

Some Challenges in TDDFT – *and Possible Solutions in Phase-Space*

Neepa T. Maitra

*Hunter College and the Graduate
Center of the City University of
New York*



TDDFT

$$n(\mathbf{r}, t) \xleftrightarrow[\Psi_0]{1-1} v_{\text{ext}}(\mathbf{r}, t)$$

*Runge-Gross Theorem,
1984*

→ TDKS system:

$$n(\mathbf{r}, t) = \sum_i^N |\phi_i(\mathbf{r}, t)|^2$$

$$i\partial_t \phi_i(\mathbf{r}, t) = (-\nabla^2/2 + v_S(\mathbf{r}, t))\phi_i(\mathbf{r}, t)$$

$$v_S[n; \Phi_0](\mathbf{r}, t) = v_{\text{ext}}(\mathbf{r}, t) + v_H[n](\mathbf{r}, t) + v_{\text{XC}}[n; \Psi_0, \Phi_0](\mathbf{r}, t)$$

→ Extract observable of interest $A[n, \Psi_0, \Phi_0]$

**in practise
approximated**

(Eg. excitation spectrum, ionization probabilities, momentum distributions, quantum backreaction on nuclear dynamics...)



TDDFT Sales Tag: unprecedented balance between accuracy and efficiency for electronic excitations

-- Can study candidates for solar cells, eg. carotenoid-diaryl-porphyrin-C60

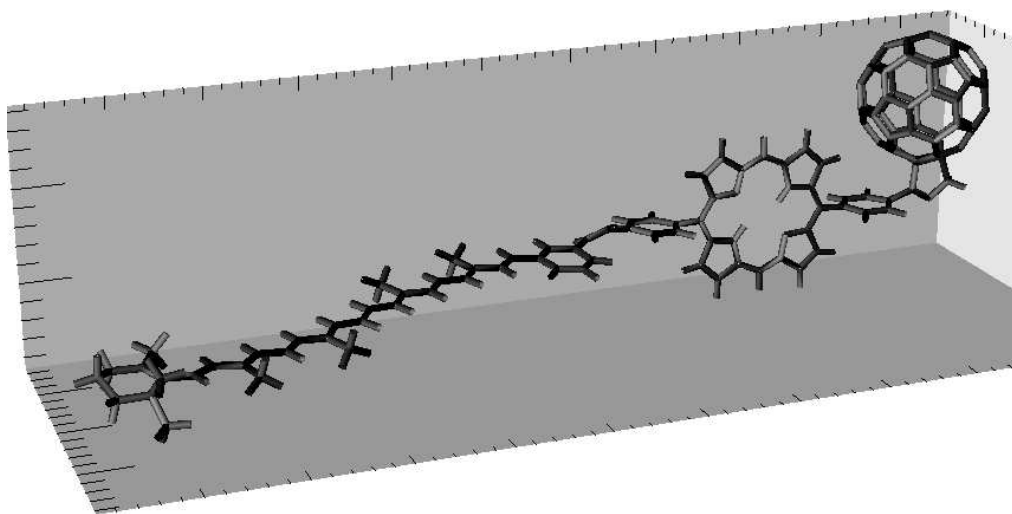
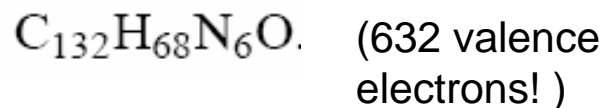


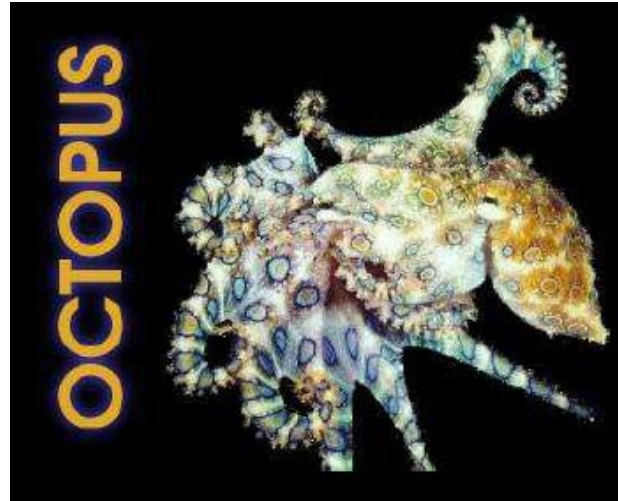
Photo-excitation of a light-harvesting supra-molecular triad: a Time-Dependent DFT study,
N. Spallanzani, C. A. Rozzi, D. Varsano, T. Baruah, M. R. Pederson, F. Manghi, and A. Rubio, *J. Phys. Chem.* (2009)

-- The usual approxs fail for certain cases eg double-excitations, long-range charge-transfer, long-chain polarizabilities... -- but recent and ongoing progress has led to improvements for these...

How about beyond linear response?

Freely-available TDDFT code
for strong and weak fields:

↓
HHG, ATI, photo-dissociation,
electronic quantum control,
coupled electron-ion
dynamics...



<http://www.tddft.org>

*Castro, Appel, Rubio,
Lorenzen, Marques,
Oliveira, Rozzi,
Andrade, Yabana,
Bertsch*



! Some models of dynamics in strong-fields show usual approximate functionals fail

! Difficult “observable functionals” needed to extract the quantity of interest from the KS orbitals

! Single-Slater Determinant (SSD) nature of KS can create severe and unnatural structure in v_{xc}

Outline

- Challenges for Present-Day Functionals
 - a (partial) overview
 - focus on real-time dynamics
- Phase-Space TDDFT
- Quasiclassical Phase-space Correlation Functionals
- Revisiting the Formal Theorems of TDDFT

Poor Performance of the Usual Functionals

Within Linear Response:

- Rydberg states
- Polarizabilities of long-chain molecules
- Optical response (gap, excitons..) of solids
- Molecular dissociation
- Long-range charge transfer
- Conical Intersections
- Double excitations

Local/semilocal approx inadequate.
Need Im fxc to open gap.

Development of **orbital-dependent fnals** (exact-exchange/sic), or **TD current-DFT**, or **Nanoquanta kernel**

Haunted by static correlation in the gs




Adiabatic approximation fails

Development of **frequency-dependent kernels**

Poor Performance of the Usual Functionals

or, questionable...

