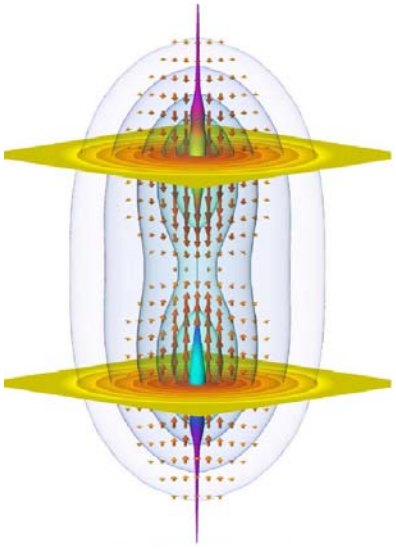
Freie Universität Berlin

Quantum Fluxes during Chemical Reactions



Jörn Manz

Freie Universität Berlin

Workshop on Quantum Dynamic Imaging
Montreal, Canada
20.10.2009

Agenda

- ~~Introduction~~
- Applications to electronic fluxes
- Applications to nuclear fluxes
- Applications to concerted electronic and nuclear fluxes

Flux densities and fluxes: Nomenclature

- Probability density ρ, dimension 1/*volume*

$$\rho = |\Psi|^2$$

Example:
one particle in 3D

- Flux density **j**, dimension 1/(*time* x *area*)
  - also called “current density”

$$\mathbf{j} = -\frac{i\hbar}{2m}\left(\Psi^*\nabla\Psi - \Psi\nabla\Psi^*\right)$$

- Flux *F*, dimension 1/*time*
  - also called “current”

$$F(t; A_{obs}) = -\int_{A_{obs}} \mathbf{j}(t)\cdot d\mathbf{A}$$

- Yield *Y*, dimension 1
  - also called “probability”

$$Y(t; A_{obs}) = \int_{V_{obs}} \rho(t)\, dV - \int_{V_{obs}} \rho(t=0)\, dV$$

I. Barth, H.-C. Hege, H. Ikeda, A. Kenfack, M. Koppitz, J. Manz, F. Marquardt, G.K. Paramonov,
Chem. Phys. Lett. 481, 118 (2009)

Continuity equations and Gauss's theorem

- Continuity equation
  - for the electron
  - for the *k*-th nucleus

$$\dot{\rho}_{el}(\mathbf{r},t) = -\nabla_{\mathbf{r}} \cdot \mathbf{j}_{el}(\mathbf{r},t)$$
$$\dot{\rho}_{nu,k}(\mathbf{R},t) = -\nabla_{\mathbf{R}} \cdot \mathbf{j}_{nu,k}(\mathbf{R},t)$$

- Gauss's theorem

$$F(t;A_{obs}) = -\int_{A_{obs}} \mathbf{j}(t)\cdot d\mathbf{A} = -\int_{V_{obs}} \nabla\cdot\mathbf{j}(t)\,dV = \int_{V_{obs}} \dot{\rho}(t)\,dV = \dot{Y}(t;A_{obs})$$

  - key equation

$$F(t;A_{obs}) = \int_{V_{obs}} \dot{\rho}(t)\,dV$$

I. Barth, H.-C. Hege, H. Ikeda, A. Kenfack, M. Koppitz, J. Manz, F. Marquardt, G.K. Paramonov, Chem. Phys. Lett. 481, 118 (2009)

Heaviside function and flux operator

- Heaviside function $h(V_{obs})$
  - flux = time derivative of the mean value of $h(V_{obs})$

$$F(t;A_{obs}) = \int_{V_{obs}} \dot{\rho}(t)\, dV = \int_{V} \dot{\rho}(t)\, h(V_{obs})\, dV = \frac{d}{dt}\langle h(V_{obs})\rangle = \left\langle \frac{i}{\hbar}[H, h(V_{obs})] \right\rangle$$

- Nuclear flux operator by W.H. Miller
  - in Schrödinger picture $\frac{i}{\hbar}[H, h(V_{obs})]$
  - in Heisenberg picture $\frac{d}{dt} h(V_{obs})$

W.H. Miller, J. Chem. Phys. 61, 1823 (1974)
W.H. Miller, Acc. Chem. Res. 26, 174 (1993)
W.H. Miller, J. Phys. Chem. A 102, 793 (2008)

Nuclear flux operator: Applications

- Thermal reaction rate constant $k(T)$
  - $H_2 + OH \rightarrow H + H_20$

Quantum mechanical calculations of the rate constant for the $H_2+OH \rightarrow H+H_2O$ reaction: Full-dimensional results and comparison to reduced dimensionality models

Uwe Manthe,[a] Tamar Seideman,[b] and William H. Miller
Department of Chemistry, University of California, and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

(Received 11 May 1994; accepted 10 June 1994)

  - $H + CH_4 \rightarrow H_2 + CH_3$

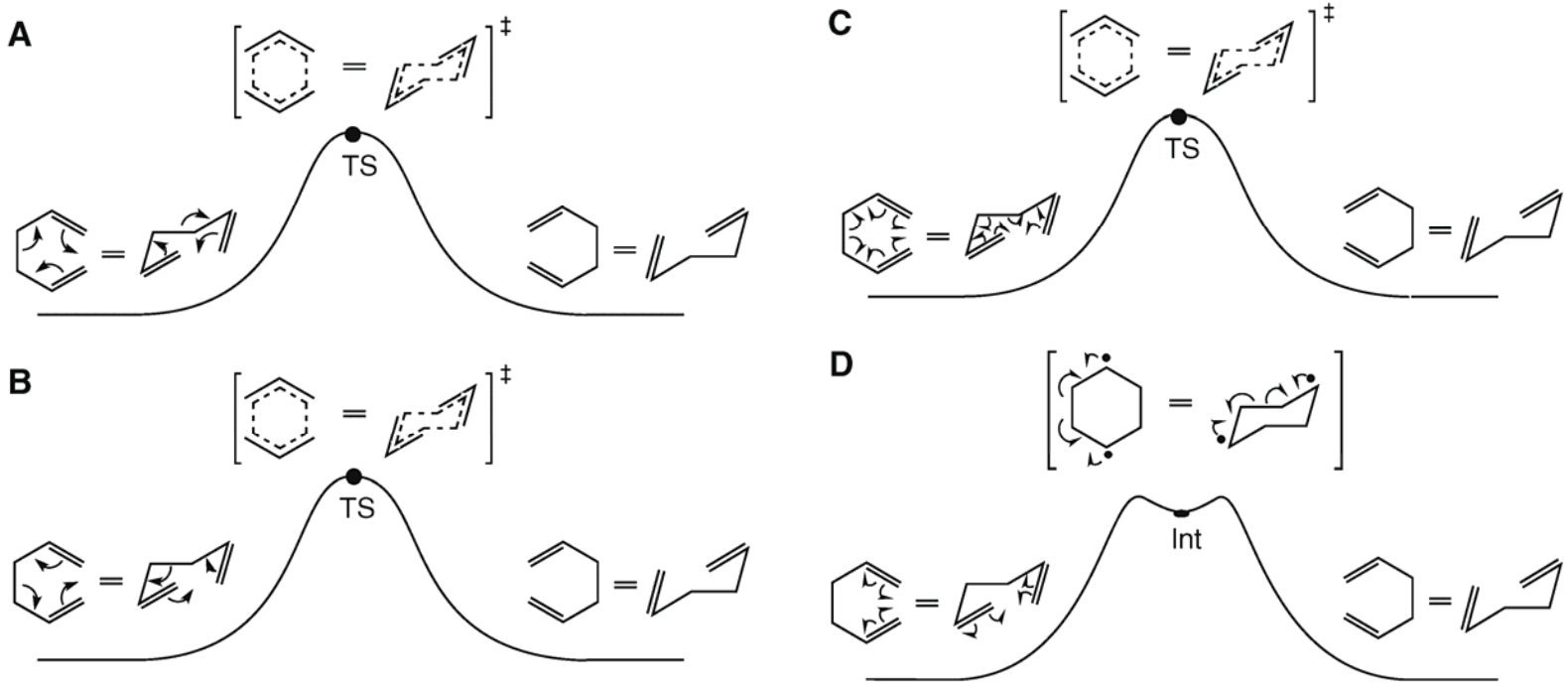
First-Principles Theory for the $H + CH_4 \rightarrow H_2 + CH_3$ Reaction

Tao Wu,[1*] Hans-Joachim Werner,[2] Uwe Manthe[3,1†]

U. Manthe, T. Seideman, W.H. Miller, J. Chem. Phys. 101, 4759 (1994)
T. Wu, H.-J. Werner, U. Manthe, Science 306, 2227 (2004)

Motivation: Nuclear and electron fluxes

- Cope rearrangement in organic chemistry
  - 1,5-hexadiene or derivatives



I. Barth, H.-C. Hege, H. Ikeda, A. Kenfack, M. Koppitz, J. Manz, F. Marquardt, G.K. Paramonov, Chem. Phys. Lett. 481, 118 (2009)

Dilemma of the BO approximation

- Born-Oppenheimer (BO) approximation

$$\Psi_{BO}(\mathbf{q},\mathbf{Q},t) = \Psi_{BO,nu}(\mathbf{Q},t)\,\Psi_{BO,el}(\mathbf{q};\mathbf{Q})$$

  - excellent for densities and nuclear flux densities
    $\Rightarrow$ powerful for quantum chemistry and nuclear dynamics
  - BUT: electronic flux densities are zero because of real electronic wavefunctions in non-degenerate states

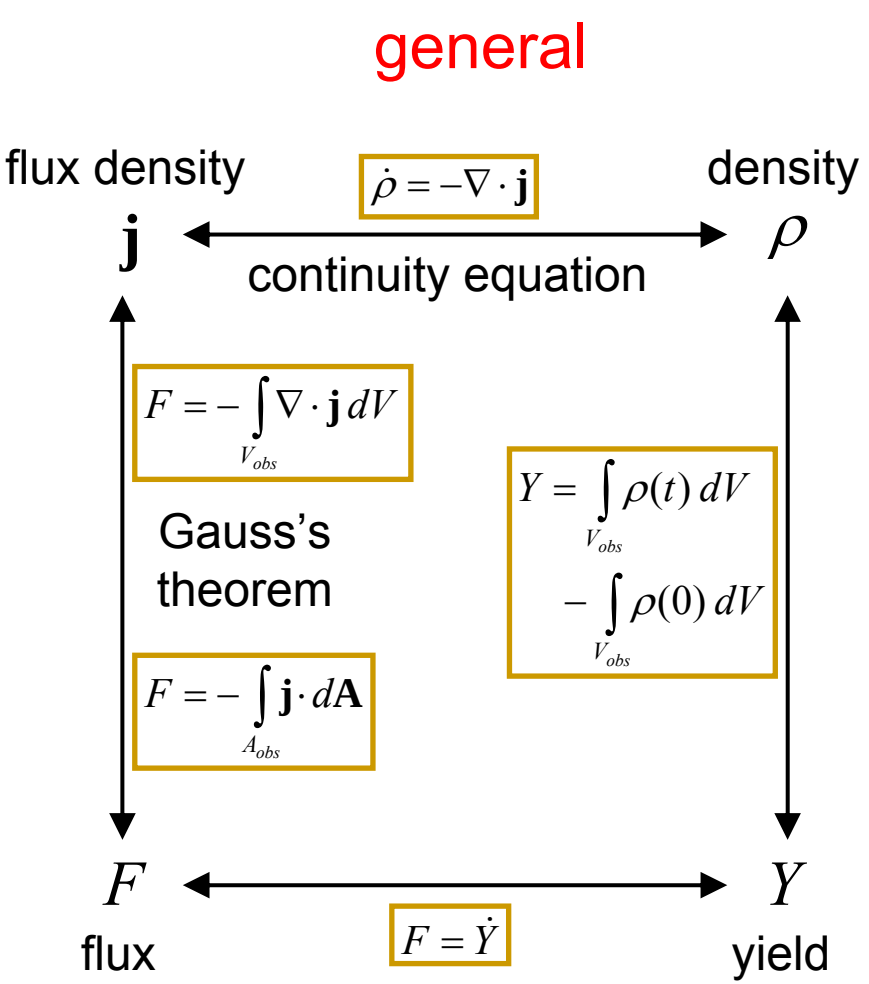
$$\mathbf{j}_{BO,el}(\mathbf{r},t) = \mathbf{0}$$

- Continuity equation for the electron is not valid in BO

$$\text{in general}: \quad \dot{\rho}_{BO,el}(\mathbf{r},t) \neq 0 \qquad \dot{\rho}_{BO,el}(\mathbf{r},t) \neq -\nabla_{\mathbf{r}} \cdot \mathbf{j}_{BO,el}(\mathbf{r},t)$$

