

TIME DEPENDENT DENSITY FUNCTIONAL THEORY: PROSPECTS AND APPLICATIONS

International Workshop and School

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School Program

time	29/8	30/8	31/8	1/9	2/9	3/9	4/9	5/9	6/9	7/9
10-11.30	DFT1	NUM	PP	free	PROP1+DP	APP1	free	APP2	BIO1	ALT1
12-13.30	VXC	TDDFT1	TDDFT2	free	TDDFT3	PROP2	free	RT	BIO2	ALT2
Lunch										
15.30-17	OCT1	OCT3	QD2	free	OCT4	PW1	free	PW3	QD5	ALT2
17.30-19	OCT2	QD1	QD3	free	QD4	PW2	free	PW4	PROJ	free
21h				School Dinner						

Theoretical Sessions

DFT1	U. von Barth	An Introduction to DFT
VXC	U. von Barth	XC functionals
NUM	X. Gonze	Numerical methods: plane waves real space methods, etc.
TDDFT	E.K.U. Gross	Time dependent density functional theory
PP	X. Gonze	Pseudopotentials
PROP	A. Castro	Propagation schemes (1h45 + 45m)
APP	A. Rubio	Applications of TDDFT for finite and infinite systems
DP	V. Olevano	Implementation of TDDFT for solids (45 m.)
RT		Round table - the past and future of TDDFT
BIO	X. López	Biological systems
ALT1	L. Reining	TDDFT vs BSE
ALT2	G. Vignale	TDDFT vs CDFT

Practical Sessions

OCT	F. Nogueira	Finite systems using octopus
QD	A. Castro	Development of a TDDFT program for quantum dots
PW	S. Botti, X. Gonze	Periodic systems with ABINIT+DP
PROJ		Project

Propagators for the time-dependent Kohn-Sham equations

Alberto Castro

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In this lesson we address the problem of the numerical integration of the time-dependent Schrödinger equation $i\partial_t\varphi = \hat{H}\varphi$. In particular, we are concerned with the important case where \hat{H} is the selfconsistent Kohn-Sham Hamiltonian that stems from time-dependent functional theory. As the Kohn-Sham potential depends parametrically on the time-dependent density, \hat{H} is in general time-dependent, even in the absence of an external time-dependent field. The present analysis also holds for the description of the excited state dynamics of a many-electron system under the influence of arbitrary external time-dependent electromagnetic fields. Our discussion is separated in two parts: i) First, we look at several algorithms to approximate $\exp(\hat{A})$, where \hat{A} is a *time-independent* operator [e.g. $\hat{A} = -i\Delta t\hat{H}(\tau)$ for some given time τ]. In particular, polynomial expansions, projection in Krylov subspaces, and split-operator methods are investigated. ii) We then discuss different approximations for the time-evolution operator, like the mid-point and implicit rules, and Magnus expansions. Split-operator techniques can also be modified to approximate the full time-dependent propagator. As the Hamiltonian is time-dependent, problem ii) is not equivalent to i). All these techniques have been implemented and tested in our computer code `octopus`, but can be of general use in other frameworks and implementations.

Numerical methods (I and II)

Xavier Gonze

Louvain la Neuve

We take as starting point the equations of Density-Functional Theory and examine the basic ideas leading to actual computer programs.

In this respect, one encounters two kinds of high-level problems : (1) mathematical quantities (like the electronic density or wavefunctions) must be represented by finite sets of numbers ; (2) mathematical equations must be solved. Supposing a representation, with some inevitable numerical inaccuracies, algorithms for solving equations will lead to computer predictions, also with a finite numerical precision. In both cases, the size of the numerical errors must be weighted against the inherent error present in any approximation to the "true" DFT. They can be reduced, at the expense of more memory space or more CPU time. In order to use properly the different computer programs, the user must be aware of this trade-off.

First, we will focus on the algorithms needed to find the optimized geometry for molecules, clusters or solids, including the resolution of the Kohn-Sham equations (in order for the electrons to be in their ground state). The similarities between geometry optimization, Kohn-Sham self-consistency, and iterative resolution of the Kohn-Sham (or Schroedinger) equation will be highlighted. Basic iterative methods will be described, as well as more advanced methods like conjugate gradients, Broyden, and damped dynamics algorithms.

Then, we examine the concept of pseudopotential, a crucial ingredient for several representation methodologies. Pseudopotentials allow to avoid treating explicitly core electrons. They introduce quite small errors, compared to the inherent (in)accuracy of present day exchange-correlation functionals. The freezing of the core electrons will be distinguished from the actual pseudopotential construction. The historical Kleinman approach will be described, followed by the discussion of more recent norm-conserving pseudopotentials, and a brief introduction to ultrasoft pseudopotentials, and projector augmentation.

We will then focus on a particular representation, based on planewaves, well-adapted to the case of crystalline solids : Bloch theorem, set of planewave coefficients in reciprocal space, Brillouin zone, computation of the density from wavefunctions, computation of the electrostatic and exchange-correlation potential, treatment of metals.

Finally, we present the ABINIT software : availability, structure, features, and present status of development.

Chromophores in biological environments

Xabier López

Kimika Fakultatea; Euskal Herriko Unibertsitatea

An introduction of chromophores in biological environments will be given. Biochromophores that absorb in the visible light mainly consist of prosthetic groups or cofactors covalently bound to proteins. In this lecture, we will see some basic examples of these prosthetic organic molecules and how the absorption of light is coupled with their complex biological functions. In addition, and since the optical response of these prosthetic groups is often modulated by their protein environment, an introduction to protein structure and its modelization will be given. Finally, we discuss some illustrative examples of chromophores embedded in proteins and how their optical absorption is a consequence of both chromophore chemical nature and interaction (structural and electrostatic) with its protein surroundings.

How to describe exchange and correlation effects in the response properties of valence electrons? Answers from TDDFT and Many-Body Perturbation Theory

Lucia Reining

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Today, one of the big challenges of theoretical condensed matter physics is to find ways for describing accurately and efficiently the response of electrons to an external perturbation. In fact, the knowledge of response functions allows one to directly derive spectra (such as absorption or electron energy loss); moreover, response functions enter the description of correlation effects, for example through the screened Coulomb interaction W in Hedin's GW approximation to the electron self-energy. Two main developments for the *ab initio* calculation of response functions of both finite and infinite systems are, on one side, the solution of the Bethe-Salpeter equation (BSE), and, on the other hand, Time-Dependent Density Functional Theory (TDDFT). Both approaches are promising, but suffer from different shortcomings: the solution of the Bethe-Salpeter equation is numerically very demanding, whereas for TDDFT, despite recent progress a generally reliable but at the same time very efficient description of exchange-correlation effects has still to be developed. Therefore, one would ideally like to combine the advantages of both pictures.

In this lesson, we will show that both approaches can be interpreted as containing the same physics, but in a different world. We focus on their comparison by putting them on the same footing. The meaning and importance of different contributions to the induced potentials will be analyzed. The similarities will allow us to propose combinations of TDDFT and the BSE approach that are leading to a class of exchange-correlation kernels which yield excellent spectra and are potentially very efficient in numerical calculations.

