MULTI-DIMENSIONAL ELECTRON DYNAMICS AND THEIR CONTROL

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Theoretische Chemie
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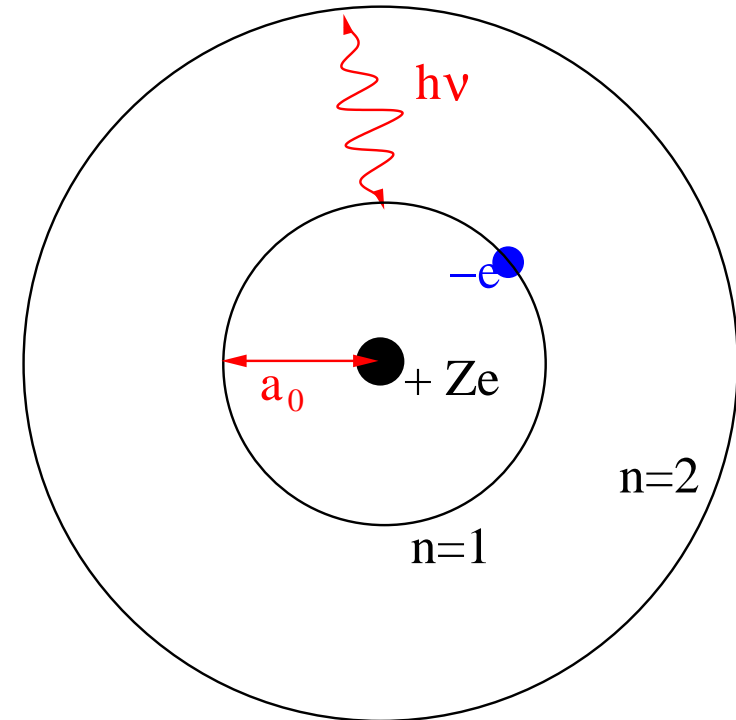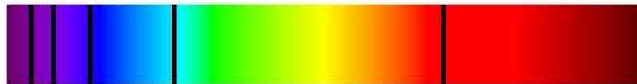
1. INTRODUCTION

1.1 Attosecond dynamics

- **Bohr's model of the H atom (1913)**

Niels Bohr, 1885-1962

$$E_{kin}^{n=1} = \left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{m_e}{2\hbar^2} = \tfrac{1}{2}m_e v^2 = \tfrac{1}{2}m_e \left(\frac{2a_0\pi}{\tau_1}\right)^2$$

"roundtrip time" $\boxed{\tau_1 = 152 \text{ as}}$

- **1 attosecond (as) $= 10^{-15}$ s**

- **Electron dynamics is attosecond dynamics**

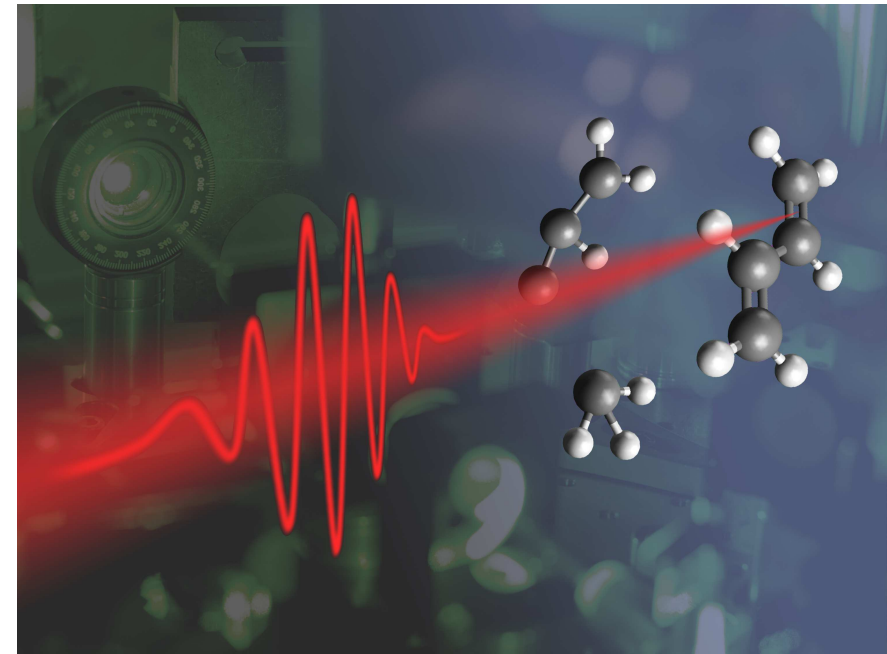# 1.1 Attosecond dynamics (2)

