Abstracts of Invited and Contributed Talks, Sep. 6

6A1-1I

Interesting bonds formed by heavier main group elements

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Carbon plays a central role in many fields of chemistry and provides a wide variety of important saturated and unsaturated compounds. It is of considerable interest to replace the skeletal carbons of these compounds by heavier homologues such as silicon, germanium, tin, and lead to create new compounds featured by interesting bonds and structures, which are not expected for carbon compounds. In this talk, I present our recent research on the bonds and structures of hypervalent, aromatic, and multiply-bonded compounds containing heavier main group elements (and transition metals), which is performed in collaboration with experiment.

6A1-3I

Donor-acceptor complexes of main group elements with unusual bonds

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The lecture will focus on three classes of donor-acceptor complexes of main-group elements which possess unusual bonds. One topic are divalent E(0) compounds EL_2 of group-14 elements E = C – Pb where L is a σ-donor ligand. The topic includes an extension to complexes $(EH)L_2$ of group-13 atoms B – Tl and group-15 complexes $(ER)L_2$ where E = N – Bi. The second topic concerns complexes of diatomic species $E_2(NHC)_2$ where E = Si – Pb, P – Bi and NHC = N-heterocyclic carbene. Finally, the third topic focuses on complexes with the formula $D\text{-}C_6F_4\text{-}BF_3$ where D is a donor species Xe, N_2, CO.

6A1-5C

Accurate evaluation of very-low ionization potentials of group VI metal-metal coordination compounds

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I. Introduction

Coordination compounds composed by two group VI metal centers (M) supported by four hpp ligands (the anion of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-a]pyrimidne), $M_2(hpp)_4$ [1], exhibit quadruple metal-metal bonds. The most characteristic feature of this series of compounds is their very-low ionization potentials. Photoionization experiments [1] indicated that the first ionization energy (IE) corresponding to the removal of the electron from the δ orbital can be as low as 3.514 eV for $W_2(hpp)_4$. In this work, *ab initio* methods were utilized to accurately evaluate the lowest four ionization energies of $Mo_2(hpp)_4$ and $W_2(hpp)_4$.

II. Computations

The authentic structures of $Mo_2(hpp)_4$ and $W_2(hpp)_4$ were initially optimized with BP86 density functional theory, and the performance of several basis sets of triple-ζ quality was compared. In the best combinations the deviations of metal-metal bond length are less than 0.02 Å between the computed and experimental geometries.

The ionization energies were calculated first using simplified models with multi-configuration wavefunction to assist orbital selections. Complete active space self-consistent field (CASSCF) theory was performed followed by energy correction with multi-reference configuration interaction (MRCI) method. The active space concluded from the model study is CASSCF(8,8) and CASSCF(7,8), respectively, in the neutral singlet and cation doublet states, and then applied to the authentic molecules. Relativistic effect was explicitly included for the tungsten system. The outcoming IE values were also compared with other high-level *ab initio* methods.

III. Results

- Computed IEs using the authentic structure of $W_2(hpp)_4$ are listed in Table 1.

Table 1. Vertical IEs (in eV) of $W_2(hpp)_4$ compared with experimental data.

	δ (A_g)	π (A_u)	π (B_u)	σ (A_g)
Exp.[a] onset	3.514			
vertical	3.76			
CASSCF	2.329	4.885	4.899	5.554
MRCI [b]	3.594	6.223	6.241	6.841

[a] Reference [1]. [b] Using second order Douglas-Kroll-Hess Hamiltonian.

[1] F.A. Cotton *et al*., Science 298 (2002) 1971.

6A1-6C

State-of-the-art calculation of the ground state of the Sc_2 dimer

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The problem of calculation of the electronic structure of transition-metal clusters still presents a challenge for computational chemistry. The reason is that the expansion of the ground state wave function on electronic configurations does not contain a principal configuration and a large number of reference configurations must be treated equally. Thus, the multi-reference (MR) approaches are, in general, mandatory.

In our study of the scandium dimer we used the multi-reference configuration interaction approach (MRCISD(+Q)) at the complete basis set (CBS) limit [1]. This is the first MRCISD(+Q) calculation of 3d transition-metal clusters at the CBS limit. Although the Sc atom has only one 3*d* electron, its dimer presents an extremely complex system, since it has 270 low laying almost degenerate molecular states. According to our calculations, the ground state of Sc_2 corresponds to a quintet, $^5\Sigma_u^-$ with an agreement with ESR experiment and previous precise calculations. Spin S = 2 can be realized only if one of Sc atoms dissociates in an excited state. The employment of the C_{2v} symmetry group, allowed us to obtain the Sc atoms in different states at the dissociation limit. It is proved that in the asymptotic dissociation limit one of Sc is created in the second quartet excited state Sc* ($3d^14s^14p^1\ ^4F$). The spectroscopic parameters of the ground potential curve, obtained by the Dunham analysis at the MRCISD(+Q)/CBS level, $R_e = 5.20$ bohr, $D_e = 50.37$ kcal/mol, and $\omega_e = 234.5$ cm^{-1}. The calculated value for the harmonic frequency agrees very well with the experimental one, $\omega_e = 239.9$ cm^{-1}. In respect to the experimentally measured dissociation limit Sc ($3d^14s^2\ ^2D_g$) + Sc ($3d^14s^2\ ^2D_g$) $D_e = 9.98$ kcal/mol. In contrast with the Mn_2 dimer, which is bonded by the weak van der Waals (dispersion) forces with $D_e = 0.62$ kcal/mol [2]. Sc_2 dimer is a valence-bonded molecule stabilized by the covalent bonding on the hybrid atomic orbitals.

1. U. Miranda and I.G. Kaplan. Eur. Phys. J. D (2011); DOI: 10 1140/epjd/e2010-10607-y.
2. D. Tzeli, U. Miranda, I.G. Kaplan, and A. Mavridis, J. Chem. Phys., **129**, 154310 (2008).

6A2-1C

An Optimized Genetic Algorithm for the Functionalization of Fullerenes

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I. Introduction

The placement of n functional groups on a fullerene presents a combinatorial explosion problem. For example, there are over 5.4 million ways to place 5 functional groups on a C_{60} fullerene. Adding another functional group results in over 50 million possible structures. The number of possible structures for $C_{60}X_n$ scales factorially, given by the formula 60!/[n!(60-n)!]. To locate the global minimum, we propose a tuned, canonical Genetic Algorithm (GA). In order to find the most efficient tunings for the GA, a second GA - a meta-genetic algorithm [1] - was used to tune the first genetic algorithm to reliably find the already known *a-priori* correct answer for $C_{20}H_4$ (4845 structures, 57 distinct isomers), using minimum computational resources. GA optimization was undertaken using Huckel, Density Functional Tight Binding (DFTB) and Density Functional Theory (DFT) methods to determine whether the level of theory employed altered the optimum GA parameters.

II. Meta-Genetic Algorithm

A total of 8 parameters were simultaneously optimised by the meta-GA, being: population size, mutation rate, crossover probability, use of elitism, mutation type, crossover type, parental selection method and scaling method. Regression analysis was used to determine the effect of each parameter on the efficiency of the GA. Population size, mutation rate and selection method were found to have the greatest effect on the efficiency of the GA, while mutation type and selection method have the greatest effect on the reliability of the GA. These results were consistent across all levels of theory employed.

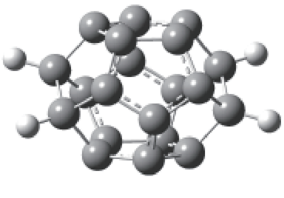

Figure 1: Global minimum geometry of $C_{20}H_4$.

[1] B. Friesleben and M. Hartfelder. In R. Albrecht, C. Reeves, and N. Steele, ed. *Artificial Neural Networks and Genetic Algorithms*, pg 392–399. Springer-Verlag, Heidelberg, 1993.

