ЦФ РАН

Школа-конференция Атомистическое моделирование функиональных материалов ASFM2015-1

Тезисы докладов

[23-24 Декабря 2015 г.]

Оглавление

Using the methods for treatment of environment effects for modeling the photoactive materials

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Quantum Mechanics/Molecular Mechanics (**QM/MM)** method was used for calculations of absorption spectra of Bis(8-hydroxy-2-methylquinoline)-(4-phenylphenoxy)aluminum (BAlQ). In this part the obtained results in QM/MM was compared with QM results.
Empirical Valence Bond (**EVB**) Method was used for modeling the Proton Transfer from the Retinal Schiff Base in Bacteriorhodopsin. The retinal molecule changes its conformation when absorbing a photon, resulting in a conformational change of the surrounding protein and the proton pumping action. Proton transfer observed at the first step of the Bacteriorhodopsin photocycle.
Effective Fragment Potential (**EFP**) research was used for simulation of exciton formation between 2 organic layers of 4,4'-bis[1-naphthyl (phenyl) amino]-1,1'biphenyl (a-NPD) and aluminum (III) bis (2-methyl-8-quinolinato)4-phenylphenolato (BAlQ). The obtained results of 1 "live" molecular and EFP environment was compared with "live" results.
This work was supported by RSF (project № 14-43-00052).

Simulation of Cytochrome P450 Catalyzed Aromatic Oxidation

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Cytochromes P450s are the principal monooxygenases expressed particularly in the human liver and metabolizing drugs and toxicants. These enzymes contribute most extensively to the biotransformation of benzene and its derivatives. On the basis of the quantum chemical calculations, the dependences of biological oxidation and hazard effects of the mono- and multisubstituted benzene derivatives on the nature of substituents are studied using an oxenoid model. According to this model, the P450 enzyme breaks the dioxygen molecules and generates the active atomic oxygen species (oxens) that readily react with benzenes. In the terms of MO LCAO approach, we calculated the differences ΔE of the total energies of aromatic compounds C_6H_5-X and corresponding arene oxides OC_6H_5-X with tetrahedrally coordinated carbon atoms. The arene oxide stability ΔE parameter determines activation energy of oxidation reaction and is shown to be adequate characteristic of the biological effects of benzenes. Particularly, we obtained that the ΔE values determine the positions of the enzyme mediated oxidation, rate of substrate biotransformation, acute toxicity, as well as carcinogenicity of the benzene derivatives. The benzenes with the low ΔE values are noncarcinogenic and those with high ΔE values belong to carcinogenic compounds series. The carcinogenicity of amino- and nitro-substituted benzenes is also determined by N-oxidation of amino and reduction of the nitro group. As the phenylhydroxylamines XC_6H_4NHOH and nitrenium ions $XC_6H_4NH^+$ are the common metabolites of the nitro- and amino-substituted benzenes and the nitrenium ions $XC_6H_4NH^+$ are the ultimate carcinogens, the energy difference $\Delta E_N = E(XC_6H_4NH^+) - E(XC_6H_4NHOH)$ is the second parameter characterizing the carcinogenic activity of amino- and nitro-substituted benzenes. We conclude that the oxenoid model together with quantum chemical calculations reasonably predict and explain a variety of the in vivo and in vitro experimental data on the biological behavior of the substituted benzenes.

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[1] P.N. D'yachkov, N.V. Kharchevnikova, et el. *Intern. J. Quantum Chem*. 2007, **107**, 2454.
[2] P.N. D'yachkov, N.V. Kharchevnikova, et el. *Intern. J. Quantum Chem*. 2010, **110**, 1402.
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Multireference Methods in Organic Electronics and Photonics: Problems and Applications

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The computational problems that typically arise in organic electronics are the problems of light absorption and emission, charge separation and recombination, and charge transport. These problems are usually addressed with the relatively cheap and fast density functional theory, which allows for large-scale calculations. However, this approach has intrinsic deficiencies that lead to qualitatively wrong results. Among these are overestimation of charge delocalization in extended molecular systems, underestimation of the energy of charge-transfer states, and different errors in the energies of singlet and triplet states, which lead to wrong transition probabilities of nonradiative processes.

Multireference methods, such as CASSCF/XMCQDPT, provide qualitatively correct and accurate description of the processes of interest. In particular, they correctly describe charge and exciton localization in extended systems through including the states with different localization with equal weights. They also provide balanced treatment of states of different multiplicity and different orbital character. Therefore, multireference methods give deeper insight into the nature of the systems under study. Understanding the mechanism of the target process will help one to find simple molecular descriptors that can be calculated by cheap methods in large scale.

We outline the problems in which multireference treatment is necessary, give some basics of the CASSCF and XMCQDPT methods, and demonstrate the application of multireference computational methods to the problems of light emission, charge and energy transfer, and chemical stability of typical OLED materials.

This work was supported by RSF (project № 14-43-00052).

