A New TDDFT^2 Method for *Isolated* Systems

Xiao-Min Tong

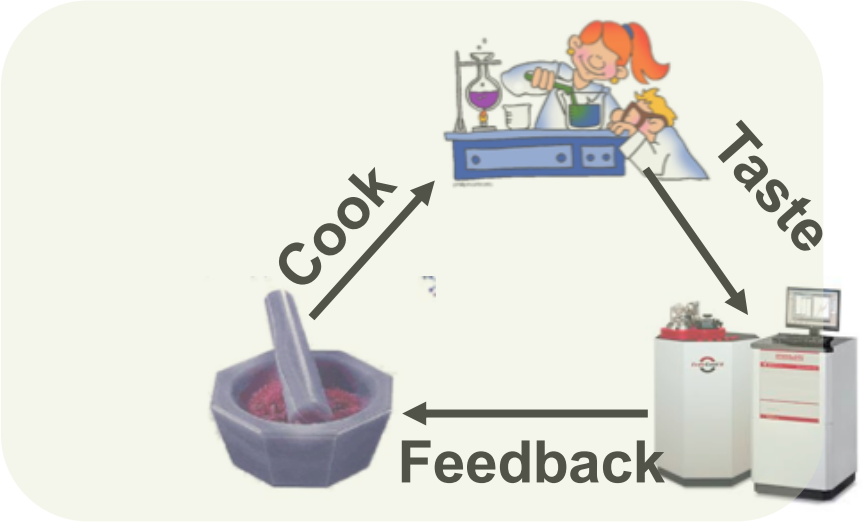
Center for Computational Sciences
University of Tsukuba, Japan

TD-DFT^2: Time-Dependent Density Functional Theory
with Discrete Fourier Transform

Outline

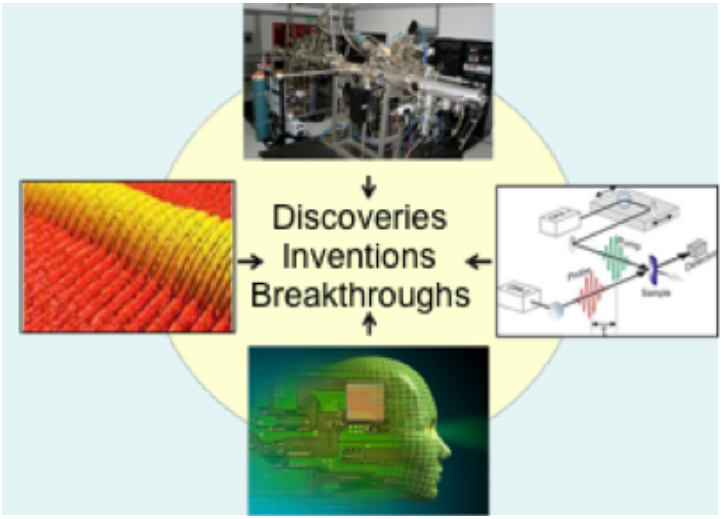
- **What we are working on and Why**
  - **Objects:** Atoms, Molecules, Solids, and Optics (AMO)
  - **Tools:** (Optics) ultra-fast intense laser pulse
  - **Goals:** ***Understand*** the mechanism and
    Control material properties in ultrafast time scale
    Built a tool to "see" what happens in a quantum system
- **What is New ?**
  - **Poisson Solver:** improve the numerical precision
  - **Self-Interaction-Correction:** improve the exchange-correlation
- **Future works**

Research Methods

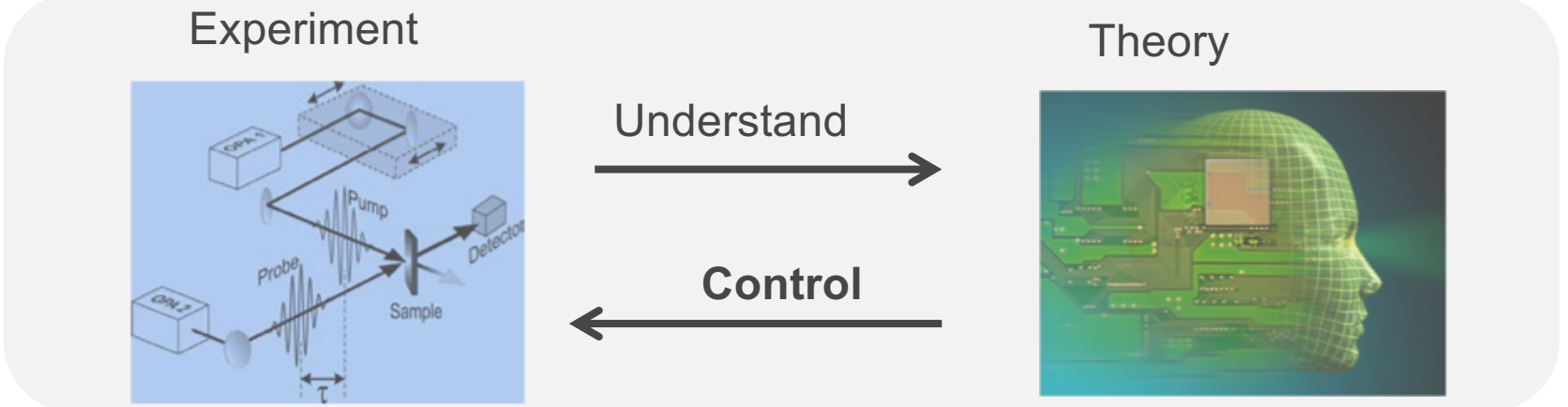


Solids for function **(2012~**

Materials and Synthesis
Properties and Functionality
Theory and Modelling
Applications and Devices



