

CHALLENGES 2024

INTERNATIONAL SCHOOL AND CONFERENCE
"CURRENT CHALLENGES IN
CHEMICAL PHYSICS AND THEORETICAL CHEMISTRY"

BOOK OF ABSTRACTS



Moscow region, Klyazma
2024

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Сборник включает в себя программу и аннотации докладов, представленных на Международной школе-конференции по современным проблемам химической физики и теоретической химии «CHALLENGES 2024» (пос. Поведники, Московская область, 1-5 июля 2024 г.). Тематика школы-конференции охватывает следующие направления фундаментальных исследований:

- Современные методы квантовой химии;
- Высокопроизводительные вычисления и алгоритмы машинного обучения;
- Молекулярная спектроскопия и физика планетных атмосфер;
- Радиационные аспекты моделирования климата и дистанционного зондирования; природных и антропогенных процессов;
- Фотофизика и фотохимия молекул при линейном и нелинейном возбуждении.

Сборник представляет интерес для специалистов в области физики и квантовой химии.

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General Information

Challenges 2024

The international school & conference on current challenges in chemical physics and theoretical chemistry Challenges 2024 aims at bringing together quantum chemists and physicists across various multidisciplinary fields of science. The conference themes span from the development of modern electronic structure theory methods to their application in classical and quantum molecular dynamics simulations, astrophysics, linear and nonlinear molecular spectroscopy. Key lectures on application of machine learning techniques in high-tech production and on innovation technologies for high-performance computing will be delivered by industrial representatives. To complement a more traditional program, which will include plenary and invited talks as well as poster sessions, round-table discussions on hot topics will be organized. This event will be an excellent opportunity to engage in new collaborations with scientific groups across Russia and abroad, as well as with industrial partners.

Summer school

The summer school on modern electronic structure theory methods and high-performance computing will be held within the conference. The participants of the school will be granted certificates of advanced training from the MSU School of Advanced Engineering Studies.

Themes

- Quantum Theory
- Computational and Theoretical Chemistry
- Machine Learning and High-Performance Computing
- Molecular Spectroscopy and Physics of Planetary Atmospheres
- Radiative Aspects of Climate Modeling and Remote Sensing
- Photoinduced Processes in Molecules

Round-table discussions

- Classical and quantum dynamics in molecular spectroscopy
- Modern Software for Modeling Electronic Structure and Properties of Molecular Systems
- Science and industry collaboration
- Photoinduced nonadiabatic molecular dynamics

Organizers

- Joint Stock Company RT-Techpriemka, Moscow
- Department of Chemistry, Lomonosov Moscow State University, Moscow
- Institute of Quantum Physics, Irkutsk
- Petersburg Nuclear Physics Institute, Gatchina
- Moscow Institute of Physics and Technology, Dolgoprudny
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List of Abstracts – Invited Talks

How true are our estimates of PES based on experimental data: A theorist's view of internal rotation barriers

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In the experimental studies of the structure and conformational dynamics of non-rigid molecules based on the methods of vibrational or electron-vibrational spectroscopy, the heights of barriers to conformational transitions and potential functions of internal rotation are obtained by solving inverse vibrational problems.

In this case, the vibrational Schrödinger equation is solved using the variational principle, and the desired structural information (conformer energy differences and conformational transition barriers) is obtained from the optimal effective potential functions. The described problems are mathematically incorrect: they usually do not have a unique solution and, moreover, their solutions are often unstable with respect to small variations in the initial data.

The described approach remains productive only if the set of coordinates used (in practice it is usually one coordinate — a one-dimensional approximation) for constructing the PES (Potential Energy Surface) sections properly represents the selected nuclear motions of the molecular system. Analysis of the shape of the PES often allows one to qualitatively evaluate the adequacy of the chosen coordinate to the problem being solved, for example, by the degree of curvature of the minimal energy path without much effort. The data on the shape of the PES are obtained from quantum-chemical calculations, and largely due to this, the use of quantum chemistry methods in the processing of experimental data from molecular spectroscopy has become the modern standard for such studies.

However, the kinetic part of the Hamiltonian does not lend itself to such a simple analysis. An example of insufficient consideration of the features of the kinetic part of the Hamiltonian is the almost twofold discrepancy in the estimates of the barrier to internal rotation in the benzaldehyde molecule, obtained by various methods of quantum chemistry and from three sets of experimental data [1].

Using the example of molecules containing planar fragments (benzene, furan, and others rings), the report discusses the structural features of molecular systems in which internal rotation can have a multimode character due to the relatively large off-diagonal elements of the matrix of kinematic coefficients B . The author presents an attempt, by comparing the results of one- and two-dimensional vibrational problems based on quantum-chemically calculated PES cross sections, to evaluate possible errors in the one-dimensional model and the stability of the inverse problem for internal rotation, which has a complex character.

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Current state of the coupled cluster method in quantum chemistry: present situation, objectives, and challenges

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In today's literary realm, it is a common notion that the coupled cluster method serves as an optimal tool for calculating the ground state energy of molecular systems composed of several dozen atoms. Over the past decade, we've witnessed a surge in theoretical research focusing on the evolution of this method to enable calculations involving excited states or systems encompassing hundreds of atoms.

The first portion of this report presents a comprehensive overview of the method's basic principles and the current status quo. The challenges of dimensional consistency, the incorporation of an exponential ansatz, and the derivation of the method's operative equations are highlighted. Evolution of the method, in terms of quantum computing and machine learning implementations, is depicted. The progression towards f_{12} and EOM approaches, as well as the orbital localization method to lessen computational complexity, is also detailed.

The secondary part centers around the issue of molecular systems' property calculations. Given the fact the original design of the coupled cluster method is not intended for calculating the wave function, in practical terms the linear response method is utilized to compute properties thus obtaining density matrices of the necessary order. An explanation follows regarding the principal strategies for these mathematical entities' calculation and their subsequent analysis.

The final portion discloses unique results derived from our research team studies. A technique for calculating the operational expressions for arbitrary order's coupled clusters methods is unveiled, this extends to both the excitation operator amplitudes and single particle density matrix calculation coefficients. The procedure involved in numerical optimization of the computation algorithm through intermediate expression calculation is delineated. The demonstration of using a two particle density matrix to analyze basis completeness in van der Waals system calculations is shown.

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Radiolabeled carbon-based nanostructures for targeted delivery to tumor cells

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Despite significant advances in therapeutic and diagnostic approaches, successful cancer treatment remains challenging. Cancer treatments such as surgery, chemotherapy, ionizing radiation therapy, immunotherapy, hyperthermia, photodynamic therapy, hormonal therapy, and combination therapy have several critical disadvantages, such as low efficacy, unfavorable pharmacokinetics and poor bioavailability, serious side effects, low specificity, and, as a result, toxicity to healthy cells. Carbon-based nanomaterials (CBN), which are complex multifunctional structures, can improve the effectiveness of traditional cancer treatment methods [1]. CBN can act as carriers for the delivery of significant quantities of radionuclides, as well as agents for targeted delivery by attaching various ligands. Various types of CBN, including carbon nanotubes [2], graphene [3], fullerenes [4], have been used to improve radionuclide delivery and even as theranostic systems.

In our study, folic acid (FA) functionalized fullerenes are used as a carrier of the radioactive isotope ¹⁷⁷Lu. FA has been used as a vector for folate receptors (FR) overexpressed by certain types of tumor cells. Polyvinylpyrrolidone (PVP) was used as a biocompatible linker that increases the solubility of fullerene and FA in water.

The synthesized FA-PVP-C₆₀ conjugate has the parameters necessary for use in therapy or diagnostics, namely, it has good biocompatibility and stability both in aqueous solutions and in culture media containing salts, amino acids, proteins and other components of biological fluids. In addition, the increased accumulation of the conjugate in cells with overexpression of folate receptors indicates the possibility of using it for delivery to target cells. At the same time, the accumulation of the drug does not lead to a decrease in the viability of FR-positive cells compared to FR-negative ones, since the conjugate demonstrates the absence of toxicity for the different types of cells used in our study. Despite the fact that our data contradict previously obtained information about the increased toxicity of C₆₀ towards tumor cells, this fact opens up a good opportunity for further modification of the obtained conjugate as a means for photodynamic therapy or as a targeted radiopharmaceutical.

Funding The work is supported by the Russian Science Foundation grant no. 23-73-01085.

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Applications of quantum chemistry for mapping electron transfer pathways in photoinduced DNA repair

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Absorption of UV photons by DNA leads to the formation of photodimers between the adjacent pyrimidine bases which is detrimental for DNA biological function. In some organisms these photodimers are inverted by photolyase enzymes operating by means of photoinduced electron transfer. Photoexcited flavin cofactor of photolyases serves as an electron donor to the photodimers. The quantum yield of the repair reaction is determined by competing forward and backward electron transfer reactions. Studies of photolyases [1] are focused on identifying electron transfer pathways that control the repair quantum yield. Determination of the photolyase 3D structure

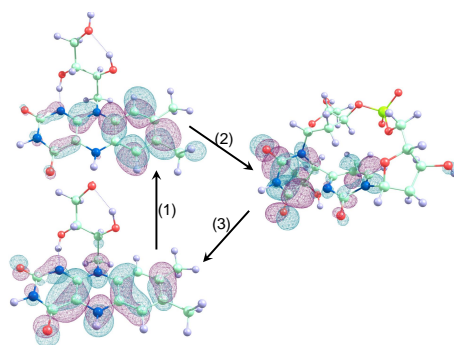


Figure 1: Electron transfer pathways of photoinduced DNA repair. Flavin photoexcitation initiates DNA repair (1), the excited flavin donates an electron to the DNA lesion (2), back electron transfer from the DNA lesion to flavin reduces the repair quantum yield (3). Multireference quantum chemistry calculations provide excitation energies and dipole moments for evaluating electron transfer rates.

initiated computational investigations of the DNA photorepair reactions. One issue to be address by computational studies is evaluation of electron transfer rates to facilitate comparison with experimental findings. We apply multireference quantum-chemistry calculations for characterizing electron transfer between the flavin and DNA lesion (see Figure). In particular, the maximal electron transfer rates are estimated from the excited state calculations with the help of generalized Mulliken-Hush scheme. The obtained maximal rates map the most probable electron transfer pathways and render some previously suggested pathways [1] to be inconsistent with experimental observations. The analysis of maximal rates establishes that energy tuning, e.g. via electrostatic interactions, is crucial for increasing the repair quantum yield. The obtained results pave the way to evaluating controversial proposals and to eventually establishing the mechanism of photoinduced DNA repair by combining computational and experimental results.

Funding The work is supported by the Russian Science Foundation grant no. 22-23-00418.

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Electronic cylindrical waves in nanotubes

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Nanotubes are the nanometer-scale chemical compounds with cylindrical geometry having different compositions and structures. All the single-walled nanotubes can be constructed by rolling up a monoatomic sheet and can differ in their chiralities and diameters. They are currently the focus of intense multidisciplinary studies because of their unique physical and chemical properties and their prospects for practical applications in molecular electronics and spintronics that are perhaps the most intriguing area of nanotechnology. Particularly, the carbon nanotubes are the aromatic conjugated compounds, and theoretical simulation of their electronic structure has received much attention since 1992, when the first calculations for the band structures of all-carbon nanotubes were done using the π -electron tight-binding techniques. We are developing a linearized augmented cylindrical wave (LACW) method for the nanotubes band structure. The LACW method is an extension for the one-dimensional multiatomic systems with tubular structure of the linearized augmented plane wave (LAPW) theory well-known for the bulk materials. Now the LAPW technique and calculations have reached the point at which, with the aid of computers, a solution of the band structure problem may be obtained for particular nanotubes, including those with heavy metals like the gold tubules. The main argument for using cylindrical waves is to account for the cylindrical geometry of the nanotubes in an explicit form that offers the obvious advantages.

Here we give the physical basis and detailed exposition of the LACW method. The experimental detection of spin-orbit gaps in the nanotubes stimulated an interest to the spin-dependent band structure calculations of tubules, and a relativistic version of LACW theory is presented. The nanotubes may have various atomic-scale point impurities, which can appear during the nanotube growth or can be created by external action in order to change the nanotubes composition and properties. Based on the LACW and Green's function techniques, a method for calculating the electronic structure of the point substitutional impurities in nanotubes was developed. This approach is closely related to the Green's function method designed for the point defects in the bulk materials. The LACW method was used to study the electronic structure of double-walled carbon nanotubes and single-walled tubules embedded in a crystal matrix. Similar to the LAPW method, the LACW technique is also applicable to non-carbon inorganic compounds up to the gold and platinum tubules; the calculations of non-carbon systems do not require any new methodical receptions [1].

We demonstrate the results of application of the LACW method to the various carbon and non-carbon, achiral and chiral, pure, intercalated, and doped single-walled, double-walled, and embedded nanotubes and nanowires [1, 2, 3, 4, 5, 6, 7]. These results are used for a deeper understanding of the properties of specific materials and their practical use in nanoelectronics. Particularly, we predict a formation of a Rashba effect in the nonchiral hexagonal and gear-like armchair and zigzag silicon nanotubes (SiNTs) [2]. We determine the spin-dependent band structures as well as the electron and spin transport and formation of magnetic field in the single-walled chiral gold and platinum nanotubes [3, 4, 5, 6, 7]. It is shown that very large electromagnetic fields can be realized in the nano-volumes using the gold nanotubes solenoid nanoantennas and that the eigenfrequencies of field components lie in the x-ray range. We show that spin transport and chirality induce spin selectivity in nanotubes can be controlled by the twisting, stretching, and compression of tubules.

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High resolution infrared spectroscopy as a tool to study the Mars' and Venus' atmospheres

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Mars and Venus are our nearest neighbors and, in contrast to Earth, they have the CO₂ atmosphere (~96%) with other gases, such as Ar, N₂, CO, O₂, H₂O, HCl, O₃, as minor species. The investigation of their climate system, the dynamical phenomena and a composition are in priority of space missions and large ground-based telescopes. The effective tool to decide these tasks is the infrared spectroscopy, benefiting from ro-vibrational spectral bands of atmospheric gases in the IR range.

High-resolution spectroscopy occupies a special place here, since it allows to search trace gases, measure isotopic ratios and study the atmospheric structure. It has a long history of providing the compositional discoveries on both planets. The ground-based telescopes with high resolution spectrometers like CRIRES, TEXES, SCHELL, NIRSPEC and others [1], allowed mapping of water distribution, HDO/H₂O ratio on both planets, H₂O₂ on Mars and SO₂ on Venus, discovered methane on Mars.

The first orbital high-resolution IR spectrometer on Venus was SOIR onboard Venus-Express working from 2006 to 2015 and provided information about vertical distribution of many gases in Venus' mesosphere at latitudes from 70 to 110 km and atmospheric density and temperature [2]. On Mars, the first high resolution IR spectrometers were delivered in frame of Trace Gas Orbiter (TGO) Exomars mission. The Atmospheric Chemistry Suite (ACS) [3] and NOMAD [4] cover the spectral range from visible to long-wavelength infrared and provide 3D spatial distribution and temporal variations of atmospheric constituents from nadir and solar occultation measurements. Among their discoveries: the first detection of HCl and its seasonal variations in the Martian atmosphere, first observation of the magnetic dipole CO₂ absorption band at 3.3 μm, study of carbon and oxygen isotopes in H₂O and CO₂ and seasonal and spatial variations of HDO/H₂O ratio as a tracer of water evolution on Mars, hunting for methane, phosphine and volcanic gases, study of aerosols, thermal structure and water vertical distribution in the wide range of altitudes from troposphere to thermosphere, seasonal cycles of non-condensable CO and O₂.

The success of TGO and Venus-Express has shown that high-resolution IR spectrometers are very effective in studying the atmosphere from orbit. Recently selected new missions to Venus, which plan to be launched next decade, include such kind of spectrometers. VenSpec-H spectrometer for EnVision (the new European mission to Venus) and VIKA, a set of near and mid-IR spectrometers, for Venera-D will continue a study of the CO₂ atmosphere of Venus from its orbit.

Based on the success in the Solar System, the ground-based high-resolution spectrometers are being considered as a promising tool for detecting molecules in atmospheres of terrestrial exoplanets. Together with James Webb telescope (JWST) instruments launched in December 2021 they open new challenges in discovering of exoplanetary atmosphere composition.

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Fractional Fourier Transform and distributions in the phase space

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The concept of the phase space plays a key role in the analysis of oscillating signals. For a 1-D signal, the coordinates of the 2-D phase space are the observation time and the instant frequency. For measurements of propagating wave fields, the time and instant frequency are linked to the spatial location and wave normal, defining a ray. In this case, the phase space is also termed the ray space. Distributions in the ray space find important applications in the analysis of radio occultation (RO) data because they allow the separation of interfering rays in multipath zones. Examples of such distributions are the spectrogram, Wigner distribution function (WDF), and Kirkwood distribution function (KDF). In this study, we analyze the application of the fractional Fourier transform (FrFT) to the construction of distributions in the ray space. The FrFT implements the phase space rotation. We consider the KDF averaged over the rotation group and demonstrate that it equals the WDF convolved with a smoothing kernel. We give examples of processing simple test signals, for which we evaluate the FrFT, KDF, WDF, and smoothed WDF (SWDF). We analyze the advantages of the SWDF and show examples of its application to the analysis of real RO observations.

Consider a generic signal $\psi(x)$ as a function of coordinate x . This signal can be both $u(t)/u_r(t)$ or $\hat{u}(p)$. If the signal is quasi-monochromatic, it can be written as follows:

$$\psi(x) = A(x) \exp \left(ik \int \xi(x) dx \right),$$

where ξ is the momentum conjugated to the coordinate x , and k is the wavenumber in wave propagation problems, or the inverse Planck constant $1/\hbar$ in quantum mechanics. More generally, k is a problem-specific scaling factor. In the general case, the signal is a superposition of quasi-monochromatic signals. The dependence $\xi(x)$ in the simplest case, or the set of dependencies $\xi_j(x)$ for multiple quasi-monochromatic components of the signal, specify the structure of the ray manifold.

In the interpretation of RO data, we have observations of $\psi(x)$ and we need to recover the complicated structure of ray manifold [1, 2]. There are different approaches to this problem. One of them uses the linear representations of wave fields implemented by FIOs [1]: the wave field is transformed into the representation of the impact parameter, which in most cases ensures the single-valued projection of the ray manifold. The other approach uses the non-linear representations of wave fields and operates with the pseudo-density in the whole phase space. The maximums of the pseudo-density follow the ray manifold, regardless of the type of its projection to any specific coordinate axis. In this study, we follow the latter approach.

The distribution function in the ray space is the symbol of the quantum density operator. Because operators $\hat{\xi}$ and \hat{x} do not commute, the symbol depends on the chosen ordering of these operators. If we choose the symmetric, or Weyl ordering, we arrive at the WDF [2, 3]:

$$\rho^W(x, \xi) = \frac{k}{2\pi} \int \psi \left(x - \frac{s}{2} \right) \psi^* \left(x + \frac{s}{2} \right) \exp(iks\xi) ds,$$

where ψ^* is the complex conjugate of ψ . If, however, we choose the $\hat{x}\hat{\xi}$ ordering, we arrive at the KDF [4, 5]:

$$\rho^K(x, \xi) = \sqrt{\frac{-ik}{2\pi}} \exp(-ikx\xi) \psi(x) \tilde{\psi}^*(\xi),$$

where $\tilde{\psi}(\xi)$ is the Fourier transform of $\psi(x)$.

There is a relationship between these two distributions [5]:

$$\rho^K(x, \xi) = \rho^W(x, \xi) * T_W^K(x, \xi), \quad T_W^K(x, \xi) = \frac{k}{\pi} \exp(-2ik\xi x).$$

where the asterisk denotes convolution.

Consider the rotation of the phase space $(x, \xi) \rightarrow (y, \eta)$ by angle α . The corresponding FIO has the following form [5]:

$$\tilde{\psi}_\alpha(y) = \hat{F}_\alpha \psi(y) = \frac{1}{\sqrt{2\pi i \sin \alpha}} \int \exp\left(i \frac{y^2 \cos \alpha - 2xy + x^2 \cos \alpha}{2 \sin \alpha}\right) \psi(x) dx.$$

This transform is termed the fractional Fourier transform (FrFT) [6]. For $\alpha = \pi/2$ it turns into the Fourier transform, and it possesses the group property:

$$\hat{F}_{\alpha+\beta} = \hat{F}_\alpha \hat{F}_\beta.$$

From the tomographic definition of the WDF [2] it follows that it is invariant with respect to phase space rotations:

$$\rho_\alpha^W(y(x, \xi, \alpha), \eta(x, \xi, \alpha)) = \rho^W(x, \xi).$$

Unlike the WDF, the KDF does not possess such a nice property. However, we can consider its averaging over phase space rotations. Then, using the fact that convolution commutes with rotations, we can infer

$$\frac{1}{2\pi} \int_0^{2\pi} \rho_\alpha^K(y(x, \xi, \alpha), \eta(x, \xi, \alpha)) d\alpha = \rho^W(x, \xi) * \frac{1}{2\pi} \int_0^{2\pi} T_W^K(y(x, \xi, \alpha), \eta(x, \xi, \alpha)) d\alpha.$$

The integral in the right-hand part evaluates analytically:

$$\frac{1}{2\pi} \int_0^{2\pi} T_W^K(y(x, \xi, \alpha), \eta(x, \xi, \alpha)) d\alpha = \frac{1}{\pi} J_0(x^2 + \xi^2),$$

where J_0 is the Bessel function. Therefore, the averaging of the KDF evaluated for the FrFTs of the signal, with different rotation angles, results in the WDF convolved with the smoothing kernel, which is close to the Fresnel transform of the WDF [7]. We will denote the smoothed WDF (SWDF) ρ_α^{WK} . Figure 1 shows an examples of processing COSMIC-2 data. We chose RO events with deep penetration, indicating a complicated multipath propagation structure. The analysis was performed in the time domain. For the analysis, we chose the tropospheric part of the signal. COSMIC-2 observations have a sampling rate of 100 Hz. We down-sampled the signals to 50 Hz because in most cases the signal spectrum lies within a 50 Hz band [8]. We plotted the WDF and SWDF in the time–frequency coordinates, where the frequency is understood as the difference between the Doppler frequencies of the measured signal and the reference one. According to the sampling rate, the frequency lies between -25 and 25 Hz. In all the cases, the WDF indicates a

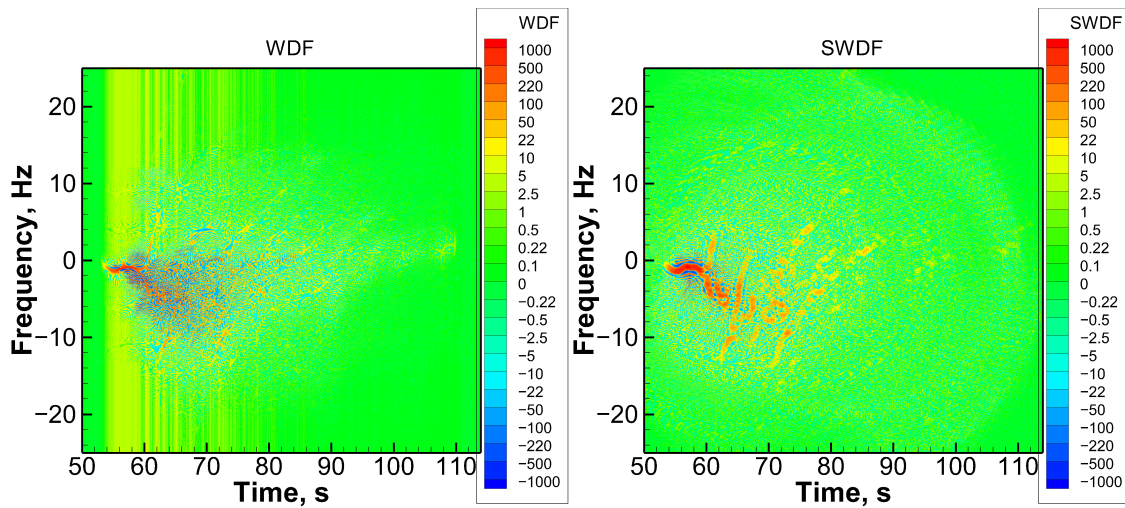


Figure 1: COSMIC-2 setting RO event observed on 15 May 2020 UTC 12:29, 0.65°N 167.78°E. Left: WDF, right: SWDF.

complicated structure, where the ray manifold is traced at a high resolution, but it is mixed with a lot of additional oscillating structures. The SWDF allows a significantly clearer visualization of the ray manifold and suppresses most of the additional oscillating structures. This is achieved at a price of a lower resolution.

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Modern predictive quantum chemical calculations for thermochemistry and kinetics: procedures and limitations

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Highly accurate theoretical values of formation enthalpies, bond energies, and activation barriers of elementary reactions are crucial for reliable quantitative modeling of reaction mechanisms and many related issues (e.g., estimations of the detonation parameters of energetic materials, EM). However, due to the prohibitive computational cost, high-level *ab initio* calculations had been impractical for a large number of "medium-size" molecules, containing dozens of CNOF atoms. The widely used DFT calculations very often could not provide the uniform "chemical accuracy" (~ 1 kcal mol⁻¹) and, ultimately, the convincing mechanistic evidence on the decomposition pathways of important EMs.

