Quantum Chemical Analysis of the Dielectric Constant Concept at Atomic Scale: an Interaction of Probing Point Charges with Silica Cristobalite-Like Cluster

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The quantum chemically simulated interaction of probing point charges with the silica cristobalite-like cluster $Si_{48}O_{122}H_{52}$ [= $Si_{48}O_{70}(OH)_{52}$] proves that the macroscopic dielectric constant can not be used at atomic scale distances due to quantum chemical interactions.

Key words: Dielectric Constant; Quantum Chemistry; Semi-Empirical Method; PM3; Silica.

The dielectric constant as a macroscopic term informs us on the ability of matter to decrease an electric field and it is frequently used when results of molecular simulation are discussed [1 – 4]. But the literature data show that the application of the dielectric constant to molecular interactions is problematic [2 – 4]. A quantum chemical (QC) approach can clarify the interaction of an external electric field with matter.

In the present paper a silica cluster, interacting with a positive and negative point charge, has been chosen for a QC simulation to discuss the meaning of the dielectric constant on the atomic level. The semiempirical method PM3 [5] has been used in the framework of the "QuChem" software [6], because this method has some important features for silica calculations [7]. The ability to simulate clusters in an electric field [8] and to calculate the forces needed to keep the system under a defined mechanical stress (along the axis of interaction), implemented in the "QuChem" and approved by recent studies [6], has been used to compute the forces of interaction between point charges.

Semiempirical QC calculations have been chosen, because the size of the investigated cluster (222 atoms) exceeds the computational potential of the density functional theory (DFT) STO 6G-311 while a smaller basis can not be used because of the incorrect reproduction of the essential structural parameters of silica [9]. Also, the accuracy of the calculation of the binding energy in *ab initio* and DFT methods is smaller than the heat of formation in the PM3 method. Thus the force, applied to the atoms, evaluated as a derivative of the heat of formation of the cluster along the axis of interaction, is more precise. Also, standard *ab initio* program packages do not allow the computation of the force, applied to the atoms.

The application of molecular dynamics (MD) methods is problematic for several reasons. Firstly, the potentials of charge-to-charge interactions, implemented into the MD, are based on the macroscopic Coulomb law. Thus the influence of quantum effects can not be studied. Secondly, the position of the examined clusters should be strictly defined, which is not allowed in the context of the model (see below).

The previously described cluster $Si_{48}O_{122}H_{52}$ [10, 11], consisting of two cristobalite-like layers with a completely hydroxylated surface, has been used as model of silica glass. The F^- ion has been used as a probing negative point charge, since it is small, the most electronegative and "rigid" to polarization.

Three QC systems are shown in Fig. 1: a positive point charge with a probing F^- ion (System 1); a positive point charge with a probing F^- ion and a silica cluster positioned outside the axis between the charges (System 2); a positive point charge with a probing F^- ion and a silica cluster positioned exactly between the charges (System 3). The distance between the charges has been varied from 20 (15 in System 1) to 60 Å. The mechanical forces needed to keep the defined distance between the charges have been QC derived and plotted vs. the distance in Figure 2. The QC

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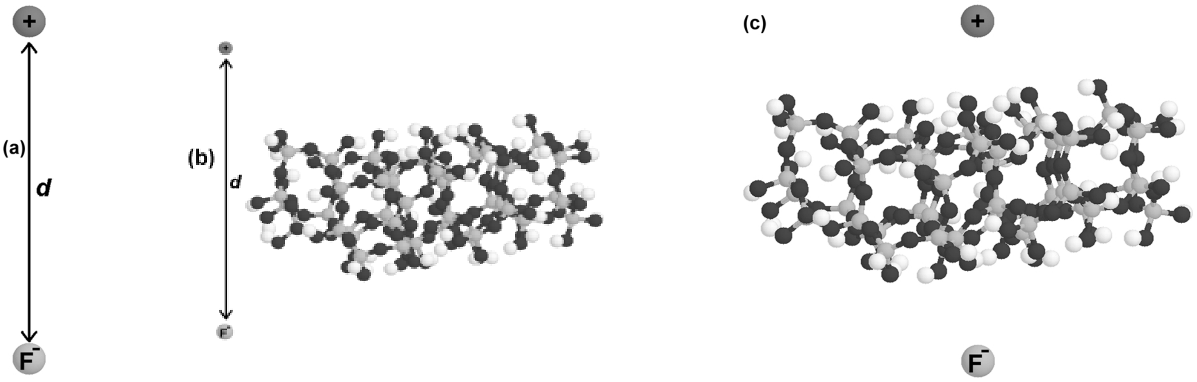

Fig. 1. Models of electrostatic force calculations: (a) positive point charge and probing F$^-$ ion (System 1); (b) positive point charge and probing F$^-$ ion with a silica cluster positioned aside from the axis of interaction between the charges (System 2); (c) positive point charge and probing F$^-$ ion with a silica cluster positioned between the charges (System 3).