Applications of TDDFT: optical absorption and electron energy loss spectroscopy of nanostructures and extended systems

Angel Rubio

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In this set of lectures we will present a comparison between TDDFT and other approaches for the description of the response properties of many electron systems [1]. We will provide a short review of the computational issues related to the practical implementation of TDDFT for finite and extended systems (within the octopus project [2]). This general scheme allows to treat on the same footing arbitrary external electromagnetic fields. As application we will show results for the optical absorption and photoinduced fragmentation of small clusters as well as the photoresponse of biomolecules (Green-Fluorescent protein and azobenzene) [3]. At the end we will discuss some of the deficiencies of the standard DFT-based approaches to cope with the response function of extended systems (one, two and three-dimensional) [1]. The problem is traced back to the lack of long-range interaction in the exchange-correlation kernel. We will show how this can be incorporated in TDDFT by deriving a formally exact exchange-correlation kernel based on many-body-perturbation theory [4] in connection with Lucia Reining lectures. Also we will present an alternative, nonperturbative way to treat the electric response of extended systems by a time-propagation scheme in the same spirit done for nanostructures[2].

Work done in collaboration with M.A.L. Marques, A. Castro, X. Lopez, E.K.U. Gross, D. Varsano, G. Bertsch, L. Reining, A. Marini, R. Del Sole and G. Onida. We acknowledge support from the European Community Research Training Network NANOPHASE (HPRN-CT-2000-00167), Network of Excellence NANOQUANTA (NOE 500198-2), Spanish MCyT (MAT2001-0946) and the University of the Basque Country (9/UPV 00206.215-13639/2001). The computer time was granted by DIPC and CEPBA (Barcelona).

[1] G. Onida, L. Reining and A. Rubio, *Rev. Mod. Phys.* **74**, 601 (2002).

[2] M. A. L. Marques, A. Castro, G. F. Bertsch and A. Rubio, *Computer Phys. Commun.* **151**, 60 (2003). The code OCTOPUS is available at <http://www.tddft.org/programs/octopus>. A. Castro, M.A.L. Marques, J.A. Alonso and A. Rubio *Journal of Computational and Theoretical Nanoscience* (in press 2004)

[3] M.A.L Marques, X. López, D. Varsano, A. Castro, and A. Rubio, *Phys. Rev. Lett.* **90**, 258101 (2003); and work to be published for azobenzene and DNA basis.

[4] A. Marini, R. Del Sole, and A. Rubio, *Phys. Rev. Lett.* **91**, 256402 (2003); F. Sottile, V. Olevano and L. Reining, *Phys. Rev. Lett.* **91**, 056402 (2003); L. Reining, V. Olevano, A. Rubio, and G. Onida, *Phys. Rev. Lett.* **88**, 066404 (2002); R.D. Sole, G. Adragna, V. Olevano and L. Reining, *Phys. Rev. B* **67**, 045207 (2003).

Lectures on TDDFT vs CDFT

G. Vignale

Univ. Missouri, USA

1. THE ELASTICITY OF THE ELECTRON LIQUID

In this lecture I review the two classical macroscopic theories of collective dynamics, hydrodynamics and elasticity, and I show that the usual description of the macroscopic dynamics of an electron liquid in terms of exchange-correlation fields can be viewed as a combination of these two theories, where the frequency-dependent visco-elastic coefficients are determined by the quantum excitation spectrum. Exact results and approximate expressions for the visco-elastic coefficients are presented.

2. TIME-DEPENDENT CURRENT DENSITY FUNCTIONAL THEORY

Here I show how the results obtained for the homogeneous electron liquid can be used to construct a local approximation for the exchange-correlation potential for non-homogeneous electronic systems. Such a construction must be done within the framework of the current-density functional theory (CDFT), in which the basic variable is the current density, and the exchange-correlation effects are described in terms of a vector potential. The explicit form of the exchange correlation potential beyond the adiabatic local density approximation is then discussed.

Workshop

Day I: Wednesday 8th

09h00 - 09h10	Angel Rubio	Opening remarks
09h10 - 10h00	Robert van Leeuwen	An overview of basic concepts in TDDFT and some new extensions
10h00 - 10h50	Ilya Tokatly	Quantum many-body dynamics in Lagrangian frame: Geometric formulation of TDDFT
10h50 - 11h20		Caffeine break
11h20 - 12h10	Neepa Maitra	Aspects of non-adiabaticity in TDDFT
12h10 - 13h00	Shaul Mukamel	Spontaneous Density Fluctuations, Intermolecular Forces and Nonlinear TDDFT Response; Superoperator Approach
13h00 - 15h00		Lunch break
15h00 - 15h50	Juerg Hutter	Plane-wave TDDFT calculations of molecules in solution
15h50 - 16h40	Michiel Sprik	Car-Parrinello TDDFT computation of electronic spectra of some transition metal aqua ions in solution
16h40 - 17h10		Beer break
17h10 - 18h00	Yoshiyuki Miyamoto	Excited State Molecular Dynamics with use of the code FPSEID: First Principles Simulation tool for Electron Ion Dynamics
18h00 - 19h00		Poster Session

Day II: Thursday 9th

09h10 - 10h00	Giovanni Vignale	Advances in time-dependent spin density functional theory
10h00 - 10h50	Roi Baer	Time dependent density functional theory: new functionals and applications
10h50 - 11h20		Caffeine break
11h20 - 12h10	Tuomas Torsti	Real-space multigrid methods for DFT and TDDFT
12h10 - 13h00	M. Marques	Octopus: present, past, and future
13h00 - 15h00		Lunch break
15h00 - 15h50	Raffaele Resta	Localization and polarization in the insulating state of matter
15h50 - 16h40	I. Tavernelli	Excited state ab initio MD of photochemical processes in model compounds
16h40 - 17h10		Beer break
17h10 - 18h00	Giacomo Mulas	Using ab initio tools to solve the astrophysical puzzle of interstellar PAHs

Day III: Friday 10th

09h10 - 10h00	Kieron Burke	Rigorous DFT treatment of transport through single molecules
10h00 - 10h50	Roberto Car	Electron transport and dissipation in nanoscale devices
10h50 - 11h20		Caffeine break
11h20 - 12h10	Carl-Olof Almbladh	Time-dependent quantum transport by means of TDDFT
12h10 - 13h00	Rex Godby	Self-Energy Approaches for Excited and Ground States: Lessons for and from DFT
13h00 - 15h00		Lunch break
15h00 - 15h50	Martin Fuchs	Use of the the adiabatic-connection fluctuation-dissipation approach to exchange-correlation in the ground state
15h50 - 16h40	P. Garcia Gonzalez	TD-DFT as an useful tool to calcute accurate correlation energies
16h40 - 17h10		Beer break
17h10 - 18h00		Presentations from the best posters.

