

松山湖材料实验室 材料计算与超算应用网络课程

SLAB Webinar on
Supercomputing & Materials Computation

密度泛函和含时密度泛函初步

孟胜

2020年2月26日

OUTLINE

I. Backgrounds

- Era of supercomputing and data science
- Computation + Materials

II. Basics of Density Functional Theory (DFT)

- Concept
- Elements for DFT calculation
- Typical applications

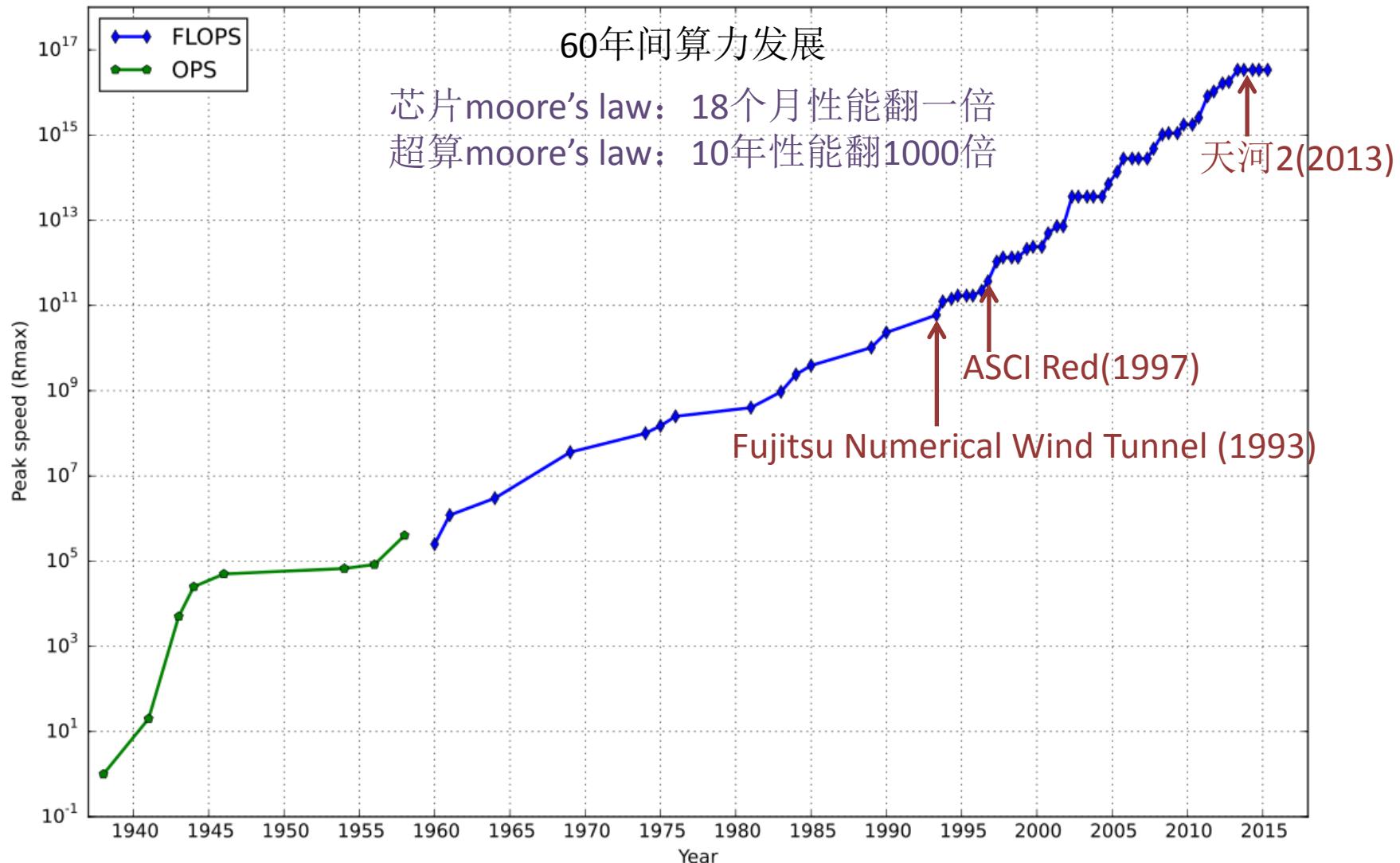
III. Basics of Time-dependent DFT (TDDFT)

- Why TDDFT ?
- TDDFT theorems, implications
- Current status, typical applications, challenges

