MCTDH Approach to Strong Field Dynamics

Suren Sukiasyan[1], Thomas Brabec[1] and Misha Ivanov[2]

[1]University of Ottawa, Canada
[2]Imperial College, London, UK

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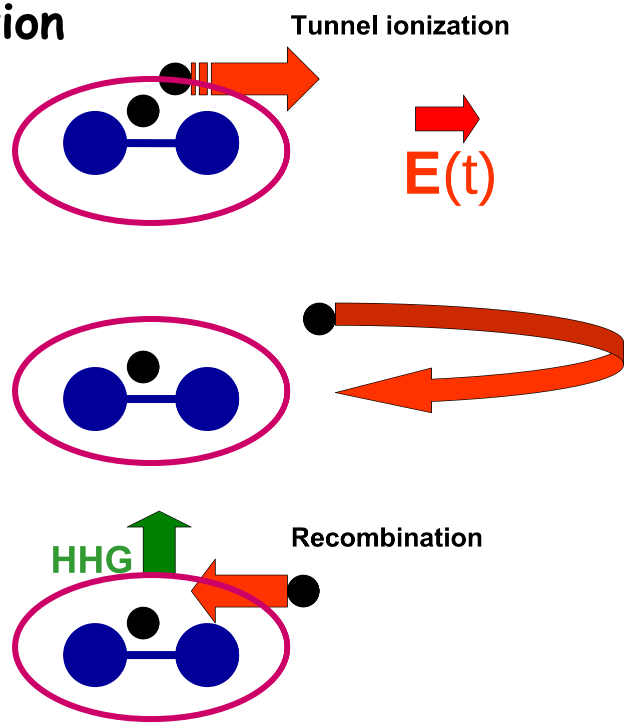
Motivation

Strong field dynamics – Role of electron correlation

HHG - Three-Step model

Single active electron approximation (SAE)



What is the role of higher excited states of the ion in strong field dynamics?

Overview

- Multi-Configuration Time-Dependent Hartree (MCTDH)
  Application to the strong field dynamics.
  Numerical exact solution of TDSE for diatomic system with 2 electrons in 2D each.

- Strong field dynamics
  Role of electron correlation.
  Origin of multi-electron excitations.

- High harmonic generation (HHG)
  Ionic Eigenstate Resolved Harmonic Generation.
  Role of multi-electron correlation in harmonic emission.

Multiconfiguration Time-dependent Hartree (MCTDH)

MCTDH Wave Function Ansatz

$$\Psi(q_1,q_2,\cdots,q_f,t)=\sum_J A_J\Phi_J \equiv \sum_{j_1=1}^{n_1}\cdots\sum_{j_f=1}^{n_f} A_{j_1\cdots j_f}(t)\prod_{\kappa=1}^{f}\varphi_{j_\kappa}^{(\kappa)}(q_\kappa,t)$$

$A_{j_j\cdots j_f}(t)$ - Expansion Coefficients

$\varphi_{j_\kappa}^{(\kappa)}(q_\kappa,t)$ - Basis Functions

Dirac-Frenkel Variational Principle

$$\left\langle \partial\Psi \middle| H - i\partial_t \middle| \Psi \right\rangle = 0$$

Constraints to define coefficients and functions uniquely

$$\left\langle \varphi_j^{(\kappa)}(0) \middle| \varphi_l^{(\kappa)}(0) \right\rangle = \delta_{jl}$$

$$\left\langle \varphi_j^{(\kappa)}(0) \middle| \dot{\varphi}_l^{(\kappa)}(0) \right\rangle = 0$$

MCTDH TD Basis Functions optimally represent the WF !

Reference: M.H.Beck,A.Jāckle,G.A.Worth and H.-D.Meyer, Phys.Rep. 324, 1 (2000)

MCTDH Equations of Motion

$$i\dot{A}_J = \sum_J \langle \Phi_J | H | \Phi_L \rangle A_L$$

$$i\dot{\varphi}_{j_\kappa}^{(\kappa)} = (1 - P^{(\kappa)})(\boldsymbol{\rho}^{(\kappa)})^{-1} \langle H \rangle^{(\kappa)} \varphi_{j_\kappa}^{(\kappa)}$$

$$P^{(\kappa)} = \sum_{j=1}^{n_\kappa} |\varphi_j^{(\kappa)}\rangle\langle\varphi_j^{(\kappa)}|$$ - Projector

$$\Phi_J \equiv \prod_{\kappa=1}^{f} \varphi_{j_\kappa}^{(\kappa)}$$

$$\rho_{jl}^{(\kappa)} = \langle \Psi_j^{(\kappa)} | \Psi_l^{(\kappa)} \rangle$$ - Density matrix

$$\langle H \rangle_{jl}^{(\kappa)} = \langle \Psi_j^{(\kappa)} | H | \Psi_l^{(\kappa)} \rangle$$ - Mean-Field matrix

where $\Psi_l^{(\kappa)} = \sum_{j_1} \cdots \sum_{j_{\kappa-1}} \sum_{j_{\kappa+1}} \cdots \sum_{j_f} A_{j_1 \cdots j_{\kappa-1} l j_{\kappa+1} \cdots f} \varphi_{j_1}^{(1)} \cdots \varphi_{j_{\kappa-1}}^{(\kappa-1)} \varphi_{j_{\kappa+1}}^{(\kappa+1)} \cdots \varphi_{j_f}^{(f)}$ - Single-Hole Functions

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Complete basis set – $n_\kappa \to N_\kappa$ $\quad \dot{\varphi}_{j_\kappa}^{(\kappa)} = 0 \quad \to \quad i\dot{A}_J = \sum_L H_{JL} A_L$ Standard approach

MCTDH WF monotonically converges toward the numerical exact solution !

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Hamiltonian representation in MCTDH

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The multi-dimensional integrations in $\langle H\rangle_{jl}^{(\kappa)}, \langle\Phi_J|H|\Phi_L\rangle$ can be efficiently calculated if

The Hamiltonian is represented

$$H=\sum_{r=1}^{s}c_r\prod_{\kappa=1}^{f}h_r^{(\kappa)}$$

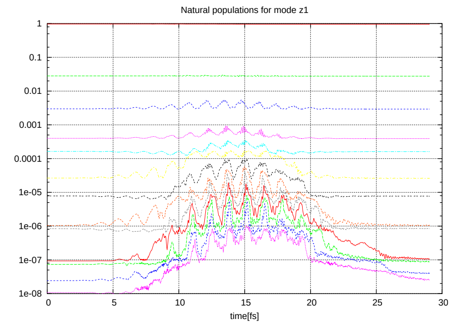
Matrix elements -

$$\langle\Phi_J|H|\Phi_L\rangle=\sum_{r=1}^{s}c_r\prod_{\kappa=1}^{f}h_r^{(\kappa)}\langle\varphi_{j_\kappa}^{(\kappa)}|h_r^{(\kappa)}|\varphi_{l_\kappa}^{(\kappa)}\rangle$$

Convergence in MCTDH

Density operator

$$\hat{\rho}^{(\kappa)}(Q_\kappa,Q'_\kappa)=\sum_{j,l=1}^{n_\kappa}\varphi_j^{(\kappa)}(Q_\kappa)\rho_{jl}^{(\kappa)}\varphi_l^{(\kappa)}(Q'_\kappa)$$



Reference: **M.H.Beck,A.Jāckle,G.A.Worth and H.-D.Meyer, Phys.Rep. 324, 1 (2000)**

MCTDH Applications

- Photodissociation
- Photoabsorption
- Molecule-surface scattering
- Reactive scattering
- Electron-scattering processes
- Density operator propagation

$$\Psi(q_1,q_2,\cdots,q_f,t)=\sum_{j_1=1}^{n_1}\cdots\sum_{j_f=1}^{n_f}A_{j_1\cdots j_f}(t)\prod_{\kappa=1}^{f}\varphi_{j_\kappa}^{(\kappa)}(q_\kappa,t)$$

MCTDHF – Applications to multi-electron strong field dynamics

$$\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_n,t)=\sum_{j_1\ldots j_n}A_{j_1\ldots j_n}(t)\,\varphi_{j_1}(\mathbf{r}_1,s_1,t)\cdots\varphi_{j_n}(\mathbf{r}_n,s_n,t)$$

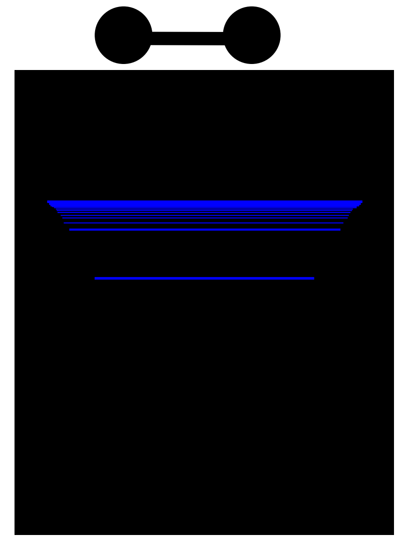
MCTDH vs MCTDHF (few-electron systems)

MCTDHF - $(x_1; y_1; z_1); (x_2; y_2; z_2)$ - $n(n-1)/2$ configurations

MCTDH - $(x_1; x_2); (y_1; y_2); (z_1; z_2)$ - n^3 configurations
- $(x_1; y_1); (x_2; y_2); (z_1; z_2)$ - n^3 configurations
- $(x_1; y_1); (x_2; y_2); z_1; z_2$ - n^4 configurations

Model diatomic system in strong laser fields

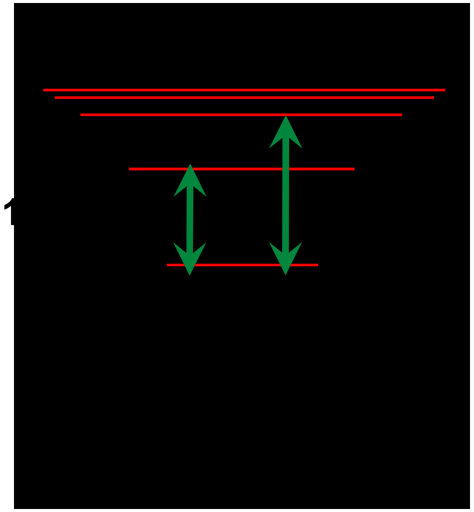
Model system : H_2 with 2D electrons (N_2)



MCTDH Wave Function

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,t) = \sum_{j_1 j_2 j_3 j_4} A_{j_1 j_2 j_3 j_4}(t)\,\varphi_{j_1}(x_1,t)\,\varphi_{j_2}(x_2,t)\,\varphi_{j_3}(y_1,t)\,\varphi_{j_4}(y_2,t)$$

Initial state: Ψ_g *is symmetric*



$$\hat{\mathbf{S}}\,\hat{\mathrm{H}}(t) - \hat{\mathrm{H}}(t)\,\hat{\mathbf{S}} = 0$$

Spin is included in calculation !

