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**13th International Workshop on
Computational Physics and Materials Science:
Total Energy and Force Methods**

11 - 13 January 2007

TDDFT: An overview

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TDDFT: An overview

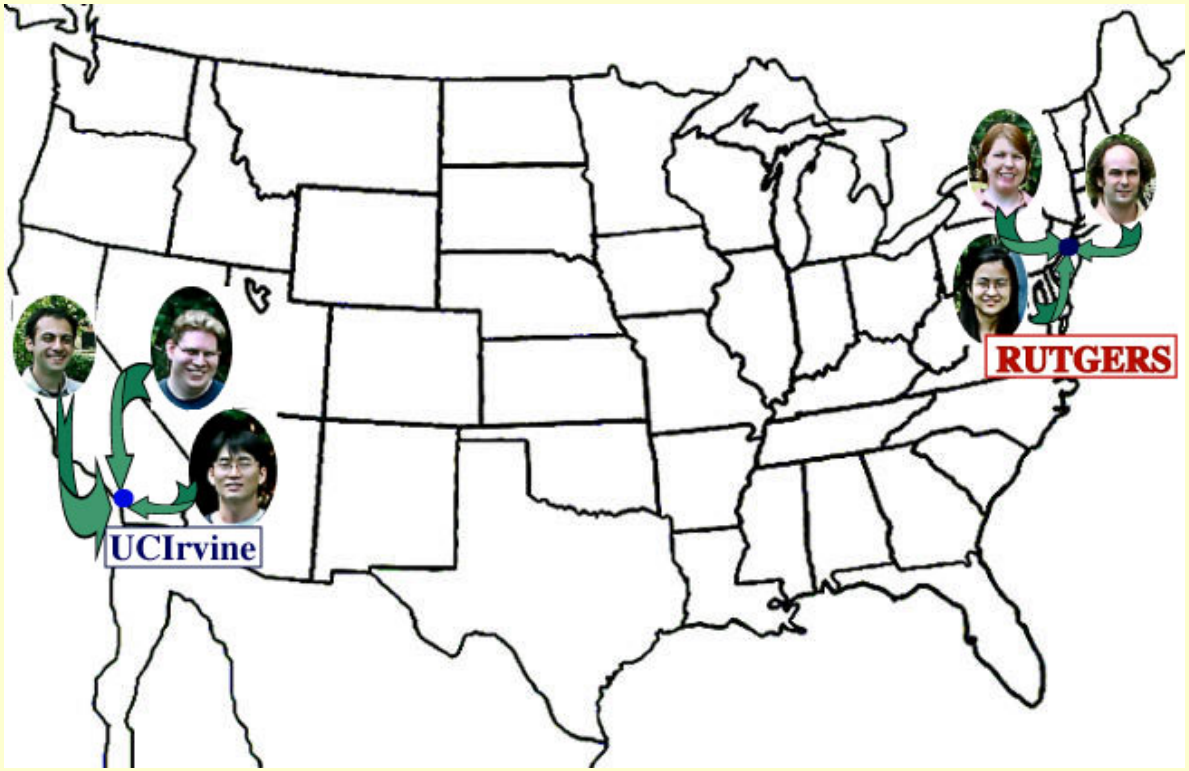
Kieron Burke and friends

Chemistry and Physics

UC Irvine

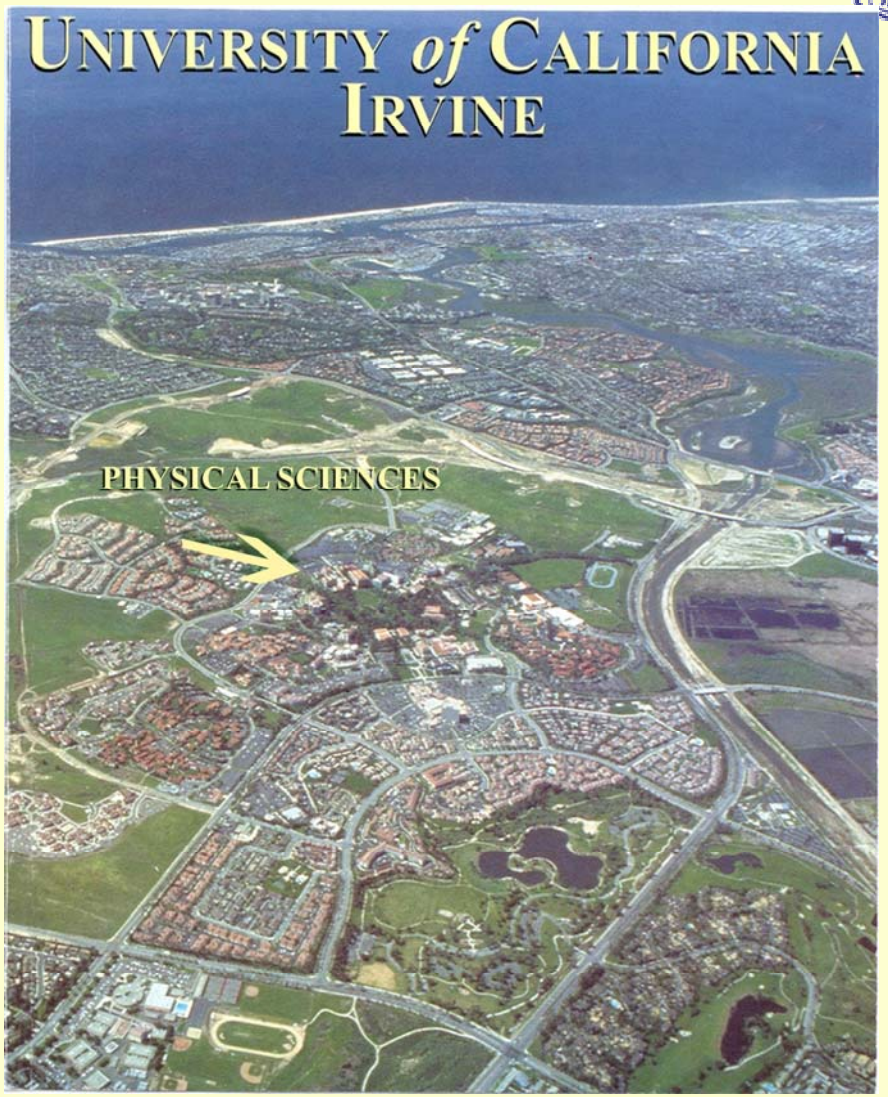
http://dft.ps.uci.edu

Fractured group



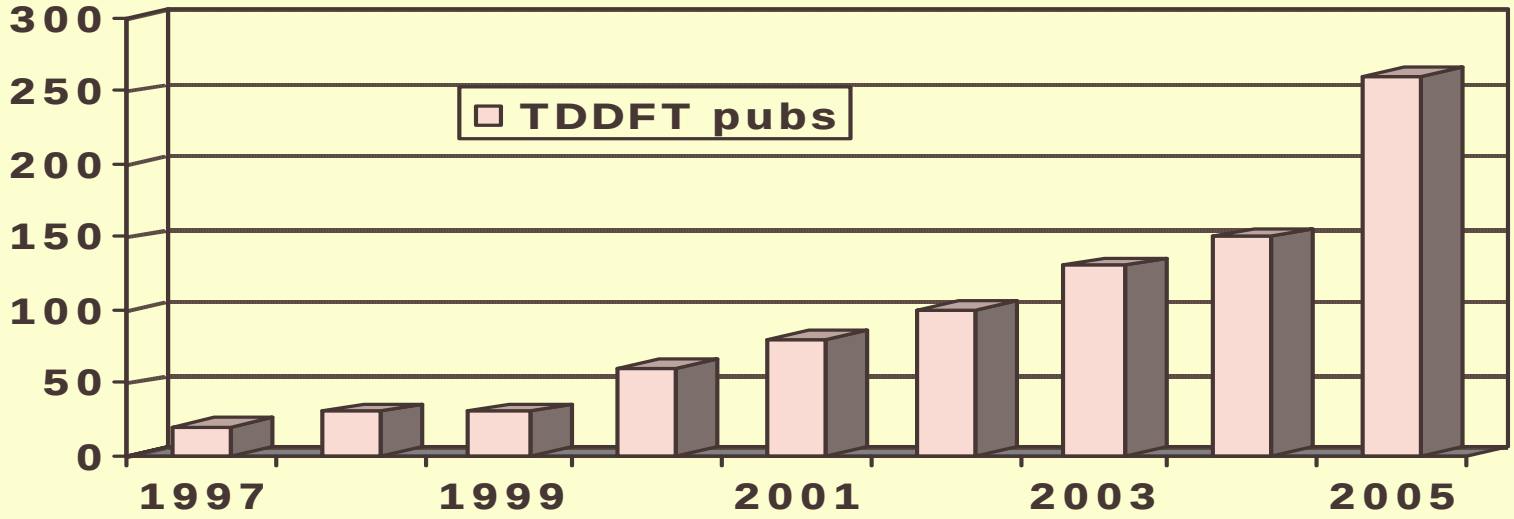
UC Irvine

- Growing theory in chemistry
- CHAMP=chem phys/cond mat program.
- Top 20 dept, working toward top 10.
- Huge opportunities for interaction.
- Housing guaranteed.



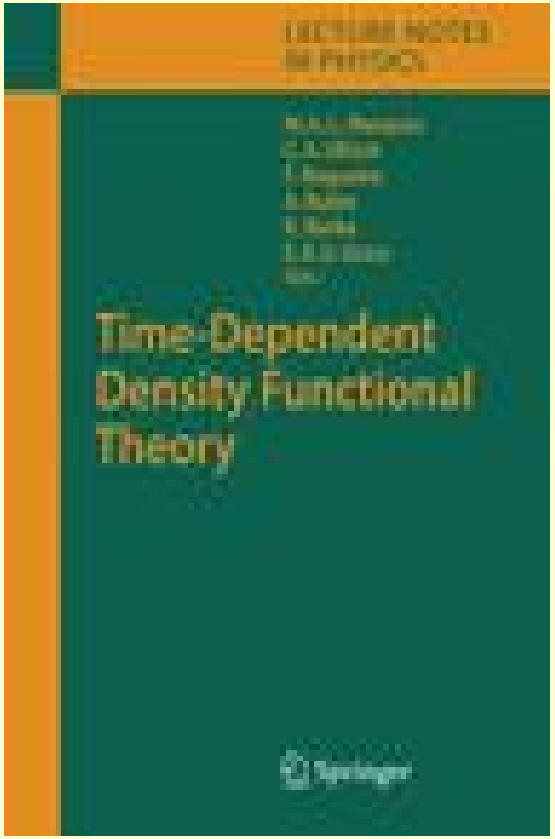
TDDFT publications in recent years

Search ISI web of Science for topic ‘TDDFT’



- Warning! By 2300, entire mass of universe will be TTDFT papers

Book: TDDFT from Springer



Recent reviews of TDDFT

(Some corrections may occur before final publication online and in print

Annu. Rev. Phys. Chem. 2004. 55:427–55
doi: 10.1146/annurev.physchem.55.091602.094449

TIME-DEPENDENT DENSITY FUNCTIONAL THEORY

M.A.L. Marques and E.K.U. Gross
Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany; email: marques@tddft.org, hardy@physik.fu-berlin.de

Key Words exchange-correlation functionals, linear response theory, optical absorption spectra, strong lasers

In *Computational Photochemistry*, edited by M. Olivucci, Elsevier, Amsterdam, 2005, in press.

