

Electron Dynamics in Strong Fields using Time-Dependent Density Functional Theory

Neepa T. Maitra

Hunter College of the City University of New York



The dynamical electronic problem

For any atom, molecule, cluster, solid... within Born-Oppenheimer,

$$H\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{t}) = i \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{t})$$

where

$$H = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^N v_{\text{ext}}(\mathbf{r}_i; \mathbf{t})$$

Kohn-Sham potential $V_S(\mathbf{r}_i; \mathbf{t})$

eg. nuclear attraction + external laser field

Atomic units: $e^2 = \hbar = m = 1$

e-e interaction leads to exponential scaling with the number of electrons N .

Prohibitively expensive for more than 2 or 3 electrons in intense fields.

From the Kohn-Sham non-interacting system, exact properties of the interacting dynamics can be extracted.

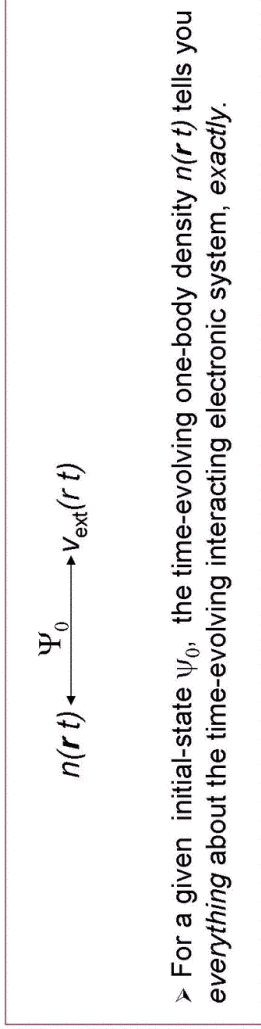
- Wide and varied applications, eg. dielectric functions, nanotube excitation spectra, spectra of large chemically interesting molecules, photosynthesis, spectra of DNA fragments, nano-tech - molecular wires ...
- In principle, all properties of the system are determined exactly but in practice approximations are required (more shortly)
- Strong-Field Physics – HHG, ATI, photo-dissociation, attosecond dynamics...
 - *How well does TDDFT work here? What are the key issues involved?*
 - Can TDDFT help to understand the underlying mechanisms of the processes? What are possibilities for electronic quantum control?*

Outline

- TDDFT Formalism
- Functional dependence: Memory
- Functional dependence: Importance, or not, of Coulomb tail
- Challenges for attosecond quantum control
- Phase-space-density functional theory
- Challenges for correlated electron-ion dynamics

Time-Dependent DFT

- Runge - Gross (1984) proved the 1-1 mapping:



i.e. you don't need to know the far more complex $(3N + 1)$ -dimensional correlated wavefunction

- Map interacting system onto a non-interacting Kohn-Sham (KS) system of orbitals, that reproduces the exact $n(\mathbf{r}, t)$ (van Leeuwen, 1999: existence of KS)
- Extract exact excitations and dynamics from KS system, much faster to solve
- Thus enables the quantum mechanical study of much larger systems than is possible using wavefunction methods.

TDDFT Formalism

Time-dependent Kohn-Sham (KS) equation:

$$\left\{ -\frac{1}{2}\nabla^2 + v_s(\mathbf{r}, t) \right\} \phi_j(\mathbf{r}, t) = i \frac{\partial \phi_j(\mathbf{r}, t)}{\partial t}$$

where

$$n(\mathbf{r}, t) = \sum_{i=1}^N |\phi_i(\mathbf{r}, t)|^2 = \text{exact, interacting density}$$

$$v_s[n; \Phi_0](\mathbf{r}, t) = v_{\text{ext}}(\mathbf{r}, t) + \int d^3r' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{xc}}[n; \Psi_0, \Phi_0](\mathbf{r}, t)$$

↑ Hartree

For initial KS state, choose any SSD that reproduces true initial n and dn/dt

Need functional approximations here for the xc potential

$v_{\text{xc}}[n; \Psi_0, \Phi_0](\mathbf{r}, t)$ -- much more complicated object than in the ground-state case: depends on the entire history of the density, the true initial state Ψ_0 and the choice of initial KS state Φ_0 .

Memory-dependence

Functionals in TDDFT

Although the theory is formally exact, in practise approximations are needed for the exchange-correlation (xc) effects.

