

CYCLIC CLUSTER MODELS WITH QUANTUM-CHEMICAL HAMILTONIANS

By

P. DEÁK

INSTITUTE OF PHYSICS, TECHNICAL UNIVERSITY
1521 BUDAPEST, HUNGARY

(Received 27. I. 1981)

The calculation of the electronic structure of point defects causing deep levels is a widely investigated problem. Various attempts have been done to solve this by applying defect containing clusters with various boundary conditions and semiempirical hamiltonians. We have shown in this paper the equivalency of the methods applying cyclic boundary conditions and we proposed for them a very simple and efficient form. Using this modified version we calculated the band structure of diamond and the electronic structure of a vacancy in it by the CNDO/S—CI method with reasonable agreement with the experimental data.

Introduction

The development of quantum chemistry, stimulated by the appearance of fast and big computers, opened up the road to the applications in solid state physics. A possible field of application may be the calculation of the band spectra of covalent (and partially ionic) solids and the determination of defect electron structure in these. This paper is devoted to this latter problem while the other problems will be only mentioned. In Section I the experiences of early cluster calculations are summarized. In Section II a foundation of the cyclic cluster model is given in order to show the equivalence of the different methods published in the literature. Finally, in Section III calculations on diamond are presented applying a CNDO-hamiltonian in order to investigate the capabilities of the model.

I. The cluster model

After the “defect-molecule” model [1, 2, 3] the cluster model has introduced quantumchemical methods in the calculation of deep levels. In the cluster model a small part of the solid around the defect is treated as a molecule. The energies of the occupied orbitals of such a “molecule” are intended to correspond to the valence band, while *the energies of the virtual orbitals are thought to reproduce the conduction band*. The first attempts were made using nonselfconsistent methods [9], [14] or [5, 6].

The experience of the early cluster calculations can be summarized in three points.

i) Unless the symmetry of the cluster is controlled, the identification of crystalline k states in the defectless cluster is accidental, and the convergence of the band edges with the arbitrary increase of the cluster size is slow [7, 8].

ii) The dangling bonds on the defect surface cause "surface states" and charge inhomogeneity, moreover they interact with the defect wave function. Various attempts were made to push the energy of these states out of the gap by filling them with electrons [9], saturating them with hydrogen [10] or with monovalent quasiatoms (a monovalent atom with the same parameters as those in the cluster e.g. [11]). However, neither the problem of charge inhomogeneity [12, 13] nor that of interaction with the defect [14, 15] can be solved by these methods.

iii) Furthermore, in contrast to the valence band, the description of the conduction band is not satisfactory [16]. (With various modifications, scaling procedures, etc. the results can be improved, but not with the parameters tested in quantum chemistry). And finally, the charge rearrangement cannot be neglected (among others, this can increase the localization of the defect wavefunction [14]). While the last problem can be solved by the IEHT [17] making the Fock matrix dependent on net atomic charges, the former two problems require a better approximation.

Therefore the problems in cluster calculations are the symmetry of the cluster, the boundary condition and the hamiltonian applied.

II. The cyclic cluster model

A) *QLUC (MUCA) method*

By applying the methods of band structure calculation, most of the problems mentioned above can be avoided. Instead of the elementary cell one can use a cluster which is the L^3 times that (or is a Bravais cell) and which is containing the defect (supercell method). Then applying periodic boundary conditions, an appropriate hamiltonian and a reasonable basis set, all but one of the difficulties shall be over (e.g. [18]). This only one is the fact that the interaction of the defect with the cluster surface is substituted by the interaction between the periodically repeated defects. We note, however, that this latter is considerably lower because the defect separation is twice as long as the defect—surface distance and, on the other hand, the number of first neighbour defects is much lower than that of the surface atoms. Therefore a much faster convergence can be expected with cluster size, than for free clusters. For the case of the perfect cluster, the reproduction of the experimental band structure obviously depends only on the approximation used to solve

the Schrödinger equation. However, the conventional methods applied to covalent materials result in uncertainties in some points. E.g. in the case of diamond, selfconsistent OPW calculations result in a 8.7 eV direct gap between Γ_{25} and Γ_{15} [61], while the DVM of [20] resulted in 6.0 eV for the same separation. Moreover, the application of a pseudopotential yielded a direct gap between Γ_{25} and Γ_2 [20]. On the other hand the direct parametrization methods depend on the experimental data chosen for fitting, which are not always unambiguous either as it is just the case for the direct gap of diamond. Much higher uncertainties appear in the case of partially ionic materials as e.g. SiO_2 . Presumably, the advanced LCAO—MO type quantumchemical methods, which apply atomic orbitals and well tested hamiltonians may help to clear the dark points. Even more promising is their application for deep levels. The general formulas of the extension of quantumchemical LCAO—MO to band structure calculation was performed by ANDRÉ et al [21].

