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

September 26 - September 29, 2017
CECAM-HQ-EPFL, Lausanne, Switzerland

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1 Description

In 1959, at the Colorado conference on Molecular Quantum Mechanics, Charles Coulson pointed out that the description of atoms and molecules involves the two-electron reduced density matrix (2-RDM), only [1]. Indeed, since electrons interact only pairwise by Coulomb repulsion, the energies and other electronic properties of atoms and molecules can be computed directly from the 2-RDM. This remarkable conceptual insight has defined the starting point for the development of new theoretical approaches in quantum chemistry, "banishing" the N-electron wave function with its exponentially many degrees of freedom. The entire quantum problem can then be recast in the form of a very simple linear functional on the 2-RDM. Yet, since this description in the 2-electron picture involves highly-nontrivial N-representability conditions (constraining to 2-RDMs representing N-electron wave functions) new approaches in the reduced electron picture were explored [2-4]. The most successful one so far is Density Functional Theory (DFT). It is based on the Hohenberg-Kohn theorem revealing a 1-1-correspondence between the external potential, corresponding ground state wave function and its electron density. This correspondence implies the existence of a "magic" functional on the electron density whose minimization yields the correct ground state energy and the corresponding density. Although DFT has seen a tremendous success in quantum chemistry, material science and condensed matter physics the search for more accurate functionals has suffered from a lack of systematic improvements: Not only the exact functional for the exchange-correlation is unknown but also the one for the kinetic energy.

It is quite promising that Gilbert in 1975 has established in the form of `Reduced Density Matrix Functional Theory’ (RDMFT) a natural extension of DFT [5]. RDMFT exploits the 1-electron picture by seeking a `magic’ functional on the whole 1-electron reduced density matrix (1-RDM). The big advantage compared to DFT is therefore that the kinetic energy can be described in an exact way and any scientific effort can be solely spent on improving the exchange-correlation functional. In addition, it is worth noting that in contrast to the 2-electron picture, the representability conditions for the 1-RDMs are known, coinciding with the Pauli exclusion principle. While DFT is resorting to a large zoo of hundreds of engineered density-functionals only about a dozen 1-RDM-functionals were proposed so far [6,7]. Remarkably, those few and less developed functionals already allowed one to describe closed-shell atoms and molecules with accuracies higher by one order in magnitude than DFT [8]. Moreover, RDMFT has succeed in predicting more accurate gaps of conventional semiconductors than DFT does and has demonstrated insulating behaviour for Mott-type insulators [9]. On the other hand, the theory has been hampered by the absence of a set of single particle equations. Unlike DFT or Hartree-Fock theory, RDMFT implies a set of coupled self-consistency conditions for the natural orbitals [10]. Therefore, it is one of the big challenges in RDMFT to find ways to improve the efficiency of the computational methods. Since the natural orbitals are known from the very beginning for translationally invariant 1-band lattice models the condensed matter regime in particular and the concept of 1-electron symmetries in general are promising direction for the future [11].

Due to tremendous recent progress on the 1-body pure and the 2-body ensemble N-representability problem, in the form of a mathematical breakthrough by A. Klyachko on the quantum marginal problem [12], new analytic tools were provided within the last ten years which can help to systematically construct more accurate 1-RDM functionals. This includes the important case of open-shell systems as well and would provide the starting point for time-dependent RDMFT. In that context, another important challenge is to explore the bridge between RDMFT and DFT- or 2-RDM-based methods including the concepts of orbital entanglement or intracular functional theory [13].

The immediate impact of these programs of research has been the development of new electronic structure methods with improved accuracy for small-to-medium-sized atoms and molecules.
The international interactive workshop will discuss and explore new aspects and challenges in "Reduced Density Matrix Functional Theory" such as
(1) New insights about RDMFT from recent progress on the 1- and 2-body N-representability problem;
(2) Implementation of 1-particle symmetries and macroscopic regime;
(3) Extension of RDMFT to open-shell atoms and molecules,
(4) Time-evolution.

The workshop will therefore address and carefully discuss the following questions manifesting themselves in four open challenges:

[C1] Derivation of universal structural insights about the exact functional in RDMFT
- What do the 1-body pure N-representability constraints (generalized Pauli constraints) imply for the structure of the `magic' 1-RDM functional for such systems?
- How does the algebraic decay of the natural occupation numbers (NON) due to the cusp reflect itself on the level of functionals?
- According to E. Lieb the `magic' functional depends explicitly on the particle number. Can we understand this dependency in specific physical regimes?

[C2] Simplification of the orbital self-consistent field equation in case of 1-electron symmetries
- For translationally invariant 1-band lattice models the functional depends only on the NON. Can we construct a meaningful functional?
- How do such functionals generalize in case of more than one band?
- How does an orbital symmetry in atoms or molecules manifest itself in simpler natural orbital self-consistency equations?
- What are the computational complexity efforts in practice for solving the self-consistency conditions for the NON and natural orbitals, respectively?

[C3] Extension of RDMFT to open-shell atoms and molecules
- Why is the description of open-shell systems much more involved?
- Can we suggest a meaningful functional for electronic systems in strong external magnetic fields (i.e. for fully-polarized electrons)?
- Can we split the description into closed shells and valence shells?

