Fourteenth International Workshop on

Quantum Systems in Chemistry and Physics

San Lorenzo de El Escorial, Madrid (Spain)
September 13-19 (2009)

Book of Abstracts

It is our great pleasure to welcome you to the Fourteenth International Workshop on Quantum Systems in Chemistry and Physics (QSCP-XIV) at San Lorenzo de El Escorial, Spain. This conference is held every year. The aim of the QSCP meetings is to show the advances in areas such as Concepts and New Methods in Quantum Chemistry, Molecular Structure and Spectroscopy, Atoms and Molecules in Strong Electric and Magnetic Fields, Condensed Matter, Complexes and Clusters, Surfaces and Interfaces, Nano-Materials and Electronics, Reactive Collisions and Chemical Reactions, Computational Chemistry, Physics and Biology, and Biological Modeling. In this edition we have about sixty speakers and more than forty posters divided in two sessions.

The previous QSCP meetings were organized in
San Miniato/Pisa, Italy (1996),
Oxford, United Kingdom (1997),
Granada, Spain (1998),
Marly le-Roi/Paris, France (1999),
Uppsala, Sweden(2000),
Sofia, Bulgaria (2001),
Bratislava, Slovakia (2002),
Spetses Island/Athens, Greece(2003),
Les Houches, France (2004),
Carthage, Tunisia (2005),
St. Petersburg, Russia (2006),
Windsor/London, United Kingdom (2007), and
East Lansing, Michigan, USA (2008)

We hope that you will find the present QSCP Workshop at least as inspiring, fruitful, and enjoyable as the previous meetings in the QSCP series. The remarkable progress in the study of quantum systems in chemistry, physics, and biology will be shown by excellent talks and poster presentations during the workshop. The level of all contributions guarantees the success of QSCP-XIV.

We are grateful for the financial support provided to us by our sponsors (listed on the next page) in particular in this year with a very strong economical crisis. Without their kind assistance, the QSCP-XIV Workshop would not be possible. We have been delighted to receive the support from The Ministerio de Ciencia e Innovación, from the Consejo Superior de Investigaciones Científicas (CSIC), from the Real Sociedad Española de Física (RSEF) and for several private organizations. We would also like to thank all of you for participating in the Fourteenth International Workshop on Quantum Systems in Chemistry and Physics.

Finally, we hope that you will enjoy your visit to San Lorenzo de El Escorial during the QSCP-XIV.

Gerardo Delgado-Barrio (Chair)
Pablo Villarreal and Octavio Roncero (Co-chairs)
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WEDNESDAY September 18

THURSDAY September 17

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Quantum Dynamics of Chiral Molecules Including Electroweak Parity Violation

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The most important fundamental questions relating to the quantum dynamics of chiral molecules concern the influence of the electroweak parity violating interaction. This effect was suggested to be of potential importance shortly after the discovery of parity violation about five decades ago, but it has been understood quantitatively only recently. It leads to a small "parity violating" energy difference $\Delta_{pv}E$ between the quantum mechanical ground states of the enantiomers of chiral molecules. By introducing appropriate techniques of electroweak quantum chemistry, we showed in 1995, that this energy difference is about one to two orders of magnitude larger [1-3] than previously anticipated, and is of the order of 100 aeV typically (for a molecule like CHFClBr, for instance [4]). This theoretical discovery has in the meantime been confirmed by further calculations in our group and by numerous other groups (see the reviews [5-8])

The most challenging current questions concern the quantitative interplay between stereomutation tunnelling and parity violation in chiral molecules [9, 10]. In the lecture we shall report about the current status of the work on these problems in our group, in particular in relation to advancing current spectroscopic experiments to measure $\Delta_{pv}E$ based on the proposal in ref. [11]. If time permits we shall address also CP and CPT violation in chiral molecules [12-14].

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Semiclassical disentangling of spin-networks: exact computation and large angular momentum asymptotics of 3*nj*-symbols

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The 3nj-symbols of quantum angular momentum theory, which originated in spectroscopic applications to molecular, atomic, nuclear and particle physics, have been found crucial to many important fields of science, playing a role for example as spin networks in approaches to quantum gravity, as simulators in quantum computing, as discrete polynomials in computational science.
The basic building block can be considered the 6j symbols or Racah coefficients, while 3j symbols and rotation matrices are derived quantities, since they can be obtained in the semiclassical limits, *i.e* when some of the j's entering the symbols are large in units of $\hbar$. The 3nj symbols for n>2 and the related nontrivial spin networks are built as specific sums of products of 6j symbols. The focus of this presentation is both on the 9j symbol, well known in its role as the matrix element of the transformation between LS and jj coupling schemes, but exhibiting prototypical features, and of more complex entangled spin networks, whose semiclassical behaviour is investigated.

V. Aquilanti, H.M. Haggard, R.G. Littlejohn, L. Yu "Semiclassical analysis of Wigner 3j-symbol" *J.Phys. A* **40**, 5637-5674 (2007)

V. Aquilanti, A.C. P. Bitencourt, C. da S. Ferreira, A. Marzuoli, M. Ragni "Quantum and semiclassical spin networks: from atomic and molecular physics to quantum computing and gravity" *Physica Scripta*, **78**, 058103 (2008)

R.W. Anderson, V. Aquilanti, C.da Silva Ferreira "Exact computation and large angular momentum asymptotics of 3nj symbols: semiclassical disentangling of spin-networks" *Journal of Chemical Physics* **129**, 161101 2008

V. Aquilanti, A.C. P. Bitencourt, C. da S. Ferreira, A. Marzuoli, M. Ragni " Combinatorics of angular momentum recoupling theory: spin networks, their asymptotics and applications" *Theoretical Chemistry Accounts*, **123**, 237 (2009)

M. Ragni, A.C.P. Bitencourt,C. da S. Ferreira, V. Aquilanti, R.W.Anderson, R.G. Littlejohn" Exact computation and asymptotic approximation of 6j symbols. Illustration of their semiclassical limits" *Int. J. Quantum Chem.*, in press (2009)

R. W. Anderson, V. Aquilanti, A. Marzuoli "3nj morphogenesis and semiclassixal disentangling" *J. Phys Chem A* submitted (2009)

CCSD(T) study of the far-infrared spectrum of various isotopomers of ethyl-methyl-ether

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The correlation between abundance of ethers and alcohols in astrophysical sources has been frequently pointed out, as both compound types are involved in common chemical processes. Then, it appears reasonable to presuppose the existence of Ethyl Methyl Ether (EME) in objects where ethanol abundance is significant, in the same way as dimethyl-ether and methanol usually coexist [1-2]. Recently, EME has been tentatively proposed as responsible of some rotational spectral lines observed in hot cores associated with regions of high-mass star formation, where the abundance of ethers like dimethyl-ether, is evident [1].

It is commonly accepted that *ab initio* calculations can help experimental research, if the level of the theory is high enough, as occurs with the size-consistent couple cluster theory (CCSD(T)) applied to monoconfigurational systems. For non-rigid molecules, the theory can help the understanding of many aspects related with the effects of barriers on the splitting of the levels. In this work [3-4], band positions and intensities for the far infrared bands of various isotopomers of ethyl-methyl-ether are variationally determined from a three-dimensional potential energy surface calculated with CCSD(T)/cc-pVTZ theory. For this purpose, the energies of 181 selected geometries computed optimizing 3n-9 parameters are fitted to a three dimensional Fourier series depending on three torsional coordinates. The *zero point vibrational energy* correction and *the search of a correct definition of the methyl torsional coordinate* are taken into consideration for obtaining very accurate frequencies. For the variational-vibrational calculation, we employ our code ENEDIM[5].

Second order perturbation theory is applied on the two molecular conformers, *trans* and *cis-gauche*, in order to test the validity of the 3D-model. Consequently, a new assignment of previous experimental bands, congruent with the new "*ab initio"* results, is proposed. For the most stable *trans*-conformer, the ν_{30}, ν_{29}, and ν_{28} fundamental transitions, computed at 115.3, 206.5 and 255.2 cm^{-1}, are correlated to the observed bands at 115.4, 202 and 248 cm^{-1} [6]. For the *cis-gauche* the three band positions are computed at 91.0, 192.5 and 243.8 cm^{-1}. Calculations on the –d$_3$ isotopomer confirm our assignment.

Intensities are determined at room temperature and at 10K. Structural parameters, potential energy barriers, anharmonic frequencies for the 3n-9 neglected modes, and rotational parameters (rotational and centrifugal distortion constants), are also provided. Computed data are compared with previous experimental results [6-8].

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Classical theory of atom-surface rainbow scattering

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Rainbows in atom surface scattering have been observed experimentally forty years ago. The phenomenon itself was well understood in terms of vanishing derivatives of the deflection function with respect to the impact parameter. Over the years quite a few systems have been measured and various characteristics elucidated. Typically rainbow scattering appears in the form of a double peaked distribution about the specular angle. The center of the distribution may be sub-specular or super-specular, the distribution is typically asymmetric. The distance between the rainbow peaks is a function of both incident energy and incident angle. The higher the energy and the larger the angle the smaller the distance between the peaks. However, much of the experimental data has not been analyzed in any detail.

Until recently the "standard" theoretical model with which some of these features have been modeled was the washboard model of Tully, in which the vertical interaction between the atom and the surface is a hard wall potential. We have recently developed a perturbation theory of atom surface scattering in the presence of corrugation and taking into account surface phonons in a Langevin equation framework [1-4], which accounts for the phenomena described above and more. The theory introduces the concept of phonon induced rainbows, phonon induced asymmetry, corrugation induced asymmetry, and nonlinear induced asymmetry in atom surface scattering. Specific systems to be discussed and analyzed include Ar-Ag(111), Ar-LiF(100), Xe-Ge(100), Ar-Ag(100), Kr-Ag(100) and Ar-2H-W(100).

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Theoretical study of solvent effects on Pterin Acid/Basic Equilibrium and UV-Visible Spectra

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Pterins are a family of heterocyclic compounds present in a wide variety of biological systems. Interest in photochemistry and photophysics of pterins and derivatives is, in part, due to their functions in physiological receptors of UV light. Some biomedical studies suggest that pterins are involved in changes of the skin pigmentation, which depend on the amount of these compounds in the cell[1]. In this work combined Monte Carlo simulations and quantum mechanical calculations have been used to study the solvent effect of aqueous environment in the UV-vis absorption spectra of Pterin. Additionally, the free energy perturbation (FEP)[2] technique has been used to study the solvent effect on the acid/basic equilibrium due to the tautomeric proton transfer reaction of Pterin in water. In the first stage, the both polarization of Pterin in the acid and basic forms were calculated in the presence of the water environment using an iterative procedure combining Monte Carlo simulations and MP2/aug-cc-pvdz quantum calculation[3]. The basic form, that has a smaller dipole moment than the acid form (1.53 and 3.68D, respectively) presents a larger polarization 85% while the acid form presents only 67% of polarization. Our best calculated values for the two π-π^* absorption transitions of Pterin (acid and basic forms) in water solution were in very good agreement with the experimental results. For the basic form the calculated values are 347 and 265nm and the experimental results[4] are 358 and 252nm, and for the acid form they are 338 and 270nm and 340 and 270nm, respectively. For the acid/basic equilibrium, two reaction pathways were considered: the direct and water-assisted transfer. For calculations with isolated molecules, the intramolecular transfer indicates that the acid form is more stable than the basic form by –1.4 kcal/mol with a free energy barrier of 34.2 kcal/mol. The proton transfer with the assistance of one water molecule indicates that the acid form is still more stable by –3.3 kcal/mol with a Drstic reduction of 70% of the barrier. The bulk water effect was found to be substantial and decisive when the reaction path involves the water-assisted mechanism. In this case the free energy barrier was only 6.7 kcal/mol and the relative free energy for the two tautomers was –11.2 kcal/mol. This last value was used to calculate the pKa of 8.3±0.6 that is in excellent agreement with the experimental result[5] of 7.9.

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Wave-function-based approaches to describe doped He clusters and its interaction with metal-oxide surfaces

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Infrared (IR) spectra of the carbonyl sulfide (OCS) molecule inside He nanodroplets provided the first experimental evidence for the onset of microscopic superfluidity[1] motivating numerous, both experimental and theoretical, studies of small doped He clusters. As an alternative to diffusion and path-integral Monte-Carlo methods, wave-function-based quantum-chemistry-type treatments, which consider the He atoms as "electrons" and the dopant as a structured ``nuclei", have been developed[2-9] to study energetic, structural and spectroscopic aspects of these aggregates. As a first step, Hartree/Hartree-Fock (H/HF) methods were implemented[3]. Simulated H/HF infrared/Raman spectra have stressed the key role of spin quantum statistic effects in the different spectra experimentally observed[5,6,8] Major difficulties in developing more rigorous approaches, including explicitly the He-He correlation and the excited states, are caused by the very repulsive He-He interaction at short distances. As a benchmark treatment, a Full-Configuration-Interaction (FCI) approach to treat the "hard-core" interaction problem have been recently developed.[4,7,9]. As an illustrative example, the results obtained with this method, as applied to Br_2 and Cl_2-doped Helium clusters, will be presented.[9]

As a second subject, an approach to treat the interaction of doped Helium nanodroplets with metal-oxide surfaces will be presented[10,11], the study being motivated by its application to the "soft-landing" adsorption of the dopant species.[11]

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Energy level alignment at metal-organic interfaces, energy gap selfinteraction corrections and Density Functional Theory

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Convencional LDA or GGA calculations for organic interfaces are limited by the “energy gap problem of the organic material”, because LDA (or GGA) Kohn-Sham energy levels have to be corrected by the selfinteraction energy of the corresponding wavefunction to provide the appropriate molecule transport energy gap. Image potential and polarization effects at metal/organic (M/O) interfaces tend to cancel these selfinteraction corrections [1,2].

We present a complete theoretical study of the approach of two Au(111)-based tips to a C_{60} molecule, whereby combining a DFT-LDA-calculation with a full analysis of the M/O interface barrier formation, making use of the IDIS (Induced Density of Interface States) model [3], we are able to calculate selfconsistently the effective intrasite Coulomb interaction for electrons in the buckyball, the selfinteraction corrections and the molecule energy gap [4]. We also present results for a single molecule adsorbed on a Au(111)-surface and compared them with independent experimental and theoretical results [2,5]

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The Chemical Bond as a Quantum Interference Phenomenon.

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A simple quantum-electrodynamical-like analysis will be presented to show that the interference among one-electron states is the driving force for the bonding phenomena [1]. This sort of analysis not only reveals the origin of the quantum effect responsible for bond formation but also indicates which MPI should be used to perform such analysis. From the energetic point of view, this sort of analysis also clearly indicates how to partition the total molecular electronic energy for a proper investigation of the chemical bond formation. Although the problem of how to partition the energy in order to analyze the formation of a chemical bond has been previously discussed [2], the actual application of the proposed methodologies has been limited to a few cases. This has to do with the difficulty in partitioning the density of complex molecules in a chemically intuitive and physically meaningful way. We use the Generalized Product Functions (GPFs) [3] for such an analysis, since their first order reduced density matrices are blocked by electron group and their second order reduced density matrices are neatly partitioned in intergroup and intragroup blocks. In particular, by describing valence electron groups with modern Valence Bond methods (GVB, SC, etc.), the arbitrariness of the choice for atomic orbitals inherent to the interference partition is removed. The conservation relations for the reduced density matrices and the equations for the interference partitioning for this type of wave function allow the interference contributions of σ and π electrons, for example, to the molecular energy to be separately analyzed. Results for N_2, C_2H_4 and for other saturated and unsaturated compound will be presented. (FAPERJ, CNPq).

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Novel Approaches for Core Excitations and Weak Interactions in Density Functional Theory

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This paper addresses the recent development of density functional methods for (I) core excitations and (II) weak interactions.

(I) Core Excitations: Time-dependent density functional theory (TDDFT) has become one of the most popular methods to compute low-lying excited states because of its reasonable accuracy with low-computational cost. However, TDDFT fails to describe core and Rydberg excitations with high accuracy [1]. We have proposed a hybrid exchange-correlation functionals for core and Rydberg excitations: core-valence-Rydberg B3LYP (CVR-B3LYP) [2] that possesses different portions of the Hartree-Fock (HF) exchange for core, valence, and Rydberg orbitals.

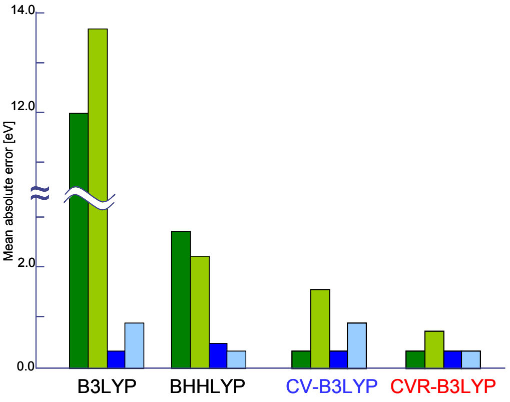

Fig. 1. Mean absolute errors of the C→V, C→R, V→V, and V→R excitation energies of C_2H_2, C_2H_4, CH_2O, CO, and N_2 molecules calculated by TDDFT with CVRB3LYP, CV-B3LYP, B3LYP, and BHHLYP (cc-pCVTZ plus 1s1p Rydberg functions).

(II) Weak Interactions: Based on the local-response approximation and the Zaremba-Kohn expression of the exact second-order dispersion energy [3], Dobson and Dinte derived doubly-local density functional for the dispersion energy between nonoverlapping fragments [4]:

$$E_{\text{disp}} = -\frac{3}{16\pi^{3/2}} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{1}{r_{12}^6} \frac{\sqrt{\rho(\mathbf{r}_1)}\sqrt{\rho(\mathbf{r}_2)}}{\sqrt{\rho(\mathbf{r}_1)}+\sqrt{\rho(\mathbf{r}_2)}} \qquad (1)$$

The same functional was also derived by Andersson, Langreth, and Lundqvist (ALL), from the different physical context [5]. Combining the ALL functional with the long-range corrected (LC) density functional [6], Hirao and coworkers [7] have successfully described various inter-molecular interactions. However, the computational cost of the ALL functional is high because of the numerical double integral. We have proposed the local-response dispersion (LRD) coefficients, $\{C_6^{AB}, C_8^{AB}, C_{10}^{AB}, \cdots\}$ [8]. The LRD coefficients are then combined with the LC-DFT through the damped atomwise expression:

$$E = E_{\text{LC-DFT}} + \sum_{n\geq 6}\sum_{A>B} \frac{C_n^{AB}}{R_{AB}^n} f_{\text{damp}}^{(n)}\left(R_{AB}\right) \qquad (2)$$

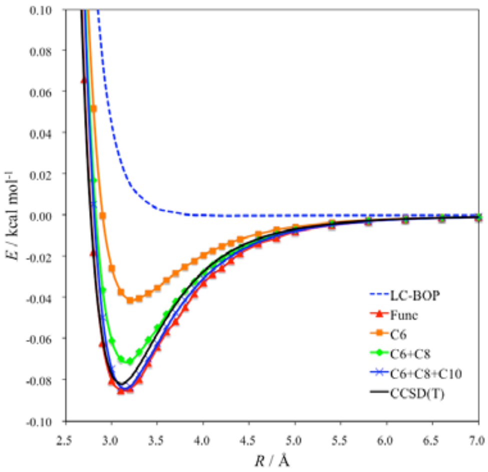

Fig. 2. Potential energy curves for Ne_2 dimer calculated by LC-BOP with and without the dispersion energy term by Eq. (1) or (2), comparing with the CCSD(T) results.

