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20-th V.A. Fock Meeting on
Theoretical, Quantum and
Computational Chemistry
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BOOK OF ABSTRACTS
**of the 20-th V.A. Fock Meeting on Theoretical,
Quantum and Computational Chemistry**

A.L. Tchougréeff - Editor

Velikiy Novgorod

2024

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Тезисы 20-й конференции им. В. А. Фока
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Под редакцией А. Л. Чугреева.

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Tentative Schedule

"Life is richer than whatever scheme."

Monday August, 26th - Friday August, 30th

Time	Mon	Tue	Wed	Thu	Fri
10.00-11.00	Arrivals and Registration	Evarestov L 2437	Kvashnin L 2442	Zakharov L 2443	Tchougreeff L 2462
11.00-11.30		Coffee break			
11.30-12.00		Pomogaeva O 2448	Turchenko O 2460	Raenko O 2461	Demin O 2452
12.00-14.00	Opening 13:45	Lunch			General Discussion and Closing
14.00-15.00	Ruelle L 2435	Sabirov L 2440		Bezrukov L 2445	
15.00-15.30	Coffee break		Boat trip	Coffee break	
15.30-16.00	Yuldasheva O 2438	Domnin O 2450		Sabirov O 2463	
16.00-16.30	Голованова O 2441	Prosnyak O 2453		Luscheev O 2464	
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17.00-17.30					Departures
17.45-18.15					
18.15-20.00	Welcome Party		Conference Dinner		

20-th Session of the V.A. Fock Meeting on Theoretical, Quantum and Computational Chemistry

Invited and Plenary Lectures

2435

Calculations of a nanographene (coronene) Ni-SAC (single atom catalyst) for hydrogenation reactions.

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SACs have been in the last years widely investigated in various catalytic reactions [1] because they have several advantages. (1) In SACs, the utilization of atomic active center atoms improves reactivity respect to an atomic cluster, due to its high dispersion. (2) Similar to homogeneous catalysis, SACs have the characteristics of maximum atomic utility efficiency and a well-designed catalytic center to ensure high catalytic performance. Furthermore, the interaction at the active center-support interface of SACs can be tuned by changing the electronic properties in nano-supports, leading to a catalyst with adaptive chemical reactivity. A computational study of a Ni atom in a coronene (Cor) molecule (Ni-Cor), as a model of a single-atom catalyst (SAC) with nanographene like nano-support, was carried out using a DFT. The electronic metal-support interaction (EMSI) has been used as bridge between theoretical electronic study and the design and synthesis of heterogenous catalysts. The adsorption energy results of Ni on pristine Cor are similar to those reported for extended graphene [2]. Ni-Cor adsorption is preferred at edge sites and electron transfer from Ni to Cor occurs. The location of the HOMO density in Ni-Cor determines the orientation of the H₂ molecule in the coronene structure. Good correlations were obtained between the H₂ activation energies and charge on Ni atom. Calculations using DFT and EH (effective Hamiltonian) shown that a substitution of a H atom of Cor by an attractor electron groups (X = O, Cl, and NO₂) improved activation of the H₂ molecule. Then, the interaction of ethene with those hydrogenated sites (H₂-Ni-Cor-X) resulted in its hydrogenation to ethane. These theoretical findings suggest that Ni-Cor could be used for hydrogen storage because of adsorption energies (1.24-1.03 eV) and also for catalytic hydrogenation of hydrocarbons; for example, hydrogenation of olefines and CO₂.

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Electronic and phonon states in the helical Brillouin zone using the example of chalcogen chains and nanorods

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Modern nano-synthesis methods make it possible to create atomic chains. Helical chains of sulfur [1], selenium [2] and tellurium [3] atoms placed in carbon nanotubes have recently been synthesized. Such objects have unique electronic and optical properties. As is known, crystalline tellurium and selenium can be considered as an ensemble of atomic helices of symmetry 31, interconnected by van der Waals forces (i.e. forming nanorods). However, the free atomic helix of chalcogens even their nanorods in the general case has a symmetry different from the crystallographic one. Moreover, for such objects a more natural description is based on line symmetry groups [4]. Accordingly, the description of the electronic or phonon states of helical nanoobjects is carried out within the framework of the helical Brillouin zone [5]. The classification of states in translational and helical Brillouin zones is different as the corresponding intervals of wave vector change are $(-\pi/a, \pi/a]$ and $(-\pi/f, \pi/f]$ respectively (here f is partial translation). This makes it possible to consider the continuous evolution of states under both axial and torsional deformations [6].

