# Cluster and supercell calculations for carbon-doped silicon

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**Abstract.** The substitution of carbon in bulk silicon is investigated at the Hartree–Fock level using a cluster model, and the results compared directly with periodic 'supercell' calculations based on the same Hamiltonian, basis set and computational scheme. To study variations in calculated properties with cluster size, hydrogen-saturated clusters containing five, thirty-five and eighty-seven Si atoms are considered, with relaxation of up to the second shell of neighbours surrounding carbon impurities. The calculated atomic relaxations and charge distributions in supercells and large clusters are reasonably similar. In relaxed clusters however, boundary effects lead to appreciable differences in calculated defect formation energies.

## 1. Introduction

The cluster approach is widely used to study local defects [1–4], chemisorption at crystalline surfaces [5–10], molecular crystals [11–13] and, in extreme cases, the properties of bulk solids [14, 15]. A particular advantage of this method, in which the infinite system is approximated by a finite cluster containing a relatively small number of atoms, is the fact that the most sophisticated many-body techniques of quantum chemistry may be used in a straightforward way to estimate electron correlation effects. Nevertheless, there are a number of disadvantages as compared to the more realistic supercell [16–19] and embedded-cluster [20, 21] schemes, the most important of which are related to the spurious perturbation arising from the abrupt truncation of the infinite lattice. For ionic systems, the most important contribution from the missing ions is the Coulomb field, which may be approximated through the introduction of either a finite set [5, 8, 10] or an infinite array [22] of point charges. In metals and covalent solids by contrast, border quantum effects are important and not easily simulated. In covalent solids the atoms at the surface of the cluster would normally be bound to other atoms and, to simulate these bonds whilst retaining the possibility of working with a finite cluster, the usual approach is to saturate the 'dangling bonds' of the cluster with hydrogen atoms [6, 7, 9]. A number of ambiguities remain however, such as the importance of overlap terms between the cluster and the missing infinite crystal, the field modification arising from the presence of the hydrogen atoms and the appropriate method to use in the case of mixed ionic–covalent situations. A justification of the cluster models is often found *a posteriori* in the inner consistency of the method, i.e. convergence of results with cluster size, and comparison with other calculations or experimental data. However, such comparisons can of course only be qualitative, since they are generally made between methods differing not only in the description of the local features around
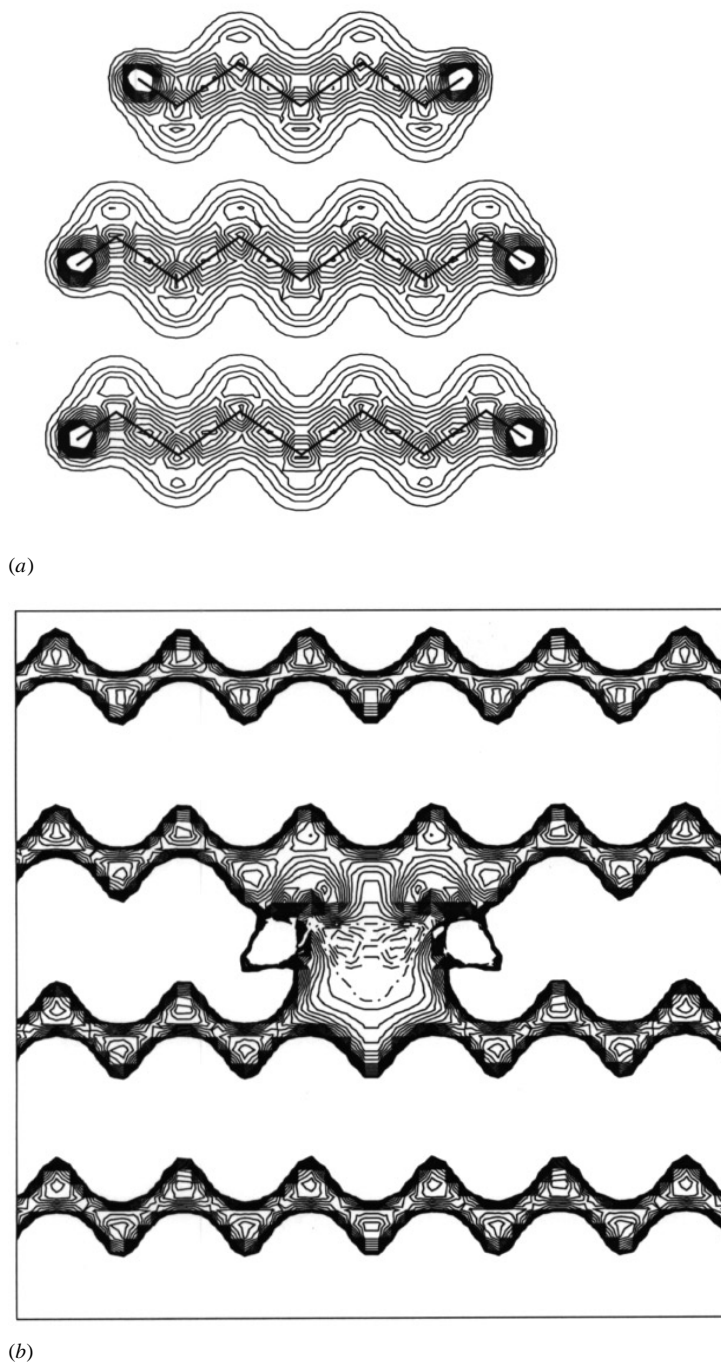
(a)



