# *TDDFT for non linear phenomena in solids and nanostructures: fundamentals and applications*


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# OUTLINE

Introduction: TDDFT

Four linked concepts:

* Molecular dissociation: bumps in Vxc
* Electron many-body tunneling
* Rabi Oscillations population analysis
* Photochemistry...

Some illustrative applications (recent work)

- Monitor excitations: Time and energy resolved spectroscopies
- Correlations: H2 and Mott insulators (how do they look in TD-DFT)
- Optimal control theory: High-harmonic generation

**Publications:**


Quantum coherence controls the charge separation in a prototypical artificial light harvesting system, C. A. Rozzi, S. M. Falke, N. Spallanzani, AR, E. Molinari, D. Brida, M. Maiuri, G. Cerullo, H. Schramm, J. Christoffers, C. Lienau Nature Communications (2013)

Simulating pump-probe photo-electron and absorption spectroscopy on the attosecond time-scale with time-dependent density-functional theory, U. De Giovannini, G. Brunetto, A. Castro, J. Walkenhorst, A.R, Chemphyschem (2013)

Universal Dynamical Steps in the Exact Time-Dependent Exchange-Correlation Potential
Peter Elliott, Johanna I. Fuks, Angel Rubio, Neepa T. Maitra, Physical Review Letters 109, 266404 (2012)

Fundamentals of Time-Resolved Charge-Transfer in Time-Dependent Density Functional Theory,
Johanna I. Fuks, Peter Elliott, AR, Neepa T. Maitra Journal Of Physical Chemistry Letters (2013)

# Beyond linear response: Real-time dynamics

E.g.

High-harmonic generation

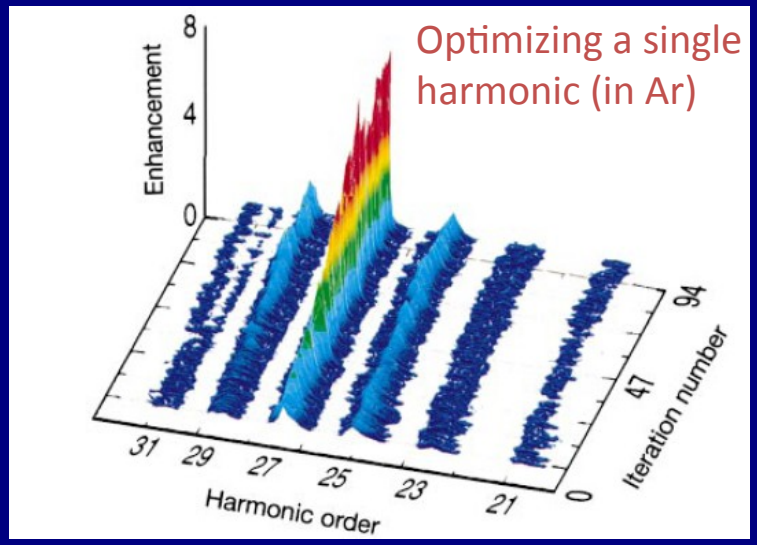
Multiple-ionization

Photo-dissociation

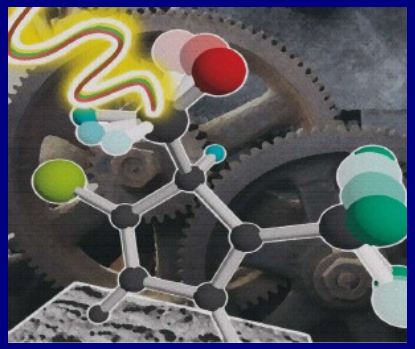
Photo-isomerization

Enhanced ionization

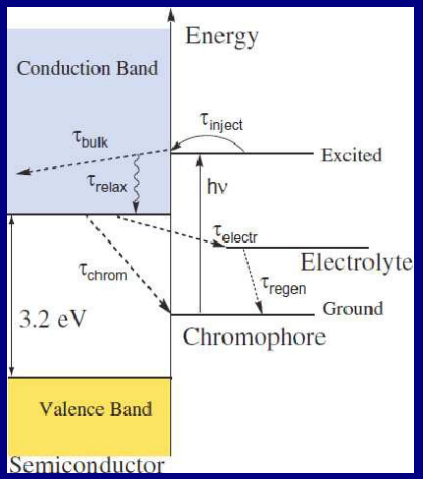
Electronic quantum control




*Murnane & Kapteyn et al, Nature 2000*



*Light-driven chiral molecular motors, Yamaki, Nakayama, Hoki, Kono, Fujimura, Phys. Chem. Chem. Phys.* ***11****, 1649 (2009)*




*Dye-Sensitized Solar Cell*

***But how well do the TDDFT approximations work ?***

# *Theoretical framework: DFT&TDDFT*

## *DFT (static- ground state)*

- The ground state energy of a many body system is a unique functional of the density i.e, can be inverted Hohenberg-Kohn (1964)

$$n(r)=n[\Psi]=\left\langle \sum_i \delta(r-r_i)\right\rangle$$

$$\Psi(r_{1,}r_{2,.}\ldots,r_N)=\Psi[n(r)] \rightarrow E[R_{ions}]=min_n\left\langle \Psi H_e \Psi\right\rangle \equiv min_n E[n]$$

- The functional has a minimum at the 'equilibrium' density

**DFT Success "~chemical accuracy"**

# Time Dependent Density Functional Theory (Runge and Gross 1984)

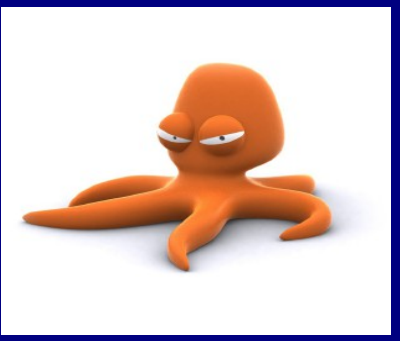
All observables are functionals of the TD density

One-to-one correspondence between the time-dependent density and the external potential, v(r,t) <------> ρ(r,t)

$$i\hbar\frac{d}{dt}\Phi = H\Phi \quad \rightarrow \quad i\hbar\frac{d}{dt}\psi_i = H_{KS}\left[\{\psi_j\}\right]\psi_i, \quad i=1,\cdots N$$

$$H_{KS} = \frac{\hbar^2}{2\mathrm{m}}\left(i\nabla - \frac{e}{c\hbar}\left(A + A_{xc}\right)\right)^2 + V_{external} + V_{hartree} + V_{exchange} + V_{correlation}$$

?



*Linear and non linear phenomena accessible*

*Octopus Code http://www.tddft.org*

*Time-Dependent Density Functional Theory, Lecture Notes in Physics, Springer Vols. 837, 706 (2012, 2006)*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## ..... and where we are?

Theoretical framework: DFT&TDDFT and MBPT

- Optical and magnetic responses, Dichroism, EELS, IXS, linear and nonlinear properties, .....
  Solids, nanostructures, biomolecules,.....
- **Correlations** ( "Mott insulators", e.g. H-chain);

*Open Question: develop accurate XC functionals*

# Some illustrative applications (recent work)

- Monitor excitations: Time and energy resolved spectroscopies
- Excite state dynamics for energy store/harvesting applications

  *Organic photovoltaics: triads "carotene-porphyrine-$C_{60}$"*
- Optimal control theory: High-harmonic generation

# *Photoelectron spectroscopy: spatial and energy resolved*

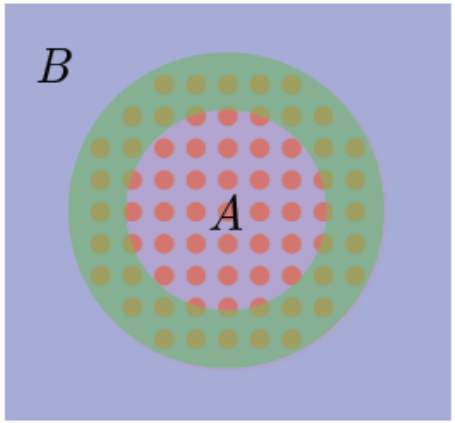
## Evolution scheme

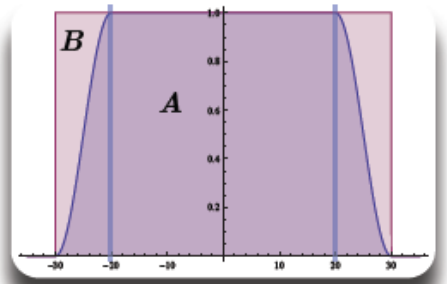
For every orbital

$$\varphi(\mathbf{r},t) = M(\mathbf{r})\varphi(\mathbf{r},t) + (1 - M(\mathbf{r}))\varphi(\mathbf{r},t)$$

$\varphi_A(\mathbf{r},t)$ $\varphi_B(\mathbf{r},t)$

$M(\mathbf{r}) =$

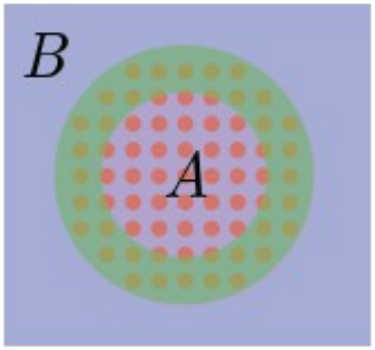



### Full mask method (FMM)

$$\begin{cases} \varphi_A(r,t') = M(r)U(t,t')(\varphi_A(r,t) + \int \mathrm{d}p\, \tilde{\varphi}_B(p,t)e^{ipr}) \\ \tilde{\varphi}_B(p,t') = \int \mathrm{d}r\, (1 - M(r))U(t,t')(\varphi_A(r,t) + \varphi_B(r,t))e^{-ipr} \end{cases}$$

U. De Giovannini, D. Varsano, H. Appel, M. A. L. Marques,, E.K.U. Gross and and A. Rubio (2012)




# The full mask method (FMM)

$$\begin{cases} \varphi_{A,i}(\mathbf{r},t') = \eta_{A,i}(\mathbf{r},t') + \eta_{B,i}(\mathbf{r},t') \\ \tilde{\varphi}_{B,i}(\mathbf{p},t') = \tilde{\xi}_{A,i}(\mathbf{p},t') + \tilde{\xi}_{B,i}(\mathbf{p},t') \end{cases}$$

$$\eta_{A,i}(\mathbf{r},t') = M(\mathbf{r})U(t',t)\varphi_{A,i}(\mathbf{r},t)$$

$$\eta_{B,i}(\mathbf{r},t') = M(\mathbf{r})\int \frac{\mathrm{d}\mathbf{p}\, e^{i\mathbf{p}\cdot\mathbf{r}}}{(2\pi)^{\frac{d}{2}}} U_V(t',t)\tilde{\varphi}_{B,i}(\mathbf{p},t)$$

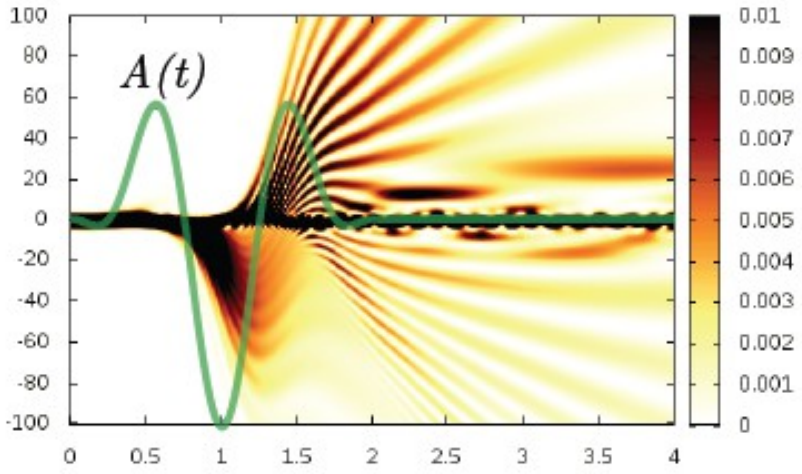
$$\tilde{\xi}_{A,i}(\mathbf{p},t') = \int \frac{\mathrm{d}\mathbf{r}\, e^{-i\mathbf{p}\cdot\mathbf{r}}}{(2\pi)^{\frac{d}{2}}} (1-M(\mathbf{r}))U(t',t)\varphi_{A,i}(\mathbf{r},t)$$

