

Quantum Days Bilbao 2013:

“Recent Developments in the Theory of Chemical Reactions”



Sarriko Campus, Bilbao, July 24th 2013

Chair: **Dmitri Sokolovski**

□ Invited Lectures:

Momentum Space Orbitals, Sturmians and Spin Networks: Hyperspherical Harmonics and Discrete Polynomials in Quantum Chemistry

Vincenzo Aquilanti, Gaia Grossi

Università di Perugia, Italy

vincenzoaquilanti@yahoo.it

Cecilia Coletti

Università di Chieti, Italy

ccoletti@unich.it

An introduction is presented to progress in analytical tools for tackling quantum mechanical few-body problems of increasing complexity. Development and classifications of complete orthonormal basis sets exploit extensions of group theoretical representation functions, basic for angular momentum theory (spin networks).

Families of continuous and discrete polynomials provide complete orthonormal basis sets for the expansions of atomic and molecular orbitals, related to hyperspherical harmonics in momentum space and to Sturmians in configuration space.

Connections between Sturmians and Slater orbitals and use in spectroscopy and reactions will be discussed as time will permit.

Efforts of recent applications and numerical implementations regard both analytical and computational advances in the generation of matrix elements and molecular integrals.

References:

1. Vincenzo Aquilanti, Dmitri Marinelli, Annalisa Marzuoli, "Hamiltonian dynamics of a quantum of space: hidden symmetries and spectrum of the volume operator, and discrete orthogonal polynomials" *J. Phys. A: Math. Theor.* **46**, 175303 (2013)
2. Roger W. Anderson, Vincenzo Aquilanti, Ana Carla P. Bitencourt, Dimitri Marinelli, and Mirco Ragni "The Screen representation of spin networks: 2D recurrence, eigenvalue equation for 6j symbols, geometric interpretation and Hamiltonian dynamics" *Lecture Notes in Computer Science, II – 46*, 2013
3. Mirco Ragni, Robert G. Littlejohn, Ana Carla P. Bitencourt, Vincenzo Aquilanti, and Roger Anderson. "The Screen representation of spin networks. Images of 6j symbols and semiclassical features" *Lecture Notes in Computer Science, II – 60*, 2013
4. Danilo Calderini, Cecilia Coletti and Vincenzo Aquilanti "Continuous and discrete algorithms in quantum chemistry: polynomials sets, spin networks and Sturmian orbitals" *Lecture Notes in Computer Science, II - 32*, 2013
5. Cecilia Coletti, Danilo Calderini and Vincenzo Aquilanti "d-dimensional Kepler-Coulomb Sturmians and Hyperspherical Harmonics as Complete Orthonormal Atomic and Molecular Orbitals" *Adv. Quantum Chem., in press*, 2013

Rationalizing atom-diatom insertion reaction dynamics using a simple semi-classical statistical model momentum Space Orbitals, Sturmians and Spin Networks: Hyperspherical Harmonics and Discrete Polynomials in Quantum Chemistry

Pascal Larregaray

ISM, Université Bordeaux1/CNRS, 351 cours de la libération, 33405 Talence, France
p.larregaray@ism.u-bordeaux1.fr

In the last decade, quantum and semi-classical statistical models have proven fairly accurate at predicting reactive cross-sections as well as state/spatial distributions in the products of triatomic insertion processes such as the title reaction. The main advantages of such theoretical treatments are numerical simplicity and interpretative power.

As an example, a simple semi-classical statistical model is presented here and its relevancy down to very low collision energies (5-120K) is evidenced for the S(1D)+ H₂ reaction by comparison with recent exact quantum scattering calculations [1-3] and molecular beams experiments [1-2].