Model diatomic system in strong laser fields

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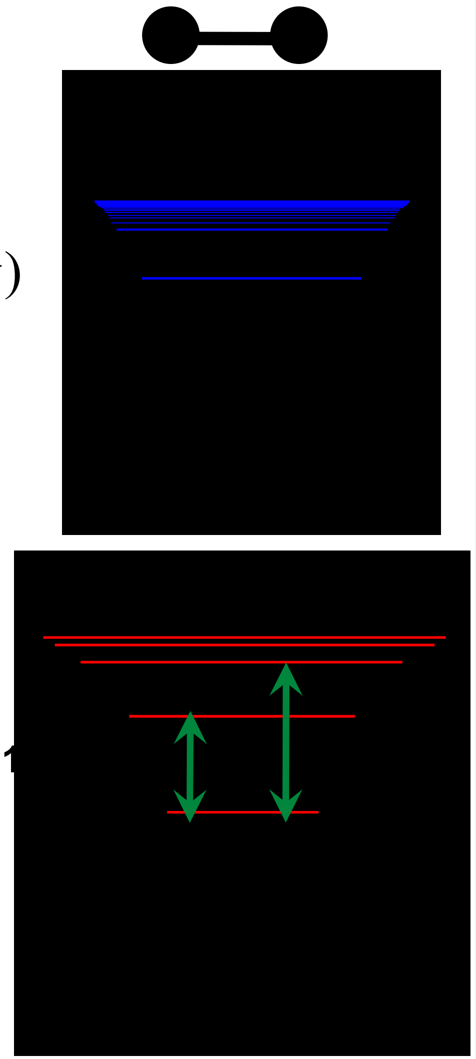

MCTDH Wave Function

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Electron-electron potential expansion

$$V_{ee}(\mathbf{r}_1,\mathbf{r}_2)=\frac{1}{\sqrt{(x_1-x_2)^2+(y_1-y_2)^2+a^2}}=\sum_{i=1}^{s} v_i(x_1-x_2)\,u_i(y_1-y_2)$$

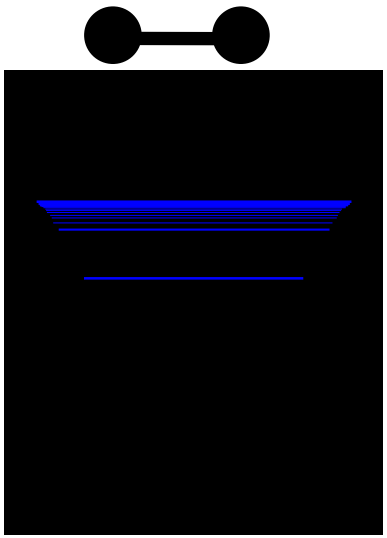
Matrix elements using the Convolution Theorem (**FFT**)

$$\langle v_i\rangle_{j_1j_2l_1l_2}=\langle \varphi_{j_1}(x_1)\varphi_{j_2}(x_2)|v_i(x_1-x_2)|\varphi_{l_1}(x_1)\varphi_{l_2}(x_2)\rangle$$
$$=\int \varphi^*_{j_1}(x_1)\varphi_{l_1}(x_1)\,dx_1\int \varphi^*_{j_2}(x_2)\varphi_{l_2}(x_2)\,v_i(x_1-x_2)\,dx_2$$

Numerical scaling: $2N\log N+N$

Model diatomic system in strong laser fields

Model system : H_2 with 2D electrons (N_2)

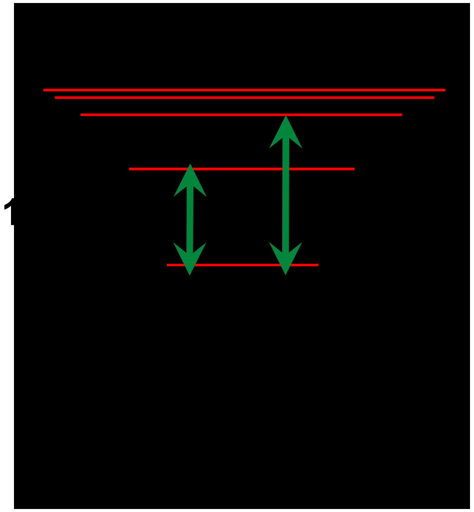


MCTDH Wave Function

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,t) = \sum_{j_1 j_2 j_3 j_4} A_{j_1 j_2 j_3 j_4}(t)\,\varphi_{j_1}(x_1,t)\,\varphi_{j_2}(x_2,t)\,\varphi_{j_3}(y_1,t)\,\varphi_{j_4}(y_2,t)$$

Computational times

Field : $\mathrm{E}(t) = \mathrm{E}_0 \mathrm{Sin}^2(\pi t/T)\,\mathrm{Cos}(\omega t)$ $\qquad T = 2\pi N/\omega$



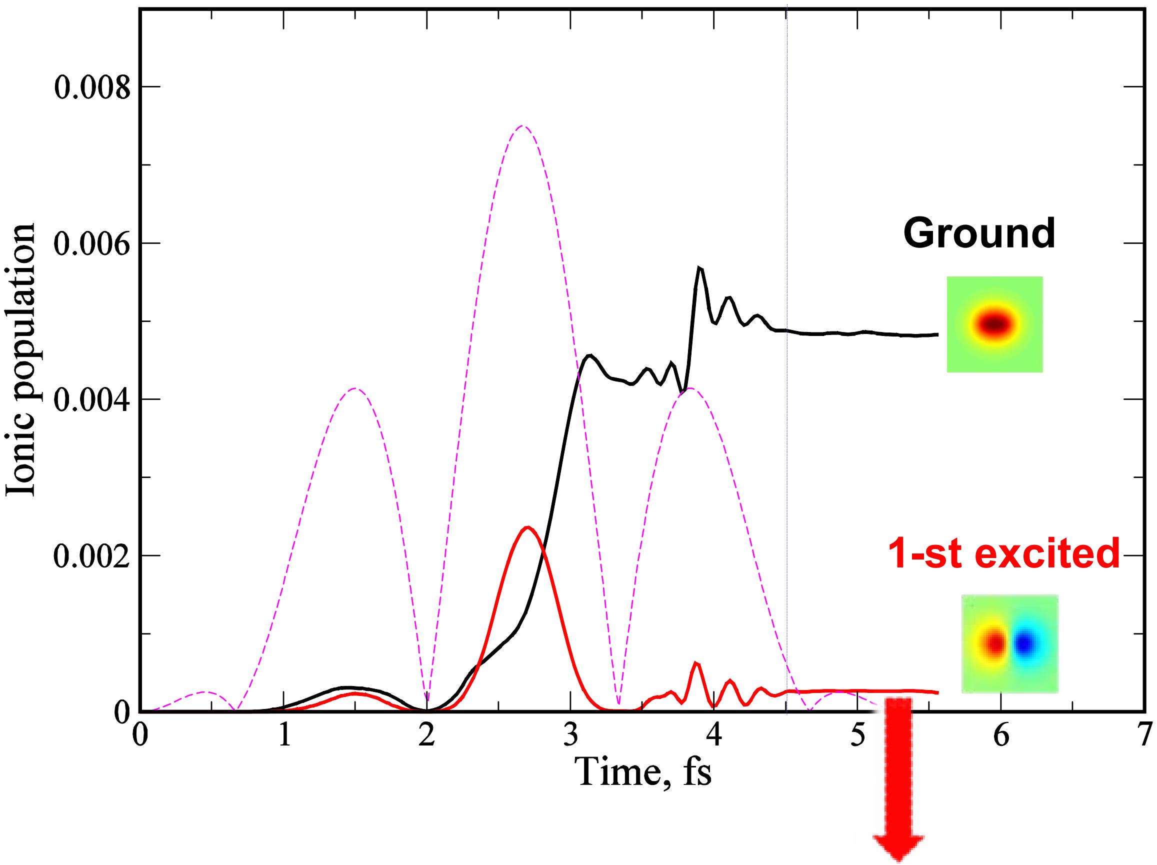
HHG : **$I=1.10^{14}$ W/cm^2 , λ=800 nm , N=10**

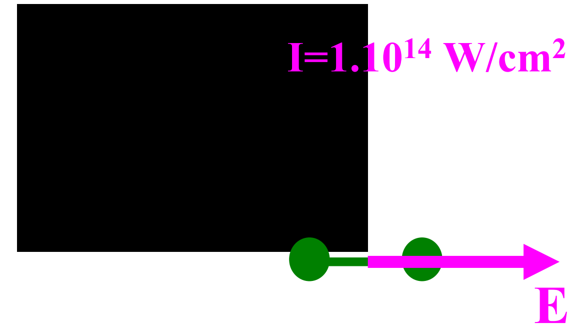
n =15 -- ~ 4 h

NSDI : **$I=2.10^{14}$ W/cm^2 , λ=800 nm , N=2**

n =29 -- ~ 120 h (single core CPU)

Ionization – Ionic bound state dynamics





Ionization WF

$$\Psi_I(t) = \Psi(t) - \sum_m \langle \Psi_m | \Psi(t) \rangle \Psi_m$$

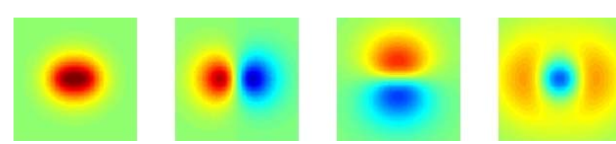
Ionic WF

$$\phi_i(\mathrm{r}_1, t) = \langle \varphi_i(\mathrm{r}_2) | \Psi_I(\mathrm{r}_1, \mathrm{r}_2\ t) \rangle$$

Ionic population

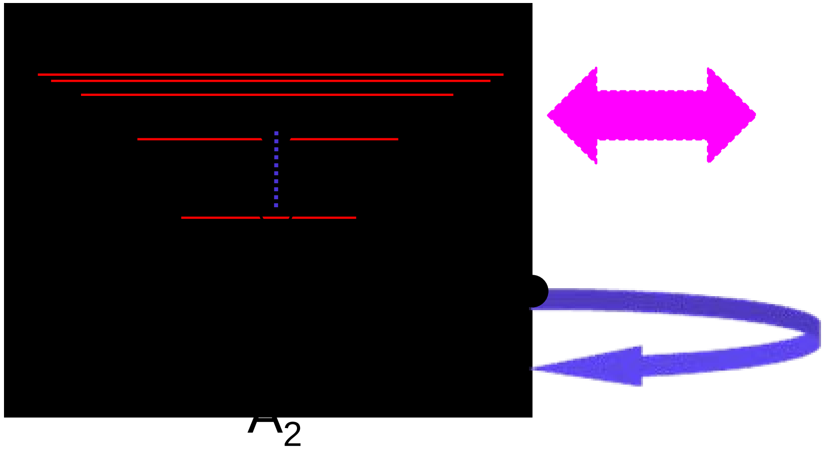
$$p_i(t) = 2\langle \phi_i | \phi_i \rangle$$

