European Research Council

ERC Consolidator Grant 2014
Research proposal [Part B1]

Improving the accuracy and reliability of electronic structure calculations: New exchange-correlation functionals from a rigorous expansion at infinite coupling strength

corr-DFT

- Principal Investigator (PI): **Dr. Paola Gori-Giorgi**
- Host institution: **VU University Amsterdam, The Netherlands**
- Proposal full title: **Improving the accuracy and reliability of electronic structure calculations: New exchange-correlation functionals from a rigorous expansion at infinite coupling strength**
- Proposal short name: **corr-DFT**
- Proposal duration in months: **60**

By virtue of its computational efficiency, Kohn-Sham (KS) density functional theory (DFT) is the method of choice for the electronic structure calculations in computational chemistry and solid-state physics. Despite its enormous successes, KS DFT's predictive power and overall usefulness are still hampered by inadequate approximations for near-degenerate and strongly-correlated systems. Crucial examples are transition metal complexes (key for catalysis), stretched chemical bonds (key to predict chemical reactions), technologically advanced functional materials, and manmade nanostructures.
I aim to address these fundamental issues, by constructing a novel framework for electronic structure calculations at all correlation regimes. This new approach is based on recent formal developments from my group, which reproduce key features of strong correlation within KS DFT, without any artificial symmetry breaking. My results on the exact infinite-coupling-strength expansion of KS DFT will be used to endow that theory with many-body properties from the ground up, thereby removing its intrinsic bias for weak correlation regimes.
This requires novel combinations of ideas from three research communities: chemists and physicists that develop approximations for KS DFT, condensed matter physicists that work on strongly-correlated systems using lattice hamiltonians, and mathematicians working on mass transportation theory. The strong-correlation limit of DFT enables these links by defining a natural framework for extending lattice-based results to the real space continuum. On the other hand, this limit has a mathematical structure formally equivalent to the optimal transport problem of mathematics, enabling adaptation of methods and algorithms.
The new approximations will be implemented with the assistance of an industrial partner and validated on representative benchmark chemical and physical systems.

Section a: *Extended Synopsis of the scientific proposal*

The electronic-structure problem

Accurately predicting electronic structure from first principles is crucial for many research areas such as chemistry, solid-state physics, biophysics, materials science, and biochemistry. In principle, the electronic structure is determined by the Schrödinger equation, which can only be solved in practice for few electrons. Thus, chemists and physicists have developed approximate methods, most importantly, wave-function methods and density-functional-theory-based methods. The former are more accurate, but computationally very demanding, and for this reason limited as far as system size is concerned.

Density Functional Theory: successes...

Kohn-Sham (KS) Density functional theory (DFT) [1] has been a real breakthrough for electronic structure calculations. KS DFT uses the one-electron density and a non-interacting wave function as basic variables, much simpler quantities than many-electron wave-functions, allowing to treat realistic large systems. Together with its extension to time-dependent (TD) phenomena (TDDFT) [2], KS DFT made it possible to study a huge number of chemical, physical, and biological processes, with a large impact on different fields (inorganic and organic chemistry, solid state physics, materials science, surface physics, biochemistry and biophysics).

The key idea of KS DFT is an exact mapping [3] between the physical, interacting, many-electron system and a model system of non-interacting fermions with the same density, allowing for a realistic treatment of the electronic kinetic energy. All the complicated many-body effects are incorporated in the so-called exchange-correlation (xc) energy functional. Although, in principle, the exact xc functional is unique (or "universal"), it needs to be approximated, and there is no well defined path to do that. Mainstream strategies follow the idea of a "Jacob's ladder" [4], based on an ansatz for the dependency of the xc functional on the relevant "ingredients", increasing the complexity of the approximations in a hierarchical manner (local density, local density gradients, local KS kinetic energy, KS occupied orbitals, up to the KS virtuals). A (sometimes very large) number of parameters can be also introduced and fitted to specific data sets [5]. The scientific community who tries to improve the approximate KS xc functionals is relatively small, but it has an enormous potential impact because of the huge number of DFT users: the most successful approximations are applied to a large variety of problems in chemistry and physics, and are used every year by thousands of scientists in different research areas.

... and failures

Despite all these efforts, present-day KS DFT is not yet able to accurately capture the physics of systems in which electronic correlation plays a prominent role. For example, we see often that approximations working well for main group chemistry fail for transition metals (which are the workhorse of catalysis). More generally, for systems containing *d* and *f* elements, spin- and spatial-symmetry breaking occurs erratically in DFT, and are very sensitive to the functional chosen. When many symmetries are broken, it is difficult to keep the potential energy surfaces continuous. Another consequence of symmetry breaking is that spin densities are not correctly described, resulting in wrong characterizations of several properties [6,7]. The breaking of the chemical bond (key to predict chemical reactions) is also characterized by strong ("static") correlation and is highly problematic for the current approximations [8]. Other important examples are given by the delicate physics of functional materials and manmade nanostructures [6,7,9,10]. These inherent difficulties can severely (and sometimes in an unpredictable way) hamper calculations, depending on their relative importance with respect to other effects that are better captured by the available approximate functionals [10]. KS DFT electronic structure calculations are important building blocks to model systems with multiscale approaches. Thus, their errors may affect in a drastic way the final results. Addressing the fundamental problems of KS DFT can make the difference between using computations to *understand* experiments (as it is mainly done nowadays) and to be able to really *predict* them.

This proposal aims at addressing the fundamental DFT problems inherent to the description of strongly-correlated systems following a physically and mathematically sound strategy radically different from mainstream ones.

A rigorous starting point: The exact strong-correlation limit of DFT

KS DFT is based on a system of *non-interacting* fermions, treating the electron-electron interactions in an approximate way. Current approximations work when the physics of the true, interacting, system is not too different than the non-interacting one of Kohn and Sham: for these cases the "Jacob's ladder" strategy is able to accurately capture the (relatively small) xc effects. Strongly-correlated systems, however, are radically different from non-interacting ones [11]. In these cases, **the xc functional needs to be a drastic correction**, and traditional strategies have failed so far.

My research efforts of the last four years, as group leader of a project mainly funded by the Dutch career-grant VIDI, have been mainly devoted to develop **a rigorous starting point to build this drastic correction**, which, as we showed, works in prototypical cases. This rigorous starting point is the exact xc functional in the limit in which correlation becomes infinitely strong, called "strictly-correlated electrons" functional (SCE). The SCE functional has a highly non-local dependence on the density that encodes new information with respect to the traditional ingredients of the "Jacob's ladder" approach. Despite this high non-locality, I have recently found an elegant and powerful shortcut to compute the SCE functional derivative [12], yielding a one-body multiplicative Kohn-Sham potential that is truly able to make non-interacting electrons reproduce key features of strongly-correlated ones, without artificially breaking any symmetry, as shown by our results on model semiconductor quantum wires and quantum dots [13,14].
I have also extended the SCE formalism to fractional electron numbers in a rigorous way [15], and shown that the SCE xc functional displays a derivative discontinuity at integer electron numbers in low-density systems even in a spin-restricted framework, a key property to describe the ground-state of strongly-correlated systems, as well as important applications such as quantum transport [9,10,16], missed by all the available approximate xc functionals [9,10].
The importance of these results is well recognized in the fundamental DFT scientific community: I have been invited to present them at most of the key conferences in the field, and the xc SCE functional is mentioned in the most recent DFT review articles as a promising new route [8,9].
Another important result I have obtained, crossing disciplinary boundaries, is the reformulation of the SCE functional as a mass transportation theory (or optimal transport) problem, an important field of mathematics and economics [17]. This reformulation paves the way to a cross-fertilization between two very different research areas, and has already triggered a huge interest in the mass transportation theory community, as shown by the increasing number of groups that are publishing on the subject [18-20] and by the many invitations I have received to speak at optimal transport and mathematics conferences.
The goal of this ERC proposal is to transform these rigorous results into a complete framework for electronic structure computations, working at all correlation regimes, and for a vast range of chemical and physical systems.

From the exact strong-coupling expansion to functionals for chemistry and solid-state physics: Challenges
Interesting systems in chemistry and solid-state physics, however, are more challenging for the SCE functional than the low-density nanostructures I have treated so far, because the kinetic correlation energy and the electron-electron repulsion often have similar importance. This requires corrections to the SCE functional, which are one of the objectives of this proposal, and will be built in a rigorous way by importing ideas from different research areas in a novel way, as detailed below.
The other big challenge is that the physics of strong correlation encoded in the highly non-local density dependence of the SCE functional does not come for free: the SCE problem is sparse but nonlinear, and a general algorithm for its evaluation following our original formulation is still an open problem. Progress has been made very recently by a group in Berkeley [20] using our reformulation of the SCE functional as a mass transportation theory problem [17], although the procedure is still cumbersome and needs further developments. The transformation of the SCE formalism into a practical xc functional is the other main pillar of this research proposal.

Goal and Objectives
In order to achieve the goal of an accurate, computationally affordable, *ab initio* description of the ground-state energy and other properties of strongly-correlated many-electron systems, my team and I will attain the **following objectives**:

1. Add higher-order corrections to (go beyond) the KS SCE approach, especially introducing the spin dependence into the xc SCE functional
2. Develop dedicated algorithms to evaluate the SCE functional in the general three-dimensional case.
3. Construct controlled approximations of the results of objectives 1 and 2 to increase the computational efficiency. This is necessary for very large systems, and it can also be used in general in case the exact implementation of objectives 1 and 2 turns out to be computationally too demanding.
4. Test the new approximate functionals and algorithms of Objectives 1-3 in representative chemical and physical benchmark systems.

A new interdisciplinary approach
In pursuing the end goal of this project, I will unite efforts from research fields that, although aiming at similar objectives, traditionally (with few exceptions) keep a distance from each other: the chemistry/physics

community that develops xc functionals and kernels for DFT and TDDFT, and the physics community that develops strongly-correlated techniques in the context of lattice hamiltonians. As I will explain in detail in the Methodology part, this will be possible because the KS SCE provides a new framework to import results from lattice hamiltonians into the DFT real-space "continuum". Moreover, as already mentioned, the SCE theory has a mathematical structure formally equivalent to an optimal transport (or mass transportation theory) problem [17]. This link will be potentiated and exploited in this project, both for the algorithmic part and for the construction of corrections to SCE.

I have designed two parallel strategies: a "top-down" and a "bottom-up" approach synergistically combining chemistry, physics and mathematics. For the top-down approach, my team and I will develop and implement the exact SCE (and beyond) functionals and, if needed, make approximations at a later stage. For the bottom-up approach, we will directly begin with approximations inspired to the SCE form and learn by implementing and testing them. These two complementary strategies reinforce each other, as schematically shown in Fig. 1.

In practice, in the top-down strategy I will use strongly-correlated-electrons techniques from lattice hamiltonians and mass transportation theory ideas to design corrections to KS SCE (Objective 1). Mass transportation theory will be also crucial for the algorithmic part (Objective 2). In the bottom-up strategy I will build approximate functionals inspired to the SCE form and to the higher-order terms of Objective 1 and combine them with gradient corrections (and beyond) specifically designed (Objective 3) and I will extensively test them (Objective 4).

I propose to create and lead a multidisciplinary research group of 3 graduate students and 2 postdoctoral associates with expertise in the three relevant research areas, embedded into several collaborations at the local and international level, as described below, where the feasibility of the objectives is also addressed.