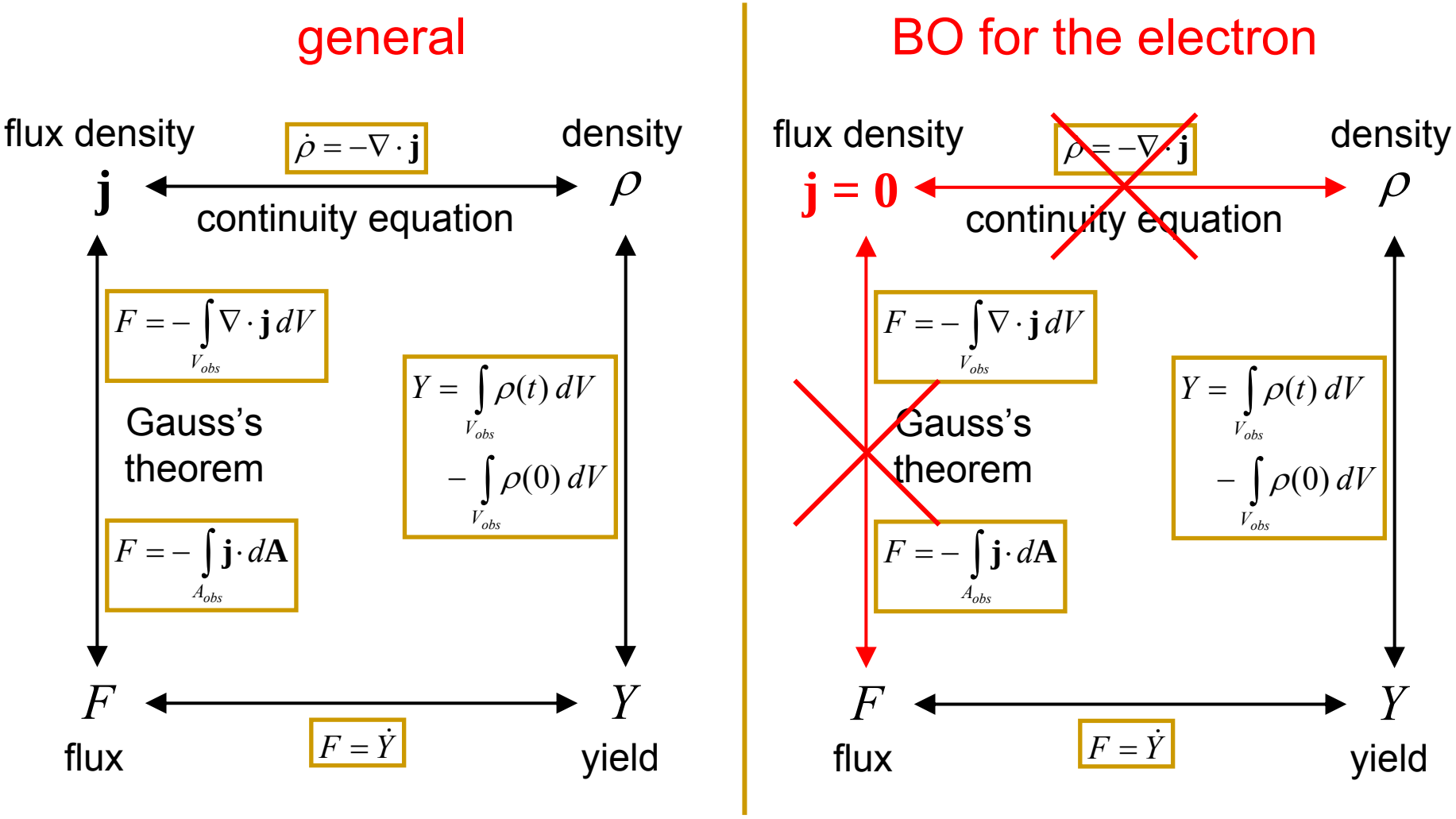
I. Barth, H.-C. Hege, H. Ikeda, A. Kenfack, M. Koppitz, J. Manz, F. Marquardt, G.K. Paramonov, Chem. Phys. Lett. 481, 118 (2009)

Schematic overview



I. Barth, H.-C. Hege, H. Ikeda, A. Kenfack, M. Koppitz, J. Manz, F. Marquardt, G.K. Paramonov, Chem. Phys. Lett. 481, 118 (2009)

Schematic overview



I. Barth, H.-C. Hege, H. Ikeda, A. Kenfack, M. Koppitz, J. Manz, F. Marquardt, G.K. Paramonov, Chem. Phys. Lett. 481, 118 (2009)

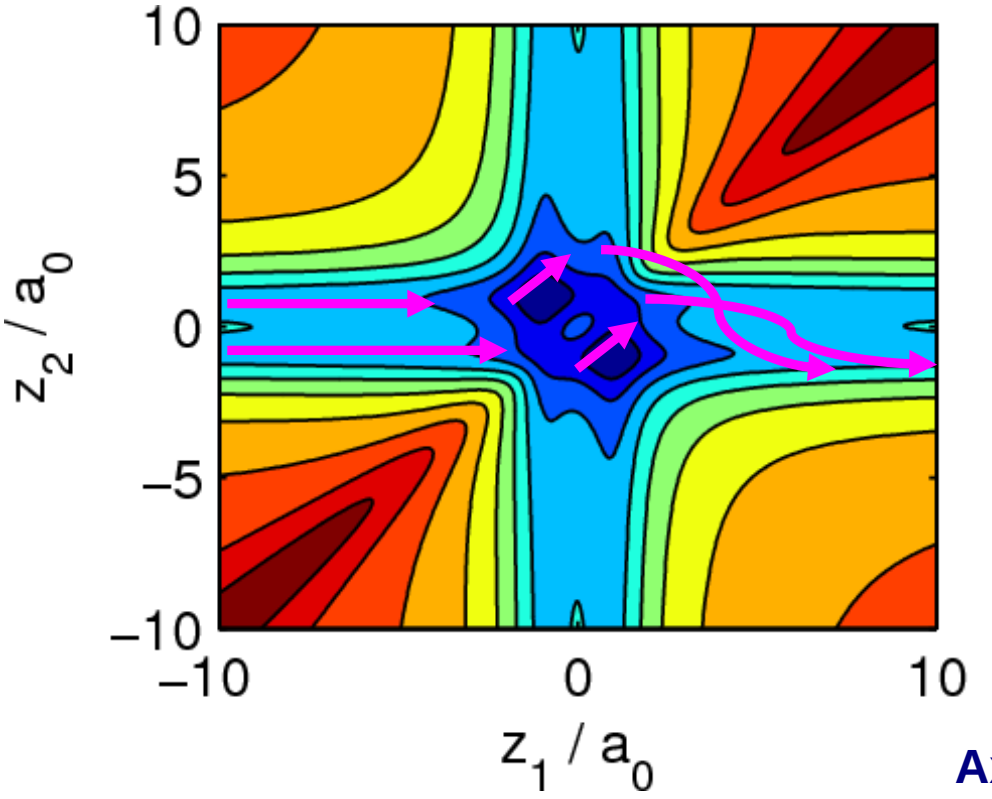
Agenda

- ✓ Introduction

- ✘ Applications to electronic fluxes
  - Electron impact dynamics: $e^- + H_2^+$ (2D)
  - Electronic ring current: Mg-porphyrin, AlCl, atoms (multi-D)
- Applications to nuclear fluxes

- Applications to concerted electronic and nuclear fluxes

Attosecond electron impact dynamics: quantum model simulation for $e^- + H_2^+$



Axel Schild
with kind support by Ingo Barth

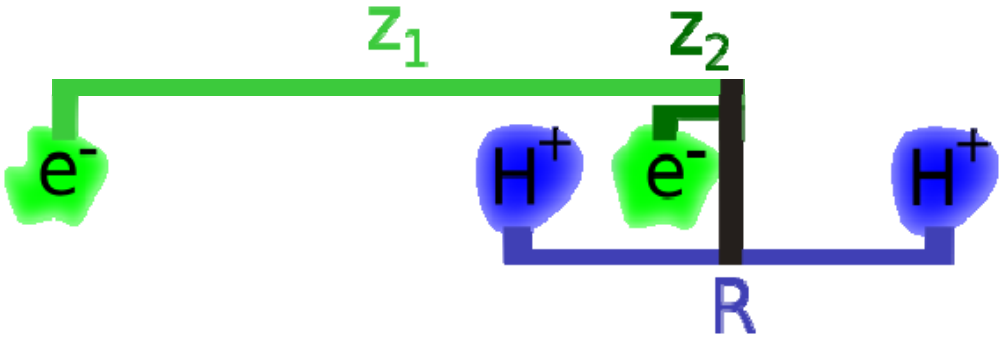
Motivation

- New method of investigation of attosecond electron dynamics:
  Zewail proposed compression of ~30 keV electron pulse to 15 as with the help of a moving intensity grating
  P. Baum, A.H. Zewail, Chem. Phys 2009, special issue Attosecond Molecular Dynamics (Eds. Bandrauk, Manz, Vrakking)
- Do high-energy electrons change the target?
- This work: Quantum model scattering of 0.5 – 1.5 keV electron off H_2^+

$$
\begin{aligned}
e + H_2^+ &\longrightarrow H_2^+ + e \\
&\longrightarrow H_2^{+*} + e \quad ? \\
&\longrightarrow p + p + e + e \; ? \\
&\longrightarrow \ldots
\end{aligned}
$$

The model

one-dimensional H_2-molecule:



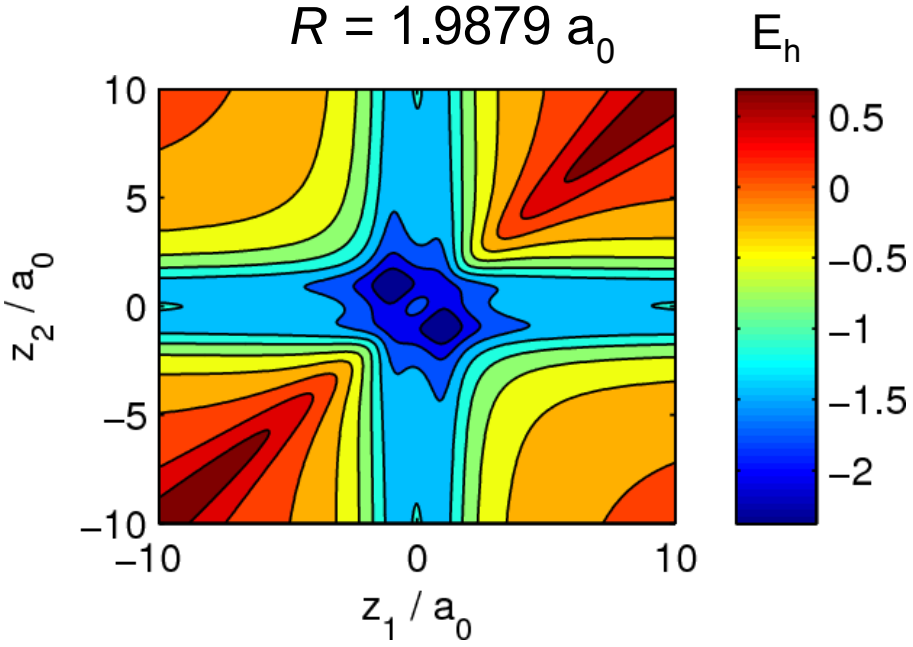
- z_1, z_2 electron distance from c.o.m.
- internuclear distance *R* kept fixed

$$i\frac{d}{dt}\Psi(z_1,z_2,t) = \left[-\frac{1}{2}\frac{\partial^2}{\partial z_1^2} - \frac{1}{2}\frac{\partial^2}{\partial z_2^2} + V(z_1,z_2)\right]\Psi(z_1,z_2,t)$$

- Solved with WavePacket program / Split-Operator method (B. Schmidt, U. Lorenz, http://wavepacket.sourceforge.net)

The model

$$V_{H_2} = \sum_{j=1}^{2} \left[-\frac{1}{\sqrt{(z_j + R/2)^2 + c}} - \frac{1}{\sqrt{(z_j - R/2)^2 + c}} \right] + \frac{1}{\sqrt{(z_1 - z_2)^2 + d}} + \frac{1}{R}$$



to reproduce electronic excitation energies of H_2:

$c = 0.7\ a_0^2$, $d = 1.2375\ a_0^2$

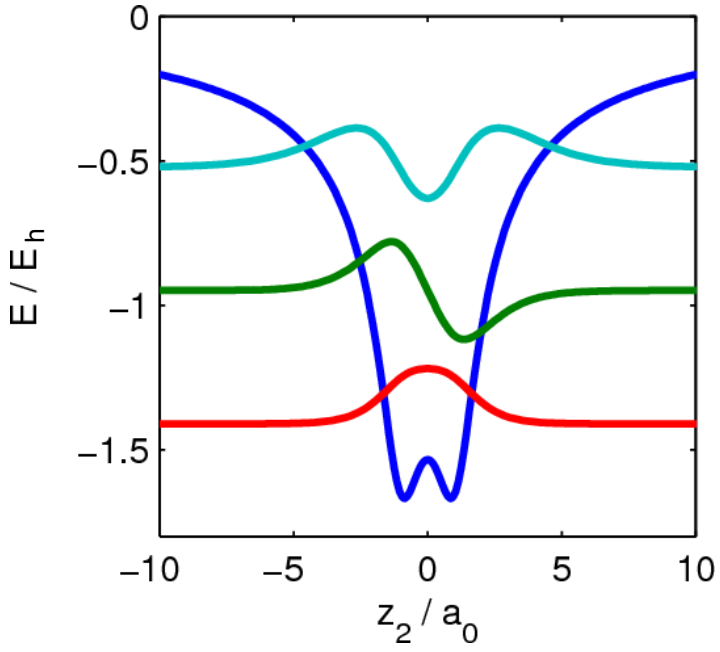
adapted from

A.D. Bandrauk, S. Chelkowski, S. Kawai, H. Lu, PRL 101, 153901, 2008

The model

$$V_{H_2^+} = -\frac{1}{\sqrt{(z+R/2)^2+c}} - \frac{1}{\sqrt{(z-R/2)^2+c}} + \frac{1}{R}$$

R = 1.9879 a_0



ε_{01} = 0.461 E_h

compare:

ε_{01} = 0.435 E_h

(J.M. Peek, J. Chem. Phys. 43, 3004, 1965)

Initial state

Product of Gaussian in z_1-direction

with ground state of H_2^+ in z_2-direction:

distinguishable electrons

$$\Psi(z_1, z_2, t = 0) = \psi(z_1)\phi_0(z_2)$$

$$\psi = Nexp\left(-\alpha_0(z_1 - z_{1,0})^2 + \frac{i}{\hbar}p_0(z_1 - z_{1,0}) + \frac{i}{\hbar}\gamma_0\right)$$

Kinetic energy: ~ 544 eV

D.J. Tannor, Introduction to Quantum Mechanics –
A Time Dependent Perspective
(University Science Books: USA 2007)

Electron dynamics

Time-dependent scattering theory

$$H = H^{ela} + V^{inela}$$

$$V_{H_2}^{ela} = \sum_{j=1}^{2} \left[-\frac{1}{\sqrt{(z_j + R/2)^2 + c}} - \frac{1}{\sqrt{(z_j - R/2)^2 + c}} \right] + \frac{1}{R}$$

$$V^{inela} = \frac{1}{\sqrt{(z_1 - z_2)^2 + d}}$$

causes electron correlation

Time-dependent scattering theory

for reference: elastic scattering

Initial state $$\Psi_j^{ela}(z_1, z_2, t = 0) = \psi_j^{ela}(z_1)\phi_j(z_2)$$

TDSE $$i\frac{d}{dt}\Psi_j^{ela}(z_1, z_2, t) = H^{ela}\Psi_j^{ela}(z_1, z_2, t)$$

Expansion in terms of elastic wavefunctions:

$$\Psi(z_1, z_2, t) = \sum_{j=0}^{\infty} c_j^{ela}(t)\Psi_j^{ela}(z_1, z_2, t) \text{ for } t \to \infty$$

$$c_j^{ela}(t) = \int^{\infty} dz_1 dz_2 (\Psi_j^{ela}(z_1, z_2, t))^* \Psi(z_1, z_2, t)$$

