International Workshop on 'New challenges in Reduced Density Matrix Functional Theory: Symmetries, time-evolution and entanglement'

A two-pronged approach to electron correlation in RDMFT

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In addressing the correlation problem of electronic structure theory, understanding and utility has been found in the partitioning of electron correlation into static and dynamic components [1]. Recently, we have taken this partitioning a step further in combining significantly different approaches to the correlation problem, density functional theory (DFT) and reduced density matrix functional theory (RDMFT), to separately capture both components of electron correlation [2]. I will discuss the key advantages of such an approach, along with, our recent progress in extending the method to open shells, and deriving an "on-top" density functional for dynamic correlation.

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Effective potentials to minimise the total energy functional in DFT and RDMFT

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Effective local potential theories in electronic structure underlie most single-particle schemes including the Kohn Sham theory and local reduced density matrix functional theory [1-3]. These theories share a common mathematical problem: quite different effective local potentials can lead to similar ground state densities and wave functions. This problem is in addition to well-known pathologies of the equations determining the effective potential when the latter and the orbitals are expanded in finite basis sets[4]. Finally, self interaction errors in approximate XC functionals in DFT manifest in the wrong asymptotics of the XC potential. A few years ago, to deal with all these issues, we restricted the admissible set of effective potentials by writing the Hartreeexchange and correlation potential, in any approximation in DFT or local RDMFT, as the electrostatic potential of an effective charge density that is non-negative and for an N-electron system it integrates to N-1 electrons. These constraints guarantee that two N-electron densities that are close to each other arise from effective potentials that are close to each other too and also, they enforce the correct asymptotic behaviour of the XC potential at large distances away from the electronic system [5,6], curing the effects of self interactions that are present in the approximate XC energy as a functional of the density or the density matrix. In this talk, I shall give an overview of our approach to determine the effective potential, which is common in applications of our method using DFT or RDMFT approximations.

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Finite Uniform Electron Gases

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Traditional density functional theory (DFT) emerged from, and remains firmly connected to, the study of the infinite uniform electron gas (IUEG) and many popular DFT functionals are constructed so that they yield correct exchange / correlation energies when applied to such systems [1]. Recently, we have shown that the IUEG is a limiting case of a much larger class of finite uniform electron gases (FUEGs) and that there are strong arguments for reconstructing DFT functionals so that they are also correct when applied to these finite systems [2,3]. In this lecture, I will discuss the mathematical treatment of FUEGs and argue that they are also potent sources of information for the construction and testing of new RDMFT models.

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Novel approaches towards constructing reduced density matrix functionals within random phase approximation framework

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Over years there has been a constant progress in development density matrix functionals (or natural orbital functionals) [1]. The accuracy and general usefulness of the most successful functionals still lag behind widely used density functionals. Recently Random Phase Approximation (RPA) electron correlation methods have re- emerged in the Kohn-Sham DFT framework leading to a new class of correlation orbital-dependent functionals (for a review of RPA methods see Ref.[2]). Foundations of most RPA approaches trace back to an exact expression for two-electron reduced density matrix written in terms of one-electron density matrix and dynamic one-electron response functions presented i.g. in the seminal paper of MacLachlan and Ball [3]. Interestingly, the MacLachlan and Ball expression lead to formulations of the density matrix functional if combined with the extended random phase approximation. In other words, two-electron reduced density matrix can be reconstructed from one-electron functions. Another way of exploiting the MacLachlan and Ball expression leading to novel density matrix functionals employs the adiabatic connection construction. The latter is only viable if one can define a 0thorder Hamiltonian (or a reference state). Both ways have been explored recently [4,5]. In my presentation first I will give a short introduction to the derivation of the MacLachlan and Ball expression and RPA functionals in DFT. Then two routes leading to density matrix depending correlation energy expression, which exploit random phase approximations will be presented. It will be shown that the “direct” approach resulting in reconstructing a full two-electron density matrix from approximate one-electron functions leads to strong overcorrelation when applied to molecules. The adiabatic connection route is much more promising and yields excellent results if one employs a Hamiltonian for a group product function as a reference.

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Separation of dynamic and nondynamic correlation

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The account of electron correlation and its efficient separation into dynamic and nondynamic parts plays a key role in the development of computational methods such as hybrid, range- separated [1] or local methods [2]. In this work, we split the correlated part of the pair density into two correlation functions that account for nondynamic and dynamic correlation effects [3]. These functions are used in a two-electron model, giving rise to dynamic and nondynamic cor- relation functions that (i) depend only on natural orbitals and their occupancies, (ii) can be straightforwardly decomposed into orbital contributions, and (iii) admit a local form [4] (see Fig. 1). Finally, using the same strategy we present a separation of the Coulomb Hole into dynamic and nondynamic correlation. The long-range part of the dynamic-correlation hole can be used to identify dispersion interactions [5] as confirmed by perturbation analysis [6]. These expressions can aid in the development of density matrix functional theory (DMFT), density functional theory (DFT) and the development of local hybrid methods.

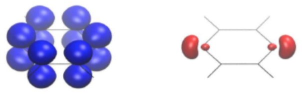

Fig. 1 DYNAMIC NONDYNAMIC

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Combining methods without double counting in RDMFT context

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Ideas that were presented as seamlessly combining wave function methods with density functionals can be seen from a reduced density matrix perspective:
- some derivations appear natural in this context,
- the wave function part can be replaced by a reduced density matrix part [1]. The usage of density functionals can be motivated by the slow convergence of the kinetic energy with basis set size, due to the singularity in the Coulomb potential [2]. Two strategies are discussed: (a) using natural orbitals [3, 4] and (b) using orbital spaces [5, 6]. Furthermore, the adiabatic connection can be reformulated, and applied from different perspectives:
- for computing the correlation energy using the kinetic energy evolution [7, 8, 9],
- by using extrapolation [10, 11, 12].

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Density and kinetic energy density -to- potential mapping on a lattice

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In the simple two-site Hubbard model one cannot reproduce the ground state 1-body Reduced Density Matrix (1-RDM) of the interacting system by a non-interacting one, even with non-local potentials and/or with some artificial temperature (grand canonical ensemble). Motivated from this fact, we show that in a lattice model we can reconstruct any density and kinetic energy density with properly adjusted potentials (local and non-local) of a fictitious non-interacting Hamiltonian. We achieve this by solving a system of non linear equations resulting from the steady state equations of motion of the fictitious system, which for a given density and kinetic energy density reproduce the functionals of the local and non-local potentials.

Correlation and Spectroscopy in Reduced Density-Matrix Functional Theory

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In this work we explore the performance of approximations to electron correlation as well as to observables in reduced density-matrix functional theory (RDMFT) [1]. Particular focus is put on the spectral function, which determines, for example, photoemission spectra, and which cannot be obtained in a straightforward way from the one-body density matrix, and on the regime of strong electron correlation, which is difficult to treat by standard methods. Using the simple Hubbard model as test case shines light on the content, successes and limits of current RDMFT approaches.

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