РОССИЙСКАЯ АКАДЕМИЯ НАУК
РОССИЙСКИЙ ФОНД ФУНДАМЕНТАЛЬНЫХ ИССЛЕДОВАНИЙ
РОССИЙСКОЕ ХИМИЧЕСКОЕ ОБЩЕСТВО ИМ. Д.И.МЕНДЕЛЕВА

СБОРНИК ТЕЗИСОВ ДОКЛАДОВ

международного симпозиума "Компьютерное обеспечение химических исследований"
Москва, 22-23 мая 2001 г.

и

3-ей Всероссийской школы-конференции
по квантовой и вычислительной химии им. В.А.Фока
Новгород Великий, 21-25 мая 2001 г.

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Институт органической химии им. Н.Д.Зелинского РАН
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Новгородский государственный университет им. Ярослава Мудрого
ОТКРЫТЫЕ СИСТЕМЫ

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Сборник тезисов докладов Второго международного симпозиума "Компьютерное обеспечение химических исследований" и Третьей сессии школы конференции по квантовой и вычислительной химии им. В.А. Фока. Представленные в сборнике тезисы доклады охватывают все аспекты применения компьютеров в химии: молекулярное моделирование, использование компьютеров в обучении, электронные библиотеки и базы данных по химии, интернет-ресурсы для химиков, вычислительную и квантовую химию, визуализацию данных химических исследований, и т.п. Основная масса докладов посвящена различным аспектам вычислительной и квантовой химии, как методологическим, так и прикладным.

Ответственный за выпуск к.х.н. И.Н.Сенченя

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академик, директор Института органической химии им.Н.Д.Зелинского РАН

Дорогие друзья,

Я рад представить Вашему вниманию совместный сборник тезисов докладов международного симпозиума "Компьютерное обеспечение химических исследований" и 3-ей школы-семинара по квантовой и вычислительной химии им. В.А.Фока. Публикация совместного сборника не является случайной, так как современные информационные технологии позволили интегрировать территориально удаленные, специализированные мероприятия средствами видеоконференц-связи.

Мы - огромная страна, а географические размеры выдвигают и свои требования. Использование современных информационных и телекоммуникационных средств позволило сблизить научное сообщество. Большое количество докладов, представленных в этом сборнике, - результат работы исследовательских групп, члены которых работают в удаленных друг от друга научных центрах. Более того, при подготовке симпозиума и школы было полностью исключено использование традиционных бумажных носителей, весь обмен информацией происходил в электронной форме - регистрация, подготовка тезисов, рассылка информационных сообщений и т.д. Это существенного ускорило весь процесс подготовки обоих мероприятий. Я хочу надеяться, что на следующий симпозиум большинство участников приедет с портативными компьютерами, а те, кто по каким-либо причинам не смогут приехать, будут иметь возможность участвовать виртуально. Разумеется, фактор личного общения между учеными несомненно является чрезвычайно важным и сохранится на долгое время.

Я считаю симпозиум и семинар чрезвычайно важными по следующим причинам. Прежде всего, примечательно, что одни из первых научных мероприятий в новом тысячелетии связаны с использованием компьютерных технологий и их применением в химии. Компьютеры преобразили наш мир, сделали наши контакты друг с другом более продуктивными. Прогресс в науке в огромной степени определяется скоростью обмена информацией. Именно поэтому мы всячески поддерживаем и содействуем развитию информационно-вычислительной инфраструктуры в нашем Институте, и надеемся, что эта структура является сейчас одной из лучших в стране. Кроме того, несмотря на объективные, серьезные трудности для отечественной науки, российские ученые-химики по-прежнему демонстрируют высокий уровень научных исследований и данный сборник - еще одно тому подтверждение. И наконец, приобщение к современным компьютерным технологиям

молодого поколения российской науки, очевидно, будет иметь огромное значение для развития российской химии.

Я желаю участникам симпозиума и школы семинара удачной работы и надеюсь, что новые тенденции в вычислительных методах и информационных технологиях в химии, выявленные во время дискуссий, разовьются успешно и продуктивно. У нас впереди много работы. И я твердо верю, что новые компьютерные технологии внесут свой достойный вклад в развитие российской химии.

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The concepts of atomic charge, bond order, and bond index are considered, various definitions are analyzed, and the use of these concepts in the high accuracy ab initio molecular electronic structure calculations is discussed, both Hartree-Fock and correlation included methods being taken into consideration. A new minimal quasi-atomic basis for the population analysis of the results of high accuracy HF calculations is proposed. In this basis the quasi-atomic orbitals for each atom of a molecule are constructed as linear combinations of all occupied and several lowest virtual molecular orbitals. Hence the expansion of each molecular orbital in this minimal quasi-atomic basis is exact. This is an advantage of the proposed method compared with the method employed the projection technique where the corresponding expansions are only approximate. To calculate the quasi-atomic orbitals the variational principle is employed, the energy functional for a given atom being one of two configuration averaged energies. One of them is the energy averaged over all states of the configurations and another is the energy calculated with the electronic density averaged over the configuration. No symmetry is assumed, therefore the configuration of the valence state of an atom in a molecule is simply an array of orbital populations. The calculation of the minimal quasi-atomic basis is carried out to selfconsistency, i.e. for each atom the populations assumed in the orbital calculations must coincide with the populations resulted from the population analysis with the obtained basis. The values of atomic charge and bond order obtained in the new quasi-atomic basis population analysis of the results of HF calculations of several molecules with bases of different length are presented and discussed in the paper. A possibility to apply the proposed minimal quasi-atomic basis to the population analysis of the calculations with correlations is also considered.

THE GENERATION OF THE SILICON AND OXYGEN SEPARABLE POTENTIALS MODELLING THE CHEMICAL BOND

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In previous works (see for example, Book of Abstracts 2-nd V.A.Fock on Quantum and Computational Chemistry, Novgorod the Great,2000) a new type of separable potential operator was introduced for several kinds of applications in electronic structure calculations. It is well known that any cluster selected from the crystal or large molecule with comparatively strong covalent bonding encounters the problem of the correct description the boundary atoms, as these are atoms with dangling (unsaturated) bonds. The main idea is to employ the one-electron \"pseudoatom\" with the specially constructed separable potential to saturate and restore the broken bond. Another application concerns the atomic pseudopotentials where the new potential operator avoids the possibility of \"ghost\" states that sometimes plague the widely used Kleinman-Bylander form of the pseudopotential. In this work the proposed separable pseudo-potentials were generated for silicon and oxygen

atoms with the help of SiH4 and H2O as the reference molecules. The potential generation scheme consists of several stages. At the first stage the all-electron Hartree-Fock calculations of the SiH4 and H2O molecules were performed. At the second stage the non-canonical Hartree-Fock orbitals localized on bonds considered were calculated. These localized orbitals we interpret as bond wave functions. At the last stage the 3-dimensional separable potentials were constructed to reproduce exactly the bond wave functions, obtained on the previous stage. The obtained separable potentials can be used in the covalent compounds of Si and O for the saturation and restoration of the broken chemical bonds. The constructed potentials were tested in calculations the electronic structure and properties of the diatomic molecules X-(SI_ps), X=F,Cl,Br,I and X-(O_ps), X=F,Cl,Br. The results of these calculations were compared with all-electron Hartree-Fock calculations of the bond characteristics of SiH3-X and OH-X molecules. In particular the atomic charges, bond orders and bond dipole moments were calculated.

CORRELATION EFFECTS IN THE OXYGEN-OXYGEN INTERACTION IN MgO CRYSTAL

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Oxygen-oxygen interaction is important for understanding the properties of oxide materials. However, even in the MgO crystal, which is the simplest oxide material and which oftenly serves as an object to test a new computation methods on, this interaction is difficult to investigate due to the high flexibility of the doubly charged negative oxygen ion. Recently (Russian~J.Phys.Chem.~vol.74,~suppl.2,~p.253~(2000)) we had developed the effective potential simulating the influence of the crystal environment on the oxygen ion in the MgO perfect crystal. This effective potential enabled us to calculate the localized orbitals of the oxygen ion in MgO and hence all the interaction energies in the Hartree-Fock (HF) approximation. Besides, it helped to calculate the intraionic correlation corrections to the energy. In the present paper the crystal environment potential was partitioned into the contributions due to each ion of the environment. The magnesium ion contribution was taken to be the usual semilocal norm-conserving pseudo-potential. The main problem was to develop the oxygen ion contribution, i.e. the potential which simulates the influence of one oxygen ion onto another oxygen ion. The special semilocal one-center form with parameters convenient for calculations with Gaussian type orbitals was assumed for the oxygen contribution and the parameters were adjusted to reproduce the correct localized oxygen orbitals in MgO. The crystal environment potential as a collection of separate ions contributions enable us to calculate any cluster of MgO crystal in the HF approximation. The new developed crystal environment potential allows one to go beyond the HF approximation and to take account of the correlation corrections. In the present paper several two-ion clusters were considered made of two negative oxygen ions at various distances consistent with MgO crystal structure and embedded in the crystal environment potential. The electronic structure of such clusters had been calculated in the HF approximation first, to ensure the accuracy of the embedding potential, and then with the configuration interaction method with moderate number of configurations taken into account. The results of calculations presented

in the paper show that for the distant oxygen pairs the correlation correction to the interaction energy corresponds to the Van der Waals interaction, while for oxygen ions being the second neighbors the correlation correction differs significantly from the Van der Waals energy.

ELECTRONIC STRUCTURE OF P_2O_5 WITH Ag_2 AND Ag_2O MOLECULAR IMPURITIES: AB INITIO TOTAL-ENERGY CALCULATIONS

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The investigaton of silver-activated phosphate glasses is important for understanding of the defect formation mechanism on exposure to ionizing radiation. Along with a single Ag atom the Ag2 molecule also can be the radiophotoluminescent center in Ag-activated phosphates glasses. It is also interesting to check the Ag2O molecule as a candidate for the impurity center, because it is the Ag2O which is added to the host when forming the Ag-activated phosphate glasses. A knowledge of the electronic structure, geometry and the charge state of these impurity centers could clarify physics of a radiophotoluminescence process. Both crystalline and vitreous P2O5 could be described equally well in terms of PO4 tetrahedra with one double-bonded oxygen atom and three bridging oxygen atoms. As the local structures in crystal and in glass are similar it is expedient to investigate the influence of various Ag impurity centers on the crystalline P2O5 first. A single Ag atom impurity case was studied in our previous paper (Phys.Rev.B, 60, 7881 (1999)), and the molecular impurity centers Ag2 and Ag2O are the subjects of the present work. To investigate the local structure of the said impurity centers the quantum-mechanical ab initio total-energy calculations of P2O5:Ag2 and P2O5:Ag2O were carried out for the first time within the density functional theory approach for the supercell periodic defect model. For this the CASTEP code had been employed, which uses the plane wave basis set for valence electrons and the first-principles separable Kleinman-Bylander pseudopotentials to incorporate the atomic cores. To make the periodic model the supercell consisting of two unit cells of P2O5 joined along the shortest unit cell vector and containing 56 atom has been used. An inputity was inserted in each supercell. So the used periodic cluster contains 16 phosphorus atoms, 40 oxygen atoms and a single impurity molecule Ag2 or Ag2O. The experimental unit cell parameters of P2O5 were employed. For starting configuration of regular atoms the experimental geometry of P2O5 crystal was taken and several different variants of the impurity molecules positions were tried. The positions of all atoms, including the impurity atoms, were optimized in calculations. As a result the equilibrium geometries of P2O5:Ag2 and P2O5:Ag2O crystals were found. In both cases the obtained electronic structure is explained in terms of the density of states and of atomic charges (on Mulliken and Lowdin) along with the bond orders (Wiberg indexes) calculated from the Kohn-Sham crystal orbitals obtained in the plane-wave basis set and then projected onto the space of the atomic Kohn-Sham orbitals. Besides the displacements of atoms from their equilibrium positions, the distortion of the electronic density and changes of the atomic charge values were determined too. The calculated impurity-induced deformation of the host lattice was found to be considerable. Its analysis in terms of PO4 tetrahedra is also given. The present work was supported by the Russian Foundation for Basic Research grant N 00-03-33040 and by NATO collaborative research

grant N 960521.

ДВУМЕРНАЯ МОДЕЛЬ ТОРСИОННО-ИНВЕРСИОННЫХ КОЛЕБАНИЙ МОЛЕКУЛ

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Разработана программа для решения задачи о многомерных колебаниях молекул с большой амплитудой. Гамильтониан колебательного движения рассматривается в виде

$$H(\varphi_1,\ldots,\varphi_n) = -\sum_{i=1}^{n}\sum_{j=1}^{n}\frac{\partial}{\partial\varphi_i}B_{ij}\frac{\partial}{\partial\varphi_j} + V(\varphi_1,\ldots,\varphi_n),$$

где n – число учитываемых колебательных координат φ_i, B_{ij} – элементы симметричной матрицы кинетических параметров, V – потенциальная функция.

Программа применялась для исследования торсионно-инверсионного движения молекул карбонильных соединений CX_3-CHO и CX_2Y-CHO (X, Y = H, F, Cl) в низших возбужденных электронных состояниях (где карбонильный фрагмент имеет пирамидальное строение) [1]. В качестве координат внутреннего вращения и инверсии приняты, соответственно, φ_1 – угол относительного поворота альдегидной и CX_2Y- (или CX_3-) групп, φ_2 – угол выхода связи CH_{ald} из плоскости CCO. Двумерные потенциальные поверхности и геометрические параметры, необходимые для вычисления величин B_{ij}, были получены путем неэмпирического квантово-механического расчета.

Анализ торсионно-инверсионных волновых функций позволил отнести рассчитанные колебательные состояния к различным конформерам и приписать им определенные значения торсионного и инверсионного квантовых чисел. Вместе с тем показано, что с ростом колебательного возбуждения взаимосвязь движений по координатам φ_1 и φ_2 становится все более заметной, и адекватное описание поведения молекулы возможно только в рамках двумерной модели. Результаты подобных расчетов существенно облегчают исследование электронно-колебательных спектров конформационно нежестких молекул.

Работа выполнена при финансовой поддержке РФФИ (гранты №№ 00-15-97346 и 01-03-32841а).

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COOPERATIVITY AND STABILITY OF WATER CLUSTERS WITH A COMPLICATED STRUCTURE OF HYDROGEN BONDS

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It is known for a long time about cooperative properties of water. At the same time, the models of complicated systems with a developed grid of hydrogen bonds find a use in various areas: to physics of liquid water, theory solvatation, etc. Set of structures, which correspond to local minima at potential energy surface obtained using semi-empirical methods, are artefacts, however structures with most expressed cooperative properties answer are more stable of them. We assume that such stable structures should be topologically equivalent. If to compare to each structure a digraph, in which tops - molecule or the chemical groups linked by hydrogen bonds, and vector designate hydrogen bond formed between them, it is possible to select structures answering minimum energy, among similar (inherings to one base column) proceeding from their topology. Because of these suppositions the account of a number of clusters of water was conducted within the framework of an approximation PM3, and obtained in a course it the accounts completely will be agreed expressed reasons.

REACTIVITY OF SINGLET DIOXYGEN ON THE SURFACE OF THE IONIC CRYSTALS

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The possibility of the existence of singlet ground state for the molecular oxygen adsorbed on the surface of the fcc type ionic crystals has been considered (the case of strong nonuniform crystal field). The adsorption energies of the various multiplet electronic states of the molecular oxygen on the crystal surface have been estimated using the approach being developed earlier by us [1] in the frame of semi-empirical quantum-chemical SCF MO LCAO method. The coulomb cluster with the lattice of fcc-type has been considered as the crystal model. The modeling cluster parameters (q - ion charge, d - lattice parameter) which can affect on the relative position of the singlet and triplet terms of the adsorbed dioxygen have been varied (in case of the gas phase the triplet-singlet splitting is equal to 0.98eV). It was shown that crossing of the triplet and singlet terms of dioxygen can take place in the presence of quite reasonable effective charge of ion q (+2 – +4) and lattice parameter d [2]. The calculations of the dioxygen adsorption on the MgO crystal (ion charge q= 2) with a defect have been performed. The positively charged ions (charge q+2) have been considered as the defect, which co-ordinates the adsorbed singlet O2. The reactions of singlet dioxygen, which take place in the gas phase, has been considered on the active site(AS) obtained in this way (AS – singlet O2, adsorbed on the highcharged defect cation of the crystal): specific oxidation of C=C bonds and aliphatic hydrocarbons with formation of peroxidates. This work was supported by the Russian Foundation for Basic Research , project no. 99-03-32145a. 1. I.D. Mikheikin, G.M. Zhidomirov, V.B. Kazanskii, Zhurn.fiz.khimii (rus.), 48 (1974) 2920.

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THEORETICAL STUDY OF CATALYTIC TRIPLE BOND ACTIVATION AND C-C COUPLING BY Pt(IV) COMPLEXES.

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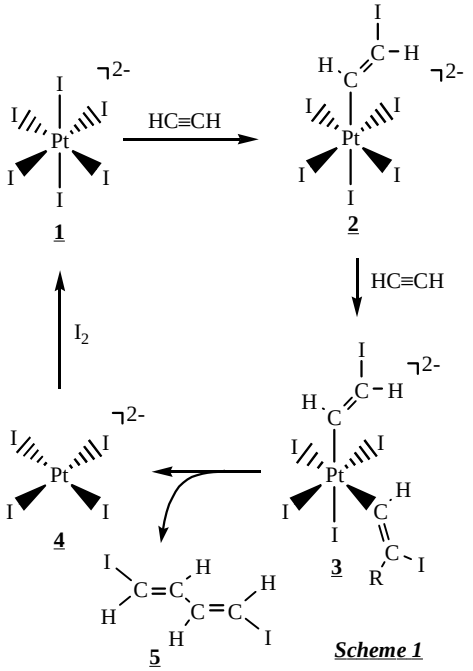
A density functional theoretical study has been performed for the mechanisms of platinum(IV)-catalyzed alkyne-to-conjugated diene conversion reaction (*Scheme 1*), which involves two subsequent triple bond activation steps (**1** → **2** and **2** → **3**) followed by vinyl-vinyl coupling (**3** → **4** + **5**) [1]. Calculations have shown that acetylene triple bond activation by $[PtI_6]^{2-}$ in water or methanol solution proceed through external nucleophile addition of I^-, thus making the activation stage stereoselective. The rate-determining step of the entire catalytic cycle is found to be the formation of platinum(IV) cis-divinyl derivative (**3**).

Although vinyl-vinyl coupling reaction may take place from both six-coordinated octahedral and five-coordinated square-pyramidal Pt(IV) divinyl complexes, the five-coordinated derivative was found to react with a significantly lower barrier. The results obtained here are in good agreement with available experimental data and reveal important details of the catalytic reaction mechanism. The present investigation also has shown that no reliable conclusions may be drawn without taking solvent effect into account.

The details of the performed theoretical study will be presented and discussed.



Scheme 1

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ИНФРАСТРУКТУРА ДЛЯ ОБЕСПЕЧЕНИЯ ПОИСКА ХИМИЧЕСКОЙ ИНФОРМАЦИИ. ПОПЫТКИ ИНТЕГРАЦИИ В РОССИИ.

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Химическая информация быстро растет, но медленно стареет. В этой связи организация возможности доступа через Internet к отечественным и зарубежным базам данных по химии является исключительно актуальной задачей. Если организация доступа к полнотекстовым ресурсам приобретает уже некие оформленные черты (www.elibrary.ru, EBSCO, LibNet и др.), то проблема **поиска** информации, т.е. формирование инфраструктуры для отыскания тех самых текстов, которые необходимо прочесть, весьма далека от решения. Такая работа при поддержке РФФИ начата в ряде региональных научных центров (Москва, Санкт-Петербург, Новосибирск, Ростов). В качестве национального WWW-сервера РФ в рамках международного Ливерпульского проекта обеспечения системы ссылок на Web-серверы организаций, работающих в области химии, выбрана интегрированная информационная система (ИС), ядром которой является Web-сервер ИОХ РАН www.chem.ac.ru. Его особенностью является преднамеренно "аскетическое" представление информации, содержащее минимум графических данных. Это сделано с учетом того, что используемые российскими химиками каналы связи часто отличаются низкой скоростью и невысокой надежностью. В ИС входит общероссийский список рассылки (телеконференция) Russian Chemical List (RCL), Rcl@www.chem.ac.ru, которым пользуются также наши коллеги из стран ближнего зарубежья. В рамках данной ИС разработан программный интерфейс между современными квантово-химическими комплексами неэмпирических программ Gaussian-94/98 и СУБД PostgreSQL в ОС Linux, а также решена проблема с тем, что принято называть "унаследованным программным обеспечением". Для него проведена инсталляция и настройка эмулятора MS DOS в ОС Linux, что позволяет организовать многопользовательский сетевой доступ через Internet к БД, разработанным для этой среды. В результате всем желающим уже можно предложить бесплатно разместить свои химические БД, созданные в среде MS DOS, на общем сервере, имеющем высокоскоростной доступ в Internet, сделав их доступными по сети. Аналогичные возможности планируется обеспечить и для среды ОС Windows.

Главное направление в создании инфраструктуры поиска химической информации - это интеграция, осуществление коллективных проектов. Если сетевой доступ в ходе их реализации оказывается невозможным, то для передачи информации используется электронная почта. В Москве свои возможности в той или иной мере объединили Химический факультет МГУ (www.chem.msu.su), Институт органической химии РАН, Центр фотохимии РАН. К примеру, внутри сети МГУ возможен доступ к значительному фонду зарубежных и отечественных баз данных (Chemical Abstracts 1996-2000 годы, INSPEC 1989-1999гг., Cambridge Structural Database System версия 2000 г., Brookhaven Protein Data Bank версия 2000 г., электронная библиотека научно-образовательных изданий по химии и др.), возможность работы с которыми предоставляется сотрудникам как МГУ, так и других научных организаций России. На

базе Института катализа Сибирского отделения РАН (www.catalysis.nsk.su) и компьютерной сети Новосибирского Научного Центра при участии ГПНТБ СО РАН создается объединенная информационная система по химическим наукам СО РАН. Проводится работа по формированию баз данных по физико-химическим методам исследования веществ. Однако материальная база таких работ существенно отстает от мирового уровня, наблюдается спад в создании отечественных баз данных. Так, почти втрое сократилось число химических журналов, реферируемых ВИНИТИ, база данных "Химия" предоставляет в доступ 3,5 млн. документов и ежегодно пополняется примерно на 150 тысяч, тогда как мировой лидер - Chemical Abstracts - 16 миллионов и пополняется на 800 тысяч. В ходе выполнения этих и других проектов предстоит освоить и внедрить технологию создания распределенных БД химической информации (фактографической, полнотекстовой, библиографической), в частности, образующейся непосредственно в процессе научного эксперимента (рентгеновская дифракция, ЯМР, ЭПР, ИК, экологический мониторинг и др.).

Ключевую роль в поиске и обучении поиску платной некоммерческой информации в теледоступе играет сейчас Московский информационный центр в ИОХ (МИЦ, khutor@ioc.ac.ru). Благодаря Соглашению с Chemical Abstracts Service и грантам РФФИ удалось снизить цены на поиск химической информации для всех пользователей центра из ВУЗов, РАН и РАМН в 10 раз по сравнению с мировым уровнем. Ежегодно услугами МИЦ по поиску пользуются 30-40 институтов страны, примерно по ста грантам РФФИ предоставляются результаты бесплатных поисков. За год в МИЦ проходят обучение около ста студентов и аспирантов, а также разрабатываются учебные пособия и оптимальные схемы поиска. Второй год идет создание сети филиалов МИЦ (Академсеть) в регионах страны. Прошло обучение будущих специалистов по поиску и преподавателей из Новосибирска, Ростова, Санкт-Петербурга. Принимаются заявки от желающих присоединиться к проекту.

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ПРИМЕНЕНИЕ ИСКУССТВЕННЫХ НЕЙРОННЫХ СЕТЕЙ В СОЧЕТАНИИ С ПОДСТРУКТУРНЫМ ПОДХОДОМ ДЛЯ ПРОГНОЗИРОВАНИЯ ФИЗИКО-ХИМИЧЕСКИХ СВОЙСТВ ОРГАНИЧЕСКИХ СОЕДИНЕНИЙ

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Для прогнозирования физико-химических свойств органических соединений интересным оказался подход на основе фрагментного метода для описания дескрипторов (разбиение молекулярного графа на множество фрагментов и подсчет количества появлений каждого из них в соединениях исследуемой базы данных) в сочетании с нейросетевым статистическим аппаратом. Для практической реализации этой идеи был разработан дескрипторный блок Fragment, работающий в рамках

программного комплекса NASAWIN, включающего статистический блок на основе искусственных нейронных сетей.
В докладе обсуждается применение такого комбинированного подхода для прогнозирования ряда физических свойств: температуры кипения, энтальпии образования, теплоты неспецифической сольватации в циклогексане, энтальпии растворения в воде для различных органических соединений.

Для температуры кипения коэффицинт корреляции на обучающей выборке равен 0.9946, среднеквадратичная ошибка на обучающей выборке равна 6,4 градуса, а среднеквадратичная ошибка на контрольной выборке – 10,1 градус. Для энтальпиии образования результирующий коэффициент корреляции составил 0.9977, среднеквадратичная ошибка на обучающей выборке - 3,5 ккал/моль и среднеквадратичная ошибка на контрольной выборке - 6,8 ккал/моль. Для теплоты неспецифической сольватации коэффицинт корреляции на обучающей выборке равен 0.9994, среднеквадратичная ошибка на обучающей выборке равна 0.4 ккал/моль, а среднеквадратичная ошибка на контрольной выборке – 1.0 ккал/моль. Для энтальпии растворения органических веществ в воде результирующий коэффициент корреляции составил 0.9936, среднеквадратичная ошибка на обучающей выборке – 0,3 единицы log (моль/м^3) и среднеквадратичная ошибка на контрольной выборке - 0.4 единицы log (моль/м^3). Все эти данные подтверждают возможность успешного применения данной методологии для прогнозирования физико-химических свойств органических соединений.

THE LOW TEMPERATURE RATE EXPRESSION INCLUDING TUNNELING IN CONDENSED PHASE

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A new approach for studying the rate constant of a chemical reactive process in condensed phase in a deep tunneling regime is considered. The Golden Rule rate expression is modified and reformulated in terms of spectral line shapes of energy levels, which are involved in a chemical rearrangement. Computations of a reactive tunneling transition and of spectral line profile are treated as two separate steps: this allows one to extract qualitative conclusions on the reaction rate and its temperature dependence basing on a structure of the general formula. This approach is extended for treating hydrogen abstraction reactions in molecular crystals within a multimode model. A strong temperature dependence of the rate at low temperature is predicted.

QUANTUM-MECHANICAL INVESTIGATIONS OF THE FLUORINE SUBSTITUTED ACETALDEHYDES IN THE LOW LYING ELECTRONIC STATES

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The results of the quantum-mechanical calculations (RHF, MP2, UHF, CASSCF, CIS, CISD etc.) of the non-rigid carbonyl molecules CXYZCHO (X, Y, Z = H, F) in the lowest excited singlet (S0) and triplet (T1) electronic states are considered. The computational results are in good agreement with the available experimental data. The structure regularities of the investigated molecules are analyzed. The one- and two-dimensional quantum mechanical models of the pyramidalization of the carbonyl fragment and the internal rotation caused by the S1<--S0 and T1<--S0 electronic excitation are discussed. This work was financially supported by RFBR (Project N 00-15-97346 and 01-03-32841).

QUANTUM-MECHANICAL INVESTIGATION OF A STRUCTURE OF THE MOLECULES OF CARBONYL COMPOUNDS IN THE GROUND AND LOWEST EXCITED ELECTRONIC STATES

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The results of the quantum-mechanical calculations of a structure of a number of the non-rigid carbonyl molecules in the ground and lowest excited electronic states are presented. To solve the electronic problem the potential energy surfaces was calculated by various ab initio methods (RHF, MP2, UHF, CASSCF, CIS, CISD etc.). On this basis the torsion and inversion nuclear motions are considered by the one- and two-dimensional quantum-mechanical approximations. The results were used for the S1<--S0 and T1<--S0 vibronic spectra analysis of X2CO and CXYZCHO molecules. This work was financially supported by RFBR (Project Nos 00-15-97346, 01-03-32116, and 01-03-32841).

МОДЕЛИРОВАНИЕ АМИНОКОНЦЕВЫХ ДОМЕНОВ МЕТАБОТРОПНЫХ ГЛУТАМАТНЫХ РЕЦЕПТОРОВ И ИХ КОМПЛЕКСОВ С ЛИГАНДАМИ С ПОМОЩЬЮ МЕТОДА МОЛЕКУЛЯРНОЙ ДИНАМИКИ

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С помощью компьютерного моделирования по гомологии с бактериальными периплазматическими белками и методом “протягивания нити” построены модели открытых и закрытых форм аминоконцевых доменов метаботропных глутаматных рецепторов и проведено сравнение полученных моделей. Показано, что для случаев низкой гомологии аминокислотных последовательностей лучшие результаты дает метод “протягивания нити”. Оценена возможность использования метода молекулярной динамики для исправления локальных структурных дефектов в построенных моделях для участков, имеющих отрицательное значение 3D-1D профиля. Проведен молекулярный докинг как известных агонистов и антагонистов к активным центрам смоделированных рецепторов, так и новых лигандов и обсуждены способы их связывания с рецептором.

С использованием метода молекулярной динамики с учетом растворителя проведен расчет свободных энергий связывания лигандов с рецептором в молекулярных комплексах белок-лиганд и оценены константы связывания лигандов в этих комплексах. Проведено сравнение констант связывания лигандов для открытых и закрытых форм аминоконцевых доменов рецепторов. Объяснена роль иона кальция в качестве коагониста при связывании эндогенного нейромедиатора – глутаминовой кислоты, предложен возможный механизм схлопывания комплементарных глобул, входящих в состав аминоконцевого домена метаботропного глутаматного рецептора, в основе которого лежит электростатическое взаимодействие. Расчеты проводились на рабочей станции SGI Octane.

POTENTIAL ENERGY SURFACE STRUCTURE OF HALOBENZENE RADICAL ANIONS

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Potential energy surfaces (PES) of a wide series of the halobenzene radical anions including anions of C6H6, C6F6, C6H5X (X=F, Cl) and some polyfluorobenzenes has been studied with ab initio (ROHF/6-31+G* and MP2/6-31+G*//ROHF/6-31+G*) calculations. The stationary points of PES have been located and their types and interrelations have been determined. Results of calculations show that for all the anions considered PES structure is of vibronic nature. The PES peculiarities were found to come from two reasons. The first one is relatively small energy gap between the radical anions\' pi state levels degenerated in the parent C6H6- . As a result, the Hartree-Fock PES of all the anions are the surfaces of pseudorotation. The second reason is a presence of vibronically active excited sigma state. This leads to out-of-plane distortions of halosubstituted radical anions. For both highly symmetric C6H6- and C6F6- anions pi state is degenerated. The Jahn-Teller and pseudo-Jahn-Teller effects with different active modes combining in C6F6- results in doubling of the stationary point number at the pseudo-rotational surface in comparison with the JTE alone case, C6H6-. C6H5Cl- represents a case of quasi-degenerated pi states. Its PES is similar to those of parent C6H6-: in both cases pseudo-rotation of planar pi radical structures occurs, which includes six stationary points. Qualitative distinction in the PES structure of the two anions comes from existing of low-lying repulsive sigma state in case of C6H5Cl- . This results in out-of-plane distortions followed by C-Cl bond cleavage. The anion metastable pi state has been found, and transition state for C-Cl cleavage has been located. Asymmetrical non-planar structure of the transition state indicates that the reaction coordinate is rather complicated. Besides the bond stretching, it includes both pseudorotation and Cl atom out-of-plane deviation because of double symmetry forbiddance for the anion ground p state cleavage. The pseudorotation contribution in reaction coordinate was found also for ortho- and meta-benzonitrile anions cleavage, while in case of para-isomer this contribution is absent. For polyfluorobenzenes C6FnH6-n (n=2-4) the energy splitting of pi MO levels generated by the benzene e2u MO varies within rather wide limit. Nevertheless, the Hartree-Fock PES of corresponding radical anions reveal pseudorotation, involving different number of planar and distorted stationary structures. On the whole, PES structure of these anions reflects main features of the C6H6- and C6F6- PES. The electron correlation effects must be

taken into account to describe correctly the result of a gas phase experiments. However, the mechanism of intramolecular transfer of unpaired electron density through the pseudorotation is independent on correlation including.

NANOPACK: PARALLEL CODES FOR SEMIEMPIRICAL QUANTUM-CHEMICAL CALCULATIONS OF LARGE SYSTEMS

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Package NANOPACK is dedicated to semiempirical quantum-chemical (QCh) calculations of nano-sized systems by using multiprocessor computers. The package is based on two one-processor software CLUSTER-Z1 [1] and CLUSTER-Z2 [2] each of which provides extended QCh calculations of structural and electronic characteristics of large polyatomic systems with up to 2960 atomic orbitals in the sp- and spd-basis, respectively, as well as of force fields, harmonic vibrational frequencies and IR R-scattering intensities. Additional blocks provide calculations of the above characteristics in the presence of electric field and under external stress. CLUSTER-Z1 is based on widely used AM1 and PM3 techniques while CLUSTER-Z2 implements a non-restricted Hartree-Fock technique in a modified NDDO approximation which exploits a computational scheme based on a set of weighted factors (NDDO-WF approach) [3]. Test calculations were carried out for two atomic systems. One presents an octamer of silicon fullerene 8*Si60 (1920 AOs, MNDO, AM1, PM3 techniques) while the other simulates carboxylic acids adsorption on TiO2 nanoparticles (cluster involves 2014 AOs, NDDO-WF method). The computation speed-up is about 4 when using 8 processors in both cases. [1]. V.A.Zayatz, \"Software CLUSTER-Z1 for quantum-chemical calculations in the sp-basis\". . Institute of Surface Chemistry, Nat.Ac,Sci of the Ukraine, Kiev, 1991. [2]. V.A.Zayatz, \"Software CLUSTER-Z2 for quantum-chemical calculations in the spd-basis\". . Institute of Surface Chemistry, Nat.Ac,Sci of the Ukraine, Kiev, 1993. [3]. A.G.Grebenyuk, V.A.Zayets, Yu.I.Gorlov, React. Kinet. Catal. Lett. 50, 257 (1993).

РЕПАРАМЕТРИЗАЦИЯ ПОЛУЭМПИРИЧЕСКОГО КВАНТОВО-ХИМИЧЕСКОГО МЕТОДА ZINDO/S ДЛЯ РАСЧЕТА СПЕКТРАЛЬНЫХ ХАРАКТЕРИСТИК КРАСИТЕЛЕЙ

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С использованием методов PM3 и ZINDO/S исследовано влияние гидратации молекулы на её энергетические и оптические свойства. Получена энергетическая характеристика сольватации. Предполагаемое влияние последней на электронный спектр молекулы (сольватохромный эффект) не обнаружилось. Из этого следует, что метод ZINDO/S недостаточно подходит для решения данной проблемы. Следствием этого является неправильная последовательность σ- и π-уровней, что, в свою очередь приводит к «ультрафиолетовому» сдвигу длинноволновой полосы поглощения.

Нами был проведён ряд расчётов спектров индиго с пошаговым изменением коэффициентов σ-σ- и π-π-взаимодействий, вследствие чего была получена картина чередования σ- и π-уровней и соответствующий им спектр, наиболее приближенный к экспериментальному

DFT PBE AND AM1 CALCULATIONS ON CONFORMATIONS OF N-SUBSTITUTED ENAMINES

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Conformational potential energy surfaces (PES) of N-substituted enamines CH2=CH-N(OR)2 (R=H, SiH3, SiMe3) corresponding to rotation around C-N bond and pyramidal N atom inversion were investigated. AM1 and DFT PBE/TZ computations were carried out on the fragments of conformational PES. The barriers for nitrogen inversion and rotation around C-N bond were calculated. AM1 and PBE calculation give qualitatively different shapes of PES, but the latter results are in better agreement with existing experimental data. In contrast to planar vinylamine, the N atom in N-disubstituted enamines has pyramidal configuration with high inversion barrier of 12-15 kcal/mol. The barrier of rotation around C-N bond (2-3 kcal/mol) is significantly lower than the N atom inversion. In contrast to AM1 calculations, rotational curve obtained using DFT PBE method shows an additional potential energy minimum, which become lower in enamines with more bulky substituents. The results are used to estimate influence of substitents on the structure of the most stable conformer of N,N-bis(trialkylsiloxy)enamines and to explain conformational changes detected in dynamic NMR studies. Acknowledgments: This work has been supported by the RFBR (project No 99-03-32015). Authors thanks Dr. Dmitry N. Laikov who make available program Priroda used for DFT PBE calculations.

SCHROEDINGER EQUATION FOR THE DIATOMIC MOLECULAR SYSTEMS INSIDE THE SPHERICAL CAVITY

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The study of the molecule encapsulated into the cavity is a natural problem that has a lot of applications in chemistry, spectroscopy and solid state physics. Effective solution of such problem requires the advanced computational and theoretical tools. Detailed analysing of the diatomic system is an interesting problem that allows to accumulate expirience for the more complex systems.

Assuming adiabatic electronic potential to be known (depending on the internuclear distance only) we have to solve nuclear six-dimensional eigenvalue differential equation with the Dirichlet boundary conditions on the sought-for wave function to find the energy spectrum of the system. There is no sense to separate the inertia center of the system. However, due to the form of the boundary conditions and potential the problem has spherical symmetry. It implies classification of the states by the total momentum value (with respect to the center of the cavity). The using of the spherical coordinates (Euler angles) and Hirschfelder's expansion by D-func-tions give rise to derive the number of individual coupled three-dimensional problems for each value of the total momentum. For the state with zero momentum the problem reduced to one equation being an analog of that one derived by Hylleraas for the ground state of the Helium atom (investigated by Fock (1953)). The coupled systems of three equations for j=1, five equations for j=2, etc. is studied. All the equations have the similar structure of its differential part just as in Hylleraas's equation. The choice of the coordinates, boundary conditions, numerical methods are considered in details. (RFSR, No 01-03-32116)

COMPUTER SIMULATION OF SiC SURFACE BEHAVIOR DURING GROWTH BY MBE

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SiC is a wide-band-gap semiconductor material of great technological interest for device designed to operate at high temperatures, high power, high frequency and in harsh environment. It crystallizes in numerous structural modifications, having different physical properties. Therefore, heterostructures of different SiC polytypes may be also of interest for future applications. Moreover, the growth of Si quantum dots on SiC may be suitable for an integration of group IV materials, especially Si, into the optoelectronics. For device application, high quality crystallinity and interface formation are necessary, and therefore, layer by layer growth has to be achieved. Furthermore, a wavy step morphology may be useful as a template for ordered quantum dot arrays. It is the aim of this work to perform computer simulation regarding the step morphology. Atomic steps are basic units of surface roughness on semiconductor surfaces. Therefore, designing of the step arrangement will be a key technique of the nanostructure self-organization for large-scale quantum dots arrays.

Authors report about the role of adatom diffusion along steps in step stabilization. Therefore, the kinetic Monte-Carlo model incorporating fast edge diffusion was developed. The kinetic Monte Carlo simulations on a solid-on solid model clearly show the stable step flow growth mode and the pattern formation for the different misorientation direction of the substrate. The parameters ratio controls the ordering and abruptness of a wavy shaped step edges. Our kinetic MC model uses 14 configurational parameters and groups of time and temperature depended parameters. Usually, the computational results of a SiC growth do not rely on one set of exact values for the model parameters. The values are not unique but are used self-consistently in the model. To increase the predictive capability of this Monte-Carlo model current work will focus on choosing values for the model parameters based on experimental measurements.

СХЕМЫ G2(MP2,SVP) В ИССЛЕДОВАНИЯХ ЭНЕРГО-НАСЫЩЕННЫХ СТРУКТУР СО СВЯЗЯМИ NN И (ИЛИ) NO

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Исследования, проведенные в последнее десятилетие, позволили существенно продвинуться в понимании природы электронной, структурной, термодинамической и кинетической стабильности (метастабильности) многих известных и гипотетических химических соединений, а также прогнозировании возможностей их использования непосредственно или в качестве компонентов энергонасыщенных веществ.

Одной из важнейших в таких исследованиях является проблема корректной оценки термохимических параметров, особенно газофазных, которые для многих структур со связями NO и (или) NO не удается определить экспериментальными методами. Возможности прогнозирования таких параметров на основе эмпирических или полуэмпирических схем, использующих методологию изодесмичности, ограничены существующим набором групповых (или иных) вкладов. Аналогичный недостаток свойственен схемам классификации, выявляющим структурную обусловленность экстремальных свойств. В связи с этим весьма актуальной представляется проблема расширения существующих границ надежной структурной и термохимической информации на основе апробированных неэмпирических методов квантовой химии.

Для многоатомных систем наиболее приемлемыми в настоящее время представляются схемы G2(MP2,SVP)[1,2]. Сохранив элементы полной схемы расчетов термохимических параметров[1,3], но используя иное выражение для полной энергии систем с открытыми оболочками: E=E(QCISD(T)/6-31G*)) - E(PUMP2/6-31G*} + E(PUMP2/6-311+G(3DF,2P)) + E(HLC) + ..., более совершенные способы оценки значений колебательного терма, поправок высшего уровня (HLC), мы провели дополнительную апробацию модифицированной схемы MG2(MP2,SVP), включив в рекомендованный список тестовых структур[2] ряд достаточно охарактеризованных соединений со связями NN и (или) NO. Одновременно решался вопрос об

адекватности описания их структуры методами MP(FC)/6-31G** и функционала плотности (B3LYP) с различными базисными наборами.

Улучшенный вариант теории использован для оценки структурной, термодинамической и, в ряде случаев, кинетической стабильности реальных и гипотетических структурных изомеров CN_2O, CN_2O_2, CN_2O_3, ряда сопряженных ковалентных и биполярных (цвиттерионных или мезомерных бетаиновых, включающих 3-центровые 4-π-электронные фрагменты или фрагменты, изосопряженные триметиленметану) гетероциклических структур CHN_3O (1,2,3,5-оксатриазол), $C_2H_2N_2O$ (фуразан), изомеров $C_2H_2N_2O_2$ (производные 1,2,3- и 1,2,5-оксадиазолов), изомеров CH_2N_4O (производные тетразола), $C_3H_4N_2O_2$ (ковалентный гидантоин и мезоионный 3-метилсиднон), потенциальных окислителей F_3NO, N_2O_4, тринитрамина N_4O_6, N-оксидов триметиламина C_3H_9NO и пиридина C_5H_5NO, недавно описанного[4] фуразано-1,4,3,4-тетразин-1,3-диоксида $C_2N_6O_3$, а также ряда азидов, в том числе кабонилдиазида N_3CON_3.

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ТЕОРЕТИЧЕСКОЕ ИССЛЕДОВАНИЕ ЭНЕРГОНАСЫЩЕННЫХ СТРУКТУРНЫХ ИЗОМЕРОВ N_4O_2 И МОЛЕКУЛЫ N_6O_3 (D_3h) МЕТОДАМИ ФУНКЦИОНАЛА ПЛОТНОСТИ И MG2(MP2,SVP)

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Методом функционала плотности (B3LYP) в базисах D95** и D95+G** исследованы стационарные точки (локальные минимумы и переходные состояния) синглетной поверхности потенциальной энергии системы N_4O_2, относящиеся к недавно идентифицированному[1] нитроазиду O_2NN_3, его структурным изомерам, топологически соответствующим различным формам димера молекулы N_2O (ковалентным ациклическим и шестичленным циклическим, и биполярным пятичленным циклическим с N-оксидной функцией), а также тримера N_6O_3 (D_3h). Для сравнения указанными методами рассчитаны структурные параметры и частоты гармонических колебаний ряда известных соединений с одной или несколькими связями NN и (или) NO, а также изомеров N_4O (известного ONN_3 и окситетразола)[2,3], N6 (локального минимума симметрии C_S и переходной структуры D_6h), оценены возможные погрешности и определена эффективная процедура коррекции рассчитанных структурных параметров. Энергии стационарных точек уточнялись методами B3LYP/6-311+G(2df) и MG2(MP2,SVP) (см. предыдущее сообщение).

