tSURFF - Photo-Electron Emission from One-, Two- and Few-Electron Systems

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Quantum Dynamics - Theory
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Munich Advanced Photonics
Excellence Cluster

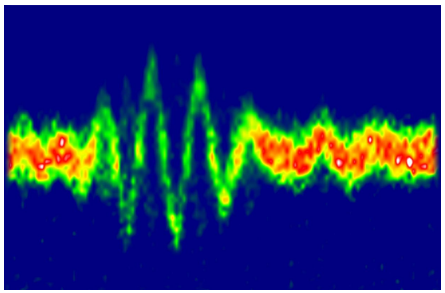
Vienna Computational Materials Science
FWF Special Research Program

Marie Curie ITN

A wealth of measured photo-electron spectra...

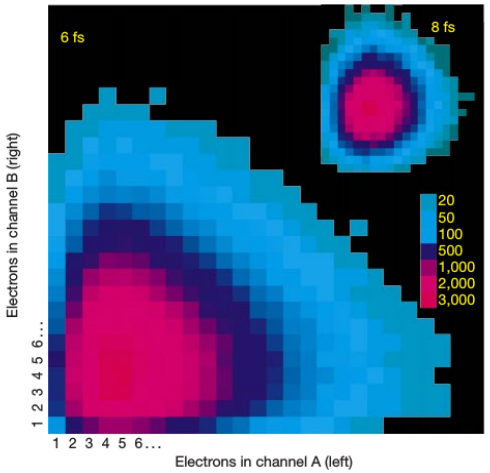
in “attosecond physics”:

Few-cycle IR pulse



Direct image of a laser pulse

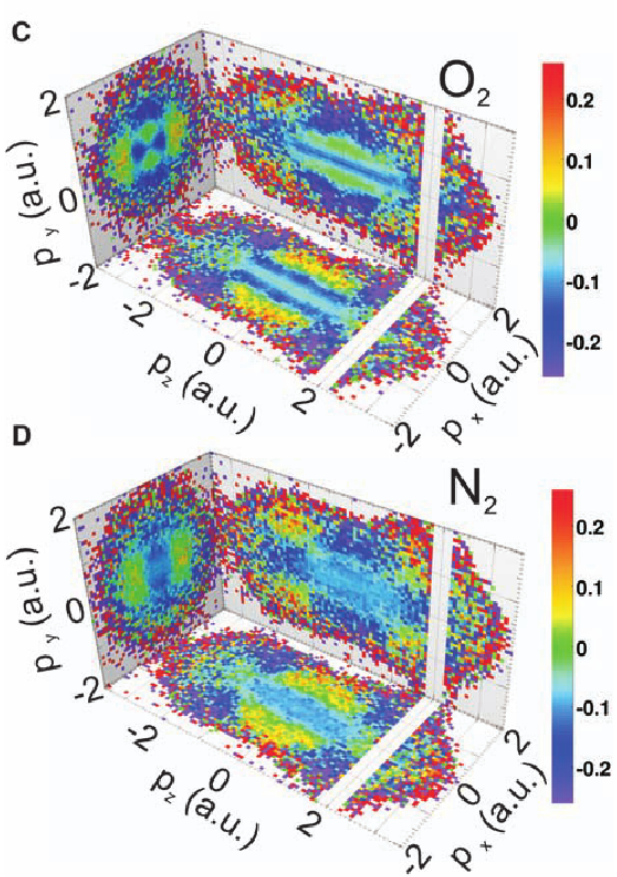
Double emission



Correlation

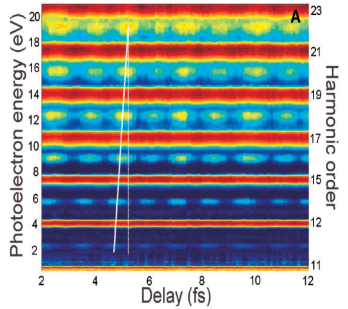
Laser-Induced Electron Tunneling and Diffraction

M. Meckel,[1,2] D. Comtois,[3] D. Zeidler,[1,4] A. Staudte,[1,2] D. Pavičić,[1] H. C. Bandulet,[3] H. Pépin,[3] J. C. Kieffer,[3] R. Dörner,[2] D. M. Villeneuve,[1] P. B. Corkum[1]*



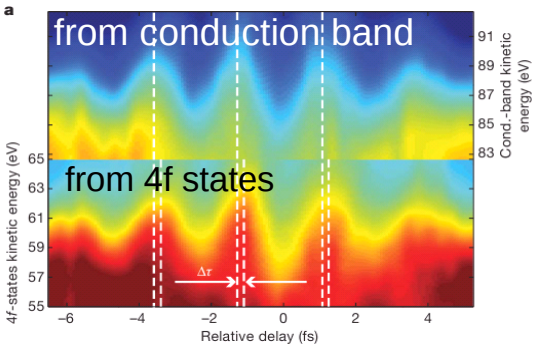
Details of molecular electronic structure

RABITT spectrogram



Complete diagnosis of sub-fs pulses

Emission from surface



Miniscule (10 as) time differences

...but modelling and calculation are hard

Two main difficulties:

(1) solution covers large (phase) space

(2) complexity of few-electron calculations

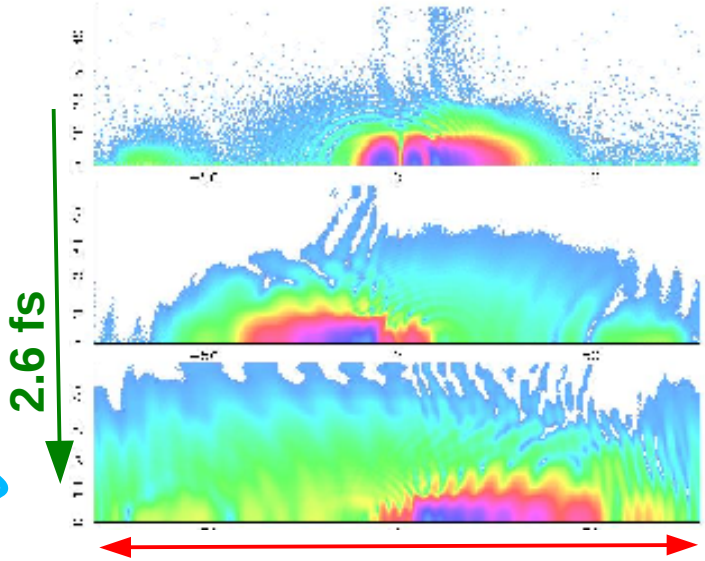
Large box sizes due to ionization:

irECS perfect absorption method

Spectra from a truncated calcuation:

tSurff time dependent surface flux

Single electron density during 2.6 fs



Complexity of quantum chemistry wave function:

→ Integrate quantum chemisty with strong field dynamics

One-electron systems

- ✔ Discretization beyond basis sets (high order FEM)
- ✔ Control box size by perfect absorption (irECS)
- ✔ Determine spectra from truncated calculation (tSURFF)
- ✔ Efficiency example: strong field photo-emission

Discretization: why finite elements?

Required basis sizes

d degrees of freedom
phase space volume ***V***

$$N > V/h^d$$

There are no smart tricks to beat this number unless we have additional information

Additional information

E.g. perturbative ionization, i.e. initial state or free motion
or SFA: initial state or Volkov wave packet
or: we “know” only bound states play a role or …

Basis sets

Pseudo-spectral (e.g. field-free eigenstates, momentum-space)

Build **energy- or momentum**-information into ansatz

Local basis sets (B-splines, finite-element, FEM-DVR)

Exploit **locality** of operators (differentiation, multiplication)
Numerically robust

High order finite elements

Locally adjustable (→ irECS)
Well-defined points of non-analyticity (element boudaries)
Rapid convergence due to high order (e.g. 10-20)
Parallelization: communication independent of order

Exterior complex scaling (ECS)

General approach for perfect absorbers (PML, ECS)

[A.S., H-P. Stimming, N. Mauser, J. Comp. Phys., to appear]

Outside some inner region $[0,R_0]$

analytically continue a **unitary transformation** U_λ (e.g. coordinate scaling)

to **contractive** (non-unitary) U_θ

$$i\frac{d}{dt}\Psi = H(t)\Psi \rightarrow i\frac{d}{dt}\Psi_\theta = U_\theta H(t) U_\theta^{-1}\Psi_\theta$$

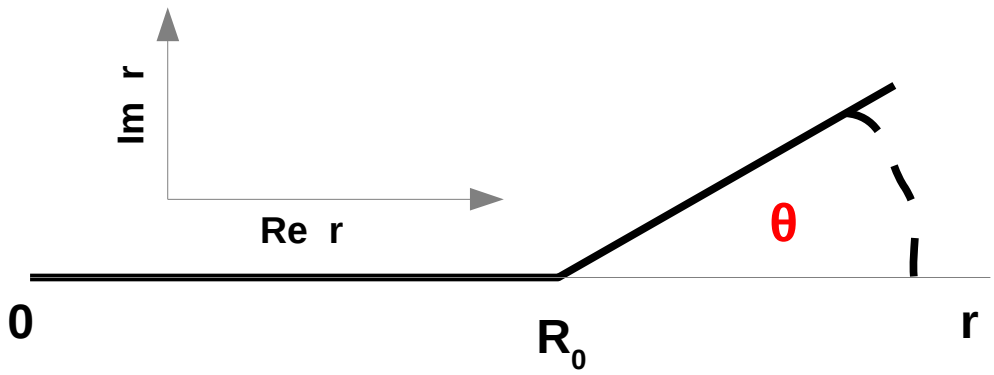
Unitarity + analyticity guarantee unchanged solution Ψ_θ on $[0,R_0]$

!!! Caution: Domain issues for $U_\theta H(t) U_\theta^{-1}$!!!

Translates into:
Complex coordinates
beyond a finite distance R_0

$r \rightarrow r$ for $r < R_0$

$r \rightarrow R_0 + e^{i\theta}(r-R_0)$ for $r > R_0$



Implementation of exterior complex scaling

Important technical complication

Bra and ket functions are not from the same set!!!

