Time-dependent density-functional theory

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Outline

1. **A survey of time-dependent phenomena**   C.U.

2. **Fundamental theorems in TDDFT**   N.M.

3. **Time-dependent Kohn-Sham equation**   C.U.

4. **Memory dependence**   N.M.

5. **Linear response and excitation energies**   N.M.

6. **Optical processes in Materials**   C.U.

7. **Multiple and charge-transfer excitations**   N.M.

8. **Current-TDDFT**   C.U.

9. **Nanoscale transport**   C.U.

10. **Strong-field processes and control**   N.M.

Time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N, t) = \left(\hat{T} + \hat{V}(t) + \hat{W} \right) \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N, t)$$

kinetic energy operator:

$$\hat{T} = \sum_{j=1}^{N} -\frac{\hbar^2 \nabla_j^2}{2m}$$
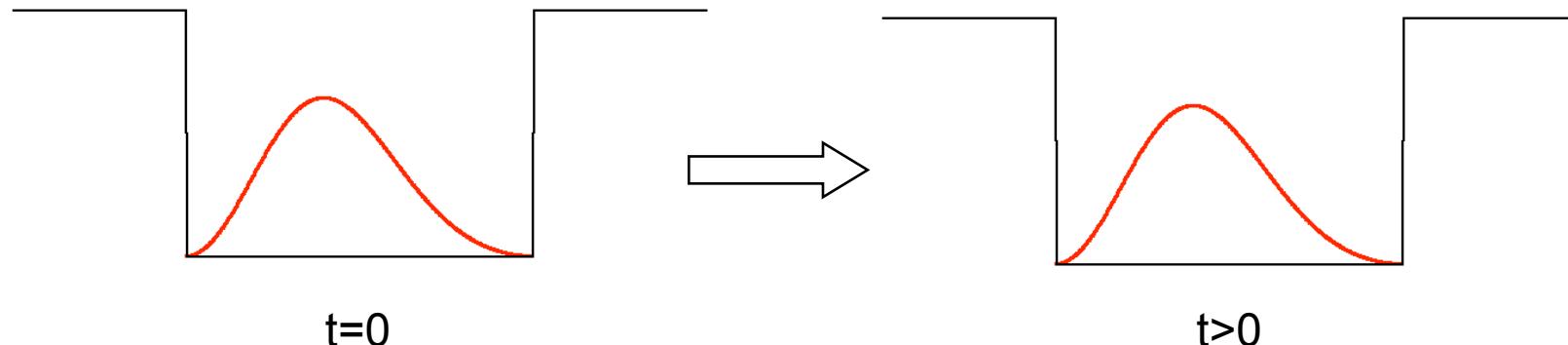
electron interaction:

$$\hat{W} = \frac{1}{2} \sum_{\substack{j,k \\ j \neq k}}^{N} \frac{e^2}{\left| \mathbf{r}_j - \mathbf{r}_k \right|}$$

The TDSE describes the time evolution of a many-body state $\Psi(t)$, starting from an initial state $\Psi(t_0)$, under the influence of an external time-dependent potential $\hat{V}(t) = \sum_{j=1}^{N} V(\mathbf{r}_j, t)$.
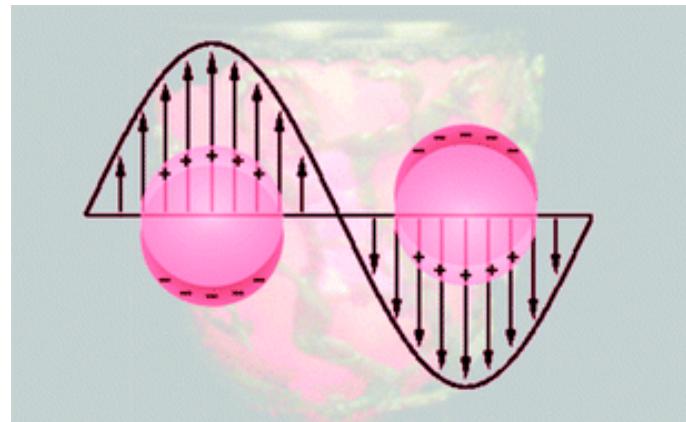
From now on, we'll (mostly) use atomic units (e = m = ħ = 1).

**Real-time electron dynamics: first scenario**
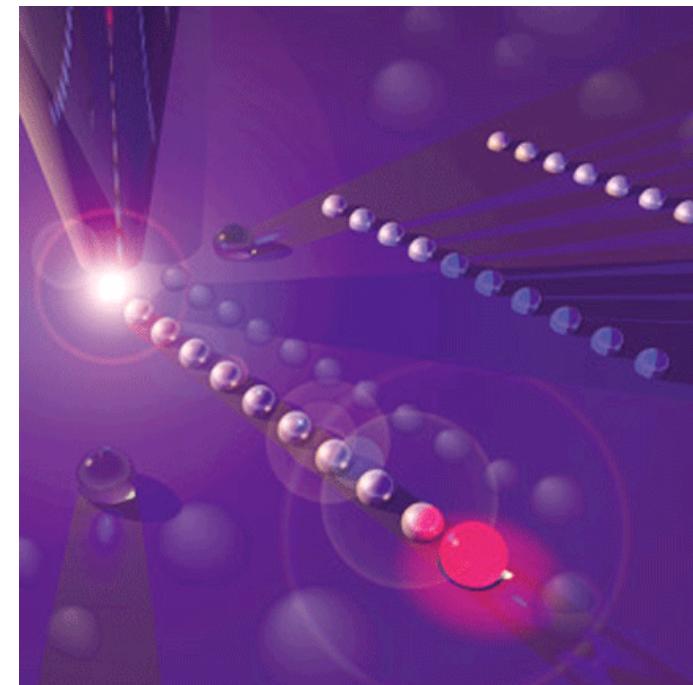
Start from nonequilibrium initial state, evolve in static potential:

t=0   t>0
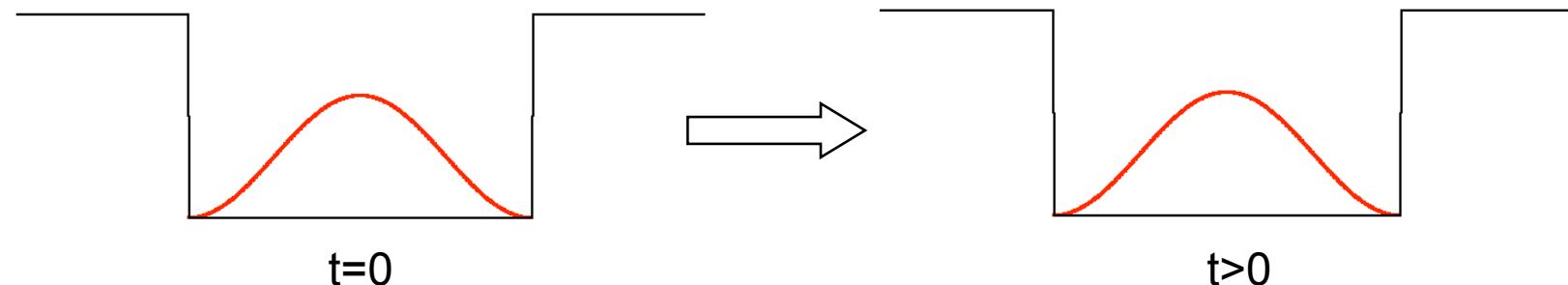
Charge-density oscillations in metallic
clusters or nanoparticles (plasmonics)
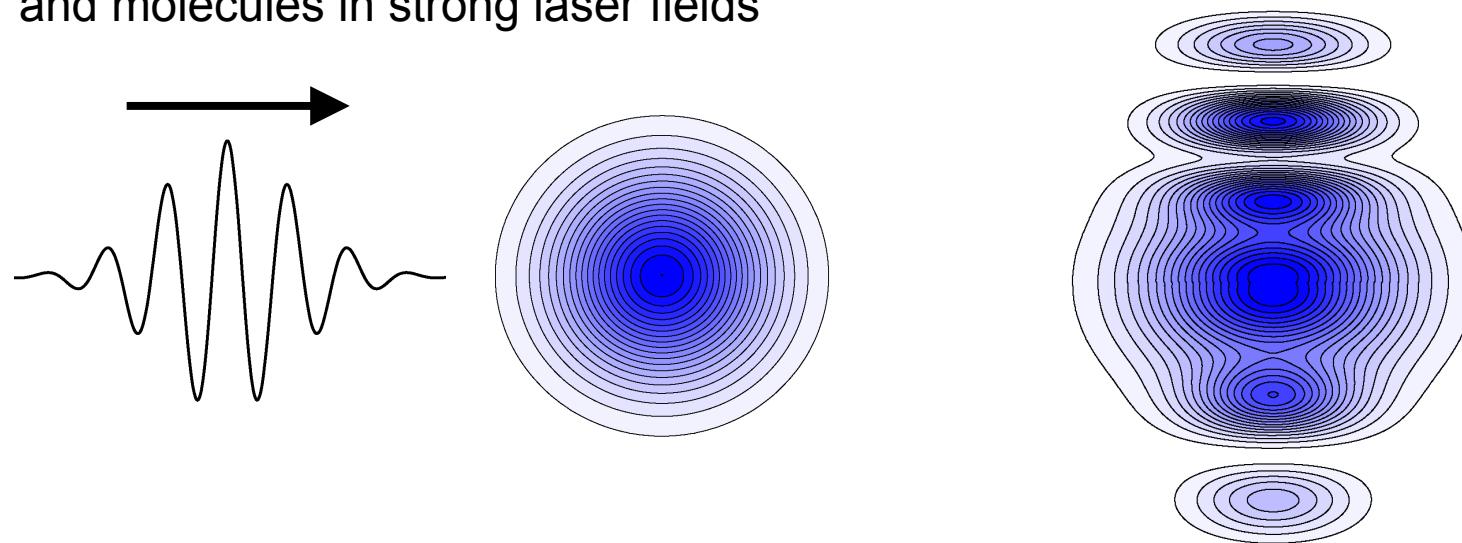
New J. Chem. **30**, 1121 (2006)
Nature Mat. Vol. **2** No. 4 (2003)
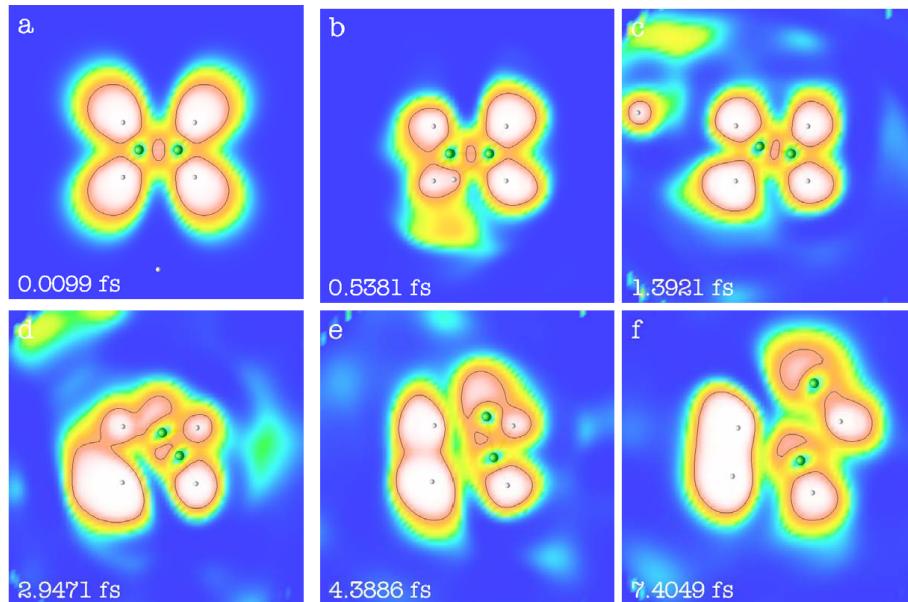
Start from ground state, evolve in time-dependent driving field:

t=0   t>0

Nonlinear response and ionization of atoms
and molecules in strong laser fields

Coupled electron-nuclear dynamics

- Dissociation of molecules (laser or collision induced)
- Coulomb explosion of clusters
- Chemical reactions
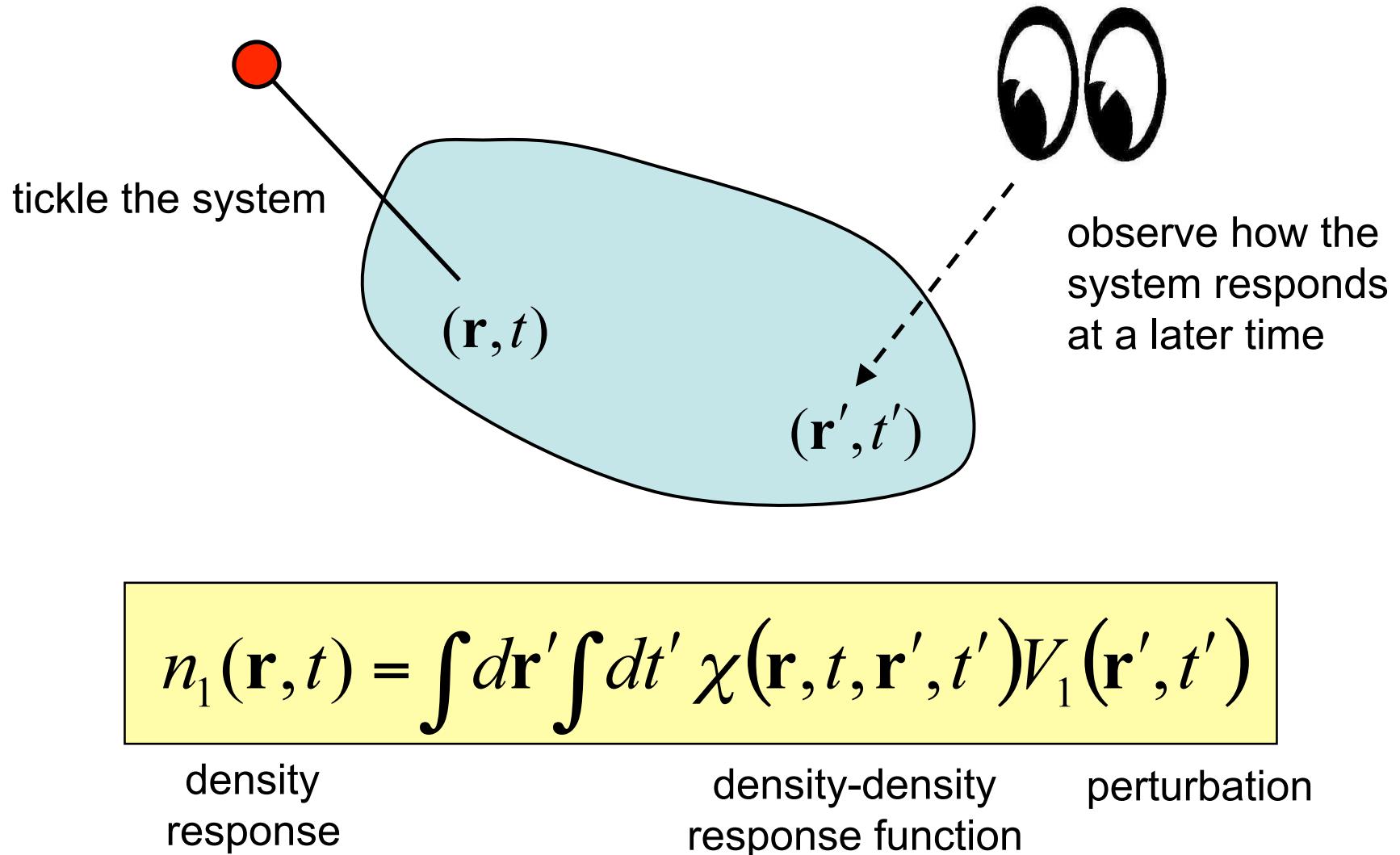
High-energy proton hitting ethene
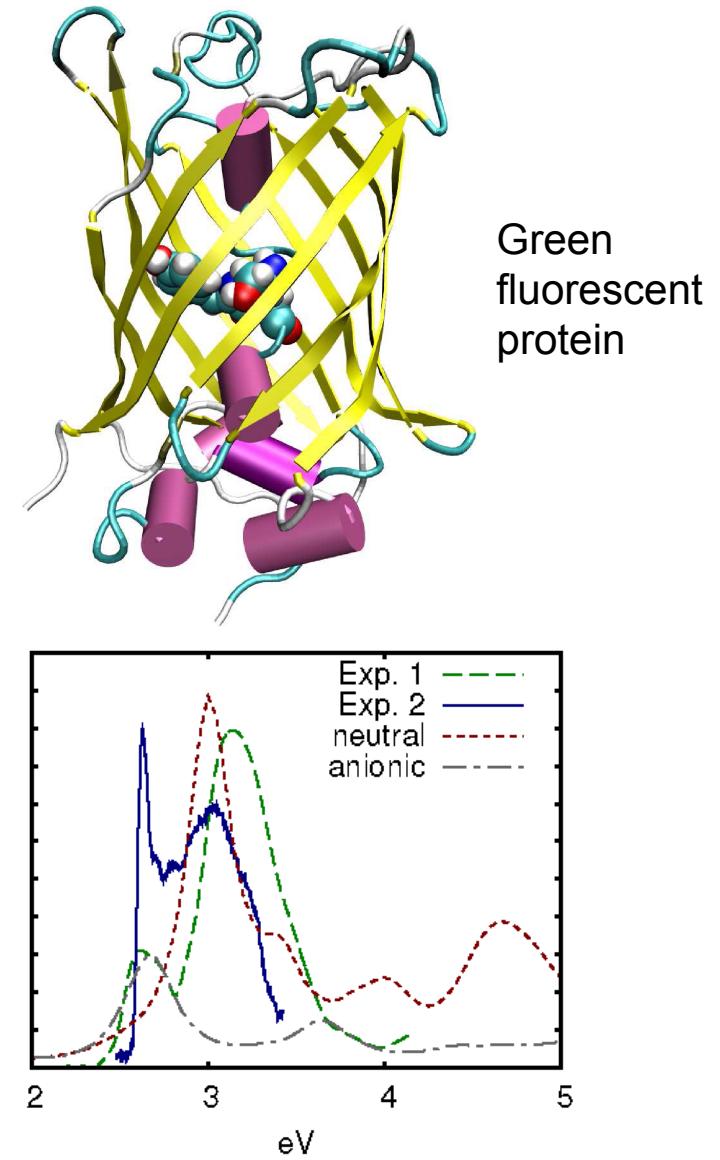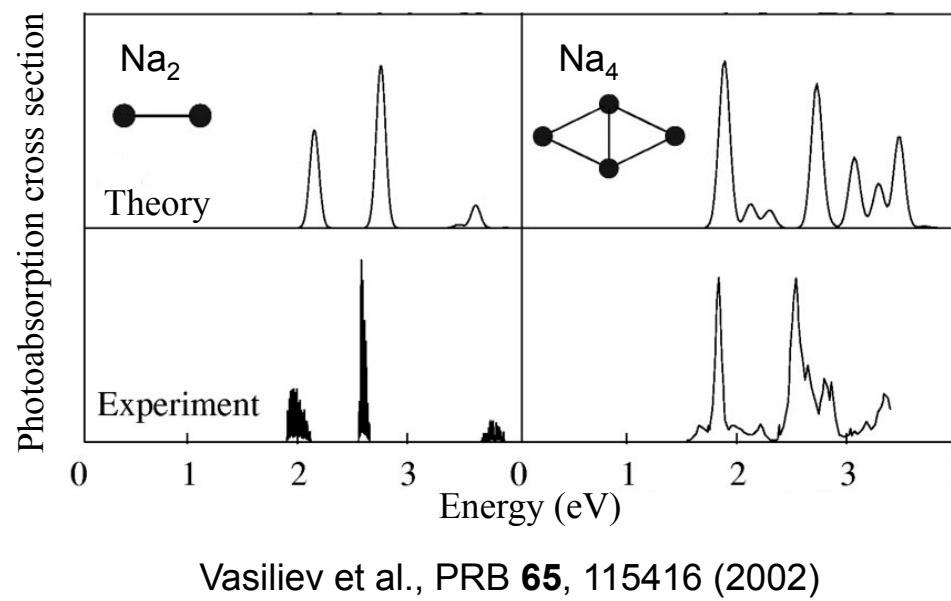
T. Burnus, M.A.L. Marques, E.K.U. Gross,
Phys. Rev. A **71**, 010501(R) (2005)

Nuclear dynamics
treated classically

For a quantum treatment of nuclear dynamics within TDDFT (beyond the scope of this tutorial), see O. Butriy et al., Phys. Rev. A **76**, 052514 (2007).

Linear response

tickle the system

$(\mathbf{r}, t)$

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

observe how the
system responds
at a later time

$$n_1(\mathbf{r}, t) = \int d\mathbf{r}' \int dt' \, \chi(\mathbf{r}, t, \mathbf{r}', t') V_1(\mathbf{r}', t')$$

density
response

density-density
response function

perturbation

Optical spectroscopy

- Uses weak CW laser as <u>Probe</u>

- <u>System Response</u> has peaks at electronic excitation energies

Green fluorescent protein

Vasiliev et al., PRB **65**, 115416 (2002)

Marques et al., PRL **90**, 258101 (2003)

Outline

For any system with Hamiltonian of form $H = T + W + V_{ext}$,

- kinetic (T)
- external potential (V_{ext})
- e-e interaction (W)

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

$$n(r\ t) \xleftarrow{\quad \Psi_0 \quad} V_{ext}(r\ t)$$

➤ For a given initial-state ψ_0, the time-evolving one-body density $n(r\ t)$ tells you *everything* about the time-evolving interacting electronic system, *exactly*.