- **Attosecond laser pulses: E(t)**

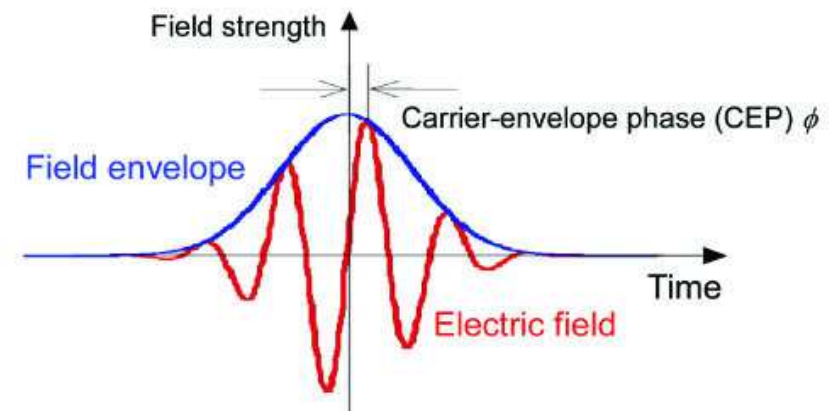Ferenc Krausz[1], Munich

shortest pulse (2012)[2]: 67 as

- **"Control" parameters**

$$\underline{E}(t) = \underline{E}_0 \; s(t) \; \cos(\omega(t)t + \phi)$$

- electric field amplitude $|\underline{E}_0|$ ($\rightarrow$ intensity)
- polarization $\underline{\varepsilon}$: $\underline{E}_0 = E_0 \, \underline{\varepsilon}$
- pulse length (FWHM), envelope function $s(t)$
- carrier frequency ω
- carrier envelope phase ϕ

[1] Krausz, Ivanov, Rev. Mod. Phys. **81**, 163 (2009)   [2] Zhao *et al.*, Opt. Lett. **37**, 3891 (2012)   -6-

1.1 Attosecond dynamics (3)

- **General (strong-) field-matter interaction phenomena[1]**

  - Polarization and linear response
  - Non-linear response and High Harmonic Generation
  - State-to-state transitions and electronic wavepacket creation
  - Above Threshold Ionization (ATI)
  - Tunneling ionization
  - Charge tansfer
  - Electron localization
  - Bond softening and hardening
  - Above Threshold Dissociation (ATD)
  - Coulomb explosion
  - Field-induced phase transitions
  - Charge migration

  - ... and many phenomena after core and inner-valence excitations:
    Autoionization, Intermolecular Coulomb Decay (ICD), ETI, Auger decay, ETMD, ...

Here: $I = \varepsilon_0 c E_0^2 \sim 10^{10} - 10^{15}$ W/cm^2 $\Longrightarrow$ non-perturbative, non-relativistic regime

[1] Krausz, Ivanov, Rev. Mod. Phys. **81**, 163 (2009)

