Quantum Control by Laser Pulses: From nuclear to electron dynamics, and back

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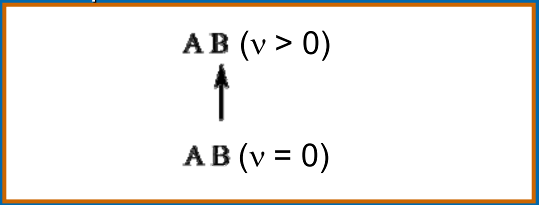
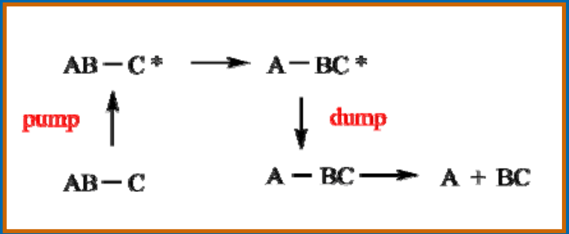
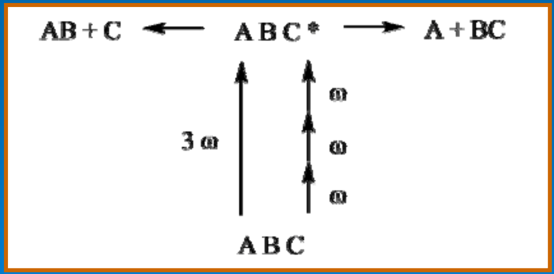
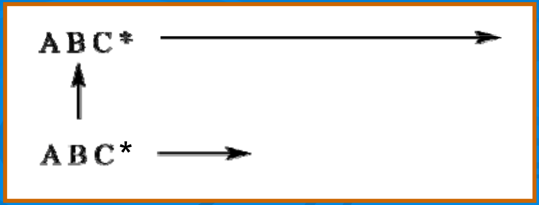
Interpreters English ←→ German Sign Language
Ralf Wiebel + Silke Brendel-Evan

Quantum Control of Light and Matter, KITP, UCSB, April 22, 2009

Quantum laser control of nuclear dynamics: history

<table>
<tr><th>year</th><th>pioneer /Ref.</th><th>mechanism</th><th>parameters</th></tr>
<tr><td>1983</td><td>G. K. Paramonov, V. A. Savva, Phys. Lett. 97A, 340 (1983)</td><td>π pulse: vibrational excitation

</td><td>few, frequency, Intensity, duration</td></tr>
<tr><td>1985</td><td>D.J. Tannor, S.A. Rice JCP 83, 5013 (1985)</td><td>„pump - dump“ (or several UV pulses)

</td><td>few, frequencies, delay time</td></tr>
<tr><td>1985</td><td>D.J. Tannor, S.A. Rice JCP 83, 5013 (1985)</td><td>optimal control, weak fields</td><td>few, frequencies, delay time</td></tr>
<tr><td>1986</td><td>P. Brumer, M. Shapiro CPL 126, 541 (1986)</td><td>coherent control

</td><td>few, phase</td></tr>
<tr><td>1986</td><td>T. Joseph, J. Manz Mol. Phys. 58, 1149 (1986)</td><td>IR π pulse

</td><td>few</td></tr>
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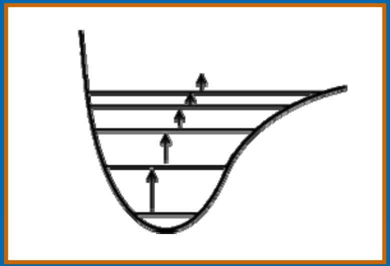
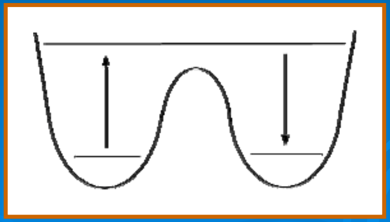
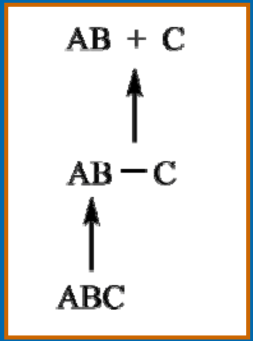
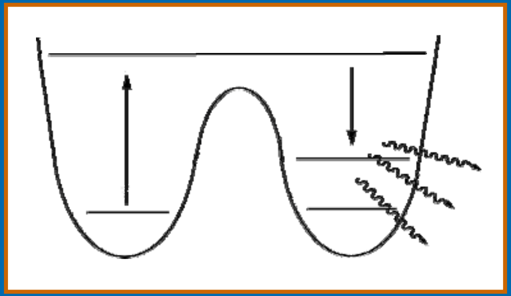
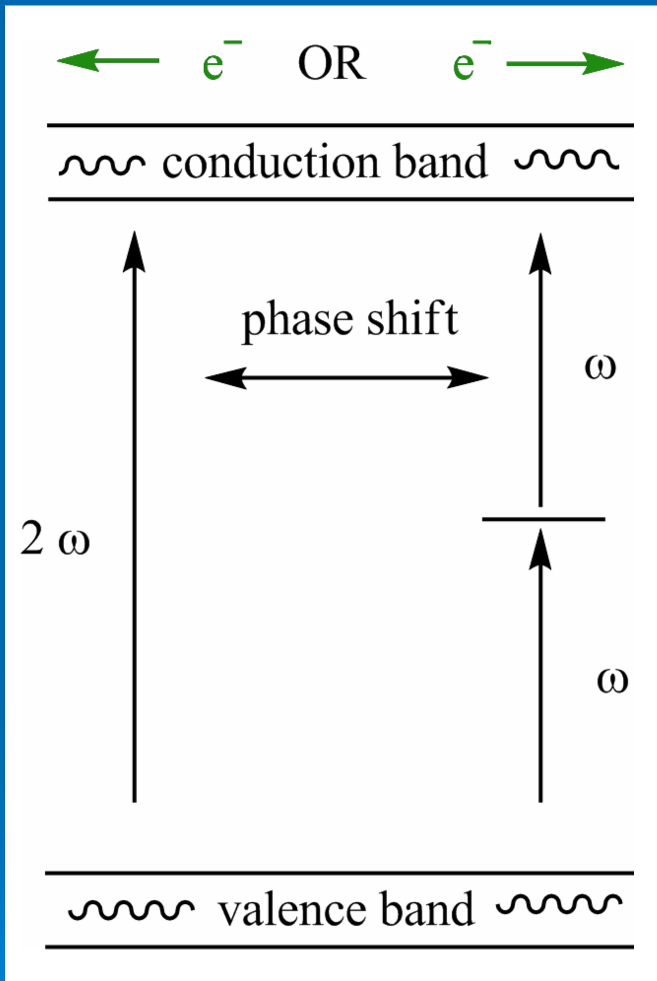
Quantum laser control of nuclear dynamics: history

year	pioneer / Ref.	mechanism	parameters
1988	S. Shi, A. Woody, H. Rabitz JCP 88, 6870 (1988)	optimal control, strong fields	"∞"
1988	U. Gaubatz, P. Rudecki, M. Becker, S. Schiemann, M. Külz, K. Bergmann CPL 149, 463 (1988)	STIRAP	few
1989	R. Kosloff, S.A. Rice, P. Gaspard, S. Tersigni, D.J. Tannor CP 139, 201 (1989)	local optimal control	"∞"
1990	S. Chelkowski, A.D. Bandrauk, P.B. Corkum PRL 65, 2355 (1990)	chirping 	few
1991	J.E. Combariza, B. Just, J. Manz, G.K. Paramonov JPC 95, 10351 (1991)	2 IR π pulse 	few
1992	J.S. Judson, H. Rabitz PRL 68, 1500 (1992)	optimal control, feedback learning evolutionary algorithms	"∞"

Quantum laser control of nuclear dynamics: history

year	pioneer / Ref.	mechanism	parameters
1992	N. Henriksen, B. Armstrup JCP 97, 8285 (1992)	IR + UV  	few
1996	M.V. Korolkov, J. Manz, G.K. Paramonov JCP 165, 10874 (1996)	IR control in open system 	few
2004	A.D Bandrauk, E.-W.S. Sedik, Ch.F. Matta JCP 121, 7764 (2004)	CEP control $X\cdot + CH_4 \longrightarrow HX + CH_3\cdot$	few

Quantum laser control of electron dynamics: coherent control



RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 39, NUMBER 5 15 FEBRUARY 1989-I

Phase-coherent control of photocurrent directionality in semiconductors

Gershon Kurizki and Moshe Shapiro
Chemical Physics Department, Weizmann Institute of Science, Rehovot, Israel 76100

Paul Brumer
Chemical Physics Theory Group, Department of Chemistry, University of Toronto, Toronto, Canada M5S 1A1

(Received 27 June 1988)

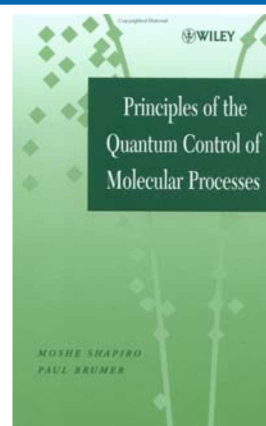
We demonstrate that one can generate and control photocurrents in semiconductors, without bias voltage, through multiple-frequency phase-coherent laser excitation of donors.

