

# **Tutorial: Time-dependent density-functional theory**

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## **Outline**

### **PART I:**

- Formal framework of TDDFT
- Time-dependent Kohn-Sham formalism

### **PART II:**

- TDDFT in the linear-response regime
- Calculation of excitation energies

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### Time-dependent Schrödinger equation

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

kinetic energy  
operator:

$$\hat{T} = \sum_{j=1}^N -\frac{\nabla_j^2}{2}$$

electron  
interaction:

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

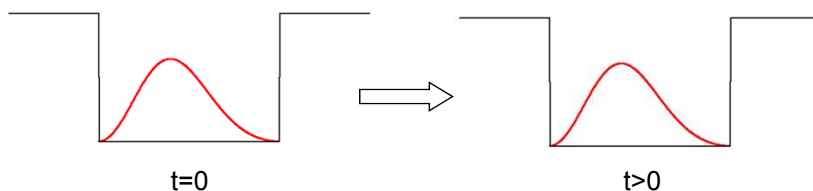
The TDSE describes the time evolution of a many-body state  $\Psi(t)$ , starting from an initial state  $\Psi(t_0)$ , under the influence of an external time-dependent potential  $\hat{V}(t) = \sum_{j=1}^N V(\mathbf{r}_j, t)$ .

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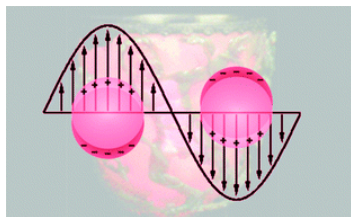


### Real-time electron dynamics: first scenario

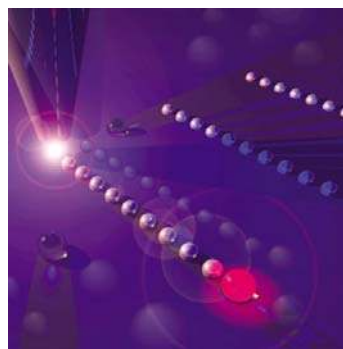
Start from nonequilibrium initial state, evolve in static potential:



Charge-density oscillations in metallic clusters or nanoparticles (plasmonics)



New J. Chem. **30**, 1121 (2006)  
Nature Mat. Vol. **2** No. 4 (2003)

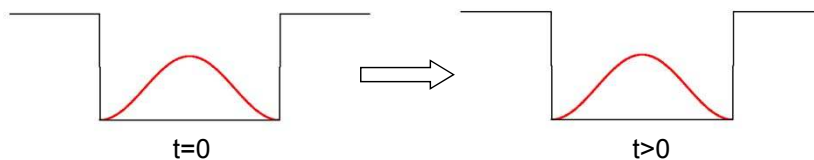


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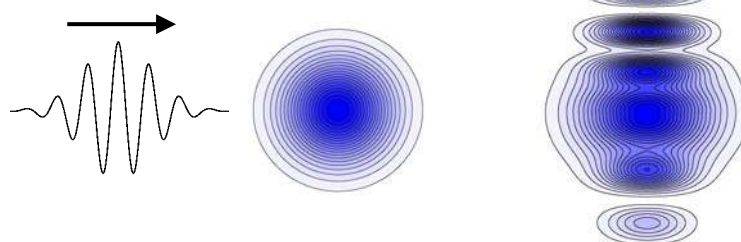


## Real-time electron dynamics: second scenario

Start from ground state, evolve in time-dependent driving field:



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

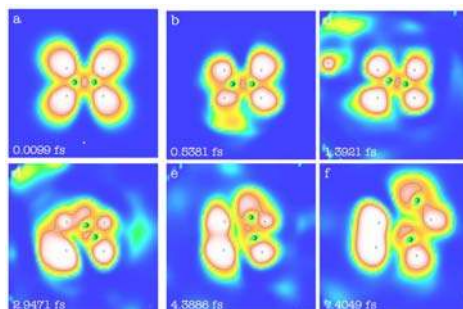


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## Coupled electron-nuclear dynamics

- 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

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## Density and current density

$$\hat{n}(\mathbf{r}) = \sum_{l=1}^N \delta(\mathbf{r} - \mathbf{r}_l) \quad n(\mathbf{r}, t) = \langle \Psi(t) | \hat{n}(\mathbf{r}) | \Psi(t) \rangle$$

$$\hat{\mathbf{j}}(\mathbf{r}) = \frac{1}{2i} \sum_{l=1}^N [\nabla_l \delta(\mathbf{r} - \mathbf{r}_l) + \delta(\mathbf{r} - \mathbf{r}_l) \nabla_l] \quad \mathbf{j}(\mathbf{r}, t) = \langle \Psi(t) | \hat{\mathbf{j}}(\mathbf{r}) | \Psi(t) \rangle$$

Heisenberg equation of motion for the density:

$$i \frac{\partial}{\partial t} n(\mathbf{r}, t) = \langle \Psi(t) | [\hat{n}(\mathbf{r}), \hat{H}(t)] | \Psi(t) \rangle$$

$$\frac{\partial}{\partial t} n(\mathbf{r}, t) = -\nabla \cdot \mathbf{j}(\mathbf{r}, t)$$

Similar equation of motion for the current density (we need it later):

$$i \frac{\partial}{\partial t} \mathbf{j}(\mathbf{r}, t) = \langle \Psi(t) | [\hat{\mathbf{j}}(\mathbf{r}), \hat{H}(t)] | \Psi(t) \rangle$$

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## The Runge-Gross Theorem (1984)

The time evolution and dynamics of a system is determined by the time-dependent external potential, via the TDSE.

The TDSE formally defines a map from potentials to densities:

$$V(\mathbf{r}, t) \xrightarrow[\text{fixed } \Psi_0]{i\partial\Psi(t)/\partial t = \hat{H}(t)\Psi(t)} \Psi(t) \xrightarrow{\langle \Psi(t) | \hat{n}(\mathbf{r}) | \Psi(t) \rangle} n(\mathbf{r}, t)$$

To construct a time-dependent DFT, we need to show that the dynamics of the system is completely determined by the time-dependent density. We need to prove the correspondence

$$V(\mathbf{r}, t) \xleftrightarrow[\text{for a given } \Psi_0]{\text{unique 1:1}} n(\mathbf{r}, t)$$

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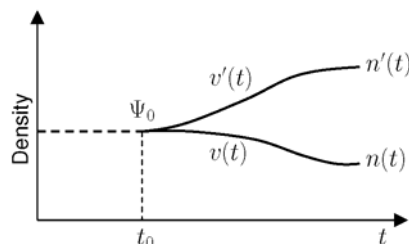


## Proof of the Runge-Gross Theorem (I)

Consider two systems of  $N$  interacting electrons, both starting in the same ground state  $\Psi_0$ , but evolving under different potentials:

$$V(\mathbf{r}, t) - V'(\mathbf{r}, t) \neq c(t)$$

The two potential differ by more than just a time-dependent constant.



The two different potentials can never give the same density!

What happens for potentials differing only by  $c(t)$ ? They give same density!

$$\tilde{V}(\mathbf{r}, t) = V(\mathbf{r}, t) + c(t) \Rightarrow \tilde{\Psi}(t) = e^{-i\alpha(t)}\Psi(t), \quad \frac{d\alpha(t)}{dt} = c(t)$$

$$\tilde{n}(t) = \langle \tilde{\Psi}(t) | \hat{n} | \tilde{\Psi}(t) \rangle = \langle \Psi(t) | e^{i\alpha(t)} \hat{n} e^{-i\alpha(t)} | \Psi(t) \rangle = \langle \Psi(t) | \hat{n} | \Psi(t) \rangle = n(t)$$

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## Proof of the Runge-Gross Theorem (II)

We assume that the potentials can be expanded in a Taylor series about the initial time:

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

Two different potentials:

there exists a smallest  $k$  so that  $V_k(\mathbf{r}) - V'_k(\mathbf{r}) \neq \text{const}$

**Step 1: show that the current densities must be different!**

We start from the equation of motion for the current density.

$$\begin{aligned} \frac{\partial}{\partial t} \{ \mathbf{j}(\mathbf{r}, t) - \mathbf{j}'(\mathbf{r}, t) \}_{t=t_0} &= -i \langle \Psi_0 | [\hat{\mathbf{j}}(\mathbf{r}), \hat{H}(t_0) - \hat{H}'(t_0)] | \Psi_0 \rangle \\ &= -n(\mathbf{r}, t_0) \nabla \{ V(\mathbf{r}, t_0) - V'(\mathbf{r}, t_0) \} \end{aligned}$$

If the two potentials are different at the initial time, then the two current densities will be different infinitesimally later than  $t_0$

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### Proof of the Runge-Gross Theorem (III)

If the potentials are not different at the initial time, they will become different later. This shows up in higher terms in the Taylor expansion. Use the equation of motion  $k$  times:

$$\frac{\partial^{k+1}}{\partial t^{k+1}} \{ \mathbf{j}(\mathbf{r}, t) - \mathbf{j}'(\mathbf{r}, t) \}_{t=t_0} = -n(\mathbf{r}, t_0) \nabla \{ V_k(\mathbf{r}, t_0) - V'_k(\mathbf{r}, t_0) \}$$

This proves the first step of the Runge-Gross theorem:

$$V(\mathbf{r}, t) \xleftrightarrow[\text{for a given } \Psi_0]{\text{unique 1:1}} \mathbf{j}(\mathbf{r}, t)$$

**Step 2: show that if the current densities are different, then the densities must be different as well!**

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### Proof of the Runge-Gross Theorem (IV)

Calculate the  $(k+1)$ st time derivative of the continuity equation:

$$\begin{aligned} \frac{\partial^{k+2}}{\partial t^{k+2}} \{ n(\mathbf{r}, t) - n'(\mathbf{r}, t) \}_{t=t_0} &= -\nabla \cdot \frac{\partial^{k+1}}{\partial t^{k+1}} \{ \mathbf{j}(\mathbf{r}, t) - \mathbf{j}'(\mathbf{r}, t) \} \\ &= -\nabla \cdot \{ n(\mathbf{r}, t_0) \nabla \{ V_k(\mathbf{r}) - V'_k(\mathbf{r}) \} \} \\ &\equiv -\nabla \cdot (n_0(\mathbf{r}) \nabla w_k(\mathbf{r})) \quad \neq 0 \end{aligned}$$

We must show that right-hand side cannot vanish identically!