~ 6% of ground state population



Ionization – Ionic bound state dynamics

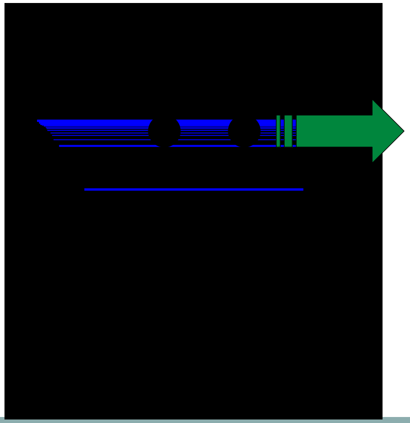
Origin of Ionic excitations



1. Electric Field

2. Electron rescattering

3. Tunneling via excited states of the neutral



Ionization – Ionic bound state dynamics

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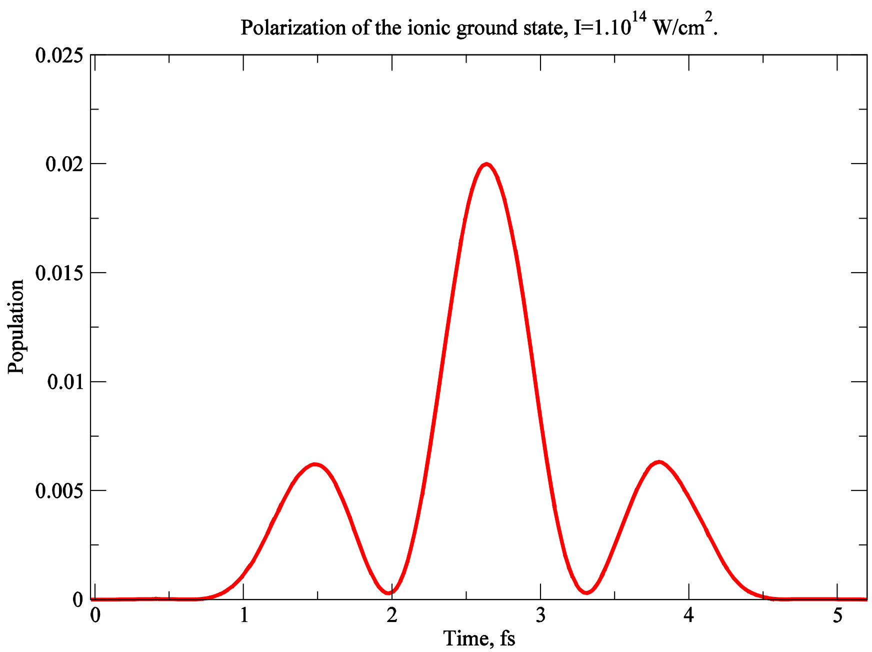
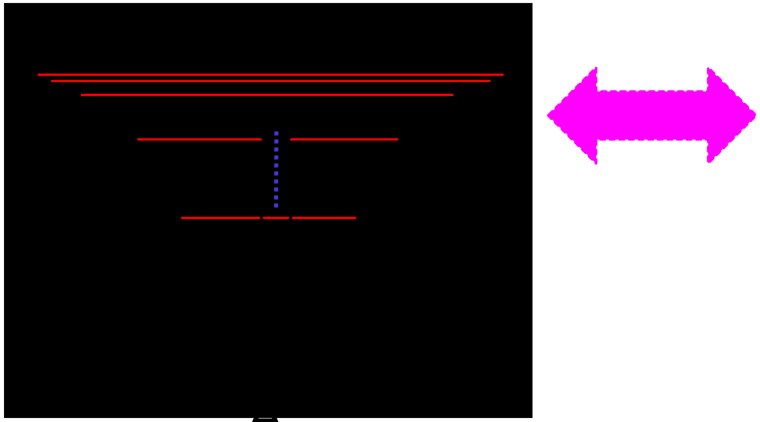




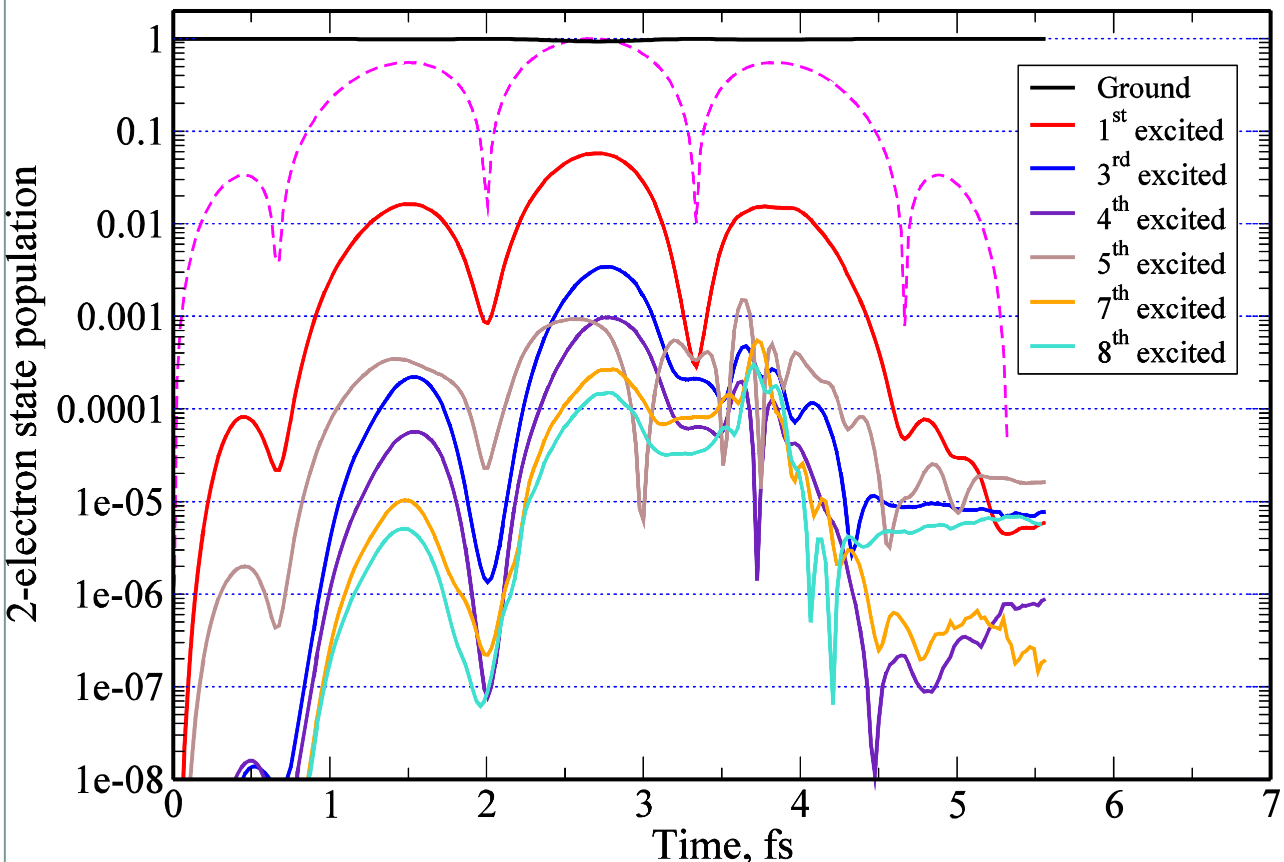
A_2

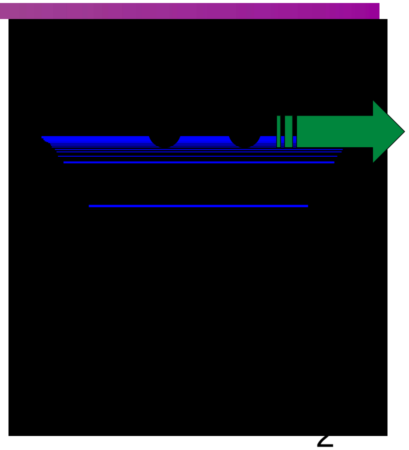
Population of 1-st ionic excited state

$$p_1(t) = \left| \left\langle \varphi_1 \middle| \phi(t) \right\rangle \right|^2$$

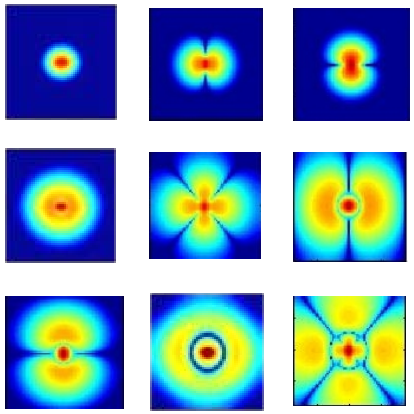
Ionization – Ionic bound state dynamics

3. Tunneling via excited states of the neutral





$$p_m(t) = \left|\left\langle \Psi_m \middle| \Psi(t) \right\rangle\right|^2$$



Ionization – Ionic bound state dynamics

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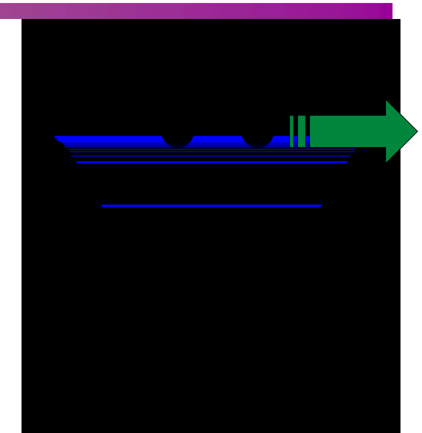
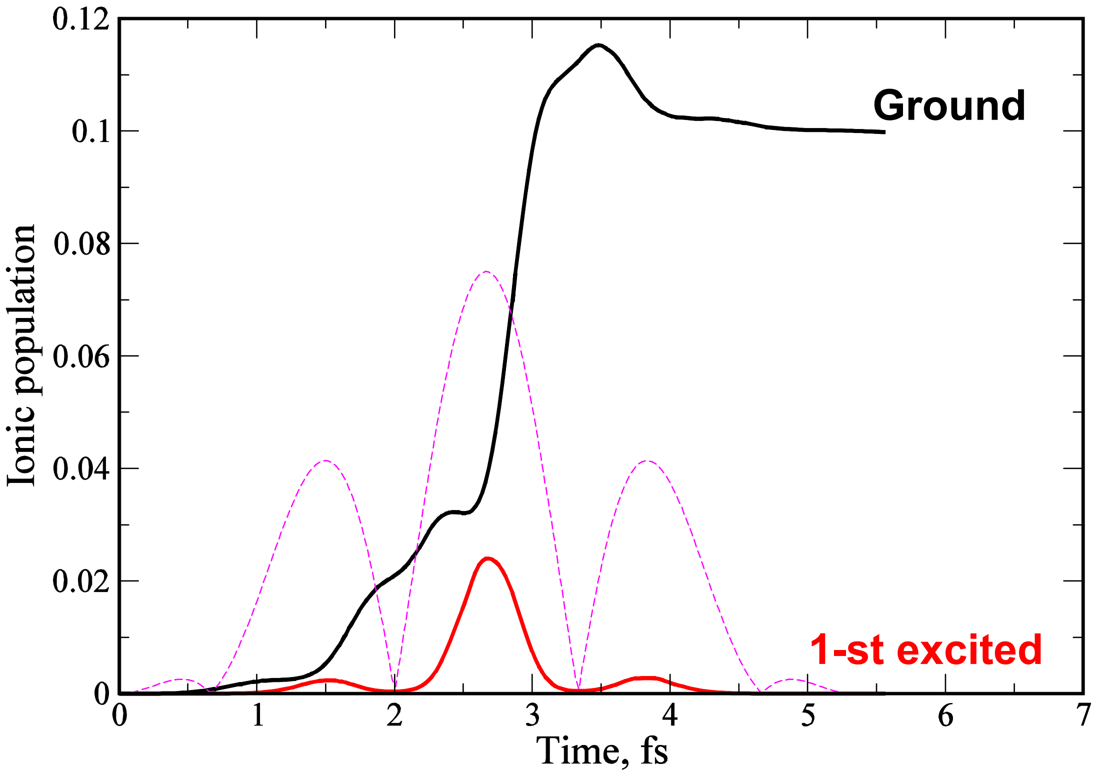
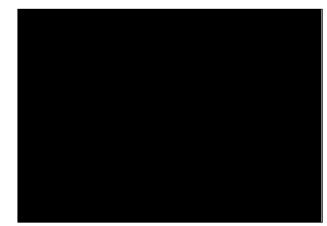
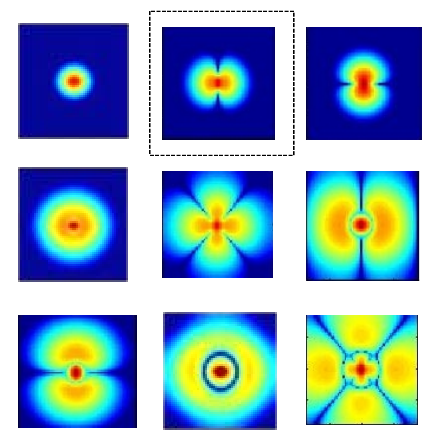






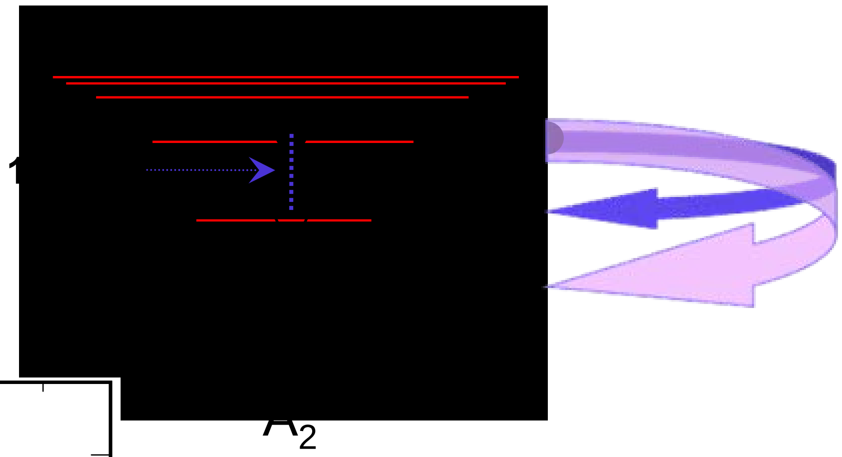


Is possible for realistic 3D multi-electron systems!

