

GLASS NETWORKS VIA SEMIEMPIRICAL QUANTUM CHEMICAL METHODS

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Received 14. 11. 1990

Various up to date approaches for theoretical investigation of glasses are compared. A new type of ZDO-class method for study of electron structure of glassy systems is proposed. The method proposed can distinguish between models representing network structure and the unrealistic models resembling more isolated structural units.

INTRODUCTION

Application of methods of quantum chemistry in the field of glass research meets severe problems. Absence of the periodicity makes the methods used in studies of crystalline phases difficult applicable. The problem may be solved either by use of suitable clusters for modelling the basic units occurring in the glass or by use of great periodic models of glass structure. However, in methods using clusters still remains questionable how to involve the influence of the environment as well as how to finish the cluster. On the other hand, in case of great periodic models of glass structure the main problem for many laboratories represent the extensive time and memory demands of such calculations. Moreover, this treatment involves a fundamental contradiction between the stochastic character of glass structure and the superimposed periodical boundary conditions.

In regard to serious questions concerning the electron—and atomic structure of amorphous systems, there have been recently developed several theoretic methods enabling to study disordered materials [1—4]. Nevertheless, in the mean time no method unlimitedly applicable for all kinds of objects and questions to be studied is available. The objects to be studied may be in principle divided in two major groups. To the first of them belong the metal glasses and the disordered alloys. The questions most frequently occurring in respect to these systems concern [2—4]: the density of states, partial density of states, photoelectron spectra, relationship of the atomic and electron structure, distance of valence and conductivity bands etc. The second type of objects under investigation involves materials with defined chemical and structural short-range arrangement and with amorphous phase consisting of non-arranged set of elementary units forming predominantly three-dimensional network. Oxidic glasses represent a typical example of these systems. Often asked questions, to be answered by the methods of quantum chemistry concern the properties of elementary units forming the three-dimensional structure: the local arrangement of atoms, energetics of changes in bond lengths, bond angles and dihedral angles. These properties determine the flexibility of the elementary unit and the flexibility of their arrangement which is closely related to the glass-forming ability [5, 6, 35, 36]. Theoretical investigations of vibrational spectra reveals the harmonical frequencies and force constants of suitable model clusters [7—9]. The methods of theoretical chemistry enable standard resolution of electron structure of oxidic glasses and their models

[1, 5—17]. Further problems which may be elucidated by means of quantum chemical calculations are: i) changes in atomic and electron structure of the network forming systems in regard to different additives; ii) behaviour of the band gaps as a function of concentration of additives; iii) correlation of the density of states with the short range environment of the atom and its binding conditions; localization of one-electron states [10] etc. An often studied problem represent also the optical properties of the given material [18, 19] and the influence of diverse additives on the spectral properties of glasses [20, 21].

In small clusters modelling the basic structural units of glass moiety *ab initio* methods [5—9, 14, 15, 22] were applied for resolution of their geometries and electron properties. Ching et al. [1, 10, 12, 13, 19] used the *ab initio* OL LCAO method [23] involving infinite electrostatic summation which enables to resolve crystals. These authors [1] applied the above method in resolution of quasicubic model of natrium silicate glass [24] consisting of three dimensionally, translatory replicated basic cell containing 162 atoms. In principle, this method is based on creation of a big cluster offering at three dimensional translatory replication logically continuous structure to which the apparatus of Bloch's functions is applied. The problem formulated this way, may be then solved by any of the current *ab initio* methods (different bases) or semiempirical methods of quantum chemistry.

The method of cyclic clusters involving infinite electrostatic summation of interaction with the translatory periodic environment was successfully applied for calculation of regular and also defect structures of crystals and surfaces [25—30].

METHOD

For glass as amorphous material the absence of translatory symmetry is characteristic. In this case it is extraordinary difficult to imply in calculation long range interactions which would reflect the randomized structure. Hence, methods based on the presumption of three-dimensional translatory symmetry may not be applied for summation of the latter interactions. In the case of fluids this problem is solved by application of diverse solvation models which consider the environment as a continuum [31—33]. Glass preserves the dominant structural features of liquid since it represents a frozen metastabil state which may be characterized by so called structural temperature T_f . Accordingly, the methods valid for liquids would provide qualitatively similar results for glass the more, that time and ensemble means are considered as equal.

Nevertheless, the selection of an elementary representant of the structure i.e. the true object of solvation remains still an important problem. Optimal solution may represent the construction of a cluster topologically equivalent to the given type of infinite structure. Such a cluster should meet the following criteria:

- i) stoichiometry;
- ii) chemical bonds oriented outwardly from the cluster should form pairs capable of topological encycling as concerns their direction and the local chemical environment as well as towards the topology of the infinite network;
- iii) among the bonds inside the cluster some should be equivalent to the artificially cyclized ones.

