Monte Carlo simulation of amorphous systems with the fragment self-consistent field method[1]

Gergely Tóth[a], Gábor Náray-Szabó[a,*], György G. Ferenczy[b,c], Gábor Csonka[d]

[a]*Department of Theoretical Chemistry, Loránd Eötvös University Budapest, P.O. Box 32, H-1518 Budapest 112, Hungary*
[b]*Chemical Works of Gedeon Richter Ltd, P.O. Box 27, H-1475 Budapest, Hungary*
[c]*Department of Chemical Information Technology, Technical University of Budapest, Szt. Gellért tér 4, H-1111 Budapest, Hungary*
[d]*Department of General and Inorganic Chemistry, Technical University of Budapest, Szt. Gellért tér 4, H-1111 Budapest, Hungary*

Abstract

We present an overview on the application of our semiempirical 'neglect of diatomic differential overlap fragment self-consistent field' method to the Monte Carlo simulation of amorphous carbon and silicon. The covalent model is partitioned into a relatively small subsystem treated at the conventional molecular orbital level and an environment perturbed by the former. The wave function is expanded either on a Slater-type atomic orbital or on a hybrid orbital basis set, and a self-consistent field calculation is made for the subsystem in the field of the iteratively determined electronic distribution of the environment. For energy calculation of the infinite amorphous systems a Monte Carlo version of the fragment self-consistent field method has been developed. Radial and angular distribution functions, obtained for amorphous silicon, are in good agreement with experiment. We calculated the same quantities for amorphous carbon with a hypothetical 100% sp^3 hybridization, but these cannot be compared directly to experiment. © 1997 Elsevier Science B.V.

Keywords: Fragment SCF method; Amorphous carbon; Amorphous silicon

1. Introduction

Partitioning of large covalent molecules into a subsystem, where essential chemical changes take place and which is described in terms of the molecular orbital theory, and an environment, treated at a simpler level, was first proposed by Warshel and Levitt in their classical paper on lysozyme [1]. In the same year we proposed the use of strictly localized molecular orbitals (SLMO) for the treatment of very large covalent systems [2]. We combined these two ideas in the framework of the semiempirical complete neglect of differential overlap (CNDO/2) approximation and we formulated the fragment self-consistent field (FSCF) method that was applied to the conformational analysis of the chymotrypsin active site [3,4]. Since then, quantum mechanical/molecular mechanical (QM/MM) hybrid methods have been developed on the basis of subsystem/environment partitioning where the subsystem is treated by an ab initio [5,6] or semi-empirical [7–9] molecular orbital method or by density functional theory [10,11], while the environment is described in terms of molecular mechanics.

The drawback of hybrid QM/MM methods is the problem with the definition of the subsystem/environment boundary. In QM/MM simulations of amorphous systems the dangling bonds should be closed by hydrogen

atoms in order to provide a classical closed-shell sub-system that is appropriate for molecular orbital calculations. The FSCF approach is similar to the combined QM/MM method but solves the partition problem in a natural way by expanding the total wave function on a basis of SLMOs. Recently we formulated this method at the neglect of diatomic differential overlap (NDDO) level, with both the AM1 [12–14] and PM3 [15,16] parametrizations, and applied this version to small molecules [13,14], enzymes [17] and condensed systems, where we derived an extension to Monte Carlo simulations [16,18]. In the following, we outline basic features of the method and present results of the statistical simulation of amorphous materials, carbon and silicon.

2. Method

2.1. Basic equations

The method is described in Ref. [13] in detail and here only its main features are recapitulated. The same way as we build up molecules from more or less transferable chemical bonds, we put together the wave function from two-centre σ, one-centre lone-pair and many-centre π SLMOs obtained as combinations of atomic hybrid orbitals (HYOs). The ith HYO on atom A in the ath SLMO has the following form:

$$i_{Aa} = b_{Aa}^{ns} u_A^{ns} + b_{Aa}^{npx} u_A^{npx} + b_{Aa}^{npy} u_A^{npy} + b_{Aa}^{npz} u_A^{npz}, \qquad (1)$$

where $u_A^{ns}, u_A^{npx}, \ldots$, are atomic Slater-type orbitals with principal quantum number n and the appropriate symmetry. For example, σ-type SLMO involves two atomic centres and represents the bond between these atoms. HYOs of such an SLMO are directed toward each other. According to the applied NDDO approximation, HYOs centred on different atoms do not overlap. To achieve orthogonality of HYOs centred on the same atom, they are Löwdin-orthogonalized [19] in order to obtain the b coefficients in Eq. (1). The HYO coefficients within SLMOs are obtained by solving a set of coupled secular equations which involve a simplified Fockian of the following form (α and β stand for an SLMO):