Установлено, что все рассмотренные ковалентные (ациклические и циклические шестичленные) и, в меньшей степени, биполярные циклические термодинамически нестабильны даже по отношению к нитроазиду. Наименее термодинамически стабильной является непланарная шестичленная структура со связью ОО, формально являющаяся предшественницей N_4. Весьма низкой, судя по рассчитанным значениям энергий активации, должна быть кинетическая стабильность других циклических изомеров N_4O_2 по отношению к диссоциации на молекулы N_2O ($C_{\infty v}$). Видимо, по этим причинам они никогда не фиксировались экспериментальными методами[4]. В расчете на моль выделившейся N_2O энергия связывания кинетически стабильной, как полагают[4], частицы N_6O_3 (D_3h) меньше, чем у исследованных биполярных пятичленных структур.

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РЕАЛЕН ЛИ ЭНЕРГОНАСЫЩЕННЫЙ ИЗОМЕР $N_2O(C_{2v})$?

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Изомеры N_2O являются простейшими структурами, содержащими связи NN и NO. Это один из примеров ситуации, когда энергия льюисовой ковалентной структуры ($^1A_1$,C_{2v}) значительно превышает[1,2] энергию ее реального биполярного антипода ($^1\Sigma^+$,$C_{\infty v}$). Хоппер[2], используя метод MCSCF/CI, показал, что энергонасыщенный циклический изомер термодинамически устойчив по отношению к его диабатической и, возможно, адиабатической асимптотикам N_2+O(^{3}P,^{1}D). Однако по понятным причинам структура циклического изомера была охарактеризована весьма приблизительно и не были проанализированы другие факторы, определяющие стабильность (метастабильность) или нестабильность этой частицы. Экспериментальные подтвержения возможности ее образования, по-видимому, отсутствуют[3].

В настоящей работе неэмпирическими методами SCF (RHF,CRHF,UHF) и MCSCF, MP2, CRMP2, QCISD, QCISD(T) в базисе 6-31G* и для сравнения методом функционала плотности (B3LYP/D95*) исследованы области синглетноq и триплетных ППЭ, соответствующие минимумам ($C_{\infty v}$, C_{2v}) и переходным структурам (C_s, C_{2v}). На уровне QCISD(T) длины связей NO и NN циклического изомера равны 1.550 и 1.205 Å (в работе[2] 1.5 и 1.2 Å). Реальным представляется и спектр гармонических колебаний (270, 759 и 1767 см$^{-1}$), рассчитанный в этом приближении. В переходной структуре C_{2v} длина связей NO увеличена до 1.976, 2.190 и 2.212 Å на уровнях CAS(8,7), QCISD и QCISD(T) соответственно, а длина связи NN (1.119, 1.120 и 1.127 Å) приближается к

межъядерному расстоянию в молекуле N_2 - 1.103 (CAS(6,5)), 1.115 и 1.120 Å соответственно (в базисе 6-31G*). Анализ относительных энергий стационарных точек, рассчитанных на более высоких уровнях теории, показывает, что циклический изомер мог бы рассматриваться как метастабильная частица, имеющая определенное время жизни при низких температурах. Однако из исследования каналов диссоциации $N_2O(C_{2v})$--N_2 + $O(^1D,^3P)$ методом CAS(8,7), а также области, примыкающей к переходному состоянию методом QCISD (базис 6-31G*), следует, что точка пересечения синглетной и триплетной ППЭ (в симметриях $^1A_1$ и $^3B_1$) находится на координате реакции между локальным минимумом и переходным состоянием. Таким образом, синглетный циклический изомер скорее должен рассматриваться как некоторая преддиссоционная структура, разложение которой идет с изменением суммарного спина системы.

HYBRID *AB INITIO* QM/MM MOLECULAR SIMULATIONS USING THE EFP METHOD

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A new computational methodology for hybrid quantum mechanical/molecular mechanical (QM/MM) calculations is introduced. Non-covalent boundary between QM and MM parts of the system is treated according the Effective Fragment Potential Method (EFP). The basic idea of the EFP method is to perform a regular *ab initio* calculation only for the active part of the system, while the chemically inert part is replaced by the model potentials, that incorporate the most important nonbonded interaction energy terms, namely, Coulomb interaction, polarization and exchange repulsion. The effective fragment potentials are generated by separate *ab initio* calculations. All energy terms of the EFPs are treated as one-electron terms in the quantum mechanical Hamiltonian of the active part of the system. In the new approach the inert part of the system, such as MM-sized biochemical molecule, is divided into specified number of small fragments with fixed internal structures, typical for biochemical systems. The fragments obtained are replaced by the EFPs. Like in the original EFP method, the interaction between the *ab initio* system and fragments enter via one-electron operators in the *ab initio* Hamiltonian, while the fragment-fragment interactions are replaced by Molecular Mechanics force field. The most important advantages of such methodology are the flexibility of the inert biochemical molecule and significant timesavings compared to full *ab initio* calculations on the same system. The new approach has been implemented into the PC-GAMESS package. The new methodology has been tested on calculations of the relative conformational energies and geometries of alanin dipeptide, treated as six EFPs, with four water molecules, which represent the *ab intio* part of the system. The Restricted Hartree-Fock calculations with different basis sets were applied for the QM-part of the system and for the construction of the effective fragment potentials. The MM part was treated with the MM3 force fields implemented in the TINKER program. The results obtained are in good agreement with pure QM calculations and experimental results.

PARTIAL CHEMICAL MODIFICATION OF CARBON NANOTUBES AS A WAY TO CREATE NANOMETER-SCALED HETEROJUNCTIONS

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We discuss the opportunity to design nanometer-scaled heterojunctions via partial chemical modification of carbon nanotubes, an alternative to mechanical connection of nanotubes of different geometries. We assume that addend atoms are attached to adjoint carbon atoms along the the chain parallel to the tube axis, which is the most favourable variant of attachment, according to our previous investigation. Since the attachment of an addend atom removes one pi-orbital, in the framework of pi-electronic and nearest-neighbour approximation, it is equivalent to the removal of the corresponding carbon atoms; therefore, we consider the ribbon of graphene hexagons. Hьckel pi-electronic band structures show that such a modification of carbon nanotubes of zigzag type changes the width of forbidden gap or even the type of the band structure, semiconducting to metallic or vice versa. Similar modification of armchair-type nanotubes changes the type of the band structure from metallic to semimetallic. All the said changes can be used to devise a broad range of heterojunctions with various electronic properties. This work has been supported by Russian Foundation for Basic Research, grant № 00–03–32968; the program «Topical Problems in Condense Matter Physics,» division «Fullerenes and Atomic Clusters,» № 98061; and 5th Contest of Basic and Applied Projects of Young Scientists of RAS.

COMPUTER MODELING OF C_2 CLUSTER ADDITION TO C_{60}

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Reaction of C_2 cluster insertion into lower fullerenes (reaction of C_2 ingestion by fullerenes) has been proposed to be one of the steps in formation and growth of higher fullerenes and nanotubes. We investigated, using semiempirical MNDO-PM3 method, the model reaction of C_2 ingestion by fullerene C_{60}. The geometries and energies of extremal points on the C_{62} potential energy surface were calculated. Several reaction pathways leading to formation of three different closed C_{62} fullerenes were investigated. All reactions proceed stepwise through intermediates of different structures. The main reaction pathways were found to be addition of C_2 by its one side to the 6-6 (see Fig.1) or 5-6 bond of C_{60} with formation of unclosed C_{62} intermediates of "ball-with-needle" structures. The results of calculations explain recent experimental data on the formation of unstable adducts upon addition of C_2 to C_{60}, obtained using the time-of-flight mass spectrometer with laser desorption.

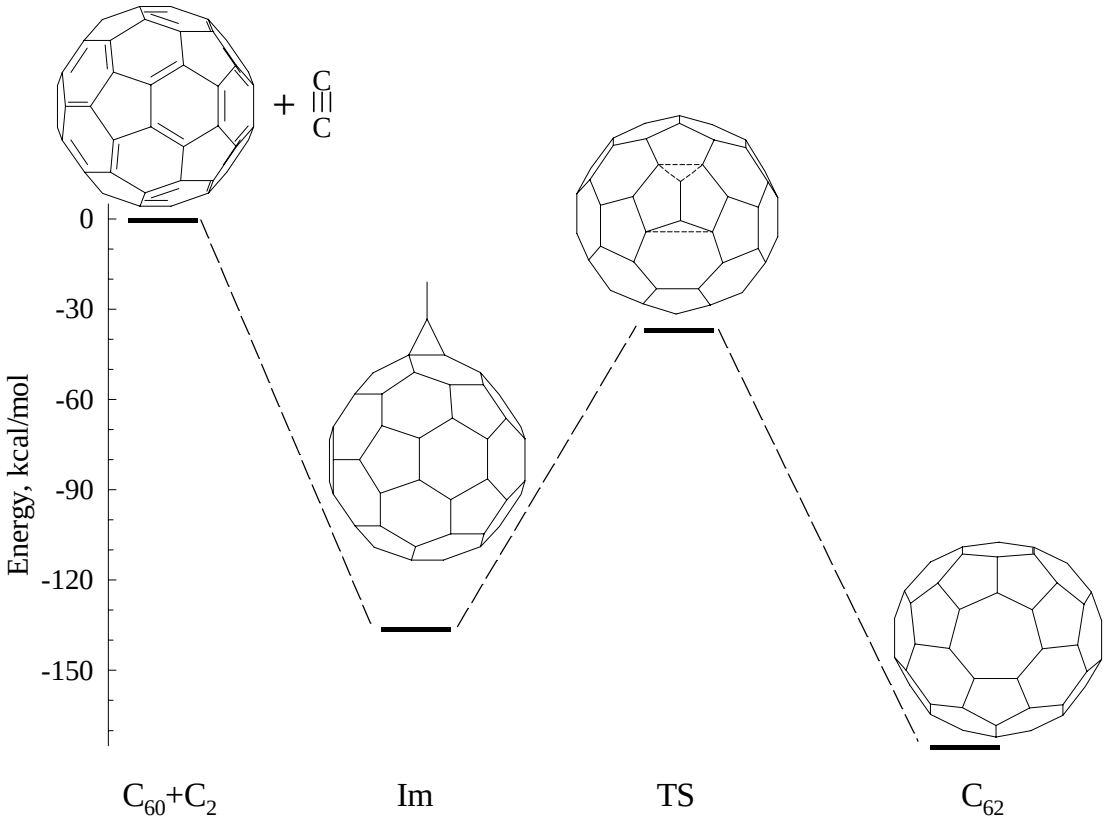

Fig. **1**. PM3-calculated stationary points (reactants, intermediate, transition state, and product) on minimal energy pathway of the reaction of C_2 cluster addition to fullerene C_{60}.
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CONCERTED HIGH-PRECISION SOLUTION OF ELECTRONIC AND VIBRATIONAL-ROTATIONAL PROBLEMS FOR THE HI MOLECULE.

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The HI molecule differs by its properties from other hydrogen halide molecules. These distinctions are caused not only by the large mass and charge of the iodine nucleus, but also by the specific structure of the molecular electronic shell. In particular, its electric dipole moment as a function of internuclear separation, has an anomalous behaviour, which causes the anomalous intensity values for vibrational-rotational lines of the fundamental and overtone vibrational bands. These anomalies cannot be described by considering small perturbations of the spectrum of a standard molecule, whose dipole moment depends linearly on the vibrational coordinate. This work is devoted to a concerted solution of electronic and vibrational-rotational problems for the HI molecule. At the first stage ab initio multiconfiguration calculations of the ground-state wave function (WF) were carried out. The total electronic energy and the dipole moment of HI were calculated for different values of

the internuclear distances by the proposed new version of ab initio valence bond method. In this method the electronic configuration of molecule is constructed as a set of configurations for separate atoms, including ionic configurations along with the covalent ones. The total ground-state WF was written as a linear combination of Slater determinants constructed from nonorthogonal atomic-like numerical orbitals localized at different centers. These orbitals were found from a numerical solution of the Hartree-Fock equations. To eliminate the continuous spectrum states from the basis set, the virtual orbitals were constructed in the form of the Sturmian-type localized orbitals. The basis set contained the ns, np and nd (n=1-7) atomic orbitals for the iodine and ns, np and nd (n=1-3) functions for the H atom, 5s and 5p I and 1s H orbitals being valence shell orbitals. The CI expansion included all configurations generated from the covalent H(1s)I(5s2,5p5) configuration with the help of single, double and partially triple excitations of electrons to different valence-shell and virtual orbitals. Only those triple excitations were taken into account, when no more than two electrons were excited to virtual Sturmian orbitals. The calculated results were compared with experimental data and the recent calculations by coupled cluster method (G.Maroulis, Chem.Phys. Lett., 318(2000), 181-189) and proved to be the better of the two and very close to experiment. At the second stage, the vibrational-rotational problem was solved by using the correct kinetic energy operator for a singlet sigma electronic state and the adiabatic potential computed at the first stage. The variational vibrational-rotational WF was taken as an expansion in products of harmonic-oscillator WF and spherical harmonics. The matrix elements of the Hamiltonian were evaluated, in particular, by quadratures, using the potential energy function calculated at the corresponding nodes. To determine the intensities of vibrational-rotational transitions, we evaluated the nondiagonal matrix elements of the dipole moment in the basis of solutions obtained, using the dipole moment values calculated at the nodes of integration. The analysis of results allowed us to examine the influence of mechanical and electrical anharmonicities and centrifugal distortion on the intensity distribution in the spectrum. The calculated results confirmed the anomalous dependence of intensities of vibrational-rotational lines on the quantum numbers and, at the same time, showed their strong sensitivity to the quality of solution of the electronic problem. This work was supported by Russian Foundation for Basic Research (grants N 00-03-33040a, N 00-03-33041a).

AB INITIO ANALYSIS OF THE STATIONARY POINTS ON THE H5+ CLUSTER ION POTENTIAL ENERGY SURFACE AND ITS DIM DESCRIPTION

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Ab initio quadratic configuration interaction QCSD(T) calculations in the cc-pVQZ basis set are performed for the stationary points on the potential energy surface (PES) of the H5+ cluster ion composed of H3+ and H2 fragments. As many as ten stationary points with different number of imaginary frequencies are located and investigated. The results remarkably update previous data of Yamaguchi et al. [J.Chem.Phys. 86, 5072 (19987)]. A simple analytical formula for the PES is derived using the diatomics-in-molecule first order

perturbation theory (DIM PT1). The topology of this function is shown to match the ab initio data reproducing the number and symmetry of stationary points. It is concluded that DIM PT1 approach can be used to represent global nine dimensional ab initio PES of the H5+ cluster ion in an analytical form.

PHOTOELECTRON SPECTROSCOPY OF THE WEAKLY-BOUND ANIONS

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The theory for ab initio simulation of the photoelectron spectra of the diatomic anions is developed and applied to the weakly bound ArO-, ArCl-, and KrCl- anions. Its essential ingridients are (i) state-of-the-art ab initio calculations of the non-relativistic potential energy curves; (ii) atoms-in-molecule (AIM) approach for constructing adiabatic spin-orbit (SO) coupled potentials and electronic wave functions; (iii) Rau-Fano model for atomic photodetachment probabilities which are converted to the molecular electronic photodetachment transition dipole moments using AIM approach. This theory allows one to calculate both transition frequencies and relative intensities almost from the first principles.The examples considered prove the high accuracy of the theory and demonstrate unexpectedly high selectivity of the photodetachment process with respect to the symmetry of the fine-structure] states of the anion and neutral species.

INVESTIGATION OF STRUCTURE OF Fe3+ MAGNETIC CENTER IN POLY-PARA-PHENYLENE

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Polymeric films doped with metals of variable valency, the ferriciron ion in particular, possess interesting optical and magnetic properties making their range of production and application wider. The EPR spectrum of poly-para-phenylene (PPP) doped with Fe3+ ions is studied in the paper. The measurements were made in the temperature range 4.2 to 300 K at the microwave frequency n = 9.246 GHz. It has been found that the EPR spectrum is described by two resonance lines with g-factors g1 = 4.21 ± 0.05 and g2 = 2.00 ± 0.09. Those lines corresponded to two magnetic centers of the Fe3+ ion in poly-para-phenylene. To estimate the structure of nonequivalent positions of the Fe3+ ion, a calculateion was done of

the energy of magnetic center. The calculation was based on the SCF MO all-valent method within the UHF approximation using the ZINDO/1 method. It was show that the \"pyramidal\" and \"sandwich\"-like structures may be formed. When the magnetic center is of \"pyramidal\" structure, the Fe3+ ion forms p-complex with one phenylene ring of the polymer. In the second case of \"sandwith\"-type structure the Fe3+ ion is surrounded by two phenylene rings of different molecules of the polymer. An unusual temperature dependence of the EPR spectrum is characterized by magnetic-ion oscillation in the potential well having two minima.

SEMIEMPIRICAL MODELING FREE ENERGY SURFACES FOR PROTON TRANSFER IN POLAR APROTIC SOLVENTS

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A method of calculation of a free-energy surface (FES) of the proton transfer (PT) reaction in a polar aprotic solvent is developed. It is based on the two-state VB description of the solute combined with recent continuum medium models. Its essential new feature is an explicit quantum-chemical treatment of VB wave functions including internal electronic structure of a chemical subsystem. The FES includes a pair of intrasolute coordinates, R the distance between hydrogen-bonded atoms and s, the proton coordinate, together with the collective medium polarization mode. Two hydrogen-bonded systems immersed in a polar solvent (freon) were considered. The first one is the H5O2+ ion, a model system which was used as a benchmark testifying validity of our semiempirical calculations. The second system is the neutral (CN)(CH3)N-H...N(CH3)3 complex in freon. PT for this system has been studied experimentally. The dependencies of basic parameters controlling FES properties (the overlap integral, the coupling matrix element and the reorganization energy Er) on intrasolute coordinates R and s are evaluated and discussed. In particular, for the neutral complex Er depends on s linearly, its dependence on R is weak. The FES for the neutral system has two potential wells separated by the energy barrier of ~ 7 kcal/mol. Quantum-mechanical averaging over the proton coordinate, s, reduces the barrier from 7.0 to 1.2 kcal/mol. The value of the non-adiabatic parameter on the averaged FES is equal to 0.13. This implies that the PT in the second system corresponds to an intermediate dynamic regime and that proton tunneling effects are hardly significant for this reaction.

ABOUT QUANTUM-CHEMICAL DESCRIPTION OF ADSORPTION OF MOLECULES ON THE SURFACE OF METAL IN SOLUTIONS OF ELECTROLYTES

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Processes of adsorption on a metal surface occupy an important place in studies of the

mechanism of protective action of rust inhibitors of metals. In this paper quantum chemical model of adsorption an organic molecules on a surface of metal in solutions of electrolyte put forward. The basis for this approach is the method of the electrostatic images modified on a case of presence of a double electrical layer (for which the model of a parallel-plate capacitor is used). It realized within the framework of PPP method. In addition, it was assumed, that minimum distance between atoms of adsorbate and surface of a conductor is determined by the sum of their Van der Waals radiuses, and the spatial arrangement is function of degree of fullness and potential of a metal surface. For simplicity sake the electric field strength was taken to be equal the ratio of exterior affixed potential to effective radius of ions of background electrolyte. On an example of a series of model calculations is displayed that to utilize the characteristics of an isolated molecule for calculation of adsorptive parameters is incorrect and consequently application of dipole or quadruple approaches of an electrostatics are usable only as zero approach. Is shown, that at potentials on metal even insignificantly distinguished from potential of a zero charge the contributions to an adsorption energy on mechanisms of reflection and interaction with an electric field it appear of one order and consequently to neglect any of these contributions it is incorrect. As approbation of the offered approach the adsorption of a series of aromatic compounds on a surface of tin is treated. To correct for - contribution on adsorption energy were restricted to the term proportional to an electric field strength (in the equation of regression the vector differences between complete (calculated AM1 method) and -electronic electrical dipole moments are included). The results of calculation are in agreement with the available experimental data. Since at considerable potentials on metal the one-electron transfer is possible, the magnitude of an interaction energy of metal - ion-radical is calculated and the value of potential is determined, when this interaction is equal to zero, i.e. there is a desorption of molecules. The obtained results are qualitatively conformed to potentials of desorption from C, E-curves. Key words:

CALCULATION OF THE THERMOCHEMICAL PROPERTIES OF CONJUGATED HYDROCARBON RADICALS

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The enthalpies of formation of 30 conjugated hydrocarbon radicals with different chemical structure in the framework of a unrestricted Hartree-Fock method on the basis of a uniform set of p-Hamiltonian parameters for systems with closed and opened electronic shell are calculated. It is shown, that this approach only with two additive constants on an s-skeleton allows describing simultaneously both neutral molecules, and radicals with experimental accuracy. Usefulness of the very simple superposition-additive approach for account of physical-chemical properties of complex polycyclic molecules or radicals, based on a postulate on additively of the contributions of atoms to chemical bonds at superposition of molecular graphs are discussed. In terms of an p-electronic perturbation theory the model of aromatic annelation are developed that enable to calculate thermochemical and others properties of radicals based on calculated, or experimental data for less extended analogs. On the basis of perturbation theory the effects of substituents on the physical-chemcial properties of radicals has been treated. It is shown that experimental heats of formation, proton coupling

constants of some substituted alternant systems and activation energy of methylencyclopropane rearrangement are described in the second order of the theory. One more approach for description of heats of formation of radicals with exocyclic methene group, developed in this work, is grounded on assumption to treat these radicals as substituted of neutral molecules. On the basis of this approach the linear dependence of RCH2-H bond dissociation energy on mutual polarizability of the conjugated molecule RH is obtained. The results of direct calculations and on the basis of a perturbation theory are well agree with each other and with available experiment.

POLIMER STRUCTURES OF (6,0) NANOTUBES: GEOMETRY AND ELECTRONIC PROPERTIES

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Single-walled carbon nanotubes (NT) have stimulated great interest in chemistry and physics with a special relevance to potential applications in electronics and material science [1].

In present research new polymerized structures of «zig-zag» type (6,0) NT's have been considered. The geometry structures of base polymer fragments have been calculated by MNDO/PM3 approach. The electronic spectra have been computed by crystal orbital method with EHT approach.

First the planar polymer has been analyzed. Each (6, 0) carbon tube in this structure is bonded with two neighbors by (2+2) cycles. This polymer demonstrates metallic behavior.

Second structure is a zeolite type [1]: each NT in this structure is bonded with six neighbor tubes by (2+2) cycles. Bonds between tubes is equal 1.61 A, in (2+2) cycles bondlength between tube atoms is equal 1.52 A, distance between neighbor NT is equal 6.98 A. Thus in each tube a half of atoms is in sp^3-hybrid state. Electronic spectrum of this (6,0) NT crystal has band gap 1.5 eV. Such polymerization lead to conductance character changing from semimetalic (for molecular crystal of (6,0) carbon NT's) to semiconducting. It should be noted that obtained structure also has to have high hardness like 3D polimerised C_{60} fullerite.

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МОДЕЛИРОВАНИЕ СТРУКТУРЫ И ЭЛЕКТРОННОГО СТРОЕНИЯ КВАЗИ-ДВУМЕРНОГО ПОЛИМЕРНОГО СЛОЯ НА ОСНОВЕ ФУЛЛЕРЕНОВ $[C_{36}]_n$ МЕТОДАМИ КВАНТОВОЙ ХИМИИ

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Проведено компьютерное моделирование структуры и электронного строения квази-двумерного углеродного слоя (**1**) с тригональной решеткой, состоящего из фуллеренов C_{36} (**2**) топологической симметрии D_{6h}. В этом полимерном слое **1** каждый полиэдрический кластер **2** окружен шестью аналогичными фуллеренами и связан с каждым из них двумя ковалентными связями. Координаты атомов повторяющегося звена слоя **1** оценивались на основании результатов оптимизации методом MNDO/PM3 полной энергии углеводородной молекулы (D_{6h})-$C_{132}H_{48}$, углеродный остов которой совпадает с достаточно большим фрагментом полимерного слоя **1**.

Методом кристаллических орбиталей в валентном приближении PMX проведен расчет электронного спектра квази-двумерной системы **1**. Установлено, что ширина запрещенной зоны в ее электронном спектре составляет ~1.5 эВ. Рассчитана также структура и электронное строение некоторых олигомеров кластера D_{6h}-C_{36}, линейной макромолекулы $[—C_{36}—]_n$, а также квази-графитового слоя, состоящего из супербензольных кластеров углерода $(C_{36})_6$.

Методом HF/3-21G исследованы эндоэдральные комплексы $M@C_{36}$ (V= Cr, Ti, Ni, Fe). Для всех рассмотренных систем найдены геометрические параметры и распределение эффективных зарядов.

В приближении координаты реакции проведено моделирование взаимодействия двух фуллеренов C_{36}.

Работа поддержана Российским Фондом Фундаментальных Исследований, а также Российской научно-технической программой «Актуальные направления в физике конденсированных сред», подпрограмма «Фуллерены и атомные кластеры».

НОВЫЙ МЕХАНИЗМ АКТИВАЦИИ АЛКАНОВ (НА ПРИМЕРЕ МОЛЕКУЛЫ ПРОПАНА) СУПЕРЭЛЕКТРОФИЛАМИ НОВОГО ПОКОЛЕНИЯ

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Проведено теоретическое исследование взаимодействия пропана с суперэлектрофилами нового поколения. С этой целью методом MNDO/PM3 рассчитаны фрагменты поверхностей потенциальной энергии (ППЭ) систем: $C_3H_8 + AlBr_5$ (I), $C_3H_8 + CBr_3^+$ (II), $C_3H_8 + CBr_3^+ {}^*Br_2AlBr_2^-$ (III).

Ключевой стадией классического механизма активации алканов электрофилами E^+ (механизма Ола) является атака электрофилом σ-связей С—Н или С—С с образованием

циклических трехцентровых двухэлектронных (3c-2e) интермедиатов или переходных состояний (ПС). Ключевой стадией другого механизма активации алканов является атака электрофилом атома С с синхронным образованием 3c-2e связи этого атома с квазимолекулой H_2. Нами ранее (на примере такого мощного электрофила, как "голый" катион Br^+) найден новый механизм активации алканов, сводящийся к атаке суперэлектрофила по атому Н алкана с образованием интермедиатов R—H—E^+. При удалении атома Br от углерода он увлекает за собой атом Н: $Br^+ + CH_4 \rightarrow CH_3^+ + HBr$.

Таким образом, реакция отрыва гидрид иона от метана проходит без образования циклических интермедиатов или ПС типа Ола.

Проведено исследование области применимости нового механизма активации алканов. Установлено:

1. Реакции пропана C_3H_8 как с катионом CBr_3^+, так и с нейтральным в целом комплексом $CBr_3^+ * Br_2AlBr_2^-$ (системы II, III), идут по найденному нами новому механизму без образования циклических интермедиатов или ПС типа Ола.

2. Изучение системы I привело к обнаружению только таких реакций пропана C_3H_8, которые идут через переходные состояния Ола.

Высказано предположение, что возможность осуществления активации алканов электрофилами по найденному нами новому механизму зависит от соотношения прочности разрывамой в алкане связи и мощности атакующего электрофила.

Работа выполнена при финансовой поддержке РФФИ.

AN EFFICIENT ALGORITHM AND ITS IMPLEMENTATION FOR LARGE-SCALE VIBRONIC COUPLING CALCULATIONS

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Various non-adiabatic effects are known to be of a great importance for problems of molecular spectroscopy. A wide class of phenomena can be successfully described within the formalism of a linear vibronic coupling model (H.Кцppel, W.Domcke, and L.S. Cederbaum, Adv. Chem. Phys. Vol. 57, 1984, p. 59). In the present work we propose an efficient algorithm and report on its implementation for calculations using the linear vibronic coupling model (LVCM) formalism. The new algorithm and associated with it MULVIB program should considerably facilitate the studies of vibronic structure in the electronic and photoelectronic spectra of larger poliatomic molecules. Our approach is quite general and can almost without limitations be applied to problems with several interacting states (multistate vibronic coupling) and with arbitrary number of totally-symmetric (tuning) and non-totally-symmetric (coupling) vibrational modes. According to the LVCM-formalism, the spectrum is calculated using Lanczos diagonalization procedure applied to the model Hamiltonian expressed in the harmonic oscillator basis. Since the dimension of such basis is often prohibitively large, we make use of a \"direct\" diagonalization requiring no disk storage for matrix elements of the Hamiltonian. The result of the matrix-vector multiplication step is evaluated on the fly. The molecular symmetry at the extent of the largest Abbelian subgroup can be used to further reduce the computational efforts at this stage. For a large two-state problem, where the vector size does not allow to complete the matrix-vector multiplication step within the available amount of main memory, an algorithm with the disk vector storage

can be invoked. The latter algorithm can also be used for vibronic coupling calculations on the computer systems with small main memory. The capabilities of the new approach are demonstrated on the example of furan and thiophene molecules, where it has been used to study the vibronic structure of the lowest photoabsorption band. The vibronic coupling problem here involves (at least) four interacting electronic states coupled via several in-plain and out-of-plain non-totally symmetric and all totally-symmetric vibrational modes, excluding hydrogen motions. The Hamiltonian matrices of the dimension up to 40 millions have been treated in course of the calculations of the spectra. The calculated spectra compare favorably with the results of measurements.

ELECTRONIC TRANSMISSION COEFFICIENT IN THE REACTIONS OF HETEROGENEOUS CHARGE TRANSFER: QUANTUM CHEMICAL CALCULATIONS

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Electronic transmission coefficient (ETC) is known to be a key quantity in modern quantum mechanical theory of charge transfer in polar media [1]. In the case of homogeneous processes ETC can be computed with high accuracy [2], whereas for Redox-reactions proceeding on a metal electrode the reliable calculations of ETC are lacking so far. In this work we have discussed earlier attempts to estimate this parameter for electrochemical reactions, as well as performed some quantum calculations of ECT in the framework of an approach developed recently [3-5]. The electronic coupling in such an approach is treated in terms of the electronic density of a metal; the latter was computed for a mercury electrode in several ways. First, the jellium model was employed [3]. The electronic density in the «spill-over» region was also described using the cluster model. Several calculations were done for a five-layer slab on the basis of the «muffin-tin» approximation and linearized planar waves as a basis set. Main attention in this work was put on some important qualitative effects. ETC as a function of the electrode-reactant distance were calculated for different orientations of [Co(oxalate)]3- and S2O82- relative to the metal surface. The dependence of electronic transmission coefficient on the electrode charge density was studied as well. Quantum chemical calculations of the acceptor wave functions of reactants were performed at SCF and DFT (B3LYP) level. References [1] A.M. Kuznetsov, J. Ulstrup. Electron Transfer in Chemistry and Biology, Wiley, Chichester, 1999. [2] M.D. Newton //Chem. Rev. 1991. v.91. p.767. [3] A.A. Kornyshev, A.M. Kuznetsov, J. Ulstrup //J. Phys. Chem. 1994. v.98. p.3832. [4] A.A. A.A. Kornyshev, A.M. Kuznetsov, J. U. Nielsen, J. Ulstrup //Phys.Chem. Chem. Phys. 2000. v.2. p.141. [5] R.R. Nazmutdinov, G.A. Tsirlina, O.A. Petrii, Yu.I. Kharkatz, A.M. Kuznetsov, Electrochim. Acta. 2000. v.45. p.3521. This work was supported by the RFBR, projects No. 99-03-32367, 00-03-32140, 01-03-02006, INTAS 99-1093 and Russian Ministry of Education.

ПАРАЛЛЕЛЬНАЯ РЕАЛИЗАЦИЯ РАСЧЕТА ЭНЕРГЕТИЧЕСКОГО ВКЛАДА ТРЕХКРАТНЫХ ВОЗБУЖДЕНИЙ В ЧЕТВЕРТОМ ПОРЯДКЕ ТЕОРИИ ВОЗМУЩЕНИЙ В ВАРИАНТЕ МЁЛЛЕРА-ПЛЕССЕ (MP4) ДЛЯ СИСТЕМ С ЗАКРЫТЫМИ ОБОЛОЧКАМИ.

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В современной неэмпирической квантовой химии широко используются методы, основанные на использовании техники многочастичной теории возмущений. Для систем с закрытыми оболочками, хорошо описывающихся в нулевом приближении одним детерминантом Слетера, чаще всего используются поправки к энергии в низших (2-4) порядках теории возмущений в варианте Мёллера-Плессе (**MP2-MP4**). Помимо чисто теоретико-возмущенческих подходов, методы теории возмущений используются также и для приближенного учета поправок на возбуждения высшей частичности (как правило, речь идет об описывающихся связными диаграммами трехкратных и, реже, четырехкратных возбуждениях) в таких, например, подходах, как **CCSD**, **QCISD**, и **BD**. Это приводит к методам типа **CCSD(T)**, **QCISD(T)**, **BD(T)**, и **BD(TQ)**, являющимися своего рода эталонами качества в современных квантовохимических исследованиях высокого уровня.

В рамках четвертого порядка теории возмущений традиционно выделяют четыре основных типа вкладов в энергию электронной корреляции – вклады, обусловленные однократными (**S**), двукратными (**D**), трехкратными (**T**), и четырехкратными (**Q**) возбуждениями. Вычислительные затраты, необходимые для расчета поправок на одночастичные возбуждения **E(MP4-S)**, в общем случае растут как **пятая** степень $\mathbf{N}^5$ размера молекулы **N**, а затраты на расчет энергетических вкладов от двукратных и четырехкратных возбуждений **E(MP4-DQ)** пропорциональны **шестой** степени размера молекулы $\mathbf{N}^6$. В то же время, вычислительные затраты, связанные с расчетом вкладов трехкратных возбуждений **E(MP4-T)**, пропорциональны ***седьмой*** степени размера молекулы $\mathbf{N}^7$. Таким образом, расчет **E(MP4-T)** требует гигантских вычислительных затрат и является лимитирующей стадией в расчете полной энергии электронной корреляции в четвертом порядке теории возмущений **E(MP4-SDTQ)** уже для сравнительно небольших молекул. При этом **E(MP4-T)** является, как правило, доминирующей составляющей полной энергии **E(MP4-SDTQ)**.

Очевидно, что для проведения расчетов молекул среднего и большого размера на уровне **MP4**, **CCSD(T)**, **QCISD(T)**, и **BD(T)** необходима эффективная параллелизация стадии расчета **E(MP4-T)**.

В спин-орбитальном формализме E(MP4-T) дается следующим выражением:

$$\mathbf{E(MP4-T)} = -\frac{1}{36}\sum_{i,j,k}^{n}\sum_{a,b,c}^{V}\frac{\left|w_{ijk}^{abc}\right|^2}{\Delta_{ijk}^{abc}} \qquad \mathbf{(1).}$$

Однако непосредственное использование полученного в рамках спин-орбитального формализма выражения для w_{ijk}^{abc} в случае систем с закрытыми оболочками крайне неэффективно в силу двух причин.

Во-первых, требуется явный учет специфики систем с закрытыми оболочками (одинаковые пространственные компоненты у спинорбиталей, отличающихся значением спина). Таким образом, необходимо перейти от спинорбитальной нотации к орбитальной путем интегрирования по спиновым переменным. **Во-вторых**, эффективный формализм должен быть сформулирован на языке простых матричных операций (матричное умножение).

Нами было показано, что бесспиновые амплитуды $\overline{w}_{ijk}^{abc}$ могут быть представлены в виде простых линейных комбинаций некоторых вспомогательных величин, которые, в свою очередь, могут быть получены как результат некоторой последовательности матрично-матричных умножений, сложений и транспозиций матриц. При этом:

1. **Число элементарных операций** (сложений и умножений), необходимых для расчета $\overline{w}_{ijk}^{abc}$, равно $2 \cdot n \cdot (n^2 - 1) \cdot V^3 \cdot (n + V)$ и **является лучшим из описанных в литературе**;
2. $\overline{w}_{ijk}^{abc}$ рассчитываются “порциями” – для **фиксированной** тройки индексов *i, j, k* одновременно находятся амплитуды $\overline{w}_{ijk}^{abc}$ для **всех** значений *a, b, c*. При этом **все операции над матрицами, необходимые для вычисления очередной “порции” амплитуд,** являются независимыми **и могут производиться параллельно на SMP системах с *разделяемой* памятью. (**Очевидно, что суммирование отдельных вкладов в формуле (1) также может производиться параллельно).
3. **Все** операции, необходимые для расчета амплитуд $\overline{w}_{ijk}^{abc}$ для **разных троек** индексов *i, j, k*, являются независимыми и **могут производиться параллельно на системах с *распределенной* памятью.**

Параллельная реализация алгоритма, основанного на описанном подходе, практически очевидна из описания его основных свойств.

Различные тройки индексов *i, j, k* распределяются между отдельными узлами вычислительного кластера таким образом, чтобы обеспечить максимальную загруженность каждого узла. В нашей реализации алгоритма в рамках программы PC GAMESS используется статическая балансировка нагрузки и MPI в качестве интерфейса для обмена данными между узлами кластера.

Каждый узел кластера распределяет работу, необходимую для вычисления амплитуд $\overline{w}_{ijk}^{abc}$ для обрабатываемой в данное время тройки индексов *i, j, k*, между всеми доступными ему процессорами. Используется многопотоковый параллелизм (multithreading) в сочетании с динамическим распределением нагрузки и полностью асинхронным вводом-выводом.

THE INFLUENCE OF LIGAND NATURE ON STRUCTURAL AND ENERGETIC CHARACTERISRICS OF SiX4*nL ADDUCTS.

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Ab initio calculations of adducts of Al, Ga, In halides with ammonia [1] and Ga halides with pyridine [2] allowed us to analyse the influence of central and terminal atoms on stability and energetics of the donor-acceptor (DA) complexes. Good agreement between theoretical and experimental gas phase dissociation enthalpies evidences the reliability of theoretical approach for studying such systems. Results obtained allow us to proceed with theoretical study of more complex DA substances, for which experimental investigation of the dissociation process in gas phase is not possible at present time. The adducts of silicon halides with nitrogen-containing donors (NH3, py) were studied. All calculations have been carried out using the GAUSSIAN 94 program package. The geometries of all complexes were optimized by RHF/DZP and B3LYP/DZP methods. Optimized geometries correspond to minima on the potential energy surface. Two isomers of SiX4□L adducts have been considered: axial (C3v) and equatorial (Cs). The fact of transition Cs in C3v during optimization has been established for SiX4□NH3. For all ligands axial isomer is more stable. For SiX4□2L complexes the trans- and cis-isomers have been considered. The Si-N distance of cis- and trans-isomer of SiX4□2L is decreased compared to SiX4□L, which indicates that donor-acceptor bond Si-N in adducts with coordination number 6 is stronger than in adducts with coordination number 5. The gas phase dissociation enthalpies of adducts decrease in order F-Cl-Br for all complexes. For SiX4□2L adducts the Si-N distance is approximately constant in order F-Cl-Br and there is no correlation between dissociation enthalpy and distance of donor-acceptor bond. We obtain the following sequence of the thermodynamic stability of adducts with respect to dissociation process: SiF4SiCl4 SiBr4 SiH4. 1. Timoshkin A.Y., Suvorov A.V., Bettinger H.F., Schaefer III H.F. // J. Amer. Chem Soc. 1999. Vol.121. N 24. P. 5687-5699. 2. Timoshkin A.Y., Suvorov A.V., Bettinger H.F., Schaefer III H.F.// Russ. J. Gener. Chem. 1999. Vol. 69. № 8. P.1250-1257.

RELATIONSHIP BETWEEN THE ENERGY OF DONOR-ACCEPTOR BOND AND THE REORGANISATION ENERGY IN MOLECULAR COMPLEXES

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The halides of the III-IV group elements form molecular complexes (adducts) with different electron-donor molecules. One of the important characteristics of these adducts is the energy of donor-acceptor (DA) bond, which can be derived from the enthalpy of the complex dissociation in the gas phase. For the halides of the IV group elements the major process during vaporization is the dissociation process of the solid complex on free components. Therefore experimental investigation of dissociation process in gas phase is impossible. The information about stability of DA bond in these compounds can be obtained only from

quantum-chemical calculation.
The adducts of silicon halides with nitrogen-containing donors (NH_3, py, 2,2'-bipy) have been chosen for the present study.
All calculations have been carried out using the GAUSSIAN 94 program package. The geometries of all complexes were fully optimized by RHF/DZP and B3LYP/DZP methods with subsequent vibrational analysis. All structures correspond to minima on the potential energy surface.
The gas phase dissociation energy of complex can be represented as difference between the DA bond energy and the reorganization energies of donor and acceptor [1]:
$E^{diss} = nE^{bond} - [E^{reorg}(A) + nE^{reorg}(D)] - D\,E^{bsse}$ (1),
where n - number of bonds; E^{diss} - the dissociation energy of complex in gas phase; E^{bond} - the bond energy; $E^{reorg}(A)$ - the reorganization energy of acceptor; $E^{reorg}(D)$ - reorganization energy of donor; $D\,E^{BSSE}$ - basis set superposition error. $D\,E^{BSSE}$ has been calculated using counterpoise method. All values are given in kJ/mol.
According to equation (1) bond energy and dissociation energy are equal only in case of negligible distortion of free component during complex formation. However, as can be seen from two representative examples in the table, the reorganization energy for halides of IV group elements is very large in contrast to group III halides. We conclude that it is the reorganization energy that determines the value of the dissociation energy of DA complexes of group IV elements.

Adduct	E^{diss}	$E^{reorg}(A)$	$E^{reorg}(nD)$	$D\,E^{BSSE}$	E^{bond}
$AlCl_3$ NH_3	149,0	28,2	0,2	-14,6	170± 7
trans-$SiCl_4$ $2NH_3$	71,5	280,2	15,0	-32,9	175± 8

1. *A.Y. Timoshkin, A.V. Suvorov, H.F. Schaefer III //* Russ. J. Inorg. Chem. 2000. Vol.45. №3. P.509-512.

MOLECULAR MECHANICS – EFFECTIVE CRYSTAL FIELD CALCULATIONS OF LOW- AND HIGH-SPIN Fe(II) COMPLEXES WITH PYRIDINE-CONTAINING LIGANDS

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A new method of potential energy surfaces (PES) modeling for transition metal complexes is applied to four Fe(II) complexes with pyridine-containing ligands, where metal center takes both low- and high-spin states. The method presents a combined molecular mechanics (MM) – quantum mechanics (QM) approach. Here the QM part is based on the effective crystal field (ECF) approach [1], which is able to describe electronic spectra and estimate the spin of ground state of transition metal ion, and used for the d-shell energy evaluating. As a MM part, the Charmm-force field based molecular mechanics method, utilizing Gillespie-Kepert model of «bonds repulsion» for metal ion coordination sphere description (MM-GK) [2] is used for ligand backbone and coordination sphere energy calculation. Accordingly [3], the total energy of a complex is a sum of d-shell energy of metal ion, calculated within ECF

paradigm, and the energy of the rest of a molecule, calculated with MM-GK method. Molecular mechanics parameters found, which allow to describe with good accuracy the experimental geometry of the complexes mentioned above, as well as predict the ground spin state of metal ion. Note, that the same MM-GK parameters are applicable for different metal ion spin states (while Fe-N distance varies from 1.88 to 2.26 E). 1. A. V. Soudackov, A. L. Tchougreeff, I. A. Misurkin Theor. Chim. Acta. 1992. V. 83. P.389. 2. M. G. Razumov, V. L. Melnikov and I. V. Pletnev J. Comput. Chem. 2001. V. 22(1). P.38. 3. M. B. Darkhovskii, A. L. Tchougreeff. Khim. Fiz. 1999. V 18(1). P. 73 [in Russian].; A. L. Thougreeff in Molecular Modeling and Dynamics of Bioinorganic Systems. NATO ARW Proceedings. L. Banci, P. Comba (eds.) Kluwer, Dordrecht (1997).

RELATIVISTIC TREATMENT OF HIGHLY-CHARGED HEAVY IONS COLLISIONS BY FINITE SET OF HERMITIAN B-SPLINES BASIS

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We introduce a numerical method for relativistic calculation time-dependent process in atom and molecular systems. The method utilizies the finite basis set of Hermitian B-splines basis for calculation of localizated states.