Here I will report on the recent methodological advantages in the theoretical thermochemistry and kinetics achieved with the use of novel explicitly correlated (CCSD(T)-F12) and local modifications of the coupled cluster technique (DLPNO-CCSD(T)). The benchmarking on a representative set of EM made in the present work revealed that both approaches do not deteriorate the quality of the coupled cluster procedure. More specifically, we obtained the accurate bond energies for novel promising energetic materials CL-20 and octanitrocubane. These values are ~ 10 kcal mol⁻¹ more accurate than the best available theoretical values so far. In addition, due to the very favorable scaling with the size of the molecule, this level of theory is still affordable, e.g., for the dimers of the latter species. The obtained highly accurate activation barriers and bond energies are particularly useful for benchmarking and calibration of the existing force fields, which are indeed highly desirable for reliable predictions of thermal decomposition and detonation-related phenomena of energetic materials.

As a rule, DLPNO-CCSD(T) allows for routine QZ-quality coupled cluster calculations with reasonable turnaround computational times for the energetic species comprised of ~ 30 -40 non-H atoms. In a more general sense, this offers a new level of predictive computational thermochemistry and kinetics for important EMs. The reliable DLPNO-CCSD(T) key thermochemical values comprise a viable step beyond the commonly used DFT procedures.

We also proposed a new approach for the determination of standard (solid) state enthalpy of formation of EM based on complementary high-level quantum chemical calculations (W1-F12 and W2-F12) of the gas-phase values and advanced thermal analysis techniques yielding sublimation enthalpies. We performed a massive benchmarking of the proposed procedure on a large set of EMs.

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Applying machine learning methods to optimize production processes, identify safety threats and improve management systems

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Currently, the main trend in the development of quality management systems is the digitalization of business processes. Modern digital technologies can significantly improve the effectiveness of many quality management tools. Today, one of the main digital technologies being introduced into production for the purpose of quality control is artificial intelligence technology. The Competence Center for the Quality Management System of the Rostec State Corporation (JSC RT-Tekhpriemka) has the necessary experience and competencies both in the field of quality management in general and in the application of machine learning technologies in particular. The work examines the results of the implementation of projects of the Competence Center in the interests of the largest industrial enterprises and government bodies in Russia. The main result of the work is the substantiation of the need and feasibility of the widespread practical use of classical methods of predictive analytics and proactive management in order to optimize production processes, identify security threats and improve management systems. In comparison with other materials related in topic and purpose, the work contains the results of a system analysis of the subject area of quality management both within the framework of traditional management processes and in terms of the use of end-to-end technologies for effective digitalization and digital transformation, and also provides the results of an analysis of the successful implementation of specific methods of machine learning and artificial intelligence in the practice of functioning of modern industrial enterprises.

Assessing containerisation overhead for running Firefly quantum chemistry program

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Containerisation technology is widely used nowadays in various software stacks including those require high performance from underlying hardware platforms [1, 2]. The Artificial Intellect (AI) and Deep Learning (DL) may be the most vivid examples. The Firefly quantum chemistry program is quite popular in the theoretical chemists community with thousands of users around the world. Unfortunately, Firefly is notoriously difficult to install, as highly-optimized kernel require legacy 32-libraries to work. We hope that containerisation approach can be beneficial to Firefly quantum chemistry program, but the related overhead is an open question. Thus in this work we compare execution time of Firefly for test jobs in both native and containerised environments. It was used computational server with following configuration:

- CPU 2x Intel(R) Xeon(R) CPU E5-2603 v4@ 1.70GHz w/o hyperthreading
- memory DDR4 2133 MHz 128 GB;
- server board Intel(R) S2600WT2R;
- hypervisor VMware ESXi™, client version 1.33.4, ESXi version 6.5.0.

Containerised environment was obtained by Docker containerization system running on 1 or 2 virtual machines (denoted further as vnodes) under Rocky Linux 9 operating system government. The total number of containers within vnodes was 0 for native and 1/2/4/8 for containerised mode. In test series with 2 vnodes, containers were evenly distributed between them. Our Docker image was based on Rocky Linux 9 Minimal image (rockylinux:9.0-minimal) and NLKNguyen:alpine-mpich image [3] from the public Docker repository [4].

Table 1: Mean runtime for tests with fixed input size.

		User+System Time, sec		
		Native	Containerization	Delta
1 vnode	1 MPI-process	73.9 (0.4)	73.8 (0.5)	-0.1
	2 MPI-processes	43.4 (1.4)	42.0 [0.2]	-1.4
	4 MPI-processes	26.5 (1.0)	25 [2.2]	-1.5
	8 MPI-processes	19.5 (1.2)	17.4 [1.9]	-2.1
2 vnodes	2 MPI-processes	42.8 (1.0)	41.7 (0.8)	-1.1
	4 MPI-processes	30.0 (1.4)	27.75 [0.03]	-2.25
	8 MPI-processes	25.1 (1.7)	24 [2.5]	-1.1
Notifications: (...) - standard deviation, <i>sd</i> ; [...] = max – min $\approx 2sd$				

To run our test calculations we used Firefly quantum chemistry software(version 8.2.0/mpich1 for Linux, 32-bit) [5]. As test job we chose optimization of geometry configuration of n-propane molecule by quadratic gradient descent method and DFT/B3LYP5 approximation (basis set 6-31G*, 61 basis set functions). For one series of test runs we fixed the number of optimization steps to 12 and increased it proportionally with a number of MPI-processes in another series (12/24/48/96 optimization steps for 1/2/4/8 MPI-processes, respectively). During test runs all MPI-processes were evenly distributed among containers. We run 32 tests for each meta-parameters combination

such as nodes/containers/MPI-processes. Then we used average numbers for analysis. Time measurements were done with the help of strace profiler and duplicated by Firefly outputs (wall time). Usage of strace profiler functionality allowed us to evaluate the influence of containerization on various quantities which describe runtime process e.g. user and system runtimes or number of system calls. Moreover, our tests show that profiler overhead was negligibly small in comparison to the variance of job execution times. Test job execution times for fixed numerical complexity i.e. for fixed number of optimization steps are presented in the table below. On the Figure 1 we show the graph of execution time respectfully to MPI-process number for two modes (containerised and native), when number of optimization steps increased proportionally to MPI-processes number (weak scaling). The comparison of various quantities, such as mean execution time, standard

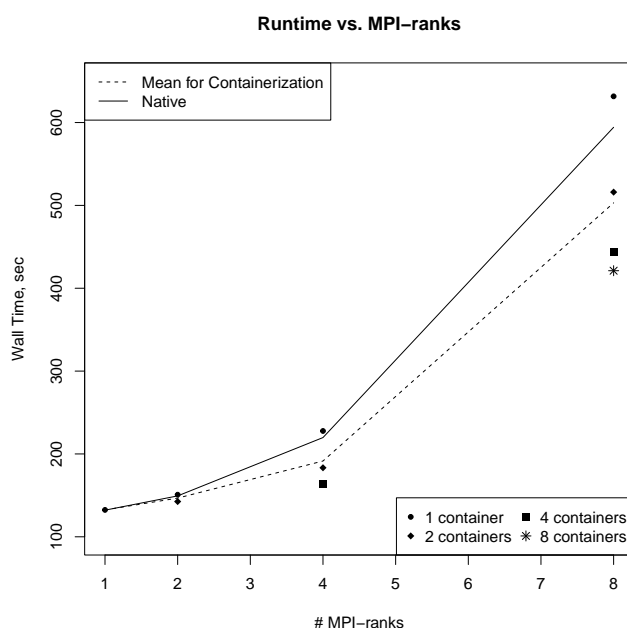


Figure 1: Execution time for scaled input test (1 vnode).

deviation of runtime, system time to wall time ratio and so on, measured for all MPI-processes (i.e. for master rank as well as slave ranks) revealed that in the case of relatively small computational complexity and in the case of parallel multiprocess computation there is no performance degradation of containerised Firefly run versus native Firefly execution. Moreover, choosing the right distribution of containers on nodes it is possible to reduce execution time. We attribute the performance gains to better memory localization and execution of some system calls in user mode by containerised version. Thus we conclude that Firefly can be successfully containerised and take full advantage of simplified software configuration management, resource allocation and capping, as provided by this infrastructure solution.

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Raman spectra induced by binary collisions: retrospective and the current status of research

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In the dipole approximation, the parity-changing transitions in centrosymmetric molecules are forbidden in Raman, but the ban is lifted due to collisions in a real gas. The thus arising intermolecular interactions not only perturb the dynamics of molecular degrees of freedom, but – what is more important for the considered subject – induce additional terms of microscopic polarizability for which the selection rules valid for isolated molecules do not hold. Because of the weakness of the induced polarizability, which is 2-3 decades smaller than the polarizabilities of free molecules, the discovery of Collision-Induced Raman Spectra (CIRS) occurred in 1969, soon after the advent of laser sources. There are two characteristic CIRS features in gas under the binary-collision regime, (1) quadratic scaling of the intensity with density, and (2) anomalously large width of CIRS bands and lines. The second feature is explicable by short collision durations (about one picosecond) when the induced polarizability is distinct from zero. As a result, the CIRS band shapes, like those of collision-induced absorption, provide a direct information on the intracollisional dynamics. This is in sharp contrast with the case of allowed spectra whose transformation with density usually does not require a detailed picture of intracollisional evolution.

The CIRS advancements will be traced and typical spectral patterns will be demonstrated. For a deeper insight into the integrated CIRS characteristics, we are to consider different induction mechanisms of collisional polarizability, with their history amazingly dating back to 1917 (the well-known “dipole-induced dipole” model), i.e., long time ago before the CIRS discovery. Now, thanks to the Feynman diagram method, one can classify and separate all long-range contributions to both induced polarizability and dipole moment casting them into invariant expressions.

Compound-tunable embedding potential method to model local electronic excitations on f-element ions in solids: Study of Ce and Th impurities in yttrium orthophosphate, YPO₄

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Yttrium orthophosphate (mineral xenotime, YPO₄) is characterized by high chemical and radiation resistance and is considered, along with other orthophosphates, as natural analogue of matrices for immobilization of actinides. Due to the high symmetry of the crystal structure of this compound, quantum chemical calculations of its properties, as well as the properties of impurity ions of Cerium and Thorium, require less computational resources and also provide more reliable results that can be analyzed theoretically, compared to other orthophosphates.

For a quantum mechanical study of the states of these impurities in crystals, one need to construct cluster models, since periodic models cannot provide the required accuracy. A cluster model of xenotime using core potentials of a special type [1, 2, 3] was constructed in [4]. The size of this cluster model (on the order of 150 atoms with 300 electrons explicitly included in the calculation) makes it difficult to use precision electronic structure calculation methods such as coupled clusters.

In the present work, a method to simulate local properties and processes in crystals with impurities via constructing cluster models within the frame of the compound-tunable embedding potential (CTEP) and highly accurate ab initio relativistic molecular-type electronic structure calculations is applied to the Ce- and Th-doped yttrium orthophosphate crystals YPO₄. Two embedded cluster models are considered, the “minimal” one, YO₈@CTEPmin [5], consisting of the central Y³⁺ cation and its first coordination sphere of eight O²⁻ anions (i.e., with broken P–O bonds), and its extended counterpart, and Y(PO₄)₆@CTEPext, implying the full treatment of all atoms of the PO₄³⁻ group nearest to the central Y³⁺ cation. CTEPmin,ext denote here the corresponding cluster environment described within the CTEP method. The Fock space relativistic coupled cluster (FS RCC) theory is applied to the minimal cluster model to study electronic excitations localized on Ce³⁺ and Th³⁺ impurity ions. Calculated transition energies for the cerium-doped xenotime are in a good agreement with the available experimental data (mean absolute deviation less than 0.1 eV for 4f→5d type transitions).

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Climate and its forecasting

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What is the climate and what is the difference between climate and weather? Climate is the statistical characterization of the climate system and It represents the average weather over a period of 30 years. Earth's climate system is a complex system with some interacting components such as the atmosphere, the hydrosphere, the cryosphere, the lithosphere and the biosphere. The main driving force of Earth's climate is the Solar radiation. Due to the uneven heating of the Earth's surface occurs circulation in the atmosphere and oceans transports heat from the tropical regions to high latitudes regions. What else is important to know about the climate? We will touch upon such important issues as the Earth's heat balance, greenhouse effect, global warming and its causes, types of climate models, climate forecasting, critical transitions in the climate.

The possibility and expediency of using multiscale modeling to predict and describe the structure and properties of new carbon nanocomposite materials based on polylactic acid for medical purposes

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One of the modern strategies of regenerative medicine and tissue engineering in the field of bone grafting is the use of implants capable of integration with native tissues. Materials being perspective for these purposes should at once show sufficient biocompatibility, antibacterial and anti-inflammatory activity, have suitable mechanical and surface characteristics, and biodegrade to non-toxic compounds in a controlled manner. One of the materials with a number of the named characteristics is polylactic acid (polylactide, PLA), however, its use in the field of bone grafting has limitations associated with its physical and mechanical properties.

Modification of PLA with carbon nanoparticles (fullerenes and their hydrophilic derivatives, related nanocarbons: nanodiamonds of detonation synthesis and graphenes) and ionizing radiation are effective ways to optimize the physico-chemical and biological properties of polylactide, leading to increased hydrophilicity, improved mechanical characteristics, increased antibacterial and anti-inflammatory activity, changes in the degree of crystallinity, and also allowing for a controlled change in the rate of biodegradation. Identifying the dependence of the structure and properties of composites on the composition, method of formation and processing of the materials obtained is a laborious and multifactorial task, and clarifying the exact mechanisms of chemical and biological action of carbon nano-components and their polymer composites often turns out to be inaccessible for experimental research. Computer modeling and simulation of energetically advantageous structural states of nanoparticles, radicals and ions formed from these particles under the influence of ionizing radiation, and the mechanisms of their reactions, to predict the properties of polymer materials with nanomodifiers and the optimal conditions for obtaining and modifying such materials makes it possible to accelerate the development of technologies for the production of medical devices based on such materials. The complexity of modeling carbon nanocomposites based on polylactide lies in their simultaneous belonging to both quantum and macromolecular systems. The solution to this problem can be the use of mathematical multiscale modeling technology [1, 2], which includes the consistent use of a number of methods to describe and predict multi-level systems:

- nanostructures description - density functional theory (DFT), density-functional theory-based tight-binding (DFTB)
- simulation of dispersion of carbon nanoparticles in a polylactide matrix - dissipative particle dynamics (DPD)
- simulation the effects of ionizing radiation - molecular dynamics (MD)
- biodegradation process simulation - the Monte Carlo method

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Direct simulations of ultrafast chemical dynamics with *ab initio* multiple cloning approach

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We present the recent developments and applications of our *ab initio* multiple cloning (AIMC) method [1, 2]. The idea of the method is to run non-adiabatic molecular dynamics using the basis of Gaussian coherent states moving along branching Ehrenfest trajectories, thus combining some best features of Multiple Spawning [3] and Multiconfigurational Ehrenfest approaches [4]. The dynamics is run “on the fly” with energies, forces and non-adiabatic coupling matrix elements provided by electronic structure calculations. The AIMC approach is implemented in NEXMD v2.0 software package [5].

We applied AIMC method to simulate the processes of ultrafast photodynamics in a number of molecular systems, such as photodissociation and vibrationally mediated photodissociation (VMP) of various heterocyclic amines [6, 7, 8] and energy transfer in light harvesting dendrimers [9, 10].

Another area of our simulations is the dissociation of hydrofluorocarbon molecules after electron impact in plasma. Hydrofluorocarbons and other fluoroorganic molecules are used in the microelectronics industry to generate free radicals for plasma etching, one of the main technological processes in microchip production. Although AIMC was originally developed for the simulation of nonadiabatic dynamics of excited molecules in singlet states in photochemistry, it can equally be used for the dynamics of molecules in low-energy triplet states produced by electron impact. We have run the simulations for two hydrofluorocarbon molecules in low triplet states and calculated the reaction channels branching ratios [11]. The calculations appear to yield very simple rules that can be used to predict dissociation channels.

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Chemical bonding in biomolecules

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The report will present the results of the recent theoretical investigations of biomolecules, which have shown that amino acids in them are mutually polarized [1, 2, 3]. An analysis of the charges distribution in entailed biomolecules has been carried out on example of the 1VM2 molecule. For this purpose the natural partial atomic charges as well the Mulliken partial atomic charges in 1VM2 biomolecule have been calculated and the partial charges of amino acids have been introduced as a sum of corresponding partial atomic charges of all amino acid atoms. The mutual amino acid polarization in 1VM2 biomolecule can be clear observed on figure below by comparing the electrostatic potentials calculated in *ab initio* calculation with the similar potential obtained with the Amber atomic charges.

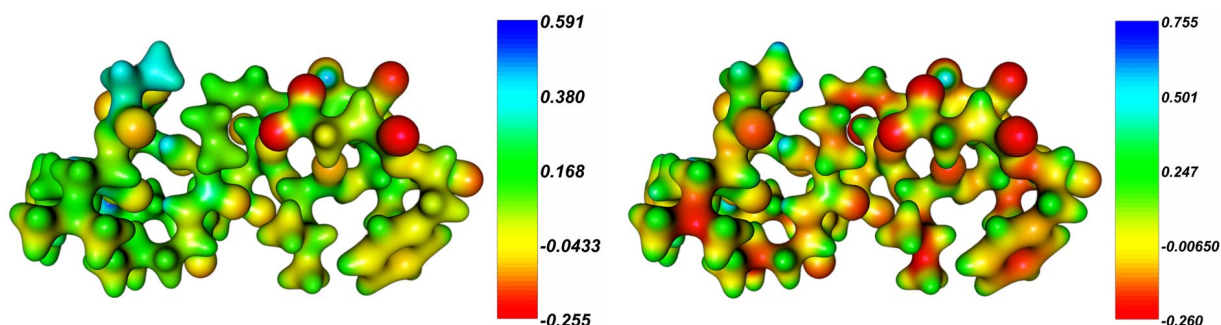


Figure 1: The electrostatic potential calculated with partial natural atomic charges obtained in B3LYP/6-31G** calculations and projected on the corresponding electron density (right) and the similar potential calculated with the Amber atomic charges (left).

The further investigations of the chemical bonding in biomolecules demonstrate that the total energy and the enthalpy of chemical bond breaking in biomolecules exceed the corresponding values in other molecules. This fact has been demonstrated in B3LYP/6-31G** calculations of C-N bond breaking between the amino acids for different blocks of 1VM2 biomolecule.

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Microelectronic technology trends and numerical simulation tools

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While numerical simulation necessity was a primary reason for the modern computer architecture inception, today's computers are mostly used for other applications. Moreover, numerical simulations are insufficient to financially justify development of specialized computational devices in the context of rapid technology development during the last decades (so called Moore's law [1]). Over the last 30 years, we witnessed numerical simulations conducted on devices, primarily targeted at various broad commercial markets. The latest shift is to General Purpose Graphic Processing Units (GP-GPUs). This family of architectures evolved from gaming personal computer (PC) industry to vehicles behind the most recent artificial intelligence (AI) boom. From a point of view of computational chemist, doing some complex modeling, this recent development gives mix of opportunities and challenges. On one hand, modern GPU can elicit, theoretically, hundreds of trillions of operations even for a humble devices, but at the cost. Its needed to re-write old software for CPU-GPU tandem, support some new floating point number formats and abide to more complex memory constraints. The 64-bit precision floating point numbers cannot be considered as supported seamlessly by hardware. Memory hierarchy may now include performant high bandwidth memory (HBM) with low latency, traditional DDR/GDDR and/or even some non-volatile segments.

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Tiny-core generalized relativistic pseudopotentials for extremely accurate electronic structure calculations

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Both the valence and several outercore shells of the considered atom are explicitly treated in calculations with the tiny-core generalized relativistic pseudopotentials (TC-GRPP) [1]. Only very deep-lying innercore shells are excluded from the TC-GRPP calculations that together with exclusion of the small components of Dirac spinors results in significant computational savings for the TC-GRPP calculations in comparison with the case of using Dirac-Coulomb Hamiltonian. Moreover, the TC-GRPP method allows one to take into account with sufficient accuracy the contributions of Breit interactions, Fermi nuclear charge distribution, the self-energy and vacuum polarization diagrams of the quantum electrodynamics (QED) [2]. In the present work, the TC-GRPP is constructed for the case of 60 explicitly treated electrons of the Yb atom and 10 excluded innercore ($1s^2 2s^2 2p^6$) ones. The contributions of various effects and errors of the TC-GRPP are demonstrated in the Table. It is planned that the generated TC-GRPP will be used in the most accurate calculations of electronic structure for low-lying states of the YbF molecule needed for analysis of systematic errors in experiments to search for a hypothetical electric dipole moment of the electron on this molecule as a particular phenomenon of New physics.

Nonrelativistic configuration	TE from HFDB (Fermi, QED)	QED contribution	Finite nucleus contribution	Breit contribution	TC-GRPP error
$\dots 4f^{14}6s^2 \rightarrow$					
$\dots 4f^{14}6s^1 6p^1$	15296	-47	-9	-3	0
$\dots 4f^{14}6s^1 5d^1$	23014	-62	-11	-53	-2
$\dots 4f^{13}6s^2 5d^1$	5851	161	21	806	31
$\dots 4f^{13}6s^2 6p^1$	9512	219	30	913	32
$\dots 4f^{13}6s^1 5d^1 6p^1$	23729	100	10	798	32

Table 1: The transition energies (TE) between the states of ytterbium averaged over the nonrelativistic configurations from Hartree-Fock-Dirac-Breit (HFDB) calculations with accounting for the QED effects and Fermi nuclear charge distribution, the various contributions to them, and the TC-GRPP errors (in cm^{-1}).

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Seamless multilayer (SML) formulation of hybrid QM/MM approach and its application to inorganic oxide compounds

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In this work we provide general formulation of a multi-layer approach combining different methods of computational chemistry in a description of the same system. Our general formulation covers both additive and subtractive QM/MM as special cases. After that we suggest a novel definition of QM/MM total energy based on the consideration of a system divided into three layers. In a simplified form it is

$$E = E_{QM}(1 + 2; \phi_3) - E_{QM}(2; \phi_3) + E_{MM}(2 + 3; \phi_1)$$

where layers 1, 2 & 3 represent inner QM, outer QM and classical MM regions, while electrostatic potentials ϕ_1 and ϕ_3 are created by regions 1 and 3, respectively. The novel formulation also is not limited by only QM/MM combination of methods - in fact, any computational methods can be combined in a hybrid calculation. In this paper we call the new approach Seamless Multi-Layer (SML).

In this work, we applied a new approach to quartz glasses synthesized from quartz and cristobalite to identify their structural differences and memory effect. Test calculations performed for silica and boric oxide show that new approach requires no QM/MM interface parametrization as well as no or very simple correction terms for boundary atoms. However, calculations of α -Al₂O₃ show that for ionic compounds the new method requires some additional development.

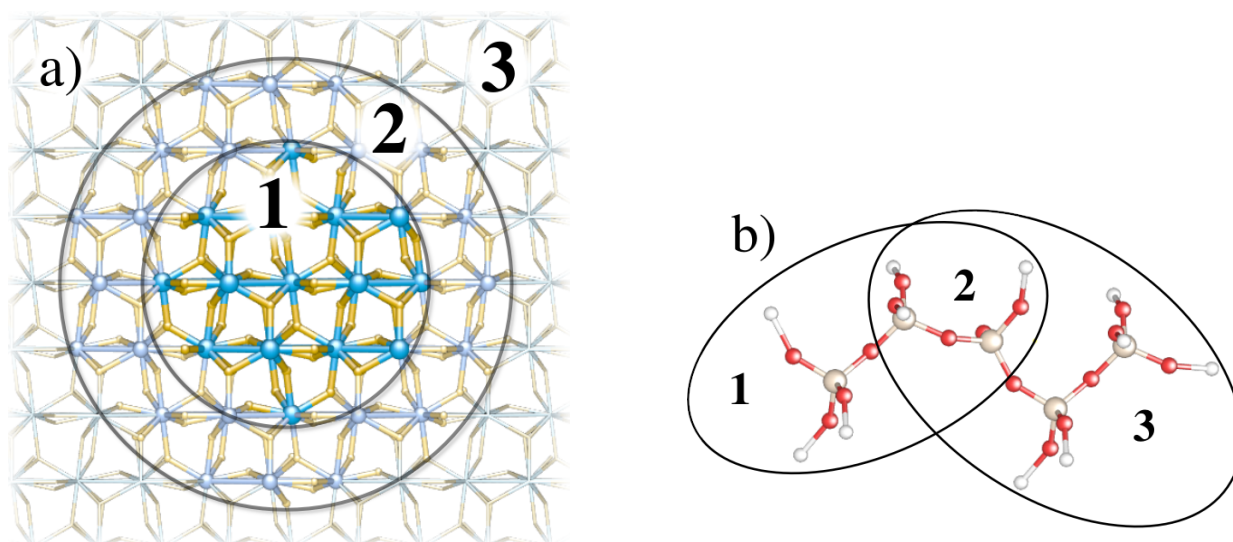


Figure 1: Schematic view of system division: a) solid state; b) linear molecules.