This follows from :

$$\Psi_0,\ n(r,t) \rightarrow \text{unique } v_{ext}(r,t) \rightarrow H(t) \rightarrow \Psi(t) \rightarrow \text{all observables}$$
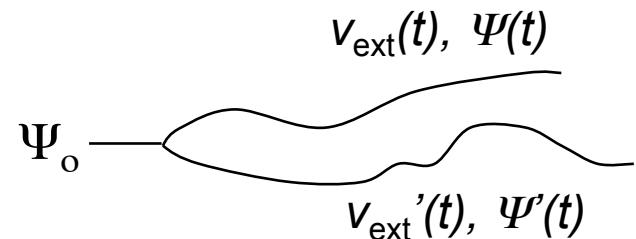
Consider two systems of N interacting electrons, both starting in the same Ψ_0, but evolving under different potentials $v_{ext}(r,t)$ and $v_{ext}'(r,t)$ respectively:

$$v_{\text{ext}}(\boldsymbol{r}, t) - v'_{\text{ext}}(\boldsymbol{r}, t) \neq c(t)$$

$v_{ext}(t)$, $\Psi(t)$

Ψ_o

$v_{ext}'(t)$, $\Psi'(t)$
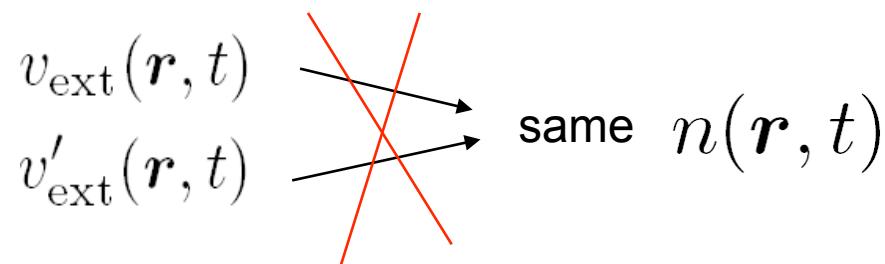
Assume Taylor-expandability:

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

$$v'(\mathbf{r}, t) = \sum_{k=0}^{\infty} \frac{1}{k!} v'_k(\mathbf{r})(t - t_0)^k.$$

RG prove that the resulting densities $n(r,t)$ and $n'(r,t)$ eventually must differ, i.e.

$$v_{\text{ext}}(\boldsymbol{r}, t)$$
$$v'_{\text{ext}}(\boldsymbol{r}, t)$$

same $n(\boldsymbol{r}, t)$

The <u>first part</u> of the proof shows that the **current-densities** must differ.

Consider Heisenberg e.o.m's for the current-density in each system,

$$\frac{\partial}{\partial t}\langle\Psi(t)|\hat{Q}(t)|\Psi(t)\rangle = \langle\Psi(t)|\left(\frac{\partial\hat{Q}}{\partial t} - i[\hat{Q}(t),\hat{H}(t)]\right)|\Psi(t)\rangle$$

$$\hat{j}_{\mathrm{P}}(\mathbf{r}) = \frac{1}{2i}\sum_{j=1}^{N}\left(\nabla_{\mathbf{r}_j}\delta(\mathbf{r}-\mathbf{r}_j) + \delta(\mathbf{r}-\mathbf{r}_j)\nabla_{\mathbf{r}_j}\right)$$

the part of H that differs in the two systems

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

At the initial time:

$$\frac{\partial}{\partial t}\{j(r,t)-j'(r,t)\}_{t=0} = -i\langle\Psi_0|\left[\hat{j}(r,t),\{\hat{H}(0)-\hat{H}'(0)\}\right]|\Psi_0\rangle$$

$$= -i\langle\Psi_0|\left[\hat{j}(r),\{v_{\text{ext}}(r,0)-v'_{\text{ext}}(r,0)\}\right]|\Psi_0\rangle$$

$$= -n_0(r)\nabla\{v_{\text{ext}}(r,0)-v'_{\text{ext}}(r,0)\}$$

initial density

→ if initially the 2 potentials differ, then j and j' differ infinitesimally later ☺

If $v_{ext}(r,0) = v'_{ext}(r,0)$, then look at later times by repeatedly using Heisenberg e.o.m :

$$\ldots \quad \frac{\partial^{k+1}}{\partial t^{k+1}} \{j(r,t) - j'(r,t)\}_{t=0} = -n_0(r)\nabla \frac{\partial^k}{\partial t^k} \{v(r,t) - v'(r,t)\}_{t=0} \qquad *$$

As $v_{ext}(r,t) - v'_{ext}(r,t) \neq c(t)$, and assuming potentials are Taylor-expandable
at t=0, there must be some k for which RHS $\neq$ 0 → $\qquad j(r,t) \neq j'(r,t)$

$$\rightarrow \text{proves } j(r,t) \quad \xleftrightarrow[\Psi_O]{1\text{-}1} \quad v_{ext}(r,t) \qquad \checkmark 1^{st} \text{ part of RG } \odot$$

The <u>second part</u> of RG proves 1-1 between *densities* and potentials:

Take div. of both sides of * and use the eqn of continuity, $\qquad \dfrac{\partial n(r,t)}{\partial t} = -\nabla \cdot j(r,t) \quad \ldots$

$$\cdots \quad \frac{\partial^{k+2}}{\partial t^{k+2}}\{n(\boldsymbol{r},t)-n'(\boldsymbol{r},t)\}_{t=0}=\nabla\cdot\left[n_0(\boldsymbol{r})\nabla\underbrace{\frac{\partial^k}{\partial t^k}\{v_{\text{ext}}(\boldsymbol{r},t)-v'_{\text{ext}}(\boldsymbol{r},t)\}_{t=0}}\right]$$

$\equiv u(r)$ is nonzero for some k, but
must taking the div here be nonzero?
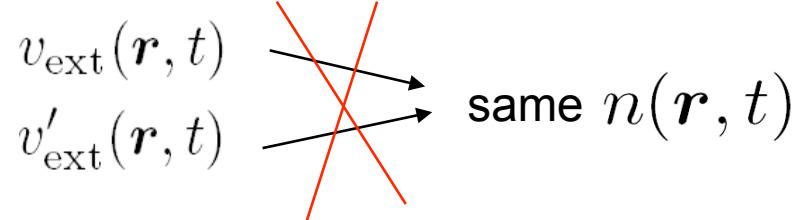
Yes!

By reductio ad absurdum: assume $\quad \text{div}[\,n(\vec{r}\,t_0)\nabla u(\vec{r}\,)\,]=0$ with $u(\vec{r}\,)\neq$ const:

Then $\quad 0=\displaystyle\int d^3r\,u(\vec{r}\,)\,\text{div}[\,n(\vec{r}\,t_0)\nabla u(\vec{r}\,)\,]$ assume fall-off of n_0 rapid enough
that surface-integral $\to 0$

$$=-\int d^3r\,n(\vec{r}\,t_0)[\nabla u(\vec{r}\,)]^2+\frac{1}{2}\oint n(\vec{r}\,t_0)[\nabla u^2(\vec{r}\,)]\cdot d\vec{f}$$

integrand ≥ 0, so if integral 0, then $\nabla u=0$ $\to$ contradiction

i.e. $\begin{array}{c}v_{\text{ext}}(\boldsymbol{r},t)\\ v'_{\text{ext}}(\boldsymbol{r},t)\end{array}$ same $n(\boldsymbol{r},t)$

➡ **1-1 mapping between time-dependent densities and potentials, for a given initial state**

● $n \rightarrow v$ for given Ψ_0, implies any observable is a functional of n and Ψ_0

　　　-- So map interacting system to a non-interacting (Kohn-Sham) one, that reproduces the same $n(\textbf{\textit{r}},t)$.

All properties of the true system can be extracted from TDKS → "bigger-faster-cheaper" calculations of spectra and dynamics

KS "electrons" evolve in the 1-body KS potential:

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

functional of the history of the density

and the initial states

-- memory-dependence (see more shortly!)

● If begin in ground-state, then no initial-state dependence, since by HK,

　　$\Psi_0 = \Psi_0[n(0)]$ (eg. in linear response). Then $v_{\text{XC}} = v_{\text{XC}}[n](\mathbf{r}t)$

● But how do we know a non-interacting system exists that reproduces a given interacting evolution *n(r,t)* ?

✓ **van Leeuwen** *(PRL, 1999)*
      (under mild restrictions of the choice of the KS initial state Φ_0)

● The KS potential is *not* the density-functional derivative of any action !

If it were, causality would be violated:

      Vxc[n,Ψ_0,Φ_0](**r**,t)   must be causal – i.e. cannot depend on *n(r t'>t)*

But *if* $v_{\mathrm{XC}}[n](\mathbf{r}t) = \dfrac{\delta A_{\mathrm{XC}}[n]}{\delta n(\mathbf{r}t)}$ then $\dfrac{\delta v_{\mathrm{XC}}[n](\mathbf{r}t)}{\delta n(\mathbf{r}'t')} = \dfrac{\delta^2 A_{\mathrm{XC}}[n]}{\delta n(\mathbf{r}t)\delta n(\mathbf{r}'t')}$

But RHS must be symmetric in (*t,t'*) → symmetry-causality paradox.

✓van Leeuwen *(PRL 1998)* showed how an action, and variational principle, may be defined, using Keldysh contours.

Clarifications and Extensions

⬤ Restriction to Taylor-expandable potentials means RG is technically not valid for many potentials, eg adiabatic turn-on, although RG is assumed in practise.

van Leeuwen *(Int. J. Mod. Phys. B. 2001)* extended the RG proof in the linear response regime to the wider class of Laplace-transformable potentials.

⬤ The first step of the RG proof showed a 1-1 mapping between *currents* and potentials → **TD current-density FT**

In principle, must use TDCDFT (not TDDFT) for

　　　　-- response of periodic systems (solids) in uniform E-fields

　　　　-- in presence of external magnetic fields

　　　　　　　(Maitra, Souza, Burke, PRB 2003; Ghosh & Dhara, PRA, 1988)

In practice, approximate functionals of current are simpler where spatial non-local dependence is important

　　　　　　　(Vignale & Kohn, 1996; Vignale, Ullrich & Conti 1997) … Stay tuned!

Outline

Consider an N-electron system, starting from a stationary state.

Solve a set of static KS equations to get a set of N ground-state orbitals:

$$\left(-\frac{\nabla^2}{2} + V_{ext}(\mathbf{r}, t_0) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) \right) \phi_j^{(0)}(\mathbf{r}) = \varepsilon_j \phi_j^{(0)}(\mathbf{r})$$

The N static KS orbitals are taken as initial orbitals and will be propagated in time:

$$\phi_j^{(0)}(\mathbf{r}) = \phi_j(\mathbf{r}, t_0), \quad j = 1,\ldots,N$$

$$i\frac{\partial}{\partial t}\phi_j(\mathbf{r}, t) = \left(-\frac{\nabla^2}{2} + V_{ext}(\mathbf{r}, t) + V_H(\mathbf{r}, t) + V_{xc}(\mathbf{r}, t) \right) \phi_j(\mathbf{r}, t)$$

Time-dependent density: $n(\mathbf{r}, t) = \sum_{j=1}^{N} \left| \phi_j(\mathbf{r}, t) \right|^2$

Only the N initially occupied orbitals are propagated. How can this be sufficient to describe all possible excitation processes?? Here's a simple argument:

Expand TDKS orbitals in complete basis of static KS orbitals,

$$\phi_j(\mathbf{r},t) = \sum_{k=1}^{\infty} a_{jk}(t)\phi_k^{(0)}(\mathbf{r})$$

finite for $k > N$

A time-dependent potential causes the TDKS orbitals to acquire admixtures of initially unoccupied orbitals.

$$V_H(\mathbf{r}, t) = \int d^3 r' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|}$$

depends on density at time t
(instantaneous, no memory)

$$V_{xc}[n](\mathbf{r}, t) \quad \text{is a functional of} \quad n(\mathbf{r}', t'), \quad t' \le t$$

The time-dependent xc potential has a memory!
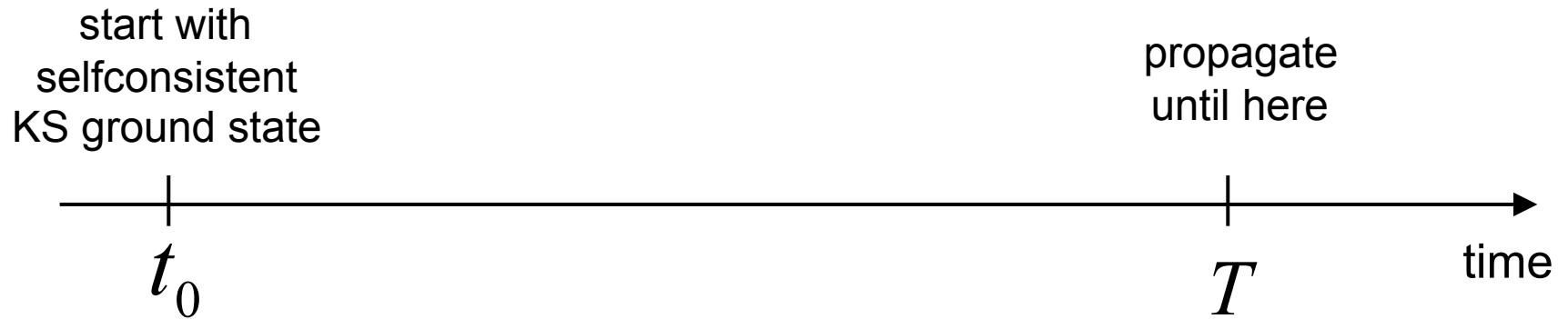
Adiabatic approximation:

$$V_{xc}^{adia}[n](\mathbf{r}, t) = V_{xc}^{gs}[n(t)](\mathbf{r})$$

(Take xc functional from static DFT and evaluate with time-dependent density)

ALDA:

$$V_{xc}^{ALDA}(\mathbf{r}, t) = V_{xc}^{LDA}(n(\mathbf{r}, t)) = \left. \frac{d^2 e_{xc}^{hom}(\bar{n})}{d\bar{n}^2} \right|_{\bar{n} = n(\mathbf{r}, t)}$$

start with
selfconsistent
KS ground state

propagate
until here

t_0

T

time

I. Propagate $\quad i\dot{\phi}_j = \left[-\frac{\nabla^2}{2} + V_{KS}^{old}(t) \right]\phi_j , \quad t \in [t_0, T]$

II. With the density $\quad n(t) = \sum_j |\phi_j(t)|^2 \quad$ calculate the new KS potential

$V_{KS}^{new}(t) = V_{ext}(t) + V_H(n(t)) + V_{xc}[n(t)] \quad$ for all $\quad t \in [t_0, T]$

III. Selfconsistency is reached if $\quad V_{KS}^{old}(t) = V_{KS}^{new}(t), \quad t \in [t_0, T]$

Propagate a time step Δt:

$$\phi_j(\mathbf{r}, t + \Delta t) = e^{-i\hat{H}\Delta t} \phi_j(\mathbf{r}, t)$$

Crank-Nicholson algorithm:

$$e^{-i\hat{H}\Delta t} \approx \frac{1 - i\hat{H}\Delta t/2}{1 + i\hat{H}\Delta t/2}$$

$$\left(1 + \tfrac{i}{2}\Delta t\hat{H}\right)\phi_j(\mathbf{r}, t + \Delta t) = \left(1 - \tfrac{i}{2}\Delta t\hat{H}\right)\phi_j(\mathbf{r}, t)$$

Problem: $\hat{H}$ must be evaluated at the mid point $t + \Delta t/2$

But we know the density only for times $\leq t$

Predictor Step:

$$\phi_j(t) \xrightarrow{\hspace{3cm}} \phi_j^{(1)}(t + \Delta t) \Rightarrow \hat{H}^{(1)}(t + \Delta t)$$

n$^{\text{th}}$ Corrector Step:
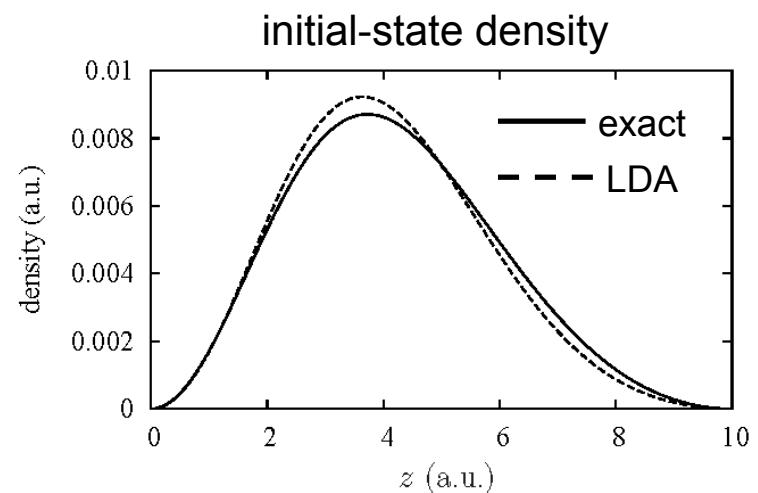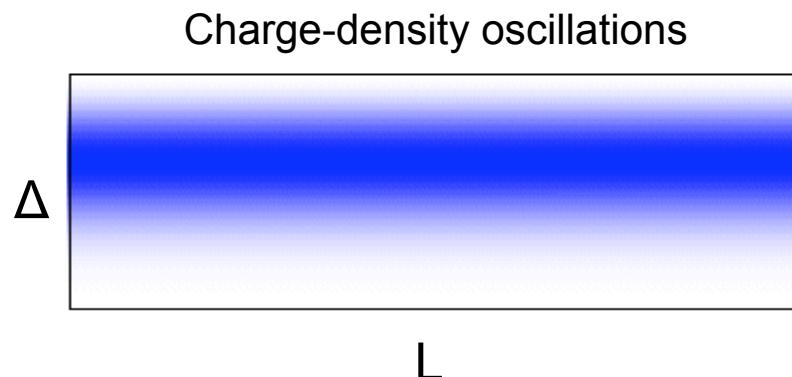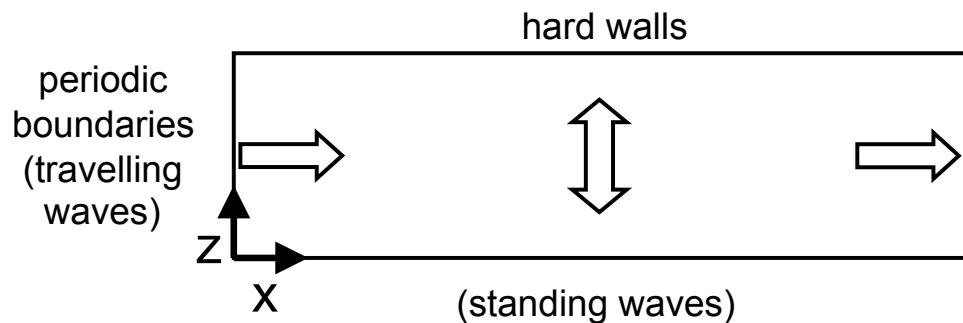
$$\phi_j(t) \xrightarrow[\substack{\hat{H}(t + \Delta t/2)= \\ \frac{1}{2}\left[\hat{H}(t) + \hat{H}^{(n)}(t + \Delta t)\right]}]{\hspace{3cm}} \phi_j^{(n+1)}(t + \Delta t) \Rightarrow \hat{H}^{(n+1)}(t + \Delta t)$$

Selfconsistency is reached if $n(t)$ remains unchanged for $t \in [t_0, T]$ upon addition of another corrector step in the time propagation.

Summary of TDKS scheme: 3 Steps

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

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

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

Example: two electrons on a 2D quantum strip

hard walls

periodic
boundaries
(travelling
waves)

Z
X

(standing waves)

initial-state density

density (a.u.)

—— exact
- - - LDA

z (a.u.)