(b)

**Figure 1.** Total (a) and difference (b), (c), (d) valence charge-density maps for the unsubstituted Si clusters in the (110) plane. Difference maps are for differences between the charge density of the perfect periodic Si crystal and the clusters calculated with the same geometry, basis set and computational conditions. (a) and (d) refer to a large cluster (87 Si atoms), (b) to a small cluster (5 Si atoms) and (c) to a medium-sized cluster (35 Si atoms). Adjacent isodensity lines are separated by $0.01e$ Bohr$^{-3}$ in (a) and $0.0005e$ Bohr$^{-3}$ in (b), (c) and (d). Continuous, dashed and chain lines correspond to positive, negative and zero differences respectively. Density differences greater than $0.01e$ Bohr$^{-3}$ are not represented. The positions of the atoms in the covalent network are highlighted by straight black lines.
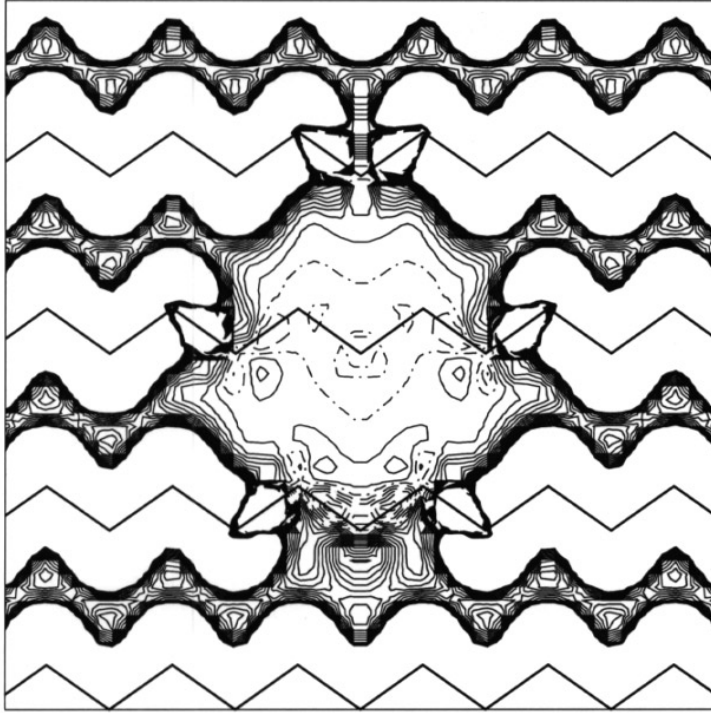
(*c*)
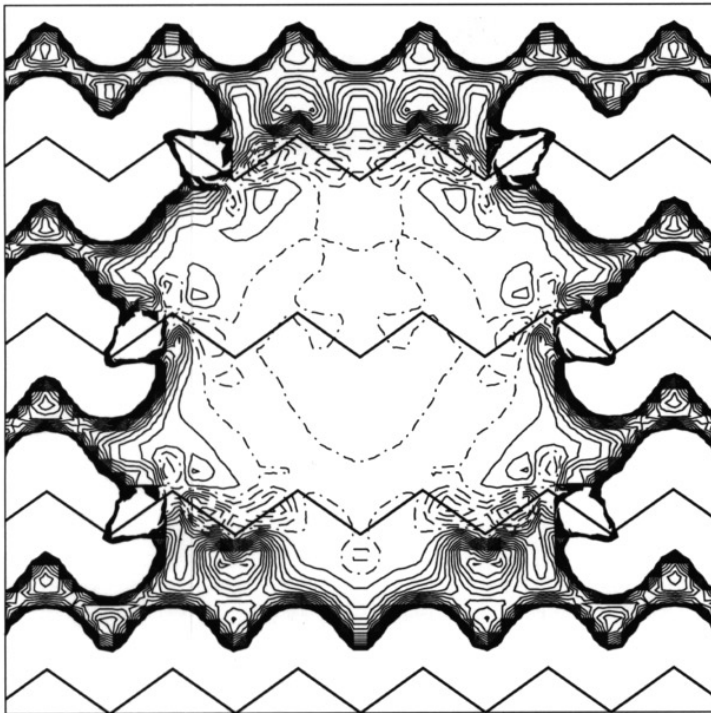