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Femtosecond laser spectroscopy of primary events of charge separation in photosynthetic centers

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The application of femtosecond laser spectroscopy to the study of PS I and PS II photosystems containing Chl d, Chl f chlorophyll molecules made it possible to reveal new features in the mechanism and kinetics of light quantum transformation into chemically active radical ion states. Experiments were carried out on native reaction centers and PS I reaction centers with amino acid substitution by point mutations. By adjusting the wavelength of the pump pulse, changes in the initial excited state were achieved in the complex system of pigments included in the reaction center. The dependence of the femto- and picosecond dynamics of the transient absorption spectra on the initial excitation state has been studied. A model of primary charge separation in PS I according to the adiabatic electron transfer mechanism is proposed. The spectral features of Chl d and Chl f, which differ significantly from Chl a, as well as the known structural data on the localization of Chl d and Chl f in photosystems, made it possible to determine the kinetics and sequence of elementary acts of energy and electron transfer in PS I and PS II photosystems.

Vibrating quantum fields — the foundation of the universe

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Quantum field theory (QFT) represents a revolutionary fusion of quantum mechanics and the theory of special relativity, fundamentally altering our understanding of the forces of nature. Breaking free from the confines of classical physics, QFT has opened new horizons in the study of atoms and elementary particles. Despite long-standing struggles with absurd infinities in calculations, the solution found not only resolved this issue but also enriched our understanding of the nature of mass and electric charge. This lecture will highlight the key developments in QFT, emphasizing its triumphs and challenges.

Exohedral and endohedral complexes of the C₆₀ fullerene with boron and beryllium – optimal configurations and the potential barriers for penetration

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Novel carbon nanomaterials such as graphene and endofullerenes continue to attract much attention of researchers from various scientific fields. This is related to fundamental aspects of their characteristics, and also, is certainly driven by numerous possible applications in physics, chemistry, material science and biology. One of the discussed application is to use boron-containing endofullerenes for the boron neutron capture therapy (BNCT) in oncology treatment. Aiming at that goal, in the presentation, I will discuss various conformations in the exohedral and endohedral molecular complexes of boron and beryllium with the C₆₀ fullerene, studied on the basis of ab initio molecular calculations. In particular, we have studied theoretically the bound states of one and two boron atoms in the exohedral and endohedral C₆₀ fullerene. The optimal position of one boron atom is found above the midpoint of the C₆₀ double bond in the exohedral complex, and at the center of C₆₀ or below a carbon atom in the endohedral complex. However, the optimal position of a boron atom is often altered when the second boron atom is added to the molecular complex. Remarkably, some of these optimal arrangements have different spin states: in the exohedral complex B₂C₆₀ S = 1, in the endohedral B₂@C₆₀ S = 2 (as in the isolated B₂ molecule) The effective (Bader) charge of boron in these configurations varies appreciably – from 0.06e at the center of C₆₀ to 2e in the B₂C₅₈ molecule with two boron atoms substituting for two carbon atoms in C₆₀.

We have also studied the potential barriers for the penetration of atomic beryllium or boron inside the C₆₀ fullerene by performing ab initio density functional theory (DFT) calculations (including the dispersion interaction) with three different variants for the exchange and correlation: B3LYP (hybrid functional), PW91 and PBE. Four principal trajectories to the inner part of C₆₀ for the penetrating atom (i.e. Be or B) have been considered: through the center of six-member-carbon ring (hexagon), five-member-carbon ring (pentagon), and also through the center of the double C-C bond (D-bond) and the center of the single C-C bond (S-bond). Averaging over the three DFT variants yields the following barriers for beryllium penetrating inside a deformable fullerene: 3.2 eV (hexagon), 4.8 eV (S-bond), 5.3 eV (D-bond), 5.9 eV (pentagon). These barriers correspond to the slow and adiabatic penetration of Be, in contrast to the fast (non-adiabatic) penetration through the rigid cage of C₆₀ resulting in 5.6 eV (hexagon), 16.3 eV (pentagon), 81.8 eV (S-bond) and 93.4 eV (D-bond). The potential barriers for the boron penetrating inside deformable/rigid C₆₀ are: 3.7/105.4 eV (D-bond), 4.0/86.8 eV (S-bond), 4.7/7.8 eV (hexagon), 6.8/14.0 eV (pentagon). The binding energy of both Be@C₆₀ and B@C₆₀ is negative ($E_c < 0$), which implies that the potential barriers for Be and B escaping from the inner part of C₆₀ are higher by the value of $-E_c \sim 0.84$ eV for Be and ~ 0.81 eV for B. The considerable reduction of the potential barriers for the deformable fullerene is ascribed to the formation of the corresponding Be-C and B-C bonds. We discuss the difference between the lowest barriers for Be and B, compare three variants of DFT, and analyze the role of the dispersion interaction.

The pilot application of the CCSD (Coupled Cluster Singles and Doubles) method for calculating the structural parameters of perovskites using the Compound-tunable Embedding Potential method

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Perovskites have proved themselves to be materials with unusual physical and chemical properties. For instance, BaTiO₃ perovskite has a high permittivity, and many microelectronics have already been developed based on it. A little over ten years ago, solar panels started to be developed based on perovskite materials. These panels have a much higher efficiency than traditional silicon panels and their production cost is much lower. However, the lifespan of these batteries is still not long enough.

One of the important applications of BaTiO₃ in this work was the use of spectroscopic experiments based on Ba_{0.5}Eu_{0.5}TiO₃ crystals to measure the electric dipole moment (EDM) of electrons [1]. To process the results of these experiments, it is necessary to have fairly accurate information about the electronic structure near the core of the heavy core being studied. Therefore, theoretical studies of the various properties of perovskites, including optical properties, are a very urgent task in the search for new and effective technological solutions based on them.

The most accurate way to reproduce the electronic structure of a specific area of a crystal is through quantum chemical calculations using the technology of the CTEP [2].

In this work, the geometry of the BaTiO₃ crystal was calculated using the DFT-PBE0 method. Minimal clusters (TiO₆)⁸⁻@CTEP and (BaO₁₂)²²⁻@CTEP were constructed with high precision fragment reproduction. The relaxation of the cluster geometry was calculated using DLPNO-CCSD.

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Recent advances in relativistic coupled cluster methods for open shell states

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Relativistic coupled cluster (RCC) theory, including its multi-reference formulations for accessing electronic states of open-shell systems, seems to be a promising background for high precision *ab initio* modeling of electronic structure and properties for low-lying states of systems containing heavy atoms. In particular, the version of the method formulated for the Fock space (FS RCC) [1] has proven itself to be a highly effective tool for obtaining information about excitation energies and transition probabilities, allowing this method to be routinely used as an auxiliary tool in molecular spectroscopy. To increase the accuracy of modeling of atomic and small molecular systems the versions of the FS RCC theory accounting for connected triple excitations in the cluster expansions were proposed and implemented and the importance of these high-order correlation effects was demonstrated for several examples [2]; their inclusion allowed us to decrease the error in excitation energies to nearly 100 cm^{-1} for all the studied cases. Such an outstanding accuracy became possible after the introduction of generalized relativistic pseudopotentials accounting for the most of subtle effects, e.g. quantum electrodynamics corrections, into the practice of *ab initio* modeling. Several recent applications of the developed theoretical models and corresponding software are to be highlighted, including calculations of electronic states of small molecules (ThO, AcF) and probabilities of *E1* transitions between these states; the obtained data made it possible the first experimental spectroscopic study of the AcF molecule. The other direction of our work concerned the extension of the scope of applicability of FS RCC to localized properties of solids. Results of the pilot application of the RCC theory to model local excitations at the Ce^{3+} and Th^{3+} impurity centers in the crystalline matrix of the mineral xenotime YPO_4 [3] are to be discussed. Finally, we focus on several other formulations of multireference coupled cluster theory which seem to be promising as alternative tools suitable for the most hopeless situations including several (more than three) open shells. These alternative ways are analyzed in terms of their computational efficiency, potential scope of applicability and classes of electronic states available for modeling within these approaches.

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Search for new physics in molecules

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The non-zero electron electric dipole moment (*eEDM*, d_e) value measured at the level of the current experimental sensitivity would be a clear signature of the physics beyond the Standard model (SM) [1]. Recently the JILA group has obtained a new constraint on the *eEDM*, $|d_e| < 4.1 \times 10^{-30} e \cdot \text{cm}$ (90% confidence) [2, 3] using the $^{180}\text{Hf}^{19}\text{F}^+$ ions trapped by the rotating electric field. It further improves the latest ACME collaboration result obtained in 2018, $|d_e| < 1.1 \cdot 10^{-29} e \cdot \text{cm}$ [4] by a factor of 2.4 and the first result $|d_e| < 1.3 \times 10^{-28}$ on the $^{180}\text{Hf}^{19}\text{F}^+$ ions [5] by a factor of about 32.

The main goal of our work [6, 7] is to calculate energy spectrum of the ground rotational level of the $^3\Delta_1$ electronic state at presence of external variable electro-magnetic field and to compare it with the experimental data. The agreement between the measured and calculated values is a good test for examination of possible systematic uncertainties. For example, at the first stage of the $^{180}\text{Hf}^{19}\text{F}^+$ experiment the disagreement between calculations and experiment led to a conclusion about the existence of a large “doublet population background” systematic error [5]. Then it was shown in Refs. [8, 9] that the disagreement between calculation and experiment in Ref. [5] is on the level of interactions with $^3\Pi_{0\pm}$ and $^3\Delta_2$ states which were not taken into account and new advanced scheme which included all the perturbations important for the *eEDM* spectroscopy was proposed. However, the previous experimental data were not accurate enough to check our method. Excellent agreement of our new calculations [6, 7] with new highly accurate experimental data [2, 3] resolves the problem, declare the accurate theoretical tool and give prospect to control the systematics on the level of $10^{-31} e \cdot \text{cm}$ and lower for the HfF^+ (and similar systems like ThF^+) experiment.

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Uniqueness of spin $1/2$

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This lecture discusses the historical background of spin experiments and associated hypotheses. The unexpected appearance of spin $1/2$ in the context of a relativistic electron wave equation is analyzed. We question the direction of spin and investigate the theorem on the largest projection of spin $1/2$. We then cover the theory of generalized angular momentum, specifically, the case of orbital momentum and spin $1/2$.

The information-entropy concepts in chemistry

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The information entropy h was introduced to theory of information and communication by the pioneers of the field, Claude Shannon and Ralph Hartley in the first part of XX century. It is defined as:

$$h = - \sum_{j=1}^n p_j \log p_j$$

and describes the complexity of a message made up with n symbols, which appear in the message with probabilities p_j . The p_j values are also called statistic weights of the symbols in the message. If the base of logarithm equals two, the information entropy is expressed in bits. Mathematically, the above equation relates to the set of elements that could be divided into the nonintersecting subsets. In this sense, p_j are called the cardinalities of the subsets. The information entropy in the original and modified forms entered chemical sciences but chemical audience in general is non-familiar with the title concepts. The talk is devoted to different ways of applying the information-entropy concepts to solving chemical problems. These applications deal with quantifying chemical and electronic structures of molecules, signal processing, structural studies on crystals, and molecular ensembles. Advances in the mentioned fields make information entropy a central concept for interdisciplinary studies on digitalizing chemical reactions, chemico-information synthesis, crystal engineering, as well as digitally rethinking basic notions of structural chemistry. In general, the applications of the h -based quantities become efficient when describing chemical objects and chemical phenomena have probabilistic nature or representable as the sets. The report is based on the published and upcoming reviews [1, 2].

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Quantum electrodynamics effects in heavy atomic systems

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The present status of quantum electrodynamics (QED) theory of heavy atomic systems is reviewed. It is demonstrated that ab initio QED calculations for these systems and their comparison with available experimental data can provide tests of QED at strong fields and determination of fundamental constants. As an alternative to the ab initio QED approach, the model QED operator can be used. This operator allows one to evaluate the QED effects on the binding energies in cases when the use of the ab initio methods becomes extremely difficult. In particular, it can be applied to evaluate the QED effects in molecules.

Recent progress on studying QED effects in supercritical Coulomb field is also discussed. The supercritical Coulomb field can be created in slow collisions of two nuclei with the total charge number larger than the critical value, $Z_1 + Z_2 > Z_c = 173$. In this field, the initially neutral vacuum can spontaneously decay into the charged vacuum and two positrons. Detection of the spontaneous emission of positrons would be the direct evidence of this fundamental phenomenon. However, the spontaneous positron emission is generally masked by the dynamical positron emission, which is induced by a strong time-dependent electric field created by the colliding nuclei. For many years it was believed that the vacuum decay can be observed only in collisions with nuclear sticking, when the nuclei are bound for some period of time due to nuclear forces. But to date there is no evidence for the nuclear sticking in such heavy-ion collisions. In our recent papers [1, 2, 3, 4], it was shown that the vacuum decay can be observed without any sticking of the nuclei. This can be done via measurements of the pair-production probabilities or the positron spectra for a given set of nuclear trajectories. The results of this study will be presented in the talk.

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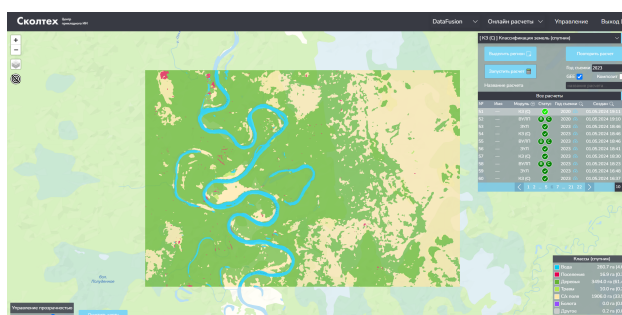
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Computer vision methods for multimodal data processing and solving remote sensing tasks

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Artificial intelligence (AI) methods have widely spread and shown efficiency in solving different problems over the last few years. It has become easier to apply AI methods across various domains due to the availability of a variety of frameworks that include implementations of state-of-the-art architectures, training pipelines, and labeled datasets. The remote sensing domain is no exception; recently, computer vision and machine learning algorithms in this field have demonstrated practical advantages over traditional methods for remote sensing data analysis. One of the most significant advantages is that machine learning methods enable the automatic processing of large amounts of data, leading to the ability to analyze more territories with reduced labor. Another benefit is that machine learning methods can identify non-obvious, nonlinear spatial and spectral dependencies in data, providing more information about objects or analyzed surfaces. These methods can also work with multispectral and hyperspectral data, automatically identifying the best spectral combinations that characterize target objects, enhancing their detection or segmentation capabilities. These advantages are crucial for Earth remote sensing tasks due to the vast amount of data that needs processing and the use of multispectral sensors in satellite technology. However, there are still limitations in applying machine learning to remote sensing data analysis. Firstly, there is a limited amount of labeled and open-source data available in the remote sensing domain, which hinders the training of complex models that require a high volume of relevant and representative data. This limitation also poses challenges for rare object detection. Another limitation is the availability of high spatial resolution data, typically at 1-2 meters per pixel or less, which is essential for accurately detecting and segmenting small objects like buildings, power lines, and roads. Additionally, utilizing multimodal data to analyze and predict environmental events, such as using satellite remote sensing data for weather forecasts, presents another challenge. In our research, we address these issues and challenges in solving practical problems. We demonstrate advanced image augmentation algorithms for synthesizing labeled data, super-resolution algorithms to enhance satellite data resolution, and multimodal data processing techniques to tackle real-world tasks. Our focus is primarily on environmental monitoring and predicting natural hazards, including monitoring surface and forest characteristics, carbon balance monitoring, infrastructure monitoring, fire spread prediction, and flood monitoring. These solutions are integrated into a single framework, and we have developed a web platform for easy access to these implementations.



Web platform DataFusion for environmental monitoring.

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An overview of trajectory guided coherent state basis sets methods of quantum dynamics with examples of applications in photochemistry and in physics

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Experiments in chemistry can now probe the dynamics of ultrafast photochemistry with femtosecond resolution. On the other hand, theory is now able to simulate quantitatively ultrafast photochemistry on the time scale of few picosecond solely from the first principles. *Ab initio* Multiple Cloning (AIMC) [1] approach uses the ensembles of Gaussian wave packets, also called Coherent States, to represent nuclear basis functions, and the electronic structure to describe potential energies of several excited electronic states. The nuclear basis functions are moving in a manner similar to classical molecular dynamics, but with the difference that an ensemble of Ehrenfest trajectories is used instead of a single classical trajectory [1]. With the appropriate sampling and branching techniques they can yield well converged results for molecules with tens of vibrational degrees of freedom treating all them on a fully quantum level [2]. Although the AIMC is similar in spirit to other methods that use trajectory guided Gaussian wave packets, such as *Ab initio* Multiple Spawning (AIMS) [3] and variational Multiconfigurational Gaussians (vMCG) [4], the difference is that AIMC pays particular attention to the way how trajectories are guided and sampled. AIMC has been benchmarked on a number of models and, most importantly, on the experiment yielding accurate description of many features of ultrafast photodissociation observed experimentally. The methods that use trajectory guided Gaussian wave packets developed for simulations in chemistry are now migrating to physics, where they are used to simulate the dynamics of ensembles of Bose particles described by second quantisation Hamiltonians [5] or the dynamics of electrons in a strong field [6, 7]. Other types of Coherent States, such as Coherent States of two level systems, can be used to describe fermions and to obtain Born-Oppenheimer electronic energies and coupled qubits [8].

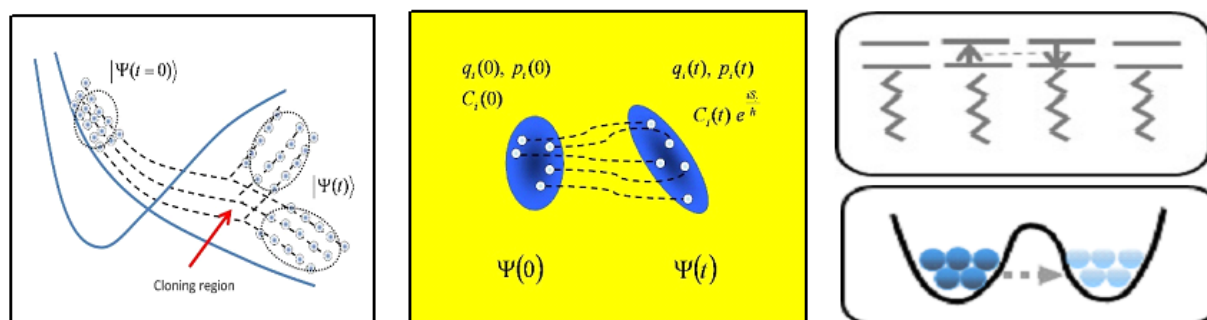


Figure 1: Trajectory guided basis sets in the middle can be applied to simulations of nonadiabatic dynamics in chemistry and for simulations in physics.

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Intermolecular Coulombic decay – an ultrafast intermolecular energy transfer mechanism. The case of biologically relevant systems

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In general, ionization of molecules results in the excited states of cation-radicals. The subsequent de-excitation allows for multiple relaxation scenarios as the system attempts to reach the energetically preferable electronic state. If the possessed single ionization energy is higher than the lowest double ionization potential of the system, the emission of an additional (secondary) electron is possible. This process can efficiently compete with fluorescence and internal conversion, which dominate in the lower energy region. In the case of a single molecule, such relaxation corresponds to the classical Auger decay, while the presence of neighbors can substantially change the scenario, introducing the number of alternative nonlocal electronic decays. One of such mechanisms is called intermolecular Coulombic decay (ICD) and occurs when the energy released by the relaxation of the inner-valence vacancy induces the emission of a secondary electron from the neighboring molecule. This results in the formation of a low-energy electron (LEE) and two cations, which typically undergo a Coulomb explosion. The ICD was first proposed theoretically by L. Cederbaum and coworkers in 1997 and later was discovered experimentally. Studies over the past two decades have revealed that ICD is a general effect that is operative from the extreme quantum system of the He dimer to water, biomolecules, systems in cavities, and quantum dots [1].

An overview of recent achievements concerning ICD in biologically relevant systems will be given, including results of our theoretical studies performed in collaboration with experimental groups, confirming the manifestation of ICD in hydrated biomolecular fragments [2] and between organic molecules [3]; revealing the potential of the ICD as a sensitive tool for the structural imaging of molecular complexes [4]; uncovering the relationships between intermolecular donor-acceptor interactions and the probability of competing relaxation mechanisms [5].

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Studying the magnetic properties of nuclei using atoms and molecules

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Molecules and atoms can be used for precision measurements of nuclear properties, such as magnetic dipole, electric quadrupole and other moments. These fundamental properties of nuclei are necessary for solving various atomic problems, developing the theory of nuclear structure, etc. In [1], a strong discrepancy was discovered between the theoretical prediction [2] of hyperfine splitting in highly charged ^{209}Bi ions and experiment. This discrepancy is called the "puzzle of the hyperfine structure of bismuth". We have established [3] that the reason for the discrepancy is the incorrect reference value of the magnetic moment of the ^{209}Bi nucleus. To solve this problem, we have developed a fully relativistic approach to calculating the shielding constants needed to extract magnetic moment values from data from NMR experiments on heavy element compounds. This approach was further applied to refine the magnetic moments of the ^{207}Pb [4], ^{185}Re , ^{187}Re nuclei. In [5], we were the first to take into account the contribution of the finite nuclear magnetization distribution effect to the shielding constant and showed that this effect can be more important than the solvent effect. In Ref. [6] we showed that it is possible to calculate and observe not only the effect of the interaction of the nuclear magnetic moment with electrons in the molecule (hyperfine structure), but also a more delicate effect of its distribution within the nucleus. This has been recently confirmed experimentally [7].

In [8], we proposed a new method for measuring the anapole moment of a nucleus. This nuclear moment arises as a result of violation of spatial parity symmetry P in intranuclear interactions and was measured only once about 27 years ago. The approach is based on measuring the P-violating contribution to the spin-spin interaction between the nuclei (J-coupling) of the molecule. The theoretical method we have developed is the most accurate for solving the problem of interpreting this experiment in terms of the anapole moment of the nucleus.

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First-principles molecular dynamics models of electronic excitations in dense media

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To solve a large number of physical, chemical and materials science problems, methods for calculating the electronic structure of crystalline and disordered solids from first principles are required. The report will describe the difficulties that arise when using such approaches to describe the properties of such dense media, taking into account the effects of electronic excitations. The complexities of describing nonadiabatic coupling between the electronic and ionic subsystems will be illustrated. As examples, applications to first-principles molecular dynamics of methods such as finite-temperature density functional theory (FT-DFT), wave packet molecular dynamics (WPMD), and restricted open-shell Kohn-Sham (ROKS) will be discussed.

Time-resolved broadband two-dimensional spectroscopy with ultrashort pulses in the visible and mid-infrared

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Two-dimensional Fourier-transform infrared (2D-FTIR) spectroscopy is most widely used to analyze the dynamics of complex organic compounds, in particular, new types of molecular markers used in the analysis of biological complexes. Two-dimensional IR spectroscopy makes it possible to obtain information about the environment of proteins reflected in a two-dimensional line shape, to measure the characteristic times of excitation transfer from one vibrational mode to another, to distinguish between solvent affected and disordered proteins, and to increase the spectral resolution due to the so-called off-diagonal cross-peaks. For example, new features of the relationship between the vibrational degrees of freedom in nucleic acids were discovered with 2D-FTIR spectroscopy. The high temporal resolution of the technique allows analyzing the dynamics of peptide folding and protein oligomerization, including the technique of labelling cells with the carbon-13 isotope.

Here we present a versatile laser platform for time-resolved broadband 2D spectroscopy using ultrashort pulses in visible and mid-IR range [1, 2]. The Ti:Sapphire based laser source generates optically synchronized pulses in visible, near- and mid-infrared range with a duration of less than 60 fs and a wavelength tunable in the range of 0.4 – 10 μm . Additional pulse compression methods based on bulk materials and hollow photonic-crystal fibers are developed to decrease pulse duration up to single cycle [3, 4], this broadband radiation then can be used to directly excite and/or probe electronic and vibrational degrees of freedom, which in combination with the heterodyne detection technique implemented in the mid-IR range, open up possibilities for studying ultrafast dynamics of molecular coherence, as well as ultrafast population kinetics and energy exchange between different degrees of freedom in a wide class of complex molecular systems (fig. 1).

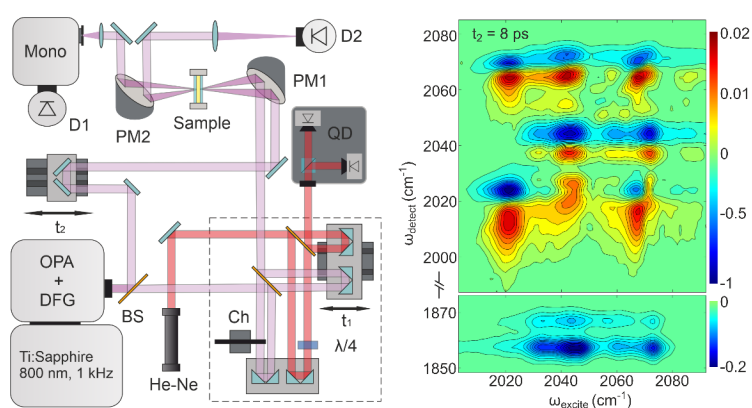


Figure 1: (Left) Schematic of a two-dimensional IR spectrometer; (right) two-dimensional IR spectrum of dicobalt octacarbonyl measured for a delay $t_2 = 8$ ps.