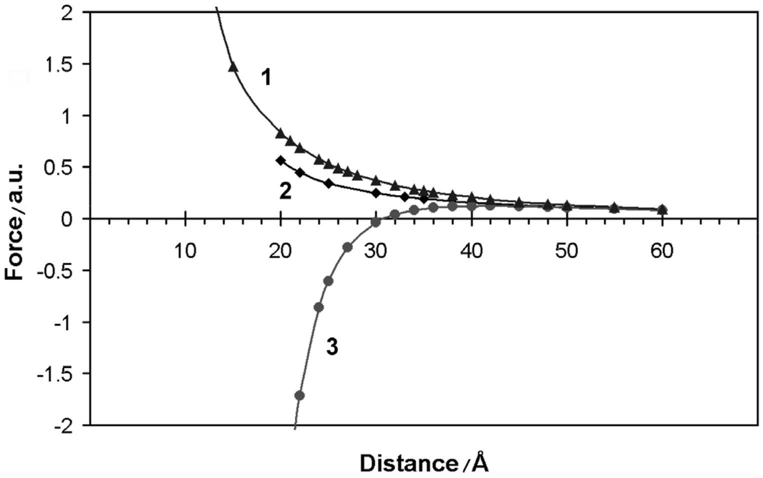

Fig. 2. The electrostatic force on the probing ion F$^-$ as a function of the distance between the point charge $+1$ and the F$^-$ ion. Line 1 shows the force of the electrostatic interaction, derived from the Coulomb law in System 1; triangles are the quantum chemically (QC) derived mechanical forces. Line 2 and diamonds are the QC derived mechanical force curve and values in System 2. Line 3 and circles are the QC force curve and values in System 3.

derived mechanical forces in System 1 reproduce excellently the curve of the electrostatic interaction, derived from the Coulomb law. The silica cluster is too small to reproduce the macroscopic values, related to the dielectric constant, but is sufficient for the study of the phenomena.

The QC computed charge of the probing F$^-$ ion is -1.000000 at any distance from the surface of the silica cluster that exceeds 6 Å. The Wiberg index [12–14] of the interaction between the F$^-$ ion and the silica cluster is below 0.001. The sum of the Wiberg indexes [9] over the F$^-$ ion is 0.000000. Therefore, there is neither charge transfer nor covalent interaction between the F$^-$ ion and the silica cluster, so the interaction is completely electrostatic.

As one can see in Fig. 2, a repulsion between opposite charges is unexpectedly observed in System 3 at distances below 30 Å. The analysis of the static component of the dielectric constant, derived from the QC calculated forces of interaction between point charges according to the Coulomb law (Fig. 3), shows that below 30 Å it is negative, which has no physical sense. Only at distances about 35 Å the QC derived static component of the dielectric constant becomes close to the experimentally known silica glass dielectric constant equal to 3.91. The further decrease of the value to the plateau, infinitely tending to 1, is explained by the finite size of the silica cluster, since the electrostatic interaction is not linear and the silica cluster does not "screen" the charges.

The QC simulation of the positive point charge and the probing F$^-$ ion with the silica cluster positioned aside form the axis of interaction between the charges (System 2) leads to a result similar to that of Sys-

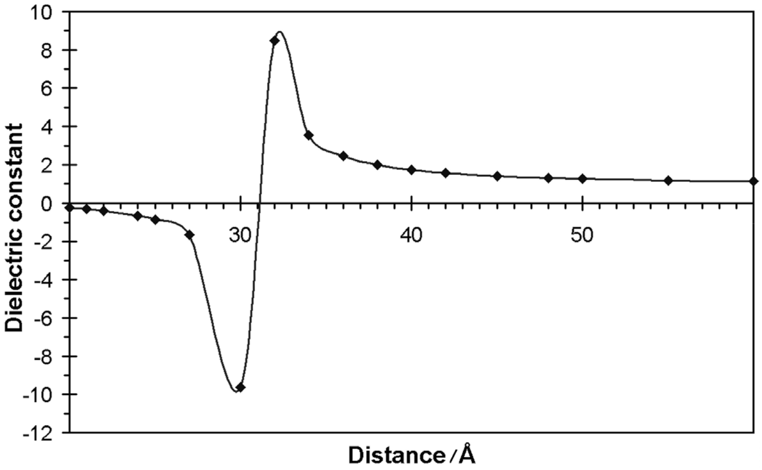

Fig. 3. The QC derived static dielectric constant between the F^- ion and point charge in System 3 as a function of distance.

tem 1, i. e. the interaction between the charges is not disturbed. However, the step-by-step insertion of the silica cluster between the charges gradually decreases the mechanical forces needed to keep the defined distance between charges, finally resulting in a situation similar to System 3.

A detailed analysis of the interactions in System 3 shows that two components can be distinguished namely, 1.) the electrostatic interaction between the positive point charge and probing F^- ion, and 2.) the electrostatic interactions of the positive point charge and probing F^- ion with the positively charged nuclei and negatively charged electrons of the atoms in the silica cluster which form the internal electric field of the silica. It has been shown in [8] that the external electric field with an intensity higher than that of the internal one causes a collapse of the molecular structure of the cluster. At distances exceeding 35 Å this field can be considered as integral of the local electric fields and, therefore, the macroscopic meaning of the dielectric constant has a sense. But below 35 Å the value of interactions between point charges and local electric fields becomes significant and leads to a radical deviation from the Coulomb law. The sign and value of such interactions depend on the local atomic structure of the considered substance and can not be predicted form the macroscopic physical laws. The phenomenon of the negative sign of the QC derived dielectric constant can not be explained by the influence of the thermal motions of the atoms. The local electromagnetic fields, induced by the thermal motions of the atoms, may influence the value of the dielectric constant but can not change the sign. So, no atomic-scale phenomena, such as bond length, atomic charges, local defects of crystalline structure, can be discussed in terms of the dielectric constant.

Therefore, the concept of the dielectric constant can only be used in macroscopic distances above 35 Å. The QC interactions should be accounted for at lower distances.

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