Closing the loop: 2014, NSF



Relation to Other Fields

Atom, Molecule and Optics
(a few body with known interactions, high precision simulation)

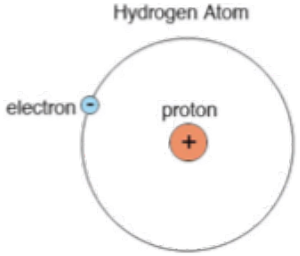
Provide data

Plasma (ITER)

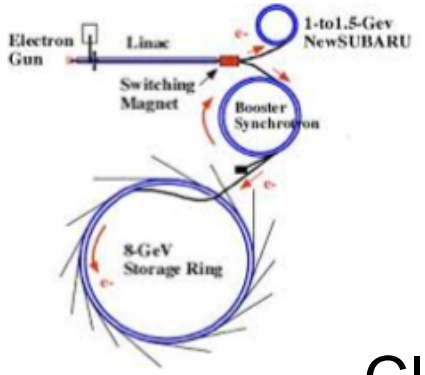
Med.: (CT)

Astro.: (ITAMP)

Play ground:



Quantum



Classical

CPT symmetry （standard model）

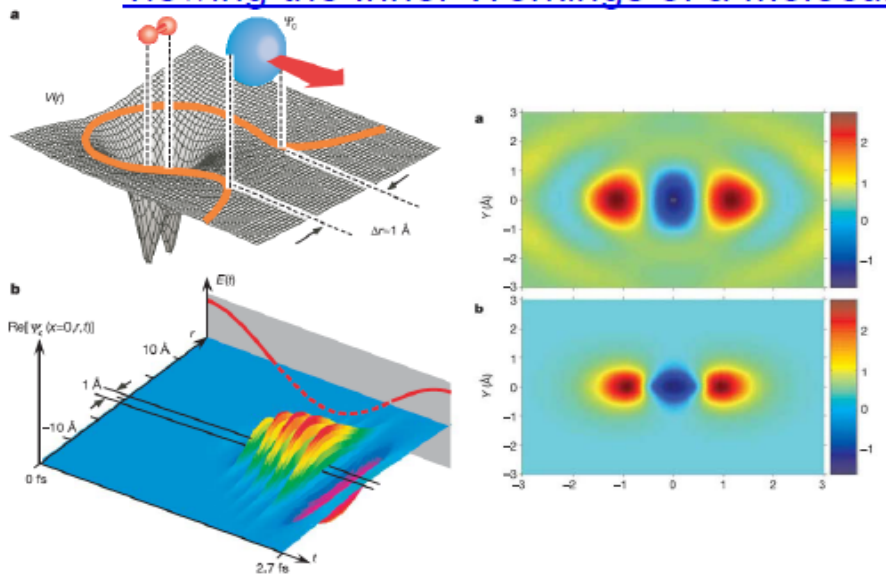
DFT: exch-corr. functionals

Quantum ⇔ Classical

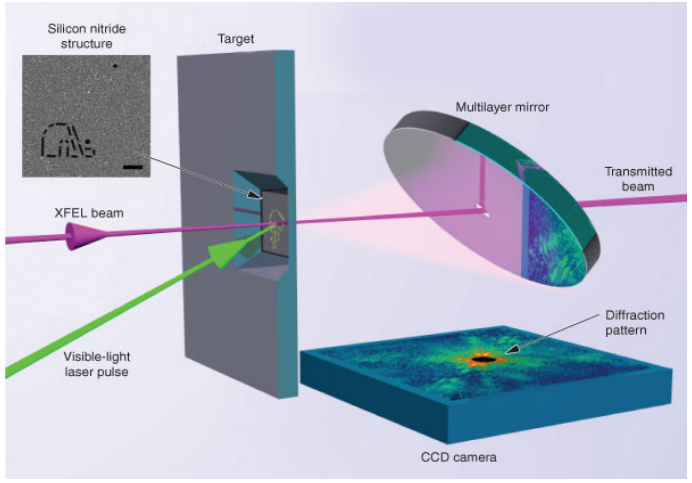
Hot Topics: Make a Molecular Movie

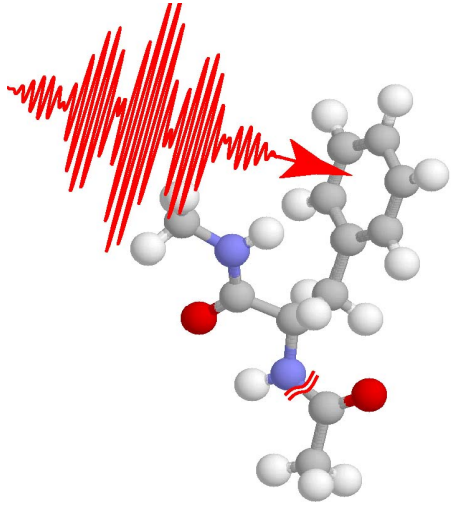
amo2010

Attosecond time scales:
viewing the Inner Workings of a Molecule



A snapshot image of a molecule
obtained from field ionization and electron-molecule recollision in <2fs