Time evolution

$R = 1.9879\ a_0$

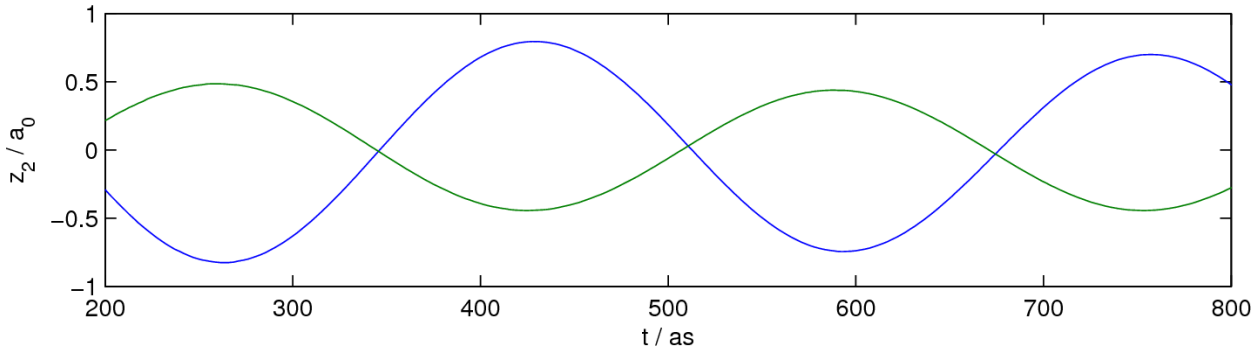
- Dispersion, but little trace of the scattering event
  → major part is elastic scattering

Time evolution

$$\Psi(z_1, z_2, t) - c_0^{ela}(t)\Psi_0^{ela}(z_1, z_2, t)$$

→ Two oscillating parts, head and tail

Period T = 329 as, $h\nu$ = 0.462 E_h compare ε_{01} = 0.461 E_h



Time evolution

$$\Psi(z_1, z_2, t) - \sum_{j=0}^{1} c_j^{ela}(t)\Psi_j^{ela}(z_1, z_2, t)$$

→ no oscillation

removing further contributions $c_j^{ela}(t)\Psi_j^{ela}(z_1, z_2, t)$

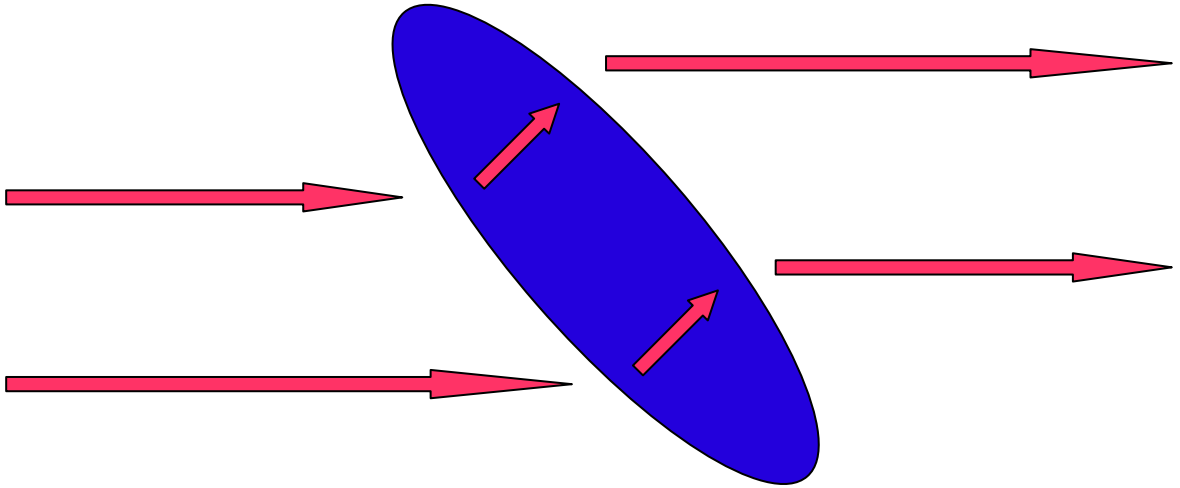
for j > 1 has no visible effect on the density

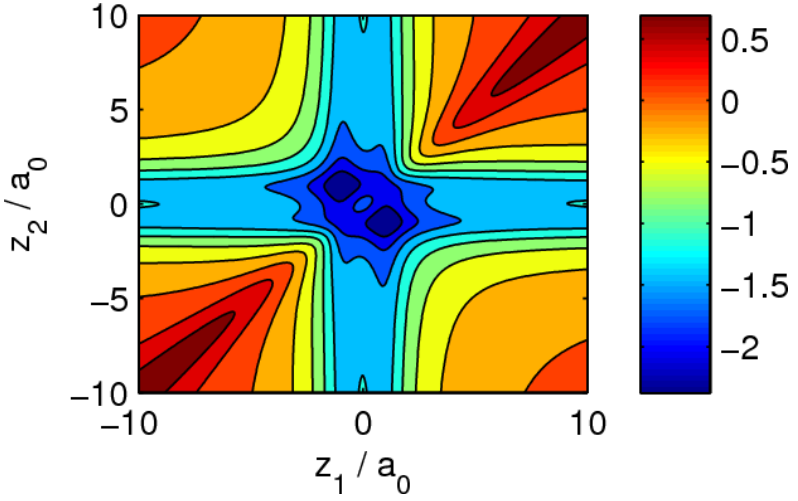
Electronic flux density

Electronic flux density

Electronic flux density

Mechanism





redirection along z_2

→ oscillation

two minima

→ two parts

Conclusion

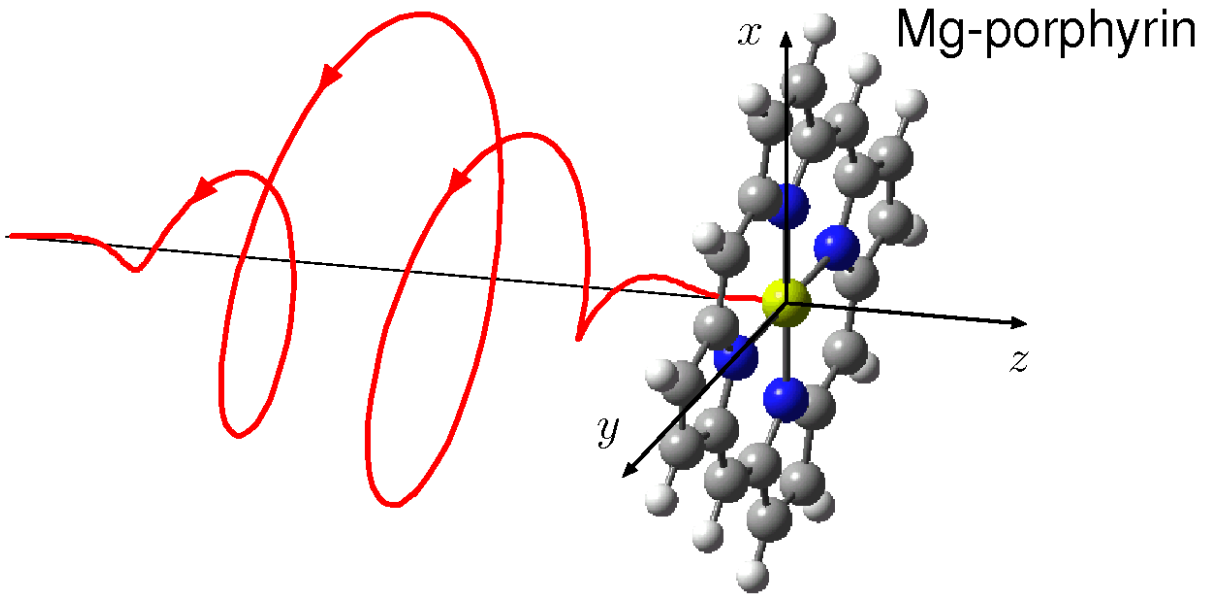
Take home message:

1) Analysis of mechanisms by flux density

2) Experiment by Baum & Zewail is promising!

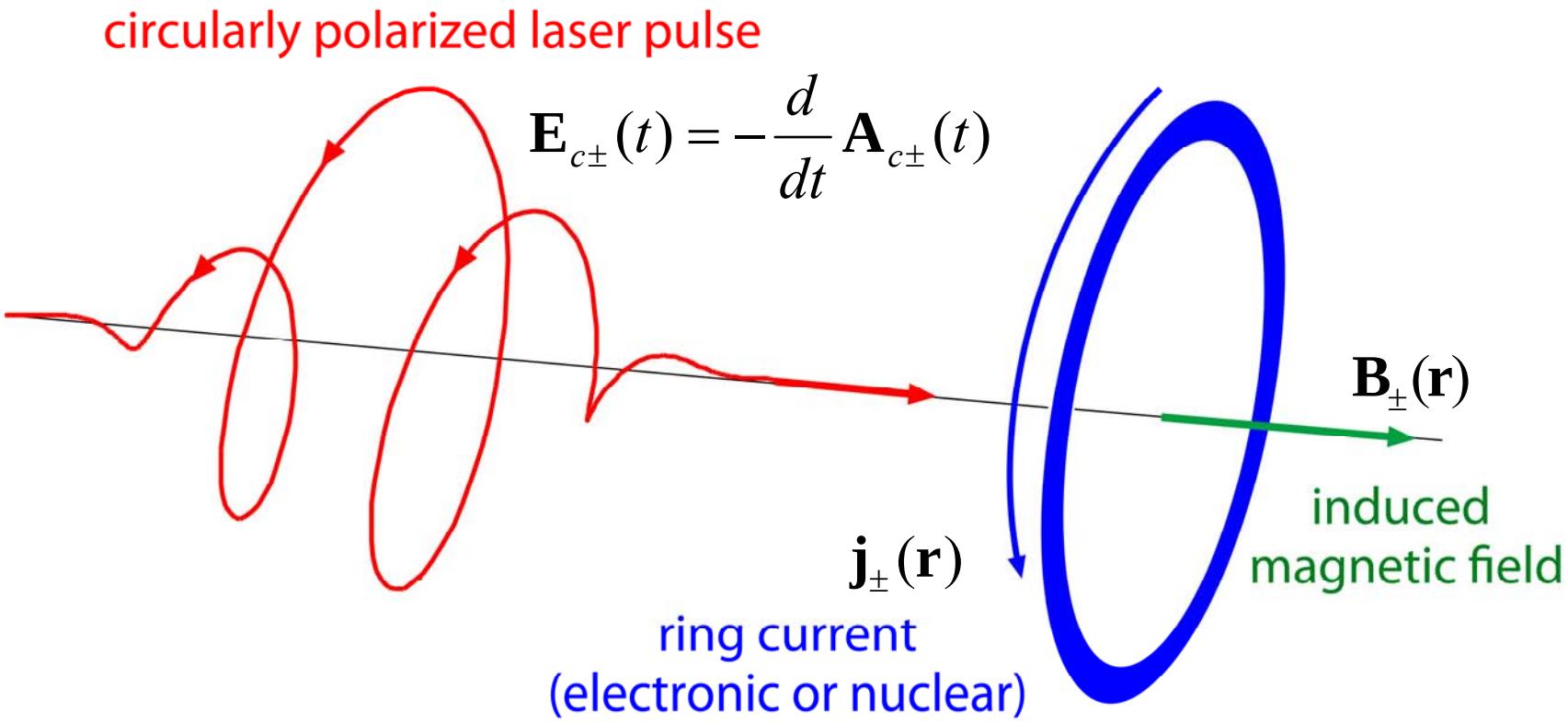
$$e + H_2^+ \longrightarrow H_2^+ + e$$
$$\dashrightarrow H_2^{+*} + e \qquad (< 3 \cdot 10^{-3})$$
$$(\dashrightarrow p + p + e + e)$$

Control of electronic ring currents by circularly polarized laser pulses



I. Barth, J. Manz, Y. Shigeta, K. Yagi, J. Am. Chem. Soc. 128, 7043 (2006)
I. Barth, J. Manz, Angew. Chem. Int. Ed. 45, 2962 (2006)
I. Barth, J. Manz, Phys. Rev. A 75, 012510 (2007)
I. Barth, J. Manz, L. Serrano-Andrés, Chem. Phys. 347, 263 (2008)
I. Barth, L. Serrano-Andrés, T. Seideman, Chem. Phys. 347, 263 (2008)
I. Barth, PhD thesis, FU Berlin (2009)

Concept



related: inverse Faraday effect

Model assumptions for ring currents

- Fixed orientation of molecule

  H. Stapelfeldt, T. Seideman, Rev. Mod. Phys. 75, 543 (2003)

  M. Leibscher, I. S. Averbukh, H. Rabitz, Phys. Rev. A 69, 013402 (2004)

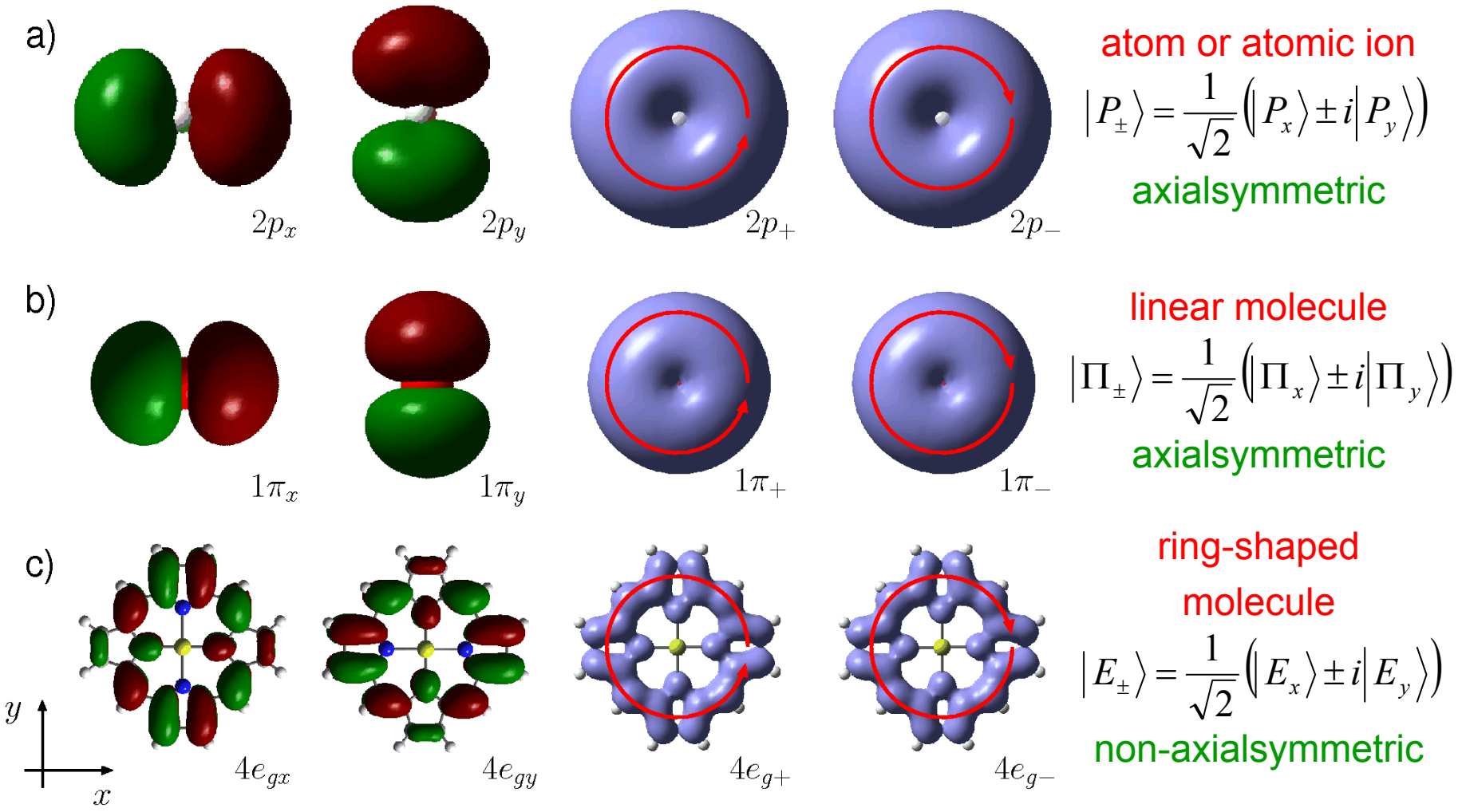
  E. Hamilton, T. Seideman, T. Ejdrup, M. D. Poulsen, C. Z. Bisgaard, S. S. Viftrup, H. Stapelfeldt, Phys. Rev. A 72, 043402 (2005)

