Correlated two-electron quantum dynamics in intense laser fields

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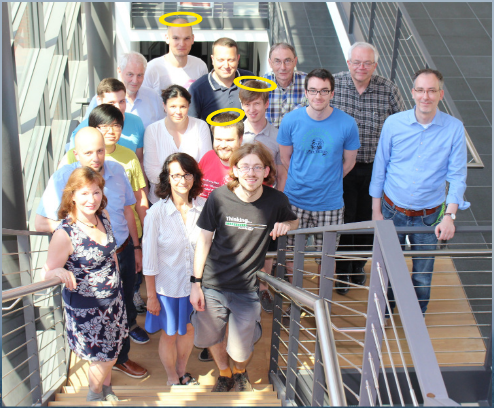
People



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Outline

Motivation to simulate few-body systems such as He or H_2^+ in intense laser fields

- *Ab initio* simulation far behind experiment.
- $N = 2$ at the boundary of what is treatable on a TDSE level.
- Highly correlated systems.
- Ideal test bed for "many"-body approaches.
- First step towards $N > 2$ in a systematic bottom-up approach.

Functional Specification Document

for a useful strong-field *ab initio* code

- Method must work for high (yet nonrelativistic, $A = E/\omega \ll 137$) laser intensities in a wide frequency regime and for arbitrary pulse forms.
  - Configurations far away from the ground state.
  - Several electrons might be in the continuum.
  - Interaction might be resonant.
  - Autoionization, Auger, interatomic Coulomb decay, ...

- Method must allow for the calculation of:
  - ion yields,
  - emitted radiation,
  - (correlated) photoelectron spectra.

- Code must have typical run times $t \ll T_{\text{PhD}}$.

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Obvious idea:

use a basic variable that is "more differential" than $n_\sigma(\vec{r}, t)$ but less than $\Psi(\vec{r}_1\sigma_1, \ldots, \vec{r}_N\sigma_N)$

Reduced density matrices and natural orbitals

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Time-dependent natural orbital (NO) theory

- **1-RDM**

everything in color is time-dependent!

$$\hat{\gamma}_1 = N \ \mathrm{Tr}_{N-1}\left\{|\Psi\rangle\langle\Psi|\right\}$$

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$$\hat{\gamma}_1 = \sum_{k=1}^{\infty} n_k |k\rangle\langle k|, \qquad \sum_k n_k = N$$

- **NOs are eigenvectors of 1-RDM**

$$\hat{\gamma}_1 |k\rangle = n_k |k\rangle$$

Occupation numbers (OCs) n_k are eigenvalues

$$\text{Non-integer } \ n_k \quad \Leftrightarrow \quad \text{correlation} \sim S \sim \sum_k n_k \ln n_k$$

Equation of motion (EOM)

Our goal: Derive **useful** EOM for NOs and OCs

- **EOM for 1-RDM involves 2-RDM (BBGKY)**

$$\mathrm{i}\dot{\hat{\gamma}}_1 = \boxed{\text{1-body part with } \hat{\gamma}_1,\ \hat{h}} + \mathrm{Tr}_2\left\{\boxed{\text{2-body part with } \hat{\gamma}_2,\ \hat{v}_{\mathrm{ee}}}\right\}$$

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- **2-RDM expanded in NOs**

$$\hat{\gamma}_2 = \sum_{ijkl} \gamma_{2,ijkl}\, |i\rangle|j\rangle\langle k|\langle l|$$

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- **Approximations of $\gamma_{2,ijkl}$**

  Hartree-Fock limit: $\gamma_{2,ijkl} = \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}$, OCs $n_k = 1$ (or 0)

  (others: Müller, Goedecker & Umrigar, Baerends, Piris)

  $\rightarrow$ problem of **observables** relaxed

Useful EOM for NOs

$$i\dot{\hat{\gamma}}_1 = \boxed{\text{1-body part with } \hat{\gamma}_1,\ \hat{h}} + \mathrm{Tr}_2\left\{\boxed{\text{2-body part with } \hat{\gamma}_2,\ \hat{v}_{ee}}\right\}$$

Left hand side:

$$i\frac{d}{dt}\sum_k n_k|k\rangle\langle k| = i\sum_k\left\{\dot{n}_k|k\rangle\langle k| + n_k|\dot{k}\rangle\langle k| + n_k|k\rangle\langle\dot{k}|\right\}$$

Introduce

$$i|\dot{k}\rangle = \sum_m \alpha_{km}|m\rangle, \qquad \alpha_{mk} = \alpha^*_{km} = i\langle k|\dot{m}\rangle$$

$\Rightarrow$

$$\sum_k\left\{i\dot{n}_k|k\rangle\langle k| + in_k|\dot{k}\rangle\langle k| - n_k\sum_m \alpha_{mk}|k\rangle\langle m|\right\} = \text{right hand side}$$

Determination of the α_{km}

$$\left\langle m \right| \sum_l \left\{ \mathrm{i}\dot{n}_l |l\rangle\langle l| + n_l \sum_p \alpha_{lp} |p\rangle\langle l| - n_l \sum_p \alpha_{pl} |l\rangle\langle p| \right\} = \text{right hand side} \left| k \right\rangle$$

$$\Rightarrow \quad \mathrm{i}\dot{n}_k\,\delta_{km} + (n_k - n_m)\alpha_{km} = \left\langle m \right| \text{right hand side} \left| k \right\rangle$$

- For $k = m$ follows with $\hat{H} = \sum_{i=1}^{N} \hat{h}^{(i)} + \sum_{i<j} \hat{v}_{\mathrm{ee}}^{(i,j)}$:

$$\dot{n}_k = 4\ \mathrm{Im} \sum_{ijl} \gamma_{2,ijkl} \langle lk | \hat{v}_{\mathrm{ee}} | ji \rangle$$

EOM for n_k ... but α_{kk} is undetermined

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- For $k \neq m$ and $n_k \neq n_m$:

$$\alpha_{km} = \langle m | \hat{h} | k \rangle + \frac{2}{n_m - n_k} \sum_{pjl} \left\{ \gamma_{2,mpjl} \langle lj | \hat{v}_{\mathrm{ee}} | pk \rangle - \left[\gamma_{2,kpjl} \langle lj | \hat{v}_{\mathrm{ee}} | pm \rangle \right]^* \right\}$$

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- If $n_k = n_m$ despite $k \neq m$: α_{km} undetermined

Useful EOM for NOs

$\mathrm{i}|\dot{k}\rangle = \sum_m \alpha_{km}|m\rangle$ is *not* a useful EOM. Instead,

$$\left\langle 1 \right| \sum_k \left\{ \mathrm{i}\dot{n}_k |k\rangle\langle k| + \mathrm{i} n_k |\dot{k}\rangle\langle k| - n_k \sum_m \alpha_{mk} |k\rangle\langle m| \right\} = \text{right hand side} \left| p \right\rangle$$

$$\Rightarrow \quad \mathrm{i} n_p \partial_t \phi_p(1) = -\mathrm{i}\dot{n}_p \phi_p(1) + \sum_k n_k \alpha_{pk} \phi_k(1) + \left\langle 1 \middle| \text{right hand side} \middle| p \right\rangle$$

has already the useful form

$$\mathrm{i}\partial_t \vec{\phi}(1) = \underline{\underline{\hat{\mathcal{H}}}}\, \vec{\phi}(1)$$

but what about α_{kk} and degeneracy?

The general two-fermion case

P.-O. Löwdin, H. Shull, Phys. Rev. 101, 1730 (1956)

- Two-fermion state $|\Psi\rangle$, expanded in orthonormal single-particle basis $\{|\psi_i\rangle\}$ (comprising spin and other degrees of freedom)

$$|\Psi\rangle = \sum_{ij} \Psi_{ij} |\psi_i, \psi_j\rangle,$$

$$\Psi_{ij} = \langle \psi_i, \psi_j | \Psi \rangle.$$

- Define matrix $\underline{\underline{\boldsymbol{\Psi}}} = \left[\Psi_{ij}\right]$. Antisymmetry implies

$$\underline{\underline{\boldsymbol{\Psi}}}^{\mathsf{T}} = -\underline{\underline{\boldsymbol{\Psi}}}.$$

The general two-fermion case

- With

$$\boldsymbol{\psi} = \begin{pmatrix} |\psi_1\rangle \\ |\psi_2\rangle \\ \vdots \end{pmatrix}, \qquad \boldsymbol{\psi}^* = \begin{pmatrix} \langle\psi_1| \\ \langle\psi_2| \\ \vdots \end{pmatrix},$$

$$\boldsymbol{\psi}^\mathsf{T} = \left(|\psi_1\rangle, |\psi_2\rangle, \ldots\right), \qquad \boldsymbol{\psi}^\dagger = \left(\langle\psi_1|, \langle\psi_2|, \ldots\right)$$

one can write

$$\boldsymbol{\psi}^*\boldsymbol{\psi}^\dagger = \begin{pmatrix} \langle\psi_1,\psi_1| & \langle\psi_1,\psi_2| & \cdots \\ \langle\psi_2,\psi_1| & \langle\psi_2,\psi_2| & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}$$