Use Green's integral theorem:

$$\int d^3r n_0(\mathbf{r}) (\nabla w_k(\mathbf{r}))^2 = \int d^3r w_k(\mathbf{r}) \nabla \cdot (n_0(\mathbf{r}) \nabla w_k(\mathbf{r})) + \oint d\mathbf{S} n_0(\mathbf{r}) w_k(\mathbf{r}) \nabla w_k(\mathbf{r})$$

positive, cannot  
vanish

so, this term  
cannot vanish!

= 0

Therefore, the densities  
must be different  
infinitesimally after  $t_0$ .  
This completes the proof.

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## The Runge-Gross Theorem

$$V(\mathbf{r}, t) \xleftrightarrow[\text{for a given } \Psi_0]{\text{unique 1:1}} n(\mathbf{r}, t)$$

E. Runge and E.K.U. Gross, Phys. Rev. Lett. **52**, 997 (1984)

The potential can therefore be written as a functional of the density and initial state, which determines the Hamiltonian:

$$V(\mathbf{r}, t) = V[n, \Psi_0](\mathbf{r}, t) \Rightarrow \hat{H}(t) = \hat{H}[n, \Psi_0](t) \Rightarrow \Psi(t) = \Psi[n, \Psi_0](t)$$

All physical observables become functionals of the density:

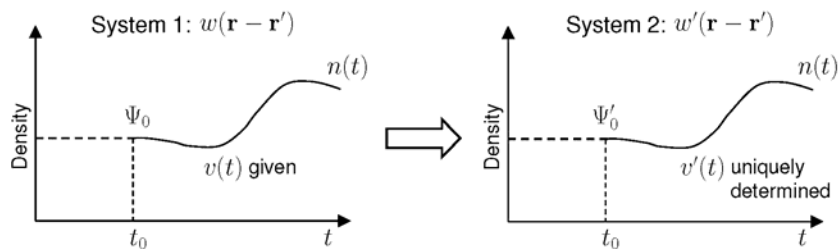
$$O(t) = \langle \Psi[n, \Psi_0](t) | \hat{O}(t) | \Psi[n, \Psi_0](t) \rangle = O[n, \Psi_0](t)$$

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## The van Leeuwen Theorem

In practice, we want to work with a noninteracting (Kohn-Sham) system that reproduces the density of the interacting system. But how do we know that such a noninteracting system exists? (this is called the “noninteracting V-representability problem”)



R. van Leeuwen, Phys. Rev. Lett. **82**, 3863 (1999)

- Can find a system with a different interaction that reproduces the same density. In particular,  $w=0$  is a noninteracting system.
- This provides formal justification of the Kohn-Sham approach
- Proof requires densities and potentials to be analytic at initial time. Recently, examples of nonanalytic densities were discovered:  
Z.-H. Yang, N.T. Maitra, and K. Burke, Phys. Rev. Lett. **108**, 063003 (2012)

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## Situations not covered by the RG theorem

- 1 TDDFT does not apply for time-dependent **magnetic fields** or for **electromagnetic waves**. These require **vector potentials**.
- 2 The original RG proof is for **finite** systems with potentials that vanish at infinity (step 2). **Extended/periodic** systems can be tricky:

- TDDFT works for periodic systems if the time-dependent potential is also periodic in space.
- The RG theorem does not apply when a homogeneous electric field (a linear potential) acts on a periodic system.

**Solution: upgrade to time-dependent **current**-DFT**

N.T. Maitra, I. Souza, and K. Burke, PRB **68**, 045109 (2003)

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## Time-dependent Kohn-Sham scheme

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:

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

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

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

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

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



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## The time-dependent xc potential

Dependence on initial states,  
except when starting from the ground state

$$V_{xc} \left[ n, \overbrace{\Psi(0), \Phi_{KS}(0)} \right] (\mathbf{r}, t)$$

Dependence on densities:

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

(nonlocal in space and time)

Static DFT:  $V_{xc}[n](\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})}$

TDDFT: more complicated!  
(stationary action principle)

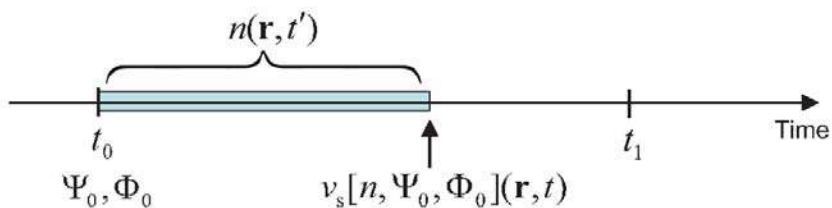
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## Time-dependent self-consistency

$$\left[ -\frac{\nabla^2}{2} + v_s[n](\mathbf{r}, t) \right] \varphi_j(\mathbf{r}, t) = i \frac{\partial}{\partial t} \varphi_j(\mathbf{r}, t) \longrightarrow \sum_j |\varphi_j(\mathbf{r}, t)|^2 = n(\mathbf{r}, t)$$

Density  $n(\mathbf{r}', t')$  over all space and times  $t' \leq t$  (initial value problem)



Time propagation requires keeping the density at previous times  
stored in memory! (But this is almost never done in practice....)

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## Adiabatic approximation

$$V_H(\mathbf{r}, t) = \int d^3 r' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} \quad \text{depends on density at time } t \text{ (instantaneous, no memory)}$$

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

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 the instantaneous time-dependent density)

ALDA:

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

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## Numerical time propagation

$$\text{Propagate a time step } \Delta t: \quad \varphi_j(\mathbf{r}, t + \Delta t) = e^{-i\hat{H}\Delta t} \varphi_j(\mathbf{r}, t)$$

$$\text{Crank-Nicholson algorithm:} \quad e^{-i\hat{H}\Delta t} \approx \frac{1 - i\hat{H}\Delta t/2}{1 + i\hat{H}\Delta t/2}$$

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

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

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

→ use “predictor-corrector scheme”

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### Summary of TDKS scheme: 3 steps

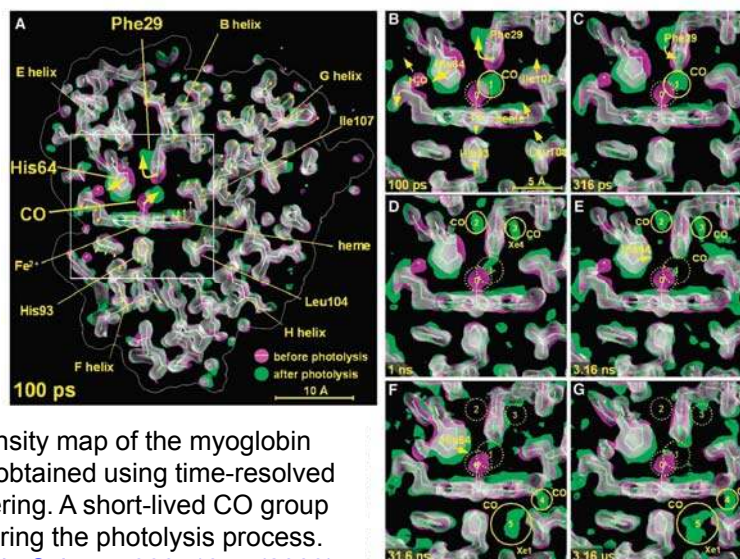
- 1 Prepare the initial state, usually the ground state, by a static DFT calculation. This gives the initial orbitals:  $\varphi_j^{(0)}(\mathbf{r}, 0)$
- 2 Solve TDKS equations selfconsistently, using an approximate time-dependent xc potential which matches the static one used in step 1. This gives the TDKS orbitals:  $\varphi_j(\mathbf{r}, t) \rightarrow n(\mathbf{r}, t)$
- 3 Calculate the relevant observable(s) as a functional of  $n(\mathbf{r}, t)$

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### Observables: the time-dependent density

The simplest observable is the time-dependent density itself:  $n(\mathbf{r}, t)$



Electron density map of the myoglobin molecules, obtained using time-resolved X-ray scattering. A short-lived CO group appears during the photolysis process.

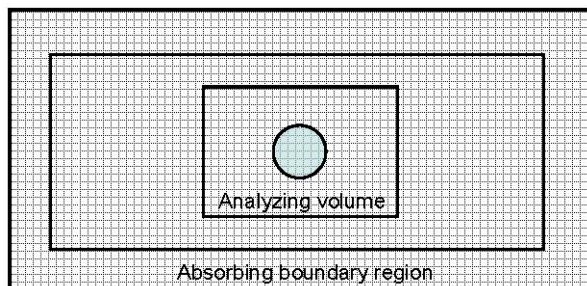
Schotte et al., *Science* **300**, 1944 (2003)

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### Observables: the particle number

Unitary time propagation: 
$$\int_{\text{all space}} d^3r n(\mathbf{r}, t) = N$$



During an ionization process, charge moves away from the system.

Numerically, we can describe this on a finite grid with an absorbing boundary.

