

Fundamental Aspects of DFT

January 8–10 2015

The Norwegian Academy of Science and Letters

Drammensveien 78, Oslo, Norway

Organizing Committee

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Centre of Theoretical and Computational Chemistry
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Dear participant,

The organizing committee has great pleasure in welcoming you to Oslo for the workshop “Fundamental Aspects of DFT”, held in the beautiful surroundings of the Norwegian Academy of Science and Letters and devoted to recent progress and developments in density-functional theory, with emphasis on fundamental aspects of the field.

During the next two days, more than 57 participants from 13 countries will give 25 oral presentations and 14 poster presentations at the workshop. It is our hope that these presentations and our discussions will stimulate us all towards new directions and developments in the field.

The workshop is sponsored by European Research Council through the Advanced Grant ABACUS and by the Centre for Theoretical and Computational Chemistry (CTCC), a Centre of Excellence established by the Research Council of Norway for the period 2007–2017 and shared by the University of Oslo and UiT The Arctic University of Norway.

Trygve Helgaker and Simen Kvaal

Organizing committee

Thursday January 8 – Afternoon

13:00 *Lunch*

Session 1

Chair: Andreas Savin

14:00 Mel Levy
*Ground-State Energy as a Simple Sum of Orbital Energies in DFT
(L1)*

14:35 Eric Cancès
*DFT for disordered materials
(L2)*

15:10 Florian Eich
*Density-Functional Theory for Thermoelectric Phenomena
(L3)*

15:45 *Coffee*

Session 2

Chair: Andreas Görling

16:15 Erik Tellgren
*Current density functional theory for molecular systems in strong mag-
netic fields
(L4)*

16:50 Andre Laestadius
*Non-existence of a Hohenberg-Kohn Variational Principle in Total Current
Density Functional Theory
(L5)*

17:25 David Gontier
*Pure-state and mixed-state N-representability in CSDFT
(L6)*

18:00 *Break*

19:30 *Poster Session*

Friday January 9 – Morning

Session 3

Chair: Simen Kvaal

- 09:00 Evert Jan Baerends
Orbitals and orbital energies in DFT and TDDFT
(L7)
- 09:35 Klaas Giesbertz
Two-body interactions and the physics of natural occupation numbers and amplitudes
(L8)
- 10:10 Lin Lin
Compressed representation of Kohn–Sham orbitals via selected columns of the density matrix
(L9)

10:45 *Coffee*

Session 4

Chair: Paul W. Ayers

- 11:15 Andreas Savin
Density functional theory without density functionals
(L10)
- 11:50 Jan Philip Solovej
Thomas-Fermi Theory revisited
(L11)
- 12:25 David Tozer
Molecular binding in post-Kohn–Sham orbital-free DFT
(L12)

13:00 *Lunch*

Friday January 9 – Afternoon

Session 5

Chair: David Tozer

- 14:00 Andreas Görling
Density-functional methods based on the adiabatic-connection fluctuation-dissipation theorem combining high accuracy and wide applicability (L13)
- 14:35 Viktor Staroverov
Reduction of Wavefunctions to Kohn-Sham Effective Potentials (L14)
- 15:10 Alex Borgoo
Excitation energies from ensemble DFT (L15)
- 15:45 Elisa Rebolini
Molecular excitation energies with a range-separated second-order dynamical Bethe-Salpeter kernel (L16)
-

16:20 *Coffee*

Session 6

Chair: Robert van Leeuwen

- 16:45 Paola Gori-Giorgi
Exchange-Correlation Functionals from the Strong Coupling Limit of DFT (L17)
- 17:20 Gero Friesecke
Scaling limits of density functional theory: cross-over from mean field theory to optimal transport (L18)
- 17:55 Huajie Chen
Pair Densities in Density Functional Theory (L19)
-

18:30 *Break*

19:30 *Conference Dinner*

Saturday January 10 – Morning

Session 7

Chair: Paola Gori-Giorgi

09:00 Paul W. Ayers
On Degeneracy, Convexity, and Related Issues
(L20)

09:35 Julien Toulouse
Density-functional theory at noninteger electron numbers
(L21)

10:10 Ulf Ekström
The universal density functional as an eigenvalue optimization problem
(L22)

10:45 *Coffee*

Session 8

Chair: Trygve Helgaker

11:15 Markus Penz
The time-dependent potential-density mapping from a density-functional perspective
(L23)

11:50 Michael Ruggenthaler
Invertibility of the time-dependent potential-density mapping
(L24)

12:25 Robert van Leeuwen
Fixed-point approach to time-dependent density-functional theory
(L25)

13:00 *Lunch*

14:00 *End of Workshop / Discussions*

Abstracts of Lectures

Ground-State Energy as a Simple Sum of Orbital Energies in DFT

Mel Levy^{1*}

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We have very recently observed [M. Levy and F. Zahariev, *Phys. Rev. Lett.* **113**, 113002 (2014)] that the exact interacting ground-state energy may be obtained, in principle, as a simple sum of orbital energies when a universal density-dependent constant is added to the Kohn-Sham potential or to one of its generalizations. The resultant shifted potential has intriguing features, including the fact that a significant component of it changes relatively little on average when the density changes and the fact that the potential does not undergo a discontinuity when the number of electrons increases through an integer. Thus, the approximation of this shifted potential represents an alternative direct approach for the approximation of the ground-state energy and density.

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DFT for disordered materials

Eric Cancès

DFT models for periodic systems (perfect crystals at zero temperature) have been used for decades in solid states physics and materials science and are well-understood mathematically. On the other hand, the modeling of the electronic structures of disordered materials such as alloys, doped semiconductors, crystals at finite temperature, or amorphous materials, still is a challenging task.

Together with Salma Lahbabi and Mathieu Lewin [1], we have introduced a new mathematical framework to set up mean-field electronic structure models of Hartree-Fock or Kohn-Sham types for disordered systems. In this talk, I will (try to) give a pedagogical introduction to this mathematical framework, state the results we have obtained so far, and point out some of the open questions we would like to address in the future.