Fulfilling the above criteria the "Topologically Cyclized Cluster" (TCC) may be constructed in a way securing the replacement of interatomic interactions of cyclized pairs with artificial bonds by equivalent interactions originating from inside the cluster (Figs. 1–3). This is correct in the framework of nearest neighbour approximation. The model allows, however, to rewrite in matrix of the Hamiltonian also elements corresponding to interaction over two, three, ... etc. bonds.

The magnitude of error made by use of a definitive topologically cyclized cluster instead of an infinite topologically linear one may be characterized by the error of spectral radius of the matrix of Hamiltonian \mathbf{H} . The estimate of the spectral radius may be expressed [34] as

$$\rho(\mathbf{H}) \leq \max_i \sum_{k \neq i}^M |h_{i,k}|.$$

Changing $M = \infty$ for $M = N$ (definite) the estimate of the error will represent

$$\Delta\rho = \sum_{k=N+1}^{\infty} |h_{i,k}|.$$

When performing that with increase of the distance the nondiagonal matrix element will decrease exponentially

$$h_{i,(N+k)} = h_{i,N} \cdot \exp(-k \cdot d) = h_{i,N} \cdot q^k.$$

In this case

$$\Delta\rho(\mathbf{H}) = |h_{i,N}|/(1 - q).$$

A very rough estimate of $\Delta\rho$ may be made from differences in the values of ρ for the nearest neighbour—second nearest neighbour—third nearest neighbour—...etc. nearest neighbour approximation in a given TCC.

The proposed method may be demonstrated on any network forming oxide. For its testing may be with advantage to choose systems enabling construction of several simple models of different size. This possibility is provided particularly by three-coordinated network formers and among them the most common boron which we have chosen too. The quantum — chemical method INDO was used.

RESULTS AND DISCUSSION

The smallest possible stoichiometric models of B_2O_3 glass structure consist of five atoms and they enable to construct two TCCs. Other five-atomic models namely involve interactions which should be, but could not be transcribed, because they represent a real chemical bond or cluster does not contain any bonds allowing replacement of interaction to be transcribed (Fig. 1).

Moreover, the limited cluster size allows the approximation of nearest or next nearest neighbour only. The studied TCCs offer rather polar even explicitly ionic bonds with small orders. The solvation effect is further enhancing the unfavourable charge distribution (Tab. I).

On the other hand, ten atomic models enable to test besides the approximation of the next nearest also the third nearest neighbour. These approximations offer already acceptable results. With the nearest neighbour approximation the obtained

Table I
Bond orders of five-atomic models

MODEL A				
Bond	nearest neighb.		2 nd nearest neighb.	
	vacuum	solvated	vacuum	solvated
B ₁ -O ₂	0.327	0.100	0.947	0.981
B ₁ -O ₄	0.521	0.080	1.163	1.109
B ₁ -O ₅	0.445	0.080	0.832	1.013
O ₂ -B ₂	0.414	0.141	0.974	0.925
B ₃ -O ₄	0.504	0.110	0.974	1.125
B ₃ -O ₅	0.517	0.101	1.054	1.249
MODEL B				
Bond	nearest neighb.		2 nd nearest neighb.	
	vacuum	solvated	vacuum	solvated
B ₁ -O ₂	0.397	0.072	0.984	0.490
B ₁ -O ₄	0.333	0.051	0.698	0.602
B ₁ -O ₅	0.324	0.051	0.636	0.600
O ₂ -B ₂	0.396	0.071	0.984	0.490
B ₃ -O ₄	0.321	0.051	0.636	0.600
B ₃ -O ₅	0.333	0.051	0.698	0.602

Table II
Bond orders of ten-atomic models. Third nearest neighbour approximation

MODEL A			MODEL B		
Bond	vacuum	solvated	Bond	vacuum	solvated
O ₁ -B ₂	0.451	0.417	O ₁ -B ₂	1.166	1.168
O ₁ -B ₆	1.236	1.227	O ₁ -B ₆	1.128	1.121
B ₂ -O ₃	0.459	0.429	B ₂ -O ₃	1.076	1.072
B ₂ -O ₁₀	0.237	0.295	B ₂ -O ₁₀	1.106	1.106
O ₃ -B ₄	1.242	1.243	O ₃ -B ₄	1.071	1.059
B ₄ -O ₅	0.937	0.909	B ₄ -O ₅	1.072	1.060
B ₄ -O ₉	1.109	1.103	B ₄ -O ₉	1.066	1.052
O ₅ -B ₆	1.106	1.096	O ₅ -B ₆	1.047	1.035
B ₆ -O ₇	1.253	1.258	B ₆ -O ₇	1.079	1.066
B ₆ -O ₁₀	0.479	0.441	B ₆ -O ₁₀	1.142	1.139
O ₇ -B ₈	1.041	1.027	O ₇ -B ₈	1.052	1.044
B ₈ -O ₉	1.139	1.139	B ₈ -O ₉	1.090	1.079