The number of bound/escaped particles at time  $t$  is approximately given by

$$N_{\text{bound}} = \int_{\text{analyzing volume}} d^3r n(\mathbf{r}, t), \quad N_{\text{esc}} = N - N_{\text{bound}}$$

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### Observables: moments of the density

dipole moment: 
$$d_{\mu}(t) = \int d^3r r_{\mu} n(\mathbf{r}, t), \quad \mu = x, y, z$$

sometimes one wants higher moments, e.g. quadrupole moment:

$$q_{\mu\nu}(t) = \int d^3r (3r_{\mu}r_{\nu} - r^2\delta_{\mu\nu})n(\mathbf{r}, t)$$

One can calculate the Fourier transform of the dipole moment:

$$d_{\mu}(\omega) = \frac{1}{t_i - t_f} \int_{t_i}^{t_f} d_{\mu}(t) e^{-i\omega t} dt$$

Dipole power spectrum:

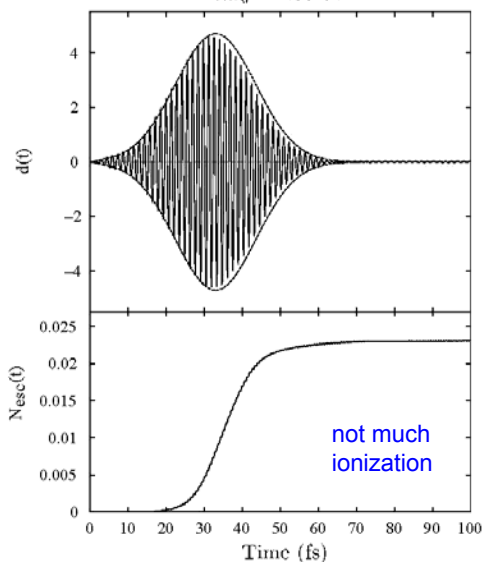
$$D(\omega) = \sum_{\mu=1}^3 |d_{\mu}(t)|^2$$

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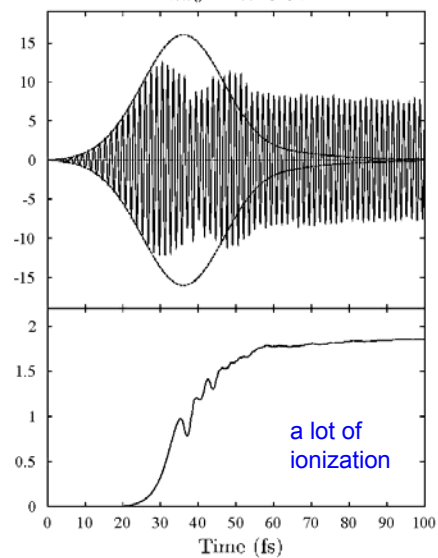


### Example: $\text{Na}_9^+$ cluster in a strong laser pulse

off resonance  $\hbar\omega_0 = 2.95 \text{ eV}$



on resonance  $\hbar\omega_0 = 2.725 \text{ eV}$

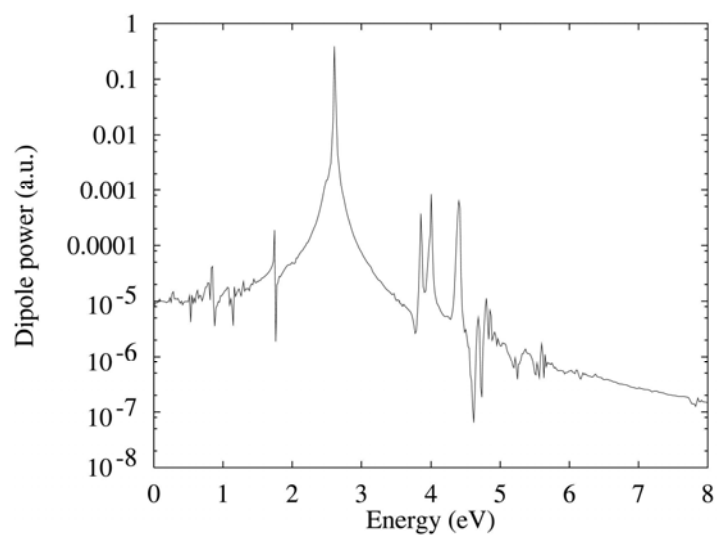


Intensity:  $I = 10^{11} \text{ W/cm}^2$

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### Example: dipole power spectrum of $\text{Na}_9^+$ cluster



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## Implicit density functionals

We have learned that in TDDFT all quantum mechanical observables become density functionals:

$$\alpha[n](t) = \langle \Psi[n](t) | \hat{\alpha} | \Psi[n](t) \rangle$$

Some observables (e.g., the dipole moment), can easily be expressed as density functionals. But there are also difficult cases!

- Probability to find the system in a k-fold ionized state

$$P_k(t) = \langle \Psi(t) | \left\{ \sum_l |\Psi_{0l}^k\rangle \langle \Psi_{0l}^k| \right\} | \Psi(t) \rangle$$

Projector on eigenstates  
with k electrons in the  
continuum

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## Implicit density functionals

- Photoelectron kinetic-energy spectrum

$$P(E)dE = \lim_{t \rightarrow \infty} \sum_{k=1}^N \left| \langle \Psi_E^k | \Psi(t) \rangle \right|^2 dE$$

- State-to-state transition amplitude (S-matrix)

$$S_{i,f} = \lim_{t \rightarrow \infty} \langle \Psi_f | \Psi(t) \rangle$$

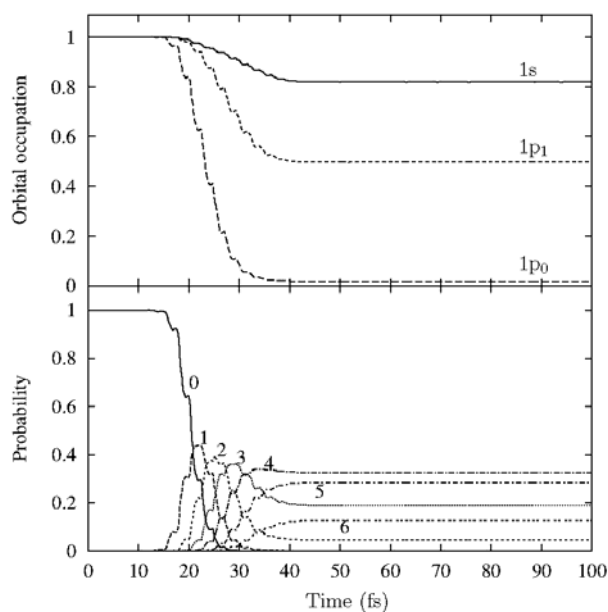
All of the above observables are easy to express in terms of the wave function, but very difficult to write down as explicit density functionals.

Not knowing any better, people often calculate them approximately using the KS Slater determinant instead of the exact wave function. This is an uncontrolled approximation, and should only be done with great care.

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## Ionization of a $\text{Na}_9^+$ cluster in a strong laser pulse



25 fs laser pulses  
0.87 eV photon energy  
 $I = 4 \times 10^{13} \text{ W/cm}^2$

For implicit observables  
such as ion probabilities  
one needs to make two  
approximations:

(1) for the xc potential  
in the TDKS calculation

(2) for calculating the  
observable from the  
TDKS orbitals.

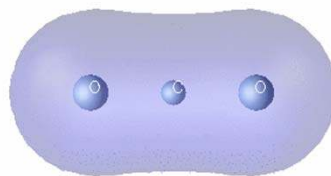
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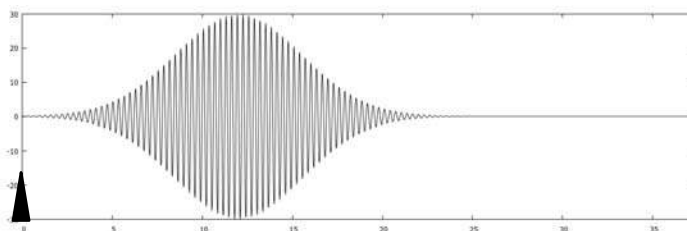
## $\text{CO}_2$ molecule in a strong laser pulse

$$\hbar\omega = 20 \text{ eV}$$

$$I = 1.2 \times 10^{15} \frac{\text{W}}{\text{cm}^2}$$



Calculation done  
with octopus



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## Outline

### PART I:

- Formal framework of TDDFT
- Time-dependent Kohn-Sham formalism

### PART II:

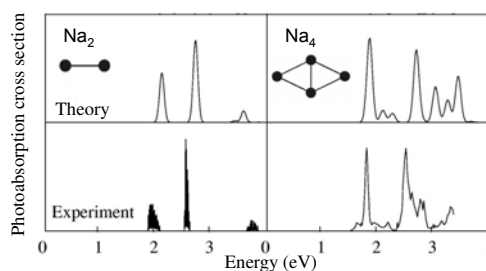
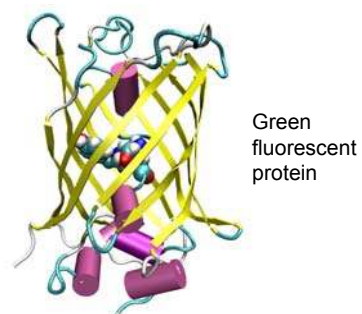
- TDDFT in the linear-response regime
- Calculation of excitation energies

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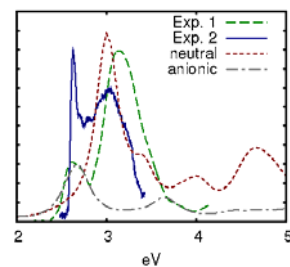


## Optical spectroscopy

- Uses weak laser as Probe
- System Response has peaks at electronic excitation energies



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



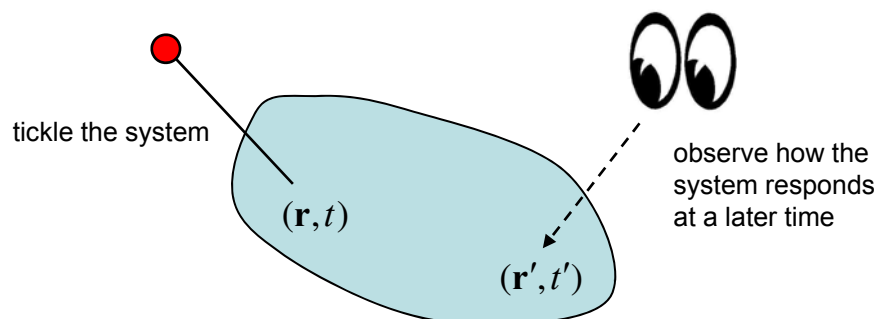
Marques et al., PRL **90**, 258101 (2003)



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## Linear response



The formal framework to describe the behavior of a system under weak perturbations is called **Linear Response Theory**.

