Advanced Laser and Photon Science
レーザー・光量子科学特論E

First principles simulations (1)

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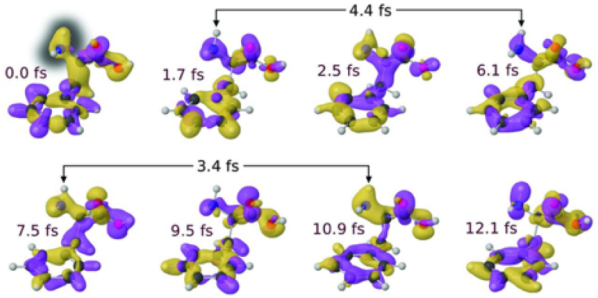
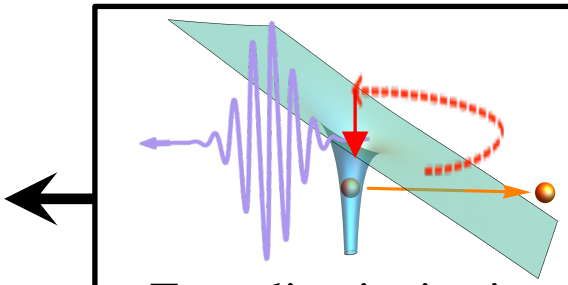
High-field & Ultrafast science

Ultrafast charge migration

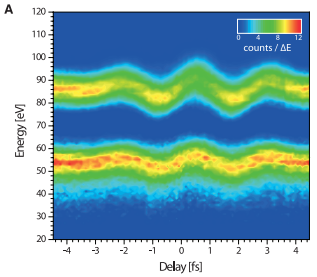


Calegari et al, 2014

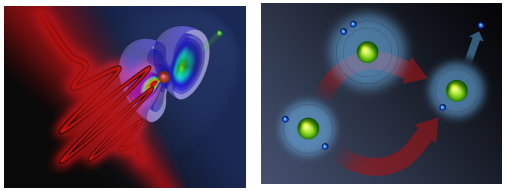


Tunneling ionization
recombination

Attosecond science

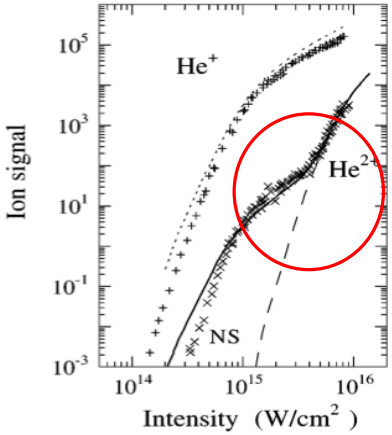


Schultze et al, 2010



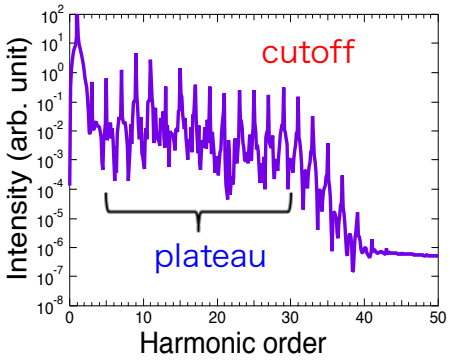
Kaldun et al, 2016,
Ossiander et al, 2017

Nonsequential double ionizatoin

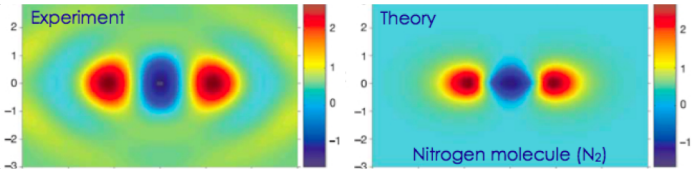


Watson et al, 1997

High-order harmonic generation



Molecular orbital tomography



Itatani et al, 2004

Time-dependent Schrödinger Equation (TDSE)

時間依存シュレーディンガー方程式

$$\hat{H}\Psi(\vec{r}_1,\vec{r}_2,\vec{r}_3,\cdots,\vec{r}_N,t) = i\frac{\partial}{\partial t}\Psi(\vec{r}_1,\vec{r}_2,\vec{r}_3,\cdots,\vec{r}_N,t)$$

$$\hat{H}(t) = \sum_{i=1}^{N}\hat{h}(\boldsymbol{r}_i,t) + \sum_{i=1}^{N}\sum_{j>i}\frac{1}{|\boldsymbol{r}_i-\boldsymbol{r}_j|}$$

$$\hat{h}(\boldsymbol{r},t) = -\frac{1}{2}\nabla^2 - \sum_{A=1}^{M}\frac{Z_A}{|\boldsymbol{r}-\boldsymbol{R}_A|} + \boldsymbol{E}(t)\cdot\boldsymbol{r} \qquad \text{or}$$

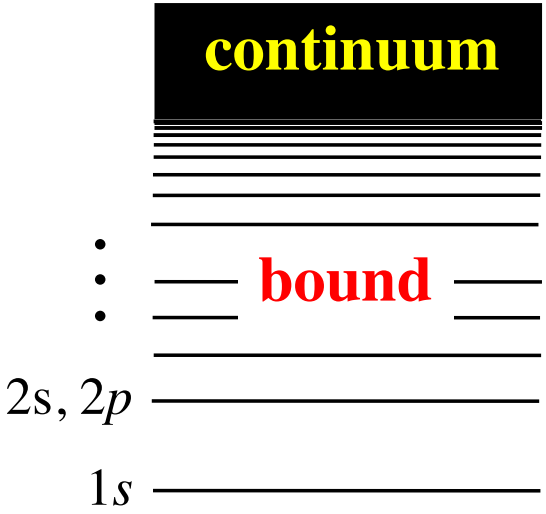
$$\hat{h}(\boldsymbol{r},t) = \frac{1}{2}\left|-i\boldsymbol{\nabla} + \boldsymbol{A}(t)\right|^2 - \sum_{A=1}^{M}\frac{Z_A}{|\boldsymbol{r}-\boldsymbol{R}_A|}$$

First principles simulations

Hydrogen atom

$$i\dot{\psi}(\vec{r},t) = \left[-\frac{\nabla^2}{2} - \frac{1}{r} + zE(t)\right]\psi(\vec{r},t)$$

Fixed orbital expansion?



$$\psi(t) = C_{1s}(t)\phi_{1s} + C_{2s}(t)\phi_{2s} + C_{2p}(t)\phi_{2p} + \cdots$$

$$i\dot{C}_I(t) = \sum_J \{\epsilon_I\delta_{IJ} + E(t)z_{IJ}\}C_J(t)$$

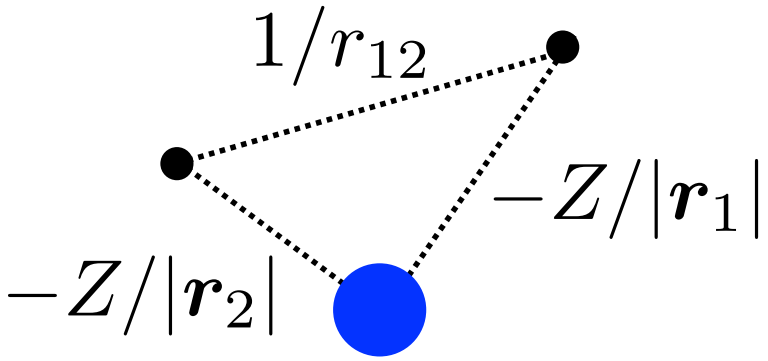
Original PDE is transformed into ODE
Difficult to include highly-excited/continuum states

Directly numerical simulation of TDSE has been proved
more advantageous for strong-field phenomena

高強度場現象を扱うにはTDSEを直接離散化した方が有利

Helium atom

$$i\dot{\Psi}(\vec{r}_1,\vec{r}_2,t)=\left[-\frac{\nabla_1^2}{2}-\frac{\nabla_2^2}{2}-\frac{2}{r_1}-\frac{2}{r_2}+(z_1+z_2)E(t)+\frac{1}{r_{12}}\right]\Psi(\vec{r}_1,\vec{r}_2,t)$$



He atom: already the limit of direct TDSE simulation

He原子ですでに限界

To solve many-electron TDSE
within a *reasonable* approximation

First principles simulations

✓ Time-dependent density functional theory (TDDFT)

$$\rho(\boldsymbol{r}_1) = N \int d\boldsymbol{r}_2 \cdots d\boldsymbol{r}_N |\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots \boldsymbol{r}_N)|^2$$

Fast. Atoms, molecules, clusters, and solids 計算コストが低い、原子から固体まで

Accuracy NOT systematically improvable 計算精度を系統的に向上できない

Difficult to treat ionization **process** イオン化**過程**の記述が困難

Difficult to extract observables in general 一般の物理量の計算が困難

✓ Time-dependent wavefunction theory

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots \boldsymbol{r}_N)$$

Demanding 計算コストが高い

Systematically improvable accuracy 計算精度を系統的に向上できる

Can properly describe excitation/ionization **process** イオン化**過程**を記述できる

Can access to observables 任意の物理量を計算できる

✓ Time-dependent reduced density matrix theory

✓ Time-dependent R-matrix-based approaches

Time-dependent density functional theory (TDDFT)

Electron density as a basic variable, not total wave function

全電子波動関数ではなく電子密度を基本的な変数とする

Exact in principle, approximate in practical

原理的には厳密、実際は近似

$$\rho(\boldsymbol{r},t) = 2\sum_{i}^{N/2} |\psi_i(\boldsymbol{r},t)|^2$$

Electron density　　Kohn-Sham orbital

$$i\dot{\psi}_i(\boldsymbol{r}) = \left\{ \hat{h}(\boldsymbol{r},t) + \int d\boldsymbol{r}' \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + V^{\mathrm{XC}}[\rho](\boldsymbol{r}) \right\} \psi_i(\boldsymbol{r})$$

Hartree potential　　Exchange-correlation potential

TDDFT equation

Time-dependent wavefunction theory

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots \boldsymbol{r}_N)$$

(1) Time-dependent Hartree (TDH)

$$\Psi_{\mathrm{TDH}}(\boldsymbol{x}_1, \boldsymbol{x}_2, \cdots \boldsymbol{x}_N) = \psi_1(\boldsymbol{x}_1)\psi_2(\boldsymbol{x}_2)\cdots\psi_N(\boldsymbol{x}_N)$$

Total wavefunction as a (Hartree) product of orbitals

全波動関数を
軌道関数の積（ハートリー積）で近似

$\boldsymbol{x} = \{\boldsymbol{r}, \boldsymbol{\sigma}\}$
$\boldsymbol{r}$: spatial coordinate 空間座標
$\boldsymbol{\sigma}$: spin coordinate スピン座標

$$\psi_{2i-1}(\boldsymbol{x}) = \psi_i(\boldsymbol{r})\alpha(\sigma)$$
$$\psi_{2i}(\boldsymbol{x}) = \psi_i(\boldsymbol{r})\beta(\sigma)$$

$$i\dot{\psi}_i(\boldsymbol{r}) = \left\{\hat{h}(\boldsymbol{r}, t) + \int d\boldsymbol{r}' \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}\right\}\psi_i(\boldsymbol{r})$$