Almost all calculations today use an “**adiabatic approximation**” :
Just upgrade a ground-state functional,

$$v_{xc}^A[n; \Psi_0, \Phi_0](\mathbf{r}t) = v_{xc}^{GS}[n(\mathbf{r}t)]$$

e.g. $v_{xc}^{ALDA}(\mathbf{r}t) = v_{xc}^{LDA}[n(\mathbf{r}t)] = \frac{de_{xc}^{unif}(n(\mathbf{r}t))}{dn}$



Completely forgetful: zero memory effects.

Development of memory-dependent functionals:

Vignale & Kohn (1996), Vignale, Ullrich, Conti (1997), Tokatly (2005)

Orbital functionals also capture some memory

Memory-dependence

? How valid is the adiabatic approximation (AA) – can we really ignore memory?

• First, consider **linear response** – excitations and response properties:

-- AA seems to work well – not entirely understood why.

-- For some excitations, AA fails badly

eg. double excitations (*Maitra, Zhang, Cave, Burke, JCP 2004*)

eg. excitations of certain long-range molecules (including charge-transfer)
(*Maitra, JCP 2005, Maitra & Tempel sub. 2006*)

eg. interaction-induced chaos in wells (AA fails to give Wigner-Dyson level statistics) (*Wasserman, Maitra, Heller, in prep. 2006*)

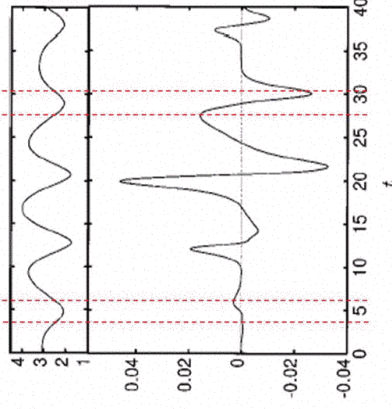
• **How about for strong-field dynamics?** Not always easy to test, since exact solutions are hard to come by...

• Examples where exact solutions are available indicate memory plays a significant role and AA fails.

Memory-dependence

- Dependence on the history of the density: $v_{xc}[n]; \Psi_0, \Phi_0](rt)$ $n(\mathbf{r}t'), t' < t$

Eg. Time-dependent Hooke's atom – exactly solvable



2 electrons in parabolic well, time-varying force constant $k(t) = 0.25 - 0.1 * \cos(0.75 t)$

Any adiabatic (or even semi-local-in-time) approximation would incorrectly predict the same v_c at both times.

parametrizes density

$$\int d^3r v_{xc}(\mathbf{r}t') \hat{n}(\mathbf{r}t')$$

Hessler, Maitra, Burke, JCP **117**, 72 (2002).

Maitra, Burke, Woodward PRL **89**, 023002 (2002) has other arguments showing xc potential is generally **ultranonlocal** in time.

- Dependence on the initial-states:

$$v_{xc}[n; \Psi_0, \Phi_0](\mathbf{r}t)$$

If we start in different Ψ_0 's, can we get the same $n(\mathbf{r}t)$ by evolving in different potentials?

Yes!

- Say this is the density of an interacting system. Both top and middle are possible KS systems.

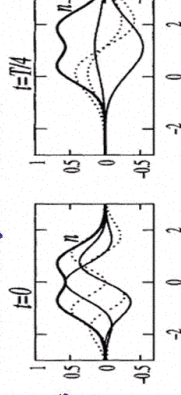
➤ v_{xc} different for each. Cannot be captured by any adiabatic approximation

- Consequence for Floquet DFT: No 1-1 mapping between densities and time-periodic potentials.

Maitra & Burke, PRA **63**, 042501 (2001); **64** 039901 (E)

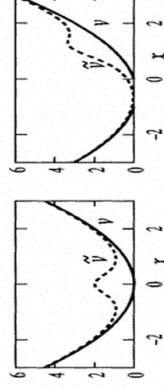
Maitra & Burke, CPL **359**, 237 (2002).