(*d*)

**Figure 1.** (Continued)

the defect (cluster, supercell, embedding scheme), but also in the Hamiltonian, basis set and computational parameters. Convergence with respect to the number of atoms in the cluster is a questionable procedure since the surface perturbation increases with cluster size. Furthermore, the cost of such calculations quickly becomes enormous, so in most cases the largest clusters considered contain rather a small number of atoms (less than 100).

The aim of the present work is to investigate the performance of the cluster approach for the case of carbon substitution in bulk silicon. This system is particularly appropriate for a study of the variation of properties with cluster size, since the appreciable difference in the electronegativities and covalent radii of carbon and silicon imply that charge transfer and relaxation effects are considerable (the Mulliken net charge in SiC is $\pm 1.81|e|$ [30], and the interatomic distances in diamond, SiC and silicon are 1.56, 1.90 and 2.36 Å respectively). In this paper, defect substitution energies, atomic relaxations, charge distributions and electrostatic potentials are investigated as functions of the cluster size, and are compared directly with the results of well-converged supercell calculations. This latter method involves a periodic array of unit cells of the host crystal containing the carbon impurity at the centre. If the cell is sufficiently large, interaction between the defects belonging to different cells is negligible; it was shown in a previous paper [23] that a 64-atom supercell containing the carbon impurity is large enough to describe an isolated defect consistently. Both supercell and cluster calculations were performed using the same computer code, namely CRYSTAL92 [24, 25, 26]. In this way, differences between the results of the two methods may be attributed completely to the assumption of cluster or periodic boundary conditions, rather than to differences in the Hamiltonian, basis set or computational scheme.

**Table 1.** Structure and Mulliken charges of undoped Si clusters. Roman numerals refer to successive stars of neighbours around the centre of the cluster.