Day IV: Saturday 11th

09h10 - 10h00	Andreas Goerling	Exact-exchange TDDFT methods for molecules and solids
10h00 - 10h50	P. de Boeij	The time-dependent current-functional approach for the response of solids and polymers
10h50 - 11h20		Caffeine break
11h20 - 12h10	Lucia Reining	TDDFT and Many-Body Perturbation Theory: comparisons and combinations
12h10 - 15h00		Lunch break
15h00 - 17h30		Discussions
17h30 - 17h45	E.K.U. Gross	Closing remarks

Time-dependent quantum transport by means of TDDFT

Gianluca Stefanucci and Carl-Olof Almbladh

Department of Theoretical Physics, University of Lund, Lund, Sweden

An exact theoretical framework based on Time Dependent Density Functional Theory (TDDFT) is proposed in order to deal with the time-dependent quantum transport in fully interacting systems. We use a partition-free approach by Cini in which the whole system is in equilibrium before an external electric field is switched on. Our theory includes the interactions between the leads and between the leads and the device. It is well suited for calculating measurable transient phenomena as well as a.c. and other time-dependent responses and is valid for finite as well as macroscopic electrodes. We show that the steady-state current results from a *dephasing mechanism* provided the leads are macroscopic and the device is finite. In the d.c. case, we obtain a Landauer-like formula when the effective potential of TDDFT is uniform deep inside the electrodes.

The time-dependent current-functional approach for the response of solids and polymers'

Paul L. de Boeij

Groningen, The Netherlands

The first-principles description of the response of crystalline systems to external fields relies heavily on the use of periodic boundary conditions. This treatment has important implications for the time-dependent density functional framework. I will show how intrinsic, i.e. material properties can be obtained and how extrinsic, i.e. size and shape dependent effects can effectively be removed from the computational scheme. The result of this analysis is that a uniform component of the current-density appears as an extra degree of freedom, which is not uniquely fixed by the lattice periodic density. A natural way to treat the periodic systems is now obtained by changing the basic dynamical variable from the time-dependent density to the induced current-density. Observable quantities, like for instance the induced macroscopic polarization can then be given in closed form as current functionals. The response to both longitudinal and transverse fields can be treated in this unified approach. I will give the linear response and excitation formulation for the resulting time-dependent Kohn-Sham system, and show how (non)-adiabatic density and current-density dependent exchange-correlation functionals are included. The approach is equally well suitable to treat finite systems as infinite metallic or insulating systems. I apply the time-dependent current-density functional approach to the response properties of periodic systems and finite systems. The periodic structures include several (semi)metallic and semiconducting crystals and polymers. The finite systems cover several pi-conjugated and non-conjugated oligomers and small molecules. In these systems some failures of the ALDA are discussed and results are presented for the current-density dependent exchange-correlation functional derived by Vignale and Kohn. The influence of this functional on the linear response and excitation energies is discussed. For the oligomer polarizabilities the asymptotic relation to the polymer susceptibilities is discussed.

Rigorous DFT treatment of transport through single molecules

Kieron Burke

Dept of Chemistry and Chemical Biology, Rutgers University

Transport through single molecules has become a hot topic since the first experiments several years ago. But it is unclear if the present methodology (Landauer formalism plus ground-state DFT) is the correct approach for calculating conductance in these devices. I'll discuss the problems, and show some recent results in the weak bias limit, derived using TDDFT. I'll also discuss a new methodology for handling dissipation in electronic systems using a Kohn-Sham master equation.

Electron transport and dissipation in nanoscale devices

Roberto Car

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We present a quantum-kinetic scheme for the calculation of non-equilibrium transport properties in nanoscale systems. Our approach is based on a time-dependent Kohn-Sham master equation for the reduced electronic density operator and represents a generalization of the well-known Boltzmann kinetic equation. The approach allows us, in particular, to model transport situations under high applied fields by adopting periodic boundary conditions. Applications to nanoscale devices and molecular structures are discussed

The time-dependent current-functional approach for the response of solids and polymers

Paul L. de Boeij

Groningen, The Netherlands

The first-principles description of the response of crystalline systems to external fields relies heavily on the use of periodic boundary conditions. This treatment has important implications for the time-dependent density functional framework. I will show how intrinsic, i.e. material properties can be obtained and how extrinsic, i.e. size and shape dependent effects can effectively be removed from the computational scheme. The result of this analysis is that a uniform component of the current-density appears as an extra degree of freedom, which is not uniquely fixed by the lattice periodic density. A natural way to treat the periodic systems is now obtained by changing the basic dynamical variable from the time-dependent density to the induced current-density. Observable quantities, like for instance the induced macroscopic polarization can then be given in closed form as current functionals. The response to both longitudinal and transverse fields can be treated in this unified approach. I will give the linear response and excitation formulation for the resulting time-dependent Kohn-Sham system, and show how (non)-adiabatic density and current-density dependent exchange-correlation functionals are included. The approach is equally well suitable to treat finite systems as infinite metallic or insulating systems. I apply the time-dependent current-density functional approach to the response properties of periodic systems and finite systems. The periodic structures include several (semi)metallic and semiconducting crystals and polymers. The finite systems cover several pi-conjugated and non-conjugated oligomers and small molecules. In these systems some failures of the ALDA are discussed and results are presented for the current-density dependent exchange-correlation functional derived by Vignale and Kohn. The influence of this functional on the linear response and excitation energies is discussed. For the oligomer polarizabilities the asymptotic relation to the polymer susceptibilities is discussed.

Use of the adiabatic-connection fluctuation-dissipation approach to exchange-correlation in the ground state

Martin Fuchs

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The adiabatic-connection fluctuation-dissipation theorem (ACFDT) provides an exact formula for the exchange-correlation (XC) energy in terms of the dynamical linear density-density response function, a quantity given by time-dependent density-functional theory. Approximate “ACFDT” XC functionals may be generated from suitable response functions, opening the way for improvements beyond present functionals such as the LDA, GGA, or hybrids: (i) proper treatment of van der Waals interactions, and (ii) systematically higher accuracy for the bond energetics of molecules and solids.

Here we consider ACFDT XC functionals based on the random phase approximation (RPA) alone and the RPA augmented by an (approximate) exchange kernel (RPA+X), which we have recently implemented in a pseudopotential plane-wave framework [1,2]. Calculating the groundstate potential energy curves for H_2 and Be_2 , we find that the RPA gives excellent results for the binding energy, equilibrium bond length and fundamental vibrational frequency. Considering stretched H_2 , we show that the RPA largely overcomes the long-standing symmetry dilemma of DFT: the molecule dissociates properly into two atoms without taking recourse to artificial symmetry breaking as in the usually applied spin-unrestricted Kohn-Sham schemes. The RPA thus captures the strong static (left-right) correlations when the bond breaks, as is apparent from the corresponding adiabatic connection curves. At intermediate bond lengths, the RPA as well as the RPA+X potential energy curves remain too repulsive however. We discuss implications of this finding on the construction TD-DFT XC kernels for ACFDT XC functionals beyond the RPA.

[1] M. Fuchs and X. Gonze, Phys. Rev. B 65, 235109 (2002); M. Fuchs, K. Burke, Y.-M. Niquet, and X. Gonze, Phys. Rev. Lett. 90, 189701 (2003).

[2] X. Gonze et al., Comput. Materials Science 24, 478 (2002).

work performed with Yann-Michel Niquet (SP2M/L_Sim, CEA Grenoble, France), Kieron Burke (Dept. of Chemistry and Chemical Biology, Rutgers Univ., U.S.), and Xavier Gonze (Unite PCPM, Univ. Catholique de Louvain, Belgium).