References

- [1] E. Cancès, S. Lahbabi and M. Lewin, *Mean-field models for disordered crystals*, J. Math. Pures App. 100 (2013) 241-274.

Density-Functional Theory for Thermoelectric Phenomena

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Thermoelectric phenomena attract renewed interest due their potential impact on the development of sustainable energy sources. On a fundamental level thermoelectricity requires the description of charge and energy (or heat) transport. In order to address the energy transport from first principles, we recently proposed a novel density-functional theory (DFT) [1]. Based on an idea due to Luttinger [2] we include the energy density as fundamental variable in addition to the charge density. The potential conjugated to the energy density is Luttinger's " ψ "-field, which acts as a proxy for a temperature distribution that varies in time and space.

In this talk I review our DFT for thermoelectric phenomena and highlight important differences to TD-DFT. To this end I discuss subtle deviations from the usual Kohn-Sham scheme. Furthermore, I present two basic approximation strategies: an adiabatic local-density approximation, and a generalization of the VK functional, which introduces a mechanism for relaxation. Finally, I compare our approach to the Landauer-Büttiker approach [3], commonly employed to describe thermoelectric transport through nanoscale devices, and discuss routes towards a mapping theorem.

1. F.G. Eich, M. Di Ventura, and G. Vignale, *Phys. Rev. Lett.* 112, 196401 (2014)
2. J.M. Luttinger, *Phys. Rev.* 135, A1505 (1964)
3. F.G. Eich, A. Principi, M. Di Ventura, and G. Vignale, *Phys. Rev. B* 90, 115116 (2014)

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Current density functional theory for molecular systems in strong magnetic fields

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Whereas conventional density functional theory is now the workhorse of quantum chemistry, current-dependent functionals for molecular systems have received relatively little attention. Within the framework of Vignale and Rasolt's paramagnetic current density functional theory, the exchange-correlation functional should depend on the current density via the vorticity. The use of the physical current density has been proposed as an alternative, but has so far not been developed into an adequate density functional framework. A more pragmatic alternative is to let a current-dependence enter via a gauge-invariant kinetic energy density in a meta-GGA functional. I will discuss the present status of, and challenges related to, vorticity-dependent functionals and meta-GGAs in the context of molecular systems subject to strong magnetic fields.

Non-existence of a Hohenberg-Kohn Variational Principle in Total Current Density Functional Theory

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For a many-electron system, whether the particle density $\rho(\mathbf{r})$ and the total current density $\mathbf{j}(\mathbf{r})$ are sufficient to determine the one-body potential $V(\mathbf{r})$ and vector potential $\mathbf{A}(\mathbf{r})$, is still an open question. For the one-electron case, a Hohenberg-Kohn theorem exists formulated with the total current density. Here we show that the generalized Hohenberg-Kohn energy functional $\mathcal{E}_{V_0, \mathbf{A}_0}(\rho, \mathbf{j}) = \langle \psi(\rho, \mathbf{j}), H(V_0, \mathbf{A}_0) \psi(\rho, \mathbf{j}) \rangle$ can be minimal for densities that are not the ground-state densities of the fixed potentials V_0 and \mathbf{A}_0 . Furthermore, for an arbitrary number of electrons and under the assumption that a Hohenberg-Kohn theorem exists formulated with ρ and \mathbf{j} , we show that a variational principle for Total Current Density Functional Theory as that of Hohenberg-Kohn for Density Functional Theory does not exist. The reason is that the assumed map from densities to the vector potential, written $(\rho, \mathbf{j}) \mapsto \mathbf{A}(\rho, \mathbf{j}; \mathbf{r})$, enters explicitly in $\mathcal{E}_{V_0, \mathbf{A}_0}(\rho, \mathbf{j})$.

Pure-state and mixed-state N -representability in CSDFT.

David Gontier

Abstract: The pure-state or mixed-state N -representability problem can be formulated as follows: *what is the correct minimization set in DFT?* When no magnetic field is involved, one only has to characterize a set of electronic densities $\{\rho\}$, which was done in the 1980's. Whenever there is a magnetic vector potential, one should also characterize the set of spin angular momenta \mathbf{m} , and of the paramagnetic currents \mathbf{j} (this leads to the Current-Spin-Density Functional Theory CSDFT). In this talk, we will answer the problem of representability of the set $\{(\rho, \mathbf{m}, \mathbf{j})\}$ completely in the mixed-state setting, and partially in the pure-state setting.

Orbitals and orbital energies in DFT and TDDFT

Evert Jan Baerends

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The status and meaning of orbitals and orbital energies in the Kohn-Sham one-electron model of DFT has been controversial. Often heard opinions are that the orbitals would not have the same meaning as in the competitive one-electron model of Hartree-Fock, they would just be auxiliary quantities in the theory to build the total density. And the orbital energies would not have physical meaning, except for the HOMO orbital energy being equal to the first ionization energy.

We will argue the opposite: the exact Kohn-Sham orbitals of DFT are “better” than HF orbitals and their orbital energies are much closer to ionization energies than HF orbital energies are. The status of the Slater-Janak theorem and the “band gap problem” in molecules and in solids will be discussed. The orbital energies of common approximations to the KS potential (LDA, GGA) are so far from the exact values that better approximations are called for. These lead, with due recognition of the nature of the fundamental gap in solids, to a possible solution for the calculation of the band gap.