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The authors appreciate the assistance of Saint Petersburg State University Computer Center in high-performance computing.

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Information entropy in the theory of chemical reactions

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Chemical reaction is usually represented as a transformation of one molecular ensemble into another one, and information entropy is used for quantitative describing changes in the molecular complexity. The information entropy of chemical reaction is introduced as the difference between the information entropies of the ensembles of products and reactants [1, 2]. We have deduced that the information entropy of molecular ensemble depends on the information entropies of individual molecules and cooperative entropy, an emergent parameter that reflects uniting the molecules into the ensemble [1]. Accounting this parameter defines the peculiarities of calculating the information entropy for interdependent chemical reactions. We have derived a general formula that connects the information entropy of the complex chemical process with the parameters of its elementary stages and demonstrated its work on typical examples of successive, parallel, and conjugated chemical reactions. Notably, the view of the derived formula differs from the equations used when Hess' law is applied to the thermodynamic parameters of interdependent reactions. The only case when the Hess' law has the same analytical expression for both information-entropy and thermodynamic parameters is the isomegetic set of chemical reactions, viz. the system of the successive reactions, in which the size of the molecular ensemble remains constant [3].

The authors acknowledge financial support from Russian Science Foundation, grant number 22-13-20095.

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Graphene oxide. Promising platform for electronic and optical applications. An overview of recent progress

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Graphene oxide, a derivative of graphene, is a highly versatile and promising material with a wide range of potential applications in various industries. Its unique structure, which consists of a single layer of carbon atoms arranged in a two-dimensional honeycomb lattice, combined with oxygen-containing functional groups, gives graphene oxide distinctive properties that differentiate it from its pure form. Graphene oxide can also be used as a component in water treatment to adsorb pollutants. The synthesis of graphene oxide typically involves the oxidation of graphite flakes using strong oxidizing agents such as sulfuric acid and potassium permanganate. This process introduces oxygen-containing functional groups (such as hydroxyl, epoxy, and carboxyl groups) onto the graphene sheets, leading to the formation of a layered structure with sp^2 and sp^3 hybridized carbon atoms. Here, I present an overview of the study in atomic structure, synthesis, possible modifications, and applications of graphene oxide and reduced graphene oxide in optoelectronic devices, including our recent results in this field. According to this topic the following publications have been released:

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Principles of relativistic molecular dynamics in condensed matter physics

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A method is proposed for studying the dynamics of systems of interacting atoms in terms of an auxiliary field, which in the state of rest of the atoms is equivalent to given interatomic potentials, and in the dynamic mode is a classical relativistic field. Within the framework of the auxiliary field concept, the following results were obtained.

- It has been established that for central static interatomic potentials that admit a Fourier transform, the auxiliary field is a superposition of elementary auxiliary fields, each of which satisfies equations of the Klein-Fock-Gordon type with complex mass parameters [1,2].
 - It has been proven that the elementary parameters are uniquely determined by the singular points of the Fourier transform of the static interatomic potential on the complex plane of the modulus of the wave vector [2,3]. • A variational formulation of the problem of the dynamics of a system consisting of relativistic atoms and the relativistic auxiliary field created by them is proposed [1].
 - The form of the action functional was established and a complete system of equations for the dynamics of atoms and auxiliary fields in two forms was derived [1,2].
1. The first form contains equations for the evolution of elementary auxiliary fields and atomic dynamics. It has been shown that signs of thermodynamic behavior are characteristic equally for both many-particle and few-particle systems [3,4].
 2. The second form of the system dynamics equations is a closed functional-differential equation of retarded type for the microscopic distribution function of atoms.
- The relativistic effect of interaction delay leads to the phenomenon of heredity, since the solution to the Cauchy problem depends not only on the initial conditions, but also on the prehistory of the system.

