on the surface atoms are modified by the presence of the impurity. This indicates that the size of the cluster is not large enough to contain the whole wave function of the impurity.

From the results described here it can be concluded that the size of the cluster is not large enough to allow a good representation of the electronic structure of a defect. But they illustrate clearly several advantages that a SCF procedure brings in, as compared to a noniterative method such as EHT used by MW.

2. Clusters of 47 atoms

The energy levels and charge distributions for the different clusters studied are given in Tables IV and V. These tables show clearly that the 47C cluster provides a reasonable representation of the perfect crystal. For the calculation performed with "0"'s W_p, the forbidden gap (5.14 eV) and the valence band width (21 eV) are the values expected from band structure calculations. The charges over the different atoms are the charges in the perfect crystal within 2%.

Self-consistency brings the same improve-

TABLE IV. Conduction (E_c), valence (E_v) bands, position of the impurity level (E_T) in a 47 atoms cluster. The energies are given in electron volts. The types of value (MW or "0," see text) taken for the W_p are indicated.

Cluster	E_c	E_v	E_T	
47C[a]	0.68	−8.49	···	MW
47C[b]	0.69	−8.61	···	MW
47C[a]	0.67	−4.65	···	0
47C[b]	0.70	−4.77	···	0
46C + B[a]	1.14	−8.51	−8.47	MW
46C + B[b]	1.12	−8.54	−8.41	MW
46C + B[a]	0.70	−5.11	−4.75	0
46C + B[b]	0.66	−4.85	−4.48	0
46C + N[a]	1.14	−8.51	−1.55	MW
46C + N[b]	1.13	−8.62	−1.50	MW
46C + N[b]	0.67	−4.63	−0.59	0
46C + N[a]	0.70	−4.78	−0.68	0

[a] First iteration.
[b] After convergence.

TABLE V. Charge per atom (electron) for each of the fourth layers in a 47 atoms cluster. The types of value ("MW" or "0," see text) used for the W_p are indicated.

Cluster	1	2	3	4	4'	4''	
47C [a]	3.99	4.13	3.85	4.02	4.02	4.07	MW
47C [b]	4.00	4.07	3.91	4.02	4.00	4.04	MW
47C [b]	4.00	4.07	3.85	4.03	4.01	4.09	0
46C + B [a]	2.49	4.45	3.85	4.00	4.01	4.04	MW
46C + B [b]	2.74	4.23	3.90	4.01	3.99	4.03	MW
46C + B [b]	2.55	4.25	3.84	4.03	4.01	4.08	0
46C + N [a]	5.62	3.93	3.87	4.02	4.02	4.07	MW
46C + N [b]	5.31	3.97	3.91	4.02	4.00	4.04	MW
46C + N [b]	5.41	3.96	3.85	4.03	4.02	4.09	0
46C + N [a]	5.63	3.95	3.78	4.02	4.06	4.13	0

[a] First iteration.
[b] After convergence.

ments as in the 17 atoms cluster. The energy levels are only slightly changed but the charge redistribution can reach up to $0.4e$. As in the 17C cluster "0" values of W_p provide a better description of the perfect crystal. The hypothesis taken for the boundary conditions appear to be quite satisfactory: all the surface atoms, although they have a different number of dangling bonds, have the same charge of $4e$, within 2%. We therefore have no need to investigate further the problem of the boundary conditions.

Introduction of a substitutional impurity changes slightly the energy gap. The energy levels obtained with "0"'s W_p can be directly compared with the experimental ones, since the gap provided in this case is nearly the experimental indirect gap. The acceptor boron level lies at $E_v + 0.36$ eV, practically the experimental value. The donor level associated with nitrogen is deep: $E_c - 1.26$ eV. Again this value should be strongly modified by the introduction of a Jahn-Teller distortion. The energy level diagrams are given in Fig. 2. The molecular orbital corresponding to the donor state localized on nitrogen has a pure $2p$ character. The square of the wave-function coefficients we determined for nitrogen and for the C_4 carbon neighbor situated on the ternary axis are given in Table VI. These coefficients, as shown in Table VI, are slightly modified by the iterations.

