



Time-dependent density functional theory in attoscience: Promises and Challenges

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Rutgers->UC Irvine

<http://dft.rutgers.edu/>
(DFT book, TDDFT book, Benasque)

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Theme

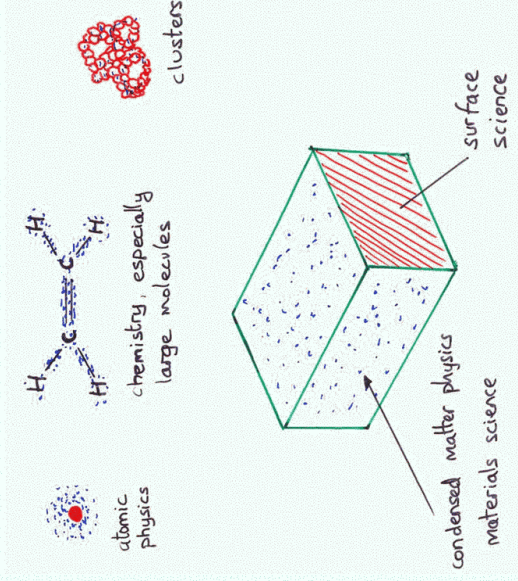
- DFT is method-of-choice for solids and large molecules
- TDDFT includes response to external TD fields
- Both enormously successful and popular
- So why aren't all calculations DFT?

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Ground-state DFT

What atoms, molecules, and solids exist, and what are their properties?

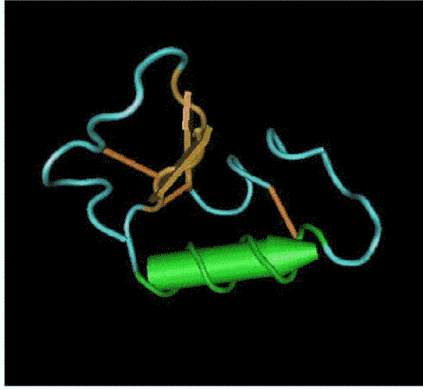


Ground-state DFT

- DFT is an utterly ALIEN way to treat interacting electrons.
- Many users, few developers.
- Often misleading, sometimes downright nasty
- But..
 - runs faster and is far more accurate than Hartree-Fock!

DFT possibilities

Crambin



GS energy 7:40 h
 GS gradient 1:58 h
 TURBOMOLE V5-7-1, RIDFT/TPSS/SV(P), 1.5
 GHz HP Itanium

645 atoms, 5587 basis functions

F. F., J. P. Perdew, *J. Chem. Phys.* **124** (2006), 0144103

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What are the Kohn-Sham equations?

- The Kohn-Sham equations (1965) are just the Schrödinger equation for fictitious, independent electrons
- In principle, they produce the exact density
- All modern DFT calculations are for these fictitious electrons, so NEVER find true wavefunction.

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Kohn-Sham equations (1965)

$$\left[-\frac{1}{2}\nabla^2 + v_s[\rho](\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

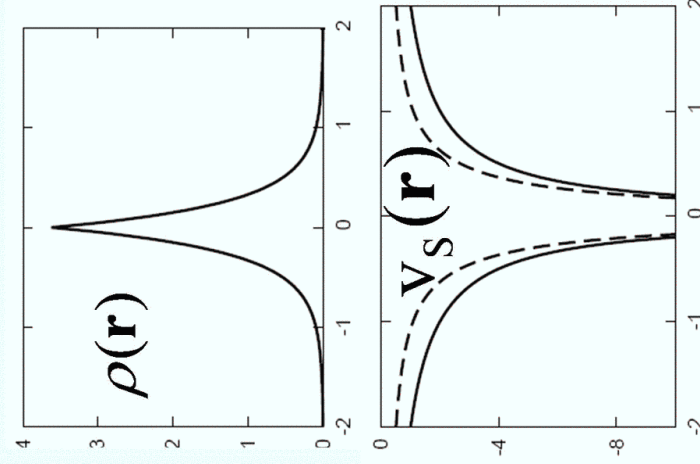
$$\rho(\mathbf{r}) = \sum_{i=1}^N |\phi_i(\mathbf{r})|^2 = \text{ground-state density of interacting system}$$

$$v_s(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{xc}}[\rho](\mathbf{r})$$

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He atom in Kohn-Sham DFT



Dashed-line:
EXACT KS
potential



In reality...

