# Atomic Charge Distribution in Diamondlike
# Amorphous Carbon

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Based on semiempirical molecular orbital calculations, we propose an empirical formula for the calculation of net atomic charges in diamondlike amorphous carbon. These charges are in a linear relationship with bond angle distortions involving first and second neighbors. On the basis of the estimated charge fluctuation we predict that the integrated infrared absorption intensity will be within the range of 70000 to 120000 cm$^{-2}$.

KEYWORDS: amorphous carbon, charge, infrared absorption

## §1. Introduction

Owing to its technological importance, pure and hydrogenated amorphous carbon (a-C) has attracted considerable interest in the past decade.[1] Different methods, such as evaporation, sputtering, ion-beam deposition, chemical vapor-deposition, and plasma chemical vapor-deposition have been used for preparation of a-C film.

There is considerable evidence indicating that a-C consists of sp$^3$ and sp$^2$ atomic sites.[2-9] The former corresponds to the diamond structure where each valence electron of carbon is assigned to a tetrahedrally directed sp$^3$ hybrid orbital forming a strong $\sigma$ bond with the adjacent atom. In the latter configuration three of the four electrons are assigned to the trigonally oriented sp$^2$ hybrids forming three $\sigma$ bonds with adjacent, atoms and the fourth one participates in a $\pi$ bond delocalized over all centers lying in the same plane. Since the $\pi$ states are weakly bound their energies are closer to the Fermi level than those of the $\sigma$ ones[10] and in specific cases of topological disorder several $\pi$ states lie even at $E_f$.[11] This $\pi$ electron structure in a-C causes different properties of conductivity compared to a-Si or to a-Ge.[12,13]

The sp$^2$:sp$^3$ ratio is one of the most important parameters of a-C. Previous structural investigations indicated the presence of sp$^2$ sites in a ratio of up to 90% in various types of a-C.[2-5] In the past few years, tetrahedrally coordinated a-C with a majority of sp$^3$ sites attracted much interest because of its extreme hardness and an optical gap in the range of 3 eV. Recently Savvides[14] succeeded in increasing the upper limit of sp$^3$ sites to 76% applying an ion-beam deposition method. It seems to be a realistic goal in the near future to increase the concentration of diamondlike carbon sites in a-C to 100%.

By symmetry, the carbon atoms in diamond have no charge at their equilibrium positions, but in the amorphous case they carry charges because of the geometric distortions. These charges have never been measured or calculated even though they play an important role in the determination of some experimental properties, such as the integrated infrared absorptivity. In this paper we determine the charge accumulation in finite aperiodic clusters of a-C by means of a semiempirical molecular orbital method based on the CNDO parametrization.

## §2. Method and Model

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.[15-19] A cluster of bulk atoms are described by a wave function expanded in terms of strictly localized molecular orbitals (SLMO). SLMOs are linear combinations of sp$^3$ atomic hybrids directed along the corresponding bond axis and subsequently orthogonalized on each atom.[17-19] Hybrid coefficients in SLMOs are derived through the solution of a coupled $2 \times 2$ 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 yields reliable charge distributions.[20]

In order to eliminate the edge effects, we place pseudoatoms, denoted by C*, at the boundary modelling the bulk. These have only one or two neighbors to which they are connected by a $\sigma$ bond. The corresponding SLMO is composed of the appropriately oriented hybrids, one of them centered at C* the other at the neighboring atom. In order to ensure electroneutrality, the effective core charge of C* is set equal to 1 or 2, depending on the number of hybrid orbitals attached to it. A test of this model was carried out for a crystalline diamond cluster containing 35 ordinary and 36 pseudocarbon atoms. The calculation yielded a uniformly neutral

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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.

At present there is no geometry available which contains only $sp^3$ sites for a-C. Therefore we constructed it on the basis of a continuous random network model (CRNM) for a-Si by Wooten et al.[21] This seems to be the best CRNM 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.[21,22] Based on the close analogy between classical saturated carbon and silicon compounds, we may suppose that scaling down the closest-neighbor atom-atom and atom-pseudoatom distances in a-Si from 235 pm to 155 pm[2] yields an adequate model for a-C, as well. Each of our model clusters consisted of at least 17 carbon atoms and more than 25 pseudocarbon atoms located at the surface.

## §3.  Results and Discussion

From the molecular orbital calculation we obtained charges for 65 different types of carbon atoms and we concluded that charge accumulation in a-C is a three-atom effect, and atomic net charges are generated by bond angle distortions, which are reflected by changes in the hybridization effect. Let us consider an elementary triad of carbon atoms, denoted by K, L and M, forming two bonds KM and LM with a KML angle denoted by $\theta$ (Fig. 1). The net charge $q^{el}$ on the atoms of the triad depends linearly on the deviation of $\theta$ from the ideal tetrahedral value ($\Delta\theta = \theta - 109.47°$):

$$q_M^{el} = 2A\Delta\theta$$
$$q_K^{el} = q_L^{el} = -A\Delta\theta, \tag{1}$$

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

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

where $\theta_i = $ XMY< and $\theta_j = $ MXZ< (X and Y are bonded to M, Z to X or Y; see Fig. 1.).

In order to derive the fitting parameter $A$, we compared net charges as calculated by eq. (2) to those obtained by our molecular orbital method. As is shown on Fig. 2, a fairly linear correlation was obtained with $A = -0.51$ ($q$ in millielectron units). We estimate rms charge fluctuations ($\Delta q$) in diamondlike a-C using all 216 atoms of the scaled model proposed by Wooten et al.[21] Applying eq. (2) we obtain $\Delta q = 0.015$ electron units.