The reason the 47 atoms cluster gives a better representation than the 17 atoms clusters is due to the fact that it is large enough to contain all the wave function associated with the impurity. Indeed the charges on the atoms of the fourth layer are *not* modified *at all* by the introduction of the impurity. A modification occurs at the first step of iteration but the self-consistency increases the localization of the wave function which then becomes localized within the three first atomic layers.

III. ATOMIC CONFIGURATION

A. Evaluation of the Roothaan-Hartree-Fock energy of a cluster

In order to determine the stable configuration of a defect and of the atoms which surround it, we have to determine a minimum in the variation of the total energy of the cluster versus the position of the different atoms which constitute it. The exact expression of the total energy of the system in the Hartree-Fock approximation is

$$E_T = \sum_i \epsilon_i + R_N - \sum_{i,j}(J_{ij} - \tfrac{1}{2}K_{ij}) . \qquad (8)$$

In this expression, $\sum_i \epsilon_i$ is the sum over the occupied molecular orbitals (MO's), indexed by i, of the monoelectronic energies (i.e., the eigenvalues of F). The second term R_N is the repulsion energy between the atomic cores. The third term, corresponding to the Coulomb
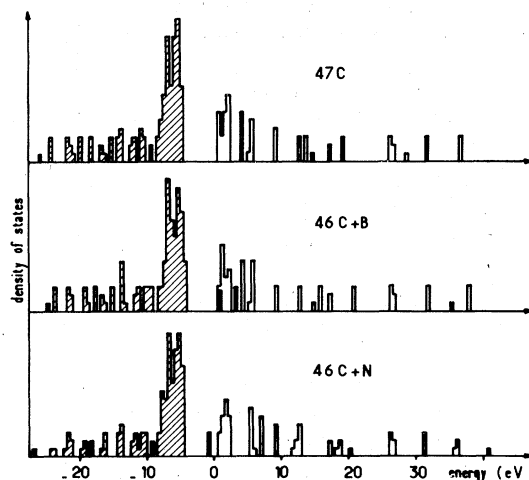

FIG. 2. Energy diagrams obtained for the 47C, 46C + B, and 46C + N clusters after the convergence has been reached (using "0" values of W_p).

TABLE VI. Wave-function coefficients determined by the calculation (using "0" values of W_p) for the nitrogen and the C_4 carbon neighbor on the ternary axis at the first iteration (a) and after convergence.

	a	b
N_{2s}	0.0	0.002
N_{2p}	0.28	0.29
C_{2s}	0.03	0.02
C_{2p}	0.42	0.41

and exchange integrals between the occupied MO's, is the repulsion energy between electrons, which is twice included in $\sum_i \epsilon_i$.

Let us consider now how the last two terms in expression (8) are evaluated. The $1s$ core AO's of different atoms have a negligible overlap, and R_N can be written

$$R_N = \sum_{R \neq P} \frac{Z_R^* Z_P^* e^2}{\rho_{RP}} = \sum_{r \neq p} n_r n_p N_{pr}, \qquad (9)$$

with

$$N_{pr} = e^2 / \rho_{PR}, \qquad (10)$$

where ρ_{PR} is the distance between R and P atoms, the cores of which bear respectively the net charges Z_R^* and Z_P^*. The last term is calculated using the Mulliken's approximation, which yields to

$$\sum_{i,j} J_{ij} = \frac{1}{2} \sum_{p,r} q_p q_r J_{pr}. \qquad (11)$$

The summation over the occupied MO's is transformed into a summation over the χ_p and χ_r AO's. The calculation of the exchange term $\sum_{i,j} K_{ij}$ is much more lengthy; we have performed it in some cases and we observed that, for the distortions to be considered in practice, the variation of $\sum_{i,j} K_{ij}$ is negligible compared to the variation of all other terms. Consequently, we shall neglect $\sum_{i,j} K_{ij}$ in the calculation of the variations of the total energy E_T.

The final expression of E_T is then

$$E_T = \sum_i \epsilon_i + \sum_{r \neq p} n_p n_r N_{pr} - \frac{1}{2} \sum_{r,p} q_p q_r J_{pr}. \qquad (12)$$

As indicated in Sec. II, the dicentre J_{pr} integrals are evaluated following Mataga,[24,25] i.e., using expressions (6) and (7) in which α can be an adjustable parameter. As was shown by Fisher-Hjalmars[27] and Sinanoglu,[28] the Mataga's formula provides indeed more realistic values for the J_{pr} integrals than the values calculated using Slater's parameters, adjusted on spectroscopic data.[29] In Sec. II we used $\alpha = 2$ in expression (7), which is a convenient value in the

limit $\rho \to 0$; we showed that this choice leads to very satisfying charge distributions on all cluster atoms.