Beyond Linear Response

- Some strong-field dynamics calculations  Adiabatic approx fails -- memory-dependence crucial
 - Certain electronic quantum control problems
 - Momentum distributions (eg in ion-recoil experiments)
 - Non-sequential double ionization
 - Coupled correlated electron-ion dynamics
-  TD Static correlation
-  Cannot extract observable simply from KS system

Challenges for Real-Time Dynamics with TDDFT

Two types of ingredients required:

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

Exact depends on entire history of the density, as well as on initial-states → “memory”

“Adiabatic approx”

$$v_{xc}^A[n; \Psi_0, \Phi_0](\mathbf{r}, t) = v_{xc}^{gs}[n(\mathbf{r}t)](\mathbf{r}t) \quad \text{- workhorse of linear response TDDFT}$$

Difficulties: -- for strong fields, **memory-dependence** often important (see later)

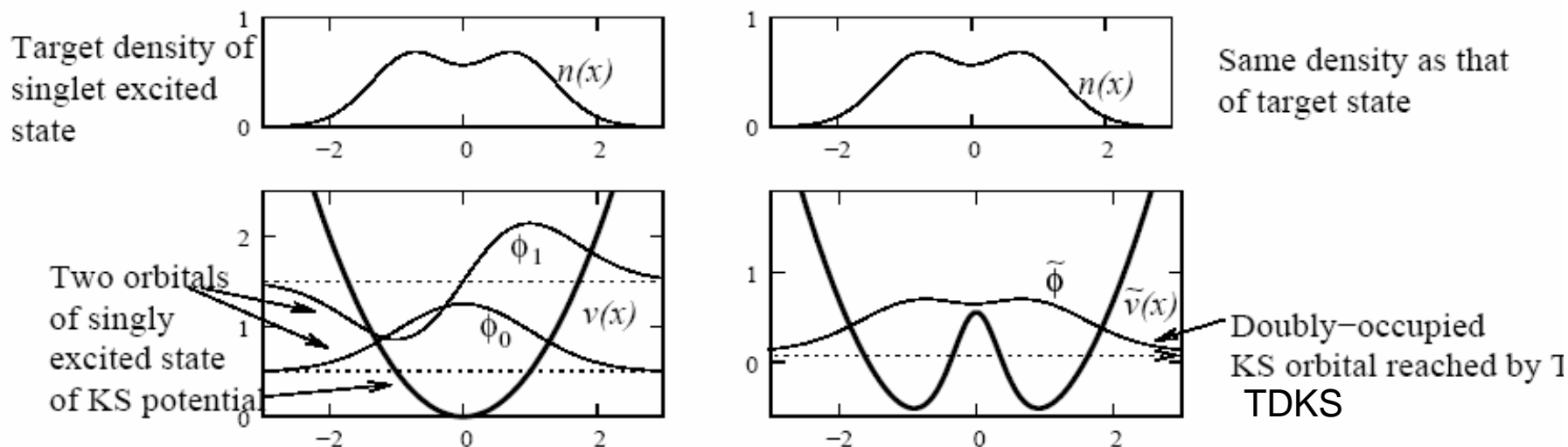
-- when *true* evolved state contains significant mixtures of more than one SSD, the exact v_{xc} develops unnatural structures, difficult to model
– **TD analog of “static correlation”**

Example: Some Quantum Control problems

Consider pumping He from ground ($1s^2$) to first accessible excited state ($1s2p$).

Problem!! The KS state remains doubly-occupied throughout – *cannot* evolve into a singly-excited KS state under any 1-body H.

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 achieves the target excited-state density, but with a doubly-occupied *ground-state* orbital !!

-- Yet this is how *exact TDDFT* describes the dynamics – the exact v_{xc} is unnatural and difficult to approximate.

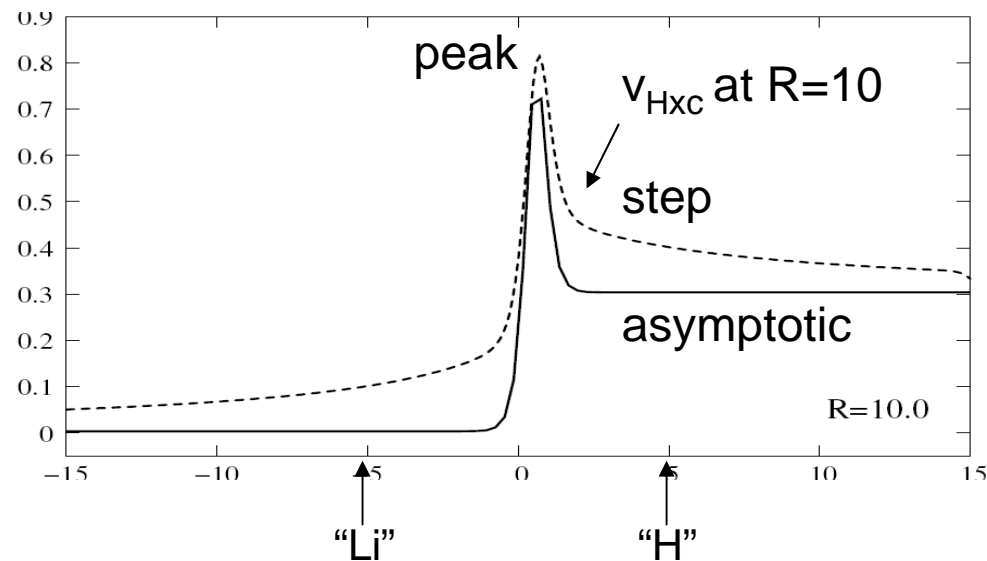
Maitra, Burke, Woodward PRL (2002)

- This difficulty is caused by the inability of the TDKS system to change occupation #'s
- TD analog of “static correlation” – which also haunts ground-state DFT

Eg. Molecular dissociation in heteroatomics

Step and peak structures in exact v_{XC} appear in the bond midpoint region,

which has negligible density – so don't affect energetics, but *do* have consequences for response and excitations.



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-- when *true* evolved state contains significant mixtures of more than one SSD, the exact v_{xc} develops unnatural structures, difficult to model – **TD analog of “static correlation”**

(2) “**Observable functionals**” to extract property of interest from KS Φ_s

Sometimes simple, eg dipole moments in HHG – directly related to $n(\mathbf{r}, t)$

But often, not simple:

eg. pair density for double-ionization yields (but see *Wilken & Bauer PRL (2006)*)

eg. Kinetic energies (ATI spectra) or recoil ion-momentum distributions
Wilken and Bauer (PRA 2007))

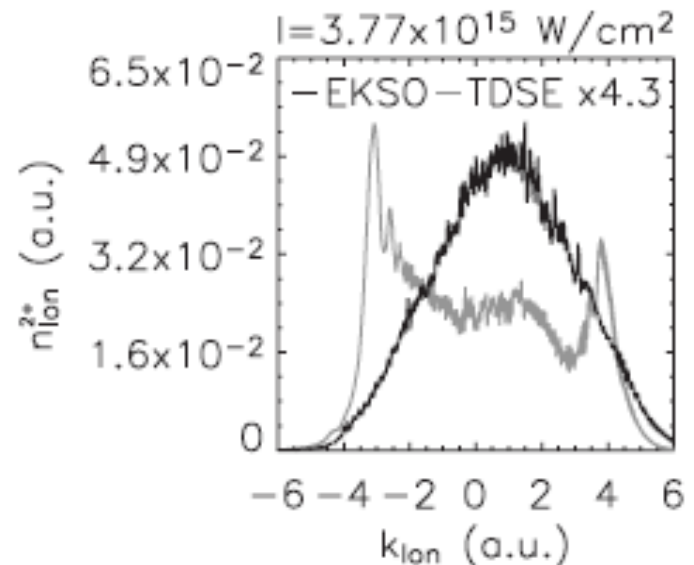
Example: Ion-recoil in Non-sequential Double Ionization

Progress has been made for approxs in TDDFT to get accurate *yields* for NSDI and capture the famous “knee” [Lein & Kuemmel PRL (2005); Wilken & Bauer PRL (2006)]

But what about **momentum distributions**?

