Models for Time-Dependent Phenomena

I. Laser-matter interaction: atoms

II. Laser-matter interaction: molecules

III. Model systems and TDDFT

Manfred Lein, TDDFT school Benasque 2012

Outline

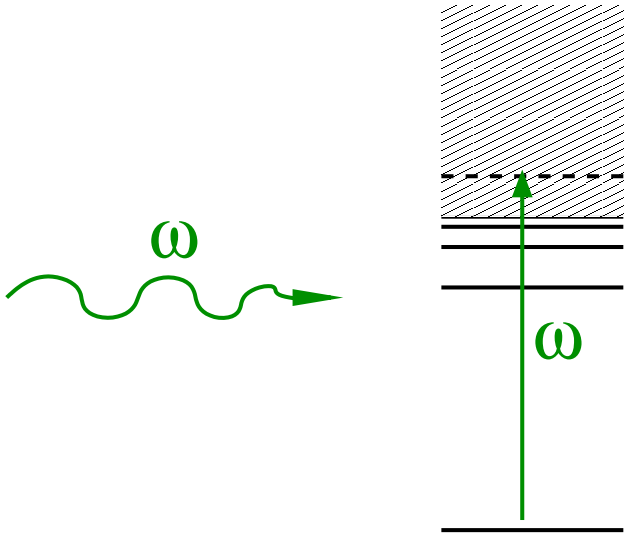
Laser-matter interaction: atoms

- Classical models and quantum description
- Floquet theory, Volkov states
- Multiphoton processes, tunneling ionization
- Recollision, high-harmonic generation, double ionization
- Strong-field approximation
- Recent examples of research on atoms in strong fields

Laser-matter interaction

“Weak” light field

(normal light, synchrotron)

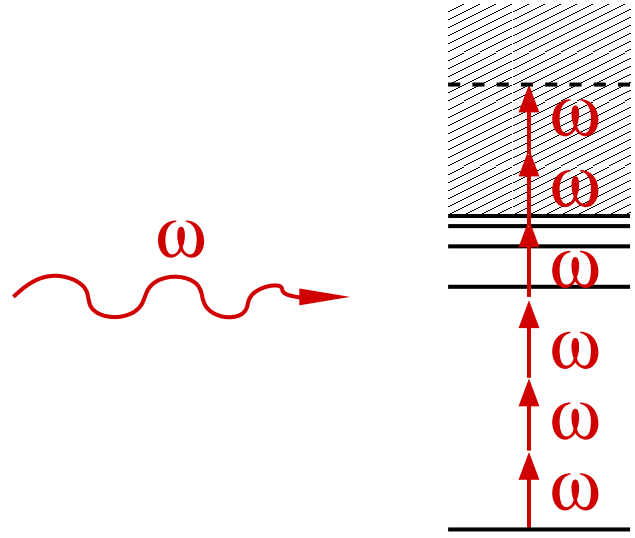


Single-photon absorption

$$P \sim |\langle 1|\mathbf{r}\cdot\mathbf{E}|0\rangle|^2$$

Strong light field

(laser pulses)



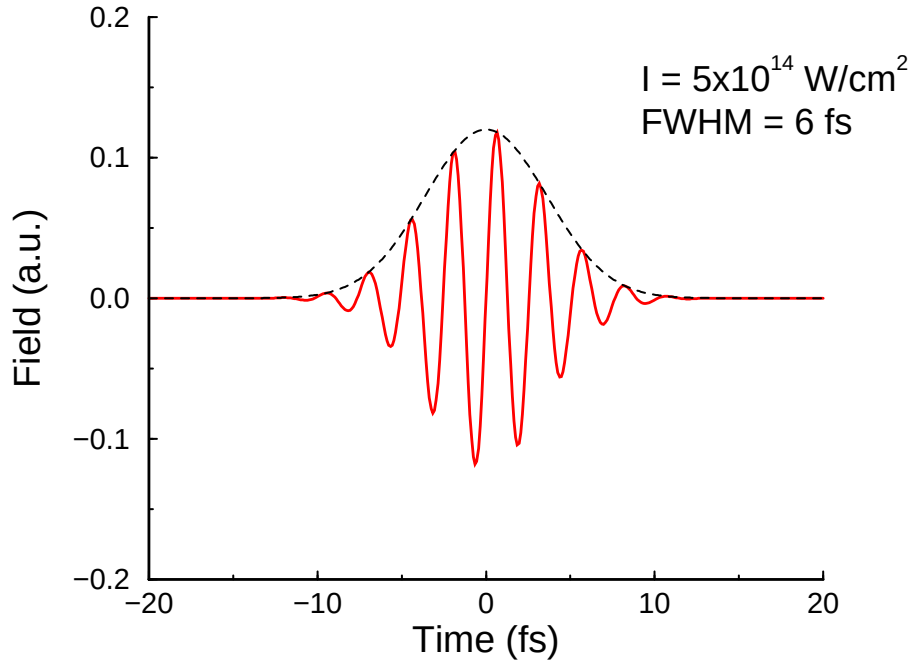
Multiphoton absorption

perturbative or

nonperturbative

Ultrashort laser pulses

Femtosecond pulses are available:



→ cause ionization of atoms, fragmentation of molecules

→ allow ultrafast time-resolved measurements (pump-probe)

→ “carrier-envelope phase” becomes important

Classical preliminaries

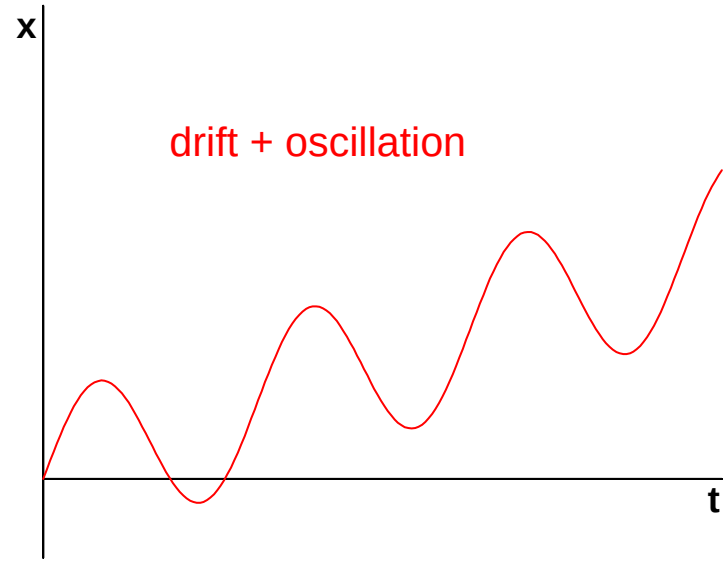
Free classical electron in a monochromatic laser field