Density functional methods for excited states: equilibrium structure and electronic spectra

Filipp Furche* and Dmitrij Rappoport

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THE JOURNAL OF CHEMICAL PHYSICS **122**, 1 (2005)

Time-dependent density functional theory: Past, present, and future

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(Received 18 August 2004; accepted 17 March 2005)

Time-dependent density functional theory (TDDFT) is presently enjoying enormous popularity in quantum chemistry, as a useful tool for extracting electronic excited state energies. This article discusses how TDDFT is much broader in scope, and yields predictions for many more properties. We discuss some of the challenges involved in making accurate predictions for these properties.
 [DOI: 10.1063/1.1904586]

Annual Reports in Comp Chem 1

Chapter XX. Time-dependent density functional theory in quantum chemistry

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New Gordon Conf 2007

2007 GRC on Time-Dependent Density-Functional Theory Page 1 of 1

Time-Dependent Density-Functional Theory

July 15-20, 2007
Colby College
Waterville, ME

Chairs: **Kieron Burke** & **Carsten A Ullrich**
Vice Chair: **Angel Rubio**

Time-dependent density-functional theory (TDDFT) provides an efficient, elegant, and formally exact way of describing the dynamics of interacting many-body quantum systems, circumventing the need for solving the full time-dependent Schrödinger equation. In the 20 years since it was first rigorously established in 1984, the field of TDDFT has made rapid and significant advances both formally as well as in terms of successful applications in chemistry, physics and materials science. Today, TDDFT has become the method of choice for calculating excitation energies of complex molecules, and is becoming increasingly popular for describing optical and spectroscopic properties of a variety of materials such as bulk solids, clusters and nanostructures. Other growing areas of applications of TDDFT are nonlinear dynamics of strongly excited electronic systems and molecular electronics.

The purpose and scope of this Gordon Research Conference is to provide a platform for discussing the current state of the art of the rapidly progressing, highly interdisciplinary field of TDDFT, to identify and debate open questions, and to point out new promising research directions. The conference will bring together experts with a diverse background in chemistry, physics, and materials science, and will cover the following topics from the perspective of TDDFT:

- Fundamental framework and recent formal and computational developments
- Excitation energies and photochemistry of complex molecular systems
- Atoms and molecules in strong fields
- Dynamics and spectroscopy of clusters, nanocrystals and materials
- Polarizabilities and optical spectra of insulating solids
- Ultrafast spectroscopy and coherent control in chemistry and materials science
- Van der Waals interactions
- Transport through nanostructures, molecular electronics

Last Updated: **2/6/2006** by Jeff Carroll

Other recent work I'll not talk about

- Semiclassical scaling of density functionals (Perdew et al,KB, PRL 06)

- Negative atomic ions in DFT
  (Donghyung Lee & KB, in prep.)

Green fluorescent Protein

TDDFT approach for Biological Chromophores, Marques et al, Phys Rev Lett **90**, 258101 (2003)

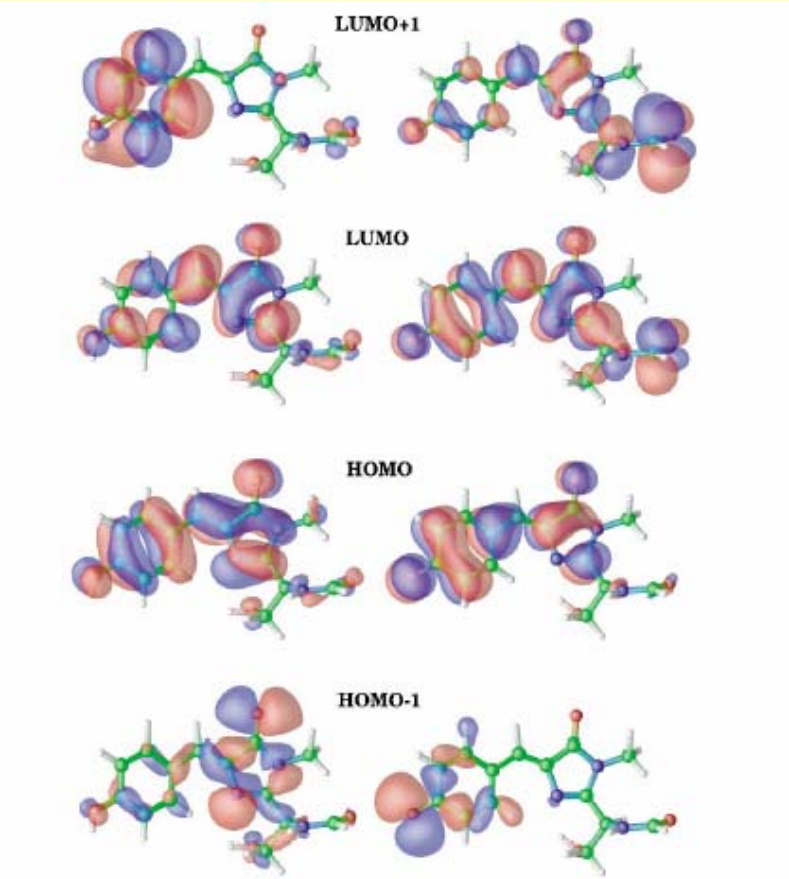


FIG. 3 (color). Kohn-Sham wave functions of the neutral (left) and anionic (right) GFP chromophores (red +, blue −). These are the most important states involved in the main collective excitation of Fig. 2, although the contribution of several other occupied and unoccupied states is not negligible.

