Bastien Mussard

My research consists in developments in electronic structure of molecular and solid systems. A part of my part focuses in the description of **London dispersion forces** in Density Functional Theory (**DFT**) in the context of **range-separated theories** coupled with the Random Phase Approximation (**RPA**). I have more recently been working in Quantum Monte-Carlo (**QMC**) and implementing in the **CHAMP** software. I currently am working on implementations of efficient **multi-reference perturbation theory (MRPT)** for applications to systems of interest in biological processes and energy conversion and storage.

Post-doctoral position

Department of Chemisty and Biochemistry
University of Colorado at Boulder, Boulder, CO, USA
Contact : sandeep.sharma@colorado.edu

Post-doctoral position

Institut des Sciences du Calcul et des Données and Laboratoire de Chimie Théorique
Université Pierre et Marie Curie, Paris, France
Contact : julien.toulouse@upmc.fr

Visit (1 month) to the Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, USA.
Contact : CyrusUmrigar@cornell.edu

PhD. in Theoretical Chemistry

Modelisation of London dispersion forces by random phase approximation (RPA) : methodological developments , under the supervison of J. G. Ángyán, S. Lebègue
Laboratoire of Cristallographie, Résonnance Magnétique et Modélisation
Université de Lorraine, Nancy, France
Contact : janos.angyan@univ-lorraine.fr

Defense on the 13th of december, 2013

Visit (3 months) to the Kémiai Intézet, Eötvös Loránd Tudományegyetem, Budapest, Hungaria.
Contact : szalay@chem.elte.hu

Master of Analytical, Physical and Theoretical Chemistry - Theoretical branch

École Normale Supérieure and Université Pierre et Marie Curie, Paris, France

Internship : (6 months) | **Implementation and Test of Valence Bond Wavefunction for Quantum Monte-Carlo** , under the supervision of B. Braida and J. Toulouse.
Laboratoire de Chimie Théorique, Université Pierre et Marie Curie, Paris, France
Contact : benoit.braida@upmc.fr ; julien.toulouse@upmc.fr

Internship : (6 months) | **Electrostatic Potential Derived Atomic Charges For Periodic Systems Using A Modified Error Functional** , under the supervision of T. Woo.
Centre for Catalysis Research and Innovation, University of Ottawa, Ottawa, Canada
Contact : twoo@uottawa.ca

Bachelor of Science - Chemistry

École Normale Supérieure and Université Pierre et Marie Curie, Paris, France

Internship : (2 months) | **Studies of the Intrusion of Water in Confined Hydrophobic Environment via Monte-Carlo Simulations** , under the supervision of F. Cailliez.
Équipe Simulation Moléculaire, École Nationale Supérieure de Chimie de Paris, Paris, France
Contact : fabien.cailliez@u-psud.fr

Skills

- Unix/Linux, Bash, LaTeX
- F77/F90, Python, Mathematica, parallel code
- Code management, in-depth use of GIT
- Use of clusters for calculations
- Developments in the `MOLPRO` commercial package
- Developments in the `CHAMP` package
- Developments of personal packages
- Interfaces between packages

Teaching and Outreach Activities

Teacher Assistant at Université de Lorraine (2010 - 2013)
PACES (translates to : Common First Year for Medical Studies) - Faculté de Médecine - 64h/year
<u>Contact</u> : virginie.pichon@univ-lorraine.fr

Stands of Quantum Chemistry (2014 - 2015)
at the "Fête de la Science" (Science Festival) of the Université Pierre et Marie Curie, Paris, France.

Publications [ResearcherID] [ORCID] [arXiv] [HAL] [GoogleScholar] [ResearchGate] [Academia]

11. A. Buksztel, O. Franck, I. Grabowski, E. Luppi, **B. Mussard**, S. Smiga, J. Toulouse, *Self-consistent double-hybrid density-functional theory using the optimized-effective-potential method.* J. Chem. Phys. *145* 144102 (2016) [doi]

10. **B. Mussard**, J. Toulouse, *Fractional-charge and fractional-spin errors in range-separated density-functional theory.* Mol. Phys. *115* 161 (2017) [doi]

9. E. Coccia, **B. Mussard**, M. Labeye, J. Caillat, R. Taieb, J. Toulouse, E. Luppi, *Gaussian continuum basis functions for calculating high-harmonic generation spectra.* Int. J. Quantum Chem. *116* 1120 (2016) [doi]

