Nonperturbative quantum dynamics

I. Laser interactions with atoms/molecules

II. Model systems and TDDFT

Manfred Lein, TDDFT school Benasque 2014

Outline

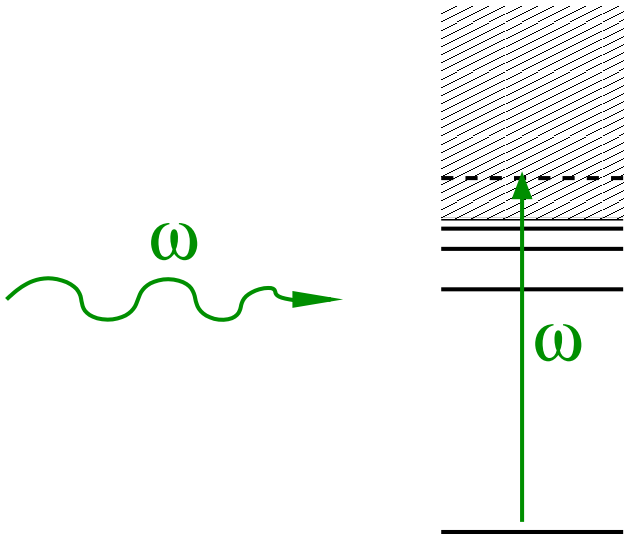
Laser interactions with atoms/molecules

- Classical models and quantum description
- Multiphoton processes, tunneling ionization
- Recollision, high-harmonic generation, double ionization
- Strong-field approximation
- Molecules, laser-induced alignment
- Examples of open problems in strong-field dynamics

Laser-matter interaction

“Weak” light field

(normal light, synchrotron)

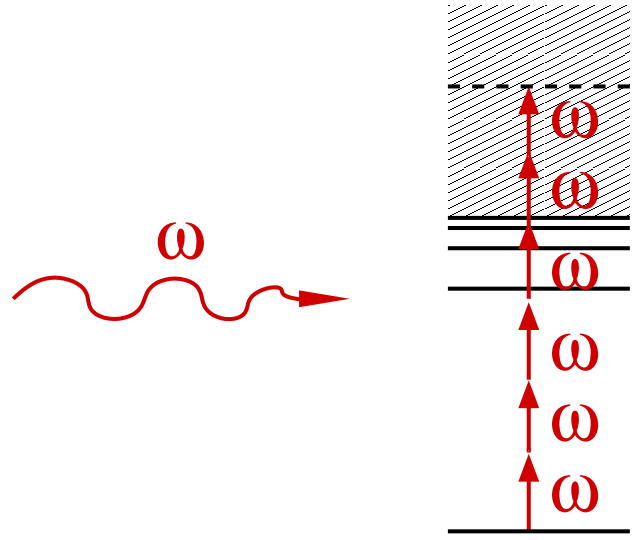


Single-photon absorption

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

Strong light field

(laser pulses)



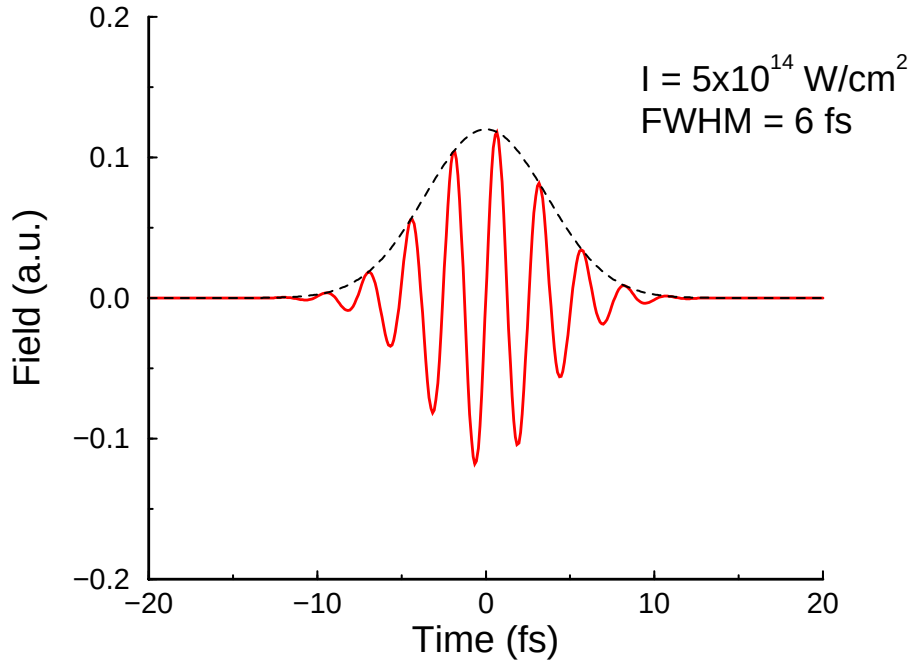
Multiphoton absorption

perturbative or

nonperturbative

Ultrashort laser pulses

Few-femtosecond light pulses are available:



→ cause ionization of atoms, fragmentation of molecules

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

→ “carrier-envelope phase” becomes important

Classical preliminaries

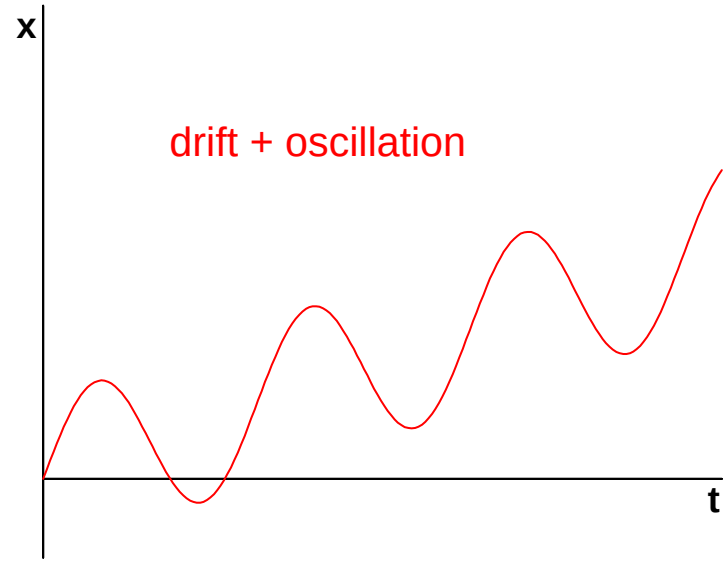
Free classical electron in a monochromatic laser field

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.

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**:

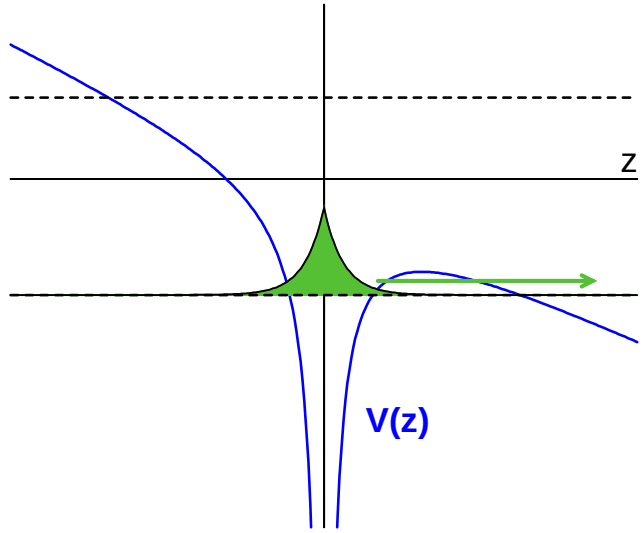
$$\boxed{\Psi^{\mathrm{V}}_{\mathbf{p}}(\mathbf{r}, t) = e^{-iS(\mathbf{p},t,t')} e^{i[\mathbf{p}+\mathbf{A}(t)]\cdot\mathbf{r}}}$$

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.