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Modeling of matrix isolated systems.

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The report is devoted to a description of our group's research in the field of modeling matrix-isolated atoms and diatomic systems. At the beginning of the report, various objects are presented that are objects of study using the matrix isolation technique. Methods for calculating the internal energy of a system are then presented. Since the object being studied is systems with predominantly van der Waals interactions, various versions of the method of diatomic fragments in a molecule are an effective semi-empirical technique that allows one to obtain correct quantitative estimates. Next, we discuss quantum chemistry methods that make it possible to obtain these curves at a good level of accuracy. The contributions of many-particle interactions and methods for taking into account the energy of zero-point oscillations are discussed. The option of modifying the matrix-matrix interaction potentials is considered, which allows us to move on to quantitative modeling of the interaction of free energies of the crystalline body.

The main achievement of the group is a computational technique that makes it possible to determine the number of thermodynamically stable capture sites and their geometry. The method is based on thermodynamic analysis of a large canonical ensemble using "free energy"- "number of atoms" diagrams. Several examples of determining stable sites are shown, and the influence of matrix creation conditions on the relative amounts of populated sites is discussed. Using model Lennard-Jones potentials, an analysis of possible sites was carried out in a wide range of potential parameters.

The next part of the report is devoted to modeling various spectroscopic properties of matrix-isolated systems. Raman spectroscopy, electron absorption spectroscopy, EPR spectroscopy. Methods for calculating spectrum parameters and their shifts relative to gas-phase systems are shown, and how these data are used to validate the results obtained for determining the number of stable sites is shown. The report then discusses the description of dynamic processes of atomic migration in noble gas matrices. The calculation methods we developed, being equipped with an apparatus for searching for transition states, made it possible to explain a number of barriers observed in experiment.

Finally, a description of some interesting unsolved problems in this area is presented.

DFT study of diamane-like structures based on twisted bilayers

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Passivation of AA- or AB-stacked bilayer graphene outer sides by hydrogen or fluorine atoms leads to interlayer bonds formation with following transformation from layered to 2D fully sp³-hybridized carbon structures named as “Diamane” [1]. In 2020, genuine diamane was obtained experimentally by fluorination [2]. This has increased interest in the study of diamanes and diamane-like structures. This material has been reported to possess a tunable bandgap, excellent heat transfer ability, ultralow friction, and high natural frequency, which can be a potential asset for cutting-edge technological applications. Properties of diamanes depend significantly on the type of coverage as well as on the type of parent bilayer. One of the most interesting modifications is the use of twisted bilayers as a base for diamanes [3]. This leads to the formation of a significantly different structure, which affects the properties. The results of DFT studies of the stability and properties of diamanes based on twisted bilayers depending on the type of functionalization will be presented.

The calculations were performed using the resources provided by the Joint Supercomputer Center of the Russian Academy of Sciences. This research was supported by Russian Science Foundation № 24-22-00444, <https://rscf.ru/project/24-22-00444/>.

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Towards 100-th Anniversary of Quantum Mechanics

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In 1925 by seminal papers [1-3] on matrix mechanics accompanied in 1926 by [4] on wave mechanics and followed by [5] gave birth to the quantum mechanics as we know it. Immediately after that, its *wave* (Schrödinger) form heavily relying on the *wave function* ψ has been applied to chemistry in [6] giving birth to *quantum chemistry*. Since then, the development was extremely intense so that some important details disappeared from studies curricula, particularly from those of chemistry students. Specifically, the *principle of superposition* of the wave functions is not sufficiently highlighted, whereas it is the key difference from the classical picture – it is responsible for the non-Kolmogorovian character of the quantum probability with its fundamentally important consequences: the covalency, “resonance” etc. These topics remain points of discussion until now, particularly on the discipline borders, e.g. between quantum theory and crystallography. In the present lecture we address and try to clarify these issues. Also the relation of the quantum measurement theory and Blokhintsev’s (ensemble) interpretation [7] to chemistry are briefly discussed.

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Molecular mechanism of synergistic effect of rifampicin and drug FS-1 on drug-resistant tuberculosis mycobacteria when administered together.