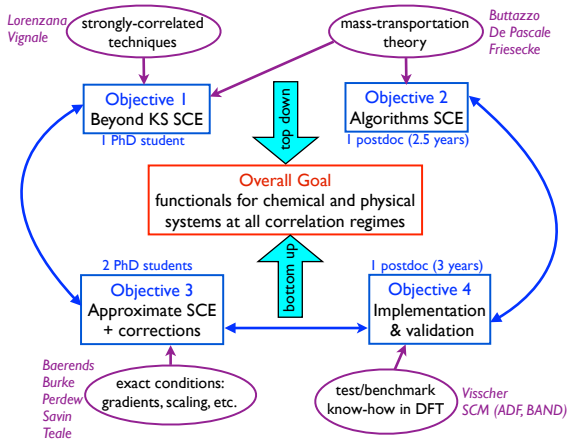

Fig. 1: Schematic overview of how the project is organized, showing the objectives, their interactions and the "top-down" and "bottom-up" strategies towards the final goal. For each objective, the team members are also shown in blue. The international and local collaborations involved in each objective are reported in purple italics, together with the main input research areas/ideas.

Objective 1: Beyond KS SCE through a new merging of strong-correlation techniques and KS DFT

Team member: 1 PhD student [Focus Area: Physics]

International Collaborations: J. Lorenzana (Physics, Rome "La Sapienza", Italy), G. Vignale (Physics, University of Columbia Missouri, USA)

A sort of "first-order" correction beyond SCE has been already formulated by myself and my coworkers in terms of local quantum fluctuations [21]. However, this correction does not distinguish between different spin states, which are taken into account only in the KS kinetic energy, but not in the xc SCE functional. Instead, for the delicate physics and chemistry of strongly-correlated materials and nanoscopic systems, the subtle interplay of the spin state and of correlation needs to be captured by the xc functional. The SCE functional is an infinite superposition (characterized by a three-dimensional single collective variable $\boldsymbol{r}$) of configurations of localized electrons, which allows us to define, for each $\boldsymbol{r}$, a lattice model with suppressed double occupation. Thus, we may construct correcting terms in the same fashion as it is done with lattice hamiltonians, exporting the main concepts to the continuum (here the word "continuum" is used to stress the difference with lattice formulations). This can be done by computing magnetic exchange and superexchange corrections as a function of the collective variable $\boldsymbol{r}$. The needed overlap integrals can be obtained from the quantum fluctuation SCE corrections [21]. We will start by calculating exact magnetic exchange and superexchange corrections in simpler systems such as quasi-one-dimensional wires or electrons trapped in two dimensions, studying first smaller number of particles for which wave-function methods are viable for validation. These corrections will be then transformed into density functionals, making and testing approximations at various levels, and will then be implemented and extensively tested in interaction with the other objectives. This is conceptually very different from mainstream approaches in physics such as LDA+U or LDA+DMFT [22,23], which, instead, only correlate some of the LDA orbitals *after* a KS LDA calculation (introducing a basis dependence and double counting problems).

I will collaborate on this project with J. Lorenzana, who has long-standing experience with lattice hamiltonians, and G. Vignale, who will contribute to develop higher-order classical corrections to SCE.

Objective 2: Algorithms for the exact SCE functional from mass transportation theory
Team member: 1 postdoc (2.5 years) [Focus Area: Mathematics]
International Collaborations: G. Buttazzo and L. De Pascale (Mathematics, University of Pisa, Italy), G. Friesecke (Mathematics, Munich Technical University, Germany)
Using concepts and collaborations in optimal transport (or mass transportation theory), I have reformulated the nonlinear SCE functional as a dual Kantorovich problem, consisting in a maximization under linear constraints [17]. This paves the way to readapting algorithms developed in the framework of optimal transport to the SCE problem, which is the main task of this objective. Indeed, very recently, building on our results, a research group in Berkeley has implemented the first prof-of-principle Kantorovich dual solution to compute the SCE functional in arbitrary 3D geometry [20]. We will start by trying to extend this approach to larger systems, reformulating the constraints in a problem given in a basis set, exploring several levels of approximations. Mass transportation theory can be also used to construct corrections to go beyond KS SCE (for example modifying the constraints), complementing the approach described in Objective 1. We will also pursue the Monge formulation, trying to develop algorithms and approximations based on the sparsity of the SCE problem.

Objective 3: xc functionals from approximations inspired to the SCE form and its corrections
Team members: 2 PhD students [Focus Area: Chemistry and Physics]
International Collaborations: K. Burke (Chemistry & Physics, University of California Irvine, USA), J. P. Perdew (Physics, Temple University, Philadelphia, USA), A. Savin (Chemistry, CNRS Paris, France), A. Teale (Chemistry, University of Nottingham, UK)
Local Collaborations, E. J. Baerends
In parallel and in synergy with the efforts described in the previous two objectives, in which a rigorous treatment starting from strongly-correlated techniques and mass transportation theory will be used to develop corrections to KS SCE (making approximations at a later stage), in this part of the project I will start to directly build new approximate functionals by using a functional form inspired to the SCE, and to test them.
The SCE functional has a non-local dependence on the density via one-body quantities called co-motion functions, which dictate the positions of all the electrons as function of a collective single-particle variable **r**. We will start by building *approximate* co-motion functions, constructing and testing new functionals with formal properties taken from the SCE theory: the new ingredient here is the non-locality brought in by the one-body approximate co-motion functions and the higher-order corrections to SCE developed in Objective 1. In order to accurately describe all correlation regimes, we will also combine functionals that work for moderate correlation with our approximate SCE functionals. This can be done by following two main strategies. The first one is based on a rigorous (and size-consistent) approach that avoids any double counting by a local interpolation along the adiabatic connection [24], and will be pursued by collaborating with A. Teale and A. Savin, who can provide accurate reference results along the adiabatic connection for small systems [25,26]. This will allow us to understand at the very basic level the accuracy of our construction. The quantities at weak correlation will be constructed from exchange functionals (exact or approximate [27]) and from a perturbative approach based on the pair density [28,29].
The second strategy consists in building GGA's and metaGGA's functionals specifically designed to be combined with the xc SCE functional. The idea here is to retain the ability of (approximate) SCE to capture strong correlation while carefully adding to it the accuracy of standard semilocal functionals to describe moderate correlation regimes. In a way, this is a "Jacob's ladder" with a starting point different than the usual one in KS: here the starting point is already able to accurately describe the non-local physics of very correlated systems. This will be done by readapting recent exact results on the gradient expansion [30], in collaboration with J. P. Perdew and K. Burke.

Objective 4: Testing the approximations in a systematic way
Team members: 1 postdoc (3 years) [Focus Area: Chemistry]
Local Collaborations: L. Visscher, SCM (industrial partner, responsible for the DFT codes ADF/BAND)
The approximations and algorithms developed in Objectives 1-3 will be extensively tested and validated. This is actually far from obvious: validating and benchmarking functionals is, in many ways, a research field by itself. Especially in chemistry, the scientific community has acquired an enormous know-how on validating and benchmarking approximate functionals, producing an extensive set of reference data that I intend to fully exploit (for extensive reviews, see, e.g. [5,6]).
In general, the benchmark data used for validation can be either from experiment or, for simple enough systems, from wave-function calculations. However, we must be very cautious about wave-function results

when dealing with strongly-correlated systems, because even very high-level wave function calculations might not be reliable if static correlation is too complex (e.g., in transition metal chemistry). On the other hand, the comparison with wave-function calculations is generally more instructive because it allows for a deeper understanding of the problems inherent to our approximations. For example, we can extract quantities such as the density and the spin densities [31], providing way more insight than the simple energetics.
At the validating stage it is thus crucial to interact with chemists with experience in benchmarking functionals using wave-function techniques with the needed care, as well as experimental data sets carefully chosen. I will then collaborate, on this aspect, with the group of L. Visscher located in my same institution, who has a long-standing experience in benchmarking quantum chemical methods. The aim is to improve the KS DFT accuracy for systems containing *d* and *f* elements, for transition states, and, in general, for systems with multireference character. We will thus focus on test sets containing this kind of systems and quantities for validation.
In a first stage, these accurate and controlled tests will provide a deep understanding of the key features of approximate SCE -based functionals needed to capture the relevant many-body effects and, at the same time, will allow for a careful analysis of the consequences of each approximate step done in the top-down strategy.
In the final stage, validation using the plethora of available test sets, including chemical and physical systems, will be essential to deliver new reliable xc functionals [5].
Regarding the practical implementation of new approximations into DFT codes, this project will benefit of the technical support of SCM (the spinoff company that develops and maintains the chemistry code ADF and the solid-state code BAND), located in my same host institution.
At the end of this project I will thus deliver to the community a novel, reliable and accurate, instrument for electronic structure calculations.

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Section b: Curriculum Vitae

PERSONAL INFORMATION

Family name, First name	Gori Giorgi, Paola
Researcher unique identifier	ResearcherID A-1017-2009
Date and place of birth	30 April 1971, Rome (Italy)
URL for web site	http://paolagorigiorgi.org/

EDUCATION

PhD

University	Department of Physics, University of Perugia (Italy)
Date of Award	14 February 2000
Supervisors	Prof. F. Sacchetti and Prof. G. B. Bachelet
Title of thesis	Electronic pair-distribution functions of jellium and real solids

Master ("Laurea")

University	Department of Physics, University of Rome "La Sapienza" (Italy)
Date of Award	29 February 1996
Supervisors	Prof. F. Melchiorri and Prof. F. A. Gianturco
Main subject	Cosmology and Astrochemistry
Title of thesis	Molecules in the early Universe
Final mark	110/110 ***cum laude***

CURRENT POSITIONS

2012 – present	Tenured Associate Professor, Department of Theoretical Chemistry, VU University, Amsterdam (The Netherlands)
2009 – present	Tenured Senior Researcher (CR1), French National Research Council (CNRS), Laboratoire de Chimie Théorique, Université Pierre et Marie Curie, Paris (France) [in temporary leave (détachement) since 2010]

PREVIOUS POSITIONS

2010 – 2012	Tenured Assistant Professor, Department of Theoretical Chemistry, VU University Amsterdam (The Netherlands)
2005 – 2009	Tenured Junior Researcher (CR2), French National Research Council (CNRS), Laboratoire de Chimie Théorique, Université Pierre et Marie Curie, Paris (France)
2004	EU Marie Curie Fellow, Laboratoire de Chimie Théorique, Université Pierre et Marie Curie, (France)
2002 – 2003	Postdoctoral Fellow, Italian National Institute for Physics of Condensed Matter (INFM), Center for Statistical Mechanics and Complexity, Rome (Italy)
2001	Researcher, Department of Physics, University of Rome "La Sapienza" (Italy)
2000 – 2001	Postdoctoral Fellow, Department of Physics and Quantum Theory Group, Tulane University, New Orleans, Louisiana (USA)
1999 – 2000	Researcher, Department of Physics, University of Rome "La Sapienza" (Italy)
1996 – 1999	PhD Student, Department of Physics, University of Perugia (Italy)

VISITING SCIENTIST POSITIONS

2006	Quantum Theory Project, University of Florida (USA)
2002	Max Planck Institute for Physics of Complex Systems, Dresden (Germany)

FELLOWSHIPS AND AWARDS

2011 The Netherlands Organisation for Scientific Research (NWO) Aspasia prize for excellent female scientists (100K€)

2010 The Netherlands Organisation for Scientific Research (NWO) Innovational Research Incentives Scheme **Vidi** (Talent scheme) *Electronic density functional theory for strong-interacting systems* (800K€)