B. Discussion

1. Introduction

We shall limit the calculation to lattice distortions around the defect which include only the first neighbors. The analysis in terms of vibrational eigenmodes gives the three following irreducible representations of the T_d group: the nondegenerate (symmetric) A_1 representation, often called "breathing mode," the twofold degenerate E representation, and the threefold degenerate (translational) T_2 representation. A displacement of the central atom of the cluster (the defect) belongs to the T_2 representation (translational mode) and therefore leads to a possible coupling between the displacement of the central atom and of its first neighbors.

Consider first displacements of the four nearest neighbors of the central atom in a cluster of 46 carbon atoms containing a nitrogen atom in its centre. Then the variation of E_T provides a stable configuration which corresponds to a rhomboedric distortion (depicted in Fig. 3), such that: C_1 atom $(1, -1, -1)$ is displaced of $(-v, 0, 0)$; C_2 atom $(-1, 1, -1)$ is displaced of $(0, -v, 0)$; C_3 atom $(-1, -1, 1)$ is displaced of $(0, 0, -v)$; C_4 atom $(1, 1, 1)$ is displaced of (v, v, v); where $v \sim 10\%$. But when this distortion is coupled with a (u, u, u) translation of the central atom, it appears that the energy surface $E_T (u, v)$ has no minimum
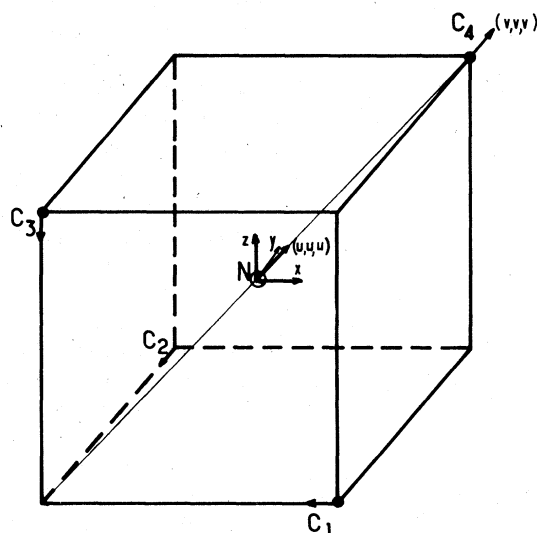

FIG. 3. Representation of the displacements of a nitrogen atom and of its four carbon neighbors in the T_2 distortion.
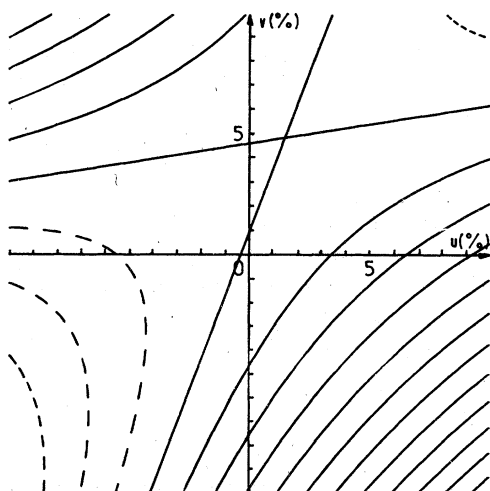
FIG. 4. Curves of constant energy of the surface E_T (u, v) for the $46C + N$ cluster, calculated using F_{pp} given by expression (3b). The energy difference between two adjacent curves is 1 eV. The curves are calculated, assuming E_T (u, v) is a second degree polynomial in u and v, from a least mean square fit on values of E_T determined for u, $v = 0$, $+ 10\%$, -10%. The surface E_T (u, v) exhibiting a saddle point, full lines are used for the curves corresponding to energies larger than the energy at the saddle point and for the asymptots, and dotted lines are used for curves corresponding to energies smaller than the saddle-point energy.