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Development and Applications of Spin-Adapted Multi-Reference Coupled Cluster Formalisms using Multi-exponential Type Cluster Ansatz: State-universal and State-specific Approaches

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A succinct account will be presented in this talk delineating the various aspects of generating spin-adapted versions of various Multi-Reference Coupled Cluster (MRCC) formalisms which use multi-exponential type cluster ansatz of the Jeziorski-Monkhorst kind. While a naive use of a spin-orbital based formalism will lead to spin-broken solutions for non-singlet cases, a spin-free analogue can be formulated which obviates this shortcoming. We would discuss the various facets of the spin-adaptation problem for both state-universal and state-specific MRCC approaches. The major novel component of our formulation is the use of a combinatoric cluster ansatz of the wave operator. In this ansatz, the associated cluster operators are defined in terms of orbital rather than spin-orbitals. The associated excitation operators are defined in terms of spin-free unitary generators. The real issues of spin-adaptation in the case of a multi-exponential cluster ansatz are: (a) Coverage of the full excitation space, (b) Choice of the rank of the cluster operators which are the most economical in the sense of being of the lowest excitation rank, (c) Avoidance, if possible, of redundant cluster operators that (a) demands and (d) Choice of a cluster ansatz which ensures a finite power series expansion of the ‘direct term’ of the working equations for determining the cluster amplitudes. The combinatoric cluster ansatz necessitates the use of excitation operators containing spectator excitations of the active orbitals, and they are allowed to contract vis these spectator orbitals. The factors associated with the connected composites thus generated are the inverse of the ‘automorphic factors’, viz. the number of various ways in which the factors in the composites can be joined leading to the same excitations. We show that this ensures the finiteness of the power series of the cluster operators for the ‘direct terms’. We will discuss, with illustrative numerical examples, how very compact working equations are generated for both state-universal and state-specific MRCC formalisms using the combinatoric ansatz. The pilot applications will indicate the efficacy of the formalisms. In particular, we show how the intruder problem can be bypassed in a compact spin-free manner in the state-specific MRCC version.

Exceptional points in molecular photodissociation

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The interaction of a molecule with a cw laser field is described by a time-periodic Hamiltonian. The wave equation has solutions given by the Floquet formalism, with eigenvalues called the quasi-energies. If the field can lead to photodissociation of the molecule, these quasi-energies are complex, with an imaginary part yielding the photofragmentation rate. These resonance energies are in fact the poles of the scattering matrix. In the case of intense fields, there is a richness of new processes. We are here interested by the possibility, with an appropriate choice of laser frequency and intensity, to provoke the degenerescence of two Floquet quasi-energies. The corresponding point in parameter plane is called exceptional [1]. This is to be distinguished from the well known situation where the same energy is associated with two different eigenfunctions, as is the case when the degeneracy is due to symmetry. Such points have recently been studied in many areas of physics, either classical or quantum [2]. They have a number of very important consequences which will be presented for the case of molecular photodissociation [3].

A condition for two resonances to yield such a point is that they correspond to respectively a shape-like resonance and a Feshbach-like one.

At an exceptional point the two resonance wave functions merge into a single one, which is "self-orthogonal". The concept of self-orthogonality is due to the special scalar product valid for resonance wave functions.

With an adiabatic variation of the parameters along a closed contour around an exceptional point, it is possible to go from one non-degenerate resonance pole to another.

In order to realize such a transfer, it is necessary to reach a compromise between two conflicting conditions: the laser pulse must vary slowly enough for an adiabatic transfer to take place, but fast enough to keep a fair amount of undissociated molecules. This can be checked through the adiabatic Floquet theory.

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Radiationless Decay of Excited States of Tetrahydrocannabinol through the S_1-S_0 Conical Intersection

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The dynamics triggered in a molecule after absorbing a photon is usually discussed in terms of the Born-Oppenheimer theory[1] , where the fast electronic degrees of freedom are treated separately from the slow nuclei. In this picture, electrons and nuclei do not easily exchange energy. Yet, in some nuclear configurations called conical intersections (CIs) energy exchange can become significant[2,3]. Characterizing and localizing these electronic energy degeneracies is important for describing and controlling electronic energy flow in molecules[4-6].

Extensive research in the last 10 years has revealed that CIs are indeed ubiquitous in polyatomic molecules and internal conversion takes place through them. CIs thus are the key mechanistic elements for photostability, as they provide a "photochemical funnels" for the highly efficient photochemical decay mechanism[7-9].

The ground and the electronically excited singlet states of THC molecule have been studied theoretically using DFT and TDDFT methods focusing on the mechanism of radiationless decay back to the ground state[10]. Based on the characterization of the ground and the first excited singlet states potential-energy profiles an ultra-fast and photostable molecular photo-switch based on the excited-state intramolecular proton transfer (ESIPT) process has been theoretically designed.

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Microscopic Self-organization and Self-referential Systems

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It is argued that the emergence of Jordan blocks in the generator of the time evolution plays a part corresponding to those of paradoxes and self-references in philosophy and logic[1]. We will briefly discuss the manifestation of these triangular units in properly generalized quantum theory of microscopic- as well as open systems with organizations appearing on the fundamental- as well as on higher order levels of explanation. The formulation centers on specific transformations within coherent-dissipative ensembles that display particular factorization properties, cf. the Gödel encoding system used in deriving the celebrated incompleteness theorem. This brings about the proposition of an additional meta-code, cf. the genetic code that may be recognized for the map between the genotypic and phenotypic spaces.

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A separable model of N interacting particles

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A system of coupled harmonic oscillators described by an N-particle Hamiltonian can be decoupled by a linear transformation of the coordinates. In the new coordinates, referred to as the normal coordinates, the Hamiltonian describes a set of independent harmonic oscillators. The resulting Schroedinger equation is separable and exactly solvable and commonly used to describe a broad set of physical systems ranging from the shell structure of atoms and vibrations of polyatomic molecules to the internal structure of atomic nuclei.

We demonstrate that the separability of the model is retained if the interactions between disjoint pairs of particles are described by arbitrary two-particle potentials which depend on the distance between the particles only. The two-particle potentials may be chosen in such a way that the model is either exactly or quasi-exactly solvable. Additionally to the well known combinations of the Coulomb and Hooke potentials leading to the Hooke atom[1] and to the Hookean hydrogen molecules[2], quasi-exact solvability is retained for a number of power-law potentials, including the ones with fractional negative powers, as well as for several kinds of screened Coulomb and quasi-relativistic potentials.

This model supplements the family of separable N-particle models[3] and may be useful in studying various aspects of separability of quantum systems related to the electron correlation effects, non-adiabatic effects, intermolecular interactions. It is applicable to a description of systems in which interactions between specific pairs of particles are different than the remaining interactions. Several systems relevant in quantum-chemistry, as the Hooke atom[1] and the Hookean hydrogen molecules[2], appear to be special cases of this model.

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The G-particle-hole Hypervirial equation: Iterative solution and computational efficiency enhancements.

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The iterative solutions either of the second-order Correlation Contracted Schrödinger equation (2-CCSE)[1] or of its anti-Hermitian part, the G-particle-hole hypervirial (GHV) equation[2,3], lead to very accurate results for the electronic structure of an N-electron system. Both of them pay attention directly to the correlation effects but the GHV equation is easier to solve because it does not depend on the 4-order effects. New procedures to reduce the storage requirements and to speed up the iterative process are here described. This new methodology has been applied to a variety of atomic and molecular systems. The improvements on the computational efficiency are discussed.

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Some theoretical questions about the G-particle-hole hypervirial equation

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The *G*-particle-hole hypervirial (GHV) equation[1,2,3] is the anti-Hermitian part of the second-order Correlation Contracted Schrödinger equation (2-CCSE) [4]. It has been shown that an iterative solution of the GHV equation leads to a very precise description of the electronic structure of an N-electron system. Some theoretical as well as applicative questions are however only partially answered. The aim of this work is to discuss these questions and describe the trends of our present quest in order to optimize further this methodology.

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Recent progress on global potential energy surfaces: an *ab initio* cost-effective strategy

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We survey recent progress on a general cost-effective strategy to generate a potential energy surface (or surfaces) at a high level of accuracy with conventional *ab initio* methods. The key feature of the approach lies on scaling and extrapolating to a given target level the energy calculated with small basis sets, without resorting to parameters alien to the *ab initio* theory. Progress on the analytic modelling of the calculated raw *ab initio* energies using double many-body expansion theory is also surveyed. Case studies to be discussed at the conference include up to tetratomics systems and electronic manifolds. Time permitting, work on medium size interactions or use in reaction dynamics of the calculated potentials will also be presented.

Dynamics simulations of collisions of gases with a perfluorinated self-assembled monolayer

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Self-assembled monolayers (SAMs) are organic assemblies formed by the adsorption of molecular constituents in which one end of the molecule, the "head group", has a specific affinity for a substrate.[1] The rest of each molecular constituent includes a tail as well as a final functional group, which controls the particular properties of the SAM. SAMs are very valuable materials for exploring the dynamics of collisions of gases with organic surfaces because their highly ordered and well-characterized structures simplify the elucidation of the microscopic mechanisms of energy transfer. In this talk, we will present our recent results on classical trajectory simulations of collisions of CO_2 molecules with a perfluorinated alkanethiol SAM (F-SAM) on gold.[2,3] The potential energy surface comprises an analytical intramolecular potential for the projectile CO_2 molecule, a force field for the F-SAM surface, and a gas-surface interaction potential. The final rotational distributions calculated for the scattered CO_2 molecules are found to be in good agreement with experimental observations.[4,5] We will also show preliminary results on collisions of silyl ions ($SiNCS^+$ and Me_2SiNCS^+) with F-SAM surfaces. In this case, we will analyse the probability of "soft-landing", that is, the deposition of intact projectile ions onto a surface, which is the basis of a method of preparing modified surfaces, first introduced by Cooks and co-workers.[6]

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A statistical quasiclassical trajectory model for insertion reactions: Application to the $H^+ + H_2$ reaction.

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A detailed comparison of statistical models based on quasi-classical trajectories (SQCT) and quantum mechanical (SQM) methods is presented in this work with application to the proton exchange reaction $H^+ + H_2$ and isotopic variants. The SQCT model [1] complies with the principle of detailed balance and conservation of the triatomic parity. The basic difference with its QM counterpart lies in the fact that trajectories instead of wavefunctions are propagated in the entrance and exit channels. Other than this the two formulations are entirely equivalent. Reaction probabilities, integral and differential cross sections for the $H^+ + H_2$, $H^+ + D_2$, $D^+ + H_2$ will be shown and discussed. The agreement between the SQCT and SQM results is excellent and indicates that the effect of tunnelling through the centrifugal barrier is negligible [1].

These results are compared with recent fully converged, close coupling exact (CCQM) calculations [2, 3]. Since these calculations are computationally expensive, it is pertinent to assess the validity of other simpler treatments such as QCT and statistical QCT or QM models [4, 5]. For the $H^+ + D_2$ reaction, it has been found that the QCT method accounts for the dynamical behaviour reasonably well at low collision energies and low values of the total angular momentum, *J*. The agreement quickly deteriorates with increasing energy and *J*, the QCT results predicting a substantially lower reactivity. In contrast, the SQCT model predicts a higher reactivity than that obtained with CCQM calculations. The main conclusion is that the accuracy of rigorous statistical descriptions is limited and depends on the isotopic variant. By and large these reactions cannot be deemed as purely statistical and important dynamical effects seem to take place. In particular, at sufficiently high energies and *J* values, the decrease of the reactivity is related with the appearance of an effective repulsive centrifugal motion within the deep well of the triatomic complex that occurs beyond the capture radius that cannot be accounted for by statistical models. CCQM results lie in between those obtained with the QCT and SQCT methods. As a result of this, an accurate description of the reaction requires a full QM treatment.

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Reaction dynamics of complex-forming triatomic processes: Recent developments around Phase Space Theory

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State and spatial distributions in the products of gas-phase processes are among the finest information on chemical reactivity. Predicting and understanding the shape of these distributions is thus a major goal in theoretical chemistry.

For elementary triatomic reactions governed by long-range forces and proceeding via a sufficiently long-lived intermediate complex (~ 1ps), one possible approach is Phase Space Theory (PST), the main advantages of which are numerical simplicity and interpretative power. The basic assumptions of PST as well as recent developments discussing the validity of such an approach are here presented.

Vector correlation analysis for unimolecular and bimolecular reactions

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Inelastic and reactive collisions as well as unimolecular processes such as photofragmentation, in general produce anisotropic distributions of the products fragments' relative velocity v and their angular momenta *j*. These vector properties have received considerable experimental and theoretical attention lately as a mean to obtain detailed information on energetics and reaction mechanisms. The angular momentum polarization of the atomic or molecular fragments are particularly important in this context. The detailed study of the anisotropy of the fragments' angular momenta can provide crucial information on structure, symmetry and dynamics in the continuum. They can give access to the relative phases of some transition matrix elements in addition to the amplitudes and they are extremely sensitive to interference effects when coherent excitation of several continua occurs. Electronic angular momentum polarization for instance, provides a direct probe of the motion of the electrons during the reaction as well as information on electronic structure, symmetries, and non-adiabatic couplings. The study of the product rotational angular momentum polarization provides on the other hand information about the bending and torsional forces acting during the reaction. The detailed information and understanding of these properties can provide means to control the production of polarized fragments to use in applications such as: spin-dependent effects in atomic, molecular, and surface physics. It is also worth noting that if the products are excited, the light emitted reflects the anisotropy of the fragments through its angular distribution and polarization.

The most detailed information on reaction dynamics is obtained if angular resolved moments are measured (the so-called complete experiment), i.e., when the correlation between the fragments' relative velocity v and the angular momentum j (v-j correlation) is determined. In this talk the unified quantum theory of vector correlations for uni- and bi-molecular reactions will be presented. The validity of semiclassical treatments will be discussed. In the photofragmentation for instance in many cases the fragments fluorescence polarization can be calculated by using the simple semiclassical treatment in terms of absorption and emitting oscillators. For the angular distributions of the fragments, it has been shown that when the rotational and electronic angular momentum J and its projection Ω along the body-fixed z axis Ω, are well defined in the initial state the quantum and quasiclassical expressions are identical for any initial polarization of the molecule prior to photolysis and for all values of J and Ω. These conclusions apply to preparation schemes employing optical excitation, static inhomogeneous and/or homogeneous electric and/or magnetic fields, as well as to molecules physisorbed on solids or clusters. This can be important for the interpretation of photofragment distributions when some other angular momenta are involved, such as electronic angular momentum, with and without nuclear spin, coupled to molecular rotation, asymmetric top rotational angular momentum, or internal vibrational angular momentun in polyatomics.

Calcium atoms attached to mixed helium nanodroplets: A probe for the ^{3}He-^{4}He interface

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Theoretical and experimental results for mixed helium droplets doped with one calcium atom are reported[1]. The absorption spectrum around the $4s4p \leftarrow 4s^2$ transition is calculated as a function of the composition of the droplet and compared to the experiment. Our study reveals the distinct feature that for specific ^{3}He concentrations, Ca atoms sit at the ^{3}He-^{4}He interface. This particular property of Ca, likely not shared with any other atomic or molecular species but the heavier alkaline-earth atoms, might offer the possibility of using it to probe the ^{3}He-^{4}He interface of the droplet. Preliminary results for Na atoms attached to $^3\text{He}_{N3}$+$^4\text{He}_{N4}$ when N3«N4 will also be discussed.

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Rare gas trimers: The Efimov effect and thermal properties

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Molecular clusters formed by rare gas atoms exhibit a rich variety of properties which have led many authors in the past to focuss their efforts on these systems. In particular, few body molecules have been ideal prototypes to probe the possible occurence of effects observed in larger aggregates such as molecular superfluidity or phase transitions. In addition, the trimer formed with the lightest rare gas, helium, as He_3 [1,2], have been found to manifest the so-called Efimov effect [3]. Thus, by conveniently enlarging the corresponding pair interactions, it is possible to observe that the first excited state becomes energetically less stable than the energy of the He_2 bound state. These bound states, on the other hand, are characterised by a extreme spatial delocation, in clear contrast with the case observed for heavier systems such as Ar_3 or Ne_3.

The energetics and geometries of the bound states found for these systems have been studied by means of a variational quantum mechanical approach based in the use of distributed Gaussian functions to describe interparticle distances [4,5]. The rovibrational spectra for the case of a nonzero total angular momentum, $J \neq 0$, can be analysed with a recently proposed method in which the eigenstates of the purely vibrational problem are used as radial functions in the basis set for the total Hamiltonian [6,7].An example of the application for Ar_3 will be presented in the conference.

Finally, recent results of the investigation of some properties of the Ar trimer as a function of the temperature will be also discussed.

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Dimers of open-shell oxygen molecules: from *ab initio* interaction potentials to comparison with experiments

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Interactions between two $^3\Sigma$ diatomics give rise to three different intermolecular potentials of singlet, triplet and quintet multiplicities that might exhibit different properties. While accurate calculations of potential energy surfaces (PES) are possible for the quintet multiplicity (since a single reference wave function is valid), calculations of the other two multiplicities are very challenging as methods based in multiconfigurational reference wave functions are unavoidable. This is the case of the $O_2(\,^3\Sigma_g^-)$-$O_2(\,^3\Sigma_g^-)$ dimer, of interest in atmospheric chemistry and physics, condensed phases, and, more recently, in low and ultralow temperature physics.

We will report on recent theoretical progress of the oxygen dimer. A full rigid rotor PES for the quintet state has been obtained at the CCSD(T) level of theory[1]. The singlet and triplet PESs are obtained by combining the CCSD(T) quintet potential with multiconfigurational calculations of the singlet-quintet and triplet-quintet splittings[2]. Multiconfigurational calculations are performed at both the MRCI and the CASPT2 levels of theory. In addition, the PESs are extrapolated at long range using accurate *ab initio* dispersion coefficients.

The new CCSD(T)-MRCI and CCSD(T)-CASPT2 PESs are compared and checked against a variety of experiments. Spectroscopy should be the most sensitive probe for the performance of the MRCI vs. the CASPT2-based PES, since the main differences between them are given around the absolute minimum of the interaction. We have performed calculations of the rovibrational bound states and compared against experiments involving the singlet and triplet states. In addition, we have carried out accurate close-coupling calculations[3] in order to compare with scattering and rotational energy-transfer experiments, which are also sensitive to the hard wall and long range behavior of the PESs. A comparison with observables obtained from previous (semi-*ab initio* and experimentally derived) PESs will be also presented.

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High Precision Theoretical Spectroscopy of Artificial Fluorescent Biosensor, Organic Light Emitting Diodes, and Inner-shell Electronic Processes

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Development of the state-of-the-art theories has made us possible to obtain the precise knowledge of the excited states of molecules. We have investigated wide varieties of "excited-state chemistry" and achieved "theoretical fine spectroscopy" with the SAC-CI method.[1] In this talk, we present our recent challenges to the high-precision theoretical spectroscopy and photochemistry of artificial fluorescent biosensor, organic light emitting diodes, and inner-shell electronic processes.

Artificial fluorescent biosensor has been extensively developed, since it enables the direct and real-time measurements of the biological activities. We have studied the photochemistry of novel *artificial fluorescent biosensor* which can selectively monitor the phosphoprotein and ATP where the probe of "anion species" is the most difficult subject in this field. We clarified the photoinduced electron transfer mechanism which is relevant in fluorescent biosensor based on the geometry relaxation and solvation effect.