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Rifampicin DNA-dependent RNA polymerase resistant Mycobacterium tuberculosis In vivo experiments have established the effect of returning sensitivity to rifampicin of resistant Mycobacterium tuberculosis if administered together with the drug FS-1. The experimental results clearly demonstrate the synergistic effect of rifampicin and FS-1. The drug FS-1 can be classified as a nanostructured drug capable of selectively delivering active complexes to the bacterial target, disrupting vital processes and causing the death of the bacterial cell. Using the DFT/B3PW91/6-31G** approach has proposed a mechanism of synergistic effect on resistant Mycobacterium tuberculosis of rifampicin and drug FS-1 when administered together. The FS-1 drug is an ionic nanostructured complex containing α -dextrin nanocomplexes with a size of $\sim 40\text{-}48$ Å. The structures of the active centers of drug FS-1 in two dextrin rings had been calculated. The active centers of the $[\text{MgI3LiI2}]^+$ drug and LiI2 , taking into account the van der Waals interactions between the hydrogen atoms of the dextrin ring and the iodine and triiodide atoms, can be built into two dextrin rings. The active center of $[[\text{MgI3LiI3}]^+$ able form a complex with mutated triplets, causing the loss of sensitivity of mycobacteria to rifampicin. These complexes become the center of the nucleoprotein complex and bind both bacterial DNA and the $\text{Mg}^{2+}(\text{COO}^-)_3$, the active catalytic complex of DNA-dependent RNA polymerase (RNAP). The conditions responsible for vital processes in the bacterial cell are disrupted, resulting in cell lysis. The X-ray diffraction data, together with biochemical studies, explain the effect of rifampicin as a direct blockade of the RNAR β -loop region. Calculations have shown that rifampicin can form a stable complex with the active center $[\text{MgI3LiI3}]^+$, significantly enhancing the interaction of rifampicin with the RNAR β -loop region. The results of quantum-chemical studies have made it possible to explain the synergistic effect of rifampicin and drug FS-1 on resistant Mycobacterium tuberculosis when administered together by the ability of FS-1 to inhibit resistant Mycobacterium tuberculosis and enhance the effect of rifampicin on them.

Comparison of MP2 and DFT methods for calculating the structure and IR spectra using the example of magnesium compounds with amino acids.

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Structural and dynamic models of magnesium compounds with valine and glycine using the second-order Moeller-Plesset method (MP2) and the density functional method (DFT) (B3LYP functional) in the 6-31G(d) basis have been constructed using the standard quantum-chemical modelling software package GAMESS (US). The frequencies of normal vibrations in the harmonic approximation in the IR spectrum of the models of the presented compounds have been calculated. Magnesium(II) complexes with valine and glycine have been synthesised from aqueous solutions, the corresponding magnesium chloride salt and the amino acid. The calculated and experimental IR spectra of the synthesised compounds are presented and interpreted. Comparison of the calculated IR spectra with each other and with the spectra of the synthesised compounds is shown, and conclusions about their structure are drawn. A comparative characterisation of quantum-chemical calculation methods MP2 and DFT from the point of view of their application to the calculation of organometallic compounds is given. The obtained data on the coordination of magnesium ionic compounds with amino acids can help to reliably establish the structure of their little-studied complexes, and will also make it possible to improve methods for the synthesis of these complex compounds of a given composition and structure.

Molecular dissociation vs. heterolytic bond splitting in complexes of halogen molecules with Lewis bases.

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Formation of molecular and ion-pair complexes of di- and interhalogen molecules with nitrogen-containing Lewis bases (LB) is computationally studied at M06-2X/def2-TZVPD levels.

Interacting with strong Lewis bases, Cl₂ forms mostly heterolytic splitting products, while I₂, or ICl, predominantly forms molecular complexes in the gas phase [1,2]. Molecular σ complexes of halogen molecules with LBs are formed via so called halogen bonds and feature a linear arrangement. T-shaped π halogen complexes are similar in stability to van der Waals complexes, although their nature includes the presence of the charge transfer component, as in the case of σ complexes. Somewhat surprisingly, the larger electronegativity of chlorine results in easier heterolytic Cl-Cl bond breaking in Cl₂·LB with [Cl·LB]⁺·Cl⁻ formation. Reaction pathways in the gas phase indicate that in the case of Cl₂·LB complexes the activation energies for the heterolytic Cl-Cl bond splitting are lower than the activation energies of the homolytic splitting of Cl₂ molecules into chlorine radicals.

