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ATOMIC CHARGE DISTRIBUTION IN FOURFOLD COORDINATED AMORPHOUS MATERIALS. CARBON AND SILICON*

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Based on Strictly Localized Molecular Orbitals (SLMO) type calculations we propose an empirical formula for the calculation of net atomic charges in tetrahedrally bonded amorphous group IV elements. These charges are in a linear relationship with bond angle distortions involving first and second neighbours. The charge distributions show maxima or shoulders and the location of these can be related to the number of fivefold rings containing the same atoms. The results are compared to ab initio Hartree–Fock calculations.

1. Introduction

In spite of theoretical understanding of electronic states in crystalline systems, amorphous structures cause more difficult problems for theoretical investigations. Because of the absence of translational periodicity the electronic states cannot be described within the context of Bloch's theory. The quantum chemical cluster methods are useful tools to investigate such systems. In these types of small finite cluster Hartree–Fock (HF) calculations there is a difficulty in separating electron properties of the bulk and the surface because of the appearance of spurious surface states. The application of hydrogen for saturation of dangling bonds is a possible way. However, putting H atoms onto the surface of a silicon cluster results in a 0.1 electron charge transfer in the H–Si bonds from hydrogen to silicon which may lead to artifacts in the calculations. In case of a-C this charge transfer is lower [1]. Increasing the size of the clusters is a further possible way to eliminate the influence of this effect but using *ab initio* methods two other problems appear. There is a

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*Dedicated to Prof. R. Gáspár on his 70th birthday serious limit because of the computer capacity and over 10 silicon atoms the convergence problems may increase. These problems reduce if a suitable semiempirical quantum chemical method is used.

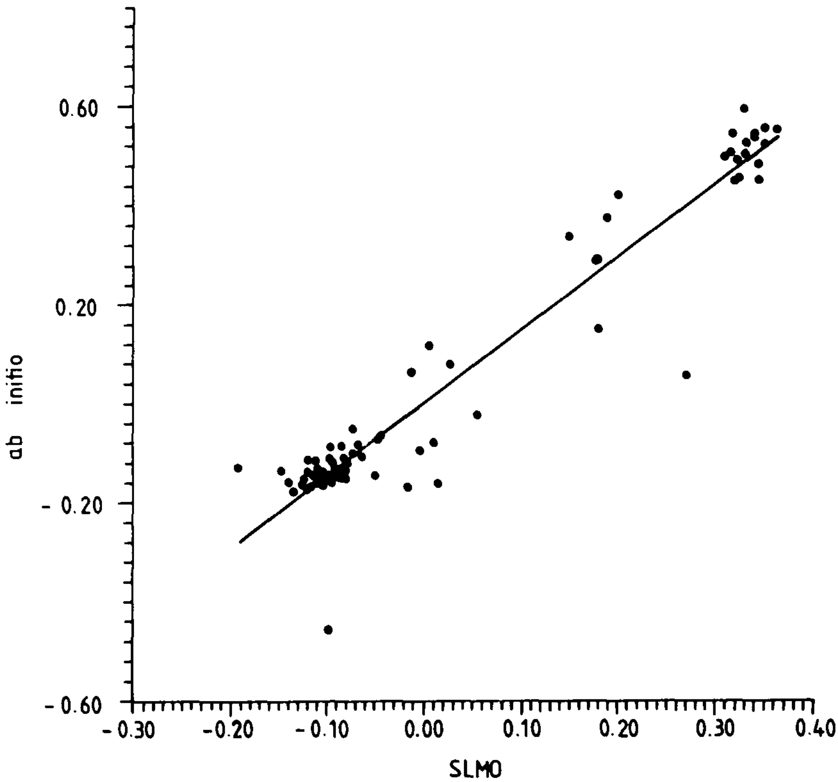

Fig. 1. Comparison of net atomic charges (in millielectrons) in a-Si:H calculated by HF *ab initio* and by SLMO methods. Each point represents a silicon or a hydrogen atom

By symmetry the atoms in crystalline silicon and carbon have no charge at their equilibrium positions but in the amorphous case they carry charges due to geometric distortions. These charges have never been directly measured or calculated though they play an important role in the determination of some experimental properties, like high resolution core-level spectra or infrared absorptivity. In this paper we summarize our earlier studies on the determination of the charge accumulation in finite aperiodic clusters of fourfold coordinated amorphous carbon and silicon by means of a semiempirical molecular orbital method and we present an empirical formula depending on angle distortions for calculating their net atomic charges. Applying our formula we calculate the charge fluctuations which are comparable to the experimental data.