[C4] Describing quantum dynamics within RDMFT
- How do we describe time-evolutions in DFT?
- Why can this not be done in a similar way in RDMFT?
- How does the concept of reduced orbital entanglement simplify the description of time-evolutions in RDMFT?
- Can we tackle the weak coupling regime?

The list of workshop participants has been carefully chosen to include leading experts in various disciplines required for the success of our proposed scientific program. To maximize this success, the speakers have been asked to provide rather informal presentations which have been shared with all participants prior to the workshop. This has allowed all participants to prepare for the workshop accordingly. This `homework' will enable fruitful scientific discussions as they are planned as an important part of our event. The workshop is also supposed to initiate several new collaborations tackling the four important open challenges [C1-C4] in the next few years.

Key references

Bibliography

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2 Program

Day 1 - Tuesday September 26, 2017

Welcome!

- 8:30 to 8:50 - Registration
- 8:50 to 9:15 - Welcome and Introduction

Session 1: Gill & Pernal (chair Hardy Gross)

- 9:15 to 10:00 - Presentation - **Peter Gill**
  Finite uniform electron gases
- 10:00 to 10:30 - Discussion

10:30 to 11:00 - **Coffee Break**

- 11:00 to 11:45 - Presentation - **Kasia Pernal**
  Novel approaches towards constructing reduced density matrix functionals within random phase approximation framework
- 11:45 to 12:15 - Discussion

12:15 to 13:45 - **Lunch**

Session 2: Savin, Gidopoulos, Berakdar & Theophilou (chair Schilling)

- 13:45 to 14:30 - Presentation - **Andreas Savin**
  Combining methods without double counting in RDMFT context
- 14:30 to 14:45 - Discussion
- 14:45 to 15:30 - Presentation - **Nikitas Gidopoulos**
  Effective potentials to minimise the total energy functional in DFT and RDMFT
- 15:30 to 15:45 - Discussion

15:45 to 16:15 - **Coffee Break**

- 16:15 to 17:00 - Presentation - **Jamal Berakdar**
  Reduced density matrix applied to quantum thermodynamics
- 17:00 to 17:15 - Discussion
- 17:15 to 18:00 - Presentation - **Iris Theophilou**
  Density and kinetic energy density -to- potential mapping on a lattice
- 18:00 to 18:15 - Discussion

Poster session

- 18:30 to 20:30 - Poster Session with cold buffet sandwiches

Day 2 - Wednesday September 27, 2017

Session 3: Piris & Giesbertz (chair Pernal)

- 9:00 to 9:45 - Presentation - **Mario Piris**
  NOF-MP2: a global method for the electron correlation

- 9:45 to 10:15 - Discussion

10:15 to 10:45 - **Coffee Break**

- 10:45 to 11:30 - Presentation - **Klaas Giesbertz**
  One-body reduced density matrix to potential mapping in finite basis sets at elevated temperatures

- 11:30 to 12:00 - Discussion

12:00 to 13:45 - **Lunch**

Session 4: Romaniello, Matito, Knowles & Helbig (chair Gill)

- 13:45 to 14:30 - Presentation - **Pina Romaniello**
  Correlation and spectroscopy in reduced density-matrix functional theory

- 14:30 to 14:45 - Discussion

- 14:45 to 15:30 - Presentation - **Eduard Matito**
  Separation of dynamic and nondynamic correlation

- 15:30 to 15:45 - Discussion

15:45 to 16:15 - **Coffee Break**

- 16:15 to 17:00 - Presentation - **Peter Knowles**
  Density matrix functionals: existence, uniqueness and applicability

- 17:00 to 17:15 - Discussion

- 17:15 to 18:00 - Presentation - **Nicole Helbig**
  Spin and pure state N-representability constraints in reduced density matrix functional theory

- 18:00 to 18:15 - Discussion

Day 3 - Thursday September 28, 2017

Session 5: Gritsenko & Lathiotakis (chair Matito)

- 9:00 to 9:45 - Presentation - **Oleg Gritsenko**
  Natural excitation orbitals as descriptors of single excitations and fractional occupation numbers as descriptors of double excitations in time-dependent response density matrix functional theories

- 9:45 to 10:15 - Discussion

10:15 to 10:45 - Coffee Break

- 10:45 to 11:30 - Presentation - **Nektarios Lathiotakis**
  Effective hamiltonians in RDMFT and single particle properties

- 11:30 to 12:00 - Discussion

12:00 to 13:45 - Lunch

Session 6: Mauser & Legeza (chair Marques)

- 13:45 to 14:30 - Presentation - **Norbert Mauser**
  Measures for electron correlation: nonfreeness

- 14:30 to 14:45 - Discussion

- 14:45 to 15:30 - Presentation - **Örs Legeza**
  Tensor network state ansatz for systems of continuously confined fermions

- 15:30 to 15:45 - Discussion

15:45 to 16:15 - Coffee Break

Contributed talks (chair Gritsenko)
- 16:15 to 16:40 - Presentation - **Christian Krumnow**
  Adapting tensor network states to the structure of interacting fermions

