TECHNISCHE UNIVERSITÄT WIEN
VIENNA UNIVERSITY OF TECHNOLOGY

AURORA
ADLIS

Strong field electron dynamics in molecules

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Why molecules ?

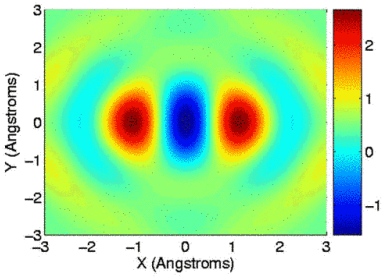
In molecules

- we really want to know how charges move
- we want to see structural rearrangement
- we would like to know how photochemistry works
- we would like to control...

Recover the image of
the molecular valence orbital
from high harmonic radiation

$2\sigma_g$ HOMO orbital of N_2 (?)

[Itatani, Nature **432,** 867 (2004)]



What's new in a molecule ?

A molecule is an extended object

- extended electron cloud
- excited electronic states close by
- pronounced structure of electronic wave function
- orientation of the molecular axis

Nuclear motion (but that is a whole different story...)

In this talk

Ionization rates

The importance of correlation

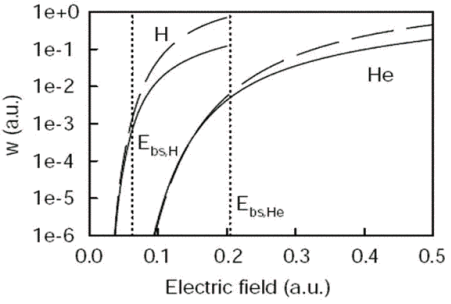
Re-scattering electron spectra

Ionization by a static field

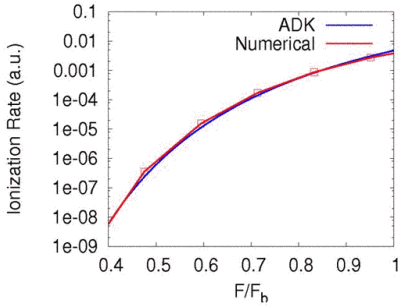
How good ADK is

ADK vs. numerical results

Hydrogen and Helium



2d atomic model "Ar"



Agreement on the 10 % level in the tunneling regime

Remember: the only system-specific information in ADK is the field-free electron wave function

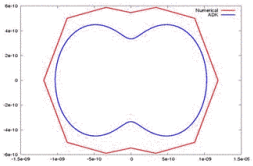
ADK: stitch together the field-free wave function with the WKB solution at the right place ("under the tunneling barrier")

Ionization

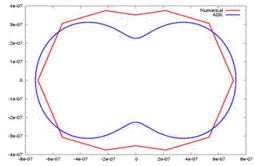
How good is ADK for molecules ?

Molecular ADK formula by X.M. Tong et al. vs. accurate complex scaling rates

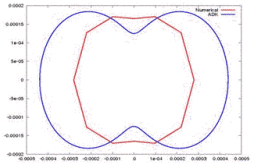
2d molecular model "N_2"
Ionization for different orientations of the molecular axis



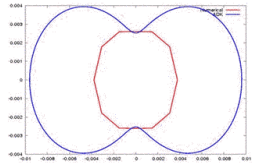
F = 0.35 F_b



F = 0.5 F_b



F = 0.6 F_b



F = 0.95 F_b

Rates accurate within factor ~ 2

ADK determined by the asymptotic field free electron density

Single electron model !

Beyond the single active electron approximation

MCTDHF in a nutshell: definition and features

$$\Psi(r_1,r_2,\ldots,r_f;t) = \Sigma_J\, A_J(t)\, \Phi_J(r_1,r_2,\ldots,r_f;\, t)$$

Linear combination of Slater determinants Φ_J

$$\Phi_J(r_1,r_2,\ldots,r_f;t) = \det |\varphi_{j1}(r_1;t)\ \varphi_{j2}(r_2;t)\ \ldots\ \varphi_{jf}(r_f;t)|$$

$A_J(t)$ time-dependent
$\varphi_j(r;t)$, $j = 1,\ldots,n$
single electron orbitals, time-dependent !
variationally optimal for each t
(Dirac-Frenkel variational principle)

+ compact representation of Ψ
+ complete representation (exact for n→∞)
+ superposition states
+ systematic inclusion of correlation

- non-linear equations
- non-local operators
- poor for hard e-e collisions
  (like all single-particle expansions)

MCTDHF: range of applicability

Range of applications:

- ionization
- quasi-bound state dynamics
- single electron spectra
- more general systems (quantum dots)

H_2 energy at R=1.4

n, f	energy
2, 2	-1.8466
4, 2	-1.8652
6, 2	-1.8725
8, 2	-1.8732

(exact -1.8887)

At present:

- up to 6 active electrons in cylindrical symmetry
- few-cycle laser pulses @ 800 nm, I < 10^{15} W/cm^2
- < 1000 Slater determinants
- ~10 hours runtime on ~ 30 CPUs

The influence of correlation on ionization

Models of Ar and N_2
two active electrons
ionization potential = 0.58 a.u.,
N_2 nuclear separation of 3 a.u.

