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## Application of embedded-cluster models in the theory of local centres in graphite

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**Abstract.** Different approaches to the theoretical study of the local centres in solids are discussed. Particular attention is paid to the embedded-cluster models. There are given the mathematical formulation, the computational scheme and applications for some local centres on/in graphite monolayers of the moderately large embedded cluster and the large-unit-cell-embedded-cluster (LUC-EC) models. It is shown that both models are based on related approximations and give comparable results for the centres considered. At the same time the LUC-EC scheme is, in practice, realised more easily and enables one to study the charged centres. A study of some charged states of adsorbed hydrogen and substitutional boron and nitrogen atoms on/in graphite monolayers is used to illustrate the LUC-EC-model applications.

### 1. Introduction

The theory of the electronic structure of local centres in crystalline solids employs a wide range of methods and computational schemes (Stoneham 1975). In the one-electron approximation this theory has been developed on the basis of one of the following three approaches: (1) perturbed crystal model, commonly realised by the Green function technique; (2) different cluster models; (3) models of periodic defects.

As a rule, changes in the perfect-crystal electronic structure caused by the perturbative potential of a defect are of major interest in the theory of local centres in solids. Investigations of this type can be undertaken in a consistent way only if the perfect and imperfect crystals are considered in the framework of the same computational scheme.

Quite often a comparative study of the same local centre in different crystalline matrices is useful. The computational scheme in this case should be easily transferable from one type of solid to another.

Finally, consideration of charged centres is of great interest due to their increasing practical importance. This is the most complicated problem as charged centres are usually deep centres with strong potentials of large radii.

In the charged-centre environment two regions can normally be distinguished. The first one is usually referred to as the 'short-range perturbation' region. It includes some spheres of the nearest neighbours of the defect centre, where the perturbative potential is changing in a strong way. The second region is that with the most essential influence of long-range polarisation. The defect potential in it is not sufficiently small to be neglected, but it changes much more slowly than the host-crystal potential.

It is usually assumed that the problem for these two regions can be treated separately: for the first region, in the framework of the quantum-chemical approaches mentioned above; and for the second region, in the Mott–Littleton (Mott and Littleton 1938) or polarised-ions (Tolpygo 1957) approximation. A scheme realising the self-consistent consideration of both regions was proposed by Kantorovich (1983).

The consistent description of the short-range perturbation in region 1 (embedding this region into the host crystal) causes the most serious difficulties in the local-centre electronic structure calculations.

In this paper we briefly review the main advantages and drawbacks of the well known quantum-chemical approaches (§ 2), consider the formulation of two different versions of the embedded-cluster approach (§§ 3 and 4) and compare the results obtained with those for some local centres in/on a graphite monolayer (§ 5).

## 2. The main approaches to local-centre electronic structure theory

In the framework of the approach using periodic boundary conditions a crystal with a single local centre is replaced by a crystal with local centres periodically distributed over the lattice. There are known different realisations of such a model: the periodic cluster (PC) model (Bennett *et al* 1971), the large-unit-cell (LUC) approach (Evarestov *et al* 1975, Lindefelt 1978, Smith *et al* 1985) and the band model (Ermoshkin *et al* 1983). In all these approaches the period of the defect is usually taken to be as large as possible. This is made in order to simulate a single defect by reducing the direct and indirect interactions of defects from different cells.

In fact, large unit cells of the perfect crystal and corresponding primitive cells of the periodically perturbed crystal are considered. For the perfect crystal each LUC is composed of an integer number ( $L$ ) of primitive unit cells (PUC) of the host crystal. The reduced Brillouin zone (RBZ) corresponding to the LUC is  $L$  times smaller than the Brillouin zone (BZ) constructed for the PUC and each  $k$ -point in the RBZ corresponds to a family  $k, k, \dots, k$  of points of the BZ.

The LUC  $k = \mathbf{0}$  approximation is widespread in the theory of perfect and imperfect solids (Smith *et al* 1985). The density matrix of a crystal in the LUC model is approximated by a sum over the finite set of one-electron states (corresponding to the  $k = \mathbf{0}$  point of the RBZ). The accuracy of this approximation depends on the type of crystal under investigation and on the choice of size and form of the LUC.

The LUC model was successfully applied to various types of perfect crystals (insulators, semiconductors) and non-charged deep centres in them. The applicability of this model to point defects in metals has not been investigated till now.

It is obvious that the model of periodic defects is unrealistic for charged centres since the charge of the centre is translated in this model over the whole crystal.

The most natural theoretical approach in the local-centres theory is the perturbed crystal approach based on the one-electron Green function (GF) method (see, for example, Pisani *et al* 1983). In this approach the Dyson equation for the whole crystal Green function is solved (Lannoo and Bourgoïn 1981). The Dyson equation connects the Green function of the imperfect crystal with that of the perfect one and the perturbative potential of the defect. The GF of the perfect crystal is usually calculated from the results of preliminary band-structure calculations. The perturbative potential of the defect is normally unknown before the problem is solved. That is why its matrix elements are usually calculated on the basis of simple semi-empirical schemes.