Charge-density oscillations

Δ

L

- Initial state: constant electric field, which is suddenly switched off

- After switch-off, free propagation of the charge-density oscillations

C.A. Ullrich, J. Chem. Phys. **125**, 234108 (2006)

Step 1: solve full 2-electron Schrödinger equation

$$\left[-\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} + V(z_1,t) + V(z_2,t) + \frac{1}{|\vec{r}_1 - \vec{r}_2|} - i\frac{\partial}{\partial t} \right] \Psi(\vec{r}_1,\vec{r}_2,t) = 0$$

Step 2: calculate the exact time-dependent density

$$\sum_{s_1,s_2} \int d\vec{r}_2 \left| \Psi(\vec{r},\vec{r}_2,t) \right|^2 = n(z,t) = 2\left| \varphi(z,t) \right|^2$$

Step 3: find that TDKS system which reproduces the density

$$\left[-\frac{1}{2}\frac{d^2}{dz^2} + V(z,t) + V_H(z,t) + V_{xc}(z,t) - i\frac{\partial}{\partial t} \right] \varphi(z,t) = 0$$

Ansatz: $\quad \varphi(\vec{r},t) = \sqrt{\dfrac{n(\vec{r},t)}{2}} \exp(i\alpha(\vec{r},t))$

$$\Longrightarrow V_{xc}(\vec{r},t) = \underbrace{\begin{array}{l} -V(\vec{r},t) - V_H(\vec{r},t) \\[2mm] + \dfrac{1}{4}\nabla^2 \ln n(\vec{r},t) + \dfrac{1}{8}\left|\vec{\nabla} \ln n(\vec{r},t)\right|^2 \end{array}}_{\displaystyle V_{xc}^{A}} \underbrace{\begin{array}{l} \\ -\dot{\alpha}(\vec{r},t) - \dfrac{1}{2}\left|\vec{\nabla}\,\alpha(\vec{r},t)\right|^2 \end{array}}_{\displaystyle V_{xc}^{dyn}}$$

V_{xc}^{A}

V_{xc}^{dyn}

2D quantum strip: charge-density oscillations
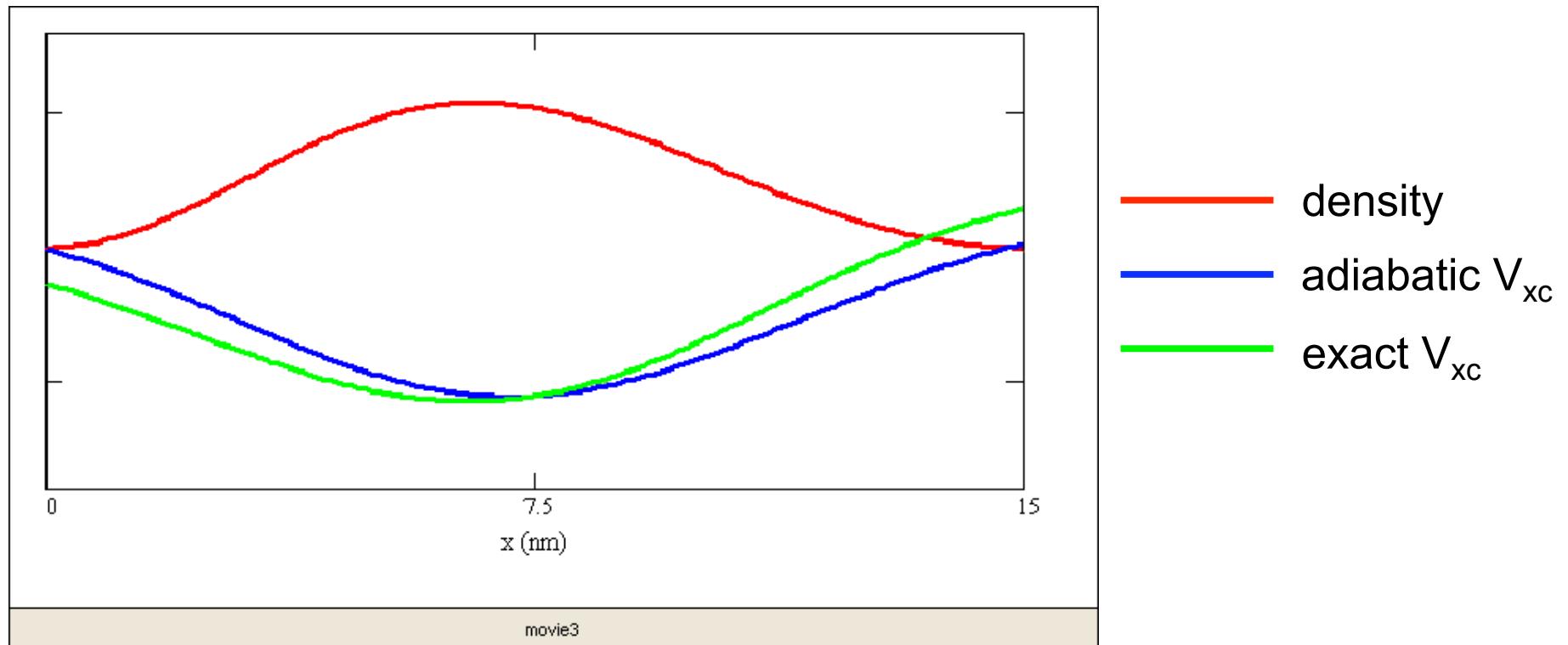
Legend:
- density (red)
- adiabatic V_{xc} (blue)
- exact V_{xc} (green)

- The TD xc potential can be constructed from a TD density
- Adiabatic approximations get most of the qualitative behavior right, but there are clear indications of nonadiabatic (memory) effects
- Nonadiabatic xc effects can become important (see later)

Outline

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

functional dependence on history, *n(r t'<t)*,
and on initial states

Almost all calculations today ignore this, and use an **"adiabatic approximation"** :

Just take xc functional from static DFT and evaluate on instantaneous density

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

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

v_{xc}

But what about the exact functional?
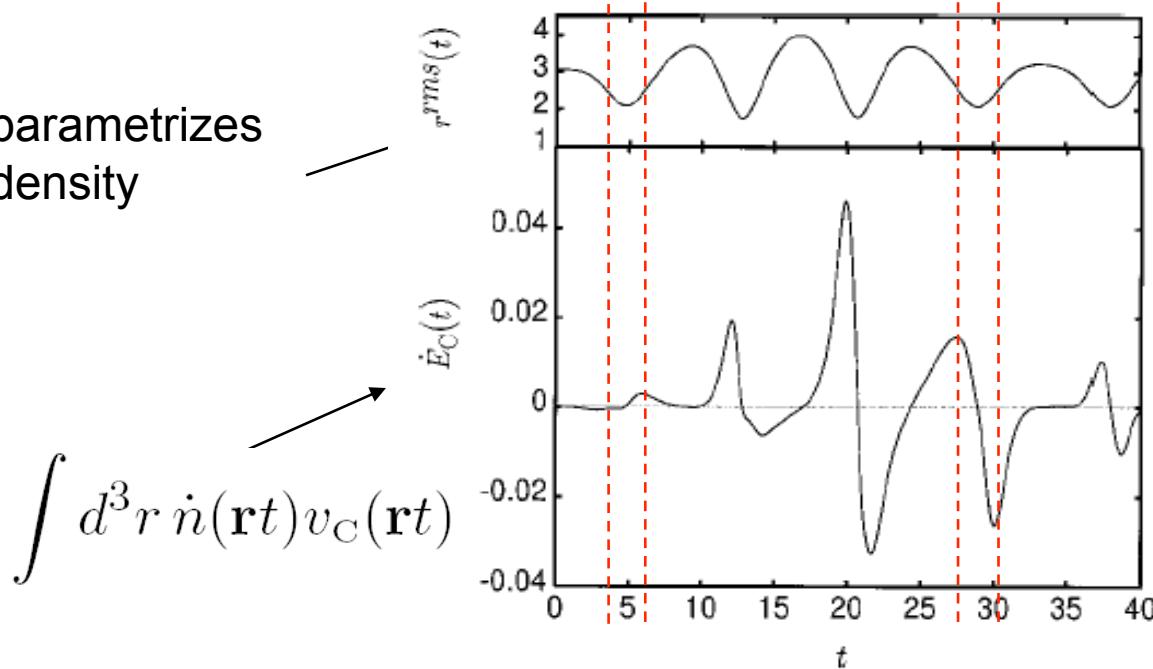
Eg. Time-dependent Hooke's atom –exactly solvable

$$v_{\text{xc}}[n; \Psi_0, \Phi_0](\mathbf{r}t)$$
$$n(\mathbf{r}t'), t' < t$$

2 electrons in parabolic well,
time-varying force constant

parametrizes
density

$$\int d^3 r\, \dot{n}(\mathbf{r}t) v_{\text{C}}(\mathbf{r}t)$$

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

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

Hessler, Maitra, Burke, (J. Chem. Phys, 2002); Wijewardane & Ullrich, (PRL 2005); Ullrich (JCP, 2006)

• Development of History-Dependent Functionals: *Dobson, Bunner & Gross (1997), Vignale, Ullrich, & Conti (1997), Kurzweil & Baer (2004), Tokatly (2005)*

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

A non-interacting example:
Periodically driven HO

If we start in different Ψ_0's, *can* we get the same *n(r t)* by evolving in different potentials?
Yes!

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

Doubly-occupied Floquet orbital with same *n*

• Say this is the density of an interacting system. Both top and middle are possible KS systems.
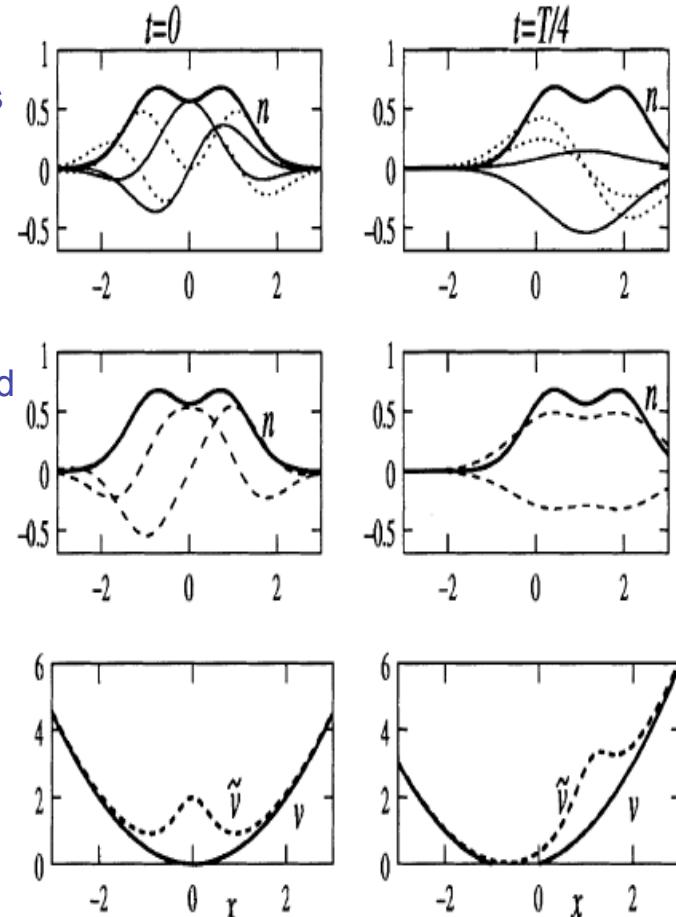
➢ v_{xc} different for each. Cannot be captured by any adiabatic approximation

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

Maitra & Burke, (PRA 2001)(2001, E); Chem. Phys. Lett. (2002).

$$0 = i \sum_{j=1}^{N_\sigma} \int_{-\infty}^{t} dt' \int d^3 r' \left[V_{xc\sigma}(\mathbf{r}',t') - u_{xcj\sigma}(\mathbf{r}',t') \right]$$

$$\times \sum_{k=1}^{\infty} \phi_{k\sigma}(\mathbf{r}',t') \phi_{k\sigma}^*(\mathbf{r},t) \phi_{j\sigma}(\mathbf{r},t) \phi_{j\sigma}^*(\mathbf{r}',t') \; + \; c.c.$$

where $\quad u_{xcj\sigma}(\mathbf{r},t) = \dfrac{1}{\phi_{j\sigma}^*(\mathbf{r},t)} \dfrac{\delta A_{xc}\left[\{\phi_{i\sigma}\}\right]}{\delta \phi_{j\sigma}(\mathbf{r},t)}$

exact exchange: $\quad u_{xj\sigma}(\mathbf{r},t) = -\dfrac{1}{\phi_{j\sigma}^*(\mathbf{r},t)} \sum_{k=1}^{N_\sigma} \int d^3 r' \dfrac{\phi_{j\sigma}^*(\mathbf{r}',t)\phi_{k\sigma}(\mathbf{r}',t)\phi_{k\sigma}^*(\mathbf{r},t)}{\left|\mathbf{r}-\mathbf{r}'\right|}$

C.A.Ullrich, U.J. Gossmann, E.K.U. Gross, PRL **74**, 872 (1995)
H.O. Wijewardane and C.A. Ullrich, PRL **100**, 056404 (2008)

Outline

$$\delta n(\mathbf{r}\omega) = \int d^3 r' \chi[n_0](\mathbf{r r'}\omega)\delta v_{\text{ext}}(\mathbf{r'}\omega)$$

$$= \int d^3 r' \chi_s[n_0](\mathbf{r r'}\omega)\delta v_{\text{s}}(\mathbf{r'}\omega)$$

$$\chi(\mathbf{r},\mathbf{r}';\omega) = \sum_I \left\{ \frac{F_I(\mathbf{r})F_I^*(\mathbf{r}')}{\omega - \omega_I + i0^+} - \frac{F_I^*(\mathbf{r})F_I(\mathbf{r}')}{\omega + \omega_I + i0^+} \right\} \quad F_I(\mathbf{r}) = \langle \Psi_0 | \hat{n}(\mathbf{r}) | \Psi_I \rangle$$

Poles at true excitations

Poles at KS excitations

$$1/|\mathbf{r}-\mathbf{r}'| + f_{\text{XC}}[n_0](\mathbf{r},\mathbf{r}',\omega)$$

adiabatic approx: no ω-dep

$$\overleftrightarrow{\chi}^{-1}(\omega) = \overleftrightarrow{\chi}_{\text{S}}^{-1}(\omega) - \overleftrightarrow{f}_{\text{HXC}}(\omega)$$

Need (1) ground-state $v_{S,0}[n_0](r)$, and its bare excitations

(2) XC kernel $f_{\text{xc}}[n_0](\mathbf{r},\mathbf{r}',t-t') = \delta v_{\text{xc}}(\mathbf{r}t)/\delta n(\mathbf{r}t')|_{n_0}$

Yields exact spectra in principle; in practice, approxs needed in (1) and (2).

Petersilka, Gossmann, Gross, (PRL, 1996)

Quantum chemistry codes cast eqns into a matrix of coupled KS single excitations (*Casida 1996*) : Diagonalize

$$\tilde{\Omega}(\omega)_{qq'} = \delta_{qq'}\omega_q^2 + 4\sqrt{\omega_q\omega_{q'}}[q|f_{\text{HXC}}(\omega)|q']$$

$q = (i \rightarrow a)$

$$[q|f_{\text{HXC}}(\omega)|q'] = \int d\mathbf{r}\, d\mathbf{r}'\, \phi_i^*(\mathbf{r})\phi_a(\mathbf{r})f_{\text{HXC}}(\mathbf{r},\mathbf{r}',\omega)\phi_{i'}(\mathbf{r}')\phi_{a'}^*(\mathbf{r}')$$

→ Excitation energies and oscillator strengths

Useful tools for analysis: "single-pole" and "small-matrix" approximations (SPA,SMA)

Zoom in on a single KS excitation, q = i→ a

Well-separated single excitations: SMA $\omega^2 = \omega_q^2 + 4\omega_q[q|f_{\text{HXC}}(\omega_q)|q]$
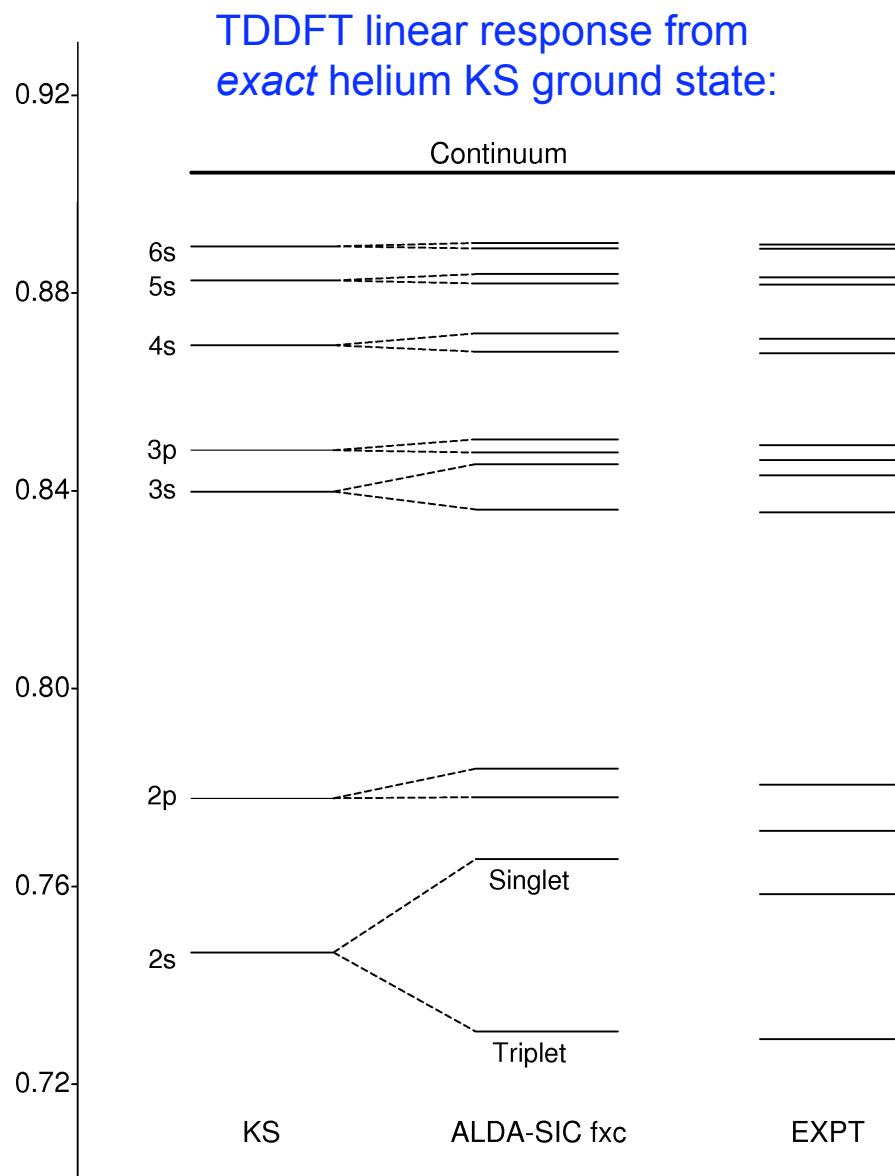
When shift from bare KS small: SPA $\omega = \omega_q + 2[q|f_{\text{HXC}}(\omega_q)|q]$

How it works: atomic excitation energies

TDDFT linear response from *exact* helium KS ground state:

LDA + ALDA lowest excitations

Atom	Exp.	full matrix	SMA	SPA	ω^{KS}
Be	5.28	4.94	5.07	5.43	3.50
Mg	4.34	4.34	4.56	4.76	3.39
Ca	2.94	3.22	3.36	3.56	2.39
Sr	2.69	2.96	3.10	3.28	2.22
Zn	5.79	5.71	6.30	6.54	4.79
Cd	5.41	5.10	5.60	5.86	4.12

Vasiliev, Ogut, Chelikowsky, PRL **82**, 1919 (1999)

From Burke & Gross, (1998); Burke, Petersilka &Gross (2000)

Look at other functional approxs (ALDA, EXX), and also with SPA. All quite similar for He.

- Energies typically 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^3, vs N^5 for wavefunction methods of comparable accuracy (eg CCSD, CASSCF)

- Available now in many electronic structure codes

TDDFT Sales Tag

- Unprecedented balance between accuracy and efficiency
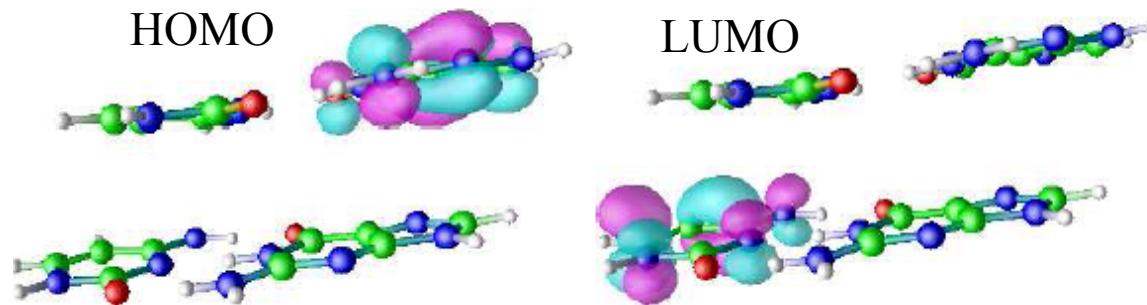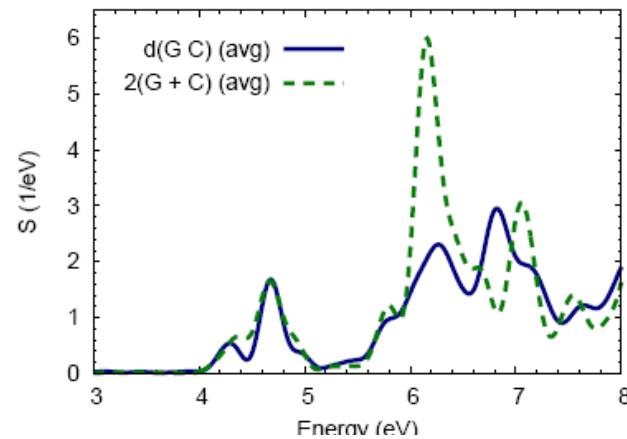
Can study big molecules with TDDFT !