2004 Marie Curie Intra European Fellowship, *From rigorous models to accurate energy density functionals* (150 K€)

2000 Fellowship of the Italian Foundation "Angelo della Riccia" (15.3 K€)

SUPERVISION OF GRADUATE STUDENTS AND POSTDOCTORAL FELLOWS

2010 – present 3 Postdocs, 2 PhD Students
Department of Theoretical Chemistry, VU University Amsterdam (The Netherlands)

2001 – 2004 3 Master ("Laurea") Students
Department of Physics, University of Rome "La Sapienza" (Italy)

TEACHING ACTIVITIES

2010 – present Coordinator and lecturer of several courses in the bachelor and master programs in Chemistry: Quantum Mechanics, Calculus, Classical Mechanics, Electromagnetism, Solid State and Molecular Physics – VU University Amsterdam (The Netherlands)

2011 Dutch University Teaching Certification (BKO)

2002 – 2004 Lecturer for Solid State and Molecular Physics in the master ("Laurea") program in Physics – University of Rome "La Sapienza" (Italy)

2013 Lecturer at the doctorate Han-sur-Lesse Winter School in Theoretical Chemistry and Spectroscopy (Belgium)

ORGANIZATION OF SCIENTIFIC MEETINGS

2008 Co-organizer of the international workshop *Density Functional Theory methods coupled to wave function methods,* University of Paris VI, France

INSTITUTIONAL RESPONSABILITIES

2011 – present Member of the Public Relation Committee, Department of Chemistry, VU University Amsterdam (The Netherlands)

2012 – present Member of the Trade Union Council, Faculty of Exact Sciences, VU University Amsterdam (The Netherlands)

2012 – present Organizer of the Amsterdam Center for Multiscale Modeling (ACMM) Symposia (see http://www.acmm.nl/)

COMMISSIONS OF TRUST

2014 Review panel member for the ECHO (Excellent Chemical Research) grants, the Netherlands Organisation of Scientific Research (NWO)

2014 Member of the search committee for a full professor in *Biomimetic Synthesis for Molecular Complexity,* Department of Chemistry, VU University Amsterdam

MAJOR COLLABORATIONS

- K. Burke (Physics, University of California Irvine, USA): *Gradient expansions and SCE*
- G. Buttazzo and L. De Pascale (Mathematics, University of Pisa, Italy): *Optimal Transport and DFT*
- G. Friesecke (Mathematics, Munich Technical University, Germany): *Optimal Transport and DFT*
- S. Kurth (Physics, Basque Country University, Spain): *Applications of SCE to Quantum Transport*
- J. Lorenzana (Physics, University of Rome "La Sapienza", Italy): *Lattice hamiltonians and SCE DFT*
- S. Moroni (SISSA, Trieste, Italy): *Functionals for range-separated DFT from QMC*
- J. P. Perdew (Physics, Temple University, USA): *Functionals from exact constraints and SCE*
- E. Räsänen (Physics, Tempere University, Finland): *Lieb-Oxford bound and SCE*
- S. M. Reimann (Physics, Lund University, Sweden): *SCE applications: quantum dots, cold atoms,...*
- A. Savin (Chemistry, CNRS, University Paris VI, France): *SCE and range separation*
- M. Seidl (Phyiscs, University of Regensburg, Germany): *SCE formalism*
- A. Teale (Chemistry, Nottingham University, UK): *exact quantities along the adiabatic connection*
- C. J. Umrigar (Physics, Cornell University, USA): *QMC results to benchmark SCE DFT*
- G. Vignale (Physics, University of Missouri, USA): *higher-order corrections to SCE*

CAREER BREAKS

September 2010 – January 2011 Maternity leave (6 months)
January 2007 – June 2007 Maternity leave (6 months)

Appendix: All on-going and submitted grants and funding of the PI (Funding ID)

On-going Grants

Project Title	*Funding Source*	*Amount*	*Period*	*Role PI*	*Relation to this ERC CoG*
Time-dependent density functional theory for strongly-interacting electrons	EU – FP7 People Marie Curie **Intra European Fellowship** Physics Panel (Fellow: Dr. G. Lani)	180 K€	2014-2016	host scientist in charge	Complementary: this IEF is devoted to the extension of SCE to the time domain and applications in quantum transport.
The strictly-correlated-electrons approach at work for Chemistry: Density Functionals for transition metals and accurate excitation energies	The Netherlands Organisation for Scientific Research (NWO) - Free competition **ECHO-STIP**	260 K€	2013-2017	PI	The ECHO-STIP funds one PhD student. A first part (on transition metals) is a pilot for this ERC CoG. The second part (on excitation energies) is complementary.
Strictly-correlated Density Functional Theory: methodology development and application to semiconductor nanostructures and ultracold atom gases	EU – FP7 People Marie Curie **Intra European Fellowship** Physics Panel (Fellow: Dr. F. Malet)	180 K€	2013-2015	host scientist in charge	Complementary: this IEF is devoted to applications of SCE DFT to semiconductor nanostructures and to the extension of the formalism to ultracold atoms gases with dipolar interactions.
Electronic density functional theory for strong-interacting systems	The Netherlands Organisation for Scientific Research (NWO) – Innovational Research Incentives Scheme **Vidi** (Talent scheme)	800 K€	2010-2015	PI	The Vidi ends in April 2015. The ERC CoG builds on the formal results obtained during the Vidi. In the ERC CoG these formal results will be transformed into practical xc functionals for chemical and physical applications.

Submitted Grants
none

Section c: Early achievements track-record

PUBLICATIONS

I have published **50** articles in peer-reviewed international journals. My results have been featured in *Physics* (APS), have been reported in several textbooks and cited in many abstracts by authors that have built on them. My h-index on the ISI Web of Science is **20** (Notice: double last name, to be searched as **gori-giorgi p OR gorigiorgi p OR giorgi pg**) and the total number of citations is **1160**.

TEN REPRESENTATIVE PUBLICATIONS: HIGHLIGHTS

1) *Energy Density Functionals From the Strong-Coupling Limit Applied to the Anions of the He Isoelectronic Series,*
A. Mirtschink, C. J. Umrigar, J. D. Morgan III, and P. Gori-Giorgi, **J. Chem. Phys.** 140, 18A532 (2014)
- Invited article for the Special Topic issue **"Advances in Density Functional Theory"**

We have tested the xc SCE functional for the delicate physics of loosely bound anions, showing that it captures effects that are missed by the other functionals. We have also used accurate wave function results to validate our findings.

2) *The derivative discontinuity in the strong-interaction limit of density functional theory*
A. Mirtschink, M. Seidl, and P. Gori-Giorgi, **Phys. Rev. Lett.** 111, 126402 (2013) [citations: 3]

We have generalized the exact strong-interaction limit of DFT to fractional electron numbers, showing that it displays the correct derivative discontinuity at integer electron numbers even in a spin-restricted framework. This is a key feature, missed by standard approximations, to describe the ground state of strongly-correlated systems and important applications such as quantum transport.

3) *Kohn-Sham density functional theory for quantum wires in arbitrary correlation regimes*
F. Malet, A. Mirtschink, J. C. Cremon, S. M. Reimann, and P. Gori-Giorgi, **Phys. Rev. B** 87, 115146 (2013); selected as **"Editor's suggestion"** [citations: 8]

We have extensively tested the performances of our new KS SCE self-consistent scheme on model semiconductor quantum wires, comparing energies, densities and ionization potentials with full CI calculations. KS SCE proved able to capture the "$2k_F$ - $4k_F$" crossover without breaking the spin symmetry, a feature that several previous attempts in the literature, including GGA's, hybrids and self-interaction corrections, had failed to capture. The SCE KS potential is uniquely capable to create barriers between the electrons that give raise to charge localization in the non-interacting KS framework.

4) *Strong correlation in Kohn-Sham density functional theory*
F. Malet and P. Gori-Giorgi, **Phys. Rev. Lett**. 109, 246402 (2012) [citations: 14]

This paper shows how to compute the functional derivative of the highly non-local SCE functional, making possible the use of SCE as an approximation for the exchange-correlation functional of KS theory.

5) *Optimal-transport formulation of electronic density-functional theory*
G. Buttazzo, L. De Pascale, and P. Gori-Giorgi, **Phys. Rev**. **A** 85, 062502 (2012) [citations: 20]

Crossing disciplinary boundaries, I have collaborated with a leading group in optimal transport (a research field of mathematics and economics) showing that the SCE is formally equivalent to a Monge-Kantorovich problem with Coulomb cost. This paper has triggered interest in the optimal transport community and inspired the first proof-of-principle calculation by a group in Berkeley.

6) *Density functional theory for strongly interacting electrons*
P. Gori-Giorgi, M. Seidl, and G. Vignale, **Phys. Rev. Lett**.103, 166402 (2009) [citations: 34]
- Article highlighted by the APS with a synopsis in ***Physics*** and selected as **"Editor's suggestion"**
- Selected for the **Virtual Journal of Nanoscale Science & Technology**

This article presents the first formal DFT theory for strongly-correlated systems, in which the electron-electron interaction is treated in an exact DFT framework and the kinetic energy is approximated as a density functional. In a way, this is an orbital-free version of the KS SCE theory of articles 1-4.

7) *Electronic zero-point oscillations in the strong-interaction limit of density functional theory*
P. Gori-Giorgi, G. Vignale, and M. Seidl, **J. Chem. Theory Comput**. 5, 743 (2009) [citations: 23]

Exact second-order correction expansion in the strong-interaction limit of DFT, formulated in a curvilinear space with a metric dictated by the density.

8) *Simple model for the spherically-and system-averaged pair density: Results for two-electron atoms*
P. Gori-Giorgi and A. Savin, **Phys. Rev. A** 71, 032513 (2005) [citations: 38]

We have generalized the "Overhauser model" to non-uniform systems, and combined it with range-separated multideterminant DFT. This article has inspired many subsequent works and refinements.

9) *Spin resolution of the electron-gas correlation energy: Positive same spin contributions*
P. Gori-Giorgi and J. P. Perdew, **Phys. Rev. B Rapid Communications** 69, 041103 (2004) [citations: 26]
Accurate spin resolution of the correlation energy in the uniform electron gas.

10) *Short-range correlation in the uniform electron gas: Extended Overhauser model*
P. Gori-Giorgi and J. P. Perdew, **Phys. Rev. B** 64, 155102 (2001) [citations: 63]

We have formalized and solved the "Overhauser model", a physically motivated approximate scheme to compute the pair density of the uniform electron liquid. This work has inspired many subsequent researches, and its results are reported in the textbook *Quantum Theory of the Electron Liquid* by Giuliani & Vignale.