The mathematical formulation of the GF method is straightforward, but its practical implementation is accompanied by some serious problems. These problems are the following: the complexity of the computational scheme; the necessity of performing the preliminary band-structure calculation; and the rapid increase of computational difficulties with the increase of the perturbative potential radius.

That is why the GF method is practically applied mainly in non-self-consistent calculations of simple local centres of small radius (Pantelides 1978) and also in qualitative consideration of oversimplified model centres (Lannoo and Bourgoin 1981). At the same time this method is practically useless in calculations of rather complex or charged centres (Telezhkin and Tolpygo 1982) if some essential modifications are not made.

It is the cluster approach that is most commonly used in the local-centres theory. This approach is based on the consideration of a comparatively small group of atoms (cluster) instead of consideration of the whole crystal. The main attractive features of a cluster model are the following: the simplicity of mathematical formulation; the possibility of direct transfer of computational schemes, worked out in quantum chemistry of molecules; and applicability to almost all types of solids and local centres in them.

At the same time the validity of the results obtained within the cluster approach is often questionable due to some serious drawbacks of the approach under discussion. Among these drawbacks are: the strong unpredictable influence of the cluster form and size on the results of calculations; the difficulties arising when relating the cluster one-electron energy levels with the band energies of the perfect crystal; and the appearance of 'pseudo-surface' states in the one-electron energy spectrum of the cluster. The appearance of the pseudo-surface states is accompanied by the unrealistic distortion of electronic density on the cluster boundaries and can lead to artefactual resonances between the pseudo-surface and the local-centre one-electron states.

In order to make the cluster model more realistic, a large number of embedding schemes have been developed (Zhidomirov *et al* 1987). Most of them are oriented on special types of crystal (ionic, simple covalent) or are based on the use of special approximations in the Hamiltonian operator (local exchange, tight-binding approximations).

The other group of cluster models is based on adding the effective-potential operator (the embedding operator) to the unperturbed-cluster Hartree-Fock operator, giving the proper one-electron solution for the perfect crystal. When the cluster form and size are chosen, this embedding operator can be determined and used in the following perturbed-cluster calculations. This so-called embedded-cluster approach is sufficiently general and can be applied to different types of solids. The only characteristic that to a certain extent depends on the nature of the solid and local centres in it is the minimal appropriate cluster size. This size is limited by the extent of localisation of one-electron states in the perturbed and non-perturbed solid. At the same time the extent of the defect-potential localisation is not so critical if the cluster is chosen in such a way that the long-range polarisation outside the cluster can be taken into account as mentioned above (for example, as in Kantorovich's model).

The embedded-cluster approach was realised in the framework of two different models: the moderately large embedded-cluster (MLEC) model (Pisani 1978, Pisani *et al* 1979, Pisani *et al* 1983) and the large-unit-cell-embedded-cluster (LUC-EC) model (Sokolov and Evarestov 1984a, b, Plachenov *et al* 1986, Evarestov and Verjazov 1987). The last was originally called in Russian 'the cyclically embedded cluster' but the term LUC-EC now seems to be more appropriate.

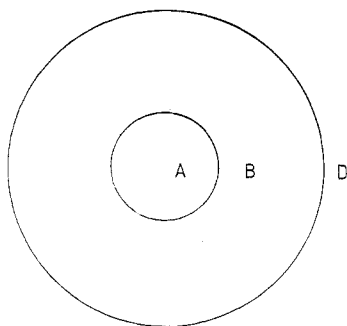


Figure 1. Scheme for the partition of the solid in embedded-cluster models.

### 3. The moderately large embedded-cluster (MLEC) model

According to Pisani (1978) we denote by A the defect itself, by B the defect-surrounding cluster region and by D the rest of the imperfect solid. The region  $C = A \cup B$  defines the embedded cluster (figure 1). Let  $\{\chi_A\}$ ,  $\{\chi_B\}$ ,  $\{\chi_C\}$ ,  $\{\chi_D\}$ , be localised basis functions (e.g. atomic orbitals) given in the regions A, B, C, D, respectively. The corresponding subset of basis functions in the region A of unperturbed crystal (which can be 'empty' for some types of local centres) is denoted by  $\{\chi_A\}$  and the corresponding subset in the region C by  $\{\chi_C\}$ .