Optical Spectrum of DNA fragments

d(GC) π-stacked pair

HOMO   LUMO

*D. Varsano, R. Di Felice, M.A.L. Marques, A Rubio, J. Phys. Chem. B **110**, 7129 (2006).*

Circular dichroism spectra of chiral fullerenes: D_2C_{84}

F. Furche and R. Ahlrichs, JACS **124**, 3804 (2002).

Outline

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \lim_{\eta\to 0^+}\left[\sum_j \frac{\langle\Psi_0|\hat{n}(\mathbf{r})|\Psi_j\rangle\langle\Psi_j|\hat{n}(\mathbf{r}')|\Psi_0\rangle}{\underbrace{\omega - E_j + E_0}_{\Omega_j} + i\eta} + c.c.(\omega\to-\omega)\right]$$

The full many-body response function has poles at the exact excitation energies

► Discrete single-particle excitations merge into a continuum
(branch cut in frequency plane)
► New types of <u>collective excitations</u> appear off the real axis
(finite lifetimes)
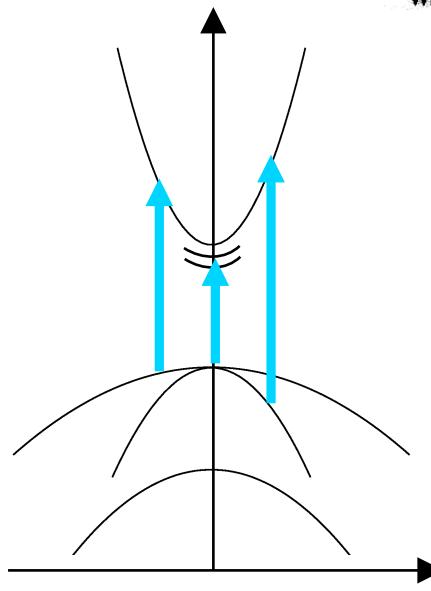
Excitation spectrum of simple metals:
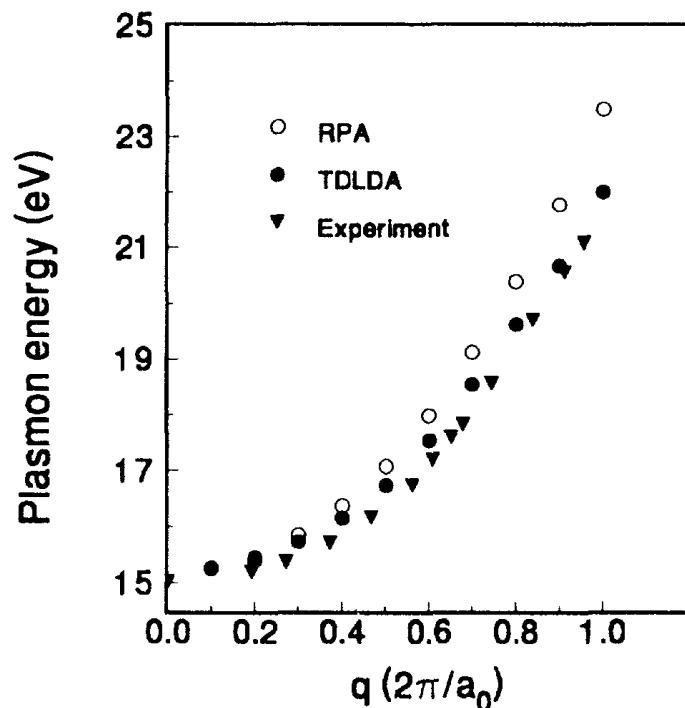
- single particle-hole continuum
  (incoherent)
- collective <u>plasmon</u> mode

Optical excitations
of insulators:

- interband transitions
- <u>excitons</u> (bound
  electron-hole pairs)

Plasmon dispersion of Al

Quong and Eguiluz, PRL **70**, 3955 (1993)

▶ RPA (i.e., Hartree) gives already reasonably good agreement
▶ ALDA agrees very well with exp.
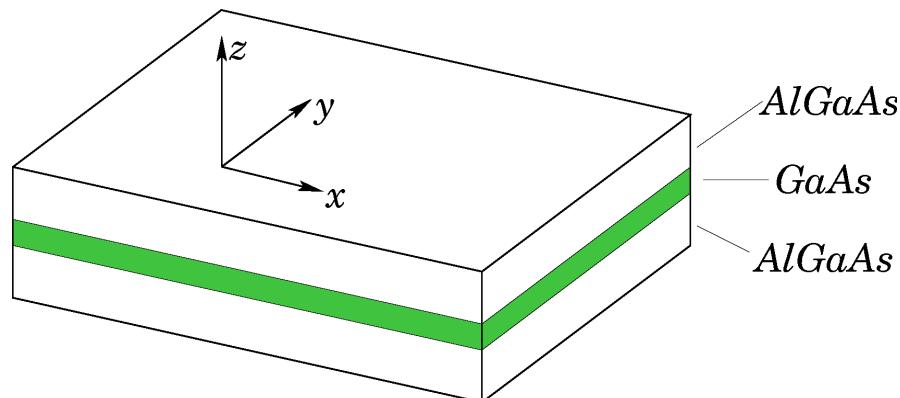
In general, (optical) excitation processes in (simple) metals are very well described by TDDFT within ALDA.

Time-dependent Hartree already gives the dominant contribution, and f_{xc} typically gives some (minor) corrections.

This is also the case for 2DEGs in doped semiconductor heterostructures

# Semiconductor heterostructures

- semiconductor heterostructures are grown with MBE or MOCVD
- control and design through layer-by-layer variation of material composition
- widely used class or materials: III-V compounds
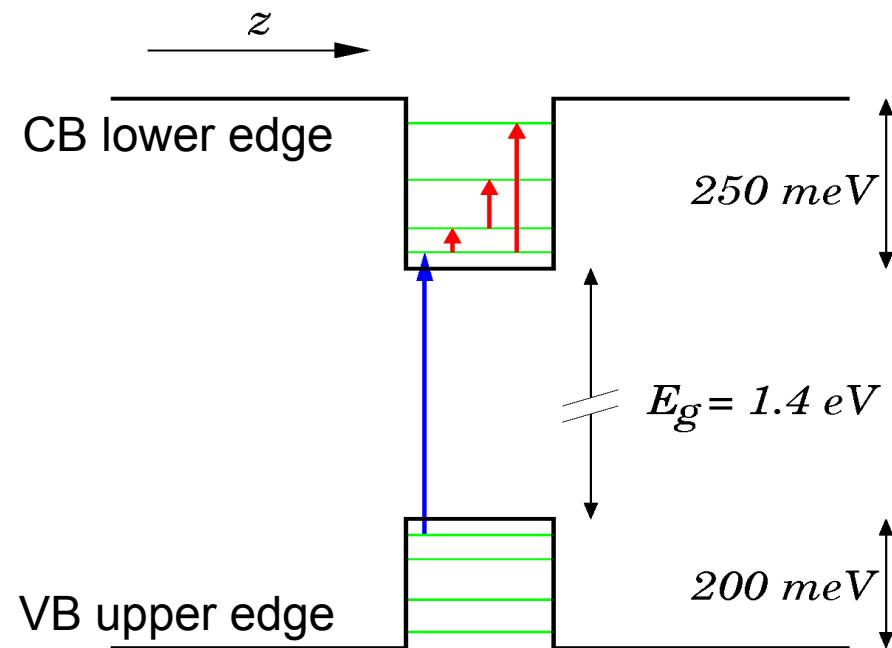
Interband transitions:
of order eV
(visible to near-IR)

Intersubband transitions:
of order meV
(mid- to far-IR)

z

CB lower edge

$250\ meV$

$E_g = 1.4\ eV$

VB upper edge

$200\ meV$
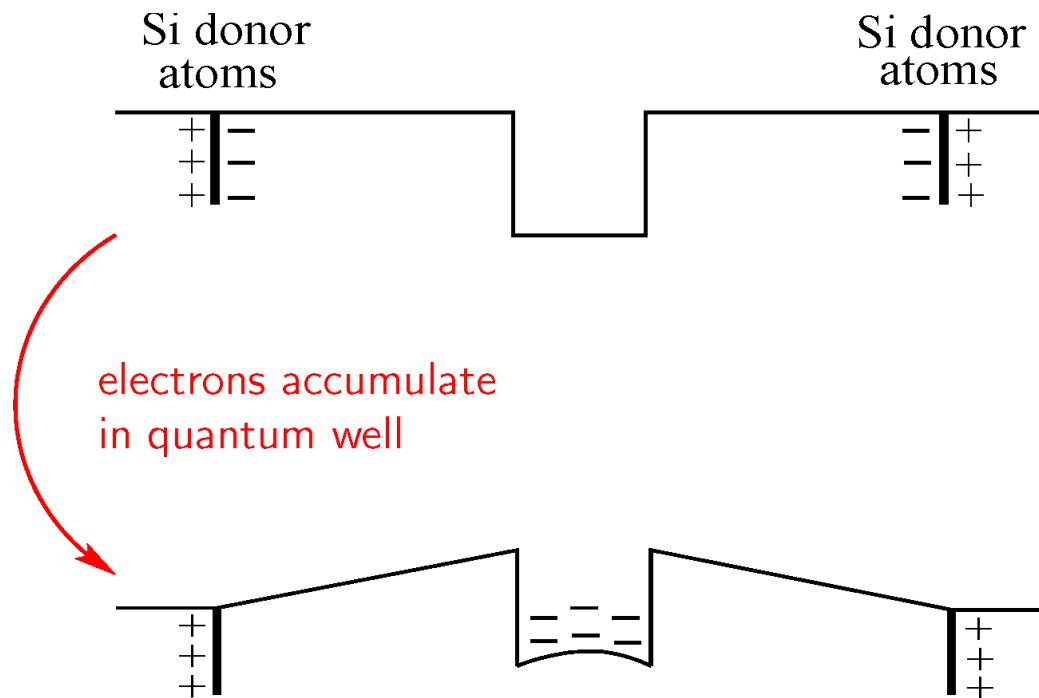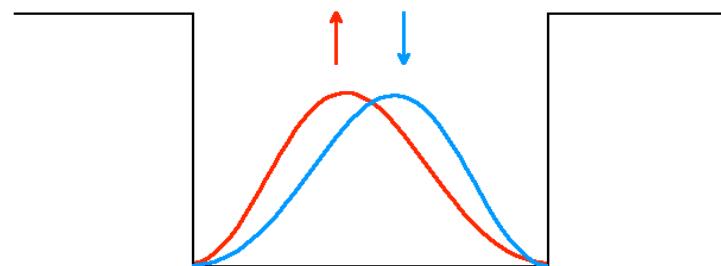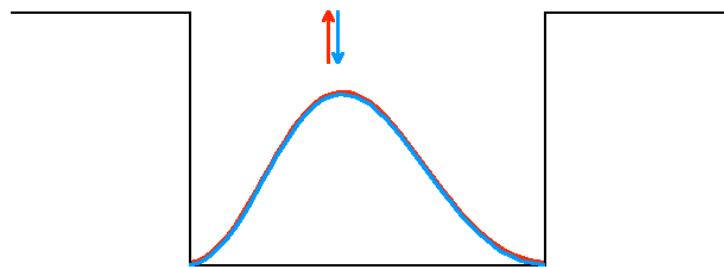
| AlGaAs barrier | GaAs well | AlGaAs barrier |

AlGaAs

GaAs

AlGaAs
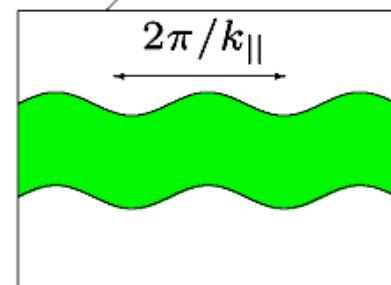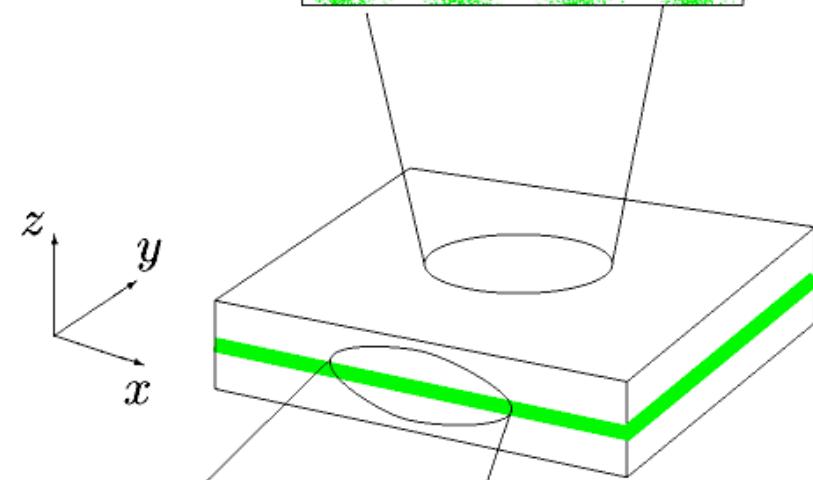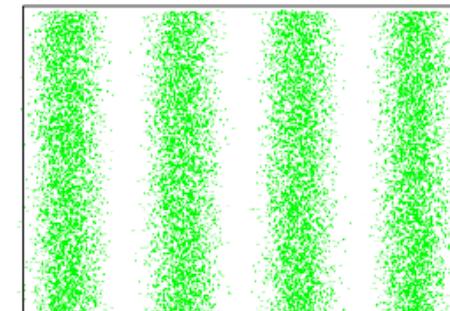
● Donor atoms separated from quantum well: **modulation delta doping**

● Total sheet density N_s typically ~10^{11} cm^{-2}

Si donor atoms

Si donor atoms

electrons accumulate in quantum well

Intersubband charge and spin plasmons: ↑ and ↓ densities in and out of phase

2D Plasmon (in-plane motion)

$2\pi/k_{||}$

Intersubband Plasmon (out-of-plane motion)
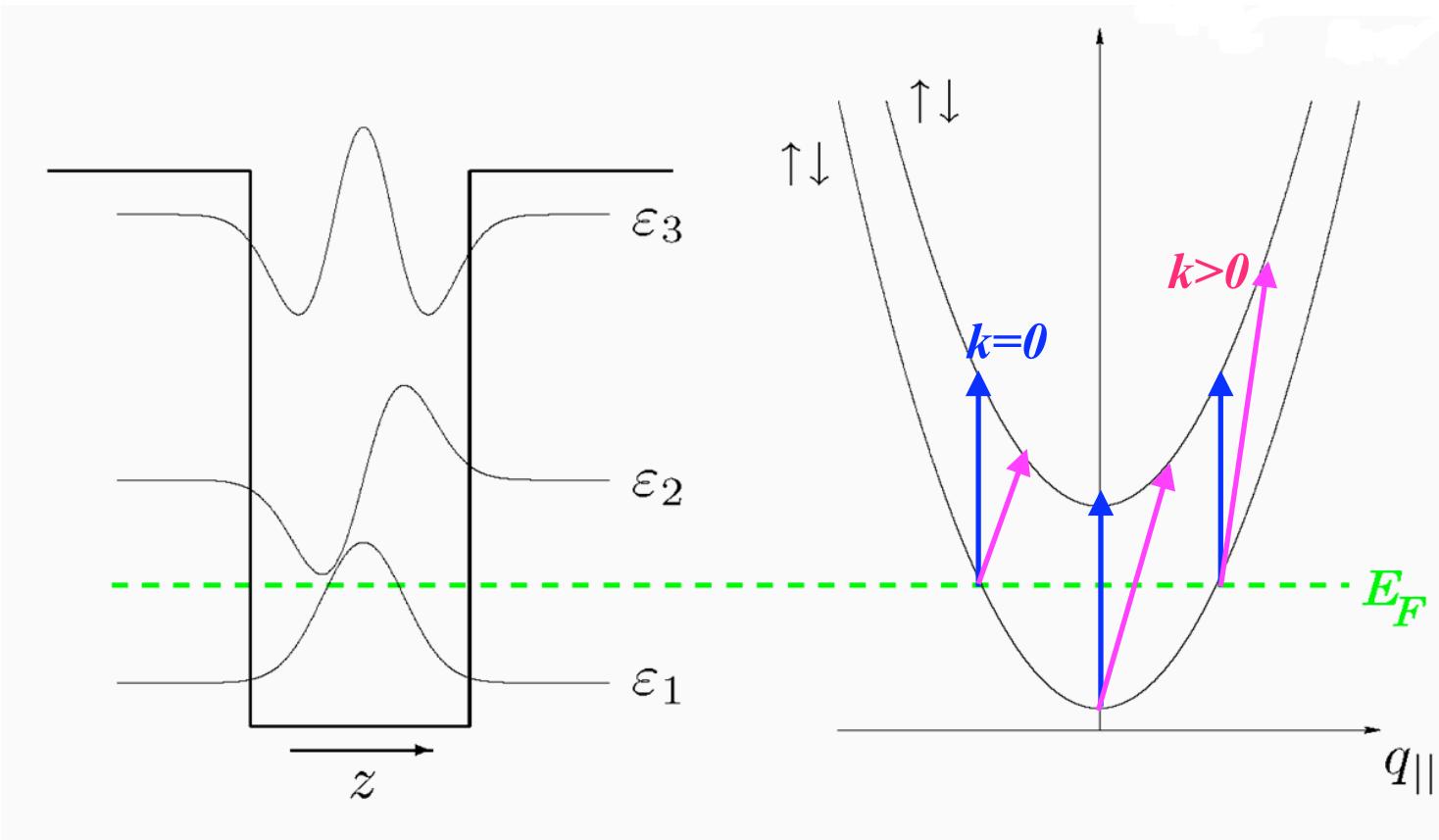
Effective-mass approximation: $m^* = \mu m$ $e^* = e/\sqrt{\kappa}$

$$(\text{for GaAs}: \mu = 0.067, \ \kappa = 13)$$

Electrons in a quantum well: plane waves in *x-y* plane, confined along *z*

$$\psi_{jq_{\parallel}}(\vec{r}) = \frac{1}{\sqrt{A}} e^{iq_{\parallel}r_{\parallel}} \varphi_j(z)$$ with energies $$E_{jq_{\parallel}} = \frac{\hbar^2 q_{\parallel}^2}{2m^*} + \varepsilon_j$$
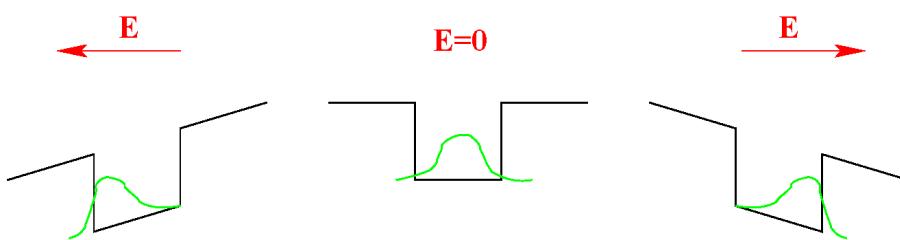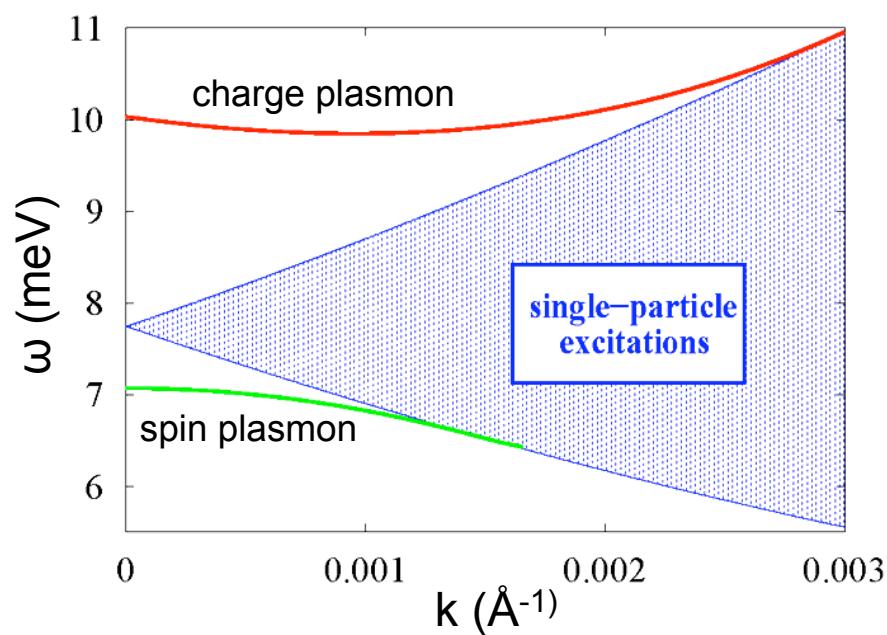
quantum well
confining potential