  I. Barth, L. Serrano-Andrés, T. Seideman, Chem. Phys. 347, 263 (2008)

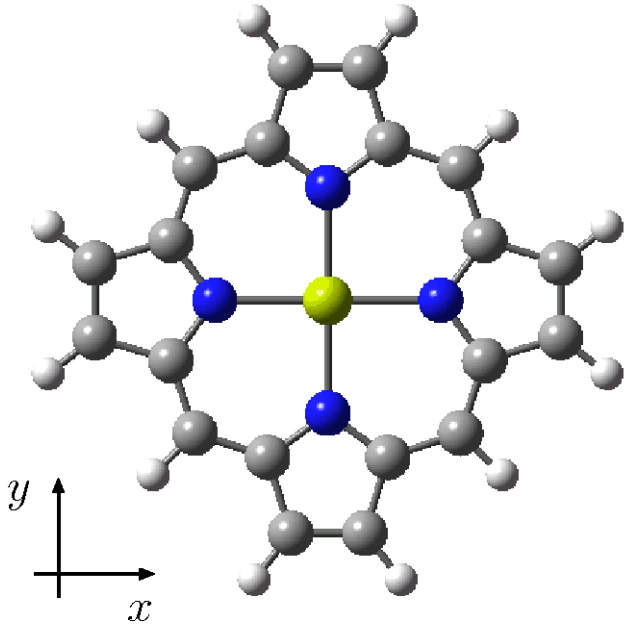
- Transition from ground state

- No spin-orbit interaction, spin conservation

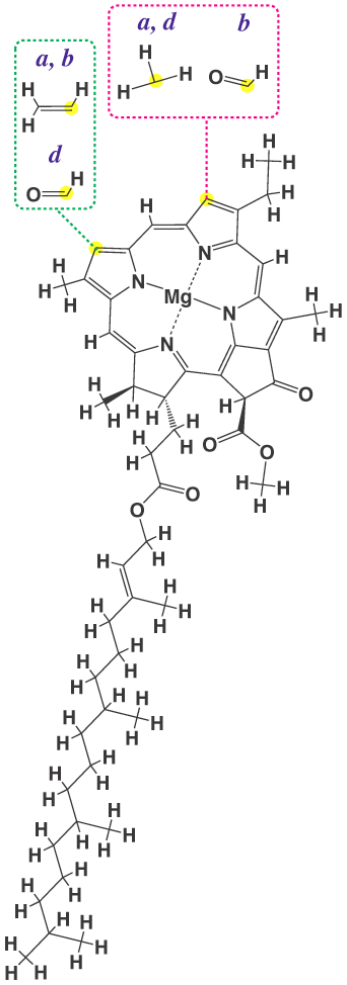
Electronic degenerate orbitals/states



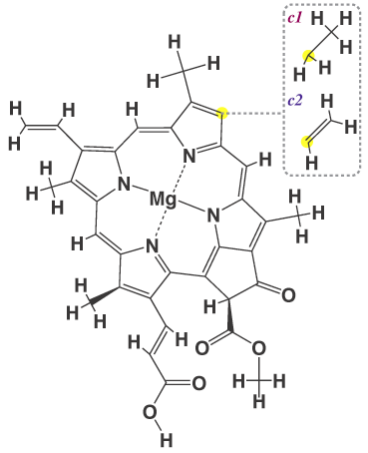
Model: Magnesium porphyrin (MgP)



- Ground state: X^1A_{1g}
- Symmetry: D_{4h}



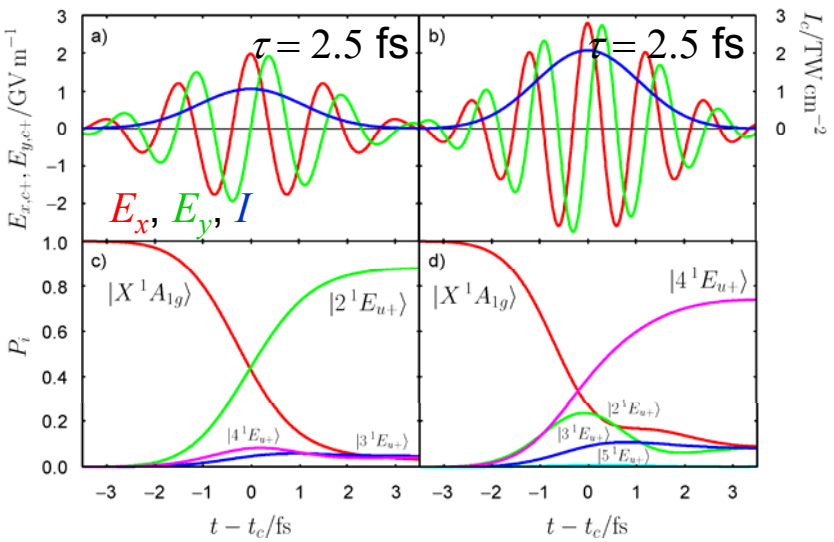
Chlorophyll a, b, d



Chlorophyll c1, c2

Electronic ring currents in MgP

- Selective population transfer $\left| X\ {}^1A_{1g} \right\rangle \rightarrow \left| n\ {}^1E_{u+} \right\rangle$ by means of a right circ. pol. optimized π laser pulse with $\cos^{20}$ envelope



$\left| 2\ {}^1E_{u+} \right\rangle$ $\left| 4\ {}^1E_{u+} \right\rangle$

Difference of the electronic probability density

$\Delta\rho(\mathbf{r},t) > 0$ (red)

$\Delta\rho(\mathbf{r},t) < 0$ (green)

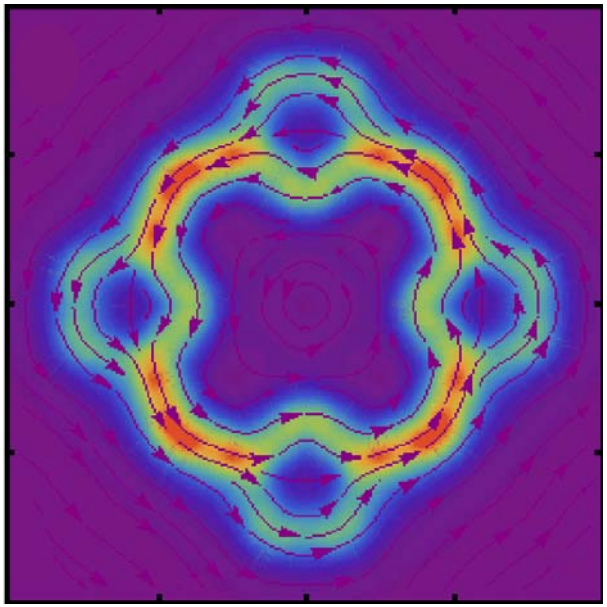
I. Barth, J. Manz, Y. Shigeta, K. Yagi, J. Am. Chem. Soc. 128, 7043 (2006)

I. Barth, C. Lasser, J. Phys. B (2009), in press

I. Barth, PhD thesis, FU Berlin (2009)

Electronic ring currents in MgP

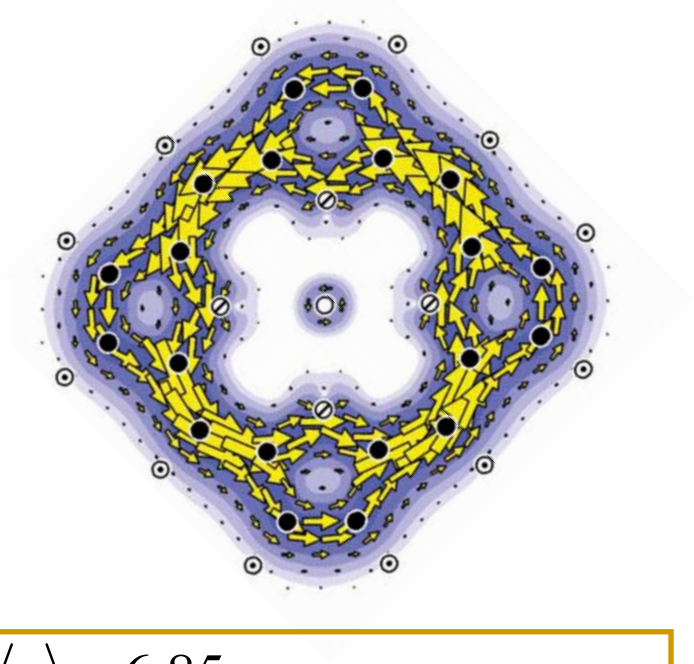
laser pulse



$$\langle r \rangle = 6.32\ a_0$$
$$I = 84.5\ \mu\text{A}$$
$$B_{ind} = 0.159\ \text{T}$$

I. Barth, J. Manz, Y. Shigeta, K. Yagi,
J. Am. Chem. Soc. 128, 7043 (2006)

permanent magnetic field



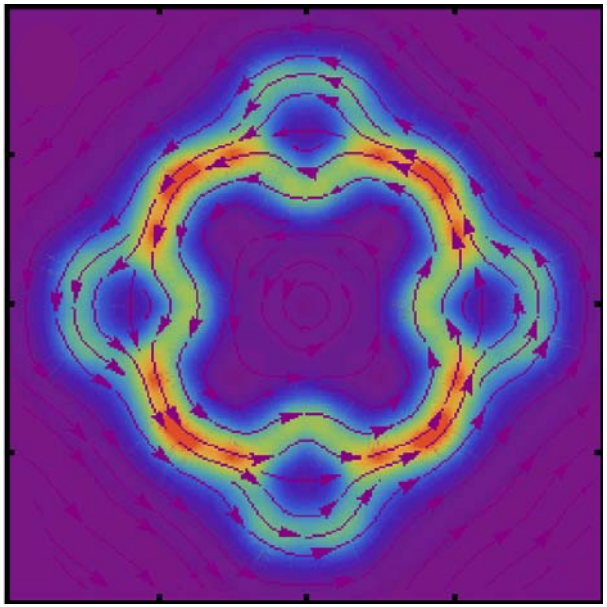
$$\langle r \rangle = 6.85\ a_0$$
$$I = 84.5\ \mu\text{A} \quad \text{if} \quad B = 8048\ \text{T}$$

Present technology:
< 100 T (permanent), 34000 T (10 ps)
(Rossendorf / Dresden, Rutherford Appleton)

E. Steiner et al, Org. Biomol. Chem. 3, 4053 (2005)
J. Jusélius et al, J. Org. Chem. 65, 5233 (2000)

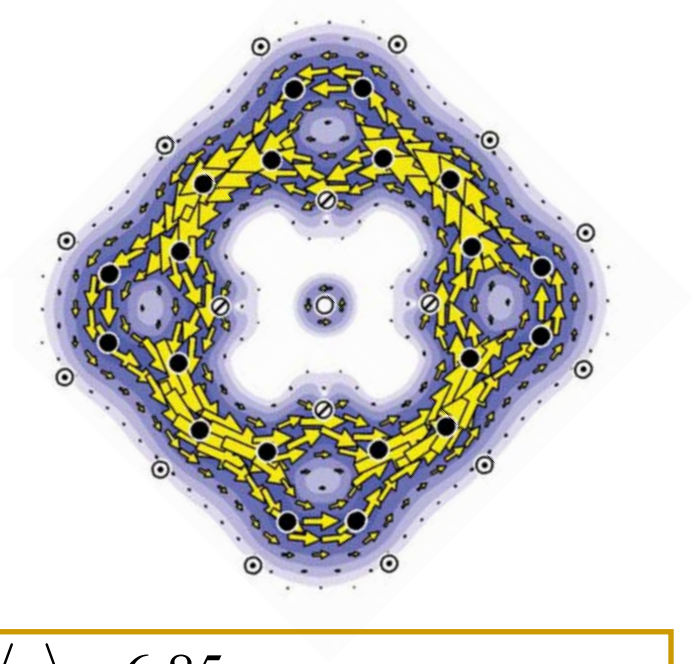
Electronic ring currents in MgP

laser pulse



strong ring current
active control

permanent magnetic field



$$\langle r \rangle = 6.85\ a_0$$

$$I = 84.5\ \mu\text{A} \quad \text{if} \quad B = 8048\ \text{T}$$

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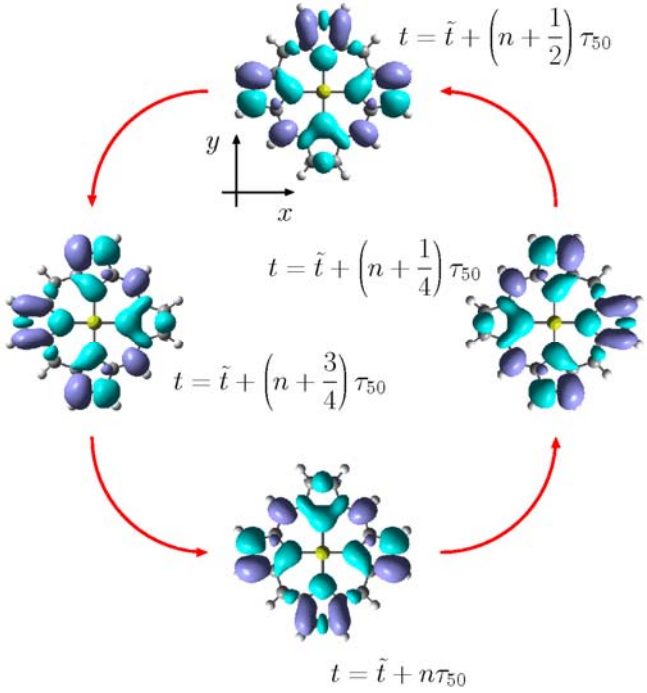
E. Steiner et al, Org. Biomol. Chem. 3, 4053 (2005)
J. Jusélius et al, J. Org. Chem. 65, 5233 (2000)

