Time-dependent density-functional theory for strong-field electron dynamics

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Outline

1. TDDFT in a nutshell

2. Observables and Applications
   - Atoms in strong fields
   - Nonlinear electron dynamics in metal clusters
   - The Helium knee: worst-case scenario for TDDFT

3. The time-dependent xc potential
   - Asymptotic behavior
   - Discontinuity
   - Beyond the adiabatic approximation

Static and time-dependent density-functional theory

Hohenberg and Kohn (1964): $n(\vec{r}) \Longleftrightarrow v(\vec{r})$

All physical observables of a static many-body system are, in principle, functionals of the ground-state density $n(\vec{r})$.

➡ most modern electronic-structure calculations use DFT.

Runge and Gross (1984): $n(\vec{r},t) \Longleftrightarrow v(\vec{r},t)$

Time-dependent density $n(\vec{r},t)$ determines, in principle, all time-dependent observables.

➡ TDDFT: universal approach for electron dynamics.

Time-dependent Kohn-Sham equations (1)

Instead of the full N-electron TDSE,

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r}_1,...,\vec{r}_N,t) = \left(\hat{T}+\hat{V}_{ext}(t)+\hat{W}_{e-e}\right)\Psi(\vec{r}_1,...,\vec{r}_N,t)$$

one can solve N single-electron TDSE's,

$$i\hbar\frac{\partial}{\partial t}\varphi_j(\vec{r},t) = \left(-\frac{\hbar^2\nabla^2}{2m}+V_{KS}(\vec{r},t)\right)\varphi_j(\vec{r},t)$$

such that the time-dependent densities agree:

$$\int dr_2 ... \int dr_N \left|\Psi(\vec{r},\vec{r}_2,...,\vec{r}_N,t)\right|^2 = n(\vec{r},t) = \sum_{j=1}^{N}\left|\varphi_j(\vec{r},t)\right|^2$$

Time-dependent Kohn-Sham equations (2)

The TDKS single-particle effective potential is

$$V_{KS}(\vec{r},t) = V_{ext}(\vec{r},t) + \int dr' \frac{n(\vec{r}',t)}{|\vec{r}-\vec{r}'|} + V_{xc}[n](\vec{r},t)$$

Hartree

exchange-correlation

$V_{xc}[n](\vec{r},t)$ is an (unknown) functional of the density, which needs to be approximated (more later).

The TDKS equations give the exact density, but not the wave function!

$$\Phi_{KS}(\vec{r}_1,...,\vec{r}_N,t) = \frac{1}{\sqrt{N}} \det\{\varphi_j(\vec{r}_j,t)\} \neq \Psi(\vec{r}_1,...,\vec{r}_N,t)$$

TDDFT: a 3-step process

1. Prepare the initial state, usually the ground state, by a static DFT calculation. This gives the initial orbitals: $\varphi_j(\vec{r},0)$

2. Solve TDKS equations self-consistently, using an approximate time-dependent xc potential which matches the static one used in step 1. This gives the TDKS orbitals: $\varphi_j(\vec{r},t) \rightarrow n(\vec{r},t)$

3. Calculate the relevant observable(s) as a functional of $n(\vec{r},t)$

"Easy" and "tough" observables in TDDFT

Easy

- Dipole moment: $d(t) = \int dr \; z\, n(\vec{r},t)$

  $\Longrightarrow$ HHG power spectrum: $|d(\omega)|^2$

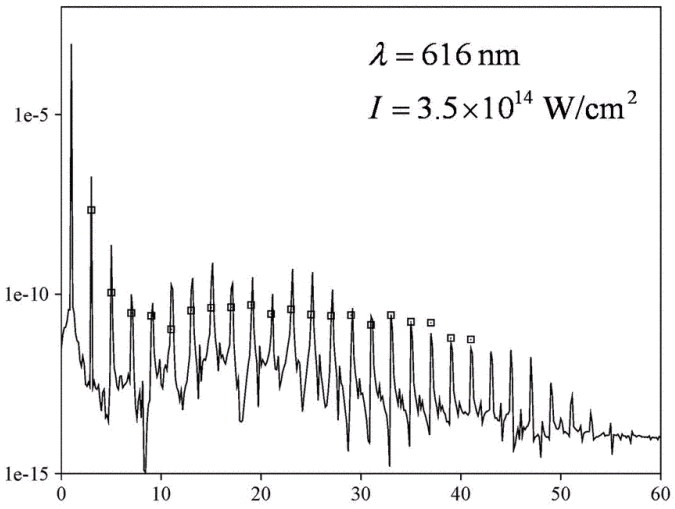
- Total number of escaped electrons:

$$N_{esc}(t) = N - \int_{box} dr \; n(\vec{r},t)$$

More difficult

- Photoelectron spectra and ATI
- Ion probabilities
- Transition probabilities $|S_{i\to f}|^2$ (J. Burgdörfer)

HHG in Helium (3D)



Calculation: TDDFT exact exchange
(C.A.U., S. Erhard, E.K.U. Gross, 1996)
Experiment: Miyazaki and Sakai (1992)