TD Hartree equation

Violate Pauli's antisymmetricity principle

パウリの反対称性
原理を満たさない

(2) Time-dependent Hartree-Fock (TDHF)

$$\Psi_{\mathrm{TDHF}}(\boldsymbol{x}_1, \boldsymbol{x}_2, \cdots \boldsymbol{x}_N) = \frac{1}{N!} \det \begin{bmatrix} \psi_1(\boldsymbol{x}_1) & \psi_1(\boldsymbol{x}_2) & \cdots & \psi_1(\boldsymbol{x}_N) \\ \psi_2(\boldsymbol{x}_1) & \psi_2(\boldsymbol{x}_2) & \cdots & \psi_2(\boldsymbol{x}_N) \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \psi_N(\boldsymbol{x}_1) & \psi_N(\boldsymbol{x}_2) & \cdots & \psi_N(\boldsymbol{x}_N) \end{bmatrix}$$

$$\equiv \left| \psi_1 \psi_2 \cdots \psi_N \right|$$

Single Slater determinant　　単一のスレーター行列式

$$i\dot{\psi}_i(\boldsymbol{r}) = \left\{ \hat{h}(\boldsymbol{r}, t) + \int d\boldsymbol{r}' \frac{\rho(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \right\} \psi_i(\boldsymbol{r}) - \sum_{j=1}^{N/2} \int d\boldsymbol{r}' \frac{\psi_j^*(\boldsymbol{r}')\psi_i(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \psi_j(\boldsymbol{r})$$

Exchange interaction

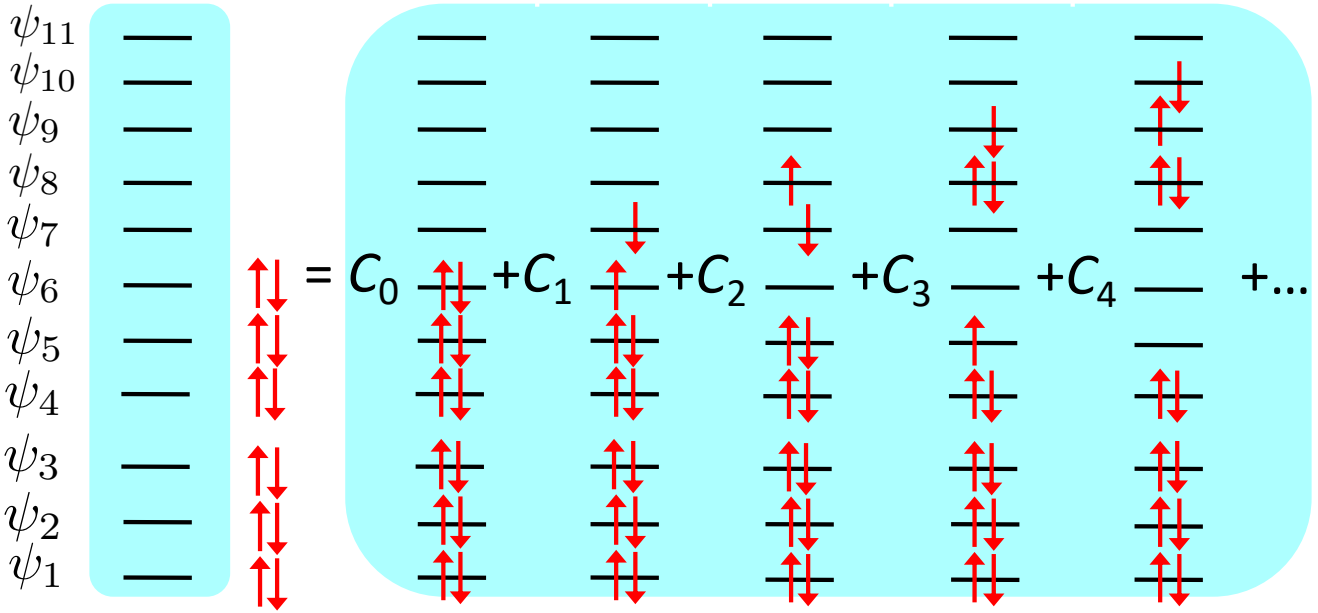
TD Hartree-Fock equation

(3) Multiconfiguration TDHF (MCTDHF)

Superposition of
Many Slater determinant
(Multi Configurations)

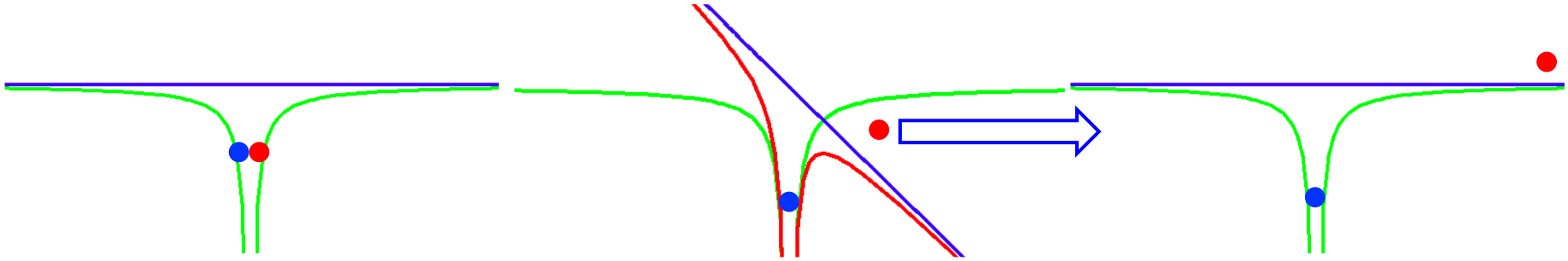
多数のスレーター行列式
（多配置）
の線型結合

$$\Psi_{\mathrm{MCTDHF}}(\boldsymbol{x}_1, \boldsymbol{x}_2, \cdots \boldsymbol{x}_N) = \sum_{i,j,\cdots,k} C_{ij\cdots k} \left| \psi_i \psi_j \cdots \psi_k \right| \equiv \sum_I C_I \Phi_I$$



TDHF (and TDDFT)
cannot appropriately
describe **strong** ionization ***process***.
Why?

Singlet two electron system (e.g, He)



Spatial part of TDHF wavefunction:

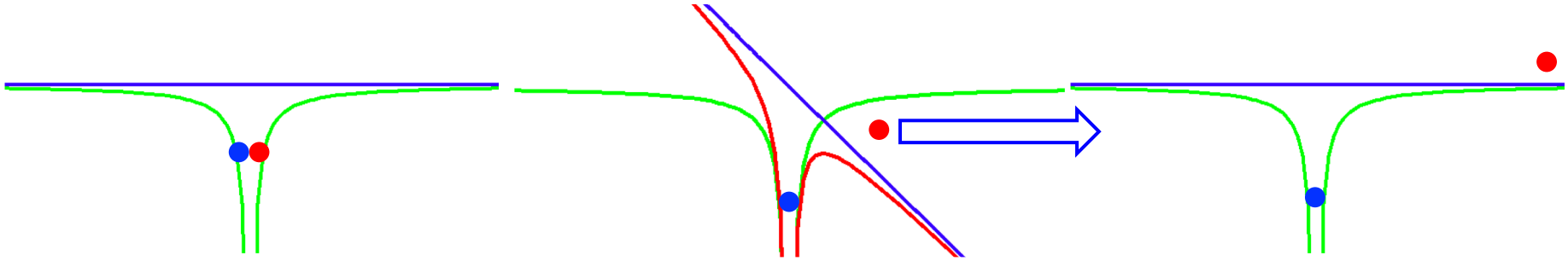
$$\Psi_{\mathrm{HF}}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \psi_1(\boldsymbol{r}_1)\psi_1(\boldsymbol{r}_2)$$

$$i\dot{\psi}_1(\boldsymbol{r}) = \left\{ \hat{h}(\boldsymbol{r}, t) + \int d\boldsymbol{r}' \frac{|\psi_1(\boldsymbol{r}')|^2}{|\boldsymbol{r} - \boldsymbol{r}'|} \right\} \psi_1(\boldsymbol{r})$$

TDHF and TDDFT, with only 1 orbitals for 2 electrons,
CANNOT describe bound and ionized electrons

1軌道で2電子を記述するTDHFでは束縛電子と
電離電子を同時に記述できない

Singlet two electron system (e.g, He)



At least two spatial orbitals are required

少なくとも2軌道必要

$$\Psi_{\mathrm{GVB}}(\boldsymbol{r}_1,\boldsymbol{r}_2) \propto \psi_1(\boldsymbol{r}_1)\psi_2(\boldsymbol{r}_2) + \psi_2(\boldsymbol{r}_1)\psi_1(\boldsymbol{r}_2)$$

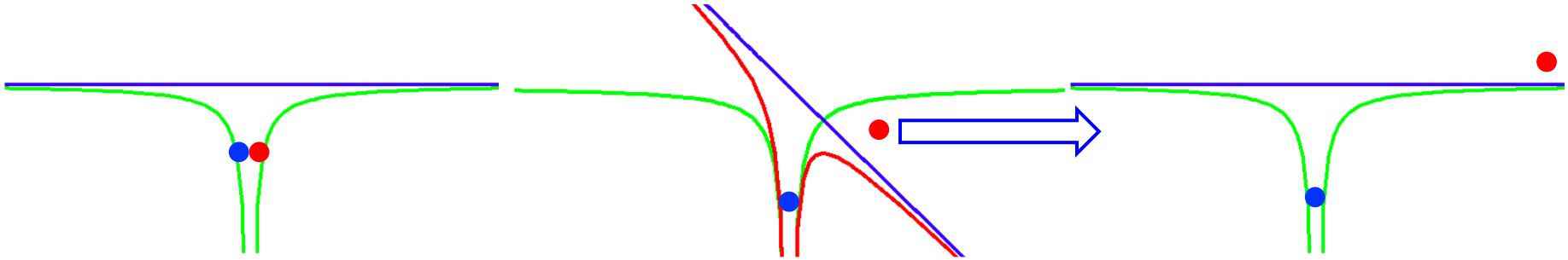
Generalized Valence Bond (Chemistry)