MULTY-REFERENCE CONFIGURATION INTERACTION STUDY OF THE VALENCE AND TRIPLET ION-PAIR STATES OF THE FLUORINE MOLECULE

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Potential curves for some fluorine valence singlet and triplet ion-pair states are calculated by means of the multi-reference configuration interaction (MRD-CI) method with the Davidson extrapolation to the full CI energies. Two molecular orbitals derived from the 1S atomic orbitals are frozen after the SCF procedure, i.e. they are not correlated. Among the excited singlet and triplet species of the fluorine molecule, which dissociate into the ground state atoms, only the ^3P_u state is found to be very weakly bound (De ~ 0.05 eV), while the remaining valence states are strictly repulsive. The calculated spectroscopic constants for the ground state are in a good agreement with the corresponding measured values. Spectroscopic constants of the lower tier ion-pair states have been also calculated. Vertical excitation energies and some moment functions of the dipole transitions between valence, as well as valence and triplet ion-pair states have been determined. In particular, a detailed analysis of the 1P_u <- 1S_g+ absorption is carried out. The treatment of the triplet ion-pair states is especially emphasized because they are found to be essential for understanding the VUV lasing in F_2. The ion-pair 3P_u state is found to be responsible for the 157 nm laser emission observed by J.R. Woodwarth and J.K. Rice [J. Chem. Phys. 69(6), 15 Sept. 1978]. Emission spectrum f3P_g -> a3P_u transition is calculated and compared with the

experimental data. Some special spectroscopic properties such as the homogeneous and heterogeneous mixing of the ion-pair states in F_2 are discussed.

КВАНТОВО-МЕХАНИЧЕСКАЯ МОДЕЛЬ ДВИЖЕНИЯ ИОНА В ГРАМИЦИДИНОВОМ КАНАЛЕ МЕМБРАНЫ

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Грамицидин А – пептидный антибиотик, который при встраивании в мембрану способен образовывать катионселективный канал. Основной целью представленной работы является моделирование движения ионов H^+, Na^+ и K^+ в полости HHSH (head-to-head single-stranded helix) пептидного димера (Ketchem R.R. J. Biol. NMR, 1996, 8, P.1). Атомные координаты димера взяты из Банка белковых структур (PDB, Brookhaven National Laboratories, USA). Потенциал электростатического поля в полости димера оценивался исходя из данных о распределении электронной плотности в пептидном димере, полученных методом EHMO (Extended Huckel MO) в стандартной параметризации. Показано, что основной вклад в электростатический потенциал димера вносят CO-группы аминокислотных остатков, ориентированных вдоль оси спирали. Установленная функция потенциальной энергии иона в электростатическом поле грамицидинового канала согласуется с экспериментальными данными. Составлено и получены решения стационарного уравнения Шредингера, описывающего движение иона в электростатическом поле грамицидинового канала мембраны. Проведен сравнительный анализ энергетических спектров и волновых функций ионов H^+, Na^+ и K^+. Исследование поддерживается грантом КЦФЕ (код ГРНТИ 34.17.15. - Биофизика, шифр 97-0-10, 0-167).

SIMULATION OF THE PROTON TRANSFER IN ACID PROTEINASE (RHIZOPUSPEPSIN) USING HYBRID QM/MM METHOD BASED ON EFP METHODOLOGY.

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Acid Proteinase (Rhizopuspepsin) belongs to the large group of ferments named hydrolases. Hydrolases are the main enzymes which catalyze initial phase of partitioning of proteins and complicated carbohydrates to the simple substances. When hydrolases attack substrate, intermolecular bonds are breaking. This process takes place in presence of water molecules. Hydrolases are divided on several groups peptidases being one of them. These enzymes catalyze breaking up the peptide bond in peptide molecules. It is assumed that this reaction depends strongly on pH, and by this reason we model the stage of proton transfer from the Asp residue from the Rhizopuspepsin to the water molecule. It is also assumed that the reaction depends on the presence of Ser residue, geometry of the protein and other details of the entire system. We apply the hybrid ab initio QM/MM molecular simulations using based

on the EFP methodology by using the GAMESS and TINKER packages. This method allows us to separate ab initio («active») part of substance and replace residuary part (chemically «inert») by the model potentials. In the present work, the water molecule is treated as an ab initio part, MM-sized enzyme molecule is subdivided into a series of fixed geometry fragments.

N-BODY INTERATOMIC POTENTIALS CALCULATED IN QUASI-FERMION APPROXIMATION: THEORY AND APPLICATIONS

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The basic ideas of quasi-fermion approximation and their last developments are considered in aspects of its application to calculation of N-body interatomic potentials destined for solid state physics and chemistry studies. In the simplest case the quasi-fermion approximation gives an algebraic equation which connects the total energy of many electron system with two first moments of Hamiltonian matrix. This value of energy has been proved is a lower bound of the exact one. There are the different ways to improve this estimation of energy involving the higher order moments of Hamiltonian. Taking into account a particular form of Hamiltonian and evaluating its moments we can represent the approximate total energy as a nonlinear function of molecular integrals. Thus using the Hartree-Fock LCAO theory and some additional simplifying assumptions it is possible to express total energy in the form of N-body interatomic potential including only one and two center molecular integrals. The most interesting result may be obtained in the framework of general manyelectron theory outgoing the Hartree-Fock limits. It turns out that in this case first order of quasi-fermion approximation leads to the total energy expression and the N-body interatomic potential, which is similar to those in Hartree-Fock theory but containing an additional electron-correlation term. The N-body interatomic potentials constructed in quasi-fermion approximation in their semiempirical version was used for modeling different processes and phenomena in solids (deformations, fracture, diffusion, phase transitions etc.). The ways of further development of the suggested approach are discussed with special emphasis on its application to computer simulations in the field of material science.

ПАРАЛЛЕЛЬНАЯ НЕЙРОННАЯ СЕТЬ С УДАЛЕННЫМ ДОСТУПОМ НА БАЗЕ РАСПРЕДЕЛЕННОГО КЛАСТЕРА ЭВМ

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Рассматривается параллельная реализация нейронной сети на распределенном вычислительном кластере. Описан созданный WWW–интерфейс для удаленного управления программно-аппаратным комплексом. Обсуждается возможность применения нейровычислений для решения химических задач.

Нейросети используются для решения самых разнообразных задач, для которых невозможна четкая алгоритмизация, но существует достаточный набор пар «известное

воздействие – известный отклик» из предметной области. Подавая на вход нейросети известное воздействие и изменяя веса связей (а, возможно, и геометрическую структуру сети), можно добиться соответствия между выходом и известным откликом. Проведя такую операцию на всем наборе известных пар «воздействие – отклик», получаем обученную нейросеть, способную выдавать ответы на неизвестные вопросы из предметной области. Именно обучение требует наибольшего количества времени и вычислительных мощностей.

Вся работа пользователя с нейросервером осуществляется с помощью Web-интерфейса со страницы http://neural.chg.ru/. Нейросервер развернут на распределенном вычислительном кластере Института теоретической физики им. Л.Д. Ландау. Одной из главных задач работы является распараллеливание. Наиболее ресурсоемкими операциями в нейровычислениях вообще и в используемом нами алгоритме обратного распространения ошибок, в частности, являются матричные операции. Нами реализован алгоритм Parallel error back propagation с использованием библиотеки MPI.

Для типичной тестовой задачи (5 входов, 5 выходов, 15 скрытых нейронов на одном промежуточном слое (250 синапсов), 1000 векторов для обучения) производительность обучения нейросети на одиночном процессоре (P-III/450MHz) составила 1.6 MCUPS (количество измененных элементов матрицы весов в секунду). Та же задача, выполняющаяся на 2-х процессорах двухпроцессорной машины с использованием MPI, дает производительность 3.0 MCUPS. При использовании всех процессоров кластера ИТФ производительность поднимается до 16-18 MCUPS.

Авторы благодарят Л.Н.Щура за поддержку работы и полезные обсуждения.

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QUANTUM-CHEMICAL INVESTIGATION OF THE NITROSOMETHANE MOLECULE STRUCTURE IN THE GROUND AND LOWEST EXCITED ELECTRONIC STATES

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The systematic theoretical investigation of the nitrosomethane molecule potential energy surfaces structure in the ground (S0) and the lowest excited singlet (S1) and triplet (T1) electronic states was considered on the basis of the RHF, MP2, CASSCF, CIS, CISD etc. calculations. The geometrical parameters, heights of the internal rotation barriers, harmonic frequencies and the one-dimensional torsional energy levels are compared with the experimental data. The theoretical and experimental results were compared to study the adequacy of the various ab initio methods to describe the conformational effects in the ground and lowest excited electronic states. In particular the change of the methyl tops orientation is found in our calculations in agreement with the experimental observations for the S1<--S0-transition. This work was financially supported by RFBR (Project N 00-15-97346 and 01-03-32841).

QUANTUM CHEMISTRY OF FERROELECTRIC SOLIDS: ELECTRONIC STRUCTURES AND PECULIAR PROPERTIES OF 0D $K_3H(SO_4)_2$ - TYPE MATERIALS

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The major task of quantum chemistry of ferroelectric (FE) solids is the study of FE behavior origin using the quantum chemical models and calculations. Regarding the H-bonded FE crystals two problems arise. The first one is the elucidation of molecular mechanisms of cooperative proton coupling. The second one is related to theoretical determination of coupling parameters for the Ising-type Hamiltonians used for microscopic description of the physical - thermodynamic and dielectric properties of the FE materials. These interconnected problems are studied at the example of the 0-D materials of K3H(SO4)2 (TKHS) family, that is investigated very actively nowadays due to its peculiar FE behavior. The determination of the Ising parameters Jij of the pseudospin Hamiltonian is examined from classical and quantum viewpoints. It is found that the values of Jij depend on the indirect effective proton-proton coupling mechanism. These Jij values are estimated by means of various quantum-chemical computational techniques and applied to the FE behavior description of the TKHS materials in the frameworks of mean field approximation and Bethe clusters approach. The results allow to explain the existence of low-temperature anti-FE phase transitions in D-derivatives of the TKHS family materials and the quantum paraelectric state of the correspondent H-derivatives. The problem of estimation of the proton and deuteron tunneling splitting for H-bonded systems studied is also discussed. This work is supported by the Russian Fundamental Research Foundation, project No 99-03-33234.

AN APPLICATION OF THE MC SIMULATIONS TECHNIQUE TO THE CVD-INDUCED SURFACE GROWTH DYNAMICS

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Computer simulations are rightfully regarded as one of the most powerful tools of theoretical analysis. The computational technique known as Monte-Carlo (random number) simulations provides an adequate and perfect description for the phenomena, which are random in their nature. In the present paper, we report on a theoretical analysis of the formation of tungsten surface by means of chemical vapor deposition (CVD). The aim of our work is to understand the relationship between the CVD growth parameters and film composition and morphology. In general, growth of a film is a nonequilibrium phenomenon where kinetics and thermodynamics play essential roles in determining the microstructure of growing film. Growth kinetics depend not only on surface migration of the adatoms on the substrate and on the film, but also on surface chemical reactions.

Simulations were carried out based on a lattice-gas model. The substrate is represented as a regular plane triangle lattice (with coordination number z=6) with periodic boundary conditions. We took into account the adsorption of $W(CO)_6$ followed by the decomposition

process $W(CO)_6 \rightarrow W + 6CO$ and a variety of surface reactions involving tungsten oxides, tungsten carbides, carbon and carbon monoxide (in the adsorbed form). Besides that, the migration of metal atoms over the surface, the diffusion and spontaneous desorption of the adsorbed CO molecules were also taken into consideration.

The interplay of the processes mentioned results in a rather complicated composition of the deposited material, which also shows strong temperature dependence. Low temperatures favour the formation of carbide and oxide containing materials. As the temperature increases, the production of carbides and oxides decreases significantly. Clean metal covers can be grown at relatively high temperatures. Variations in temperature also induce considerable changes in the surface morphology. At low temperatures, the surface is composed of chaotically distributed small grains. At high temperatures show relatively large flat clusters with well-outlined rounded boundaries.

The work is supported by the Russian Foundation for Basic Research (grant no. 99-03-32061).

AUGMENTED WAVES METHODS FOR ONE- AND ZERO-DIMENTIONAL SYSTEMS

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Linear augmented waves methods for nanowires, nanotubes, and qubic and spherical clusters are developed. The methods are based on muffin-tin and local density approximations. These methods are the generalizations of the well-know in the solids band structure Slaters APW method on the low-dimentional systems.

ЭЛЕКТРОННОЕ СТРОЕНИЕ, ОТНОСИТЕЛЬНАЯ СТАБИЛЬНОСТЬ И МАГНИТНО-РЕЗОНАНСНЫЕ ПАРАМЕТРЫ РАДИКАЛОВ, ОБРАЗУЮЩИХСЯ ПРИ РАДИАЦИОННОМ ОБЛУЧЕНИИ ШЕРСТИ.

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Радиационная обработка в качестве одной из стадий переработки волокон является перспективной для получения текстильных материалов с заранее заданными свойствами. Результаты исследования γ-облученных шерстяных волокон методом ЭПР показали, что при этом образуется ряд свободных радикалов, для которых были предложены возможные структуры. Более точная информация о строении таких радикалов и их роли во вторичных превращениях, может быть получена методами квантовой химии.

Полуэмпирическими методами ССП МО ЛКАО в валентных приближениях РМ3 и INDO проведенных расчеты возможных структур и энергетики образования свободных радикалов в олигомерных полипептидных фрагментах, содержащих фрагменты глицина, глутаминовой кислоты и серина. Показано, что наиболее устойчивыми

являются радикалы, образуемые отрывом атомов водорода от атомов азота пептидной связи и атомов углерода в аминокислоте полипептидного фрагмента. Для полученных оптимальных структур рассчитаны магнитно-резонансные параметры исследованных радикалов (константы СТВ и g-факторы). Результаты расчетов сравниваются с экспериментом и подтверждают заключения, сделанные на основе расчетов относительной стабильности радикальных структур.

S-*CIS*- AND S-*TRANS*-BUTADIENE COORDINATION ON ACTIVE CENTERS WHICH ARE GENERATED AT DIENES POLYMERIZATION ON CATALYSTS ON THE BASIS NDCl3.3TBF-AlR3

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Quantum-chemical calculations of the model complexes of 6 types of active centers (AC), taking part in polymerization reaction, with S-cis- and S-trans-butadien, were carried out with the help of the extended Huckel method. It was found, that the coordination of S-trans-butadiene is energetically more advantage than the coordination of S-cis butadiene to all types of AC. In a row of AC 1-6 the charge of atom Nd decreases with the reduction of quantity of Cl atoms in the nearest environment of atom Nd and the energy of a complexing with S-cis- and S-trans-butadiene falls. The constants of growth and termination of chain are bound to drop with the reduction of energy of a complexing of a butadiene with AC in this row. On the basis of this it was suspected, that the spikes on a curve of molecular-mass distribution of polybutadiene corresponds to polymerization on definite types of AC.

ELECTRON DENSITY DISTRIBUTION ANALYSIS IN NEUTRAL, MONO- AND DIANIONIC B6 OCTAHEDRONS

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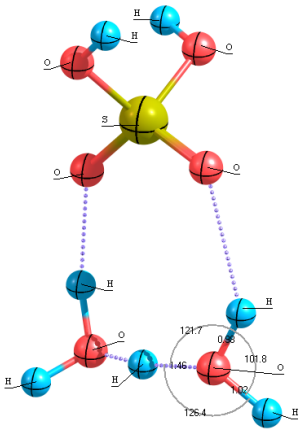
Octahedron B6 is a structure unit of rare-earth borides MB6, which have many interesting properties (see e.g. [1]). Exploring the possibility of a cluster modeling of these compounds, we studied neutral, anionic and dianionic B6 octahedrons at UMP2/6-311+G* level of theory. The most stable from these species is monoanion: doublet ground state, geometry in D4h point group. The ground state of neutral cluster is triplet and highly symmetrical (Oh) in accord to previous studies [2,3]. The ground state of dianion is singlet and has symmetry D4h. Unexpectedly increasing of spin multi-plicity does not lead to forcing electrons out of inner sphere and its localization on the octahedron apexes, but rather to a redistribution of electron density in inner sphere right up to breaking B-B bonds. For example, B6 with 6 unpaired electrons misses four B-B bonds. This information was obtained in the frame of the topological analysis of elec-tron density distribution [4]. An attempt to emulate the B-B bonds with other octahedrons in the lattice by hy-drogen atoms saturation leads to displacing of the H atoms to the space regions with concentrated negative charge, if only no geometrical

constraint is applied. These regions are reflected by critical points (3,-3) of electron density laplacian and was found above the centers of the octahedron faces [5]. Thus, cluster modeling of bulk phase MB6 compounds is impossible due to the strong electron acceptor character of structure units B6. References: 1. Phys.Rev., B49, 1564 (1994). 2. Phys.Rev., B55, 16426 (1997). 3. J.Chem.Phys., 107, 132 (1997). 4. R.F.W.Bader. Atoms in Molecules: A Quantum Theory. – Oxford: Calendon Press, 1990. 5. J.Chem.Phys., 80, 1943 (1984).



CHEMCRAFT – A POWERFUL TOOL FOR MOLECULAR BUILDING, TREATMENT AND PRESENTATION OF CHEMICAL DATA

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ChemCraft is a graphical tool for treatment of the chemical data with special emphasis on molecular building and working out computational results. ***ChemCraft*** is an affordable, convenient graphical user interface for *Gaussian* and *Gamess* program packages with efficient molecular building capacities and advanced visualisation facilities. It allows:

- to view *Gaussian* or *Gamess* computational results (optimised geometry, geometry for each optimisation step, etc.) and to animate vibrational frequencies);
- to build molecules using simple mouse operations by atom, ring or other fragments and to prepare input files for calculations easily;
- to examine any structural parameter (interatomic distances, angles, dihedrals) by clicking on object (atom, fragment, etc.);
- to examine displayed molecules even of very large size in three dimensions: rotation, translation and zooming are all accomplished via simple mouse or keyboard operations;
- to display molecules in different visualisation modes with very customisable schemes;
- to modify easily the displayed molecule by adding/removing fragments or atoms with controlling any parameters for desired placement;
- to prepare high-quality true-colour images in different graphical styles and export them as bitmaps or metafiles;
- to produce graphical outputs containing any of the images with necessary clarifications (bond lengths, bond angles, interatomic distances, any text, lines, charges of atoms, etc.);

Additional features will be implemented in future: database of output files systematising them by different categories and allowing quick search of any information, integration with other program packages, improved molecular building capacities, performance and graphic possibilities.

ChemCraft allows to work more efficiently with results of calculations, to prepare new jobs and to present the results of your analysis. ***ChemCraft*** is also good tool implementing majority molecular visualisation, analysis and presentation needs.

ПЕРСПЕКТИВЫ ИСПОЛЬЗОВАНИЯ ЕДИНОЙ СРЕДЫ РАСПРЕДЕЛЕННЫХ РЕСУРСОВ (GRID) ДЛЯ ИНФОРМАЦИОННОГО ОБЕСПЕЧЕНИЯ ХИМИЧЕСКИХ ИССЛЕДОВАНИЙ

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Единая среда распределенных ресурсов

Работа по объединению всех ресурсов Интернета в единый интегрированный комплекс проводится в рамках создания единой среды распределенных ресурсов (ECP, GRID), которая составит информационно-вычислительную инфраструктуру будущего [1,2].

Мы рассматриваем GRID как исходно распределенную систему, которая сводит воедино данные, вычислительные мощности и ресурсы для визуализации. Основу, суть ECP составляют протоколы, сервисы, API (Application Programming Interfaces) и SDK (Software Development Kits).

Для пользователя обращение к ECP будет в некотором роде аналогично использованию электроэнергии посредством обычной розетки - единый интерфейс будет предоставлять доступ ко всем необходимым ресурсам так, словно мы имеем дело с одним огромным метакомпьютером. Все задачи, как традиционные для обычных компьютеров (управление процессами, памятью, файловой системой, вводом/выводом и пр.), так и принципиально новые (учет, контроль, способ доступа и распределение ресурсов, обеспечение безопасности, совместная работа над набором данных в реальном масштабе времени и пр.) будет решать специализированный комплекс программного обеспечения (например, разрабатываемый в проекте Globus [3,4]) на базе соответствующей аппаратной инфраструктуры.

Цели создания ECP

Главная долговременная цель развития ECP - информационное обеспечение принятия решений группами экспертов, занимающихся определенными проблемами, в составе отдельных кластеров понятийных сетей [1].

Термин "понятийная сеть" (knowledge network) можно определить, как совокупность информации, экспертов и знания по определенной дисциплине, которые могут быть использованы с применением компьютерных технологий для анализа различных проблем. Т.е. это люди, знания и инфраструктура. В случае научных сетей в число экспертов должны входить как профильные специалисты, так и компьютерщики, призванные организовать и обеспечить обработку информации. Инфраструктура включает ECP, информационно-ориентированный программный комплекс, модели и соответствующие приложения. Знание представлено в том числе гипотезами (прогнозами) о возможных эффектах (например, о влиянии техногенных аэрозолей на изменение глобального климата) и интерпретацией существующих данных (например, социологических опросов).

Программное обеспечение

Перечислим некоторые принципиальные задачи, которые необходимо решить при создании ECP:

- поддержка интероперабельности между объектами и ресурсами в ECP;

- диспетчеризация, включая идентификацию доступных ресурсов, статистика использования и загрузки ресурсов и пр.;
- система безопасности и контроля доступа, в т.ч. привилегии пользователей;
- обращение к наборам данных в удаленных архивах (включая протоколы, которые необходимо использовать для работы с гетерогенными источниками данных).

Базовое программное обеспечение, необходимое для создания инфраструктуры для обработки больших объемов информации включает в себя:

- создание в рамках ECP согласованной объектной среды, позволяющей поддерживать выполнение необходимых приложений и сервисов в реальном масштабе времени;
- создание СПИ, обеспечивающих поиск данных по атрибутам, выделение метаданных (metadata mining), семантическую интероперабельност'fc, общие онтологии и улучшенные системы аннотирования данных;
- разработку технологий цифровых библиотек, поддерживающих публикацию, каталогизирование и хранение наборов данных;
- создание систем управления данными, снабженных каталогами системных метаданных для обеспечения интероперабельност'е8 между объектами и ресурсами в ECP;
- создание механизма т.н. "брокера ресурсов" (storage resource broker), обеспечивающего единый механизм доступа к гетерогенным источникам данных;
- создание комплексов "база данных + хранилище", как основу для специализированных коллекций;
- создание архивных систем для долговременного хранения данных.

Интеграция ECP, технологий обработки больших объемов информации и технологий цифровых библиотек в перспективе приведет к появлению уникальной инфраструктуры для доступа, анализа и генерации информации.

Интенсивно развивающиеся последние годы технологии электронных библиотек также предоставляют достаточно мощный и совершенный набор инструментов (сервисов) для манипуляции с наборами данных и включают [5]:

- · публикацию/регистрацию новых наборов данных;
- · база метаданных для поиска данных по атрибутам;
- · доступ к гетерогенных ресурсам посредством брокера ресурсов;
- · контроль аутентификации и доступа;
- · диспетчирование вычислительных ресурсов и ресурсов ввода/вывода;
- · распределенное исполнение сервисов ЦБ.

Соответствующие сервисы могут регистрироваться в специальной базе данных и вызываться для обработки любого набора данных, хранящегося в библиотеке (ее репозитории). Комбинация возможности доступа к данным через базу метаданных, каталожных сервисов, зарегистрированного набора методов обработки данных позволяет решать практически все задачи для создания среды обработки данных в ECP.

В России коллаборация НИИЯФ МГУ, ИТЭФ, ИПМ и АНО ТЦ «Наука и общество» на базе Южной Московской Опорной Сети создает российский сегмент ECP (RGRID).

Информационное обеспечение химических исследований

Очевидно, что достигнутый уровень информационных технологий позволяет вплотную приступить к решению задачи не просто информационного обеспечения химических исследований – но к решению задачи создания «химической понятийной сети». Россия располагает значительным числом высококвалифициров'е0нных химиков, научной информации в этой области. Представляется, что соединение имеющегося потенциала с новейшими информационными технологиями способно придать новое качество развитию химии в нашей стране. Естественно, создание такой понятийной сети предполагает теснейшую интеграцию в международные сети, организации, сообщества.

К сожалению, тенденции последних лет позволяют, на наш взгляд, говорить скорее об ухудшении информационного обеспечения химических исследований. В значительной степени утратило свое былое значение ВИНИТИ, очень сильно сократилась подписка на иностранную периодику, уменьшилось число издаваемых книг.

Положение усугубляется тем, что химия как отрасль знания, науки – имеет свою специфику. При том, что химическая информация, по некоторым оценкам, составляет до 70% от общего объема, практически вся она доступна лишь за плату.

Раньше, в отсутствие Интернета и практики бесплатного распространения информации, химия принадлежала – вслед за физикой – к числу лидеров в использовании информационных технологий.

В настоящее время положение резко изменилось. Исследователи ряда областей смогли договориться о том, что реферативная (библиографическая) научная информация доступна бесплатно. Классический пример – медицинская база Medline. Эту позицию поддержало правительство США, в 1996 г. законодательно обязавшее бесплатно предоставлять доступ к информации, созданной в ходе исследований, проводимых за счет государственного бюджета.

Развитие сетевых технологий и веба резко убыстрило скорость распространения, циркуляции научной информации. Огромное число полных текстов статей доступно на домашних страницах отдельных ученых, научных лабораторий, институтов, центров и пр.

Естественно, что созданы и интенсивно развиваются коммерческие источники научной информации, поддерживающие высококачественные базы данных, в т.ч. по химии. Примеры – базы данных Chemical Abstract, Beilshtein, Web of Science.

Из рассмотрения текущей ситуации, по нашему мнению, вытекают следующие выводы:

- Неоходимо осознание изменившейся реальности химическим научным сообществом России;
- Необходимы последовательные настойчивые усилия по формированию «информационного сознания» в химическом сообществе страны. Глобальность современной науки, высокие информационные технологии диктуют новые способы существования в науке, новые методы проведения научных исследований.
- Необходимо изменение дифференцированное изменение отношения к научной информации. Большая часть ее была создана за счет государственного финансирования, не представляет коммерческой ценности, не содержит «добавленной стоимости» как источник качественной

информации – поэтому может и должна предоставляться бесплатно, например, в составе федеративных электронных библиотек. В тоже время, необходимо воссоздать в стране организации, специализирующееся на создании высококачественной научной информации. Доступ к такой информации должен быть платным.

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МОДЕЛИРОВАНИЕ РАВНОВЕСНОЙ ГЕОМЕТРИИ АМИНОКИСЛОТ ВО ВНЕШНЕМ ЭЛЕКТРОСТАТИЧЕСКОМ ПОЛЕ

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Целью представленной работы является моделирование равновесной геометрии молекул аминокислот во внешнем электростатическом поле методами квантовой химии и молекулярной механики. Внешнее электростатическое поле последовательно ориентировалось по направлениям главных осей инерции молекул аминокислот. Квантовохимические расчеты равновесной геометрии молекул, в присутствии внешнего электростатического поля, проводились методом ССП МО ЛКАО в базисе 3-21G (валентно-расщепленный базис (9*s*,6*p*)→[4*s*,3*p*]). Минимизация функции энергии молекулы проводилась методом сопряженных градиентов Полака-Рибьера. Для моделирования равновесной геометрии молекул в присутствии внешнего электростатического поля методом молекулярной механики использовалось силовое поле AMBER (Assisted Model Building and Energy Refinement) дополненное энергиями собственных и индуцированных дипольных моментов связей во внешнем электростатическом поле. Минимизация потенциальной энергии молекулы проводилась с использованием общематематического пакета MathCAD. Проведен сравнительный анализ полученных результатов. Исследование поддерживается грантом КЦФЕ (код ГРНТИ 34.17.15. - Биофизика, шифр 97-0-10, 0-167).

AB INITIO QUASIRELATIVISTIC CALCULATIONS OF ELECTRONIC TRANSITION PROPERTIES BY THE MULTIREFERENCE MANY-BODY PERTURBATION THEORY

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A quasirelativistic method of ab initio calculations on ground and excited molecular electronic states within the relativistic core pseudopotential model is formulated and implemented. The method is based on the perturbative construction of a state-specific (intermediate) many-electron effective Hamiltonian in the model space spanned by an appropriate set of Slater determinants. The effective spin-orbit interactions outside of the model space are neglected. This allows to exploit relatively high non-relativistic (point-group and spin) symmetry during the evaluation of second order perturbative corrections and therefore to dramatically reduce the cost of computations; at the same time the errors arising from this approximation can be efficiently suppressed by the use of moderately large incomplete model spaces built by a numerical configuration selection procedure. The \'perturb-then- diagonalize\' computational strategy offers the possibility to adequately describe the interplay of correlations and spin-orbit interactions. Provided that the multipartitioning many-body form of perturbation theory is employed, the results of calculations are nearly separable with respect to the fragmentation of the molecular system under study. The evaluation of radiative transition probabilities within the present approach is performed via the perturbative construction of spin-free one-body transition density matrices with subsequent computation of transition dipole moment functions. The presented scheme is demonstrated to yield accurate energies and intensities of radiative electronic transitions in molecules involving electronic states strongly affected by spin-orbit interactions. The work is partially supported by the Russian Foundation for Basic Researches under the grant No.00-03-33004.

ELEMENTARY EXCITATIONS IN CLASSICAL STATISTICAL MECHANICS

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1. Functional-integral representations of classical partition function for one-component systems with arbitrary interatomic potentials. Equivalence of functional integrals in configuration and wave-vector spaces. 2. Equivalence of interatomic interactions to random external complex-valued fields. Renormalizations of external fields. Inverse problems. 3. External fields and renormalization of interatomic potentials. Analogy between of classical statistical mechanics and spectral problems with random potentials. 4. Equivalence of statistical mechanics of classical particles to field-theoretical problems. Non-linear oscillators and anomalous phonons. Mechanisms of phase transitions in field models.

STATISTICAL THERMODYNAMICS OF TERNARY SOLID SOLUTIONS WITH MUTUALLY RELATED COMPONENTS

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A ternary solid solutions with two types of short-range action are considered. The first type of short-range action is a chemical bond due to join of atoms of two kinds in unique complexes (molecules) $A_\\alpha B_\\beta$ and, as a consequence, to mutual relation of corresponding components of solution. The second form of short-range action is the strong repulsion like a \"hard core\" is taken into account by introducing the proper volumes of atoms of components based on a generalized lattice model. The long-range part of interatomic interactions is taken into account in the mean-field approximation. Thermodynamic description of the ternary solutions is given taking into account indicated types of short- and long-range actions. A closed set of equations for equillibrium ternary solid solution with mutually related components is obtained. The stability given solution against spinodal decomposition is investigated, the critical temperature is obtained. This work was partly financially supported by the \"Universities of Russia - Fundamental Stadies\" program (grant N 990019).

DIFFUSION KINETICS OF TERNARY SOLID SOLUTIONS WITH MUTUALLY RELATED COMPONENTS

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In the present work a phenomenological theory of ternary solid solutions with mutually related components has been developed. A closed set of evolution equations for description of diffusive rearrangement of such chemical nonequillibrium systems is derived, corresponding Cauchy problem is formulated. The concentrate relation of the effective coefficient of diffusion, which plays a role of coefficient of mutual diffusion in such pseudobinary systems, is obtained and investigated. The conditions of presence in the solution both normal diffusion and decomposition are obtained. This work was partly financially supported by the \"Universities of Russia - Fundamental Stadies\" program (grant N 990019).

AB INITIO AND DFT SIMULATION OF MOLECULAR AND ELECTRONIC STRUCTURE OF CALIX[4]ARENES [-C6H3(O-HO)-Y-]-4, Y=CH2, NH, O, SIH2, PH, S, P(O)H

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The molecular design of new calix[4]arenes is an important problem of the supramolecular chemistry. We report here results of DFT and ab initio HF/3-21G* studies with the GAMESS and PRIRODA programs of some known (Y= CH2, S) and hypothetical calix[4]arenes (I, Y= CH2, NH, O,) and (II, Y= SiH2, PH, S.). We have found periodic changes in properites of studied molecules. It was shown that all the compounds have C4 symmetry conformations with coop-erative hydrogen bonds and regularity in geometric changes. The dihedral angle between opposite phenol rings (a) is decreasing in the series I (69°, 67°, 64°) and even more considerably in II (105°, 81°, 80°). The non-valence side C...C triangle CYC defines a. Intramolecular circular hydrogen bond has four vibrational frequences. The more intensive degenerate IR vibrations are 3010, 2985, 3041 in the series I and 3172, 3100, 3288/cm in II (DFT). We calculated H-bond energy as the difference be-tween heats of formation of supramolecular phenol tetramer and four phenol molecules. Circular hydrogen bond energy is about 5 ккal/mol. Calix[4]arenes with Y=NH, PH and P(O)H have a number of geometric isomers with different a values. The axial isomers (Y=NH, PH) are more stable than equatorial isomers. The relative energies are 1.01 (Y=NH) and 3.34 (Y= PH) kcal/mol (DFT) and 2.04 and 5.79 kcal/mol (HF/3-21G*). The most stable isomer (Y= P(O)H) has PO...H hydrogen bonds and a little a value (29°). The 1,3-alternante conformers, charges, ionization potentials and frontier orbital energies are discussed. It is shown the theoretical results are experimental data are similar. This study was supported by theAcademy of Sciences of Tatarstan.

ISOMERS OF THE RADICAL CATION OF 1-METHYLTRICYCLO[4.1.0.02,7]HEPTANE

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By method PM3 within the framework of an unlimited Hartri - Fock method with use of the program MOPAC 6.0 molecular and electronic structure of radical cations of 1-methyltricyclo[4.1.0.02,7]heptane (I) in a vertical status (A*), and also some products by its thermal isomerization are investigated. In contradistinction to unsubstituted tricyclo[4.1.0.02,7]heptane (II) are studied earlier the same method, in a case of hydrocarbon (I) it fails to locate a radical cation (A) with the loosened central bicyclobutane bond C1-C7. At a choice of geometry (IA*) as starting, gradient optimization results in isomer (IB) with

the completely broken bond C1-C7. It can exist as syn- and anti-conformers, differing by orientation of atom C4 and methyl group concerning a plane C2C3C5C6 (head of formation H 1021.2 and 1020.2 kJ/mol). The isomerization (IA*) accompanying by opening of side bond C1-C2, results in a radical cation (IC) with a skeleton of 7-methylbicyclo[4.1.0]heptane, for which the conformations chair and twist are optimized (H 1009.9 and 998.9 kJ/mol accordingly). At break of bond C2-C7 is formed 1-methylbicyclo[4.1.0]heptyl radical cation (ID), having the conformation chair (H 1036.4 kJ/mol). Deeper reorganization of (IA*) results in a radical cation (IE) with skeleton of 6-methylbicyclo[3.2.0]hept-6-ene, existing as cis- and trans-conformers (H 927.8 and 932.3 kJ/mol accordingly), and also to a radical cation (IF) with a skeleton of 2-methylcyclohepta-1,3-diene (H 834.5 kJ/mol). For comparative study of radical cation (A) and (B) of compounds (I) and (II) the methods of density functional theory (DFT/3Z) and ab initio (UHF and ROHF/3-21G, GAMESS program) also are used. However the local minimum for structure (IIB) by a method UHF/3-21G fails to find. At the same time DFT/3Z and ROHF/3-21G methods fail to locate structure (IA). The specified difficulties, apparently, grow out of only mathematical complexities of formation of two minima at insignificant quantity of a dividing barrier and can be overcome on more high levels of the theory. This work was supported by Ministry of education of Russian Federation (grant E 00-5.0-30).

INTRODUCTION TO QUANTUM CHEMISTRY OF FUNCTIONALLY SUBSTITUTED FULLERENES

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The structure of molecules of a series functionly substituted of methanofullerenes and pyrrolidinofullerenes C60 and C70 containing electron donating and accepting groups, is studied by the methods of density functional theory, ab initio HF and ROHF/3-21G* and semiempirical PM3 (GAMESS and PRIRODA) The following results are discussed. The utilised methods result in a general sequence of increasing of olefinic bonds lengths of methano- and pyrrolidinofullerenes eq2, eq1, tr4, tr1, tr2, tr3, cis3, cis2. The most significant influence on bond lengths renders the transformation of two carbon atoms to sp3-state. Except for separate compounds the preferential conformations of functional groups in fullerenes and more simple compounds are similar. The asymmetry of atoms and bonds in different properties of fullerene shell in substituted derivatives C60 is expressed in a different degree. In a considerable degree the asymmetry is displayed in values of atom charges and chemical shifts, to a lesser degree in atomic populations of the HOMO and the LUMO and bond lengths. The frontal orbitals of the studied fullerene derivatives are localized on a fullerene shell or functional groups. Also it was found out high localization of frontal orbitals on some olefinic bonds. For compounds under study, HOMO atomic populations for eq1 bonds are close to zero and are maximal for eq2 bonds. LUMO has knots on eq2 bonds and the maximal population on eq1 bonds. Accordingly in cation- and anion-radicals the greatest changes are found for the lengths of eq1 and eq2 bonds (DFT). The IE and EA are designated as a difference of the total energies of the-molecules and their cation- and anion-radicals,

from comparison of the HOMO and LUMO energies and the energies of the upper single-electron level in DFT method. It was found that the theoretical values are proportional to the experimental values of the oxidation and reduction potentials. The structure and fragmentation of the anion-radicals and negatively charged ions are discussed. Chemical C13 shifts of sp2-hybridized carbons are compared to the effective charges calculated by DFT, PM3 and AM1 methods. The correlation was found for these values, the largest deviations obtained for atoms belonging to cis1-bonds. For C70 , the largest deviation is found for the signal of aromatic equatorial atoms. The splitting of the signals of these atoms caused by functional groups is discussed. The results of ab initio calculations of shielding constants are also discussed. The authors thank RFBI (grant 99-03-32888), program \"Fullerenes and atomic clusters \" (grant \" Gemo-2 \") and Academy of Sciences of Tatarstan for financial support of research.

POTENTIAL OF IONIZATION AND ELECTRON AFFINITY. CATION AND ANION RADICALS OF FUNCTIONALLY SUBSTITUTED DERIVATIVES OF FULLERENES

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The structure of molecules and their cation- and anion-radicals of a series methanofullerenes and fulleropyrrolidines C60 and C70, containing electron donor and electron-withdrawing groups is studied by methods of density functional theory, ab initio at a level ROHF/3-21G* and semiempirical method PM3 with GAMESS and PRIRODA programs. The values of adiabatic and vertical potentials of ionization (IP) and electron affinity (EA) as a difference of total energies of initial molecules and their cation- and anion- radicals, on a basis comparison of energies of HOMO and LUMO and energy of the upper one-electron level in a method DFT are designed. Is shown the calculated values IP and EA are proportional to experimental data of potentials of oxidation and reduction. Is shown the change of potentials of oxidation and reduction and the geometrical parameters feature cation- and anions - radicals explored by one-electron orbital models. This model are confirmed by the method of density functional theory calculations of cation- and anions - radicals to the greatest distension subjected of the bond eq2 and eq1, on which are mainly localized the HOMO and LUMO. The solvatations and stabilities of cation- and anions - radicals of substituted fullerenes are explored the mechanism of decomposition of their anion - radicals and dianions in which the effective charge is mainly localized on addends or fullerene moiety. The reactions of electrochemical reduction of methanofullerenes bearing phosphonate and alkoxycarbonyl groups at the exo-carbon atom by DFT were studied. The mechanism of the retro-Bingel reaction at the cleavage of two C-C bonds between the C(61) atom and the fullerene shell accompanied by electrochemical electron transfer was preposed. This study was supported by RFBI (grant 99-03-32888, Program \" Fullerenes and Atomic Clusters \" (grant 98008 \"Gemo-2\") and Academy of Science of Tatarstan

VARIATIONAL CALCULATION OF ELECTRONIC CHEMICAL POTENTIAL OF A MANY-ELECTRON SYSTEM

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In this work the possibility of quantumchemical evaluation of the electronic chemical potential (electronegativity) of a many-electron system is discussed.
We thoroughly consider Valone\'s formulation [1,2] of the Donnelly-Parr variational principle [3] and elucidate unproved statements supposed to be truth. We display the weakest point in the Donnelly-Parr theory; that is an parametrization of the two-electron part of the exact energy functional which violates the functional N-representability. This implies that this theory is no longer variational. We consider some possible parametrizations for the Donnelly-Parr energy functional and demonstrate with simple closed-shell molecules that the Euler-Lagrange equations for those parametrizations have no solutions within the set of N-representable density matrices. Therefore, these equations are unusable in determination of the electronic chemical potential of a system, and physical consequences from the Donnelly-Parr theory are open to question. This is especially true in regard to Sanderson\'s principle of electronegativity equalization which can not be founded presently in the framework of density functional theory.
Finally, we briefly characterize the techniques allowing to evaluate the electronic chemical potential of isolated molecules. The approximation of the electronic chemical potential with the three-point finite-difference scheme seems to be the most relevant route to its evaluation at the present stage of development.

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КВАНТОВО-ХИМИЧЕСКОЕ ИССЛЕДОВАНИЕ СУПРАМОЛЕКУЛЯРНЫХ КОМПЛЕКСОВ 4,4'-ДИПИРИДИЛИЛЭТИЛЕНА С НИТРАТОМ СЕРЕБРА.

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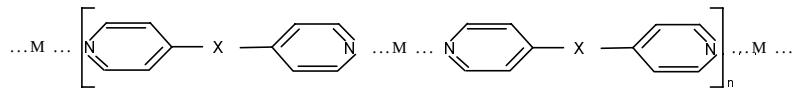
В последние годы впечатляющие успехи достигнуты в синтезе новых супрамолекулярных систем на основе дипиридиловых металлокомплексных полимеров [1], структуру которых можно условно представить формулой:



где M – ион металла. Например, в результате координационной полимеризации 2,7-диазапирена и $[Cu(MeCN)_4]PF_6$ была получена необычная кристалличекая структура, представляющая собой три взаимопроникающие адамантоидные сетки, расположенные

под углом 90^o друг к другу [1c]. В растворах $AgNO_3$ и транс-4,4'-дипиридилэтилена (DPyEt) при достижении определенного критического соотношения [DPyEt]/ [$AgNO_3$] происходит образование супрамолекулярных агрегатов, о чем свидетельствует характерное изменение спектров поглощения и образование твердой микродисперсной фазы [4]. В данном докладе представлены результаты квантово-химических расчетов супрамолекулярных комплексов на основе DPyEt различной структуры и состава, отвечающего формуле $(DPyEt)_n$ $(AgNO_3)_n$ (n=1÷6, m=1÷13). Расчеты проводились полуэмпирическим методом AM1/d (пакет MOPAC 2000, версия 1.06) и в рамках теории функционала плотности (B3LYP). Энергии синглет-синглетных электронных переходов рассчитывались в рамках метода TDDFT с базисами и 6-31+G* на атомах C,N,O,H и LanL2DZ с псевдопотенциалом LanL2 на атоме Ag. Показана возможность образования нескольких типов супрамолекулярных комплексов, причем при избытке металла наиболее устойчивы комплексы типа «спиральных цепей», которые, взаимодействуя между собой, поперечно сшиваются. Наблюлаемые изменения экспериментальных спектров поглощения растворов хорошо коррелируют с теоретически рассчитанными энергиями электронных переходов.

Работа выполнена при финансовой поддержке РФФИ (код проекта IR-97-1230).