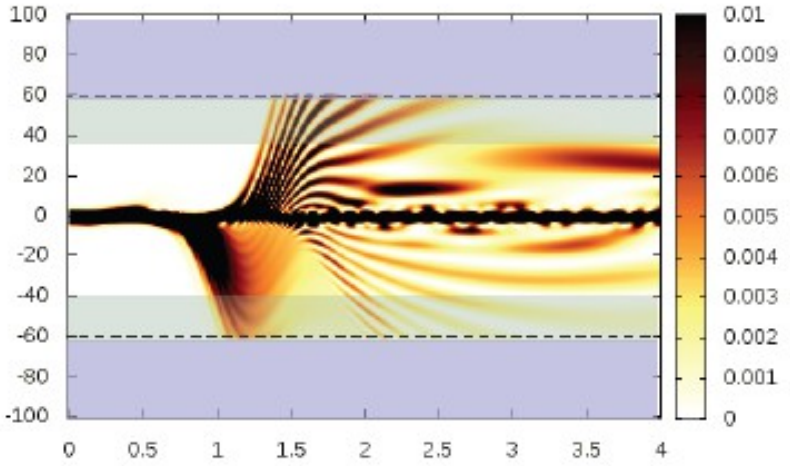
$$\tilde{\xi}_{B,i}(\mathbf{p},t') = U_V(t',t)\tilde{\varphi}_{B,i}(\mathbf{p},t) - \int \frac{\mathrm{d}\mathbf{r}\, e^{-i\mathbf{p}\cdot\mathbf{r}}}{(2\pi)^{\frac{d}{2}}} \eta_{B,i}(\mathbf{r},t')$$

Can evaluate with discrete FT

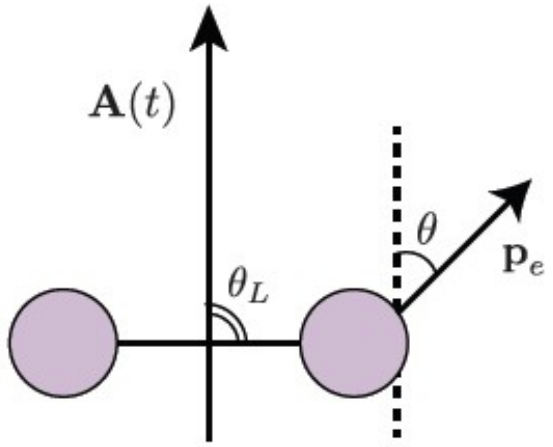
localized in momentum

localized in space



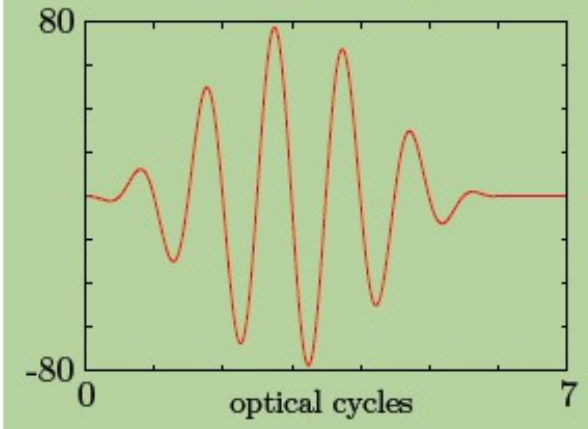
# N2 few-cycles infrared pulse

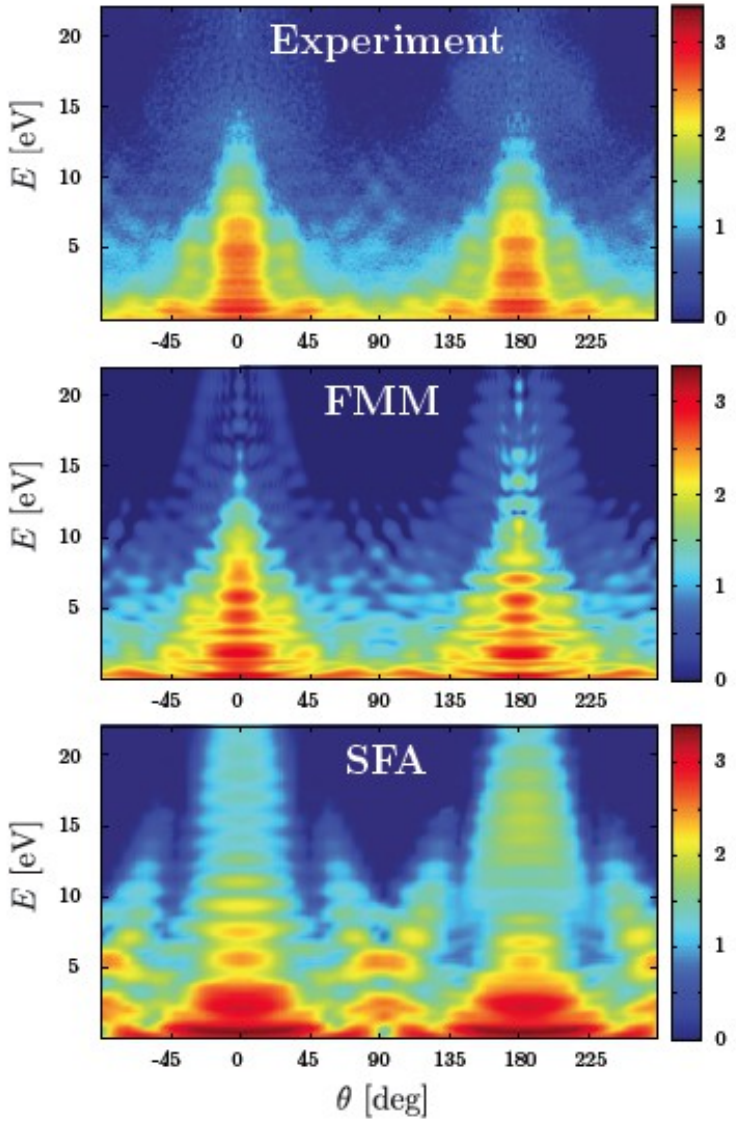



**Laser Pulse**

$\lambda = 750$ nm

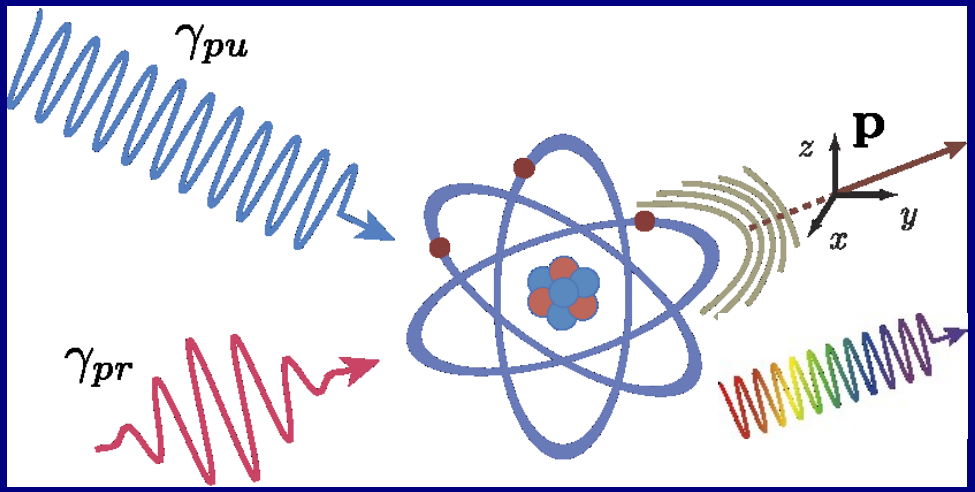
$I = 4.3 \times 10^{13}$ W/cm$^2$




A. Gazibegović-Busuladžić, E. Hasović, M. Busuladžić, D. Milosevic, F. Kelkensberg, W. Siu, M. Vrakking, F. Lepine, G. Sansone, M. Nisoli, I. Znakovskaya, and M. Kling, *Phys. Rev. A* **84**, (2011).

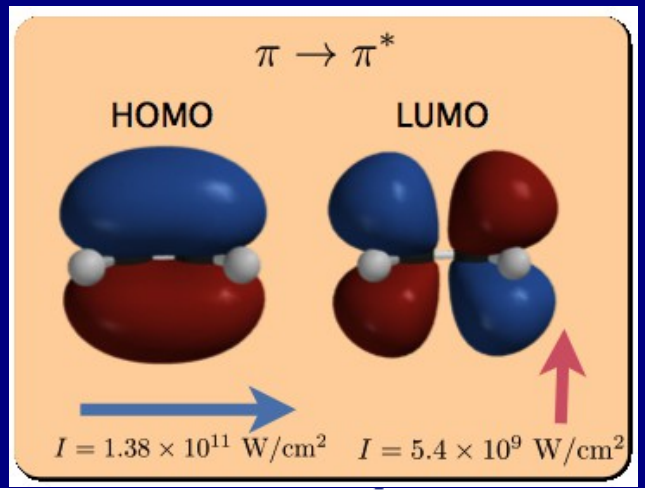
# Transient Absorption and Photoelectron Spectroscopies