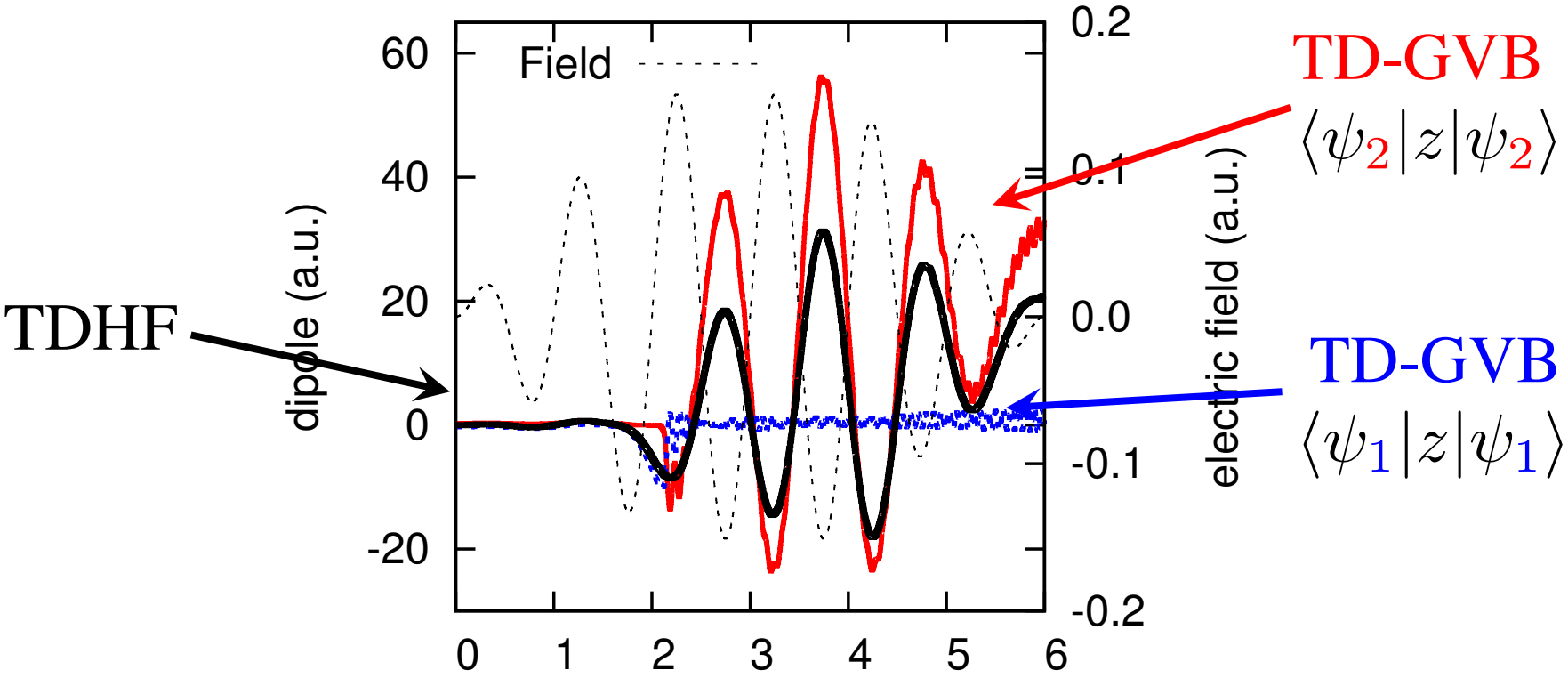
Extended Hartree-Fock (Physics)

$$S_{12} \equiv \langle\psi_1|\psi_2\rangle \neq 0$$

$$dS_{12}/dt \neq 0$$

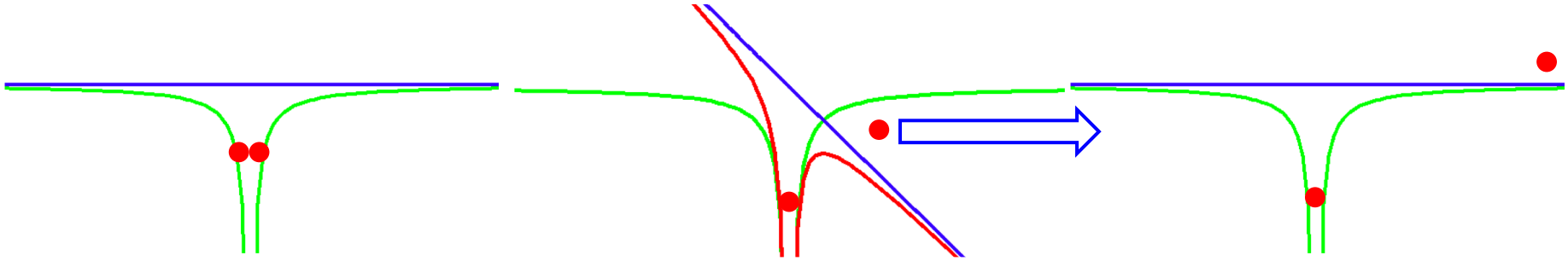
Singlet two electron system (e.g, He)





Dipole moment (mean position)

Singlet two electron system (e.g, He)



TD-GVB

$$\Psi_{\mathrm{GVB}}(\boldsymbol{r}_1,\boldsymbol{r}_2) \propto \psi_1(\boldsymbol{r}_1)\psi_2(\boldsymbol{r}_2) + \psi_2(\boldsymbol{r}_1)\psi_1(\boldsymbol{r}_2)$$

$$S_{12} \equiv \langle\psi_1|\psi_2\rangle \neq 0$$

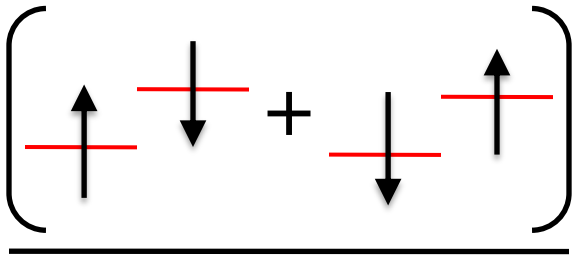
Good for $N = 2$, but

Too complicated for $N > 2$

二電子で成功も、より多電子への拡張は困難

Orbital redundancy

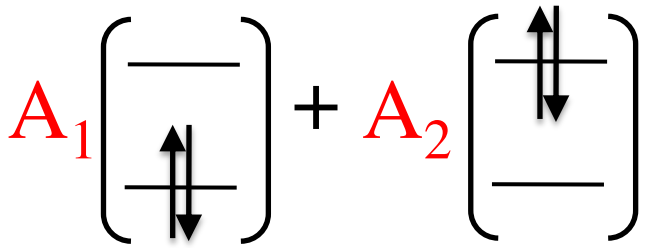
Linear transformation of orbitals,
that leaves **total wavefunction invariant**.



$$\Psi_{\mathrm{GVB}}(\boldsymbol{r}_1,\boldsymbol{r}_2) = \frac{1}{\sqrt{2}}\left[\psi_1(\boldsymbol{r}_1)\psi_2(\boldsymbol{r}_2) + \psi_2(\boldsymbol{r}_1)\psi_1(\boldsymbol{r}_2)\right]$$
$$= A_1\phi_1(\boldsymbol{r}_1)\phi_1(\boldsymbol{r}_2) + A_2\phi_2(\boldsymbol{r}_1)\phi_2(\boldsymbol{r}_2)$$

$$\psi_1\psi_2 + \psi_2\psi_1$$

Equivalent! 等価



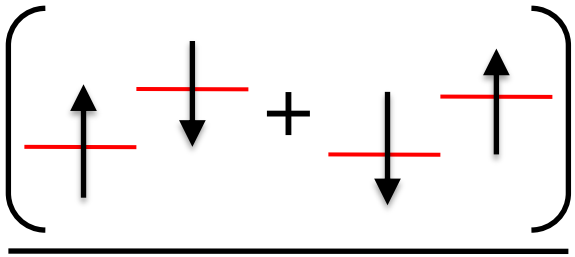
$$\langle\phi_1|\phi_2\rangle = 0$$

$$A_1 = \frac{1+|S_{12}|}{\sqrt{2(1+|S_{12}|^2)}}\frac{S_{12}^*}{|S_{12}|},$$
$$A_2 = \frac{1-|S_{12}|}{\sqrt{2(1+|S_{12}|^2)}}\frac{S_{12}}{|S_{12}|},$$

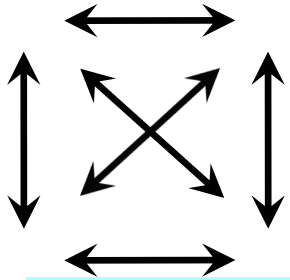
$$\phi_1 = \frac{1}{\sqrt{2(1+|S_{12}|)}}\left\{\frac{S_{12}}{|S_{12}|}\psi_1 + \psi_2\right\}$$
$$\phi_2 = \frac{1}{\sqrt{2(1+|S_{12}|)}}\left\{\frac{S_{12}^*}{|S_{12}|}\psi_2 - \psi_1\right\}$$