Solvation effects are studied by the SMD implicit solvent method. Results indicate that complexes of Cl₂ with all but the weakest Lewis bases undergo spontaneous ionization in the acetonitrile solution. Dissociation process of molecular σ complexes is found to be extremely sensitive to the solvent polarity of weakly polar ($\epsilon < 20$) solvents as well as to the donor ability of the LBs. A slight increase in the dielectric constant of the solvent can lead to the spontaneous ionization of the complex.

Thus, the control of the generation of cationic [LB·X·Solv]⁺ species is possible by varying the nature of LB, varying the nature of the solvent, and varying the nature of the halogen X. Molecular Cl₂ has the best tendency to form ionic species in polar solvents. On the other hand, such a weak LB as pyrazine, even in polar solvents, retains the molecular structure of the σ complex with halogen molecules. π complexes are found to be rather insensitive to solvent polarity.

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EZFF2 – software for global optimization of force-field potentials: development of force-field potentials for modeling multi-walled WSe₂ nanotubes.

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The study presents a novel force field designed to model the properties of multi-walled nanotubes (MWNTs) composed of tungsten diselenide (WSe₂), addressing the limitations of ab initio methods for such large systems. Traditional quantum chemistry methods are computationally prohibitive for simulating MWNTs with experimentally relevant diameters. Thus, force field approaches remain essential, although many existing force fields are not optimized for MWNTs.

Using a gradient-free optimization algorithm, specifically the PSO [1], we calibrated the force field parameters to accurately reflect the properties of WSe₂ MWNTs. Our methodology involved computer tuning the force field to match a training set of experimental data and ab initio calculations for bulk phases, nanolayers, and single-walled nanotubes. The GULP [2] program was utilized for both force-field fitting and subsequent molecular mechanics or molecular dynamics simulations.

The developed force field was validated through comparisons with quantum chemical calculations and experimental data. Results indicate that the new force field accurately reproduces the structural and energetic properties of WSe₂ nanotubes, including interlayer distances and stability metrics. Notably, the interlayer interactions in WSe₂ contribute more significantly to nanotube stability than in WS₂, attributed to the larger and more polarizable selenium atoms.

Key findings include the successful simulation of the structure and stability of chiral and achiral MWNTs with diameters approaching experimental values. The force field's ability to predict properties of multi-walled nanotubes with various chirality angles and interlayer distances shows good agreement with experimental measurements.

This work underscores the potential of optimized force fields in modeling complex nanomaterials and provides a robust tool for future studies of WSe₂ MWNTs. Our findings pave the way for further theoretical exploration and potential experimental validation, contributing to advancements in nanoelectronics and optoelectronics.

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Search for T, P-violating axionlike-particle-mediated interactions in molecules

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Molecules that include heavy element atoms can be used to search for "new" physics beyond the Standard Model through precision experiments aimed at detecting violations of spatial parity (P) and time reversal (T) symmetries in fundamental interactions. One of the most frequently discussed source of T and P violation in molecules is the electric dipole moment (EDM) of the electron [1]. Currently, a non-zero EDM of the electron has not been observed, but limitations on its value have been established. The most precise constraint to date was achieved by the JILA group in their experiment with hafnium monofluoride (HfF⁺) molecular cation [2]. Also, in the future experiment with barium monofluoride (BaF) molecule, a very close independent constraint is expected to be achieved [3]. Nevertheless, the T, P-violation of fundamental interactions in molecules can be induced not only by the electron's electric dipole moment (EDM), but also by the exchange of virtual axionlike particles between two electrons, as well as between the electron and the nucleus. In this study we considered this effect for HfF⁺ molecular cation and BaF molecule. In the case of electron-nuclear interaction, the calculations were performed with taking into account the finite size of the nucleus. Using the calculated molecular parameters of the considered interactions, we established constraints on the products of interaction coupling constants corresponding to current sensitivity of experiment with HfF⁺ molecular cation [2], as well as to expected sensitivity of the future experiment with the BaF molecule [3]. The obtained results were published in papers [4] and [5]. In addition, new results on the study of parity violation effects not presented in these papers will be discussed.

