Collaborative development of a modern program based on Maximum Probability Domains search

Four dates in 2016 (do be defined). Location : Paris

Benoît BRAÏDA
LCT[1]-UPMC, France
benoit.braida@upmc.fr

Pascal FREY
LJLL[2] et ICS[3]-UPMC, France
pascal.frey@upmc.fr

Patrick BULTINCK
Ghent University, Belgium
patrick.Bultinck@ugent.be

Ángel Martín PENDÁS
Universitad de Oviedo, Spain
angel@fluor.quimica.uniovi.es

[1] Laboratoire de Chimie Théorique
[2] Laboratoire Jacques-Louis Lyons
[3] Institut du Calcul et de la Simulation

1. Proposal

1.1. Introduction and motivation

As the standard interpretation of quantum theory is probabilistic in nature, the most natural way of extracting chemical information from an accurate wave function is to consider the probability of finding specific numbers of electrons in some given regions of space.[4] The last few years, the idea to search for the regions of 3D space for which the probability of finding a given number of electrons is maximal has been investigated.[5] These regions, and the associated interpretative method, are thus called « maximum probability domains (MPDs) ». In the case of two spin-paired electrons, MPD-representations are homomorphic to Lewis structures, as they are able to give an indication of the most probable regions of space which should contain exactly two spin-paired electrons.

In the light of recent results the MPD method looks a very promising interpretative tool for chemistry, overcoming shortcomings and limitations of older and more widely used interpretative methods.[6] However, it is necessary to deliver to the chemical community a simple-to-use, robust, accurate and fast program able to compute MPDs and related properties.

1.2. State of the art

MPDs obtained from current implementations suffer from severe limits. The programs used to calculate MPDs are still exploratory and represent the domains as collections of small cubes. They optimize the domain shapes by either randomly adding and deleting cubes or exploiting the availability of shape derivatives. Both optimization methods give rise to numerical inaccuracy which clouds the properties of MPDs, and are not well-controled in the current implementations. It has been shown analytically that MPDs suffer from an inherent instability and multiple degeneracies at the Hartree-Fock level.[2e] These results indicate that there is a need for: (i) the inclusion of electron correlation, and: (ii) a need for numerical measure of the optimality of the domain, i.e. the second shape derivative). The latter would allow also a second-order type of

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[4] Savin A. (2002), In: Sen KD (ed), Reviews of modern quantum chemistry: a celebration of the 252 contributions of Robert G. Parr, World Scientific, Singapore

[5] Recent articles: (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 (i) Braïda, B. ; Menendez, M. ; Pendas, A. M. ; Savin, A. manuscript in preparation.

[6] A recent CFCAM discussion meeting has taken place last May 2015 which was very fruitful and sucessful. Web site: https://wiki.lct.jussieu.fr/workshop/index.php/Discussion_meeting_on_Maximum_Probability_Domains. Most pdf files of the talks given there could be downloaded from the following Dropbox shared folder: https://www.dropbox.com/sh/ftbuebebm9clw9u/AAC3H6dEMdsezgUJ28GZPESCa?dl=0.

algorithm to be developed. Last, currently available MPD programs are difficult to maintain, due to a lack of adherence to software engineering principles.

The effort is now focused both on coding implementations and developing theoretical frameworks, which includes in particular the following threads, all already ongoing in parallel:
1. The development and maintenance of an efficient and user-friendly general-purpose MPD program ;
2. Visualization of the resulting MPDs, making use of state-of-the-art 3D virtual reality systems in development in the ICS-UPMC ;
3. The improvement of current algorithms, including numerical analysis and the use of adaptive non-regular grids, in particular with regard to the difficulty of a multiple solution problem ;
4. The development and implementation of the second shape derivative ;
The theoretical investigation and practical implementation of this second derivative, will allow true maxima to be characterized ;
5. Extension of the algorithm to multi-determinant wavefunctions ;
6. Theoretical analysis of MPDs and development of related concepts for the analysis of the chemical bond.
7. Development of multi-domain optimization, to derive a direct Lewis-like resonance description from quantum chemical wavefunctions.

1.3. Objectives

A collaboration between the LCT-UPMC and LJLL-UPMC has started in 2012 on all the mathematically related aspect. More recently, the development of a new generation MPD program, capitalizing on the LCT/LJLL collaboration has been undertaken and involved as the third party the Ghent Quantum Chemistry group, Belgium (though the thesis of Guillaume ACKE). In the near future, it is planed to make this program development a true multicenter collaborative development, involving also the group of Ángel Martín PENDÁS in Oviedo, Spain and Paul W. AYERS, Canada.

The development of the new MPD program is thus at the moment in an early stage. Due to the collaborative nature of the development, a « GitHub » platform[7] has been set up, but it is highly necessary in the medium term (the year 2016) that all the researchers directly involved in the development meet regularly (every ~3 months), in order to have short meetings to share current advances and difficulties in the recent implementation work, collectively address the technical and theoretical issues, coordinate and distribute the tasks for the next three months. We think that ~4 meetings of that kind, each lasting no more than ~1-2 days, would be necessary in the year 2016 to efficiently advance the development of the program. Most of these meetings will probably takes place Paris in order to minimize the global cost of housing plus travel expenses of the participants.

[7] Private at the moment

Our goal will be, in the medium term, to be able to deliver to the chemical community a robust, user-friendly and reliable version of the program, in order to build around the core of researchers involved in the MPD project[8] in order to start building a community of users of the MPD method.

1.4. Participant List

Benoit BRAIDA, France (benoit.braida@upmc.fr)
Andreas SAVIN, France (andreas.savin@lct.jussieu.fr)
Pascal FREY, France (pascal.frey@upmc.fr)
Jeremy DALPHIN, France (jeremy.dalphin@univ-lorraine.fr)
Jeremy FOULON, France (jeremy.foulon@upmc.fr)
Patrick BULTINCK, Belgium (patrick.Bultinck@ugent.be)
Guillaume ACKE, Belgium (guillaume.acke@UGent.be)
Sofie VAN DAMME, Belgium (sofie.VanDamme@UGent.be)
Ángel Martín PENDÁS, Spain (angel@fluor.quimica.uniovi.es)
Paul W. AYERS, Canada (ayers@mcmaster.ca)

2. Financial Support

Requested to CECAM-FR-IDF : 3000€
An application to the « tournesol » program (4000€) between France and Belgium has also been sent.

The financial help is requested to support the housing and meal expenses of the participants, and travel expenses of the non-local European participants.

[8] Basically, at the moment the list of names in section 1.4