6A2-2C

Mechanisms of Carbon-Based Nanostructure Self-Assembly: Insights from Density-Functional Tight-Binding Molecular Dynamics

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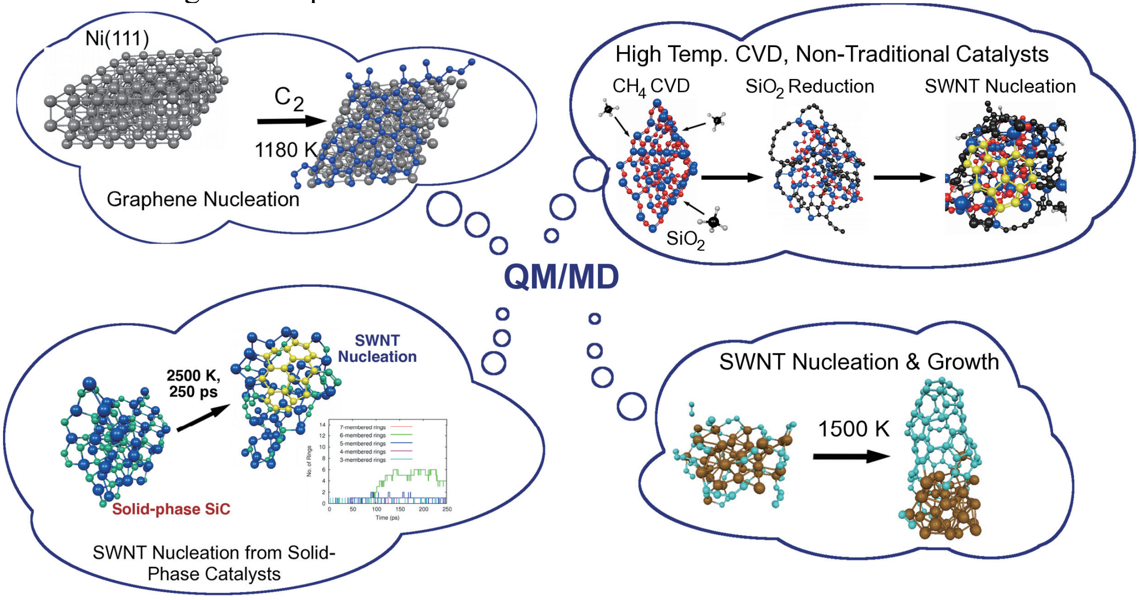
Carbon nanostructures, such as fullerenes, carbon nanotubes and graphene, are currently at the forefront of nanoscale molecular and material sciences. Yet in many cases, a precise, atomistic understanding of how such nanostructures form is currently lacking. In this work, we will review our recent non-equilibrium, high-temperature QM/MD simulations of the formation of graphene and carbon nanotubes on catalysts ranging from transition metals [1] to main-group oxide materials [2]. The approach employed is based upon the self-consistent-charge density-functional tight-binding approximation to DFT (SCC-DFTB) [3]. We are therefore able to simulate these phenomena with an accuracy approaching that of conventional DFT, but at a cost that is comparable to classical force-field-based methods. The simulations reviewed here have recently furnished a detailed understanding of mechanisms of the nucleation and growth of these nanostructures over timescales ranging from picoseconds to nanoseconds. They have therefore served to complement, and, in some cases, predate experimental understanding of such phenomena.



[1] A. J. Page *et al.*, *Acc. Chem. Res.*, **43**, (2010), 175.
[2] A. J. Page *et al.*, *J. Am. Chem. Soc.*, **133**, (2011), 621.
[3] M. Elstner *et al.*, *Phys. Rev. B*, **58**, (1998), 7260.

6A2-3C

New Insights from Quantum Chemical Molecular Dynamics Simulations on the Formation Mechanism of Metallofullerenes

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Since the discovery of fullerenes and metallofullerenes, theoreticians and experimentalists alike have been eager to reveal their formation mechanisms. Many hypotheses were put forward, but none has been directly verified by experiment observations. In this contribution we present QM/MD simulations aimed at elucidating the formation mechanism of endohedral metallofullerenes (EMFs) and endohedral metal carbide fullerenes (EMCFs). As transition metal elements we selected Sc, Ti, and Fe atoms embedded in ensembles of randomly placed C_2 molecules. The self-consistent-charge density-functional tight-binding (abbreviated as SCC-DFTB) method [1] in conjunction with electronic temperature was used as quantum chemical potential for the direct MD simulations. The MD simulations were performed using the Nose-Hoover-chain thermostat at an environmental temperature of 2000 K for up to about two hundred picoseconds. Each system was replicated 10 times.

In the beginning of the trajectories, metal atoms become incorporated in the growing sp^2 carbon network. Around the 60 picosecond mark, we could observe fullerene formation similar to the previous carbon-only simulations [2], but here some metal atoms became incorporated into the cage network. The probability of the cage formation was comparable to carbon-only simulations. However, the cage metal atoms became occasionally “pushed in” by outer carbon structures, with the consequence that the metal atoms become endohedrally trapped, most often with small carbon fragments attached. Thus, Sc_xC_y formation was observed frequently, while Sc_xC_0 was not so common. Our results therefore suggest that EMCF formation dominates the early stage of endohedral metal GF formation. This finding seems unexpected at first sight but can be reconciled by our observation that C_y fragments can re-attach to the cage walls during GF shrinking to produce the familiar EMFs as well as EMCFs.

[1] M. Elstner, D. Porezag, G. Jungnickel, J. Elstner, M. Haugk, Th. Frauenheim, S. Suhai, G. Seifert, *Phys. Rev. B,* **58**, 7260 (1998).

[2] S. Irle, G. Zheng, Z. Wang, K. Morokuma, *J. Phys. Chem. B,* **110**, 14531 (2006).

6A3-1I

Multi-Paradigm Simulations at the Nanoscale: Methodology and Applications to Functional Carbon Materials

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Abstract

Multiparadigm methods to span the scales from quantum mechanics to practical issues of functional nanoassembly and nanofabrication are enabling first principles predictions to guide and complement the experimental developments by designing and optimizing computationally the materials compositions and structures to assemble nanoscale systems with the requisite properties. In this talk, we employ multi-paradigm approaches to investigate functional carbon materials with versatile character, including fullerene, carbon nanotube (CNT), graphene, and related hybrid structures, which have already created an enormous impact on next generation nano devices. The topics will cover the reaction dynamics of C60 dimerization and the more challenging complex formation dynamics in the nano carbon structures; the predicted magnetic state in NanoBuds; and opto-electronic properties of graphene nanoribbons.

6A3-3C

Stone-Wales Rearrangement in Pyrene *via* the S_1 State

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Stone-Wales rearrangement (SWR, Figure 1) is a major mechanism for defect formation in nanocarbons such as graphene and carbon nanotubes (CNTs) [1]. SWR is regarded as a key step of fullerene formation from graphite [2]. This reaction changes the electronic and magnetic properties of nanocarbon drastically [1]. Recent experimental [3] and theoretical studies [4, 5] suggest that there is some reaction path *via* electronic excited state (EES). However, the detailed mechanism of the EES paths remains unknown. What kind of EES paths of SWR exist in graphene? The EES processes of SWR *via* EES can be controlled photochemically, e.g., by optimal control of femtosecond laser pulses. This provides a new way of tuning the EMPs of nanocarbons optically.

We have investigated the SWR paths of graphene and CNT *via* EES quantum chemically by using pyrene as a model system (Figure 1). By potential energy surface scan on the IRC of the T_1 state at the MS-CASPT2//UB3LYP level of theory we found that electronic excitation reduces the activation energy $\Delta E^{\ddagger}$(Table 1) [6]. We also found an avoided crossing point between the S_1 and the S_2 state due to the distortion of the carbon frame. This suggests that SWR can have a few EES paths branched by nonadiabatic transitions. The detailed mechanism at the MS-CASPT2//SA-CASSCF level of theory will be reported.

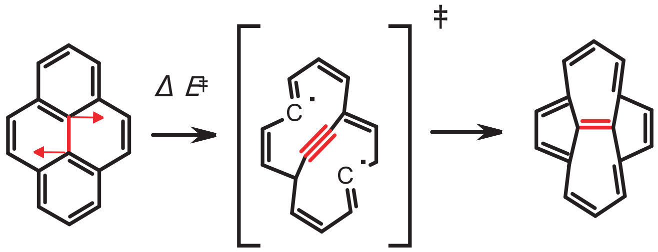

Figure 1: The Stone-Wales rearrangement in pyrene

Table 1: Relation between the activation energy of SWR in pyrene ($\Delta E^{\ddagger}$) and the excitation energy (vertical: ΔE_{ve}, adiabatic: ΔE_{ad}) in pyrene at the MS-CASPT2//IRC-UB3LYP level of theory (in eV).

State	ΔE_{ve}	ΔE_{ad}	$\Delta E^{\ddagger}_{\mathrm{opt}}$	$\Delta E^{\ddagger}_{\mathrm{scan}}$
S_0	0.00	0.00	8.88	9.52
T_1	2.17	1.95	8.02	8.05
S_1	2.93	2.77	—	7.97

Reference: [1] Neto, C. *et al.*, *Rev. Mod.Phys.* **2009**, *81*, 109-162. [2] Chuvilin, A. *et al., Nat. Chem.* **2010**, *2,* 450-452. [3] Mayer, J. *et al.*, *Nano. Lett*. **2008**, *8* (11), 3582-3586. [4] Valencia, F. *et al.*, *Phys. Rev. B.* **2006**, *74*, 075409. [5] Romero, H. *et al.*, *Nano. Lett.* **2005**, *5* (7), 1361-1365. [6] Yamazaki, K. *et al.*, in preparation.