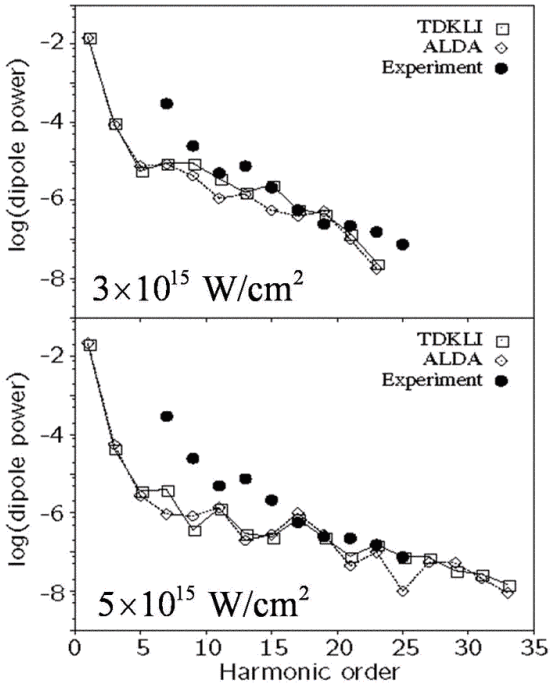
HHG in Neon: all-electron calculation

$\lambda = 248\,\text{nm}$

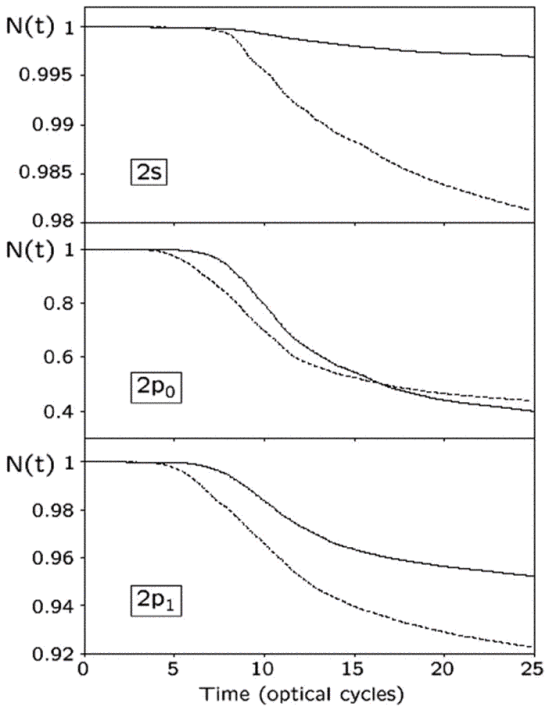
Experiment: Sarukura et al., PRA **43**, 1669 (1991) at 4×10^{17} W/cm^2

TDKS calculation for all outer-shell orbitals.

C.A.U. and E.K.U. Gross, Comments At. Mol. Phys. **33**, 211 (1997)



Neon: Kohn-Sham orbital norms



$\lambda = 248\,\text{nm}$

$I = 3\times10^{15}$ W/cm^2

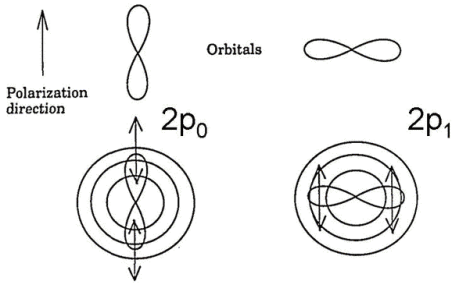
$$N_j(t) = \int_{box} dr\,\left|\varphi_j(\vec{r},t)\right|^2$$

——— TDKLI ("exact" exchange)

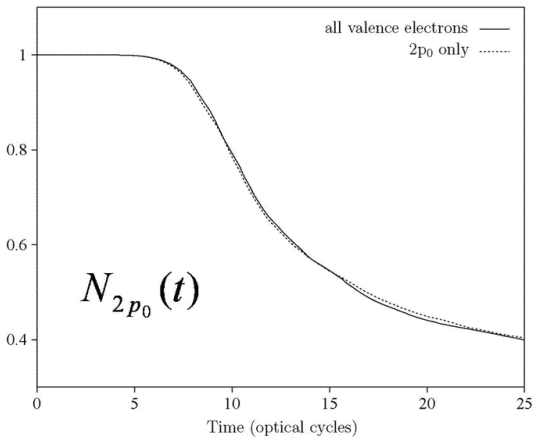
····· ALDA

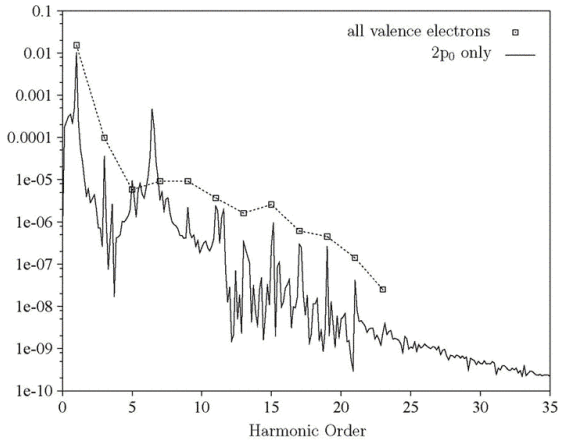
The KS orbital norms have no rigorous physical meaning, but can be a useful diagnostic tool.