Laser
single-cycle laser pulse @ 800 nm,
peak intensity 3x10^{14}W/cm^2

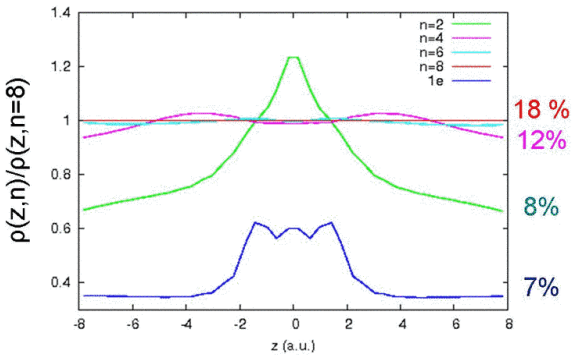
Ground state depletion

	Atom "Ar"	Molecule "N_2"
Single active electron	4.4 %	7.1%
Time-dependent Hartree-Fock	1.8 %	8.2%
MCTDHF: 2 extra orbitals	4 %	12%
MCTDHF: 4 extra orbitals	5.1 %	18%
MCTDHF: 6 extra orbitals	6.2%	18%

Strong multi-electron effects in total ionization !?
(~ same in atoms and molecules)

Convergence of electron density of N_2

Ratio of field free electron densities to best converged density



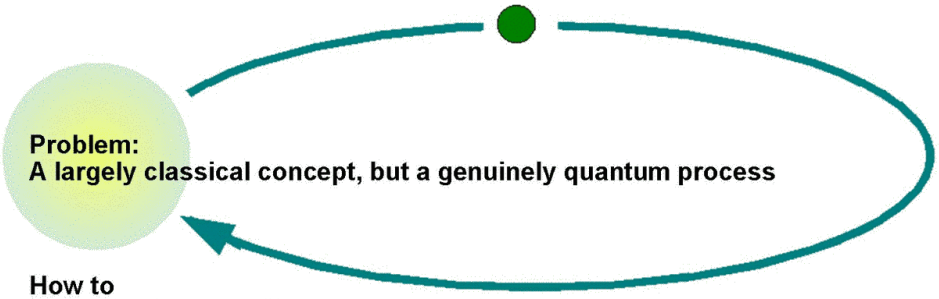
Convergence of ionization is related (not proportional) to electron density at larger distances

For correct ionization rates we need single-electron models
with correct asymptotic electron density !
(minimal requirement)

Recollision electron spectra

What is the "recollision current" ?

Is this a meaningful concept ?
How does it depend on the host molecule ?



Problem:
A largely classical concept, but a genuinely quantum process

How to
separate electrons that are returning to the nucleus
from electrons that always have stayed there ?

NOTE:
no unambiguous distinction
between bound and continuous states in strong fields !

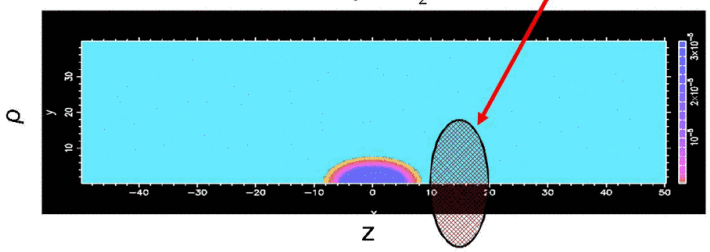
Watch electrons from a distance

Solution of the time-dependent Schrödinger equation $\Psi(r,t)$

Multiply by a local probe function M_Z at a save distance Z from the molecule

"Measure" the electrons passing through a barrier

Electron density of N_2 below 10^{-4}



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Solution of the time-dependent Schrödinger equation $\Psi(r,t)$

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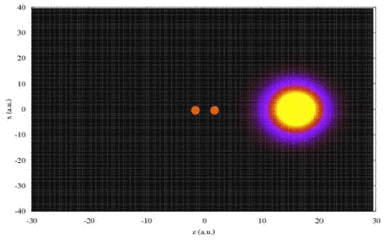
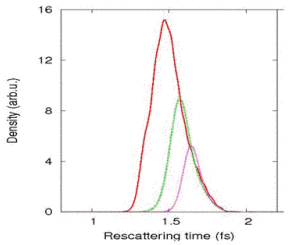