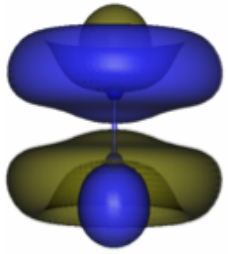
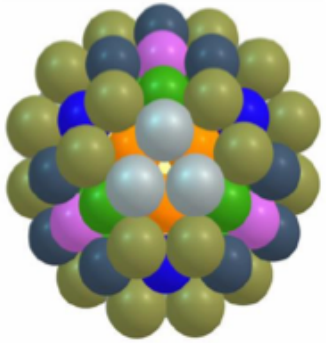
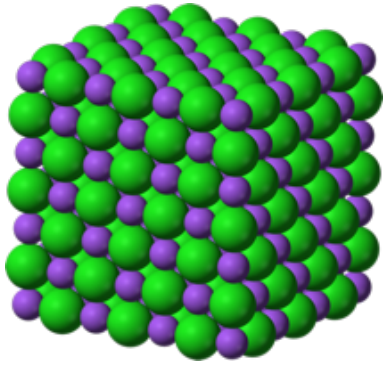




Our Research Targets

➢ Physical Processes and Current Status

- Atoms, molecules, clusters in strong fields
- *Understand* and *control* the dynamical processes
- Generate ultrashort X-ray laser and decode the information in ATI
- Many first principles calculations (Elk, Salmon, Octopus, VASP …)

Atoms	diatomic molecules	many-atom systems	crystals
			
Spherical	Cylindrical	???	Translational

A typical problem size: 10^7 to 10^9 space grids

Theoretical Method

Electron motion: Time-Dependent Schrodinger Equation (TD-DFT)

$$i\frac{\partial}{\partial t}\Psi(t) = H(t)\Psi(t) \quad \text{with} \quad \Psi(t=-\infty) = \Psi_0(t)$$

(1) Structure	Time-independence SE		$H\psi_i(\boldsymbol{r}) = \epsilon_i \psi\_\mathrm{i}(\boldsymbol{r})$
(2) Perturbation	IPA $M_{if} = \langle\psi_i\|\hat{T}\|\psi_f\rangle$	or	Linear response (TDDFT)
(3) Strong Field	TDDFT		

Nucleus motion: Newton Equations (large time)

$$M_i\ddot{\boldsymbol{R}}_i = \boldsymbol{F}_i$$

Optical Fields: Maxwell's equations (large space)

$$\nabla\cdot\boldsymbol{B} = 0 \qquad \nabla\times\boldsymbol{H} - \frac{\partial \boldsymbol{D}}{\partial t} = \boldsymbol{j}$$

$$\nabla\cdot\boldsymbol{D} = \rho \qquad \nabla\times\boldsymbol{E} - \frac{\partial \boldsymbol{B}}{\partial t} = 0$$

TDDFT: simulation flowchart

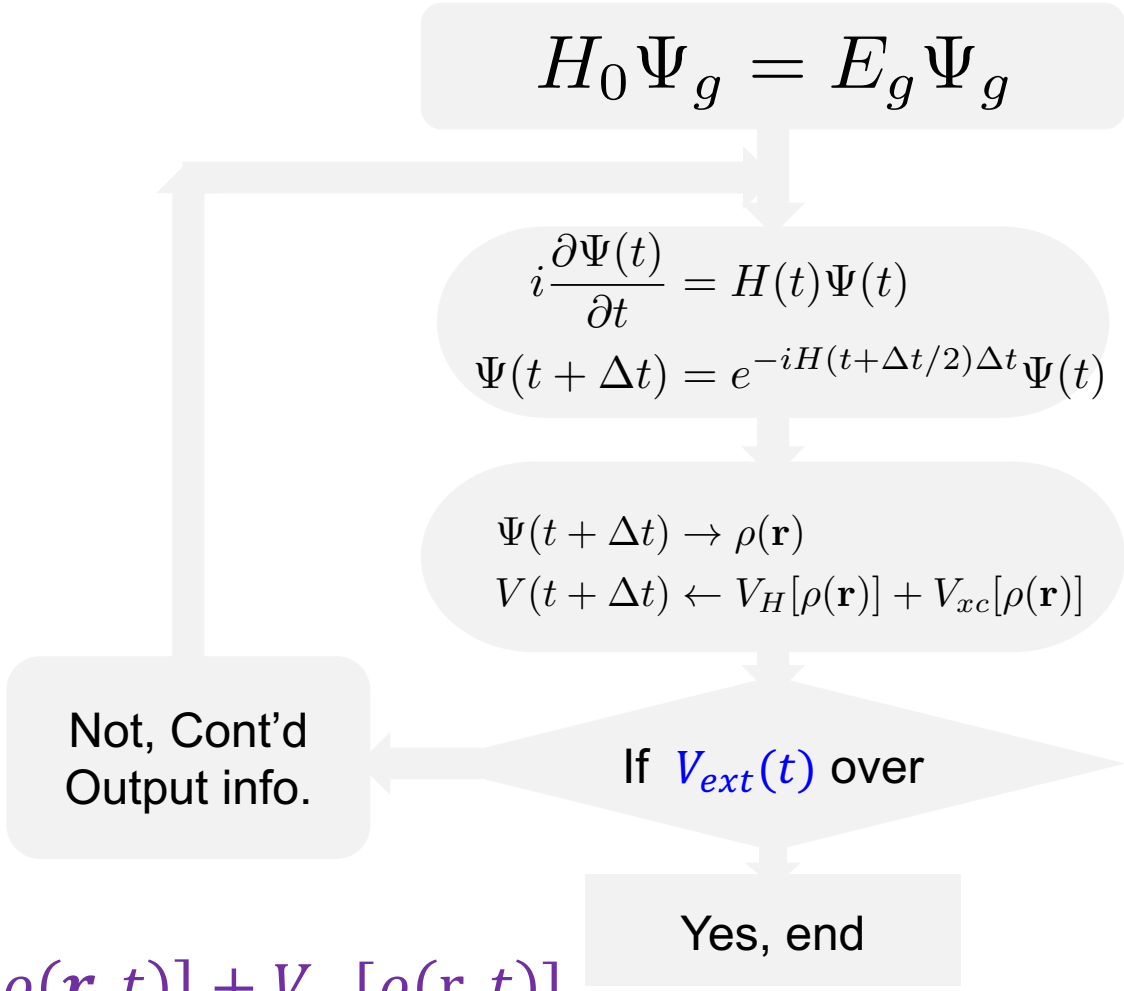
Prepare the initial state
(Kohn-Sham equation)