Neon: failure of the SAE approximation

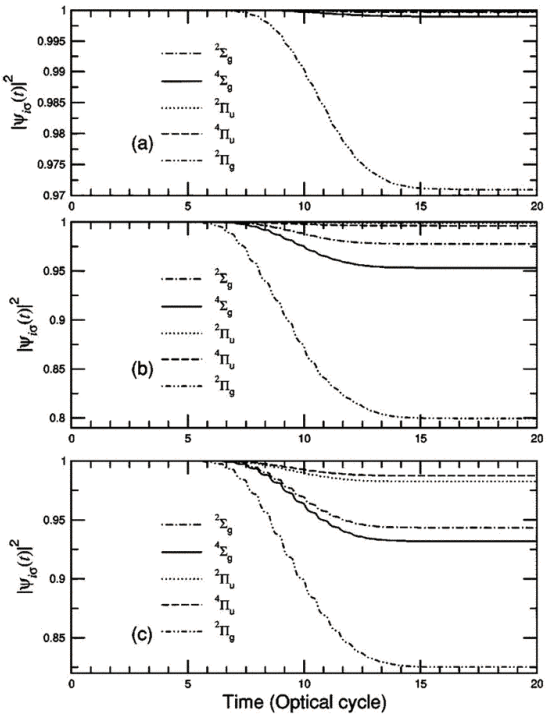


$2p_0$ orbital dominates ionization and HHG, but gives spurious resonance





Diatomic molecules



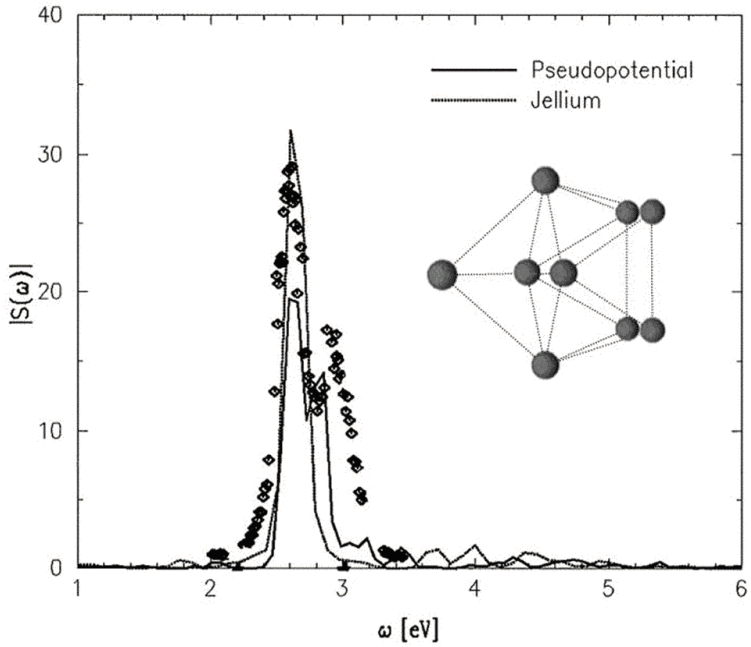
O_2, fixed nuclei, 800 nm pulses,

$1x10^{14}$, $3x10^{14}$, $5x10^{14}$ W/cm^2

X. Chu and S.-I Chu
PRA **63**, 023411 (2001)
PRA **64**, 063404 (2001)
PRB **70**, 061402 (2004)

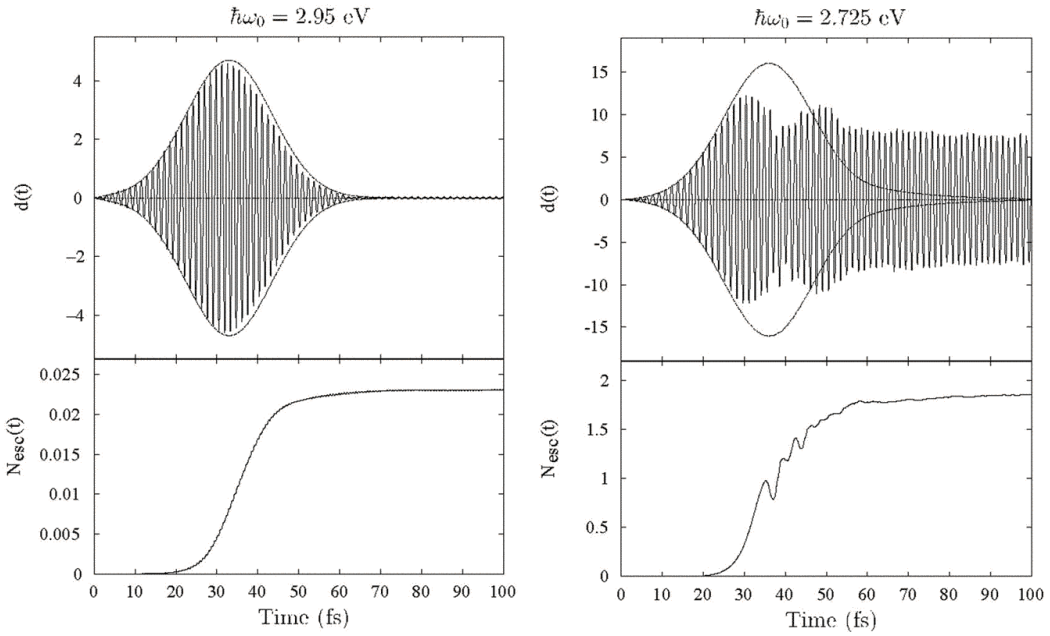
D. Dundas and J.M. Rost
PRA 71, 013421 (2005)

Na_9^+ cluster: the Mie plasmon



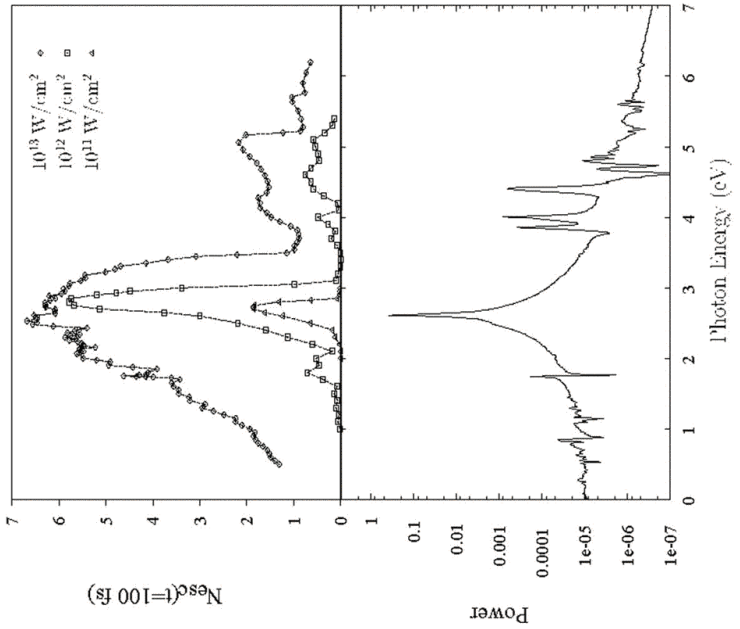
F. Calvayrac, P.-G. Reinhard, E. Suraud, C.A.U., Phys. Rep. **337**, 493 (2000)

Na_9^+ in spherical jellium model

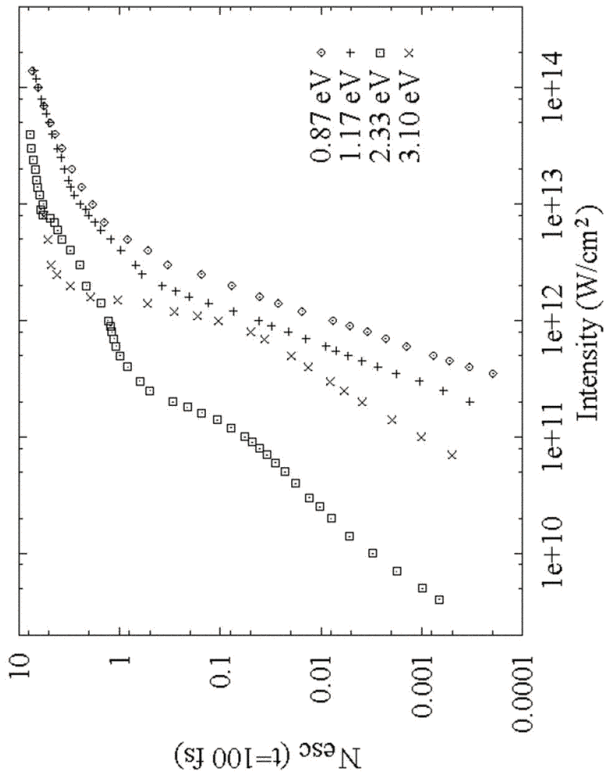


C.A.U., P.-G. Reinhard, E. Suraud, J. Phys. B **30**, 5043 (1997)