- Must approximate a small unknown piece of the functional, the exchange-correlation energy $E_{xc}[\rho]$.
- Early 90's:
 - Approximations became accurate enough to be useful in chemistry
 - 98 Nobel to Kohn and Pople

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Functional soup

- **Good:** choose one functional and stick with it (e.g., LDA or PBE or B3LYP).
- **Bad:** Run several functionals, and pick 'best' answer.
- **Ugly:** Design your own functional with 2300 parameters.

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Time-dependent DFT

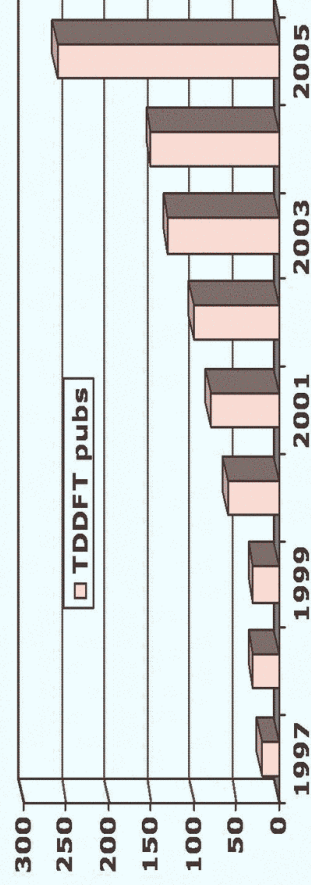
- New theorem (Runge-Gross 1984) applied to time-dependent Schrödinger equation, showing potential a functional of $\rho(\mathbf{r},t)$.
- Define TD Kohn-Sham equations for independent electrons producing right $\rho(\mathbf{r},t)$.

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TDDFT publications in recent years

Search ISI web of Science for topic 'TDDFT'

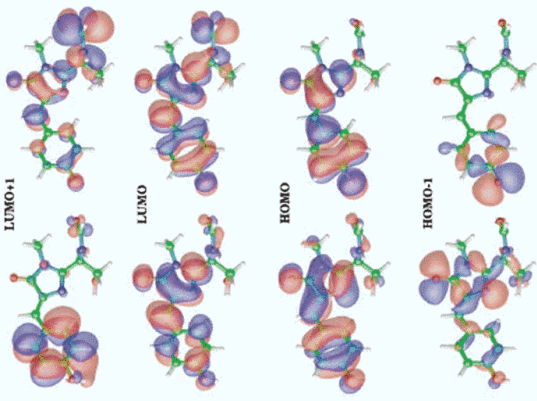


- Warning! By 2300, entire mass of universe will be TDDFT papers



Green fluorescent Protein

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




LUMO+1
LUMO
HOMO
HOMO-1


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.

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Recent reviews of TDDFT



(Some corrections may occur before final publication online and in print.)
 Ann. Rev. Phys. Chem. 2004. 55:427-55.
 DOI: 10.1146/annurev.physchem.55.020104.085537
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TIME-DEPENDENT DENSITY FUNCTIONAL THEORY

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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
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THE JOURNAL OF CHEMICAL PHYSICS 121, 1 (2005)

3F COPY 708522JCP

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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 reviews the current status of TDDFT, its strengths and weaknesses, and the challenges ahead. We discuss some of the challenges involved in making accurate predictions for these properties. © 2005 American Institute of Physics. [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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 Department of Chemistry and Chemical Biology, Rutgers University, 610 Taylor Rd., Piscataway, NJ 08854, USA

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Recent mug shot



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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 14-20, 2007
 Coxy College
 Vintonville, NC

Chair: Kieron Burke & Charles A. Ulrich
 Vice Chair: Aiguo Jitianu

Time-dependent density functional theory (TDDFT) provides an efficient, elegant, and formally exact way of solving the many-body Schrödinger equation. In the 20 years since it was first rigorously established in 1984, the field of TDDFT has grown rapidly, with applications in chemistry, physics and materials science. Today, TDDFT has become the method of choice for calculating the ground state and excited state electronic structure of molecules and materials. 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 field, to present new results, and to point out new promising research directions. The conference will bring together experts with a broad 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
- Dynamics and spectroscopy of solids, nanocrystals and materials
- Frustrated and other spectra of insulating solids
- Applications of TDDFT to the study of molecular electronics and materials science
- Van der Waals interactions
- Transport through nanocrystals, molecular electronics



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Last Updated: 2/20/06 by Jeff Carroll

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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:

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

- 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 $v_{\text{XC}}^{\text{unif}}(\rho(\mathbf{r}t))$



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

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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

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

and XC kernel

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



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).