Energetically balanced reaction coordinate for the biosynthesis of Spinosyn A

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Cycloaddition reaction (Diels-Alder reaction) is a powerful method for fine organic synthesis. This method allows to obtain cyclic or polycyclic products including biologically active compounds. Until recently it was assumed that the cycloaddition reaction is solely a synthetic method and not found in nature. However, a number of enzymes which catalyze the Diels-Alder reaction (Diels-Alderases) were discovered at the last decades. Recently a new enzyme (SpnF) was discovered inside the cells of the bacterium *Saccharopolyspora spinosa*. SpnF catalyzes the reaction of intramolecular [4+2] cycloaddition in the process of obtaining of natural insecticide spinosyn A

In this work, we propose a new mechanism of enzymatic catalysis, which allows to achieve a significant catalytic effect and preserve the concerted character of the cycloaddition stage.[i]

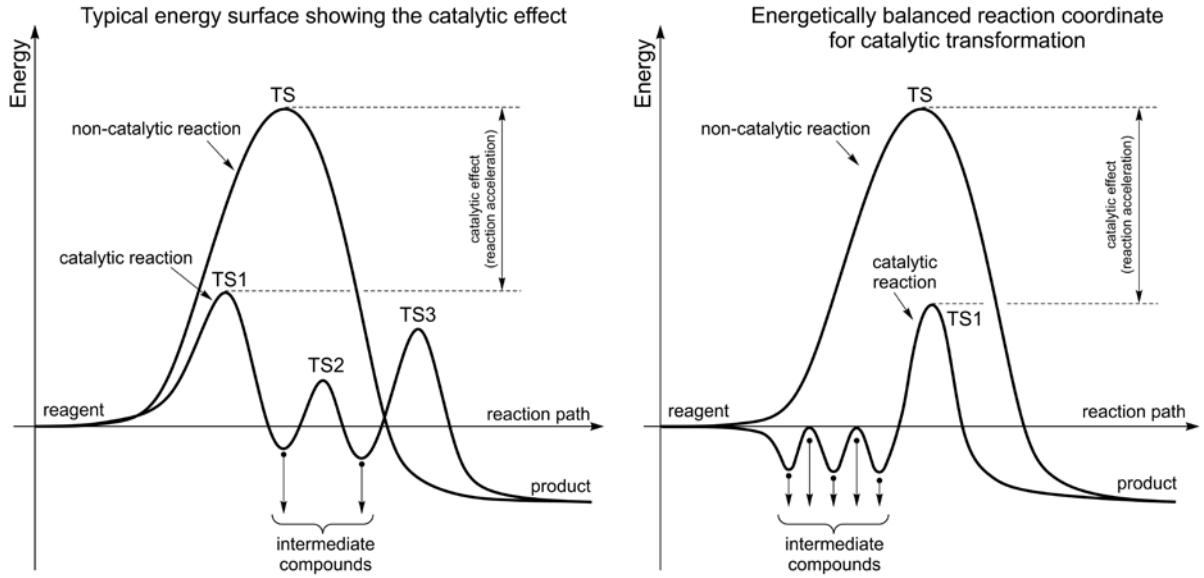

Fig. 1. Reaction path for a typical catalytic reaction (left) and energetically balanced catalytic pathway.

By quantum chemical methods it was shown that the classical model of enzymatic catalysis provides only a small catalytic effect (3-5 kcal/mol). The new model of catalysis includes a sequential compression of the substrate molecule in the cavity of the enzymatic active center. After each stage of compression increasing of the energy caused by compression is compensated by hydrogen bonds formation. Several cycles of compression/compensation lead to the convergence of the diene and the dienophile and to significant decrease in the activation energy of the reaction. The calculated catalytic effect of the proposed mechanism is 18 kcal/mol.

This work was supported by RFBR (project № 14-03-31752) and Russian Science Foundation (RSF grant 14-50-00126).

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Моделирование анизотропных плёнок органических полупроводников методом молекулярной динамики.

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Построение реалистичной морфологии материала является важной ступенью на пути численного описания его функционирования. Органические полупроводники на основе молекул малой молекулярной массы представляют собой тонкие (порядка 10-100 нм) плёнки, получаемые вакуумным напылением. Примечательной особенностью таких структур является частичная анизотропность. Она существенным образом влияет на транспорт носителей заряда, а также на излучение света. Воспроизведение этих эффектов в процессе численного эксперимента невозможно без адекватной анизотропной модели.

Нами была разработана методика и созданы программные средства по реализации алгоритма «виртуального напыления», в котором осуществляется моделирование роста плёнки вещества в результате постепенного добавления в систему молекул. В основе моделирования лежит метод молекулярной динамики в рамках популярного программного пакета GROMACS, работающего под управлением внешнего скрипта. Доступен как конечный вариант программы, так и бесконечный «конвейер», в котором молекулы добавляются и удаляются из системы с сохранением их полного числа.

Метод виртуального напыления с успехом использовался для моделирования анизотропной морфологии аморфных органических полупроводников. Внесение минимальных изменений позволяет легко моделировать с его помощью структуру органико-неорганических и органико-органических интерфейсов в наноразмерных гетероструктурах, а также генерировать морфологию материалов, в состав которых входят примесные молекулы.