Exterior scaled Laplacian $\Delta_{R0,\Theta}$ is defined on discontinuous functions

$$\Psi(R_0 - 0) = e^{3i\theta/2}\Psi(R_0 + 0)$$

Discontinuity because start from unitary transformation

Discontinuity is reversed for the left hand functions

$$\Psi^*(R_0 - 0) = (e^{-3i\theta/2}\Psi)^*(R_0 + 0)$$

Matrix elements of $\Delta_{R0,\Theta}$

are computed by piece-wise integration $[0,R_0] + [R_0,\infty)$

Conditions easy to implement with a local basis set

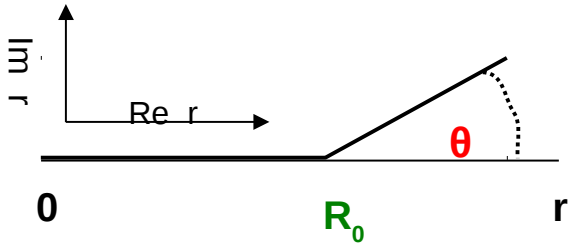
irECS – a perfect absorber

[A.S., Phys. Rev. A81, 53845 (2010)]

Infinite range Exterior Complex Scaling

ECS: $r \rightarrow r$ for $r < R_0$

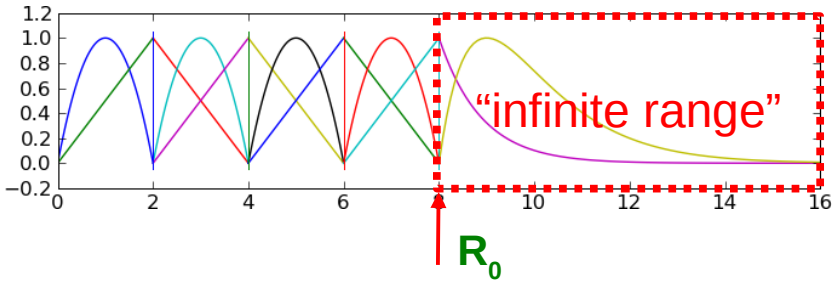
$r \rightarrow R_0 + e^{i\theta}(r-R_0)$ for $r > R_0$



Discretization

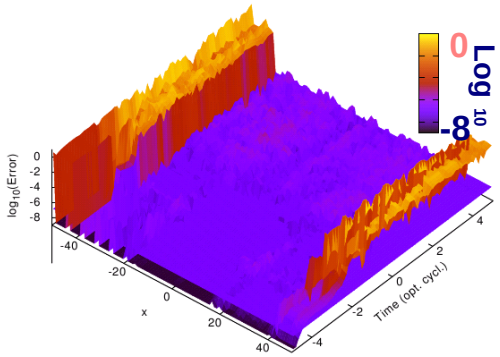
High (~8th) order finite elements

infinite size last element $[R_0,\infty)$



Accuracy

$|\Psi_{\theta R0}(x,t) - \Psi(x,t)| / |\Psi(x,t)|$



Accuracy inside R_0 ~ 10^{-7}

Efficiency

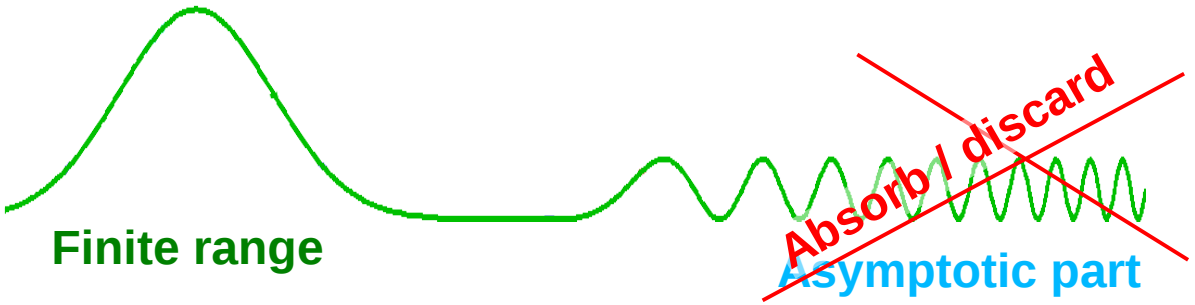
Number of points — Accuracy

Method	M_A	A	θ or σ	q	$\mathcal{E}[-R_0, R_0]$
irECS	21	∞	0.6	—	2×10^{-15}
ECS	20	10	0.6	—	2×10^{-4}
ECS	40	20	0.5	—	1×10^{-7}
CAP	20	10	10^{-4}	4	3×10^{-3}
CAP	20	10	2×10^{-6}	6	4×10^{-3}
CAP	40	20	4×10^{-6}	4	3×10^{-4}
CAP	60	30	6×10^{-7}	4	1×10^{-5}

CAP = complex absorbing potential

tSURFF – how to obtain spectra from a finite range wave function

Scattering spectra = asymptotic information by definition



If we solve only on a finite range, exactly the asymptotic information is **missing**

Solution:

Continue beyond the box using some **known solution – Volkov**

[Caillat et al., Rev. A 71 , 012712 (2005)]
[L. Tao and A.S., New. J. Phys. 14, 013021 (2012)]

How we usually calculate spectra from TDSE

Get Ψ(r,t) at the end of the pulse t=T: ***Ψ(r,T)*** ← **problem 1** Needs very large box

Scattering solution ψ_k $H(T)|\psi_{\vec{k}}\rangle = \frac{\vec{k}^2}{2}|\psi_{\vec{k}}\rangle$ ← **problem 2** Time-independent scattering

With asymptotics $\psi_{\vec{k}}(\vec{r}) \sim (2\pi)^{-3/2}\exp(i\vec{k}\cdot\vec{r})$

Spectrally analyze Ψ(x,t) $b(\vec{k}) = \langle\psi_{\vec{k}}|\Psi(T)\rangle$

Spectral density $\sigma(\vec{k}) \propto |b^2(\vec{k})|$

Solve by using additional information

(1) TDSE is a 2nd order PDE

Value and derivative at a surface $r = R_c$ suffice
to continue the solution beyond the surface

(2) Beyond distances R_c ~ 50 a.u. motion is free

Use Volkov solution for free motion in the field instead of numerically solving

Compare R-matrix theory!

How things are done...

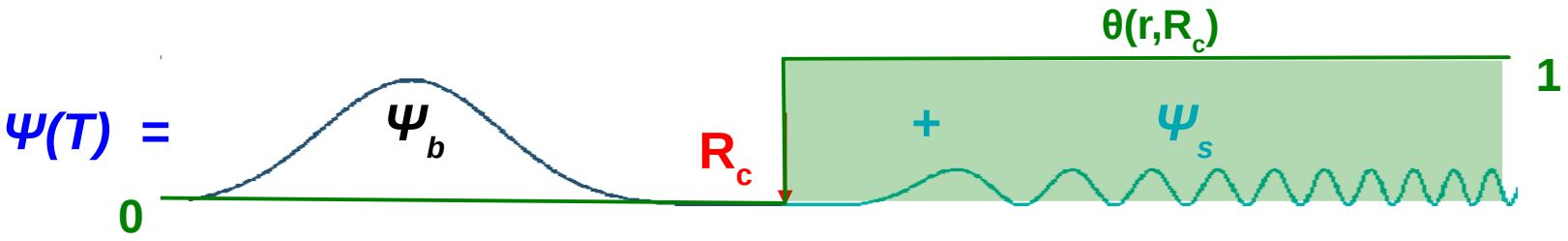
- for a given pulse, **solve** with irECS absorption (box size ~ 50 a.u., laser-dependent)
- save surface values and derivatives at surface(s) as function of time
- properly **time-integrate** surface values for asymptotic momenta ***p*** of your choice
  (one integration for each ***p,*** ordinary integrals, very cheap!)
- can zoom in onto areas of interest (important for 2-electron problems)
- Effort grows only linearly with pulse duration T (cf. T^2 ~ T^4 if time and box-size grow)

t-SURFF – time-dependent surface flux method

[L. Tao and A.S., New. J. Phys. 14, 013021 (2012)]

Propagate until large T where bound Ψ_b and scattering Ψ_s parts separate

Beyond distance R_c scattering solutions χ_k are known



Spectral amplitude σ(k):

with *Volkov solutions* χ_k

$$\sigma(\vec{k}) \propto \left| \langle \chi_{\vec{k}} | \theta(R_c) | \Psi(T) \rangle \right|^2$$

Volume integral → Time-integral & surface integral

$$\langle \chi_k(T) | \theta(R_c) | \Psi_s(T) \rangle = i \int_0^T dt \langle \chi_k(t) | \left[-\frac{1}{2}\Delta + i\vec{A}(t)\cdot\vec{\nabla}, \theta(R_c) \right] | \Psi_s(t) \rangle$$

Commutator depends only on $\Psi(R_c,t)$ and $\partial\Psi(R_c,t)$

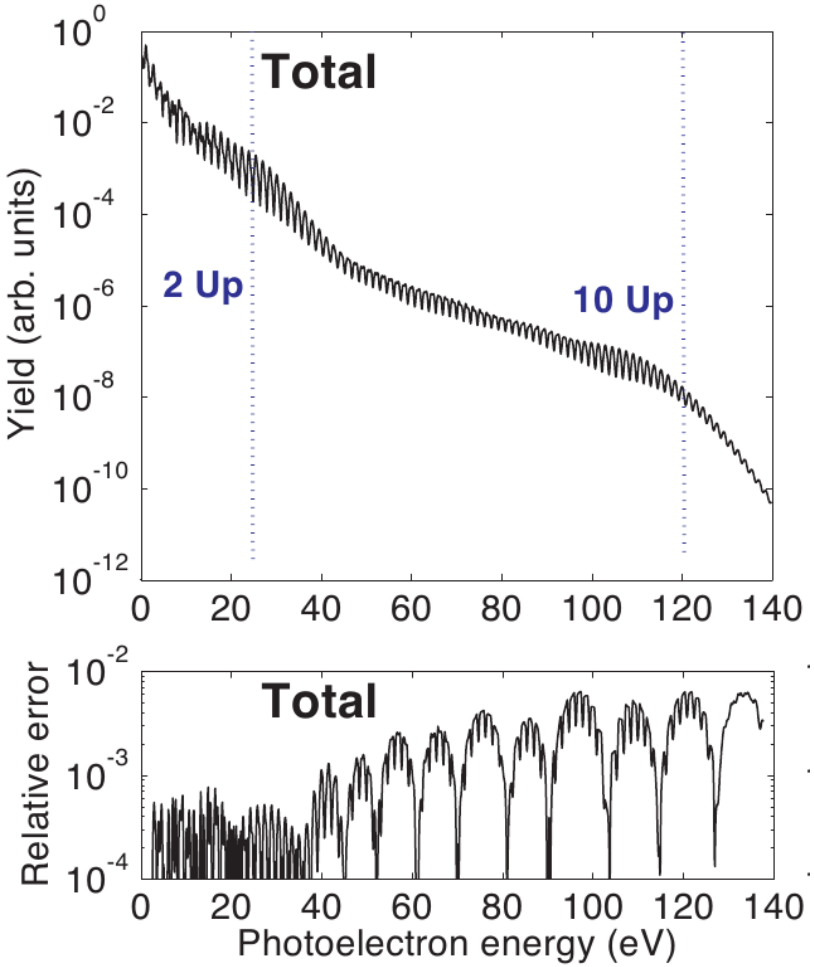
Note: need time-dependent bra-solutions ≈ ***Volkov (or better, if available)***