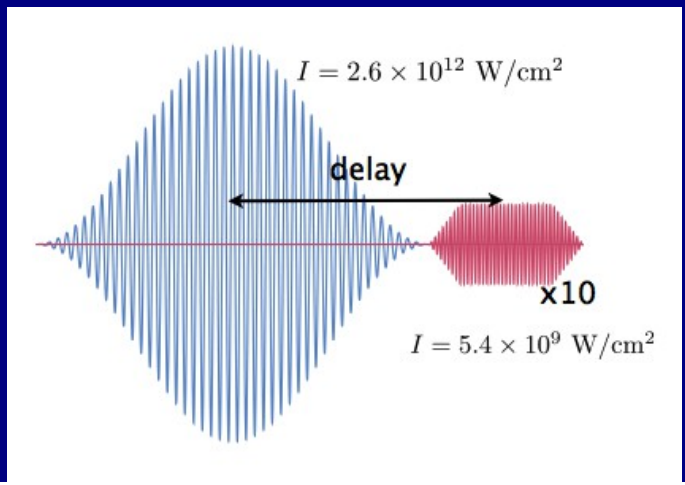


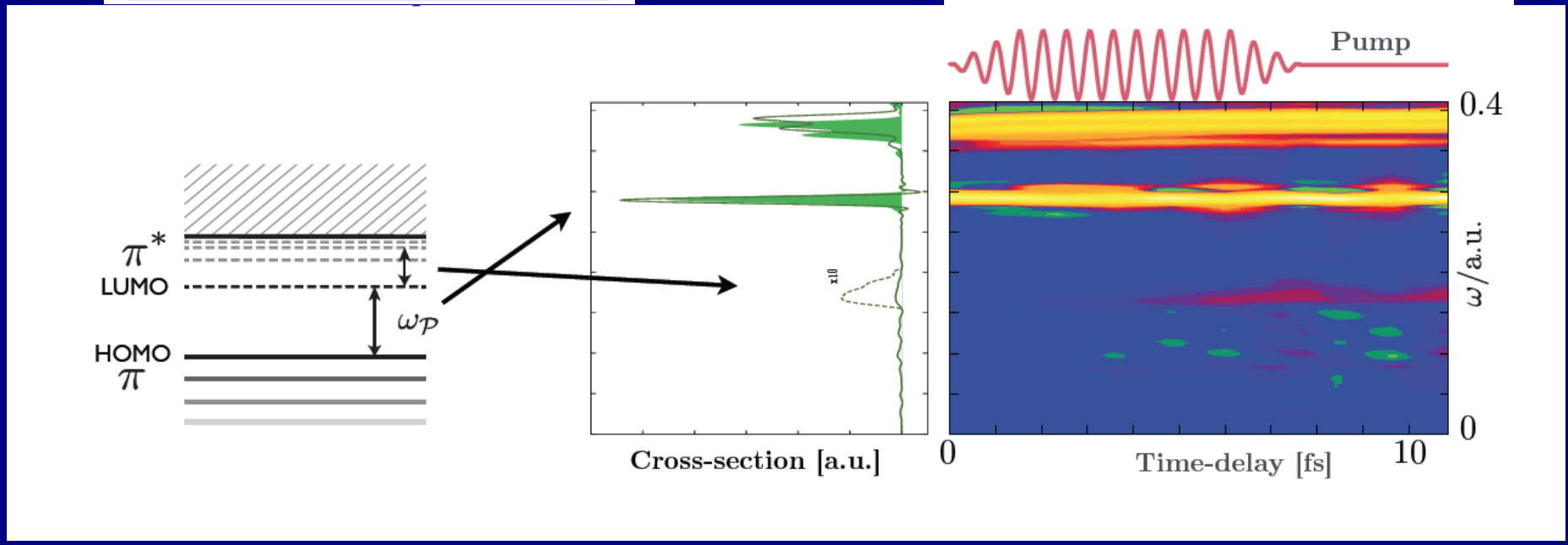

## Time resolved pump-probe spectroscopy

## Image reconstruction and monitoring electron-ion dynamics in finite and extended systems

# Ethylene: $C_2H_4$ Transient Absorption Spectroscopy




*Simulating pump-probe photo-electron and absorption spectroscopy on the attosecond time-scale with TDDFT*
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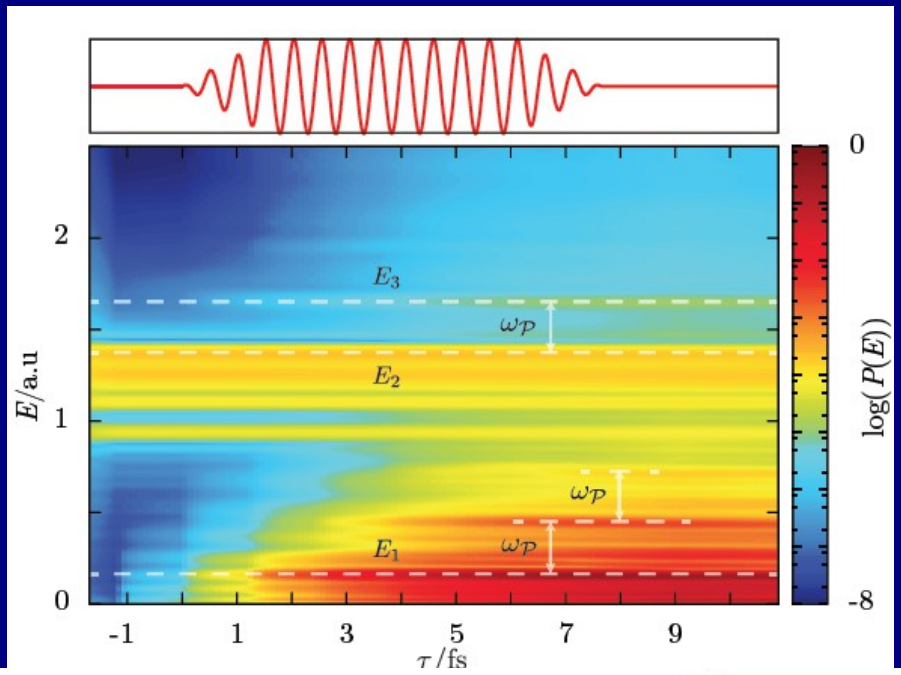
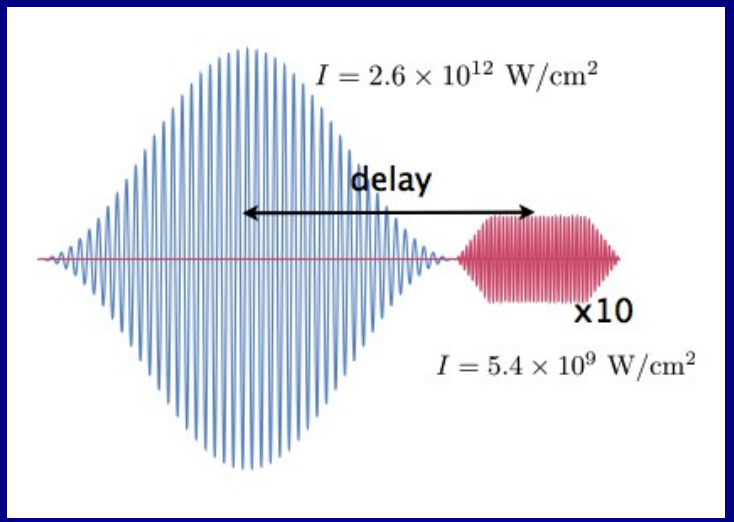
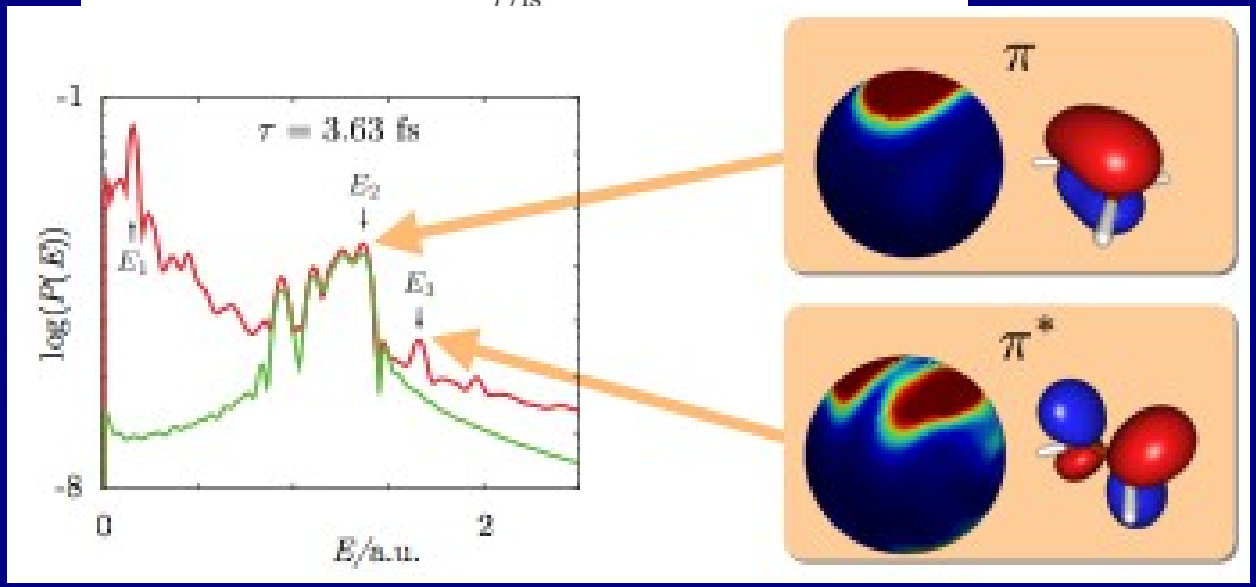



$w_{pump}$=0.291
$w_{probe}$= 1.8

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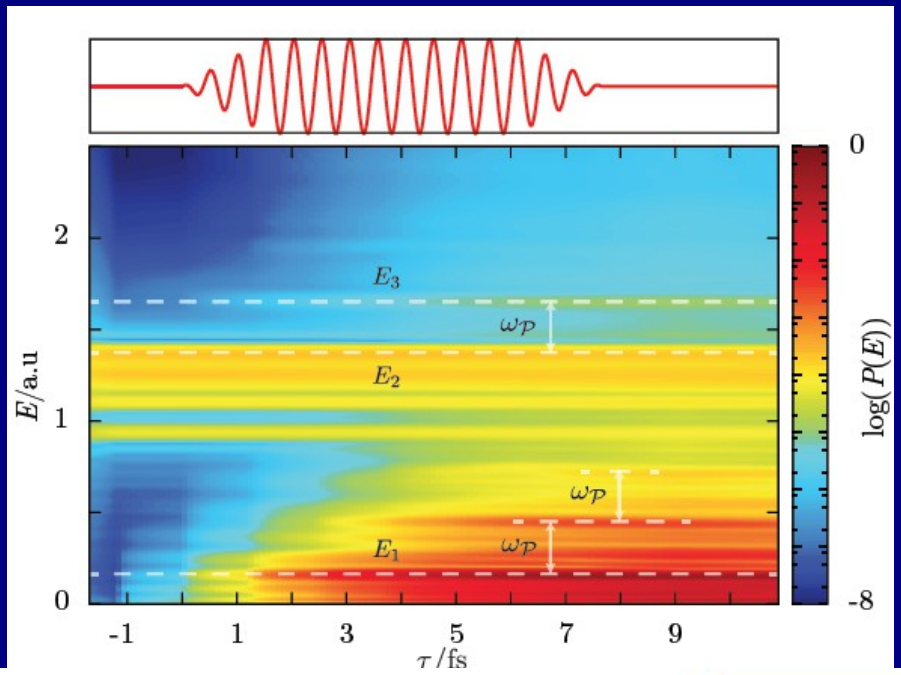
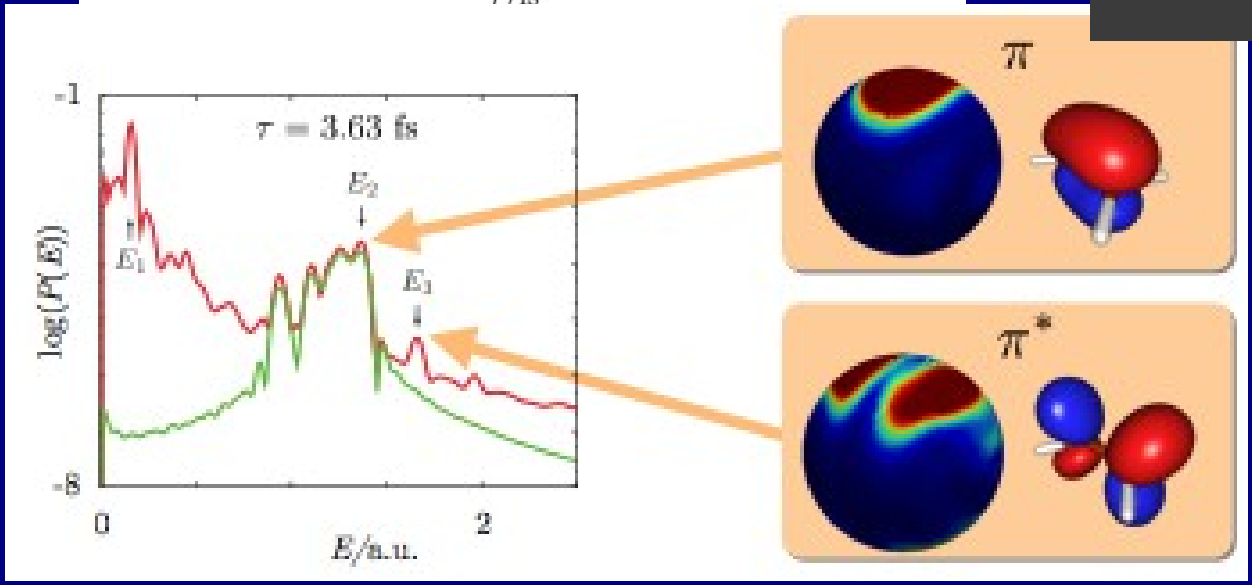
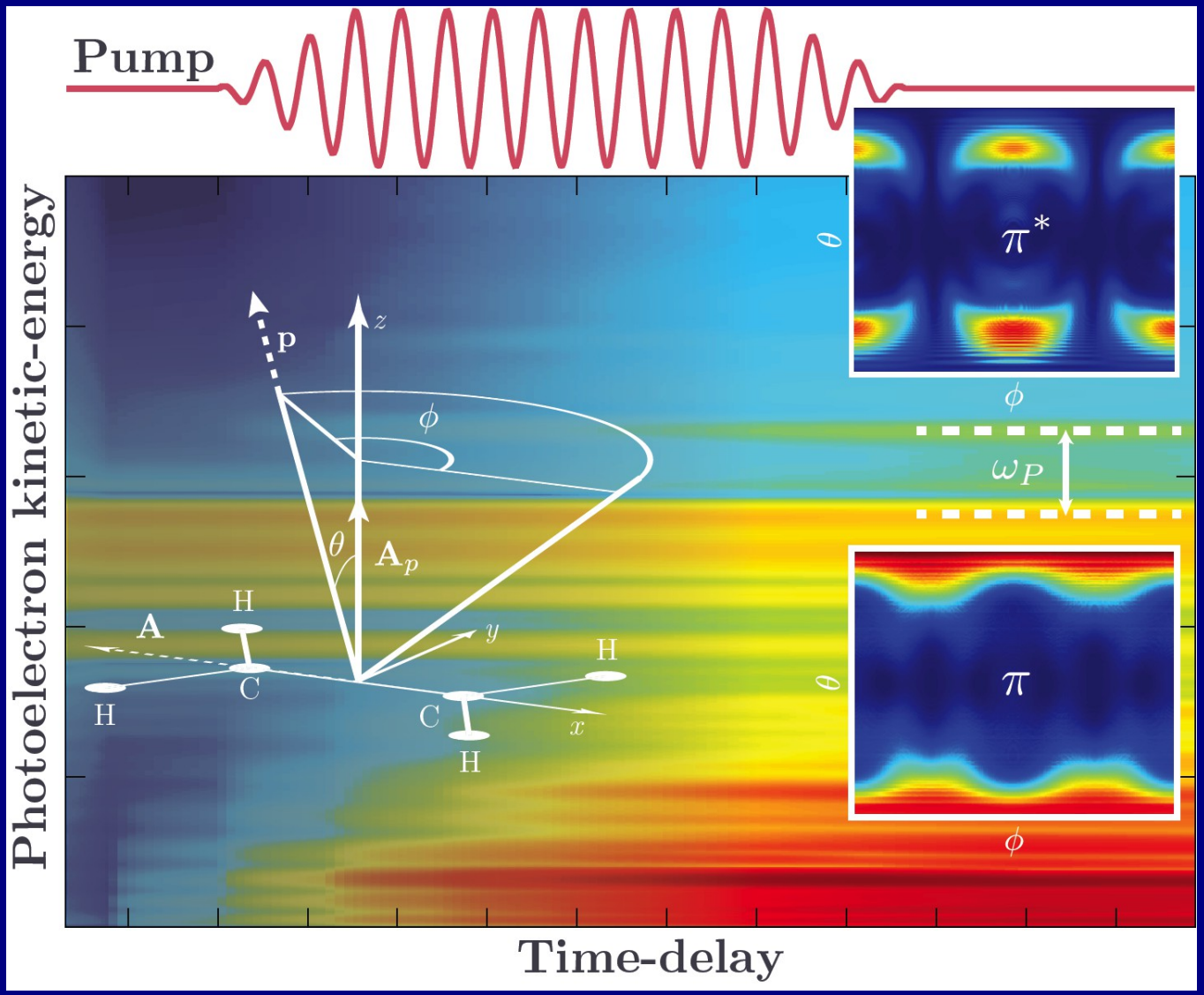