Organic light emitting diodes (OLED) are recognized as the important materials for the next generation electro-optical devices. Theory can predict the photo-physical properties of OLED aiming at the molecular design of color-tuning. We have investigated optical properties, photo-electronic processes, and excited-state dynamics of some OLED molecules like polyphenylenevinylene, fluorene-thiophene, and Ir complexes.[2]

Recent developments in high-resolution spectroscopy require *highly accurate theory* that can clarify the underlying physics behind the complex phenomena. We have investigated various kinds of *core-electronic processes* like geometry relaxation, inner-shell shake-up satellites with vibrational progression, irregular valence-Rydberg coupling and its thermal effect, keto-enol isomerization induced by inner-shell excitations, and scalar relativistic effect in *K*-shell ionizations.[3]

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Energy Approach and QED Lines Moments Technique for Atoms and Nuclei in a Strong Laser Field

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QED theory is developed for studying interaction of atoms with an intense and superintense laser field. Method bases on a description of system in the field by the k-photon emission and absorption lines. The lines are described by their QED moments of different orders, which are calculated within Gell-Mann and Low adiabatic formalism [1,2]. The corresponding energy approach uses the adiabatic Gell-Mann and Low formula for an energy shift ΔE with QED scattering matrice, which includes an interaction with the photon vacuum field and external electromagnetic (laser) field [1,3]. There are gpresented new data for multi-photon resonance and ionization profile in *Cs, Yb, Gd* atoms. The analogous energy approach is for the first time developed for consistent description of the laser-nucleus interaction and corresponding multi-photon phenomena. The natural actual application of the presented approach is formulaion of the consistent theory for the resonant process of nuclear excitation by electron capture NEEC (transition NEET) , in which a continuum electron is captured into a bound state of an ion with the simultaneous excitation of the nucleus. The preliminary estimates are obtained for the case of electric and magnetic multipole E2, M1 transitions in $^{236,238}_{92}U$, $^{173,174}_{70}Yb$, $^{154-157}_{64}Gd$. AC and DC strong field Stark effect for atoms is also studied within the energy approch and operator peturbation theory formalism. The zeroth order Hamiltonian, possessing only stationary states, is determined only by its spectrum without specifying its explicit form. We present here the calculation results of the Stark resonances energies and widths for a number of atoms (*H, Li, Tm,U* etc.) and for a whole number of low-lying and also Rydberg states [2]. We discovered and analyzed the weak field effect of the giant broadening of widths for Letokhov-Ivanov re-orientation decay autoionization resonances in *Tm* etc. For the first time this effect is discovered in the *U* atom. We consider the nuclear dynamic (AC) Stark shift of low-lying nuclear states due to the off-resonant excitation by the laser field (laser intensity ~10^{25}-10^{35} W/cm^2). It is confirmed that the direct laser-nucleus interaction has to become of relevance together with other super-intense light-matter interaction processes such as pair creation.

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Electronic properties of molecular structures by inelastic x-ray scattering

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The detection of high-energy x-rays that are inelastically scattered from matter provides advanced methods to study the electronic structure both at the ground- and the excited state. The experiments are typically performed at large-scale synchrotron radiation facilities. In the so-called Compton regime (high energy and momentum transfer to the system) the scattering cross section is sensitive to the ground-state momentum density of the electrons. The momentum density is itself strongly dependent on the covalent and hydrogen bonds in the system. Even small geometrical changes, i.e. 0.1-0.01 Å in the bond lengths, lead to observable changes in the experimental spectra. We have recently analyzed a large set of molecular systems in the solid and liquid states experimentally and by quantum mechanical calculations at the density-functional theory level (see Refs. 1-2). The studies comprise cases such as the range of applicability of different models for the structure of water, aqueous solvation of ions and isomeric differences of small alcohols. These studies have provided new insight into the hydrogen bond networks, intra- and intermolecular geometries and nearest neighbor coordination.

The other technique, so-called x-ray Raman scattering (XRS), can be used to probe the excited electronic states in the vicinity of a core-excited atom in the system. When the momentum transferred from x-rays to the studied system is small, XRS provides information similar to x-ray absorption, and the dipole-allowed transitions from an inner shell to the unoccupied electronic states are probed. However, by increasing the momentum transfer one is able to probe non-dipolar transitions, e.g. *s* to *s* and *s* to *d* type, which gives complementary and new information on the excited states. The recent development in the experimental and computational aspects of XRS enables a detailed analysis of the experimental spectrum.[3] For example, one can decompose the spectrum with respect to the symmetry properties of the unoccupied electronic states. In this way, one obtains new information on the electronic and structural properties of molecular systems. The XRS methodology has been used e.g. for polymeric systems.[4]

The interpretation of both the x-ray Compton and Raman scattering spectra relies essentially on quantum mechanical calculations for the electronic structure. In this contribution I will cover the recent advances and applications of the x-ray techniques on molecular systems.

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Active-space electron-attached and ionized equation-of-motion coupled-cluster methods

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The electron-attached (EA) and ionized (IP) equation-of-motion coupled-cluster (EOMCC) methods, which utilize the idea of applying a linear electron-attaching or ionizing operator to the correlated, ground-state, CC wave function of an *N*-electron closed-shell system in order to generate the ground and excited states of an (*N*±1)-electron system provide an ideal framework for performing orthogonally spin-adapted calculations for radical species. The problem with these approaches is that their basic, low-order approximations are often insufficient for accurately describing excited states and potential energy surfaces along bond-breaking coordinates of radicals, and so higher order excitations must be accounted for.[1-4] Unfortunately, the inclusion of higher order excitations in the EA- and IP-EOMCC schemes makes the resulting calculations prohibitively expensive, restricting the use of these approaches to relatively small systems and basis sets. To deal with this difficulty, we have recently developed the active-space variants of the EA- and IP-EOMCC[1-3] and related SAC-CI (symmetry-adapted-cluster configuration interaction)[4] methods, in which one considers only small subsets of all higher-than-double, higher than 2-particle-1-hole (2*p*-1*h*), and higher than 2-hole-1-particle (2*h*-1*p*) excitations in the cluster, electron-attaching, and ionizing operators, respectively, which are selected through the use of a suitably defined set of active orbitals. In this presentation, we will discuss the fundamental theoretical aspects of the active-space EA- and IP-EOMCC methodologies, with an emphasis on the active-space EA- and IP-EOMCC methods including up to 3*p*-2*h* and 3*h*-2*p* excitations, referred to as EA- and IP-EOMCCSDt,[1-3] and active-space SAC-CI methods including up to 4*p*-3*h* and 4*h*-3*p* excitations.[4] To illustrate the performance of the resulting approaches, we will present the results of calculations for the excitation energies and potential energy surfaces of the low-lying states of CH, OH, SH, C_2N, CNC, N_3, and NCO.[1-6] These calculations reveal that active-space methods with up to 3*p*-2*h* and 3*h*-2*p* terms provide accurate results for low-lying electronic states within the Franck-Condon region while active-space methods with up to 4*p*-3*h* and 4*h*-3*p* terms are needed to accurately describe potential energy surfaces along bond breaking coordinates. Furthermore, the calculations show that the active-space schemes are capable of producing results that are virtually identical to those produced by their expensive parent EA- and IP-EOMCC and SAC-CI schemes with 3*p*-2*h*/3*h*-2*p* and 4*p*-3*h*/4*h*-3*p* excitations at a fraction of the computational cost.

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From microscopic to macroscopic time scales: towards a unified theory of dynamics and thermodynamics

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Since Gibbs, at the end of the 19th century, the formulation of equilibrium thermodynamics (thermostatics) is well defined and unique. Despite continuous progress from that time, there still remain many competing formulations of non-equilibrium thermodynamics. The main reason is that there are many ways to pass from thermostatics to thermodynamics. We go a step further on the road opened in the mid-1950s by Jaynes and Prigogine towards a unified description of dynamics and thermodynamics of irreversible processes[1,2].

Our approach is based on the concepts and methods originating in the quantum theory of resonance[3-5] .The Liouville-von Neumann equation is solved by means of effective Liouvillians which are similar to the effective Hamiltonians derived from the Schrödinger equation. Hierarchies of effective Liouvillians enable to obtain long macroscopic times for the observables from short microscopic characteristic times.

For that purpose, standard perturbation theory is used in the complex plane. A straightforward determination of generalized Langevin-type equations offers a simple way to understand the relationship between fluctuation and dissipation. As an application, we derive the kinetic equations of a simple chemical reaction proceeding towards equilibrium. The model implies a transition state assimilated to a short lived resonance. A dynamical illustration for the evolution of the entropy and its rate of production, as a function of time, is presented.

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Explicitly correlated local coupled cluster methods

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The two major bottlenecks of conventional coupled-cluster calculations are the extremely slow convergence of the correlation energy with basis sets size and the very steep scaling of the computational cost as a function of molecular size. It has recently been demonstrated that the explicitly correlated CCSD(T)-F12*x* (*x*=a,b) methods [1,2] greatly enhance the basis set convergence for a wide variety of molecular properties [2-4] and thus overcome the basis set problem. The steep scaling of the computational cost of coupled-cluster methods can be reduced by using localized orbitals and local approximations [5]. Here we present a new local CCSD(T)-F12 method [6] which combines the ideas of local and explicit correlation methods. It is shown that the explicitly correlated terms not only improve the basis set convergence, but to a large extent also eliminate the errors caused by the domain approximation in local wavefunctions. This is achieved by a modified ansatz of the explicitly correlated wavefunction [7,8], which makes it possible that the configurations neglected in the domain approximation are accounted for in the explicitly correlated part. This ansatz not only improves the accuracy, but also reduces the computational effort and makes it possible to achieve linear cost scaling. It is demonstrated for a large set of reaction energies and other molecular properties that the CCSD(T)-F12 and LCCSD(T)-F12 methods yield similar accuracy.

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Extending electronic structure theory to complex molecular problems: Local correlation coupled-cluster and correlation energy scaling methodologies

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Electronic structure theory faces considerable challenges when dealing with complex molecular problems, including prohibitive costs of high-level calculations for larger systems and difficulties with determining multi-dimensional molecular potential energy surfaces (PESs). To address the first challenge, we have extended[1] a number of coupled-cluster (CC) methods, including CCSD, CCSD(T), and the completely renormalized extension of CCSD(T), termed CR-CC(2,3),[2] to larger systems with hundreds of correlated electrons through the use of the local correlation 'cluster-in-molecule' (CIM) ansatz.[1,3] The resulting CIM-CCSD, CIM-CCSD(T), and CIM-CR-CC(2,3) methods are characterized by (i) the linear scaling of the CPU time with the system size, (ii) the use of orthonormal orbitals in the CC subsystem calculations, (iii) the natural parallelism, (iv) the high computational efficiency, enabling calculations for much larger systems and at higher levels of CC theory than previously possible, and (v) the purely non-iterative character of local triples corrections to CCSD energies. By comparing the results of the canonical and CIM-CC calculations for normal alkanes and water clusters, we have demonstrated that the CIM-CCSD, CIM-CCSD(T), and CIM-CR-CC(2,3) approaches accurately reproduce the corresponding canonical CC correlation and relative energies, while offering savings in the computer effort by orders of magnitude.[1] To address the second challenge of difficulties with determining multi-dimensional PESs, we have developed an extrapolation scheme exploiting the concept of correlation energy scaling which predicts, to within a fraction of a millihartree, the PES corresponding to large basis set calculations using high-level CC and multi-reference configuration-interaction methods from a single point on the molecular PES[4] or lower-order electronic structure calculations.[5]

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Recent Developments in Quantum Monte Carlo Approaches for Studying Rotation/Vibration Spectroscopy and Dynamics of Molecules that Undergo Large Amplitude Vibrational Motions

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Quantum Monte Carlo techniques have proven to provide an efficient and effective approach for obtaining ground state properties of a variety of molecular systems, including ones that display very large amplitude motions. In this talk we review earlier work on DMC for evaluating ground state properties of a variety of molecules, specifically CH_5^+. We then move on to several recent developments made in our group that enable us to extend the range of systems and properties that we can investigate. These include rotational and vibrational excited states as well as investigations of how molecular wave functions evolve as a bond in the molecule is dissociated. In the studies of rotational states the states are generated by a fixed-node approach in which the nodes are defined using the eigenstates of a symmetric top Hamiltonian. This approach has been applied to H_3O^+ and CH_5^+. One challenge with the above approaches is that each excited state must be evaluated separately. We have recently developed an approach for evaluating properties of the excited states with one or two quanta of vibrational excitation, based on only information from the ground state probability amplitudes. Results for $H_5O_2^+$ and $H_3O_2^-$ as well as larger protonated water clusters will be discussed.

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Excitation spectra of small para-Hydrogen clusters

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Small $(pH_2)_N$ clusters have been produced in a cryogenic free jet expansion and studied by Raman spectroscopy(1). Clusters with N=2-8 molecules have been unambiguously identified, and broad maxima were observed at N≅13, 33, and perhaps 55, indicating the existence of magic sizes related to geometric shells. Quantum Monte Carlo methods have been used in recent years as a theoretical tool to study $(pH_2)_N$ clusters(2-5). Both diffusion Monte Carlo (DMC) and path integral Monte Carlo (PIMC) calculations show that these clusters exhibit a clear structural order, with the molecules occupying concentric spherical shells, which could be related to some polyheDrl arrangement. Whereas up to N≅22 these calculations are substantially in agreement, for heavier clusters there are noticeable differences between DMC and PIMC magic sizes.

We present here our DMC simulations for clusters with N=3-40. The energies of all stabilized excitations with angular momentum from L=1 to 13 have been calculated, as well as those of the first L=0 vibrational excited state, assuming the isotropic pairwise interaction of Buck et al(6). Para-hydrogen clusters exhibit very rich spectra and no regular pattern can been guessed in terms of the angular momenta and the size of the cluster, at variance with the situation found for helium droplets. The partition function has been calculated from the excitation spectra, thus allowing for an estimate of finite temperature effects. An enhanced production is predicted for cluster sizes N=13, 26, 31 and 36, at any temperature, and also for N=19, 29 and 34 at some specific temperatures. The DMC and PIMC differences in the predicted magic sizes are thus explained as being mostly due to thermal effects.

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Fragmentation dynamics inside helium droplets

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Helium droplets provide a unique low-temperature (0.38K), inert, liquid environment, with superfluid properties that can be studied at the molecular level. In particular, they were initially considered as a potential refrigerant for cooling newly formed ions, with the hope that parent ions could be observed. This idea was based on the exceptionally high heat conductivity and the specific type of heat propagation in bulk (superfluid) helium II. On the other hand, bulk helium II also exhibits a vanishing viscosity for the flow through fine capillaries, which could imply that dissociation inside superfluid helium should occur exactly like in the gas phase, without any interference from the superfluid ``solvent''. Experimental results have shown that the ``caging'' effect is important, although fragmentation is usually not completely hindered. Photodissociation experiments inside helium droplets have lead to the conclusion that binary collisions play an important role in high kinetic energy dynamics. In addition, the cooling by helium atom evaporation has been found to be highly non thermal for some ions in small droplets. It is therefore of great importance to understand the mechanisms that are responsible for energy dissipation inside helium droplets.

We present simulation results on the effect of a helium nanodroplet environment on the fragmentation dynamics of embedded molecular systems. Ionized rare gas clusters are chosen as model systems because they are well known for extensively fragmenting upon ionization. In addition, their well known fragmentation patterns allow for comparisons with experiments both in the gas phase and inside helium nanodroplets.

The helium atoms are treated explicitly using the ZPAD (zero-point averaged dynamics) method, in which zero-point effects taken into account through an effective helium-helium interaction potential. Previous attempts at describing the helium environment implicitly through a friction force have given good results compared to experiment. However, the value obtained for the friction coefficient by fitting this sole parameter to the experimental fragment distribution was very large, indicating that some other processes must be playing an important role. All the nonadiabatic effects between electronic states of the ionized rare gas cluster are taken into account in the same fashion as in our previous works on rare gas cluster dissociation upon ionization in the gas phase. The results show good agreement with available experimental data, and have revealed new mechanisms (non thermal dissociation of the helium atoms, ejection of the intermediate ionic species...).

Recent Development in the General Method of Solving the Schrödinger Equation

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We have formulated and established a general method of solving the Schrödinger equation (SE) and the Dirac-Coulomb (DCE) equation of atoms and molecules [1-9]. In this method, the complement functions that span the exact wave function of atoms and molecules are generated (almost automatically using Maple or Mathematica) with the use of the Hamiltonian and the scaling function of the system [3]. *Complement* (element of complete) functions are central in our theory and are guaranteed to span the exact wave function of the system [3]. So, we call our theory as Hamiltonian Generated Complement Function (HGCF) theory. We have IC, FC, and PC. IC is renamed from the ICI method [1,2] and FC is renamed from the free ICI method [3]. PC (piecewise complement) was recently invented [4]. Through many applications of our method to few-electron systems, the fundamental accuracy and the general utility of our theory have been confirmed [5-8]. The formulation of the local Schrödinger equation (LSE) method [6] has opened a way to use the HGCF method as a general practical method of solving the SE of atoms and molecules. However, to make our methodology truly applicable to real science, we have to remove some computational obstacles.

In the HGCF formalism, the exact wave function ψ is shown to be written as

$$\psi = \sum_i c_i \phi_i \tag{1}$$

where $\{\phi_i\}$ are the complement functions, FC, PC, or IC, that are generated with the use of the Hamiltonian and the g function applied to the initial function ψ_0 [3,1,4]. The exactness (or accuracy) of the ψ is guaranteed by eq (1). Namely, eq.(1) represents the *sufficient* condition for the Schrödinger equation. Then, all we have to do is to calculate the coefficients $\{c_i\}$ using some *necessary* conditions for the Schrödinger equation. In the LSE method, we use the local SE's at different coordinates as necessary conditions. There, we have some practical problems. (1) Complement function generation: FC, PC, or IC? What initial function do we use? Different principles between atoms and molecules? (2) Sampling: In the LSE, we do not do integrations but do sampling. The LSE principle is not a stationary condition of the energy, but an equi-local-energy condition at the sampled points. So, wide, numerous sampling is preferable, but from computational standpoints, efficient sampling should be considered. We have proposed *local sampling* that is transferable and gives continuous results [9]. This is a simple order-*N* sampling. (3) Calculations of the matrix elements: in LSE, this is simply the calculations of ϕ_i and $H\phi_i$ at the sampled *N*-electron coordinates, but a problem here is the indistinguishability of *N* electrons. A naive formulation involves *N!* process, but as is well known the calculation of a determinant is N^3 process. In our case, we have correlated electrons $r_{\mu\nu}$, so that the order is higher, but when only one $r_{\mu\nu}$ appears, the calculations are essentially reduced to an N^3 process. When four $r_{\mu\nu}$ terms appear, the computation would be roughly N^6 process. Not bad.

We will show our recent development in the formalism of general and efficient method of solving the Schrödinger equation.

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The Sc_2 dimer revisited

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The Sc_2 molecule is the simplest of all first row transition metal neutral diatomics M_2, M=Sc to Cu. Nevertheless is complicated enough that even its ground state is not known with certainty after 45 years of both experimental and theoretical work.

We have performed large scale MRCI calculations in conjunction with adequate correlation consistent basis sets constructing for the first time at this level valence potential energy curves of ${}^{3,5}\Sigma_u^-$, ${}^{1}\Pi_{g,u}[2]$, ${}^{3}\Delta_u[2]$, ${}^{1}\Phi_{g,u}[2]$, and ${}^{3}\Gamma_u$ a total of 11 states. Our results indicate that the ${}^{5}\Sigma_u^-$ is the ground state with the ${}^{3}\Sigma_u^-$ one being a strong competitor. For the ${}^{5}\Sigma_u^-$ state we predict a binding energy D_e^o of about 8 kcal/mol at r_e =2.75 Å.

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Energies, structures, and properties of large molecules from *ab initio* energy-based fragmentation approaches

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In this talk, I will present our recent developments in energy-based fragmentation (EBF) approach, which provide a fast and reliable theoretical tool for evaluating energies, structures, and properties of large systems at various ab initio levels.[1-5] The essence of our fragmentation method is to obtain the approximate energy (or various properties) of this molecule from energies (or properties) of various subsystems. To treat systems with charged or polar groups, the generalized EBF (GEBF) approach is developed, in which all subsystems are placed in the presence of background point charges. The GEBF approach is applied to investigate relative energies of different conformers, optimized structures, vibrational frequencies and intensities, and some molecular properties for a number of medium-sized or large molecules including small proteins, carbon nanotubes, and water clusters. It is shown that total energies, structures, and properties of these systems predicted with the GEBF approach agree well with those from the corresponding conventional calculations. Within dispersion-corrected DFT, the GEBF approach has been applied to investigate the driving forces for the formation of molecular self-assembling processes.[6]

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Generalizations and Limitations of Quasiparticle Pictures of Molecular Electronic Structure

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The Dyson equation of electron propagator theory provides a formally exact means to calculating electron binding energies, corresponding spectroscopic transition probabilities, one-electron properties and total energies. Approximate solutions may be classified according to the form of the nonlocal, energy-dependent self-energy operator that supersedes Coulomb-exchange potentials by including correlation and relaxation effects. In the simplest cases, Hartree-Fock quasiparticles require only perturbative improvements in the self-energy; efficient implementations of this class of approximations now enable applications to fullerenes, nucleotides and substituted metalloporphyrins. The quasiparticle picture may be retained even when orbital relaxation effects are strong through the use of grand-canonical reference ensembles; applications to core electron binding energies illustrate the accuracy and efficiency of this approach. Strong correlation effects in final states may require renormalized self-energies that are capable of describing collapses of the quasiparticle picture. Results on metallophthalocyanines demonstrate that such flexibility may be needed to determine the lowest ionization energy of a large, closed-shell molecule. Strong initial-state correlation may necessitate the employment of approximate Brueckner orbitals in the construction of the self-energy. Applications to double-Rydberg anions show the predictive power of these methods and their success in retaining quasiparticle descriptions of electron binding energies.