A non-interacting example: Periodically driven HO



Re and Im parts of 1st and 2nd Floquet orbitals

Doubly-occupied Floquet orbital with same n

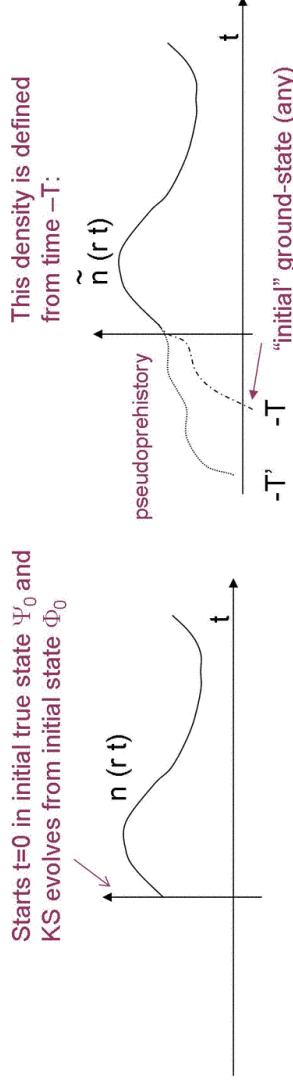


Eliminating initial-state dependence (ISD)

Evolve initial states backward in time, in some potential, to a *ground-state* → no ISD (due to Hohenberg-Kohn DFT) → instead, must tack on extra piece of “pseudo pre-history”

$$V_{xc}[n; \psi_0, \Phi_0](\mathbf{r}, t) = V_{xc}[\tilde{n}](\mathbf{r}, t)$$

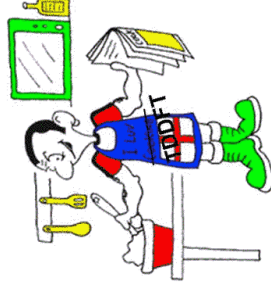
Starts $t=0$ in initial true state ψ_0 and KS evolves from initial state Φ_0



• The pseudoprehistory is not unique – may find many ground-states that evolve to the same state at $t=0$, in different amounts of time, in different potentials.

• Eqn applies to all – and gives a strict exact test for approximate history-dependent functionals.

Ingredients for strong-field TDDFT calculations



(1) Approximation for $v_{xc}[n; \psi_0, \Phi_0](\mathbf{r}, t)$

- Adiabatic versus Non-Adiabatic ?
(Time-nonlocality i.e. memory)

- Long-range Coulomb tail needed or is short-range LDA OK?
(Spatial non-locality)

- Derivative discontinuity ?
Important in NSDI (multi-e ionization)

(Lein & Kuemmel, 2005)

(2) Observable as a functional of $n(\mathbf{r}, t)$

- Is the relevant KS quantity physical ?
Certainly measurements involving only density (eg dipole moment) can be extracted directly KS.

✓ HHG

ATI
NSDI

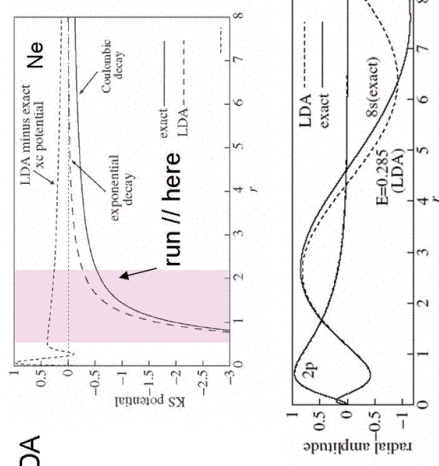
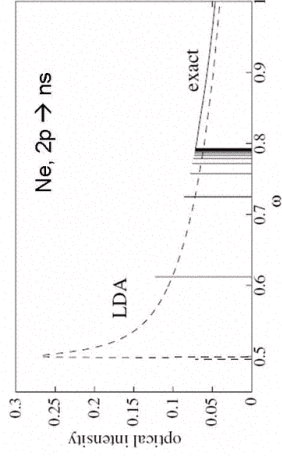
Attosecond Quantum Control
Correlated electron-ion dynamics

Harder: need functional approx

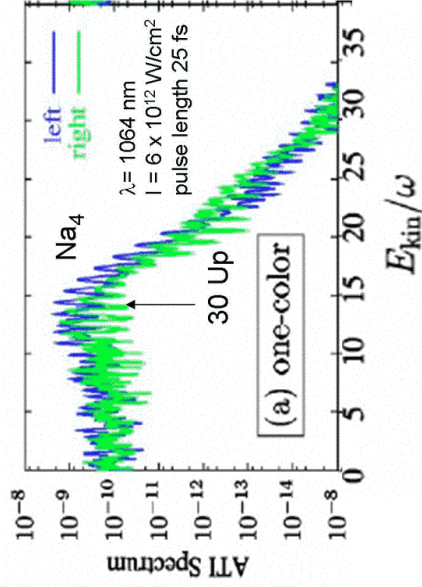
Long-range Coulomb tail needed or not?