FIG. 5. Curves of constant energy of the surface R_N (u, v) core repulsion energy, given by expression (9) for the $46C + N$ cluster. Specifications are identical to those of Fig. 4. The fact that the saddle point does not coincide with the origin of the displacements u and v is due to the anharmonicity of the energy surface.

within a range of reasonable atomic displacements (the calculations have been performed for u or v values up to about 40%). The surface E_T (u, v) exhibits clearly a saddle point: E_T decreases both in the $(1, 1)$ and in the $(- 1, - 1)$ directions, although it exhibits minima for displacements corresponding to constant values of u or v (Fig. 4).

Such an instability, when the two modes of distortion are coupled, indicates that the evaluation of E_T presents some deficiencies. It is thus necessary to examine in detail the behavior of the three terms which contribute to E_T.

2. Variations of the different terms of the total energy

The one-electron energy term $\sum_i \epsilon_i$ exhibits a minimum. But, according to Lannoo,[30] the origin of such a minimum is related to the repulsive energy provided by the overlap between adjacent bonding orbitals and therefore a realistic evaluation of E_T cannot be limited to this term. Further illustration that the approximation $E_T \simeq \sum_i \epsilon_i$ is not physically realistic is provided by the comparison between the results described here and those obtained by Messmer and Watkins[4] when they investigated the same problem (a cluster containing a substitutional nitrogen atom):
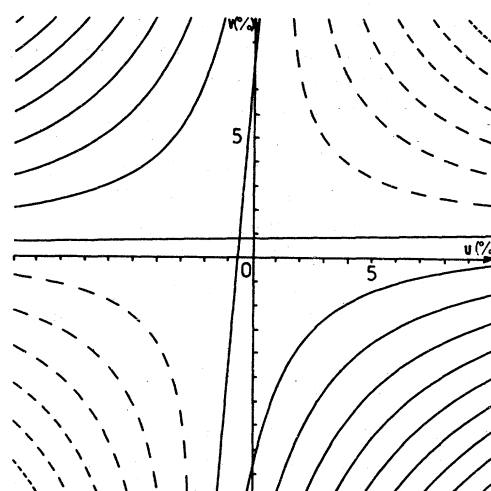
they found an energy curve E_T (u or $v =$const) with a curvature such that, when extrapolated, the energy would go through a maximum (see Table III in Ref. 4).

When examining the behavior of the two other terms which contribute to E_T, it can be easily seen that the decrease of the core repulsion R_N in the $(1, 1)$ direction (Fig. 5) is only partially compensated by the electronic repulsion energy. This led us to investigate the validity of the calculation of these two terms. Consider first the contribution to the energy due to core repulsions. The calculation of this energy versus the number of atomic layers in the cluster shows that the central atom and its first neighbors are responsible for 90% of the variation of the energy due to the (u, v) displacements. The third atomic layer, and the following layers which can be added to the cluster, close to spherical shells, give a nearly constant potential in the inner part of the cluster and therefore do not contribute significantly to the variation of E_T. The interactions between nearest neighbors play thus a dominant part in the instability. As a consequence, in the evaluation of the different interactions, it will be sufficient to analyze carefully the variations of the interactions for distances close to the first neighbors spacing (ρ of the order of 2.5 to 3 $a.u.$). As we indicated in Sec. III A, formula (9) provides a reasonable evaluation for R_N. The variations of R_N due to $1s$ core electrons can be evaluated, and are found to remain of the order of $1\%_{oo}$.

On the other hand, the variations of the electron-electron interactions, given by the J_{pr} integrals, are underestimated by the Mataga's formulas (6) and (7). The J_{pr} integrals depend on an adjustable parameter α which was first taken equal to two. Using a different value for α (1.5 or 1), we observed that the instability could actually be decreased. Indeed, it can be seen using expression (12) of E_T that a better compensation between the J_{pr} and N_{pr} terms is obtained with increasing J since, according to formula (6):

$$\partial J_{pr}/\partial \rho = (\partial N_{pr}/\partial \rho)(J_{pr}/N_{pr})^2 .$$ (13)

For the distance ρ corresponding to the interatomic distance and using $\alpha = 2$, one gets $\partial J_{pr}/\partial \rho \simeq 0.3(\partial N_{pr}/\partial \rho)$, a value very close to the ratio of the variations of the electron repulsion to the core repulsion for the total energy of the cluster. Consequently (i) the interactions between nearest neighbors are dominant and (ii) the atomic charges are not sensitive to distortions. Note that the value of $\partial J/\partial \rho$ for the Slater-type orbital ($\xi = 1.625$ for carbon $2s$ AO) is $\partial J/\partial \rho \simeq 0.8 \partial N/\partial \rho$.