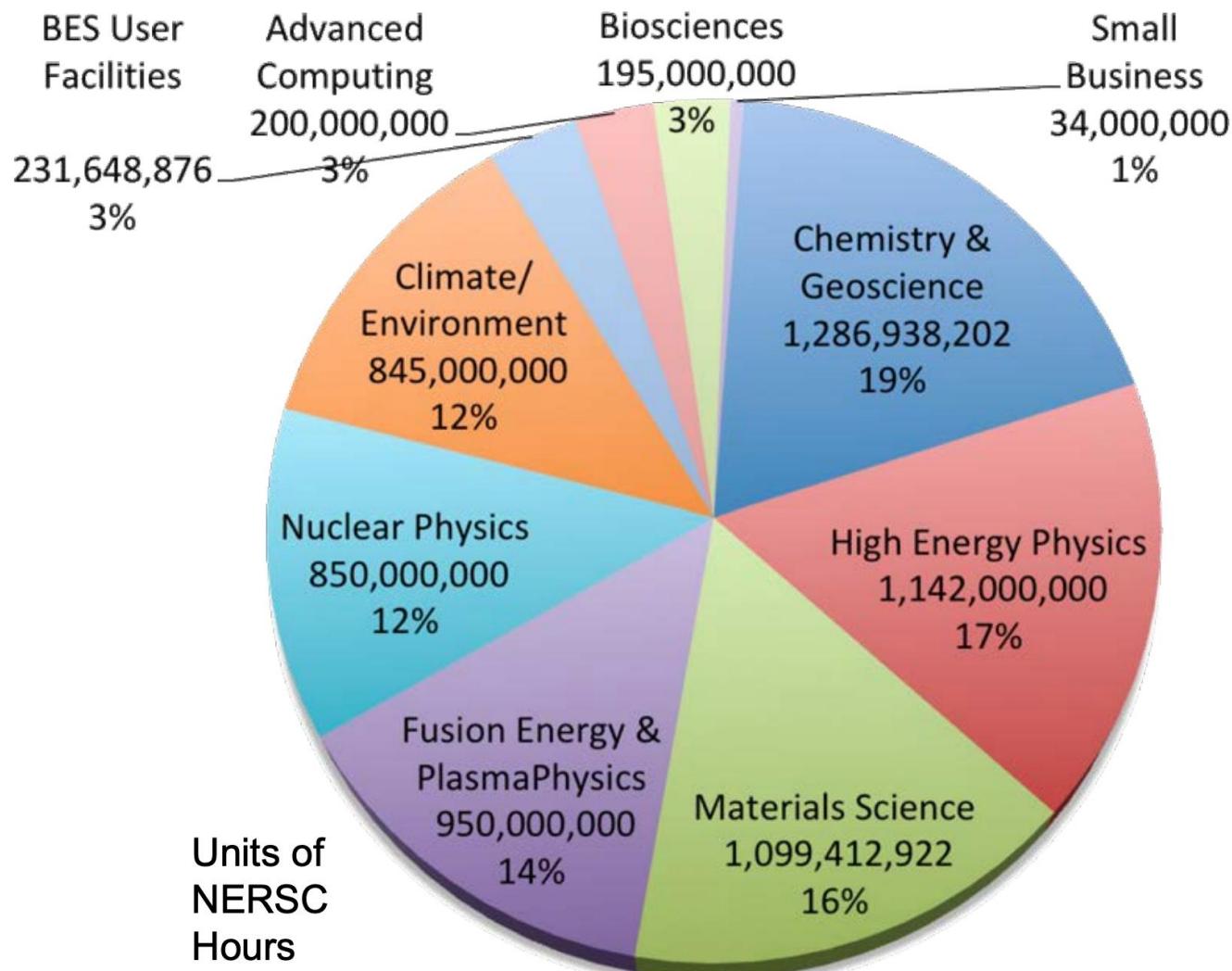


Supercomputing
超级计算

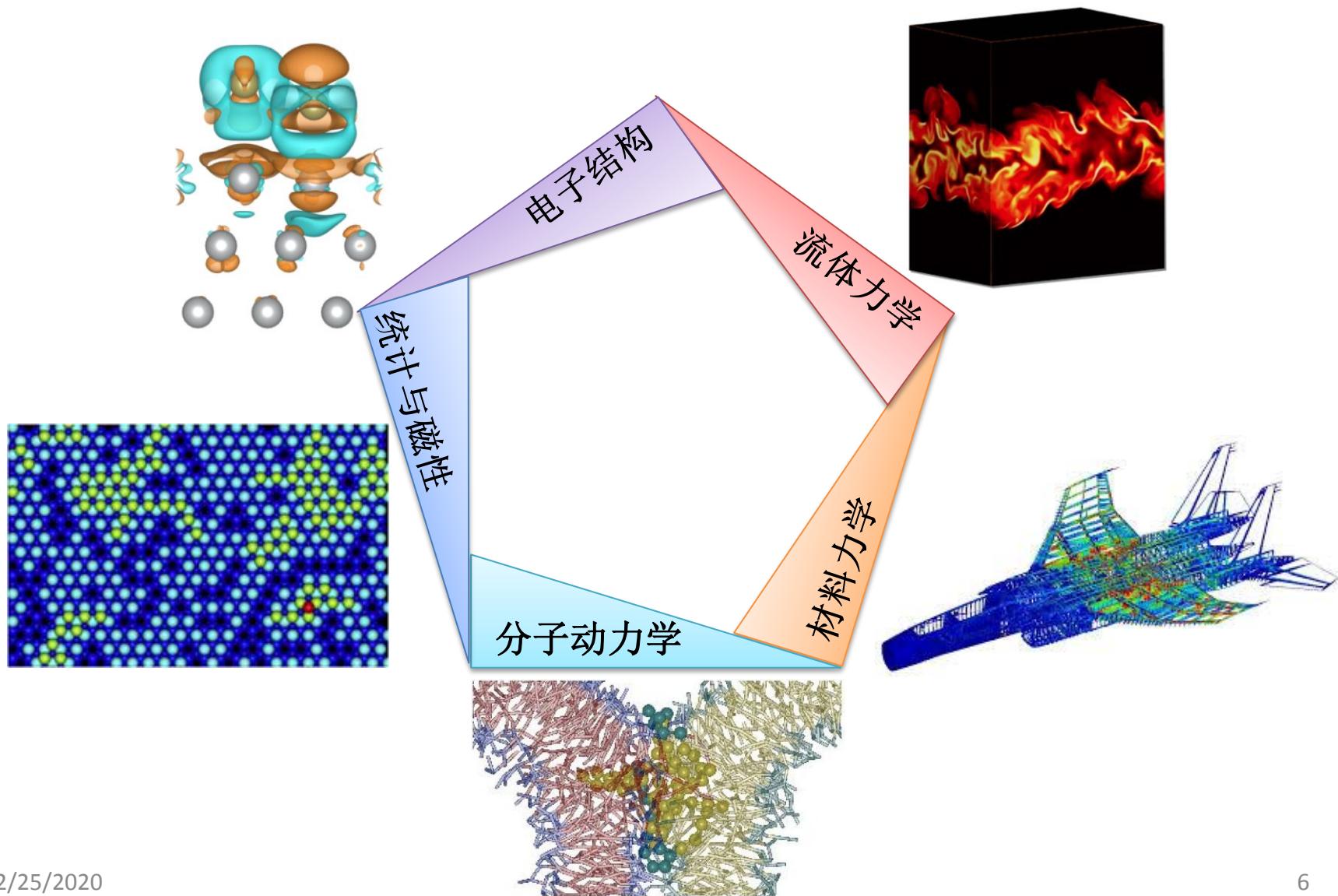
超算发展历程



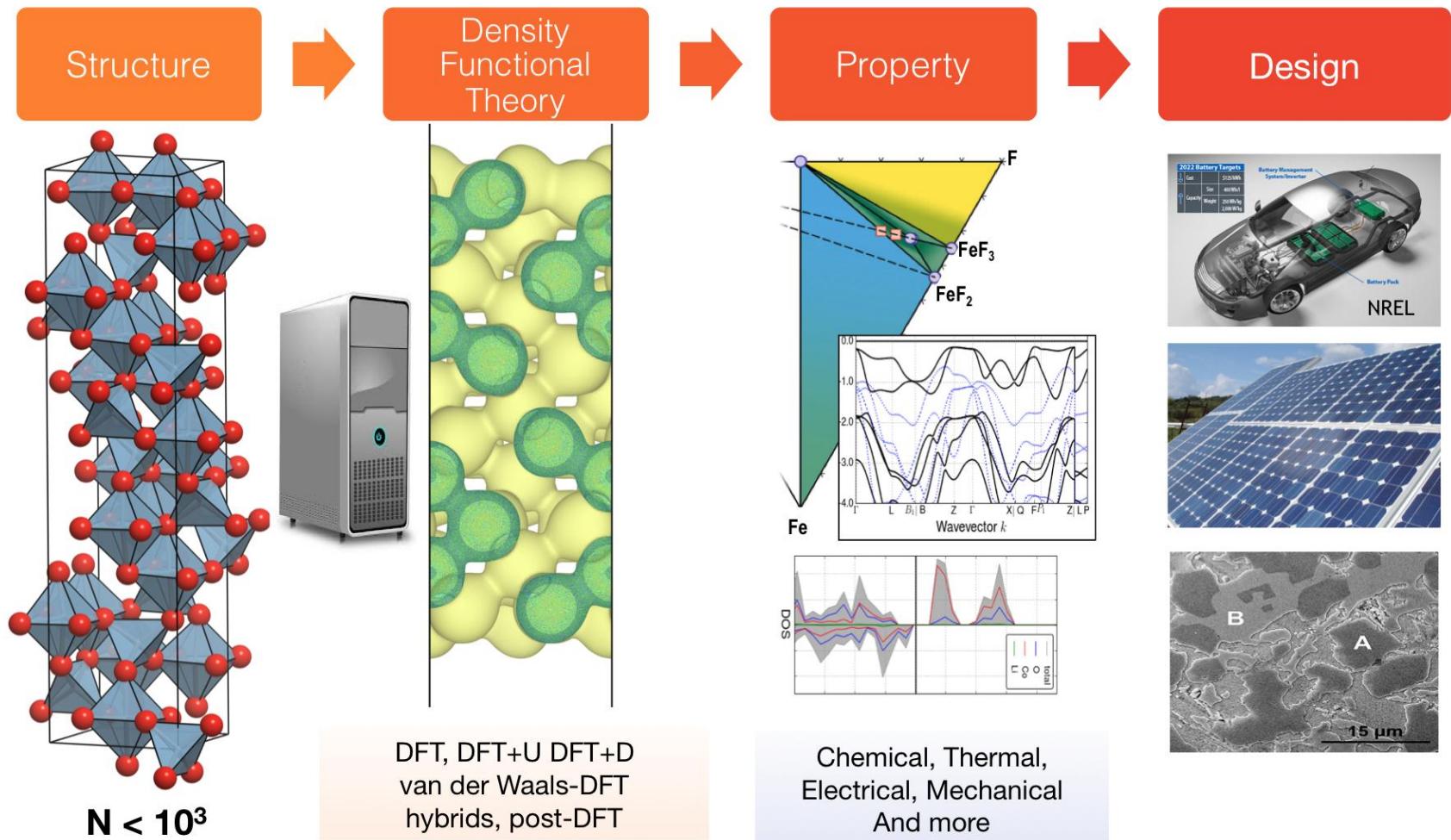
科学计算与超算



超算在材料科学领域的应用



材料计算的威力



材料计算的威力

Electronic Structure

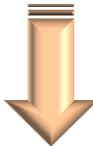
- Density Functional Theory
- Wave Function Method
- Quantum Monte Carlo



1998 Nobel Prize in Chemistry

Walter Kohn (DFT)

John A. Pople (Quantum chemistry methods)



Simulation of Atomic Nuclei in Materials Based on Electronic Structure

- Molecular Dynamics
- Structure Prediction
- Quantum-Classical Hybridization Method



2013 Nobel Prize in Chemistry

Martin Karplus

Michael Levitt

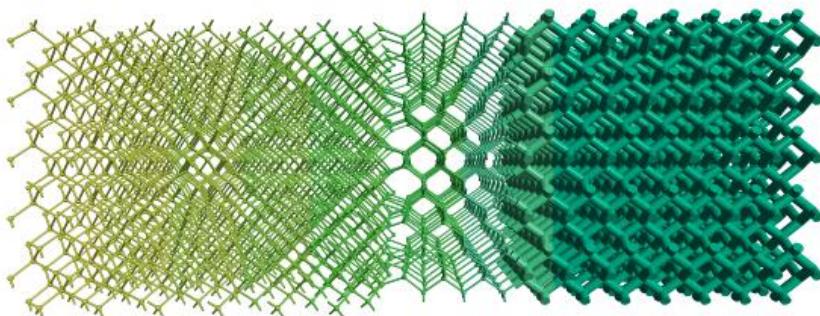
Arieh Warshel

Multiscale models for complex chemical systems

松山湖材料计算与数据库平台



- 180计算节点（含GPU节点，胖节点）6776核
- 8台**国产CPU**（海光）计算节点
- 100Gb/s 超高速低延时网络
- 计算能力 \sim 500 TFLOPS



单节点算力 \approx 天河二号 3.6倍
 \approx 天河一号 30+倍

超算应用与材料计算网课

Webinars on supercomputing and material computation

What we hope to cover:

1. Supercomputing Technology
2. Materials Computation
3. Materials Data

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II. Basics of Density Functional Theory (DFT)

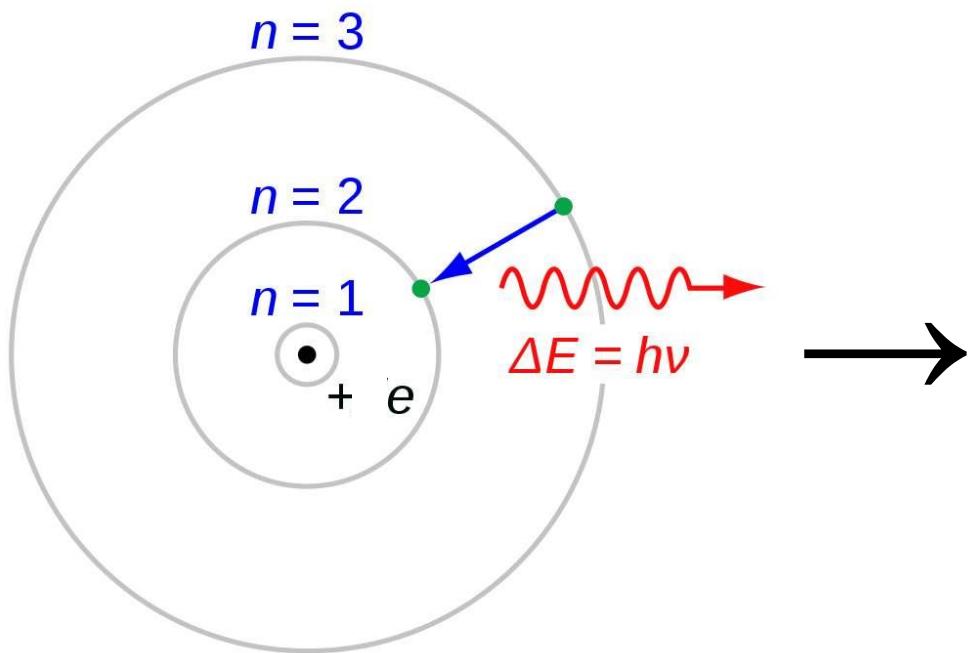
- Concept
- Elements for DFT calculation
- Typical applications

III. Basics of Time-dependent DFT (TDDFT)

- Why TDDFT ?
- TDDFT theorems, implications
- Current status, typical applications, challenges

The Problem

Hydrogen atom



Real materials



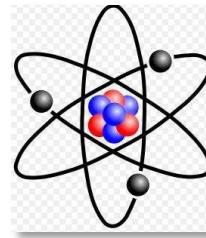
$$E_n = -\frac{e^4 m}{8n^2 \hbar^2 \epsilon_0^2}$$

$$r_n = \frac{4\pi\epsilon_0 n^2 \hbar^2}{me^2} \equiv n^2 a_0$$

?

Microscopic Description of Atoms

Physical Model: Electrons + Nucleus



Math Description: Schrödinger Equation:

$$\hat{H} \psi(\mathbf{r}, \mathbf{R}) = E \psi(\mathbf{r}, \mathbf{R})$$

Electron

Nucleus

$$\hat{H} = -\sum_I \frac{\hbar^2}{2m_I} \nabla_I^2 + \sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 + \sum_i \sum_I \frac{e^2 Z_I}{r_{iI}} + \sum_{i < j} \frac{e^2}{r_{ij}} + \sum_{I < J} \frac{e^2 Z_I Z_J}{r_{IJ}}$$

Kinetic energy

Kinetic energy

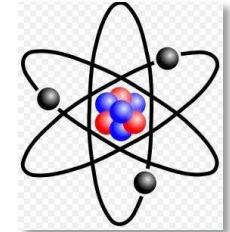
Coulomb interaction

Coulomb interaction

Electron-nucleus coupling

Born-Oppenheimer approximation

(Adiabatic approximation)



$\psi(\mathbf{r}, \mathbf{R}) = \psi_N(\mathbf{R}) \cdot \psi_{el}(\mathbf{r}; \mathbf{R}) \longrightarrow$ Separate electronic and nuclear motions

$\hat{H}_{el}(\mathbf{R})\psi_{el}(\mathbf{r}) = E(\mathbf{R})\psi_{el}(\mathbf{r}) \longrightarrow$ Only include electrons as quantum particles

$$\hat{H}_{el} = -\sum_I \frac{\hbar^2}{2m_I} \nabla_I^2 - \sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 - \sum_i \sum_I \frac{e^2 Z_I}{r_{il}} + \sum_{i < j} \frac{e^2}{r_{ij}} + \sum_{I < J} \frac{e^2 Z_I Z_J}{r_{IJ}}$$

- **Many-body problem**
- **A function of nuclear geometry**

Electronic Structure

Hartree-Fock Approximations

Slater Determinant of many-particle wave function:

$$\psi_{SD}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(1) & \varphi_2(1) & \cdots & \varphi_N(1) \\ \varphi_1(2) & \varphi_2(2) & \cdots & \varphi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_1(N) & \varphi_2(N) & \cdots & \varphi_N(N) \end{vmatrix} = |\varphi_1, \varphi_2 \dots \varphi_N\rangle$$
$$\hat{h}_i \varphi_i = \varepsilon_i \varphi_i$$

Limitation: lacking electron correlation

Post HF methods: more elaborate approximation for many-body wave function

- Configuration Interaction (CI) method
- Moller-Plesset (MP) perturbation theory
- Couple-Cluster(CC) method

Can be very accurate, But, ...scaling

Hartree-Fock Approximations: Scaling



Doubling every
18 months



30 years



10^6 increase in
performance

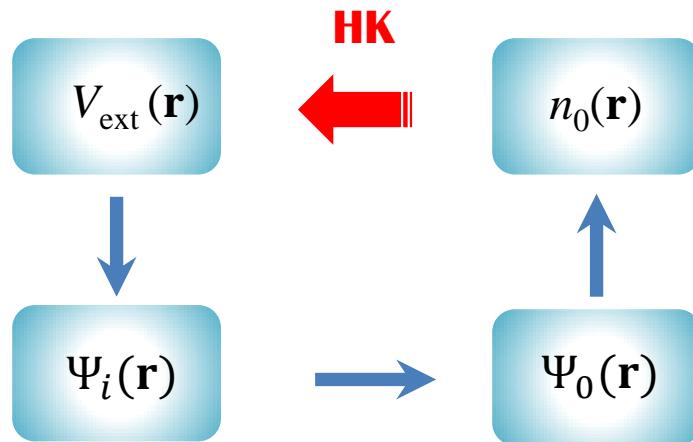
What does more computing buy us ?

Method	Today (electrons)	30 years	
HF + CI (N^6)	10	100	Atoms Small molecules
Potentials	10^8	10^{14}	
DFT (N^3)	1000	100,000	Molecules Condensed matter

Density Functional Theory: HK Theorems

Hohenberg-Kohn Theorem I: External potential $V_{\text{ext}}(\mathbf{r})$ is determined uniquely by the ground state particle density $n_0(\mathbf{r})$.