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Analytical capabilities of the diatomic quantum defect theory

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Analytical properties of the quantum defect theory (QDT) in modelling the structure and dynamics of atomic Rydberg's states within the experimental accuracy are well-known [1]. The propagation of the QDT framework into diatomic molecules [2] has overcome an inevitable breakdown of the Born-Oppenheimer (BO) approximation for highly excited molecular rovibronic states in a vicinity of ionization threshold. The original QDT concept is found to be very useful in solving the particular quantum-chemical problems such as constructing effective core potentials (ECP), core polarization potentials (CPP) and diffusive atomic basis suitable for Rydberg's electronic states. Furthermore, the QDT modelling is naturally complementary to conventional multi-electron calculations based on a variation principle since the QDT reliability is expected to be generally increased as the electronic excitation and angular momentum of Rydberg's electron increase.

The effective quantum numbers $\nu_i(R)$ and quantum-defect function $\mu_{l\Lambda}(R)$ internuclear distance R , determining all key properties of the diatomic QDT machinery, could be derived from the BO potential energy curves $U_{nl\Lambda}^{BO}(R)$ *ab initio* calculated for the n -th lowest members of the molecular Rydberg's series:

$$\mu_{l\Lambda} = n - \nu_i; \quad \nu_i = \frac{1}{\sqrt{2(U_+^{BO} - U_{nl\Lambda}^{BO})}}$$

Alternatively, the $\mu_{l\Lambda}$ values corresponding to the high angular momentum l states can be estimated analytically by using of the *ab initio* polarization potential for the molecular cation.

The unique behaviour of the Rydberg electronic wave function inside and outside of a core region provides the amazing analytical capabilities of the QDT. Within the framework of single-channel QDT approximation the closed expressions were invented, for instance, for radial B_{ij} , angular L_{ij}^{\pm} and electronic coupling matrix elements [3] between Rydberg's diatomic states

$$B_{ij} = \frac{d\mu_{l\Lambda}/dR}{\nu_j - \nu_i}; \quad L_{ij}^{\pm} = \frac{\sin(\pi(\nu_i - \nu_j))}{\nu_i - \nu_j} \sqrt{l(l+1) - |\Lambda|(|\Lambda| \pm 1)}$$

along with their adiabatic corrections and regular non-adiabatic energy shifts [4]. These formulae have been implemented for the lowest $^3\Sigma_u^+$ and $^3\Pi_u$ states of molecular hydrogen isotopomers. A fraction contribution of the embedded continuum Rydberg's states into both adiabatic correction and non-adiabatic shifts was established. The modelling QDT results are thoroughly compared with their *ab initio* and experimental counterparts available in a literature.

Funding The work is supported by the Russian Science Foundation (RSF) grant No.23-13-00207.

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Hyperfine structure in the microwave spectrum of (*para*)-NH₃-(*ortho*)-H₂ van der Waals complex

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The spectra of the NH₃-H₂ complex provide detailed information on the NH₃-H₂ potential energy surface, which is of astrophysical interest for accurate modelling of the collisional excitation of ammonia in interstellar clouds. In the previous study the pure rotational (end-over-end rotation) spectra of two nuclear spin isomers, namely (*o*)-NH₃-(*o*)-H₂ and (*p*)-NH₃-(*o*)-H₂ ((*o*) denotes (*ortho*) and (*p*) denotes (*para*)) were detected [1]. Hyperfine quadrupole structure due to the ¹⁴N nuclear spin ($I = 1$) interaction was well resolved for the (*o*)-NH₃-(*o*)-H₂, but not for the (*p*)-NH₃-(*o*)-H₂ species.

The present work demonstrates the first observation of the hyperfine structure for (*p*)-NH₃-(*o*)-H₂ using a newly built millimeter-wave (50-170 GHz) jet spectrometer [2]. A coaxial propagation of the molecular jet and millimeter-wave radiation results in the narrow linewidths of the 30-40 kHz that was very advantageous for resolving the closely spaced hyperfine structure components. The $J = 2 - 1$ and $J = 3 - 2$ pure rotational transitions of (*p*)-NH₃-(*o*)-H₂ in the $\Pi_{e/f}(K = 1)$ states were detected. The observed lines are split by the quadrupole interaction of the nitrogen nucleus ($I_N = 1$), and each component is split further due to the magnetic nuclear spin interaction of the H nuclei ($I_{(o)-H_2} = 1$). The rotational frequencies are consistent with those from previous work, but now the hyperfine components are well resolved and can be determined with an accuracy of 5-7 kHz, compared to 100 kHz for the rotational line centers in the earlier study. PGOPHER fitting program [3] was used to determine the quadrupole, spin-rotational and spin-spin coupling parameters. These results provide the dynamical information about the angular orientation of ammonia and hydrogen monomers in the complex, its structure and intermolecular potential.

Funding The work is carried out within the framework of the theme no. FFUU-2022-0004 of the Institute of Spectroscopy RAS.

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Cartesius fort – object fortran library for chemistry and materials science. 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 [2]: 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 [3]. We developed a series of targeted numeric tools based on this library: Liqulon – a tool for modeling thermodynamical properties of ionic liquids [4] and adamas – a tool targeted on description of carbon allotropes [5] and providing their crystalline structures, relative energies and elastic properties. GoGreenGo – local perturbations of periodic systems: chemisorption and point defects [6]. jakontos – Effective Hamiltonian Crystal Field for periodic systems with transition and rare-earth elements [7, 8]. They available through the NetLaboratory system [9].

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Modern problems of quantum theory of materials containing elements of the lower half of Mendeleev periodic table

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The creation of new materials based on heavy transition metals (*d*-elements), lanthanides and actinides (*f*-elements), which are located in the lower half of Mendeleev’s table, is one of the key direction in the evolution of the scientific and technical base of the most developed countries of the world in the coming decades. Digital materials science, including computer modeling of such materials, is one of the most important components of such development. Theoretical study of materials containing *d*- and *f*-elements with high accuracy is necessary for a correct understanding of the processes occurring in them at the atomic level, predicting the properties of materials and developing new technologies. Computer modeling can play an important role in the creation of new magnetic, optical, quantum, radiopharmaceutical, and other materials with unique properties.

The problems of modeling such materials are discussed in the report, as well as the ways to overcome these problems with using the relativistic pseudopotential models, which can be applied not only for accurate treatment of frozen core electrons in heavy atoms (see [1] and refs) but may be efficiently utilized for constructing embedding potentials in studying the crystal fragments (see [2] and refs). In the latter case they can provide most accurate calculation of various properties of materials (both periodic structures with *d*- and *f*-elements, and structures with the impurity centers containing them) in the framework of cluster modeling of materials. First of all, this concerns calculations of the properties of “atoms in compounds” [3], such as chemical shifts of the X-ray emission (fluorescent) spectra of heavy atoms in a crystalline environment, fine and hyperfine splitting, and other properties, which are, in particular, required to search for a “new physics” [4] and solve other actual problems. Some further developments based on the concept of “atoms in compounds” are suggested and briefly discussed, which can be used to overcome some present problems of quantum theory of molecules and materials.

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Propagator methods in the ADC approximation: Theory, development and current state

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The algebraic diagrammatic construction (ADC) approximation for propagators (Green's functions) provides very useful approach to derivation of computational schemes for studies of electron excitations in molecules, atoms, and clusters [1]. These schemes, referred to as ADC(n) methods (where n denotes the order of the consistent perturbative treatment of the lowest excitation class for the electronic states under study), have been employed with considerable success for, e.g., studies of the photoabsorption and photoionization spectra (involving the outer-, inner- and K-shell electrons) as well as of the diverse excited-state relaxation processes, such as the intermolecular Coulomb decay (ICD) in molecular systems and clusters.

Historically, the ADC approach was devised by J. Schirmer in earlier 1980-th in an attempt to extend the treatment of the self-energy in the Dyson equation for the one-particle Green's function (electron propagator) beyond second order. This allowed the first consistent third-order approximation for the electron propagator to be obtained. Very soon, however ADC was recognized as a powerful tool applicable to other types of propagators, so that second-order schemes for the polarization and two-particle propagators were obtained. Currently, the ADC schemes for most chemistry-relevant types of propagators up to fourth order are available. The higher-order derivations became possible due to the discovery of J. Schirmer in 1990-th of the fact that the ADC schemes can be formulated entirely in terms of the familiar many-electron states without any reference to Feynman diagrammatic representation of propagators. The key quantities here are the so-called intermediate states (IS) [1].

The ADC schemes are often considered as less demanding alternatives to closely related popular equation-of-motion coupled cluster (EOM-CC) approaches. The latter are believed to be superior to ADC in particular because of the coupled cluster treatment of the ground state involving summations of certain terms up to infinite order. In fact, however, this makes the EOM-CC models quite unbalanced compared to the ADC schemes relying on the strict perturbative approach and can lead in some cases to their severe failures. The origins of such failures will be briefly discussed in the talk, as well as the advantages and disadvantages of the most common ADC and EOM-CC methods. Some representative examples of the ADC applications will be given.

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Weakly interacting molecular pairs in planetary atmospheres

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Each planetary atmosphere is unique as regards both its molecular composition or density and temperature height profiles. In all of the presently known atmospheres the most abundant species are neutral symmetrical molecules having no permanent electric dipole [1]. The slight dipole moment can arise, however, through interaction of these molecules with each other via weak Van der Waals type forces. As a result, the opacity of known atmospheres may be affected to various extent by the mechanisms lying beyond conventional electric-dipole permitted absorption of individual molecules. The foundation of molecular spectroscopy thus must be extended by inclusion a somewhat unconventional but its integral part – “supermolecule” spectroscopy – relevant to weakly interacting molecular pairs [2]. Current review emphasizes the importance of this extension for solution of some radiative problems relevant to planetary atmospheres. Special attention is paid to recent theoretical methods which are now developing to permit simulation of “supermolecular” spectra basing on *ab initio* characterization of electronic energy and induced dipole as a function of nuclear coordinates. The benefits and drawbacks of such methods as molecular dynamics and trajectory based simulation of the interaction induced spectra are discussed.

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The Development of the QM/MM Interface and Its Application for the on-the-fly QM/MM Nonadiabatic Dynamics in JADE Package: Theory, Implementation and Applications

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Understanding the nonadiabatic dynamics of complex systems is a challenging task in computational photochemistry. Herein, we present an efficient and user-friendly quantum mechanics/molecular mechanics (QM/MM) interface to run on-the-fly nonadiabatic dynamics. Currently, this interface consists of an independent set of codes designed for general-purpose use. Herein, we demonstrate the ability and feasibility of the QM/MM interface by integrating it with our long-term developed JADE package. Tailored to handle nonadiabatic processes in various complex systems, especially condensed phases and protein environments, we delve into the theories, implementations, and applications of the on-the-fly QM/MM nonadiabatic dynamics. The QM/MM approach is established within the framework of the additive QM/MM scheme, employing electrostatic embedding, link-atom inclusion, and charge-redistribution schemes to treat the QM/MM boundary. Trajectory surface-hopping dynamics are facilitated using the fewest switches algorithm, encompassing classical and quantum treatments for nuclear and electronic motions, respectively. Finally, we report simulations of nonadiabatic dynamics for two typical systems: azomethane in water and the retinal chromophore PSB3 in a protein environment. Our results not only illustrate the power of the QM/MM program but also reveal the important roles of environmental factors in nonadiabatic processes.

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On the experience of using AI-tools to represent experimental data in the form of partial empirical theories

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The possibilities and experience of representing empirical data constantly accumulated during the experimental analysis and study of a given target effect in the form of so-called partial (possibly rearranged with the arrival of new irrelevant information) formalized (by special mathematical means) *theories* (PT) are discussed. Each such PT represents a consistent set of formulas of some mathematical language generated from the current set of precedents - the facts of the presence (examples), as well as the facts of the absence (counterexamples) of the studied effect in appropriate situations (tests, experiments characterized by the corresponding values of pre-selected parameters of different "nature" - Boolean, numerical, structural, etc.). The formulas collected in PT - empirical dependencies (ED) - are special logical conditions generated on the analyzed set of precedents - dataset in its current (and assuming further replenishment with new data) state - by interpolation. At the same time, it is required that each of the use cases of the analyzed dataset (covering examples and counterexamples) It could be represented as a logical consequence of certain formulas of a given PT (i.e. generated in a given PT as a logical consequence). It is also necessary that, when supplementing the current dataset with examples and/or counterexamples of the same "nature" (for example, in medical diagnostics - with descriptions of new patients of the same nosology), at least part of the previously found EDs would be inherited to the extension of the existing dataset generated by the new data (i.e. the current PT, considered for example, as a set of partially defined functions, it would demonstrate stability with respect to extensions of the analyzed dataset that are "homogeneous" with already available data). The EDs forming the current version of the PT can be used to forecast the target effect on new precedents by checking their extrapolability to descriptions of such precedents.

It is easy to make sure that most of the interpolation-extrapolation mathematical techniques popular in modern machine learning do not provide and ensure the heritability of the EDs generated by them when expanding the original dataset. The obvious "material" basis for the desired stability of the effects generated from empirical data may be a reflection (i.e. representation) of the *causality* of the analyzed effect by the corresponding EDs.

The possibilities of using the well-known in AI research and development *heuristics* of the so-called *causal similarity* to form the required type of PT are considered. To clarify this heuristic, the mathematical formalization of the concept of similarity by means of a binary algebraic operation and the similarity relation generated on its basis are used. The proposed PTs are formed using the well-known mathematical techniques of Galois connections and closure. At the same time, EDs of a causal nature, forming a PT, with accuracy related to a set of precedents in the current analyzed dataset, characterize the fixed points of the Galois closure generated on it. A number of aspects and features characterizing the computational complexity of the combinatorial search arising here are discussed [1].

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Multipartitioning perturbation theory in quantum chemistry

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The formulation of stationary quantum-mechanical quasidegenerate perturbation theory employing several zero-order Hamiltonians simultaneously (multipartitioning perturbation theory, MPPT; [1] and references therein) opens the way towards natural multistate multireference generalizations of state-specific perturbative many-body methods of quantum chemistry. During almost three decades of its existence MPPT have given rise to several efficient and economical techniques of *ab initio* non-relativistic and quasirelativistic calculations on energetic, electric, magnetic and radiative properties of electronically excited states of molecules and clusters. We focus on the two main schemes, analyzing their advantages and shortcomings in view of improved implementations and applications to the studies of electronic transitions in rather large systems containing heavy atoms (first of all, *f*-elements).

The simple second-order MPPT versions employing one-electron zero-order Hamiltonians provide consistent multistate/multireference generalizations of the conventional second order Møller-Plesset perturbation theory. In contradistinction to most approaches based on the use of universal one-electron zero-order operators, MPPT schemes offer the possibility to avoid the nightmare of intruder states without contracting the model space determinants or/and introducing artificial denominator shifts. Their advantages in *d*- and *f*-element compound modeling may be related to automatic suppression of systematic errors in relative energies of states with different number of open electronic shells, typical for most single-partitioning second-order schemes. The “diagrammatic” formulation for arbitrary incomplete model spaces paves the way for economical parallel implementations.

The use of more sophisticated state-specific zero-order Hamiltonians with partial retention of two-body terms (Dyall-type Hamiltonians) within the MPPT framework leads to multistate formulations of the *N*-electron valence state perturbation theory (see [2] and references therein) which are usually considered as promising tools for transition metal and lanthanide chemistry modeling. It should be noticed that the applicability of such techniques to the simulation of extremely dense electronic spectra of lanthanide-containing systems with numerous open-shell electrons may be seriously restricted by the rapid increase of computational cost with the extension of contracted many-electron model space basis.

Finally, we discuss the prospects of applying MPPT-based techniques to *ab initio* studies on local excitations in lanthanide-doped crystals in the frames of the compound-tunable embedding potential approach [3].

Funding The work of AZ and AVO on MPPT applications to *f*-element compounds at NRC “Kurchatov Institute” - PNPI was supported by the Russian Science Foundation (grant no. 20-13-00225-P, <https://rscf.ru/en/project/23-13-45028/>).

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Nonadiabatic Dynamics, Time-Resolved Spectra and Machine Learning

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Nonadiabatic dynamics widely exist in photophysics, photochemistry and photobiology. We tried to develop theoretical approaches to study the photoinduced nonadiabatic dynamics. A few topics will be discussed.

We combined the doorway-window representation of the nonlinear response theories and ab initio nonadiabatic dynamics to simulate the time-resolved pump-probe spectra, including both transient absorption spectra and time-resolved fluorescence spectra. Two interesting examples, including photoinduced energy transfer and photoisomerization, are discussed.

We tried to combine deep learning method and numerical accurate quantum dynamics approach to simulate the long-time quantum evolution of open quantum system. This approach allows us to obtain the evolution of reduced density matrix of open quantum system with a low computational cost. It demonstrates that the deep learning approach is the important tool to speed up the long-time quantum evolution. The similar time-series analysis tool can also be used to propagate all nuclear and electronic degrees of freedom in the trajectory evolution of the SQC-MM dynamics.

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List of Abstracts – Posters

Theoretical insight into lithiation of N-doped molybdenum disulfide

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Molybdenum disulfide (MoS_2) is a promising anode material due to its layered structure and high theoretical capacity of $670 \text{ mAh} \cdot \text{g}^{-1}$, provided by both intercalation and conversion reactions. However, due to the low electrical conductivity and poor reversibility of the conversion reaction, pure MoS_2 requires modification, the simplest of which is doping.

Nitrogen can act as an impurity element from available precursors and is suitable for MoS_2 doping according to existing methods [1, 2]. Several experimental works showed that the presence of nitrogen heteroatoms leads to enhanced electrochemical capacity in MoS_2 [2], as well as in MoS_2 based composites [3]. Since the capacity of pristine MoS_2 is mainly attributed to released sulfur after conversion reaction, the role of nitrogen in the improvement of the MoS_2 performance remains unclear. In this work, we use the quantum-chemical calculations to study lithiation of N– MoS_2 and provide an insight to this process. For the DFT calculations, we used the plane-wave based package Quantum Espresso. The DFT calculations were accompanied by ab initio Car Parrinello molecular dynamics simulations to verify the dynamical stability of the MoS_2 models considered.

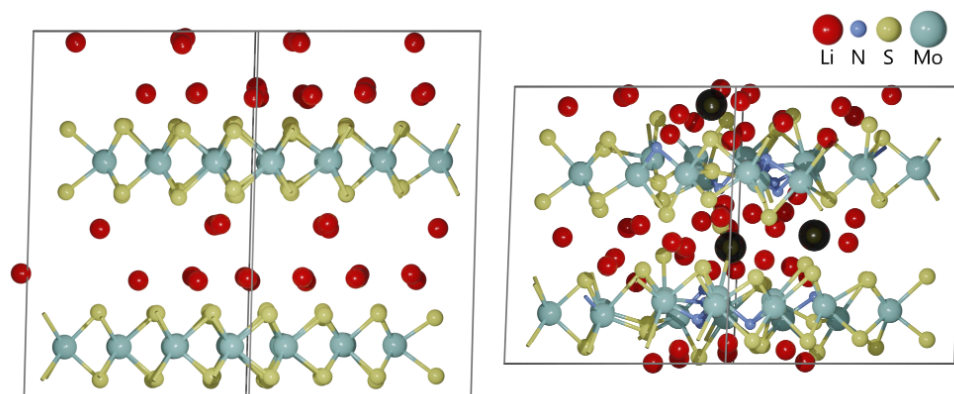


Figure 1: Final snapshots of bulk $\text{Li}_{1.5}\text{MoS}_2$ and $\text{Li}_{1.5}\text{MoN}_{0.375}\text{S}_{1.625}$ molecular dynamics simulations. Black highlights released sulfur

During our investigation MoS_2 models with 0, 4.2, 12.5 at. % nitrogen concentrations were constructed as $4 \times 4 \times 1$ supercells. Using supercell program, for each of the doping ratios we generated series of structures with inequivalent heteroatoms distributions. Structures with the lowest total energies after optimisation were used to study lithiation. We inserted Li atoms at 1:1 ratio of Li: MoS_2 inside both pristine MoS_2 and N– MoS_2 , which corresponds to the final stage of intercalation process. We considering dense Li accommodation around high energy nitrogen sites for the N– MoS_2

case and performed static optimizations for models with different Li arrangements. In order to study N–MoS₂ at deeper lithiation stage, we performed Ab-initio molecular dynamics simulations on models with stoichiometries Li_{1.5}MoN_xS_{2-x}. For Li_{1.5}MoN_xS_{2-x} series, we considered both bilayer and bulk structures to study dimensional effect.

Overall, we tested behaviour of N–MoS₂ and pristine MoS₂ interacting with Li at concentrations, associated with conventionally known intercalation and conversion stages of pristine MoS₂. Although nitrogen heteroatoms bind Li with higher energy, Li tend to shift towards octahedral cavities inside interlayer space as in MoS₂, stating that intercalation stage provides similar theoretical capacity in both N–MoS₂ and MoS₂. Molecular dynamics simulations of Li_{1.5}MoN_xS_{2-x} showed that Nitrogen insertion leads to lower stability and earlier conversion reaction. Additionally, it was shown that conversion reaction is expected to undergo on the surface of N–MoS₂.

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Effect of quantum entanglement on two-photon absorption probabilities in fluorescent proteins

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Quantum entanglement in a system of two particles is a specific correlation manifested in the fact that they, in some sense, behave like a single quantum object. For instance, the absorption rate of entangled photon pairs linearly depends on the flux density, whereas in classical two-photon absorption experiments this dependence is quadratic. This allows spectroscopic measurements to be carried out at significantly lower excitation light intensities than in classical experiments. Although the effect of a significant enhancement of two-photon absorption in the case of entangled photons compared to classical two-photon absorption has been repeatedly observed in experimental studies, the magnitude of this enhancement remains to be the subject of active debate.

Here we perform a theoretical study of the use of correlated and uncorrelated photon pairs in the two-photon $S_0 \rightarrow S_1$ absorption by the EGFP protein and its modification EGFP T203I.

The absorption probabilities of correlated and uncorrelated photon pairs are calculated using the sum-over-states formalism. We consider two-photon resonant absorption of a degenerate photon pair. Excitation energies and transition moments are calculated using the XMCQDPT2-based QM/MM approach. The convergence of a series of the N -level models with increasing number of states N is shown to be very fast for the $S_0 \rightarrow S_1$ transition in EGFP and EGFP T203I. When considering the $0 \rightarrow 0 \rightarrow f$ and $0 \rightarrow f \rightarrow f$ permanent dipole pathways (PDP) by restricting the summation to the initial and final states only, we obtain the following approximate relation for the entangled two-photon absorption (ETPA) probability δ_e :

$$\delta_e = \delta_c(1 - \cos(\Omega_f T_e/2))^2 + \delta_+ \sin^2(\Omega_f T_e/2)$$

where δ_c is the classical TPA probability, δ_+ is the non-classical contribution due to the entanglement of the two photons absorbed, Ω_f is the $S_0 \rightarrow S_1$ energy gap, and T_e is the entanglement time.

We show that under nonlinear two-photon excitation of the $S_0 \rightarrow S_1$ transition in EGFP and EGFP T203I, the PDP channels dominate for the absorption of both the correlated and uncorrelated photons. The ETPA enhancement is determined by the value of the non-classical contribution δ_+ , which primarily depends on the sum of the permanent dipole moments of the final and initial states, while the classical probability δ_c is determined by the difference of these dipole moments. The ETPA probability as a function of entanglement time rapidly oscillates on the femtosecond timescale. It changes from zero to the values significantly exceeding the classical one, and its average value is 2 orders of magnitude higher than δ_c . Remarkably, the T203I modification of EGFP enhances the ETPA probability, whereas it diminishes the classical one. This can be rationalized by analysing the derived equation for δ_e and considering the internal protein field and its influence on the permanent dipole moments of the EGFP chromophore in the initial and final states.

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Theoretical modeling of the adsorption, desorption and migration of heavy and superheavy atoms on a metal surface: beyond a mobile adsorption model

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Experimental study of chemical properties of superheavy elements (SHE) is a non-trivial challenge due to the difficulty of the radioisotopes synthesizing and their short half-life times. The online chemical experiments imply synthesis of a superheavy nucleus, its separation from other products of nuclear reactions, transport into a chromatographic system, adsorption on a surface and alpha decay detection. In the thermochromatographic experiments important chemical information is provided by an adsorption temperature on metals and other surfaces, as well as by the corresponding chromatographic peak profiles. Comparing theoretical predictions with experimental chromatographic results it is possible to conclude about SHE chemical form observed in the experiment.