2. Methods

Recently a quantum chemical method has been elaborated for the determination of net atomic charges in tetrahedrally coordinated amorphous materials such as carbon or silicon [2–6]. A cluster of bulk atoms is described by a wave function expanded in terms of strictly localized molecular orbitals. SLMO's are linear combinations of sp^3 atomic hybrids directed along the corresponding bond axis and subsequently orthogonalized on each atom. Hybrid coefficients in SLMO's are derived through solution of a coupled 2×2 secular equation which is based on the diagonalization of a valence electron effective Hamiltonian. Owing to geometry distortions charges will accumulate on atoms and their relative magnitude can be estimated reliably by our method since inductive effects are correctly accounted for and the CNDO parametrization we used yields reliable charge distributions [7].

In order to eliminate the edge effects we put pseudoatoms at the boundary modelling the bulk. These have only one or two neighbours to which they are connected by a sigma bond. The corresponding SLMO is composed of the appropriately oriented hybrids, one of them centered at pseudoatoms the other at the neighbouring atom. To ensure electroneutrality, the effective core charge of pseudoatoms is put equal to 1 or 2 depending on the number of hybrid orbitals attached to it.

In both cases a test of this model was carried out for a crystalline diamond cluster containing 35 ordinary and 36 pseudoatoms. The first neighbour distances in a-Si and a-C were put equal to 235 pm and 155 pm, respectively. The calculation yielded a uniformly neutral charge distribution, less than 10^{-4} electron units charge accumulation was observed on any atom. This indicates that our method is free from the spurious accumulation of surface charges.

3. Finite cluster models

In diamondlike crystalline silicon or carbon the nearest-neighbour arrangement of atoms is perfectly tetrahedral as expected from sp^3 hybridization. In the amorphous form the short range order is retained, only limited bond-length and bond-angle deviations can be found. Previous structural investigations indicated that amorphous carbon usually is a mixture of diamond-like and graphite-like configurations [8]. In the past few years tetrahedrally coordinated a-C with a majority of sp^3 sites attracted much interest. Recently Savvides [9] could increase the upper limit of sp^3 sites to 76 %. It seems to be a realistic goal in the near future to increase the concentration of diamond-like carbon sites in a-C up to 100 %, this is why our studies on this modification seem to be interesting.

In our calculation we have used the continuous random network (CRN) model for the structure of a covalently bonded amorphous material [10]. There are no coordination defects nor dangling bonds inside the model. The CRN model can be considered to be an idealized structure of bulk, tetrahedrally coordinated amorphous carbon and silicon. The finite clusters have been constructed on the basis of a CRN model for a-Si by Wooten et al [10]. This, so-called Sillium model consists of a network of 216 silicon atoms interacting through the Keating local potential [11]. It seems to be the best CRN model at present since it has a periodic boundary condition and reproduces the experimental one-dimensional radial distribution function of tetrahedrally coordinated amorphous semiconductors excellently within the interval of 0–800 pm [12].

At present, there is no geometry available containing only sp^3 sites for a-C, therefore based on the close analogy between classical saturated carbon and silicon compounds we may suppose that scaling down the closest-neighbour atom–atom and atom–pseudoatom distances in a-Si from 235 pm to 155 pm [13] yields an adequate model for a-C, too.

Each of our model clusters consisted of at least 17 atoms and more than 25 pseudoatoms located at the surface.