Hohenberg-Kohn Theorem II: For any given $V_{\text{ext}}(\mathbf{r})$, the exact ground state energy is the global minimum of $E[n(\mathbf{r})]$, and the density $n(\mathbf{r})$ minimizing $E[n(\mathbf{r})]$ is the exact ground state density $n_0(\mathbf{r})$.



Exact theory of many-body systems

Density Functional Theory: KS Scheme

Kohn-Sham scheme: A practical scheme

$$E[n(\mathbf{r})] = \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})] \quad (\text{HK Theorem I}) \quad n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2$$

$$E[n(\mathbf{r})] = \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + G[n(\mathbf{r})]$$

Hartree energy Unknown universal functional

$$E[n(\mathbf{r})] = \int V_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r} + \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{xc}[n(\mathbf{r})] + T^s[n(\mathbf{r})]$$

Exchange-correlation term Kinetic energy
Non-interacting system

KS scheme maps the complex, interacting electronic systems into a non-interacting systems, moving in an effective local potential.

Density Functional Theory: KS Scheme

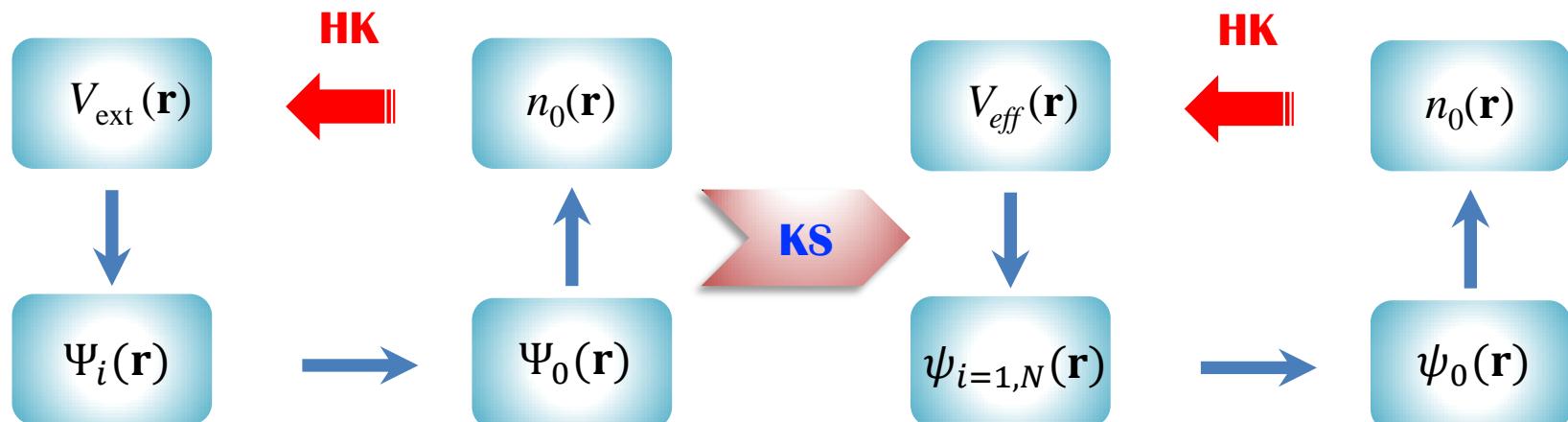
Kohn-Sham Hamiltonian of independent-particle system:

$$\hat{H}_{KS} = -\frac{1}{2}\nabla^2 + V_{eff}(\mathbf{r})$$

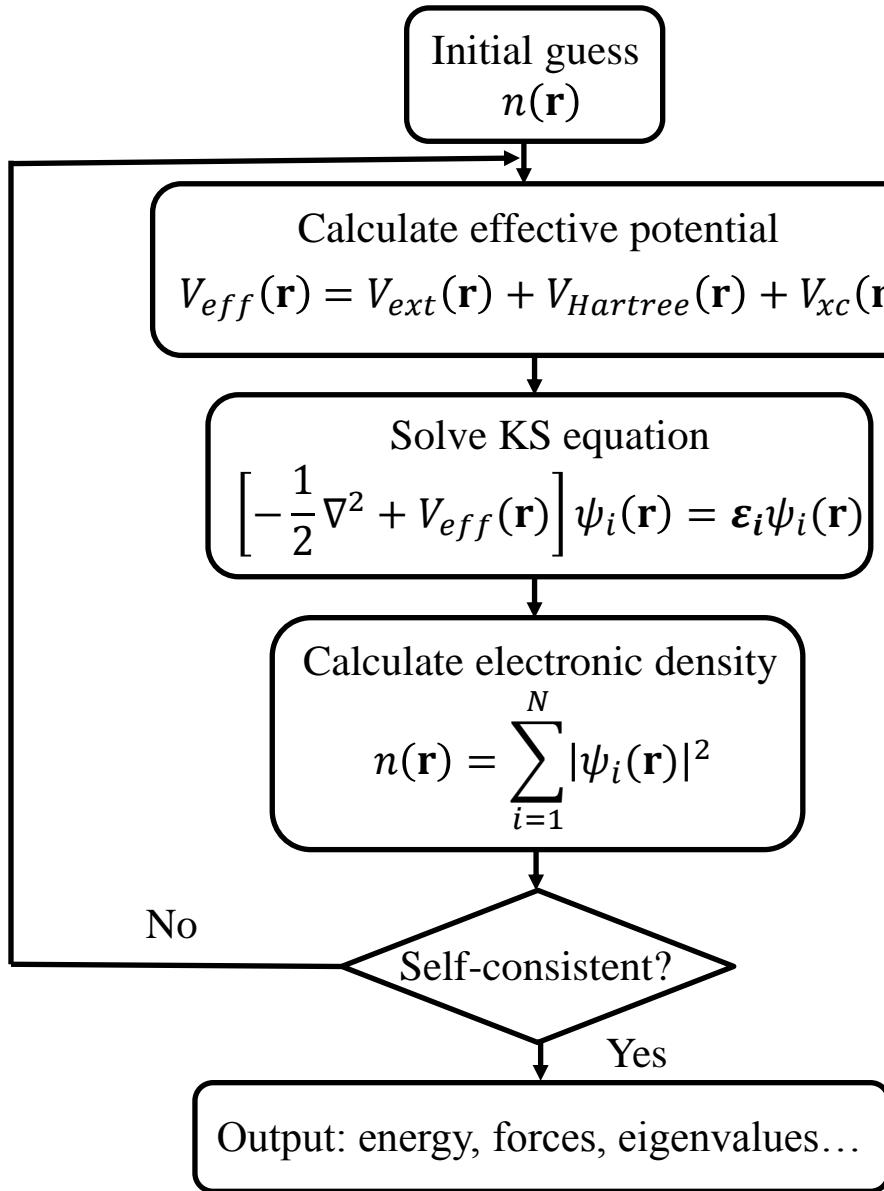
$$V_{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_{Hartree}(\mathbf{r}) + V_{xc}(\mathbf{r})$$

Kohn-Sham Equation: $\left[-\frac{1}{2}\nabla^2 + V_{eff}(\mathbf{r})\right]\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r})$

Two assumptions: “System of non-interacting particles” and “ $V_{eff}(\mathbf{r})$ ”



Flowchart of Solving KS Equation



Exchange and Correlation Functional

In KS scheme, all the many-body interaction complexity is put into exchange-correlation energy $E_{xc}[n(\mathbf{r})]$.

Exact expression is unknown, approximation is required!

- **Local density approximation (LDA)**

$$E_{xc}[n(\mathbf{r})] = \int n(\mathbf{r}) \varepsilon_{xc}[n(\mathbf{r})] d\mathbf{r} \quad \text{Homogeneous electron gas}$$

- **Generalized gradient approximation (GGA)** (PBE, PW, BLYP...)

$$E_{xc}[n(\mathbf{r})] = \int n(\mathbf{r}) \varepsilon_{xc}[n(\mathbf{r}), \nabla n(\mathbf{r})] d\mathbf{r} \quad \text{Gradient of the density}$$

- **Meta-GGA (SCAN)**

$$E_{xc}[n(\mathbf{r})] = \int n(\mathbf{r}) \varepsilon_{xc}[n(\mathbf{r}), \nabla n(\mathbf{r}), \tau(\mathbf{r}), \nabla^2 n(\mathbf{r})] d\mathbf{r}$$

Kinetic energy density τ and/or
the Laplacians of the density ∇^2

Exchange and Correlation Functional

- **vdW density functional** Dispersion corrections (vdW-DF2, optPBE-vdW, optB88-vdW)

$$E_{vdw-DF} = E_x^{GGA} + E_c^{LDA} + E_c^{nl}$$

$$E_c^{nl} = \frac{1}{2} \iint d^3\mathbf{r}_1 d^3\mathbf{r}_2 n(\mathbf{r}_1) \phi(\mathbf{r}_1, \mathbf{r}_2) n(\mathbf{r}_2)$$

- **DFT-D**

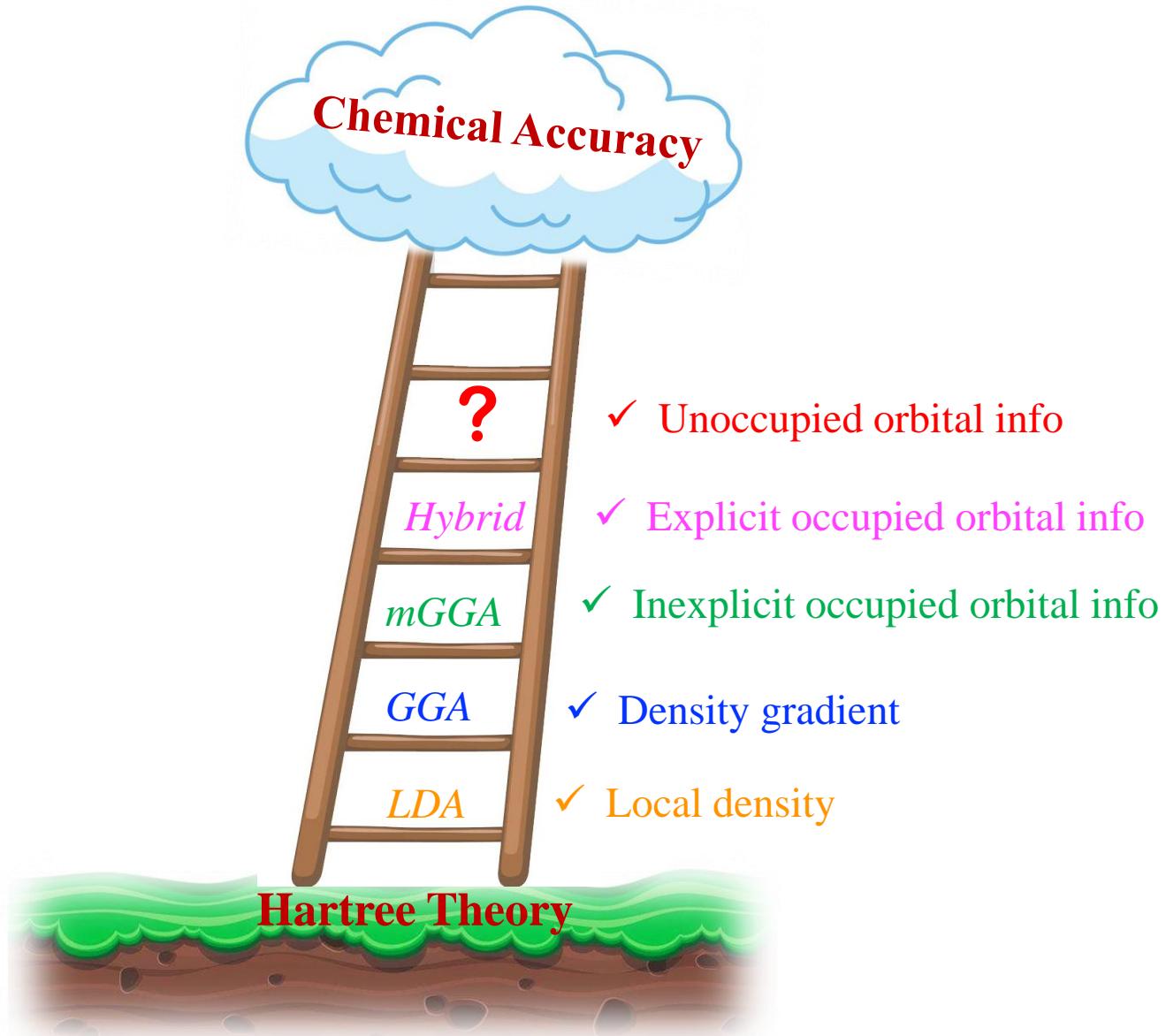
$$E_{DFT-D} = E_{KS} + C_6 R^{-6} f_{dmp}(R) \quad (\text{TS, DFT-D2})$$