Within the simple mobile adsorption model theoretical Monte Carlo simulation and modeling of the chromatographic profiles [1] requires knowledge of the adsorption energies E_a which can be obtained from relativistic ab initio quantum chemistry calculations [2]. The average desorption time is determined by the Arrhenius-Frenkel-like equation and depends both on E_a and on the harmonic vibration frequencies of an adsorbent lattice [1]. Therefore, a mobile adsorption approach considers the retention time as a function of an adsorbent lattice dynamics, ignoring dynamical effects caused by chemical interactions between adatom and surface [3]. It has been shown, however, that a mobile adsorption model is justified only in a physisorption case when E_a values are small [4]. For strong atom-surface interactions desorption is a multiphonon process that depends not only on the adsorption energy and lattice vibrations but also on the chemical nature of adatom. As a result, a mismatch between theoretical estimations and experimental results is possible. To the best of our knowledge no any theoretical predictions of the chromatographic profiles for heavy and superheavy atoms have been made to date beyond a mobile adsorption approximation.

In this work we consider several possible modifications of the Arrhenius-Frenkel equation, explicitly taking into account a potential energy of the atom-surface interaction. Using the adiabatic approximation and activated complex theory, we propose a tool for estimation of atomic mobility, desorption times, adsorption energies, enthalpies and entropies of heavy and superheavy atoms. This model is used to simulate atomic adsorption of a heavy element Tl and a superheavy element Fl on a gold surface.

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Impact of intramolecular hydrogen bonding on the photophysics of the modified GFP chromophore anion

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Green Fluorescent Proteins (GFP) are indispensable tools in molecular and cellular biology due to their high fluorescence quantum yields. However, fluorescence is lost at room temperature when the GFP chromophore is taken out of the native protein environment due to much faster internal conversion, which proceeds on a picosecond timescale through a conical intersection between the excited and ground electronic states [1]. The intramolecular rotation about the single and double bonds in the bridge moiety of the chromophore is known to be responsible for promoting internal conversion. The addition of a hydroxyl group to the ortho-position of the phenolic ring of the chromophore inhibits twisting across these bonds due to the formation of an intramolecular hydrogen bond, resulting in the increase of the fluorescence quantum yield. By using time-resolved action absorption spectroscopy of cryogenically cooled molecular ions combined with high-level *ab initio* calculations, we provide direct evidence for the influence of hydrogen bonding on the photoresponse of the modified deprotonated GFP chromophore — opDHBDI⁻.

By using the XMCQDPT2/SA(2)-CASSCF(14,13)/(aug)-cc-pVDZ level of theory, we calculate the potential that hinders internal rotation about the single and double bonds of the chromophore in the ground and first excited singlet states. The excited-state potential for rotation about the single bond exhibits multiple minima with twisted geometries of the chromophore due to the presence of the intramolecular hydrogen bond. Vertical transitions from the planar minima of the *s-cis* and *s-trans* conformers in S_0 correspond to the population of the transition states in S_1 , and the twisting about the single bond becomes highly active upon the $S_0 \rightarrow S_1$ transition in opDHBDI⁻. The torsional levels and the corresponding wavefunctions are calculated using these highly anharmonic periodic potentials in S_1 and S_0 . The photoabsorption spectrum is then calculated using the linear coupling model in the harmonic approximation for all modes except the torsional mode treated explicitly. The simulated $S_0 \rightarrow S_1$ absorption profile is used to interpret the vibrationally-resolved action-absorption spectrum obtained experimentally at cryogenic temperatures. We show that the most intense transition is significantly blue shifted from the band origin and corresponds to the vertical transition of the *s-cis* rotomer, whereas the weak band origin can be attributed to the transitions of the higher-energy *s-trans* rotomer. The located lowest-energy conical intersection between the S_1 and S_0 states lies 0.3 eV above the minimum in S_1 , unlike that in the non-modified chromophore. We discuss the impact of the higher-lying conical intersection on the excited-state decay channels of the modified chromophore, as well as on its excited-state lifetimes, which are found to be strongly dependent on excitation wavelength across the $S_0 \rightarrow S_1$ absorption band.

Funding The work is supported by the Russian Science Foundation grant no. 22-13-00126. The calculations are carried out using the equipment of the shared research facilities of HPC computing resources at Lomonosov Moscow State University as well as the local resources (RSC Tornado) provided through the Lomonosov Moscow State University Program of Development.

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MCSF Approach to Many-Electron Pauli Equation

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Nowadays, the main way to obtain information about distant astrophysical objects, study their structure, evolution and processes occurring in them is to study their spectra. At the same time, the state of matter in space may be significantly different from usual. We focused on studying the behavior of atoms in strong magnetic fields, such as those present on the surface of neutron stars and white dwarf stars. Knowledge of the behavior of the electronic spectrum of atoms in such magnetic fields will make it possible to compare the predicted spectrum with the experimental one [1], which will subsequently make it possible to draw conclusions about the atomic composition of these astrophysical objects.

The approach that we develop in this work is based on the representation of an atom in a uniform magnetic field of a white dwarf as a quantum non-relativistic many-electron system in the external Coulomb field of the atomic nucleus and an external uniform magnetic field [2]. The electron energy values in this approach will be solutions of the eigenvalue problem for the many-electron Pauli Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2} + B_z \hat{S}_z + \frac{1}{2} B_z \hat{L}_z^O + \frac{1}{8} B_z^2 (X^{O2} + Y^{O2}) + \hat{V}_{ne}$$

In this work, we applied a well-proven approach using the MCSF method to describe the excited states of atoms to this model.

This work will provide technical details of the implementation of all main stages

- Matrix elements calculation
- Solution of the optimization problem in the basis of molecular orbitals (Self Consistent Field procedure)
- Solution of the optimization problem in the basis of Slater determinants (Configuration Interaction procedure)

A comparative analysis of the of various algorithms for solving various stages of the problem as applied to the systems under consideration is presented.

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Model-based reinforcement learning for Iterative Prisoner's Dilemma in a Multi-agent environment

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The Iterative Prisoner's Dilemma (IPD) is a fairly common problem within game theory. In a multi-agent environment in which agents play different strategies (even if they are stationary), there is no single optimal stationary strategy since the agent has to adapt to different opponents. Reinforcement learning (RL) is one of the prominent machine learning methods that can be applied to find optimal strategies in the IPD framework. However, existing research on using RL for IPD mainly considers situations where the learning agent plays with only one opponent [1, 2, 3]. Although in these cases the trained agents rank high in the IPD tournament simulations and their comparative results are higher than those of the opponents, the resulting strategies may be far from optimal.

In this study, we have tested machine learning algorithms proposed in the [3]. We have found that model-free RL indeed allows finding optimal strategies when learning on games with a single opponent, but in an environment with several opponents, the results turn out to be worse. Moreover, the learning process becomes unstable when we expand the agent's memory, due to an increase in the number of possible states of the environment. The reason is that the IPD formulation under consideration cannot be reduced to a Markov decision-making process (MDP), since while playing with different opponents the agent's making the same decisions can lead to different new states, and to make a decision it is necessary to consider the entire history of the game with one opponent. In this regard, the work also tested the model-based RL algorithm proposed in [4] and improved in [5]. Its main advantage is the absence of assumption that the environment should be Markovian. We have managed to obtain a near-optimal strategy in a multi-agent environment in which the agent was trained by playing against three different types of stationary strategies.

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Quantum chemical study of 1,3-cyclopentadiene trimerization mechanism

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1,3-cyclopentadiene (CPD), being a conjugated cyclic diene, has a tendency to undergo [4+2]-cycloaddition with various dienophiles, including other CPD molecules. Two stereoisomers of dicyclopentadiene (DCPD) are formed: *exo*- and *endo*-DCPD, the latter being a product of kinetic control. Both dimers have a C=C bond both in the norbornene (NB) and the cyclopentene (CP) fragments of the molecule. Due to this, a diverse amount of tricyclopentadiene (TCPD) isomers can be formed by [4+2]-cycloaddition of CPD and DCPD. A total of 14 TCPD isomers are formed in the reaction of CPD and *exo/endo*-DCPD (fig. 1). However, experimental observations only show the formation of 2 to 7 trimers [1, 2]. The aim of this study was to determine the patterns of the resulting product distribution.

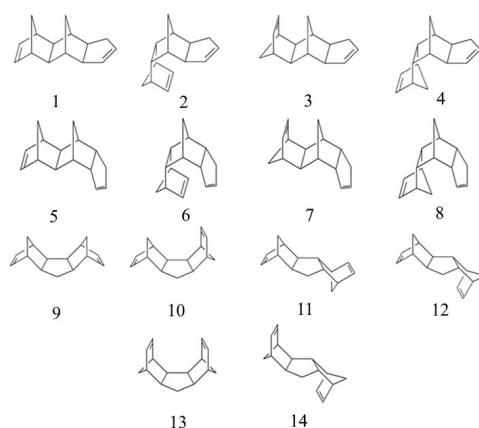


Figure 1: TCPD structures

According to DFT-PBE0/cc-pVTZ calculations, experimentally observed TCPD isomers are both the most thermodynamically stable ($\Delta G_{298} = -21.3...-37.3$ kJ/mol) and kinetically preferred ($\Delta G_{298} = 141.1...158.8$ kJ/mol). Ring strain energies for all trimers were calculated using the homodesmotic reaction method. In almost all the cases the determined ring strain energies were smaller in case of CPD addition to the NBE-end of DCPD. Energy decomposition analysis according to the activation strain model showed the steric hindrance, which causes significant deformation of reagents upon reaching the transition state, to be the determining factor of the activation energy magnitude.

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Multiscale quantum chemical calculations of highly efficient narrowband deep-blue fluorophores

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Until now, one of the main problems in the production of a commercially successful organic light-emitting diode (OLED) is the creation of a stable blue emitter with a narrow emission spectrum. One solution to this problem is the use of rigid fluorophores, in which various vibrations of the structure are hindered by the absence of single chemical bonds. However, such structures consist of a large number of atoms, as a result of which vibronics calculations are very limited for them. On the other hand, multiscale modeling allows one to calculate quite accurately the shape and width of spectral lines of large molecules.

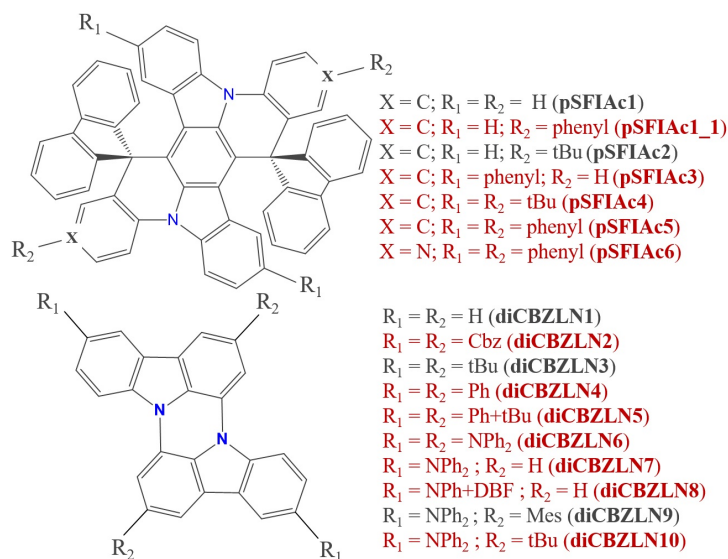


Figure 1: Structures of studied pSFIAC and diCBZLN derivatives. Grey - literature structures, Red - new structures

In this work the spectral properties of pSFIAC and diCBZLN based deep-blue luminophores is studied taking into account their environment. The structures of the dopants with different hosts were generated using molecular dynamics. The fluorescence spectra of the dopants with hosts were calculated using TD-DFT method. The environment of the chromophores was modelled as a QM/MM approach, and as effective fragment potentials (EFP) method. It was found that the use of a multiscale approach allows one to increase the accuracy of the results obtained, without using computationally expensive functionals, and also to accurately predict the shape of spectral lines without calculating vibration frequencies.

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Prediction of proton conductivity of metal-organic frameworks using a multimodal transformer

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Metal-organic frameworks (MOFs) are a class of promising, potentially porous materials, which properties can be fine-tuned by changing the metal centers and organic ligands (linkers). One of these properties is proton conductivity, which can vary significantly at different humidity and temperature values, which makes it possible to use MOFs as electrolytes in fuel cells. The impressive variety of MOFs complicates experimental design and make to use a high-speed predictive method — machine learning. The aim of this work is to train a model based on a multimodal transformer to predict the proton conductivity of MOFs, taking into account global features and, then, to perform a screening of databases to obtain new promising proton conductors.

Experimental data for training were collected from literary sources. The dataset consisted of 2,396 data points for 223 different crystalline structures. Relative humidity values ranged from 0 to 100%, and temperature was in the range of 230–415 K.

For predicting proton conductivity, a multimodal transformer MOFTransformer [1] was used; the model was modified to take into account the global features of the structure (humidity, temperature, acidity constant of the solvent in the pores, protonation of the solvent). The model was trained using the cross-validation method to more accurately estimate the generalizing ability of the model by means of the testing on the entire available dataset. Optimal hyperparameters are obtained by grid search technique. The mean absolute error (MAE) of predicting the natural logarithm of proton conductivity is 2.05 for a range of values from -23 to -2. Moreover, the uncertainty of predictions was assessed: the experimental error of the data was estimated by adding an additional neuron to the last fully connected layer of the neural network to obtain the variance of the predicted value, and by modifying the loss function. The error of the algorithm was estimated by training an ensemble of models with different initialization of weights with further calculation of prediction variances.

In addition, a similar architecture was trained for the task of classification the conduction mechanism, which depends on the value of the activation energy. The latter is calculated from experimental data using the Arrhenius equation. The classification accuracy score is 0.73.

As a result of screening a database of 20,000 structures, potential candidates for new promising proton conductors were obtained.

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Nonadiabatic electronic excitations as a trigger mechanism of plasma phase transition in dense fluid H₂ and N₂

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The nature of the transition of a dense hydrogen fluid from an isolated molecular state to a conducting state is one of the fundamental problems that has attracted much attention over the last two decades, starting with the first detailed experiment to study the electrical conductivity of the H₂/D₂ fluid under shock compression. Subsequent shock compressions and heating in diamond anvils have generated a large amount of experimental data. However, to date there is no theory that describes the dynamic and static experiments from a unified point of view and explains the differences in their results.

The intensive development of computational methods has led to classical and quantum molecular dynamics being firmly established in almost all areas of condensed matter physics. However, these methods have so far proved inadequate for describing the transition in an element as simple as hydrogen. This raises the question of the reliability of modern methods and the need to determine the limits of their applicability. Thus, the importance of describing this transition from the point of view of computational methods arises not only from the practical importance of dense hydrogen, but also from the need to verify modern approaches.

The modelling of the transition mechanisms in dense hydrogen and nitrogen fluids allows us to explain all experimental observations, as well as the difference in the transition points observed by different groups [1, 2, 3]. The results of this work allow us to better understand the processes occurring inside the giant planets, and also demonstrate the importance of non-adiabatic electron dynamics and the insufficiency of the description by classical models, without taking into account excitations.

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Investigation of the structure and stability of boron-carbon clusters using the DFT method

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Boron carbides stand out for their unique combination of high melting temperature, exceptional hardness, and low weight, making them indispensable in industries such as refractories, abrasives, body armor, as well as in nuclear technologies due to their neutron absorption capability. Boron carbides are also promising as high-temperature semiconductors for electronics. Boron-carbon nanoclusters may serve as fullerene analogues, H₂ and N₂ gas nanosensors, quantum dots, thermoelectric energy converters, and more. The purpose of this study is to elucidate the properties of these systems depending on their size, as well as to understand the mechanism by which the properties of their bulk samples are achieved. Another objective is to determine the stable structures of intermediate molecules formed in the growth process of boron-carbon systems [1, 2, 3].

In this study, we have predicted the optimal atomic structures of boron-carbon clusters containing up to 24 atoms. To find the most stable structures, we used the evolutionary algorithm USPEX (see also <http://uspex-team.org>) coupled with *ab initio* calculations. The final refinements of structures, energies and magnetic moments were done using the Gaussian 16 code.

The stability of B_nC_m clusters was investigated, for which the minimum second-order energy differences by the number of atoms of different types (Δ_{\min}^2), fragmentation energies (E_{frag}), and HOMO-LUMO gaps depending on the composition (n, m) were calculated. Figure 1 displays the graph of $\Delta_{\min}^2(n, m)$, demonstrating the existence of "ridges" and "islands" of stability, corresponding to the most stable clusters.

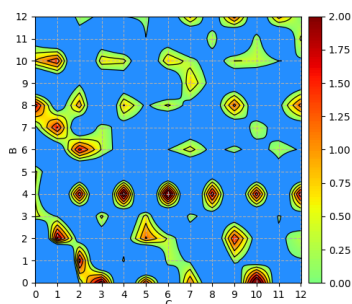


Figure 1: The graph of $\Delta_{\min}^2 E(n, m)$, showing the stability of B_nC_m clusters ($n, m = 0 - 12$).

Knowledge of stable atomic configurations provides an understanding of the structural foundations of the objects under consideration, helps to predict the course of chemical reactions involving them, and also explains the processes of their growth in experiments.

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Experimental and theoretical study of intermolecular interactions in water-acetonitrile system

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Liquid systems are the complex objects for their study due to lack of the translational invariance and presence of the cooperative motions of a large number of particles. Only the combination of the experimental and theoretical (e.g. quantum chemical or molecular dynamics) methods makes possible to obtain significant information about the structure and molecular interactions in such systems.

At the solutions formation, the interactions between the molecules of the solute and the solvent appear. It leads to a structural reorganization of both of them. In the present work the acetonitrile (ACN) - water liquid solutions were studied. The density and the speed of ultrasound were measured throughout the full concentration range at the various temperatures (20 – 40°C) [1]. From the experimental data, the adiabatic compressibility, excess molar volume and adiabatic compressibility were calculated. Based on the analysis of the concentration and temperature dependences of these parameters, the entire concentration range was divided into five intervals with different intermolecular structures: 0.0 – 0.1, 0.1 – 0.35, 0.35 – 0.6, 0.6 – 0.9, 0.9 – 1.0 molar fractions of ACN. It was shown that the structures peculiarities in each interval can be explained by the formation of different molecular associates.

To clarify in detail the structure of these associates, the optimal geometry configurations and the formation energies for clusters $(\text{CH}_3\text{CN})_n$ and $(\text{CH}_3\text{CN})_{n-1} \cdot \text{H}_2\text{O}$ ($n = 3 - 7$) were calculated by the DFT method with the B3LYP/cc-pvdz functional with dispersion correction term [2]. Intermolecular interactions are easier to analyze in clusters than in condensed phase, and the finite size clusters of can be related to molecular associates in the solutions. When constructing ACN clusters, we assumed that ACN molecules prefer the antiparallel orientation. At the number of molecules in the cluster increase, the cyclic configurations with the molecules orientation “head to tail” were also realized, It was found that at the same n , the formation of clusters including a water molecule is energetically preferable, and, starting from $n = 6$, water is located inside the cavity of the ACN molecules.

The obtained data on the structure of the clusters were used to construct a structural model of acetonitrile–water solutions, which correlates well with the model proposed based on the analysis of experimental studies.

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Development of descriptors for assessing maximum resistance to the principles of independence and reverse thermal isomerization time in computer-assisted screening of photopharmacological methods

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Photopharmacology is a field of research aimed at developing drugs that are converted into active form only when exposed to light. This approach allows for significant spatial localization of the action of drugs and, thus, reducing the side effects of their use [1]. One of the main approaches to the development of photopharmacological compounds is the “cross-linking” of the biologically active part and the molecular photoswitch, the most promising of which are azobenzenes and azoheterocyclic compounds [2]. Absorption of a photon causes isomerization of the switch, which brings the drug into the active form, and the drug is subsequently returned to the inactive form by reverse thermal isomerization of the molecular switch [3]. When computer screening of new photopharmacological drugs, in addition to the standard set of compound parameters optimized in pharmacology, the maximum of the absorption (activation) spectrum and the rate of reverse thermal isomerization of the molecular switch are added. Both parameters require quantum chemical calculations and their assessment requires significant time and computational resources, especially for the rate of reverse thermal isomerization [4]. To be able to conduct computer screening, it is necessary to find quickly calculated descriptors that correlate with the values of the specified properties. In this work, descriptors of molecular photoswitches were found that make it possible to estimate the maximum absorption spectrum and the rate of reverse thermal isomerization of compounds based on fast quantum chemical calculations and, thus, can be used in computer screening of photopharmacological drugs.

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Possible room-temperature superconductivity in Ca-Y-H system at high pressure

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Achieving room-temperature superconductivity is a one of the major goal of modern science. Hydrogen-based materials at high pressure have shown promise in this regard, with LaH₁₀ currently holding the record for the highest superconducting transition temperature (250-260 K) in this class of materials. Exploring ternary hydride systems theoretically could lead to further progress towards this goal. In this work, we present a theoretical investigation of ternary superconducting hydrides in Ca-Y-H system under high pressure. The thermodynamic stability, considering the zero-point energy, was studied by the evolutionary algorithm USPEX and the program package Phonopy applying the Convex hull method. State-of-the-art methods for modeling the electronic structure of materials such as VASP and Quantum ESPRESSO, were applied to explore the band structure and density of states of the materials. The Python programming language was used for numerical solutions of the isotropic Migdal-Eliashberg equations.

As a result, it was found that $P\bar{6}m2$ -CaYH₁₈ exhibits a high superconducting critical temperature: for 300 GPa, T_c (Eliashberg) = 270–292 K, the electron-phonon interaction coefficient (λ) is equal to 2.480; 350 GPa - T_c (Eliashberg) = 272–295 K, λ = 2.131; 400 GPa - T_c (Eliashberg) = 278–302 K, λ = 2.033. $P\bar{6}m2$ -CaYH₁₈ is a combination of the characteristic $C2/m$ -CaH₉[1] and $P6_3/mmc$ -YH₉[2] polyhedra, which have been studied earlier in the literature.

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Photoionization of γ -pyrone: Nonadiabatic nuclear dynamics in the low-lying electronic states of the γ -pyrone radical cation

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The latest photoelectron studies of γ -pyrone provide well-resolved spectrum, which shows complex features representing combinations of the main and satellite lines [1]. In our recent work, the outer valence ionization of γ -pyrone was studied using the IP-ADC(3) and other accurate electronic structure methods, and the results were used to interpret the experimental data [2].

The results of our high-level quantum chemical calculations showed that the electronic structure of γ -pyrone is quite complex due to electron correlation effects. These effects are reflected in the complex structure of the ionization spectrum and also can be seen from the disagreement between the results of different methods with respect to the sequence of cationic states. In many occasions, the spacing between the electronic states is quite small, which indicates that their vibronic interaction is possible and should be taken into account when studying the vibronic structure of the photoelectron bands. Such, the first maximum in the experimental spectrum with an energy of ~ 9.5 eV arises from the two closely located transitions $8b_2$ (2B_2) and $3b_1$ (2B_1), whose sequence is indicated in accordance with the most accurate data of the CC3 method.

In this work, the vibronic structure of the ~ 9.5 eV band was studied using a proper theoretical framework. For this, the vibronic interaction of the 2B_2 and 2B_1 states of the γ -pyrone radical cation was taken into account by means of the linear vibronic coupling model employing vibronic Hamiltonians expressed in a basis of diabatic electronic states [3] and parameters derived from our IP-EOM-CCSD calculations. The model allows the interaction of the 2B_2 and 2B_1 states to be quantified in terms of the conical intersection energy and linear vibronic coupling constants associated with totally and non-totally symmetric vibrational modes of γ -pyrone. The nonadiabatic nuclear dynamics in the coupled 2B_2 and 2B_1 states was studied using MCTDH method. Also, the resulting vibronic spectrum was computed. The agreement obtained between the theoretical and experimental spectra confirms the adequate level of our modeling and allows for qualitative assignment of the observed spectrum.

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Prediction of photophysical properties of organometallic compounds using machine learning algorithms

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Recently, a broad field of study has been developed in the realm of chemistry, focusing on the development of luminescent materials. For determining the suitability of a molecule as a phosphor, the knowledge of its photophysical and photodynamic properties, including excitation wavelength and fluorescence wavelength, is considered essential. Currently, the demonstration of machine learning applications is limited exclusively to organic molecules devoid of metal atoms. The objective of this research is to devise a model that can predict the photodynamic properties of organometallic complexes.

A combination of a 12×12 Coulomb matrix, which describes the coordination environment of most metal atoms, Morgan FingerPrints, which describe the ligand environment, and persistence Barcodes, which describe the topology of the complex as a whole, was used to encode organometallic compounds. Additionally, good results were shown by the SLATM descriptor.

Acceptable predictive ability was shown by gradient boosting CatBoost; the best results were obtained with neural network architectures such as CNN and RNN, which were found capable of predicting the photodynamic properties of organometallic phosphors with high accuracy. The resulting metrics to predict absorption and emission wavelengths are shown in Figure. For comparison, the results of quantum chemical modeling of absorption wavelengths at the TD-DFT/PBE0-D3BJ/def2-tzvppd/CPCM(Acetonitrile) level in the Orca software package are presented.

As a result, machine learning models that are capable of predicting photodynamic properties at the level of quantum chemical modeling and higher for organometallic compounds were able to be created.