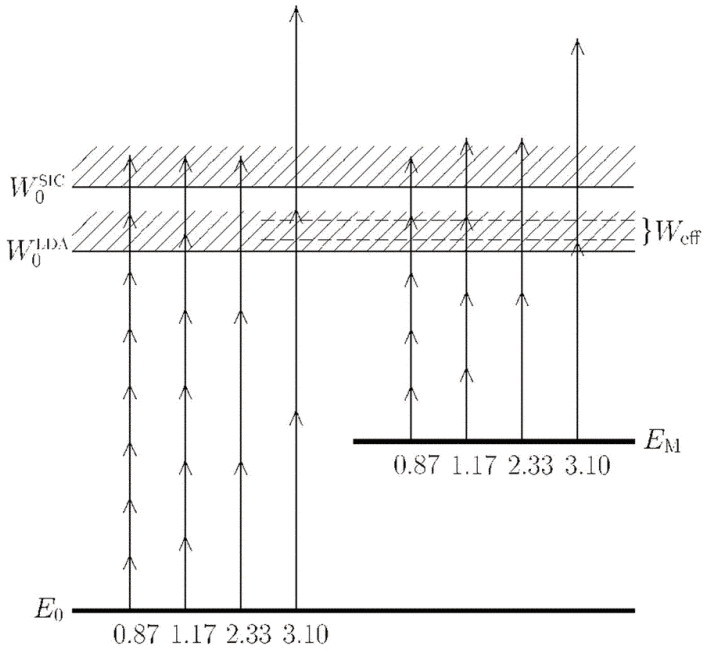
Na_9^+ strong-field ionization



Na_9^+ multiphoton ionization



Cluster multiphoton ionization



Resonant ionization with Plasmon mode as "doorway" state

C.A.U., P.-G. Reinhard, E. Suraud, J. Phys. B **31**, 1871 (1998)

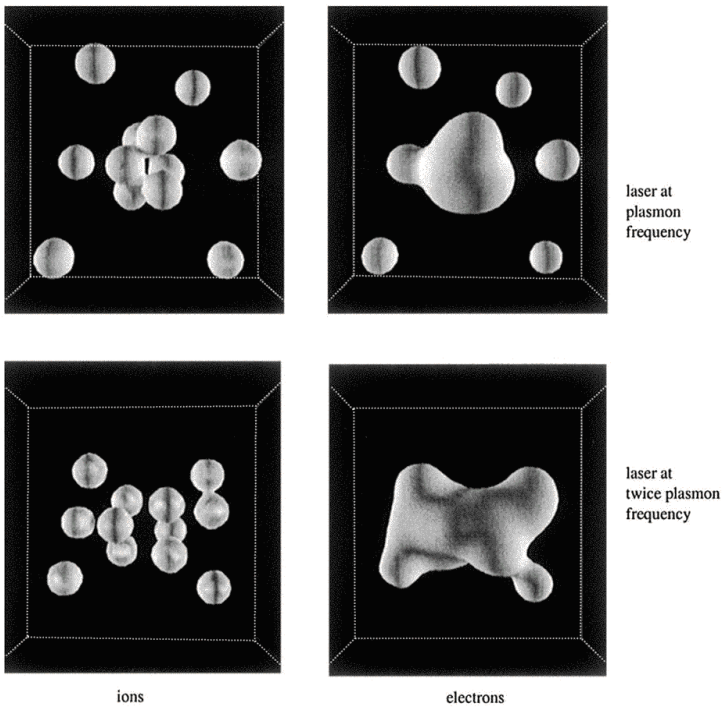
Na_{12} Coulomb explosion

Calvayrac, Reinhard, and Suraud (1998)

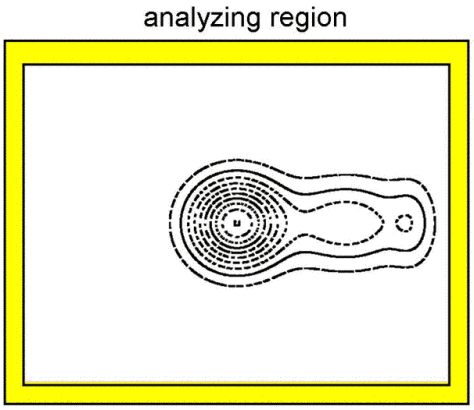
50 fs laser pulse

$Na_{12} \longrightarrow Na_{12}^{3+}$

Non-BO dynamics



Photoelectron spectra and ATI



A. Pohl, P.-G. Reinhard, E. Suraud, PRL **84**, 5090 (2000)

$$P_{KS}(E) = \sum_j \left|\varphi_j(\vec{r}_a, E)\right|^2$$

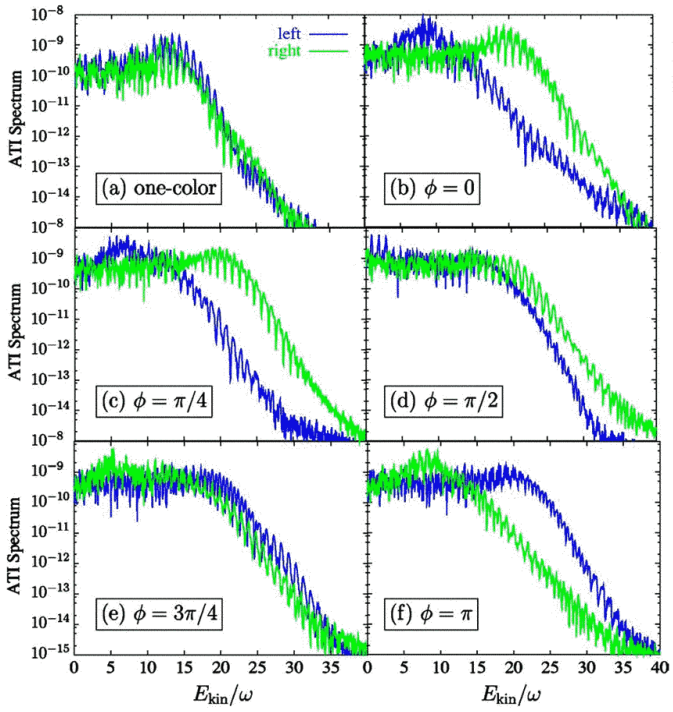
(Fourier transform of KS orbitals)

