

Experimentally Constrained Wave Function Methods: Current Developments and Future Perspectives

Nancy, June 19-20, 2017

Organizer 1:

Alessandro Genoni,

CNRS & Université de Lorraine, UMR CNRS 7565, Nancy-Metz, France

E-mail: Alessandro.Genoni@univ-lorraine.fr

Organizer 2:

Simon Grabowsky

Institute for Inorganic Chemistry and Crystallography, University of Bremen, Germany

E-mail: simon.grabowsky@uni-bremen.de

1. Proposal

1.1 Introduction and motivation

The determination of wave functions or density matrices from experimental data has been an open research field for about fifty years. There are three main reasons that continuously prompt different research groups to pursue the development of new “experimental” wave function/density matrix methods: *i*) the necessity of summarizing all the experimental observations into an object of unquestionable physical meaning and, in this sense, the wave function and the density matrix represent the best theoretical options available from the quantum mechanical point of view; *ii*) the possibility of obtaining reliable wave functions also in all those cases in which it is not possible to perform very accurate (e.g., highly correlated) quantum mechanical calculations on the systems under exam; *iii*) the fact that extracting wave functions from experimental data (especially X-ray diffraction data) could give important insights into unsolved theoretical problems, such as the Hohenberg & Kohn mapping between the ground-state electron densities and the ground-state wave functions of many-electron systems.

1.2 State of the art

The first attempt of obtaining an experimentally constrained wave function dates back to 1963 when Mukherji and Karplus [1] proposed a perturbation approach to extract a meaningful single Slater determinant from experimental values for the dipole moment and the electric field gradient of the simple hydrofluoric acid. However, the real milestones in this area are represented by the series of papers by Clinton and coworkers since 1969, in which they have mainly devised original methods to obtain idempotent one-particle density matrices from theoretically generated X-ray structure factors [2-4].

Nevertheless, a first intrinsic and important limitation of all the strategies based on the Clinton approach is their only focus on single Slater determinants (or, equivalently, to idempotent density matrices). To overcome this drawback, Hibbs and coworkers have developed a new interesting linear scaling technique (MOON approach) where the occupation numbers of predetermined (occupied and virtual) molecular orbitals are optimized through a fitting to experimental data [5-6].

Furthermore, more advanced approaches have also explicitly taken into account conditions for the wave functions (or density matrices) N -representability, which is not automatically guaranteed in the Clinton-like methods. In this context, a prominent role is occupied by the techniques proposed by Weyrich and coworkers [7,8] and, more recently, by Gillet and collaborators [9-11] that have interestingly demonstrated over the years that the wealth of information about chemical bonding effects contained in inelastic Compton scattering data can be efficiently exploited to reconstruct one-particle density matrices.

Unfortunately, even introducing N -representability conditions may not be enough. In fact, in 1975 Gilbert showed that, in principle, an infinite number of N -representable one-particle density matrices can reproduce a desired electron density distribution

[12]. Therefore, fitting to density data alone is a necessary but not sufficient criterion to guarantee the determination of physically meaningful experimentally constrained wave functions or density matrices. To overcome this drawback, Henderson and Zimmerman [13] have suggested that of all the possible single Slater determinants that are compatible with a given experimental electron density, the optimal one is that which minimizes the Hartree–Fock energy. This idea is actually at the basis of the X-ray Constrained Wave Function (XCWF) approach developed by Jayatilaka, an approach [14,15] that basically consists in finding single Slater determinants that not only minimize the electronic energy of the investigated systems, but that also reproduce as much as possible sets of experimentally collected structure factors.

The Jayatilaka approach has been initially proposed in the framework of the Hartree–Fock method (both restricted [14, 15] and unrestricted [16]) and it has been afterwards extended introducing density functionals, the treatment of relativistic effects [16], and the possibility of extracting extremely localized molecular orbitals from experimental data [17-18]. The XCWF technique has been shown to be successful not only in the determination of physically meaningful “experimental” electron densities, but also in the study of chemical and physical properties such as in-crystal molecular dipole moments, in-crystal polarizabilities and refractive indices [19, 20]. For all these reasons, the X-ray constrained wave function approach is probably the most promising among all the modern “experimental” wave function methods.