Equation of motion: $\boxed{\ddot{\mathbf{r}}(t) = -\mathbf{E}_0 \sin(\omega t)}$

(using dipole approximation; $\mathbf{E}_0 \sin(\omega t) =$ electric field, linearly polarized)

Velocity: $\dot{\mathbf{r}}(t) = \mathbf{v}_{\text{drift}} + \frac{\mathbf{E}_0}{\omega} \cos(\omega t)$

Position: $\mathbf{r}(t) = \mathbf{r}_0 + \mathbf{v}_{\text{drift}} t + \frac{\mathbf{E}_0}{\omega^2} \sin(\omega t)$



Oscillation amplitude: $\alpha = \mathbf{E}_0/\omega^2$

Classical preliminaries

Kinetic energy: $T(t) = \frac{v_{\mathrm{drift}}^2}{2} + \mathbf{v}_{\mathrm{drift}} \cdot \frac{\mathbf{E}_0}{\omega} \cos(\omega t) + \frac{E_0^2}{2\omega^2} \cos^2(\omega t)$

Average kinetic energy: $\boxed{\bar{T} = \frac{v_{\mathrm{drift}}^2}{2} + \frac{E_0^2}{4\omega^2}}$

$\rightarrow$ Define **ponderomotive potential**: $\boxed{U_{\mathrm{p}} = \frac{E_0^2}{4\omega^2}}$

If field amplitude is position dependent, there will be a ponderomotive force $\mathbf{F}_{\mathrm{p}} = -\nabla U_{\mathrm{p}}(\mathbf{r})$.

(But in an ultrashort laser pulse, the electron has not enough time to follow this force).

Quantum mechanical description

Time evolution is described by the time-dependent Schrödinger equation (TDSE): $\boxed{i\frac{\partial}{\partial t}\Psi(t) = H(t)\Psi(t).}$

Hamiltonian in dipole approximation ($\lambda >>$ system size):

$\boxed{H(t) = H_0 + \mathbf{E}(t)\cdot\sum_j \mathbf{r}_j}$ with $\mathbf{E}(t)$ = electric field.

This is called *length gauge*.

Alternatively:

$\boxed{H'(t) = H_0 + \mathbf{A}(t)\cdot\sum_j[\mathbf{p}_j + \mathbf{A}(t)/2]}$ with

$$\mathbf{A}(t) = -\int_{-\infty}^{t} \mathbf{E}(t')dt'.$$

This is called *velocity gauge*.

Quantum mechanical description

The velocity-gauge wave function $\Psi'(t)$ is related to the length-gauge wave function $\Psi(t)$ by

$$\boxed{\Psi'(t) = e^{-i\mathbf{A}(t)\cdot\sum_j \mathbf{r}_j}\ \Psi(t)}$$

Are there problems with TDDFT and velocity gauge (momentum-dependent interaction)?

No, because gauge transformation does not change density .

$\rightarrow$ TDKS equations may be solved in either gauge.

But: orbitals change under gauge transformation.

Floquet theory

Consider monochromatic field $\mathbf{E}(t) = \mathbf{E}_0 \sin(\omega t)$

$\rightarrow$ periodic Hamiltonian $H(t+T) = H(t)$

$\rightarrow$ **Floquet theorem** (cf. Bloch theorem in solid-state physics):

TDSE has solutions of the form

$$\boxed{\Psi(t) = e^{-i\mathcal{E}t}\Phi(t)}$$

with time-periodic wave functions $\Phi(t)$,

$$\boxed{\Phi(t+T) = \Phi(t).}$$

Floquet theory

The Floquet states $\Phi(t)$ are eigenstates of the **Floquet operator** $\mathcal{H}(t) = H(t) - i\frac{\partial}{\partial t}$,

$$\boxed{\mathcal{H}(t)\Phi(t) = \mathcal{E}\Phi(t),}$$

where $\mathcal{E}$ is the **quasienergy**.

If $\mathcal{E}$ and $\Phi(t)$ are solutions, then also
$\mathcal{E}' = \mathcal{E} + n\omega$ and $\Phi'(t) = \Phi(t)e^{in\omega t}$ are solutions.

$\Phi(t)$ are called **dressed states**
(analog to stationary eigenstates for time-independent Hamiltonian).

Volkov states

Free electron in the presence of a time-dependent electric field is described by the Hamiltonian (length gauge):

$$H(t) = -\frac{\nabla^2}{2} + \mathbf{E}(t) \cdot \mathbf{r}$$

Possible solutions of the TDSE are **Volkov states**:

$$\boxed{\Psi^{\mathrm{V}}_{\mathbf{p}}(\mathbf{r}, t) = e^{-iS(\mathbf{p},t,t')} e^{i[\mathbf{p}+\mathbf{A}(t)]\cdot\mathbf{r}}}$$

with the action integral $S(\mathbf{p}, t, t') = \frac{1}{2}\int_{t'}^{t} [\mathbf{p} + \mathbf{A}(t'')]^2 dt''$ and arbitrary, fixed t'.

These are plane waves with momenta depending on time as in classical mechanics.

Volkov states

For a monochromatic field, the Volkov states can be written as

$$\Psi^{\mathrm{V}}_{\mathbf{p}}(\mathbf{r},t) = e^{-i(p^2/2+U_{\mathrm{p}})t}\ \Phi_{\mathbf{p}}(\mathbf{r},t)$$

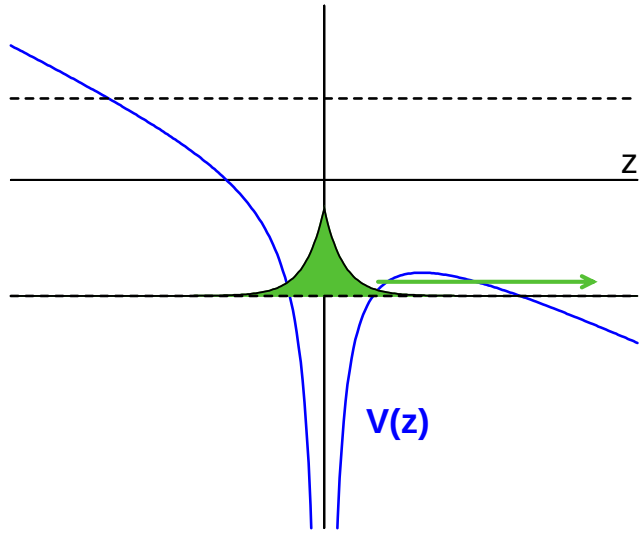
with a time periodic function $\Phi_{\mathbf{p}}$, i.e. this is a Floquet state with quasienergy

$$\boxed{\mathcal{E}_{\mathbf{p}} = p^2/2 + U_{\mathrm{p}}.}$$

The ponderomotive potential is the ac Stark shift of plane waves!