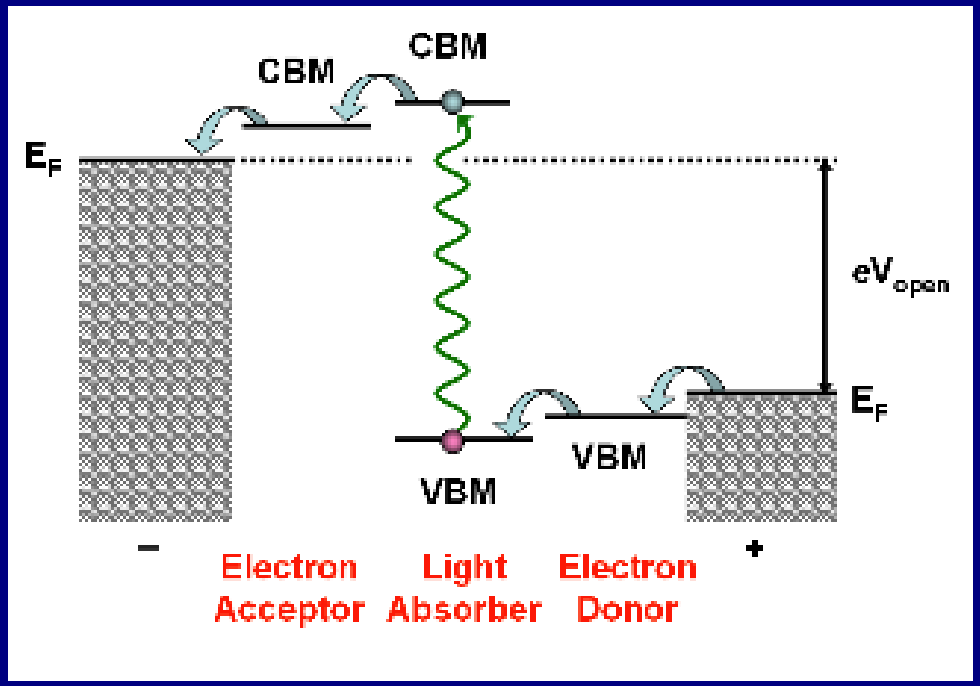

Momentum-resolved photoelectron distribution (3D)

# TRPES for $C_2H_4$




Simulating pump-probe photo-electron and absorption spectroscopy on the attosecond time-scale with time-dependent density-functional theory, U. D Giovannini, G. Brunetto, A. Castro, J. Walkenhorst, A.R, Chemphyschem (2013)

# Problems with extended systems in finite fields?




- Absorption of ligh (matching solar spectra) "Level alignment"
- Exciton dynamics and splitting
- Transport at the interface Extracting charges

*Efficiency*

# Macroscopic Polarisation Theory and real-time simulation

$$i\hbar\frac{\partial}{\partial t}\psi_i=\left[\frac{1}{2\mathrm{m}}\left(\vec{p}+\frac{e}{c}\vec{A}\right)^2+V_{ion}+V_H+V_{xc}\right]\psi_i$$

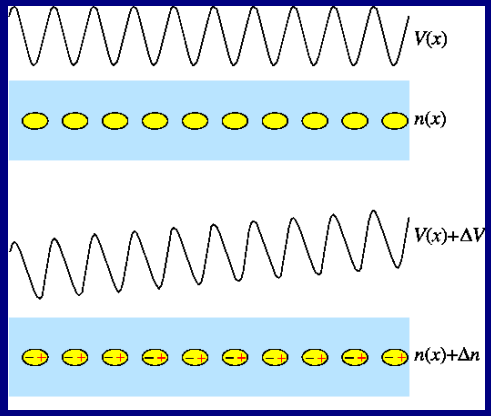
$$\vec{E}=\frac{-1}{c}\frac{d\vec{A}(t)}{dt}$$

$A(t) = A_{ext}(t) + A_{ind}(t)$

$E_{mac} = 4\pi P(t)$

$H = H + H_{em}$

P=polarisation




$$\frac{1}{4\pi}\frac{d^2\vec{A}}{dt^2}=-e^2\frac{n}{m}\vec{A}-c\frac{e}{V}\sum_i\langle\psi_i|\frac{\vec{p}}{m}|\psi_i\rangle=c^2\,j_{mac}(t)=-c^2\frac{d\vec{P}(t)}{dt}$$

What is the link to the “modern theory of polarisation”?
(see the recent review by Vanderbilt, Resta)

*G.F. Bertsch, J.I. Iwata, AR, K. Yabana, PRB62, 7998 (2000)*

# Macroscopic Polarisation Theory <-->real-time **A(t)**

$$\vec{j}_{\mathrm{mac}}(t) = -\frac{e}{c}\frac{1}{\Omega}\sum_{n\vec{k}}\int_{\Omega} d\vec{r}\, u^{*}_{n\vec{k}}(\vec{r},t)\frac{-i\hbar}{m}\left(\vec{\nabla}+i\vec{k}+\frac{ie}{\hbar c}\vec{A}(t)\right)u_{n\vec{k}}(\vec{r},t)$$

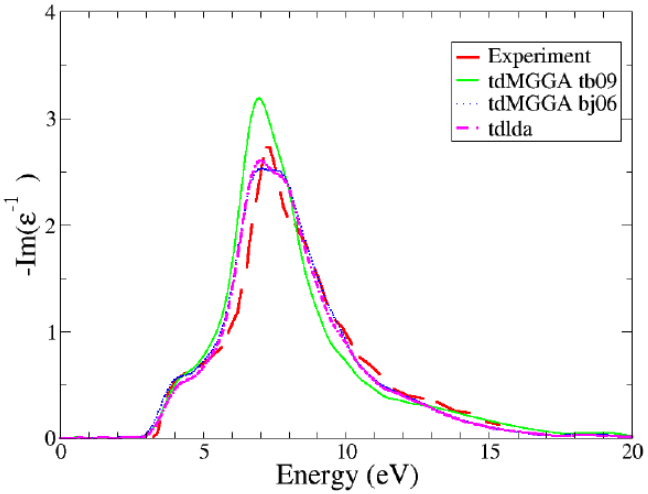
$$i\hbar\frac{\partial}{\partial t}u_{n\vec{k}}(\vec{r},t)=\left\{-\frac{\hbar^2}{2m}\left(\vec{\nabla}+i\vec{k}+\frac{ie}{\hbar c}\vec{A}(t)\right)^2+V(\vec{r},t)\right\}u_{n\vec{k}}(\vec{r},t)$$

$$\frac{d\vec{P}(t)}{dt}=\frac{ie}{c}\frac{1}{\Omega}\int_{\Omega} d\vec{r}\sum_{n\vec{k}}\left\{\frac{\partial u^{*}_{n\vec{k}}}{\partial t}\frac{\partial u_{n\vec{k}}}{\partial \vec{k}}+u^{*}_{n\vec{k}}\frac{\partial^2 u_{n\vec{k}}}{\partial t\partial \vec{k}}\right\}$$

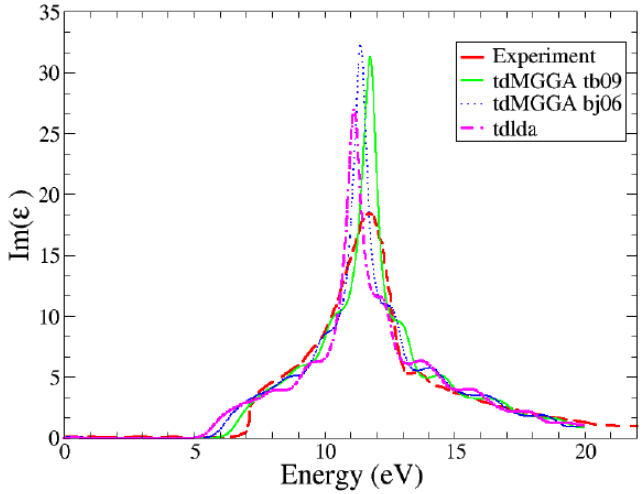
Berry Phase

$$\vec{P}(t)=\frac{ie}{c}\frac{1}{\Omega}\int_{\Omega} d\vec{r}\sum_{n\vec{k}} u^{*}_{n\vec{k}}(\vec{r},t)\frac{\partial}{\partial \vec{k}}u_{n\vec{k}}(\vec{r},t)$$

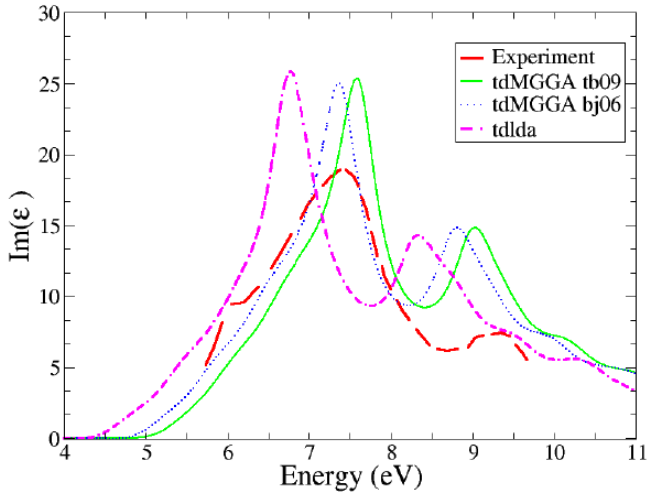
# Simple test cases: Li, C, SiC, AlP



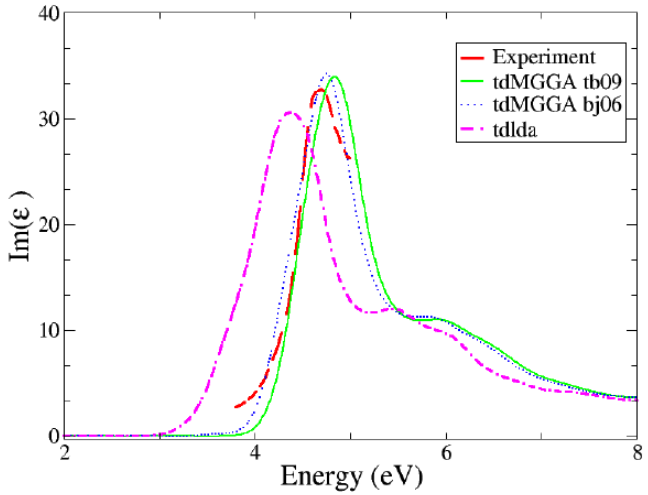

(a) EELS of Li (bcc)




(b) Photoabsorption of C (diamond).