$$\left[-\frac{\hbar^2}{2m^*}\frac{d^2}{dz^2} + V_{conf}(z) + V_H(z) + V_{xc}^{LDA}(z) \right] \varphi_j(z) = \varepsilon_j \varphi_j(z)$$
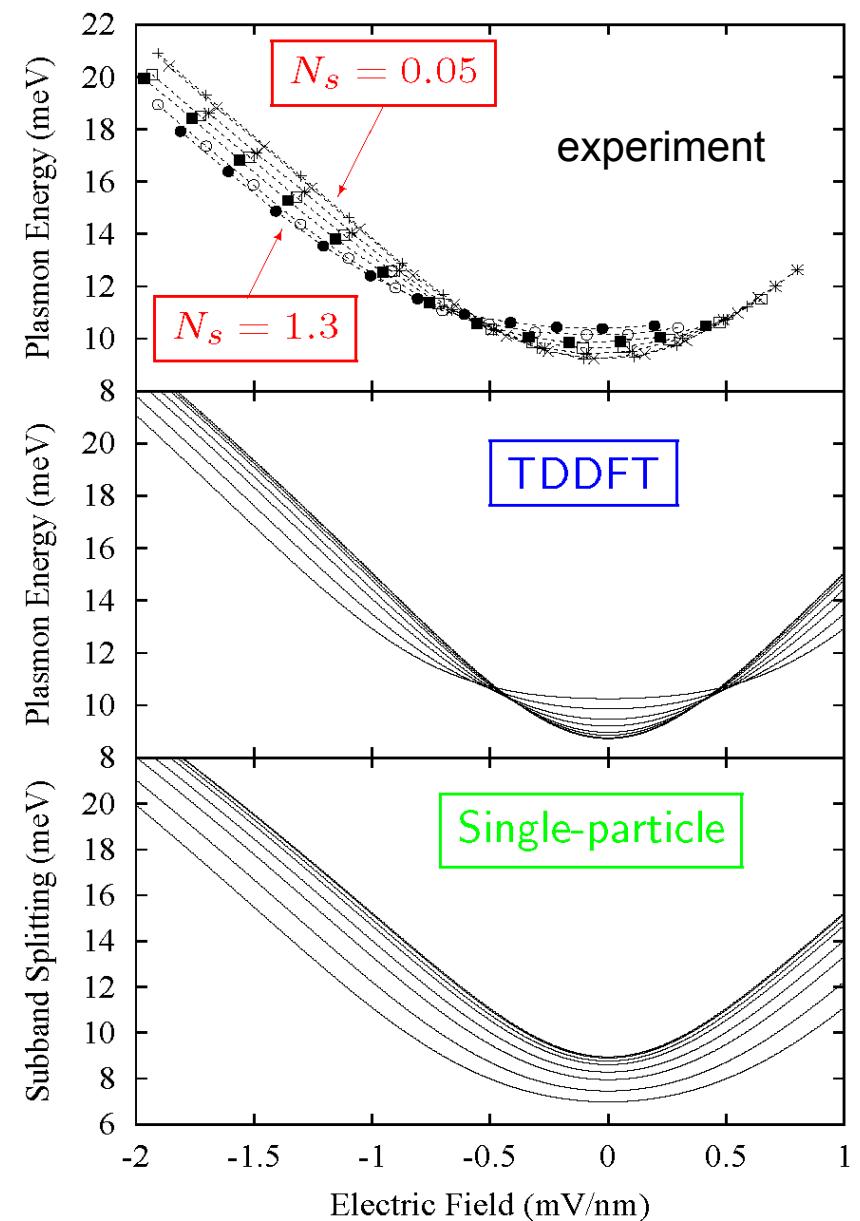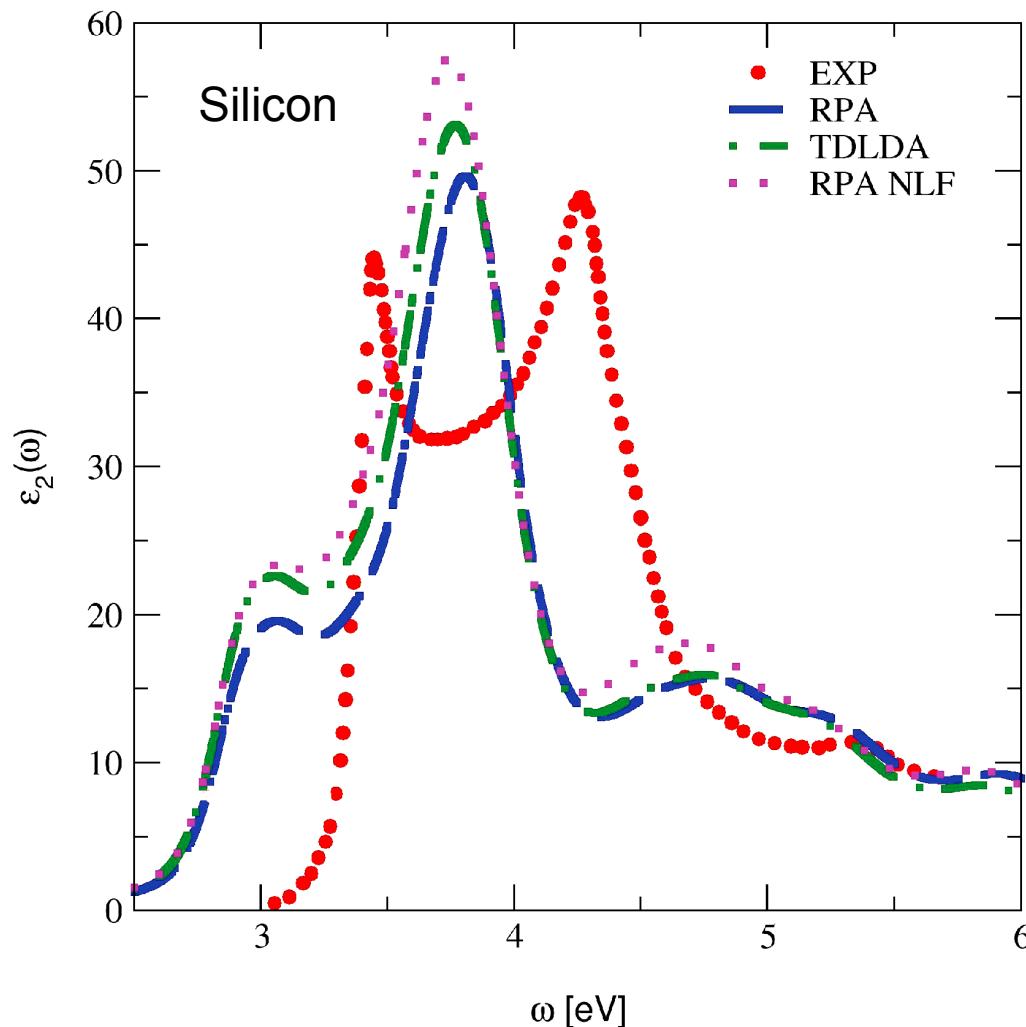
Intersubband plasmon dispersions

charge plasmon

spin plasmon

single–particle excitations

ω (meV)

k (Å⁻¹)

$N_s = 0.05$

$N_s = 1.3$

experiment

Plasmon Energy (meV)

TDDFT

Plasmon Energy (meV)

Single-particle

Subband Splitting (meV)

Electric Field (mV/nm)

E

E=0

E

C.A.Ullrich and G.Vignale, PRL **87**, 037402 (2002)

Optical absorption of insulators

Silicon

- EXP
- RPA
- TDLDA
- RPA NLF

RPA and ALDA both bad!

► absorption edge red shifted (electron self-interaction)

► first excitonic peak missing (electron-hole interaction)

Why does the ALDA fail??

G. Onida, L. Reining, A. Rubio, RMP **74**, 601 (2002)
S. Botti, A. Schindlmayr, R. Del Sole, L. Reining, Rep. Prog. Phys. **70**, 357 (2007)

Optical absorption requires imaginary part of macroscopic dielectric function:

$$\text{Im}\{\varepsilon_{mac}\} = -\lim_{\mathbf{q}\to 0} V_{\mathbf{G}}(\mathbf{q})\,\text{Im}\{\overline{\chi}_{\mathbf{GG}}\}$$

where $\quad \overline{\chi} = \chi_{KS} + \chi_{KS}\left(\overline{V} + f_{xc}\right)\overline{\chi}, \quad \overline{V}_{\mathbf{G}} = \begin{cases} V_{\mathbf{G}}, & \mathbf{G} \neq 0 \\ 0, & \mathbf{G} = 0 \end{cases}$

$\boxed{\mathbf{q} \to 0 \text{ limit:}}$ $\sim q^2$ Long-range excluded, so RPA is ineffective

Needs $1/q^2$ component to correct χ_{KS}

But ALDA is **constant** for $\mathbf{q} \to 0$:

$$f_{xc}^{ALDA} = \lim_{q\to 0} f_{xc}^{hom}(q, \omega = 0)$$

- **LRC** (long-range correlation) kernel (with fitting parameter α):

$$f_{xc}^{LRC}(\mathbf{q}) = -\frac{\alpha}{q^2}$$

- **TDOEP** kernel (X-only):

$$f_x^{OEP}(\mathbf{r}, \mathbf{r}') = -\frac{\left|\sum_k f_k \phi_k(\mathbf{r}) \phi_k^*(\mathbf{r}')\right|^2}{2|\mathbf{r} - \mathbf{r}'| n(\mathbf{r}) n(\mathbf{r}')}$$

Simple real-space form: Petersilka, Gossmann, Gross, PRL **76**, 1212 (1996)
TDOEP for extended systems: Kim and Görling, PRL **89**, 096402 (2002)

- **"Nanoquanta"** kernel (L. Reining et al, PRL **88**, 066404 (2002)
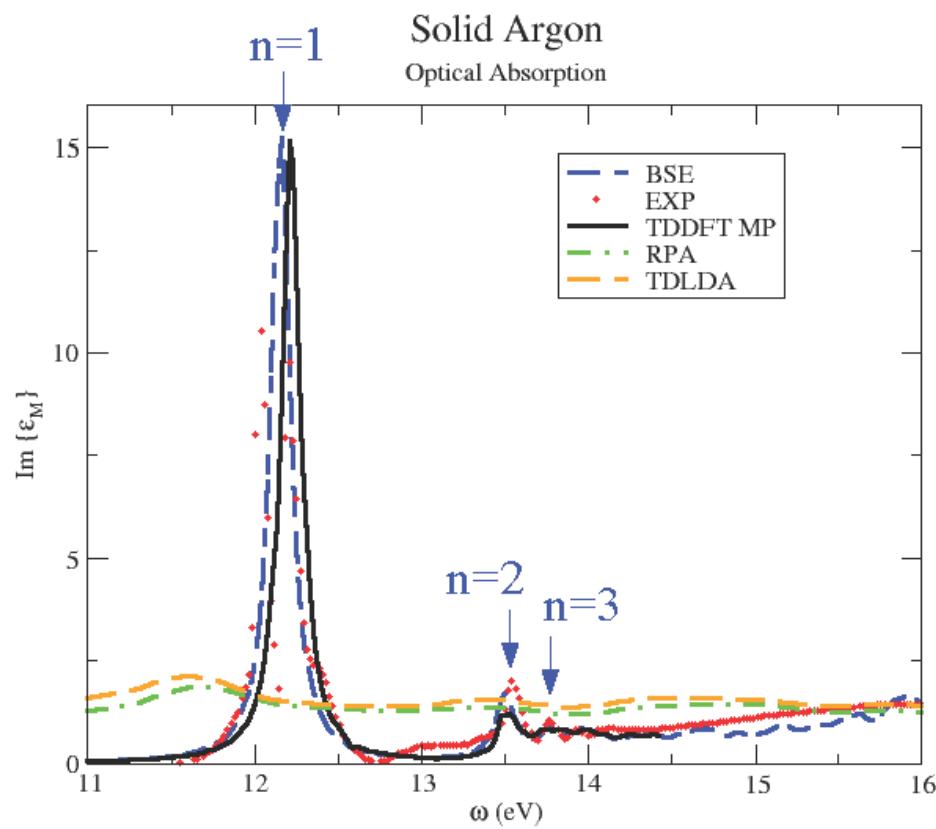
$$f_{xc}^{BSE}(\mathbf{q} \to 0, \mathbf{G}, \mathbf{G}') = \sum_{vck, v'c'k'} \Phi_{\mathbf{G}}^{-1}(vk\,ck; \mathbf{q} \to 0) F_{vck, v'c'k'}^{BSE} (\Phi^*)_{\mathbf{G}'}^{-1}(v'\mathbf{k}'c'\mathbf{k}'; \mathbf{q} \to 0)$$

pairs of KS wave functions
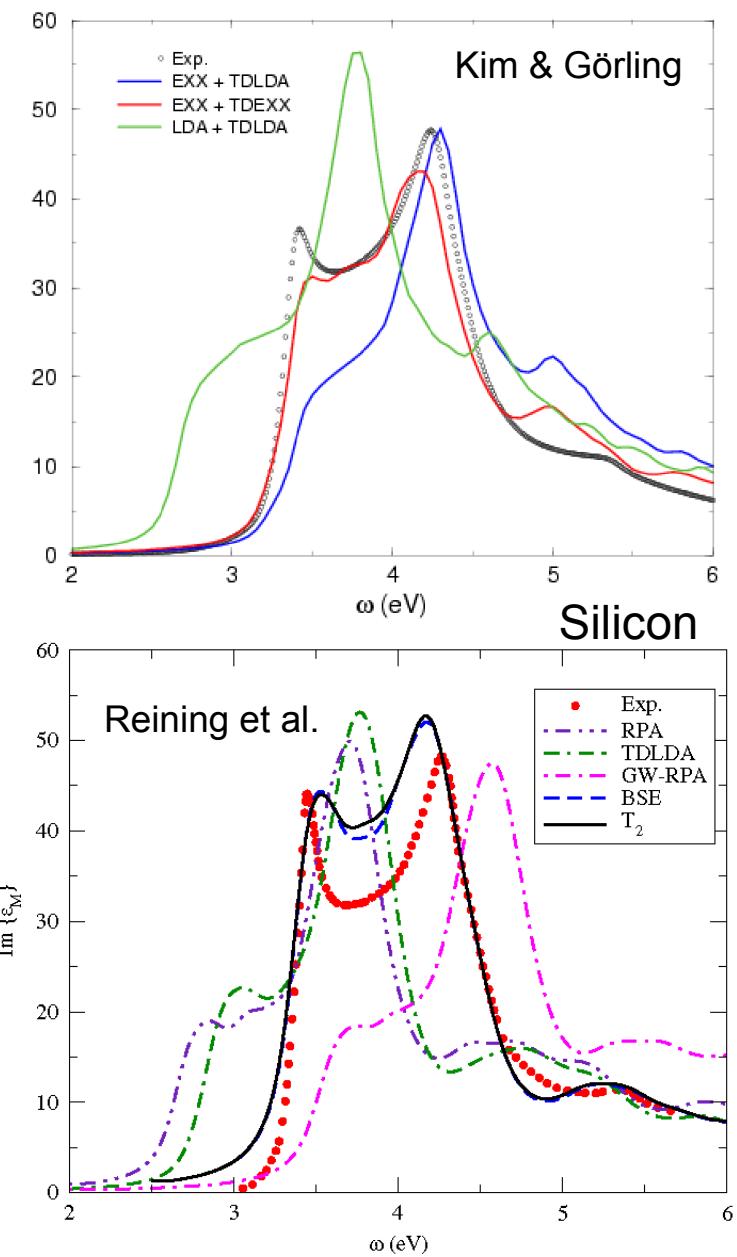
matrix element of screened Coulomb interaction (from Bethe-Salpeter equation)

Optical absorption of insulators, again

F. Sottile et al., PRB **76**, 161103 (2007)

► TDDFT works well for metallic and quasi-metallic systems already
at the level of the ALDA. Successful applications for plasmon modes
in bulk metals and low-dimensional semiconductor heterostructures.

► TDDFT for insulators is a much more complicated story:

   ● ALDA works well for EELS (electron energy loss spectra), but
   not for optical absorption spectra

   ● difficulties originate from long-range contribution to f_{xc}

   ● some long-range XC kernels have become available,
   but some of them are complicated. Stay tuned….

   ● Nonlinear real-time dynamics including excitonic effects:
   TDDFT version of Semiconductor Bloch equations
   V.Turkowski and C.A.Ullrich, PRB **77**, 075204 (2008) (Wednesday P13.7)

Outline

meaning, semi-local in space
and local in time

- Rydberg states

- Polarizabilities of long-chain molecules

- Optical response/gap of solids

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

Can cure with orbital- dependent fnals
(exact-exchange/sic), or **TD current-DFT**

- Double excitations

- Long-range charge transfer

- Conical Intersections

Adiabatic approx for fxc fails.

Can use frequency-dependent
kernel derived for *some* of these
cases

Ailments – and some Cures (II)

● Quantum control phenomena ← Single-determinant constraint of KS leads to unnatural description of the true state → weird xc effects

● Other strong-field phenomena ? ← ? Memory-dependence in $v_{xc}[n;\psi_0.\Phi_0](r\ t)$

● Observables that are not directly related to the density, eg NSDI, NACs… ← Need to know observable as functional of $n(r\ t)$
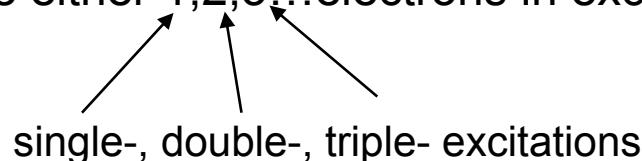
● Coulomb blockade ← Lack of derivative discontinuity

● Coupled electron-ion dynamics ← Lack of electron-nuclear correlation in Ehrenfest, but surface-hopping has fundamental problems

Excitations of interacting systems generally involve mixtures of (KS) SSD's
that have either 1,2,3...electrons in excited orbitals.

single-, double-, triple- excitations

Now consider:

$$\chi(\mathbf{r}, \mathbf{r}'; \omega) = \sum_I \left\{ \frac{F_I(\mathbf{r})F_I^*(\mathbf{r}')}{\omega - \omega_I + i0^+} - \frac{F_I^*(\mathbf{r})F_I(\mathbf{r}')}{\omega + \omega_I + i0^+} \right\} \qquad F_I(\mathbf{r}) = \langle \Psi_0 | \hat{n}(\mathbf{r}) | \Psi_I \rangle$$

χ – poles at true states that are mixtures of singles, doubles, and higher excitations

χ_S -- poles only at single KS excitations, since one-body operator $\hat{n}(\mathbf{r})$ can't
connect Slater determinants differing by more than one orbital.

➡ χ has more poles than χ_s
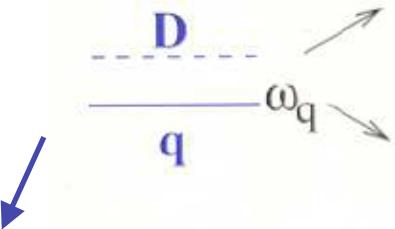
? How does f_{xc} generate more poles to get states of multiple excitation character?

Exactly Solve a Simple Model: one KS single (q) mixing with a nearby double (D)

$$\chi_s(\mathbf{r},\mathbf{r}',\omega) \approx \frac{A(\mathbf{r},\mathbf{r}',(\omega))}{\omega - \omega_q}$$

$$\chi(\mathbf{r},\mathbf{r}';\omega) \approx A(\mathbf{r},\mathbf{r}';\omega)\left(\frac{1-m^2}{\omega-\omega_a} + \frac{m^2}{\omega-\omega_b}\right)$$

Invert and insert into Dyson-like eqn for kernel →*dressed* SPA (i.e. ω-dependent):

$$2[q|f_{\text{HXC}}(\omega)|q] = 2\left([q|\chi_s^{-1}|q] - [q|\chi^{-1}|q]\right)$$

$$= (\bar{\omega} - \omega_q) + \frac{\bar{\omega}'\bar{\omega} - \omega_a\omega_b}{(\omega - \bar{\omega}')}$$

$$\bar{\omega} = (1-m^2)\omega_a + m^2\omega_b$$

$$\bar{\omega}' = m^2\omega_a + (1-m^2)\omega_b$$

Strong non-adiabaticity!

General case: Diagonalize many-body H in KS subspace near the double ex of interest, and require reduction to adiabatic TDDFT in the limit of weak coupling of the single to the double →

usual adiabatic matrix element

$$2[q|f_{\mathsf{XC}}(\omega)|q] = 2[q|f_{\mathsf{XC}}^A(\omega_q)|q] + \frac{|H_{qD}|^2}{\omega - (H_{DD} - H_{00})}$$

dynamical (non-adiabatic) correction

*NTM, Zhang, Cave,& Burke JCP (2004), Casida JCP (2004)*
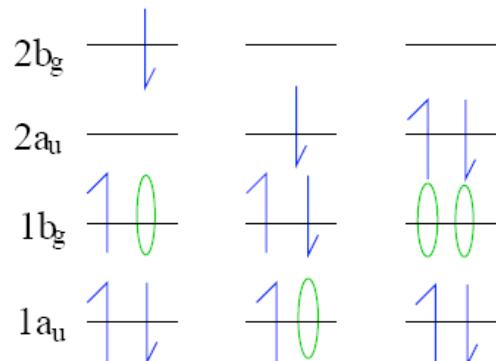
Example: Short-chain polyenes

Lowest-lying excitations notoriously difficult to calculate due to significant double-excitation character.