Эта работа была поддержана Российским Научным Фондом (проект № 14-43-00052)

Excited State Dynamics in Complex Systems for Solar Energy Harvesting: Time-Domain Ab Initio Studies

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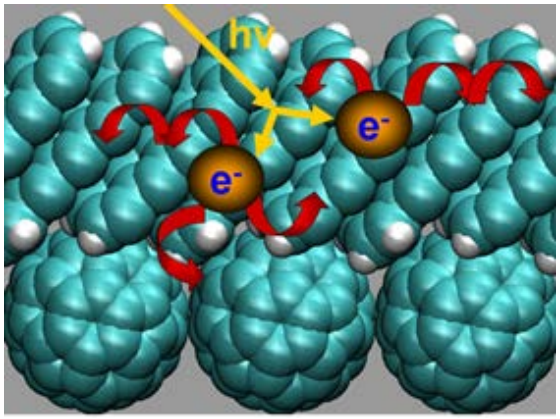

Figure 1. An interface between pentacene and C_{60} layers. The photoinduced dynamics at the interface is much more complex than in isolated singlet fission material (pentacene), since it involves a variety of interfacial charge transfer states, in addition to the pentacene states.

organic molecules, water, semiconductor quantum dots and graphene, GaN/water interface, carbon nanotube bundles, interfaces of C_{60} with pentacene and inorganic particles, etc. Photoinduced charge separation across such interfaces creates many challenges due to stark differences between molecular and periodic, and organic and inorganic systems. Our simulations provide a unifying description of quantum dynamics on nanoscale, characterize the rates and branching ratios of competing processes, resolve debated issues, and generate theoretical guidelines for development of novel systems for solar energy harvesting.

Photo-induced processes at various interfaces form foundation of photovoltaic and photo-catalytic applications. They require understanding of dynamical response of novel materials on atomic and nanometer scales. Our non-adiabatic molecular dynamics techniques, implemented within time-dependent density functional theory, allow us to model such non-equilibrium response in real time. We focus on photo-initiated charge and energy transfer at interfaces involving organic and inorganic nanoscale materials. Examples include TiO_2 sensitized with

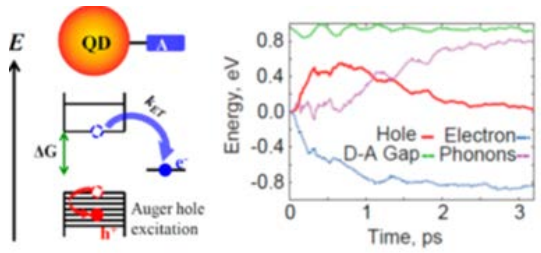

Figure 2. Auger-assisted electron transfer (ET) strongly influences ET rate and eliminates the Marcus inverted regime. Significant electron-hole coupling and high density of states available in nanomaterials allows hole excitation during electron transfer. Our time-domain atomistic study will provide a detailed description of Auger-assissted ET. It shows that the hole supporting the Auger mechanism is excited only transiently and restorers its initial energy within several picosecond by transferring energy to phonons.

Influence of structural anisotropy on mesogenity of Ln(III) adducts by means of quantum chemistry

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Liquid-crystalline lanthanide (Ln) complexes are of particular interest due to their potential applications as advanced multifunctional materials. Their distinctive anisotropy of magnetic and optical properties allows to create luminescent materials that emit polarized monochromatic light.[2] Quantum-chemical simulation of Ln(III) complexes with various ligand environments makes it possible to foresee and afterward to synthesize compounds with obviously predictable liquid-crystalline properties. Such a prediction can be made on the basis of the value of geometric anisotropy. Quantum-chemical simulation of the equilibrium geometry of complexes was performed using the Priroda 06 software by the DFT method with the PBE exchange correlation functional. The rL11 relativistic basis set was applied for Ln(III) and the rL1 basis set for other atoms. In the studied complexes of Ln(III) with different substituted β-diketones and 1,10-phenanthroline (Phen) (Fig. 1) the highest contribution to the value of geometric anisotropy of a molecule is brought by the length of terminal alkyl substituents of ligands. An increase in the length of alkyl substituents in the investigated complexes leads to a simultaneous increase in both the length and width and as the result to the decrease in the anisometry. Contrary to the complexes with 5,5'-dimethyl-2,2'-bipyridine ($Bpy_{17\text{-}17}$) the length of which brings a crucial contribution to the overall geometric anisotropy of molecules, the anisometry of the complexes with Phen depends on the molecular sizes of β-diketones to a greater extent. Though the anisotropy value for the majority of known organic calamitic liquid crystals lies in the range from 4 to 8, it reaches values 1.6÷1.8 in the case of liquid-crystalline complexes with Phen and 2.0÷3.0 with $Bpy_{17–17}$. Such a difference could be the result of participation of the latter molecules in the lateral intermolecular interactions between Ln(III) complexes, the geometry of molecules become more branched on transition to the longer hydrocarbon radicals. That result in reducing of intermolecular ligand-ligand and Ln-Ln interactions. The calculations were performed using the facilities of the Joint Supercomputer Center of Russian Academy of Sciences and the Supercomputing Center of Lomonosov, Moscow State University.[3]

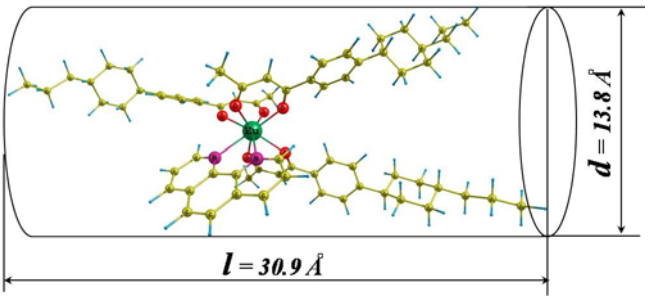

Fig. 1. Optimized structure and geometry parameters of Eu(III) complex

This work was supported by the Ministry of Education and Science of the Russian Federation (state contract no. 4.323.2014/K).