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GAS-PHASE INTERACTION OF SILICON TETRAFLUORIDE WITH WATER. A COMBINED AB INITIO AND FTIR STUDY

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The silicon tetrafluoride is evolved abundantly to the atmosphere in the fertilizer production and many modern technology processes. In atmosphere, it undergoes the hydrolysis by the atmospheric water forming the various toxic products: hydrogen fluoride, fluorosiloxanes and, probably, polyhydroxoderivatives of different composition and structure. The mechanisms of these processes are sufficiently different from the well-known liquid-phase hydrolysis of silicon tetrafluoride and poorly understood yet. The main objective of this work is a studying the reaction mechanism of the silicon tetrafluoride gas-phase hydrolysis under small water concentration conditions, the structure and stability of short-living intermediates, and the estimation of thermodynamic and kinetic parameters of elementary reactions of atmospheric hydrolysis. The important information on the structure and properties of short-living intermediates can be obtained with modern quantum-chemical methods combined with Fourier-transform IR spectroscopy of gas-phase mixtures. In this work, we studied theoretically the structures, association energies, electronic distribution, vibrational frequencies, IR intensities, and thermodynamic parameters for various weak-bonded complexes of silicon tetrafluoride with water as initial intermediates of hydrolysis process, and the hydrolysis products of two different classes - polyhydroxoderivatives and fluorosiloxanes. The calculations were carried out by the ab initio method with correlation correction at the MP2 and MP4 levels, and by density functional theory (B3LYP) using the 6-

311++G(d,p), 6-311++G(2d,p), 6-311++G(2d,2p), and aug-cc-pVTZ basis sets with full geometry optimization and the basis set superposition correction for the binding energies. On the basis of optimized molecular structure and the calculated vibrational frequencies, the energetic and thermodynamic parameters of elementary reactions of gas-phase hydrolysis process were estimated. The high-accuracy G2 and G2MP2 procedures were used for the thermodynamic calculations. The transition state structures were optimized for most thermodynamically preferable reactions and the activation energies and absolute rate constants of various elementary stages were estimated. The potential energy hypersurface (PES) of SiF4+H2O system was studied with an original computer program ADANIMEHS specially designed for the adaptive analysis of PES of weak-interacting systems. The PES analysis performed with the new program provided a way of correct recognition of local minima and correct estimation of their curvatures in order to take into explicit account the anharmonicity contribution to the thremodynamic properties and estimate the low-lying vibrational modes. It was found that the hexafluorodisiloxane SiF3-O-SiF3 formation is more thermodynamically preferable in comparison with the polyhydroxoderivatives SiF4-n(OH)n formation process. However, the activation barrier of the hexafluorodisiloxane formation is 5-9 kcal/mol higher. This fact may have a serious influence on the mechanism of silicon tetrafluoride hydrolysis under conditions far from the thermodynamic equilibrium. The conclusion on the hydroxoderivative formation at the initial stages of gas-phase hydrolysis under non-equilibrium conditions and small water concentrations is supported by the FTIR spectroscopy of gas phase mixtures and the dilute solutions of SiF4 in CCl4 with small impurity of H2O modeling the atmospheric SiF4 hydrolysis conditions. The observed IR bands of OH vibrations are in a good agreement with the calculated frequencies of hydroxoderivatives, and the positions and intensities of Si-F vibrations and their time-dependence correlate with conclusions about the formation of several fluorine-containing derivatives together with hexafluorodisiloxane.

MOLECULAR COMPLEXES OF SILICON TETRAFLUORIDE WITH WATER, METHANOL, AND DIMETHYL ETHER FROM THE LOW-TEMPERATURE IR SPECTROSCOPY AND QUANTUM CHEMICAL DATA

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The molecular structure, binding energies, and vibrational spectrum of binary molecular complexes of silicon tetrafluoride with water, methanol and dimethyl ether molecules observed earlier by the IR spectroscopy in the low temperature (12-15K) inert matrices were studied with the quantum chemical electron correlated ab initio method (MP2) using the different basis sets up to 6-311++G(2d,2p). It was found that the molecular structure of these adducts is a trigonal bipyramide with the five-coordinated silicon atom and the donor-acceptor bond between silicon and oxygen. This structure is additionally stabilized by the hydrogen bonds between hydrogen and fluorine atoms. No local minima of the potential energy surface corresponding to the pure hydrogen-bonded structures were located. The estimation of the binding energy corrected by the basis set superposition error and the zero point energy are 6.3, 9.7, and 12.5 kJ/mol for the SiF4 H2O, SiF4 O(H)CH3, SiF4 O(CH3)2

complexes, correspondingly. The calculated IR shifts of the monomer molecules in the SiF4 H2O and SiF4 O(CH3)2 complexes are in a good agreement with the experimental values whereas the band 844 cm-1 observed under matrix isolation conditions in the case of SiF4 O(H)CH3 complex can not be unambiguously assigned in the framework of models used. The most probable explanation of this band is a formation of essentially anharmonic hydrogen bond O…H…F or even ionic structure F…H+…O– resulting to the very large shifts of the H-F or O-H vibrations.

COMPLETE INTERMOLECULAR POTENTIAL ENERGY SURFACE OF WEAK-BONDED COMPLEXES CH4 H2O AND SiH4 H2O

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A new method for the fast estimation of the intermolecular interaction energy for the potential energy surface (PES) exploration was applied to the PES study of two systems with a weak intermolecular binding: binary molecular complexes of silane and methane with water CH4 H2O and SiH4 H2O. One of the key features of these weak-bonded systems is very flat intermolecular PES. Abundant studies of analogous systems (CH4 HCl, CH4 NO, SiF4 H2O) show that the standard procedure of theoretical investigation (full geometry optimization following the vibrational frequency calculation) is not effective for these systems: the vibrational analysis fails to correctly determine the type of stationary point because the low-lying vibration modes (0-100 cm-1) are strongly mixed with rotations and translations resulting in the negative hessian eigenvalues even for the true (but very flat) minima. In contrary, for the stationary points of higher orders, standard procedures often results to the positive determined hessian matrix. The hessian purification methods can rarely be successful in correcting the situation as well as the reaction coordinate following because of extremely low PES curvature. In this work, the intermolecular PES of CH4 H2O and SiH4 H2O was explored using the adaptive scanning algorithm consisting in energy calculation performed in the nodes of equal-mesh grid following the interpolation, and the grid specification in the regions of interpolation function minima. Using this approach, the complete 6-dimensional PES\'s of the H2O molecule movement relatively to the X molecule (X=CH4, SiH4) with frozen intramolecular monomer structure. The energy was calculated with ab inition method at the MP2/6-311++G(2d,2p) level. All the results were obtained using original program specially designed for the adaptive PES scanning ADANIMEHS. The results of the PES scanning are compared with available experimental results of the CH4+H2O microwave spectroscopy and previous ab initio study of this system using the standard quantum-chemical procedures. The effect of various interaction components on the total binding energy in different PES regions is discussed.

GRECP/MRD-CI CALCULATION OF THE ELECTRONIC STRUCTURE OF PbH

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Calculations of the potential curves and spectroscopic constants for the low-lying electronic states of molecules with heavy atoms are of substantial interest from both experimental and theoretical points. We carried out 5-electron correlation calculations of electronic structure of PbH by MultiReference single and Double Configuration Interaction method (MRD-CI) (Buenker & Peyerimhoff Theor.Chim.Acta, v.35, 33 (1974); v.39, 217(1975), Titov et al., Int.J.Quant.Chem.(2001), in press) with the 22-electron Generalized Relativistic Effective Core Potential (GRECP)(Mosyagin et al., Int.J.Quant.Chem. 63, 1107(1997), Titov et al., Int.J.Quant.Chem., 71(5), 359(1999)).The pseudospinors describing the 5s, 5p and 5d shells of Tl are frozen using the level-shift technique (Titov et al., Int.J.Quant.Chem., 71(5), 359(1999)). Basis set for Pb is generated and optimized with the help of the technique recently developed in PNPI (Mosyagin et al., J.Phys.B, 33, 667(2000), Isaev et al., J.Phys.B, v.33, 5139(2000)). The results are compared with the experimental data and recently calculated spectroscopic values for PbH by Alexeev A. et al. and discussed.

POLYMORPHISM OF HYDROGEN BONDING IN THE SHORT DOUBLE HELIXES OF OLIGONUCLEOTIDES. QUANTUM-CHEMICAL SEMIEMPIRICAL STUDY.

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Physical mechanism of nucleotide sequence dependence of DNA and RNA secondary structure is a problem of current interest in molecular biophysics. A precise knowledge of crucial conformational and energetic parameters, which determine the unique spatial packing of nucleotide pairs in the double-strained molecules, is of extreme importance. The existing concept of stacking accumulation of base pairs noncoplanarity in double helix structure cannot ambiguously describe a sizeable distortion of hydrogen bonding of base pairs observed both in the structure of single crystals of nucleosides and nucleotides and in the native and synthetic forms of DNA molecules. In the report the hypothesis of a «hidden» polymorphism in the mechanism of nitrous bases hydrogen bonding in the structure of short oligonucleotide duplexes is developed by using quantum-chemical semi-empirical MNDO-PM3 approach. Main goal of the study is to show, that rather large «propeller-like» and «step-like» deformations of Watson-Crick base pairs is a permanent intrinsic property of pairs packing. The energetic and structural properties of the plurality of canonical base pairing forms were examine at the raw of oligonucleotide complexes:

a. d(ApA)Чd(TpT), d(ApT)Чd(TpA),d(GpG)Чd(CpC),d(GpC)Чd(CpG)
b. d(ApApA)Чd(TpTpT),d(ApTpA)Чd(TpApT), d(GpGpG)Чd(CpCpC), d(GpCpG)Чd(CpGpC)

c. d(ApApApA)Чd(TpTpTpT), d(GpGpGpG)Чd(CpCpCpC)
It is concluded, that structural polymorphism of the pairs as a non-trivial factor of bases H-bonding most likely determines the unique packing of complementary pairs and their flexibility in DNA structure. The work is supported by Russian Fund for Basic Research, Grant № 99-04-48162. REFERENCE 1. V.M.Komarov, Biophysics 43, 917-924 (1998) 2. V.M.Komarov, J.Biol.Phys., 24, 167-184 (1999)

ИСПОЛЬЗОВАНИЕ ДАННЫХ КВАНТОВО-ХИМИЧЕСКИХ РАСЧЕТОВ ДЛЯ ОПРЕДЕЛЕНИЯ РЕАКЦИОННОЙ СПОСОБНОСТИ НЕКОТОРЫХ ФУЛЛЕРЕНОВ И ИХ ПРОИЗВОДНЫХ В ПРОЦЕССCАХ РАДИКАЛЬНОГО ПРИСОЕДИНЕНИЯ

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Известно, что при взаимодействии высокосимметричного C_{60} с углерод- и элемент-центрированными радикалами образуется фуллеренильный спин-аддукт только одного типа $^{\bullet}C_{60}R$. Понижение симметрии молекулы, связанное с увеличением числа углеродов в каркасе или присоединением к нему различных органических или металлоорганических фрагментов, приводит к появлению неэквивалентных групп атомов, обладающих различной реакционной способностью по отношению к атакующим их частицам.

Нами показано, что в условиях радикального фосфорилирования C_{76} и $C_{60}(CH_2)_2C_6H_2(OMe)_2$ происходит избирательная атака атомов углерода фуллереновых молекул, приводящая к образованию кинетически- и термодинамически стабильных изомеров. Методом MNDO/PM3 в приближении ROHF были определены энтальпии образования для всех возможных изомерных спин-аддуктов. В совокупности с данными о порядках связей в исходных фуллеренах оказалось возможным определить участки углеродного каркаса, присоединение к которым оказывается наиболее вероятным. Методом B3LYP вычислены значения спиновой электронной плотности в изомерных спин-аддуктах и значения констант СТВ неспаренного электрона с ядром атома фосфора фосфорильной группы, присоединенной к фуллереновому ядру. Сравнение экспериментальных и расчетных констант СТВ позволяет провести соотнесение сигналов, наблюдаемых в спектре ЭПР, с образующимися спин-аддуктами.

Работа выполнена при поддержке РФФИ и Государственной программы “Фуллерены и Атомные Кластеры”.

ELECTRONIC EXCITATION IN ANIONIC POLYMERIZATION OF BUTADIENE. NON EMPIRICAL CALCULATIONS OF REACTION COMPLEXES

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A new mechanism of anionic polymerization of butadiene is proposed. In the elementary chemical act, the \"living\" polymer - monomer complex is excited into the low-lying triplet state. This state has the character of charge (electron) and cation (Li+ or Na+) transfer from the terminal unit of the active center to the monomer molecule. In the framework of this concept the probability of chemical bond formation is determined by spin density on radical centers of reagent molecules. Semi-empirical and ab initio 6-31G** quantum- chemical calculations showed stable interaction between components of the complex in the ground electronic state (9-11 kcal/mole) and low energy levels of triplet excited states (< 14 kcal/mole). This new approach is shown to be useful in the analysis of polymerization kinetics and the microstructure of polybutadiene depending on the cation type and the ion pair state. The mechanism of cis-trans isomerization in the terminal unit of the \"living\" polymer consists in concerted rotation about the Cb-Cg bond and the migration of Li between Ca and Cg atoms.

NATURE OF BINDING IN CLUSTERS WITH CLOSED VALENCE-SUBSHELL ATOMS: ALKALINE-EARTHS

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The study of binding in clusters with closed valence-subshell atoms is performed [1]. The study is based on the accurate calculations of Ben, Mgn and Can (n=2,3)clusters at the Moller-Plesset electron correlation level(MP4)using a resonably large basis set [6-311 + G(3df)].The two- and three-body decompositions of binding energy at the MP4 and SCF levels, the NBO population analysis and the electron density difference maps allow to elucidate the nature of binding in the alkaline -earth clusters. In the dimers, the only stabilization factor is the dispersion forces. So, the alkaline-earth dimers can be attributed to the van der Waals molecules. The trimers are stabilized by the two-body localized dispersion forces and three-body delocalized exchange forces. Thus, the binding in the alkaline-earth trimers has a mixed physical (van der Waals) and chemical (non-additive exchange) nature. Three-body exchange forces cause the pi-in-plane bonding. [1] I.G.Kaplan, S.Roszak, and J.Leszczinski, J. Chem. Phys.v.113, 6245 (2000).

ACTYLENE-ALLENE REARRANGEMENT IN SUBSTITUTED PROPYNES: A THEORETICAL STUDY

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The ab initio investigation of the acetylene-allene rearrangement of propargyl systems XCH2CCH (X = Me, NMe2, OMe, F and SMe) towards allene (XCH=C=CH2) and propynyl (XCCCH3) structures has been performed. The n-pi-conjugation is shown to dominate in allene stabilization, while the effect of electronegative hetheroatom makes at least comparative contribution to stabilization (or destabilization) of the propynyl form. In particular, the relative instability of 1-methoxypropyne is rationalized by high electronegativity of oxygen atom that dramatically decreases total electronic charge of the neighboring C-C triple bond.
The MP2 level of theory is shown to be insufficient to obtain the correct energy differences between propynes and corresponding allenes. The MP4 calculations combined with a ZPE correction are in a good agreement with the experimental data available.

A THEORETICAL ANALYSIS OF PYRROLE ANIONS ADDITION TO CARBON DISULFIDE

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Quantum-chemical analysis (MP2/6-31+G*) of the pyrrole anions addition to carbon disulfide and the substitution effects therein shows that pyrrole-2(5)-carbodithioates are thermodynamically the most stable compounds, whilst 1- isomer obtained from the unsubstituted pyrrole is likely a kinetic product. Steric hindrances destabilize N-adducts when a methyl substitutor appears in a 2(5) position and the 2,5-dimethyl-1-pyrrolecarbodithioate anion turns over to be even less stable then the 2,5-dimethyl-3-pyrrolecarbodithioate one.

ЭЛЕКТРОННАЯ СТРУКТУРА АДАМАНТАНА

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Одной из важных характеристик электронной структуры адамантана, во многом определяющей физико-химические свойства самого адамантана и его многочисленных производных, является распределение валентной электронной плотности внутри адамантанового полиэдра и на его гранях. Обсуждаемые распределения зарядовой плотности валентных электронов детально вычислены на основе результатов квантово-химических расчетов неэмпирическим ограниченным методом Хартри-Фока (RHF) в двух атомных базисах – в минимальном базисе MINI и расширенном базисе 6-31G* с включением поляризующих *d*-функций на атомах углерода. При этом установлено, что

в центральных областях полиэдра и в центральных областях его граней электронная плотность весьма мала. В частности, значения полной электронной плотности в полости молекулы были рассчитаны при сканировании по оси третьего порядка (она проходит через центр полиэдра) от вершины C1 до расстояний 3A от нее; по мере удаления от вершины полная электронная плотность очень быстро убывает до значений ~ 0.01 и лишь незначительно возрастает (до ~0.02) при прохождении через плоскость, в которой расположены вершины C5, C6, C7, и через плоскость, в которой расположены вершины C8, C9, C10. Индексы кратностей для трансаннулярных взаимодействий несопоставимо малы по сравнению с индексами кратностей двухцентровых связей C-C, для которых эти значения близки 1.

Аналогичные результаты были получены при вычислении полной электронной плотности для полиэдрических молекулярных катионов $(CH)^{1+}_5$ и $(CH)^{2+}_6$.
Распределение электронной плотности в полиэдрах C_nH_n из атомов углерода принципиально отлично от распределения электронной плотности в полиэдрах B_nH_n из атомов бора, в которых зарядовая плотность валентных электронов в центральных областях полиэдров и на их гранях весьма значительна.

Причина этих различий в распределении зарядовой плотности валентных электронов, по-видимому, в том, что в электронной структуре B_nH_n возможны и часто реализуются орбитальные взаимодействия *двух связевых электронов B – H (двух электронов связывающей молекулярной орбитали B – H) с вакантной 2p – орбиталью другого атома B* (показательно, что валентности атомов B в B_nH_n значительно больше 3 и часто достигают значений 3.5 – 3.8). Напротив, в электронной структуре C_nH_n аналогичные орбитальные взаимодействия, естественно, невозможны из-за отсутствия вакансий на валентных орбиталях атомов C (с классической валентностью ~4). Взаимодействие же электронной пары, локализованной преимущественно на атоме C (имеющей преобладающий *2sC* – вклад), с подходящей по симметрии одной из низших свободных MO нереалистичны из-за отсутствия таких слаборазрыхляющих MO с достаточно низкой энергией.

THE ELECTRONIC STRUCTURE OF ADAMANTANE

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The distrbutions of valent electron density within adamantane polyhedron and on its sides are one of the most important characteristic features of adamantane electronic structure that regulates to a large extent the physical-chemical properties of right adamantane and its numerous derivatives. The discussed distributions of valent electron charge density were in detail computed on the base of results of quantum-chemical calculations by non-empirical restricted Hartree-Fock (RHF) method with use of minimum atom basis MINI and extended atom basis 6-31G* including polarizing *d*-functions for carbon atoms. Under this it was established that electron density is very small in central regions of polyhedron and in central regions of its sides. In particular the values of total electron density within molecule cavity have been computed under displacement along the third order axis (it crosses the polyhedron center) from vertex C1 up to 3 A; as moving off the vertex the total electron density is very quickly decreased and this density grows insignificantly only passing the plane of vertexes

C5, C6, C7 and the plane of vertexes C8, C9, C10. The index values of transannular interactions are non-comparably small with comparison of bond orders of twocenter bonds C-C that near 1.

Analogous results have been obtained computing of total electron density for polyhedral molecilar cations $(CH)^{1+}_5$ и $(CH)^{2+}_6$.

Electron density distributions in polyhedrons C_nH_n including carbon atoms differ on principle from electron density distribution in polyhedrons B_nH_n including boron atoms: valent electron charge density in central regions of boron polyhedrons and on its sides is highly substantial.

The reason of these different distributions of valent electron charge density consists evidently in that the orbital interactions *between two bond electrons B – H (two electrons of bonding molecular orbital B – H) and vacant 2p-orbital of the other boron atom* is possible and is often realized in electron structure B_nH_n (that is extremely significant that boron atom valencies in B_nH_n are meaningfully more than 3 and reach values 3.5 – 3.8 often). On the contrary analogous interactions are naturally impossible in electronic structure of C_nH_n owing to absence of any vacancies on carbon atom valent orbitals. The interaction between the electron pair that is preferentially localized on carbon atom (with predominant *2sC* – contribution) and symmetry proper lower unoccupied MO is rather non-realizable owing to absence of such weak antibonding MO having sufficiently low energies.

QUANTITATIVE STRUCTURE-ACTIVITY RELATIONSHIP STUDY OF SUBSTITUTED AMINOTETRALINE ACTIVITY TO 5-HT1A SEROTONINE RECEPTOR USING THE CHARGE DESCRIPTORS

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The structural features of substituted aminotetralines and their effect on the 5-HT1A serotonine receptor agonist/antagonist activity were investigated. The molecular geometry was calculated by ab initio and AM1 methods, and the charge distribution was estimated using Mulliken approach. A number of classical electronegativity equalization techniques was also employed. The charge descriptors obtained in this way were combined with other local parameters (steric, lipophilicity, hydrogen bonding characteristics) and used to derive the quantitative structure-activity relationship models by the Molecular Field Topology Analysis (MFTA) technique. It is based on the construction of a molecular supergraph enabling the correct matching of such parameters for different structures. Statistical treatment of the resulting descriptor sets with the partial least squares (PLS) regression and artificial neural networks leads to the models of high predictivity. Using this data, different charge computation schemes are compared with respect to structure-bioactivity relationship studies of organic compounds. The properties for novel structures were also predicted, and the priority targets for synthesis of prospective serotonine receptor agonists and antagonists were determined.

INTERACTION POTENTIALS AND COLLISION PROPERTIES OF THE RARE GAS - SULFUR OPEN-SHELL SYSTEMS

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Interaction potentials of the rare gas - sulfur (RgS, Rg=He-Xe) open-shell systems are computed at the coupled cluster CCSD(T) level of ab initio theory using the extended correlation-consistent basis sets augmented by bond functions. Ab initio potentials are found to be in good agreement with empirical potentials determined from the absolute total scattering cross section measurements in molecular beams. Two sets of potentials are implemented for calculating the cross sections and rate constants of collision-induced transitions between the fine-structure levels of the S(3Pj) atom in a wide range of translational temperatures. The role of electrostatic and Coriolis couplings in governing the intramultiplet mixing dynamics is analyzed and it is illustrated that the rate constants for the j=0 -- j=1 transitions in S + Ar, Kr and Xe collisions, forbidden if the body fixed projection of j is conserved, are greater in magnitude than the rate constants for \"allowed\" j = 0 -- 2 and j = 1 -- 2 transitions. References: 1. R. Burcl, R.V. Krems, A.A. Buchachenko, M.M.Szczesniak, G.Chalasinski, and S.M. Cybulski, J. Chem. Phys., 109, 2144 (1998). 2. R.V. Krems, A.A. Buchachenko, J. Phys. B., 33, 4551 (2001). 3. A.A. Buchachenko, J. Jakowski, G.Chalasinski, M.M.Szczesniak, S.M. Cybulski, J. Chem. Phys., 112 5852 (2000).

TO QUESTION ON NONIDEALITY OF CATALYTIC CHEMICAL REACTIONS IN THE SLOGL MODEL

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We consider the chemical catalytic reacations in the Shlogl model when an initial substance A is transformed to a product B by a transient formation X catalyzing itself production. We propoze that nonideality in the Shlogl model is taken into account by adding four derivative with respect to space coordinate of the X concentration to a diifusion flow in the evolution concentration equation. Besides there is the Buregers nonlinearity describing the total rate of the X production component in the evolution equation. All of these leads to Kuramoto-Sivashnsky evolution equation for the reagent concentration X that gives quasiperiodical solutions having been interpreted as space structure.

МОДЕЛИРОВАНИЕ ВЗАИМОДЕЙСТВИЯ ПРОСТЫХ СПИРТОВ С ЛЬЮИСОВСКИМИ ЦЕНТРАМИ ЦЕОЛИТОВ МЕТОДОМ DFT

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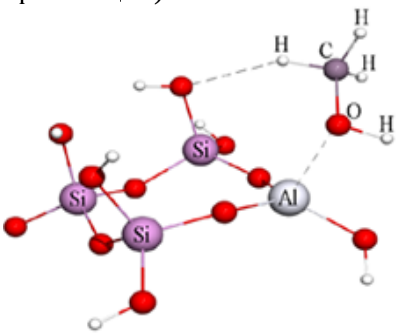
Экспериментально и квантовохимическим моделированием было показано, что молекулы воды, аммиака и сероводорода, адсорбированные на кислотном центре типа Льюиса, приобретают протоно донорные свойства. Этилен, взаимодействующий с кластером вода –циклический фрагмент структуры цеолита, по своим свойствам близок к неклассическому иону карбения. Мы предположили, что взаимодействие простых спиртов с цеолитом должно происходить аналогичным образом.

Для подтверждения этого методом DFT с использованием функционалов BLYP и PBE было изучено взаимодействие молекул метанола и этанола с фрагментом цеолита (рисунок). Взаимодействие двух молекул и димера метанола моделировали с использованием фрагмента с 6 тетраэдрическими атомами (2 атома Al).

Было установлено, что молекулы спиртов координированы на атоме алюминия фрагмента (для комплекса метанол –«цеолит» равновероятны две близкие по структуре ориентации).



Анализ изменения геометрии и распределения электронной плотности в комплексе позволяет утверждать, что связь O–H группы молекул спиртов ослабляется, а протон может быть источником бренстедовской кислотности. В «адсорбированном» димере только одна молекула координирована атомом алюминия. Взаимодействие с координационно-ненасыщенным атомом Al приводит усилению взаимодействия между молекулами метанола, что согласуется с представлениями о том, что образование C–C связи происходит при атаке молекулой метанола комплекса метанол – цеолит. Рассчитанные величины энергии образования комплексов сопоставимы с литературными данными по значениям теплоты адсорбции. Разумно совпадали и значения экспериментальных и рассчитанных частот колебаний в молекулах спиртов. В структуре фрагментов цеолита межатомные расстояния изменялись незначительно, наибольшие изменения отмечены в значениях углов связей между атомами.

Использование функционалов PDE и BLYP давало близкие результаты, сопоставление которых с данными, полученными методом MP2 (SCF/6-31G**), показало удовлетворительное совпадение. Учитывая меньшие требования DFT к вычислительным ресурсам, это позволяет рекомендовать метод для расчета сложных каталитических и адсорбционных моделей.

AB INITIO QUANTUM-MECHANICAL CALCULATIONS OF A STRUCTURE OF THE PROPANAL MOLECULE IN LOWEST SINGLET AND TRIPLET EXCITED ELECTRONIC STATES

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The structure of the non-rigid propanal molecule (CH3CH2CHO) in the lowest excited triplet (T1) and singlet (S1) electronic states was investigated by one- and multiconfigurational SCF methods. The T1<--S0 and S1<--S0 electronic excitations of propanal are followed by the CH3CH2 top rotation and the pyramidal distortion of carbonyl fragment. The similarity of the structure of the propanal potential energy surfaces in S1 and T1 state was demonstrated. On the basis of the potential energy surfaces calculated the vibrational problems for the torsion ethyl top and inversion motions of the carbonyl fragment was solved using one- and two-dimensional quantum mechanical approximations. This work was financially supported by RFBR (Project N 00-15-97346 and 01-03-32841).

THEORETICAL EVIDENCE OF AROMATICITY IN ALL-METAL SPECIES

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Reasons why certain molecules are stable relative to others have long been sought by chemists. Among the useful concepts is *aromaticity*, the simplest and yet the most successful description of the particular stability of cyclic, planar, or conjugated organic molecules which possesses (4*n*+2) π-electrons and have specific chemical and structural stability. The concept of aromaticity may seem foreign for metal systems. Although it has been extended to include hetero-systems and organometallic compounds, aromaticity has never been considered in pure all-metal species. We have recently reported experimental and theoretical evidence of aromaticity in an all-metal system, the Al_4^{2-} dianion in a series of bimetallic and ionic clusters MAl_4^- (M = Li, Na, or Ca)[1]. The Al_4^{2-} dianion, both as an isolated species and in the bimetallic molecules (MAl_4^-), was found to be square-planar and possess two delocalized π-electrons, thus conforming to the structural criterion and the (4*n*+2) electron-counting rule for aromaticity. Delocalization of the two π-electrons was found to be critical for the planar structure and aromaticity of Al_4^{2-}. Also, the possibility of aromaticity in a series of hetero-systems, XAl_3^- (X = Si, Ge, Sn, and Pb) which are isoelectronic to Al_4^{2-}, has been explored[2]. We found that all the XAl_3^- species have two lowest singlet isomers; a four-membered hetero-cyclic structure (C_{2v}) and a pyramidal structure (C_{3v}). The hetero-cyclic structure was found to be aromatic with two delocalized π-electrons, analogous to Al_4^{2-}. The substitution of one Al in Al_4^{2-} by Si, Ge, Sn, and Pb allow us to investigate systematically how the delocalized -orbital, thus aromaticity, effects the relative stabilities and properties of the hetero-cyclic and pyramidal structures. In previous study of the lighter CAl_3^- species, it was found the pyramidal isomer to be the only minimum3. The instability of the CAl_3^--planar

cyclic isomer is due to the compete localization of the two π-electrons on the C atom because of its much higher electronegativity relative to that of Al.

These findings may not only expand the aromaticity concept into all-metal systems but may also indicate whole classes of new inorganic aromatic species. Some of them may eventually serve as the basis for novel materials with as-yet unimagined properties.

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A SIMPLE MODEL FOR THE IONIC ADSORPTION ON ELECTRODE SURFACES FROM POLAR SOLUTIONS: DENSITY FUNCTIONAL THEORY AND CONTINUUM SOLVATION MODEL

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Investigations of the adsorption processes of different ionic and molecular components of electrolytes on the electrode surfaces are of great interest for electrochemistry, in particular, the double electric layer theory. The main peculiarity of the theoretical treatment of the ionic adsorption from a polar solution is the necessity of taking into account the partial desolvation of the ion on its way from the bulk of solution into the state of adsorption.

In the present work we have calculated the potential curves for a single chloride ion adsorbed on the cooper, silver and gold electrode from the water solution as functions of the metal-ion distance. The calculations were carried out using the Density Functional Theory (version B3LYP) by means of the GAUSSIAN 94 program package.

The electrode surface was simulated by means of a two-layer Me_{13} cluster (Me=Cu, Ag, Au). The whole adsorptional $Me_{13}Cl^-$ complex was immersed into a dielectric continuum with the dielectric constant □, corresponding to the water solution. The effect of the polar medium on this system was included using the self-consistent reaction field model (SCRF), namely, the isodensity polarized continuum model (SCIPCM) in which the dielectric cavity is determined self-consistently from the electron isodensity of solute.

The potential curves for the chloride adsorption on the three metals under study are characterized by an energy barrier, the height of which increases in the sequence Ag<Cu<Au. The position of this barrier corresponds to the distance of ca. 350 pm between the ion center and the electrode plane (this value is close to the effective radius of the first hydration shell of the chloride ion in the bulk of solution).

At the calculation of the chloride ion adsorption energy we assumed that one of the water molecules of the electrode dense part is desorbed into the bulk of solution. Note, that the adsorption energies calculated by such a way are substantially lower than the gas phase adsorption energies. This may be explained by a partial dehydration of the ion in the

adsorption state compared with its complete hydration in solution.

It is somewhat surprising that the absolute values of the adsorption energy follow the same sequence as the energy barrier on the potential curves (Ag<Cu<Au). The electronic charge density transfer from the adsorbed chloride to the metal (ca. 0.5 of the elementar electron charge) is also maximum in the case of gold.

The calculational results were analyzed in comparison with some available experimental data and quantum-chemical results on the cyanide ion adsorption, for which a similar adsorptional behaviour on the metals considered here had been found.

This work was supported by the RFBR (grant No. 00-03-32140).

A QUANTUM-MECHANICAL TREATMENT OF THE ELECTROREDUCTION MECHANISM OF Cu(I) CYANO-COMPLEXES FROM WATER SOLUTION

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One of the important problems in the study of the electrochemical copper deposition from cyanide solutions is the elucidation of the electrochemically active particle participating directly in the discharge and also the mechanism of the elementary act of electroreduction

In this work we have optimized the geometrical structure of $[Cu(CN)_n]^{1-n}$ (n= 1,2,3,4) complexes using the B3LYP Density Functional Theory (Becke\'s three parameter hybrid method including the non-local correlation functional of Lee, Yang and Parr) which takes into account precisely enough the electron correlation effects. The stability of these complexes in the water solution was investigated taking into account their interaction with the polar medium using the self-consistent reaction field model (SCRF), namely, the isodensity polarized continuum model (SCIPCM) in which the dielectric cavity is determined self-consistently from the electron isodensity of solute. The $[Cu(CN)_4]^{3-}$ and $[Cu(CN)_3]^{2-}$ complexes were found to be the most stable species in the bulk of solution. As the next step, we attempted for the first time to study quantum-chemically the complexation processes at the electrode surface within the framework of a cluster model. For this aim, the adsorptional $Cu_{15}[Cu(CN)_n]^{1-n}$ complexes were calculated. The analysis of the calculated free energies of the surface complexation processes shows that only [CuCN] and $[Cu(CN)_2]^-$ species can exist in the direct contact with the electrode surface, whereas $[Cu(CN)_4]^{3-}$ and $[Cu(CN)_3l^{2-}$ have tendency to decreasing the coordination number with their transformation into the $[Cu(CN)_2]^-$ complex. On the base of these results one can conclude that this particle takes part directly in the discharge on the electrode surface.

Basing on the quantum-mechanical theory of charge transfer in polar media, we calculated the outer-sphere and inner-sphere contributions into the reorganization energy and estimated the activation energy for the elementary act of the outer-sphere electron transfer The activation energy we calculated is very large in comparison with available experimental data on the Cu(I) discharge. For this reason, the possibility of an alternative mechanism of discharge was considered, namely, the transfer of the heavy particle (the central copper ion) along the adiabatic potential curve describing the interaction of the complex ion with the electrode surface. As the effective reaction coordinate, the distance between the central copper ion and the electrode surface was chosen. For every fixed values of this parameter, the

geometry structure of the inner shell of the complex under study was completely optimized. On the potential curve obtained by such a way, an energetical barrier is observed. The height of this barrier is remarkably lower in comparison with the activation energy estimated for the outer-sphere electron transfer. This fact allows to conclude that such mechanism may be more preferable compared with the outer-sphere electron transfer mechanism. One of the possible reasons for a relatively low barrier on the potential curve is probably the high affinity of the cyanide ions to the copper electrode, which compensates to some extent the energetical losses caused by a partial dehydration of the reduced complex on its way from the bulk of solution to the final state of discharge.
This work was supported by the RFBR (grant No. 00-03-32140).

OPTIMIZATION OF GEOMETRY OF TRIATOMIC MOLECULAR COMPLEXES Ag3, Ag3^{+}, Ag^{+2}: AB INITIO CALCULATIONS

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A knowledge of geometrical and electronic structure of triatomic molecular complexes Ag3, Ag3^{+},Ag3^{+2} is the key to understanding a process of radiophotoluminescence in the irradiated silver-doped phosphate glasses. The matter is that in some models of the defect formation process in the said glasses these triatomic complexes on exposure to ionizing radiation are anticipated to be radiophotoluminescence centers. Before proceeding to study these impurity centers in crystals or glasses we were faced with a more simple problem - an investigation of geometry and electronic structure of complexes Ag3, Ag3^{+}, Ag3^{+2} in a free state. The aim of the present paper is a solution of the said problem. With this in mind we undertaken for Ag3-species the ground-state ab initio calculations. Three groups of methods were used, namely, density functional methods, different variants of Hartree-Fock (HF) method (RHF, ROHF, UHF, HF+MP2), and Multiconfiguration Self-Consistent Field (MCSCF) methods (CASSCF, RASSCF). In course of the HF and MCSCF calculations with the use of the GAMESS code we implemented 11-electron semilocal Relativistic Effective Core Potential (RECP) for Ag atom, that was constructed with the help of 5s, 5p and 4d orbitals with 1s2-4p6 core, and was checked by the RASSCF calculations of spectroscopic constants and low-lying electronic states of Ag2, and Ag2^{+} molecules in our previous papers (Optics and Spectroscopy, Vol.84,No.3,1998,pp.307-312; Vol.87,No.6,1999,pp.877-887). For Ag atom RECP was obtained from numerical Hartree-Fock-Dirac (HFD) calculations for the state that is an average over the nonrelativistic [...]4d^{10}5s^{0.5}5p^{0.5} configuration with [Kr] as an inner core. In more exact terms we used in our nonrelativistic calculations within the framework of LS coupling the spin-averaged component of RECP, called AREP, which takes into account all relativistic effects contained in the HFD equations, except for the spin-orbit interaction. Numerical AREP pseudo-valence orbitals needed for molecular calculations were obtained in HF calculations with this AREP component of RECP and approximated by Gaussian Type Orbitals (GTO). The HF and MC SCF calculations were carried out using partially contracted GTO basis set (4s3p3d)/[3s3p3d], presented in our previous paper. In our calculations linear and triangle geometries of Ag3-species were investigated. In the process of the geometry optimization the

arbitrary triangle was used as a starting geometry along with the equilateral triangle and isosceles triangle. Apart from calculations without any symmetry restrictions in some cases the spatial symmetry corresponding to the point groups C3v, C2v and Cs was explicitly taken into account. Where it was possible our results were compared with the experiment and the results obtained by other authors. The present work was supported by the Russian Foundation for Basic Research (grant N 00-03-33040).

ELECTRONIC STRUCTURE OF SIO2: AB INITIO MULTIDETERMINANT METHOD WITH LOCALIZED ORBITALS WITHIN A QUASI-COMPLEX APPROACH

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An ab initio LCDLO (linear combination of determinants with localized orbitals) cluster approach to calculate the electronic structure of SiO2 is proposed. A cluster which can represent the solid is chosen and its wave function is written as a linear combination of Slater determinants built up of nonorthogonal pseudo-valent orbitals localized at different atoms. The determinants under consideration correspond to the various schemes of the chemical bonding including also the ionic schemes. The many-electron states of this cluster are found with the help of CI procedure which reduces to solving a generalized eigenvalue problem. The proposed approach includes a new kind of cluster \"boundary conditions\" applicable to covalent as well as to ionic-covalent solids with tetrahedral bonds. In order to avoid the artificial saturation of dangling bonds by hydrogen atoms or by additional electrons, the hybridized AO\'s (HAO\'s) directed outside the cluster are considered together with HAO\'s \"belonging to the cluster\", however in another way than HAO\'s \"belonging to the cluster\". The potential of a boundary atom is written in the form including so-called \"charges on HAO\'s\", which are defined as Mulliken charges in the Hartree-Fock method or in terms of the bond-order matrix and the non-orthogonality matrix in the LCDLO method. It allows one to obtain the mean values of atomic charges in glass in the course of multideterminant self-consistent ground-state calculations of quasi-complex (cluster with the said \"boundary conditions\"). The method proposed has the well defined advantages. It makes the selection criteria of the most important configurations physical and transparent as compared with CI MO LCAO method. Besides, the LCDLO approach is particularly suited for description of the defect-related processes in SiO2. Indeed, first, it gives a correct behaviour of adiabatic curves at large atomic displacements as opposed to the Hartree-Fock method. Second, the use of localized nonorthogonal basis within a cluster approach is especially natural for dealing with point defects, as their wave functions are usually highly localized. And finally, the approach proposed is useful for the disordered systems investigation. For example, together with a concept of glass-forming complex unit (I.V.Abarenkov et al., Phys.stat.sol.,1970, v.A2, pp.865-873) it makes the simulation of diagonal disorder straightforward. Two interesting problems were considered using the LCDLO quasi-complex approach. The first problem is the analysis (in terms of the valence-bond-schemes weights) of the genealogy of the ground and excited states related to the peaks in optical absorption spectrum of SiO2. Another problem is a study of the angular stability of Si-O-Si bridge in silica. The LCDLO

calculations for both problems were performed within the simple model of a chain quasi-complex Si_{1/4} - O - Si_{1/4} in the minimal basis set. The results of calculations show that the ionic configurations Si^{+1}-O^{-2}-Si{+1} and Si^{+0.5}-O^{-1}-Si{+0.5} are dominant for the ground state term. As for excited states, the covalent configurations Si^{0}-O^{0}-Si{0} became appreciable as they may contribute up to a 30 percents to the calculated value. The results obtained for the bridge stability predict bending to an equilibrium angle of approximately 130 degrees with an energy gain of approximately 1.1 eV. This work was supported by Russian Foundation for Basic Research (grant N 00-03-33040a).

ВЫСОКОПРОИЗВОДИТЕЛЬНЫЕ ВЫЧИСЛЕНИЯ В ХИМИИ: СОВРЕМЕННЫЕ ТЕНДЕНЦИИ

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Рассмотрено современное состояние и перспективы использования высокопроизводительных вычислительных систем для исследований в различных областях химии и некоторых смежных областях науки, в частности, биохимии. Дана краткая характеристика состояния в области высокопроизводительных вычислений для химии в России.

Проанализированы тенденции развития процессоров различной архитектуры (векторных, CISC,RISC, VLIW) с точки зрения их производительности при решении задач вычислительной химии, в частности, квантовой химии. Рассмотрены преимущества и недостатки различных архитектур суперЭВМ (PVP, SMP и ccNUMA, MPP). Доступные в настоящее время технологии связывания узлов кластеров сопоставлены с аналогичными архитектурными элементами суперЭВМ. Обсуждены, в частности, результаты измерений производительности работы стека протоколов TCP/IP поверх Fast Ethernet при использовании ОС Linux. Сделан вывод о перспективности применения кластеров, в частности, для задач квантовой химии.

Показано, что основной проблемой кластеров является эффективность распараллеливания соответствующих программ. На основе оригинальных результатов и литературных данных проведен анализ современного состояния с распараллеливанием программ в области квантовой химии и молекулярной динамики. Проведено сопоставление различных моделей (общего поля памяти и обмена сообщениями) и инструментальных средств распараллеливания (типа OpenMP, MPI, Linda и т.д.).

Сделан вывод, что для расчетов больших и сверхбольших молекулярных систем, актуальных для многих задач химии и биохимии (протеины и ДНК, нанотехнологии и проч.) необходима разработка принципиально новых специализированных расчетных схем полуэмпирической и неэмпирической квантовой химии. Показано, что перспективными (в т.ч. с точки зрения распараллеливания) для неэмпирических и полуэмпирических расчетов сверхбольших, в первую очередь биологических, молекулярных систем являются методики, основанные на использовании локализованных орбиталей, разрабатываемые в Центре компьютерного обеспечения химических исследований ООТХ РАН.

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КОМПЬЮТЕРНОЕ МОДЕЛИРОВАНИЕ КИНЕТИКИ ГЕТЕРОГЕННЫХ ПРОЦЕССОВ В ХИМИЧЕСКИХ СИСТЕМАХ МЕТОДОМ ВЕРОЯТНОСТНОГО КЛЕТОЧНОГО АВТОМАТА

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Построение комплексной модели сложной гетерофазной химической системы в рамках классического подхода, т.е. с помощью дифференциальных уравнений, содержит ряд трудностей, связанных, в первую очередь, с разнообразием физико-химических процессов. Кроме того, гетерофазные химические системы являясь многокомпонентными, могут включать широкий спектр низко- и высокомолекулярных атомно-молекулярных комплексов, что значительно усложняет решение дифференциальных уравнений. Следует отметить, что не только аналитическое, но и численное решение такой системы дифференциальных уравнений представляет значительные трудности. Поэтому для моделирования сложных гетерофазных химических систем необходимо использовать аппарат, более приспособленный для решения такого рода задач. Этот аппарат можно получить, используя клеточные автоматы.

Клеточные автоматы позволяют изучать кооперативное поведение – важную составную часть физики и химии конденсированных систем. При моделировании гетерофазных систем методом клеточного автомата рассматриваемая система разбивается на сеть ячеек. Состояние каждой ячейки характеризуется целым числом, которое указывает на заполненность ячейки или на тип молекулы, содержащейся в ней. Рассматриваемые состояния ячеек изменяются синхронным образом через дискретные интервалы времени в соответствии с локальными вероятностными правилами, которые могут зависеть от состояния переменных в соседних узлах и не меняются со временем. Локальность законов поведения и дискретность переменных позволяют естественным образом учитывать флуктуации или внутренние шумы системы без каких-либо дополнительных предположений.

В разработанной методике моделирования все физико-химические процессы делятся на две группы: процессы взаимодействия ячеек с внешней средой и процессы взаимодействия ячеек между собой. Процессами взаимодействия ячеек с внешней средой являются адсорбция, десорбция и радиационное возбуждение. Процессами взаимодействия ячеек между собой являются диффузия и химические прецессы.

Приведенный набор физико-химических процессов, разумеется, не является полным. При решении конкретных задач в этот список могут быть добавлены новые факторы, что приведет к еще большему уточнению результатов моделирования.

Результатами компьютерного моделирования гетерофазных химических систем методом вероятностного клеточного автомата являются пространственные и временные картины распределения концентраций компонент химических соединений в исследуемой системе. Результаты моделирования могут быть представлены в наглядной форме, удобной для дальнейшего использования.

В результате проведенного исследования нами разработана методика моделирования сложных гетерофазных химических систем методом вероятностного клеточного автомата; создана компьютерная программа, позволяющая моделировать

сложные гетерофазные химические системы на основании совокупности физико-химических факторов.