Time-dependent DFT

- New theorem (Runge-Gross 1984) applied to time-dependent Schrödinger equation, showing potential a functional of $\rho(\mathbf{r},t)$.

- Define TD Kohn-Sham equations for independent electrons producing right $\rho(\mathbf{r},t)$.

TD Kohn-Sham equations

- Time-dependent KS equations:

$$\left\{-\frac{1}{2}\nabla^2 + v_S(\mathbf{r}t)\right\}\phi_i(\mathbf{r}t) = i\frac{d\phi_i(\mathbf{r}t)}{dt}$$

- Density:

$$\rho(\mathbf{r}t) = \sum_{i=1}^{N}\left|\phi_i(\mathbf{r}t)\right|^2$$

- XC potential:

$$v_S(\mathbf{r}t) = v_{\text{ext}}(\mathbf{r}t) + \int d^3r' \frac{\rho(\mathbf{r}'t)}{|\mathbf{r}-\mathbf{r}'|} + v_{\text{XC}}[n;\Psi(0),\Phi(0)](\mathbf{r}t)$$

Depends on entire history(MEMORY)

initial state(s) dependence(MEMORY)

Overview of ALL TDDFT

1. General Time-dependent Density Functional Theory

- Any e$^-$ system subjected to any $v_{\text{ext}}(\mathbf{r}t)$
- Only unknown: $v_{\text{XC}}[\rho](\mathbf{r}t)$
- Treat atoms and molecules in INTENSE laser fields

2. TDDFT linear response to weak fields

- Linear response: $\delta\rho(\mathbf{r}t) = \int d^3r' \int dt' \, \chi(\mathbf{r}\mathbf{r}', t-t') \, \delta v_{\text{ext}}(\mathbf{r}'t')$
- Only unknown: $v_{\text{XC}}(\mathbf{r}t)$ near ground state

$$v_{\text{XC}}[\rho_0 + \delta\rho](\mathbf{r}\omega) = v_{\text{XC}}[\rho_0](\mathbf{r}) + \int d^3r' \, f_{\text{XC}}[\rho_0](\mathbf{r}\mathbf{r}'\omega) \, \delta\rho(\mathbf{r}'\omega)$$

- Treat electronic excitations in atoms + molecules + solids

3. Ground-state Energy from TDDFT

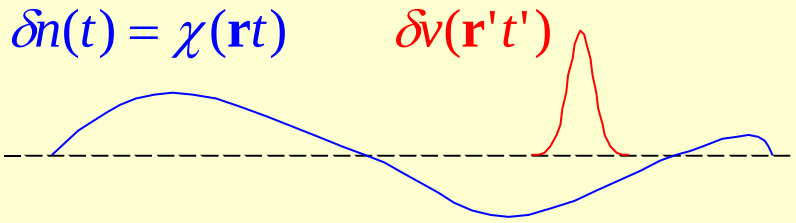
- Fluctuation–dissipation theorem: Exc from susceptibility
- Van der Waals; seamless dissociation

Basic approximation: ALDA $v_{\text{XC}}^{\text{unif}}(\rho(\mathbf{r}t))$

Linear response in TDDFT

Key quantity is susceptibility

$$\chi(\mathbf{r}\mathbf{r}', t-t') = \frac{\delta n(\mathbf{r}t)}{\delta v(\mathbf{r}'t')}$$



Dyson-like equation for a susceptibility:

$$\chi(\mathbf{r}\mathbf{r}', \omega) = \chi_S(\mathbf{r}\mathbf{r}'\omega) + \int d^3r_1 \int d^3r_2\, \chi_S(\mathbf{r}\mathbf{r}_1\omega) \left\{ \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + f_{XC}[\rho_0](\mathbf{r}_1\mathbf{r}_2\omega) \right\} \chi(\mathbf{r}_2\mathbf{r}'\omega)$$

Two inputs: KS susceptibility

$$\chi_S(\mathbf{r}\mathbf{r}', \omega) = \sum_{jk} (f_k - f_j) \frac{\phi_j(\mathbf{r})\phi_k^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_j(\mathbf{r}')}{\omega - (\varepsilon_j - \varepsilon_k) + i0_+}$$

and XC kernel

$$f_{XC}(\mathbf{r}, \mathbf{r}', t-t') = \delta v_{XC}(\mathbf{r}, t) \Big/ \delta\rho(\mathbf{r}', t')$$

TDDFT linear response

- Probe system with AC field of freq ω
- Ask at what ω you find a self-sustaining response
- That's a transition frequency!
- Need a new functional, the XC kernel, $f_{xc}[\rho_0](\mathbf{r},\mathbf{r}',\omega)$
- Almost always ignore ω-dependence (called adiabatic approximation)
- Can view as corrections to KS response

Success of TDDFT for excited states

- Energies to within about 0.4 eV
- Bonds to within about 1%
- Dipoles good to about 5%
- Vibrational frequencies good to 5%
- Cost scales as N^2, vs N^5 for CCSD
- Available now in your favorite quantum chemical code

TABLE III: Performance of various density functionals for the first six singlet excitation energies (in eV) of naphthalene. An aug-TZVP basis set and the PBE/TZVP/RI ground state structure was used. The "best" estimates of the true excitations were from experiment and calculations, as described in text.