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Vibronic band structure in the absorption spectra of dibenzoylmethanatoboron difluoride derivatives: an analysis based on ab initio calculations

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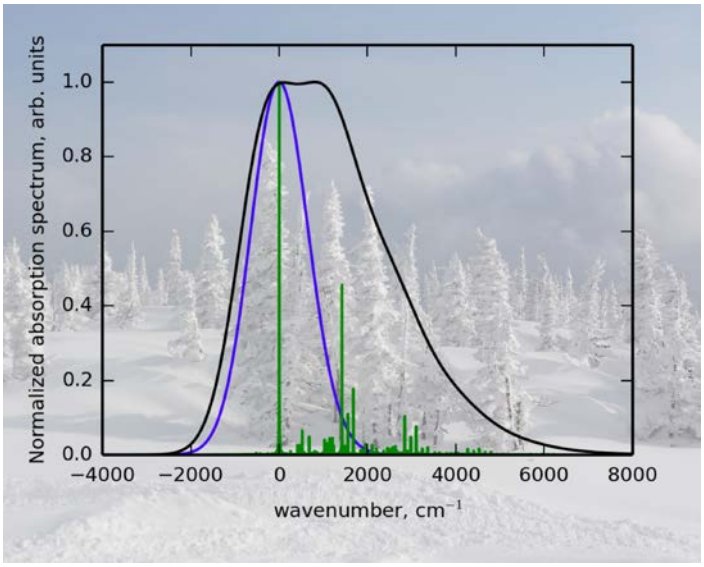

Fig. 1. The calculated absorption spectrum of $DBMBF_2$, $I(\Omega)$ (black) deconvoluted into the "soft" $\overline{I}_{soft}$ (blue) and "hard" $\overline{I}_{hard}$ (green) components.

The nature of absorption bandshapes of dibenzoylmethanatoboron difluoride ($DBMBF_2$) dye substituted in ortho-, meta-, and para-positions of the phenyl ring is investigated using DFT and TD-DFT with the range-separated hybrid CAM-B3LYP functional and the 6-311G(d,p) basis set. The solvent effects are taken into account within the polarized continuum model. The vibronic bandshape is simulated using time-dependent linear coupling model with vertical gradient approach through an original code. For flexible chromophores, the spectra of individual conformers are summed up with Boltzmann factors. It is shown that the long-wavelength absorption band shape of $DBMBF_2$ derivatives is determined by three factors: the relative statistical weights of conformers with different electronic absorption patterns, the relative position and intensity of the second low-energy electronic transition, and the vibronic structure of individual electronic peaks. The simulated spectra of the dyes in study are in a good agreement with the available experimental data and explain the observed spectral features.[4]

This work was supported by RFBR (project № 14-43-00052).

[4] Rukin P.S., Freidzon A.Ya., Scherbinin A.V., Saznikov V.A., Bagaturyants A.A., Alfimov M.V. *Phys.Chem.Chem.Phys.*, 2015 accepted.

The structure of *N*'-(adamantan-2-ylidene)benzohydrazide, a potential antibacterial agent, in solution: DFT, CASSCF/XMCQDPT2 and UV/Vis studies

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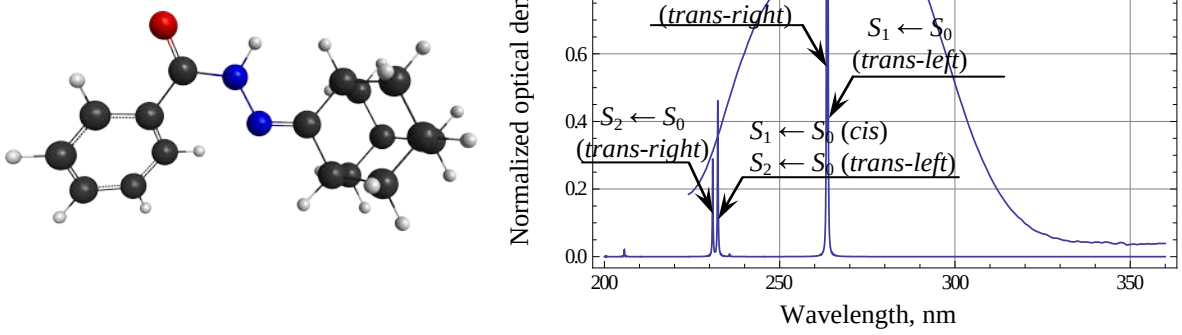
The incorporation of an adamantyl moiety into several molecules results in compounds with relatively high lipophilicity, which in turn can modify the biological availability of these molecules. In almost all cases, an adamantyl-bearing compound will be more lipophilic than the des-adamantyl analogue. Several adamantane derivatives were associated antimicrobial and anti-inflammatory activities. The title compound ($C_{17}H_{20}N_2O$) was recently synthesized[1] as among a series of *N*'-(adamantan-2-ylidene)aroylhydrazides which displayed potent broad-spectrum antibacterial activity.

In this study, the title molecule's structure (Fig. 1, *a*) has been obtained by DFT and CASSCF/MRPT level of theory calculations. The results of these simulations were used for interpretation of the UV/Vis spectrum of the title molecule's solution in ethanol (Fig. 1, *b*). At the B3LYP/cc-pVDZ + PCM (ethanol) level of theory we found four stable conformers of the title molecule: one *cis*-conformer (for C=O and N–H bonds) and three *trans*-conformers (one "central" and two "side"). These three conformers correspond to rotation around N–N bond. The calculations at the SA-CASSCF(2,8)/XMCQDPT2[2] level of theory were performed for the B3LYP/cc-pVDZ + PCM optimized equilibrium configurations.