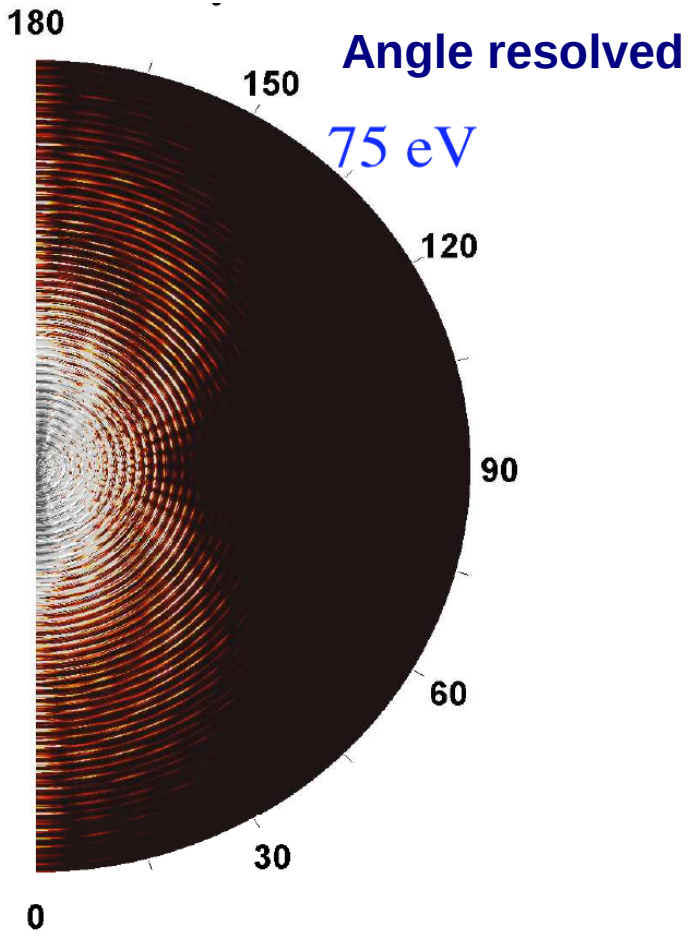
Single photo-electron spectra

Photo-electron spectra – single electron, 3d

[L. Tao and A.S., New. J. Phys. 14, 013021 (2012)]

Hydrogen atom, **Laser:** 2 x 10^{14} W/cm^2 @ 800 nm, **20 opt.cyc. FWHM**
Linear polarization





90 radial discretization points, 30 angular momenta

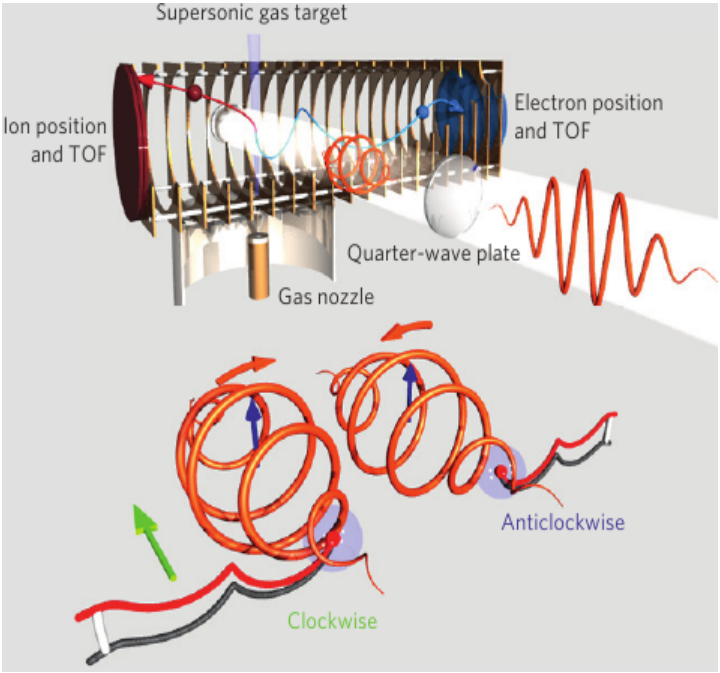
Attoclock – ionization by elliptically polarized IR

[Pfeiffer et al, Nat. Phys. 8, 76 (2012)]

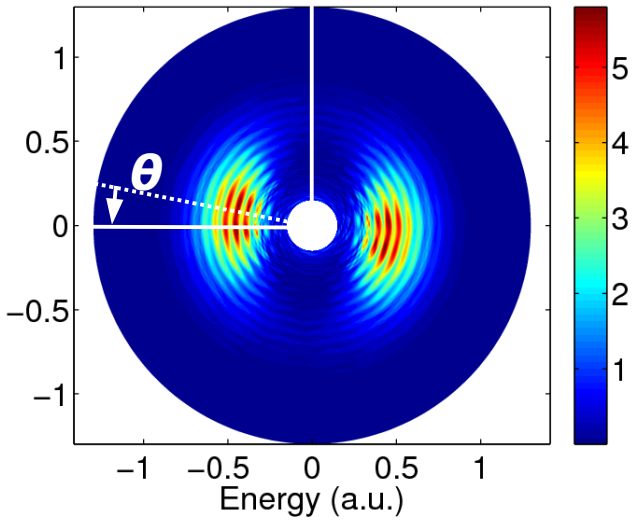
Angle-resolved photo-electron spectra

Peak emission direction
deviates from
Peak field direction

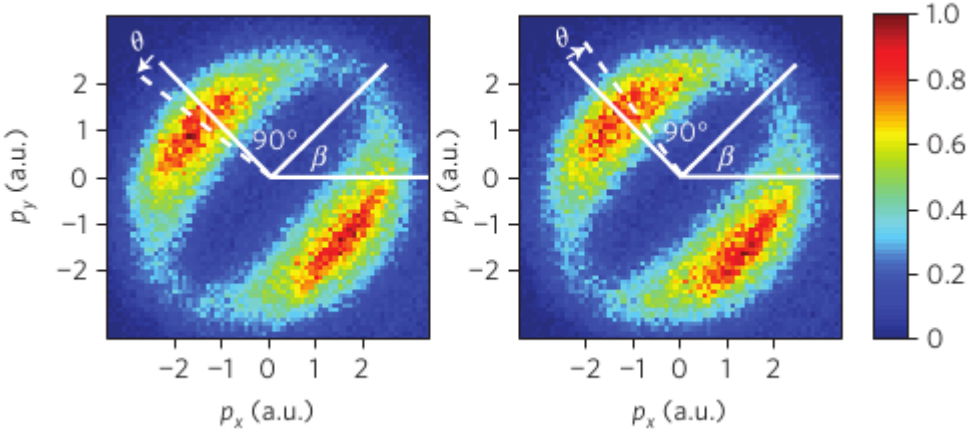
=> deduce delay in release of electron



Solution of the TDSE



Use oppositely handed polarizations
to calibrate peak field direction



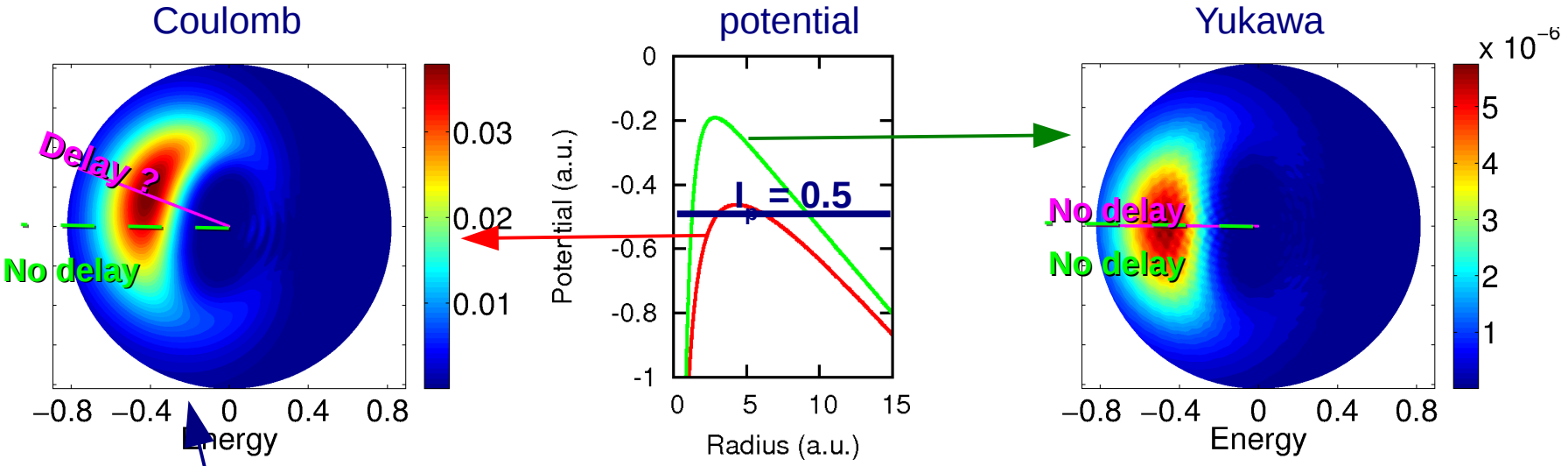
Tunneling times (?) in IR ionization

Is the offset angle θ related to a "tunneling time"?

If the time-delay is related to tunneling,
expect wider barrier longer tunneling delay?