Method	$1\,^1B_{3u}$	$1\,^1B_{2u}$	$2\,^1A_g$	$1\,^1B_{1g}$	$2\,^1B_{3u}$	$1\,^1A_u$
Pure density functionals						
LSDA	4.191	4.026	5.751	4.940	5.623	5.332
BP86	4.193	4.027	5.770	4.974	5.627	5.337
PBE	4.193	4.031	5.753	4.957	5.622	5.141
Hybrids						
B3LYP	4.393	4.282	6.062	5.422	5.794	5.311
PBE0	4.474	4.379	6.205	5.611	5.889	5.603
"best".	4.0	4.5	5.5	5.5	5.5	5.7

TABLE IV: Performance of various wavefunction methods for the excitations of Table I. The aug-TZVP basis set and the PBE/TZVP/RI ground state structure was used for all except the CASPT2 results, which were taken from Ref. [185]. Experimental results are also from Ref. [185].

Method	$1\,^1B_{3u}$	$1\,^1B_{2u}$	$2\,^1A_g$	$1\,^1B_{1g}$	$2\,^1B_{3u}$	$1\,^1A_u$
CIS	5.139	4.984	7.038	6.251	6.770	5.862
CC2	4.376	4.758	6.068	5.838	6.018	5.736
CASPT2	4.03	4.56	5.39	5.53	5.54	5.54
expt.	3.97, 4.0	4.45, 4.7	5.50, 5.52	5.28, 5.22	5.63,5.55 5.89	
"best".	4.0	4.5	5.5	5.5	5.5	5.7

TDDFT results for vertical singlet excitations in Naphthalene

Elliot, Furche, KB, Reviews Comp Chem, sub. 07.

Methodology for TDDFT

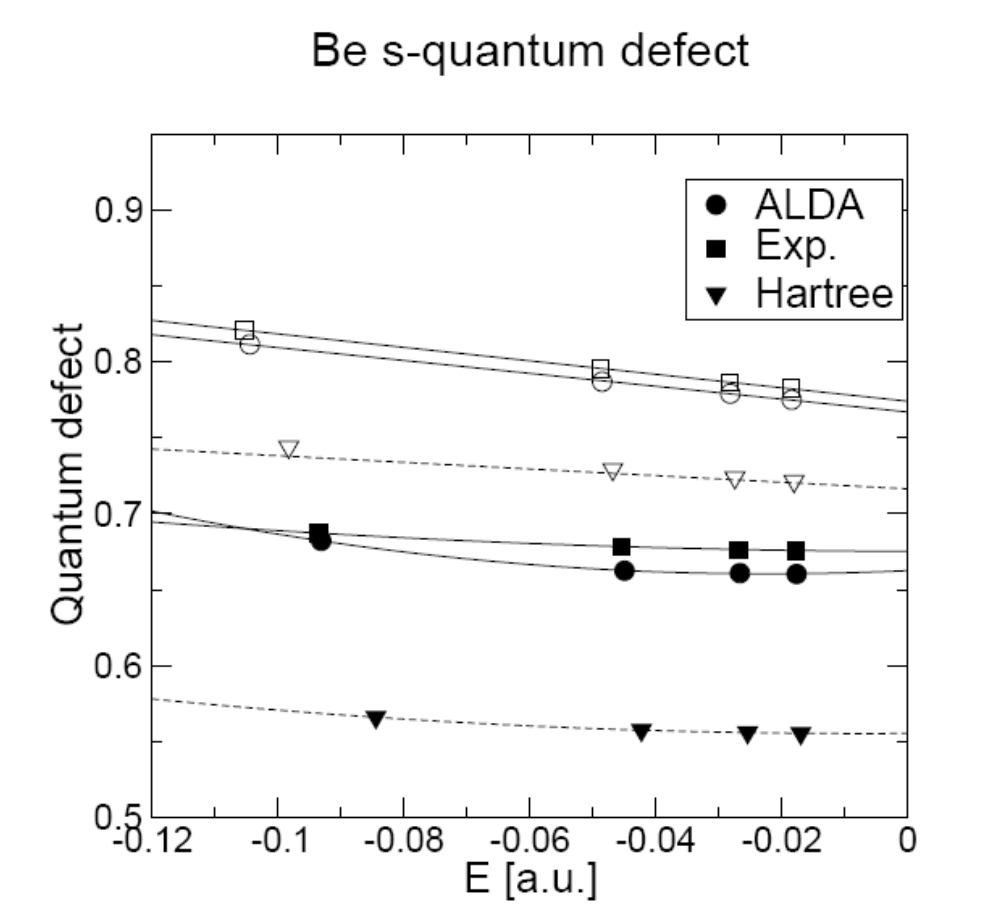
- In general: Propagate TDKS equations forward in time, and then transform the dipole moment, eg. Octopus code

- Linear response: Convert problem of finding transitions to eigenvalue problem (Casida, 1996).

General notes

- Most papers are lin resp, looking at excitations: need gs potential, plus kernel
- Severe problems with Rydbergs
- Lots of physics explored with non-standard functionals
- Simple generalization to current TDDFT

Does TDDFT really work?



Open symbols are triplet, closed are singlet; all using exact ground-state potential; Meta van Faassen + KB, in prep.

Complications for solids

- Locality of XC approximations implies no corrections to (g=0,g'=0) RPA matrix element in thermodynamic limit!*
- $f_H = 1/|\mathbf{r}-\mathbf{r}'|$, but $f_{xc}^{ALDA} = \delta^{(3)}(\mathbf{r}-\mathbf{r}')\, f_{xc}^{unif}(n(\mathbf{r}))$
- As q->0, need $q^2\, f_{Hxc}$ -> constant to get effects.

