Describing Quantum Phases of Matter and their Dynamics within DFT and TDDFT

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The Hamiltonian of Condensed Matter (atoms, molecules, solids)

Hamiltonian for the complete system of N_e electrons with coordinates $(\mathbf{r}_1 \cdots \mathbf{r}_{N_e}) \equiv \underline{\underline{\mathbf{r}}}$ and N_n nuclei with coordinates $(\mathbf{R}_1 \cdots \mathbf{R}_{N_n}) \equiv \underline{\underline{\mathbf{R}}}$

$$\hat{H} = \hat{T}_n(\underline{\underline{R}}) + \hat{W}_{nn}(\underline{\underline{R}}) + \hat{T}_e(\underline{\underline{r}}) + \hat{W}_{ee}(\underline{\underline{r}}) + \hat{V}_{en}(\underline{\underline{R}}, \underline{\underline{r}})$$

with $\hat{T}_n = \sum_{\nu=1}^{N_n} -\frac{\nabla_\nu^2}{2M_\nu}$ $\hat{T}_e = \sum_{i=1}^{N_e} -\frac{\nabla_i^2}{2m}$ $\hat{W}_{nn} = \frac{1}{2}\sum_{\substack{\mu,\nu \\ \mu\neq\nu}}^{N_n} \frac{Z_\mu Z_\nu}{|R_\mu - R_\nu|}$

$$\hat{W}_{ee} = \frac{1}{2}\sum_{\substack{j,k \\ j\neq k}}^{N_e} \frac{1}{|r_j - r_k|} \qquad \hat{V}_{en} = \sum_{j=1}^{N_e}\sum_{\nu=1}^{N_n} -\frac{Z_\nu}{|r_j - R_\nu|}$$

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Stationary Schrödinger equation

$$\hat{H}\Psi(\underline{\underline{r}}, \underline{\underline{\underline{R}}}) = E\Psi(\underline{\underline{r}}, \underline{\underline{\underline{R}}})$$

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Time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\Psi(\underline{\underline{r}}, \underline{\underline{R}}, t) = \left(H(\underline{\underline{r}}, \underline{\underline{R}}) + V_{laser}(\underline{\underline{r}}, \underline{\underline{R}}, t)\right)\psi(\underline{\underline{r}}, \underline{\underline{R}}, t)$$

$$V_{laser}(\underline{\underline{r}}, \underline{\underline{R}}, t) = \left(\sum_{j=1}^{N_e} r_j - \sum_{\nu=1}^{N_n} Z_\nu R_\nu\right) \cdot E \cdot f(t) \cdot \cos\omega t$$

Born-Oppenheimer approximation

solve

$$\left(\hat{T}_e(\underline{\underline{r}}) + W_{ee}(\underline{\underline{r}}) + \hat{W}_{nn}(\underline{\underline{R}}) + V_{en}(\underline{\underline{r}}, \underline{\underline{R}})\right)\Phi^{BO}_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right) = \in^{BO}\left(\underline{\underline{R}}\right)\Phi^{BO}_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)$$

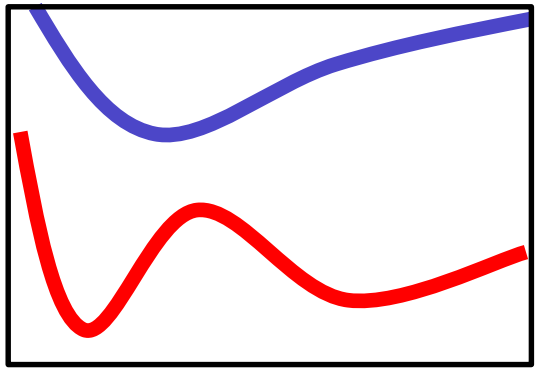
for each fixed nuclear configuration $\underline{\underline{R}}$.

Make adiabatic ansatz for the complete molecular wave function:

$$\Psi^{BO}\left(\underline{\underline{r}}, \underline{\underline{R}}\right) = \Phi^{BO}_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right) \cdot \chi^{BO}\left(\underline{\underline{R}}\right)$$

and find best χ^{BO} by minimizing $\langle \Psi^{BO} | H | \Psi^{BO} \rangle$ w.r.t. χ^{BO} :

Born-Oppenheimer approximation



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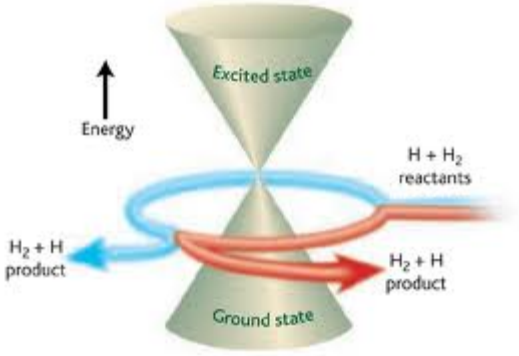
Nuclear equation

$$\left[\text{资}_{\mathbf{n}}(\underline{\underline{R}}) + W_{nn}(\underline{\underline{R}}) + \sum_{\upsilon} \frac{1}{M_{\upsilon}} A_{\upsilon}^{BO}(\underline{\underline{R}})\,(-i\nabla_{\upsilon}) + \in^{BO}(\underline{\underline{R}}) \right.$$

$$\left. + \int \Phi_{\underline{\underline{R}}}^{BO\,*}(\underline{\underline{r}})\hat{T}_{n}(\underline{\underline{R}})\Phi_{\underline{\underline{R}}}^{BO}(\underline{\underline{r}})d\underline{\underline{r}} \right] \chi^{BO}(\underline{\underline{R}}) = E\chi^{BO}(\underline{\underline{R}})$$



Berry connection

$$\mathbf{A_{\upsilon}^{BO}(\underline{\underline{R}}) = \int \Phi_{\underline{\underline{R}}}^{BO\,*}(\underline{\underline{r}})(-i\nabla_{\upsilon})\Phi_{\underline{\underline{R}}}^{BO}(\underline{\underline{r}})d\underline{\underline{r}}}$$

$\gamma^{BO}(C) = \oint_{C} \vec{A}^{BO}(\underline{\underline{R}}) \cdot d\vec{R}$ **is a geometric phase**

In this context, potential energy surfaces $\in^{BO}(\underline{\underline{R}})$ **and the vector potential** $\vec{A}^{BO}(\underline{\underline{R}})$ **follow from an APPROXIMATION (the BO approximation).**

To start: Focus on the Electronic-Structure Problem (i.e. make Born-Oppenheimer approximation):

$$\left(\hat{T}_{e}(\underline{\underline{r}}) + W_{ee}(\underline{\underline{r}}) + \hat{W}_{nn}(\underline{\underline{R}}) + V_{en}(\underline{\underline{r}}, \underline{\underline{R}})\right)\Phi^{BO}_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right) = \in^{BO}\left(\underline{\underline{R}}\right)\Phi^{BO}_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)$$

for fixed nuclear configuration $\underline{\underline{R}}$.

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for fixed nuclear configuration $\underline{\underline{R}}$.

Note: This is still an exponentially hard problem!!

Two fundamentally different classes of ab-initio approaches:

- **Wave function approaches**

  -- Quantum Monte Carlo
  -- Configuration interaction
  -- Tensor product decomposition

- **"Functional Theories"**

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  -- Configuration interaction
  -- Tensor product decomposition

- **"Functional Theories"**

  Write total energy as functional of a simpler quantity and minimize

“Functional Theories”

MBPT **RDMFT** **DFT**

$G(r, r', t - t')$ $\gamma(r, r') = G(r, r', 0^+)$ $\rho(r) = \gamma(r, r)$

“Functional Theories”

MBPT	RDMFT	DFT
$G(r, r', t - t')$	$\gamma(r, r') = G(r, r', 0^+)$	$\rho(r) = \gamma(r, r)$
Functional: $\Phi_{xc}[G]$ or $\Sigma_{xc}[G]$	Functional: $E_{xc}[\gamma]$	Functional: $E_{xc}[\rho]$ or $v_{xc}[\rho]$

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easy (e.g. GW)	difficult	very difficult

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easy (e.g. GW)	difficult	very difficult
numerically		
heavy	moderate	light

ESSENCE OF DENSITY-FUNTIONAL THEORY

- **Every observable quantity of a quantum system can be calculated from the density of the system ALONE**

- **The density of particles interacting with each other can be calculated as the density of an auxiliary system of non-interacting particles**

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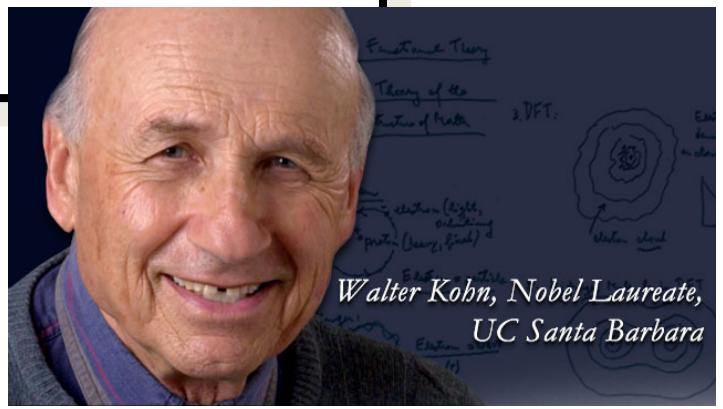
Hohenberg-Kohn theorem (1964)
Kohn-Sham theorem (1965)
(for the ground state)



HOHENBERG-KOHN THEOREM

1. $v(r) \xleftrightarrow{1\text{—}1} \rho(r)$

   one-to-one correspondence between external potentials v(r) and ground-state densities ρ(r)

2. <u>Variational principle</u>

   Given a particular system characterized by the external potential **$v_0(r)$**. There exists a functional, $E_{HK}[\rho]$, such that the solution of the Euler-Lagrange equation

$$\frac{\delta}{\delta\rho(r)} E_{HK}[\rho] = 0$$

   yields the exact ground-state energy **E_0** and ground-state density **$\rho_0(r)$** of this system

3. $$E_{HK}[\rho] = F[\rho] + \int \rho(r)\, v_0(r)\, d^3r$$

   F[ρ] is <u>UNIVERSAL</u>. **In practice, F[ρ] needs to be approximated**

KOHN-SHAM EQUATIONS

Rewrite HK functional as:

$$E_{HK}[\rho] = T_S[\rho] + \int \rho(r)\, v_0(r)\, d^3r + E_H[\rho] + E_{xc}[\rho]$$

where $T_S[\rho]$ is the kinetic energy functional of non-interacting particles

$$\frac{\delta}{\delta\rho(r)} E_{HK}[\rho] = 0$$ yields the Kohn-Sham equations:

$$\left(-\nabla^2/2 + v_o(\mathbf{r}) + v_H[\rho](\mathbf{r}) + v_{xc}[\rho](\mathbf{r})\right)\phi_j(\mathbf{r}) = \epsilon_j\, \phi_j(\mathbf{r})$$

Walter Kohn: "The KS equations are an Exactification of the Hartree mean-field equation"

$E_{xc}[\rho]$ is a universal functional of the density which, in practice, needs to be approximated (e.g. LDA, GGAs, hybrid functionals).

Time-dependent density-functional formalism

(E. Runge, E.K.U.G., PRL 52, 997 (1984))

Basic 1-1 correspondence:

$$v(rt) \xleftrightarrow{1\text{-}1} \rho(rt)$$

The time-dependent density determines uniquely the time-dependent external potential and hence all physical observables for fixed initial state.

KS theorem:

The time-dependent density of the interacting system of interest can be calculated as density

$$\rho(rt) = \sum_{j=1}^{N} \left|\varphi_j(rt)\right|^2$$

of an auxiliary non-interacting (KS) system

$$i\hbar \frac{\partial}{\partial t}\varphi_j(rt) = \left(-\frac{\hbar^2\nabla^2}{2m} + v_S[\rho](rt)\right)\varphi_j(rt)$$

with the local potential

$$v_S\left[\rho(r't')\right](rt) = v_0(rt) + \int d^3r' \frac{\rho(r't)}{|r-r'|} + v_{xc}\left[\rho(r't')\right](rt)$$

EXTENSIONS

1. Relativistic systems

KS equations:

$$\left[\vec{\gamma}\cdot\left(-i\hbar\vec{\nabla}-\vec{A}_s(r)\right)+mc^2+\gamma_o v_s(r)\right]\psi_n(r)=\varepsilon_n\gamma_o\psi_n(r)$$

$$\vec{A}_s(r) = -e\left\{\vec{A}_{ext}(r)+\int d^3r'\frac{\vec{j}(r')}{|r-r'|}+\frac{\delta E_{xc}\left[\rho,\vec{j}\right]}{\delta\vec{j}(r)}\right\}$$

$$v_s(r) = -e\left\{\underbrace{A^0_{ext}(r)}_{v_{nuc}(r)}+\int d^3r'\frac{\rho(r')}{|r-r'|}+\frac{\delta E_{xc}\left[\rho,\vec{j}\right]}{\delta\rho(r)}\right\}$$

KS orbitals are Dirac spinors

Relativistic local spin-density approximation is available

EXTENSIONS

2. Finite temperature

KS equations:

$$\left(-\frac{\hbar^2\nabla^2}{2m}+v_{nuc}(r)+\int\frac{\rho(r')}{|r-r'|}d^3r'+v_{xc}^{(T)}(r)\right)\varphi_j(r)=\varepsilon_j\varphi_j(r)$$

$$\rho(r)=\sum_j \underbrace{f_T(\varepsilon_j)}_{\text{Fermi distribution}}\cdot|\varphi_j(r)|^2$$

3. Quantum phases: Magnetism and superconductivity

DENSITY-FUNTIONAL THEORY OF MAGNETIC SYSTEMS

Quantity of interest: Spin magnetization density m(r)

In principle, Hohenberg-Kohn theorem guarantees that m(r) is a functional of the density: $m(r) = m[\rho](r)$. In practice, good approximations for the functional $m[\rho]$ are not known.

Include m(r) as basic variable in the formalism, in addition to the density ρ(r).

Start from fully interacting Hamiltonian with Zeeman term:

$$\hat{H}_{v,\vec{B}} = T + V_{ee} + \int \hat{\rho}(r)\, v(r)\, d^3r - \int \hat{\vec{m}}(r) \cdot \vec{B}(r)\, d^3r$$

$$\hat{\vec{m}}(r) = \mu_0 \sum_{\alpha\beta} \psi^{+}_{\alpha}(r)\, \vec{\sigma}_{\alpha\beta}\, \psi_{\beta}(r)$$

HK theorem

$$\left[\rho(r), \vec{m}(r)\right] \xleftrightarrow{1\text{-}1} \left[v(r), \vec{B}(r)\right]$$

total energy:

$$E_{v,\vec{B}}[\rho, \vec{m}] = F[\rho, \vec{m}] + \int d^3r \left(v(r)\rho(r) - \vec{B}(r) \cdot \vec{m}(r)\right)$$

universal

KS scheme

For simplicity: $\vec{B}(\boldsymbol{r}) = \begin{pmatrix} 0 \\ 0 \\ B(\boldsymbol{r}) \end{pmatrix}$, $\vec{m}(\boldsymbol{r}) = \begin{pmatrix} 0 \\ 0 \\ m(\boldsymbol{r}) \end{pmatrix}$

$$\left(-\frac{\nabla^2}{2m} + \left[v(\mathbf{r}) + v_H(\mathbf{r}) + \mathbf{v_{xc}(r)} \right] \pm \mu_o \left[B(\mathbf{r}) - \mathbf{B_{xc}(r)} \right] \right) \varphi^j_{\pm}(\mathbf{r}) = \in^j_{\pm} \varphi^j_{\pm}(\mathbf{r})$$

$$\mathbf{v_{xc}[\rho,m] = \delta E_{xc}[\rho,m]/\delta \rho} \qquad \mathbf{B_{xc}[\rho,m] = \delta E_{xc}[\rho,m]/\delta m}$$

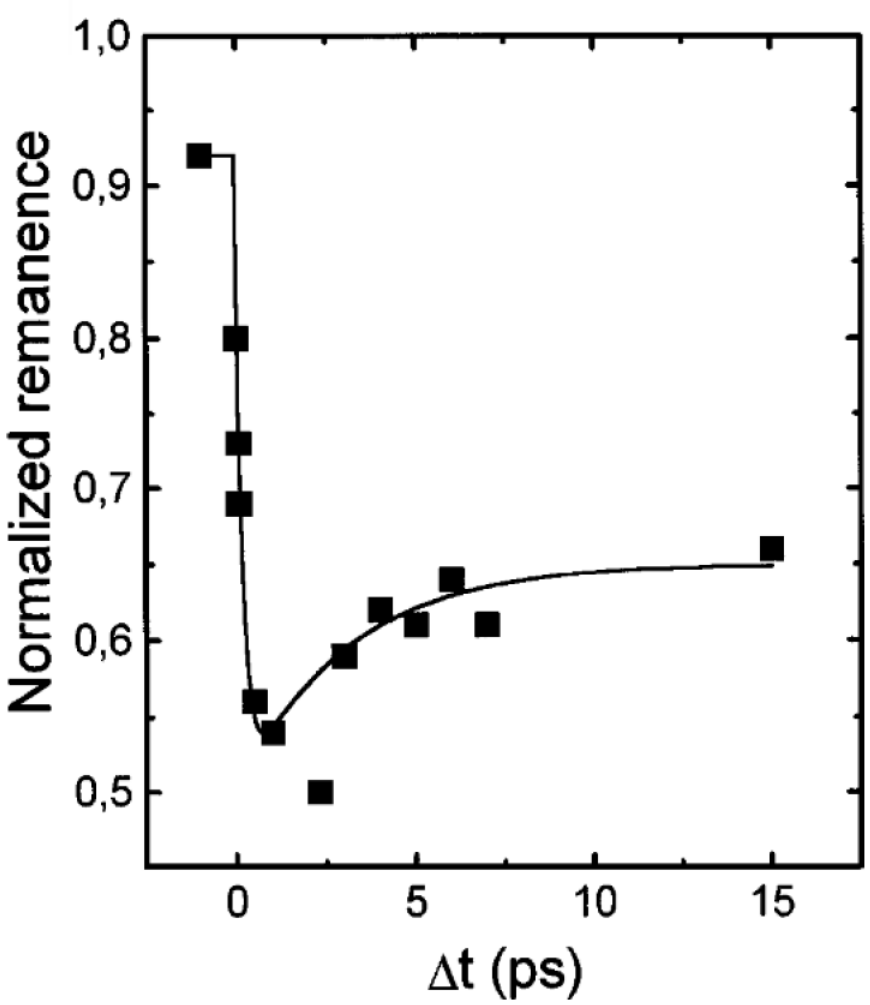
$$\rho(\mathbf{r}) = \rho_+(\mathbf{r}) + \rho_-(\mathbf{r}) \ , \ m(\mathbf{r}) = \rho_+(\mathbf{r}) - \rho_-(\mathbf{r}) \ , \ \rho_\pm = \Sigma \left| \varphi^j_\pm \right|^2$$

B $\longrightarrow$ 0 limit

These equations do not reduce to the original KS equations for B $\rightarrow$ 0 if, in this limit, the system has a finite m(r).

An application:
Ultrafast laser-induced demagnetization of solids

First experiment on ultrafast laser induced demagnetization



Beaurepaire et al, PRL 76, 4250 (1996)

More recent experiments show demagnetization in around 50 fs

Possible mechanisms for demagnetisation

- Spin-lattice relaxation causing global demagnetization
  Huebner, Bennemann, PRB **53**, 3422 (1996)

- Direct interaction of spins with the magnetic component of the laser
  Zhang, Huebner, PRL **85**, 3025 (2000)

- Elliott-Yafet mechanism: electron-phonon and electron-impurity scattering
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- **Our proposal for the first 50 fs:**
  Laser-induced charge excitation followed by spin-orbit-driven demagnetization of the remaining d-electrons

Quantity of prime interest:
vector field of spin magnetization

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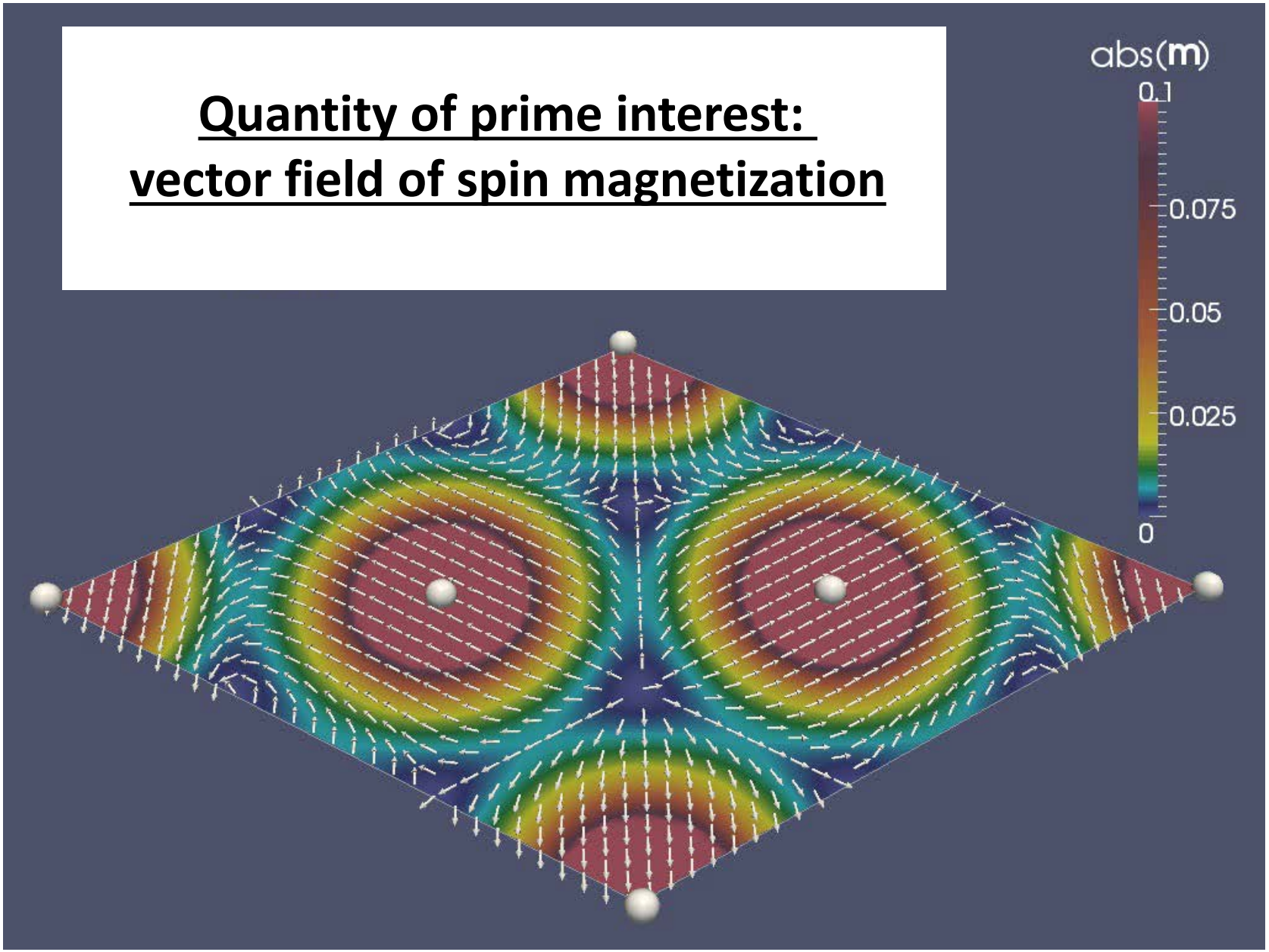


Cr monolayer in ground state

Real-time TDDFT with SOC

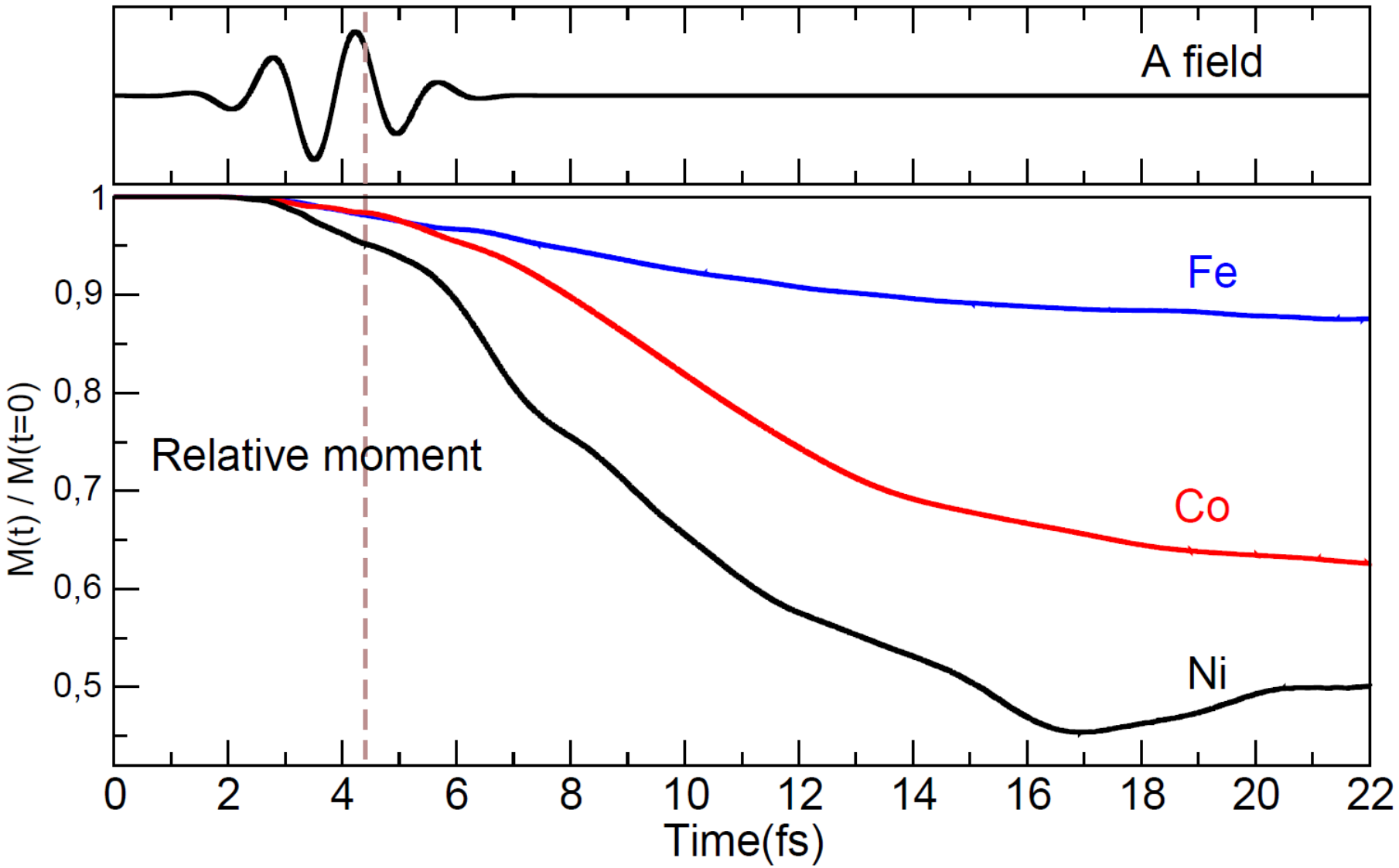
$$i\frac{\partial}{\partial t}\varphi_k(r,t) = \Bigg[\frac{1}{2}\left(-i\nabla - A_{laser}(t)\right)^2 + v_S[\rho,\boldsymbol{m}](r,t) - \mu_B\sigma\cdot B_S[\rho,\boldsymbol{m}](r,t) + \frac{\mu_B}{2c}\sigma\cdot\left(\nabla v_S[\rho,\boldsymbol{m}](r,t)\right)\times\left(-i\nabla\right)\Bigg]\varphi_k(r,t)$$

$$v_S[\rho,\boldsymbol{m}](r,t) = v_{lattice}(r) + \int\frac{\rho(r',t)}{|r-r'|}d^3r' + v_{xc}[\rho,\boldsymbol{m}](r,t)$$

$$B_S[\rho,\boldsymbol{m}](r,t) = B_{external}(r,t) + B_{xc}[\rho,\boldsymbol{m}](r,t)$$

where $\varphi_k(r,t)$ are Pauli spinors

Demagnetisation in Fe, Co and Ni



K. Krieger, K. Dewhurst, P. Elliott, S. Sharma, E.K.U.G., JCTC 11, 4870 (2015)

Aspects of the implementation

- Wave length of laser in the visible regime
  (very large compared to unit cell)

  ⇨ Dipole approximation is made
  (i.e. electric field of laser is assumed to be spatially constant)

  ⇨ Laser can be described by a purely time-dependent vector potential

- **Periodicity of the TDKS Hamiltonian is preserved!**

- **Implementation in ELK code (FLAPW) (http://elk.sourceforge.net/)**

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Kay Dewhurst

ELK = Electrons in K-Space
or
Electrons in Kay's Space

Sangeeta Sharma

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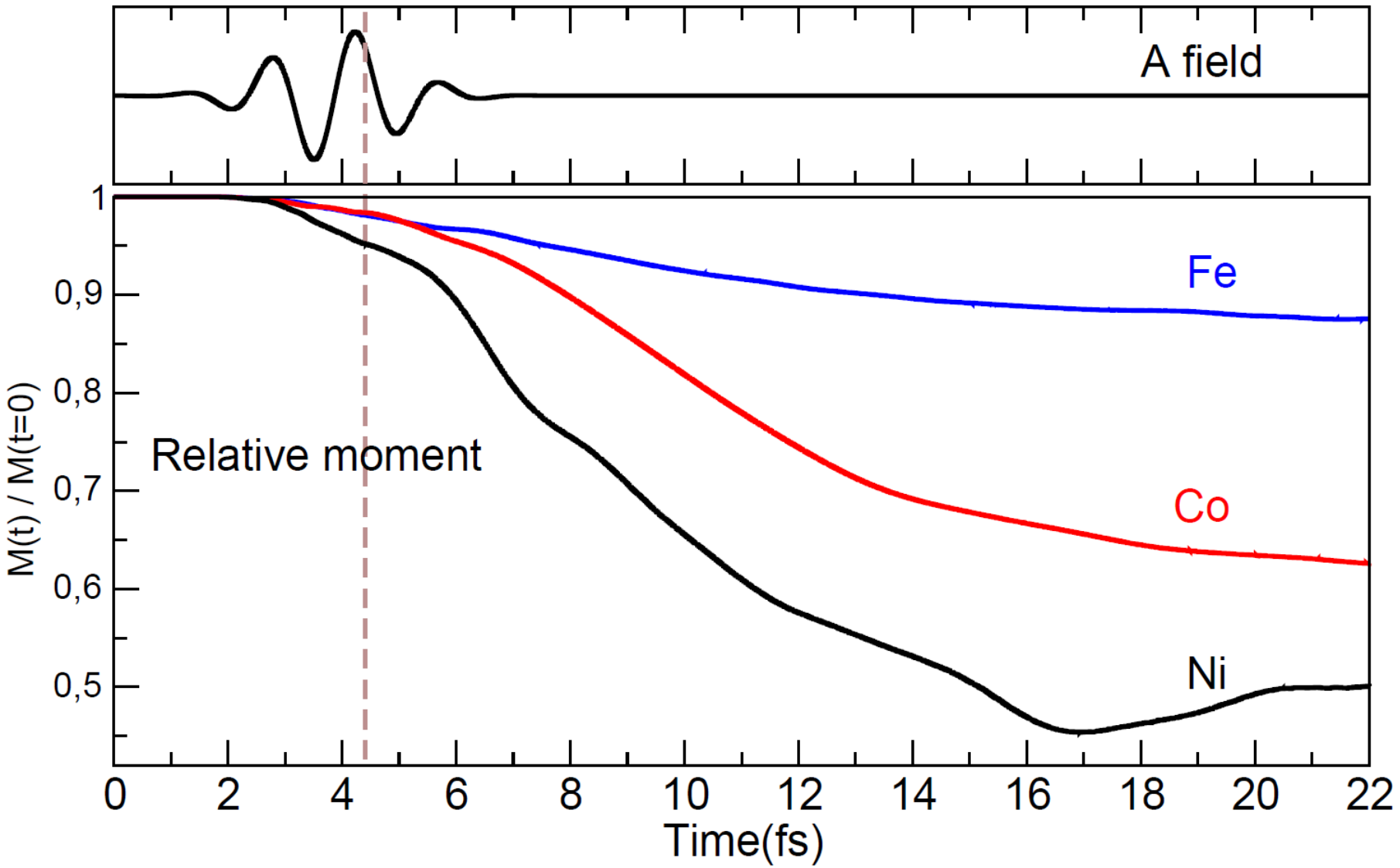
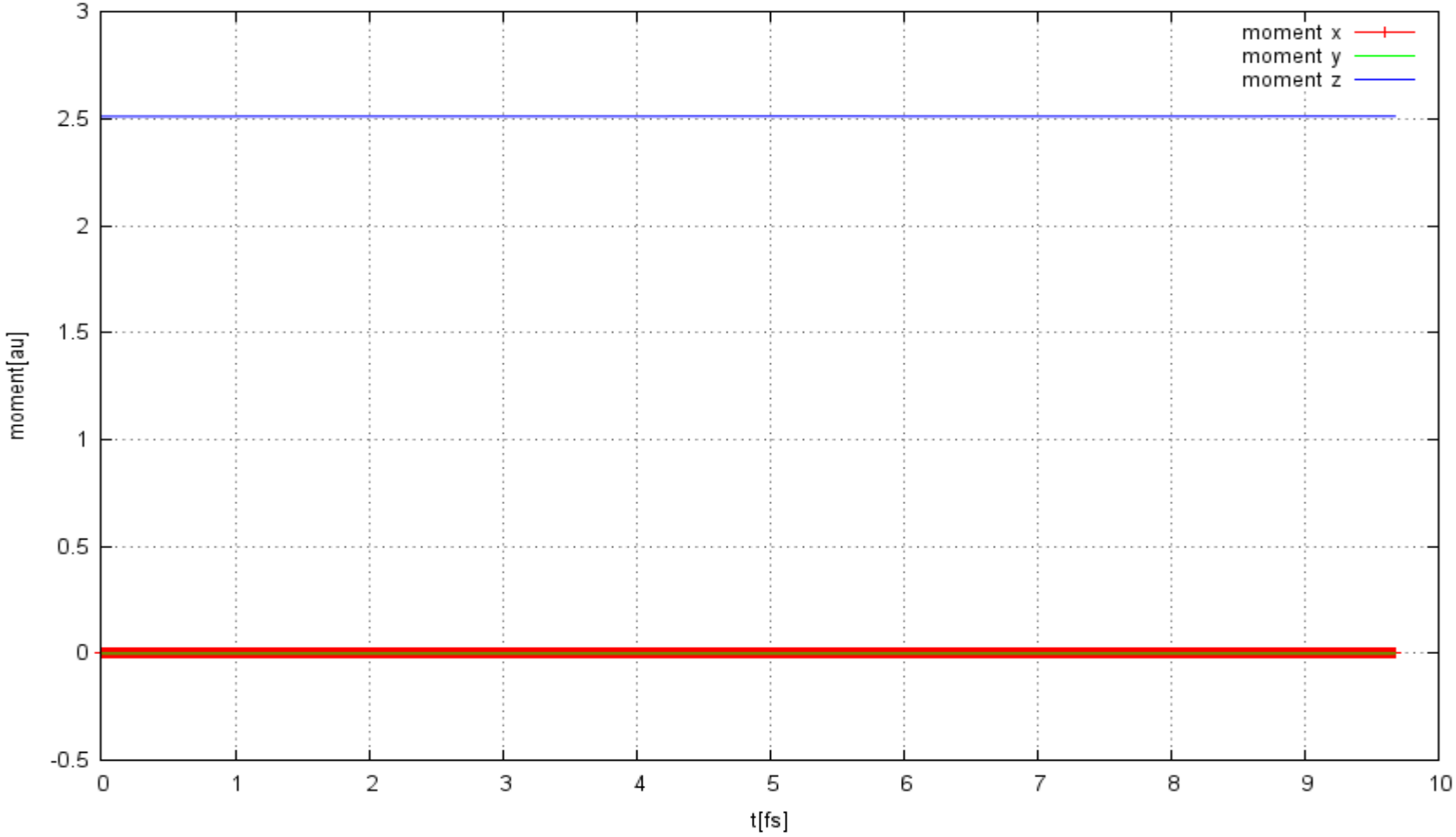


M(t) is the **total** spin magnetic moment, i.e. m(r,t) integrated over the unit cell

Analysis of the results

Calculation without spin-orbit coupling

components of total spin moment



Exact equation of motion for the total spin moment

$$\frac{\partial}{\partial t} M_z(t) = \frac{i}{\hbar}\left\langle \left[\hat{H}_{KS}, \hat{\sigma}_z \right] \right\rangle$$

$$= \int d^3r \left\{ m_x(r,t) B_{xc,y}(rt) - m_y(r,t) B_{xc,x}(rt) \right\}$$

$$+ \int d^3r \frac{1}{2c^2} \left\{ \text{盜} \left[\nabla v_s(r,t) \times j_y(r,t) \right] - y \cdot \left[\nabla v_s(r,t) \times j_z(r,t) \right] \right\}$$

$$- \int d^3r \left\{ \nabla \cdot j_z(r,t) \right\}$$

$$\overleftrightarrow{j}(r,t) = \left\langle \hat{\sigma} \otimes \hat{p} \right\rangle$$ spin current tensor

SOC is the only term which can change the <u>total</u> moment!

Exact equation of motion for total moment

$$\frac{\partial}{\partial t} M_z(t) = \frac{i}{\hbar}\left\langle \left[\hat{H}_{KS}, \hat{\sigma}_z \right] \right\rangle$$

Global torque exerted by B_{xc} = 0 (zero torque theorem)

$$= \int d^3r \left\{ m_x(r,t) B_{xc,y}(rt) - m_y(r,t) B_{xc,x}(rt) \right\}$$

$$+ \int d^3r \frac{1}{2c^2} \left\{ \text{盜}\left[\nabla v_s(r,t) \times j_y(r,t) \right] - y \cdot \left[\nabla v_s(r,t) \times j_z(r,t) \right] \right\}$$ **SOC**

$$- \int d^3r \left\{ \nabla \cdot j_z(r,t) \right\}$$ **=0**

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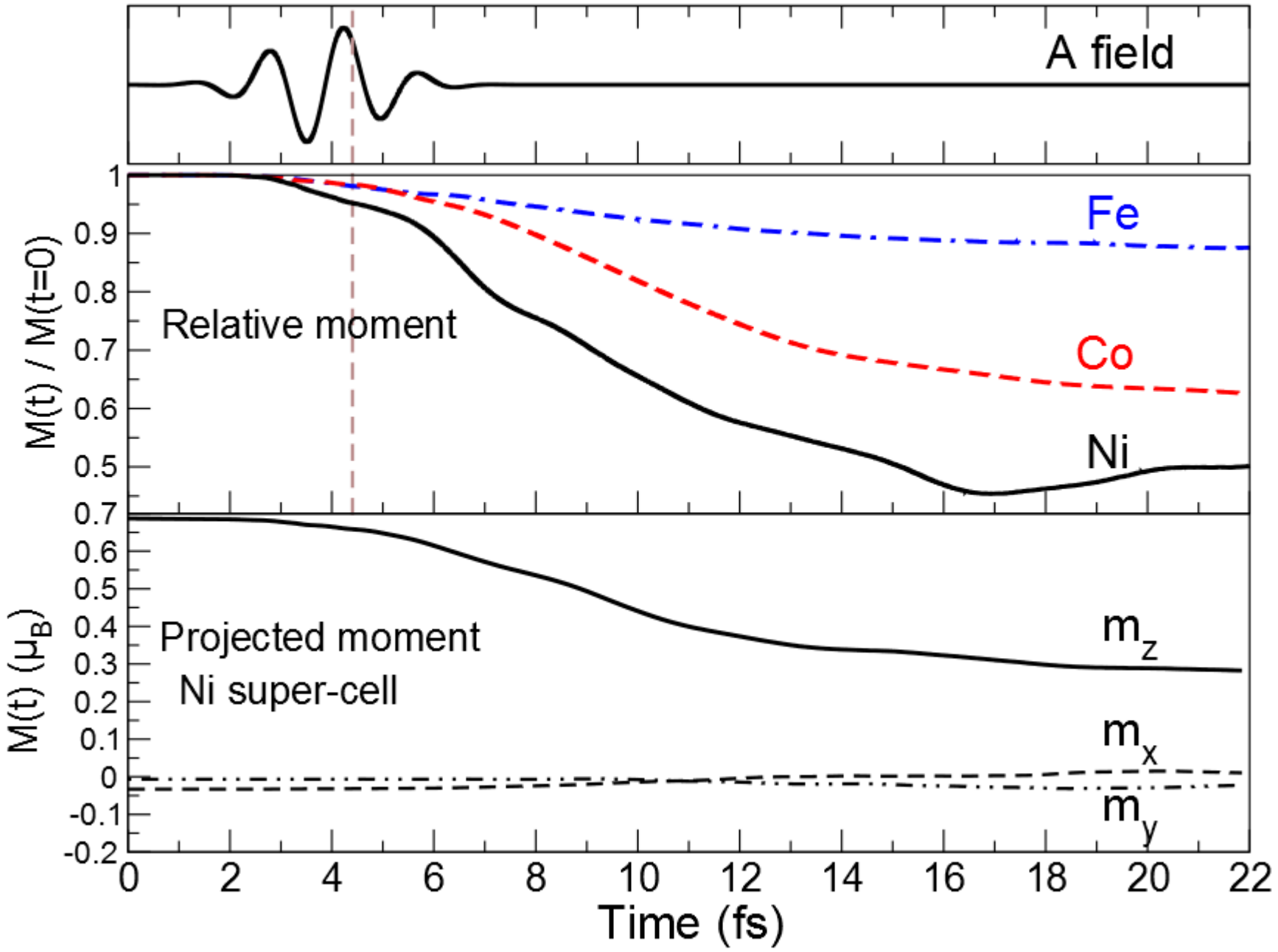
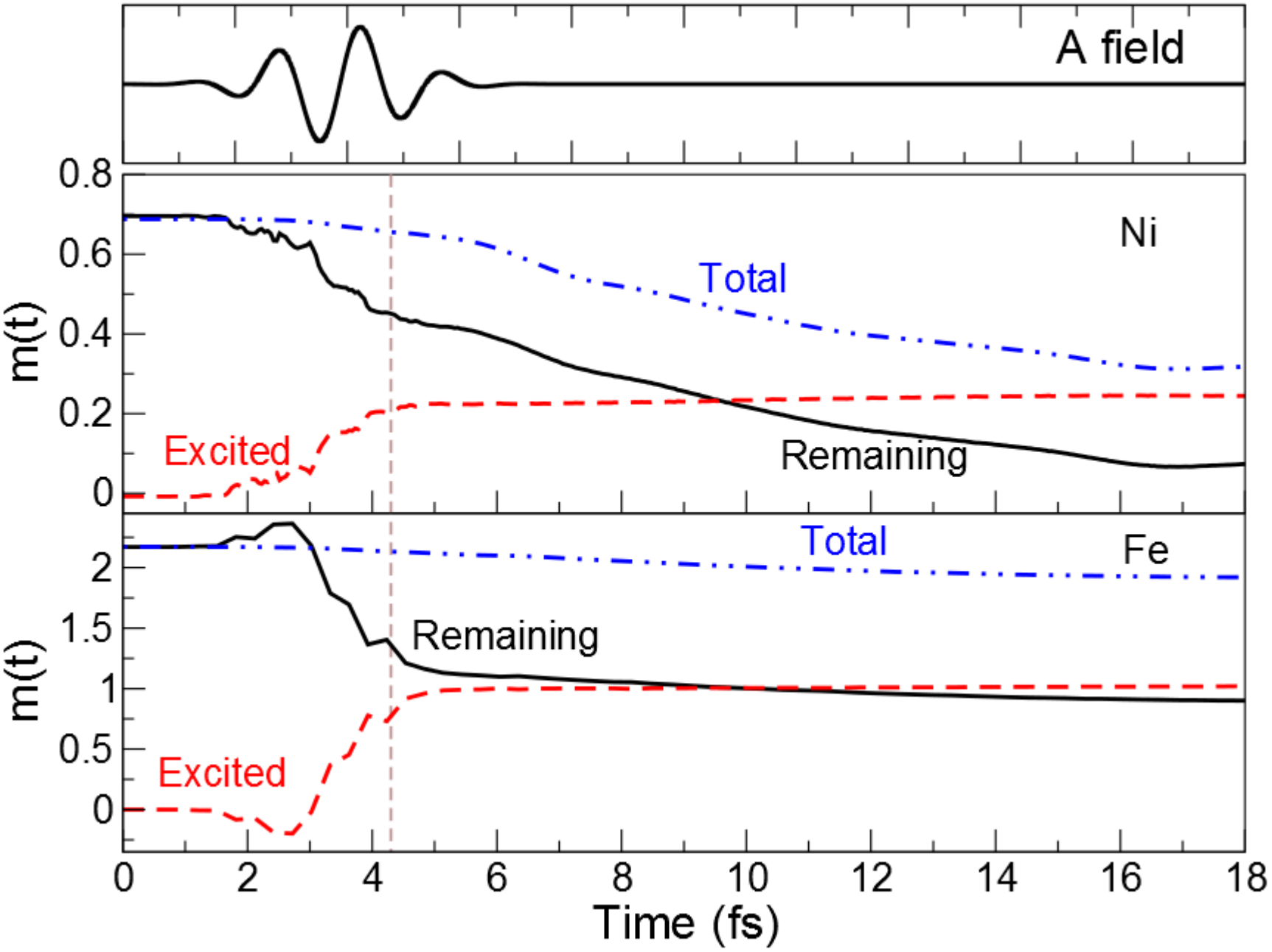
SOC is the only term which can change the total moment!