References:

1. Berteloite et al., Phys. Rev. Lett., 2010, 105, 203201
2. Lara et al., Phys. Chem. Chem. Phys., 2011, 13, 8127
3. Lara et al., Phys. Chem. Chem. Phys., 2011, 13, 8359

Recent results on the H_3^+ system: The dynamics at the low energy regime

Tomas González Lezana

*Instituto de Matemáticas y Física Fundamental, Dpto. Física Atómica, Molecular y de Agregados,
CSIC, Spain*

t.gonzalez.lezana@csic.es

Recent investigations on the H_3^+ system and isotopical variants might shed some light about the dynamics of the corresponding reactive processes at the low energy regime. On the one hand studies of the stabilization of $\text{H}^+ + \text{H}_2$ collision complexes reveal deviations from the standard association models based on statistical assumptions and on the separation of the complex formation besides competition afterwards between stabilization and decay [1,2]. However, on the other hand, a statistical quantum study of the $\text{D}^+ + \text{H}_2$ reaction [3] revealed that experimental rate coefficients in terms of the energy [4] can be reproduced theoretically despite previous failures with time independent quantum mechanical approaches [5]. The agreement observed between the statistical predictions and the measured coefficients down to 10^{-3} eV collision energies suggests a complex-forming reaction mechanisms at such low energy regime.

References:

1. D. Gerlich et al. J. Phys. Chem. A, DOI: 10.1021/jp400917v (2013)
2. R. Plasil et al. Philos. Trans. R. Soc. 370, 5066 (2012)
3. T. Gonzalez-Lezana, P. Honvault and Y. Scribano, J. Chem. Phys. (accepted 2013)
4. D. Gerlich Adv. Chem. Phys. 82, 1 (1992)
5. P. Honvault and Y. Scribano, J. Phys. Chem. A, DOI: 10.1021/jp3124549 (2013)

High accuracy quantum description of the chemistry of the early universe

Dario de Fazio

Istituto Metodologie Inorganiche e dei Plasmi del CNR, 00016, Roma, Italy

IKERBASQUE, Basque Foundation for Science, E-48011 Bilbao, Spain

defazio.dario@yahoo.it

Benchmark quantum dynamical calculations are very important to properly understand crossed molecular beam experiments as well as to properly assess dynamical approximations necessary to extend the numerical treatment to more complex systems where exact calculations are too expensive. Moreover, it is the only class of methods which allow for a realistic description of the dynamics at cold and ultra-cold temperatures as those involved in the interstellar medium, where accurate evaluation of quantum effects is critical to describe the dynamics.

In the last thirty years, the development of powerful hyperspherical methods and the fast increase of the computer technology have permitted to solve very efficiently and with high accuracy the time independent Schroedinger nuclear equation for the three bodies reactive problem. In particular the advent of multi-core chips has allowed to build parallel supercomputer machines with hundred thousands computational cores. These machines, when opportunely exploited, permit to calculate reactive observables on a wide range of collision energies, typically covered by the experiments, in few hours of elapsed time. The bottleneck in high accuracy calculations of the reaction dynamics is the calculation of the electronic potential energy surfaces (PESs) where the real accuracy is often very difficult to be predicted, depending from several factors such as the extension of the basis set, the geometries of the points used to generate the fit, the accuracy of the *ab-initio* method used and of the analytical fit. However, efficient dynamical calculations can help the quantum chemistry work, establishing the sensitivity of the dynamics at the different features of the PES, and suggesting new criteria¹ to do quantum chemistry calculations in more efficient ways. These prototypical studies are very important for extend high accuracy calculations at a larger numbers of atoms where the higher number of degree of freedom increase drastically the number of the nuclear geometries to be probed.

In the meeting, the results of our studies in this direction on some prototypical chemical system will be presented. In particular, we have investigated the fast barrier-less reactions of the HeH_2^+ system. Besides being a test case of methods for ion-molecule reactions, this system is also important from the astrophysical point of view. In fact, the exothermic $\text{H} + \text{HeH}^+ \rightarrow \text{He} + \text{H}_2^+$ reaction is considered of great importance² in the chemical network of the early universe evolution, so that the rate constant of this reaction are very important to determinate the abundance of the main molecular species during the gravitational collapse which led to the first stars formation. The small number of electrons involved in this system as well as the development of novel infinite basis set extrapolation techniques,³ permit to perform Born-Oppenheimer quantum chemistry calculations with spectroscopic accuracy (1 cm^{-1}). Moreover, recent experimental data⁴ are available to test the accuracy of the description of the interaction. Reactive observables ranging from differential cross sections to rate constants will be presented for the direct and inverse reactions of this system. The range of the temperatures covered extends from ultra-cold to thermal conditions. Results on several PESs^{1,5} will be analysed and compared⁶ to the experiments to explore the accuracy of the ab-initio methods employed.