Ion-recoil p-distributions computed from *exact* KS orbitals are poor, eg.

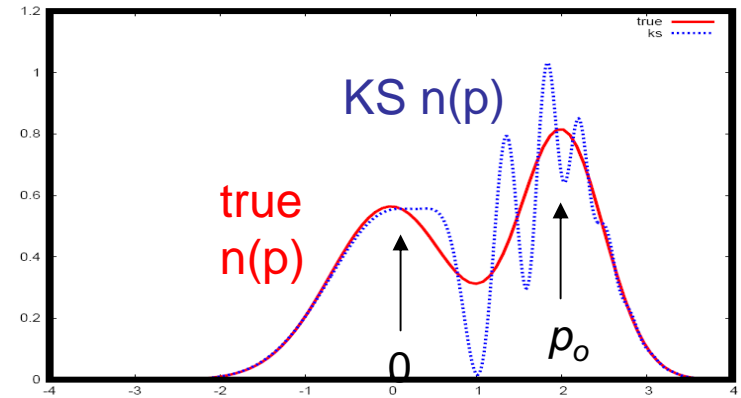
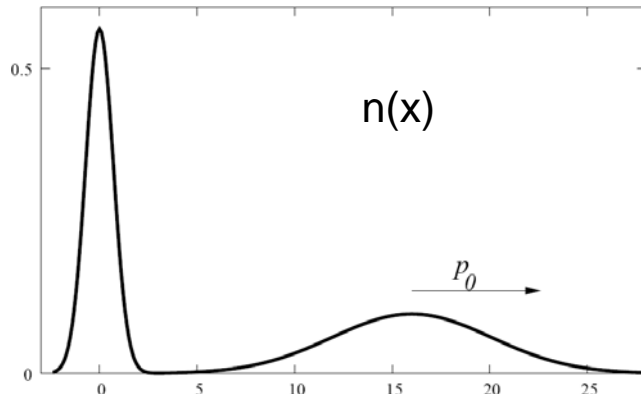
(Wilken and Bauer, PRA **76**, 023409 (2007))



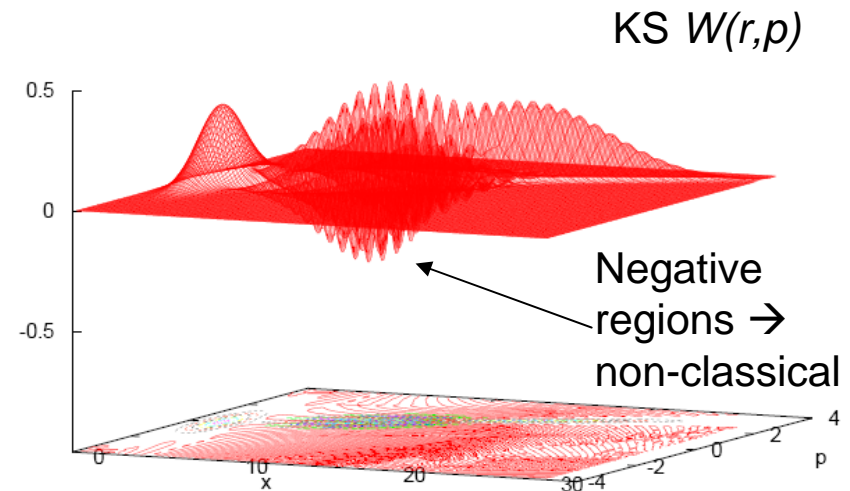
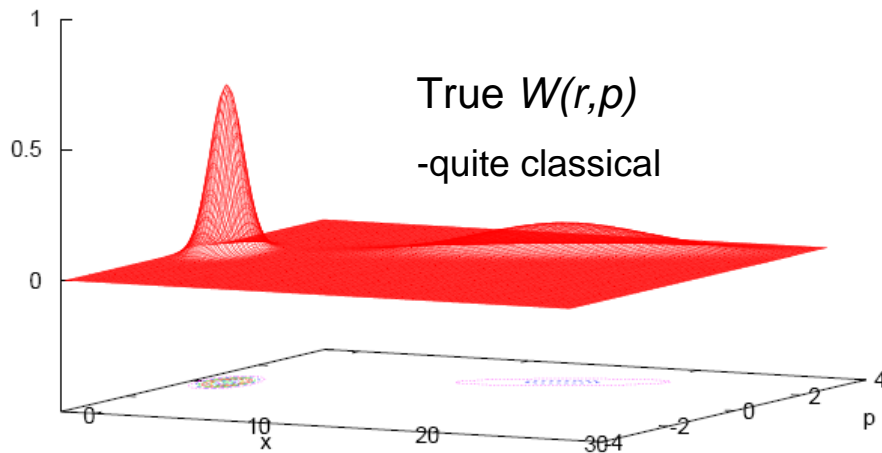
- Generally time-dependent KS momentum distributions don't have anything to do with the true p-distribution

(in principle the true p-dist is a functional of the KS system...but what functional?!)

A simple example: 2-el 1-d Model of Ionization



QM Wigner phase-space densities:



KS = doubly-occupied orbital, that gets $n(x)$ exactly right, but must therefore be delocalized \rightarrow non-classical.

KS describes an essentially classical situation highly non-classically!

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$$w(\mathbf{r}, \mathbf{p}, t)$$

Develop a generalized DFT based on **Phase-Space (quasiprobability) density**

Basic variable has more information \rightarrow simpler functionals may be more accurate

More observables directly obtained without additional observable-functionals
eg., momentum, kinetic energy

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Wigner function

One-body reduced Wigner fn:

$$w(r, p, t) = \int \rho_1(r + y/2, r - y/2, t) e^{ip \cdot y} dy$$

↑
1-body density matrix (1-DM)

w contains both r and p information

$$\left\{ \begin{array}{l} n(r, t) = \int w(r, p, t) dp \\ \tilde{n}(p, t) = \int w(r, p, t) dr \end{array} \right.$$

Literature notes:

-- Wigner function mostly used for one-particle problems, esp. to make classical-quantum analogies.

-- Some work on many-electron problems, particularly for transport,

eg. Jacoboni, *Rep. Prog. Phys.* **67** 1033 (2004); Cancellieri, Bordone, Bertoni, Ferrari & Jacoboni, *J. Comp. Elec.* **3**, 411 (2005)

-- “Phase-space intracule” approach of Gill et al. involves contractions of the two-body Wigner function

Wigner Phase-Space-Density Functional Theory

Basic variable $w(r, p, t) = \int \rho_1(r + y/2, r - y/2, t) e^{ip \cdot y} dy$ replaces $n(r, t)$

- In principle, *all* observables may be obtained from knowledge of $w(r, p, t)$ and the initial state Ψ_0 : 1-1 $w \leftrightarrow v$ (local) mapping follows from Runge-Gross theorem.