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The Molecular Parameter Characterizing Nuclear-spin-dependent Interactions in the Silicon Monoxide Cation $^{29}\text{Si}^{16}\text{O}^+$

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The study of diatomic molecules provides a powerful test of the Standard Model in the sector of weak interactions and opens avenues for discovering new physics [1]. These effects are manifested as nuclear-spin-dependent parity-violating effects localized within nuclei with nonzero spin. Notable results include the detection of parity-violating effects in the atom ^{133}Cs [2] and in the molecule $^{138}\text{Ba}^{19}\text{F}$ (a restriction established in the ^{19}F nucleus) [3]. Currently, an experiment is in the preparatory stage [4]. In this experiment, the $^{29}\text{Si}^{16}\text{O}^+$ cation has been chosen as the studied system, primarily due to the presence of degenerate rotational levels of opposite parity in terms of energy [5, 6].

In the present work, within the framework of fully relativistic descriptions of many-electron systems, the electronic molecular parameter characterizing parity-violating interactions in the $^{29}\text{Si}^{16}\text{O}^+$ cation, necessary for the interpretation of the experiment [4], was calculated. The result features a detailed description of various contributions and their uncertainties related to variations in the basis sets of single-electron wave functions, the number and degree of electron correlation, as well as considering other sources of calculation errors.

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Next-generation semi-empirical method for modeling of metal-organic frameworks: present developments

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Metal-organic frameworks (MOFs) are a relatively new and actively studied class of materials that attract scientific attention due to their high adsorption capacities, wide range of pore sizes (5 – 30 Å), and synthetic availability. Current and prospective use cases for MOFs include transportation and storage of gases, catalysis, as well as optical and magnetic sensing. Experimental research of MOFs is however hindered both by the vastness of the space of such compounds and by the lack of sufficiently fast and reliable computational methods. Provided in the present work are preliminary results obtained with $\Sigma H\Theta\Omega$, an in-development semiempirical software package created with the aim of performing high-throughput quantum chemical calculations on MOF structures. The current main focus of the work is correct prediction of ground state spin and LS-HS energy gaps for transition metal ions in MOFs. The accuracy of the method is tested against available experimental data for MOFs and simple MOF-like systems: (Mn,Fe,Co,Ni)NCN, (Fe,Co,Ni)(HNCN)₂, (Fe,Co,Ni)MOF-74, FeBDC, FeBDC(pyz), FeBTC; with results being sufficiently accurate for proof of concept computations. Computational efficiency of the $\Sigma H\Theta\Omega$ package is determined to be $O(N^{1.33})$ wrt AO basis size, and results from a rational decomposition of the electronic system into justified electronic subsystems.

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A DFT study of polarizability of $(C_{60})_n$ nano-aggregates: molecular and periodic models

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The polarizability increase, called exaltation of polarizability is typical for oligomers $(C_{60})_n$, in which the C_{60} units are covalently bonded with cyclobutane moieties. The exaltation comprises the superadditive polarizability growth with the number of the fullerene units in the structure [1]. We compare the DFT-computed polarizability, obtained for molecules $(C_{60})_n$, and periodic model of quasi-1D covalently-bonded fullerene chains. We found that the increment of the $(C_{60})_n$ mean polarizability growth (95.88 cubic Angstroms for $n = 6$) approaches the value, obtained for the periodic model (97.49 cubic Angstroms) [2]. Site-specific analysis of polarizability within the molecular model is also discussed [3].

