Reduced Density-Matrix Functional Theory: Improving its foundation

Report of Contributions

https://indico.ectstar.eu/e/153

Contribution ID: **1** Type: **not specified**

Introduction

Monday, 3 October 2022 10:30 (30 minutes)

Contribution ID: **2** Type: **not specified**

Welcome

Monday, 3 October 2022 11:30 (1h 30m)

Presenter: SCHILLING & CARLOS BENAVIDES-RIVEROS, Christian

Contribution ID: **13** Type: **not specified**

Registration

Monday, 3 October 2022 10:00 (30 minutes)

Contribution ID: **14** Type: **not specified**

DFT, RDMFT, and the challenge of strong correlations

Monday, 3 October 2022 14:30 (30 minutes)

Presenter: GROSS, Eberhard

Contribution ID: **15** Type: **not specified**

Density Functional Theory Transformed into a One-electron Reduced Density Matrix Functional Theory for the Capture of Static Correlation

Monday, 3 October 2022 15:00 (30 minutes)

Presenter: MAZZIOTTI, David

Contribution ID: **16** Type: **not specified**

One-body Reduced Density-matrix Functional Theory for the Canonical Ensemble

Monday, 3 October 2022 15:30 (30 minutes)

Presenter: SUTTER, Sarina

Contribution ID: **17** Type: **not specified**

Convex N-Representability

Monday, 3 October 2022 16:30 (30 minutes)

Presenter: CASTILLO, Federico

Contribution ID: **18** Type: **not specified**

Relating the pure and ensemble density matrix functional

Monday, 3 October 2022 17:00 (30 minutes)

Presenter: SCHILLING, Christian

Contribution ID: **19** Type: **not specified**

Implications of pinned occupation numbers for natural orbital expansions

Monday, 3 October 2022 17:30 (30 minutes)

Presenter: MACIAZEK, Tomasz

Contribution ID: **20** Type: **not specified**

Obstacles on the road to practical implementation of RDMFT

Wednesday, 5 October 2022 09:30 (30 minutes)

Presenter: CIOSLOWSKI, Jerzy

Contribution ID: **21** Type: **not specified**

Global Natural Orbital Functional

Wednesday, 5 October 2022 10:00 (30 minutes)

Appropriate representations of the electronic structure of atoms, molecules, and solids without explicit recourse to the N-particle density matrix can alternatively be obtained by the one-particle reduced density matrix (1RDM) functional theory [1]. Regrettably, computational schemes based on the exact constrained search formulation are too expensive; so the 1RDM functional requires a practical approach. For a Hamiltonian involving no more than two-body interactions, the ground-state energy can be cast as an exact functional of the two-particle reduced density matrix (2RDM). In practical applications, we employ this exact energy functional but using an approximate 2RDM that is built from the 1RDM.

Approximating the energy functional has an important consequence: the functional N-representability problem arises. In this presentation, the role of the N-representability in approximate functionals [2] will be analyzed. The 1RDM functional is called Natural Orbital Functional (NOF) when it is based upon the spectral expansion of the 1RDM. So far, several approximate functionals have been proposed [3], but solely PNOFs [4,5] are based on the reconstruction of the 2RDM subject to necessary N-representability conditions. For the latter, an open source software is available [6] for quantum chemistry calculations. These functionals are capable of producing a correct description of systems with a multiconfigurational nature, however, they also suffer from an important lack of dynamic correlation. To recover this correlation, second-order perturbative corrections have been implemented with significant results [5,7]. Nevertheless, our goal is to recover the missing dynamic correlation only within the NOF theory framework.

The 1RDM functional is called Natural Orbital Functional (NOF) when it is based upon the spectral expansion of the 1RDM. So far, several approximate functionals have been proposed [3], but solely PNOFs [4,5] are based on the reconstruction of the 2RDM subject to necessary N-representability conditions. For the latter, an open source software is available [6] for quantum chemistry calculations. These functionals are capable of producing a correct description of systems with a multiconfigurational nature, however, they also suffer from an important lack of dynamic correlation. To recover this correlation, second-order perturbative corrections have been implemented with significant results [5,7]. Nevertheless, our goal is to recover the missing dynamic correlation only within the NOF theory framework.