References:

1. D. P. Palmieri, C. Puzzarini, V. Aquilanti, et al; *Mol. Phys.*, **98**, (2000) 1835.
2. S. Bovino, M. Tacconi, F.A. Gianturco and D. Galli; *Astronomy & Astrophysic*, **529** (2011) A140.
3. L. Velilla, B. Lepetit, A. Aguado, J. Beswick, and M. Paniagua; *J. Chem. Phys.* **129**, (2008) 084307.
4. X. N. Tang, H. Xu, T. Zhang, et al; *J. Chem. Phys.* **122**, (2005) 164301.
5. C. N. Ramachandran, D. De Fazio, S. Cavalli, et al.; *Chem. Phys. Lett.*, **469**, (2009)
6. D. De Fazio, M. de Castro, A. Aguado, V. Aquilani and S. Cavalli; *J. Chem. Phys.* **137** (2012) 244306

Kepler-Coulomb Sturmian Orbitals and Hyperspherical Harmonics as Building-blocks for Quantum Chemical Applications

Cecilia Coletti

*Dipartimento di Farmacia, Università G. d'Annunzio Chieti-Pescara, Via dei Vestini, 66100
Chieti, Italy*
ccoletti@unich.it

Gaia Grossi

Dipartimento di Chimica, Università di Perugia, Via Elce di Sotto 8, 06100 Perugia, Italy
gaia.grossi@unipg.it

Vincenzo Aquilanti

Università di Perugia, Italy
vincenzoaquilanti@yahoo.it

In the last years, Sturmian orbitals are emerging as an interesting alternative to Slater-type and Gaussian-type orbitals to solve quantum chemistry problems [1,2]. One of their main strengths lies in the complete reciprocity between these basis sets in configuration space and their counterparts in momentum space, hyperspherical harmonics. Because the superposition integrals between these functions can be written as elements of angular momentum algebra and its generalizations [3], they can also be used to connect alternative Sturmian bases, arising from the separation of the hydrogenic Schrödinger equation in different sets of coordinates [4,5]. This provides a most powerful tool to be exploited for building up the most appropriate basis sets to solve multielectron and/or multicenter problems. Moreover, this approach is completely general and can be extended to any dimension, allowing, for instance, the use of alternative basis sets to deal with the d -dimensional hydrogen atom, though the usual tridimensional Sturmians (and the corresponding $O(4)$ hyperspherical harmonics) are most commonly employed in applications.

The quantum mechanics of atoms and molecules can be discussed in terms of the breaking of the hyperspherical symmetry of a d -dimensional hydrogenoid atom, $d=3(N-1)$ for N body Coulomb problems, due to the introduction of further charged particles (electrons and/or nuclei). Thus, in configuration space, Sturmian basis functions can be used as expansion basis sets to build up atomic and molecular orbitals. Additionally, one can choose among alternative hyperspherical harmonics pertaining to different subgroup chain reductions of the original $(d+1)$ -dimensional rotation group and thus possessing different symmetry properties [6].