Taking into account possible deviation of calculated versus experimental values of the transition energies (i), the Boltzmann's weight of the each conformer (ii) and long-wave shifts due to polar solvent (ethanol) effect (iii) one can suggest that there are two bands with one (long-wave, 280 nm) containing contributions from the "side" conformers $S_1 \leftarrow S_0$ transitions and another one (shot-wave, 248 nm) containing possible contributions from the "side" conformers $S_2 \leftarrow S_0$ transitions and the "central" conformers $S_1 \leftarrow S_0$ transitions.



a *b*

Fig. 1. *Cis*-conformer (*a*), experimental absorption spectrum of the title molecule in ethanol (1) and calculated at the CASSCF/XMCQDPT2 level of theory absorption bands (2) (*b*)

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Ab initio multi-reference perturbation theory calculations of the low-lying singlet and triplet states of the KRb molecule

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One of the possibilities of obtaining of molecular quantum matter with controlled properties is the transferring of the polar diatomic molecules to the ground rovibronic state by initial optical excitation into the overlying rovibronic states with specific forms of electronic terms. In this case for the high efficiency of excitation and subsequent relaxation of the molecular system it is required knowledge of the exact forms of the potential energy curves (PECs) of the combining electronic states. The construction of exact "experimental" terms[1] is performed on the basis of the analysis and interpretation of high-resolution rovibronic spectra, and may be based on *ab initio* potential curves.

The diatomic polar molecule KRb is a typical example of the above-mentioned compounds. *Ab initio* calculations of the KRb's electronic terms are traditionally[2,3] performed in multi-configuration CASSCF/MRCI approximation. A common feature of these calculations is both sufficiently successful reproduction of the experimental value[1] of the ground electronic state $X^1\Sigma^+$ equilibrium internuclear distance R_e (4.06770 Å), and significantly lower value of the ground state dissociation energy[1] D_e (4217.815 cm^{-1}).

In this study, the SA-CASSCF(2,14)/XMCQDPT2[4] calculations of the low-lying singlet ($X^1\Sigma^+$, $2^1\Sigma^+$, $3^1\Sigma^+$, $1^1\Pi$ and $2^1\Pi$) and triplet ($1^3\Sigma^+$, $2^3\Sigma^+$, $3^3\Sigma^+$, $1^3\Pi$ and $2^3\Pi$) states of the KRb molecule performed. The Stuttgart RSC ECPs have been used in calculations. Further the vibrational energies have been calculated. The results of our calculations of the spectroscopic parameters of the KRb's ground state $X^1\Sigma^+$ very well agree with experimental data (R_e = 4.07481 Å, D_e = 4211 cm^{-1}, see Fig. 1, *a*). The differences of the experimental and calculated vibrational frequencies for the $^{39}K^{85}Rb$ ground state are less then 1 cm^{-1} (Fig. 1, *b*). This is the best agreement among all previously performed for KRb molecule *ab initio* calculations.

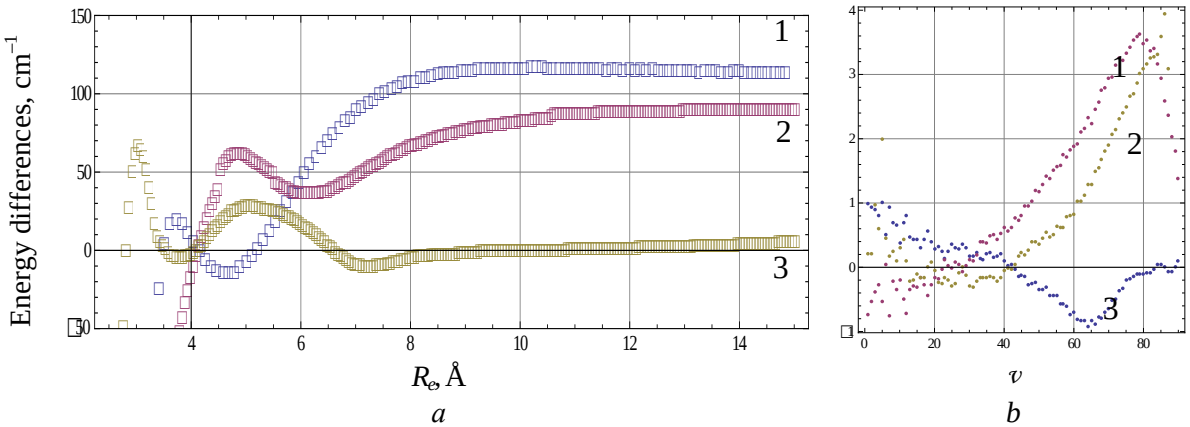

Fig. 1. Differences of the experimental and calculated ground term PECs (*a*) and differences of the experimental and calculated vibrational frequencies for the $^{39}K^{85}Rb$ ground state: (1)[2], (2)[3] and this study (3) (*b*)

This work was supported by SCST of the Republic of Belarus (project № F14LAT-060).

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[4] A.A. Granovsky. *J. Chem. Phys.* 2011, **134**, 214113.