Tunneling

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



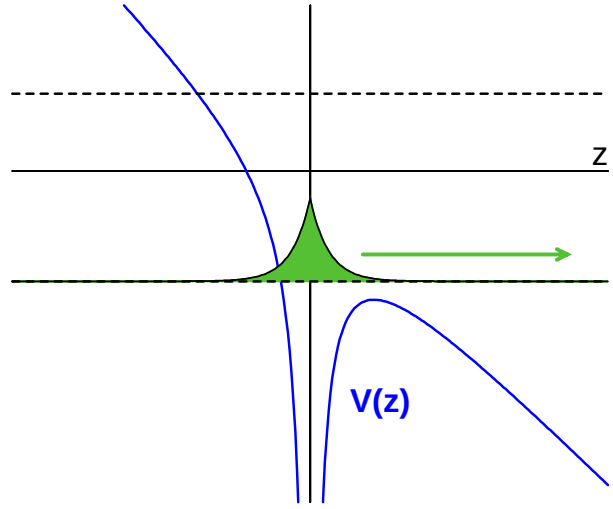
Tunneling rate for the hydrogen atom (see Landau & Lifshitz):

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

(derived from quasiclassical theory)

Over-barrier ionization

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

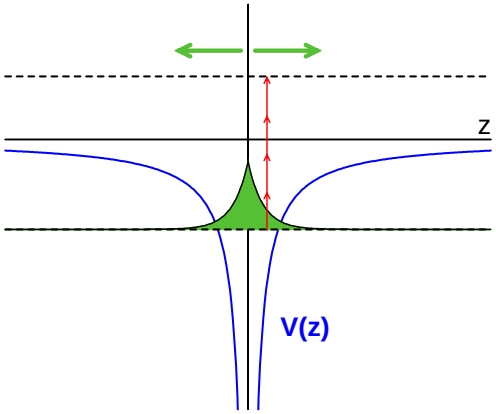


$\rightarrow$ Classical escape of the electron.

$E_{\rm BS} =$ **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)

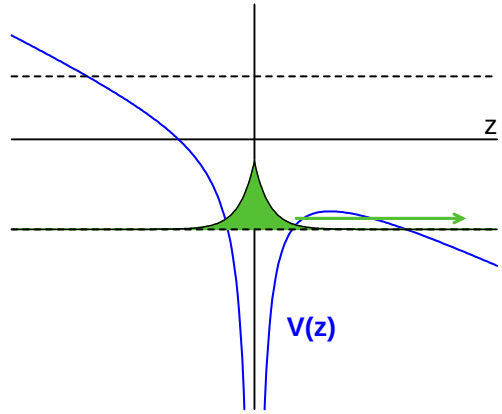
Ionization regimes

multiphoton ionization



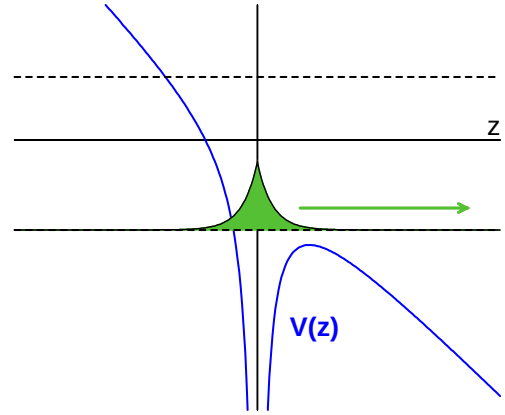
$\gamma = \omega/\omega_{\rm t} > 1$

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

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).

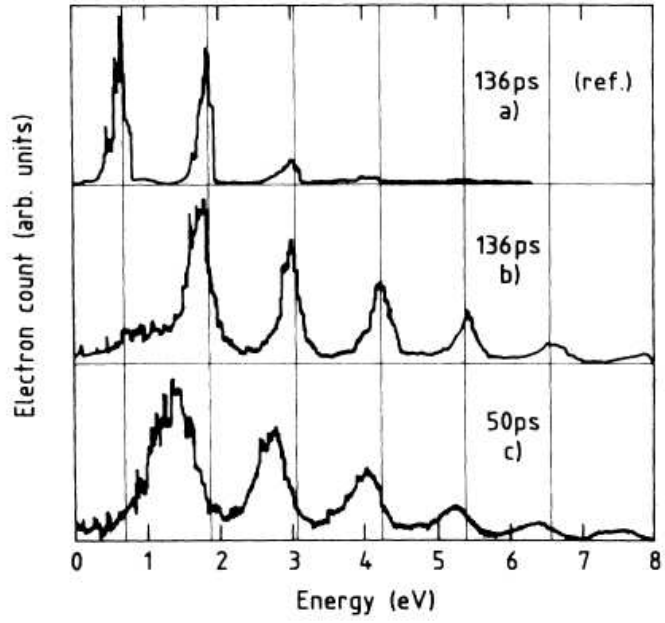


FIG. 2. Electron energy spectra for different laser intensities and pulse durations. (a) reference spectrum, $I = 2.2 \times 10^{12}$ W cm^{-2}; (b) and (c) $I = 7.5 \times 10^{12}$ W cm^{-2}.

Recollision mechanism

3-step process:

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

Recollision mechanism

3-step process:

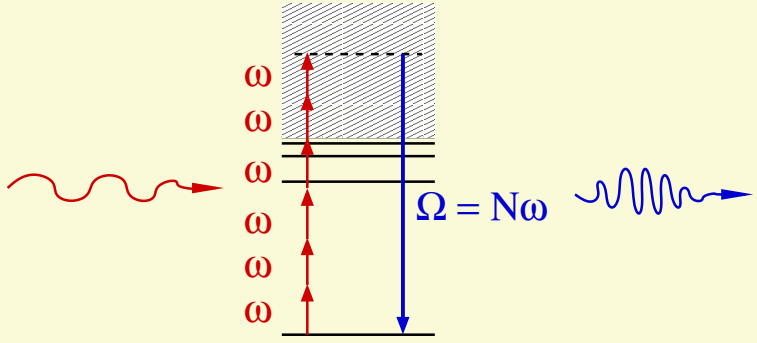
1. ionization
2. acceleration by the field
3. return to the core