- **Hybrid density functional** Exact exchange

$$E_{xc} = \alpha E_x^{exact} + (1 - \alpha) E_x^{GGA} + E_C^{GGA} \quad (\text{PBE0})$$

- ❖ Three-parameter hybrid functional (B3LYP)
- ❖ Screened hybrid functional (HSE)

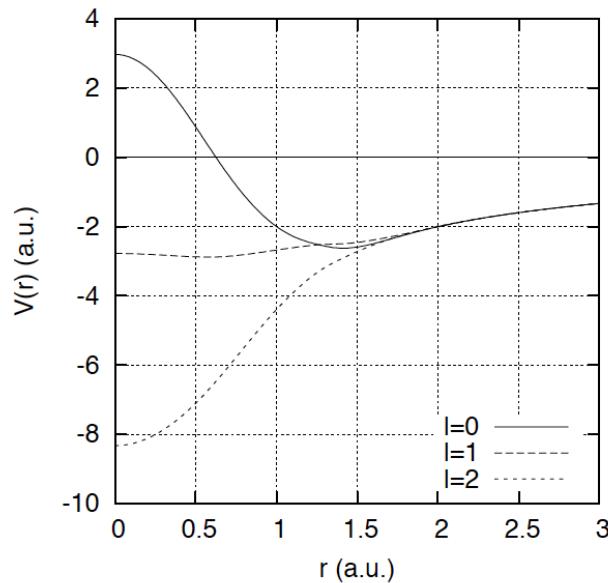
Jacob's Ladder



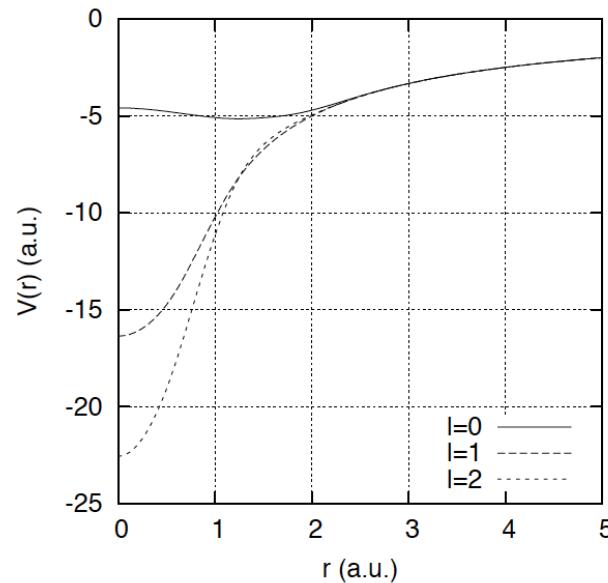
Pseudopotentials

Core electrons + Valence electrons

Core electrons can be replaced by an angular dependent **pseudopotentials**.



R_c

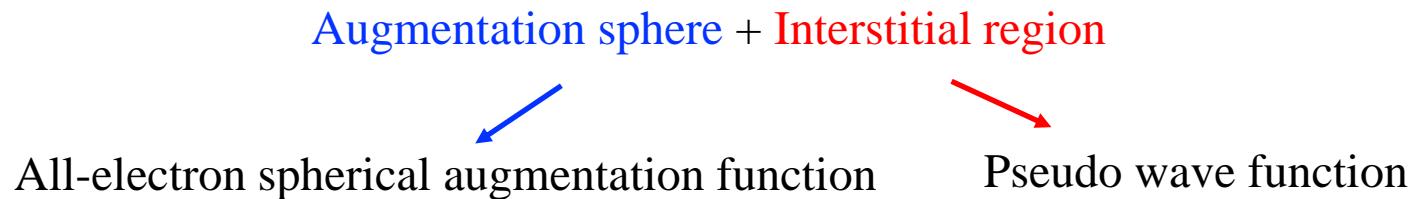


Si: $1s^2 2s^2 2p^6 3s^2 3p^2$
valence electron # = 4

Ti: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
valence electron # = 10

Pseudopotentials

- “**Norm-conserving (NC)**”: Integral of core region charge density = All-electron one
High accuracy, high transferability
Large cut-off radius of PW basis set
- “**Ultra-soft (US)**”: Smooth wave function in the core region, but not accurate in there
Small cut-off radius of PW basis set
- “**Projector augmented wave (PAW) method**”: All-electron + pseudopotential methods



Basis Sets

Plane waves: Bloch Theorem:

$$\begin{aligned} \text{Periodic potential } V(\mathbf{r} + \mathbf{T}) &= V(\mathbf{r}), & \mathbf{T} &\text{ lattice vector} \\ \psi_{\mathbf{k}}(\mathbf{r}) &= e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) & \mathbf{G} &\text{ reciprocal lattice vector} \\ u_{\mathbf{k}}(\mathbf{r} + \mathbf{T}) &= u_{\mathbf{k}}(\mathbf{r}) \end{aligned}$$

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_n e^{i\mathbf{G} \cdot \mathbf{r}} \quad \xrightarrow{\text{red arrow}} \quad \psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_n e^{i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}} \quad \text{Cut-off radius}$$

Localized orbitals: $\chi_{m\mathbf{k}}(\mathbf{r}) = A_{m\mathbf{k}} \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} \chi_m[\mathbf{r} - (\tau_m + \mathbf{T})]$

Scaling “order- N ”

Linear combination of atomic orbitals (LCAO)

Size: number of orbitals per atom

single- ζ to multiple- ζ with polarization and diffuse orbitals

DFT packages

According to the Potential:

Pseudo potential: VASP, CASTEP, ABINIT, STATE

Full potential: WIEN2K, FLEUR

According to the Basis:

Gaussian orbital or atomic orbital: GAUSSIAN, OpenMX

Plane wave: VASP, CASTEP, ABINIT

LMTO: TB-LMTO

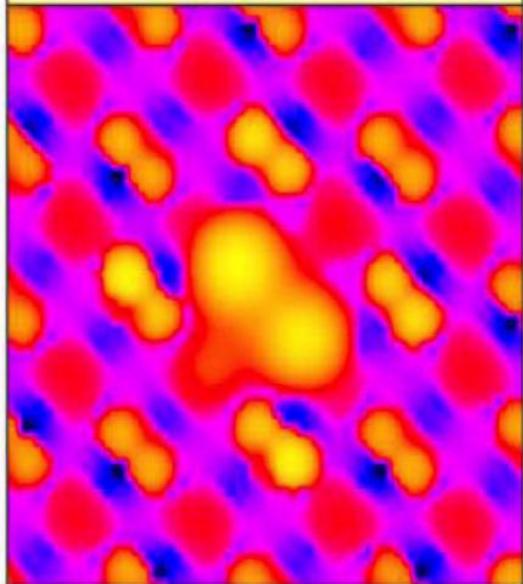
According to Money:

Free: ABINIT, PWSCF, STATE

Charged: VASP, WIEN2K

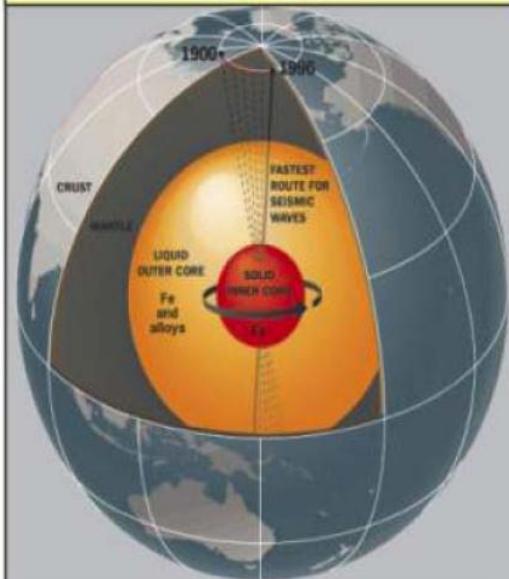
Typical Applications

**INTERPRET and
COMPLEMENT
Experiments**



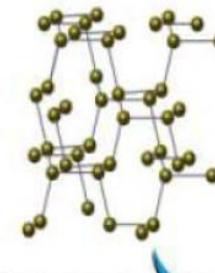
Determining surface
structure

**INVESTIGATE Properties
Not Directly Accessible
to Experiments**



Matter under extreme
conditions

**PREDICT Physical
Properties**



Polymeric



Diatomeric

Design of novel materials

Predicting the properties of matter based on laws of quantum mechanics!

Success of DFT

Surface chemistry and heterogeneous catalysis:

- 1) Adsorbate structure and energetics
- 2) Metals, ceramics, semiconductors, zeolites, etc.
- 3) Reaction pathways and transition states

Materials science

- 1) Bulk, surface, interface, defects
- 2) Electronic structure
- 3) Mechanical properties
- 4) Magnetic properties

Failures and extensions

Physics missing or incorrect:

- 1) Strongly correlation systems (late transition metal oxides, sulfides, actinides, etc.)
- 2) Excited states
- 3) Band gaps
- 4) Open shell systems

Extensions

- 1) Strongly correlated systems:
DMFT+DFT, LDA +U
- 2) Excited states:
GW+DFT, TDDFT, etc.
- 3) Nonequilibrium transport:
DFT+DEGF, TDDFT+NEGF

.....

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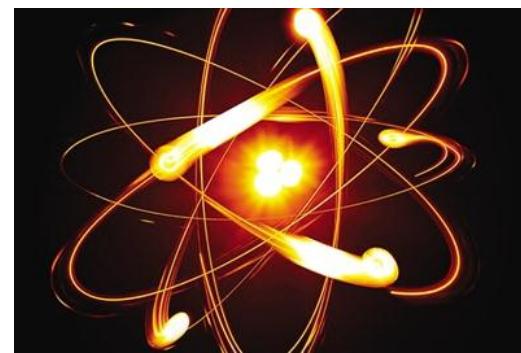
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Things Density Functional Theory (DFT) Cannot Describe Well

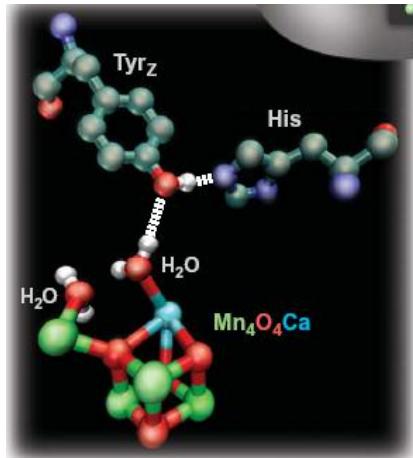
Lighting



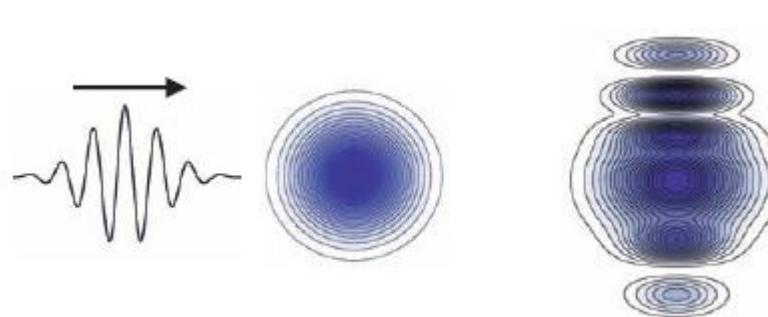
Ultrafast (10^{-18} s)



Photosynthesis



Detection



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

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

Theorem I.

$$\left\{ \begin{array}{ccc} \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) & \xrightarrow{\hspace{1cm}} & \rho(\vec{r}) = \int |\Psi(\vec{r}, \vec{r}_2, \dots, \vec{r}_N)|^2 \prod_{j=2}^N d\vec{r}_j \\ \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) & \xleftarrow{\hspace{1cm}} & \rho(\vec{r}) \end{array} \right.$$

Theorem II.