V. Véniard, R. Taïeb, and A. Maquet, Laser Phys. **13**, 465 (2003)

$$P(E,t) = n\left(t\sqrt{2(E \pm \Delta E)}\right)$$

(time-of-flight analysis of density at large t)

ATI spectra of Na_4 in two-color pulses



H.S. Nguyen, A.D.Bandrauk, C.A.U., PRA **69**, 063415 (2004)

2-color 25 fs pulses:
1064 nm, 6x10^{12} W/cm^2
532 nm, 1.5x10^{12} W/cm^2

ATI cutoffs at 20-40 U_p

Ion probabilities

Exact definition:

$$P^0(t) = \int_{box} d^3r_1 \ldots \int_{box} d^3r_N \left|\Psi(\vec{r}_1,\ldots,\vec{r}_N,t)\right|^2$$

$$P^{+1}(t) = N \int_{\overline{box}} d^3r_1 \int_{box} d^3r_2 \ldots \int_{box} d^3r_N \left|\Psi(\vec{r}_1,\ldots,\vec{r}_N,t)\right|^2$$

$$\vdots$$

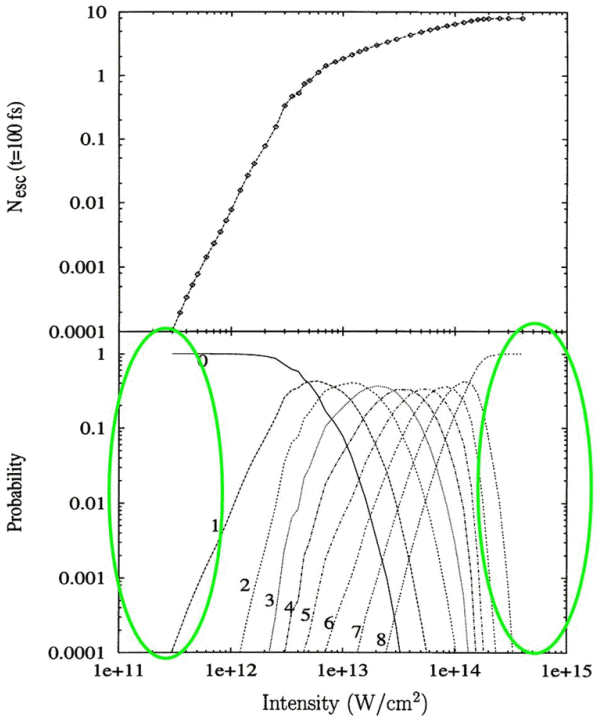
$P^{+n}(t)$ is the probability to find the system in charge state +n

$P^{+n}_{KS}(t)$: evaluate the above formulas with $\Phi_{KS}(\vec{r}_1,\ldots,\vec{r}_n,t)$

A deadly sin in TDDFT!

KS Ion probabilities of a Na_9^+ cluster

25-fs pulses
0.87 eV photons



KS probabilities exact for

$N_{esc} \to 0, \quad N_{esc} \to N$

Ion probabilities for 2-electron systems

$$P^0(t) = \frac{1}{2}\int_{box} d^3r_1 \int_{box} d^3r_2\, n(\vec{r}_1,t)n(\vec{r}_2,t)g(\vec{r}_1,\vec{r}_2,t)$$

$$P^{+1}(t) = 2N(t) - 2P^0(t), \qquad P^{+2}(t) = 1 - P^{+1}(t) - P^0(t)$$

$$N(t) = \frac{1}{2}\int_{box} d^3r\, n(\vec{r},t), \qquad g[n](\vec{r}_1,\vec{r}_2,t) = \frac{2\,|\Psi(\vec{r}_1,\vec{r}_2,t)|^2}{n(\vec{r}_1,t)n(\vec{r}_2,t)}$$

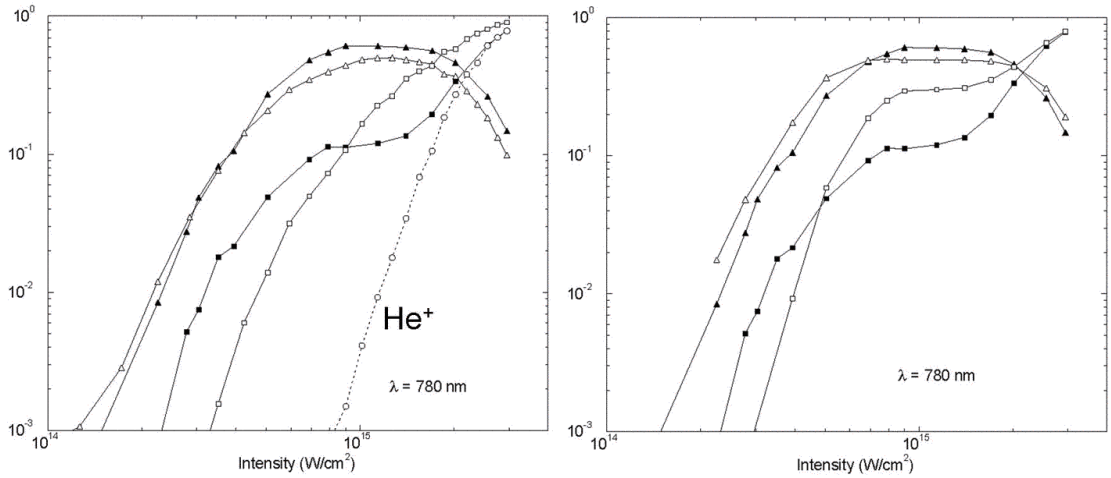
pair correlation function

Using x-only limit, $g(r_1,r_2,t)=1/2$, gives the KS probabilities:

$$P^0_{KS} = N(t)^2, \qquad P^{+1}_{KS}(t) = 2N(t)[1-N(t)], \qquad P^{+2}_{KS} = [1-N(t)]^2$$