- Hence

$$\underline{\underline{\boldsymbol{\Psi}}} = \boldsymbol{\psi}^*\boldsymbol{\psi}^\dagger|\Psi\rangle, \qquad |\Psi\rangle = \boldsymbol{\psi}^\mathsf{T}\underline{\underline{\boldsymbol{\Psi}}}\boldsymbol{\psi}.$$

The general two-fermion case

- Any skew-symmetric matrix $\underline{\underline{\boldsymbol{\Psi}}} = -\underline{\underline{\boldsymbol{\Psi}}}^\mathsf{T}$ can be factorized into unitary matrices $\boldsymbol{U}$, $\boldsymbol{U}^\mathsf{T}$ and a block-diagonal matrix,

$$\underline{\underline{\boldsymbol{\Psi}}} = \boldsymbol{U}\boldsymbol{\Sigma}\boldsymbol{U}^\mathsf{T}, \qquad \boldsymbol{\Sigma} = \mathrm{diag}(\boldsymbol{\Sigma}_1, \boldsymbol{\Sigma}_3, \boldsymbol{\Sigma}_5, \ldots),$$

$$\boldsymbol{\Sigma}_i = \begin{pmatrix} 0 & \xi_i \\ -\xi_i & 0 \end{pmatrix}, \qquad i \text{ odd}.$$

- Hence,

$$|\Psi\rangle = \psi^\mathsf{T}\boldsymbol{U}\boldsymbol{\Sigma}\boldsymbol{U}^\mathsf{T}\psi = \phi^\mathsf{T}\boldsymbol{\Sigma}\phi, \quad \phi = \boldsymbol{U}^\mathsf{T}\psi$$

and thus

$$|\Psi\rangle = \sum_{i \text{ odd}} \xi_i \Big[|\phi_i, \phi_{i+1}\rangle - |\phi_{i+1}, \phi_i\rangle \Big].$$

The general two-fermion case

- For the **1-RDM** follows

$$\hat{\gamma}_1 = \sum_{k \text{ odd}} 2|\xi_k|^2 \Big[|\phi_k\rangle\langle\phi_k| + |\phi_{k+1}\rangle\langle\phi_{k+1}| \Big],$$

which proves that $|k\rangle = |\phi_k\rangle$, i.e., the set $\{|\phi_k\rangle\}$ *is* a set of NOs, and $2|\xi_k|^2$ are the pairwise degenerate ONs

$$n_k = n_{k+1} = 2|\xi_k|^2, \qquad k \text{ odd}.$$

- Hence

$$\hat{\gamma}_1 = \sum_{k \text{ odd}} n_k \big[|k\rangle\langle k| + |k+1\rangle\langle k+1| \big]$$

The general two-fermion case

- **Exact 2-fermion state**

$$|\Psi\rangle = \sum_{k \text{ odd}} \sqrt{\frac{n_k}{2}} e^{i\varphi_k} \left[|k\rangle |k+1\rangle - |k+1\rangle |k\rangle \right]$$

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- **Exact 2-DM**

$$|\Psi\rangle\langle\Psi| = \hat{\gamma}_2 = \sum_{ijkl} \underbrace{(-1)^{i-k} e^{i(\varphi_i - \varphi_k)} \frac{\sqrt{n_i n_k}}{2} \delta_{ij'} \delta_{kl'}}_{\gamma_{2,ijkl}} |i\rangle|j\rangle\langle k|\langle l|$$

$j' = j \pm 1$ for j odd or even, respectively

The general two-fermion case

- Plugging the 2-fermion state

$$|\Psi\rangle = \sum_{k\ \text{odd}} \sqrt{\frac{n_k}{2}} e^{i\varphi_k} \left[|k\rangle |k'\rangle - |k'\rangle |k\rangle \right]$$

into the TDSE and multiplication from the left by $\langle k|\langle k'|$ yields

$$\alpha_{kk} + \alpha_{k'k'} = \langle k|\hat{h}|k\rangle + \langle k'|\hat{h}|k'\rangle + \frac{2}{n_k} \mathrm{Re} \sum_{ijl} \gamma_{2,ijkl} \langle kl|\hat{v_{ee}}|ij\rangle$$

Phase freedom

- **1-RDM** independent of NO phases

$$\hat{\gamma}_1 = \sum_{k \text{ odd}} n_k \left[|k\rangle\langle k| + |k'\rangle\langle k'| \right]$$

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$$|\Psi\rangle = \sum_{k \text{ odd}} \sqrt{\frac{n_k}{2}} e^{i\varphi_k} \left[|k\rangle|k'\rangle - |k'\rangle|k\rangle \right]$$

not because

$$|\bar{j}\rangle = e^{i\vartheta_j}|j\rangle$$

leads to

$$|\Psi\rangle = \sum_{k \text{ odd}} \sqrt{\frac{n_k}{2}} e^{i\bar{\varphi}_k} \left[|\bar{k}\rangle|\bar{k}'\rangle - |\bar{k}'\rangle|\bar{k}\rangle \right]$$

with a new phase

$$\bar{\varphi}_k = \varphi_k - \vartheta_k - \vartheta'_k$$

Phase choices

- “Standard choice”

$$\mathrm{i}\langle k|\dot{k}\rangle = \alpha_{kk} = 0 \quad \Leftrightarrow \quad \vartheta_k(t) = \mathrm{i}\int^{t} \langle k(t')|\partial_{t'}|k(t')\rangle \, \mathrm{d}t'$$

  leads to time-dependent phases $\bar{\varphi}_k$ and $\dot{n}_k = 0$ during imaginary-time propagation

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- Giesbertz's phase-including NOs (PINOs)

$$\vartheta_k(t) = \vartheta_{k'}(t) = \frac{1}{2}[\varphi_k(t) - \varphi_k(0)]$$

  shift time-dependence to the NOs,

$$|\Psi\rangle = \sum_{k\ \mathrm{odd}} \sqrt{\frac{n_k}{2}} \mathrm{e}^{\mathrm{i}\varphi_k} \left[|k\rangle|k+1\rangle - |k+1\rangle|k\rangle\right],$$

  and imaginary-time propagation yield real groundstate NOs with
  - $\mathrm{e}^{\mathrm{i}\varphi_1} = 1$, $\mathrm{e}^{\mathrm{i}\varphi_3} = \mathrm{e}^{\mathrm{i}\varphi_5} = \ldots = -1$ (singlet)
  - $\mathrm{e}^{\mathrm{i}\varphi_1} = \mathrm{e}^{\mathrm{i}\varphi_3} = \mathrm{e}^{\mathrm{i}\varphi_5} = \ldots = 1$ (triplet)

TDRNOT in position space

- Get rid of spin degrees, i.e., write

$$|\Psi\rangle = |\Phi_{0,1}\rangle \otimes \frac{1}{\sqrt{2}}\big[|+-\rangle \mp |-+\rangle\big], \qquad |\Psi\rangle = |\Phi_1\rangle \otimes |\pm\pm\rangle$$

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- Go to position space ($\phi_k(x) = \langle x|k\rangle$) and derive EOM for spatial NOs

$$\mathrm{i}\dot{\vec{\phi}}(x) = \underline{\underline{\hat{\mathcal{H}}}}(x)\,\vec{\phi}(x)$$

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$$\mathrm{i}\dot{\vec{\phi}}(x) = \underline{\underline{\hat{\mathcal{H}}}}(x)\,\vec{\phi}(x)$$

- Unify $\dot{\phi}_k(x)$ and $\dot{n}_k$ into **single EOM**

$$\boxed{\mathrm{i}\dot{\vec{\tilde{\phi}}}(x) = \underline{\underline{\hat{\tilde{\mathcal{H}}}}}(x)\,\vec{\tilde{\phi}}(x)}$$

by **renormalizing** $|\tilde{k}\rangle = \sqrt{n_k}|k\rangle$,

$$\int \mathrm{d}x\,|\tilde{\phi}_k(x)|^2 = n_k$$

NO-Hamiltonian $\hat{\tilde{\mathcal{H}}}$

everything in color is time-dependent!

$$\hat{\tilde{\mathcal{H}}}_{km} = (\hat{h} + \mathcal{A}_k)\delta_{km} + \mathcal{B}_{km} + \hat{\mathcal{C}}_{km}$$

with

$$\hat{h} = \hat{p}^2/2 + \hat{v} + A\hat{p},$$

$$\mathcal{A}_k = -\frac{1}{n_k}\,\mathrm{Re}\sum_{jpl}\tilde{\gamma}_{2,kjpl}\langle\tilde{p}\tilde{l}|\hat{v}_{ee}|\tilde{k}\tilde{j}\rangle, \quad n_k = \langle\tilde{k}|\tilde{k}\rangle,$$