Cave, Zhang, NTM, Burke, CPL (2004)

E.g. Butadiene, dark 2^1A_g state

$2b_g$

$2a_u$

$1b_g$

$1a_u$

- 2^1A_g Vertical excitation energies (eV) for butadiene and hexatriene

System	CASPT2	ATDDFT	D-TD-TDDFT
C_4H_6	6.27	7.02	6.28
C_6H_8	5.20	5.83	5.16

- 2^1A_g Vertical and 0-0 excitations for butadiene at the estimated planar stationary point for 2^1A_g
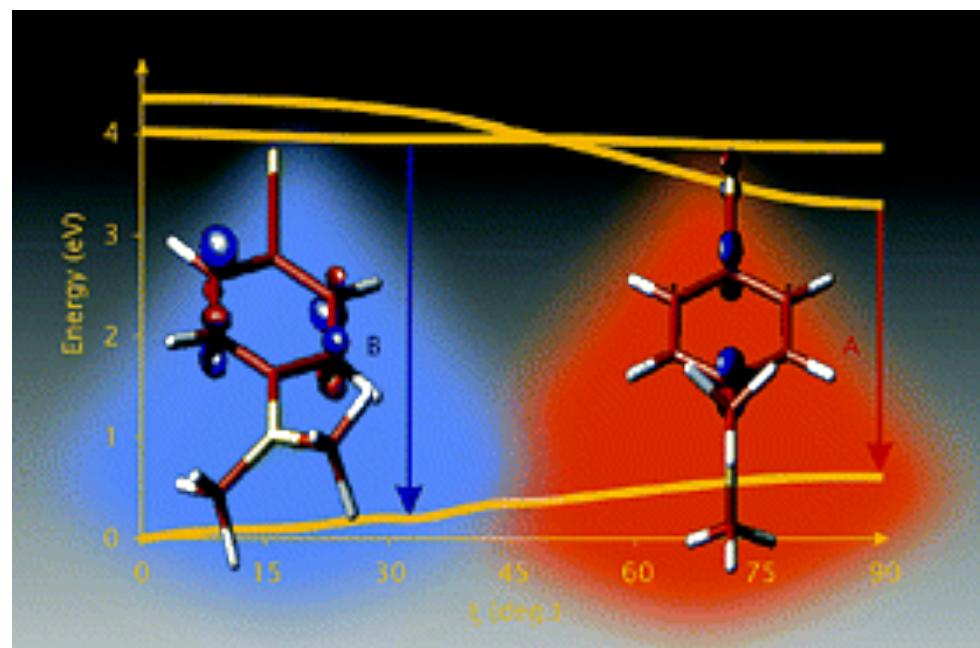
ΔE	CASPT2	ATDDFT	D-TD-TDDFT
Vertical	4.3	5.8	4.16
0-0	5.2	6.8	5.28

• Note importance of accurate double-excitation description in **coupled electron-ion dynamics** – propensity for curve-crossing

Levine, Ko, Quenneville, Martinez, Mol. Phys. (2006)

Example: Dual Fluorescence in DMABN in Polar Solvents

Rappoport & Furche,
JACS 126, 1277 (2004).
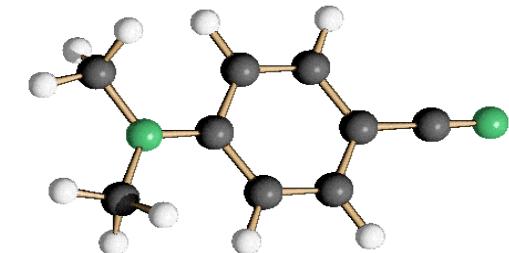
"normal"   "anomalous"

"Local" Excitation (LE)   Intramolecular Charge Transfer (ICT)

TDDFT resolved the long debate on ICT structure (neither "PICT" nor "TICT"), and elucidated the mechanism of LE -- ICT reaction
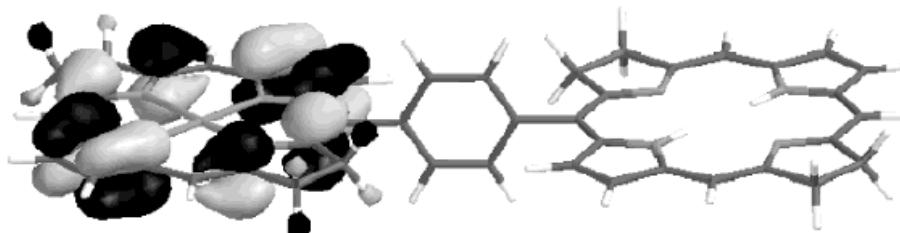
Success in predicting ICT structure – How about CT energies ??

Long-Range Charge-Transfer Excitations

TDDFT typically **severely underestimates** long-range CT energies

Important process in biomolecules, large enough that TDDFT may be only feasible approach !

Eg. Zincbacteriochlorin-Bacteriochlorin complex
(light-harvesting in plants and purple bacteria)

Dreuw & Head-Gordon, JACS 126 4007, (2004).

TDDFT predicts CT states energetically well below local fluorescing states.
Predicts CT quenching of the fluorescence.
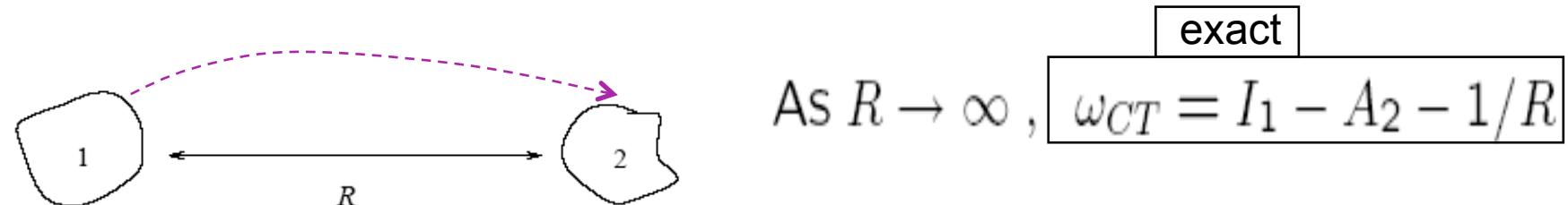
! Not observed !

TDDFT error ~ 1.4eV

Why do the usual approximations in TDDFT fail for these excitations?

We know what the *exact* energy for charge transfer at long range should be:

exact

$$\text{As } R \to \infty, \quad \boxed{\omega_{CT} = I_1 - A_2 - 1/R}$$

$$\omega = \omega_q + 2[q|f_{\text{HXC}}(\omega_q)|q]$$

Why TDDFT typically severely underestimates this energy can be seen in SPA

$$\omega = \epsilon_2^L - \epsilon_1^H + \int \int d\mathbf{r} d\mathbf{r}' \underbrace{\phi_1^H(\mathbf{r})\phi_2^L(\mathbf{r})}_{\sim 0 \text{ overlap}} f_{\text{HXC}}(\mathbf{r}, \mathbf{r}'\omega) \underbrace{\phi_1^H(\mathbf{r}')\phi_2^L(\mathbf{r}')}$$

$-A_{s,2}$ $-I_1$

~0 overlap

$$\approx I_1 - A_{s,2}$$

i.e. get just the bare KS orbital energy difference: <u>missing xc contribution to acceptor's electron affinity, $A_{xc,2}$, and -1/R</u>

(Also, usual g.s. approxs underestimate I)

Long-Range Charge-Transfer Excitations

What are the properties of the unknown exact xc kernel that must be well-modelled to get long-range CT energies correct ?
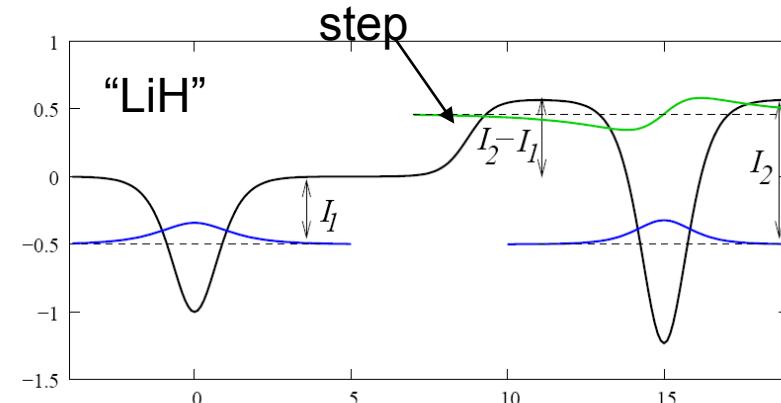
➢ Exponential dependence on the fragment separation R,

$$f_{xc} \sim \exp(aR)$$

➢ For transfer between open-shell species, need strong frequency-dependence.

Step in V_{xc} re-aligns the 2 atomic HOMOs → near-degeneracy of molecular HOMO & LUMO → static correlation, crucial double excitations → frequency-dependence!

(It's a rather ugly kernel…)

Gritsenko & Baerends (PRA, 2004), Maitra (JCP, 2005), Tozer (JCP, 2003) Tawada et al. (JCP, 2004)

Outline

- In general, the adiabatic approximation works well for excitations which have an analogue in the KS system (single excitations)

- formally justified only for infinitely slow electron dynamics. But why is it that the frequency dependence seems less important?

> The frequency scale of f_{xc} is set by correlated multiple excitations, which are absent in the KS spectrum.

- Adiabatic approximation fails for more complicated excitations (multiple, charge-transfer)

- misses dissipation of long-wavelength plasmon excitations

Fundamental question: what is the proper extension of the LDA into the dynamical regime?

Visualize electron dynamics as the motion (and deformation)
of infinitesimal fluid elements:

Nonlocality in time (memory) implies nonlocality in space!

Dobson, Bünner, and Gross, PRL **79**, 1905 (1997)
I.V. Tokatly, PRB **71**, 165105 (2005)
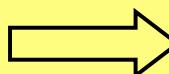
Zero-force theorem:
$$\int d^3r \, n(\vec{r},t) \vec{\nabla} V_{xc}(\vec{r},t) = 0$$
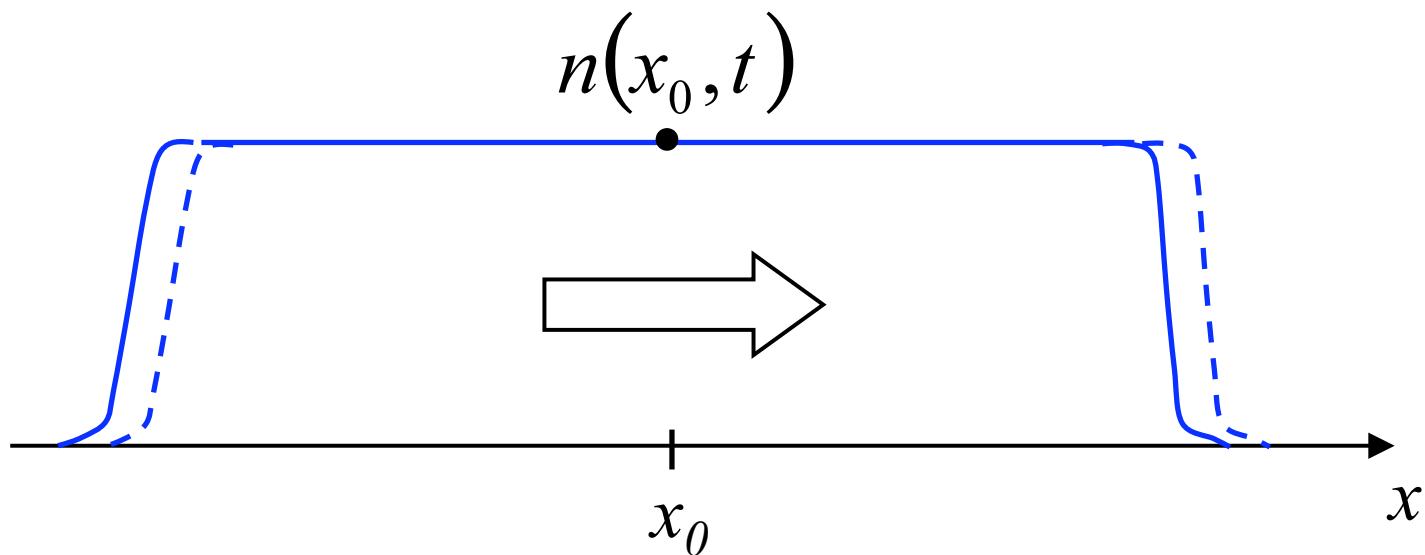
Linearized form:
$$\int d^3r' \vec{\nabla} n_0(\vec{r}') f_{xc}(\vec{r},\vec{r}',\omega) = \vec{\nabla} V_{xc,0}(\vec{r})$$

If the xc kernel has a **finite range**, we can write for slowly varying systems:

$$\vec{\nabla} n_0(\vec{r}) \underbrace{\int d^3r' \, f_{xc}(\vec{r},\vec{r}',\omega)}_{\Rightarrow \, f_{xc}^{\text{hom}}\left(\vec{k}=0,\omega\right)} = \vec{\nabla} V_{xc,0}(\vec{r})$$

l.h.s. is frequency-dependent, r.h.s is not: **contradiction!**
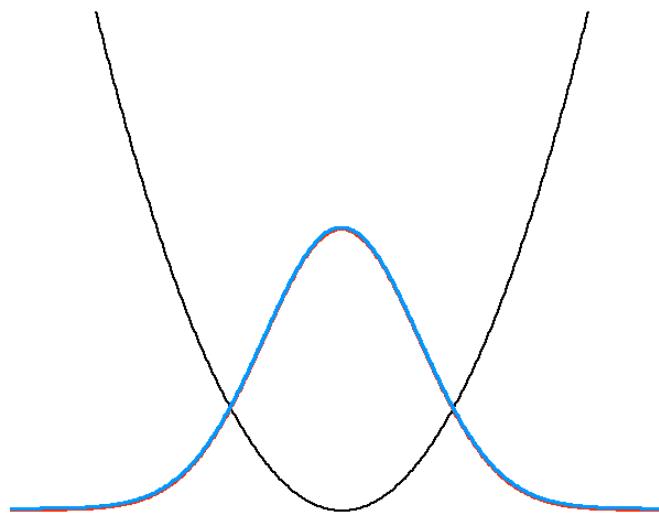
$$\Rightarrow f_{xc}(\vec{r},\vec{r}',\omega)$$ has infinitely long spatial range!

$$n(x_0, t)$$

$$x_0$$

$$x$$
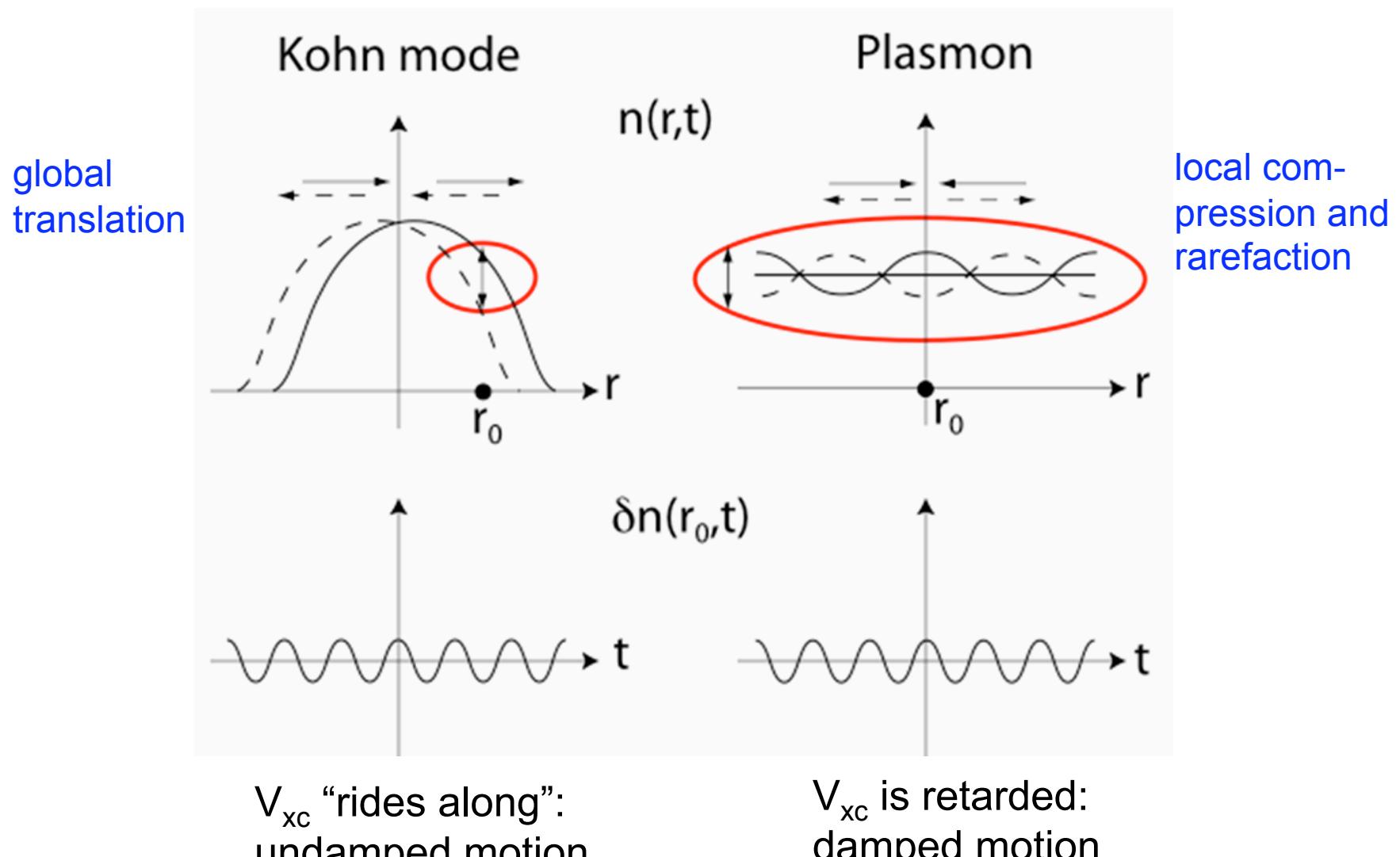
An xc functional that depends only on the local density (or its gradients) cannot see the motion of the entire slab.

A density functional needs to have a long range to see the motion through the changes at the edges.