| Star | Structure of cluster | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 0 | I | II | III | IV | V | VI | VII |
| Distance from origin (Å) | 0.0 | 2.36 | 3.86 | 4.53 | 5.46 | 5.95 | 6.69 | 7.09 |
| Number of atoms in star (number of bonds to H per Si) | | | | | | | | |
| $Si_5H_{12}$ | 1(0) | 4(3) | — | — | — | — | — | — |
| $Si_{35}H_{36}$ | 1(0) | 4(0) | 12(1) | 12(1) | 6(2) | — | — | — |
| $Si_{87}H_{76}$ | 1(0) | 4(0) | 12(0) | 12(0) | 6(0) | 12(1) | 24(1) | 16(2) |
| Mulliken charges | | | | | | | | |
| $Si_5H_{12}$ | −0.18 | +0.58 | — | — | — | — | — | — |
| $Si_{35}H_{36}$ | −0.07 | −0.10 | +0.17 | +0.15 | +0.38 | — | — | — |
| $Si_{87}H_{76}$ | +0.01 | −0.01 | −0.05 | −0.06 | −0.08 | +0.17 | +0.27 | +0.33 |

## 2. Computational details

CRYSTAL92 is a widely established code that has been used to study a variety of solid-state problems. A description of the periodic Hartree–Fock crystalline orbitals (LCAO) self-consistent-field computational scheme embodied in this program may be found in [25] and [26]. Recent modifications to the code now allow cluster calculations to be performed using

an option for the automatic selection of atoms from the infinite perfect crystal, according to distance and/or connectivity criteria. In this work we have examined clusters containing 5, 35 and 87 silicon atoms, which will be referred to as small, medium and large. Bond distances and angles are the same as in the bulk crystal. The dangling bonds were saturated with hydrogen atoms along Si–Si directions of the perfect crystal. The optimized Si–H distance (1.5 Å) for the small cluster was used throughout. The medium and large clusters were constructed subject to the constraint that silicon atoms at the cluster surface were connected to a maximum of two hydrogens.

The Gaussian basis sets adopted for silicon and carbon were the same as in previous bulk [27] and supercell [23] studies. Two sp shells and one d shell (13 atomic orbitals) per atom were used, with core electron states represented by Durand–Barthelat pseudopotentials [28]. For hydrogen, a standard 21G basis set [29] was used. The computational conditions that control the truncation of the Coulomb and exchange series, as defined in [25, 26], were set at 5, 5, 6, 6 and 12, which provides reasonably high numerical accuracy; the total energy per Si atom of the perfect crystal evaluated for supercells containing 2, 8, 16, 32 and 64 atoms lies always within a range of less than $10^{-5}$ Hartree (3.770 42 Hartree) [23].

## 3. Results and discussion

Before we examine the substitution of carbon, the quality of the cluster approach as a model of the undoped infinite silicon crystal will be considered. In table 1, the net Mulliken charges of atoms belonging to stars of neighbours at increasing distances from the centre of the cluster are shown. Compared to the necessarily uncharged atoms of bulk Si, it is apparent that only silicon atoms not directly bonded to hydrogen have net charges of less than $0.1|e|$. Due to the packed nature of the diamond structure, the small, medium and large clusters contain only zero, one and four stars of silicon atoms that satisfy this criterion. In the large cluster (shown in figure 1(a)), the charge distribution in the zone containing the central atom and its first neighbours is quite close to the bulk one, with net charges smaller than $\pm0.01|e|$. For the medium cluster, the zone similar to the bulk is much smaller, with a charge of $-0.07|e|$ at the central atom and $-0.1|e|$ on the first star of neighbours. The charges on the small cluster are quite different from those of the bulk. The relative sizes of the bulk-like zone can be appreciated from figures 1(b)–(d) where maps of the charge-density difference between supercell and cluster calculations are shown.

**Table 2.** Relaxation effects in the undoped clusters for the first- and second-nearest neighbours of the central Si atom. $\Delta E$ is the total relaxation energy (eV). $\Delta R$ is the change in distance (Å) between a star of neighbours and the central atom, compared to the perfect-crystal geometry. The optimized Si–Si distance in the bulk (obtained with the same basis set) is 2.3642 Å.

| Cluster | I | | II | |
|---|---|---|---|---|
| | $\Delta E$ | $\Delta R$ | $\Delta E$ | $\Delta R$ |
| $Si_5H_{12}$ | 0.0025 | 0.01 | — | — |
| $Si_{35}H_{36}$ | 0.0113 | 0.02 | 0.0406 | 0.01 |
| $Si_{87}H_{76}$ | 0.0004 | 0.00 | 0.0039 | 0.01 |