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Success of TDDFT for excited states

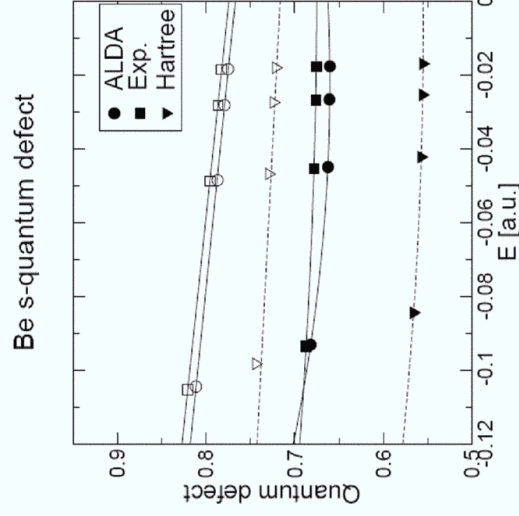
- Energies to within about 0.4 eV
- Bonds to within about 1%
- Dipoles good to about 5%
- Vibrational frequencies good to 5%
- Cost scales as N^2 , vs N^5 for CCSD
- Available now in your favorite quantum chemical code

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TDDFT from exact KS potential



Open symbols
are triplet,
closed
are singlet.

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Strong fields: Promises and challenges

1. HHG seems to work well, but need orbital dependent potentials.
2. Difficulty with eg multiple ionization.

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Simple problem with ground-state potential

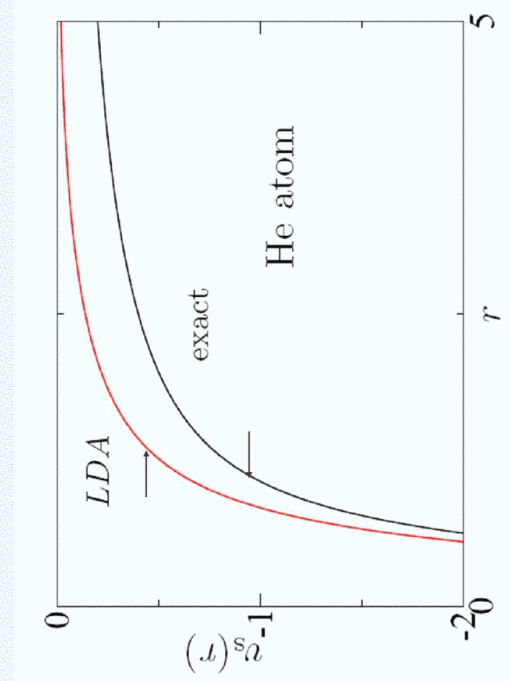
- Density functionals usually have bad potentials!
- Orbital-dependent functionals are much better.