1. E. J. Baerends, O. V. Gritsenko, R. van Meer, *Phys. Chem. Chem. Phys.* **15** (2013) 16408
2. R. van Meer, O. V. Gritsenko and E. J. Baerends, *J. Chem. Theor. Comp.* **10** (2014) 4432
3. M. Kuisma, J. Ojanen, J. Enkovaara, T. T. Rantala, *Phys. Rev. B* **82** (2010) 115106

Two-body interactions and the physics of natural occupation numbers and amplitudes

Klaas Giesbertz^{1*}

¹⁾ *VU Amsterdam, Netherlands*

The non-vanishing of the natural orbital occupation numbers of the one-particle density matrix of many-body systems has important consequences for the existence of a density matrix-potential mapping for nonlocal potentials in reduced density matrix functional theory and for the validity of the extended Koopmans' Theorem. We analyze for a number of explicit examples of two-particle systems that in case the wave function is non-analytic at its spatial diagonal and derive a more general criterium for the non-vanishing of natural occupations for two-particle wave functions with a certain separability structure. Singlet two-electron systems also allow for a diagonal representation of the wave function with the natural orbitals as its eigenfunctions and the squares of its eigenvalues, the natural amplitudes, are equal to the occupation numbers. We demonstrate that the sign pattern of the natural amplitudes is related to the long-range structure of the wave function, which is in turn dictated by the tail of the Coulomb interaction.

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Compressed representation of Kohn-Sham orbitals via selected columns of the density matrix

Lin Lin

Abstract:

Given a set of Kohn-Sham orbitals from an insulating system, we present a simple, robust, efficient and highly parallelizable method to construct a set of, optionally orthogonal, localized basis functions for the associated subspace. Our method explicitly uses the fact that density matrices associated with insulating systems decay exponentially along the off-diagonal direction in the real space representation. Our method avoids the usage of an optimization procedure, and the localized basis functions are constructed directly from a set of selected columns of the density matrix (SCDM). Consequently, the only adjustable parameter in our method is the truncation threshold of the localized basis functions. Our method can be used in any electronic structure software package with an arbitrary basis set. We demonstrate the numerical accuracy and parallel scalability of the SCDM procedure using orbitals generated by the Quantum ESPRESSO software package. We also demonstrate a procedure for combining SCDM with Hockney's algorithm to efficiently perform Hartree-Fock exchange energy calculations with near linear scaling. (Joint work with Anil Damle and Lexing Ying)

Density functional theory without density functionals

Elisa Rebolini^{1,2,4,*}, Julien Toulouse^{1,2,†}, Andrew M. Teale^{3,‡}, Trygve Helgaker^{4,§}, and Andreas Savin^{1,2¶}

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The adiabatic connection in density functional theory provides a series of model Hamiltonians. Could such Hamiltonians be used for providing physically reasonable results? Can perturbation techniques be used to improve them systematically? What numerical methods are adapted to them? Some simple attempts [1,2] to answer these questions are presented.

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2. E. Rebolini, J. Toulouse, A. M. Teale, T. Helgaker, A. Savin, *J. Chem. Phys.* **141**, 044123 (2014), and papers to be published

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Thomas-Fermi Theory revisited

Jan Philip Solovej, University of Copenhagen

Abstract: As crude as Thomas-Fermi theory may be in totally ignoring exchange-correlation effects it still predicts certain aspects of atomic and molecular structure better than expected, at least qualitatively.

I will discuss a rigorous mathematical result implying that Thomas-Fermi theory gives a much better estimate on the size of atoms than one would have expected. This led to a proof of what is known as the ionization conjecture in the Hartree-Fock approximation.

I will compare this to experimental data for the size of alkali atoms as well as to computational results on the Born-Oppenheimer potential curves for diatomic molecules. The latter computational part is joint work with Natalie Gilka and Peter Taylor.

Molecular binding in post-Kohn–Sham orbital-free DFT

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Molecular binding in post-Kohn-Sham orbital-free DFT is investigated, using non-interacting kinetic energy functionals that satisfy the uniform electron gas condition and which are inhomogeneous under density scaling. A parameter is introduced that quantifies binding and a series of functionals are determined from fits to near-exact effective homogeneities and/or Kohn-Sham non-interacting kinetic energies. These are then used to investigate the relationship between binding and the accuracy of the effective homogeneity and non-interacting kinetic energy at the equilibrium geometry. For a series of 11 molecules, the binding broadly improves as the effective homogeneity improves, although the extent to which it improves is dependent on the accuracy of the non-interacting kinetic energy; optimal binding appears to require both to be accurate simultaneously. The use of a Thomas-Fermi-von Weizsäcker form, augmented with a second gradient correction, goes some way towards achieving this, exhibiting molecular binding on average. The extent to which the functionals can reproduce the system-dependence of the near-exact effective homogeneity is quantified and potential energy curves are presented for selected molecules.

The findings are discussed in terms of the non-interacting kinetic potential and the Hellmann-Feynman theorem. Kinetic potentials from the new functionals are presented for selected systems and are a clear improvement over those from Thomas-Fermi theory.

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2. A. Borgoo and D. J. Tozer, *J. Chem. Theory Comput.* **9** 2250 (2013)
3. A. Borgoo, J. A. Green, and D. J. Tozer, *J. Chem. Theory Comput.* **10** 5338 (2014)

Density-functional methods based on the adiabatic-connection fluctuation-dissipation theorem combining high accuracy and wide applicability

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A new generation of density-functional methods exploiting the adiabatic-connection fluctuation-dissipation (ACFD) theorem is presented. These methods belong to the class of approaches based on orbital-dependent exchange and correlation functionals. The exchange energy and the local multiplicative exchange potential, not to be confused with the nonlocal Hartree-Fock exchange potential, are treated exactly. Functionals for the correlation energy are derived from the adiabatic-connection fluctuation-dissipation theorem via time-dependent density-functional theory. In the latter either the simple Coulomb kernel or the Coulomb kernel plus the full frequency-dependent exact exchange kernel is employed, leading to the correlation energy either in the straightforward direct random phase approximation (dRPA) or in a highly accurate approximation termed exact-exchange ACFD (EXX-ACFD). In self-consistent dRPA and EXX-ACFD methods the correlation potential corresponding to the dRPA or EXX-ACFD correlation energy is obtained via the optimized effective potential method. The new approaches, in particular the EXX-ACFD method, are shown to be highly accurate and, in contrast to traditional density-functional methods, to be well-suited for the treatment of Van-der-Waals interactions or situations characterized by strong correlation. Due to their ability to describe situations with static correlation, i.e., multi-reference cases, EXX-ACFD methods have a wider range of applicability than standard, high-level quantum chemistry methods, like single-reference coupled cluster methods. The relation of singlet-singlet instabilities in exact exchange-only Kohn-Sham methods to the frequency integration in EXX-ACFD methods is discussed.