Double ionization of He at 780 nm

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

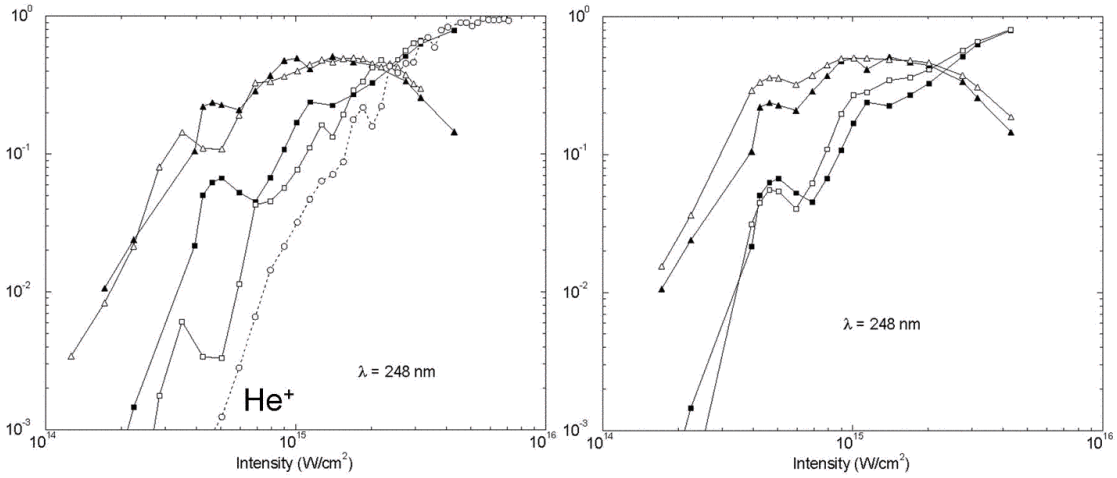


TDHF

KS ion probs. with exact density

Double ionization of He at 248 nm

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



TDHF

KS ion probs. with exact density

Nonsequential double ionization

- Worst-case scenario for TDDFT: highly correlated 2-electron dynamics described via 1-particle density
- Not a **fundamental** failure of TDDFT! Our present-day functionals are simply not good enough.
- TDDFT works better for sequential ionization.

The time-dependent xc potential

$$i\hbar\frac{\partial}{\partial t}\varphi_j(t) = \left(-\frac{\hbar^2\nabla^2}{2m} + V_{ext}(t) + V_H(t) + V_{xc}(t)\right)\varphi_j(t)$$

Adiabatic approximation: just take any xc potential from ground-state DFT and plug in time-dependent density.

$$V_{xc}^{ALDA}(\vec{r},t) = V_{xc}^{LDA}\left(n(\vec{r},t)\right)$$

- depends only on density at same space-time point
- OK for SLOW variations in **r** and t.

The time-dependent xc potential: requirements

quasi-static

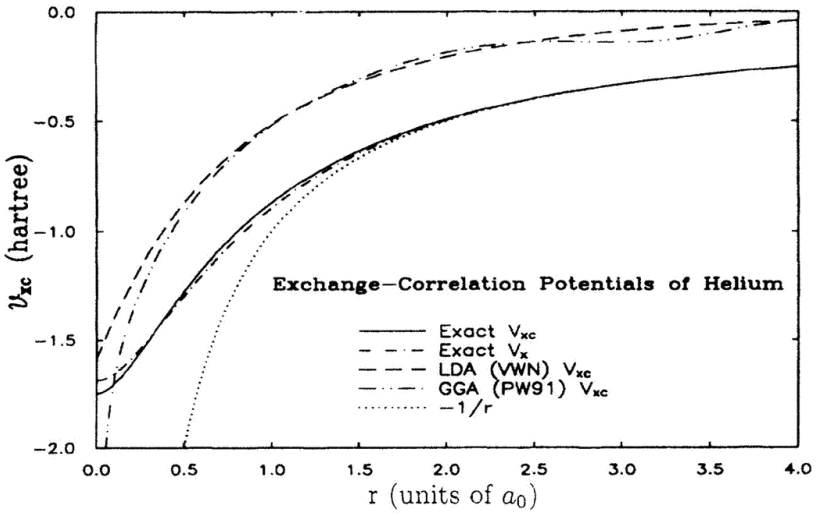
- long-range asymptotic behavior
- discontinuity as particle number changes

truly dynamic

- non-adiabatic: memory of previous history

Asymptotics of V_{xc}: ground state

C.J. Umrigar and X. Gonze, PRA **50**, 3827 (1994)



Exact:

$$V_{xc} \to -\frac{1}{r}$$

LDA, GGA:

$$V_{xc} \to -e^{-\alpha r}$$

Correct asymptotics: • bound negative ions and KS Rydberg states

• $\varepsilon_{HOMO} = I_p$

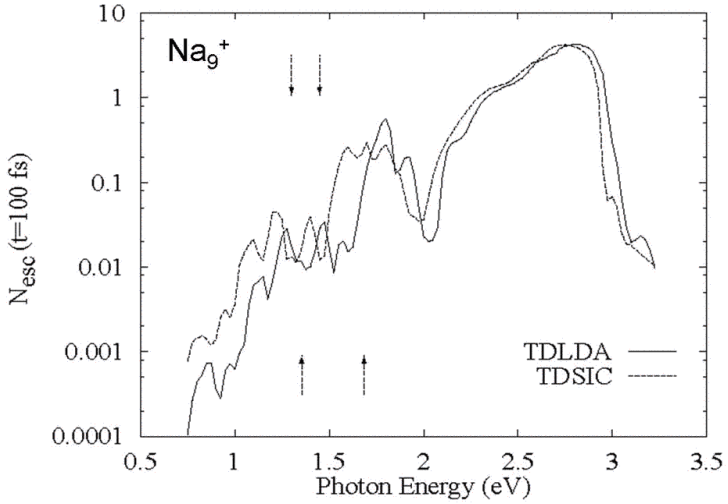
Asymptotics of V_{xc}: excitation energies

Atom	$\Delta\epsilon_{\mathrm{LDA}}$	$\Omega_{\mathrm{LDA/ALDA}}$	$\Delta\epsilon_{\mathrm{EXX}}$	$\Omega_{\mathrm{EXX/PGG}}$	Ωexp
Be	0.129	0.200	0.130	0.196	0.194
Mg	0.125	0.176	0.117	0.164	0.160
Ca	0.088	0.132	0.079	0.117	0.108
Zn	0.176	0.239	0.157	0.211	0.213
Sr	0.082	0.121	0.071	0.105	0.099
Cd	0.152	0.214	0.135	0.188	0.199