Note: Ground state of bulk Fe, Co, Ni is collinear

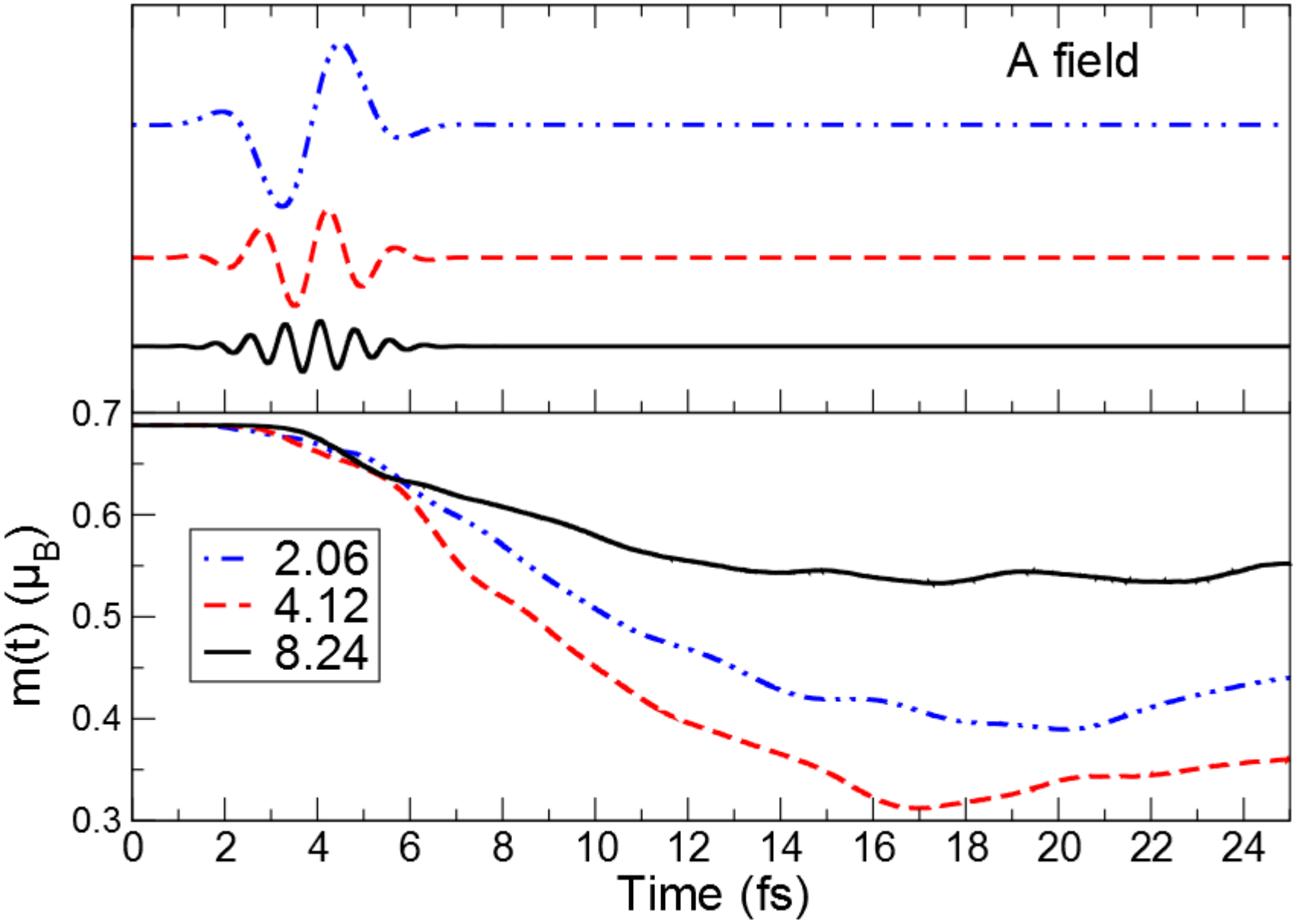

A field
Ni
Total
Excited
Remaining
m(t)
Fe
Total
Remaining
Excited
m(t)
Time (fs)

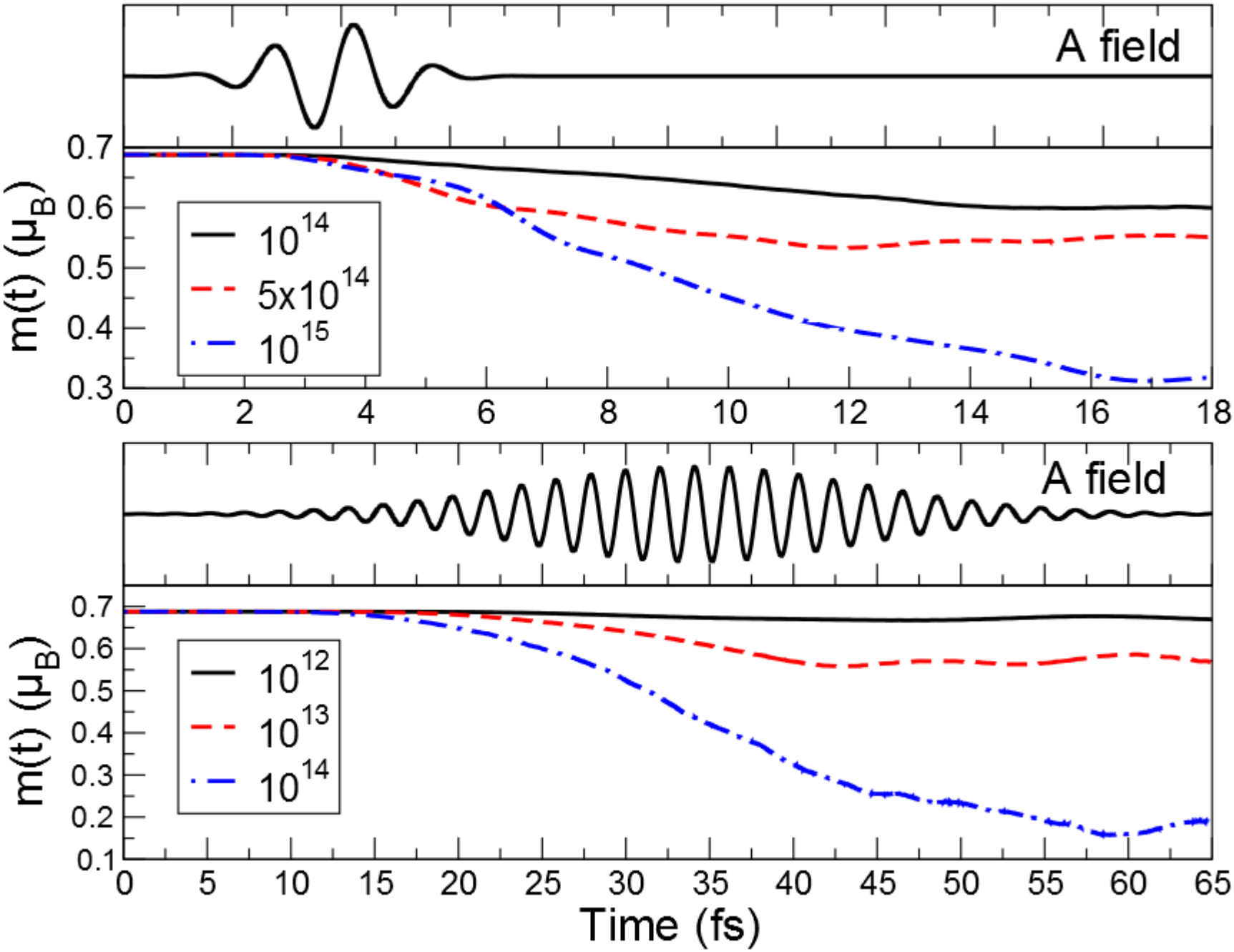
Demagnetization occurs in two steps:

- Initial excitation by laser *moves* magnetization from atomic region into interstitial region. Total Moment is basically conserved during this phase.

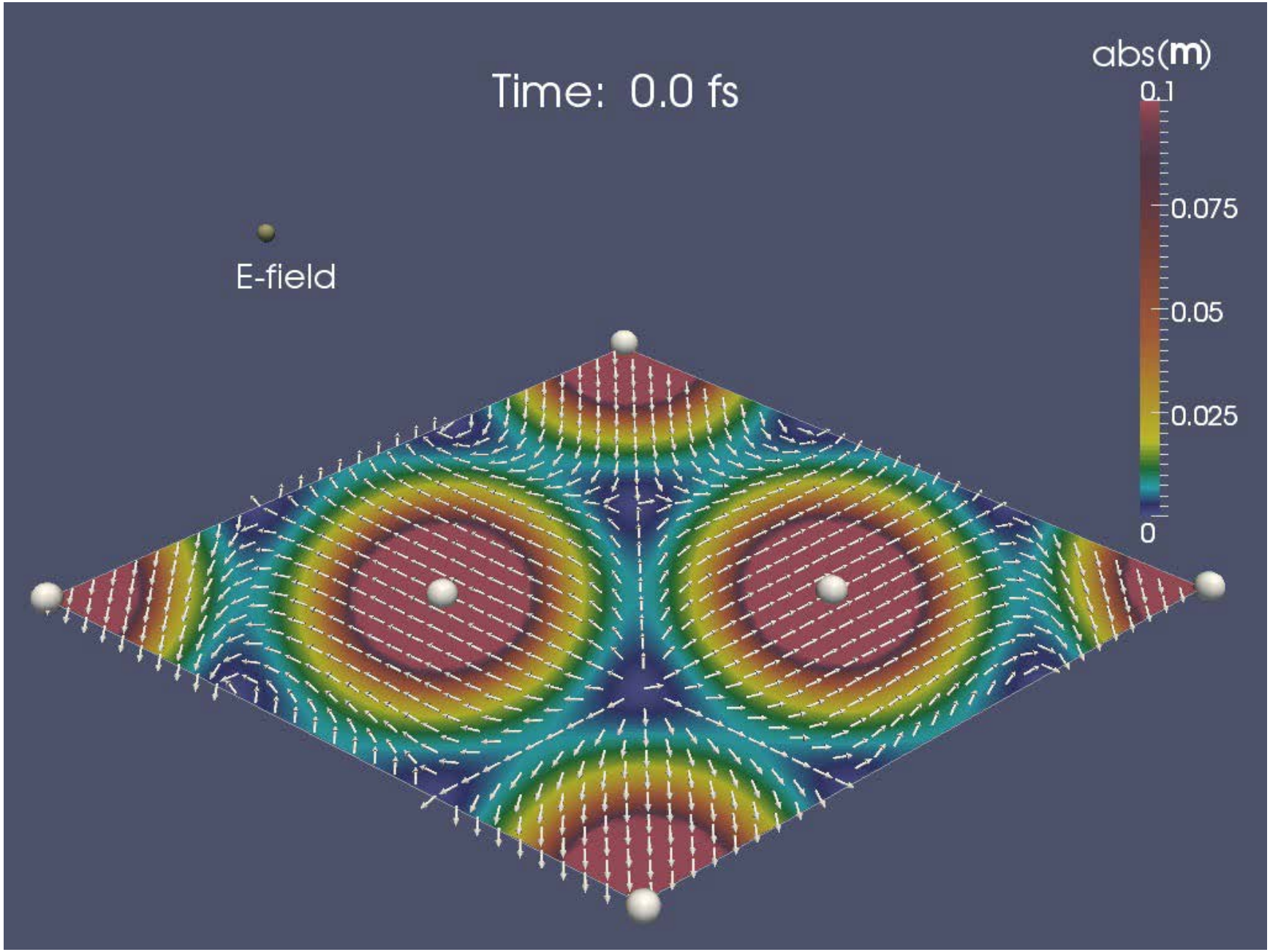
- Spin-Orbit term drives demagnetization of the more localized electrons until stabilization at lower moment is achieved

Playing with laser parameters

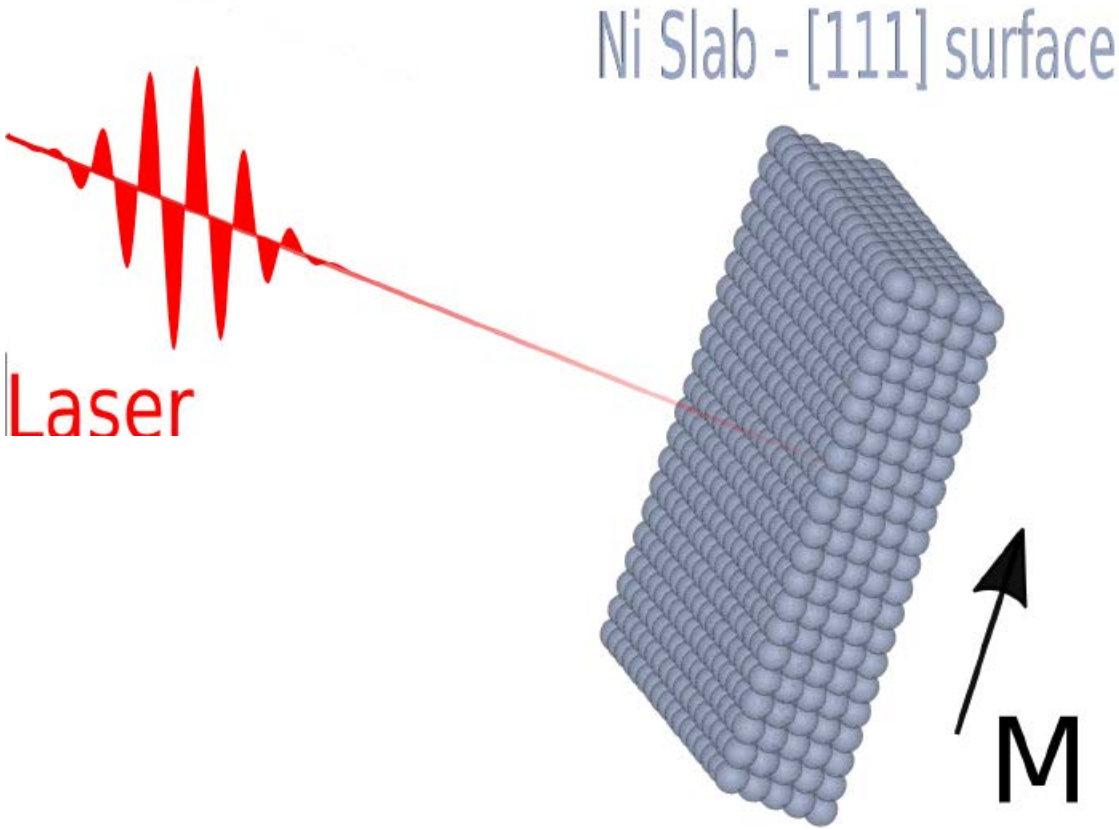

A field
0.7
0.6
0.5
0.4
0.3
m(t) (μB)
2.06
4.12
8.24
0
2
4
6
8
10
12
14
16
18
20
22
24
Time (fs)

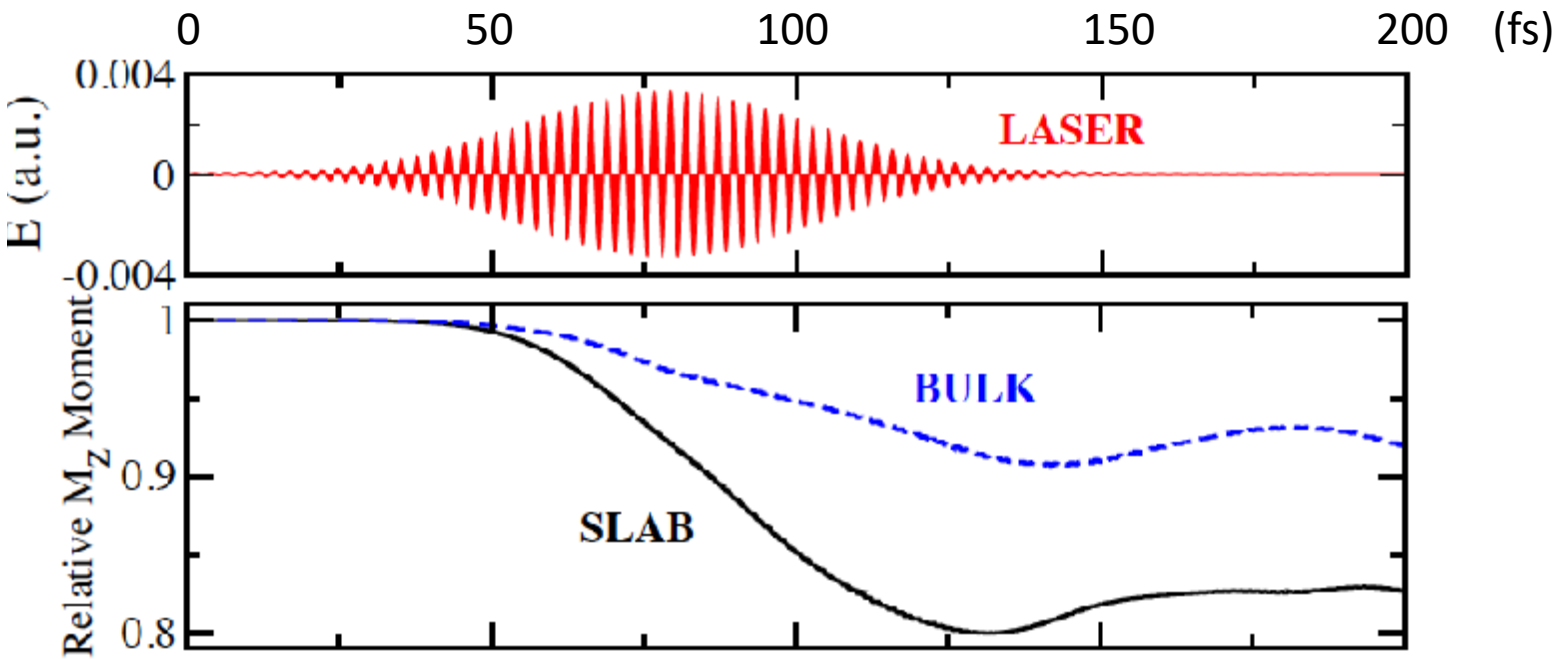

A field
m(t) (μB)
0.7
0.6
0.5
0.4
0.3
10^14
5x10^14
10^15
0
2
4
6
8
10
12
14
16
18
A field
m(t) (μB)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
10^12
10^13
10^14
0
5
10
15
20
25
30
35
40
45
50
55
60
65
Time (fs)

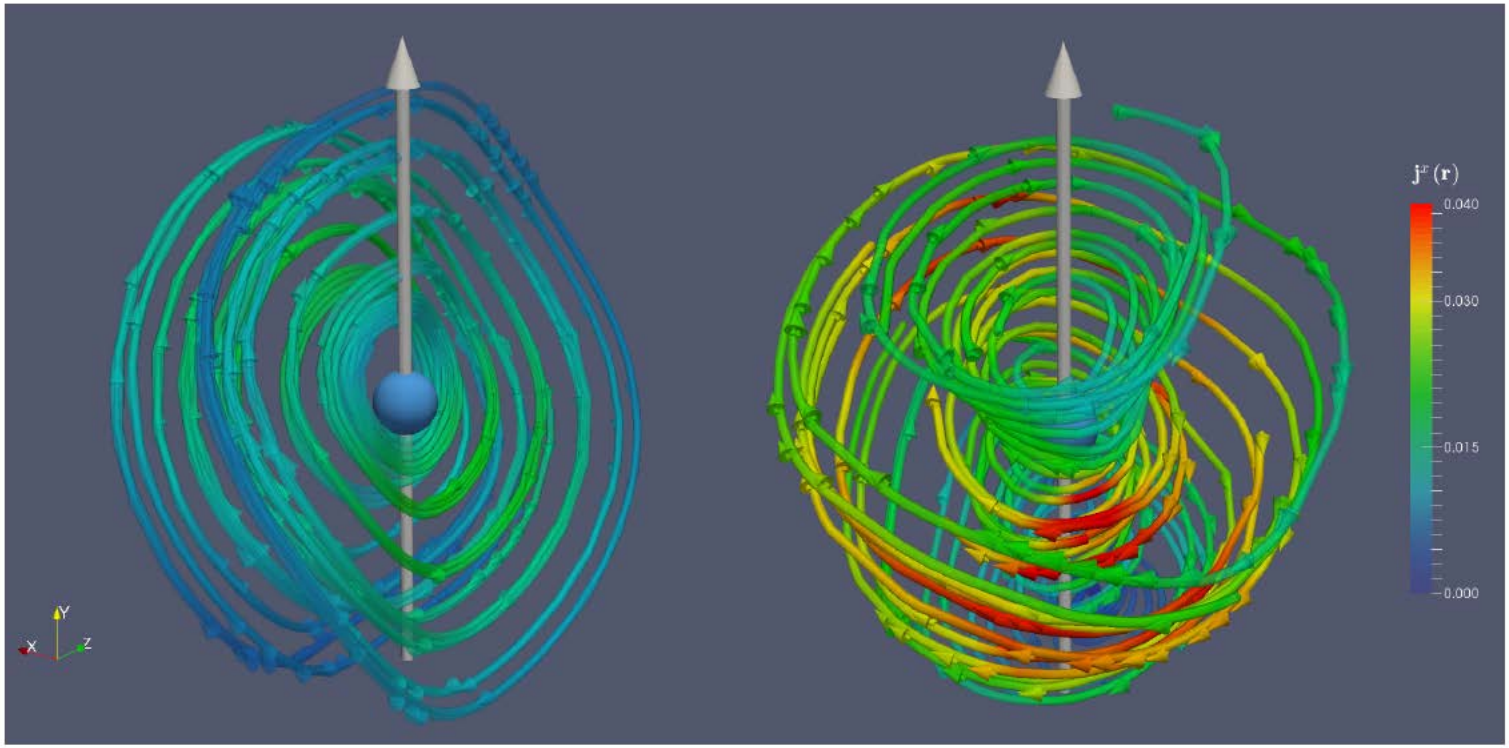
Beyond 3D bulk



Cr monolayer


Ni Slab - [111] surface
Laser
M

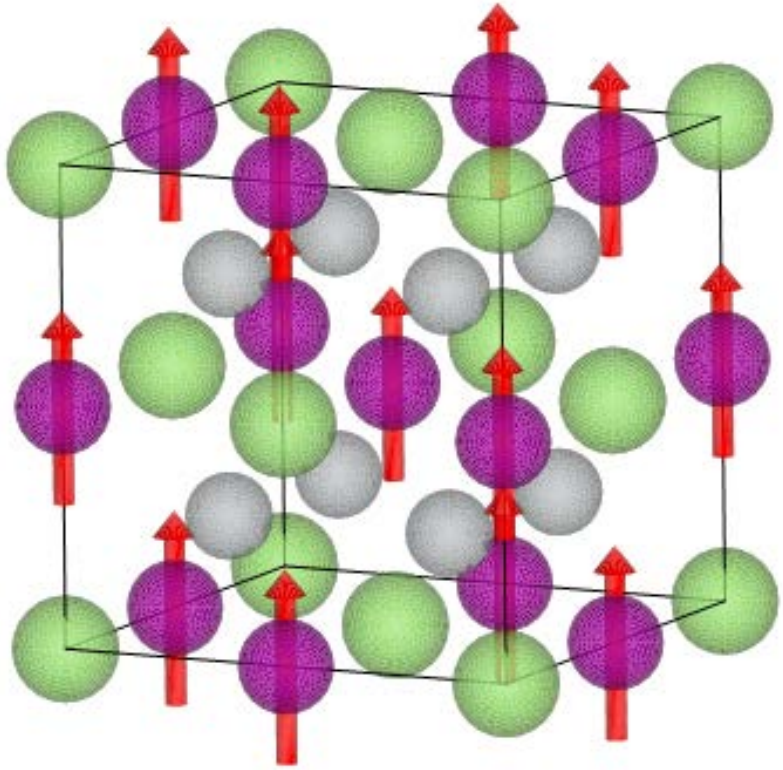

0
50
100
150
200
(fs)
E (a.u.)
0.004
0
-0.004
LASER
Relative M_Z Moment
1
0.9
0.8
BULK
SLAB



Streamlines for J_x, the spin-current vector field of the x component of spin, around a Ni atom in bulk (left) and for the outermost Ni atom in the slab (right).

Magnetisation transfer between sublattices

Ni_2MnGa

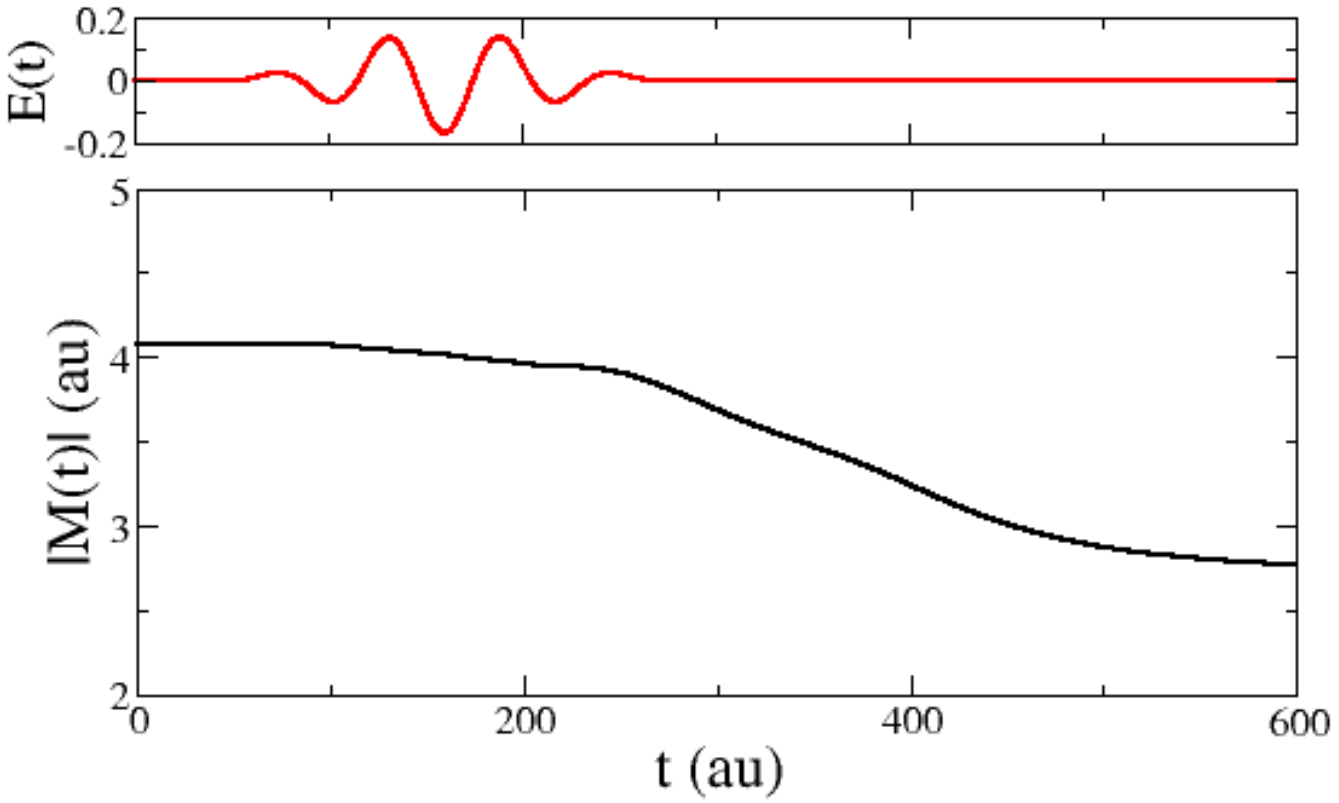


Ga	0.02 μB
Mn	-3.14 μB
Ni	-0.37 μB

Ni_2MnGa

Laser parameters: ω=2.72eV Ipeak= 1x1015 W/cm2 J = 935 mJ/cm2 FWHM = 2.42 fs

Loss in global moment

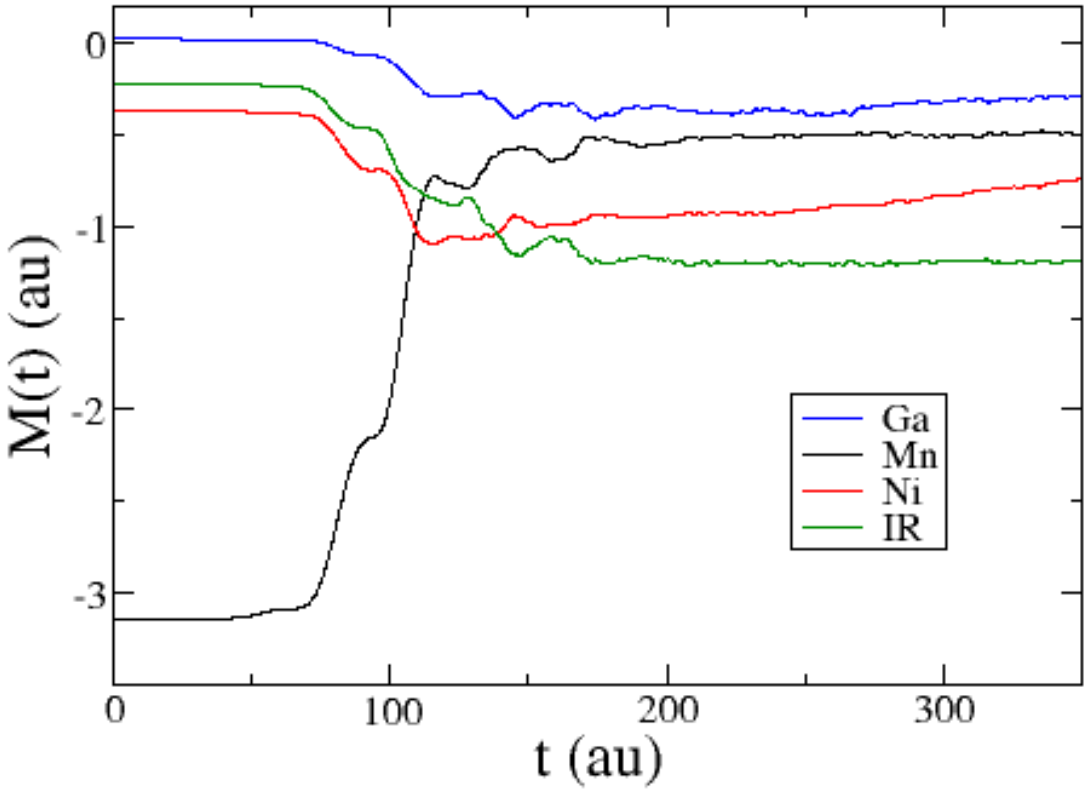


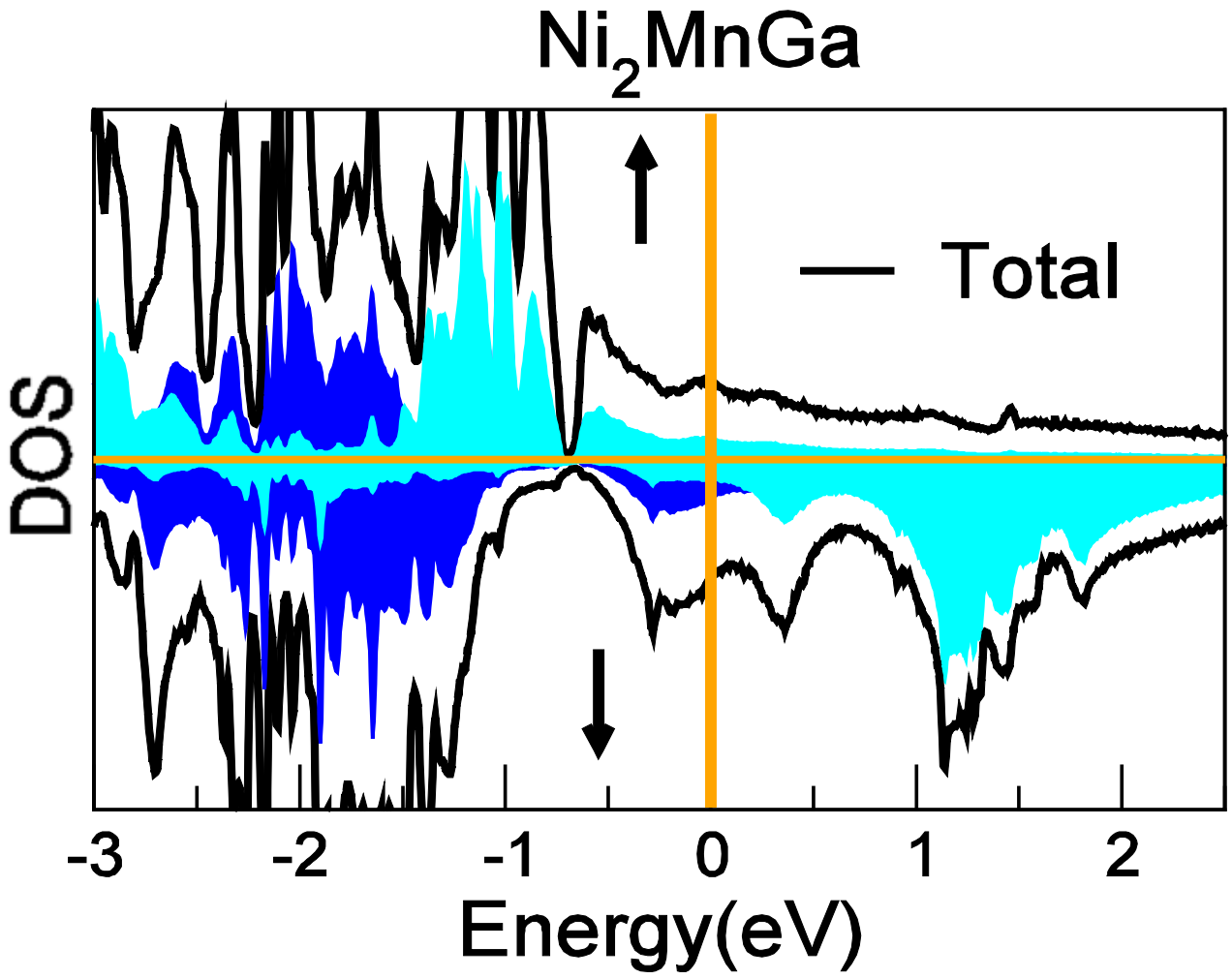
Ni_2MnGa

Also change in local moments

Transfer of moment from Mn to Ni (does not require SOC)

Followed by spin-orbit mediated demagnetization on Ni





P. Elliott, T. Mueller, K. Dewhurst, S. Sharma, E.K.U.G.,
Scientific Reports 6, 38911 (2016)

Future:

- **Include relaxation processes due to el-el scattering**
  - in principle contained in TDDFT,
  - but not with adiabatic xc functionals
  - need xc functional approximations with memory $v_{xc}\left[\rho(r't')\right](rt)$

- **Include relaxation processes due to the motion of nuclei**

- **Include relaxation due to radiative effects**
  simultaneous propagation of TDKS and Maxwell equations

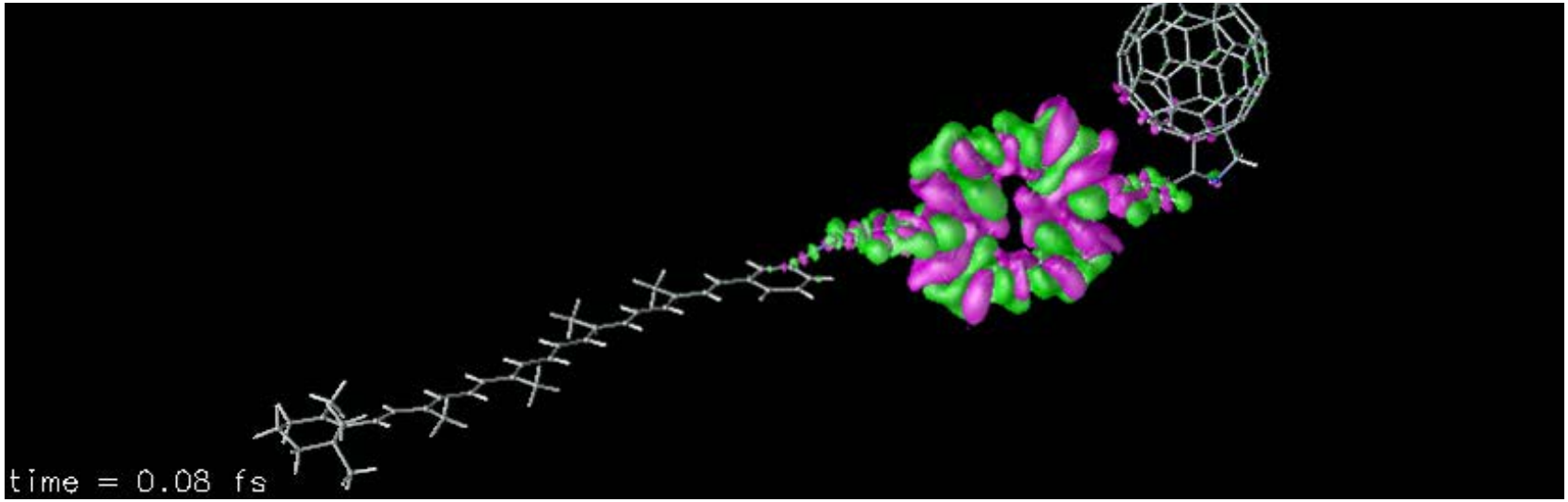
- **Include dipole-dipole interaction to describe motion of domains**
  construct approximate xc functionals which refer to the dipole-int

- **Combine TDDFT with Optimal Control Theory to find lasers pulses that remagnetise the sample**

"Triad molecule": Candidate for photovoltaic applications

C.A. Rozzi et al, Nature Communications 4, 1602 (2013)

S.M. Falke et al, Science 344, 1001 (2014)