Numerical result

Laser: 800nm, single cycle, 10^{14}W/cm^2, ellipticity as in Pfeiffer et al.
Ionization potential: 0.5 a.u. (Hydrogen)



No evidence for "tunneling time" in this setting

(Reasons for the observed delay in Coulumb – long range correction)

Comparison theory and experiment

Angles of peak photo-emission

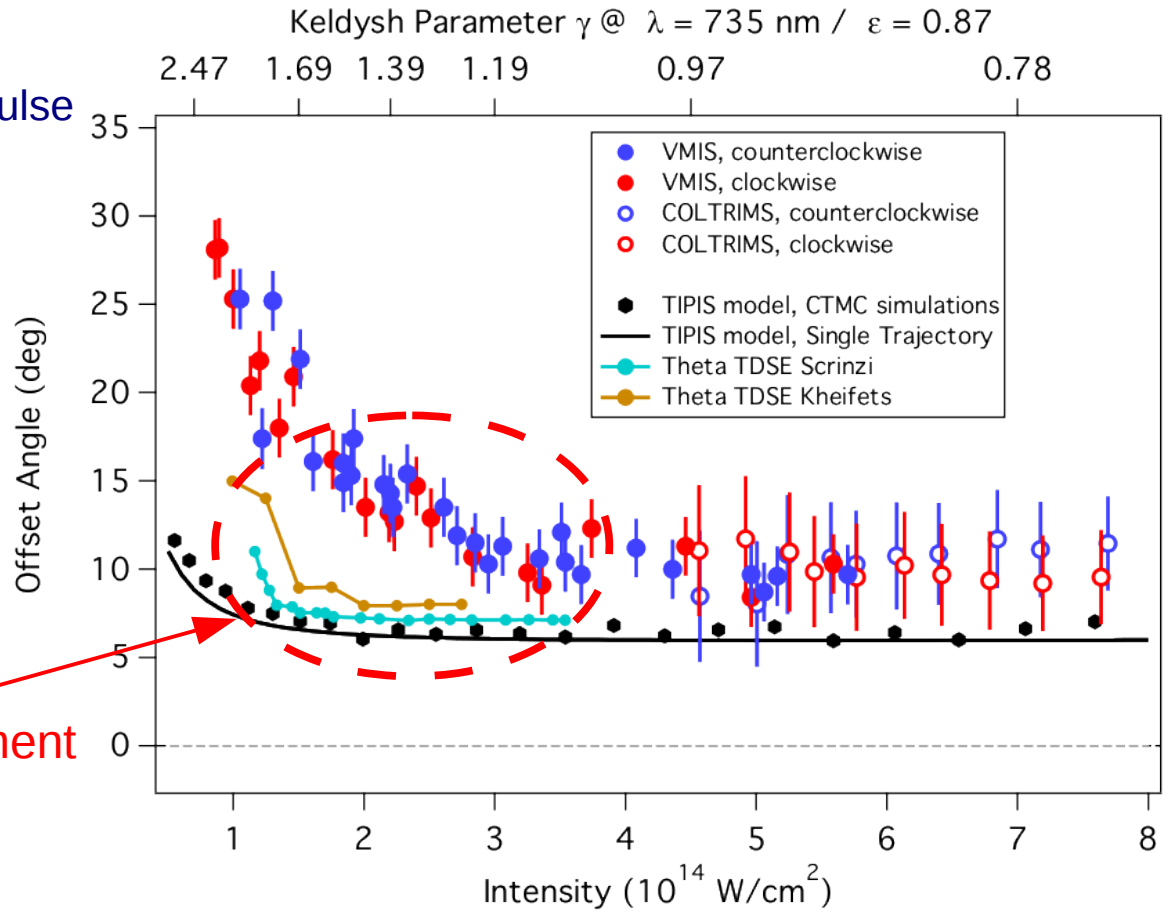
Helium, elliptically polarized pulse

Measurements:

C. Cirelli et al. ETH

Calculations:

L. Madsen(TIPIS)
Kheifets/Ivanov
A. Zielinski/A.S.



Very disquieting disagreement

Note: calculations are all single-electron...

Multi-electron effects?

Two-electron systems

- ✔ Extension of tSURFF to multi-channel emission
- ✔ Extension to double-emission
- ✔ Technical remarks
- ✔ Fano-resonances, correlation in double emission

t-SURFF for 2-electron systems

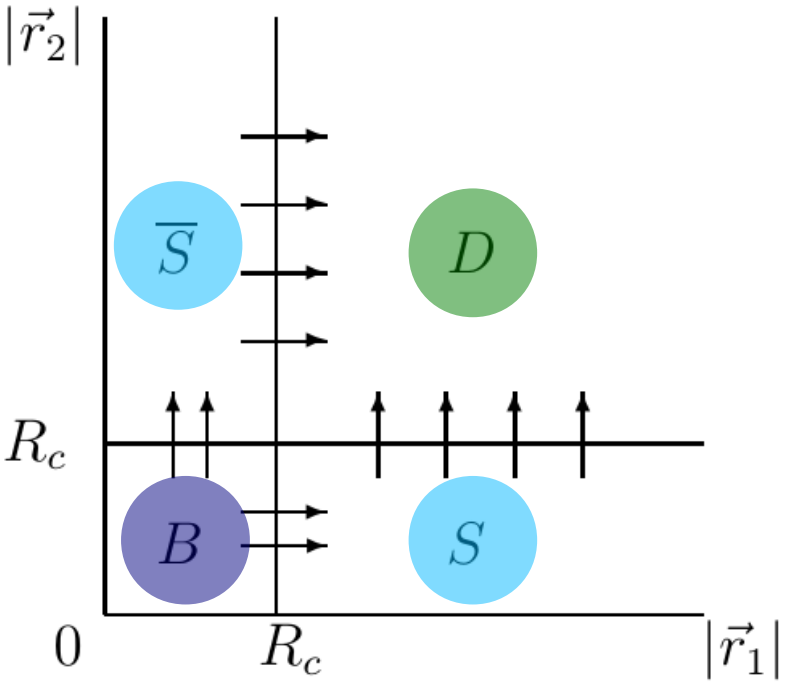
[A. S., New. J. Phys., 14, 085008 (2012)]

Split two-electron coordinate space

B... $|\mathbf{r}_1|,|\mathbf{r}_2| < R_c$ "bound" region
Numerical solutions on $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$

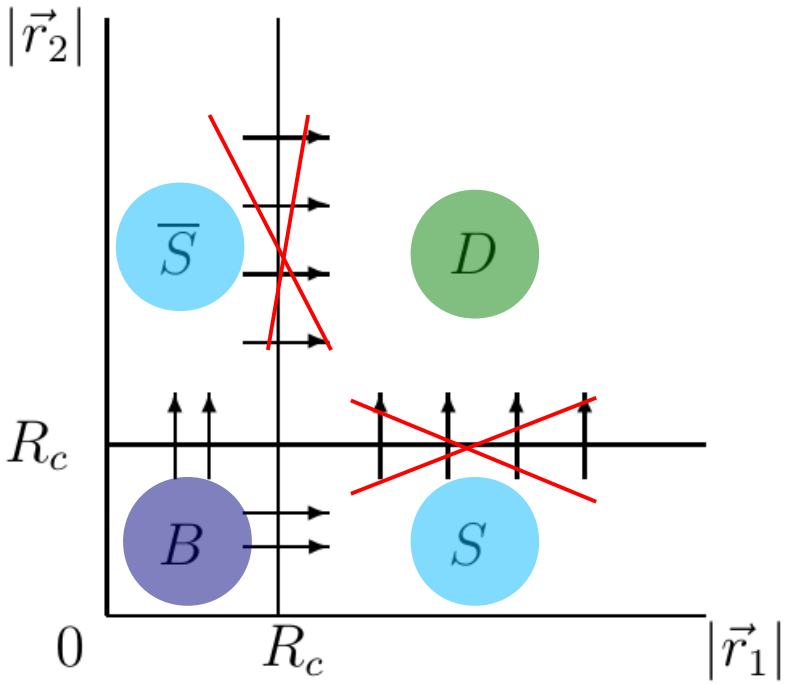
S... $|\mathbf{r}_2| < R_c$, $|\mathbf{r}_1| > R_c$ "singly asympotic" region
Numerical ionic solution on $\boldsymbol{r}_2$: $\Phi_c(\boldsymbol{r}_2,t)$
Volkov solution on $\boldsymbol{r}_1$

D... $|\mathbf{r}_1|,|\mathbf{r}_2| > R_c$ "doubly asymptotic" region
Volkov solutions on $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$



R_c as before:

Multi-channel single emssion



If one can neglect double ionzation

Computational tasks for ionic channels reduces to:

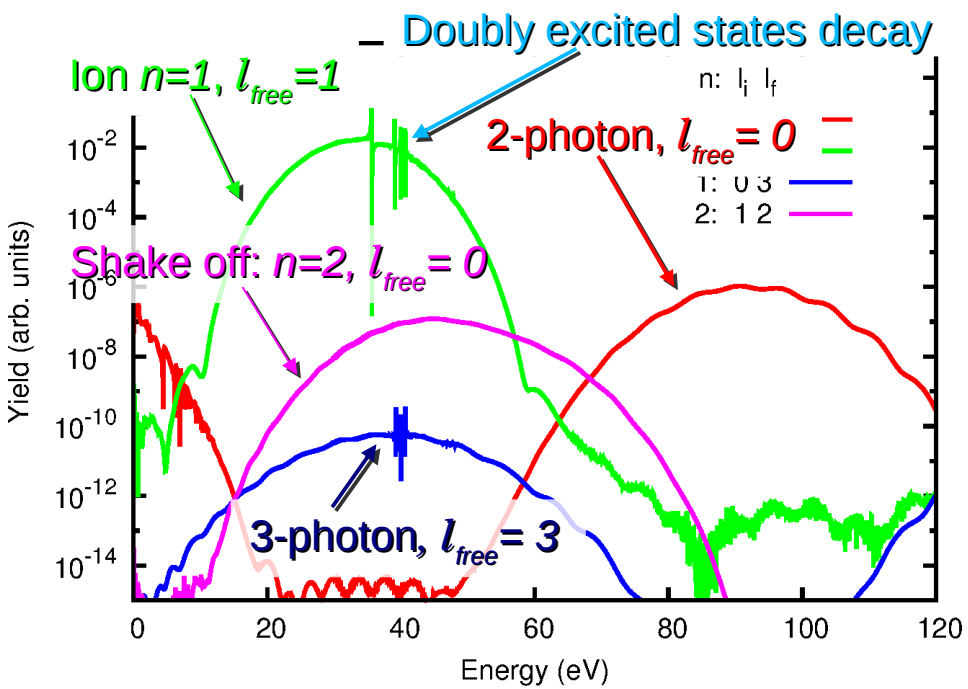
- solve full 2-electron problem on B

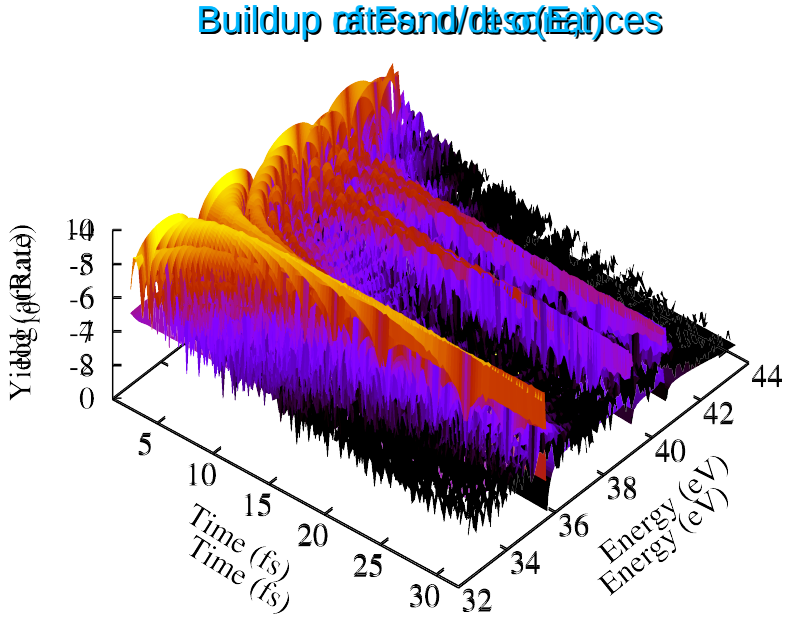
- for each single ionization channel, solve a single ionic problem in $[0,R_c]$