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A. Heßelmann and A. Görling, *Phys. Rev. Lett.* **106**, 093001 (2011).

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Reduction of Wavefunctions to Kohn–Sham Effective Potentials

Viktor N. Staroverov

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Conventional methods for computing exact exchange-correlation potentials attempt to recover $v_{\text{XC}}(\mathbf{r})$ from a given ground-state electron density that is obtained from an *ab initio* wavefunction. We present a conceptually different approach in which the wavefunction is “folded” into $v_{\text{XC}}(\mathbf{r})$. The approach relies on a closed-form expression connecting the Kohn–Sham effective potential with a special reduced form of the Schrödinger equation. As a numerical procedure, the method is free from basis-set artifacts that beset conventional Kohn–Sham inversion algorithms. This new development provides an explicit connection between the Kohn–Sham density-functional scheme and wavefunction methods, and allows one to directly probe the functional derivative of the true exchange-correlation energy functional.

Excitation energies from ensemble DFT

Alex Borgoo, Andy Teale, Trygve Helgaker

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We study the evaluation of the Gross-Oliveira-Kohn expression for excitation energies.

$$E_1 - E_0 = \epsilon_1 - \epsilon_0 + \left. \frac{\partial E_{xc}^w[\rho]}{\partial w} \right|_{\rho=\rho_0} \quad (1)$$

In particular Eq. 1 gives the difference between an excitation energy $E_1 - E_0$ and the corresponding Kohn–Sham orbital energy difference $\epsilon_1 - \epsilon_0$ as a partial derivative of the exchange–correlation energy of an ensemble of states $E_{xc}^w[\rho]$. Through Lieb maximisation, on input full-CI density functions, the exchange–correlation energy is evaluated exactly and the partial derivative is evaluated through finite difference. The equality is studied numerically for different geometries of the H_2 molecule and different ensemble weights. Furthermore we explore the adiabatic connection for the ensemble exchange–correlation energy. The latter may prove useful when modelling the unknown weight dependence of the exchange–correlation energy.

1. *Density-functional theory for ensembles of fractionally occupied states*,
E.K.U. Gross, L.N. Oliveira, W. Kohn
Phys. Rev. A **37** (1988) 2809

Molecular excitation energies with a range-separated second-order dynamical Bethe-Salpeter kernel

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In the past years, time-dependent density functional theory (TDDFT) [1] within the usual local (LDA) or semi-local (GGA) approximations has become very popular to calculate excitation energies of medium-sized systems because of its low computational cost and good accuracy. It has been shown very reliable in predicting excitation energies to the low-lying valence states but still present several shortcomings, especially concerning the underestimation of the high-lying Rydberg excitation energies, a poor description of charge transfer excitations and the lack of double or higher order excitations. Range separation of the electronic interaction has been proposed as one way to correct these deficiencies and has been shown very efficient when applied to the exchange part of the functional to recover good Rydberg and charge transfer excitation energies [2,3]. However, situations such as the dissociation of the hydrogen molecule and the treatment of excitation with multiple character are still pathological in this approach. These problems have been attributed to a bad description of the correlation kernel which is frequency independent in TDDFT within the adiabatic approximation.

In this talk, I will present an extension of the range separation technique to the correlation kernel where the long-range part of the correlation kernel is removed. Then I will show how to construct a long-range second-order frequency-dependent correlation kernel inspired by the Bethe-Salpeter kernel [4-6] and give some numerical results on atoms and molecules.

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EXCHANGE-CORRELATION FUNCTIONALS
FROM THE STRONG COUPLING LIMIT OF DFT

Paola Gori-Giorgi

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In this talk, I will show how the exact strong-interaction limit of the Hohenberg-Kohn energy density functional can be used to approximate the KS exchange-correlation energy. This corresponds to constructing a highly non-local density functional whose functional derivative (the KS potential) can be easily constructed. Otherwise said, we transform exactly, in a physically transparent way, an important part of the electron-electron interaction into an effective local one-body potential able to capture essential features of strong correlation that (restricted) Kohn-Sham calculations using the currently available approximations cannot describe. Some applications to model quantum wires and quantum dots, as well as negative ions and simple model chemical systems will be illustrated, and open problems and future perspectives will be discussed.

Acknowledgements: This research was supported by NWO through a Vidi grant and by EU-fp7 through a Marie Curie IEF fellowship.

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Scaling limits of density functional theory: cross-over from from mean field theory to optimal transport

Gero Friesecke^{1*}

¹⁾ *Technische Universität München, Germany*

The exact Hohenberg-Kohn-Lieb-Levy functional is computationally just as unfeasible as the original Schroedinger equation, but it is a formidable tool to gain theoretical insight into electron correlation. In my talk I discuss two natural scaling limits of the exact functional which involve only (i) the 'dilute'-ness and (ii) the particle number of the system, but no artificial parameters. The ensuing behaviour of correlations (as encoded by the 'exact' Hohenberg-Kohn electron pair density) is found to differ dramatically depending on the scaling regime, ranging from extreme correlation governed by optimal transport alias SCE theory over 'exchange correlations' governed by Pauli exclusion to independence, with interesting crossover phenomena. The main shortcoming of our work is that in the, for practical purposes most interesting, 'crossover' regime we have currently no proposal how to turn our insights into improved exchange-correlation functionals, except in the case of one-dimensional systems.