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

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

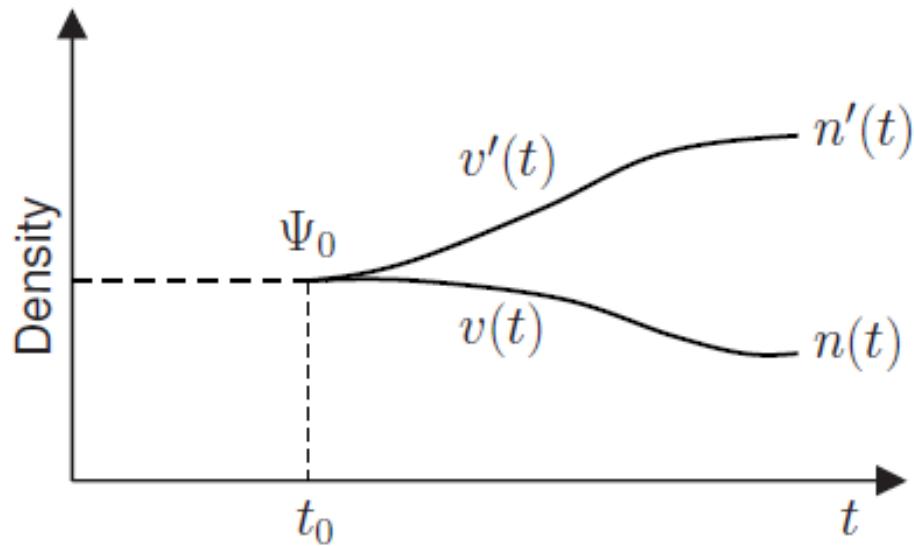
$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N; t) \xrightleftharpoons{\hspace{1cm}} \rho(\vec{r}, t) = \int |\Psi(\vec{r}, \vec{r}_2, \dots, \vec{r}_N; t)|^2 \prod_{j=2}^N d\vec{r}_j$$

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

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

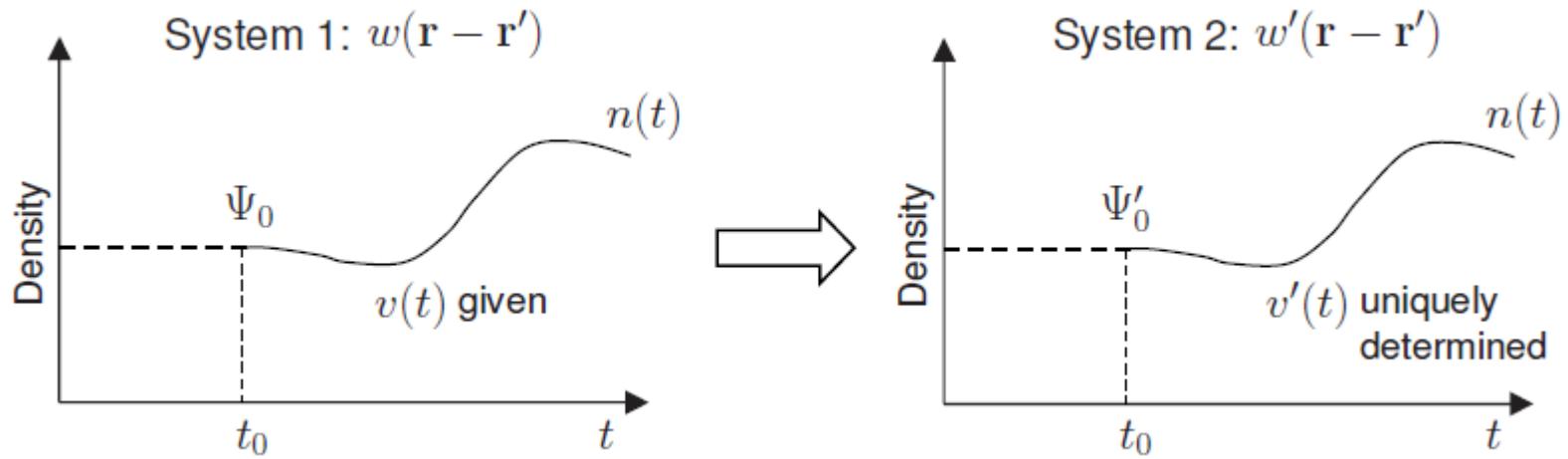
TDDFT Theorem I.

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.



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.



DFT vs TDDFT

Static DFT:

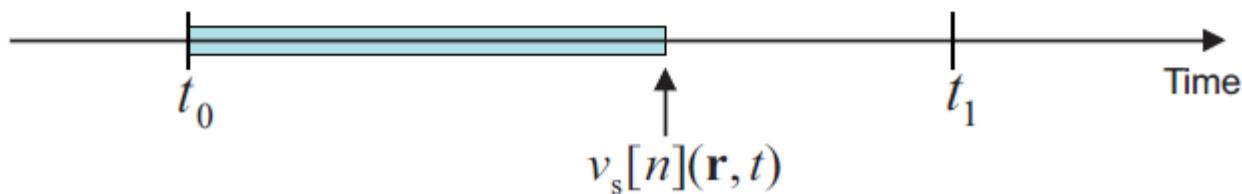
$$\left[-\frac{\nabla^2}{2} + v_s^0[n_0](\mathbf{r}) \right] \varphi_j(\mathbf{r}) = \varepsilon_j \varphi_j(\mathbf{r}) \longrightarrow \sum_j |\varphi_j(\mathbf{r})|^2 = n_0(\mathbf{r})$$

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

TDDFT:

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

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



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

TDDFT is a fundamental tool for many-body physics

Adiabatic-Connection Fluctuation-Dissipation Theorem

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

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

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

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

Three xc functionals

- **Exc**

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

- **V_{xc}**

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

- **f_{xc}**

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

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

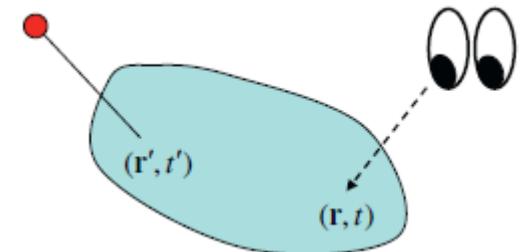
TDDFT is an exact theory for dynamics and excited state properties

A). Linear response TDDFT:

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

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

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



Modified Sternheimer method:

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

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

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

$$\delta n(\mathbf{r}, t) = \delta n(\mathbf{r}) e^{-i\omega t} + \delta n^*(\mathbf{r}) e^{i\omega t} \quad \Rightarrow \quad \delta n(\mathbf{r}) = \sum \phi_i^*(\mathbf{r}) \delta\psi_i^{(+)}(\mathbf{r}) + \phi_i(\mathbf{r}) \delta\psi_i^{(-)*}(\mathbf{r})$$

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

$$A_{ij} = (h_0(\mathbf{r}) - \varepsilon_i) \delta(\mathbf{r} - \mathbf{r}') \delta_{ij} + \phi_i(\mathbf{r}) \frac{\delta h(\mathbf{r})}{\delta n(\mathbf{r}')} \phi_j^*(\mathbf{r}')$$

$$B_{ij} = \phi_i(\mathbf{r}) \frac{\delta h(\mathbf{r})}{\delta n(\mathbf{r}')} \phi_j(\mathbf{r}')$$

Only occupied states are considered!

TDDFT is an exact theory for dynamics and excited state properties

More generally, assume:

$$\psi_i^{(+)}(\mathbf{r}) = \sum_m X_{im} \phi_m(\mathbf{r}) \quad \psi_i^{(-)}(\mathbf{r}) = \sum_n Y_{in}^* \phi_n(\mathbf{r})$$

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

Casida Equation

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

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

This is called frequency domain (linear response) TDDFT.

Advantages:

- Straightforward 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: $i\frac{\partial \varphi}{\partial t}(t) = \hat{H}(t)\varphi(t)$

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

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

Advantages:

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

Current status of TDDFT

Many popular codes now contain TDDFT:

Frequency domain:

- Gaussian
- MolPro
- ABINIT
- YAMBO
- OCTOPUS
- exciting
- ...

Real time:

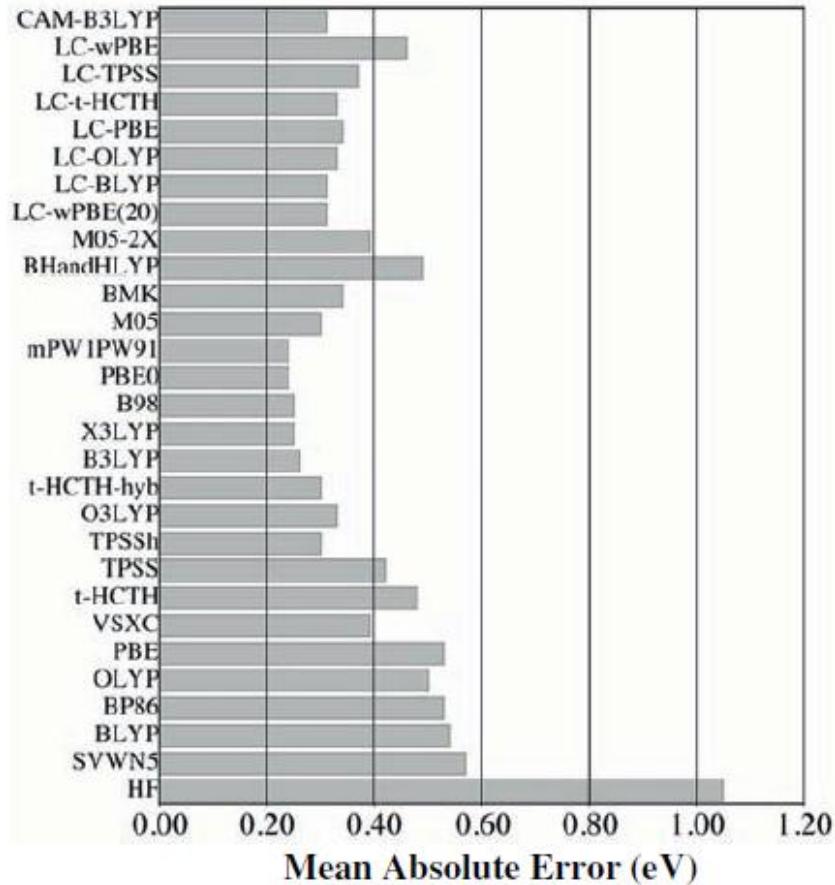
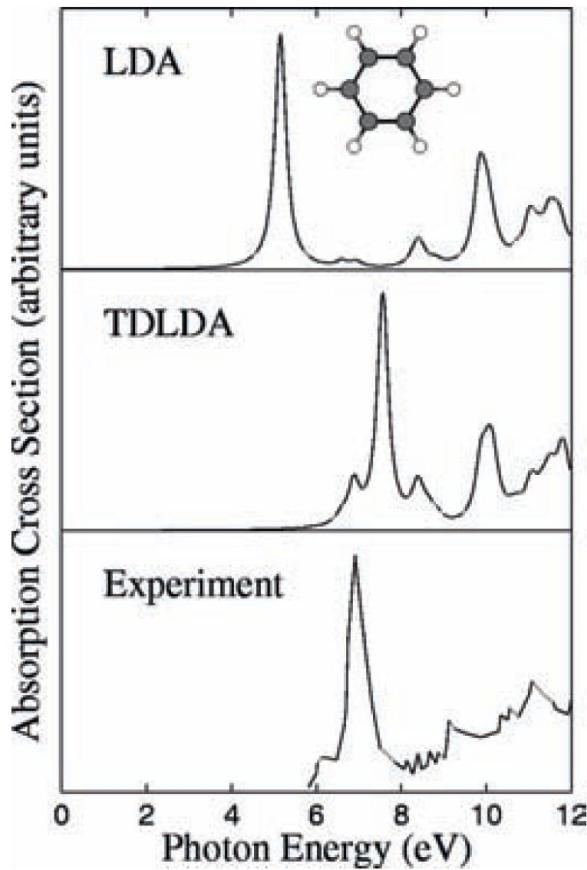
- NWChem
- GPAW
- CP2K
- SALMON
- OCTOPUS
- ...
- many home-made ones

