2 News from the ESF Programme

”Towards Atomistic Materials Design”

2.1 Reports on the ESF Psi-k Programme Workshops/Conferences

2.1.1 Report on International Workshop and School on "TIME DEPENDENT DENSITY FUNCTIONAL THEORY: PROSPECTS AND APPLICATIONS"

2006, August 27 – September 11

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The School and workshop was hosted by the Benasque Center for Science, located at the heart of the Pirinees. The aim of the school was to introduce theoretical, practical, and numerical aspects of Time-dependent-density functional theory (TDDFT) to young graduate students, post-docs and even older scientists that are envisaging a project for which TDDFT would be the tool of choice. During the school we incentivated a close and informal contact between the students and the teachers. Furthermore, the students presented their current research activities and future interests (six of those presentations were selected as oral contributions to the international workshop). We felt that this was an important point, since young scientists should be involved in the building up of a strong community. The number of applications (above 190) surpassed all expectations and, of course, the limit of 43 places that we had to satisfy in order for the students to get the maximum benefit from the school, and also due to space and computer resource limitations. The students (graduate and postgraduate) also did participate in the workshop held just after the 10 days of school. The total number of participants was 90 from all over the world (including 16 females; three as invited speakers/lectures). The distribution was:

	Organizers	Teachers	Students	Invited	Participants	School	Workshop
Australia	0	0	0	0	1	0 1	
Austria	0	0	3	1	0	3	4
Belgium	0	1	1	1	0	2	3
Brazil	0	0	2	0	0	2	2
Chile	0	0	1	0	0	1	1
Finland	0	0	3	1	0	3	3
France	0	3	2	4	1	5	7
Germany	1	4	5	7	1	9	16
Holland	0	1	3	1	0	4	5
Iran	0	0	3	0	0	3	3
Israel	0	0	0	1	0	0	1
Italy	0	1	4	3	1	5	8
Japan	0	0	0	1	1	0	2
Mexico	0	0	2	0	1	2	3
Portugal	2	3	3	0	1	6	7
Spain	1	3	3	1	0	6	7
Sweden	0	0	2	0	0	2	2
Switzerland	0	0	0	2	0	0	2
UK	0	1	0	1	2	1	3
USA	0	1	6	3	1	7	10
TOTAL	4	18	43	27	10	61	90

The aim of the Workshop was to assess the present status of TDDFT approaches to the study of spectroscopic properties of real materials, and explore their capability for applications in further systems with technological and biological interest. The recent developments of TDDFT covered during the workshop include TDDFT versus current-DFT, van der Waals interactions, applications to biological systems, new functionals, transport phenomena, optical spectra of solids , etc. Due to the different methods used to tackle this problem (Many-Body Theory, Density Functional Theory, Configuration Interaction, semi-empirical approaches), this Workshop was intended as a way to promote links among scientists coming from different communities working or interested in electron excited states. Also it was intended as a follow-up event for the students attending the school as it was a good opportunity for them to see the real implications of the school lectures and get the new theoretical advances in the the development of exchange-correlation functionals as well as applications to complex systems (nanostructures, bio-molecules, interstellar molecular analysis, solids, etc.) Our goal was to bring together scientists working on foundations and different applications of TDDFT and many-body theory, trying to assess the capability of current approximations to be applied to real systems of increasing complexity. The invited and contributed talks covered:

I) Fundamental topics on TDDFT, Many-Body Theory, and electron transport theory.

II) New approximations and techniques.

III) Ab-initio calculations of spectroscopic properties of complex materials.

As a consequence, there was a broad variety of participants which helped to get an interdisciplinary vision of the field. Thus, although some of the more specific topics were far from the research interest of many participants, the meeting was an excellent opportunity to see how the same techniques are used by members of other communities.

School Program

Day	Hour	Title	T/P
28/8	9:30 - 11:00	TDDFT I - Introduction (EG)	T
	11:30 - 13:00	TDDFT II - Linear Response Theory (EG)	
	15:00 - 18:30	Introduction to the practical classes (codes Octopus, Self, Abinit) (MM+AM+YP)	P
29/8	9:30 - 11:00	TDDFT as a tool in chemistry I (FF)	T
	11:30 - 13:00	TDDFT III - Strong Fields (EG)	
	15:00 - 18:30	Quantum Dots I (AC+MM+MO+FN)	P
30/8	9:30 - 11:00	Many-Body I - Introduction (RG)	T
	11:30 - 13:00	TDDFT as a tool in chemistry II (FF)	
	15:00 - 18:30	Quantum Dots II (AC+MM+MO+FN)	P
31/8	9:30 - 11:00	Many-Body II - GW and BSE (RG+LR)	T
	11:30 - 13:00	TDDFT IV - Keldish formalism (RvL)	
	15:00 - 18:30	Quantum Dots III (AC+MM+MO+FN)	P
1/9	9:30 - 11:00	Many-Body III - Many-Body vs TDDFT (LR)	T
	11:30 - 13:00	Propagation schemes (AC)	
	15:00 - 18:30	OCTOPUS I (FN+MO+MM+AC)	P
2/9		Free (excursion to be announced)	
3/9	9:30 - 11:00	TDDFT V - Advanced topics I (RvL)	T
	11:30 - 13:00	Models for time-dependent phenomena I (ML)	
	15:00 - 18:30	OCTOPUS II (FN+MO+MM+AC)	P
4/9	9:30 - 11:00	TDDFT VI - Advanced topics II (RvL)	T
	11:30 - 13:00	Models for time-dependent phenomena II (ML)	
	15:00 - 18:30	ABINIT+SELF I (AM+LW+MB+PG+SB+YP)	P
5/9	9:30 - 11:00	TDDFT as a tool in biophysics (AR+MM)	T
	11:30 - 13:00	Nonadiabatic electron dynamics in TDDFT I (CU)	
	15:00 - 18:30	ABINIT+SELF II (AM+LW+MB+PG+SB+YP)	P
6/9	9:30 - 11:00	Nonadiabatic electron dynamics in TDDFT II (CU)	T
	11:30 - 13:00	Challenges in TDDFT and Final remarks (AR)	