THE SOLVENT EFFECT MODELING OF THE VIBRATIONAL SPECTRUM OF HYDROGEN SULFIDE

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The vibration spectrum of hydrogen sulfide in water was simulated by different quantum chemistry approaches. According to the Raman spectra of the hydrogen sulfide solution the stretch vibration frequencies have a red shift (~ 26 cm-1) with respect to gaseous phase data. Both continuum (SCRF, PCM) and discrete models of solvent were considered. Ab initio calculations were carried out at SCF and MP2 level with aug-cc-pDZV basis set. The approaches based on the continuum solvent model could not simulate the blue shift for the bend frequency and predict small red shifts for all vibration frequencies. On the contrary, modeling solvent effect on the basis of H2S…H2O cluster treatment (with only one water molecule) leads to qualitatively correct shifts of hydrogen sulfide vibration frequencies in both direct ab initio calculations and within the effective fragment potential model (EFP). The EFP model based on the simulating the solvent molecule by some effective potential (such as multipoles, polarization and repulsive points) allowed consideration of the large size clusters up to H2S. 38H2Oeff. The molecules H2S. nH2Oeff (n=1,2,4,12,38) were calculated and the exact agreement with the experimental shift take place for the case n=4. The results are quite stable with respect to the increase of number of water molecules in hydrate shell model. (RFBR 01-03-32116).

DIASTEREOMERIC COMPOSITION OF 1,2-DIHYDROHETERINES

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As a rule, nonplanar 1,2-dihydro monoheterines and 1,2-dihydro-1,2-diheterines with pyramidal het-eroatom(s) have as a minimum two types of chirality elements: chirality centre(s) (one or two asymmetric pyramidal heteroatoms) and three chirality planes describing the torsions of six member cycle (it is con-venient to describe these torsions in the terms of helicity). So these heterocycles can exist in the form of a few diastereomeric conformers. We have estimated conformational composition of some 1,2-dihydroheterines and 1,2-dihydro-1,2-diheterines. Calculations in more full basis sets as well as with due regard to an electronic correlation re-sult in localization of a greater number of conformers. For instance 1,2-dihydropyridine has planar N atom according to 3-21G basis set calculations, so this molecule can be realized as only 8 different con-formers, i.e. 4 enantiomeric pairs (diastereomers). Nevertheless only one diastereomer has been localized as energy minimum. According to 6-31G(d) calculations, N atom is pyramidal, so 16 conformers (8 di-astereomers) are possible, but again only one enantiomeric pair has been

localized. Only MP2/6-31G(d) calculations localize two different diastereomeres of 1,2-dihydropyridine. Similarly, the calculations of 1,2-dihydropyridazine in the 3-21G and 6-31G basis sets result in localization of only one diastereomer, the calculations in the basic sets 6-31G(d), 6-311G(d), 6-31+G(d) give two diastereomeres, and the MP2/6-31G(d), MP2/6-311G(d), MP2/6-31+G(d) calculations result in three diastereomeres. The same is true for 1,2-dihydro-1,2-diphosporine. Diastereomeric composition of 1,2-dihydrophosphorine doesn't depend on the basis set: all above sets without or with MP2 give two diastereomeres. Such independence is also true for 1,2-dihydro-1,2-azaphosphorine (one diastereomer, N is planar), as well as for its substituted analogues, such as 1-methyl-, 2-chloro-, 1-methyl-2-chloro-: only one di-astereomer hem has been localized for all of them. The same is true for 1,2-dihydro-1,2-oxaphosphorine systems. The attempts to localize new diastereomeres with inverted P atom and not inverted cycle, by means of starting from such guess geometry, resulted not in the corresponding new diastereomeres, but in the enantiomeres of the structures, localized earlier, the cycle being inverted relative to the guess geome-try. Similarly the narcissistic reaction of enantiomerization of one enantiomorph of 1,2-dihydro-1,2-azaphosphorine to another via chiral transition state represents inversion of the cycle, but not the P atom inversion. The attempts to restrict this inversion and to localize different diastereomers by the flanking the 3,4-, 4,5-, 5,6-, 6,1- bonds in the cycle by two methyl and fluoro substituents failed as well as the flanking of 3,4-, 4,5-, 5,6- bonds by two chloro substituents. Only the flanking the most short C–N (6,1-) bond by two chloro substitutients was successful and the second diastereomer of 1,2-dihydro-1,2-azaphosphorine system has been localized.

UNCONVENTIONAL CONSIDERATION OF THE SYMMETRY PROPERTIES. NEW TECHNIQUES AND COMPUTER CODES. APPLICATION FOR HIGH-TEMPERATURE SUPERCONDUCTORS

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The conventional technique for solving the equations of quantum chemistry is untraditionally extended to the structures possessing certain symmetries. This proposal allows to release the unoccupied electronic states located lower than the ground state Fermi level of a specific system. Application of this technique, in particular, when calculating the electronic structure of the HTSC-compound YBa2Cu3O7-x ($0 < x < 1$) results in the following. The above-mentioned unoccupied electronic states of high spatial localization are found, being located, mainly at the Py- orbitals of the apex oxygens. These orbitals overlap and form linear chains which are parallel to the known Cu(1)-O chains, disappearing when x is closed to 1. One can suppose, that the linear chains of such overlapping states form a «superconducting channel». Some other parameters related closely to the critical characteristics of HTSC-materials are also calculated. The calculations show that «the superconducting channel» is broken when the oxygen chain atoms O(1) are removed ($x > 0$).

SIMPLIFIED MODELS OF INTERMOLECULAR INTERACTIONS OF LARGE SYSTEMS

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Some computational techniques for estimating intermolecular interaction (IMI) energies are considered in the framework of density matrix formalism. One of the general problems is an evaluation of the Hamiltonian matrix elements in the basis set involving strongly orthogonalized wavefunctions of separated molecules. It is shown that calculations on typical charge-transfer states may easily be performed if using the so-called Dyson orbitals and geminals in the spin-free formulations given in ref.[1]. Some more general operator constructions pertinent to IMI problems are discussed as well. A new quantum-mechanical scheme is proposed for estimations of dispersion interactions and transfer matrix elements of electronic excitations. The key step in the implementation of the scheme is the use of singular value decomposition for matrices of the two-electron operator responsible for interactions between two molecules [2]. Thus obtained decomposition contains only few leading terms having asymptotics of conventional multipole terms. It turns out that the first of these terms (a quasi-monopole term), usually ignored by conventional approaches, may give a marked contribution to the transfer amplitudes. Within this technique some calculations on pi-systems of aromatic molecules and fullerenes are performed. A quite simple scheme for estimating nonexpanded dispersion energy for large molecules is also given. It is based on average excitation energy approximation and a semiempirical method which reduces the problem to a suitable form via the Wiberg bond indices.The latter are approximated by a topological matrix for sigma-bonds and by Hueckel's bond orders for pi-bonds [3]. The method is illustrated by calculating two- and three-body dispersion energies for fullerenes and carbon nanotubes. In this vein the problem of chirality recognition in IMI processes is treated on the base of the Goossens model. Satisfactory correlations of the proposed dissymmetry pseudoinvariant with twisting power of the chiral molecules in nematics are reported. REFERENCES: 1. A.V.Luzanov, V.V.Ivanov, I.V.Boichenko, J. Mol. Struct. (Theochem), 360 (1996) 167. 2. A.V.Luzanov, A.D.Bochevarov, Khim. Fisika, 19, No 10 (2000) 21. 3. A.V.Luzanov, L.N.Lisetski, Zh.Struct. Khim., 42 (2001).

THE VARIATIONAL SOLUTION OF THE NUCLEAR DYNAMICS PROBLEM FOR LARGE AMPLITUDE MOTION IN THE MkXO4 (k = 1, 2) MOLECULES

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The MReO4 and M2XO4 (M = Li, Na, K; X = S, Se, Te, Cr, Mo, W) molecules were studied at the CISD+Q level of theory. The calculations have shown that the molecules are non-rigid systems with a hindered rotation of the alkali metal cations M+ with respect to the (XO4)^k- moiety. The nuclear dynamics problem was solved for some of the MReO4 and M2XO4 molecules. The effective Hamiltonian was constructed using the adiabatic separation of the M+ intramolecular motion and the (XO4)^k- vibrational motion. The potential energy was

expressed as a function of the polar coordinates which define the position of the M+ cations with respect to the(XO4)^k- anion. The radial and angular parts of the potential function were constructed by fitting the ab initio data to a series expansion in the basis set of the symmetry-adapted spherical harmonics and, in the case of M2XO4 molecules, with the inclusion of a term corresponding to the Coulomb interaction between the two M+ cations. The matrix of the effective Hamiltonian was set up and diagonalized in the basis set of the functions which are products of the harmonic oscillator and rigid rotor eigenfunctions. The energy levels, the transition dipole moments, and the state-averaged geometry parameters were calculated. This work was supported by the Russian Federation Education Ministry, Grant N 97-0-9.1-262.

QUANTUM-CHEMICAL INVESTIGATION OF THE SUBSTITUTION OF CH3COO- -GROUPS BY BIS-ARSINES IN THE ACETATE COMPLEXES OF RH(II)

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It is well known from the literature [1-3], that the substitution reactions of $Rh_2(OAc)_4(H_2O)_2$ are accompanied by the elimination of axial water molecules. The attempts to substitute the acetate groups lead to the destruction of complexes [4,5]. In the present study we have investigated the bis-arsines as bidentate ligands, which on principle can substitute the acetate groups. At the same time, they can play the role of a reducing agent in the redox transformations of Rh(II).

The geometry optimization of the initial acetate complex of Rh(II) and of supposed structures which can be formed in the course of substitution of water molecules and acetate ligands have been carried out by means of the density functional method (B3LYP version) using the standard 6-31G(d,p) basis set. The calculations were performed using the GAUSSIAN 98 [6] program package. As a model ligand, the bis-arsinomethane ($H_2AsCH_2AsH_2$ or dam) was chosen for simplicity. The obtained geometrical parameters are in good agreement with available crystallographic experimental data.

The calculations showed that the energetically most preferable is the dissociative substitution of the two water molecules by bis-arsine ligands

$$[Rh_2(CH_3COO)_4(H_2O)_2] + 2(AsH_2)_2CH_2 = [Rh_2(CH_3COO)_4(\{AsH_2\}_2CH_2)_2] + 2H_2O$$

with the enthalpy of 51.2 kJ/mol. The calculated enthalpy of the successive substitution of the two acetate ligands by bis-arsines is equal to 107.8 and 266.7 kJ/mol, correspondingly. The first value is not a large, and one may assume that this reaction can be realized at the certain conditions of the synthesis, e.g. in polar solvents. The substitution of the second acetate ligand is less probable from the viewpoint both of the energetics and steric factors.

The calculational conclusions were confirmed experimentally. We have investigated the interaction of the Rh(II) acetate with bis-(diphenylarsino)alkanes

$Rh_2AsCH_2AsRh_2$(dam); $Rh_2As(CH_2)_2AsRh_2$(dae); $Rh_2As(CH_2)_4AsRh_2$(dab).

As a result of these investigation, the following compounds were synthesized:

$Rh_2(CH_3COO)_2$(dam)$(OH)_2$; $[Rh_2(CH_3COO)_4(dae)]_n$; $[Rh_2(CH_3COO)_4(dab)]_n$.

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СОВРЕМЕННАЯ МОДЕЛЬ КОМПЬЮТЕРНОГО ОБЕСПЕЧЕНИЯ ХИМИЧЕСКИХ ИССЛЕДОВАНИЙ

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Данная работа посвящена совершенствованию модели компьютерного обеспечения химических исследований с учетом, как современных достижений информационных технологий, так и новых тенденций в использовании информационных, вычислительных и телекоммуникационных ресурсов в области химии.

В работе проводится анализ эволюции в течение последнего десятилетия концепции компьютерного обеспечения как естественнонаучных исследований в целом, так и химических исследований в частности. Для этой цели наряду с привлечением опубликованных в литературе данных используется обобщенный опыт функционирующего на базе ИОХ РАН Центра компьютерного обеспечения химических исследований (ЦКОХИ ООТХ РАН) в области применения высокопроизводительных вычислений и телекоммуникационных технологий для решения исследовательских задач.

Результаты анализа позволили выявить ряд характерных тенденций в компьютерном обеспечении естественнонаучных исследований. В частности, они показывают, что в последние годы наряду с автоматизацией экспериментальных работ и использованием средств вычислительных техники для проведения вычислительного эксперимента сформировались и интенсивно развиваются два новых направления: высокоэффективные распределенные мультимедийные информационные системы (в том числе электронные библиотеки) и системы обеспечения функционирования территориально распределенных коллективов. В работе отмечается особое значение последнего направления для российской науки, и подробно излагаются результаты работ ЦКОХИ по созданию соответствующих технологий и систем.

В работе также анализируется причины, по которым за последние пять лет, при сохранении общей положительной динамики, произошло относительное, по сравнению с другими науками, понижение уровня компьютерного обеспечения химических исследований. Делается вывод о необходимости формирования новой концепции компьютерного обеспечения химических исследований, и определяется, какие именно из новейших достижений в области информационных технологий могут послужить технической основой этой концепции. В частности описываются результаты работ в области создания специализированных вычислительных ресурсов и специализированных телекоммуникационных инфраструктур.

НОВЫЕ ТЕХНОЛОГИИ ТРЕХМЕРНОГО ПРЕДСТАВЛЕНИЯ ОБЪЕКТОВ В ПУБЛИКАЦИЯХ ПО ХИМИИ В ИНТЕРНЕТЕ

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Для публикации химической информации ключевую роль играет представление трехмерных объектов - молекулярных и кристаллических структур. Для понимания теоретических понятий некоторых разделов химии, например кристаллохимии, общение с трехмерными объектами оказывается необходимым, а представление в трехмерном виде экспериментальных результатов может позволить сделать новые выводы. С развитием сети Интернет и ростом объема размещаемой в ней химической информации растет и потребность в использовании интерактивных трехмерных иллюстраций в публикуемых в Сети материалах.

В настоящее время используется очень немного инструментов трехмерной визуализации химических объектов в Интернете. В основном это - программа Chime компании MDL Information Systems, предназначенная для просмотра молекулярных объектов; язык виртуальной реальности VRML – более универсальное, но менее распространенное из-за трудоемкости средство, и еще более редкие Java апплеты. Однако, в связи с растущими потребностями электронной торговли, все более охватывающей Интернет, в последнее время были разработаны новые универсальные технологии трехмерной визуализации объектов в Сети. Выбрав две наиболее перспективных технологии, VET компании Viewpoint и Cult3D компании Cycore, мы опробовали их для решения химических задач.

На примерах интерактивных иллюстраций к курсу стереохимии, визуализации динамики элементарного акта реакций изомеризации и внутримолекулярной вращательной подвижности фрагментов молекул, в настоящей работе представлен опыт применения авторами указанных технологий. Обе технологии характеризуются универсальностью, интерактивностью, способностью к сопряжению с другими мультимедийными форматами, а также очень высоким качеством формируемого изображения. С одной стороны технологии практически снимают ограничения с реализации идей автора публикаций, с другой стороны – сам процесс визуализации достаточно трудоемок. В связи с этим в данной работе обсуждается вопрос о выборе технологий визуализации для решения конкретных химических задач, оцениваются перспективы использования новых технологий.

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CATEGORIZATION OF VISUALIZATION TOOLS IN ASPECT OF CHEMICAL RESEARCH AND EDUCATION

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Chemistry is an experimental science. The subject of its research is not often directly available within close dimensions of time or space. To optimize the research and teaching process it is required to analogize or visualize phenomena, processes or objects. In effect visualization is significant to problem solving. In the last years in the Laboratory of Chemical Education at Adam Mickiewicz University in Pozna? the research was undertaken. The main aim of the research was to determine educational effectiveness of different types of chemical visualization. The methods of visualization of chemical issues were worked out. A series of original video and animation sequences presenting different aspects of chemical visualization were prepared. Interactive Internet Instructions Sets were prepared. Methods of visualization were categorized. The effectiveness of use of different types of chemical visualization was estimated. The main aspect of visualization is obviously its application to teaching or research. Thus the choice of techniques depends on whether it is used for recognition, explanation, memorization, inspiration or motivation. In the research the importance as well as area of usefulness of three main categories of visualization was also established. These categories are: illustration - relating to the presentation of an existing picture of object; representation - the presentation of an image assigned to an object; visualization - related to the presentation of an image created for the object. Research work on preparing visualization means confirms that depending on the particular aspect of categorizing visualization, it may be useful, as well, to assign additional criteria such as dimensions, degree, functions, methodological contexts, experimental relationship and mediality of visualization.

THEORETICAL INVESTIGATION OF THE METATHESIS REACTION OF ALKANES CATALYZED BY SUPPORTED TRANSITION METAL HYDRIDE COMPLEXES

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The activation of alkanes by transition metal hydride complexes immobilized on a SiO2 surface was considered theoretically using ab initio quantum chemical calculations. The active site of these catalytic systems was modeled by (H4Si2O5)O2Ta(III)R and (H4Si2O5)O2Ta(V)RR\'R\'\' clusters (R = H, Me, Et; R\', R\'\' = H). The geometrical and electronic structure of these clusters was examined using ab initio quantum chemical calculations at the B3LYP level. The interaction of C2H6 with the hydride active site modeled as (H4Si2O5)O2Ta(III)H and the reaction path of the formation of the (H4Si2O5)O2Ta(III)(Et) complex in this reaction were studied in detail. Two possible mechanisms were considered. The first mechanism involves the direct transfer of the migrating hydrogen atom from C2H6 to the hydride ligand through a four-membered transition state to form molecular hydrogen (one-step mechanism). The second mechanism

consists of two steps. The first step is the oxidative addition of C2H6 with the formation the (H4Si2O5)O2Ta(V)(Et)(H)(H) dihydride ethyl intermediate, and the second step is the reductive elimination of molecular hydrogen from the dihydride complex. Various isomer structures of the (H4Si2O5)O2Ta(V)(Et)(H)(H) dihydride ethyl intermediate complex were considered. One of these intermediate structures corresponds closely to the tentative structure of the four-membered cyclic transition state postulated within the first mechanism. Therefore, the entire reaction proceeds through the two-step mechanism rather than the one-step four-center mechanism postulated in the literature.

СИСТЕМА ЭФФЕКТИВНОГО ИСПОЛЬЗОВАНИЯ ИНДИВИДУАЛЬНЫХ И КОЛЛЕКТИВНЫХ ВЫЧИСЛИТЕЛЬНЫХ РЕСУРСОВ В НАУЧНЫХ ИССЛЕДОВАНИЯХ. ПРОЕКТ “ПЕЛЕТОН

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Доклад посвящен анализу системы эффективного использования индивидуальных и коллективных вычислительных ресурсов в научных исследованиях. Особое внимание уделено рассмотрению следующих вопросов:

- Вычислительные кластеры на Linux в химии и биоинформатике: перспективы использования.
- Функции и задачи системы «Пелетон»
- Построение информационной системы для совместной работы сотрудников с данными, документами и отчетами.
- Организация централизованного механизма для доступа и поиска информации вне зависимости от местоположения хранения данных и формата их представления.
- Объединение разнородных компьютеров и платформ в единую информационную среду.

TO MODELING OF VIBRONIC INTERACTION AND CHAOTIC DYNAMICS IN ELECTRONIC AND NUCLEAR SUBSYSTEMS OF MOLECULES

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One of the simplest variant of description of vibronic interaction (VI) in molecular systems is the account of shift equilibrium position their nuclear oscillators at transition of an electronic subsystem from basic born-oppenheimer state in exited state. At such account VI do not consider as a possible source chaos of molecular dynamics. Classical analogue such VI, as it is easy to show, is the interaction between electronic and nuclear oscillators, caused by nonlinear (cubic on product of their coordinates) coupling, which efficiency is characterized

in some parameter a. The nonlinearity of the appropriate equations of movement of such coupled classical oscillators system under some conditions of their excitation, as is known, causes chaos of their dynamics. In the present work the study of dynamics of such system is carried out at action on it quasiharmonic force with using of results of the numerical solution of the appropriate equations of movement, and also of appropriate quantum-classical system, in which the electronic subsystem is considered as quantum oscillator, and nuclear - as classical oscillators with above mentioned shift S. It is shown, that at condition S=aA2 (where A – «zero amplitude vibrations» of the quantum electronic oscillator) intensity of Raman line for above mentioned systems (the reflecting efficiency VI in these systems) is identical, and their dynamics does not contain elements of chaos at an irradiation by weak enough light fields. The criteria of an opportunity of occurrence chaotic dynamics of such systems under certain conditions of their excitation are established. This work was supported by RFBR, project no. 00-03-32957 and 00-15-97307.

GENERALIZED RELATIVISTIC EFFECTIVE CORE POTENTIAL AND RELATIVISTIC COUPLED CLUSTER METHODS FOR PRECISE ELECTRONIC STRUCTURE CALCULATIONS. CALCULATIONS ON MERCURY HYDRIDE AND ITS ION

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The Relativistic Effective Core Potential (RECP) method is most intensively used in a few last decades for electronic structure calculations on molecules containing heavy atoms because it allows one to reduce drastically computational efforts with respect to the corresponding all-electron calculation. In paper [1], the generalized RECP (GRECP) was generated for mercury and was tested in numerical two-component Hartree-Fock calculations by comparison with all-electron Dirac-Fock and other RECP calculations. The suitability of the GRECP for describing the correlation effects was examined in atomic calculations [2]. Significant improvement of accuracy in reproducing the all-electron Dirac-Coulomb data for the GRECP as compared with the tested RECPs of other groups was demonstrated in these calculations. The same number of electrons, 20, is explicitly treated in the considered RECP versions. Therefore, comparison of accuracy for these RECPs is correct. In turn, the coupled cluster (CC) method is one of the most powerful approaches for precise correlation structure calculations of atoms and molecules. Important advantages of the CC method include size-extensivity and straightforward summation of some high-order perturbation theory diagrams. In the present report, the GRECP and Relativistic CC (RCC) methods are discussed for the case of electronic structure calculations on the HgH molecule [3]. The calculated spectroscopic constants are compared with experimental data and results of calculations of other groups. Errors of the performed calculations are analyzed. The magnitude of the Basis Set Superposition Errors (BSSE) is estimated and discussed. [1] N.S.Mosyagin, A.V.Titov, Z.Latajka, Int.J.Quant.Chem. 63, 1107 (1997). [2] N.S.Mosyagin, E.Eliav, A.V.Titov, U.Kaldor, J.Phys.B 33, 667 (2000). [3] N.S.Mosyagin, A.V.Titov, E.Eliav, U.Kaldor, E-print: http://xxx.lanl.gov/abs/physics/0101047 .

QUANTUM CHEMICAL JUSTIFICATION OF EMPIRICAL MODEL OF TRANSANNULAR INTERACTION IN SILATRANES

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Considerable interest in chemistry of silatranes primarily depends upon the fact that some of these compounds possess high and specific biological activity. At the same time structure of silatranes is quite interesting by itself. Relying on available experimental data on electronic and spatial structure of 1-substituted silatranes $XSi(OCHRCH_2)_3N$, we proposed an empirical orbital $n\sigma^*$-model of transannular interaction N→Si in endo-silatrane. According to this model the equilibrium distance between azote and silicon atoms in gas phase is determined by competition of the strain energy of silatrane structure and the energy of $n\sigma^*$-interaction between lone electron pair of azote atom and fragment Si-X.
In order to verify the proposed $n\sigma^*$-model, the semiempirical (PM3) and nonempirical (MP2/3-21G//MP2/3-21G) calculations of some 1-substituted silatranes have been performed. Localized orbitals and potential curves of inversion of azote atom have been constructed for all structures being tested. Systematical study of the influence of different factors (electronic structure method, method of geometry optimization, basis set) on the degree of interaction between azote atom and fragment Si-X has been carried out on the nonempirical level of theory. It has been demonstrated that in isolated molecules of silatranes the increase in the rings strain prevents from the formation of the coordination bond N→Si, and there exists only a weak nonvalent interaction of the $n\sigma^*$ type. These results confirm the $n\sigma^*$-model and correlate with its propositions concerning the gaseous state molecules.

THE INVESTIGATION OF THE REACTION PATH OF THE N,N\'-DIPHENYLGUANIDYNE WITH THE DIMETHYLPHOSPHORIC AND DIETHYLPHOSPHORIC ACIDS

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Recently, we have reported quantum-chemical calculations of N,N\'-diphenylguanidynic salts of dialkylphosphoric acids [1, 2]. These compounds are of great interest because they are widely used in rubber tire industry. In the present work, we have carried out quantum-chemical PM3 calculations to the study of reactions of dimethylphosphoric (DMPA) and diethylphosphoric (DEPA) acids with N,N\'-diphenylguanidyne (DPG). Initially, for each of the reactions under study we calculated the structures of separated reactants and after that the both reactants were combined into a prereactional complex. At the second step, the same algorythm was used for the products of the reaction. The transition states were searched by the method of a linear synchronous transit in the case of DMPA...DPG and by the EF method for DEPA...DPG. Basing on these calculations and the results of IRC calculations the potential energy curves and dependencies of most significant interatomic distances as functions of a reaction coordinate were built. The most significant changes are observed for

the distances between the nitrogen atoms of NH-group of DPG and for polarized bonds in dimethyl- and diethylphosphoric acids. Note, that the potential energy curve for the reaction of diethylphosphoric acid with DPG is characterized by a remarkable bend on the way from the reactants to the transition state which can be explained by the influence of steric factors caused by the presence of the methyl group in the vicinity of the reaction center which leads to a delay in the formation of the transition state. The energetical characteristics allowed to calculate the activation energy and the corresponding equilibrium constant K= of the transition state. The obtained values $K^{=} = 7.87 \cdot 10^{-4}$ for DMPA and $5.7 \cdot 10^{-6}$ for DEPA and DPG demonstrate a reversible character of the reactions mentioned above and correlate with available data for transition states of reactions with participation of organic molecules [5].

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QUANTUM-CHEMICAL STUDY OF THE CONDENSATION REACTIONS WITH PARTICIPATION OF p-DIMETHYLAMINOBENZALDEHYDE

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The analytical method of the detection of dimethyldioxane (DMD) in the air is based on its interaction with p-dimethylaminobenzaldehyde. However, it is known from available experimental data, that besides of DMD there is more than 20 substances which can react with p-dimethylaminobenzaldehyde [1]. Dimethyldioxane is the substance with a narcotic effect, possesses cumulative properties and influences on the liver and kidneys, causing irreversible processes. That is why, the analytical control of its content in the air is of great importance. It should be noted that the study of the actual influence of a number of by-products on the results of analysis and also of the concentration range at which their influence is essential, is a rather complicated problem from the experimental viewpoint. We believe that the use of quantum-chemical approaches can be useful for the elucidation of some details of the problem mentioned above. In this communication we report quantum-chemical results on the condensation reactions of p-dimethylaminobenzaldehyde with a number of organic compounds. The thermodynamic parameters, the structures of transition states and the activation energies were calculated on the B3LYP level. The calculational results are analysed in detail and some of them may be recommended for working out analytical methods directed at the increase of the selectivity and accuracy of the analytical control of the content of dimethyldioxane in the air based on the accessible reactants and means of measurements. **Bibliography:**I.M.Korenman, Photometricheskii analiz. Methody opredelenija organicheskikh soedinenii.

CHLORINATION REACTIONS OF RESORCINOL. QUANTUM-CHEMICAL CALCULATIONS OF THERMODYNAMIC AND KINETIC PARAMETERS

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Chlorination is widely used in the practice of drinking water disinfection. Upon that process, natural organic matter (NOM) ubiquitously present in drinking water interacts with chlorine to form a variety of harmful by-products, including carcinogens such as chlorinated furanones. Although the chemical structure of NOM is largely unknown, it has been established that the behavior of the chlorine attack sites in NOM is similar to that of resorcinol (RC). The goal of the present study was to elucidate the reaction pathways of the RC chlorination in aqueous solutions. This was done by quantum-chemical calculations of thermodynamic and kinetic parameters corresponding to the sequential replacement of the hydrogen atoms in RC by chlorine. The calculations were carried out using the semi-empirical method PM3 and functional density method (version B3LYP), which employed the 6-31G(d,p) basis set.

In aqueous solutions at pH>3, chlorine is virtually completely hydrolyzed to form acids HCl and HClO. Since the reactions pertinent to the replacement of the hydrogen atoms in the aromatic ring by chlorine have an electrophilic nature, it was initially assumed that the main acting agent in these reactions was the weakly dissociated molecule of HClO, in which the chlorine oxidation state is +1. However, the reaction barriers calculated for the reactions involving this species were found to be fairly high (>50 kcal/mol), which appears to exclude the participation of HClO in the fast substitution reactions. A positively charged Cl^+ particle, which theoretically can be formed by the reaction $HClO + H^+ <=> Cl^+...H_2O$ was considered as an alternative reactive species. The strength of the $Cl^+ ...H_2O$ bond was shown to be weak thus justifying the calculations of the transition states and activation energies for this species. In addition to the modeling performed for the molecular (neutral) form of RC, calculations were also carried out for two anionic forms of RC, which are formed by the sequential deprotonation at elevated pHs of the first and second hydroxyl groups in RC, respectively.

In was found that the electrophilic substitution to varying positions in the aromatic ring of the molecular form of RC is not associated with notable thermodynamic differences, while the chlorination to all these positions appears to involve similar transition states and activation barriers (ca. 20 kJ/mol). However, for the anionic forms of RC the differences in the thermodynamics and kinetics of the substitution reactions are more pronounced. In this work, the thermodynamic and kinetic parameters of the RC chlorination are described in detail. A qualitative conclusion was made that the rate of RC chlorination may decrease with the pH due to the depletion of the reactive Cl^+ species.

PUZZLE OF THE ELECTROCHEMICAL REDUCTION OF A PERSULPHATE ION: A QUANTUM CHEMICAL STUDY

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The electrochemical reduction of persulphate-anion S2O82- on a mercury electrode is known to have a puzzling qualitative feature - a 'pit' on the polarization curve at high overvoltages. Moreover, the electron transfer entails the O-O bond rupture. Such features are of common nature for a number of interfacial reactions for which a great deal of reliable experimental data have been collected. Up to now, the relevant data are explained by using a purely phenomenological approach. In this work we attempted to address the mechanism of electrochemical reduction of S2O82- on the basis both of the charge transfer theory in polar media and quantum chemical methods. Quantum chemical calculations were performed at SCF and DFT (B3LYP) level by using 6-31G(d, p) basis set. The polarized continuum model (PCM) was employed in order to describe the solvation effects. The interaction with the Electrical Double Layer (EDL) field was treated on the basis of detailed charge distribution in reactants. For a single S2O82- a trans-isomer was found to be more favourable compared with the cis-form (a corresponding difference in the total energies amounts to 15 kcal mol-1). The potential energy surface along the innermolecular reorganization was built and fitted by functions in analytical form. It has been demonstrated that the electron transfer proceeds in the vicinity of activationless region. A qualitative behaviour of the polarization curve was concluded to depend crucially upon the interplay between different reactants (S2O82-, [Na(H2O)6*S2O8]-) and their orientations relative to the electrode surface. It has been shown that the solvent reorganization energy affects slightly the model current values, whereas the role of the works of approach is the most significant. The 'pit' on the experimental curves might be explained only involving a scenario with «cation» catalysis, as well as the dependence of electronic transmission coefficient on the electrode charge. This work was supported by the RFBR, projects No. 99-03-32367, 00-03-32140, 01-03-02006, INTAS 99-1093, and Russian Ministry of Education.

QUANTUM CHEMICAL MODELLING OF THE ADSORPTION OF CHLORIDE IONS AT P-METALS FROM AN AQUEOUS SOLUTION

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Adsorption of chloride-ions and chlorine atoms at In(111), In(100), and liquid gallium surfaces was studied at the ab initio SCF and the DFT (B3LYP) level. The metals surface was modelled by a two-layer Me16(10+6) cluster. The adsorption energy of Cl- from gas phase (corrected on BSSE) was found to be –38 kcal/mol and –34 kcal/mol in the case of In(111) and Ga, respectively, and to increase in the row: (hollow)-(bridge)-(on-top) both for Cl-ions and Cl-atoms. It has been shown that the charge of the both adsorbed species amounts to –

0.5e. The solvation effects were treated by exploring the Newns-Anderson model combined with results of quantum chemical calculations. The solvation of chloride ions leads to the noticeable decreasing of the partial charge transfer. The potential energy profile including different contributions was built in order to describe the «electrochemical» adsorption of ions. The ions adsorbed were assumed to form a monolayer at the electrode surface and the lateral interactions were treated in the framework of Vorotyntsev's theory. The spatial solvent dispersion and the screening of electrostatic interactions by both electrons in metal and electrolyte solution were addressed in the model employed. The penetration of electric field into the metal was found to affect crucially the ion-ion interactions. An average inter-ionic distance corresponding to the transition to a two-dimentional plasma was estimated as well. The parameters of virial isotherm were calculated and compared with the available experimental data. The second virial coefficient values do not differ much for the both metals. This work was supported by the RFBR, projects No. 99-03-32367, 00-03-32140, 01-03-02006, INTAS 99-1093, and Russian Ministry of Education.

QUANTUM-CHEMICAL STUDY OF HYPERPOLARIZABILITY FOR PUSH-PULL POLYENES

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Electro-optic polymer electrets are promissing materials for high-speed waveguide modulators and switches which are developing to promote fiber-optic communications. An electro-optic electret is built from dipolar chromophores with the improved first hyperpolarizability and from a polymer matrix that maintains dipolar polarization of chromophores in the polymer glassy state. Donor-acceptor substituted or push-pull polyenes are the most promissing nonlinear optical (NLO) chromophores. From the chemical viewpoint, a push-pull polyene consists of a stereoregular polyene chain with the length and of two terminal groups inducing the mesomeric shift of electrons along the chain longitudinal axis. The macroscopic second-order susceptibility of a polymer depends mainly on the longitudinal hyperpolarizability that can vary significantly with and with donor-acceptor strengths of terminal substituents. We represent here the hyperpolarizability mesomeric model based on the results of quantum chemical calculations performed for the wide series of push, pull and push-pull polyenes. The model calls into play the scale of mesomeric constants which characterize an ability of substituents to be conjugated with a polyene bridge. These constants and chain length are the only structural parameters of a chromophore which are in need to estimate hyperpolarizability in the framework of the model under consideration. The analitical expression connecting hyperpolarizability to mesomeric constants and n has been obtained. Guidelines for molecular design of NLO chromophores are formulated and the most promissing chemical structures are evaluated.

DFT THEORETICAL STUDY OF SILYLENES, GERMYLENES AND STANNYLENES Me_2M (M = Si, Ge, Sn) REACTIONS WITH PHOSPHORUS AND ARSENIC YLIDES

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The chemistry of group 14A organoelement compounds containing double bonds $R_2M=CR'_2$ (M = Si, Ge, Sn) develops intensively in last 20 year. New perspective method of synthesis of **I** is the interaction of heavy analogs of carbenes Me_2M (M = Si, Ge, Sn) with phosphorus and arsenic ylides $H_2C=EMe_3$ (E = P, As). The PESs of these reactions in gas phase at T= O K where calculated at DFT PBE/TZ2P level. The formation of betaines $Me_2M^-\text{-}CH_2\text{-}E^+Me_3$ (**I**) in all cases proceeds without energy barrier as rather exothermic process (dE -29,4 - -35 kkal/mol). Further transformations of **I** can proceed with elimination of phosphine (arsine) EMe_3 and formation of $Me_2M=CH_2$ (**II**) or with proton migration from carbon atom to anionic center yielding metal containing ylides $Me_2HM\text{-}CH=EMe_3$ (**III**). The ylides $Me_2HM\text{-}CH=PMe_3$ (**III**) formed in the reactions of silylenes and germylenes Me_2M (M = Si, Ge) with phosphorus ylide $H_2C=PMe_3$ are the most thermally stable products. In similar reactions of silylenes and germylenes with arsenic ylide $H_2C=AsMe_3$ the global minima of PESs correspond to the formation of **II** ($Me_2M=CH_2$, M = Si, Ge). The formation of betaines $Me_2Sn^-\text{-}CH_2\text{-}E^+Me_3$ (**I**) is most favourable in the reactions of stannylenes with both ylides $H_2C=EMe_3$ (E = P, As). The activation energy of transformation **I a II** changes in a range from 8 up to 37 kcal/mol. The values for the phosphorus derivatives are approximately 10 kcal/mol higher than for arsenic ones and increase in the series from silicon to tin. The intramolecular isomerization **I a III** requires high activation energies (31,5 - 48,4 kcal/mol) and should probably run intermolecularly. The carbenic decomposition of ylides **III** (E = As) with subsequent migration of methyl group resulting in formation of MeHM=CHMe (M = Si, Ge, Sn) is improbable due to high energy barriers (from 40.1 up to 66.8 kcal/mol).

DFT THEORETICAL STUDY OF PHOSPHORUS AND ARSENIC YLIDES REACTIONS WITH KETONES, THIONES AND IMINES

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Reactions of phosphorus and arsenic ylides $R_2C=ER'_3$ (E = P, As) with carbonyl compounds $R»_2C=O$ and their analogs – thiocarbonyl compounds $R»_2C=S$ and imines $R»_2C=NR»'$ make a basis of important general synthetic methods known as Wittig and Corey-Chaykovsky reactions. The PES's of model reactions of $CH_2=EMe_3$ (E = P, As) with Me_2CO, Me_2CS and $Me_2C=NMe$ (gas phase, T= 0 K) have been investigated for the first time in detail at the PBE/TZ2P level of theory. Reactions of $Me_2C=O$ with phosphorus and arsenic ylides follow Wittig pathway. 1,2-Oxaphosphetanes and 1,2-oxaarsetanes, containing cyclic fragments O-C-C-E (E = P, As) are the intermidiates in these reactions in agreement with experimental and theoretical data known. $Me_2C=CH_2$ is kinetically and thermally most favourable product. Theoretical grounds have been presented to the experimental data on the interaction of thiones with Wittig ylides. The reaction follows the Corey-Chaycovsky pathway with the

formation of thiirane under kinetic control conditions (low temperature). More stable Wittig product $Me_2C=CH_2$ is formed under thermal conditions. Betaine containing structural fragment $^-S\text{-}C\text{-}C\text{-}P^+$ is the intermidiate of this reaction, which has contracted cis-gauch-conformation. The interaction of $Me_2C=NMe$ with phosphorus ylides procceds by Wittig-type pathway. 1,2λ^5-Azaphosphetidine, containing cyclic fragment N-C-C-P, is the intermidiate of the reaction which is in agreement with experimental data. The reactions of thione $Me_2C=S$ and imine $Me_2C=NMe$ with arsenic ylides can proceed both via Corey-Chaykovsky and Wittig pathways. Gas phase reactions of thiones with $CH_2=AsMe_3$ is barrierless, but activation barriers are rather high in the reaction of $Me_2C=NMe$ (about 15 kcal/mol).

MECHANICAL BEHAVIOUR OF THE SYSTEM SILICA/POLYDIMETHYLSILOXANE UNDER DEFORMATION. IMPACT OF SILICA SURFACE MODIFICATION. QUANTUM-CHEMICAL STUDY

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Polydimethylsiloxane (PDMS) elastomers filled by highly dispersed silica reveal peculiar mechanical behaviour. Intermolecular interactions in the system and chemical modifications of the silica surface control this process in general. Here are presented the results of microscopical quantum-chemical study of mechanical properties of the silica/PDMS ad-system. Behaviour of a silicone polymer fragment interacting with silica model cluster under deformation has been considered in a framework of mechanochemical-reaction approach. The quantum-chemical realisation of this approach was based on a mechanochemical internal coordinate (MIC) concept. Determined in a special way MIC was changed in a constant-pitch elongation, while other atomic configuration of deformed ad-complex was optimised over all other coordinates. The related force of response on deformation was calculated as the total-energy gradient along the MIC. The approach has been applied to ad-complexes of different linear polydimethylsiloxane oligomers with hydroxylated and silylated silica clusters. An impact of silica particle adsorption and silica surface modification on stress-strain characteristics of PDMS, i.e., Young\'s modulus, energy and force of deformation, tensile strength at break has been studied at molecular level. QCh study revealed microscopical peculiarities of unfilled and filled elastomer molecular model network mechanical behaviour, bond breaking in the systems and their post-fracture relaxation.

NONEMPIRICAL PREDICTION ON THE IONIZED CONDENSED WATER STATE

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The problem of describing and predicting the states of condensed phase species in terms of nonempirical modeling is one of the most complex and intriguing in the modern theoretical chemistry. One of the main difficulties lies in the possibility of extrapolating the results obtained for individual size-restricted systems to essentially unrestricted species that could represent liquids or solids. The problem can be solved only for the systems, relatively small parts of which possess all the main peculiarities inherent in the bulk. As our nonempirical simulations show water clusters do actually meet this condition. The geometrical features and energetic characteristics of neutral and charged water clusters involving up to 40 molecules were obtained in the second order of the Moeller-Plesset perturbation theory with the unrestricted Hartree-Fock functions with the conventional or modified 6-31++G** basis set augmented with diffuse functions centered in the internuclear space and with the use of the effective potential technique for describing a part of water molecules. Instantaneous positive ionization of water clusters may occur under ultraviolet radiation with the photon energy of about 10.9 to 11.9 eV depending on whether open and branched chainlike or predominantly cyclic configurations are taken into account. The adiabatic relaxation, that results in the formation of hydronium ions and hydroxyl radicals, decreases the necessary external impact to about 8.5 eV when all possible structural types are involved in the consideration, which corresponds to an amorphous ice sample. The degree of the structure reorganization upon the lost of an electron can be estimated from the extrapolated vertical energy of an electron attachment to the cationic species: it equals about 4.7 eV, which means that thus formed neutral structure has an excess energy of ca. 3.7 eV over the stable neutral configuration. Instantaneous attachment of an electron to optimal neutral clusters comprising up to 40 molecules always requires some energy to be supplied to the system. At the same time, the relaxed anionic species, when formed by two to four subfragments not directly H-bonded to each other, are stable and have substantial positive vertical energies of the electron detachment. These energies, being extrapolated to an infinite size of water cluster, provide a value of about 5.5 eV in unexpectedly good agreement with the experimental estimate for the same characteristic measured for the anions formed under the conditions of molecular water flow. This value enabled us to clarify the structure of anions formed in molecular beams and to indirectly estimate the adiabatic affinity of an infinite water cluster of an arbitrary structure, which would correspond to an amorphous ice sample. The work is financially supported by the Russian Foundation for Basic Research (project no. 99-03-33251) and the Ministry for Higher Education in the framework of the program \"Universities of Russia-Fundamental Research\".

THE DYNAMICAL MECHANISM OF COVALENT BONDING

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The covalent bond is the heart of microscopic and molecular chemistry. It has been the subject of a fascinating sequence of intuitive and empirical models culminating in the computational methods of quantum chemistry. Among the users of modern quantum chemistry it may be a prevalent feeling that covalent bonding is now thoroughly understood and more a matter of the number of significant figures in our computational results than of principle. The discussion of principle and mechanism behind covalent bonding has, however, generated spirited debate between supporters of lowering of electrostatic potential energy and the supporters of kinetic energy lowering as the main cause. As a result textbooks on bonding offer a variety of explanations or simply abstain from presenting a mechanistic explanation leaving the physical basis of covalent bonding in a state of some confusion and controversy. In this talk I will put forth a resolution of the controversy based on a dynamical mechanism of covalent bonding. The confusion surrounding lowering of potential and kinetic energy will be shown to arise due to a paradoxical feature of the Coulombic potential well. The key delocalization concept will be found to explain both the virial theorem and the Ruedenberg orbital contraction phenomenon. The delocalization mechanism is directly related to the ergodic properties of electron dynamics in atoms and molecules. It becomes clear why the original form of density functional theory, the Thomas-Fermi theory, does not explain covalent bonding while the Kohn-Sham interpretation does. The simple Huckel theory will be used to illustrate the concept of quantum ergodicity and its relationship to the covalent bonding mechanism.

DYNAMIC STRUCTURES OF PROTEIN COMPLEXES STUDIED BY NORMAL MODE ANALYSIS

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Normal Mode analysis of Trypsin-BPTI and Monoclonal antibody D1.3-lysozyme complexes was performed to investigate the dynamics at the interface between proteins. Experimental studies of these complexes shown that nature of forces driven interactions in studied system are opposite i.e. trypsin-BPTI interaction is classical entropy driven but bunding of lysozyme to D 1.3 is enthalpy controlled.