Table 1 shows that the presence of hydrogen atoms, which are more electronegative than Si, induces a positive charge on neighbouring Si atoms, the magnitude of which depends approximately on the degree of saturation. This effect propagates and, for the large

undoped silicon clusters, between three and four bond distances from the surface hydrogens are necessary to restore charge distributions similar to those of the bulk. The large cluster can be crudely described as a locally neutral core, consisting of the central atom and its first shell of neighbours, surrounded by a double layer of positive charge (from $+0.17|e|$ to $+0.33|e|$) and negative charge (up to $-0.10|e|$ on H). For the small and medium clusters, the neutral region disappears because the central atom is still influenced by boundary effects. It might be thought that the atomic positions at the centre of the cluster may be affected by the spurious electrostatic field set up by this double layer. Table 2 shows, however, that for the undoped silicon cluster the field is not strong enough to cause significant atomic displacements, presumably since covalent and short-range repulsion effects predominate in determining the interatomic forces in this system.

The energy gap of the clusters, defined as the energy difference between the highest occupied and the lowest unoccupied molecular orbitals, tends to the bulk value as the size of the silicon cluster increases. The calculated gaps were 13.40 eV (small), 9.69 eV (medium) and 8.65 eV (large), compared with 6.20 eV for the periodic crystal, i.e. still around 2.5 eV greater in the large cluster. These values are all much larger than the experimental optical gap, which is of the order of 1.2 eV [31]. However, it should be remembered that differences in Hartree–Fock eigenvalues do not strictly correspond to excitation energies even within a frozen orbital picture; the experimental data will also be affected by correlation, and, probably more importantly, relaxation effects which will considerably lower the observed excitation energies. It can therefore safely be concluded that the Hartree–Fock band gap is a considerable overestimate of the observed optical gap, and that it is not appropriate to interpret spectroscopic data in terms of Hartree–Fock eigenvalues. A final point regarding the electronic structure is that the proportion of hydrogen in the highest occupied and lowest unoccupied orbitals as measured by the coefficients in the molecular orbital expansion was significant in all the cluster calculations, although a decrease with increasing cluster size was observed.

We now consider the substitution of carbon into silicon clusters. In our previous supercell study of this system [23], it was shown that the purely *electrostatic* perturbation due to the negatively charged carbon impurity is screened almost completely by its first shell of neighbours (four Si atoms). This is apparent in figures 2(a) and 3(a), where we show the difference between the charge densities and electrostatic potentials of the unrelaxed C-doped and undoped supercells. The rearrangement of charge is seen to affect essentially only first-nearest neighbours of the carbon. Figures 2(b) and 3(b), which are the equivalent diagrams for the large cluster, show that these features are adequately described by the cluster model. If the polarization field is extended to include the atomic positions however, the perturbation is found to propagate through the covalent chain as far as the *fifth* shell of neighbours via displacements of the Si atoms in the vicinity of the carbon atom [23]. The adequacy of the cluster model in describing this process may be discussed by examining defect formation energies, which we define as

$$E_{\mathrm{S}} = [E_{\mathrm{cluster}}(\mathrm{Si}) - E_{\mathrm{atom}}(\mathrm{Si})] - [E_{\mathrm{cluster}}(\mathrm{C}) - E_{\mathrm{atom}}(\mathrm{C})].$$

Here $E_{\mathrm{cluster}}(\mathrm{C})$ and $E_{\mathrm{cluster}}(\mathrm{Si})$ are the total energies of doped and undoped clusters, and $E_{\mathrm{atom}}(\mathrm{Si})$ and $E_{\mathrm{atom}}(\mathrm{C})$ are the appropriate atomic energies (3.6550 and 5.2876 Hartree for Si and C respectively).