Denoting by  $Q(e)$  the energy-dependent inverse of the Green operator  $G(e) = ((e + i0)S - F)^{-1}$ , where  $F$ ,  $S$  are the Hartree-Fock operator and overlap matrices of the solid, respectively, one can write

$$\begin{pmatrix} Q_{AA} & Q_{AB} & Q_{AD} \\ Q_{BA} & Q_{BB} & Q_{BD} \\ Q_{DA} & Q_{DB} & Q_{DD} \end{pmatrix} \begin{pmatrix} G_{AA} & G_{AB} & G_{AD} \\ G_{BA} & G_{BB} & G_{BD} \\ G_{DA} & G_{DB} & G_{DD} \end{pmatrix} = \begin{pmatrix} I_A & 0 & 0 \\ 0 & I_B & 0 \\ 0 & 0 & I_D \end{pmatrix} \quad (1)$$

$$\begin{pmatrix} \bar{Q}_{AA} & \bar{Q}_{AB} \\ \bar{Q}_{BA} & \bar{Q}_{BB} \end{pmatrix} \begin{pmatrix} \bar{G}_{AA} & \bar{G}_{AB} \\ \bar{G}_{BA} & \bar{G}_{BB} \end{pmatrix} = \begin{pmatrix} I_A & 0 \\ 0 & I_B \end{pmatrix}. \quad (2)$$

Here equation (1) corresponds to the perturbed crystal, and equation (2) to the perturbed (but isolated!) cluster.

The main idea of the MLEC model is to calculate the whole GF submatrix  $G_C$  from the isolated cluster matrix  $\bar{G}_C$  and some submatrices obtained from the perfect-crystal calculation. To this purpose, some approximations are introduced. It is supposed that the  $Q$  and  $G$  matrices of the perturbed crystal may be represented in the following form:

$$Q(e) = \begin{pmatrix} \cdot & \cdot & 0 \\ \cdot & \cdot & f \\ 0 & f & f \end{pmatrix} \quad (3)$$

$$G(e) = \begin{pmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & f \\ \cdot & f & \cdot \end{pmatrix}. \quad (4)$$

Here  $f$  stands for the blocks identical to those in the perfect crystal.

The final expression for  $G$  was obtained in the MLEC model in two forms. The first one appeared as the result of an additional approximation  $G_{AD}Q_{DB}^f = 0$  (Pisani 1978):

$$G_C = \begin{pmatrix} \bar{G}_{AA} & \bar{G}_{AB} \\ G_{BC}^f Q_{CB}^f \bar{G}_{BA} & G_{BC}^f Q_{CB}^f \bar{G}_{BB} \end{pmatrix}. \quad (5)$$

The second one was based on using the symmetry of the  $G_C$  submatrix without introducing any additional approximations (Pisani *et al* 1983):

$$G_C = \begin{pmatrix} \bar{\bar{G}}_{AA} - G_{AB} Q_{BA} \bar{\bar{G}}_{AA} & (G_{BC}^f Q_{CB}^f \bar{G}_{BA})^T \\ G_{BC}^f Q_{CB}^f \bar{G}_{BA} & G_{BC}^f Q_{CB}^f \bar{G}_{BB} \end{pmatrix} \quad (6)$$

where  $\bar{\bar{G}}_{AA} = Q_A^{-1}$ .

In the self-consistent calculations the density matrix  $P_C$  of a cluster is to be recalculated at each step of the iterative process. Its direct calculation by integration of the GF up to the Fermi level of the perfect crystal is somewhat cumbersome.

To avoid this integration and to simplify the calculation of the  $P_C$  matrix, an energy-dependent non-symmetric coupling matrix  $M(e)$  was introduced (Pisani 1978, Pisani *et al* 1983). Within such an approach the  $P_C$  matrix may be represented as the result of matrix multiplications, involving the eigenvectors of the embedded-cluster Hartree-Fock operator and matrix  $M(e)$ . The set of matrices  $M(e)$  for different energies  $e$  may be calculated if one-electron energies of the perfect crystal are known. No integration of the GF at each iteration is needed and the self-consistent determination of the density matrix is simplified drastically. As was shown in Pisani (1978), the  $M(e)$  function provides the correct behaviour for the density matrix when the embedded cluster is enlarged. This function differs essentially near the Fermi level from the commonly used step function  $\theta(e - e_F)$ .

An additional approximation is introduced when using the  $M(e)$  matrix: it is assumed that the Fermi level of the perturbed embedded cluster is fixed at the value appropriate for the unperturbed solid. This leads to the necessity of adding to the cluster electronic subsystem an excess electron or hole charge in order to compensate for the Fermi-level shift. The value of the artificial excess charge is adapted to the choice of cluster form and size and depends on the strength of the perturbative potential. The consideration of singly charged centres (whose charges are not the same as the artificial cluster charge) is impossible in the MLEC model.

The serious drawback of the MLEC model is the complexity of the computational scheme. That is the reason why this model has been practically implemented till now only for two-dimensional systems (local centres in graphite) and for the simple model of a tight-binding cubic metal (Pisani 1978, Pisani *et al* 1979, 1983).

It is obvious that the approximations (3) and (4) used in the MLEC approach lead to the following relations:

$$\begin{aligned} F_{AD} &= P_{AD} = S_{AD} = 0 \\ F_{BD} &= F_{BD}^f & P_{BD} &= P_{BD}^f & S_{BD} &= S_{BD}^f \\ F_{DD} &= F_{DD}^f & P_{DD} &= P_{DD}^f & S_{DD} &= S_{DD}^f. \end{aligned} \quad (7)$$

These approximations are exploited also in the LUC-EC model considered in the next section.