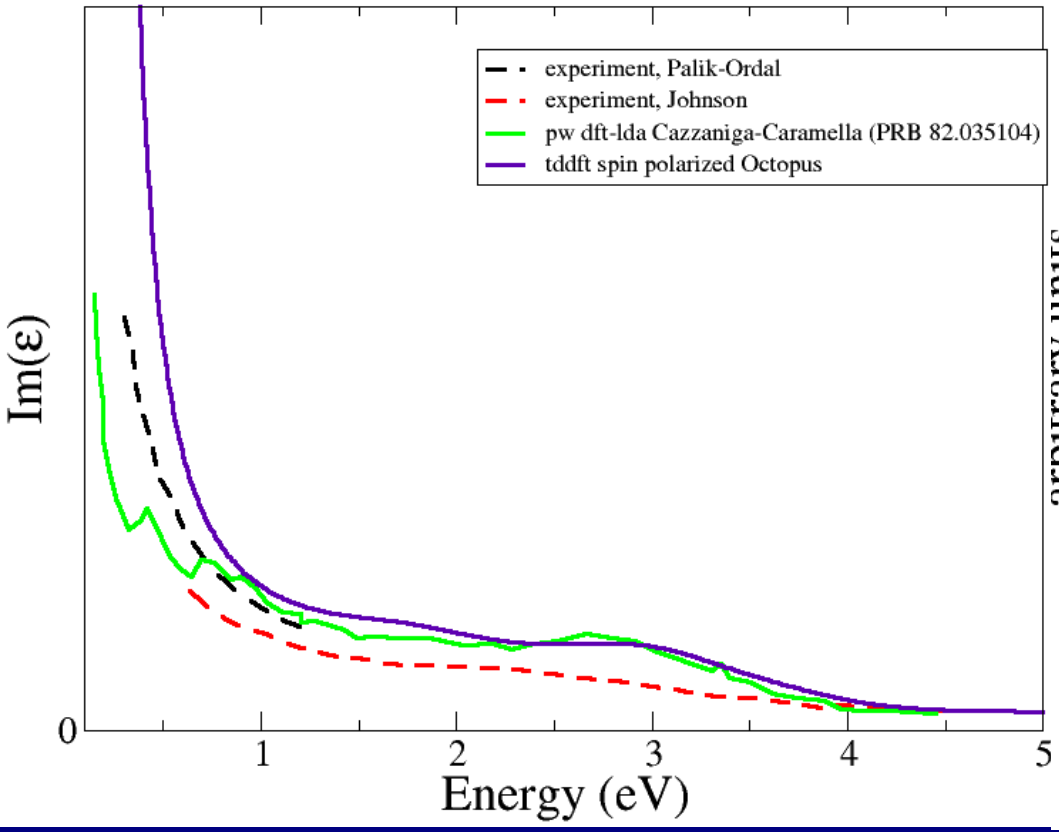


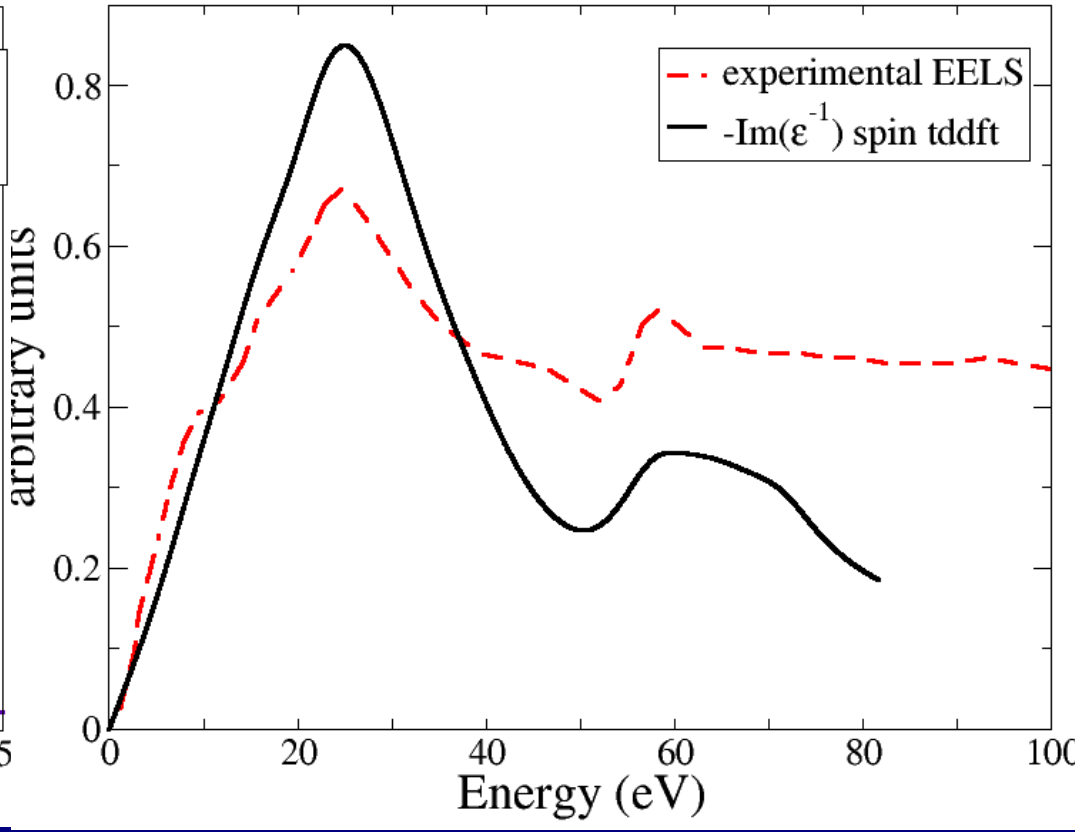

(c) Photoabsorption of SiC (Zinc-Blende )




(d) Photoabsorption of AlP (Zinc-Blende)

# Fe-response function spin-polarised (and spinorial calculation, not shown)



# Finding the exact time-dependent xc potential for a given known density-evolution

- In general, not easy.
- But for 2 electrons, starting in a doubly-occupied orbital, it's easy

$$\Phi(x_1, x_2, t) = \phi(x_1, t)\phi(x_2, t)$$ $(\uparrow\downarrow - \downarrow\uparrow)/\sqrt{2}$

Must have

$$\phi(x,t) = \sqrt{n(x,t)/2}\, e^{i\int^x dx' u(x',t)} \qquad u(x,t) = j(x,t)/n(x,t)$$

Insert $\phi(x,t)$ into TDKS equation, and solve for :

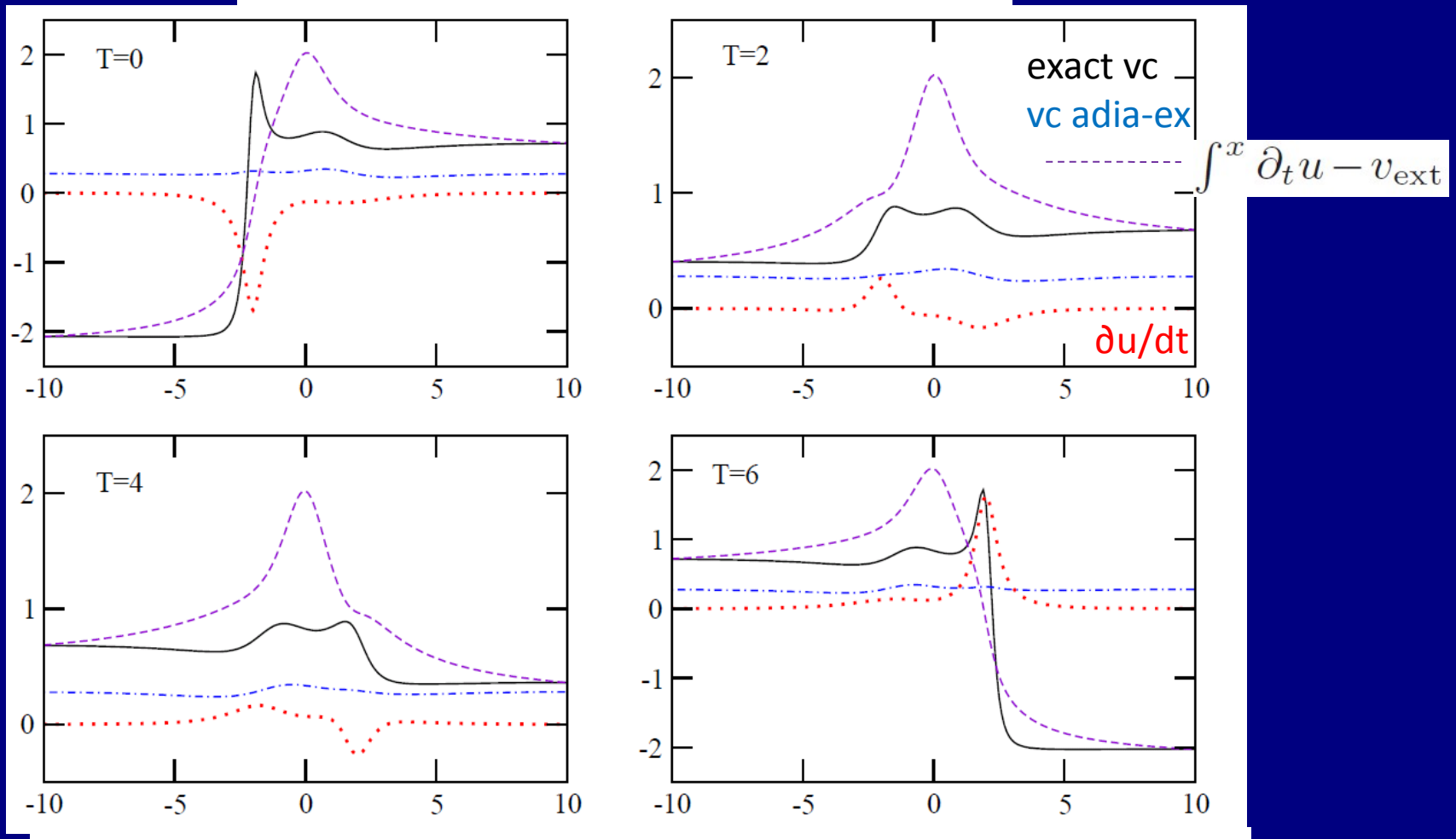
$$v_{\rm S}(x,t) = \frac{\partial_x^2 n(x,t)}{4n(x,t)} - \frac{(\partial_x n(x,t))^2}{8n^2(x,t)} - \frac{u^2(x,t)}{2} - \int^x \partial_t u(x',t)dx'$$

Further, we have $v_{\rm X}(x,t) = -v_{\rm H}(x,t)/2$

so we can extract $v_{\rm C}(x,t) = v_{\rm S}(x,t) - v_{\rm ext}(x,t) - v_{\rm H}(x,t)/2$

# Example 1: Field-free evolution of a non-stationary state  He-atom

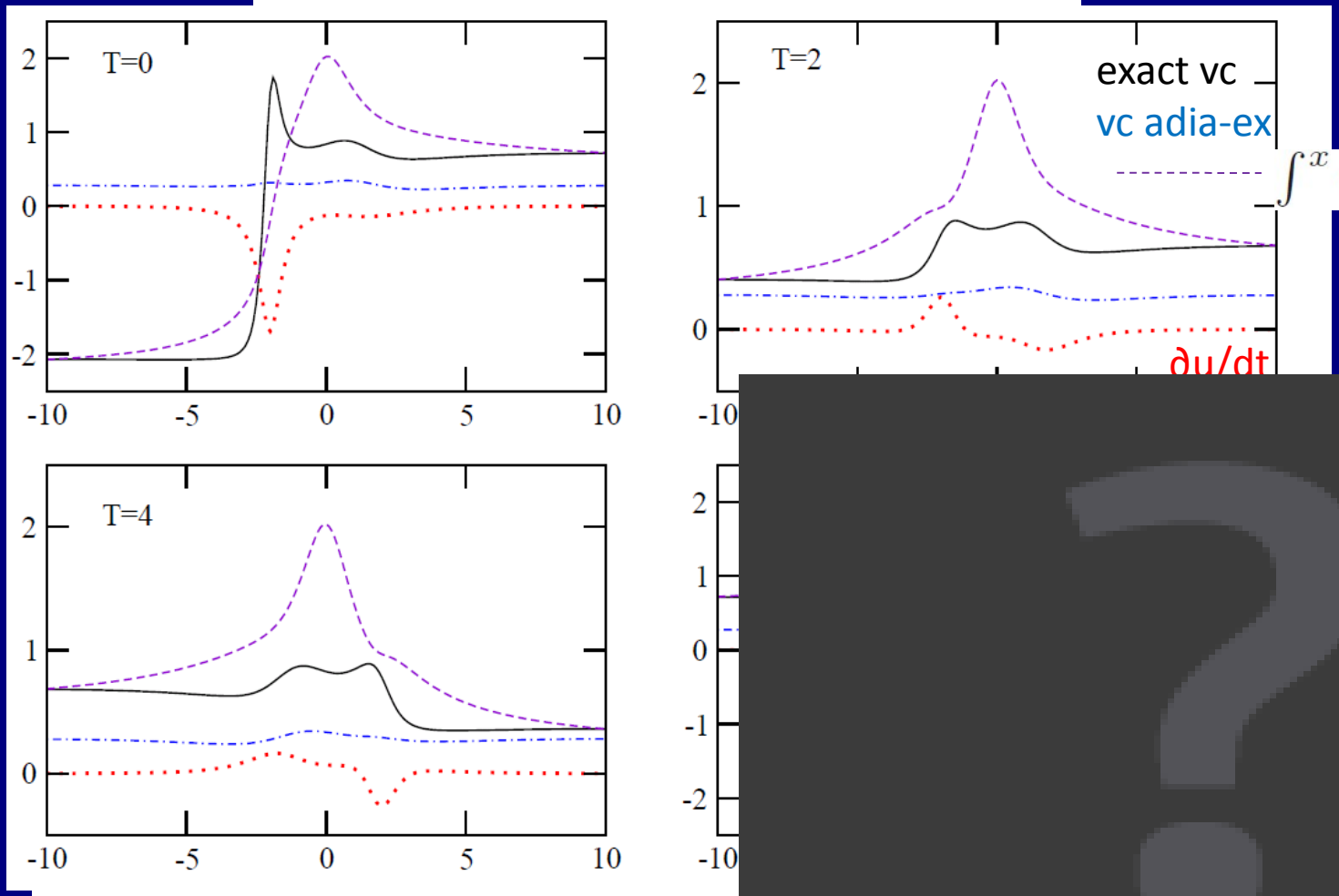
$$|\Psi(t)\rangle = \left(e^{-iE_g t}|\Psi_g\rangle + e^{-iE_e t}|\Psi_e\rangle\right)/\sqrt{2}$$




$$v_{\rm S}(x,t) = \frac{\partial_x^2 n(x,t)}{4n(x,t)} - \frac{(\partial_x n(x,t))^2}{8n^2(x,t)} - \frac{u^2(x,t)}{2} - \int^x \partial_t u(x',t)dx'$$