A NEW METHOD AND PROGRAM TOOL FOR TREATING MOLECULAR ELECTROSTATICS

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Electrostatic interactions play important role in the modeling of physicochemical properties and chemical reactivity. The model of point charges has become a widely used theoretical ground in such modeling [1]. A number of rapid empirical methods of atomic charge calculation was developed by various research groups [2]. Recently we have proposed [3] a novel efficient approach to the calculation of atomic charges and other electronic descriptors. This approach is based on an analogy between a molecule and an ideal electrical network where the atoms are represented by the nodes of the network and the chemical bonds are simulated by conducting branches. Atomic (or orbital) electronegativities (EN) of the constituent atoms are implied to be equilibrated in such a manner as potentials in the nodes of an electrical circuit. An appropriate algebraic formalism based on the theory of electrical circuits is developed for the modeling of such equilibration. Given molecular topology and tabulated EN values one can obtain effective electronegativities of atoms in a molecule and then partial atomic charges. A special attention is paid to the treatment of aromatic and conjugated species. Good quality of the values obtained can be confirmed by excellent correlations with observable physicochemical and spectral properties. The method proposed is implemented in the form of Windows95/NT computer program written on C++ pragramming language. The program has a suitable user-friendly interface and enables one to calculate molecular charge distribution in a fast and efficient way. References: [1] Cramer C., Truhlar D. Theor.Chem.Acc. 1997, 98, 206-211. [2] Mortier W., Van Genechten K., Gasteiger J. J.Am. Chem.Soc. 1985, 107, 829-835. [3] Oliferenko A.A., Palyulin V.A., Zefirov N.S. Doklady Chemistry. 1999, 368, 209-212.

DERIVATION OF ATOMIC ELECTRONEGATIVITIES FROM THE ANALYSIS OF THE ELECTRON DENSITY LAPLACIAN

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Quantum theory of \"atoms in molecules\" (AIM)developed by R.Bader has become a promising interpreting and computational tool in the learning of chemical bonding and molecular structure. One of the sections of the AIM theory, analysis of the electron density Laplacian scalar field enables one to achieve additional insights in the constitution of atomic valence shells. A one-to-one correspondence was established by Bader and coworkers between the valence shell charge contentrations represented by critical points of signature (3,-3) and the electron pairs of Gillespie\'s VSEPR model. Analyzing the electron density Laplacian of a number of simple hydrides, we have found a Laplacian-derived descriptor that correlates well with the electronegativity values of the following atoms: from Li to F, from Si to Cl, and from Ge to Br. This descriptor (designated by tau)is written as a normalized ratio of the critical point Laplacian value L(r) and the corresponding value of characteristic radius. The wavefunctions were obtained via the MO-LCAO SCF calculations by using PC-

GAMESS and the basis set 6-311++G(2d,2p) with six d-functions. The electron density Laplacian was constructed and analyzed with the help of BUBBLE program (cortesy of R.F.W.Bader). Then a scatter plot of atomic electronegativities vs the calculated tau values was built. Five electronegativity scales were tested, those of Pauling, Sanderson, Allred-Rochow, Batzanov, and Hinze-Jaffe. The best correlations was achieved with Batzanov (r=0.95) and Hinze-Jaffe (r=0.94) scales. Therefore, the intuitively clear qualitative notion of electronegativity can be quantitavely realized in terms of the electron density Laplacian features.

PUMP-INDUCED PHOTOPROCESSES IN THE MOLECULES AND LOCALIZATION OF SPIN-ORBITAL COUPLING OR THE NEAR-LYNG SINGLET AND TRIPLET EXCITED STATES

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This paper considers series organic heterocyclic azoles to investigate the dependence of the main optics characteristics of these compounds on the magnitude of pump-induced triplet-triplet losses within fluorescence band. It is shown that only organic compounds with a definite type of spatial structure satisfy the condition of maximum separation of the band of limiting gain and the spectra of pump-induced singlet-singlet and triplet-triplet reabsorbtion in excited states.

The total energy E_{tot} of quantum mechanical system in the stationary state is a single measurable variable, and the determination of local portions corresponding to atoms and molecular bonds is a nontrivial problem. In the adiabatic approximation of the Born-Oppenheimer method, the motion of nuclei is characterized by the potential energy of electrons which corresponds to the energy of electrons of the Schrodinger equation for electronic wave functions with fixed coordinates of nuclei (involved in the equation as parameters): $\hat{H}_0 \Psi_m(r,R) = E_m(R)\Psi(r,R)$, where $E_m(R)$ is the electron energy corresponding to the given nuclear configuration (equilibrium geometry) of a molecule and $\hat{H}_0$ is the statistical Hamilton operator describing the energy of a molecular system before the interaction with the excitation quantum. According to the main principle of quantum mechanics, the excited singlet and triplet states with the minimal energy of the molecule are the most probable ones. A complex multiatomic molecule can be represented as a system of excited electronic states with different spin and orbital structures where the energy of a quantum evolves under the action of intramolecular mechanisms with determine photophysical and photochemical properties of organic molecules.

Obukhov A. E. [1-7]: -*Laser Physics*. 1997. Vol. 7. №. 5. pp. 1102 – 1131; - Ibid. 1999. Vol. 9. № 3. pp. 699 – 722; - Ibid. 1999. Vol. 9. №. 3. pp. 723 – 735; - Ibid. 1999. Vol. 9. №. 4. pp. 927 – 939; - Ibid. 2000. Vol. 4. №. 2. pp. 347 – 358; - Ibid. 2000. Vol. 10. №. 2. pp. 644 – 664; - Ibid. 2000. Vol. 10. № 5. pp. 1101 – 1135.

THE PHYSICAL PRINCIPLES OF SIMULATING THE STRUCTURE AND PHOTOPHYSICAL PROPERTIES OF N,O,S GETEROAROMATIC COMPOUNDS BY OF THE QUANTUM-CHEMICAL LCAO MO SCF CI METHODS

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When organic molecules are pumped by various UV excitation sources with an energy E_{exit} > 2 eV and the time interval within which the excitation pulse is applied is comparable with the lifetime of an excited-state quantum system, spectra of pump-induced reabsorption through $S_1^* \rightarrow S_n^*$ and $T_1 \rightarrow T_n$ transitions are formed in systems of excited states before the emission of a photon, and a pumping pulse applied to an organic substance opens up an efficient channel of active losses. In LCAO MO SCF CI INDO/S quantum-chemical models, this phenomenon is attributed to the fact that only certain compounds of azoles in excited fluorescent (and phosphorescent) states allow the excessive electron-vibrational excitation to be delocalized exclusively on atoms and bonds with similar positions and nature.

The Robinson-Frosch formula modified for fundamental problems of laser-physics is employed to calculate the c onstants of optical and non-optical deactivation of electron-vibrational excitation energy and cross sections of stimulated emission and secondary reabsorption in spectra of pump-induced reabsorbtion and the calculated rate constants of radiative decay and intercombination conversion and fluorescence quantum yields of excited molecules in vapor and solutions are used to determine the characteristic limited duration of the pumping pulse - $t_{lp} = 2/\sum_i k_{ST} \left\{ \frac{\sigma_{31}^{osc}(\nu_{osc}^{\max}) - \sigma_{2,T-T}^{reabs}(\nu_{osc}^{\max})}{\sigma_{3,S-S}^{reabs}(\nu_{osc}^{\max})} \right\}$. For molecules the growth in the energy stored in excitation, which occurs within the time interval no less than the characteristic time of initiation of multiphoton processes in excited molecules with $k_{ST} \approx k_{nr} = 10^{12} - 10^{13} c^{-1}$, is shown to give rise $S_1^* \Leftrightarrow S_n^*$ transitions populating those highly excited S_n^* states that are involved in spin-orbital interaction with triplet states (T_n).

Obukhov A. E. [1-7]: -*Laser Physics*. 1997. Vol. 7. №. 5. pp. 1102 – 1131; - Ibid. 1999. Vol. 9. № 3. pp. 699 – 722; - Ibid. 1999. Vol. 9. №. 3. pp. 723 – 735; - Ibid. 1999. Vol. 9. №. 4. pp. 927 – 939; -Ibid. 2000. Vol. 4. №. 2. pp. 347–358;- Ibid. 2000. Vol. 10. №. 2. pp. 644–664;-Ibid. 2000. Vol. 10. № 5.pp.1101– 1135.

COMPUTATION OF ADATOM PROPERTIES ON Si(111)(7X7) SURFACE USING CLUSTER APPROXIMATION

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The possibly adsorption centers on 7x7-reconstructed Si(111) surface are the atoms of the far incomplete top atomic layer, called in the well-known Dimer-Adatom Stacking Fault (DAS) model [1] by adatoms. With the purpose of determining of properties of adatoms and its environment, we selected the pseudopotential basis set of double-zeta quality, which the most precisely reproduces the equilibrium geometry of disilane molecule. Further in all geometry optimizations was used the mixed basis set: Stuttgart pseudopotential [2] with d-function added for Si atom, -31G splitted [3] for H atom. We determined equilibrium geometry of the clusters containing atoms of incomplete two (Si5H7) and incomplete four (Si22H23, Si23H25) coordination shells around the adatoms, in UHF and UMP2 approximations. Adatom bond lengths are found larger than other Si-Si bond lengths in the clusters. This can be explained by a significantly deviation of hybridization type of the first coordination shell atoms from sp3-type. Properties of the atoms of three coordination shells are analyzed. It is established that the atom of the first atomic plane of bulk bilayer, directly connected to the atom of dimer layer, has spin density ca. 0.15 a.u. This is anomal for an four-coordinated atom Si ever on cluster surface. The topological analysis [4] of electron density distribution is to be carried out using elec-tron density derived from a full-electron computation. The electron density from MP2/6-31G(d) in the best way reproduces \"atoms in molecule\" properties [4] of disilane, computed in pseudo-potential basis set mentioned above. The topological analysis of electron density distribution from UHF/6-31G(d) and UMP2/6-31G(d) for Si22H23 and Si23H25 is carried out. References: 1. J.Vac.Sci.Technol., A3, 120 (1985). 2. Mol.Phys., 80, 1431 (1993). 3. J.Chem.Phys., 98, 5555 (1993). 4. R.F.W.Bader. Atoms in Molecules: A Quantum Theory. – Oxford: Calendon Press, 1990.

NON-NUCLEAR ATTRACTORS ON Si-Si BOND IN DISILANE AS BASIS SET INADEQUACY

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Using topological analysis of electron density (ED) [1], we have found anomalies of Si-Si bond ED distribution in disilane molecule, known as \"non-nuclear attractors\". These are flat local maxima of ED near or at the center of the bond. Such anomalies exhibits a large set of EDs computed using the various basis sets and methods: 6-31G(dp), 6-31G(3d3p), 6-311G(dp), 6-311++G(dp) (HF, DFT B3LYP), aug-cc-pvDZ, aug-cc-pvTZ (all methods applied: HF, DFT B3LYP, MP2, MP4(SDQ), CI-2), aug-cc-pvQZ (all applied: HF, DFT B3LYP) and ever Roos ANO TZ [2] (HF, MP2). Neither total energy nor Si-Si axial component of quadrupole moment is sensitive to presence of such ED anomaly, while Si-Si bending normal mode usually is. Comparing its frequency to experimental value 434 cm-1

[3], we found the best results for basis sets do not leading to non-nuclear attractors in ED. For instance, 6-311G(2d2p) gives better value than 6-311G(3d3p) at the same level of theory. Consequently, the presence of the non-nuclear attractors at Si-Si bond is to be directly referred to basis set quality, and much less to electron correlation effects accounting. Particularly, the success of 6-311G(2d2p) basis set is explained by position of radial maxima of the 2nd d-shell nearly the center of the bond (1.236 A, Si-Si bond length 2.35-2.45 A), and failure of 6-311G(3d3p), as well as of 6-311G(dp), is explained by a considerably large distances from ra-dial maxima of its d-shells to the center of the bond. The excellent test of basis set quality rep-resents ED computed just at HF level of theory, and non-nuclear attractors on Si-Si bond are to be considered as artefact of computation. All this means also that in studying the non-nuclear attractors by itself, particularly in Li2 molecule [4,5], the full accounting of electron correlation effects in small basis sets (as FCI in 6-31G(d) [5]) is meaningless. References: 1. R.F.W.Bader. Atoms in Molecules: A Quantum Theory. – Oxford: Calendon Press, 1990. 2. Theor.Chim.Acta, 77, 291 (1990); ibid., 79, 419 (1991). 3. J.Chem.Phys., 26, 1107 (1957). 4. J.Chem.Phys., 97, 2592 (1992). 5. J.Chem.Phys., 97, 9323 (1993).

AROMATIC SUBSTITUTION REACTIVITY: QUANTUM CHEMICAL PREDICTIONS FOR REACTIONS RATES AND YIELDS

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The cationic localization energies (Λ^+) [1] for the reaction of monosubstituted benzenes interaction with nitronium cation have been computed by the PM3 method. The subjects of investigation are molecules C_6H_5X, where X = CH_3, C_2H_5, $CH(CH_3)_2$, $C(CH_3)_3$, CH_2CN, $CH_2COOC_2H_5$, $CH_2N^+(CH_3)_3$, CH_2NO_2, CH_2OCH_3, CH_2F, CF_3, CH_2Cl, $CHCl_2$, CCl_3, CN, CHO, $COCH_3$, $CONH_2$, COOH, $COOC_2H_5$, COCl, $N^+(CH_3)_3$, NO_2, OH, OCH_3, F, $Si(CH_3)_3$, $S^+(CH_3)_2$, Cl, Br, I.

We have found the linear correlations between $\ln Y^*$ and Λ^+, where Y^* are product yields (Y) refered to a quantity of the atoms of uniform type ($Y^*_{ortho} = 0.5Y_{ortho}$, $Y^*_{meta} = 0.5Y_{meta}$, $Y^*_{para} = Y_{para}$), for *ortho*, *meta* and *para* positions in molecules. For the series of compounds, the linear dependences $\ln Y$ *vs* Λ^+ for permanent positions in aromatic ring have been also established. The equalities $\ln Y = a + b\Lambda^+$ and $\ln Y^* = a + b\Lambda^+$ agree with both the Arrhenius equation and the linear free energy relationships [2].

The anionic localization energies (Λ^-) [1] for the interaction of 1-chloro-2-nitro-4-X-benzenes (X = H, CH_3, CF_3, CN, CHO, $COCH_3$, COC_6H_5, $CONH_2$, $CON(CH_3)_2$, $COOCH_3$, $N{=}NC_6H_5$, $N{=}NOC_6H_5$, $NO{=}NC_6H_5$, N_3, NO_2, SCH_3, SO_2CH_3, $SO_2C_6H_{11}$, $SO_2C_6H_5$, $SO_2N(CH_3)_2$, $SO_2N(CH_3)C_6H_5$, F, Cl, Br, I) with methoxide anion have been computed. Substituent rate factors correlate linearly with the Λ^- values.

The correlations obtained could be used for the facilitated semiempirical *a priori* estimation of nitration yields of positional isomers (*ortho*, *meta* or *para*), as well as for the evaluation of kinetic characteristics of the aromatic series reactions. These dependences open up the way to molecular design of aromatic compounds.

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A PRIORI PREDICTIONS FOR ANALYTICAL REDOX REAGENTS SELECTIVITY

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Diphenylamine (DPA), phenothiazine and their substituted derivatives are widely distributed analytical redox reagents, antioxidants, drugs. Their application is based on oxidation reactions. The analytical significance of DPA and phenothiazine derivatives, their selectivity to different oxidants and other important properties are due to the standard redox potentials E^0 (instead of those, essentially the same formal potentials E^f found by the Walden method are often used), or due to the potentials of voltammetric oxidation $E_{1/2}$, and also depend upon protolytic and polar characteristics.

For diphenylamines, on the base of PM3 computations, the following type correlations have been found: E^0 (E^f) = a + bI (1), pK_a = c + d·PA (2), $\mu_{эксп} = e\mu_{теор}$ (3), where I is ionization potential of amine or its protonated form, K_a is acidity constant of the diarylamine conjugate acid or constant of the compounds' acidity dissociation *via* carboxylic group, PA is gaseous-phase proton affinity.

By means of the MNDO, AM1 and PM3 methods, we have studied spatial and electronic structure of the phenothiazine series molecules. In all the cases, heterocycle is featured by the bath conformation, more planarized when substituents at the nitrogen atom are absent. Relationships of the $E_{1/2}$ = f + gI (4) type have been established.

Using the relations (1) - (4) one can predict the E, pK_a and μ values for the DPA and phenothiazine series redox reagents, construct the compounds with the desired protolytic, oxidative-reductive properties, as well as polarity, and, consequently, with regulated analytical selectivity.

We have shown the predictive power of the relations (1) on the following example. Recently Mushtakova *et al.* have synthesized new redox reagents 4-sulphotriphenylamine, 4,4'-disulphotriphenylamine, 2-nitro-4'-sulpho-DPA, 3-nitro-4'-sulpho-DPA, 4-nitro-4'-sulpho-DPA, and determined their E^f_{exper} values. By means of the PM3 method, for the above compounds and their conjugate acids we have computed first ionization potentials. Inserting the latter in (1) lets one obtain E^f_{theor} values, which are in good agreement with the experimental data:

THERMODYNAMIC AND MOLECULAR PROPERTIES OF AS-, SB-, BI-CONTAINING SPECIES AND SPATIAL STRUCTURE OF THE $(C_6H_5)_3XYZ$ MOLECULES (X = AS, SB, BI)

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By the PM3 method, standard values of entropy, heats and Gibbs energies of formation, first ionization potentials and dipole moments of the molecules have been computed for series of inorganic and organic arsenic and antimony compounds. The species under study were As, As^+, As^{2+}, As_2, As_3, As_4, As_4^+, PAs_3, P_2As_2, P_3As, AsH_2, AsH_3, As_2H_4, AsN, AsO, AsO^+, AsF_2, AsF_3, AsF_5, AsS, AsCl, $AsCl_3$, AsSe, $AsBr_2$, $AsBr_3$, AsTe, AsI_3, As_4O_6 {2,4,6,8,9,10-hexaoxa-1,3,5,7-tetraarsatricyclo[3.3.1.1(3,7)]decane}, CH_3AsH_2, $(CH_3)_2AsH$, $(CH_3)_2As$, $(CH_3)_3As$, $(C_2H_5)_3As$, $(n\text{-}C_3H_7)_3As$, $(n\text{-}C_4H_9)_3As$, $(CF_3)_2AsH$, $(CH_3)_2AsCF_3$, $(CF_3)_2AsCH_3$, $(CF_3)_3As$, CH_3AsF_2, $(CH_3)_2AsF$, CH_3AsCl_2, $C_2H_5AsCl_2$, $(CH_3)_2AsCl$, $(CF_3)_2AsCl$, CH_3AsBr_2, $(CH_3)_2AsBr$, CH_3AsI_2, $(CH_3)_2AsI$, 4-$CH_3C_6H_4As(C_2H_5)$-*n*-C_4H_9, $(C_6H_5)_2AsCN$, $(C_6H_5)_2AsCl$, $(C_6H_5)_3As$, $(4\text{-}CH_3C_6H_4)_3As$, $(C_6H_5)_3AsO$, $(C_6H_5)_3AsS$, $(C_6H_5)_3AsCl_2$, $(CH_3O)_3As$, $(C_2H_5O)_3As$, $(n\text{-}C_3H_7O)_3As$, *trans*-C_6H_5-N=N-C_6H_5, *trans*-ClCH=$CHAsCl_2$, (*trans*-ClCH=$CH)_2AsCl$, (*trans*-ClCH=$CH)_3As$, 10-chloro-5,10-dihydrophenarsazine (Pankratov A.N., Uchaeva I.M.. *J. Mol. Struct. Theochem*. 2000. Vol. **498**, No. 1-3. P. 247-254); Sb, Sb^+, Sb^{2+}, Sb_2, Sb_4, Sb_4^+, SbH_3, Sb_2H_4, $Sb_2H_4^+$, SbN, SbO, Sb_2O_3, SbF, SbF_3, SbF_5, SbS, SbCl, $SbCl_2$, $SbCl_3$, $SbCl_5$, SbOCl, SbSe, SbBr, $SbBr_3$, InSb, $InSb_2$, SbTe, Sb_2Te_2, SbI, SbI_3, Sb_3Bi, $(CH_3)_2Sb$, $(CH_3)_3Sb$, $(C_2H_5)_3Sb$, $(C_6H_5)_3Sb$, $(4\text{-}CH_3C_6H_4)_3SbO$, $(C_6H_5)_3SbS$, $(C_6H_5)_3SbCl_2$, $(C_6H_5)_3Sb(OH)Cl$, $(C_2H_5O)_5Sb$, $(C_6H_5O)_5Sb$; Bi^+, Bi^{2+}, Bi_2, BiH, BiO, BiF, BiS, BiS^+, BiCl, $BiCl_2$, $BiCl_3$, BiSe, BiBr, $BiBr_3$, BiTe, BiI, BiI_3, $(CH_3)_2Bi$, $(CH_3)_3Bi$, $(C_2H_5)_3Bi$, $(C_6H_5)_3Bi$, $(C_6H_5)_3BiCl_2$, $(C_6H_5)_3Bi(ONO_2)_2$. Linear relationships have been stated, allowing *a priori* evaluation of thermodynamic and molecular characteristics of As- and Sb-containing substances. For arsine, the PM3 method overestimates gaseous-phase proton affinity not more than by 10 %. A quantum chemical computation reproduces well adiabatic ionization potential of BiH_3. It has been concluded that the molecules $(C_6H_5)_3AsCl_2$, $(C_6H_5)_3SbCl_2$, $(C_6H_5)_3Sb(OH)Cl$, $(C_6H_5)_3BiCl_2$, $(C_6H_5)_3Bi(ONO_2)_2$ exist as solutes in the form of trigonal bipyramid with two axial inorganic ligands.

THE INTERACTION OF 1-NAPHTHYLAMINE WITH NITRITE ION: HOW THE AQUEOUS MEDIUM ADJUSTS THE REGIOSELECTIVITY AND PRODUCT STRUCTURE

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The reactions of diazotization and azo coupling of 1-naphthylamine are of importance for spectrophotometric determination of nitrite ion in different objects.

A choice of the semiempirical quantum chemical MNDO, AM1, PM3 methods for studying the aforesaid coupling reaction has been justified.

Quantum chemical (MNDO, AM1, PM3) analysis of electron density in highest occupied molecular orbital and modelling (PM3) a reaction barrier within the localization approximation have enabled us to substantiate regioselectivity of the 1-naphthylamine reaction with 1-naphthyldiazonium cation proceeding by 2 and 4 positions of amine molecule.

The electronic structure of molecules of 1-amino-2,1'-azonaphthalene (I) and 4-amino-1,1'-azonaphthalene (II) geometric isomers has been computed. *Trans* isomer of II is slightly over 2 kcal/mol more thermodynamically stable than *cis* form. Non-planar structure of the molecules of *cis* azo compounds doesn't allow the conjugation between π-systems of naphthyl bicycles and azo fragment. The molecules of *trans* isomers are planar. A contributor of analytical signal (bright color carrier) is the product II.

Azo tautomers of I and II are more thermodynamically stable as compared to the corresponding quinone-hydrazonic forms in both gaseous phase and aqueous solution.

In gaseous phase, the compound I is protonated by amino group. For II, conjugate acids are close to each other in thermodynamic characteristics.

Quantum chemical PM3 computations with an explicit account for aqueous medium have been performed for supermolecules containing the systems of I, II, their quinone-hydrazonic tautomers and conjugate acids. The hydration enthalpies of all the above molecular systems apart from azonaphthalene II protonation product by N_β atom are positive, that obviously corresponds to the negative hydration.

In aqueous medium, preferable is protonation of both *trans* aminoazonaphthalenes by β nitrogen atom of azo group. Therewith quinoidization of the molecular system of II takes place leading to an analytical signal appearance.

On the contrary, the N_β-protonated compound I does not exist in the quinone-hydrazonic form, since the unshared electron pair axis of the primary amino group nitrogen atom is located in the plane whole molecule.

By the methods of quantum chemistry, electron absorption spectroscopy, high performance liquid chromatography and preparative synthesis, it has been established that medium factors provide the decision between two alternative routes of reaction predicted by gaseous-phase computations. In aqueous solutions, azo coupling with a participation of 4 position and the substance II formation from two possible azo compounds take place.

AN APPROACH TO PREDICTION OF REDUCTION POTENTIALS, ELECTRON AFFINITIES AND VIBRATIONAL FREQUENCIES OF ARYLDIAZONIUM CATIONS - SEMIPRODUCTS OF SYNTHESYS OF ANALYTICALLY IMPORTANT AZO COMPOUNDS

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The reactions of azo coupling of aromatic amines and phenols with the aryldiazonium catons are of great importance in analytical chemistry, in dyes production.

A tendency of diazo cations for reduction could be a measure of their electrophilic activity on azo coupling.

Diazonium cations are capable of decomposing to form nitrogen molecules. A measure of diazonium cations stability (and at the same time an indicator of their activity as electrophilic agents) can be, in particular, frequencies of valent vibrations of the atomic group $C\text{-}N^{+}{\equiv}N$ bonds.

By the fact of finding 43 relationships, we have shown that the reduction potentials, dimerization potentials and potentials in half-equivalent point on titration of aryldiazonium cations are related linearly to the quantum chemically evaluated electron affinities and to the stabilization energies of radicals formed on diazonium cations reduction.

We have found 66 linear correlations of frequencies characterizing a collection of bonds valent vibrations of the $C\text{-}N^{+}{\equiv}N$ fragment in the $XC_6H_4N^{+}{\equiv}N$ cations, with the bonds orders of N≡N and C-N, with the charges on carbon atoms in *para* positions of the C_6H_5X molecules aromatic rings, with the mesomeric dipole moments of X substituents. On an example of 43 diazonium cations, it has been shown that bond orders of N≡N and C-N correlate linearly to each other.

Twelve quantitative relationships combining the mesomeric dipole moments of atomic groups with the Koopmans quantities of electron affinities and vibrational spectra frequencies of the substituted phenyldiazonium cations have been established.

The correlations revealed allow one to predict actual values of the potentials, electron affinities, vibrational spectra frequencies not always available to experimental measurments, as well as mesomeric dipole moments.

THERMODYNAMICS OF INTRAMOLECULAR HYDROGEN BOND IN ORGANIC COMPOUNDS: SEMIEMPIRICAL EVALUATIONS AS AN ALTERNATIVE TO THE *AB INITIO* APPROACH

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Using the MNDO/H, I-MNDO, MNDO/HB, MNDO/M methods we have evaluated thermodynamic characteristics of the intramolecular hydrogen bond (IHB) for salicylic aldehyde, salicylic acid, its methyl, ethyl, phenyl ethers, 2-methoxybenzoic acid, 2-nitro-, 2-methoxy-, 2-fluoro-, 2-chloro-, 2-bromo-, 2-iodophenols, 8-hydroxy- and 8-mercaptoquinolines, tropolone. The results agree with the experimental data.

The correctness of the above quantum chemical methods is confirmed by the substances experimental heats of formation reproduction. At geometry optimization of the tropolone molecule, we have avoided the system “rolling down” to the alternative energy minimum corresponding to the non-planar conformation and displaying an artefact of the MNDO group schemes. The errors relativation at the IHB energetic parametes differential evaluation leads to satisfactory accordance of the computed IHB enthalpy of 2-nitrophenol with the experimental one, in spite of the fact that the MNDO calculation scheme is unfit for the heats of formation of nitro compounds. For tropolone, semiempirical computations of the

IHB thermodynamics appeared more successful as compared to the RHF/6-31G and RHF/6-31G* consideration (Redington R.L., Bock Ch.W. *J. Phys. Chem.* 1991. Vol. **95**, No. 25. P. 10284-10294).

We have computed thermodynamic functions of the IHB formation for tropolone in the hexane, diethyl ether, acetone, ethanol and aqueous media being modelled in the point dipole approximation. Potential energy surface profiles have been obtained for the rotation of the O-H bond around the C-O one, as well as for the intramolecular proton transfer both in the gas phase and in the aforementioned solvents.

The MNDO/H, I-MNDO, MNDO/HB, MNDO/M methods are applicable for *a priori* estimation of the IHB thermodynamic properties aimed at molecular design of compounds with given IHB enthalpies and free energies. In view of ingenious parameterization, the above methods may present a real alternative to the *ab initio* approach.

ELECTRONEGATIVITY OF SUBSTITUENTS IN LINEAR ALIPHATIC MOLECULES

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The aim of the present work is systematic *ab initio* RHF/6-31G*//RHF/6-31G* investigation into the distance and specificity of the atomic groups electronegativity effect in linear aliphatic molecules $C_6H_{13}X$ at X = H, CH_3, C_2H_5, CH_2CN, CH_2OCH_3, COOH, COO^-, NH_2, NO_2, OH, O^-, F, Cl.

Charges on atoms were obtained within Mulliken orbital population analysis. For 1-aminohexane, ^{13}C NMR chemical shifts correlate linearly with charges on atoms. The atomic groups electronegativities found by Inamoto and Masuda for the model HX compounds, are related linearly to the sums of charges on the C_6H_{13} fragment's atoms. Therefore the correctness of our estimations for charge distribution in aliphatic molecules has been proved.

All the substituents studied cause a decrease in negative charge on C-1 atom. Therewith the substituents OH, O^-, F alter a sign of charge on C-1 atom to positive one. As for C-2 atom, the groups CH_3, C_2H_5, NH_2, O^- do not practically influence its charge. The other substituents under consi-deration shift charge on C-2 atom toward the negative side.

The electronegativity effect leads to alternating the signs of charge changes in aliphatic chain. The above fact is in agreement with a knowledge on α and β effects in ^1H NMR spectroscopy. The C-3 atom does not practically undergo the effect over the chemical bonds chain from such substituents as CH_3, C_2H_5, CH_2CN, CH_2OCH_3, COOH, NH_2, O^-. Somewhat gain in negative charge on γ carbon atom occurs in the case of NO_2, OH, F, Cl groups. In contrast, carboxylate-ion decreases slightly negative charge on C-3 atom. The most considerable effect of substituent with re-spect to charge changes takes place in the case of C-1 atom (changes in the first digit). Changes in the second digit occur for C-2 and C-3. The electronegativity effect distance over aliphatic chain does not exceed three atoms. Besides, the distance and specificity of electronegativity effect do not depend directly upon the overall electron-acceptor ability of atomic groups.

THE N-NITROSAMINES HEATS OF FORMATION AND THE DIPHENYLAMINE NITROSATION REGIOSELECTIVITY: A QUANTUM CHEMICAL STUDY

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N-Nitrosamines, including N-nitrosodiphenylamine, are dangerous environmental pollutants. Of importance is information on the reaction of diphenylamine (DPA) nitrosation. Using the MNDO, AM1, PM3 methods we have studied the DPA molecule interaction with nitrosonium ion. The possible reaction paths resulting in 2-, 3-, 4- and N-nitroso-DPA formation have been considered. Standard changes in enthalpy and free energy of the reactions DPA + $NO^+ \rightarrow$ x-NO-DPA + H^+, where x = 2, 3, 4, are close to each other. The N-nitroso-DPA molecule is thermodynamically less stable by 8-16 kcal/mol (according to the AM1 and PM3 data), as compared to C-nitrosodiphenylamines. The N-N bond lability is confirmed by the known mass spectrometry data: spectra of N-DPA and DPA are fairly close to each other.

Preferable nitrosation of DPA by the nitrogen atom is related to the kinetic control of reaction occurring with the involvement of the greatest negative charge's location site. It has been stated that the enthalpies and free energies of cationic localization (simulating the activation barrier) on electrophilic attack of different x positions of the DPA molecule, change in the series: 4 > 2 > N > 3, that is in agreement with the N-nitroso-DPA ability to transform into the corresponding C-nitroso compound.

With the examples of bis(2,2,2-trinitroethyl)-N-nitrosamine, bis(2,2-dinitroethyl)-N-nitrosamine, 1-nitrosopiperidine, 1,4-dinitrosopiperazine, 4-nitrosomorpholine, nitrosobenzene, pentafluoronitrosobenzene it has been shown that the adequate evaluation of the NO-containing substances' heats of formation decreases in the series PM3 > AM1 > MNDO. For dimethyl-N-nitrosamine, the corresponding sequence is MNDO > AM1 > PM3, and in the case of diisobutyl-N-nitrosamine - AM1 > MNDO > PM3. The PM3 method was used for computing profiles of potential energy surface for the DPA interaction with nitrosonium cation and for reversible homolytic dissociation of N-nitroso-DPA.

QUANTUM CHEMICAL AND KINETIC STUDY OF LIGAND SUBSTITUTION IN Pd (II) - NaCl - H_2O AND Pd (II) - HCl - H_2O REACTION SYSTEMS

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The behaviour of potassium tetrachloropalladate (II) in media modelling biological liquids (gastric juice, blood plasma) has been studied. It has been shown that in NaCl aqueous solutions, the aquation rate is higher than the rate of chloro ligand introduction into the internal coordination sphere of palladium atom. In HCl solutions, the process of palladium chloro complexes formation predominates. The latter is obviously due to the protonation of water molecules entering a composition of aqua complexes. Aquation and accumulation of palladium chloro complexes obey the regularities of first-order reactions.

By means of the ZINDO/1 method, a quantum chemical study of the substitution reaction of ligands as water molecules and hydronium ion in palladium (II) planar complexes by chloride ion has been performed. For all the complexes containing H_2O and H_3O^+ ligands, apart from $[Pd(H_2O)_4]^{2+}$, characteristic is the presence of intramolecular hydrogen bonds. In the complexes of $[Pd(H_2O)_3(H_3O)]^{3+}$ and *trans*-$[Pd(H_2O)_2(H_3O)Cl]^{2+}$ "non-classical" symmetric hydrogen bond of the type $O^{\cdots}H^{\cdots}O$ has been established. The substitution of hydronium ion in the palladium atom internal sphere is thermodynamically more favourable (excluding the last step) as compared to the displacing of water molecules. The agreement of the results of kinetic behaviour studies for the $K_2[PdCl_4]$ - NaCl - H_2O and $K_2[PdCl_4]$ - HCl - H_2O systems with the data of quantum chemical investigations of ligands exchange thermodynamics is of no doubt.

Logarithms of stepwise stability constants of the palladium (II) chloride complexes have been found to correlate linearly with the enthalpies of the substitution of water molecules by chloride ion. The use of similar correlation equations for another centre atoms and ligands allows *a priori* evaluation of the stepwise complex-formation constants, as well as directive synthesis of the complexes with a given ratio of stability constants by different steps.

QUANTITATIVE STRUCTURE - PROPERTY RELATIONSHIPS IN THE PYRIDINE SERIES

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By means of the MNDO, AM1, PM3 methods, we have computed standard heats of formation (ΔH_f), entropies (S), ionization potentials (I) and molecular dipole moments (μ) of pyridine and its 231 derivatives, the molecules of which contain C, H, N, O, F, Si, S, Cl, Br, I atoms. Linear dependences $P_{exper} = bP_{theor}$ ($P = \Delta H_f$, S, I, μ) have been established, which let one *a priori* evaluate the pyridines thermodynamic and molecular properties. Using the correlations found, it is possible to predict real substances' properties, not always available to the experimental measurement. In doing so, the computed values have to be corrected by the multiplier b. *A priori* evaluation of the said parameters by quantum chemical methods is important for molecular design of compounds with given properties, may serve as a base for expert decision on reasonability of synthesis that is sometimes labour- and time-consuming, requiring complicated device, rigid conditions, expensive and toxic chemicals.

2,2'-Bipyridine and its derivatives are important chelating reagents and redox indicators. Their protonation exhibits a competing reaction in relation to complexation. Molecular design of 2,2'-bipyridines demands for quantitative relationships for the pK_a evaluations.

We have performed quantum chemical computations of proton affinity (PA) for 2,2'-

bipyridine and a series of its 4-substituted derivatives (for which the experimental basicity data do exist) with the substituents $CONH_2$, $NHCOCH_3$, NO_2, OCH_3, OC_2H_5, $OCH_2C_6H_5$, Cl, Br. The pK_a and PA values of 4-X-2,2'-bipyridines with X = H, $CONH_2$, NO_2, $OCH_2C_6H_5$, Cl, Br satisfy the linearity condition of the interrelation between the above quantities, which probably corresponds to the permanent medium contribution to the substances' basicity. On the MNDO, AM1 and PM3 methods computations results, for PA = $\Delta\Delta H_f$, $\Delta\Delta G_f$ positive deviations from the trend line in the case of methoxy and ethoxy substituted 2,2'-bipyridines, and negative deviations with reference to the compound with the $NHCOCH_3$ substituent turn attention on itself. The data both for the species with obviously hydrophilic ($CONH_2$, NO_2), as well as with relatively hydrophobic ($OCH_2C_6H_5$, Cl, Br) atomic groups are put in dependences pK_a *vs* PA. Deviations from the trend take place for sufficiently bulky substituents, in which the hydrophilic-hydrophobic balance has been more or less kept.

STRUCTURE - PROPERTY RELATIONSHIPS BASED ON QUANTUM CHEMICAL COMPUTATIONS

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Based on quantum chemical investigations, correlation equations have been obtained for *a priori* predictions of standard heats and free energies of formation, entropies, ionization potentials, electron affinities, potentials of chemical and electrochemical oxidation and reduction, pK_a quantities, stability constants, dipole moments, vibrational frequencies of inorganic, organic, organoelement, coordination compounds, electronegativities, inductive parameters *iota*, mesomeric moments, for the forecasting of products yields and substituet rate factors in electrophilic and nucleophilic aromatic substitution, analytical reagents selectivity, substrate selectivity of the amines and phenolic species oxidation catalyzed by laccase of basidiomycete *Lentinus edodes*, transport rates of surfactant ions through molecular sieves. The results are of interest for molecular design of substances with given properties [1-9]. Oxidation mechanisms and homolytic coupling regioselectivities for diphenylamines and their heterocyclic analogs have been elucidated using spectroscopic, kinetic, voltammetric, electrophoretic and quantum chemical techniques [10-14].

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COMPARATIVE BASICITIES OF ANILINES IN WATER AND IN THE GASEOUS PHASE: POSSIBLE HYDROPHOBIC HYDRATION IN AQUEOUS MEDIA

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Reactivity of aniline and its derivatives is influenced by their protolytic properties.

By means of the PM3 method, we have computed proton affinities for aniline and its 62 derivatives with different kinds of electron-donor and electron-acceptor substitution in aromatic ring and at nitrogen atom.

For the cations of 4-methoxyaniline, 4-aminobenzoic acid and 4-nitroaniline conjugate acids, we have computed clusters including the aforesaid molecular systems along with 107 water molecules. A density of water molecules distribution approaches to this value for liquid state therewith, i. e. real aqueous solutions are modelled. The explicit hydration shell account showed that the anilines protonation occurs *via* the amine nitrogen, even in the cases when alternative protonation centres exist in the molecules.

Provided that the differences in anilines basicity are owing to intramolecular factors, and medium makes a constant contribution, the pK_a *vs* PA dependences must be linear. However, for the whole set of considered substances, such linear dependences are not observed. Obvious is differentiating effect of medium upon the protolytic properties of the aniline series.

We have established linear relationships pK_a vs PA for the series of 39-42 substances. Deviations from the linear dependences take place for N-substituted anilines, as well as for amines the molecules of which contain a bulky substituent in *ortho* position of aromatic ring (including those participating in intramolecular hydrogen bond: COOH, $COOCH_3$, NO_2). The *ortho* effect is probably connected with an increase in hydrophobicity of molecular fragments in the vicinity of protonation centre, with hydrophobic hydration of atomic basins including the reaction centre. Fallout of the data for N-alkyl anilines from the correlation series would be explained by considerable structural difference of the above compounds from primary aromatic amines. Using the relations obtained one can predict the pK_a values for anilines, construct the compounds with the desired acid-base properties. The approach proposed for evaluating pK_a values of anilines, aimed at their molecular design, can be extended to other classes of compounds.

ПЕРЕНОСИМОСТЬ МАСШТАБИРУЮЩИХ МНОЖИТЕЛЕЙ ПРОТИВ ПЕРЕНОСИМОСТИ СИЛОВЫХ ПОСТОЯННЫХ

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При решении обратной колебательной задачи на базе квантово-механического силового поля как исходного приближения и перенесении полученных силовых постоянных на родственные молекулы считают [1], что *силовые постоянные одинаковы* для квазиэквивалентных координат в сходных структурных группах родственных молекул. Тем самым указанный подход игнорирует характерные особенности силового поля каждой отдельной молекулы и делает обратную матрицу кинетической энергии полностью ответственной за возможные сдвиги частот колебаний и другие спектральные особенности родственных молекул, на которые переносятся силовые постоянные.

При масштабировании квантово-механических силовых полей родственных молекул принимают *одинаковыми относительные ошибки*, привносимые в квантово-механические силовые постоянные для квазиэквивалентных координат в сходных структурных группах при расчете на определенном теоретическом уровне. Это предположение накладывает гораздо менее жесткие ограничения, чем предположение о переносимости силовых постоянных в серии родственных молекул. В качестве примера приведены расчеты частот колебаний плоского *транс* и неплоского *гош* ротамеров бутадиена-1,3 [2,3].

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СРАВНЕНИЕ РЕЗУЛЬТАТОВ НЕЭМПИРИЧЕСКОГО КОЛЕБАТЕЛЬНОГО АНАЛИЗА И РЕШЕНИЯ ОБРАТНОЙ КОЛЕБАТЕЛЬНОЙ ЗАДАЧИ

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На примере *транс*- и *цис*-изомеров молекулы глиоксаля сопоставлены результаты решения прямой колебательной задачи с масштабированным неэмпирическим силовым полем в приближении МП2/6-31 ГФ*// МП2/6-31 ГФ* с результатами решения обратной колебательной задачи с использованием так называемой бэджеровской модели силового поля в качестве исходного приближения [1]. Показана неприменимость последнего подхода к многоатомным молекулам [2] и отмечена несостоятельность претензий на возможность конкуренции решения обратной колебательной задачи с начальным приближением по Бэджеру с неэмпирическими квантово-механическими расчетами.

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СОПОСТАВЛЕНИЕ ПРОГРАММ ДЛЯ ОПРЕДЕЛЕНИЯ МАСШТАБИРУЮЩИХ МНОЖИТЕЛЕЙ ДЛЯ КВАНТОВО-МЕХАНИЧЕСКИХ СИЛОВЫХ ПОЛЕЙ МОЛЕКУЛ

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Рассмотрены некоторые особенности и вычислительные возможности ряда программ для определения масштабирующих множителей, позволяющих эмпирически корректировать квантово-механические силовые поля по методу Пулаи. Обсуждена проблема устойчивости решений, получаемых рассматриваемыми программами. Численный пример нахождения стабильного решения при определении масштабирующих множителей по методу Тихонова [1] и по программе, рассмотренной в [2], приведен для перфторэтана. Показано [2], что программа [1] в наибольшей мере дает неудовлетворительные результаты для квантово-механических силовых полей, рассчитанных в приближении Хартри-Фока.

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КОЛЕБАТЕЛЬНАЯ АНГАРМОНИЧНОСТЬ И МАСШТАБИРОВАНИЕ КВАНТОВО-МЕХАНИЧЕСКОГО СИЛОВОГО ПОЛЯ МОЛЕКУЛЫ

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В рамках потенциала Морзе рассмотрена связь между масштабирующими множителями, полученными по методу Пулаи [1-4] из ангармонических и гармонизированных частот колебаний легкой молекулы и ее тяжелого аналога. Показано [5], что определение масштабирующих множителей из частот колебаний легкой молекулы приводит к меньшим отклонениям рассчитанных частот от их экспериментальных аналогов для тяжелой молекулы, чем обратная процедура. В этом контексте обсуждена степень выполнимости правила Деннисона.

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СОВРЕМЕННЫЕ ТЕНДЕНЦИИ КОМПЬЮТЕРИЗАЦИИ ХИМИЧЕСКИХ ИССЛЕДОВАНИЙ

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В настоящее время программное обеспечение для научных исследований развивается в направлении создания интегрированных проблемно ориентированных сред. Одновременно преобразованию подвергаются программные методологии, учитывая специфику прикладной области. Традиционно в химии применяются разные математические методы и модели хорошо известные из стандартных курсов обучения. Сегодня разрабатываются собственные методы программирования, структуры данных и технологии проблемно ориентированной среды в химии. Следует отметить четыре новые тенденции:

Персонализация: Научная система ПО становится более восприимчивой контексту пользователя, компьютерной среде и вычислительной задаче. Данный контекст охватывает информационные ресурсы предметной области.

