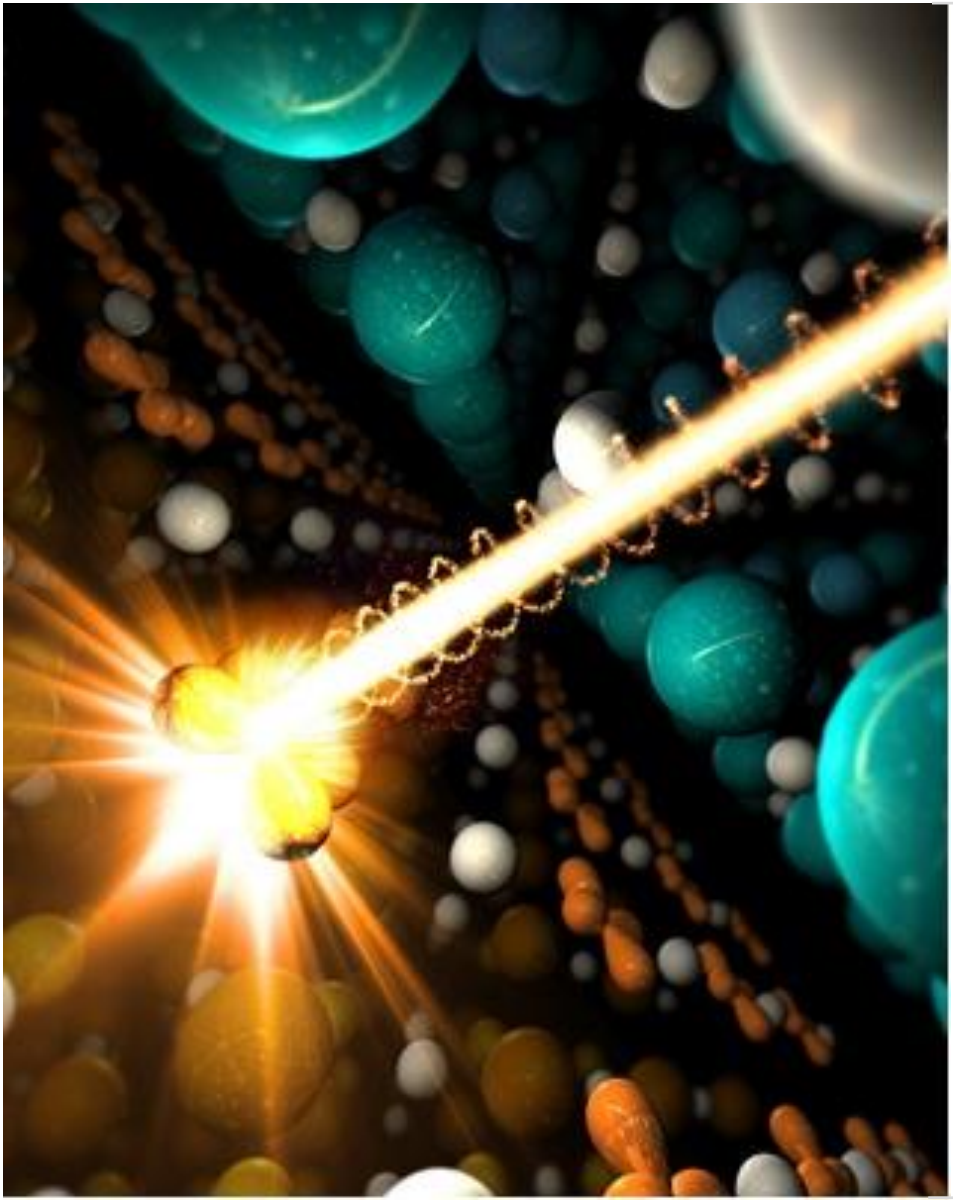

含时密度泛函理论

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2019.7.24

Time-Dependent Density Functional Theory

OUTLINE

I. What is TDDFT? What it does?

II. Current status and typically applications

- spectroscopy
- excited state
- dynamics

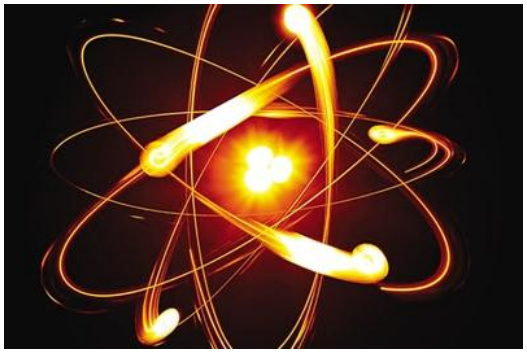
III. Implementation, progress, and prospect

- implementation
- some examples
- remarks

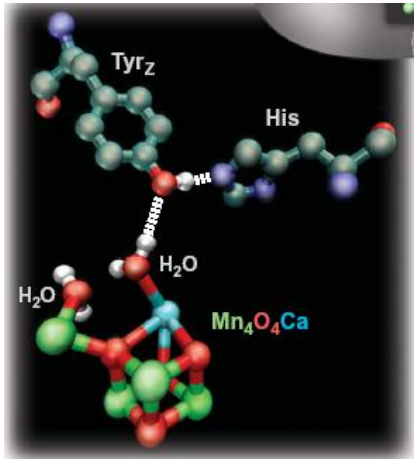
1.1 Things Density Functional Theory (DFT) Cannot Describe Well

Lighting

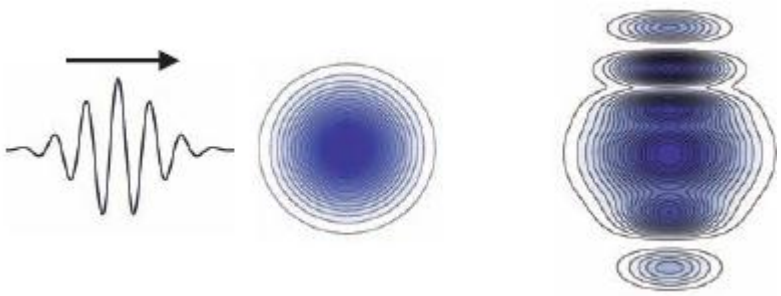
Ultrafast (10^{-18} s)



Photosynthesis



Detection



From Density Functional Theory (DFT) to Time-dependent DFT (TDDFT)

Density functional theory (DFT) and single-particle approximation (Kohn, 1964)

Theorem I.

$$\begin{cases} \Psi(\vec{r}_1,\vec{r}_2,...,\vec{r}_N) \longrightarrow \rho(\vec{r}) = \int \left|\Psi(\vec{r},\vec{r}_2,...,\vec{r}_N)\right|^2 \prod_{j=2}^{N} d\vec{r}_j \\ \Psi(\vec{r}_1,\vec{r}_2,...,\vec{r}_N) \longleftarrow \rho(\vec{r}) \end{cases}$$

Theorem II.

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + V_{external}(\vec{r}) + \int dr' \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} + V_{xc}[\rho]\right\}\varphi_i(\vec{r}) = E_i\varphi_i(\vec{r})$$

Time-dependent density functional theory (TDDFT) (EKU Gross, 1984)

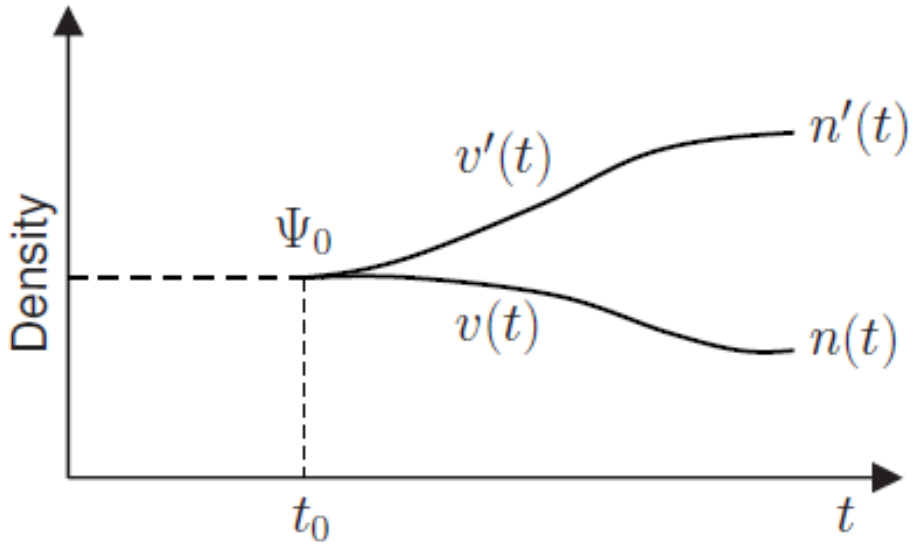
$$\Psi(\vec{r}_1,\vec{r}_2,...,\vec{r}_N;t) \rightleftharpoons \rho(\vec{r},t) = \int \left|\Psi(\vec{r},\vec{r}_2,...,\vec{r}_N;t)\right|^2 \prod_{j=2}^{N} d\vec{r}_j$$

Given $\Psi(0)$, $\quad i\hbar\frac{\partial\Psi(t)}{\partial t} = \hat{H}\left[\rho(\vec{r},t),t\right]\Psi(t)$

E Rouge & EKU Gross, PRL 52, 997 (1984).

TDDFT Theorem I.

Runge–Gross theorem. Two densities $n(\mathbf{r},t)$ and $n'(\mathbf{r},t)$, evolving from a common initial many-body state Ψ_0 under the influence of two different potentials $v(\mathbf{r},t)$ and $v'(\mathbf{r},t) \neq v(\mathbf{r},t)+c(t)$ (both assumed to be Taylor-expandable around t_0), will start to become different infinitesimally later than t_0. Therefore, there is a one-to-one correspondence between densities and potentials, for any fixed initial many-body state.