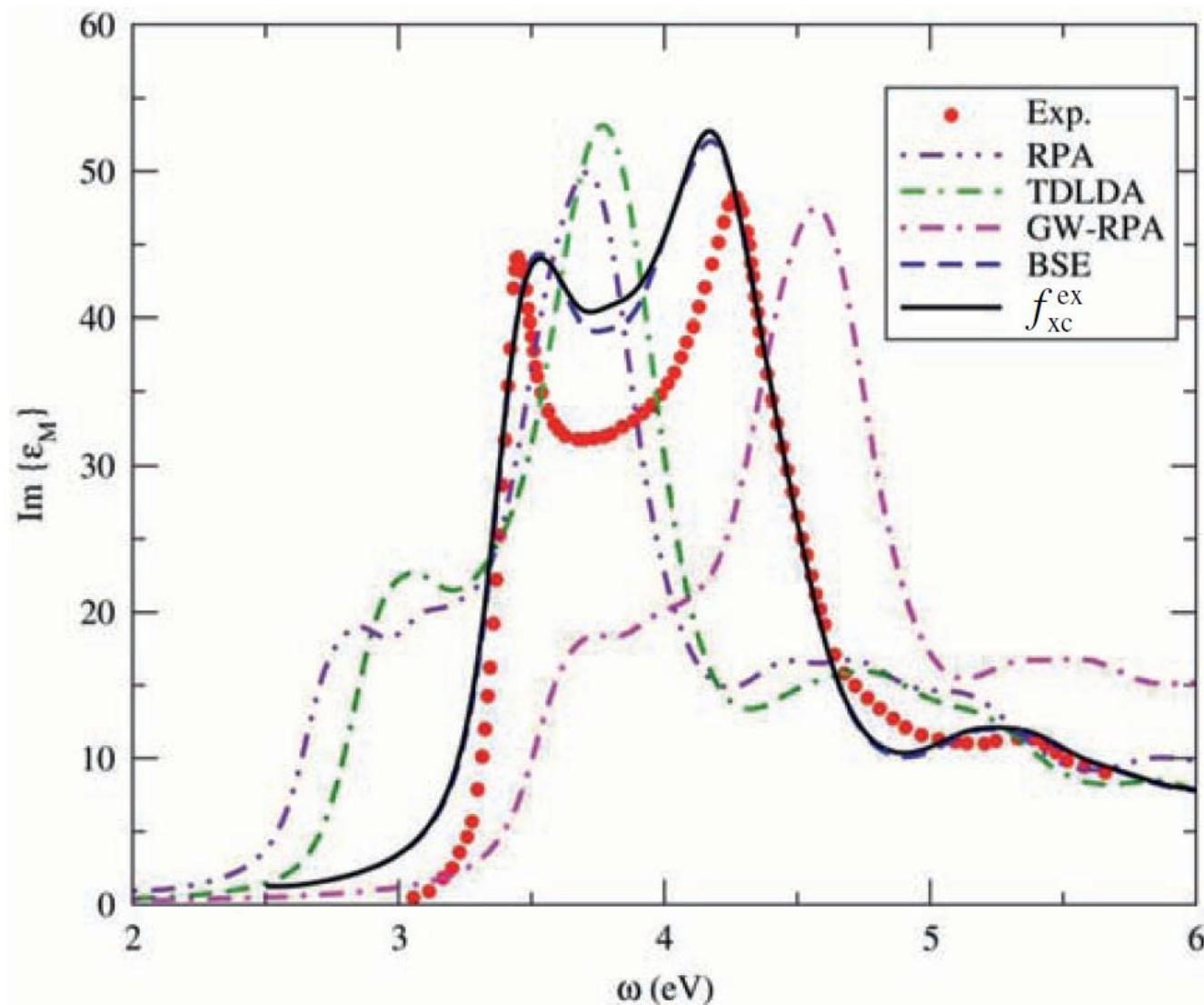
Major developers

- 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
- ...

Applications of TDDFT

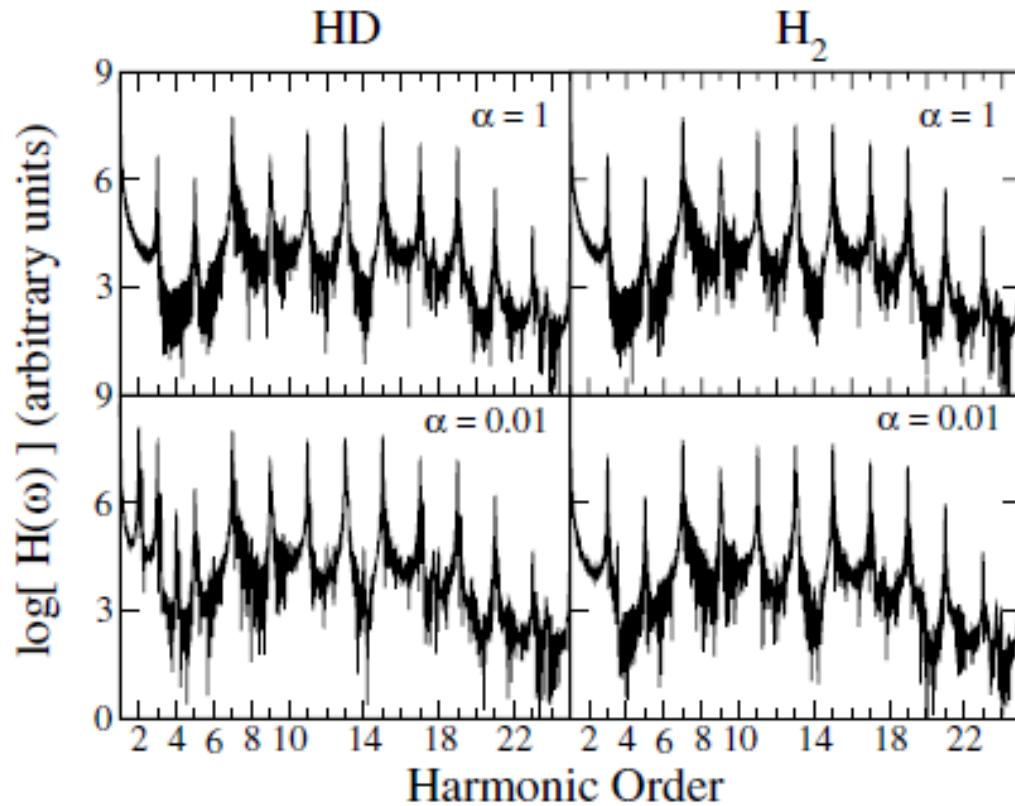
- Photoabsorption spectrum (Corrected Optical Bandgap)



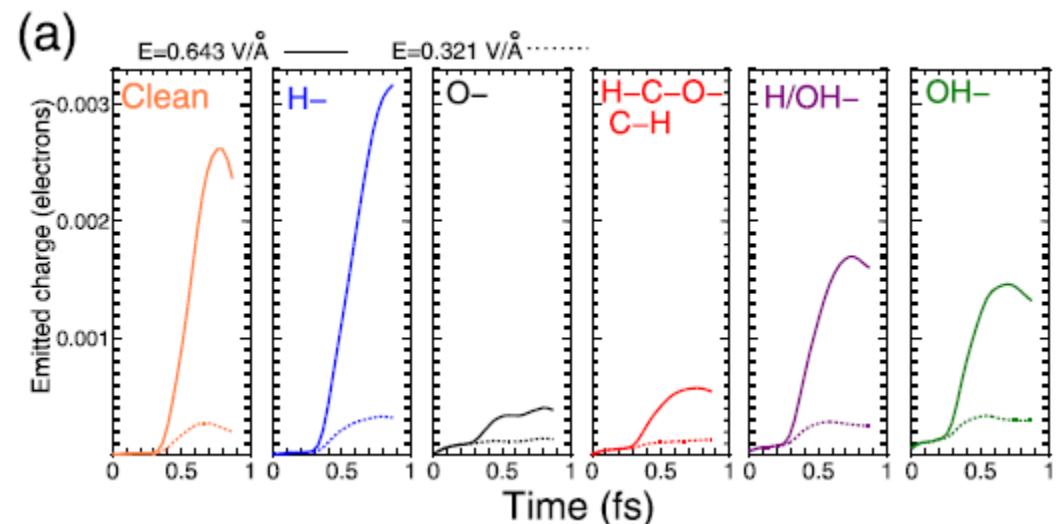
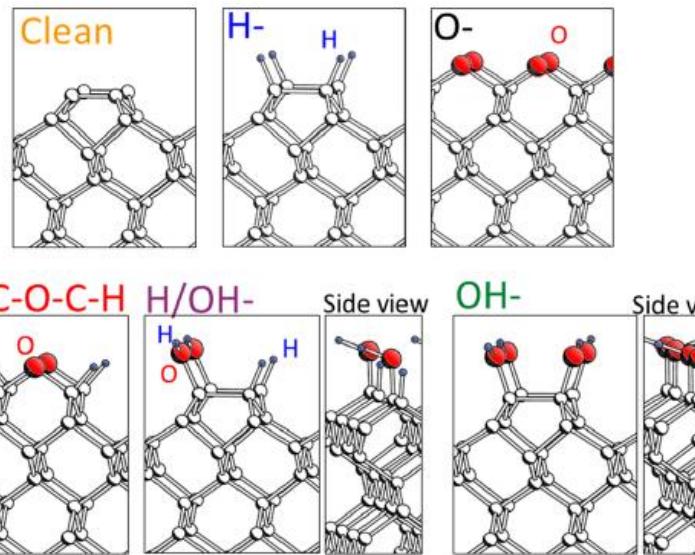


- Nonlinear optics

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

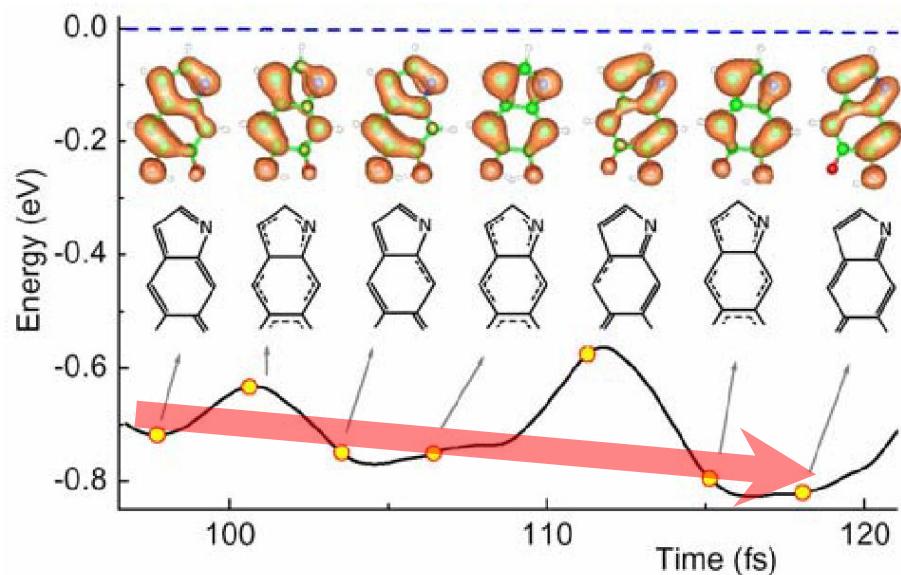
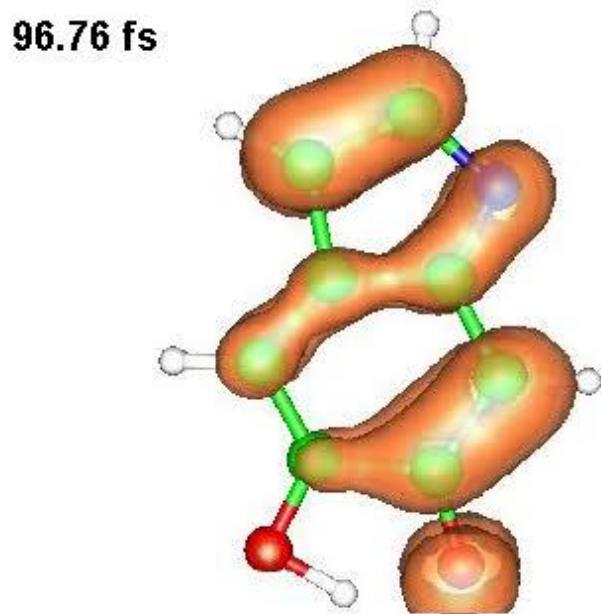