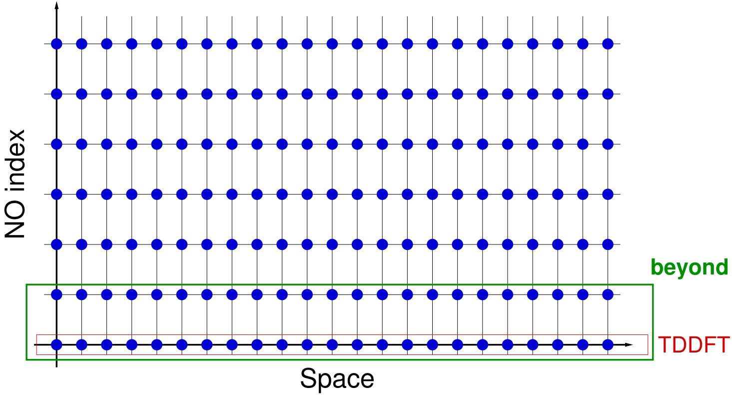
$$\mathcal{B}_{km} \overset{m\neq k}{=} \frac{2}{n_m - n_k}\sum_{jpl}\left\{\tilde{\gamma}_{2,mjpl}\langle\tilde{p}\tilde{l}|\hat{v}_{ee}|\tilde{k}\tilde{j}\rangle - \left[\tilde{\gamma}_{2,kjpl}\langle\tilde{p}\tilde{l}|\hat{v}_{ee}|\tilde{m}\tilde{j}\rangle\right]^*\right\},$$

$$\hat{\mathcal{C}}_{km} = 2\sum_{jl}\tilde{\gamma}_{2,mjkl}\langle\tilde{l}|\hat{v}_{ee}|\tilde{j}\rangle.$$

J. Rapp, M. Brics, D. Bauer; Phys. Rev. A 90, 012518 (2014)

TDRNOT in position space

- Unitary propagation on a grid



- Use favorite unconditionally stable unitary propagator

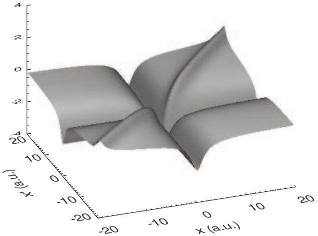
Results

Test system
1D model He in intense laser fields

- in TDSE:

$$V(x,x',t) = -\frac{2}{\sqrt{1+x^2}} - \frac{2}{\sqrt{1+x'^2}} + E(t)(x+x'),$$

$$V_{ee}(|x-x'|) = \frac{1}{\sqrt{1+(x-x')^2}}$$



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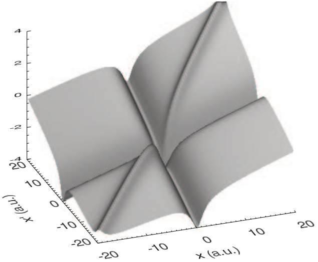

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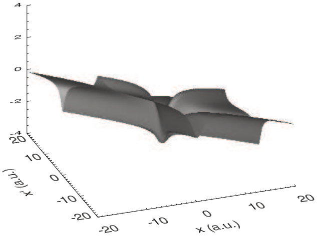
- in TDSE:

$$V(x, x', t) = -\frac{2}{\sqrt{1+x^2}} - \frac{2}{\sqrt{1+x'^2}} + E(t)(x+x'),$$

$$V_{ee}(|x-x'|) = \frac{1}{\sqrt{1+(x-x')^2}}$$



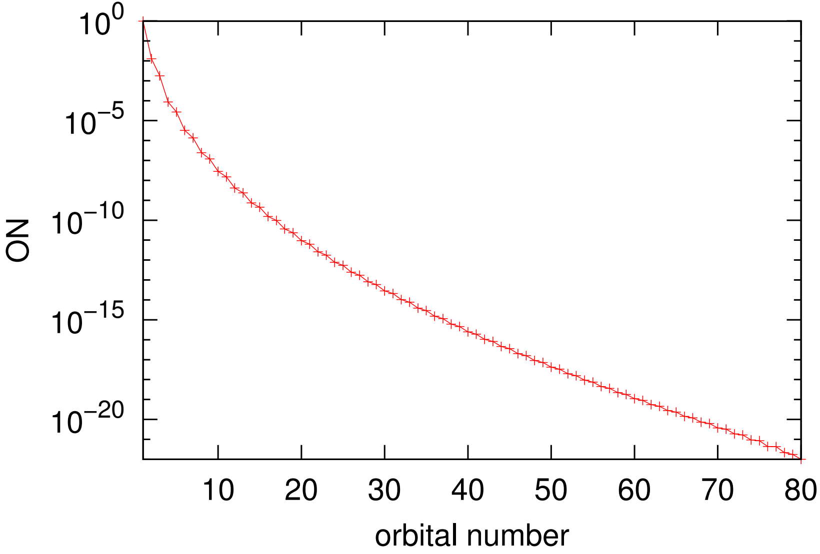
Ground states

via imaginary propagation

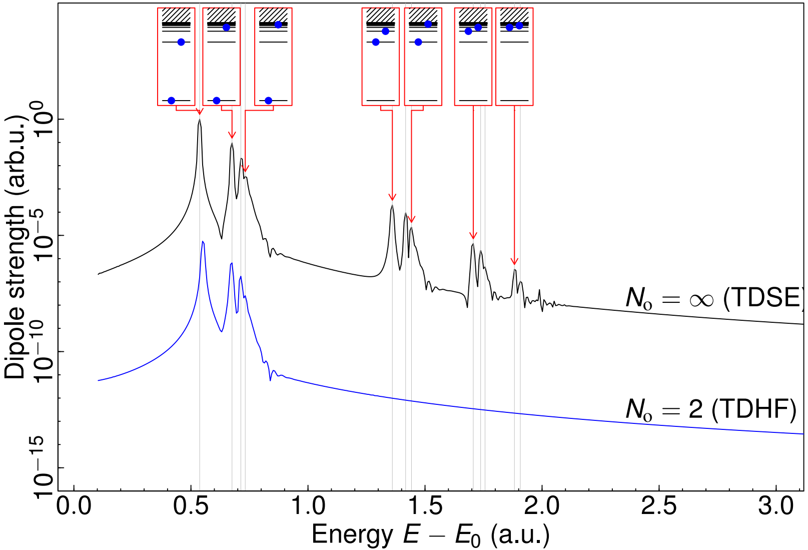
Number of RNOs N_o	Total energy E_0 (a.u.)	Dominant occupation numbers n_1	$n_3/10^{-3}$	$n_5/10^{-5}$
		Spin-singlet		
2 (TDHF)	−2.224318	1.0000000		
4 (TDRNOT)	−2.236595	0.9912665	8.7335	
6 (TDRNOT)	−2.238203	0.9909590	8.3142	72.683
8 (TDRNOT)	−2.238324	0.9909438	8.3221	70.229
∞ **(TDSE)**	−2.238368	0.9909473	8.3053	70.744
		Spin-triplet		
2 (TDHF)	−1.8120524	1.00000000		
4 (TDRNOT)	−1.8160798	0.99764048	2.35952	
6 (TDRNOT)	−1.8161870	0.99760705	2.36464	2.8298
8 (TDRNOT)	−1.8161945	0.99760656	2.36267	2.9581
∞ **(TDSE)**	−1.8161954	0.99760677	2.36220	2.9610

Ground state ONs

***via* imaginary propagation (spin-singlet)**



Linear response



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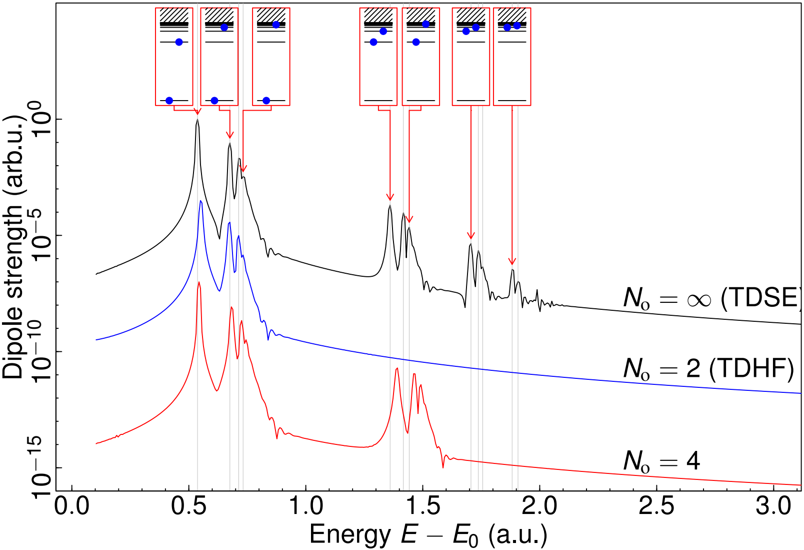