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

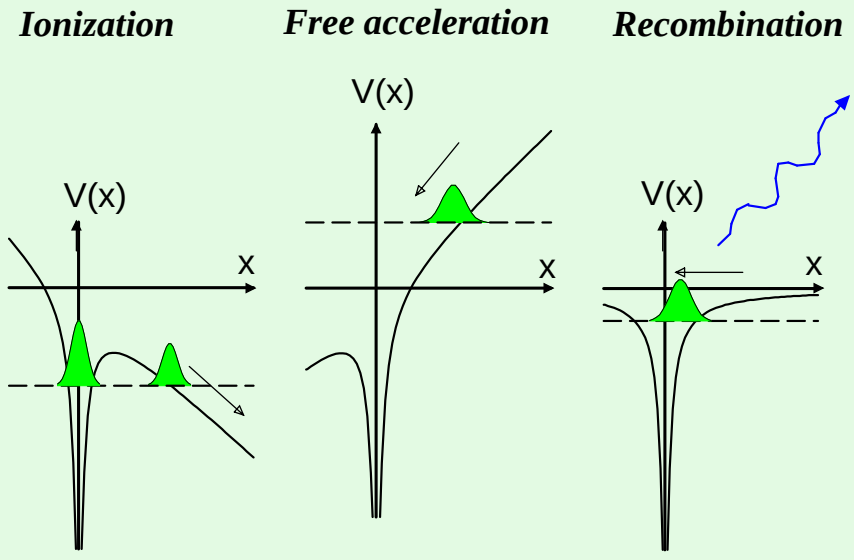


N photons of frequency ω

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

High-harmonic generation

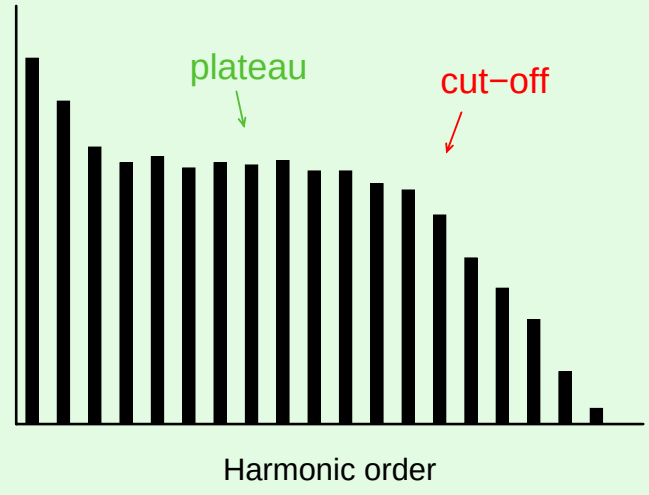
Recollision picture



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,

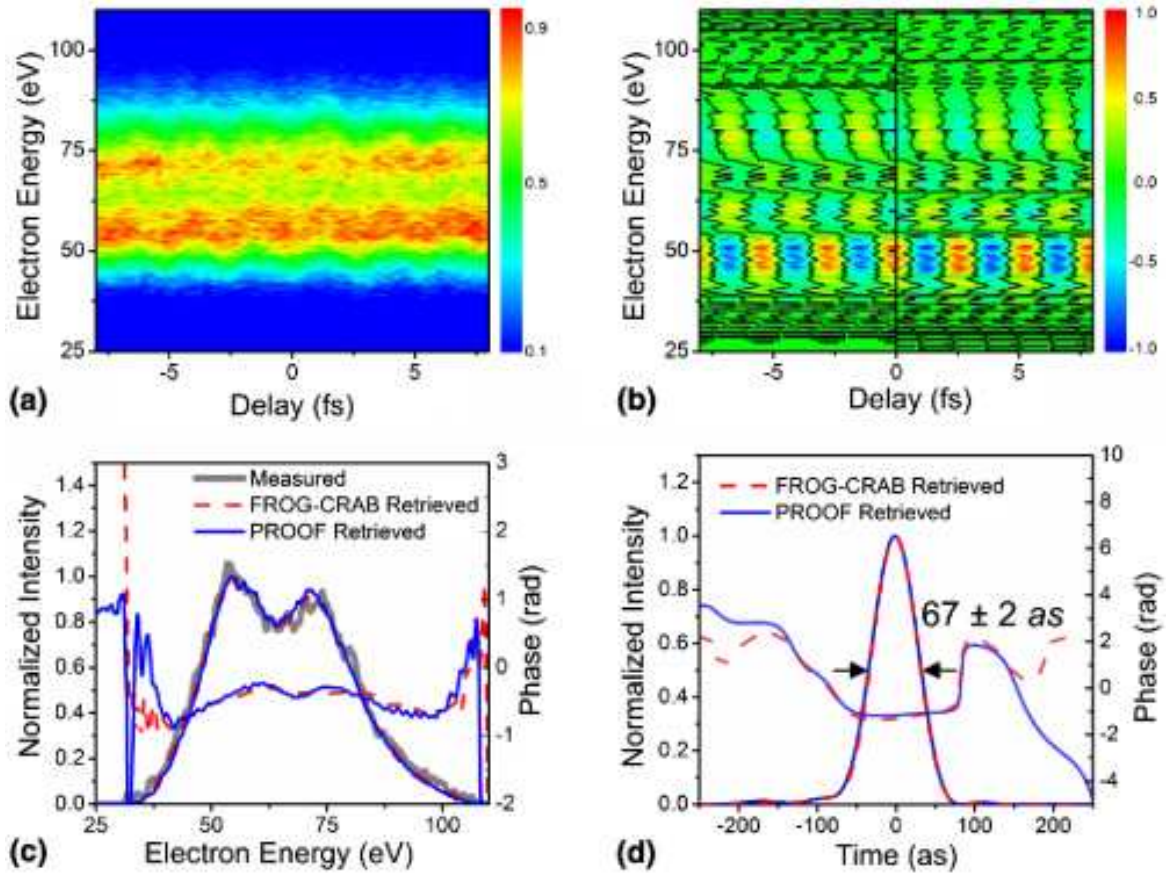
$$\boxed{\mathbf{a}(\Omega) = \int_0^T \mathbf{a}(t) f(t) e^{i\omega t}}$$

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 $\mathbf{v}(t)$

Attosecond pulses

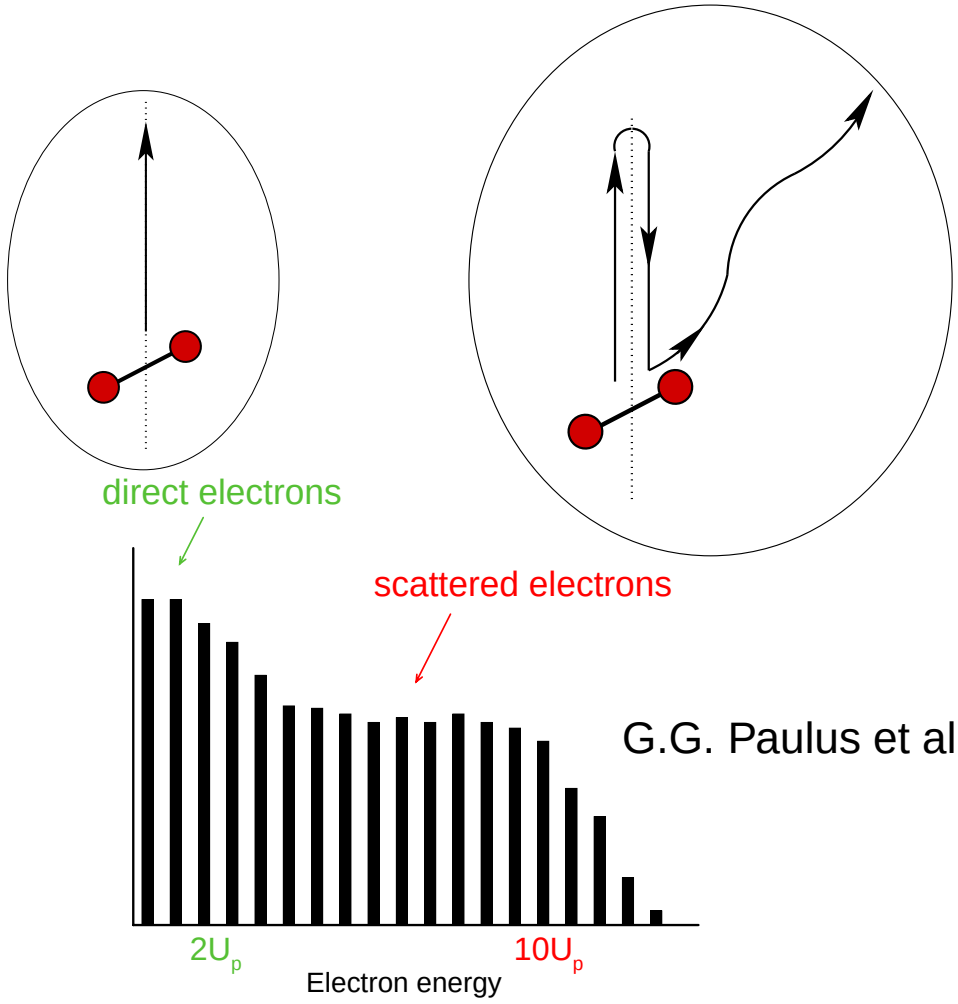
Currently shortest achieved coherent light pulses: 67as



Zhao et al., Opt. Lett. 37, 3891 (2012)

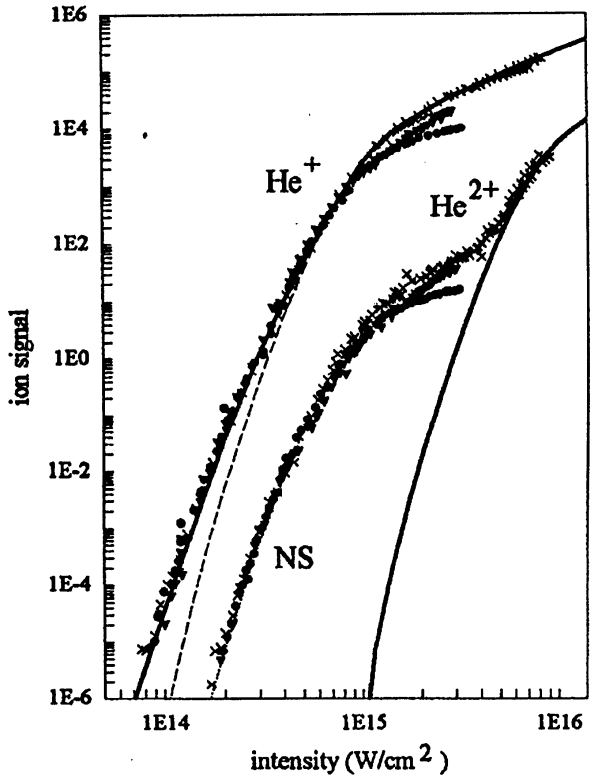
Rescattered photoelectrons

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):

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

Molecules

Set of nuclear and electronic coordinates $\mathbf{R}_j$ and $\mathbf{r}_k$.

Hamiltonian:

$$H_0 = \sum_j \frac{P_j^2}{2M_j} + \sum_k \frac{p_k^2}{2} + \sum_{j,k} w_{j,\mathrm{e}}(\mathbf{R}_j, \mathbf{r}_k) + \sum_{j_1 \neq j_2} w_{j_1,j_2}(\mathbf{R}_{j_1}, \mathbf{R}_{j_2}) + \sum_{k_1 \neq k_2} w_{\mathrm{ee}}(\mathbf{r}_{k_1}, \mathbf{r}_{k_2})$$

with w_{j_1,j_2} nucleus-nucleus interaction, $w_{j,\mathrm{e}}$ nucleus-electron interaction, and w_{ee} electron-electron interaction.