Generalizable to vector potentials: $w \xleftrightarrow[\Psi_0]{1-1} \mathbf{A}$

- PSDFT formally equivalent to TD-density-matrix-FT:

recent developments in the linear response regime, Pernal, Gritsenko, Baerends *Phys. Rev. A* (2007), Giesbertz, Baerends, Gritsenko *Phys. Rev. Lett.* (2008)

Phase-space formulation may prove useful for visualization, approximations and semiclassical analyses.

- NO KS counterpart! No non-interacting system can reproduce the phase-space density of a given interacting system.
- No additional “observable functionals” are needed for the expectation value of *any* one-body operator.

Equation of motion:

kinetic energy done *exactly*
(unlike in TDDFT)

$$\dot{w}(\mathbf{r}, \mathbf{p}, t) = \left[-\mathbf{p} \cdot \nabla - i \int d^3 p' \int d^3 y e^{-i(\mathbf{p}-\mathbf{p}') \cdot \mathbf{y}} \left[v_{ext}(\mathbf{r} + \frac{\mathbf{y}}{2}) - v_{ext}(\mathbf{r} - \frac{\mathbf{y}}{2}) \right] \right] w(\mathbf{r}, \mathbf{p}, t) \\ - i \int d^3 y d^3 p_1 d^3 p_2 d^3 r_2 e^{i(\mathbf{p}-\mathbf{p}_1) \cdot \mathbf{y}} \left(\frac{1}{|\mathbf{r} - \mathbf{r}_2 + \frac{\mathbf{y}}{2}|} - \frac{1}{|\mathbf{r} - \mathbf{r}_2 - \frac{\mathbf{y}}{2}|} \right) w_2(\mathbf{r}, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2, t)$$

Would like this in terms of w
and Ψ_0 .

Approximations needed here.

We'd like these to:

Capture correlation

Change occupation #'s of TD natural
orbitals (elec qm control)

BBGKY truncation, but gets rapidly
messy esp. when preserving trace
relation

Quasi/Semiclassical? *stay tuned!!*

(Adiabatic ones based on ground-state density-
matrix functionals don't work: Pernal et al. JCP
2007, Appel & Gross, *arXiv* (2008))

Before we describe a possible approach to this, can we say anything about their memory-dependence?

- TDDFT Memory arises because of the reduced description of the system in terms of density alone.
- So, could functionals of the phase-space density $F[w]$ be *less non-local* in time?
- Consider Hooke's atom example...

TDDFT History-dependence in Hooke's atom

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

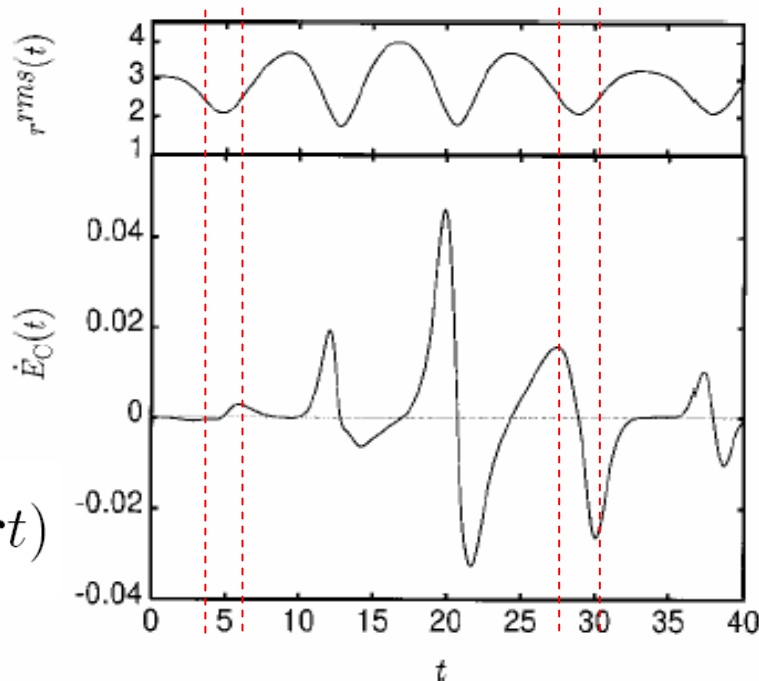
$$v_{xc}[n; \Psi_0, \Phi_0](\mathbf{r}t)$$

$n(\mathbf{r}t'), t' < t$

2 electrons in parabolic well,
time-varying force constant

parametrizes
density

$$\int d^3r \dot{n}(\mathbf{r}t) v_c(\mathbf{r}t)$$



$$k(t) = 0.25 - 0.1 * \cos(0.75 t)$$

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

Time-slices where $n(t)$ is locally and semi-locally identical but v_c is quite distinct $\rightarrow v_c$ is generally a very non-local functional in time of the density