Joint work with Huajie Chen (TUM/Warwick), Codina Cotar (University College London), Claudia Klueppelberg (TUM), Christian Mendl (TUM), Brendan Pass (Alberta)

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4. H. Chen, G.F., "Pair densities in density functional theory", soon on *arXiv*

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Pair Densities in Density Functional Theory

Huajie Chen

For a many-electron system, the exact Coulomb repulsive energy is completely determined by the electron pair density, which has not been intensively studied in standard density functional models. We simulate the true pair densities of two groups of one dimensional systems with homogeneous and inhomogeneous single-particle densities, respectively. With the given single-particle densities, we carry out numerical simulations of Hohenberg-Kohn functionals for both bosons and fermions from a strongly interacting limit to a weakly interacting limit. This is a joint work with Gero Friesecke (TU Munich).

On Degeneracy, Convexity, and Related Issues

Paul W. Ayers^{1*}

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Present-day density-functional approximations are often unreliable for systems with nearly degenerate ground states. For this reason, it is useful to study the behavior of the exact density functional for degenerate ground states, along with the closely related issues of systems with fractional charge or fractional spin. This presentation will show how degenerate (and fractionally-charged) states lead to fundamental difficulties, primarily because they impel one to consider strongly nonlocal exchange-correlation functionals. Fortunately, the exact form of the exact exchange-correlation functionals and exchange-correlation potential in these cases is strictly constrained by the degeneracy of the energy for the infinite family of degenerate ground-state densities. Unfortunately, incorporating these constraints into practical approximate exchange-correlation functionals seems difficult.

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Density-functional theory at noninteger electron numbers

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Within exact electron density-functional theory, we investigate Kohn-Sham (KS) potentials, orbital energies, and noninteracting kinetic energies of the fractional ions of Li, C, and F. We use quantum Monte Carlo densities as input, which are then fitted, interpolated at noninteger electron numbers N , and inverted to produce accurate KS potentials $v_s^N(\mathbf{r})$. We study the dependence of the KS potential on N , and in particular we numerically reproduce the theoretically predicted spatially constant discontinuity of $v_s^N(\mathbf{r})$ as N passes through an integer. We further show that, for all the cases considered, the inner orbital energies and the noninteracting kinetic energy are nearly piecewise linear functions of N . This leads us to propose a simple approximation of the KS potential $v_s^N(\mathbf{r})$ at any fractional electron number N which uses only quantities of the systems with the adjacent integer electron numbers.

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THE UNIVERSAL DENSITY FUNCTIONAL AS AN EIGENVALUE OPTIMIZATION PROBLEM

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The universal density functional can be defined in two equivalent ways, either directly as a constrained minimization (ensemble Lévy–Lieb)

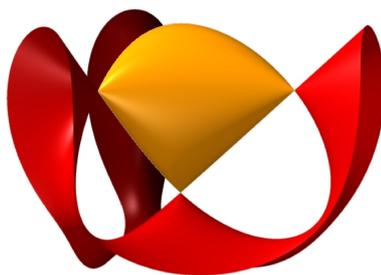
$$(1) \quad F_{\text{LL}}(\rho) = \inf_{\Gamma \in \mathcal{D}_N, \Gamma \rightarrow \rho} \text{Tr} H_0 \Gamma,$$

or as a Legendre–Fenchel transform of the energy (Lieb),

$$(2) \quad F_{\text{Lieb}}(\rho) = \sup_{v \in X^*} \inf_{\Gamma \in \mathcal{D}_N} \text{Tr}((H_0 + v)\Gamma) - (\rho, v).$$

Both formulations are amenable to approximation by discretization of the wave function and potential spaces. The Lévy–Lieb functional leads naturally to a *semidefinite programming* (SDP) problem, while the Lieb functional is an *eigenvalue optimization problem*. In the first case the objective function is linear, and the challenge lies in the constraint set and the curse of dimensionality. The Lieb functional allows approximations to the ground state energy to be used, but the optimization problem is not guaranteed to be smooth.

I will present a new black box algorithm for solution of the non-smooth Lieb maximization problem. The method combines quasi-Newton type approximate Hessians with a low dimensional bundle method for the non-smooth (degenerate) potential degrees of freedom. As a by-product we will also show how the standard Hartree term in Kohn–Sham theory implies smoothness of the Lieb problem, and how this suggests a particularly well conditioned choice of potential basis set.



The yellow set is a *spectrahedron*, a possible feasible set in Eq. 1 and a central object in semidefinite programming.

From P. Rostalski, <http://www.math.uni-frankfurt.de/~rostalsk/>.

The time-dependent potential-density mapping from a density-functional perspective

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Any study of the fundamental properties of the density-potential mapping in time-dependent density-functional theory (TDDFT) as an inverse problem must be preceded by a thorough analysis of the direct problem that is the solution of the time-dependent many-body Schrödinger equation. TDDFT specifically demands for time-dependent potentials and thus the usual $\exp(-iHt)$ evolution operator does not apply any more and more general proofs for existence and uniqueness of solutions come into play. Further conditions on the regularity of solutions, such that specific physical quantities that become important in the setting of TDDFT are well-defined, put certain limits on the space of possible potentials. Within such spaces the notion of a functional derivative with respect to potentials can be set up which yields a rigorous framework for linear response techniques.

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Invertibility of the time-dependent potential-density mapping

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We present basic conditions for the invertibility of the potential-density mapping, which is defined by the solutions of the time-dependent Schrödinger equation for a fixed initial state. We do so by investigating the local-force equation of quantum mechanics and by considering it as a non-linear equation that determines a potential for a given time-dependent density. We propose a constructive solution of this control problem by an iterative sequence. For this iterative sequence to be well-defined we find restrictions on the initial state and the temporal and spatial properties of the time-dependent densities and potentials.