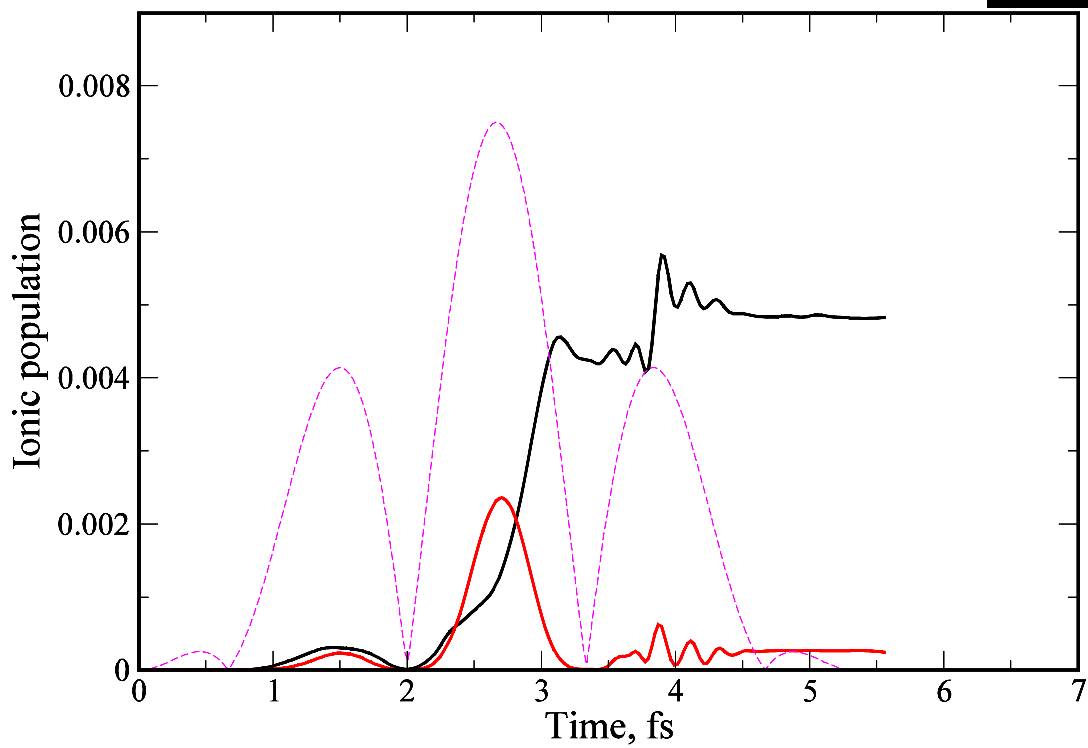
Ionization – Ionic bound state dynamics

2. Electron rescattering

$$E_{\max} \cong 3.2U_p \approx 18\,\mathrm{eV}$$



$$\mathrm{E}(t) = \mathrm{E}_x(t) + \varepsilon\,\mathrm{E}_y(t)$$



Ionization – Ionic bound state dynamics

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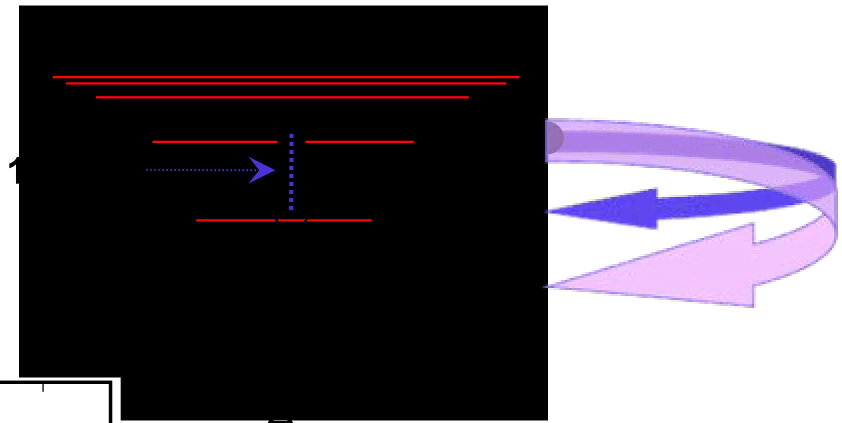
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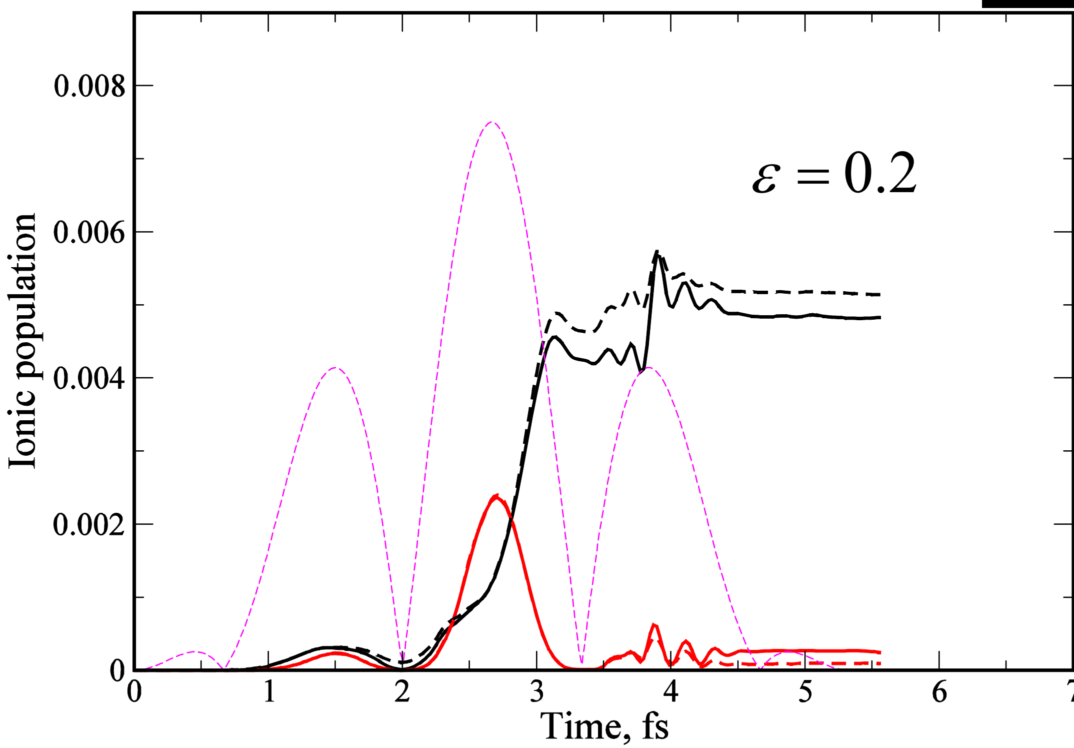
$$\mathrm{E}(t) = \mathrm{E}_x(t) + \varepsilon\,\mathrm{E}_y(t)$$



Ionization – Ionic bound state dynamics

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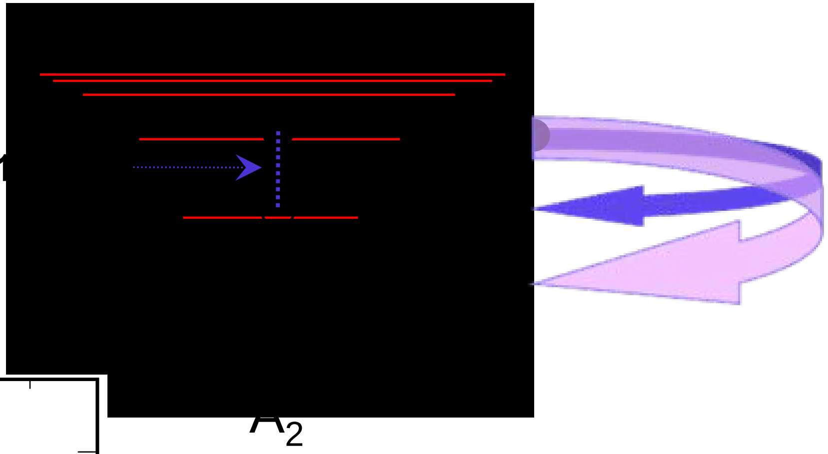

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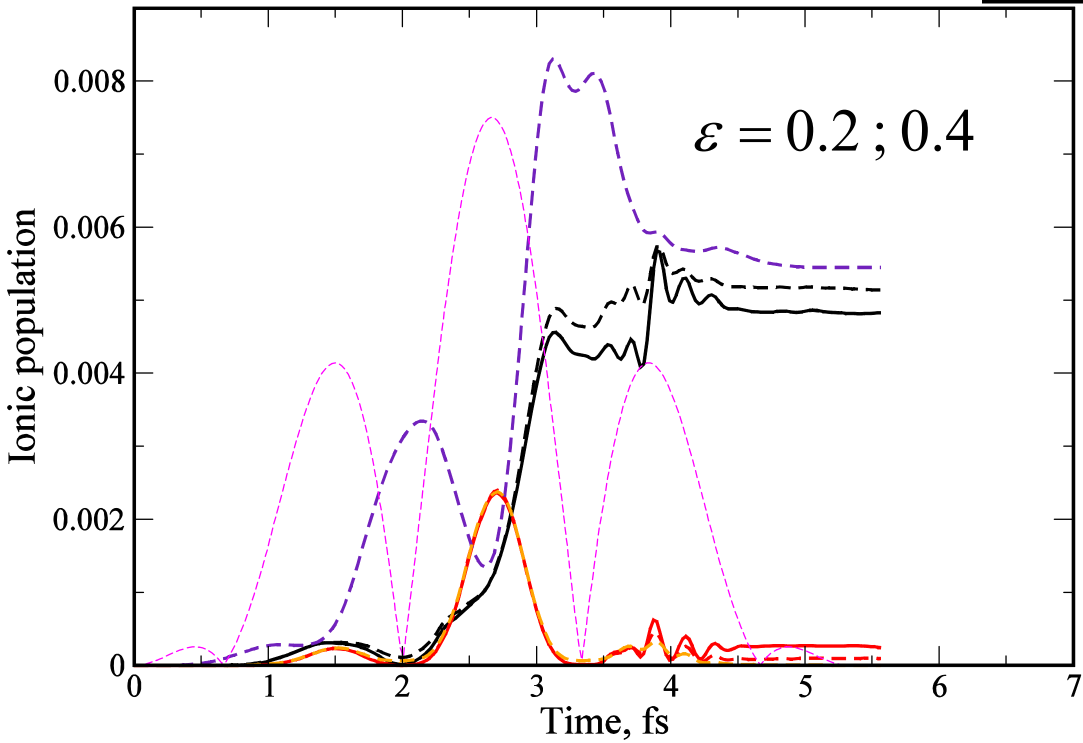