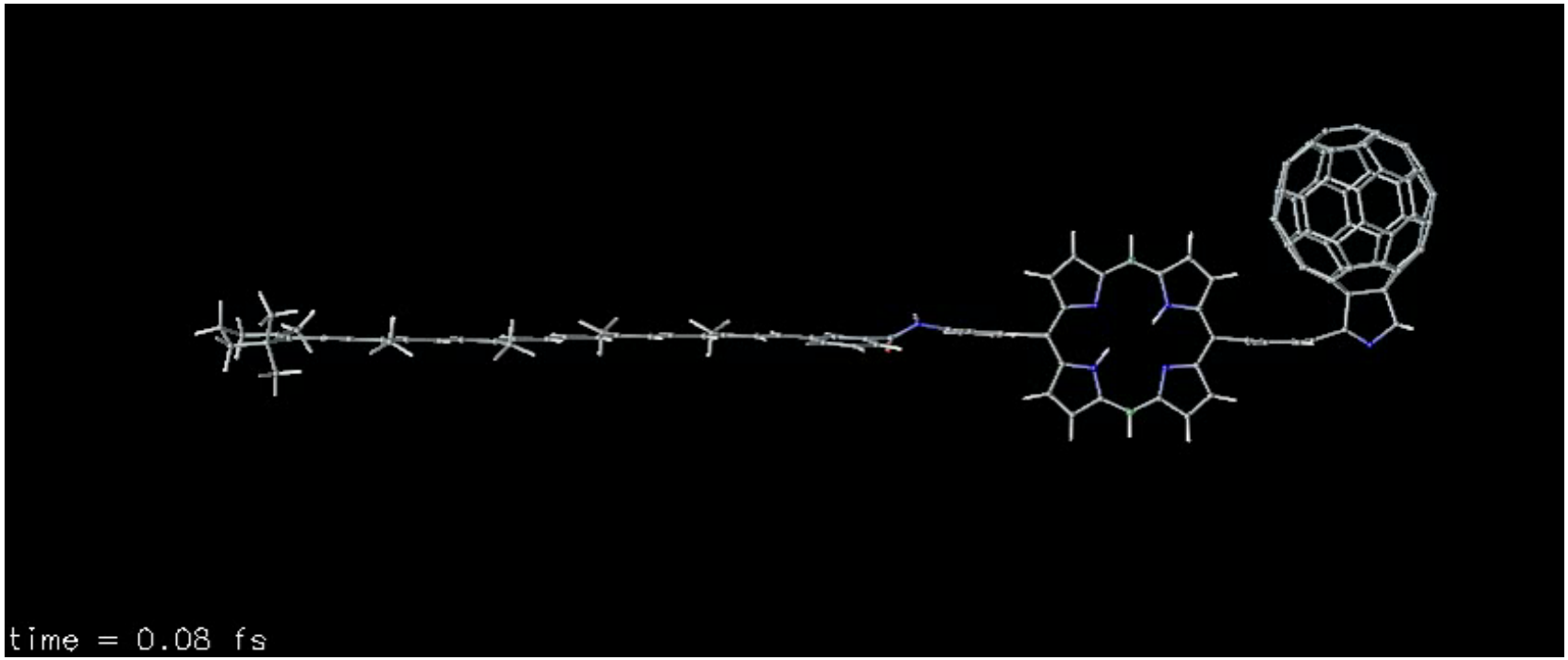


TDDFT propagation with clamped nuclei

"Triad molecule": Candidate for photovoltaic applications

C.A. Rozzi et al, Nature Communications 4, 1602 (2013)

S.M. Falke et al, Science 344, 1001 (2014)



Moving nuclei

DENSITY-FUNTIONAL THEORY OF THE SUPERCONDUCTING STATE

BASIC IDEA:

- **Include order parameter, χ , characterising superconductivity as additional "density"**

  L.N. Oliveira, E.K.U.G., W. Kohn, PRL **60**, 2430 (1988)

- **Include N-body density, Γ, of the nuclei as additional "density"**

  T. Kreibich, E.K.U.G., PRL **86**, 2984 (2001)

General (model-independent) characterization of superconductors:
Off-diagonal long-range order of the 2-body density matrix:

$$\rho^{(2)}(xx', yy') = \left\langle \hat{\psi}^{+}_{\downarrow}(x')\hat{\psi}^{+}_{\uparrow}(x)\hat{\psi}_{\uparrow}(y)\hat{\psi}_{\downarrow}(y') \right\rangle$$

$$\xrightarrow[|X-Y|\to\infty]{} \underbrace{\left\langle \hat{\psi}^{+}_{\downarrow}(x')\hat{\psi}^{+}_{\uparrow}(x) \right\rangle}_{\chi^{*}(x,x')} \cdot \underbrace{\left\langle \hat{\psi}_{\uparrow}(y)\hat{\psi}_{\downarrow}(y') \right\rangle}_{\chi(y,y')}$$

$$X = \frac{x+x'}{2} \qquad Y = \frac{y+y'}{2}$$

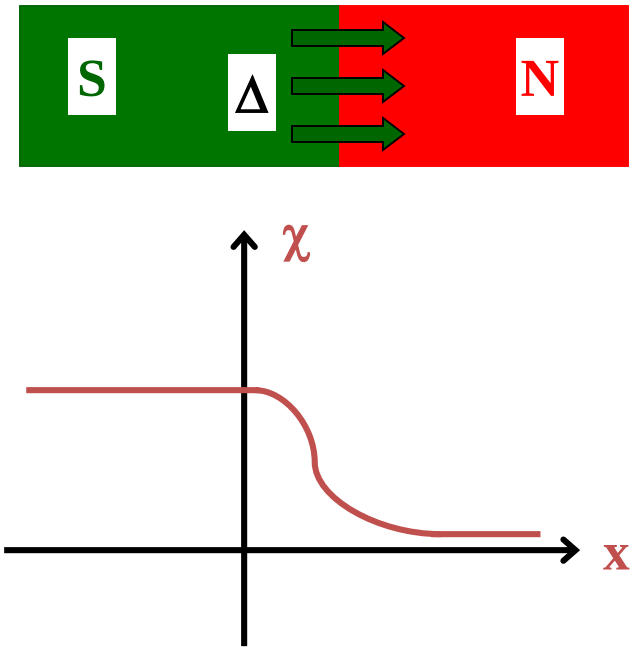
$$\chi\ (r, r') = \left\langle \hat{\psi}_{\uparrow}(r)\hat{\psi}_{\downarrow}(r') \right\rangle$$

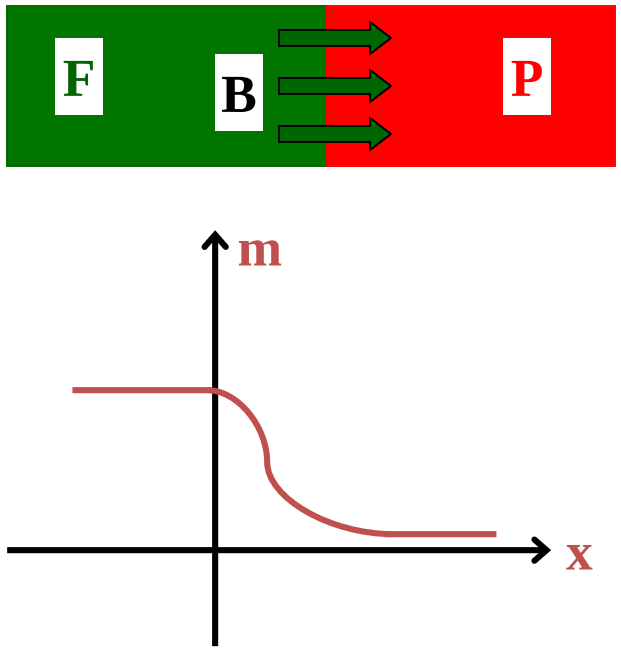
order parameter of the N-S phase transition

Hamiltonian

$$\hat{H}_e = \hat{T}_e + \hat{W}_{ee} + \int \hat{\rho}(r) v(\mathbf{r}) d^3r - \int d^3r \int d^3r' \left(\hat{\chi}(r, r') \Delta^*(r, r') + \text{H.c.} \right)$$

ANALOGY





“proximity effect”

Hamiltonian

$$\hat{H}_e = \hat{T}_e + \hat{W}_{ee} + \int \hat{\rho}(r)\, v(\mathbf{r})\, d^3r - \int d^3r \int d^3r' \left(\hat{\chi}(r,r')\, \Delta^*(r,r') + \text{H.c.} \right)$$

$$\hat{H}_n = \hat{T}_n + \int d^{N_n} R\, \hat{\Gamma}(\underline{\underline{R}}) W(\underline{\underline{R}})$$

$$\hat{H} = \hat{H}_e + \hat{H}_n + \hat{U}_{en}$$

3 densities:

$$\rho(r) = \left\langle \sum_{\sigma=\uparrow\downarrow} \hat{\psi}^+_\sigma(r) \hat{\psi}_\sigma(r) \right\rangle$$ electron density

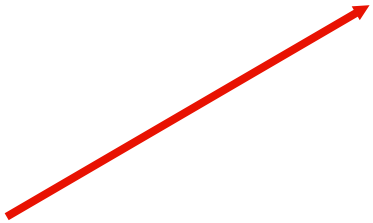
$$\chi(r,r') = \left\langle \hat{\psi}_\uparrow(r) \hat{\psi}_\downarrow(r') \right\rangle$$ order parameter

$$\Gamma(\underline{\underline{R}}) = \left\langle \hat{\phi}^+(R_1) \hat{\phi}^+(R_2) \cdots \hat{\phi}(R_1) \hat{\phi}(R_2) \cdots \right\rangle$$

diagonal of nuclear N_n-body density matrix

Hohenberg-Kohn theorem for superconductors

$$[v(r),\Delta(r,r'),W(\underline{\underline{R}})] \xleftrightarrow{\textbf{1-1}} [\rho(r),\chi(r,r'),\Gamma(\underline{\underline{R}})]$$



Densities in thermal equilibrium at finite temperature

Electronic KS equation

$$\left(-\frac{\nabla^2}{2}-\mu+v_s[\rho,\chi,\Gamma](r)\right)u(\boldsymbol{r})+\int \Delta_s[\rho,\chi,\Gamma](r,r')\,v(\boldsymbol{r}')d^3\boldsymbol{r}'=Eu(\boldsymbol{r})$$

$$\int \Delta_s{}^*[\rho,\chi,\Gamma](\mathbf{r},\mathbf{r}')\,u(\boldsymbol{r}')d^3\boldsymbol{r}'-\left(-\frac{\nabla^2}{2}-\mu+v_s[\rho,\chi,\Gamma](\mathbf{r})\right)v(\boldsymbol{r})=Ev(\boldsymbol{r})$$

Nuclear KS equation

$$\left(\sum_{\alpha=1}^{N_n}-\frac{\nabla_\alpha^2}{2M_\alpha}+W_s[\rho,\chi,\Gamma](\underline{\underline{R}})\right)\psi(\underline{\underline{R}})=E\psi(\underline{\underline{R}})$$

3 KS potentials: v_s Δ_s W_s

No approximation yet!

"Exactification" of BdG mean-field eqs.

KS theorem: There exist functionals $v_s[\rho,\chi,\Gamma]$, $\Delta_s[\rho,\chi,\Gamma]$, $W_s[\rho,\chi,\Gamma]$, such that the above equations reproduce the exact densities of the interacting system

Electronic KS equation

$$\left(-\frac{\nabla^2}{2}-\mu+v_s[\rho,\chi,\Gamma](r)\right)u(\boldsymbol{r})+\int \Delta_s[\rho,\chi,\Gamma](r,r')\,v(\boldsymbol{r}')d^3\boldsymbol{r}'=Eu(\boldsymbol{r})$$

$$\int \Delta_s{}^*[\rho,\chi,\Gamma](\mathbf{r},\mathbf{r}')\,u(\boldsymbol{r}')d^3\boldsymbol{r}'-\left(-\frac{\nabla^2}{2}-\mu+v_s[\rho,\chi,\Gamma](\mathbf{r})\right)v(\boldsymbol{r})=Ev(\boldsymbol{r})$$

Nuclear KS equation

$$\left(\sum_{\alpha=1}^{N_n}-\frac{\nabla_\alpha^2}{2M_\alpha}+W_s[\rho,\chi,\Gamma](\underline{\underline{R}})\right)\psi(\underline{\underline{R}})=E\psi(\underline{\underline{R}})$$

Solved in harmonic approximation

3 KS potentials: v_s Δ_s W_s

No approximation yet!

"Exactification" of BdG mean-field eqs.

KS theorem: There exist functionals $v_s[\rho,\chi,\Gamma]$, $\Delta_s[\rho,\chi,\Gamma]$, $W_s[\rho,\chi,\Gamma]$, such that the above equations reproduce the exact densities of the interacting system

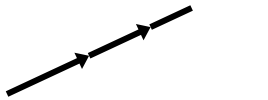
CONSTRUCTION OF APPROXIMATE F_{xc} :

$$\hat{H} = \hat{H}_o + \hat{H}_1$$

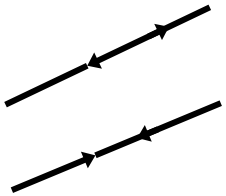
$$\hat{H}_o = \sum_\sigma \int \hat{\psi}^+_\sigma(r)\left(-\frac{\nabla^2}{2} - \mu + v_s\,(r, \underline{\underline{R}}_o) \right)\hat{\psi}_\sigma(r)d^3r$$

$$- \int d^3r \int d^3r' \left[\hat{\psi}_\uparrow(r)\hat{\psi}_\downarrow(r')\Delta^*_s(r,r') + \text{H.c.}\right] + \sum_q \Omega_q \left(\hat{b}^+_q \hat{b}_q + \frac{3}{2} \right)$$

develop diagrammatic many-body perturbation theory on the basis of the H_o-propagators:



G_s normal electron propagator (in superconducting state)



F_s

F_s*

anomalous electron propagators

D_s phonon propagator

Immediate consequence:

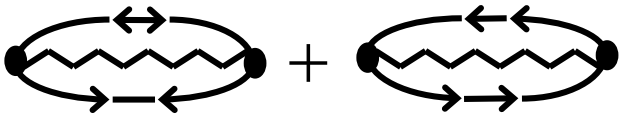
$$F_{xc} = F^{ph}_{xc} + F^{el}_{xc}$$

all diagrams containing D_s

all others diagrams

Phononic contributions

First order in phonon propagator:

$$F_{xc}^{ph}[n,\chi,\Gamma] =$$ 

$$= -\frac{1}{2}\sum_{ij}\int d\Omega \alpha^2 F_{ij}(\Omega)\frac{\Delta_i \Delta_j^*}{E_i E_j}\left(I(E_i,-E_j,\Omega) - I(E_i,E_j,\Omega)\right)$$

$$-\frac{1}{2}\sum_{ij}\int d\Omega \alpha^2 F_{ij}(\Omega)\left[\left(1+\frac{(\epsilon_i-\mu)(\epsilon_j-\mu)}{E_i E_j}\right) I(E_i,E_j,\Omega)\right.$$

$$\left. +\left(1-\frac{(\epsilon_i-\mu)(\epsilon_j-\mu)}{E_i E_j}\right) I(E_i,-E_j,\Omega)\right]$$

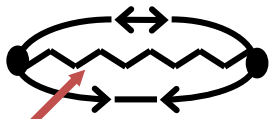
Input to $\mathbf{F_{xc}^{ph}}$: Full k,k' resolved Eliashberg function

$$\alpha^2 F_{nk,n'k'}(\Omega) = \sum_{\lambda q}\left|g_{nk,n'k'}^{\lambda q}\right|^2 \delta\left(\Omega-\Omega_{\lambda q}\right)$$

Calculated with Quantum Espresso code

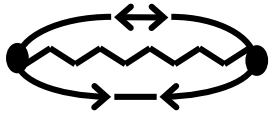
Purely electronic contributions

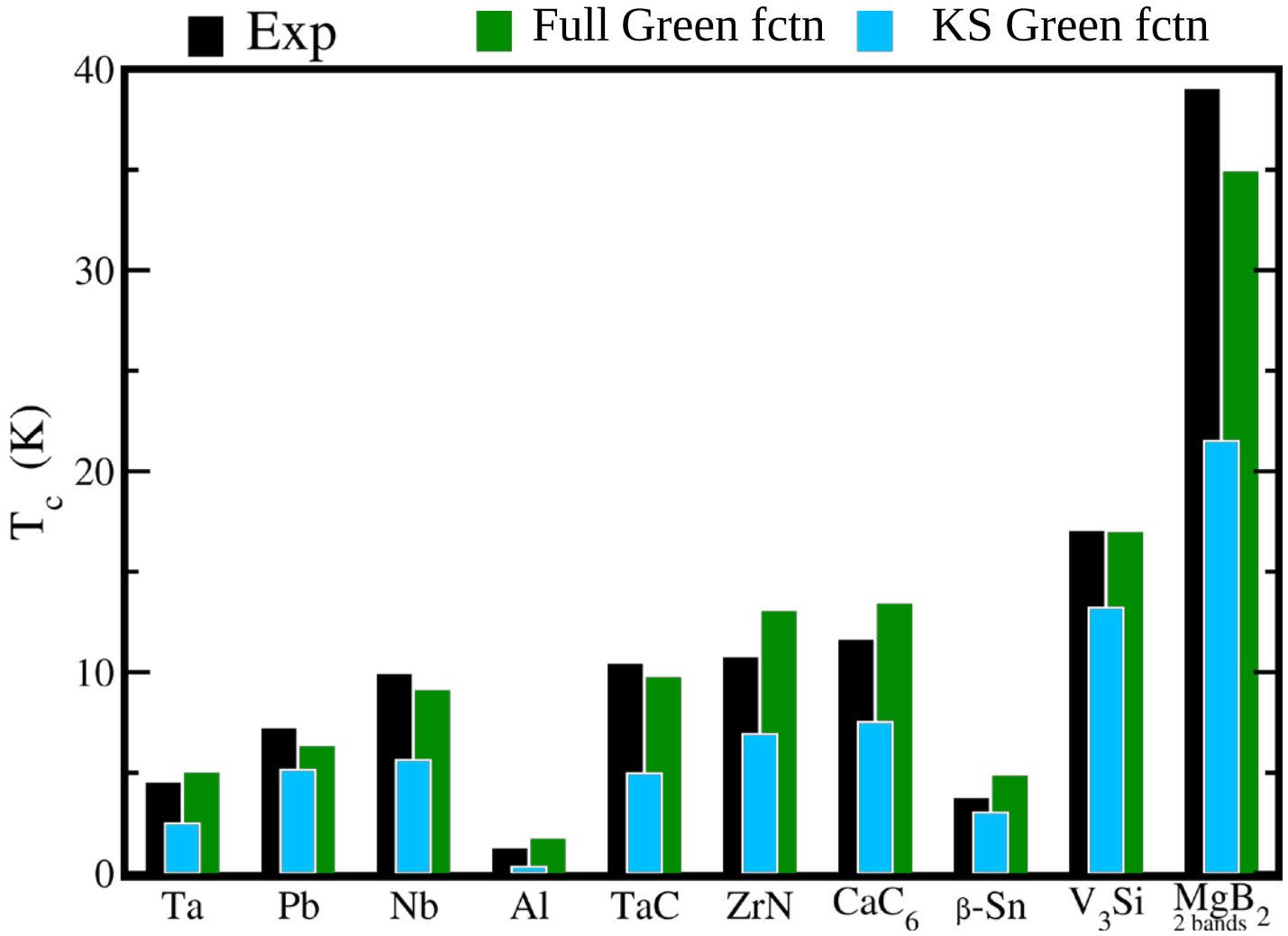
$$F_{xc}^{ee}[\rho,\chi] = \quad + F_{xc}^{GGA}[\rho]$$



RPA-screened electron-electron interaction

Crucial point: NO ADJUSTABLE PARAMETERS




Exp
Full Green fctn
KS Green fctn
T_c (K)
40
30
20
10
0
Ta
Pb
Nb
Al
TaC
ZrN
CaC_6
β-Sn
V_3Si
MgB_2
2 bands

Isotope effect:

$$T_c \propto M^{-\alpha}$$

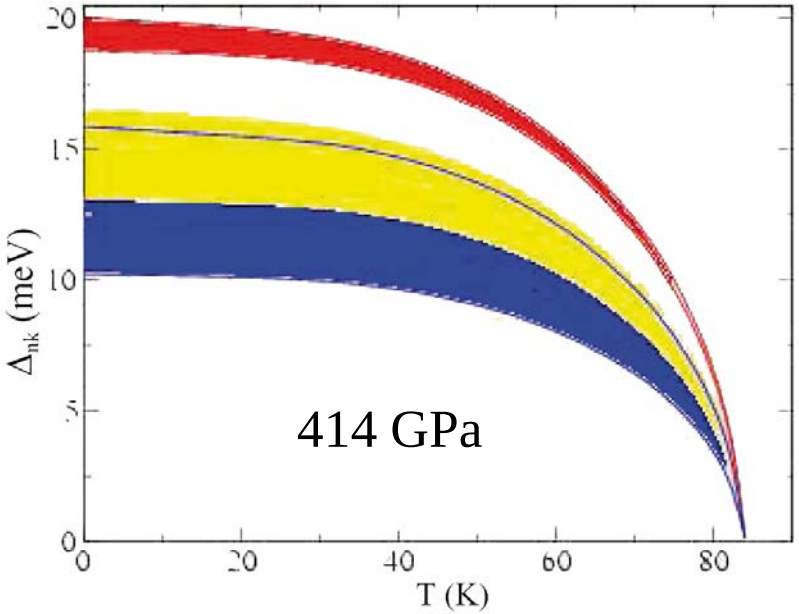
	Calculations			Experiment		
Pb		0.47			0.47	
Mo		0.37			0.33	

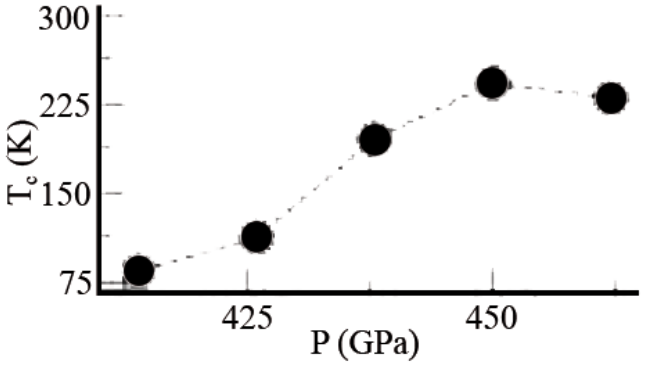
The deviations from BCS value α=0.5 are correctly described

Jump of specific heat at T_c

	Theory	Experiment
Pb	2.93	3.57-3.71
Nb	2.87	2.8-3.07
Ta	2.64	2.63
Al	2.46	2.43

Hydrogen under extreme pressure





Predictions:

- Three-gap superconductivity
- Increase of T_c with increasing P until T_c ~ 242K at 450 GPa

P. Cudazzo, G. Profeta, A. Sanna, A. Floris, A. Continenza, S. Massidda, E.K.U.G., Phys. Rev. Lett. 100, 257001 (2008).

Order parameter of superconductivity:

$$\chi(r,r') = \langle \psi_{\uparrow}(r)\psi_{\downarrow}(r') \rangle = \sum_{nk} \chi_{nk} \varphi_{nk}(r) \varphi^{*}_{nk}(r')$$

$$\chi_{nk} = -\frac{1}{2} \frac{\tanh\left(\frac{\beta}{2}\sqrt{(\epsilon_{n'k'} - \mu)^2 + |\Delta_{n'k'}|^2}\right)}{\sqrt{(\epsilon_{n'k'} - \mu)^2 + |\Delta_{n'k'}|^2}} \Delta_{n'k'}$$

$$\Delta(r,r') = \sum_{nk} \Delta_{nk} \varphi_{nk}(r) \varphi^{*}_{nk}(r')$$

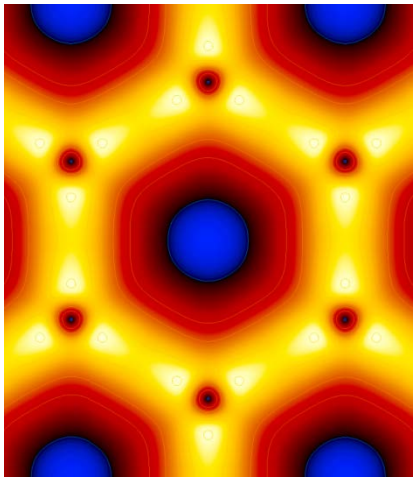
with Δ_{nk} being the solution of the SCDFT gap equation

Ab-initio calculation of SC order parameter χ(r,r') for MgB_2

$\chi(r,r') \equiv \chi(R,s)$

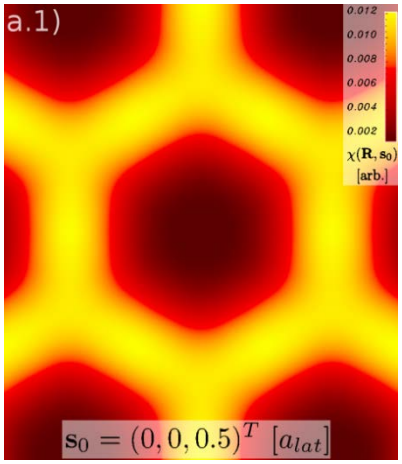
$R = (r+r')/2$

$s = r-r'$

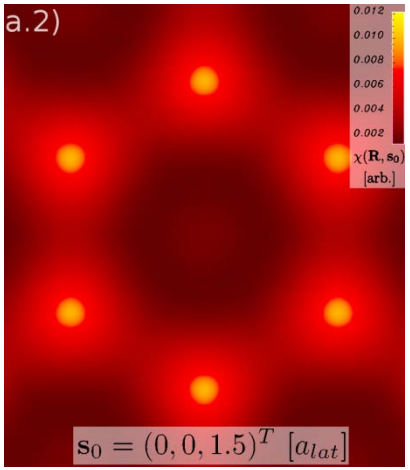


s = 0

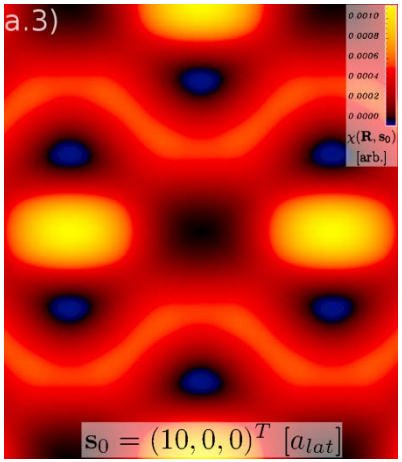
χ(R,s) as function of R for fixed s.



s = (0,0, 0.5)



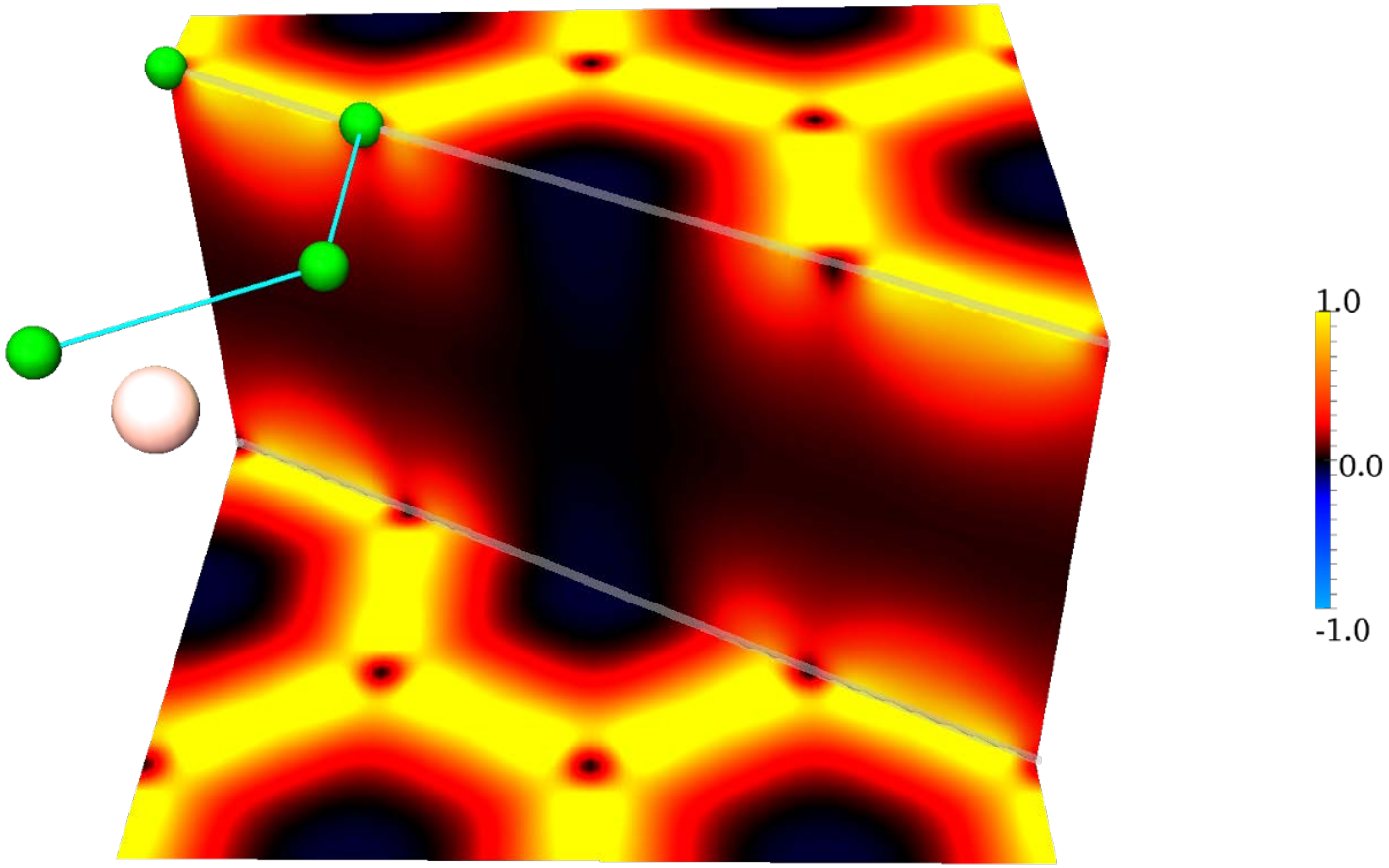
s = (0,0, 1.5)



s = (10,0,0)

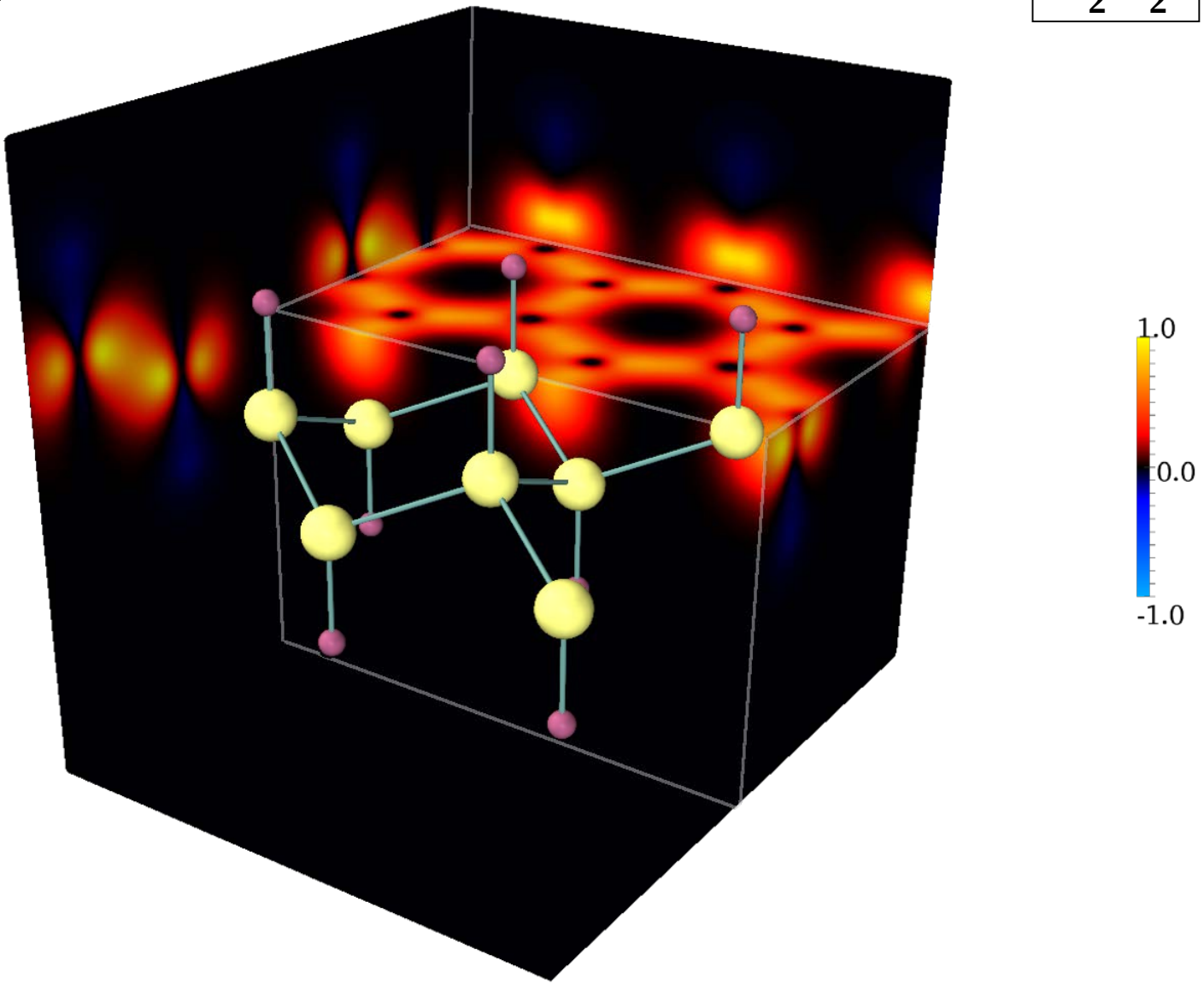
$\chi(R, s=0)$ as function of R

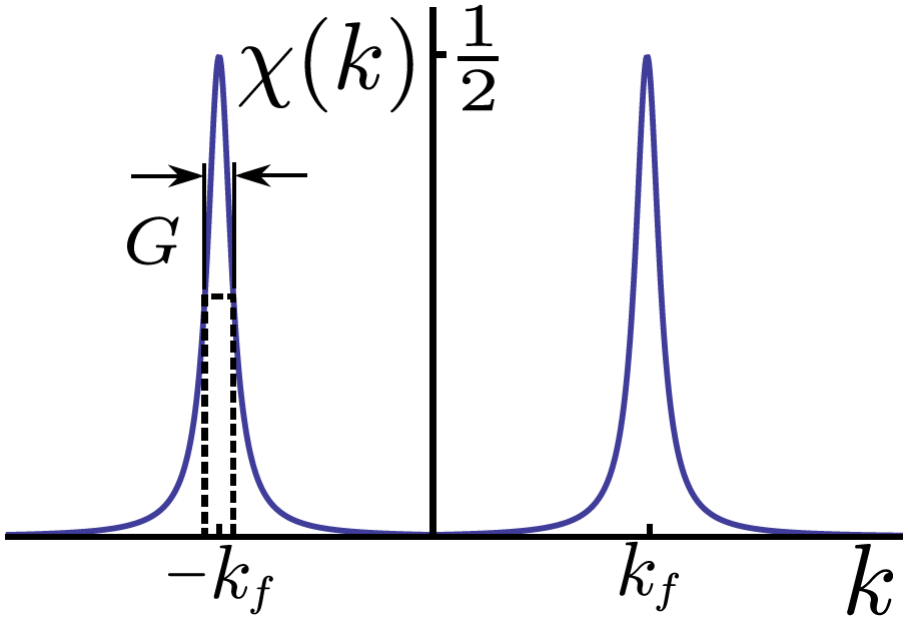
MgB_2

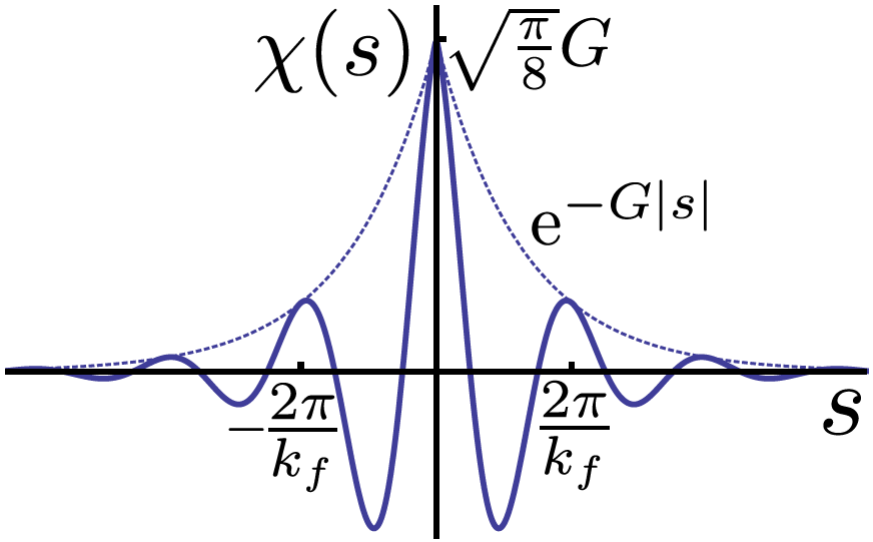


χ(R, s=0) as function of R

C_2H_2





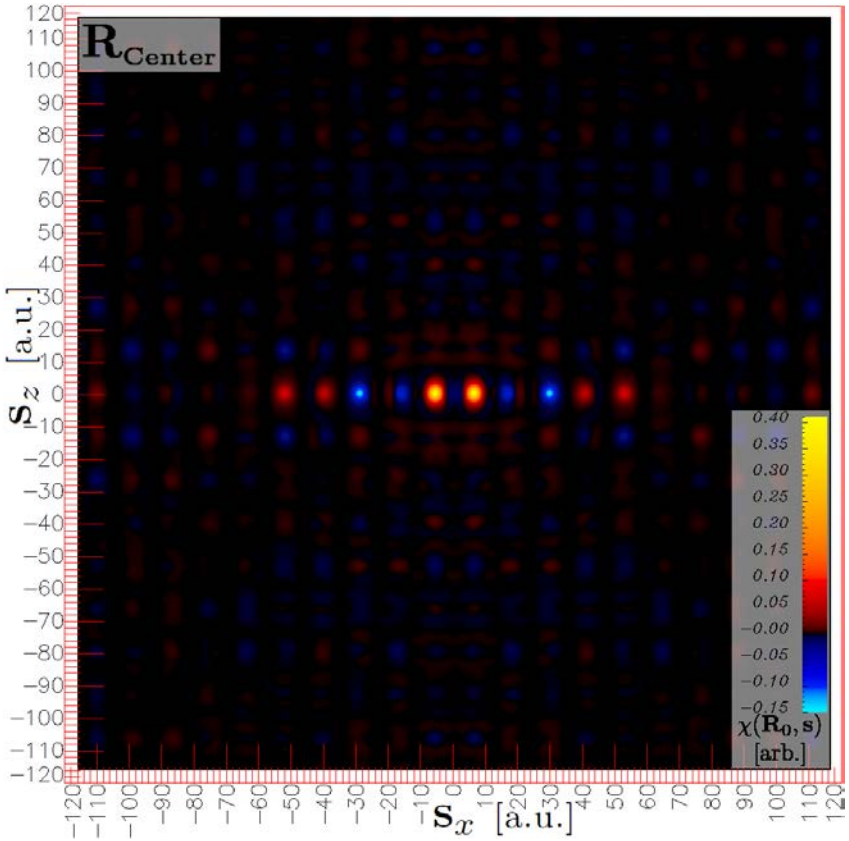


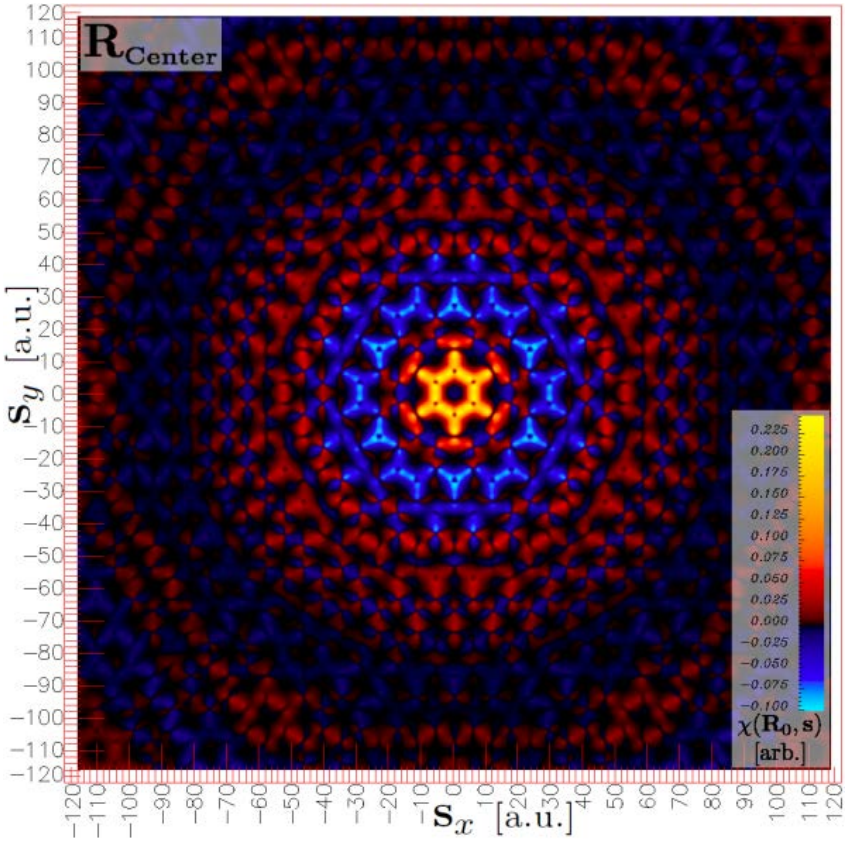
Lorentzian peaks of $\chi(k)$ in a 1D model system around the Fermi vectors $\pm k_F$ with width G.

Its real space transform (panel c) shows oscillations of periodicity $2\pi/k_F$ and exponential damping eGjsj.