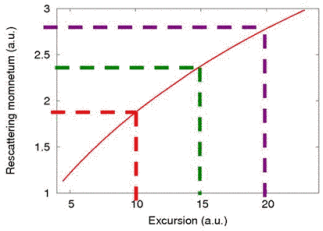
(A): Quantum mechanically propagate the masked function $M_Z\Psi$

or (B): Transform to a phase-space distribution (Wigner distribution) and propagate classically

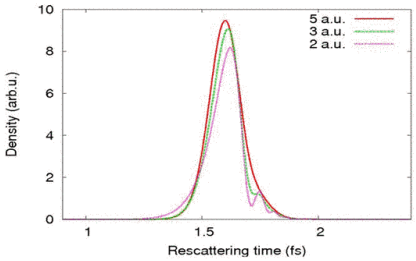
Does it work ? -
Current on target obtained by probing a different distances



Not all electrons reach our probe barrier:
Max distance vs. recollision momentum

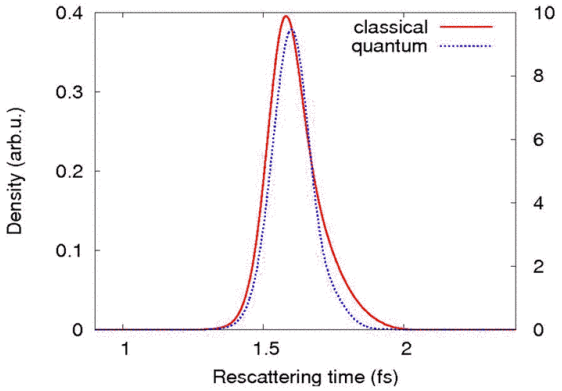


Dependence on probe width



Probed electrons behave classically

Current on target as obtained by
quantum vs. classical (Wigner) propagation



Probing at a distance gives the
(high momentum part of)
the electron wave function on target

Application to model Ar and N_2

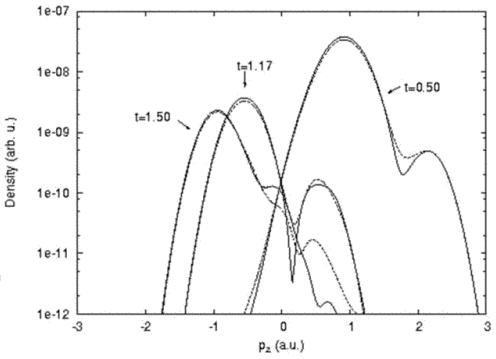
Electron detachment from Ar and N_2

Comparison of electron spectra
at distance z=15 a.u.
three different time slices

Models of Ar and N_2
two active electrons
ionization potential = 0.58 a.u.,
N_2 nuclear separation of 3 a.u.

Laser
single-cycle laser pulse @ 800 nm,
peak intensity $3 \times 10^{14} W/cm^2$

(Compensated for different total yields)



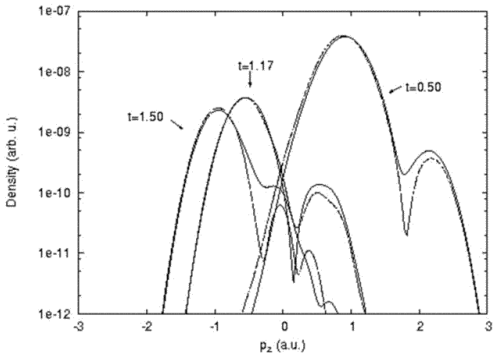
Reasonable agreement !
BUT: N_2 axis aligned with the laser field

Justification of SAE models

Correlation plays a minor role

Electron current of Ar calculated
with 2 and 8 single electron orbitals

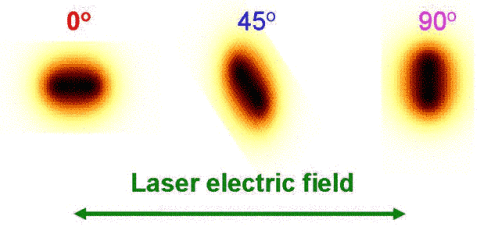
(compensated for different total yields)



Single active electron models should give good qualitative results

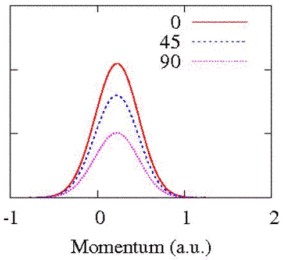
Orientation dependence of momentum distributions for 2-dimensional single active electron models