Time-propagation

Construct new potential
(**Poisson Solver** +
Exchange correlation)

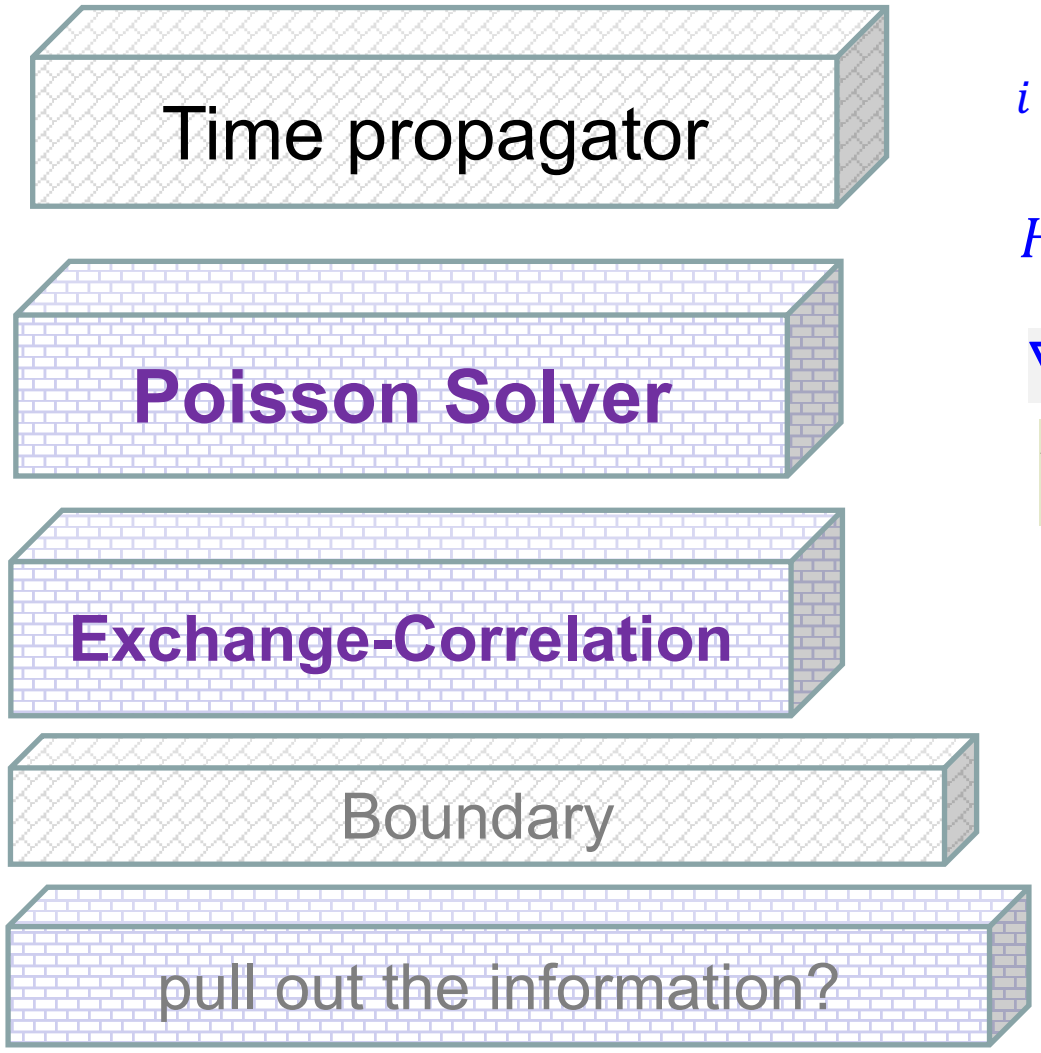
Information output

End



$$H(t) = -\frac{\boldsymbol{\nabla}^2}{2} + V_{ion}(\boldsymbol{r}) + V_H[\rho(\boldsymbol{r},t)] + V_{xc}[\rho(\mathrm{r},t)]$$