*Thanks to Lucia Reining for pointing out error in original statement.

New functionals

- Current-density functionals
  - Gross-Kohn (96): Gradient expansion in current
  - Various attempts to generalize

- Orbital-dependent functionals
  - Build in exact exchange, good potentials, no self-interaction error, improved gaps(?),...

Improvements for solids: currents

- Current-dependence: Snijders, de Boeij, et al – improved optical response via ‘adjusted’ VK
  - Also yields improved polarizabilities of long chain conjugated polymers.
  - Can relate to modern theory of polarization (Maitra, Souza, KB, PRB 03).

Other features of Vignale-Kohn

- Provides XC correction to current in molecular electronics
- Finite lifetime to plasmons in double quantum wells
- But wrongly gives finite lifetime to electronic transitions in molecules
  (Ullrich + KB, JCP 04)

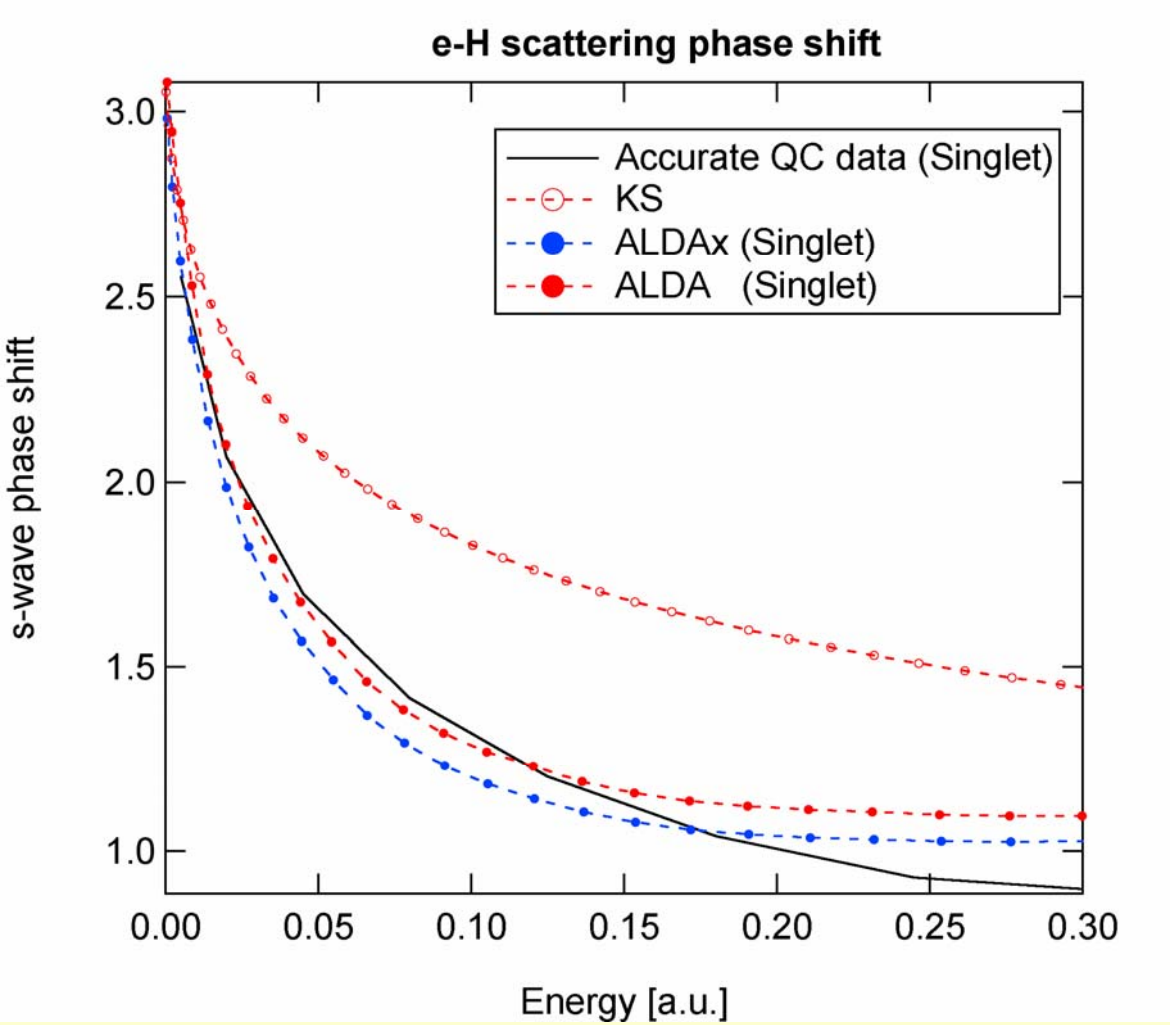
Solids: orbital-dependence

- Reining, Rubio, etc.
- Find what terms needed in f_{xc} to reproduce Bethe-Salpeter results.
- Reproduces optical response accurately, especially excitons, but not a general functional.

Much recent work

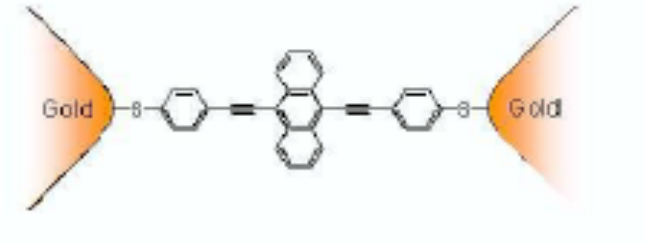
- Double excitations
- Understanding how it works
- X-ray spectra
- Rydberg series from LDA potential
- Errors in DFT for transport
- Failure for charge transfer excitations
- Elastic electron-atom scattering
- Quantum control
- Double ionization in He in strong fields
- ...