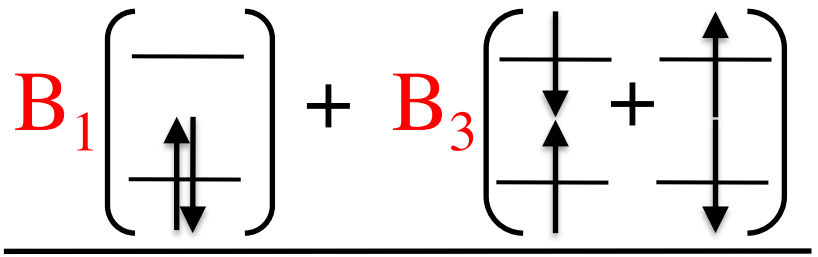
Orbital redundancy

All Equivalent 全て等価

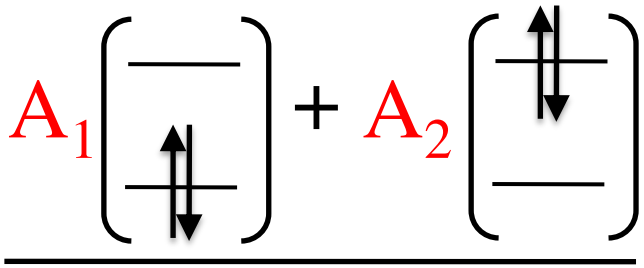


$$\psi_1\psi_2 + \psi_2\psi_1$$



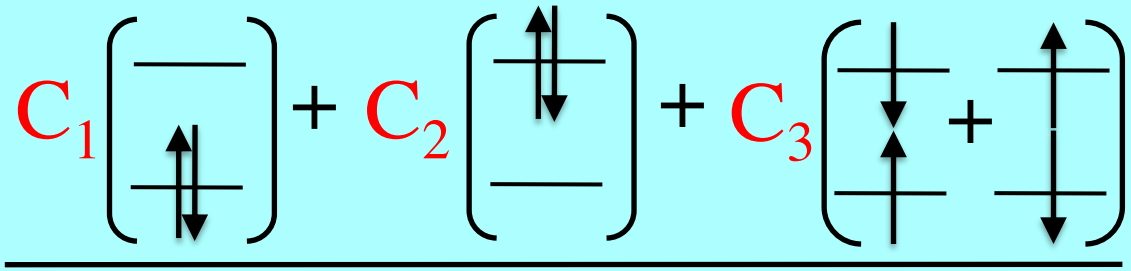


$$\langle\phi_1|\phi_2\rangle = 0$$



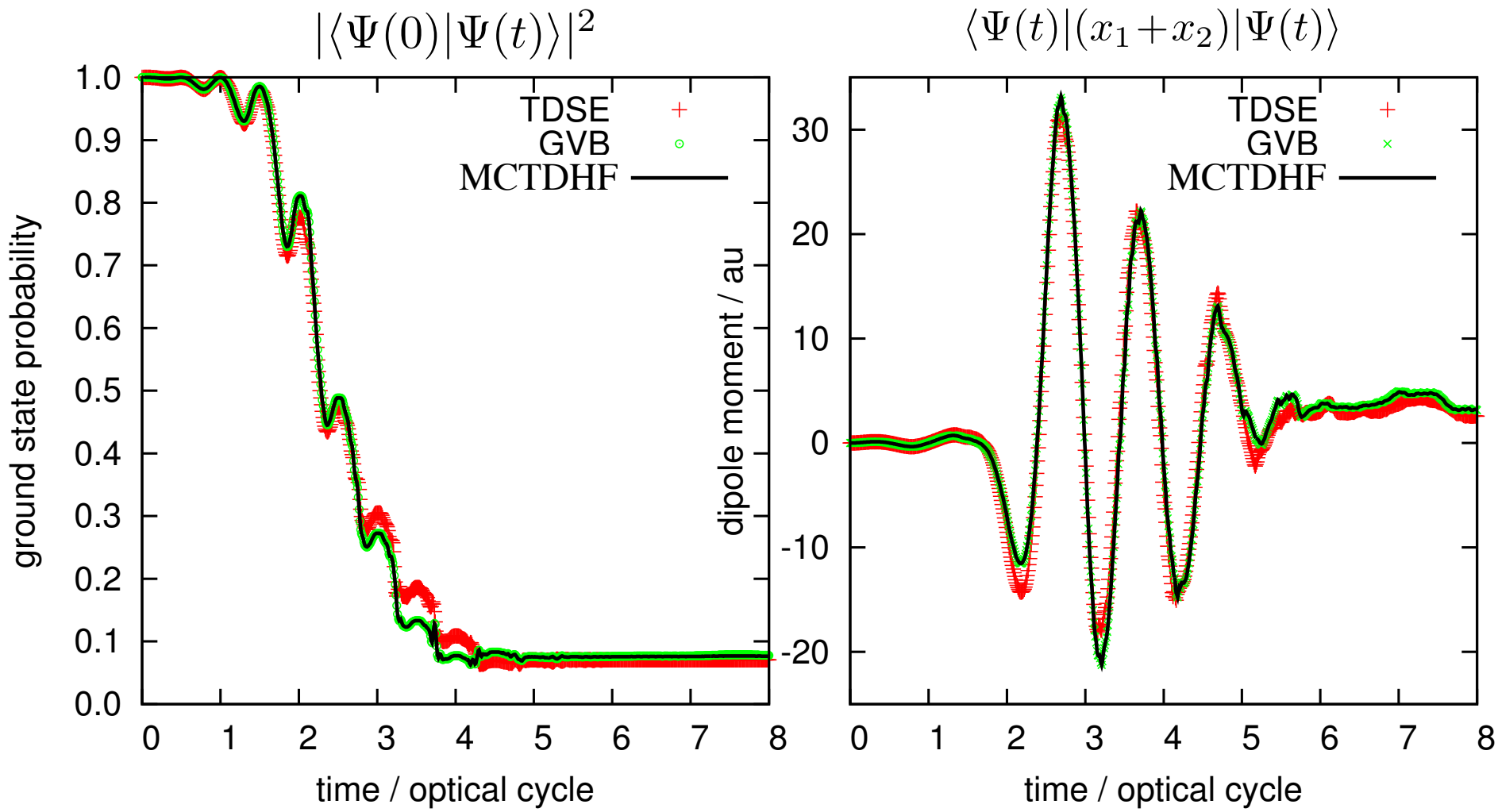
$$\langle\phi_1|\phi_2\rangle = 0$$

MCTDHF



$$\langle\phi_1|\phi_2\rangle = 0$$

May be based on the most convenient ansatz



$$\Psi(t) = \sum_{ij}^{2} C_{ij}(t)\phi_i(1,t)\phi_j(2,t) \propto \psi_1(1,t)\psi_2(2,t) + \psi_2(1,t)\psi_1(2,t)$$

MCTDHF with two orbitals and TD-GVB are equivalent, with

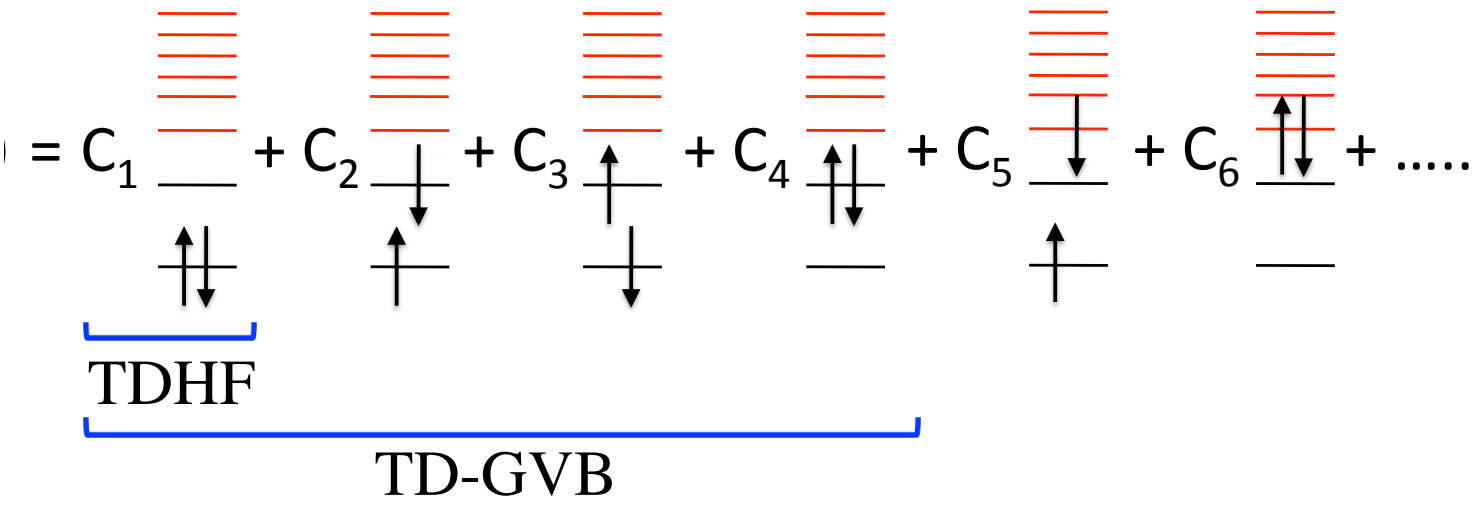
MCTDHF being much simpler

MCTDHF method for two electron systems

$$\Psi(t) = \sum_{ij}^{2} C_{ij}(t)\phi_i(1,t)\phi_j(2,t) \propto \psi_1(1,t)\psi_2(2,t) + \psi_2(1,t)\psi_1(2,t)$$

- ✓ Propagate both CI coefficients and orbitals
- ✓ Can improve accuracy by increasing orbitals

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, t) = \sum_{ij}^{n} C_{ij}(t)\phi_i(\boldsymbol{r}_1, t)\phi_j(\boldsymbol{r}_2, t)$$



Nonsequential Double Ionization of Helium 非逐次二重電離

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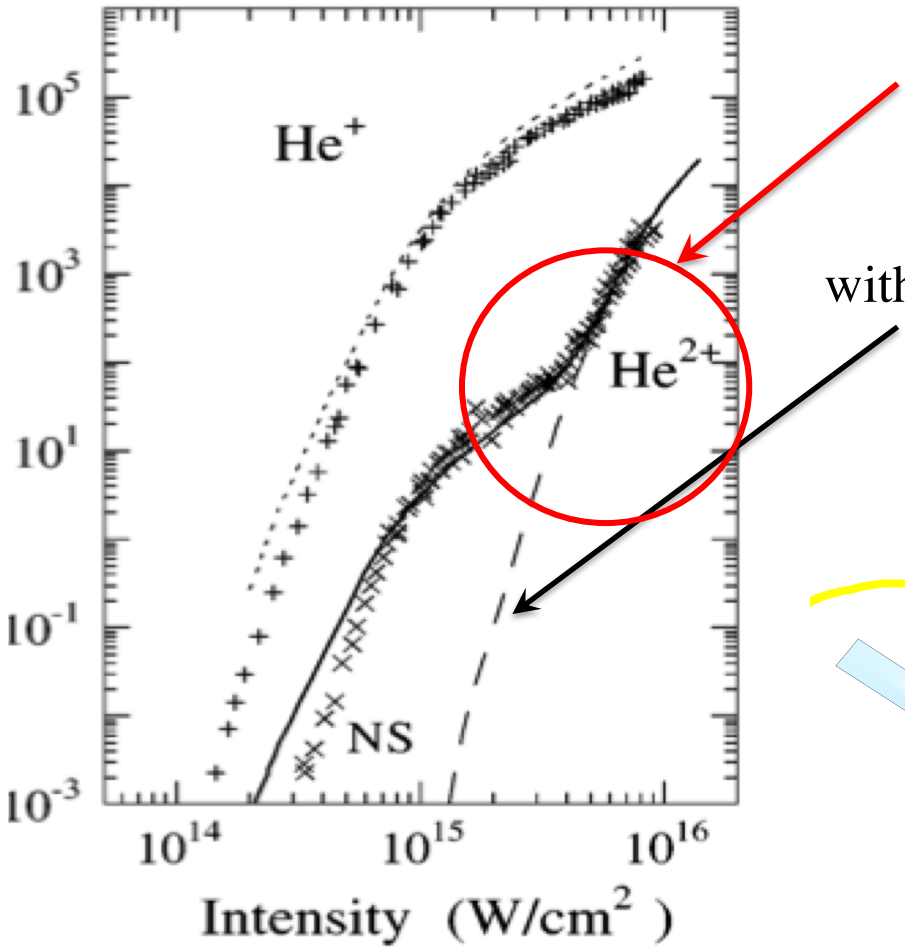
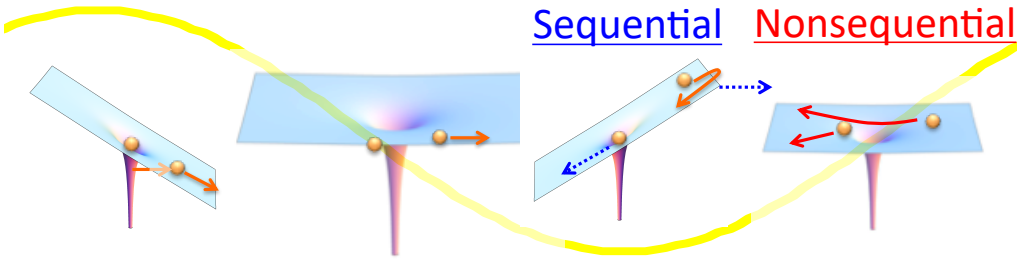
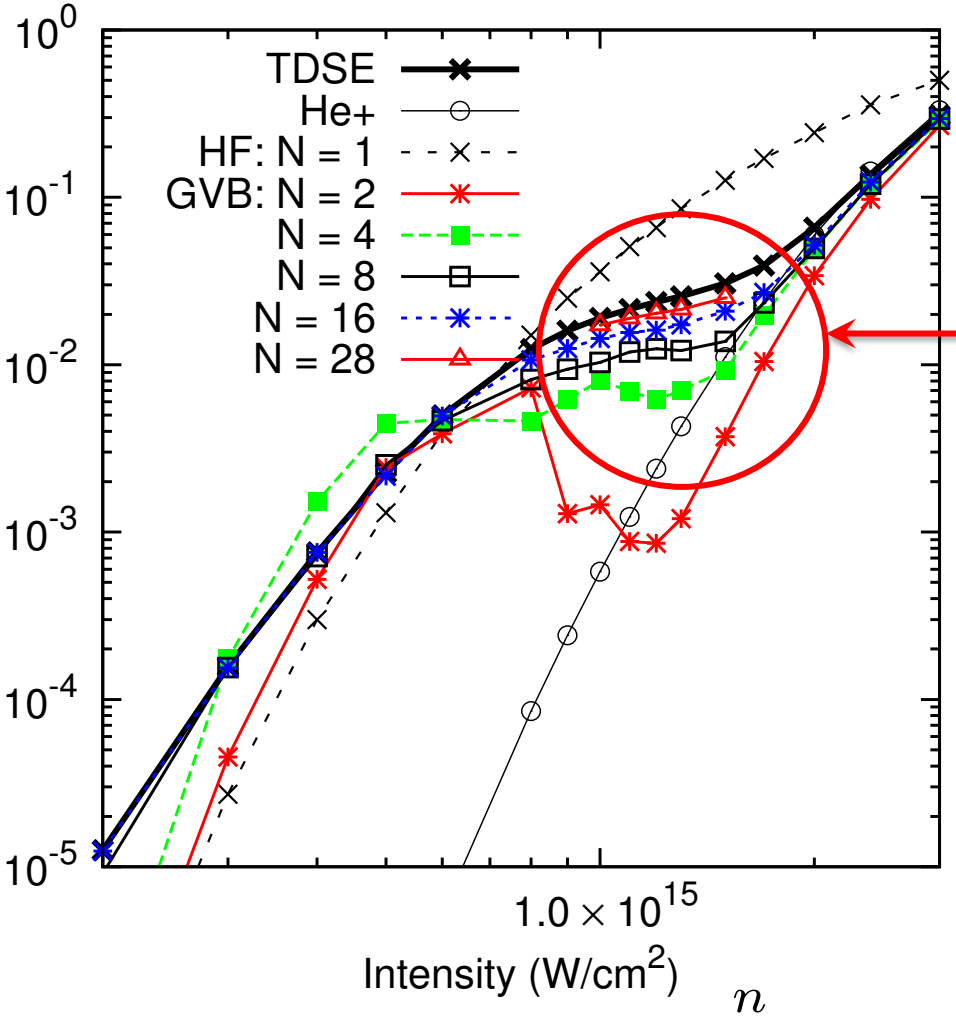
(Received 27 August 1996)
PRL, 78, 1884 (1997)