$$F_{ii} = H_{ii} + \tfrac{1}{2} P_{ii}(ii|ii) + \sum_{j(\neq i)\epsilon\alpha} P_{jj}(ii|jj)$$

$$+ \sum_{\beta(\neq\alpha)} \sum_{k\epsilon\beta} P_{kk}(ii|kk), \quad i\epsilon\alpha$$

$$F_{ij} = H_{ij} - \tfrac{1}{2} P_{ij}(ii|jj), \quad i,j\epsilon\alpha, \; i \neq j \qquad (2)$$

$$F_{ik} = 0, \quad i\epsilon\alpha, \; k\epsilon\beta, \; \alpha \neq \beta$$

The core hamiltonian, H, and the density matrix, P, are block diagonal. The differential overlap of orbitals i and j is nonzero only if they belong to the same SLMO.

The subsystem, S, is defined as the place where the chemical event (in this case displacement of a particle) takes place. Its Hamiltonian is similar to that used in conventional MNDO calculations except for a perturbation term in the Fockian originating from the environment, E. A further specificity is that all calculations are done on a hybrid orbital basis:

$$F_{ij}^{S} = H_{ii} + \sum_{k,l\epsilon S} P_{kl}\left[(ij|kl) - \tfrac{1}{2}(il|kj)\right] + \sum_{\alpha\epsilon E}\sum_{k\epsilon\alpha} P_{kk}(ij|kk)$$

$$- \tfrac{1}{2}\sum_{\alpha\epsilon E}\sum_{k,l\epsilon\alpha} P_{kl}(il|kj). \qquad (3)$$

2.2. Monte Carlo simulation

Subsystem/environment partition is shown schematically in Fig. 1.

The periodic cubic box contained 216 atoms with a number density of 50 and 153 nm^{-3} and subsystem radii of 480 and 330 pm for a-Si and a-C, respectively.
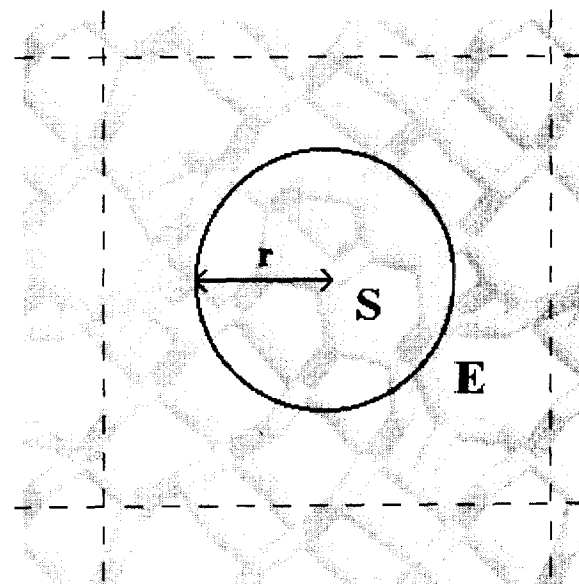

Fig. 1. Schematic representation of the definition of S and E for the Wooten model of a-Si.

The AM1 and PM3 semiempirical parametrizations were used for a-C and the PM3 one for a-Si. The starting configuration was a distorted version of the Wooten model [20]. It has only tetracoordinated silicon atoms, which means that in the first approximation exclusively σ-type SLMOs were used to construct the wave function both for the environment and the subsystem. The distortion was performed by a constrained hard-sphere Monte Carlo procedure in which a coordination number constraint of 4 was applied. Equilibrium was reached in approximately 10 000 steps, whereas the radial distribution functions and cosine distributions were calculated over the next 30 000–40 000 steps.

At the beginning of the calculations we evaluated all integrals for the first SCF approximation, then solved the coupled, typically 2×2 secular equations of Eq. (2) for the whole system. For each Monte Carlo step we chose a particle and defined the subsystem around it, then evaluated the integrals for the subsystem without moving the particle and solved the SCF equations of Eq. (3). Afterwards, we displaced the particle, recalculated the changed integrals, and solved the equations of Eq. (2) for the whole system and then the equations of Eq. (3) for the subsystem. The Metropolis criterion was applied to accept or reject the new configuration. If the step was not successful, we returned to the old configuration for a new trial. Since we needed to calculate only integrals containing displaced atomic centres and most of the HYO coefficients did not change drastically, a considerable amount of computational work could be saved. More details about the method and its application to amorphous silicon can be found in the original publication [16].

