Bastien Mussard

My research consists in developments in electronic structure of molecular systems. There are two fundamental aspects to my work. On the one hand, my approach is analytic and theoretical and consists in developing new methods and approximations. On the other hand, an integral part of my work is technical and is concerned with implementing these developments in widely used quantum chemistry packages.

My work has branched into three main parts which are intimatly linked :

- I have been focused 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 most currently am working on implementations of efficient **multi-reference calculations**, most notably using **semistochastic heat-bath configuration interaction (SHCI)** and **multi-reference perturbation theory (MRPT)** for applications to systems of interest in biological processes and energy conversion and storage.

Main information in one glance

30 ans

Education : 2009-2010 Master at École Normale Supérieure, Paris, France
2011-2013 PhD at Université de Lorraine, Nancy, France
2014-2016 Post-doc at Université Pierre et Marie Curie, Paris, France
2017 Post-doc at University of Colorado at Boulder, CO, U.S.A.

14 publications, 8 as first author

Skills

- Unix/Linux, Bash, LaTeX
- F77/F90, C/C++, Python, Mathematica
- Parallel codes
- Code management, in-depth use of GIT
- Use of clusters for calculations

Softwares contributions

- `Molpro` commercial package [link]
- `CHAMP` package [link]
- `Dice` package [link]
- Developments of personal packages
- Interfaces between packages

Contact

Sandeep Sharma's group
University of Colorado at Boulder, CO, U.S.A.
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Main coworkers

- Julien Toulouse [link]
- János G. Ángyán [link]
- Cyrus J. Umrigar [link]
- Sandeep Sharma [link]

Post-doctoral position (2017 Current position)

Sandeep Sharma's group
Department of Chemisty and Biochemistry
University of Colorado at Boulder, CO, U.S.A.
Contact : sandeep.sharma@colorado.edu

Post-doctoral position (2014-2016)

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, U.S.A.
Contact : CyrusUmrigar@cornell.edu

PhD. in Theoretical Chemistry (2011-2013)

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

Reviewers : Benoit Champagne (Université de Namur, Namur, Belgium), Andreas Savin (Université Pierre et Marie Curie, Paris, France)
Thesis committee : Xavier Assfeld (Université de Lorraine, Nancy, France), Georg Jansen (Universität Duisburg-Essen, Essen, Germany), Peter Reinhardt (Université Pierre et Marie Curie, Paris, France), Ágnes Szabados (Eötvös Loránd Tudományegyetem, Budapest, Hungaria), János Ángyán (Université de Lorraine, Nancy, France), Sébastien Lebegue (Université de Lorraine, Nancy, France)

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

Master of Analytical, Physical and Theoretical Chemistry (2009-2010)

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 (2006-2008)

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

Publications

14. **B. Mussard**, S. Sharma *One-step treatment of spin-orbit coupling and electron correlation in large active spaces* J. Chem. Theory Comput. (submitted) [arxiv]
13. J. E. T. Smith, **B. Mussard**, A. A. Holmes, S. Sharma, *Cheap and near exact CASSCF with large active spaces* J. Chem. Theory Comput. (2017) ***Editors' Choice for 2017*** [doi]
12. **B. Mussard**, E. Coccia, R. Assaraf, M. Otten, C.J. Umrigar, J. Toulouse, *Time-Dependent Linear-Response Variational Monte Carlo.* Adv. Quantum Chem. (2017) [doi]
11. **B. Mussard**, J. Toulouse, *Fractional-charge and fractional-spin errors in range-separated density-functional theory.* Mol. Phys. *115* 161 (2017) [doi]
10. S. Śmiga, O. Franck, **B. Mussard**, A. Buksztel, I. Grabowski, E. Luppi, J. Toulouse, *Self-consistent double-hybrid density-functional theory using the optimized-effective-potential method.* J. Chem. Phys. *145* 144102 (2016) [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]

Teaching and Outreach Activities

Teacher Assistant at Université de Lorraine (2011 - 2013)
PACES (translates to : Common First Year for Medical Studies) - Faculté de Médecine - 64h/year
Contact : 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.

Key Oral Communications

- **Cheap and near exact calculations with large active spaces.**
  -Laboratoire de Chimie Théorique, ENS Lyon, France, Octobre 2017
  -Laboratoire Modélisation et Simulation Multi-Échelle, Marne-la-Vallée, France, Octobre 2017
  -Laboratoire de Physique des Lasers, Atomes et Molécules, Lille, France, Octobre 2017
  -CEISAM, Nantes, France, Octobre 2017
  -ISM Theoretical Chemistry and Modeling Group, Bordeaux, France, Octobre 2017
  -Laboratoire de Chimie Quantique, Strasbourg, France, Octobre 2017
  -Chimie Théorique et Modèles, Marseille, France, Octobre 2017
- **Time-dependent linear-response variational Monte Carlo.**
  Stochastic Methods in Electronic Structure Theory, Telluride, Colorado, 2017
- **Multireference Perturbation Theory using extended active space wavefunctions.**
  XLIII Congress of Theoretical Chemists of Latin Expression, Paris, France, 2017
- **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^{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

Multireference methods (see [arxiv] and [arxiv])
I have most lately been involved in a number of developments of new features for the recently-introduced heat-bath configuration interaction (HCI) and its semistochastic extension. This algorithm was proven to successfully prune the large Hilbert space to retain the most important determinants regardless of their excitation distance to a reference determinant, allowing calculations with large active spaces. A self-consistent field method, called HCISCF, was devised and we showed the SHCI convergence is greatly improved by the use of the optimized orbitals. We also extended the algorithm to include relativistic effects treated on an equal footing with the electron correlation, with large active spaces.

Implementation in the `MOLPRO` package
From 2014 to 2016, I have been among other things in charge of the management and support of the `MOLPRO` package at the Laboratoire de Chimie Théorique at the Université Pierre et Marie Curie, 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 improved the performance of the code (memory management, 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.

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 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 literature. 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 expects the convergence of the calculations with respect to the size of the gaussian basis set to be faster since the long-range wavefunction is freed form the treatment of the electron-electron coalescence. Indeed, we showed, on the one hand, the exponential convergence of the quality of the partial-wave expansion 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.

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.