Proof of Runge-Gross Theorem

The action integral: $A = \int_{t_0}^{t_1} dt \langle \Phi(t) | i\partial/\partial t - \hat{H}(t) | \Phi(t) \rangle$

$$\hat{H}(t) = \hat{T} + \hat{V}(t) + \hat{W}$$

$$\hat{T} = \sum_s \int d^3r\, \hat{\psi}_s^\dagger(\vec{r}) \left(-\tfrac{1}{2}\nabla^2\right) \hat{\psi}_s(\vec{r})$$

$$\hat{V}(t) = \sum_s \int d^3r\, v(\vec{r}\,t) \hat{\psi}_s^\dagger(\vec{r}) \hat{\psi}_s(\vec{r})$$

$$\hat{W} = \tfrac{1}{2} \sum_s \sum_{s'} \int d^3r \int d^3r'\, \hat{\psi}_s^\dagger(\vec{r}) \hat{\psi}_{s'}^\dagger(\vec{r}\,') w(\vec{r}, \vec{r}\,') \hat{\psi}_{s'}(\vec{r}\,') \hat{\psi}_s(\vec{r})$$

Assume $v(\vec{r}\,t) - v'(\vec{r}\,t) \neq c(t)$ then

$$\frac{\partial^k}{\partial t^k} [v(\vec{r}\,t) - v'(\vec{r}\,t)]\big|_{t=t_0} \neq \text{const.}$$

$$\vec{j}(\vec{r}\,t) = \langle \Phi(t) | \hat{\vec{j}}(\vec{r}) | \Phi(t) \rangle \qquad \hat{\vec{j}}(\vec{r}) = (2i)^{-1} \sum_s \{ [\nabla \hat{\psi}_s^\dagger(\vec{r})] \hat{\psi}_s(\vec{r}) - \hat{\psi}_s^\dagger(\vec{r}) [\nabla \hat{\psi}_s(\vec{r})] \}$$

$$i\partial \vec{j}(\vec{r}\,t)/\partial t = \langle \Phi(t) | [\hat{\vec{j}}(\vec{r}), \hat{H}(t)] | \Phi(t) \rangle$$

$$i\frac{\partial}{\partial t} [\vec{j}(\vec{r}\,t) - \vec{j}'(\vec{r}\,t)]\big|_{t=t_0} = \langle \Phi_0 | [\hat{\vec{j}}(\vec{r}), \hat{H}(t_0) - \hat{H}'(t_0)] | \Phi_0 \rangle = in(\vec{r}\,t_0) \nabla [v(\vec{r}\,t_0) - v'(\vec{r}\,t_0)]$$

$$\left(i\frac{\partial}{\partial t}\right)^{k+1} [\vec{j}(\vec{r}\,t) - \vec{j}'(\vec{r}\,t)]_{t=t_0} = in(\vec{r}\,t_0) \nabla \left\{ \left(i\frac{\partial}{\partial t} \right)^k [v(\vec{r}\,t) - v'(\vec{r}\,t)]\big|_{t=t_0} \right\} \neq 0$$

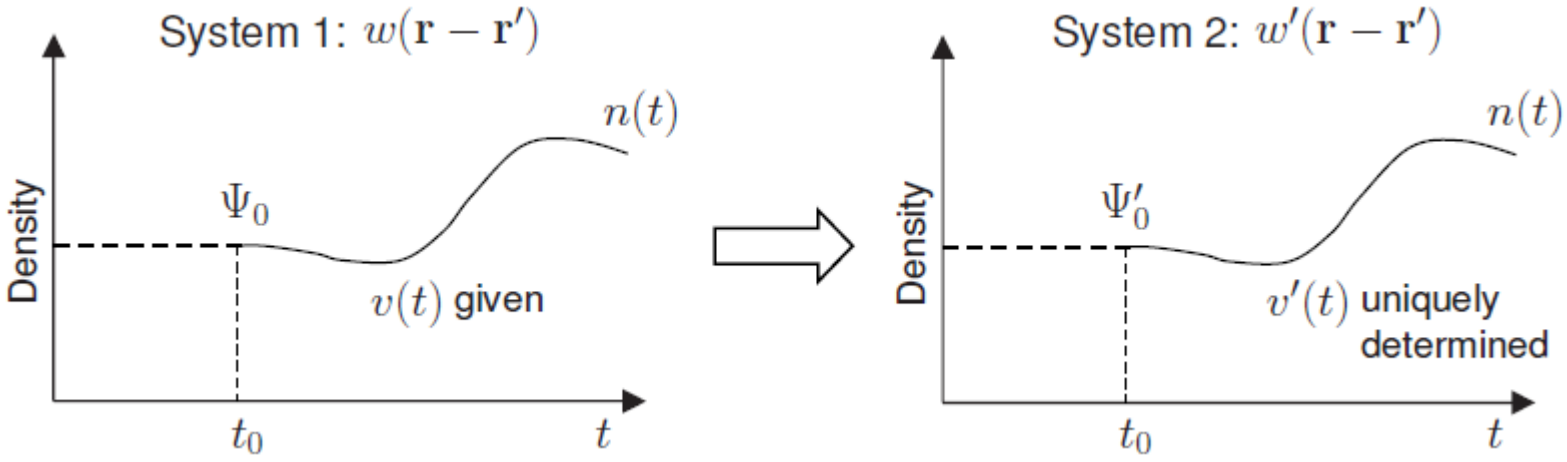
$$(\partial/\partial t)[n(\vec{r}\,t) - n'(\vec{r}\,t)] = -\operatorname{div}[\vec{j}(\vec{r}\,t) - \vec{j}'(\vec{r}\,t)]$$

$$\frac{\partial^{k+2}}{\partial t^{k+2}} [n(\vec{r}\,t) - n'(\vec{r}\,t)]\big|_{t=t_0} = -\operatorname{div} n(\vec{r}\,t_0) \cdot \nabla \left\{ \frac{\partial^k}{\partial t^k} [v(\vec{r}\,t) - v'(\vec{r}\,t)]\big|_{t=t_0} \right\} \neq 0$$

E Rouge & EKU Gross, PRL 52, 997 (1984).

TDDFT Theorem II.

Van Leeuwen theorem. For a time-dependent density $n(\mathbf{r},t)$ associated with a many-body system with a given particle–particle interaction $w(|\mathbf{r}-\mathbf{r}'|)$, external potential $v(\mathbf{r},t)$, and initial state Ψ_0, there exists a different many-body system featuring an interaction $w'(|\mathbf{r}-\mathbf{r}'|)$ and a unique external potential $v'(\mathbf{r},t)$ [up to a purely time-dependent $c(t)$] which reproduces the same time-dependent density. The initial state Ψ_0' in this system must be chosen such that it correctly yields the given density and its time derivative at the initial time.



Van Leeuwen, PRL 82, 3863 (1999).

DFT vs TDDFT

Static DFT:

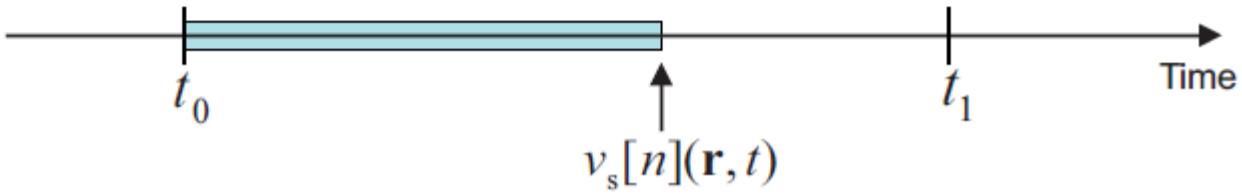
$$\left[-\frac{\nabla^2}{2}+v_s^0[n_0](\mathbf{r})\right]\varphi_j(\mathbf{r})=\varepsilon_j\varphi_j(\mathbf{r}) \longrightarrow \sum_j\left|\varphi_j(\mathbf{r})\right|^2=n_0(\mathbf{r})$$

Density $n_0(\mathbf{r}')$ over all space

TDDFT:

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

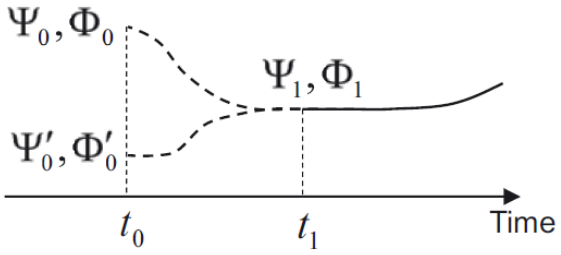
Density $n(\mathbf{r}',t')$ over all space and times $t'\le t$



$$v_s[n](\mathbf{r},t)=v(\mathbf{r},t)+\int d^3r'\frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}+v_{\mathrm{xc}}[n](\mathbf{r},t)$$

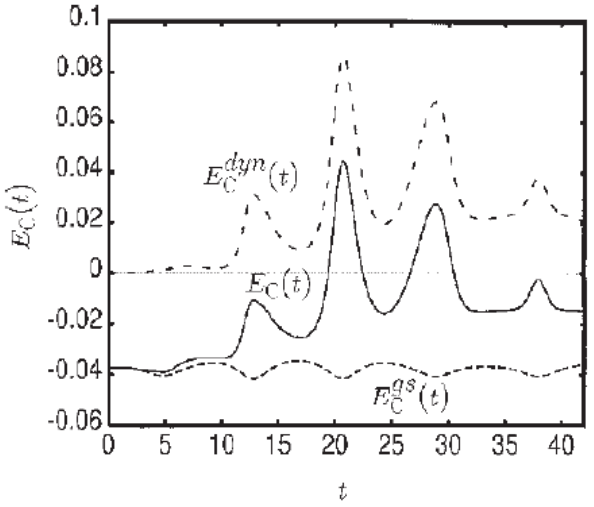
Some important notes on TDDFT

- **Initial-state/history dependent, Memory, Causality**



- **Adiabatic xc**

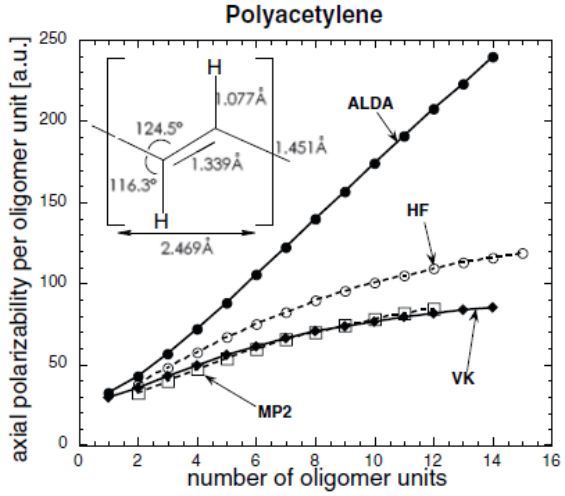
$$v_{\rm xc}(\mathbf{r},t) \longrightarrow v^0_{\rm xc}[n(t)](\mathbf{r})$$



- **ALDA/APBE: not good for double excitation, charge transfer, Rydberg**

- **Hydrodynamic xc (Vignale-Kohn)**

$$A_{{\rm xc}1,\mu}(\mathbf{r},\omega) = A^{\rm ALDA}_{{\rm xc}1,\mu}(\mathbf{r},\omega) - \frac{1}{i\omega\bar{n}}\sum_\nu \nabla_\nu \sigma_{{\rm xc},\mu\nu}$$



- **TDDFT ≈ DFT**

Hessler et al. (2002); Faassen et al. (2002).

