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CHARGE DISTRIBUTION FUNCTIONS FOR CHARACTERIZATION OF COMPLEX SYSTEMS

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A set of characteristics calculated within the scope of quantum chemistry methods may be assigned to local ones changing from atom to atom in complex systems. Simple averaging of the related values gives rather poor characteristics of the systems because various fractions of certain atoms can have different surrounding and, therefore, different characteristics, which may not correspond to the average one. The aim of this study is searching a more appropriate pathway to transform local characteristics, e.g., atomic charges, into nonlocal ones based on the distribution functions. The distribution functions of atomic charges (CDF) could be considered as a simple tool to analyze nonuniform complex systems since specificity of different fractions of atoms reflects in the CDF shape. As a whole, the approach accuracy and efficiency depend on the quality and appropriateness of molecular and cluster models used, as well as on the quantum chemical methods (ab initio, DFT, and semiempirical) and the basis sets used. Nanosystems with dozens of molecules (clusters, domains, nanodroplets), modelling a liquid phase or interfacial layers, and solid nanoparticles of almost real sizes (> 40 units, > 2 nm) may be considered as more appropriate models of real systems than the models with several molecules and small clusters (< 20 units, < 1 nm). This approach has been applied to a set of representatives of such various materials as activated carbon, porous and nanoparticulate silicas unmodified and modified interacting with nitrogen, methane, water, human serum albumin (HSA) binding doxorubicin molecules. This approach may give information useful upon the analysis of any complex system.

Keywords: *atomic charges, distribution functions, DFT method, semiempirical method*

INTRODUCTION

According to quantum chemical calculations, the electronic characteristics of molecular and cluster systems could be divided into local (e.g., atomic charges, magnetic shielding tensors or chemical shifts, bond length, strength and vibrations, etc.) and nonlocal (molecular orbitals, MO, electron bands, total energy, solvation energy, etc.) ones [1–9]. Some of the latter may be represented as local or quasi-local characteristics (e.g., localized MO, spin density, etc.). On the other hand, the transformation of the local characteristics into nonlocal ones is of interest to obtain a more generalized picture of the electronic structure, to analyze various phenomena and related experimental data, etc. [10–13]. In the present work, this transformation was realized for values of atomic charges (q). This was done upon calculations of interfacial structures with water, methane, nitrogen, and human serum albumin (HSA) binding doxorubicin (DOX) interacting with nanoparticles of unmodified and modified silicas, alumina, alumina/silica, titania/silica, and activated carbon as representatives of different systems using the density functional theory (DFT) and semiempirical (PM7) methods [14, 15].

CALCULATION METHODS

Solid nanoparticles, free water clusters and interfacial layers at surfaces of hydrophilic and hydrophobic silicas, alumina, alumina/silica, and titania/silica were calculated using DFT methods with the Gaussian 09 [14] and GAMESS 2020 R2 [15] program suits. The DFT calculations were done using a hybrid functional ω B97X–D and cc–pVDZ basis set. The solvation effects were analyzed using the SMD method [16] implemented in the Gaussian and GAMESS. The calculations were performed taking into account zero-point and thermal corrections to the Gibbs free energy in the gas phase and for solvated molecules and silica clusters using the geometry optimized using ω B97X–D/cc–pVDZ (with or without SMD). Note that ω B97X–D introduces empirical damped atom-pairwise dispersion terms into the functional containing range-separated Hartree-Fock exchange for better description of van-der-Waals interactions [17, 18]. Therefore, ω B97X–D was selected to obtain more adequate results for the gas and liquid phases (water, hydrophilic and hydrophobic organic solvents) interacting with hydrophilic and hydrophobic silica nanoparticles. Large systems up to 15200 atoms were calculated using the PM7

method (MOPAC 2016, versions 20.015L, 20.268L, and 21.002L) [19, 20].