- 16:40 to 17:05 - Presentation - **Stefan Donsa**
  The time-dependent two-particle reduced density matrix method

- 17:05 to 17:30 - Presentation - **Mauricio Antonio Rodríguez Mayorga**
  Steeplechase for 2-RDM approximations

- 17:30 to 17:55 - Presentation - **Ion Mitxelena**
  Recent advances in nof theory

- 17:55 to 18:20 - Presentation - **Martin Hebenstreit**
  SLOCC hierarchy for generic states in 2 x m x n level systems

- 18:20 to 18:45 - Presentation - **Mojdeh Banafsheh**
  Analytically inverted non-additive kinetic potential functional at small density overlaps

Social dinner: le port de pully
- 19:30 to 22:30 - Social Dinner

Day 4 - Friday September 29, 2017

Session 7: Sharma & DePrince (chair Romaniello)

- 9:00 to 9:45 - Presentation - **Sangeeta Sharma**
  Spectrum within Reduced Density Matrix Functional Theory: application to transition metal oxides

- 9:45 to 10:15 - Discussion

10:15 to 10:45 - Coffee Break

- 10:45 to 11:30 - Presentation - **Eugene DePrince**
  Analytic energy gradients, excited states, and pure-state N-representability in v2RDM-driven CASSCF

- 11:30 to 12:00 - Discussion

12:00 to 13:45 - Lunch

Session 8: Ayers & Hollett (chair DePrince)

- 13:45 to 14:30 - Presentation - **Paul Ayers**
  Refining non-N-representable density matrices

- 14:30 to 14:45 - Discussion

- 14:45 to 15:30 - Presentation - **Joshua Hollett**
  A two-pronged approach to electron correlation in RDMFT

- 15:30 to 15:45 - Discussion

Finis

- 15:45 to 16:15 - Closing Word

Finite Uniform Electron Gases

Peter Gill
Australian National University

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.

[1] R. G. Parr and W. Yang, Density-functional theory of atoms and molecules, Oxford, Clarendon Press, 1989.
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Novel approaches towards constructing reduced density matrix functionals within random phase approximation framework

Kasia Pernal
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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 0th-order 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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Combining methods without double counting in RDMFT context

Andreas Savin
CNRS and University of Paris 6 - Sorbonne University, Paris, France

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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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 Hartree-exchange 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.

[1] N. N. Lathiotakis, N. Helbig, A. Rubio, and N. I. Gidopoulos, Phys. Rev. A 90 032511 (2014).
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Reduced density matrix applied to quantum thermodynamics

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[2] University of Kaiserslautern, Germany

Recently considerable research efforts were devoted to study of the thermodynamic behaviour of nanoscale quantum structures [1] with an emphasis on the question as to which extent the quantum nature of the system, and in particular entanglement, can be exploited to enhance the performance of quantum heat engines. Motivated by the fact that entanglement entails mixedness and correlation we investigated theoretically correlated many body systems. We focus on the low-energy excitations that can be captured by an effective quantum spin model, possibly with a topologically non-trivial spin order. Thermodynamic quantities are formulated in terms of the reduced density matrices making possible to trace the role of entanglement [1,2]. For instance, we find that an efficient spin-dependent Otto heat engine can be constructed with the working substance being Ni2 dimer driven by non-resonant THz field. As evidenced by full ab-initio calculations the entanglement enhances the cycle efficiency. The same applies to quantum spin systems with non-collinear magnetic order. In particular, we studied quantum heat engines with a working substance being a helical multiferroic structure, meaning a system which is susceptible to external electric and magnetic fields allowing to perform electromagnetic work. We will discuss how to exploit the inherent spin non-collinearity to enhance the thermodynamic cycle efficiency [2]. Practical applications such as the entanglement-assisted thermal pumping of spin currents will be presented.

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

Iris Theophilou[1], M. Ruggenthaler[1], F. Bucholz[1], F.G. Eich[1] and A. Rubio[1,2]
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[2] Universidad del Pais Vasco UPV/EHU, San Sebastian, Spain.

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.

NOF-MP2: A global method for the electron correlation

Mario Piris
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The energy of an electron system can be determined exactly from the knowledge of the one- and two-particle reduced density matrices (1- and 2-RDMs). In practical applications, we employ this exact energy functional but using an approximate 2-RDM that is built from the 1-RDM. Approximating the energy functional has important consequences: the theorems obtained for the exact functional of the 1-RDM [1] are no longer valid.

As a consequence, the functional N-representability problem arises, that is, we have to comply the requirement that reconstructed 2-RDM must satisfy N-representability conditions to ensure a physical value of the approximate ground-state energy. In the first part of this talk, the role of the N-representability in approximate one- particle functional theories [2] will be analyzed. The 1-RDM functional is called Natural Orbital Functional (NOF) [3] when it is based upon the spectral expansion of the 1-RDM.