3. Results and discussion

Distribution functions for a-Si and a-C are displayed in Figs. 2 and 3. As is seen from Figs. 2a and 3a, our simulations on a-Si are in excellent agreement both with the results obtained from the original Wooten model and with those from a reverse Monte Carlo (RMC) calculation [21] based on experimental data [22]. A coordination number constraint of 4 was applied in the RMC simulation. The first sharp peak on the radial distribution function is at 235 pm,
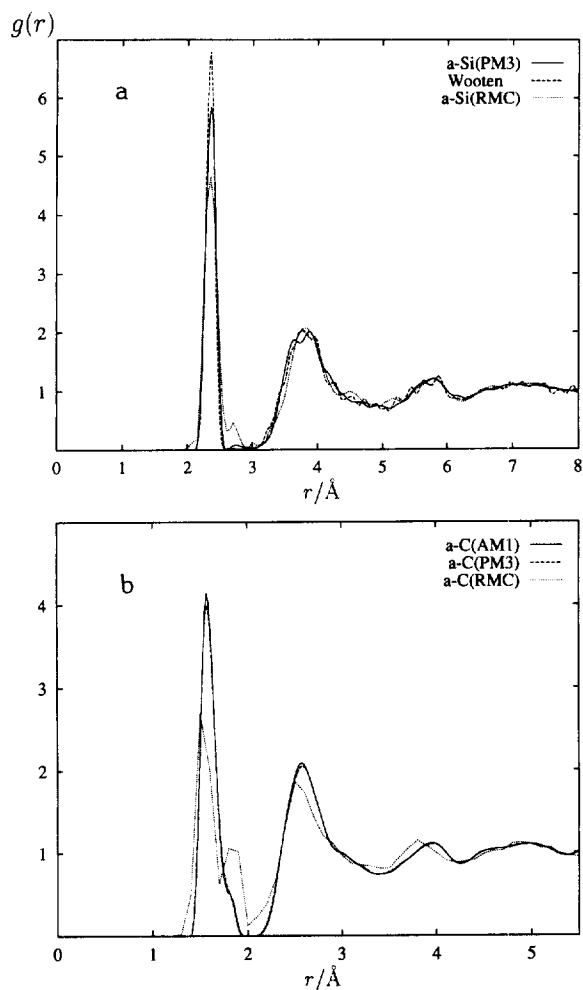

Fig. 2. Radial distribution functions: (a) a-Si; (b) a-C. It is important to notice that the $g(r)$ functions provided by the FSCF Monte Carlo method are continuous and smooth at the S/E boundary (480 and 330 pm, respectively).

exactly the same as the experimental Si–Si single-bond length, indicating that in a-Si nearly all silicon atoms participate in undistorted single bonds. The peak on the angular distribution function is around the tetrahedral value, 104.5°.

It is more complicated to compare our results for a-C with experiment. As is known, it is very difficult to provide a-C samples with 100% sp^3-hybridized carbon atoms; up to now the maximum percentage reached is around 80 [23,24]. A further problem is that samples contain voids, dislocations and impurities,
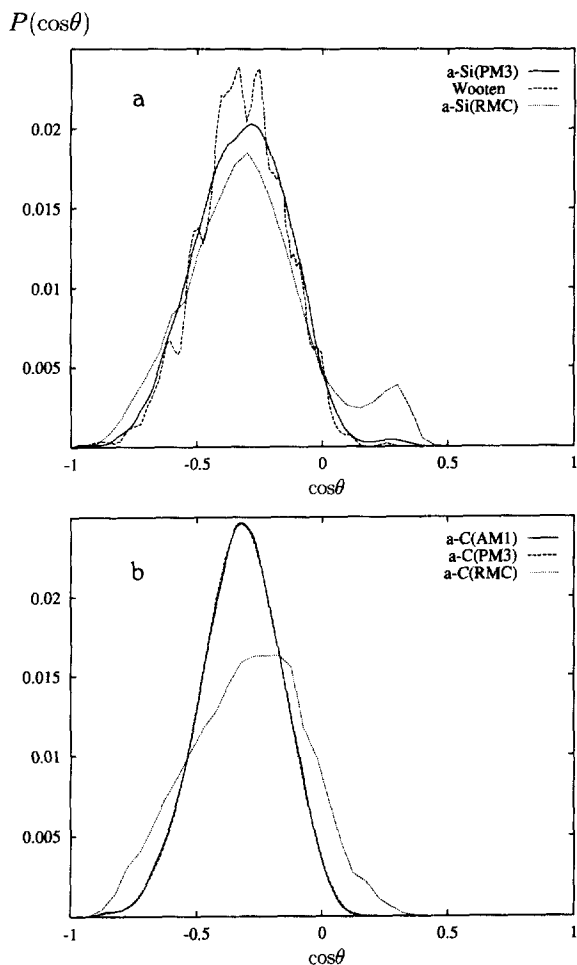
$P(\cos\theta)$

Fig. 3. Cosine distribution functions: (a) Si–Si–Si angles in a-Si; (b) C–C–C angles in a-C. The maximal distances of two atoms forming a common SLMO were defined to be 270 pm for a-Si and 200 pm for a-C.

shown in Figs. 2 and 3 are provided by a simulation based on the experiment of Ref. [24]. A coordination number constraint of 4 was applied in this RMC calculation.