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## Linear response theory (I)

Consider a quantum mechanical observable  $\hat{\alpha}$  with ground-state expectation value

$$\alpha_0 = \langle \Psi_0 | \hat{\alpha} | \Psi_0 \rangle$$

Time-dependent perturbation:  $\hat{H}_1(t) = F(t)\hat{\beta}$ ,  $t \geq t_0$

The expectation value of the observable  $\hat{\alpha}$  now becomes time-dependent:

$$\alpha(t) = \langle \Psi(t) | \hat{\alpha} | \Psi(t) \rangle, \quad t \geq t_0$$

The **response** of the system can be expanded in powers of the field  $F(t)$ :

$$\begin{aligned} \alpha(t) - \alpha_0 &= \alpha_1(t) + \alpha_2(t) + \alpha_3(t) + \dots \\ &= \text{linear} + \text{quadratic} + \text{third-order} + \dots \end{aligned}$$

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## Linear response theory (II)

For us, the **density-density response** will be most important.  
The perturbation is a scalar potential  $V_I$ ,

$$\hat{H}_1(t) = \int d^3r' V_1(\mathbf{r}', t) \hat{n}(\mathbf{r}')$$

where the density operator is  $\hat{n}(\mathbf{r}) = \sum_{l=1}^N \delta(\mathbf{r} - \mathbf{r}_l)$

$$n(\mathbf{r}, t) = \langle \Psi(t) | \hat{n}(\mathbf{r}) | \Psi(t) \rangle$$

The linear density response is

$$n_1(\mathbf{r}, t) = \int_{-\infty}^{\infty} dt' \int d^3r' \chi_{nn}(\mathbf{r}, \mathbf{r}', t - t') V_1(\mathbf{r}', t')$$

$$\chi_{nn}(\mathbf{r}, \mathbf{r}', t - t') = -i\theta(t - t') \langle \Psi_0 | [\hat{n}(\mathbf{r}, t - t'), \hat{n}(\mathbf{r}')] | \Psi_0 \rangle$$

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## Linear response theory (III)

Fourier transformation with respect to  $(t - t')$  gives:

$$n_1(\mathbf{r}, \omega) = \int d^3r' \chi_{nn}(\mathbf{r}, \mathbf{r}', \omega) V_1(\mathbf{r}', \omega)$$

$$\chi_{nn}(\mathbf{r}, \mathbf{r}', \omega) = \sum_{n=1}^{\infty} \left\{ \frac{\langle \Psi_0 | \hat{n}(\mathbf{r}) | \Psi_n \rangle \langle \Psi_n | \hat{n}(\mathbf{r}') | \Psi_0 \rangle}{\omega - \Omega_n + i\eta} - \frac{\langle \Psi_0 | \hat{n}(\mathbf{r}') | \Psi_n \rangle \langle \Psi_n | \hat{n}(\mathbf{r}) | \Psi_0 \rangle}{\omega + \Omega_n + i\eta} \right\}$$

where  $\Omega_n = E_n - E_0$  is the  **$n^{\text{th}}$  excitation energy**.

- The linear response function has poles at the excitation energies of the system.
- Whenever there is a perturbation at such a frequency, the response will diverge (peak in the spectrum)

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## Spectroscopic observables

First-order induced dipole polarization:  $\mathbf{p}_1(\omega) = \boldsymbol{\alpha}(\omega)\mathbf{E}(\omega)$

In dipole approximation, one defines a scalar potential associated with a monochromatic electric field, linearly polarized along the z direction:

$$V_1(\mathbf{r}, t) = \mathcal{E} z \sin(\omega t)$$

This gives 
$$p_{1,z}(\omega) = -\int d^3r z n_1(\mathbf{r}, \omega)$$

And the dynamic dipole polarization becomes

$$\begin{aligned} \alpha_{zz}(\omega) &= -\frac{2}{\mathcal{E}} \int d^3r z n_1(\mathbf{r}, \omega) \\ &= -\int d^3r \int d^3r' z z' \chi(\mathbf{r}, \mathbf{r}', \omega) \end{aligned}$$

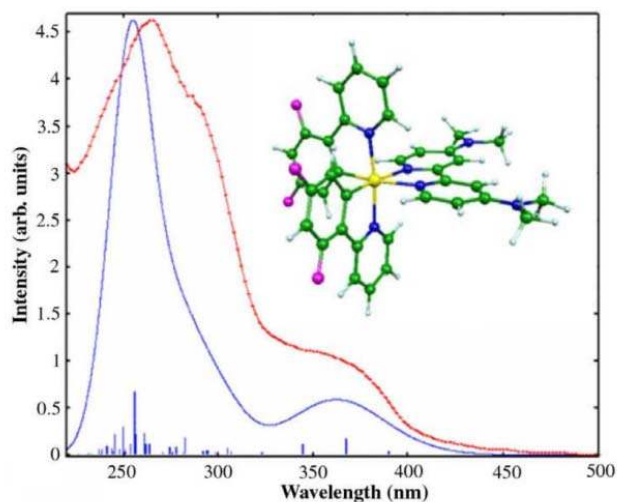
From this we obtain the photoabsorption cross section:

$$\sigma_{zz}(\omega) = \frac{4\pi\omega}{c} \text{Im} \alpha_{zz}(\omega)$$

38



## Spectrum of a cyclometallated complex



F. De Angelis, L. Belpassi, S. Fantacci, J. Mol. Struct. THEOCHEM **914**, 74 (2009)

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## TDDFT for linear response

Gross and Kohn, 1985:

$$\begin{aligned} n_1(\mathbf{r}, t) &= \int d^3 r' \int dt' \chi(\mathbf{r}, t, \mathbf{r}', t') V_1(\mathbf{r}', t') \\ &= \int d^3 r' \int dt' \chi_s(\mathbf{r}, t, \mathbf{r}', t') V_{1,s}(\mathbf{r}', t') \end{aligned}$$

Exact density response can be calculated as the response of a **noninteracting system** to an **effective perturbation**:

$$V_{1,s}(\mathbf{r}, t) = V_1(\mathbf{r}, t) + \int dt' \int d^3 r' \left[ \frac{\delta(t-t')}{|\mathbf{r}-\mathbf{r}'|} + f_{xc}(\mathbf{r}, t, \mathbf{r}', t') \right] n_1(\mathbf{r}', t')$$

$$\text{xc kernel: } f_{xc}(\mathbf{r}, t, \mathbf{r}', t') = \left. \frac{\delta V_{xc}[n](\mathbf{r}, t)}{\delta n(\mathbf{r}', t')} \right|_{n_0(\mathbf{r})}$$

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## Frequency-dependent linear response

$$\begin{aligned} n_1(\mathbf{r}, \omega) &= \int d^3 r' \chi(\mathbf{r}, \mathbf{r}', \omega) V_1(\mathbf{r}', \omega) \\ &= \int d^3 r' \chi_s(\mathbf{r}, \mathbf{r}', \omega) V_{1,s}(\mathbf{r}', \omega) \end{aligned}$$

many-body  
response  
function:

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = \sum_m \frac{\langle 0 | \hat{n}(\mathbf{r}) | m \rangle \langle m | \hat{n}(\mathbf{r}') | 0 \rangle}{\omega - (E_m - E_0) + i\delta} + c.c.(-\omega)$$

exact excitations  $\Omega$

noninteracting  
response  
function:

$$\chi_s(\mathbf{r}, \mathbf{r}', \omega) = \sum_{j,k} (f_k - f_j) \frac{\phi_k^*(\mathbf{r}) \phi_j(\mathbf{r}) \phi_j^*(\mathbf{r}') \phi_k(\mathbf{r}')}{\omega - (\epsilon_j - \epsilon_k) + i\eta}$$

KS excitations  $\omega_{KS}$

$$V_{1,s} = V_1 + \int d^3 r' \left[ \frac{1}{|\mathbf{r}-\mathbf{r}'|} + f_{xc}(\mathbf{r}, \mathbf{r}', \omega) \right] n_1(\mathbf{r}', \omega)$$

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## The xc kernel: approximations

$$f_{xc}(\mathbf{r}, \mathbf{r}', \omega) = \chi_s^{-1}(\mathbf{r}, \mathbf{r}', \omega) - \chi^{-1}(\mathbf{r}, \mathbf{r}', \omega) - \frac{1}{|\mathbf{r} - \mathbf{r}'|}$$

Formally, the xc kernel is frequency-dependent and complex.

**Random Phase Approximation (RPA):**  $f_{xc}^{RPA} = 0$

**Adiabatic approximation:**  
frequency-independent  
and real

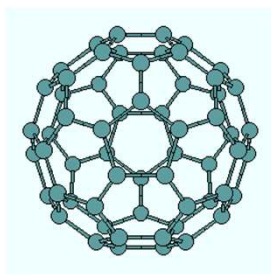
$$f_{xc}^{adia}(\mathbf{r}, \mathbf{r}') = \frac{\delta V_{xc}^{g.s.}[n](\mathbf{r})}{\delta n(\mathbf{r}')} = \frac{\delta^2 E_{xc}[n]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')}$$

**Adiabatic LDA (ALDA):**  $f_{xc}^{ALDA}(\mathbf{r}, \mathbf{r}') = \frac{d^2 e_{xc}^{unif}(n)}{dn^2} \bigg|_{n=n_0(\mathbf{r})} \delta(\mathbf{r} - \mathbf{r}')$

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## Analogy: molecular vibrations



Molecular vibrations are characterized by the **eigenmodes** of the system.

Using classical mechanics we can find the eigenmodes and their frequencies by solving an equation of the form

$$\sum_j (A_{jk} - \omega_r^2 m_{jk}) \xi_{jr} = 0$$

dynamical coupling  
matrix (contains  
the spring constants)

frequency of  
r<sup>th</sup> eigenmode

mass tensor

eigenvector  
gives the  
mode profile

So, to find the molecular eigenmodes and vibrational frequencies we have to solve an eigenvalue equation whose size depends on the size of the molecule.

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## Electronic excitations

An electronic excitation can be viewed as an **eigenmode of the electronic many-body system**.