However the charge distribution over the different atomic layers of the cluster is found to be less satisfactory when the value $\alpha = 1$ is used instead of $\alpha = 2$.

The same behavior is observed when the central atom is not a nitrogen atom but a carbon atom (see Fig. 6). We are therefore led to a more fundamental problem: is the method we use able to account for the stability of a cluster
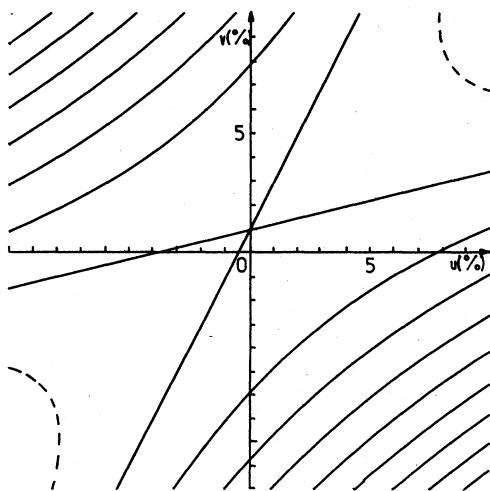

FIG. 6. Curves of constant energy of the surface E_T (u, v) for the 17C cluster, calculated using F_{pp} given by expression (3b). Specifications are identical to those of Fig. 5.

assumed to represent a perfect crystal? In order to answer this question, we shall analyze some of the approximations which are made in Sec. II.

3. Importance of the penetration integrals

We have shown that it was reasonable to neglect the penetration integrals in the determination of the electronic states of the cluster. We argued that, because these integrals are estimated using *semiempirical* values of J_{pr} and *exact* values for the nuclear terms $Z_R^* A_{pr}$ with

$$A_{pr} = \left\langle \chi_p \left| \frac{e^2}{\rho_{PR}} \right| \chi_p \right\rangle ,$$ (14)

this would introduce an error in their estimation larger than the error resulting from their neglect, and consequently a change in the eigenvalues and eigenvectors, since the Wolfsberg-Helmholtz's approximation is not invariant under a shift of the zero of energy. But the variations of these integrals with atomic displacements *should not* be neglected. In order to take into account only *the variations* of the penetration integrals from their undistorted geometry values, we introduce an additional term in the expression (3b) of the matrix element of the Fock's operator, which we now write down as follows:

$$F_{pp} = F_{pp}^0 + \sum_r q_r \left(J_{pr} - \frac{1}{2} K_{pr} \right)$$

$$- \sum_{r \in R \neq P} n_r A_{pr} + \sum_{r \in R \neq P} (n_r A_{pr} - q_r J_{pr})_0 .$$ (15)

The values of J_{pr} used here are the same as in the preceding calculation, i.e., semiempirical values. The index 0 on the last term means that the corresponding quantities are calculated for the undistorted geometry (perfect crystal)—i.e., the eigenvectors for the undistorted geometry are those obtained from expression (3a).

If we neglect multipolar effects, we have $J_{pr} < A_{pr} < N_{pr}$ for all interatomic distances (see Fig. 7). If we use the lower value $A_{pr} = J_{pr}$, we have the situation depicted above, which we found unsatisfactory because the J_{pr} values used are unable to balance the nuclear repulsion term. Let us then consider expression (15) using the upper value

$$A_{pr} = e^2/\rho_{pR} ,$$ (16)