Lecturers for the theoretical classes

	Lecturer
AC	Alberto Castro (FU Berlin, Germany)
AR	Angel Rubio (San Sebastian, Spain)
CU	Carsten Ullrich (Missouri, USA)
EG	E. K. U. Gross (FU Berlin, Germany)
FF	Filipp Furche (Karlsruhe, Germany)
LR	Lucia Reining (Paris, France)
ML	Manfred Lein (MPI Heidelberg)
MM	Miguel Marques (Coimbra, Portugal)
RG	Rex W. Godby (York, UK)
RvL	Robert van Leeuwen (Groningen, The Netherlands)

Tutors for the practical classes

	Tutor
AC	Alberto Castro (FU Berlin, Germany)
AM	Andrea Marini (Rome, Italy)
FN	Fernando Nogueira (Coimbra, Portugal)
LW	Ludger Wirtz (Lille, France)
MB	Michel Bockstedte (San Sebastian, Spain)
MM	Miguel Marques (Coimbra, Portugal)
MO	Micael Oliveira (Coimbra, Portugal and San Sebastian, Spain)
PG	Pablo Garcia (Madrid, Spain)
SB	Silvana Botti (Paris, France)
YP	Yann Pouillon (Louvain-la-Neuve, Belgium)

Workshop

Workshop Program

Day I: Thursday 7th		
09:00	Hardy Gross	Opening remarks
09:10	Neepa Maitra	Some challenges for time-dependent density functional approximations - and some partial solutions
10:00	N. Lathiotakis	Reduced density matrix functionals for finite and periodic systems
10:50	Caffeine break	
11:20	Mark Casida	Two-electron excitations in TDDFT
12:10	Stephan Kummel	Strong-field excitations and derivative discontinuities in TDDFT
13:00	Lunch break	
15:00	E. J. Baerends	Avoided crossings of excited state surfaces and vibronic coupling in TDDFT
15:50	Ivano Tavernelli	Non-adiabatic TDDFT MD: from gas phase to complex environments
16:40	Caffeine break	
17:10	Juerg Hutter	TDDFT calculations with the Gaussian augmented plane wave approach
18:00	Rodolfo del Sole	Calculation of optical properties of complex systems within TDDFT
18:50	Dmitrij Rappoport	Practical aspects of molecular TDDFT calculations
Day II: Friday 8th		
09:10	Andreas Goerling	Exact exchange spin current density functional methods
10:00	Myrta Grüning	The effect of nonlocality on the band gap within density functional theory
10:50	Caffeine break	
11:20	Matteo Gatti	Nonlocality and frequency dependence of effective potentials
12:10	Rex Godby	Exchange-correlation functionals and kernels for conductance and polarization
13:00	Lunch break	
15:00	Massimiliano di Ventra	Transport in nanoscale systems: new approaches to an old problem
15:50	Gianluca Stefanucci	Time dependent transport phenomena within TDDFT
16:40	Beer break	
17:10	Carsten Ullrich	Time-dependent generating-coordinate method
18:00		Poster session, cheese and wine

Day III: Saturday 9th		
09:10	Eckhard Pehlke	Molecular dynamics simulations of non-adiabatic processes
10:00	Roi Baer	Nonadiabatic functionals and their effects on electron dynamics in molecules and metal clusters
10:50	Caffeine break	
11:20	Esa Räsänen	Optimal laser control of quantum rings
12:10	Silvana Botti	How do rewritable DVDs work: optical properties of phase-change materials
13:00	Lunch break	
15:00	Ludger Wirtz	Electronic excitations in hexagonal layered systems (C and BN)
15:50	Deborah Prezzi	The role of excitons in the optical properties of carbon nanotubes
16:40	Beer break	
17:10	Marti Pi	TDDFT description of electronic systems in semiconductor heterostructures
18:00		Oral presentation of the best posters

Day IV: Sunday 10th		
09:10	Stefano Baroni	Turbocharging time-dependent density-functional theory with Lanczos chains
10:00	Yoshi Miyamoto	TDDFT-MD simulation of nano-carbons: decay dynamics of hot-carriers and electronic shakeup by high-speed ions/atoms
10:50	Caffeine break	
11:20	Patrick Rinke	The band gap of InN and ScN: a quasiparticle energy study based on exact-exchange density-functional theory
12:10	C Ambrosch-Draxl	The role of core states on the excitation spectra of solids
13:00	Angel Rubio	Closing remarks