1.2 TDDFT is a fundamental tool for many-body physics

Adiabatic-Connection Fluctuation-Dissipation Theorem

$$E_{\rm xc}[n] = -\frac{1}{2}\int_0^1 d\lambda \int d^3r \int d^3r' \frac{1}{|\mathbf{r}-\mathbf{r}'|}\left\{ n(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') + \frac{1}{\pi}\int_0^\infty d\omega\, \Im\chi^\lambda(\mathbf{r},\mathbf{r}',\omega)\right\}$$

$$\chi^\lambda(\mathbf{r},\mathbf{r}',\omega) = \chi_0(\mathbf{r},\mathbf{r}',\omega) + \int d^3x \int d^3x'\, \chi_0(\mathbf{r},\mathbf{x},\omega)\left\{\frac{\lambda}{|\mathbf{x}-\mathbf{x}'|} + f_{\rm xc}^\lambda(\mathbf{x},\mathbf{x}',\omega)\right\}\chi^\lambda(\mathbf{x}',\mathbf{r}',\omega)$$

$$n_1(\mathbf{r},\omega) = \int d^3r' \chi_{nn}(\mathbf{r},\mathbf{r}',\omega) v_1(\mathbf{r}',\omega)$$

- **Accurate exchange-correlation functional**
- **RPA, GW, high-order process,…**
- **Van der Waals force**
- **Nonlinear; Non perturbative; Non-equilibrium**

Three xc functionals

- **Exc**

$$E_{\mathrm{xc}}[n] = T[n] - T_s[n] + W[n] - \frac{1}{2}\int d^3r \int d^3r' \, \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

- **Vxc**

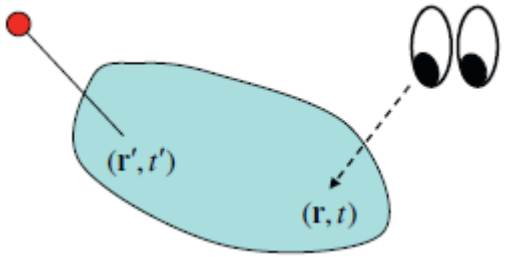
$$v_{\mathrm{xc}}[n](\mathbf{r}) = \frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\mathbf{r})}$$

- **fxc**

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

$$\chi(\mathbf{r},t,\mathbf{r}',t') = \chi_s(\mathbf{r},t,\mathbf{r}',t') + \int d\tau \int d^3x \int d\tau' \int d^3x' \, \chi_s(\mathbf{r},t,\mathbf{x},\tau)\left\{\frac{\delta(\tau-\tau')}{|\mathbf{x}-\mathbf{x}'|} + f_{\mathrm{xc}}(\mathbf{x},\tau,\mathbf{x}',\tau')\right\}\chi(\mathbf{x}',\tau',\mathbf{r}',t')$$

1.3 TDDFT is an exact theory for dynamics and excited state properties



A). Linear response TDDFT:

$$\delta n(\boldsymbol{r},t) \equiv n(\boldsymbol{r},t) - n_0(\boldsymbol{r}) = \int_{-\infty}^{t} \mathrm{d}t' \int \mathrm{d}\boldsymbol{r}'\, \chi(\boldsymbol{r},\boldsymbol{r}',t-t')\, V_{\mathrm{ext}}(\boldsymbol{r}',t')$$

$$\chi(\boldsymbol{r},\boldsymbol{r}',t-t') = \frac{1}{i\hbar}\theta(t-t')\,\langle \Phi_0 |[\hat{n}(\boldsymbol{r},t), \hat{n}(\boldsymbol{r}',t')]| \Phi_0\rangle$$

$$\chi(\boldsymbol{r},\boldsymbol{r}',\omega) = \int_{-\infty}^{\infty} \mathrm{d}t\ \mathrm{e}^{i\omega t}\,\chi(\boldsymbol{r},\boldsymbol{r}',t) = \sum_n \frac{\langle \Phi_0|\hat{n}(\boldsymbol{r})|\Phi_n\rangle\langle\Phi_n|\hat{n}(\boldsymbol{r}')|\Phi_0\rangle}{\hbar\omega + i\eta - (E_n - E_0)} - \frac{\langle \Phi_0|\hat{n}(\boldsymbol{r}')|\Phi_n\rangle\langle\Phi_n|\hat{n}(\boldsymbol{r})|\Phi_0\rangle}{\hbar\omega + i\eta + (E_n - E_0)}$$

Modified Sternheimer method:

For given ω, assume $\psi_i(\boldsymbol{r},t) = (\phi_i(\boldsymbol{r}) + \delta\psi_i(\boldsymbol{r},t))\,\mathrm{e}^{-i\varepsilon_i t/\hbar}$ ⇨ $\delta n(\boldsymbol{r},t) = \sum_{i\in \mathrm{occ}} \phi_i^*(\boldsymbol{r})\,\delta\psi_i(\boldsymbol{r},t) + \phi_i(\boldsymbol{r})\,\delta\psi_i^*(\boldsymbol{r},t)$

$$i\hbar\frac{\partial}{\partial t}\delta\psi_i(\boldsymbol{r},t) = (h_0(\boldsymbol{r}) - \varepsilon_i) + \left(\int \mathrm{d}\boldsymbol{r}'\,\frac{\delta h_{\mathrm{KS}}[n(\boldsymbol{r})]}{\delta n(\boldsymbol{r}')}\,\delta n(\boldsymbol{r}',t) + V_{\mathrm{ext}}(\boldsymbol{r},t)\right)\phi_i(\boldsymbol{r})$$

$$\delta\psi_i(\boldsymbol{r},t) = \delta\psi_i^{(+)}(\boldsymbol{r})\,\mathrm{e}^{-i\omega t} + \delta\psi_i^{(-)}(\boldsymbol{r})\,\mathrm{e}^{i\omega t}$$

$$\delta n(\boldsymbol{r},t) = \delta n(\boldsymbol{r})\,\mathrm{e}^{-i\omega t} + \delta n^*(\boldsymbol{r})\,\mathrm{e}^{i\omega t}$$

⇨ $\delta n(\boldsymbol{r}) = \sum \phi_i^*(\boldsymbol{r})\,\delta\psi_i^{(+)}(\boldsymbol{r}) + \phi_i(\boldsymbol{r})\,\delta\psi_i^{(-)*}(\boldsymbol{r})$

$$\left\{\hbar\omega\begin{pmatrix}\boldsymbol{I} & 0\\ 0 & -\boldsymbol{I}\end{pmatrix} - \begin{pmatrix}\boldsymbol{A} & \boldsymbol{B}\\ \boldsymbol{B}^* & \boldsymbol{A}^*\end{pmatrix}\right\}\begin{pmatrix}\delta\psi^{(+)}\\ \delta\psi^{(-)*}\end{pmatrix} = V_{\mathrm{ext}}\begin{pmatrix}\phi\\ \phi^*\end{pmatrix}$$

$$\boldsymbol{A}_{ij} = (h_0(\boldsymbol{r}) - \varepsilon_i)\,\delta(\boldsymbol{r}-\boldsymbol{r}')\,\delta_{ij} + \phi_i(\boldsymbol{r})\,\frac{\delta h(\boldsymbol{r})}{\delta n(\boldsymbol{r}')}\,\phi_j^*(\boldsymbol{r}')$$

$$\boldsymbol{B}_{ij} = \phi_i(\boldsymbol{r})\,\frac{\delta h(\boldsymbol{r})}{\delta n(\boldsymbol{r}')}\,\phi_j(\boldsymbol{r}')$$

Only occupied states are considered!

TDDFT is an exact theory for dynamics and excited state properties

More generally, assume: $\psi_i^{(+)}(\boldsymbol{r}) = \sum_m X_{im}\phi_m(\boldsymbol{r})$ $\psi_i^{(-)}(\boldsymbol{r}) = \sum_n Y_{in}^*\phi_n(\boldsymbol{r})$

$$\begin{pmatrix} \boldsymbol{A} & \boldsymbol{B} \\ \boldsymbol{B}^* & \boldsymbol{A}^* \end{pmatrix} \begin{pmatrix} \boldsymbol{X} \\ \boldsymbol{Y}^* \end{pmatrix} = \hbar\omega \begin{pmatrix} \boldsymbol{X} \\ -\boldsymbol{Y}^* \end{pmatrix}$$

Casida Equation

$$A_{im,jn} = (\varepsilon_m - \varepsilon_i)\,\delta_{mn}\delta_{ij} + \left\langle \phi_m\phi_j \left| \frac{\delta h}{\delta n} \right| \phi_i\phi_n \right\rangle$$

$$B_{im,jn} = \left\langle \phi_m\phi_n \left| \frac{\delta h}{\delta n} \right| \phi_i\phi_j \right\rangle$$

This is called frequency domain (linear response) TDDFT.

Advantages:

- **Straighforward for implementation**
- **Good description of optical spectra of molecules**
- **Excited state properties: PES, force, NAC**

TDDFT is an exact theory for dynamics and excited state properties

B). Real time TDDFT: $i\frac{\partial \varphi}{\partial t}(t) = \hat{H}(t)\varphi(t)$

$$\phi_j(t) = \mathcal{U}(t, t_0)\phi_j(t_0), \quad j = 1, \ldots, N_e,$$

$$\mathcal{U}(t, t_0) = \hat{T} \exp\left(-i \int_{t_0}^{t} \mathcal{H}_{KS}(\tau)\, d\tau\right)$$

Advantages:

- **Beyond linear response**
- **Non-equilibrium**
- **Local information, transport**
- **TDDFT + MD → Nonadiabatic dynamics**

Beyond Born-Oppenheimer (BO) dynamics

$$\Psi(\mathbb{r},\mathbb{R},t)=\sum_{l=0}^{\infty}\Psi_l(\mathbb{r},\mathbb{R})\,\Xi_l(\mathbb{R},t)$$ **(Born-Huang expansion)**

$$i\frac{\partial}{\partial t}\Xi_k(\mathbb{R},t)=\left[-\sum_{j=1}^{N_n}\frac{\nabla^2_{\mathbf{R}_j}}{2M_j}+E_k(\mathbb{R})\right]\Xi_k(\mathbb{R},t)-\sum_{l=0}^{\infty}\sum_{j=1}^{N_n}\frac{1}{2M_j}\left[\boldsymbol{\tau}^j_{kl}\cdot\nabla_{\mathbf{R}_j}+\widetilde{\tau}^j_{kl}\right]\Xi_l(\mathbb{R},t).$$

$$\boldsymbol{\tau}^j_{kl}=\int d\mathbb{r}\;\Psi^*_k(\mathbb{r},\mathbb{R})\nabla_{\mathbf{R}_j}\Psi_l(\mathbb{r},\mathbb{R})$$

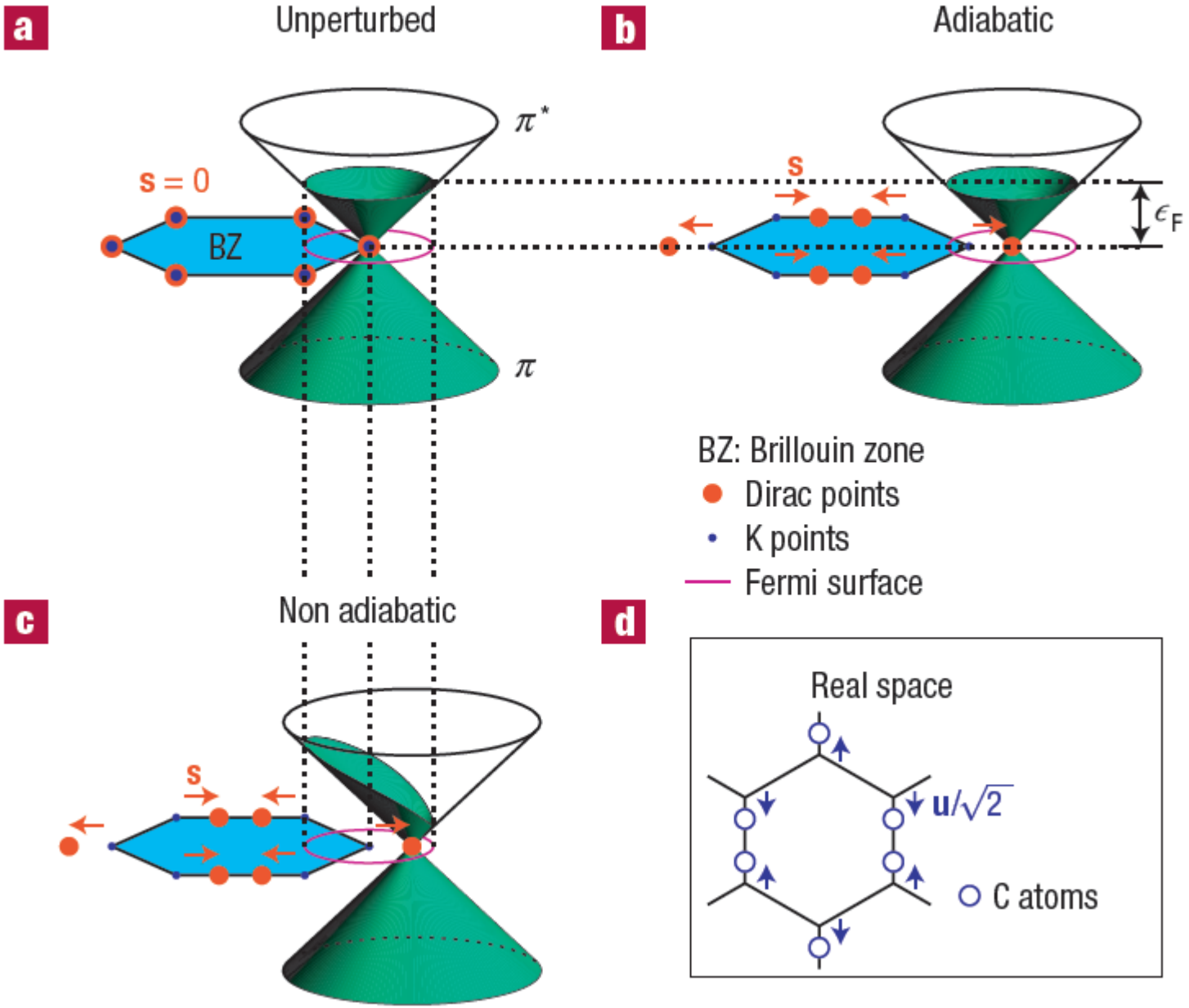
$$\widetilde{\tau}^j_{kl}=\int d\mathbb{r}\;\Psi^*_k(\mathbb{r},\mathbb{R})\nabla^2_{\mathbf{R}_j}\Psi_l(\mathbb{r},\mathbb{R})$$