Tunneling

Static electric field $E \rightarrow$ potential barrier, allows tunneling.



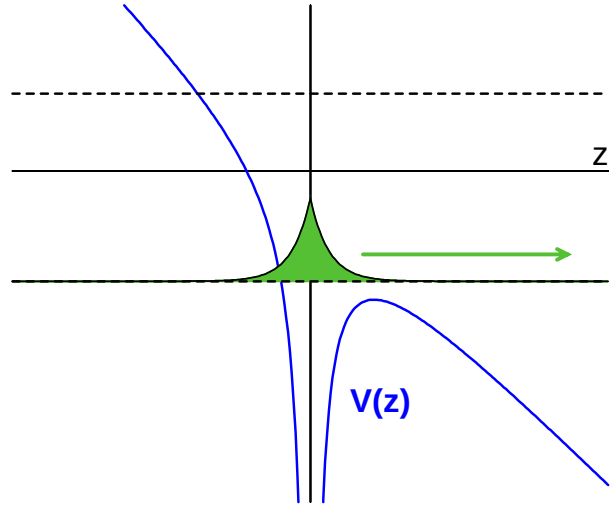
Tunneling rate for the hydrogen atom (see Landau & Lifshitz):

$$\boxed{w = \frac{4}{E} e^{-2/(3E)}}$$

(derived from quasiclassical theory)

Over-barrier ionization

For sufficiently large field $E >$ critical field $E_{\rm BS}$
$\rightarrow$ ground-state energy above barrier maximum

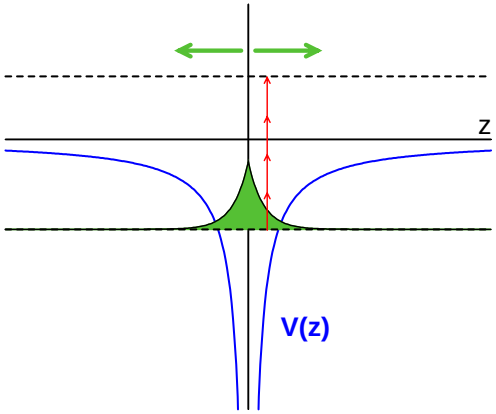


$\rightarrow$ Classical escape of the electron.

$E_{\rm BS} =$ **barrier suppression field strength**
H atom: $E_{\rm BS} = 0.113$ a.u.
(corresponds to laser intensity $I_{\rm BS} = 4.5 \times 10^{14}$ W/cm^2)

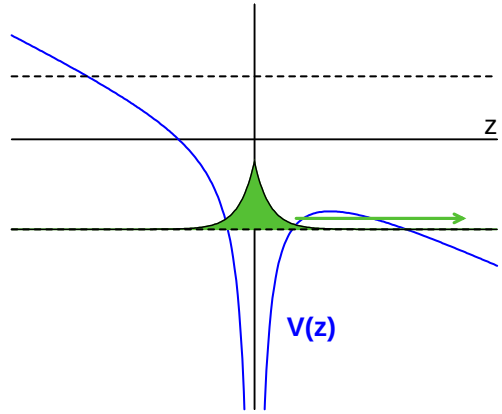
Ionization regimes

multiphoton ionization



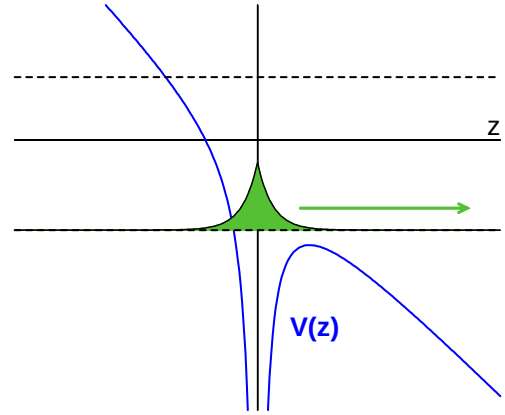
$\gamma = \omega/\omega_{\rm t} > 1$

tunnel ionization



$\gamma = \omega/\omega_{\rm t} < 1$

over-barrier ionization



$E > E_{\rm BS}$

$\gamma = \frac{\text{tunneling time}}{\text{laser period}}$ (Keldysh parameter)

H atom: $\gamma = \omega/E$

in general: $\gamma = \sqrt{I_{\rm p}/(2U_{\rm p})}$,

$I_{\rm p}$ = ionization potential, $U_{\rm p}$ = ponderomotive potential

Simple man's model of ionization

- At each instant t_0, the ionization rate is given by a simple estimate (e.g. tunneling formula) using the instantaneous field strength.
- Electron appears with zero velocity at position zero.
- Subsequent dynamics is described classically.

Simple man's model of ionization

- At each instant t_0, the ionization rate is given by a simple estimate (e.g. tunneling formula) using the instantaneous field strength.
- Electron appears with zero velocity at position zero.
- Subsequent dynamics is described classically.

For monochromatic field: $\dot{\mathbf{r}}(t) = \frac{\mathbf{E}_0}{\omega}[\cos(\omega t) - \cos(\omega t_0)]$

i.e. drift velocity $\mathbf{v}_{\mathrm{drift}} = -\frac{\mathbf{E}_0}{\omega}\cos(\omega t_0)$

$\rightarrow$ Estimate of maximum photoelectron energy:

$$|\cos(\omega t_0)| = 1 \quad \rightarrow \quad \boxed{E_{\mathrm{max}} = \frac{E_0^2}{2\omega^2} = 2U_{\mathrm{p}}}$$

Above-threshold ionization

Absorption of more photons than needed to overcome the ionization threshold

$\rightarrow$ Peaks separated by the photon energy in the electron spectrum

Example:
experiment with Xe atoms,
Agostini et al. PRA **36**, R4111 (1987).