Abstracts

Some challenges for time-dependent density functional approximations - and some partial solutions

Neepa T. Maitra

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The burst of activity and applications using TDDFT is evidence of its remarkable success in predicting a range of phenomena for a wide range of systems. The simple functional approximations, bootstrapped from ground-state approximations, appear to fare very well in the general case. There are however exceptions where these functionals fail, and where challenges lie in the development of more accurate functionals. I will discuss three very different cases, and offer partial solutions for them. First, excitations of a long-range heteroatomic molecule composed of open-shell units. Both local and charge-transfer excitations require strong non-adiabaticity in the exchange-correlation kernel. These excitations are necessary to get right if TDDFT is to be used for potential energy curves in electron-ion dynamics involving dissociation, for example. A key feature of this problem is step structure in the exact ground-state potential, which eludes the usual (semi-)local LDA/GGAs, and even exact exchange. A new approach that extracts a ground-state potential from the Vignale-Kohn current-density response functional will be shown to capture the steps well for the closely-related problem of homoatomic species in electric fields. Second, in strong-field dynamics, the underlying single Slater-determinant nature of the Kohn-Sham wavefunction is at the root of severe difficulties particularly important in attosecond quantum control problems. To treat this, initial work towards a new extension of the theory to phase-space density functionals will be presented. Finally, time allowing, the question of whether the presently available TDDFT approximations can capture quantum chaos induced by electron-electron interaction alone will be addressed.

Reduced density matrix functionals for finite and periodic systems

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Reduced Density Matrix Functional Theory (RDMFT) is based on Gilbert's theorem, which guarantees that every observable is a functional of the one-body-reduced density matrix (1-RDM). We discuss several aspects of RDMFT, review its application to finite systems and finally, we emphasize on its application to periodic systems. The implementation of 1-RDM functionals for periodic systems is based on a Wannier- or Bloch-states description of the system. In a similar fashion to DFT, we explore the possibility of using the discontinuity of the chemical potential as a measure of the fundamental gap. Finally, we apply last generation functionals of the 1-RDM to the case of the Homogeneous Electron Gas (HEG). It is demonstrated that they offer a better description than their predecessors. In addition, by using suitable fitting parameters, we show that the exact correlation energy of the HEG can be reproduced. The derivative functionals are expected to be useful in the application of RDMFT to metallic systems.

Polarization Propagator Corrections to Linear Response Time-Dependent Density-Functional Theory for Molecules with Closed- and Open-Shell Ground States

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A decade ago time-dependent density-functional theory (TDDFT) was introduced to the quantum chemistry community in its linear response (LR) for calculating excitation spectra [C95]. Since that time LR-TDDFT has become a method of choice for calculating molecular vertical excitation energies because of its demonstrated accuracy within the domain of applicability [C01] determined by present-day approximate exchange-correlation functionals. One limitation of the method comes from the wide-spread use of the TDDFT adiabatic approximation which limits LR-TDDFT to quasiparticle spectra (i.e., one-electron excitations). Two-electron excitations are important when calculating the excitation energies of closed-shell molecules both (i) because of the importance in some molecules of excited states with substantial two-electron character and (ii) because the inclusion of two-electron excitations allows a better description of biradical ground states. Spin-flip excitations are a particular type of two-electron excitation which is important for a correct description of the excitation spectra of molecules with open-shell ground states. Some of these points are nicely illustrated in Ref. [CIC06]. In this talk I plan to outline how the equation-of-motion superoperator approach may be used to derive nonadiabatic polarization propagator corrections [C05] to adiabatic LR-TDDFT for application to the above mentionned problems.

[CIC06] M.E. Casida, A. Ipatov, and F. Cordova, in *Time-Dependent Density-Functional Theory*, edited by M.A.L. Marques, C. Ullrich, F. Nogueira, A. Rubio, and E.K.U. Gross, *Lecture Notes in Physics* (Springer: Berlin, 2006). “Linear-Response Time-Dependent Density-Functional Theory for Open-Shell Molecules”

[C05] M.E. Casida, J. Chem. Phys. **122**, 054111 (2005). “Propagator Corrections to Adiabatic Time-Dependent Density-Functional Theory Linear Response Theory”

[C01] M.E. Casida, in *Accurate Description of Low-Lying Molecular States and Potential Energy Surfaces*, ACS Symposium Series 828, edited by M.R. Hoffmann and K.G. Dyall (ACS Press: Washington, D.C., 2002), p. 199. “Jacob‘s ladder for time-dependent density-functional theory: Some rungs on the way to photochemical heaven”

[C95] M.E. Casida, in *Recent Advances in Density Functional Theory*, Vol. I, edited by D.P. Chong (World Scientific: Singapore, 1995), p. 155. “Time-dependent density-functional response theory for molecules”

Preprints of Refs. [C95], [C01], and [CIC06] may be downloaded from

http://www-ledss.ujf-grenoble.fr/PERSONNEL/LEDSS7/casida/research/complete.html

Strong-field excitations and derivative discontinuities in time-dependent density functional theory

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Time-dependent density functional theory with local or semi-local approximations for the exchange-correlation potential has been quite successful in the linear response regime. However, non-linear, non-perturbative excitations like the ionization of finite systems by strong laser fields are not well described by approaches like the adiabatic local density approximation (ALDA). We argue [1] that this failure is due to the fact that in time-dependent Kohn-Sham theory, there is an analog of the particle-number discontinuity that is well known in ground-state Kohn-Sham theory [2]. This discontinuity is missing in approaches like the ALDA. We demonstrate the importance of this discontinuity by calculating the exact (within numerical limits) time-dependent exchange-correlation potential for an ionization process. Finally, we discuss in how far this discontinuity can be incorporated into Kohn-Sham theory via the time-dependent optimized effective potential formalism.