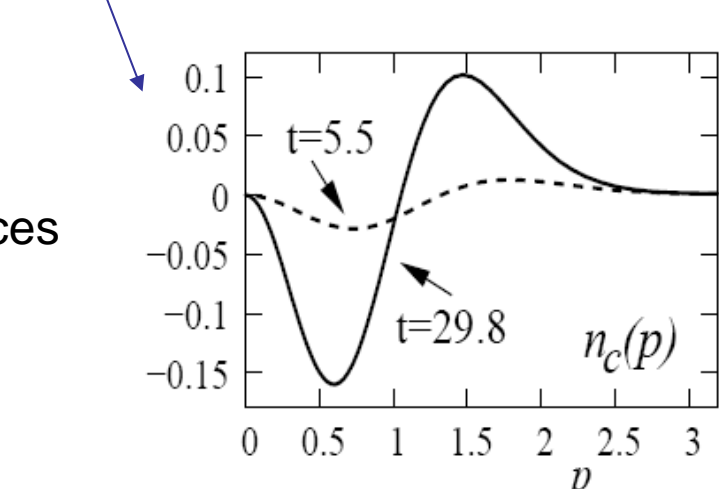
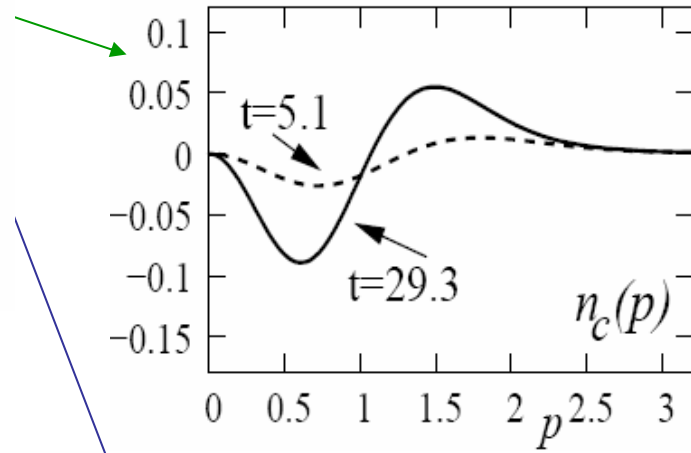
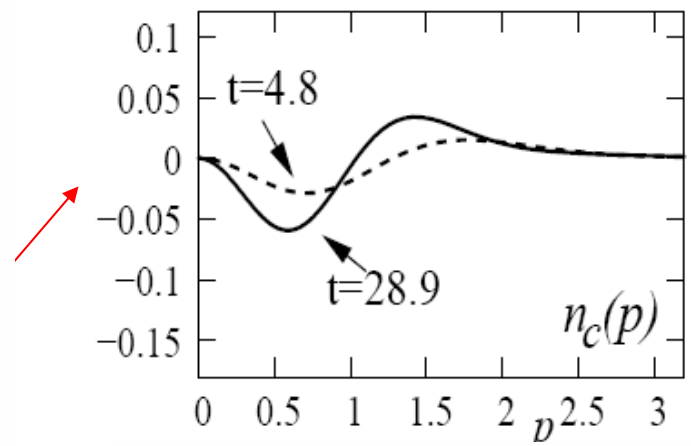
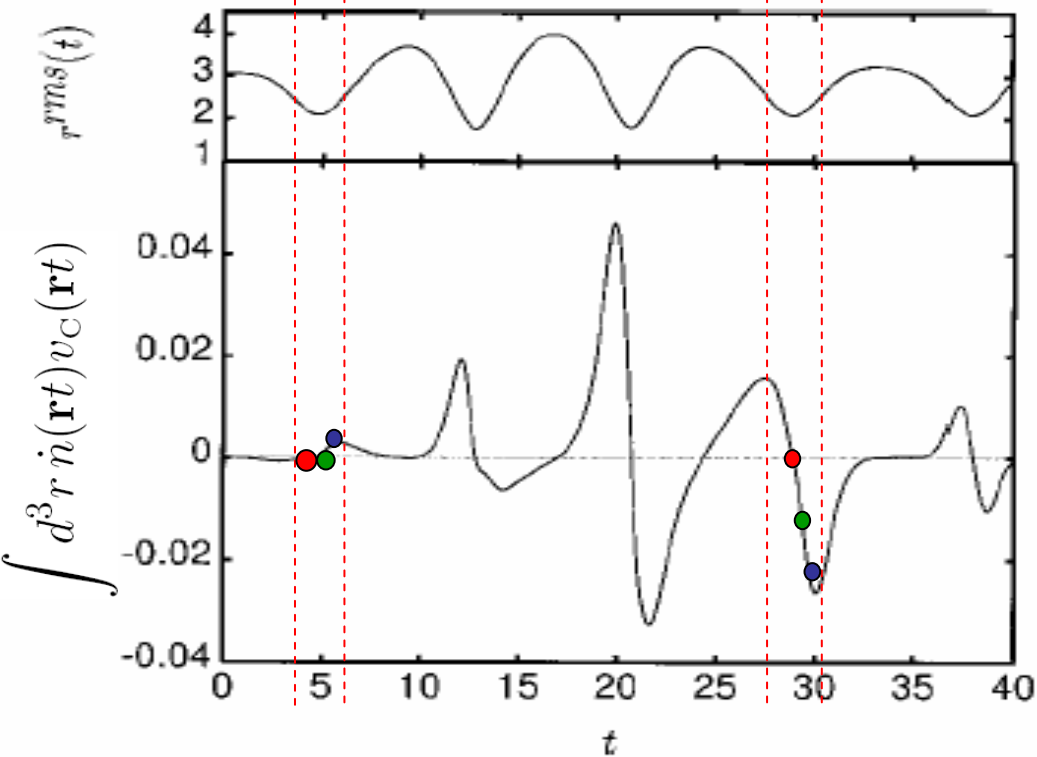
Using Hooke's Atom to ask:

- Could functionals of the phase-space density $F[w]$ be *less non-local* in time?
- **Exploration:** If we find $w(r,p,t)$ distinguishes the system at those times when $n(r,t)$ cannot, then
 - memory-dependence in PSDFT milder than in the usual TDDFT

To simplify: we actually look at $\tilde{n}(p,t)$

and define

$$\tilde{n}_c(p,t) = \tilde{n}(p,t) - \tilde{n}_s(p,t)$$



At each pair of times on the right:

$n(r,t)$ identical, $v_c(r,t)$ different, $n_c(p,t)$ different

And, larger difference in $v_c \rightarrow$ larger difference in n_c

\rightarrow Instantaneous p -densities *do* distinguish differences in $v_c(r,t)$ in cases where instantaneous $n(r,t)$ are identical, i.e. functionals of $w(r,p,t)$ reduce memory-dependence compared to those of $n(r,t)$ alone

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A Quasi(Semi)classical Treatment of w_2

$$\dot{w}(\mathbf{r}, \mathbf{p}, t) = \left[-\mathbf{p} \cdot \nabla - i \int d^3 p' \int d^3 y e^{-i(\mathbf{p}-\mathbf{p}') \cdot \mathbf{y}} \left[v_{ext}(\mathbf{r} + \frac{\mathbf{y}}{2}) - v_{ext}(\mathbf{r} - \frac{\mathbf{y}}{2}) \right] \right] w(\mathbf{r}, \mathbf{p}, t) \\ - i \int d^3 y d^3 p_1 d^3 p_2 d^3 r_2 e^{i(\mathbf{p}-\mathbf{p}_1) \cdot \mathbf{y}} \left(\frac{1}{|\mathbf{r} - \mathbf{r}_2 + \frac{\mathbf{y}}{2}|} - \frac{1}{|\mathbf{r} - \mathbf{r}_2 - \frac{\mathbf{y}}{2}|} \right) w_2(\mathbf{r}, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2, t)$$

Decompose $w_2(\mathbf{r}, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2, t) = w(\mathbf{r}, \mathbf{p}_1, t) w(\mathbf{r}_2, \mathbf{p}_2, t) + w_{2xc}(\mathbf{r}, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2, t)$

w_{2xc} is the correction to independent particle two-body phase-space distribution

Idea: obtain w_{2xc} via a quasi- or semi-classical dynamics of the many-body wavefunction, while evolving all other terms (one-body) *exactly*.