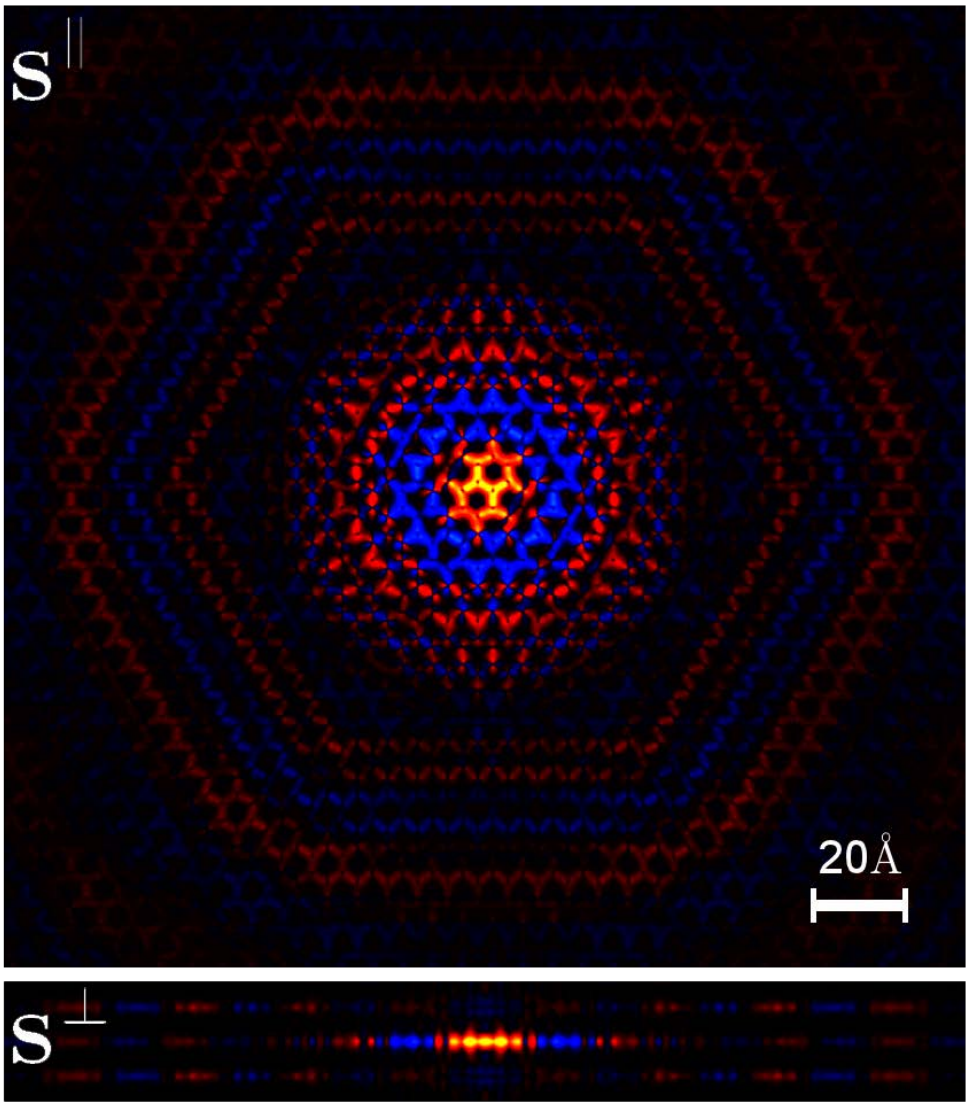
$\chi(R_0,s)$ as function of s (R_0 fixed at center of B hexagon)

MgB_2



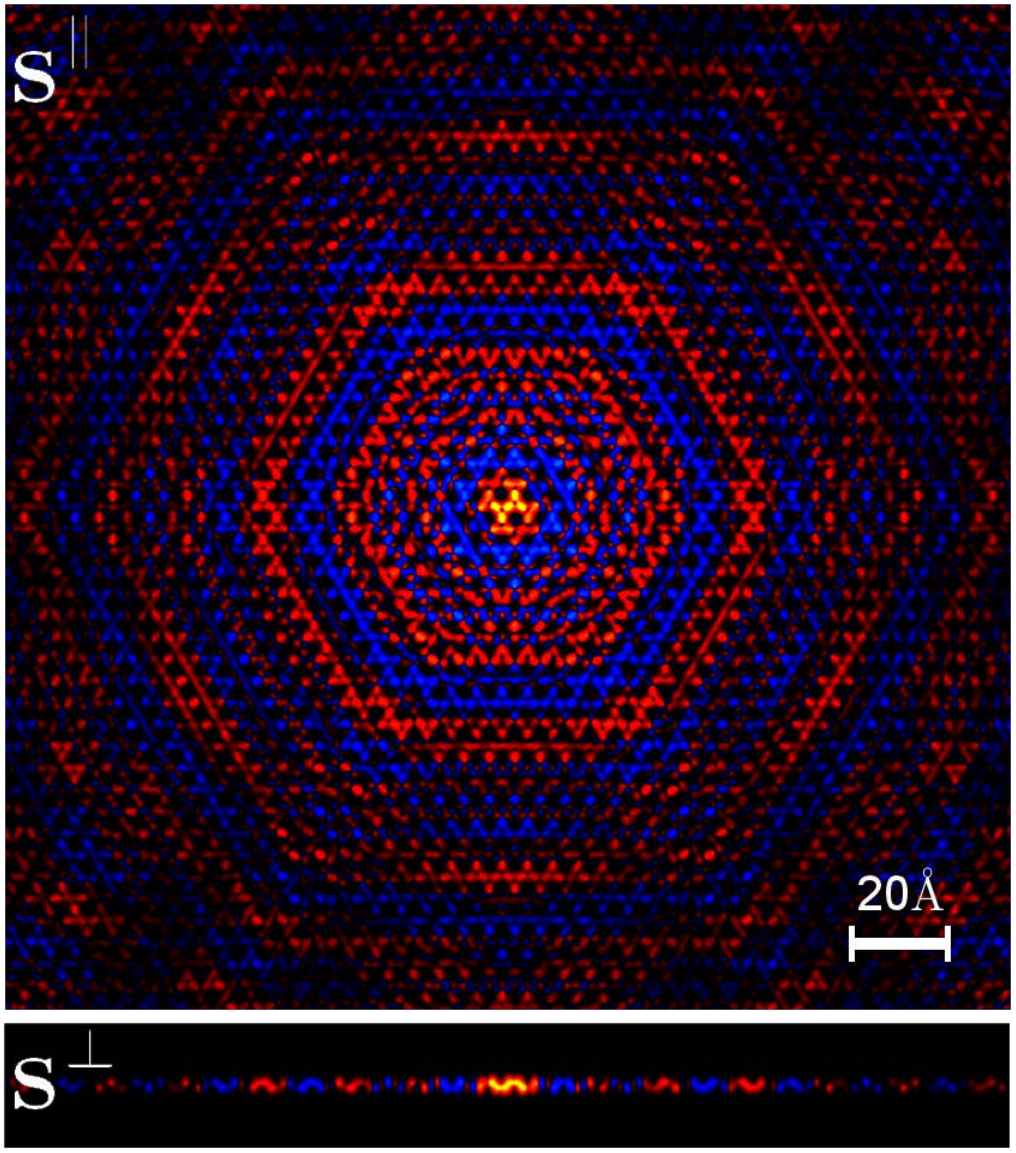


$\chi(R_0,s)$ as function of s (R_0 fixed at middle of B-B σ bond)

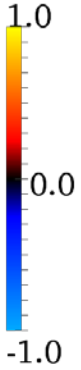


MgB_2

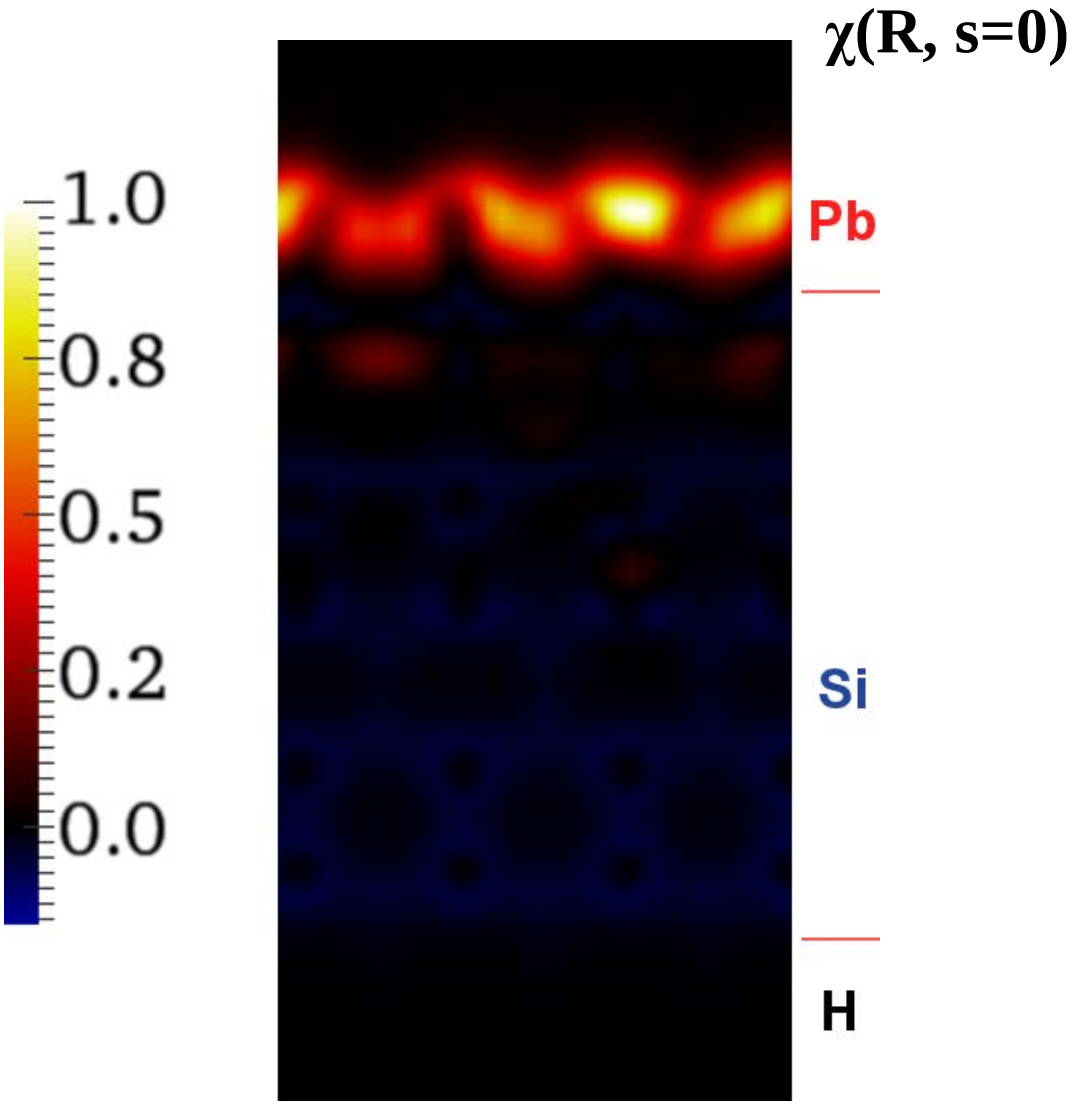
$\chi(R_0,s)$ as function of s (R_0 fixed at middle of C-C σ bond)



C_2H_2

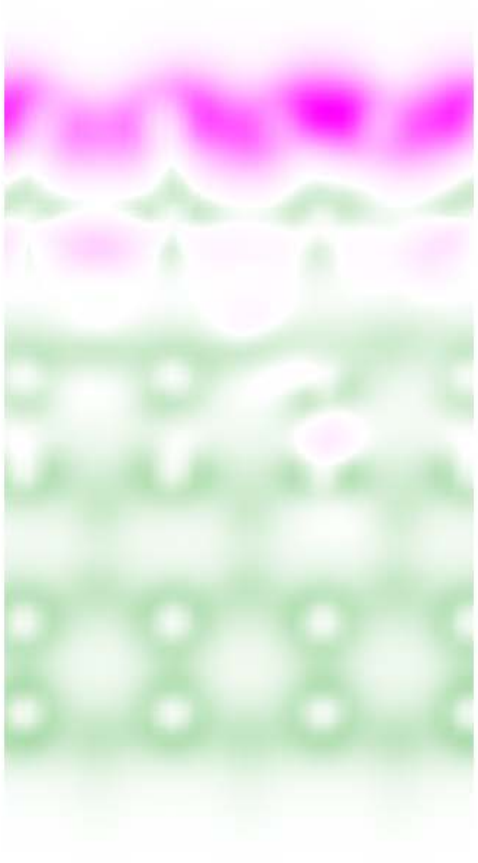


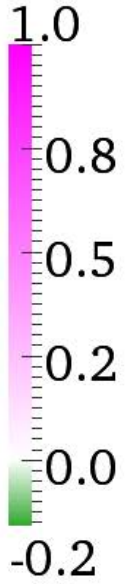
Pb monolayer on Si

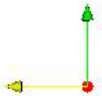


Pb monolayer on Si

$\chi(R, s=0)$

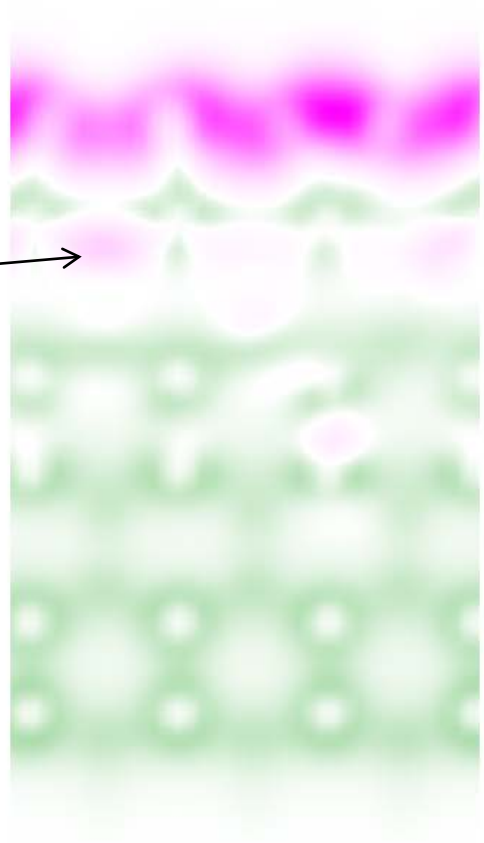




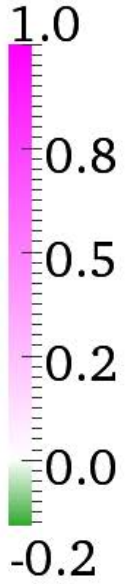


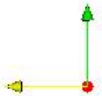
Pb monolayer on Si

$\chi(R, s=0)$



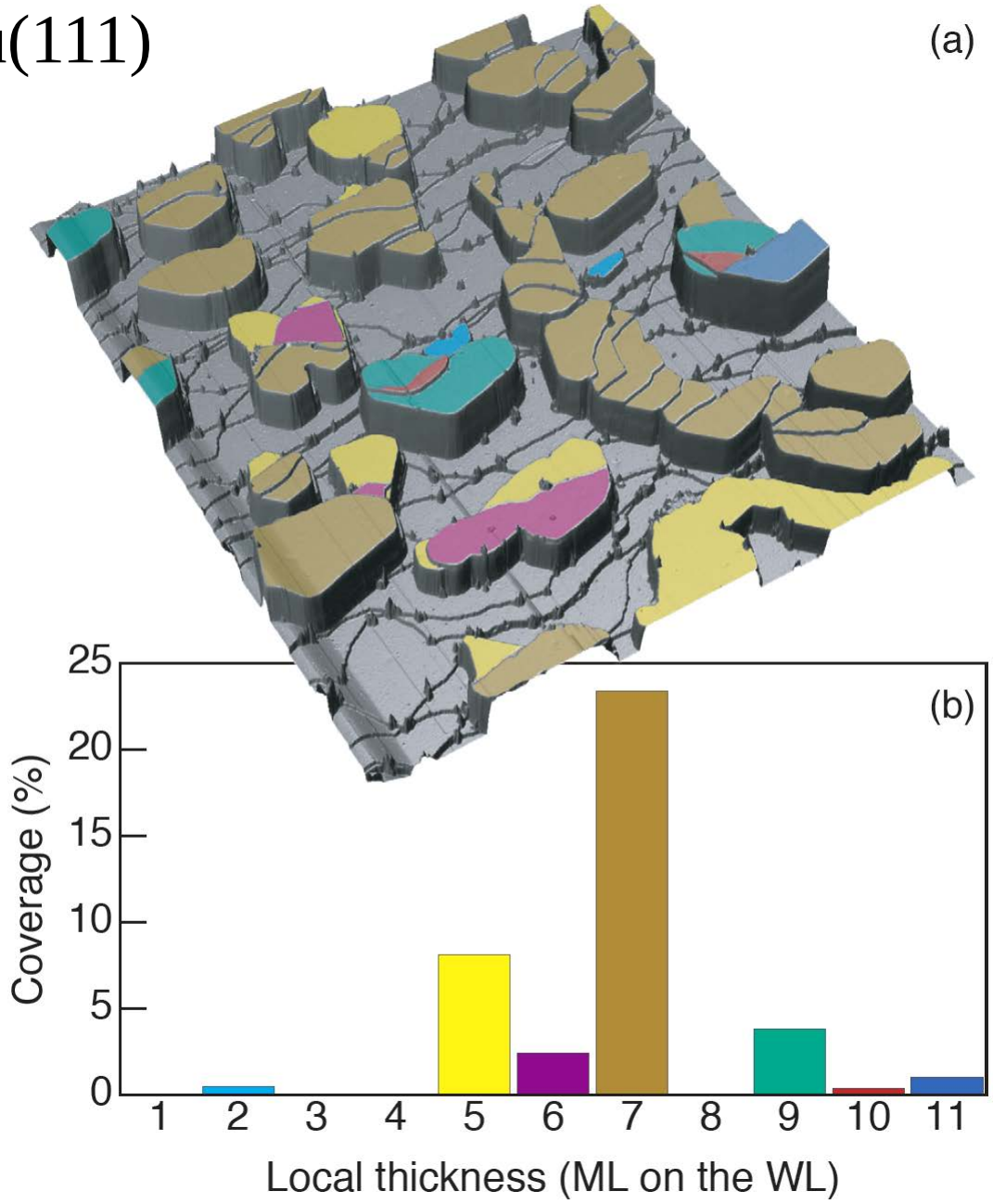
superconducting
metallic band of Si

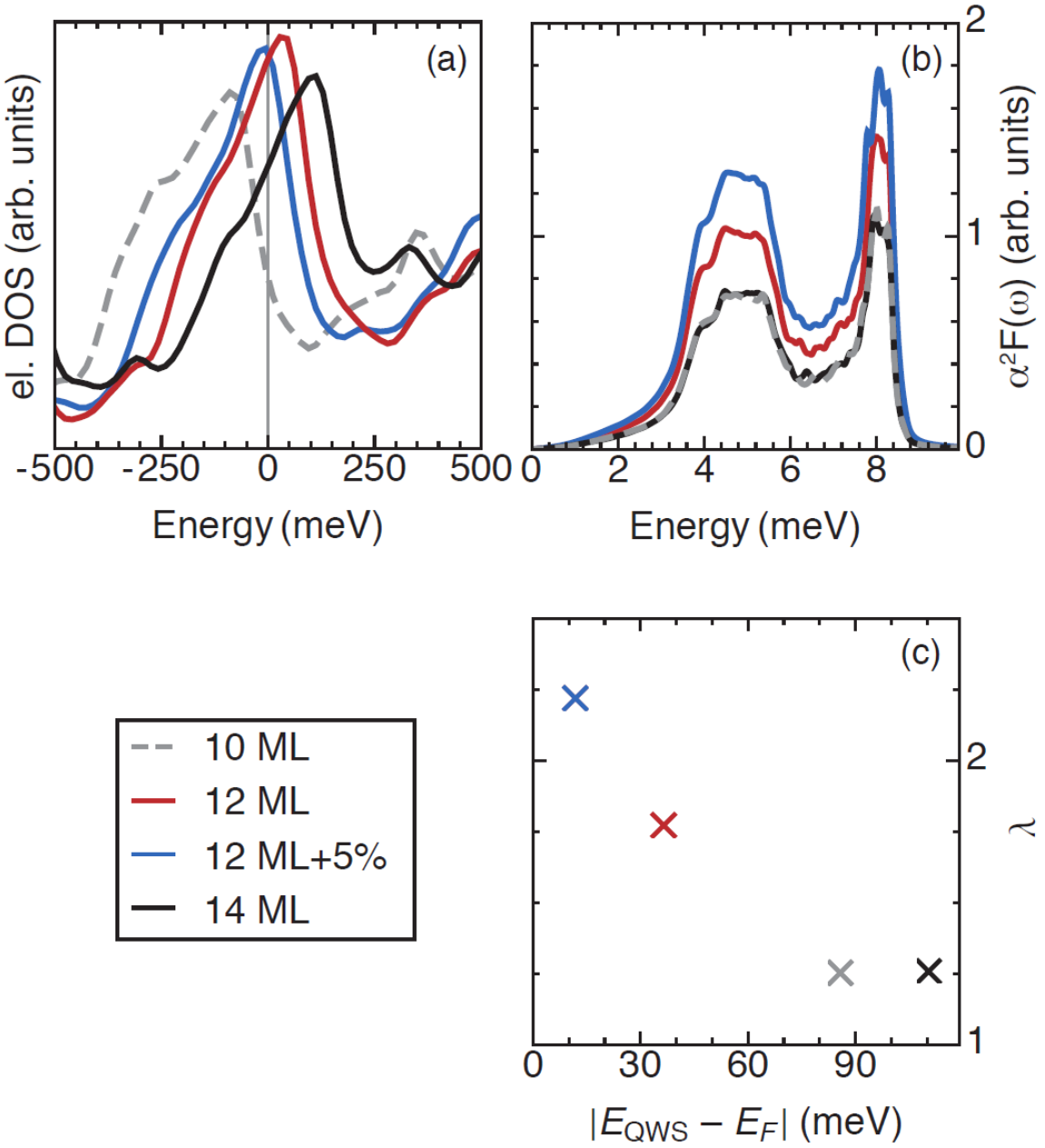




Tailoring the local order parameter

Pb islands on Cu(111)





M. Schackert, T. Märkl, J. Jandke, M. Hölzer, S. Ostanin, E. K. U. Gross, A. Ernst, W. Wulfhekel, Phys. Rev. Lett. (2015)

Correlation of T_c with bonding properties (localization of σ charges)

CaBeSi: T_c= 0.4 K (experiment and calculation)
CaBeB: T_c= 3.1 K (calculation)
MgB_2: T_c= 39.5 K (experiment and calculation)
LiBC: T_c= 75 K (calculation: Picket et al)

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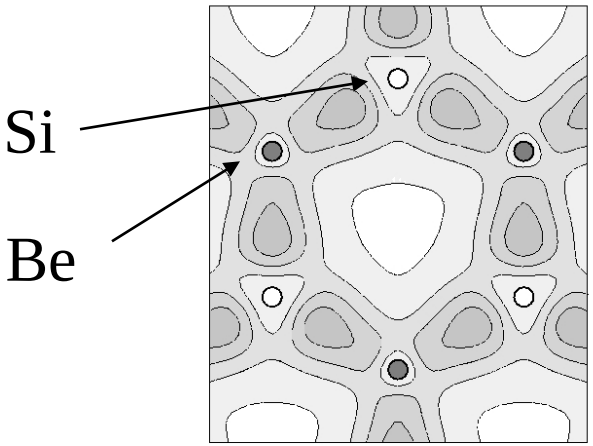
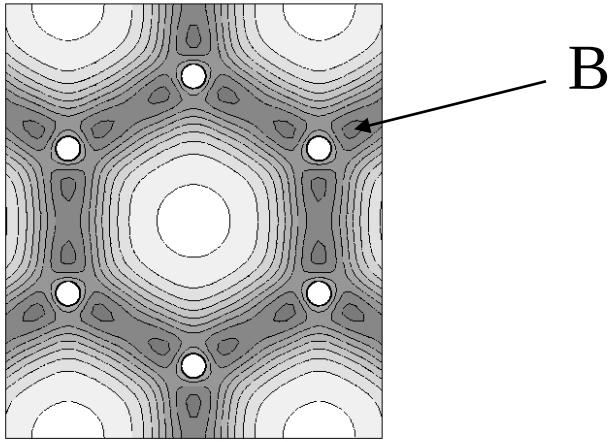
$$\chi(r,r) = \sum_{nk} \chi_{nk} \varphi_{nk}(r) \varphi^{*}_{nk}(r) \approx \sum_{k=k_F} |\varphi_{nk}(r)|^2$$

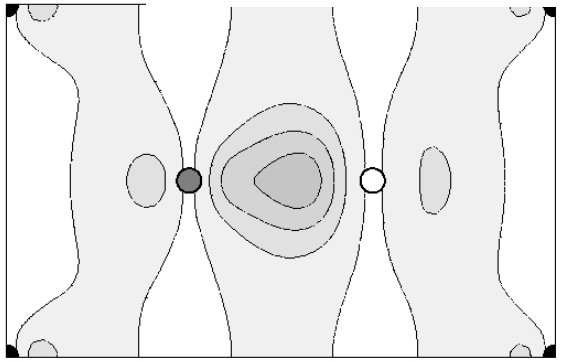
σ charge in CaBeSi vs MgB_2

C. Bersier, A. Floris, A. Sanna, G. Profeta, A. Continenza, EKUG, S. Massidda, Phys. Rev. B 79, 104503 (2009)

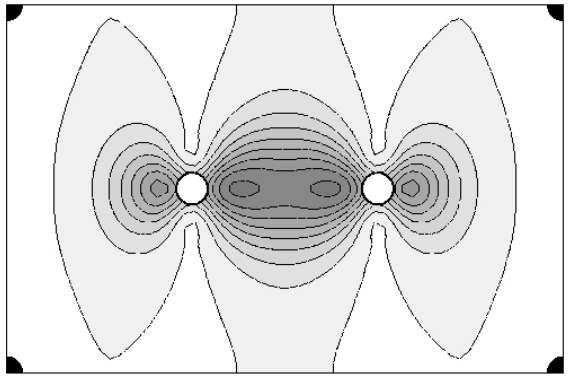


in plane





out of plane



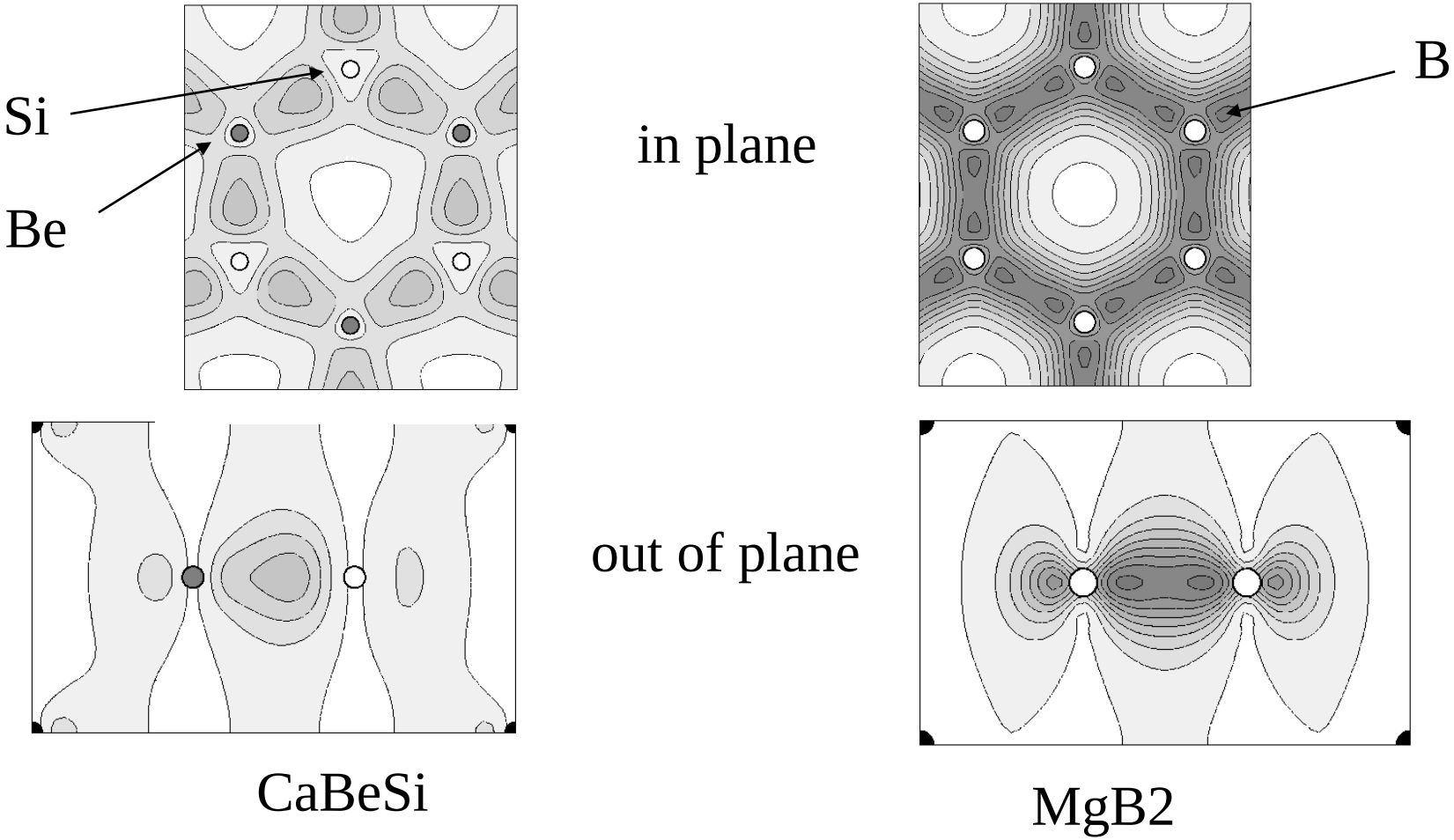
CaBeSi

MgB2

In MgB_2 much stronger σ charge localization than in CaBeSi

σ charge in CaBeSi vs MgB_2

C. Bersier, A. Floris, A. Sanna, G. Profeta, A. Continenza, EKUG, S. Massidda, Phys. Rev. B 79, 104503 (2009)



In MgB_2 much stronger σ charge localization than in CaBeSi

T_c correlates with the strength of the σ charge localization

Correlated motion of electrons and nuclei beyond the Born-Oppenheimer approximation

Hamiltonian for the complete system of N_e electrons with coordinates $(\mathbf{r}_1 \cdots \mathbf{r}_{N_e}) \equiv \underline{\underline{r}}$ and N_n nuclei with coordinates $(\mathbf{R}_1 \cdots \mathbf{R}_{N_n}) \equiv \underline{\underline{R}}$

$$\hat{H} = \hat{T}_n(\underline{\underline{R}}) + \hat{W}_{nn}(\underline{\underline{R}}) + \hat{T}_e(\underline{\underline{r}}) + \hat{W}_{ee}(\underline{\underline{r}}) + \hat{V}_{en}(\underline{\underline{R}}, \underline{\underline{r}})$$

with

$$\hat{T}_n = \sum_{\nu=1}^{N_n} -\frac{\nabla_\nu^2}{2M_\nu} \qquad \hat{T}_e = \sum_{i=1}^{N_e} -\frac{\nabla_i^2}{2m} \qquad \hat{W}_{nn} = \frac{1}{2}\sum_{\substack{\mu,\nu \\ \mu\neq\nu}}^{N_n} \frac{Z_\mu Z_\nu}{|R_\mu - R_\nu|}$$

$$\hat{W}_{ee} = \frac{1}{2}\sum_{\substack{j,k \\ j\neq k}}^{N_e} \frac{1}{|r_j - r_k|} \qquad \hat{V}_{en} = \sum_{j=1}^{N_e}\sum_{\nu=1}^{N_n} -\frac{Z_\nu}{|r_j - R_\nu|}$$

Time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\Psi(\underline{\underline{r}}, \underline{\underline{R}}, t) = \left(H(\underline{\underline{r}}, \underline{\underline{R}}) + V_{laser}(\underline{\underline{r}}, \underline{\underline{R}}, t)\right)\psi(\underline{\underline{r}}, \underline{\underline{R}}, t)$$

$$V_{laser}(\underline{\underline{r}}, \underline{\underline{R}}, t) = \left(\sum_{j=1}^{N_e} r_j - \sum_{\nu=1}^{N_n} Z_\nu R_\nu\right) \cdot E \cdot f(t) \cdot \cos\omega t$$

Standard representation of the full TD wave function

Expand full molecular wave function in complete set of BO states:

$$\Psi\left(\underline{\underline{r}},\underline{\underline{\underline{R}}},t\right)=\sum_{J}\Phi^{BO}_{\underline{\underline{\underline{R}}},J}\left(\underline{\underline{r}}\right)\cdot\chi_{J}\left(\underline{\underline{\underline{R}}},t\right)$$

and insert expansion in the full Schrödinger equation → standard non-adiabatic coupling terms from T_n acting on $\Phi^{BO}_{\underline{\underline{\underline{R}}},J}\left(\underline{\underline{r}}\right)$.

Plug Born-Huang expansion in full TDSE:

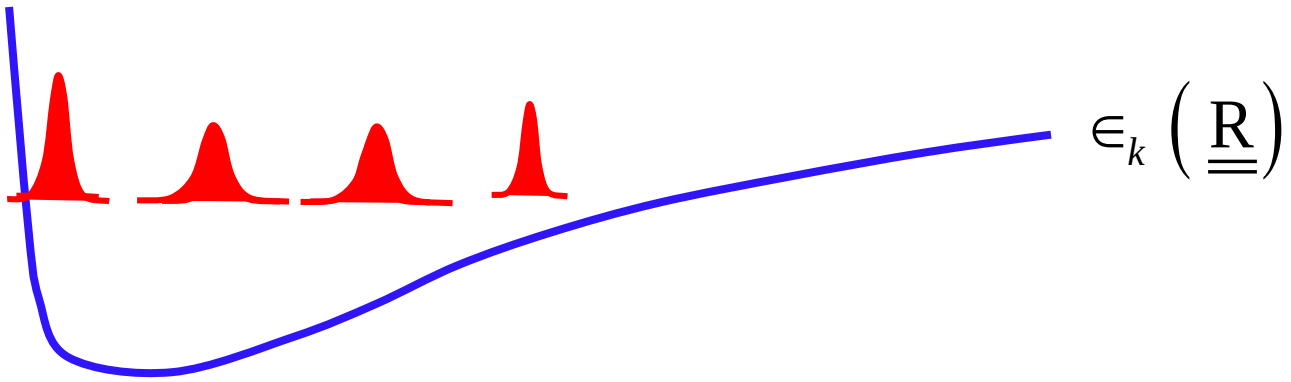
$$i\partial_t \chi_k\left(\underline{\underline{R}},t\right) = T_n \chi_k\left(\underline{\underline{R}},t\right) + \in_k\left(\underline{\underline{R}}\right)\chi_k\left(\underline{\underline{R}},t\right)$$

$$+\sum_{j\alpha}\left(\frac{\hbar^2}{M_\alpha}\right)\underbrace{\left\langle \phi^{BO}_{\underline{\underline{R}},k}\left|-i\nabla_{\underline{\underline{R}}_\alpha}\right|\phi^{BO}_{\underline{\underline{R}},j}\right\rangle}_{\text{NAC-1}}\left(-i\nabla_{\underline{\underline{R}}_\alpha}\chi_j\left(\underline{\underline{R}},t\right)\right)$$

$$+\sum_{j\alpha}\left(-\frac{\hbar^2}{2M_\alpha}\right)\underbrace{\left\langle \phi^{BO}_{\underline{\underline{R}},k}\left|\nabla^2_{\underline{\underline{R}}_\alpha}\right|\phi^{BO}_{\underline{\underline{R}},j}\right\rangle}_{\text{NAC-2}}\chi_j\left(\underline{\underline{R}},t\right)$$

Plug Born-Huang expansion in full TDSE:

$$i\partial_t \chi_k\left(\underline{\underline{R}},t\right) = T_n \chi_k\left(\underline{\underline{R}},t\right) + \in_k\left(\underline{\underline{R}}\right)\chi_k\left(\underline{\underline{R}},t\right)$$



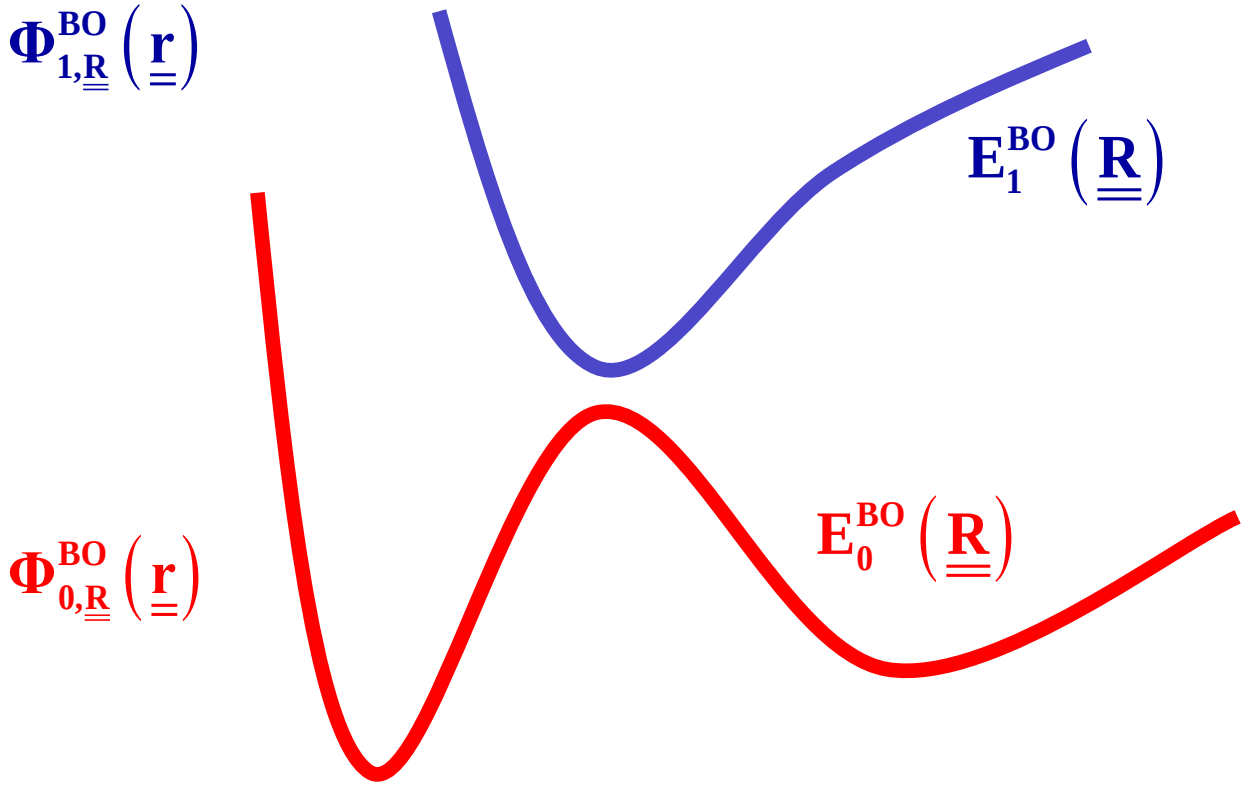
Plug Born-Huang expansion in full TDSE:

$$i\partial_t \chi_k\left(\underline{\underline{R}},t\right) = T_n \chi_k\left(\underline{\underline{R}},t\right) + \epsilon_k\left(\underline{\underline{R}}\right)\chi_k\left(\underline{\underline{R}},t\right)$$

$$+\sum_{j\alpha}\left(\frac{\hbar^2}{M_\alpha}\right)\underbrace{\left\langle \phi^{BO}_{\underline{\underline{R}},k}\left|-i\nabla_{\underline{\underline{R}}_\alpha}\right|\phi^{BO}_{\underline{\underline{R}},j}\right\rangle}_{\text{NAC-1}}\left(-i\nabla_{\underline{\underline{R}}_\alpha}\chi_j\left(\underline{\underline{R}},t\right)\right)$$

$$+\sum_{j\alpha}\left(-\frac{\hbar^2}{2M_\alpha}\right)\underbrace{\left\langle \phi^{BO}_{\underline{\underline{R}},k}\left|\nabla^2_{\underline{\underline{R}}_\alpha}\right|\phi^{BO}_{\underline{\underline{R}},j}\right\rangle}_{\text{NAC-2}}\chi_j\left(\underline{\underline{R}},t\right)$$

