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Tentative Schedule

Monday September, 4th - Friday September, 8th

Time	Mon	Tue	Wed	Thu	Fri	
9.00-10.00	Arrivals	Tupitsyn	Zakharov	Sabirov	Kolobov	
		L 2360	L 2374	L 2419	L 2409	
Raenko		Leibin	Stepanov	Levina		
O 2370		O 2396	O 2418	O 2427		
10.00-10.30						
10.30-11.00		Coffee break				
11.00-12.00						
		Shakhova	Kozlov	Tchougreeff	Panova	
12.00-12.30						
		L 2362	L 2375	L 2391	L 2388	
12.30-14.00	Registration	Jalolov	Mezentsev	Starostin	General discussion and Closing	
		O 2372	O 2415	O 2422		
12.30-14.00	Opening 13:45	Lunch				
14.00-15.00	Evarestov	Kvashnin	Bezrukov	Medvedev	Departures	
	L 2355	L 2364	L 2389	L 2393		
15.00-15.30	Domnin			Posters		
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15.30-16.00	Coffee break		Coffee break			
16.00-16.30	Porsev	Bokarev				
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	O 2365	O 2383				
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18.00-20.00	Welcome Party		Conference Dinner			

Symmetry and quantum-chemical calculations of one-periodic systems.

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All the calculations of monoperiodic (1D) nanostructures (nanohelicenes, nanotwistans, nanotubes) are performed with geometry optimization using hybrid density functional PBE0, HSE06, LCAO basis set and computer code CRYSTAL17 [1]. Nanohelicenes are helically periodic carbon sp^2 nanostructures. Calculations [2-5] demonstrate that nanohelicene electronic and magnetic properties essentially depend on the variations in the shape (hexagonal or trigonal), edge termination (zig-zag or arm-chair), ribbon width or inner shaft lead. Polytwistane is helically periodic sp^3 benzene-derived carbon nanostructure and was found to be the most stable nanothread. In [6] the electronic band gap and mechanical properties of polytwistane were calculated. The symmetry of single wall (SW) and multiwall (MW) nanotubes is investigated in [7-8]. The results of first principle DFT calculations of inorganic achiral nanotubes are summarized in [9] for different crystals (binary and ternary oxides, transition metal chalcogenides). We studied in [10] single-wall pristine and Janus nanotubes based on post-transition metal chalcogenides and in [11] the results of our quantum chemical simulation of DW nanotubes based on Ga and In chalcogenides are discussed.

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References

- [1] R. Dovesi, A. Erba, R. Orlando, C.M. Zicovich-Wilson, B. Civalleri, L. Maschio, M. Rérat, S. Casassa, J. Baima, S. Salustro, B. Kirtman. *WIREs Comput. Mol. Sci.* 8 (2018) e1360.
- [2] V.V. Porsev, A.V. Bandura, S.I. Lukyanov, R.A. Evarestov, *Carbon* 152 (2019) 755.
- [3] V.V. Porsev, R.A. Evarestov. *Comp. Mat. Sci.* 203 (2022) 111063.
- [4] V.V. Porsev, R.A. Evarestov. *Comp. Mat. Sci.* 213 (2022) 111642.
- [5] R.Evarestov, V.Porsev, *Nanomaterials*, 13 (2023), 415
- [6] A.V.Domnin, V.V.Porsev, R.A.Evarestov, *Comp. Mat. Sci.* 214 (2022) 111704
- [7] M. Damnjanović, I. Milošević. "Line Groups in Physics. Theory and Applications to Nanotubes and Polymers" *Lect. Notes in Phys.*, 801. Berlin: Springer, 2010.
- [8] E.Dobardzić, I. Milošević, T.Vuković, B.Nicolić, M. Damnjanović, *Eur. Phys. J. B* 34, 409 (2003)
- [9] R.A. Evarestov, *Theoretical Modeling of Inorganic Nanostructures. Symmetry and Ab Initio Calculations of Nanolayers, Nanotubes and Nanowires*, second ed., Springer, Berlin - Heidelberg, 2020
- [10] A.V.Bandura, D.D.Kuruch, V.V.Porsev, R A.Evarestov *Physica E* 147, 115611 (2023)
- [11] A.V.Bandura, D.D.Kuruch, S.I.Lukyanov, R A.Evarestov *Russian Journal of Inorganic Chemistry*, 67, 1795 (2022)

Specific features of the electronic structure of super-heavy elements of the 8-th period

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In this work, the results of the electronic-structure calculations for a number of super-heavy elements (SHE) of the 8th period with atomic numbers $Z = 119-170$ are presented [1,2]. Various chemical properties of these elements such as ionization potentials, electron affinities, root mean square radii and widths of the electron-density distribution, electron localization functions (RELf) and Shannon entropy of valence shells are calculated. Based on the obtained results, the role of the relativistic and QED effects on the electronic structures of SHEs was analyzed, and conclusions about the extension of the Mendeleev's periodic law to the region of SHEs were drawn. However, the electronic structure of SHEs is unique in several aspects:

(i) Spin-orbital splitting of valence p-shells reaches up about 10 eV in Og ($Z=118$) and about 400 eV in element with atomic number $Z=165$. As a result, due to the strong relativistic contraction, the radial distribution of the electron density of the valence $p_{1/2}$ -shell starts to overlap with the outer core shells and RELf is close to 0.5 in the valence region. In Ref. [3], this effect in Og was interpreted as smearing out the valence electron density distribution and its approaching to the case of the homogeneous electron gas. A similar effect is observed for the strongly-bound core shells in element with $Z = 165$. In this case, the electron densities of the 1s- and $2p_{1/2}$ - shells begin to overlap and the RELf value becomes close to 0.5. However, this behavior of the electron density in the core region cannot indicate that it is close to a homogeneous electron gas.

(ii) Starting from the $Z = 125$ element, the 5g-shell with the large angular momentum ($l = 4$) is occupied with electrons. The effective radial potential for the 5g-electron, which includes a large centrifugal repulsive term, has two potential wells which lead to the so-called orbital collapse. In this case, the problem of understanding the meaning of the numerical solutions, and the physical origin of the transition between these two wells arises. The orbital collapse is also observed for the f-electrons in rare-earth elements [4].

References

- [1] M. Y. Kaygorodov, L. V. Skripnikov, I. I. Tupitsyn, E. Eliav, Y. S. Kozhedub et al., Phys. Rev. A, 104, 012819 (2021).
- [2] I. I. Tupitsyn, A. V. Malyshev, D. A. Glazov, M. Y. Kaygorodov, Y. S. Kozhedub, et al., Opt. Spectr. 129, 1038 (2021).
- [3] P. Jerabek, B. Schuetrumpf, P. Schwerdtfeger, and W. Nazarewicz, Phys. Rev. Lett. 120, 053001 (2018).
- [4] J.-R Connerade and R.C. Kamatak, Handbook on the Physics and Chemistry of Rare Earths, v. 28, p. 1 (2000).

Compound-tunable embedding potential method for precise electronic-structure modeling: ytterbium halides

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Theoretical studies of crystals containing lanthanides are limited by the current capabilities of modern quantum chemical methods for describing periodic structures: density functional theory, scalar-relativistic versions of "soft" semi-local pseudopotentials and atomic basis sets of moderate size. Precise theoretical research of such structures could become a powerful tool that allows one to solve many fundamental and applied problems. In this research, the electronic structure of ytterbium halide crystals YbF_2 , YbF_3 , YbCl_2 , YbCl_3 , are studied. For investigating such structures the combined method is applied. It contains "compound-tunable pseudopotentials" (CTPP) and "compound-tunable embedding potentials" (CTEP) [1-3]. The investigation of a crystal by the CTEP method is carried out in three stages. First, a perfect crystal with periodic boundary conditions is calculated by the CRYSTAL code. Second, short-range large-core CTPP is built for the chosen crystal by using the CRYSTAL code as well. Third, cluster calculations of the crystal fragment are performed, and the long-range Coulomb potential of the environment is constructed as a part of CTEP. A crystal fragment of a "required minimal size" (minimal cluster include a heavy atom and its immediate environment) is cut out, within which the electron density must be reproduced with high accuracy. The atoms of the near environment of the crystal fragment are described by point charges and CTPPs ("pseudoatoms" below) to take into account the influence on a chosen fragment of the "whole crystal" excluding the atoms of the fragment. It is important to note that the relaxation of the crystal fragment environment is considered as negligible by appropriate choosing the fragment, and the whole system is generally electroneutral taking into account the pseudoatoms of the near environment. The crystal fragment built by the CTEP method using CTPP reproduces the electron density from periodic calculations in the vicinity of the Yb atom with the error less than 0.25%. In the framework of periodic calculations, the use of precise small-core PP and saturated basis sets is practically impossible. Consequently, the accuracy of such calculations is at the level of 0.1 eV for the energetic characteristics, which is insufficient for precise study of materials with lanthanide atoms. In turn, such a problem does not arise in cluster CTEP calculations, since both good basis sets and PPs are used, and the calculation errors associated with them are drastically reduced. This was shown in the framework of the analysis of the structural parameters of crystals and corresponding clusters.

1. Lomachuk Yu.V. et al. PCCP. 2020. 22. 17922-17931.
2. Maltsev D.A. et al. PRB. 2021. 103. 205105. 3. Shakhova V.M. et al. PCCP. 2022. 24. 19333-19345.