6A3-4C

Symmetry Broken Edge States of Linear Acenes: Artifact or Reality?

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Half-metallicity has been recently predicted for graphene nanoribbons on the ground of Density Functional Theory (DFT) [1]. Peculiar states localize at the edges of the nanoribbon and form a twofold degenerate flat band at the Fermi energy within one third of the first Brillouin zone when the single graphite layer is terminated by zig-zag edges (polyacetylenic strands) on both sides [2]. These edge states have been observed in monoatomic graphitic step edges using scanning tunneling microscopy [3]. According to DFT calculations, they are believed to relate to ferromagnetically ordered states with opposite spin orientation across the ribbon, yielding a total spin equal to zero [4]. DFT calculations of linear acenes confirmed the singlet biradical or multiradical ground state of long linear acenes [5]. Unfortunately, a detailed investigation of the wave function reveals that the symmetry-broken spin-densities in unrestricted calculations are numerical artifacts, yielding an *unphysical* energy lowering of the electronic wave function into an open shell singlet ground state. A benchmark theoretical study (1 kcal/mol or 0.04 eV accuracy) of the electronic ground state and of the vertical and adiabatic ionization energies [6], electron affinities [7], and singlet-triplet (S_0-T_1) excitation energies [8] of benzene (n=1) and n-acenes ($C_{4n+2}H_{2n+4}$) ranging from naphthalene (n=2) to hexacene (n=6) or heptacene (n=7) is presented. Many different criteria demonstrate that all investigated systems exhibit a ^1A_g singlet closed-shell electronic ground state. In line with the absence of Peierls distortions, extrapolations of results indicate a vanishingly small S_0-T_1 energy gap of ~–1 to ~1.5 kcal/mol in the limit of an infinitely long polyacene.

[1] Y-W. Son, M. L. Cohen, S. G. Louie, Nature, **444**, 347 (2006); [2] L. Nakada et. al,. Phys. Rev. B, **54**, 17954 (1996); K. Wakabayashi et. al., Phys. Rev. B, **59**, 8271 (1999); Y. Miyamoto et. al., Phys. Rev. B, **59**, 9858 (1999); [3] Y. Kobayashi et. al., Phys. Rev. B, **71**, 193406 (2005); T. Enoki, Y. Kobayashi, J. Mat. Chem., **15**, 3999 (2005); Y. Niimi et. al., Phys. Rev. B, **73**, 085421 (2006); [4] S. Okada et. al., Phys. Rev. Lett., **87**, 146803 (2001); H. Lee et. al., Phys. Rev. B, **72**, 174431 (2005); [5] M. Bendikov et. al., J. Am. Chem. Soc., **126**, 7416 (2004); J. Hachmann et. al., J. Chem. Phys. **127**, 134309 (2007); M. C. dos Santos et. al., Phys. Rev. B, **74**, 045426 (2006); D-E. Jiang, S. Dai, J. Phys. Chem. A, **112**, 332 (2008); Z. Qu et. al., J. Phys. Chem. A, **113**, 7909 (2009); [6] M. S. Deleuze, L. Claes, E. S. Kryachko and J. -P. François, J. Chem. Phys., **119**, 3106 (2003); [7] B. Hajgató, M. S. Deleuze, D. J. Tozer, F. De Proft, J. Chem. Phys., **129**, 084308 (2008); [8] B. Hajgató, M. S. Deleuze, D. Szieberth, F. De Proft, and P. Geerlings, J. Chem. Phys., **131**, 224321 (2009).

6A3-5C

Alkali Halides Nanotubes: Structure and Stability

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In this talk we report the results of accurate quantum mechanical calculations on some alkali halide (LiF, NaCl, KBr) neutral clusters. The relative stability of $(MX)_{n=2-28}$ structural isomers was studied using DFT (B3LYP/LAVCV3P**). For the members of the cubic and nanotube series Coupled Cluster calculations at the CCSD/SDD level were also performed. Møller-Plesset perturbation theory at the MP2/LAVCV3P** level of calculation was also used to check for possible inconsistencies in the DFT results for the $(MX)_{n=1-10}$ clusters. Quantum dynamics calculations, at room temperature and atmospheric pressure, were also performed for the $(LiF)_{28}$ octagon nanotube. A variety of structures has been found but in this talk we limit the discussion on the tube-like ones. Structural properties and possible mechanisms of formation will be discussed.

The alkali halide nanotubes present much smaller diameters, ranging from 0.241 nm to 0.67 nm (LiF, tetragonal-KBr hexagonal) when compared to the more traditional covalent nanotubes of C (1-2 nm), BN (1-3 nm) or GaN (30-200 nm). This is a consequence of the fact that the interactions are dominantly electrostatic and, therefore, much less strain is involved in making ring-type structures than in the covalent ones.

The results obtained for the $(LiF)_n$ clusters show that overall the cubic series is highly stable as expected from structures which are debris of a crystalline bulk. Surprisingly, however, nanotube clusters with hexagonal and octagonal cross section present similar or higher stability than the corresponding cubic clusters. This result represents a new paradigm for 3D macro assembly of alkali halide clusters. This work was funded by CNPq, FAPERJ and Instituto Nacional de Materiais Complexos Funcionais. F.A.F-L acknowledges support from the National Institute of Health (Grant No. 1K99RR030188-01).

6A3-6C

Favorable confinement of water inside the carbon nanotubes is driven by hydrogen bond and entropy

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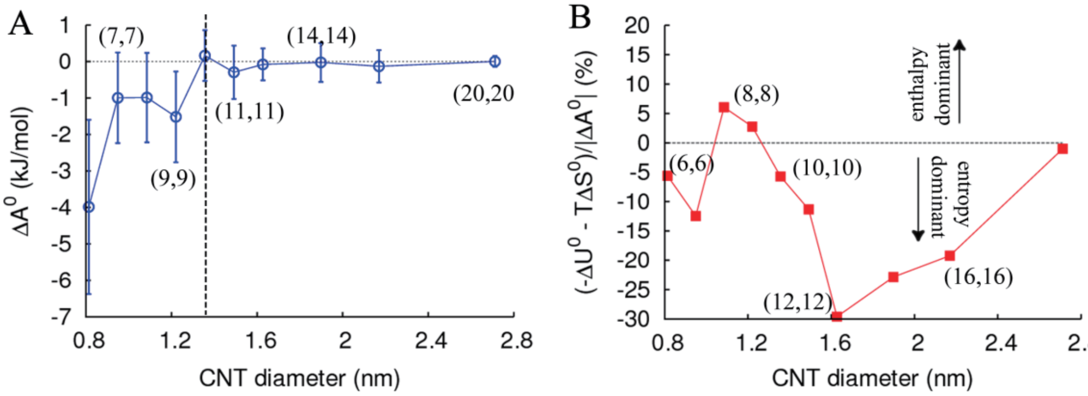
Nanofluidics and nanofiltration have emerged quite recently as an intriguing interdisciplinary science, with applications to sensing, desalination and efficient energy storage and conversion technologies. Water confined in carbon nanotubes (CNTs) exhibits unexpected properties such as fast conduction rates and a variety of structural and phase transitions. Future progress would undoubtedly depend on obtaining a basic understanding of the fundamental driving forces in these systems. In particular, both experimental and theoretical studies have revealed that CNTs spontaneously fill with water, a counter-intuitive proposition since hydrophobic confinement is generally expected to decrease both entropy and bonding due to the breaking of water-water hydrogen bonds upon creating a surface. While there has been some speculation as to the reasons for this remarkable phenomenon, it has not yet been explained.



In this talk, I present the first thermodynamic analysis of the favorable confinement of water in hydrophobic CNTs over the range of CNT diameters from 0.8 to 2.7 nm by molecular dynamics simulations and the Two-Phase Thermodynamics method of extracting absolute entropies and quantum corrections to the internal energy. We find for all sizes that water inside the CNTs has lower free energies than bulk water, but the nature and stability of the confined water changes dramatically with CNT sizes: from entropy-dominated vapor-like phase of water for small CNTs, to enthalpy-dominated ice-like phase for medium sized CNTs, and to a bulk-like liquid phase for larger tubes stabilized by the increased translational entropy. We find it to arise from the tetrahedral H-bonded structure of liquid water.