Light-molecule interaction:

$$H(t) = H_0 - \mathbf{D} \cdot \mathbf{E}(t)$$

with dipole moment $\mathbf{D} = (\sum_j Z_j \mathbf{R}_j) - (\sum_k \mathbf{r}_k)$

Born-Oppenheimer approximation

Separation of time scales for nuclear and electronic motion due to great mass difference

$\rightarrow$ Electrons adjust "instantaneously" to nuclear positions.

Born-Oppenheimer (BO) Ansatz for wave function:

$$\boxed{\Psi(\mathbf{R},\mathbf{r},t) = \sum_m \chi_m(\mathbf{R},t)\,\Phi_m(\mathbf{R},\mathbf{r}),}$$

$\Phi_m(\mathbf{R},\mathbf{r}) =$ electronic eigenstates at fixed nuclear positions.

Inserting into the field-free TDSE yields

$$i\tfrac{\partial}{\partial t}\chi_m(\mathbf{R},t) = \left[T_\mathrm{n} + V_m^\mathrm{BO}(\mathbf{R})\right]\chi_m \quad \leftarrow \textbf{BO approximation}$$

$$+ \sum_{m'} \langle \Phi_m | T_\mathrm{n} | \Phi_{m'} \rangle \chi_{m'} \quad \leftarrow \text{nonadiabatic couplings}$$

(T_n acting on both $\Phi_{m'}$ and $\chi_{m'}$)

Born-Oppenheimer approximation

Including the laser-molecule interaction, the BO TDSE becomes:

$$i\frac{\partial}{\partial t}\chi_m(\mathbf{R},t) = \left[T_{\rm n} + V_m^{\rm BO}(\mathbf{R})\right]\chi_m(\mathbf{R},t) \; - \; \mathbf{E}\cdot\sum_{m'}\langle\Phi_m|\mathbf{D}|\Phi_{m'}\rangle\chi_{m'}$$

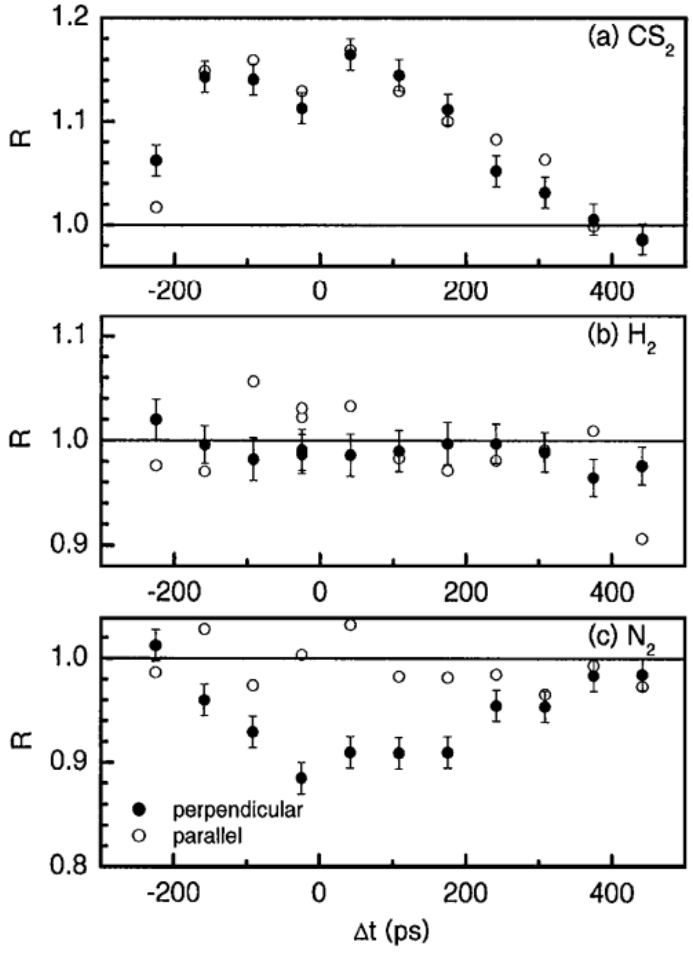
$\rightarrow$ Functions χ_m coupled only by the dipole matrix elements.

BO approximation breaks down for highly excited electrons:

- Rydberg molecules
- Electrons in the continuum

Controlling harmonic generation with molecular alignment

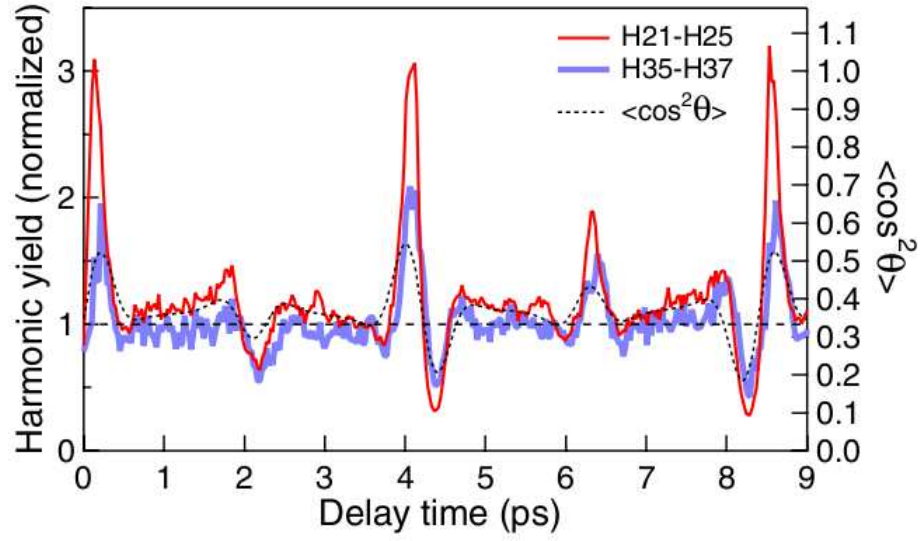
CS_2, H_2, N_2



9th harmonic, adiabatic alignment

Hay et al. PRL 87, 183901 (2001)

N_2



impulsive alignment

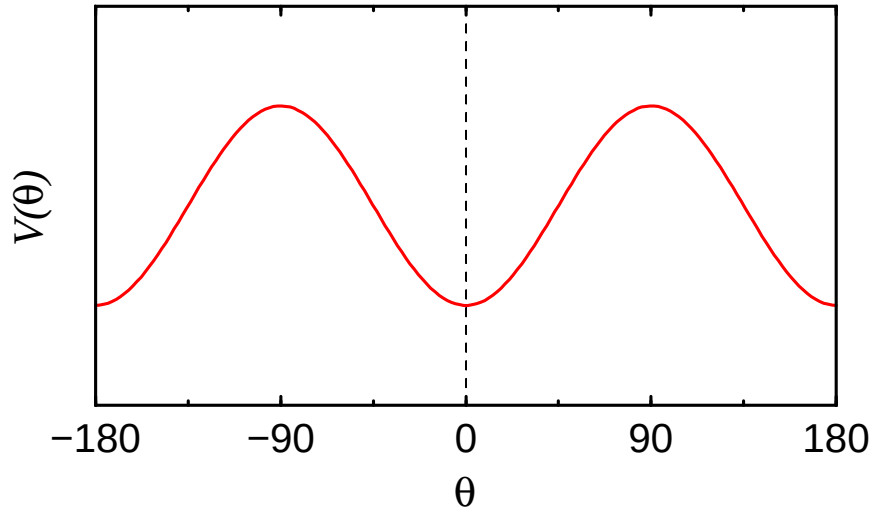
Itatani et al., PRL 94, 123902 (2005)

Adiabatic alignment of molecules

Linear molecule with dipole moment μ and polarizabilities $\alpha_{||}$, $\alpha_{\perp}$ interacts with laser field $E = E_0 \cos(\omega t)$ as

$$V_\mu(\theta) = -\mu E \cos\theta, \quad V_\alpha(\theta) = -\frac{1}{2} E^2 \left(\alpha_{||} \cos^2\theta + \alpha_\perp \sin^2\theta\right)$$

Sufficiently high frequencies: $\langle E \rangle \to 0$, $\langle E^2 \rangle \to E_0^2/2$