3d He: shake up photo-electron spectra @ XUV

Ionic channels & partial waves

(Laser: 2 opt.cyc. FWHM @ hυ=54eV, perturbative intensity regime)





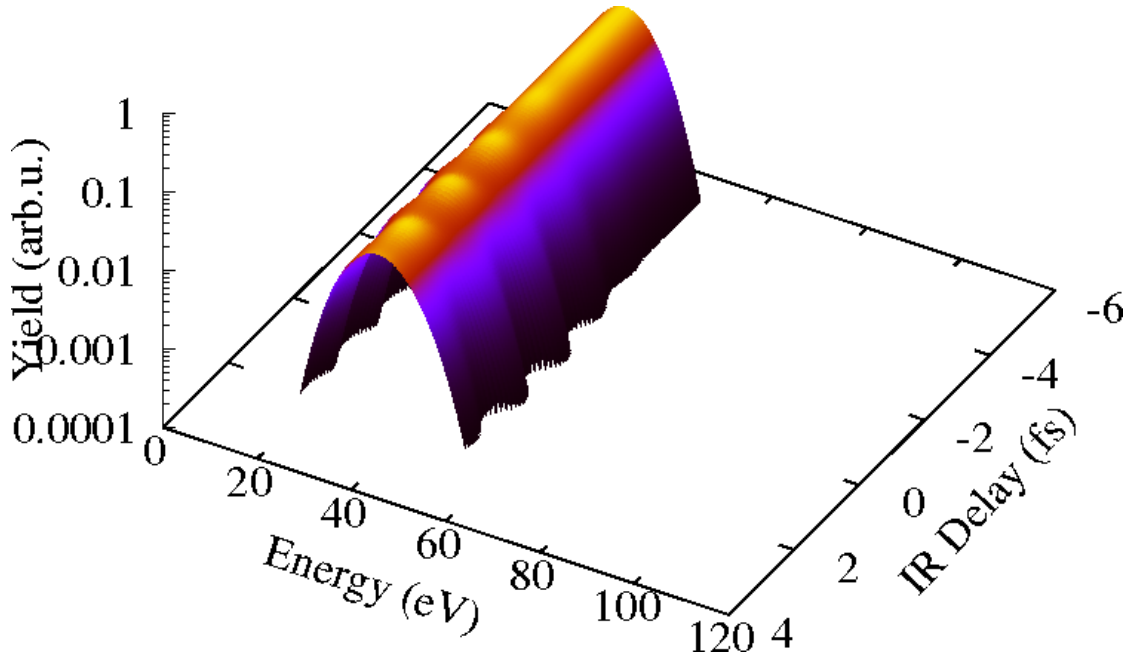
Note:

Doubly excited content after the end of the pulse
can also be obtained by projection / window operator

XUV-IR spectra

Single electron model

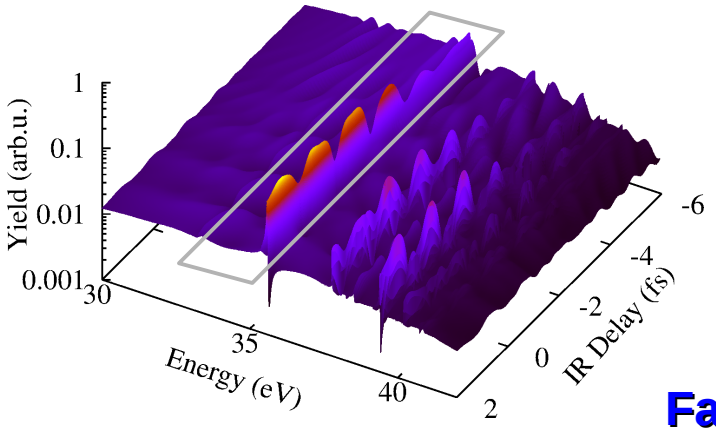
Actual streaking field
Spectrogram @ IR 2 x 10^{12} W/cm^2



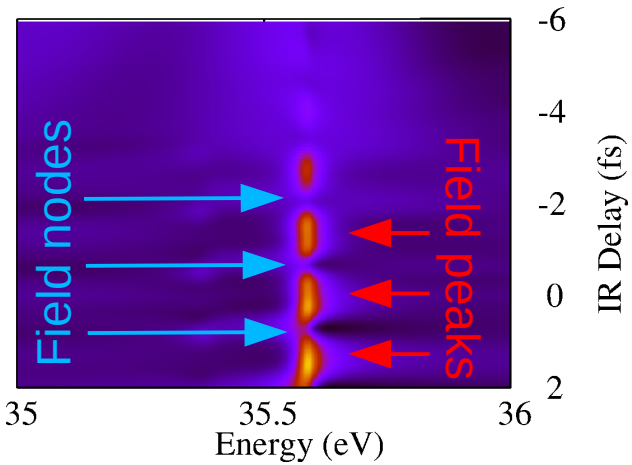
XUV photo-electron spectra in presence of IR

Ion ground state channel

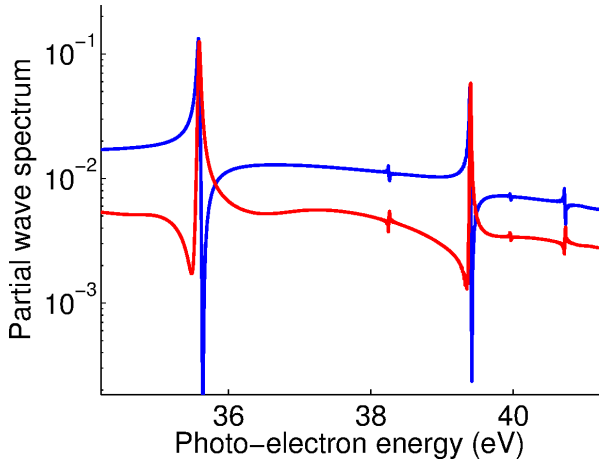
Time-delayd 800 nm few-cycle IR probe
Intensity 2 x 10^{12} W/cm^2



L=1 partial wave



Fano / anti-Fano
(No IR / peak IR)



Shift of the Fano peaks?

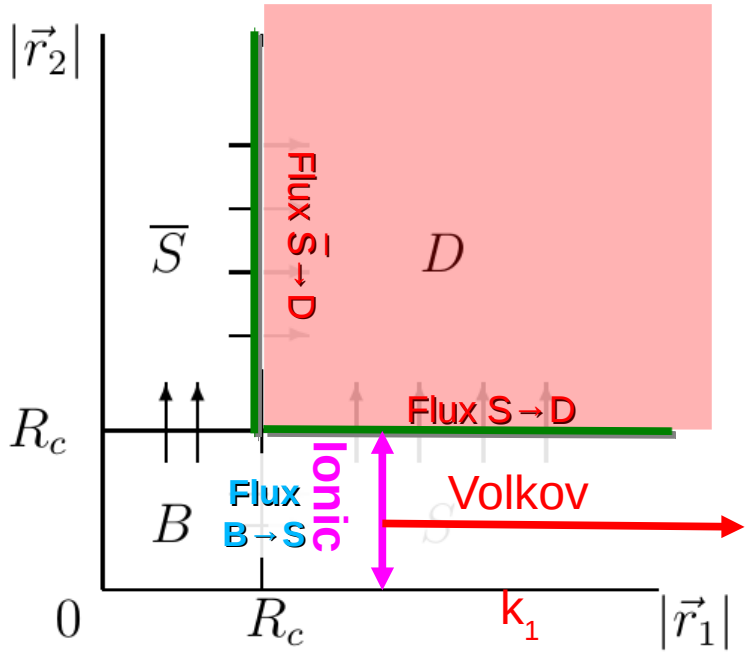
Compare experiment by Ott et al. Science 340, 716 (2013)

Double-ionization

t-SURFF for two-electron systems: double ionization

[A. S., New. J. Phys., 14, 085008 (2012)]

Spectrum in D – integrate flux S → D



S-D-surface values/derivatives

Need solution in region ***S***

Dynamics is entangled:

Independently for each Volkov k_1,

solve one ionic problem in $[0,R_c]$

(perfectly parallelizable)

Similar for flux $\overline{S}$ → D

Equations on *S*

$b(k_1,n,t)$ … coefficients for ionic basis $|\xi_n\rangle$ in $[0,R_c]$

$$i\frac{d}{dt}b(\vec{k}_1,n,t) = \sum_m \langle\xi_n|H_{ion}(t)|\xi_m\rangle b(\vec{k}_1,m,t)$$ …ionic time-evolution

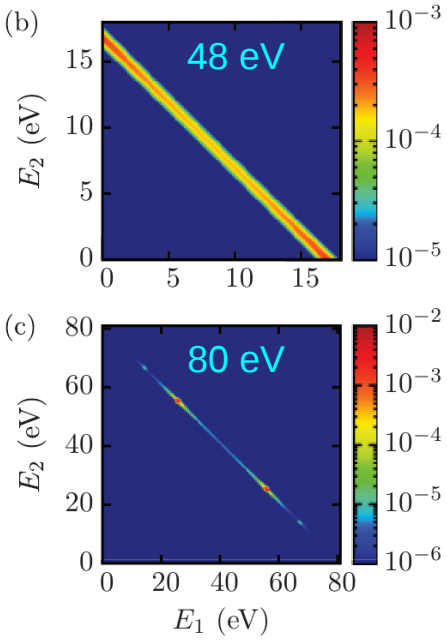
$$- \langle\vec{k}_1,t|[H_v(t),\theta_1]\langle\xi_n|\Psi(t)\rangle\rangle$$ …flux B → S

Demonstration in Helium: 2 x 3d @ 42 – 80 eV

Angle-integrated photo-ionization spectra $\sigma(E_1,E_2)$

Photon energies from below 1-photon single ionization (42 eV)
to above 1-photon double ionization (80 eV)