THE JOURNAL OF CHEMICAL PHYSICS **128**, 244905 (2008)

Femtosecond dynamics and laser control of charge transport in *trans*-polyacetylene

Ignacio Franco,[1] Moshe Shapiro,[2] and Paul Brumer[1,a)]
[1]*Chemical Physics Theory Group, Department of Chemistry and Center for Quantum Information and Quantum Control, University of Toronto, Toronto, Ontario M5S 3H6, Canada*
[2]*Chemical Physics Department, The Weizmann Institute, Rehovot 76100, Israel and Department of Chemistry and Department of Physics, The University of British Columbia, Vancouver, British Columbia V6T 1Z1, Canada*

(Received 15 January 2008; accepted 16 May 2008; published online 27 June 2008)



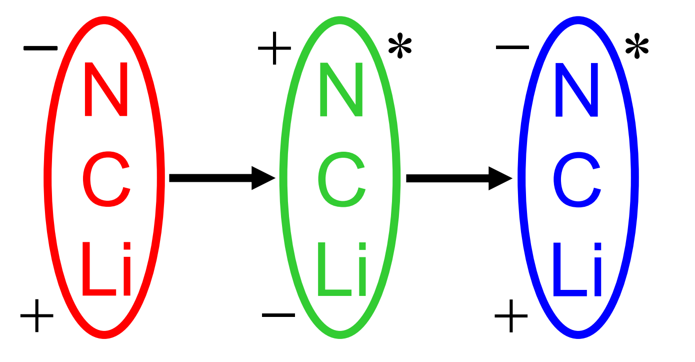
See: **Principles of the Quantum Control of Molecular Processes**

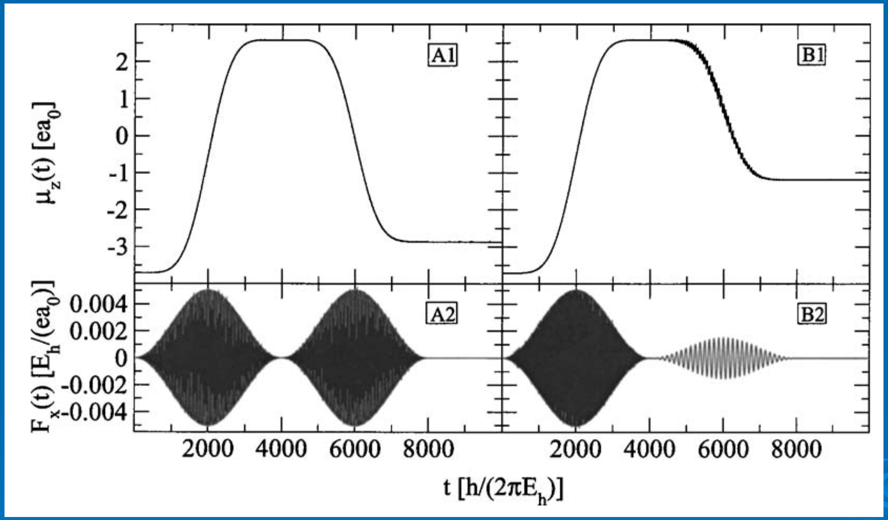
by Paul W. Brumer and Moshe Shapiro

"...a compilation of the authors' own contributions to the topic over the last two decades and represents the height of the first principles of understanding of quantum control for simple atomic and molecular systems."
(*Journal of the American Chemical Society*, Vol. 125, 2003)

Quantum laser control of electron dynamics:
dipole switching in molecules

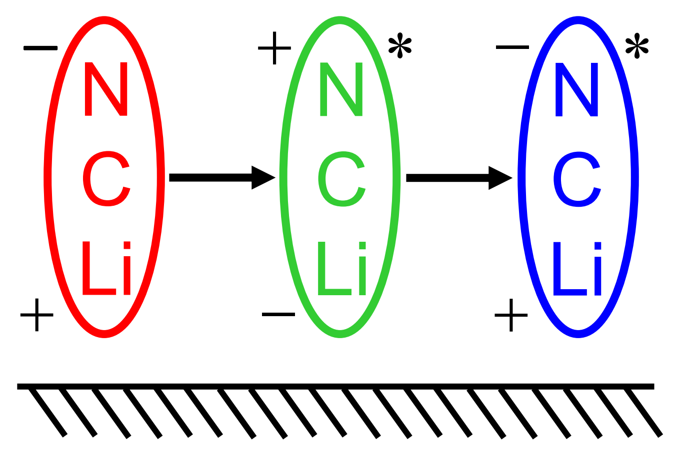
- using series of π pulses (TD-CIS(D))
  P. Krause, T. Klamroth, P. Saalfrank, JCP 123, 074105 (2005)



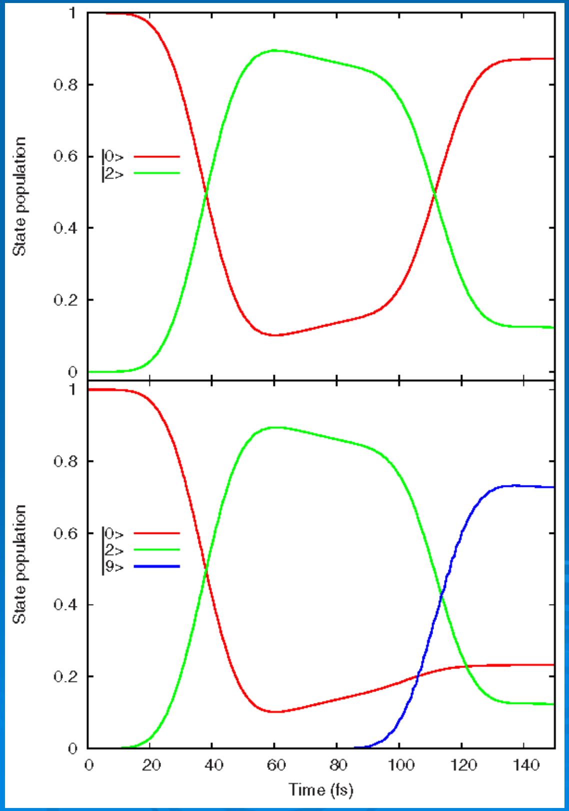


Quantum laser control of electron dynamics:
dipole switching in "open system"

- using series of π pulses (TD-CIS(D))
  J.C. Tremblay, T. Klamroth, P. Saalfrank, JCP 129, 084302 (2008)



surface enhanced relaxation approach (SERA)



A possible analogy to the Tannor-Rice approach:

Quantum control of electron transfer (?)

- attosecond charge migration in small peptides
  F. Remacle, R.D. Levine, PNAS 103, 6793 (2006)