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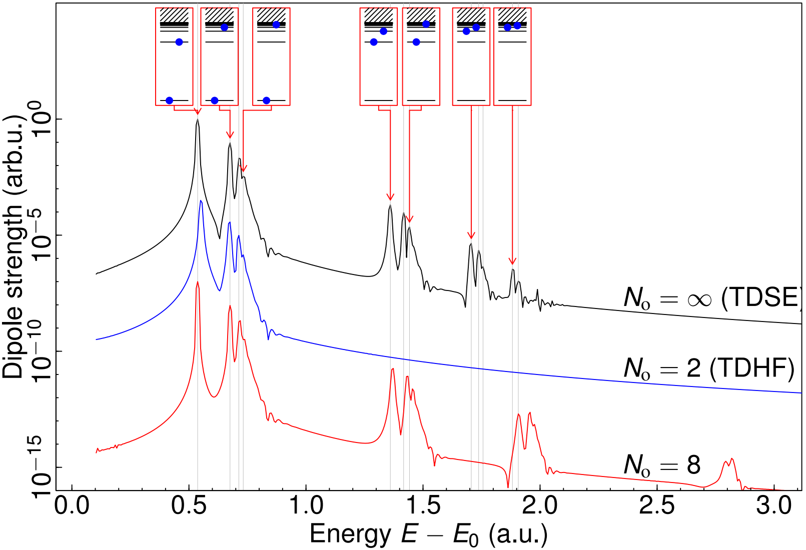

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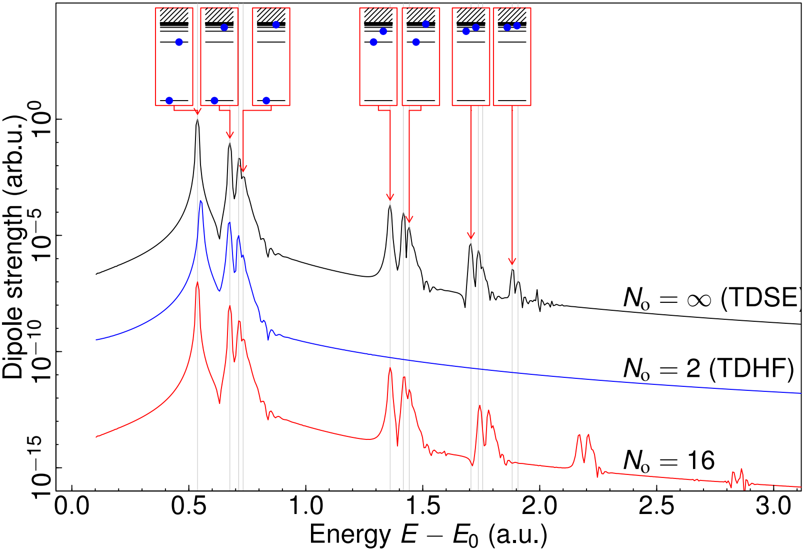
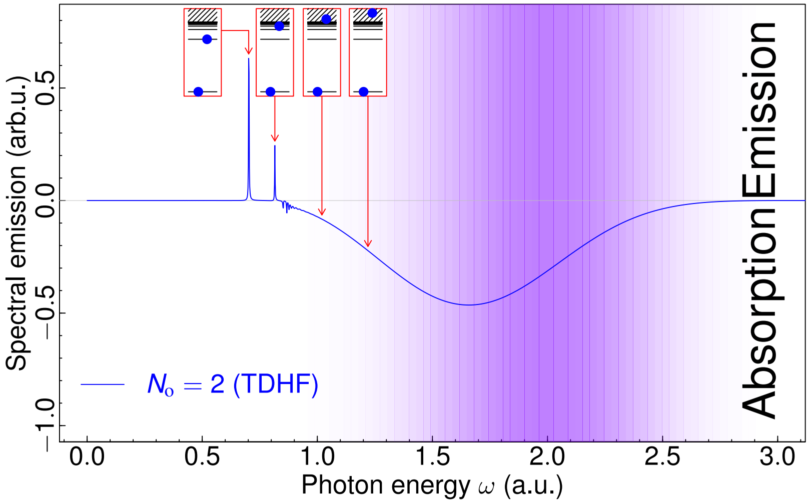


Absorption spectroscopy

Lorentz *vs* Fano

C. Ott *et al.*, Science 340, 716 (2013)



$\omega = 1.84$, 3-cycle $\sin^2$ + postprop., 10^{12} Wcm^{-2}

Absorption spectroscopy

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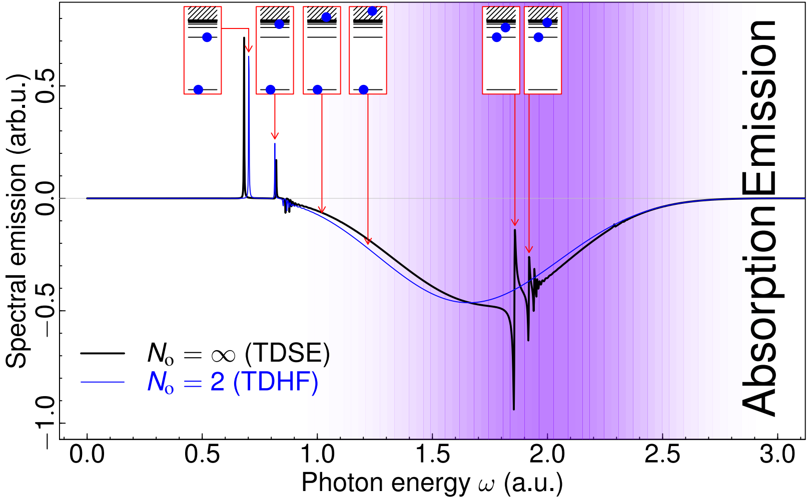
C. Ott *et al.*, Science 340, 716 (2013)



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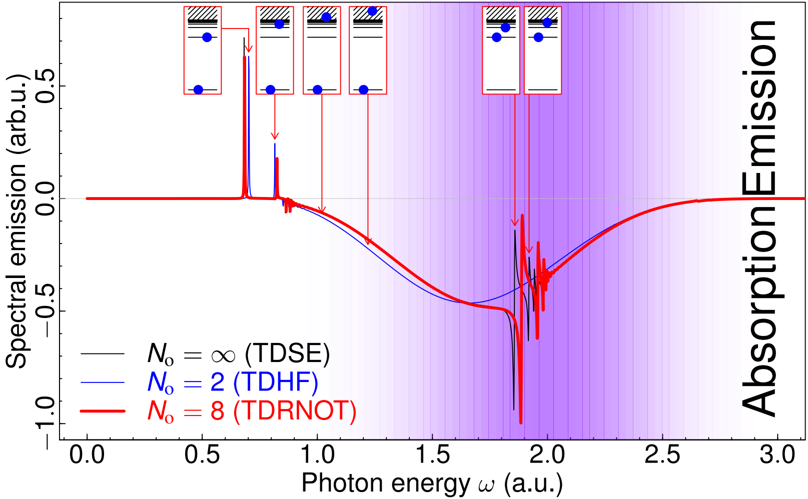
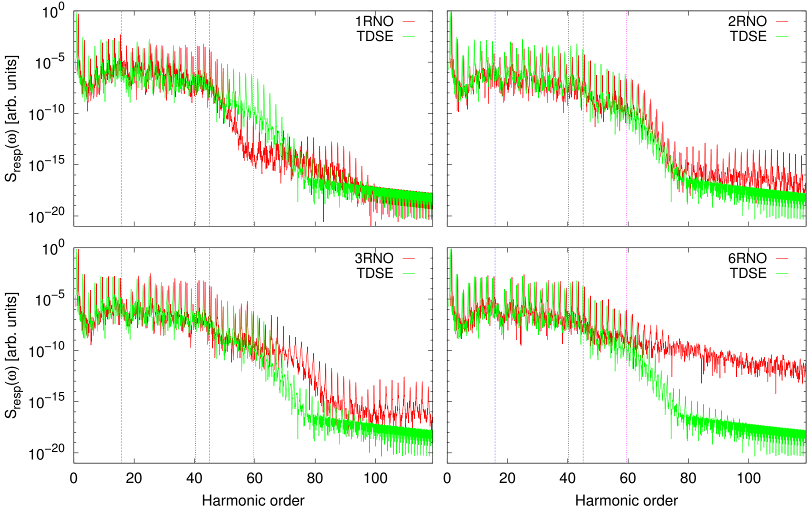