Exact-exchange TDDFT methods for molecules and solids

Andreas Goerling

Bonn University

The Kohn-Sham formalism is reconsidered in order to introduce the concept of orbital-dependent functionals for exchange-correlation energies, potentials, and kernels. Adiabatic connection perturbation theory for a systematic construction of functionals in the static as well as in the time-dependent case is discussed. Response properties (excitation energies, NMR chemical shifts) of molecules based on effective exact-exchange KS orbitals and eigenvalues are presented. An exact-exchange TDDFT approach for solids is presented and compared to methods based on the Bethe-Salpeter equation.

TD-DFT as an useful tool to calcute accurate correlation energies

P. Garcia-Gonzalez (1), J. Jung (1), A. Marini (2), J. Dobson (3), R.W. Godby (4), and A. Rubio (2)

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(2) Donostia International Physics Center, Apartado 1072, E-20018 San Sebastian, Spain

(3) School of Science, Griffith University, Nathan, Queensland 4111, Australia

(4) Department of Physics, University of York, Heslington, York YO10 5DD, United Kingdom

The adiabatic-connection fluctuation-dissipation theorem (ACFDT) in the framework of Time Dependent Density Functional Theory (TD-DFT) has emerged as a promising alterative to standard implementations of Kohn-Sham (KS) theory to calculate correlation energies. In this approach, the correlation energy is calculated from the knowledge of the interacting density response, without resorting to mean-field-like approximations. Thus, using the ACFDT scheme we can easily describe many-body effects that are absent in the KS-LDA or KS-GGA without the numerical expense of diffusion quantum Monte Carlo calculations.

If we neglect local-field corrections in the construction of the density response, it is well known that the absolute correlation energies so obtained are not accurate at all. Nonetheless, it is believed that even at this RPA level, the "binding" correlation energies are very accurate. To confirm this trend, we have calculated the RPA energies of model jellium-like systems as well as the structural properties of simple solids (Si, NaCl), where the KS-LDA performs quite well. As expected, there are minor differences between the KS-LDA and the RPA results. However, in model layered systems, where layer-layer interactions are very weak, there are evident discrepancies between the KS and the TD-DFT binding energies. This is due to the presence of long-ranged correlations that cannot be described at all by mean-field approximations.

In the ACFDT framework, local-field corrections mainly account for short-ranged electron-electron correlations. They can be built in either through LDA/GGA functionals or by including non-local XC kernels in the evaluation of the density response. Since we are interested on correlation energies, both corrections are constructed by imposing the reproduction of the exact homogeneous electron gas energies. We will see that these procedures are very robust, since the corrected correlation energies are rather insensitive to the details of the method used to implement the local-field corrections. The comparison with the corresponding RPA energies suggests that the RPA slightly overcorrects the KS-LDA results.

Self-Energy Approaches for Excited and Ground States: Lessons for and from DFT

Rex Godby

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Density-functional theory was originally a theory for the ground-state total energy which more recently, through TDDFT, has been applied to calculations of certain excited-state properties. On the other hand, self-energy approaches (within the framework of many-body perturbation theory) are theories of the one-electron Green's function which is most directly related to spectral properties such as quasiparticle energies and lifetimes for added electrons or holes, but can also be applied to the calculation of ground-state properties such as the total energy.

In situations where both methods are applicable, each has advantages and disadvantages. (TD)DFT is typically inexpensive, but in systems where electronic exchange and correlation has more than a peripheral role, the uncontrolled (and sometimes quite pathological) errors in the usual density-based exchange-correlation functionals (such as the LDA and GGA) limit its applicability. *Ab initio* many-body perturbation theory provides, in principle, a convergable series of successive approximations to the exact answer, but the numerical complexity in practice restricts its application to relatively low-order approximations such as the *GW* approximation, which is the first-order term in an expansion of the self-energy operator Σ in powers of the dynamically screened electron-electron interaction, W . It may be thought of as exact exchange (the Hartree-Fock exchange operator), together with an partial inclusion of correlation diagrams through dynamical screening of the Coulomb interaction. From Σ , the one-electron Green's function G may be calculated, from which various spectral and ground-state properties are available. For transport properties (as well as certain other excited-state properties), the two-electron Green's function is required, which may also be formulated at the same level of approximation as *GW*.

By way of introduction to *GW*, I shall give a brief review of key applications to spectral properties such as quasiparticle energies and lifetimes for added electrons or holes.

In applying *GW* to the ground-state total energy, the choice of whether G and/or W are made to be consistent with the Green's function that arises *from* Σ is particularly important: G_0W_0 , GW_0 and fully self-consistent *GW*, where G_0 generally indicates the LDA Green's function. I shall present results for finite and infinite systems at all three levels of self-consistency. These include converged results resulting from the incorporation of self-consistency and *GW* total-energy techniques into our general-purpose GWST "space-time" supercell code suite [1], which interfaces with pseudopotential plane-wave DFT calculations as its input. This allows the extension of the *GW* total-energy approach from high-symmetry test systems [2] to general systems, and opens the possibility of applications to systems whose energetics is not described sufficiently reliably within the usual DFT-based approaches.

I shall also describe our recent formulation [3] of the conductance of a junction between two nanowires in a form which permits the inclusion of electronic correlation effects in a *GW*-like framework.

[1] "Space-time method for *ab initio* calculations of self-energies and dielectric response functions of solids", H. N. Rojas, R. W. Godby and R. J. Needs, Phys. Rev. Lett. **74** 1827 (1995)

[2] "Many-body *GW* calculations of ground-state properties: quasi-2D electron systems and van der Waals forces", P. García-González and R. W. Godby, Phys. Rev. Lett. **88** 056406 (2002)

[3] “Conductance and polarization in quantum junctions”, P. Bokes and R.W. Godby, Phys. Rev. B **69** 245420 (2004)

Further details at <http://www-users.york.ac.uk/~rwg3/>.

Plane-wave TDDFT calculations of molecules in solution

Juerg Hutter

Physical Chemistry Institute, University of Zurich

A formulation of time dependent linear response density functional theory within the plane-wave pseudopotential framework has recently been introduced [J. Hutter, J. Chem. Phys., 118, 3928 (2003)]. This implementation allows for efficient calculations of excitation spectra, excited state properties and coupling to classical force fields in QM/MM approaches. The scheme has been applied in combination with Car-Parrinello molecular dynamics to study the solvent shift and intensity enhancement effects of the first electronic transition in acetone-water systems [L. Bernasconi et al., J. Chem. Phys., 119, 12417 (2003)]. In agreement with experiment a general increase in the mean oscillator strength and a blue shift of 0.19 eV of the transition was found. However, this analysis was severely hampered by shortcomings of traditional density functionals. Both, the poor eigenvalues of occupied and virtual Kohn-Sham orbitals and the lack of a correct representation of charge transfer (CT) in the response kernel result in many unphysical solute-solvent and solute-solute CT states overlapping with the acetone $n \rightarrow \pi^*$ transition. These problems are partially solved using hybrid functional, although only with drastically increased computational costs [L. Bernasconi et al., Chem. Phys. Lett., 394, 141 (2004)]. Another approach combines standard DFT calculations with TDDFT using the statistical average of orbital model exchange-correlation potentials. The improved representation of orbital energies helps to isolate low-lying local transitions and is a first step towards an accurate description of CT states.