Finally, we can draw some conclusions. Since our results on amorphous silicon are in good agreement with experiment, the calculation on amorphous carbon may correctly describe the structure of the currently hypothetical 100% sp^3 a-C. We hope that experiment will provide such samples in the near future to test our calculations.

Acknowledgements

References

[1] A. Warshel and M. Levitt, J. Mol. Biol., 103 (1976) 227.
[2] G. Náray-Szabó, Acta Phys. Acad. Sci. Hung., 40 (1976) 261.
[3] G. Náray-Szabó and P.R. Surján, Chem. Phys. Lett., 96 (1983) 499; G. Náray-Szabó, Croat. Chem. Acta, 57 (1984) 901.
[4] G. Náray-Szabó, P.R. Surján and Á.I. Kiss, J. Mol. Struct. (Theochem), 123 (1985) 85.
[5] U.C. Singh and P.A. Kollman, J. Comput. Chem., 7 (1986) 718.
[6] N. Vaidehi, T.A. Wesolowski and A. Warshel, J. Chem. Phys., 97 (1992) 4264.
[7] P.A. Bash, M.J. Field and M. Karplus, J. Am. Chem. Soc., 109 (1987) 8092.
[8] J. Gao, J. Phys. Chem., 96 (1992) 537.
[9] B. Waszkowycz, I.H. Hillier, N. Gensmantel and D.W. Payling, J. Chem. Soc. Perkin Trans., 2 (1991) 225.
[10] R.V. Stanton, D.S. Hartsough and K.M. Merz, Jr, J. Phys. Chem., 97 (1993) 11 868.
[11] D. Wei and D. Salahub, Chem. Phys. Lett., 224 (1994) 291.
[12] M.J.S. Dewar, E.G. Zoebisch, E.F. Healy and J.J.P. Stewart, J. Am. Chem. Soc., 107 (1985) 3902.
[13] G.G. Ferenczy, J.M. Rivail, P.R. Surján and G. Náray-Szabó, J. Comput. Chem., 13 (1992) 830.
[14] G. Náray-Szabó and G.G. Ferenczy, J. Mol. Struct. (Theochem), 261 (1992) 55.
[15] J.J.P. Stewart, J. Comput. Chem., 10 (1989) 209.
[16] G. Tóth and G. Náray-Szabó, J. Chem. Phys., 100 (1994) 3742.
[17] G. Náray-Szabó, G. Tóth, G.G. Ferenczy and G. Csonka, Int. J. Quant. Chem. Quantum Biol. Symp., 21 (1994) 227.
[18] G. Tóth, O. Gereben and G. Náray-Szabó, J. Mol. Struct. (Theochem), 313 (1994) 165.

therefore the density cannot be determined unequivocally (see tables in Ref. [25]). Thus, simulations and experiments provide incomparable results. While the radial distribution function obtained by the FSCF Monte Carlo method has a sharp peak at 157 pm, only 3 pm larger than the experimental value for the CC single bond (154 pm), other calculations and experiments [25,26] yield 142–150 pm, sometimes close to the length of the CC bond in graphite (142 pm), due to the high percentage of tricoordinated carbon atoms in the samples. The a-C RMC results [26]

[19] P.O. Löwdin, Phys. Rev., 97 (1955) 1474.

[20] F. Wooten and D. Wearie, Solid State Phys., 40 (1987) 1.

[21] R.L. McGreevy and L. Pusztai, Mol. Simulations, 1 (1988) 359.

[22] S. Kugler, L. Pusztai, L. Rosta, R. Bellissent and P. Chieux, Phys. Rev. B, 48 (1993) 7685.

[23] N. Savvides, J. Appl. Phys., 59 (1986) 4133.

[24] P.H. Gaskell, A. Saeed, P. Chieux and D.R. McKenzie, Philos. Mag. B, 66 (1992) 155.

[25] G. Galli, R.M. Martin, R. Car and M. Parrinello, Phys. Rev. Lett., 62 (1989) 555.

[26] O. Gereben and L. Pusztai, Phys. Rev. B, 50 (1994) 14 136.