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АЛГОРИТМ ПОИСКА ПЕРЕХОДНОГО СОСТОЯНИЯ С УЧЁТОМ ХИМИЧЕСКОЙ ИНТУИЦИИ

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Квантовохимический расчет кинетики химической реакции невозможен без моделирования её переходного состояния (ПС), в частности, оптимизации его геометрии. Существующие алгоритмы поиска ПС [1] решают задачу математически и не учитывают химическую природу целевого ПС (разрывающиеся и образующиеся связи), поэтому от исследователя требуется много опыта и времени, чтобы вручную направить оптимизацию в сторону искомой геометрии. В данной работе предложен и реализован метод оптимизации ПС, который использует дополнительную информацию о его химической природе, то есть задействованных связях и направлениях движения (разрыв/образование). Направление шага оптимизации рассчитывается из вектора сил и предполагаемого направления движения от реагентов к продуктам: сила разбивается на 2 компоненты, первая из которых расслабляет геометрию, а вторая отвечает за перемещение по реакционному пути, и смещение на каждом шаге оптимизации пропорционально первой, и, в обратном направлении, второй [2]. Предполагаемое направление реакции может быть взято из графового представления реакции. Тестирование на разнообразных реакциях показало, что этот метод позволяет систематически находить целевые ПС. Метод успешно локализует ряд ПС, на которых стандартные методы из Gaussian и ORCA не сходятся. Отдельным достоинством нового метода является отсутствие необходимости в вычислительно затратном расчете Гессиана, который требуется стандартным алгоритмам.

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The influence of the DFT method and the dispersion correction models in ONIOM methodology on the calculation of the activation energy of the process of butadiene polymerization on a neodymium-based Ziegler-Natta catalyst.

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In this work, using the double layer ONIOM methodology, we simulated the stages of initiation and growth of the polymer chain during the polymerization of butadiene on a neodymium-based Ziegler-Natta catalyst.

The DFT methods B3LYP and PBE0 in combination with the def2-TZVP atomic basis set were used as high-level methods in ONIOM. Grimme's semi-empirical XTB1 method was used as a low-level method. Optimization of geometric parameters was carried out taking into account the influence of the solvent (hexane) in the ALPB continuum model. All calculations were performed with full optimization of geometric parameters without any symmetry restrictions. All found transition states had one imaginary mode, which indicated the presence of a first-order saddle point. To establish the correspondence of the found saddle point to the transition state of the reaction under consideration, the “descents” were calculated according to the procedure IRC - following the internal coordinate of the reaction.

In our previous work [1], the mechanism of butadiene polymerization on a neodymium-containing Ziegler-Natta catalyst was studied in detail. The polymerization activation energy of 61 kJ/mol was found to be slightly higher than the experimentally determined values of this parameter. In the present work, the influence of a high-level method and a model of taking into account dispersion interactions on the quality of calculation of activation parameters of the polymerization reaction was studied. Experimental activation energy for the polymerization of dienes in the presence of Ziegler-Natta catalysts is in the range of 30–60 kJ/mol, but neodymium-based catalysts have an activation energy somewhat closer to the lower limit of this range. For comparison, semi-empirical Grimme models D3 and D4 were used.

It has been established that the both models reveal within the B3LYP method the activation energy practically the same, while within the PBE0 method it decreases to 41 kJ/mol. Thus, using the PBE0 as a high-level method within the ONIOM methodology and taking into account dispersion interactions within the D4 model leads to results in much better agreement with experimental data.

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Structure and Thermodynamic Properties of Adducts Based on Cucurbit[6]uril and Fe(III)/Fe(II) Aqua Complexes: a DFT Examination.

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In this work, successive stages of incorporation of Fe(III/II) aqua ions into the CB[6] cavity from the bulk of aqueous solution to the state of inclusion were studied. The structures of hydrated Fe(III/II) ions were represented by the aqua complex $[\text{Fe}(\text{H}_2\text{O})_6]^{3+/2+} \cdot 12\text{H}_2\text{O}$. For CB[6] in solution, four H₂O molecules were taken into account inside the cavity and six molecules on one of the two oxygen portals, on which the entry of ions into the cavity was studied. Possible stable structures of adducts with different types of Fe(III/II) aqua complex interactions with CB[6] were obtained, which differ in the geometry and composition of the hydrate environment of the ions.

The resulting structures of the adducts correspond to the following states:

1. interaction of water molecules of the second coordination sphere of the aquacomplex with the portal oxygen atoms through hydrogen bonds;
2. interaction through the hydrogen bonds of the water molecules of the first coordination sphere with portal oxygen atoms and water molecules in the CB[6] cavity;
3. formation of one Fe-O bond with the portal oxygen atom CB[6];
4. formation of two Fe-O bonds with the portal CB[6] atoms and
5. the final stage of formation of the inclusion compound.