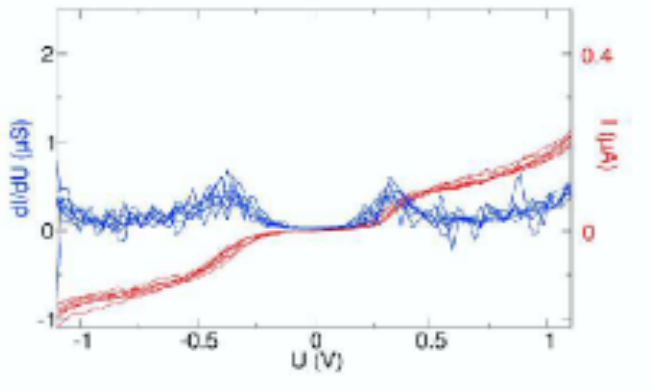
Singlet scattering from H



Meta van Faassen's most recent results

Break junction expts





Experiments:

H. Weber, R. Ochs, J. Reichert,

M. DiLeo, J. Würfel, INT Research Center Karlsruhe

PRL 88, 176804 (2002); PNAS 102, 8815 (2005)

Simple view of single-molecule transport

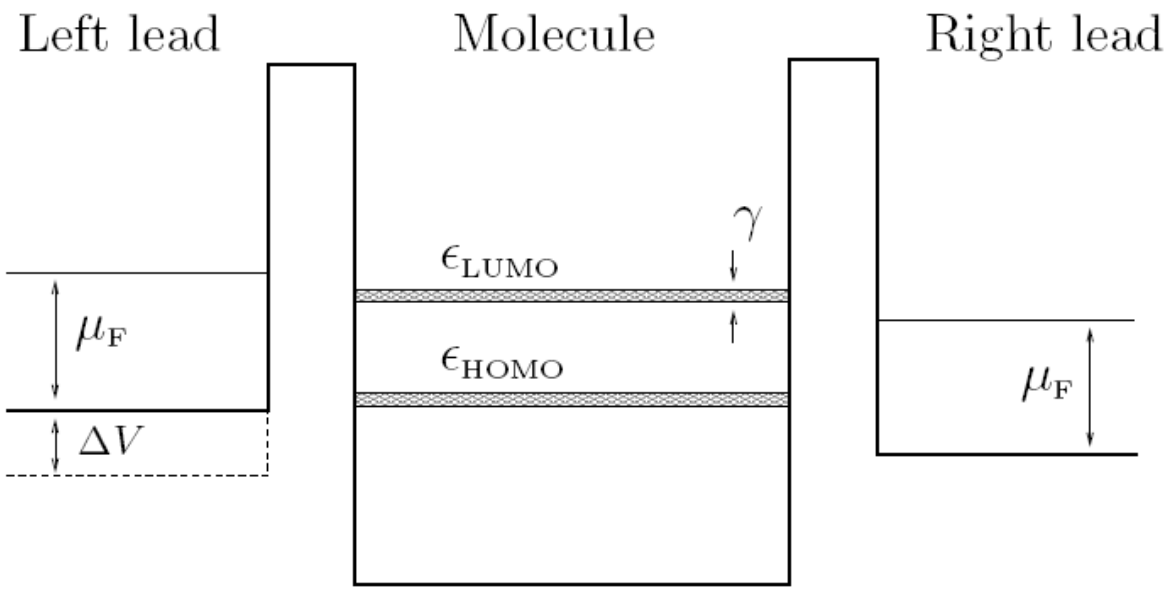
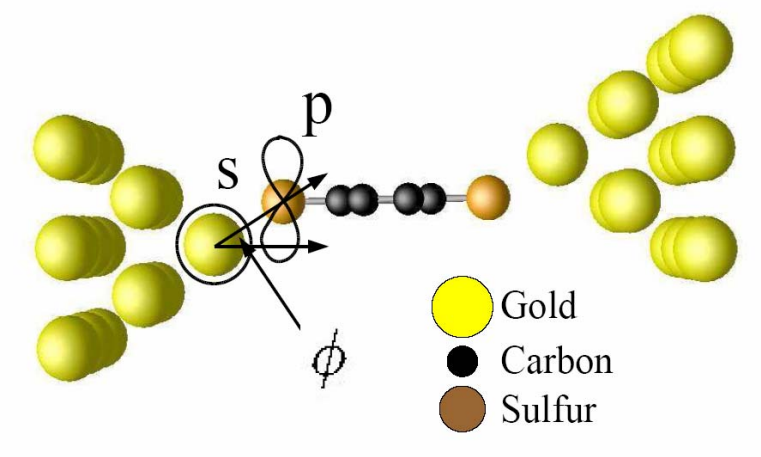


FIG. 1: Schematic of the potential of a resonant tunneling device with the LUMO level of the device molecule sandwiched between the Fermi levels of the leads which are shifted relative to each other by an applied bias voltage ΔV. When $\Delta V = 0$, the chemical potential is μ_F. The LUMO and HOMO levels have a small width γ, indicating weak coupling to the leads.

Chang, Koentopp, KB, and Car, in prep, JPhysB

Orbital-dependent calculations

Tohar, Filipetti, Sanvito, and KB (PRL, 05).