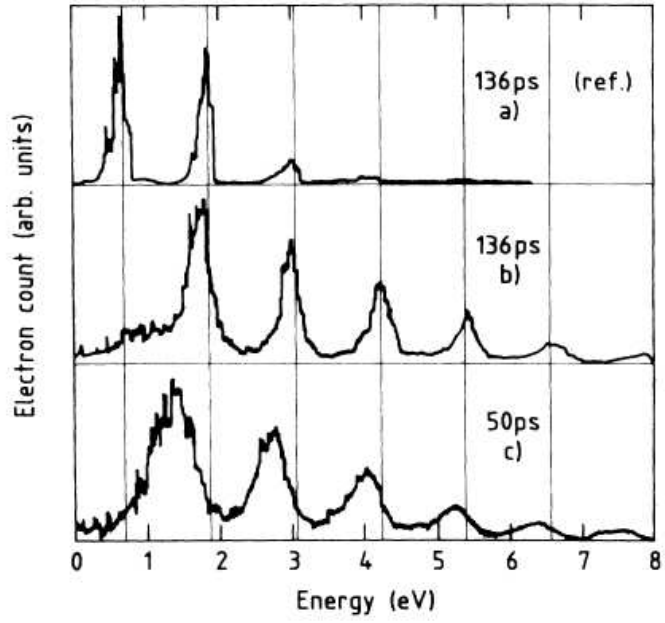


FIG. 2. Electron energy spectra for different laser intensities and pulse durations. (a) reference spectrum, $I = 2.2 \times 10^{12}$ W cm^{-2}; (b) and (c) $I = 7.5 \times 10^{12}$ W cm^{-2}.

Above-threshold ionization

Ponderomotive shift of the ATI peaks

- continuum dressed states have energies $\mathcal{E}_k^{\mathrm{d}} = k^2/2 + U_{\mathrm{p}}$

- shift of ground-state energy is small: $\mathcal{E}_{\mathrm{g}}^{\mathrm{d}} \approx E_{\mathrm{g}}$,
  so absorption of n photons yields electrons with energy $E_{\mathrm{g}} + n\omega$.

$\rightarrow$ Photoelectron kinetic energies $\boxed{k^2/2 = E_{\mathrm{g}} + n\omega - U_{\mathrm{p}}}$

Recollision mechanism

3-step process:

1. ionization
2. acceleration by the field
3. return to the core

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3-step process:

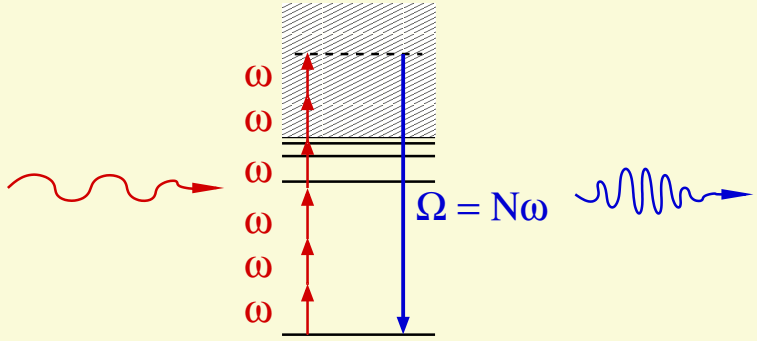
1. ionization
2. acceleration by the field
3. return to the core

Possible consequences:

- recombination (high harmonic generation – coherent light)
- elastic scattering $\rightarrow$ fast photoelectrons
- inelastic scattering $\rightarrow$ e.g. double ionization

High-harmonic generation

Photon picture

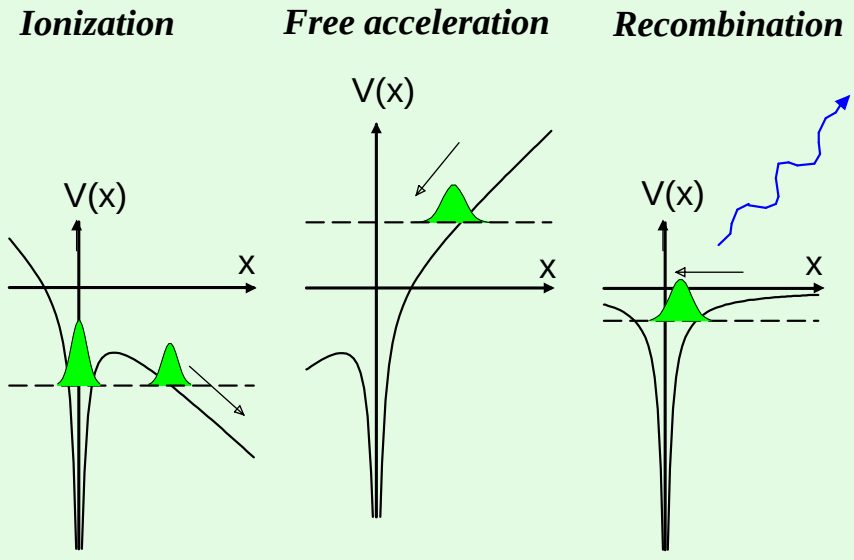


N photons of frequency ω

$\rightarrow$ 1 photon of frequency $N\omega$.

High-harmonic generation

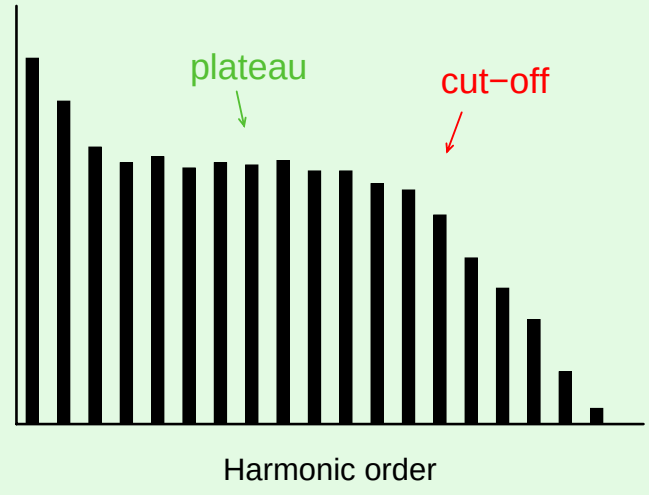
Recollision picture



Maximum return energy: $E_{\max} = 3.17 U_{\mathrm{p}}$

$\hookrightarrow$ Cut-off at $\boxed{\hbar\omega = 3.17 U_{\mathrm{p}} + I_{\mathrm{p}}}$