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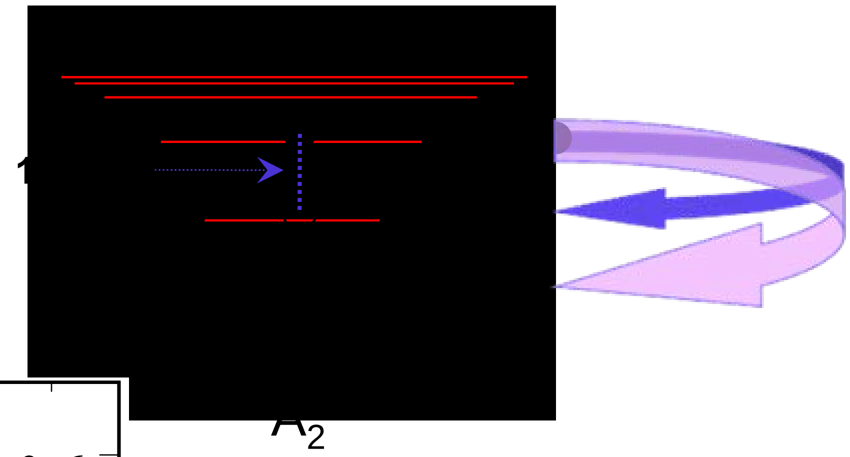

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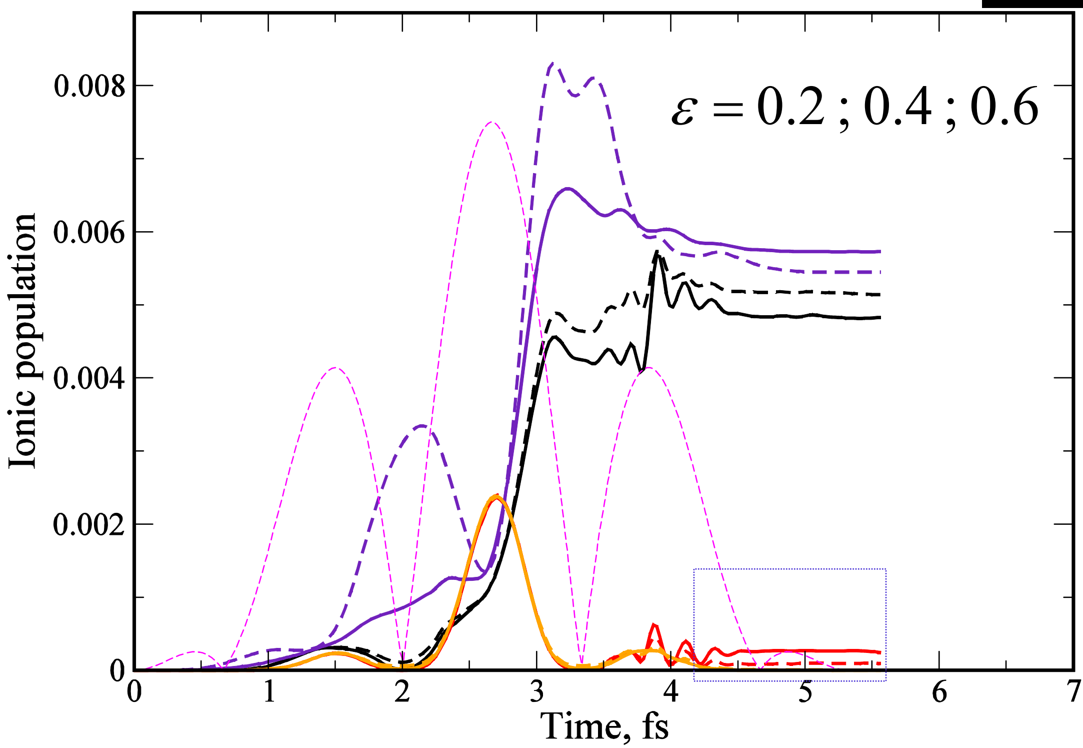

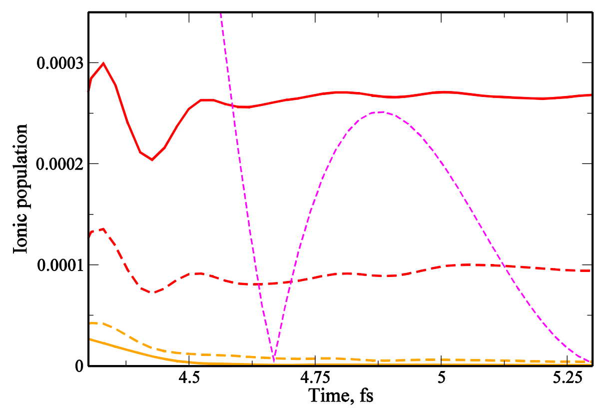

Ionization – Ionic bound state dynamics

2. Electron rescattering

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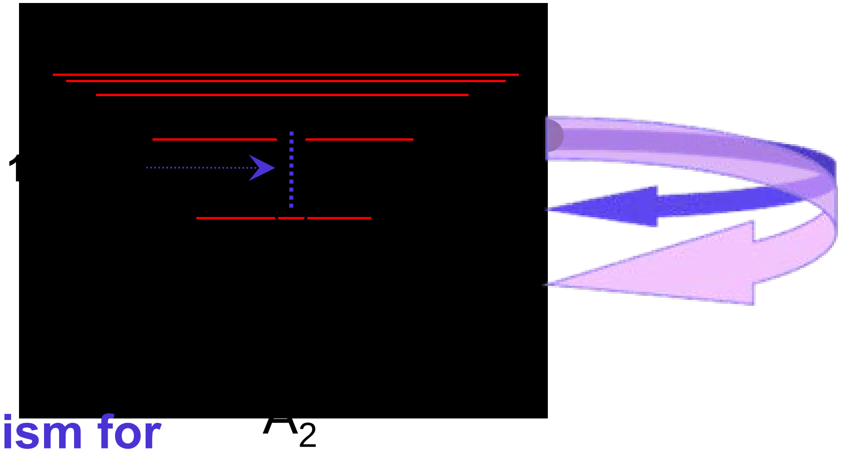
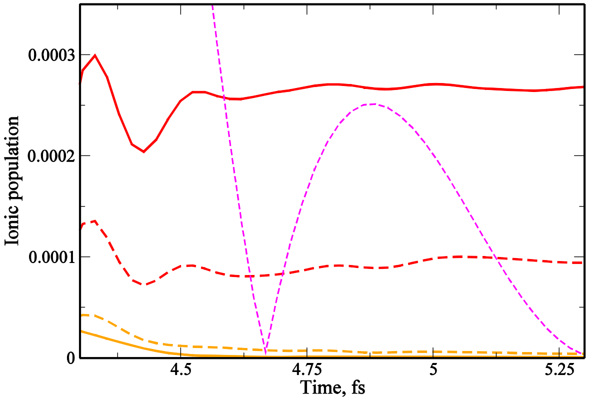


Conclusions

Electron rescattering is the main mechanism for the ionic excitation for the model A_2 diatom!

$$E(t) = E_x(t) + \varepsilon\, E_y(t)$$

For higher laser intensities the effect may be enhanced!



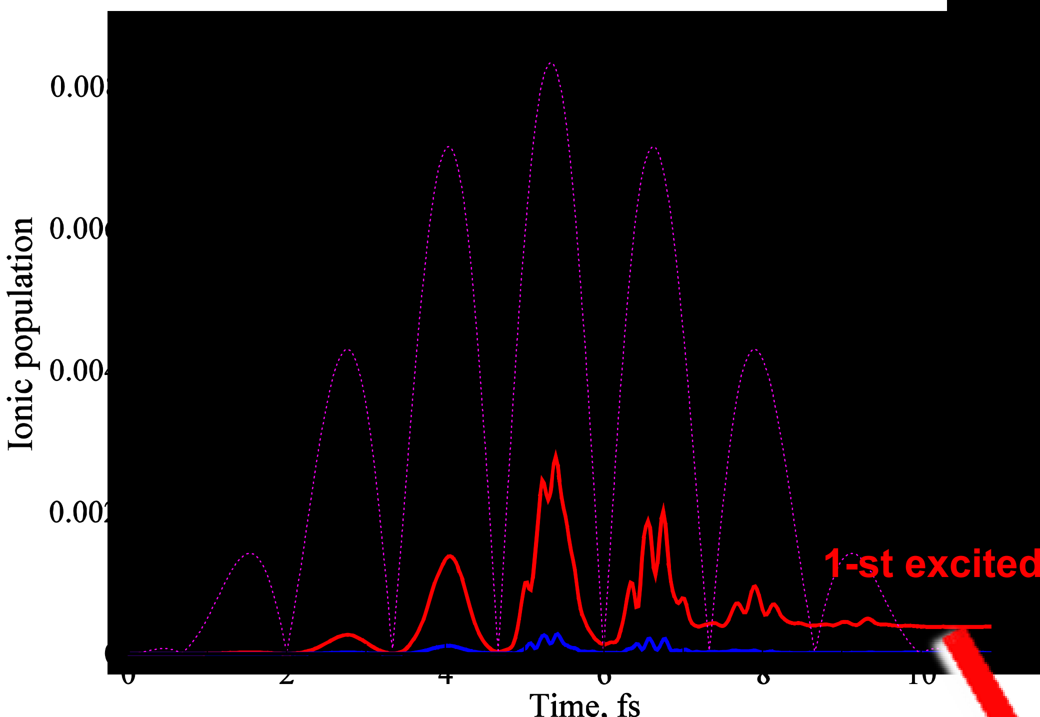
The effect will be more pronounced for realistic 3D multi-electron systems!

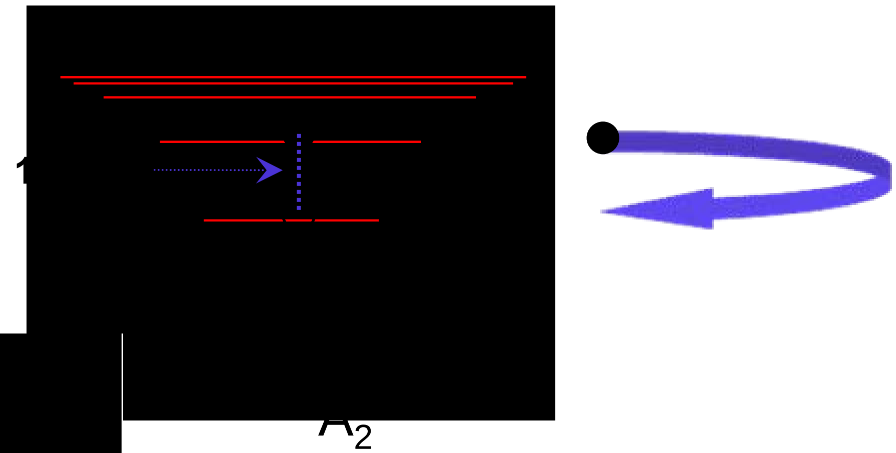
SAE is not valid for precise description of strong field multi-electron dynamics!