0D/2D heterostructures for photonics and sensors

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Recent development of 2D materials opens a new way for the fabrication of low-dimensional structures with desired properties via controllable way. The most promising materials for nanoelectronics devices in the near future are graphene and different heterostructures based on them. Thus, it is necessary to create mechanisms of controlled modification of graphene electronic and magnetic properties to expand the application of graphene. Previous studies showed that this can be done by various techniques, for example, by using different substrates, mechanical deformations, chemical functionalization, introducing of various defects in graphene structure, and formation of heterostructures based on graphene. By combining different two-dimensional (like graphene, BN) and quasi-two-dimensional materials (for example, TMD) layered structures with van der Waals interlayer interaction can be obtained. In such materials the properties of individual components can be not only preserved but also new unique features can appear. Here an overview of theoretical and experimental results of effective way of modifying of physical and chemical properties of 2D structures via organic compounds and inorganic 2D materials functionalization were presented [1-4]. Features of the atomic structure and physical and chemical properties in a pair with possible ways for tuning of magnetic properties and shift the absorption spectra toward the visible range of the wavelength was performed.

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[1] E. V. Sukhanova, D. G. Kvashnin, Z. I. Popov, *Nanoscale* 2020, 12, 23248.

[2] E. V. Sukhanova, Z. I. Popov, D. G. Kvashnin, *Jetp Lett.* 2020, 111, 627.

[3] M. Y. Lukianov, A. A. Rubekina, J. V. Bondareva, A. V. Sybachin, G. D. Diudbin, K. I. Maslakov, D. G. Kvashnin, O. G. Klimova-Korsmik, E. A. Shirshin, S. A. Evlashin, *Nanomaterials* 2023, 13, 1982.

[4] A. N. Toksumakov, G. A. Ermolaev, M. K. Tatmyshevskiy, Y. A. Klishin, A. S. Slavich, I. V. Begichev, D. Stosic, D. I. Yakubovsky, D. G. Kvashnin, A. A. Vyshnevyy, A. V. Arsenin, V. S. Volkov, D. A. Ghazaryan, *Commun Phys* 2023, 6, 1.

Principles of classical relativistic dynamics of interacting particles with applications to microscopic thermodynamics and kinetics

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A method is proposed for describing the dynamics of systems of interacting particles in terms of an auxiliary field, which in the static mode is equivalent to given interatomic potentials, and in the dynamic mode is a classical relativistic composite field. It has been established that for interatomic potentials that admit the Fourier transform, the auxiliary field is a composition of elementary fields that satisfy the Klein-Gordon equation with a certain spectrum of complex masses. The interaction between particles carried by the auxiliary field is nonlocal both in space variables and in time. The temporal non-locality is due to the dynamic nature of the auxiliary field and can be described in terms of functional-differential equations of retarded type. Due to the finiteness mass of the auxiliary field, the delay in interactions between particles can be arbitrarily large. A qualitative analysis of the dynamics of few-body and many-body systems with retarded interactions has been carried out, and non-statistical mechanisms for both the thermodynamic behavior of systems and synergistic effects has been established. In particular, a microscopic non-statistical mechanism for establishing thermodynamic equilibrium is proposed.

References

- [1] Zakharov, A.Y.; Zakharov, M.A. Microscopic Dynamic Mechanism of Irreversible Thermodynamic Equilibration of Crystals. *Quantum Rep.* 2021, 3, 724-730. <https://doi.org/10.3390/quantum3040045>
- [2] Zakharov, A.Y.; Zubkov, V.V. Field-Theoretical Representation of Interactions between Particles: Classical Relativistic Probability-Free Kinetic Theory. *Universe* 2022, 8, 281. <https://doi.org/10.3390/universe8050281>
- [3] Zakharov, A.Y. Field Form of the Dynamics of Classical Many- and Few-Body Systems: From Microscopic Dynamics to Kinetics, Thermodynamics and Synergetics. *Quantum Rep.* 2022, 4, 533-543. <https://doi.org/10.3390/quantum4040038>

Excitation of the ^{229}Th nucleus using the hole in inner electronic shells

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The ^{229}Th nucleus has a long-lived isomeric state A^* at 8.338(24) eV [Kraemer et al, Nature, **617**, 706 (2023)]. This state is connected to the ground state by an M1 transition. For a hydrogenlike Th ion in the 1s state the hyperfine structure splitting is about 0.7 eV. This means that the hyperfine interaction can mix the nuclear ground state with the isomeric state with a mixing coefficient β about 0.03. If the electron is suddenly removed from this system, the nucleus will be left in the mixed state. The probability to find the nucleus in the isomeric state A^* is equal to $\beta^2 \sim 10^{-3}$. For the 2s state the effect is roughly two orders of magnitude smaller. An atom with a hole in the ns shell with $n = 1$ or 2 is similar to the hydrogenlike atom, only the hole has a short lifetime τ . After the hole is filled, there is a non-zero probability $P^*(ns)$ to find the nucleus in the A^* state. We found that $P^*(1s) = 1\text{E-}5$ and $P^*(2s) = 2\text{E-}5$. The reason why the probability is higher for the 2s hole is the much longer lifetime. The lifetime of the isomeric nuclear state for the bare nucleus is expected to be of the order of 1000 seconds. In the neutral and singly charged thorium the lifetime is orders of magnitude smaller because of the internal conversion. In order to study nuclear isomeric state we need to place thorium ion in the crystal with the broad band gap where internal conversion is suppressed. One example of such a crystal is ThF_4 . Then we can produce the holes in thorium 2s shell by irradiating this crystal with 20 - 25 keV X-ray beam. This way one can produce 10^6 isomeric nuclei, or more per accumulation cycle of about 1000 sec. This opens new possibilities to study such properties of the isomeric state A^* , as its energy, charge radius, and the hyperfine constants. An accurate knowledge of the transition energy is crucial for making an optical clock on this transition. Other parameters are necessary to use this transition to search for "new physics", in particular, to study possible variation of the fundamental constants.

Conformational space of glycosyl cations

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Quantum chemistry plays the central role in elucidating the structures of glycosylation reaction intermediates (in particular, glycosyl cations), since common analytic methods usually cannot detect such short-living species under operando conditions. Naturally, starting geometries significantly affect the results of glycosyl cations optimization, so conformational searches are mandatory in order to obtain lowest-energy geometries.

Still, lowest-energy geometries tell us only part of the story. We show, how systematic analysis of glycosyl cation conformations – both low- and high-energy ones – allowed us to shed light on substitution effects and glycosyl cations' dynamics in glycosylation reactions involving neuraminic acid [1, 2] and arabinofuranose disaccharide Ara- β -(1 \rightarrow 2)-Ara.

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1. Panova M. V., Medvedev M. G., Orlova A. V., Kononov L. O. *ChemPhysChem*, 2022, 23, e202200017. 2. Panova M. V., Orlova A. V., Kononov L. O. *Russ. Chem. Bull.*, 2018, 67, 1573–1579.

Calculation of observables in coupled clusters methods

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This abstract is devoted to the description of problems in the calculation of observables in the method of coupled clusters. To date, one can often find statements in the literature that this method is the gold standard for calculating the energy of the ground state of molecular systems containing several tens of atoms.

The first part is devoted to a general overview of the fundamentals of the method and the current state of affairs. The problem of dimensional consistency, the introduction of an exponential ansatz, and the derivation of working equations of the method are discussed. The application of modern hot topics in the field of development of computational approaches is described: quantum computing and the use of ML techniques. The development of the method towards f_{12} and EOM implementations is shown, as well as the orbital localization technique to reduce the computational complexity of the problem.

The second part is devoted to the problem of calculating the properties of molecular systems. Since the initial construction of the coupled cluster method does not imply the calculation of the wave function, in practice, to calculate the properties, the linear response technique is used to obtain the density matrices of the required order. The main approaches to the calculation of these mathematical objects and their analysis are described.

In the last part presents the original results obtained in our scientific group. A method for calculating the working expressions for the arbitrary-order coupled cluster methods is shown for both the amplitudes of the excitation operator and the coefficients for calculating the single-particle density matrix. The procedure for numerical optimization of the calculation algorithm through the calculation of intermediate expressions is described. The use of a two-particle density matrix for the analysis of the completeness of the basis in the calculation of van der Waals systems is demonstrated.

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cartesius fort – object fortran library for representing chemistry and materials science objects. Recent developments

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Modeling structure and properties of molecules and materials based on their electronic structure is one of the principal consumers of computer resources (time, memory and storage). The known attempts to improve the efficiency of such a modeling stumble upon the enormous diversity of types of structures and behaviors. Even worse, this diversity is not reflected in the dominating paradigm of molecular/material modeling, which can be characterized as naïve monism: it is believed that everything must be calculated by the same, possibly most precise available theory. This, of course, leads to a deadlock. Truly scientific approach is based on a thorough analysis of physics governing the observed diversity. We followed this route and built a series of methods targeted upon specific classes of molecules/materials: inorganics with open d-shells, organics featuring local two-center bonds and conjugated π -systems. The approach is described in [1]. The experience gained through these studies led to a new vision of semi-empirism [3]: selecting the electronic wave function of a system as a product of observable electronic groups (chromophores) present in it. This requires a development of a library of objects representing different types of chromophores to be freely combinable to represent an arbitrary system so that its respective parts are modeled by the most efficient method suitable for the specific type of the chromophore and taking into account interactions between them. This is done within our project library Cartesius [4]. We developed a series of targeted numeric tools based on this library: LiquIon – a tool for modeling thermodynamical properties of ionic liquids [5] and adamas – a tool targeted on description of carbon allotropes [6] and providing their crystalline structures, relative energies and elastic properties. atoms – implements calculations of atomic properties in exponential bases [7]. GoGreenGo – local perturbations of periodic systems: chemisorption and point defects [8]. jakontos – Effective Hamiltonian Crystal Field for periodic systems with transition and rare-earth elements [9]. They available through the NetLaboratory system [2].

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References.