Table III

Bond orders of fifteen-atomic models. Third nearest neighbour approximation

Bond	Vacuum	Solvated
O ₁ -B ₂	1.023	0.997
O ₁ -B ₄	1.017	0.985
B ₂ -O ₃	0.952	0.920
B ₂ -O ₇	1.009	0.974
O ₃ -B ₄	0.954	0.918
B ₄ -O ₅	0.988	0.943
O ₅ -B ₆	0.963	0.928
B ₆ -O ₇	1.012	0.980
B ₆ -O ₈	0.879	0.825
O ₈ -B ₉	0.879	0.823
B ₉ -O ₁₀	0.964	0.926
B ₉ -O ₁₄	1.012	0.983
O ₁₀ -B ₁₁	0.986	0.943
B ₁₁ -O ₁₂	0.953	0.923
B ₁₁ -O ₁₅	1.024	0.998
O ₁₂ -B ₁₃	0.953	0.916
B ₁₃ -O ₁₄	1.011	0.972
B ₁₃ -O ₁₅	1.017	0.983

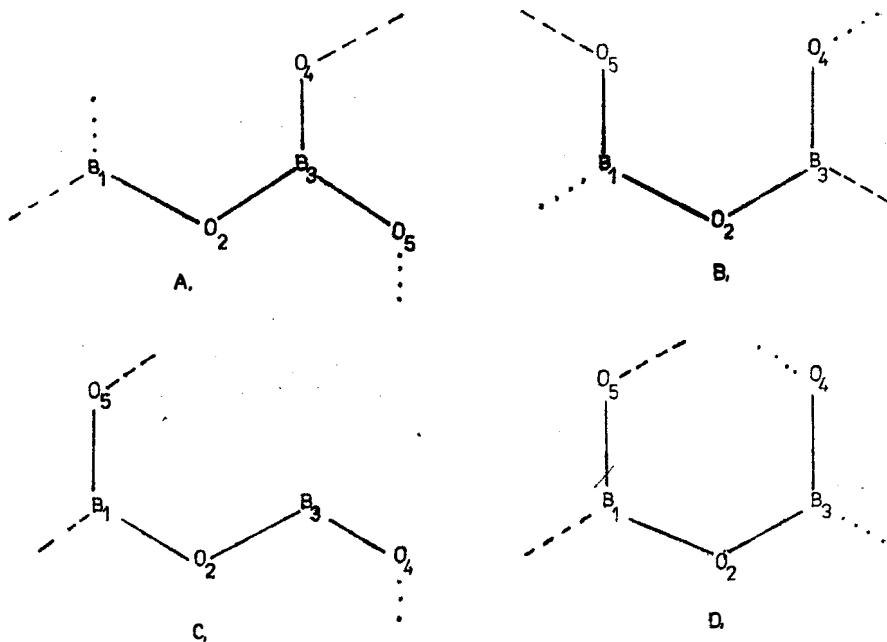


Fig. 1. Five-atomic B₂O₃ clusters. A, B - true TCCs, C, D - not TCC's.