TDDFT: building blocks



$$i\frac{\partial}{\partial t}\Psi(t) = H(t)\Psi(t)$$

$$H(t) = -\frac{\nabla^2}{2} + V_{ion}(\boldsymbol{r}) + V_H[\rho(\boldsymbol{r},t)] + V_{xc}[\rho(\mathrm{r},t)]$$

$$\nabla^2 V_H[\rho(\mathbf{r})] = -4\pi\rho(\mathbf{r})$$

$$V_H[\rho(\mathbf{r})] = \int \frac{\rho(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}|} d\mathbf{r}_1$$

$$V_{xc}[\rho(\mathbf{r})]$$

Problem dependent parts

Poisson Solver for Isolated System

Working equation $$\nabla^2 V_C(\mathbf{r}) = -4\pi\rho(\mathbf{r})$$

Available methods:

Differential equation (need boundary information):

- Finite Difference + CG iteration: $\alpha N \times N_{iter}$
- Finite Difference + FFT $10N\log_2 N$
- other iteration methods

Kernel method

$$\begin{aligned} V_C(\mathbf{r}) &= \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3\mathbf{r}' \\ &= \int G(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}')d^3\mathbf{r}' \\ &= \sum K_{i-i',j-j',k-k'}\rho_{i',j',k'} \end{aligned}$$

- Scaling function
- Gaussian function
- Present work

$$FFT^{-1}[FFT(K)FFT(\rho)] \qquad 10(8N)\log_2(8N)$$

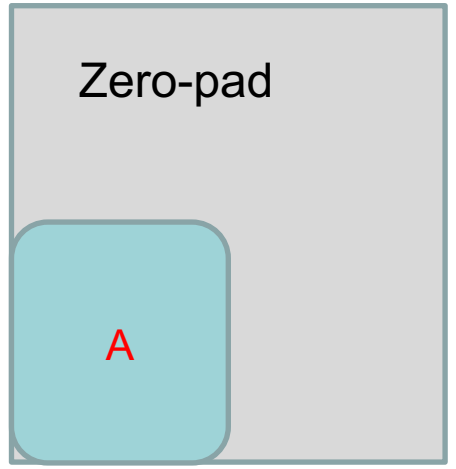
Kernel-Type Poisson Solver

Basic idea

$$\rho(\mathbf{r}) = \sum \rho_{i,j,k}\ \phi_i(x)\phi_j(y)\phi_k(z)$$

Choose a function

$$\phi_i(x_j) = \delta_{i,j}, \qquad \int \phi_i(x)dx = 1$$



Free boundary condition

$$V_C(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}' = \sum \int \frac{\phi_{i'}(x)\phi_{j'}(y)\phi_{k'}(z)}{|\mathbf{r}-\mathbf{r}'|}d^3\mathbf{r}'\ \rho_{i',j',k'}$$
$$= \sum K_{i-i',j-j',k-k'}\,\rho_{i',j',k'}$$

$$\frac{1}{r^a} = \frac{4}{\Gamma(a/2)}\int_0^\infty e^{-r^2e^{2s}+as}ds$$

FFT for **8** ($N_xN_yN_z$), which is eight times larger than the density!

Scaling function: L. Genovese *et al.,* J. Chem. Phys. **125**, 074105 (2006).
Gaussian bases: MH Hejlesen *et al.,* J. Comp. Phys. **326**, 188-196 (2016).

Poisson Solver - cont'd

Replace the scaling function with

$$\phi_0(x) = \frac{\sin(\pi x)}{\pi x} e^{-x^2/36}$$

$$\phi_i(x) = \frac{\sin(\pi(x-i))}{\pi(x-i)} e^{-(x-i)^2/36}$$

(i < =16)
Calculate

$$\phi_i(x_j) = \delta_{i,j}, \quad \int \phi_i(x)dx = 1 \qquad \delta < 10^{-30}$$

$$\int x^m \phi_0(x)dx \approx 0 \quad \text{for } m = 2, 4, 6, ...16$$

$$m = 8 \quad \delta < 10^{-26}$$

$$m = 16 \quad \delta < 10^{-12}$$

$$K_i(p) = \int \phi_i(x) e^{-px^2} dx = \int \frac{\sin(\pi(x-i))}{\pi(x-i)} e^{-(x-i)^2/36} e^{-px^2} dx$$