This means that the electronic density of the system (atom, molecule, or solid) can carry out oscillations, at certain special frequencies, which are self-sustained, and do not need any external driving force.

$$n_1(\mathbf{r}, \omega) = \int d^3 r' \chi(\mathbf{r}, \mathbf{r}', \omega) V_1(\mathbf{r}', \omega)$$

finite density  
response: the  
eigenmode of  
an excitation

diverges when  $\omega$   
equals one of the  
excitation energies

set to zero  
(no external  
perturbation)

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## Electronic excitations with TDDFT

$$n_1(\mathbf{r}, \omega) = \int d^3 r' \chi_s(\mathbf{r}, \mathbf{r}', \omega) \int d^3 r'' \left[ \frac{1}{|\mathbf{r}' - \mathbf{r}''|} + f_{xc}(\mathbf{r}', \mathbf{r}'', \omega) \right] n_1(\mathbf{r}'', \omega)$$

Find those frequencies  $\omega$  where the response equation, without external perturbation, has a solution with finite  $n_1$ .

M. Petersilka, U.J. Gossmann, E.K.U. Gross, PRL **76**, 1212 (1996)  
H. Appel, E.K.U. Gross, K. Burke, PRL **90**, 043005 (2003)

We define the following abbreviation:

$$f_{Hxc}(\mathbf{r}, \mathbf{r}', \omega) = \frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{xc}(\mathbf{r}, \mathbf{r}', \omega)$$

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### Warm-up exercise: 2-level system

Noninteracting response function, where  $\omega_{jk} = \varepsilon_j - \varepsilon_k$  :

$$\chi_s(\mathbf{r}, \mathbf{r}', \omega) = \sum_{j,k} (f_k - f_j) \frac{\varphi_k^*(\mathbf{r}) \varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}') \varphi_k(\mathbf{r}')}{\omega - \omega_{jk} + i\eta}$$

We consider the case of a system with 2 real orbitals, the first one occupied and the second one empty. Then,

$$\begin{aligned} \chi_s(\mathbf{r}, \mathbf{r}', \omega) &= \frac{\varphi_1(\mathbf{r}) \varphi_2(\mathbf{r}) \varphi_2(\mathbf{r}') \varphi_1(\mathbf{r}')}{\omega - \omega_{21}} - \frac{\varphi_1(\mathbf{r}) \varphi_2(\mathbf{r}) \varphi_2(\mathbf{r}') \varphi_1(\mathbf{r}')}{\omega + \omega_{21}} \\ &= \varphi_1(\mathbf{r}) \varphi_2(\mathbf{r}) \varphi_2(\mathbf{r}') \varphi_1(\mathbf{r}') \frac{2\omega_{21}}{\omega^2 - \omega_{21}^2} \end{aligned}$$

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### 2-level system

$$\begin{aligned} n_1(\mathbf{r}, \omega) &= \int d^3 r' \chi_s(\mathbf{r}, \mathbf{r}', \omega) \int d^3 r'' f_{Hxc}(\mathbf{r}', \mathbf{r}'', \omega) n_1(\mathbf{r}'', \omega) \\ &= \frac{2\omega_{21}}{\omega^2 - \omega_{21}^2} \int d^3 r' \varphi_1(\mathbf{r}) \varphi_2(\mathbf{r}) \varphi_1(\mathbf{r}') \varphi_2(\mathbf{r}') \int d^3 r'' f_{Hxc}(\mathbf{r}', \mathbf{r}'', \omega) n_1(\mathbf{r}'', \omega) \end{aligned}$$

Multiply both sides with  $\varphi_1(\mathbf{r}''') \varphi_2(\mathbf{r}''') f_{Hxc}(\mathbf{r}''', \mathbf{r}, \omega)$  and integrate over r. Then we can cancel terms left and right, and

$$1 = \frac{2\omega_{21}}{\omega^2 - \omega_{21}^2} \int d^3 r \int d^3 r' \varphi_1(\mathbf{r}) \varphi_2(\mathbf{r}) f_{Hxc}(\mathbf{r}, \mathbf{r}', \omega) \varphi_1(\mathbf{r}') \varphi_2(\mathbf{r}')$$

$$\omega^2 = \omega_{21}^2 + 2\omega_{21} \int d^3 r \int d^3 r' \varphi_1(\mathbf{r}) \varphi_2(\mathbf{r}) f_{Hxc}(\mathbf{r}, \mathbf{r}', \omega) \varphi_1(\mathbf{r}') \varphi_2(\mathbf{r}')$$

$$\omega^2 = \omega_{21}^2 + 2\omega_{21} \langle 12 | f_{Hxc} | 12 \rangle$$

TDDFT correction to  
Kohn-Sham excitation

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## The Casida formalism for excitation energies

Excitation energies follow from eigenvalue problem (Casida 1995):

$$\begin{pmatrix} \mathbf{A} & \mathbf{K} \\ \mathbf{K}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \Omega \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}$$

$$A_{ia\sigma, i'a'\sigma'} = \delta_{ii'} \delta_{aa'} \delta_{\sigma\sigma'} (\varepsilon_{a\sigma} - \varepsilon_{i\sigma}) + K_{ia\sigma, i'a'\sigma'}$$

$$K_{ia\sigma, i'a'\sigma'} = \int d^3r \int d^3r' \phi_{i\sigma}^*(\mathbf{r}) \phi_{a\sigma}(\mathbf{r}) \left[ \frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{xc, \sigma\sigma'}(\mathbf{r}, \mathbf{r}', \omega) \right] \phi_{i'\sigma'}(\mathbf{r}') \phi_{a'\sigma'}(\mathbf{r}')$$

For real orbitals and frequency-independent xc kernel, can rewrite this as

$$\sum_{i'a'\sigma'} \left[ \delta_{ii'} \delta_{aa'} \delta_{\sigma\sigma'} \omega_{ai\sigma}^2 + 2\sqrt{\omega_{ai\sigma} \omega_{a'i'\sigma'}} K_{ia\sigma, i'a'\sigma'} \right] Z_{i'a'\sigma'} = \Omega^2 Z_{i'a'\sigma'}$$

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## The Casida formalism for excitation energies

The Casida formalism gives, in principle, the exact excitation energies and oscillator strengths. In practice, three approximations are required:

- ▶ KS ground state with approximate xc potential
- ▶ The infinite-dimensional matrix needs to be truncated
- ▶ Approximate xc kernel (usually adiabatic):

$$f_{xc}^{adia}(\mathbf{r}, \mathbf{r}') = \frac{\delta V_{xc}^{stat}(\mathbf{r})}{\delta n(\mathbf{r}')}$$

**advantage:** can use any xc functional from static DFT ("plug and play")

**disadvantage:** no frequency dependence, no memory

→ missing physics (see later)



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## How it works: atomic excitation energies

### LDA + ALDA lowest excitations

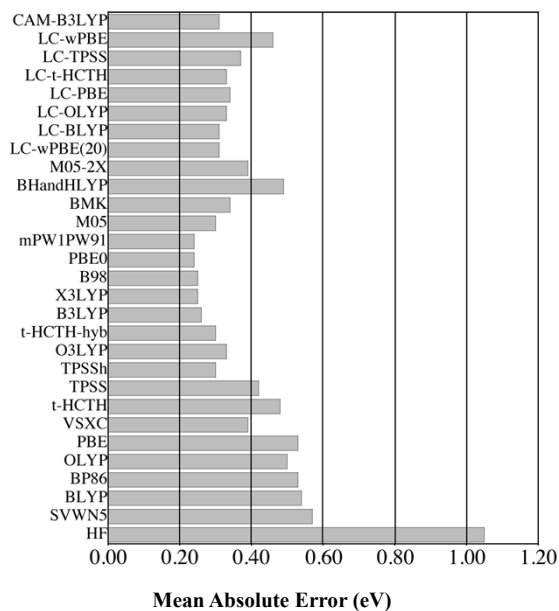
Atom	Exp.	full matrix	SMA	SPA	$\omega^{\text{KS}}$
Be	5.28	4.94	5.07	5.43	3.50
Mg	4.34	4.34	4.56	4.76	3.39
Ca	2.94	3.22	3.36	3.56	2.39
Sr	2.69	2.96	3.10	3.28	2.22
Zn	5.79	5.71	6.30	6.54	4.79
Cd	5.41	5.10	5.60	5.86	4.12

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

50



## A comparison of xc functionals



Study of various functionals  
over a set of ~ 500 organic  
compounds, 700 excited  
singlet states

D. Jacquemin et al.,  
J. Chem. Theor. Comput.  
**5**, 2420 (2009)

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## Excited states with TDDFT: general trends

- Energies typically accurate within 0.3-0.4 eV
- Bonds to within about 1%
- Dipoles good to about 5%
- Vibrational frequencies good to 5%
- Cost scales as  $N^2$ - $N^3$ , vs  $N^5$  for wavefunction methods of comparable accuracy (eg CCSD, CASSCF)
- Available now in many electronic structure codes

### challenges/open issues:

- complex excitations (multiple, charge-transfer)
- optical response/excitons in bulk insulators

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## Single versus double excitations

$$n_1(\mathbf{r}, \omega) = \int d^3 r' \chi_s(\mathbf{r}, \mathbf{r}', \omega) \int d^3 r'' \left[ \frac{1}{|\mathbf{r}' - \mathbf{r}''|} + f_{xc}(\mathbf{r}', \mathbf{r}'', \omega) \right] n_1(\mathbf{r}'', \omega)$$

Has poles at KS single excitations. The exact response function has more poles (single, double and multiple excitations).

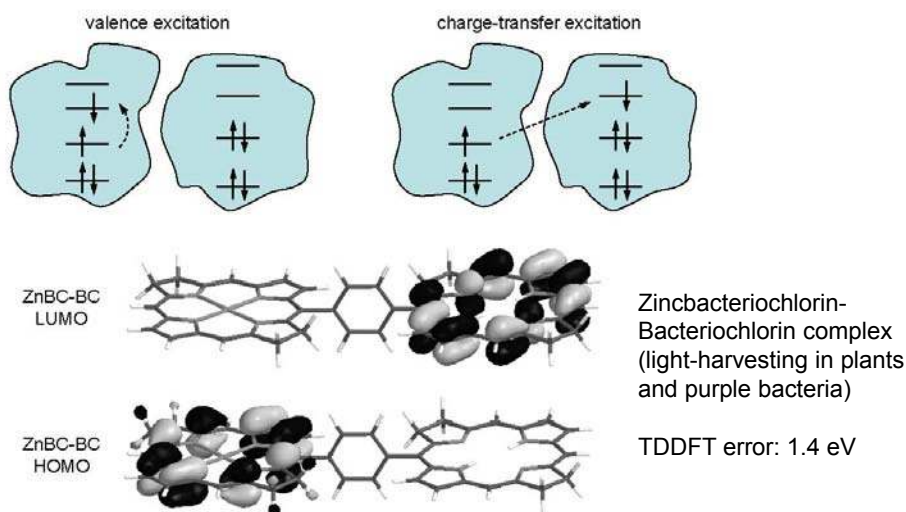
Gives dynamical corrections to the KS excitation spectrum. Shifts the single KS poles to the correct positions, and creates new poles at double and multiple excitations.