This procedure is based on the construction of crystalline orbitals (CO) as a linear combination of Bloch sums, which are in turn given from the identical orbitals in the various primitive cells:

$$\psi_n(\mathbf{k}) = \sum_{A=1}^h \sum_{\mu=1}^{\delta} c_{\mu n}^A(\mathbf{k}) \varphi_{\mu}^A(\mathbf{k}), \quad (1a)$$

$$\varphi_{\mu}^A(\mathbf{k}) = N^{-1/2} \sum_{l=0}^{N-1} x_{\mu}(r - R_l - \mathbf{d}_A) e^{i\mathbf{k}R_l}. \quad (1b)$$

Here and in the following n, m will mean the band index: i, j, k, l will correspond to one of the N cells of the crystal, and

$$x_{\mu}(r - R_l - \mathbf{d}_A) \quad (\mu = 1, \dots, \delta; A = 1, \dots, h)$$

is the atomic orbital of type μ on the centre A of the l -th primitive cell. For the sake of brevity we shall write:

$$x_{\mu}(r - R_l - \mathbf{d}_A) =: \mu_l^A.$$

The periodic boundary condition is fulfilled by the statement:

$$\mu_{l+N}^A \equiv \mu_l^A. \quad (2)$$

Within this scheme a modified set of Roothaan's equations must be solved with any kind of quantumchemical methods:

$$\sum_B \sum_{\nu} [F_{\mu\nu}(\mathbf{k}) - \varepsilon_n(\mathbf{k}) S_{\mu\nu}(\mathbf{k})] c_{\nu n}^B(\mathbf{k}) = 0, \quad (3)$$

where:

$$F_{\mu\nu}(k) = \sum_j F_{\mu\nu}^{0j} e^{ikR_j}. \quad (4)$$

$F_{\mu\nu}(k)$ is the element of the Fock matrix between Bloch sums which are constructed from μ orbitals of the A -type centres and ν orbitals of B -type centres, respectively, and

$$F_{\mu\nu}^{0j} = H_{\mu\nu}^{0j} + \sum_{k'} \sum_{C,D} \sum_{\lambda,\sigma} \frac{P_{\lambda\sigma}(k')}{N} \sum_{k,l} \left[(\mu_0^A \nu_j^B | \lambda_k^C \sigma_l^D) - \right. \\ \left. - \frac{1}{2} (\mu_0^A \lambda_k^C | \nu_j^B \sigma_l^D) \right] e^{ik'(R_k - R_l)}. \quad (5)$$

In (5) $H_{\mu\nu}^{0j}$ is the core hamiltonian matrix between the μ orbital of the 0-th cell and the ν orbital of the j -th one, and:

$$P_{\lambda\sigma}(k) = 2 \sum_m^{\text{occ}} c_{\lambda m}^{\lambda}(k')^* c_{\sigma m}^{\sigma}(k'), \quad (6)$$

$$S_{\mu\nu}(k) = \sum_j S_{\mu\nu}^{0j} e^{ikR_j} = \sum_j (\mu_0^A | \nu_j^B) e^{ikR_j}. \quad (7)$$

Eq. (3) has to be solved for all k states of the reduced Brillouin zone (BZ). Since the Fock matrix contains the $c_{\mu n}^A(k)$ coefficients, the solution can be found in an iterative SCF procedure. To perform this with an *ab initio* hamiltonian is quite a hard task regarding the sum of multicentre integrals over the BZ and over all orbitals in every cell. A simplification of the problem can be reached by applying approximate semiempirical methods, which is the usual way of the quantum chemistry for large molecules. This has also the advantage that through the empirical data a certain part of correlation is also accounted for in some of the methods.

The simplest case is the EHT [19], which neglects electron—electron (and also core—core) interaction, making the sum in Eq. (5) disappear. The remaining term $H_{\mu\nu}^{0j}$ is parametrized semiempirically. In this case the energies at various k points can be calculated independently (e.g. [4]).

If one applies a supercell, all K points of the corresponding BZ collect more k points of the original one. By a careful choice of the supercell [22, 23] the important symmetry points (all branches of a given k^*) can be involved in the $K = 0$ state. This is important from the viewpoint of the defect calculation, because it was shown [24] that the defect levels originate from the critical points of the band structure, which are in turn usually at or near to the high symmetry points of the BZ. Therefore, to obtain the defect levels it is sufficient to calculate the $K = 0$ state of the appropriately chosen large unit cell. For the case of the EHT, when all K states are independent, this supercell calculation is equivalent to a cluster model with periodic boundary

conditions as applied by [25], [26] and [27], [24] [14], [28]. The procedure was called MUCA (molecular unit cell approach) by MESSMER and WATKINS and QLUC (quasimolecular large unit cell) by EVARESTOV et al.

Regarding the shortcomings of the EHT as mentioned previously, a somewhat better approximation of the Fock matrix is necessary. The next step in approximation is usually the CNDO with different parametrizations which are very suitable for calculating wavefunction related properties (e.g. dipole moments and geometry) as the CNDO/2 [29], [30], [31], or for energy values as the CNDO/SW [32], [33] and CNDO/S [34], [35] and [36]. The formulae of the LCAO—CO in the CNDO approximation were elaborated by [37]. The Roothaan equations are reduced to

$$\sum_B \sum_v F_{\mu\nu}(k) c_{\nu n}^B(k) = \varepsilon_n(k) c_{\mu n}^A(k) \quad (8)$$

and the Fock matrix is ($\mu \in A$):