"Gerade" type orbital

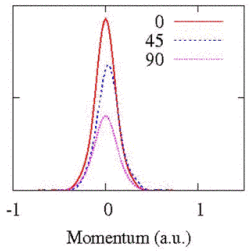


Momentum distribution
as probed at Z=15

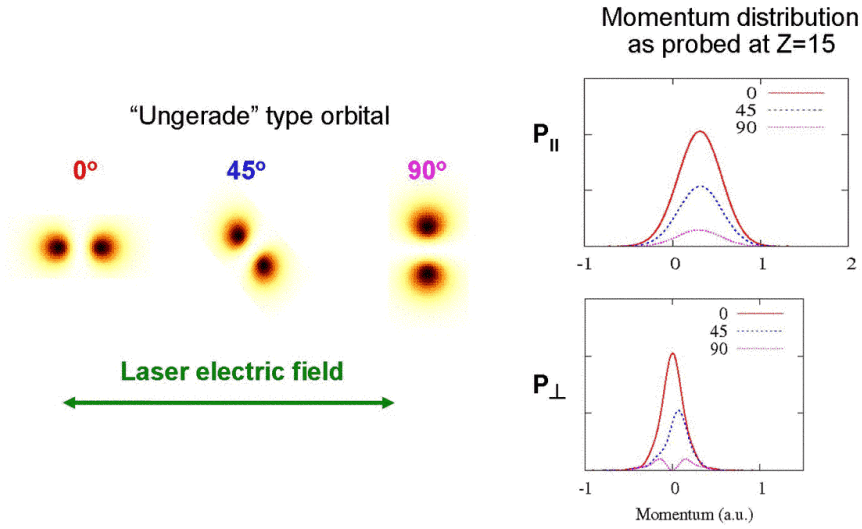
$P_{||}$



$P_{\perp}$



Momentum distributions for different orbital symmetry

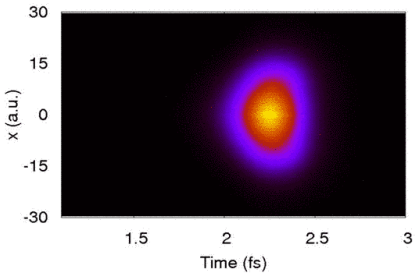


Node-structure of the outer electrons persists !

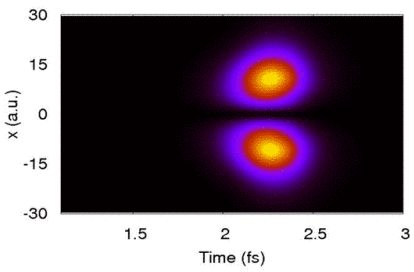
Distribution of re-colliding electrons on target

Ungerade type orbital

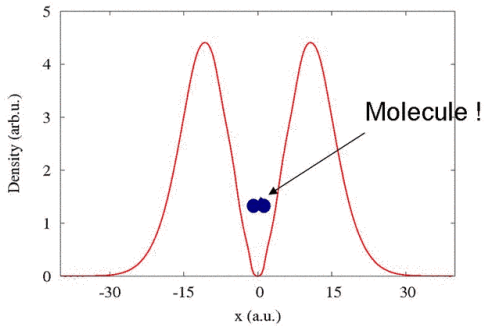
Parallel alignment



Perpendicular alignment



Distribution of re-colliding electrons on target



Most electrons will miss the target !

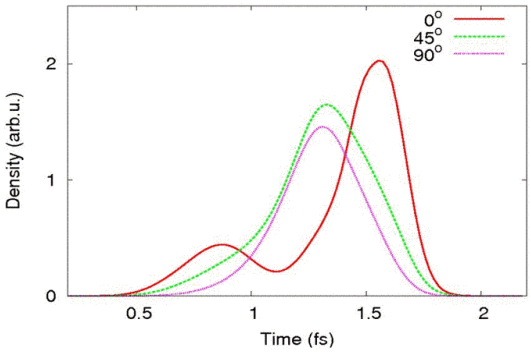
Orientation-dependent effect

We CANNOT deduce total ionization from re-scattering on molecules

Orientation dependence of the timing

Current through the probe as a function of time

Nuclear separation 6 a.u.



Peak current shifts by ~ 0.3 fs

Consequences for rescattering imaging

If the initial orbital is unknown,
we can not know the momentum re-scattering electron spectra

If harmonics are sensitive to the initial orbital,
we still may extract the information

How ?
Single electron effects dominate
Iteratively adjust the outer orbital to the measured spectra
(Quite a bit harder than the tomographic reconstruction)

Theory-dependent interpretation of measurements !

Lots of numerics and/or new analytic models

Summary

Total (tunnel) ionization similar to atoms
- performance of ADK as good for molecules as for atoms
- highly sensitive to the field free electronic wave function at larger distances

Correlation
- important for initial state
- little effect on rescattering

Rescattering electrons
- “measure” at a distance and follow to target
- essentially classical behavior confirmed

The rescattering electron wave function is NOT universal
Not in momentum and not in time

Re-scattering imaging needs a joint effort of theory and experiment

Thanks to

Xinhua Xie: re-scattering electrons

Gerald Jordan: MCTDHF calculations

Marlene Wickenhauser: 2d ADK calculations