In this talk, a new accurate NOF will be presented for all electronic structure problems, that is, a global NOF [8,9]. Note that the adjective “global” is used instead of “universal” to differentiate our approximate multipurpose NOF from the exact functional. The concept of the dynamic part of the occupation numbers will be introduced. The emergent functional describes the complete intrapair electron correlation and the correlation between orbitals that make up both the pairs and the individual electrons. The interorbital correlation is composed of static and dynamic terms. Different examples will be analyzed where the weak and strong electron correlations are revealed. Our results will be compared with those obtained by established accurate theoretical methods and experimental data.

1. T. L. Gilbert, Phys. Rev. B 12, 2111 (1975); M. Levy, Proc. Natl. Acad. Sci. USA 76, 6062 (1979); S. M. Valone, J. Chem. Phys. 73, 1344 (1980).
2. M. Piris, in Many-body approaches at different scales: a tribute to N. H. March on the occasion of his 90th birthday, Chap. 22, pp. 231-247. New York: Springer (2018).
3. K. Pernal and K. J. H. Giesbertz, Top Curr Chem 368, 125-184 (2016); I. Mitxelena, M. Piris, J. M. Ugalde, Adv. Quantum Chem. 79, 155-177 (2019).
4. M. Piris, J. M. Ugalde, Int. J. Quantum Chem. 114, 1169-1175 (2014).

5. M. Piris, Phys. Rev. Lett. 119, 063002 (2017); Phys. Rev. A 98, 022504 (2018); Phys. Rev. A 100, 032508 (2019).
6. M. Piris, I. Mitxelena, Comp. Phys. Comm. 259, 107651 (2021).
7. M. Piris, X. Lopez, M. Piris, Theor. Chem. Acc. 138, 89 (2019).
8. M. Piris, "Global Natural Orbital Functional: Towards the Complete Description of the Electron Correlation", Phys. Rev. Lett. 127, 233001 (2021).
9. I. Mitxelena, M. Piris, "Benchmarking GNOF against FCI in challenging systems in one, two and three dimensions", J. Chem. Phys. 156, 214102 (2022).

Keywords:
Electron Correlation, Reduced Density Matrix Functional Theory (RDMFT), Natural Orbital Functional Theory (NOFT)

Presenter: PIRIS, Mario

Contribution ID: **22** Type: **not specified**

Functional-Based Description of Electronic Dynamic and Strong Correlation

Wednesday, 5 October 2022 10:30 (30 minutes)

The slow progress in systematically eliminating intrinsic errors in commonly used approximate functionals limits the applicability of functional-based descriptions to strongly correlated systems. Kohn-Sham density functional theory (KS-DFT) and reduced density matrix functional theory (RDMFT) represent two formally exact theoretical frameworks for the many-electron problem. Commonly, approximate functionals in KS-DFT and RDMFT have advantages in dealing with dynamic correlation and strong correlation, respectively. Hence, establishing a connection between both theories and developing an effective approach to combine functional approximations in both theories can create new possibilities for improving the predictive power of functional-based methods. This talk is about some effort in this direction in our group.

Presenter: QIANG SU, Neil

Contribution ID: **23** Type: **not specified**

Towards an in-principle-exact density matrix functional embedding theory

Wednesday, 5 October 2022 11:30 (30 minutes)

Presenter: FROMAGER, Emmanuel

Contribution ID: **24** Type: **not specified**

Self-consistent-field method for correlated many-electron systems with an entropic cumulant energy

Wednesday, 5 October 2022 12:00 (30 minutes)

Using an entropic functional for the correlation energy, an SCF method is found within the density-matrix functional theory. The method is efficient as the SCF method in Hartree-Fock or DFT theory.