The distribution functions of atomic charges (CDF) were calculated using a simple equation [10–13]

$$f_n(q) = (2\pi\sigma_n^2)^{-0.5} \sum_j \frac{\exp[-(q_{n,j} - q)^2]}{2\sigma_n^2}, \quad (1)$$

where j is the number of an atom of the n -th kind, σ_n^2 is the distribution dispersion for the atoms of the n -th kind, and $q_{n,j}$ is the Mulliken charge value, and q is the current value. For the electron-donor atoms (H, Al, Si, Ti), $\sigma = 0.01$ a.u., and $\sigma = 0.05$ a.u. for electron-acceptor atoms (C, N, O, S). This difference in the σ values is due to broadening of the CDF for atoms with excess electron density (*i.e.*, for electron-acceptor atoms) more strongly affected by the surroundings in comparison to the atoms with deficiency in the electron density (electron-donor atoms) with more compact electron clouds. Additionally, the distribution functions of integral density of electron states (IDES) of some silica clusters were calculated using an equation similar to Eq. (1) with

the molecular orbital energy (E) instead of the atomic charge, q [21].

RESULTS AND DISCUSSION

The CDF shapes for silica clusters at 8, 22, and 44 units (Fig. 1 *a*) show that the curves for the smallest cluster are incomplete and simpler than those for larger silica models with the same σ value. As a whole, the CDF shapes are quite appropriate for the cluster at $n = 44$ since the curves give information on a difference in the O atoms in the siloxane bridges and silanols, H atoms without or with the hydrogen bonds, as well as for the Si atoms with different surroundings. Thus, one may assume that silica clusters at $n > 40$ (> 2 nm in size) could be considered as appropriate models of silica nanoparticles. Additionally, a set of the CDF (Fig. 1 *a*) is more informative and sensitive to the cluster size than the IDES (Fig. 1 *b*). However, instead of the IDES local DES (*i.e.*, local density of electron states for each atom in the system) could be calculated that give detailed but purely local pictures of the electron states of complex systems [21]. Therefore, the IDES/LDES are not considered here as a tool to transform the local characteristics into nonlocal ones.

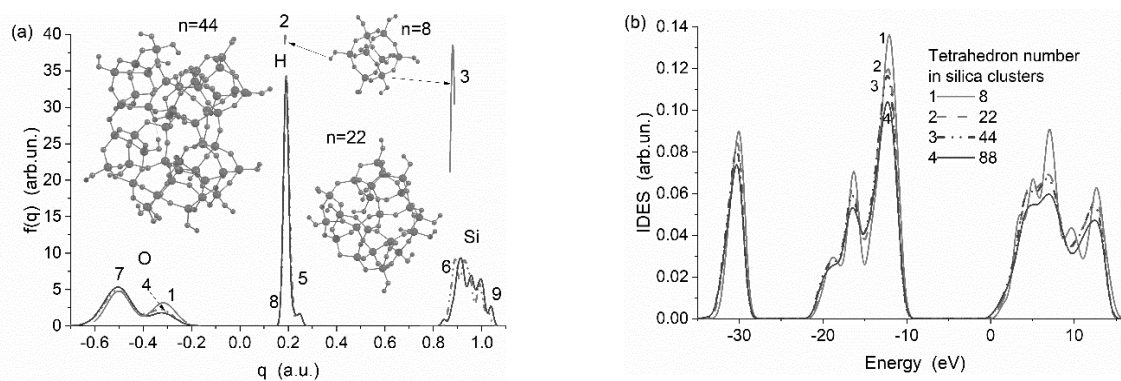


Fig. 1. Distribution functions of (a) charges of H (curves 2, 5, 8), O (1, 4, 7), and Si (3, 6, 9) atoms for silica clusters with 8 (curves 1-3), 22 (4-6), and 44 (7-9, size ~ 2 nm) $\text{SiO}_{4/2}$ units and silanols (solid lines at $n = 8$ and 44, and dashed lines at $n = 22$); (b) integral density of electron states for the same silica clusters calculated using the $\omega\text{B97X-D/cc-pVDZ}$ method

Upon the adsorption of nitrogen molecules (40N_2) onto the cluster at $n = 44$, the maximal difference in the CDF calculated using the DFT and PM7 methods is observed for the H atoms (Fig. 2), since for others (N, O, and Si) the positions of the CDF peaks are close. However, the calculations with the PM7 method give less detailed CDF curves; *i.e.*, the electronic structure of the atoms is

less sensitive to the surroundings upon calculations with only the valence basis (PM7). This aspect also appears upon the calculations of the NMR spectra with the DFT (or *ab initio*) methods and estimation of the ^1H NMR spectra (δ_{H}) using calculations with the PM7 (or PM6, *etc.*) method (q_{H}) and correlation functions for δ_{H} vs. q_{H} [10–13, 22]. This approach does not work for non-hydrogen multi-electron

atoms. One of the reasons of this restriction is the use of the MO only of valence electrons with frozen core electrons in the semiempirical methods (PM7, *etc.*). Thus, if it is possible that the use of the DFT methods is preferable than the use of the semiempirical methods to study various complex systems.