[1] T. Pascal, W. Goddard, Y. Jung, Submitted

6A4-1I

The structure of the water oxidizing complex in photosystem II

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Hybrid density functional theory has been used for the past decade to study the mechanisms of a large number of transition metal containing enzymes. The present strategy for treating these systems using larger and larger clusters, entirely treated quantum mechanically, will be briefly outlined. DFT studies on the mechanism for dioxygen formation in photosystem II are then described, and it will be concluded that these studies have now reached a level of convergence. After the first X-ray structures of PSII appeared a few years ago, the understanding of this fundamental reaction has improved significantly. A detailed mechanistic proposal will be presented including a complete energy diagram. During the past years major progress has also been made concerning the structure of the oxygen evolving complex. I have previously argued that the theoretical prediction of the structure was more accurate than, and even qualitatively different from, what had been obtained by X-ray crystallography or EXAFS. It was also quite different from what had been obtained with other theoretical approaches. Very recently (Shen et al, Nature, 2011), a new X-ray structure with much higher resolution than before (1.9 Å) has been described. The structure is very similar to the one predicted by theory.

6A4-3I

Exciton coupling and energy transfer: From prototypical bichromophores to photosynthetic proteins

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We investigate exciton coupling in several prototypical bichromophores, such as benzene dimer, diphenylmethane (DPM), and chlorophyll dimers, as well as in photosynthetic proteins such as the Fenna-Matthews-Olson (FMO) complex. Accurate description of interactions between the electronic states is challenging for theory. For instance, in flexible diphenylmethane, a small splitting between the exciton states and a sensitivity of the transition dipole moment to the relative orientation of the aromatic rings leads to curious shapes and crossings of the potential energy surfaces of the exciton states. Exciton couplings are evaluated by using a perturbative approach, in which the coupling strength is estimated by using transition densities of the individual chromophores. By using the effective fragment potential (EFP) and fragment molecular orbital (FMO) methods, we explicitly include and characterize the effect of the protein environment on interactions between the electronic states of chromophores in photosynthetic complexes.

6A4-5I

Electronic Coherence Effects in Photosynthetic Light Harvesting

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Highly efficient energy harvesting and trapping performed by photosynthetic systems are critical to the success of photosynthesis; however, the physical mechanisms that are responsible for the remarkable efficiency remain largely unclear. Recent experimental and theoretical investigations into the mechanisms of excitation energy transfer in photosynthetic complexes have provided evidences that quantum coherence effects can contribute to optimize the efficiency of photosynthetic light harvesting. In this work, we investigate quantum coherence effects in photosynthetic complexes, including electronic coherences manifested in delocalized electronic exciton states and excitonic coherences manifested in superposition between electronic excitons. We show how quantum mechanical rules play important roles in the speedup of excitation energy transfer, the stabilization of electronic excitations, and the robustness of light harvesting. In addition, we present the results of our recent work using a simple model to investigate quantum coherence effects in inter-complex excitation energy transfer in natural photosynthesis, with a focus on the likelihoods of generating excitonic coherences during the process. Finally, the implications of all these combined experimental and theoretical works to important open questions that remain to be answered will be discussed in this work.

6B1-1I

Coherent Quantum Processes in Thermal and Nonequilibrium Environments

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In this talk, we describe recent work on investigating the role of the environment in influencing coherent quantum dynamics. We describe numerical methodology for simulating quantum coherent processes using classical-like molecular dynamics simulation and ensemble averaging, and apply the approach to simulating vibrational dephasing of I_2 in cryogenic rare gas matrices and the quantum vibrations of OH stretches of HOD in D_2O. We then describe simple analytic and numerical models that highlight novel behavior that can be exhibited by quantum coherent processes in the presence of an environment that is not at thermal equilibrium. We finish with some speculations on the role of nonequilibrium bath effects in quantum biological processes.

6B1-3I

Energy relaxation pathways in liquid water

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The mechanisms of vibrational (bend) and rotational relaxation in liquid water are examined via a detailed analysis of energy fluxes between molecular modes [1,2,3].

Classical nonequilibrium MD runs are conducted for neat liquid water (SPC/E model) at different temperatures. Results are averaged for sets of trajectories in which at the initial time either: (a) the bend mode of a single flexible water molecule is excited or, (b) a purely rotational excitation is created for a single rigid molecule.

Analysis of energy fluxes is possible through the computation of the various contributions to the power and the work. In this way one can determine, for instance, which percentage of vibrational energy flows into self-rotation through centrifugal coupling, and to which particular axis this flow is maximal [1,2]. Moreover the spatial extent of energy flow into other water molecules can be ascertained as well, together with the specific molecular modes (translational, rotational) to which excess energy is transferred.

Bend relaxation is found to be dominated by energy flow to the hindered rotation (libration) of the bend excited water molecule, due to a 2:1 Fermi resonance for the centrifugal coupling between the water bend and rotation. The remaining energy flow from the excited water bend is dominated by transfer to the first hydration shell. A slowdown of vibrational relaxation with increasing temperature is observed [3], compatible with recent experimental findings [4].

The energy flow from (the ensuing) rotational excitation of the central water molecule is less local in character, with slightly more than half of the energy being directly transferred to molecules in the first hydration shell of the initially excited water, and almost half of it being transferred to molecules beyond that shell.

Finally, it is observed that, following an initial increase in interaction energy, transfer to hindered rotational (librational) modes of neighbours is substantially more important than that to translational motions [3].

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6B1-5C

Ab initio path integral simulations of hydrogen bonded systems

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The “floppiness” or “flexibility” is one of the key characters that is shared by hydrogen bonded systems. Large-amplitude vibrations, hydrogen-bonded network rearrangements, proton transfers, etc., are caused by thermal and quantum effects of the hydrogen bonding moiety; Thermal excitation of soft modes leads to anharmonic motion and quantum fluctuation of proton is associated to zero-point vibration and tunneling. These are important factors that are relevant to rich chemical/physical behavior of hydrogen bonds.

The family of path integral simulations (path integral molecular dynamics [1], path integral hybrid Monte Carlo [1,2], and ring polymer molecular dynamics [3], etc.) allows one to compute quantum statistics and quasiclassical dynamics of complex many-body systems at finite temperatures. When the method is combined with ab initio electron structure calculations, the whole molecular entity composed of electrons and nuclei are treated quantum mechanically based on first principles within the framework of Born-Oppenheimer approximation [4,5]. Using these ab initio path integral simulations, I study the nature of strong hydrogen bonds in protonated and deprotonated water clusters and their isotopomers at finite temperatures [6-8]. It is shown that the quantum mechanical nature of proton not only have noticeable influence on the structure hydrogen bond but also affect the electronic properties such as the chemical shift in nuclear magnetic resonance [9].

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6B1-6C

Interpolated potential energy surfaces for condensed phase molecular dynamics

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In this talk, we will present an extension of the interpolation scheme for constructing intramolecular potential energy surfaces for conducting molecular dynamics simulations in condensed phase. We show that our scheme can be feasibly used for the purpose when it is supplemented with additional terms for describing intermolecular interactions, and that the method can be used for reliably building the "force field" of any arbitrary molecule without any *a priori*-defined potential shape. We then apply the approach for studying the resolvation process of coumarin 153 in a number of polar solvents. We find that the interpolated surface actually reproduces experimental features much better than the conventional force field based potential in terms of both solvent relaxation and solute vibrational coherence. This shows that the solute vibrational effect is actually important along the solvent relaxation and should be modeled properly for accurate description of the related dynamics. Implication toward the simulations of biological systems is also discussed.

6B2-1I

Incorporation of nuclear quantum effects to ab initio molecular dynamics approach

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We developed an AIMD code for excited-state reactions, which takes into account nonadiabatic transitions between adiabatic electronic states explicitly by the fewest switches algorithm [1]. The surface-hopping AIMD method has been applied to several dissociative recombination (DR) reactions, $HCNH^+ + e^-$ [2], $H_3O^+ + e^-$ [3], and $HD_2O^+ + e^-$ [4], as well as a photoisomerization reaction of azobenzene [5], to examine the tendency in the branching ratio of the products and to give insight to dynamical processes accompanying non-adiabatic transitions. Very recently, we also implemented the semiclassical tunneling method [6] to our AIMD code, and performed test calculations for the tunneling splitting in the umbrella inversion of ammonia and the intramolecular hydrogen transfer in malonaldehyde [7]. In the application to malonaldehyde, effects of multi-dimensionality were examined by assigning quantum zero-point energies only to significant vibrational modes and changing the amount of energy given to bath modes. In this talk, our extension of the AIMD approach to excited-state reactions and tunneling reactions is introduced and discussed.

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6B2-3C

The role of Rydberg state in the photochemistry of ethylene

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Photoinduced *cis-trans* isomerization is one of the fundamental topics in photochemistry because of the way it converts photon energy into mechanical motion. Ethylene is considered to be the simplest model for this purpose, and it has been studied extensively to understand the mechanism and dynamics. While the overall mechanism has been well described, the role of the low-lying Rydberg state is still not clear. Especially, there is little knowledge about how this state contributes to the dynamics.

