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Theoretical estimation of static charge fluctuation in amorphous silicon

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A quantum-chemical method has been developed to determine charge fluctuations in finite aperiodic clusters of amorphous silicon. Calculated atomic net charges are in a close linear relationship to bond-angle distortions involving first and second neighbors. Applying this relationship to a continuous-random-network model of 216 silicon atoms proposed by Wooten *et al.*, we obtained 0.021 electron units for the rms deviation from charge neutrality.

Fluctuation of charge density in amorphous silicon (*a*-Si) has been the subject of several theoretical and experimental studies.[1-5] Since atomic net charges are not observable, experimental determination of their fluctuations from high-resolution Si 2*p* core-level spectra[2] or integrated infrared absorptivity[3] may be ambiguous. On the other hand, theoretical calculations are more or less approximate;[1,4,5] therefore it is rather difficult to compare results obtained by different methodologies.

Recently, we elaborated on a quantum-chemical method for the determination of charge fluctuation in various *a*-Si models.[6,7] The sample is modeled by finite clusters in which the geometry of atoms can be constructed using, e.g., the coordinates of the continuous-random-network (CRN) model of Wooten *et al.*[8] A cluster of bulk silicon atoms is described by a valence-electron effective Hamiltonian written down in a hybridized atomic basis. The sp^3-like hybrids are directed along the corresponding Si—Si bond axis, and subsequently orthogonalized on each atom. This orthogonalization is effective only if the geometry of the cluster is different from the diamondlike one and it may result in a deviation of the actual form of hybrids (*s* characters) from the standard sp^3 types. Accordingly, geometry distortions in *a*-Si are reflected by hybridization changes.

The wave function of the cluster is constructed in terms of molecular orbitals ϕ_i which are constrained to be localized on one Si—Si bond *i* spanned by two hybrids h_{a_i} and h_{b_i}:

$$\phi_i = c_{a_i} h_{a_i} + c_{b_i} h_{b_i} \; , \tag{1}$$

with $c_{a_i}^2 + c_{b_i}^2 = 1$. Within this constraint the Hartree-Fock problem is solved for the cluster; that is, the c_{a_i} coefficients are optimized variationally. The matrix elements of the Hamiltonian are parametrized according to the complete neglect of differential overlap (CNDO/2) scheme.[9]

The Hartree-Fock problems for different bonds are coupled due to interbond Coulomb integrals; thus the model is capable of describing interbond electrostatics (inductive effects).

To eliminate end effects as much as possible, we put special pseudoatoms (Si*) at the boundary modeling the bulk. These pseudosilicon atoms possess one or two neighbors only and they are described by one (or two) hybrids, their effective core charges (Z_a^*) being 1 (or 2).

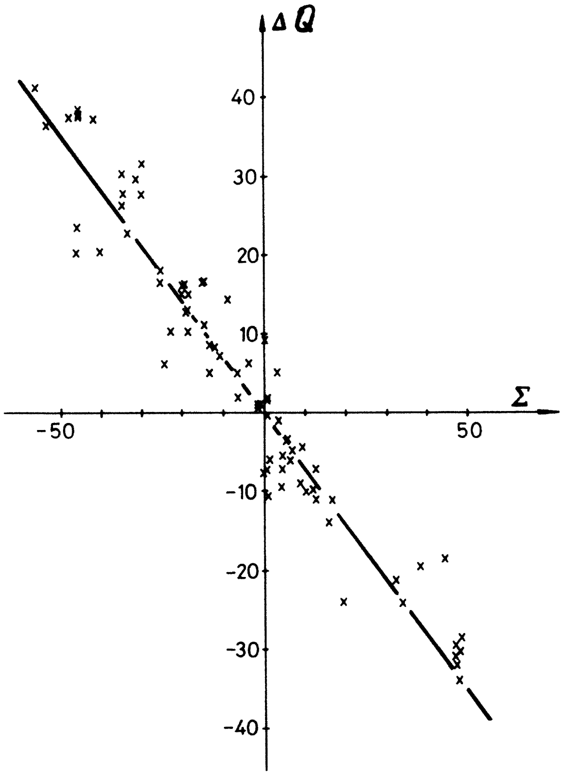

FIG. 1. Comparison of silicon atomic net charges calculated quantum chemically (crosses) and by Eq. (4) (solid line). $\Delta Q = (-0.69 \pm 0.024)\Sigma$, where Σ denotes the quantity in parentheses in Eq. (4); ΔQ is in 10^{-3} electrons, Σ is in degrees.