Electron circulation in MgP

- Half population transfer $\left|X\ {}^1A_{1g}\right\rangle \rightarrow \left|n\ {}^1E_{u+}\right\rangle$ by means of a right circ. pol. optimized $\pi/2$ laser pulse with $\cos^{20}$ envelope



- Period of the electronic density

$\left|5\ {}^1E_{u\pm}\right\rangle$: $\tau_{50} = 2\pi / \omega_{50} = 907$ as

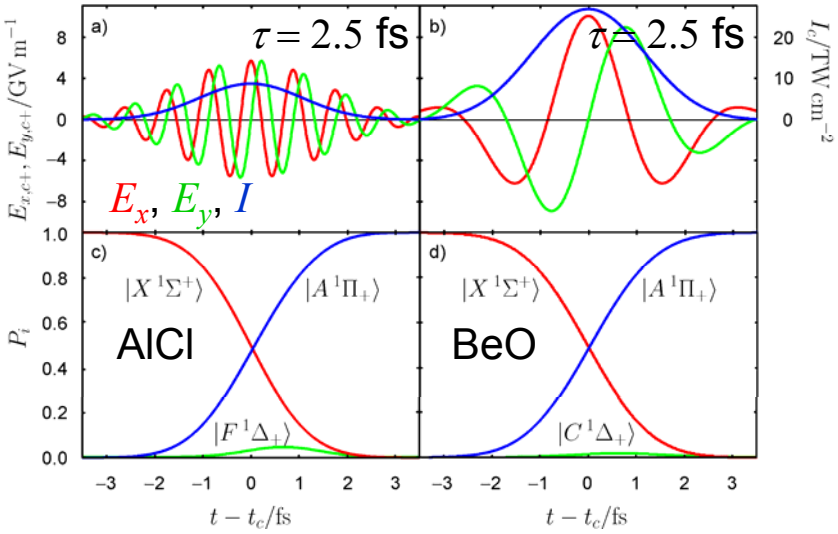
$\Delta\rho(\mathbf{r},t) > 0$ (blue), $\Delta\rho(\mathbf{r},t) < 0$ (cyan)

I. Barth, J. Manz, Angew. Chem. Int. Ed. 45, 2962 (2006), Angew. Chem. 118, 3028 (2006)

I. Barth, J. Manz, in: A.W. Castleman, Jr., M.L. Kimble (eds.), *Femtochemistry VII: Fundamental Ultrafast Processes in Chemistry, Physics, and Biology* (Elsevier, Amsterdam, 2006), p. 441

Electronic ring currents in AlCl and BeO

- Complete population transfer $\left|X\ ^1\Sigma^+\right\rangle \rightarrow \left|A\ ^1\Pi_+\right\rangle$ by means of a right circ. pol. optimized π laser pulse with $\cos^{20}$ envelope



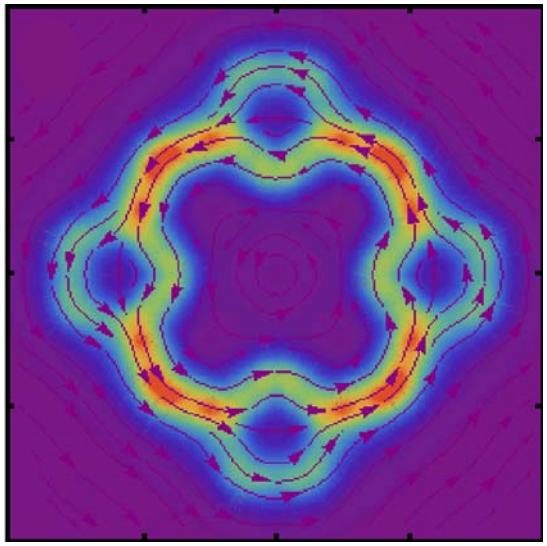
Difference of the electronic probability density

$$\Delta\rho(\mathbf{r},t) = \rho(\mathbf{r},t) - \rho(\mathbf{r},t_0)$$
$$\Delta\rho(\mathbf{r},t) > 0 \quad \text{(red)}$$
$$\Delta\rho(\mathbf{r},t) < 0 \quad \text{(green)}$$

I. Barth, J. Manz, L. Serrano-Andrés, Chem. Phys. 347, 263 (2008)
I. Barth, L. Serrano-Andrés, T. Seideman, J. Chem. Phys. 129, 164303 (2008); 130, 109901(E) (2009)

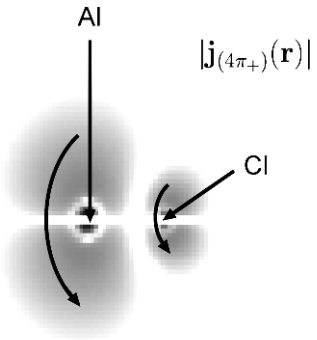
Comparison: Electronic ring currents

MgP



$$\langle r \rangle = 6.32\ a_0$$
$$I = 84.5\ \mu\text{A}$$
$$T = 1.90\ \text{fs}$$
$$B_{ind}(\text{Mg}) = 0.16\ \text{T}$$
$$\langle L_{z,el} \rangle \approx 2.5\ \hbar$$

AlCl



$$\langle r^{-1} \rangle^{-1} = 0.18\ a_0$$
$$I = 405\ \mu\text{A}$$
$$T = 396\ \text{as}$$
$$B_{ind}(\text{Al}) = 7.68\ \text{T}$$
$$\langle L_{z,el} \rangle = 1\ \hbar$$

Biot-Savart law for ring loop model:

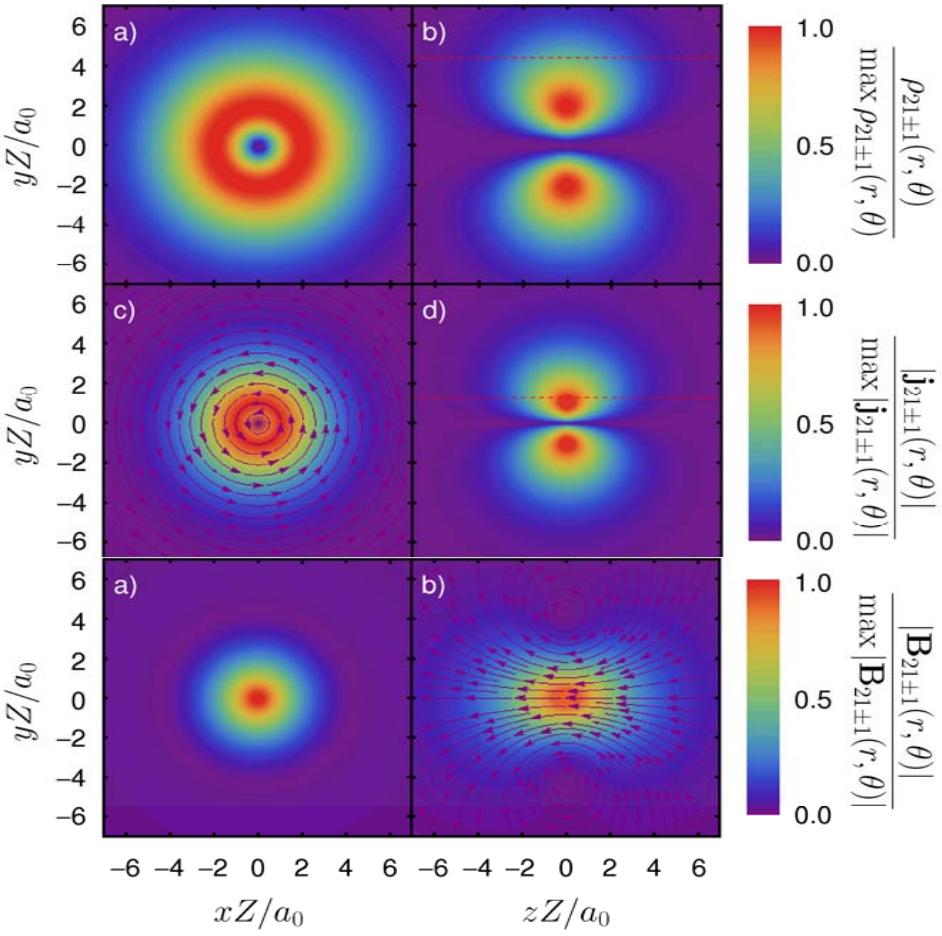
$$\mathbf{B}(\mathbf{r}=\mathbf{0}) \approx -\frac{\mu_0 I}{2R}\mathbf{e}_z$$

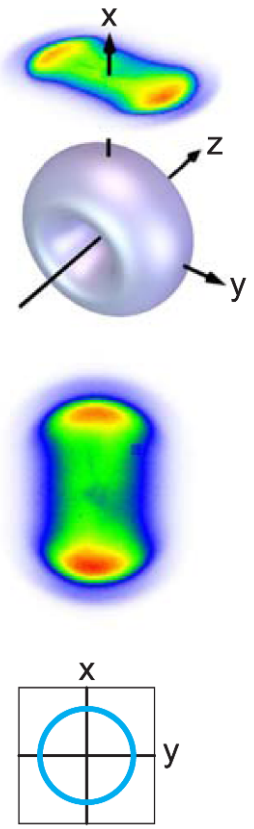
$$I = \frac{Q}{T}$$

I. Barth, J. Manz, Y. Shigeta, K. Yagi, J. Am. Chem. Soc. 128, 7043 (2006)

I. Barth, J. Manz, L. Serrano-Andrés, Chem. Phys. 347, 263 (2008)

Electronic ring currents in atomic orbitals





ionized
f(*m*=±3) orbital
of the K atom

experimentally observed

by means of
circularly polarized
laser pulses

I. Barth, J. Manz, Phys. Rev. A 75, 012510 (2007)
I. Barth, PhD thesis, FU Berlin (2009)

M. Wollenhaupt et al,
Appl. Phys. B 95, 245 (2009)

Agenda

- ✓ Introduction
- ✓ Applications to electronic fluxes
- ✘ Applications to nuclear fluxes
  - Double proton transfer: porphyrin (2D)
- Applications to concerted electronic and nuclear fluxes

From Synchronous to Sequential Double Proton Transfer:

Quantum Dynamics Simulation for the Model Porphine

***A. Accardi*, I. Barth, O. Kühn, J. Manz**

MOTIVATION

System:

• Porphyrins and metalloporphyrins, as well known as the "pigments of life", play a decisive role in biological processes[1] , such as:

- ➢Photosynthesis (*chlorins*)
- ➢Oxygen transport (*hemoglobin and myoglobin*)
- ➢Oxygen activation (*Cytochromes*)

Processes:

• Double Proton Transfer is important (for example, it may cause mutation of DNA base pair)[2] .

[1] H.-H. Limbach, J.T. Hynes,J.P. Klinman, R. L. Schowen, *Hydrogen-Transfer Reaction, Vol. 1*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2007.

[2] M. Meuwly, A. Müller and S. Leutwyler, *PCCP*, **5**, 2663-2672 (2003)

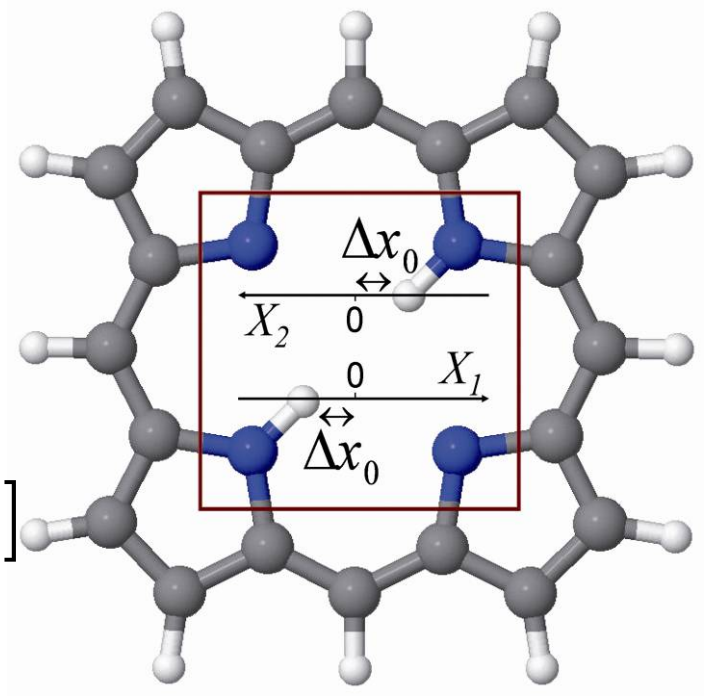
MODEL [3]

$$H = T(X_1, X_2) + V(X_1, X_2)$$

$$T = \frac{P_1^2}{2m_{H_1}} + \frac{P_2^2}{2m_{H_2}}$$

$$V = \frac{U_0}{\Delta x_0^4}\left[(X_1^2 - \Delta x_0^2)^2 + (X_2^2 - \Delta x_0^2)^2 - 4G\Delta x_0^2 X_1 X_2\right]$$

$$U_0 = 0.473eV \;\; , \;\; \Delta x_0 = 1.251 a_0 \;\; \text{and} \;\; G = 0.063$$



Parameters based on:

- *Experimental value U_0* [5], [6], [7] → *NMR, Laser-Induced Fluor.-Spect.*
- *Quantum chemistry for other values* [8] → *DFT/B3LYP/6-31G**

Two dimensional model supported in [4]: not RRKM, slow IVR.

[3] Z. Smedarchina, W. Siebrand, A. Fernandez-Ramos, *J. Chem. Phys.* **127**, 174513 (2007)

[4] T. J. Butenhoff, R. S. Chuck, H.-H. Limbach, C. B. Moore *J. Phys. Chem.* **1990**, *94*, 7847-7851.