Appropriate forms of the two-particle cumulant have led to different implementations [4], being the most recent an interacting-pair model called PNOF7 [5]. The latter is able to treat properly the static (non-dynamic) correlation and recover an important part of dynamic correlation. However, accurate solutions require a balanced treatment of both types of correlation. In the second part of the talk, a new method capable of achieving dynamic and static correlation even in those difficult cases in which both types of correlation are equally present will be presented. The starting-point is a determinant wavefunction formed with PNOF7 natural orbitals. Two new energy functionals are defined for both dynamic (Edyn) and static (Esta) correlation. Edyn is derived from a modified second-order Møller-Plesset perturbation theory (MP2) [5], while Esta is obtained from the static component of the PNOF7. Double counting is avoided by introducing the amount of static and dynamic correlation in each orbital as a function of its occupation. The total energy is represented by the sum Ehf + Edyn + Esta. The resulting working formulas allow for correlation to be achieved in one shot. Some challenging examples will be presented as well.

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One-body reduced density matrix to potential mapping in finite basis sets at elevated temperatures

Klaas Giesbertz
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Density functional theory in finite basis sets tends to degenerate to one-body reduced (1-RDM) functional theory. As all calculations are done in finite basis sets, a rigorous foundation of 1-RDM functional theory is desirable. To avoid uniqueness problems in the potential to 1RDM mapping, I will discuss the foundations of 1-RDM functional theory in finite basis sets at finite temperatures, both for fermions and bosons. The fermionic case turns out to be relatively straightforward, but the bosonic case requires more care. The main result is that we can rigorously proof v-representability and functional differentiability in this setting.

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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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.

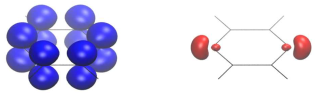

Fig. 1 DYNAMIC NONDYNAMIC

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Density matrix functionals: existence, uniqueness and applicability

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Many popular approximations of the two-electron density matrix are formulated as algebraic functions of the one-electron density matrix, typically in the N-in-N active orbital space. Whilst good accuracy can often be achieved, there are examples of wavefunctions with identical one-electron, but strongly different two-electron density matrices, which mean that algebraic density-matrix functionals cannot be exact everywhere [1]. The implications of this to the design of approximations to the static and dynamic correlation energy are discussed.

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Spin and pure state N-representability constraints in reduced density matrix functional theory

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Reduced Density Matrix Functional Theory is a method that relies on the 1-1 correspondence between the many-body ground-state wave function and the first order reduced density matrix (1RDM) and uses the latter as its fundamental variable. The ground state of a system is determined within this approach by minimizing the energy functional with respect to the 1RDM under the constraint that the 1RDM corresponds to a fermionic ensemble (Coleman's conditions). Additional constraints can be employed to ensure the existence of a fermionic ensemble with a specific S_z . However, there remain the two questions if the fermionic system corresponds to a specific total spin and if the system can be represented by a pure state. We show that generally the answer to both questions is negative unless additional constraints are enforced and discuss these constraints exemplary for several small systems.

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Natural excitation orbitals as descriptors of single excitations and fractional occupation numbers as descriptors of double excitations in time-dependent response density matrix functional theories

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Physical interpretation is given to the elements of the matrix diagonalization problem of time-dependent response Hartree-Fock (TDHF) and density matrix functional (TDDMFT) theories. A simple description of single excitations calculated in TDHF and TDDMFT is given in terms of natural excitation orbitals (NEOs) [1,2]. The NEOs are obtained by diagonalization of a submatrix in the diagonalization problem and they closely resemble virtual Kohn-Sham orbitals of density functional theory (DFT). A crucial role of fractional occupation numbers (FONs) of the natural orbitals (NOs) in description of double excitations obtained in TDDMFT is demonstrated. An analytical expression for the energy of a double excitation as a function of the FON ratio is derived in a simple model [3].

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Effective Hamiltonians in RDMFT and single particle propeties

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In DFT, the electron density of any interacting particle system in the ground state is reproduced by an independent electron system, the Kohn Sham system. Thus, KS theory, apart from leading to a system of single particle equations that are solved self-consistently, it offers a very useful single-particle description from which spectral properties like orbital energies, electronic bands and densities of states are routinely used to characterize physical systems and describe several phenomena. On the contrary, in RDMFT, there is no "default" single particle Hamiltonian like KS in DFT. Ionization energies, however, can be obtained by applying Extended Koopmans' theorem [1]. There are several attempts to define effective Hamitlonians in RDMFT [2] with mainly two targets: (1) to minimize effectively the total energy in RDMFT which is a relatively complicated task and (2) to define a useful single particle picture. In the present talk, we review several Hamiltonian schemes that have been proposed for RDMFT.

We focus on the local-RDMFT [3] in which the occupation numbers are given as usual by minimizing the energy functional but the natural orbitals are replaced by those orbitals that optimize the same energy functional under the constraint that they obey a single particle Schroedinger equation with a local potential. We present applications of local RDMFT [4] as well as recent ideas to improve its efficiency and performance [5]. We also compare the effective potential of local RDMFT with that obtained by inverting the density of a full RDMFT minimization [6].

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Measures for electron correlation: Nonfreeness

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The relative entropy of a correlated state and an uncorrelated reference state is a reasonable measure for the degree of correlations [1]. A particular measure, coined “nonfreeness” was introduced by Gottlieb and Mauser [2]. A key question is to which uncorrelated state to compare to. The relative entropy becomes minimal for the uncorrelated reference state that has the same one-particle density matrix as the correlated state, so “nonfreenes” is unique and reasonable. Held and Mauser have demonstrated [3] that for relevant physical situations, such as finite temperatures or a correlation enhanced orbital splitting, other choices of the uncorrelated state, even educated guesses, overestimate correlations.