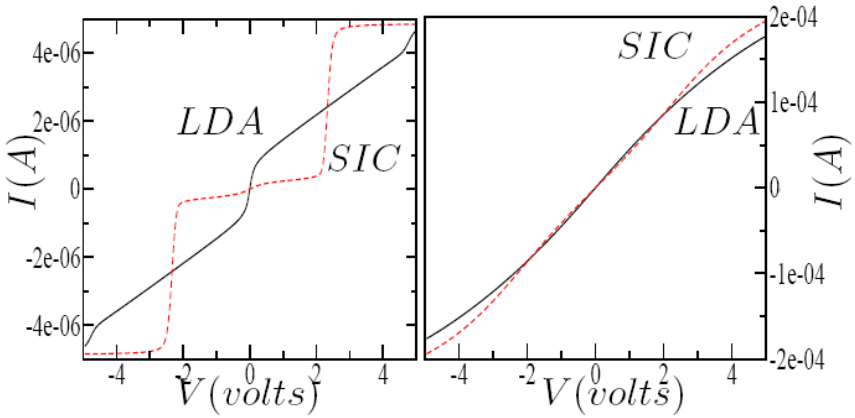


FIG. 11: Current of a single energy level coupled to two metallic leads as a function of bias. Left figure corresponds to the case of weak coupling and right figure corresponds to the case of strong coupling. Solid lines are results for LDA and the dotted lines are results using self-interaction corrected LDA (LDA-SIC). From ref. [51].

- For weak coupling, see much lower conductance when SIC turned on.

Weak bias results

(Koentopp, Evers, Burke, PRB 05)

- As $\omega \to 0$, σ_s indep of **r**,**r'** and -> $T_s(\varepsilon_F)$.

$$\delta j(\mathbf{r}\omega) = \int d^3r' \sigma_s(\mathbf{r}\mathbf{r}'\omega) \bullet (\mathrm{E}_{ext}(\omega) + \mathrm{E}_H(\mathbf{r}'\omega) + \mathrm{E}_{xc}(\mathbf{r}'\omega))$$

Becomes

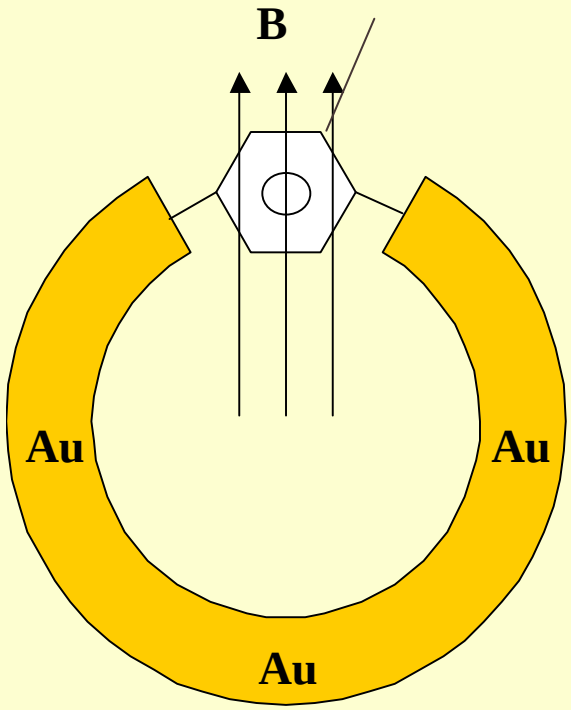
$$\delta I(\omega = 0) = \frac{T_s(\varepsilon_F)}{\pi} \int d^3r' (\mathrm{E}_{ext}(\omega) + \mathrm{E}_H(\mathbf{r}'\omega) + \mathrm{E}_{xc}(\mathbf{r}'\omega))$$

Compare with

$$I = \frac{1}{\pi} \int_{\mu}^{\mu+V} d\varepsilon \, T_s(\varepsilon, V) \left(f_L(\varepsilon) - f_R(\varepsilon) \right) = \frac{T_s(\varepsilon_F)}{\pi} V$$

Finite Electric Fields WITHOUT open boundaries (Burke, Gebauer, Car, PRL 05)

- Treats electric field in periodic potential correctly: no left and right chemical potentials
- No empirical parameters
- Leads chemically accurate (CP code)
- Entire problem becomes time-dependent, with no ground state, but only steady-state solutions
- So must have dissipation, including via DFT Master equation.



$$\mathbf{A} = -c\int_0^t dt'\mathbf{E}(t')$$

Master equation for dissipation

- $H = H_{el} + H_{ph} + K_{el\text{-}ph}$
- Assume relaxation time much longer than time for transitions or phonon periods
- Coarse-grain over electronic transitions and average over bath fluctuations
- Master equation for system density matrix:

$$\frac{dS}{dt} = -i[H, S] + C(S(t))$$

Kohn-Sham Master equation

- Define a Kohn-Sham Master equation yielding same $\rho(\mathbf{r},t)$ from $v_s(\mathbf{r},t)$, but choose C_s to equilibrate to the Mermin-Kohn-Sham $S_s(0)$

$$\frac{dS_s}{dt} = -i[H, S_s] + C_s(S_s(t))$$

Return to weak bias

- Usual Kubo calculation yields *adiabatic* conductivity
- Our approach produces true *isothermal* conductivity
- Can show, as C_s->0, it becomes $i\eta$ in Kubo formula

Summary

- TDDFT allows calculation of electronic excitations with DFT via linear response.
- Complications in solids as need nonlocality, using currents or orbitals
- New theories being developed for molecular electronics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Eye alt 3342.27 mi