1. A.L. Tchougréeff. Hybrid Methods of Molecular Modeling. Springer, 2008.
2. NetLaboratory system. <https://netlab.cartesius.info/>
3. A.L. Tchougréeff. J. Struct. Chem., 48 (2007) S32.
4. Cartesius library. <https://cartesius.info/doxygen/index.html>.
5. I.V. Popov, A.L. Tchougréeff. Comp. Theor. Chem., 1116 (2017) 141.
6. I.V. Popov, V.V. Slavin, A.L. Tchougréeff, R. Dronskowski. PCCP, 21 (2019) 18138.
7. P. Reinhardt, I.V. Popov, A.L. Tchougréeff. IJQC, 121 (2021) e26687.
8. I.V. Popov, T.S. Kushnir, A.L. Tchougréeff. J. Comp. Chem., 42 (2021) 2352.
9. I. Popov, E. Plekhanov, A. Tchougréeff, E. Besley. Mol. Phys., 121 (2023) e2106905.

Building a digital twin of an ICP-CVD process

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Next-generation nanoelectronics requires development of new thermally and mechanically stable materials with relative permittivity (k) as close to 1 as possible. In June 2020, Hong et al. presented ICP-CVD-deposited amorphous boron nitride (a-BN) with very low k of 1.78 [1]. This a-BN also turned out to be thermally, chemically, and mechanically stable, and having high breakdown voltage, thus fulfilling all requirements for practical applications. A three-nanometer thick layer of this material was obtained by low-temperature remote inductively coupled plasma–chemical vapor deposition (ICP-CVD) with borazine as the precursor.

Two years later Lin et al. conducted seemingly identical synthesis, but obtained a compound with noticeably different properties [2]. When synthesis conditions were identical (based on the information in the article) to those of the Hong experiment, the boron to nitrogen ratio (B:N) was ~ 2.64 , whereas the B:N in the original article films was 1.0. To obtain the same B:N, Lin's team had to explicitly add nitrogen molecules to the gas flow.

In order to understand why supposedly equivalent conditions lead to different products, it is necessary to understand the process at the atomic level, which is not possible with current experimental techniques. As Richard Feynman famously quoted: "What I cannot create, I do not understand." Following this principle, we have constructed a digital twin of this system to comprehensively reconstruct the ICP-CVD process, encompassing all its intricate details and established the most likely reason for the discrepancy between Hong's and Lin's experiments.

1. Hong S., Lee C.-S., Lee M.-H., Lee Y., Ma K.Y., Kim G., Yoon S.I., Ihm K., Kim K.-J., Shin T.J., Kim S.W., Jeon E., Jeon H., Kim J.-Y., Lee H.-I., Lee Z., Antidormi A., Roche S., Chhowalla M., Shin H.-J., Shin H.S. Ultralow-dielectric-constant amorphous boron nitride // *Nature*. – 2020. – Vol. 582, № 7813. – P. 511–514. – DOI: 10.1038/s41586-020-2375-9.
2. Lin C., Hsu C., Huang W., Astié V., Cheng P., Lin Y., Hu W., Chen S., Lin H., Li M., Magyari Kope B., Yang C., Decams J., Lee T., Gui D., Wang H., Woon W., Lin P., Wu J., Lee J., Liao S.S., Cao M. Ultralow k Amorphous Boron Nitride Based on Hexagonal Ring Stacking Framework for 300 nm Silicon Technology Platform // *Advanced Materials Technologies*. – 2022. – Vol. 7, № 10. – P. 2200022. – DOI: 10.1002/admt.202200022.

Atomic and electronic structure of binary 3D semiconductors in the 2D limit

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When the thickness of a three-dimensional crystal is decreased to the limit of a few monolayers, surface effects start to play a dominant role. Surfaces of such semiconductor slabs possess a large number of dangling bonds. In addition, because of the different electronegativities of the constituent species, the opposite are polar. Polar surfaces are intrinsically unstable thanks to the divergence of the surface energy. Several mechanisms have been considered that may stabilize such surfaces, among which the formation of planar graphene-like structures was proposed as a stabilization mechanism for wurtzite structures, whereby the trigonal-planar configuration of the cations and anions minimizes the surface dipole moment. In this talk, we consider GaN and CdTe as two examples. Our calculations demonstrated that in a few monolayer limit the wurtzite phase of GaN becomes unstable and the materials transforms into a graphite-like flat and then into a 4|8 Haeckelite phase, in which the dipoles, existing in the wurtzite phase, disappear [1]. This phase is a direct-gap semiconductor, whose properties can be controlled by application of strain. A single monolayer becomes flat, also minimizing the surface dipoles. In CdTe, on the other hand, the electronegativity difference is much smaller and, while a monolayer partially flattens, it does not become fully flat. Consequently, the formation of a Haeckelite phase is not possible. At the same time, for a two monolayer thick slab, it becomes energetically favourable to swap atomic planes from the Cd-Te-Cd-Te stacking, to a symmetric Te-Cd-Cd-Te stacking, where the metal planes are sandwiched between two chalcogen planes [2]. The structure of this slab is very similar to a generic structure of layers in van der Waals solids, where typically one-to several atomic planes are encapsulated by chalcogen atomic planes (X-Mo-X, X-In-In-X, X-Sb-X-Sb-X being examples). Consequently, a van der Waals bulk CdTe crystal can be built, whose stability has been verified by calculations of phonon dispersion curves [3]. Implications from these results for engineering new materials are further discussed.

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1. Kolobov, A. V., Fons, P., Tominaga, J., Hyot, B., & Andre, B. (2016). Instability and spontaneous reconstruction of few-monolayer thick GaN graphitic structures. *Nano Letters*, 16(8), 4849-4856.
2. Kolobov, A. V., Kuznetsov, V. G., Fons, P., Saito, Y., Elets, D. I., & Hyot, B. (2021). Polymorphism of CdTe in the Few Monolayer Limit. *Physica Status Solidi (RRL)–Rapid Research Letters*, 15(11), 2100358.
3. Kuznetsov, V.G., Gavrikov A.A., & Kolobov A.V. (to be published) Bandgap Engineering in Ultimately Thin Slabs of CdTe with Different Layer Stacking

COMPUTATIONAL ASTROCHEMISTRY AND MATERIALS SCIENCE OF CARBON-RICH MOLECULES

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Fullerenes, polycyclic aromatic hydrocarbons and their derivatives are carbon-rich compounds, whose molecules are constructed with sp²-carbon atoms [1]. The latter means their richness with remarkably responsive pi electrons. This feature makes fullerenes and PAHs promising for diverse nanotechnology and materials science applications. Meanwhile, the title compounds are currently known as one of the most widespread and survivable molecules of interstellar media. Thus, there is a fundamental interest in studying their properties. In this talk, we discuss computational studies on carbon-rich compounds focusing on their molecular properties, especially dipole polarizability. The corresponding numerical estimates allows predicting efficiency of the fullerene-containing organic solar cells, screening endo-atoms of endofullerene-implemented qubits, abundances of carbon-rich compounds under laboratory and environmental (space) conditions [2, 3]. A part of the report deals with the reactivity of the interiors of the endofullerenes under high pressures that might lead to a novel, currently unknown compounds [4]. The results obtaining with molecular dynamics simulations and quantum chemical methods are compared. Quantum chemical techniques and models of polarizability used in computational chemistry of fullerenes and PAHs, such as additive schemes and site-specific analysis, are discussed [5]. In the report, we focus on the minimum-polarizability principle that allows studying chemical dynamics beyond the energy estimates. This allowed us predicting non-planar helicenes under space conditions [6], which were further identified as the main compounds formed in circumstellar envelopes of carbon stars. The found regularities are discussed in a tight conjunction with relevant experiments [2, 5, 7].

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References

1. Sabirov D.Sh., Osawa E. J. Chem. Inf. Model. 2015, 55, 1576.
2. Sabirov D.Sh. RSC Adv. 2014, 4, 44996 (review).
3. Sabirov D.Sh. Fullerene Nanotube Carbon Nanostruct. 2020, 28, 71 (review).
4. Sabirov D.Sh. J. Phys. Chem. C 2013, 117, 1178.
5. Sabirov D.Sh., Tukhbatullina A.A. Nanomaterials 2022, 12, 4404.
6. Sabirov D.Sh., Garipova R.R., Cataldo F. Mol. Astrophys. 2018, 12, 10.
7. Sabirov D.Sh., Tukhbatullina A.A., Shepelevich I.S. ACS Earth Space Chem. 2022, 6, 1 (review).

Development of force field potentials for modeling multi-walled WS₂ nanotubes

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Despite extensive experimental studies of multi-walled nanotubes based on transition metal chalcogenides, there are few works on their theoretical modeling. However, simulations of their properties are necessary for interpreting the observed properties of known nanomaterials and predicting the properties of nanosystems that have not yet been synthesized. Due to the high computational requirements, the ab initio methods of quantum chemistry cannot be used to simulate multi-walled nanotubes with diameters close to the experimental values. In this regard methods based on force fields, remain relevant. Unfortunately, most of existing force fields are not designed for modeling multi-walled nanotubes and should be optimized.

In this work, we present the results of applying a genetic algorithm to fit force fields intended for modeling the properties of WS₂-based multi-walled nanotubes. We applied NSGA-III [1], a multi-objective optimization algorithm, to tune force fields. It was used to explore the Pareto-optimal front of the force field parameters and select the best solutions according to different criteria. We have demonstrated the effectiveness of our method and shown that it can produce superior force fields compared to those obtained by other methods using the relatively simple potential models. The authors considered their experience in modeling multi-walled nanotubes based on MS₂ [2] and gallium monochalcogenides [3] when choosing the dependences of the contributions to the potential energy of the system.