Ionization – Role of electron rescattering

Dependence of rescattering on

1. Laser pulse duration





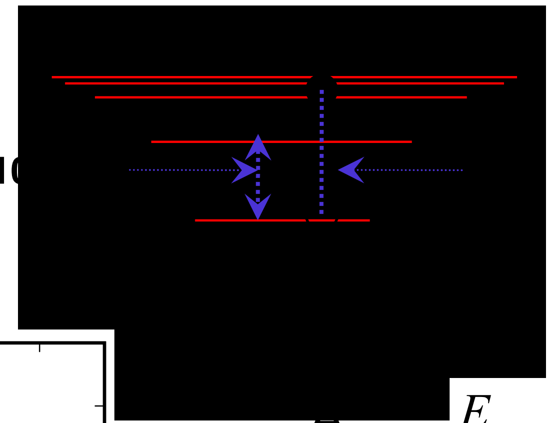
$$E_{\max} \cong 3.2 U_p \approx 18\,\mathrm{eV}$$

~ 8% of ground state population

Ionization – Role of electron rescattering

Dependence of rescattering on

2. Molecular orientation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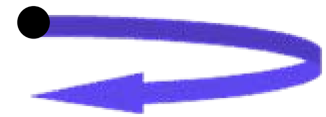

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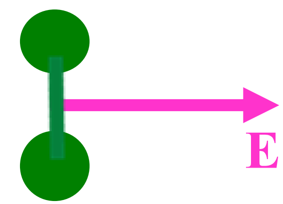
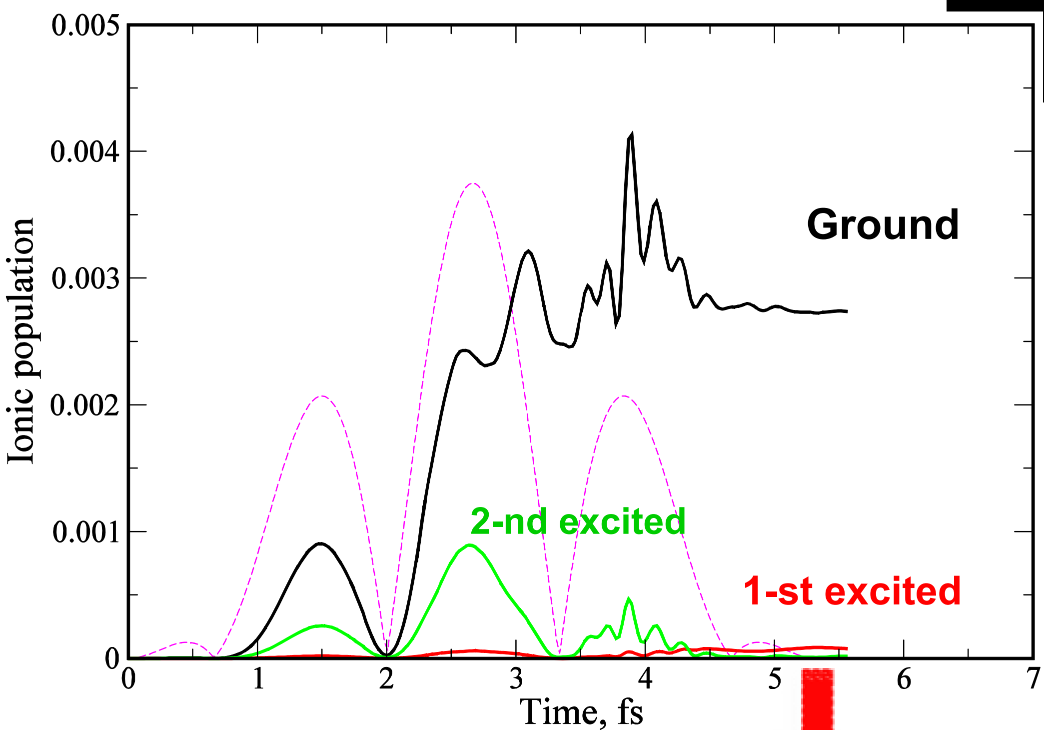
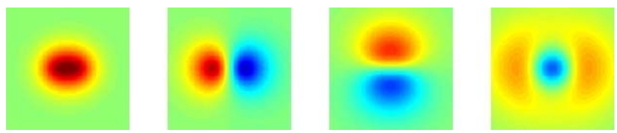


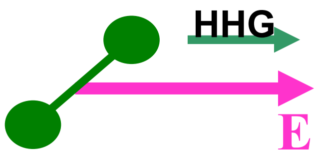




~ 3% of ground state population

Excitation via rescattering depends on ionic orbital symmetry!

High harmonic generation (HHG) - Role of Ionic excitations



I=1.10^14 W/cm^2 , λ=800 nm , N=10

Ionic Eigenstate Resolved HHG

$\varphi_i(\mathbf{r})$ **Ionic Eigenstates**

$$\Psi_{\text{IER}}^{(M)}(\mathbf{r}_1,\mathbf{r}_2,t)=\sum_{i=1}^{M}\left[\phi_i(\mathbf{r}_1,t)\,\varphi_i(\mathbf{r}_2)+\varphi_i(\mathbf{r}_1)\,\phi_i(\mathbf{r}_2,t)\right]$$

$$\boxed{\phi_i(\mathbf{r}_1,t)=\left\langle \varphi_i(\mathbf{r}_2)\middle|\Psi(\mathbf{r}_1,\mathbf{r}_2,t)\right\rangle}$$

HHG spectrum

$$\mathbf{I}_M(\Omega)=\left|\int\left\langle \alpha_g(t)\Psi_g\right|\hat{a}\left|\Psi_{\text{IER}}^{(M)}\right\rangle e^{i\Omega t}dt\right|^2$$

$$\hat{a}(\mathbf{r})=-\frac{\partial V}{\partial \mathbf{r}}-\mathbf{E}(t)$$

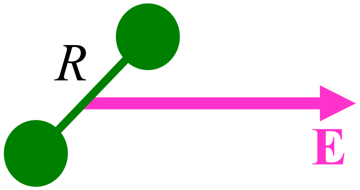
Direct

$$\left\langle \alpha_g(t)\Psi_g\middle|\hat{a}(\mathbf{r}_1)\middle|\phi_i(\mathbf{r}_1,t)\,\varphi_i(\mathbf{r}_2)\right\rangle=\alpha_g(t)\left\langle \psi_i^{\text{D}}(\mathbf{r}_1)\middle|\hat{a}(\mathbf{r}_1)\middle|\phi_i(\mathbf{r}_1,t)\right\rangle$$

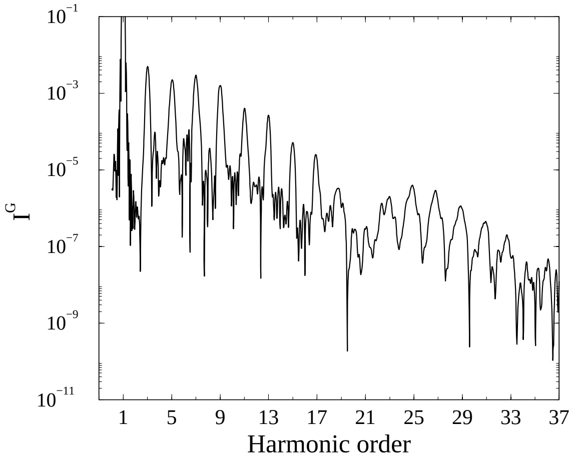
Exchange

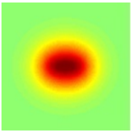
$$\left\langle \alpha_g(t)\Psi_g\middle|\hat{a}(\mathbf{r}_1)\middle|\varphi_i(\mathbf{r}_1)\,\phi_i(\mathbf{r}_2,t)\right\rangle$$

Two-center Interference in HHG



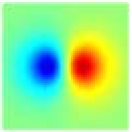
$$R \cos\theta = \frac{\lambda}{2} k$$





k=2n+1 - Destructive interference

k=2n - Constructive interference

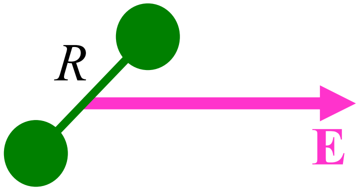


k=2n+1 - Constructive interference

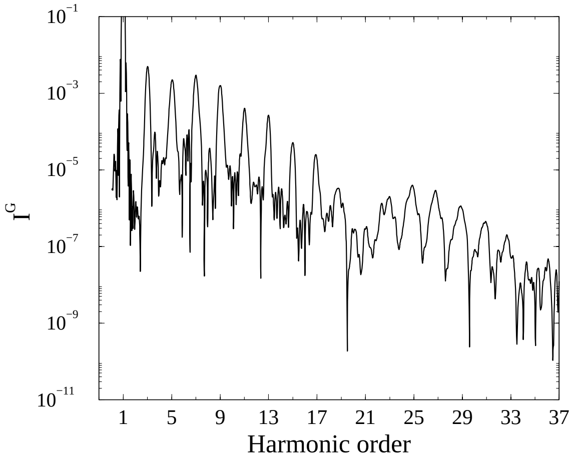
k=2n - Destructive interference

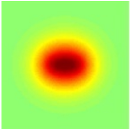
Reference: **M.Lein** *et al*, **Phys.Rev.Lett. 183903 (2002)**

Two-center Interference in HHG



$$R\,\mathrm{Cos}\,\theta = \frac{\lambda}{2}k$$





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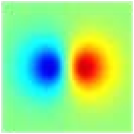


k=2n+1 - Constructive interference

k=2n - Destructive interference

Two-center Interference is present only in *Direct* harmonic emission

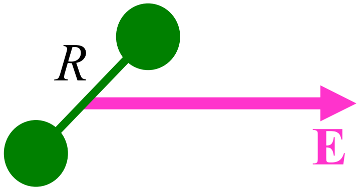
Direct

$$\left\langle \alpha_g(t)\Psi_g \middle| \hat{a}(\mathbf{r}_1) \middle| \phi_i(\mathbf{r}_1,t)\,\varphi_i(\mathbf{r}_2) \right\rangle = \alpha_g(t)\left\langle \psi_i^{D}(\mathbf{r}_1) \middle| \hat{a}(\mathbf{r}_1) \middle| \phi_i(\mathbf{r}_1,t) \right\rangle$$

