

Structure and Energetics of Mineral-Water Interfaces: Application to Clay-Based Building Materials*

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Abstract. The article provides an overview of the existing clay minerals for building purposes, methods for quantum-chemical modeling of clays and "green" nanomaterials based. Examples cover a wide class of clay minerals, processes and applications ranging from construction, geotechnics and geochemistry to biotechnology.

Keywords: Clay minerals, layered silicate minerals, building materials, phyllosilicates, computer modeling of new materials

In the last decade, a surge in scientific research in the nanosystems industry has stimulated a significant increase in interest in phyllosilicate minerals, especially clay minerals. To date, nanostructured materials based on minerals of the phyllosilicate subclass are increasingly being used in many branches of life [1].

The crystal structures of these minerals are a regular combination of two types of structural polyhedra - tetrahedra and octahedrons, in which O, OH, F anions are located at the vertices, and small cations are located inside. The tetrahedral positions can be predominantly occupied by Si atoms, which can be partially replaced by Al atoms and less often by Fe atoms. Octahedral sites can contain Al, Fe, Cr, Mg, Zn, Li, etc [2]. Fig. 1 shows the structure of layered silicates.

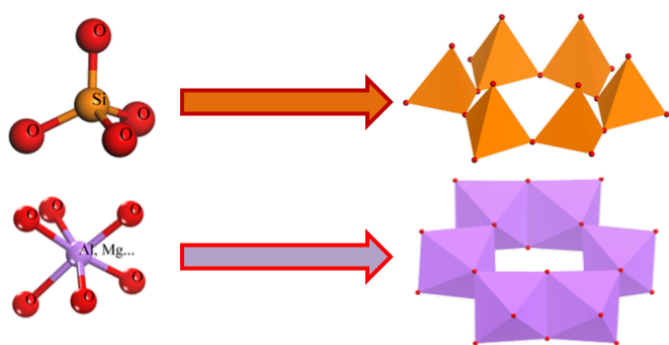


Fig. 1. Structure of layered silicates

In the crystal structures of layered silicates, tetrahedra, articulated in space by the vertices of their bases, and octahedrons, by their lateral edges, form two-dimensional hexagonal networks. In turn, tetrahedral and octahedral networks, having similar sizes, articulate with each other into layers, which for each mineral group are a combination of these networks (packages) [3-6].

So, for example, the combination of one octahedral and one tetrahedral network forms a 1:1 type package, which is represented by minerals of the kaolinite group. Three-storied packages of two tetrahedral networks adjacent from above and below to one intermediate octahedral network form a 2:1 type package and compose the structure of minerals of the smectite, micas, and illites group [7-10].

A distinctive feature of minerals of the smectite group, designated by the numerical index 2:1, is that in their crystal lattice there are two tetrahedral meshes with their vertices facing each other, between which there is an octahedral layer. The crystallochemical formula of one of the main representatives of this group - dioctahedral montmorillonite, corresponds to the form $(Ca, Mg, \dots)(Al, Fe^{3+}, Mg)_2(OH)_2[(Si, Al)_4O_{10}] nH_2O$. In this formula, in the first place are the cations that are located in the interpacket spaces, the composition of which may vary depending on the composition of the surrounding solution; in the second place are the cations located in the octahedrons; in the third place - hydroxyl groups located in the tops of the octahedral grid, through which there is no connection with the tetrahedral layer; in the last place in the formula there is an expression indicating an indefinite number of water molecules located in the interpacket spaces in the form of hydrate shells of interpacket cations.

It can be seen that the number of studies conducted on this topic is increasing not only over the years, but also over the range of subject areas of science. Fig. 2 shows the increase in the number of publications on layered silicates.

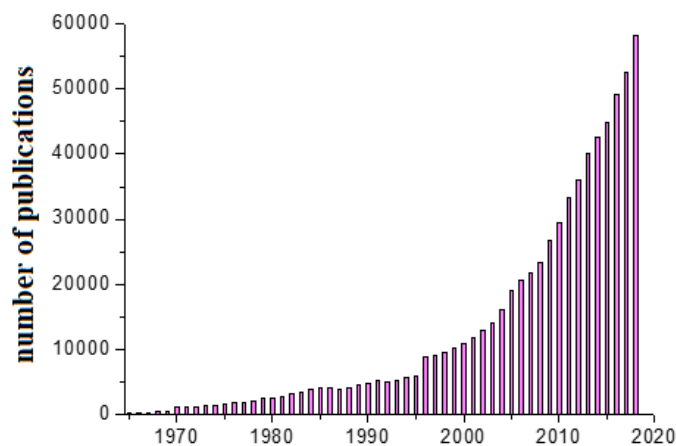


Fig. 2. Dynamics of the number of publications on the subject of layered silicates