(nonadiabatic couplings)

$$i\frac{\partial}{\partial t}\Xi_k(\mathbb{R},t)=\left[-\sum_{j=1}^{N_n}\frac{\nabla^2_{\mathbf{R}_j}}{2M_j}+E_k(\mathbb{R})\right]\Xi_k(\mathbb{R},t),$$

$$M_j\frac{\partial^2}{\partial t^2}\mathbf{R}_j(t)=-\nabla_{\mathbf{R}_j}E_k(\mathbb{R})$$

(BOMD/CPMD; AIMD)



Pisana et al., Nat. Mater. 6, 198 (2007).

II. Current status and applications of TDDFT

Many popular codes now contain TDDFT:

Frequency domain:

- **Gaussian**
- **MolPro**
- **ABINIT**
- **YAMBO**
- **OCTOPUS**
- **exciting**
- **…**

Real time:

- **NWChem**
- **GPAW**
- **CP2K**
- **SALMON**
- **OCTOPUS**
- **…**
- **many home-made ones**

Major developers

- **EKU Gross**
- **E Casida**
- **K Yabana/GF Bertsch**
- **K Burke**
- **A Rubio**
- **S Baroni**
- **Y Miyamoto**
- **I Tavernelli**

- **OV Prezhdo**

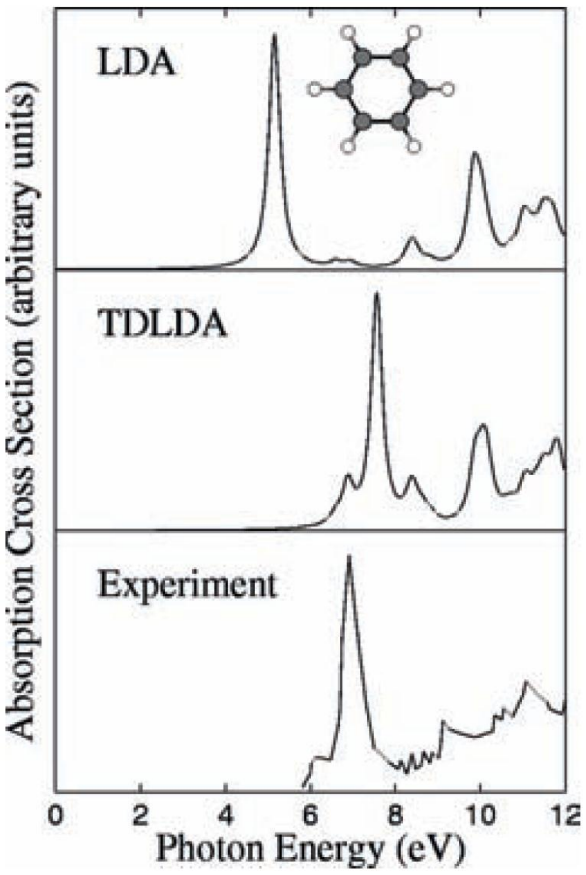
- **JM Li**
- **SW Gao**
- **GH Chen (LODESTAR)**
- **H Zhang**
- **J Zhao**
- **S Meng**
- **…**

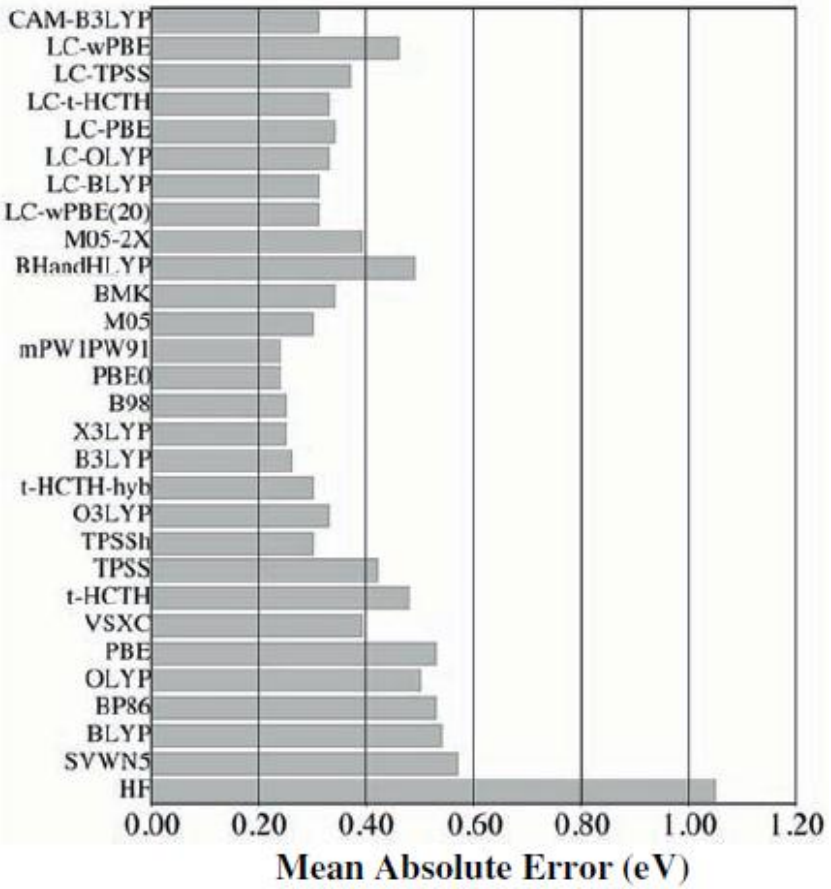
Some common features:

- **Tiny timestep ~1-10 as**
- **Stability, convergence**
- **Heavy computation, > 10-1000 times heavier than DFT**
- **Functionals**
- **How to prepare physically-sound initial states?**
- **Open systems**
- **Nonadiabatic effects**
- **Spin-orbital coupling? Relativistic effect?**

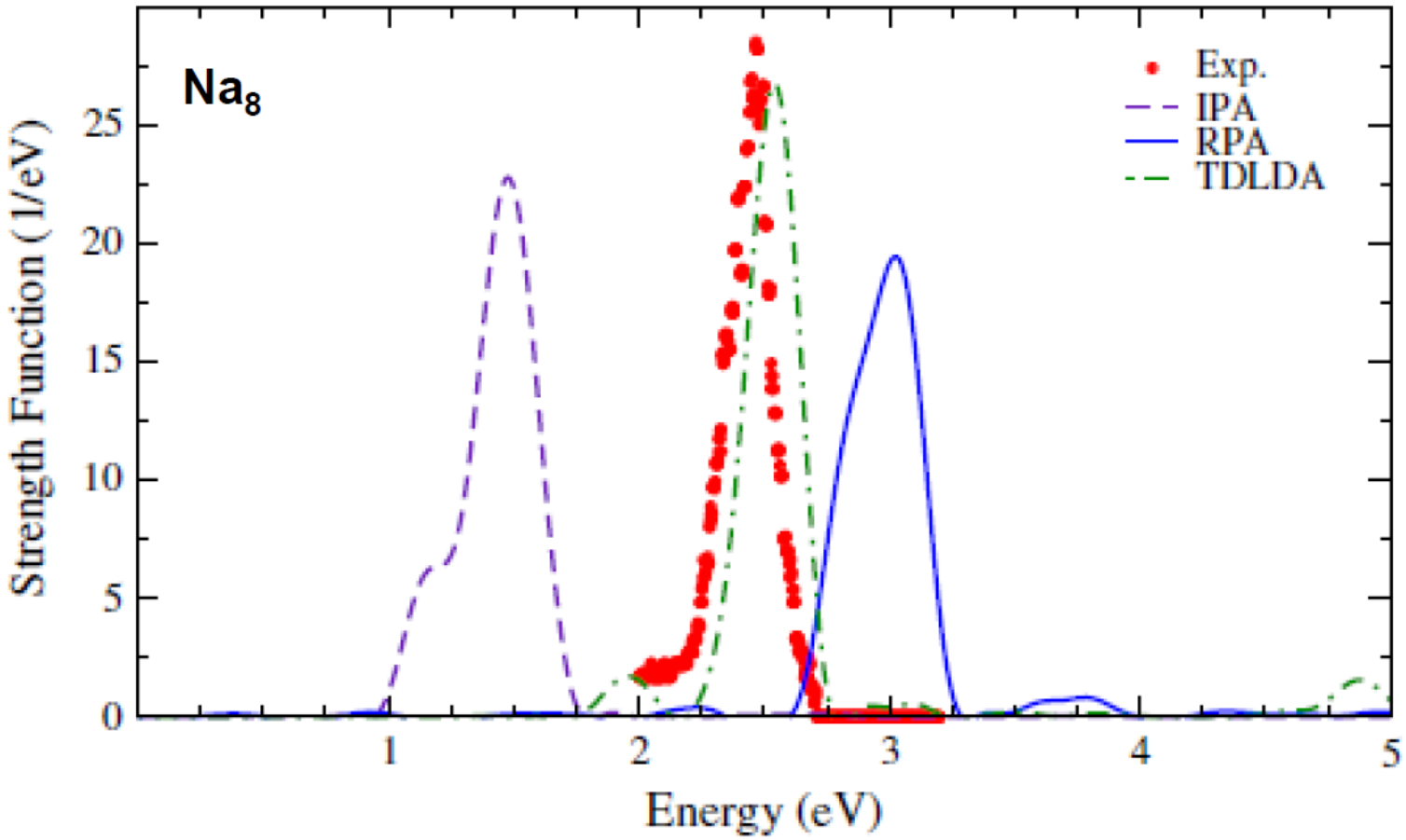
Applications of TDDFT

- Photoabsorption spectrum (Corrected Optical Bandgap)