Symmetry-based Theoretical Approach to Spin-hybrid Molecular Magnets

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The goals of quantum-chemical studies on metal-organic magnetic materials are the elucidation of the nature and mechanism of exchange interaction and the development of an adequate algorithm for theoretical prediction of sought magnetic characteristics. The main obstacle to modelling of such systems is that small variation of the molecular geometry may result in substantially different exchange and thus affect the observed magnetic behaviour. Therefore, in the literature solely quantum-chemical calculations on available X-ray structures are reported, aiming at analysis of the experimental observations rather than at prediction of novel spin-hybrid magnetic materials. The main purpose of the present theoretical study is to establish a new purely quantum-chemical approach to the design of metal-organic magnetics.

Two well-characterized copper(II) complexes with aminoxyl radicals [Cu(hfac)2(p-NOPy)2] and [Cu(hfac)2(m-NOPy)2][1] were chosen as objects of investigation. Density functional theory was used for the modelling, addressing the influence of various parameters on the qualitative and quantitative description of the magnetic characteristics of these compounds. The theoretical treatment was carried out from two different perspectives. The first one was based on the X-ray geometry with intrinsic symmetry point group [1] and was focused on the search for conditions providing satisfactory reproducibility of the experimental data. The second tactic was to obtain the proper magnetic characteristics of the structures through geometry optimization of each of the possible Jahn-Teller isomers by means of imposing adequate symmetry.

The results for structure, energy and spin density distribution obtained with the two approaches are compared, showing very good agreement. The nature of the magnetic interaction is clarified after performing molecular orbital analysis. It is established that the presence of symmetry restraints on the wavefunction is crucial for an accurate description of the exchange interaction. Specifically, we show that by careful treatment of the molecular geometry upon optimization, the obstacle to future molecular design can be circumvented. The good convergence of the two modelling strategies allows us to propose a simulation protocol for theoretical prediction of the magnetic ground state of systems with molecular formula Cu(acac)2(L)2 (L being a stable organic radical). This scheme can be applied in the design of novel metal-organic magnetic materials.

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Quantum Mechanical Study of Protein Structure and Dynamics

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Efficient fragment-based quantum mechanical method for accurate calculation of protein in solution is developed and applied to study protein structure and dynamics. The quantum calculation of protein is further employed to generate new force field that features polarized protein-specific charges (PPC). The PPC provides a realistic description of the polarized electrostatic state of the protein than the widely used mean field charges such as AMBER and CHARMM. Extensive MD simulations have been performed to study the efficacy of PPC through direct comparisons between results obtained from PPC, the standard AMBER charges and experimental results. The impact of PPC on protein electrostatic interaction, stability of hydrogen bonds, protein-ligand binding and protein dynamics are presented in this talk. The results clearly demonstrate that the correct description of the electronic polarization of protein is crucial and PPC shall have important applications for MD simulation studies of protein structure and dynamics.

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Dynamics of bielectronic processes in intermediate ion-atom and ion-molecule collisions

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The quality of the calculations of potential energy surfaces for multi-electronic molecular structures is in general very high for the ground and first excited states. It allows for the detailed predictions of various characteristics of these systems, such as excitation threshold energy, vibrational and rotational spectra, ... However the knowledge of the dynamics of similar scattering systems (e.g. ion-atom, ion-molecule collisions) involving only two active electrons is far to be as precise, especially in the intermediate (keV/amu) impact energy range where many electronic processes are strongly coupled and the characteristic time of interaction is far below the femtosecond time scale.

In the workshop we shall present an original theoretical approach[1] to deal with such systems, based on the non-perturbative *coupled channel* solution of the time-dependent Schrödinger equation. We have recently developped a code which allows for the description of bound-bound transitions (excitation, electron transfer or capture), as well as bound-free ones (ionisation), as well as all combinations of theses processes for two electrons (double capture, capture - excitation, excitation - ionisation, ...). We shall present two applications of this treatment, in relation with recent experimental and theoretical investigations.[2-4]

The first one concerns the shape of the double transfer cross sections in a wide domain of impact energy, ranging from 0.06 to 50 keV/amu, for collision between H^- and H^+. This system is the benchmark to model correlation both statically (in the initial channel) and dynamically since the electronic repulsion is of the order of the other interactions which induce the transitions. We shall present our predictions for the dominant channels, in comparison with various existing theoretical and experimental results. The discussion will be focused on the double capture process for which we present a model to explain the series of oscillations[2] observed experimentally by various groups and which have not been so far interpreted in a coherent way.

The second illustration concerns the predictions of the cross sections of double electron transfer into metastable states, for collisions between He^{2+} and H_2. In general this process is very weak but can be enhanced in the low energy domain (typically 100 eV/amu and below). Predictions do not exist for this system and are highly required in order to predict the faisability of a collision experiment in which Young-typed interference patterns should be observed in the unique electron regime.

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Orbital polarization of the chemical reaction products: Determination of the dynamical amplitudes and phases.

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The field of stereodynamics and vector correlations in chemical and photochemical reactions attracts much attention for decades. The importance of the vector properties in the reactions bases on the fact that practically all interactions within a reaction complex are intrinsically anisotropic which in many cases results in the electronic and nuclear motion anisotropy in the reaction products.

The lecture reviews recent study on spin and orbital angular momentum recoil distributions of the products of chemical and photochemical reactions of diatomic and polyatomic molecules. It will be shown that in both cases the recoil-angle-dependent part can be completely separated from the dynamical part. The dynamical part can be expressed in terms of the set of the *anisotropy parameters* which contain all information about the reaction dynamics and can be either directly determined from experiment, or calculated from theory. The measurement of the anisotropy parameters is usually based on the ion imaging technique and polarized Doppler spectroscopy of the chemical reaction products and provides a powerful tool for experimentalist. In particular, it allows for investigation of the symmetries of the quantum states involved in the reaction, determination of the amplitudes and phases of nonadiabatic interactions between different quantum states, investigation of the vibration (bending) motion in the reaction complex and long-range interaction between the reaction products.

The talk reviews recent advantages in the field and obtained theoretical and experimental results on photodissociation of a number of diatomic and thiatomic molecules, particularly: RbI at 266 nm, BrCl at 467 nm, OCS and O_3 at 193 nm. The investigation of the determined values of the speed-dependent parameter β and higher rank anisotropy parameters supported the interpretation of the photodissociation dynamics.

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Correlated many electron dynamics from different perspectives

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In this talk various approaches to the correlated quantum dynamics of electrons in atoms and molecules are discussed. We do so by solving the Time-Dependent Schrödinger Equation with first principle methods for several systems. The emphasis is on wave function based methods, especially Multi-Configuration Time-Dependent Hartree-Fock (MCTDHF). Selected applications, like the controlled manipulation of the electronic state of LiH, and the onset of thermalization of electrons in Na_8 clusters, serve to illustrate the opportunities and challenges of first principles electron dynamics. Also, the relation to Configuration Interaction based methods, and ansaetze to go beyond the fixed nuclei approximation are presented.

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Quantum linear superposition theory from chemical processes

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The standard semi-classic scheme is extended to include diabatic representations of electronic basis functions. An alternative to BO scheme is proposed. This one permits representin the quantum state of an electronuclear system as linear superpositions on a generalized BO approach.Distinction between fragments and whole system is quentum mechanically implemented.

Inclusion of external quantized electromagnetic field leads to a theoretical scheme able to represent chemical processes as a clean quantum mechanical time evolution process. Application to the representation of a two-electrons and two-protons quantum states is reported.

Photoinduced Energy, Electron and Proton Transfer: A Computational Approach

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Photoinduced energy, electron and proton transfer are elementary photophysical and photochemical processes in many chemical and biological systems, conforming an extensive field of experimental and theoretical research. Here we present some recent advances in the theoretical and computational prediction of the mechanistic aspects of these processes, as well as their relation with the molecular and electronic structure of the studied systems.[1] Concretely, we analyze the role of the internal coordinates in the non-vertical triplet energy transfer, in different systems, as is the case of stilbenes. Similarly, we have studied photoinduced proton and electron transfer in different model systems.[2] The results provide insight into the mechanism and viability of these processes, showing the importance of the different internal coordinate of the system in controlling the processes, as well as the fundamental role of the intersection space (crossing of the electronic states) in order to modulate the efficiency of these photoinduced processes.

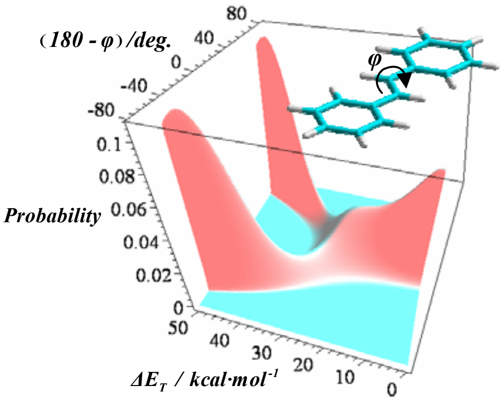

Figure. Probability distribution of ϕ torsional coordinate as a function of the triplet energy deficit between donor and *trans*-Stilbene (*t*-Stb) (i.e. $\Delta E_T = E_T(\text{Donor}) - E_T(\text{t-Stb})$ in the *t*-Stb triplet quenching. Note that for triplet donors with similar triplet energy, ϕ probability is centered in zero, and when the triplet energy donor decreases, the torsion becomes increasingly important in quenching process.

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The role of rotational relaxation in the intersystem crossing between triplet and singlet electronic states

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Thiophosgene is an exception among the group of small thiocarbonyl compounds in that the first excited triplet state of Cl_2CS is dark (nonradiative). This lack of phosphorescence can be attributed to a very fast ISC (intersystem crossing) that Drins energy from the first triplet T_1 excited state to the S_0 ground state.

A calculation of the rate of ISC relaxation at 0 K requires a knowledge of the spin-orbit coupling, and the vibrational overlap integrals (Franck-Condon factors) between the T_1 and S_0 states. At elevated temperatures the population of the rotational states needs to be taken into account through the overlap of the rotational wavefunctions between the interacting T_1/S_0 electronic states.

In this presentation we discuss effect of the singlet–triplet selection rules on the number and magnitude of the rotational overlap factors for the J= 5 and J = 50 rotational manifold of levels of thiophosgene. Of equal importance is the influence of the rotational fragmentation factors on the ISC survival probability. The discussion will also include a comparison to experimental data.

Intense laser assisted molecular dissociation dynamics: From simulation to control

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Intense laser fields, by applying forces that in energetic terms are comparable to electron binding energies, produce strong internal distorsions in molecules and induce selective dynamical effects that can be exploited in designing control strategies. These strategies rest on some basic mechanisms which act either in complementary or antagonistic ways and can further be used in optimal control schemes.

In the high frequency visible-UV wavelength regime, the molecule feels an optical cycle-averaged force field. Its dynamics is described through a Floquet representation based on light-induced potentials. The strong radiative interaction generally facilitates fragmentation through the Bond Softening (BS) process, which results from the lowering of some potential barriers accomodating shape resonances. More unexpectedly, the dissociation may, under specific conditions, be delayed or even suppressed through the complementary, non-intuitive, Vibrational Trapping (VT) that occurs for Feshbach resonances supported by some “upper” adiabatic potentials.

In the low frequency IR wavelength regime, a quasi-static adiabatic picture is appropriate. The molecular vibrational motion follows the field’s oscillations. An appropriate synchronization, either completely suppress potential barriers, or produces reflection of the wavepacket on them. This is the Dynamical Dissociation Quenching (DDQ) mechanism.

BS and VT have been well documented in the literature [1,2], whereas a first experimental confirmation has only been recently given for DDQ [3,4]. After a thorough review of these mechanisms, we consider two applications on the illustrative example of H_2^+. One deals with the interpretation of some recent pump (XUV atto-pulse)-probe (Intense IR pulse) experiments [5] and the other with an efficient and selective laser-induced molecular stabilization mechanism leading to so called Zero Width Resonances [6] opening the way to control scenarios for a selective preparation of a given molecular vibrational level, including the possibility of obtaining ro-vibrationaly cold molecules.

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Experimental RF-GIB and *ab initio* study of some dehydrohalogenation gas phase reactions induced by Li^+ in their ground electronic state.

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In recent times, gas-phase ion-molecule reactions have attracted a renewed interest, in particular at low collision energies because of their relevance inf many reactive processes occurring in interstellar media [1] as well as in systems of biological interest.[2]

Recently, we have built an octopole radio frequency guided ion beam (RF-GIB) apparatus[3] for the study of alkali ion-molecule collisions at energies ranging from thermal to about 20 eV. Using it we have studied some alkali ion association reactions [4] (with butanone, cyclohexanone, benzene) as well as the isopropyl chloride [5] and propyl chloride dehydrohalogenation reactions induced by collisions with lithium ions together with other observed decomposition reactions.

The interpretation of the experimental results requires some knowledge of the potential energy surfaces (PES) where reactions take place. For this, *ab initio* calculations have been carried out, exploring and investigating the main traits of the low-lying singlet PES adiabatically correlating reactants and products. Recent results for the dehydrohalogenation reactions will be reported at the meeting.

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Ultrafast electron dynamics following outer-valence ionization

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About ten years ago it was shown[1] that after a sudden ionization the electronic many-body effects *alone* can beget rich ultrafast electron dynamics. The positive charge created after the ionization can migrate throughout the system on a femtosecond time scale *solely* driven by the electron correlation and electron relaxation. Although typical for the inner-valence ionized states it appeared only recently that this charge migration phenomenon can take place also after ionization out of the outer-valence shell[2]. Using an *ab initio* method for multielectron wave packet propagation[3] in the present work we study the electron dynamics following ionization out of the highest occupied molecular orbital of different systems. The mechanisms underlying the charge migration phenomenon are analysed and discussed in terms of simple models.

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Ground and excited states of the H_2 molecule

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The first fifteen $^1\Sigma_g^+$ states and the first fourteen $^1\Sigma_u^+$ states of the H_2 molecule are computed with full configuration interaction both from Hartree-Fock molecular orbitals and Heitler-London atomic orbitals and correlated by a comprehensive analysis. The full CI computations cover the inter-nuclear distances from R=0.01 to R=10000 bohr. Two types of basis sets are used, Gaussian and Slater type functions. The computations nicely compare with Kolos and Wolniewicz data.

We focus on the characterization of the orbitals in the wave functions, on the electronic density evolution from the united atom to dissociation, on quantitative decomposition of the total energy into covalent and ionic components. These analyses lead to CI computations on related systems, like the H^- negative ion interacting with a proton and the H^+H^- ion pair. Preliminary data of other symmetries are also reported.

Response properties of finite systems: An atomic-level analysis*

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A methodology for atomic-level analysis of the dipole moments and polarizabilities of finite systems[1] will be presented and analyzed. The methodology is based on partitioning the space into volumes associated with the individual atoms of the system and defining the contributions of each atom to the total dipole moment and total polarizability from the charge density within its volume. The atomic dipole moments and polarizabilities are then further decomposed into the so-called dipole and charge-transfer parts. The dipole parts of the dipole moments and the polarizabilities characterize dielectric types of responses of the atoms to the intrasystem bonding and to a small external electric field, respectively. The corresponding charge transfer parts represent the respective metallic types of responses. The systems' total dipole moments and polarizabilities can also be partitioned into dipole and charge transfer parts. These are defined as sums of the atomic dipole and charge transfer parts, respectively.

The utility of the methodology will be illustrated through applications to atomic clusters of different sizes and composition.[1-4] Its power as an analysis tool will be demonstrated through characterization of the site-specificity of the atomic moments and polarizabilities; through analyses of structure- (i.e., isomer-), shape-, and size-dependent trends in the total moments and polarizabilities, as well as their dipole and charge-transfer components; and through its use as a tool for comparative evaluation of the degree of nonmetallic *vs* metallic character of clusters of different materials and sizes.

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Accurate evaluation of interaction properties

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Interaction properties play a main role in many physical and chemical phenomena and are the subject of a considerable number of experimental and theoretical studies. Taking into account the high accuracy of the experimental results available, the computational studies of these interactions are challenging, as not only large basis sets, but also high level correlation methods are mandatory in order to compete with the experiments.

We evaluated accurate interaction properties, using the coupled-cluster singles and doubles (CCSD) and the CCSD including connected triples (CCSD(T)) models and augmented correlation consistent polarized valence basis sets extended with a set of 3s3p2d1f1g midbond functions. As models we selected van der Waals complexes. These systems are characterized by an interaction dominated by dispersion, that is essential in processes like the solvation or adsorption of molecules, and the most difficult to describe from the theoretical point of view.

We obtained ground and excited state intermolecular potential energy surfaces and calculated the bound van der Waals states. We compared the results with those of previous theoretical studies and the experimental data available, improving considerably the former, getting a very good agreement with the latter, and in some cases being able to correct and complete the assignments. Results for the ground states of the Ne-N_2, and the CO-Ar complexes, and for the first singlet excited state of the fluorobenzene-Ar complex[1] will be presented.

With the CCSD response theory we evaluated interaction induced (hyper)polarizabilities and the corresponding virial coefficients.[2] We will show results for the CO-Ar complex.

With the increase of the complex size the use of accurate electron correlation methods is still prohibitive. We carried out an extension of the CCSD(T) code in order to be able to apply it to the study of larger systems, programming it using the Cholesky decomposition. We studied large-size van der Waals complexes like those formed by benzene and a fluorobenzene derivative.[3]

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Topological models of magnetic-field induced electron current density forthe interpretation of molecular magnetic response.

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Concise information on the general features of the quantum-mechanical current density induced in the electrons of a molecule by a spatially uniform, time-independent magnetic field is obtained via a stagnation graph that shows the isolated singularities and the lines at which the current density vector field vanishes. Stagnation graphs provide a compact description of current density vector fields and help the interpretation of molecular magnetic response, e.g., magnetic susceptibility and nuclear magnetic shielding. A few noticeable examples are discussed.

The stagnation graph of cyclopropane, obtained at the Hartree-Fock level via a procedure based on continuous transformation of the origin of the current density formally annihilating the diamagnetic contribution, shows that the current interpretation of this molecule as an archetypal sigma-aromatic system should be revised. The stagnation graphs of lithium hydride, acetylene, carbon dioxide, and azulene provide the first evidence of the existence of electronic toroidal currents inducing orbital anapole moments.

The induced orbital paramagnetism of boron monohydride, cyclobutadiene and clamped cyclooctatetraene are explained via stagnation graphs showing that vortical lines occur at the intersection of nodal surfaces of real and imaginary components of the the electronic wave function.

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Detection of parity violation in chiral molecules by external tuning of electroweak optical activity

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Since the prediction and subsequent discovery of parity violation in weak interactions [1], the role of discrete symmetries in fundamental interactions is an intriguing field of research. The effect of electroweak interactions between electrons and nuclei mediated by the Z^0 have been extensively studied and observed in atoms [2], and only predicted in molecules, where an energy difference between the two enantiomers of chiral molecules has been estimated to be between 10^{-16} and 10^{-21} eV [3]. In the laboratory, no conclusive energy difference has been reported in experimental spectroscopic studies reaching an energy resolution of about 10^{-15} eV [4]. In addition, since the effect of parity violation in the optical activity (OA) was reported [5], several authors have focused their attention in the possibility of measuring the parity-violating energy difference (PVED) between enantiomers via optical rotation experiments, looking for time dependent evolution of either chiral states [6] or parity states [7]. However, no experimental results have been reported up to date. The main difficulties for obtaining information about the PVED from OA experiments is the predicted very small size of the effect that can be asked by racemization processes and loss of phase coherence due to collisions with the environment. In this work [8], a proposal is made to measure the PVED between enantiomers of chiral molecules by modifying the dynamics of the two-state system using an external chiral field, in particular, circularly polarized light. The intrinsic molecular parity-violating energy could be compensated by this external chiral field, with the subsequent change in the OA. From the observation of changes in the time-averaged optical activity of a sample with initial chiral purity and minimized environment effects, the value of the intrinsic parity-violating energy could be extracted. A discussion is made on the feasibility of this measurement.