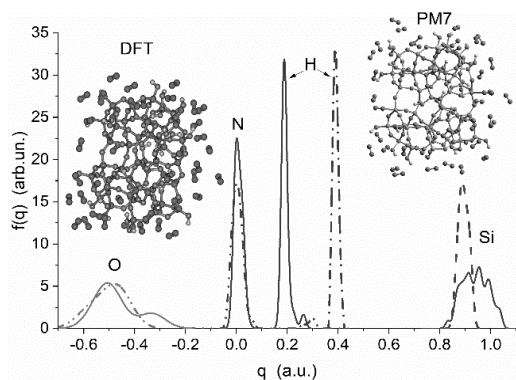


Fig. 2. Charge distribution functions of H, N, O, and Si atoms for a silica cluster (44 $\text{SiO}_{4/2}$ units and 24 OH) and adsorbed nitrogen molecules (40 N_2) calculated using the $\omega\text{B97X-D/cc-pVDZ}$ (solid lines) and PM7 (dashed lines) methods

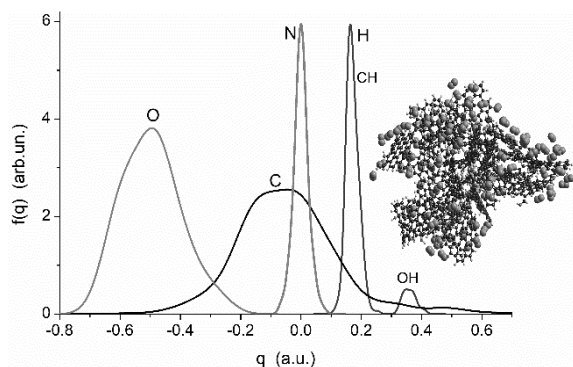


Fig. 3. Charge distribution functions of H, C, N, and O atoms for a model cluster (1787 atoms in total) of activated carbon decorated by various O-containing functionalities and adsorbed nitrogen molecules (see insert)

Comparison of the CDF of the nitrogen atoms upon the adsorption of nitrogen molecules onto silica clusters (Fig. 2) and AC (Fig. 3) shows that in the case of a more polar surface of silica, there is certain asymmetry in the CDF with a larger contribution of $q_N > 0$ due to transfer of the electron density toward the silica surface (*e.g.*, onto H in the SiOH groups). For the latter, the q_H values are greater than that for AC. This effect leads to stronger variations in the orientation of the N_2 molecules at a silica surface, and, therefore, the

occupied area for N_2 adsorbed onto silica could be smaller (0.135–0.137 nm^2) than that upon the adsorption onto basal planes of carbons (0.162 nm^2).

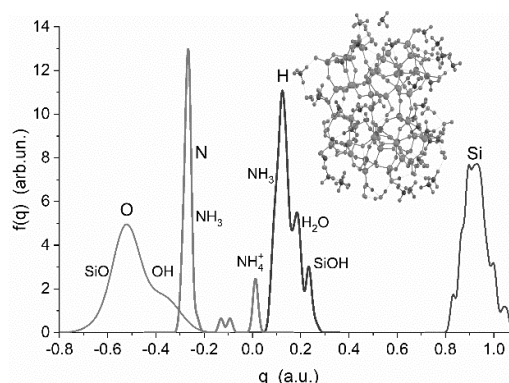


Fig. 4. Charge distribution functions of H, N, O, and Si atoms for silica cluster (44 units + 19 OH and 5 SiO^-) and adsorbed NH_3 (5 NH_4^+ and 30 NH_3) and 16 H_2O molecules calculated using the SMD/ $\omega\text{B97X-D/cc-pVDZ}$ method

The CDF of the O atoms are broader for AC than for silica (PM7 method) because of a larger variety in the surroundings of the O atoms in AC than in silica.