# Example 1: Field-free evolution of a non-stationary state  He-atom

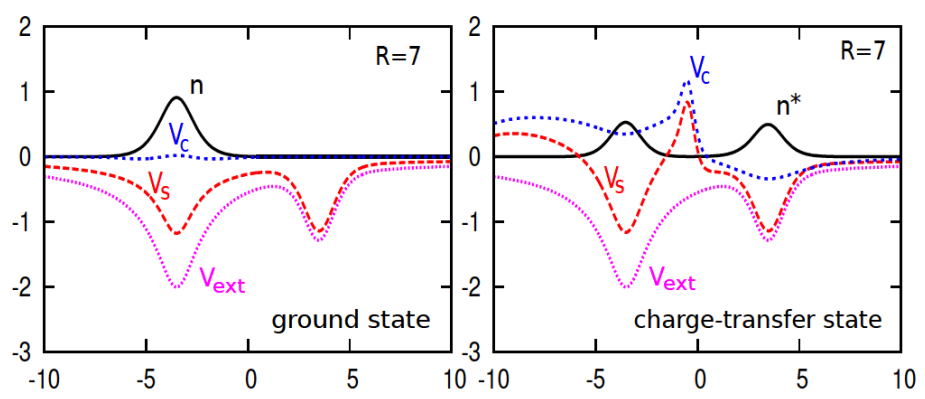
$$|\Psi(t)\rangle = \left(e^{-iE_g t}|\Psi_g\rangle + e^{-iE_e t}|\Psi_e\rangle\right)/\sqrt{2}$$

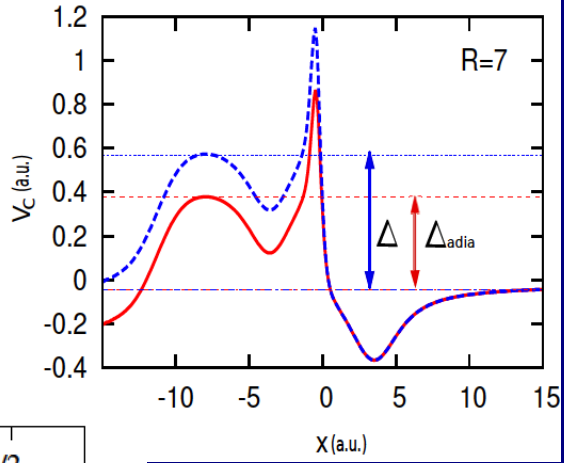


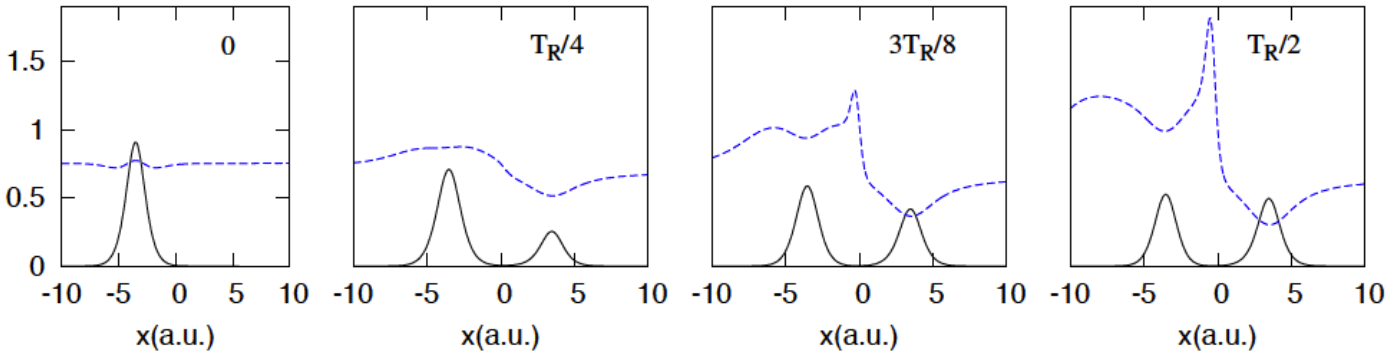

$$v_S(x,t) = \frac{\partial_x^2 n(x,t)}{4n(x,t)} - \frac{(\partial_x n(x,t))^2}{8n^2(x,t)}$$

# Example 2: Time resolved Charge transfer

## CT-resonant excitation of two closed shell fragments



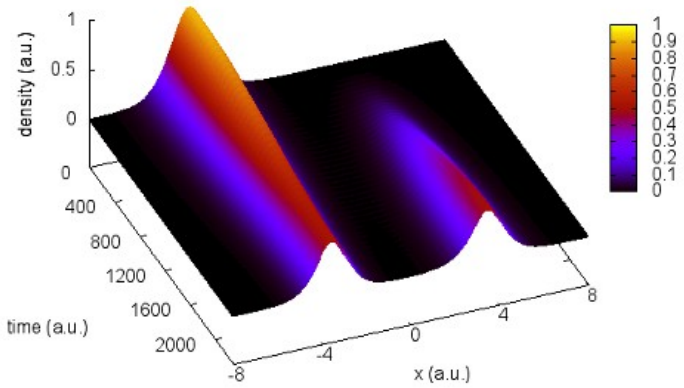



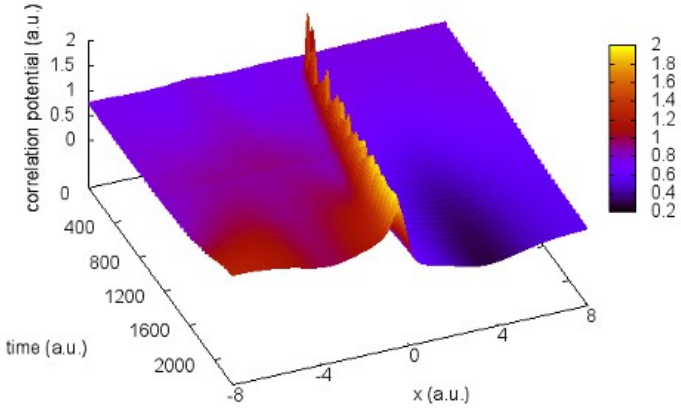

$$\mathcal{E}(t) = 0.006\cos(0.112t)$$

$(2\pi/T_R) = 0.00136$ Ha

$$\Delta = |I_D^{N_D-1} - I_A^{N_A+1}|$$

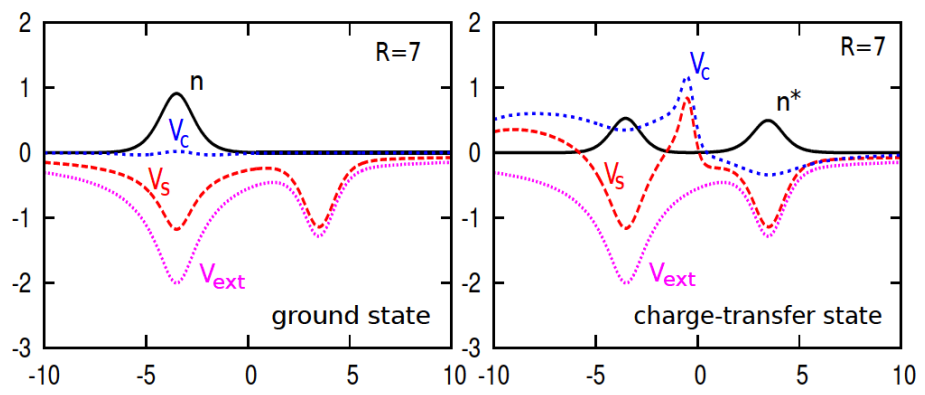
$$\Delta_{adia} = |I_D^{N_D-1} - A_D^{N_D-1}|$$