Experiment: 実験
"Shoulder" region, or
"Knee" region

Simulation: 計算
with electron-electron correlation **neglected**
電子間相互作用を無視





Accuracy can be improved systematically by increasing orbitals

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, t) = \sum_{ij}^{n} C_{ij}(t)\phi_i(\boldsymbol{r}_1, t)\phi_j(\boldsymbol{r}_2, t)$$

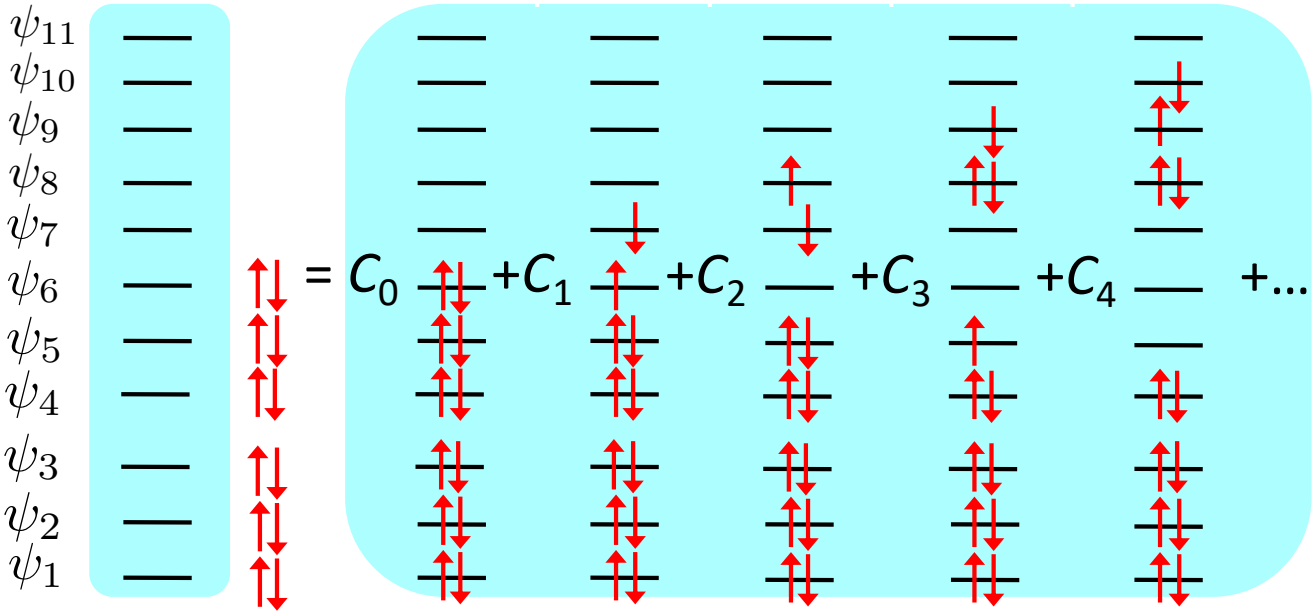
MCTDHF is a powerful tool for multielectron dynamics

(3) Multiconfiguration TDHF (MCTDHF)

Superposition of
Many TD Slater determinants

多数の時間に依存する
スレーター行列式
の線型結合

$$\Psi_{\mathrm{MCTDHF}}(\boldsymbol{x}_1, \boldsymbol{x}_2, \cdots \boldsymbol{x}_N) = \sum_{i,j,\cdots,k} C_{ij\cdots k} \left| \psi_i \psi_j \cdots \psi_k \right| \equiv \sum_I C_I \Phi_I$$



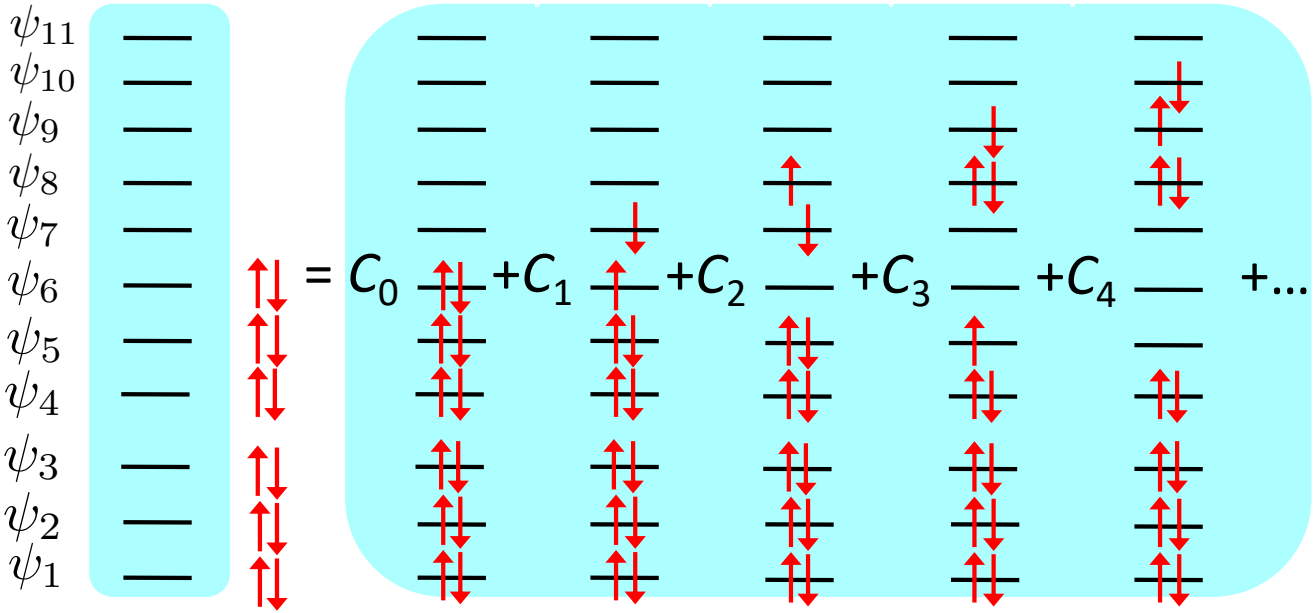
(3) Multiconfiguration TDHF (MCTDHF)

Problem:

Factorial cost scaling w.r.t number of electrons

計算コストが電子数の**階乗**で増加

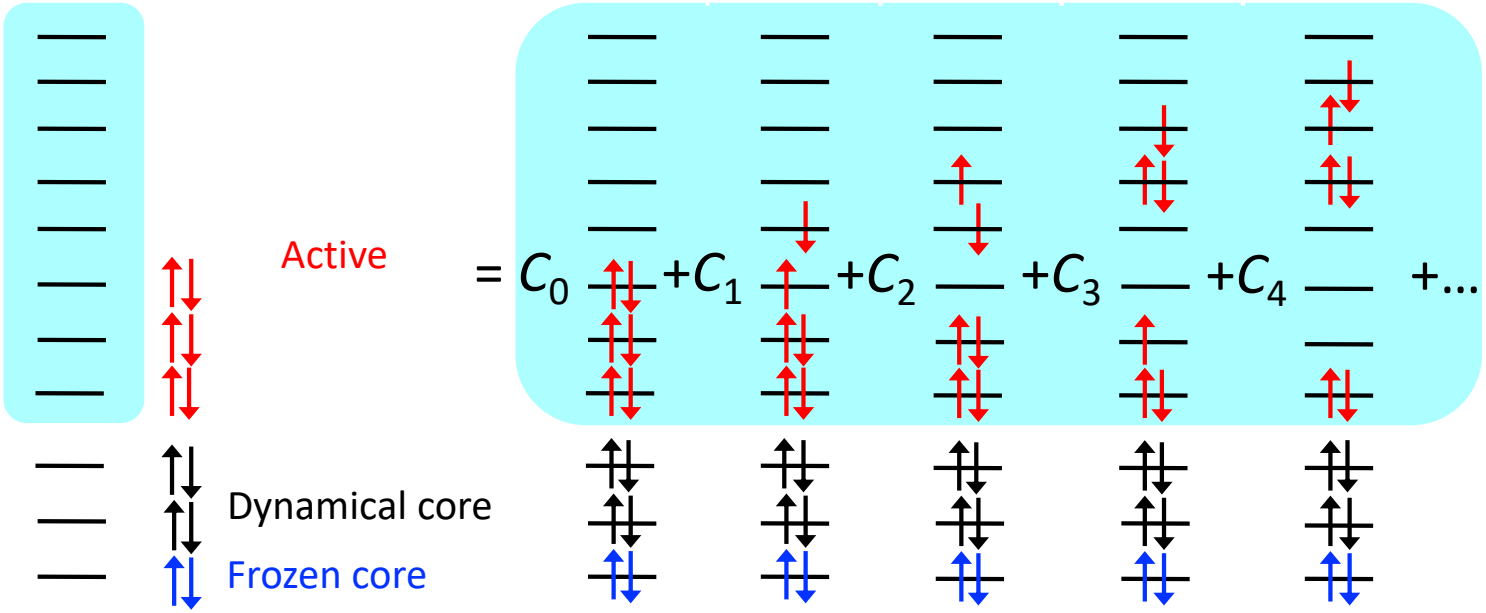
$$\Psi_{\mathrm{MCTDHF}}(\boldsymbol{x}_1, \boldsymbol{x}_2, \cdots \boldsymbol{x}_N) = \sum_{i,j,\cdots,k} C_{ij\cdots k} \left| \psi_i \psi_j \cdots \psi_k \right| \equiv \sum_I C_I \Phi_I$$