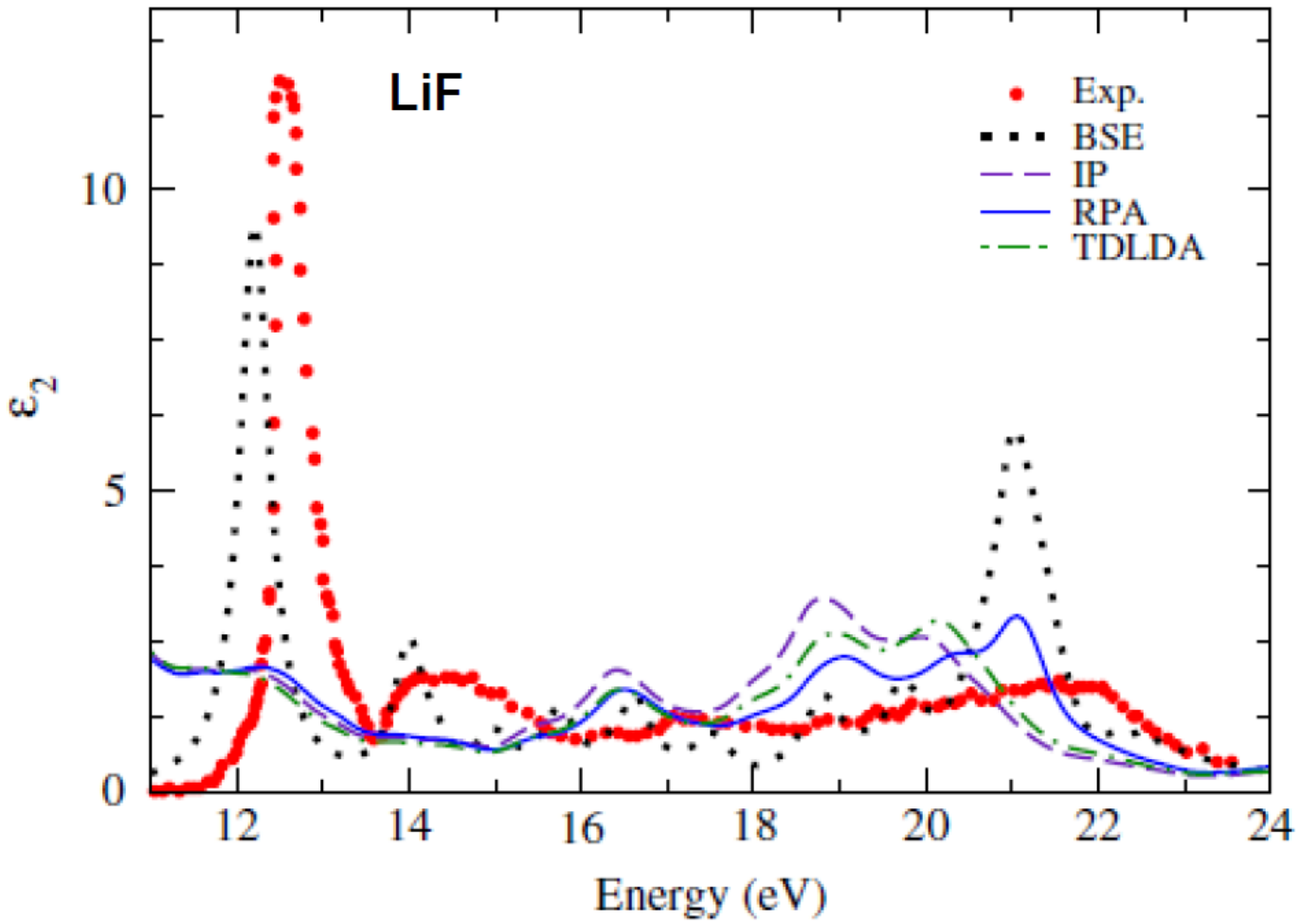




Vasiliev et al. (2002); Jacquemin et al. (2009)



S. Botti et al., Rep. Prog. Phys. 70, 357 (2007).



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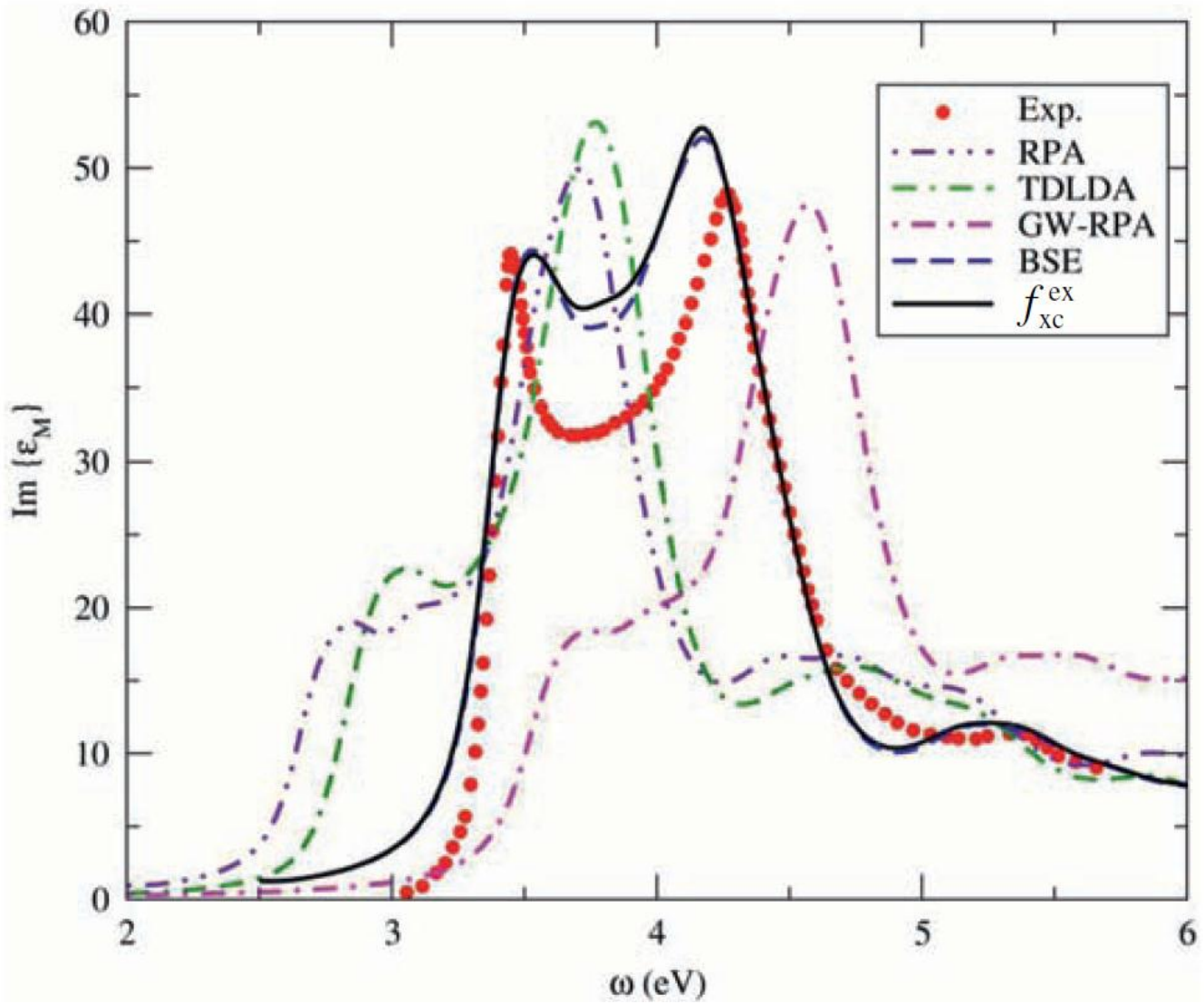
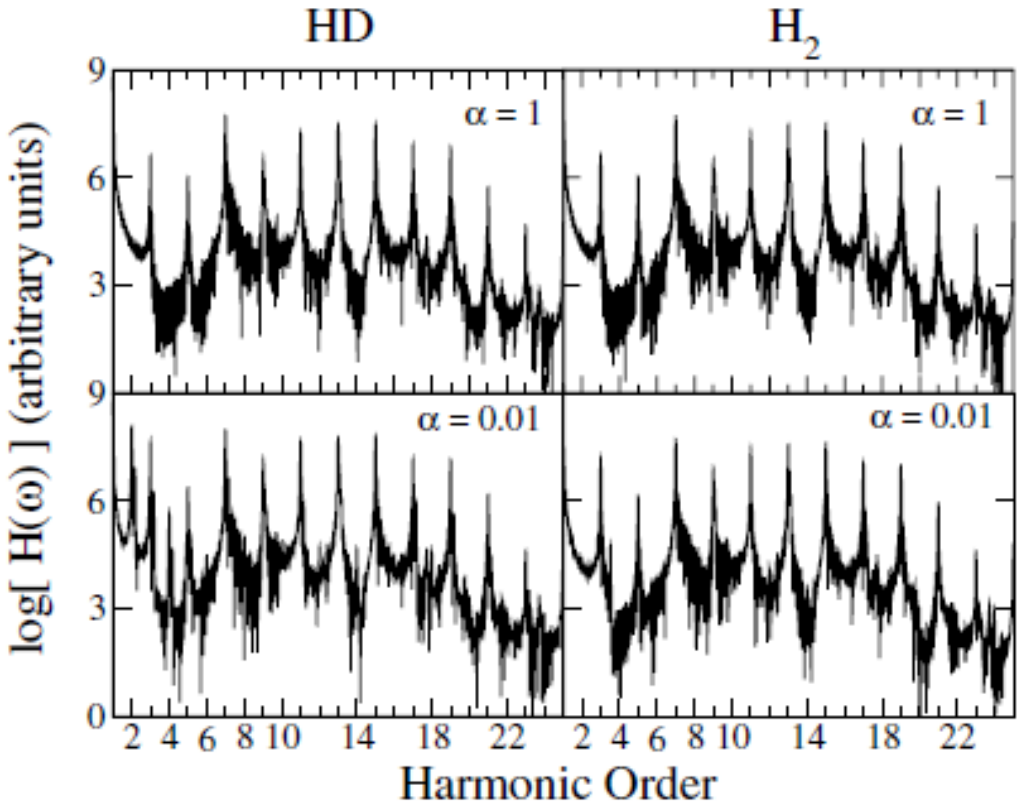