The proposed procedure is linked to Gulp [4] program which can be used both for force -field fitting and molecular mechanics or molecular dynamic simulations. Training set includes experimental data, and results of ab initio calculations of bulk phases, nanolayers, and single-walled nanotubes. Several variants of the parameterization of the force field were obtained by us, which satisfactorily reproduce the properties of training systems. The finest parameters were selected by comparing the properties of double-walled nanotubes with small diameters calculated using ab initio methods and those obtained by molecular mechanics modeling. The finally selected force field was applied to simulate multi-walled nanotubes WS₂, and comparison of calculated results with experimental data shows good agreement.

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References

1. K. Deb, H. Jain, IEEE Transactions on Evolutionary Computation 2014, 18, 577-601.
2. A. V. Bandura, S. I. Lukyanov, D. D. Kuruch, R. A. Evarestov, Physica E 2020, 124, 114183
3. S. I. Lukyanov, A. V. Bandura, R. A. Evarestov, Physica E 2021, 133, 114779.
4. J. D. Gale, A. L. Rohl, Molec. Sim. 2003, 29 291-341.

First principles study of nanohelicenes using line symmetry groups

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Nanohelicenes [1] or graphene spirals are examples of helically periodic nanostructures, which can be considered as a generalization of the idea of polymeric $[\infty]$ helicene. It is known that variations in the shape (hexagonal or trigonal), edge termination (zig-zag or arm-chair), ribbon width or inner shaft lead to the manifestation of metallic or semiconductor properties in nanohelicenes, as well as ferromagnetic or antiferromagnetic ordering. The unique spring topology of such structures makes it possible to manipulate the electronic and magnetic properties by reversible mechanical strains. So far the properties of nanohelicenes under axial deformations have been studied, ignoring the importance of torsion strains. The study of the latter requires the use of the line symmetry groups [2] which can be written in two factorizations: the crystallographic one $L = TF$ (T is translation subgroup of L) and $L = ZP$ (Z includes screw axis rotations while P is point group). Moreover, using of line groups makes it possible to describe the symmetry of one-periodic structures having no translational periodicity but with helical one.

A general algorithm for ab initio modeling of helically periodic nanostructures was recently successively applied by us to nanohelicenes. Calculations were performed using CRYSTAL17 [3] computer code based on the atomic basis sets and using built-in possibility to take into account the helical symmetry operations of one-periodic systems. By this way it was shown in [4] that the true nanohelicenes symmetry groups differ from the traditionally accepted $L6_1$ or $L3_1$ rod groups. The superposition of torsional and axial deformations was used to obtain the two-parameter maps of the electronic and magnetic properties of nanohelicenes. It was also shown that torsion, as well as axial, deformations are reversible in a large region, which is a consequence of the spring topology. The electronic band gap depends to a large extent on the magnitude of the strains. In particular, the torsion regulates the type of metal-insulator transition (Mott-Hubbard or Peierls) which occur in metallic nanohelicenes [5].

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- [1] V.V.Porsev, A.V.Bandura, S.I.Lukyanov, R.A.Evarestov, Carbon 152 (2019) 755.
- [2] M.Damnjanovic, I.Milosevic, "Line Groups in Physics. Theory and Applications to Nanotubes and Polymers" Lect. Notes in Phys., 801. Berlin: Springer, 2010.
- [3] R.Dovesi, A.Erba, R.Orlando, C.M.Zicovich-Wilson, B.Civalleri, L.Maschio, M.Rerat, S.Casassa, J.Baima, S.Salustro, B.Kirtman, WIREs Comput.Mol.Sci. 8 (2018) e1360.
- [4] V.V.Porsev, R.A.Evarestov, Comp.Mat.Sci. 203 (2022) 111063.
- [5] V.V.Porsev, R.A.Evarestov, Comp.Mat.Sci. 213 (2022) 111642.

The CROP algorithm to accelerate convergence of iterative solution of relativistic coupled cluster theory equations

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The theoretical toolbox of studying materials with lanthanides and actinides is usually limited to density functional theory and scalar-relativistic (without accounting for the spin-dependent interactions) approaches. In most cases, these methods do not allow one to obtain reliable results for such materials, since wave functions for f-element compounds often have a pronounced multi-configuration character, and a spectrum of states is characterized by a high density of low-lying electronic states. Relativistic versions of coupled-cluster theory for multidimensional model spaces (MR-CC) allow one to solve these problems, however, they require serious developments to increase the computational efficiency of program implementations of these techniques. The present report is devoted to the implementation of computational algorithms that improve the convergence of iterative procedures for solving amplitude equations of the coupled cluster method. The DIIS (direct inversion in the iterative subspace) algorithm is widely used to accelerate the convergence of the iterative procedure at the moment. However, when considering models with high computational cost, in particular, explicitly considering the contributions of triple excitations (the CCSDT model), this algorithm requires a large amount of RAM to store the values of amplitudes from previous iterations. To solve this problem, the CROP (the conjugate residual with optimal trial vectors) algorithm was proposed in [1]. Within this approach, the iterative subspace can be reduced to a three-dimensional one without loss of convergence rate with respect to DIIS. The CROP algorithm was implemented in the EXP-T software package [2]. It is demonstrated that the CCSD method using DIIS and CROP has the same convergence rate, while for the CROP algorithm were stored arrays of cluster amplitudes obtained at three last iterations compared to ten for DIIS. Tests were carried out for water and AcO^+ .

1. Ziolkowski, M.; Weijo, V.; Jorgensen, P.; Olsen, J. J. Chem. Phys. 128, 204105, 2008
2. A. V. Oleynichenko, A. Zaitsevskii, E. Eliav, Towards High Performance Relativistic Electronic Structure Modelling: The EXP-T Program Package. Commun. Comp. Inf. Sci. 1331, 375-386 (2020)

Ring kinematics-informed conformational space exploration of macrocyclic molecules

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Conformational searches and ML-driven geometry predictions (e.g., AlphaFold [1]) operate within the space of molecular degrees of freedom. When dealing with cycles, cyclicity constraints impose complex interdependence between degrees of freedom, so that arbitrary changes of cyclic dihedral angles lead to heavy distortions of some bond lengths and valence angles of the ring. This renders navigation through conformational space of cyclic molecules to be very challenging.

Inverse kinematics is a theoretical framework that offers a rigorous mathematical solution to this problem. It enables the identification of independent degrees of freedom for polycyclic molecules, i.e., the dihedral angles that can be set independently from one another. Subsequently, for any given values of degrees of freedom, inverse kinematics can reconstruct the remaining dihedrals so that all rings are closed with given bond lengths and valence angles. This approach offers a handy and efficient way for navigating conformational space of any molecule using either naive Monte-Carlo sampling or sophisticated machine learning models [2,3].

Through inverse kinematics, the conformational space of polycyclic molecules can be significantly narrowed down to encompass the regions that preserve cyclicity. Thus, it can be considered a physical constraint imposed on the model, enforcing on it the principles of kinematics that govern conformations of molecular cycles. We believe that inverse kinematics will become an essential tool in the rapidly expanding field of geometry prediction for (poly)cyclic molecules.

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References

1. *Nature*, **2021**, 596, 7873, 583-589.
2. *J. Chem. Inf. Model.*, **2022**, 62, 4, 785-800.
3. *J. Comput. Chem.*, **2022**, 43, 27, 1880-1886.

Development of a new-generation semiempirical method for modeling metal-organic frameworks

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Metal-organic frameworks (MOFs) are a relatively new class of adsorbents which, in addition to having unprecedented surface areas, exhibit exciting physico-chemical properties. Among those, are optical and magnetic chemical sensing capabilities, the usefulness of which warrants development of a computational screening method capable of discerning candidate materials for use in industrial and commercial applications. In the present work, Effective Hamiltonian of Crystal Field (EHCF), a hybrid method for calculating accurate d-d spectra of transition metal complexes, has been applied to transition metal carbodiimides (NCN^{2-}), hydrocyanamides (HNCN^-), and MOFs. Two methods, tight-binding SCF and SCF/SLG, were used to calculate the states of the ligand subsystems of the studied systems. Both methods are shown to be capable of accurately reproducing experimental spin multiplicities and spatial symmetries of the d-shell in the transition metal. The SCF/SLG approach is, however, much more computationally effective, having time complexity $O(N)$, which makes it a prime candidate for use in the aforementioned screening of MOFs.

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References

1. A.V. Soudackov, A.L. Tchougréeff, I.A. Misurkin. Electronic structure and optical spectra of transition metal complexes by the effective Hamiltonian method. *Theor. Chim. Acta* 83 (1992) 389-416.
2. M.B. Darkhovskii, A.M. Tokmachev, A.L. Tchougréeff. MNDO parameterized hybrid SLG/SCF method as used for molecular modeling of Zn(II) complexes. *Int. J. Quant. Chem.* 106 (2006) 2268-2280.
3. I. Popov, E. Plekhanov, A.L. Tchougréeff, E. Besley. Effective Hamiltonian of Crystal Field Method for Periodic Systems Containing Transition Metals. *Mol. Phys.* (2022) e2106905.

Mechanical properties of complex solids from machine learning based approach

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Modern methods of computational simulations allow one to predict the structure and physical properties of new materials mostly with single crystal structure and a certain stoichiometry. Ideally obtained theoretical data can be used for further targeted synthesis of these materials, which should lead to a significant reduction in the time from search to development and implementation of a new material in practical applications. However, experimentally synthesized materials usually consist of polycrystallites or multiple phases. This leads to conclusion that experimentally measured properties of synthesized samples may significantly differ from calculated properties for single crystals. Thus, it is required to propose new methods towards description of physical properties of such complex systems. We propose new computational technique toward efficient calculations of mechanical properties of complex solids from atomistic point of view with high accuracy and reasonable computational cost by using machine learning interatomic potentials (MLIPs) based on moment tensor potentials (MTPs). MLIPs were trained on a number of local atomic configurations for which forces, stresses and energies were calculated by using ab initio calculations. Developed automated approach allows one to perform calculations of elastic tensor, bulk and shear moduli of complex systems by using active learning of MLIPs on local atomic environments in automatic. This technique allows one to perform large scale calculations of mechanical properties of complex solids with high accuracy.