(4) More flexible methods

TS and K. L. Ishikawa, *Phys. Rev. A*, **88**, 023402 (2013): core & active: **TD-CASSCF**
TS and K. L. Ishikawa, *Phys. Rev. A*, **91**, 023417 (2015): occupation restriction: **TD-ORMAS**

Flexibly classifying electrons into
active , dynamical core, and frozen core



Less demanding (yet accurate), allowing deeper **physical insight** than fully correlated MCTDHF

Deriving Equations of motion

$$\Psi_{\mathrm{MCTDHF}}(\boldsymbol{r}_1,\boldsymbol{r}_2,\cdots\boldsymbol{r}_N)=\sum_{i,j,\cdots,k}C_{ij\cdots k}\left|\psi_i\psi_j\cdots\psi_k\right|\equiv\sum_I C_I\Phi_I$$

Time-dependent variational principle

$$S[\Psi]=\int dt\langle\Psi|\left(\hat{H}-\mathrm{i}\frac{\partial}{\partial t}\right)|\Psi\rangle$$

$$\delta S=\langle\delta\Psi|\left(\hat{H}-\mathrm{i}\frac{\partial}{\partial t}\right)|\Psi\rangle+c.c.=0$$

Equations of motion

$$i\dot{C}_I=\sum_J\langle\Phi_I|\hat{H}|\Phi_J\rangle C_J$$

$$i\dot{\psi}_i(\boldsymbol{r})=\hat{Q}\left[\{h_0+V_{\mathrm{ext}}(t)\}\psi_i(\boldsymbol{r})+\sum_{jklm}\int d\boldsymbol{r}'\frac{\psi_k^*(\boldsymbol{r}')\psi_l(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\psi_j(\boldsymbol{r})P_{mk}^{jl}(D^{-1})_i^m\right]+\sum_j\psi_j(\boldsymbol{r})R_i^j$$

Field free one-electron terms

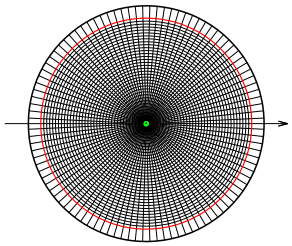
Electron-laser interaction

Electron-electron interaction

Real-space implementation

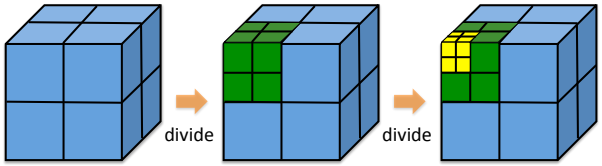
Local Potential $V(x)f(x) \longrightarrow V(x_i)f(x_i)$ 局所ポテンシャル

Kinetic energy $\dfrac{\partial^2}{\partial x^2} f(x) \longrightarrow \dfrac{f(x_{i-1}) - 2f(x_i) + f(x_{i+1})}{\Delta x^2}$ 運動エネルギー



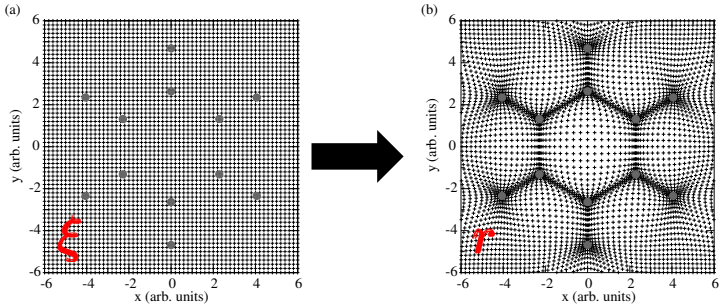
Spherical coordinate for atoms

$$\psi_p(t) \longrightarrow \sum_{klm} c_{p,klm}(t) \frac{f_{klm}(r)}{r} Y_{lm}(\theta, \phi)$$



Multiresolution cartesian grids

$$\psi_p(t) \longrightarrow \psi_p(x_i, y_j, z_k, t)$$



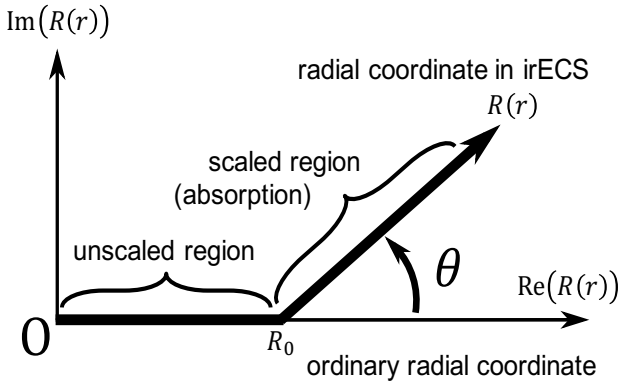
Curvilinear coordinate

$$\psi_p(t) \longrightarrow \bar{\psi}_p(\xi_i, \xi_j, \xi_k, t),$$

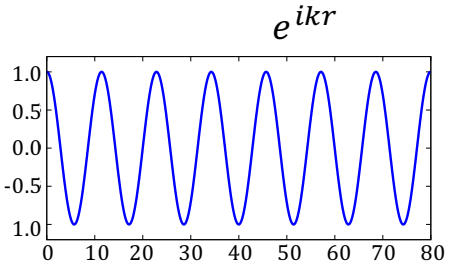
$$\bar{\psi}_p(\boldsymbol{\xi}, t) = |J(\boldsymbol{\xi})|^{1/2} \psi_p(\boldsymbol{r}(\boldsymbol{\xi}, t))$$

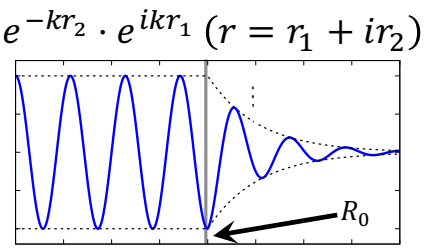
Absorbing boundary condition
吸収境界条件

Mask function, Complex absorbing potential (CAP), Exterior complex scaling (ECS), etc

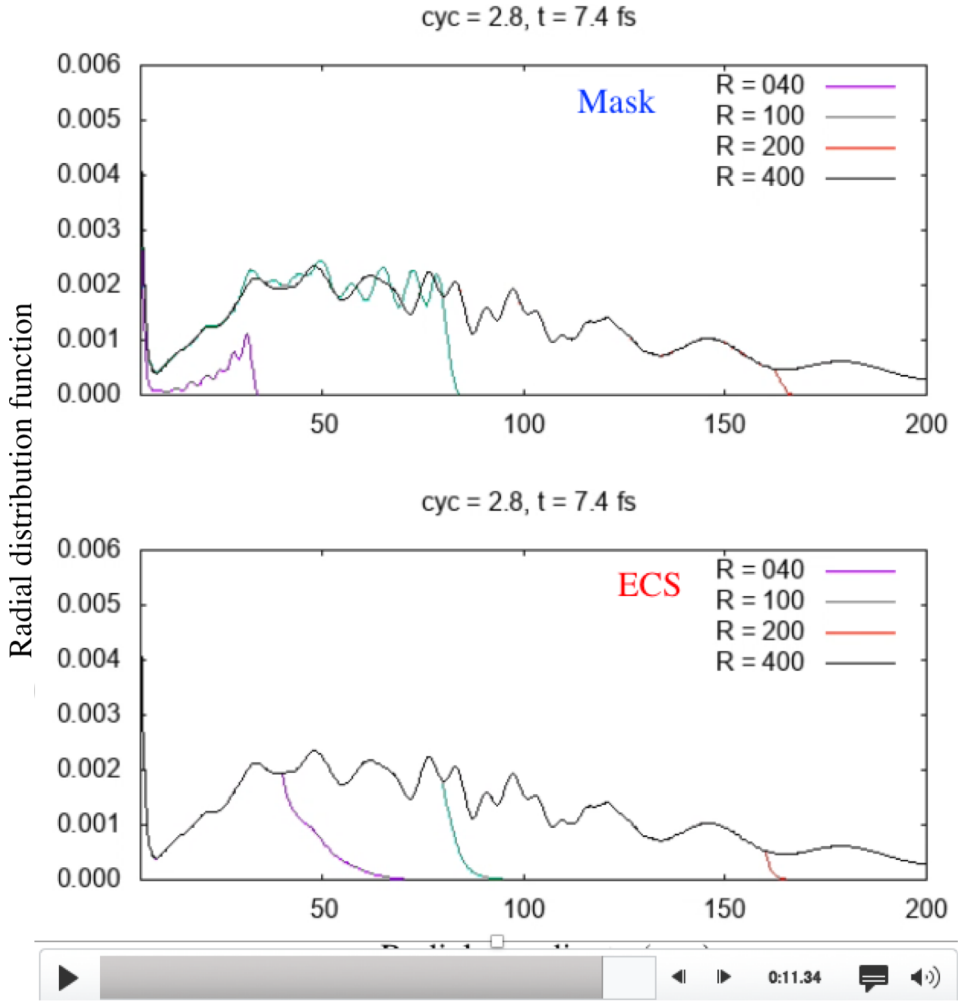


$$r \to R(r) = \begin{cases} r & (r < R_0) \\ R_0 + (r - R_0)\mathrm{e}^{i\eta} & (r \geq R_0) \end{cases}$$