S. Botti et al., Rep. Prog. Phys. 70, 357 (2007)

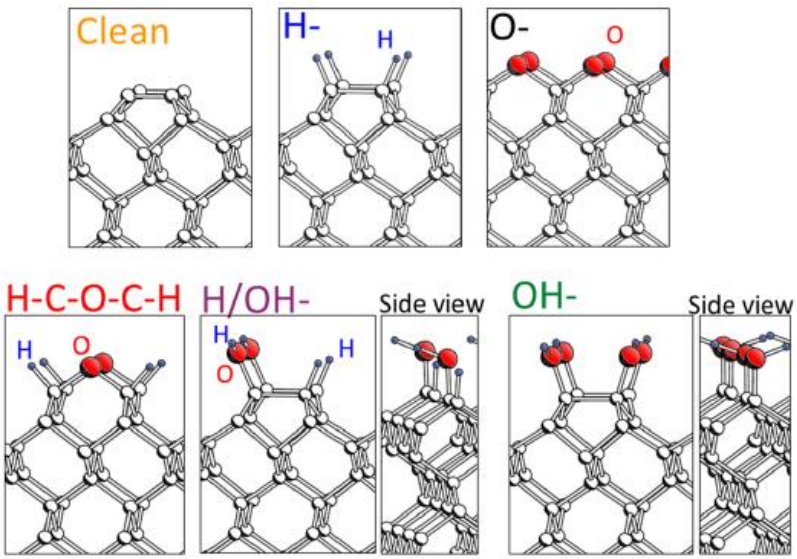
- Nonlinear optics

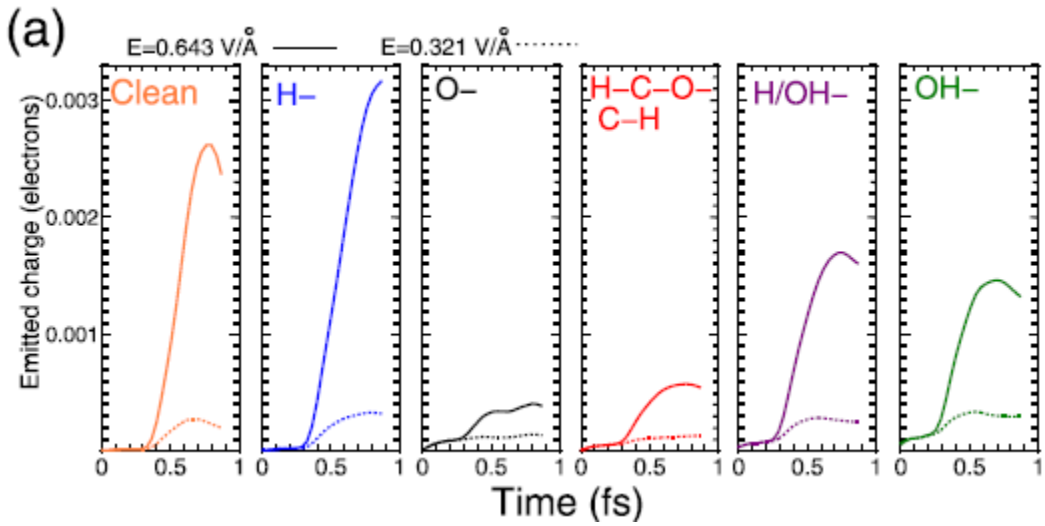
High harmonic generation $H(\omega) \sim \left| \int \mathrm{d}t \, e^{i\omega t} \frac{\mathrm{d}^2}{\mathrm{d}t^2} \langle \Psi(t) | \, \hat{e} \cdot \boldsymbol{D} \, | \Psi(t) \rangle \right|^2$



Castro et al. Eur. Phys. J. D 28, 211(2004).

- Photoemission

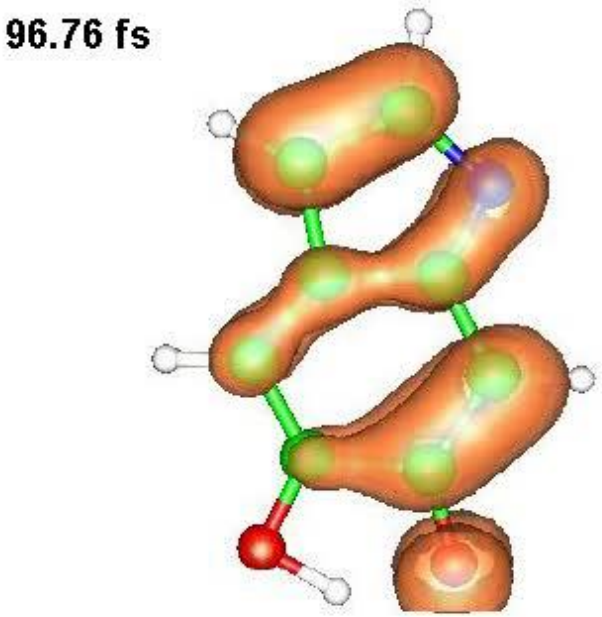


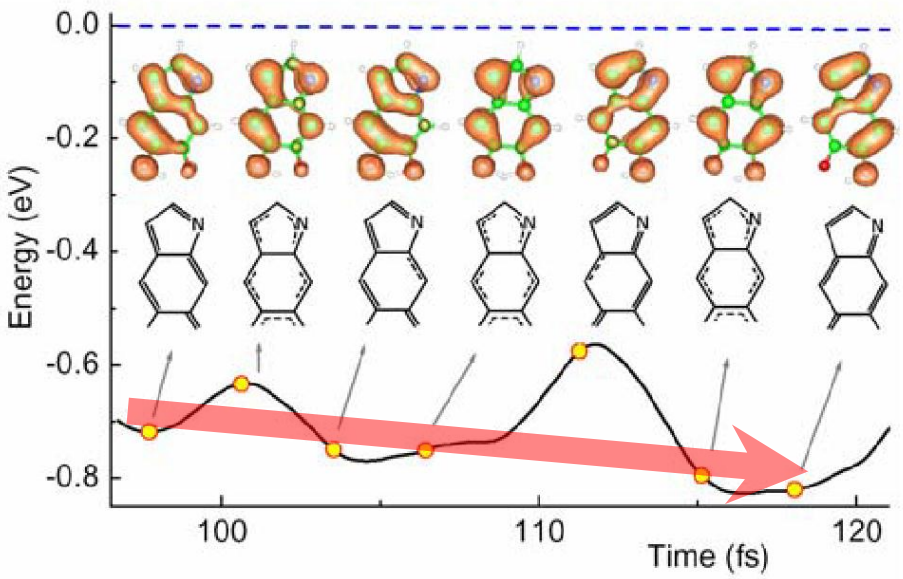


Miyamoto et al. APL (2013).