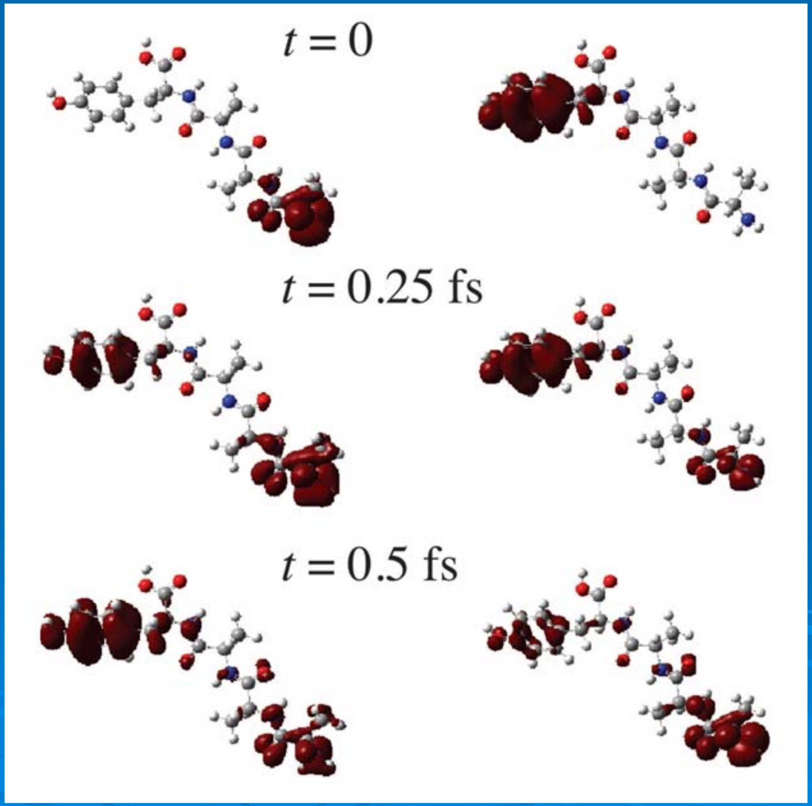
Tyr-Ala-Ala-Ala

↓

Tyr-Ala-Ala-Ala$^+$ + e$^-$

↓

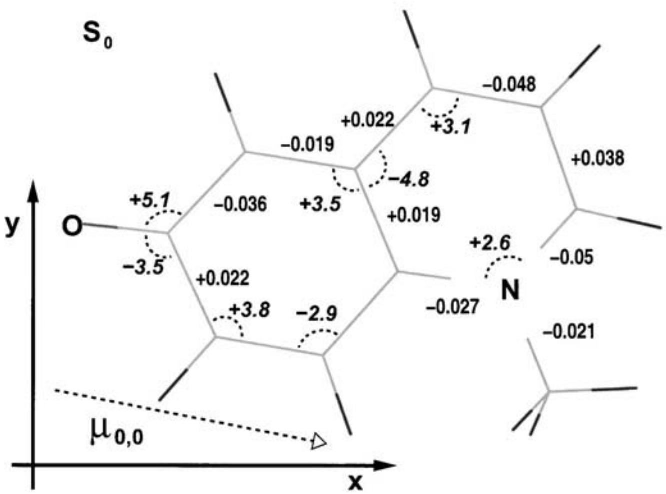
Tyr$^+$-Ala-Ala-Ala + e$^-$

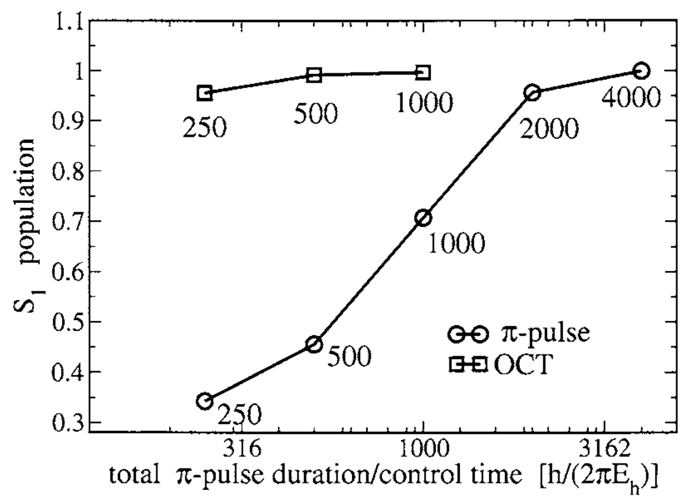


HOMO HOMO - 1

Quantum laser control of electron dynamics: optimal control

- using TD-CIS,
  application: S0 → S1 transition of N-methyl-6-quinolone
  T. Klamroth, JCP 124, 144310 (2006)





$$J = \langle \Psi(t_f)|\hat{O}|\Psi(t_f)\rangle - \int_0^{t_f} \alpha(t)|\mathbf{F}(t)|^2 dt$$

$$- 2\,\mathrm{Re}\left[\int_0^{t_f} \langle \chi(t)|\frac{\partial}{\partial t} + i(\hat{H}_0 - \hat{\boldsymbol{\mu}}\mathbf{F}(t))|\Psi(t)\rangle dt\right]$$

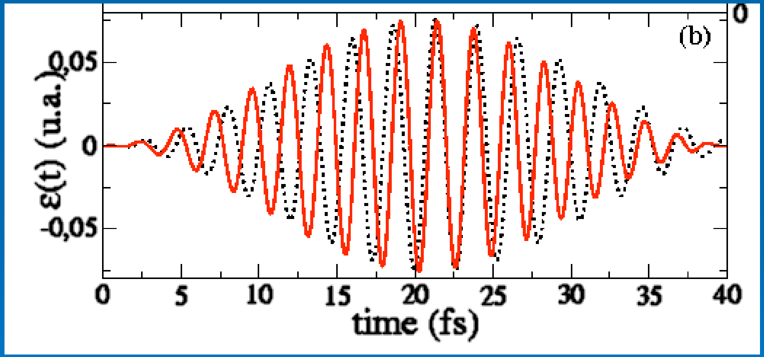
$$i\dot{\Psi}(t) = (\hat{H}_0 - \hat{\boldsymbol{\mu}}\mathbf{F}(t))\Psi(t) \quad \text{with } \Psi(t_0) = \Psi_0,$$

$$i\dot{\chi}(t) = (\hat{H}_0 - \hat{\boldsymbol{\mu}}\mathbf{F}(t))\chi(t) \quad \text{with } \chi(t_f) = \hat{O}\Psi(t_f),$$

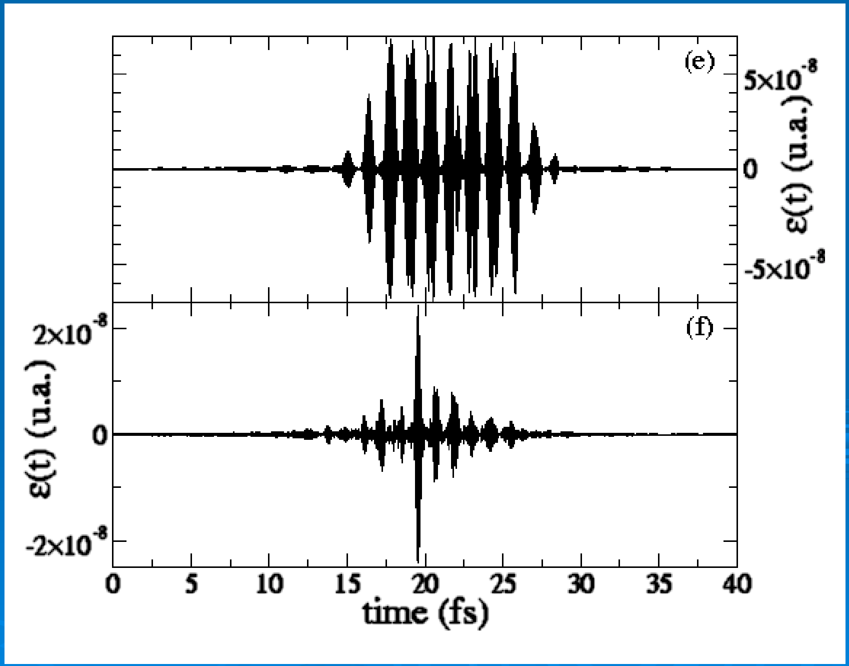
$$\mathbf{F}(t) = -\frac{1}{\alpha(t)}\,\mathrm{Im}[\langle \chi(t)|\hat{\boldsymbol{\mu}}|\Psi(t)\rangle].$$

Quantum laser control of electron dynamics:
chirping (restricted optimal control)

- target:
  generation of attosecond pulse by high harmonic generation (HHG)
  A. Ben Haj Yedder, C. Le Bris, O. Atabek, S. Chelkowski, A.D. Bandrauk,
  PRA 69, 041802(R) (2004)



excitation fs laser pulse



emitted as laser pulse

Quantum laser control of electron dynamics: carrier envelope phase (CEP) control

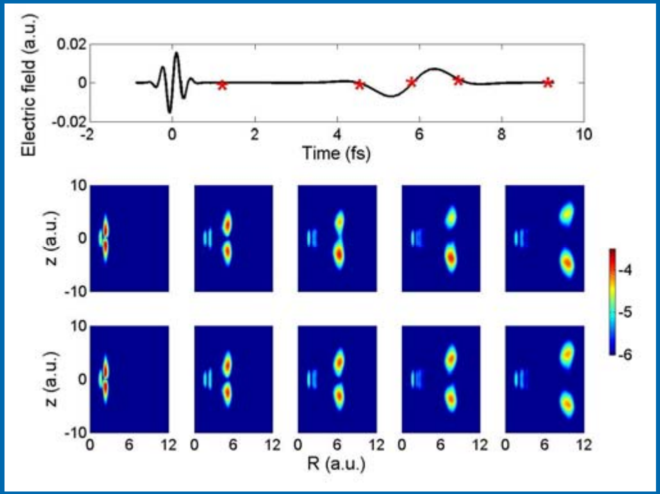
control of HHG		applications
A. Baltuška, …, F. Krausz, Nature 421, 611 (2003)	→	250 as pulse
E. Goulielmakis, …., F. Krausz, Science 320, 1614 (2008)	→	80 as pulse
Z. Zhai, R.-F. Yu, X.-S. Liu, Y.-J. Yang, PRA 78, 041402(R) (2008)	→	45 as pulse
E.V. van der Zwan, M. Lein, JPB 41, 074009 (2008)	→	molecular orbital tomography
A.D. Bandrauk, S. Barmaki, G. L. Kamta, PRL 98, 013001 (2007)	←	electron transfer in H_3^{2+} $H^+ + H_2^+(1\sigma_g, 1\sigma_u)$