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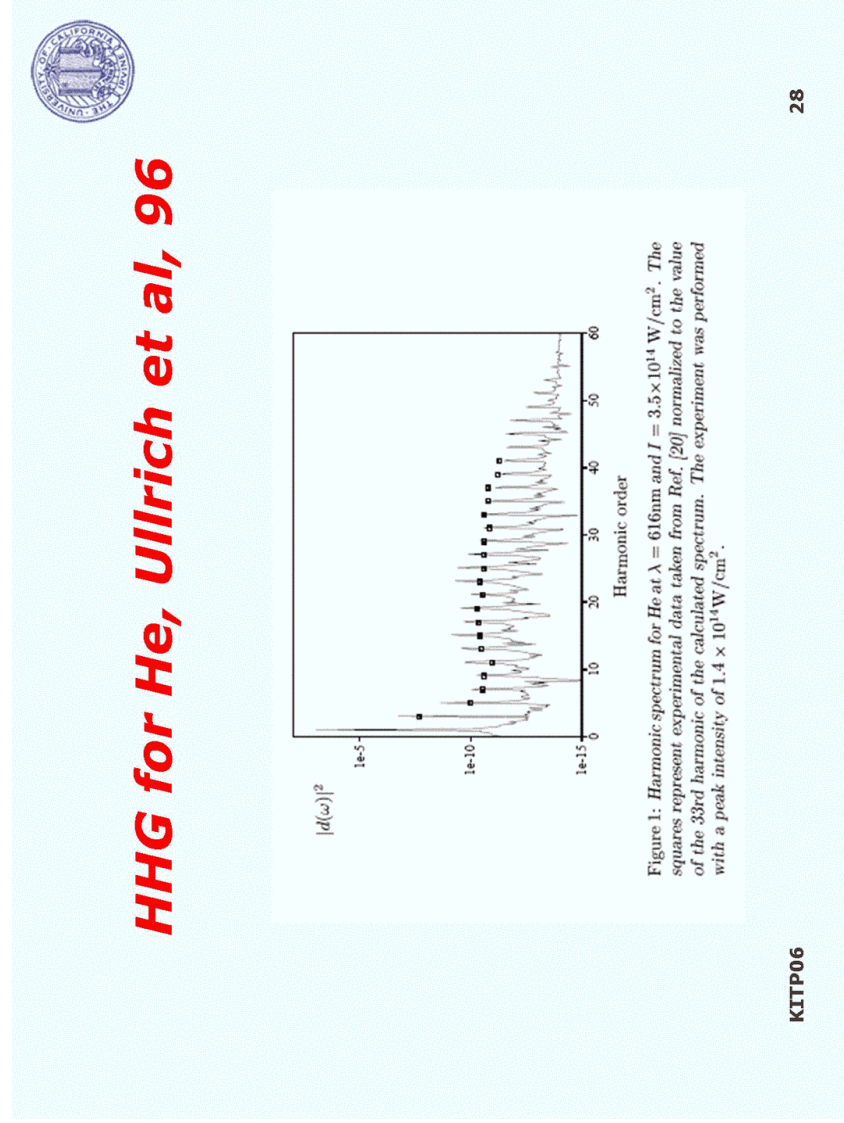
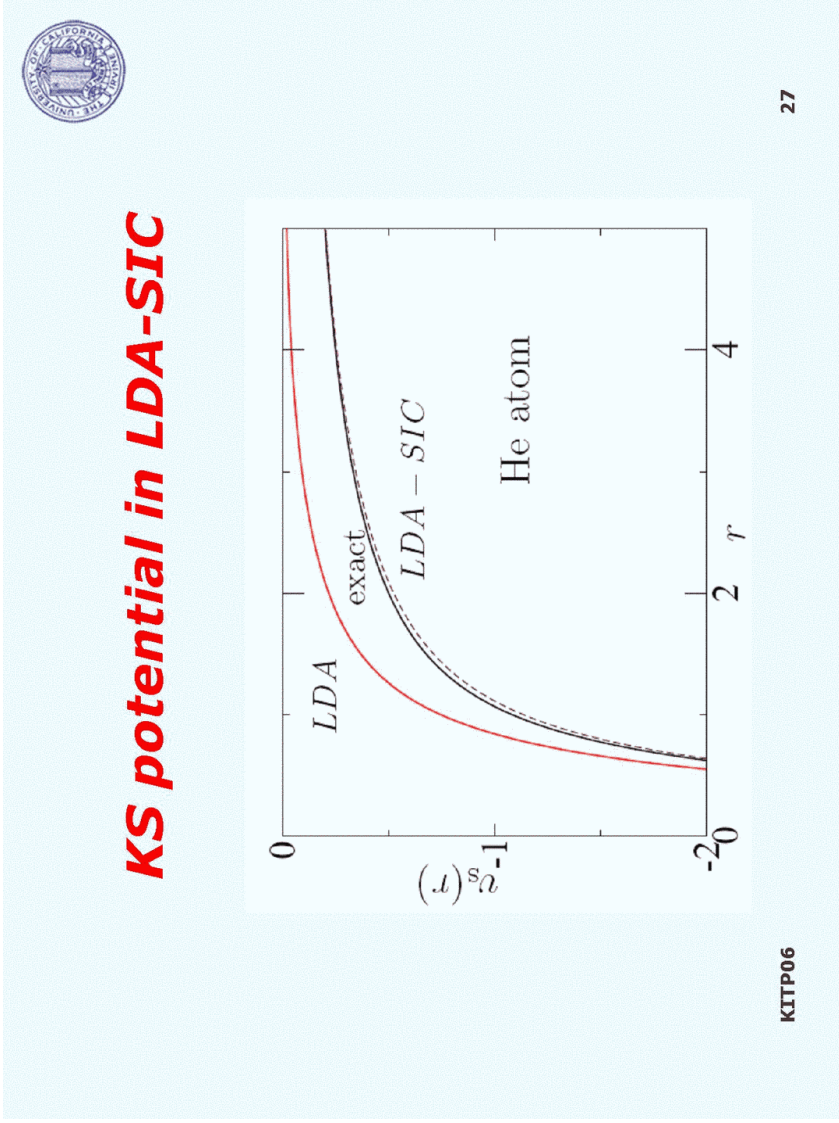