Carbon allotropes as a playground for ‘structure-properties’ search.

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Arguably, carbon is the most important chemical element. It provides the basis for life on Earth, it is used for many technological applications: from drugs to synthetic material. Importance of carbon origins from its ability to bind to itself and nearly all other elements, which allows it to construct many hypothetical allotropic forms. The structural diversity of carbons lead to a broad range of chemical and physical properties.[1] Naturally, there are two 3D natural allotropes of carbon: diamond and graphite. Diamond possess the highest values for some important industrial properties like hardness, thermal conductivity or electrical conductivity and heat up the search for new carbons with similar properties. Allotropes of carbon are also important for fundamental search for ‘structure-properties’ relation due to simplicity. Presently, there are more than 1000 hypothetical carbon allotropes and almost all of them are indexed in Samara Carbon Allotrope Database (SACADA) [2]. All entries in SACADA are calculated ab initio by using the Vienna Ab Initio Simulation Package (VASP) with the same settings. Based on SACADA dataset, we have established some simple relations between the density of allotropes and some mechanical parameters like bulk modulus or hardness. [3]

References

- [1] Hirsch A. The era of carbon allotropes //Nature materials. – 2010. – T. 9. – №. 11. – C. 868-871.
- [2] Hoffmann R. et al. Homo citans and carbon allotropes: for an ethics of citation //Angewandte Chemie International Edition. – 2016. – T. 55. – №. 37. – C. 10962-10976.
- [3] Kabanov A. A., Bukhteeva E. O., Blatov V. A. A topological approach to reconstructive solid-state transformations and its application for generation of new carbon allotropes //Acta Crystallographica Section B: Structural Science, Crystal Engineering and Materials. – 2023. – T. 79. – №. 3.

Quantum computing library for quantum chemistry applications

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Quantum computing is aimed to solve tasks, which are believed to be exponentially hard to existing computational devices and tools. A prominent example of such classically-hard problems is simulating complex quantum many-body systems, in particular, for quantum chemistry. However, solving realistic quantum chemistry problems with quantum computers encounters various difficulties, which are related, first, to limited computational capabilities of existing quantum devices and, second, the efficiency of algorithmic approaches. In the present work, we address the algorithmic side of quantum chemistry applications by introducing a Python 3 code library, whose primary objective is to speed up the development of variational quantum algorithms for electronic structure problems. The code library allows the calculation of energies for the ground and excited states of molecular systems, both on a classical computer and emulator of a quantum processor. The library implements both the general structure of variational algorithms and built-in versions of known algorithms (Variational Quantum Eigensolver [1], Adapt-VQE [2,3]). A distinctive feature of the library is the ability to flexibly modify the algorithm to meet the user's needs, which is especially important for developers of new algorithms and researchers. Additionally, the library supports classical quantum chemical computation packages, which facilitates benchmarking when testing newly developed algorithms.

References.

1. Cerezo M, Arrasmith A, Babbush R, Benjamin S, Endo S, Fujii K, Mcclean J, Mitarai K, Yuan X, Cincio L and Coles P 2021 Nature Reviews Physics 3 1–20
2. Grimsley H, Economou S, Barnes E and Mayhall N 2019 Nature Communications 10 3007
3. Sapova M and Fedorov A 2022 Communications Physics 5 199

Modeling of electronic levels of atoms of period II in the presence of strong magnetic fields

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At present, the only way to study stars and other astrophysical objects, their structure, and processes occurring within them is to study their spectra. Amazing examples of such celestial bodies are "white dwarf" stars. To understand the structure of the life cycle of stars, it is important to study their chemical composition at different stages of development. The literature provides a qualitative analysis of the chemical composition of white dwarfs [1]. It is reported that, in addition to light hydrogen and helium, their composition also contains a number of elements of the second period [2].

This work continues the study of modeling the electronic structure of atoms of the second period in strong magnetic fields. Current best approach to carry out such calculations today is the method based on the modification of the one-electron part of the electron Hamiltonian by introducing additional terms in the presence of a uniform magnetic field [3-4]. This method modifies the standard algorithms of quantum chemistry, the electron Hamiltonian contributions explicitly depend on the spin and orbital momentum of the electron. Thus, the matrices with which one has to work are already clearly not just self-adjoint, but also complex, and the spin-orbitals for electrons with different spin values can no longer have the same spatial parts. All this significantly slows down the calculation speed.

In this work we proposed a method for calculating the electronic structure in the version of the UHF, UMP2 methods and the full CI method in the framework of a similar formalism, also the MCSCF method is considered. The elements of the II period were calculated; the pattern of changes in the orbital energy and composition of orbitals in the case of a successive increase in the value of the external magnetic to extreme values was studied. Separately, the energy contributions to various components of magnetic interactions are calculated and general regularities are revealed in the dependences of the energies of electronic levels on the external magnetic field on the parameters of the system under study.

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Bibliography

1. Kepler S. O., Koester D., Ourique G. A white dwarf with an oxygen atmosphere // *Science*. 2016. Vol. 352. P. 67-69.
2. Dufour P. et al. White dwarf stars with carbon atmospheres // *Nature*. 2007. Vol. 450. P. 522-524.
3. Stopkowicz S. et al. Coupled-cluster theory for atoms and molecules in strong magnetic fields // *The Journal of Chemical Physics*. 2015. Vol. 143. P. 074110.
4. Hampe F., Stopkowicz S. Equation-of-motion coupled-cluster methods for atoms and molecules in strong magnetic fields // *The Journal of Chemical Physics*. 2017. Vol. 146. P. 154105.

Trapping and thermal migration of the first- and second-row atoms in Ar, Kr and Xe crystals

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Single atoms isolated in rare gas (RG) crystals represent a perfect model system for studying dynamics of non-reacting atomic impurities and gaining valuable insights for the mechanisms of diffusion-limited reactions in solid state. In the present work atoms from the first two rows of Periodic Table (H-Ne), isolated in Ar, Kr, Xe crystals were investigated and their trapping sites, atomic migration barriers and diffusion coefficients were calculated. Pair potential approximation with diatomic energy curves calculated using high-level quantum chemistry methods (aug-cc-pV5Z/CCSD(T)) was used for all systems. Additionally, for B,C,O,F@RG, anisotropic calculations were performed with the help of recently developed [1] diatomics-in-molecules-based method. Two main trapping sites – single substitutional and interstitial – were discovered to be thermodynamically stable for all atoms in Ar, Kr and Xe with only a few exceptions. Both sites turned out to have several structural variants with the most stable one depending on guest atom properties. One previously undiscussed variant of interstitial site was discovered for B, C and F atoms, which possess particularly high degree of interaction anisotropy with RG. Atomic mobility in the present work is discussed mainly in context of interstitial atoms. Overall, three migration mechanisms were discovered, two of which are realized only for anisotropic atoms. Isotropic ones and O travel in an almost straight line, from one octahedral void to another through their common edge. Meanwhile a critical phenomenon which changes the transition state was discovered for C@RG and F@RG and a completely different migration path – for C@Xe and F@Xe. From the mechanism with the smallest migration barrier for any given system, jump frequency and the diffusion coefficient was calculated using simple transition state theory. The results were compared to the available experimental data with satisfactory agreement.

References

1. I. V. Leibin, I. S. Kalinina, D. S. Bezrukov, and A. A. Buchachenko, Modeling of the thermal migration mechanisms of atomic oxygen in Ar, Kr and Xe crystals, *J. Chem. Phys.* 154, 044305 (2021)

Virtual Sites Fitting for Molecular Mechanics Based on Electron Density Topology Analysis

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Molecular mechanics is a widely used tool in biology and materials science, as it provides possibility to model systems of hundreds and thousands of atoms [1,2]. Noncovalent (electrostatic and dispersion) interactions are of a great importance for most systems of interest. Common way to describe electrostatic interactions is to use Coulomb law with point charges, located at the atomic positions. Though this representation is computationally effective, it sometimes is unable to reproduce charge distribution around an atom, the most common example being halogen atoms [3]. The so-called sigma hole at line connection carbon atom and heteroatom can be described by an additional virtual charge, improving the quality of approximation. The positions for such virtual sites are usually chosen based on chemical intuition or quantum mechanical data.

This work suggests analyzing the electron density topology to locate virtual sites positions. The method helps to make virtual sites localization automatic and provides physical argumentation for their positions. It is shown that virtual sites fitted that way improve the description of noncovalent interactions in biological molecules and halogenated molecules.

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References.

1. Chen Z.; Pei J.; Li R.; Xiao F. *Construction and Building Materials* 2018, 189, 695.
2. Cisneros G.A.; Karttunen M.; Ren P.; Sagui C. *Chemical Reviews* 2014, 114, 779.
3. Inakollu V.S.; Geerke D.P.; Rowley C.N.; Yu H. *COSB* 2020, 61, 182.