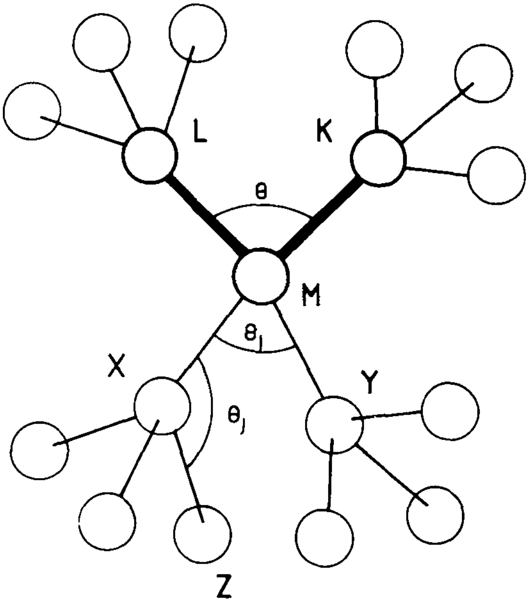

Fig. 2. Atomic arrangement in a CRN model. An elementary triad of tetrahedrally bonded atoms (heavy lines) with the surrounding environment (light lines)

4. Comparison to ab initio quantum chemical calculations

Ab initio quantum chemical calculations have been carried out on small a-Si:H clusters in order to determine the net atomic charges and to make a comparison to SLMO type results. The clusters having 4–11 ordinary silicon atoms have been constructed on the basis of a computer simulated model structure for hydrogenated amorphous silicon [14]. To model the bulk we put hydrogen on the boundary. We have used the MUNGAUSS *ab initio* program [15] and a standard 3-21G basis set

[16]. A fair linear correlation has been obtained between *ab initio* and SLMO results (cf. Fig. 1). The *ab initio* charges are greater than the results calculated by the other method ($q_{ab\ initio} \approx 1.4\, q_{\mathrm{SLMO}}$). On the basis of this comparison, we feel that SLMO is a very convenient method for calculating the net atomic charges since, as is known, the HF *ab initio* method (with standard 3-21G basis set) a little bit overestimates the net atomic charges.

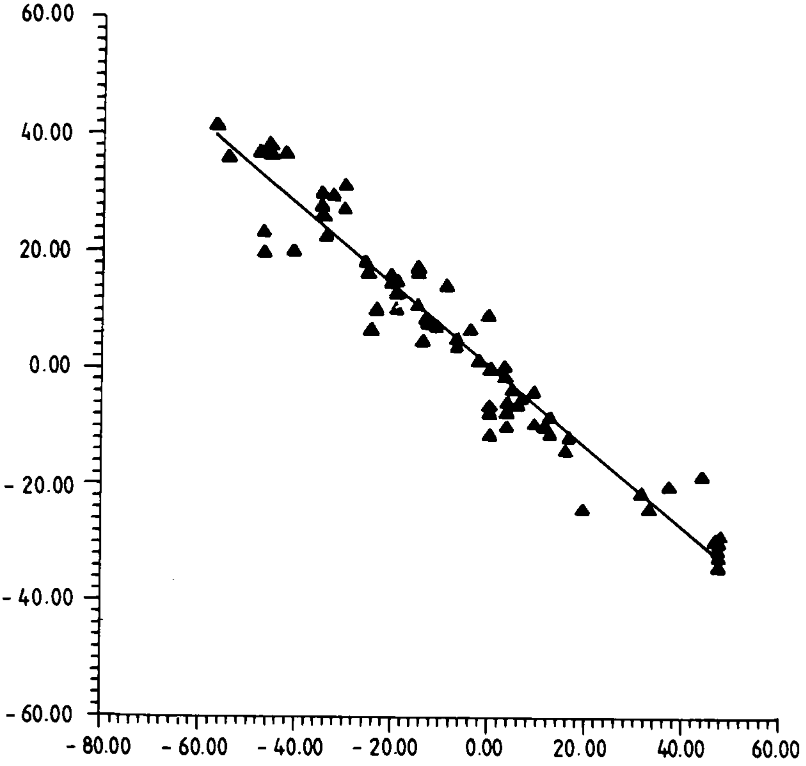

Fig. 3a. Comparison of net atomic charges in a–Si (in millielectrons) calculated by the SLMO method (y axis) and the quantity in parentheses of Eq. (2) (x axis, measured in degrees). Each point represents a silicon atom. $A = -0.69$ millielectrons/degrees