Atomic HF and DFT calculations of exchange interaction in dilute magnetic semiconductor $Ga_{1-x}Mn_xAs$

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Despite the fact that dilute magnetic semiconductors have been known for a long time, there is no general consensus on the electronic structure and the nature of ferromagnetism in these compounds[i,ii]. Recent studies have revealed that the electrons as of an impurity and of the host compound found at the Fermi level [iii]. There are models of p-d- exchange and double exchange for description of ferromagnetism in these compounds[iii].

In present work a direct atomistic approach to ferromagnetism in these compounds is developed and calculations are performed. The electrons in conduction band are plane-wave shape between atoms, and are excited atomic shape at the atomic centers. In the ionic model the excited electrons on Mn centers are of 4*s*-type and their energy depends on the spin orientation with respect to $Mn3d^5(^6S)$ ground term. In parallel spin coupling this energy, estimated making use of atomic Hartree-Fock wave functions and angular momentum coupling technique, is 0,48 lower than the energy of average term. The calculations of the density of states in GaAs and $Ga_{0,875}Mn_{0,15}As$ crystal were also performed. The main peak of DOS of *d*- states is 3 eV lower with a small peak at the Fermi level, what is in excellent agreement with the experiment [iii].

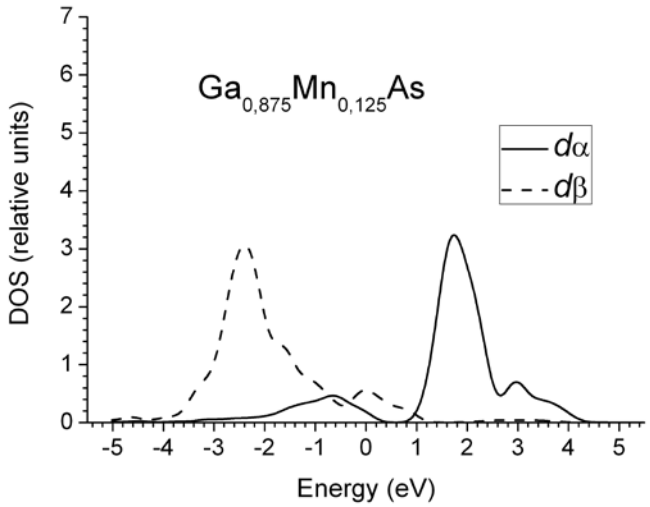

Fig. 1. Spin-polarized DOS of *d*-electrons in $Ga_{0,875}Mn_{0,15}As$

The DOS of *s*-states of $Ga_{0,875}Mn_{0,15}As$ show a small peak at the Fermi level, which is absent in pure GaAs, which corresponds to Mn4*s*- states To estimate the spin polarization energy in our model we calculated $Ga_{0,875}Mn_{0,15}As$ with the Mn *s*- energy shift (Hubbard energy), which is equal to atomic spin-polarization energy. The resulting total energy is 0.009 eV lower, then the average energy. The obtained energy is in agreement with the results of other authors 0,007 eV. Thus the theoretical DOS and spin polarization energy are in agreement with experiment and other theoretical results.

This work was supported by RFBR (project № 15-03-05370).

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Структура и агрегация супрамолекулярных комплексов β-циклодекстрин-пирен-аналит: спектры электронного поглощения и флуоресценции, компьютерное моделирование.

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Исследована возможность использования пирена (Ру) в качестве флуоресцентного зонда (ФЗ) в трёхкомпонентных комплексах «циклодекстрин – пирен – аналит» для аналитов (А) различной полярности в водных растворах. Спектр флуоресценции (СФ) пирена имеет хорошо разрешенную вибронную структуру. Характеристикой пирена как ФЗ является отношение $I_1/_3I$, где I_1 интенсивность линии 0-0 перехода, а I_3 интенсивность третьей вибронной линии с $\Delta\nu$~800 см$^{-1}$, относящейся к колебательному переходу типа A_g, в процессе которого растяжение скелета Ру вдоль длинной оси сопровождается сжатием скелета вдоль короткой оси. Результатом является вибронная связь между этими переходами, которая проявляется в том, что запрещенный по симметрии 0-0 переход в СФ Ру никогда не тушится, а величина $I_1/_3I$ чувствительна к диэлектрической проницаемости аналита, показанной для комплексов типа A_2·Ру@2βCD в [1,2]. Изучение спектров электронного поглощения (СП) водных растворов пирена показало, что добавление βЦД приводит к появлению новой полосы, сдвинутой на 400 см$^{-1}$ в красную область спектра и относящейся к агрегатам, в которых роль активной фотохимической частицы играет комплекс Ру@2βCD. Совместный анализ СП и СФ показывает, что рост температуры вызывает распад агрегата, а вместе с ним, по-видимому, и самого Ру@2βCD, поскольку при 50° С его СФ имеет сходство со спектром Ру в воде. Однако этот процесс обратим. Другим важным результатом является установленный нами факт, что СФ трехкомпонентных комплексов A_2·Ру@2βCD имеют одинаковый контур и различаются для аналитов разной полярности только отношением $I_1/_3I$, которое чувствительно к добавлению А в микромольных количествах.