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Tensor network state ansatz for systems of continuously confined fermions

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In this contribution, we overview tensor network states techniques that can be used for the treatment of high-dimensional optimization tasks used in many-body quantum physics with long range interactions and ab initio quantum chemistry. We will also discuss the controlled manipulation of the entanglement, which is in fact the key ingredient of such methods, and which provides relevant information about correlations. Recent developments on fermionic orbital optimization, externally corrected coupled cluster density matrix renormalization group (TCCSD-DMRG) will be presented. Finally, new results will be shown for systems of continuously confined fermions in light of Generalized Pauli Principle.

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Adapting tensor network states to the structure of interacting fermions

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The direct computation of the ground state of interacting fermionic systems becomes quickly infeasible with increasing system size due to the exponential size of the Hilbert space. Additional structure present in many physical systems needs to be exploited in order to advance and simulate realistic systems. In recent years, it was noted that tensor network states (TNS) are able to capture naturally occurring correlations efficiently such that ground states of distinguishable particles can be approximated using the density matrix renormalization group algorithm [1]. Applied to fermionic systems however, TNS capture correlations partially in the wrong picture as individual Slater determinants might not be efficiently representable. We correct this shortcoming by augmenting TNS with additional degrees of freedom [2] which allow to systematically optimize the single particle basis. By this we are able to construct ground state search and time evolution methods which adapt the single particle basis according to the correlation structure of the problem automatically. Widening the scope, similar ideas of identifying more optimal structures can be exploited in DFT and establish links between TNS and DFT as we will discuss.

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The time-dependent two-particle reduced density matrix method

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Describing time-dependent many-body systems where correlation effects play an important role remains a major theoretical challenge. The full solution of the full N-body Schrödinger equation is prohibitive for large systems due to the exponential scaling with the number of particles. Frequently employed approaches to treat time-dependent many-body systems are based on effective mean-field approaches, e.g. time-dependent density functional theory, or multi-configurational methods like the multi-configurational time-dependent Hartree Fock method. While the first one makes computation of large systems feasible but is lacking the accuracy of wave-function based methods, the second approach is in principle exact but the exponential scaling with the number of particles limits its application to small system sizes. To bridge the gap between those two descriptions we developed the time-dependent two-particle reduced density matrix (TD-2RDM) method [1, 2], which allows to treat correlations up to the two-particle level exactly and circumvents the exponential scaling of multi-configurational methods. The TD-2RDM method is based on a contraction consistent reconstruction of the three-particle reduced density matrix, as required for the proper closure of the equations of motion for the TD-2RDM. Contraction consistency and enforcing N-representability constraints are key to achieve accurate and stable propagation of correlated dynamics. We show benchmark results for atoms in strong laser fields [2] and the non-equilibrium dynamics in Hubbard clusters. We will highlight the importance of two-particle correlations and discuss future developments and applications of the method.

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Steeplechase for 2-RDM approximations

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In this work, we will present some tests that we have performed to analyse the goodness of second-order reduced density matrices approximations (2-RDM) when the effects of correlation become important. The approximations studied are used to construct functionals in natural orbital functional theory [1-3]. The battery of tests presented here include: the delocalization index, the calculation of the 2-RDM trace, the termwise error for diagonal elements and for the whole matrix, the fulfilment of some N-Representability [2,4] 4conditions, the attainment of symmetry properties and magnitudes related to the intracule density. Unlike common tests that are based on the reproduction of the electronic energy, this battery of tests offer a wide variety of assessments that permit to check relevant features of the 2-RDM that are normally not put into test. To tune the correlation effects and dispose of a wide range of correlation regimes, we have chosen the Harmonium atom (HA) model [5] as our reference system. In HA, the effects of correlation are driven by one single parameter called the confinement strength. This model systems provides a realistic description of electron correlation effects and renders itself to analytic solutions for some values of the confinement strength. Harmonium has been used to calibrate DFT functionals [6] and third-order reduced density matrices [7].

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Recent advances in NOF theory

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General expressions for analytic gradients with respect to nuclear motion are derived for NOFT [1,2], in such a way that resulting equations do not require resorting to linear-response theory. Recently published PNOF7 [3] is used to yield accurate equilibrium geometries in agreement with experimental data. The latter is also tested by using the 2-, 4- and 6-sites Hubbard model, together with a set of commonly used NOFs [4,5]. Encouraging results point out the importance of imposing (2,2)-positivity N-representability conditions on the 2-RDM [6] in order to obtain accurate and consistent results, as well as the balanced treatment of static and dynamic electron correlation.

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SLOCC hierarchy for generic states in 2 x m x n level systems

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We consider entanglement in the three partite system consisting of a qubit, an m-level and an n-level system. In particular, we use tools introduced in [1] to characterize entanglement transformations under stochastic local operations and classical communication (SLOCC). We identify the generic SLOCC classes for the two inherently distinct cases n=m and n≠m. Furthermore, we derive the full hierarchy of the generic SLOCC classes, i.e., we characterize transformations to lower dimensions. Moreover, we investigate common resource states, i.e., states in a higher-dimensional Hilbert space that can reach all 2 x m x n states. In a continuation of the project, we would like to investigate the properties of specific SLOCC classes. In particular, we are interested in the arising entanglement polytopes.