- Adiabatic approximation ( $f_{xc}$  does not depend on  $\omega$ ): only single excitations!
- $\omega$ -dependence of  $f_{xc}$  will generate additional solutions of the Casida equations, which corresponds to double/multiple excitations.
- Unfortunately, nonadiabatic approximations are not easy to find.

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## Charge-transfer excitations



TDDFT predicts CT states energetically well below local fluorescing states. Predicts CT quenching of the fluorescence. **Not observed!**  
*Dreuw and Head-Gordon, JACS (2004)*

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## Charge-transfer excitations: large separation

$$\Omega_{ct}^{exact} = I_d - A_a - \frac{1}{R}$$

(ionization potential of donor minus electron affinity of acceptor plus Coulomb energy of the charged fragments)

What do we get in TDDFT? Let's try the single-pole approximation:

$$\Omega_{ct}^{SPA} = \varepsilon_L^a - \varepsilon_H^d + 2 \int d^2r \int d^3r' \varphi_L^a(\mathbf{r}) \varphi_H^d(\mathbf{r}) f_{Hxc}(\mathbf{r}, \mathbf{r}', \omega) \varphi_L^a(\mathbf{r}') \varphi_H^d(\mathbf{r}')$$

The highest occupied orbital of the donor and the lowest unoccupied orbital of the acceptor have exponentially vanishing overlap!

$$\Omega_{ct}^{TDDFT} \approx \varepsilon_L^a - \varepsilon_H^d$$

For all (semi)local xc approximations, TDDFT significantly underestimates charge-transfer energies!

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## Charge-transfer excitations: exchange

$$\Omega_{ct}^{TDHF} = \varepsilon_L^{a,HF} - \varepsilon_H^{d,HF} - \int d^2r \int d^3r' \frac{\varphi_L^a(\mathbf{r}) \varphi_L^a(\mathbf{r}) \varphi_H^d(\mathbf{r}') \varphi_H^d(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$\rightarrow \varepsilon_L^{a,HF} - \varepsilon_H^{d,HF} - \frac{1}{R} \quad \text{and use Koopmans theorem!}$$

TDHF reproduces charge-transfer energies correctly. Therefore, hybrid functionals (such as B3LYP) will give some improvement over LDA and GGA.

Even better are the so-called **range-separated hybrids**:

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \frac{f(\mu|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} + \frac{1 - f(\mu|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} \quad f(\mu x) = e^{-\mu x}, f(\mu x) = \text{erfc}(\mu x)$$

$$E_{xc} = E_x^{SR-GGA} + E_x^{LR-HF} + E_c^{GGA}$$

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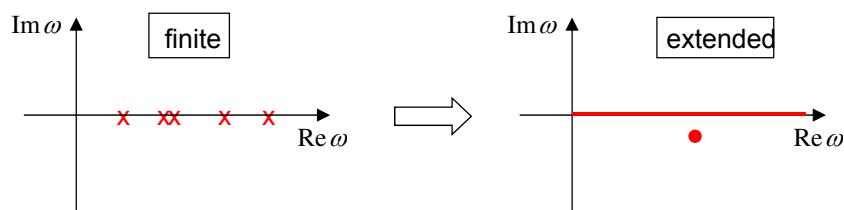


## Excitations in finite and extended systems

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

$\underbrace{\hspace{10em}}_{\Omega_j}$

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



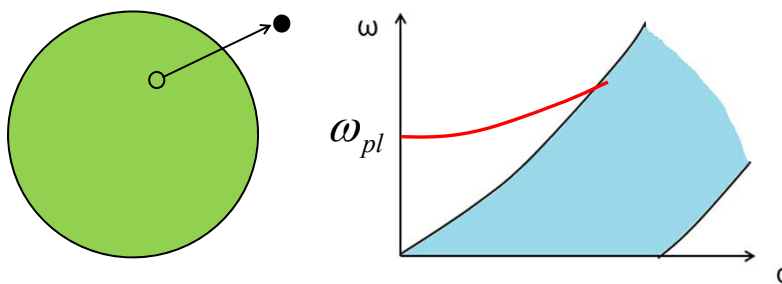
- ▶ Discrete single-particle excitations merge into a continuum (branch cut in frequency plane)
- ▶ New types of collective excitations appear off the real axis (finite lifetimes)

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## Metals: particle-hole continuum and plasmons

In ideal metals, all single-particle states inside the **Fermi sphere** are filled. A **particle-hole excitation** connects an occupied single-particle state inside the sphere with an empty state outside.



From linear response theory, one can show that the plasmon dispersion goes as

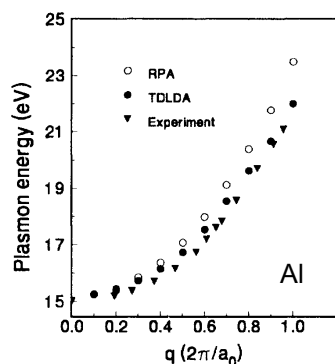
$$\Omega(q) = \omega_{pl} + \alpha q^2 + \dots$$

$$\omega_{pl} = \sqrt{\frac{4\pi n e^2}{m}}$$

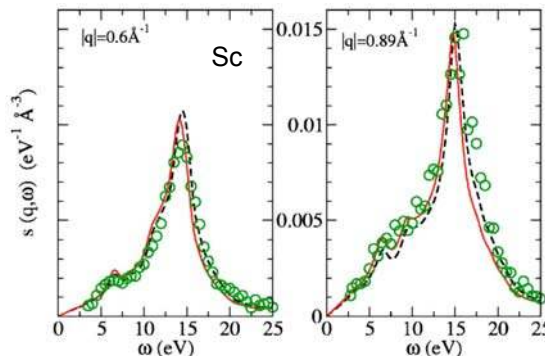
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## Plasmon excitations in bulk metals



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



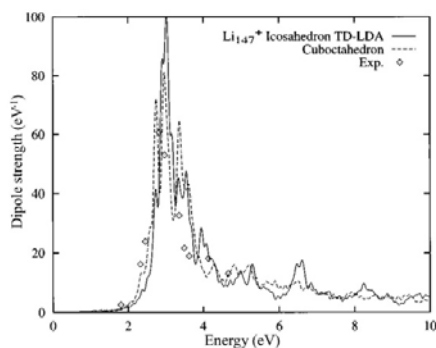
Gurtubay et al., PRB **72**, 125114 (2005)

- In general, excitations in (simple) metals very well described by ALDA.
- Time-dependent Hartree (=RPA) already gives the dominant contribution
- $f_{xc}$  typically gives some (minor) corrections (damping!)
- This is also the case for 2DEGs in doped semiconductor heterostructures

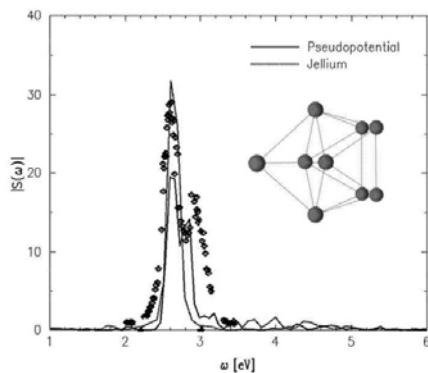
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## Plasmon excitations in metal clusters



Yabana and Bertsch (1996)



Calvayrac et al. (2000)

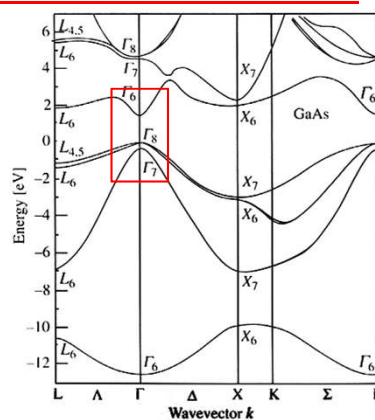
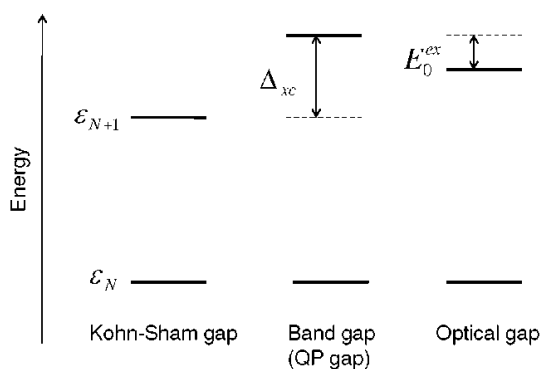
Surface plasmons ("Mie plasmon") in metal clusters are very well reproduced within ALDA.

**Plasmonics:** mainly using classical electrodynamics, not quantum response

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## Insulators: three different gaps



Band gap:  $E_g = E_{g,KS} + \Delta_{xc}$

Optical gap:  $E_g^{optical} = E_g - E_0^{exciton}$

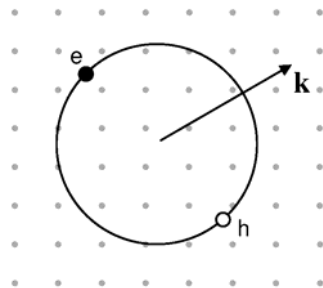
The Kohn-Sham gap approximates the optical gap (neutral excitation), not the band gap!