[1]M. Lein and S. Kümmel, Phys. Rev. Lett. **94**, 143003 (2005);
M. Mundt and S. Kümmel, Phys. Rev. Lett. **95**, 203004 (2005).
[2]J.P. Perdew, R.G. Parr, M. Levy, and J.L. Balduz, Jr., Phys. Rev. Lett. **49**, 1691 (1982).

Avoided crossings of excited state surfaces and vibronic coupling in TDDFT

E. J. Baerends

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Time-dependent DFT has become a very powerful tool in spectroscopical investigations in chemistry for several reasons.
In the first place, it is remarkably accurate, if sufficiently accurate (not LDA or GGA but "shape-corrected") Kohn-Sham potentials are used. Approximations to the exchange-correlation kernel are much less critical, the adiabatic LDA usually suffices.
In the second place the Kohn-Sham orbitals and the orbital energies are physically meaningful, much more so than the Hartree-Fock orbitals. The occupied orbital energies are very close to ionization energies, and unoccupied-occupied orbital energy differences represent to very good approximation excitation energies. Moreover, excitations are often represented for more than 90% by single orbital excitations, affording very s traightforward interpretation of excitation spectra.

The accuracy of the TDDFT excitation energies is such that it should be sufficient to describe properly the potential energy curves even in regions of avoided crossings. This poses the questions whether it would be possible to calculate non-Born-Oppenheimer effects (vibronic coupling) with TDDFT. The crucial step is that one needs a so-called diabatization method to extract from the calculated adiabatic excited state surfaces properly diabatized surfaces, and coupling constants. A method for calculating vibronic coupling will be discussed.

This vibronic coupling method has been implemented in the ADF TDDFT code. We will discuss two applications. The first is to N_2.
The N_2 excitation spectrum has proved surprisingly difficult to calculate correctly, partly because of a crossing of the three lowest excited states of $^1\Pi_u$ symmetry. The ordering of these states at R_e has been incorrectly given, compared to the standard experimental assignment, in many recent *ab initio* and all TDDFT calculations. This has led to the suggestion that the experimental assignment might have to be revised. However, using the vibronic coupling to obtain fully comparable theoretical and experimental spectra, we can rule out this possibility and we have to conclude that the excitation energy for one of the

$^1\Pi_u$ states is actually in error in TDDFT by ca. 1 eV at R_e, and even more at elongated bond length. We can trace the singularly large error in this case to inability of the linear response based TDDFT method to incorporate double excitation character.

The second application is to permanganate, MnO_4^-. The spectrum of this tetrahedral metaloxo-anion has been obtained with detailed vibrational structure in 1964. Since then virtually all quantum chemical methods have been benchmarked against this spectrum, but still the interpretation of the spectrum remains controversial. We will reproduce, using TDDFT with vibronic coupling, for the first time the full vibrational structure. This leads to a definitive assignment.

N_2: M. Grüning, O.V.Gritsenko, S.J.A. van Gisbergen and E.J. Baerends "Shape corrections to exchange-correlation Kohn-Sham potentials by gradient-regulated seamless connection of model potentials for inner and outer region", J. Chem Phys. **114** (2001) 652-660; J. Neugebauer, E.J. Baerends, "Vibronic coupling and double excitations in linear response time-dependent density functional calculations: dipole-allowed states of N_2", J. Chem. Phys. **121** (2004) 6155-6166.

MnO_4^-: J. Neugebauer, E.J. Baerends, M. Nooijen, "Vibronic structure of the permanganate absorption spectrum from time-dependent density functional calculations", J. Phys. Chem. A **109** (2005) 1168-1179

Non-adiabatic TDDFT MD: from gas phase to complex environments

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TDDFT calculations with the Gaussian augmented-plane wave approach

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The Gaussian augmented plane wave (GAPW) approach combines the description of the Kohn-Sham orbitals as a linear combination of Gaussian functions with a mixed basis representation of the electron density. The density is separated in a smooth part, described in a plane wave basis and a rapidly varying part expanded in local Gaussian functions. This scheme leads to efficient algorithms for all-electron ground state Kohn-Sham calculations with periodic boundary conditions. We have further extended the GAPW method to include linear response TDDFT calculations. A series of approximations to the full equations (within the ALDA approach) was tested on molecular systems.

Calculation of optical properties of complex systems within TDDFT

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The microscopic study of complex systems has nowadays reached a high level of accuracy that allows for a deep understanding of the electronic excitations. Ab-initio descriptions of experiments such as direct or inverse photoemission, optical absorption, electron energy loss, have become possible thanks to the huge progress in theory and the increased computational power. Charged excitations, as well as neutral excitations, can now be studied within the Many-Body Perturbation Theory based on the Green's function formalism. Optical spectra can be calculated with inclusion of the electron hole interaction by solving the Bethe Salpeter equation (BSE) within the framework of Green's function theory.