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Analytically inverted non-additive kinetic potential functional at small density overlaps

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In density-dependent embedding methods [1], non-additive kinetic potential plays an important role. This functional is a bi-functional depending on a pair of electron densities ρA and ρB. We report here the first time use of the numerical inversion procedure to generate reference non-additive kinetic potentials for weakly overlapping ρA and ρB. To obtain exact quantity of non-additive kinetic potential, analytically inverted procedure is proposed [2]. It is especially suited for small overlap cases and it is applicable only for a special case of ρA being a two-electron density. The procedure requires particular constraint on the choice of pair of electron densities to assure their admissibility as well as the smallness of the overlap between ρA and ρB. The constraint is applied over total density to provide the pair of electron densities. Mathematical challenge of this preparation and the accuracy of the pair electron densities will be presented in detail. All reported are obtained using basis set free numerical solver of Kohn-Sham equation for diatomic systems [3]. The non-additive kinetic potential at small overlap is constructed for different systems of four electrons ($LiHe^+$, $BeHe2^+$, LiH and BeH^+).

The exact potential was calculated for a chosen four electron system changing interatomic distance. For all investigated systems, the non-additive kinetic potentials derived by means of the proposed analytical inversion method was compared to the potential obtained using the common approximations to the density functional of the kinetic energy. We showed that exact potential is smooth in overlap region for all system and a system with different interatomic distances.

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Analytic energy gradients, excited states, and pure-state N-representability in v2RDM-driven CASSCF

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The direct variational optimization of the ground-state two-electron reduced-density matrix (2-RDM) can routinely be achieved via semidefinite programming techniques. The resulting variational 2-RDM (v2RDM) approach can be used to realize polynomially-scaling complete active space self-consistent field (CASSCF) computations applicable to active spaces comprised of 50 electrons in 50 orbitals, or more [1]. Analytic energy gradients for v2RDM-CASSCF are readily available, and excited-state information can be extracted from the time-evolution of the one-electron RDM [2] or within the framework of the extended random phase approximation (ERPA) [3,4]. However, within the ERPA, a proper treatment of excitations from degenerate ground states requires the application of pure-state N-representability conditions [5,6].

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Refining non-N-representable Density Matrices

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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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Spectrum within Reduced Density Matrix Functional Theory: application to transition metal oxides

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Despite decades of intensive research on approximations to the exchange correlation functional in density functional theory (DFT) several ground state properties, most famously the insulating state of transition metal oxides (TMO), remain intractable problems. Furthermore, away from the ground-state TMOs show the rich physics of insulator-metal phase transitions and the physics of this phase transition is totally different for different methods; DFT based method, even with most sophisticated functionals, do not agree with many-body methods like dynamical mean field theory. In this regard, reduced density matrix functional theory (RDMFT) shows tremendous promise [1,2,3,4] in that (i) it is able to capture the correct insulating state of TMOs under ambient conditions and (ii) away from ambient pressure RDMFT correctly captures the physics of the insulator to metal phase transition. In my presentation I will talk about RDMFT in general and treatment of strong correlations and existing problems with RDMFT in particular.

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Studying the effect of spin-orbit coupling on electronic properties of $BiFeO_3$

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We have studied the electronic properties of of BFO under the effect of spin-orbit coupling. We have determined the band structures in two different directions [-101] and [111]. Our results show that there is no effect of changing directions on electronic character of BFO, the band gaps in both directions are nearly the same (0.84 eV), which is in good agreement with available literature. The magnetic moment of Fe atoms is found to be 3.40 μB. The value to polarization in each direction is found to be 0.5 μC/cm2 in [111] and 1.1 μC/cm2 in [-101] direction. Thus we can say that the electronic properties of BFO are isotropic in nature as no significant change has been observed in our study.

Reduced Density Matrix Theory for Fermion-Boson Coupled Systems

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Reduced density matrix (RDM) theory proved in the last decades to be successful in describing many many- body problems that are not easily accessible by the more common many-body perturbation theories or density funtional theory. Especially as RDM theories are typically non-perturbative, there are advantages in strong coupling scenarios. However, the RDM was to our knowledge never applied to systems with more than one active particle type. The focus of the present work is to analyze the possibilities and problems of an extension to Fermion-Boson coupled theories. Comparing a typical bilinear interaction term of the form di cj (bk + ak), where d /c and b/a indicate Fermion and Boson creation/annihilation operators, respectively and the Fermionic 2-body interaction term di dj ck cl, the former should have a considerably reduced definition space, which we hope to be exploitable somehow. On the other hand, the bilinear interaction has a very different structure and it is not clear at all, how to define a RDM that carries all information to compute the expectation value ⟨di cj(bk + ak)⟩. To overcome this fundamental problem, we construct a higher dimensional auxiliary system that allows for a quasiparticle basis with Fermionic and Bosonic degrees of freedom. In this particular basis, the Hamiltonian becomes a new structure that has only one-body and two-body parts. Hence, the theorems of the “pure” RDM theory can be transferred.