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Quantum Chemical Calculations of Water Oxidation at the Semiconductor-Aqueous Solution Interface

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In an effort to understand how water is oxidized to molecular oxygen at the surface of a semiconductor photocatalyst for direct water splitting, we are focusing on the properties of the GaN/ZnO solid solution and its pure components at the aqueous interface. This work is motivated in part by the report by Domen's group that not only is the GaN/ZnO photocatalyst capable of direct water splitting (at < 5% efficiency for light between 420 and 440 nm) with the aid of an attached nanoparticle co-catalyst for proton reduction, the quantum yield for O_2 production is as high as 51% when the proton-reduction half reaction is "short-circuited" by the addition of an electron scavenger ($AgNO_3$) to the solution. This suggests that the photocatalyst itself is also a good water oxidation catalyst.

We have entered into a multi-disciplinary collaboration (the Solar Water Splitting Simulation Team, or "SWaSSiT") of chemists and physicists to understand this interfacial water oxidation mechanism at the atomic and molecular level using quantum chemistry, bulk solid-state, surface science, and first-principles simulation techniques. While striving to construct an accurate physical model of the composition and structure of the GaN/ZnO solid solution at such an interface, we have simultaneously begun to study the interfacial properties of pure GaN, which also functions as a water splitting photocatalyst (but only in the ultra-violet region of the spectrum). Our calculations indicate that a monolayer (or sub-monolayer) of H_2O on the non-polar GaN($10\underline{1}0$) surface is completely dissociated (dissociation barrier ca. 1 meV), with the protons occupying surface N-sites and the hydroxide ions occupying surface Ga-sites. The hydroxide ions form hydrogen bonds to each other along the rows of surface Ga atoms. When, however, the water coverage is several monolayers or a bulk solvent as modeled by first-principles MD simulations, the hydrogen bonding structure of the monolayer coverage is transformed into one dominated by hydrogen bonding of the adsorbed hydroxide ions to water molecules in the overlayers or the bulk solvent. We consider this phenomenon significant for acid-base reactions that are responsible for removing protons from surface-adsorbed species to the bulk solution in connection with proton-coupled electron-transfer (PCET) reactions.

We have also devised a cluster model of the water oxidation process at the GaN/aqueous solution interface consisting of a fragment of the periodic slab model of the surface with passivated non-surface atoms, a number of explicit solvent molecules and a polarizable continuum model of the bulk solvent. On the basis of calculations using this model, we have proposed a four-step water oxidation mechanism in which each step involves a PCET oxidation of an adsorbed water fragment by a hole at a surface Ga site. In contrast to a similar mechanism proposed by Norskov, our mechanism never involves a vacant active site on the surface because of concerted interactions with explicit solvent molecules.

Dynamics of irradiated clusters and molecules

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We discuss the non adiabatic dynamical response to laser irradiation of clusters and small organic molecules, possibly in contact with an environment (insulating substrate or matrix). The electronic degrees of freedom are treated at a microscopic quantum level through Density Functional Theory (DFT) in the time domain [1]. Mind that a proper account of electronic emisson requires some dedicated treatment, especially when ionization is to be explicitly followed in time. We have thus included elaborate theoretical methods to treat the well known hinDrnce constituted by the Self Interaction Problem in the simple and robust Local Density Approximation of DFT [2, 3]. The description of electrons is complemented by a classical Molecular Dynamics treatment of ions. Environment is, when necessary, included via a dynamical hierachical modelling in the spirit of Quantum Mechanical/ Molecular Mechanical approaches of quantum chemistry [4, 5, 6, 7].

A major focus of these studies concerns the properties of ionized electrons. We discuss in particular photoelectron spectra (PES) and photoelelectron angular distributions (PAD) in relation to recent experimental results. Experimental results provide here a challenging environment for theoretical modelling. But such observables are easily attainable within the formalism we have developed and calculations lead to encouraging results.

We also consider the impact of variations of laser frequencies, especially when exploring the newly and widely opening domain of FEL frequencies. We show that the use of such frequencies at moderate laser intensities might also constitute a key tool of analysis of cluster properties, in complement to studies performed in the visible. The complementing case of organic molecules is also considered in this respect.

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Theoretical study of the structural and electronic properties of aggregates and crystals formed from 3d-metal doped silicon clusters as super-molecular units.

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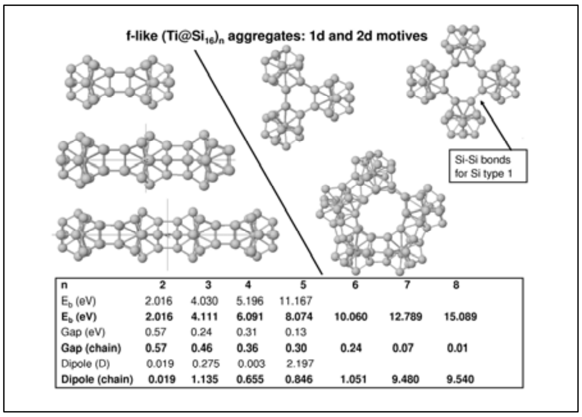
The cage-like M@Si_{16} endoheDrl clusters (M = Sc^-, Ti, V^+) have been proposed as basic units to construct optoelectronic materials due to their large Homo-Lumo gap (> 1.5 eV) [1, 2]. In this work, we studied by means of first principles calculations the formation of aggregates and bulk crystal phases built from super-molecular units like Ti@Si_{16}, Sc@Si_{16}K and V@Si_{16}F. Firstly are studied the trends in the formation of [Ti@Si_{16}]$_n$, [Sc@S_{16}K]$_n$, and [V@Si_{16}F]$_n$ aggregates as their size increases, going from linear to planar to three dimensional arrangements. The more favourable configurations for n ≥ 2 are those formed from the fullerene-like (FL) D_{4d} isomer of M@Si_{16}, instead of the ground state Frank-Kasper T_d symmetry of the isolated M@Si_{16} unit. These units are joined preferably by Si-Si bonds between the Si atoms of their square facets and can form linear (wires), planar (multilayer), and three dimensional aggregates with several arrangements. In all cases the Homo-Lumo gap for the most favourable structure decrease with the size n. Trends for the binding energy, dipole moment, orbital-proyected density of states, and other electronic properties are also discussed. Figure 1 shows a few structures of the aggregates [Ti@Si_{16}]$_n$ (n = 2-5).



n	2	3	4	5	6	7	8
E_b (eV)	2.016	4.030	5.196	11.167			
E_b (eV)	**2.016**	**4.111**	**6.091**	**8.074**	**10.060**	**12.789**	**15.089**
Gap (eV)	0.57	0.24	0.31	0.13			
Gap (chain)	**0.57**	**0.46**	**0.36**	**0.30**	**0.24**	**0.07**	**0.01**
Dipole (D)	0.019	0.275	0.003	2.197			
Dipole (chain)	**0.019**	**1.135**	**0.655**	**0.846**	**1.051**	**9.480**	**9.540**

With respect to bulk phases we have found meta-stable sc, fcc, bcc, NaCl CsCl, and hcp (this only for TiSi_{16}) structures built from Ti@Si_{16}, Sc@Si_{16}K, and V@Si_{16}F super-molecules. The orientation of the molecule in the cell plays a critical roll. Both, Ti@Si_{16} and Sc@Si_{16}K, have the largest cohesive energy for the bcc crystal with the D_{4d} FL isomer as basic unit. For V@Si_{16}F the NaCl structure, results to be the more stable one.

We further study the electronic and structural properties of these materials at finite temperature and pressure. A phase transition of V@Si_{16}F from NaCl to CsCl structure occurs at 0.24 GPa. Other extended systems, like wires and nanotubes composed of M@Si_{16}-Z units, have been studied.

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Molecular dynamics simulations of rigid and flexible water models: Temperature dependence of viscosities

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Molecular dynamics simulations were carried out on a system of rigid or flexible model water molecules at a series of temperatures between 279 and 368 K. Transport coefficients, such as shear and bulk viscosity, are calculated and their behaviour was systematically investigated as a function of flexibility and temperature. It was found that including the intramolecular stretching and bending terms the obtained viscosity values are in overall much better agreement than that of the rigid SPC/E model, compared to ealier and recent experimental data available. The effect of the intramolecular degrees of freedom on transport properties of liquid water was analysed and incorporation of polarizability was discussed for further improvements. To our knowledge the present study constitutes the first such compendium of results for pure water that has been assembled [1].

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Bifurcation Phenomena in Vibrationally Excited Small and Large Molecules and their Spectroscopic Signatures

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Understanding molecular behaviours at vibrational excited states requires knowledge of the motions of atoms close and above isomerization and dissociation thresholds. The most successful theories for assigning and extracting the dynamics from complex spectra stem from nonlinear mechanics. Here we present these theories and the spectroscopy of several molecules that show localized motions even above dissociation. Examples of triatomic molecules that show chaotic behaviors [1] and polyatomic biomolecules [2,3] with regular motions are presented. The dynamics are elucidated by applying theories of nonlinear mechanics and semiclassical correspondence between stationary objects in phase space (periodic orbits, tori) and eigenfunctions. On the route to isomerization or dissociation of a molecule new type of motions appear via bifurcations of the normal modes. With the assistance of bifurcation theory of periodic orbits concepts like local stretching modes are generalized to any type of vibrational mode. The role of nonlinear mechanics to comprehend molecular dynamics is to reveal those stationary objects that act as organizing structures of the classical mechanical motions and as localization centers for quantum mechanical eigenstates [4].

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H_2 reactivity on gold nano-structures: a cluster and embedding potential approach

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Gold is the noblest of the transition metals and presents a very low reactivity and catalytic activity in bulk. However, in small gold nano-structures, the reaction barriers get lower for many reactions and the chemisoprtion wells deeper. There is a recent increasing interest in determining their catalytic properties because their possible industrial impact [1]. The dissociation of H_2 on nanowires [2] and clusters [3] have been studied recently, showing no barrier for the reaction. In order to understand in detail the factors determining such high reactivity and the transition from clusters to bulk, here we present a study for different coordinations of gold atoms on model systems, linear and planar, paying special attention to their fluxionality [4]. It is found that appart from the coordination of gold atoms, being a fundamental factor, the reactivity is modulated by the hybridization of the gold atoms involved, explaining the reactivity change from planar to linear configurations or edges. An extension of a recently developed embedding potential method [5] is used to simplify the study of larger clusters. Moreover, such embedding techniques are used to analyze the hybridization of the gold atoms involved in the reaction and, hence, as an analysis tool to understand the reaction mechanisms.

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Protocols for assessing relativistic, relaxation, and correlation contributions, and charge-transfer effects for 1s-, 2s-, 2p-, and 1s-2p- core ionization energies in elements up to Barium

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This report is an integrated review of previous work on various protocols, mostly of allometric type, for rapid assessment of core ionization energies in atoms of molecular systems[1-9]. On the basis of numerical *ab-initio*, DBF and MCDBF computations (including qed and nuclear corrections), we have investigated the relativistic, relaxation, and correlation contributions to 1s-, 2s-, 2p-, and 1s-2p- core ionization energies in relevant atoms of the Periodic Table up to Barium. Effects of shell structure on core energies have been considered in defining families appropriate for allometric fits, with special care for the peculiarities of transition-metal series. For atoms, computations made by mixing the ground and ionized configurations yielded significant improvements in relaxation energies and better agreement with available experimental results. For molecules, a combined - rigorous-atomic/approximate-molecular (RAAM) - protocol was devised, involving the well-documented dependence of core ionization chemical shifts on charge transfer to or from ligands[10].

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Posters

MONDAY September 14

FRIDAY September 18

Ab initio study of beryllium hydrides

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In the context of plasma wall interaction and beryllium used as a first-wall material for the future fusion experiment ITER, the retention of hydrogen isotopes into the beryllium bulk and the deposition of beryllium hydride layers issued from the plasma could be a serious concern for plasma devices utilizing tritium. Numbers of experiments have been proposed in the last few years on solid hydrides deposition under beryllium seeded plasma action [1] or on high-energy hydrogen implantation in metallic beryllium [2]. It would be beneficial to supplement these investigations with theoretical calculations, and a first contribution has already been published on quantum study of hydrogen adsorption on beryllium surface [3].

Crystalline beryllium hydrides can be produced via a rather complicated procedure [4], the structure and properties of which have been theoretically explored using quantum methods [5,6]. However, this material can only be considered as a model and a more specific study must be led on the amorphous possible structures more likely to be found in the fusion domain.

This communication reports on calculations carried out using *First Principles* DFT. The structures of amorphous beryllium hydride are investigated for various H/Be ratios. They are compared to the BeH_2 organized crystal, as a test of the validity of this model. The respective cohesive energies are calculated in order to predict the most probable one. We also tried to identify the constitutive patterns, BeH or BeH_2, and the possible existence of hydrogen molecules. The interaction energy of each hydrogen atom or of each constitutive element (H_n or BeH_n) can also be related to desorption spectroscopy experiments.

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Generalized Jensen divergence analysis of atomic electron densities in conjugated spaces

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Information-theoretic divergence measures are here applied to the analysis of atomic systems by means of their one-particle densities in position and momentum spaces. In doing so, the concept of *Jensen-Renyi Divergence of order q* JRD_q [1] is employed for carrying out a comparative study among the electron densities of neutral atoms throughout the whole Periodic Table, the results being interpreted according to the characteristic shell-filling patterns of those systems. Different ranges of the order *q* allow to enhance or to diminish the relative contribution of the inner or the outer atomic regions, according to their relevance on the physical or chemical properties to be compared.

The JRD_q divergence constitutes a generalization of the *Jensen-Shannon Divergence* (JSD) [2], widely employed in many different fields with comparative purposes [3,4,5]. In fact, the first order (*q=1*) JRD_1 gives rise to the JSD definition. The numerical results follow different trends depending on the considered position or momentum space densities.

Taking advantage of different relevant properties of the divergence definitions, we have also considered the *mean distance* among more than two weighted distributions as allowed by the JSD and JRD_q measures. Applications are carried out in two different ways: (i) analyzing the 'entropy excess' of the whole atomic density with respect to its basic constituents, namely all subshells, and (ii) the similar concept concerning groups and periods as composed by individual atoms.

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Coulomb Sturmian bases for *N*-electron molecular calculations

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A method is proposed for using isoenergetic configurations formed from many-center Coulomb Sturmians as a basis for calculations on *N*-electron molecules. Such configurations are solutions to an approximate *N*-electron Schrödinger equation with a weighted potential, and they are thus closely analogous to the Goscinskian configurations, which we have used previously to study atomic spectra. We show that when the method is applied to diatomic molecules, all of the relevant integrals are pure functions of the parameter $s=kR$, and therefore they can be evaluated once and for all and stored.

Radiosensitization properties of 5-halouracils in collision with carbon ions

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Severe damage to DNA may be induced by interaction of ionizing radiation with biological tissue. Early studies have shown that the replacement of thymine by 5-bromouracil in cellular DNA induces strong enhancement of DNA damage through ionizing radiation and results in significant increase of cell death [1]. Such sensitivity to ionizing radiation is also recognized for other 5-halouracils and radiosensitization properties have been widely employed in radiation therapy. In such processes, important damage is due to the secondary particles generated along the track after interaction of the ionizing radiation with the biological medium [2]. In that sense, studies have been developed in order to investigate the mechanism involved in attachment of secondary low energy electrons on such molecules [3] and experiments involving the action of singly and multiply charged ions on biological systems have been performed.

These ion/biomolecule collisions may induce different processes: excitation and fragmentation of the biomolecule, ionization of the gaseous target, and also possible charge transfer from the multicharged ion towards the biomolecule. Fragmentation and charge transfer have been shown to be complementary processes. They are highly anisotropic with a strong influence of the electronic structure and charge of the C^{q+} ion. As 5-halouracils are supposed to enhance sensitivity to ionizing radiation, the collision with carbon ions would favour fragmentation of the biomolecule in the collision involving a halouracil, compared to the same reaction with uracil. That means, on the contrary, that the charge transfer process would be less efficient. In order to check this point, we have thus undertaken a detailed study of these processes involving a comparison of the different halouracils and their influence on the collision cross-section values, and also a consideration, in each case, of the preferred geometry for the collision process. The collision of the C^{4+} projectile ion on 5-fluoro, 5-chloro and 5-bromouracil targets for a series of geometries has been investigated by means of *ab-initio* molecular calculations of the potential energies and couplings followed by a semiclassical dynamics [4]. The charge transfer appears markedly less efficient than the corresponding process with uracil which induces an enhancement of the complementary fragmentation process in agreement with the radio-sensitivity of 5-halouracils. The mechanism seems to be driven by both electronic and steric effects which induce a lowering of the charge transfer cross-sections and favour various orientations of the projectile with respect to the 5-halouracil target considered.

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Reaction paths for CH_2O, C_2H_4O and C_3H_6O molecules

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After studying peroxidic and persulfidic bonds and the effect of substituents [1-5] with respect specifically to chirality changing isomerization by torsion [6-9], we are presenting a systematic investigation of the sequence of molecules CH_2O, C_2H_4O and C_3H_6O which involve a series of dissociation and isomerization reactions. The propylene oxide (C_3H_6O) is of particular interest to us in relationship with current chirality changing experiments by aligned molecular beams[10].

We study properties of all stable isomers and activation energies of transition states and characterize paths along the intrinsic reaction coordinates, employing quantum chemistry electronic structure calculations and interpretative tools, such as hyperspherical coordinates and moment of inertia variables, for the representation of potential energy surfaces, of use for molecular dynamics.

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Potential energy surface of ionic cluster: application to H_5^+

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The potential energy surface of H_5^+ is characterized using density functional theory. The potential hypersurface is evaluated at selected configurations employing different functionals, and compared with results obtained from ab initio CCSD(T) calculations. The lowest ten stationary points (minima and saddle-points) on the surface are located, and the features of the short- and large-range intermolecular interactions are also investigated. A detailed analysis of the surface's topology shows that DFT calculations faithfully represent the H_5^+ potential, and the use for such surface for studying dynamics is discussed [1].

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Potential Energy Surface for $H_2O - X_2$, with X = H, N and O, System

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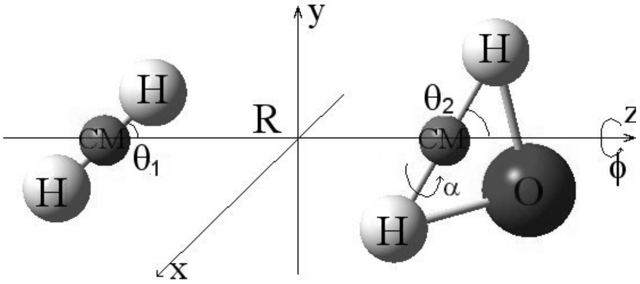
We have developed a potential energy surfaces, PES, for the $H_2O–X_2$, with X=H, N and O, system, based in the concept of the harmonic expansion functional applied to diatom-diatom interactions [1,2] and partitioned as a sum of two contribution, the external one, accounts for the interaction contribution depending on the molecules' center of mass relative distance *R* and orientation, and the internal one, depending on the oxygen position according to the radial axis that connects the two molecules, as applied to the H_2O_2–Rg [3] and H_2S_2–Rg [4] system. The framework of the supermolecular approach was used, as well as the counterpoise-corrected interaction energies [5] in MP2/aug-cc-pVQZ level. The energies were calculated in eighteen leading configuration according the orientation of the molecules (α, θ_1, θ_2, ϕ), where $0 \leq \alpha \leq 2\pi$ measure the oxygen position, $0 \leq \theta_1 \leq \pi$ and $0 \leq \theta_2 \leq \pi$ are the polar angles of the orientation of the vectors along the X_2 bonds with respect to *R* and $0 \leq \phi \leq \pi$ is the relative torsion angle of the two X_2 axis, as illustrated in figure bellow. For each leading configuration the H_2O and X_2 geometries are kept frozen, 101 energies points are calculated, and the PES for the radial part, $\upsilon_{L_1L_2L}(R)$, are constructed by fitting the energies to a fifth degree generalized Rydberg function. The final PES is given by:

$$V(R,\alpha,\theta_1,\theta_2,\phi) = \sum_i w_i(\alpha) \sum_{L_1,L_2,L} \upsilon_{L_1L_2L}(R) \begin{pmatrix} L_1 & L_2 & L \\ m & -m & 0 \end{pmatrix} Y_{L_{11}}^{m}(\theta_1,\phi) Y_{L_2}^{m}(\theta_2,\phi)$$

The isotropic average potential for the H_2, N_2 and O_2 are 0.1336 kcal mol^{-1} at 3.5704 Å, 0.2929 kcal mol^{-1} at 3.7110 Å and 0.2907 kcal mol^{-1} at 3.7024 Å, respectively.