INVITED TALKS (SELECTION) AT INTERNATIONAL CONFERENCES AND WORKSHOPS

I have been an invited speaker at **34 international conferences** in the fields of Density Functional Theory, Quantum Chemistry, Condensed Matter Physics, and Applied Mathematics. Here is a selection:

2014 *CECAM Workshop: What about U? - Strong correlations from first principles,* Lausanne, Switzerland
2014 *Promoting Female Excellence in Theoretical and Computational Chemistry II* , Oslo, Norway
2013 *7th Molecular Quantum Mechanics: An international Conference in honour of R.J. Bartlett*, Lugano, Switzerland
2013 *Semiclassical Origins of Density Functional Approximations,* Institute for Pure and Applied Mathematics (IPAM) workshop, University of California, Los Angeles, USA
2013 *Symposium "Electronic Structure" at SIAM Conference on Mathematical Aspects of Materials Science*, Philadelphia, USA
2013 *CECAM Workshop: Green's functions Methods: the next generation*, Toulouse, France
2013 *CECAM Workshop: Density Functional Theory: learning from the past, looking to the future*, Berlin, Germany
2013 *16th International Workshop on Computational Physics and Materials Science: Total Energy and Force Methods*, Trieste, Italy
2012 *ERC Workshop on Optimal Transportation and Applications*, Pisa, Italy
2012 *Low-scaling and Unconventional Electronic Structure Techniques (LUEST) Conference*, Telluride Science Research Center, Colorado, USA
2012 *Challenges in Density Matrix and Density Functional Theory*, Ghent, Belgium
2011 *14th International Density Functional Theory (DFT) Conference*, Athens, Greece
2011 *CECAM Workshop: How to speed up progress and reduce empiricism in Density Functional Theory*, Dublin, Ireland
2011 *European Seminar on Computational Methods in Quantum Chemistry 2011,* Oscarsborg, Norway
2009 *92nd Canadian Chemistry Conference and Exhibition*, Hamilton, Ontario, Canada
2008 *Sixth Congress of the International Society for Theoretical Chemical Physics (ISTCP-VI)*, Vancouver, BC, Canada
2006 *30th International Workshop on Condensed Matter Theories*, Dresden, Germany
2006 *Frontier Applications and Developments of Density Functional Theory: A Symposium in Honor of Robert G. Parr's 85th Birthday*, ACS Meeting, Atlanta, USA
2004 *28th International Workshop on Condensed Matter Theories*, St. Louis, USA

PRIZES AND AWARDS

2013 Selected by the Netherlands Organisation for Scientific Research (NWO) to appear with a quote and a picture in the vision document *Chemistry & Physics, Fundamental For Our Future.* The document describes the ambitions for physics and chemistry for the next ten years and can be downloaded at www.nwo.nl/en/news-and-events/news/2013/cw/vision-document-chemistry-and-physics-in-2025-presented.html.
2012 Selected for *AcademiaNet: Profiles of Leading Women Scientists* (www.academia-net.org)
2011 The Netherlands Organisation for Scientific Research (NWO) Aspasia prize for excellent female scientists (100K€)

ERC Consolidator Grant 2014
Research proposal [Part B2)]

Part B2: *The scientific proposal*

Section a. State-of-the-art, objectives and overall goal

The electronic-structure problem

Accurately predicting the electronic structure of atoms, molecules and solids from first principles is crucial for many research areas such as theoretical and computational chemistry solid-state physics, materials science, biophysics and biochemistry. For example, to design *in silico* novel materials with specific properties, to predict whether a protein will attach to a given site of DNA, or whether a specific chemical reaction will occur, a full quantum mechanical treatment of the electronic structure of (at least) the reactive part of the system is essential.

In principle, the electronic structure is determined by the Schrödinger equation. However, due to its complexity, solving the Schrödinger equation is in practice limited to systems with only a few electrons. To overcome this problem, both chemists and physicists have developed approximate methods to treat the many-electron Schrödinger equation. These methods can be roughly divided in two groups: wave-function methods and density-functional-theory-based methods. Wave-function methods attempt at constructing an approximation for the many-electron wave-function, in most cases optimized according to the variational principle. Typical examples are quantum chemistry methods [1,2], which make use of an expansion on a basis of Slater determinants (configuration interaction, coupled clusters,...) and quantum Monte Carlo (QMC) methods [3], which start from a more compact form of the wave-function and use stochastic techniques to project the ground state. These methods can be very accurate, and have proven to be extremely useful for solving many interesting chemical and physical questions. On the other hand, they are computationally demanding, and for this reason they are intrinsically limited as far as system size is concerned.

Density Functional Theory: successes...

Density functional theory (DFT), in its Kohn-Sham (KS) formulation [4], has been a real breakthrough for electronic structure calculations. DFT uses the one-electron density and a non-interacting wave function as basic variables, much simpler quantities to handle than a correlated many-electron wave-function. In this way, DFT can treat systems much larger than those accessible to wave-function methods. KS DFT, together with its extension to time-dependent (TD) phenomena (TDDFT) [5], made possible the theoretical study of a huge number of chemical, physical, and biological processes. These enormous successes are beautiful examples of how fundamental theoretical research can have a huge impact in many different fields (inorganic and organic chemistry, solid state physics, materials science, surface physics, biochemistry and biophysics).

The key idea of KS DFT is an exact mapping [6] between the physical, interacting, many-electron system and a model system of non-interacting fermions with the same density, allowing for a realistic treatment of the electronic kinetic energy. All the complicated many-body effects are embedded in the so-called exchange-correlation (xc) energy functional. Although, in principle, the exact xc functional is unique (or "universal"), in practice a large number of approximations has been developed in the last 30 years, often tailored to the peculiarities of different systems, different properties, and different phenomena. Common practice for DFT users is nowadays to consult the (rather extensive) benchmark literature to choose the approximate xc functional most suitable for the problem at hand. This reflects the intrinsic difficulty of building a general approximation able to recognize and capture, for each class of systems or process, the many-body effects relevant for its description [7].

... and failures

Even in this "specialized-functional" world, there are still important cases in which state-of-the-art KS DFT encounters severe problems, which is why the quest for better xc functionals continues to be a very active research field [8-10]. In particular [9,11], present-day KS DFT encounters severe problems in the treatment of near-degeneracy and strong-correlation effects (rearrangement of electrons within partially filled levels, important for describing bond dissociation but also equilibrium geometries, particularly for systems with *d* and *f* unsaturated shells, such as transition metals and actinides, technologically useful functional materials, and manmade nanostructures) and in the description of van der Waals long-range interactions (relevant, for example, for biomolecules and layered materials). While on this latter issue there has been considerable

progress in the last years through long-range energy corrections, the difficulties related to near degeneracy and strong correlation remain. These difficulties can hamper more or less severely (and sometimes in an unpredictable way) a given calculation, depending on their relative importance with respect to other effects that are better captured by the available approximate functionals [9,11].

It is important to mention that when dealing with strong (or "static") correlation, similarly to unrestricted Hartree-Fock (HF), approximate KS DFT often tries to mimic the physics of strong correlation and near degeneracy with spin and spatial symmetry breaking, which in complex systems may occur erratically and can be very sensitive to the choice of functional [10,11]. This easily leads to a wrong characterization of several properties and to discontinuous potential energy surfaces [10,11]. Being able to capture strong electronic correlation within KS DFT without resorting to symmetry breaking is arguably one of the most important open problems of electronic structure theory [7,10,11]

As the KS DFT electronic structure calculations are the starting building blocks for studying sophisticated processes on systems too large to be treated with wave-function methods (such as, for example, the damaging of DNA from a given compound, or the behavior and properties of novel materials and nanostructures), their errors can affect in a drastic way the final results and conclusions. Addressing the fundamental problems of KS DFT can make the difference between using computations to *understand* experiments (as it is mainly done nowadays) and to be able to really *predict* them.

This proposal aims at addressing the fundamental DFT problems inherent to the description of strongly-correlated systems following a strategy radically different than mainstream ones.

Mainstream strategies to construct approximate xc functionals

We have to keep in mind that a large part of the success of KS DFT stems from its highly non-perturbative nature. Already the most basic xc functional, the local density approximation (LDA), relies on the exact (obtained from QMC) solution of a many-electron system with uniform density. This exact (at all orders of perturbation theory) correlated solution is then used in each point of space in a non-uniform system. Precisely because of this non-perturbative character, there is no well defined strategy to improve DFT in a truly systematic way. Breakthroughs in the past came mainly from a combination of physical insight, mathematical study of exact conditions, and new creative ideas [7].

The community of those who try to improve the approximate functionals is relatively small, probably precisely because there is no clear, universal, path to follow. At the same time, this small scientific community has an enormous potential impact because of the huge number of DFT users: the most successful approximations make it possible to treat a large variety of problems in chemistry and physics, and are used every year by thousands of scientists in different research areas [7].

The mainstream strategies to address the unsolved problems of KS DFT consist of making an ansatz for the dependence of the xc functional on the relevant "ingredients", increasing the complexity of the approximations in a hierarchical manner ("Jacob's ladder" to the "heaven" of chemical accuracy [8]), although, as mentioned, we have to keep in mind that DFT is not really systematically improvable. At the lowest level of approximation one considers the local density only (LDA, LSDA). The next level introduces the local density gradients (GGA's), followed by the KS kinetic orbital energies (metaGGA), the occupied KS orbitals (exact exchange, hybrid functionals, self-interaction corrections,...), up to including the virtual KS orbitals (*e.g.*, random phase approximations, double hybrids,...). The ansatz can be constructed in order to fulfill as many exact constraints as possible given the ingredients used [8]. Some authors also introduce a (sometimes very large) number of parameters to be fitted to a specific data set [12]. Other approaches are based on range separation to use long-range exchange only [13,14] or to combine DFT with wavefunction methods in a rigorous way [15].

A rigorous starting point: The exact strong-correlation limit of DFT

KS DFT is based on a system of *non-interacting* fermions, treating the electron-electron interactions in an approximate way. Current approximations work well when the physics of the true, interacting, system is not too different than the non-interacting one of Kohn and Sham: for these cases the "Jacob's ladder" and related strategies are able to accurately capture the (relatively small) xc effects. Strongly-correlated systems, however, are radically different than non-interacting ones. In these cases, **the xc functional needs to be a drastic correction**, and traditional strategies have failed so far.

My research efforts of the last four years have been mainly devoted to develop **a rigorous starting point to build this drastic correction**, showing, for prototypical cases, that it works. This rigorous starting point is the exact xc functional in the limit in which correlation becomes infinitely strong, called "strictly-correlated electrons" functional (SCE), first introduced by M. Seidl and coworkers [16,17] in 1999-2000, but only treated in an approximate way. Later on, in 2007-2009, I was able, in collaboration with M. Seidl, A. Savin

and G. Vignale [18,19], to write a general solution for the SCE functional and its first-order correction. The SCE functional has a highly non-local dependence on the density that encodes new information with respect to the traditional ingredients of the "Jacob's ladder" approach.
As a group leader funded by the VIDI and other grants (two Marie Curie fellowships - devoted to applications in Physics and to the extension to the time domain - and the Dutch grant ECHO-STIP that funds one PhD student), I have made considerable steps forward concerning the formalism and the practical implementation of SCE, with a focus on the physics of low-density model nanodevices. In particular, I have found an elegant and powerful shortcut to compute the functional derivative of the highly non-local SCE functional [20], yielding a one-body multiplicative Kohn-Sham potential which creates, self-consistently, "barriers" that make non-interacting electrons reproduce key features of strongly-correlated ones, without artificially breaking any symmetry. In fact, we have shown that, when used as an approximation for the exchange-correlation functional in the self-consistent KS procedure, the xc SCE functional is able to capture strongly-correlated features such as the "$2k_F$ - $4k_F$" crossover in model quantum wires without introducing artificial magnetic order [21], and the transition to the Wigner correlated regime ("Wigner rings") in model quantum dots [22]. These features are out of reach for all the available approximate functionals.
I have also extended the SCE formalism to fractional electron numbers in a rigorous way [23], and shown that the SCE xc functional displays a derivative discontinuity at integer electron numbers when the system is very correlated, with quantitative agreement with exact results which increases as the system becomes more and more correlated. Notice that this derivative discontinuity is obtained in a spin-restricted framework, so that the KS spectrum truly jumps even when filling the same orbital. This is a unique result [23] that has never been obtained with any other approximation, and it is known to be a key feature to describe the ground-state of strongly-correlated systems and important applications such as quantum transport [9,10,24].
The importance of these results is well recognized in the fundamental DFT scientific community: I have been invited to present them at most of the key conferences in the field, and the xc SCE functional is mentioned in the most recent DFT review articles as a very promising new route [7,10].
Another important result I have obtained, crossing disciplinary boundaries, is the reformulation of the SCE functional as a mass transportation theory (or optimal transport) problem, an important field of mathematics and economics [25]. This reformulation paves the way to a cross-fertilization between two very different research areas, and has already triggered a huge interest in the mass transportation theory community, as shown by the increasing number of groups that are publishing on the subject and by the many invitations I have received to speak at optimal transport and mathematics conferences.
Finally, I have started to investigate, with proof-of-principle calculations, the performances of the SCE xc functional in chemistry, showing that is able to capture effects that are missed by the standard approximations, such as the physics of stretched bonds [26] and of loosely bound negative ions [27].
The goal of this ERC proposal is to transform these rigorous results into a complete framework for electronic structure computations, working at all correlation regimes, and for a vast range of chemical and physical systems.