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Progress in the development and use of computational chemistry methods, the development of software and computer technology have led to the widespread use of computer modeling of atoms, molecules, crystals and nanosystems [11-13]. Computer modeling methods are a relatively new and effective tool, in addition to existing analytical methods, providing a deeper understanding of the mechanisms of interlayer and surface processes in phyllosilicate minerals [14, 15].

Recently, the range of problems in the field of phyllosilicate minerals, in the solution of which computer modeling is used, has significantly expanded. If in the past computer modeling was mainly aimed at a quantitative description of the processes in these minerals, now much attention is paid to the creation of new promising nanomaterials. At the same time, the existing variety of computational algorithms, computational methods and approximations of quantum chemistry, due to the inevitability of introducing certain simplifications and limitations, requires a careful choice of the most rational computational-theoretical approach and the optimal direction of research when carrying out practical calculations.

Currently, there are many different methods that allow the theoretical study of polyatomic structures, including layered-periodic structures, which include minerals of the phyllosilicate subclass. They can be conditionally divided into the following groups: density functional theory methods, semi-empirical and empirical methods. When describing the electron subsystem in the density functional theory method, the many-electron wave function is replaced by the electron density. Semi-empirical methods take into account the parameters that are obtained in the framework of experimental studies. Empirical methods for calculating the total energy of a structure are based on the equations of classical mechanics and include a large number of experimental parameters. Such methods include, for example, molecular research methods.

The wide range of use of clay minerals is due to their high specific surface area and chemical activity, which allow them to be involved in various physicochemical and technological processes [16–20]. A significant role in these processes belongs to the contact of the mineral surface with water, which is a natural solvent and transport medium for numerous chemical compounds.

The chemical and physical properties of clay minerals are inextricably linked to some aspects of water interaction with their surface [21-28]. The hydration dynamics of phyllosilicate minerals, as well as the presence of solvation states, is the most important factor determining the macroscopic properties of these minerals, including their swelling capacity, plasticity, sorption and catalytic properties [29-40]. The mechanisms underlying these interactions have been the subject of intensive research in recent years using a wide range of experimental techniques. They include hydrogen bond formation, charge-dipole (electrostatic) interactions, ligand-ligand and van der Waals interactions. In addition, hydrolysis and redox reactions, depending on the nature of the exchangeable cations, can influence these mechanisms [41-47].

Thus, understanding the mechanisms of interaction in the "clay mineral-water" system is an important problem, the solution of which is aimed at developing theoretical concepts that explain such properties of clay material dispersions as plastic-

ity. Careful study of dispersions of clay minerals and the development of precision methods for studying their physical properties are necessary to solve these problems.

EXPERIMENTAL PART

The crystal structure of montmorillonite is formed by an octahedral sheet of aluminum atoms surrounding two tetrahedral sheets of silicon. The unit cell corresponds to the structural formula $\text{Si}_{16}\text{Al}_8\text{O}_{40}(\text{OH})_8$. The cell parameters are determined using the diffraction of synchrotron radiation on a single crystal.

Model of the siloxane surface of montmorillonite were built by optimizing the unit cell of montmorillonite with lateral dimensions of $5.18 \text{ \AA} \times 8.89 \text{ \AA}$. A vacuum space of 30 \AA is added vertically to the basal surface along the *c* axis. The results of preliminary calculations showed that such a thickness of the vacuum layer is sufficient to eliminate the interaction between the selected surfaces at a periodic boundary.

The spatial structure of the water molecule is preliminarily optimized in a $20 \times 20 \times 20 \text{ \AA}$ cell. The cell parameters are fixed during the optimization process. The gamma point is used in inverse *k*-space. The interaction between water molecules and the basal surfaces of clay minerals occurs due to forces that lead to the formation of a chemical bond.