Aligning laser field is switched on slowly $\to$ *pendular states*

Friedrich and Herschbach, PRL 74, 4623 (1995)

experiment: **Larsen et al., JCP 111, 7774 (1999)**

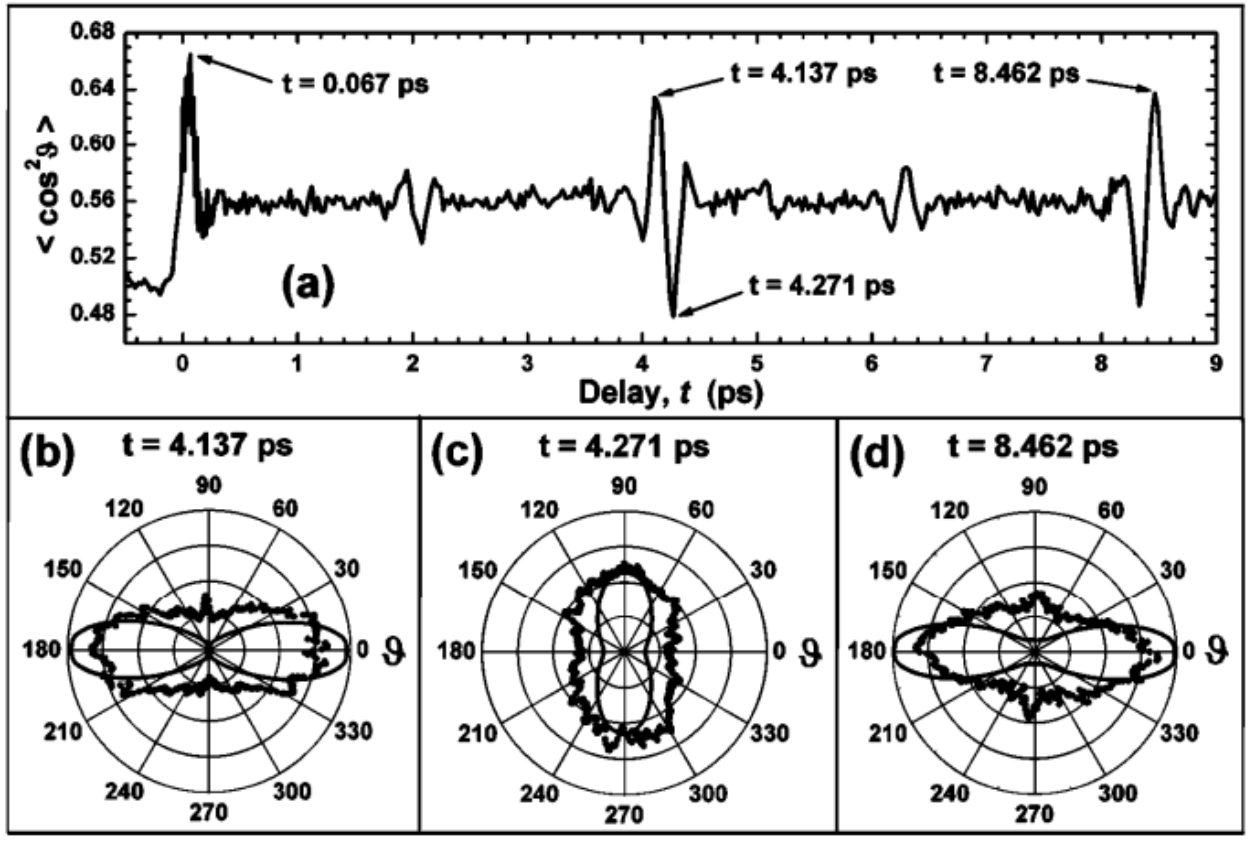
Impulsive alignment

Kick with a femtosecond pulse shorter than the rotational period

$\rightarrow$ Rotational revival structure exhibits times of *field-free alignment*.

Seideman, PRL 83, 4971 (1999), Rosca-Pruna/Vrakking, PRL 87, 153902 (2001)

Detection by Coulomb explosion of N_2 in circularly polarized pulse / ion detection:



Dooley et al., PRL 68, 023406 (2003)

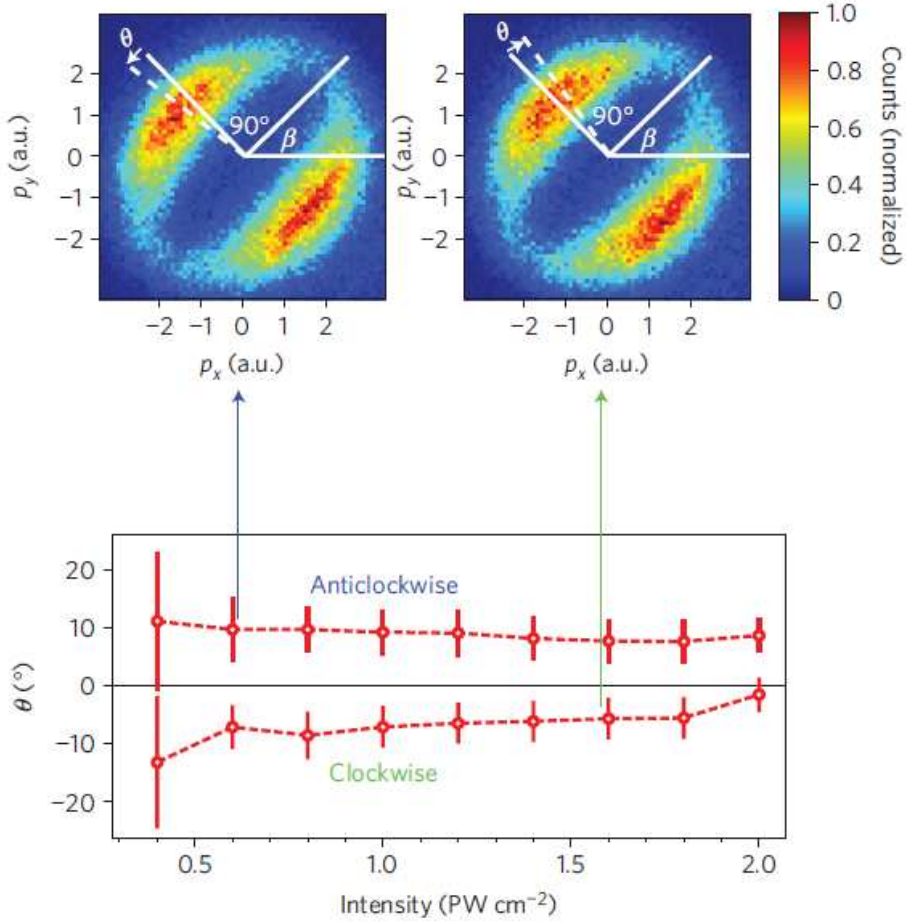
Two examples of open problems in laser atom/molecule interactions

- Tunneling times from the attoclock
- Photoelectron circular dichroism

Tunneling times from the attoclock

Attoclock principle:

- ionization by near-circular polarized pulses
- measurement of angular offset of the distribution peak

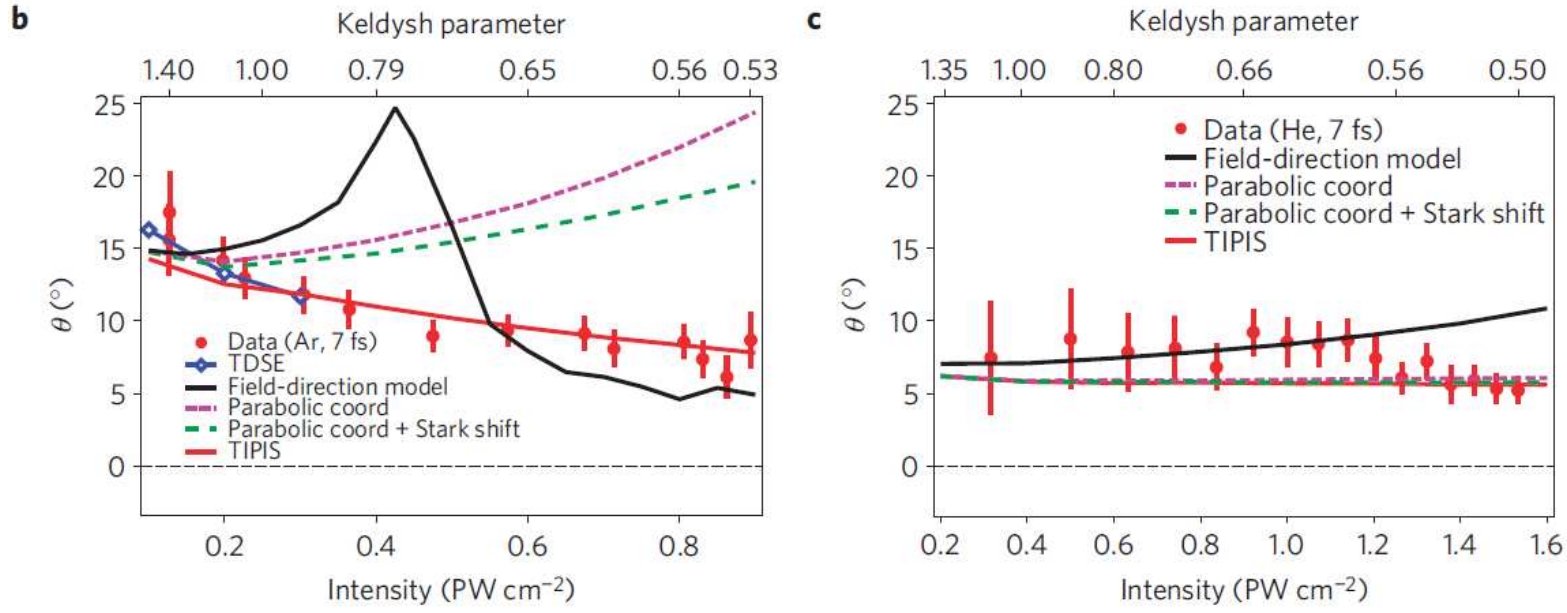


Pfeiffer et al., Nat. Phys. **8**, 76 (2011)