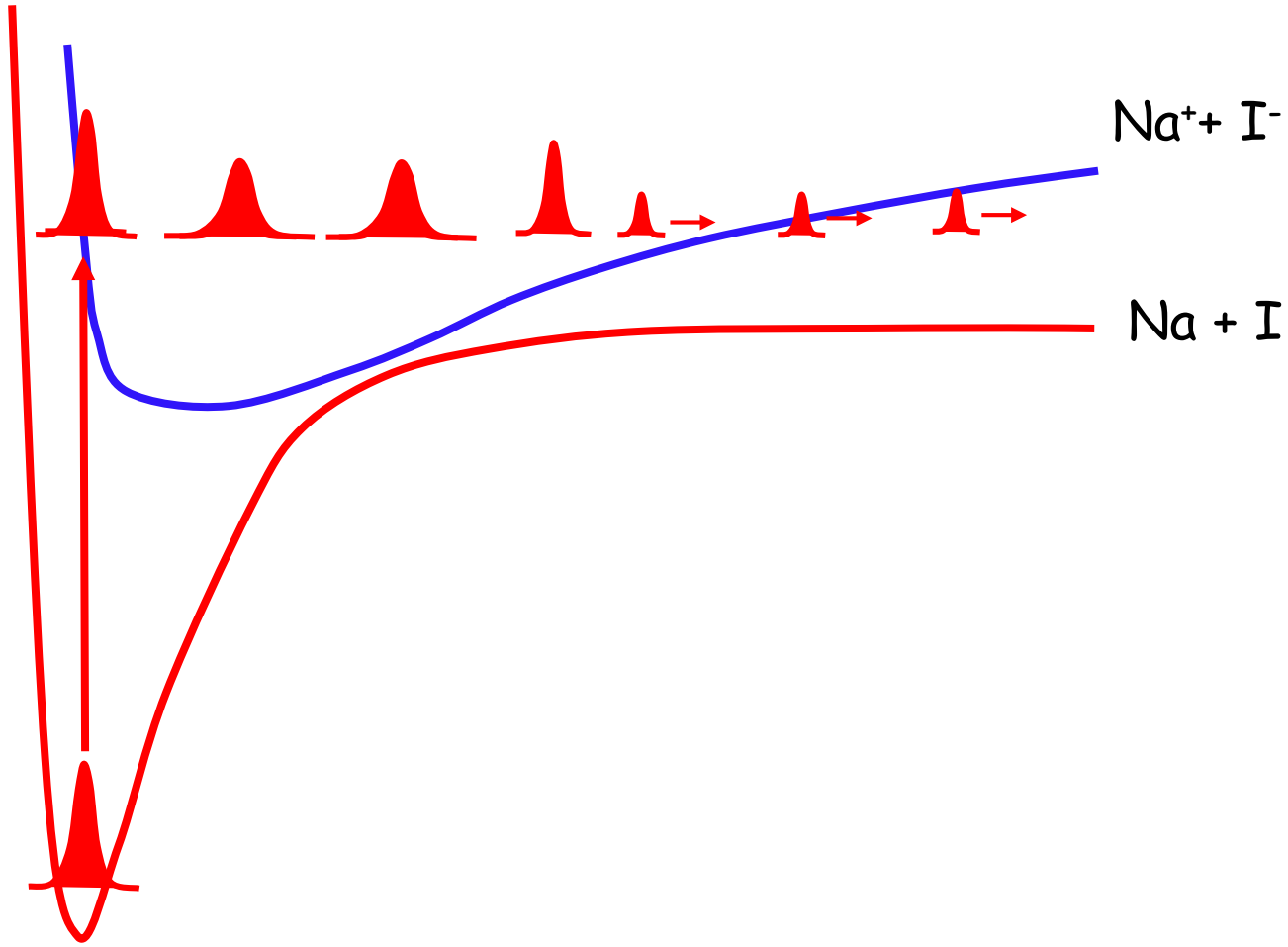
The dynamics is "non-adiabatic" when the NAC terms cannot be neglected



$$\Psi_0\left(\underline{\underline{r}},\underline{\underline{R}},t\right) \approx \chi_{00}\left(\underline{\underline{R}},t\right)\Phi^{BO}_{0,\underline{\underline{R}}}\left(\underline{\underline{r}}\right) + \chi_{01}\left(\underline{\underline{R}},t\right)\Phi^{BO}_{1,\underline{\underline{R}}}\left(\underline{\underline{r}}\right)$$

When only few BO-PES are important, the BO expansion gives a perfectly clear picture of the dynamics

Example: NaI femtochemistry



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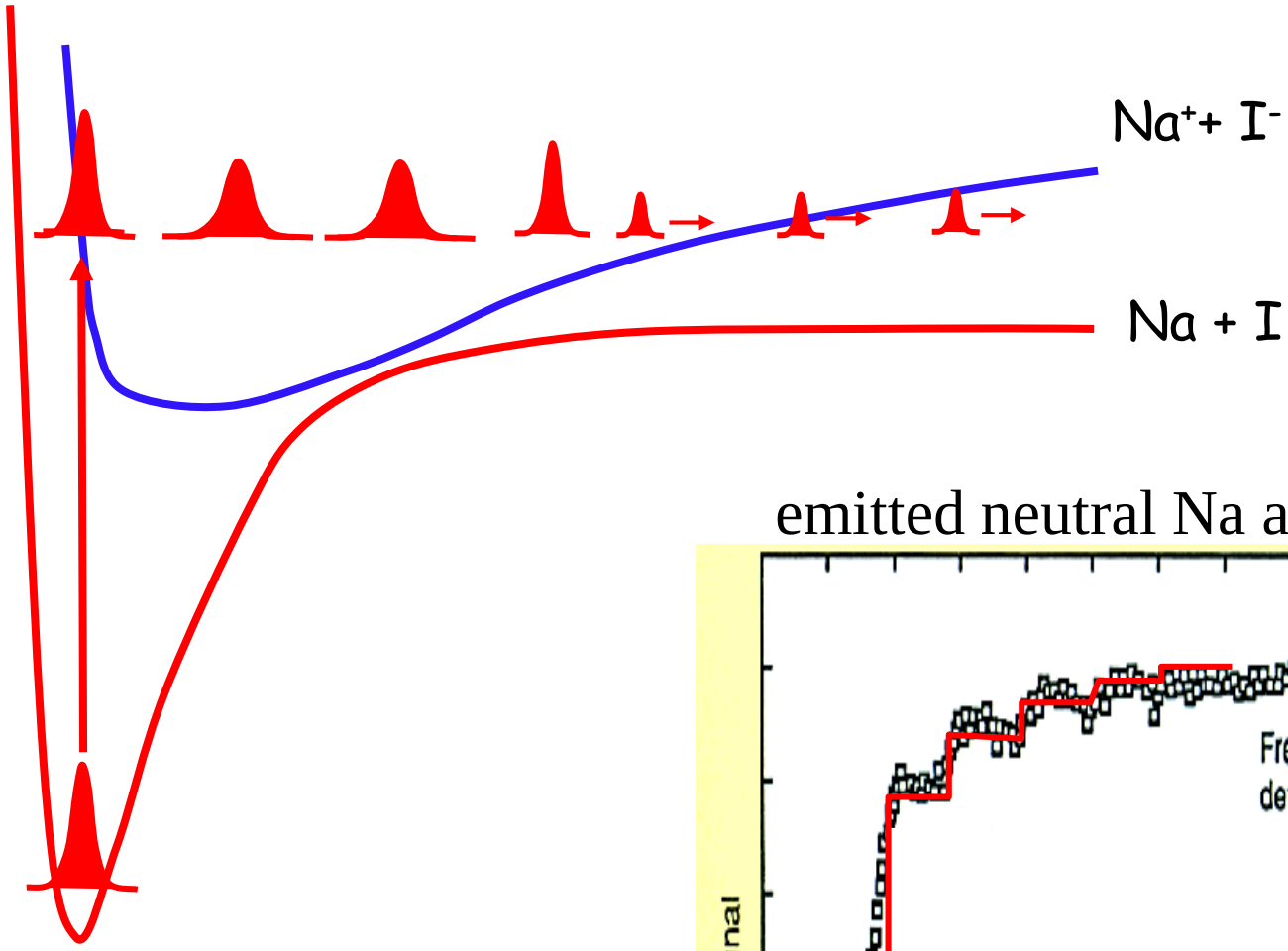
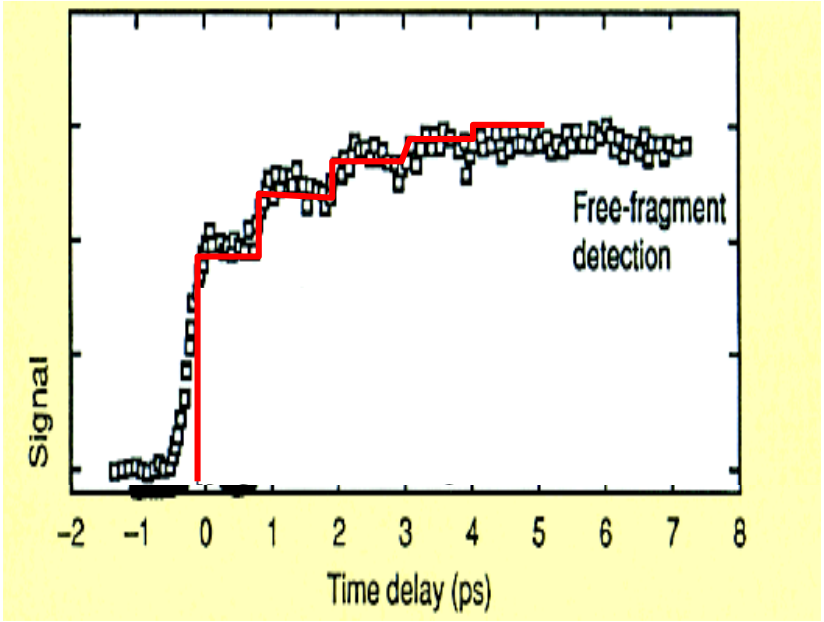
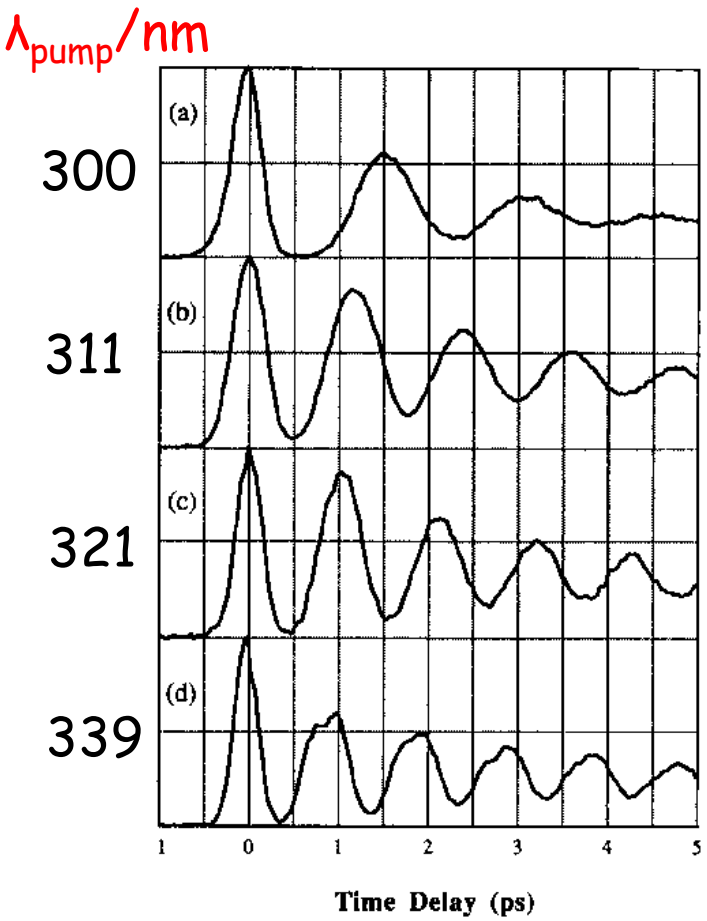
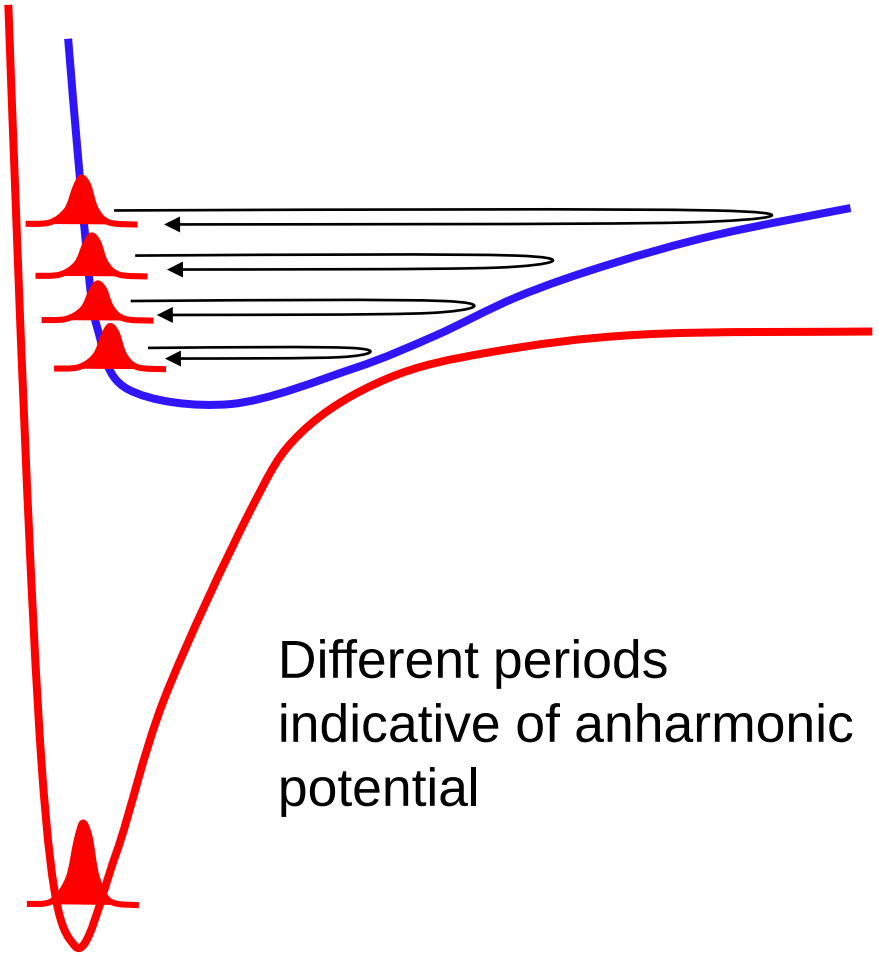


emitted neutral Na atoms



Effect of tuning pump wavelength (exciting to different points on excited surface)



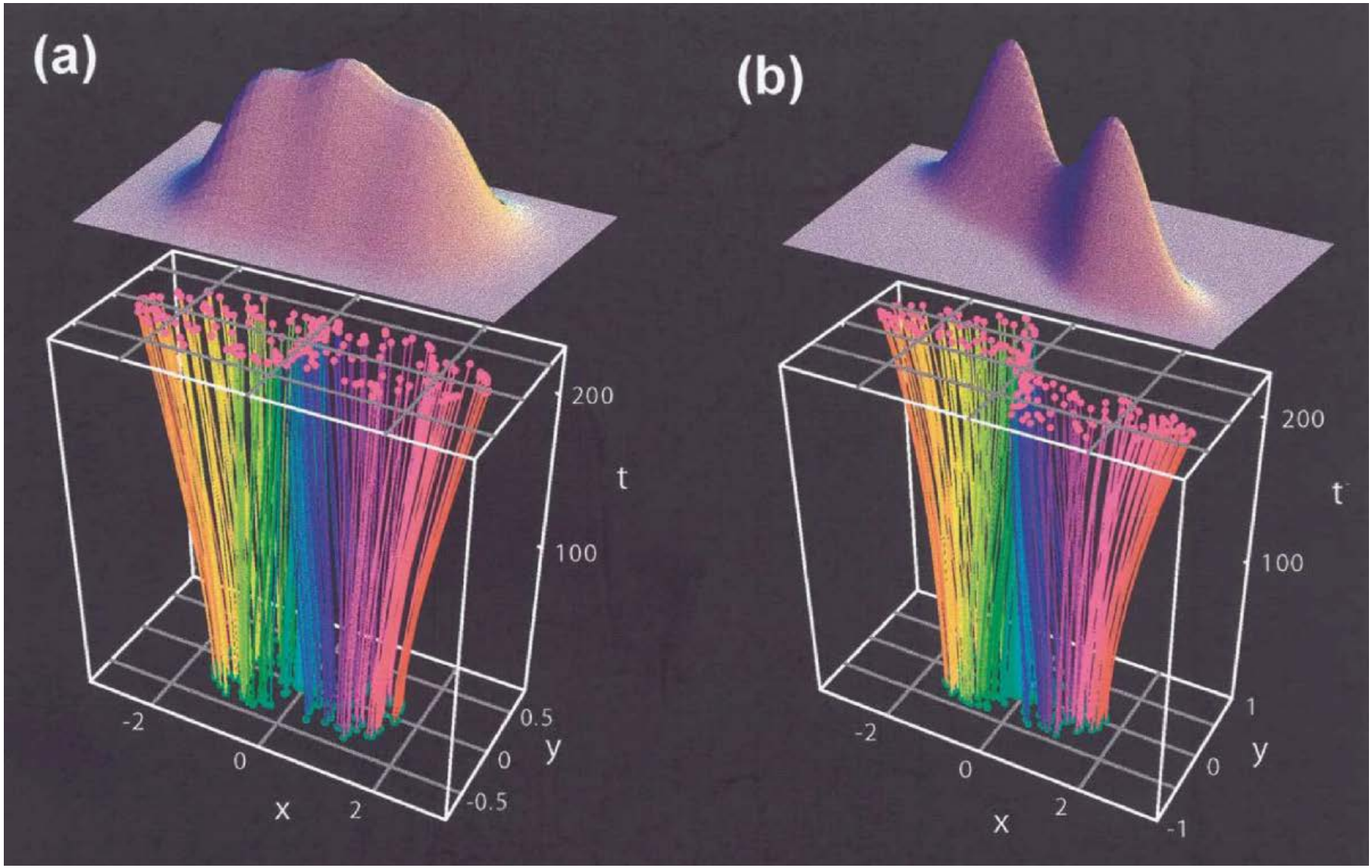


Different periods indicative of anharmonic potential

T.S. Rose, M.J. Rosker, A. Zewail, JCP **91**, 7415 (1989)

For larger systems one would like to (one has to) treat the nuclei classically.

Trajectory-based quantum dynamics



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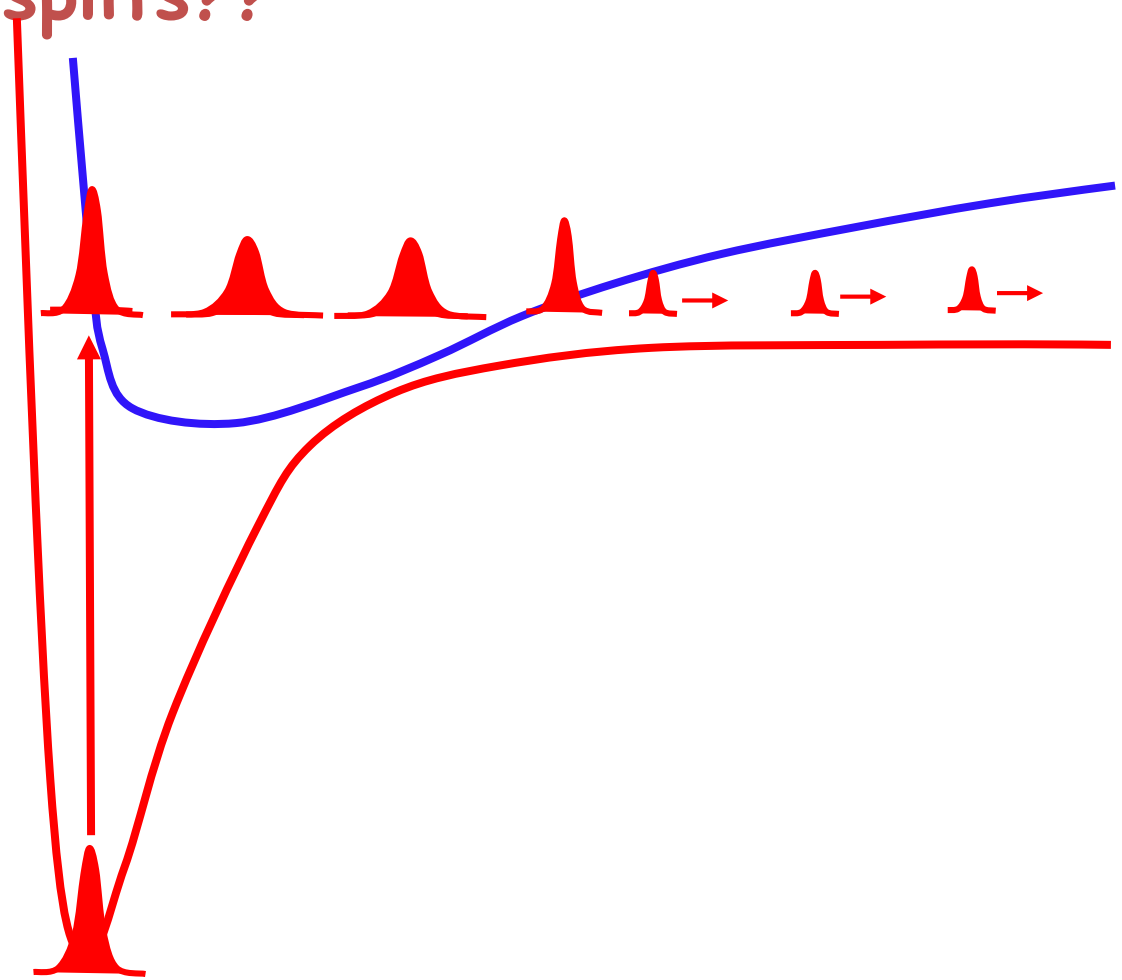

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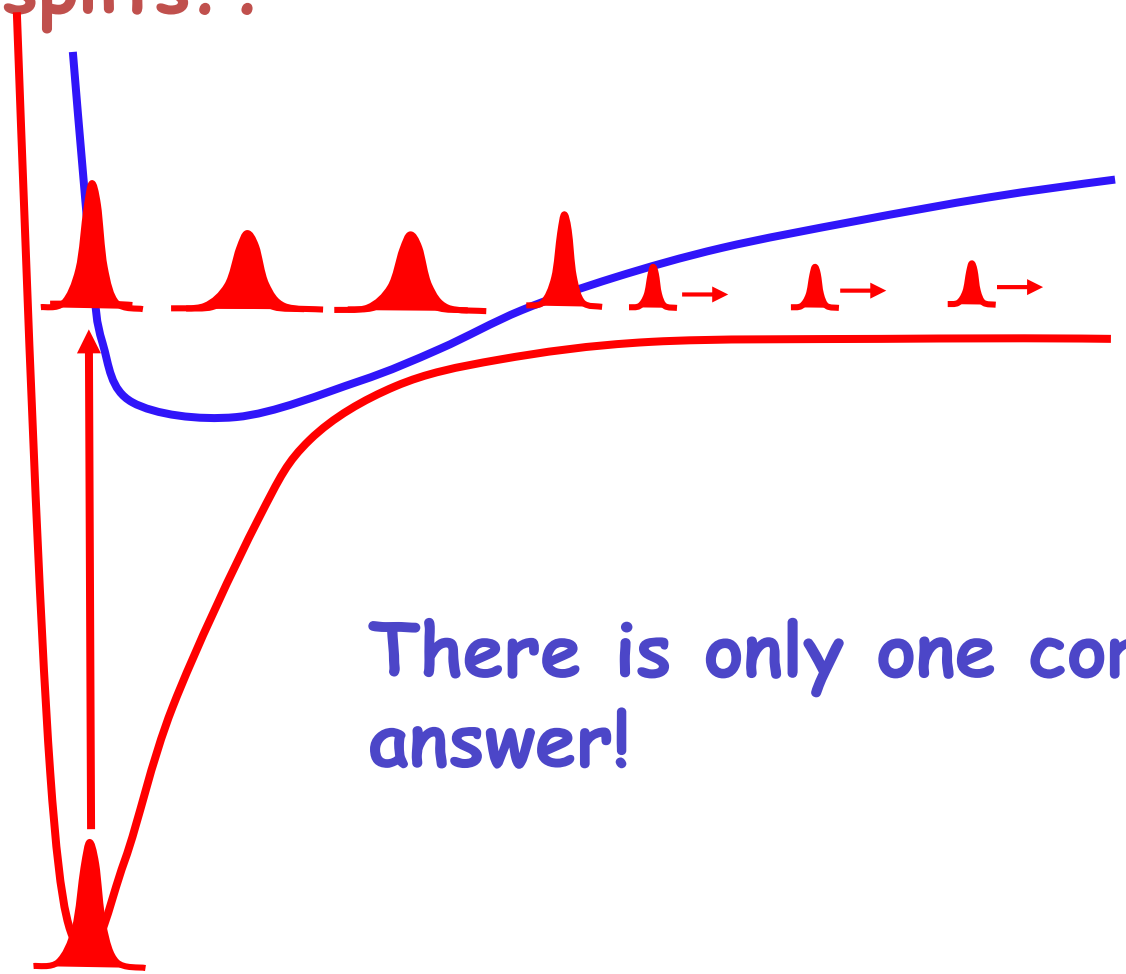

There is only one correct answer!

Outline

- **Show that the factorisation**

$$\Psi\left(\underline{\underline{r}}, \underline{\underline{\underline{R}}}\right) = \Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right) \cdot \chi\left(\underline{\underline{\underline{R}}}\right)$$

  can be made exact

- **Concept of exact PES and exact Berry phase**

- **Concept of exact and unique time-dependent PES**

- **Mixed quantum-classical algorithms**

- **Density-functionalisation of complete system of electrons and nuclei**

Theorem I

The exact solutions of

$$\hat{H}\Psi\left(\underline{\underline{r}},\underline{\underline{R}}\right)=E\Psi\left(\underline{\underline{r}},\underline{\underline{R}}\right)$$

can be written in the form

$$\Psi\left(\underline{\underline{r}},\underline{\underline{R}}\right)=\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)\cdot\chi\left(\underline{\underline{R}}\right)$$

where $\int d\underline{\underline{r}}\left|\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)\right|^2=1$ **for each fixed** $\underline{\underline{R}}$**.**

N.I. Gidopoulos, E.K.U. Gross, Phil. Trans. R. Soc. 372, 20130059 (2014)

Factorization first suggested by G. Hunter, IJQC 9, 237 (1975)

Theorem II: $\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)$ and $\chi\left(\underline{\underline{R}}\right)$ **satisfy the following equations:**

Eq. ❶

$$\left(\underbrace{\hat{T}_e + \hat{W}_{ee} + \hat{V}_e^{ext} + \hat{V}_{en}}_{\hat{H}_{BO}} + \sum_{\nu}^{N_n} \frac{1}{2M_\nu}\left(-i\nabla_\nu - A_\nu\right)^2 + \sum_{\nu}^{N_n} \frac{1}{M_\nu}\left(\frac{-i\nabla_\nu \chi}{\chi} + A_\nu\right)\left(-i\nabla_\nu - A_\nu\right)\right)\Phi_{\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{r}}\right) = \in\left(\underline{\underline{R}}\right)\Phi_{\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{r}}\right)$$

Eq. ❷

$$\left(\sum_{\nu}^{N_n} \frac{1}{2M_\nu}\left(-i\nabla_\nu + A_\nu\right)^2 + \hat{W}_{nn} + \hat{V}_n^{ext} + \in\left(\underline{\underline{R}}\right)\right)\chi\left(\underline{\underline{R}}\right) = E\chi\left(\underline{\underline{R}}\right)$$

where

$$A_\nu\left(\underline{\underline{R}}\right) = -i\int \Phi^*_{\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{r}}\right)\nabla_\nu \Phi_{\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{r}}\right) d\underline{\underline{r}}$$

N.I. Gidopoulos, E.K.U. Gross, Phil. Trans. R. Soc. 372, 20130059 (2014)

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Eq. ❷

$$\left(\sum_{\nu}^{N_n} \frac{1}{2M_\nu}\left(-i\nabla_\nu + A_\nu\right)^2 + \hat{W}_{nn} + \hat{V}_n^{ext} + \in\left(\underline{\underline{R}}\right)\right)\chi\left(\underline{\underline{R}}\right) = E\chi\left(\underline{\underline{R}}\right)$$

Exact PES

where

$$A_\nu\left(\underline{\underline{R}}\right) = -i\int \Phi^*_{\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{r}}\right)\nabla_\nu \Phi_{\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{r}}\right) d\underline{\underline{r}}$$

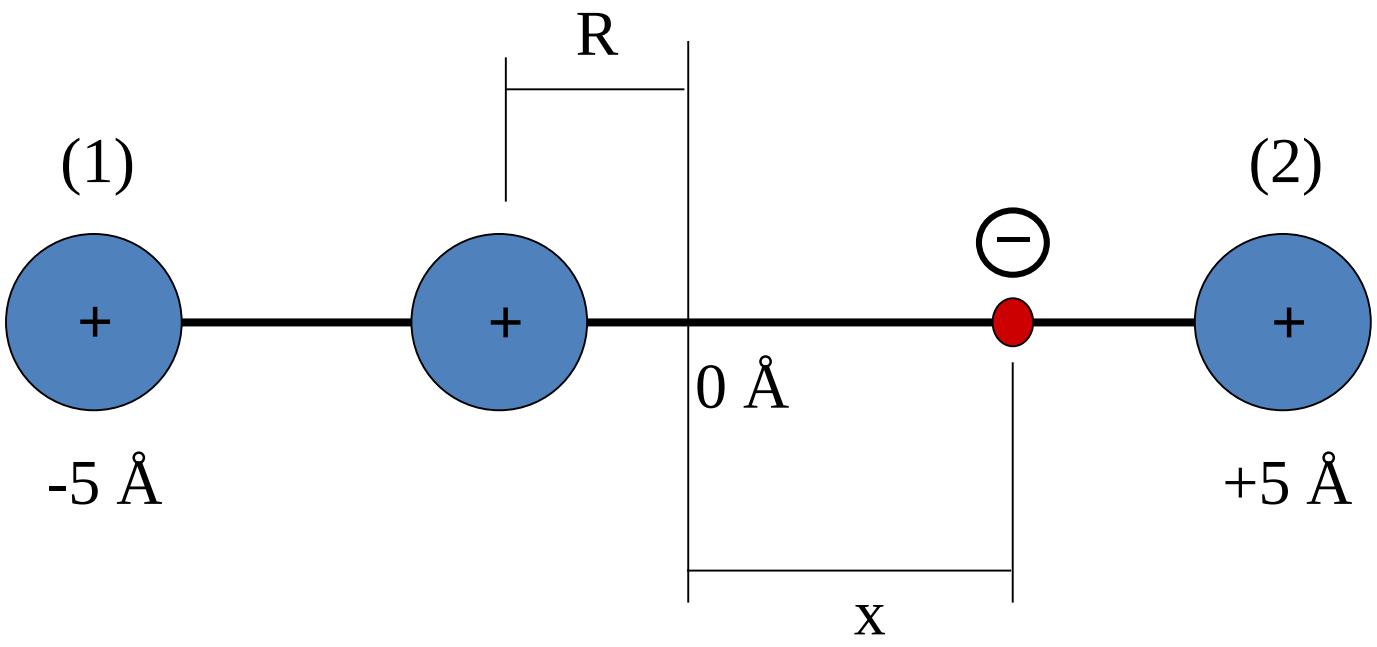
Exact Berry potential

N.I. Gidopoulos, E.K.U. Gross, Phil. Trans. R. Soc. 372, 20130059 (2014)

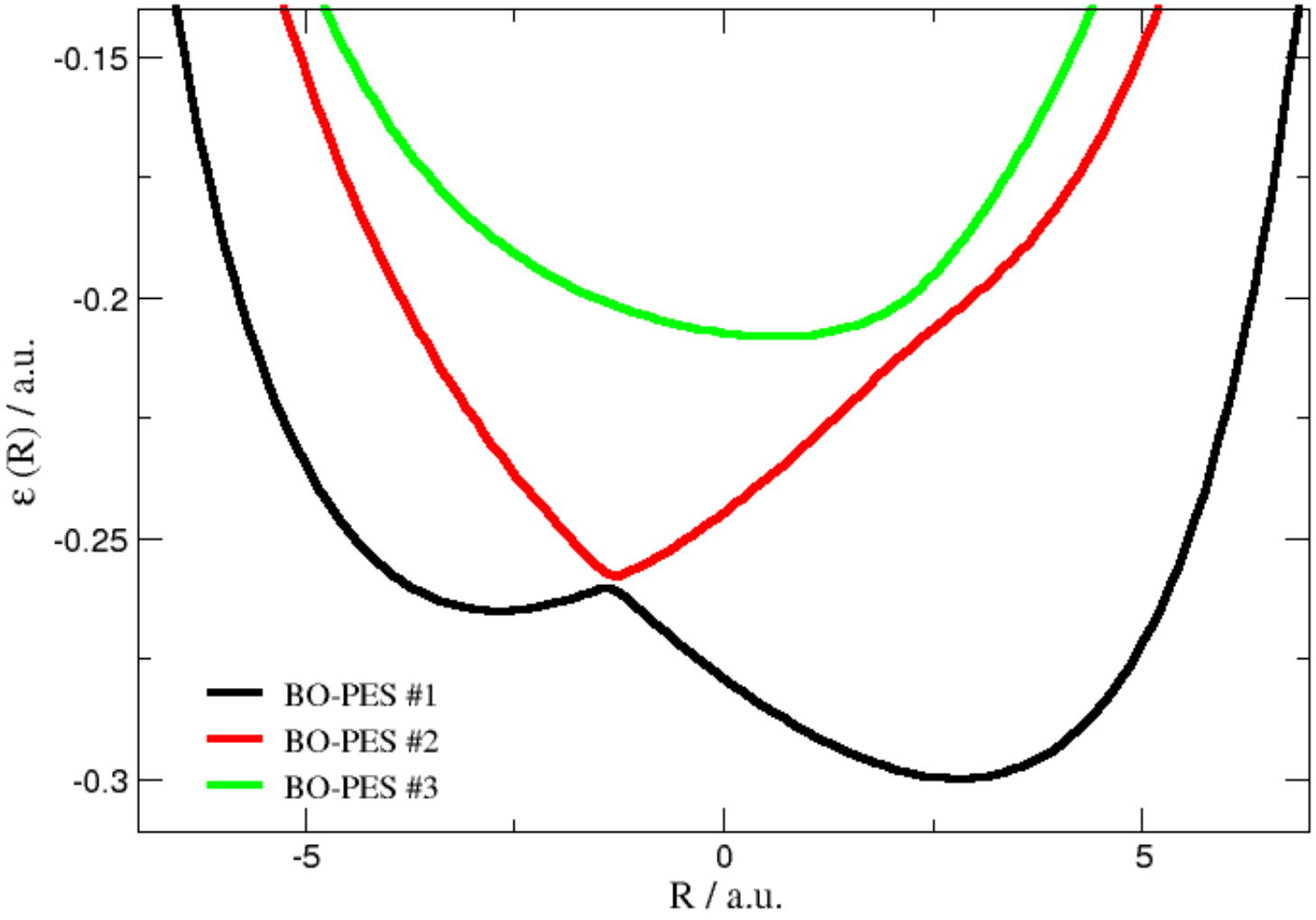
How do the exact PES look like?

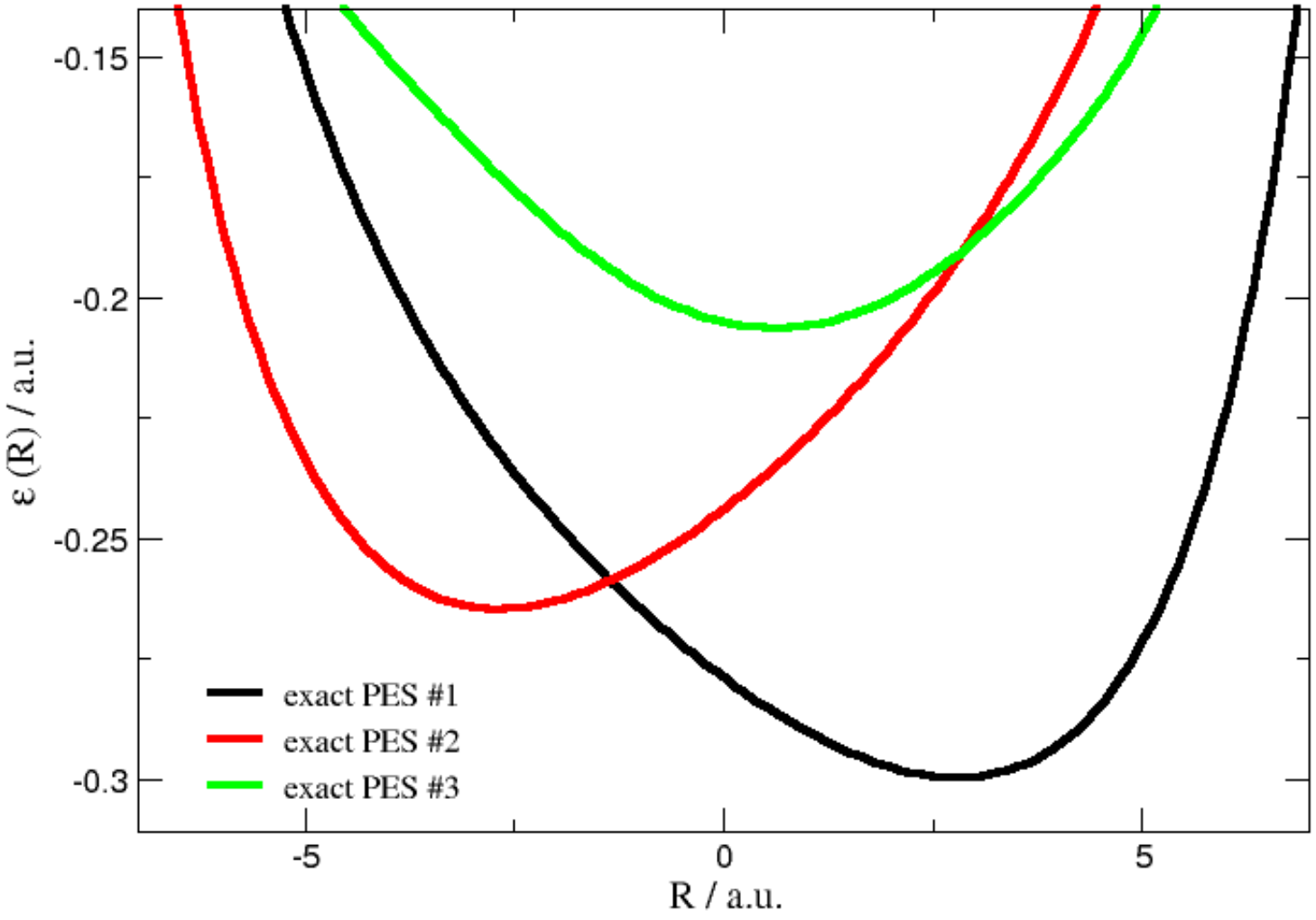
MODEL

S. Shin, H. Metiu, JCP 102, 9285 (1995), JPC 100, 7867 (1996)



Nuclei (1) and (2) are heavy: Their positions are fixed


-0.15
-0.2
-0.25
-0.3
ε (R) / a.u.
-5
0
5
R / a.u.
BO-PES #1
BO-PES #2
BO-PES #3


-0.15
-0.2
-0.25
-0.3
ε (R) / a.u.
-5
0
5
R / a.u.
exact PES #1
exact PES #2
exact PES #3

Exact Berry connection

$$A_\nu\left(\underline{\underline{R}}\right)=\int d\underline{\underline{r}}\;\Phi^*_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)\;\left(-i\nabla_\nu\right)\;\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)$$

Insert: $\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)=\Psi\left(\underline{\underline{r}},\underline{\underline{R}}\right)/\chi\left(\underline{\underline{R}}\right)$

$$\chi\left(\underline{\underline{R}}\right):=e^{i\theta\left(\underline{\underline{R}}\right)}\left|\chi\left(\underline{\underline{R}}\right)\right|$$

$$A_\nu\left(\underline{\underline{R}}\right)=\mathrm{Im}\left\{\int d\underline{\underline{r}}\;\Psi^*\left(\underline{\underline{r}},\underline{\underline{R}}\right)\;\nabla_\nu\Psi\left(\underline{\underline{r}},\underline{\underline{R}}\right)\right\}/\left|\chi\left(\underline{\underline{R}}\right)\right|^2-\nabla_\nu\theta$$

$$\boxed{A_\nu\left(\underline{\underline{R}}\right)=J_\nu\left(\underline{\underline{R}}\right)/\left|\chi\left(\underline{\underline{R}}\right)\right|^2-\nabla_\nu\theta\left(\underline{\underline{R}}\right)}$$

with the exact nuclear current density J_ν

Another way of reading this equation:

$$J_\nu(\underline{\underline{R}}) = \left|\chi(\underline{\underline{R}})\right|^2 \{A_\nu(\underline{\underline{R}}) + \nabla_\nu \theta(\underline{\underline{R}})\}$$

Conclusion: The nuclear Schrödinger equation

$$\left(\sum_\nu^{N_n} \frac{1}{2M_\nu}(-i\nabla_\nu + A_\nu)^2 + \hat{W}_{nn} + \hat{V}_n^{ext} + \in(\underline{\underline{R}})\right)\chi(\underline{\underline{R}}) = E\chi(\underline{\underline{R}})$$

yields both the exact nuclear N-body density and the exact nucler N-body current density

A. Abedi, N.T. Maitra, E.K.U. Gross, JCP 137, 22A530 (2012)

Question: Can the true vector potential be gauged away, i.e. is the true Berry phase zero?