#### 4. The large-unit-cell-embedded-cluster (LUC-EC) approach

In the LUC-EC model the crystal is divided into the set of regions  $\{C_j\}$  ( $j = 0, \dots, N-1$ ) and all of these regions are chosen in the form of a LUC of the perfect crystal. The central region  $C \equiv C_0 = A \cup B$  contains the defect with its surrounding, the other regions together form the rest of the crystal:

$$D = \bigcup_{j=1}^{N-1} C_j.$$

If the approximations (7) are used, then the Hartree-Fock-Roothaan (HFR) equations for the imperfect solid can be written in the following form:

$$\begin{aligned} F_{AA}a_A + F_{AB}a_B &= e(S_{AA}a_A + S_{AB}a_B) \\ F_{BA}a_A + F_{BB}a_B + F_{BD}^f a_D &= e(S_{BA}a_A + S_{BB}a_B + S_{BD}^f a_D) \\ F_{DB}^f a_B + F_{DD}^f a_D &= e(S_{DB}^f a_B + S_{DD}^f a_D). \end{aligned} \quad (8)$$

Here  $a_A, a_B, a_D$  are the expansion coefficients of molecular orbitals (MO) over the basis subsets  $\{\chi_A\}, \{\chi_B\}, \{\chi_D\}$  respectively.

By solving (8) with respect to  $a_D$ , eliminating this term and introducing the embedding operators  $F_{emb}, S_{emb}$ , one can rewrite the embedded-cluster equations in the form:

$$[F_{CC} + F_{CC}^{emb}(e)]a_C = e[S_{CC} + S_{CC}^{emb}(e)]a_C \quad (9)$$

where  $F_{CC}^{emb}, S_{CC}^{emb}$  are the matrix representations of the corresponding embedding operators:

$$\begin{aligned} F_{CC}^{emb}(e) &= \begin{pmatrix} 0 & 0 \\ 0 & F_{BD}^f [(F_{DD}^f - eS_{DD}^f)^{-1} (eS_{DB}^f - F_{DB}^f)] \end{pmatrix} \\ S_{CC}^{emb}(e) &= \begin{pmatrix} 0 & 0 \\ 0 & S_{BD}^f [(F_{DD}^f - eS_{DD}^f)^{-1} (eS_{DB}^f - F_{DB}^f)] \end{pmatrix}. \end{aligned} \quad (10)$$

From the approximation (3) and (4) it follows that the expression in the square brackets (let us denote it as  $K_{DB}(e)$ ) is the same for the perfect and imperfect crystals for any energy  $e$ . Matrix  $K(e)$  connects expansion coefficients  $\alpha_{C_j}$  with  $a_C$ :

$$\alpha_{C_j}(e) = K_{C_j C}(e)a_C(e).$$

For the perfect crystal Bloch's theorem leads to:

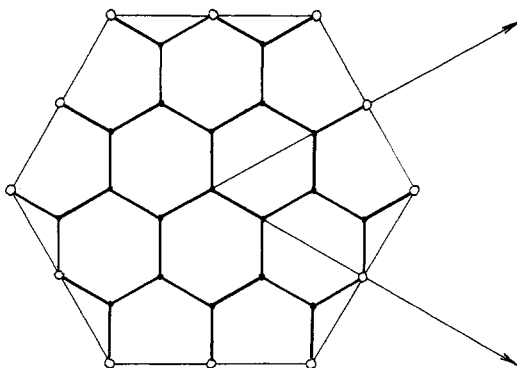
$$K_{C_j C}^f(e_k) = \exp(i\mathbf{k} \cdot \mathbf{R}_j)I_C$$

where  $I_C$  is the unit matrix.

In the LUC  $\mathbf{k} = \mathbf{0}$  approximation

$$K_{C_j C}^f = I_C \quad \text{for any } j \neq 0. \quad (11)$$

For the imperfect crystal in the LUC-EC model the  $K(e)$  matrix elements are assumed



**Figure 2.** LUC-EC  $C_{32}$  chosen in the form of Wigner-Seitz unit cells centred on a carbon atom:  $\circ$ , carbon atoms lying on the boundaries of the LUC-EC.

to be the same as in the LUC model for the perfect crystal. Taking into account (10) and (11) one can get immediately:

$$\begin{aligned}
 F_{BB}^{\text{emb}}(e) &= \sum_{j=1}^{N-1} F_{BC_j}^f & F_{AA}^{\text{emb}}(e) &= F_{AB}^{\text{emb}}(e) = F_{BA}^{\text{emb}}(e) = 0 \\
 S_{BB}^{\text{emb}}(e) &= \sum_{j=1}^{N-1} S_{BC_j}^f & S_{AA}^{\text{emb}}(e) &= S_{AB}^{\text{emb}}(e) = S_{BA}^{\text{emb}}(e) = 0.
 \end{aligned}
 \tag{12}$$