Quasiclassical (QC) evolution of $W(\underline{r}, \underline{p}, t)$

Take the initial quantum N-body Ψ_0 , find its initial quantum Wigner distribution, but then evolve it as a *classical* phase-space probability distribution:

N-body QC Wigner function $W^{QC}(\underline{r}, \underline{p}, t) = W_0(\underline{r}_{-t}, \underline{p}_{-t})$

evolve classical Hamilton's equations backward in time for each electron:

$$\begin{aligned} \frac{\partial r_i}{\partial t} &= p_i(t) \\ \frac{\partial p_i}{\partial t} &= -\frac{\partial V}{\partial r_i} - \frac{\partial V_{ee}}{\partial r_i} \end{aligned}$$

$$\begin{aligned} V(\underline{r}, t) &= \sum_i v_{\text{ext}}(r_i, t) \\ V_{ee}(\underline{r}, t) &= \sum_{i \neq j} \frac{1}{|r_i - r_j|} \end{aligned}$$

Heller, *JCP* **64**, 1289 (1976); Brown & Heller, *JCP* **75**, 186 (1981)

Now extract 1-body Wigner: $W^{QC}(r, p, t) = \int W^{QC}(\underline{r}, \underline{p}, t) d^3 r_2 \dots d^3 r_N d^3 p_2 \dots d^3 p_N$

and calculate

$$W_{2,xc}^{QC}(r_1, r_2, p_1, p_2) = \int W^{QC}(\underline{r}, \underline{p}, t) d^3 r_3 \dots d^3 r_N d^3 p_3 \dots d^3 p_N - W^{QC}(r_1, p_1, t) W^{QC}(r_2, p_2, t)$$

Insert $w^{QC}_{2xc}(r,p,t)$ into (quantum) eqn for $w(r,p,t)$:

- Captures “classical correlation”, while capturing quantum effects at the one-body level
- Has memory-dependence & initial-state dependence naturally built in!
- Classical scaling with the number of electrons
- But no guarantee for N-representability
- How about changing occupation #'s of TD natural orbitals ?

$$\rho_1(\mathbf{r}, \mathbf{r}', t) = \sum_i f_i(t) \psi_i(\mathbf{r}, t) \psi_i^*(\mathbf{r}', t)$$

$$w(\mathbf{r}, \mathbf{p}, t) = \sum_i f_i(t) w_i(\mathbf{r}, \mathbf{p}, t)$$

← one of the main reasons for the phase-space DFT!

Eg. In the electronic quantum control problem of He $1s^2 \rightarrow 1s2p$ excited state,

$f_1 \sim \text{near } 2 \rightarrow \text{near } 1$ while $f_2 \sim \text{near } 0 \rightarrow \text{near } 1$



Yes!

Next slide..

Example: Time-dependent Moshinsky atom

Niehaus, Suhai, March, J. Phys. A. 41, 085304 (2008)

Everything is harmonic

$$\hat{H} = -\frac{1}{2}(\nabla_{r_1}^2 + \nabla_{r_2}^2) + \frac{1}{2}\omega_0^2(t)(r_1^2 + r_2^2) + u(|\mathbf{r}_1 - \mathbf{r}_2|)$$

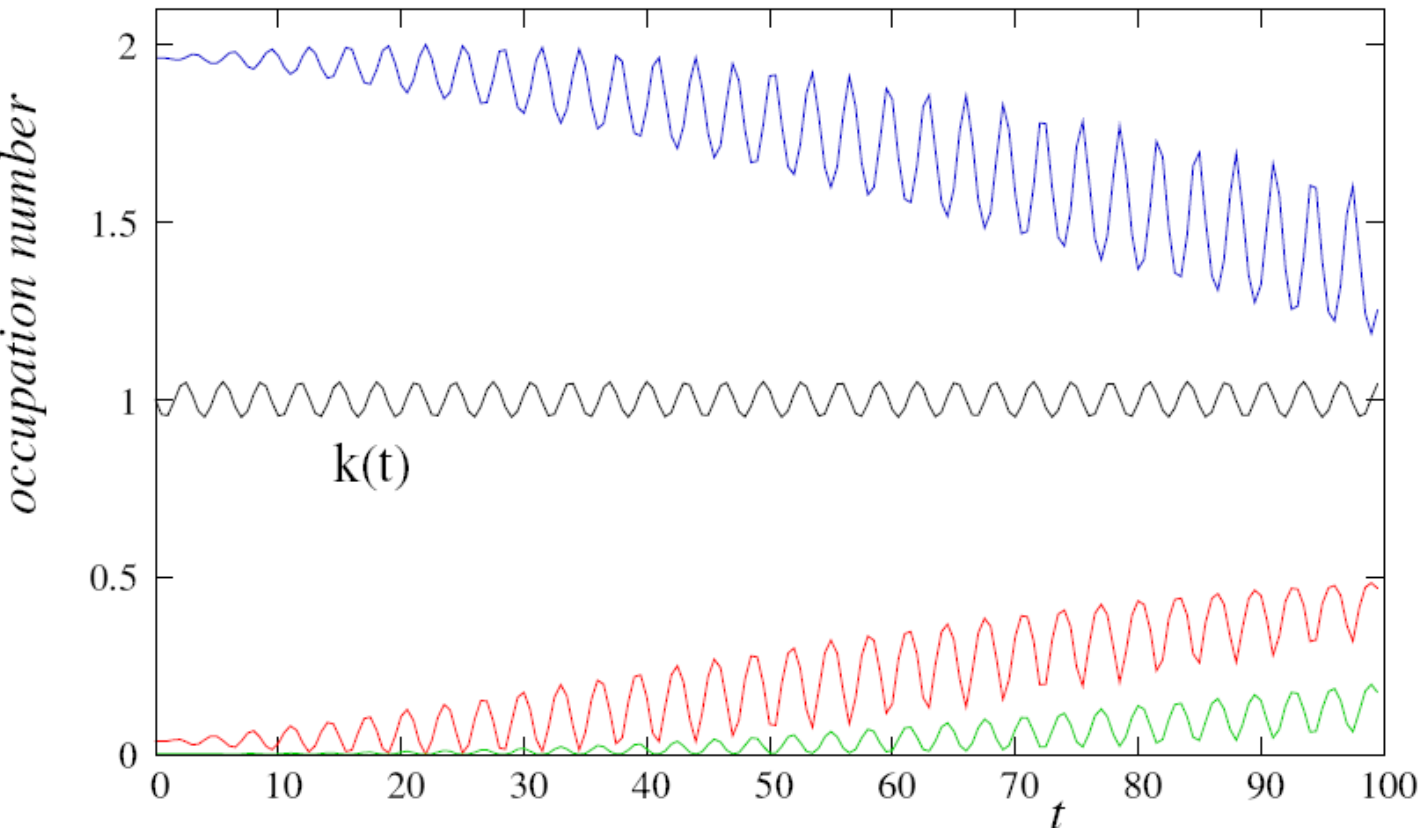
$\lambda(r_1 - r_2)^2$

Exact solution for $\Psi(r_1, r_2, t)$ is easily solvable by separating into center of mass and relative coordinates \rightarrow obtain exact occupation numbers.

Drive at a transition frequency to encourage population transfer:

$$\text{e.g. } \omega_0^2(t) = 1 - 0.05 \sin(2t)$$

Changing Occupation Numbers using w_{2xc}^{QC}



Quasiclassical
calculation = Exact
(harmonic !)