Aspects of non-adiabaticity in TDDFT

Neepa Maitra

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Memory is a feature of time-dependent density functionals that is well-known to exist but little understood. Indeed, the vast majority of TDDFT calculations utilise adiabatic approximations, where memory is entirely neglected. In this talk, I review some formal aspects of memory in TDDFT, and point out its significance in quantum control problems. I shall discuss some applications in linear response where non-adiabaticity plays a prominent role; these include the description of states of significant double excitation character and long-range charge transfer states.

Octopus: present, past, and future

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We present a computer package aimed at the simulation of the electron-ion dynamics of finite systems, both in one and three dimensions, under the influence of time-dependent electromagnetic fields. The electronic degrees of freedom are treated quantum mechanically within the time-dependent Kohn-Sham formalism, while the ions are handled classically. All quantities are expanded in a regular mesh in real space, and the simulations are performed in real time. Although not optimized for that purpose, the program is also able to obtain static properties like ground-state geometries, or static polarizabilities. The method employed proved quite reliable and general, and has been successfully used to calculate linear and non-linear absorption spectra, harmonic spectra, laser induced fragmentation, etc. of a variety of systems, from small clusters to medium sized quantum dots.

*Excited State Molecular Dynamics with use of the code FPSEID: First Principles Simulation tool for Electron Ion Dynamics

Yoshiyuki Miyamoto* and Osamu Sugino†

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Institute for Solid State Physics, University of Tokyo

In this talk, I will give molecular dynamics (MD) simulations on the adiabatic potential energy surfaces of electronic excited states. In these MD simulations, adiabatic approximation for the exchange-correlation potential is adopted, and the excitation is simply mimicked by manually promoted electronic occupations. Even with this simplified approximation, the time-dependent treatment for the Kohn-Sham equation is necessary to follow the right potential energy surface. Numerical stability for simulation-time beyond hundreds femtoseconds and difficulty in treating non-adiabatic (nonradiative) decay of excitation will be discussed. The applications are MD simulations on photo-excited carbon nanotubes, which will be related to nanotube engineering.

This work has been done in collaborations with Profs. Angel Rubio and David Tománek. Part of present works were supported by the Earth Simulator Center and by NAREGI Nanoscience Project, Ministry of Education, Culture, Sports, Science and Technology, Japan.

Spontaneous Density Fluctuations, Intermolecular Forces and Nonlinear TDDFT Response; Superoperator Approach

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Dispersive long-range forces are ubiquitous in nature and have been the subject of intense experimental and theoretical attention [1-3]. van der Waals (vdW), non-bonded interactions between neutral, polarizable molecules that play an important role in many chemical and biological dynamical processes. vdW forces may be computed using the nonlocal linear polarizabilities or charge response functions of the individual molecules [4]. By formulating quantum dynamics in terms of superoperators in Liouville space [3] intermolecular forces may be expressed to all orders in terms of both the charge density response and the spontaneous charge fluctuations of individual molecules. The building blocks of the p 'th order response are $2p$, $(p + 1)$ - point correlation functions of the charge density which differ by permutations of their time arguments. Each correlation function represents a Liouville Space pathway for the density matrix [5]. A complete description of intermolecular forces requires a set of $p+1$ combinations of these pathways denoted generalized response functions (GRF) [6]. The p 'th order polarizability is only one member of that family. Using a superoperator formulation of TDDFT [7,8,9], we calculate the GRFs of individual molecule which, in turn, are evaluated using the collective electronic oscillator (CEO) eigenmodes of the linearized TDDFT. These GRFs are used to compute the intermolecular energy in terms of CEO modes [10]. The "causality" paradox [11] of the TDDFT response is naturally resolved by the non-retarded superoperator formalism. In Liouville space all physical observables can be expressed in terms of positively ordered products of superoperators avoiding the negative time ordering required for ordinary operators in Hilbert space (the Keldysh loop). Non-equilibrium Greens functions may thus be evaluated in real (physical) time.

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Using ab initio tools to solve the astrophysical puzzle of interstellar PAHs

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The presence of a large amount of gas-phase Polycyclic Aromatic Hydrocarbons (PAHs) in the InterStellar Medium (ISM) of our galaxy was suggested about twenty years ago (Léger & Puget, 1984; Allamandola et al., 1985), to account for the ubiquitous infrared emission bands near 3.3, 6.2, 7.7, 8.6, 11.3 and 12.7 micrometers seen wherever dusty environments are excited by UV photons. In the last two decades this "PAH hypothesis" was the subject of intensive study, and these molecules and their derivatives were speculated to also give rise to other unidentified interstellar spectral features: the Diffuse Interstellar Bands (a set of 300 absorption features throughout the visible) and the far-UV rise of the interstellar extinction curve, just to name two of the most outstanding puzzles in the spectroscopy of the interstellar medium. Nonetheless, no single PAH has been identified to date in astronomical spectra.

Since a large scale, systematic experimental study of the whole family of PAHs and derivatives in conditions comparable to those in the ISM would be a hopelessly demanding task, we are using (TD)DFT techniques, together with a Monte Carlo model of the photophysics of interstellar PAHs, to prepare an atlas of their computed interstellar spectra, for direct comparison with astronomical data and as a guide for targeted experimental measures on specific molecules, which would say the final word. We here present some preliminary results of this ongoing effort.

Localization and polarization in the insulating state of matter

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At variance with what happens in metals, the electronic charge in insulators cannot flow freely under an applied dc field, and undergoes instead static polarization. Both these features owe to the different nature of the excitation spectrum, but also to a different organization of the electrons in their ground state: electrons are localized in insulators and delocalized in metals. Such localization feature, however, is hidden in a rather subtle way into the many-body wavefunction. There have been recent advances in the theory of the insulating state, which in turn are deeply rooted into the modern theory of polarization, based on a Berry phase. Localization and polarization can be regarded as two aspects of the same phenomenon, and stem from essentially the same formalism.

The theory is very general, and applies on the same footing to either correlated wavefunctions or independent electrons, and to either disordered or crystalline systems. Its implications for a Kohn-Sham crystal can be stated as follows. In insulators, a set of well localized orbitals (the Wannier functions) spans the same Hilbert space as do the Bloch orbitals of the occupied bands. The first moment (dipole) of these orbitals defines macroscopic polarization, while their spherical second moment (spread) can be made finite. In metals macroscopic polarization is ill-defined, while it is impossible to span the Hilbert space of the occupied Bloch states using localized orbitals whose spread is finite.