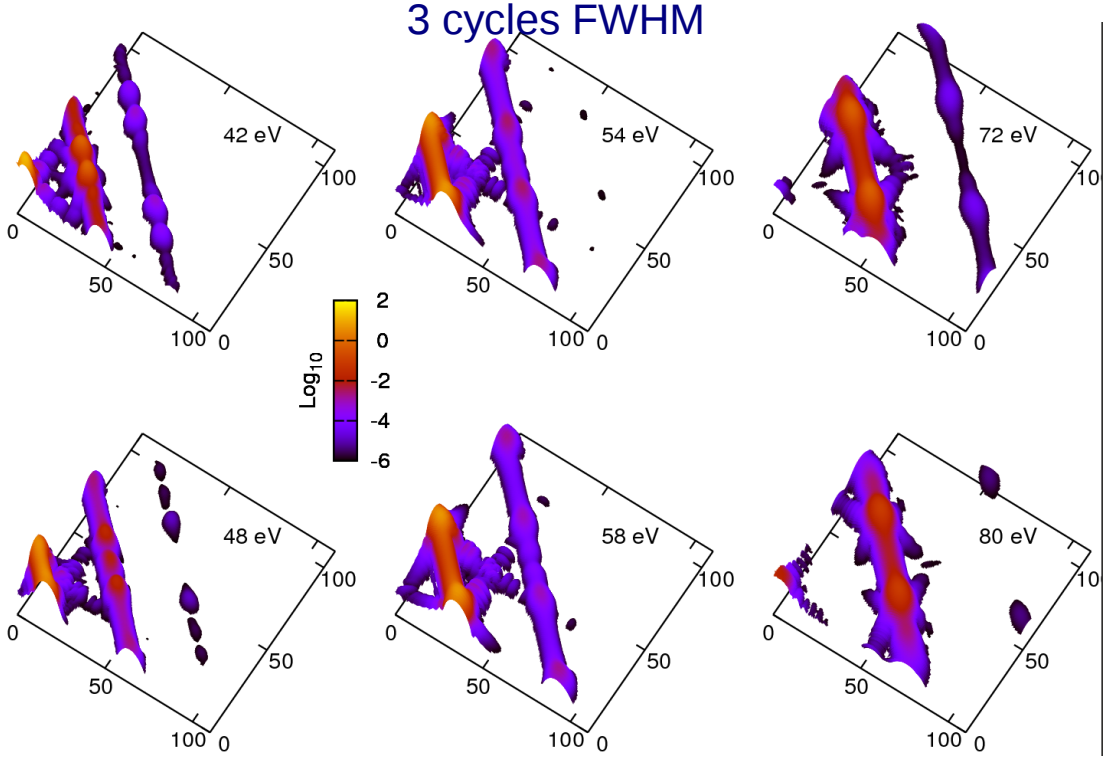
2.25 fs FWHM



[R. Pazuourek et al.
Phys.Rev.A 83, 053481 (2011)]

Box size:	2000 bohr
Grid points:	~ 10^6
Hardware:	~ 100s of CPUs

3 cycles FWHM



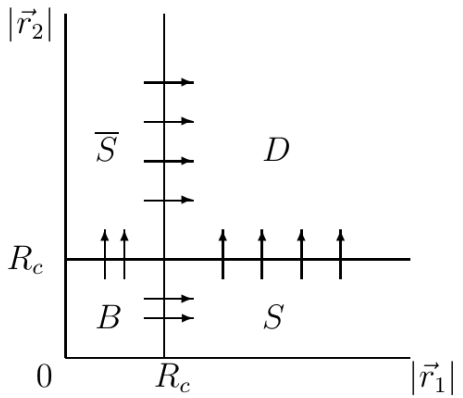
[our results]

Box size:	30 bohr
Grid points:	~ 6400
Hardware:	1 CPU (my desktop)

Effort for two-electron calculations

Inner region (B)

Meaningful results with box sizes R_c x R_c ~ 20 x 20 a.u.
With total radial discretization points N_1 x N_2 ~ 40 x 40
Angular momenta: strongly wave-length dependent
XUV: M x L_1 x L_2 ~ 2 x 4 x 4
NIR: M x L_1 x L_2 ~ 4 x 40 x 40



Single ionization spectra (S)

For each channel ***c***,
solve one (hydrogen-like) ionic TDSE

$$i\frac{d}{dt}\Phi_c(\vec{r}_1) = H_{ion}(\vec{r}_1)\Phi_c(\vec{r}_1)$$

For each momentum ***p*** in the channel
one time-integration over channel surface:

$$\int dt\ \mathrm{f}[\vec{p}, \Phi_c(|\vec{r}_1| = R_c)]$$

Double ionization spectra (D)

For each momentum $\boldsymbol{p_2}$,
solve one ionic TDSE with source term

$$i\frac{d}{dt}\Phi_{\vec{p}_2}(\vec{r}_1) = H_{ion}(\vec{r}_1)\Phi_{\vec{p}_2}(\vec{r}_1) + S_{\vec{p}_2}(\vec{r}_1)$$

For each momentum pair ($\boldsymbol{p_1}$,$\boldsymbol{p_2}$)
one time-integration over surface:

$$\int dt\ \mathrm{g}[\vec{p}_1, \Phi_{\vec{p}_2}(|\vec{r}_1| = R_c, t)]$$

Entanglement and correlation

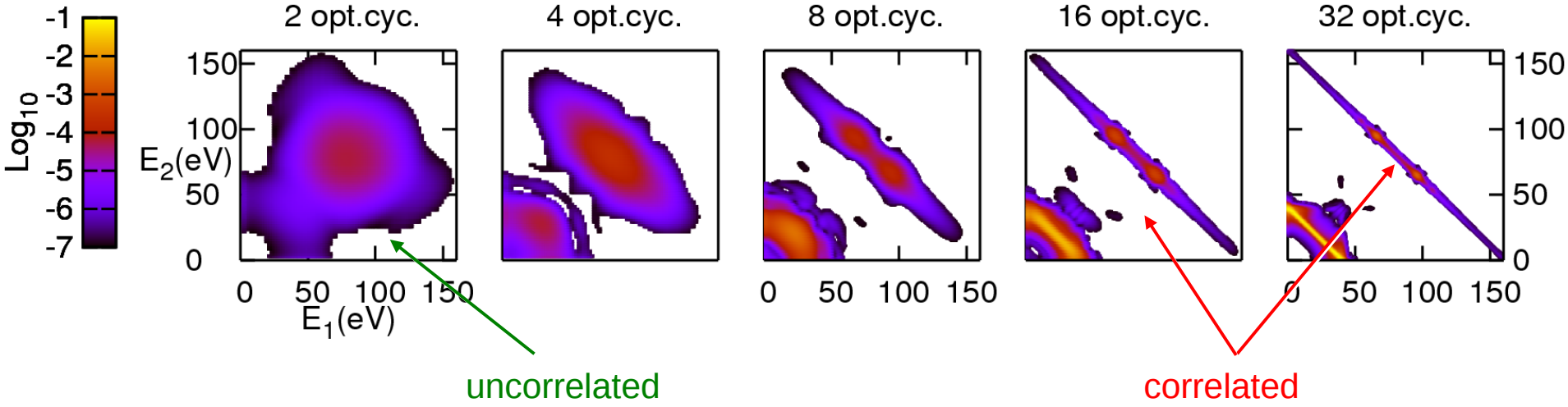
in double emission

Entanglement in double emission

Dependence of double-spectra on pulse duration

@ $\hbar\omega$ = 120 eV, constant pulse energy

Idea: if pulse duration << $T_{corr} = 2\pi\hbar/E_{corr}$
emitted spectra are uncorrelated



Quantify - “measure of entanglement / correlation”

Measure of entanglement / correlation

"Number of terms needed when expanding into products of single particle factors"

Unique (Schmidt) representation as a sum of products

$$\Psi(\vec{k}_1, \vec{k}_2) = \sum_i c_i \Phi_i(\vec{k}_1)\Phi_i(\vec{k}_2)$$

Single particle density matrix

$$\rho(\vec{k}_1, \vec{k}_2) = \int d^{(3)}k\, \Psi(\vec{k}_1, \vec{k})\Psi^*(\vec{k}, \vec{k}_2) \;\; = \sum_i \Phi_i(\vec{k}_1)|c_i|^2\Phi_i^*(\vec{k}_2)$$

Yield

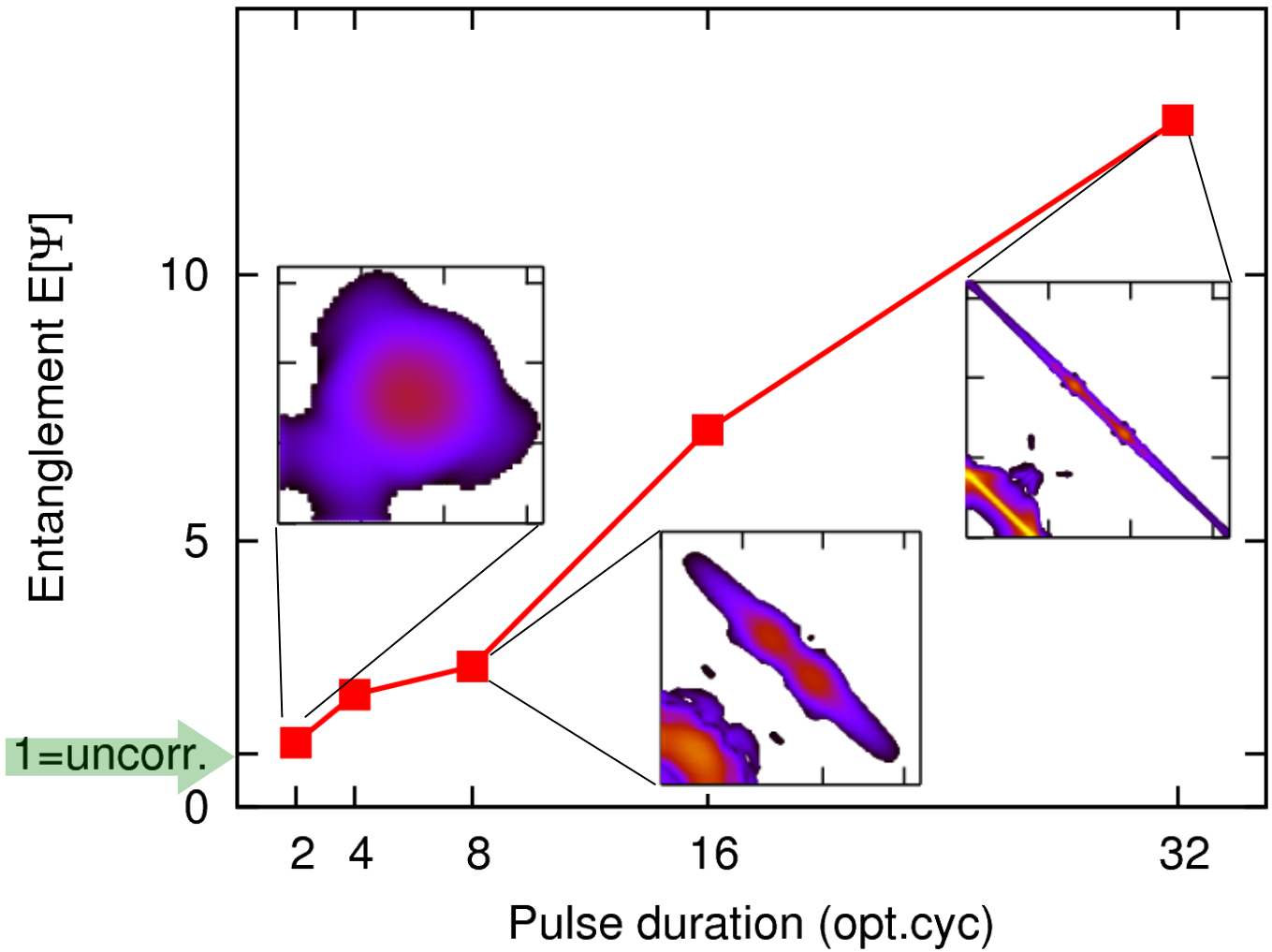
$$Y[\Psi] = \sum_i |c_i|^2 = \int d^{(3)}k\, \rho(\vec{k}, \vec{k}) =: \mathrm{Tr}\, \hat{\rho}$$