- Photodynamics in a molecule

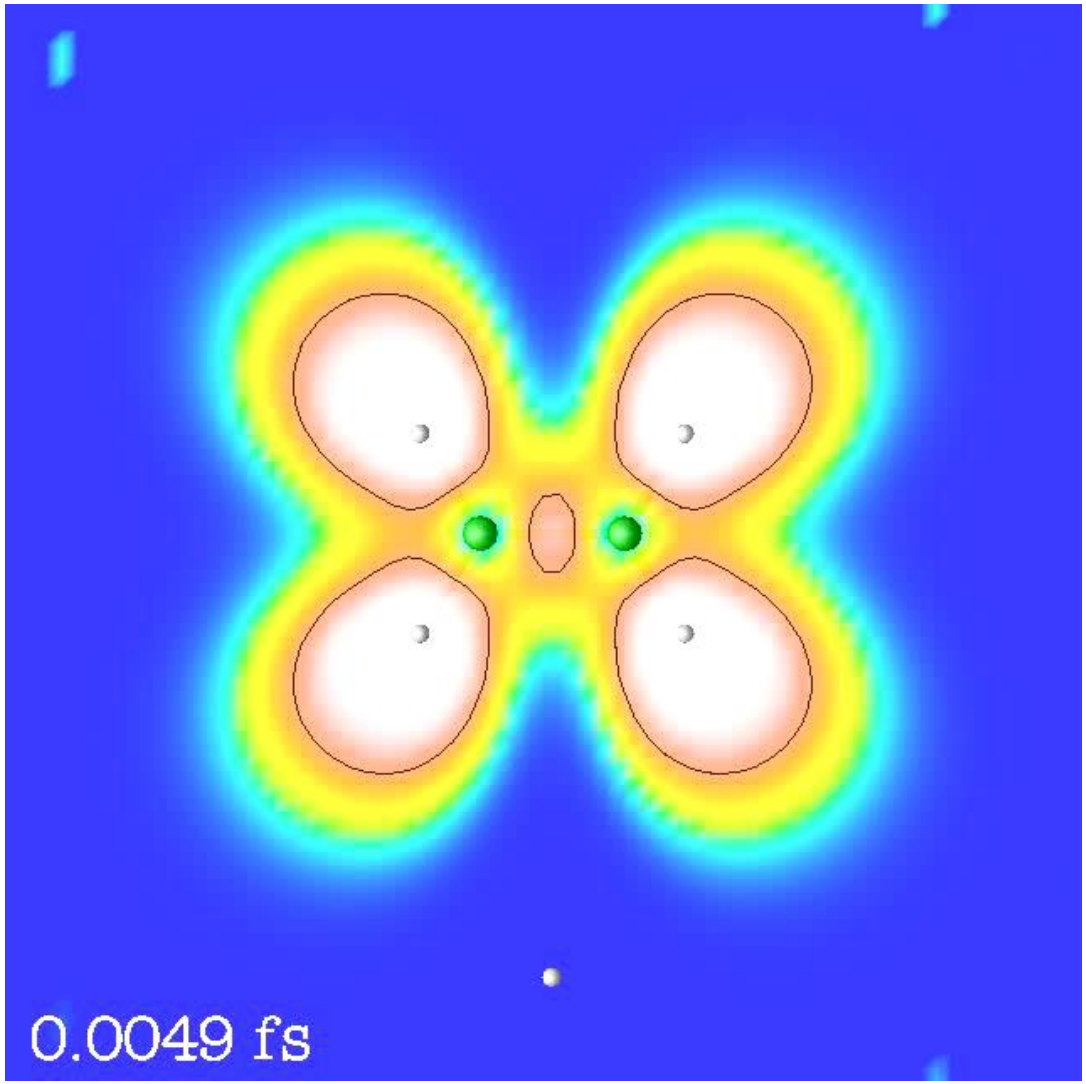
e-proton concerted dynamics





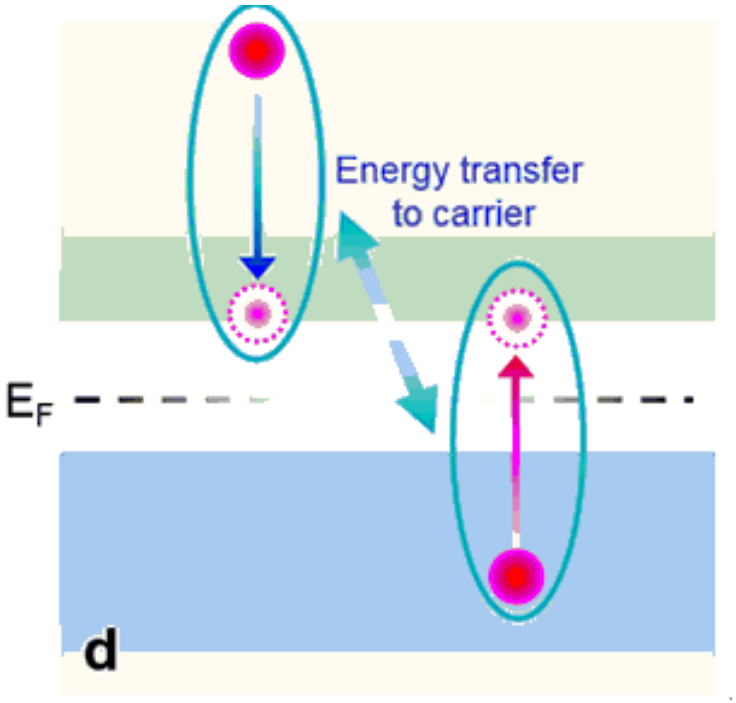
Clouds = e density in excited state

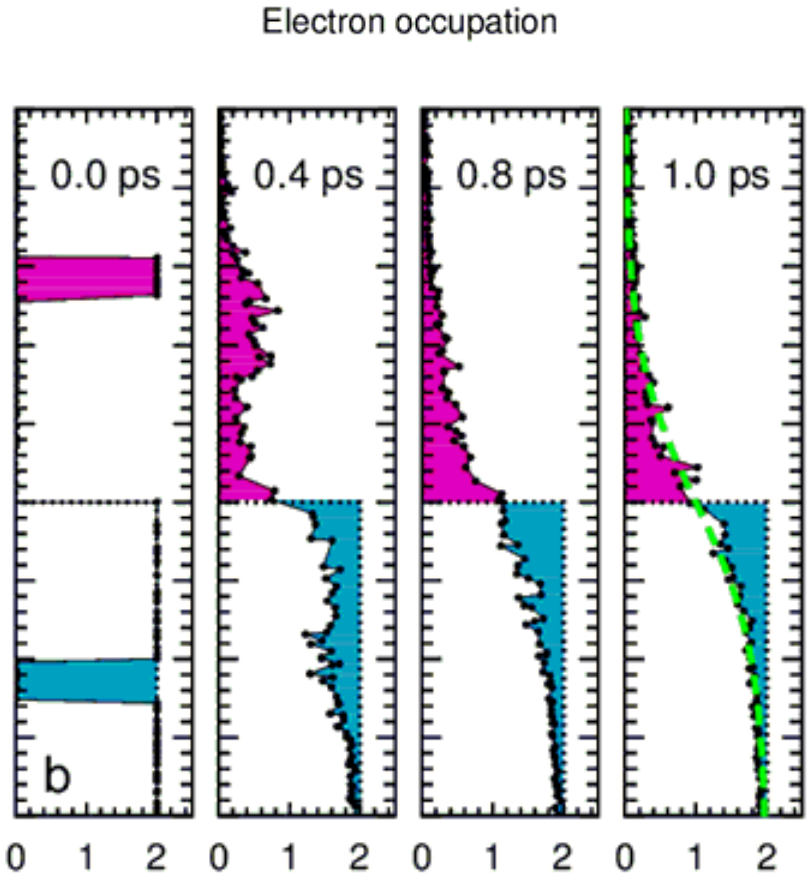
- Femtosecond dynamics



Burnus et al. PRA 71, 10501 (2005).

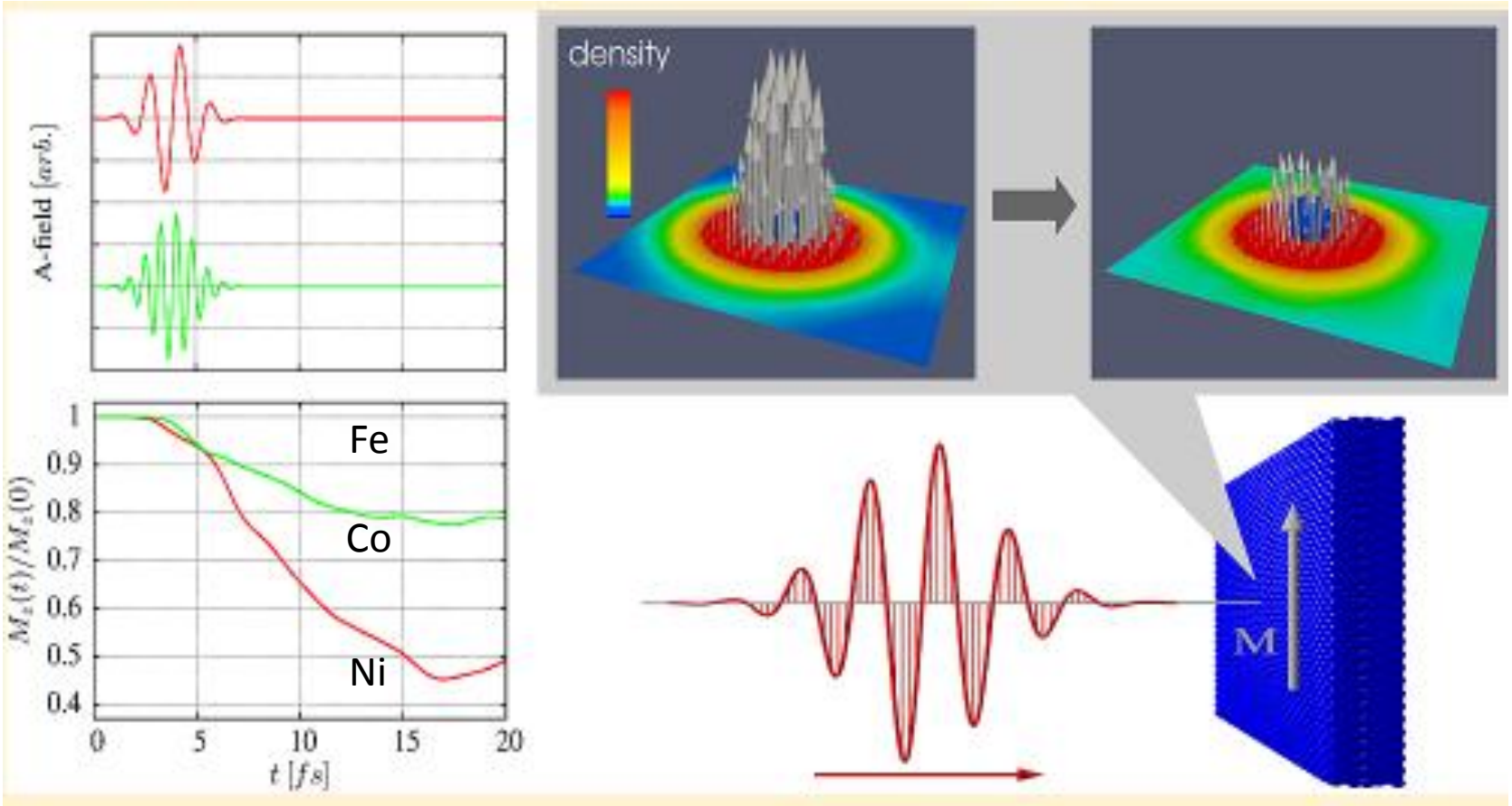
- Nonadiabatic process





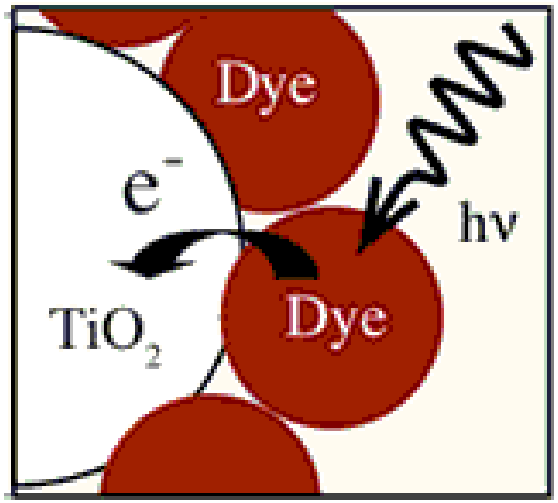
Bang et al.

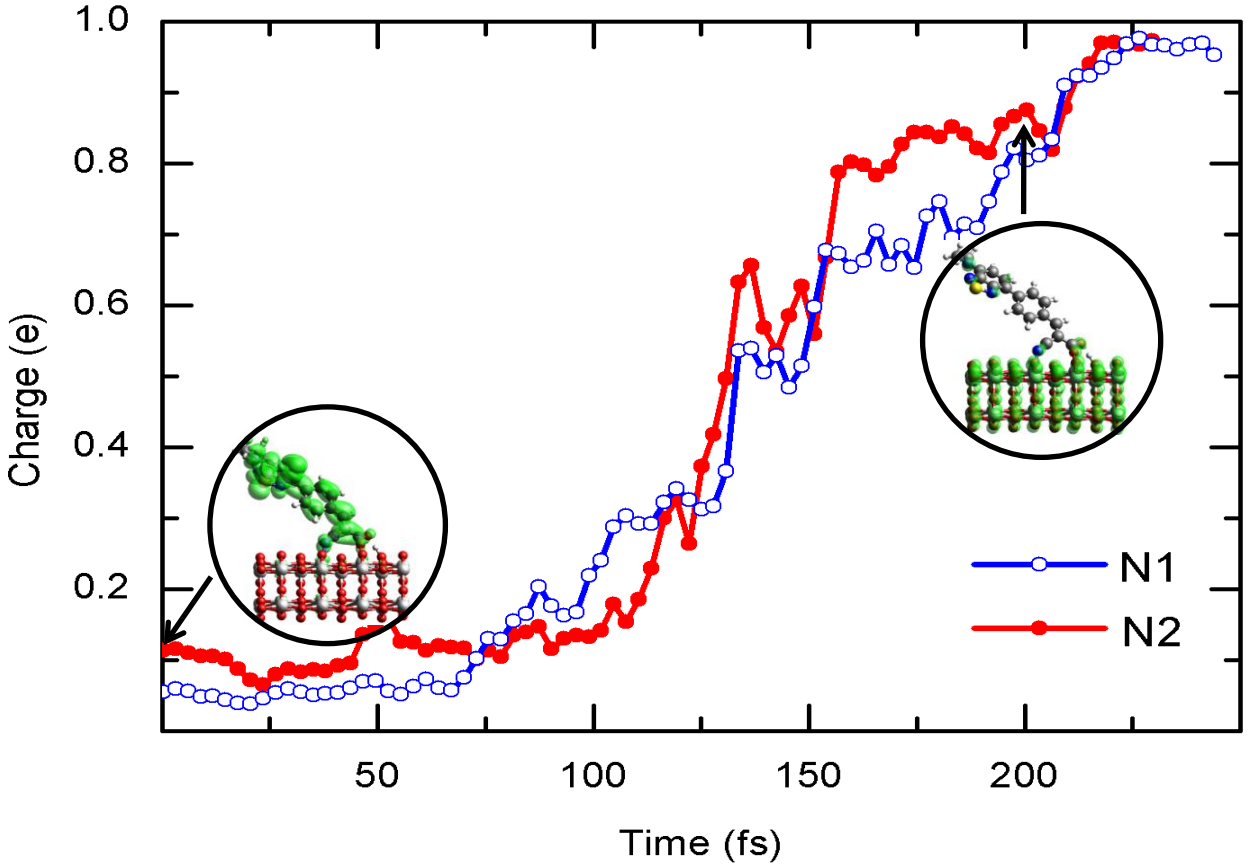
- Ultrafast demagnetization



Kreiger et al. JCTC (2015).