KS potential in LDA



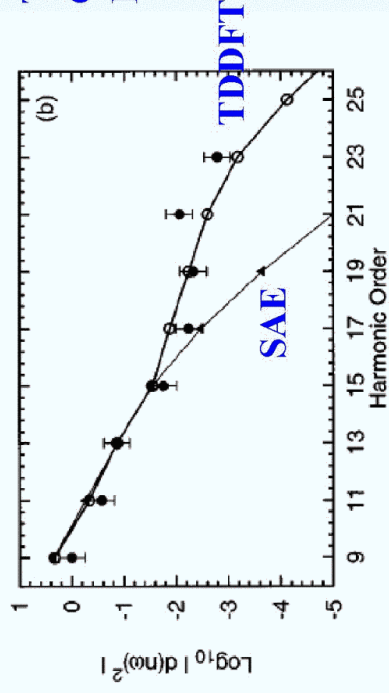
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Improvement over SAE

HHG in He atom, $\lambda=246\text{nm}$, $I=3\times 10^{15}\text{W/cm}^2$



Tong and
Chu,
PRA 1998

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Two key differences for multiple ionization

- The XC potential, far from the ground-state, is not well-approximated by standard functionals.
- The KS wavefunction can be very different from the true wavefunction.

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Pumping to an excited state

- Imagine exact TDKS in which He atom is pumped into 2p excited state.
- But ALWAYS stays in single doubly-occupied orbital.
- If stationary, KS potential is highly non-spherical (Maitra et al PRL 2002).

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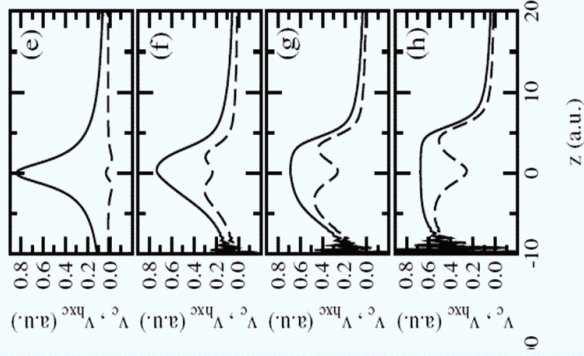
Exact KS potential for multiple ionization

- Do exact calculation, and invert TDKS equations (Hessler et al, PRL 99) to find $v_s(\mathbf{r},t)$.
- See what's going on, and try to approximate.

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TDKS potential during ionization



From Lein and Kummel, PRL 05: Step in correlation potential as one electron leaves

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Multiple ionization from model TDKS potential

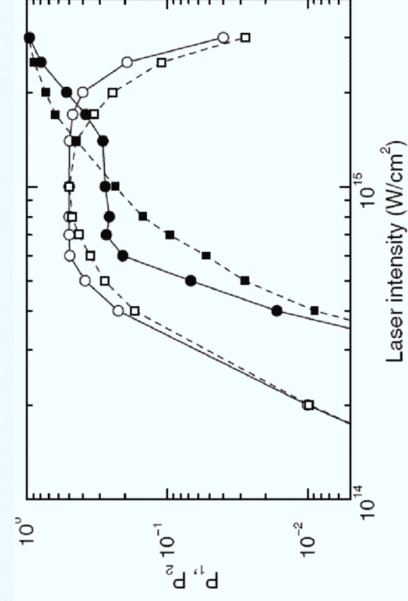


FIG. 3. Probabilities for laser-induced single- ionization (open symbols) and double ionization (filled symbols) from TDDFT (circles) and TDHF (squares) calculations.