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Fixed-point approach to time-dependent density-functional theory

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In this presentation we will discuss the one-to-one correspondence between densities and potentials which forms the foundation of time-dependent density-functional theory. The central idea is to restate this correspondence as a global fixed-point question for potentials on a given time interval using the local force equation. We show that the unique fixed point, i.e. the unique potential generating a given density, is reached as the limiting point of an iterative procedure. This approach avoids the usual restrictions of Taylor-expandability in time of the uniqueness theorem by Runge and Gross. We further present a numerical implementation of the method that can handle different interactions, initial states and densities. Finally we present an overview of open problems.

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Abstracts of Posters

Towards improved local hybrid functionals by calibration of exchange energy densities

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In contrast to traditional (global) hybrid functionals like B3LYP, PBE0, or TPSSh with a *constant* amount of the exact-exchange (EXX) admixture, local hybrid functionals (local hybrids) [1] are characterized by the *dependence* of the EXX admixture *on the position in real space*, governed by a so-called local mixing function (LMF). While the success of local hybrids in the simultaneous accurate prediction of various molecular properties is remarkable [2-4], their further development is hampered by fundamental ambiguities in defining the exchange energy density [5,6]: it can be modified by adding some *calibration function* (CF) which integrates to zero. The effect of the latter evidently vanishes for global hybrids (LMF=const), but can be dramatic for non-trivial LMFs, as we show in this presentation.

In contrast to a recently proposed, rather sophisticated CF involving the exact-exchange energy density itself and its spatial derivatives [6], we suggest a CF employing only the electron density and its spatial derivatives up to second order [7]. Our calibration function fulfills the seven more important out of nine known exact constraints. It is shown that calibration improves substantially the definition of a non-dynamical correlation energy term for GGA-based local hybrids. Moreover, gauge artifacts in the potential-energy curves of noble-gas dimers may be corrected by calibration. The developed calibration functions are then evaluated for a large range of energy-related properties (atomization energies, reaction barriers, ionization potentials, electron affinities, total atomic energies) of three sets of local hybrids, using a simple one-parameter local-mixing. It is shown that calibration allows a dramatic improvement of atomization energies, accompanied by only a small deterioration of reaction barriers. We expect that the present calibration approach will pave the way towards new generations of more accurate hyper-GGA functionals based on a local mixing of exchange-energy densities.

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Recipe of a transferable van der Waals density functional

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The van der Waals density functional (vdW-DF) includes the London dispersion forces required for describing inter-molecular binding fully within a density functional theory (DFT) account. Early versions of the functional helped expand the frontiers of DFT to vdW-bounded systems but has issues with describing weak chemisorption and were inferior to standard GGAs for intra-molecular binding. A recent version called vdW-DF-cx [K. Berland *et al.*, *J. Chem. Phys.* **140**, 18A539 (2014), K. Berland and P. Hyldgaard, *Phys. Rev. B* **89**, 035412 (2014)] resolves these issues within a constraint-based framework by using a consistent combination of exchange and non-local correlation. The potential of vdW-DF as a general purpose method can be traced to the fact that the non-local correlation arises as a coupling between characteristic modes of semilocal exchange-correlation holes [P. Hyldgaard *et al.*, *Phys. Rev. B* **90**, 075148 (2014)]. The good performance of vdW-DF-cx validates the robustness of the vdW-DF plasmon pole model, which can be shown to be closely linked to the exchange-correlation hole at the GGA level.

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The Linear Response Kernel from Conceptual Density Functional Theory

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Density Functional Theory (DFT) is a branch of theoretical chemistry which takes the electronic density $\rho(\mathbf{r})$ as its central ingredient rather than the many electron wavefunction. Parallel to DFT, Conceptual Density Function Theory¹ (CDFT) was developed, which tried to formalize well known chemical concepts from first principles. It does so by introducing *indices*, defined as (mixed) functional derivatives of the electronic energy $E[N, v]$ w.r.t. the number of electrons N and the external potential $v(\mathbf{r})$. Contrary to some other indices which arise, the linear response function $\chi(\mathbf{r}, \mathbf{r}')$ has received relatively little attention. Even then, most of the work that has been done on the chemical relevance of the linear response kernel (pertaining to, among others, inductive, mesomeric and hyperconjugative effects as well as (anti)aromaticity of molecules²) has focussed on its atom-condensed form χ_{AB} while less is known however about its non-condensed form. The work presented here is first systematic study of the linear response kernel $\chi(\mathbf{r}, \mathbf{r})$ for the elements Hydrogen through Argon^{3,4}. The function in question is studied using a single Slater determinant KS type ansatz and a first order perturbational approach, giving us a relatively easy expression to evaluate:

$$\chi(\mathbf{r}, \mathbf{r}') \approx 2 \sum_{i,a,\sigma} \frac{\psi_i^{\sigma,*}(\mathbf{r})\psi_a^\sigma(\mathbf{r})\psi_a^{\sigma,*}(\mathbf{r}')\psi_i^\sigma(\mathbf{r}')}{\epsilon_i - \epsilon_a}. \quad (1)$$

The results which we obtained reveal a close relation to the shell structure and polarizability of the atoms in question.

In order to further deepen the understanding of this kernel, complementary methods for calculating $\chi(\mathbf{r}, \mathbf{r}')$ are investigated as well as the related polarizability density, which relates to the linear response function through

$$\alpha_{ij}(\mathbf{r}) = \int d\mathbf{r}' r_i \chi(\mathbf{r}, \mathbf{r}') r'_j, \quad i, j = 1, 2, 3 \quad (2)$$

where r_i denotes the i^{th} component of the position vector \mathbf{r} .