Moreover, optical spectra can be nowadays also well described within the Time Dependent Density Functional Theory (TDDFT). The derivation of a long range exchange-correlation kernel suitable for optical spectra calculations will be briefly reviewed. Its performance, as well as those of simpler approximations, will be tested in the case of complex systems, like surfaces or liquids.

Practical aspects of molecular TDDFT calculations

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Universität Karlsruhe, Germany

Photochemistry has to date accumulated an immense amount of experimental data on molecular excitations and luminescence characteristics. Efficient implementations of TDDFT excited state Cartesian gradients [1,2] now provide computational tools for their interpretation and systematic investigation of excited state reactions. This is demonstrated for 7-azaindole dimer ((7-AI)$_2$) which is a very much investigated example for excited state intramolecular proton transfer. When excited to the S_1 state, (7-AI)$_2$ undergoes double proton transfer forming the tautomer [3]. Both concerted and stepwise mechanisms have been proposed for the double proton transfer, and the existence of an intermediate has been addressed in many experimental and theoretical studies.

TDDFT calculations using B3LYP functional and TZVPP basis reveal 3 excited state state minima in the S_1 state of (7-AI)$_2$. The excited state structures of normal dimer S_1^{N} and tautomer S_1^{T} show symmetry breaking which leads to full localization of the excitation on one monomeric unit. The third excited state structure corresponds to single proton transfer intermediate S_1^{I} and appears very low in energy due to strong charge transfer between the monomers. The mechanism of tautomerization has been investigated by 2-dimensional potential energy surface calculations along the proton transfer coordinates. The TDDFT results suggest that the tautomerization occurs by concerted yet not synchronous transfer of both protons, which is supported by recent experimental results [4]. The stepwise mechanism via S_1^{I}

intermediate seems to be rather a channel to fast radiationless relaxation to the ground state.

[1] F. Furche, R. Ahlrichs, J. Chem. Phys. **117**, 7433 (2002).
[2] J. Hutter, J. Chem. Phys. **118**, 3928 (2003).
[3] C. A. Taylor, M. A. El-Bayomi, M. Kasha, Proc. Natl. Acad. Sci. **69**, 253 (1969).
[4] K. Sakota, A. Hara, H. Sekiya, Phys. Chem. Chem. Phys. **6**, 32 (2004).

Exact-exchange spin-current density-functional theory

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A brief introduction of the optimized effective potential (OEP) method and exact-exchange Kohn-Sham approaches is given. Then a spin-current density-functional formalism that generalizes the current-spin-density- functional theory of Vignale and Rasolt is presented. The introduced spin-current density-functional theory (SCDFT) takes into account spin-currents, i.e., currents of the magnetization, in addition to the variables considered in current-spin-density-functional theory, i.e., the density, the spin-density, and currents of the density. An implementation of the presented SCDFT within an exact-exchange (OEP) framework is presented. The inclusion of relativistic effects, in particular of spin-orbit coupling, via relativistiv OEP pseudopotentials is discussed. Results for atoms and semiconductors are presented. It is shown that spin-orbit interactions are accompanied by spin-currents. Finally the perspectives of time-dependent SCDFT are briefly considered.

A. Görling, J. Chem. Phys. **123**, 062203 (2005) and references therein.
S. Rohra and A. Görling, Phys. Rev. Lett. **97**, 013005 (2006).
S. Rohra, E. Engel, and A. Görling, cond-mat/0608505.

The effect of nonlocality on the band gap within density functional theory

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In this talk I compare the eigenvalue band gap found with a nonlocal potential within the generalized KS (GKS)[1] scheme and within the KS scheme using the the optimized effective potential(OEP)[2] approach. Since I use the same exchange-correlation approximation (Coulomb-Hole screened-exchange)

the difference in the band gap is due solely to the locality/nonlocality of the potential. In fact, I show that the difference between the OEP-KS and the GKS band gaps comes from the derivative discontinuity of the exchange-correlation energy that corresponds to the nonlocal potential. Once the derivative discontinuity is taken into account, the corrected KS and generalized KS gaps are very close to each other. Finally I discuss whether the GKS schemes can be successfully applied to calculations of optical absorption spectra of semiconductors and insulators.

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[1] A. Seidl et al. Phys. Rev. B **53**, 3764 (1996).
[2] R. T. Sharp and G. K.Horton Phys. Rev.**90**, 317 (1953);
J. D. Talman and W. F. Shadwick Phys. Rev. A **14**, 36 (1976);
M. E. Casida Phys. Rev. A **51**, 2005 (1995).