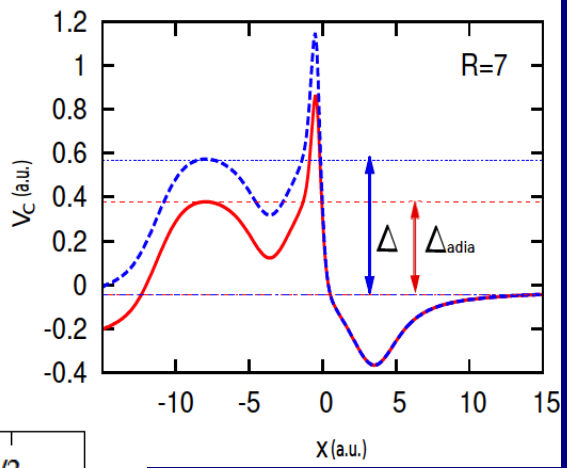


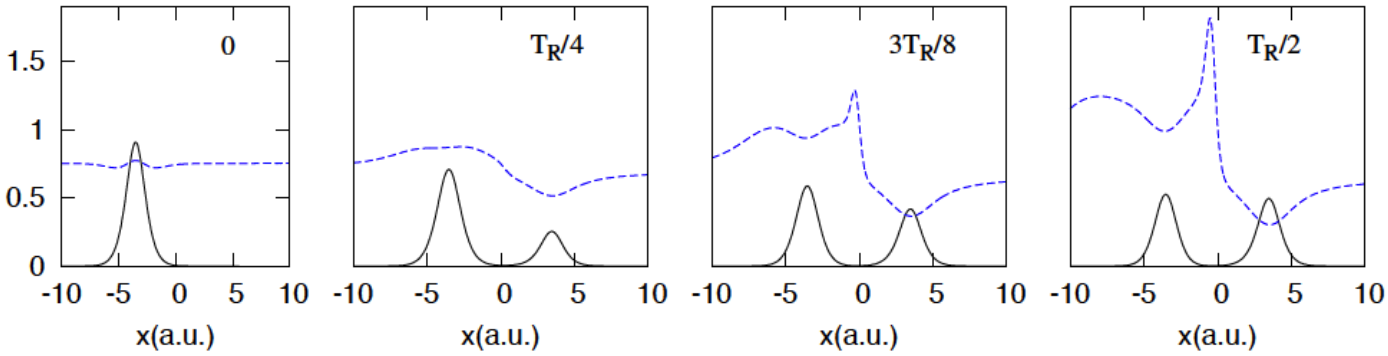



# Example 2: Time resolved Charge transfer

## CT-resonant excitation of two closed shell fragments

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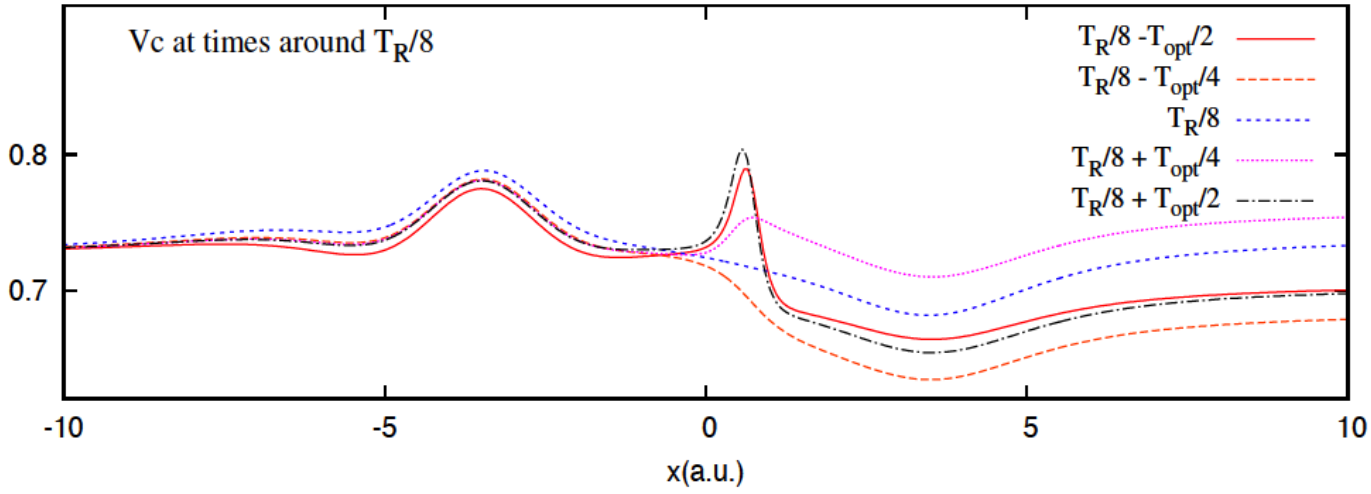
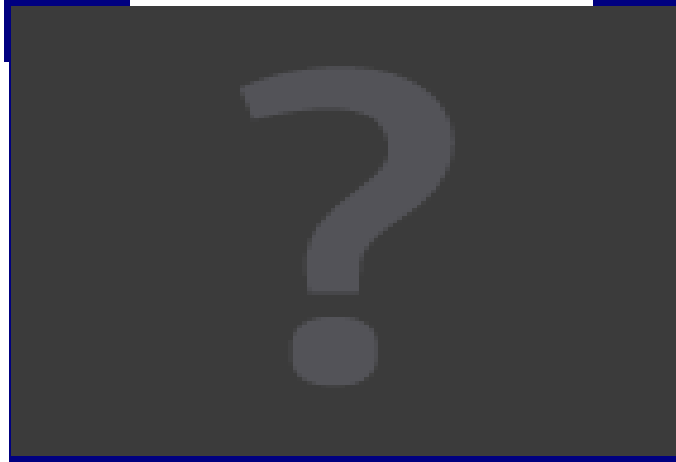
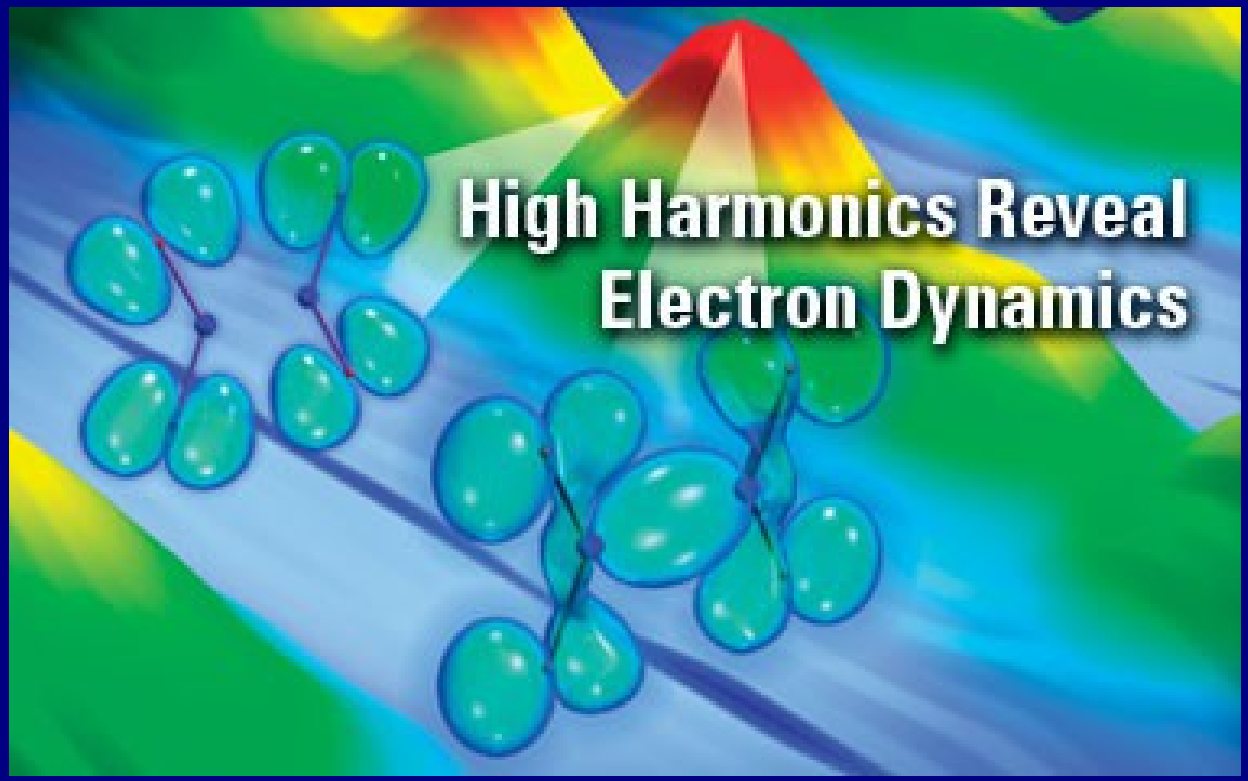
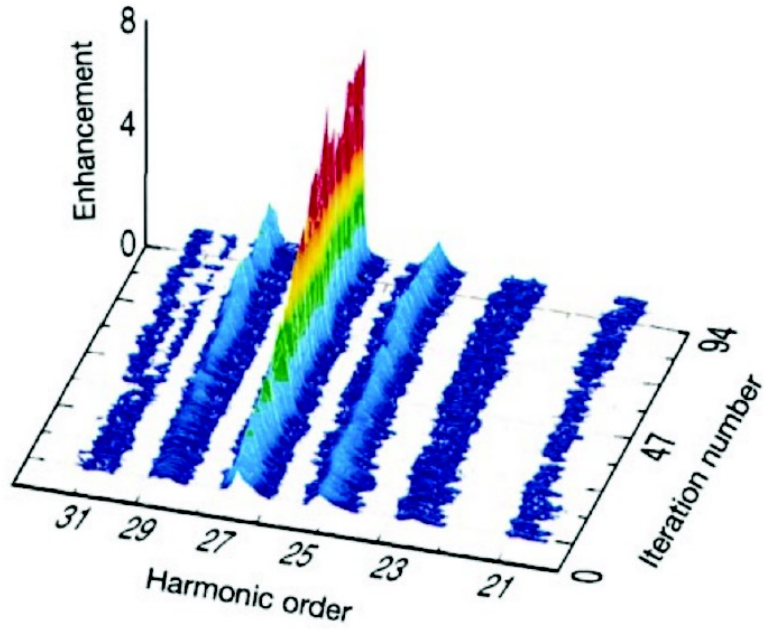




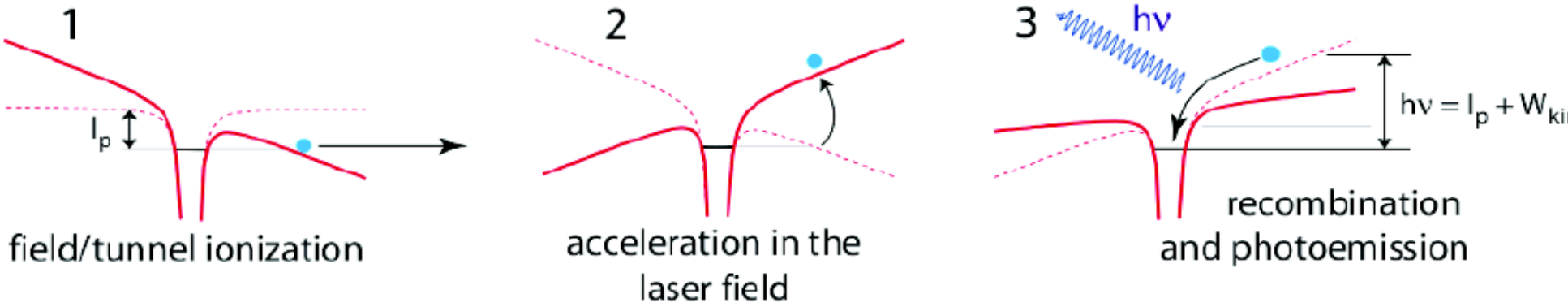

[R. Bartels *et al*, Nature **406**, 164 (2000)]

Interrogating Molecules?

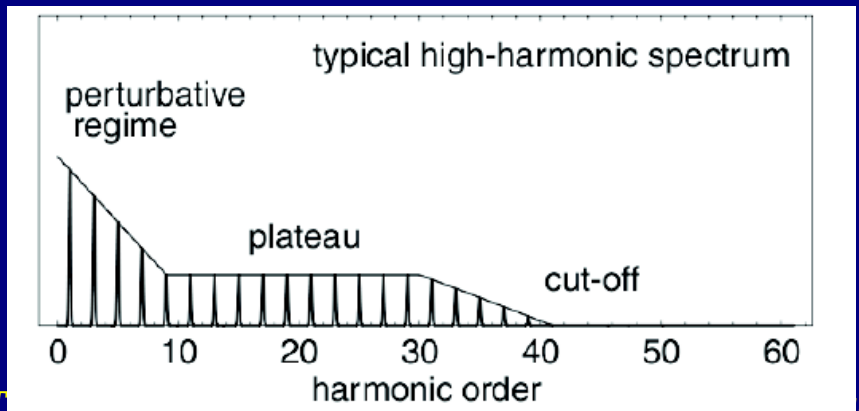
Science, Nov. 2008

# Tailoring HHG

HHG consists of the emission of integer multiples of the carrier frequency of a driving laser, due to its highly non-linear interaction with matter. It can be explained with the so-called 3-steps model:




Typically, the HH spectrum (emission intensity vs. photon frequency) consists of a rapid intensity decrease, a plateau, and a cut-off.



# Quantum Optimal control theory (QOCT)

Key question: What is the laser pulse that drives the system into a predef ned goal?

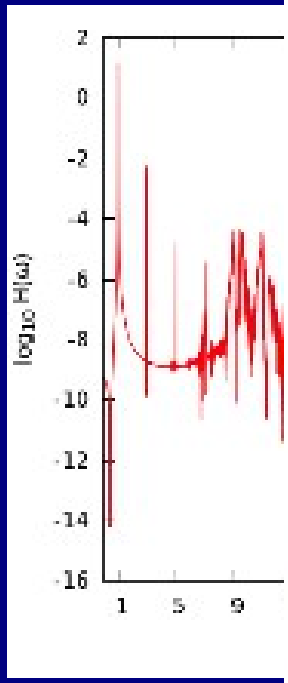
Procedure: Def ne a target operator $\hat{O}$ and at the end of the laser interaction (t = T) maximize the functional

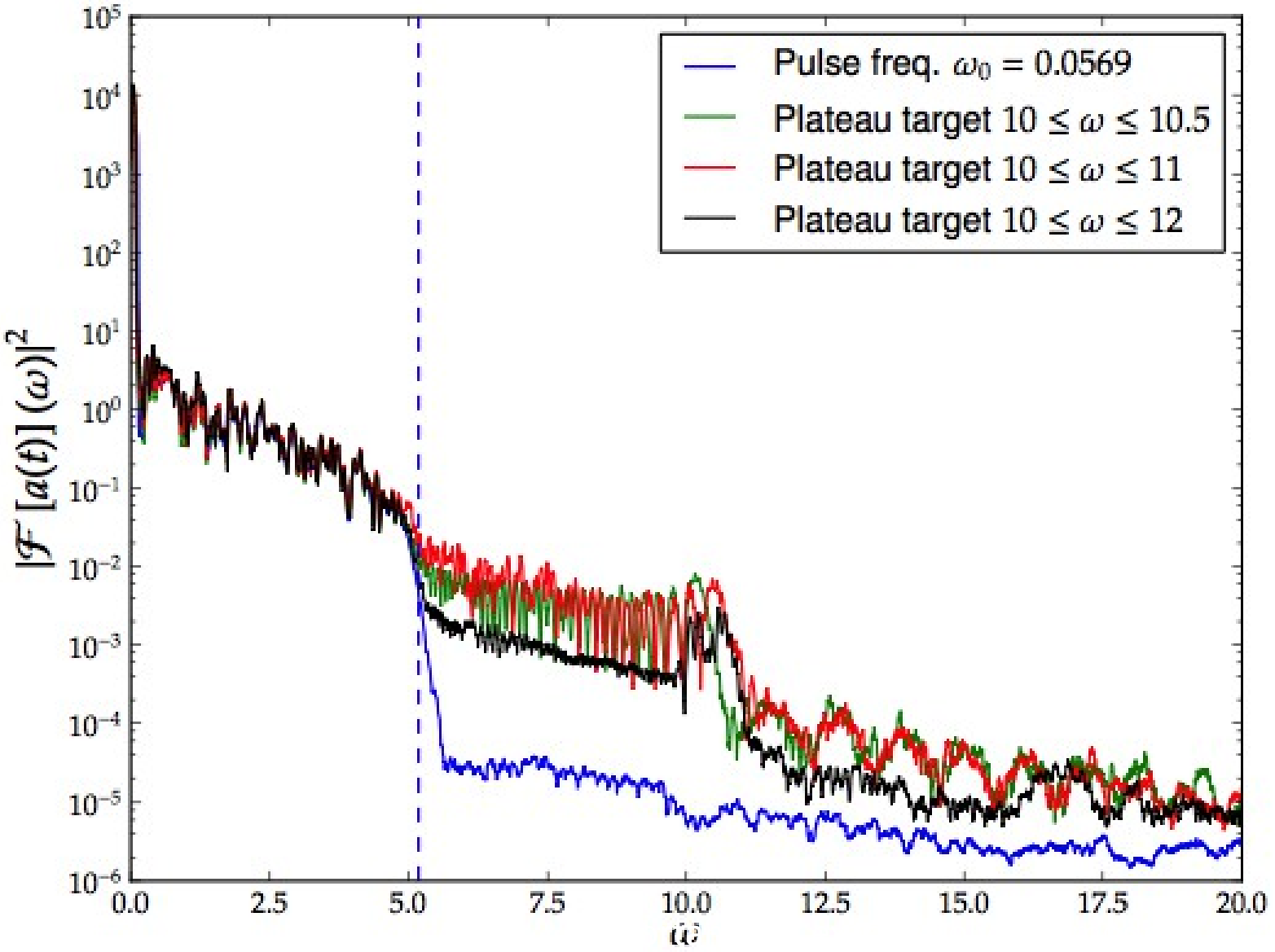
$$J_1[\Psi] = \langle \Psi(T)|\hat{O}|\Psi(T)\rangle = |\langle \Psi(T)|\Phi_F\rangle|^2$$

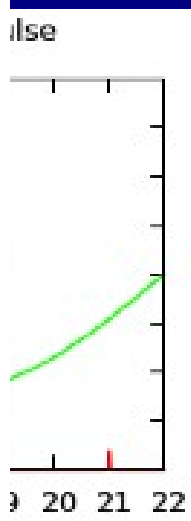
$\hat{O} = |\Phi_F\rangle\langle\Phi_F|$ target state