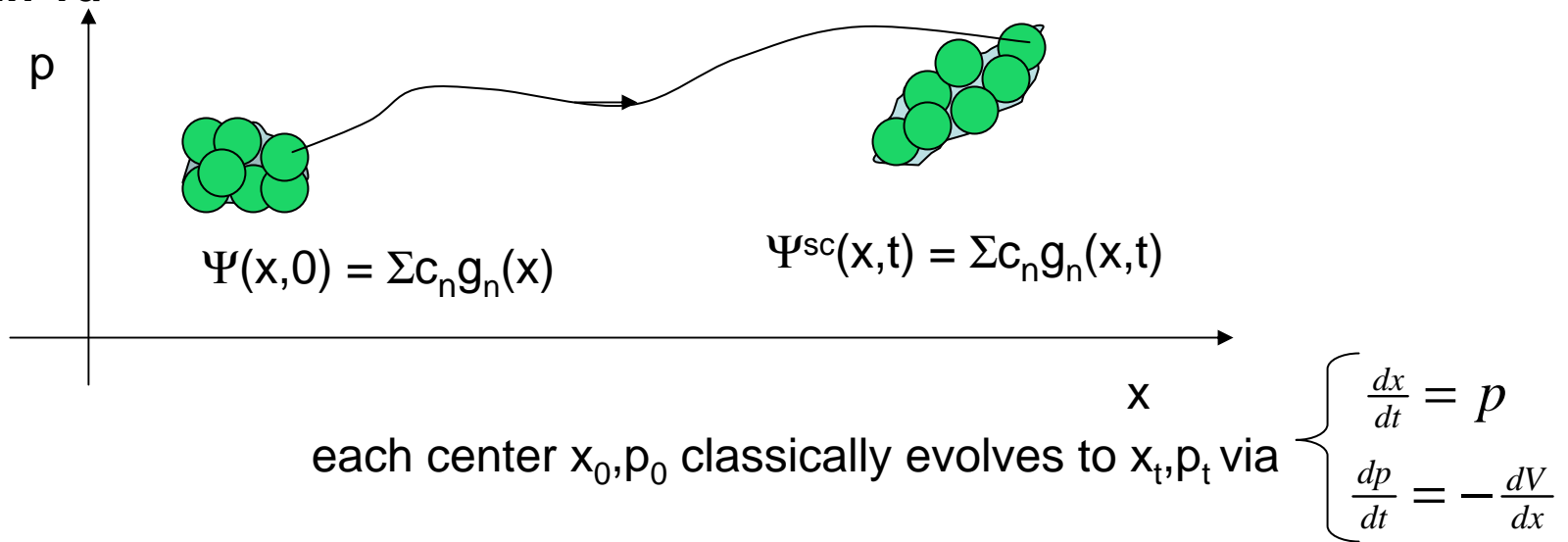
A. Rajam, I. Raczkowska, N.T. Maitra, in prep. (2010)

One step further: Semiclassical instead of Quasiclassical

to get W^{SC}_{2xc} to $O(\hbar)$

Essential Concept: Frozen Gaussians (Heller, 1981)

Eg. 1e in 1d



$$g_n(x) = N \exp[-g(x-x_0)^2 + ip_0 x]$$

$$g_n(x,t) = N \exp[-g(x-x_t)^2 + ip_t x + iS_t]$$

i.e. the Σ is really a sum over initial phase-space points (x_0, p_0)

Herman-Kluk Propagator (1984):

- made Frozen Gaussian Approach semiclassically rigorous (i.e. satisfying TDSE $O(\hbar)$).
- phase-space integral over *classical* trajectories builds the wavefn, yet captures interference, quantization
- so far mostly used for nuclear dynamics, scales “more efficiently” than QM for dozens of d.o.f. in many cases
- sign problem from oscillating phase restricts efficient use to several, not many, d.o.f, and systems of low chaos
- quasi-classical technique: pure classical evolution of an initial quantum phase-space distribution (no sign problem) – scales $\sim \sqrt{N}$ (but no interference...)

So: Insert w_{2xc} obtained from the semiclassically propagated many-body wavefunction into equation for $w(r,p,t)$...

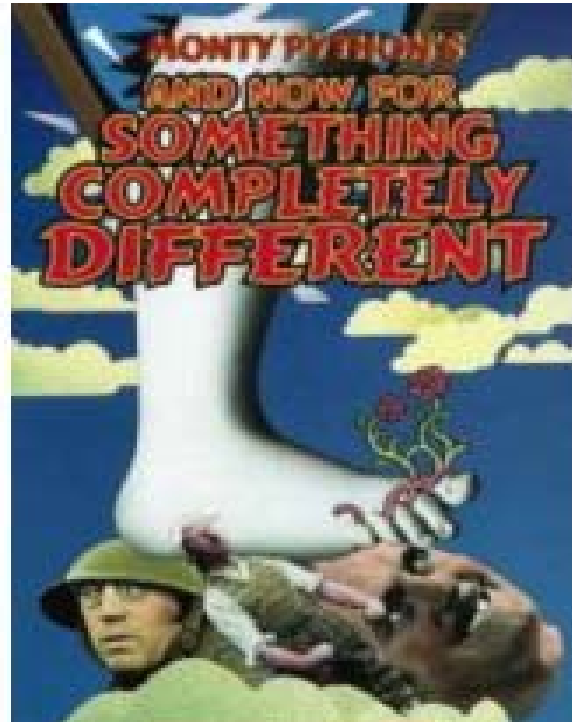
- will change occupation #'s
- naturally builds in memory, *both* initial-state-dependence and history
- scales well for many cases (low degree of chaos)



WORK IN PROGRESS

Summary so far

- Approximate TDDFT, although remarkably successful for many wide-ranging applications esp. in linear response, faces serious pitfalls for several applications for real-time dynamics
 - when true wavefunction is dominated equally by more than one SSD
 - where memory-dependence is important
 - when observable of interest is not directly related to the density
- Phase-Space TDDFT could be more successful than TDDFT in these cases, ameliorating all three problems.
- Two-body Wigner functionals of the one-body PS density are needed that dynamically change occupation #'s
- A quasi- or semi-classical treatment of the dynamics of the two-body Wigner functional may be a promising route, while naturally including the elusive initial-state-dependence and memory – should be further explored!!



Revisiting the Formal Theorems behind TDDFT

Time-Analyticity Requirements

(1) Runge-Gross (RG) Theorem:

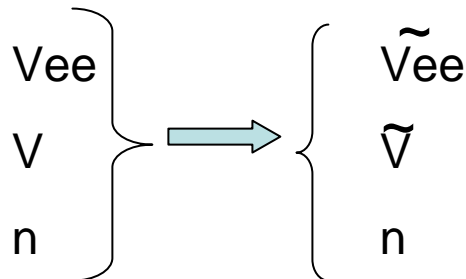
$$n(\mathbf{r}, t) \xleftrightarrow[1-1]{\Psi_0} v(\mathbf{r}, t)$$

proven only for potentials analytic in time about the initial time:

$$v(\mathbf{r}, t) = \sum_{k=0}^{\infty} \frac{1}{k!} v_k(\mathbf{r}) (t - t_0)^k$$

Proof requires v to be t-analytic

(2) van Leeuwen Theorem



v-representability under different interparticle interactions

$$(KS \quad \tilde{V}_{ee} = 0 \text{ and } \tilde{V} = V_s)$$

Proof requires both n and v to be t-analytic

How restrictive are these requirements?