Nonlocality and frequency dependence of effective potentials

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Many-body perturbation theory (MBPT) [1] is a very powerful method. The key variable is the Green's function $G(r, r', \omega)$ which contains a great deal of information, like the one-quasiparticle spectra. However, one is often interested in just a part of the information carried by G, so in these cases it is preferable to work with simpler quantities from the beginning. This is precisely the case of density-functional theory (DFT) [2], where one wants to obtain the ground-state total energy and density $\rho(r)$. In principle, one doesn't need the full G to obtain this information. In the Kohn-Sham approach [3] it is sufficient to solve an effective one-particle Schrödinger equation, with a local and static potential $V_{xc}(r)$. The Green's function, in turn, is determined by a nonlocal and frequency dependent self-energy $\Sigma(r, r', \omega)$. A possible link between DFT and MBPT is the Sham-Schlüter equation [4]:

$$V_{xc}(r_1) = \int d\omega dr_2 dr_3 dr_4 e^{i\eta\omega} \tilde{\chi}^{-1}(r_1, r_4) G_{KS}(r_4, r_2, \omega) \Sigma(r_2, r_3, \omega) G(r_3, r_4, \omega)$$

$$\tilde{\chi}(r_1, r_2) = \int d\omega e^{i\eta\omega} G_{KS}(r_1, r_2, \omega) G(r_2, r_1, \omega)$$

Here we generalize the Sham-Schlüter equation to situations where one is interested in other parts of the Green's function. For example, one can consider the trace of the spectral function, which is needed to interpret photoemission spectra. In this case a local and dynamical potential $V_{SF}(r,\omega)$ can be introduced. We show that in this case the nonlocality of the self-energy can be converted into a frequency dependence of VSF . This is illustrated for model systems. We discuss also the link with dynamical mean-field theory (DMFT) [5] and other approaches.

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Exchange-correlation functionals and kernels for conductance and polarisation

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Transport in nanoscale systems: new approaches to an old problem

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Transport in nanoscale systems is usually described as an open-boundary scattering problem. This picture, however, says nothing about the dynamical onset of steady states, their microscopic nature, or their dependence on initial conditions.[1] In order to address these issues, I will first introduce a novel formulation of transport based on the physical notion of two large but finite charged electrodes discharging across a nanoscale junction. [1,2] This "microcanonical" picture suggests the description of electron flow by means of quantum hydrodynamic equations [3], allows us to prove that the total many-body current is given exactly in Time-Dependent DFT [1], and provides an elegant connection with Time-Dependent Current DFT [3]. As a bonus, we predict a series of novel phenomena like turbulence of the electron liquid [3], local electron heating in nanostructures [4] and the effect of electron viscosity on resistance [5]. We will provide both analytical results and numerical examples of first-principles electron dynamics in nanostructures using the above approach.

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Time dependent transport phenomena within TDDFT

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We propose a rigorous approach based on TDDFT to calculate total currents through and density in a molecule attached to macroscopically large reservoirs. We clarify under what circumstances a steady state can develop, discuss the initial-state and history dependences and obtain a Landauer-like formula for the steady current. We further show that the steady-state assumption is not compatible with the presence of bound states. The density oscillates with history-dependent amplitudes and, as a consequence, the effective potential of TDDFT oscillates too. A computationally tractable scheme of the theory is also presented. We develop a numerical algorithm based on the propagation of Kohn-Sham orbitals in open systems. The scheme is used to compute the time-dependent current in response to an external dc or ac bias or time dependent gate voltages (electron pumping). Finally, possible generalization of our approach are discussed.

Time-dependent generating-coordinate method

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The vast majority of applications in TDDFT use adiabatic approximations (such as the ALDA) for exchange and correlation. While the ALDA has overall been very successful, there are many situations where it fails. To go beyond the adiabatic approximation requires an xc potential with a memory, which is computationally demanding and has so far been achieved only in few exploratory calculations.

This talk presents a new, post-TDKS variational method which extends the ALDA in a flexible and computationally simple manner. The time-dependent many-body wave function is represented as a weighted sum of single-determinant, non-orthogonal wavefunctions coming from ALDA hamiltonians featuring a generating coordinate. The weight factors are obtained from a stationary action principle. As an illustration, the method is applied to describe driven parametric oscillations of two electrons in a harmonic potential (Hooke's atom). Comparison with exact solutions of the time-dependent two-electron Schroedinger equation shows that a proper choice of generating coordinates reproduces the linear and nonlinear electron dynamics very accurately, including effects associated with double excitations that cannot be captured with the ALDA alone.

Molecular dynamic simulations of non-adiabatic processes at surfaces

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Energy transfer processes at surfaces play an important role for various surface phenomena. During chemisorption, the binding energy of the adsorbate has to be dissipated into the substrate degrees of freedom. Concurrently with energy dissipation directly into phonons, part of the chemisorption energy can be spent to excite electron-hole pairs in the substrate. This electronic dissipation will be most pronounced for light adsorbate atoms interacting with metal surfaces, thus we focus on hydrogen atoms chemisorbing on an Al(111) surface. The electronic non-adiabacity has been demonstrated experimentally by H. Nienhaus [1] and coworkers by the direct observation of chemicurrents due to electron hole pairs induced by the chemical reaction. Here we investigate two different mechanisms that can contribute to the chemicurrents by simulating the chemisorption dynamics within TDDFT.

As a second example for energy transfer processes at surfaces we calculate the excitation of coherent surface-atom motion by very intense fs laser pulses. Such excitations are well known in case of bulk phonons, they still mark an active problem in case of atomic vibrations at the Si(001) surface.