Динамическое решение задачи: Традиционная парадигма, включающая этапы программирования, компиляции, загрузки и выполнения постепенно изживает себя. Современная прикладная система допускает реконфигурирование всех параметров при поступлении новых данных, возникновению новых задач, появлению новых ресурсов и выборе новых приоритетов.

Автоматическая оптимизация ПО: Анализ и оптимизация распространяется на более высокие уровни программирования, чем просто языковые модули. Целью этих усилий является упрощение программного интерфейса, проверка альтернативных решений реорганизация данных и программ. Высокая стоимость разработки ПО является мощным фактором, стимулирующим развитие технологии программирования компонентов.

Сочетание реальных и модельных систем: Моделирование является практическим решением, если соответствующие химические структуры хорошо поняты, а их воспроизведение в реальности либо невозможно, либо слишком дорого. Комбинирование виртуальной и химической реальности позволяет создать новые модели, обеспечивающие анализ химических структур на основе потоков информации. Предложенная идеология была использована нами при создании информационного комплекса расчета частот и форм нормальных колебаний многоатомных молекул.

GRECP/RCC-SD CALCULATION OF P,T-ODD SPIN-ROTATIONAL HAMILTONIANS IN HEAVY-ELEMENT DIATOMICS

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Last years a large number of both theoretical and experimental investigations is carried out dealing with the effects of the non-conservation of the space parity (P) and time invariance (T). The most prospective objects of such investigations are heavy diatomics TlF, YbF and

PbO because of the enhancement due to the relativistic effects and high charge of the heavy nuclei. Besides, some other important chemical and spectroscopic properties of these diatomics from the experimental and computational viewpoints were taken into account when selecting them for the fundamental experiments. Interpretation of the experimental data on the search for the T-non-conservation is based on the knowledge of the P,T-odd spin-rotational Hamiltonian parameters, which are calculated using quantum chemical methods. The electronic structure calculations are also necessary for appropriate planning these experiments. In this research we used modern relativistic quantum chemistry methods, the Generalized Relativistic Effective Core Potential (GRECP) and the Fock-Space Relativistic Coupled-Cluster method with Single and Double cluster amplitudes, for calculating electronic wave functions. Some chemical and spectroscopic constants for the ground state in TlF and YbF and for excited states in PbO are also calculated. Applying the recently developed universal nonvariational technique of restoration of four-component spinors in heavy cores, the P,T-odd spin-rotational Hamiltonian parameters are calculated.

COSMOS, A PROGRAMMING LANGUAGE FOR MANIPULATING CHEMICAL OBJECTS

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Developing tools for the description and manipulating molecular objects is of permanent interest for [computational] chemistry community. The more integrated and powerful are those tools, the better. The extreme case is a whole programming language specifically intended to handle molecules and to serve as a «glue» for a variety of computational methods and software which are common in modern chemical practice. COSMOS (Chemistry Oriented System for Manipulating Objects and their Storage) represents an attempt to create such a language. COSMOS comprises: the basis, a conventional object-oriented algorithmic programming language; the hierarchical set of data structures representing molecular objects; the set of functions (methods) inherent to those objects. The basis of COSMOS is Python, highly portable, extensible and robust programming language. Its well-developed objects support enabled easy building chemistry-oriented objects upon a general language structure. The objects hierarchy currently includes the following entries: Atom; Bond; Point; Assembly; Molecule; Conformation; Structure. COSMOS and Python were and are extensively used in our own practice (mainly molecular mechanics) and in the Net Laboratory for computational chemistry [http://qcc.ru/~netlab]. Simple COSMOS scripts perform many routinely tasks related to data preparation, visualization, statistics, etc. One more complex example is the program for hard-spheres calculation of oligosaccharides which starts from a short-hand notation common in sugars chemistry (like ‘Fuc(a1-3b)Gal(b1-2a)Gal’) and ends up with 2D images representing energy maps for all the disaccharides. The authors are grateful to Russian Foundation for Basic Research (Grant No. 98-07-90155v) for the support.

AB INITIO STUDY OF THE REACTIONS OF MAGNESIUM WITH CARBON TETRACHLORIDE

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Interaction of magnesium atoms with carbon tetrachloride is studied by high level ab initio methods of quantum chemistry. Stationary points on the Mg + CCl4 potential energy surface are located at the MP2/aug-cc-pVTZ level. Single point energy calculations for the predicted points are carried out at MP4//MP2/aug-cc-pVTZ level. Two important structures on the surface have been studied in detail, namely, well known Grignard's complex configuration CCl3MgCl, and the structure Cl2C□MgCl2 (C2v symmetry). Calculated vibrational frequencies and IR intensities of these species are compared to the experimental infrared spectra of matrix-isolated Mg/CCl4 co-condensates obtained at cryogenic temperatures.

КОМПЬЮТЕРНОЕ ПРЕДСКАЗАНИЕ БИОЛОГИЧЕСКОЙ АКТИВНОСТИ ХИМИЧЕСКИХ ВЕЩЕСТВ

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Биологическая активность – одно из важнейших свойств химических соединений – позволяет найти им применение в медицине, ветеринарии, парфюмерной и пищевой промышленности, но может также стать причиной токсичности и опасности веществ. Практически все известные физиологически активные вещества не являются абсолютно специфичными и обладают целым набором видов биологической активности. Общее количество известных видов биологической активности составляет более 2000, причем это число быстро растет. Очевидно, что практически невозможно исследовать все синтезированные соединения на все известные виды биологической активности. Определить приоритеты в тестировании веществ можно на основе компьютерного прогноза спектра биологической активности с помощью разработанной нами системы PASS (Химия в России, 1999, № 2, с.8-12). PASS оценивает вероятности принадлежности к классам активных (Pa) и неактивных (Pi) веществ для более 600 фармакологических эффектов, механизмов действия и специфической токсичности. Средняя точность прогноза в условиях скользящего контроля с исключением по одному составляет 85%. Показан универсальный характер используемых в PASS структурных MNA дескрипторов (J.Chem.Inf.Comput. Sci., 1999, ***39***, 666-670) и высокая статистическая устойчивость получаемых оценок вероятностей Pa и Pi (J.Chem.Inform.Comput.Sci., 2000, ***40***, 1349-1355). На основе предсказаний PASS удалось выявить ряд новых физиологически активных соединений с противоязвенной, антиамнестической, противоопухолевой, гепатопротекторной и другими видами активности (**http://www.ibmh.msk.su/PASS**). Создан web-сервер, прогнозирующий биологическую активность веществ через Интернет (**http://www.ibmh.msk.su/PASS**). В докладе обсуждаются текущее состояние и направления дальнейшего развития

компьютерной системы PASS, а также возможности сотрудничества с химиками, заинтересованными в выявлении биологической активности у синтезируемых ими веществ.

MULTIGEN: A NEW PARADIGM FOR *"MULTICONFORMATIONAL"* ALIGNMENT OF MOLECULAR STRUCTURES IN 3D-QSAR STUDIES[§].

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Lowest energy conformers are usually assumed in 3D-QSAR studies as the active form of a drug molecule but more and more evidences clearly show that a *minimum conformation* is not critical for bioactivity.

In this paper a new algorithmic innovation called MultiGen(shortcut for Multiconformer Generation) to define *multiconformational* models of a molecular dataset is presented.

Starting from the geometry of the lowest energy conformer the approach can be decomposed into 4 steps: 1) the normal vibrational (or internal rotational) modes (directions of vibrations) are defined for the lowest energy conformer; 2) the atoms of the molecule are moved along each mode until the nearest maximum of energy is overcame; 3) the new probable conformer is defined using a local minimum search; 4) the geometry of the new conformer is saved when its energy is less than an accepted value on respect to the low energy conformer. The process is iteratively carried out for each of the newly defined conformers. The conformational search is ended when the iteration doesn't lead to any new conformer then a *multiconformers based* model is created by the BiS[1] superimposing of the generated conformers. The model includes the cartesian coordinates of the atoms of all the conformers and the probabilities of their location in each point of this space. The biological activity of a compound (A) is defined as the sum of the conformers activities: $A = a + b\sum p_i A_i$ (where A_i = partial activity of the conformer i; p_i = statistical probability of a conformation to exist; a and b = parameters which are function of units of activity but independent of the dataset itself). The proposed method has been benchmarked using the recently reported *multiconformer* data on a dataset of 5-HT_{1A} receptor agonists[2]. The MultiGen results are generally in agreement with *Guccione et al.*[2] and allowed to *pick up* the most active conformer for each structure in the dataset when used as input for BiS[1] and HASL[2] calculations.

[§]This work has been supported by the Russian Foundation of Basic Researches (Grant 01-03-96414) and is part of S. Perspicace' s graduation thesis.

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ON THE MOTION IN THE MULTY-WELL POTENTIAL

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Some features of quantum multy-well problem are considered. The energy level ordering and the structure of the wave functions are described for some model systems with special attention to the one- and two-dimensional internal rotation and inversion problems for real potential surfaces of some carbonyl systems. The details of motions are considered for the atomic system into the polarised spherical cavity for the small and the large cavity radii limits. The peculiarities of the evolution description for the multy-well potentials are also considered. (RFBR, projects N 98-03-33232, 01-03-32116).

NONEMPIRICAL VIEW ON THE IONIZATION OF HYDRATED OZONE AND NITROGEN DIOXIDE

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The problem of the mutual effect of the properties of water clusters and small inorganic oxygen-containing molecules is not only interesting, but also important in view of the atmospheric chemistry under varying conditions caused by human or solar activity. The former implies artificially produced contaminants, such as nitrogen dioxide, while the latter results primarily in relatively severe ultraviolet radiation, which reaches the upper layers of atmosphere. Nonempirical modeling of water-ozone and water-nitrogen dioxide complex systems was carried out both in the second order of the Moeller-Plesset perturbation theory (MP2) and at the configuration interaction level with the 6-31++G** basis set and the effective potential technique. Being essentially hydrophobic, both ozone and nitrogen dioxide molecules initiate the formation of a relatively distant hydration shells around them, so that they are apparently located in the centers of cavities surrounded by water molecules. These defects created in the hydrogen-bond network facilitate the capture of excess electrons, which may be liberated in the positive ionization of neighbor species. The process of the excess electron density localization is further promoted by the high positive electron affinities of both aforementioned molecules, which exceed in absolute value the disinclination of individual water clusters to attach an excess electron. The resulting anionic species resemble the most stable water anions, in which the alien oxygen-containing molecules are located in the region of the maximum of the excess electron density. The positive ionization of water vapors in the presence of ozone and nitrogen dioxide should result in the formation of the states with different multiplicity. The actually observed structural reorganization well correlates with the ionization potentials (IP) of all the constituents considered: the IP of ozone

exceeds the IPs of all water clusters, while the IP of nitrogen dioxide, being lower than IPs of water dimer and trimer, is higher than IPs of the larger water clusters. The work is financially supported by the Russian Foundation for Basic Research (project no. 99-03-33251) and the Ministry for Higher Education in the framework of the program \"Universities of Russia-Fundamental Research\".

HIGH LEVEL CALCULATIONS OF TERT-BUTYL CATION ADDUCTS WITH NUCLEOPHYLS

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Ab initio SCF, MP2 and DFT calculations using large basis sets have been performed for the structures of adducts of carbocations with several nucleophiles. Special emphasis has been done to adducts of tert-butyl cation. It has been shown that the structure of adducts depends on two factors: the basicity of the nucleophiles and the Lewis acidity of the carbocations. More basic nucleophiles form covalent structures with primary cations resulting in delocalisation of positive charge to the attached neutral molecule. On the contrary, more acidic nucleophiles form molecular ion pair complexes with the positively charged relatively flat alkyl cation fragments. Basis set and electron correlation influence on the structures of adducts has been discussed in details. The results have been used to interpret experimental data obtained by collision activation mass-spectrometry.

BASIS SET AND ELECTRON CORRELATION INFLUENCE ON OH-BOND ANHARMONICITY AND VIBRATIONAL FEATURES OF SUBSTITUTED SILANOLS

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Ab initio SCF, MP2 and DFT calculations using wide range of basis sets have been performed for silanol and fluorinated silanol molecules that have been used as the simplest models for isolated terminal silanol group at silica surface. Complexes of silanols with different molecules have been also studied in details. The in-plane and out-of-plane OH-bending vibrations are sensitive to complex formation, as is the OH stretching vibration. The letter has been studied in harmonic and anharmonic approximations, by numerically solving the related Schroedinger equation for both free and interacting molecules. It has been shown that SCF calculations overestimate all frequences by about 10% but give approximately the same values of anharmonicity. In full agreement with experimental data the interaction practically does not cause any change of OH-bond anharmonicity. Basis set and electron correlation influence of the vibrational features has been discussed..

EFFECTIVE CRYSTAL FIELD FOR CALCULATION OF D-ELECTRON EXCITATIONS IN COMPLEXES OF TRIVALENT CATIONS OF FIRST ROW TRANSITION METALS

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Semiempirical method of Effective Crystal Field (ECF) designed for calculations of Transition Metal Complexes electron structure and using a trial electron wave function of none-Hartree-Fock type have been before parametrized and employed for calculations of complexes of divalent cations of 3d-elements Cr, V, Mn, Fe, Co, Ni. In the present work the ECF method have been extended to the complexes of trivalent ions of those 3d-elements. The ECF method with such a parametrization is employed for calculation of ground states and low-energy excitation spectra of the d-shell in fluoro-, chloro-, aqua-, amino- and cyanocomplexes. The total spin and the ground state space symmetry obtained in our calculations are alwais in accord with the experimental data. Satisfactory accordance between the calculated and experimental energies of d-electron excitations is achieved.

СТРУКТУРНО-ВЕРОЯТНОСТНЫЙ ПОДХОД К ОПРЕДЕЛЕНИЮ ОБЛАСТИ ПРИМЕНИМОСТИ ЛИНЕЙНОЙ МОДЕЛИ СВЯЗИ «СТРУКТУРА – СВОЙСТВО»

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Одна из важных задач современной теоретической химии - построение и исследование математических моделей, связывающих структуру и свойства химических соединений. Построение таких моделей основывается, как правило, на анализе некоторой выборки соединений с известными свойствами. При использовании соответствующих уравнений связи «структура – свойство» для прогнозирования свойств новых соединений возникает задача нахождения их области применимости, т.е. выделения класса химических соединений, свойства которых могут быть рассчитаны на основе вышеуказанных уравнений с требуемой точностью.

Рассматривается наиболее часто применяемая на практике математическая модель, в которой изучаемое свойство аппроксимируется линейной функцией молекулярных дескрипторов, описывающих структуру химических соединений, а коэффициенты линейной функции определяются по методу наименьших квадратов. Для уравнений такого типа предлагается новый подход к построению области применимости, основанный на комбинированном использовании аппарата теории вероятностей и некоторых количественных критериев структурного сходства.

Приводится ряд примеров, иллюстрирующих предлагаемый подход.

ОБ ОДНОМ СПОСОБЕ КОДИРОВАНИЯ ХИМИЧЕСКИХ СТРУКТУР В ЗАДАЧАХ ПОСТРОЕНИЯ МАТЕМАТИЧЕСКИХ МОДЕЛЕЙ СВЯЗИ «СТРУКТУРА – СВОЙСТВО»

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При построении математических моделей связи «структура – свойство» и определении их области применимости возникает задача количественного описания химических структур.

Предлагается метод кодирования химических структур, представленных простыми молекулярными графами (МГ). Каждой структуре сопоставляется вектор $X = (x_1, x_2, ..., x_n)$, компоненты которого x_i (i=1,...,n) равны числам вхождения в МГ определенных структурных фрагментов, называемых базисными. Базисный фрагмент S_k с k вершинами (k≥2) состоит из объединения некоторого числа следующих изолированных подграфов - цепочек длины 2, 3, ..., а также циклов размера 3, 4, ..., к вершинам которых присоединены 0, 1, 2, ... цепочки единичной длины всеми неэквивалентными способами.

Разработаны алгоритм и компьютерная программа генерации базисных фрагментов для любого числа вершин k и построения соответствующих молекулярных кодов.

Выдвигаются следующие гипотезы:

1) Структуры любой заданной конечной выборки могут быть однозначно закодированы вышеуказанным способом;

2) Любой инвариант графов f, рассмотренный на графах данной выборки, может быть представлен в виде некоторого многочлена $f(x_1, x_2, ..., x_n)$ базисных параметров x_i (i=1,...,n).

Показана справедливость выдвинутых гтпотез для достаточно больших и разнообразных классов МГ. Предложены способы автоматического отбора небольшого числа базисных фрагментов для построения корреляций «структура – свойство» и определения области применимости полученной математической модели. Приведены примеры.

DEDUCTION OF THE KLEIN-FOCK-GORDON EQUATION FROM A NON-MARKOVIAN STOCHASTIC EQUATION FOR REAL PURE-JUMP PROCESS

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For the first time the Klein-Fock-Gordon equation for a relativistic particle under an external potential is derived from the real relativistic quantum transport equation (RQTE) for the probability P(x,u) positively defined on the 8-space (x,u). As for RQTE, it is deduced from the relativistic non-Markovian generalization of the Kolmogorov-Gikhman-Skorokhod

equation for a real pure-jump process. By analogy, the Schroedinger equation for a micro-particle in an external potential is derived from the non-relativistic quantum transport equation (QTE) for the probability density, P(p, x, t), positively defined on the phase space (p, x). As for QTE, it is deduced from quantum kinetic equation (QKE) that is from non-Markovian Kolmogorov-Gikhman-Skorokhod equation for the real pure-jump process. Thus all quantum mechanics as mathematical theory is a topic of the theory of real pure-jump non-Markovian stochastic processes.

ВЫВОД УРАВНЕНИЯ КЛЕЙНА-ФОКА-ГОРДОНА ИЗ НЕМАРКОВСКОГО СТОХАСТИЧЕСКОГО УРАВНЕНИЯ КОЛМОГОРОВА-ГИХМАНА-СКОРОХОДА ДЛЯ ДЕЙСТВИТЕЛЬНОГО ЧИСТО-РАЗРЫВНОГО ПРОЦЕССА

Скоробогатов Г.А.

С момента выхода в 1926 работы Е. Маделунга известно, что пара сопряженных уравнений Шредингера взаимно-однозначно соответствует двум уравнениям “гидродинамического представления” для плотности вероятности $w(\mathbf{x},t)=|\psi(\mathbf{x},t)|^2$ и среднего импульса $\mathbf{p}(\mathbf{x},t)=i(h/2\pi)(\psi\nabla_x\psi^*-\psi^*\nabla_x\psi)/2w$ Эти два уравнения получаются из **квантового транспортного уравнения (КТУ**) для плотности вероятности $P(\mathbf{p},\mathbf{x},t)$ в фазовом пространстве, как два уравнения для первых двух моментов $w(\mathbf{x},t)=\int P(\mathbf{p},\mathbf{x},t)d^3p$ и $\langle p\rangle_{x,t}=w^{-1}\int \mathbf{p}P(\mathbf{p},\mathbf{x},t)d^3p$ В свою очередь КТУ получается из **квантового кинетического уравнения (ККУ)** -немарковского стохастического уравнения Колмогорова-Гихмана-Скорохода для действительного чисто-разрывного случайного процесса. Аналогично, уравнение Клейна-Фока-Гордона выводится из **релятивистского квантового транспортного уравнения (РКТУ)**, а последнее – из **релятивистского квантового кинетического уравнения (РККУ).** Обнаружение КТУ, ККУ, РКТУ и РККУ означает создание **ПОЛНОЙ** квантовой механики.

A NON-EMPIRICAL STUDY OF THE MOLECULAR STRUCTURE OF Sc(MDA)3 AND Sc(MDA)2

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Molecular structures and vibrational spectra of the scandium complexes with the chelate ligands (Sc(MDA)3 and Sc(MDA)2, where MDA is malondial-dehyde) have been investigated by non-empirical Hartree-Fock and second-order Moller-Plesset perturbation theory methods. The total energy of the electronically lowest-lying states of the Sc(MDA)2 radical were determined with the state –averaged complete active space self-consistent-field method. The quantum chemical computations were performed by the PC GAMESS version of the program GAMESS using extended basis sets, augmen-ted with polarization p(H) and d(O,C) functions. Atomic cores were described by effective (relati-vistic for Sc) potentials of Stevens et al. Equilibrium configuration of Sc(MDA)3 is a D3 symmetry structure in which the coordination poly-hedron ScO6 is a distorted octahedron. Another con-figuration (D3h

symmetry) taken into conside-ration is a first-order saddle point and corres-ponds to a barrier of 3650 cm-1 along the D3h - D3 - D3h-… rearrangement path. For the Sc(MDA)2 radical the D2h and D2d symmetry structures have been considered. The planar D2h configuration has a lowest energy at the 2Ag elect-ronic state and corresponds to a minimum on the PES. The planar configuration at the first excited electronic state (2B3g) as well as the nonplanar D2d configu-rations at the ground (2B1) and first excited electronic state (2B2) are the 3rd-order saddle points. Distortions of the geometry along the normal coordinates corresponding to imaginary frequencies tends to the configurations of D2 and C2 symmetries. An analysis of the geometrical parameters, force fields and features of the chemical bonds formation in the molecules under study has been done. The results has been compared with the literature data for similar molecules.

WANNIER FUNCTIONS AND CHEMICAL BONDING IN CRYSTALS

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Electronic configurations of atoms forming the crystal being suppoused to be known one can analyzes the change of atomic states under atom-atom interactions. In existing methods of electronic band structure calculations, electronical Bloch functions are looking for as a sum of basis orbitals (atom-type functions, plane waves etc.). The density matrix found in the calculations is used for population analysis by means of atom-type orbitals which were basis functions in band calculations or obtained from plane waves by a special procedure. One of the shortcomings of this approach is an essential dependence of the calculated characteristics of chemical bonding (charges and valences of atoms, indexes of interatomic bonds) on the choice of atomic functions used. In the present paper a new method of chemical bonding analysis in crystals is proposed. In this approach the Wannier functions for a crystal centered on atoms are suggested to play a part of atom-like functions for population analysis (atomic orbitals in a crystal). These functions are linear combinations of Bloch states of the upper valence and low conduction bands of the crystal. The group-theoretical symmetry analysis of these states by the method of induce representations allows to pick out those band states which are related to the corresponding Wannier functions according their symmetry. The proposed method has some advantages over usually used one. 1.Wannier functions form a minimal set of atom-like orbitals which reproduce exactly the structure of the upper valence and low conduction bands. 2.These functions are real and transform according to representations of the site symmetry groups of atoms in the crystal. In crystals with inversion these functions are unique (to within linear transformations in the space of the site groups representations). The arbitrariness in the determination of the Wannier functions in crystals without inversion center may be used for the generation of the best localized Wannier functions. 3.As Wannier functions are orthonomal, the population analysis on their base is similar to Löwdin' one. There exists the variational method which generates from the set of Bloch orbitals the best localized (according some criterion), but nonorthogonal functions. On the base of these functions is possible the population analysis similar to Mulliken' one. Wannier functions are produced from these functions by a suitable symmetrical orthogonalization procedure. The results of the calculations show that the Wannier and

nonorthogonal functions are close to one another and this explains the closeness of the results of the population analysis on their bases. 4.The proposed method does not depend on the type of the basis functions and is equally applicable to Bloch states in terms of atom-like functions, plane waves and any other basis functions. 5.The enlargement of the basis function set in the variational methods of the band structure calculation gives rise to more accurate definition of Bloch states and, as a consequence, to more accurate form of Wannier states and more accurate results of the chemical bonding analysis on their base. This method is also applicable for the chemical bonding analysis in molecules as in these systems one can generate localized orbitals from canonical ones (atomic functions in molecule, the analogue of Wannier functions in crystals) The proposed approach for the analysis of local characteristics of atoms in crystals is illustrated on the examples of classical structures – silicon, gallium arsenide and silver halides crystals.

VARIATIONAL METHOD FOR THE CHOICE OF BLOCH FUNCTION PHASE FACTOR IN THE PROBLEM OF WANNIER FUNCTIONS GENERATION

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Since their introduction in 1937 Wannier functions have been often used in many theoretical considerations of electronic properties of crystals. The use of a localized basis facilitates significantly the study of local properties (atom charges, active valences, bond orders and so on) in solids. The basis of best localized Wannier functions has an irrefutable advantage over other atomic-like bases as it is the best adopted to the states of an energy band under consideration. The Wannier functions may be regarded as atomic functions modified by the crystalline surrounding The analytical behavior of Bloch functions of energy bands in k-space determines the degree of localization of corresponding Wannier functions in r-space. A useful concept of band (induced) representations has been introduced in the theory of crystals, according to which the symmetry properties of Bloch functions for a given energy band define (in many cases unambiguously) the position of symmetry localization and the symmetry properties of Wannier functions . Practical methods for the calculation of Wannier functions for simple and composite bands in perfect crystals have been elaborated and applied. The method of the localized Wannier functions construction by the Fourier transformation of Bloch functions we are proposing now consists of three steps: 1) a symmetry analysis basing on the band representation theory, 2) a variational procedure of the Bloch function\' phase factors choice and 3) a suitable orthogonalization procedure. The character of the localization of Wannier functions depends on the analytical properties of Bloch states (as a function of the wave vector) which are essentially determined by the nature of the system under consideration. One can arbitrary change only their phase factors and form arbitrary linear combinations of Bloch functions (in particular, in case of degeneracies). It is just this arbitrariness that is used in our variational approach to assure the best localization of Wannier functions. The accuracy of the Wannier functions obtained by the proposed method is determined solely by the accuracy of the Bloch functions and the size of the supercell used. The variational procedure proposed gives the system the best localized non-orthogonal functions. After the symmetrical orthogonalization this system does not loose the property to

be the best localized. The reliability of the method is demonstrated by computations of localized displacements in a one-dimensional diatomic lattice and a germanium lattice, of localized electronic states in a one-dimensional Kronig-Penney model and for the upper valence bands of Si and MgO crystals.

MOLECULAR STRUCTURE AND NUCLEAR DYNAMICS OF NBX4 (X=F, CL, BR, I)

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Molecular structure and vibrational spectra of the niobium tetrahalides have been investigated by non-empirical Hartree-Fock and second-order Moller-Plesset perturbation theory methods using PC version of program GAMESS. Atomic cores were described by effective relativistic potentials by Stevens et al. The valence electrons were described by the set of Cartesian Gauss functions augmented with polarisation d-functions for halogens. The two electronic states 2A1 and 2B1 corresponding to D2d symmetry of molecules were considered. The calculation of the set of vibrational frequencies showed that D2d structure with 2A1 symmetry of the electronic state corresponds to the minimum on the energy surface. The structure D2d with 2B1 electronic state is the first-order saddle point. The structure with Td(2E)symmetry was calculated by CASSCF taking into account five lower lying electronic states. Jahn-Teller energy stabilisation was obtained. Jahn-Teller effect manifest itself for all investigated molecules. The structural distortion decreases in the line NbF4, NbCl4, NbBr4, NbI4. The energy surface is similar to the Mexican hat with 3 minima for the D2d configurations along the trough. The nuclear dynamics of all molecules under consideration was investigated by analytical method. The one-dimensional Schrodinger equation with the potential function for the motion along the bottom of the trough (along the extremal) of the Mexican hat was solved. The formulae for the energy levels and for the wave function were obtained. The calculated structures for molecules NbCl4, NbBr4, NbI4 are in good agreement generally with the structures obtained by gas-phase electron diffraction.

REACTIVITY OF VINYL MONOMERS IN RADICAL ADDITION REACTIONS: QUANTUM CHEMISTRY MODEL

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Transition states (TS) of radical addition of CH3, CH3O, CCl3, CF3 and HOO to ethene, propene, acrylic nitryl, methyl acrilate, vinyl chloride and vinilidene chloride were calculated using MNDO UHF, both positions of attack discussed. Moreover, also considered monomers with conjugated double bond (butadiene, styrene, vinylpyridines etc. (over 100 reactions). The main aspects and results of this investigation were as follows. * Intrinsic reaction coordinate (IRC): detailed description of IRC was gained by using energy partitioning procedure and studying vibration frequencies alongside pathways; demonstrated that deformation of monomers\' reactive centers gave important part to activation barriers. *

Thermochemical aspects: found satisfactory correlation of reaction heat and activation energy in the \"radical-monomers\" series; correlations between activation barriers and deformation energies. Regularities of charge distribution: found that there was linearity between charge transfer in all reaction series. Comparison with PMO approach: correlations between directly calculated activation energies and Charge Transfer (CT) energies of PMO method were obtained; demonstrated that Frontier Orbitals approach to reactivity consideration failed, so the full sums over p-orbitals were used; proposed new reactivity index of reactivity. * Model of reactivity in radical addition. Suggested that activation energy of radical addition is a total of two effects, namely deformation energy and polar interaction. The first was evaluated by energy of some standard deformation, the second - by CT energy. All results of direct TS calculations were considered within the following equation as a general scheme of radical activity: Ea = a0 + a1 Edef + a2 ECT. Good enough correlation prompted us to transfer this model to discussion of experimental reactivity and offering new empirical scheme of reactivity. * Empirical scheme of reactivity for radical addition to vinyl monomers. Mathematical form of above-mentioned model was used as a correlation equation for known experimental kinetic data (over 200 rate constants of radical reactions considered). Parameters of 40 monomers and radicals were obtained by optimization.

NEW ASPECTS OF ELECTROPHYLIC AROMATIC SUBSTITUTION MECHANISM. COMPUTATIONAL MODEL OF NITRATION REACTION

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Systematic studies of aromatic nitration reaction were performed using gas phase model (AM1) and solvation model (SM2.1). In both cases the aspects of RHF, UHF and CI approach were considered. Several variants of possible nitration agents were examined. The known fact is that nitronium ion (NO2+) is formed from nitracidium ion (H2NO3+) at a slow reaction step and exists in essentially acid media. We found by computational simulation that both NO2+ and H2NO3+ have similar affinity to aromatic compounds, so nitracidium ion is a possible electrophile of nitration reaction in media of moderate or low acidity (solvates containing water, acetic acid and the like). Electronic and thermochemical characteristics of transition (TS) states with substituted aromatic compounds (Alk, Ph-R, CH3O, Cl, COOCH3 etc.). There were investigated in detail the electronic structure of TS, of reaction intermediate (sigma-complex), the reaction pathway by above-mentioned methods. Maps of potential energy are given. The causes and the character of influence of substitutes on reactivity and selectivity discussed. Firm correlation of activation barriers and enthalpies of sigma-complex formations were found. Possibility of electron transfer during reaction of NO2+ with aromatics discussed. Our attempt to solve the problem by semiempirical methods led to no certain results. Physicochemical model was offered to describe influence of solvents on nitration reaction. It explained high (5-7) degrees of reaction dependence on HNO3 concentration which was observed in some cases.

КВАНТОВО-ХИМИЧЕСКОЕ ИССЛЕДОВАНИЕ РАЗЛИЧНЫХ ПУТЕЙ ГЕНЕРАЦИИ КАРБЕНИЕВЫХ ИОНОВ ИЗ ОЛЕФИНОВ И АЛКИЛФТОРИДОВ В СРЕДЕ HF

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Методами Хартри-Фока (ХФ) с учетом электронной корреляции на уровне MP2 и функционала плотности Becke3LYP в базисе 6-31++G** исследованы реакции генерации карбениевых ионов из олефинов и алкилфторидов в среде жидкой HF. На основе рассчитанных энтальпий реакций определены возможные пути генерации карбениевых ионов в системе (олефин - HF), и сделан вывод, что наряду с протонизацией олефина источниками карбениевых ионов являются соответствующий алкилфторид и его протонированная форма. В рамках дискретной модели микросольватации, а также модели поляризующегося континуума (PCM) оценен вклад сольватации в понижение активационного барьера гетеролитического распада алкилфторидов в среде жидкой HF. Проведены расчеты методом MP2 поверхности потенциальной энергии (ППЭ) для двух систем ((изобутан + (CH3)3C(+) +2HF) и (изобутан + (CH3)2CH(+) +2HF)). Обнаружено, что в случае второй системы происходит безбарьерный перенос гидрид-иона от изобутана к карбениевому иону (CH3)2CH(+). Для первой системы на ППЭ обнаружен минимум, соответствующий комплексу с симметричной локализацией гидридного иона (HF..(CH3)3C(+)..H..C(CH3)3..FH), и только учет всего остального растворителя в рамках модели PCM приводит к появлению небольшого активационного барьера. Методом MP2 в базисе 6-31G** исследованы реакции присоединения (CH3)3C(+) иона к олефинам (изобутену, 1-бутену и 2-бутену) в среде жидкой HF. На основе рассчитанных энтальпий реакций перегруппировок первично образующихся карбениевых ионов (1,2 сдвиг метильной группы и 1,2 и 1,3 гидридные сдвиги) определены наиболее стабильные C(8) карбениевые ионы в исследованной системе.

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THE JAHN-TELLER EFFECT AND A SPIN-ORBIT COUPLING IN THE TANTALUM TETRAHALIDE MOLECULES

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The Jahn-Teller (JT) effect and a spin-orbit coupling (SOC)in the ground 2^E and the first excited 2^T_2 electronic states of the TaHal4 molecules (with Hal = F,Cl,Br,I)were investigated. State-averaged complete active space self-consistent field (SA-CASSCF)level of theory has been employed. The SOC effect was accounted for with the use of an effective one-electron one-center spin-orbit operator. The JT distortions, stabilization energies, coupling constants, and the vibronic molecular spectra were calculated. The structural and spectroscopic consequences of the interplay between the Jahn-Teller effect and a spin-orbit coupling were revealed. The work was supported by the Russian Foundation for Basic

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НЕКОТОРЫЕ СООТНОШЕНИЯ ДЛЯ ПОЛНЫХ ЭНЕРГИЙ ФУЛЛЕРЕНОВ C_n И ИХ ПРОИЗВОДНЫХ, СОДЕРЖАЩИХ АТОМЫ БОРА И АЗОТА В ПОЛИЭДРИЧЕСОМ КАРКАСЕ

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Среди достаточно широкого класса химических соединений, содержащих атомы бора и азота, существует много структур изоэлектронных и изоструктурных их углеродным аналогам. Анализ опубликованных расчетов показал, что замещение в углеводородных молекулах или в углеродном кластере некоторых связей C-C на связи B-N приводит во многих случаях к значительному уменьшению полной энергии. Например, разность полных энергий молекул бензола и боразола, рассчитанная методом MNDO, равна 44 эВ, а для кластеров C_{60} и $C_{58}BN$ аналогичная величина составляет 34 eV.

В докладе показано на примерах некоторых полиэдрических молекул $C_{n-2x}(BN)_x$, что такое различие между полными энергиями основных состояний изоструктурных и изоэлектронных полиэдрических углеродных кластеров C_n и их B,N-производных имеет достаточно общую природу и не зависит от метода вычислений (конечно, если такой метод теоретически обоснован).

Установлено, что для энергий основных состояний достаточно широкого класса кластеров $(BN)_xC_{n-2x}$ $(n-2x\geq 0)$ справедливы следующие соотношения

$E(\ (BN)_x C_{n-2x}\ ) + \Delta E < E(\ C_n\ )$. В этой формуле $E(Q)$ – энергия основного состояния кластера Q и $\Delta E = \sum_{\mu=1}^{n} \sum_{\mu<\nu} \frac{\pm 1}{|R_\mu - R_\nu|}$, где R_μ - координата μ-ого ядра, и индексы μ и ν относятся только к атомам B и N. Если индексы μ и ν относятся к атомам различных типов, тогда соответствующий член в выражении ΔE положителен. Если индексы μ и ν относятся к атомам одного и того же типа, то такое слагаемое будет иметь знак минус.

Работа поддержена Российским Фондом Фундаментальный Исследований, а также Российской научно-технической программой «Актуальные направления в физике конденсированных сред», подпрограмма «Фуллерены и атомные кластеры».

MEDIUM EFFECT ON A STRUCTURE SULFAMIC ACID IN A GAS PHASE. COMPARISON AB INITIO CALCULATIONS WITH EXPERIMENTAL DATA.

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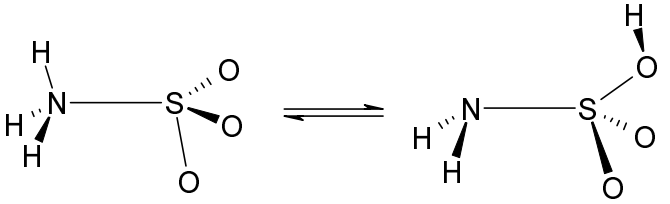
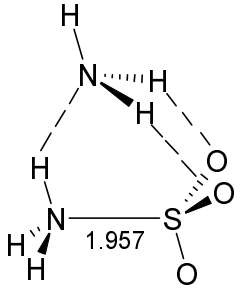
The main purpose of the present work is an to establish with the help ab initio (MP2 (full) /6-31G **) calculations the mechanism of reaction rearrangement of sulfamic acid from neutral to the zwitterionic form and to study influence of the mediators molecules (NH_3, H_2O, HF) on the energetic characteristics of the given reaction, and also estimation of cooperative environment effect**.**



1 2

According to the calculations, the zwitterionic form 1 of sulfamic acid on 3.2 kcal/mol is more stable than neutral form 2. The barrier reactions is 31.1 kcal/mol. The mediators molecules - NH_3, H_2O, HF reduce a barrier of reaction up to 7.0, 15.7, 13.5 kcal/mol accordingly. It has been shown that S-N bond is shortened from 2.106 E up to 1.835 E with increase of ammonia amount around sulfamic acid. The results of nonempirical calculations for complex 3 with one molecule NH_3 are in excellent agreement with gas phase experimental data for sulfamic acid.



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The work is financial supported by RFBR, grant 01-03-32546.

STRUCTURE AND HYDROGEN BONDING OF ADENINE IN POLYHYDRATED COMPLEXES. A DFT STUDY

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Method of the density functional theory with B3LYP functional in basis 6-31G (d) has been used for calculation of equilibrium geometry and energy of interaction in four polyhydrated complexes of adenine (W12, W13, W14, W16) with 12, 13, 14 and 16 molecules of water respectively. It is determined that hydration shell in the complexes is essentially nonplanar. It is revealed that the attempt of modeling formation hydrogen bonds such as H...pi (with coordination hydrogen atom of water to pi system of purine) results in realization of structure with two equal hydrogen bonds such as H...N on atom of nitrogen N(7). It is established that the strongest hydrogen bonds (of nucleobases-water type) form groups of atoms N(3) and N(9) -H adenine, and the weakest - C(8) -H and amino group N(10)H2. It was found that the interaction with molecules of water considerably influences molecular structure of hydrated adenine. It is demonstrated that the change in the geometrical characteristics of the amino group contradicts the classical understanding of the conjugation between the amino group and the aromatic system when hydration shell is formed and reorganized in adenine. The topological analysis of distribution of electron density in complexes identificates the presence of the (3,-1) critical point on C(8) — H...0 bond. This confirms existence of C — H...O hydrogen bond between hydrophobic part of adenine molecule and molecules of water. Calculated BSSE-corrected energy of the interaction for hydrates W12- W14 increases when adding water molecules to hydration shell and reaches maxima in W14 (-57.9 kcal/mol). Further shell reorganization up to W16 results in decrease of the value of interaction energy.

RADICAL POLYMERIZATION OF DIALLYLAMINE COMPOUNDS: FROM QUANTUM CHEMICAL MODELING TO CONTROLLABLE SYNTHESIS OF HIGH MOLECULAR WEIGHT POLYMERS

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It is known that the processes of polymerization of allyl and diallyl compounds are practically controlled by degradative chain transfer to monomer reaction with formation of nonreactive allyl «transfer» radical and obtaining of only oligomeric products. In this connection series of quantum chemical and experimental investigations has been performed of a principal possibility of obtaining of high molecular weight (HMW) polymers from the monomers of diallylamine (DAA) set. Potential energy profiles of chain propagation and chain transfer competing reactions, free radical double bond addition and a-hydrogen radical abstraction respectively, were studied for several polymerization processes[1] within polarized continuum solvent model [2] utilizing the procedure [3] based on semiempirical MNDO-PM3 background. It was established that the existence of monomer molecules in protonated form

in polymerizing system is the requisite condition of decrease in competitiveness of chain transfer to monomer reaction [1]. As a result of quantum chemical calculations the strategy was developed of obtaining of HMW polymers from monomers of DAA set. The equimolar salt of N,N-diallyl-N-methylamine and trifluoroacetic acid was first synthesized and suggested as appropriate monomer system [4]. It was shown by NMR 1H spectra that diallylmethylamine molecules are in protonated form in solutions of the salt. Novel HMW polymers were synthesized for the first time by radical polymerization of said salt at soft conditions [4]. It was determined by kinetic studying that the phenomenon of degradative chain transfer to monomer, characterizing polymerization of allyl compounds, was overcome by transformation of degradative chain transfer into the effective one [4]. The results obtained give the principal opportunity for controllable synthesis of new polymers based on monomers of DAA set. At the same time they demonstrate the potential of quantum chemical calculations in theoretical prediction and determining the way of chemical process. 1. Timofeeva, Yu. A. Vasilieva, N. A. Klescheva and D.A. Topchiev, Russ. Chem. Bull., 1999, 48, 856. 2. S. Miertus, E. Scrocco and J. Tomasi, J. Chem. Phys. ,1981, 55, 117. 3. G.E. Chudinov, D.V. Napolov and M.V. Basilevsky , Chem. Physics, 1992, 160, 41. 4. Yu. A. Vasilieva, N. A. Klescheva, G. L. Gromova, M. P. Filatova, A. I. Rebrov, E. B. Kryt'ko, L. M. Timofeeva and D.A. Topchiev. Russ. Chem. Bull., 2000, 49, 431.

AB INITIO QUANTUM-CHEMICAL CALCULATIONS OF A CLUSTER C8H12

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In connection with a problem of design organic high-spin polyradicals, ab initio calculations of a cluster C8H12 has been carried out. The calculations are performed on the program GAUSSIAN-94 as within the framework of a method UHF, and with usage of Density Functional (DFT) method (basis set 6-31G*). For calculation the quincunx conformation C8H12 with fragments H-C-H posed in a plane of an axis C-C was selected. Angles between bond at each carbonic atom tetrahedral and equal 109 degrees. The calculations are performed at fixed dihedral and valence angles of a cluster C8H12. The cluster C8H12 is calculated in single, triple, quartet and septet states. As a result of calculations was shown, that a ground state for the given conformation is septet state. On an example of a concrete system the kinematic mechanism of magnetic exchange and magnetic ordering in polyradicals is researched. The explanation is based upon the concentrational magnetism, appearing, when highly mobile electrons fall into the paramagnetic ambience. The considered cluster C8H12 serve as source of such electrons, and provide ferromagnetic ordering FMO) in them without the admixture of d-metals.

MRD-CI METHOD FOR CALCULATION OF HEAVY-ATOM MOLECULES. COMPARISON OF GRECP/MRD-CI AND GRECP/RCC-SD CALCULATIONS ON TlH

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The relativistic one-step version of the MultiReference single- and Double-excitation Configuration Interaction (MRD-CI) method is discussed. Up to now MRD-CI is most actively used in calculations of correlation structure and physical-chemical properties of low-lying states in molecules. The nonrelativistic MRD-CI method was suggested by Buenker & Peyerimhoff [Theor.Chim.Acta, v.35, 33 (1974); v.39, 217 (1975)]. The relativistic MRD-CI versions with the spin-orbit interaction taken into account were then developed by a few groups applying both the one-step and two-step techniques. Some new features, such as spin-orbit configuration selection [Titov et al., Int.J.Quant.Chem., 2001, in press] and a new criterium of automatic generating reference configurations [Mosyagin et al., in progress] for a group of states and selecting configurations were recently proposed by our group and applied to the TlH, HgH and PbH calculations. Advantages and disadvantages of MRD-CI as compared to a very rapidly evolving Relativistic Coupled-Cluster (RCC) approach are discussed. Features of these methods are demonstrated on example of the 4- and 14-electron GRECP/MRD-CI [Titov et al., Int.J.Quant.Chem., 2001, in press] and GRECP/RCC calculations [Titov et al., in progress] for the ground and a group of low-lying states in TlH. The same basis sets, [4,4,4,3,2] for thallium and [4,3,1] for fluorine, are used and the same numbers of electrons are correlated. In our calculations, the Fock-Space RCC version with Single and Double cluster amplitudes (FS RCC-SD) is used (the RCC-SD codes were developed by group of Prof. U.Kaldor). The Generalized Relativistic Effective Core Potential (GRECP) method was developed by our group (e.g., see Int.J.Quant.Chem., v.71, 359 (1999)) for accurate describing relativistic effects, interaction with core electrons etc. It is demostrated that a combination of the MRD-CI and RCC-SD methods (i.e., \"valence CI correction\" to the RCC-SD energies, see [Isaev et al., J.Phys.B, v.33, 5139 (2000)]) can considerably improve the FS RCC-SD accuracy for open shell cases in the valence region.