Finally, for the crystal with a single local centre the HFR equations in the LUC-EC scheme are the following:

$$\begin{aligned}
 F_{AA}a_A + F_{AB}a_A &= e(S_{AA}a_A + S_{AB}a_A) \\
 F_{BA}a_A + \left( F_{BB} + \sum_{j=1}^{N-1} F_{BC_j}^f \right) a_B &= e \left[ S_{BA}a_A + \left( S_{BB} + \sum_{j=1}^{N-1} S_{BC_j}^f \right) a_B \right].
 \end{aligned}
 \tag{13}$$

It should be mentioned here that the matrix  $F_{CC}$  in (9) and (13) depends on the density matrix of the whole crystal (i.e.  $F_{CC}$  is a block of the complete Hamiltonian matrix of the whole crystal). In order to calculate the density matrix of the whole imperfect solid, first of all the approximations (7) are used. Secondly, in the LUC-EC scheme all matrix elements corresponding to the 'free' (unperturbed) crystal are calculated as in the LUC ( $k=0$ ) model. For atomic orbitals (AO)  $\chi_X^n$  and  $\chi_Y^m$  centred on atoms  $X \in C_n$  and  $Y \in C_m$  this approximation gives (Evarestov and Lovchikov 1979):

$$P_{X^n X^m}^f = P_{X^n X^m}^f(\mathbf{0}) \int \exp[i\mathbf{k} \cdot (\mathbf{R}_X^n - \mathbf{R}_Y^m)] d\mathbf{k} = P_{X^n X^m}^f(\mathbf{0}) f(\mathbf{R}_X^n - \mathbf{R}_Y^m)
 \tag{14}$$

where  $\mathbf{R}_X^n$  and  $\mathbf{R}_Y^m$  are the radius vectors of the atoms  $X^n$  and  $Y^m$  respectively,  $P_{X^n X^m}^f(\mathbf{0})$  the matrix element for  $\mathbf{k} = \mathbf{0}$  of the density matrix in the Bloch representation. The integration in (14) is performed over the reduced Brillouin zone, corresponding to the LUC chosen.

There are some limitations for the choice of the LUC form and size in the LUC-EC model:

(i) All regions  $C_j$  are to be chosen in the form of Wigner-Seitz LUC with the defect being placed in the centre of the  $C_0$  region. Some atoms from  $C_0$  can belong to the Wigner-Seitz cell boundary (see figure 2). In this case one needs to use the approximation (7) for such atoms as if they belong to the D region.



(ii) The size of the LUC  $C$  must be sufficiently large to ensure that the validity of the approximations (7) and (14) be acceptable.

In the limit, when the region  $C_0$  is the whole crystal and the subset  $\{\chi_D\}$  is empty, the lattice sums disappear in (13) and the LUC–EC model gives the traditional HFR equations for a crystal considered as a large molecule. In the other limit, when the defect potential is equal to zero and  $\{\chi_A\}$  is empty, the equations (13) transform to the perfect-crystal HFR–LUC ( $\mathbf{k} = \mathbf{0}$ ) equations. Finally, if the host-crystal potential is rather weak and the matrix elements  $P_{BD}^f, P_{DD'}^f, F_{BD}^f, S_{BD}^f$  are negligible, the LUC–EC model gives the same equations for the  $C_0$  region as the simple cluster model does.

Thus, the introduction of the embedding operator matrices in the form of lattice sums (12) gives the proper limiting conditions for the cluster-type HFR equations.

The proposed LUC–EC model is rather simple in implementation and we have already used it for some different types of local centres in ionic (KCl—Sokolov and Evarestov 1984b; AgCl—Plachenov *et al* 1986) and covalent (graphite—Sokolov and Evarestov 1984a) crystals. It was shown that the model can be easily applied for the study of different single local centres (charged and neutral) in crystals.

The drawback of the LUC–EC model is that it does not take into account the polarisation of the crystal in region  $D$  by the perturbative potential of the defect. However, we suppose that if all limitations on the choice of cluster form and size are satisfied, the crystal in region  $D$  can be considered as only slightly perturbed by the defect. The methods accounting the polarisation in this case are well known and were mentioned in § 2. They can be used with the LUC–EC model exactly in the same manner as they are used with the cluster models (Plachenov *et al* 1986).

The application of the LUC–EC and MLEC models to some local centres in graphite and results obtained are discussed in the next section.

## 5. Local centres on/in a graphite monolayer in embedded-cluster models

Different local centres in graphite have been considered in a number of publications (see, for example, Bennett *et al* 1971, Pisani 1978, Sokoklov and Evarestov 1984a,b, Casanas *et al* 1983 and references therein). Various modifications of quantum-chemical approaches were used. As a rule, the results obtained for the same centre differ drastically from one another.