TDDFT is ideally suited to simulate such electronically non-adiabatic processes *ab initio*. The adiabatic approximation is applied to the time-dependent exchange-correlation potential. The integration of the time-dependent Kohn-Sham equations has been implemented both into the original version of the total-energy program fhimd from the Fritz-Haber Institut in Berlin and into the program version by M. Bockstedte *et al.* extended for spin polarization. The calculations employ pseudopotentials, a plane-wave basis-set and periodically repeated supercells. For the situations considered here the dynamics of the ions is expected to be sufficiently accurately described within the Ehrenfest approximation. A time-dependent electric field perpendicular to the slabs can be used to simulate electron-hole pair-excitation by laser pulses.

Electron-hole pair excitation during H/Al(111) chemisorption has been simulated over up to 80 fs for cells containing up to 500 electrons. Due to computational limitations, the calculations had to be performed at a small plane-wave cut-off energy of 10 Ry and one special k-point. The dynamic of the electrons is analysed by a posteriori relaxation of the wave-functions down onto the Born-Oppenheimer surface at frozen-in atomic coordinates. In this way the energy stored in electron-hole pair-excitations, the non-adiabatic contribution to the force acting on the hydrogen atom, and the electronic excitation spectrum is calculated [2]. In this talk, the energy dissipation and the excitation spectra will be presented for H/Al(111), the isotope effect and kinetic energy dependence will be discussed, and the contribution to energy dissipation from the delocalisation of the local spin moment at the H-atom will be quantified and compared to the time-dependent Newns-Andersen model by Mizielinski *et al.* [3]

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Nonadiabatic functionals and their effects on electron dynamics in molecules and metal clusters

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Large Control of electronic currents by laser in quantum rings

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We show that the excited states of N-electron semiconductor quantum rings (QRs) can be controlled by a circularly polarized laser field [1]. For this purpose, we define a realistic 2D model potential for the QR and treat the influence of a tunable laser field on the electrons with the dipole approximation. In the numerical calculations we apply the time-dependent density-functional theory within the OCTOPUS code package [2], which enables the evolution of the electronic wave functions in real time and real space. This allows us to monitor the total density and current in the QR during the propagation. As a generalization to a recent study on one-dimensional QRs [3], we find that (i) an external magnetic field creating persistent currents does not affect the controllability of the excited states, and (ii) the finite width of the QR considerably changes the dipole matrix elements required for the determination of the pulse length. Finally we discuss the prominent role of the electron-electron interactions as well as the possibilities to fully control the many-electron system by using the framework of the optimal control theory.

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How do rewritable DVDs work: optical properties of phase-change materials

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Several chalcogenide alloys exhibit a pronounced contrast in the optical absorption of the metastable rocksalt and the amorphous state. This phenomenon is the basis for their application in the optical data storage.

Here I present ab initio calculations of the optical properties of GeTe and $Ge_1Sb_2Te_4$ in the rocksalt and the amorphous phase. These calculations reveal the correlation between local structural changes and optical properties as well as the origin of the optical contrast in these materials. We find that the change in the optical properties cannot be solely attributed to a smearing of the electronic states as commonly assumed for amorphous semiconductors: in fact the optical contrast between the two phases can only be explained by significant changes in the transition matrix elements.

Electronic excitations in hexagonal layered systems (C and BN)

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We present different phenomena involving electronic excitations in layered systems. For hexagonal boron nitride*, we show that excitonic effects play an important role for the optical properties. Measured and calculated values for the band-gap still display a strong scattering between 4.3 and 6.8 eV. We show that optical absorption and electron energy loss spectroscopy cannot be explained in terms of independent-electron transitions but can be properly understood only by proper inclusion of excitonic effects. We discuss the origin of the different values for the measured/calculated band-gaps. For the interpretation of Raman spectra of graphite, the double-resonant Raman model which involves electron-hole pair excitations is qualitatively successful. Quantitative evaluation based on DFT band-structures display, however, a mismatch between theory and experiments. We discuss the achievements and short-comings of the double-resonant model for the explanation of the differences in the Raman spectra of single-layer, few-layer, and bulk graphite.

* Collaboration with Andrea Marini and Angel Rubio (DIPC, San Sebastian, Spain)

** Collaboration with Davy Graf, Francoise Molitor, Klaus Ensslin, Christoph Stampfer, Alain Jungen, and Christopher Hierold (ETH Zurich, Switzerland)

The role of excitons in the optical properties of carbon nanotubes

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We present a first-principles study of the optical properties of single-walled carbon nanotubes (SWCNT). We employed many-body theoretical methods to determine the excited states of the system. Both self-energy corrections in the treatment of single-particle energies and effects arising from the electron-hole interaction are included in our calculations [1,2]. Our symmetry-based approach exploits all the symmetries of these systems, making feasible the study of large tubes with more than 200 atoms per unit cell, which are otherwise impossible to treat in standard approches within the many-body framework. In addition, this picture gives a more complete understanding of the excited state properties, of the degeneracies and group character of the single-particle bands, and of the selection rules involved in determining optical spectra. We computed one- and two-photon absorption spectra, achieving excellent agreement with recent experiments [3-5]. We found that many-electron effects are crucial in both the peak shapes and positions for all the tubes studied. In particular, for 0.4-0.8-nm-diameter tubes, the calculated exciton binding energies range between 0.3 and 0.9 eV, showing important excitonic effects even in large diameter nanotubes.