The appearance of charged groups (SiO^-) and ions (NH_4^+) more strongly affects the CDF of N and H. This result is due to significant localization of the excess charges in solvated or adsorbed ions in comparison to the charged groups at a surface of solids (Fig. 4).

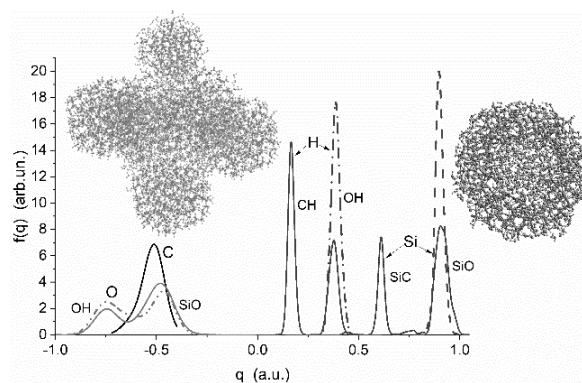


Fig. 5. Charge distribution functions of H, C, N, O, and Si atoms for silica nanoparticles (unmodified, A-300 and modified by dimethylsilyl groups pair-crosslinked, AM1, forming aggregate with six nanoparticles AM1/A-300 at 5:1, 8090 atoms in total), and pore model (pore radius $R = 0.9$ nm, 3171 atoms in total) of unmodified silica gel and adsorbed H_2O and CH_4 (only on AM1/A-300 aggregate) molecules calculated using the PM7 method

The silica particle structure (particulate or porous) weakly affects the CDF of the H, C, O, and Si atoms (Fig. 5). This result may be explained by a major contribution of atoms with similar surroundings in the particles of different morphologies. This assumption is confirmed by the calculations of complex systems (Figs. 6 and 7). The

surroundings of the Al atoms are different in $\gamma\text{-Al}_2\text{O}_3$ (Fig. 6 *a*) and alumina embedded into silica, AS (Fig. 6 *b*) due to variations in the O-coordination numbers of Al (from 3 to 6 for $\gamma\text{-Al}_2\text{O}_3$ and only 4 for alumina at a silica surface). This difference leads to a complex CDF of Al in $\gamma\text{-Al}_2\text{O}_3$ in contrast to AS (Fig. 6).

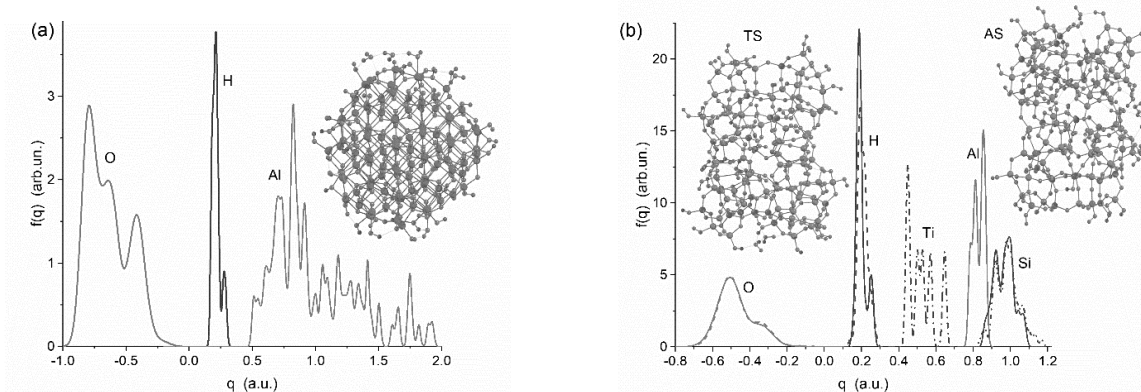


Fig. 6. Charge distribution functions of H, O, Al, Si, and Ti atoms for clusters and adsorbed H_2O molecules calculated using the $\omega\text{B97X-D/cc-pVDZ}$ method: (a) $\gamma\text{-Al}_2\text{O}_3$ (363 atoms) and (b) silica (82 units + 40 hydroxyls + 10 H_2O) with six units of alumina (AS, solid lines) or titania (TS, dashed lines)