TABLE I. Charge fluctuations (rms, in millielectrons) as obtained by different authors.

Author	dQ
Guttman *et al.* (theor.)[a]	200
Ley *et al.* (expt.)[b]	110
Klug and Whalley (expt.)[c]	180–320
Kramer *et al.* (theor.)[d]	35
Brey *et al.* (theor.)[e]	<30
Present work	21

[a] Reference 1.
[b] Reference 2.
[c] Reference 3.
[d] Reference 4.
[e] Reference 5.

This permits us to deal with a closed-shell neutral and finite cluster without imposing periodic boundary conditions or introducing artificially heteroatoms at the surface.

Since all parameters of the Hamiltonian are the same for Si and Si* atoms, we obtain exact electroneutrality within each bond in a diamondlike cluster and, as a consequence, our method is free from the spurious accumulation of charges inside the cluster and on the boundary observed if using the conventional formalism.[10] Pseudoatom effects at the boundary were tested on the following way: A cluster containing 38 atoms was chosen and one, two, or three atoms were added to the surface of it. On the five central silicon atoms there was no change of net atomic charge. The net charge on atom A in our model is defined by

$$\Delta Q_A = Z_A^* - \sum c_{A_i}^2 \,, \tag{2}$$

where the sum is extended over the four bonds in which the atom in question takes place, and Z_A^* is the effective nuclear core charge (4 for Si). Similar methods based on localized wave functions have long been utilized to calculate atomic charges and other properties in an effective manner.[11]

Using our method for diamondlike clusters, containing 35 ordinary and 36 pseudosilicon atoms (Si-Si and Si-Si* distances were set equal to 235 pm) and displacing the central atom by 30 pm in various directions, we found that charges accumulating on atoms separated by more than two bonds from this central atom are less than 10^{-4} electron units. From this we concluded that charge fluctuation in amorphous silicon is a three-atom effect and can be traced back to bond-angle distortions, which are reflected by changes in hybridization effect. In a triad of silicon atoms K, L, and M, forming two bonds KM and LM with a KML angle of θ, one may assume that the atomic charge depends approximately linearly on the deviation of the bond angle from the ideal tetrahedral value, $d\theta = \theta - 109.47°$. Accordingly, the charges may be estimated from the following equations:

$$\begin{aligned} q_M &= 2A\,d\theta \,, \\ q_K &= q_L = -A\,d\theta \,. \end{aligned} \tag{3}$$

Applying Eq. (3) on a CRN model of a-Si clusters for the net charge of atom M, we get a single-parameter equation,

$$\Delta Q_M = \sum q_i = A \left[2 \sum_{i=1}^{6} d\theta_i - \sum_{j=1}^{12} d\theta_j \right] , \tag{4}$$

where $\theta_i = XMY_<$ and $\theta_j = MXZ_<$ (X and Y are bonded to M, Z to X or Y).