Transport properties of asymmetric zigzag graphene nanoribbon built by carbon vacancy in edge

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Using nonequilibrium Green’s functions in combination with density functional theory, we investigated the electronic transport behaviors of single layer zigzag graphene Nanoribbon (ZGNR) with a Carbon vacancy in edge. The results show that electronic transport properties of the asymmetry ZGNR can be modulated by vacancy in edges, and prominent negative differential resistance (NDR) can be observed [1]. These results may be useful for designing practical devices based on graphene Nano-ribbons. Since we observed spin filtering effect, it leads us forward to using in spintronic devices. Besides, Negative Differential Resistance (NDR) is of great importance that occurred due to the electron tunneling into one of the neighboring islands (valleys) in conduction band i.e. into a system of states of reduced dimensionality. It means high energy electrons transmitting between two terminals don’t have enough space (dimensional confinement) in collector (conduction band) so that they are tunneling to second barrier in collector and finally we observe decreasing current. Our results on transport properties of defected graphene and defect free graphene indicate a great potential in applications such as spin sensitive electronic devices.

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Study of intersystem crossing between excited singlet and triplet states of halogenated BODIPY derivatives

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Halogenated BODIPY derivatives are emerging as important candidates for photodynamic therapy of cancer cells due to their high phosphorescence activity [1]. Unsubstituted BODIPY has no phosphorescence activity while incorporation of heavy halogen atoms in its molecule makes BODIPY highly phosphorescent. It can be assumed that the presence of halogen atoms induces spin-orbit coupling resulting in a higher rate of intersystem crossing from the excited singlet state to the low lying triplet states thus leading the experimentally observed high phosphorescent activity. In order to fully understand the excite state dynamics of these systems regarding the influence of halogen atoms, we perform surface hopping molecular dynamics simulations on potential energy surfaces resulting from the eigenstates of the total electronic Hamiltonian including the spin-orbit coupling. A subset of 30 initial conditions starting in S2 state was used for gas phase simulations with spin-orbit coupling utilizing implementation of the three-step propagator in the Newton-X software suit as well as two novel “one-step” approaches [2].

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Intermolecular interactions in the presence of stretched bonds: an embedded electron-pairs approach.

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Non-covalent interactions occurring between molecules in which bonds are being stretched or broken are a fascinating, yet little-studied subject. This shortage of information stems largely from the inability of the majority of computational methods to describe both strong and weak long-range correlation with sufficient accuracy. Now, by combining the generalized valence bond wavefunction [1], the extended random phase approximation correlation expression [2,3] and the reduced density-matrix embedding formalism [4], we are able to gain access to this class of systems. We show the theory and illustrative examples, including a fluorine molecule attempting a reaction with ethylene.

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DFT+RDMFT and RDMF from constrained optimization

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For strongly correlated solids like NiO it is known from the successes of DFT+dynamical mean field theory that the deficiencies of local or semi-local DFAs can be cured by treating the local atomic degrees of freedom with an advanced correlation method. We propose a new method for the calculation of the electronic and atomic structure of correlated electron systems based on a hybrid theory combining DFT and RDMFT (proposed by Bloechl, Walther and Pruschke, Phys. Rev. B 84, 205101). The local atomic physics is described with local orbitals, thus leading to a rather small one-particle basis for which we have to calculate the RDMF. For this RDMF we can now either employ parametrized explicit functionals or implicit functionals based on approximations of Levy's constrained optimization recipe. I present details about the first implementation of this approach (in our projector augmented wave DFT code) and report on results for correlated solids.

New geminal based DMFT functionals from wavefunction 2RDM analysis

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Almost all functionals that are currently used in DMFT have been created by some a priori Ansatz that generates approximate 2RDM elements. We have opted to use a more consistent approach in order to find a suitable approximate functional. The 2RDMs of rather accurate wavefunctions (in NO basis) have been analysed for several small molecules. The results show that a perfect orbital pair geminal like structure is present, even though no restrictions have been applied from the onset. In addition to this finding, it was found that the dynamical correlation between the geminals is dominated by non-JKL multipole-multipole interactions. Lastly, the analysis shows that the Exchange between unpaired electrons on fragments, present when multiple bonds are broken, is not described correctly by the standard APSG functional. In high spin cases one can fix this problem by doubling the exchange between bond broken geminals. A new functional is proposed that incorporates these corrections. This functional is capable of reproducing CASSCF curves that have a similar active space.