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Resonances in chemical reactions

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The temporary trapping of translational energy in internal degrees of freedom of the reaction complex gives rise to the resonance phenomenon whose signatures have been found in the integral and differential cross sections for the $F+H_2 \rightarrow HF+H$ and $F+HD \rightarrow HF+D$ chemical reactions. We study the dynamics of these reactions using rigorous quantum scattering calculations[1] and analyse scattering resonances from two main perspectives. One relies on the partial wave analysis of reaction lifetimes[2,3]. The other one uses poles of the scattering matrix in the first quaDrnt of the complex angular momentum plane, also known as Regge poles [4].

For the F + HD chemical reaction, we show that most of the resonances are due to van der Waals states in the entrance and exit reaction channels. The metastable states observed in the product reaction channel are assigned by calculating the energy levels and wave functions of the HFD van der Waals complex. The behaviour of resonance energies, widths, and decay branching ratios as functions of total angular momentum is analyzed[3]. The calculated differential cross section shows characteristic forward-backward peaks due to the formation of a long-lived metastable complex.

A detailed description of the metastable states in the $F+H_2$ reaction has been given in refs.[2,3]. The results of our quantum mechanical calculations reveal two interfering resonance pathways leading to the HF product to be scattered selectively in the forward direction. The origin of this quantum structure, recently observed in molecular beam experiments, has been explained using the semiclassical complex angular momentum analysis[4]. This led us to explain the signatures of the resonances in reactive scattering observables.

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Ab initio PES and bound states of ground electronic state of NeI_2 van der Waals molecule

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The structure, energetics and spectroscopy of ground state NeI2 molecule are analyzed from first principles. Ab initio methodology at CCSD(T) level of theory was employed, and large basis sets were used to compute the interaction energies. Scalar relativistic effects accounted for by relativistic effective core potentials for the iodine atoms. Special attention was paid in the choice of basis sets used, the extrapolation schemes employed, as well as the fitting and interpolation processes for its analytical representation. The complete analytical form is provided, and variational fully quantum mechanical calculations were carried out using the present surface, to evaluate vibrationally averaged structures and binding energies for the different conformers. The results obtained are in good accord with earlier and recent data available from experimental investigations of the Ne–I_2 rovibronic spectra [1] [2].

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Formamide as the Model for Photodissociation Studies of the Peptide Bond

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Photoinduced fragmentation of charged small polypeptides has been intensively investigated in recent years due to their importance in 'soft' ionization methods such as MALDI and ESI[1]. These studies revealed that photofragmentation patterns depend strongly on the peptide composition, on electronic state excited by the photon (excitation of aromatic amino acid residues at 266 nm or amide chromophore of the peptide backbone at 193 or 157 nm), on the mass analyzer employed and its time regime[1]. In this respect formamide is particularly interesting since it is the smallest molecule which incorporates the peptide linkage. As such it allows very accurate calculations to be carried out and enables testing of their reliability by comparison of the calculated values with available experimental data.

In this contribution an overview of our recent computational study on photodissociation of formamide[2], its oxygen- and nitrogen- protonated forms[3,4] and *N,N*-dimethylformamide[5] will be presented. The calculations were carried out using the multireference configuration interaction with singles and doubles (MR-CISD) method while dynamics were simulated by employing the mixed quantum-classical direct trajectory method with surface hopping based on multi-configurational self-consistent wave functions. All calculations were carried out using COLUMBUS and NEWTON-X program packages. The main dissociation paths in the S_1 and S_2 states of the parent molecule and its *N,N*-dimethyl derivative was found to be C-N dissociation, with the process from the S_2 state being considerably faster The photodeactivation from the first excited singlet state in *O*-protonated formamide resembled those found for the second valence excited state of the parent molecule. Two photodissociation processes were found: the C-N (major) and C-O (minor) dissociations with very short lifetimes. Similarly, the major process for photodecomposition in the first excited state of *N*-protonated formamide resembles that for the parent formamide, involving C-N dissociation. However, 55% of trajectories remained undissociated and undeactivated until 1000 fs, indicating existence of other deactivation processes on a longer time scale.

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Photodissociation of CH_3I in the red edge of the A band: Comparison between experiment and multisurface wave packet calculations

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The photodissociation dynamics of CH_3I in the red edge of the A band (λ=286-333 nm) has been studied through slice imaging experiments and multisurface wave packet calculations. The theoretical model applied treats the CH_3I molecule as a pseudotriatomic X-C-I system where the three H atoms are replaced by the pseudoatom X. In this model three nuclear degrees of freedom are considered, namely the XC-I dissociation coordinate, the X-C-I bending mode, and the X-C stretch mode, which approximates the umbrella mode of the CH_3I system [1-3]. The simulations consider excitation of the system to three electronic states, namely $^3Q_0$, $^1Q_1$, and $^3Q_1$, where the dynamical evolution takes place. The angle between the laser polarization direction and the direction of dissociation is included in the treatment in addition to the three nuclear degrees of freedom, which makes possible to calculate differential photodissociation cross sections [4]. Experimental and theoretical asymptotic properties like the kinetic energy distributions of the CH_3 fragment, and I/(I*+I) branching ratios, are compared and analyzed. The simulations reproduce all the trends found experimentally in the range of excitation wavelengths studied [4]. Discrepancies found are discussed in the light of the approximations of the theoretical model applied.

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The signature of orbiting resonances in the He-I_2(B) van der Waals complex

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The signature of the He-I_2(B,v) resonances embedded in the continuum of the v vibrational manifolds is investigated in two different dynamical processes. On the one hand, the continuum resonances of the v=59 and 60 vibrational manifolds are probed through vibrational predissociation of the complex initially excited to the ground intermolecular resonance in the v'=v+1 manifold. The calculated excitation spectra show that these resonances manifest a nature of overlapping and long-lived orbiting resonances, which are supported by centrifugal barriers originated in internal rotational excitation of I_2 and He within the complex [1]. These resonance states are similar to those previously found in Ne-Br_2(B,v) [2,3].

On the other hand, the vibrational relaxation process of I_2(B,v=21) through low temperature collisions with He (for collision energies < 7 cm^{-1}) has also been studied. This process was investigated experimentally [4,5], and three peaks were found in the vibrational relaxation cross section measured, which were suggested to be originated by orbiting resonances of the He-I_2(B) complex formed upon the collision. The calculated cross sections associated both with vibrational relaxation to I_2(B,v"<v=21) products and with I_2(B,v=21) products (due to tunnelling through the centrifugal barrier in the initial v=21 manifold) indeed show a number of peaks at similar energy positions as the orbiting resonances found in the vibrational predissociation process. Moreover, the positions of three of the peaks found in the calculated cross sections nearly coincide with the three peaks detected in the experimental cross section. Therefore the present results would confirm that indeed the peaks found in the experimental cross section are originated in low energy orbiting resonances of the He-I_2(B) van der Waals complex.

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Ab initio treatment of charge exchange in H^++CH collisions

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Ion-molecule collisions are important processes in several fields like fusion research, astrophysics and biological damage by ionizing radiation. In particular, proton collisions with the CH radical are relevant in tokamak plasmas, where small hydrocarbons are sputtered in the divertor region and collide with the main plasma constituents (see e.g. ref. 1). The theoretical description of low-energy collisions in ion-diatom collisions is generally carried out by expanding the collision wavefunction as a linear combination of electronic wavefunctions of the (quasi)molecule formed during the collision (CH_2^+ in the present case). This treatment requires a detailed quantum chemistry calculation to evaluate potential energy surfaces (PES) and dynamical couplings of the three-center system. In order to ensure the accuracy of the calculation, we have employed the CASSCF method with analytical and numerical evaluation of the dynamical couplings using MOLPRO [3], and a multi-reference-CI method with a numerical calculation of the couplings (see ref . 2) which uses the package MELDF [4].

In general, non-adiabatic transitions taking place in conical intersections are critical, and therefore we have studied the structure of the dynamical couplings in the neighborhood of the conical intersections. In particular, the PES of the CH_2^+ quasimolecule show asymptotic conical intersections, in both $^2A'$ and $^2A''$ subsystems, between the PES of the states dissociating into H^+ + $CH(X^2\Pi)$ (the entrance channels of the charge transfer reaction) and those dissociating into H(1s) + $CH^+(A^1\Pi)$ (the most important exit channels). The asymptotic conical intersections are similar to that found in the H_3^+ system, and we have applied the method explained in ref. 5 to remove the singularities in the dynamical couplings; this method yields a set of *regularized* states, which are coupled through an exponential interaction. These states have been employed in semiclassical calculations at the Franck-Condon level and using the sudden approximation for rotation and vibration to evaluate total charge transfer cross sections. Anisotropy effects have been considered by performing calculations for different relative orientations of the ion velocity vector with respect to the CH internuclear axis.

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Optimized Quasiparticle Dirac-Kohn-Sham DFT and its Application to Autoionization and Electron-β-Nuclear Processes

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We present the quasiparticle Fermi-liquid version of the DFT theory, starting from the problem of searching for an optimal 1-quasiparticle (1Qp) representation [1]. Some time ago Davidson suggested the optimal "natural orbitals" 1Qp [1]. However, there remain some difficulties in the realization of the Davidson program. One of the efficient recipes represents the Dirac-Kohn-Sham (DKS) DFT theory [1]. In our work the QED DFT version, based on formally exact QED perturbation theory (PT) [2], is developed and a new approach to construction of the optimized 1Qe representation is proposed within the energy approach. An interaction Lagrangian is defined in the standard DFT form (sum of the Coulomb and exchange-correlation terms), but it takes into account for energy dependence of a mass operator Σ:

$$L_q^{\text{int}} = L_K - \frac{1}{2}\sum_{i,k=0}^{2}\int \beta_{ik} F(r_1,r_2)\nu_i(r_1)\nu_k(r_2)dr_1 dr_2 \tag{1}$$

where β_{ik} are some constants. These constants in our theory possess the same universality as ones in the Landau-Migdal Fermi-liquid theory. If F is one of the standard DFT F_{XC} potentials, then without losing a community of statement β_{00} =1. The constant β_{02} can be calculated by analytical way, but is simple linked with spectroscopic factor G_{sp} of atomic or molecular system:

$$G_{sp} = \left\{1-\frac{\partial}{\partial \in}\sum{}_{kk}\left[-(I.P.)_k\right]\right\} \tag{2}$$

where I.P. is an ionization potential. In the fourth order of QED PT (the second order of the atomic PT) there appear the diagrams, whose contribution to imaginary part of the electron energy $\mathrm{Im}\Delta E_{ninv}$ accounts for many-body correlation effects. This contribution describes the collective effects and is dependent upon the electromagnetic potentials gauge [2]. Minimization of DF (3) leads to the DKS-like equations for electron density that are numerically solved. Finally, the optimal QED PT 1Qp basis can be obtained. As example, theory is applied to studying the autoionization resonances in heavy atomic systems and allowed β-decay parameters calculation with account of the bound-decay channel, chemical bond, atomic configuration effects [3].

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Exploring potential energy surfaces of van der Waals clusters using genetic algorithms

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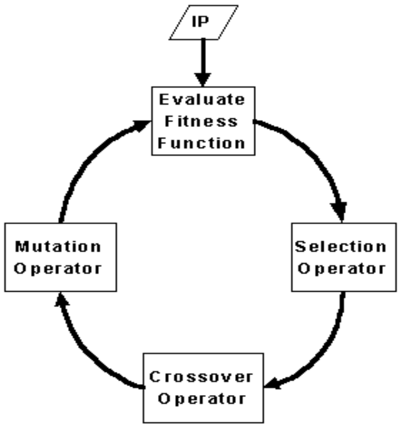
The structures and stability of molecular clusters play a key role for describing physical and chemical properties. The determination of the minima on the potential energy surface is considered crucial for at least semiquantitative analysis, thus many theoretical studies have been devoted to the goal of global optimization. However, as the number of local minima rises quasiexponentially with cluster size, global geometry optimization becomes very difficult for larger clusters, and particularly for weakly bound vdW ones. Recently, interest has been shown in the use of the genetic algorithm (GA) to solve the problem of global optimization [1]. Genetic algorithms are efficient heuristic search methods based on Darwinian evolution with powerful characteristics of robustness and flexibility to capture global solutions of complex optimizations. The GA approach is a powerful tool and it can be used not only as a replacement of traditional optimizations, but may extend and improve them – in general, better performances are reached, by using hybrid methods.

A simple GA uses repeated trials of the Selection-Crossover-Mutation sequence from an initial population (IP) as can be seen in Figure 1.