Методом молекулярной динамики (МД) рассчитана структура комплекса Ру@2βCD в присутствии ~1000 молекул воды и изучена способность к инкапсуляции в его полость молекул А из водной среды. Показано, что Ру в димере βCD может ориентироваться как перпендикулярно оси C_7 димера (1), так и под некоторым углом к ней (2), причем ориентация 2 более предпочтительна. Пустое пространство в Ру@2βCD занимают в среднем от 8 до 10 молекул воды, которые вытесняются добавленным А. При этом Ру приобретает ориентацию 1. Расчет комплексов A_2·Ру@2βCD полуэмпирическим квантово-химическим методом PM7 демонстрирует, в согласии с данными МД, бóльшую термодинамическую выгоду ориентации 2 для свободного комплекса и трансформацию её в 1 для комплексов A_2·Ру@2βCD. Причина красного сдвига электронного поглощения агрегата исследована путем сравнительного расчета методом ZINDO/S энергий электронных переходов пирена в газовой фазе и пирена, имплементированного в кластер из 14 молекул этиленгликоля, моделирующий пояс комплементарных Н-связей димера βCD, образованных между вторичными ОН-группами широкого портала βCD. Показано, что причиной сдвига является напряжение, возникающее в поясе Н-связей димера в результате имплементации жесткой молекулы пирена, которая в комплексе A_2·Ру@2βCD дополнительно сжата гидрофобными молекулами А.

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Ab initio исследование влияния кислорода на электронные и магнитные свойства нанопороводов 3d металлов на поверхности Rh(553)

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В последние десятилетия изучение магнитных свойств наноразмерных объектов открыло перед исследователями новые фундаментальные физические явления [1]. Прогресс в понимании квантовых свойств материалов в наномасштабах дал толчок для развития технологий создания новых материалов с управляемыми электронными и магнитными свойствами. С точки зрения применения в различных электронных устройствах наиболее перспективными выглядят структурно анизотропные объекты, такие как одномерные нанопровода. На свойства данных атомарных структур могут оказывать влияние множество различных факторов, в частности, присутствие примесей [2, 3]. В этой связи методом ab initio было проведено исследование электронных и магнитных свойств моноатомных проводов 3d металлов (Mn, Fe, Co, Ni) и их металл-оксидов на ступенчатой поверхности Rh(553) (Рисунок 1) с целью выявления влияния кислорода на свойства рассматриваемых нанопроводов. Интерес к данным атомарным объектам мотивирован недавней экспериментальной работой, впервые показавшей возможность образования одномерных гибридных металл-оксидных структур в процессе окисления биметаллических нанопроводов Ni-Rh на ступенях поверхности Rh(553) [4]. Так в результате окисления формируются одномерные Ni-O провода с различным содержанием кислорода в структуре никелевого провода.

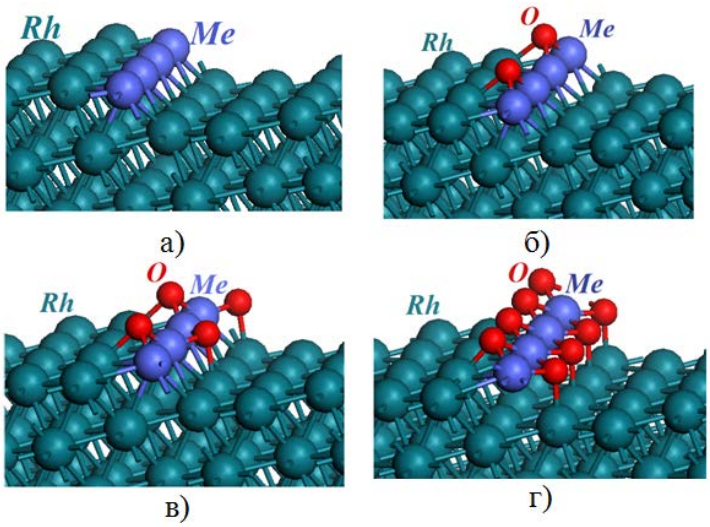

Рисунок 1. а) Нанопровод 3d металла (Mn, Fe, Co, Ni) на Rh(553); б), в), г) Металл-оксидные нанопровода 3d металлов (Mn-O, Fe-O, Co-O, Ni-O) на Rh(553) с концентрацией кислорода 0.1 ML, 0.2 ML и 0.4 ML соответственно.

Проведенные спин-поляризованные расчеты показали, что рассматриваемые моноатомные провода 3d металлов находятся в магнитном состоянии со значениями локального магнитного момента $3.67\mu_B$, $3.03\ \mu_B$, $1.96\ \mu_B$ and $0.58\ \mu_B$ соответственно приходящиеся на атомы Mn, Fe, Co и Ni в проводе. При исследовании магнитного сцепления атомов внутри провода были рассмотрены три различные конфигурации: антиферромагнитная с чередованием направлений спинов атомов (↑↓↑↓), антиферромагнитная с дублетным сцеплением спинов (↑↑↓↓) и ферромагнитная (↑↑↑↑). Важно отметить, что согласно нашим результатам атомы Mn и Fe в проводе демонстрируют устойчивое антиферромагнитное дублетное сцепление. При рассмотрении одномерных проводов Co и Ni было получено, что данные нанопровода находятся в устойчивом ферромагнитном состоянии.