Quantum laser control of electron dynamics:
fs IR + as UV pulses

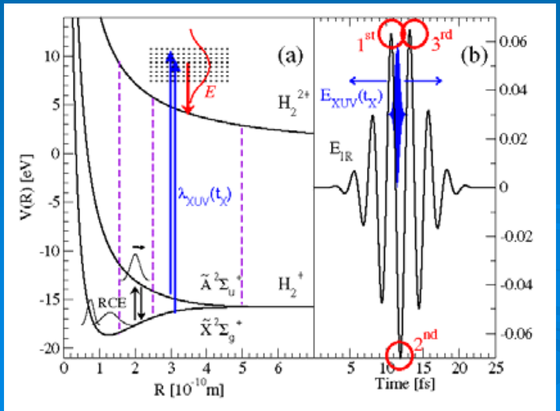
- electron localization in H_2^+ and HD^+
  F. He, C. Ruiz, A. Becker (2008), submitted

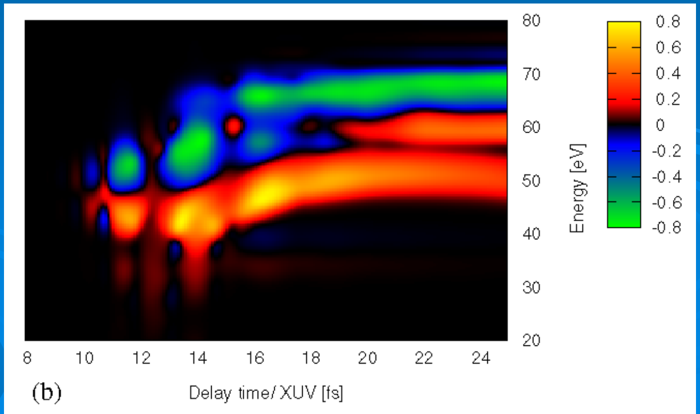
H_2^+ → p + H (with IR)

H_2^+ → H + p (without IR)



- attosecond photoelectron spectroscopy of electron tunneling in H_2^+
  S. Gräfe, V. Engel, M.Yu. Ivanov, PRL 101, 103001 (2008)



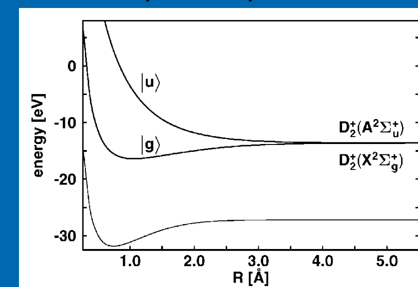


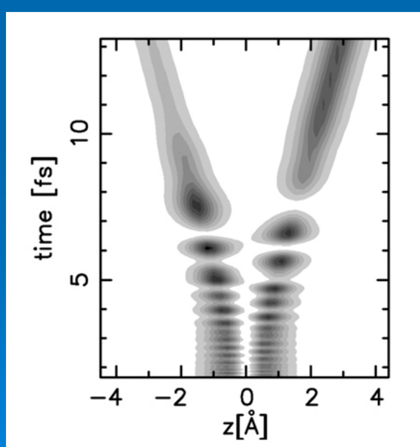
Quantum laser control of electron dynamics:
carrier envelope phase (CEP) control

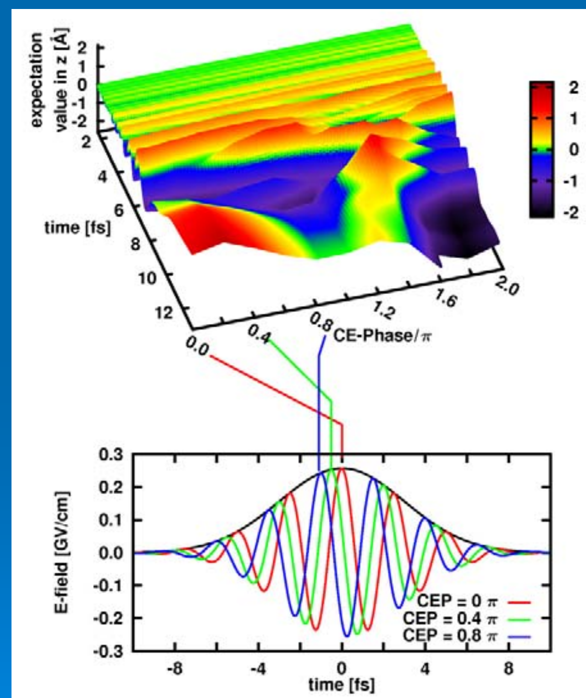
- photodissociation of D_2^+
  D. Geppert, P. von der Hoff, R. de Vivie-Riedle, JPB 41, 074006 (2008)

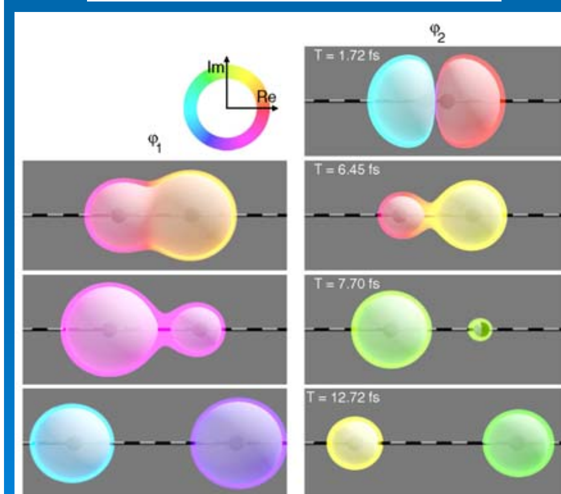
$D_2^+ \rightarrow d + D$

$D_2^+ \rightarrow D + d$





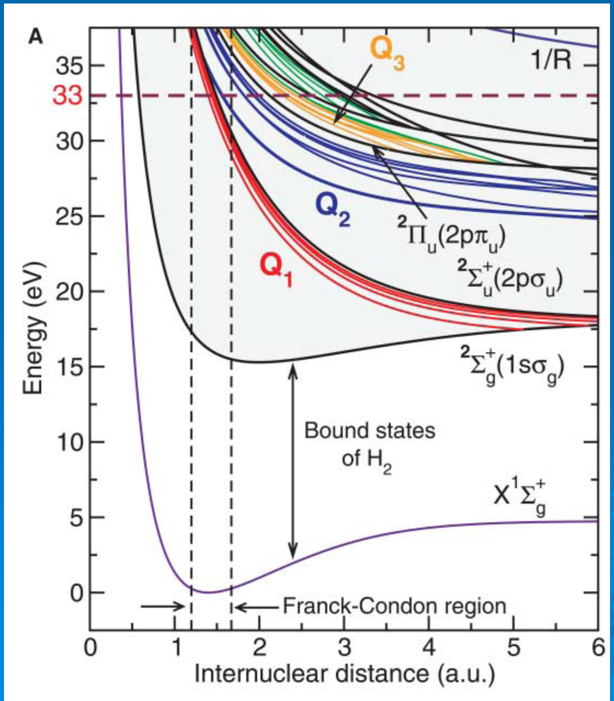


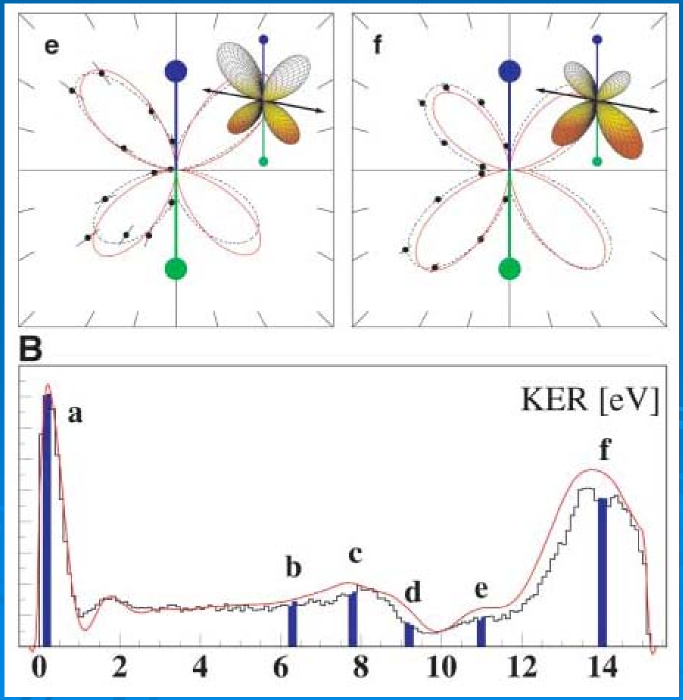


- see also: M.F. Kling, Ch. Siedschlag, A.J. Verhoef, J.I. Khan, M. Schultze, Th. Uphues, Y. Ni, M. Uiberacker, M. Drescher, F. Krausz, M.J.J. Vrakking, Science 312, 246 (2006)