In this work, we investigated the role of the 3s Rydberg state in the dynamics from an ab initio molecular dynamics simulation. Describing both the Valence and Rydberg states require a balanced electronic structure method that can include both static and dynamic electron correlation effects. For this purpose, we used the multistate second-order perturbation theory (MSPT2), and to study the nonadiabatic events, we developed a method to calculate the MSPT2 nonadiabatic coupling analytically.

$$\left\langle \phi_I^{\mathrm{MSPT2}} \left| \frac{\partial}{\partial \mathbf{R}_a} \right| \phi_J^{\mathrm{MSPT2}} \right\rangle = \sum_{M,N}^{\mathrm{CAS}} \left(E_J^{\mathrm{MSPT2}} - E_I^{\mathrm{MSPT2}} \right)^{-1} u_M^I u_N^J \frac{\partial H_{MN}}{\partial \mathbf{R}_a} + \sum_{M,N}^{CAS} u_M^I u_N^J \left\langle \phi_M^{\mathrm{CAS}} \left| \frac{\partial}{\partial \mathbf{R}_a} \right| \phi_N^{\mathrm{CAS}} \right\rangle$$

The MSPT2 method has been combined with the ab initio multiple spawning (AIMS) method. The time resolved photoelectron spectrum (TRPES) was also calculated.

Our result shows that roughly 20% of the initial population transfers from the $\pi\pi^*$ to the 3s Rydberg state within the first 10 fs, but it returns rapidly to the $\pi\pi^*$ state within 50 fs (Fig. 1). The overall excited state lifetime was about 82 fs, which is slightly longer than those calculated without the Rydberg state, thus the present result is consistent with previous experiments. On the other hand, when the trajectories were initially excited to the 3s Rydberg state, a fairly longer excited state lifetime was observed (~122 fs), implying an existence of a different path. Finally, the calculated TRPES shows a bright line as an excitation from the Rydberg state, suggesting a way to further investigate the role of Rydberg states in the dynamics from both experiments and theory.

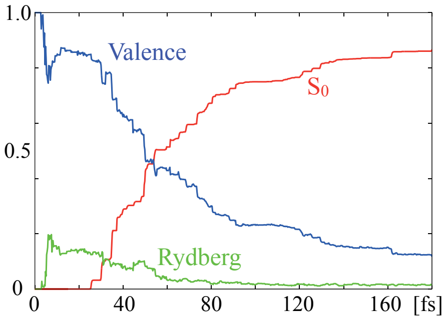

Figure 1: Rate of populations with Valence and Rydberg characters

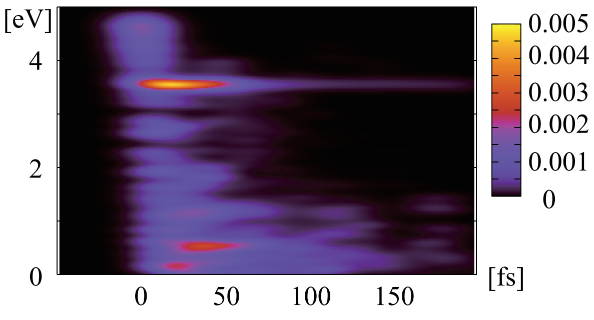

Fig. 2: Calculated TRPES spectrum with a probe energy of 7.7 eV

6B3-1I

Composite particles in quantum chemistry: from two-electron bands to cold atoms

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Ab initio quantum chemistry usually treats electrons as elementary particles, thus the theory of *composite particles* is absent from most textbooks. However, we do deal with composite particles implicitly, e.g., when considering nuclei as point-like, structureless objects. This is a trivial limiting case, as the internal interactions between hadrons gluing together the nuclei are so strong that no chemical process is comparable. Consequently, the only point where the composite nature of a nucleus enters is the counting of its total spin.

Forming composite particles from electrons is a much less trivial problem, since the binding forces between them may easily be affected by external interactions. Such composites form the basis of certain *models*, among which the BCS theory of Cooper pairs is perhaps the most successful. Another example is to consider a localized two-electron chemical bond as a composite particle, which is clearly a fragile object. In the latter case the term *composite quasi-particle* seems to be more adequate.

Distinguishing between true elementary particles and composite quasi-particles can be done most thoroughly by studying the commutation properties of their creation and annihilation operators. Quasi-particles always exhibit a complicated algebra, in contrast to elementary particles which commute or anticommute to unity in the case of bosons or fermions, respectively. A challenge here is to make predictions on the validity of the quasi-particle approximation based on the mathematical form of commutators. Another important issue is to develop correction schemes which describe the effect of the internal structure of quasi-particles on their interactions.

Going to larger composites, some applications permit one to treat a whole atom as a single particle. Approximating an atom as an elementary particle may also be permitted sometimes. The success of the Bose-Hubbard model of cold, dilute atomic gases represents such an example. Solution of the Bose-Hubbard model is another challenging field where quantum chemical techniques may find applications.

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6B3-3I

Theoretical Aspects on the Evaluation and Interpretation of the Third-Order Nonlinear Optical Properties of Diradical Compounds

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I. Introduction

Over the last decades, scientists have designed molecules and materials with unique nonlinear optical (NLO) properties targeting the realization of all-optical computing and signal processing. For many reasons (large response, short response time) organic compounds are of considerable interest. However, suitable materials for practical applications are still missing because the third-order NLO responses and the related molecular second hyperpolarizability (γ) are still too small. Increasing the conjugation length was a first strategy to maximize γ while in subsequent approaches appropriate substituents with specific donor and acceptor strengths were selected. More recent strategies consist in varying the shape and dimensionality of the chromophore and of charging it, for instance by chemical doping.

II. Diradicals and multiradicals as third-order NLO compounds

Although most of these systems are closed-shell molecules, recent studies have demonstrated that open-shell species show potential as materials with high NLO efficiency and, in particular, singlet diradical systems with intermediate diradical character. For instance, *ab initio* molecular orbital and DFT calculations performed on the *p*-quinodimethane model showed that γ attains a maximum in the intermediate diradical character region and subsequently that π-conjugated diradical systems involving imidazole rings and compounds of the family of thermally stable diphenalenyl diradical systems display significant enhancements of γ with respect to their analogous closed-shell systems. Then, the dependence of γ on the spin states makes these compounds further attractive for designing multifunctional materials. In this presentation, theoretical aspects on the evaluation and interpretation of γ of diradical and multiradical species will be discussed.

6B3-5C

Tautomeric equilibria and thermal decomposition of nitrogen-rich heterocycles: new insights from high-level ab initio calculations

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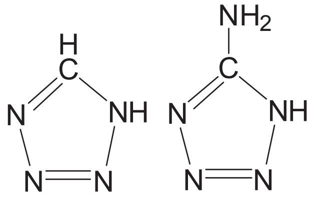
Nitrogen-rich heterocycles and their derivatives have recently attracted considerable attention as promising environmental friendly energetic compounds. Among them, tetrazole (TZ) and 5-aminotetrazole (5-ATZ) are widely used building blocks for a huge family of novel high-energy species [1-3].



TZ **5-ATZ**

The mutual interconversion and decomposition reactions of various tautomers of TZ and 5-ATZ have been studied theoretically using the W1 and G3 high-level procedures. The concerted double H atom transfer reactions in the H-bonded complexes led to fast equilibration between various tautomeric forms of the both TZ and 5-ATZ. The carbene isomer of TZ have never been considered before, however, it was predicted to be a key intermediate in the mechanism of thermal decomposition of TZ. In the case of 5-ATZ, new bimolecular reactions have been proposed to describe the experimentally detected formation of HN_3. High-level computations allowed us to reveal the role of tautomeric equilibria in thermal decomposition of TZ and 5-ATZ. The existing discrepancies in the mechanism and key intermediates of thermolysis have also been resolved. The calculated values of effective activation energy of TZ decomposition are in perfect agreement with the experimental data.

ACKNOWLEDGEMENTS. The authors are grateful to the Russian Ministry of Education and Science (project No. P1475) and SB RAS (the Lavrentiev grant programme) for financial support.

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6B3-6C

Quantum Chemical Simulations of Chemical Vapor Deposition Reactions

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Mechanism and energetics of chemical reactions, relevant for Chemical Vapor Deposition (CVD) has been investigated using quantum chemical methods, implemented in the Q-Chem and CFOUR program packages. These reactions are not only important from the practical point of view, but also have very interesting, complex mechanisms. Reaction mechanisms, structure of intermediates and transition structures have been determined using density functional theory, while accurate energies were computed using high level quantum chemical methods including Coupled Cluster computations and composite methods. The performance of these methods has been thoroughly investigated. The observed results are interpreted using the analysis of the electronic structures. Thermal parameters were evaluated at various temperatures. Reaction rates were also computed.