Car-Parrinello TDDFT computation of electronic spectra of some transition metal aqua ions in solution

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Transition metal complexes show a variety of electronic excitations often observable as absorption of light in the visible range. These transitions can be broadly divided into $d \rightarrow d$ excitations (largely metal \rightarrow metal), charge transfers between ligands and metal and $d \rightarrow s$ transitions. Using the time dependent density functional response theory method as implemented in the CPMD code[1,2], we have studied the electronic absorption spectrum of $\text{Ru}^{2+}(\text{H}_2\text{O})_6$, as an example of $d \rightarrow d$ transitions and Ag^+ and Cu^+ as examples of $d \rightarrow s$ transitions. The result of the finite temperature $t_{2g}^6 \rightarrow t_{2g}^5 e_g^1$ (visible) absorption spectrum of $\text{Ru}^{2+}(\text{H}_2\text{O})_6$ at the BLYP level of theory was found in good agreement with experiment including the splitting between the ${}^1T_{2g}$ and ${}^1T_{1g}$ terms due to electronic repulsion. Apart from minor changes in intensities we found little difference between the vacuum spectrum of the hexahydrate and the spectrum in bulk aqueous solution. The computed UV spectrum of Ag^+ , while red shifted w.r.t to experiment by 2 eV, shows a line shape in fair agreement with experiment. Our calculations suggest that the observed three peak structure is consistent with a dihedrally distorted fourfold coordination[3]. Similar to our previous calculation of the spectrum of aqueous acetone[2,4], the $\text{Ru}^{2+}(\text{H}_2\text{O})_6$ spectrum shows spurious solvent \rightarrow solute and solute \rightarrow solvent charge transfer excitations, which can be eliminated by switching over (at considerable computational cost) to a density functional which includes a fraction of exact exchange (PBE0). This also essentially cures the 2 eV redshift of the position of the Ag^+ absorption band, which because of the highly delocalized nature of the 5s state in solution can be considered as a manifestation of the well known underestimation of band gaps in DFT. Our calculations seem to confirm therefore the importance of exact exchange for the computation of excitation spectra in condensed molecular systems. Finally we will present our first results on the emission spectrum of $\text{Ru}^{2+}(\text{H}_2\text{O})_6$ obtained by a molecular dynamics simulation on the energy surface associated with the lowest $t_{2g}^6 \rightarrow t_{2g}^5 e_g^1$ excitation with special attention to solvent effects on the Stokes shift.

Excited state *ab initio* MD of photochemical processes in model compounds

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This talk will focus on two photochemical processes of chemical and biological relevance, namely photo-isomerisation and photoinduced electron transfer. Our computational approach is based on the implementation of time-dependent density functional theory [1] (TDDFT) in the *ab initio* MD code CPMD [2]. Recently, the possibility to compute excited state properties within a mixed quantum-classical (QM/MM) [3] scheme was included. This gives us the opportunity to study for the first time ET processes in large molecular systems in different complex environments.

Photo-isomerisation. Photoinduced *cis-trans* isomerisations of C=C, C=N and N=N double bonds are investigated in three model compounds, namely the 2,4-pentadiene-1-iminium cation (PSB), formalimine, and diimide. For formalimine and diimide, the results obtained using TDDFT are in agreement with experimental data and previously reported theoretical results. The molecular dynamics simulations yield new insights into the relaxation pathways in the excited state. For PSB, which is a model system for the retinal protonated Schiff base involved in the visual process, the forces computed from the LR-TDDFT S_1 surface do not lead to double bond isomerisation but to single bond rotation [4]. The same reaction was also observed for the case of photoexcited retinal in its protein environment.

Photoinduced electron transfer. Electron transfer is an important chemical process with applications in physics, chemistry and biology. ET in molecular systems is characterized by a spontaneous charge redistribution between an initially prepared reactant state and a well defined product state. It is usually described as the transport of a single electron from a donor (D) molecular orbital (MO) to an acceptor (A) MO even though all MO of the system are modified during the transition. Because of its intrinsic properties, namely charge separation and orbital reorganization, ET processes constitute a major challenge for modern DFT studies.

In the case of intramolecular photoinduced ET, the reactant state is obtained after optical excitation of an electron from the ground state into one of its excited states. The ET process proceeds then through a rearrangement of the nuclear coordinates together with the relaxation of the excited electron into the LUMO (lowest unoccupied molecular orbital) on the acceptor site. In the present work we investigate using *ab initio* molecular dynamics (MD) methods the orbital and nuclear rearrangements that follow the electronic vertical photo-excitation of small organic molecules. Of particular interest is the analysis of the dependence of electronic and nuclear rearrangements on the spacing between donor and acceptor moieties (obtained by adding a number of bridge units) and on the screening effects induced by solvents with different polarity.

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Quantum many-body dynamics in Lagrangian frame: Geometric formulation of TDDFT

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In this talk I formulate equations of time-dependent density functional theory (TDDFT) in the co-moving Lagrangian reference frame. The main advantage of Lagrangian description of many-body dynamics is that in the co-moving frame both the density of particles and the current density become the exact integrals of motion. The current density is exactly zero in every point of Lagrangian space, while the density of particles preserves its initial form. In other words, a local co-moving observer will see no currents in the system, and a stationary density distribution – the picture, which is very similar to that, seen in the equilibrium system from the laboratory frame. Reformulation of the theory in Lagrangian frame shows that the most natural complete set of basic variables in TDDFT consists of Lagrangian coordinate, ξ , a symmetric deformation tensor $g_{\mu\nu}$, and a skew-symmetric vorticity tensor, $F_{\mu\nu}$. These three quantities, one vector, one symmetric tensor, and one skew-symmetric tensor, contain twelve independent numbers, which are required for the complete local characterization of a deformed state of any continuum media. Namely, ξ , $g_{\mu\nu}$ and $F_{\mu\nu}$ respectively describe the translation, deformation and rotation of an infinitesimal fluid element. On the other hand, tensors $g_{\mu\nu}$ and $F_{\mu\nu}$ have a clear geometric meaning: $g_{\mu\nu}$ is a metric tensor in Lagrangian space, while $F_{\mu\nu}$ determines a local angular velocity of the co-moving frame. All above quantities are functionals of the fluid velocity in accordance with Runge-Gross mapping theorem. Formulation of TDDFT in terms of new basic variables allows to regularly derive a local nonadiabatic approximation for the xc potential. Stationarity of the density in the co-moving frame makes the derivation to a large extent similar to that of the static LDA. In the last part of the talk I will show a few explicit examples of nonlinear nonadiabatic xc functionals.

Real-space multigrid methods for DFT and TDDFT

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MIKA (Multigrid Instead of the K-spAce) [1] is a program package for electronic structure calculations based on density-functional theory. The central numerical technique in MIKA is the Rayleigh-quotient multigrid method (RQMG) [2] for the eigenproblem. Multigrid methods significantly speed up the solution of the ground state in the case of large-scale real-space calculations.

The main applications of the MIKA-package have been made in research of the properties of quantum dots in two-dimensional electron gas [3,4] and computationally two-dimensional axially symmetric model systems for nanostructures containing up to thousands of electrons [5]. The MIKA-code can also be used for simulations of finite as well as periodic three-dimensional systems described by norm-conserving pseudopotentials [2].

We are looking forward to extend the MIKA-code to perform real-time TDDFT calculations. We will benefit greatly from the pioneering work already done in the Octopus-project [6]. The public availability of the source code for both MIKA and Octopus should also help us, or anyone else, willing to develop real-space real-time schemes for large scale TDDFT calculations.