- Photoemission



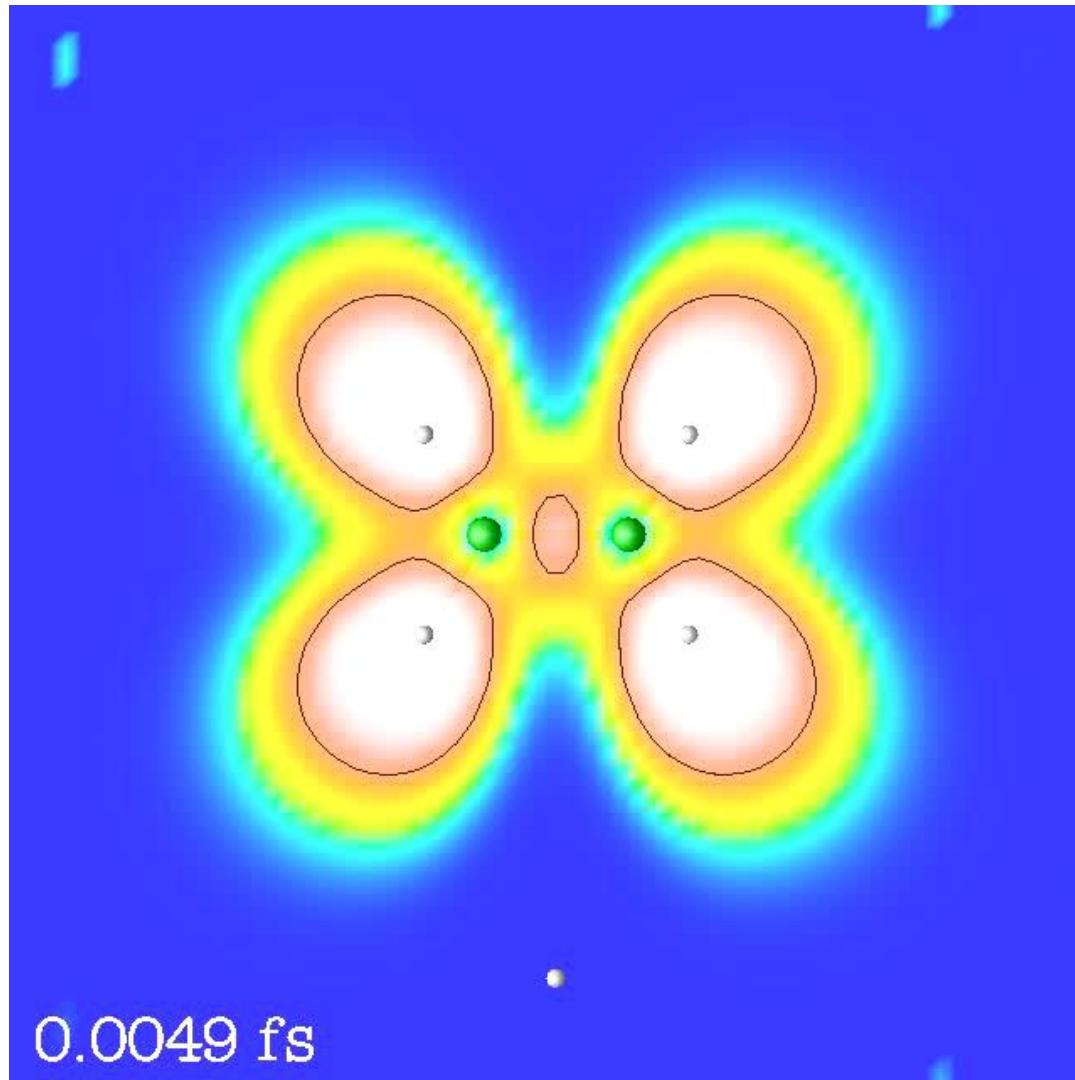
- Photodynamics in a molecule

e-proton concerted dynamics



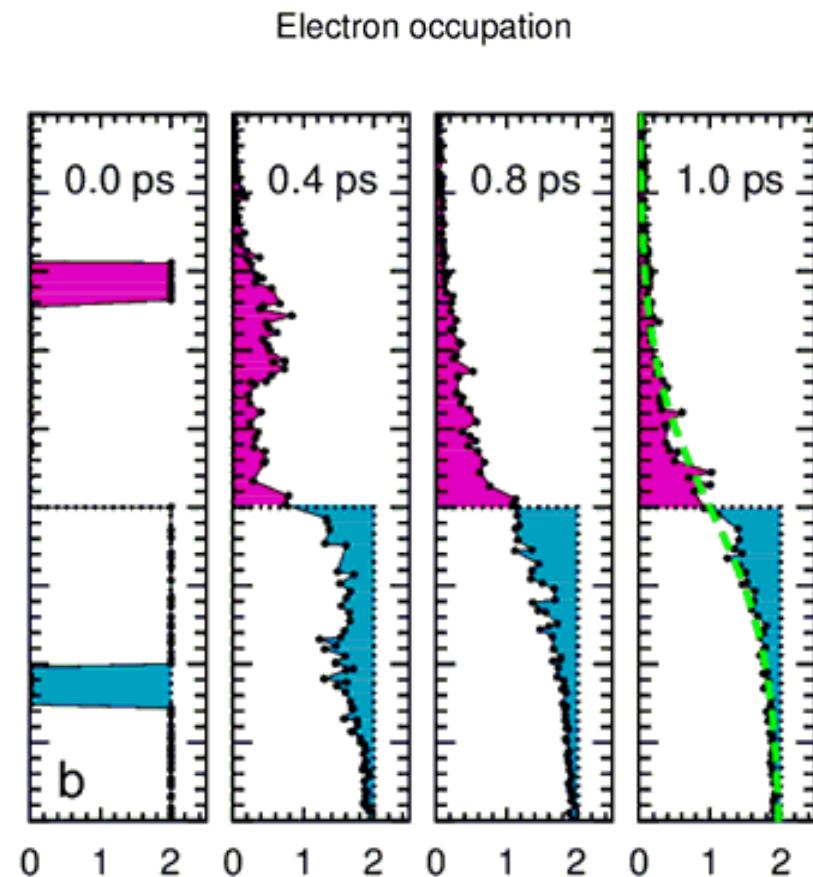
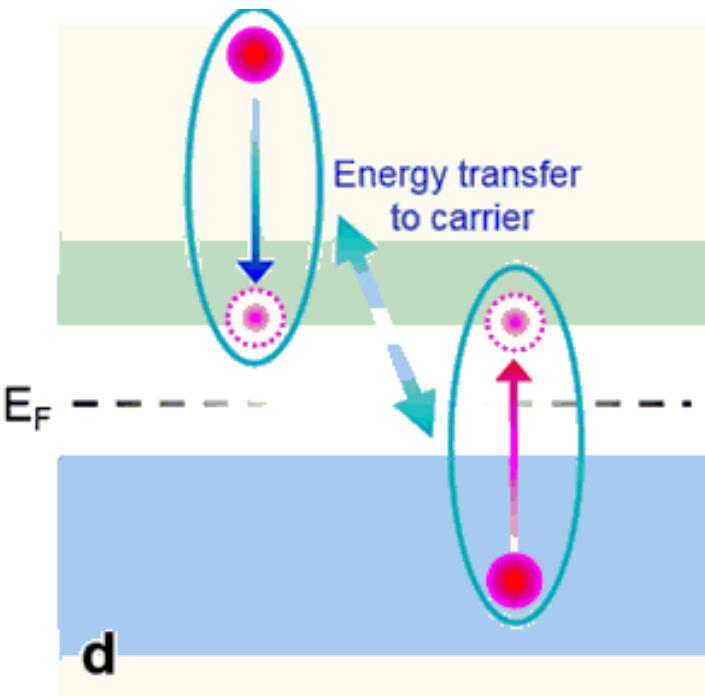
Clouds = e density in excited state

- Femtosecond dynamics

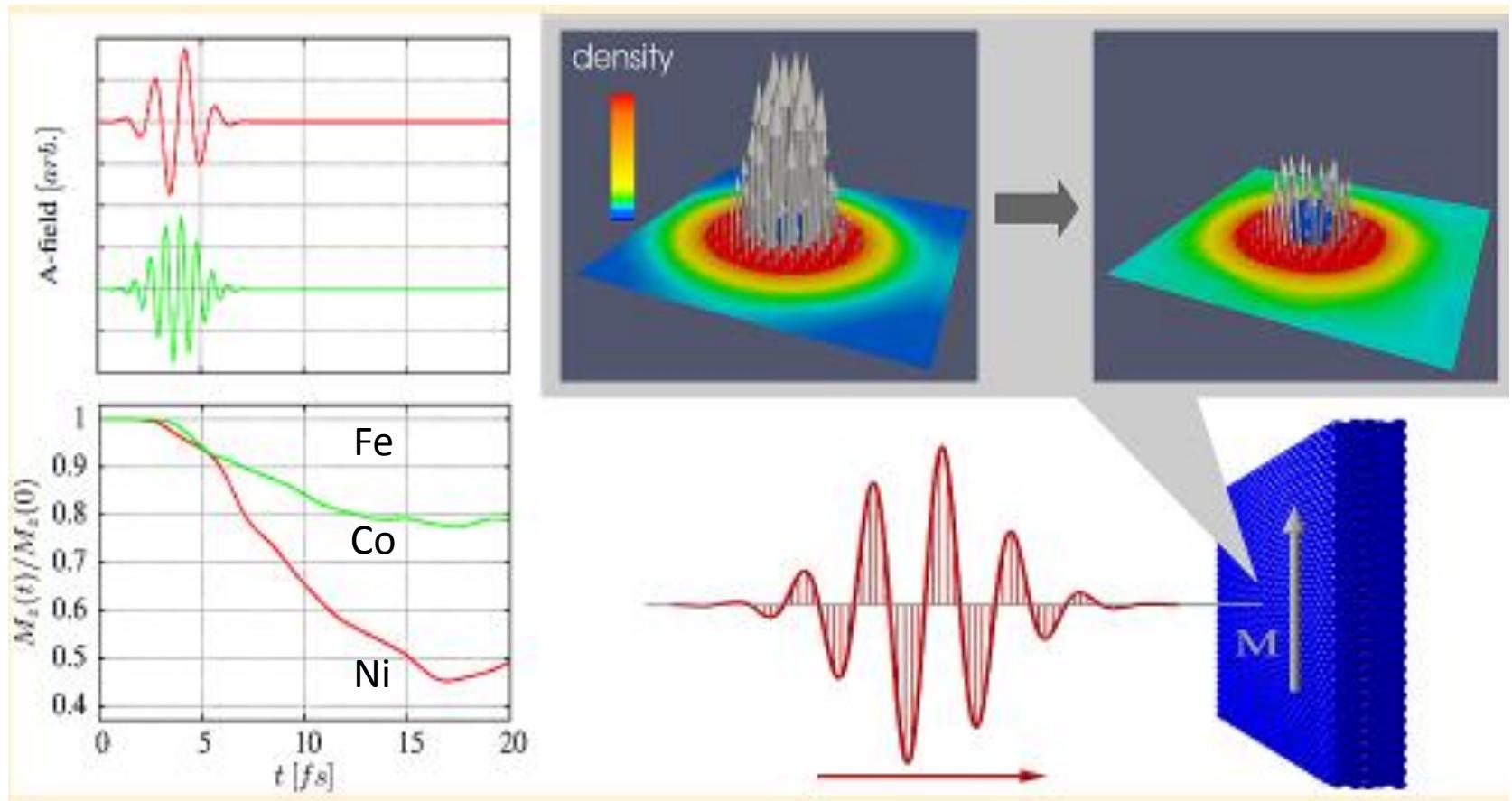


Burnus et al. PRA 71, 10501 (2005).

