

Excited states from small molecules to more complex systems

April 2014 – Université Paris-Est Marne-la-Vallée

Organizer1

Navizet Isabelle

Université Paris-Est Marne-la-Vallée

navizet@univ-mlv.fr

Organizer2

Ferré Nicolas

Université d'Aix-Marseille

Nicolas.ferre@univ-amu.fr

Organizer3

Valérie Brenner

CEA Saclay

Valerie.brenner@cea.fr

1. Proposal

1.1 Introduction and motivation

The quantum chemical description of the excited electronic states is important in order to study light-driven processes, chemi- or bioluminescent molecular systems, non-adiabatic reaction paths involving states crossings like conical intersections, electronic spectroscopic properties, but also electric and magnetic properties of organic and inorganic materials.

The accurate calculation of several excited states potential energy surfaces with the same precision is still one of the most difficult tasks in modern electronic-structure theory.

Such a challenge requires specialized and versatile computational packages. Among them, MOLCAS features some unique codes for describing both the static and dynamic electronic correlation using multi-reference and multi-configurational wavefunction calculations.

We aim to take the opportunity that Prof. Roland Lindh, one of the principal developers of the MOLCAS program, is invited for one month at the University Paris-Est Marne-la-Vallée to gather around him French developers and users of the MOLCAS program. Such a meeting will promote the exchange of new ideas and techniques between MOLCAS developers and users, with particular interest for some of the features used in the French quantum chemistry community.

1.2 State of the art

.....
The basic philosophy behind MOLCAS is to develop methods and programs that will allow an accurate *ab initio* treatment of very general electronic structure problems for molecular systems in both ground and excited states.

MOLCAS contains a number of modules that can perform single reference calculations (Perturbation theory, Coupled Cluster...). These methods, along with Kohn-Sham Density Functional Theory, treat the electron correlation starting from a single determinant reference state. When this simple approach is no more suitable, e.g. in excited states, transition states, magnetic systems, or heavy metal systems, MOLCAS offers a unique set of state-of-the-art multi-configurational SCF methods. Using the concept of active spaces, the Complete/Restricted Active Space SCF approaches can efficiently deal with the static correlation problem in many electronic states in a balanced way. At a later stage, the dynamic correlation effects are added to multi-configurational wavefunctions and energies, using the second order perturbation theory (CASPT2). Other methods like Multi-Reference Configuration Interaction, Density-Matrix Renormalization Group theory, ... complete the list of post-Hartree-Fock methods available for modeling quantum mechanically virtually any molecular system. While these methods are traditionally limited to small molecules due to their high computational costs, the size of the systems that can be studied has been increased by the introduction of the Resolution of Identity and Cholesky decomposition of the two-electron integrals and by an intense effort toward efficient parallelization of the modules. The interface with the Molecular Mechanics code TINKER implemented in MOLCAS by Nicolas Ferré (Aix-Marseille Université) allows to take into account

steric and electrostatic interactions with the environment (aka hybrid QM/MM calculations, recently acknowledged by the 2013 Nobel Prize in Chemistry awarded to Karplus, Levitt and Warshel). In order to include relativistic effects in the calculations, spin-Orbit (SO) effects can also be calculated.

Among many others, here are some examples of the state-of-the-art applications of these methods in the French community.

- QM/MM calculations of the emitted light of firefly bioluminescent systems at the CASPT2//AMBER level have shown the importance of the H-bond network in the cavity of the enzyme (Marne-la-Vallée, Marseille, Orsay).
- Electronic spectroscopy of various molecular systems, e.g. effects of the intercalation of transition metal complexes in DNA (Strasbourg).
- Electronic dynamics of biomolecules. Determination of relaxation mechanisms of the excited states (CEA).
- Multi-configurational calculations of electronic and magnetic properties of organic and inorganic materials, e.g. Single Molecule Magnets (Toulouse, Rennes, Strasbourg). Parametrization of effective Hamiltonians (Toulouse).
- Spectroscopy of actinide and lanthanide compounds, taking into account solvent effects (Lille).
- Determination of very accurate potential energy surfaces for quantum dynamics simulations (Marne-La-Vallée, Bordeaux, Marseille).

1.3 Objectives

The aim of this Discussion meeting is to gather developers and users of the MOLCAS program, as long as researchers interested to use it or willing to see new implementations in the program, in order to:

- Expose to the French community the new possibilities of the program.
- Allow users to share experiences and difficulties
- Give feedback from the users to the developers of wished new developments and alternatives programs to use.
- Discuss the generalization of “home-made” add-ons to MOLCAS.
- Form and identify the community of MOLCAS users in France.

1.4 Participant List

Isabelle NAVIZET (navizet@univ-mlv.fr)

Valérie BRENNER (valerie.brenner@cea.fr)

Nicolas FERRE (nicolas.ferre@univ-amu.fr)

Roland LINDH (roland.lindh@kemi.uu.se)

Majdi HOCHLAF (hochlaf@univ-mlv.fr)

Gilberte CHAMBAUD (gilberte.chambaud@univ-mlv.fr)

Roberto LINGUERRI (roberto.linguerr@univ-mlv.fr)
Nadia BEN AMOR (benamor@irsamc.ups-tlse.fr)
Nathalie GUIHERY (nathalie@irsamc.ups-tlse.fr)
Nicolas SUAUD (suaud@irsamc.ups-tlse.fr)
Valérie VALLET (valerie.vallet@univ-lille1.fr)
Boris LE GUENNIC (boris.leguennic@univ-rennes1.fr)
Mickaël KEPENEKIAN (mikael.kepenekian@univ-rennes1.fr)
Chantal DANIEL (c.daniel@unistra.fr)
Etienne GINDENSBERGER (egindensperger@unistra.fr)
Julien ENG (jeng@unistra.fr)
Béatrice BUSSERY-HONVAULT (beatrice.honvault@u-bourgogne.fr)
Shu-Feng CHEN (shufeng.chen@u-psud.fr)

2. **Financial Support**

The meeting will be held on two days in April 2014.

The CFCAM financial support will cover:

Refreshments served at the coffee break	100 euros
Lunches for 2 days	350 euros
Dinner	550 euros
Travelling for participants outside Paris	2200 euros
One night hotel for participants outside Paris	1100 euros
Logistics: communication material	100 euros
TOTAL	4400 euros

Therefore we request the CFCAM to fund the meeting with a grant about 4400 euros.