$$\begin{aligned} F_{\mu\mu}(k) = & U_{\mu\mu} + \beta_A \sum_j (S_{\mu\mu}^{0j} - \delta_{0j}) e^{ikR_j} - \sum_B Z_B \sum_j (1 - \delta_{AB} \delta_{0j}) \gamma_{AB}^{0j} + \\ & + \sum_{k'} \sum_B \frac{P_{BB}(k')}{N} \sum_j \gamma_{AB}^{0j} - \frac{1}{2} \sum_{k'} \frac{P_{\mu\mu}(k')}{N} \sum_j \gamma_{AA}^{0j} e^{i(k+k')R_j} \end{aligned} \quad (9)$$

and the off diagonal elements ($\mu \neq \nu$ and $\mu \in A$, $\nu \in B$) are

$$\begin{aligned} F_{\mu\nu}(k) = & \frac{1}{2} (\beta_A + \beta_B) \sum_j S_{\mu\nu}^{0j} e^{ikR_j} - \frac{1}{2} \sum_{k'} \frac{P_{\mu\nu}(k')}{N} \cdot \\ & \sum_j \gamma_{AB}^{0j} e^{i(k+k')R_j}, \end{aligned} \quad (10)$$

where $P_{BB} = \sum_{\lambda \in B} P_{\lambda\lambda}$; Z_B is the core charge and δ_{ij} is the Kronecker symbol. The first three members in (9) and the first in (10) correspond to $H_{\mu\nu}(k)$, while the remaining terms express the electron—electron interactions because of the basic limitation of the CNDO:

$$\begin{aligned} (\mu_i^A \nu_j^B | \lambda_k^C \sigma_l^D) &= (\mu_i^A \mu_i^A | \lambda_k^C \lambda_k^C) \delta_{ij} \delta_{kl} \delta_{AB} \delta_{CD} \cdot \\ \delta_{\mu\nu} \delta_{\lambda\sigma} &= \gamma_{AC}^{ik} \delta_{ij} \delta_{kl} \delta_{AB} \delta_{CD} \delta_{\mu\nu} \delta_{\lambda\sigma} \end{aligned} \quad (11)$$

for all μ on A in the i -th cell and for all λ on C in the k -th one. $U_{\mu\mu}$, β_A and γ_{AB}^{0j} are the parameters selected according to the type of the CNDO. As can be seen the CNDO maintains a certain part of the two-electron integrals and

the coupling of the k states appears again. To avoid the integration over the BZ EVARESTOV et al returned to a cluster type calculation by neglecting the interactions between the various K states in the BZ of the supercell (but preserving them between the k states involved in the $K = 0$ state) [38]. As it was mentioned above this restriction has a minor effect on the defect levels, however, it is important from the viewpoint of simulating the band structure. EVARESTOV et al [24] have shown that the energy of a given k state converges to its exact value as the number of k' states interacting with it increases. However, the improvement of the results is not monotonous by all means increasing the cluster arbitrarily [39]. In spite of this, such an extension of the QLUC model resulted in an encouraging valence band for a diamond cluster containing only the Γ , X and L points of the original BZ. EVARESTOV et al interpret this success by means of the special k -point theorem of CHADI and COHEN [40]. Namely, it was shown that the average of a smoothly varying function $f(k)$ over the BZ can be calculated as a weighted sum of the values at some special k points

$$\langle f(k) \rangle = \frac{1}{V_{BZ}} \int_{BZ} f(k) d k \approx \sum_i \alpha_i f(k_i) . \quad (12)$$

The results are extremely good even for a few number of k states. Since the supercell band structure calculation decreases the dispersion of the bands [41], one can expect the function $P_{\nu\nu}(K)$ to be smooth enough for applying the theorem in Eq. (5) with success. By the use of the summation method of [42] for the electron—electron integrals the reaching of an *ab initio* selfconsistent band structure would be also possible with a reasonable computing time.

B) The SPC method

The problem of interactions between the periodically repeated defects appears also in the QLUC model. This problem is thought to be eluded in the SPC (small periodic cluster) approach which applies periodic boundary conditions directly to the cluster. This means the prescription that the interaction of atoms A and B (both in the cluster) has to be replaced by the AB' interaction, B' being an equivalent of B closest to A in the crystalline environment (Fig. 1). If all $R_{AB'}$ distances are longer than R_{AB} then AB is maintained [26]. Due to this conception, the length of allowed interactions is restricted to be less than the half of the cluster size. This limitation excludes the direct interactions between the defects and lowers the indirect ones also considerably because all atoms interact with one defect only. The SPC was applied first in the chemisorption theory of graphite and boron nitride by [43], [44] with CNDO and by [45] with EHT, but later on it was used in other problems too (e.g.

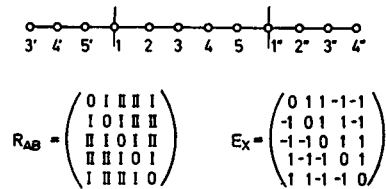


Fig. 1. The interatomic distance and direction cosine matrices in a one dimensional SPC. (Roman numbers correspond to appropriate neighbour distances)

[46] or [11]). The name SPC originates from ZUNGER who analysed this method [39, 47] in detail for one- and two-dimensional systems [48, 49]. In his formulation the interatomic distance and direction cosine matrices (Fig. 1) were constructed to be cyclic and these were used in the construction of the Fock matrix. This procedure is obviously equivalent to that described by [26].