J.F. Dobson, PRL **73**, 2244 (1994)
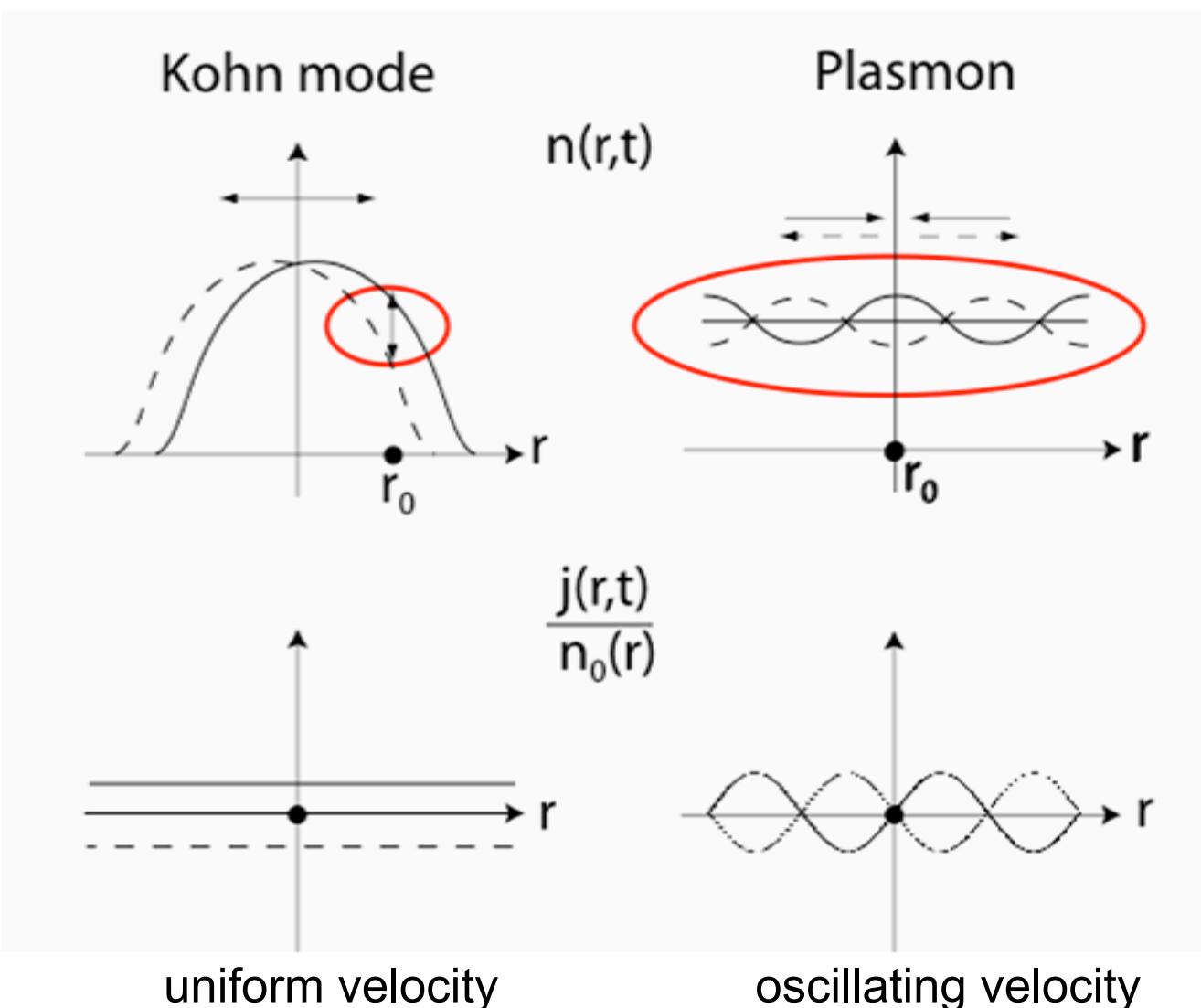
A parabolically confined, interacting N-electron system can carry out an undistorted, undamped, collective "sloshing" mode, where

$$n(\vec{r},t) = n_0\left(\vec{r} - \vec{R}(t)\right)$$ with the CM position $\vec{R}(t)$

Kohn mode — global translation

Plasmon — local compression and rarefaction

$n(r,t)$

$\delta n(r_0,t)$
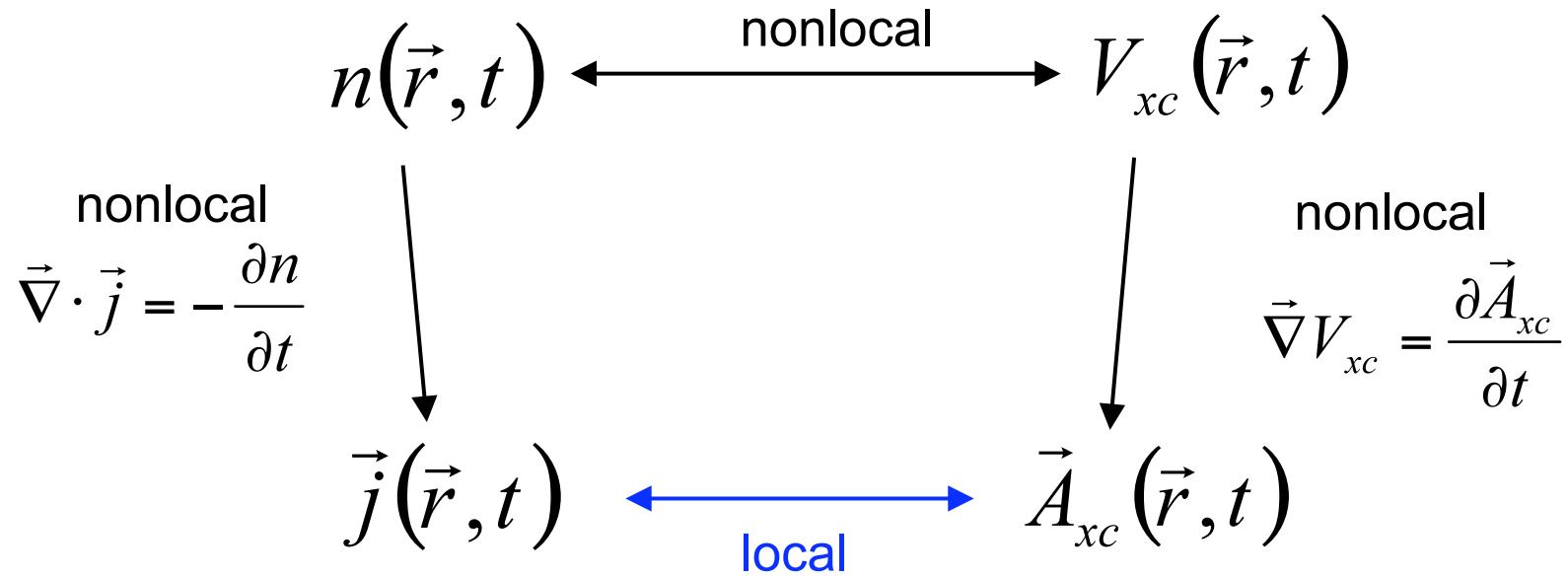
V_{xc} "rides along": undamped motion

V_{xc} is retarded: damped motion

➡ xc functionals based on local density can't distinguish the two cases!

uniform velocity   oscillating velocity

➡ much better chance to capture the physics correctly!

Upgrading TDDFT: time-dependent Current-DFT

$$n(\vec{r},t) \xleftrightarrow{\text{nonlocal}} V_{xc}(\vec{r},t)$$

$$\text{nonlocal} \qquad \vec{\nabla} \cdot \vec{j} = -\frac{\partial n}{\partial t} \qquad\qquad \text{nonlocal} \qquad \vec{\nabla} V_{xc} = \frac{\partial \vec{A}_{xc}}{\partial t}$$

$$\vec{j}(\vec{r},t) \xleftrightarrow{\text{local}} \vec{A}_{xc}(\vec{r},t)$$
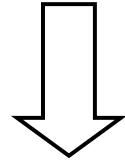
$$\vec{j}(\vec{r},t) = \vec{j}_L(\vec{r},t) + \vec{j}_T(\vec{r},t), \qquad \vec{j}_L(\vec{r},t) = \frac{\vec{\nabla}}{4\pi} \int \frac{\dot{n}(\vec{r}',t)}{|\vec{r} - \vec{r}'|}$$
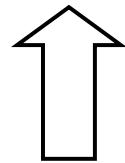
● Continuity equation only gives the longitudinal current
● TDCDFT gives also the transverse current
● We can find a short-range current-dependent xc vector potential

generalization of RG theorem: Ghosh and Dhara, PRA **38**, 1149 (1988)

G. Vignale, PRB **70**, 201102 (2004)

$$\hat{H}_{\text{int}}(t) = \sum_i \left\{ \frac{1}{2}\left[\vec{p}_i + \tfrac{1}{c}\vec{A}_{ext}(\vec{r}_i,t)\right]^2 + V_{ext}(\vec{r}_i,t) \right\} + \sum_{i>j} U(\vec{r}_i - \vec{r}_j)$$

$$\Downarrow$$

full current can be
represented by
a KS system

$$\vec{j}(\vec{r},t) = \vec{j}_L(\vec{r},t) + \vec{j}_T(\vec{r},t)$$

$$\Uparrow$$

$$\hat{H}_{KS}(t) = \sum_i \left\{ \frac{1}{2}\left[\vec{p}_i + \tfrac{1}{c}\vec{A}_{KS}(\vec{r}_i,t)\right]^2 + V_{KS}(\vec{r}_i,t) \right\}$$

uniquely determined up to gauge transformation

$$\vec{j}_1(\vec{r},\omega) = \int d^3r' \; \overleftrightarrow{\chi}_{KS}(\vec{r},\vec{r}',\omega) \left\{ \vec{A}_{ext,1}(\vec{r},\omega) + \vec{A}_{H,1}(\vec{r},\omega) + \vec{A}_{xc,1}(\vec{r},\omega) \right\}$$

KS current-current response tensor: diamagnetic + paramagnetic part

$$\chi_{\mu\nu}(\vec{r},\vec{r}',\omega) = n_0(\vec{r})\delta(\vec{r}-\vec{r}')\delta_{\mu\nu} + \frac{1}{2}\sum_{j,k}^{\infty} \frac{f_k - f_j}{\varepsilon_k - \varepsilon_j + \omega + i\eta} P_\mu^{kj}(\vec{r}) P_\nu^{jk}(\vec{r}')$$

where $$P_\mu^{kj} = \varphi_k^*(\vec{r})\nabla_\mu \varphi_j(\vec{r}) - \varphi_j(\vec{r})\nabla_\mu \varphi_k^*(\vec{r})$$

$\vec{A}_{ext,1}(\vec{r},\omega):$ external perturbation. Can be a true vector potential, or a gauge transformed scalar perturbation:

$$\vec{A}_{ext,1} = \frac{1}{i\omega}\vec{\nabla}V_{ext,1}$$

$$\vec{A}_{H,1}(\vec{r},\omega) = \frac{\vec{\nabla}}{(i\omega)^2}\int d^3r'\frac{\vec{\nabla}'\cdot\vec{j}(\vec{r}',\omega)}{|\vec{r}-\vec{r}'|}$$

gauge transformed Hartree potential

$$\vec{A}_{xc,1}(\vec{r},\omega) = \int d^3r'\,\overleftrightarrow{f}_{xc}(\vec{r},\vec{r}',\omega)\vec{j}(\vec{r}',\omega)$$

the xc kernel is now a tensor!

ALDA: $\quad \vec{A}_{xc,1}^{ALDA}(\vec{r},\omega) = \dfrac{\vec{\nabla}}{(i\omega)^2}\int d^3r'\,f_{xc}^{ALDA}(\vec{r},\vec{r}')\vec{\nabla}'\cdot\vec{j}(\vec{r}',\omega)$

TDCDFT beyond the ALDA: the VK functional

G. Vignale and W. Kohn, PRL **77**, 2037 (1996)
G. Vignale, C.A. Ullrich, and S. Conti, PRL **79**, 4878 (1997)

$$\vec{A}_{xc,1}(\vec{r},\omega) = \vec{A}_{xc,1}^{ALDA}(\vec{r},\omega) - \frac{c}{i\omega n_0(\vec{r})}\vec{\nabla}\cdot\overset{\leftrightarrow}{\sigma}_{xc}(\vec{r},\omega)$$

xc viscoelastic stress tensor:

$$\sigma_{xc,jk} = \tilde{\eta}_{xc}\left(\nabla_j v_{1,k} + \nabla_k v_{1,j} - \frac{2}{3}\vec{\nabla}\cdot\vec{v}_1\delta_{jk}\right) + \tilde{\zeta}_{xc}\vec{\nabla}\cdot\vec{v}_1\delta_{jk}$$

$$\vec{v}(\vec{r},\omega) = \vec{j}(\vec{r},\omega)/n_0(\vec{r}) \quad \text{velocity field}$$

- automatically satisfies zero-force theorem/Newton's 3rd law
- automatically satisfies the Harmonic Potential theorem
- is local in the current, but nonlocal in the density
- introduces dissipation/retardation effects

XC viscosity coefficients

$$\tilde{\eta}_{xc}(n,\omega) = -\frac{n^2}{i\omega} f_{xc}^T(n,\omega)$$

$$\tilde{\xi}_{xc}(n,\omega) = -\frac{n^2}{i\omega}\left(f_{xc}^L(n,\omega) - \frac{4}{3} f_{xc}^T(n,\omega) - \frac{d^2 e_{xc}^{unif}}{dn^2}\right)$$

In contrast with the classical case, the xc viscosities have both real and imaginary parts, describing <u>dissipative</u> and <u>elastic</u> behavior:
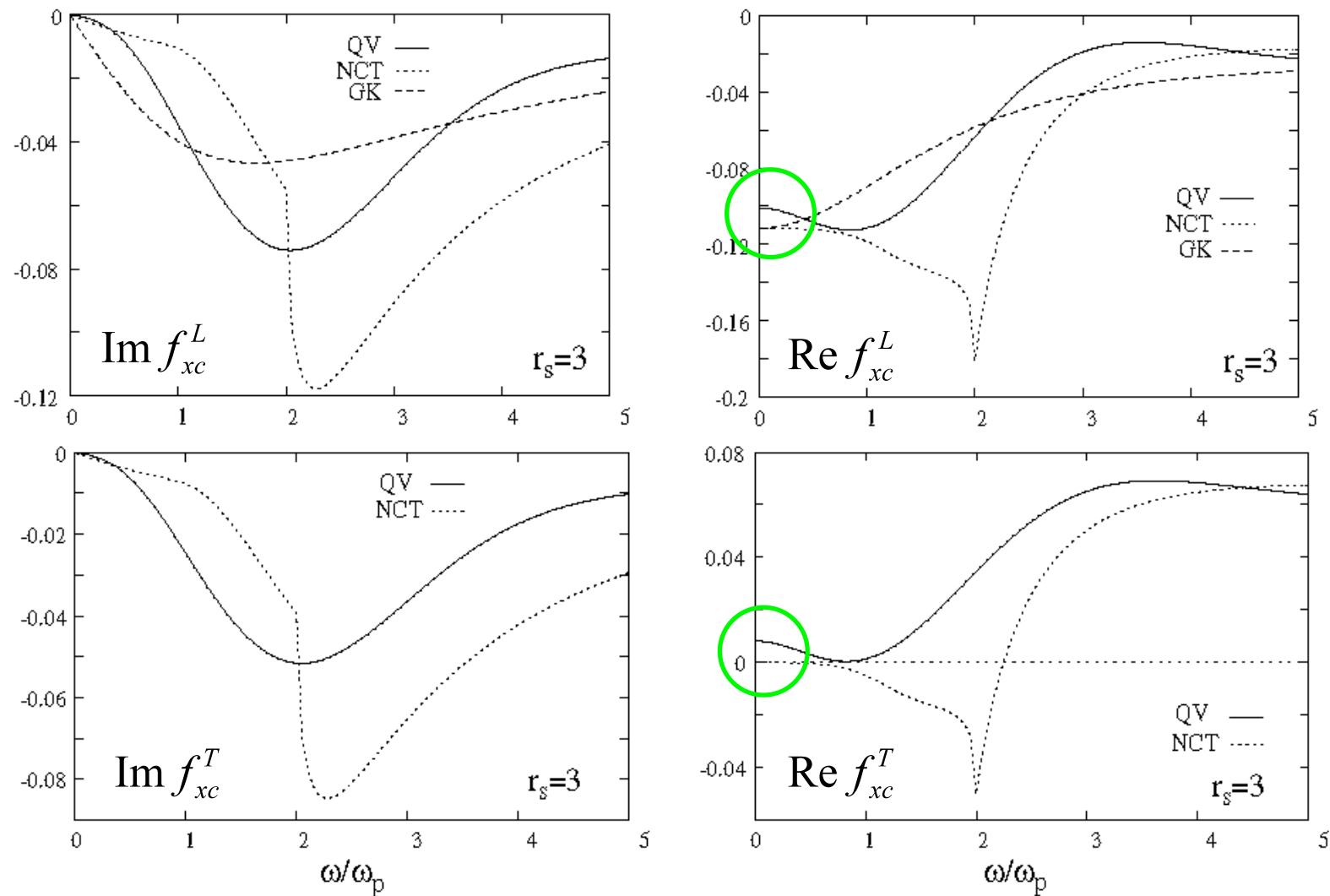
$$\tilde{\eta}(\omega) = \eta(\omega) - \frac{S_{xc}(\omega)}{i\omega}$$

shear modulus

$$\tilde{\xi}(\omega) = \xi(\omega) - \frac{B_{xc}^{dyn}(\omega)}{i\omega}$$

dynamical bulk modulus

reflect the stiffness of Fermi surface against defor- mations

GK: E.K.U. Gross and W. Kohn, PRL **55**, 2850 (1985)
NCT: R. Nifosi, S. Conti, and M.P. Tosi, PRB **58**, 12758 (1998)
QV: X. Qian and G. Vignale, PRB **65**, 235121 (2002)

$$f_{xc}^{L}(0) = \frac{d^2 e_{xc}^{unif}(n)}{dn^2} + \frac{4}{3} \frac{S_{xc}(0)}{n^2}$$
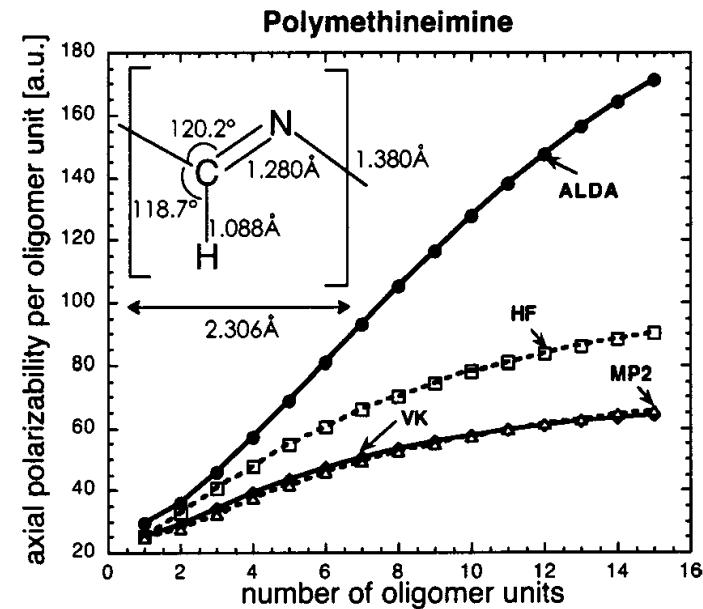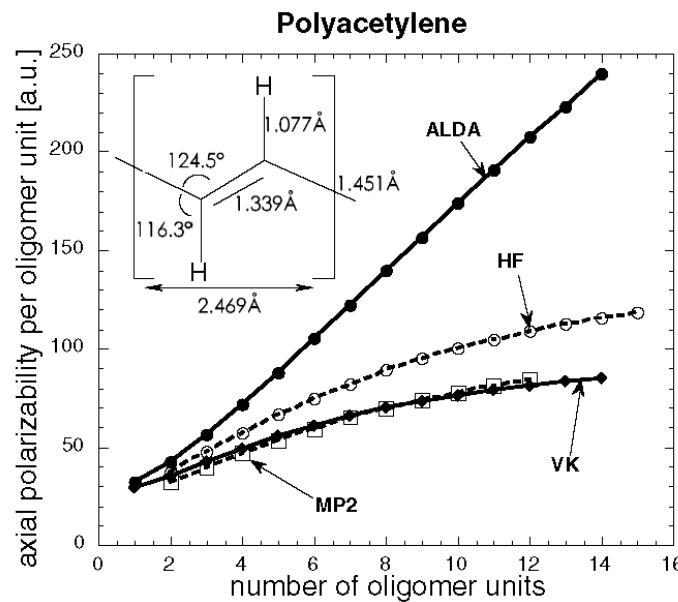
$$f_{xc}^{T}(0) = \frac{S_{xc}(0)}{n^2}$$

The shear modulus of the electron liquid does **not** disappear for $\omega \to 0$. (as long as the limit q→0 is taken first). Physical reason:
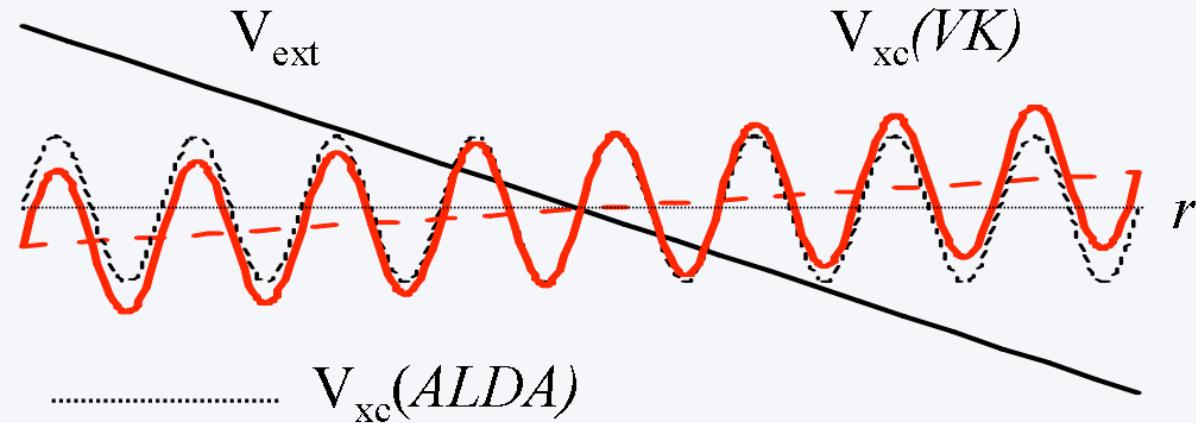
- Even very small frequencies <<E_F are large compared to relaxation rates from electron-electron collisions.
- The zero-frequency limit is taken such that local equilibrium is not reached.
- The Fermi surface remains stiff against deformations.

TDCDFT for conjugated polymers

Polyacetylene

Polymethineimine

ALDA overestimates polarizabilities of long molecular chains. The long-range VK functional produces a counteracting field, due to the finite shear modulus at $\omega \to 0$.