[Corkum, PRL **71**, 1994 (1993)]



Calculation of spectra

Calculation of the time-dependent dipole acceleration

$$\boxed{\mathbf{a}(t) = \langle \psi(t) | \nabla V_0 + \mathbf{E}(t) | \psi(t) \rangle}$$

and Fourier transform

$$\boxed{\mathbf{a}(\Omega) = \int \mathbf{a}(t) e^{i\omega t}}$$

gives emission spectrum

$$\boxed{S(\Omega) \sim |\mathbf{a}(\Omega)|^2}$$

In practice: time integration over pulse duration T,

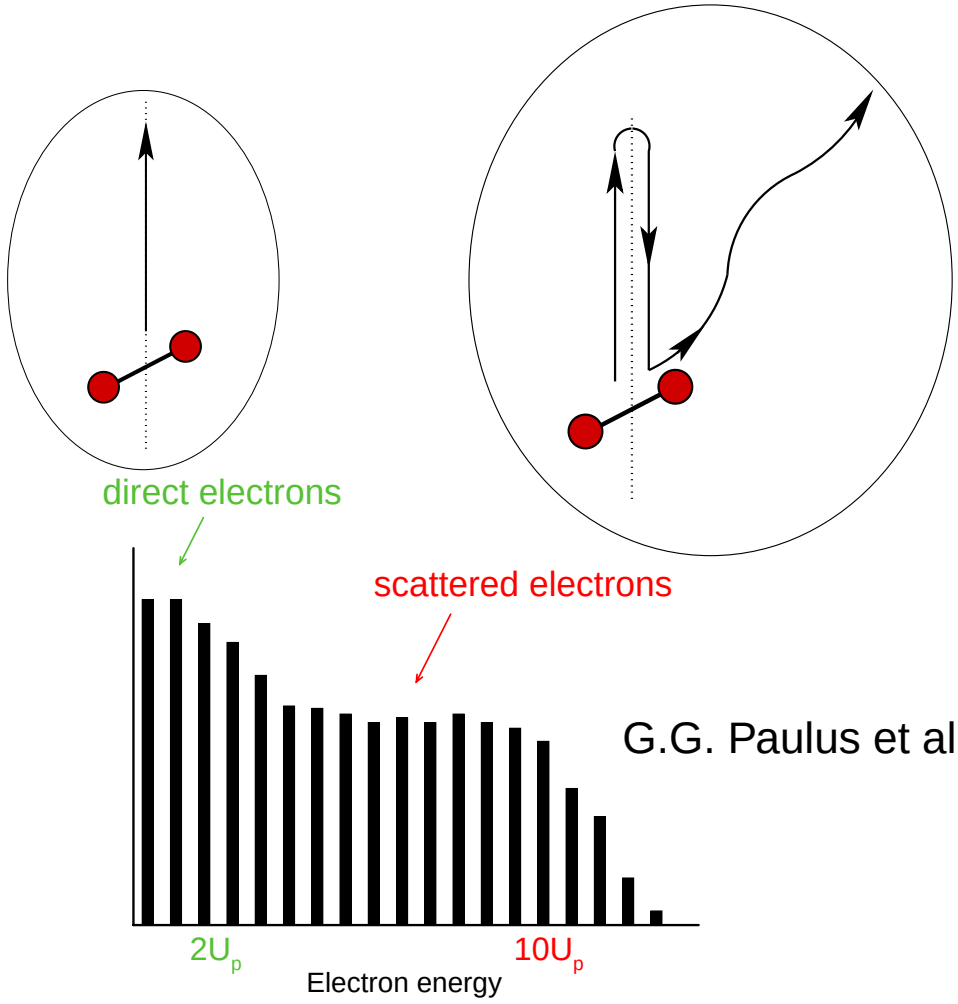
$$\boxed{\mathbf{a}(\Omega) = \int_0^T \mathbf{a}(t) f(t) e^{i\omega t}}$$

with some window function $f(t)$.

Alternatively: $\mathbf{a}(t) = \ddot{\mathbf{D}}(t)$ from time-dependent dipole moment $\mathbf{D}(t)$
or: $\mathbf{a}(t) = \dot{\mathbf{v}}(t)$ from time-dependent dipole velocity $\mathbf{v}(t)$

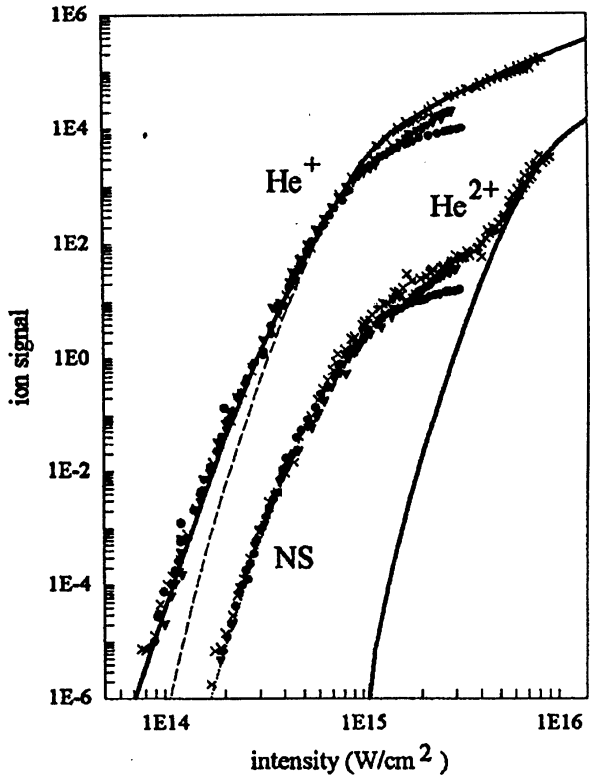
Rescattered photoelectrons

Scattered electrons (*high-order above-threshold ionization*)



G.G. Paulus et al. PRL **72**, 2851 (1994)

Double ionization



Walker et al., PRL **73**, 1227 (1994)

Double ionization is enhanced due to electron correlations by orders of magnitude.