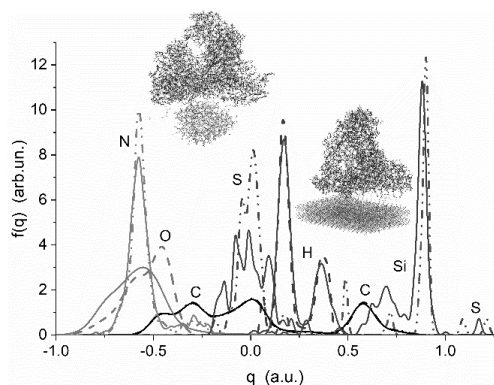


Fig. 7. Charge distribution functions of H, C, N, O, Si, and S atoms for HSA with bound 12 molecules of DOX (HSA/DOX), 194 H_2O interacting with a silica nanoparticle (~ 3.3 nm in size) (solid lines, 12304 atoms in total), and HSA/DOX, 149 H_2O , interacting with a plane fragment of a silica surface (dashed lines, 15147 atoms in total) calculated using the PM7 method

The structure of silica particles can affect the CDF of certain atoms (*e.g.*, S) in complex adsorbates such as HSA with DOX (Fig. 7). For some other atoms, the difference could be smaller due to stronger averaging of the q values for larger numbers of atoms. This result may be also explained by a small contact area between silica particles and HSA/DOX/water (Fig. 7, inserts). Additionally, the silica surface shape, hydrophilicity and other

characteristics can affect folding-unfolding processes characteristic for proteins and other complex macromolecules.

CONCLUSION

Thus, calculations of the distribution functions of atomic charges with the DFT and semiempirical PM7 methods may be considered as a simple tool to analyze various factors affecting the electronic structure of complex systems. The efficiency and accuracy of this tool depends strongly on the quality and appropriateness of the models used. The systems with dozens or hundreds of molecules of water or other low-molecular weight compounds (modeling a liquid phase or interfacial layers) and solid nanoparticles of almost real sizes (> 40 units, > 2 nm) for fumed oxides give more accurate and representative results than the systems with several molecules and too small solid clusters (< 20 units, < 1 nm). As a whole, the presented approach could be used with different quantum chemical methods (*ab initio*, DFT, and even such semiempirical methods as PM7 or PM6).

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Функції розподілу зарядів для характеристики складних систем

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Набір характеристик, розрахований у межах методів квантової хімії, може бути віднесений до локальних, що змінюються від атома до атома в складних системах. Просте усереднення пов'язаних значень дає досить погані характеристики систем, оскільки різні фракції певних атомів можуть мати різне оточення і, отже, різні характеристики, які не відповідають середньому. Метою цього дослідження є пошук більш адекватного шляху трансформації локальних характеристик, наприклад, атомних зарядів, у нелокальні на основі функції розподілу. Функції розподілу атомних зарядів (CDF) можна розглядати як простий інструмент для аналізу неоднорідних складних систем, оскільки специфічність різних фракцій відображається у формі CDF. В цілому точність та ефективність підходу залежать від якості та доцільності використаних молекулярних та кластерних моделей, а також від квантово-хімічних методів (*ab initio*, DFT та напівемпіричних) та використаних базисних наборів. Наносистеми з десятками молекул (кластери, домени, нанокрапельки), що моделюють рідку фазу або міжфазний шар, і тверді наночастинки майже реальних розмірів (> 40 одиниць) можуть розглядатися як більш відповідні моделі реальних систем, ніж моделі з декількома молекулами і невеликими кластерами (< 10 одиниць). Цей підхід був застосований до представників таких різноманітних матеріалів, як активоване вугілля, пористі та непористі наночастинки кремнезему, немодифіковані та модифіковані з адсорбованими молекулами азоту, метану, води, людський сироватковий альбумін з молекулами доксорубіцину. Цей підхід може надати інформацію, корисну при аналізі будь-яких складних систем.

Ключові слова: атомні заряди, функції розподілу, DFT метод, напівемпіричні методи

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