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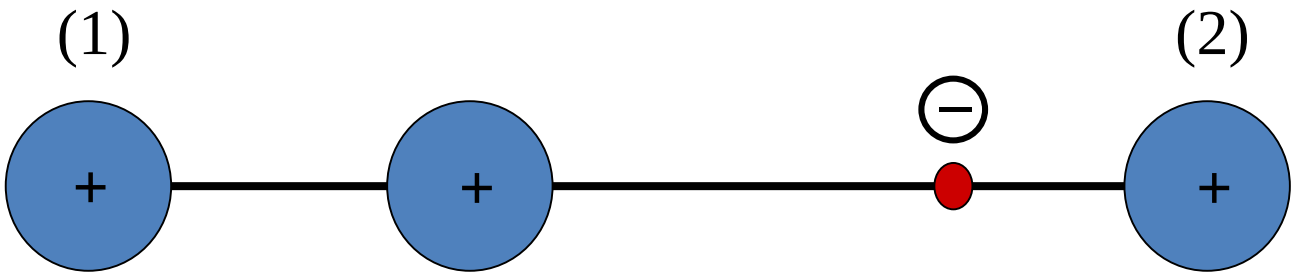
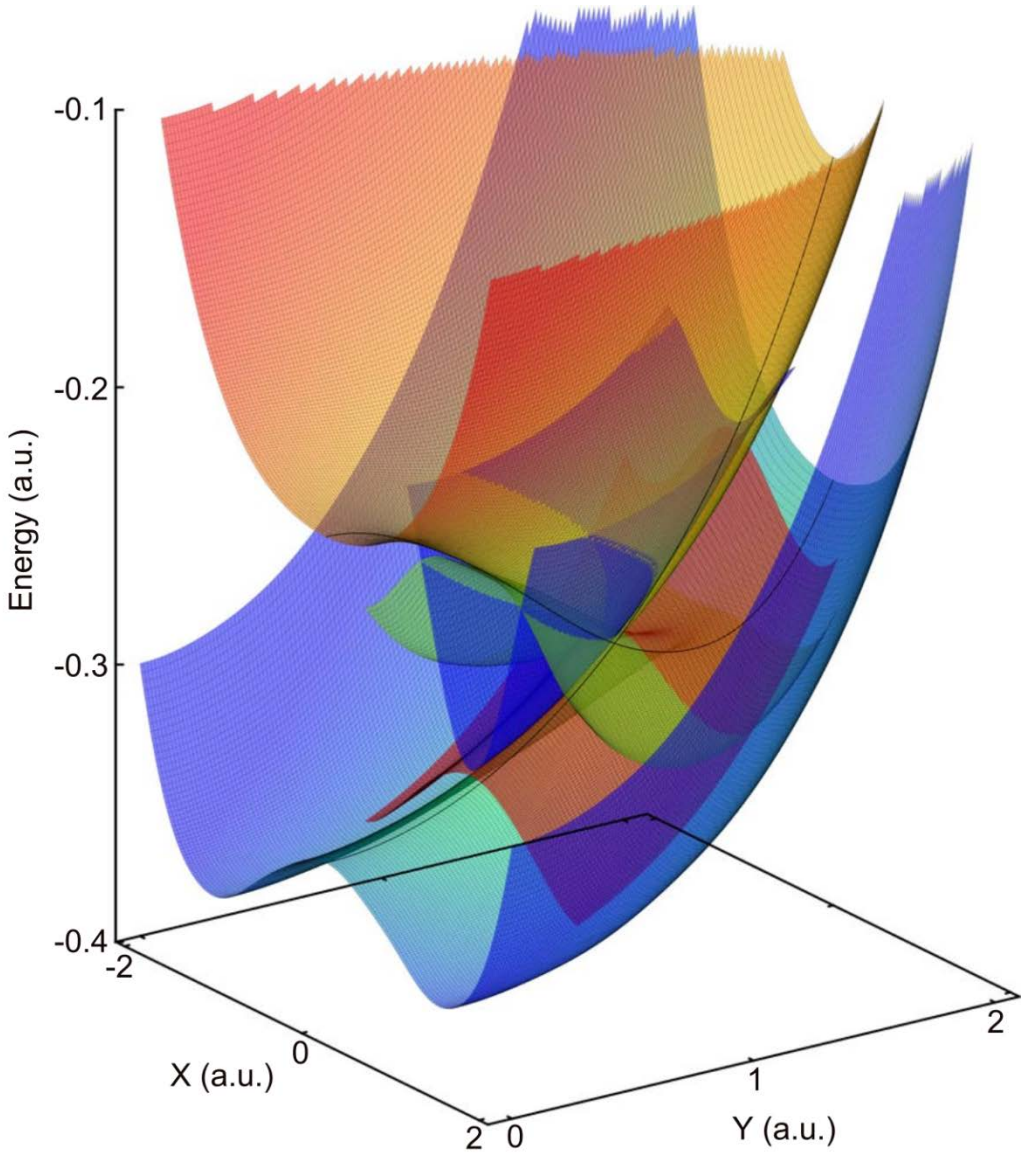
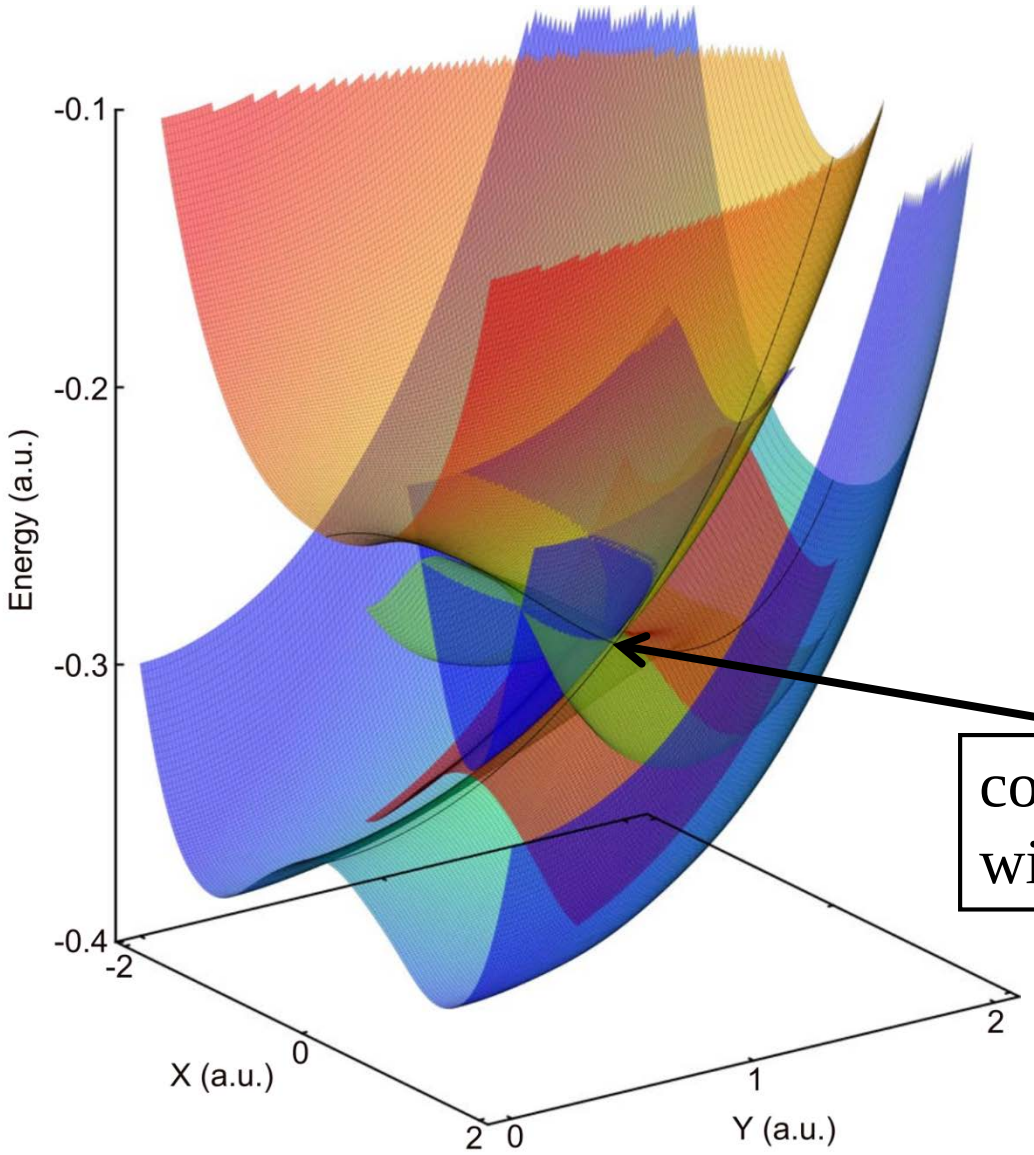
Look at Shin-Metiu model in 2D:



BO-PES of 2D Shin-Metiu model



BO-PES of 2D Shin-Metiu model



conical intersection with Berry phase π

- Non-vanishing Berry phase results from a non-analyticity in the electronic wave function $\Phi^{BO}_{\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{r}}\right)$ as function of R.

- Such non-analyticity is found in BO approximation.

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- Such non-analyticity is found in BO approximation.

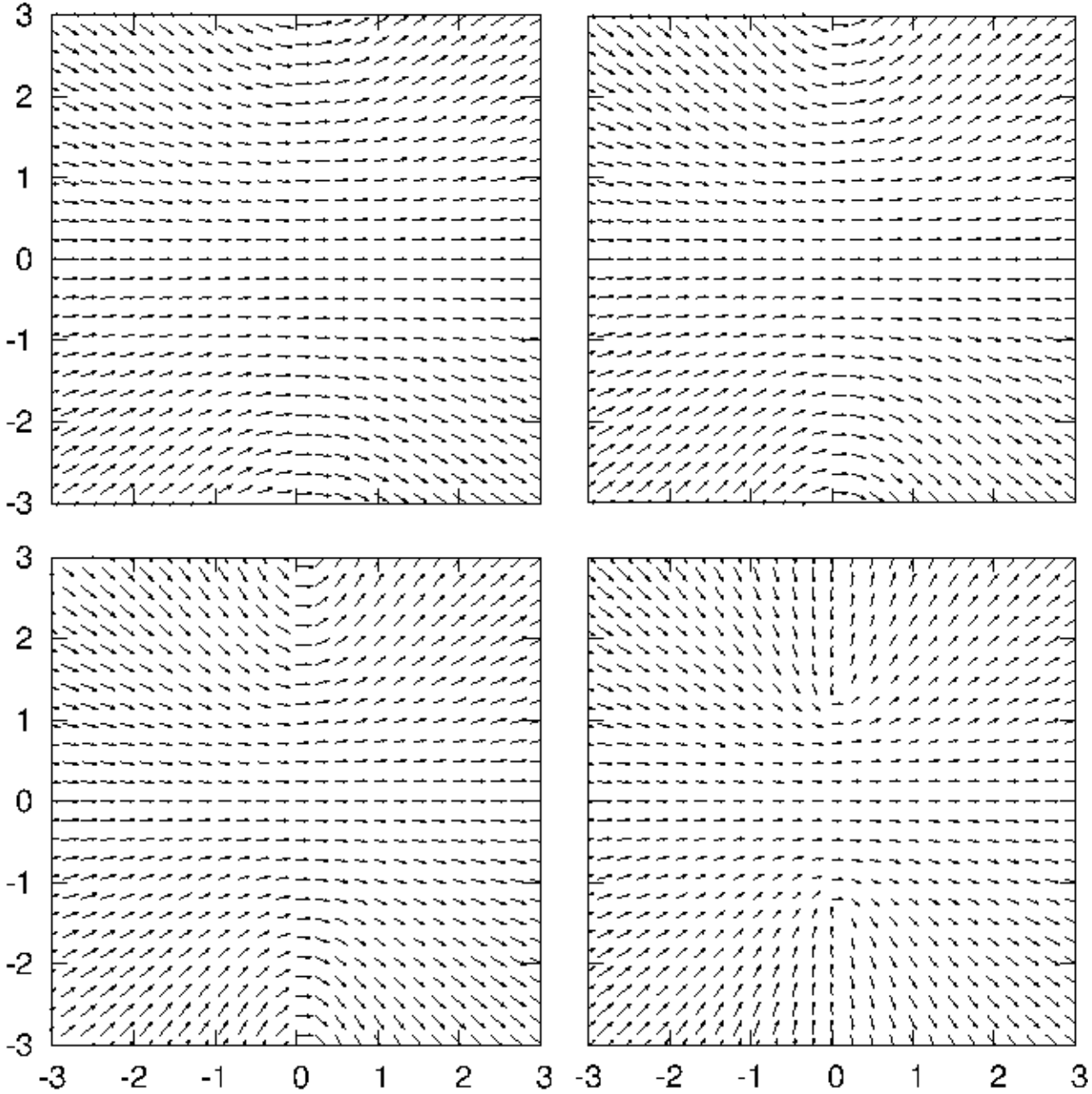
Does the exact electronic wave function show such non-analyticity as well (in 2D Shin-Metiu model)?

Look at $$D(\mathbf{R}) = \int \mathbf{r}\,\Phi_{\mathbf{R}}(\mathbf{r})\,d\mathbf{r}$$

as function of nuclear mass M.

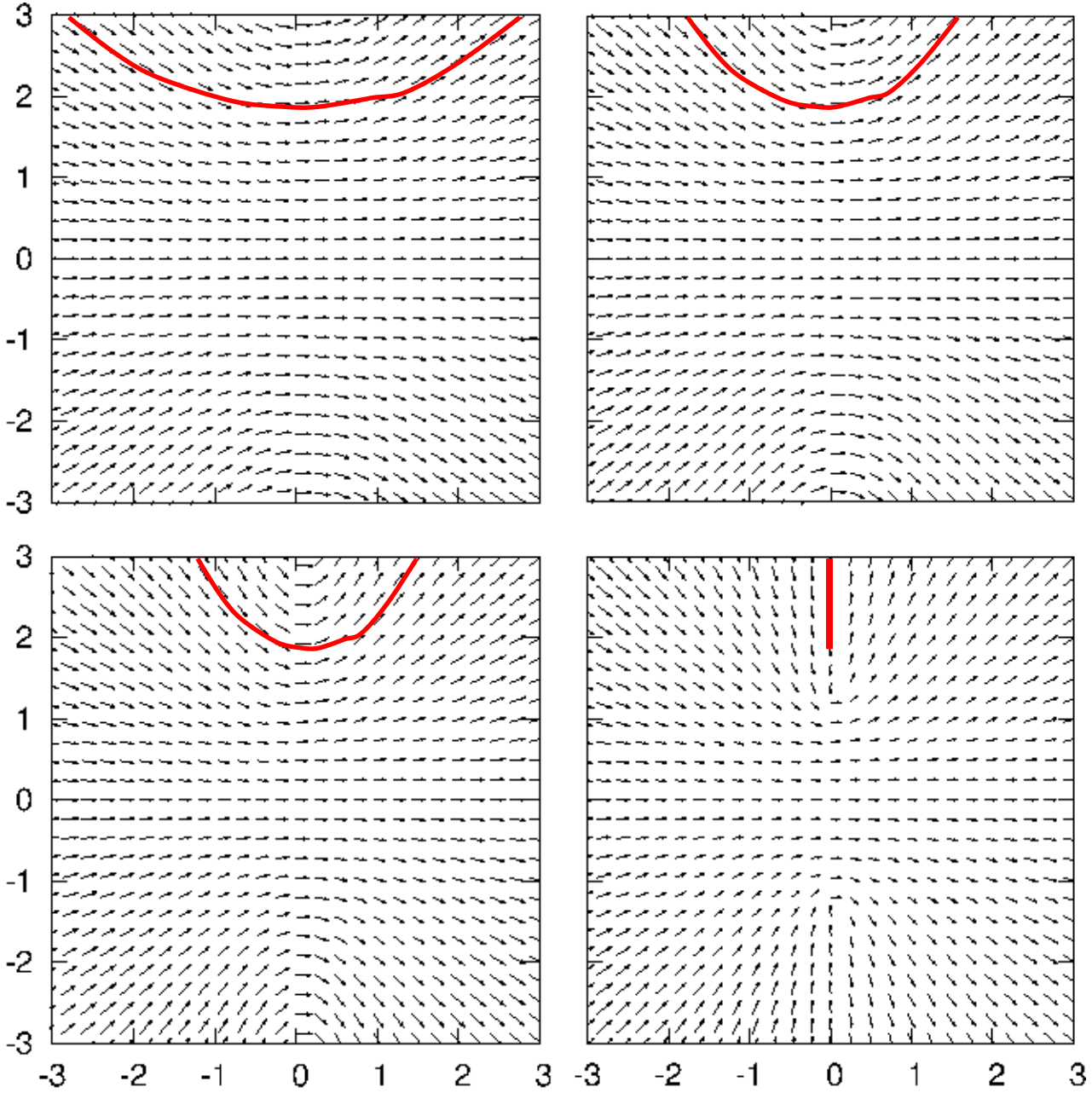
S.K. Min, A. Abedi, K.S. Kim, E.K.U. Gross, PRL 113, 263004 (2014)

D(R)



M = ∞

D(R)



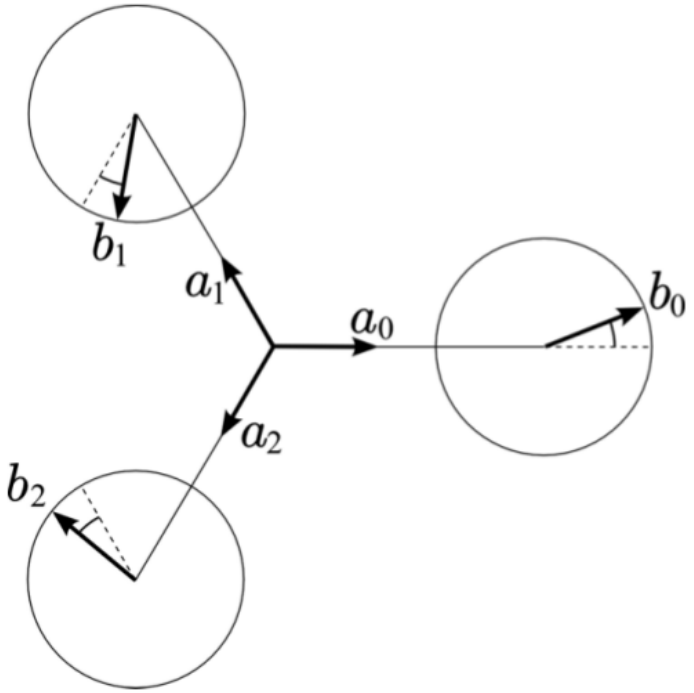
M = ∞

Question: Can one prove in general that the exact molecular Berry phase (at finite nuclear mass) vanishes?

Question: Can one prove in general that the exact molecular Berry phase (at finite nuclear mass) vanishes?

Answer: No! There are cases where a nontrivial Berry phase appears in the exact treatment.

R. Requist, F. Tandetzky, EKU Gross, Phys. Rev. A 93, 042108 (2016).



Time-dependent case

Theorem T-I

The exact solution of

$$i\partial_t \Psi\left(\underline{\underline{r}}, \underline{\underline{\underline{R}}}, t\right) = H\left(\underline{\underline{r}}, \underline{\underline{\underline{R}}}, t\right)\ \Psi\left(\underline{\underline{r}}, \underline{\underline{\underline{R}}}, t\right)$$

can be written in the form

$$\Psi\left(\underline{\underline{r}}, \underline{\underline{\underline{R}}}, t\right) = \Phi_{\underline{\underline{\underline{R}}}}\left(\underline{\underline{r}}, t\right)\ \chi\left(\underline{\underline{\underline{R}}}, t\right)$$

where $\int d\underline{\underline{r}} \left|\Phi_{\underline{\underline{\underline{R}}}}\left(\underline{\underline{r}}, t\right)\right|^2 = 1$ **for any fixed** $\underline{\underline{\underline{R}}}, t$.

A. Abedi, N.T. Maitra, E.K.U.G., PRL 105, 123002 (2010)
JCP 137, 22A530 (2012)

Theorem T-II

$\Phi_{\underline{\underline{R}}}(\underline{\underline{r}},t)$ and $\chi(\underline{\underline{R}},t)$ satisfy the following equations

Eq. ❶

$$\Big(\underbrace{\hat{T}_e+\hat{W}_{ee}+\hat{V}_e^{ext}(\underline{\underline{r}},t)+\hat{V}_{en}(\underline{\underline{r}},\underline{\underline{R}})}_{\hat{H}_{BO}(t)}+\sum_{\nu}^{N_n}\frac{1}{2M_\nu}\left(-i\nabla_\nu-A_\nu(\underline{\underline{R}},t)\right)^2$$
$$+\sum_{\nu}^{N_n}\frac{1}{M_\nu}\left(\frac{-i\nabla_\nu\chi(\underline{\underline{R}},t)}{\chi(\underline{\underline{R}},t)}+A_\nu(\underline{\underline{R}},t)\right)\left(-i\nabla_\nu-A_\nu\right)-\in(\underline{\underline{R}},t)\Big)\Phi_{\underline{\underline{R}}}(\underline{\underline{r}})=i\partial_t\Phi_{\underline{\underline{R}}}(\underline{\underline{r}},t)$$

Eq. ❷

$$\left(\sum_{\nu}^{N_n}\frac{1}{2M_\nu}\left(-i\nabla_\nu+A_\nu(\underline{\underline{R}},t)\right)^2+\hat{W}_{nn}(\underline{\underline{R}})+\hat{V}_n^{ext}(\underline{\underline{R}},t)+\in(\underline{\underline{R}},t)\right)\chi(\underline{\underline{R}},t)=i\partial_t\chi(\underline{\underline{R}},t)$$

A. Abedi, N.T. Maitra, E.K.U.G., PRL 105, 123002 (2010)

JCP 137, 22A530 (2012)

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$$\Big(\underbrace{\hat{T}_e+\hat{W}_{ee}+\hat{V}_e^{ext}(\underline{\underline{r}},t)+\hat{V}_{en}(\underline{\underline{r}},\underline{\underline{R}})}_{\hat{H}_{BO}(t)}+\sum_\nu^{N_n}\frac{1}{2M_\nu}\left(-i\nabla_\nu-A_\nu(\underline{\underline{R}},t)\right)^2$$
$$+\sum_\nu^{N_n}\frac{1}{M_\nu}\left(\frac{-i\nabla_\nu\chi(\underline{\underline{R}},t)}{\chi(\underline{\underline{R}},t)}+A_\nu(\underline{\underline{R}},t)\right)\left(-i\nabla_\nu-A_\nu\right)-\epsilon(\underline{\underline{R}},t)\Big)\Phi_{\underline{\underline{R}}}(\underline{\underline{r}})=i\partial_t\Phi_{\underline{\underline{R}}}(\underline{\underline{r}},t)$$

Exact Berry potential

Exact TDPES

Eq. ❷

$$\left(\sum_\nu^{N_n}\frac{1}{2M_\nu}\left(-i\nabla_\nu+A_\nu(\underline{\underline{R}},t)\right)^2+\hat{W}_{nn}(\underline{\underline{R}})+\hat{V}_n^{ext}(\underline{\underline{R}},t)+\epsilon(\underline{\underline{R}},t)\right)\chi(\underline{\underline{R}},t)=i\partial_t\chi(\underline{\underline{R}},t)$$

A. Abedi, N.T. Maitra, E.K.U.G., PRL 105, 123002 (2010)

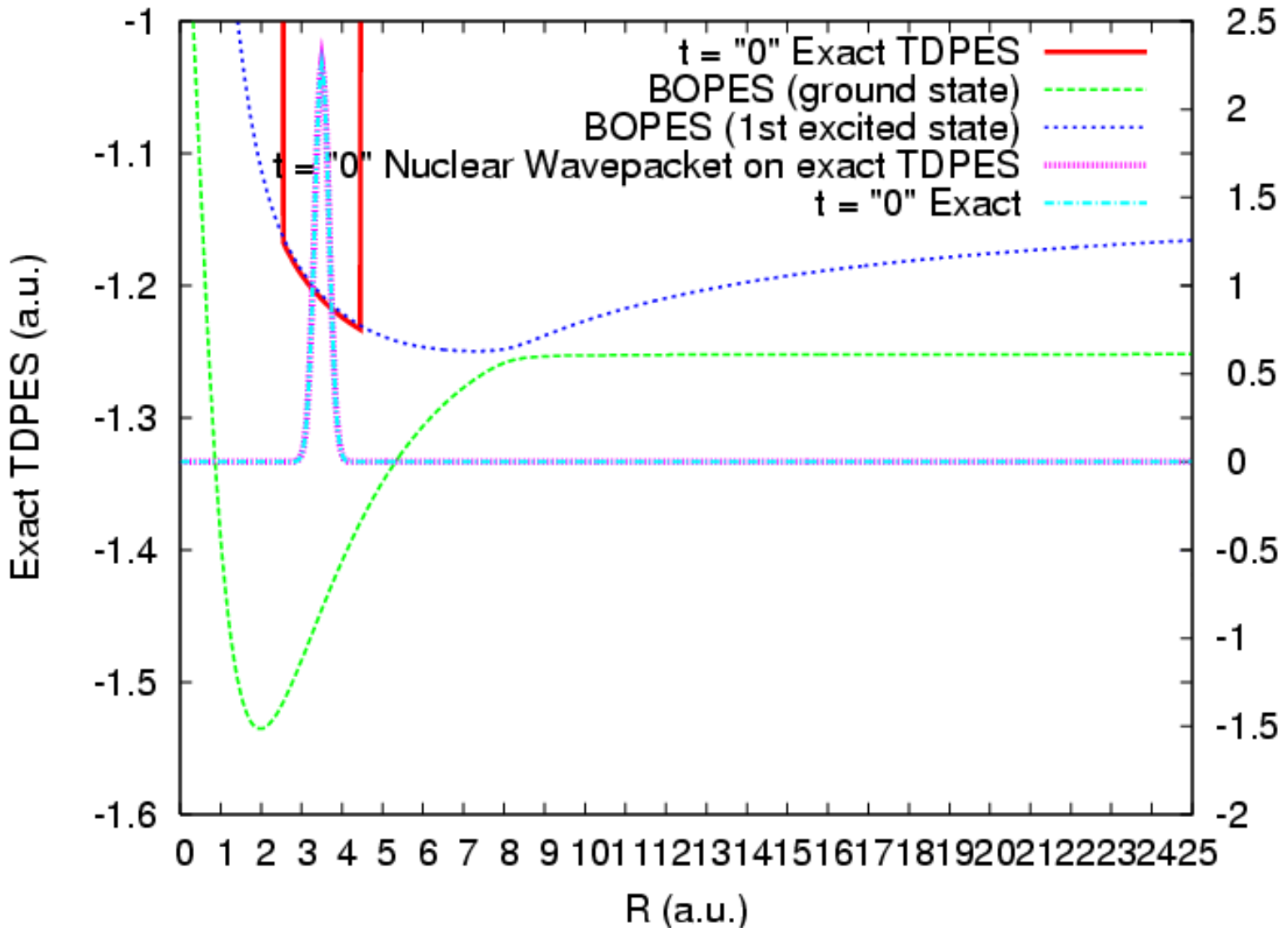
JCP 137, 22A530 (2012)

How does the exact time-dependent PES look like?

Example: Nuclear wave packet going through an avoided crossing (Zewail experiment)