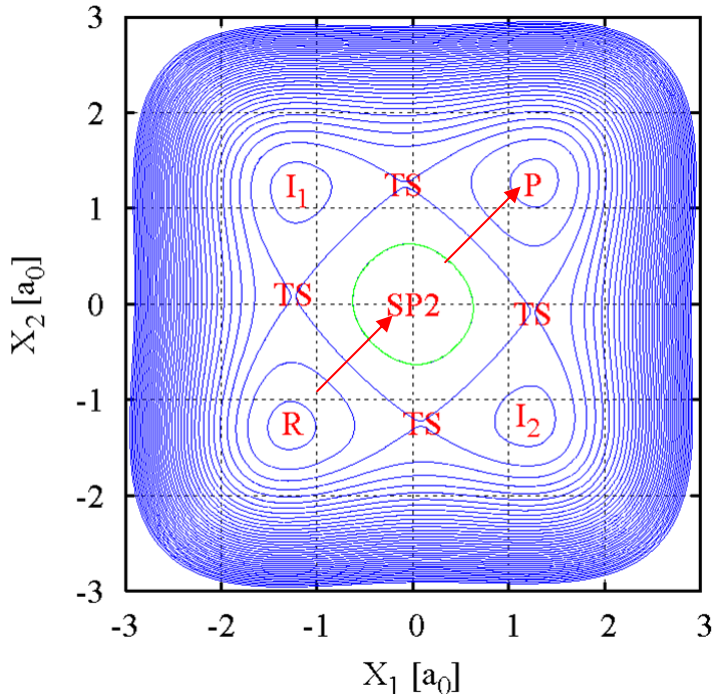
[5] J. Braun, M. Schlabach, B. Wehrle, M. Kocher, E. Vogel, and H.-H. Limbach, J. Am. Chem. Soc. **116**, 6593 (1994)

[6] J. Braun, H.-H. Limbach, P. G. Williams, H. Moromoto, and D. E. Wemmer, J. Am. Chem. Soc. **118**, 7241 (1996)

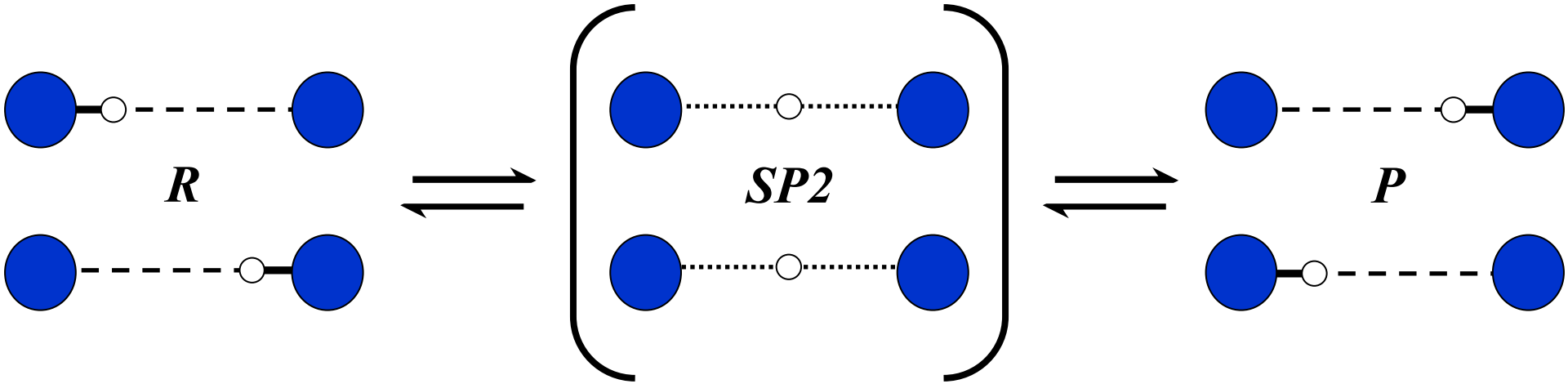
[7] T. J. Butenhoff, C. B. Moore *J. Am. Chem. Soc.* **1988**, *110*, 8336.

[8] Z. Smedarchina, M. Z. Zgierski, W. Siedbrand, and P. M. Kozlowsji, J. Chem. Phys. **109**, 1014 (1998)