Tunneling times from the attoclock

Previous experiment:

consistent with instantaneous tunneling

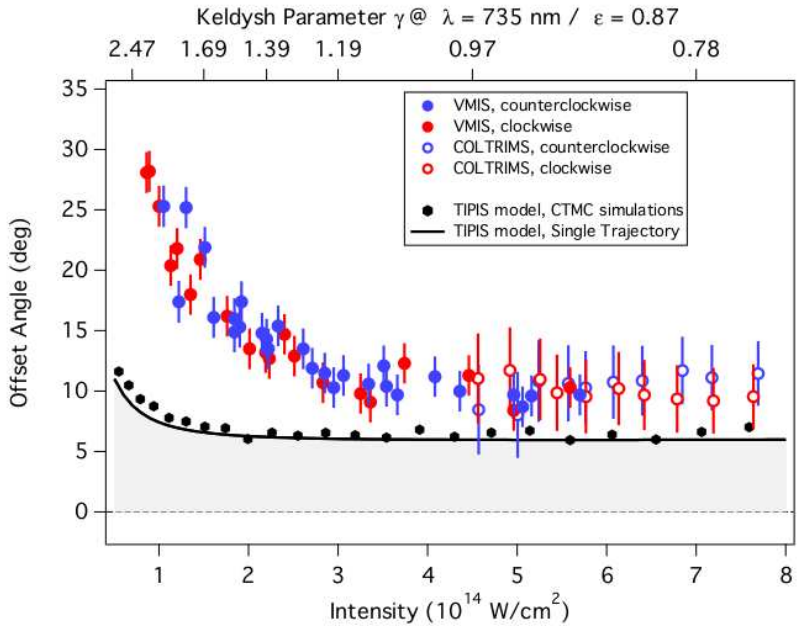


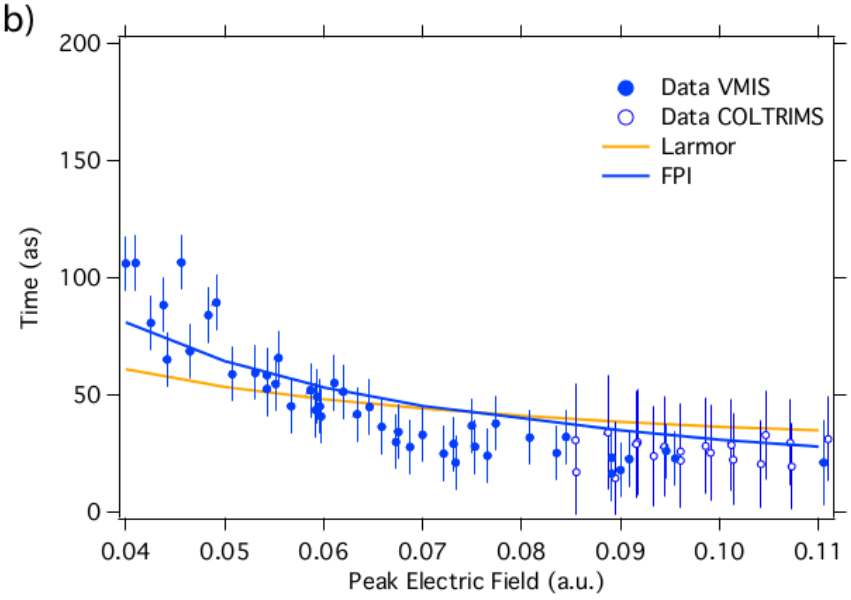
Pfeiffer et al., Nat. Phys. **8**, 76 (2011)

Tunneling times from the attoclock

Recent experiment:

appears to indicate non-zero real tunneling time

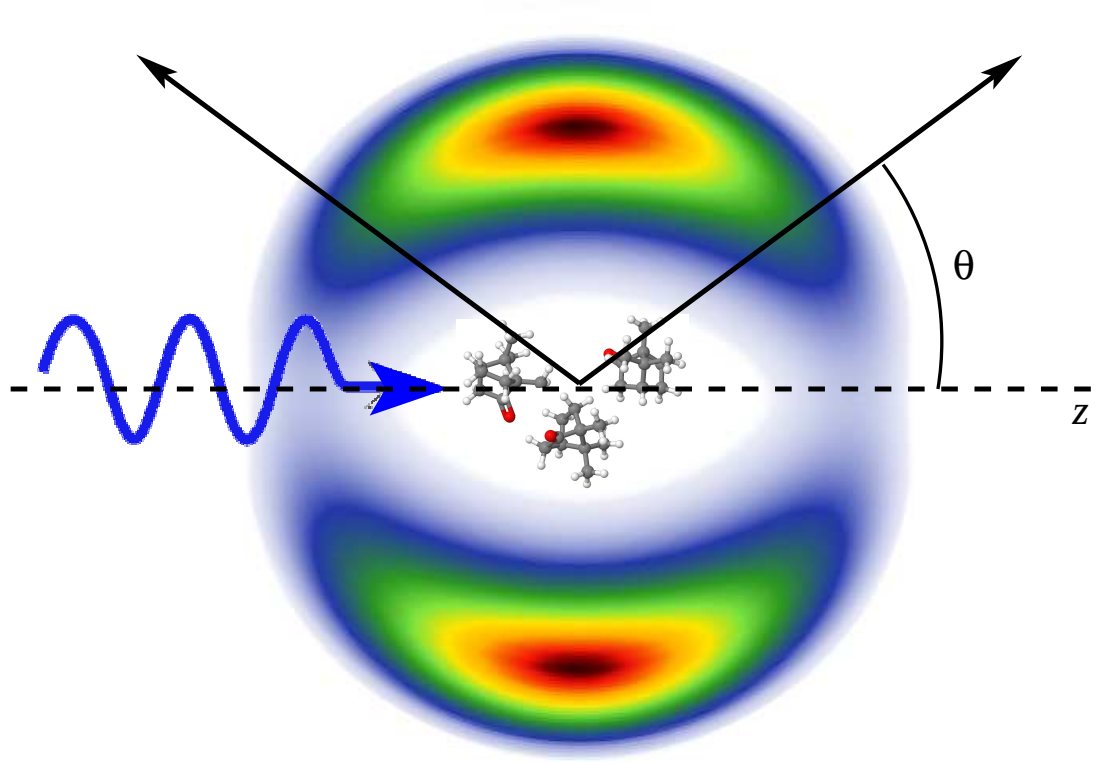




Landsman et al., arXiv:13012766v2 (2013)

Strong-field photoelectron circular dichroism

- Ionization of chiral molecules with circularly polarized laser pulses
- Observable: three-dimensional photoelectron distribution
- Search for forward-backward asymmetry