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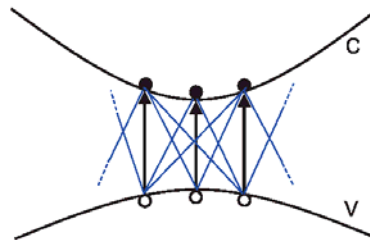
## Elementary view of Excitons

Real space:



Mott-Wannier exciton:  
weakly bound, delocalized  
over many lattice constants

Reciprocal space:

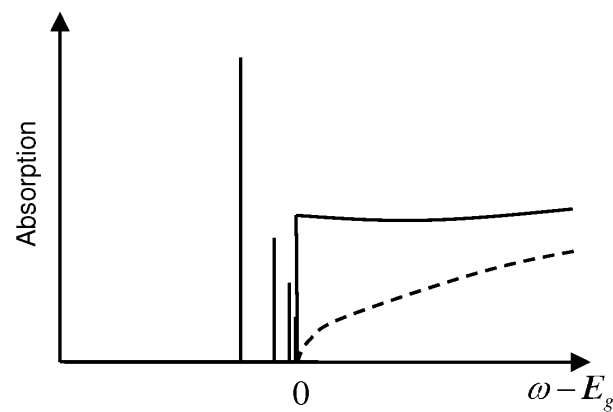


An exciton is a collective  
interband excitation:  
single-particle excitations are  
coupled by Coulomb interaction

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## Excitonic features in the absorption spectrum

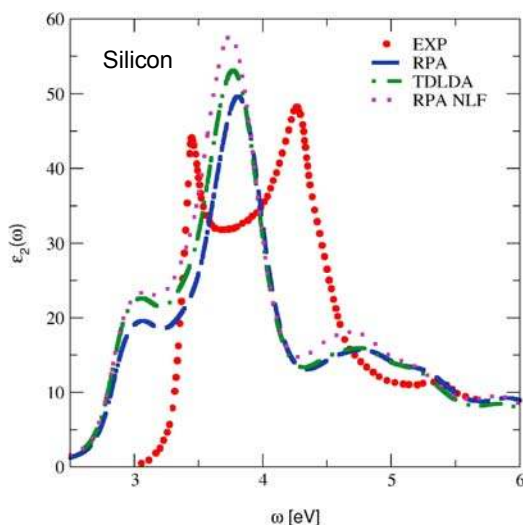


- Sharp peaks below the onset of the single-particle optical gap
- Redistribution of oscillator strength: enhanced absorption close to the onset of the continuum

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## Optical absorption of insulators



RPA and ALDA both bad!

- absorption edge red shifted (electron self-interaction)
- first excitonic peak missing (electron-hole interaction)

**Why does 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)

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## Linear response in periodic systems

$$\chi_{GG'}(\mathbf{k}, \omega) = \chi_{sGG'}(\mathbf{k}, \omega) + \sum_{G_1 G_2} \chi_{sGG_1}(\mathbf{k}, \omega) \times \{V_{G_1}(\mathbf{k})\delta_{G_1 G_2} + f_{xcG_1 G_2}(\mathbf{k}, \omega)\} \chi_{G_2 G'}(\mathbf{k}, \omega)$$

Optical properties are determined by the macroscopic dielectric function:

$$\epsilon_{mac}(\omega) = \tilde{n}^2 \quad (\text{Complex index of refraction})$$

For cubic symmetry, one can prove that

$$\epsilon_{mac}(\omega) = \lim_{k \rightarrow 0} \left[ \epsilon_{GG'}^{-1}(\mathbf{k}, \omega) \Big|_{\substack{\mathbf{G}=0 \\ \mathbf{G}'=0}} \right]^{-1}$$

Therefore, one needs the inverse dielectric matrix:

$$\epsilon_{GG'}^{-1}(\mathbf{k}, \omega) = \delta_{GG'} + V_G(\mathbf{k}) \chi_{GG'}(\mathbf{k}, \omega)$$



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## The xc kernel for periodic systems

$$f_{Hxc}(\mathbf{r}, \mathbf{r}', \omega) = \sum_{\mathbf{q} \in \text{FBZ}} \sum_{\mathbf{G}, \mathbf{G}'} e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}} f_{Hxc, \mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega) e^{-i(\mathbf{q}+\mathbf{G}')\mathbf{r}'}$$

TDDFT requires the following matrix elements as input:

$$K_{ia, i'a'}^{\mathbf{G}_0 \mathbf{G}'_0} = \sum_{\mathbf{q} \in \text{FBZ}} \sum_{\mathbf{G}\mathbf{G}'} \langle i\mathbf{k}_i | e^{i(\mathbf{q}+\mathbf{G})\mathbf{r}} | a\mathbf{k}_a \rangle f_{Hxc, \mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega) \langle a'\mathbf{k}_{a'} | e^{-i(\mathbf{q}+\mathbf{G}')\mathbf{r}'} | i'\mathbf{k}_{i'} \rangle \\ \times \delta_{\mathbf{k}_a - \mathbf{k}_i + \mathbf{q}, \mathbf{G}_0} \delta_{\mathbf{k}_{a'} - \mathbf{k}_{i'} + \mathbf{q}, \mathbf{G}'_0}$$

**Most important: long-range ( $\mathbf{q} \rightarrow 0$ ) limit of “head” ( $\mathbf{G} = \mathbf{G}' = 0$ ):**

$$\langle i\mathbf{k}_i | e^{i\mathbf{q}\mathbf{r}} | a\mathbf{k}_a \rangle \xrightarrow{\mathbf{q} \rightarrow 0} \mathbf{q} \quad f_{xc, 00}^{exact}(\mathbf{q}, \omega) \xrightarrow{\mathbf{q} \rightarrow 0} \frac{1}{q^2}$$

**but**  $f_{xc, 00}^{ALDA}(\mathbf{q}, \omega) \xrightarrow{\mathbf{q} \rightarrow 0} \text{const.}$  **Therefore, no excitons in ALDA!**

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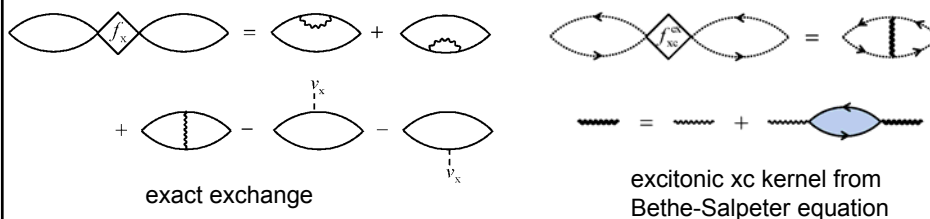
## Long-range xc kernels for solids

- **LRC** (long-range corrected) kernel (with fitting parameter  $\alpha$ ):  $f_{xc, \mathbf{G}\mathbf{G}'}^{LRC}(\mathbf{q}) = -\frac{\alpha}{|\mathbf{q} + \mathbf{G}|^2} \delta_{\mathbf{G}\mathbf{G}'}$

- **“bootstrap”** kernel (S. Sharma et al., PRL **107**, 186401 (2011))

$$f_{xc, \mathbf{G}\mathbf{G}'}^{boot}(\mathbf{q}, \omega) = \frac{\varepsilon_{\mathbf{G}\mathbf{G}'}^{-1}(\mathbf{q}, 0)}{\chi_{s00}(\mathbf{q}, 0)}$$

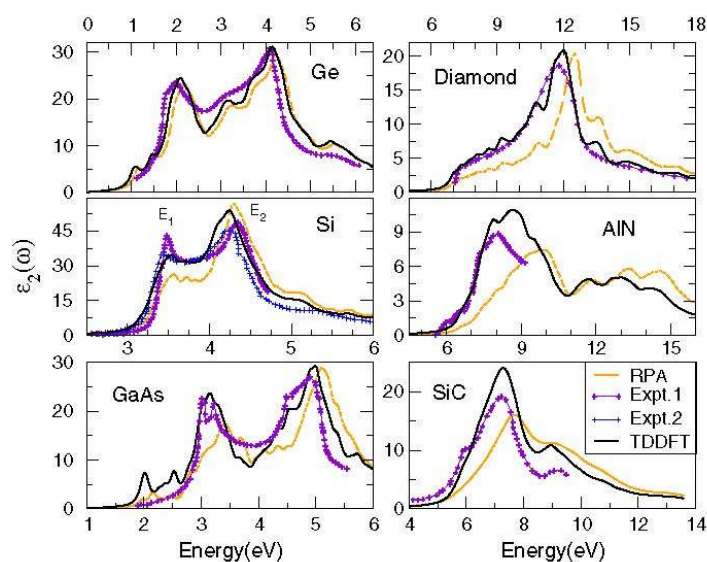
- **Functionals from many-body theory:** (requires matrix inversion)



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## Excitons with TDDFT: “bootstrap” xc kernel



S. Sharma et al., PRL **107**, 186401 (2011)

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## Excitons with TDDFT: which xc functionals to use?