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Let $P^t(\mathbf{x})$ be the population where x denotes the individuals. Then the GA algorithm is:
• Establish parameters of the GA:
  population size, maximum number of
  generations, selection operator,
  crossover operator, crossover rate,
  mutation operator, mutation rate;
• t = 0;
• Generate $P^t(\mathbf{x})$;
• While not termination criterion do
    ♦ Evaluate $P^t(\mathbf{x})$;
    ♦ Set $P'^t(\mathbf{x}) \leftarrow$ selection $\lfloor P^t(\mathbf{x}) \rfloor$;
    ♦ Set $P^t_{new}(\mathbf{x}) \leftarrow$ crossover$\lfloor P'^t(\mathbf{x}) \rfloor$;
    ♦ Set $P^{t+1}(\mathbf{x}) \leftarrow$ mutation $\lceil P^t_{new}(\mathbf{x}) \rceil$;
    ♦ Set $P^t(\mathbf{x}) \leftarrow P^{t+1}(\mathbf{x})$;
• Od
• Print solutions;
```

Figure 1. Scheme of a simple Genetic Algorithm.

In this study, we will use a GA [2] to explore an *ab initio*-based surface of He_n-ICl clusters [3]. Various local minimum structures are located and their stability is analysed. The actual results are compared with previous ones and the efficiency of the present method is discussed.

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Effects of the rotational excitation and the potential energy surface on the dynamics of the $H^+ + D_2 \rightarrow HD + D^+$ reaction

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The $H^+ + D_2 \rightarrow HD + D^+$ reaction has been theoretically investigated by means of an exact quantum mechanical approach, a quasiclassical trajectory method, and two statistical methods based in the propagation of either wave functions or trajectories. The study addresses the possible changes on the overall dynamics of the title reaction when the D_2 diatom is rotationally excited to its $v=0$, $j=1$ state. In addition, the reactivity for the ground rotational state on two different potential energy surfaces (PESs), namely, the surface by Aguado *et al.* [1] and the PES by Kamisaka [2] is examined. Reaction probabilities and cross sections at 0.524 and 0.1 eV collision energies are calculated. The major differences with respect to the reaction initiated with D_2 in its ground rovibrational state are observed for the lowest collision energy E_c=0.1 eV. Differential cross sections have been found to depend to some extend on the PES employed. In addition, at E_c=0.1 eV further discrepancies in the total and rotational cross sections are noticeable.

For the two energies considered in this study, the statistical approaches have been found to provide a fairly good description of the overall dynamics, thus confirming previous investigations by means of these methods [3-6].

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The many-electron band structure approach for the calculation of excitation energies in crystals

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One-electron band structure theory has difficulties in the prediction of accurate band gaps or excitation energies for systems where electron correlation plays an important role. Particular examples are extended systems in which ionisations or excitations have a local character. Our approach to overcome this deficiency involves the computation of correlated wavefunctions (at for example the MCSCF level of theory) for embedded clusters. These wavefunctions serve as a basis for the construction of the final delocalised many-electron wavefunctions of the crystal.

In this presentation an outline of our method is given and a comparison is made between existing methods that deal with the electron correlation problem in solids. The computational aspects will be described and its strengths and weaknesses will be discussed. Recent results of calculations on $CaMnO_3$ crystals will be presented as an example of the performance of the method.

Electronic structure and bonding of ozone

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The ground and low-lying states of ozone (O_3) have been studied by multi reference variational methods and large basis sets. We have constructed potential energy curves along the bending coordinate for $(1,\ 2)\ ^1A'$, $(1,\ 2)\ ^1A''$, $(1,\ 2)\ ^3A'$, and $(1,\ 2)\ ^3A''$ symmetries, optimizing at the same time the symmetric stretching coordinate. Thirteen minima have been located whose geometrical and energetic characteristics are in very good agreement with existing experimental data. Special emphasis has been given to the interpretation of the chemical bond through valence-bond-Lewis (vbL) diagrams; their appropriate use capture admirably the bonding nature of the O_3 molecule. The biradical character of its ground state, adopted long ago by the scientific community, does not follow from a careful analysis of its wave function.

QED Perturbation Theory: Hyperfine Structure and Atomic Parity Nonconservation in Heavy Atoms

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During the past decade, first of all the optical experiments to detect atomic parity on-conservation (PNC) have progressed to the point where PNC amplitudes can be measured with accuracy on the level of a few percents in certain heavy atoms [1]. To provide an adequate treating these experiments in terms of the standard model for a electro-weak interaction, comparison of the measured amplitudes with theoretically defined ones is required. Nowdays the PNC in atomic systems has a potential to probe a new physics beyond the standard model. In our paper we systematically apply the formalism of the QED many-body perturbation theory (PT) [2] to precise studying PNC effect in heavy atoms with taking into account the relativistic, nuclear, QED corrections. The key element is in an accurate taking into account the correlation corrections (CC) of the PT second and higher orders (dominating classes: Coulomb interaction screening; interaction «particle-hole»; mass operator iterations), which is based on using the Feynman diagrammatic technique and Green function (GF) method. The chain of the screening correlation diagrams forms the geometric progression, the mass operator iterations accouting reduces to solution of the corresponding equations. Usually the GF is defined on the basis of the direct summation. More effective procedure is based on the GF definition from solutions of the Dirac equations. Missing non-local exchange interaction, the GF is defined by the corresponding solutions of the Dirac equations: regular in zero and on indefiniteness. Earlier an efficiency of this approach was shown in the precise calculation of hyperfine structure constants, for a number of the heavy atoms and ions [3]. Here present the calculation results for energy levels, hyperfine structure intervals, E1-,M1-transitions amplitudes in heavy atoms of ^{133}Cs, ^{137}Ba^{+}, ^{207}Pb. As example, let us present the calculation data for PNC 6s-7p dipole amplitude in Cs. Our result is: D=<6s|Dz|7s>=-0.903$\cdot 10^{-11}$i|e|a(-Q_w/N). For comparison we also present other known data [1]: D=-0.91$\cdot 10^{-11}$i|e|a(-Q_w/N) by Dzuba etal (Novosibirsk); D=-0.908$\cdot 10^{-11}$i|e|a(-Q_w/N) by Bouchiat etal (Paris); D=-0.935$\cdot 10^{-11}$i|e|a(-Q_w/N) by Johnson etal (Indiana),D=-0.902$\cdot 10^{-11}$i|e|a(-Q_w/N), and D=-0.905$\cdot 10^{-11}$i|e|a(-Q_w/N) by Johnson-Sapirstein-Blundell (Notre Dame). Comparison of calculated value D with the measurement by Noeker et al allows further to define the weak nuclear charge Q_w and the Weinberg angle ϑ_W. In conclusion we also discuss possibility for observing P and PT violation using NMR frequency shift in a laser beam.

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Effect of a Valley Bifurcation Point on the semi-classical Dynamics.

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The valley regions of a potential energy surface (PES) can be defined as the set of non stationary points of the PES in which all of their projected eigenvalues are positive. This is an open set in the nuclear configuration space and it can be partitioned into a countable family of open and connected sets, disjoint each other and known as valley domains.[1] This definition is similar to that given by Mezey.[2] Both non degenerated energy minima and first order saddle points (SP) of PES are points of its boundary set. Specifically, a non degenerated minimum is the limit point of a single valley domain, while a SP is a limit point of only two valley domains. Thus, if a SP belongs to the closure of two valley domains $D_0^{(1)}$ and $D_0^{(2)}$ ($\overline{D_0^{(1)}}$ and $\overline{D_0^{(2)}}$), it will be always possible to find a minimum energy path (MEP) connecting the reactants of $\overline{D_0^{(1)}}$ with the products of $\overline{D_0^{(2)}}$ and contained in $\overline{D_0^{(1)}} \cup \overline{D_0^{(2)}}$. In general, one of these MEP travelling exclusively across the closures of valley domains describes properly the reaction pathway.[2] Hence, the valley domains play a predominant role in representation of chemical reactions on the PES. However, it has been found that this model cannot be applied to PES where the closure of $D_0^{(2)}$ contains two energy minima. In these cases, it has been demonstrated recently that there is a bifurcation region[1] on the boundary set of $D_0^{(2)}$. The most common case is that one where the bifurcation consists of one point called valley bifurcation point (VBP). This point satisfies a set of conditions which make possible to localize it on the PES being a first order SP of the PES restricted to the frontier surface of $D_0^{(2)}$.

In the current study, it is shown how the semi-classical dynamics is affected by the presence of a VBP on several surfaces of a certain one-parameter-dependent family.[3] The dynamical calculations were carried out using the classical Liouvillian formalism[4,5] with a semi-classical initial probability density. First, we studied a symmetrical surface and then the parameter was changed progressively increasing the asymmetry of the surface until the VBP disappears. We have studied the bifurcation ratio between the two possible products in each surface and probed if a VBP on a PES must cause the expected dynamical effect, i.e. a significant distribution of the dynamical trajectories between both products.

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Theoretical study of Eley-Rideal recombination of Nitrogen atoms from Tungsten (100,110) surfaces

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In the different processes taking place at the gas-surface interface, the mechanisms of molecular recombination play a decisive role. The study and understanding of such mechanisms is a fundamental goal in the chemistry of surfaces.

Using the Classical trajectory method, the dynamics of molecular recombination of nitrogen atoms from a Tungsten surface is studied in two different crystallographic planes. We focus our attention in the Eley - Rideal recombination mechanism.

The potential energy surface is an extended version of a periodic classical LEPS, recently developed in our group. The dynamics is explored in a wide range of projectile energies, the main objective being to explain the behavior of the cross section for the molecular recombination.

(^{4}He)$_N$-Cs$_2$($^2\Sigma$), N=2 up to 12, clusters: a Hartree-like approach

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Clusters and droplets of noble gases, mainly Helium, have opened up a new field or research. In particular, the study of medium-size complexes has been motivated by striking phenomena like superfluidity[1]. It is related with the completely different spectra of molecules embedded in this kind of clusters, depending on the bosonic or fermionic nature of the solvent: in the former case it is a well-defined profile, while in the latter any structure is lost.

In this work we study complexes formed by a diatomic Cs_2 molecule plus an ensemble of N ^{4}He atoms, with N=2 up to 12. In order to search the ground state wave-function of the system we have employed Hartree Quantum-Chemistry-like calculations[2], assuming adiabaticity in the diatomic stretch and decoupling of the diatomic rotation from the helium atoms. The PES is described through a sum of pairwise interactions and we have used an *ab initio* scheme for the Cs_2-He potential. We will show energetic and structural aspects of the clusters, trying to understand the arrangement of the impurity with respect to the helium cloud.

This is a part of a most comprehensive study that includes also a fermionic helium environment, whose work is being currently in progress. The overall objective of the this research is to clarify the effect of the spin statistic in the spectrum of the impurity (see Refs. 3,4 for more details).

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Theoretical studies for the O_2-N_2 intermolecular interaction: a new global potential energy surface

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The interaction between the two major components of the earth atmosphere, in their electronic ground state and considered as rigid rotors, has been obtained by means of *ab initio* electronic structure calculations. The SAPT(DFT) methodology, recently extended to treat open-shell monomers[1], has been employed to obtain interaction energies in a grid of 107 different dimer configurations. For each geometry a set of 19 intermolecular distances, covering the short range, well area and long range regions, has been used. A comparison with interaction energies obtained with the more computationally demanding RCCSD(T) method has been performed for selected dimer geometries. The multipole expansion for the electrostatic, dispersion and induction contributions needed for the extrapolation of the total interaction at larger intermolecular distances has been also obtained: for each monomer static and dynamic polarizabilities as well as permanent multipole moments have been calculated by using the CAS, MRCI and ACPF levels of theory.

The global potential energy surface, fitted with a spherical harmonic expansion, has been tested on experimental "hot" beam integral cross section[2] and second virial coefficient[3,4] data. The lowest bound rotovibrational states and spectroscopic parameters for this weakly bound dimer have been also determined. A comparison with a previous experimentally derived potential energy surface[5] is also presented.

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Quantum mechanical study of rovibrational states for the oxygen dimer from a new *ab initio* potential energy surface

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We present in this communication the quantum mechanical results on the rovibrational states of the O_2-O_2 dimer for its three different intermolecular potential spin multiplicities. The potential energy surfaces (PESs) used have been computed by using an *ab-initio* procedure at different levels of theory. For the quintet state[1] the interaction potential has been obtained from CCSD(T) calculations while for the singlet and triplet multiplicities the PESs have been obtained by combining the CCSD(T) quintet potential with the singlet-quintet and triplet-quintet energy splittings[2] carried out from multiconfigurational calculations. The latter have been performed at both the MRCI and the CASPT2 levels of theory and fitted with a spherical harmonic expansion. In addition, the PESs have been extrapolated at long range by means of accurate *ab-initio* dispersion, induction and electrostatic coefficients.

The full quantum mechanical calculations of bound states have been carried out with the BOUND[3] program for the rigid rotor O_2-O_2 dimer. The obtained bound states and associated wavefunctions have been used to assess some spectroscopic features and to determine which of the MRCI and CASPT2 splittings is more adequate to describe the experimental results. We present energies and eigenfunctions for the first bound states of the dimer in the singlet, triplet and quintet spin multiplicities, the most stable geometries of rovibrational fundamental and first excited states and also we determine dissociation energies, the singlet-triplet splitting, rotational constants and some intermolecular vibrational frequencies. The results obtained with the new *ab-initio* PESs are compared with experimental data[4,5] and quantum mechanical calculations based on previous interactions potentials[6,7].

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A Variation of MCTDH applied to System-Bath Dynamics

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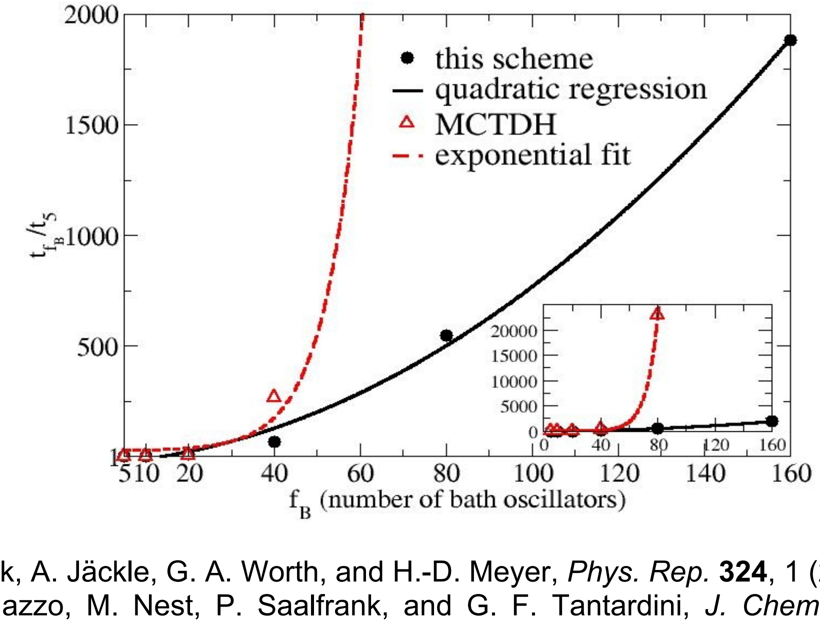
We have explored a variation of the MCTDH method [1], aiming to get around its exponential scaling problem, and especially in regard to system-bath dynamics. Very often these processes can be described by a set of strongly coupled subsystem degrees of freedom, and another set of bath modes also coupled to the subsystem, but only weakly. We can thus use the following ansatz, closely related to the local coherent-state approximation (LCSA) [2], and the continuous configuration TD-SCF method [3]. For clarity reasons, we chose a 1D subsystem described by the coordinate x_0, coupled to f 1D bath modes x_i:

$$\Psi(x_0,\ldots,x_f,t)=\sum_{\alpha=1}^{N} C_\alpha(t)\ |s_\alpha>\ \prod_{k=1}^{f}\varphi_\alpha^{(k)}(x_k,t).$$

The $|s_\alpha>$ denote N subsystem DVR points, and the $\varphi_\alpha^{(k)}$ correspond to the bath. This scheme requires all degrees of freedom to be described by the same number N of single-particle functions, but minimizes the number of included configurations by taking into account that coupling to the bath is local in subsystem coordinates. If this is interpreted as Hartree products coupled locally to a reaction path coordinate, then it is necessary to relax the condition of MCTDH, that all single particle functions are orthogonal to each other.

We present applications to quantum dissipative dynamics and an analysis of the computational effort [4]. Namely, propagation times within this scheme scale as $t_{CPU}\sim f^2$:



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Statistical quantum and quasiclassical studies on the O(^1D) + HCl reaction: a product-channel dependent dynamics

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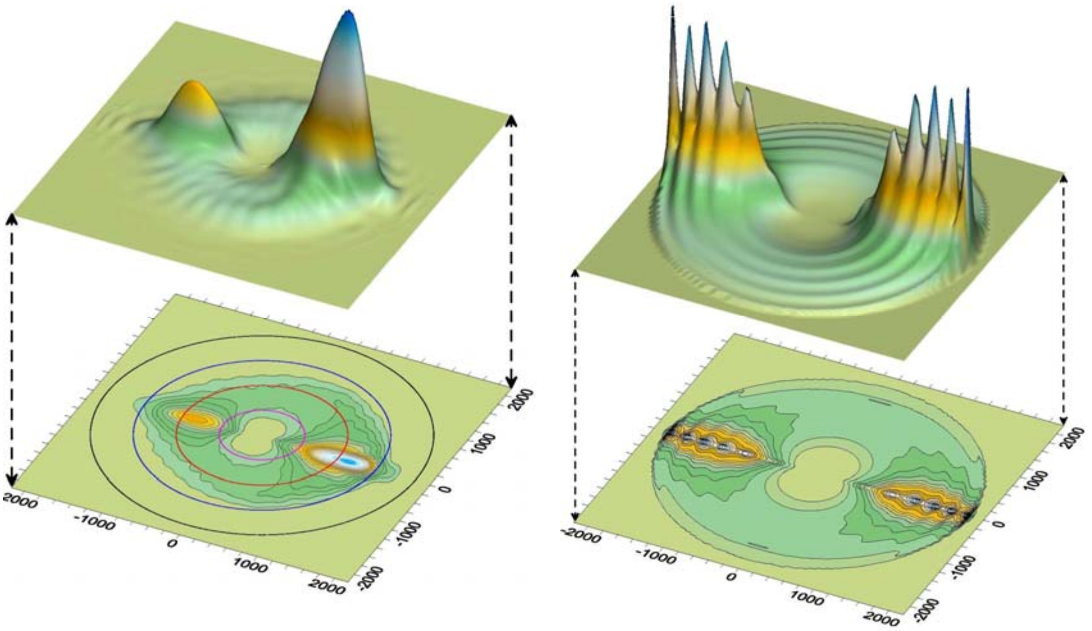
The dynamics of the double-well mediated O(^1D)+ HCl reaction has been extensively studied by means of statistical (quantum and quasiclassical) and quasiclassical approaches. In particular, reaction probabilities, integral and differential cross sections for both product channels, OH + Cl and ClO + H, have been calculated on the H2 PES [1]. When possible, theoretical results have been tested and compared with the experiment [2,3]. It is found that, in general, the formation of OH molecules is due to abstraction-like processes, while the main mechanism leading to ClO products is of complex-forming-type [4,5].



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Effects induced by nuclear deformations in ground and correlation electron energies of multiply charged Helium like ions in high-temperature plasma

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Multiply charged isoelectronic Helium like ions in high-temperature astrophysical and laboratory plasma possess specific properties and characteristics caused by the non-compensated by electrons long-range Columb field of the nuclei. This field determines the possibility one or two electrons to occupy highly excited quasidiscrete (autoionized) states, outside the ionization limit. There are two decomposition channels of the excited ion: autoionization and radiation. In that case one can observe several resonance processes, for example radiative recombination (RR) and the opposite process - photoionization. The Columb field also plays significant role in all interaction processes of multiply charged ions with electrons and photons in plasma.

In the case of electron capture the decomposition channels of double excited ion are two also: autoionization and radiation. In the case of electron "observer" the transition of ion's electron from unbound to bound state is accompanied by so called satellite lines in the spectrum. In the case of interaction with electron having the appropriate resonance energy, the radiative decomposition of double excited ion realizes by photon emission and electron transition into bound state. When the radiative transition realizes by the internal electron, the process is dielectronic recombination (DR).

The opposite effects of the influence of the specific electron processes on the nucleus, that is manifested as a deviation of the pure nuclear Coulomb potential and nuclear excitation, denoted as nuclear excitation by electron capture (NEEC).

Nuclear motion, nuclear mass and nuclear size exert an influence over the processes in the electron system also. Many theoretical investigations concern the effects of these nuclear characteristics on the electron system.

The proposed work concerns for the first time and studies the effects resulting from nuclear deformations on the formation of the electron energy quantities of multiply charged ions. In the current stage the investigations are performed on the base of obtained numerical results for the ground state energies, mass corrections and mass correlations of the electronic systems for multiply charged He like ions with charge Z from 2 to 118. The nuclides of all existing isotopes are included. A modified method is used based on explicitly correlated wave functions (ECWF) approach. Staggering effects of the electron energy quantities with nuclear magic numbers by N (number of neutrons) and A (mass number) are investigated for each value of Z (number of protons). The effects of nuclear deformations on the electron energy quantities are also investigated through the formation of all nuclear deformation multiplets.

The extremely high accuracy of the obtained numerical results allows their application in precise approaches for plasma diagnostics.

QED Many-Body Approach to Calculating Autionization widths and Electron Collision Strengths for Multicharged Ions

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We present the uniform energy approach, formally based on the QED perturbation theory (PT) [1,2], for the calculation of the autoionization states energies and widths and electron collision strengths and cross-sections in the multicharged ions (in a collisionally pumped plasma). The electron collision excitation cross-sections and rate coefficients for some plasma Ne-like multicharged ions are calculated within QED energy approach [1]. The energy shift due to the collision is arisen at first in the second PT order in the form of integral on the scattered electron energy ε_{sc}:

$$\mathrm{Im}\Delta E = \pi G(\varepsilon_{iv}, \varepsilon_{ie}, \varepsilon_{in}, \varepsilon_{sc})$$

where *G* is the squared combination of the two-particle matrix elements:

$$V(1,2;4,3) = \sqrt{(2j_1+1)(2j_2+1)(2j_3+1)(2j_4+1)}\,(-1)^{j_1+j_2+j_3+j_4+m_1+m_2} \times$$

$$\times \sum_{\lambda,\mu}(-1)^{\mu}\begin{bmatrix} j_1 \ldots\ldots j_3 \ldots\lambda \\ m_1 . -m_3 \ldots\mu \end{bmatrix}\begin{bmatrix} j_2 \ldots\ldots j_4 \ldots\lambda \\ m_2 . -m_4 ..\mu \end{bmatrix}(Q_\lambda^{Qul} + Q_\lambda^{Br})$$

The values $Q_\lambda^{\mathrm{Qul}}, Q_\lambda^{\mathrm{Br}}$ are corresponding to the the Coulomb part $exp(i|\omega|r_{12})/r_{12}$ i and Breiht part $exp(i|\omega|r_{12})\,\alpha_1\alpha_2/r_{12}$. of the inter particle interaction. The cross-section is σ =-2 ImΔE. The similar procedure has been earlier developed for treating the autoionization states in the multicharged ions [1]. We present the results of calcuation the autoionization resonances energies and widthds in heavy He-like multicharged ions and rare-earth atoms of Gd and Tm. Besides, we present data on the electron –collision strengths for Ne-like ions. To test the results of calculations we compare the obtained data for some Ne-like ions with other authors' calculations and available experimental data. The inclusion of Na-like states, accounting for diffusion-like processes, can increase the population inversion for the "lasing candidates" by at least a factor of two for a wide range of plasma conditions.

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Anharmonic molecular vibrations using local rectilinear coordinates and the Watson Hamiltonian

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.

Having in mind floppy molecules, I shall present a method that we developed[1] to construct local rectilinear vibrational coordinates for nonlinear molecules whose reference structures do not necessarily correspond to stationary points of the potential energy surface. These vibrational coordinates satisfy Eckart's conditions.