M. Petersilka, U.J.Gossmann, E.K.U. Gross, PRL **76**, 1212 (1996)

Asymptotics of V_{xc}: strong-field properties

C.A.U., P.-G. Reinhard, E. Suraud, J. Phys. B **31**, 1871 (1998)



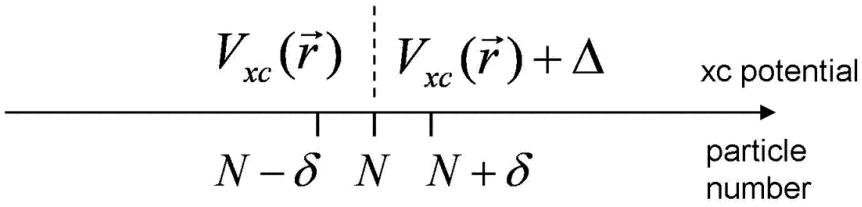
minor quantitative differences between ALDA and SIC, EXX for multiphoton ionization or HHG

The time-dependent xc potential: requirements

- long-range asymptotic behavior
- discontinuity as particle number changes
- non-adiabatic: memory of previous history

Discontinuity in V_{xc}: ground state

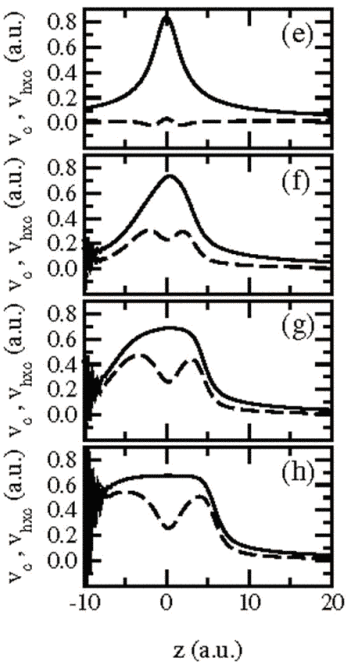
J.P. Perdew et al., PRL **49**, 1691 (1982)

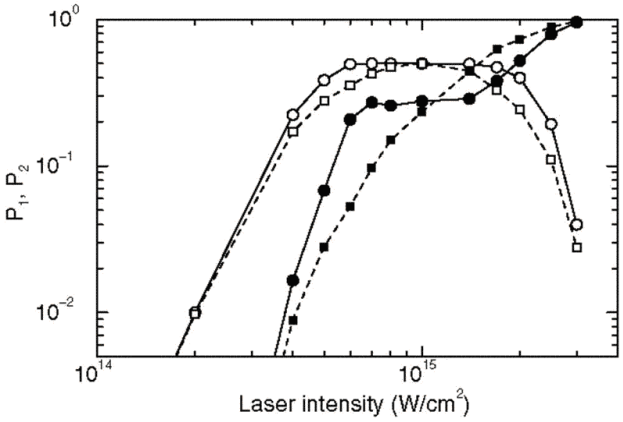


- proper description of dissociation of heteronuclear molecules
- band gap in solids include contribution from Δ

Discontinuity in V_{xc}: ioniziation

S. Kümmel and M. Lein, PRL **94**, 143003 (2005)





Exact 1D Helium: $n(x,t) \Rightarrow V_{xc}(x,t)$

As the atom ionizes, a step develops in the correlation potential.

The time-dependent xc potential: requirements

- long-range asymptotic behavior
- discontinuity as particle number changes
- non-adiabatic: memory of previous history

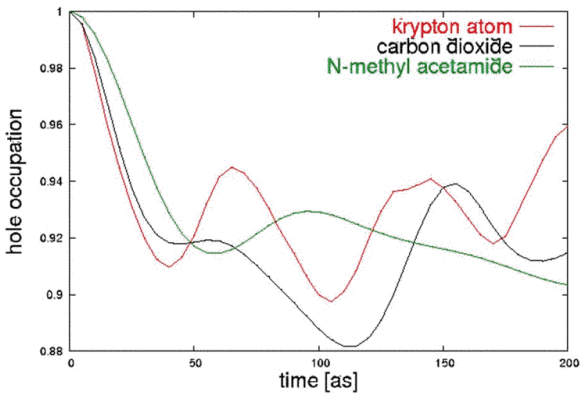
$V_{xc}[n](\vec{r},t)$ depends on previous history (t'< t)

$n(\vec{r}',t')$

Nonadiabatic xc potentials

- **Linear response:** frequency-dependent xc kernel $f_{xc}(\vec{r},\vec{r}',\omega)$ required for double excitations

- **Beyond linear response:** ALDA invalid for rapid (nonadiabatic) changes of the density

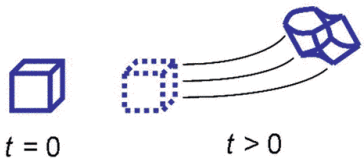


E.g.: attosecond response to the removal of an electron

J. Breidbach and L.S. Cederbaum, PRL **94**, 033901 (2005)

Nonadiabatic xc potentials

1 XC functionals using the language of hydrodynamics/elasticity



- Extension of LDA to dynamical regime: local in space, but nonlocal in time ⟹ current is more natural variable.
- Dynamical xc effects: viscoelastic stresses in the electron liquid
- Frequency-dependent viscosity coefficients / elastic moduli

J.F. Dobson, M.J. Bünner, E.K.U. Gross, PRL **79**, 1905 (1997)
G. Vignale and W. Kohn, PRL **77**, 2037 (1996)
G. Vignale, C.A.U., S. Conti, PRL **79**, 4878 (1997)
I.V. Tokatly, PRB **71**, 165105 (2005)

An xc potential with memory

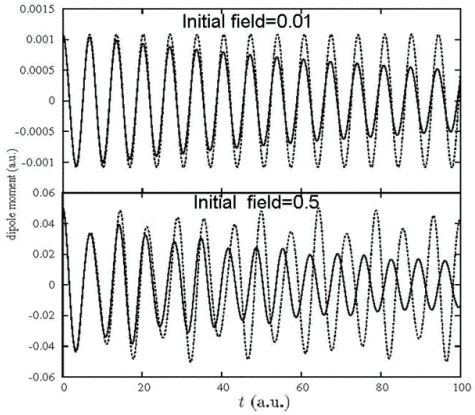
H.O. Wijewardane and C.A.U, PRL **95**, 086401 (2005)