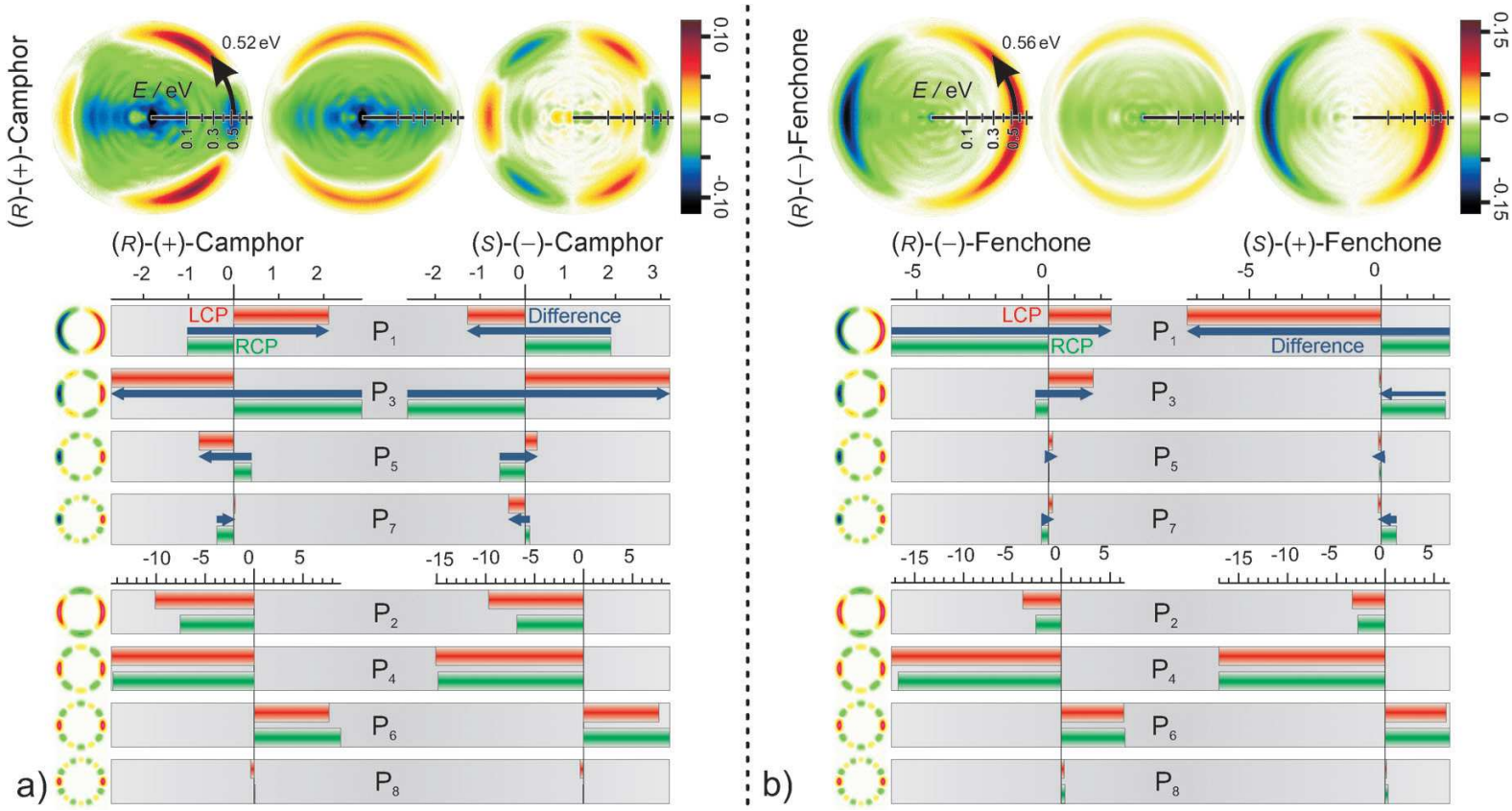


[Ritchie, PRA 13, 1411 (1976); Cherepkov, CPL 87, 344 (1982);

Powis, JCP 112, 301 (2000); Böwering et al., PRL 86, 1187 (2001)]

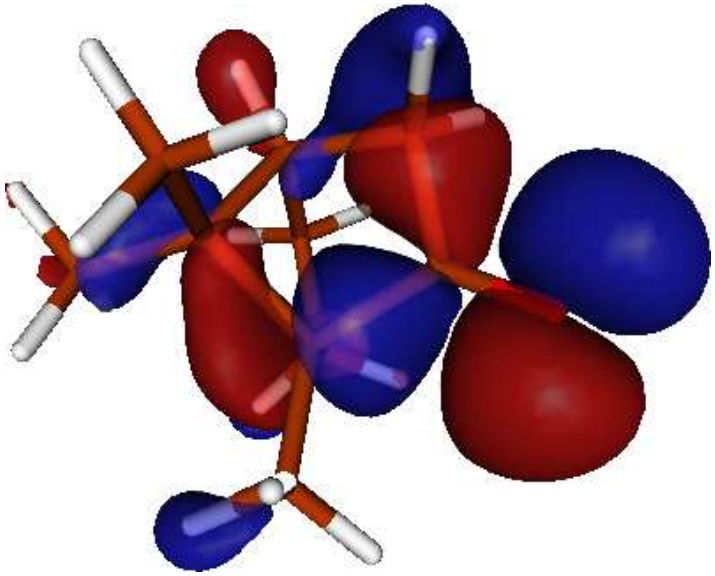
Strong-field photoelectron circular dichroism

Femtosecond pulse PECD **[Lux et al., Angew. Chem. Int. Ed. 51, 5001 (2012)]**

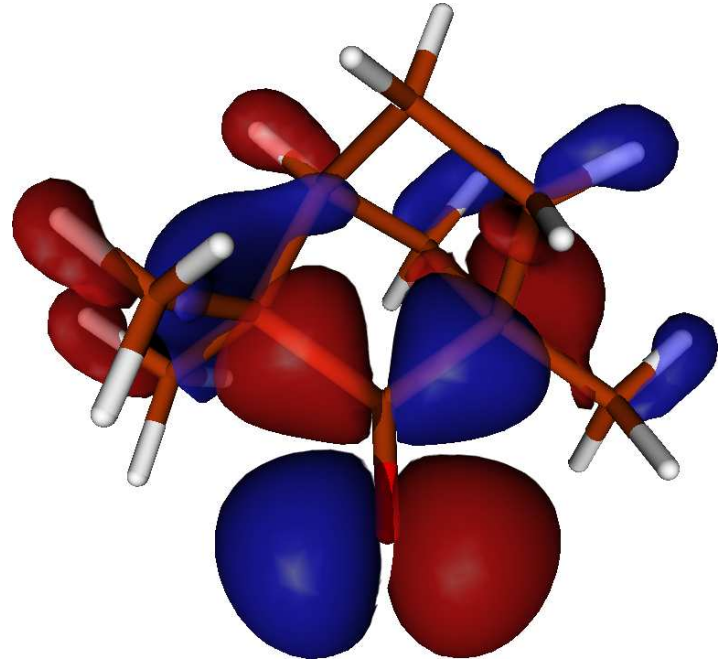


Camphor and fenchone HOMOs

R-camphor

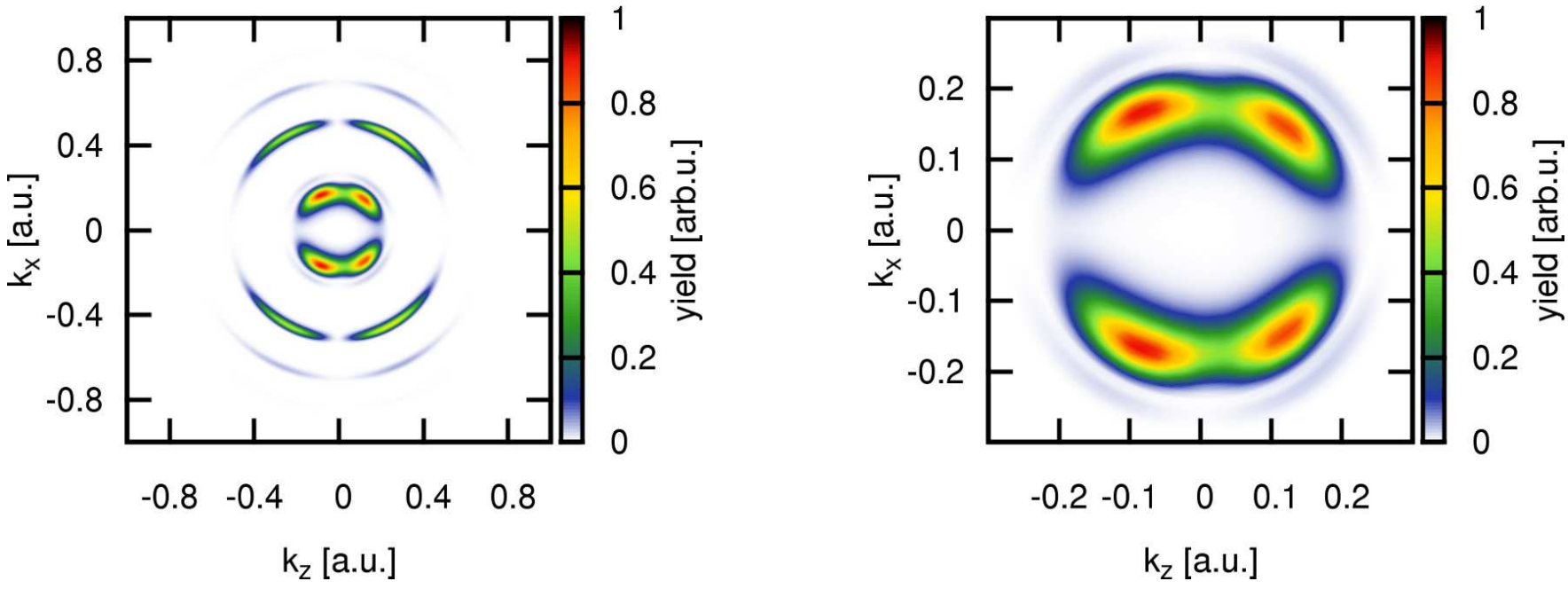


R-fenchone



Calculated electron distributions (SFA+Born approximation)