Quantum laser control of electron dynamics:
symmetry breaking

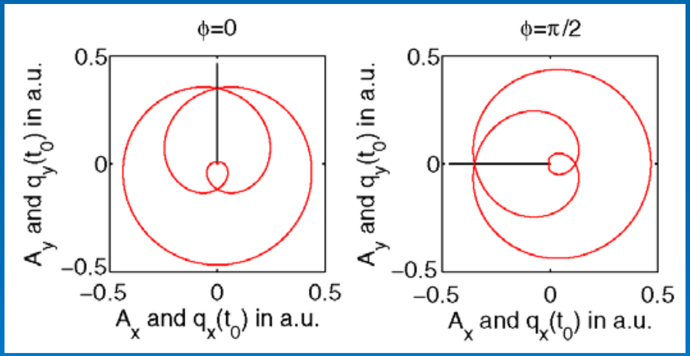
- symmetry breaking of D_2 dissociation by entanglement between symmetric and antisymmetric states caused by autoionization (1 nuclear and 6 (-1) electronic coordinates)
  F. Martín, J. Fernández, T. Havermeier, L. Foucar, Th. Weber, K. Kreidi, M. Schöffler, L. Schmidt, T. Jahnke, O. Jagutzki, A. Czasch, E.P. Benis, T. Osipov, A.L. Landers, A. Belkacem, M.H. Prior, H. Schmidt-Böcking, C.L. Cocke, R. Dörner, Science 315, 629 (2007)

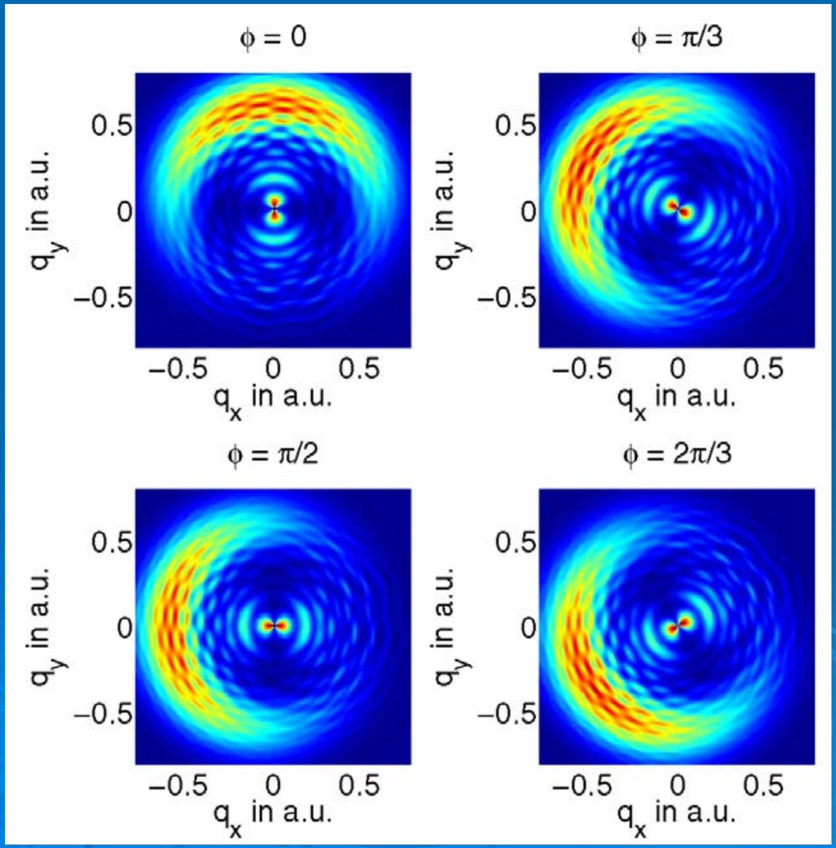




Quantum laser control of electron dynamics:
CEP control for circularly polarized laser pulses

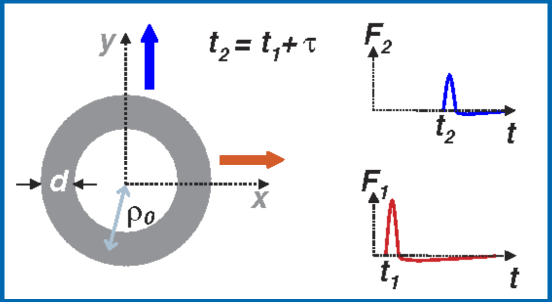
- Control of directionality of ionization of H atom
  C.P.J. Martiny, L.B. Madsen, PRL 97, 093001 (2006)



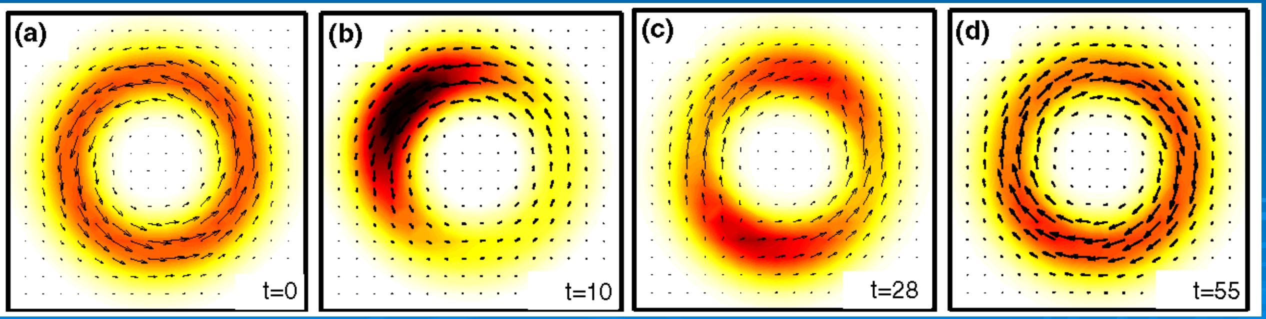


Quantum laser control of electron dynamics:
control of electron circulation/rotation/ring current

- in nanorings, using two perpendicular time-delayed pulses
  A. Matos-Abiague, J. Beradkar, PRL 94, 166801 (2005)



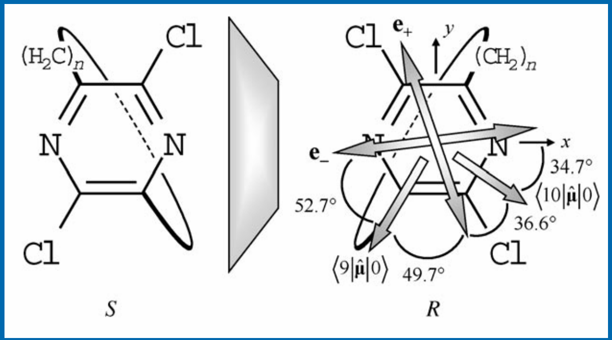
- using optimal control theory (OCT)
  E. Räsänen, A. Castro, J. Werschnik, A. Rubio, E.K.U. Gross, PRL 98, 157404 (2007)



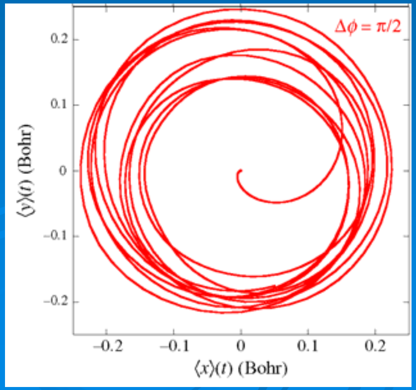
- in molecules, using circularly polarized re-optimized π pulses
  I. Barth, J. Manz, Angew. Chem. Int. Ed. 45, 2962 (2006) (etc., see below!)