The main reason for this difference is connected with the following features of the graphite electronic band structure. The perfect graphite valence band is composed of well localised  $\sigma$ -type states and delocalised  $\pi$  states. The  $\pi$ -electron subsystem is mobile. The corresponding valence and conduction sub-bands stick together in one point of the Brillouin zone, while the energy gap between the  $\sigma$ -valence and  $\sigma$ -conduction sub-bands is sufficiently large. The balance between  $\sigma$ - and  $\pi$ -electron subsystems plays a quite important role in the local-centre description, as the response of these two subsystems on the defect formation is quite different. Any localised-state energy level in graphite falls into one of the allowed energy bands of the perfect crystal. Therefore, all these states are resonant in nature. The corresponding one-electron wavefunctions extend far from the defect centre and are essentially delocalised over the whole crystal.

The non-embedded-cluster and periodic-centre models can give poor results for such states due to the artificial resonances between the localised and pseudo-surface states (in cluster models) or between the states of local centres from different unit cells of periodically perturbed solid (in periodic models).

In our opinion the GF method and embedded-cluster models are the most appropriate for the description of local centres in graphite. The GF method was used in calculations of atomic hydrogen adsorption on a graphite monolayer in the framework of the EHT (Cohen *et al* 1977). As this calculation was based on the  $\pi$ -electron and tight-binding approximations, the  $\sigma$ -electron subsystem and long-range interactions were not considered. This makes the validity of results obtained in Cohen *et al* (1977) questionable.

The embedded-cluster models were used in the study of local centres on/in a graphite monolayer in the framework of the complete neglect of differential overlap (CNDO) scheme (Pisani 1978, Pisani *et al* 1979, Pisani and Ricca 1980, Sokolov and Evarestov 1984a,b, Evarestov and Verjazov 1987).

Pisani's MLEC calculations were based on the CNDO/2 technique (Pople and Beveridge 1970), and our's on the CNDO/BW method (Boyd and Whitehead 1972).

Since the traditional CNDO scheme gives rather poor results for the perfect graphite electronic structure, we have modified it (Evarestov *et al* 1982). Modifications involved mainly the resonance integrals. The  $sp^2$  hybridisation of  $\sigma$ -type atomic orbitals was taken into account.

The equations of the CNDO/BW method in the LUC-EC model are the following:

$$FC = CE$$

$$F_{\mu\mu} = U_{\mu\mu} + (P_{AA} - \frac{1}{2}P_{\mu\mu})\gamma_{AA}^{00} - \sum_{B \in C_0}^{M_0} q_B \gamma_{AB}^{00} - 2\beta_{AA} I_{\mu} \sum_{j=1}^{N-1} S_{\mu\mu}^{0j} - \sum_{j=1}^{N-1} \sum_{B \in C_j}^M q_B^f \gamma_{AB}^{0j}$$

$$F_{\mu\nu} = -\beta_{AB} (I_{\mu} + I_{\nu}) \sum_{j=0}^{N-1} S_{\mu\nu}^{0j} - \frac{1}{2}P_{\mu\nu} \gamma_{AB}^{00} - \frac{1}{2} \sum_{j=1}^{N-1} P_{\mu\nu}^f(\mathbf{0}) f(\mathbf{R}_A^0 - \mathbf{R}_B^j) \gamma_{AB}^{0j} \quad (15)$$

where  $\mu$  and  $\nu$  are the indices of AO centred on atoms A and B from the  $C_0$  region,  $M_0$  the total number of atoms in this region,  $M$  the total number of atoms in the  $j$ th region ( $j = 1, \dots, N-1$ ),  $\gamma_{AB}$  the Coulomb integral,  $\beta_{AA}$ ,  $\beta_{AB}$ ,  $U_{\mu\mu}$  the parameters of the method, and  $I_{\mu}$  the total ionisation potential of  $\mu$ th AO.

In our calculations we have neglected all interactions between atoms that are situated at a distance of more than 10 atomic units. Open shells were handled using the half-electron method (Dewar *et al* 1968).

The results of calculations for some neutral local centres (adsorbed hydrogen atom, single vacancy, substitutional boron and nitrogen impurities on/in a graphite monolayer) are given in table 1. By  $\Delta P_A$  is denoted the mean deviation of the density matrix of imperfect solid from the perfect crystal value:

$$\Delta P_A = (1/n) \left( \sum_{\mu, \nu \in A}^n (P_{\mu\nu} - P_{\mu\nu}^f)^2 \right)^{1/2}$$

where  $n$  is the number of valence orbitals on atom A. The  $\Delta P_A$  value characterises the distortion of the electronic density on the corresponding atom by the local-centre potential.

As can be seen from table 1, the net charges on impurity atoms calculated in different embedded-cluster models differ in sign. In our opinion, the main reason for this is the discrepancy of semi-empirical calculational schemes used (CNDO/2 and modified CNDO/BW).