C) Generalization of the SPC toward the QLUC: the cyclic cluster

The SPC was criticized by EVARESTOV et al [50] in comparison with the QLUC. However, it can be shown on the basis of a somewhat different conception of SPC [51] that the two approaches are essentially equivalent. The periodic boundary conditions of the SPC can be visualized by joining the one end of the cluster to the other, i.e. making cyclic the cluster itself (Fig. 2). If the interaction length is shorter than the half of the cluster size, the orbital μ on atom A "winds" (onefold) on the cluster (Fig. 3/a). However the same can be done also without limiting the interaction length, only the "winding" will be manifold (Fig. 3/b). This causes e.g. the "self-overlap" of μ_0^A , however, as can be seen comparing Fig. 3/b, and Fig. 4, this is identical with the diagonal element of the overlap matrix on the basis Φ_μ^A where

$$\Phi_\mu^A = \frac{1}{\sqrt{N}} \sum_l \mu_l^A, \quad (13)$$

and l runs over the cells equivalent to the cluster in the whole crystal. But (13) is just the basis which is used in the QLUC after neglecting interactions between the K states ($K = 0$ is calculated only and the sum over K' disappears also,

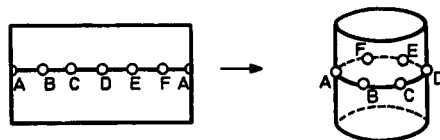


Fig. 2. Cyclic visualization of the Born-Kármán boundary conditions in one dimension

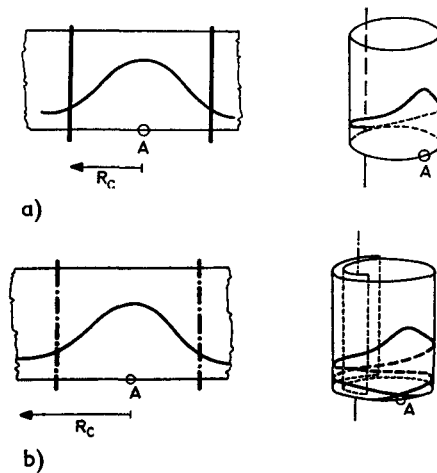


Fig. 3. The application of the cyclic boundary conditions with: a) finite range of interaction; b) infinite range of interaction

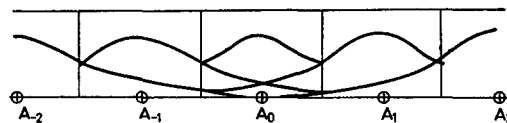


Fig. 4. Periodic visualization of the Born-Kármán boundary conditions in one dimension with infinite interaction length

in Eqs. 9–10). Therefore, if one carries out the choice of the cluster in a way prescribed in [23], the only difference is in the limitation of the interaction length. The restriction of this, however, has practical advantages. In addition to eliminating lattice sums (which causes a significant reduction of the computational time if one calculates the electron-electron integrals theoretically), the interaction of defects is also strongly suppressed.

The infinite range of interaction is kept in the QLUC to ensure exact translational invariance, i.e. the long range order. However, as it was shown [52, 53], the band character in covalent solids is determined by the short range order. (This holds even more for e.g. SiO_2 .) Therefore, the improvement introduced taking into consideration the long range order can be of the same order of magnitude as the error caused by involving the interactions of the defects in the superlattice.

In the light of these we think that the arguments in Section 5 of [23] can be ignored, except the one that the restriction of R_c below the half of the cluster size leads to the necessity of calculating too large clusters. Therefore, we suggest a compromise for keeping R_c to be equal to the half of the cluster size increasing the effect of indirect defect interactions but excluding the direct ones further. As will be shown in the next Section, this little con-

cession makes a considerable improvement possible. We note that lattice sums do not appear if care is taken to preserve charge neutrality in a similar manner as in the Madelung summation [51].

III. Calculations

We present calculations for the vacancy in diamond applying the model described above, in order to investigate its convergence properties (between our limited possibilities) and to compare its results with experimental data. Perhaps the diamond vacancy is not the best choice for such a purpose, because the localization of its wavefunction is questionable (but very likely not too strong), however, most of the previous works were carried out for the vacancy in diamond and in silicon. (The examination of Si requires further work, because no parameters exist for it in the CNDO/S scheme involving d orbitals.) Our final goal is the oxygen vacancy in SiO_2 which is a partially ionic material dominated by the short range order, i.e. with highly localized bonds.