i.e., assuming the strongest interaction possible between atomic orbital χ_p and atomic core R. Performing again the calculation on a pure cluster of 17C atoms, we obtain an energy surface $E_T (u, v)$ which exhibits the same symmetry elements than in the above situation, but the
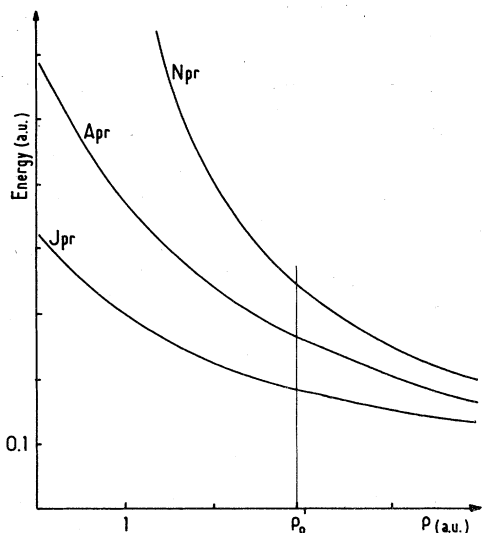
FIG. 7. Representation of the variations with the inter-atomic distance ρ of the different interaction laws. These variations are computed using Mataga's formula; if $2s$ Slater's orbitals for C or N atoms had been used, the A and J integrals would have been very close to e^2/ρ (within 1% and 3%, respectively) for $\rho \sim \rho_0$, the inter-atomic distance at equilibrium.

energy sign is different (see Fig. 8): the $u = -v$ displacements are unstable. We therefore conclude that the use of an e^2/ρ law for the interaction between atomic orbital χ_p and atomic core R provides a too large evaluation of A_{pr}, while the choice $A_{pr} = J_{pr}$ results in a too low evaluation of A_{pr} (Fig. 7).
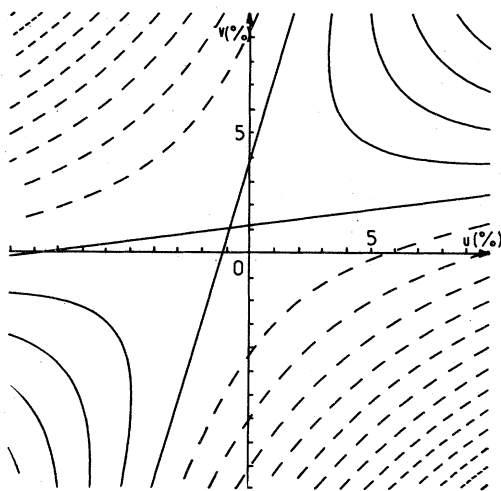
We are thus led to take for the A_{pr} terms a

FIG. 8. Curves of constant energy of the surface E_T (u, v) for the 17C cluster, calculated using F_{pp} given by expression (15), with $A_{pr} = e^2/\rho$. Specifications are identical to those of Fig. 6.

formula interpolated between the two choices described above. Let us now detail the reasons which guided our choice of an interpolation formula for A_{pr}. If, in a first approximation, we neglect exchange terms, the total energy E_T contains interactions between cores and electrons, between electrons and between nuclei which can be written, respectively, $-\sum_{p,r} q_p n_r A_{pr}$, $\frac{1}{2}\sum_{p,r} q_p q_r J_{pr}$, and $\sum_{p<r} n_p n_r N_{pr}$ in the Mulliken approximation. (Note that, when $\rho \to \infty$, J_{pr}, $A_{pr} \to N_{pr} = e^2/\rho$). For small charge transfers $(q_r \simeq n_r)$, the contribution to E_T for each electron pair is

$$Q = N_{pr} + J_{pr} - 2A_{pr} \cdot \tag{17}$$

As a result the approximations taken for J_{pr} and A_{pr} must be such that they provide reasonable values for their variations.[31] For instance, for first neighbors, $\partial Q/\partial \rho$ must be of the order of the corresponding value calculated for the best Slater type orbitals with a reasonable value of ξ. We thus chose an interpolation similar to the formula proposed by Momichioli[32] for the nuclear-nuclear repulsion terms (Momichioli takes $A_{pr} = J_{pr}$ and adjusts N_{pr} in order to get a reasonable value of $\partial Q/\partial \rho$):

$$A_{pr} = J_{pr}\exp(-\beta\rho) + (e^2/\rho)[1 - \exp(-\beta\rho)]. \tag{18}$$

This choice introduces an arbitrary parameter β. There are two or more ways to determine it: (i) either by considering the limit of A_{pr} when $\rho \to 0$, or (ii) by adjusting the value of $\partial Q/\partial \rho$ on the value given by Slater type orbitals. In the case (i), one obtains $\beta \simeq 0.07$ a.u. and in the case (ii), $\beta \simeq 0.8$ a.u. Actually, we verified that an energetically stable configuration for the perfect crystal is obtained in a range of β values which extends from 0.15 to 0.60 a.u. In the calculations performed, which will be described in the next Section, we used the value $\beta = 0.30$ a.u.