Presenter: WANG, Jian

Contribution ID: **25** Type: **not specified**

Critical reassessment of recent developments in functional theory: From Hartree-Fock to i-DMFT

Wednesday, 5 October 2022 12:30 (30 minutes)

Presenter: DING, Lexin

Contribution ID: **26** Type: **not specified**

Oportunities for RDMFT: Lee-Huang-Yang Fluids: from liquid droplets to supersolidity

Friday, 7 October 2022 09:30 (30 minutes)

Presenter: RECATI, Alessio

Contribution ID: **27** Type: **not specified**

Reduced density matrix functional theory for superconductors

Friday, 7 October 2022 12:30 (30 minutes)

Presenter: BENAVIDES-RIVEROS, Carlos

Contribution ID: **28** Type: **not specified**

Reduced density matrix functional theory for bosons

Friday, 7 October 2022 10:00 (30 minutes)

Presenter: SCHILLING, Christian

Contribution ID: **29** Type: **not specified**

Functional theory for Bose-Einstein condensates

Friday, 7 October 2022 10:30 (30 minutes)

Presenter: LIEBERT, Julia

Contribution ID: **30** Type: **not specified**

Repulsively diverging gradient of the density functional in the Reduced Density Matrix Functional Theory

Friday, 7 October 2022 11:30 (30 minutes)

Presenter: MACIAZEK, Tomasz

Contribution ID: **31** Type: **not specified**

Introducing Relativistic Reduced Density Matrix Functional Theory

Presenter: RODRIGUEZ MAYORCA, Mauricio

Contribution ID: **32** Type: **not specified**

New interpretation of the reduced density matrices

Monday, 10 October 2022 09:30 (30 minutes)

Presenter: DEUTSCH, Thierry

Contribution ID: **33** Type: **not specified**

Richardson-Gaudin Wavefunctions for Strong Correlation

Monday, 10 October 2022 10:00 (30 minutes)

Weakly-correlated systems are well-described as individual electrons. The dominant contribution to the wave function is a Slater determinant of the occupied orbitals, with small corrections from single- and double-excitations. This is not the case for strongly-correlated systems. Many Slater determinants contribute substantially and thus the correct physical picture is not independent electrons. For molecular systems, we have shown that Richardson-Gaudin (RG) states are a much better starting point. They amount to pair wave functions, but they are tractable and form a basis of the Hilbert space, allowing for systematic improvement. Pair wavefunctions are near synonymous with natural orbital functionals, and we argue that it is easier, and more reasonable physically, to consider the RG states directly.

Presenter: JOHNSON, Paul

Contribution ID: **34** Type: **not specified**

Density inversion method for local basis sets without potential auxiliary functions: inverting densities from RDMFT

Monday, 10 October 2022 10:30 (30 minutes)

Presenter: BOUSIADI, Sofia

Contribution ID: **35** Type: **not specified**

Efficient Bosonic and Fermionic Sinkhorn Algorithms for Non-Interacting Ensembles in One-body Reduced Density Matrix Functional Theory in the Canonical Ensemble

Monday, 10 October 2022 11:30 (30 minutes)

Presenter: KOOI, Derk

Contribution ID: **36** Type: **not specified**

Relating fundamentals of functional theory: An analytic case study

Monday, 10 October 2022 12:00 (30 minutes)

Presenter: LIEBERT, Julia

Contribution ID: **37** Type: **not specified**

Introducing Relativistic Reduced Density Matrix Functional Theory

Monday, 10 October 2022 12:30 (30 minutes)

Presenter: RODRIGUEZ MAYORCA, Mauricio

Contribution ID: **38** Type: **not specified**

Ensemble reduced density matrix functional theory for excited states and hierarchical generalization of Pauli's exclusion principle

Wednesday, 12 October 2022 09:30 (30 minutes)