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Orbital-free density functional theory implementation within the projector-augmented wave method

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The use of a higher (more accurate) level of theory for the study of molecular and solid matter at the quantum level is usually accompanied by an increase in the required computational power. Complex simulations involving many atoms thus require multi-million CPU-hour calculations on expensive supercomputers. Density functional theory (DFT), in its standard form based on the Kohn-Sham (KS) single-particle approximation, is arguably the most popular electronic structure method among both the physics and chemistry communities. KS DFT offers a description of matter which is satisfactory for many purposes, however it presents poor time scaling with system size. Due to the great success of KS DFT, other variants of DFT have not received enough attention. This is the case of orbital-free DFT (OFDFT) which, in the spirit of the original Hohenberg-Kohn theorems, obtains the system's properties from the knowledge of the electronic density alone, without single-particle orbitals. This approach offers linear time scaling and the potential to study large systems containing millions of atoms (Fig. 1).

We will introduce a new real-space implementation in the GPAW code of OFDFT in the context of the projector-augmented wave method (PAW) [1]. The PAW formalism allows access to all-electron values and improved convergence capabilities, compared to the pseudopotential scheme traditionally associated with OFDFT. In addition, GPAW is an open collaboration, offers full parallelization and access to different efficient algorithms, and therefore serves as an ideal platform for the future development of OFDFT as a community-driven project. We will present the current state of the implementation and will discuss open challenges of OFDFT such as accuracy, convergence and the improvement of orbital-free density functionals.

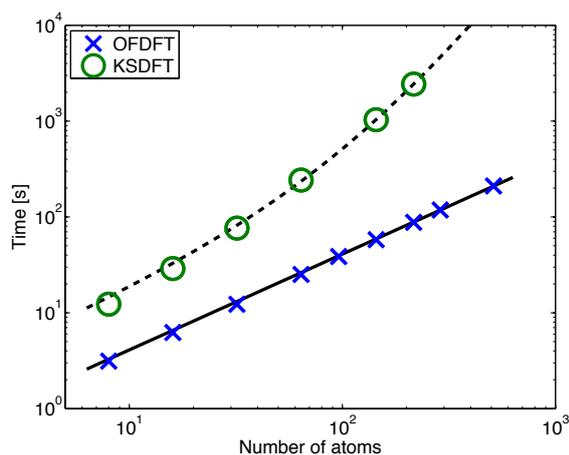


Figure 1: Time scaling comparison of the present OFDFT implementation (linear) and KS DFT.

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Local hybrid functionals with orbital-free mixing functions

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The recently introduced Density Overlap Regions Indicator (DORI) [1] is an orbital-free scalar field, that reveals regions of overlap between shells, atoms and molecules. As such, it can be also considered as an indicator of one-electron-like regions, where the density is dominated by a single orbital. The asymptotic properties of DORI at nuclei, bond critical points and infinity are the same as of the iso-orbital indicator, that is the ratio of von Weizsäcker to the exact positive-definite kinetic energy densities. The latter is often used in construction of self-interaction corrected density functionals like meta-GGAs and local hybrids.

In this contribution, we present local hybrids functionals, whose mixing functions are based on DORI [2]. We show that replacing the iso-orbital indicator with DORI leads to qualitatively similar results. Subsequently, we introduce a modest semi-empirical parametrization to fine-tune the performance of our local hybrids for standard chemical data sets. As a result, the best candidates are shown to perform uniformly better than respective global hybrids.

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Kohn-Sham DFT for Excited States: Maximum Overlap Method

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The maximum overlap method (MOM) [1, 2] allows calculation of excited states with Kohn-Sham density functional theory (DFT) [3]. This is achieved by modifying the orbital selection step in the self-consistent field (SCF) procedure: instead of using the aufbau principle, the MOM algorithm maximizes the overlap between the occupied orbitals on successive SCF iterations. This prevents variational collapse to the ground state and guides the SCF process towards the nearest, rather than the lowest energy, solution.

In this work, the MOM is explored in calculations of excited states of nitric oxide (NO) and NO-rare gas (NO-RG) van der Waals complexes. NO Rydberg and quartet valence excited states are accurately described in terms of vertical excitation energies T_e , equilibrium bond lengths r_e , and harmonic vibrational frequencies ω_e by the MOM in combination with the B3LYP and ω B97X exchange-correlation functionals. Doublet valence $\pi \rightarrow \pi^*$ excited states are not described correctly by MOM-DFT due to their multiconfigurational nature. An important property of the MOM-based calculations is that diabatic states can be determined directly. The surface crossing between the diabatic $B^2\Pi$ and $C^2\Pi$ states has been characterised and shown to be consistent with previous studies using MRCI. Description of the NO-RGs excited Rydberg A state with MOM-DFT is problematic, none of the functionals considered provides completely satisfactory results. This is likely due to an incorrect description of the non-dispersion component of the NO-RG interaction by DFT.

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Parameterization and coarse graining in density matrix theory

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We show how quantum one particle electron density matrix theory can be parameterized by a Clebsch type operator generator. We use this generator to discuss some approaches to perturbation theory and response theory. We extend our earlier derivation of hybrid fluid kinetic theory to this simpler parameterization both in the classical and quantum regime by using a Wigner-Weyl representation of the quantum electron density matrix Vlasov equation. It is demonstrated that the fluid part of the equations also can be represented as a CDFT by decomposing the stress tensor force in a divergent and rotational part. Approximate closure of these equations in terms of binary correlations and earlier DFT is attempted.

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The SCE functional in the time domain: insights into its formal properties

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Abstract

The strictly correlated electron limit (SCE) of the Hohenberg-Kohn energy functional, when employed in the DFT context, has recently shown [1] to be promising in tackling the difficult problem of strong electronic correlation. Whereas both its formal properties [2, 3] and its performance in the static case have been studied extensively, there are only a handful of studies in the time domain [4].

In this work we investigate some properties of the adiabatic SCE (ASCE) functional, ranging from the compliance to constraints of exact many-body theories, such as the generalized translational invariance [5] and the zero-force theorem, to relations peculiar to the building blocks -so called co-motion functions- of the SCE functional.