Table 3 shows that, in the absence of atomic relaxation, the formation energies from cluster calculations are very similar to those calculated using the supercell approach, even in the case of small clusters. This indicates that, for the unrelaxed system, the electronic structure around the first shell of neighbours of the carbon impurity is described equally
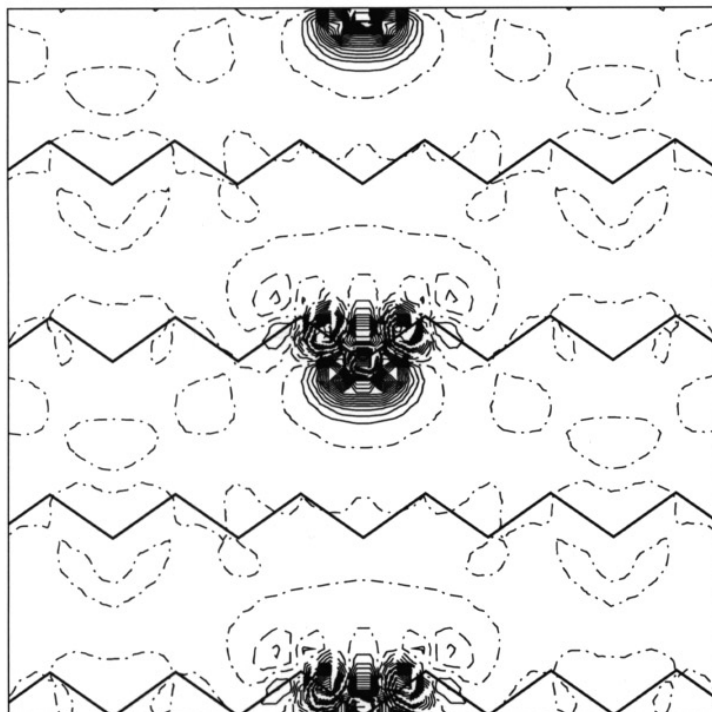
(a)
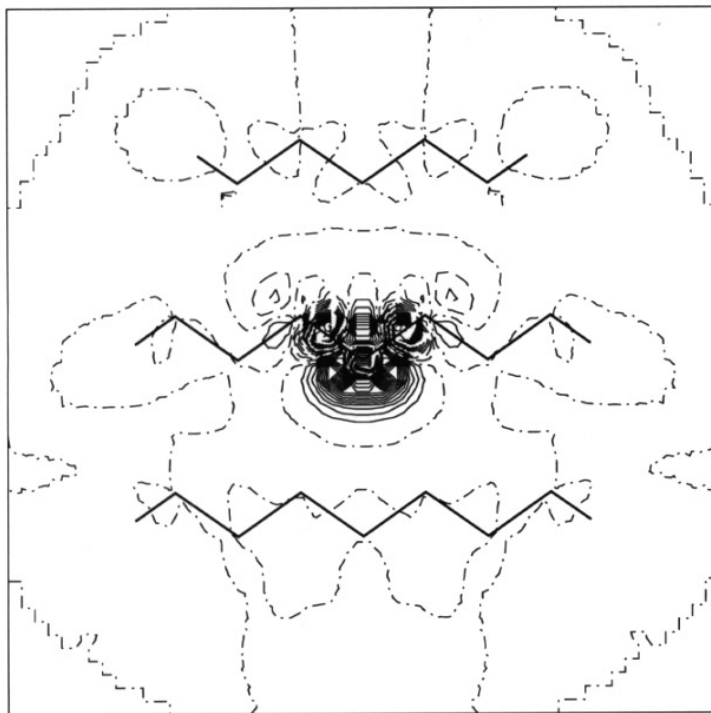
(b)

**Figure 2.** Maps of the difference between the charge density of C-substituted Si and that of unsubstituted Si; (a) refers to a periodic 64-atom supercell and (b) to a large-cluster calculation (87 Si atoms). Adjacent isodensity lines are separated by $0.001e$ Bohr$^{-3}$. The section and symbols are as in figure 1.