C. Results

The variations of E_T with T_2, E and A_1 distortions in a 17C cluster are given in Figs. 9 and 10. The energy surface E_T (u, v) for T_2 distortions in a 47C cluster is very similar in shape and amplitude to the surface given in Fig. 9 and is not represented. We obtain a minimum of energy for a zero distortion, i.e., the calculation is able to account for the stability of the system.

We then apply the calculation to the case of a nitrogen substitutional atom in a 47C cluster $(46C + N)$. The variations of $E_T(u, v)$ for the T_2 distortion show the existence of a Jahn-Teller distortion of about $u_m \sim -12\%$ and $v_m \sim -7\%$. Since the u_m and v_m have the same sign and are of the same order of magnitude, the distances
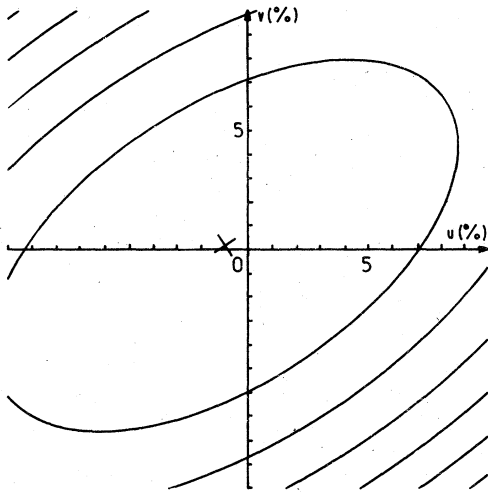
FIG. 9. Curves of constant energy of the surface E_T (u, v) for the $17C$ cluster, calculated using F_{pp} given by expression (15), in which A_{pr} is given by expression (18). The curves are calculated as those of Fig. 4. The energy difference between two adjacent curves is 1 eV. The fact that the center of the ellipse does not coincide with the origin of displacements u and v is due to the anharmonicity of the energy surface.

FIG. 10. Variations of the total energy of the $17C$ cluster with A_1 and E distortions.

between the nitrogen atom and its carbon neighbors are only slightly modified: the bonds are nearly identical to the bonds in the undistorted lattice. The curvature of the energy surface around the minimum energy provides the force constants (k_1, k_2, k_3) which can be used to deduce the vibrational modes of the nitrogen atom and its four neighbors. The nonlinear part of the energy is: $E_T = k_1 u^2 + k_2 u.v + k_3 v^2$ with $k_1 = 97.50$, $k_2 = -218.08$ and $k_3 = 201.14$ when E_T is expressed in eV and u, v in lattice constants (see Sec. III B 1 and Fig. 3).

Solving the Lagrangian equations for these five atoms we obtain two eigenmodes at: $\omega_1 = 1770$ cm^{-1} and $\omega_2 = 640$ cm^{-1}. Experimentally broad bands peaking at 1130 and 850 cm^{-1} are observed, the (weaker) last line being observed only in type-Ib diamond.[33] The difference between the ω_1 and ω_2 modes calculated and the experimental observation is not significant since the curvature of the energy surface is dependent on the value of the parameter β [see expression (18)] chosen.

As discussed in Ref. 4 a barrier height of ~ 0.7 eV can be estimated (from EPR linewidth study)[33] for the reorientation from one trigonal distortion to another. The calculated value of 0.5 eV we determine on the energy surface $E_T(u, v)$ compares favorably with this experimental result.