$\omega = 1.84$, 3-cycle $\sin^2$ + postprop., 10^{12} Wcm^{-2}

High-order harmonic generation (HOHG) in He

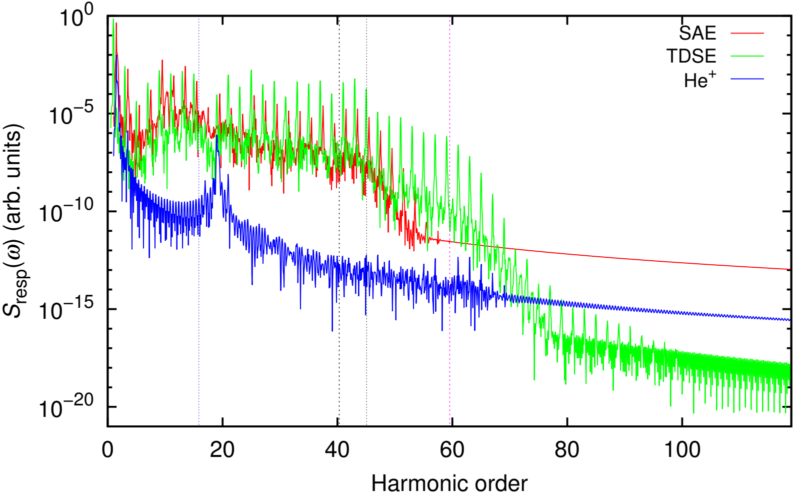


$\omega = 0.057$, 15-cycle trapez. + 2-cycle $\sin^2$ ramping, 10^{14} Wcm^{-2}

M. Brics, J. Rapp, D. Bauer, Phys. Rev. A**93**, 013404 (2016)

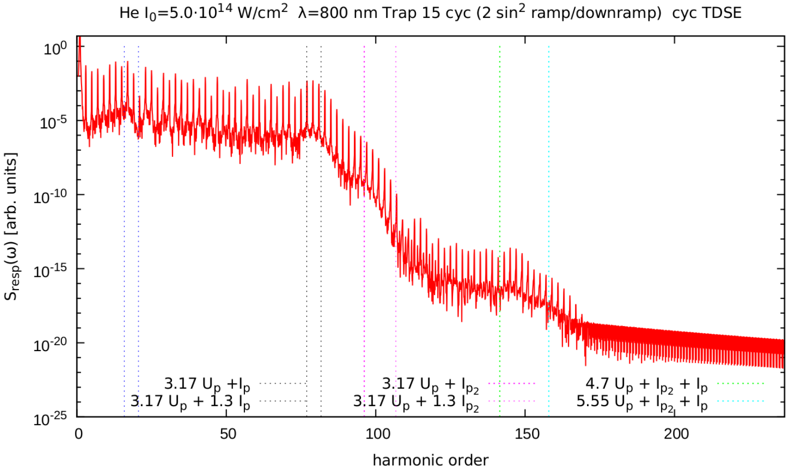
High-order harmonic generation (HOHG) in He

He^+ extension is a two-electron effect



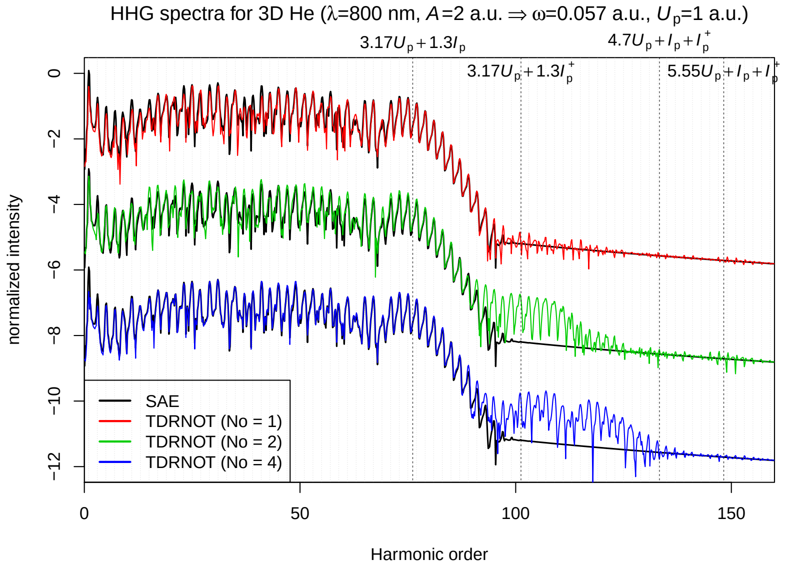
High-order harmonic generation (HOHG) in He

He^+ extension is a two-electron effect, but not NSDR



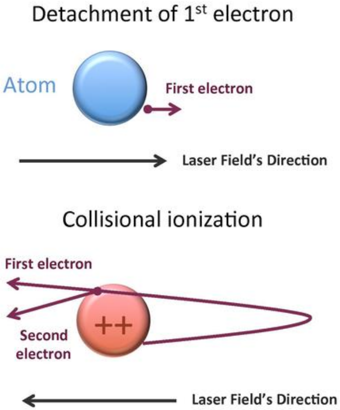
P. Koval, F. Wilken, D. Bauer, and C. H. Keitel, Phys. Rev. Lett. 98, 043904 (2007)
Kenneth K. Hansen and Lars Bojer Madsen, Phys. Rev. A 93, 053427 (2016)

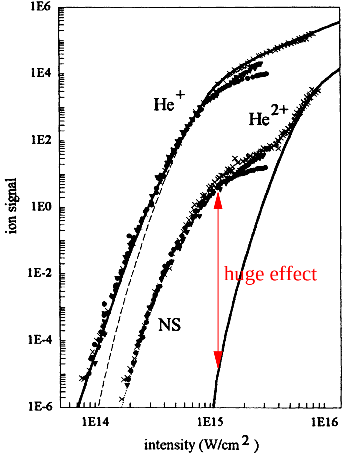
First results on HOHG in 3D He



calculations by Julius Rapp

Nonsequential double-ionization (NSDI)



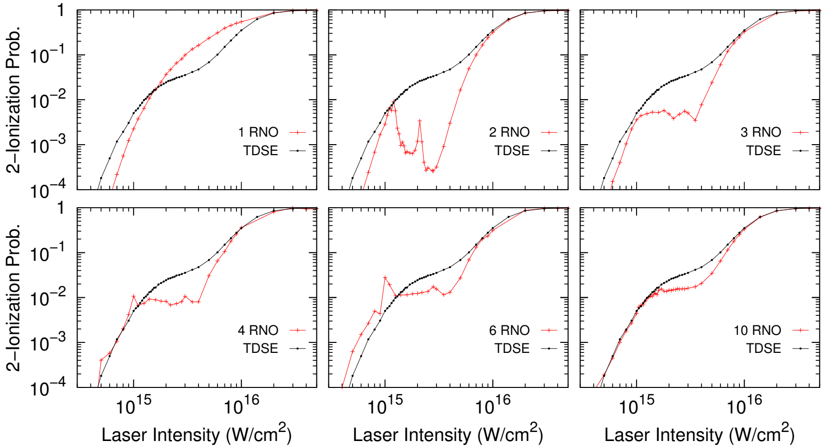


https://en.wikipedia.org/wiki/Double_ionization

B. Walker *et al.*, Phys. Rev. Lett. 73, 1227 (1994)

Nonsequential double-ionization (NSDI)

The "knee" in the double-ionization probability



M. Brics, J. Rapp, D. Bauer, Phys. Rev. A 90, 053418 (2014)

$\omega = 0.058$, 3-cycle $\sin^2$

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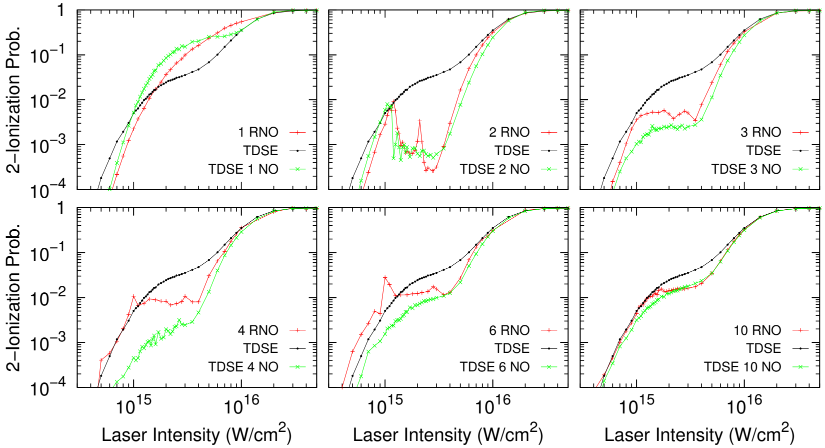