A. Abedi, F. Agostini, Y. Suzuki, E.K.U.Gross,
PRL 110, 263001 (2013)

F. Agostini, A. Abedi, Y. Suzuki, E.K.U. Gross,
Mol. Phys. 111, 3625 (2013)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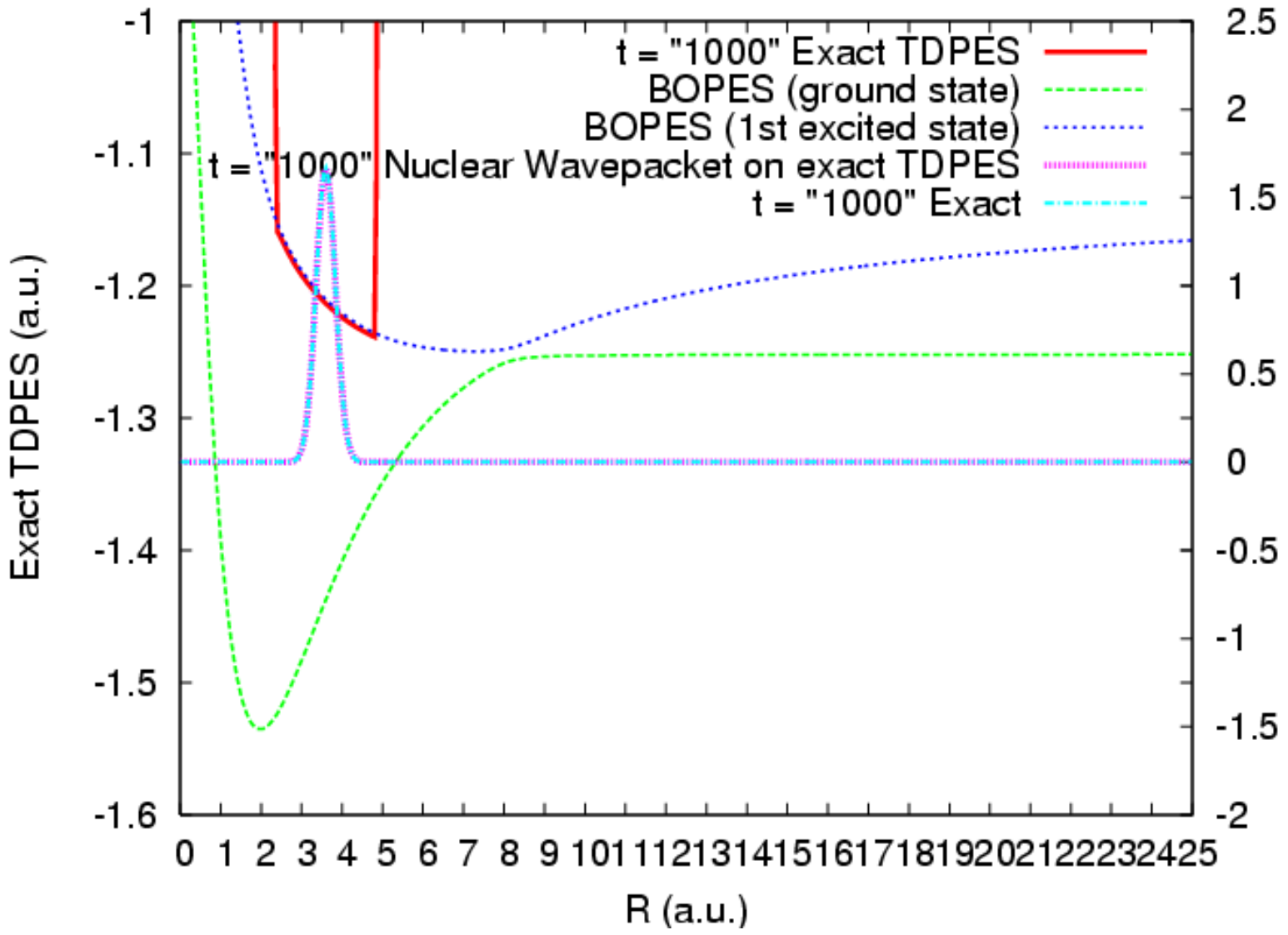
BOPES (ground state)
BOPES (1st excited state)
t = "0" Nuclear Wavepacket on exact TDPES
t = "0" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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BOPES (ground state)
BOPES (1st excited state)
t = "1000" Nuclear Wavepacket on exact TDPES
t = "1000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
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0.5
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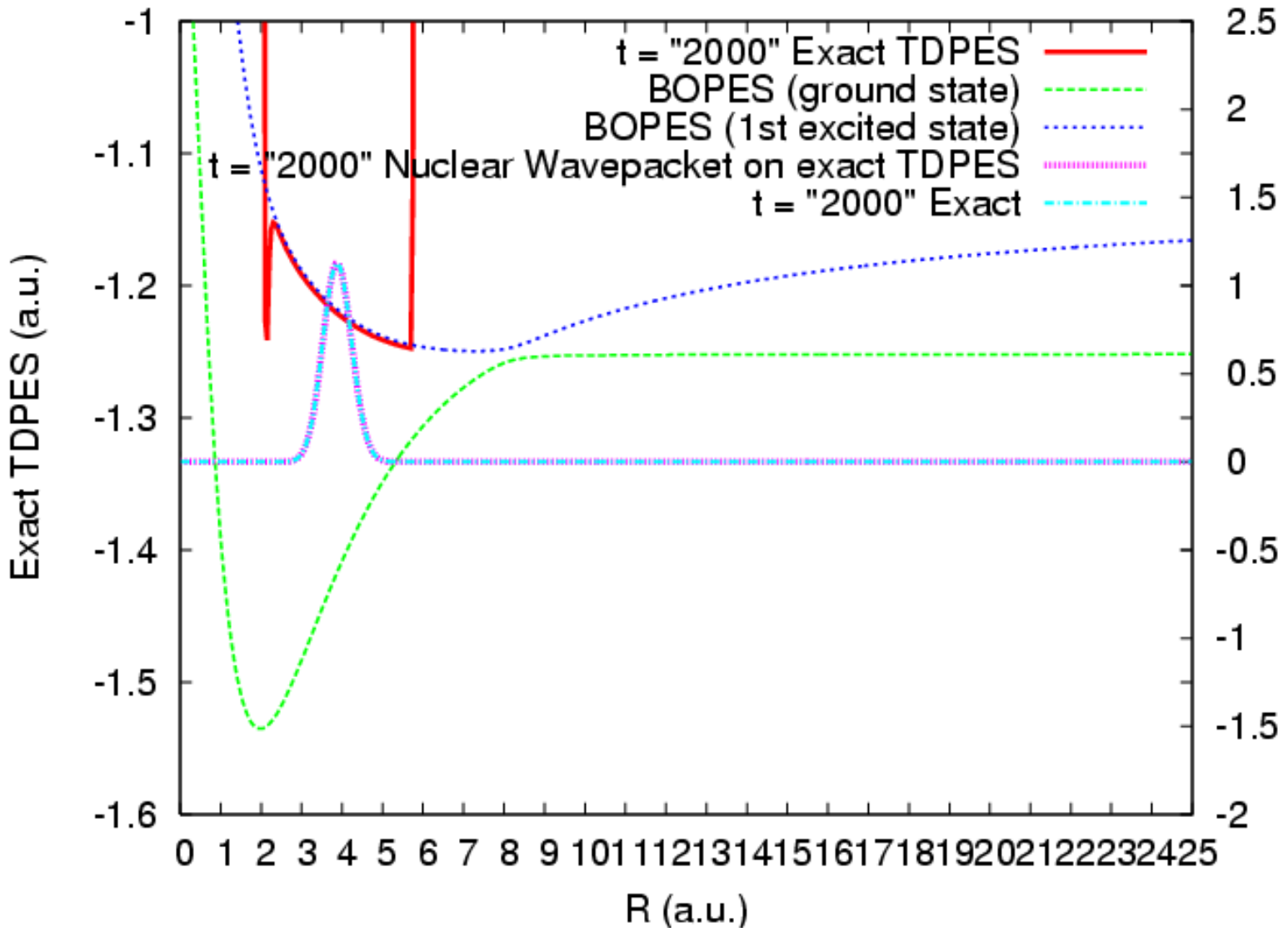
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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BOPES (ground state)
BOPES (1st excited state)
t = "2000" Nuclear Wavepacket on exact TDPES
t = "2000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
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-1
-1.5
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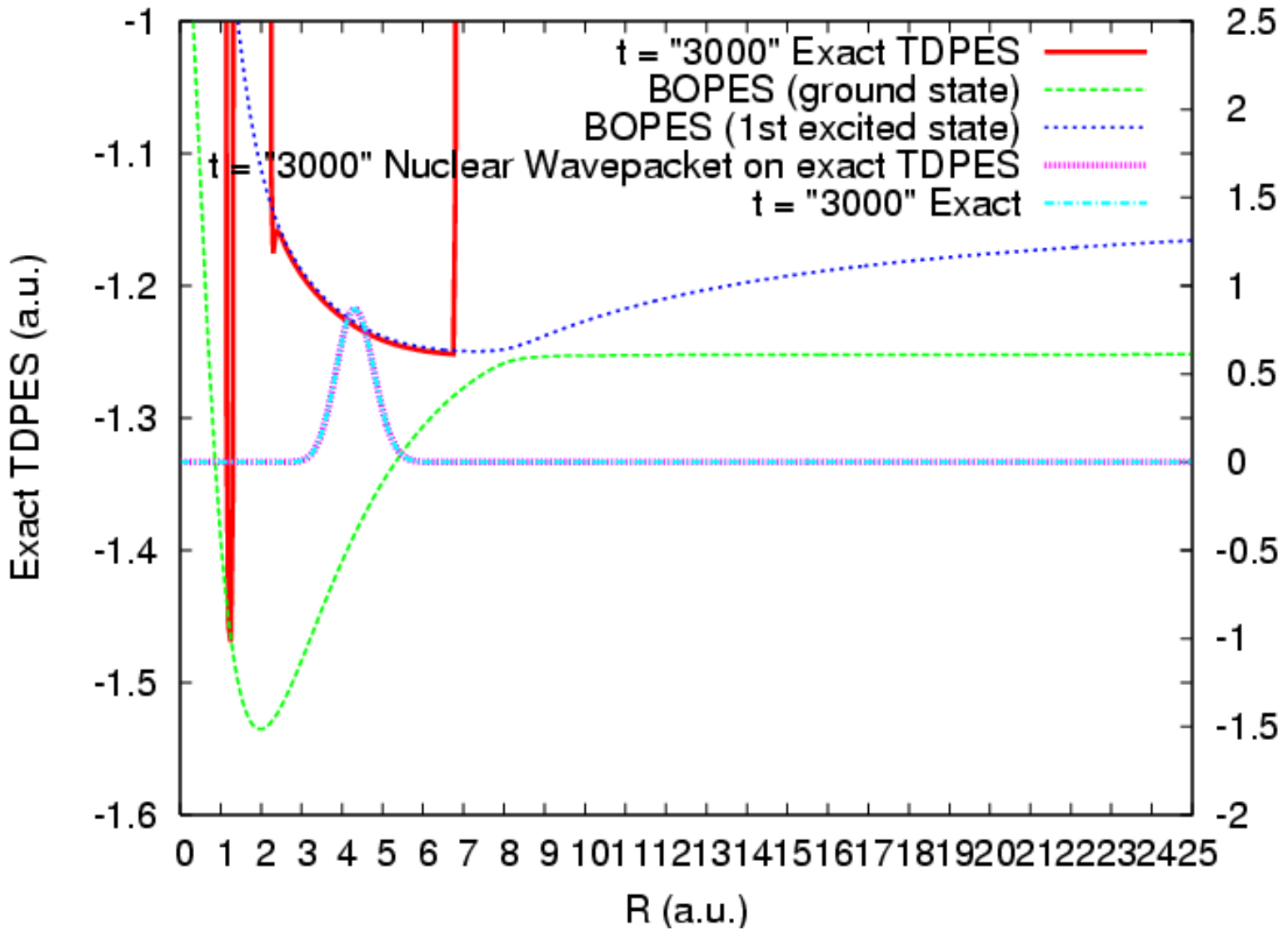
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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BOPES (ground state)
BOPES (1st excited state)
t = "3000" Nuclear Wavepacket on exact TDPES
t = "3000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
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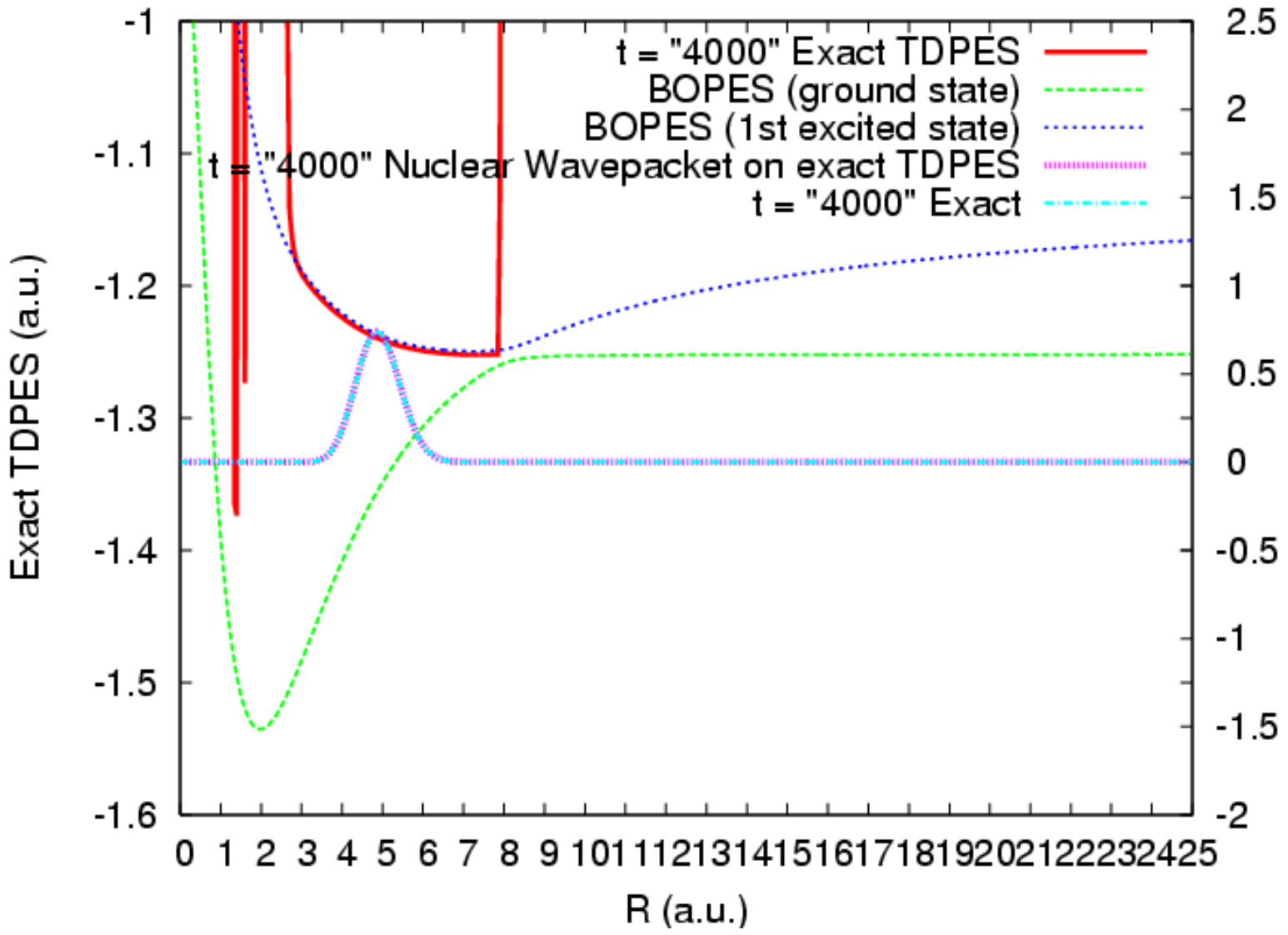
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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BOPES (ground state)
BOPES (1st excited state)
t = "4000" Nuclear Wavepacket on exact TDPES
t = "4000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
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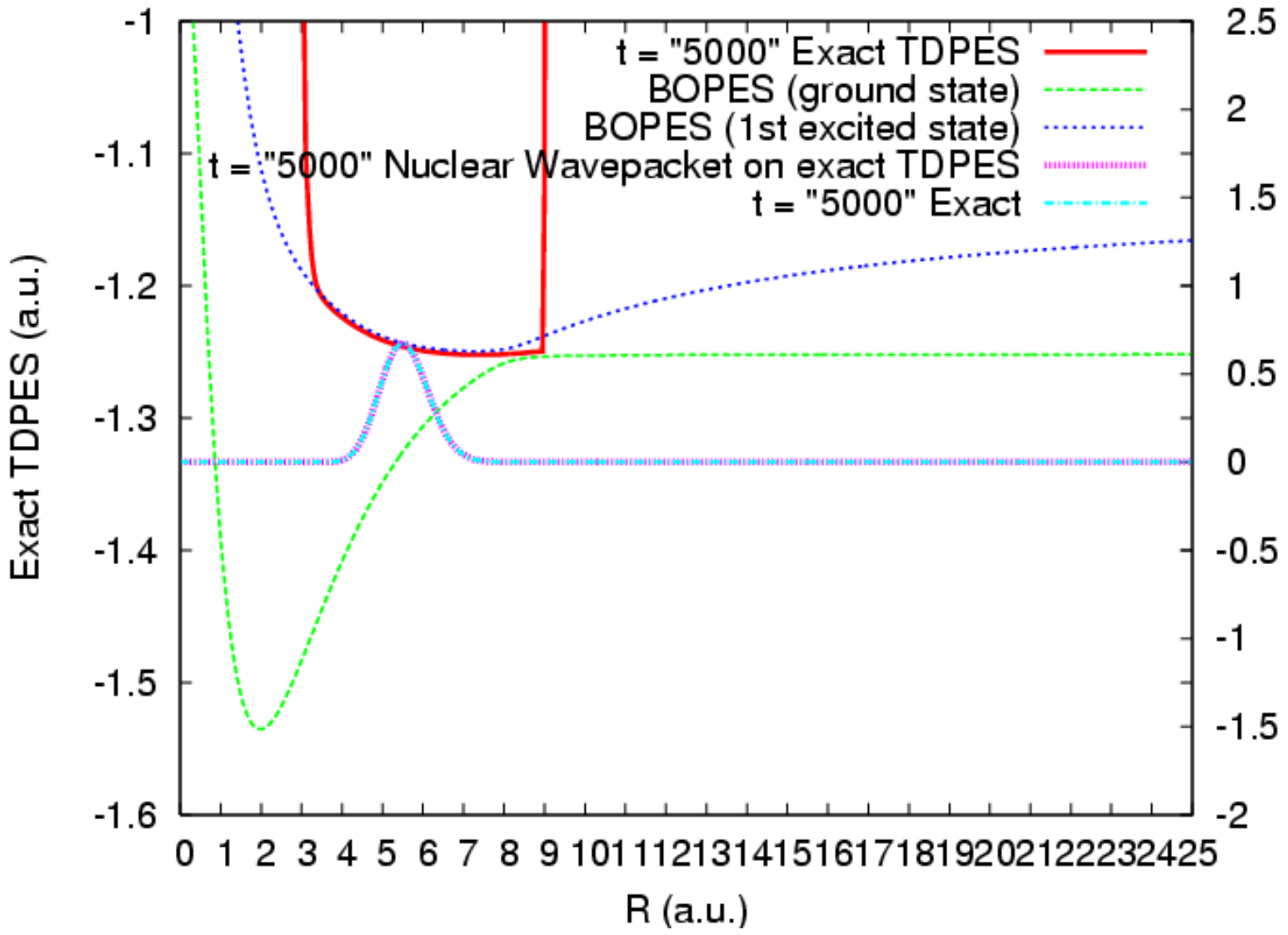
t = "5000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "5000" Nuclear Wavepacket on exact TDPES
t = "5000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
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-1.2
-1.3
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-1.5
-1.6
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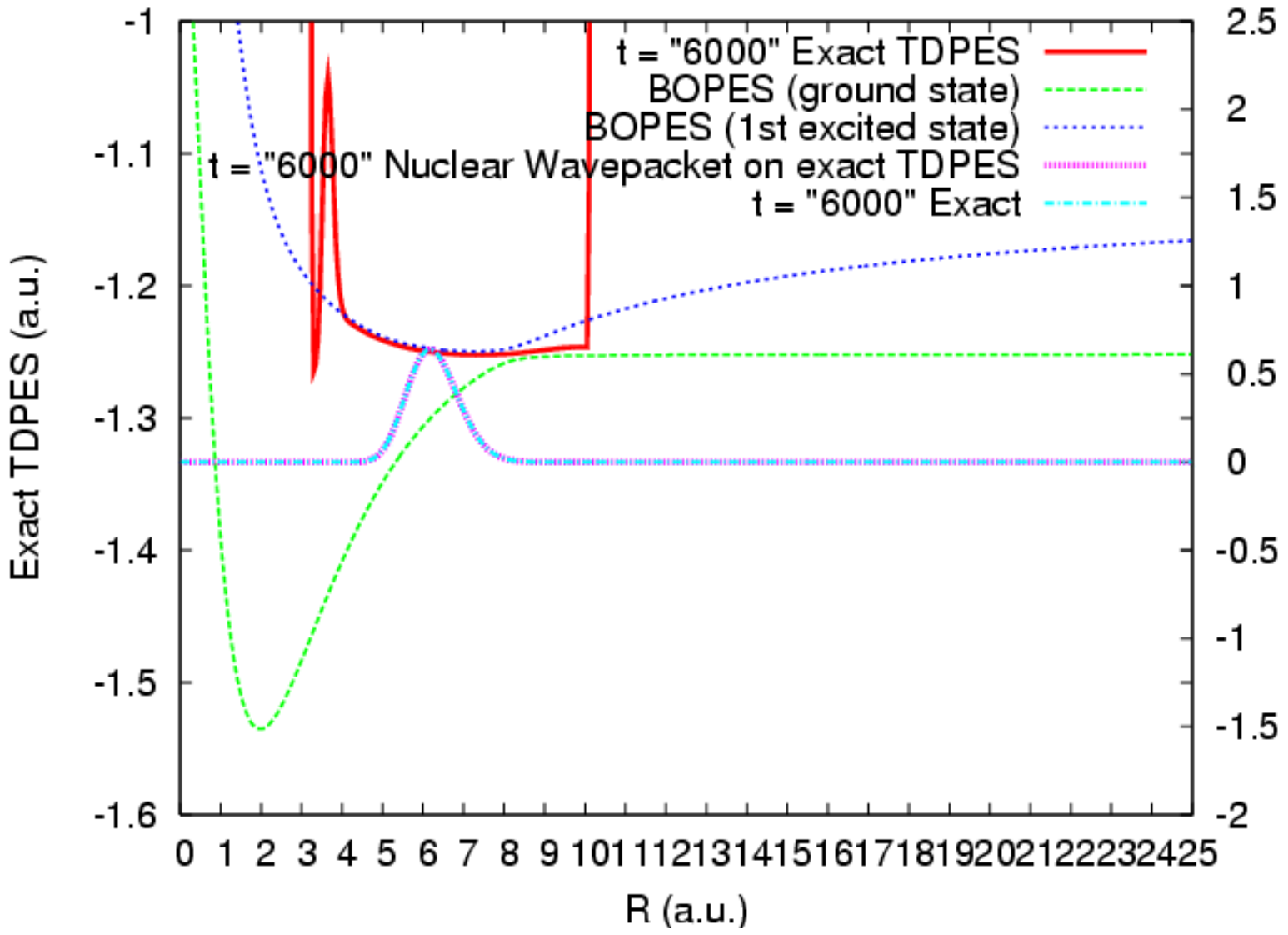
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BOPES (ground state)
BOPES (1st excited state)
t = "6000" Nuclear Wavepacket on exact TDPES
t = "6000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
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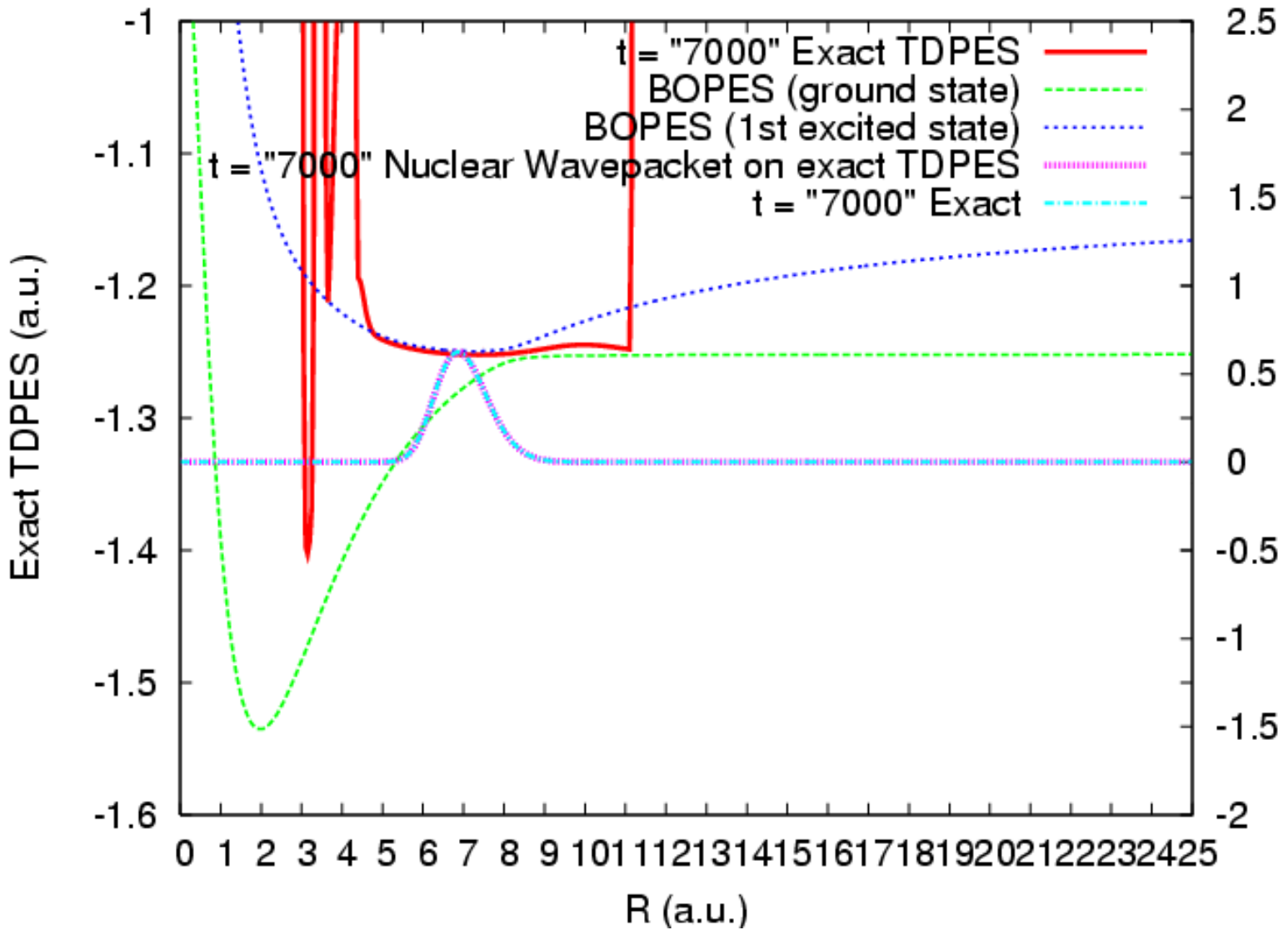
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BOPES (ground state)
BOPES (1st excited state)
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t = "7000" Exact
Exact TDPES (a.u.)
R (a.u.)
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-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
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1.5
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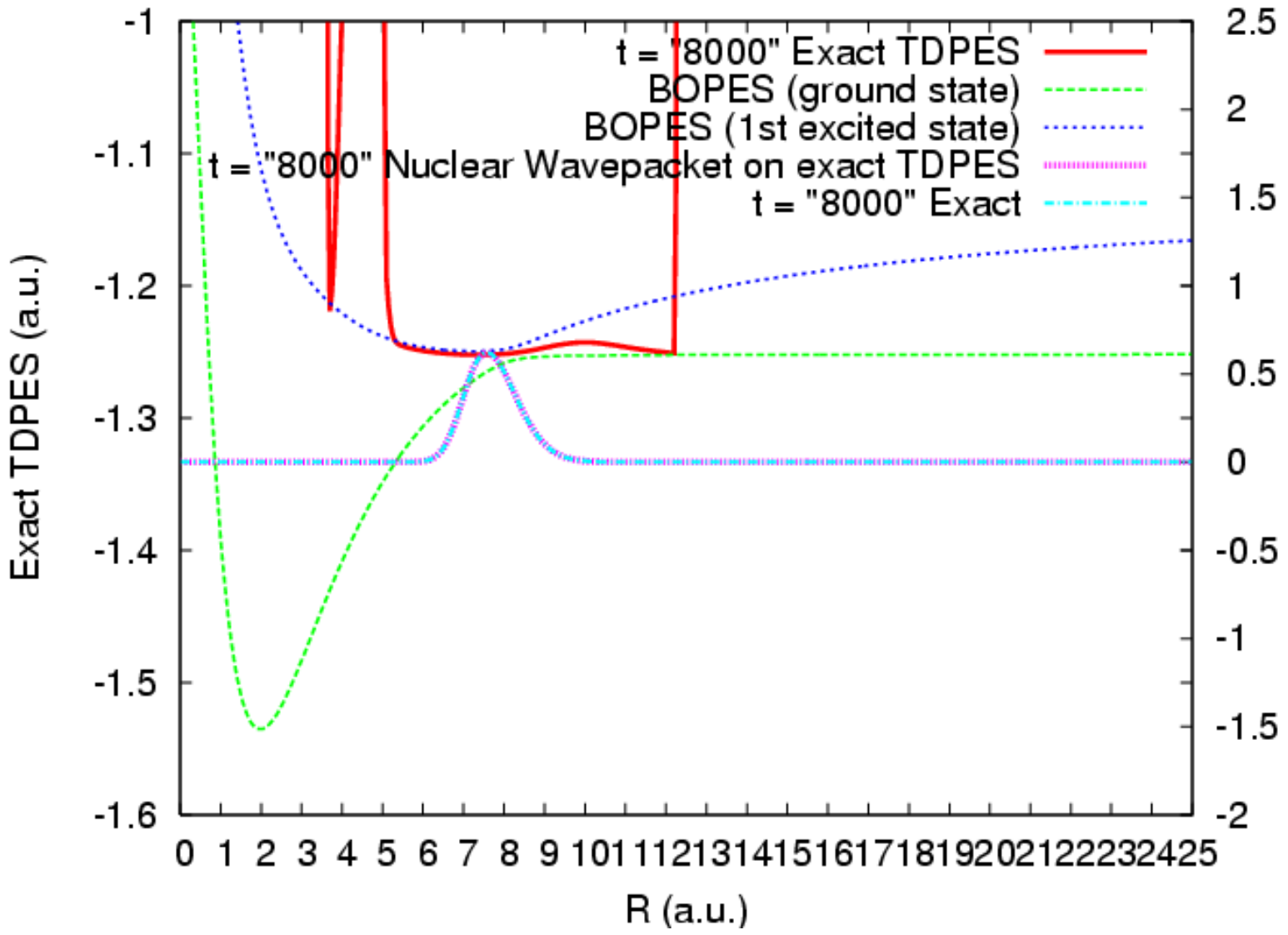
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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R (a.u.)
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-1.2
-1.3
-1.4
-1.5
-1.6
2.5
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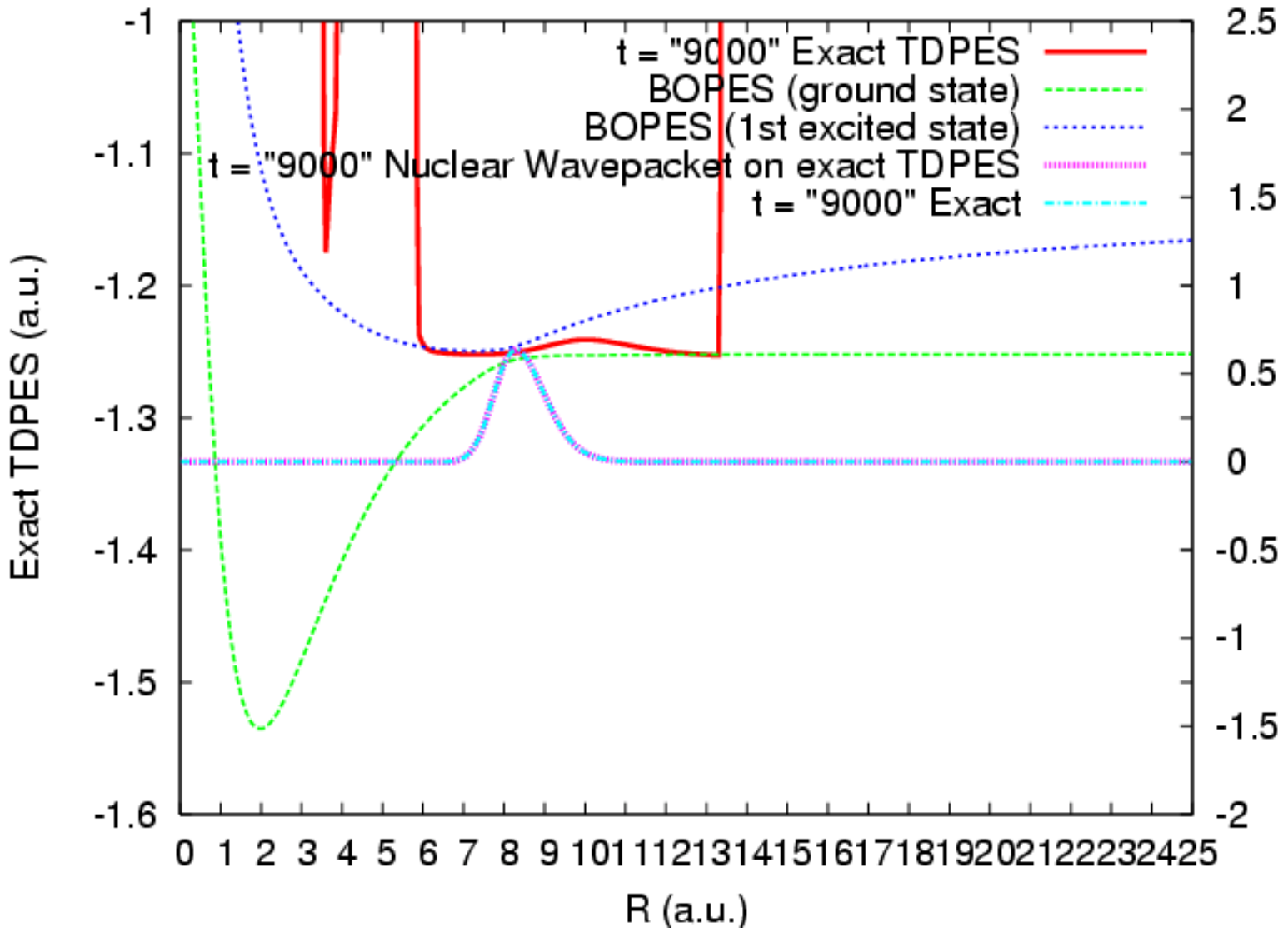
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BOPES (1st excited state)
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t = "9000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
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-1.2
-1.3
-1.4
-1.5
-1.6
2.5
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1.5
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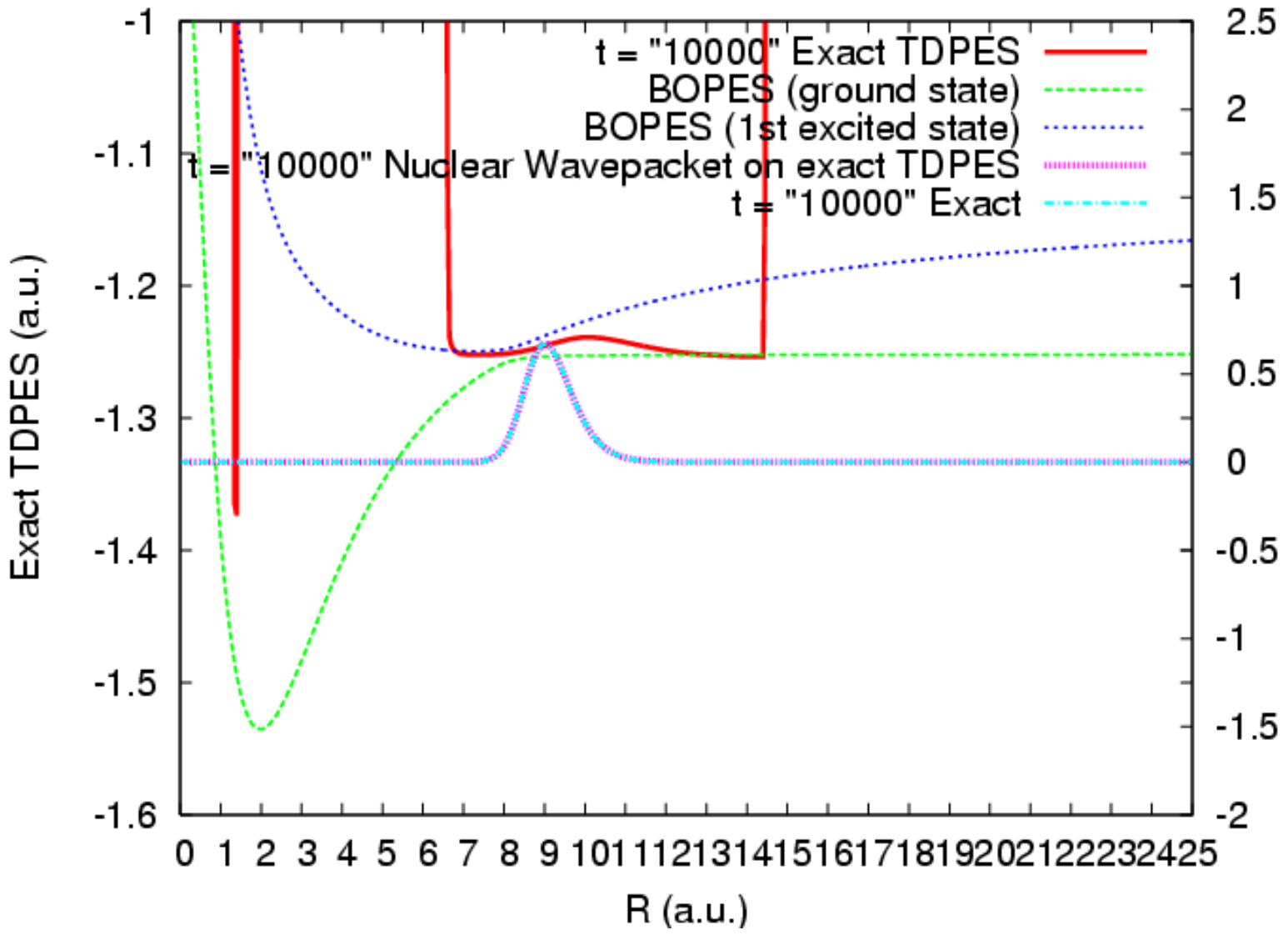
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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BOPES (ground state)
BOPES (1st excited state)
t = "10000" Nuclear Wavepacket on exact TDPES
t = "10000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
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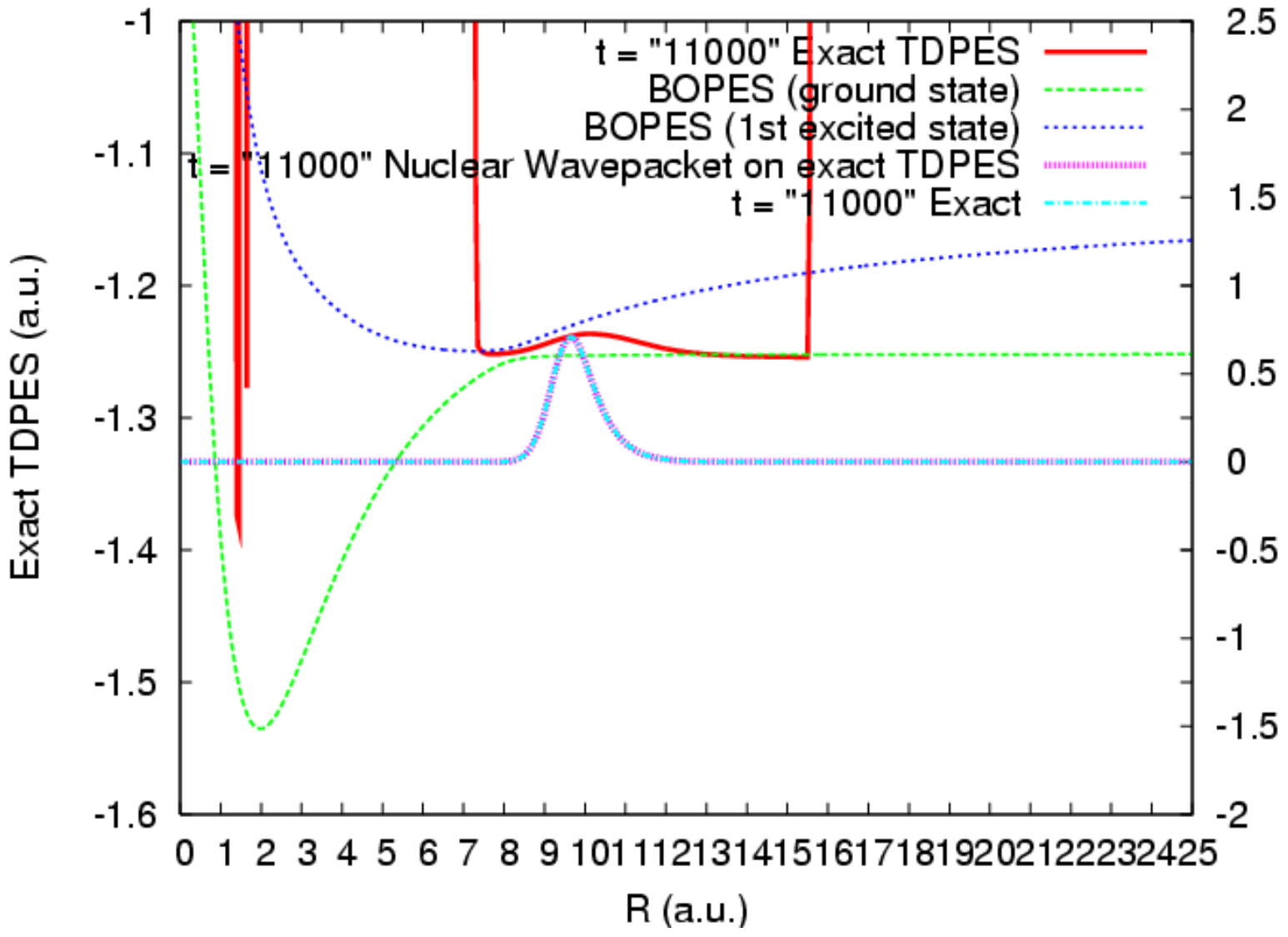
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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BOPES (1st excited state)
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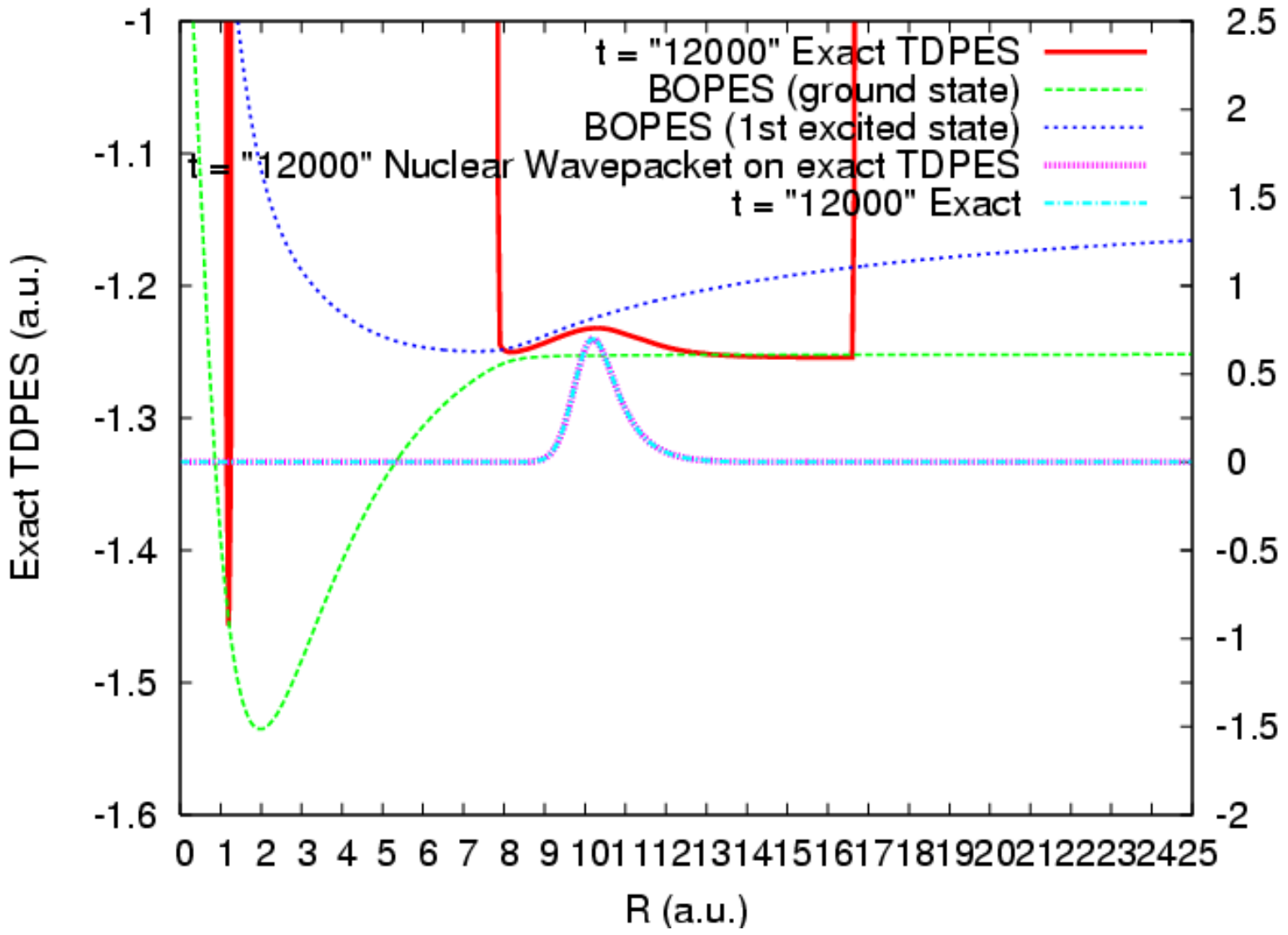
t = "11000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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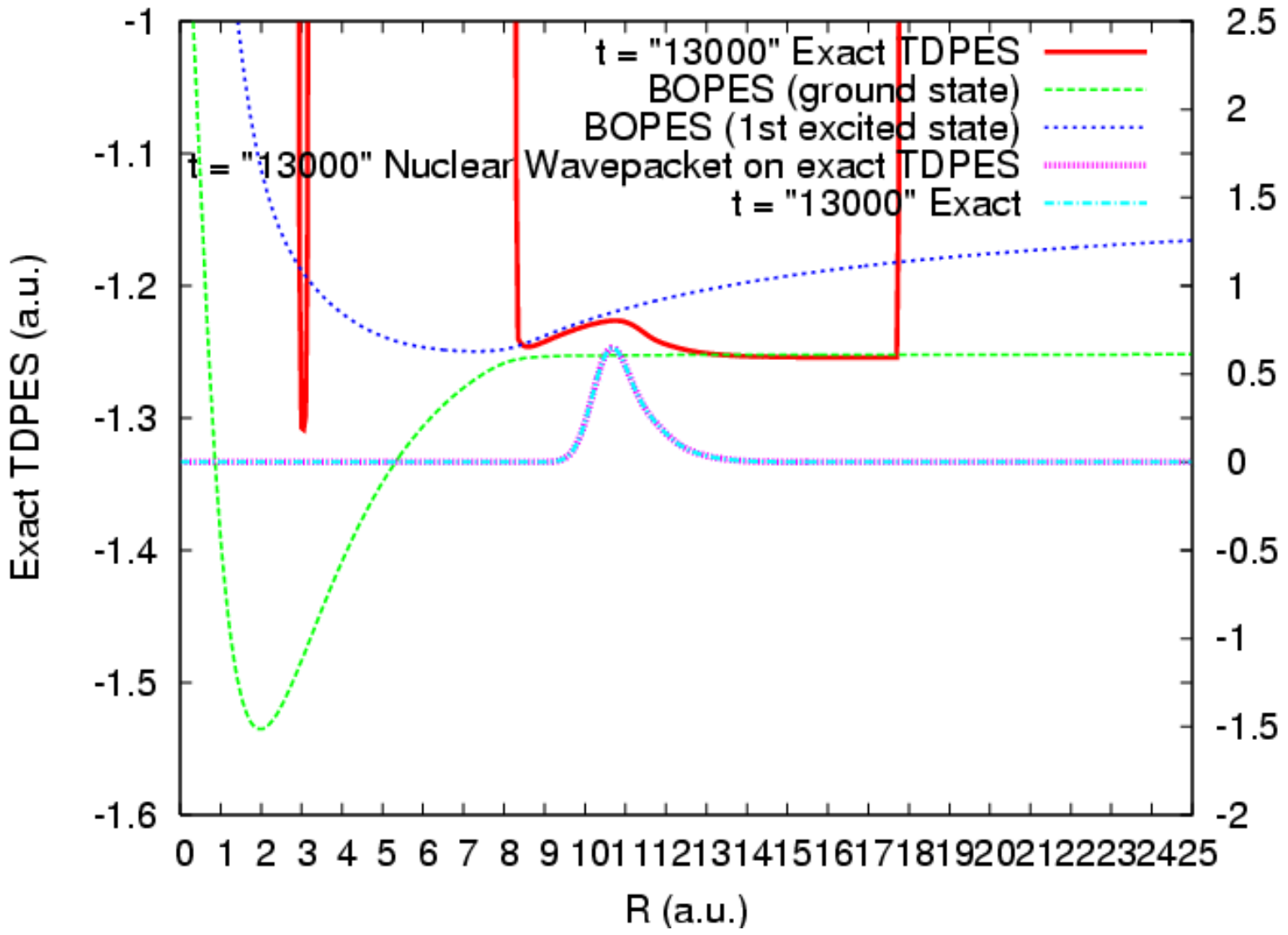
BOPES (ground state)
BOPES (1st excited state)
t = "12000" Nuclear Wavepacket on exact TDPES
t = "12000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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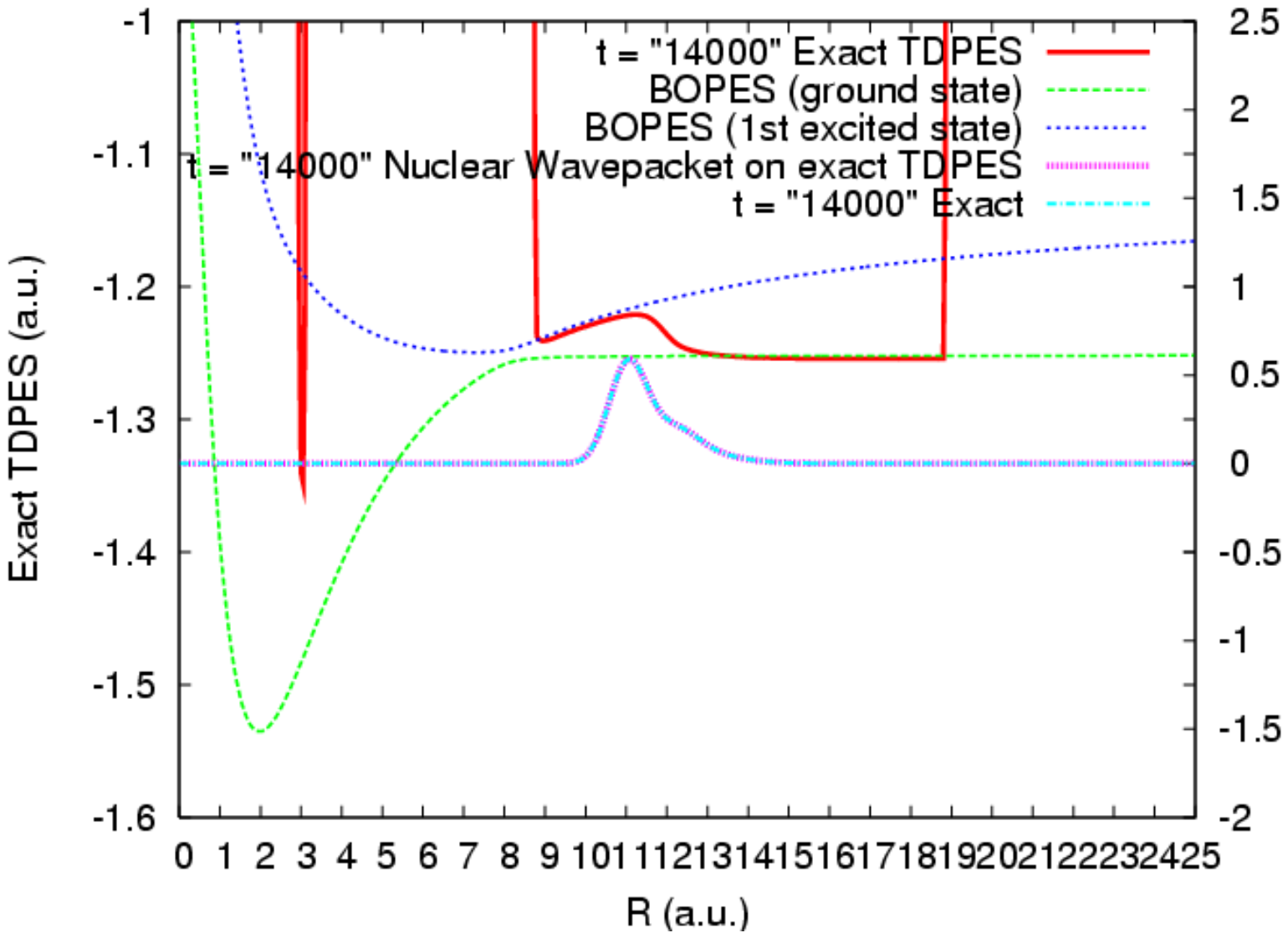
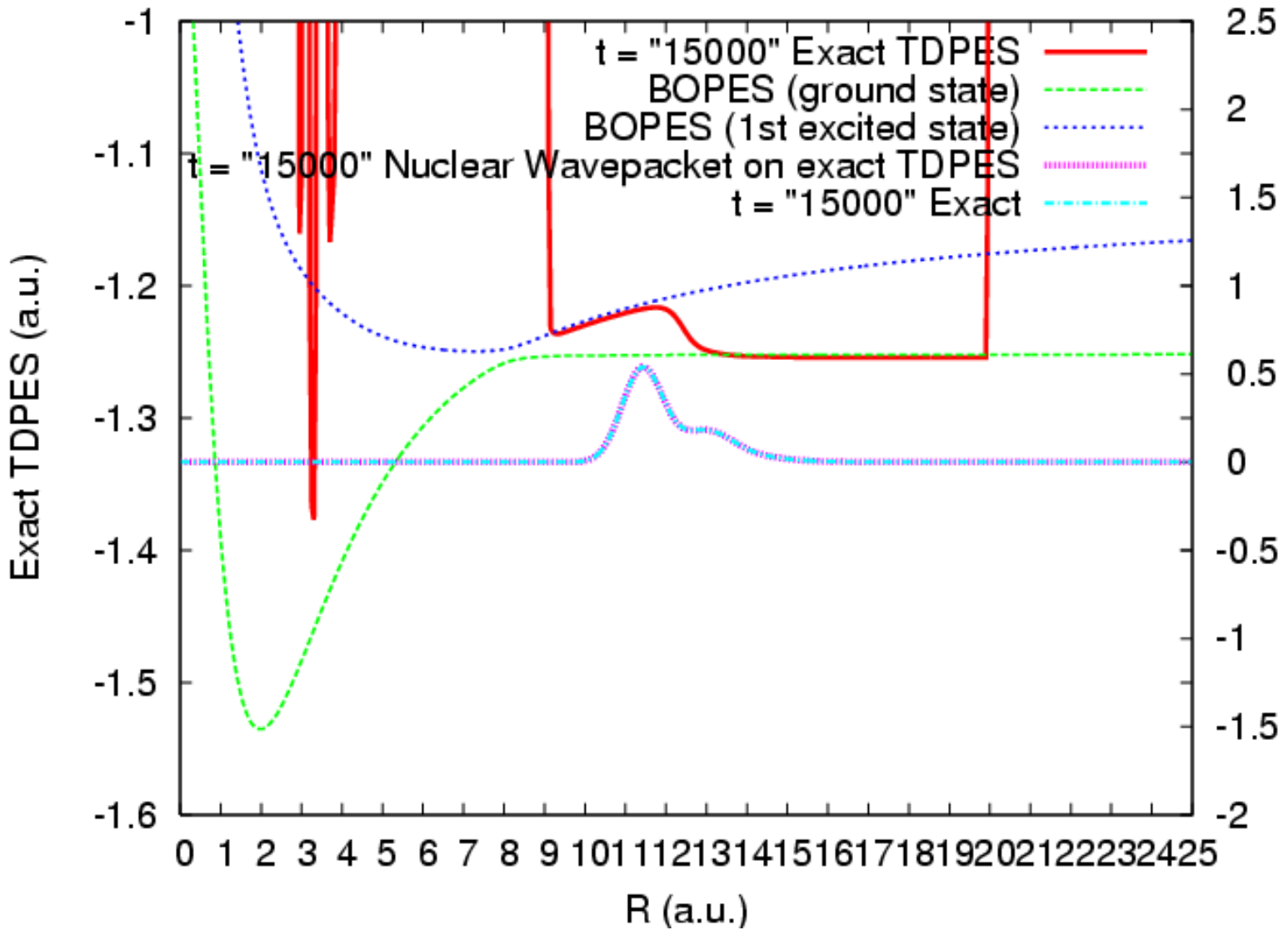
BOPES (ground state)
BOPES (1st excited state)
t = "13000" Nuclear Wavepacket on exact TDPES
t = "13000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