From the exact strong-coupling expansion to functionals for chemistry and solid-state physics: Challenges
Chemistry and solid-state physics, however, are more challenging for the SCE functional than low-density nanostructures, because the kinetic correlation energy and the electron-electron repulsion often have similar importance. For example, in a stretched bond only the bonding electrons are strongly correlated, while the others are not. Indeed, our pilot calculations have shown that KS SCE dissociates properly a chemical bond without introducing symmetry breaking, but it overcorrelates in all other aspects. This evidently requires corrections to the SCE functional, which are one of the objectives of this proposal, and will be built in a rigorous way by importing ideas from different research areas in a novel way, as detailed below.
The other big challenge is that the physics of strong correlation encoded in the highly non-local density dependence of the SCE functional does not come for free: the SCE problem is sparse but nonlinear, and a general algorithm for its evaluation following our original formulation is still an open problem. The results listed above, in fact, were obtained in special cases for which the SCE functional and its functional derivative can be evaluated exactly: one-dimensional and spherically-symmetric systems. Progress has been made very recently [28] using our reformulation of the SCE functional as a mass transportation theory problem [25], which transforms the evaluation of the SCE functional and its functional derivative into a maximization under linear constraints, although the procedure is still cumbersome and needs further developments. The transformation of the SCE formalism into a practical xc functional is the other main pillar of this research proposal.

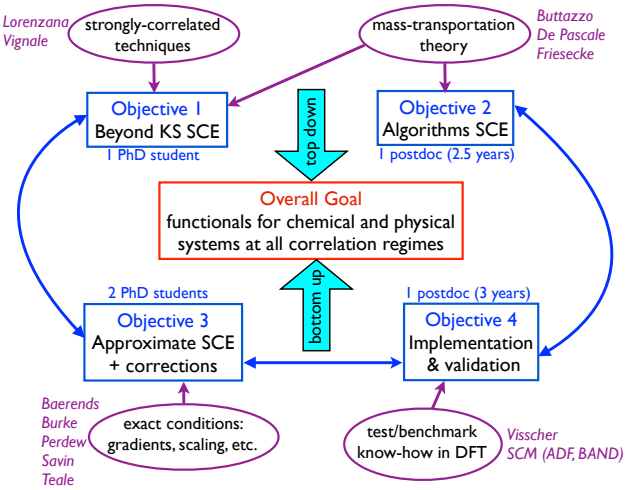

Fig. 1: Schematic overview of how the project is organized, showing the objectives, their interactions and the "top-down" and "bottom-up" strategies towards the final goal. For each objective, the team members are also shown in blue. The international and local collaborations involved in each objective are reported in purple italics, together with the main input research areas/ideas.

A new interdisciplinary approach

In pursuing the final goal of extending the applicability of DFT to strongly-correlated systems, I want to unite efforts from research fields that, although aiming at similar objectives, traditionally (with few exceptions) keep a distance from each other: the chemistry/physics community that develops xc functionals and kernels for DFT and TDDFT, and the physics community that develops strongly-correlated techniques in the context of lattice hamiltonians. As I will explain in detail in the Methodology part, this will be possible because the KS SCE provides a new framework to import results from lattice hamiltonians into the DFT real-space "continuum". Moreover, as already mentioned, the SCE theory has a mathematical structure formally equivalent to an optimal transport (or mass transportation theory) problem, an important field of mathematics and economics [25]. This link will be potentiated and exploited in this project, both for the algorithmic part and for the construction of corrections to SCE. Therefore, this proposal lies at the interface of fore-front research in chemistry, physics and mathematics.

Goal and Objectives

The goal of this ERC proposal is the generalization of the KS SCE theory to realistic problems, yielding an accurate, computationally affordable, *ab initio* description of the ground-state energy and other properties of strongly-correlated many-electron systems, based on a physically and mathematically sound framework.

In order to achieve this goal the **following objectives** must be met:

1. Add corrections to (go beyond) the KS SCE approach, which, as mentioned, is a zeroth-order expansion of the exact exchange-correlation functional at infinite coupling strength. This means adding proper higher order corrections.
2. Develop dedicated algorithms to evaluate the SCE functional in the general three-dimensional case.
3. Construct controlled approximations of the results of objectives 1 and 2 to increase the computational efficiency. This is necessary for very large systems, and it can also be used in general in case the exact implementation of objectives 1 and 2 turns out to be computationally too demanding.
4. Test and benchmark in a systematic way the new approximate functionals and algorithms of Objectives 1-3.

Strategy and Approach

I designed two parallel strategies to pursue the final goal of extending KS DFT to strongly-correlated realistic systems: I will have at the same time a "top-down" and a "bottom-up" approach synergistically combining chemistry, physics and mathematics. For the top-down approach, my team and I will develop and implement the exact SCE (and beyond) functionals and, if needed, make approximations at a later stage. For the bottom-up approach, we will begin with approximations and learn by implementing and testing them. These two complementary strategies reinforce each other, progressing towards the final common goal.

In Fig. 1, I report a graphical summary of the four objectives, showing their interactions with arrows that indicate how some of the objectives create input and/or feedback for the others. The "top down" and "bottom up" strategies are also schematically represented.

In practice, in the top-down strategy I will use strong correlation techniques from lattice hamiltonians and mass transportation theory ideas to design corrections to KS SCE (Objective 1). Mass transportation theory will also play an important role in the algorithmic part (Objective 2). Extensive tests (Objective 4) of the approximations of Objective 3 are used in the bottom-up strategy. Objectives 1 and 3 will constantly interact and affect each other, and the same will happen with algorithms (Objective 2) and the implementation and benchmarking part (Objective 4).

With this approach I am confident to significantly extend the applicability of KS DFT to systems yet unreachable, providing the scientific community with new tools for accurate *ab initio* modeling of chemical and physical systems.
In the following Section, I fully describe the four objectives, highlighting in detail the novelty of what is proposed here with respect to mainstream approaches, and addressing the unconventional methodological aspects of the project.

Section b. Methodology

Objective 1: Beyond KS SCE through a new merging of (lattice) strong-correlation techniques and KS DFT

In many-body physics, strong-correlation techniques have been traditionally developed starting from lattice hamiltonians, such as the Hubbard model, the Anderson-impurity model, the *t-J* model, etc. These theories are extremely elegant and powerful, and provide insight into the complex mechanisms arising in real materials with strong electronic correlation. On the other hand, they do not treat realistic microscopic hamiltonians (necessary to be quantitatively predictive) as it is done, instead, in KS DFT. However, present day KS DFT, as mentioned, fails when electronic correlation becomes strong: the available xc functionals often mimick the effects of strong correlation by introducing symmetry breaking (e.g., artificial magnetic order), without capturing the right physics [29,30], like in most transition metal oxides.

Comparison with approaches such as LDA+DMFT and LDA+U

There are several approaches that try to bridge the gap between the two worlds of strong-correlation lattice hamiltonians techniques and KS DFT: LDA+U [29], LDA plus dynamical-mean field theory (DMFT) [31], and LDA plus dynamical Vertex Approximation [32], are among the most popular. While these methods have been able, indeed, to successfully cure some of the KS DFT problems, they have several drawbacks, such as basis dependence, double counting and (for the most accurate ones) a high computational cost. Moreover, I will argue here that they do not completely merge the two worlds.
These approaches start from a low-level approximate xc functional, in most cases the local (spin) density approximation (L(S)DA), which gives huge errors when strong correlations are present. Starting from this qualitatively wrong description, these merged approaches use some LDA orbitals as input for strong-correlation calculations. For example, in transition metal oxides, LDA+DMFT only correlates some of the *d* and *f* valence orbitals that must be identified by hand. Since correlation in these orbitals is also taken into account in the LDA calculation, one must correct for double counting, something that, at present, can only be done in an approximate and uncontrolled way.
It is important to keep in mind that KS DFT is, in principle, an *exact* theory. If we could find a very good approximation for the exact xc functional and for the exact xc kernel we could describe strongly-correlated systems in a pure DFT framework. The main reason to undertake these combined approaches is the common feeling that, although possible in principle, it is impossible in practice to find xc functionals and kernels able to describe strong correlation.

From lattice hamiltonians to the DFT continuum

In very recent work [20-23], my group and I have shown that, instead, it is possible to construct functionals that capture strong correlation. The SCE theory, which derives from the exact strong-interaction limit of

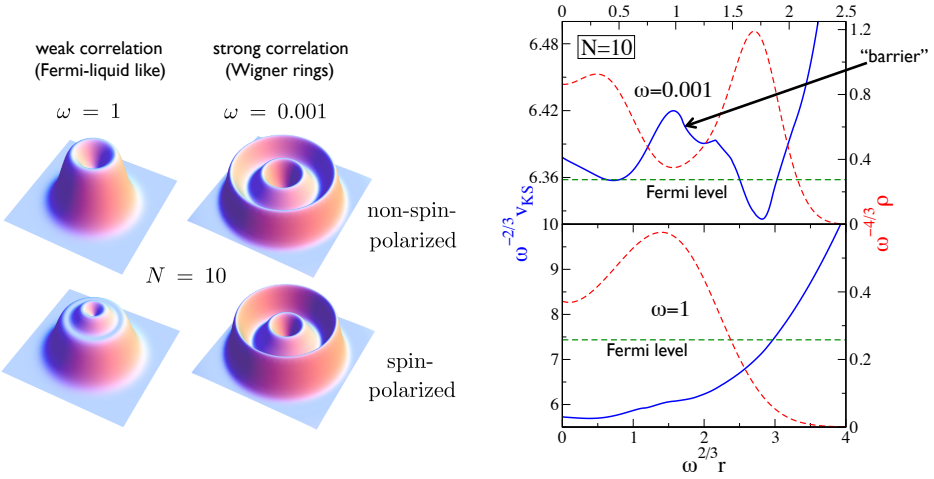

Fig. 2. Left: self-consistent KS SCE electronic densities for 10 electrons confned in a circular harmonic trap. Right: the corresponding KS SCE potential: when the system is strongly correlated (top) the KS SCE potential builds barriers inside the trap, creating classically forbidden regions [22]

DFT, provides a highly non-local density functional whose corresponding one-body KS potential is able to do what people often regarded as practically impossible: making non-interacting electrons reproduce key strongly-correlated features, without any artificial symmetry breaking. As an example, in Fig. 2 I show the results for ten electrons confined in a two-dimensional semiconductor nanostructure laterally confined by a harmonic trap. When the density in the trap is high (weak correlation) the KS SCE self-consistent density is correctly qualitatively dictated by the non-interacting orbital structure (Fermi-liquid like, equivalent to the shell structure of a simple atom, e.g., neon). When the electronic density in the trap is low, correlation effects become very strong: as well known, the density shows sharp radial rings ("Wigner rings"), which destroy the Fermi-like shell structure, and are accurately captured by the self-consistent KS SCE results. Notice that full CI at the low densities and electron number showed in the figure is already not doable [33], and even QMC needs to artificially break the fundamental circular symmetry of the system to reach convergence [34,35]. KS SCE instead, can easily treat this regime, without any symmetry breaking. The key point is that, self-consistently, the KS potential coming from the functional derivative of the xc SCE, builds "barriers" that create classically forbidden regions inside the trap (see Fig. 2), and were known from theoretical arguments to be a feature of exact KS DFT [36]. The xc SCE functional is a well defined, physically transparent, mechanism to build these barriers self-consistently.