M. Brics, J. Rapp, D. Bauer, Phys. Rev. A 90, 053418 (2014)

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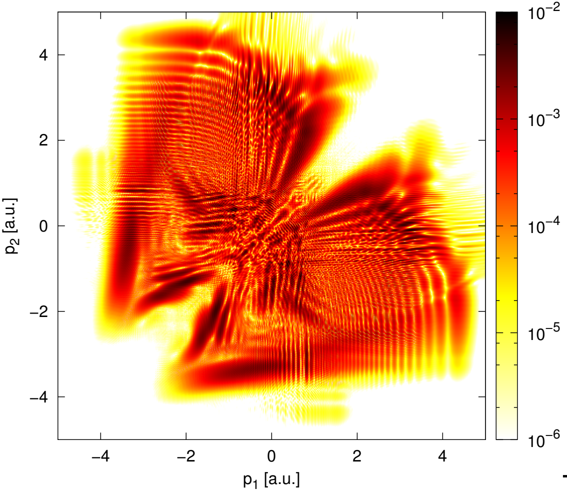
Nonsequential double-ionization (NSDI)

Correlated momentum spectra from TDSE



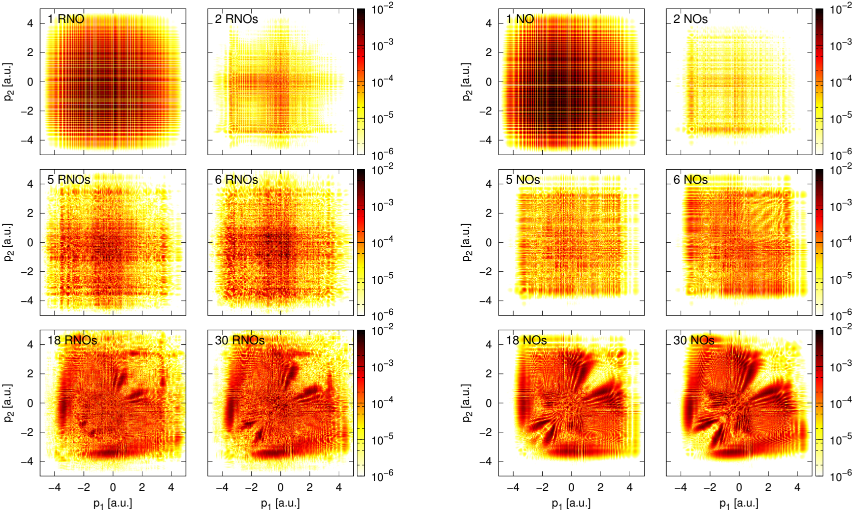
TDSE

M. Brics, J. Rapp, D. Bauer, Phys. Rev. A 90, 053418 (2014)

$\omega = 0.058$, 3-cycle $\sin^2$, 2.25×10^{15} Wcm^{-2}

Nonsequential double-ionization (NSDI)

Correlated momentum spectra from TRNOT?



TDRNOT

from TDSE

M. Brics, J. Rapp, D. Bauer, Phys. Rev. A 90, 053418 (2014)

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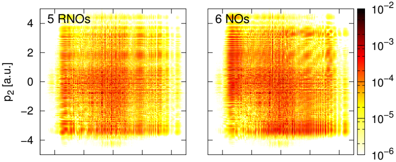
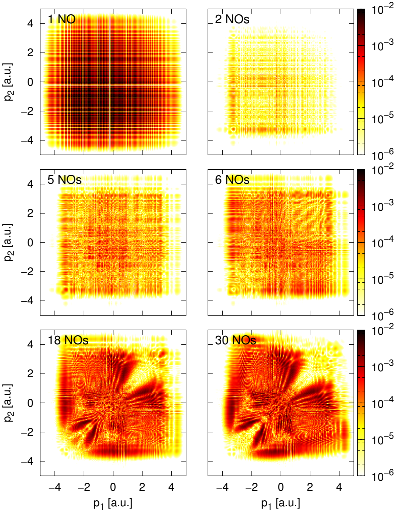


TDRNOT (30 NOs)

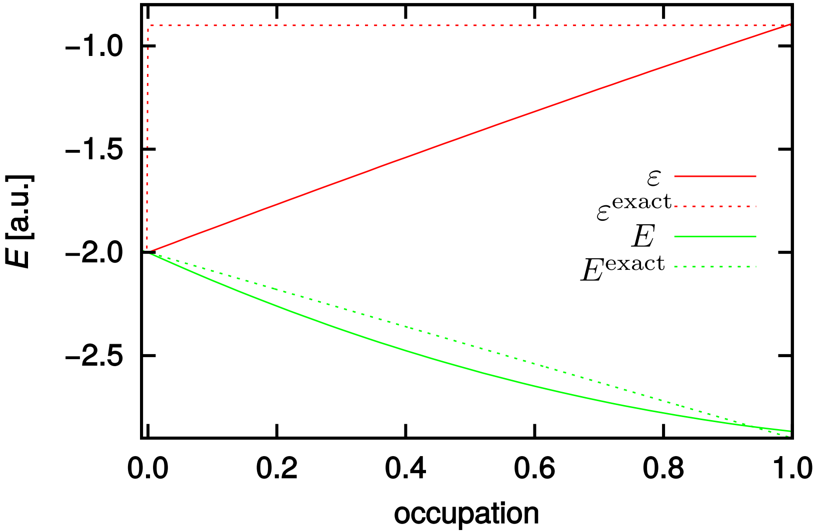


from TDSE

M. Brics, J. Rapp, D. Bauer, Phys. Rev. A 90, 053418 (2014)

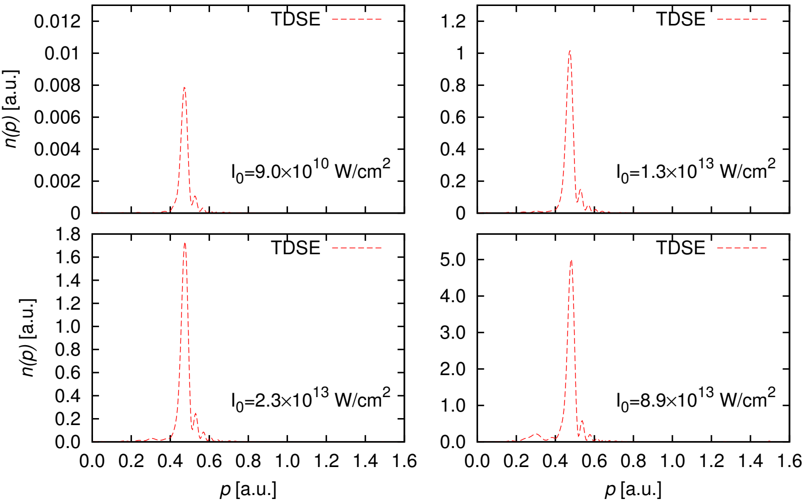
Moving photoelectron peak in TDDFT

... unless derivative discontinuity is taken care of



Moving photoelectron peak in TDDFT

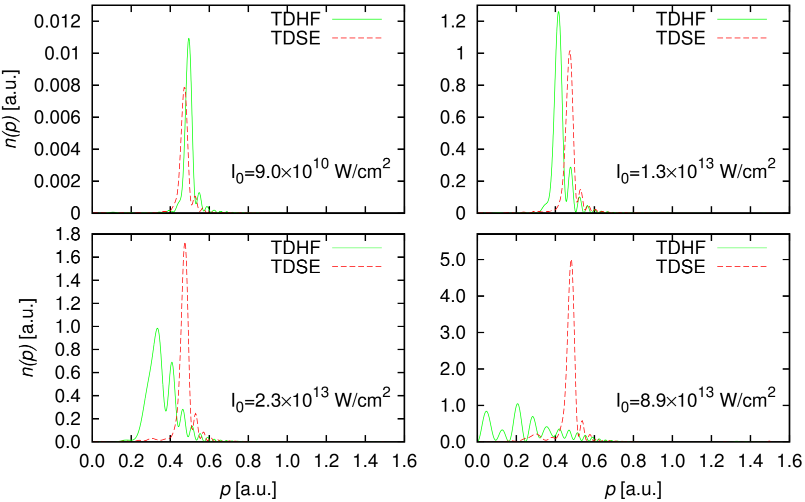
TDRNOT nails it



(2,46,2)-pulse, $\omega = 1$

Moving photoelectron peak in TDDFT

TDRNOT nails it



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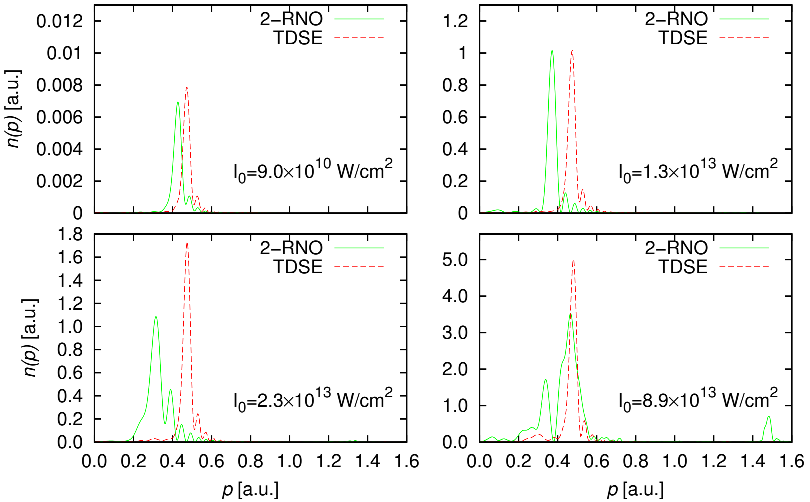