Presenter: LIEBERT, Julia

Contribution ID: **39** Type: **not specified**

Photoemission spectra from the Extended Koopmans' theorem: capturing weak and strong correlation

Wednesday, 12 October 2022 10:00 (30 minutes)

Presenter: ROMANIELLO, Pina

Contribution ID: **40** Type: **not specified**

Machine learning for reduced density matrix functional theory

Wednesday, 12 October 2022 10:30 (30 minutes)

The one-body reduced density matrix (1RDM) plays a fundamental role in describing and predicting quantum features of bosonic and fermionic systems, such as Bose-Einstein condensation. Based on a decomposition of the 1RDM, we have developed a method to design reliable approximations for such universal functionals: Our results suggest that for translational invariant systems the constrained search approach of functional theories can be transformed into an unconstrained problem through a parametrization of a Euclidian space. This simplification of the search approach allows us to use standard machine learning methods to perform a quite efficient computation of both the universal functional and its functional derivative. For the Bose-Hubbard model, we present a comparison between our approach and the quantum Monte Carlo method.

This talk is based on:
J. Schmidt, M. Fadel, and C. L. Benavides-Riveros, Phys. Rev. Research 3, L032063 (2021).

Presenter: BENAVIDES-RIVEROS, Carlos

Contribution ID: **41** Type: **not specified**

Diverging Exchange Force and Form of the Exact Density Matrix Functional

Wednesday, 12 October 2022 11:30 (30 minutes)

Presenter: SCHILLING, Christian

Contribution ID: **42** Type: **not specified**

Many-body energy density functional

Wednesday, 12 October 2022 12:00 (30 minutes)

Presenter: ORLANDINI, Giuseppina

Contribution ID: **43** Type: **not specified**

Symposium 1: Exact results in RDMFT

Monday, 3 October 2022 14:29 (1 minute)

Presenter: BENAVIDES-RIVEROS, Carlos (Max-Planck Institute for Complex Systems)

Contribution ID: **44** Type: **not specified**

Symposium 2: RDMFT for quantum chemistry: Computational and theoretical state-of-the-art and open challenges

Wednesday, 5 October 2022 09:29 (1 minute)

Presenter: SCHILLING, Christian (LMU Munich)

Contribution ID: **45** Type: **not specified**

Symposium 3: Extending the scope of RDMFT (Bosons, ultracold gases, and superconductors)

Friday, 7 October 2022 09:29 (1 minute)

Presenter: KOOI, Derk

Contribution ID: **46** Type: **not specified**

Symposium 4: conceptual aspects of RDMFT

Monday, 10 October 2022 09:29 (1 minute)

Presenter: CIOSLOWSKI, Jerzy (University of Szczecin)

Contribution ID: **47** Type: **not specified**

Symposium 5: Excited states, time evolution, machine learning and more

Wednesday, 12 October 2022 09:25 (1 minute)

Presenter: GROSS, E. K. U. (The Hebrew University of Jerusalem)

Contribution ID: **48** Type: **not specified**

Density functional theory of the superconducting state

Friday, 7 October 2022 12:00 (30 minutes)

Presenter: GROSS, Eberhard

Contribution ID: **49** Type: **not specified**

Density functional theory of the superconducting state

Presenter: GROSS, Eberhard K. U. (The Hebrew University of Jerusalem)

Contribution ID: **50** Type: **not specified**

Closing

Wednesday, 12 October 2022 12:30 (30 minutes)

Presenters: BENAVIDES-RIVEROS, Carlos (Max-Planck Institute for Complex Systems); SCHILLING, Christian (LMU Munich); GROSS, Eberhard K. U. (The Hebrew University of Jerusalem)

Contribution ID: **51** Type: **not specified**

Informal discussions

Friday, 14 October 2022 09:30 (1h 30m)

Contribution ID: **52** Type: **not specified**

Informal discussion

Friday, 14 October 2022 11:30 (1h 30m)