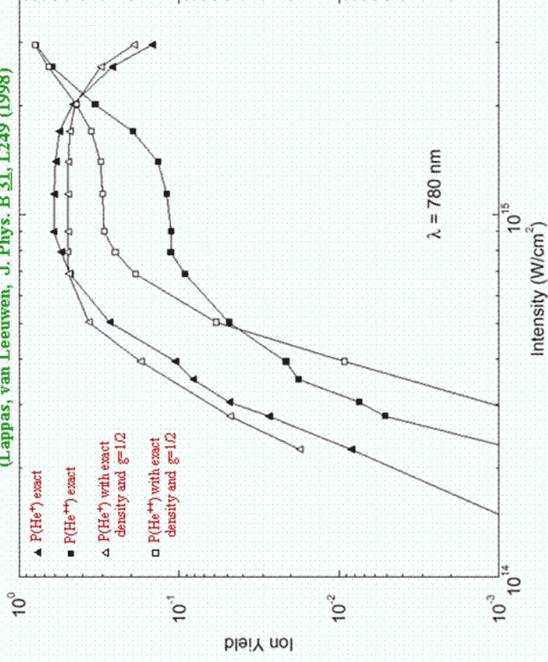
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But...still not accurate!

1D Helium atom (with soft Coulomb interaction)

(Lappas, van Leeuwen, J. Phys. B **31**, L249 (1998))



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In the meantime...

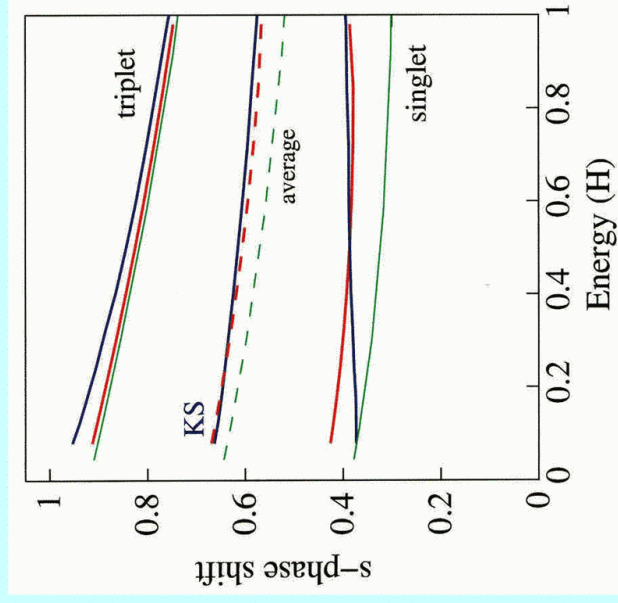
- Margaret Murnane showed neat results for probing molecular vibrations using HHG.
- Zac Walters did calculation for intensities, using static-exchange for scattering in recombination step, showing how all modes comparable.

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TDDFT lin. resp. results

e-He⁺ scattering



“Exact” from T. T. Gien,
J.Phys. B: At. Mol. Opt. Phys.
35, 4475 (2002); A.K. Bhatia,
Phys. Rev. A **66**, 064702
(2002).

Static Exchange
from R.R. Lucchese and V.
McKoy, Phys. Rev. A, **21**, 112
(1980).

TDDFT, present work:
A. Wasserman, N.T. Maitra, and
K. Burke, see [JCP 2005](#)



Ideas

- Build on good results from linear response, eg scattering theory. Where can they be used inside more demanding calculations?
- Use dipole matrix elements from lin. resp. in strong field calculations (Jan Werschnik, Berlin, for quantum control)
- A thought: almost always want evolution in same time-dependent field (an electric field).



Lessons

- DFT best when physics is understood, but computational accuracy is crucial.
- Whenever DFT used in new field, must take present approximations, and see what works and what doesn't.
- For failures, usually can rationalize why they fail, but can take a while to see how to build physics into better functionals.
- But, most important, its absolutely necessary for interface with all other DFT calculations/experience.

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Tricks: eg, double excitations

- In linear response, can show adiabatic approximation only includes single-excitations.
- We showed how to construct $f_{xc}(\omega)$ to yield doubles.
- New TDDFT ideas should be tested in linear regime.

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Unlikely, but not impossible



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