We shall use a cyclic cluster representing the Γ , X and L points of the diamond BZ (i.e. the C_{16} cluster), with an interaction length equal to the radius of the cluster (i.e. 4th neighbour). This means the reduction of Eq. (8) to the original Roothaan equation in the CNDO approximation, i.e.:

$$\sum_B \sum_\nu (F_{\mu\nu} - \varepsilon_n \delta_{\mu\nu}) c_{\nu n}^B = 0 \quad (14)$$

and

$$F_{\mu\mu} = U_{\mu\mu} + \frac{1}{2} P_{\mu\mu} \gamma_{AA} + \sum_B (P_{BB} - Z_B) \gamma_{AB}, \quad (15)$$

$$F_{\mu\nu} = \frac{1}{2} (\beta_A + \beta_B) S_{\mu\nu} - \frac{1}{2} P_{\mu\nu} \gamma_{AB}. \quad (16)$$

Such a procedure involves three kinds of convergence problems

- convergence with \mathbf{k} states involved in $K = 0$;
- convergence with the range of interaction;
- convergence with defect separation.

The first two are needed to achieve a good simulation of the perfect crystal band structure, while the third is required to eliminate indirect defect—defect interactions (direct ones are excluded automatically by R_c).

A) Simulation of the band structure (perfect cluster)

In Fig. 5 the occupied orbitals, i.e. the valence bands of various diamond clusters are plotted. The a), b), and c) parts of the Figure show the $C_2(\Gamma)$, $C_8(\Gamma, X)$ and $C_{16}(\Gamma, X, L)$ clusters in the same first neighbour approximation.

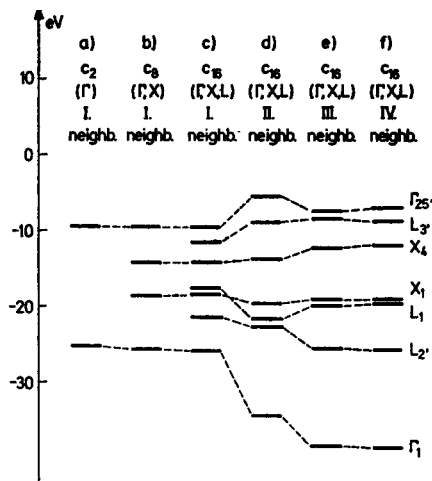


Fig. 5. Occupied orbitals of a) C_2 , b) C_6 , c), d), e), f) C_{18} diamond clusters with first (a, b, c) second (d), third (e) and fourth (f) neighbour approximations, applying CNDO/S

(The C_{64} cluster was too large for our computer). The c, d, e and f parts show the same C_{18} cluster with increasing interaction lengths (from first to fourth neighbour). The results confirm the importance of short range interactions, showing a fast convergence with R_c . On the other hand the results show very slight dependence of the included k set. Although, the few number of results do not allow far reaching conclusions, we shall see that the C_{18} cluster reproduces the experimental band structure fairly well.

Applying the cyclic cluster model, two of the problems connected with EHT truncated cluster calculations (see Section I) are overcome. The third one is the question of the choice of the hamiltonian. The CNDO is selfconsistent and its CNDO/2 version is excellent for geometry determination. The application of semiempirical methods, as the CNDO, to molecules allows the comparison of results with experiments which are in the case of the electronic structure the photoelectron and UV spectroscopy. Similarly for solids the valence band levels can be determined directly relative to the vacuum level, while those of the conduction band are determined only relative to the valence band via electronic transitions. In a solid, the excitation or the removal of an electron does not alter the state of the whole system considerably. This is not the case in molecules and consequently in our molecular cluster. By removing an electron from his level, the position of the ionic cores may alter, the system of the remaining electrons may relax, and the error caused by the neglect of the correlation effects may change. Therefore a method, which is well parametrized in the ground state, can give unreliable results for excitation or ionization energies, even if these are calculated as the difference between the initial and the final state energies.

Fortunately, for the ionization potentials the Koopmans' theorem generally holds with good accuracy, i.e. the energies of the occupied orbitals are equal to the negative of the ionization energies. This statement justifies the correctness of identifying the valence band with the occupied orbitals of the cluster.

However, this is not valid for the excitation energies. The calculation of these simply from the difference between the energies of the virtual orbital, (for which the electron will be excited) and of the occupied orbital leads to very poor results. Therefore, in the case of electronic transitions selfconsistent calculation must be carried out taking the correlation also into account. Hence a conduction band, comparable with experimental data, must be deduced in a cluster model from such a calculation.

Such a procedure is not possible in the EHT, while the CNDO/S-CI was elaborated even for calculating electronic transitions. In this method the parametrization takes into account a part of the correlation, and the transitions are calculated selfconsistently followed by a limited configuration interaction (CI) calculation. We used a reparametrized form of it which yields *both* ionization and excitation energies (similarly to CNDO/S3 of [54], but optimized for saturated hydrocarbons [55]). Our results for the C_{16} cluster (4th neighbour appr.) are shown in Fig. 6 together with experimental results [56, 57] and with results of OPW [61] and DVM [20] band structure calculations. In the lower part of the Figure the energy of the strongest transition