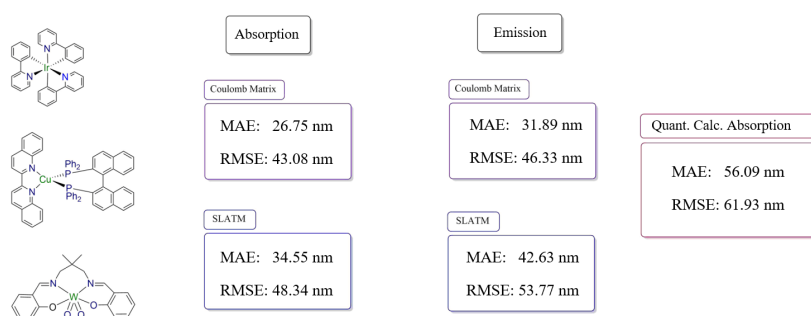


Figure 1: Photophysical properties prediction metrics

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Dataset formation for refolding of the GLP-1 agonist precursor protein

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Machine learning is a subset of artificial intelligence (AI) that focuses on enabling machines to learn from data and improve their performance over time without being explicitly programmed. In traditional programming, a programmer writes rules and instructions for a computer to follow. However, in machine learning, the computer is trained on data to learn patterns and make decisions or predictions based on that data. The prospects for machine learning are incredibly promising and continue to expand rapidly. Machine learning is widely used in various fields, including image and speech recognition, natural language processing, recommendation systems, financial forecasting, healthcare, and many others.

In order for machine learning to be possible, datasets are required. Datasets are collections of data points that are used to train, validate, and test machine learning models. They serve as the foundation for building and evaluating the performance of these models. Datasets can vary widely in size, complexity, and format depending on the specific task and domain they are designed for. As a rule, the sources of datasets are open data. However, the amount of open data is limited in some highly commercialized areas, such as the pharmaceutical industry.

The main problem that the pharmaceutical industry faces when trying to use machine intelligence is the lack of large amounts of open data. When creating datasets, each pharmaceutical company can only rely on itself. Real experiments take time and labor. Therefore, to generate datasets, approaches are needed that allow obtaining the largest amount of data in a minimum number of experiments. An example of such an approach is fractional factor analysis and the design of experiments (DoE) approach developed on its basis.

In this work, the DoE approach was applied to the refolding of the GLP-1 agonist precursor protein to determine the optimal process conditions, as well as the formation of a dataset suitable for machine learning, in particular Bayesian optimization. Based on an analysis of the literature, 12 factors were identified that could affect protein folding, including temperature, pH, urea, sucrose, arginine, SDS and others. Using MODDE 12.1 software, a D-optimal parameter screening plan was constructed, including 21 experiments. An indicator of the quantitative content of hybrid protein in the sample, determined by capillary zone electrophoresis, was used as a response. In addition, to study the component composition of the samples, the method of protein electrophoresis in polyacrylamide gel in the presence of SDS according to Laemmli was used.

Based on the screening results, a critical effect of SDS on the retention of the hybrid protein in the dissolved state was revealed. The main mechanism that ensures an increase in the solubility of a protein molecule in the presence of SDS is the shielding of the hydrophobic regions of the protein by surfactant molecules from the effects of a hydrophilic environment. It is likely that the lower effectiveness of nonionic surfactants, such as Tween 20 and Triton X-100, in the process of renaturation of the GLP-1 agonist precursor protein is associated with less shielding of the hydrophobic regions of the molecule due to the lack of surface charge and a long hydrophobic tail.

Thus, in the course of this work, the current production problem was solved, refolding conditions for the molecule were selected, and a data set was obtained that can be used in the future for machine learning.

Quantum chemical modeling of the electronic structure of ytterbium halides by the coupled cluster method

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Methods based on density functional theory are the most common in modeling the electronic structure of materials. However, when studying optical properties, such as excitation energies, in materials containing lanthanides and actinides, it is almost impossible to achieve reliable and high-precision results. This problem arises due to the fact that the electronic structure of such compounds has close energy levels, which leads to the need to take into account correlation and relativistic effects simultaneously. This can be achieved using relativistic coupled cluster methods, but there is a problem of necessity for time-consuming and memory-demanding calculations. To apply these approaches to crystals, our laboratory has developed a technology for cutting out a fragment from a periodic structure named CTEP (compound-tunable embedding potential) [1], which provides high accuracy in describing the influence of the environment on the selected fragment.

To analyze the correctness of reproducing the simulated electron density in the vicinity of a heavy nucleus, the chemical shift of the X-ray emission spectrum lines was chosen. For each atom, these spectra are characteristic and highly sensitive to the state of a d- or f-element in a particular compound. Direct methods for calculating the X-ray emission spectra lines are practically unapplicable, therefore a "two-step" method for its calculation was developed [2].

In this work ytterbium halides (YbHal_n , $\text{Hal}=\text{F, Cl}$, $n = 2, 3$) are investigated by a relativistic version of the CCSD. This approach has limited possibilities due to the rapid growth of its computational complexity with increasing the system size, therefore, it is important to carry out preliminary calculations on simpler systems and the stoichiometric molecules were chosen for this purpose. In the first part of the work, the calibration of the basic sets on molecular systems was carried out, which showed that when studying the "core properties" on the Yb atom, there is no need to use saturated basic sets on halogens. In the second part of the work, pilot calculations of chemical shifts of X-ray emission spectrum lines for fragments of CTEP crystals were carried out using the relativistic CCSD.

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Theoretical modeling of the structural and spectral properties of a magnesium atom in a methane matrix

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Matrix isolation is a well-established technique for investigating the properties of individual atoms and molecules. Initially conceived for studying metastable molecular systems or transient species, subsequent experimental advancements have revealed that the spectral properties of even well-characterized atoms and molecules exhibit a strong dependence on the surrounding matrix environment. This dependence continues to be of significant interest.

Previously, our group proposed an approach that made it possible to determine the structural parameters of matrix-isolated atoms and small molecules in noble gas matrices, which was subsequently expanded to calculate various spectral properties: Raman spectra, EPR spectra, and electronic spectra. The latter remains the most prevalent technique for investigating systems exhibiting characteristic bands, such as first and second-row atoms.

This study aimed to extend the previously developed approach for modeling a pure isotropic matrix to an almost isotropic methane matrix. The matrix-isolated magnesium atom was chosen as the system of interest, for which experimental spectra are available, but there is no reasonable theoretical interpretation and the trapping site structure has not been established. As part of this work, we carried out *ab initio* modeling of the magnesium-methane system, constructing five different potential energy surface sections using the CCSD(T)/bf/CBS method for the ground state and MRCI(+Q) for the excited state. The resulting potentials were averaged with the Jacobian to obtain isotropic potentials. Next, using the previously proposed approach, the geometries of stable structures were obtained, and the positions of the bands in the vertical excitation spectrum and their shifts relative to the vacuum state were calculated. The agreement obtained with the experiment confirms the correctness of the calculations and allows us to draw a conclusion about the method of trapping the magnesium atom in the noble gas matrix.

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Physically based water-related continuum modelling in the SubTHz range for atmospheric applications

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The concept of continuum absorption raised due to the impossibility to describe the atmospheric air absorption as the sum of the resonance lines of atmospheric molecules. Even after a century of persistent theoretical and experimental efforts on the continuum nature investigation [1], empirical and semi-empirical continuum models are still used in atmospheric physics and related studies. The accumulated knowledge about the continuum absorption spectrum (and its interpretation as a bimolecular absorption) in the subterahertz frequency range (0 – 1 THz), allows building a physically based continuum model for practical applications.

The proposed model is a modification of the MPM (millimeter-wave propagation model) [2], widely used all over the world. Water vapor self-continuum is presented as sum of contributions from absorption by stable and metastable dimers, and absorption corresponding to the unknown behavior of the far wings of the water monomer resonance lines approximated by a simple functions [3]. For the water foreign-continuum, the parameters of its empirical representation in MPM were refined to achieve a better agreement with the available experimental data in the submillimeter wave range.

We demonstrate that the new model is in a very good agreement with current versions of propagation models [4] but the deviation of the the atmospheric brightness temperature calculated with the new model from its empirical progenitor may reach up to 20 K by adding significant for the subTHz range resonance water lines.

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SubTHz molecular laboratory spectroscopy: experimental methods and results

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Today's molecular spectroscopy is addressing a wide variety of fundamental and applied key problems in physical chemistry, molecular physics, and related fields. Molecular structure and chemical bonding, intramolecular dynamics and intermolecular interactions are probed by spectroscopic methods. Astronomical and atmospheric studies, diagnosis of human diseases by analyzing exhaled air, technological processes control and many other applications utilize the molecular spectra. These applications demand accurate information on the spectra of the target molecules.

Laboratory spectroscopy can provide the required spectral information. However, the most complete and reliable data can be obtained using different (by principle of measurement) spectroscopic methods operating in a wide range of thermodynamic conditions. The wider the range of conditions, the more accurate the information about molecules, their dynamics and interactions can be revealed.

In this report we present a complex of gas spectrometers [1] that has been developed in IAP RAS (Nizhny Novgorod) for about half a century. The complex consists of three broadband BWO-based scanning instruments operating in the subTHz range that have the complementary abilities in terms of studying the molecular spectra. These instruments are the video spectrometer, the spectrometer with the radio-acoustic detection of absorption (RAD spectrometer) and the resonator spectrometer. All together they cover pressure range from about 10^{-3} Torr to 10^3 Torr allowing investigation of a variety of physical effects which can manifest themselves in experimental spectra. The examples of the comprehensive study of molecular spectra and other unique results are also presented in the report.

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Calculation of higher-order correlation effects in highly charged ions

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The properties of highly charged ions (HCIs), including both their structure and dynamics, are rigorously described from first principles by quantum electrodynamics (QED), widely acknowledged as one of the most precise theories of fundamental interactions. In comparison to neutral atoms or light ions, HCIs exhibit significantly enhanced physical phenomena. Relativistic effects, Breit interactions, QED corrections, and deviations from various selection rules are notably pronounced in HCIs, exerting considerable influence on their structural and radiative characteristics. The remarkable precision offered by QED theory presents unique scientific opportunities, particularly in the exploration of "new" physics, underscoring the ongoing necessity for rigorous experimental verification. HCIs are actively investigated experimentally utilizing heavy ion storage rings and Electron-Beam-Ion-Trap facilities of varying scales.

Precisely evaluating the structure and dynamic properties of highly relativistic, tightly bound electrons within HCIs presents one of the most formidable challenges in contemporary theoretical atomic physics. Achieving the required theoretical accuracy in the case of few-electron HCIs is a very important and complicated problem. Methodologies employed for calculating high- Z ions fundamentally differ from those used for low- Z ions due to the non-small nuclear-strength parameter αZ (where α denotes the fine-structure constant), rendering it unsuitable as an expansion parameter. Consequently, calculations necessitate consideration of all orders in αZ .

The methodologies for calculating the QED contributions from first- and second-order diagrams are actively evolving and being applied. However, the technical intricacy of directly computing QED corrections escalates rapidly with the order of perturbation theory and the number of electrons, rendering large-scale computations practically infeasible. Consequently, simplified approximate methods are often employed to incorporate these corrections [1, 2]. Enhancing the precision of theoretical calculations entails the development of methodologies that leverage the benefits of both exact and approximate approaches. Nonetheless, numerous experimental datasets exhibit greater precision than their theoretical counterparts, notably for Li-like [3], B-like [4, 5], and F-like [6, 7] ions.

To enhance the theoretical accuracy achieved through rigorous QED methods (limited to the lowest orders), higher-order correlation contributions can be incorporated within the lowest relativistic approximation by solving the Dirac-Coulomb-Breit equation (DCB). These calculations are feasible for both individual levels [8, 9] and within the framework of quasidegenerate perturbation theory to rigorously address the mixing of closely spaced levels with the same symmetry [10, 11].

To refine the prediction of QED screening corrections, we propose employing an approximate method based on the model QED operator. This entails isolating higher-order interelectronic interactions from the QED screening outcomes derived with the model operator. To achieve this, we will introduce a small parameter scaling the interelectronic interaction operator in calculations conducted with the effective QED operator [1]. This parameter enables a numerical decomposition

of the QED screening correction by this parameter. By segregating the lower-order contributions from the total value, we can deduce the higher-order contributions, which will be incorporated into the exact QED values. The accuracy of the results obtained can be gauged by the dispersion of the final values, contingent upon the initial approximation of the perturbation theory regarding the interelectronic interaction (determined by the initial screening potential).

In this study, we illustrate the integration of rigorous QED calculations up to the second order of perturbation theory with higher-order electron-correlation contributions assessed within the Breit approximation and model QED operator in HCl. To account for correlation effects within the Breit approximation, we employ the relativistic Dirac-Fock-Sturm configuration interaction method (CI-DFS) in conjunction with many-body perturbation theory [12].

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Investigation of the structure and properties of the ThF^+ molecule using relativistic coupled-cluster method

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In the next generation of experiments to search for electron electric dipole moment (EDM) at JILA, the ThF^+ molecular ion will be used [1]. The thorium monofluoride molecule is an excellent candidate for searching for EDM, as its EDM-sensitive state $^3\Delta_1$ is the ground electronic state. This allows for increased measurement accuracy, as the coherence time of the measurements will not be limited by the spontaneous lifetime of the working state [2].

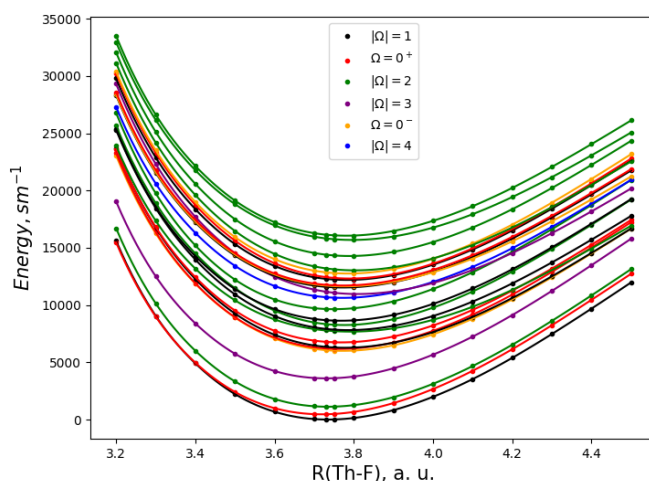


Figure 1: Potential curves of electronic states of the ThF^+ molecule

Accurate data on low-lying electronic states and radiative properties of ThF^+ were obtained using relativistic quantum chemical modeling. Potential curves were calculated using the Fock-space relativistic coupled cluster method with single and double excitations (FS RCCSD), and lifetimes of electronic states were calculated. The FS RCCSD-based spectroscopic constants agree reasonably with experimental data [3] for the four lowest states, while significant discrepancies for higher-energy states are observed. The results of the calculation of potential curves for several dozen low-lying electronic states of the ThF^+ molecule are presented in Figure 1.

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Modeling of P–O bond cleavage mechanism of nucleoside phosphates

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Chemical reactions involving the formation or cleavage of P-O bonds in phosphoric acid esters are important in biochemistry. Phosphoric acid esters of nucleosides are essential in biological systems as components of DNA, RNA, and many cofactors and metabolites. Usually P-O bond cleavage involves the substitution of the leaving group (LG) by a nucleophilic agent (Nu). The substitution might occur stepwise, creating a stable intermediate, or in a concerted manner, passing through transition state. Moreover, the reaction can follow one of two distinct paths: a dissociative mechanism, where the leaving group exit is followed by the attack of nucleophilic agent, or an associative mechanism, where the Nu initiates the attack before the leaving group departure.

In this work, various electron density descriptors and geometry criteria were considered to determine the type of mechanism based on the structure of the enzyme-substrate complex, using the hydrolysis reactions of different organophosphorus compounds in the enzyme's active site as examples. To determine the type of mechanism, it is proposed to use a combination of the distribution of the length of the breaking P-O bond during QM/MM simulation and Laplacian of electron density along the breaking P-O bond at the stationary point corresponding to the enzyme-substrate complex.

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Modeling kinetics of the photoinduced retinal fragmentation

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The retinal protonated Schiff base is a main component of photoactive proteins, which play a crucial role in sensory organs of organisms. The photon absorption in the protein environment leads to the isomerization of retinal, and the chromophore returns to the initial form via a series of intermediates, which are formed in the photocycle of these proteins. For the isolated molecule in the gas phase, the energy cannot, however, be released into the environment and its excess becomes redistributed among various vibrational modes in the ground electronic state following internal conversion and isomerization of retinal. This eventually results in the statistical fragmentation of the molecule in the hot ground state. The chromophore shows a remarkably selective photoresponse in the gas phase, which is triggered by a cyclization reaction with subsequent fragmentation, leading to one specific fragment ion, the truncated protonated Schiff base, and toluene [1, 2]. Such photoinduced fragmentation is used in action absorption spectroscopy, when the photophysics and fast photoinduced dynamics of the retinal protonated Schiff base is studied in the gas phase. Here, we introduce a theoretical model to describe the kinetics of the photoinduced retinal fragmentation.

We develop a methodology for calculating statistical lifetimes of isolated chromophores following their excitation by photons of different wavelengths. By using the MRMP2/CASSCF(12,12)/cc-pVDZ level of theory, we locate all intermediates and transition states along the reaction pathway for the statistical fragmentation of the retinal protonated Schiff base in the ground electronic state. The rate constants for all steps are calculated using the quasi-equilibrium theory for isolated molecules based on the numerical evaluation of densities and sums of vibrational states. The kinetic scheme is then analyzed based on the calculated rate constants. Three characteristic timescales are derived, and one of these time components can directly be compared to the experimental data obtained in the millisecond time window. The calculated (103 mcs and 146 mcs) and experimental (107 mcs and 125 mcs) lifetimes are compared at excitation wavelengths of 530 nm and 550 nm, showing excellent agreement.

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Molecular modeling of reagents potentially active against sulfide minerals

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The search for selective reagents-collectors of sulfide minerals for flotation extraction of noble and other valuable metals is an urgent task. To predict the properties and select flotation reagents, IPKON RAS studied quantum mechanical aspects of chemical bonds and intermolecular interactions of reagents and sulfide minerals.

The fixation of collectors on sulfide minerals during flotation is considered as a process of formation of surface coordination compounds. 3D models of minerals, collectors and their complexes were created in the ChemBio 3D program of the specialized ChemOffice complex. The resulting structures were optimized and minimized using molecular mechanics MM 2. The calculation of the main data during modeling was carried out using the PM 7 method using the MOPAC software module using ARC and Gaussian Output files.

To quantify the activity of collectors during the interaction of a collector with an atom of a mineral cluster, P.M. Solozhenkin proposed a forecast index for assessing the activity of the collector POAS [1]. It is defined as the difference between the total energy of the complex and the sum of the energy of the cluster and the energy of the collector, determined by the expression:

$$\Delta E = E_{\text{complex}} - (E_{\text{cluster}} + E_{\text{collector}}), \text{ eV}$$

The lower the value of the POAS index, the more preferable is the interaction of the collector with an atom of the mineral cluster. Reagents with a negative index can be effective collectors.

As a result of modeling the parameters of molecular interactions, new reagents were identified and recommended as collectors of sulfide minerals of gold, antimony, copper, zinc, and lead. Thus, to obtain complexes of copper, lead, zinc and antimony with (di(pyrazin-2-yl)amine), docking was carried out. Atomic charges, orbital energies, and the electron occupancy of the orbitals of the complexes were determined. The data obtained were used to calculate the POAS index. It was established that for the copper complex, POAS is equal to 6.081 eV, for the lead complex, POAS is equal to -1.39301 eV, for the antimony complex, POAS is equal to -2.82434 eV. Thus, di(pyrazin-2-yl)amine can be a collector for sulfide minerals of lead and antimony.

For flotation of zinc sulfide minerals, their preliminary activation with copper ions is used. For the CuZnS cluster, di(pyrazin-2-yl)amine and C₁₀H₇(N=N)(C=O)OH are considered as collectors. For the complexes obtained as a result of docking, the values of the POAS index were calculated. For CuZnS and (C₁₀H₇(N=N)(C=O)OH), the POAS is -1.65243 eV, and for CuZnS and di(pyrazin-2-yl)amine, the POAS is -1.7222 eV. Based on the negative values of the POAS index, it is possible to conclude that these compounds may be effective as collectors of zinc sulfide minerals.

The approach being developed allows for a preliminary selection of reagents for flotation [2]. It is especially important for the extraction of strategic metals, the compounds of which are found in complex deposits, as well as in the form of finely disseminated or emulsion associations, and therefore are difficult to isolate in pure form.

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Role of the protein environment and structural heterogeneity in the mechanisms of photochromic reactions of microbial and animal rhodopsins

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Rhodopsins are photosensitive proteins containing the retinal protonated Schiff base (RPSB) as a chromophore group. The protein environment plays an important role in establishing high quantum yields and high rates of their primary photochemical reactions: *all-trans* → *13-cis* and *11-cis* → *all-trans* photoisomerization of RPSB in microbial and animal rhodopsins, respectively [1]. However, nonreactive excited states that produce no photoproducts are also observed in rhodopsins. In this work, we investigate the influence of the protein environment on the photodynamics of RPSB in the forward and reverse photoisomerization reactions and study the role of the structural heterogeneity of the protein active centers in the formation of nonreactive states in microbial and animal rhodopsins.

By using molecular dynamics simulations and extended multiconfiguration quasi-degenerate perturbation theory (XMCQDPT2) [2] combined with the effective fragment potential method (EFP) [3], we calculate the S_0 - S_1 vibronic band shapes of RPSB in the active centers of microbial rhodopsins KR2, ESR, and bacteriorhodopsin, as well as animal bovine rhodopsin. We show that each rhodopsin selectively excite certain vibrational modes of the RPSB polyene chain upon the S_0 - S_1 transition, thus determining the different specificity and efficiency of the primary photoisomerization reaction in these proteins. Remarkably, the reverse photochromic reactions show specificity only in microbial rhodopsins, whereas the specificity of the reverse photoisomerization is lost in visual rhodopsin. The high efficiency of the direct *11-cis* → *all-trans* photoisomerization reaction and the low probability of the reverse photoreaction might indicate evolutionary much higher tuned chromophore-protein interactions in animal rhodopsins.

We also reveal structural heterogeneity of the retinal-binding pocket in the KR2 and ESR rhodopsins, characterized by several distinct conformations of their active centers. This is thought to be related to the presence of nonreactive states in the photodynamics of these proteins.

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Parametric broadening of the electronic-vibrational spectrum of a molecule caused by zero-point vibrations and thermal fluctuations of interatomic bonds

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The existence of a new type of broadening of the spectral line of an electronic-vibrational-rotational (rovibronic) transition in a molecule, caused by zero-point vibrations and thermal fluctuations of atomic nuclei near their equilibrium positions during vibrational-rotational motion inside the molecule, has been shown [1, 2, 3]. From the position of the Copenhagen interpretation of quantum mechanics, the parametric broadening of vibronic transitions is an expression of the difference between a real open (i.e., experimentally measured) system and an isolated (unobservable) system. To describe a real molecule, modified Franck–Condon diagrams have been proposed (Figure).

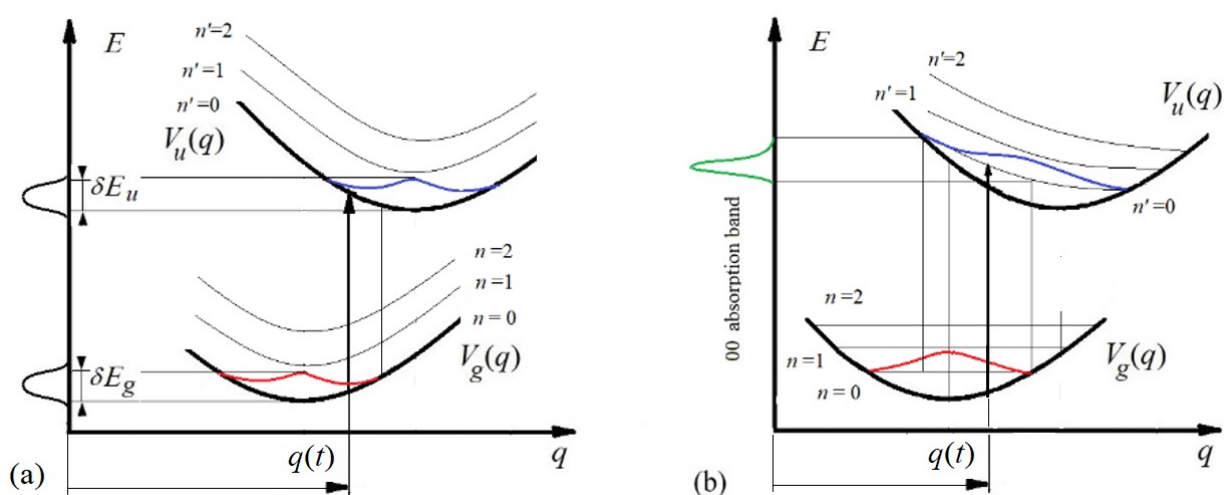


Figure 1: A modified Franck–Condon diagrams describing the occurrence of parametric broadening of vibronic levels (a) and lines (b) in a molecule [2].