- Most functionals eg LDA, GGA's, lack the tail.
- Numerically more intensive functionals eg. SIC, OEP/KLI, do have $-1/r$ tail (Eg. *Nguyen, Bandrauk, Ullrich, PRA 2004*, HHG/ATI spectra of Na-clusters)
- Sometimes not having a tail doesn't matter!

Eg. Photo-absorption spectra accurate in LDA
(*Wasserman, Maitra, Burke, PRL 2003*)



- Suggests Starace's QES/TDER analysis of HHG/ATI may be applied within TDDFT, with short-ranged LDA
(*Frolov, Khuskivadze, Manakov, Starace, J Phys B (2006)*)
- Could such analysis help to explain the extended plateaus of the TDDFT ATI in the Na-clusters?



Nguyen, Bandrauk, Ullrich, PRA 2004

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- Phase-space-density functional theory
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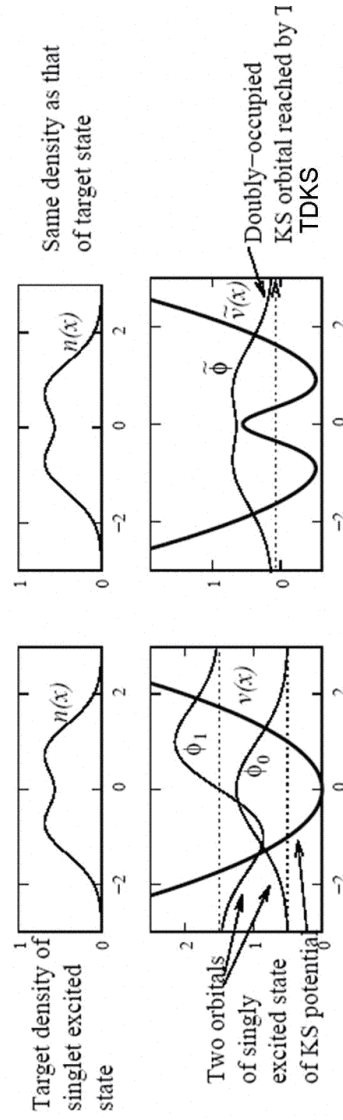
Electronic Quantum Control

What can theory predict? Electron correlation vital – use TDDFT!

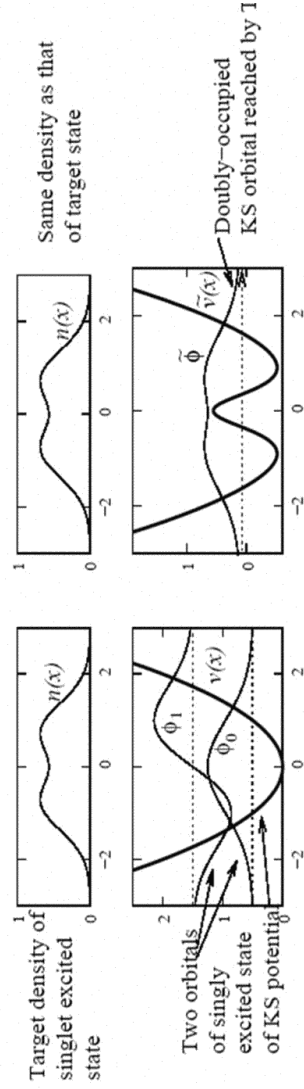
Consider pumping He from ground to first accessible excited state (1s2p).

Problem!! The KS state remains doubly-occupied throughout – *cannot* evolve into a singly-excited KS state.