Identification of the recollision mechanism:

A. Becker, F.H.M. Faisal, J. Phys. B **29**, L197 (1996)

R. Moshammer et al., PRL **84**, 447 (2000)

T. Weber et al., Nature **405**, 658 (2000)

M.L., E.K.U. Gross, V. Engel, PRL **85**, 4707 (2000)

Quantum mechanical methods for ultrashort pulses

- **Numerical solution of the TDSE (or TDKS) equations**
  - accurate,
  - but time consuming and hard to interpret,
  - approximations for TDDFT xc potential have deficiencies

- **Strong-field approximation**
  ("Keldysh-Faisal-Reiss theory", "intense field S-matrix formalism")
  - less reliable (e.g. strong dependence on gauge),
  - but fast and amenable to physical interpretation.

Strong-field approximation for ionization

Time evolution operator $U(t,t')$ obeys Schrödinger equation:

$$i\frac{\partial}{\partial t}U(t,t') = \left[H_0 + H_{\rm int}(t)\right]U(t,t'),$$

where $H_{\rm int}$ is the system-field interaction.

The solution can be written in integral form:

$$U(t,t') = U_0(t,t') - i\int_{t'}^{t} U(t,t'')H_{\rm int}(t'')U_0(t'',t')dt''.$$

Goal: calculation of transition amplitudes from ground state to continuum states with momentum $\mathbf{p}$ at final time $t_{\rm f}$:

$$M_{\mathbf{p}}(t_{\rm f},t_{\rm i}) = \langle\Psi_{\mathbf{p}}(t_{\rm f})|U(t_{\rm f},t_{\rm i})|\Psi_0(t_{\rm i})\rangle$$

Strong-field approximation for ionization

Assumption 1: time evolution after ionization is governed by the laser field *only*, not by the binding potential, i.e. $U(t,t'') \approx U_{\mathrm{V}}(t,t'')$ (Volkov-Propagator). Then

$$U(t,t') = U_0(t,t') - i\int_{t'}^{t} U_{\mathrm{V}}(t,t'')H_{\mathrm{int}}(t'')U_0(t'',t')dt''.$$

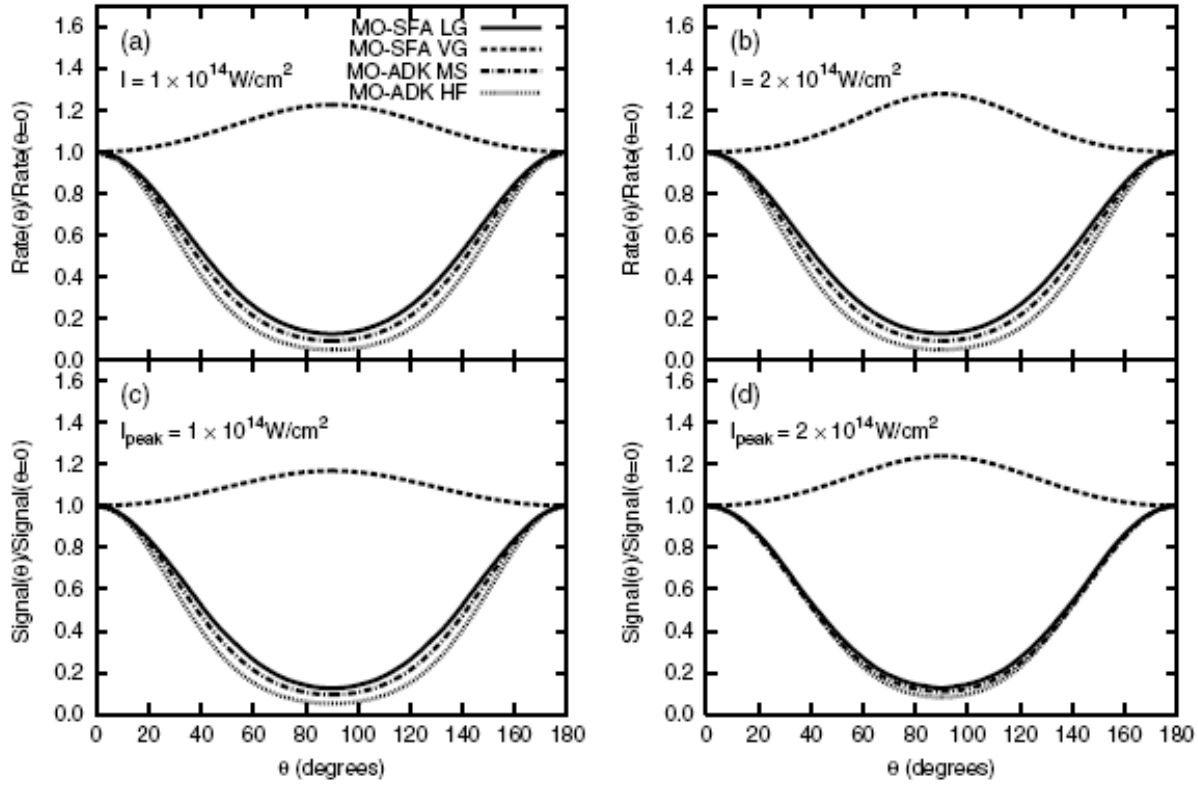
Assumption 2: final state with momentum $\mathbf{p}$ is approximated as a Volkov state.

$\rightarrow$ Ionization amplitude in strong-field approximation (SFA):

$$M_{\mathbf{p}}^{\mathrm{SFA}}(t_{\mathrm{i}},t_{\mathrm{f}}) = -i\int_{t_{\mathrm{i}}}^{t_{\mathrm{f}}} \langle \Psi_{\mathbf{p}}^{\mathrm{V}}(t)|H_{\mathrm{int}}(t)|\Psi_0(t)\rangle\, dt$$

Strong-field approximation for ionization

SFA is not gauge invariant: results for ionization of N_2



T.K. Kjeldsen and L.B. Madsen, J. Phys. B **37**, 2033 (2004)

Length gauge ($\mathbf{r} \cdot \mathbf{E}(t)$) appears favourable (except for large molecules)

Two examples of recent research in laser-atom interactions

- Low-energy structure in electron spectra from long-wavelength irradiation
- Lateral momentum width in strong-field ionization