References:

1. Avery, J.; Avery, J. *Generalized Sturmians and Atomic Spectra*. **2006**, World Scientific, Singapore.
2. Calderini, D.; Cavalli, S.; Coletti, C.; Grossi, G.; Aquilanti, V. *J. Chem. Sci*, **2012**, *124*, 187.
3. Aquilanti, V.; Caligiana, A.; Cavalli, S.; Coletti, C. *Int. J. Quantum Chem*, **2003**, *92*, 212
4. Aquilanti, V., Cavalli, S., Coletti, C. *Chem. Phys. Lett.*, **2001**, *344*, 587
5. Coletti, C.; Calderini, D., Aquilanti, V. *Adv. Quantum. Chem.*, in press
6. Aquilanti, V.; Cavalli, S.; Coletti, C.; Di Domenico, D.; Grossi, G. *Int Rev Phys Chem*, **2001**, *40*, 673

New insights into the semiclassical Wigner treatment of photodissociation dynamics

L. Bonnet

Univ. Bordeaux, CNRS, ISM, UMR 5255, Talence, France

l.bonnet@ism.u-bordeaux1.fr

Soon after the discovery of quantum mechanics, it was realized that for nuclei, the space-time propagator and stationary states may be well described by semiclassical expressions involving parameters calculated along specific classical paths. Since Hamilton equations, from which the previous paths are obtained, are much easier to solve than Schrödinger equation, the development of semiclassical methods in spectroscopy and dynamics became a central, still topical, issue.

In the field of photodissociation dynamics, Heller and co-workers proposed in the early eighties an original and elegant method of this type, called semiclassical Wigner, in order to predict state-resolved absorption cross sections measured in molecular beam experiments [1]. The method combines quantum and classical mechanics in a very natural way through the use of Wigner distributions to weight initial and final phase space states. However, the original method did not include rotation motions and could not be used to study photodissociations in realistic conditions.

We have recently solved this issue [2], and the goal of the seminar is to present the main lines of our approach as well as its application to a triatomic-like model of methyl iodide photodissociation. Important next steps are the extension of the method to photodissociations involving non adiabatic transitions and/or polyatomic species, and bimolecular collisions of the same type.

References:

1. E. J. Heller, J. Chem. Phys. 68, 2066 (1978) ; R. C. Brown and E. J. Heller, J. Chem. Phys. 75, 186 (1981).
2. W. Arbelo-Gonzalez, L. Bonnet and A. Garcia-Vela, Phys. Chem. Chem. Phys. 15, 9994 (2013)

New theoretical method for calculating the radiative association cross section of a triatomic molecule: Application to N_2H^-

T. Stoecklin

Institut des Sciences Moléculaire, UMR5255-CNRS, Université de Bordeaux, 351 cours de la Libération, 33405 Talence Cedex, France

F. Lique

LOMC - UMR 6294, CNRS-Université du Havre, 25 rue Philippe Lebon, BP 540, 76058, Le Havre, France

M. Hochlaf

Université Paris-Est, Laboratoire Modélisation et Simulation Multi Echelle, MSME UMR 8208 CNRS, 5 bd Descartes, 77454 Marne-la-Vallée, France
t.stoecklin@ism.u-bordeaux1.fr

Radiative association in ion-molecule collisions is considered to be an important step of the synthesis of polyatomic species in interstellar clouds [1]. The cosmic rays ionise the atoms and the molecules which can then recombine by radiative association to produce new molecules. About 14 positive ions have been detected in the Interstellar Medium as well as several carbon chain anions. However, whereas the radiative association of diatomic molecules is the object of many theoretical [2] studies the radiative association of a triatomic molecule has up to very recently not received much interest compared to photodissociation. The main reason of this lack of studies is the experimental difficulty to measure these cross sections. The first Close Coupling study of radiative association of a triatomic molecule was done in 2011 by Ayouz et al [3] for the H_3^- anion while a previous study was done by Mrugala et al [4] for $He-H_2$ using the CC-BF-diabatic approach.

We present here a new method [5] to treat the atom diatom radiative association within a time independent approach. This method is an adaptation of the driven equations method developed for photodissociation.

In the second part of this paper, this approach is applied to the radiative association of the N_2H^- anion. The bound states energies and wave functions of this anion which we calculated exactly in a recent study [6] are used to propagate the overlap with the initial scattering wave function. The main features of the radiative association cross sections are analysed and the magnitude of the calculated rate coefficient at 10 k is used to discuss the existence of the N_2H^- in the interstellar medium which could be used as a tracer of both N_2 and H^- .