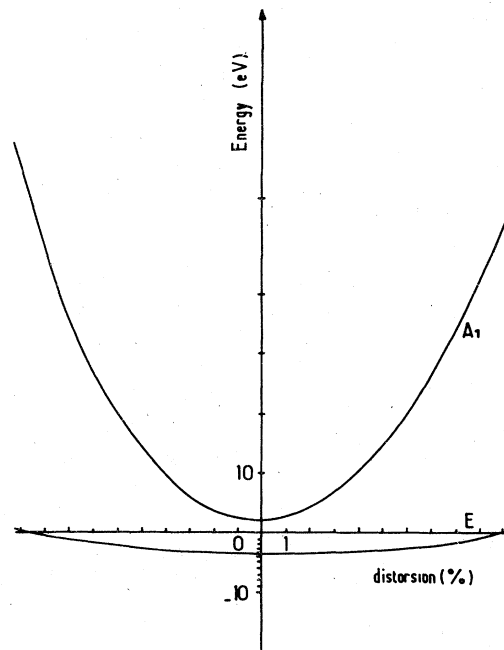For the distortion corresponding to the minimum of E_T, the donor energy level associated with

nitrogen splits and moves from the undistorted value $E_c - 1.4$ eV to $E_c - 2.1$ eV (the forbidden gap is 5.0 eV). The character of the wave-function associated with the donor level localized on nitrogen remains $2p$. The $2s$ and $2p$ coefficients of the wave-function associated with nitrogen and with the ternary carbon neighbor are compared in Table VII with the corresponding coefficients obtained from the hyperfine analysis of electron paramagnetic resonance spectrum.[33]

IV. CONCLUSION

The molecular orbital treatment in the EHT approximation, applied on a cluster of atoms surrounding a defect, which has been proposed by Messmer and Watkins, has been shown to provide a qualitative picture of the electronic states of this defect. In this paper, we des-

TABLE VII. Square of the wave function coefficients determined by the calculation (using "0" values of W_p) for the nitrogen and the ternary carbon neighbor and comparison to experiment.

	Calculated	Experiment
N_{2s}	0.0	0.06
N_{2p}	0.34	0.23
C_{2s}	0.01	0.066
C_{2p}	0.43	0.73

cribed a new molecular orbital method which includes a self-consistent procedure in order to be able to take into account the charge redistributions occurring around the defect. We demonstrated that self-consistency provides a better picture of the electronic states of the perfect crystal and greatly improves the representation of defect states, as compared to the noniterative EHT method.

We have also evaluated the total energy E_T of the cluster. The nuclear energy R_N alone, calculated for point charges ($N_{pr}=e^2/\rho$) leads to an unstable situation, as it can be foreseen from electrostatic theorems. The one-electron energy term $\sum_i \epsilon_i$ and the Coulomb repulsion $\sum_{i,j} J_{ij}$ are calculated from the electronic distribution obtained in a SCF way. The exchange integrals are neglected because they result in negligible variations, compared to the variations of the $\sum_i \epsilon_i$ and $\sum_{i,j} J_{ij}$ terms, when the atomic configuration is changed. These two terms $\sum_i \epsilon_i$ and $\sum_{i,j} J_{ij}$ are calculated in the Mulliken approximation, using in particular dicentre integrals which give interaction potential energies between electrons (J_{pr}) and between electrons and cores (A_{pr}). We discussed in detail the energy A_{pr}. It is obvious that (if we neglect

multipolar effects) we have $J_{pr} < A_{pr} < N_{pr}$, for all interatomic distances (see Fig. 7). We found that the term A_{pr} plays an important role in the stability of the system and consequently in a correct evaluation of E_T: when taking the limit value $A_{pr}=J_{pr}$, the nuclear repulsion instability is not compensated; when taking the upper limit value $A_{pr}=N_{pr}$, the instability remains, but is "inverted". In order to get a stable cluster the expression of A_{pr} must be interpolated between the two extreme values N_{pr} and J_{pr}.

With the interpolated expression of A_{pr} proposed here we verified that $17C$ and $47C$ carbon clusters are stable. We then applied the calculation to the determination of the Jahn-Teller distortion around nitrogen in diamond (on $16C+N$ and $46C+N$ clusters). The results obtained: location of the level in the gap, nature of the wave function, barrier height for the reorientation of the distortion and vibrational modes are shown to compare favorably with experiment.

ACKNOWLEDGMENT

*Laboratoire associé au C.N.R.S.

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