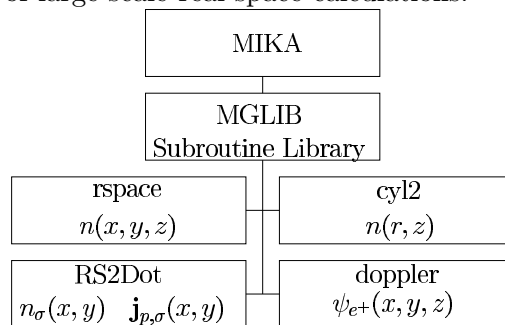


Fig. 1: Schematic of the most important components of the MIKA-package.

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An overview of basic concepts in TDDFT and some new extensions

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We give an overview of the underlying concepts of time-dependent density-functional theory (TDDFT). This includes an extension of the Runge-Gross theorem, the question of the invertibility of the density-density response function, and a discussion of the subtleties related to the action principle. We will further discuss a way to construct density-functionals that incorporate memory effects and satisfy basic conservation laws. We finally discuss a multi-component extension of TDDFT in order to treat coupled electronic and nuclear motion. This will provide a TDDFT formalism that can be applied to a treatment of the electron-phonon interaction and to molecules in strong laser fields.

Advances in time-dependent spin density functional theory

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Time-dependent density functional generally suffers from an ultra-nonlocality problem, namely the local density approximation for the exchange-correlation potential always fails, no matter how slowly varying is the density. I show that this problem is particularly severe in time-dependent spin density functional theory, but can be cured by switching to a formulation in which the spin currents are the basic variables. I discuss the physical significance of the new terms that appear in the spin-current dependent functional, and review the progress that has been made in providing explicit expressions for the latter.

Poster Session

Ground state and excited state calculations of GeTe

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Chalcogenide alloys, which show a significant change of optical reflectivity and electric conductivity under phase transformation from the amorphous to the crystalline structure are widely used for optical data storage today (e.g. DVD-RW). As they can also be used as non volatile memories (Phase-Change-RAM), they are furthermore promising candidates for future electronic data storage techniques. In this work ground state and excited state calculations are presented for GeTe, the basic phase-change-material. It is reported to crystallize in a cubic rocksalt phase and in a trigonal phase, which can be described as a distorted cubic structure. From literature relatively little is known about the amorphous structure, but the available data hints towards a tetragonal, diamond-like local coordination. The focus of the project is on the relation between optical properties and geometrical structure in different phases of GeTe, ranging from the two crystalline phases, defect structures and the amorphous phase. The origin for the difference of the optical and electronic properties in these different states is examined. The problem of obtaining a realistic amorphous structure is approached in two different ways: on one side we employ *ab initio* molecular dynamics within a 64-atom supercell and on the other side we use a simple model structure which reproduces the local configuration reported in earlier experimental work. The electronic structure is presented in the GW-correction and the theoretical spectra are calculated within TDDFT and GW-RPA. They are compared with experimental data of thin film GeTe-samples. Differences between theory and experiment are discussed as well as the changes in the optical and electronic properties upon phase transition from the crystalline to the amorphous state.

Real time dynamics of photoinduced deformation of benzene by TDDFT

Yoshitaka Tateyama, Yoshiyuki Miyamoto, Norihisa Oyama, Takahisa Ohno

Coupled dynamics of ions and electrons in the excited states of molecular and solid benzene is investigated on the femtosecond scale by TDDFT with the Suzuki-Trotter decomposition for the propagation. Within the $\pi - \pi^*$ excitations, any out-of-plane motion of the ions is not induced in the molecular system, as expected from the symmetry consideration. In the solid, however, we found that large swing of the C-H bonds and subsequent twist of the carbon ring take place, leading to sp^3 -like bonding of carbon ions. This swing-to-twist motion presents a plausible mechanism underlying the photoinduced ring opening in solid benzene experimentally observed under pressure.

Linear response at the 4-component relativistic DFT level: Application to the frequency-dependent dipole polarizability of the mercury atom and dimer

Trond Saue

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We report the implementation and application of DFT linear response theory based on the 4-component relativistic Dirac-Coulomb Hamiltonian in the DIRAC code [1,2]. Due to the separability of Hamiltonians and methods, the theory can be developed with little reference to relativity. We have based the theory on the quasienergy formalism or Floquet theory (see [3,4] and references therein), which can be applied quite generally to both variational and nonvariational wave-function methods as well as DFT using variational perturbation theory. In quasienergy DFT, the dependence of the initial state in the Runge-Gross theorem is replaced by periodic boundary conditions. Contradictions in causality and time-symmetry arguments are thereby avoided and the exchange-correlation potential and kernel can be expressed as functional derivatives of the quasienergy.

We apply the method to the calculation of the frequency-dependent polarizability of the mercury atom, which show very large effects of both relativity and correlation. We furthermore calculate the polarizability anisotropy of the mercury dimer and simulate the depolarized collision induced Raman spectrum and compare with a recent experimental study [5].

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Density functional for bosons in the path integral approach

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The density functional for a system of interacting bosons is defined as the effective action for composite operators. The functional depends on both the condensate density and the total density, the physical values of which are determined by variational principle. An expansion in powers of the Planck constant generates a systematic approximation scheme being an extension of the Kohn-Sham approach to bosonic systems.

Time-dependent exchange-correlation current density functionals with memory

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Most present applications of time-dependent density functional theory use adiabatic functionals, i.e. the effective potential at time t is determined solely by the density at the same time. Our work discusses a method that aims to go beyond this approximation, by incorporating "memory" effects: the potential will depend also on the history. We add to the adiabatic approximation an additional part that includes memory and yields a functional that is totally consistent with known dynamical properties of the homogeneous electron gas (in the linear response limit). In order to achieve this, we write down an action principle from which Kohn-Sham equations are derived for description of the time-dependent electron density and fluid velocity field. We construct the action on Lagrangian coordinate s system and pseudo time domain (Keldysh contour). Therefore, action principle is built in such a way that it is Galilean invariant and yields causal equations.

Ultrafast dissociation of adenine-water hydrogen bonds by photoexcitation.

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Recent molecular-beam studies of hydrated cluster of adenines show the anomalous loss of the solvent molecules after excitation by a nanosecond laser pulse at 262 nm[1,2].

The goal of this work is to provide the molecular mechanism behind this phenomenon working within the time-dependent density functional theory (DFT) framework.

The dissociation of the hydrogen bonds has been attributed to the dissociative character of the potential energy surface in the excited state: we investigate this hypothesis calculating the evolution of the system after the interaction with the laser pulse with real-space real-time time dependent DFT.

Preliminary ground state and linear response time dependent DFT calculations indicate that the potential energy surface in the excited state is not dissociative, but the excitation provides the complex with enough energy to dissociate.

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Scattering amplitudes from time-dependent density functional theory

Adam Wasserman, Neepa T. Maitra, and Kieron Burke

Rutgers University

The linear response formalism of time-dependent density functional theory is adapted to study low-lying electronic continuum states of atoms. Exact formulas to extract transmission amplitudes from the susceptibility are derived for one dimensional scattering, and exemplified on a simple model. Continuum states of the ground-state Kohn-Sham potential of an N -electron system can provide a good approximation to scattering from the corresponding $(N-1)$ -electron system, as shown here for the case of electron- He^+ scattering.