Analysis of the distribution of electron density is carried out in order to assess hydrophilicity, to investigate the features of the mechanism of adsorption of water molecules on the siloxane surface of montmorillonite. An energetically favorable position for water molecules above the studied surface was found. To assess the hydrophilicity and identify the features of the mechanism of adsorption of water molecules on the siloxane surface of montmorillonite, an analysis of the electron density distribution was carried out, and energetically favorable positions of water molecules on these surfaces were determined.

The main difficulty that arises in calculations of the electronic structure of polyatomic molecules, nanoclusters, and solids is the correct consideration of the effects of electron-electron interactions. The electron density functional theory developed by Kochenberg and Kohn and Kohn and Sham is a fairly simple method for describing the exchange and correlation effects of an electron gas. Kochenberg and Cohn proved that the total energy of a physical system, including the exchange and correlation effects of the electron gas, is a single-valued electron density functional. The minimum value of the total energy functional is the energy of the ground state of the system, and the electron density corresponding to this minimum is the exact single-particle density in the ground state. Kohn and Sham then showed how it was possible, formally, to replace the many-electron problem with a completely equivalent set of one-electron equations.

The Kohn-Sham total energy functional for a set of doubly occupied electronic states is expressed by eq. 1:

$$E[\psi_i] = 2 \sum_i \int \psi_i \left(-\frac{\hbar^2}{2m} \right) \nabla^2 \psi_i d^3 \mathbf{r} + \int V_{ion}(\mathbf{r}) n(\mathbf{r}) d^3 \mathbf{r} + \frac{e^2}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3 \mathbf{r} d^3 \mathbf{r}' + E_{XC}[n(\mathbf{r})] + E_{ion}[R_I] \quad (1)$$

where E_{ion} is the Coulomb energy associated with interactions between nuclei (or ions) in positions R_I , V_{ion} is the static total electron-ion potential, $n(r)$ is the electron density, determined by eq. 2:

$$n(\mathbf{r}) = 2 \sum_i |\psi_i(\mathbf{r})|^2 \quad (2)$$

In this case, only the minimum value of the Kohn-Sham functional has a physical meaning. In order to minimize the Kohn-Sham functional, it is necessary to define a set of wave functions ψ_i . This is achieved by a self-consistent solution of the Kohn-Sham equations expressed by eq. 3:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{ion}(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \quad (3)$$

where ψ_i is the wave function of the electronic state i , ϵ_i is the Kohn-Sham eigenvalue, and V_H is the Hartree potential of electrons given by eq. 4:

$$V_H(\mathbf{r}) = e \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}'. \quad (4)$$

The exchange-correlation potential V_{XC} is given, formally, by the functional derivative according to eq. 5:

$$V_{XC} = \frac{\delta E_{XC}[n(\mathbf{r})]}{\delta n(\mathbf{r})}. \quad (5)$$

The main advantage of this method is that the Kohn-Sham equations represent the system of interacting electrons as a system of non-interacting electrons moving in the effective potential created by other electrons. In addition, to simplify the solution of these equations, the exchange-correlation energy of the electronic system is presented in an approximate form. The simplest method for describing V_{XC} is the LDA local density approximation.

The local density approximation is accurate in the limit of high densities or in the limit of a weakly varying charge distribution. This approximation turned out to be more successful than originally thought, despite its extreme simplicity. For materials such as semiconductors and simple metals, the local density approximation quite accurately describes the structural and vibrational properties: adequate structure at the lowest energy, elastic moduli, vibrational frequencies with an accuracy of several percent. At the same time, the local density approximation has well-known shortcomings. The large overestimation (up to 20%) of the crystal bond and molecular bond energy is perhaps the most serious shortcoming of this approximation, along with the impossibility of describing strongly correlated systems such as transition metal oxides.

The improvement of the LDA functionality was the gradient corrections to it GGA, with the help of which it is possible to improve the accounting for electron correlations of bounded and semi-infinite systems, such as molecules and surfaces. Further improvement of the technique for taking into account electron correlations led to the emergence of hybrid potentials. Their use in terms of machine counting time is comparable to the Hartree-Fock method, and in accuracy, in some cases, significantly superior to it. One of the most well-known representatives of hybrid potentials is B3LYP, the most well-known functional, which includes three components: the Hartree-Fock exchange potential, the Becke functional, and the Slater functional, and its correlation part is a combination of the Lee-Yang-Parr (LYP) and Wasko-Wilk functionals - Nusara (VWN). The use of this functional in calculating the structure of molecules, reaction energies, vibrational frequencies, electronic moments is comparable to the accuracy of the MP2 method (Meller-Plesset theory of the 2nd order). In some cases (for example, when calculating vibrational frequencies), the accuracy of the B3LYP functional exceeds all known non-empirical methods.