Low-energy structure in electron spectra

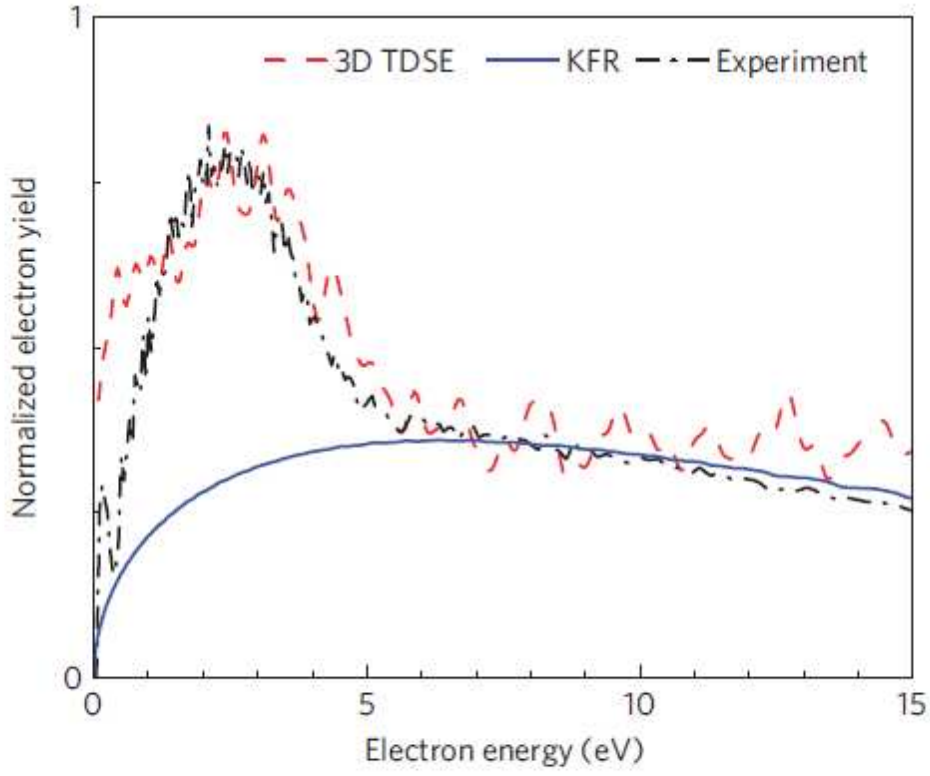
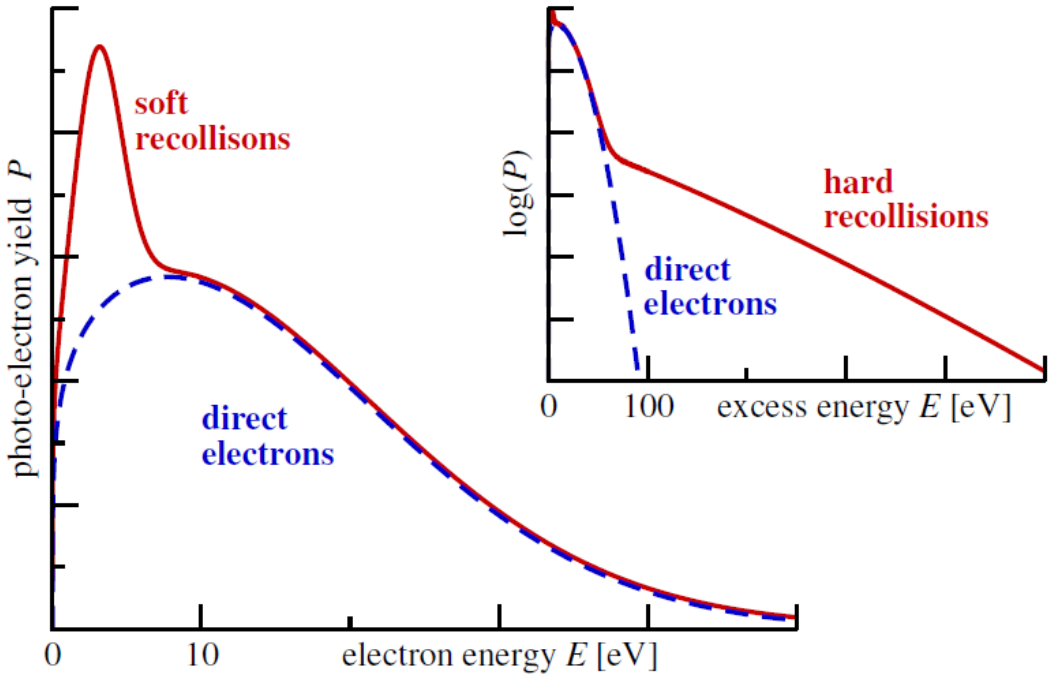


Figure 4 | Comparison of calculated and measured LES distributions for argon ionized by 150 TW cm^{-2}, 2 μm pulses. The experiment is remarkably well reproduced by the three-dimensional TDSE. For comparison, the KFR using Volkov states fails in this region. The calculated distributions are obtained using intensity averaged, 10-cycle flat-top pulses (see the Methods section).

Blaga et al., Nat. Phys. **5**, 335 (2009)