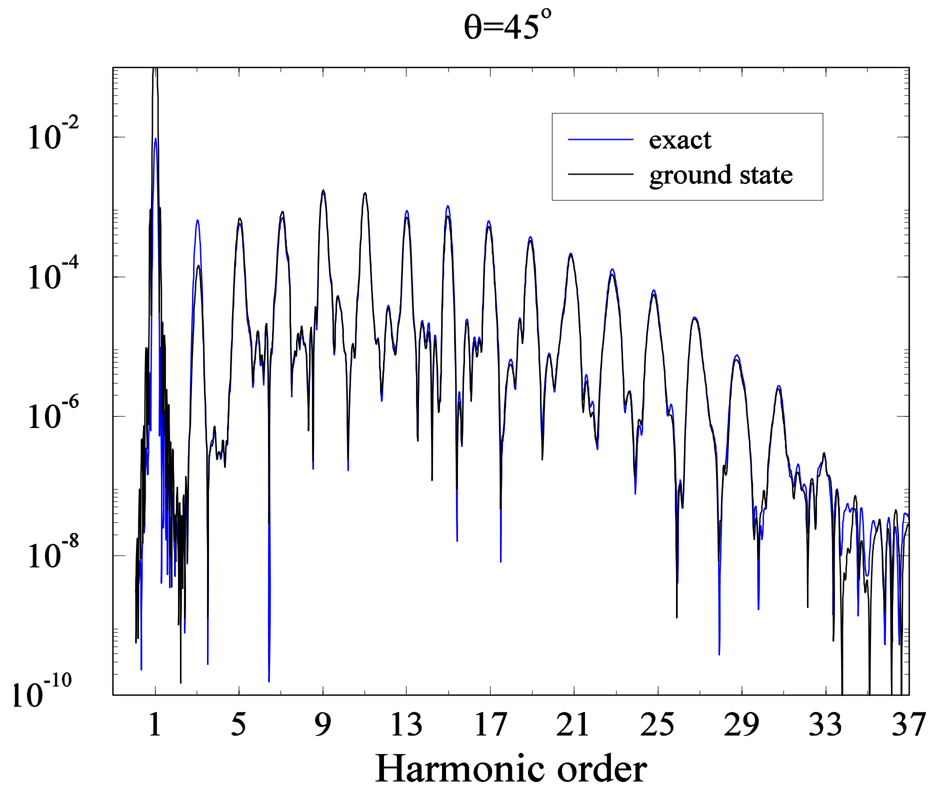
Exchange

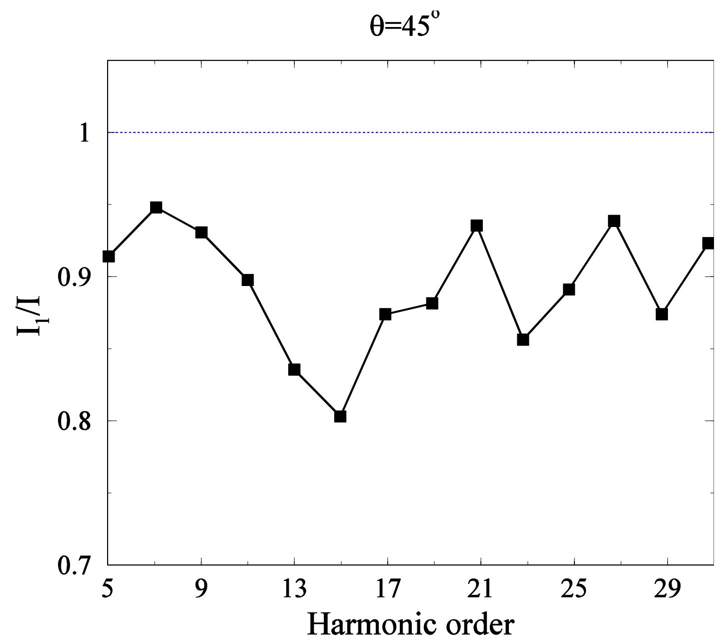
$$\left\langle \alpha_g(t)\Psi_g \middle| \hat{a}(\mathbf{r}_1) \middle| \varphi_i(\mathbf{r}_1)\,\phi_i(\mathbf{r}_2,t) \right\rangle$$