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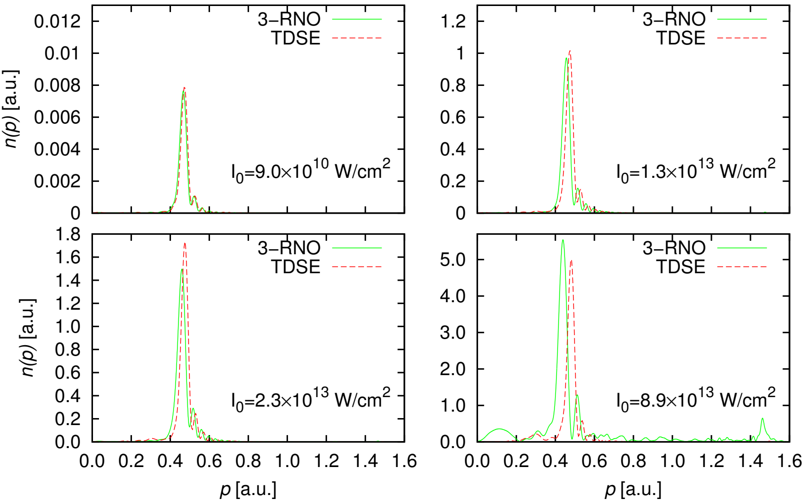

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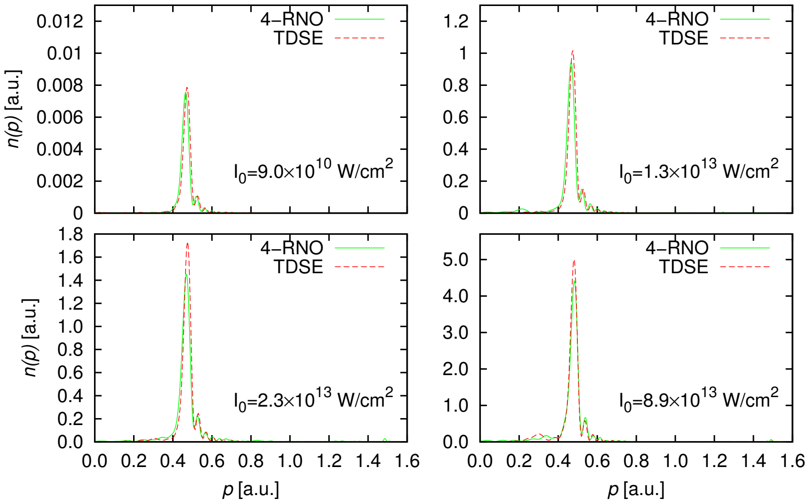

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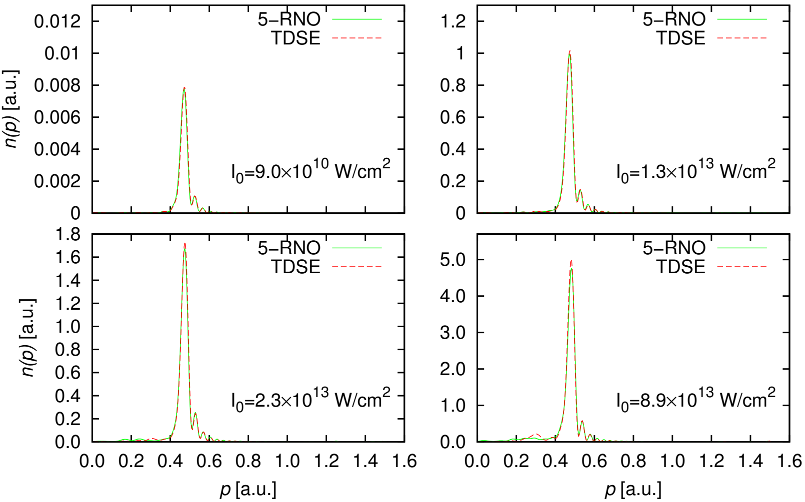

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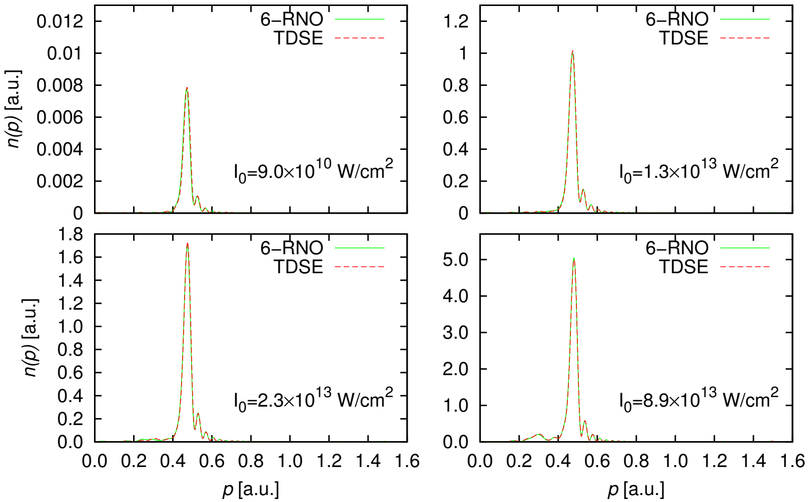
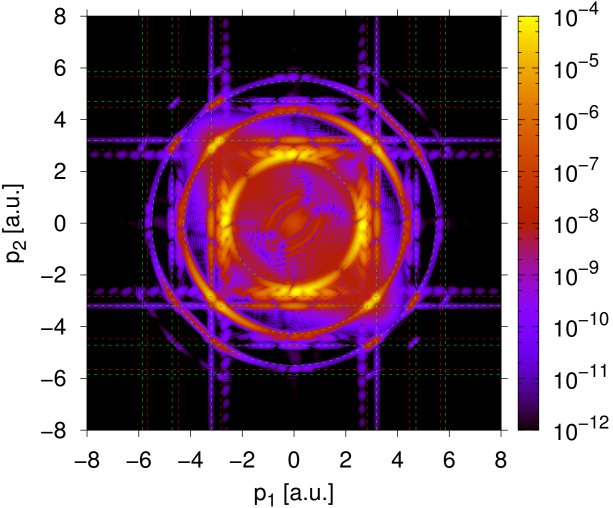


(2,46,2)-pulse, $\omega = 1$

Single-photon double ionization in He

20-cycle $\sin^2$**, 7.6 nm (**$\omega = 6$**),** 2.4×10^{14} Wcm^{-2}

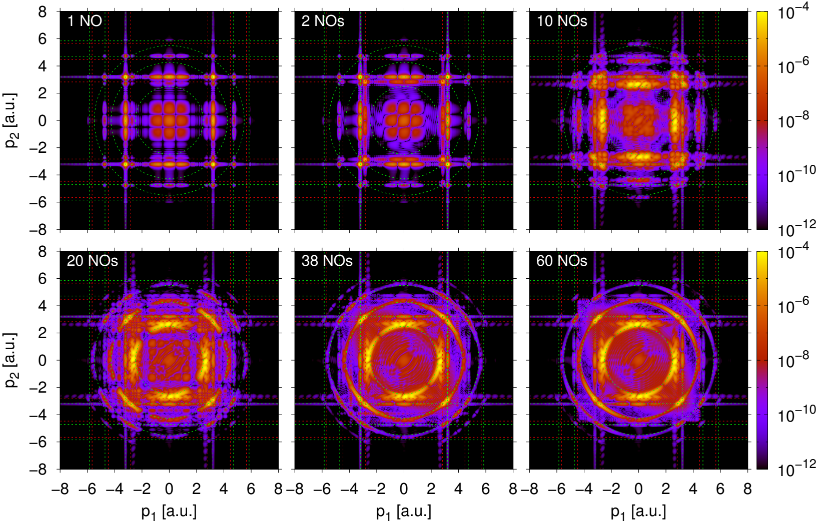
TDSE reference spectrum



Single-photon double ionization in He

20-cycle $\sin^2$**, 7.6 nm (**$\omega = 6$**),** 2.4×10^{14} $\mathrm{W cm^{-2}}$