Measure of entanglement $E[\Psi]$

$$E[\Psi] = Y^2[\Psi] / \sum_i |c_i|^4 = (\mathrm{Tr}\hat{\rho})^2 / \mathrm{Tr}(\hat{\rho}^*\hat{\rho})$$

Similarly (classical) correlation $C[\sigma]$ in the spectra $\sigma(k_1,k_2)$

Entanglement in double emission



Double ionization at 800 nm

2 x 1d and scaling to 2 x 3d

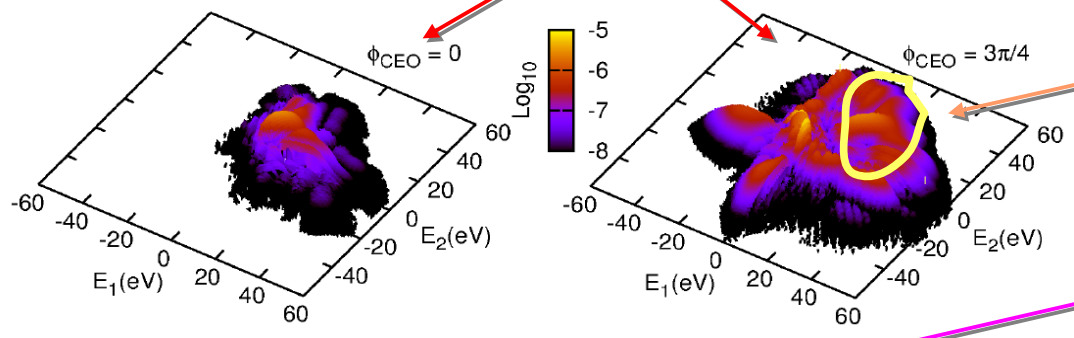
800 nm: demonstration in “1d-Helium”

[A. S., New. J. Phys., 14, 085008 (2012)]

$$H(t) = \sum_{\alpha=1,2} \frac{1}{2}\left[-i\frac{\partial}{\partial x_\alpha} - A(t)\right]^2 - \frac{2M(x_\alpha)}{\sqrt{x_\alpha^2 + 1/2}} + \frac{M(x_1)M(x_2)}{\sqrt{(x_1 - x_2)^2 + 0.3}}$$

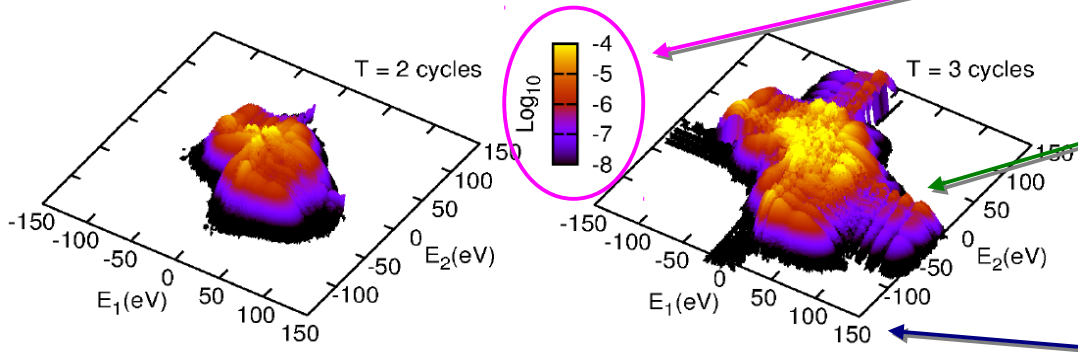
Laser pulse 2 x 10^{14} W/cm^2 @800 nm, 1~3 cycles FWHM (20% ~ 60 % ionization)

Pronounced phase dependence



correlated double emission

Large dynamical range



Recollision plateau

High energies 150 eV ~ 5 a.u.

Discretization size 49 points on [0,∞), total of 97 x 97 points

Scaling to 2 electron IR in full dimensionality

All calculations to this point are a few hours on single CPU

2 x 3d @ IR wave length:

Needs parallel code
Problem size (2 x 10^{14} W/cm^2 @ 800 nm)
Angular:
L_{max} ~ 30 (dictated by single electron quiver motion)
M_{max} ($\varphi_1 - \varphi_2$) ~ 5(?) (m conserved by laser, driven by electron interaction)

Radial: same as 2 x 1d

2 x 1d, 2-dimensional problem: $(2)^2$ x $(N_r)^2$ (2^2 for left/right directions)
2 x 3d, 5-dimensional problem: $\mathbf{(L_{max})^2}$ x $\mathbf{M_{max}}$ x $(N_r)^2$

Expected computation times for 800 nm in 2 x 3d
a few hours on 1000 CPUs

Complex atoms and small molecules

- ✔ Integration with quantum chemistry (COLUMBUS)
- ✔ Technical remarks
- ✔ Emission from He, H_2, and N_2

Ionic core dynamics (quantum chemical)

for molecular photo-emission...

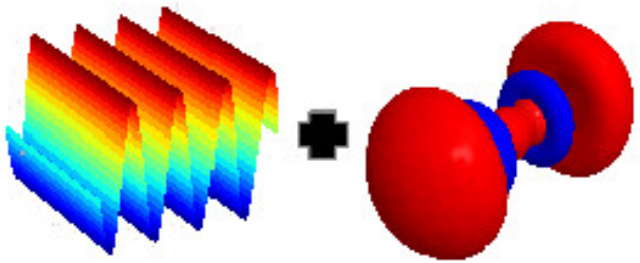
Combine complex scaled basis χ_i
with ionic CI functions Φ_c (COLUMBUS)

Goals:
Reliable strong-field ionization rates
Accurate photo-electron spectra

Anti-symmetrize

$$\psi_{i,c}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n) = \mathcal{A}\left[\chi_i(\vec{r}_1)\, \Phi_c(\vec{r}_2, \ldots, \vec{r}_n)\right]$$

$$\Psi = \sum_{c=1}^{N_{core}} \sum_{i} C_{i,c}(t)\psi_{i,c}$$



Difficulties:

- Get wave function (solved)
- Basis size (endless story)
- Messy matrix elements (solved)
- Over-completeness issues (solved)
- Gauge (currently being addressed)

Many thanks for access to COLUMBUS wave functions
H. Lischka
Th. Müller
J. Pittner

Gauge dependence of the approach

Idea of the quantum chemistry basis

Bound electron dynamics largely within field free states Ψ_i

Length gauge:

x and p have their standard meaning

Functions Ψ_i correspond to field free states also in presence of IR

Velocity gauge:

Corresponds to a time-dependent boost $p \rightarrow p + eA(t)/c$

Functions $e^{-i\vec{r}\cdot\vec{A}(t)}\Psi_i(\vec{r})$ correspond to field free state

At strong IR fields exp[-irA(t)] can strongly differ from 1 across the Ψ_i

(Compare the debate about the “correct” gauge in SFA)

Computations more efficient in velocity gauge
=> local gauge transform on the bound state range
(tricky business)

A flavor of the complexity of matrix elements

Two-particle (electron-electron) interaction: $H_2 = \sum_{i,j,i<j} h_{ij}$

Electron + ion basis function:

$$\psi_{i,I} = \mathcal{A}\left[\chi_i(\vec{r}_1)\Phi_I(\vec{r}_2 \ldots \vec{r}_n)\right]$$

Matrix element:

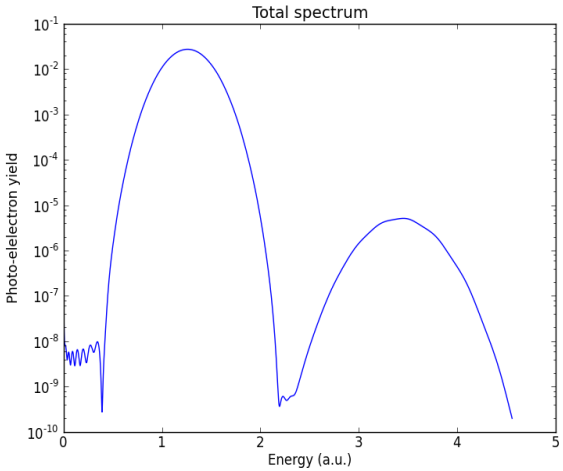
$$\begin{aligned}
\langle \psi_{i,I} | H_2 | \psi_{j,J} \rangle \quad =& (n-1)\sum_{kl}\langle \phi_k\chi_i|\phi_l\chi_j\rangle \rho^{(1)}_{kl;IJ} \\
&+\frac{(n-1)(n-2)}{2}\langle\chi_i|\chi_j\rangle\sum_{klmn}\langle\phi_k\phi_l|\phi_m\phi_n\rangle\rho^{(2)}_{klmn;IJ} \\
&-(n-1)\sum_{kl}\langle\phi_k\chi_i|\chi_j\phi_l\rangle\rho^{(1)}_{kl;IJ} \\
&-(n-1)(n-2)\sum_{klmn}\langle\phi_k\chi_i|\phi_m\phi_n\rangle\rho^{(2)}_{klmn;IJ}\langle\phi_l|\chi_j\rangle \\
&-(n-1)(n-2)\sum_{klmn}\langle\phi_k\phi_l|\chi_j\phi_n\rangle\rho^{(2)}_{klmn;IJ}\langle\chi_i|\phi_m\rangle \\
&-\frac{(n-1)(n-2)(n-3)}{2}\sum_{abcdef}\langle\phi_a\phi_b|\phi_d\phi_e\rangle\rho^{(3)}_{abcdef;IJ}\langle\chi_i|\phi_f\rangle\langle\phi_c|\chi_j\rangle
\end{aligned}$$