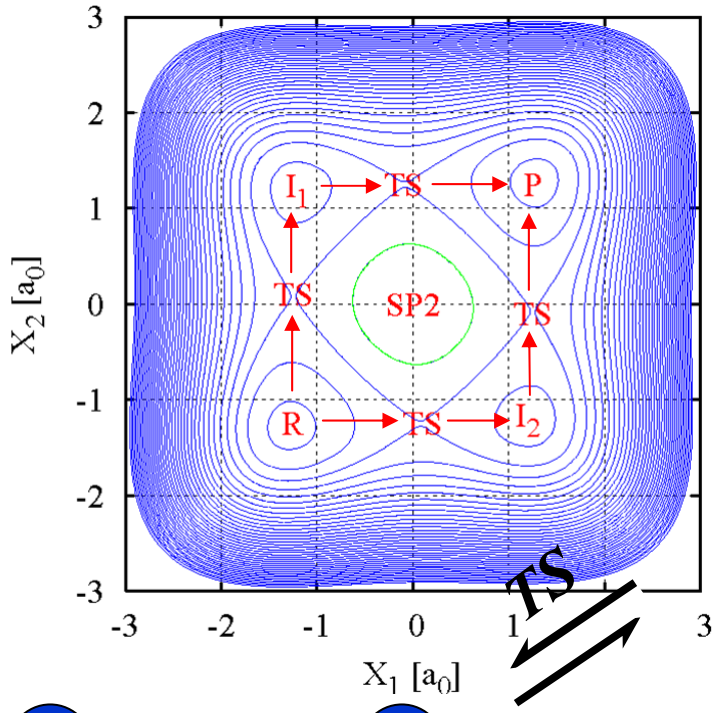
DOUBLE PROTON TRANSFER



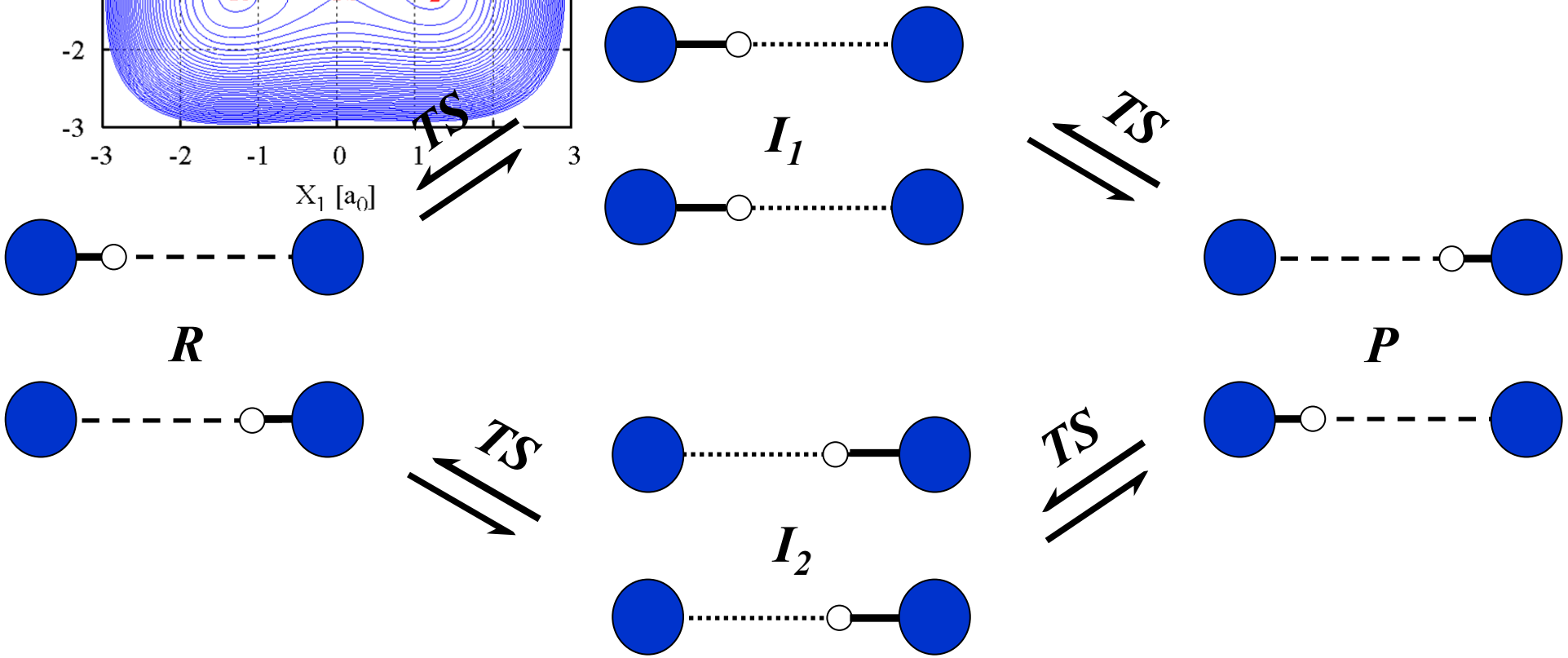
Synchronous



DOUBLE PROTON TRANSFER

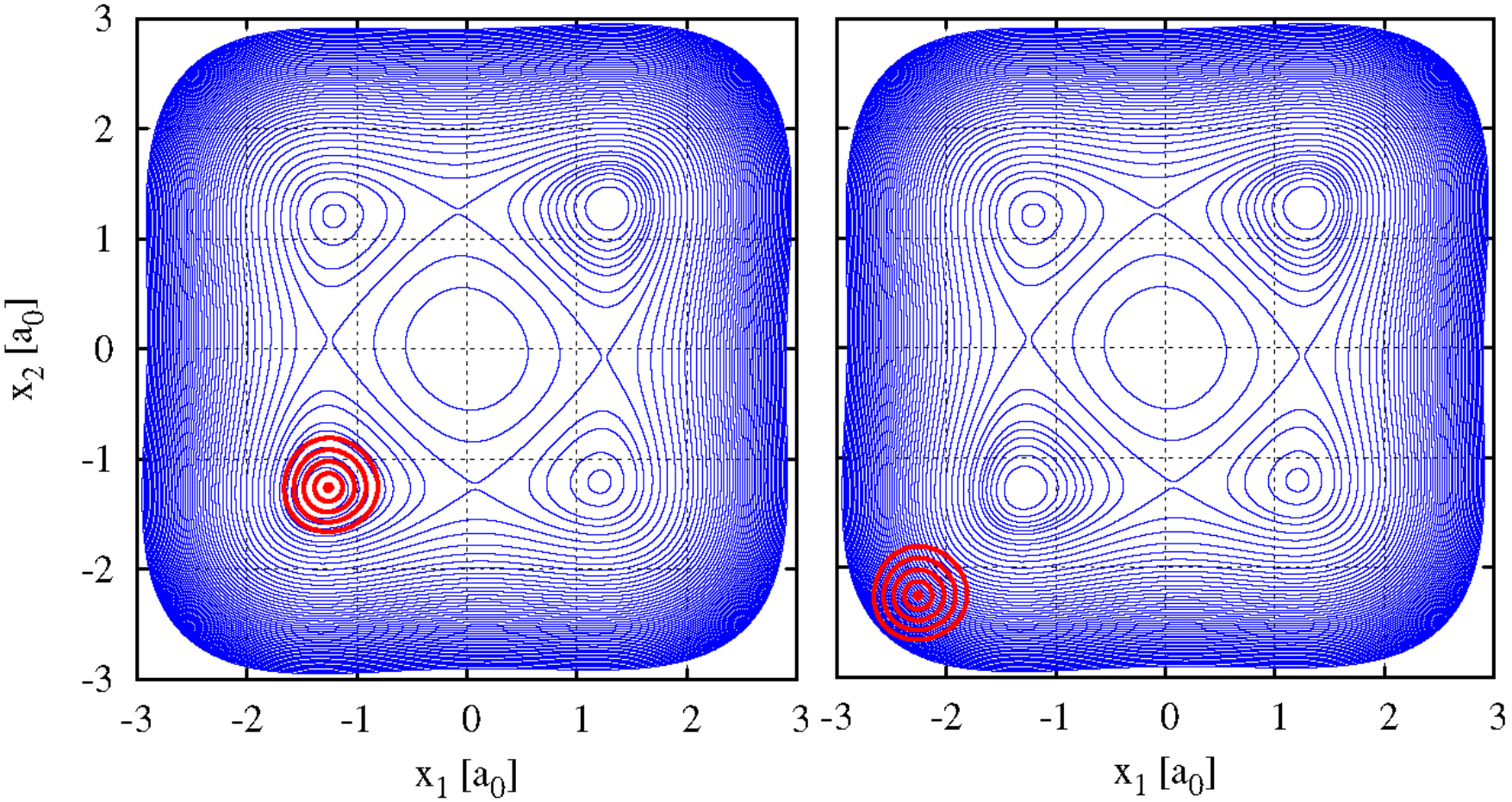


Sequential



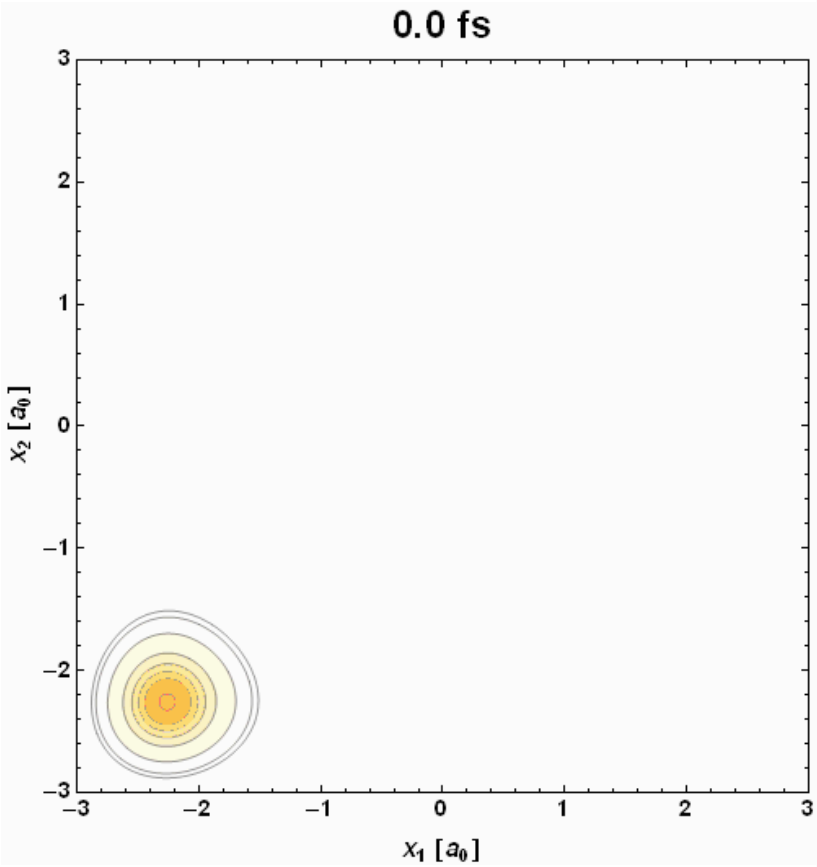
INITIAL CONDITION

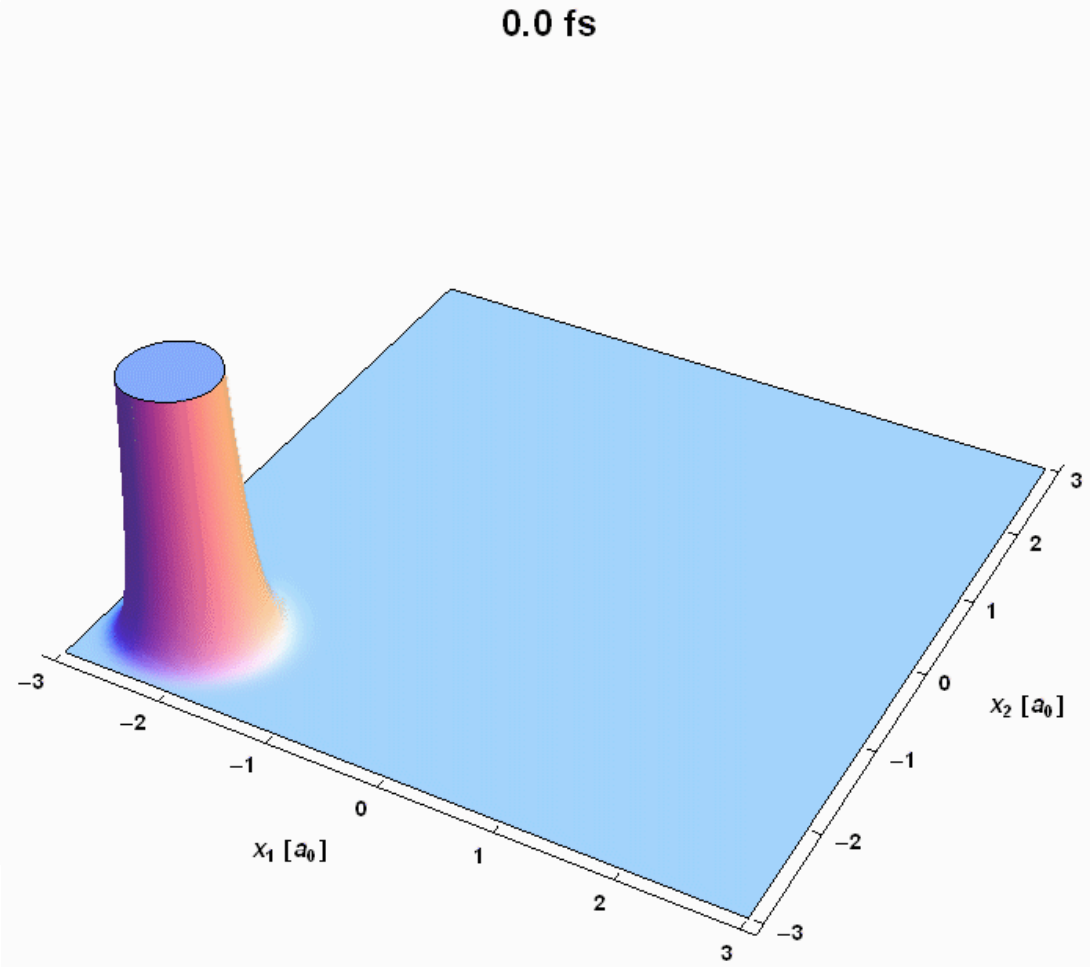
Initial displacement of the wave packet[11]



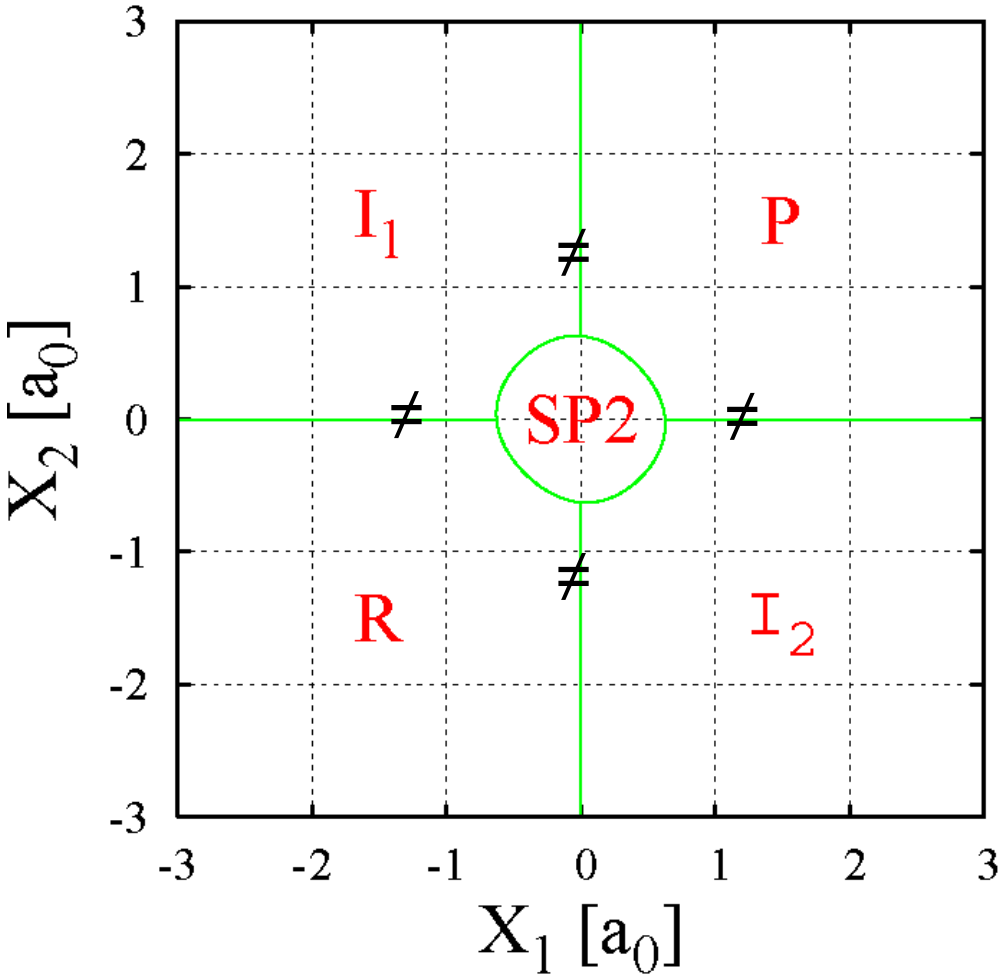
[11] W. Li, X. Zhou, R. Lock, S. Patchovskii, A. Stolow, H.C. Kapteyn, M.M. Murnane, Science, **322**, 1207 (2008)

NUCLEAR DYNAMICS





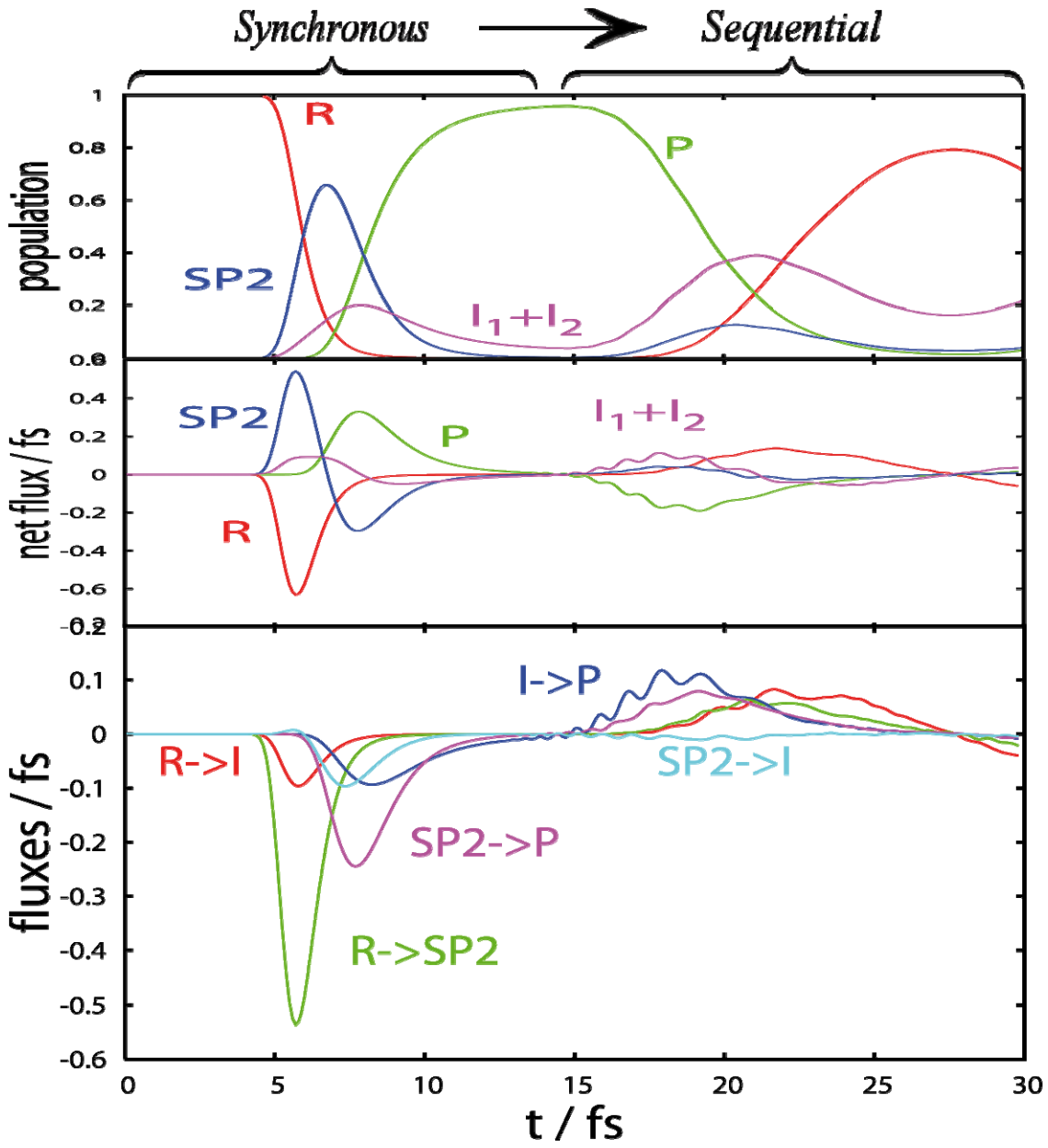
DOMAINS OF THE POTENTIAL



Time-dependent population of domains:

$$P_{Domain}(t) = \iint_{Domain} \rho(X_1, X_2, t) dX_1 dX_2$$

POPULATION AND FLUX DYNAMICS



CONCLUSIONS

Fluxes ➔ Analysis of mechanism

Double Proton Transfer

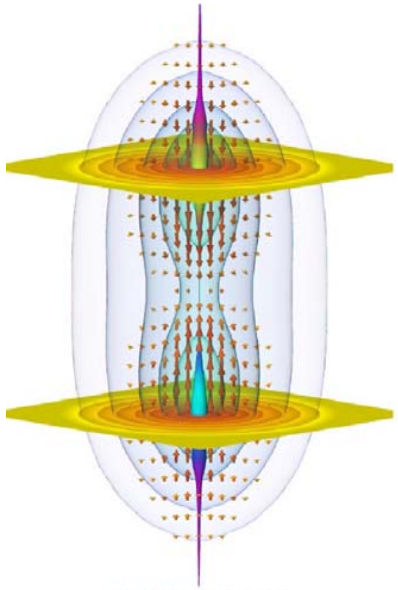
1) Synchronous ➔ sequential

2) in general:
quantum chemistry ⊙⊙ quantum reaction dynamics

Agenda

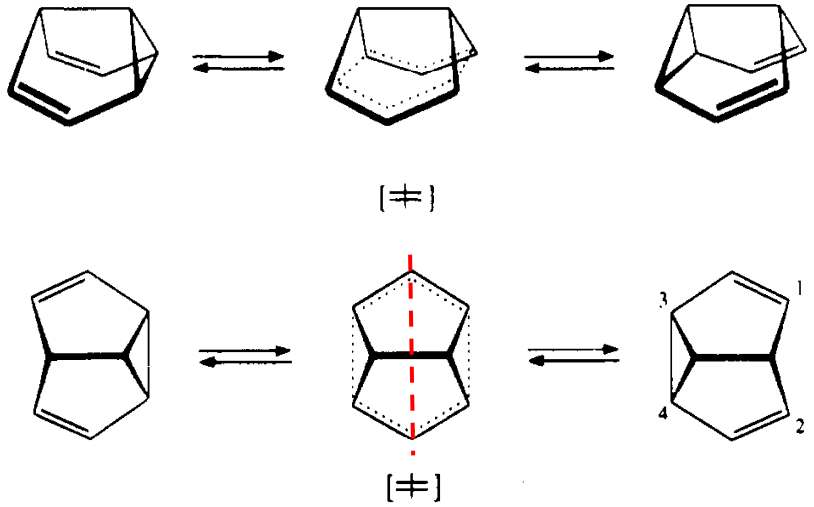
- ✓ Introduction
- ✓ Applications to electronic fluxes
- ✓ Applications to nuclear fluxes
- ✘ Applications to concerted electronic and nuclear fluxes
  - Vibration dynamics: H_2^+ (3D+1D)
  - Cope rearrangement: Semibullvalene (multi-D+1D)

Concerted electronic and nuclear fluxes in molecules



Vibration dynamics in H_2^+

I. Barth, H.-C. Hege, H. Ikeda, A. Kenfack, M. Koppitz, J. Manz, F. Marquardt, G.K. Paramonov, Chem. Phys. Lett. 481, 118 (2009)



Cope rearrangement in Semibullvalene (SBV)