8. **B.Mussard**, D. Rocca, G. Jansen, J.G. Ángyán, *Dielectric matrix formulation of correlation energies in the Random Phase Approximation (RPA) : inclusion of exchange effects.* J. Chem. Theory Comput. *12* 2191 (2016) [doi]

7. **B.Mussard**, J.G. Ángyán, *Local Random Phase Approximation with Projected Oscillator Orbitals.* Theo. Chem. Acc. *134* 1 (2015) [doi1]
and *Chapter* in Péter R. Surján : A Festschrift from Theoretical Chemistry Account 99 (2015) [doi2]

6. **B.Mussard**, P. Reinhardt, J.G. Ángyán, J. Toulouse, *Spin-unrestricted random-phase approximation with range separation : Benchmark on atomisation energies and energy barrier heights.* J. Chem. Phys. *142* 154123 (2015) [doi]

5. O. Franck, **B.Mussard**, E. Luppi, J. Toulouse *Basis convergence of range-separated density-functional theory.* J. Chem. Phys. *142* 074107 (2015) [doi]

4. **B.Mussard**, J.G. Ángyán *Relationships between charge density response functions, exchange holes and localized orbitals.* Comp. Theor. Chem. *1053* 44 (2015) [doi]

3. **B.Mussard**, P. Szalay, J.G. Ángyán, *Analytical Energy Gradients in Range-Separated Hybrid Density Functional Theory with Random Phase Approximation.* J. Chem. Theory Comput. *10* 1968 (2014) [doi]

2. E. Chermak, **B.Mussard**, J.G. Ángyán, P. Reinhardt, *Short-range DFT combined with long-range local RPA within a range-separated hybrid DFT framework.*, Chem. Phys. Lett. *552* 132 (2012) [doi]

1. C. Campañá, **B.Mussard**, T.K. Woo, *Electrostatic Potential Derived Atomic Charges for Periodic Systems Using a Modified Error Functional : REPEAT Charges.*, J. Chem. Theory Comput. *5* 2866 (2009) [doi]

Key Oral Communications

- *Fractional-charge and Fractional-spin errors in Range-Separated Density-Functional Theory with Random Phase Approximation.* General meeting of GdR "REST", Roscoff, France, 2016

- *Random Phase Approximation with Fractional Charge and Fractional Spin.*
  Kick-off "MCFUNEX" meeting, Strasbourg, France, 2016

- *Range-Separated Random Phase Approximations.*
  Workshop "Advances in electronic structure theory", Paris, France, 2015
  General meeting of the GdR "CORREL", Marseille, France, 2015

- *MOLPRO : overview and challenges.*
  Meeting CECAM "Dévelop$^{\text{t}}$ de codes de chimie théorique dans un env. HPC", Paris, France, 2015

- *Analytical Gradients of Random Phase Approximation correlation energies in a Range-Separated-Hybrid context : Theory and implementation.*
  General meeting of the GdR "CORREL", Paris, France, 2013

- *Analytical Gradients for the Range-Separated Random Phase Approximation Correlation Energies Using a Lagrangian Framework.*
  9th "Rencontre des Chimistes Théoriciens du Grand-Est", Moussy, France, 2013

- *Random Phase Approximation step by step.*
  (Seminar) Kémiai Intézet, Eötvös Loránd Tudományegyetem, Budapest, Hungaria, 2012

Research

Multi-reference Perturbation Theory (work in progress)
I have implemented a fully internally contracted version of multi-reference perturbation theories (NEVPT2/MRLC in a program interfaced with PySCF. The implementation of both the density fitting approximation for the integrals and the cumulant approximation for the high-order reduced density matrix involved in the equations allows the treatment of larger systems of interest.

Evaluation of determinant in Quantum Monte-Carlo (work in progress)
I started working on the efficient evaluation of a great number of determinants using the determinant lemma of the Sherman-Morrison-Woodbury formula, both for the Quantum Monte-Carlo steps and for the optimisation of the wave-function. This is a collaboration, at the LCT, with Cyrus Umrigar from the Cornell University and the implementation is done in the `CHAMP` software.