Quantum laser control of electron dynamics:
control of electron circulation/rotation/ring current

- using 1 or 2 linearly polarized pulses applied to chiral aromatic molecule
  M. Kanno, H. Kono, Y. Fujimura, Angew. Chem. Int. Ed. 45, 7995 (2006)

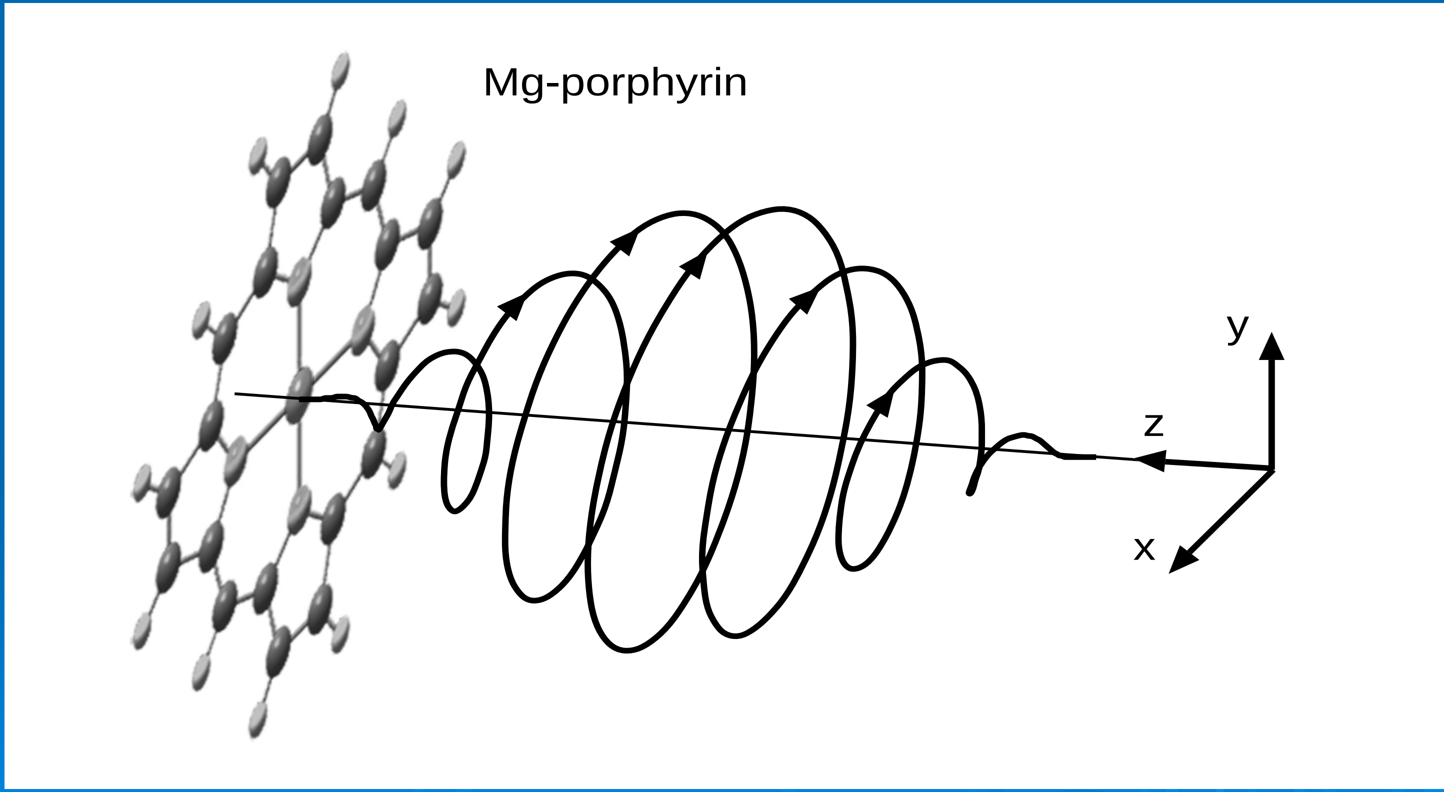


- using 2 short linearly polarized pulses (MC-TDHF), electronic wavepacket ($\Sigma^+ + \Pi + \Delta$) in LiH
  M. Nest, F. Remacle, R.D. Levine, New J. Phys. 10, 025019 (2008)



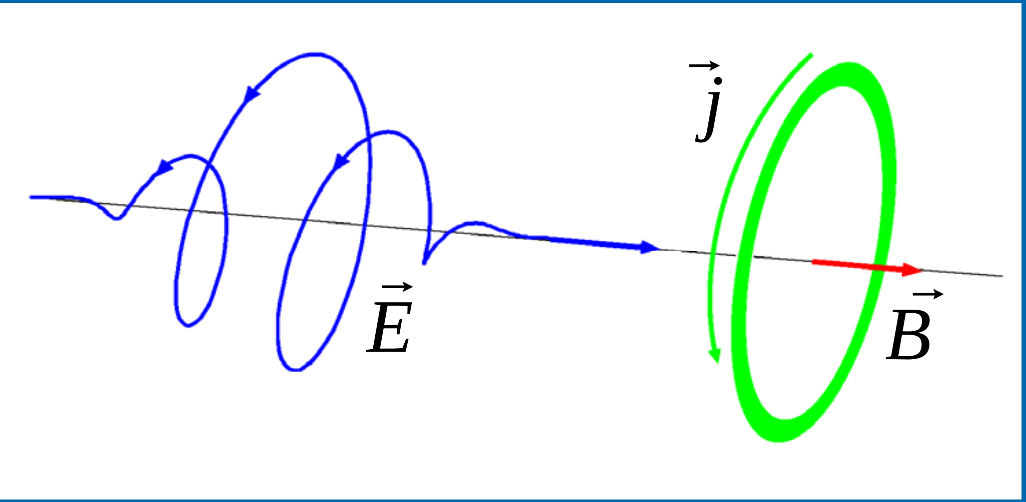
Control of Electric Ring Currents

π and π/2 pulses:
from femtoseconds to attoseconds
from nuclear dynamics to electron dynamics



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

Concept



circularly polarized laser pulse

induced magnetic field

ring current (nuclear or electronic)

related: inverse Faraday effect

Model assumptions for charge circulation and ring currents

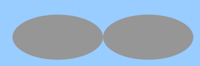
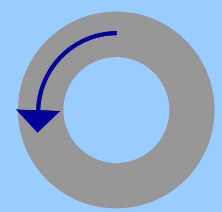
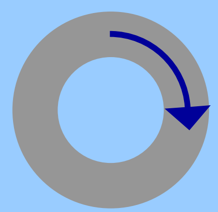
- Fixed orientation of molecule

  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

Analogy for opposite ring currents in doubly degenerate states

$1/\sqrt{2}\big($  $\pm i$  $\big) =$  , 

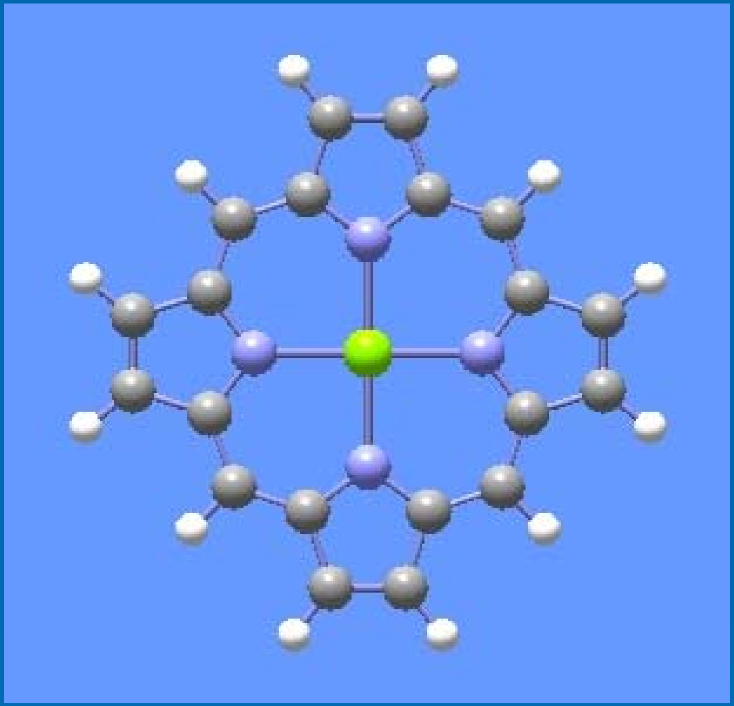
$$1/\sqrt{2}\left(p_x \pm i\, p_y \right) = p_+ \,,\; p_-$$