V_{ext} $V_{xc}(VK)$

r

$V_{xc}(ALDA)$

M. van Faassen et al., PRL **88**, 186401 (2002) and JCP **118**, 1044 (2003)

Outline

DFT and nanoscale transport

Koentopp, Chang, Burke, and Car (2008)

$$I = \frac{2}{\pi} \int_{-\infty}^{\infty} dE \, T(E) [f_L(E) - f_R(E)]$$

two-terminal Landauer formula

Transmission coefficient, usually obtained from DFT-nonequilibrium Green's function

Problems: ● standard xc functionals (LDA,GGA) inaccurate
● unoccupied levels not well reproduced in DFT
⟹ transmission peaks can come out wrong
⟹ conductances often much overestimated
⟹ need need better functionals (SIC, orbital-dep.)
and/or TDDFT

Current response:
$$\vec{j}(\vec{r},\omega) = \int d^3r'\, \overleftrightarrow{\sigma}_0(\vec{r},\vec{r}',\omega)\vec{E}_{eff}(\vec{r}',\omega)$$

$$\delta I(\omega \to 0) = \frac{T_0(\varepsilon_F)}{\pi}\int d^3r'\left[\delta E_{ext}(\omega) + \delta E_H(\vec{r}',\omega) + \delta E_{xc}(\vec{r}',\omega)\right]$$
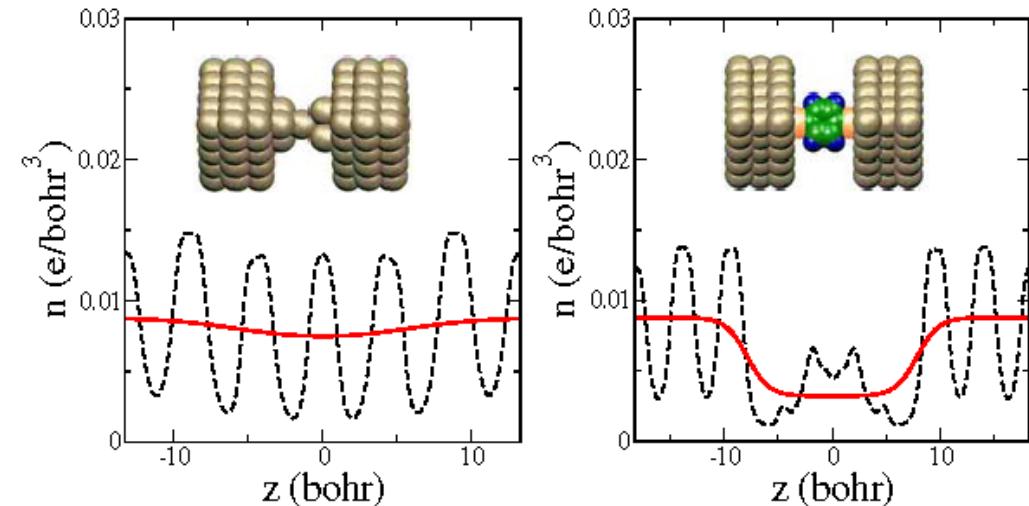
XC piece of voltage drop: **Current-TDDFT**

$$R^{dyn} = \frac{4}{3e^2 A_c}\int \eta\, \frac{(\partial_z n)^2}{n^4}\, dz$$

Sai, Zwolak, Vignale, Di Ventra,
PRL **94**, 186810 (2005)
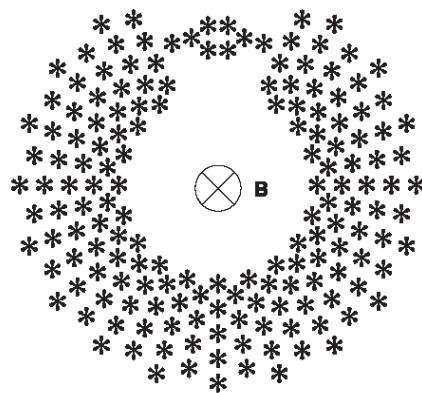
dynamical resistance: ~10% correction

BDT

point contact

TDDFT and nanoscale transport: finite bias

(A) Current-TDDFT and Master equation
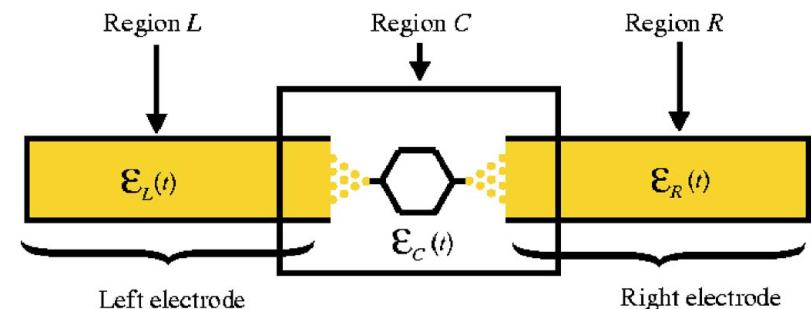
Burke, Car & Gebauer, PRL **94**, 146803 (2005)

- periodic boundary conditions (ring geometry), electric field induced by vector potential A(t)
- current as basic variable
- requires coupling to phonon bath for steady current

(B) TDDFT and Non-equilibrium Green's functions

Stefanucci & Almbladh, PRB **69**, 195318 (2004)

Region L   Region C   Region R

$\mathcal{E}_L(t)$ $\mathcal{E}_C(t)$ $\mathcal{E}_R(t)$

Left electrode   Right electrode

- localized system
- density as basic variable
- steady current via electronis dephasing with continuum of the leads

► (A) and (B) agree for weak bias and small dissipation
► some preliminary results are available – stay tuned!

Outline

In addition to an approximation for $v_{xc}[n;\Psi_0,\Phi_0](r,t)$, also need an

approximation for the <u>observables of interest</u>.

→ Is the relevant KS quantity physical ?

Certainly measurements involving only density (eg dipole moment) can be extracted directly from KS – no functional approximation needed for the observable. But generally not the case.

We'll take a look at:

High-harmonic generation (HHG)

Above-threshold ionization (ATI)

Non-sequential double ionization (NSDI)
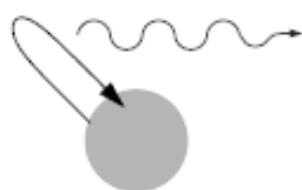
Attosecond Quantum Control

Correlated electron-ion dynamics

HHG: get peaks at
odd multiples of
laser frequency

Eg. He

TDHF

correlation reduces
peak heights by ~ 2 or 3

$|d(\omega)|^2$
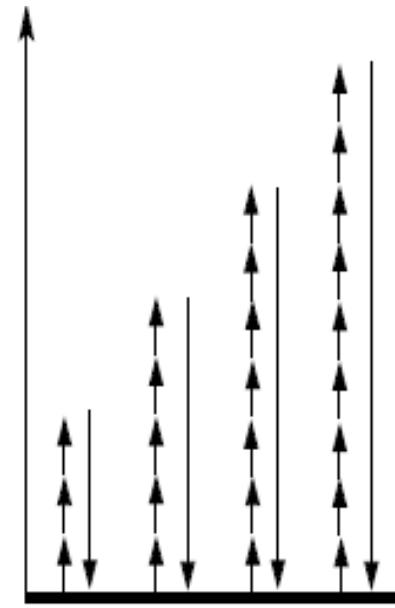
L'Huillier (2002)

Figure 7. Harmonic spectra of helium resulting from the Hartree–Fock equation (without correlation) and the Kohn–Sham equation (with correlation). The laser parameters are $\lambda = 616$ nm and $I = 7.0 \cdot 10^{14}$ W/cm^2.

Erhard & Gross, (1996)

Measures dipole moment,
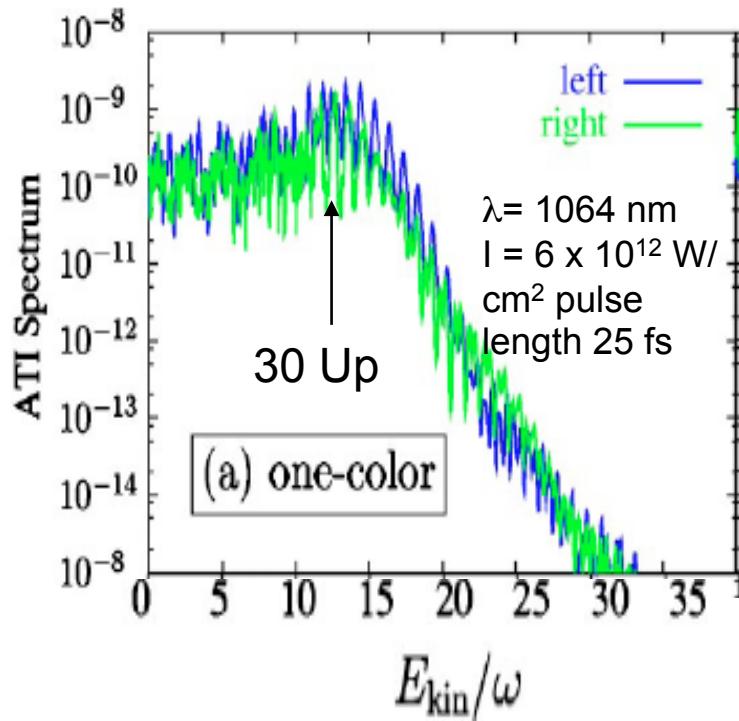
$|d(\omega)|^2 = \int n(r,t) \, r \, d^3r$

so directly available from TD KS system
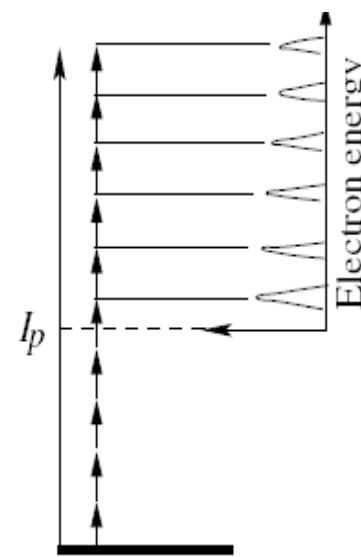
ATI: Measure kinetic energy of ejected electrons

Eg. Na-clusters

λ= 1064 nm
I = 6 x 10^{12} W/cm^2 pulse length 25 fs

30 Up

(a) one-color

E_{kin}/ω

*Nguyen, Bandrauk, and Ullrich, PRA **69**, 063415 (2004).*
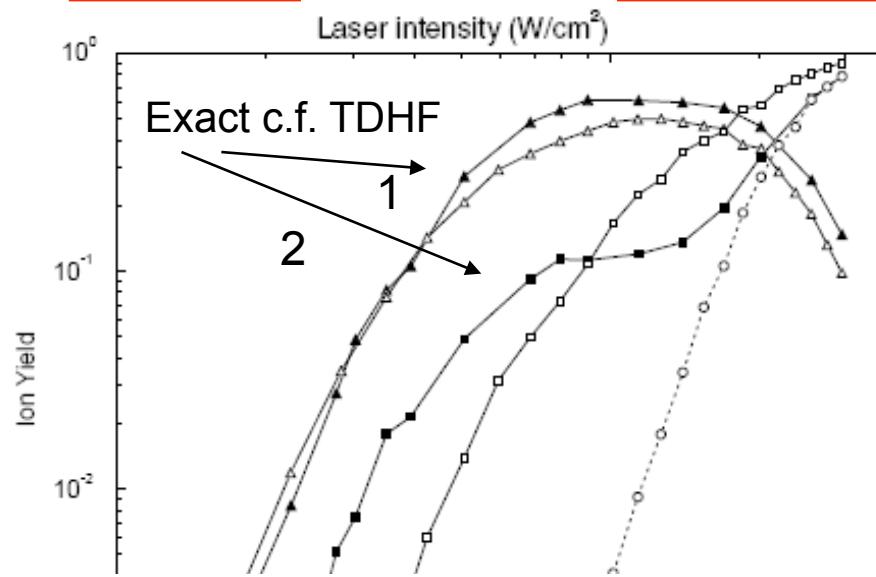
L'Huillier (2002)
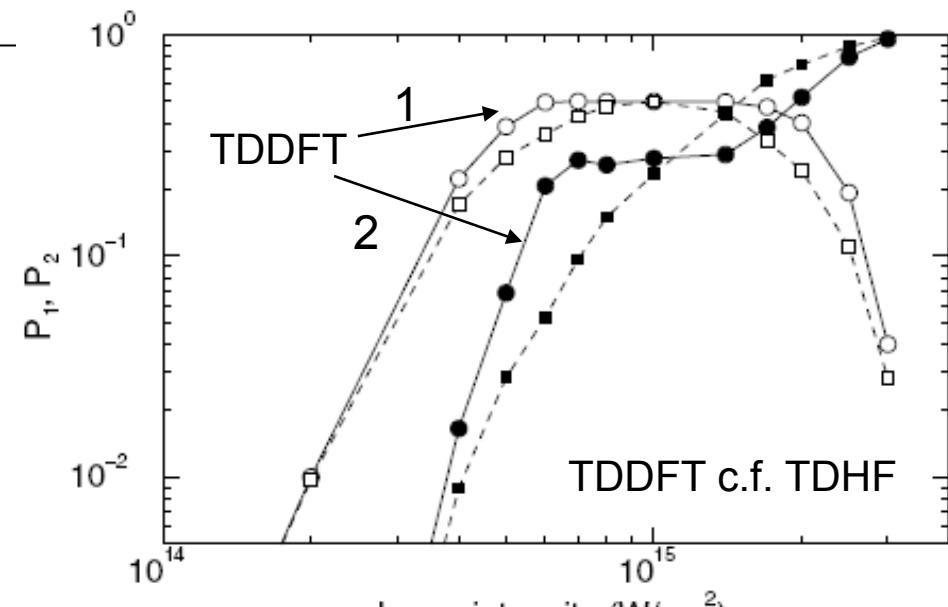
• TDDFT is the *only* computationally feasible method that could compute ATI for something as big as this!

• ATI measures kinetic energy of electrons – not directly accessible from KS. Here, *approximate* T by KS kinetic energy.

•TDDFT yields plateaus much longer than the 10 Up predicted by quasi-classical one-electron models

Lappas & van Leeuwen (1998),

Lein & Kummel (2005)

Knee forms due to a switchover from a sequential to a non-sequential (correlated) process of double ionization.

Knee missed by all single-orbital theories eg TDHF
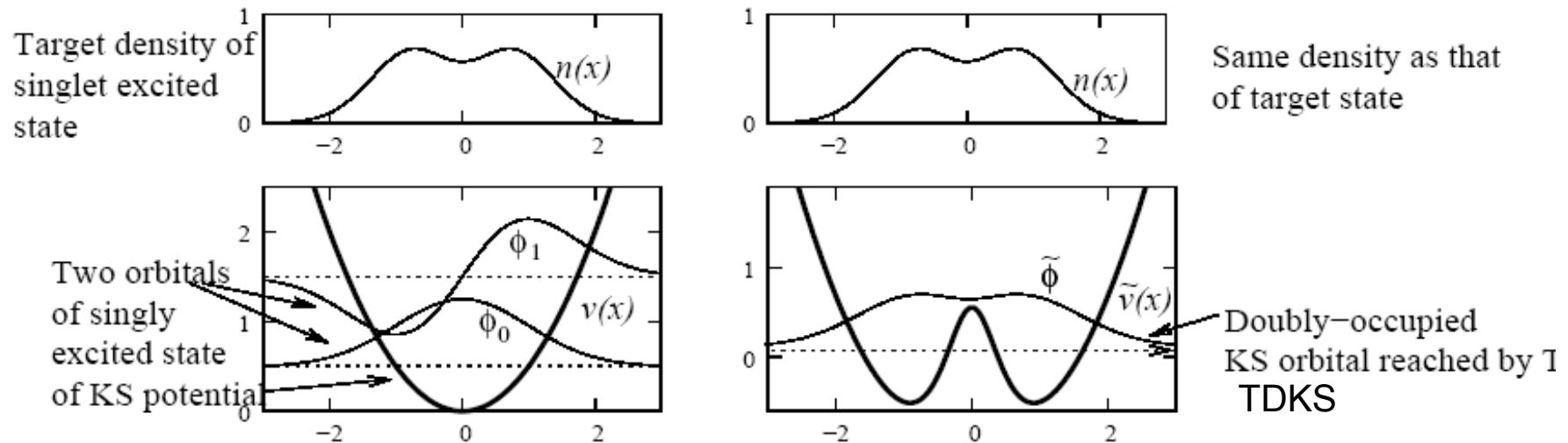
TDDFT can get it, but it's difficult :

• Knee requires a derivative discontinuity, lacking in most approxs

• Need to express *pair-density* as purely a density functional – uncorrelated expression gives wrong knee-height. *(Wilken & Bauer (2006))*

' Is difficult: Consider pumping He from ($1s^2$) → ($1s2p$)

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

<u>Simple model:</u> 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 !! The exact $v_{xc}(t)$ is unnatural and difficult to approximate.

Maitra, Woodward, & Burke (2002), Werschnik & Gross (2005), Werschnik, Gross & Burke (2007)

Classical nuclei coupled to quantum electrons, via Ehrenfest coupling, i.e.

$$M\ddot{\underline{R}} = -\nabla_R \left(W_{nn} + V_{ext,N}(t) + \langle \Phi_R | H_{el} | \Phi_R \rangle_{\underline{r}} \right)$$

$$= -\int d^3r\, n(\mathbf{r}t) \nabla_R V_{en}^R$$

Eg. Collisions of O atoms/ions with graphite clusters
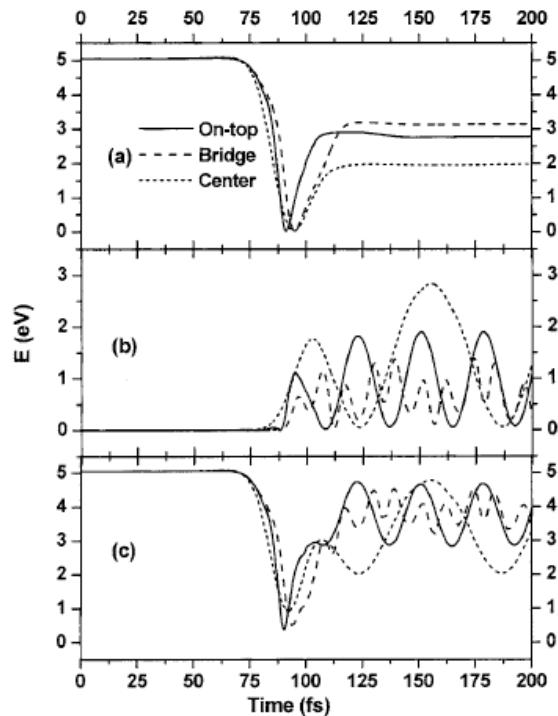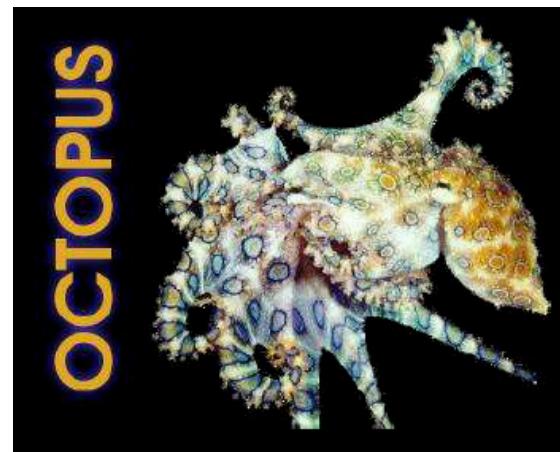
FIG. 2. Kinetic energies of (a) O(^3P), (b) the graphite cluster, and (c) the entire system.

*Isborn, Li. Tully, JCP **126**, 134307 (2007)*

Freely-available TDDFT code for strong and weak fields:

http://www.tddft.org

Castro, Appel, Rubio, Lorenzen, Marques, Oliveira, Rozzi, Andrade, 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..

Classical Ehrenfest method misses electron-nuclear correlation

("branching" of trajectories)

!! essential for photochemistry, relaxation, electron transfer, branching ratios, reactions near surfaces...

How about <u>Surface-Hopping</u> a la Tully with TDDFT ?
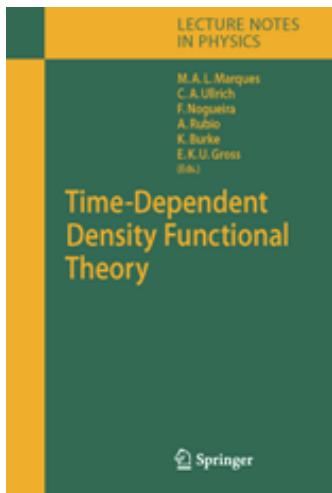
Simplest: nuclei move on KS PES between hops. But, KS PES ≠ true PES, and generally, may give wrong forces on the nuclei.

Should use TDDFT-corrected PES (eg calculate in linear response).

But then, trajectory hopping probabilities cannot be simply extracted – e.g. they depend on the coefficients of the true Ψ (not accessible in TDDFT), and on non-adiabatic couplings.

Craig, Duncan, & Prezhdo PRL 2005, Tapavicza, Tavernelli, Rothlisberger, PRL 2007, Maitra, JCP 2006

To learn more…

Time-dependent density functional theory, edited by M.A.L. Marques, C.A. Ullrich, F. Nogueira, A. Rubio, K. Burke, and E.K.U. Gross, Springer Lecture Notes in Physics, Vol. 706 (2006)

(see handouts for TDDFT literature list)

Upcoming TDDFT conferences:

● **3rd International Workshop and School on TDDFT Benasque, Spain, August 31 - September 15, 2008 http://benasque.ecm.ub.es/2008tddft/2008tddft.htm**

● **Gordon Conference on TDDFT, Summer 2009 http://www.grc.org**

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