Engineering of band structure of A^3B^6 layered semiconductors through compositional tuning and uniaxial strain

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Layered van der Waals (vdW) materials are currently at the forefront of research related to applications in next generation electronics. Such materials are primarily of interest because they contain a weak dispersion interaction vdW between covalently bonded layers. From such materials, it seems possible to create ultrathin layers and heterostructures with atomically sharp interfaces, almost independently of their lattice constant. These materials greatly expand the possibilities for transparent and flexible electronic devices. At the same time, in order to unlock the full potential of layered materials, it is necessary to fully understand the patterns of their structure, functioning, and behavior under various conditions. One of the effective approaches to control the functionality of vdW materials is to obtain quasi-binary alloys using isoelectronic materials. Another approach is to reconfigure the gap vdW under applied uniaxial compression. Investigating the influence of compositional and structural disorder, it was shown that with a random distribution of indium and gallium cations (for both tellurides and selenides) relative to the gap vdW, only the topology of the band structure changes significantly, we associate this with a change in symmetry, the band gap in this case varies insignificantly. The ordered distribution (one type of atoms in the atomic plane, forming a vdW gap) does not significantly affect the topology, but only affects the band gap. Various permutations of chalcogen atoms with respect to the vdW gap were also studied. It is found that in this case the band gap changes significantly. In particular, it was found that in the case when the gap vdW is formed on both sides by atoms of the same type, the band width will be the largest. Our study confirms the decisive influence of chalcogen atoms on the band structure and vdW gap. We believe that our results are general and can be applied to other classes of layered 2D chalcogenides. To study the reconfiguration of the gap vdW, uniaxial compression of materials was carried out. The application of pressure causes structural changes, which leads to the collapse of the vdW gap and the formation of metal-chalcogen bonds. The dimension of structures decreases to quasi-one-dimensional (q1D). The transition is accompanied by a change in the topology of bonds, the atoms in the new structure become coordinated in accordance with the 8-N rule. In addition, the new q1D structure includes a vdW binding. In the original 2D structure, the vdW interaction is due to s-orbital electrons with a lone pair, while the bond between q1D chains in the high-pressure phase occurs due to the participation of a p-orbital lone pair of electrons. It is stated that the impossibility of closing the vdW gap is a common property of A^3B^6 materials.

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Photoinduced recoordination in complexes of bis-aza-18-crown-6-containing ketocyanine dyes with cations of alkaline and alkaline earth metals

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Bis(azacrown)ketocyanine-containing dyes have attracted attention as prototypes of photo-switchable molecular devices and optical molecular chemosensors due to their ability to bind metal cations [1]. The phenomenon of metal cation recoordination in the ground and excited state was detected in crown-containing styrene dyes [2-3] and investigated by the density functional theory method [4]. It was shown that the recoordination is associated with a change in the conformation of the macrocycle, because of which the cation is either bound to all crown-ether heteroatoms, and crown-ether nitrogen is excluded from the conjugation chain, or is bound only to oxygen atoms, and crown-ether nitrogen remains in the conjugation chain. The first type of conformations leads to a hypsochromic shift of the absorption band of the complex, and for the second type, the absorption spectrum slightly differs from the spectrum of the free dye. It has also been shown that the tendency to recoordination depends on the correspondence between the size of the cation and the size of the macrocycle cavity, as well as on the ion charge, while the solvation of the cation has a key effect on recoordination. In this work, bis-aza-18-crown-6-containing ketocyanine dyes (Figure 1) and their complexes with K^+ , Ca^{2+} , Mg^{2+} cations were studied by DFT and TDDFT. Various solvate forms of complexes with stoichiometry cations have been studied 1:1, 2:1, 3:1. Recoordination was studied both in the main S_0 and in the excited S_1 states. It is found that the relative depth of the minima of both conformers types is determined by the surface charge density on the cation and the geometric correspondence between the cation and the macrocycle cavity. Changing the size of the central cycle does not lead to significant changes in photophysical properties, since it does not distort the conjugate system. For Mg^{2+} with a large surface charge density, the possibility of carbonyl oxygen atom coordination was shown, and the existence of such complexes was confirmed experimentally. The work was carried out with the financial support of the Russian Science Foundation (grant. № 22-23-00161).

1. V. V. Volchkov, M. N. Khimich., M. Ya. Melnikov, A. E. Egorov, R. O. Starostin, M. V. Fomina, S. P. Gromov. *Mendeleev Commun.*, 2023, 33, No. 3, 380.
2. A. Ya. Freidzon, A. A. Bagatur'yants, S. P. Gromov, M. V. Alfimov, *Russ. Chem. Bull.*, 2003, 52 No. 12, 2646.
3. A. Ya. Freidzon, A. A. Bagatur'yants, S. P. Gromov, M. V. Alfimov, *Russ. Chem. Bull.*, 2008, 57, No. 10, 2045.
4. A. Ya. Freidzon, A. A. Bagatur'yants, S. P. Gromov, M. V. Alfimov, *Int. J. Quantum Chem.*, 2004, 100, No. 4, 617.

Fermionic potential as a chemical bonding and electron (de)localization descriptor

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Electron (de)localization is one of the key chemical phenomena determining various properties of the matter. The lack of experimental techniques directly measuring (de)localization of electrons leads to a need for quantum chemical tools to evaluate it. In closed-shell systems electron (de)localization can be studied in terms of an exchange (Fermi) hole, since the formation and the spread of electron pairs in position space is driven by the exchange correlation. The only drawback of the immediate application of Fermi hole is its dependence on the position of two electrons, that complicates electron delocalization analysis in molecules and crystals. This fact stipulates creation of the one-electron Fermi hole-based descriptors (such as ELF, LOL, etc.). Ideally, they should retain all valuable information about exchange correlation features in a system, but in practice can lose significant parts of it [1]. To overcome these difficulties and fully take into account all effects responsible for electron (de)localization we introduce a fermionic potential $v_f(\mathbf{r})$ [1]. It originates from the Euler-Lagrange equation for electron density and, unlike other electron (de)localization descriptors, simultaneously characterizes a Fermi hole depth, its tendency to change, a sensitivity of an exchange correlation hidden in a pair density and kinetic potential to local variations in electron density. The wells in the $v_f(\mathbf{r})$ distribution correspond to the domains of maximum electron localization in the system, while the potential's barriers prevent delocalization of electrons through them. The $v_f(\mathbf{r})$ components give a unique opportunity to compare influence of the previously mentioned factors connected with exchange correlation behavior on the electron delocalization in a system. We need to note, that symmetry of the $v_f(\mathbf{r})$ distribution in the interatomic regions estimates bond orders and successfully reveals impact of the chemical modifications or environmental effects on the (de)localization of electrons in molecules and crystals. We show that fermionic potential can be applied both to theoretically computed and experimentally derived structures. The examination of the impressively large systems is possible as well, for instance, absorbed epoxy resin components on 2D periodic defected graphene. This example along with the study of benzoza(thia)zolothiazinium polyiodides single crystals with π -hole tetrel bonds demonstrate potential benefits of the $v_f(\mathbf{r})$ use in the noncovalent bonding analysis.

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Bibliography

1. Levina E. O., Tsirelson V. G. DFT potentials from a chemical perspective: Anatomy of electron (de) localization in molecules and crystals // J. Comput. Chem. – 2023. – V. 44, – P. 1817-1835.

Ring kinematics-informed conformational space exploration of macrocyclic molecules

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Conformational searches and ML-driven geometry predictions (e.g., AlphaFold [1]) operate within the space of molecular degrees of freedom. When dealing with cycles, cyclicity constraints impose complex interdependence between degrees of freedom, so that arbitrary changes of cyclic dihedral angles lead to heavy distortions of some bond lengths and valence angles of the ring. This renders navigation through conformational space of cyclic molecules to be very challenging.

Inverse kinematics is a theoretical framework that offers a rigorous mathematical solution to this problem. It enables the identification of independent degrees of freedom for polycyclic molecules, i.e., the dihedral angles that can be set independently from one another. Subsequently, for any given values of degrees of freedom, inverse kinematics can reconstruct the remaining dihedrals so that all rings are closed with given bond lengths and valence angles. This approach offers a handy and efficient way for navigating conformational space of any molecule using either naive Monte-Carlo sampling or sophisticated machine learning models [2,3].

Through inverse kinematics, the conformational space of polycyclic molecules can be significantly narrowed down to encompass the regions that preserve cyclicity. Thus, it can be considered a physical constraint imposed on the model, enforcing on it the principles of kinematics that govern conformations of molecular cycles. We believe that inverse kinematics will become an essential tool in the rapidly expanding field of geometry prediction for (poly)cyclic molecules. This work was supported by the RSF (22-73-10124). This work has been carried out using computing resources of the federal collective usage center Complex for Simulation and Data Processing for Mega-science Facilities at NRC “Kurchatov Institute”, <http://ckp.nrcki.ru/>.

References

1. *Nature*, **2021**, 596, 7873, 583-589.
2. *J. Chem. Inf. Model.*, **2022**, 62, 4, 785-800.
3. *J. Comput. Chem.*, **2022**, 43, 27, 1880-1886.

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Quantum chemical study of the electronic structure of molecules containing ytterbium

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Chemical compounds containing f- and heavy d-elements possess a number of unique properties, which are of great practical interest. However, the theoretical study of the electronic structure of such molecules is burdened by a number of difficulties. This is due to the fact that calculations of such molecules with the accuracy of interest require simultaneous consideration of relativistic and correlation effects. For the correct description of polyvalent heavy d- and f-elements, a very high accuracy of calculations is necessary since they often have a pronounced multiconfiguration character and a high density of low-lying electronic states.

The method of relativistic pseudopotential was used in the work, which allows one to significantly reduce the computational cost in the study of electronic structure. This method takes into account the electrons near the nucleus in the form of some nonlocal pseudopotential (PP). The number of electrons participating in the calculation explicitly is usually reduced dramatically, which greatly simplifies the calculation. After calculation of the electronic structure using the pseudopotential method, the restoration of wave functions in the core region is carried out to calculate various properties which are concentrated in the core region of a heavy atom.