Для исследования влияния кислорода на магнитные и электронные свойства моноатомных проводов 3d металлов были рассмотрены одномерные металл-оксидные

нанопровода 3d металлов (Mn-O, Fe-O, Co-O, Ni-O) с концентрацией кислорода 0.1 ML, 0.2 ML и 0.4 ML (см. Рисунок 1 б, в, г). Результаты показывают, что кислород оказывает сильное влияние на магнитные и электронные свойства одноатомных проводов 3d металлов. Согласно проведенным спин-поляризованным расчетам, нанопровода Ni-O находятся в устойчивом парамагнитном состоянии, в то время как одномерные провода Mn-O и Fe-O остаются в антиферромагнитном состоянии. Моноатомные провода Co-O при концентрациях кислорода 0.1 ML и 0.4 ML сохраняют ферромагнитное упорядочение спинов атомов Co, однако при концентрации 0.2 ML более энергетически выгодной оказывается конфигурация с антиферромагнитным дублетным сцеплением спинов атомов. В случае нанопроводов Fe и Co наблюдается снижение значения локального магнитного момента атома металла в проводе при увеличении концентрации кислорода в системе. Наиболее существенно данный эффект проявляется для нанопроводов кобальта. Для случая одномерных проводов Mn при концентрации кислорода 0.2 ML наблюдается падение значения магнитного момента. Таким образом, в результате работы получено, что присутствие кислорода оказывает существенное влияние на магнитные свойства проводов переходных металлов.
Работа выполнена при поддержке гранта РФФИ № 13-02-01322-а.

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Effect of impurity concentration on magnetic anisotropy of deposited nanowires

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The modern progress in nanotechnology made clear that adsorbates can be very useful in creation of new nanostructured material for various applications. There exists number of studies of different adsorbate structures, for example of self-organized growth of the adsorbates at metal surfaces include highly ordered arrays of monoatomic Cu wires on the Pd(110) surface [1], fabrication of Ag nanoislands on the Pt(111) [2] through nucleation of deposited metal atoms on carefully prepared substrates. In addition to self-assembly growth at the substrate, the adsorbates can also restructure the substrate surface [3-7]. Presence of impurity atoms can affect very significant the quantum properties of neighboring atoms and, thus, change the properties of the whole material.

For instance, in the resent study of the effect of adsorbed H atoms on magnetism in monoatomic Fe wires at Ir(100) surface is was shown that the type of exchange interaction between Fe atoms can be changed by changing of H coverage: the pristine monoatomic Fe wires deposited on nanostructured Ir(100) surface partially covered by H atoms are antiferromagnetic but at fully hydrogenated Ir surface the Fe wires themselves are decorated with hydrogen, which gives rise to the ferromagnetic coupling between adjacent Fe atoms [8]. Base on this result one can suppose that changing of H coverage can also effect on magnetic anisotropy (MA) in the Fe wire.

In this work we present the first principal study of effect of changing of H coverage on MA in the Fe wire in framework of density functional theory [9] as it is implemented in VASP code [10]. The studied Fe wire deposited on Ir(100) surface with different H coverage are presented in Fig.1.

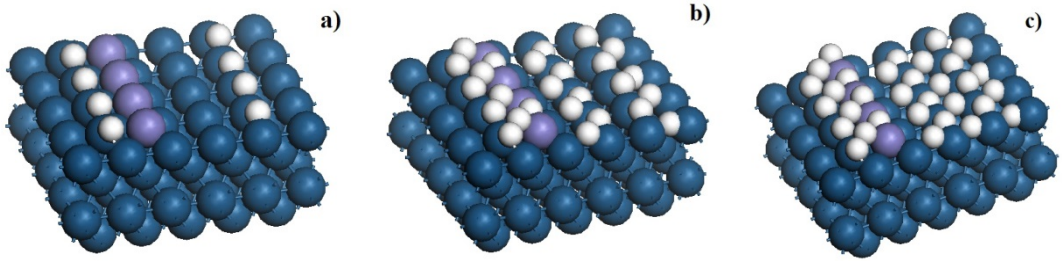

Figure 1: Fe wire on Ir(100) surface with different H coverage a) 0.4ML, b) 1.3ML, c) 1.6ML. blue – Ir, magenta – Fe, white – H.

As a first step we have repeated the results obtained in [8]. Our results also show that in the case of pure Ir(100) surface and 0.4ML of hydrogen coverage the antiferromagnetic (AFM) coupling in Fe wire is more energetically preferable then ferromagnetic (FM) one. The increasing of H coverage decreases the energy difference between AFM and FM coupling until they become almost degenerate at 1.3ML H coverage. After further H coverage increasing the FM coupling becomes more energetically preferable then AFM one.

Next step we have obtained the MA energy value for different H coverages. Results of our study are summarized in Table 1.

H concentration, ML	E^{AFM}-E^{FM}, meV	$\mu^{Fe(FM)}$, μ_B	$\mu^{Fe(AFM)}$, μ_B	MAE(FM), meV	MAE(AFM), meV
0	-130	2.89	2.90	2.778	2.543

0.4	-165	2.91	2.91	2.685	2.607
1.3	-14	2.81	2.79	3.126	3.548
1.6	156	2.66	2.63	1.151	4.329

Table 1. Magnetic properties of Fe wire deposited on Ir(100) surface with different H coverage. μ – magnetic moment value

As one can see from the table the changing of H coverage significantly effects on the MA energy value. Also it was found that magnetization easy and hard axis direction depends on H coverage also.

As a summary we can conclude that adsorbates make a strong effect on magnetic properties on deposited nanowire and changing adsorbate coverage can be used for tailoring the MA in Fe nanowire.

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