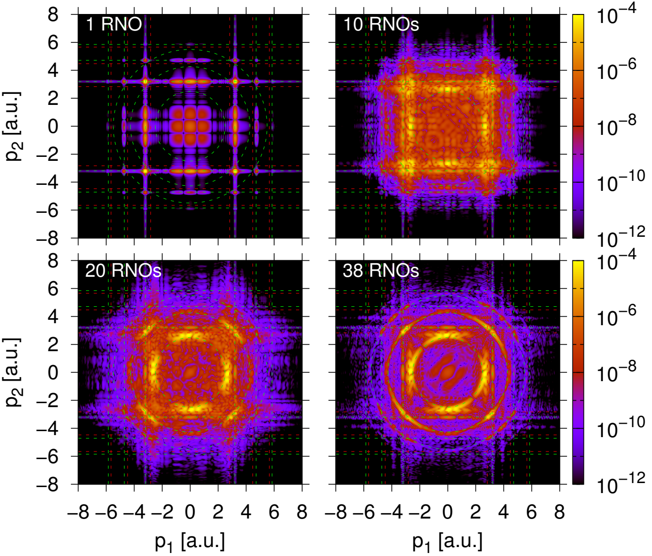
TDSE, with various numbers of NOs taken into account



Single-photon double ionization in He

20-cycle $\sin^2$**, 7.6 nm (**$\omega = 6$**),** 2.4×10^{14} Wcm^{-2}

TDRNOT, with various numbers of NOs propagated



TRNOT for simplest multi-component system: H_2^+

- Usual 1D-model of H_2^+:

$$\hat{H}(x, R, t) \;=\; \hat{h}_{\mathrm{e}} + \hat{h}_{\mathrm{n}} + V_{\mathrm{en}}(x, R),$$

where

$$\begin{aligned}
\hat{h}_{\mathrm{e}}(x, t) &= -\frac{1}{2\,\mu_{\mathrm{e}}}\,\partial_x^2 + q_e\, x\, E(t) \\
\hat{h}_{\mathrm{n}}(R) &= -\frac{1}{2\,\mu_{\mathrm{n}}}\,\partial_R^2 + V_{\mathrm{nn}}(R) \\
V_{\mathrm{en}}(x, R) &= -\frac{1}{\sqrt{(x - \frac{R}{2})^2 + \varepsilon_{\mathrm{en}}^2}} - \frac{1}{\sqrt{(x + \frac{R}{2})^2 + \varepsilon_{\mathrm{en}}^2}} \\
V_{\mathrm{nn}}(R) &= \frac{1}{\sqrt{R^2 + \varepsilon_{\mathrm{nn}}^2}}
\end{aligned}$$

TRNOT for simplest multi-component system: H_2^+

- Two types of 1-RDM from pure $\hat{\gamma}_{1,1}(t) = |\Psi(t)\rangle\langle\Psi(t)|$

$$\hat{\gamma}_{1,0}(t) = \mathrm{Tr}_{\mathrm{n}}\, \hat{\gamma}_{1,1}(t), \qquad \hat{\gamma}_{0,1}(t) = \mathrm{Tr}_{\mathrm{e}}\, \hat{\gamma}_{1,1}(t)$$

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- NOs and ONs

$$\hat{\gamma}_{1,0}(t)|k(t)\rangle = n_k(t)|k(t)\rangle, \qquad \hat{\gamma}_{0,1}(t)|K(t)\rangle = N_K(t)|K(t)\rangle$$

TRNOT for simplest multi-component system: H_2^+

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- Schmidt decomposition

$$\Psi(x, R, t) = \sum_k c_k(t)\, \varphi_k(x, t)\, \eta_k(R, t).$$

where $\varphi_k(x, t) = \langle x|k(t)\rangle$, $\eta_k(R, t) = \langle R|K(t)\rangle$

TRNOT for simplest multi-component system: H_2^+

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- One also finds $n_k(t) = N_K(t)$

TRNOT for simplest multi-component system: H_2^+

- Two types of 1-RDM from pure $\hat{\gamma}_{1,1}(t) = |\Psi(t)\rangle\langle\Psi(t)|$

$$\hat{\gamma}_{1,0}(t) = \mathrm{Tr}_\mathrm{n}\, \hat{\gamma}_{1,1}(t), \qquad \hat{\gamma}_{0,1}(t) = \mathrm{Tr}_\mathrm{e}\, \hat{\gamma}_{1,1}(t)$$

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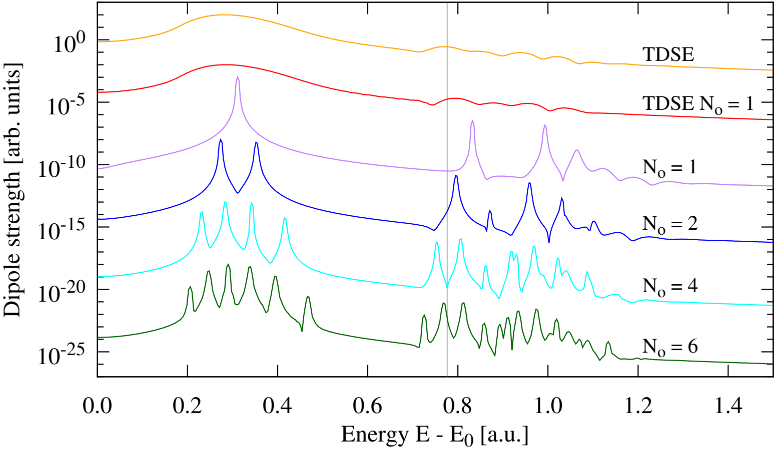
  where $\varphi_k(x, t) = \langle x|k(t)\rangle$, $\eta_k(R, t) = \langle R|K(t)\rangle$
- One also finds $n_k(t) = N_K(t)$
- Two—via matrix elements coupled—sets of EOMs for $|\tilde{k}(t)\rangle$ and $|\tilde{K}(t)\rangle$ can be derived

A. Hanusch, J. Rapp, M. Brics, D. Bauer, Phys. Rev. A**93**, 043414 (2016)

TRNOT for simplest multi-component system: H_2^+

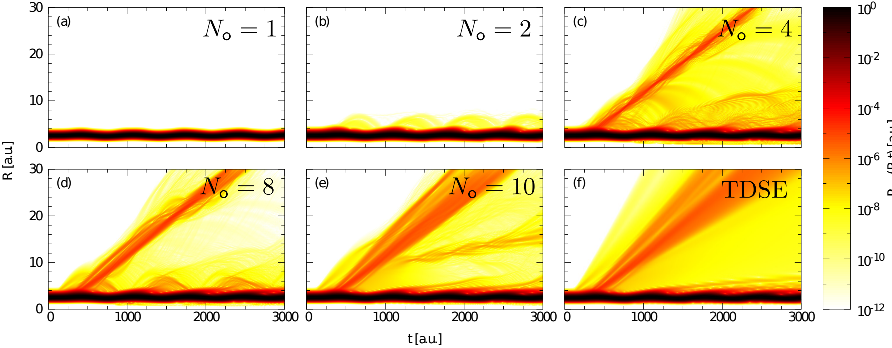
Linear response spectrum shows discrete peaks due to truncation error



A. Hanusch, J. Rapp, M. Brics, D. Bauer, Phys. Rev. A**93**, 043414 (2016)

TRNOT for simplest multi-component system: H_2^+

Nuclear density during 800-nm four-cycle $\sin^2$-shaped 10^{14} $\mathrm{Wcm^{-2}}$ pulse



A. Hanusch, J. Rapp, M. Brics, D. Bauer, Phys. Rev. A**93**, 043414 (2016)

Conclusion

TDRNOT so far

- method to simulate correlated dynamics
- exact for $N = 2$, requires approx. $\gamma_{2,ijkl}$ for $N > 2$
- no problem to calculate observables (if $\hat{\gamma}_2$ is sufficient)
- 3D He ($\rightarrow$ Julius Rapp)
- To do: TDRNOT $\neq$ MCTDHF (but work out connection, also to TDDMRG)
- No-free-lunch theorem confirmed yet another time