5 Participant List

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Sharma, Sangeeta - Max Planck Institute of Microstructure Physics, Germany
Theophilou, Iris - MPI for the Structure and Dynamics of Matter, Germany
van Meer, Robert - RIKEN Advanced Institute for Computational Science, Japan

New application

For this workshop, we have set up an application with relevant information for your mobile android, iPhone, iPad.

https://planify.io/download/

Click on the link below to add the program on the app

http://planify.io/plans/index.html?id=reducedDensity

Or enter directly the program code: reducedDensity

WIFI

SSID: PUBLIC-EPFL
Website: Enclair.epfl.ch
Username : x-cecamguest
Password : ziglam53

Notes:

Notes:

Notes:

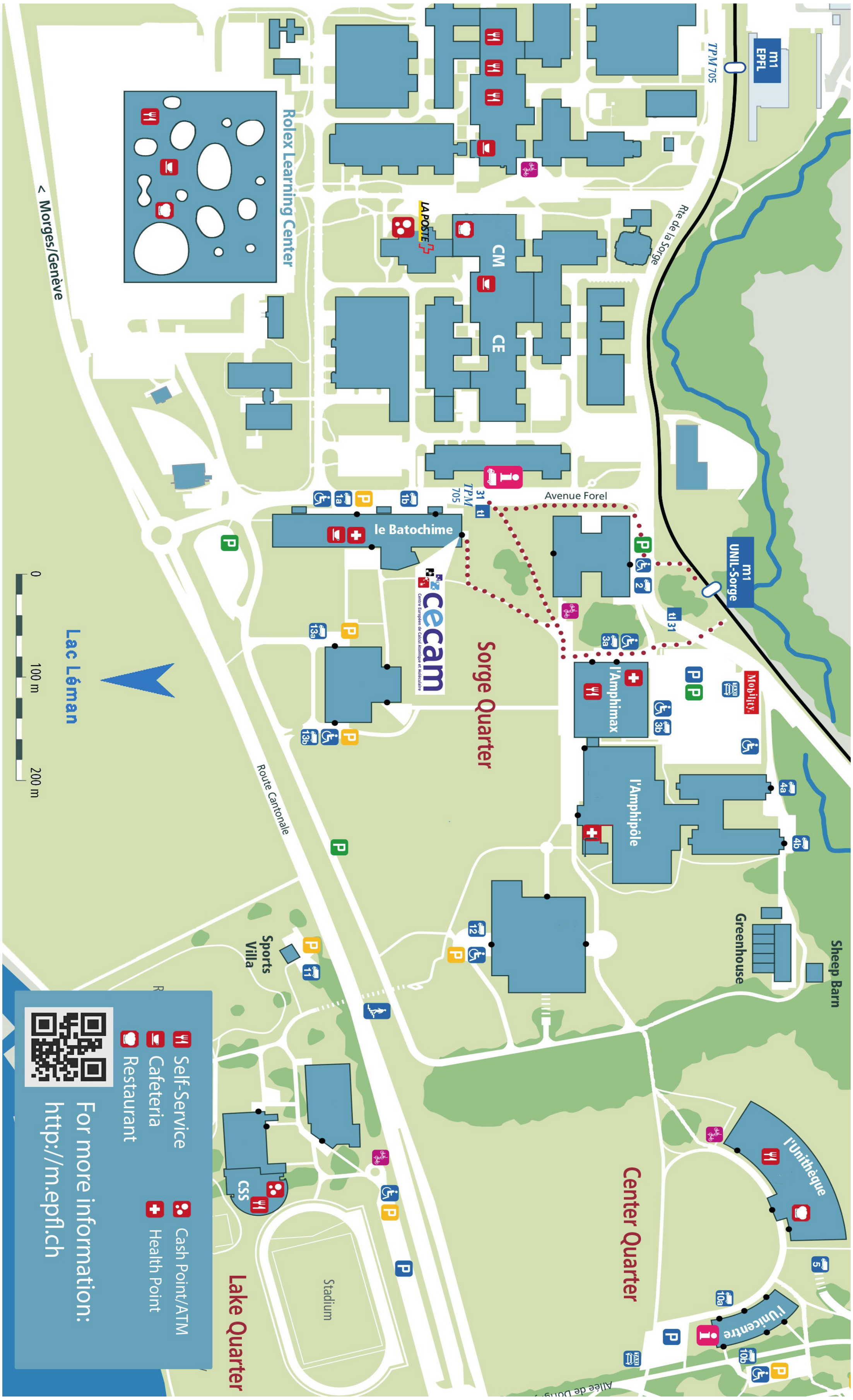
Social Dinner on Thursday 28 September 2017 at 19:30

Restaurant Port de Pully
Route du Port 7
1009 Pully
Tel +41 21 728 78 78
www.pullyport.ch

Included in the MENU are 3 course meal, 2dl wine, mineral waters, tea or coffee. Any extras will be invoiced to the individual.

Directions from CECAM
Take metro M1 from UNIL-Sorge and get off at Lausanne-Flon.
From Lausanne-Flon take elevator up and walk southeast up to Place St-Francois.
Take bus 8 from St-Francois going in the direction Verrière, and get off at Pully-Port.
Bus leaving St-Francois every 10 minutes and count 12 minutes' journey to the bus stop.

Returning to the Hotel.
Take bus Nr 8 from bus stop Pully-Port, direction Grand-Mont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31
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31
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Sorge Quarter
13a
13b
l'Amphimax
3b
Mobility
l'Amphipôle
4a
4b
Lac Léman
0
100 m
200 m
Route Cantonale
Sports Villa
11
12
Greenhouse
Sheep Barn
CSS
Stadium
Lake Quarter
Center Quarter
l'Unithèque
5
10a
l'Unicentre
10b
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