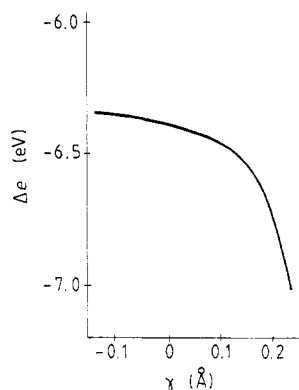
As follows from simple electronegativity considerations a carbon atom accepts positive charge being bound with nitrogen atoms and negative charge if it is bound with

**Table 1.** MLEC  $C_{22}$  and LUC-EC results for local centres in/on a graphite monolayer.

Type of centre	Number of sphere	MLEC		LUC-EC			
		$C_{22}$		$C_{24}$		$C_{32}$	
		$Q_i$	$P_i$	$Q_i$	$P_i$	$Q_i$	$P_i$
Hydrogen	$H_{\text{ads}}$	0.110	—			-0.012	
	0	0.045	—			0.048	0.022
	1	0.020	—			0.007	0.005
	2	-0.025	—			-0.009	0.001
	3	0.005	—			-0.008	0.003
	4					0.004	0.001
	5					0.010	0.001
	6					-0.009	0.001
	7					-0.011	0.001
8					0.000	0.001	
Nitrogen	$N_{\text{subs}}$	0.012		-0.248		-0.117	
	1	0.078	0.028	-0.007	0.044	0.041	0.016
	2	-0.008	0.007	-0.021	0.004	0.001	0.002
	3	0.004	0.008	0.074	0.020	-0.005	0.005
	4	-0.019	0.008	0.048	0.015	-0.002	0.001
	5	0.002	0.003	-0.029	0.016	0.007	0.002
	6			-0.015	0.010	0.008	0.001
	7					-0.003	0.002
	8					-0.012	0.003
Boron	$B_{\text{subs}}$	-0.138		0.075		0.085	
	1	-0.035	0.026	-0.046	0.019	-0.064	0.030
	2	0.009	0.006	-0.028	0.009	0.004	0.004
	3	-0.001	0.006	0.022	0.007	0.020	0.010
	4	0.005	0.004	0.051	0.009	0.004	0.002
	5	-0.002	0.003	-0.009	0.003	-0.006	0.002
	6			-0.056	0.013	-0.009	0.002
	7					0.006	0.003
	8					0.004	0.003
Vacancy	1	-0.151	0.054	-0.153	0.069	-0.032	0.064
	2	0.052	0.011	0.016	0.009	-0.015	0.011
	3	-0.029	0.032	0.069	0.016	0.047	0.019
	4	0.024	0.014	0.035	0.009	0.002	0.004
	5	0.013	0.003	-0.031	0.014	0.003	0.005
	6			0.018	0.009	-0.005	0.004
	7					0.009	0.006
	8					-0.005	0.006

boron atoms ( $\chi_C = 2.5$ ,  $\chi_N = 3.0$ ,  $\chi_B = 2.0$ ). Our results for LUC-EC  $C_{32}$  agree well with this consideration, contrary to Pisani's results.

The coincidence of  $\Delta P_A$  values is much better and the results for MLEC are quite often intermediate between the results for  $C_{24}$  and  $C_{32}$  LUC-EC. As can be seen from the comparison of calculations for  $C_{13}$  and  $C_{22}$  quasi-molecules in the MLEC model (Pisani 1978, Pisani *et al* 1979) and for  $C_{24}$  and  $C_{32}$  quasi-molecules in the LUC-EC models, the results obtained in both approaches for similar centres become closer to each other when cluster size increases.



**Figure 3.** The quasi-local  $A'_1$  level position with respect to the Fermi level ( $\Delta e = e_i - e_F$ ) as a function of relaxation parameter  $\gamma$ . The  $\gamma$  value characterises the shift of the first-sphere atoms towards the vacancy site.

The following conclusions can be made from our results presented in table 1. (i) The perturbation of the electronic density of graphite by the local centres considered is essential for the first three spheres of atoms surrounding the defect. (ii) The strength of this perturbation falls in the order: vacancy  $>$   $B_{\text{subs}} >$   $N_{\text{subs}} >$   $H_{\text{ads}}$ . (iii) The quasi-molecule  $C_{24}$  in the LUC-EC model is not sufficiently large to provide the quantitative description of centres under consideration. The  $C_{32}$  LUC-EC is sufficiently large for this purpose.

An interesting problem concerning the upper occupied quasi-local vacancy state in graphite was posed in Pisani *et al* (1979). According to Zunger and Englman (1978) the doubly degenerate singly occupied level of  $E''$  symmetry is located quite near the Fermi level ( $E_F$ ). It corresponds to  $\pi$ -type crystalline orbitals spatially localised on the atoms surrounding the vacant site. Contrary to this Pisani *et al* (1979) found only a well localised fully occupied  $\sigma$  level of  $A'_1$  symmetry. The corresponding one-electron energy is approximately 5 eV lower than  $E_F$ . About half of the electronic population of this level is associated with three atoms of the first sphere around the vacancy, the rest being delocalised over six atoms of the second sphere.