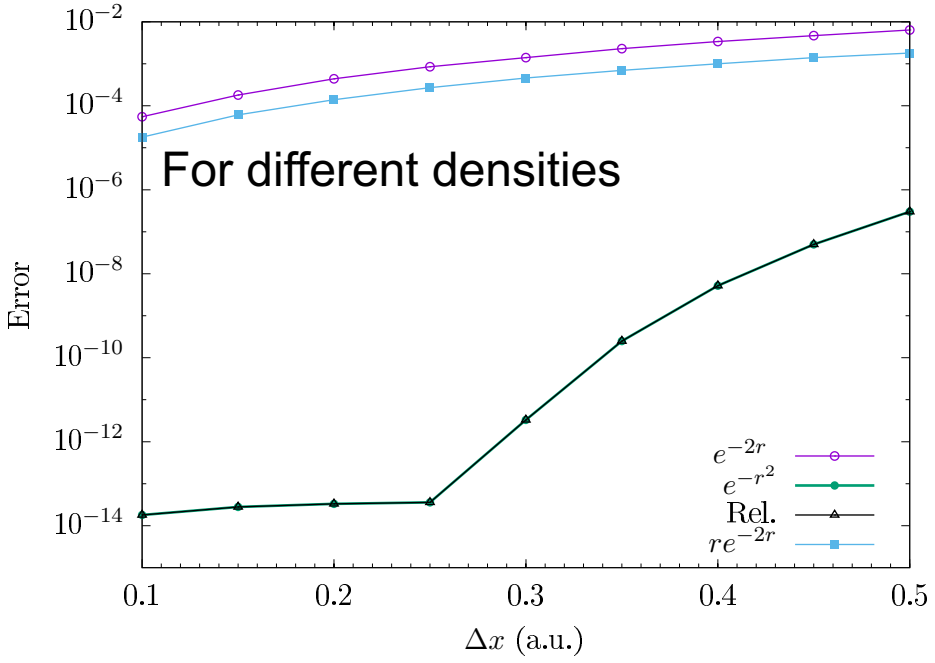
$$K_0(p) = \mathrm{Erf}[\frac{3\pi}{\sqrt{1+36p}}]$$

$$\frac{1}{r^a} = \frac{4}{\Gamma(a/2)} \int_0^\infty e^{-r^2 e^{2s} + as} ds = \frac{4}{\Gamma(a/2)} \sum_{i=0}^{N} e^{-r^2 e^{2s_i} + as_i} \Delta s$$

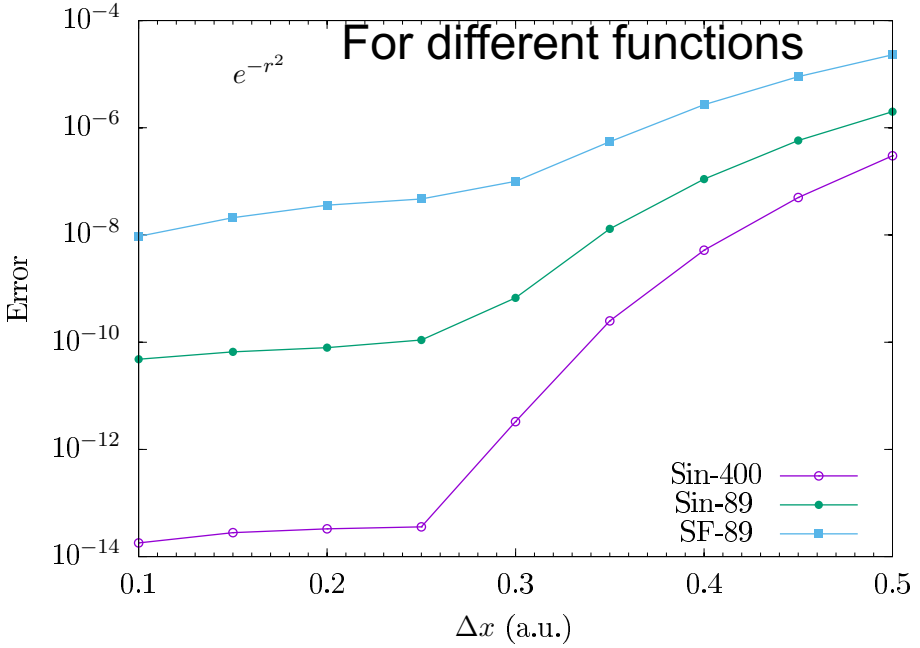
$$s_i = -30 + \frac{55i}{N}$$

Poisson Solver – cont'd

Convergence test



Absolute error (N=89, 400)



CPU time (Xeon 7250)	explicit	implicit
$(512x2)^3$	1.5 sec (215x6 GFlops)	6.17 sec (50x6 GFlops)
$(520x2)^3$	**1.0 sec (339x6 GFlops)**	**1.81 sec (168x6 GFlops)**

Exchange-Correlation

Self-interaction corrections

DFT: In principle, it works for all the many-electron systems,
no-one works ***exactly*** for H atom (LDA, GGA, meta-GGA…)
electron does not interact with itself.