Since the chemical shifts of the lines of the X-ray emission spectrum have a high sensitivity to changes in the electronic structure in core of an atom of interest in various compounds, it was chosen as a criterion for checking the quality of reproducing the electronic density. YbHal_n molecules (Hal = F, Cl, $n = 2, 3$) were selected as objects of our research. In these molecules, the ytterbium atom is in two different oxidation states: +2 and +3. In the first case, the 4f shell is completely closed, and in the second one it is open.

Structural parameters for these molecules, in particular, the lengths of Yb-Hal bonds and the angles between Hal-Yb-Hal were calculated. The chemical shifts of the $K_{\alpha 1}$ and $K_{\alpha 2}$ lines of the X-ray emission spectrum in the YbHal_3 molecule relative to the YbHal_2 molecule have also been calculated. The obtained results are compared to the experimental data. Some particular study was conducted on the dependence of the chemical shift value on the basis set size on the halogen.

Relativistic light atoms in strong uniform magnetic fields

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Relativistic atomic spectra are drastically modified by an external magnetic fields of the atomic order of magnitude 2.35×10^9 G which corresponds to the 10^6 up to 10^{15} G field range relevant to the thin atmospheres of the compact objects including white dwarfs, neutron stars, and magnetars. While the comprehensive data for a relativistic hydrogen have been available for some time, this is less the case for atoms and ions with more than one electron, which are of interest due to the features discovered in the thermal emission spectra of isolated neutron stars.

Since the perturbative treatment of the magnetic effects fails miserably for such strength the precise ab initio description of many-electron atoms represents the challenge for the relativistic quantum theory. From this perspective, it turns out to be interesting to examine the same systems in the pure relativistic framework still bypassing the full quantum electrodynamical (QED) regime but addressing the retardation effects on the electron-electron interactions.

In the present work we calculate the relativistic ground and several excited states for the H, Li, Be and B atoms in the magnetic field strengths up to 10^{12} G range using the Dirac-Coulomb-Gaunt Hamiltonian in the framework of purely relativistic FCI approach where the pair creation-annihilation problem was avoided grossly within the no-pair approximation. All computations were performed in the Slater type bispinoric basis set using the restricted kinetic balance approach. First of all, the construction of the one-electron basis was performed applying the solution of the hydrogen-like atom problem for the given field using for all considered cases. The computing of the no-pair FCI Hamiltonian on the positive energy states was invoked for the states with the select relativistic symmetries. In this case, the simplicity of the atomic problem allows to effectively evaluate all one- and two-electron integrals involved which are readily combined in the method's Hamiltonian matrix elements using the effective caching strategy. Moreover, we applied the Lanczos-inspired approach for the energy dispersion functional which have been already used for the relativistic hydrogen atom.

As a result of the study, the relativistic dependencies for the ground and first excited states energies on the magnetic field strengths were obtained for all of the above-mentioned atoms. The calculations performed indicate the necessity to include relativistic corrections given the current numerical accuracy of the nonrelativistic results. Besides the lack of bounds on the energy, the basis set applied in this work was found to be not very efficient for very strong magnetic fields and small atomic numbers, although the basis set saturation is still available in the considered cases.

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Theoretical search for new prospective chalcogen-containing solid ion conductors for multivalent-ion batteries

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The wide used lithium-ion batteries (LIB) have some disadvantages, which are connected with high lithium price and flammable electrolyte. Theoretically, batteries based on multivalent working ions, such as Mg, Ca, Zn and Al, could be have higher volumetric capacities compared to LIBs [1]. Here we carried out the high-throughput screening of the ICSD database for searching of new conducting materials for multivalent metal-ion batteries. We focused on ternary and quaternary chalcogenides (more than 1500 entries), since such compounds should exhibit higher cation conductivities than their oxide counterparts due to a lower ionicity degree in chalcogenides [2]. A wide set of methods was applied including geometrical-topological (GT) analysis, bond valence site energy (BVSE) and density functional theory (DFT) calculations, kinetic Monte-Carlo simulations and ab initio molecular dynamics (AIMD). GT analysis based on the Voronoi partition revealed 109 compounds with sufficient free crystal space for the migration of multivalent cations and previously unknown as an ionic conductors. Then, 17 structures were filtered out due to low migration energy (E_m) value from the BVSE method. Following DFT simulations resulted to twelve most promising multivalent cationic conductors with E_m less than 1.0 eV. Most interestingly, a family of $ML_n_3TQ_7$ ($M = Zn, Al$; $T = Al, Si, Ga, Ge$; $Q = S, Se$) structures possess very low migration energies (0.09-0.99 eV). AIMD simulation was performed to prove high ionic diffusion rate into $ML_n_3TQ_7$ family. The diffusion coefficient was calculated over an atomic mean squared displacement (MSD) [2]. The diffusion coefficient range was about $6.21 \cdot 10^{-8}$ - $1.18 \cdot 10^{-6}$. Additionally, based on the GT and BVSE results we have established the logarithmic dependencies of E_m on the geometrical parameters of the free crystal space: E_m of working ions expectedly increases with decreasing the free space available for diffusion. The study was supported by the Russian Science Foundation grant No. 19-73-10026, <https://rscf.ru/project/19-73-10026>.

1. Iton, Z. W. B.; See, K. A. Multivalent Ion Conduction in Inorganic Solids. *Chem. Mater.* 2022, 34 (3), 881–898.
2. Urban A., Seo D.-H., Ceder G. Computational understanding of Li-ion batteries // *npj Comput. Mater.* 2016. Vol. 2, № 1. P. 16002.

Intermolecular and intramolecular rate constants of molecule-metallic nanoparticle system within the electromagnetic field

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A theoretical model for estimating the fluorescence quantum yield (ϕ_f) a system consisting of a highly dipolar dye and a nanoparticle (NP) using quantum chemical calculations of intramolecular and intermolecular electronic transition rate constants was developed taking into account the localized surface plasmon resonance (LSPR) effect. It was shown that the LSPR effect can increase or decrease depending on the dielectric constant (ϵ_m) of the environment. For small ϵ_m values of 3–8.5, the LSPR effect will be predominantly positive for radiation processes of the dye, whereas for large ϵ_m values of 18–80, the LSPR effect is negligible. Finally, it can be concluded that the theoretical model can calculate the fluorescence quantum yield of dye near NP depending on the distance between a dye and NP based on the radius of NP, the ϵ_m , the electric dipole moment transition of molecule, the wavelength of incident electromagnetic radiation, concentration of the free electrons in per unit of NP and the damping (or electron-collision) rate constant.

Advancing Internal Conversion Rate Constants Calculation: A Comprehensive Approach Integrating Duschinsky, Anharmonic, and Herzberg-Teller Effects

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A novel method to calculate internal conversion rate constants (k_{IC}) with consideration of the Duschinsky effect has been developed. This method is based on previously established methods for calculating k_{IC} taking into account the harmonic (HARM) and anharmonic (ANH) approximations, within the Frank-Condon (FC) and Hertzberg-Teller (HT) approaches using the results of ab initio calculations and the fast method to calculate k_{IC} in the approximation of accepting X-H (X=O, C, N) stretching modes [1,2]. This method has been tested on well-known planar molecules such as tetraoxa[8]circulene, free-base porphyrin, and pyrromethene, and have small Duschinsky rotation with nearly identical normal coordinates in the ground and excited states, and on poly[n]fluorenes (P[n]F) with $n = 2-14$, which experience substantial Duschinsky rotation. The results obtained from the calculations indicate that the Duschinsky effect is significant in the HARM approximation but generally much smaller in the ANH approximation. It is most noticeable for high-frequency vibrational modes with energies of around 3300 cm^{-1} , particularly the X-H (X = C, N, and O) stretching modes. However, even in such cases, the increase in k_{IC} due to the Duschinsky effect does not exceed one order of magnitude. Overall, the calculations demonstrate that ANH contribution to k_{IC} dominate over HT contribution, which in turn are larger than the contributions from the Duschinsky effect (ANH > HT > Du). Moreover, the study confirms that an approximation considering only X-H bonds in the k_{IC} calculation remains accurate even for P[n]F with $n = 2-14$.

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1. R. R. Valiev, R. T. Nasibullin, V. N. Cherepanov, G. V. Baryshnikov, D. Sundholm, H. Agren, B. F. Minaev and T. Kurten, *Phys. Chem. Chem. Phys.*, 2020, 22, 22314-22323.
2. R. R. Valiev, R. T. Nasibullin, V. N. Cherepanov, A. Kurtsevich, D. Sundholm and T. Kurten, *Phys. Chem. Chem. Phys.*, 2021, 23, 6344-6348.

Cerium ammonium nitrate as template agent. DFT studies

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There are many approaches in synthetic chemistry to make C—X bonds via radical mechanisms, where X is heteroatom or carbon [1].

Recently, our colleagues have found that sodium sulfinate reacts with 1-azidevinylbenzene upon oxidation. Strikingly, different one-electron oxidizing agents (manganese triacetate and cerium ammonium nitrate, CAN), led to different reaction products: first produced an enamine product, but CAN resulted in formation of a dimeric product with a C=N—N=C linker instead of the enamine groups. That fact led us to hypothesize, for the first time, to the best of our knowledge, that in this reaction cerium atom acts not only as an oxidizer, but also as a template agent, carrying out the entire reaction in its first coordination sphere.

To test this hypothesis, quantum chemical calculations were carried out for possible complexes of cerium and initial agents.

1. Kvasovs N., Gevorgyan V. Contemporary methods for generation of aryl radicals // Chemical Society Reviews. – 2021. – V. 50. – №. 4. – C. 2244-2259. – DOI: 10.1039/D0CS00589D.