**Table 3.** Carbon substitutional energy and relaxation effects as a function of cluster size. $E_S$ is the substitutional energy (eV) defined in (1). $\Delta R$ is the change in distance (Å) between the defect and its first (four Si) and second (twelve Si) neighbours—these distances are 2.364 and 3.861 Å in the perfect Si crystal. 'First' means that only the first shell of neighbours is allowed to relax, while 'second' refers to relaxation of both first and second shells.

| Cluster | Relaxation | $E_S$ | $\Delta R_1$ | $\Delta R_2$ |
|---|---|---|---|---|
| $CSi_4H_{12}$ | Unrelaxed | 1.90 | — | — |
| | First | 0.87 | −0.16 | — |
| | Second | — | — | — |
| $CSi_{34}H_{36}$ | Unrelaxed | 1.97 | — | — |
| | First | 0.81 | −0.21 | — |
| | Second | 0.72 | −0.23 | −0.02 |
| $CSi_{86}H_{76}$ | Unrelaxed | 1.99 | — | — |
| | First | 0.52 | −0.24 | — |
| | Second | 0.25 | −0.27 | −0.05 |
| Supercell | Unrelaxed | 1.93 | — | — |
| | First | 0.43 | −0.24 | — |
| | Second | 0.08 | −0.28 | −0.05 |

well in both models, and that the influence of boundary effects in that region of the cluster is small. In each case, the four nearest Si neighbours have a positive net charge that compensates to a large extent the negative charge of carbon (table 4), and thus the $CSi_4$ core of each cluster appears to be sufficient to describe the electronic perturbation. Although the electrostatic field created by the double layer is appreciable, the high positional symmetry of the central impurity site minimizes its influence. This is certainly not true near the surface of the cluster, but, as the doped and the undoped cluster show very similar structures there, the corresponding terms in $E_S$ cancel almost completely.

**Table 4.** Net atomic charges and Mulliken bond populations of substituted clusters with relaxed geometry. Asterisks indicate silicon atoms bonded to one or more hydrogens.

| Cluster | Mulliken charge | | | Bond population | | |
|---|---|---|---|---|---|---|
| | 0 | I | II | 0–I | I–II | II–III |
| $CSi_4H_{12}$ | −1.18 | 0.83* | — | 0.31 | — | — |
| $CSi_{34}H_{36}$ | −1.16 | 0.23 | 0.15* | 0.30 | 0.37 | 0.39 |
| $CSi_{86}H_{76}$ | −1.18 | 0.37 | −0.08 | 0.30 | 0.38 | 0.38 |
| Supercell | −1.20 | 0.38 | −0.03 | 0.30 | 0.38 | 0.38 |