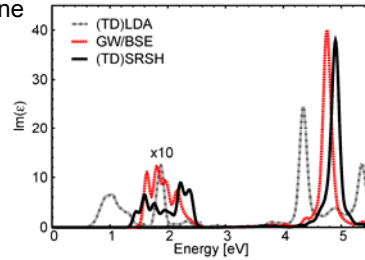
- ▶ Local functionals (ALDA/GGA) don't work
- ▶ **Nanoquanta kernel**: accurate but expensive  
Reining, Olevano, Rubio, Onida, PRL **88**, 066404 (2002)
- ▶ **Long-range corrected (LRC) kernel**: simple but ad-hoc  
Botti *et al.*, PRB **69**, 155112 (2004)
- ▶ **Bootstrap kernel**: mixed success  
Sharma, Dewhurst, Sanna and Gross, PRL **107**, 186401 (2011)
- ▶ **Jellium with a gap**: mixed success  
Trevisanutto *et al.*, PRB **87**, 205143 (2013)
- ▶ **Hybrid functionals, meta-GGAs**: few results for optical properties
  - B3LYP**: Bernasconi *et al.* PRB **83**, 195325 (2011)
  - HSE**: Paier, Marsman and Kresse, PRB **78**, 121201 (2008)
  - VS98/TPSS**: Nazarov and Vignale, PRL **107**, 216401 (2011)
  - Range separated**: Refaely-Abramson *et al.*, arXiv:1505.01602v1

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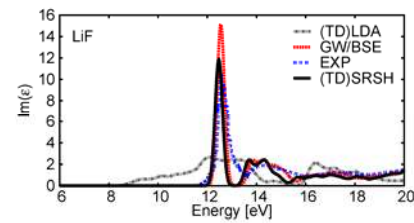
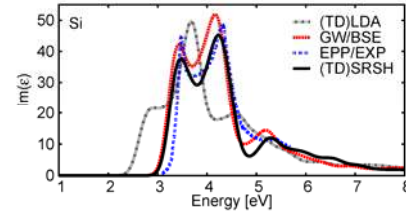


## Optical spectra with range-separated hybrid

pentacene



S. Refaely-Abramson, M. Jain,  
S. Sharifzadeh, J.B. Neaton,  
and L. Kronik, arXiv1505.01602v1  
(2015)



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## Direct calculation of exciton binding energies

$$\sum_{(mnk')} \left[ \delta_{ik,mk'} \delta_{jk,nk'} (\varepsilon_{jk} - \varepsilon_{ik}) + F_{Hxc}^{(ijk)(mnk')} \right] \rho_{\lambda}^{(mnk')} = \omega_{\lambda} \rho_{\lambda}^{(ijk)}$$

TDDFT coupling matrix:

$$F_{xc}^{(ijk)(mnk')} = \frac{2}{V_{crys}} \sum_{GG'} f_{xc,GG'}(\mathbf{q}=0) \langle j\mathbf{k} | e^{i\mathbf{G}\cdot\mathbf{r}} | i\mathbf{k} \rangle \langle m\mathbf{k}' | e^{-i\mathbf{G}'\cdot\mathbf{r}} | n\mathbf{k}' \rangle$$

xc kernel

BSE coupling matrix:

$$F_{xc}^{(ijk)(mnk')} = \frac{1}{V_{crys}} \sum_{GG'} g_{GG'}(\mathbf{q}) \langle j\mathbf{k} | e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | n\mathbf{k}' \rangle \langle m\mathbf{k}' | e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} | i\mathbf{k} \rangle \delta_{\mathbf{q},\mathbf{k}-\mathbf{k}'}$$

screened Coulomb interaction

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## Screened exact exchange (SXX)

**BSE:**  $g_{GG'}(\mathbf{q}) = -4\pi \frac{\varepsilon_{GG'}^{-1}(\mathbf{q}, \omega = 0)}{|\mathbf{q} + \mathbf{G}'|^2}$  ← full dielectric matrix

**TDHF:**  $g_{GG'}(\mathbf{q}) = -4\pi \frac{1}{|\mathbf{q} + \mathbf{G}'|^2} \delta_{GG'}$  unscreened

**SXX:**  $g_{GG'}(\mathbf{q}) = -4\pi \frac{\gamma}{|\mathbf{q} + \mathbf{G}'|^2} \delta_{GG'}$  simple screening parameter

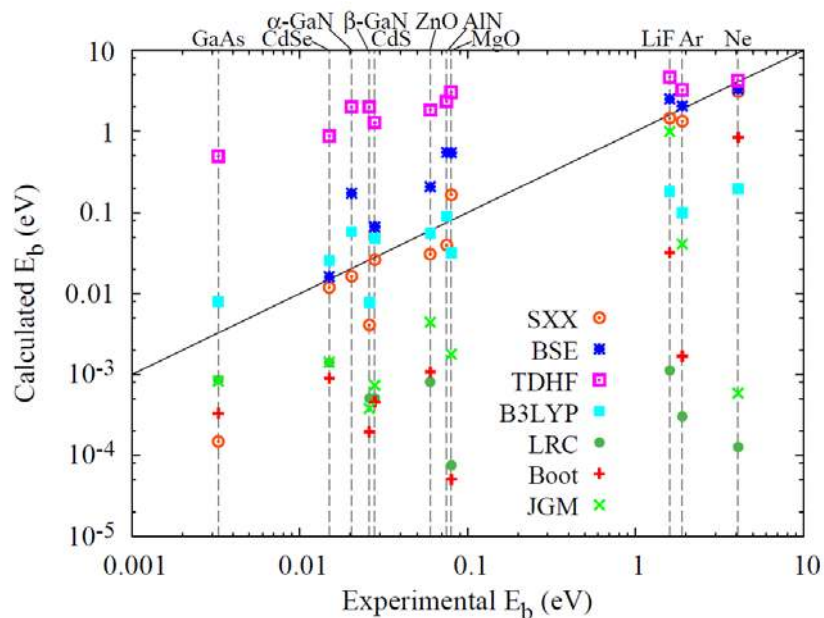
$\gamma = \varepsilon_{00}^{-1}(0,0)$  Calculated with RPA

Z.-h. Yang, F. Sottile, and C.A. Ullrich, PRB **92**, 035202 (2015)

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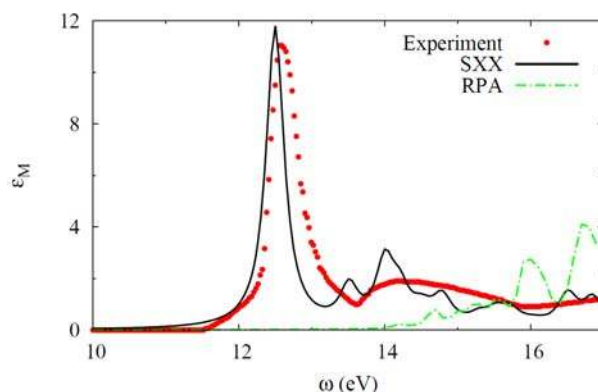
## Exciton binding energies



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## Absorption spectrum of LiF



- ▶ good oscillator strength
- ▶ second excitonic peak

Z.-h. Yang, Y. Li, and C.A. Ullrich, JCP **137**, 014513 (2012)

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## Extended systems - summary

- ▶ 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
  - Excitonic binding due to attractive electron-hole interactions, which require long-range contribution to  $f_{xc}$
  - At present, the full (but expensive) Bethe-Salpeter equation gives most accurate optical spectra in inorganic and organic materials (extended or nanoscale), but TDDFT is catching up.
  - Several long-range XC kernels have become available. Hybrid functionals seem most promising for excitons.

C.A. Ullrich and Z.-h. Yang, Topics in Current Chem. **368** (2015)

75

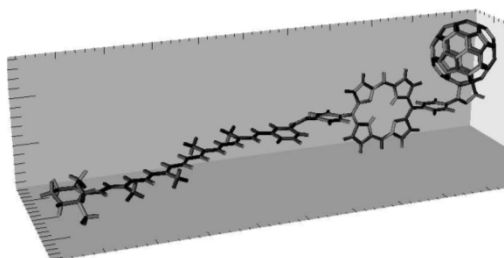


## The future of TDDFT: biological applications

(TD)DFT can handle big systems ( $10^3$ — $10^6$  atoms).

Many applications to large organic systems (DNA, light-harvesting complexes, organic solar cells) will become possible.

Charge-transfer excitations and van der Waals interactions can be treated from first principles.



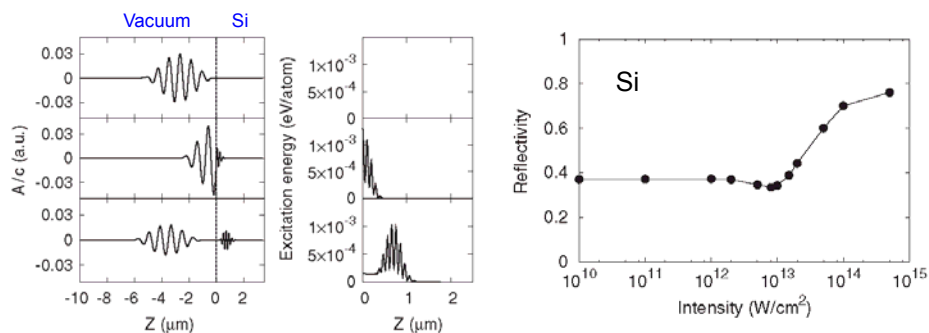
N. Spallanzani, C. A. Rozzi, D. Varsano, T. Baruah, M. R. Pederson, F. Manghi, and A. Rubio, J. Phys. Chem. (2009)

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## The future of TDDFT: materials science

K. Yabana, S. Sugiyama, Y. Shinohara, T. Otobe, and G.F. Bertsch, PRB **85**, 045134 (2012)



- Combined solution of TDKS and Maxwell's equations
- Strong fields acting on crystalline solids: dielectric breakdown, coherent phonons, hot carrier generation
- Coupling of electron and nuclear dynamics allows description of relaxation and dissipation (TDDFT + Molecular Dynamics)

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## The future of TDDFT: open formal problems

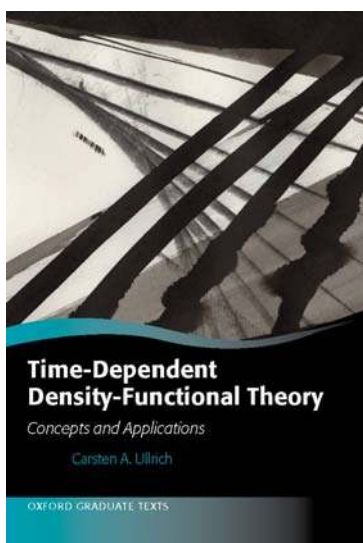
- ▶ Development of **nonadabatic xc functionals** (needed for double excitations, dissipation, etc.)
- ▶ TDDFT for **open systems**: nanoscale transport in dissipative environments. Some theory exists, but applications so far restricted to simple model systems
- ▶ **Strongly correlated systems**. Mott-Hubbard insulators, Kondo effect, Coulomb blockade. Requires subtle xc effects (discontinuity upon change of particle number)
- ▶ **Formal extensions**: finite temperature, relativistic effects...

**TDDFT will remain an exciting field of research for many years to come!**

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## Literature



Time-dependent Density-Functional Theory: Concepts and Applications (Oxford University Press 2012)

“A brief compendium of TDDFT”  
Carsten A. Ullrich and Zeng-hui Yang  
arXiv:1305.1388  
(Brazilian Journal of Physics **44**, 154 (2014))

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