Idex Sorbonne Universités
Pour l'Enseignement et la Recherche (SUPER)
Labex Calsimlab

Formulaire de soumission 2016-19

Projet doctoral ou post-doctoral

*L'appel à proposition est ouvert **jusqu'au 1er octobre 2016** pour les projets doctoraux et **jusqu'au 1er juin 2019** pour les projets postdoctoraux. Les porteurs de projet sont invités à contacter la coordination du labex pour toute question relative à l'appel à projets.*

Les demandes devront être adressées, avec l'ensemble des pièces justificatives sous forme d'archive, par voie électronique (rubrique Soumettre un projet*):*

http://ics.sorbonne-universites.fr/acces-direct/appels-a-projets/labex-calsimlab.html

*Les fichiers archive seront nommés : **ICS_Nom_du_porteur.[zip,gz,tgz,pdf]***

Un accusé de réception faisant foi du dépôt sera envoyé par retour électronique.

Les demandes seront examinées par les membres du comité de pilotage du labex et des experts extérieurs. La sélection des dossiers interviendra lors de la prochaine réunion trimestrielle du comité de pilotage du labex.

Nature du projet

Contrat doctoral ☐ Contrat post-doctoral ☒

Titre du Projet

Development of efficient 3D shape optimization techniques for the research of Maximum Probability Domains from accurate quantum chemistry wavefunctions

Domaine de recherche (mots-clés):

Porteurs du Projet

Nom et Prénom des porteurs du Projet	Unité, Laboratoire ou structure d'affiliation	Email des porteurs	Coordonnées téléphoniques

Benoît BRAÏDA	LCT	benoit.braida@upmc.fr	01 44 27 96 57
Charles DAPOGNY	LJK	charles.dapogny@univ-grenoble-alpes.fr	01 44 27 27 21
Pascal FREY	LJLL	pascal.frey@upmc.fr	01 44 27 51 02
Yannick PRIVAT	LJLL	yannick.privat@upmc.fr	01 44 27 54 07

N.B. : Les projets de thèse doivent impliquer deux co-directeurs de deux disciplines distinctes. Il est possible de déposer un projet interdisciplinaire ou à l'interface de deux disciplines avec un seul porteur. L'institut aidera le porteur du projet à identifier un co-responsable de la discipline concernée, pour finaliser le projet avant sa soumission devant le comité de pilotage du labex.

Dans le cas où l'étudiant de master est identifié au moment de soumettre la demande, joindre son CV avec mention de leur inscription dans un master de Sorbonne Universités ou d'une autre tutelle.

Résumé du Projet

2 pages maximum – interligne simple (2 000 caractères maximum)
La description du projet détaillera le contexte, l'objectif scientifique, les collaborations interdisciplinaires ou aux interfaces et le profil de l'étudiant.

Maximum Probability Domains (MPDs) are defined as regions of space where the probability of finding a given number of electrons is maximal. As the quantum theory is probabilistic in nature, this original proposition of Andreas Savin (Laboratoire de Chimie Théorique - LCT) appears as the most natural way to extract chemical information from accurate quantum calculations. Therefore, despite the fact that its development is still ongoing and the lack of large-scale numerical program to perform the needed calculations, the MPD method starts to arouse a strong interest among the chemical community.[1] MPDs overcome the limitations and shortcomings of widely used topological methods and can shed new light on the nature of chemical bonding.[2]

The first implementations of the MPD method suffered from severe restrictions. They were limited to the analysis of single-determinant wave functions, while correlated wave functions are essential in many interesting chemical situations. These simple algorithms, which notably relied on fixed cubic grids, give rise to numerical inaccuracies which cloud the properties of MPDs, and limit the efficiency of the search for maximum probability domains.

This is why a collaboration between Andreas Savin and Benoît Braïda (LCT), and Pascal Frey (Laboratoire Jacques-Louis Lyons - LJLL) including also Eric Cancès (CERMICS) has been initiated around this topic. The recent post-doctoral stay (1 year) of Jeremy Dalphin allowed very lately to make two fundamental theoretical advances:[3]

- The derivation of an algorithm potentially allowing fast calculations of probabilities and shape-derivatives on multi-determinant wave functions, which is also suitable for parallelization ;
- The derivation of an expression for the computation of second order shape derivatives.

Meanwhile, a joined development of a new-generation MPD program has started and now involves the Quantum Chemistry Group of Ghent university (thesis of Guillaume Acke), built around the advanced adaptative mesh techniques developed in the LJLL, and an adaptation of the level-set algorithm for the 3D MPDs search problem.[4,5]

The prospective candidate may work on the following applied mathematical aspects in the continuation of this project, by order of priority:

- Implementation of the probability and shape-derivative calculations for multi-determinant wave functions (QZ-algorithm, p14 of Annexe 1) ;
- Implementation of the second-order shape derivative for the characterization of these domains (critical points characterization, definition of a volume-based chemical hardness) ;
- Algorithm improvement: possibly the development of a Newton-type algorithm making use of the recently derived second-order shape derivative ;
- Numerical analysis for accuracy control of the optimization procedure.