Implementation in the `MOLPRO` package
Since February, 2014, I have been, among other things, in charge of the management and support at the Laboratoire de Chimie Théorique at the Université Pierre et Marie Curie of the `MOLPRO` package, and in particular of the part of the package where the LCT team develops the RPA code. I unified and documented different pre-existing developments and also improved the performance of the code (memory management, CPU time of the transformation of bi-electronic integrals, etc). I implemented all the necessary tools to the ongoing projects, such as the generalization to open-shell systems and the calculations using fractional occupation numbers.

Fractional occupation numbers (see doi)
To better understand the RPA properties, a study of calculations with fractional occupation numbers has been initiated. This type of analysis allows one to estimate how a method handles the N-electrons self-interaction error, or, more accurately, the delocalization error. Some early implementation in the `MOLPRO` package yields interesting results useful to compare the behavior of different RPA approximations.

High-harmonic generation spectra (see [doi])
We explored the computation of high-harmonic generation spectra in atoms by means of Gaussian basis sets in time-dependent close coupling approaches. We investigated the efficiency of Gaussian functions specifically designed for the description of the continuum proposed by Kaufmann *et al.*; we notably studied the effect of increasing the basis set cardinal number, the number of diffuse basis functions, and the number of Gaussian pseudo-continuum basis functions for various laser parameters. Our results show that the

latter significantly improve the description of the low-lying continuum states, and provide a satisfactory agreement with grid calculations.

RPA formalisms (see [doi])
I worked on the different formalisms in which the RPA equations can be derived. I in particular explored in a systematic and new way the formalism called "dielectric matrix formalism". The examination and comparison of the different RPA formalisms reveals the underlying unity between them and allows to obtain crucial information about the nature of the approximations that are made during the a priori very different derivations. I implemented this dielectric matrix formalism and the various approximations that can be made in this context in the `MOLPRO` package, including a new Clenshaw-Curtis quadrature for the integration over the frequency dimension.

Local orbitals (see [doi])
The use of local orbitals is one of the path that can be taken to reduce the computational cost of RPA calculations. I studied the virtual localized orbitals that are the "projected oscillatory orbitals" (POO), an original idea of Boys that has not been developped in the litterature. The basic equations concerning the POO have been derived during my thesis, including multipolar expansions of the bi-electronic integrals in the basis of the POO; it has also been shown that the matrix elements of the dipolar moment between an occupied localized orbital and a POO virtual localized orbital reduces to the expression of the overlap between two POOs. This non-trivial result vastly simplifies the RPA equations that can be written in the POO basis.

Spin-unrestricted generalization (see [doi])
To widen the field of applications of our RPA methods, the derivations of most of the formalisms have been generalized to open shell systems and this has been implemented in the `MOLPRO` package. Extended tests on datasets of atomisation energies (AE49) and of barrier heights energies (BH24) showed the excellent performance of a version of RPA with exchange called "SO2" when it is used in a range separation context. This variant was previously already known to have good performances on the S22 dataset, but this kind of generalizations and extensions of application field allows to better grasp the roots of the relative qualities of the different versions of RPA.

Basis convergence (see [doi])
Among the advantages of the use of range separation methods, one finds that in this context the wavefunction part on a calculation is no more burdened by the treatment of the electron-electron coalescence and it is then expected that the convergence of the calculations with respect to the size of the gaussian basis set be better. A new study of the convergence of range-separated calculations allowed us to show, on the one hand, the exponential convergence of the quality of the expansion called "partial-wave" of the long-range wavefunction at the electron-electron coalescence with respect to the angular momentum of the expansion and, on the other hand, the also exponential convergence of the error made on the total RSH+MP2 energy with respect to the cardinal number of the Dunning basis. Based on these observations, we proposed an extrapolation method for the total energy of range-separated calculations.

Direct space (see [doi])
Another axis of research is to work on functions such as the response functions, that are found when doing RPA calculations, by considering explicitly their dependance to the real space variables. In my thesis I created tools to calculate these functions on parallelepipedic real space grids, and on so-called "DFT-type" grids. A long-term goal could be the generation of grids such as to better sample the space *between* the atoms.

Gradients of the RPA correlation energy (see [doi])
I derived the equations allowing to compute the analytical gradients of the RPA correlation energies in the context of range separation. The formalism that was developped, which uses the lagrangian technique, allows an all-in-one derivation of the short- and long-range terms that emerge in the expressions of the gradient. These terms show interesting parallels. The equations were implemented in the `MOLPRO` package, and this now allows to perform geometry optimisation at the RSH-RPA levels, and to obtain dipoles calculated at the RSH-RPA levels.