- Energy conversion



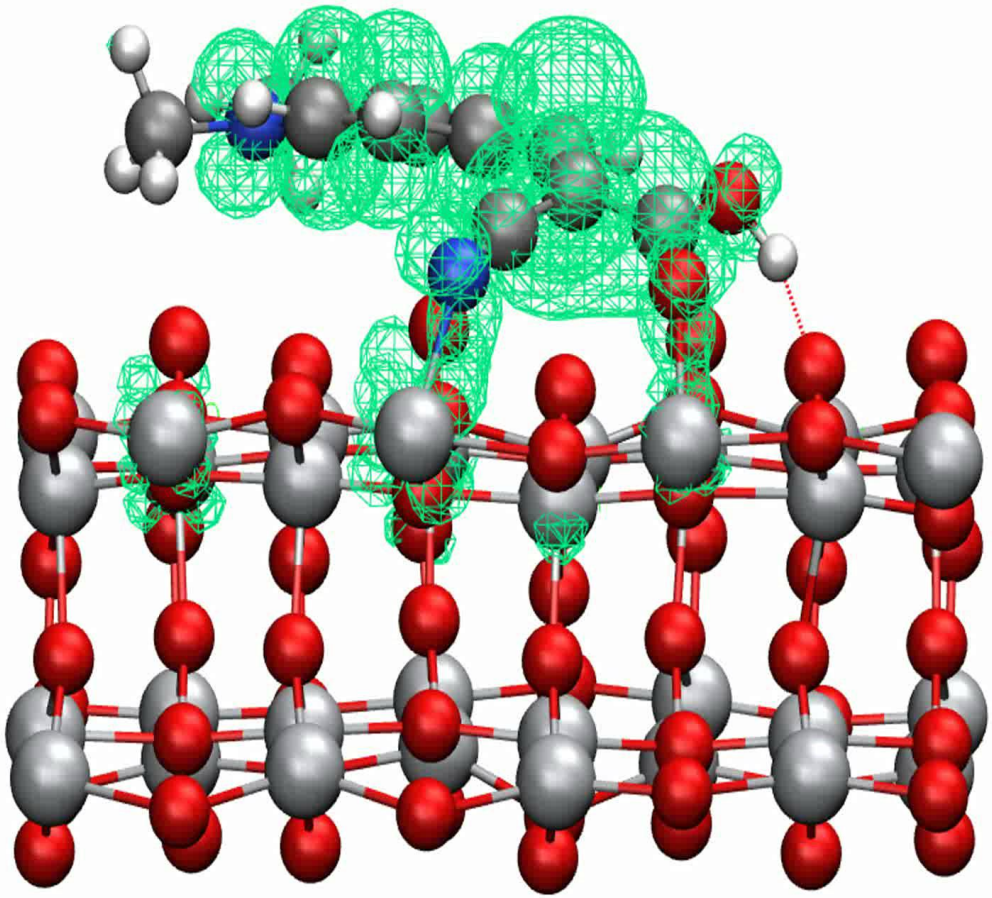


Meng*, Guo* et al. Nano Lett . (2016) .

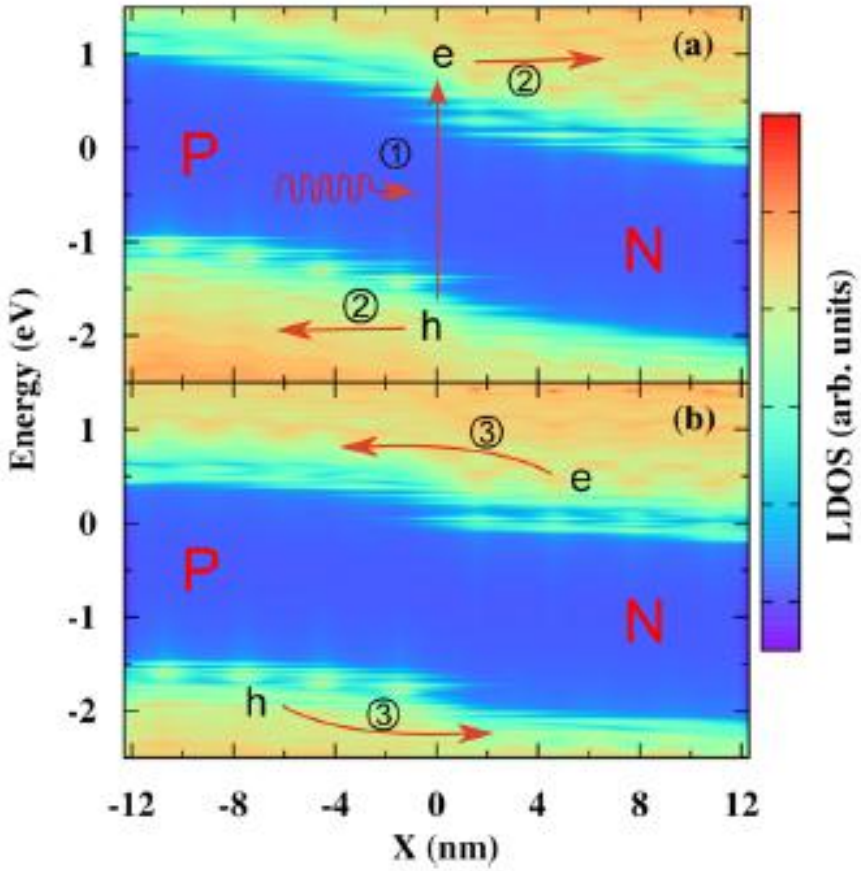
Electron Injection Dynamics

t = 5.8 fs

$$\Phi_{\text{inject}} = 1 \Big/ \left(1 + \frac{\tau_{\text{inj}}}{\tau_{\text{relax}}}\right)$$

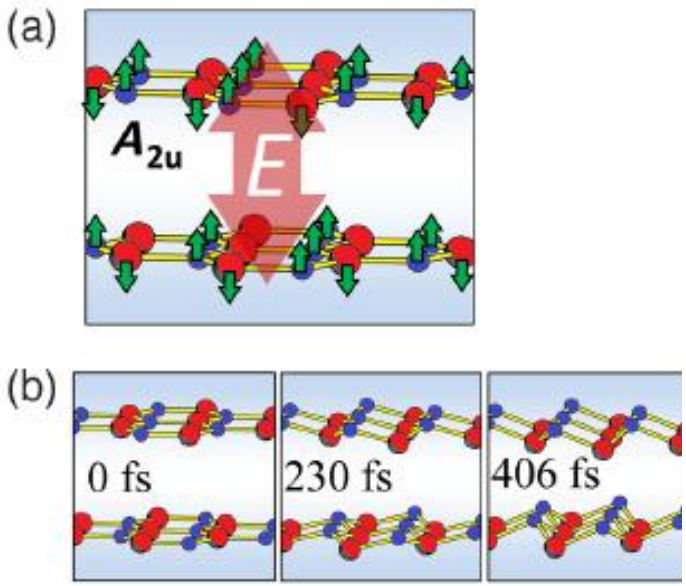


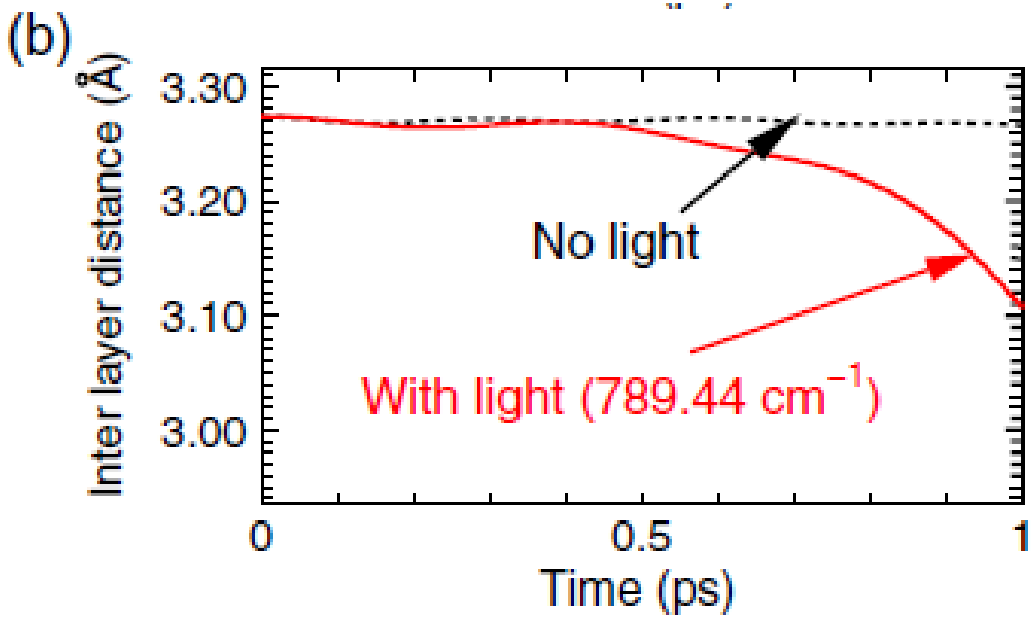
- Quantum transport



Chen GH et al. JPCL (2014).

- Light interaction with nanomaterials





Miyamoto, Zhang et al. PRL (2015).

Developing first-principle methods for e-ion dynamics

Time-dependent density functional theory (TDDFT) Gross 1984'

$$\Psi(\vec{r}_1,\vec{r}_2,....,\vec{r}_N;t) \rightleftharpoons \rho(\vec{r},t)=\int\left|\Psi(\vec{r},\vec{r}_2,....,\vec{r}_N;t)\right|^2\prod_{j=2}^{N}d\vec{r}_j$$

$$\text{Given } \Psi(0),\quad i\hbar\frac{\partial\Psi(t)}{\partial t}=\hat{H}\left[\rho(\vec{r},t),t\right]\Psi(t)$$

Coupled electron-ion dynamics **Beyond Born-Oppenheimer**

$$\begin{cases} i\hbar\dfrac{\partial\phi_j(\mathbf{r},t)}{\partial t} = \left[-\dfrac{\hbar^2}{2m}\nabla_{\mathbf{r}}^2+v_{ext}(\mathbf{r},t)+\displaystyle\int\frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'-\sum_I\frac{Z_I}{|\mathbf{r}-\mathbf{R}_I^d|}+v_{xc}[\rho](\mathbf{r},t)\right]\phi_j(\mathbf{r},t) \\ M_J\dfrac{d^2\mathbf{R}_J^d(t)}{dt^2} = -\nabla_{\mathbf{R}_J^d}\left[V_{ext}^J(\mathbf{R}_J^d,t)-\displaystyle\int\frac{Z_J\rho(\mathbf{r},t)}{|\mathbf{R}_J^d-\mathbf{r}|}d\mathbf{r}+\sum_{I\neq J}\frac{Z_JZ_I}{|\mathbf{R}_J^d-\mathbf{R}_I^d|}\right] \end{cases}$$

A new implementation:

- Real time (nonlinear, dynamics)
- Local bases: numeric atomic orbitals
- Paralleling over Kohn-Sham orbitals
- External field, spin excitation, large scale,…

TDAP

Time-Dependent
Ab-initio Package

References

- E.K.U. Gross, J.F. Dobson, and M. Petersilka, *Density functional theory of time-dependent phenomena* (Topics in Current Chemistry, vol 181, Springer, 1996).
- M. R. L. Marques, E. K. U. Gross, *Time-dependent density-functional theory*, Annu. Rev. Phys. Chem. 55, 427(2004).
- S. Botti et al., *Time-dependent density-functional theory for extended systems*, Rep. Prog. Phys. 70, 357 (2007).
- M.E. Casida and M. Huix-Rotllant, *Progress in Time-Dependent Density-Functional Theory*, Annu. Rev. Phys. Chem. 63, 287 (2012).
- C. A. Ullrich, *Time-Dependent Density-Functional Theory: Concepts and Applications* (Oxford Uni. Press, 2012).
- M. R. L. Marques et al. (ed.), *Fundamentals of Time-Dependent Density Functional Theory*, Springer (2012).