Since no theoretical or experimental estimation has been available on $\Delta q$ in a-C, it is interesting to compare our result to the value of 0.021 electron units obtained for a-Si.[15] It is hoped that from this comparison we may derive some relationship between experimental data de-
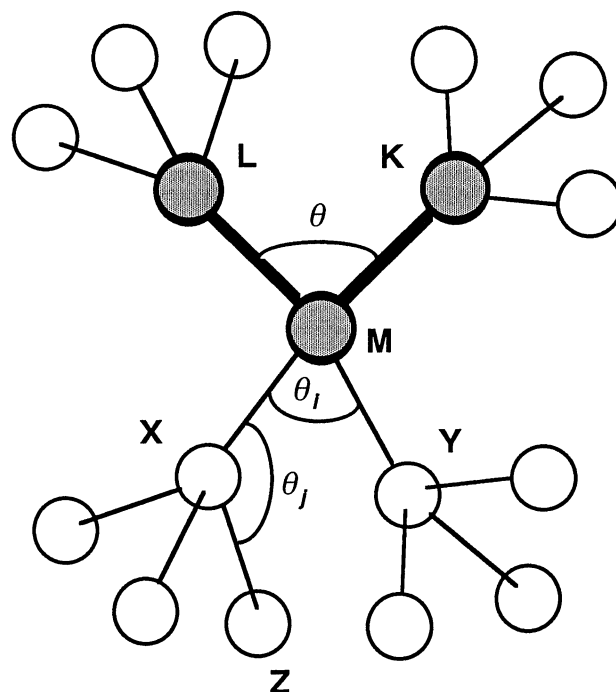


Fig. 1.  An elementary triad of carbon atoms (heavy lines) with the surrounding environment (light lines).
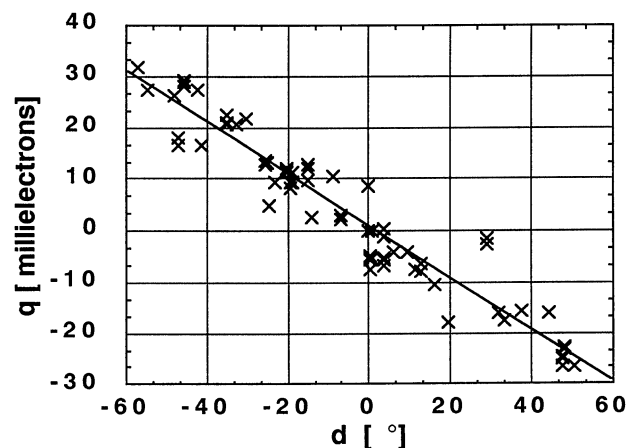


Fig. 2.  Comparison of net atomic charges calculated by a molecular orbital method (crosses) and by eq. (2) (full line). $q = -0.51 \, d$ (in millielectrons), where $d$ denotes the quantity in parentheses in eq. (2).

pending directly or indirectly on $\Delta q$. In our previous work,[15] we discussed Si 2p core-level spectra[23] and integrated infrared absorption intensities ($K_{av}$).[24] Since there exist no 2p core level exitations in a-C, we must restrict our considerations to $K_{av}$.

According to Klug and Whalley, the integrated infrared absorption intensity depends on the mass-reduced effective atomic charges[24]

$$K_x^{av} \equiv \int K_x \, dv^3 = c_x \left\langle \frac{q_x^2}{m_{ix}} \right\rangle_i, \tag{3}$$

where the $c_x$ proportionality constant depends on the complex permittivity and the real part of the refractive in-

dex. It is a plausible supposition that for these materials, $m_{ix}$ is equal to the atomic weight $M_x$. Therefore we may formulate the following relationship between a-Si and a-Ge parameters:

$$\left[\frac{K_X^{\mathrm{av}}}{K_Y^{\mathrm{av}}}\right]^{1/2} = \left[\frac{c_X}{c_Y}\cdot\frac{M_Y}{M_X}\right]^{1/2}\cdot\frac{\Delta q_X}{\Delta q_Y} \tag{4}$$

with $\Delta q_x^2 = \langle q_{ix}^2 \rangle_i$, the mean-square averaged charge fluctuation. Using the experimental data of Klug and Whalley we obtained $c_{\mathrm{Si}} = 5.5$ and $c_{\mathrm{Ge}} = 7.3$ (in arbitrary units). Since no experimental data are available for tetrahedral a-C, we extrapolate linearly from the above values of the group IV elements and propose a value of 4.0 which can be considered as a rough estimation for $c_{\mathrm{C}}$. With this we may calculate $K_{\mathrm{C}}^{\mathrm{av}}$. Substituting our estimated rms charge fluctuation values into eq. (4) ($\Delta q_{\mathrm{C}} = 0.015$, $\Delta q_{\mathrm{Si}} = 0.021$) we have

$$K_{\mathrm{C}}^{\mathrm{av}} = 0.9 K_{\mathrm{Si}}^{\mathrm{av}}. \tag{5}$$

Equation (5) means that in the same experiment, the integrated infrared intensity for diamondlike a-C will be less than for a-Si. Using the experimental values quoted in ref. 24, we predict that its value will be within the range of 70000 to 120000 cm$^{-2}$.

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