$$1/\sqrt{2}\left(\pi_x \pm i\, \pi_y \right) = \pi_+ \,,\; \pi_-$$

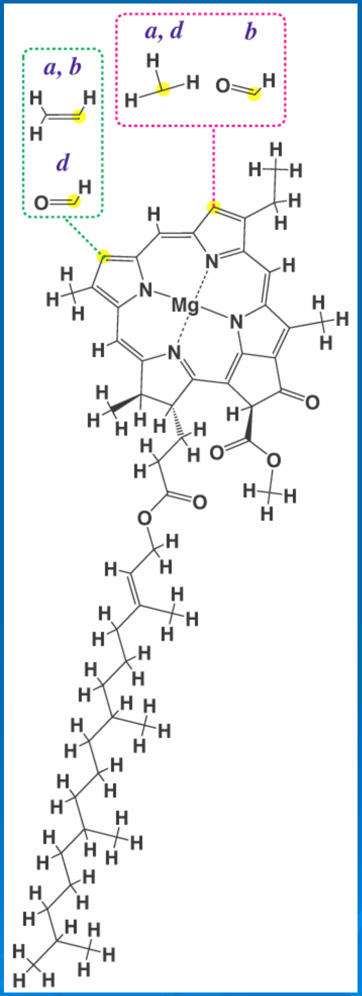
$$1/\sqrt{2}\left(E_x \pm i\, E_y \right) = E_+ \,,\; E_-$$

$$1/\sqrt{2}\left(\Phi_{v_b,x} \pm i\, \Phi_{v_b,y} \right) = \Phi_{v_b,+} \,,\; \Phi_{v_b,-}$$

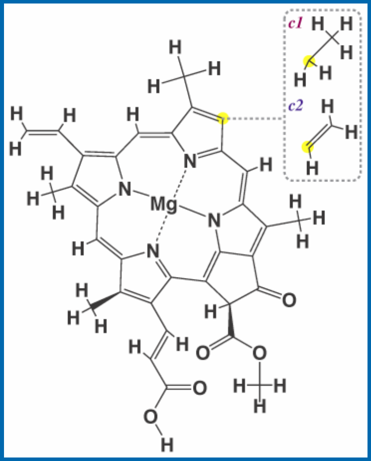
Magnesium porphyrin (MgP)



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



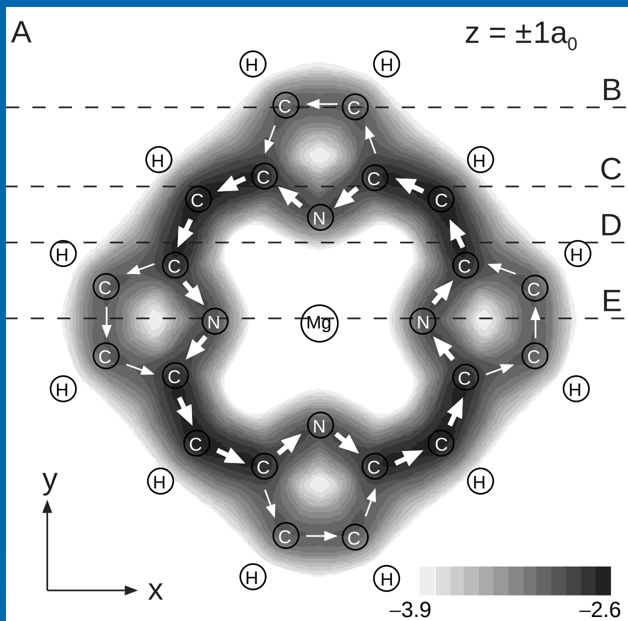
Chlorophyll a, b, d



Chlorophyll c1, c2

Electric ring current

laser pulse



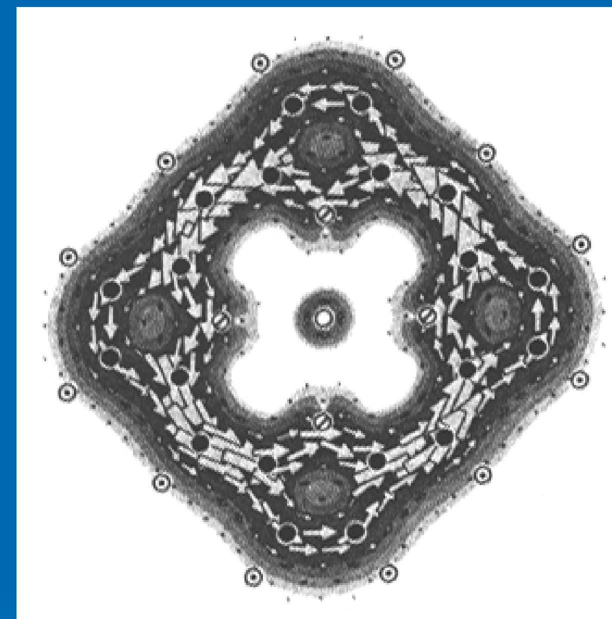
$$\langle r \rangle = 6.32\ a_0$$

$$I = 84.5\ \mu\text{A}$$

$$B_{ind} = 0.159\ \text{T}$$

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)
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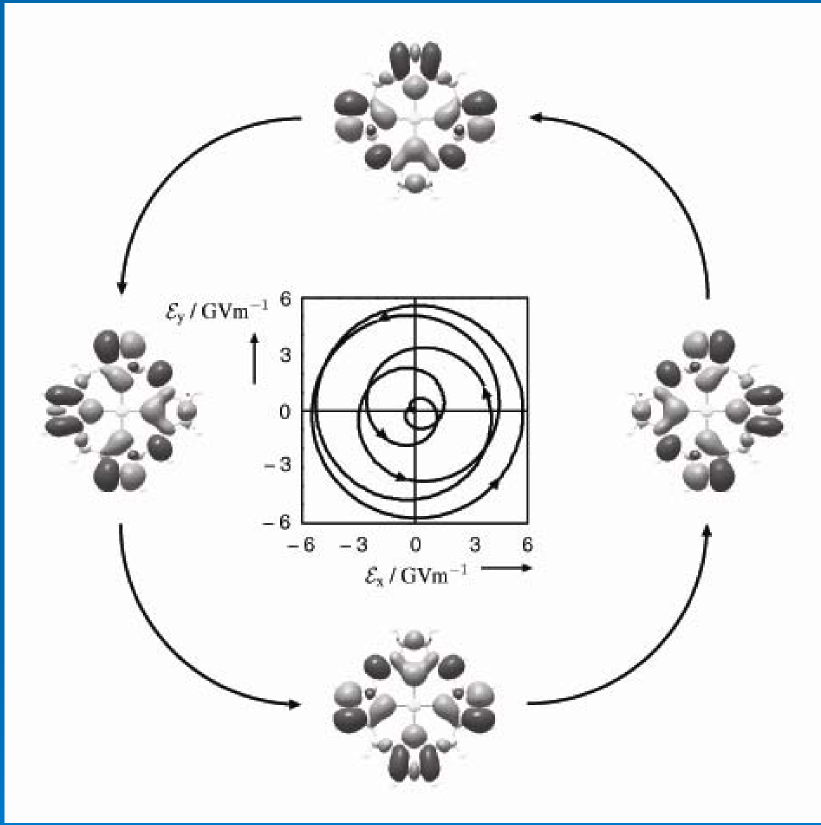
Periodic electron circulation $X \rightarrow 5^1E_{u+}$ with re-opt. $\pi/2$-pulse