Our calculations supported that the gas phase hydrolysis of tetrachlorine-silane ($SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$) is a multi-step reaction, where several intermediates and transition structures can be identified. These correspond to the step-by-step elimination of the hydrogen-chloride and the dissociation of the resulting van der Waals complex.

Formation of gallium-nitride from trimethyl-gallium and ammonia has also been investigated. Several different reaction mechanisms were suggested in the literature, including addition-elimination, oligomerization and radical reaction mechanisms. However no high level results were reported. Therefore we have performed a detailed analysis of the possible intermediates and we have computed the detailed mechanism of the most important reaction.

The formation of gallium-arsenide from trimethyl-gallium and arsine is analogous to the previous case and has also been investigated in detail. The results of the formation of gallium-arsenide and gallium-nitride have been compared and interpreted.

6B4-1I

Theoretical studies of photophysical events in π-stacked dimers of nucleobases

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The excited states of DNA and their fate after UV absorption are of extreme importance because of their biological relevance. Quantum chemistry can help address these problems but one has to limit the size of the system. Dimers of nucleobases are the smallest models one can use to look into the effect of π-stacking and hydrogen bonding on the excited states. We have studied the effect of π-stacking on the photophysical properties of π-stacked dimers of natural nucleobases or their fluorescent analogues. Fluorescent analogues of nucleobases are very useful as probes to study DNA dynamics, since natural DNA does not fluoresce significantly. In many of these analogues, such as 2-aminopurine (2AP), the fluorescence is quenched when incorporated into DNA through processes that are not well understood. So 2AP presents a case where π-stacking changes significantly the photophysical behavior of a base, making it an interesting system to focus on. We will present theoretical studies of the excited states of π-staked dimers and focus on features of the potential energy surfaces that can describe the fate of the excited state populations. Computed relaxation pathways along the excited state surfaces reveal novel mechanisms that can lead to fluorescence quenching and radiationless decay in the π-stacked dimers [1]. The importance of charge transfer and exciton states will also be discussed.

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6B4-3C

Quantum chemistry calculations in helium clusters doped with diatomic molecules

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Spectroscopic studies of simple molecules surrounded by He atoms show a drastic difference depending on the fermionic or bosonic character of the solvent atoms [1]. A quantum chemistry-like approach has been recently developed in our group to deal with HeN –BC doped helium clusters, where the BC dopant is a conventional di-atomic molecule. The central idea is to consider the He atoms as "electrons" while the B and C atoms play the role of the nuclei in standard electronic structure calculations. The procedure provides spectral simulations and, hence, making feasible to do proper comparisons with current experiments [1]. However, due to the big difference of masses of He and electrons, and also to the replacement of Coulomb potentials by molecular interactions, it is worthy to asses at what extent the approximations involved (decoupling of orbital angular momenta of the He atoms from the BC rotation and adiabaticity of the BC stretch versus de He motions) lead to accurate results [2-10].

Here, we consider several diatomic molecules as dopants. The model provides the energy levels of the cluster and the intensities of the main lines of the spectrum at low temperatures.

Up to now, Hartree/Hartree-Fock approaches involving their own limitations have been used. It is therefore desirable to implement more accurate ab initio methodologies. Encouraging "full interaction configuration" results, based on a Jacobi-Davidson diagonalization procedure, have been already obtained for small doped fermion clusters [10].

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6B4-4C

Excited states of nucleotide bases and nucleotides: matrix isolation spectroscopic and quantum chemical study[a,b]

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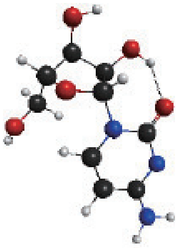
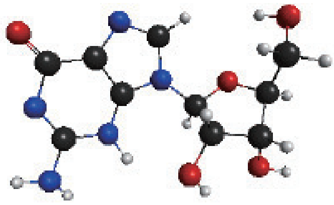
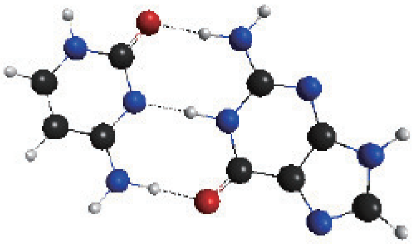
Our research focuses on the spectral properties of the building blocks of DNA and RNA, the so called nucleobases and nucleosides, in order to understand their interaction with light.

Our first target was cytosine, the smallest of the nucleobases. Here we used a combined experimental and theoretical procedure using matrix isolation (MI) spectroscopy and high level ab initio (coupled cluster) calculations. We have found that there are three tautomers of cytosine present in the MI experiment and all three need to be considered to explain the observed UV spectra. Using the obtained ratios of these tautomers, very good agreement could be found between simulated and experimental UV spectra.

The success of this first project made us confident that very accurate information can be obtained from the high level theoretical calculations. Therefore in a second step we have calculated at the EOM-CCSD(T)/aug-cc-pVDZ level of theory the excited state properties for the nucleobases (cytosine, guanine) their complexes with water and with each other (Watson-Crick base pairs and stacks) as well as corresponding nucleosides and try to answer the following questions: (1) How the order of excited states varies in different nucleobases? (2) How hydration influences the excited states and their order? (3) Is there any effect of the sugar substituent? (4) How do close lying other bases change the spectrum? The calculations involve over hundred correlated electrons and up to thousand basis functions. Such calculations are now routinely available with ACESIII code[c] and can make use of hundreds or even thousands of processors.







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[a] The Hungarian American Enterprise Scholarship Foundation (HAESF) supported the sabbatical stay of P.G.Sz. at QTP.

[b] Contribution from TAMOP, supported by the European Union and cofinanced by the European Social Fund (grant agreement no. TAMOP 4.2.1./B-09/1/KMR-2010-0003) is also acknowledged.

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6B4-5C

Distribution and Orientation of Retinol in Dipalmitoylphosphatidylcholine Bilayer

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Abstract

Vitamin A (retinol) is called fat-soluble vitamins. They are absorbed from the small intestine with dietary fat[1]. Moreover it is hydrophobic and absorbed similarly to other dietary lipids[2]. The study of absorption of retinol at the molecular level is still unclear and thus of interest[3]. In the present study, the distribution of retinol at water/membrane interface was investigated by means of molecular dynamics (MD) simulations [4]. The study of the molecular dynamics was focused on the favorable binding sites of retinol inside the DPPC bilayer. Three MD simulations of the retinol /dipalmitoylphosphatidylcholine (DPPC) were performed with a single-point charge water model [5]. The retinol preferably accommodated at the head of the bilayer upper part of the glycerol moiety. The absorption process proved that the hydrophobic aromatic part of the retinol is located inside the more ordered region of DPPC by a gradual deeper shift inside the hydrocarbon core of the bilayer. The retinol formed a weak hydrogen bonding to the glycerol group of DPPC bilayer.

Key words: Vitamin A, retinol, dipalmitoylphosphatidylcholine (DPPC), Molecular dynamics simulations, Absorption

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6C1-1I

Approximate Variational Coupled Cluster Theory

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A modification is presented of the variational configuration interaction functional in the first-order interacting space for molecular electronic structure. The modified functional is a fully-linked expression, that by construction is extensive and invariant to transformations of the underlying orbital basis, and is exact for an ensemble of separated 2-electron subsystems. The method is then extended by including additional terms in the functional that can be computed with $O(N^6)$ work, and which make it agree at low order with variational coupled-cluster with double excitations (VCCD). This method demonstrates accuracy that exceeds that of the standard coupled-cluster (CCD) method, in particular in situations where the reference Slater determinant is not a good approximation.

We also discuss the inclusion of the effect of single orbital excitations, either through minimisation of the approximate VCCD functional with respect to the orbitals, or through an explicit generalisation of the functional to approximate VCCSD.

A further extension generalises the use of the functional to a multiconfigurational reference wavefunction.

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6C1-3I

General implementation of the relativistic coupled-cluster method

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We report the development of a general order relativistic coupled-cluster (CC) code. Our implementation is based on Kramers-paired molecular spinors, utilizes double group symmetry, and is applicable with the full Dirac-Coulomb and several approximate relativistic Hamiltonians. The available methods include iterative and perturbative single-reference CC approaches with arbitrary excitations as well as a state-selective multireference CC ansatz. To illustrate the performance of the new code benchmark calculations have been performed for the total energies, bond lengths, and vibrational frequencies of the monoxides of Group IVa elements. The trends due to the simultaneous inclusion of relativity as well as higher-order electron correlation effects are analyzed. The newly developed code significantly widens the scope of the *ab initio* relativistic calculations, for both molecules and atoms alike, surpassing the accuracy and reliability of the currently available implementations in the literature.