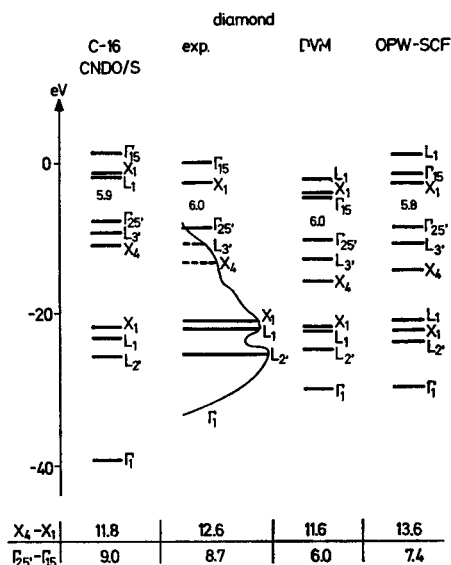


Fig. 6. Comparison of the electronic structure and electronic transitions of a $[C_{16}]$ cluster with experimental OPW-SCF and DVM data

and the width of the direct gap are indicated. As can be seen the simulation of the band structure is satisfactory despite the small cluster and the limited interaction length. (We note that applying the special parameters of [11] which were obtained by fitting to the valence band of [20], the conduction band calculated in the way described above fits also better). The energy of Γ_2 is predicted also in our calculation to be below that of Γ_{15} (not shown in the Figure). This is connected with the fact that $3a_1$ precedes $2t_2$ in CH_4 .

After all these results support the use of a cyclic cluster model supposing that the cluster is chosen appropriately and the conduction band is calculated in a correct way, too. Of course the particular size of the cluster depends on the material examined and the desired accuracy, however, it is surely in the treatable region.

B) *The energy levels of the vacancy*

The third convergence problem, connected with defect separation, has meant the hardest task, because at the moment we are not able to treat clusters as large as necessary. (The next suitable cluster after C_{16} would be the C_{64} — about 1.3 Mbyte). The rate of convergence is determined by the localization of the defect wavefunction, which is, however, questionable for the case of the vacancy in a purely covalent material. The only “experimental” fact is the conclusion of WATKINS [58] from the analysis of EPR data on silicon, namely that the wavefunction is localized about 65% to the first neighbours. The EHT calculation of MESSMER and WATKINS [14] for $C_{63}V$ and the pseudopotential calculation of LOUIE et al [18] for $Si_{53}V$ (both in supercell model) resulted equally in a dispersion of about 1.0 eV in the vacancy level (lying in the gap). However, in the former the delocalization can follow from the lack of self-consistency [14], while in the latter from the plane wave expansion. The Koster—Slater method (which implies the perfect crystal Green function) with a localized basis set [59] yielded a 70% localization to the first neighbours and a more diffuse tail. However these authors and also [60] reported that the change in the *total charge* distribution is practically zero out of the second neighbours. (We note that although these latter methods do not apply a superlattice of defects, their results are comparable with those of [18] regarding both the energies and electron density maps).

Our model calculation on a $C_{15}V$ cluster applying the CNDO/2 parametrization which is suited for calculating wavefunction related properties resulted in a localization of 75%, 17%, 7% and 1% of the wavefunction for 1st, 2nd, 3rd and 4th neighbours, respectively. The CNDO/S parametrization (which is suited for calculating energy related properties) worsens this to about 90% on first neighbours. From the viewpoint of the defect energy level, our method can be characterized by the following:

— restricting the interaction length we apply the same approximation for the localized vacancy wavefunction as for the extended wavefunctions of the crystal. Therefore, the error in the energy relative to the “defect band” must be also similar and the result deviates toward the isolated case;

— the energy difference between the isolated vacancy level and the defect band is caused by the indirect interactions (the direct ones are excluded by the restriction of the interaction length), i.e. by the change in the charge distribution of intermediate atoms due to the adjacent vacancies. The main contribution originates from the atom on the halfway, which is influenced by both vacancies. The further ones are affected by the change of this atom only;

— the Fock matrix in the CNDO contains the bond order matrix $P_{\mu\nu} = 2 \sum_n c_{\mu n}^* c_{\nu n}$ therefore it does not depend directly on the particular change in charge distribution caused by the vacancy wave function.

Therefore, to obtain reliable results for the energy levels of an isolated vacancy, it is necessary to consider a cluster in which the middle point between adjacent defects is farther than the distance where the change in the total charge distribution due to the defect becomes negligible. For the case of silicon and diamond the latter ensue after the second nearest neighbour distance (it diminishes to about 1/20 at third neighbour distance), therefore the lowest defect separation should be greater than twice the 2nd neighbour distance. This is realised by the 54 atom cluster, where the lowest defect separation is twice the 5th neighbour distance ($2a_0 \sqrt{19}/4 = 0.776$ nm for diamond). Indeed, the results of [18] for $Si_{53}V$ are very close to that of [60] (0.5 eV and 0.7 eV above the valence band, respectively).* Regarding the $C_{15}V$ cluster, the half of the shortest vacancy separation is at the second neighbours in the $\langle 110 \rangle$ direction, i.e. the effect of indirect interaction is not negligible. The direct comparison of the results for this cluster (Fig. 7) with experiments is not possible, because the relaxation effects would require a larger cluster. However, the transitions at the vacancy are well in the region of those of the GR centres, usually attributed to the vacancy. This shows that the error cannot be too much even for this small cluster, too (the reason for this is perhaps the contracting effect of the energy-oriented parametrization). Furthermore, the vacancy in diamond and silicon can be regarded as the worst case. For example the localization of the wavefunction of a nitrogen substituent in diamond is much higher [14]. The same can be expected for vacancies in partially ionic solids [49].