Expressions for the parametrically broadened spectral intensity of the vibronic transition are found. An estimate of the parametric broadening of the absorption line of the (0-0) transition in a series of monomers of polymethine dyes, which is comparable in order of magnitude with the broadening observed in the experiment, is presented. Existing quantum chemical methods for calculating molecular spectra do not take into account parametric broadening. Taking this effect into account makes it possible to clarify existing ideas, incl. when describing the photodissociation spectrum of a molecule.

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Machine learning approaches for fuel design

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Despite the development of the alternative energy industry, fuel energy remains a key industry in the global economy. High-throughput screening of mixtures in order to find the optimal fuel composition, including those based on biofuel components, is important both from an economic and environmental point of view. The key characteristics of fuels are the research and motor octane numbers (for gasoline), cetane number (for diesel), density and viscosity. Modern research in various fields is shifting towards data driven approaches that allow making highly accurate predictions based on accumulated experimental and calculated data. The use of such approaches in the field of fuel quality assessment makes it possible to solve the complex problem of efficiency, time and price costs: traditional methods of determining octane numbers and other fuel characteristics involve expensive and time-consuming laboratory tests. Machine learning models can predict octane numbers quickly, saving time and resources.

In this work, a machine learning model is implemented to predict the octane and cetane numbers of individual fuel molecules and mixtures. For individual molecule models, a comparison of the use of classical tabular ML approaches using deterministic descriptionization based on well established chemical descriptors [1] with subsequent feature engineering and a DL approach based on graph convolutional neural networks of various architectures is demonstrated. Within the framework of mixture prediction, various approaches to accounting for the properties of individual molecules have been studied: a quasi-additive model that uses only the composition and embeddings of individual molecules as input data, as well as an approach with the descriptionization of paired intermolecular interactions of molecules presented in mixture.

We used the created predictive model for individual molecules as a reward model for L-MolGAN [2] generative model, shifting the generation distribution to the region of molecules with a high octane number or cetane number and conducted high-throughput screening of mixtures, identifying potential fuel candidate mixtures.

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Modeling photoabsorption spectra of conformationally flexible calcium indicators in solution upon one- and two-photon excitation

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Fura-2 is a ratiometric fluorescent dye, which binds to free intracellular Ca²⁺ ions and is widely used for calcium imaging in living cells. Upon complexation, the absorption maximum of Fura-2 shifts from 375 nm to 340 nm, and the ratio of the emission intensities at these wavelengths can directly be related to the amount of intracellular calcium [1]. However, continuous exposure of samples to the blue and UV light has a detrimental effect, as it causes their deterioration due to photobleaching and photodamage. Moreover, the short-wavelength light is unable to penetrate tissues deeper than 40 mm. These issues can be addressed by employing two-photon excitation, which practically assembled in two-photon scanning microscopy (2PEF) with near-infrared laser light. Here, we introduce a methodology for modeling one- and two-photon absorption spectra of conformationally flexible fluorescent dyes in solution to optimize their brightness for bioimaging applications. We also apply the new methodology for calculating spectral profiles of Fura-2 in a free state and bound to Ca²⁺ ions in aqueous solution upon one- and two-photon excitation.

Our methodology explicitly accounts for both the homogeneous and inhomogeneous spectral broadening effects. It combines MD sampling techniques with high-level quantum chemistry calculations of one- and two-photon transition parameters for multiple structures taken along the MD trajectory. The following major steps are performed: MD simulations using the NPT ensemble at 300 K, QM/MM (PBE0/(aug)-cc-pVDZ/CHARMM) geometry optimization, XMCQDPT2 [2] / EFP [3] calculations of transition parameters, simulating Franck-Condon vibronic band shapes using a linear coupling model, calculations of two-photon absorption cross-sections using a sum-over-states approach, modelling overall one- and two-photon absorption spectra.

We show that the contribution from inhomogeneous broadening is crucial for accurate modeling of both the one- and two-photon absorption profiles of conformationally flexible dyes like Fura-2 in solution. We also reveal a strong correlation between the calculated two-photon absorption cross-sections and the changes in permanent dipole moments upon the transition. Chemical modifications of Fura-2, which increase the intramolecular charge transfer character upon the transition, can therefore be used to enhance its nonlinear photophysical properties.

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Ground state of the light relativistic atoms in intermediate and strong magnetic fields

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The progress of astrophysical spectroscopic methods for studying the thin hot atmospheres and accreting gas near compact objects such as neutron stars, white dwarfs, and magnetars has significantly stimulated theoretical interest in investigating electronic properties of atomic systems under extreme conditions of relativistic matter in superstrong magnetic fields ranging from 10^6 up to 10^{15} G. Since such conditions are largely unattainable in available experimental setups, this motivates the development of *ab-initio* approaches to describe Lyman series. However, the complete description of the spectroscopic features for most compact objects requires consideration many-electron atomic species, including He, Li, C, and O atomic species. In this context, there have been numerous studies dedicated to the description of non-relativistic atoms in strong magnetic fields within the framework of either standard quantum chemical strategies or kinetic diffusion methods. Against this background, there is a clear lack of research within the framework of relativistic approaches, whether QFT or relativistic quantum chemistry (RQC), which is primarily due to the peculiarities of T-symmetry accounting in most standard relativistic packages, as well as the general complexity of the resulted QFT propagator expansions.

The aim of this work was to create and implement RQC approaches, primarily DHF, MCSCF, and FCI, that allow one to bypass the NVPA when solving the problem of the spectrum of the relativistic electronic Dirac-Coulomb-Gaunt Hamiltonian. Within this framework, the Lanczos method was used in the critical points analysis for the energy dispersion functional which made it possible to avoid the problem with the lack of a lower-bound property of the Dirac Hamiltonian. All approaches, except MCSCF, were implemented without NVPA in atomic bases with correct asymptotic behavior and control of convergence by moments and the atomic basis size, where the magnetic field contributions was completely accounted for within the one-particle problem. As a result, the FCI method was applied to produce the relativistic energies dependencies on the magnetic field for the ground and several lower excited states of H, He, and Li atoms, see Fig. 1. The regions of crossing of atomic terms corresponding to the rearrangement of the symmetry of the ground state were obtained and studied.

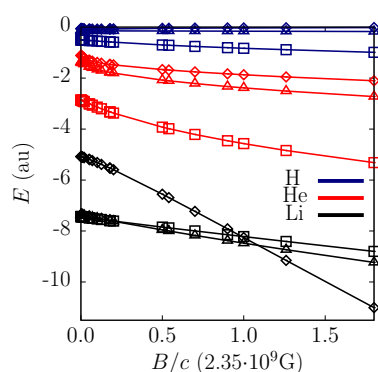


Figure 1: The dependencies of total electronic energy for the ground and a few first excited states of H, He, and Li on the magnetic field strength B .

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Branching in internal conversion of the methylene iminium cation

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The interaction of molecules with light is essential for many natural processes and vital functions of living organisms. For example, 11-*cis* retinal in the form of a protonated Schiff base is a key element of rhodopsin, which is a protein that plays an important role in human vision. The photoinduced isomerization of 11-*cis* retinal, leading to the formation of its all-*trans* form, causes structural changes in the rhodopsin protein. These changes trigger the generation of a nerve impulse. The isomerization process is one of the fastest natural processes, with nuclear rearrangements occurring within hundreds of femtoseconds. However, the mechanism behind this reaction has not yet been fully understood due to the difficulty in studying it using high-precision quantum chemistry methods, which require a significant amount of time for calculations. In order to investigate the mechanism of photochemical isomerization, a small molecular model of the methylene iminium cation has been chosen. This work aims at studying the relaxation mechanisms of the electronically excited methylene iminium cation using second-order extended multiconfiguration quasi-degenerate perturbation theory (XMCQDPT2).

By using the XMCQDPT2/SA(3)-CASSCF(12,12)/aug-cc-pVDZ level of theory, we have studied the potential energy surfaces of the methylene iminium cation in the S_0 , S_1 , and S_2 states. The S_2 state is found to be of a $\pi\pi^*$ character, while S_1 corresponds to the $\sigma\pi^*$ excited state, and the corresponding $S_0 \rightarrow S_1$ transition happens to be optically dark at the equilibrium geometry of the molecule in the ground electronic state. Therefore, the photoinduced dynamics of the molecule starts in the S_2 state. Stationary points and three conical intersections between different states are identified, and topographies of the potential energy surfaces around the conical intersections are analyzed. We show that the main relaxation pathway is associated with the passage of the excited molecule through two conical intersections, resulting in its barrierless isomerization. This finding is consistent with the internal conversion mechanism of the methylene iminium cation as described in the literature.

We also reveal another relaxation pathway through two conical intersections, S_2/S_1 and S_1/S_0 ; however, the second conical intersection is of a different nature compared to that of the main relaxation pathway. Unlike the S_1 state of the main branch, which acquires the $\pi\pi^*$ character after the passage of the first S_2/S_1 conical intersection, it remains its $\sigma\pi^*$ origin along the minor pathway. This minor channel in the relaxation mechanism of the methylene iminium cation has not been reported so far. The minor branch may lead to the re-population of the initial ground state or to the photoinduced fragmentation of the molecule through the loss of H_2 . The branching ratio of the two channels and its impact on the photoinduced dynamics of the methylene iminium cation are discussed.

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From humorous post to detailed quantum-chemical study: Isocyanate synthesis revisited

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Isocyanates play an essential role in modern manufacturing processes, especially in polyurethane production. There are numerous synthesis strategies for isocyanates both in industrial and laboratory conditions, which do not prevent searching for alternative highly efficient synthetic protocols.

In this work, we report a detailed theoretical investigation of the mechanism of sulfur dioxide-catalyzed rearrangement of the phenylnitrile oxide into phenyl isocyanate, which was first reported in 1977 [1]. The DLPNO-CCSD(T) method and up-to-date DFT protocols were used to perform a highly accurate quantum-chemical study of the rearrangement mechanism. An overview of various organic and inorganic catalysts has revealed other potential catalysts, such as sulfur trioxide and selenium dioxide. Furthermore, the present study elucidated how substituents in phenylnitrile oxide influence reaction kinetics. This study [2] was performed by a self-organized collaboration of scientists initiated by a humorous post on the VK social network.

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Search for \mathcal{T}, \mathcal{P} -violating axionlike-particle-mediated interactions in HfF^+ molecular cation

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Molecules containing atoms of heavy elements can be used to search for "new" physics beyond the Standard Model by precision experiments searching for the effects of spatial parity (\mathcal{P}) and time reversal (\mathcal{T}) symmetries violations of fundamental interactions. One of the most discussed source of \mathcal{T}, \mathcal{P} -violating interaction in molecules is the electric dipole moment (EDM) of the electron [1]. At the present moment, a non-zero EDM of the electron has not been detected, but a constraint on its value has been established. The most accurate constraint was obtained by the JILA group in the experiment with molecular cations of hafnium monofluoride (HfF^+) [2].

However, the \mathcal{T}, \mathcal{P} -violation of fundamental interactions in molecules can be induced not only by the electron EDM, but also by the effect of the exchange of virtual axionlike particles between the electron and the nucleus, as well as between two electrons. The study of this effect for a number of atoms and molecules was carried out, e.g., in Ref. [3]. A detailed theoretical study of the \mathcal{T}, \mathcal{P} -violating interactions induced by axionlike particles in the molecular cation HfF^+ with a precise account of the inter-electron correlation effects was carried out in our paper [4]. For this purpose, programs were developed to calculate the matrix elements of the corresponding interaction operators. As a result, the constraints on the interaction constants for a wide range of considered masses of axionlike particles were established.

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Transferable ML-based variational Monte Carlo

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The Quantum Monte Carlo (QMC) method is one of the most important methods for solving the Schrödinger equation ab initio. However, in QMC, the accuracy of the solution largely depends on the choice of the ansatz, which requires considerable knowledge and experience. This limits the adaptability of QMC compared to other deterministic approaches such as CCSD(T), which are widely considered the “gold standard”.

Machine learning has revolutionized the field of quantum chemistry for obtaining more accurate solutions to the Schrödinger equation. One of the pioneering approaches is the ML-based real-space variational Monte Carlo (ML-VMC), such as FermiNet, PauliNet [1] and PsiFormer [2]. The ground state wavefunction can be obtained through the variational principle, by which the expectation value of the energy is minimized. Based on this fact, ML-VMC methods utilize deep neural networks to parameterize the wavefunction and optimize the network parameters with the energy serving as the loss function. The most important disadvantage is the inability to reuse the trained ML-VMC model within the study of different molecules. This problem can not be solved by additional training with small amount of train steps: the internal structure of the model does not allow it to be reused if number of electrons is changed. The existing solution to this problem is to replace electron-dependent trainable backflow matrices, which project electron embeddings onto single-electron functions, with trainable functions of atomic descriptors obtained from a cheap DFT calculation [3].

In this work, an ML-VMC solution is presented that project electron embeddings using atomic descriptors together with information about the average density of other electrons of the same and opposite spin obtained using the seq2seq model for electron embeddings. It is shown that such additional transmission of information about other electrons bypassing the electronic embedding itself has a positive effect on the transferability of the model. In addition, a number of alternative atomic descriptors have been studied, including the joint use of data from the DFT calculation and constant atomic descriptors independent of the molecular system under consideration. Despite the growth of the trainable parameters, this expansion reduces the required number of additional training steps when transferring the model to a new molecular system.

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Non-adiabatic excited-state dynamics simulations based on highly accurate quantum chemistry and neural network interatomic potentials

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The interaction of light with biological molecules is central to the vital activity of living organisms. These processes are remarkably efficient and occur on a timescale down to sub-picoseconds. In the understanding of the photoinduced dynamics, theoretical studies play an essential role because they provide many useful physical insights, for instance, excited-state reaction pathways, impact of protein environments, and detailed molecular motion in the dynamics. However, a proper selection of electronic structure methods is essential for accurate modeling. Systems with quasi-degeneracy require multi-reference approaches, accounting for both static and dynamic electron correlation. The on-the-fly excited-state dynamics is generally very expensive due to high computational costs, particularly when a high-level electronic structure method is used. Great efforts are currently being made to construct excited-state potential energy surfaces by using machine learning approaches and to use them for speeding up dynamics simulations.

Here, we aim at developing a comprehensive computational protocol to explore general nonadiabatic dynamics in complex molecular systems by combining on-the-fly trajectory-surface hopping mixed quantum-classical dynamics with multiconfiguration quasi-degenerate perturbation theory (XMCQDPT2) [1]. To speed up the nonadiabatic dynamics simulations, we use an E(3)-equivariant neural network approach [2] for learning interatomic potentials from the XMCQDPT2 and underlying CASSCF calculations. The developed methodology is extensively tested on the photoinduced dynamics of the methylene iminium cation, CH_2NH_2^+ — a small model molecule featuring a single double bond of the retinal protonated Schiff base important in vision. The results are obtained using potentials, which are based on the XMCQDPT2/SA(3)-CASSCF(12,12)/aug-cc-pVDZ and SA(3)-CASSCF(12,12)/aug-cc-pVDZ methods. Three electronic states are monitored during the photoinduced dynamics simulations — optically bright S_2 , dark S_1 , and ground S_0 . The probability of hopping events between different electronic states are estimated based on the overlap of electronic wave functions at two successive points along the trajectory propagation. The time step for propagation is set to 0.2 fs, and each trajectory out of the total of 100 is simulated up to 500 fs. Initial conditions are generated according to the Wigner distribution for ground-state normal modes at 300 K. Population dynamics, key molecular motions, excited-state lifetimes, and branching in the nonadiabatic dynamics of CH_2NH_2^+ , occurring through three conical intersections and involving photoisomerization and photoinduced fragmentation, are analyzed and discussed.

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Tensor decomposition methods for high-precision relativistic modeling of electronic structure

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The achievement of high accuracy in theoretical modeling of the electronic structure of materials containing f-elements, in particular lanthanides and actinides, requires simultaneous consideration of relativistic and correlation effects. The most promising method that satisfies this requirement is the relativistic coupled cluster method (RCC), which leads to extremely resource-intensive calculations. It is possible to achieve increased capabilities and reduced computational complexity by using tensor decompositions to store data and optimize the algorithms used in modeling.

For this purpose, a detailed analysis of the efficiency of various tensor decomposition schemes (canonical [1], tensor train [2] and Tucker[3] decompositions) were carried out. Optimal algorithms were found for performing the approximate decomposition of tensors of molecular integrals and cluster amplitudes, and the computational complexity of algorithms implementing the basic operations of the working equations of the coupled cluster method was evaluated.

For the first time, the equations of the coupled cluster method for the ground state were formulated directly in terms of tensor trains, including versions of the method that take into account the contributions of triple excitations of reference functions. Also a software implementation was performed and include to the EXP-T quantum chemical package [4]. Pilot calculations using CCSD and CCSDT methods were carried out, in which the superiority of solving the equations of the coupled cluster method in terms of tensor trains was shown.

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Polarizability in computational astrochemistry of fullerenes and PAHs

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Organic matter of space is a challenging object to study due to diversity of the astronomical objects, wide range of conditions, limitations of spectroscopy techniques etc. Therefore, astrochemical studies operate with a combination of experimental and computational methods. It allows restoring a whole picture of chemical processes in astronomical objects and predicting their behavior.

This talk summarizes the grounds and applications of polarizability to the astrochemical studies on polycyclic aromatic hydrocarbons (PAHs) and fullerenes, which are widespread in interstellar and circumstellar media. Polarizability is introduced to physical chemistry as a parameter describing the response of the molecule's electronic cloud to the external electric field. However, it was found useful for the analysis of physicochemical processes (interactions with positrons, molecular collisions, quenching, and dielectric screening) and chemical reactions (including catalytic ones) [1, 2]. The idea of a combined use of minimum-polarizability and minimum-energy principles for searching for novel candidates for detecting in space is considered. This idea seems fruitful. Indeed, operating with the polarizability values, we predicted in 2018 the helicenes, a class of non-planar PAHs, as abundant compounds of interstellar medium [3]. In 2019, helicenes were produced in laboratory experiments simulating the conditions of the circumstellar envelopes of carbon-rich red giants [4]. Thus, we formulated the empirical rule to discriminate low-abundant and high-abundant structures in environmental conditions: planar PAHs have low energy whereas their nonplanar isomers have low polarizability [1, 5]. Low polarizability is a factor that enhances molecule's survivability under high-energy conditions, so low polarizability is associated with high abundance of chemical substances [1, 6].

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Bimolecular absorption in nitrogen

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Molecular composition of the currently known planetary atmospheres is dominated by symmetrical species that do not have resonant absorption lines in the long wave infrared and microwave spectral ranges. Nevertheless, absorption caused by weak intermolecular interactions may become crucial in microwindows of atmospheric transparency. The most abundant gas in the Earth's atmosphere, nitrogen, is transparent in the far-infrared. In contrast, collision induced absorption (CIA) in a nitrogen gas is perceptible in the Earth's stratosphere. Accounting for the nitrogen CIA is also known to be indispensable for the simulation of the thermal radiance in the Titan's atmosphere.

In this work we present a detailed experimental and theoretical characterization of the millimeter and sub-millimeter wave absorption in N_2-N_2 and N_2-Ar pairs. The measurements are carried out using a resonator spectrometer [1] at pressures up to 2 atmospheres in a broad frequency range from 70 up to 360 GHz. Spectra of pure nitrogen were measured at temperatures 296 ± 20 K and N_2 with Ar mixture spectrum was measured at room temperature. In this frequency range and under chosen conditions, the absorption of the studied gases has entirely bimolecular nature. The expected continuum pressure and temperature variations are experimentally confirmed. The data obtained so far are in agreement with previous experimental observations [2] as well as with the results of trajectory-based simulation [3]. New practical model is suggested on the basis of theoretical and experimental data, which is intended to facilitate simulation of radiative transfer of mm-submm radiation in the nitrogen rich atmospheres.

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Development of sustainable technologies for flotation plants

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The flotation method is used by about 45% of Russian mineral processing plants. Due to the deterioration of the mineral resource base, the ores supplied for processing are becoming increasingly poorer and more complex. Maintaining the quality of the resulting concentrates is becoming increasingly challenging. Digitalization of factories makes it possible to optimize management processes at a higher level for the sustainable development of technology. Machine (technical) vision helps monitor the condition of ore during crushing and grinding. Artificial intelligence can be used in digital twins of grinding and subsequent flotation processes, in automating equipment control or in preliminary modeling of processes based on the analysis of sensor readings and historical plant data in a database. Also, based on artificial intelligence, digital advisors (recommendation services) are being developed to manage the duration and efficiency of the flotation process [1]. At the Uchalinsky Mining and processing plant, the Smart Advisor system makes a forecast of the quality and quantity of the ore charge based on the quality of the feedstock and plans deliveries. When managing the flotation process, the digital advisor optimizes decision making and predicts performance as process parameters change. As a result of using the system, a 6% increase in product quality, a 12% reduction in unscheduled shutdowns, and a 5% increase in productivity were achieved. The introduction of the “Collective Flotation Optimizer” at Norilsk Nickel’s Talnakh concentrator allowed to increase the extraction of metals into concentrates: nickel by 0.1%, copper by 0.08%, and also stabilize the flotation front.

Creating optimization algorithms for controlling the flotation process is a complex task. Flotation is a dynamic process. The machine vision system must be able to process a video stream from several cameras and determine the main characteristics of the foam automatically. Foam characteristics are used to control the degree of aeration, reagent consumption, and foam level in the flotation machine. Semantic segmentation is used to determine the size, shape, and number of bubbles, and bubble tracking is used to analyze the speed and direction of foam movement.

The most famous machine vision systems were developed for their flotation machines by Outokumpu (Outotec FrothSense), Metso Minerals (Outotec FrothSense), and Russian companies RIVS (MachineVision). For the Kola Mining and Metallurgical Company, the RIVS company developed a machine vision system and built flotation algorithms [2]. The neural network model was trained by assigning the bubble size to one of the classes from 1 to 10 and comparing the image with the regulatory parameters – air flow for aeration and the flow of two reagents. The intended goal was to ensure that the specified grade (up to 6 mm bubbles) was maintained at no lower than 70-80%. When the content of bubbles of a given class decreased, a task was given to correct the consumption of the collector reagent. Thus, modernizing process control using machine vision and neural networks can improve the performance of flotation plants.

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Cryochemical synthesis and quantum chemical modeling of the IR spectrum of magnetic iron oxide nanoparticles and their hybrid systems with chloramphenicol

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During the last decade, science and engineering have seen a rapid increase in interest for nanoscale materials with dimensions less than 100 nm. Nanoparticles, due to their submicroscopic sizes intermediate between atoms and bulk (solid) materials, have unique characteristics, primarily, a large surface area per volume unit, a high proportion of surface and near-surface atoms. Magnetite and maghemite nanoparticles also possess the unique magnetic and thermal properties, easily separation, low toxicity and biocompatibility. Magnetic iron oxides nanoparticles currently have immense potential as magnetic vectors for directed drug delivery and carriers, magnetic agents for MRI and magnetic hyperthermia. If the size of these particles decreases below the critical size of the magnetic domain, they will transfer into a superparamagnetic state. Superparamagnetic nanoparticles are characterized by a high value of saturation magnetization, the absence of residual magnetism and a high magnetocaloric effect. In addition, superparamagnetic particles smaller than 10 nm are optimal agents for MRI, as they are T1 contrast agents, unlike larger particles [1, 2].

Cryochemical technologies in the case of nanomaterials production make it possible to increase the environmental friendliness of the synthesis and obtain materials with different dimensional and structural characteristics. In the course of this work, particles of magnetic iron oxides of various sizes and structures were obtained, by varying the conditions of cryochemical synthesis. Cryochemical coprecipitation of divalent and trivalent iron salts makes it possible to reduce the average size of the resulting magnetic iron oxide nanoparticles from 17 (the case of classical coprecipitation) to 6 nm. However, in this case, in addition to the main metal oxide products, goethite with undesirable magnetic properties is also formed. The deposition of iron (II) sulfate from the surface of cryogranules makes it possible to obtain nanopowder of magnetic iron oxide, freed from the admixture of goethite particles. In this case, the IR spectra of the resulting nanoparticles play an important role in determining the substance. However, in modern literature it is difficult to find spectra and use them to separate magnetite and maghemite. To solve this problem, quantum chemistry approaches can be used to model IR spectra and compare them with IR spectra of samples of known composition.

Low-temperature technologies make it possible to obtain not only nanoparticles, but also hybrid materials. Magnetite nanoparticles obtained by cryochemical method were included in chloramphenicol based nanocomposite. The resulting hybrid particles had an average size of 50-400 nm, including magnetite nanoparticles with an average size of less than 10 nm, as in the precursor used. It is important to understand how the drug is attached to the surface of the hybrid system. One of the methods for determining this problem is quantum chemistry and molecular dynamics, which allows one to calculate these interactions and construct a theoretical IR spectrum and compare it with the practical one.

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Effective collaboration between science and industry in biotechnology

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Recently, scientists and business representatives in Russia are increasingly talking about close co-operation between science and industry. It seems that this interaction can be particularly effective and serve to create high-tech products and solutions. But there is still a question of how exactly to organise this cooperation to make it really useful.