RESULTS AND DISCUSSIONS

Simulations of the behavior of water molecules on the basal surface of montmorillonite are shown in Fig. 3a. The most energetically favorable position of water molecules is the active sites formed by surface oxygen atoms. In these sites chemisorbed water forms hydrogen bonds with basal oxygen of montmorillonite. Hydrogen bond formation is due to the positively polarized hydrogen atom of the water molecule. Its single electron is displaced in the direction of the surface oxygen atom, with which the hydrogen atom forms a covalent bond. Therefore, the other side, on which "bare" positively charged nucleus, the hydrogen atom is able to approach electronegative atoms to distances close to the length of the chemical bond. The resulting stable hydrated shell of the Na⁺ ion is formed by three water molecules with an average radius of ~ 2.3 Å. The distance between the molecules and the basal surface is ~ 1.9 Å.

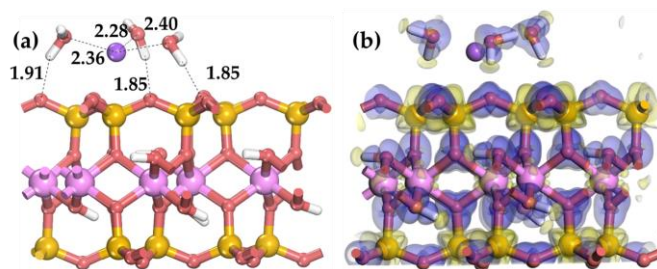


Fig. 3. Adsorption of water molecules on the basal surface of montmorillonite.

a – most stable adsorption configuration of water molecules;
b – electron density change

Fig. 3b shows the difference in electron density, which obtained by subtracting the electron density before the start interaction of the components of the montmorillonite-water system, and electron density after their interaction. Areas marked in blue indicate the accumulation of electrons in the binder, yellow areas indicate a decrease in electron density.

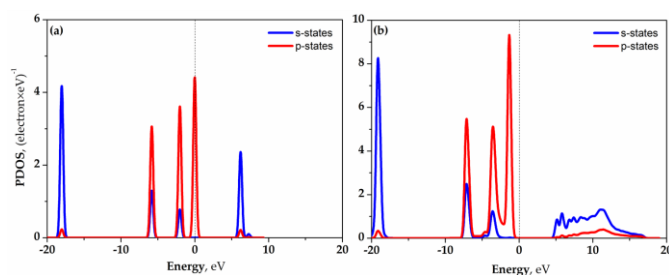


Fig. 4. Partial density of electronic states of water molecules.
a – water molecules in the gas phase;
b – water molecules adsorbed on the basal surface of montmorillonite

The calculated difference in electron densities shows a large charge accumulation between the adsorbate and the surface associated with the formation of a covalent bond, where the neighboring H atoms of the water molecule donate electrons to the oxygen atoms of the surface.

The change in the structure of electronic levels was studied H₂O molecules during its adsorption on the basal surface of montmorillonite. For this, the partial density of states of an isolated H₂O molecule and an H₂O molecule adsorbed on siloxane (001) montmorillonite surface (see Fig. 4).

CONCLUSION

Thus, in the course of the research, the following results were obtained:

1. It has been established that a wide class of natural nanomaterials, such as clay minerals are widely used in many industries, including construction, geotechnics, biotechnology, and others;

2. Theoretical aspects of computer simulation of new nanomaterials based on the Kohn-Sham density functional theory are presented;

3. Computer simulation of water adsorption on the surface of montmorillonite was carried out, the difference in electron density was experimentally obtained, which obtained by subtracting the electron density before the start interaction of the components of the montmorillonite-water system, and electron density after their interaction.

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Структура и энергетика границы раздела минерал – вода: применение к строительным материалам на основе глины

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Аннотация. В статье представлен обзор существующих глинистых минералов строительного назначения, методов квантово-химического моделирования глин и «зеленых» наноматериалов на их основе. Примеры охватывают широкий класс глинистых минералов, процессов и применений — от строительства, геотехники и геохимии до биотехнологии.

Ключевые слова: глинистые минералы, слоистые силикатные минералы, строительные материалы, слоистые силикаты, компьютерное моделирование новых материалов.