* The value 0.5 eV was obtained from the “defect band” by a tight binding method, using the values at I' and X . Since the direct interactions are included, the dispersion is quite large causing some uncertainty. On the other hand the 0.2 eV difference seems to be quite large relative to the 1.1 eV direct gap in Si. However, the results of two similar calculations [60], [59] differ also by 0.1 eV.

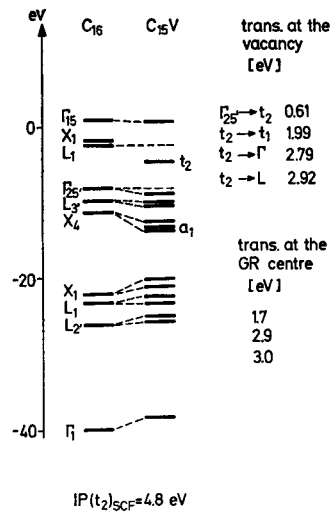


Fig. 7. Electronic structure of an unrelaxed vacancy in diamond (C_{15}). Electronic transitions at the vacancy in the first column are to be compared with those at the GR centre in the second column

Finally, we may devote some words to the relaxation problem, which is investigated very intensively in the present days. Since the CNDO/2 parametrization is fitted to dipole moments, it is quite well applicable for geometry determination. Therefore, the geometry around a defect can be calculated in the course of a conformational analysis procedure on a sufficiently large cluster (64 atoms for a diamond cluster with first neighbour displacements) as in the quantum chemistry of molecules. Demonstrating the accuracy of the CNDO/2 we note that for the equilibrium lattice constant of diamond we obtained 0.354 nm compared to the experimental 0.356 nm.

Conclusions

The early truncated cluster approaches to the deep level problem have had serious shortcomings. These can be avoided by using an appropriate cluster representing the special k points of the BZ and applying periodic boundary conditions. We have pointed out the equivalency of the various models developed independently and we have shown that such a cluster model with balanced restrictions is effective already for medium size clusters (and if the defect wavefunction is strongly localized even for small clusters, too).

The cluster model makes it possible to apply semiempirical quantum-chemical methods, which yield results comparable with experiments for molecules. We have shown that also the conduction band levels can be simulated in a cluster model well, if one calculates them selfconsistently (including

correlation effects) as final states of electronic transitions. Applying the CNDO/S—CI method for a C_{16} cluster we reproduced the energies of some high-symmetry points of the diamond band structure with reasonable accuracy. This indicates the perspective of the application of SCF LCAO MO methods combined with the special k point theorem for band structure calculation.

We have investigated the energy levels of a vacancy in diamond, which is probably the worst case for possible applications. The results of the $C_{15}V$ cluster (the largest we could compute), however, seem to be semiquantitatively correct encouraging us to apply this model for our final goal SiO_2 .

Acknowledgements

The author would like to thank Prof. J. GIBER for supporting his work and Dr. E. KAPUY for helpful discussions.

REFERENCES

1. C. A. COULSON and M. J. KEARSLEY, Proc. Roy. Soc. A, **141**, 433, 1957.
2. C. A. COULSON and F. P. LARKINS, J. Phys. Chem. Solids, **30**, 1963, 1969.
3. C. A. COULSON and F. P. LARKINS, J. Phys. Chem. Solids, **32**, 2245, 1971.
4. R. P. MESSMER, Chem. Phys. Lett., **11**, 589, 1971.
5. K. L. YIP and W. B. FOWLER, Phys. Rev. B, **10**, 1391, 1400, 1974.
6. K. L. YIP and W. B. FOWLER, Phys. Rev. B, **11**, 2327, 1975.
7. A. ZUNGER, J. Phys., **C**, **7**, 76, 1974.
8. W. P. MENZEL, K. MEDNICK, CH. C. LIN and C. F. DORMAN, J. Chem. Phys., **63**, 4708, 1975.
9. R. P. MESSMER and G. D. WATKINS, Radiation Effects, **9**, 9, 1971.
10. E. B. MOORE and C. M. CARLSON, Phys. Rev. B, **4**, 2063, 1971.
11. A. MAINWOOD, J. Phys. C, **11**, 2703, 1978.
12. I. LÁSZLÓ, Int. J. Quantum Chem., **12**, Suppl. 2, 104, 1977.
13. J. PIPEK, Thesis, 1977.
14. R. P. MESSMER and G. D. WATKINS, Inst. Phys. Conf. Ser., **16**, 255, 9173.
15. F. P. LARKINS, J. Phys. C, **4**, 3065, 3077, 1971.
16. A. M. STONEHAM, in "Theory of Defects in Solids" Clarendon Press, Oxford, 1975.
17. L. C. CUSACHS and J. W. REYNOLDS, J. Chem. Phys., **43**, S160, 1965.
18. S. G. LOUIE, M. SCHLÜTER, J. R. CHELIKOWSKY and M. L. COHEN, Phys. Rev. B, **13**, 1654, 1976.
19. R. HOFFMAN, J. Chem. Phys., **39**, 1397, 1963.
20. G. S. PAINTER, D. E. ELLIS and A. R. LUBINSKY, Phys. Rev. B, **4**, 3610, 1971.
21. J. M. ANDRÉ, L. GOUVERNEUR and G. LEROY, Int. J. Quantum Chem., **1**, 427, 451, 1967.
22. R. A. EVARESTOV, Phys. Stat. Sol. (b) **72**, 569, 1975.
23. R. A. EVARESTOV, M. I. PETRASHEN and E. M. LEDOVSKAYA, Phys. Stat. Sol. (b) **68**, 453, 1975.
24. A. M. DOBROTVORSKII and R. A. EVARESTOV, Phys. Stat. Sol. (b), **64**, 635, 1974.
25. D. BRAMANTI, M. MANCINI and R. RANFAGNI, Phys. Rev. B, **3**, 3670, 1971.
26. A. J. BENNETT and L. M. ROTH, J. Phys. Chem. Solids, **32**, 1251, 1971.
27. A. M. DOBROTVORSKII and R. A. EVARESTOV, Vestnik Leningradsk. Univ., **22**, 45, 1972.
28. T. F. LEE and T. C. MCGILL, J. Phys. C, **6**, 3438, 1973.
29. J. A. POPLE, D. P. SANTRY and G. A. SEGAL, J. Chem. Phys., **43**, S129, 1965.
30. J. A. POPLE and G. A. SEGAL, J. Chem. Phys., **44**, 3289, 1966.
31. D. P. SANTRY and G. A. SEGAL, J. Chem. Phys., **47**, 158, 1967.
32. J. M. SICHEL and M. A. WHITEHEAD, Theoret. Chim. Acta, **7**, 32, 1967.
33. J. M. SICHEL and M. A. WHITEHEAD, Theoret. Chim. Acta, **11**, 220, 239, 254, 1968.
34. J. DEL BENE and H. H. JAFFÉ, J. Chem. Phys., **48**, 1807, 1968.