Low-energy structure in electron spectra

Explanation: caustics from soft recollisions

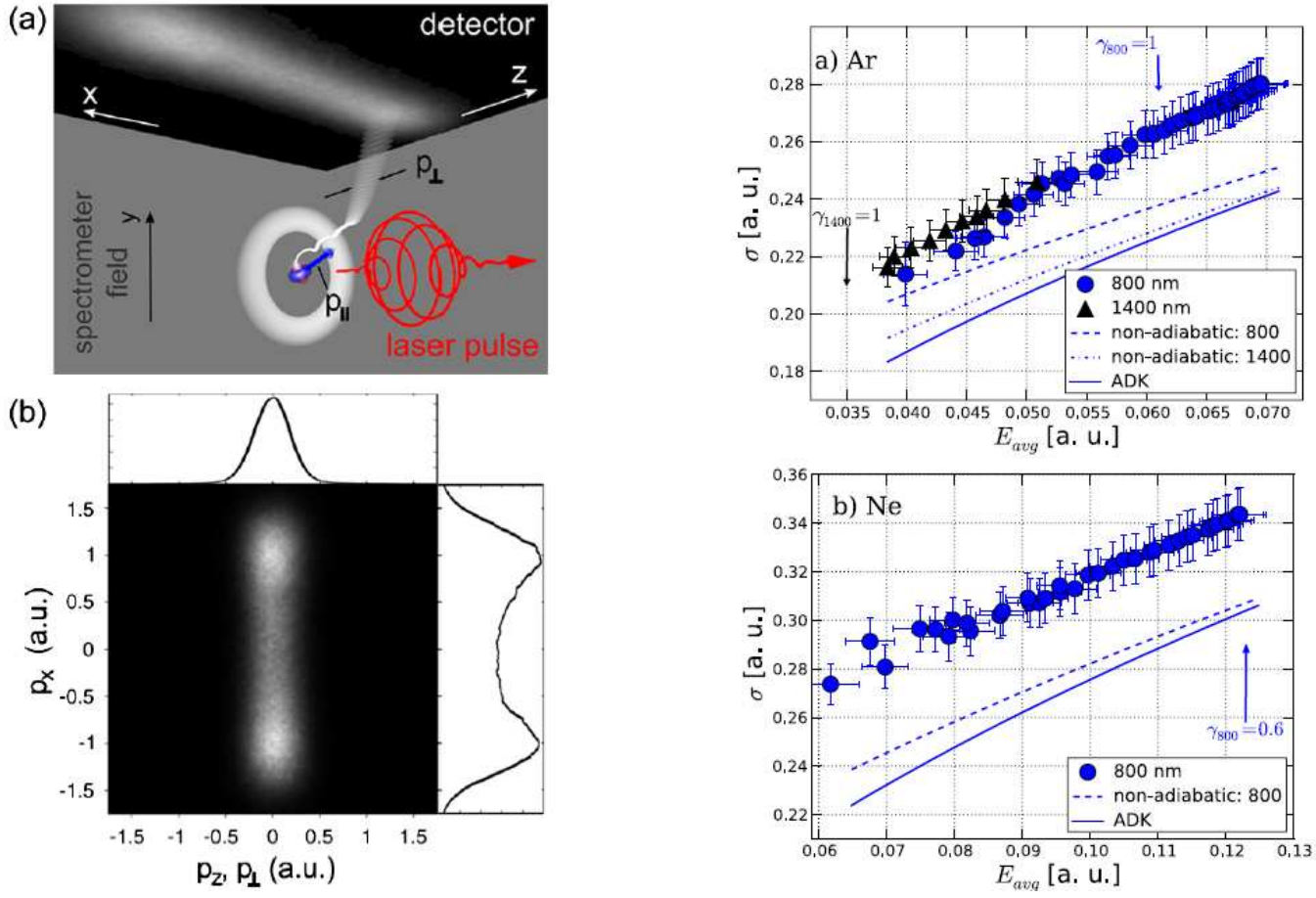


Kästner et al. arXiv:1109.3998v1 (2011)

Yan et al., PRL **105**, 253002 (2010)

Lateral momentum distribution in strong-field ionization

Measured widths of lateral distributions (circularly polarized light)



Arissian et al., PRL **105**, 133002 (2010)

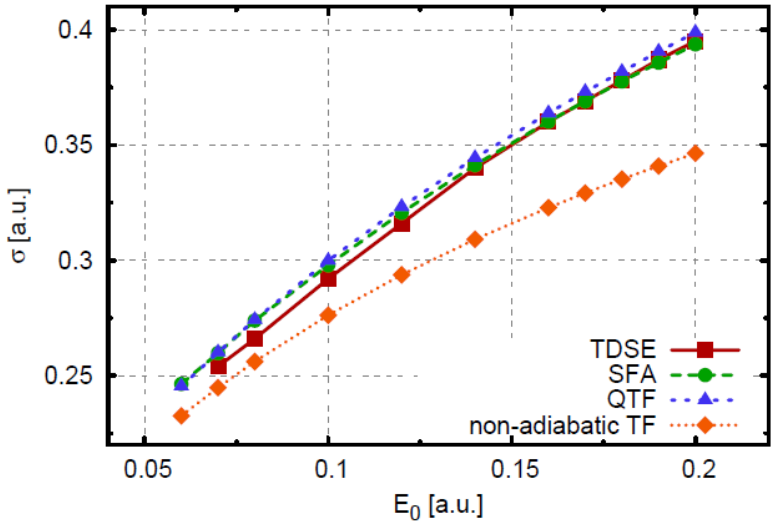
$\rightarrow$ Widths are larger than predicted by a simple tunneling formula

$$|\Psi(k_\perp)|^2 = |\Psi(k_\perp)|^2 \, \exp(-k_\perp^2 \sqrt{2I_\mathrm{p}}/E).$$

Lateral momentum distribution in strong-field ionization

Calculated widths and comparison to experiment:

H



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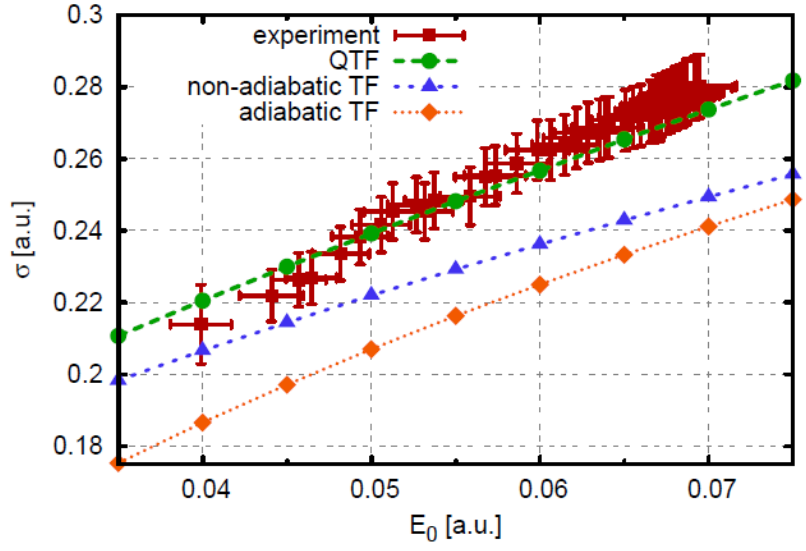

I. Dreissigacker, M.L., submitted; experimental data by Arissian et al. PRL 2010

- Very good agreement between TDSE, SFA, experiment.
- Simple tunneling model is inaccurate.

Conclusions

- Strong laser fields require nonperturbative description and large grids.
- In general, theoretical description is not quantitative and relies heavily on models.
- TDDFT is the only tractable first-principles approach, already for atoms.

Next part:

- Laser-matter interaction: molecules