6C1-5C

Unitary perturbation theory for the electron correlation problem

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The scheme proposed by Mayer for a symmetrical treatment of 2×2 Jacobi rotations [1] is investigated. The technique involves an explicit construction of the unitary matrix

$$U = \exp\left(\sum_i A_i\right) \quad ,$$

where A_i's are anti-hermitian matrices, parametrized by the single rotation angle affecting the ground state and the i'th excited state. The idea can be exploited to develop an efficient correction scheme, applicable in electron correlation theory.

Starting from an arbitrary reference function, the first column of matrix U provides a corrected function. Depending on the actual algorithm, the computational price may vary between $\sim N$ and $\sim N^2$, with N denoting the dimension of the subspace interacting with the reference. The performance of this approach is explored on the example of covalent bond breaking, based on a multideterminantal initial function. The results are contested with related methods: Jacobi-rotations and degeneracy corrected perturbation theory [2,3]. The possibility of amending the simple sum in the exponential by commutators of the form $[[A_i, A_j], A_j]$ is also examined.

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6C1-6C

Coupled cluster method in application to the double ionized and double electron attached states

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The double ionization potentials (DIP) and double electron affinities (DEA) can be described within the coupled cluster (CC) theory via the multireference (MR) or equation-of-motion (EOM) extensions. The MR approach requires inclusion of the (0,2) and (2,0) sectors of the Fock space to treat the DIP and DEA, respectively. The current work reports development of the new computational schemes aimed at the evaluation of the DIP and DEA quantities employing the powerful intermediate Hamiltonian strategy of the multireference theory.

The performance of the new methods is discussed on the basis of the test calculations for several molecules. They can be applied also to study potential energy curves (PEC) for the systems for which double positive or double negative ions dissociate into closed-shell fragments.

The significance of the DIP and/or DEA results can be appreciated by comparison with the experimental (AES - Auger electron spectroscopy, DCT - double charge transfer spectroscopy, ...) data. The new methods can be particularly useful in the studying PEC for the halogen dimers (DIP methods) or for the alkali metal dimers (DEA methods).

6C2-1I

Multireference F12 Coupled Cluster Theory

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We report development and implementation of explicitly correlated multireference coupled cluster methods that include configurations explicitly depending on the correlation factor of Slater type geminal. Namely, Brillouin Wigner [1] and Mukherjee's [2] MR CC approaches with single and double excitations are extended in this manner. Additional configurations that include pair functions with the correlation factor are generated separately for each reference determinant [3] similarly as in CCSD-F12 [4]. The performance is shown for model systems and small polyatomic molecules using variants with full optimization of the geminal amplitudes, partial optimization of those amplitudes, and fixed amplitudes corresponding to the theoretical cusp conditions. Like in single reference methods, results show a dramatically improved convergence of total energies towards the complete basis set limit as compared to a conventional MR CC approach.

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6C2-3C

Multireference Explicitly Correlated F12 Theories

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We will present the newly developed CASPT2-F12 and MRCI-F12 methods [1,2], which achieve much improved basis-set convergence compared to the conventional CASPT2 and MRCI methods by introducing a basis function explicitly dependent on the electron-electron distances. The applicability of these methods are exactly the same as the conventional CASPT2 and MRCI; they can be routinely used for systems with near degeneracy (such as avoided crossing and conical intersections) and for complicated electronic structures of electronic excited states [3]. In this presentation, numerical results for some benchmark systems, including the ozone excited states and PES of the OH ($A^2\Sigma^+$) + H_2 reaction, will be presented to illustrate the superior basis-set convergence of the multireference F12 theories. They suggest that the accuracy comparable to MRCI with a quadruple-zeta basis set can be achieved by MRCI-F12 with a double-zeta basis set with an order of magnitude smaller computational effort.

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6C3-1I

The divide–expand–consolidate (DEC) coupled cluster method. A linear–scaling approach with energy–based error control

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We present the Divide-Expand-Consolidate (DEC) coupled cluster (CC) model, where a CC calculation on a full molecular system is carried out in terms of calculations on small orbital fragments of the total molecular system. The fragmentation does not involve non–physical bond cuts and represents only an efficient way of dividing the calculation on a full molecular system into calculations on small orbital fragments. The sizes of the orbital fragment spaces are optimized during the calculation in a black box manner to ensure that that the fragment energies are determined to a preset threshold. This in turn defines the total correlation energy as a sum of fragment energies to a preset threshold compared to a full molecular calculation. The number of independent fragment calculations scales linearly with the system size, and the method is therefore linearly scaling and embarrasingly parallel.

The fragmentation of orbital spaces relies on using a set of local Hartree-Fock (HF) orbitals. We use our recently developed orbital localization strategy where powers of the orbital variances are minimized to yield a set of local occupied and virtual HF orbitals.

DEC calculations are presented for the energy using second order Møller-Plesset perturbation (MP2) theory and the coupled cluster singles doubles (CCSD) models to demonstrate the performance of the DEC model. Calculations of the molecular gradient for MP2 will also be presented.

6C3-3I

Local Coupled-Cluster Methods for Chemical Reaction Pathways Involving Large Molecular Systems and their Multi-Level Generalizations

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Coupled-cluster (CC) theory has become the *de facto* standard for high-accuracy molecular calculations, but as all electronic structure approaches that aim at the accurate description of many-electron correlation effects, it faces a number of challenges. Among them are the prohibitive costs of CC calculations for larger molecular systems. To address this challenge, we have recently extended a number of CC methods, including the size-extensive, left-eigenstate, completely renormalized CC method with singles, doubles, and non-iterative connected triples, abbreviated as CR-CC(2,3), which is known to provide an accurate description of chemical reaction profiles involving single bond breaking and biradicals, to larger systems with hundreds of atoms through the use of the local correlation, cluster-in-molecule (CIM) ansatz. The resulting CIM-CR-CC(2,3) and other CIM-CC methods are characterized by (i) the linear scaling of the CPU time with the system size when the same level of theory is applied to all CIM subsystems, (ii) the use of orthonormal orbitals in subsystem calculations, (iii) the natural coarse-grain parallelism, which can be further enhanced by the additional fine-grain parallelism of each subsystem calculation, (iv) the high computational efficiency, enabling calculations for large molecular systems at high levels of CC theory, (v) the purely non-iterative character of the local triples and other perturbative corrections to correlation energy, and (vi) the applicability to the covalently and weakly bound molecular systems. In addition, one can use the flexibility of the CIM local correlation ansatz to mix different CC or CC and non-CC methods within a single calculation, enabling the rigorous formulation of multi-level local correlation theories that combine the high-level CC methods, such as CR-CC(2,3), to treat, for example, the reactive part of a large molecular system with the lower-order *ab initio* (e.g., MP2) scheme(s) to handle the chemically inactive regions without splitting it into *ad hoc* fragments and saturating dangling bonds. The performance of the CIM-CR-CC(2,3) approach in applications involving chemical reaction profiles is illustrated by examining the bond dissociation curves in normal alkanes and alkyl radicals, the diffusion of atomic oxygen on the silicon surface, the proton transfer in the aggregates of dithiophosphinic acids with the water molecules, and the Co-C bond dissociation in methylcobalamin.

6C3-5C

Highly accurate linear scaling method -elongation method- and its applications to large systems

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The elongation method, developed for many years in our group[for examples Refs. 1-12], is the method towards O(N) with high efficiency and high accuracy for any dimensional systems. This method adapts the concept of 'quantum locality' and works on the Region Localized Molecular Orbital (RLMO) basis we proposed and has recently been extended to be applicable for three-dimensional (3D) systems. As an approach toward post-Hartree-Fock, we developed the elongation local MP2 (ELG-LMP2) method. We also confirmed that the RLMO is very useful to evaluate local excitation around chromophore center in a large system at single excitation configuration interaction (SCI) and TDHF levels. To make sure the applicability of this method to ring-shaped peptide systems, a pentapeptide argifin is chosen to test the 3D-Elongation. As the system is elongated, there are more frozen units are required to be included to achieve high accuracy. For more applications to entangled large bio-systems, 3D-Elongation method was applied to entangled insulin peptides and also we confirmed that the accuracy is good enough and also this method is applicable by increasing the active region even to the systems in which the end terminal parts have strongly polar amino acids. For any type of calculation path, the elongation method has very high accuracy, 10^{-8} a.u./atom error in total energy compared to the conventional direct calculations. These results are promising for application of our 3D-Elongation method to gigantic real bio-systems in the near future. Recently, we also succeeded to incorporate energy gradient technique into elongation method and will show the results in some bio-model systems for geometry optimization based on elongation method.

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6C3-6C

Divide-and-conquer evaluation of optical response properties

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I. Introduction

For theoretical design of optical materials, we desire that (hyper)polarizability evaluation of nano-materials becomes tractable. We have developed the linear-scaling divide-and-conquer (DC) electronic structure method [1]. Recently, we have extended the DC method to the TDHF dynamic polarizability calculations [2]. We will report its brief summary and further extension to the hyperpolarizability calculations.