Valence electronic structure and TDDFT study on RuO₄ and OsO₄

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We present a study of the valence electronic structures of RuO₄ and OsO₄, incorporating both scalar and spin-orbit relativistic corrections. Extensive comparison is made with previous experimental data on vibrational frequencies and ionization energies.

Excitation energies are also calculated using Time-Dependent Density Functional Theory. Large basis-set were used together with a range of functionals, including the LB94 potential. Comparison is made with results obtained from earlier experiments and from extended Hckel type calculations [J. Chem. Phys. 60, 3166 (1974)]

Hartree Fock exchange in Time Dependent Density Functional Theory

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The absorption spectrum of acetone in aqueous solution at finite temperature is computed using Time Dependent Density Functional Theory and Car Parrinello Molecular Dynamics at the BLYP, B3LYP and PBE0 level of theory. The role of the exchange-correlation functional in separating spectral features originating from localised (intra-molecular) and charge-transfer or collective electronic excitations is analysed. In the limit of local and frequency independent exchange-correlation kernels, admixture of Hartree Fock exchange in the density functional is proved to be a necessary requirement in order to remove the unphysical degeneracy between the intra-molecular $n \rightarrow \pi^*$ and solvent \rightarrow solvent transitions. Results for the $n \rightarrow \pi^*$ transition energy, oscillator strength and solvatochromic shift are computed in excellent agreement with experiment.

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An iterative GW approach for the (111) surface of diamond

Margherita Marsili

Università di Roma Tor Vergata

The Pandey Chain model seems to be the most stable reconstruction for the (111) surface of diamond, being the atoms on the chain neither buckled nor dimerized. Experimental data confirm the absence of dimerization but cannot exclude the presence of buckling. Within DFT the electronic band structure related to the fully relaxed structure appears semimetallic in contrast with experiments which show a gap of at least 0.5 eV. This could be due to a wrong equilibrium geometry in the calculations or to the usual DFT band gap problem. Introducing quasiparticle corrections within a self-consistent GW scheme, using an iterative procedure for updating the quasiparticle energies, we found for this surface an electronic gap close to 1 eV. Preliminary results on the optical properties are also presented and discussed.

Photoionisation using DFT wave functions

Michael Walter and Hannu Hkkinen

University of Jyväskylä, Finland

The determination of photoionisation cross sections using the Kohn-Sham wave functions from accurate DFT calculations. The continuum electron is described by an analytical wave function and the matrix elements are calculated in both in length and velocity form of the dipole operator.

The test case of water shows excellent agreement between the calculations and experiment in the ionisation energies if a vertical transition is considered. The cross sections agree well with the experiment in particular in case of the velocity form results. Differences to the length form indicate the limitations in an analytical description of the continuum.

Beyond Ehrenfest dynamics

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Here we present a method to introduce electron-ion correlations into Ehrenfest dynamics which is computationally affordable. Assuming that the ionic wavefunctions are narrow a moment expansion of the full density matrix is made. The many-electron problem is then reduced to a single-electron problem by tracing over all electrons but one. Using the first moment approximation, we carry out tight binding simulations of the effect of an electric current on a mobile atom. The classical (Ehrenfest) contribution to the ionic heating is negative (cooling) and independent of the bias. The quantum contributions shows strong heating, with a rate proportional to the bias.

Failure of time-dependent density functional theory for long-range charge-transfer excited states

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Over the last few years, time-dependent density-functional theory (TDDFT) has advanced to one of the most popular theoretical approaches to calculate excited state properties of medium-sized and large molecules up to about 200 second-row atoms. Recently, it has been pointed out that TDDFT yields substantial errors for charge-transfer (CT) excited states. Here, we focus on the failures of TDDFT to predict the excitation energies of charge-transfer states correctly and to give the correct long-range $1/R$ dependence on donor-acceptor distance. The CT states of a ethylene-tetrafluorethylene model system are investigated and the dependence of their $1/R$ asymptotic behavior on the exact exchange part in hybrid functionals is explored. While the wrong excitation energies can be related to missing discontinuities in the approximate xc-potentials, the wrong asymptote of CT excited states is due to the local character of the approximate xc-functionals leading to a so-called electron-transfer self-interaction error. Future perspectives how this failure of TDDFT might be cured are discussed.

Furthermore, a hybrid approach of TDDFT and configuration interaction singles (CIS) is suggested to yield reasonable estimates for long-range CT states of large molecular systems. This approach combines the benefits of TDDFT and CIS in yielding accurate results for valence-excited states in the one hand and correctly shaped potential energy surfaces for CT states on the other. Within this approach, the CIS curves are gauged with a electron-transfer self-interaction free Δ DFT calculation. This approach is applied to large molecular systems of biological interest.

Excited-state density functionals?

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For a given excited state there exist densities that arise from more than one external local one-body potential. This is due to a qualitatively different energy-density relationship from that of the ground state and is related to positive eigenvalues in the non-local susceptibility for excited states. Consequences for the adiabatic connection method and time-dependent density functional theory are discussed.

Understanding the dissociation of diatomic molecules in the DFT-ACFD formalism : ground-state and excited-state studies

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There is a growing need for exchange-correlation (XC) functionals going beyond the Local-Density and Generalized-Gradient Approximations (LDA and GGA), as these do not account for long-range correlations occurring for instance in weakly-bonded compounds and biomolecules. In such systems van der Waals (vdW) interactions play a crucial role and can only be taken into account by means of fully non-local XC functionals. Contrary to the LDA and GGA cases, most of the latter depend on the Kohn-Sham orbitals and their energies. One way to build such a functional is to resort to the Adiabatic-Connection Fluctuation-Dissipation (ACFD) theorem [1, 2] in conjunction with the Random-Phase Approximation (RPA). The RPA captures the physics of the vdW interactions and has been tested non self-consistently on some atoms, diatomic molecules, and solids.

However, a spurious maximum in the dissociation curve was evidenced for the N₂ [3] and H₂ [4] molecules. It may result from either (a) the RPA being insufficient to describe the dissociation regime, or (b) the lack of self-consistency, as well as (c) H₂ and N₂ being pathological cases, without forgetting (d) a possible bug in the implementation.

In parallel with studies concerning points (a), (b) and (d), we are tackling point (c) by examining the dissociation of several diatomic molecules within the ACFD-RPA framework as well as their excitation energies through Time-Dependent DFT (TDDFT) and SCF calculations. We compare some of their ground-state properties with the results obtained from LDA/GGA approximations too. In addition of being heteroatomic, and composed of low Z atoms, the LiH molecule presents very peculiar properties and is often used as a test case for new computational methods. That is why we have decided to put a particular emphasis on it. To further enhance our understanding of weakly-bonded systems we are also considering the van der Waals molecules Be₂ and Mg₂. In particular, it is known that the vdW interaction is quite larger in the latter than in all those previously tried.

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Non-additive nature of van der Waals dispersion energy in layered model-systems.

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Optimization of Effective Atom Centered Potentials for Molecular Properties

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