Similarly to the KS non-interacting kinetic energy, which is determined in terms of the KS orbitals, the SCE functional is determined by one-body quantities called co-motion functions $\mathbf{f}_i(\mathbf{r})$, which are non-local functionals of the density $\rho(\mathbf{r})$ and fix the positions of all the electrons in terms of a collective continuum real-space variable $\mathbf{r}$. The net effect of the many-body electron-electron repulsion can then be exactly transformed into a local one-body potential, to be used in the KS equations, which is also the functional derivative of the SCE functional. The SCE construction can be viewed as a sort of "floating" Wigner crystal in a metric determined by the density $\rho(\mathbf{r})$, as summarized in Fig. 3.

The KS SCE approach consists in using the exact SCE one-body potential $v_{SCE}(\mathbf{r})$ of Fig. 3 to approximate the xc potential of KS theory [20]. It can be shown from the scaling properties of DFT [37] that the KS SCE theory becomes exact both in the weak- and in the strong-interaction limits [20]. It also turned out to be qualitatively right in describing the crossover between different regimes of correlation, but it still needs improvement to be quantitatively accurate at all correlation regimes [20,21]. This is where a true merging of KS DFT and strongly-correlated techniques can take place. Using the KS SCE hamiltonian, several concepts and tools of the strongly-correlated world can now be translated into a DFT formalism in the continuum (here the word "continuum" is used to stress the difference with lattice hamiltonians) to build physically motivated corrections to KS SCE, with the ultimate goal of extending the domain of applicability of DFT to systems yet unreachable.

Task 1: xc functionals from a new merging of strongly-correlated techniques and KS DFT
Team members: 1 PhD student
Intenrational Collaborations: J. Lorenzana (University of Rome "La Sapienza"), G. Vignale (University of Columbia Missouri)

A sort of "first-order" correction has been already formulated by myself and my coworkers in terms of local

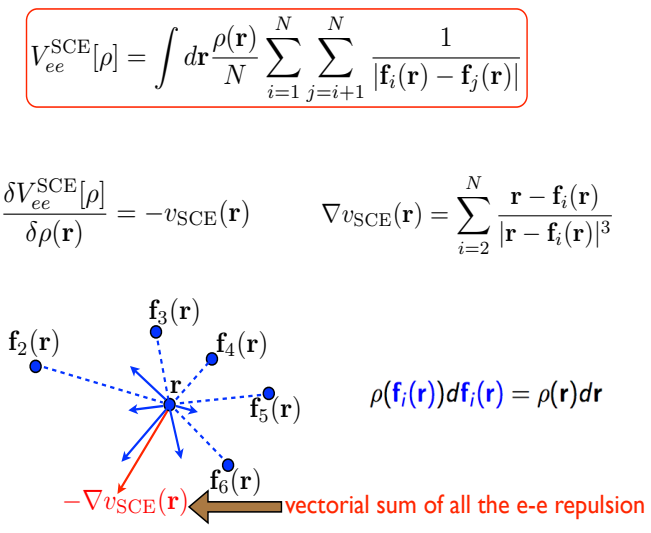

Fig. 3: The SCE functional corresponds to the minimum possible expectation value of the electron-electron interaction in a given non-uniform smooth density $\rho(\mathbf{r})$. It can be calculated through the so-called co-motion functions $\mathbf{f}_i(\mathbf{r})$, which determine the position of electron "i" as a function of the collective variable $\mathbf{r}$. The co-motion functions $\mathbf{f}_i(\mathbf{r})$ are highly non-local functionals of the density $\rho(\mathbf{r})$. The physics is similar to the one of a "floating" Wigner crystal in a metric defined by the density. Once the co-motion functions are variationally determined, the net electron-electron repulsion can be exactly transformed into a local one-body potential, $v_{SCE}(\mathbf{r})$, yielding an approximation for the xc potential that becomes asymptotically exact in the limit of infinite coupling.

quantum fluctuations [38]. However, this correction does not distinguish between different spin states, which are taken into account only in the KS kinetic energy, but not in the xc SCE functional. Instead, for the delicate physics and chemistry of strongly-correlated materials containing *d* and *f* elements and of nanoscopic systems, the subtle interplay of the spin state and of correlation needs to be taken into account in the xc functional. Since the SCE functional describes a continuum (as a function of the collective variable **r**) of configurations of localized electrons, the idea is to construct correcting terms in the same fashion as it is done with lattice hamiltonians In fact, for each **r**, the SCE construction defines a lattice in which the double occupation is suppressed, which, in turn, can be studied with models such as the *t-J* one. Corrections beyond SCE can then be constructed by computing magnetic exchange and superexchange terms as a function of the real-space continuum variable **r**. The needed overlap integrals can be obtained from the quantum fluctuation SCE correction that I already started to develop [38]. We will start by first looking at exact magnetic exchange and superexchange corrections in simpler systems such as quasi-one-dimensional wires or electrons trapped in two dimensions, studying first smaller number of particles for which wave-function methods (QMC or full CI) are viable for comparison, to validate the accuracy of these corrections. We will further transform these correcting terms into density functionals, making and testing approximations at various levels. Embedding techniques inspired to DMFT [31] or to the recent density matrix embedding theory [39] can also be used to reduce the computational effort when going to larger systems. The conceptual difference between approaches such as LDA+U or LDA+DMFT and what is proposed here is illustrated schematically in Fig. 4.

Part of this work will be done in collaboration with the group of J. Lorenzana at the University of Rome "La Sapienza" (Italy), who has long-standing experience in strongly-correlated techniques, and with G. Vignale (University of Columbia Missouri).
Finally, interacting with the other objectives that focus on the algorithmic implementation of the SCE functional (approximate or exact), the most promising approximations will be implemented into the DFT codes ADF and BAND and tested for realistic chemical systems and solids as described in Objective 3. Tests for model and realistic quantum wires, dots, and point contacts will be also performed.

Comparison with other (related) approaches
In recent years, there has been an interest from the DFT community into lattice hamiltonians [40-44], with the main goal of studying and characterizing (by inverting the exact many-body solution) the exact KS system for prototypical strongly-correlated cases [40-44], and of applying lattice DFT [44], a DFT theory adapted to lattice hamiltonians, for which some functionals based on the 1D homogeneous Hubbard model have been developed [45]. These studies have provided enormous insight into the exact KS theory, and have also shown that several strong correlation features such as some aspects of the Kondo effect [24] and a realistic dynamical description of the Coulomb blockade [44] are, in principle, accessible to KS (TD)DFT. These results support the ideas of this project, as they provide evidence that it is possible to describe many strong-correlation features within KS DFT. It is, however, also important to stress the differences between these works and what is planned for this part of this proposal: here, we have already developed a functional able to capture some of the relevant effects to describe strong correlation in a real-space (continuum) KS DFT framework, and we will use our new formulation to *translate* and *import* the concepts developed with lattice hamiltonians into a true DFT formalism in the continuum.
Other approaches that relate many-body physics and KS DFT involve the use of the unoccupied KS orbitals, performing many-body perturbation theory starting from the KS solution. These theories typically start from the random-phase approximation (RPA) and may include beyond-RPA diagrams (for a recent review see [46]). The approach proposed here is, instead, highly non-perturbative, as it uses the exact solution at infinite coupling strength and its corrections to build the exchange-correlation functional of KS DFT.

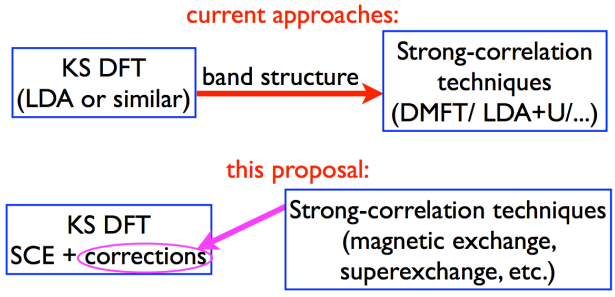

Fig. 4: Conceptual difference between current approaches such as LDA+U and LDA+DMFT, and this proposal. Here, strongly-correlated concepts and tools will be used to improve KS SCE, working in a continuum DFT framework. Current approaches, instead, use output quantities from KS LDA calculations on which, afterwards, a strongly-correlated treatment is performed.

Another strategy to cure some of the KS DFT problems for strong correlation is the inclusion of self-interaction corrections (SIC) [47], which, although successful in some aspects, have drawbacks such as the non invariance with respect to unitary rotations of the KS orbitals. Also, notice that KS DFT with SIC has been used to attempt to describe charge localization in non-magnetic quantum wires without success [48], contrary to our KS SCE theory, which proved able to perfectly capture this kind of physics [21].

Objective 2: Algorithms for the exact SCE functional from Optimal Transport

As illustrated in Fig. 2, the exact SCE functional corresponds to the minimum electron-electron interaction in a given *smooth* quantum mechanical density. This defines a problem that is neither properly classical (classical systems at zero temperature do not have smooth densities) nor quantum mechanical (there is zero kinetic energy, so that quantum effects do not enter). Notice that this does not imply that we do not take into account quantum effects: they enter when we use the SCE functional in the KS approach.

A very suitable mathematical framework for the SCE functional is optimal transport (or mass transportation theory), an important field of mathematics and economics, as I have recently shown in collaboration with a leading group in this field [25].

Optimal Transport (or Mass Transportation Theory) with Coulomb cost

Mass transportation theory dates back to 1781 when Monge [49] posed the problem of finding the most economical way of moving soil from one area to another, and received a boost when Kantorovich, in 1942, generalized it to what is now known as the Kantorovich dual problem [50]. In the last twenty years optimal transport has developed into one of the most fertile and active fields in mathematics, because long-standing issues could be finally addressed, and also because connections with classical problems in geometry, partial differential equations, nonlinear dynamics, and other problems of economics have been established [51].

The original Monge-Kantorovich problem consists in finding the most economical way to move a mass distribution into another one (according to a given definition of the cost function, which defines the work necessary to move a unit mass from one location to another). For example, one may wish to move books from one shelf ("shelf 1") to another ("shelf 2"), by minimizing the total work. The goal of solving the Monge problem is then to find an *optimal map* which assigns to every book in shelf 1 a unique final destination in shelf 2 (see Fig. 5).