5. Results

From the molecular orbital calculation we concluded that charge accumulation in tetrahedrally bonded semiconductors is a three-atom effect, atomic net charges are generated by bond angle distortions [17]. Let us consider an elementary triad of atoms, denoted by K, L and M, forming two bonds KM and LM with a KML angle denoted by θ (Fig.2). The net charge on the atoms of the triad depends linearly on the deviation of θ from the ideal tetrahedral value ($d\theta = \theta - 109.47°$):

$$\begin{aligned} q_M^{el} &= 2A\, d\theta, \\ q_K^{el} = q_L^{el} &= -A\, d\theta, \end{aligned} \tag{1}$$

where A is a fitting parameter. The total atomic net charge on atom K is a sum of contributions originating from all combinations of the triads containing K. Since in the distorted tetrahedral model of Wooten each atom is at the centre of 6 triads and at the end of 12 triads we have the following relation

$$q_M = A\left(2\sum_{i=1}^{6} d\theta_i - \sum_{j=1}^{12} d\theta_j\right), \tag{2}$$

where $\theta_i = XMY <$ and $\theta_j = MXZ <$ (X and Y are bonded to M, Z to X or Y, see Fig. 2).

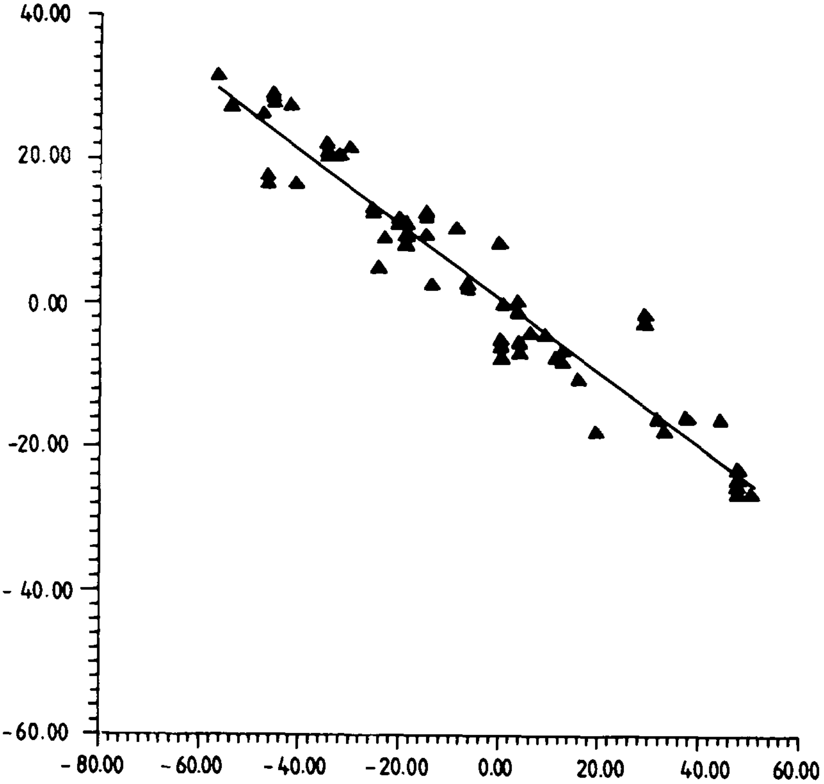

Fig. 3b. Comparison of net atomic charges in a–C (in millielectrons) calculated by the SLMO method (y axis) and the quantity in parentheses of Eq. (2) (x axis, measured in degrees). Each point represents a carbon atom. $A = -0.51$ millielectrons/degrees

We compared net charges, calculated by Eq. (2), to those obtained by our quantum chemical method. We constructed models, as described above, and only the five central silicon atoms were included in the comparison. As a whole, we calculated net charges for 79 different silicon atoms and obtained a fair linear correlation for Eq. (2) with $A = -0.69$ millielectrons/degrees (cf. Fig. 3a) [2].