We compared net charges, calculated by Eq. (4), to those obtained by our quantum-chemical method summarized in Eqs. (1) and (2). We constructed models, as described above, and used the geometry proposed for a-Si by Wooten *et al.*[8] Each cluster consisted of at least 17 ordinary and more than 25 pseudosilicon atoms, 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. (4) with $A = -0.69 \pm 0.024$, and the correlation coefficient is $r = -0.965$ (cf. Fig. 1). The rms charge fluctuation, as obtained from the quantum-chemical calculations and from Eq. (4) are 0.0195 and 0.0188 elec-

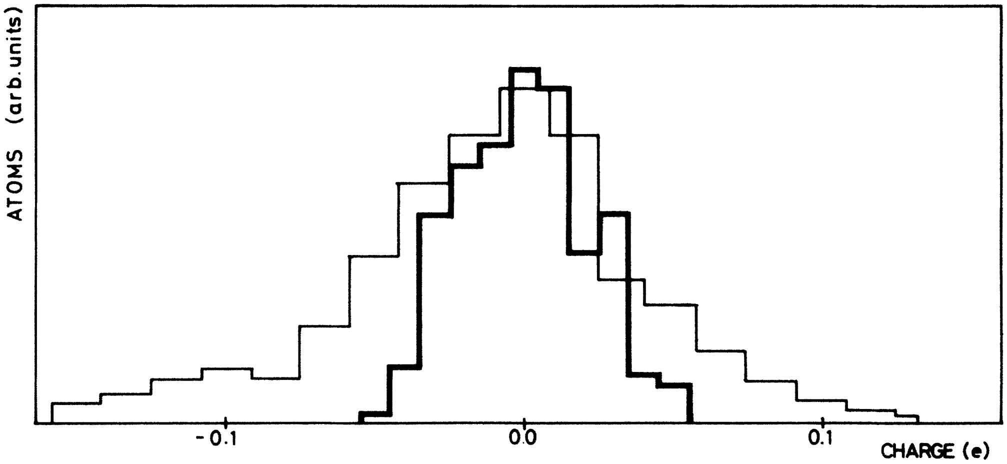

FIG. 2. Charge distributions in a-Si models. Thin solid line, Ref. 4; thick solid, present work.

trons, respectively. The good agreement justifies application of Eq. (4) to other systems, too.

Our equation is analogous, though not equivalent to that proposed by Guttman *et al.*[1] In their function to calculate the net charge on atom i, they used a term depending on the deviation of the distance to the four neighbors of i, dr_i, from the ideal value, r_0, instead of this first term in Eq. (4):

$$\Delta Q_i = a \sum_{i=1}^{4} dr_i / r_0 + b \sum_{j=1}^{12} (\theta_j - \theta_0) + c \ . \tag{5}$$

Guttman *et al.* stated that Eq. (5) has a considerable physical basis because, among other arguments, c is close to zero. However, in an ideal diamondlike structure where $r_i = r_0$, c must have a nonzero value; otherwise, identical charges of the same sign on all atoms would appear and a spurious nonzero gross charge would accumulate in the system. Our method yields exactly zero atomic net charges for systems where all bond angles are ideally tetrahedral, regardless of the actual bond distances; furthermore, the sum of charges is zero for any geometric structures. This is why the standard error of A in Eq. (4) is considerably smaller than that of b in Eq. (5) ($b = 0.174 \pm 0.022$, 0.164 ± 0.022, and 0.162 ± 0.022 for three independent models[1]).

To estimate charge fluctuations in a-Si, we used a model proposed by Wooten *et al.*[8] This seems to be the best at present since it reproduces the experimental one-dimensional radial distribution function within the interval 0–800 pm excellently. Using Eq. (4) for all 216 atoms of the model cluster, we obtain 0.021 electron for the rms charge fluctuation. This is compared with values from other studies in Table I. As can be seen, our estimate is considerably smaller than those from experimental studies. We feel that our value is realistic since, as is known, CNDO/2 net charges reproduce absolute values of experimental dipole moments within a reasonable error.[9] The discrepancy with the core-level–spectroscopic estimate of Ley *et al.*[2] may be explained on the basis of intra-atomic charge transfers,[5] while the infrared spectroscopic estimation is subject to considerable simplifications as discussed by the authors themselves.[3]

Figure 2 depicts histograms of our calculated charge distributions in the CRN model as compared to the results of Kramer *et al.*[4] Our curve indicates a pronounced maximum near 0.030 electron. Whether this is only an artifact due to the small number of atoms in our model or has a physical meaning, needs further studies.

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