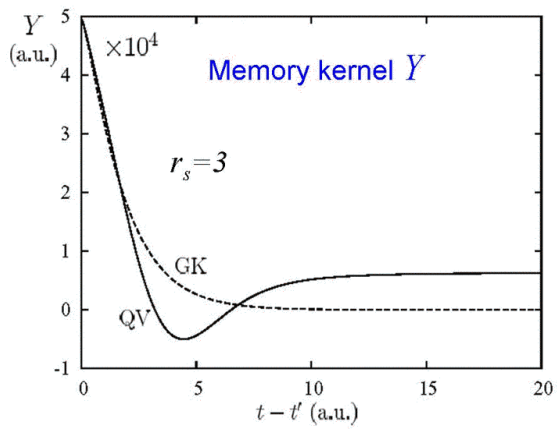
For a quantum well: $$V_{xc}(z,t) = V_{xc}^{ALDA}(z,t) + V_{xc}^{M}(z,t)$$

$$V_{xc}^{M}(z,t) = -\int_{-\infty}^{Z} \frac{dz'}{n(z',t)} \nabla_{Z'} \sigma_{xc}(z',t)$$

velocity gradient

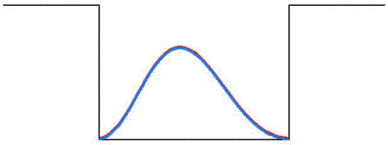
xc stress tensor : $$\sigma_{xc}(z',t) = \int_{0}^{t} dt' Y(n(z',t), t-t') \nabla_{Z'} u_{Z'}(z',t')$$



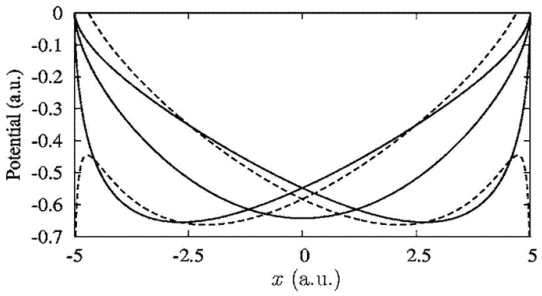


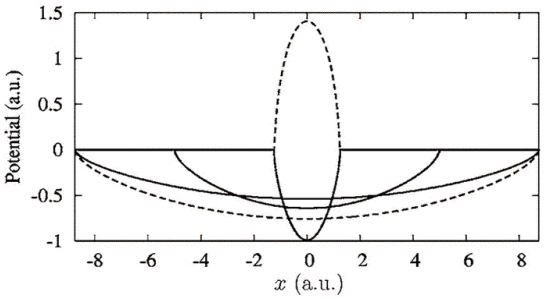
Breakdown of the ALDA

C.A.U. and I.V. Tokatly, PRB **73**, 235102 (2006)



High-frequency, purely elastic limit ($\omega >> \omega_p$)





Sloshing mode: small deformation, minor corrections to ALDA

Breathing mode: large deformation, ALDA breaks down

Nonadiabatic xc potentials

2 XC functionals using the KS orbitals:

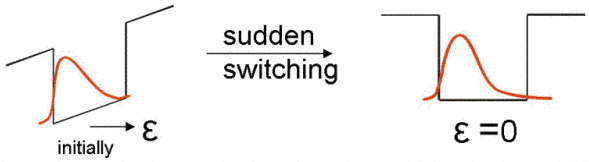
Time-dependent optimized effective potential (TDOEP)
C.A.U., U.J. Gossmann, E.K.U. Gross, PRL **74**, 872 (1995)

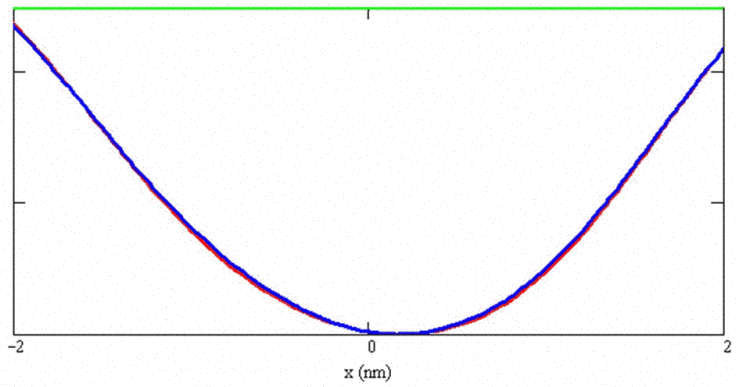
$$\sum_{j=1}^{N} \int_{-\infty}^{t} dt' \int d^3r' \left[V_{xc}(\vec{r}'t') - u_{xcj}(\vec{r}'t') \right] \varphi_j(\vec{r}t) \varphi_j^*(\vec{r}'t') K(\vec{r}t, \vec{r}'t') - c.c. = 0$$

where $K(\vec{r}t, \vec{r}'t') = \sum_{k=1}^{\infty} \varphi_k^*(\vec{r}t) \varphi_k(\vec{r}'t')$

$$u_{xcj}(\vec{r}t) = \frac{1}{\varphi_j^*(\vec{r}t)} \frac{\delta A_{xc}[\{\varphi_i\}]}{\delta \varphi_j(\vec{r}t)}$$

Full TDOEP versus TDKLI: exact exchange





full TDOEP TDKLI (no memory)

(correct asymptotics, discontinuous as a new level is filled)

Summary

- TDDFT is the most promising approach for the dynamics of large systems (molecules, materials)
- Quality of results depends on problem and functionals used:

→ ALDA works well for processes that have an analog in the KS system (single excitations, sequential ionizations)

→ Strongly correlated processes, multiple excitations, charge-transfer excitations, and ultrafast processes are much more challenging

- Dynamical xc functionals are being developed and tested for simple model systems

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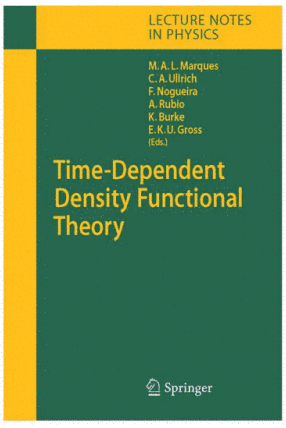
Literature



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Chapter 24: C.A. Ullrich and A.D. Bandrauk, Atoms and molecules in strong laser fields

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