For the above sequence of stages of Fe(III/II) aqua ions inclusion into the CB[6] cavity, the thermodynamic parameters were calculated. It has been found that the formation of an adduct, in which water molecules of the first coordination sphere of aqua complexes interact with portal oxygen atoms, is most preferable under standard conditions, and the entropy factor makes it possible for the reactions to proceed, whereas the reactions of adduct formation themselves are endothermic. The formation of an adduct in which there is one Fe-O(CB[6]) bond under standard conditions is beneficial only for Fe(II) aqua complexes, and for Fe(III) complexes, ΔG_{298}^0 of the reaction of formation of such a structure has a small positive value. The formation of structures with two Fe-O(CB[6]) bonds under standard conditions is unfavorable in both cases. The formation of inclusion compounds $[\text{Fe}(\text{H}_2\text{O})_4]^{3+/2+} @ \text{CB}[6]$ is also unfavorable. However, given the significant contribution of entropy, it was found that the formation of the compound $[\text{Fe}(\text{H}_2\text{O})_4]^{2+} @ \text{CB}[6]$ becomes possible at a temperature of $\sim 93^\circ\text{C}$.

Additionally, the standard redox potentials of the half-reaction $\text{Fe}^{3+}(\text{aq}) + \text{e} = \text{Fe}^{2+}(\text{aq})$ were calculated. It has been found that the formation of adducts with a stronger interaction between the aqua complex and CB[6] leads to an increase a redox potential and consequently the greater stability of Fe(II)-CB[6] complexes in an aqueous solution, and the maximum stability is manifested for the Fe(II) included in the CB[6] cavity.

Dynamic electric and magnetic polarizability of Pt-conjugated structures

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Negative refractive index metamaterials require simultaneously negative electric permittivity and magnetic permeability, as was firstly proposed by Veselago in 1968. Because of the lack of negative magnetic response in nature materials, negative refractive index may only occur in artificially constructed materials. The use of functional molecules in the constructing metamaterials represents an alternative approach to acquire the negative refractive metamaterials. One of the strategies to obtain negative electric and magnetic responses involves the use of conductive materials with antennae and capacitor elements [1]. According to this strategy, in this work molecular conjugated chains containing Pt-fragments have been considered as candidates for negative refraction index metamaterials components. The presence of Pt-fragment reduces the molecular symmetry, resulting in magnetically allowed dipole transitions necessary to achieve a negative magnetic response. The dynamic electric and magnetic polarizabilities of Pt-containing conjugated chains have been calculated using analytical expression. The analytical expression requires vertical excitation energy, electric and magnetic dipole transition moments, static electric and magnetic polarizabilities calculations. All calculations were obtained at the density functional level of theory using cam-b3lyp functional in combination with LanL2DZ basis set. The 15 electronic states were directly included to obtain dynamic polarizability. The electronic transition $S_0 \rightarrow S_3$ of the molecular systems considered characterized by simultaneously large electric and magnetic transition dipole moments. At this transition, the negative electric and magnetic dynamic polarizabilities are observed.

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Приближённое уравнение состояния жидкости с двойным экспоненциальным потенциалом в единичном секторе области устойчивости

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Исследование простой жидкости с двойным экспоненциальным потенциалом на основе интегрального представления для свободной энергии системы частиц, взаимодействующих посредством потенциалов, допускающих разложение в ряд Фурье [1], приводит чрезвычайно громоздким выражениям для термодинамических функций [2]. Показано, что трудности, возникающие при описании равновесных теплофизических свойств жидкостей, могут быть преодолены в рамках подхода, позволяющего упростить аналитические расчёты свойств в единичном секторе области устойчивости потенциала взаимодействия. В единичном секторе безразмерные отношения амплитудных параметров и параметров крутизны потенциала близки к единице. Результаты расчетов, выполненных с помощью приближённого уравнения состояния, сопоставляются с экспериментальными данными и результатами соответствующих численных расчётов. Предложенный подход может быть использован для исследования жидкостей с двойным потенциалом Юкавы.

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