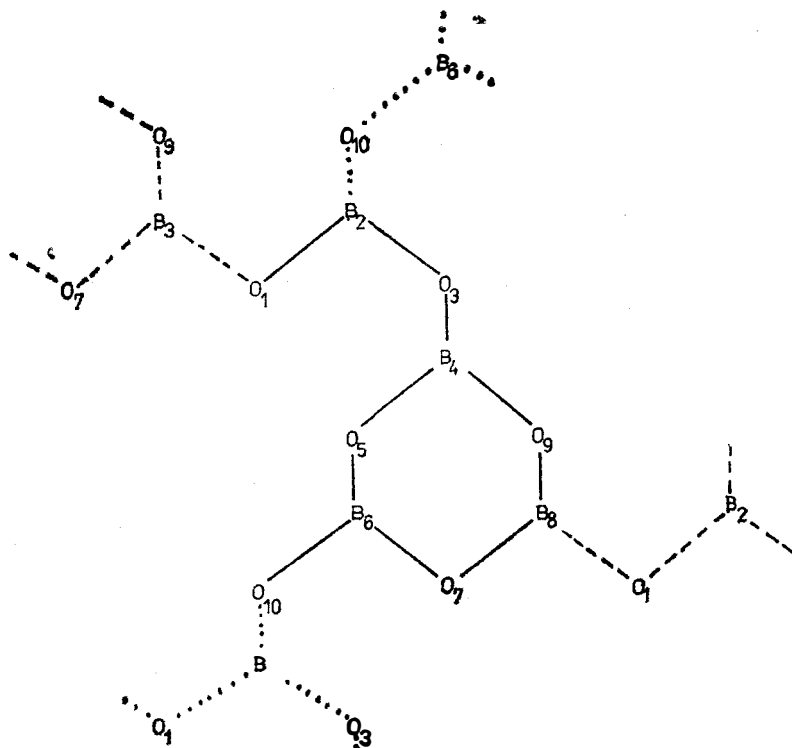


Fig. 2. Ten-atomic TCC, model A. The figure explicitly shows the continuation of the structure.

bond orders were small and the bonds too polar. These results are comparable with those obtained for five-atomic TCCs.

The approximation of the second and the third nearest neighbour yields bond orders close to one. Although the solvation enhances the polarities of bonds but their orders are not considerably influenced.

Two ten-atomic TCCs were studied: model A (Fig. 2) corresponds topologically to two-dimensional surface. Nevertheless, the bond orders revealed that although the bonds within the boroxole ring are of the order close to one, the two-dimensional network between diverse boroxole rings contains bonds of very low order only. Hence, the system resembles more a bunch of isolated structure units.

The ten-atomic model B (Fig. 3) represents a stripe. This model appears to be continual (Tab. II).

A further system studied represents the fifteen-atomic model corresponding to two infinite half-planes with mutual position ascertained by dihedral angles $O_5-B_6-O_8-B_9$ and $B_6-O_8-B_9-O_{10}$ (Fig. 4). All bond orders of this model are close to one (Tab. III) and the system „in toto” is not planar.

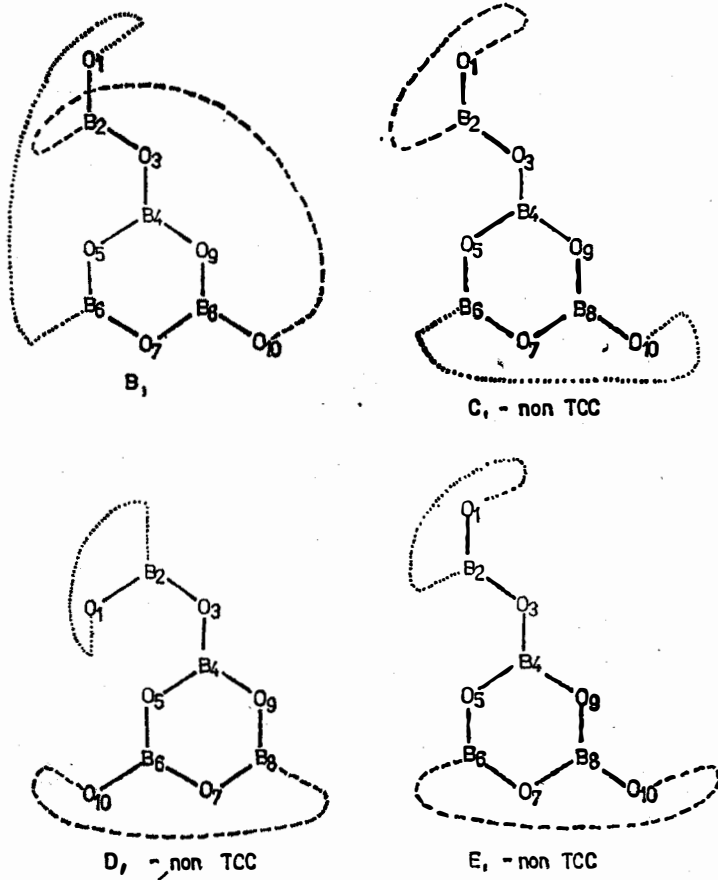


Fig. 3. Ten-atomic clusters, models B, C, D, E. Cases C, D, E are not TCCs.