In order to derive the fitting parameter A for a-C, a similar process was carried out. As it is displayed in Fig. 3b a fair linear correlation was obtained with $A = -0.51$ millielectrons/degrees [18].

6. Charge fluctuations

To estimate charge fluctuations in a-Si we used the geometric model proposed by Wooten et al [10]. Applying Eq. (2) for all 216 atoms of the model cluster we obtain $dq_{Si} = 0.021$ electron for the rms charge fluctuation. This is compared with values from other studies [19–24] in Table I.

Table I
Charge fluctuations (dq_{Si}) from theoretical and experimental studies in amorphous silicon as obtained by different authors

No.	Authors	Type	dq_{Si}[me]
1.	Guttman et al [19]	theor.	200
2.	Ley et al [20]	exp.	110
3.	Klug, Whalley [21]	exp.	180-320
4.	Kramer et al [22]	theor.	35
5.	Bose et al [23]	exp.	140
6.	Brey et al [24]	exp.	≤ 30
7.	Kugler et al [2]	theor.	21

As it is seen, our estimate is considerably smaller than those from experimental studies. We feel that our value is realistic since, as it is known, CNDO/2 net charges reproduce absolute values of experimental dipole moments within a reasonable error. In our semiempirical quantum chemical method we used the CNDO/2 parametrization. The discrepancy with the core-level spectroscopic estimation of Ley et al [20] may be explained on the basis of intra-atomic charge transfer [24] while the infra-red spectroscopic estimation is subject to considerable simplifications as discussed by the authors themselves [21]. In a real a-Si system there are a few so-called dangling bonds. Their number is about 10^{15}–10^{19}/mol. These defects also increase the charge fluctuation in a-Si.

We estimate rms charge fluctuations in diamond-like a-C using all all 216 atoms of the scaled model proposed by Wooten et al [10]. Applying again Eq.(2) we obtain $dq = 0.015$ electron units. On the basis of our rms charge fluctuation values ($dq_C = 0.015$, $dq_{Si} = 0.021$) and Klug and Whalley's formula [21] we have estimated the integrated infrared intensity for diamond-like a-C. From the experimental values quoted in [21] we predict that its value is within the range of 70 000 and 120 000 cm^{-2}.

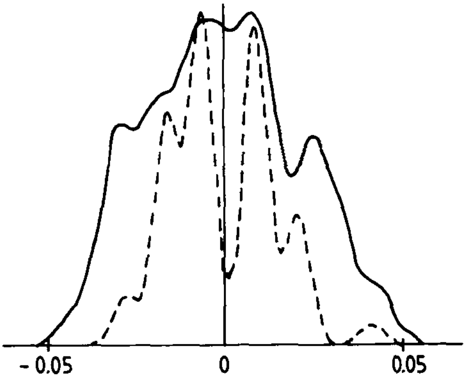

Fig. 4. Charge distribution in a-Si. Full line: from Eq. (2), dashed line: from fivefold ring statistics

The charge distribution curve for a-Si (similar for a-C), as obtained by smoothing the calculated histograms with Gaussian line broadening that corresponds to a full width of 0.064 electrons at half maximum, is presented in Fig. 4. The curve has characteristic maxima or shoulders. Analyzing the distribution of rings, we have found that the number of fivefold rings belonging to the same atom determines the charge distribution to a given extent. The charge averages for atoms with 0, 1, 2, 3, 4 and 5 fivefold rings are -0.023, -0.016, -0.005, 0.009, 0.021 and 0.035 electrons, respectively. These values show fair coincidence with maxima on the charge distribution curve. Applying the above Gaussian line broadening method we smoothed the histogram displaying the number of atoms with 0, 1, 2, 3, 4 and 5 fivefold rings (10, 45, 67, 64, 26 and 4, respectively). The fair correspondence between both curves call the attention to the primary importance of ring statistics in determining the charge distribution [25].

As a consequence, we may state that atomic charge distribution in a-Si and in diamondlike a-C are determined primarily by bond angle distortions that are dependent on the number of fivefold rings attached to the same atom.

Acknowledgements

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