t = "14000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "14000" Nuclear Wavepacket on exact TDPES
t = "14000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25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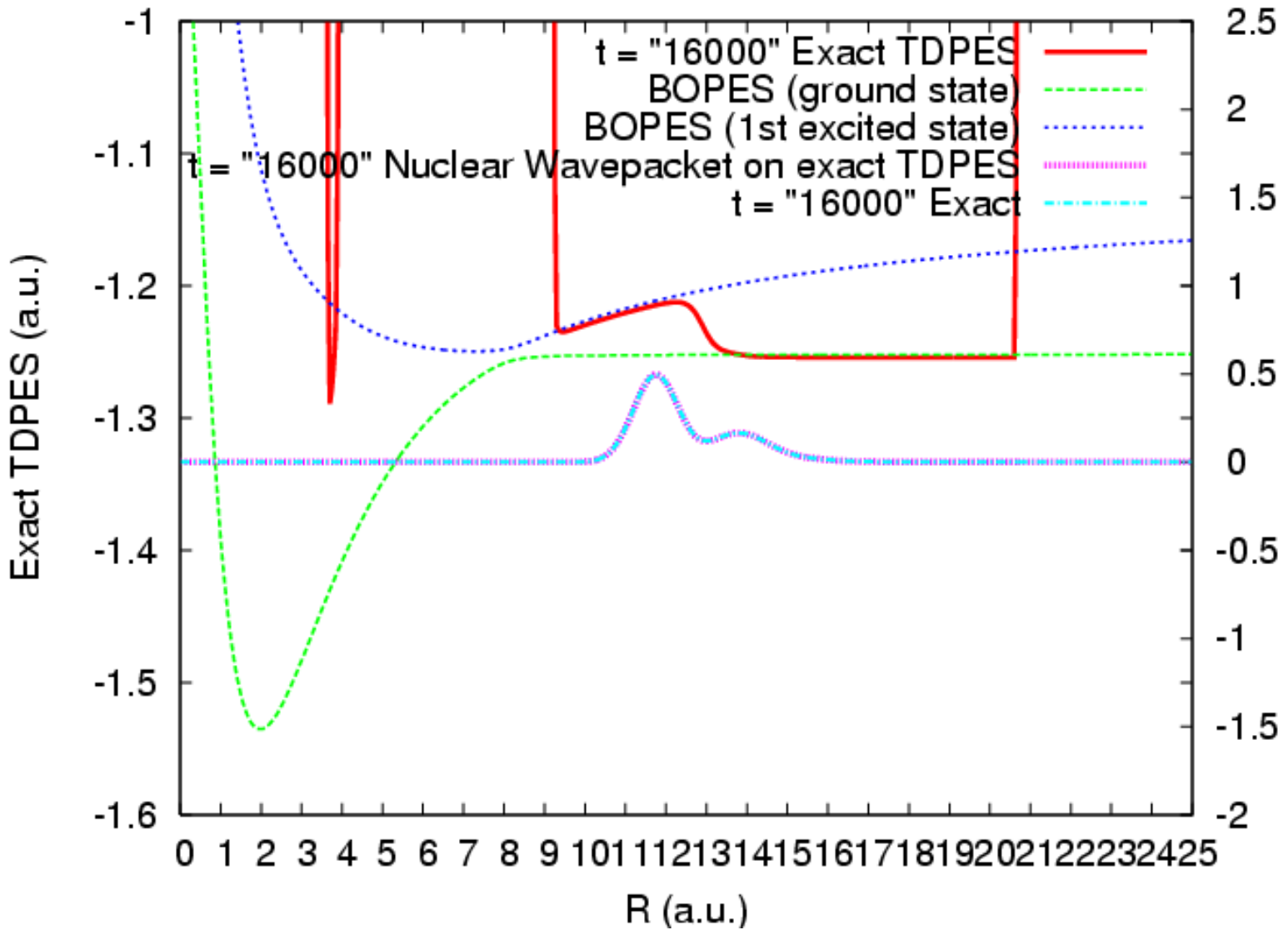
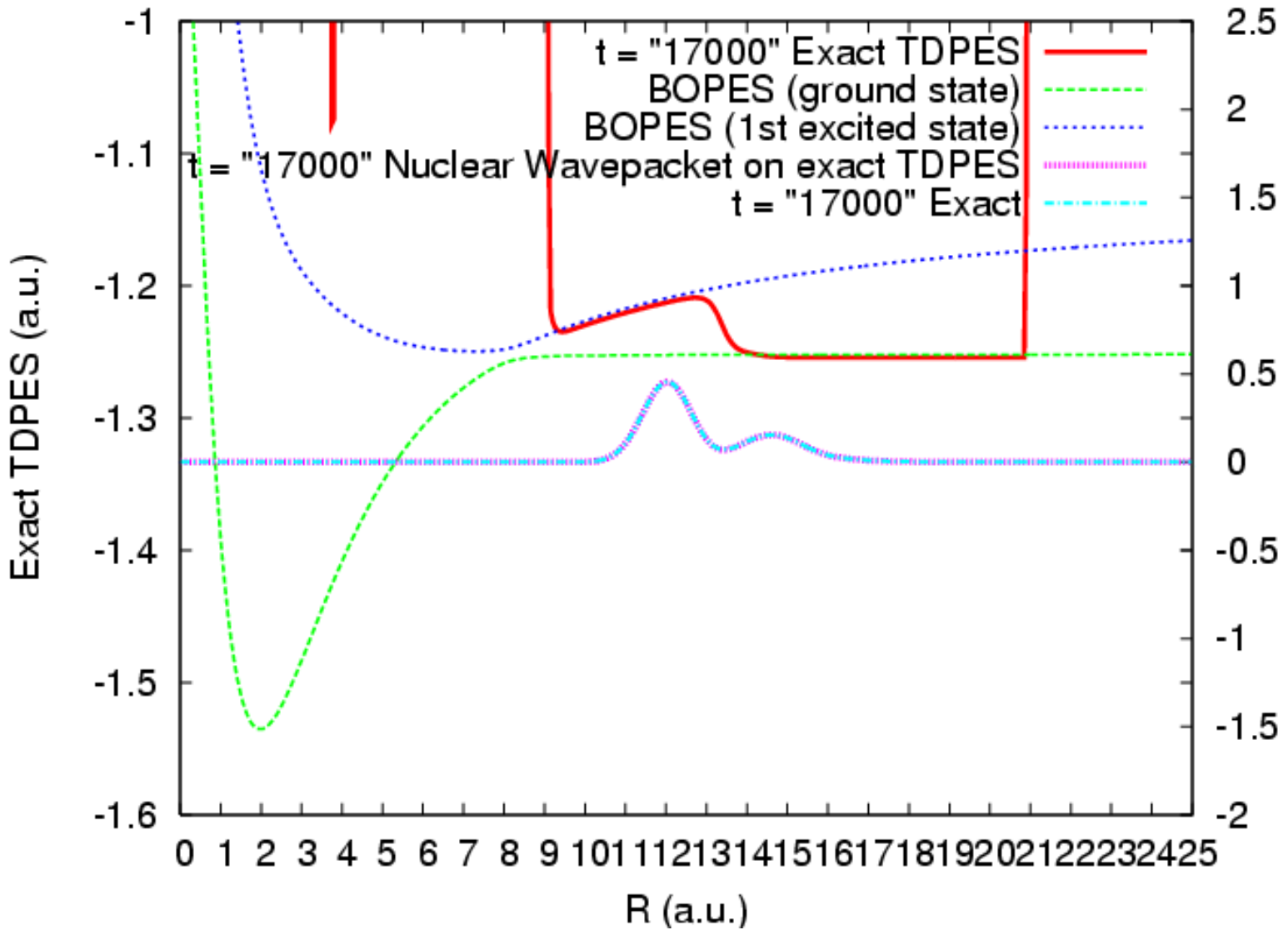
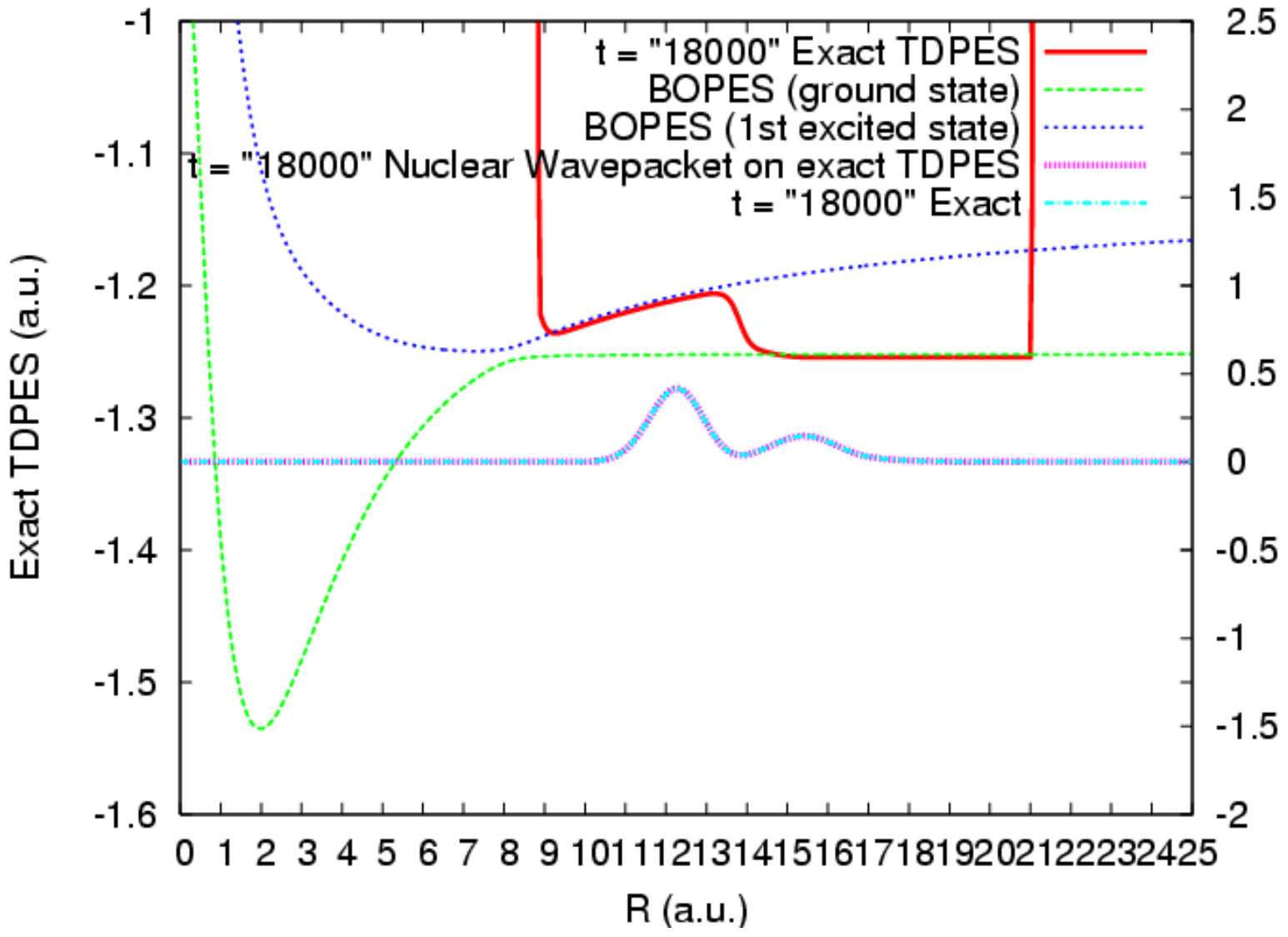
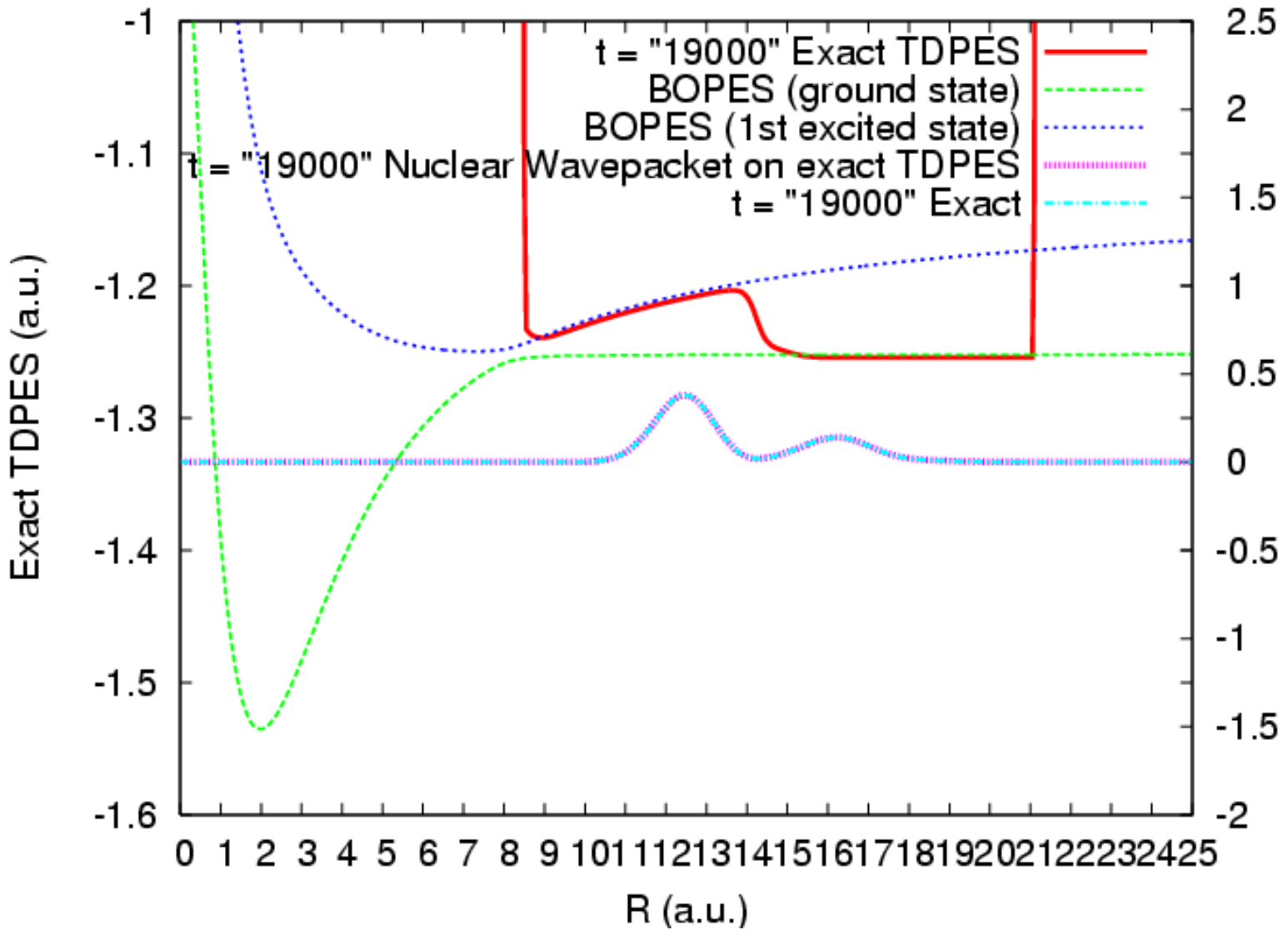
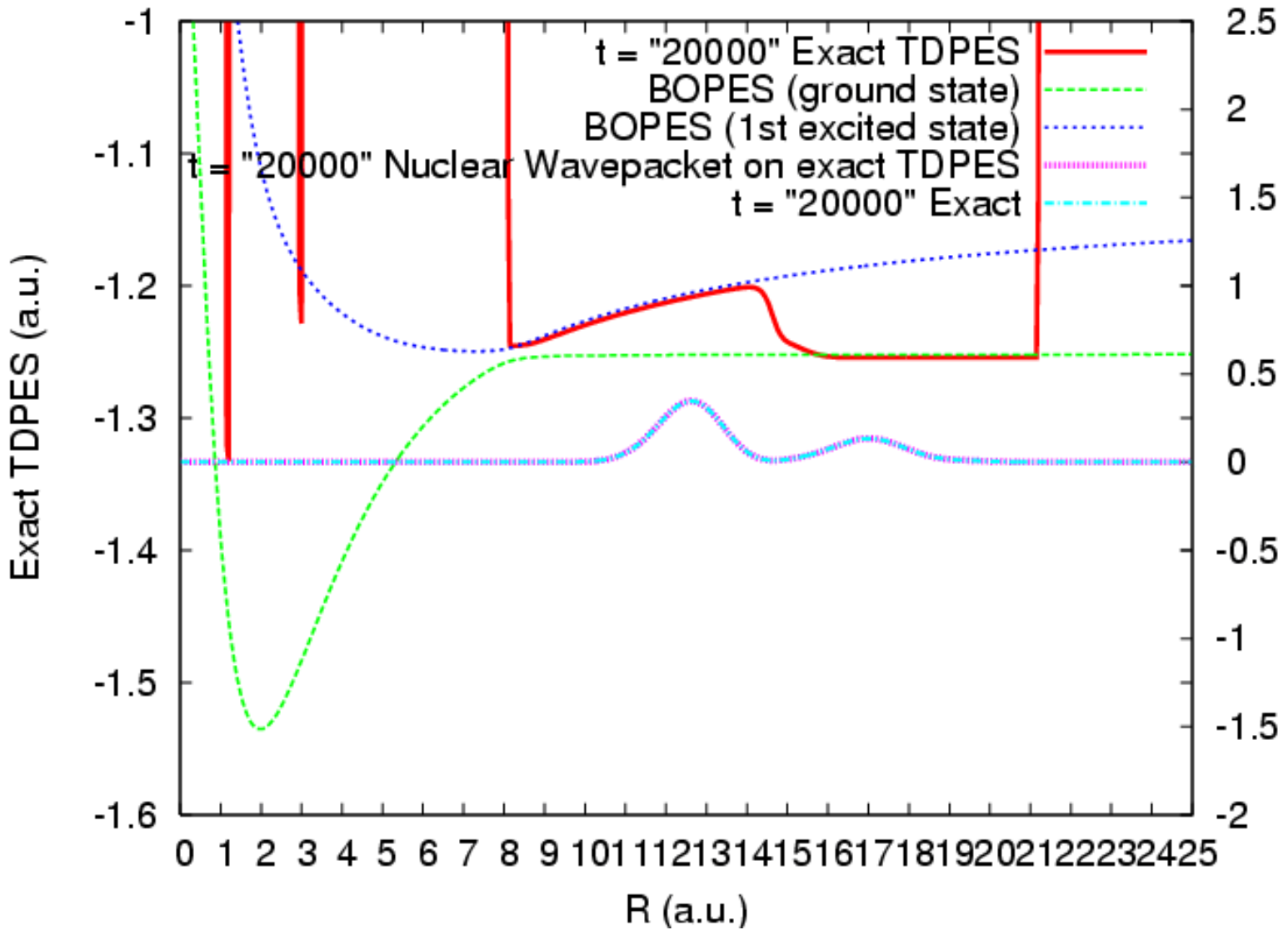
BOPES (ground state)
BOPES (1st excited state)
t = "15000" Nuclear Wavepacket on exact TDPES
t = "15000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


t = "16000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "16000" Nuclear Wavepacket on exact TDPES
t = "16000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


t = "17000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "17000" Nuclear Wavepacket on exact TDPES
t = "17000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


t = "18000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "18000" Nuclear Wavepacket on exact TDPES
t = "18000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


t = "19000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "19000" Nuclear Wavepacket on exact TDPES
t = "19000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


t = "20000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "20000" Nuclear Wavepacket on exact TDPES
t = "20000" Exact
Exact TDPES (a.u.)
R (a.u.)
-1
-1.1
-1.2
-1.3
-1.4
-1.5
-1.6
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

New MD schemes:

Perform classical limit of the nuclear equation, but retain the quantum treatment of the electronic degrees of freedom.

A. Abedi, F. Agostini, E.K.U.Gross, EPL 106, 33001 (2014)

S.K. Min, F. Agostini, E.K.U. Gross, Phys. Rev. Lett. 115, 073001 (2015)

F. Agostini, S.K. Min, A. Abedi, E.K.U. Gross, JCTC 12, 2127 (2016)

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F. Agostini, S.K. Min, A. Abedi, E.K.U. Gross, JCTC 12, 2127 (2016)

Further step: "Density-functionalization":

to make the many-electron equation of motion tractable

Ryan Requist, E.K.U. Gross, PRL 117, 193001 (2016)

Theorem II

Eq. ❶

$$\Bigg(\underbrace{\hat{T}_e + \hat{W}_{ee} + \hat{V}_e^{ext}\left(\underline{\underline{r}},t\right) + \hat{V}_{en}\left(\underline{\underline{r}},\underline{\underline{R}}\right)}_{\hat{H}_{BO}(t)} + \sum_{\nu}^{N_n}\frac{1}{2M_\nu}\left(-i\nabla_\nu - A_\nu\left(\underline{\underline{R}},t\right)\right)^2$$

$$+\sum_{\nu}^{N_n}\frac{1}{M_\nu}\left(\frac{-i\nabla_\nu\chi\left(\underline{\underline{R}},t\right)}{\chi\left(\underline{\underline{R}},t\right)} + A_\nu\left(\underline{\underline{R}},t\right)\right)\left(-i\nabla_\nu - A_\nu\right) - \in\left(\underline{\underline{R}},t\right)\Bigg)\Phi_{\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{r}}\right) = i\partial_t\Phi_{\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{r}},t\right)$$

Eq. ❷

$$\left(\sum_{\nu}^{N_n}\frac{1}{2M_\nu}\left(-i\nabla_\nu + A_\nu\left(\underline{\underline{R}},t\right)\right)^2 + \hat{W}_{nn}\left(\underline{\underline{R}}\right) + \hat{V}_n^{ext}\left(\underline{\underline{R}},t\right) + \in\left(\underline{\underline{R}},t\right)\right)\chi\left(\underline{\underline{R}},t\right) = i\partial_t\chi\left(\underline{\underline{R}},t\right)$$

Theorem II

Eq. ❶

$$\Bigg(\underbrace{\hat{T}_e + \hat{W}_{ee} + \hat{V}_e^{ext}\left(\underline{\underline{r}},t\right) + \hat{V}_{en}\left(\underline{\underline{r}},\underline{\underline{R}}\right)}_{\hat{H}_{BO}(t)} + \sum_{\nu}^{N_n}\frac{1}{2M_\nu}\left(-i\nabla_\nu - A_\nu\left(\underline{\underline{R}},t\right)\right)^2$$

$$+\sum_{\nu}^{N_n}\frac{1}{M_\nu}\left(\frac{-i\nabla_\nu\chi\left(\underline{\underline{R}},t\right)}{\chi\left(\underline{\underline{R}},t\right)} + A_\nu\left(\underline{\underline{R}},t\right)\right)\left(-i\nabla_\nu - A_\nu\right) - \in\left(\underline{\underline{R}},t\right)\Bigg)\Phi_{\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{r}}\right) = i\partial_t\Phi_{\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{r}},t\right)$$

Eq. ❷

$$\left(\sum_{\nu}^{N_n}\frac{1}{2M_\nu}\left(-i\nabla_\nu + A_\nu\left(\underline{\underline{R}},t\right)\right)^2 + \hat{W}_{nn}\left(\underline{\underline{R}}\right) + \hat{V}_n^{ext}\left(\underline{\underline{R}},t\right) + \in\left(\underline{\underline{R}},t\right)\right)\chi\left(\underline{\underline{R}},t\right) = i\partial_t\chi\left(\underline{\underline{R}},t\right)$$

Classical Newton equations for nuclear trajectories

Theorem II

Eq. ❶

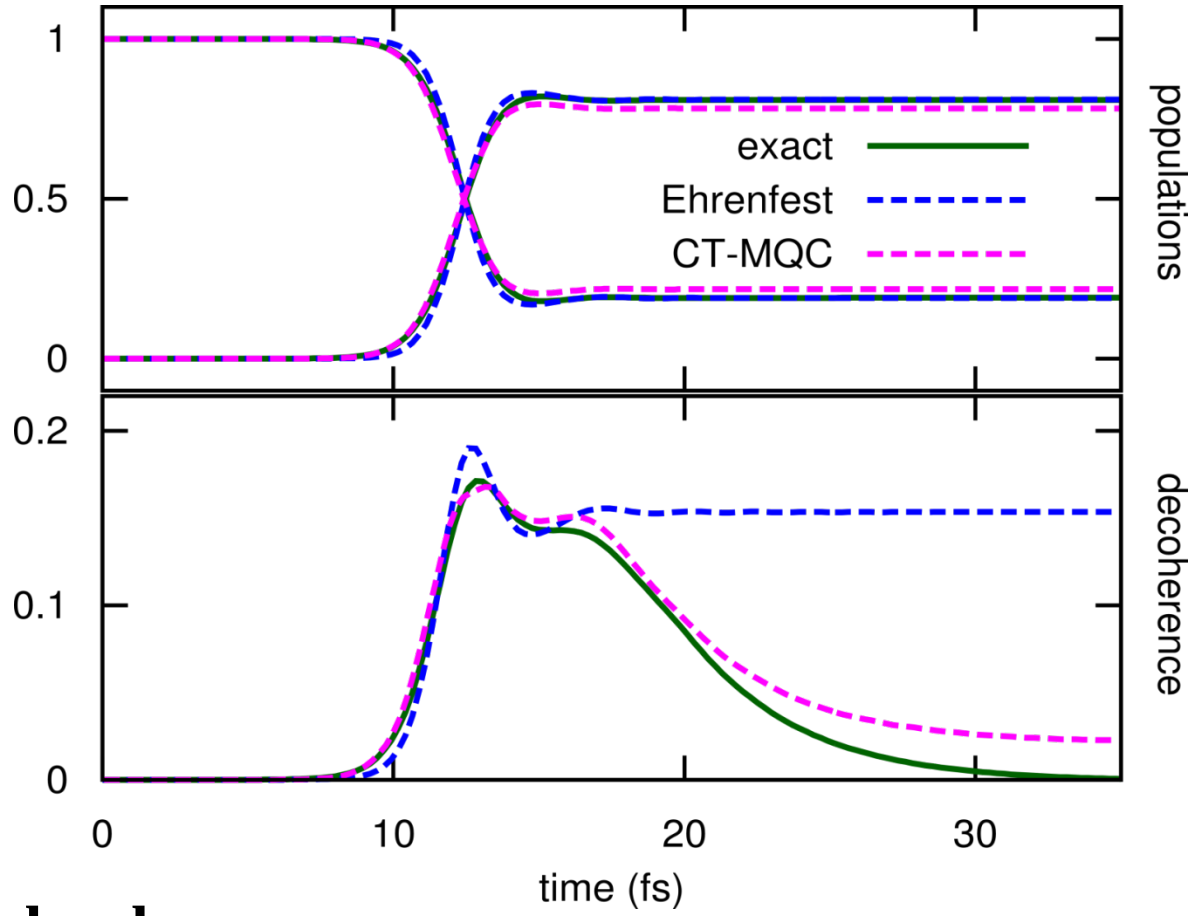
$$\Big(\underbrace{\hat{T}_e + \hat{W}_{ee} + \hat{V}_e^{ext}(\underline{\underline{r}},t) + \hat{V}_{en}(\underline{\underline{r}},\underline{\underline{R}})}_{\hat{H}_{BO}(t)} + \sum_\nu^{N_n} \frac{1}{2M_\nu}\left(-i\nabla_\nu - A_\nu(\underline{\underline{R}},t)\right)^2$$

$$+ \sum_\nu^{N_n} \frac{1}{M_\nu}\left(\frac{-i\nabla_\nu \chi(\underline{\underline{R}},t)}{\chi(\underline{\underline{R}},t)} + A_\nu(\underline{\underline{R}},t)\right)\left(-i\nabla_\nu - A_\nu\right) - \in(\underline{\underline{R}},t)\Big)\Phi_{\underline{\underline{R}}}(\underline{\underline{r}}) = i\partial_t \Phi_{\underline{\underline{R}}}(\underline{\underline{r}},t)$$

Eq. ❷

$$\left(\sum_\nu^{N_n} \frac{1}{2M_\nu}\left(-i\nabla_\nu + A_\nu(\underline{\underline{R}},t)\right)^2 + \hat{W}_{nn}(\underline{\underline{R}}) + \hat{V}_n^{ext}(\underline{\underline{R}},t) + \in(\underline{\underline{R}},t)\right)\chi(\underline{\underline{R}},t) = i\partial_t \chi(\underline{\underline{R}},t)$$

Classical Newton equations for nuclear trajectories

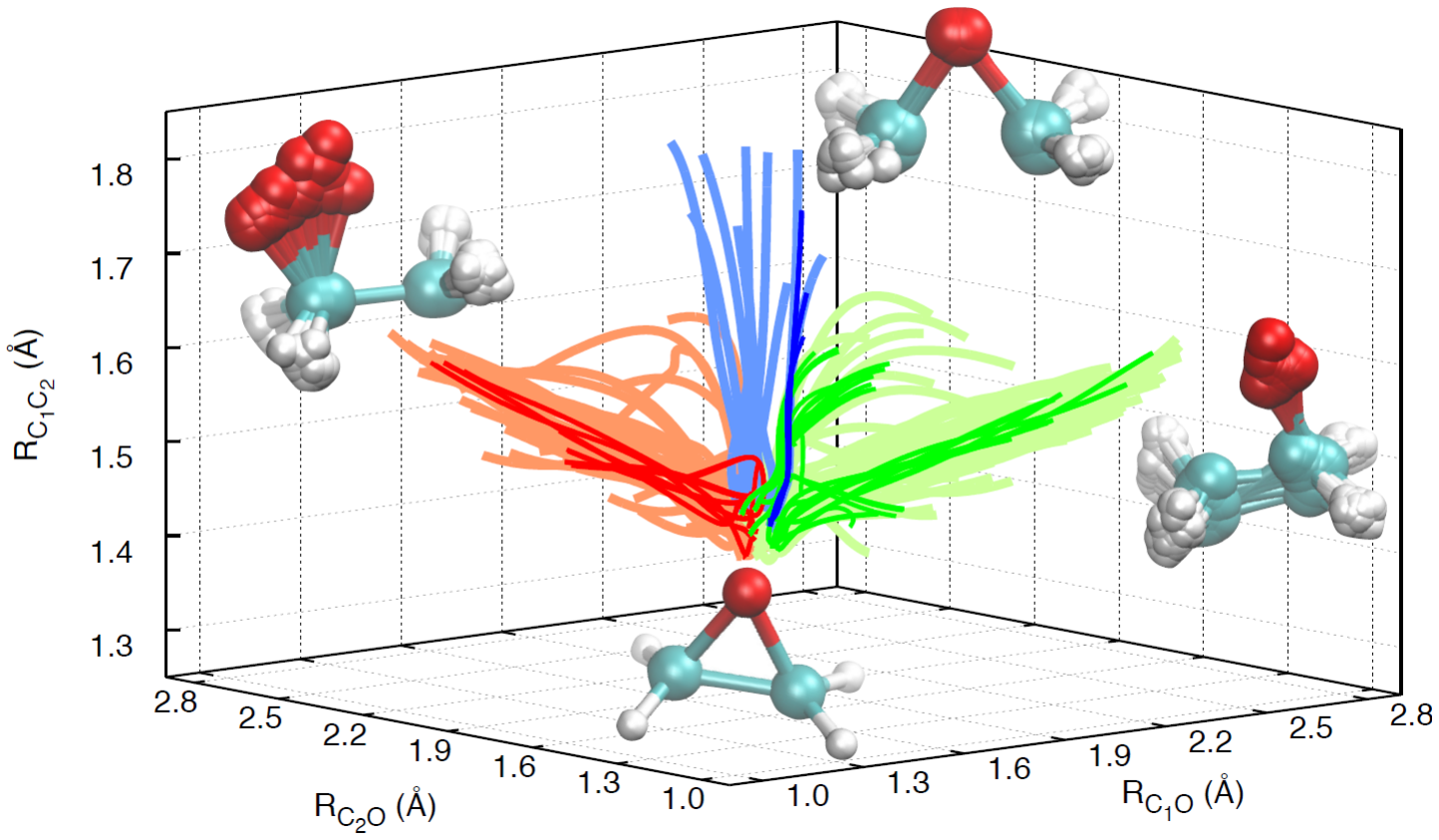


Measure of decoherence:

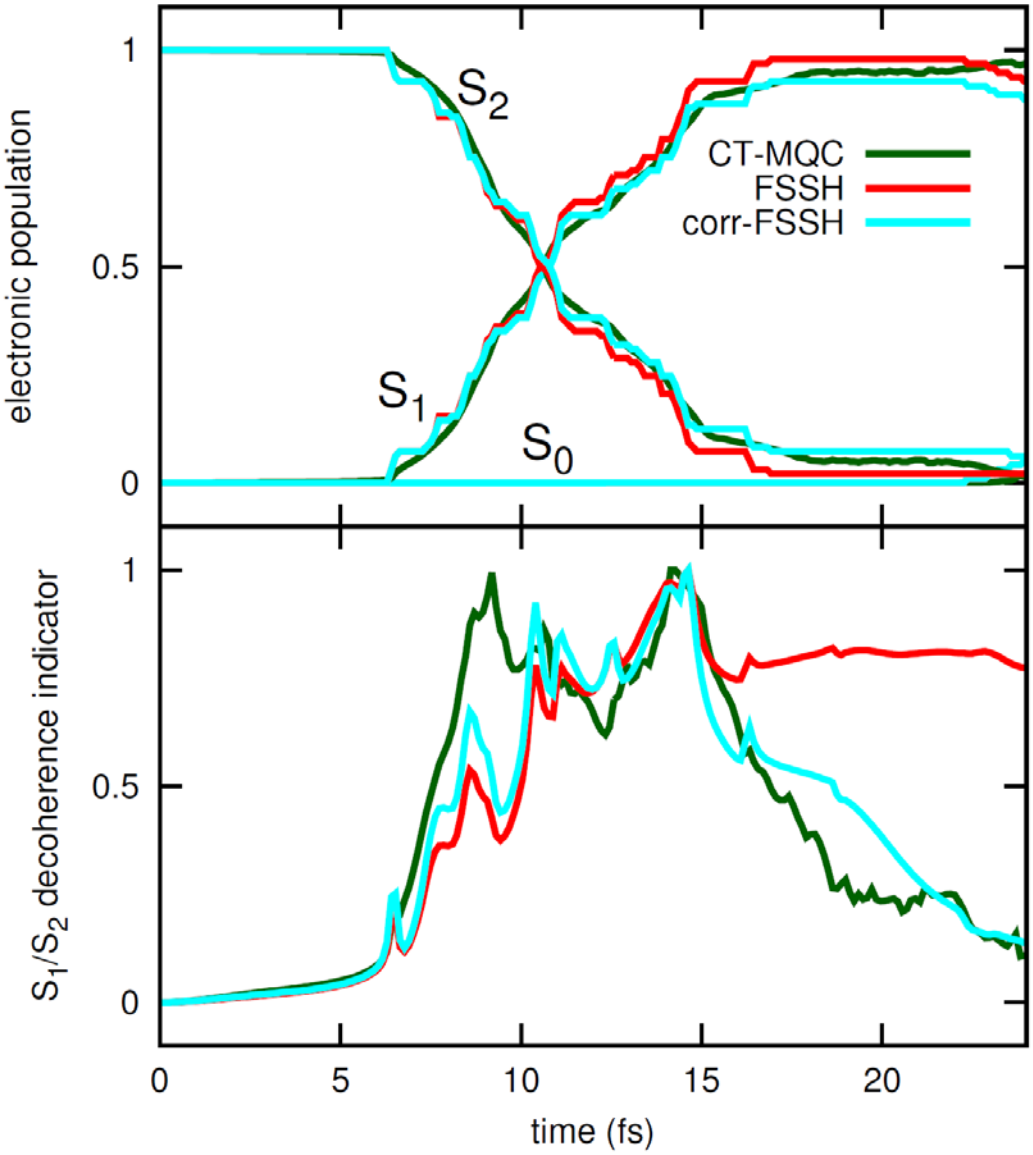
Quantum: $\int d\underline{\underline{\mathbf{R}}} \left|C_1\left(\underline{\underline{\mathbf{R}}}, t\right)\right|^2 \left|C_2\left(\underline{\underline{\mathbf{R}}}, t\right)\right|^2 \left|\chi\left(\underline{\underline{\mathbf{R}}}, t\right)\right|^2$

Trajectories $\boldsymbol{N_{traj}^{-1}} \sum_{\boldsymbol{I}} \left|\boldsymbol{C_1^{(I)}(t)}\right|^2 \left|\boldsymbol{C_2^{(I)}(t)}\right|^2$

Photo-induced ring opening in Oxirane



Identification of the three groups of trajectories that, starting from the initial geometries, yield right-open (red) or left-open (green) ring structures and CC-extended bond geometry (blue). The distributions of the final geometries are estimated as 36% (right-open structure), 47% (left-open structure), 10% (CC-extended bond structure), 7% (closed-ring structure, not represented in the figure), based on CT-MQC dynamics, whereas they are 34% (right-open structure), 54% (left-open structure), 10% (CC-extended bond structure), 2% (closed-ring structure, not represented in the figure), based on corr-FSSH dynamics. Light colors identify CT-MQC trajectories and darker colors corr-FSSH trajectories.



Upper panel: electronic populations of S0, S1 and S2 as functions of time. Lower panel: indicator of decoherence for the element S1=S2. Three sets of results are compared, based on the CT-MQC algorithm (dark-green lines), FSSH (red lines) and corr-FSSH (cyan lines).

Summary of exact factorisation

- $\Psi\left(\underline{\underline{r}},\underline{\underline{\underline{R}}},t\right)=\Phi_{\underline{\underline{\underline{R}}}}\left(\underline{\underline{r}},t\right)\cdot\chi\left(\underline{\underline{\underline{R}}},t\right)$ **is exact**

  A. Abedi, N.T. Maitra, E.K.U. Gross, PRL 105, 123002 (2010)

- **Exact Berry phase vanishes in some cases and is finite in others**

  S.K. Min, A. Abedi, K.S. Kim, E.K.U. Gross, PRL 113, 263004 (2014)

- **TD-PES shows jumps betweeen BO-PES resembling surface hopping**

  A. Abedi, F. Agostini, Y. Suzuki, E.K.U.Gross, PRL 110, 263001 (2013)

- **mixed quantum classical algorithms**

  S.K. Min, F Agostini, E.K.U. Gross, PRL 115, 073001 (2015)

- **multi-component DFT for electrons and nuclei**

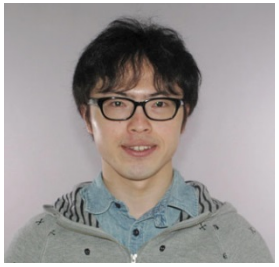
  Ryan Requist, E.K.U. Gross, PRL 117, 193001 (2016)

THANKS

Axel Schild

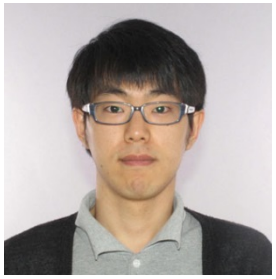
Ali Abedi

Federica Agostini



Yasumitsu Suzuki

Basile Curchod

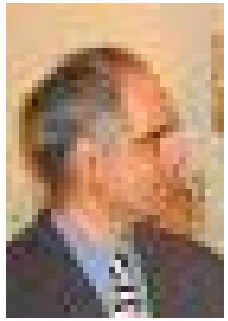


Seung Kyu Min

Ivano Tavernelli

Neepa Maitra
(Hunter College, CUNY)

Ryan Requist



Nikitas Gidopoulos

Other applications

- **Inverse factorisation:** $\Psi\left(\underline{\underline{r}},\underline{\underline{R}},t\right)=\Phi_{\underline{\underline{r}}}\left(\underline{\underline{R}},t\right)\cdot\chi\left(\underline{\underline{r}},t\right)$ **and electronic PES**

  Y. Suzuki, A. Abedi, N. Maitra, K. Yamashita, E.K.U. Gross, Phys. Rev. A 89, 040501(R) (2014)

- **<u>Factorisation for electrons only:</u> Description of processes involving "slow" and "fast" electrons such as HHG and ionisation. Concept of an exact single-active-electron potential. A. Schild, E.K.U.G., PRL 118, 163202 (2017)**

- **Exact TD-PES of systems driven by CW lasers are piecewise identical with Floquet surfaces with steps in between. Surface hopping algorithms should hop between Floquet surfaces**

  T. Fiedlschuster, E.K.U. Gross, R. Schmidt, Phys Rev A (2017 in press)

- **Calculation of vibrational circular dichroism. Beyond-BO terms are treated in 1^{st}-order perturbation theory**

  A. Scherrer, F Agostini, D. Sebastiani, E.K.U. Gross, R. Vuilleumier, JCP 143, 074106 (2015)

- **Calculation of electronic currents generated by nuclear currents. Beyond-BO terms are treated in 1^{st}-order perturbation theory**

  A. Schild, F Agostini, E.K.U. Gross, JPC A120, 3316 (2016)

- **Quantum interferences treated in mixed quantum-classical algorithm using exact TDPES**

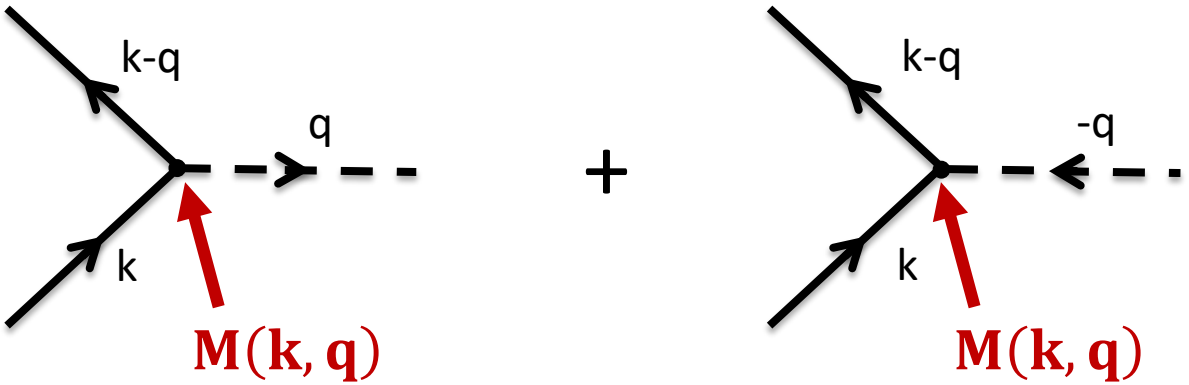
  B. Curchod, F. Agostini, E.K.U. Gross, JCP 145, 034103 (2016)

- **Implementation in** CPMD **F. Agostini, S.K. Min, I. Tavernelli, E.K.U. Gross (2017)**

- **factorisation for other degrees of freedom: e.g. electrons and photons**

- **<u>Ab-initio</u> electron-phonon interaction: What is the correct $M_\lambda(k,q)$?**

$$\hat{H}_{e-ph} = \sum_{k,q,\lambda} M_\lambda(k,q)\, c^{\dagger}_{k-q} c_k \left(b^{\dagger}_{q\lambda} + b_{-q\lambda} \right)$$



Thanks !

SFB 450
SFB 685
SFB 762
SPP 1145