Laser period: 0.94 fs

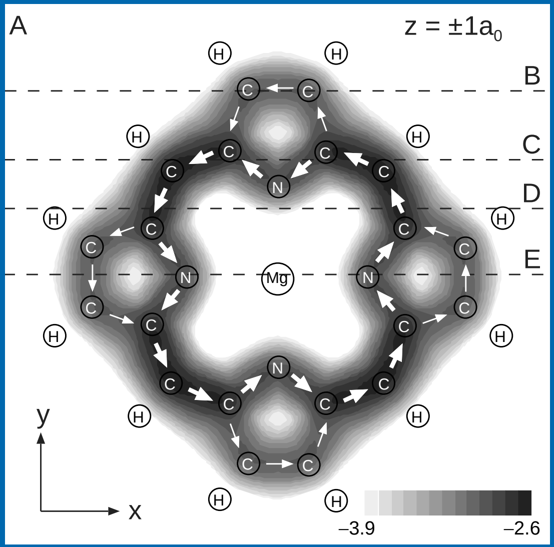
Electron period: 0.91 fs

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

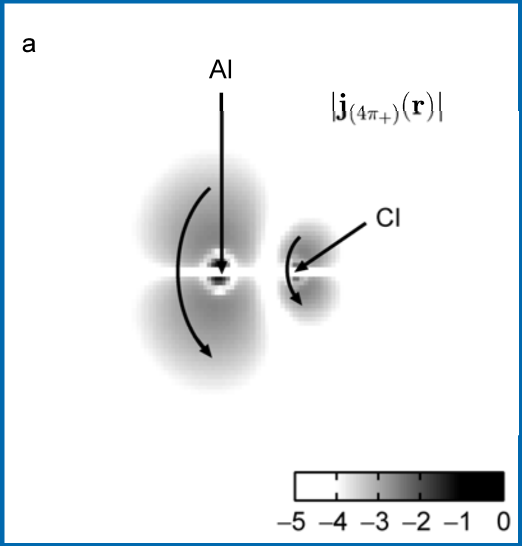
$$\left|X\right\rangle \xrightarrow{\tau=2.00\text{ fs}} \frac{1}{\sqrt{2}}\left(\left|X\right\rangle e^{-iE_X t/\hbar} \pm i\left|5^1E_{u+}\right\rangle e^{-iE_{5^1E_{u+}} t/\hbar}\right)$$

Comparison: Electric ring currents

MgP



AlCl



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

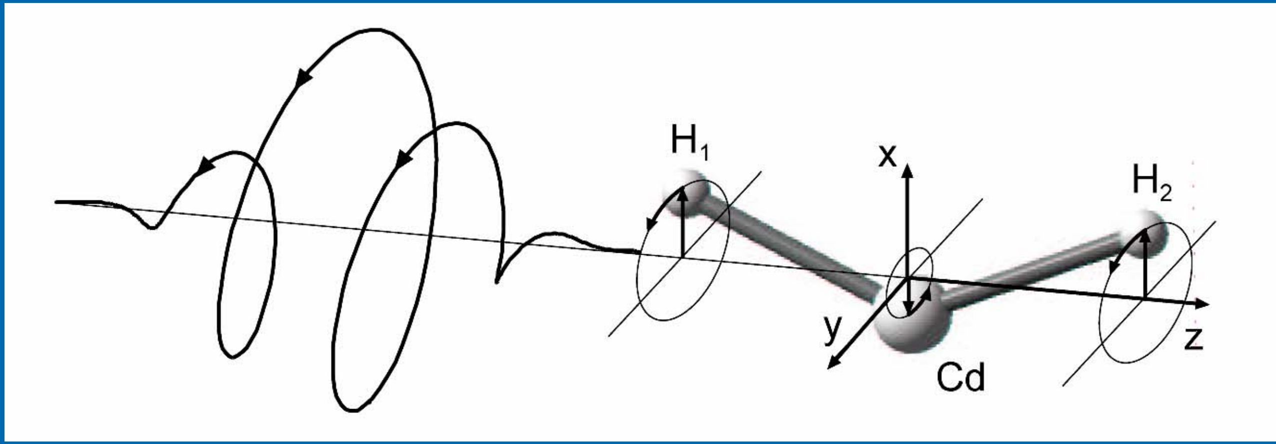
$$\langle r^{-1} \rangle^{-1} = 0.18\, a_0$$
$$I = 405\, \mu\text{A}$$
$$T = 396\,\text{as}$$
$$B_{ind}(\text{Al}) = 7.68\,\text{T}$$
$$\langle L_{z,el} \rangle = 1\hbar$$

Biot-Savart law for ring loop model:

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

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

Nuclear pseudorotation of linear triatomic molecule



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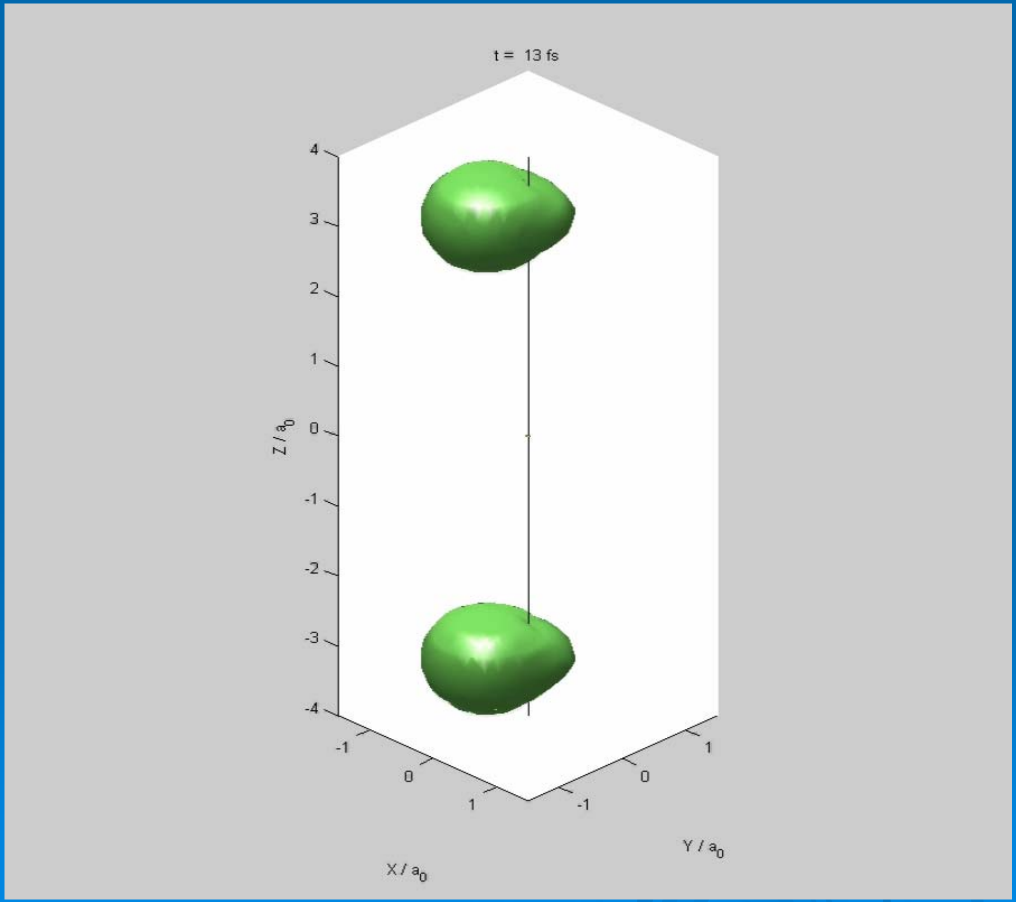
I. Barth, J. Manz, G. Pérez-Hernández, P. Sebald, Z. Phys. Chem. 222, 1311 (2008)

- Driven by circularly polarized infrared (IR) laser pulse propagated along the molecular axis
- Unidirectional pseudorotation of linear triatomic molecule, e.g. FHF^- and $^{114}CdH_2$
- Method analogous to electron circulation

From electron circulation to nuclear spinning: CdH_2 and FHF^-



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Chem. Phys. 346 (2008) 89

I. Barth, J. Manz,
G. Pérez-Hernández, P. Sebald,
Z. Phys. Chem. 222, 1311 (2008)
(toroidal hydrogen bond)

Film: A. Schild

Summary

circularly polarized laser pulse ⇒ ring current ⇒ induced magnetic field

STRONG effects by ACTIVE control

	system	Q/e	I	T	R/a_0	B/T
electronic ring current	MgP	1	84.5 μA	1.90 fs	6.32	0.16
	AlCl	1	405 μA	396 as	0.18	7.68
	BeO	1	2.49 mA	64.4 as	0.25	52.1
	H	1	132 μA	1.21 fs	1.27	0.52
	Al^{12+}	1	22.3 mA	7.18 as	0.098	1146
	U^{91+}	1	12.0 A	13.4 zs	≈ 0.004	36.4 MT
nuclear ring current	FHF^-	9	125 μA	24.4 fs	0.0044	10.9
	CdH_2	48	151 μA	53.0 fs	0.0030	318
	H	1	132 μA	1.21 fs	≈ 0.0007	≈ 1000
	He^+	2	1.05 mA	304 as	≈ 0.00009	≈ 60000

Conclusion

quantum control by laser pulses

↓

nuclear dynamics

↓

electron dynamics

↓

and back

- DFG (project Ma 515/23-1)
- GK 788 (project A1)
- Sfb 450 (project TP C1)
- Agentur für Arbeit Berlin-Nord

Partner + Coauthors

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…and international partners!

€ : DFG, FCI, Humboldt