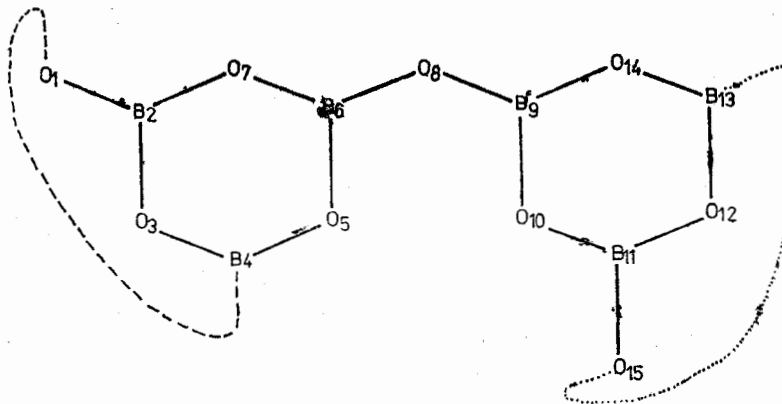


Fig. 4. Fifteen-atomic TCC.

CONCLUSIONS

It could be summarized that the method proposed seems to be acceptable on condition that the considered interactions will reach at least three bonds. The inclusion of the environmental effect in the model of continuum correspondingly increases the polarities but do not influence considerably the orders of bonds. Because of the well known limitations of the Germer's method it seems to be reasonable to test also some more developed methods for involvement of the influence of the environment in the calculation of electron structure.

The method proposed seems to be capable to distinguish between models representing network structure and the unrealistic models resembling more isolated structural units.

The actual structure of real B_2O_3 glass represents combination of many types of motives, including the three-dimensional ones. Therefore, when computing the observables of the real glass it remain still questionable how to combine for TCC approximation the results obtained in single models. In the first approach a perspective solution seems to be offered by the calculations of means using the Boltzman's relation at temperature equal to T_f .

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MODELOVANIE SIEŤOVEJ ŠTRUKTÚRY SKIEL SEMIEMPIRICKÝMI METÓDAMI KVANTOVEJ CHÉMIE

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Porovnávajú sa rozličné súčasné metódy teoretického štúdia skiel. Pre teoretické štúdium elektrónovej štruktúry skelných systémov sa navrhla nová metóda ZDO typu. Navrhnutá metóda je schopná rozlíšiť modely, predstavujúce skutočnú sieťovú štruktúru od modelov s elektrónovou štruktúrou zodpovedajúcou skôr súboru vzájomne izolovaných štruktúrnych jednotiek. Použité metódy sa ilustruje na päť, desať a pätnásť atómových topologicky cyklizovaných klastroch modelujúcich sieťovú štruktúru skelného oxidu boritého (obr. 1—4). Pritom sa porovnávajú matice poriadkov väzieb získané so zahrnutím rôzneho dosahu interakcií (tab. I—III). Ukázalo sa, že na postihnutie sieťového charakteru štruktúry treba v modeli zahrnúť minimálne interakcie na úrovni druhých najbližších susedov.

Obr. 1. Päťatómové B₂O₃ klastre.

A, B — pravé TCC; C, D — nie TCC.

Obr. 2. Desiatatómové TCC, model A. Na obrázku je explicitne znázornené pokračovanie štruktúry.

Obr. 3. Desiatatómové klastre, modely B, C, D, E. Prípady C, D, E nie sú TCC.

Obr. 4. Päťnásťatómový TCC.

МОДЕЛИРОВАНИЕ СЕТЧАТОЙ СТРУКТУРЫ СТЕКОЛ С ПОМОЩЬЮ ПОЛУЭМПИРИЧЕСКИХ МЕТОДОВ КВАНТОВОЙ ХИМИИ

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В работе сопоставляются различные новейшие методы теоретического исследования стекол. Для теоретического исследования электронной структуры системы стекол авторами предлагается новый метод ZDO типа. С помощью приводимого метода можно различать модели, представляющие действительную сетчатую структуру, от моделей с электронной структурой, соответствующей более менее комплексу взаимно изолированных структурных единиц. Использование метода иллюстрируется на пяти-, десяти- и пятнадцатиатомных топологически циклизированных кластерах, моделирующих сетчатую структуру стеклообразующего оксида трехвалентного бора (рис.1—4). В связи с тем сопоставляются матрицы порядков связей, полученные с помощью разного предела взаимосвязей (табл. I—III). Было доказано, что для описания сетчатого характера структуры приходится в модель включить минимальные взаимодействия на уровне дальнейших ближайших соседей.

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Рис. 1. Пятиатомные B_2O_3 кластеры: А, В — действительные ТСС, С, Д — не являются действительными ТСС.

Рис. 2. Десятиатомные ТСС, модель А. На рисунке наглядно изображается продолжение структуры.

Рис. 3. Десятиатомные кластеры, модели В, С, Д, Е. Приводимые С, Д, Е не являются действительными ТСС.

Рис. 4. Пятнадцатиаомные ТСС.