Perdew & Zunger, PRB 23, 5048 (1981)

$$E_{xc}^{SIC}[\rho(\mathbf{r})] = E_{xc}[\rho(\mathbf{r})] - \sum_i \left(J[\rho_i(\mathbf{r}) + E_{xc}[\rho_i(\mathbf{r}), 0]\right)$$

Optimized effective potential for Hartree-Fock

Sharp *et al.*, PR **90**, 317 (1953); Talman *et al.*, PRA **14**, 36 (1976)

$$\left(-\frac{1}{2}\nabla^2 + V^{OEP}(\mathbf{r})\right)\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r})$$

Search OEP to minimize the HF energy;
Krieger, Li & Iafrate (KLI), PRA **46**, 5453 (1992)

$\rho(\mathbf{r})$ 

Exchange-correlation

$\rho(\mathbf{r})$ 

Exchange-correlation? No

Exchange-Correlation

Self-interaction corrections

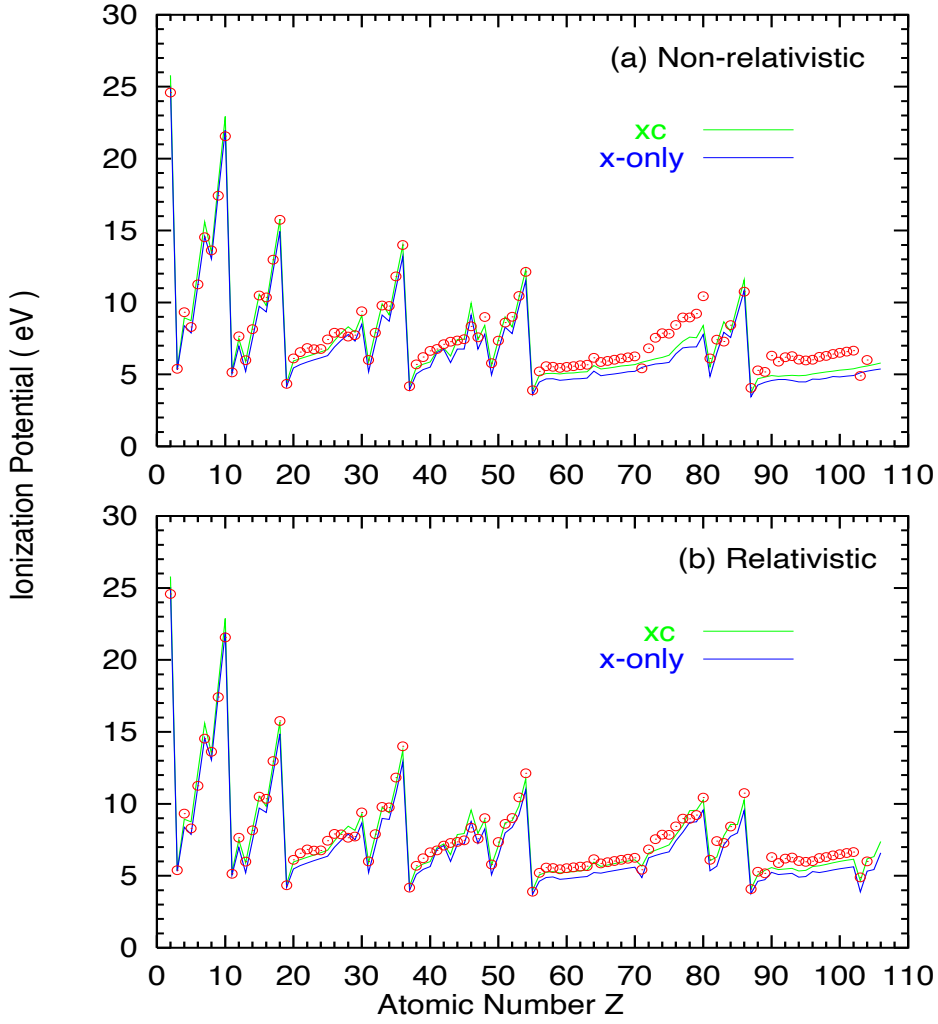
Application of SIC-LDA
to atoms

Tong & Chu, PRA **55**, 3406 (1997);
PRA **57**, 855 (1998);
(TDDFT) PRA **57**, 452 (1998)

to diatomic molecules

Chu & Chu, PRA **63**, 023411 (2001);
Otobe & Yabana PRA **69**, 053403(2004);
PRA **75**, 062507(2007)

Why not extend to other systems ?
Numerical difficulties!



Exchange-Correlation

Self-interaction corrections

Move the SIC to Ionic potential in atomic pseudo-potential

$$V^{OEP}(\mathbf{r}) = V_{ion}(\mathbf{r}) + V_H[\rho(\mathbf{r})] + V_{xc}[\rho(\mathbf{r})] + V_{SIC}(\mathbf{r})$$

For many-atom systems

$$V^{OEP}(\mathbf{r}; \{\mathbf{R}_j\}) = \sum_j V_{ion}(\mathbf{r}, \mathbf{R}_j) + V_H[\rho(\mathbf{r})] + V_{xc}[\rho(\mathbf{r})] + V_{SIC}(\mathbf{r})$$

Too complex

$$V_{SIC}(\mathbf{r}) = \sum_i \frac{\rho_i(\mathbf{r})}{\rho(\mathbf{r})} \left(V_i(\mathbf{r}) + \bar{V}^i_{SIC} - \bar{V}_i \right)$$

Suggested one:

$$V_{SIC}(\mathbf{r}) = \frac{1}{w} \sum_j V^j_{SIC}(\mathbf{r} - \mathbf{R}_j) e^{-2\kappa_j |\mathbf{r} - \mathbf{R}_j|}$$

Using atomic SIC

$$w = \sum_j e^{-2\kappa_j |\mathbf{r} - \mathbf{R}_j|}$$

Exchange-Correlation

Self-interaction corrections

TABLE I. Comparison of the calculated and experimental ionization energies of the ground state of CO. All energies are in eV units.