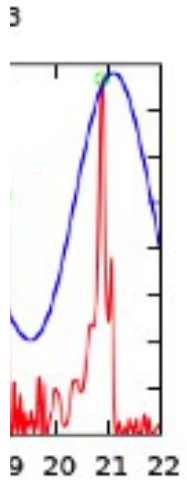
W. Zhu, J. Botina, H. Rabitz, JCP 108, 1953 (1998)

# *Tailoring HHG (He atom)*



# Conclusions and Perspectives

*Density-functional based-schemes are a powerful tool to "predictively" describe the combined dynamics of electron and ions in response to external electromagnetic fields of large scale nanostructures, biological molecules and extended systems spanning very different time scales*

*"A first principles time-dependent description of non-adiabatic couplings, decoherence and dissipation in many-body quantum systems (solids, nanostructures, etc..) including quantum control of open quantum-systems is required"*

Work to be done: "new spatial and w-dependent functionals"

# Acknowledgements


U.de Giovannini, A.Larsen, J.Fuks, A.Crawford, J.Walkenhorst, I.Tokatly, S.Kurth







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Universidad del País Vasco

Euskal Herriko Unibertsitatea


***TDDFT for non linear phenomena in solids and nanostructures: fundamentals and applications***

*"Electronic structure calculations with GPAW", CAMD-DTU, Denmark (22-May 2013)*

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***TDDFT for non linear phenomena in solids and nanostructures: fundamentals and applications***
*"Electronic structure calculations with GPAW", CAMD-DTU, Denmark (22-May 2013)*


ETSF
European Theoretical Spectroscopy Facility

*It is one of the first duties of a professor, for example, in any subject, to exaggerate a little both the importance of his subject and his own importance in it*

G. H. Hardy (1940). A Mathematician's Apology.

# Thank you!!!

*Let's increase complexity ??!!!!*

# $H_2$ Dimers

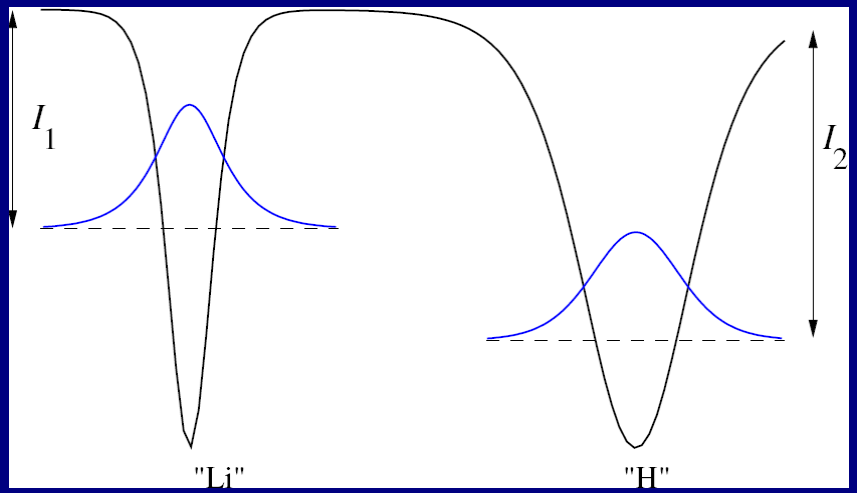
*Illustrate the problem of SIC and beyond from a different perspective*

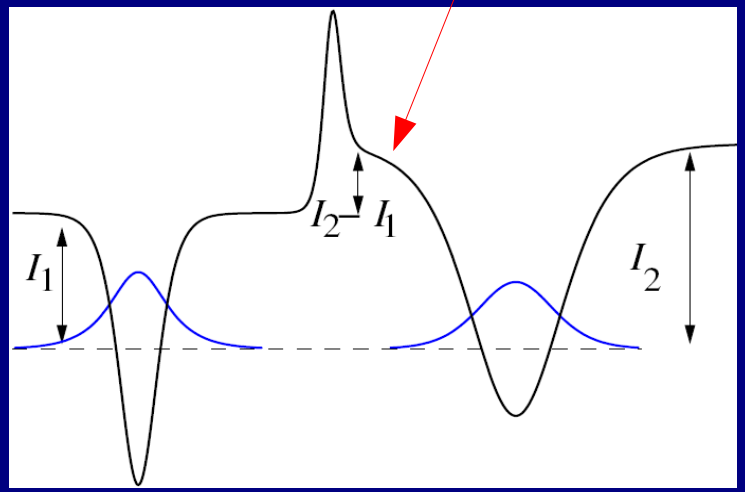
# The step in KS potential: open shell fragments

- Step aligns the atomic HOMOs
- Kohn-Sham system builds a ”wall“ to mimick the repulsion due to interaction and prevent tunneling

  *Prevents dissociation to unphysical fractional charges*
- Step-height = difference between highest eigenvalues of the two wells

Step in exact KS potential that exactly realigns the two atomic HOMOs: Step $\Delta = |ID - IA|$



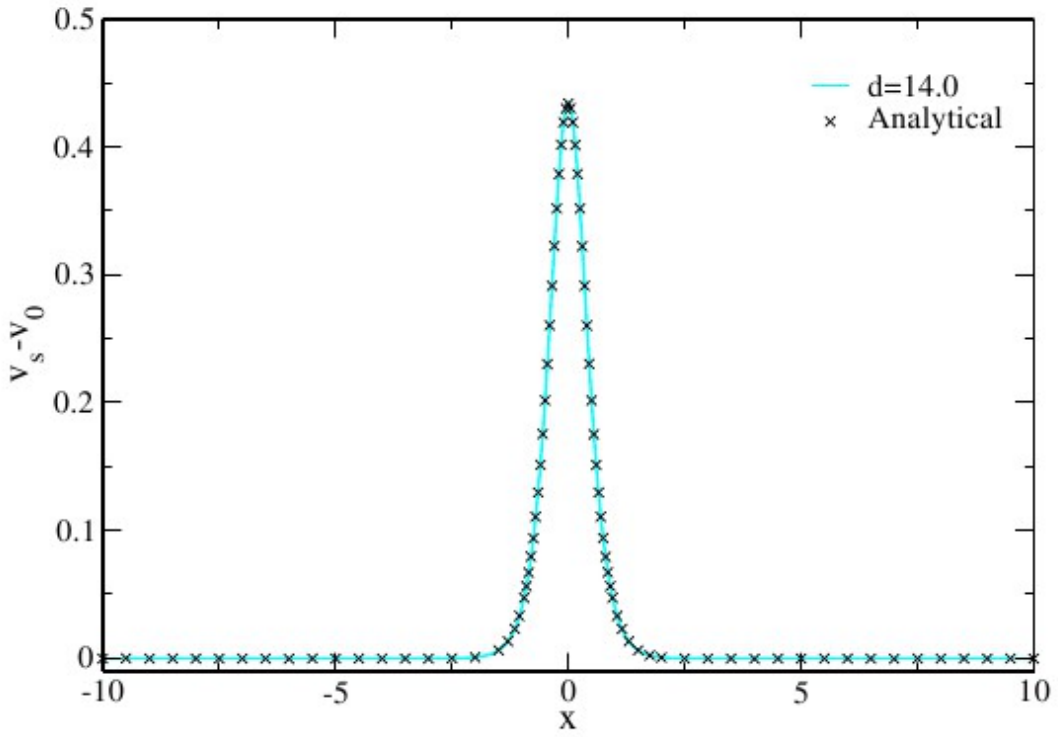




*Early work of Perdew, Almbladh& von Barth, Gritsenko & Baerends*
*Recent work of Tempel, Martinez, Maitra, JCTC (2009) and N. Helbig, I. Tokatly, A. Rubio, JCP (2009)*

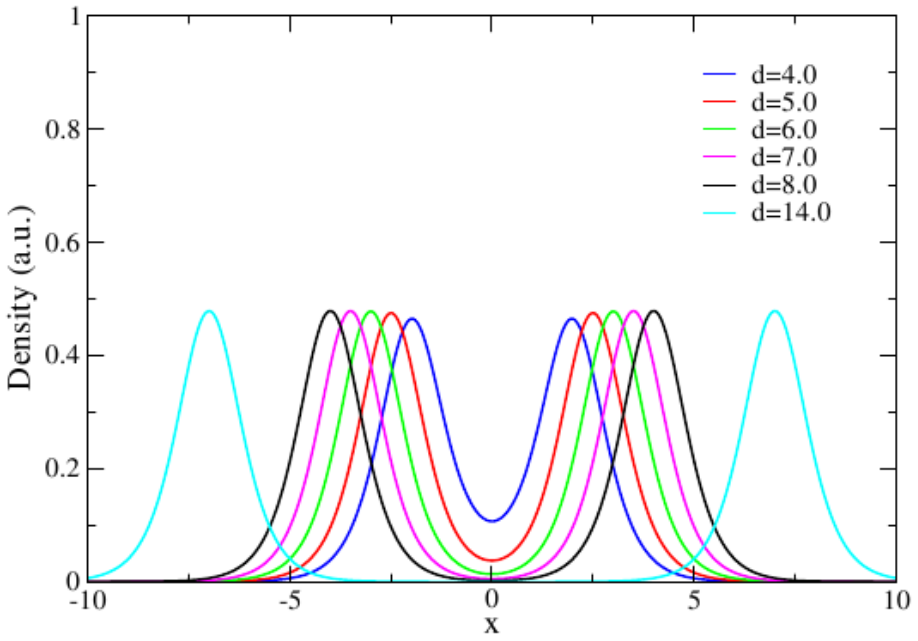
# Difference between the KS-effective potential and the external (ionic) one

$H_2$

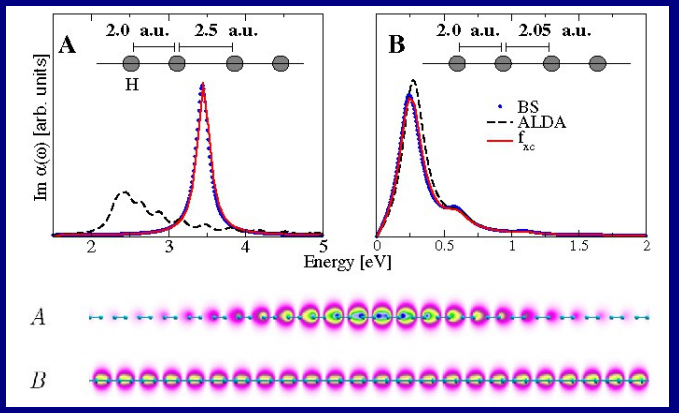
$$v_s(\mathbf{r}) = \frac{1}{2}\frac{\nabla^2\sqrt{n(\mathbf{r})}}{\sqrt{n(\mathbf{r})}} + \epsilon_1$$



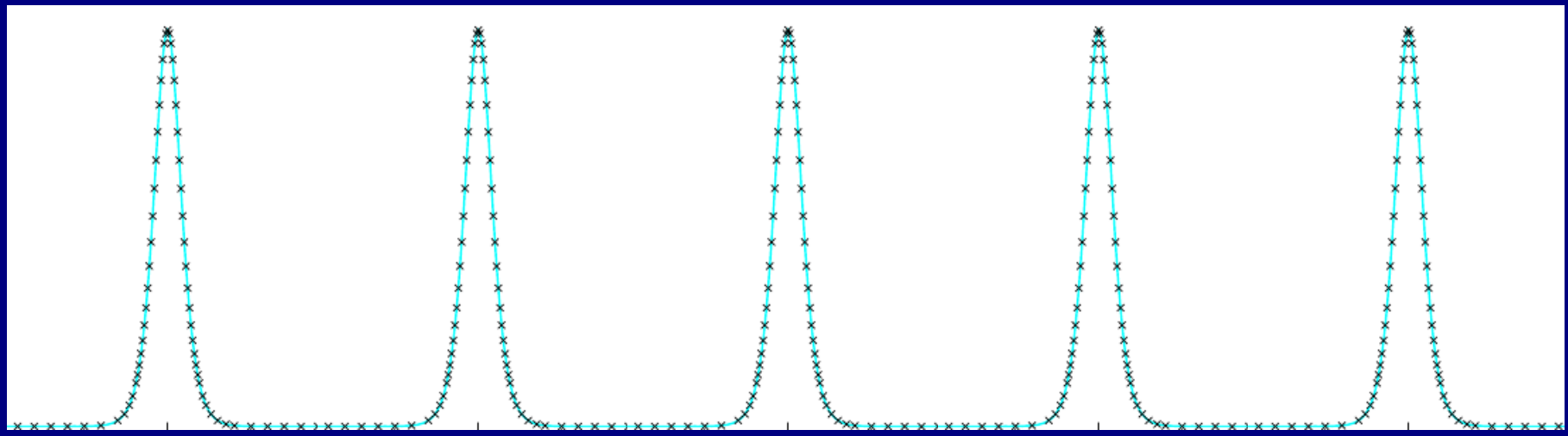

Dissociation of two symmetric wells



# H-chain
# Mott insulator : in DFT !!!




$V_{KS} - V_{ionic}$



*Clearly all local functionals and most orbital dependent functionals do not capture the step in the potential*

*The KS systems is metallic : fxc responsible for the gap*