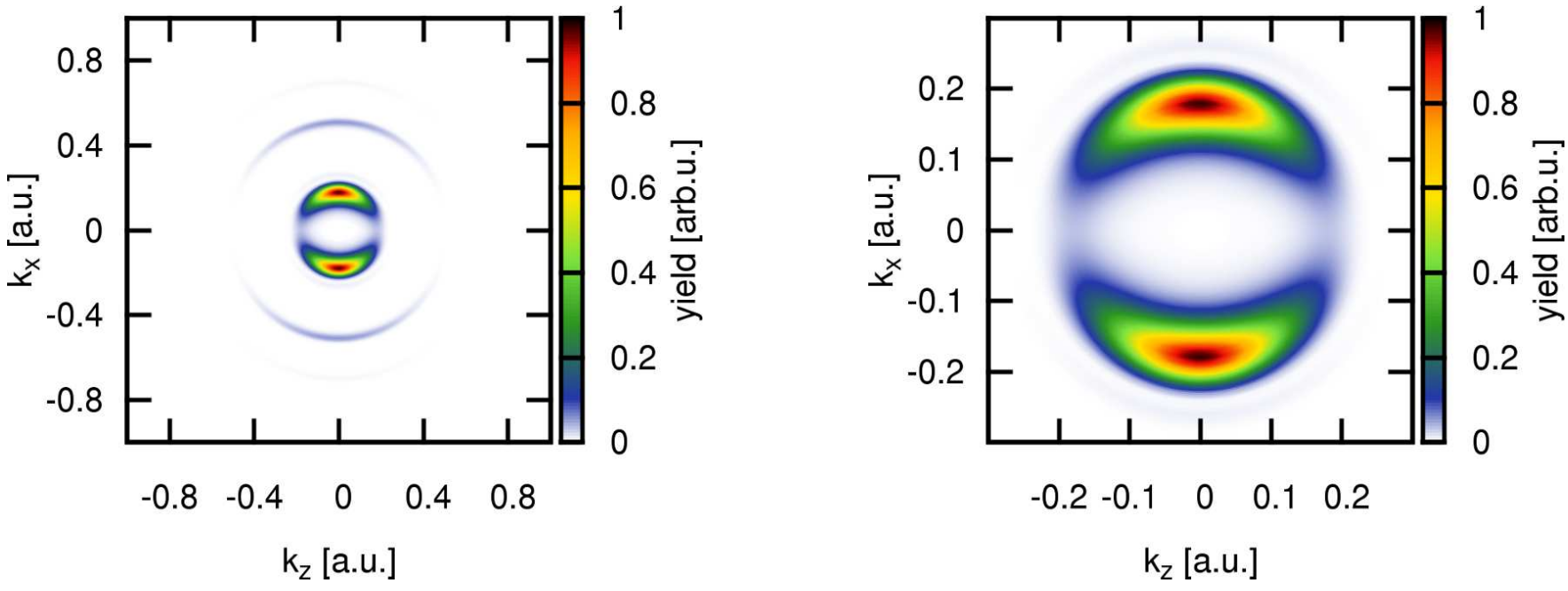
R-fenchone, single orientation, LCP pulse (total length 20 cycles)



- Three-, four- and five-photon rings are visible.
- Asymmetry due to single orientation.

Photoelectron distributions

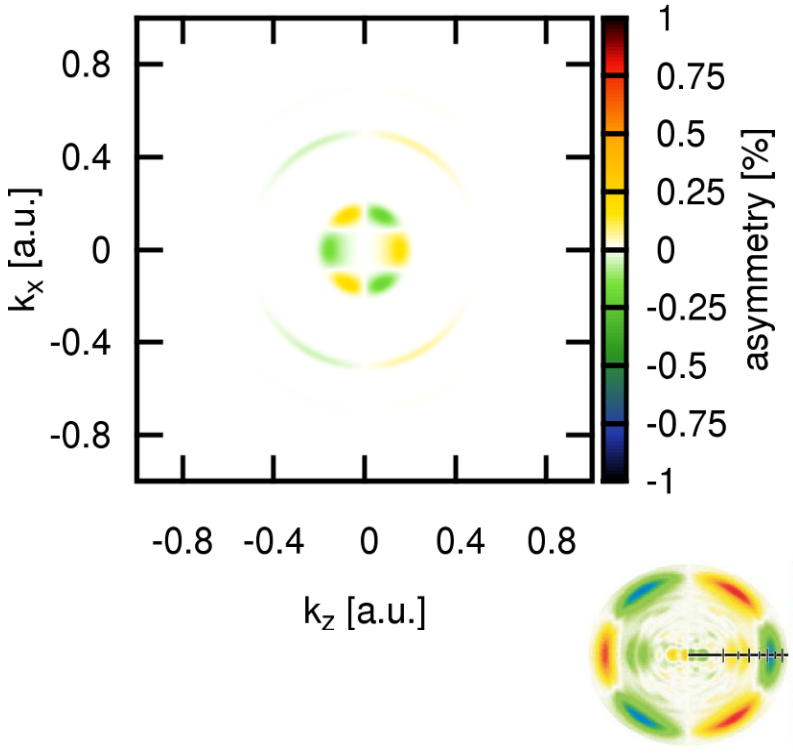
R-fenchone, random orientation (numerically averaged over Euler angles)



- Asymmetry is reduced by angle averaging.
- Camphor distribution looks practically the same as in fenchone.

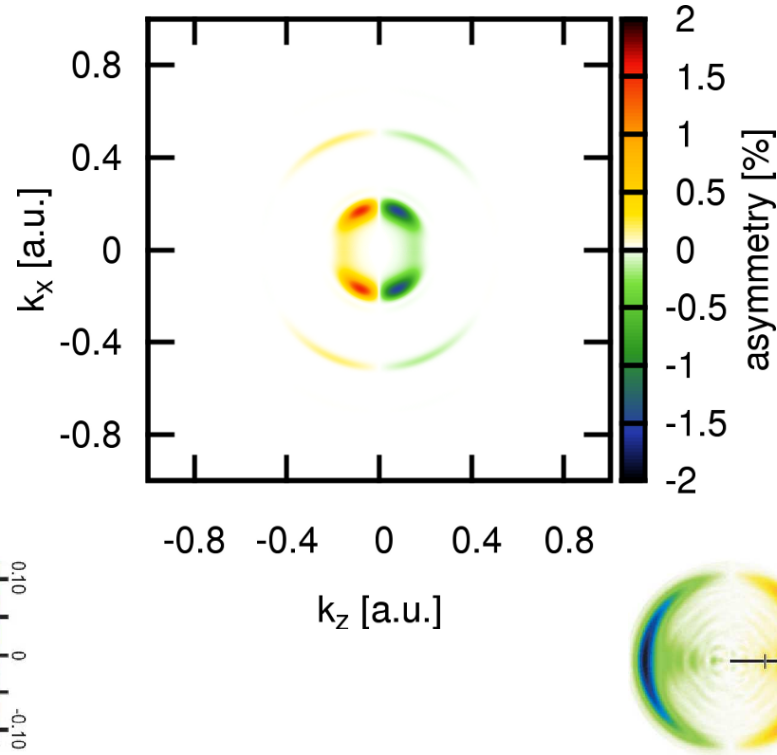
Forward-backward asymmetries

R−camphor



Lux et al.

R−fenchone



Lux et al.

- Nodal structure in good agreement with experiment
- Asymmetries smaller and of different sign compared to experiment
- Fenchone gives stronger asymmetry (matches experiment)

Conclusions

- Strong laser fields require nonperturbative description; even one-electron problem is demanding.
- In general, theoretical description relies heavily on models; open problems in simple systems
- TDDFT is the only tractable first-principles approach, already for atoms.

Next part:

- Model systems and TDDFT