For the second year in a row, we are organising a scientific and industrial biotech festival "BioTech Day" [1] on the basis of MIPT, which is dedicated to the interaction of young scientists and specialists with the biotechnology industry. Our venue brought together about 900 participants who listened to more than 20 lectures, visited more than 5 excursions and took part in a poster session.

Our main idea is that cooperation between industry and science should be organised at all levels: from universities to classical laboratories and research centres. And the implementation of this approach, in addition to the conclusion of formal co-operation agreements, should include annual festivals and conferences where all participants could communicate in a comfortable environment and discuss current tasks, problems and areas of work.

We have developed a new programme for such a festival, based on the experience of the past two years and including the best of our solutions, which we are ready to share.

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[1] BioTech Day, <https://biomed-mipt.ru/biotechday>

Ab initio study of dioxidine dimers as a tool to predict polymorphs formation

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Polymorphism of medicinal substances, understood as the crystallization of a medicinal molecule in a variety of structures depending on external conditions, is an important factor in pharmaceutical control, as well as a factor in the development of new highly effective dosage forms.

Electronic structure methods such as periodic DFT, MP2, molecular dynamics methods are widely used for crystal structure prediction and calculation of its thermodynamic parameters. However, such standard methods are less suitable for studying molecular crystals, where a more thorough exploration of the conformational space is necessary. Fragment-based approach which involves breaking down a crystal into smaller, more manageable fragments or characteristic building blocks allows to explore vast conformational space with reduced computing efforts as well as to obtain more interpretable results [1]. Thus, in the study [2], the energy of two polymorphic crystal lattices of lead (II) phthalocyanine and their UV-vis spectra were estimated using calculations of the corresponding dimers and trimers.

If the crystal structures of polymorphs have been deciphered experimentally or modeled theoretically, it becomes possible to predict the formation of a particular crystal structure depending on external conditions, in particular on the solvent. The effect of the solvent is to stabilize certain structures of solute on the way to the formation of a critical size nuclei [3] as well as block specific centers of hydrogen bond formation thus destabilizing the oligomer of the corresponding crystal structure [4]. For the first stages of this process, the formation of dimers and lower oligomers, the thermodynamic effect will be maximal and decisive in the formation of the nuclei of a particular crystalline phase. Thus, the approach consists in the precise description of molecular dimers and oligomers structurally corresponding to appropriate crystalline phases in a solvent medium.

In our study dimers and oligomers of antibacterial drug dioxidine have been shown to exhibit structural properties of two polymorphic forms - triclinic (T) and monoclinic (M). In the absence of any solvent oligomers corresponding to triclinic phase are shown to be more thermodynamically stable, being in accordance with the experiment. When the CO₂ carrier gas is used as a solvent during dioxidine nanoparticles formation, the M phase becomes more stable according to the experimental data [5], and its content increases with increasing CO₂ concentration. Calculations of T and M dioxidine dimers with different numbers of CO₂ molecules have shown that with an increase in the number of CO₂ molecules in the system up to four, the difference in the ΔG of formation of these dimers changes by more than 20 kJ/mol, making the M dimer more stable than T dimer. This approach is planned to be applied to other drug-solvent systems, as well as to solvate crystalline forms in the future. Quantum chemistry program ORCA, DFT B3LYP-D3 method, (aug)-cc-pVDZ basis were used for calculations.

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Predicting emulsion type in octane-C₁₀E₄-water systems using dissipative particle dynamics simulation

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Hydrocarbon production in the modern world is an extremely important issue. Nowadays one of the most useful approaches for increasing the efficiency of oil recovery is the injection of chemical agents into the oil well. These agents reduce interfacial energy in the oil-water system, which increases the efficiency of oil recovery. Quite effective reagents for this goal are surfactant mixtures with alkalis. Due to the complex composition of oil, an important task is to optimize the composition of the reagents and production conditions. Experimental selection of the optimal surfactant composition is highly complicated and requires significant time. Improvement of molecular modeling tools and computer technology provides great opportunities for predicting the properties and effectiveness of surfactant mixtures used to reduce interfacial tension in the oil-water system [1]. Dissipative particle dynamics (DPD) simulation is a very useful technique for estimating properties of large molecular systems [2]. DPD it takes less computational forces than similar molecular dynamics and DFT-methods but still provides accurate results.

In DPD simulations all particles are represented as soft beads, interacting with each other by weak repulsive force. Repulsion parameters could be estimated from experimental data or using DFT.

In the present work DPD simulations in a model octane-C₁₀E₄-water system were used for prediction of interfacial properties and microemulsion stability in different conditions. Repulsion parameters were optimized for better accordance with experimental data. To estimate the microemulsion type we used the 'method of moments' approach, based on the calculation of the first moment of surface tension [3].

Acknowledgements The calculations are carried out using the equipment of the shared research facilities of HPC computing resources at Lomonosov Moscow State University as well as the local resources (RSC Tornado) provided through the Lomonosov Moscow State University Program of Development.

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Band Alignment transformations in heterostructures by applying external stimuli: a first principal investigation

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To create ultrafast multifunctional nanoelectronic devices, it is necessary to develop some new approaches to common semiconductor systems based on different band alignment of individual heterostructure components. It is generally accepted to distinguish three types of band alignment between semiconductors distinguishing on the relative positions of the valence band maxima and conduction band minima of the semiconductors [1]. And one of the suggestions is to use 2D nanomaterials to create different heterostructures. Due to the absence of broken bonds 2D nanomaterials can be vertically aligned in van der Waals (vdW) heterostructures by both top-down and bottom-up techniques and such hybrid nanomaterials not only preserve the properties of individual components but also can acquire new features and expand the application of the initial monolayers. To design novel biomimetic devices with excellent characteristics it is required to manipulate and do engineering of the band alignment between individual heterostructure components which can be achieved by applying a reversible external stimuli like electric field or strain.

To date, many 2D nanomaterials are known and a large amount of them have been not only theoretically predicted but also were successfully fabricated like transition metal dichalcogenides (TMD), MXenes, hexagonal boron nitride (h-BN) therefore the number of perspective heterostructures which should be investigated is significant and to solve this theoretical calculations can help experimental studies. The goal of the work was to carry out a theoretical investigation to find possible candidates for creating a two-component heterostructure in which it is possible to change the type of heterojunction by applying a small external stimulus. All quantum-chemical calculations were performed using density functional theory (DFT) [2, 3] realized in the VASP program package [4, 5, 6]. To create unit cells of the considered heterostructures the “HETEROTOOL” software package written in Python3 was used.

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High-precision measurements of the $J = 1 - 0$ rotational transitions of the jet-cooled rare CO isotopologues

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High-precision measurements of the $J = 1 - 0$ (J is the quantum number for the rotational angular momentum of the molecule) pure rotational transitions of isotopically substituted carbon monoxide species, i.e., $^{13}\text{C}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}$, $^{13}\text{C}^{18}\text{O}$, $^{12}\text{C}^{17}\text{O}$ and $^{13}\text{C}^{17}\text{O}$, were performed using recently developed millimeter-wave jet spectrometer [1]. A coaxial propagation of the molecular jet and millimeter-wave radiation resulted in the narrow linewidths of the 30-40 kHz that proved to be useful for measuring line center frequencies with high accuracy (3-4 kHz) and resolving the closely spaced hyperfine structure components. In the carbon monoxide isotopologues the hyperfine splitting arises from the oxygen ^{17}O electric quadrupole moment (larger effect) and the carbon ^{13}C magnetic moment (smaller effect). The high spectral resolution of the spectrometer allowed us to observe hyperfine patterns from the both effects. We report here the first observations of the resolved structure of the $J = 1 - 0$ rotational lines for $^{13}\text{C}^{18}\text{O}$ and $^{13}\text{C}^{17}\text{O}$, more precise determination of the nuclear spin-rotation constant $C_I(^{17}\text{O})$ for $^{12}\text{C}^{17}\text{O}$ and the first determination of this constant for $^{13}\text{C}^{17}\text{O}$. The new results were compared with other available high-precision data on the CO isotopologues from saturation dip spectroscopy (Lamb dip) [2, 3, 4, 5].

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Molecular Parameter of Spatially-Odd Nuclear-Electron Interactions in the $^{29}\text{Si}^{16}\text{O}^+$ Cation

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In a diatomic molecule parity violation (PV) properties are dominated by the nuclear-spin-dependent interactions (NSD-PV). Studying them will contribute to the refinement of the theory of interactions in atomic nuclei that violate spatial invariance. In recent years, many experiments to detect PV properties have been initiated — effects have been measured in the atom ^{133}Cs [1] and in the $^{138}\text{Ba}^{19}\text{F}$ molecule (restriction obtained in the ^{19}F nucleus) [2], and a series of experiments is in the planning stages [3, 4, 5]. The advantage of diatomic molecules is the presence of closely spaced rotational levels of opposite parity in terms of energy [6, 7], which among other things influenced the choice of $^{29}\text{Si}^{16}\text{O}^+$ cation for the upcoming experiment [5].

In this work, within the framework of fully relativistic descriptions of many-electron systems, the value of the molecular parameter of spatially-odd nuclear-electron interactions in the $^{29}\text{Si}^{16}\text{O}^+$ cation was calculated, which is necessary for the interpretation of the experiment [5]. In solving this problem, various contributions and their uncertainties due to variations in the basis sets of the single-electron wave function, the number and degree of electron correlation were considered. Currently, non-adiabatic contributions are being studied.

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Speed-dependent broadening and shifting of water lines in the subTHz range

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Radiometric studies in the subTHz range play an important role in the tasks of remote sensing of the Earth's atmosphere and the underlying surface. The technical capabilities of modern radiometers require high-accurate models of the radiation absorption in the atmosphere. This requires accurate laboratory measurements of the shape parameters of the resonance lines of atmospheric molecules (first of all H₂O) and continuum.

The aim of this work is to increase the accuracy of modeling the resonant absorption of atmospheric water vapor by acquiring new laboratory information about the line profile of all the most intense rotational transitions in the frequency range up to 1 THz. Line profiles are recorded using two spectrometers [1] differing in the principle of operation and the range of operating pressures, which significantly increases the reliability of the experimental information. The first instrument is a classical direct absorption spectrometer (video spectrometer) based on a frequency-stabilized backward wave oscillator and an InSb bolometer cooled by liquid helium, which allows recording the molecular spectra in the pressure range from fractions of mTorr to about 1 Torr. The second instrument is a spectrometer with radio-acoustic detection of the absorption (RAD spectrometer), which operates in the pressure range from several mTorr to tens of Torr. The experimental spectra are analysed using the Voigt profile modified to take into account the dependence of collisional relaxation rate on molecular speed which was investigated in the framework of the quadratic approximating function [2]. The multispectrum fitting procedure, which applied the simultaneous fitting of the model function to all experimental spectra of a chosen line, was used to minimize possible correlation of the line shape and baseline parameters in the model function.

The results of the study are collisional broadening and shifting parameters and their speed dependence measured for the studied water lines at room temperature for several perturbing partners (H₂O, N₂, O₂, Ar). The reliability of the results is well confirmed by the agreement of the data obtained using various experimental techniques. The obtained information can be used for verifying results of theoretical calculations, updating spectroscopic databases and refining the models of atmospheric absorption.

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Influence of Mode-specific Excitation on the Nonadiabatic Dynamics of Methyl Nitrate (CH₃ONO₂)

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The impact of mode-specific vibrational excitations in the initial preparations on the nonadiabatic dynamics of methyl nitrate (CH₃ONO₂) were studied by examining the excited-state population decay rates. In particular, exciting a few specific modes by adding a single quantum of energy clearly decelerated the nonadiabatic dynamics population decay rates. The underlying reason for this slow population decay was explained by analyzing the profiles of the excited-state potential energy surfaces in the Franck-Condon regions and the topology of the S₁/S₀ conical intersection. This study not only provides physical insights into the key mechanisms controlling nonadiabatic dynamics but also shows the possibility of controlling nonadiabatic dynamics via mode-specific vibrational excitations.

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Multilevel Calculation Schemes as a New Approach to Molecular Docking Calculations

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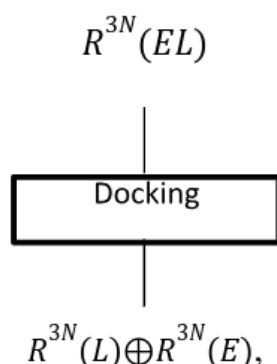
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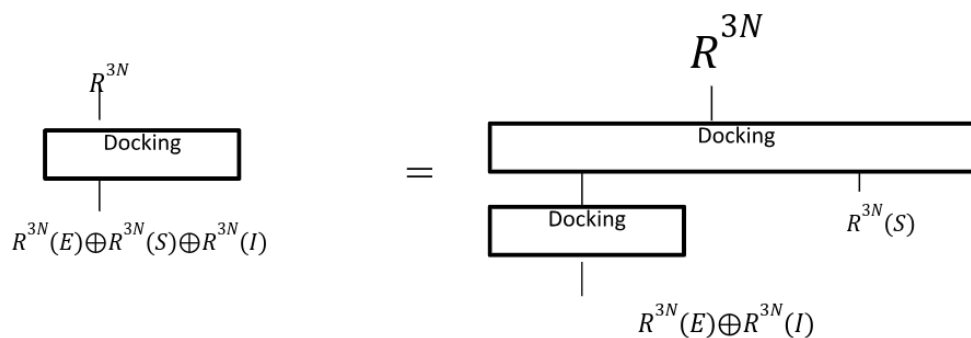
The study of various key mechanisms of antiviral activity is a necessary important step in the development of antiviral drugs. It is important to determine not only a target enzyme for the drug molecule, but also to understand, in detail, how the enzyme is inhibited. That is, to identify the active sites of the enzyme, to understand how the binding of the enzyme to the inhibitor impedes access to the active sites, etc. Computational methods play an important role during this process: quantum chemical calculations are used for modeling of the molecular structures, while molecular docking is used to reveal the binding sites of inhibitor and the target protein.

Molecular docking is a semi-empirical calculation method, so it has accuracy limitations and does not take into account the quantum effects of intermolecular interactions. However, due to the high calculation speed, this method can be widely used for approximate calculations in modeling of protein-ligand interactions.

We formulate the molecular docking problem as follows: find such a position of the ligand \vec{x} , so that $\Delta G_{\text{bind}} \rightarrow \Delta G(\vec{x}) = \min$, where ΔG - is molecular docking scoring function. Briefly, this can be represented by the following calculation diagram:



where $R^{3N}(L)$ is set of ligand coordinates, $R^{3N}(E)$ - the set of enzyme coordinates, and $R^{3N}(EL)$ - set of coordinates of an intermolecular complex. This scheme is single-level, because it contains only one calculational layer. Single-level molecular docking schemes used in practice do not provide a complete picture of enzyme inhibition. An alternative approach is the multilevel calculation schemes presented in this work:



This algorithm includes the calculation of the binding free energy not only for the interaction of an enzyme macromolecule with an inhibitor or substrate, but also the calculation of the binding free energy of an enzyme-inhibitor complex with a substrate, as well as the calculation of the free energy of binding of an enzyme-substrate complex with an inhibitor. This report will describe the mathematical foundations of the construction and the application of the multilevel schemes, as well as the practical application of these schemes with an example of antiviral activity (anti-influenza and anti-HIV) mechanisms modeling for penta-substituted fullerene derivatives (Figure 1), synthesized in the Laboratory of Functional Materials for Electronics and Medicine of the Federal Research Center of Chemical Physics and Physical Chemistry of the Russian Academy of Sciences. The calculation results will be presented, as well as their comparison with the experimental data. Also, in addition to using multilevel schemes for calculating enzyme inhibition, we are currently adapting these schemes for quantum chemical modeling of the antitumor and neuroprotective activity of fullerene derivatives.

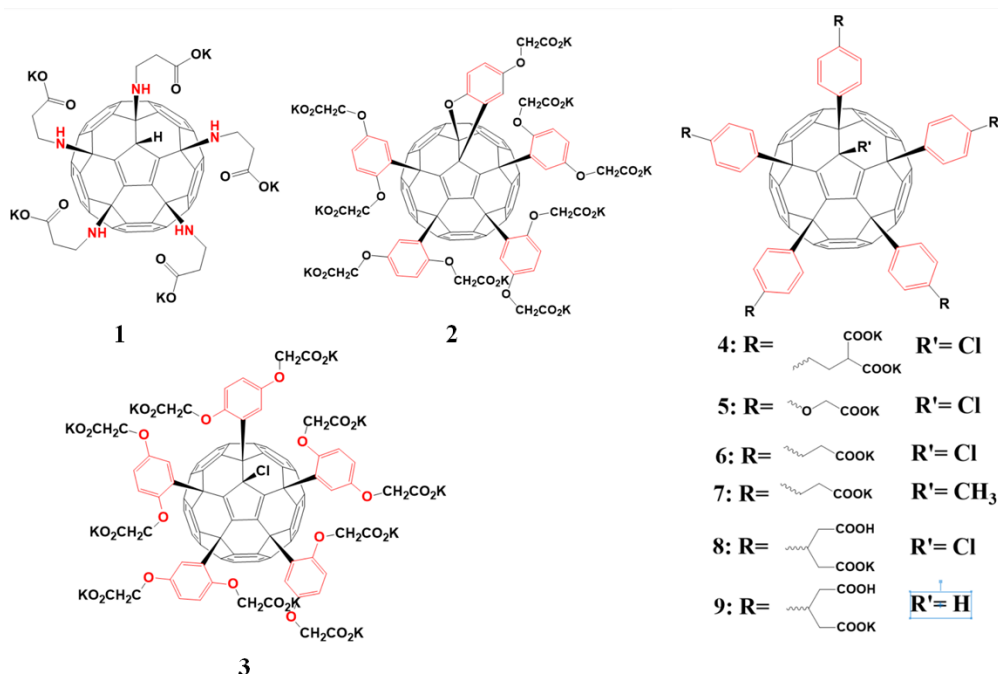


Figure 1: Structures of some fullerene derivatives selected for calculation

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Unsupervised Machine Learning in the Nonadiabatic Surface Hopping Dynamics

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The analysis of the leading active molecular motions in the on-the-fly trajectory surface hopping simulation provides the essential information to understand the geometric evolution in nonadiabatic dynamics. When the ring deformation is involved, the identification of the key active coordinates becomes challenging. A “hierarchical” protocol based on the dimensionality reduction and clustering approaches is proposed for the automatic analysis of the ring deformation in the nonadiabatic molecular dynamics. The representative system keto isocytosine is taken as the prototype to illustrate this protocol. The results indicate that the current hierarchical analysis protocol is a powerful way to clearly clarify both the major and minor active molecular motions of the ring distortion in nonadiabatic dynamics.

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Multiscale modeling of heterogeneous oxygen loss in plasma conditions

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Plasma finds many applications in various fields: in the production of microelectronics, chips, micromechanical systems, in surface treatment and plasma cutting of materials. In the production of modern devices, it is required to achieve extremely high manufacturing accuracy, therefore it is necessary to achieve a high degree of control over the concentration of active particles in the discharge. In low-pressure discharges in molecular gases, the death of active particles, as well as practically significant reactions, occur mainly on the walls of the discharge chamber or the surface of the processed material, therefore, high-quality models of plasma interaction with the surface of a solid are required for the needs of industry.

Oxygen plasma is one of the main types of plasma used in the technology, however, so far models of the interaction of oxygen plasma with the surface have low predictive power, poorly explain the dependencies of experiment and almost do not explain the interaction process at the molecular level.

In the experiment, the probability of heterogeneous recombination of oxygen atoms from various discharge parameters was obtained, analyzing this dependence using microkinetic models – kinetic Monte Carlo and deterministic models, the inverse problem of restoring reaction parameters and surface characteristics from experimental data was solved. The influence of the model parameters on the probability of reaction and the analysis of the sensitivity of the results to the model parameters were analyzed, which made it possible to identify the most reliable values of the model parameters and explain the discrepancy in the results of data analysis obtained by different researchers and describe practically important features of the behavior of the system for reaction kinetics.

Using DFT modeling, the interaction of oxygen atoms with the surface of various amorphous silica-like materials was studied, taking into account various surface groups and the presence of admixture of various substances in the material. The results were compared with the results of microkinetic models and the most significant features of the system and the most likely candidates for adsorption centers were identified.

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Information entropy changes in elementary and complex chemical reactions

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In mathematical chemistry, a chemical reaction is 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 a chemical reaction is the difference between the values of the ensembles of products and reagents:

$$\Delta h_{\text{R}} = h_{\text{ME}}^{\text{prod}} - h_{\text{ME}}^{\text{react}}$$

The information entropy of molecular ensemble (ME) depends on the information entropies of individual molecules h_i and, additionally, on the cooperative entropy H_{Ω} , an emergent parameter that reflects uniting the molecules into the ensemble:

$$h_{\text{ME}} = H_{\Omega} + \sum_{i=1}^m \omega_i h_i$$

where ω_i is the fraction of the atoms of ME belonging to i -th molecule, and m is the total number of molecules in the ensemble:

$$\omega_i = N_i / \sum_{i=1}^m N_i$$

and H_{Ω} is the cooperative entropy:

$$H_{\Omega} = - \sum_{i=1}^m \omega_i \log_2 \omega_i$$

Then the information entropy change in chemical reaction (or information entropy of chemical reaction) is represented as:

$$\Delta h_{\text{R}} = H_{\text{redistr}} - H_{\text{reorg}}$$

In the above equation, the first terms is the redistribution entropy that depends only on the size of the reaction participants:

$$H_{\text{redistr}} = H_{\Omega}^{\text{prod}} - H_{\Omega}^{\text{react}}$$

The second term depends on both structure, size of the molecules, and is called reorganization entropy:

$$H_{\text{reorg}} = \sum_{i=1}^{\text{prod}} \omega_i h_i - \sum_{j=1}^{\text{react}} \omega_j h_j$$

As we found [1], the information entropy of complex reaction scheme with K chemical reactions depends on the stage parameters $\Delta h_{\text{R}(k)}$ as follows:

$$\Delta h_{\text{R}} = \sum_{k=1}^K \omega_k \Delta h_{\text{R}(k)}$$

where ω_k is the contribution of k -th reaction to the total value. In the talk, we demonstrate the work of this equation with typical examples of successive, parallel, catalytic, and conjugated chemical

reactions [1, 2, 3].

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Round-Table A

Classical and Quantum Dynamics in Molecular Spectroscopy

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Molecular spectra are subject to pronounced modifications caused by intermolecular interactions. Rigorous quantum mechanical description of such intermolecular effects requires huge computational efforts, thus making it affordable presently only for relatively small molecular species. Semiclassical methods can be regarded as a reasonable alternative to pure quantum calculations. Molecular dynamics or trajectory based simulations were proved recently to be sufficiently accurate and feasible methods. However, a number of yet unresolved problems still remain of how quantum corrections have to be introduced into classical formalism in order to satisfy critical quantum properties of molecular spectra. We suggest this round-table discussion to focus on several topics interconnecting quantum and classical dynamics with selected problems of molecular spectroscopy.

Main topics

- Requantization of classically simulated profiles;
- Desymmetrization of classical band shapes;
- Wigner functions and Moyal-brackets formalism;
- Feynman's path integrals;
- Intercollisional interference.

Round-Table B

Modern Software for Modeling Electronic Structure and Properties of Molecular Systems

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Despite the significant progress in computational quantum mechanics of multi-particle systems achieved in recent decades, high-precision modeling of atoms and molecules and their properties in different electronic states still remain a significant problem. This situation is primarily due to the fact that the most sophisticated and accurate models of electronic structure and computational methods remain unimplemented in popular software packages, existing only at the conceptual level intended to demonstrate the capabilities of a new method but are not applicable to real challenging problems. We suggest this round-table discussion to focus on some recent achievements in the development of computational quantum mechanics methods and quantum chemical packages.

Main topics

- Methods for excited states;
- Calculations of atomic and molecular properties, including those determined by interactions with nuclei;
- High-performance computing for theoretical chemistry and physics.

Round-Table C

Photoinduced Nonadiabatic Molecular Dynamics

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Nonadiabatic dynamics simulations are powerful tools for elucidating complicated photoinduced processes in molecules. Due to high computational costs, mixed quantum–classical dynamics is often used to propagate nuclear dynamics through classical trajectories, whereas electrons are treated at the quantum mechanical level. To recover nonadiabatic information various algorithms are employed. The advantage of treating the nuclei classically is the ability to simulate molecular systems in full dimensionality. The electronic properties are usually computed on-the-fly; however, the costs of such simulations are prohibitively high when accurate electronic structure theory methods are used. Moreover, the local approximation implied by the classical trajectories also fails to describe non-local quantum effects, as tunneling and quantum interference, as well as the results can be affected by decoherence errors. We suggest this round-table discussion to focus on recent advances in developing theoretical frameworks and efficient computational algorithms for simulating ultrafast photoresponse of molecular systems. We also aim at bridging the gap between the experimentalists and theoreticians to discuss various topics of mutual interest, such as ultrafast time-resolved spectroscopy.

Main topics

- Mixed quantum-classical molecular dynamics;
- Neural network potentials;
- Time-resolved spectroscopy;
- Two-dimensional vibrational-electronic spectroscopy;
- Entangled two-photon absorption spectroscopy.

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