In Ref. [25] we have shown that the co-motion functions of the SCE theory are exactly the Monge optimal maps for a mass transportation problem with cost function given by the Coulomb repulsion. However, it is well known in mass transportation theory that the Monge problem is very delicate and that proving in general the existence of the optimal maps (the co-motion functions in the SCE case) is extremely difficult, even if we have hints that in the special case of Coulomb cost it might be possible to prove their general existence under rather mild assumptions. In 1942 Kantorovich proposed a relaxed formulation of the Monge problem, in which the goal is now to find a *transport plan*, which gives the probability that, when minimizing the total cost, a certain mass element in the first mass distribution be transported into another one in the second mass distribution. This is evidently more general than the Monge transportation map, which assigns a unique final destination in the second mass distribution to every element in the first one. We have extended the relaxed Kantorovich formulation to the SCE problem [25]. This way, we have also been able to generalize the dual Kantorovich problem to the SCE functional, transforming the non linear SCE problem into a maximization under linear constraints that yields, in one shot, the functional and its functional derivative (needed for the KS potential). This reformulation paves the way to readapting algorithms based

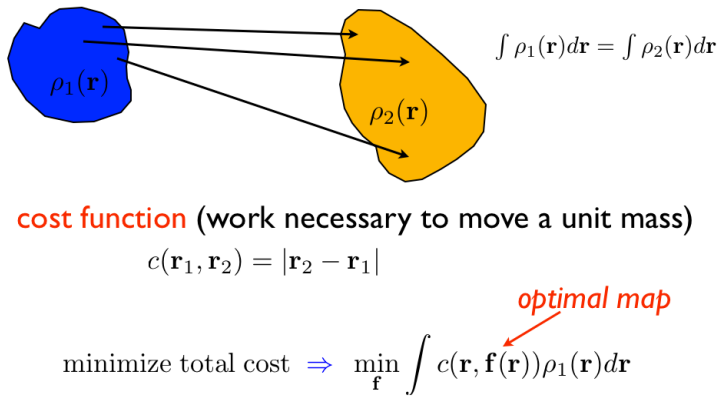

Fig. 5: The Monge problem of finding the most economical way of moving a mass distribution into another one. Usually, the work necessary to move a unit mass from one location to another is set equal to the distance between the two locations. The SCE functional defines a similar problem in which, instead, the cost function is given by the Coulomb repulsion, and the goal is to transport N-1 times the density into itself.

on linear programming developed in the framework of optimal transport to the SCE problem. Indeed, very recently, building on our results, a research group in Berkeley has implemented the first proof-of-principle Kantorovich dual solution to compute the SCE functional in arbitrary 3D geometry [28].

Task 2: From mass transportation theory to algorithms and corrections for the SCE functional
Team members: 1 postdoc (2.5 years)
International Collaborations: G. Buttazzo and L. De Pascale (Mathematics, University of Pisa, Italy), G. Friesecke (Mathematics, Munich Technical University, Germany)
In this part of the project I plan to continue and expand my interaction with the optimal transport community in order to 1) import and readapt algorithms developed in this framework, and 2) gain insight into the exact SCE functional and its corrections.
The implementation of the exact SCE functional in the general two- and three- dimensional cases poses new challenges also for the field of mass transportation theory. The first challenge is that the Coulomb repulsion as cost function has never been considered in the field, until very recently, when triggered by our work. The second challenge is that the SCE functional is an optimal transport problem with many mass distributions (while in the classical Monge-Kantorovich problem one treats normally just two mass distributions), for which the literature is scarce. Fortunately, all the mass distributions are the same in the SCE case, equal to the electronic densities. This gives to the problem additional symmetries that highly simplify it [52,53]. The very recent work done by the Berkeley group [28] showed that it is possible to solve the dual Kantorovich problem to compute the SCE potential. However, they could only address small systems, with less than 10 electrons. We will start by trying to extend this approach to larger systems, reformulating the constraints in a problem given in a basis set, exploring several levels of approximations. A key point is to understand the sensitivity of the KS SCE approach to the actual accuracy of the SCE one-body potential, which is the output of the Kantorovich dual problem. Several results in KS DFT for the optimized potential method showed that the density is not very sensitive to the fine details of the potential, but only to some key features. The challenge will be to identify these key features in the SCE case, and to impose them as constraints in a simplified Kantorovich formulation. We will also pursue the Monge approach based on the co-motion functions, since they provide very useful physical information on the system, as explained in the approach of Obective 1.
Mass transportation theory can also be used to construct corrections beyond KS SCE, complementing the approach described in Objective 1. This can be done by defining a different transport plan, which is not optimal for the electron-electron interaction energy alone, but for the original quantum mechanical problem, or, at least, for some parts of it. This can be done by partially relaxing the constraints in the Kantorovich formulation. Approximations for the co-motion functions will be also studied, interacting with Objective 3.
Notice that there is already a big interest of the Optimal Transport community in the problem defined by the SCE functional. I have been an invited speaker in the 2012 European symposium on Optimal Transport Applications [http://crm.sns.it/event/251/], where I was explicitly asked to illustrate the connection between the Monge-Kantorovich problem and DFT. Also, very recently, other mass transportation theory groups have started to work on the SCE problem [52-54]. This interest clearly increases the chances of importing algorithms and ideas from this research field.

Objective 3: xc functionals from approximate SCE and its corrections, and beyond
Important examples of strongly-correlated chemical systems for which state-of-the art KS DFT has severe problems are transition metals (key agents in catalysis) and the stretching and breaking of the chemical bond (crucial for predicting chemical reactions). Not surprisingly, these problems have the same roots as the problems just mentioned in Objective 1, with strong electronic correlation being mimicked by the approximate functionals with spin and spatial symmetry breaking, which, especially for transition metal complexes, occurs erratically, and is very sensitive to the functional chosen. The consequences are wrong characterizations of the ground and excited states, and problems in keeping the potential energy surfaces continuous [11]. This is particularly striking, considering that KS DFT is regarded as the workhorse for transition metal chemistry, because, due to the large electronic correlations, wave-function methods are just not viable: already the simple transition metal dimers Cr_2 and Fe_2 have presented enormous hurdles for wave-function theory. It is then crucial to address all these problems within a KS DFT framework.
While in the strongly-correlated-electron physics community most effort is put into approaches that correct the errors of KS DFT via a correlated treatment *after* a KS calculation done with a low-level functional (see Fig. 3), in chemistry there has been an enormous flourishing of research aimed at directly improving the xc functionals. As already mentioned, this is done, basically, by following two main strategies: 1) the inclusion of more and more exact properties in the approximate xc functional by adding more ingredients (gradients of

the density, orbital-kinetic-energy density, exact exchange, unoccupied KS orbitals - summarized in the so-called "Jacob's ladder" towards the "heaven" of chemical accuracy [8]), and 2) more pragmatically, by fitting a (often quite large) number of parameters on empirical data sets, resulting in functionals highly optimized for specific systems or processes [8,12]. The drawback of approach 1) is that it has not given, yet, approximations with the desired accuracy, and the problems with approach 2) is that these highly-optimized functionals can easily fail for systems other than those used for their fine-tuning.
In any case, the accuracy for transition metal chemistry and for predicting chemical reactions is, with both strategies, far from satisfactory, presenting all the problems mentioned above.

New xc functionals from approximate SCE + corrections: bottom up strategy
In parallel and in synergy with the efforts described in the previous two objectives, in which a rigorous treatment starting from strongly-correlated-electron techniques will be used to develop corrections to KS SCE (making approximations at a later stage), in this part of the project I will start to directly build new approximate functionals by using a functional form inspired to the SCE theory, and to test them. The idea is to start to learn since the beginning which aspects of SCE and its higher order corrections are crucial and which ones can be neglected or approximated.
An important part of this objective will be also to design and test seamless ways to combine some aspects of standard functionals with SCE. This is necessary to be able to describe in a quantitative accurate way systems at moderate and intermediate correlation regimes.
As already anticipated in Fig. 1, I will have at the same time a "top-down" approach (Objectives 1-2: develop and implement the exact functionals and then, if needed, make approximations at a later stage) and a "bottom-up" approach (start since the beginning with approximations and learn by testing them). These two strategies will continuously interact and affect each other, progressing towards the final common goal.

Building Approximations
As illustrated in Fig. 3, the SCE functional depends on one-body quantities called co-motion functions that perfectly correlate all the electronic positions, and are highly non-local functionals of the density. Once the co-motion functions are known, the corresponding KS potential can be easily built, as I have recently shown [20]. While for the quasi-one-dimensional case that we have treated in our preliminary tests [21] the computational effort of the KS SCE approach was similar to the one of standard KS LDA, computing the *exact* co-motion functions in the general three-dimensional case might turn out to be too expensive or not doable, as discussed in the previous Objective 2. The key idea, here, is to build *approximate* co-motion functions, leading to new functionals totally inspired to the SCE theory. This is very different than the traditional ingredients of the "Jacob's ladder" strategy: the new information here is the non-locality brought in by the one-body approximate co-motion functions, and, at a later stage, in the approximate higher order corrections inspired to the results of Objective 1.
Moreover, as already discussed, our pilot calculations on chemical systems have shown that the SCE functional is essentially complementary to the standard approximations: it correctly describes very correlated situations (e.g., a stretched bond), but gives energies way too low for cases in which simple xc functionals such as GGA's work well.
It seems thus very attractive to combine the SCE functional with GGA's or metaGGA functionals. This, however, needs to be done in a rigorous way, to avoid any double counting and empiricism.
In this respect I will follow two main strategies:

Task 3: Local interpolation along the adiabatic connection
Team member: 1 PhD student
International Collaborations: M. Seidl (Physics, University of Regensburg, Germany), A. Savin (Chemistry, CNRS Paris, France), A. Teale (Department of Chemistry, University of Nottingham, UK)
The first one is based on a *local interpolation* along the standard adiabatic connection of DFT (in which the electron-electron interaction is switched on – at fixed electronic density - by multiplying it by a real constant varying between 0 and 1). The idea is inspired to the work of Seidl et al. [55], who constructed an interpolation for the total xc energy between the weakly correlated regime (taking the two leading terms in the Taylor expansion, corresponding to exact exchange and second-order perturbation theory) and the strongly-correlated regime (SCE and first-order correction to SCE - at the time both terms could only be approximated in a semilocal way, as the exact SCE solution was not known). The problem with the original idea of Seidl at al. [55] is that it yields an approximate xc energy functional that is not size-consistent, because the size-consistent ingredients enter necessarily in a non-linear way. With the exact SCE solution, we have also access to *local* quantities, also called energy densities. If we construct the interpolation locally

(that is, in each point of space, interpolating between energy densities at weak and strong correlation) we recover in a very natural way size-consistency (at least in the usual DFT sense). When constructing this local interpolation it is important to keep in mind that energy densities are not uniquely defined, so that the local interpolation makes sense only if all the input quantities (at weak and strong correlation) are defined in the same way (people use often the term *gauge*). Together with my coworkers, I have already shown how to construct the SCE energy density in the gauge of the exchange-correlation hole from the co-motion functions [56]. This gauge is probably the most natural one, and can be easily combined, at weak correlation, with the exact (or approximate, like the metaGGA Becke-Roussel exchange hole functional [57], which is in the correct gauge) exchange energy density obtained from the exchange hole.
Another key point here is to have a local indicator of correlation, that is, a quantity that tells us, in each point of space, if our system is closer to the weak- or to the strong-correlation limit. This local indicator should have a role similar to second-order perturbation theory in the original (non size-consistent) global interpolation of Seidl at al. [55]. To construct this local indicator I will proceed exploring different routes. A first one is based on the idea of Becke [58] of using the local normalization of the exact exchange hole: in situations of strong correlation the exact exchange hole is highly delocalized on many centers and its local normalization is thus different from minus one (smaller in absolute value) and would signal a situation in which strong "static" correlation is present. Another idea is based on the "Overhauser model", a physically sound way of constructing the pair density of a many-electron system, that I have contributed to develop [59,60]. By using the Overhauser model in a perturbative way, one could get an estimate of the effect of second-order perturbation theory on the exchange-correlation hole, thus directly having an indicator in the right gauge. A third promising idea is to use the (exact or approximate) co-motion functions, as they provide, in each point $\boldsymbol{r}$, a local estimate of the average electron-electron distance, $r_{12}(\boldsymbol{r})$. In other words, the co-motion functions are able to exactly transform a two-body observable (the electron-electron distance) into a local one-body quantity. A comparison of the local average electron-electron distance with the Bohr radius a_0 will allow us to establish whether a system is closer to the weakly correlated regime ($a_0 >> r_{12}(\boldsymbol{r})$) or to the strongly-correlated one ($a_0 << r_{12}(\boldsymbol{r})$).
Collaborating with A. Teale, who contributed to develop a sophisticated machinery to extract nearly exact quantities along the adiabatic connection by using accurate wave function results and the Legendre transform formulation of DFT [61,62], I will also analyze "exact" local second-order corrections, built from accurate pair densities. This will allow us to compare our approximate local indicators of correlation with an exact one, and to get ideas for constructing improved approximations.
Finally, collaborating with A. Savin, I will also explore non linear adiabatic connections like the one based on range separation [63], as it might be simpler to construct interpolations in such cases.