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Pilot Applications of the SCE Functional for the Description of Strong Correlation in Adiabatic TDDFT

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The strictly-correlated electrons (SCE) concept [1] allows for an alternative construction of approximate energy density functionals in Kohn-Sham density functional theory. Contrary to the non-interacting KS reference system, in the SCE reference system infinitely strongly interacting electrons are bound to give the density of the physical system. When implemented in the self-consistent solution of the spin-restricted KS equations – thus notably without spin-symmetry breaking – the SCE functional is able to capture strong-correlation physics in KS-DFT [2,3].

Pilot applications of the SCE functional for the description of strong correlation in a 1D model for stretched H₂ will be presented. In an adiabatic TDDFT framework the *spin-restricted* SCE functional correctly describes the electron hopping transition HH → H⁺H⁻ [4], which is notoriously difficult to obtain from functional approximations that can not bind the Hydrogen anion [5] and do not exhibit a derivative discontinuity [6]. Implications for the modeling of electron dynamics in long-range charge transfer [4] and charge transport [7] will be drawn.

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Exchange-Correlation Energy from a Correlation Factor Model Based Hybrid Scheme

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Recent developments of density functionals for the exchange-correlations energy focus on approximations that build on exactly computed exchange (X). Construction of such functionals without empirical parameters remains challenging and successful solutions have been elusive. To address this problem, we have recently developed¹ a correlation factor (CF) model, little explored in the literature so far. The model is based on building the exchange-correlation hole as a product of an exchange hole and a correlation factor that turns the exchange-hole into an exchange-correlation hole. We apply the Becke-Roussel model to design an X-hole reproducing the exact exchange energy per electron. Two versions of the Becke-Roussel hole are employed that differ in constraints used in the exchange hole construction. Each of the two X-holes or their linear combination is then subject to a multiplication by a correlation factor. We propose a simple five-parameter ansatz for the CF and determine all parameters of the correlation factor model exclusively through exact constraints. We argue that combining the two model exchange holes can be viewed as constructing a hybrid functional. A correlation factor model with the combined X-holes exhibits an improved performance for the atomization energies when compared to a CF model relying on one of the exchange holes only.

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The general, recursive, open-ended response code OPENRSP

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A recent open-ended formulation of response theory allows the calculation of any molecular property at the SCF level of theory in the atomic orbital basis [1]. We have created a code based on this formulation called OPENRSP, using recursive programming [2], that can calculate any molecular property analytically as long as the appropriate contributions from one-electron [3] and two-electron [4-6] integral codes and exchange/correlation [7,8] contributions are available. The implementation can also be augmented to allow for the calculation of residues of arbitrary-order response functions [9]. The properties can be calculated at Hartree-Fock and DFT levels of theory, using any rule [10] between and including the $(n + 1)$ and $(2n + 1)$ rules for determining the highest non-truncated order of (perturbed) matrices used in the calculation, in particular the density, Fock, and overlap matrices. We show some applications to vibrational spectroscopies that demonstrate the code's versatility.

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Capturing strong electron correlation with nonlocal density functionals

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Tackling strong electron correlation is a high priority for present electronic structure methods, and yet often thought out of reach of Kohn–Sham density functional theory (KS-DFT) methods. But this is not true. Recent work has uncovered an energy functional which is correct in the strongly correlated limit — the strictly correlated electron (SCE) functional. The SCE functional uses a classical picture of electrons to find their interaction energy for a given electron density. Yet there are still challenges: SCE is an extremely nonlocal functional of the density. In 3d, SCE algorithms are currently applicable only to spherically symmetric systems. Furthermore, SCE requires suitable corrections to make it useful for chemistry. We present an alternative functional which behaves similarly to the SCE functional, but which is easier to implement and may more readily accept corrections. It also includes nonlocal information about the density, via the nonlocal Wigner–Seitz radius $R(r)$, so we call it the nonlocal radius (NLR) method.

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meta-GGAs in Current-Density-Functional Theory

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We explore the use of meta-GGA functionals in current-density-functional theory [1, 2] using a fully-self consistent implementation in the LONDON program [3, 4]. For meta-GGAs current effects may be introduced by a simple modification of the kinetic energy density to restore gauge-invariance of the exchange–correlation energy, as suggested by Becke and Dobson [5, 6]. In the weak field regime modified B98 and TPSS functionals show modest improvements in the calculation of magnetizabilities and NMR shielding constants compared with standard GGAs. However, as shown in Figure 1, in the strong field regime these functionals show significant promise being numerically stable and capturing the essential physics of the recently predicted perpendicular paramagnetic bonding mechanism [7].

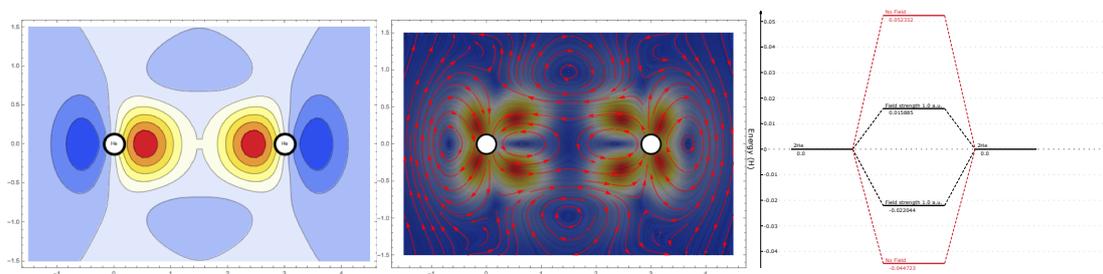


Figure 1: The density change $\Delta\rho = \rho_{\text{He}_2} - 2\rho_{\text{He}}$ (left panel), physical current change $\Delta\mathbf{j} = \mathbf{j}_{\text{He}_2} - 2\mathbf{j}_{\text{He}}$ (central panel) and orbital energy changes (right panel) due to perpendicular paramagnetic bonding in a strong magnetic field as described by a modified TPSS functional.

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