МОЛЕКУЛЯРНОЕ МОДЕЛИРОВАНИЕ NR1 И NR2B СУБЕДИНИЦ NMDA-РЕЦЕПТОРА И МОЛЕКУЛЯРНЫЙ ДОКИНГ ЛИГАНДОВ.

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Построены трехмерные модели NR1 и NR2B субединиц NMDA-рецептора, содержащих сайты связывания возбуждающего нейромедиатора глутамата (агониста NMDA-рецептора) и коагониста глицина, по гомологии на основе координат атомов AMPA-подобного водорастворимого рецептора. На основе построенных моделей и литературных данных по сайт-специфическому мутагенезу был проведен молекулярный докинг агонистов и антагонистов к вышеперечисленным сайтам, а также обсуждены способы их связывания. Построенные модели комплексов были использованы для объяснения известных зависимостей «структура-свойство»:

зависимость агонистических (антагонистических) свойств от длины и от природы щ-кислотной группы , предпочтительность замещения атома азота аминогруппы и D-конфигурации хирального центра. Проведено молекулярно-динамическое исследование полученных комплексов «лиганд-рецептор». Полученные данные могут быть использованы для дизайна новых лигандов, которые могли бы стать терапевтическими средствами для лечения ряда острых и хронических нейродегенеративных заболеваний.

ADDITION OF THE PHENYL RADICAL TO ETHYLENE AND ACETYLENE: REACTION PATHWAYS, POTENTIAL ENERGY PROFILES AND ABSOLUTE RATE COEFFICIENTS

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The C6H5 + C2H2/C2H4 addition reactions and subsequent transformations have been studied within a framework of the G2M composite method [1]. Full geometry optimization was performed using the B3LYP density functional [2,3] with the 6-311++G(d,p) basis set [4]. Higher level ab initio single point calculations were carried out on the optimized structures of the local minima and first-order saddle points to provide more accurate estimates of reaction barriers and enthalpies. The theoretical analysis of these reactions revealed that chemically activated adducts can undergo several isomerization pathways in competition with well-known deactivation and H-elimination channels. Thus formed isomeric C8H7/C8H9 vinylic/aliphatic, aromatic and bicyclic radicals can serve as active agents in the mass growth reactions with C2H2, C2H4 and other light unsaturated hydrocarbons and radicals. The latter processes are relevant to the PAH formation in hydrocarbon combustion. P,T-dependent rate coefficients for various elementary steps involved in the two title reactions have been calculated and closely correlated with the available experimental kinetic data. References: 1. Mebel, A. M.; Morokuma, K.; Lin, M. C. J Chem Phys 1995, 103, 7414. 2. Becke, A. D. J Chem Phys 1993, 98, 5648. Becke, A. D. J Chem Phys 1992, 96, 2155. Becke, A. D. J Chem Phys 1992, 97, 9173. 3. Lee, C.; Yang, W.; Parr, R. G. Phys Rev B 1988, 37, 785. 4. Pople, J. A.; Head-Gordon, M.; Raghavachari, K. J Chem Phys 1987, 87, 5768.

TRANSITION METAL COMPLEXES WITH OXYGEN ACTIVE LIGAND AS STUDIED BY EFFECTIVE ELECTRON HAMILTONIAN APPROACH

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Many transition metal complexes are known as active catalysts of the oxygenation processes.

The mechanism of their catalytic activity is however not clearly understood. It is assumed that the reorganization of the electronic structure of reactants under adsorption or coordination to a catalyst plays an important role in the oxygenation processes. In this work we consider the changes of oxygen state under coordination of molecular and atomic oxygen to transition metal complex. The electrons in the d-shell of transition metal atom and electrons of reactants are highly correlated in the catalytic complex. The oxygenation catalysts are usually extended molecular systems or even solid-state catalysts and can not be attacked by standard correlated quantum chemical methods. The hybrid scheme developed previously [1] is used for description of electronic structure of these complexes. The variables of quantum part is chosen as the occupation numbers of the d-shell of transition metal atom and those of certain one-electron reactant states. The quantum part is then treated on the full configuration interaction level. This scheme is applied to analysis of the electronic states of atomic and molecular oxygen coordinated by transition metal porphyrines and adsorbed on the surfaces of transition metal oxides. The latter are modeled by clusters containing 125 ions. We studied the electronic structure of adsorbed oxygen species as function of the geometry parameters (the metal-oxygen separation, type of coordination of the oxygen molecule (side-on or end-on), bending angle for the oxygen molecule, exit of metal atom from the plane of the catalyst). Our calculations show variation of the weights of the singlet, triplet and negatively charged oxygen configurations regarding the geometry variations. The metal-oxygen separation seems to be the most important factor affecting the weights of the singlet and charged oxygen configurations. The results also demonstrate how the state of oxygen atom depends on the electronic structure of catalyst. 1) A.M. Tokmachev, A.L. Tchougreeff, Russ. J. Phys. Chem., 2000, v. 74, ¦ 1, p. 66.

GENERALIZED MOLECULAR MECHANICS AS DERIVED FROM LOCAL QUANTUM MECHANICAL DESCRIPTION OF MOLECULAR ELECTRONIC STRUCTURE

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Molecular mechanics (MM) is very powerful and extensively used tool for modeling potential energy surfaces of large molecular systems. At the same time its potential functions (force fields) and their parameters are purely empirical and the validity of the MM itself is confirmed only empirically. On the other hand the parameters of MM potentials of fixed form are often determined from the quantum chemical calculations. At the same time not only parameters but also the form of MM potential are reasonable to be derived from quantum mechanical considerations. Previously we developed a semiempirical quantum chemical method using the wave function in the form of antisymmetrized product of strictly localized geminals (APSLG) [1]. Starting from that local APSLG description of molecular electronic structure we constructed a generalized MM scheme. It can be termed as molecular mechanical since it does not contain any diagonalization or iteration processes and expresses the energy as a function of intrabond and interbond contributions. By contrast to the usual MM which takes the energy as an explicit function of nuclear coordinates the constructed generalized scheme represents the energy as a function of not only geometry parameters but

also some electronic parameters (form of the hybrid orbitals; ionicity and polarity of the bonds) which are determined by simple algorithms. It is noteworthy that no parameters are added to the underlying semiempirical APSLG scheme [1]. The results of our calculations show that the scheme obtained has the same accuracy as the underlying quantum mechanical APSLG approach.

1) A.M. Tokmachev, A.L. Tchougreeff, Russ. J. Phys. Chem., 1999, v. 73, No 2, p. 259.

COMPUTING THE KEKULÉ STRUCTURE COUNT FOR ALTERNATE HYDROCARBONS

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A fast computer algorithm brings computation of the permanents of sparse matrices, specifically, chemical adjacency matrices. Examples and results are presented, along with a discussion of the relationship of the permanent to the Kekulé structure count. A simple method is presented for determining the Kekulé structure count of alternate hydrocarbons. For alternate hydrocarbons, the square of the Kekulé structure count is equal to the permanent of the adjacency matrix. Also, for alternate structures, the adjacency matrix for N atoms can be written in such a way that only an $N/2 \times N/2$ matrix need be evaluated. The Kekulé structure count correlates with topological indices. The number of cycles improves the fit. When comparing with previous results, the variance decreases 74%. The calculated standard heats of formation correlate with the logarithm of the Kekulé structure count. This heat increases 151kJ$\cdot$mol^{-1} each time that the Kekulé structure count is multiplied by number *e*.

РАСПОЗНАВАНИЕ СТРУКТУРНЫХ ФОРМУЛ ДЛЯ РЕШЕНИЯ ЗАДАЧ ОРГАНИЧЕСКОЙ КОМПЬЮТЕРНОЙ ХИМИИ

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При решении широкого круга задач органической компьютерной химии часто возникает необходимость ввода в компьютер информации о химических структурах органических соединений с бумажного носителя (книги, журнала, справочника и т.д.). Предлагаемая в данной работе методика автоматического ввода структурной информации представляет собой композицию ряда широко известных алгоритмов машинной графики и распознавания образов (таких, например, как преобразование Хафа), адаптированных с учетом конкретной специфики предметной области - органическая химия. Программная реализация методики выполнена на компьютерной платформе Macintosh. Входным потоком является изображение структур - набор молекулярных графов (МГ) в растровом графическом формате (например, стандартный для Макинтоша файл данных типа PICT). Выходной поток составляют: матрицы смежности МГ и матрицы координат вершин для изображения МГ. Процесс

распознавания каждой структуры состоит из следующих трех стадий: сканирования, собственно распознавания и формирования МГ. После выполнения этого процесса для очередной структуры он циклически повторяется для следующей, пока весь входной поток не будет исчерпан. Эксперименты с реальными структурными формулами, взятыми из литературных источников свидетельствуют, что для распознавания кратных связей необходимы усложнения, причем измерения программных реализаций показывают, что эти усложнения в 2 и более раз удлиняют время распознавания, а в некоторых случаях снижается его достоверность. Поэтому при реализации методики представляется оправданным принять разумные ограничения на возможные способы представления структур подлежащих распознаванию, кроме того, в программной реализации стоит предусмотреть возможность отключения функции распознавания кратных связей. Отдельной задачей, вне рамок данной работы, является задача компьютерного распознавания структурных формул, содержащих гетероатомы и другую сопутствующую алфавитно-цифровую информацию (например, значения длин связей, включенных непосредственно в рисунок структуры). Путями к решению подобных задач может быть как комбинация данной методики с типовыми методами OCR (Optical Character Recognition), так и переход на полуавтоматический режим распознавания – при котором программа распознает лишь структурный скелет, а ввод гетероатомов и прочей дополнительной информации производится затем вручную с помощью специализированного редактора МГ. Этот же редактор служит целям просмотра и коррекции выходных данных.

РАСЧЕТ ПАРАМЕТРОВ ЯМР ДЛЯ ЦИКЛИЧЕСКИХ МОЛЕКУЛ ОРГАНИЧЕСКИХ СОЕДИНЕНИЙ

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Предлагаемый расчетный метод базируется на предложенном ранее авторами способе расчета электроотрицательностей атомов органических молекул с введением поправки на топологические особенности для циклосодержащих молекул [1]. Метод не требует трудоемких вычислений и может применяться для экспресс-оценки фундаментальных свойств циклосодержащих (в том числе ароматических) органических соединений при решении широкого круга задач органической компьютерной химии. Компьютерная реализация предлагаемой модели представляет собой модуль программы EDIP[2]. С ее помощью метод испытан для различных классов органических соединений путем сравнения вычисленных значений константы спин-спинового взаимодействия $^{J}13_{C\text{-}H}$ с экспериментальными, взятыми из литературных источников.

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ORBITAL OPTIMIZATION IN THE AB INITIO GENERALIZED RELATIVISTIC VALENCE BOND METHOD

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In the previous works we introduced ab initio nonrelativistic and relativistic Generalized-Valence-Bond (GVB and RGVB) full-electron methods with nonorthogonal numerical basis set build up of one-electron atomic-like functions localized at different centers. These numerical function were obtained by solving the integro-differential Hartree-Fock-Dirac (HFD) equations for each atom of the molecule. To eliminate the continuum states from complete basis set we used as virtual atomic orbitals the Sturmian-type orbitals, which were found by solving the integro-differential Dirac-Fock-Sturm equations. The total molecular wave function was taken as a linear combination of Slater determinants, each of them was the antysimmetric product of Slater determinants for the separate atoms, Various electron configurations (including ionic one) were considered for different atoms, consisting the molecule. The many-electron states of molecule within the proposed RGVB method were found as a result of the configuration interaction (CI) procedure based on solving the generalized eigenvalue problem. The aim of the present work was to improve a quality of CI expansion in the proposed RGVB method using an optimization procedure of the atomic-like functions. This procedure is based on the unitary rotations within the space of orthogonal orbitals belonging to one center. It is the well known property of the unitary matrix that it can be written as the exponential of an anti-Hermitian matrix. The latter can be arranged to a four-block form with submatrices corresponding to transformations of atomic-like orbitals within and between occupied and unoccupied atomic one-center spaces. We don\'t consider rotations within both spaces, putting two diagonal submatrices to zero. The rest off-diagonal submatrix elements we find using generalized Brillouin\'s theorem for total wave function of molecule. To demonstrate the advantages of the proposed improved ab initio RGVB method with orbital optimization we performed the full-electron multicofiguration RGVB calculations of the adiabatic curves, spectroscopic constants and dipole moments for a number of diatomic molecules. All single, double and partially triple excitations of electrons were taken into account. As objects the molecules AgH, AuH, HJ, HBr, HCl and YbF were chosen.

THE ACTIVE CENTERS DISTRIBUTION ON STRUCTURE AND STEREOSPECIFICITY OF ACTION UNDER THE POLYMERIZATION OF DIENES ON NdCl3 3TBF-AlR3 CATALYTIC SYSTEM

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The formation of different active centers types is possible under diene polymerization on lanthanide catalytic systems. These centers differ in structure, stereospecificity of action and polymerization constants. The difference in structure is concluded in the fact that the nearest environment of lanthanide atom on which polymerization occurs contains various number of chlorine and carbon atoms. Active centers may be divided into six types by this indication. It was shown with the help of quantum-chemical calculations, that for the first five active centers types the terminal units of propagating polymer chain are is bonded preliminary by pi-allyl bonds and they show cis-stereoregulating action. In the sixth active center type the sigma-bonds are formed mainly and shows trans-regulation action. The influence of different factors on the formation of either these or another active centers set and consequently on the stereoregulation was analyzed.

MOLECULAR DYNAMICS SIMULATIONS OF THE SH(A) RADICALS IN KRYPTON MATRICES

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Properties of the SH radical both in the free state and in different environments attract considerable attention of several research groups. Also, the structure and spectra of the van der Waals clusters containing the SH fragment and rare gas atoms, have been extensively investigated. In particular, the emission spectrum of SH radicals in solid krypton at 7.5K shows two peaks. The dominating peak is located at the wavelength 413 nm and possesses the lifetime 750 ns. The other one is located at 375 nm with the lifetime 350 ns. We check the assumption that these two peaks corresponded to the same system of bands A (v\'=0) - X (v\'\'), but originate from two different trapping sites in the excited electronic state. Potential energy surfaces of the SH@Krn cluster was constructed with the diatomics-in-molecules (DIM) method. In the excited state the potential surface possesses two minima (of 1706 cm-1 for SH...Kr and about of 1400 cm-1 for Kr...SH geometry) separated by a saddle point. The molecular dynamics procedure is organized as follows. The SH species is inserted into a random position near the center of the fragment of the krypton fcc lattice composed of 256 atoms in a random orientation of its diatomic axis with respect to the lattice origin. Then the krypton atoms found closer to both S and H centers than rmin are deleted. At the beginning, each trajectory proceeds on the lower potential energy surface, correlating with the channel SH(X) + Krn. The scaling of velocities is performed. The length of this part of a trajectory is about 10-12 s. Then the trajectory is switched to the upper electronic surface, by starting from

the positions of all atoms on the lower surface. The length of the second part is about 10-11 s with the time integration step varying within 0.2 - 0.5 fs. At every 10th integration step the current data are selected for calculations of the spectrum, lifetimes and spatial correlation functions which are finally obtained after averaging over integration steps. Usual periodical boundary conditions are imposed on the trajectories. By numerical integration of the one-dimensional Schrodinger equation with DIM-modified one-dimensional potentials the sets of vibrational levels are computed along trajectories. After averaging over time steps energy differences and overlap integrals of the vibrational wavefunctions (the Franck-Condon factors), the spectrum associated with a given trajectory is therefore obtained. Calculation of the lifetimes is performed using the formula: t-1=(4/3c2)<v\'|DU3D2|v\', where |v\' denotes the corresponding vibrational eigenfunction of the upper state, DU is the difference potential of both electronic states, D is the transition dipole moment function, c is the velocity of light. In this work the representation of the spatial distribution of krypton atoms surrounding the trapped SH radical is used as distribution maps, which are constructed in temporary coordinate systems associated with the SH fragment. We subdivide the trajectories to two types by location of dominating peak in spectra. We can assign trajectories of type (a) to the spectrum with the dominating peak (#1) at a shorter wavelength (340-350 nm), and trajectories of type (b) to the spectrum with the dominating peak (#2) at a longer wavelength (390-400 nm). According to the calculations of lifetimes, for all trajectories of type (a), the values between 550 and 600 ns are obtained, while for trajectories of type (b) noticeably higher values 800 - 840 ns are computed. The distinctively different values of lifetimes of peaks (#1) and (#2) in a correct sequence provide strong support to the suggested interpretation of the observed spectrum: shorter-lived peak (#1) is associated with a trapping site with a movement of SH (A) inside the lattice, and longer-lived peak (#2) is associated with a site, where a relatively tight tri-atomic complex is formed. A reasonable correspondence of the parameters, which can be obtain both in experiment and theory, supports a description of the matrix sites, which can drawn only from simulations. Namely, emission of SH in krypton environment originates from two different matrix sites in the excited electronic state.

THEORETICAL INVESTIGATIONS OF 1,4-BUTANEDIOL AND 2-BUTENE-1,4-DIOL CYCLODEHYDRATION USING POSTPROCESSING VISUALIZATION OF QUANTUM CHEMICAL CALCULATION DATA

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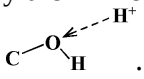
The cyclodehydration of 1,4-butanediol and 2-butene-1,4-diol into tetrahydrofuran and 2,5-dihydrofuran, respectively is industrially important reaction occuring in the presence of acidic dehydrating agents such as silica gel, alumosilicate, zeolites or, for example, cobalt catalysts supported on γ-Al_2O_3, kieselguhr and silica-alumina.

The reactions are carried out in vapour phase at 190-300°C and the yields of tetrahydrofuran and 2,5-dihydrofuran reach 93-100%.

In the present work the transformation of diols on acidic and basic active centers of heterogeneous catalysts was studied by AM1 Hamiltonian. The data on the changes in geometry during the optimization process were converted to the form suitable for molecular animation programs. Such method gave the possibility to establish the peculiarities of the reaction mechanism and the difference between the transformations of both diols.

The protonation of OH group was simulated by the H^+ ion directed to the O atom along the C–O bond of the alkanol molecule fragment 

. The basic sites were modelled by $(HO)_3SiO^-$ clusters. In accordance with our calculation the semicyclic conformers take part in cyclodehydration reaction in both cases. 1,4-Butanediol after protonation of one OH group, proton annexation from other OH group by basic surface center and loss of water, transformed into five-membered cycle – tetrahydrofuran. The linear conformer of 1,4-butanediol after the loss of water and proton annexation from the second OH group gaves as the intermediate the five-membered cycle *via* C(2)---H---O bonds formation which then transformed to unsaturated alcohol 3-buten-1-ol.

2-Butene-1,4-diol interacted at first with basic center forming surface O-H group. Then protonation of other OH group, dehydration and five-membered ring closure resulted in 2,5-dihydrofuran formation occurred.

MULTICONFIGURATIONAL GREEN\'S FUNCTION APPROACH WITH QUASI-DEGENERATE PERTURBATION THEORY

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Green's function or propagator approaches providing direct determination of electronic transition characteristics, ionization potentials, and electron affinities in atoms and molecules may allow to produce estimation techniques of higher accuracy and computational efficacy with respect to traditional quantum chemical ones, which are primarily oriented toward evaluation of individual states wave functions and properties. However, realization of these potential advantages is restrained with the two shortcomings of current propagator approach techniques. The first of them is the absence of criteria, based on the very propagator formalism, for consistent choice of reference state wave function (RSWF) and excitation operators system (EOS) in all current methods of propagator poles and residues evaluation, besides those based on the apparatus of perturbation theory for non-degenerate level. The absence of these criteria and employment of RSWF and EOS not properly balanced in the framework of unique approach result in violations of estimated and narrows the applicability area of propagator approach. We suggest a new approach to evaluation of propagator poles and residues with RSWF constructed on the base of multidimensional model space with the aim to remove aforementioned shortcomings. This approach is constructed for model spaces

of special structure, but the restriction introduced here for associated basis set composition is regularly adopted in multireference approaches. As it is illustrated by several examples, the types of model spaces suggested in the framework of the presented approach do not create hindrances for exploiting size-extensive RSWF derived by some versions of multireference coupled cluster method or quasi-degenerate perturbation theory (QDPT) on the base of incomplete model spaces. It is proved that the energy dependent polarization propagator (PP) expression in this approach may be formed with the modified EOS, which contains the subsystem of operators associated with transitions within the cluster of quasi-degenerate states including the reference one. The main aim of this modification realizing the structure concordance of RSWF and EOS consists in providing the subdivision of PP expression according to the orders of QDPT. Receding from the assumption that one configuration state function dominates in RSWF and consistency of the RSWF and EOS structures master the main encumbrance for creation internally consistent methods of PP poles and residues estimation with a multireference RSWF of an arbitrary composition, and the perspective of PP formalism application for evaluation of characteristics of transitions between electronic states of molecules as functions of nuclear coordinates becomes actual. On the base of the suggested composition of (RSWF, EOS) pairs the approximations of PP in zeroth order and through the first order of QDPT are constructed. The delivered PP approximations are juxtaposed with variational methods, response theory and traditional PP approaches. In particular, the multiconfiguration random phase approximation is revealed to hold an intermediate position between the two PP approximations constructed on the base of QDPT. An analogous scheme for the evaluation of electron propagator poles and residues is presented.

HYDROGEN ATOM DYNAMICS INSIDE A SPHERICAL CAVITY

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The one-electron atom in a spherical cavity with impenetrable walls is known as the simplest model of influence of the environment on the behaviour of atomic and molecular systems since at least 1937. In the present work, we calculate the transition spectrum of the one-electron atom in a spherical cavity, i.e. frequencies and intensities of transitions between stationary states. The solution of the Schrodinger equation was carried out within the adiabatic approximation, and the calculation of the transition probabilities - within the dipole one. The electronic problem was solved within different approximate methods: perturbation theory, variational and finite-difference ones, and the results obtained are compared with each other. The adiabatic potentials are calculated for different cavity radii and their behaviour is analysed qualitatively. A criterion is formulated that permits to determine the equilibrium position of the nucleus at the centre of the cavity or off-centre. The matrix elements of the dipole momentum operator between the electronic wavefunctions are also calculated as functions of the displacement of the nucleus off the centre, the behaviour of the curves obtained is analysed qulitatively. The nuclear motion problem is solved by using the finite-difference method with subsequent evaluation of squared transition momenta and intensities of spectral lines. The rovibrational spectrum in the ground electronic state is calculated and its qualitative features are explicated within the three-dimensional isotropic harmonic

oscillator model. The harmonic frequency asymptotics in the limit of small cavity radii is found. The relative positions and contour forms of the spectral bands are discussed. The work presented gives a consecutive and rather complete analysis of the problem considered. The qualitative conclusions made would be of interest for the purpose of interpretation of real molecule-medium interactions. (RFBR N 98-03-33232, 01-03-32116).

AN APPROACH TO THE SOLUTION OF THE ONE-DIMENSIONAL SCHROEDINGER EQUATION

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Since the pioneer investigation of Swimm and Delos [1] there are many works(see, for example [2-8]) that are devoted to the quantisation problem of the classical Hamiltonian systems on the basis of the Birkhoff-Gustavson normal form (BGNF) method [9,10]. In order to find the energy spectrum of the one-dimensional Schroedinger equation we are going the following way. At first we introduce the auxiliary scalar function that plays the role of the classical Hamiltonian function. Making then the canonical transformation to new canonically conjugated variables we reduce the auxiliary Hamiltonian function to the classical BGNF. With the help of the Weyl correspondence rule we construct the quantum BGNF as differential operator which gives the approximated expression for the Hamiltonian operator in the initial Schroedinger equation. The eigenproblem for quantum BGNF one solves easily and its solution gives us the analytical approximated formula for the energy spectrum of the initial Schroedinger equation. For a partial type of Hamiltonian operator with quartic part the calculations are performed and a comparison with known results of other authors is made [11,12]. It should be noted that the proposed approach is limited to a sufficientlly small nonlinear part of the Hamiltonian operator. But in spite of the partial choice of the Hamiltonian operator this approach is valid for wider classes of the Hamiltonian operator and evidently may be applied to many-dimensional systems. This work is supported partially by the Russian Foundation for Basic Research (grant No.00-02-16337) and the St.-Petersburg University (grant No.97-0-143-5). 6. References 1. Swimm R.T. and Delos.J.B. J. Chem. Phys., 1979, 71, 1706. 2. Jaffe Ch. and Reinhardt W.P. J. Chem. Phys., 1982, 77, 5191. 3. Shirts R.B. and Reinhardt W.P. J. Chem. Phys 1982, 77, 5204. 4. Robnik M. J. Phys.: Math. Gen., 1984, A17, 109. 5. Uzer T., Marcus R.A. J. Chem. Phys., 1984, 81, 5013. 6. N. A. Chekanov N.A. Jad. Fiz., 1989, 50, 344. 7. Farrelly D. et.al. Phys. Rev., 1992, A45, 4738. 8. Chekanov N.A., Gusev A.A., Krasilnikov V.V. Ghurn. Fiz. Khim., 2000, 74, 101. 9. Birkhoff G.D. Dynamical Systems. New York, A.M.S. Coll. Publ., 1927. 10. Gustavson F.G. The Astronomical Journal, 1966, 71, 670. 13. Ali M.K. J. Math. Phys., v. 26, No. 10, 1985, p. 2565. 14. Banerjee K., et. al. Proc. R. Soc. Lond., 1978, A 360, 575.

DMRG STUDY OF ZERO-TEMPERATURE MAGNETIC ORDERING IN POLYALLYL SPIN 1/2 CHAIN

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We studied zero-temperature magnetic ordering in a model organic ferrimagnet- polyallyl spin-1/2 chain as a function of the exchange integral J describing the interaction between spins of radical centers and the main chain. Density matrix renormalization group method (DMRG) and exact diagonalization study of finite lattice clusters demonstrated that for small applied field, the difference in zero-temperature magnetization of the sublattices takes maximum values at J=0.70 (in units of exchange integral for the main chain). It is shown that there is a critical value of magnetic field, above which this ferrimagnetic ordering is destroyed. We also present the results of DMRG calculations that show the gap character of excitations without decrease of total spin for the values of J more than 0.40.

POLYMERIZATION AND COALESCENCE OF SINGLE-WALLED NANOTUBES

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Mechanism of polymerization for both doubly crossed (n,m) the single-walled nanotubes (SWNT) and two parallel SWNT's by means of cycloaddition process is discussed. Coupling of two parallel neighbor nanotubes is energetically favorably under the «zipper» scheme. After readjustments of 2+2 cycloaddition of some atom pairs, step by step polymerization takes place along line between the tubes. Role of hydrogenation in the process of coupling and coalescence of SWNT is discussed. The «zipper» mechanism is used to explain: 1) formation of double diameter nanotubes under high temperature and light atom flow treatment [1] – we considered nonchiral and chiral SWNT's; 2) transformation of molecular coupled nanotube rope into graphite needle under high pressure treatment [2]; 3) formation of different zeolite structures like considered ones in [3].

Geometrical and electronic structures of the new polymer forms have been computed by using molecular mechanics and a generalized tight-binding molecular-dynamic (GTBMD) method [4]. Energetic characteristics show high stability for all considered structures. Furthermore, electronic band structures and DOS of SWNT polymers show changing of electronic properties of original SWNT ropes, for example, from original (6,6) SWNT metal molecular crystal (all sp^2 atoms) to high dielectric gap crystal with all sp^3 atoms.

Some of considered structures have good agreement with experiments [1, 2, 5]).

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ГИДРИДЫ КОРАННУЛЕНА И ФУЛЛЕРЕНА C_{60} КАК ПОТЕНЦИАЛЬНЫЕ ЛИГАНДЫ В η^4- И η^3-π-КОМПЛЕКСАХ С ПЕРЕХОДНЫМИ МЕТАЛЛАМИ.-

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С целью поиска способов химической модификации полиэдрических молекул типа фуллеренов и их чашеобразных предшественников, способствующих стабилизации η^n-π-комплексов (n>2) таких систем с атомами переходных металлов неэмпирическим методом HF/3-21G, а также полуэмпирическим методом MNDO/PM3, рассчитан ряд таких гидридов фуллерена C_{60} и молекулы кораннулена $C_{20}H_{10}$, в которых атомы водорода выделяют в углеродных остовах этих систем или бутадиеновые, или фульвеновые, или аллильные фрагменты. А именно, проведено моделирование структуры и электронного строения следующих углеводородных молекул и радикалов на основе кораннулена и фуллерена: $C_{20}H_{16}$ (**1**), $C_{20}H_{12}$ (**2**), $C_{20}H_{14}$ (**3**), $C_{20}H_{18}$ (4), $C_{20}H_{18}$ (**5**), $C_{60}H_4$ (**6**), $C_{60}H_3$ (**7**), $C_{60}H_6$ (**8**). Дополнительные атомы водорода в этих системах расположены таким образом, что в каждой из них выделяется или бутадиеновый или фульвеновый, или аллильный фрагменты.

Результаты расчетов использованы для качественных оценок возможности существования η^4- и η^3-π-комплексов этих соединений.

Методами HF/32-1G и функционалом плотности в приближении PBE (D.N. Laikov, Chem.Phys.Lett.,281 (1997 151) рассчитаны следующие гипотетические η^4-π комплексы: $C_{20}H_{14}Fe(CO)_3$ (**10**), $C_{20}H_{16}Fe(CO)_3$ (**11**), $C_{60}H_4Fe(CO)_3$ (**12**) и $C_{60}H_6Fe(CO)_3$ (**13**). Определено геометрическое и электронное строение комплексов **10 - 13**. Полученные оценки энергий η^4-π-связей в этих соединениях, полученные этими методами, согласуются между собой. Однако они оказались немного ниже, но сравнимыми с энергиями η^5-π-связей в комплексах $C_{60}H_5FeCp$ (**15**), $C_{40}H_5FeCp$ (**16**) $C_{20}H_5FeCp$ (**16**) и $FeCp_2$ (**17**).

Работа поддержfна Российским Фондом Фундаментальных Исследований, Российской научно-технической программой «Актуальные направления в физике конденсированных сред», подпрограмма «Фуллерены и атомные кластеры», а также грантом 9.4.06 Миннауки, промышленности и технологии.

AUTOMATIC QUANTUM CHEMICAL PROCEDURE OF CORRECTION OF OPTIMIZED GEOMETRIES OF FREE RADICALS

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The structural parameters of free radicals calculated by semiempirical methods are often very different from the experimental ones. It immediately causes the poor description of experimental magnetic resonance parameters with the use of geometries optimized by these methods. We have analyzed structural parameters of a test set of free radicals calculated by *ab initio* (UHF/6-31G**) and DFT (UB3LYP/6-31G**) methods as well as semiempirical variant MNDO/UHF. The first two methods, unlike the third one, provide structural information well corresponded to the experimental data. For the formyl and vinyl radicals the differences between the reliably determined valence angle and one calculated by MNDO method exceed a few tens of degrees. We propose the criterion (G-function) which makes it possible to evaluate the quality of the whole set of calculated magnetic resonance parameters (isotropic hyperfine coupling constants, anisotropic hyperfine coupling tensors and g-tensors). It is established that the largest differences between the calculated by MNDO method and experimental magnetic resonance parameters are observed for sigma-electron radicals when their calculated structural parameters are far from experimental ones. In going from the energy-optimized geometry to the experimental one the quality of calculated magnetic resonance parameters is significantly improved. It allows the automatic procedure of correction of structural parameters of free radicals to be developed by means of minimizing the G-function, i.e. the discrepancies between the calculated and experimentally determined magnetic resonance parameters. The application of this procedure to free radicals which geometries are poorly described by MNDO method causes the structural parameters to be well corresponding to those observed experimentally or calculated by DFT. When the differences between the calculated and experimental magnetic resonance parameters are small (G-function is no more than 10) the application of geometry correction procedure is redundant.

COMPARATIVE EFFICIENCY OF QUANTUM CHEMICAL METHODS IN CALCULATIONS OF PROTON ISOTROPIC HYPERFINE COUPLING CONSTANTS IN FREE RADICALS

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Extraction of structural information from ESR spectra can be brought off successfully by application of suitable quantum chemical procedures. We have compared the efficiency of standard *ab initio* (UHF/6-311G**) and DFT (UB3LYP/6-311G**) methods as well as semiempirical MNDO variant in calculations of proton isotropic hyperfine coupling constants taking 15 well experimentally studied free radicals as examples. To estimate the proton isotropic hyperfine coupling constants in the framework of MNDO approach we used the

new MNDORU procedure [1,2] based on the separate account of delocalization and polarization contributions to the spin population of 1s-AO of H atom [3]. The comparison of calculation results with the experimental data gives evidence of the preference of DFT approach in estimating the proton isotropic hyperfine coupling constants in free radical systems with small number of atoms. Within the scope of *ab initio* approach the same quality of the results can be achieved only by adoption of more extended (than 6-311G**) basis sets. The MNDORU procedure can successfully replace the DFT approach in analyzing the constants of isotropic hyperfine coupling with nuclei of heavy atoms even in the case of relatively small radicals provided that their structural characteristics are correct. For fairly complex paramagnetic systems the DFT methods become rather time-consuming, and hence the use of MNDORU procedure seems to be expedient since it results in quite satisfactory estimates of proton isotropic hyperfine coupling constants. References.1) N.D. Chuvylkin, A.M. Tokmachev, *Izv. AN, Ser. Khim.*, 1999, p. 1459. 2) N.D. Chuvylkin, A.M. Tokmachev, *Mend. Comm.*, 1999, p. 183. 3) N.D. Chuvylkin, A.M. Tokmachev, *Izv. AN, Ser. Khim.*, 1999, p. 245.

SOLVATION OF MOLECULAR COMPLEXES. A COMBINED SELF-CONSISTENT-FIELD AND INTEGRAL EQUATION STUDY

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The study of electronic structure of molecular complexes in solution is of considerable interest to theoretical chemistry since most of the chemical reactions are observed in solution. The main goal of this report to develop a method, which can take account for the relations between quantum chemical and solvent thermodynamic properties. This method is based on a hybrid approach including quantum chemical calculations and the integral equation theory (IET). We suppose that the electronic and the solvent distributions are coupled through the electrostatic interactions between the interaction sites assigned to solute and solvent. We apply reference-interaction-site-model (RISM) to treat molecular aspects of solvent within a reasonable cost of computation. The latter version of integral equation method is widely used to investigate a wide variety of processes in liquids, in particular, to calculate the local microstructure of solvent around a solvated molecular complex. The RISM allows us to calculate site-site correlation functions and find distribution of solvent molecules around the solvated complex. These solvent molecules induce an electrostatic potential, which can be calculated via the site-site correlation functions. The above potential can be considered as external field acting on the electronic structure of solvated complex. Therefore, we can use conventional quantum-chemical methods (for example MOPAC package) to calculate the electronic structure of the solvated complex subjected to the external field. The evaluation of the electrostatic potential and electronic structure is to be optimized in a self-consistent manner resulting in microscopic self-consistent field (SCF) calculations of combined RISM—SCF equations. We have applied the method to calculate energetic and structural characteristics of solvated positronium and electron and compared the obtained results with the experimental data. The results obtained by us indicate that although the absolute values of energies of solvated electron and positronium, found by the RISM-SCF method, can be quantitatively differ from the experimental values, such calculations are very promising for

evaluation of structural parameters of solvated complexes. The work was supported by RFBR grants 01-03-32529 and 01-04-97032.

MOLECULAR MAGNETISM OF SILICON NANOSTRUCTURES: QUANTUM-CHEMICAL PREDICTIONS AND EXPERIMENTAL EVIDENCES

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In the current paper molecular magnetism is considered for the first time for inorganic species, namely, for silicon nanostructures. Small clusters, fullerenes of a buckyball type, nanowires, crystal surfaces and a porous body present the species. Quantum-chemical view of molecular magnetism is outlined on the basis of detailed SCF LCAO MO calculations, the main part of which has been performed by using a semiempirical AM1-approach incorporated in both one-processor CLUSTER-Z1 [1] and multi-processor MP-AM1 [2] packages making allowance for large atomic systems to be tackled. In the last case the calculations were carried out at a PC-cluster system combining 16 processors. The observed peculiarities of the molecular magnetism of silicon nanostructures are suggested to be connected with a strong tendency of silicon atoms to keep sp3-configuration of their valence electrons predominantly. Unpaired electrons which do not participate in interatomic bonding populate delocalized antibonding molecular orbitals and take part in spin density formation. The density, rather significant by value, causes a pronounced stabilization of the high spin ground states of silicon nanostructures. 1. V.A.Zayatz, Software CLUSTER-Z1 for quantum-chemical calculations in sp-basis\". Institute of Surface Chemistry, Nat.Ac,Sci of the Ukraine, Kiev, 1991. 2. P.K.Berzigijarov, V.A.Zayatz, I.Ya.Ginzburg, V.M.Razumov, E.F.Sheka, MP-AM1: parallel code for quantum-chemical calculations in sp-basis\". Institute of Chemical Physics Problems, Russ.Ac,Sci., Chernogolovka, 2000.

FULLERENIC MODEL OF SILICON NANOWIRES

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Silicon nanowires, recently produced from silicon atom gas on a HOPG surface [1], have revealed a new type of silicon nanostructures. In the current paper. a nanowire is suggested to be formed as a result of two polymerization processes. A primary one implies oligomer chain formation and is responsible for keeping a discretely calibrated thickness of the wire. The secondary process occurs between oligomer chains and provides the wire growth in length. A buckyball fullerene Si60 is suggested as the basic building element, with a cross-sectional width about 1 nm. A computational design of 4-nm and 7-nm wires has been performed by using semiempirical software PM-AM1 [1], which makes allowance for calculations of large

polyatomic systems in both sequential and massively parallel regimes. As shown, both processes are energetically favourable with a clearly seen preference towards high spin states. Therefore, the wires are expected to be magnetic, although in a rather peculiar manner since instead of regular ordering in atomic spins inherent for crystalline surfaces, a distribution of spin density is characteristic for oligomers which looks like a fractal one. 1. P.K.Berzigijarov, V.A.Zayatz, I.Ya.Ginzburg, V.M.Razumov, E.F.Sheka, MP-AM1: parallel code for quantum-chemical calculations in sp-basis\". Institute of Chemical Physics Problems, Russ.Ac.Sci., Chernogolovka, 2000.

MOLECULAR STRUCTURE AND CONFORMATIONAL DYNAMICS OF NUCLEIC ACID BASES IN THE GAS PHASE AND WATER SOLUTIONS

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Quantum chemical calculations at the HF, DFT and MP2 levels of theory demonstrate that pyrimidine ring in nucleic acid bases uracil, thymine, cytosine, isocytosine and guanine possesses high conformational flexibility. Transition from a planar equilibrium conformation to a sofa with relevant torsion angle 20 deg. results in an increase of energy of molecule less than 1 kcal/mol. This property of heterocycle is determined by deviation of character of its cyclic conjugated system from aromatic. Combined analysis of results of scan of potential energy surface and vibrational data reveals at least two possible directions of easy deformation of ring. Based on this approach it was demonstrated that population of non-planar conformers every moment of time is 40-55 % at the room temperature. Results of calculations indicate that pyrimidine ring in adenine also possesses notable degree of conformational non-rigidity despite of its pure aromatic character. Analysis of ring out-of-plane vibrations and potential energy surface topology around global minimum for adenine and related compounds (purine, 4-aminopyrimidine and pyrimidine) reveals that deformability is an intrinsic property of aromatic pyrimidine ring. Energy of deformation of this heterocycle should be associated with change of degree of aromaticity. The relationship between aromaticity and conformational flexibility was also established for such aromatic compounds as benzene and azines. It was demonstrated that about 15% of benzene molecules possess considerably non-planar geometry every moment of time at the room temperature. Analysis of geometry of uracil, thymine and cytosine in polyhydrated complexes (11 water molecules for uracil and thymine, and 14 for cytosine) calculated using B3LYP/6-31G(d) method reveals significant deformation of nuclobases toward zwitter-ionic structure. Especially great changes of geometry were found for cytosine. It was demonstrated that structure of cytosine in polyhydrated complex can not be described by canonical formula. It corresponds to superposition of two resonance structures with higher contribution of zwitter-ionic one. However, frequencies of out-of-plane vibrations of the pyrimidine ring remain almost unchanged. This allow to assume that deformability of heterocycle in these complexes does not change significantly at least for relatively small amplitudes of deformations. This conclusion is also supported by values of ring deformation energy for adenine-thymine and guanine-cytosine Watson-Crick base pairs.

EFFECTS OF ELECTRON CORRELATION ON LOCAL CHARACTERISTICS OF ELECTRONIC STRUCTURE OF SOLIDS

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Review of electronic structure calculations performed by authors to study the effects of electron correlation on chemical bonding in crystals is presented. Molecular-crystalline (MC) approach and periodic model of crystal (PM) were employed. Changes of charge values on atoms, bond indices, and atomic covalencies when electron correlation is accounted on the base of Post HF methods (MC approach) and DFT methods (PM approach) both in local density approximation and with gradient corrections are considered. Basis of Gaussian type orbitals and LCAO approximation of molecular and crystalline orbitals was used. As concrete systems, crystals with different type of chemical bonding were chosen: purely covalent silicon, ionic-covalent crystals SiC and cubic BN, crystalline titanium oxide TiO2 (rutile structure) and Ti2O3 (corundum structure). For crystals Si, SiC,BN, TiO2 atomic charges and overlap populations obtained in periodic model in basis of plane waves (with subsequent projecting on AO of minimal basis) are compared with the results of LCAO calculations. Both in MC approach and in periodic model account of electron correlation results in decrease of atomic charges and bond indices as compared with the data of Hartree-Fock calculations. Both in LCAO and plane waves bases trends in local characterisics changes of electronic structure are similar in the series of crystals studied.

DFT THEORETICAL STUDY OF THE ALKANE FUNCTIONALIZATION BY HETEROBINUCLEAR COMPLEXES CONTAINING EARLY–LATE TRANSITION METAL PAIRS

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Development of effective catalytic systems of alkanes functionalization under mild biological conditions is one of the most important problems of the modern chemistry. Heterobinuclear complexes of macrocyclic Schiff bases containing early-late pairs of transition metals (Pt-Zr, Rh-Zr) inside of the large ligand cavity in the close proximity to each other have been studied as promising components of such catalytic systems. Unsymmetrical macrocycles were constructed as the products of condensation of 2,6-diformylpyridine and 2,2\'-dipyrrol-5,5\'-dicarbonic acid with diamines (1,2-diaminobenzene, 1,2-diaminoethane, 1,3-diaminopropane, etc). Calculations have been performed by means of the gradient corrected DFT using PBE exchange-correlation functional and large Gaussian basis sets with the help of analytical first and second derivatives as implemented in the program PRIRODA developed by Dr.D.N.Laikov. Structures of starting complexes and potential energy surfaces corresponding to their interactions with methane, CO, CO_2 and C_2H_4 have been studied in detail as well as the model reactions of methane carbonylation (CH_4+CO) and carboxylation (CH_4+CO_2). Theoretical results show that heterobinuclear complexes under consideration able to bind small molecules mentioned above and to activate C-H bonds in alkanes due to concert push-pull type interaction of both metals with substrate. Activation barriers for methane oxidative

addition are rather low. These results open a new approach to the design of catalytic systems for alkane mild functionalization.

MODELING OF INTERNAL MOBILITY OF THE MOLECULE OF DNA

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Recent investigations of the DNA molecule showed that the molecule has a rather moveable structure. Moreover it was shown that the studies of the DNA mobility is of most interest because the internal mobility plays an important role in biological activity of the molecule. In this work we describe one of possible ways of modeling the internal DNA mobility based on the hamiltonian formalism. To illustrate the approach we consider, as an example, the modeling of the internal DNA motions associated with the process of unwinding of the DNA double helix. We obtain corresponding dynamical equations and find their solutions. We discuss merits and demerits of the model obtained. Different ways to improve the model and the approach by applying new computer methods, new databanks and new methods of visualizations are considered in details.

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