Candidates should have a solid background in numerical methods including shape optimization techniques and 3D numerical simulations techniques, together with good programing experience and skills in C language.

(1) Recent publications on the field: (a) Mafra Lopez Jr., O. ; Braïda, B. ; Causa, M. ; Savin, A. in Progress in Theoretical Chemistry and Physics, vol 22, ed Hoggan, Springer UK, London (**2011**). (b) Causa, M ; Savin, A (**2011**) Z. Anorg. Allg. Chem. 637, 882 (c) Causa, M ; Savin, A (**2011**) J. Phys. Chem. A. 115, 45, 13139 (d) Causa, M ; D'Amore, M ; Garzillo, C ; Gentile, FS ; Savin, A (**2013**) in Applications of Density Functional Theory to Biological and Bioinorganic Chemistry, Structure and Bonding Volume 150, p119-141 (e) Menendez, M. ; Pendas, A. M. (**2014**) Theor. Chem. Acc. 133:1539 (f) Menendez, M. ; Pendas, A. M. ; Braïda, B.; Savin, A. (**2015**) Comput. Theor. Chem. 1053, 142 (g) Agostini, F. ; Ciccotti, G. ; Savin, A. (**2015**) J. Chem. Phys. 142, 6 (h) Causa, M ; D'Amore, M ; Gentile, F ; Menendez, M ; Calatayud, M (**2015**) Comput. and Theor. Chem. 1053, 315.
(2) For instance: for a new view of ionic bonding see Annexe 2, for a revisit of bonding in phosphonium oxydes and ylides: see Annexe 3.
(3) See annexe 1, two articles from this work are in preparation.
(4) The development of the program can be followed from this repository: https://github.com/guacke/MPD.
(5) Supported by the CECAM initiative (http://www.cecam.org/ssd_initiative.html)

Caractère interdisciplinaire du Projet et complémentarité des partenaires

1 page maximum – interligne simple (1 000 caractères maximum)
Préciser le rôle de chaque encadrant ainsi que les compétences scientifiques apportées. Montrer la valeur ajoutée des complémentarités entre disciplines.

Benoît Braïda (BB), MCF at the LCT is one of the renowned experts in Valence Bond theory.[6] His work more generally focuses on the development of interpretative methods and chemical concepts, and their application to fundamental problems in chemistry. BB is also the project coordinator of a developing network around the MPD project.[7-9] BB will take care of all chemically-driven aspect related to the project, including full support in electronic structure theory to the candidate (that is minimal).

Charles Dapogny (CD), researcher at CNRS, Pascal Frey (PF), Pr. at the LJLL and Yannick PRIVAT (YP), researcher at CNRS are experts of theoretical and numerical aspects of geometrical and topological shape optimization including the derivation of workable optimality conditions, the mesh deformation management methods. PF is also Head of the research center Institut des sciences du calcul et des données (ISCD). All three will take care of both mathematical and computational aspects of the project.

(6) Recent publication on this topic: (a) Braïda B.* ; Hiberty P. C.* Nature Chemistry 2013, 5, 417 (b) Braïda B.* ; Hendrickx K. ; Domin D. ; Hiberty P. C. J. Chem. Theory Comput. 2013, 9, 2276 (c) Wu W. ; Zhang HY ; Braïda B., Shaik S. ; Hiberty P. C. Theor. Chem. Acc. 2014, 133, 1441 (d) Zhang HY ; Danovich D. ; Wu W. ; Braïda B ; Hiberty P. C. ; Shaik S. J. Chem. Theory Comput. 2014, 10, 2410 (e) Mo Y. ; Wang, C. ; Guan, L. ; Braida, B ; Hiberty, P. C. ; Wu, W Chem. Eur. J. 2014, 20, 8444 (f) Braïda B.* ; Ribeyre T. ; Hiberty P. C.* Chem. Eur. J. 2014, 20, 9643 (g) Anderson P ; Petit, A ; Ho J ; Mitoraj M ; Coote M. L. ; Danovich D ; Shaik, S ; Braida, B* ; Ess, D H* J. Org. Chem. 2014, 21, 9998 (h) Hendrickx, K ; Braida, B* ; Bultinck, P ; Hiberty,

PC* Comp. Theor. Chem. 2015, 1053, 180 (i) Bruckner, C ; Walter, C ; Stolte, M ; Braida, B ; Meerholz, K ; Wurthner, F ; Engels, B J. Phys. Chem. C 2015, 119, 17602.
(7) A collaboration on chemical applications involving MPD analysis has started with the Quantum Chemistry group in Brussels, see Annexe 4.
(8) Together with Paris, Ghent and Brussels, also includes researchers from Oviedo (Spain) and Hamilton (Canada).
(9) Two scientific network events has been organized last year, in Paris (https://wiki.lct.jussieu.fr/workshop/index.php/Discussion_meeting_on_Maximum_Probability_Domains), and Ghent (http://www.quantum.ugent.be/mediawiki/index.php?title=Maximum_Probability_Domains).

Coordonnées du candidat

Nom et Prénom	Université d'origine, département du master	Email du candidat	Date de naissance

Avis motivé sur le candidat

1 page maximum – interligne simple (1 000 caractères maximum) *Préciser la formation*