HHG – Role of Ionic excitations

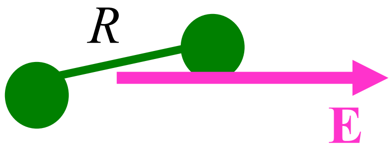


$I = 1.10^{14}$ W/cm^2 , $\lambda = 800$ nm , N=10

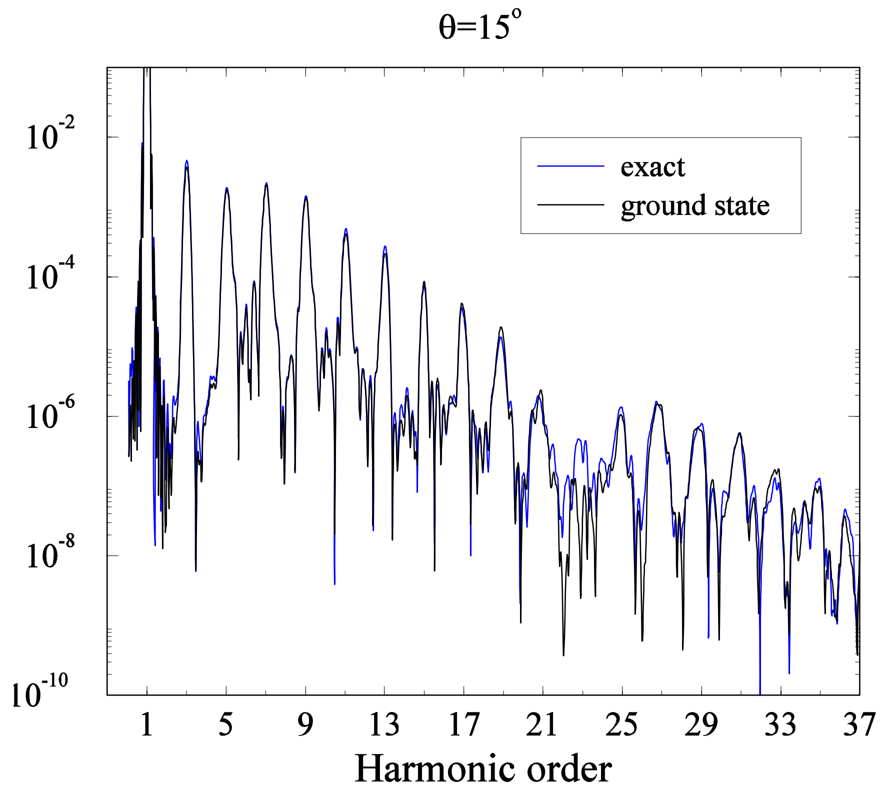


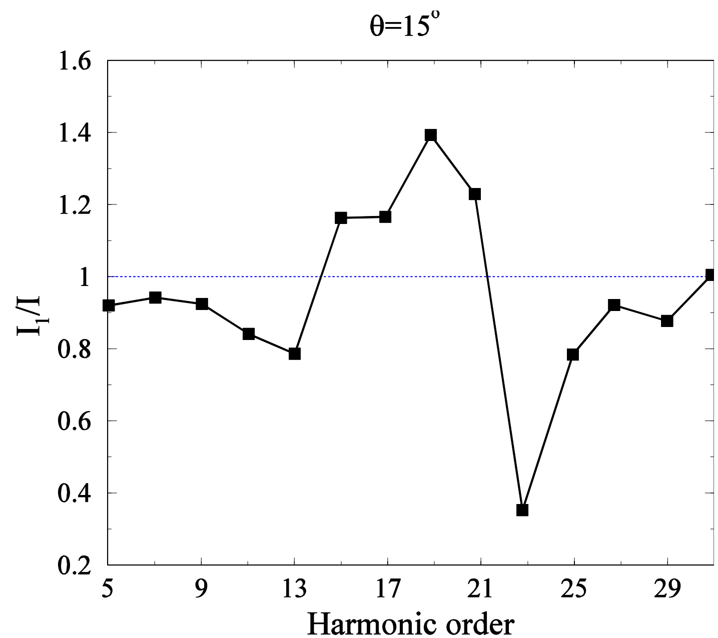


HHG – Role of Ionic excitations

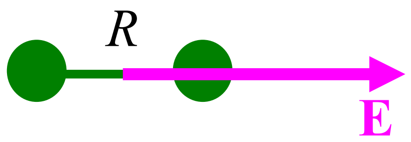


I=1.10^{14} W/cm^2 , λ=800 nm , N=10

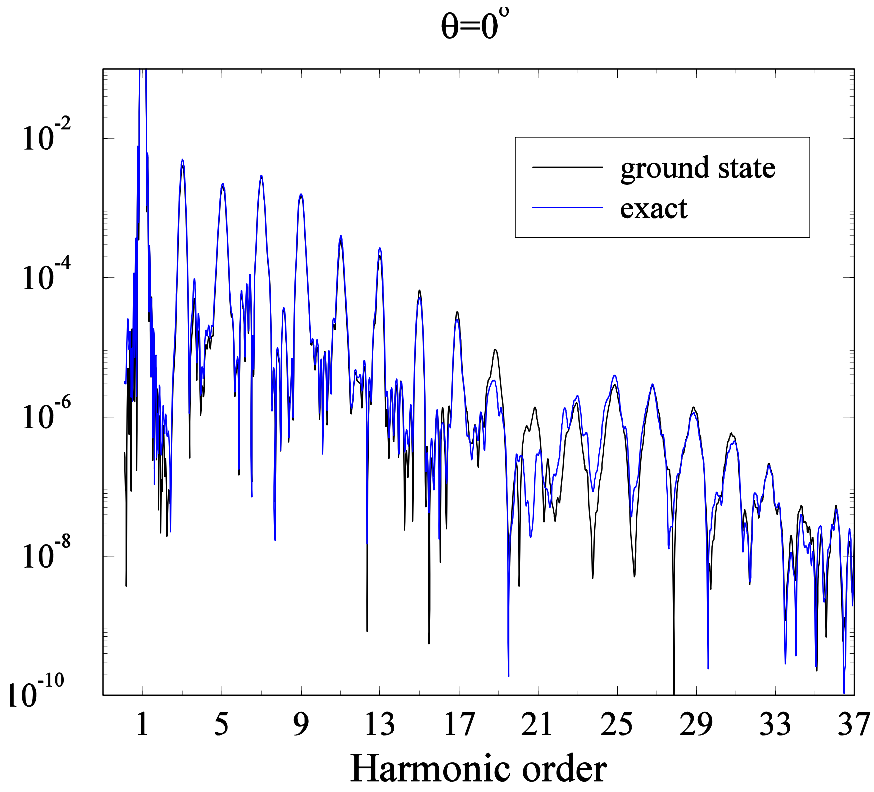


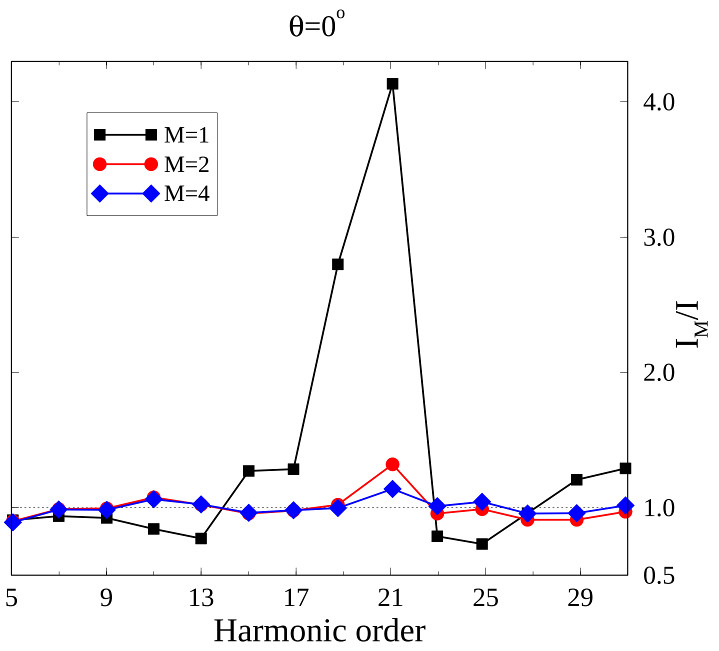


HHG - Role of Ionic excitations

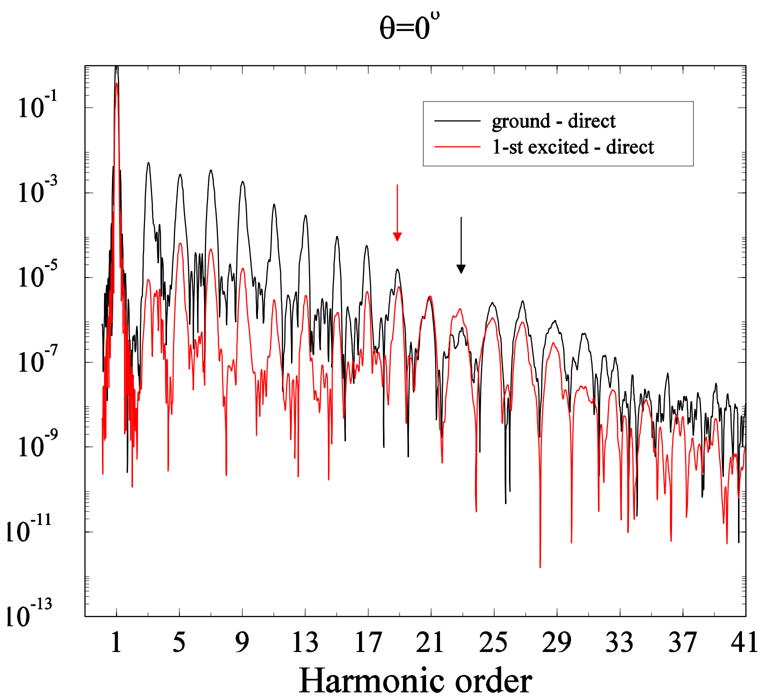


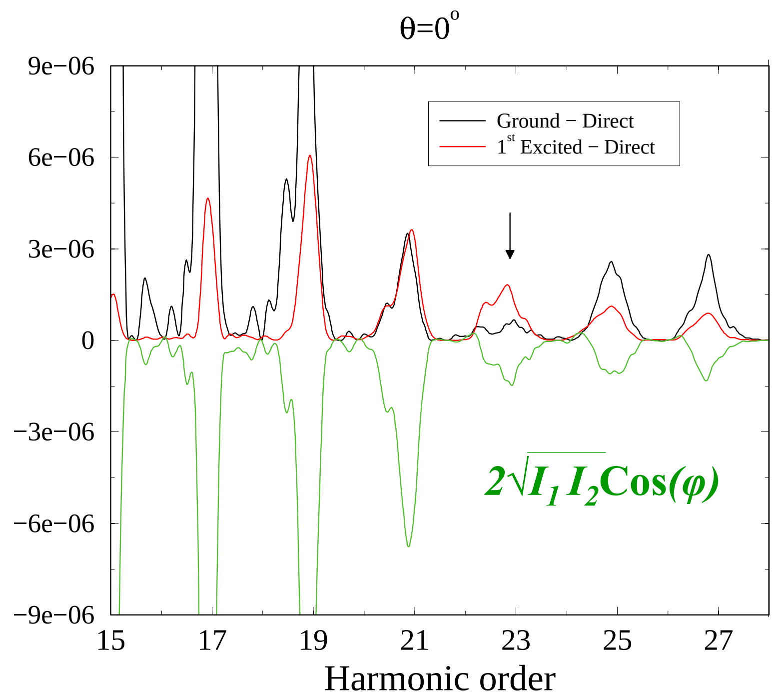
I=1.10^{14} W/cm^2 , λ=800 nm , N=10





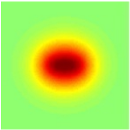
HHG – Role of Ionic excitations



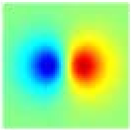


$$\left\langle \psi_1^D(\mathbf{r}) \middle| \hat{a} \middle| \phi_1(\mathbf{r},t) \right\rangle$$

$$\left\langle \psi_2^D(\mathbf{r}) \middle| \hat{a} \middle| \phi_2(\mathbf{r},t) \right\rangle$$



$\psi_1^D(\mathbf{r})$

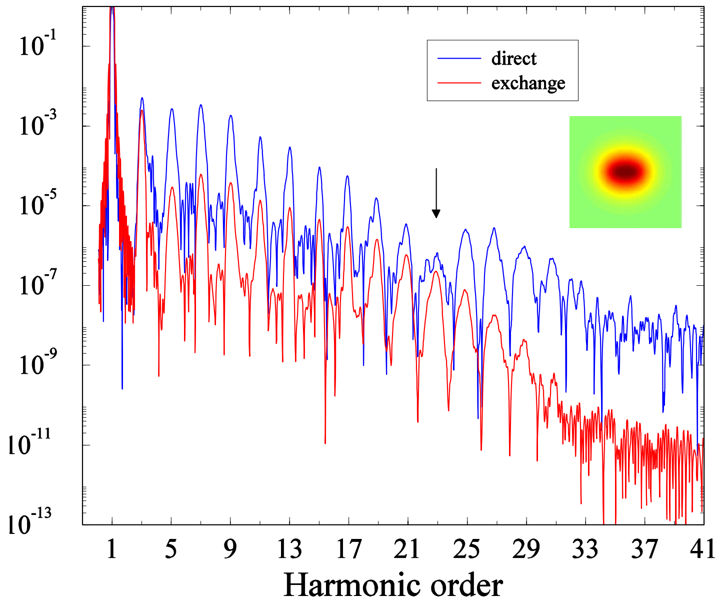


$\psi_2^D(\mathbf{r})$

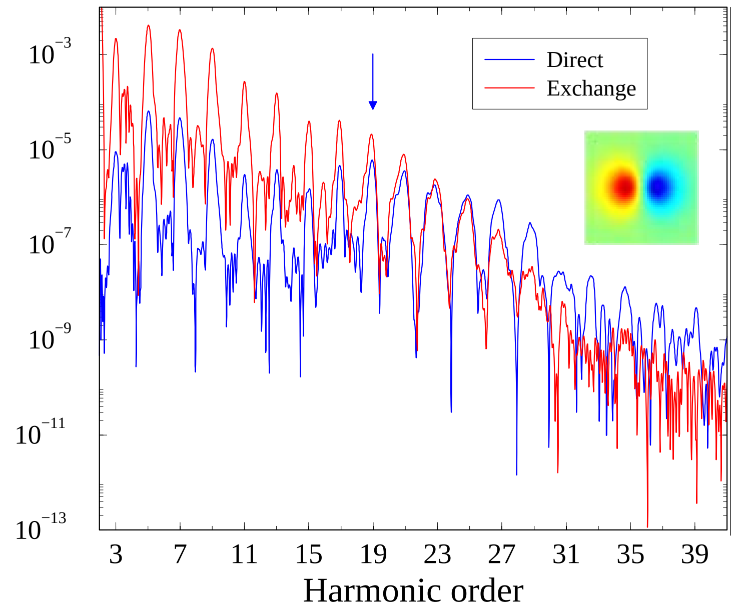
Destructive interference!

HHG – Role of Ionic excitations

θ=0°



θ=0° – 1st Excited state



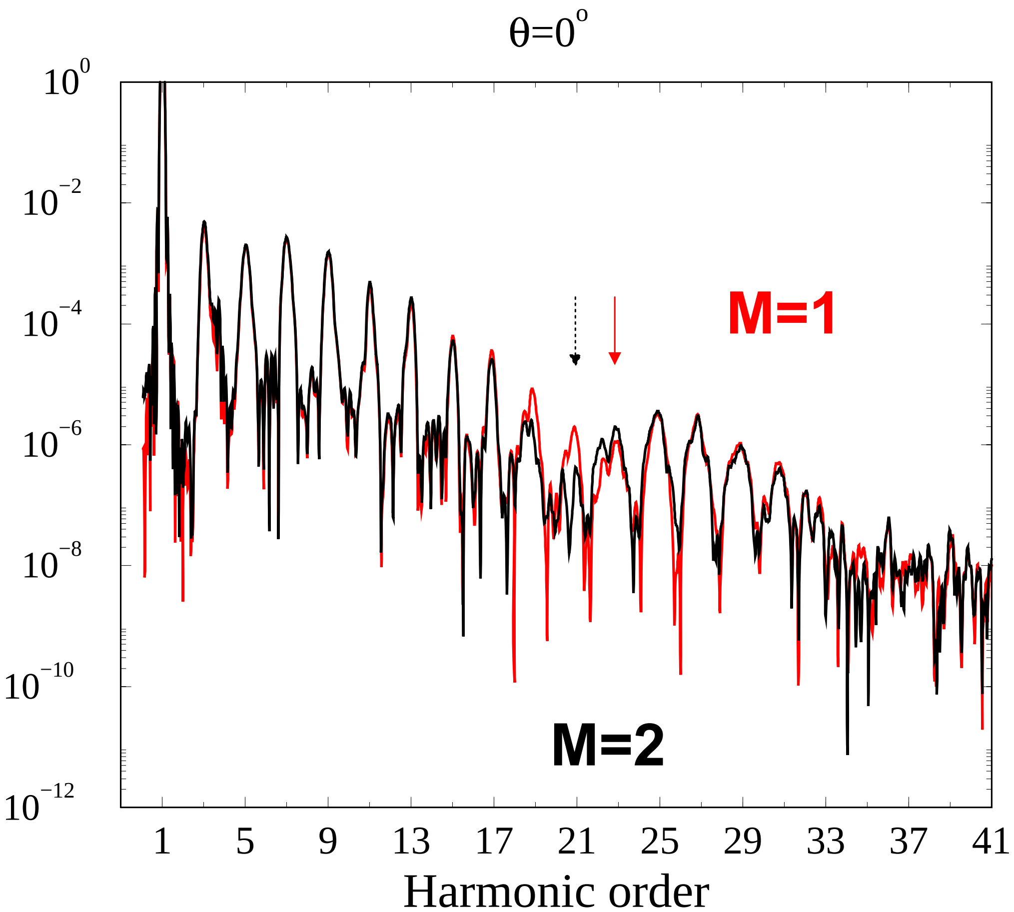
Destructive interference!

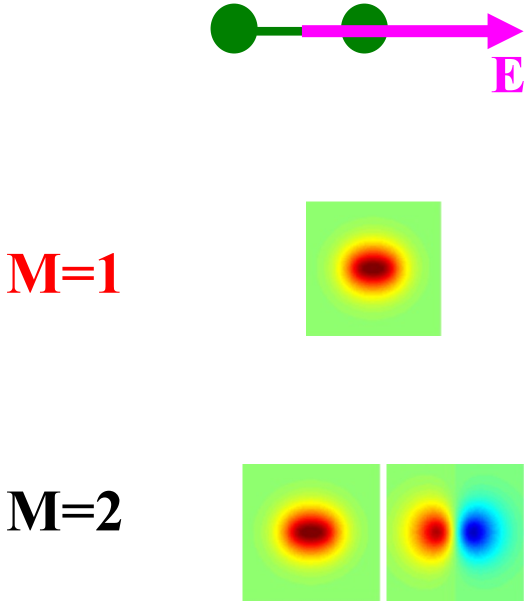
Direct	$\propto \left\| \psi_1^D \right\|^2$	$\propto \left\| \psi_2^D \right\|^2$
Exchange	$\propto \left\| \psi_2^D \right\|^2$	$\propto \left\| \psi_1^D \right\|^2$

$$\psi_i^D(\mathbf{r}_1) = \left\langle \varphi_i(\mathbf{r}_2) \middle| \Psi_g(\mathbf{r}_1, \mathbf{r}_2) \right\rangle$$

$$\left\| \psi_1^D \right\| >> \left\| \psi_2^D \right\|$$

HHG – Role of Ionic excitations





Role of ionic excitations in HHG (reconstruction of Molecular Orbitals) is significant!

Summary

- ✓ MCTDH is implemented to study the correlated dynamics of electrons in strong laser fields.
- ✓ Role of electron rescattering in the multi-electron excitations is significant.
- ✓ Development of Ionic Eigenstate Resolved HHG technique to analyze the role of ionic eigenstates in harmonic emission.
- ✓ The influence of multi-electron excitations and exchange in HHG is significant.
- ✓ Electron correlation can lead to increasing/lowering of Two-Center Interference in HHG.