References:

1. A. Mukherji, M. Karplus, *J. Chem. Phys.* **38**, 44 (1963).
2. W. L. Clinton, J. Nahkleh, F. Wunderlich, *Phys. Rev.* **177**, 1 (1969).
3. W. L. Clinton, L. J. Massa, *Phys. Rev. Lett.* **29**, 1363 (1972).
4. W. L. Clinton, C. A. Frishberg, L. J. Massa, P. A. Oldfield, *Int. J. Quantum Chem. Symp.* **7**, 505 (1973).
5. D. E. Hibbs, S. T. Howard, J. P. Huke, M. P. Waller, *Phys. Chem. Chem. Phys.* **7**, 1772 (2005).
6. M. P. Waller, S. T. Howard, J. A. Platts, R. O. Piltz, D. J. Willock, D. E. Hibbs, *Chem. Eur. J.* **12**, 7603 (2006).
7. H. Schmider, V. H. Smith, W. Weyrich, *Trans. Am. Cryst. Assoc.* **26**, 125(1990).
8. H. Schmider, V. H. Smith, W. Weyrich, *J. Chem. Phys.* **96**, 8986 (1992).
9. J.-M. Gillet, P. J. Becker, *J. Phys. Chem. Sol.* **65**, 2017 (2004).
10. J.-M. Gillet, *Acta Cryst. A* **63**, 234 (2007).
11. J.-M. Gillet, P. J. Becker, P. Cortona, *Phys. Rev. B* **63**, 235115 (2001).
12. T. L. Gilbert, *Phys. Rev. B* **12**, 2111 (1975).
13. G. A. Henderson, R. K. Zimmermann, *J. Phys. Chem.* **65**, 619 (1976).
14. D. Jayatilaka, *Phys. Rev. Lett.* **80**, 798 (1998).
15. D. Jayatilaka, D. J. Grimwood, *Acta Cryst. A* **57**, 76 (2001).
16. M. Hudák, D. Jayatilaka, L. Perasínova, S. Biskupic, J. Kozísec, L. Bucinsky, *Acta Cryst. A* **66**, 78 (1010).
17. A. Genoni, *J. Phys. Chem. Lett.* **4**, 1093 (2013).
18. A. Genoni, *J. Chem. Theory Comput.* **9**, 3004 (2013).
19. A. E. Whitten, D. Jayatilaka, M. Spackman, *J. Chem. Phys.* **125**, 174505 (2006).
20. D. D. Hickstein, J. M. Cole, M. J. Turner, D. Jayatilaka, *J. Chem. Phys.* **139**, 064108 (2013).

1.3 Objectives

- 1) The first goal of the meeting will be the discussion of the most recent advancements and of the possible improvements in the modern experimentally constrained wave function/density matrix methods (not exclusively the X-ray Constrained Wave Function approach) with all the original and active authors of the prominent methods.
- 2) Another important aspect of the meeting will be the involvement of experimentalists (mainly crystallographers), whose expertise will be necessary to address the problem of the experimental data quality that should be required for the current and future “experimental” wave function/density matrix techniques.
- 3) A third objective will be the discussion about the possible exploitation of the XCWF method to shed light on the Hohenberg & Kohn mapping between ground-state electron densities and ground-state wave functions of many-electron systems and, consequently, to develop new density functionals starting from experimental (or theoretical) X-ray structure factors.
- 4) A fourth goal will be to discuss which properties of chemical and physical interest can be deduced from the obtained wave functions, which are not otherwise available, or not available with the same accuracy or speed of determination. It should be also evaluated how the use of the XCWF methods can be made available to a broader community.

1.4 Participants List

Alex Borgoo (alex.borgoo@kjemi.uio.no)
Lukas Bucinsky (lukas.bucinsky@stuba.sk)
Nicolas Claiser (nicolas.claiser@univ-lorraine.fr)
Birger Dittrich (birger.dittrich@hhu.de)
Carlo Gatti (carlo.gatti@istm.cnr.it)
Alessandro Genoni (Alessandro.Genoni@univ-lorraine.fr)
Jean-Michel Gillet (jean-michel.gillet@centralesupelec.fr)
Simon Grabowsky (simon.grabowsky@uni-bremen.de)
Dylan Jayatilaka (dylan.jayatilaka@uwa.edu.au)
Claude Lecomte (claudio.lecomte@univ-lorraine.fr)
Piero Macchi (piero.macchi@dcb.unibe.ch)
Lou J. Massa (LMassa@Hunter.CUNY.edu) (To Be Confirmed)

2. Financial Support

- 4000 Euros from the CECAM-FR MOSER node to cover the expenses for the meals during the meeting and the accommodation expenses of all the invited speakers;
- 1000 Euros from other possible sources (e.g., Réseau Français de Chimie Théorique, Région Lorraine, University of Lorraine, International Union of Crystallography, European Association of Crystallography).