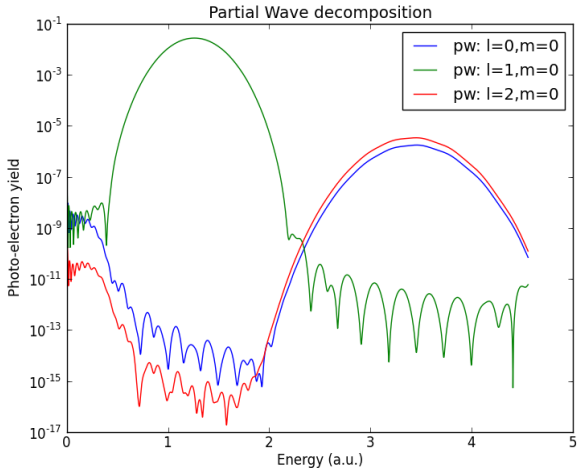
Non-standard 3-particle reduced density matrix for ionic states Φ_I, Φ_J

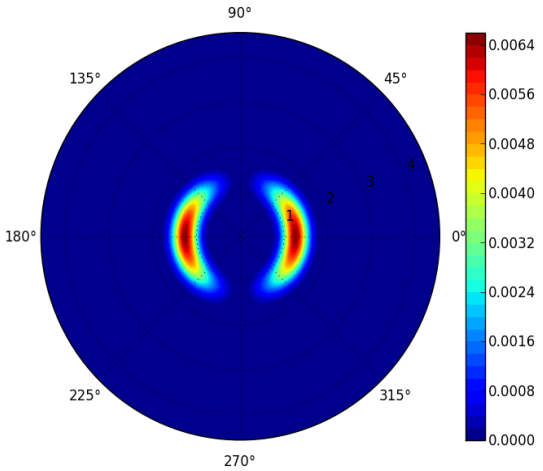
XUV photo-ionization of Helium

Pulse parameters: λ = 21nm, 3-cycle, $\cos^8$ envelope, linear polarization

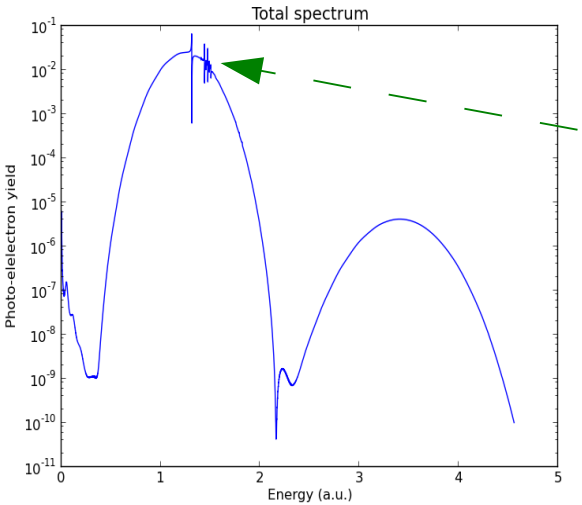
1 ionic state

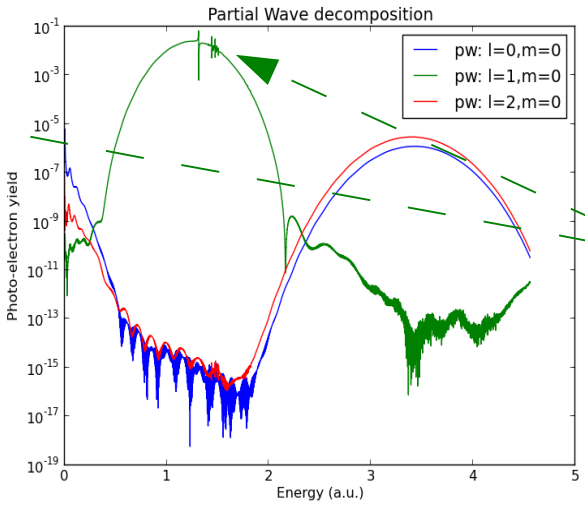






6 ionic states





Doubly excited states / Fano resonances

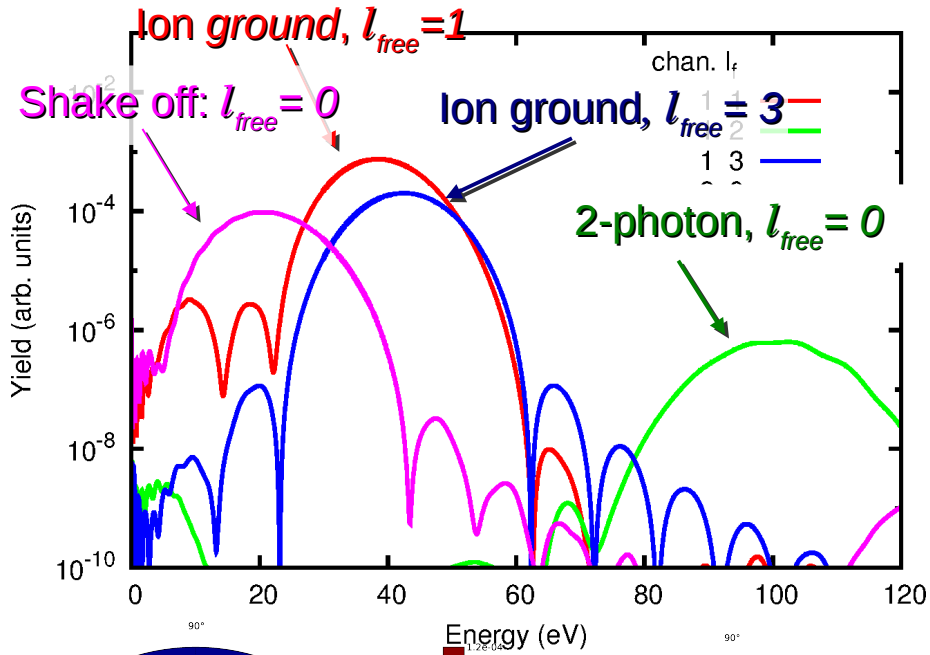
State	Literature[a]	Calculation
2s 2p	1.307	1.313
2s 3p	1.436	1.441
2s 4p	1.466	1.474

[a] J Chem. Phys. 139, 104314 (2013)

Photo-ionization of H_2 and N_2

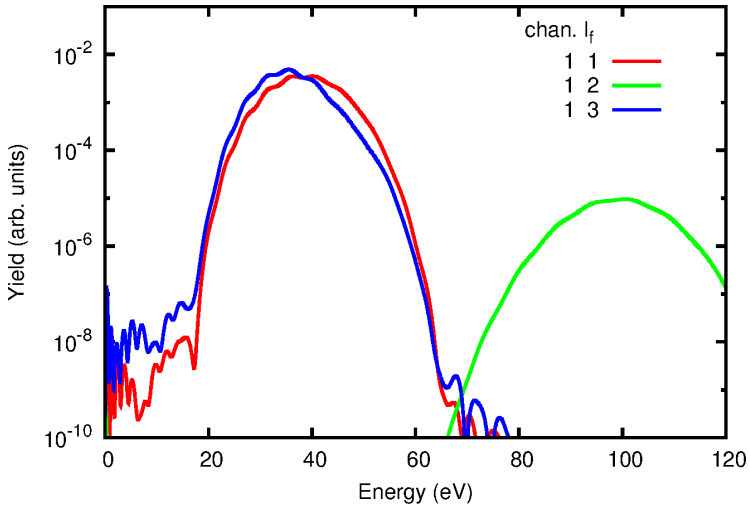
H_2 XUV photo-ionization

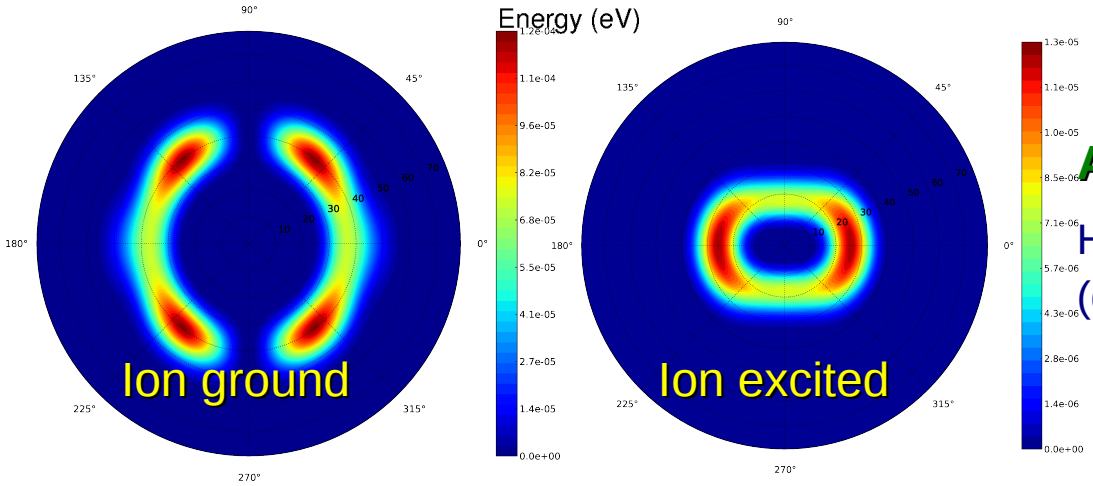
Pulse: 21 nm, 3 cycle FWHM, 10^{15}W/cm^2



N_2 XUV photo-ionization

More of the same...





Angle-resolved spectra

H_2 ionic channels
(disc diameter=80 eV)

Team

Vinay Majety
2-electron
& molecules

Mattia Lupetti
Solids and
surfaces

Alejandro “the convergator” Zielinski
1-e elliptic
2-electron

Jakob Liss
Solids and
surfaces

Publications

[A.S., Phys. Rev. A81, 53845 (2010)]
[L. Tao and A.S., New. J. Phys. 14, 013021 (2012)]
[A. S., New. J. Phys., 14, 085008 (2012)]
[A.S., HP. Stimming, N. Mauser, J.Comp.Phys, accepted (2014)]

Finances

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Excellence Cluster

Vienna Computational Materials Science
FWF Special Research Program

CORINF
Correlated Multielectron Dynamics in Intense Laser Fields

Marie Curie ITN

Code: tRecs = tSURFF + irECS (working title)

All codes united in a single, C++ code based on recursive structures

General dimensions and coordinate systems

PDEs of the form $d/dt\Psi = D\Psi$

(includes e.g. Maxwell's equations)

Preparing for public access
Can be made available for collaborations immediately

Screenshots of the Doxygen documentation