It might be expected, however, that differences between substitution energies from cluster and supercell calculations could increase when relaxation is taken into account, because the defect perturbation then extends further from the impurity into regions where the screening of the border effect is only partial. The results shown in table 3 confirm this; defect substitution energies from the cluster calculations differ from the supercell results by 0.44 (small), 0.38 (medium) and 0.09 (large) eV when first nearest neighbours are allowed to relax, and 0.64 (medium) and 0.17 (large) eV with the addition of relaxed second-nearest neighbours. For a consistent description of the defect energetics in this system, it thus appears that relaxation of the covalent network needs to be accurate to large numbers of stars of neighbours, implying much worse agreement for smaller and medium clusters where
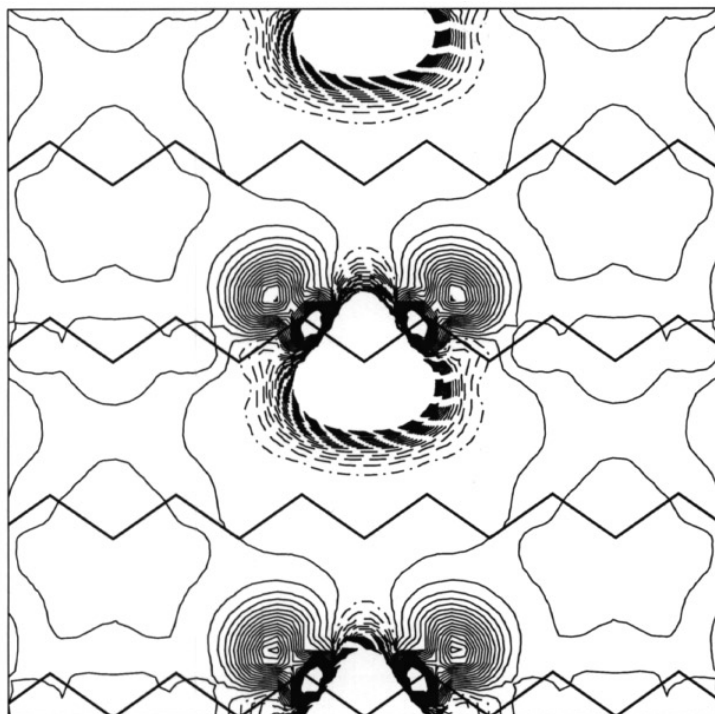
(a)
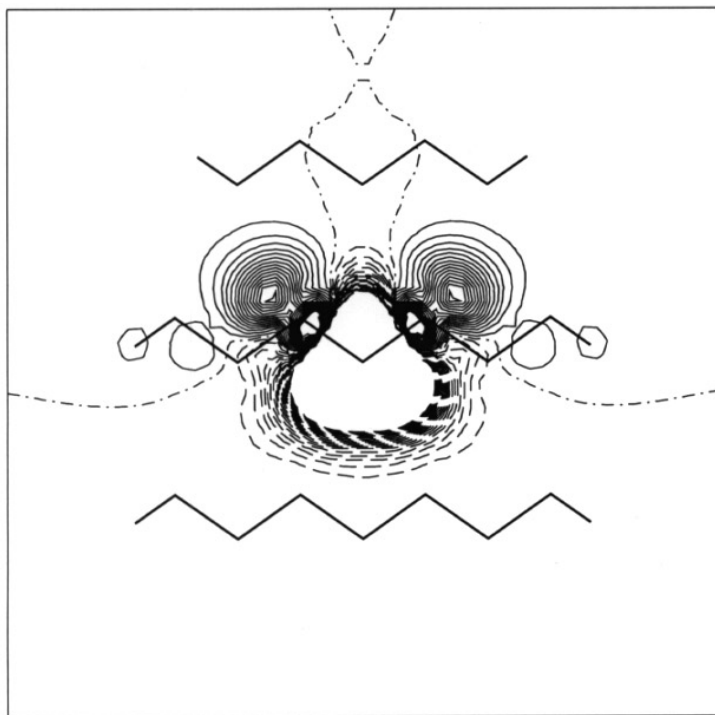


(b)

**Figure 3.** Maps of the difference between the electrostatic potential in C-substituted Si and that of unsubstituted Si; (a) refers to a periodic 64-atom supercell and (b) to a large-cluster calculation (87 Si atoms). Adjacent isopotential lines are separated by 0.027 eV. The section and symbols are as in figure 1.

these neighbours are either absent or are significantly perturbed by border effects.

## 4. Conclusion

In this study, we have compared the description of carbon substitution in bulk silicon at the Hartree–Fock level using various cluster models and a periodic supercell model. The cluster model proves to be adequate to describe the local charge distribution surrounding the defect. As was found in periodic supercell calculations [23], the purely electrostatic perturbation due to the carbon impurity is very short ranged and screened virtually completely by the nearest Si neighbours, to the extent that it is described well even in the smallest cluster. In the absence of relaxation, we find a difference of only 0.03 eV in substitution energy compared to supercell calculation with the same basis set and computational conditions. However, atomic relaxation effects are much more sensitive to cluster termination and the energetic effect of such relaxations surrounding the defect is high (around 2 eV). Large clusters are thus required if accurate results are to be obtained. The error in the substitution energy is still considerable in our largest cluster (containing 87 Si atoms) even though the magnitude of the relaxation is reasonably accurate. These results highlight the care with which one should approach such calculations, particularly when discussing results obtained with small covalently bonded clusters (e.g. [7] where less than five non-hydrogen atoms per cluster were used).

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