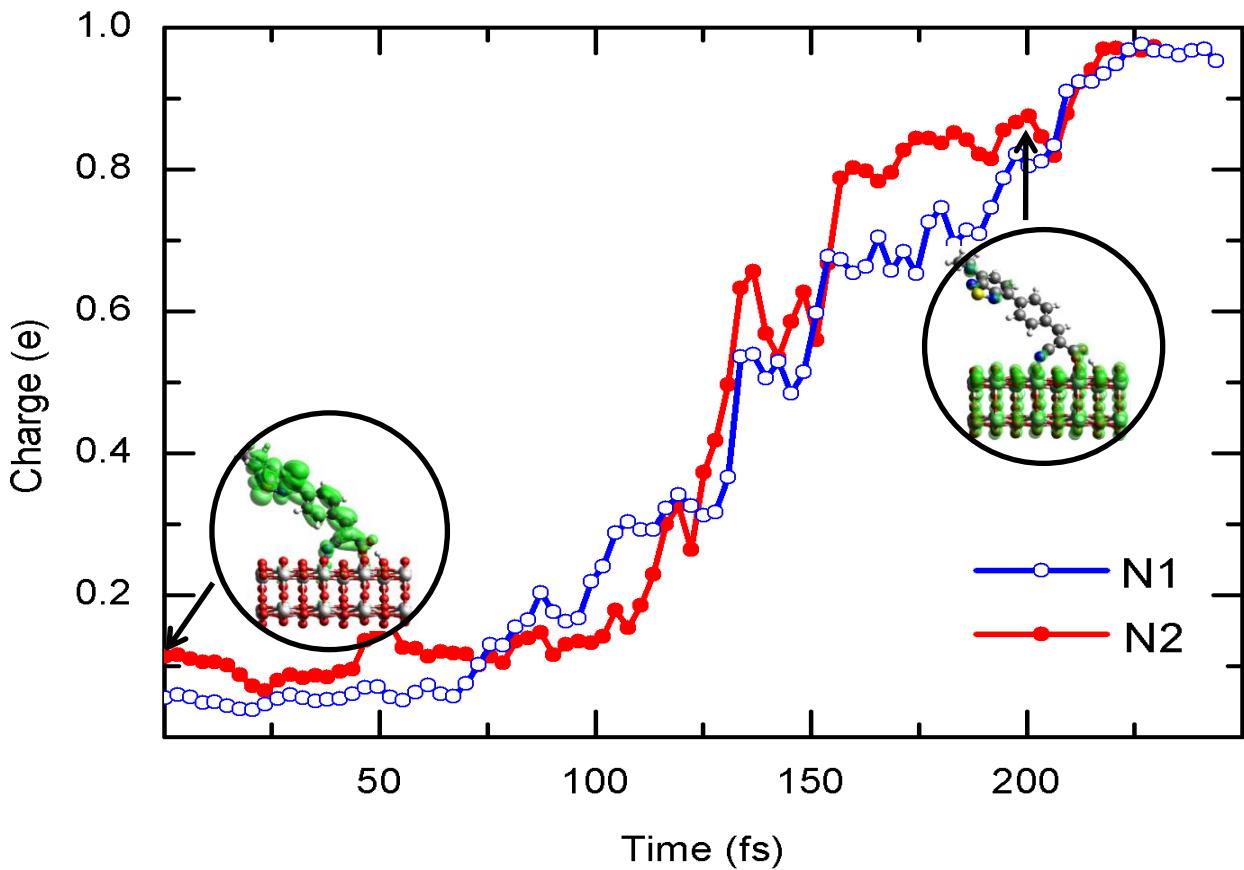
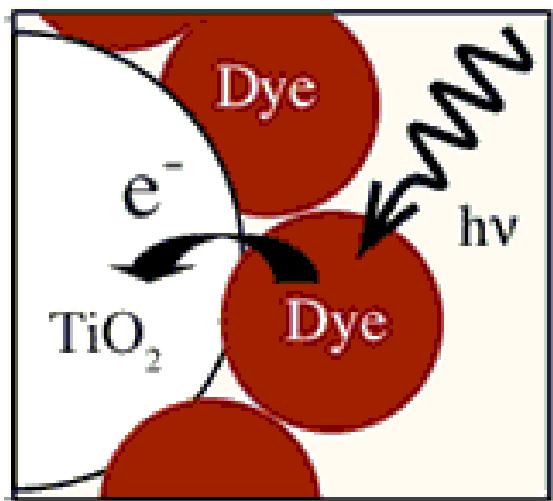
- Nonadiabatic process



- Ultrafast demagnetization



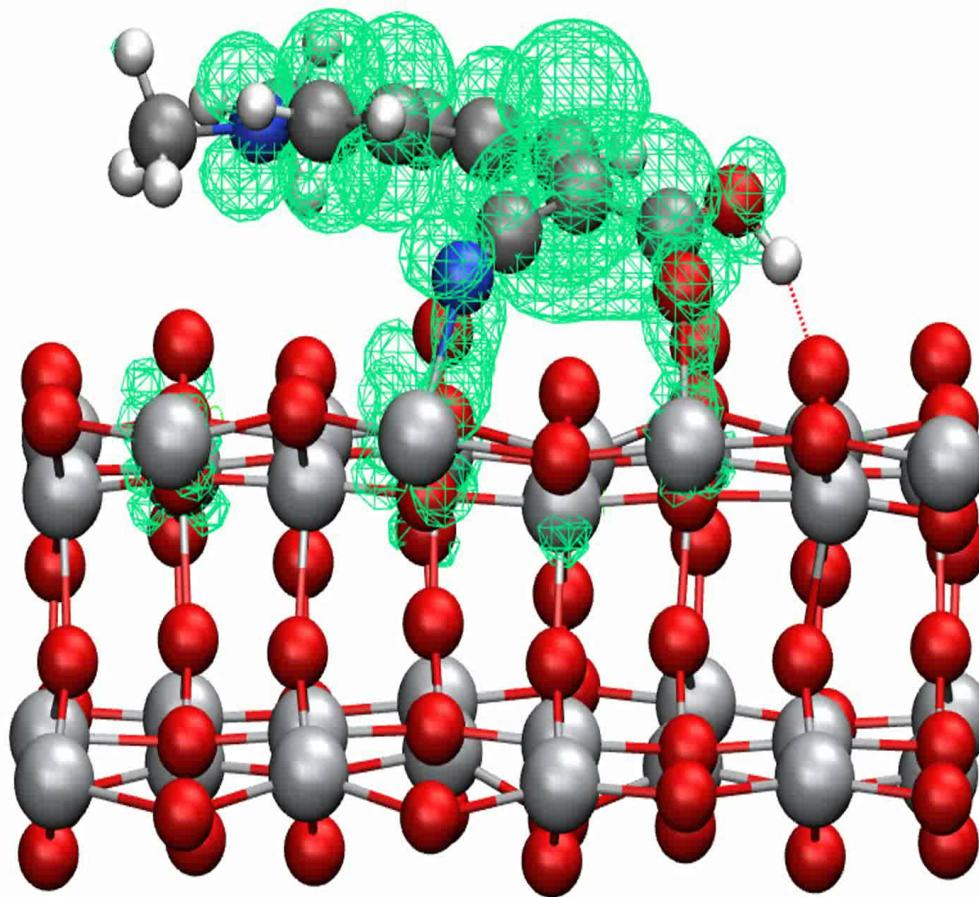
- Energy conversion



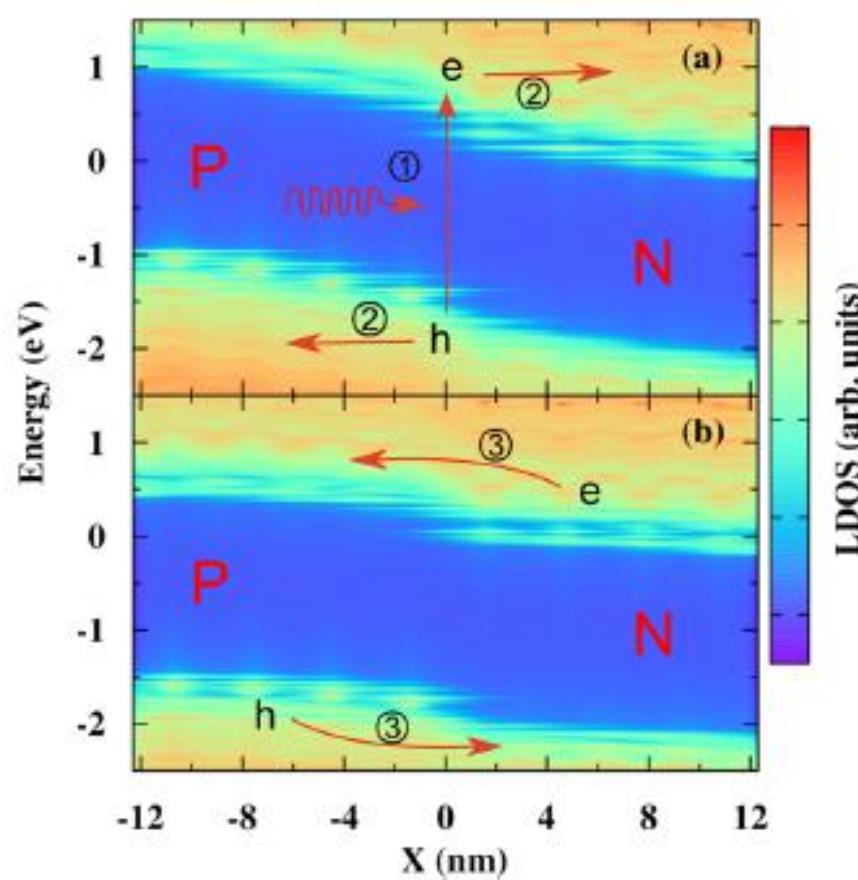
Electron Injection Dynamics

$t = 5.8 \text{ fs}$

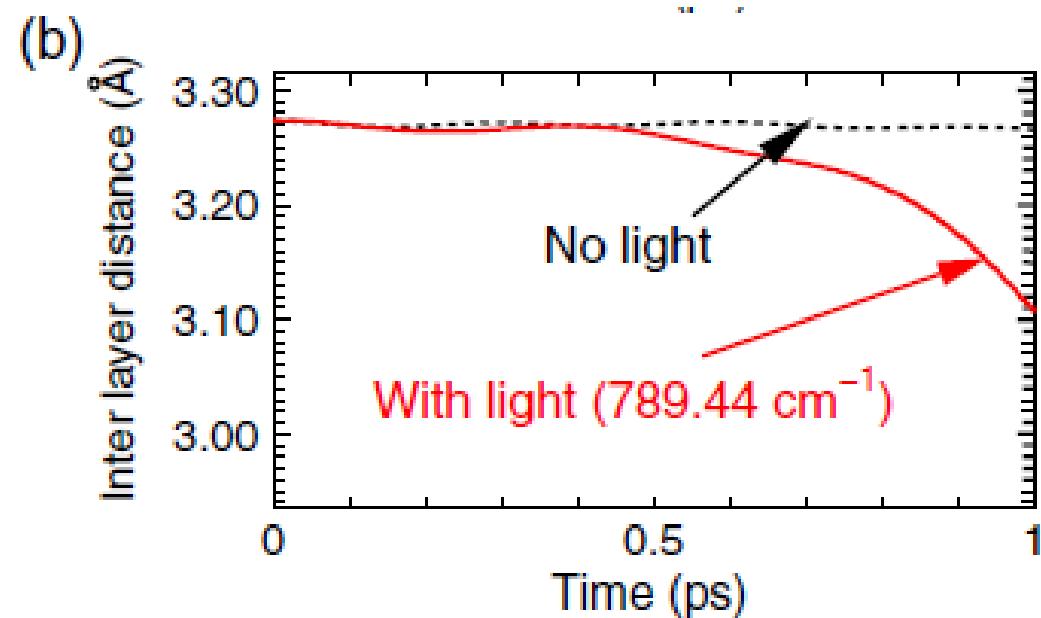
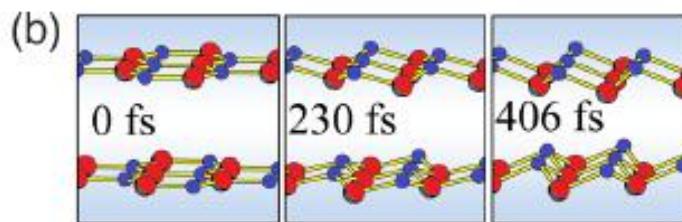
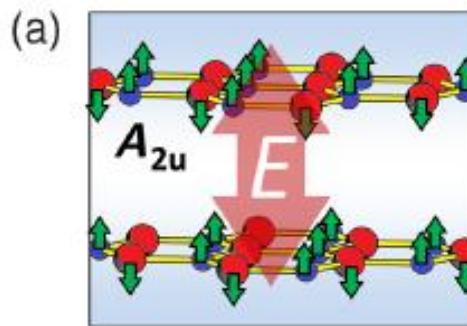
$$\Phi_{\text{inject}} = 1 / \left(1 + \frac{\tau_{\text{inj}}}{\tau_{\text{relax}}} \right)$$



- Quantum transport



- Light interaction with nanomaterials



Current challenges for TDDFT

- Lack of non-adiabatic $f_{XC}(\omega)$
- Charge transfer excitation: nonlocal exchange
- Double excitation; Rydberg states
- Tiny timestep ~ 1 as;
- Inefficient propagation: stability; convergence
- Heavy computation: $10^3 \times$ heavier than AIMD; $10^6 \times$ than static DFT
- How to prepare physically-sound initial states?
- Calculation of time-dependent properties ?
- Beyond Ehrenfest dynamics ?
- Open systems ? ...

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2/25/2020

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