Orbital	LDA	LDA-SIC	Expt.	HF[d]
3σ	29.31	34.79	38.3[a]	38.16
4σ	14.18	19.62	19.72[b]	18.76
1π	12.15	17.49	16.91[b]	13.81
5σ	9.13	14.17	14.01[b]	11.99
2π	2.27	7.32	7.61[c]	–

[a] from Table V in Ref.[10]
[b] from Table 3.1 in Ref.[11]
[c] from LUMO energy in Ref.[12]
[d] from Ref.[13]

TABLE II. Comparison of the calculated and experimental ionization energies of the ground state of N_2. All energies are in eV units.

Orbital	LDA	LDA-SIC	Expt.[a]	HF[b]
$2\sigma_g$	28.32	33.93	37.3	38.33
$2\sigma_u$	13.40	18.96	18.81	19.80
$1\pi_u$	11.91	17.39	16.73	14.93
$3\sigma_g$	10.45	15.83	15.61	14.43

[a] from table 3 in Ref.[14]
[b] Ref.[13]

TABLE III. Comparison of the calculated and experimental ionization energies of the ground state of H_2O. All energies are in eV units.

Orbital	LDA	LDA-SIC	Expt.[a]	HF[b]
$2a_1$	23.87	31.01	32.4	34.22
$1b_2$	11.97	18.93	18.7	16.16
$3a_1$	8.11	15.11	14.8	12.51
$1b_1$	6.15	13.01	12.6	10.68

[a] from table 3 in Ref.[16]
[b] Ref.[14]

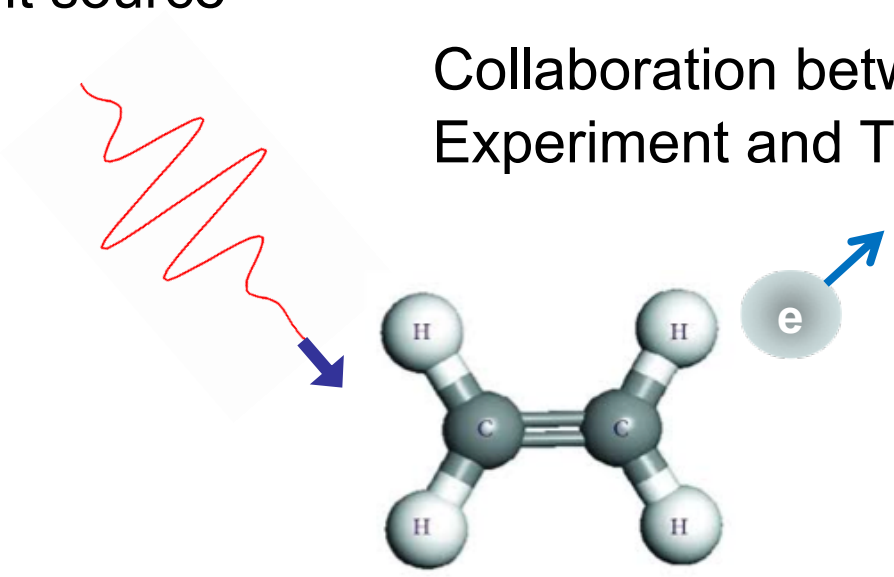
Future works

Decode information from measurements

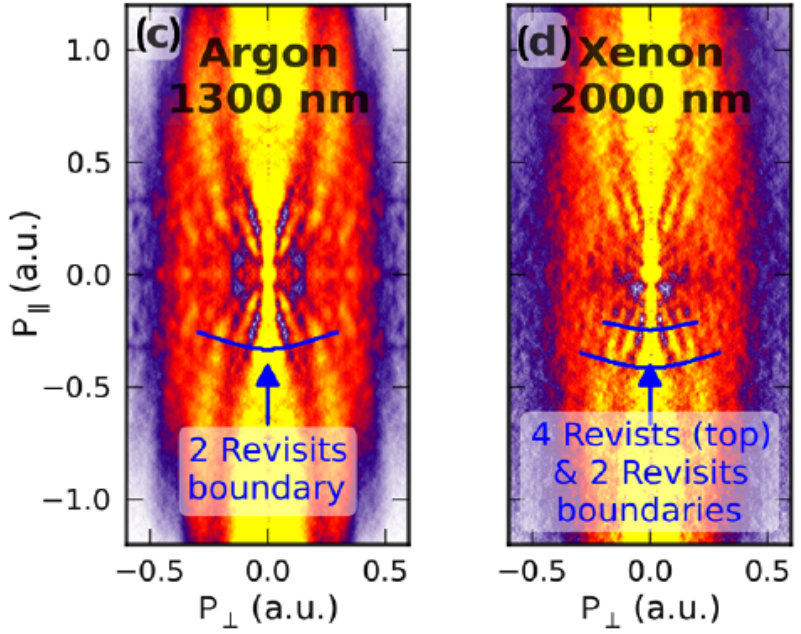
Light source

Measured electrons
What information?

Collaboration between
Experiment and Theory



Atoms, Molecules, Clusters



PRL: **109** (2012) 073004.