Simple model: evolve two electrons in a harmonic potential from ground-state (KS doubly-occupied ϕ_0) to the first excited state (ϕ_0, ϕ_1) :



- KS system can achieve the target density, but with a doubly-occupied orbital !!
- Yet this is how exact *TDDFT* describes the dynamics – the exact v_{xc} is unnatural and difficult to approximate.
- v_s does not return to its initial value, as v_{ext} does, after pumping complete.
- What functional to define the control target?
 If try to optimize $\langle \Phi(T) | 1s2p \rangle$ - max would be $1/2$
 (c.f. close to 100% in the interacting He problem – *Werschnik & Gross (2005)*)
 i.e. the interacting system is controllable in this sense, but the non-interacting is not



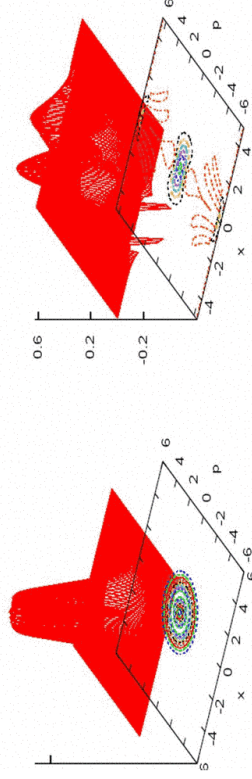
An alternative approach...

- Construct a *generalized density-functional theory* based on a phase-space density, eg Wigner function:

$$W(\mathbf{r}, \mathbf{p}) = \int dy \rho_1(\mathbf{r} + y/2, \mathbf{r} - y/2) e^{i\mathbf{p}\cdot\mathbf{y}}$$

1st order density matrix

The Wigner function for the two states in the harmonic oscillator control problem are distinct -



So although an adiabatic functional of the *density* predicts the same result for both states, an adiabatic functional of the *phase-space density* distinguishes them

TD Phase-Space FT



Currently under investigation

- Idea is that as more information is contained in the basic variable, functionals of it ought to be simpler – less non-local in time
- 1-1 mapping, $v_{\text{ext}} \leftrightarrow W(\mathbf{r}, \mathbf{p}, t)$, given Ψ_0 , exists:
 $W(\mathbf{r}, \mathbf{p}, t) \rightarrow n(\mathbf{r}, t)$ by integration over $\mathbf{p} \rightarrow v_{\text{ext}}(\mathbf{r}, t)$ by RG thm
- Closely related to the first-order density matrix (1DM), $\rho_1(\mathbf{r}, \mathbf{r}', t)$
c.f. 1DM-FT in the *ground-state* (Lathiotakis, Helbig, & Gross (2005), Buijse & Baerends, *Mol. Phys.* 2001)
- Deal directly with $W(\mathbf{r}, \mathbf{p}, t)$ – no KS system
- The kinetic part of the time-evolution can be done exactly (unlike in TDDFT)
- May help with some observable problems eg. directly gives momentum distributions of ionized electrons in some region of space

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- Phase-space density functional theory
- **Challenges for correlated electron-ion dynamics**

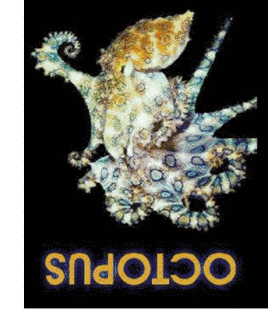
Coupled electron-ion dynamics

- A common approach: classical nuclei coupled to quantum electrons with Ehrenfest forces providing the quantum “backreaction”.

Eg. Study of photo-dissociation in N_2^+ using TDDFT for the electrons: capturing Coulomb explosion following ionization

(Castro, Marques, Alonso, Bertsch, Rubio, 2004)

- Now programmed into freely-available octopus code:



<http://www.tddft.org>,

Marques, Castro, Rubio, Yabana, Bertsch

octopus is a program aimed at the *ab initio* virtual experimentation on a hopefully ever increasing range of systems types. Its main characteristics are:

- Electrons are describe quantum-mechanically within the Density-Functional Theory (DFT), in its time-dependent form (TDDFT) when doing simulations in time. Nuclei are described classically as point particles.

- Electron-nucleus interaction is described within the Pseudopotential approximation..

- But Ehrenfest methods cannot capture *correlations* between nuclear and electronic motion eg. atomic collisions, amount of electronic excitation is correlated with resulting nuclear velocities – single averaged nuclear trajectory inadequate.