The molecular vibrations can then be described exactly by the Watson Hamiltonian. Often in the literature, within such a description, the Coriolis coupling is omitted, especially for large systems. We point out that, unlike the exact Watson solution, the omission leads to results that depend on the initial choice of molecular reference structure. Nevertheless, the self-consistent solution, yields a molecular geometry that coincides with the quantum averaged geometry of the exact Watson Hamiltonian and appears to be a promising way for the computation of the vibrational spectra of strongly anharmonic molecules.

It is worth noting that the application of the Watson Hamiltonian for the description of floppy nonlinear molecules is not straightforward, because at linear molecular configurations the Watson Hamiltonian becomes singular, resulting in spurious, unphysical solutions close to the linear geometry[2]. I shall present our analysis of the problem and how we propose to eliminate these unphysical solutions. Our results on the water molecule show an improvement compared with previous methods. Finally, I shall present results for the extremely floppy $XeHe_2$ molecule.

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Theoretical Studies on Reduction Potential of Type I copper Proteins

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About one-half of all known proteins in the Protein Data Bank (PDB) contain metal ion cofactors. Metalloproteins are simply metal complexes but with remarkably intricate and complex ligands. The transition metal ions are bridged by oxide or sulfide ligands or coordinately bonding with organic atoms in residues around the metal ions. The metal ions play vital roles in charge neutralization, structure, and function. Solomon et al. [1] have summarized functions of blue copper proteins and have investigated electronic structures of the active sites in the proteins by quantum chemical calculations with computational models. For these metalloproteins, the metal ion and its environment are important from the viewpoint of catalysis in active sites. The functions of metalloproteins are summarized in 2; (1) allosteric interactions between the active sites in different subunits, (2) organization of metal sites within a protein molecule for directional electron transfer (ET) to a catalytic site, (3) surface recognition sites for interactions with donor and acceptor proteins, (4) covalent ET pathways within the protein, (5) forming substrate access channels to the active site, (6) providing an active site hydrophobic environment within the protein in aqueous solution, (7) forming a substrate binding pocket near the metal active site, (8) assembling additional reactive covalently or non covalently bound organic cofactors for catalysis, (9) providing specific charge and hydrogen-bonding residues near the metal site to assist in catalysis, and (10) imposing a unique geometry on the metal site.

In this study, we analyze the reduction potentials of type I copper proteins by using quantum chemical calculations [3] and a simple model [4]. We discuss the reduction potentials of blue copper proteins in relation to the dependence of the solvation and that of the protonation effects by a continuum solvent model approach and partial geometry optimization with DFT/B3LYP calculation. The simple model used in this study is based upon the field theory, and the dependence of the reduction potentials of type I copper proteins on the partial spin density of the copper ion is discussed with the concept of the strongly correlated electron systems.

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Thermal properties of a small cluster: The Ar trimer

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Small clusters offer an ideal scenario halfway through atomic/molecular systems and continuum media (liquids or solids), providing a way to understand how properties of macroscopic systems arise from those of their atomic contituents, properties such as phase changes, equilibrium geometries or superfluidity.

In this work the Ar_3 system has been studied in the thermal interval up to T=40K by means of Path Integral Monte Carlo (PIMC) [1] calculations and a model based on the Boltzmann average of the rovibrational spectrum of the system at sufficiently high values of the total angular momentum, which has been made with a method [2,3] based on the use of Distributed Gaussian Functions (DGF)[4] for the interparticle distances.

The comparison between the average energies of the system as a function of the temperature reveals a reasonably good agreement up to moderate temperatures T~20K. Beyond that temperature, the Ar_3 system starts exploring more configurations apart from the strictly equilateral geometry, namely, both linear and Ar_2-Ar arrangements. The use of a confinement radius in Monte Carlo calculations in this thermal regime in order to prevent this behaviour has been extensively used but also questioned by some authors [5], and will be discussed in detail in this work.

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PES, bound and Vibrational Predissociation of He–I_2 van der Waals molecule

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Ab initio CCSD(T) and MRCI approaches were employed to construct potential energy surfaces of the ground and the B electronic excited states of He–I_2 complex, while full quantum mechanical methods were applied to study its spectroscopy and dynamics. A description of the approach adopted, together with the results obtained and their comparison with recent experimental data, as well as further improvements are presented.

HeI_2 was the first rare gas-dihalogen van derWaals molecule studied by Levy and co-workers [1]. So far, experimental data are available for spectral blueshifts and predissociation linewidths for low and high $I_2(B,v')$ vibrational levels form earlier experiments, as well as the binding energies of the X and B states, from a recent experimental study [1]. Interestingly, high-level electronic structure calculations had predicted minima in the X-state potential in the linear configurations [2], while experimental evidence of such conformer has been first observed in the spectra reported by Levy and co-workers in 1976, although was not definitively assigned until recently [1].

For a direct comparison with the experiment, theoretical, accurate global PESs for both electronic states involved are required together with a first principles dynamics simulations. Here, we present a fully quantum computation of the HeI2 dynamics using high-level ab initio surfaces of the X and B states. This allows us to make a first comparison with experiment based on first principles model potentials [2, 3]. Binding energies, vibrationally averaged structures for both electronic states are determined, and their values are found to be in excellent accord with recent experimental measurements. Further, spectral blueshifts and vibrational predissociation lifetimes are also computed and their comparison with the experimental data, in order to evaluate the quality of the *ab initio* surfaces, is discussed.

Such accurate model interaction potentials continue to be in demand for studying collisions of molecules with ultracold rare-gas atoms in optical traps, as well as spectroscopy of larger rare gas-dihalogen clusters, where a diatomic molecule interacts with a solvent system of rare gas atoms.

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H_2 reactivity on gold nano-structures: a cluster and embedding potential approach

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Gold is the noblest of the transition metals and presents a very low reactivity and catalytic activity in bulk. However, in small gold nano-structures, the reaction barriers get lower for many reactions and the chemisoprtion wells deeper. There is a recent increasing interest in determining their catalytic properties because their possible industrial impact [1]. The dissociation of H_2 on nanowires [2] and clusters [3] have been studied recently, showing no barrier for the reaction. In order to understand in detail the factors determining such high reactivity and the transition from clusters to bulk, here we present a study for different coordinations of gold atoms on model systems, linear and planar, paying special attention to their fluxionality [4]. It is found that appart from the coordination of gold atoms, being a fundamental factor, the reactivity is modulated by the hybridization of the gold atoms involved, explaining the reactivity change from planar to linear configurations or edges. An extension of a recently developed embedding potential method [5] is used to simplify the study of larger clusters. Moreover, such embedding techniques are used to analyze the hybridization of the gold atoms involved in the reaction and, hence, as an analysis tool to understand the reaction mechanisms.

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Assessment of the CTOCD-DZ approach in a hierarchy of coupled cluster methods

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Gauge origin independent calculations of nuclear magnetic shielding tensors are carried out inside the formalism of the continuous transformation of the origin of the current density leading to formal annihilation of its diamagnetic contribution (CTOCD-DZ)[1]. We employ the unrelaxed linear response approach with a hierarchy[2-4] of different coupled cluster (CCS, CC2, CCSD and CC3) methods in order to assess the importance of the level of approximation in the coupled cluster expansion. The basis set dependence of the computed nuclear magnetic shielding constants is also analyzed in the series of correlation consistent basis set from Dunning and coworkers[5], with the aim of designing optimized basis sets of relatively small size.

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Excited states of SiH_4. Low lying Rydberg states

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The study of silane molecule is of interest because both its practical application in plasma chemistry and for fundamental reasons to understand the evolution of the properties of group IVb hydrides. Its structure (a central third period atom surrounded by light H atoms) makes it convenient for the present study. The electronic spectrum of SiH_4 was reported by Tronc et al.[1]

Diverse basis sets and calculation conditions are compared through the results of vertical excitation energies and electronic excited states obtained from LR-CCSD[2] (equivalently EOM-CCSD)[3] and some more involved methods including effects of *triples* (CCSDR(3)[2], CR-EOM-CCSD(T)[3],...). Three basis set classes are compared: 1) ANO[4] + "ad hoc" single series of Rydberg ANO's[5], 2) Dunning's diversely augmented pVXZ basis sets[6] and 3) Descompensated Dunning's pVXZ where the central atom is much better described in order to favour the description of Rydberg states. On the basis of all these calculations, an attempt is made of assignment of the low lying states of silane, paying special attention to Rydberg series and their quantum defects. Distorting the T_d tetraheDrl structure along normal modes allows for taking into account the occurrence of several Rydberg series due to Jahn-Teller effect.

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Scattering Physics: A Quantum Trajectory Approach

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The trajectory-based formalism of Bohmian mechanics[1,2,3] constitutes an alternative (but equivalent at a predictive level) approach to the standard formulation of quantum mechanics. Here, we show the advantages of this formalism in providing both an accurate description and a novel interpretation when it is applied to different phenomena of interest in scattering problems[4,5,6], such as diffraction by "hard" and "soft" slits[4], the Talbot effect and its connection to wave guides[7], and the quantum vortical dynamics induced by the presence of single adsorbates on metal surfaces[8,9]. These problems illustrate fairly well how quantum trajectories are able to satisfactorily reproduce the main features of real scattering experiments[10] as well as to provide a causal insight of the underlying dynamics without taking into consideration other philosophical connotations.

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Quantum-Cumulant theory for vibration excited states

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Recently, we have developed a quantal cumulant dynamics (QCD) in order to treat large quantum systems with low costs [1-6]. The key ideas are that a coordinate shift operator acting on a potential operator is introduced and that a cumulant expansion technique is applied to evaluate the expectation value of the shift operator. In the presentation, we derive the coupled equations of motion of coordinates, momenta, cumulants that consist of symmetric-ordered products of the coordinate and the momentum fluctuation operators. We apply the methodology to describe quantum nature of structural transitions of Morse clusters. In the last QSCP, We have evaluated a Lindemann index of small quantum clusters and observed quantum isotope effects on their melting behavior. The quantum effects shallow the potential and elongate the equilibrium distance of the Morse potential. These features result in increase of transition temperatures of freezing and melting toward those of classical ones.

In this work, we propose an excitation operator approach to treat the vibrational excited states based on QCD method. We construct a general wave function by means of a product of excitation operators with expansion coefficients acting on the reference wave function used in the previous work, where the excitation operators are expressed as a function of both coordinate and momentum fluctuation operators and the expansion coefficients are determined by solving secular equation on the fly. This method is applied to the vibrational motions of polyatomic molecules. We derive a "*classical approximation*" to the vibrational excited states, which has not been explored yet.

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Theoretical study of the adsorption of CO molecules on $MAu_nO_2^+$ clusters (M = Ti, Fe; n = 1, 4-7)

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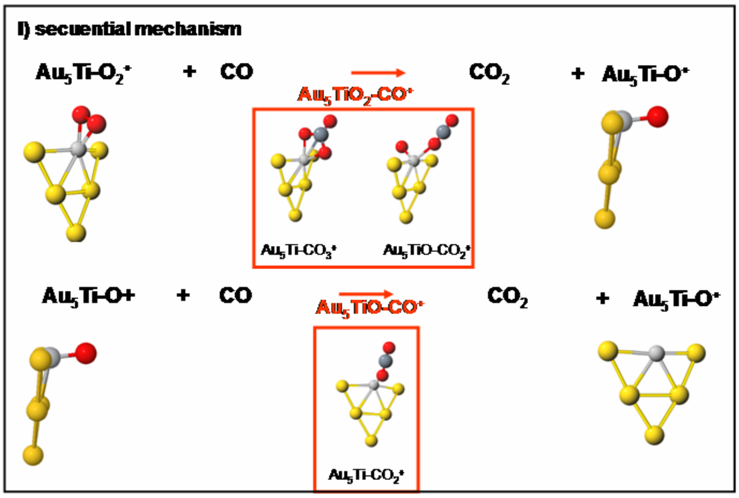
We have studied the adsorption of CO molecules on several low lying energy isomers of $MAu_nO_2^+$ clusters (M=Ti, Fe; n= 1, 4-7). These isomers were previously obtained[1] in a study of the adsorption of O_2 on MAu_n^+ clusters. Some preliminary results have been already published[2]. This study is based on first-principles calculations using the Siesta code[3] within the spin dependent PBE-GGA[4]. Norm conserving pseudopotentials and multiple-zeta basis sets for this problem were tested and used in previous works[1,2]. Auxiliary tools to find the transition state and reaction barriers have been taken from the Gaussian code[5] and from the ASE interface[6] to the Nudged Elastic Band (NBE) method.

We have studied two different CO adsorption mechanisms: i) sequential, and ii) simultaneous. In the case i), the adsorption of a CO on $Au_nMO_2^+$ leads to the formation of Au_nMO^+ cluster and a CO_2 desorbed molecule. Then, a second CO molecule is adsorbed on the product Au_nMO^+, and a second CO_2 is desorbed, leading to the clean MAu_n^+ cluster. This mechanism involves the calculation of several reaction intermediates for each one of the steps, as shown in the Figure (M=Ti, n=5).



For several cases in the range n=1, 4-7 and M=Ti, Fe, we have calculated the vibration frequencies of [$MAu_nO\text{-}CO_2^+$ and $MAu_n\text{-}CO_3^+$] complexes to distinguish between reaction intermediates and transition states. Intrinsic reaction coordinate (IRC) calculations are also performed so that a transition state connects two appropriate local minima in the reaction pathwayIn the mechanism ii) we have optimized complexes of the type [$MAu_nO_2\text{-}(CO)_2^+$] from which two CO_2 can be desorbed leading to the clean MAu_n^+. Among these complexes $MAu_n\text{-}C_2O_4^+$, with the oxalate C_2O_4 bonded to M, and $MAu_n\text{-}(CO_2)_2^+$, with two preformed CO_2 molecules bonded to M, can be highlighted.

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Density Functional Theory study of the photo-oxidation of water on tungsten trioxide (WO3)

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The photo-oxidation of water on the monoclinic P21/n WO3 (200, 020 and 002) surfaces is investigated using density functional theory (DFT) calculations, employing the PW91-generalized gradient approximation, and the method developed by Norskov and coworkers[1] based on the free energy differences between the reaction intermediates. We first relax the bulk material unit cell and then investigate the relative stability of different surface terminations of WO3 and analyze the overpotential needed for the photo-electrolysis of water. We found that the rate limiting step is the transfer of a proton from the surface adsorbed OH to the electrolyte, and that the computed overpotential for O2 evolution (1.04 V) is available upon illumination of the surface with visible light.

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"A priori" inclusion of long-range interaction behaviour in fitted potential energy surfaces.

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For ion-molecule reactions, like the $H_2 + H^+$ or $H_2^+ + H$ reactions at low temperatures, the long-range interactions are very important. These ion-molecule reactions are of great importance in gas phase environments such as the molecular hydrogen plasma occurring in interstellar clouds, planetary ionospheres, ion sources and thermonuclear experiments. On the other hand, the H_3^+ play an important role as a benchmark system for high accuracy *ab initio* molecular theory and reaction dynamics. Full reviews of the experimental and theoretical work on H_3^+ have been presented by McNab [1] and Tennyson [2]. In order to obtain the rovibrational states and simulate the experimental spectrum, it is necessary an accurate Global Potential energy surface (GPES) for the ground electronic 1A' state, that it includes the long-range behaviour.

The two possible channels of dissociation correspond with $H_2 + H^+$ or $H_2^+ + H$. For the lowest dissociation channel, $H_2 + H^+$, the relevant long-range interaction has two contributions [3], the charge-cuadrupole term, $V_3 = Q_{H2}\, P_2(\cos\theta)\, R^{-3}$ and the charge-induced dipole term, $V_4 = -(A_0 + A_2\, P_2(\cos\theta))\, R^{-4}$, where Q_{H2} is the quadrupole moment of H_2, $(\alpha_{\parallel} - \alpha_{\perp}) = 3A_2$ is the anisotropy in the polarizability of the H_2 molecule whose mean polarizability is $\alpha_0 = ⅓(\alpha_{\parallel} - 2\alpha_{\perp}) = 2\, A_0$. Both $\alpha_{\parallel}$ and $\alpha_{\perp}$ are functions of the internuclear distance of H_2, r.

We analyze a new method [4] of embedding the long-range interaction terms in the functional form used to represent the Potential Energy Surface ground electronic state of H_3^+. For this electronic state of H_3^+ we use the Diatomics in Molecules (DIM) approach as a starting point [5,6], because it describes correctly the channels of dissociation. Usually the long-range terms are included *a posteriori* by using a switching function $f(R)$ that goes smoothly from zero at short values of R to one at long ones. The most widely used damping functions are probably those of Tang and Toennies [7], later modified to be an incomplete gamma function [8].

We will propose to introduce the long-range terms *a priori*, by including them in the DIM approach [4]. Due to the high interest in highly rotationally excited states of H_3^+, we have computed the H_3^+ full rovibrational spectra up to the $H_2 + H^+$ dissociation energy limit. Where the correlation function, even when convoluted with a smoothing function, exhibits oscillations similar to those observed experimentally by Carrington *et al* [1,9,10,11], in the extraordinarily complex IR predissociation spectrum (almost 27000 lines between 872 and 1094 cm^{-1}), grouped in four separated peaks for a pseudo-low-resolution spectrum.

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Integral and differential cross sections in A+BC reactions using a new wave packet method.

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The differential cross sections for some triatomic systems have been calculated using a new wave packet code, MAD-WAVE3 [1], which uses either reactants or products Jacobi coordinates along the propagation. In order to show the accuracy and efficiency of the coordinate transformation required when using reactants Jacobi coordinates, as recently proposed [2], the method is first applied to H+D_2 reaction as a benchmark, for which exact time independent calculations are also performed. It is found that the use of reactants coordinates yields to accurate results, with a computational effort slightly lower than when using products coordinate. The reactant coordinates, which are particularly well adapted to describe H+H'L reactions (H for heavy atom and L for light) and have then been applied to simulate the Li+HF collision on which quantum differential cross sections results were not available. The obtained results are compared to recent QCT calculations and experimental results [3]. We will end presenting preliminary results obtained for the reactions O+HF on the $1^3A''$ and $2^3A''$ states using both adiabatic and diabatic PESs [4]. New results calculated on the recently built PES of the $^4A''$ excited state [5] for C+OH reaction will also be shown.

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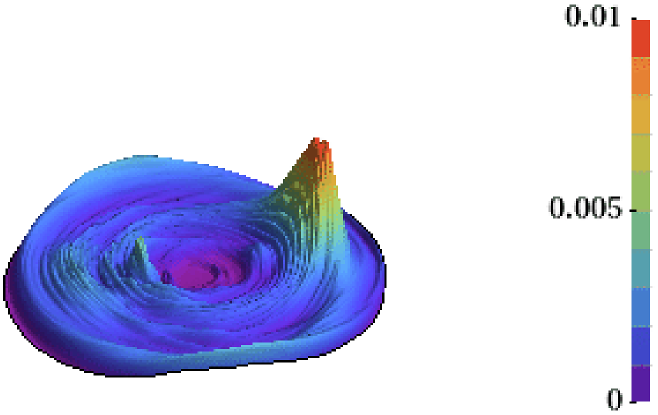

Velocity map distribution of the differential cross section (Å^2/sr.) for Li+HF(v=0,j=0)→LiF+H for a collision energy of 0.341 eV.

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Sunday, Sept 13	**Monday, Sept 14**	**Tuesday, Sept 15**	**Wednesday, Sept 16**	**Thursday, Sept 17**	**Friday, Sept 18**	**Saturday, Sept 19**
	7:30-9:00 ***Breakfast***	**7:30-9:00** ***Breakfast***	**7:30-9:00** ***Breakfast***	**7:30-9:00** ***Breakfast***	**7:30-9:00** ***Breakfast***	**7:30-9:00** ***Breakfast***
	9:00-9:30 Opening **9:30-11:00** **Session M1** *M. Quack* *V. Aquilanti* *M.L. Senent*	**9:00-11:00** **Session T1** *E. Brändas* *J. Karwoski* *L. Tel* *C. Valdemoro*	**9:00-12:00** **Session W1** *A. Glushkov* *M. Hakala* *J.R. Gour* *I. Paidorová*	**9:00-10:00** **Session Th1** *H.J. Werner* *P. Piecuch* **10:15-11:45** Visit to Monasterio	**9:00-11:00** **Session F1** *O.Vasiyutinskii* *M. Nest* *O. Tapia* *O.D. Castaño*	**9:00-11:00** **Session S1** *J.T. Muckerman* *E. Suraud* *L.C. Balbás* *J. Medina*
	11:00-11:30 ***Coffee Break***	**11:00-11:30** ***Coffee Break***			**11:00-11:30** ***Coffee Break***	**11:00-11:30** ***Coffee Break***
	11:30-13:30 **Session M2** *E. Pollak* *K. Coutinho* *M.P. de Lara Castells* *F. Flores*	**11:30-13:30** **Session T2** *A.J.C. Varandas* *S. Vázquez* *F.J. Aoiz* *P. Larrégaray*	**12:00-19:00** Excursion to Segovia	**12:00-13:30** **Session Th2** *A. McCoy* *J. Navarro* *N. Halberstadt*	**11:30-13:30** **Session F2** *D.C. Moule* *O. Atabek* *A. Aguilar* *A. Kuleff*	**11:30-12:30** **Session S2** *S. Farantos* *A. Zanchet* *J. Maruani* **12:30-13:30** Closing Remarks
	13:30-15:30 ***Lunch***	**13:30-15:30** ***Lunch***		**13:30-15:30** ***Lunch***	**13:30-15:30** ***Lunch***	**13:30-15:30** ***Lunch***
16:30-21:30 Registration	**15:30-17:00** **Session M3** *M.A.C. Nascimento* *H. Nakai* *D. Mukherjee*	**15:30-17:00** **Session T3** *A.Beswick* *M. Barranco* *T. González-Lezana*		**15:30-17:30** **Session Th3** *H. Nakatsuji* *A. Mavridis* *S. Li* *J.V. Ortiz*	**15:30-17:00** **Session F3** *G. Corongiu* *J. Jellinek* *B. Fernández*	
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20:00-21:30 Dinner	**17:30-18:30** **Session M4** *R. Lefebvre* *A. Vibok*	**17:30-18:30** **Session T4** *M.I. Hernández* *M .Ehara*		**18:00-19:30** **Session Th4** *A. Tadjer* *J.Z.H. Zhang* *A. Dubois*	**17:30-18:30** **Session F4** *P. Lazzeretti* *P. Bargueño*	
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	20:00-21:30 ***Dinner***	**21:00-22:30** ***Dinner***	**20:00-21:30** ***Dinner***	**20:00-23:00** ***Banquet Reception*** ***Dinner***	**20:00-21:30** ***Dinner***	
	21:30-23:00 Poster Session I				**21:30-23:00** Poster Session II	