- Means that potentials that turn on like $\sim e^{-C/t^n}$, t^p p non-integer, or $t^n \ln(t)$ are not covered in RG
- Can we extend RG to apply to such potentials?
 - ✓ linear response from gs (van Leeuwen 2001)
 - ? Response from non-gs? Non-linear response?
- If we accept the restriction to $v(r,t)$ being t-analytic, is it reasonable to assume resulting $n(r,t)$ is also t-analytic?

No!

Spatial non-analyticities \rightarrow time non-analyticity via TDSE, even for the most innocently evolving potentials!

\rightarrow ν -representability proof falls through i.e. existence and uniqueness of KS system thrown into question.

Example: The Disapparated* Nucleus

Remove nucleus from H-atom and watch e-density evolve in free-space:

Propagate $\psi(x, 0) = \sqrt{\kappa} e^{-\kappa|x|}$ using $G(x, t; x', 0) = \sqrt{\frac{m}{2\pi i\hbar t}} e^{i(x-x')^2 m/2\hbar t}$



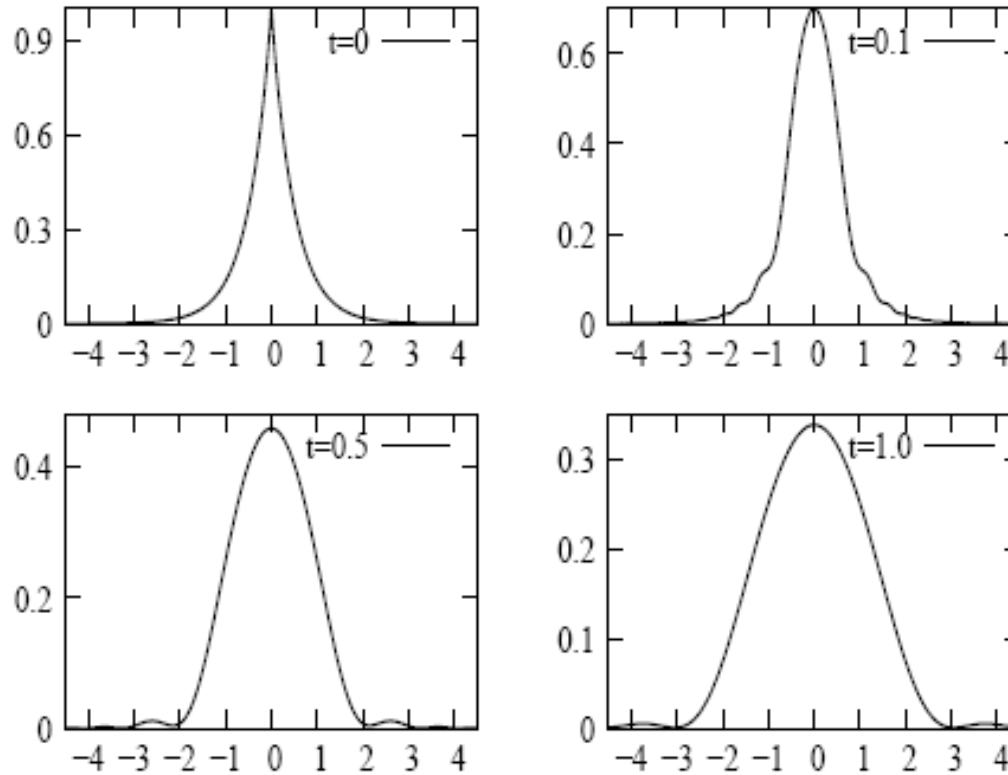
$$\psi(x, t) = \frac{\sqrt{\kappa}}{2} e^{i\hbar\kappa^2 t/2m} \left\{ e^{\kappa x} \left[1 - \operatorname{erf} \left(\frac{x + i\hbar\kappa t/m}{\sqrt{2i\hbar t/m}} \right) \right] + e^{-\kappa x} \left[1 - \operatorname{erf} \left(\frac{-x + i\hbar\kappa t/m}{\sqrt{2i\hbar t/m}} \right) \right] \right\}$$

Non-analytic in t and completely different from its (fixed-x) Taylor-series:

$$\psi_T(x \neq 0, t) = \sqrt{\kappa} e^{i\hbar\kappa^2 t/2m} e^{-\kappa|x|}$$

* J. K. Rowling, *Harry Potter and the Half-Blood Prince* (Bloomsbury, 2005)

- This is how the exact $n(x,t)$ looks:



True solution loses its cusp at $t=0+$, disperses and develops oscillations in the tails.

But the Taylor series does nothing!

- Although Taylor series solves free-particle TDSE for $x \neq 0$ it yields a delta-fn error at $x=0$:

$$i\hbar \dot{\psi}_T(x,t) = -\frac{\hbar^2}{2m} \psi_T''(x,t) - \frac{\hbar^2 \kappa}{m} \delta(x) \psi_T(x,t)$$

(Note – essentially the same analysis for the 3D H-atom with disapparatated nucleus)

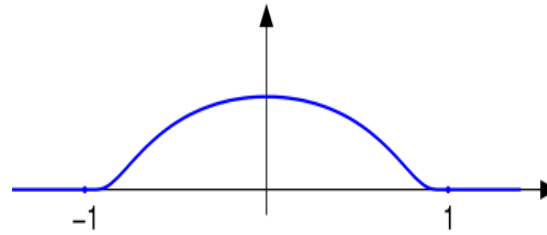
N.T. Maitra, T. N. Todorov, C. Woodward, K. Burke, in prep. (2009)

Non-t-analytic densities

- Non-t-analytic $n(r,t)$ also arises in other examples -- even where the initial wavefunction and potential are spatially smooth:

Eg. Evolve a “bump-state” like this:

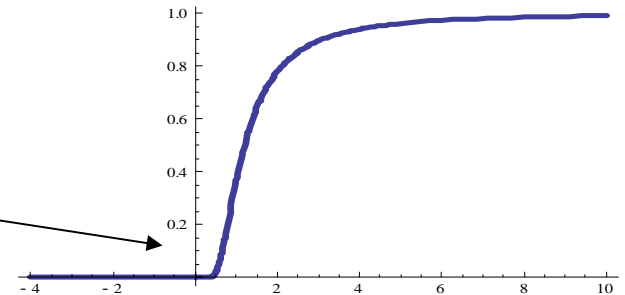
in free-space – Taylor series doesn't disperse but true solution does



Or, evolve some general initial state in an potential like:

Taylor series predicts nothing happens in the flat region – *wrong!*

infinitely-differentiable everywhere



Upshot:

$v(r,t)$ t-analytic \rightarrow RG holds, but

$v(r,t)$ t-analytic often leads to $n(r,t)$ non-t-analytic \rightarrow existence and uniqueness of KS system is not (yet) proven.

\rightarrow Can we prove TDDFT thms without assuming t-analyticity ?

Group @ Hunter

Phase-space DFT: Arun Rajam, Iza Raczkowska



Collaborators on time-analyticity requirements:

Chris Woodward
(Rutgers)



Tchavdar Todorov
(Queens, Belfast)



Kieron Burke
(UC Irvine)



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