Task 4: GGA's, metaGGA's and hybrid corrections to SCE
Team member: 1 PhD student
International Collaborations: J. P. Perdew (Physics, Temple University, USA), K. Burke (Chemistry & Physics, University of California Irvine, USA)
Local Collaborations: E. J. Baerends (host institution)
The second strategy consists in directly building xc functionals to be combined with the approximate SCE (and its corrections developed in objectives 1-2). As already mentioned (see Fig. 2), in exact KS DFT strong correlation is captured with "barriers" (or "bumps") in the Kohn-Sham potential that create internal classically forbidden regions for the KS orbitals, describing the physics of charge localization.
GGA's, metaGGA's or hybrids are not able to create these barriers self-consistently, while self-consistent KS calculations with the xc SCE functional creates them, at least partially, in a physically and mathematically sound way. Once the barriers and the internal classically forbidden regions are created with the xc SCE functional, we can build GGA's correction specifically designed to deal with these regions. In fact, in recent years, it has been proven that the gradient expansion for classically forbidden regions is different than the one for classically allowed regions [64]. This new mathematical insight has lead to a formal derivation of GGA parameters previously obtained by fitting procedures [65], and to improved GGA's for solids, either by including the new exact expansion [66] or by using an expansion derived from surface effects [67]. The idea here is to use the exact properties of the gradient expansion for classically forbidden regions to improve the results from KS SCE. This can be realized by designing GGA's that treat in a correct way both the internal classically forbidden regions due to strong correlation and the normal (classically allowed) regions, recovering the accuracy of GGA's for weak and moderate correlation, while retaining and improving the accuracy of SCE to treat strong correlation. I will collaborate on this aspect with K. Burke and J.P. Perdew, who have long-standing experience in building approximate functionals.

Another related strategy to construct GGA, metaGGA's and/or hybrid corrections to the xc SCE functional is based on the scaling properties of the functionals [37]. A given approximate functional can be scaled to the low-density limit to extract its strong-coupling contribution, which can be subtracted to avoid double counting when combined with SCE and its higher order corrections.
Other ways to retain the non-local (exact or approximate) physics of the SCE functional and to go beyond it is to consider the exact partition of the KS potential that is obtained from the equation for the square root of the density [68,69]. This equation can be written, more generally, along the adiabatic connection, and thus also for the limit of infinite coupling strength. By comparing the potential with the one at the physical coupling strength and with the KS one it is possible to gain insight in the construction of a kinetic correlation correction to the SCE, and to its functional derivative. I will collaborate on this aspect with E.J. Baerends from my same host institution.

Task 5: Testing the approximations in a systematic way
Team members: 1 postdoc (3 years), 1 Technician (5 years, 0.2 fte)
Local Collaborations: L. Visscher (host institution), SCM (spinoff company that develops and maintains the codes ADF and BAND)
A crucial role in this proposal is played by testing and validating the approximate functionals. This is actually far from obvious: validating and benchmarking functionals is, in many ways, a research field by itself. Especially in chemistry, the scientific community has produced an enormous know-how on validating and benchmarking approximate functionals, producing an extensive set of reference data that I intend to fully exploit (for extensive reviews, see, e.g. [11,12]).
In general, the benchmark data used for validation can be either from experiment or, for simple enough systems, from wave-function calculations. However, we must be very cautious about wave-function results when dealing with correlated systems, because even very high-level wave function calculations might not be reliable if static correlation is too complex (e.g., in transition metal chemistry). On the other hand, the comparison with wave-function calculations is generally more instructive because it allows for a deeper understanding of the problems inherent to our approximations. For example, we can extract quantities such as the density and the spin densities [70], providing way more insight than the simple energetics.
At the validating stage it is thus crucial to interact with chemists with experience in benchmarking functionals using wave-function techniques with the needed care, as well as experimental data sets carefully chosen. I will then collaborate, on this aspect, with the group of L. Visscher located in my same institution, who has a long-standing experience in benchmarking quantum chemical methods. The aim is to improve the KS DFT accuracy for systems containing *d* and *f* elements, for transition states, and, in general, for systems with multireference character. We will thus focus on test sets containing this kind of systems and quantities for validation.
In a first stage, these accurate and controlled tests will provide a deep understanding of the key features of approximate SCE -based functionals needed to capture the relevant many-body effects and, at the same time, will allow a careful analysis of the consequences of each approximate step done in the top-down strategy.
In the final stage, validation will be essential to deliver new reliable xc functionals.
Regarding the practical implementation of new approximations into DFT codes, this project will benefit of the technical support of SCM (the spinoff company that develops and maintains the chemistry code ADF and the solid-state code BAND), located in my same host institution.

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Section c. Resources (incl. project costs)

Research Team
To successfully build a new theoretical framework for accurate electronic structure calculations, I propose to create a multidisciplinary research group of graduate students and postdoctoral associates with expertise in the three relevant research areas:

Position	Key expertise	Focus area	Role in project
PI (myself)	xc functionals and SCE	Chemsitry and Physics	group leader
Post-doc 1	Mass transportation theory	Mathematics	Task 2: Algorithms
Post-doc 2	Benchmarking xc functionals	Chemistry	Task 5: test xc functionals
PhD student 1	Strongly-correlated techniques	Physics	Task 1: corrections to SCE
PhD student 2	Density functional theory	Chemistry and Physics	Task 3: xc functionals from SCE + local interpolation
PhD student 3	Density functional theory	Physics and Chemistry	Task 4: SCE + adapted GGA's, metaGGA's, etc.
System analyst	System administration/ Programming	Computer Science	Cluster administration

My documented expertise in the three areas involved (not only in terms of publications, but also as a frequent invited speaker in conferences in the three scientific communities) will allow me to efficiently direct and coordinate this mixed research group, defining the research directions and also translating between different scientific languages, **dedicating 60% of my time to the project**. This way, all the members of the group will be able to go beyond the boundaries of their domain and to establish fruitful interactions with each other. The tasks assigned to each member of the team and an estimated timeline is reported in Fig. 6.

Host Institution and Local Collaborations
My host institution is the **Theoretical Chemistry Department of the VU University in Amsterdam**, which has a long-standing tradition of excellence in the field of fundamental development in DFT, embedding the project in one of the best possible environments. In particular, I will benefit of collaborations and discussions with leading scientists in DFT such as **E. J. Baerends** and **O. Gristenko**, and of working with **L. Visscher** in benchmarking and validating the new functionals (Objective 4). The **spinoff company SCM**, which develops and maintains the DFT codes **ADF** (chemistry) and **BAND** (extended systems) is located in the same department and will assure all the needed technical assistance when dealing with the implementation of the new functionals.

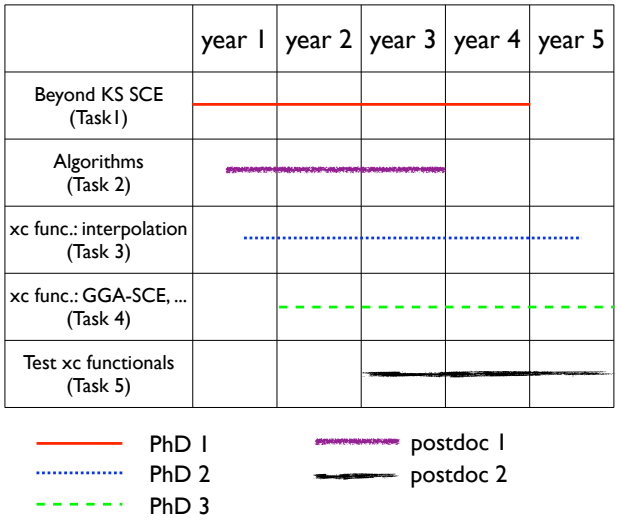

Fig. 6 Schematic timeline for the entire project, including all funded scientific personnel.

Moreover, the science faculties of the VU University and of the University of Amsterdam will form together, in the next years, a new institution called Amsterdam Faculty of Science. Our department will then move in 2018 to be merged with other Chemistry and Physics departments in a unit called **Amsterdam Center for Multiscale Modeling**, which will be an even better host for this interdisciplinary project.

Cost Category			**Total in Euro**
Direct Costs	**Personnel**	PI	331.000
		Senior Staff	
		Postdocs (2x)	382.000
		Students (3x)	592.000
		Other (Technician)	64.000
	i. Total Direct Costs for Personnel (in Euro)		**1.369.000**
	Travel		59.000
	Equipment		163.000
	Other goods and services	Consumables	
		Publications (including Open Access fees), etc.	5.000
		Other (please specify)	
	ii. Total Other Direct Costs (in Euro)		**227.000**
A – Total Direct Costs (i + ii) (in Euro)			**1.596.000**
B – Indirect Costs (overheads) 25% of Direct Costs (in Euro)			**399.000**
C1 – Subcontracting Costs (no overheads) (in Euro)			
C2 – Other Direct Costs with no overheads (in Euro)			**5.000**
Total Estimated Eligible Costs (A + B + C) (in Euro)			**2.000.000**
Total Requested EU Contribution (in Euro)			**2.000.000**

For the above cost table, please indicate the % of working time the PI dedicates to the project over the period of the grant:	**60 %**

International Collaborations
As already mentioned in the Methodology section, I also build on several international collaborations with groups specialized in the research fields involved.
All the collaborations involved in this proposal are also summarized below

- K. Burke (Chemistry & Physics, University of California Irvine, USA)
- G. Butazzo and L. De Pascale (Department of Mathematics, University of Pisa, Italy)
- J. Lorenzana (Department of Physics, University of Rome "La Sapienza", Italy)
- J. P. Perdew (Physics Department, Temple University, Philadelphia, USA)
- A. Savin and J. Toulouse (Theoretical Chemistry, CNRS Paris, France)
- M. Seidl (Institute of Theoretical Physics, University of Regensburg, Germany)
- A. Teale (Department of Chemistry, University of Nottingham, UK)
- G. Vignale (Department of Physics and Astronomy, University of Missouri, USA)

Equipment and Technical Staff
I will need extensive computer resources to carry on the different aspects of this proposal, especially the part concerning benchmarking the approximations. I thus plan to buy a computer cluster and to employ for one day per week a technician and programmer to provide the technical support.