Eg. HHG in non-centrosymmetric diatomics: 1-d H—D

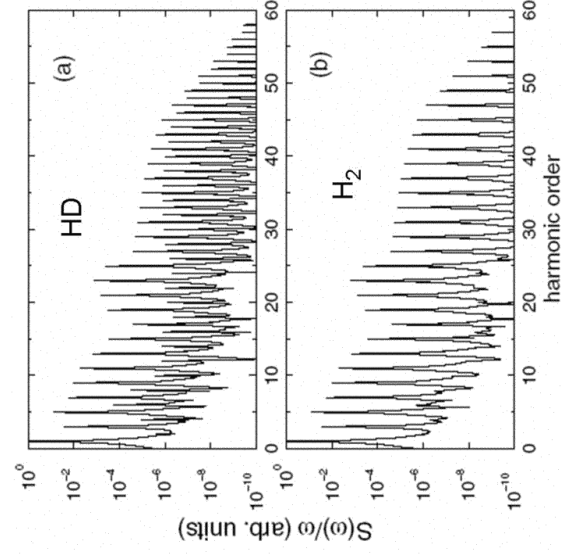
Exact quantum treatment of both electrons plus nuclei reveals **even** harmonics are generated. Must go beyond Born-Oppenheimer.

(Kreibich, Lein, Engel, Gross, PRL 2001)

- How well does approach with classical nuclei & Ehrenfest capture this?

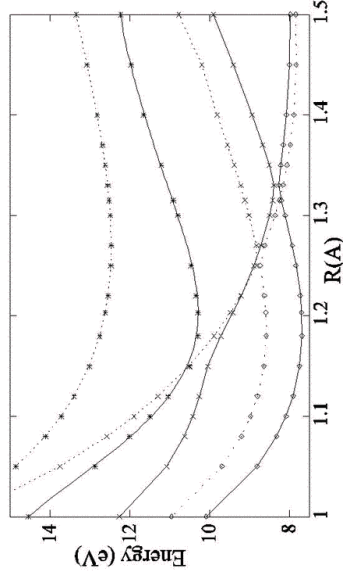
Find even harmonics are produced but with dramatically less intensity. (Hardly detectable unless decrease nuclear masses by 100)

(Castro, Marques, Alonso, Bertsch, Rubio, 2004)



Correlated electron-ion dynamics using TDDFT?

- Prezhdo - first calculation of surface-hopping using TDDFT. (*Craig, Duncan, & Prezhdo PRL 2005*)
- Showed significant improvement in calculations of nonradiative relaxation of GFP chromophore, and solar cell electron transfer
- Prezhdo's method: Evolve electrons via TDKS eqns, coupled to classical nuclei moving on KS potential energy surfaces (PES), making hops between them according "fewest-switches surface-hopping" scheme of Tully.
- But the KS PES's are not true adiabatic PES's \rightarrow should use TDDFT-corrected ones (eg from linear response) to get correct forces on the nuclei.



Eg. PES of formaldehyde 1A_1 excited states along C-O bond:

Gradients of TDDFT curves (solid) quite different from bare KS curves (dashed).

- But, if correct adiabatic PES are obtained from TDDFT linear response, the trajectory hopping probabilities cannot be simply extracted:

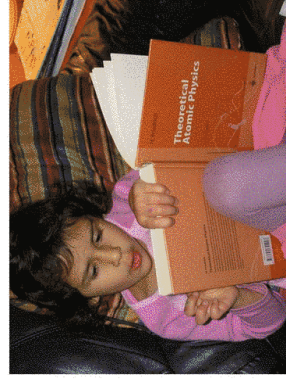
These depend on

- coefficients of the time-evolving ψ expanded in the e-states \leftarrow But DFT doesn't give ψ !
- non-adiabatic couplings (NAC) between electronic PES \leftarrow NAC density-functionals known for ground to excited states only

Maitra, JCP (2006)

Summary

- TDDFT is an enticing method for the treatment of atomic and molecular dynamics in strong fields, scaling favorably with the system size while including electron correlation
- Challenges remain in the development of memory-dependent exchange-correlation functionals, as well as density-dependence of physical observables
- Impacts many important problems eg. attosecond quantum control, coupled correlated nuclear-electron dynamics...
- These challenges raise lots of interesting fundamental questions !
- Addressing future challenges:



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• *And to you all for listening!!*