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TDDFT description of electronic systems in semiconductor heterostructures

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Turbocharging time-dependent density-functional theory with Lanczos chains

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The large-scale application of TDDFT to nano-structured materials is currently hindered by our poor knowledge of the relevant exchange-correlation functionals in the dynamical regime, as well as by the lack of efficient algorithms applicable to systems larger than few (or few tens at the very best) independent atoms. In this talk a new algorithm will be described which allows for the application of TDDFT to systems of the same complexity as those currently treatable using state-of-the-art ground-state DFT techniques.

Using a super-operator formulation of linearized time-dependent density-functional theory, the dynamical polarizability of a system of interacting electrons is represented by a matrix continued fraction whose coefficients can be obtained from the non-symmetric block-Lanczos method. The resulting algorithm, which is particularly convenient when large basis sets are used, allows for the calculation of the full spectrum of a system with a computational workload only a few times larger than needed for static polarizabilities within time-independent density-functional perturbation theory. The method is demonstrated with calculations of the spectra of benzene and of fullerene, and prospects for its application to the large-scale calculation of optical spectra, particularly in what concerns the acceleration of the Lanczos recursion, are discussed.

TDDFT-MD simulation of nano-carbons: Decay dynamics of hot-carriers and electronic shakeup by high-speed ions/atoms

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In this talk, I will show applications of the TDDFT on molecular dynamics in nano-carbons. Since both electron dynamics and ionic motions are treated simultaneously, the TDDFT-MD simulation can treat both electron-electron interaction (within DFT) and electron-phonon interaction.

I show two examples of the applications: hot-carrier decay in carbon nanotubes and stopping power acting on high-speed hydrogen atom/ion passing through a graphene sheet.

The electronically excited carbon nanotubes are placed under particular lattice temperature, and time-evolution of expectation values of electrons and the potential energy of ions (the total energy) were monitored. We observed two-major time-domains of the electron-hole gap reduction which were respectively interpreted as electron-electron and electron-phonon interactions. This interpretation was further confirmed by monitoring a dependence of the decay dynamics on initial lattice temperatures.

Next example is high-energy hydrogen irradiation on a graphene sheet which shows significant reduction on the hydrogen kinetic energy even when kinetic energy transfer on carbon atoms in the graphene sheet is negligible. The reason of the significant stopping power is electronic shakeup which corresponds to collective excitation of valence electrons of graphene. This shakeup can be seen when the incident kinetic energy of hydrogen atom/ion exceeds 1 KeV. Meanwhile, the conventional Born-Oppenheimer approximation is found to be valid when the incident kinetic energy is less than 100 eV.

If time is allowed, I will discuss possible future applications of the TDDFT-MD simulation.

The present works have been done in collaboration with Profs. A. Rubio, D. Tománek, and Dr. A. Krasheninnikov. Part of the present calculations were performed by using the Earth Simulator.

The band gap of InN and ScN: a quasiparticle energy study based on exact-exchange density-functional theory

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The group-IIIA nitride InN and the group-IIIB nitride ScN have recently received increased attention in the field of opto-electronics and optical coatings. Due to the difficulty of growing clean samples, however, the size of their band gap has not been well established, yet. We have recently shown, that quasiparticle energy calculations in the G_0W_0 approximation based on density-functional theory (DFT) calculations in the exact-exchange (EXX) approach yield band gaps in very good agreement with experiment for GaN and II-VI compounds [1]. For wurtzite InN our approach predicts a gap of 0.7 eV supporting recent experimental observations [2,3,4]. Extrapolating the G_0W_0 data to higher carrier concentrations, which are prevalent in most InN samples, results in an increase of the apparent band gap with increasing concentration (Burnstein-Moss effect) in good agreement with the observed blue shift of the optical absorption edge [4]. Moreover, the concentration dependence of the effective mass, which is a result of the non-parabolicity of the conduction band, agrees well with the experimental findings [4]. For ScN there exists a longstanding controversy if the material is a semimetal or semiconductor, which has only very recently been resolved in favor of the latter. Our calculations for rocksalt ScN predict an indirect band gap of 0.9 eV in good agreement with recent experimental observations [5].

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The role of core states in the excitation spectra of solids

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All-electron full-potential methods are highly precise and allow to explore the physics of the core region of solids, since no shape approximation is made for the potential when solving the Kohn-Sham equation. Thus they are reliable tools when heavy atoms are involved in a material, and they are also often used as a benchmark for other codes in terms of accuracy. But they are quite demanding regarding the computational effort and when it comes to the implementation of new features, particularily those related to excited states. Several discrepancies with respect to planewave calculations, which have been reported in literature, ask for clarification, and hence, for a wider range of applications. In this talk, the implementation of various methods into the full-potential linearized augmented planewave (LAPW) method is presented, comprising the exact exchange scheme (EXX), many-body perturbation theory (MBPT), as well as time-dependent density functional theory (TDDFT). Discrepancies with respect to planewave results – which show up in the EXX Kohn-Sham band gaps, the GW self-energies, as well as the electron-hole wavefunctions obtained by the Bethe-Salpeter Equation (BSE) – will be discussed, highlighting the importance of the core-valence interaction and the proper treatment of the wavefunctions close to the nucleus. Finally, first all-electron TDDFT spectra will be presented.