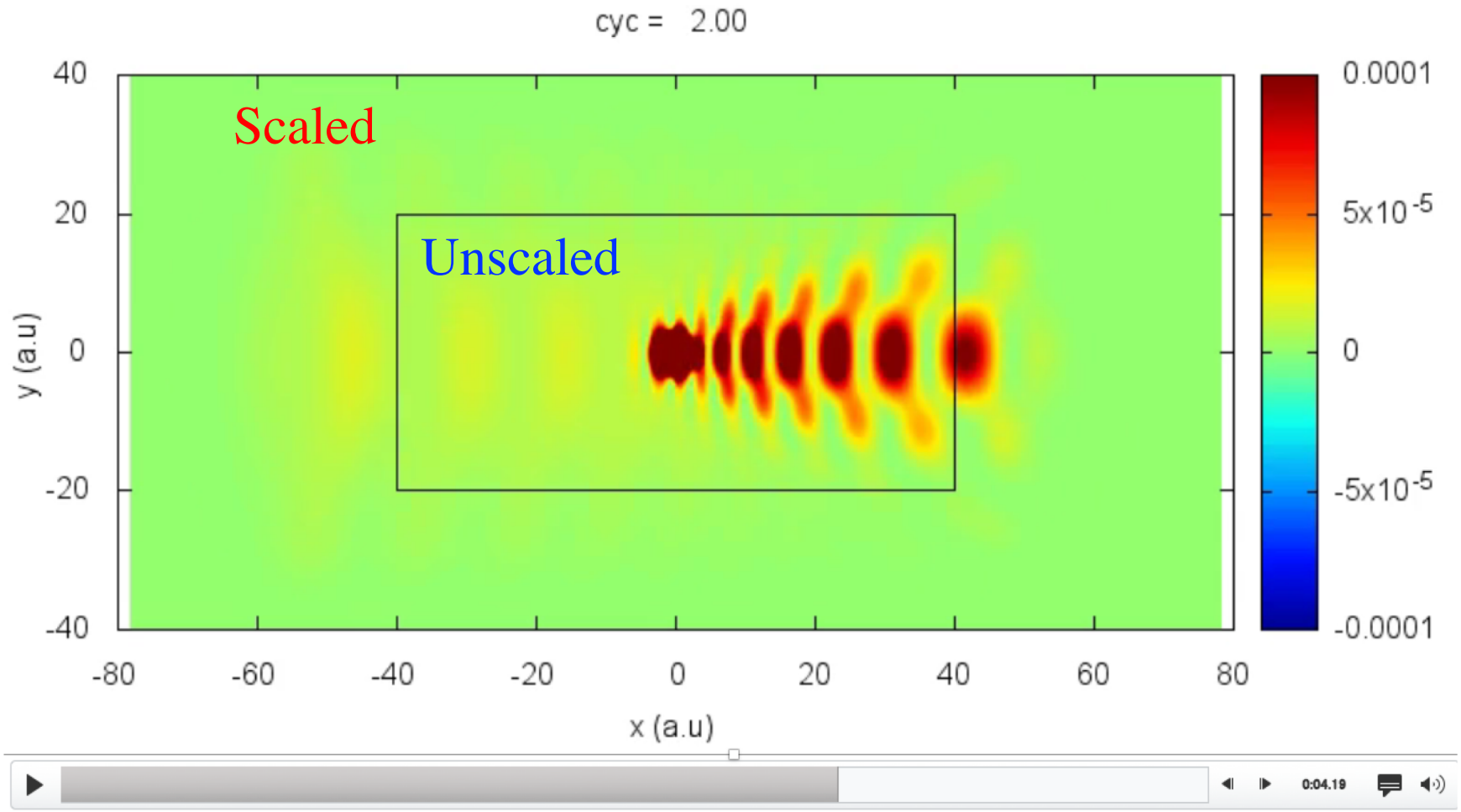
Radial coordinate



H, 800 nm, 4×10^{14} W/cm^2

Absorbing boundary condition

吸収境界条件

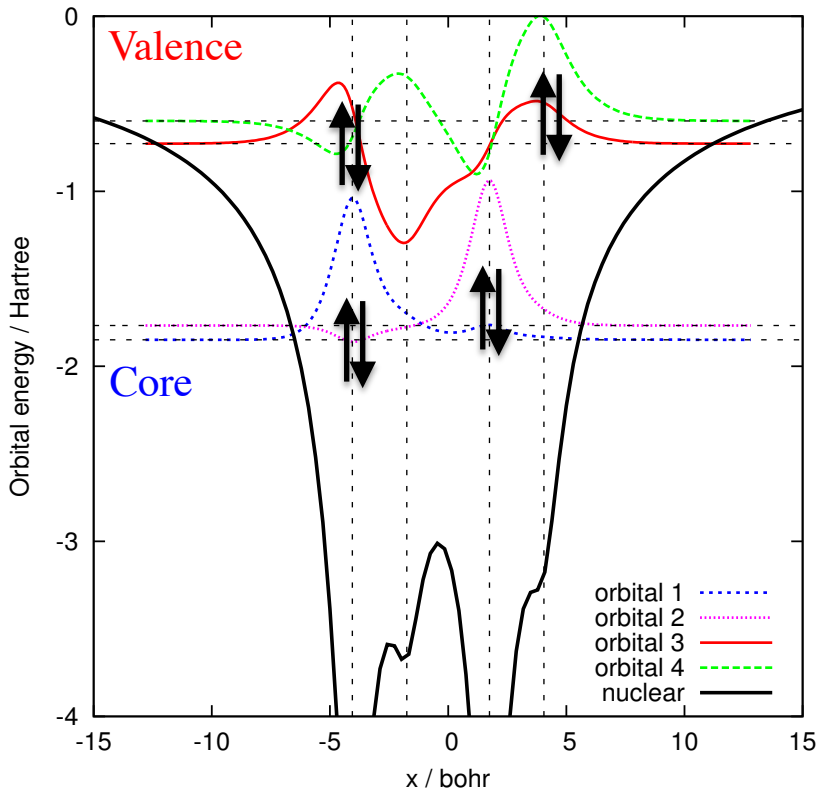


Numerically converged simulation with a finite simulation box

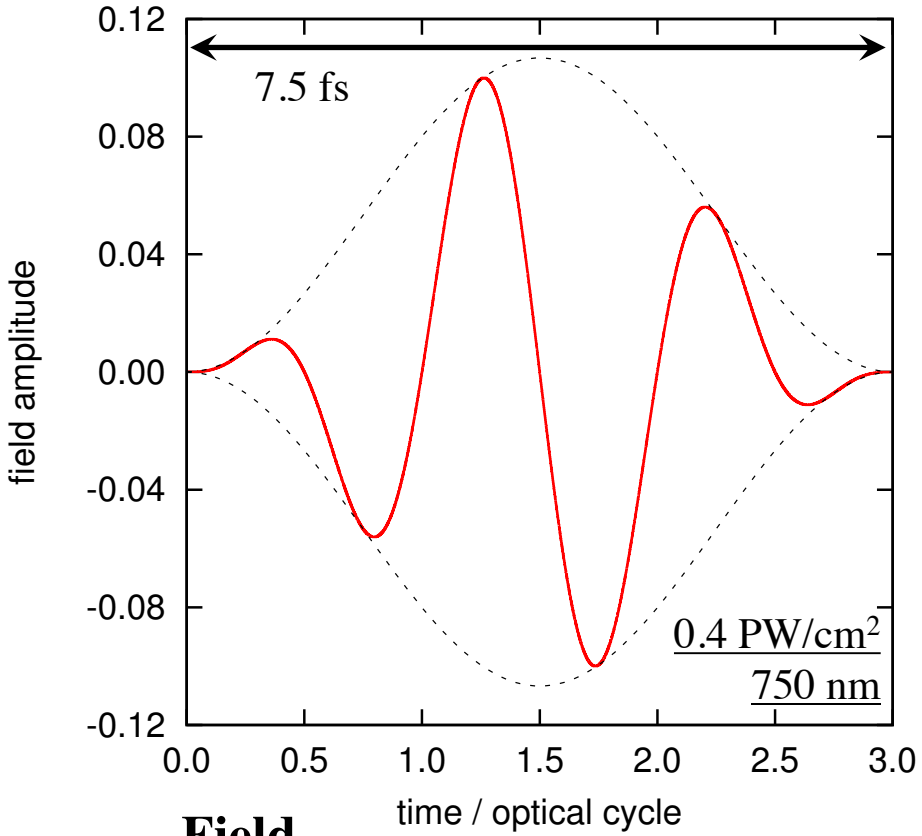
有限の計算領域で数値的に収束したシミュレーションが可能

Applicaions

$$H = \sum_{i=1}^{N} \left\{ -\frac{1}{2}\frac{\partial^2}{\partial x_i^2} - \sum_{a=1}^{M} \frac{Z_a}{\sqrt{(x_i - X_a)^2 + c}} - x_i E(t) \right\} + \sum_{i>j}^{N} \frac{1}{\sqrt{(x_i - x_j)^2 + d}}$$