In our calculations we have obtained the quasi-local occupied level of symmetry  $A'_1$ , located approximately at 5 eV below the Fermi level. The main contribution to the electronic density on this level is given by atoms of the first and second spheres (55 and 15% respectively).

The shift of the  $A'_1$  level position as a function of lattice relaxation about the vacancy is shown on figure 3. The results for the upper occupied quasi-local level obtained in both embedded-cluster models are in qualitative agreement. These results disagree with those obtained in periodic-cluster calculations of Zunger and Englman (1978). At the same time  $\pi$  and  $\sigma$  electronic charges on the carbon atoms nearest to the vacancy obtained by us (3.74 and 0.40 electrons respectively) are in good agreement with Zunger's results.

In order to determine the direction of shift of the first-sphere atoms (towards or away from the vacancy site), we have calculated the Wiberg index (Wiberg 1968) for bonds towards and away from the vacancy site. For perfect graphite we have obtained the values 0.006 and 1.211 for the bonds of a first-sphere atom with its neighbours in this sphere and in the second sphere, respectively. In the imperfect crystal the Wiberg index increases for a bond across the vacancy site (0.018) and decreases for a bond with a second-sphere atom (1.196). This result agrees well with the result obtained on the basis of MLEC calculations (Pisani *et al* 1979), where the shift towards the vacancy site was predicted in contrast with the predictions of Zunger and Englman (1978).

**Table 2.**  $C_{32}$  LUC-EC results for charged local centres in/on a graphite monolayer.

Type of centre	Number of sphere	Total charge of centre			
		+1		-1	
		$Q_i$	$P_i$	$Q_i$	$P_i$
Hydrogen	$H_{ads}$	0.063		-0.076	
	0	0.057	0.032	0.038	0.014
	1	0.048	0.018	-0.043	0.016
	2	-0.044	0.010	0.041	0.008
	3	0.049	0.012	-0.068	0.017
	4	0.045	0.005	-0.047	0.012
	5	0.078	0.006	-0.083	0.007
	6	0.019	0.002	-0.021	0.002
	7	0.029	0.005	-0.031	0.006
8	0.054	0.005	-0.042	0.006	
Nitrogen	$N_{subs}$	-0.078		-0.030	
	1	0.094	0.021	-0.014	0.028
	2	-0.042	0.008	0.048	0.012
	3	0.056	0.011	-0.059	0.020
	4	0.043	0.005	-0.046	0.005
	5	0.091	0.007	-0.075	0.007
	6	0.031	0.002	-0.011	0.004
	7	0.029	0.004	-0.032	0.007
	8	0.032	0.003	-0.065	0.008
Boron	$B_{subs}$	0.150		0.020	
	1	-0.031	0.028	-0.099	0.034
	2	0.036	0.007	0.043	0.009
	3	0.083	0.026	-0.041	0.008
	4	0.051	0.005	-0.042	0.005
	5	0.078	0.007	-0.092	0.007
	6	0.012	0.003	-0.029	0.003
	7	0.038	0.009	-0.024	0.003
	8	0.046	0.008	-0.041	0.003

The Wiberg index is usually considered as the order of the corresponding bond in molecules. Its value for the bond between an impurity boron atom and the nearest carbon atom (1.096) is much larger than the analogous value for a nitrogen impurity (0.617). This result correlates well with the results of Pisani's calculations and well known experimental results of lower stability of nitrogen impurities in comparison with boron ones.

As was pointed out above, the LUC-EC model is applicable to charged centres. For  $C_{32}$  LUC-EC we have calculated the electronic structure of some positively and negatively charged centres. The values of atomic charges and density matrix deviations obtained are given in table 2.

It can be seen from this table that the excess charge does not cause a drastic distortion of the local centre's structure. Again, as for neutral defects, the local centre consists of a strongly perturbed region (including about 3-5 atomic spheres) and the rest of the perturbed solid. Of course, the rest of the solid perturbation is larger for charged centres than for uncharged ones.

The excess charge is not localised on the defect or in its neighbourhood, but extends

over the whole embedded cluster. This result coincides with the well known semi-metal properties of graphite. Note that a smaller deviation of the electronic density has been obtained for defects isoelectronic with the carbon atom ( $N_{\text{subs}}^+$ ,  $B_{\text{subs}}^-$ ) than for centres of opposite charge.

## 6. Conclusions

In this paper we have briefly discussed the advantages and drawbacks of the main approaches to local-centre electronic structure theory. Based on this discussion we regard the embedded-cluster models as the most appropriate for consideration of various local centres in different types of solids. Then we have compared the formulation, limitations and approximations behind the moderately large embedded-cluster (MLEC) and the large-unit-cell-embedded-cluster (LUC-EC) models. It has been shown that both models are close, but the second one is simpler in practical implementation and is applicable to charged centres. Finally the results obtained for some local centres on/in a graphite monolayer have been discussed. It has been shown that both embedded-cluster models give comparable results for neutral centres. Charged centres have been considered for the first time in the framework of the LUC-EC model.

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