Ab Initio Investigation of the Band Structure of Bismuth-Antimony Alloys

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Bismuth-antimony solid solutions are of interest due to their transport properties of charge carriers' sensitivity to various impact. The band structure of bulk crystals of bismuth-antimony alloys, depending on the concentration of antimony, undergoes changes. It has been experimentally shown there is a change from a semimetallic state to a gapless state (at 4 at.% Sb), then to a semiconductor state (7–22 at.% Sb), and again to a semimetallic state. In this case, the parameters of overlap and the band gap vary in the ranges of tens and hundreds of meV. This makes calculating the bismuth antimony system from first principles quite a challenge.

Bismuth-antimony alloys play an important role in the low temperature thermoelectric devices industry. Despite the fact that these materials have a rich history of research, this system continues to be a source of discovery of novel properties. Thus, the state of a topological insulator was first discovered in bismuth-antimony crystals. The high mobility of surface topological states in bismuth-antimony films can allow to increase electrical conductivity of the material, while its thermal conductivity is determined by the bulk properties. This would make it possible to achieve an increase in thermoelectric figure of merit, which requires a combination of high electrical conductivity and low thermal conductivity. Thus, the study of bismuth-antimony crystals from the first principles is of theoretical and practical interest, however, the data on such studies are not fully presented in modern literature.

Here we present the results of first principles modeling of the effect of the antimony concentration on the band structure of bismuth rich bismuth-antimony alloys. Ab-initio calculations were carried out using the density-functional theory method within the GGA for exchange-correlation functional with the PBE functional as implemented in the VASP code. The norm-conserving full relativistic pseudopotentials constructed were used to describe the electron-ion interactions. The cutoff point for planewave kinetic energy cutoff and the Monkhorst-Pack k-mesh for each rhombohedral supercell was chosen to ensure the convergence of the total energy within 1 meV. In this study, all calculations were performed taking into account the spin-orbit interaction.

We have studied the evolution of structural parameters depending on the antimony concentration. It is found that the position of antimony atoms does not affect the modeling results. Comparison of the results of calculations of the parameters of the band structure with the experimental values shows that taking into account the van der Waals interaction leads to discrepancies. The parameters of the band structures obtained in the calculations are in qualitative agreement with the experimental data. The results of the work can be used for further research of crystals and films of the bismuth-antimony system from first principles.

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Electronic Structure and Optical Absorption of the Ligated Magic-Size Clusters with Cd₈Se₁₃ Core

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In the field of semiconductor nanoclusters there exists a special interest for the structures with predefined number of atoms, so called magic-size clusters (MSC). They can provide the knowledge of exact atomic structure rather than just size-dependent variation in properties. A number of MSC of various compositions has been successfully prepared to date through the elaborated protocols, characterized in detail using different spectroscopic techniques and treated theoretically interpreting the properties through the high-level electronic structure calculations. The examples of these clusters are rather numerous, for Cd derivatives they include the cores with Cd_{4,8,10,13,17,28}, etc. [1,2]. Among these MSC of various compositions, clusters of the lower size range can result in identification of the earliest steps of nucleation and growth of nanoparticles and quantum dots. On the other hand, the lowest size range provides significant challenge to get true experimental information on their structure. In the present communication, we concern the series of Cd₈-species those were treated considerably rare to date. An experimental verification of the MSC of this size range is also not very easy because their extreme reactivity, rapid growth and strong deviation from the stoichiometric Cd/Se=1/1 ratio of the bulk counterpart. Meanwhile, there is experimental information on the MSC with Cd₈Se₁₃-core stabilized by N-terminated pyridine derivatives [3]. Theoretical treatment of them is of great demand for understanding structure-properties relation and comparison with more elaborated other series of CdSe MSC. This Cd₈-series is featured by the geometry built with Se atom in the centre. We performed the DFT calculations of the MSC with Cd₈Se₁₃-core terminated by hydrogen, amine ligands and pyridine group. Before discussion of the calculation data for these MSC, we pay more attention on justification of the correct functional in DFT and basis set with the best correspondence to experimental and high-level theoretical data for the simpler systems: CdSe diatomic, Cd₂Se₂ molecules, and the ligated Cd₂Se₂. Optical absorption spectra of the clusters with Cd₈Se₁₃-cores are simulated through the TDDFT method. The results on the ligand effects are in consistence with experimental observations for the MSC produced in the medium of N-coordinating molecules those provide efficient luminescence. The work was supported by the State Program of Scientific Research of Belarus "Nanostructure".

References

1. J. Lee, J. Yang, S.Gu Kwon, T. Hyeon. Nature Rev. Mater. 1 (2016) 16034.
2. C. Palencia, K. Yu, K. Boldt. ACS Nano 14 (2020) 1227.
3. A.V. Antanovich, A.V. Prudnikau, V.S. Gurin, M.V. Artemyev. Chem. Phys. 455 (2015) 32.

Theoretical study of structure and photophysics of the bis(arylidene)cycloalkanones homological series

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Bis(arylidene)cycloalkanones with various donor substituents, also known as ketocyanine dyes or symmetric cross-conjugated dienones, are D- π -A- π -D type dyes with interesting photophysical properties (Figure 1). They were investigated using stationary and time-resolved spectroscopy [1-3]. It was found that the compounds are characterized by effective reactions of (E,E)-(E,Z) photoisomerization. The paper presents a quantum-chemical study of the photophysical properties of dienones as a function of the molecular structure, and the influence of the structure on the possibility of deactivation of excitation through emission and non-radiative channels is estimated. The results obtained will provide a deeper understanding of the relationship between the structure and properties of the studied dienones and facilitate the search for a targeted molecular design. The structures of model dienones in the ground and excited states are established. It is shown that increasing the central cycle to a six-membered one strongly distorts the conjugate π -system, which leads to a non-monotonic change in the properties of a series of dyes. The bathochromic shift of the main transition band in the absorption spectra as the donor capacity of substituents increases is due to an increase in the energy of the HOMO (an increase in the oxidative potential) and a decrease in the gap of the HOMO-LUMO. It was found that photoinduced (E,E)-(E,Z)-isomerization underlies the mechanism of non-radiative relaxation of the excited dye. The ability to relax through fluorescence or photoisomerization is determined by the height of the barrier between the Frank-Condon region and the area of the conical intersection S_1 - S_0 . The calculation showed that the height of the barrier also correlates with the donor ability of substituents and the efficiency of coupling between the central and π -donor fragments. The work was carried out with the financial support of the Russian Science Foundation (grant. №22-13-00064).

1. Fomina, M.V.; Vatsadze, S.Z.; Freidzon, A.Y.; Kuz'mina, L.G.; Moiseeva, A.A.; Starostin, R.O.; Nuriev, V.N.; Gromov, S.P. Structure–Property Relationships of dibenzylidenecyclohexanones. *ACS Omega* 2022, 7, 10087–10099.
2. Fomina, M.V.; Freidzon, A.Y.; Kuz'mina, L.G.; Moiseeva, A.A.; Starostin, R.O.; Kurchavov, N.A.; Nuriev, V.N.; Gromov, S.P. Synthesis, Structure and Photochemistry of Dibenzylidenecyclobutanones. *Molecules* 2022, 27, 7602.
3. A. Gutrov, V.N.; Zakharova, G.V.; Fomina, M.V.; Nuriev, V.N.; Gromov, S.P.; Chibisov, A.K. Molecular photonics of dienones based on cycloalkanones and their derivatives. *J. Photochem. Photobiol. A* 2022, 425, 113678.

Catalytical activity of WB_{5-x} from the first principles

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Nowadays the most widely used catalysts for organic synthesis mainly made of noble and rare earth metals that significantly increases the cost of many products. Moreover, 80% of catalyst used in domestic industry including oil and chemical production are imported and it can cause problems in the present political situation.

Obviously, the new class of materials for the catalysts is needed. Suggested alternative to the pricey catalysts is the transition metals borides [1]–[3]. Along with the cobalt, molybdenum, nickel, and vanadium borides, tungsten borides were studied as potential catalysts for hydrogen evolution reaction (HER) and CO_2 reduction, then, their usage as the catalysts for organic synthesis was proposed.

Moreover, the catalytic activity of transition metal borides increases with the boron stoichiometric content [4], [5]. Hence, the higher tungsten boride (WB_{5-x}) is the most promising one beyond the other tungsten borides.

Here we performed the comprehensive study of surfaces of WB_{5-x} using density functional theory.

We studied the surface energies of WB_{5-x} slabs with various crystallographic orientations. Since WB_{5-x} has also been proposed as the alternative to the catalysts for an automotive motor, the adsorption of the different atmosphere gases (CO , CO_2 , H_2 , N_2 , O_2 , NO , NO_2 , H_2O , NH_3 , SO_2) on its stable surfaces was investigated. It was shown that at the (010) surface the lowest adsorption energies have the NO , CO and H_2 molecules. On the contrary, WB_{5-x} surface doesn't adsorb SO_2 gas. On (101) surface O_2 , NH_3 and NO_2 have the lowest adsorption energies.

The activation barriers for CO oxidation reaction are 1.29 eV and 1.35 eV for (010) and (101) surface, respectively. Such results makes WB_{5-x} promising catalyst for automotive motor and CO_2 reduction reaction.

References.

1. M. M. Dorri и др., Scripta Materialia, V. 200, P. 113915
2. C. Zhu, C. Wen, M. Wang, Z. Min, Y. Geng, и Z. Su, Chemical Science, № 13, P. 1342–1354, 2022
3. W. Zhao и др., Catalysts, V. 2, № 12, P. 222, 2022
4. S. Gupta, M. K. Patel, A. Miotello, и N. Patel, Advanced Functional Materials, № 30, P. 1906481, 2020
5. Q. Li и др., Chemical Communications, 2020