35. J. DEL BENE and H. H. JAFFÉ, *J. Chem. Phys.*, **50**, 1126, 1969.
36. R. L. ELLIS, G. KUEHNLENZ and H. H. JAFFÉ, *Theoret. Chim. Acta*, **26**, 131, 1972.
37. R. DOVESI, C. PISANI, C. ROETTI and F. RIGGA, *Chem. Phys. Lett.*, **39**, 103, 1976.
38. R. A. EVARESTOV and V. A. LOVCHIKOV, *Phys. Stat. Sol. (b)*, **79**, 743, 1977.
39. A. ZUNGER, *J. Phys. C*, **7**, 96, 1974.
40. D. J. CHADI and M. L. CUHEN, *Phys. Rev. B*, **7**, 692 and **8**, 5747, 1973.
41. A. ZUNGER and R. ENGLMAN, *Phys. Rev. B*, **17**, 642, 1978.
42. L. PIELA and J. DELHALLE, *Int. J. Quantum Chem.*, **13**, 605, 1978.
43. A. J. BENNETT, M. MCCAROLL and R. P. MESSMER, *Phys. Rev. B*, **3**, 1397, 1971.
44. M. MCCAROLL and R. P. MESSMER, *Surf. Sci.*, **27**, 451, 1971.
45. D. J. M. FASSAERT, H. VERBECK and A. v. D'AVOIRD, *Surf. Sci.*, **29**, 501, 1972.
46. T. SHIMIZU and N. ISHII, *J. Noncrystalline Solids*, **27**, 109, 1978.
47. A. ZUNGER, *J. Chem. Phys.*, **62**, 1861, 1975.
48. A. ZUNGER, *J. Chem. Phys.*, **63**, 1713, 1975.
49. A. ZUNGER and A. KATZIR, *Phys. Rev. B*, **11**, 2378, 1975.
50. R. A. EVARESTOV, M. I. PETRASHEN and E. M. LEDOVSKAYA, *Phys. Stat. Sol. (b)*, **76**, 377, 1976.
51. P. DEÁK, J. KAZSOKI and J. GIBER, *Phys. Lett. A*, **66**, 395, 1978.
52. J. M. ZIMAN, *J. Phys. C*, **4**, 3129, 1971.
53. J. KELLER, *J. Phys. C*, **4**, 3143, 1971.
54. N. O. LIPARI and C. B. DUKA, *J. Chem. Phys.*, **63**, 1748, 1975.
55. P. DEÁK, to be published.
56. F. R. McFEELY, S. P. KOWALCZYK, L. LEY, R. G. CAVELL, R. A. POLLÁK and D. A. SHIRLEY, *Phys. Rev. B*, **9**, 5268, 1974.
57. J. C. PHILLIPS, *Sol. State Phys.*, **18**, 55, 1966.
58. G. D. WATKINS, *Chinese J. Phys.*, **15**, 92, 1977.
59. J. BERNHOLC, S. T. PANTELIDES and N. O. LIPARI, *Inst. Phys. Conf. Ser.*, **43**, 429, 9179.
60. G. A. BARAFF and M. SCHLÜTER, *Inst. Phys. Conf. Ser.*, **43**, 425, 1979.
61. F. HERMANN, R. L. KORTUM and C. D. KUGLIN, *Int. J. Quantum Chem.*, **1A**, 533, 1967.