References:

1. Bates, D. R., Herbst E., in 'Rate coefficients in Astrochemistry', T. J. Millar, D. A. Williams editors, Kluwer Academic, Dordrecht 1998, p 17
2. Bennett O. J., Dickinson A. S., Leininger T. and Gadea F. X. Mon. Not. R. Astron. Soc., 2003, 341, 361.
3. M. Ayouz M., Lopes R., Raoult M., Dulieu O., and Kokoouline V., Phys. Rev. A., 2011 83, 052712.
4. Mrugala F., Spirko V. and Kraemer W. P., J. Chem. Phys., 2003, 118, 10547
5. Stoecklin T., Lique F., Hochlaf M., arXiv:1303.1114
6. Lique F., Halvick P., Stoecklin T. and Hochlaf M., J. Chem. Phys. 2012, 138, 244302

□ Poster:

Detailed Complex Angular Momentum (CAM) Analysis of Resonances in the F+HD Reaction

D. Sokolovski

*Department of Physical Chemistry, University of the Basque Country, Leioa, 48940, Spain,
IKERBASQUE, Basque Foundation for Science, E-48011 Bilbao, Spain
dmitri.sokolovski@ehu.es*

C. Echeverría-Arrondo

IKERBASQUE, Basque Foundation for Science, E-48011 Bilbao, Spain

E. Akhmatskaya

Basque Center for Applied Mathematics (BCAM), Bilbao, Bizkaia, Spain

D. De Fazio

*Istituto Metodologie Inorganiche e dei Plasmi del CNR, 00016, Roma, Italy
IKERBASQUE, Basque Foundation for Science, E-48011 Bilbao, Spain*

We analyse in detail the resonance effects in the differential (DCS) and integral (ICS) cross sections of the state-to-state F+HD($v=0, j=0$) \rightarrow FH($v'=3, j'=0$) + D reaction, in the collision energy range 80-200 meV. We found many such resonances just above the reaction threshold. The reaction dynamics was studied on the FXZ potential energy surface [1]. The Regge trajectories are obtained with help of the PADEII code [2]. The CAM technique of [3] was used for the semiclassical analysis of the DCS. Mulholland decomposition of [4] and [5] was employed to assign the peaks in the ICS to resonant Regge trajectories.

References:

1. B. Fu, X. Xu and D. H. Zhang, *J. Chem. Phys.*, **129**, 011103 (2008).
2. D. Sokolovski and E. Akhmatskaya, *Comp. Phys. Comm.*, **182**, 448 (2011).
3. D. Sokolovski and A. Z. Msezane, *Phys. Rev. A*, **70**, 032710 (2004).
4. J. H. Macek, P. S. Krstic, and S. Yu. Ovchinnikov, *Phys. Rev. Lett.* **93**, 183203 (2004).
5. D. Sokolovski, D. De Fazio, S. Cavalli and V. Aquilant, *J. Chem. Phys.*, **126**, 121101 (2007).

□ List of Attendees:

1. Aquilanti Vincenzo, vincenzoaquilanti@yahoo.it
2. Akhmatkaya Elena, akhmatkaya@bcamath.org
3. Bonnet Laurent, l.bonnet@ism.u-bordeaux1.fr
4. Coletti Cecilia, ccoletti@unich.it
5. De Fazio, Dario, defazio.dario@yahoo.it
6. Echeverría-Arrondo Carlos, carlos.echeverria@terra.com
7. González Miguel, miguel.gonzalez@ub.edu
8. González-Lezana Tomás, t.gonzalez-lezana@csic.es
9. Larregaray Pascal, p.larregaray@ism.u-bordeaux1.fr
10. Sokolovski Dmitri, dmitri.sokolovski@ehu.es
11. Stoecklin Thierry, t.stoecklin@ism.u-bordeaux1.fr