D. Andrae, I. Barth, T. Bredtmann, J. Manz, B. Paulus, in preparation

A.D. Bandrauk, S. Chelkowski, P.B. Corkum, J. Manz, G.L. Yudin, J. Phys. B 42, 134001 (2009)
M. Okuyama, K. Takatsuka, Chem. Phys. Lett. 476, 109 (2009)
K. Nagashima, K. Takatsuka, J. Phys. Chem. A (2009), in press

Concerted electronic and nuclear fluxes in molecules: Vibration dynamics in H_2^+

- *Example: Vibration dynamics in H_2^+*

- *Initialization:*

W. Li, X. Zhou, R. Lock, S. Patchkovskii, A. Stolow, H.C. Kapteyn, M.M. Murnane, Science 322 (2008) 1207.

I. Barth, H.-C. Hege, H. Ikeda, A. Kenfack, M. Koppitz, J. Manz, F. Marquardt, G.K. Paramonov, Chem. Phys. Lett. 481, 118 (2009)

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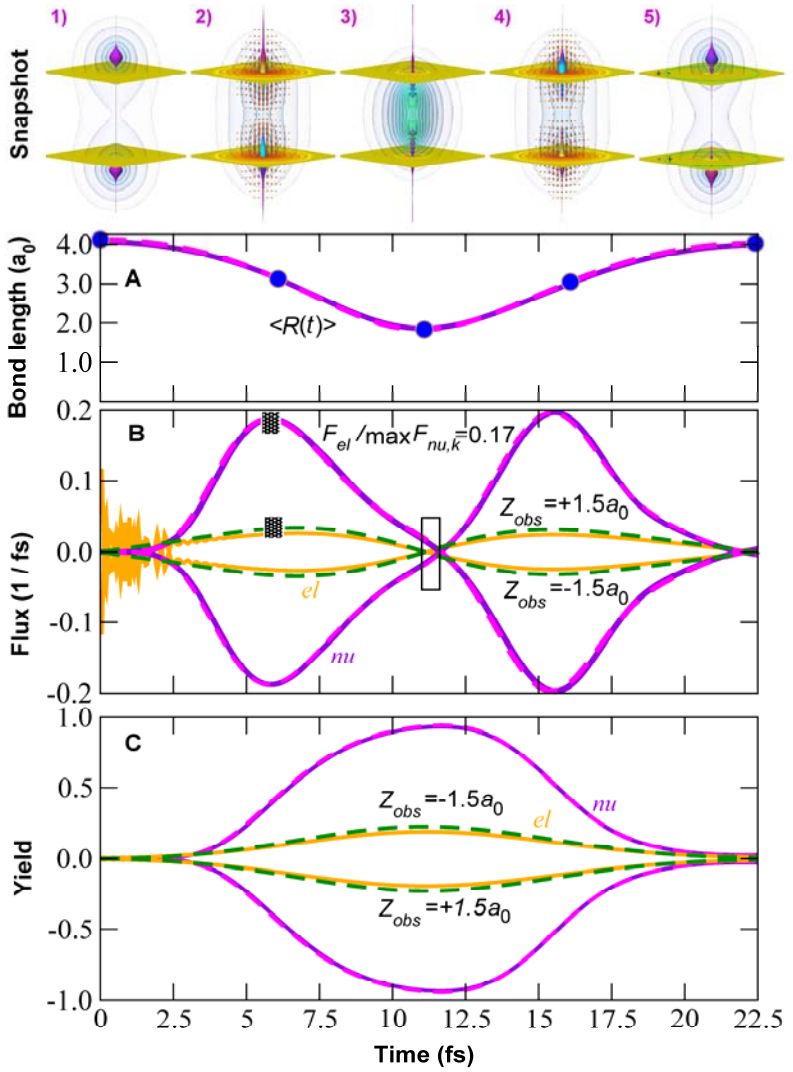

I. Barth, H.-C. Hege, H. Ikeda, A. Kenfack, M. Koppitz, J. Manz, F. Marquardt, G.K. Paramonov, Chem. Phys. Lett. 481, 118 (2009)

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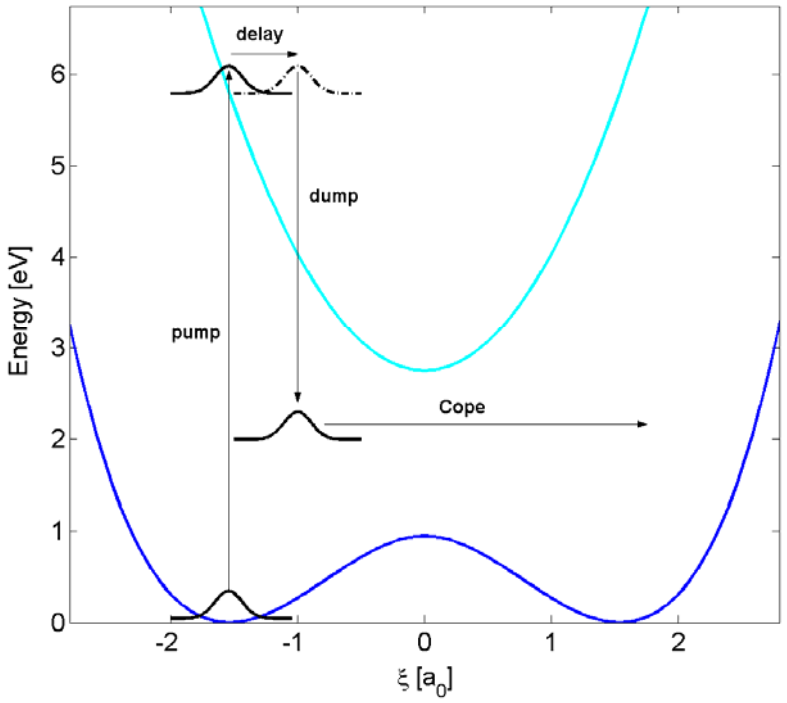
K. Bergmann, S. Görtler, J. Manz, and H. Quast, J. Am. Chem. Soc. **1993**, 115, 1490-1495.

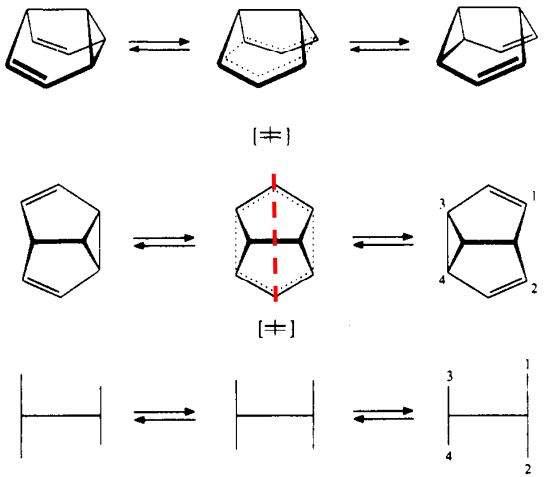
M. Dohle, J. Manz, G.K. Paramanov, H.Quast, Chem. Phys. **1995**, 197, 91-97.

M. Dohle, J. Manz, G.K. Paramonov, Ber. Bunsenges. Phys. Chem. **1995,** 99, 478-484.

- *Initialization:*

W. Li, X. Zhou, R. Lock, S. Patchkovskii, A. Stolow, H.C. Kapteyn, M.M. Murnane, Science 322 (2008) 1207.





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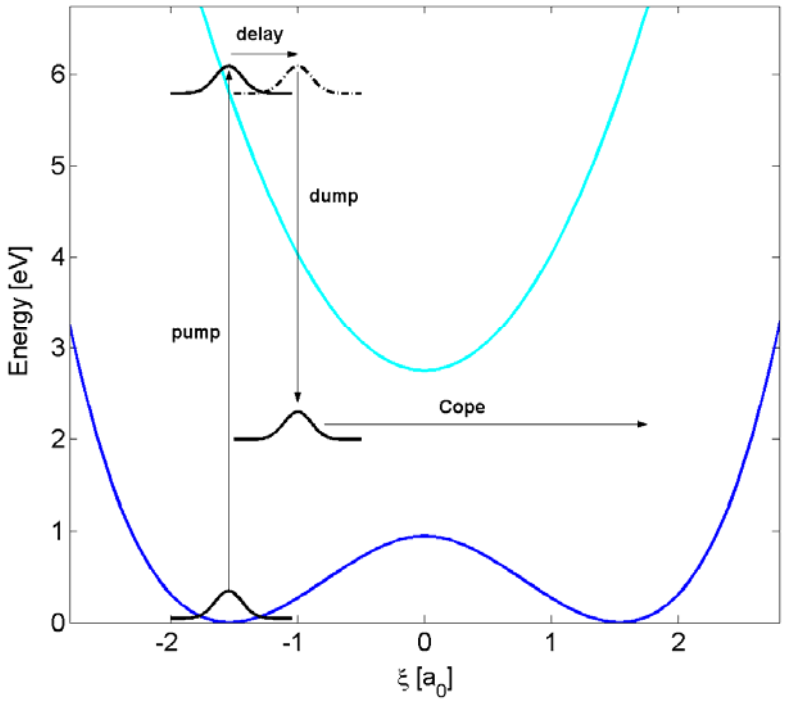

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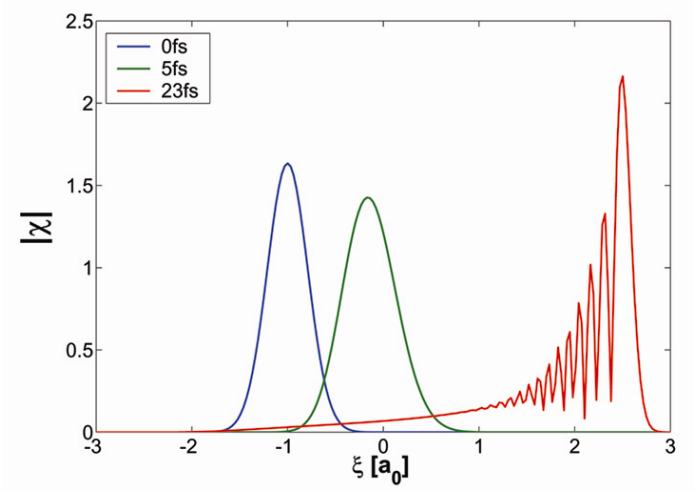

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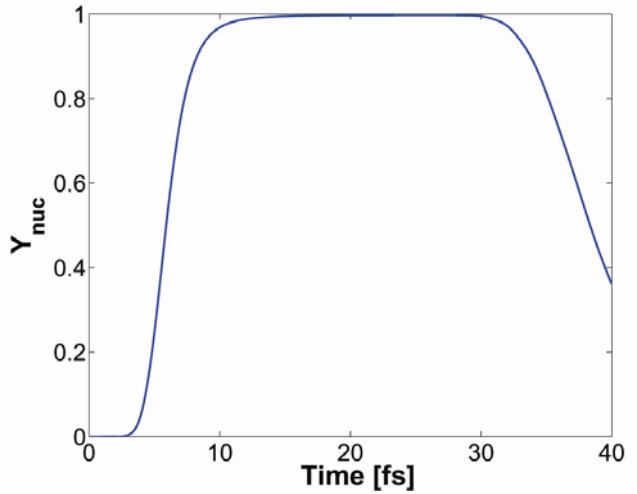
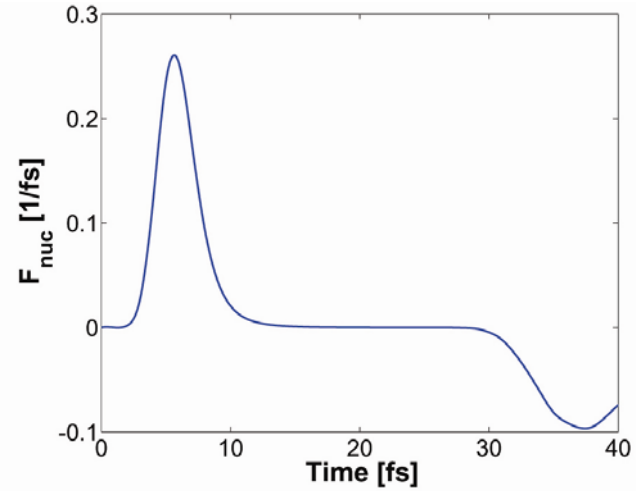
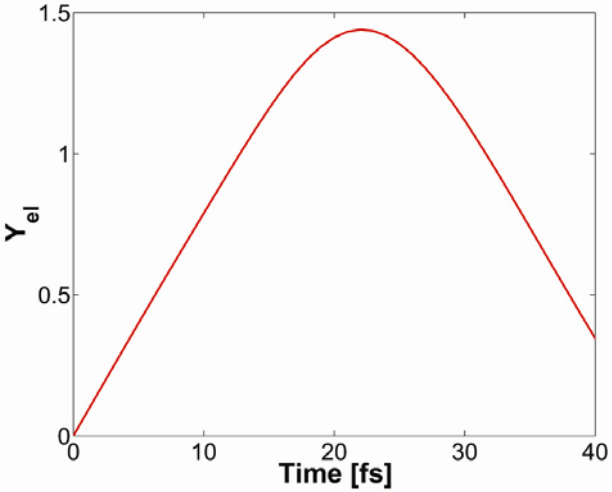
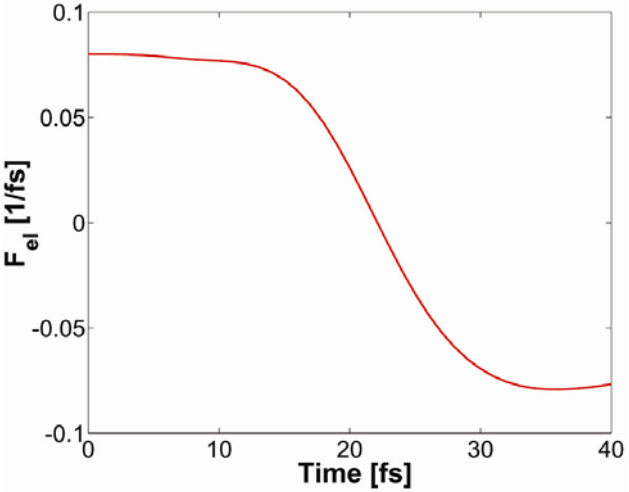
Concerted electronic and nuclear fluxes in molecules: Cope rearrangement in SBV









Conclusions and outlook

Flux: ➔ analysis of reaction mechanism

➔ concerted effects of coupled nuclei and electrons

Challenges for future

Calculation of the time-dependent electronic flux density in large molecules

Experiments for coupled quantum effects of electron and nuclear dynamics

Thanks to…

- The group at FU Berlin
- international partners


DFG (project Ma 515/23-1 and Sfb 450)


GK 788 (project A1)


CSS


FCI

Group at FU Berlin