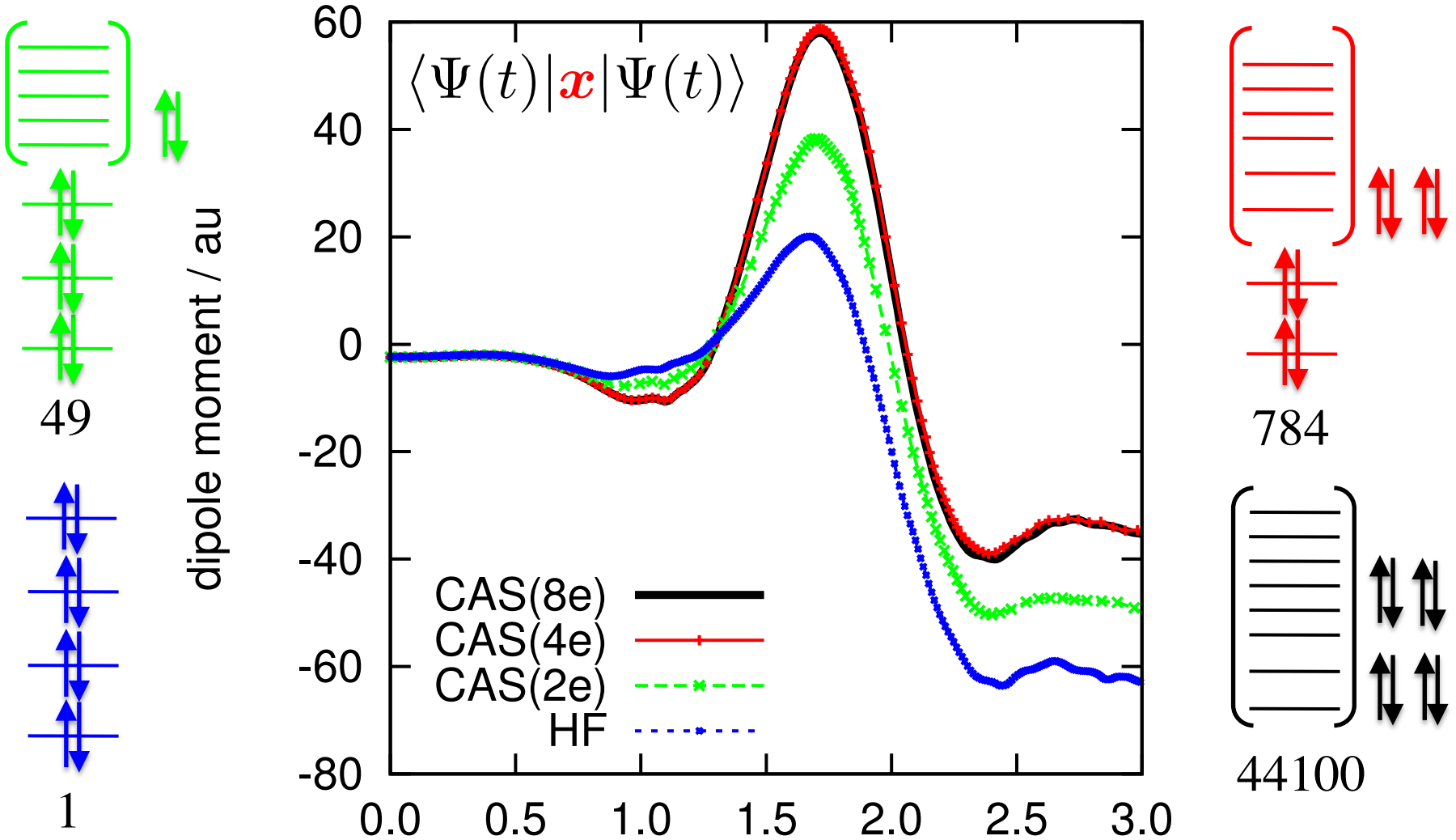
Ground-state



Field

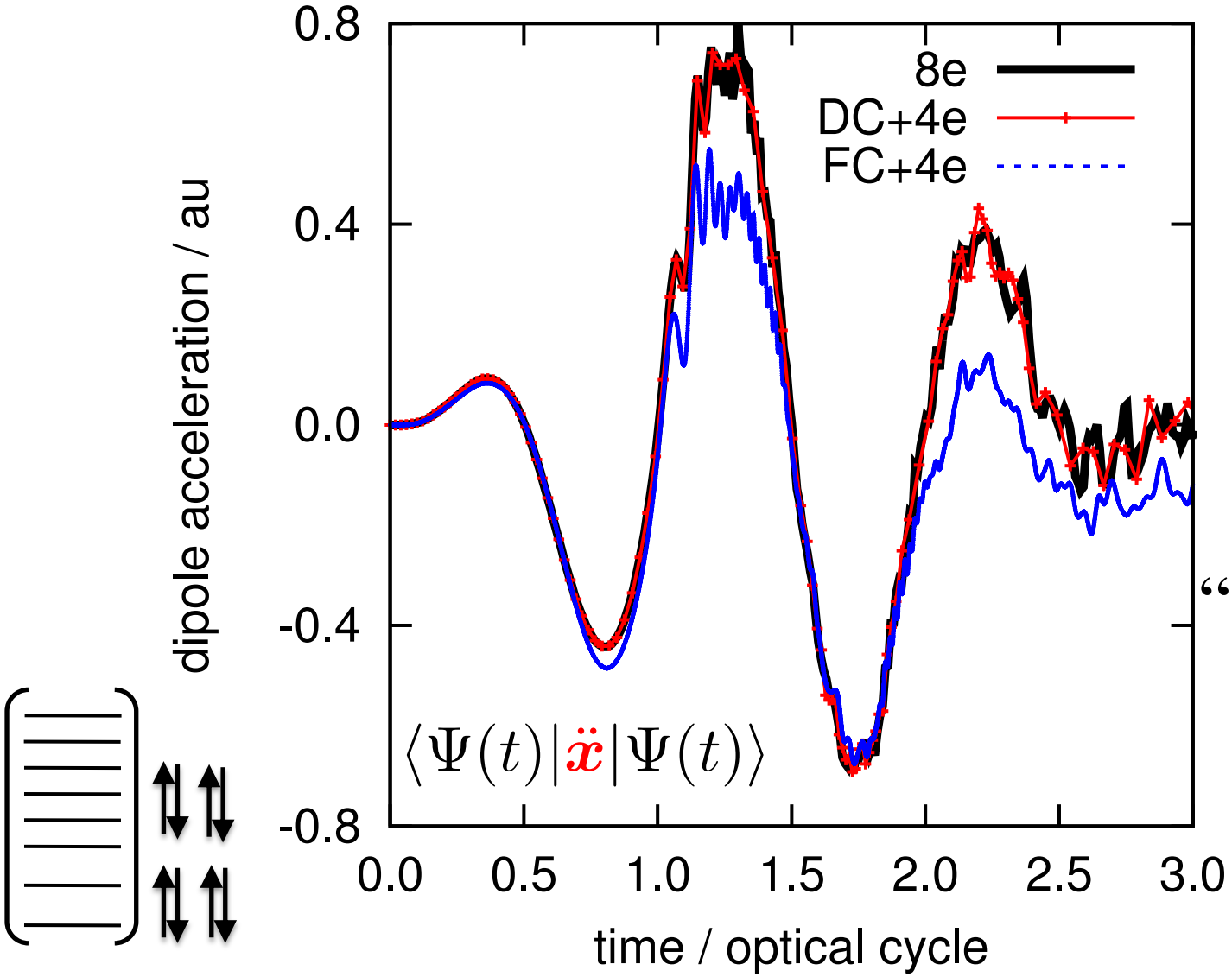
1D "LiH dimer" 4 valence and 4 core electrons

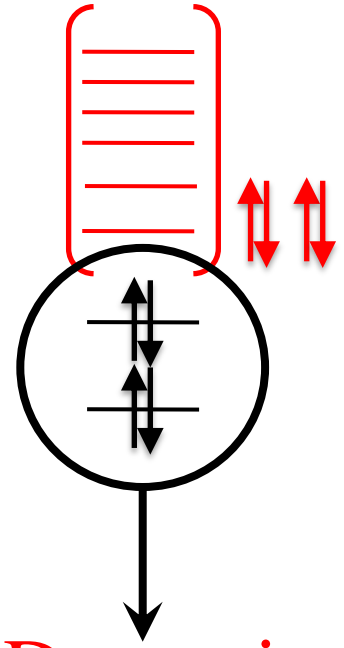
Applicaions



TD-CASSCF(4e, 8a) reproduces MCTDHF(8o, 10o)

Applicaions





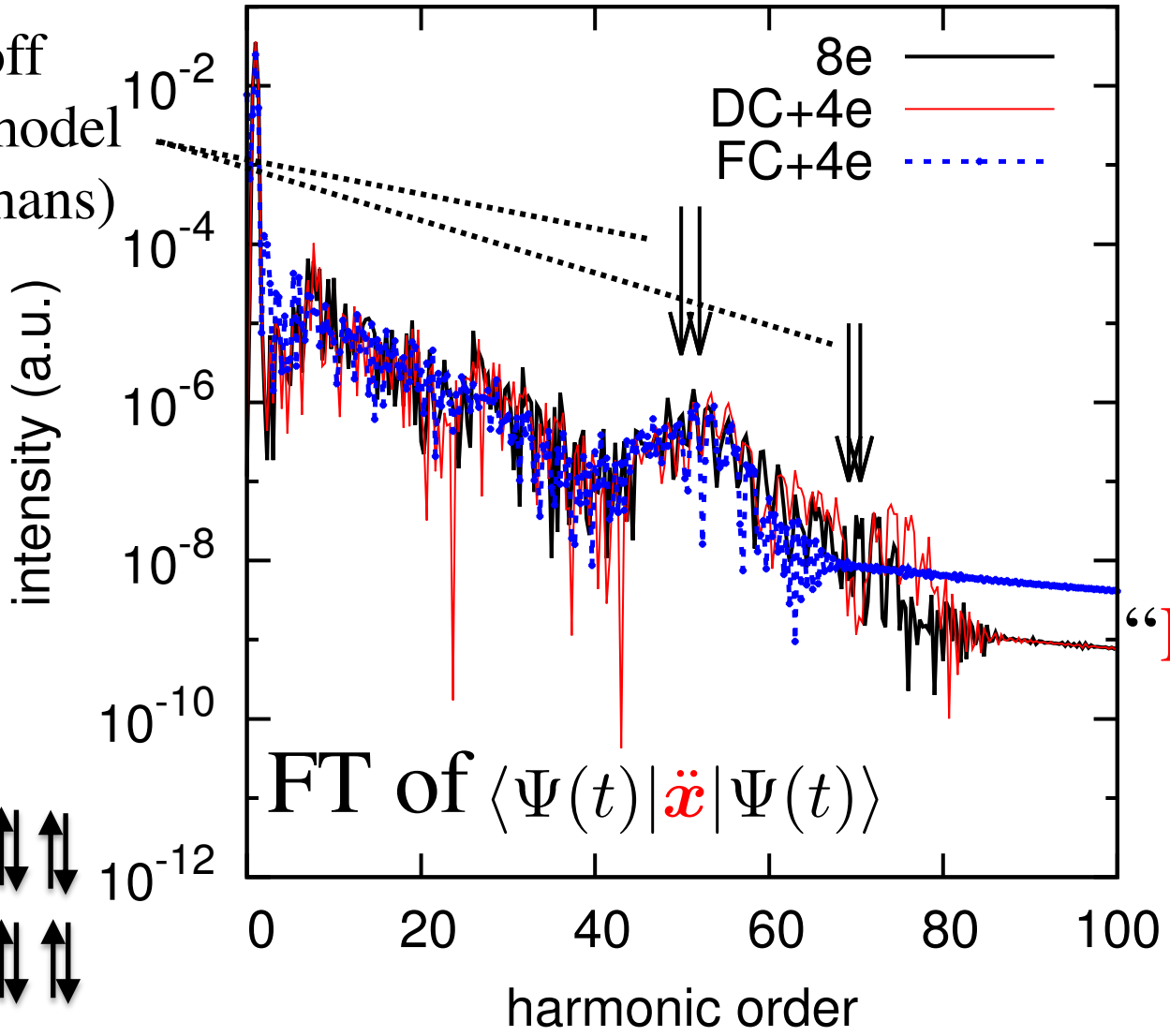
“Dynamical”

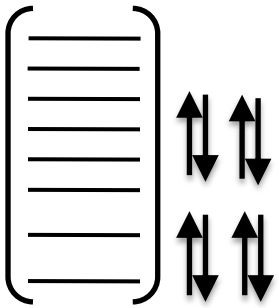
or

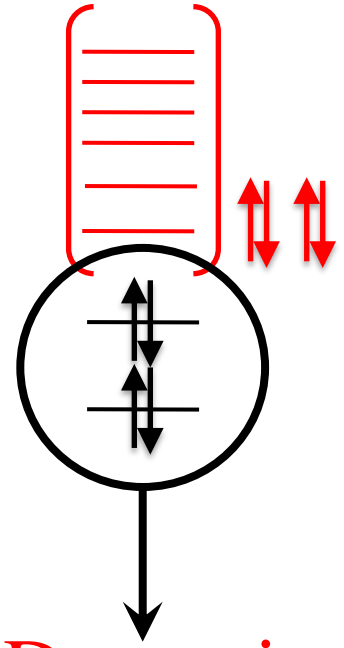
“Frozen”

Applicaions

Cutoff
3-step model
(Koopmans)







“Dynamical”
or
“Frozen”

Elucidating roles of valence and core dynamics