II. DC-TDHF method for dynamic first hyperpolarizability evaluation

In the standard calculation, the first hyperpolarizability can be evaluated from the first-order CPHF solution as:

$$\beta_{\eta_1\eta_2\eta_3}(\omega_1;\omega_2,\omega_3)=\hat{P}_{\eta_1,\eta_2,\eta_3}\mathrm{Tr}\left[\mathbf{D}'^{\eta_1\eta_2}(\omega_1,\omega_2)\mathbf{F}^{\eta_3}(\omega_3)-\mathbf{W}'^{\eta_1\eta_2\eta_3}(\omega_1,\omega_2,\omega_3)\mathbf{S}\right], \qquad (1)$$

where $\mathbf{D}'^{\eta_1\eta_2}(\omega_1,\omega_2)$ and $\mathbf{W}'^{\eta_1\eta_2\eta_3}(\omega_1,\omega_2,\omega_3)$ can be constructed in the same form as the density and energy-weighted density matrices, respectively. In the present scheme, these two matrices are calculated in the DC manner as:

$$D'^{\eta_1\eta_2}_{\mu\nu}(\omega_1,\omega_2)=\sum_s p^s_{\mu\nu}\sum_i C^{\eta_1,s}_{\mu i}(\omega_1)C^{\eta_2,s*}_{\nu i}(\omega_2)\,. \qquad (2)$$

Figure shows the frequency dependence of (a) polarizability $\alpha(\omega)$, (b) Pockels coefficient $\beta(-\omega;0,+\omega)$, and (c) second-harmonic generation (SHG) coefficient $\beta(-2\omega;+\omega,+\omega)$ of a normal saturated aldehyde $C_{60}H_{121}CHO$ calculated with conventional and DC-TDHF methods. The DC results agree with the conventional results within 0.0002%, 0.06%, and 2.6% errors for (a), (b), and (c), respectively. The SHG curve has a pole at 4.89 eV, the half of C=O π-π* excitation energy (9.77 eV). The position of the pole is also reproduced accurately in the DC scheme.

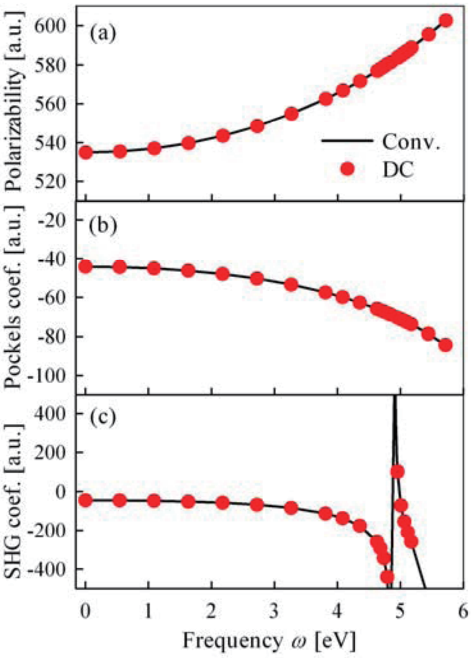

Fig. (a) Polarizability, (b) Pockels coefficient, and (c) SHG coefficient of $C_{60}H_{121}CHO$ (TDHF/6-31G**).

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6C4-1I

Correcting model energies by numerically integrating along the adiabatic connection and a link to density functional theory

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Model Hamiltonians are considered for which electrons interact via long-range forces. It is assumed that their eigenvalues can be obtained with satisfying accuracy. Extrapolation techniques using asymptotic behavior considerations provide estimates for the energy of the physical system. Results for the uniform electron gas and some two-electron systems show that very few quadrature points can already produce good quality results. Connections to the density functional theory are discussed.

6C4-3I

Assessing the Performance of Density-Functional and Wavefunction Quantum Chemical Methods for Noncovalent Interactions

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Very high quality benchmark data, from CCSD(T) and high-order symmetry-adapted perturbation theory (SAPT), has been obtained for a significant collection of van der Waals dimers (469 high-quality single-point energies, and growing). This data is allowing for a thorough assessment of the quality of various wavefunction-based and modified DFT methods for noncovalent interactions. We have examined various DFT-D methods, Becke and Johnson's exchange dipole moment (XDM) method, various double-hybrids (ωB97X-D, XYG3), the Minnesota functionals (M05-2X, M06-2X), MP2C, and wavefunction-based methods such as lower-order SAPT, spin-component-scaled MP2, spin-component-scaled CCSD, and MP2.5. Results are analyzed for various classes of noncovalent interactions (hydrogen-bonded, dispersion-dominated, and mixed systems). Basis set effects are examined. We also explore how the quality of results is expected to behave as one moves to larger noncovalent complexes, and we consider the nature of noncovalent interactions in large systems.

L. A. Burns, A. Vazquez-Mayagoitia, B. G. Sumpter, and C. D. Sherrill, *J. Chem. Phys.* **134**, 084107 (2011).

6C4-5C

Dispersionless density functional theory with physically sound dispersion correction.

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Symmetry-adapted perturbation theory based on the density functional theory description of the monomers [SAPT(DFT)] has become the method of choice for calculating interaction energies for systems with a few dozen atoms [1]. Its accuracy has been proved in several applications for both dispersion-dominated and hydrogen-bonded systems, including successful predictions of structure of molecular crystals [2]. On the other hand, its reasonable scaling enabled its use for systems as large as coronene dimer [3]. Additionally, the method provides a physical decomposition of the interaction energy, including high-accuracy dispersion contribution.

The dispersion energy obtained from SAPT(DFT) has been used in developing a density functional (dlDF) designed to contain only the non-dispersion part of the interaction energy. Such dispersionless energy contains only terms that the local and semi-local density functionals can model. The SAPT(DFT) dispersion energy was also used in parameterization of an atom-atom dispersion (D) correction. The dispersionless functional with the dispersion correction (dlDF+D) approach [4] provides physically correct decomposition of the interaction energy. It is accurate for a wide range of intermolecular separations, including both the potential well and the asymptotic region. Correct modeling of these two regions had been particularly difficult for standard (dispersion-corrected) DFT functionals. An alternative approach to modeling of the dispersionless energy is also presented. It uses the Hartree-Fock method corrected by low-order SAPT(DFT) terms [5]. The method does not require adjustable parameters and does not rely on error cancellations.

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6C4-6C

Cubic scaling doubly hybrid density functional method close to chemical accuracy and its gradient theory

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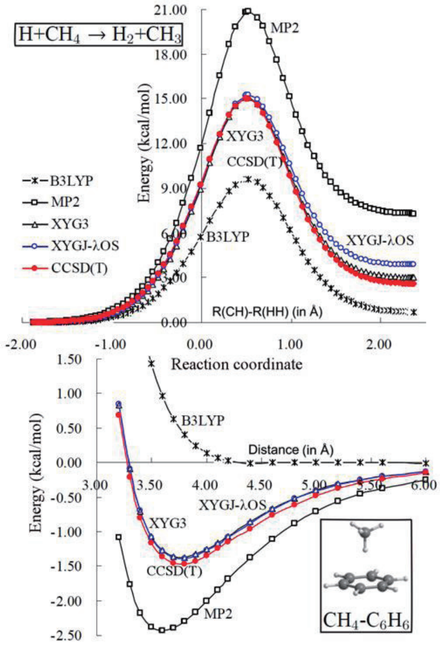
Obtaining chemical accuracy (0.04 eV) to quantify key chemical quantities (e.g. heats of formation, bond dissociation energies, and reaction barrier heights) using quantum mechanics has been a major focus in the development of the theory. This has led to, for example, the Gn method that approaches to this accuracy. Because G3 is a coupled cluster based method, it scales on the order of N^7, where N measures the system size, limiting to fairly small molecules for routine use. Present-day density functional methods are generally believed to provide a sweet spot between feasibility and accuracy, yet still lead to significant errors for some systems. For example, current density functionals give a poor description of London dispersion, which is essential to predict the packing of molecules into solids, and the binding of drug molecules to proteins. They are also poor in predicting the magnitude of reaction barriers often cases.



In this talk, I will present a new doubly hybrid density functional we developed which includes the perturbative correlation treatment of opposite-spin electrons only and therefore provides a unique combination of high accuracy and speed, namely XYGJ-λOS. Scaling of the method is shown to be cubic by utilizing the local characteristics and sparsity of the electron correlations, two orders lower than the scaling of conventional doubly hybrid methods. The analytic gradient theory of this opposite-spin based doubly hybrid functional is also formulated and implemented into Q-CHEM for geometry optimization. Some interesting chemical applications are presented for geometries and potential energy surfaces.

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