1.2 Ultrafast electron dynamics in molecules
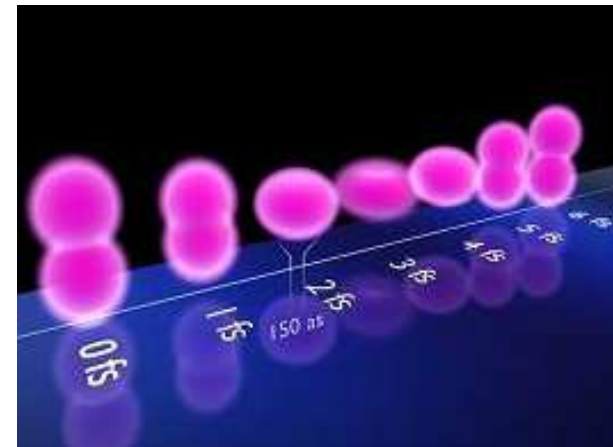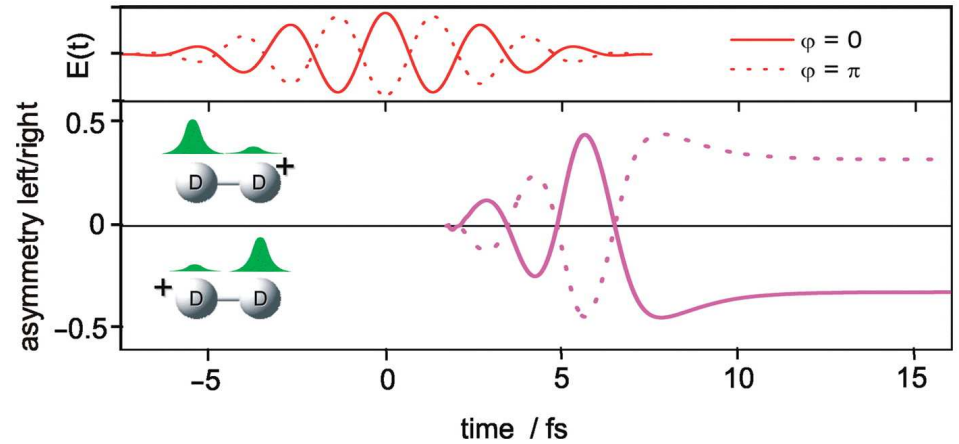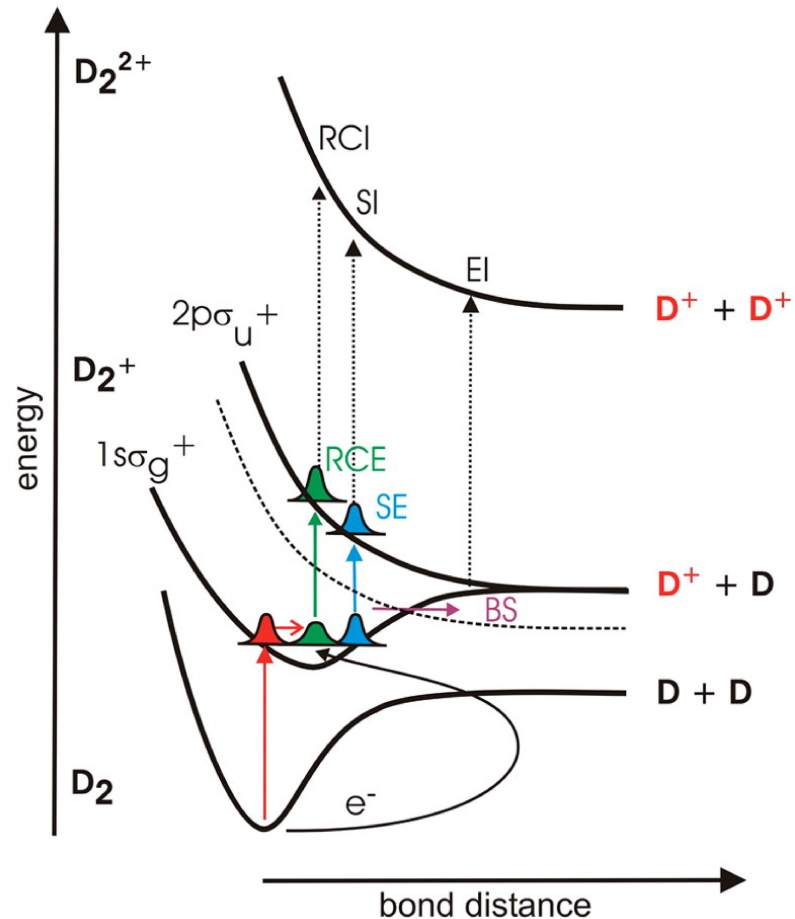
- **Electron wavepackets and their control: D_2^+**
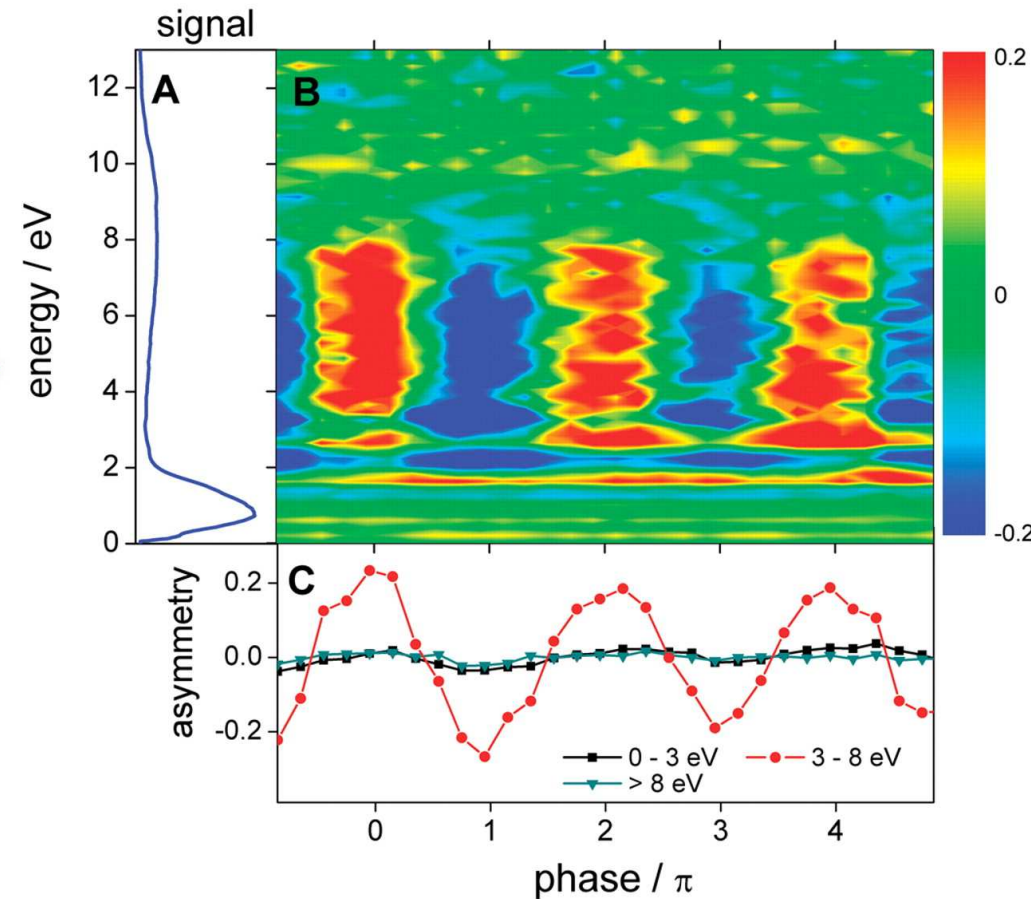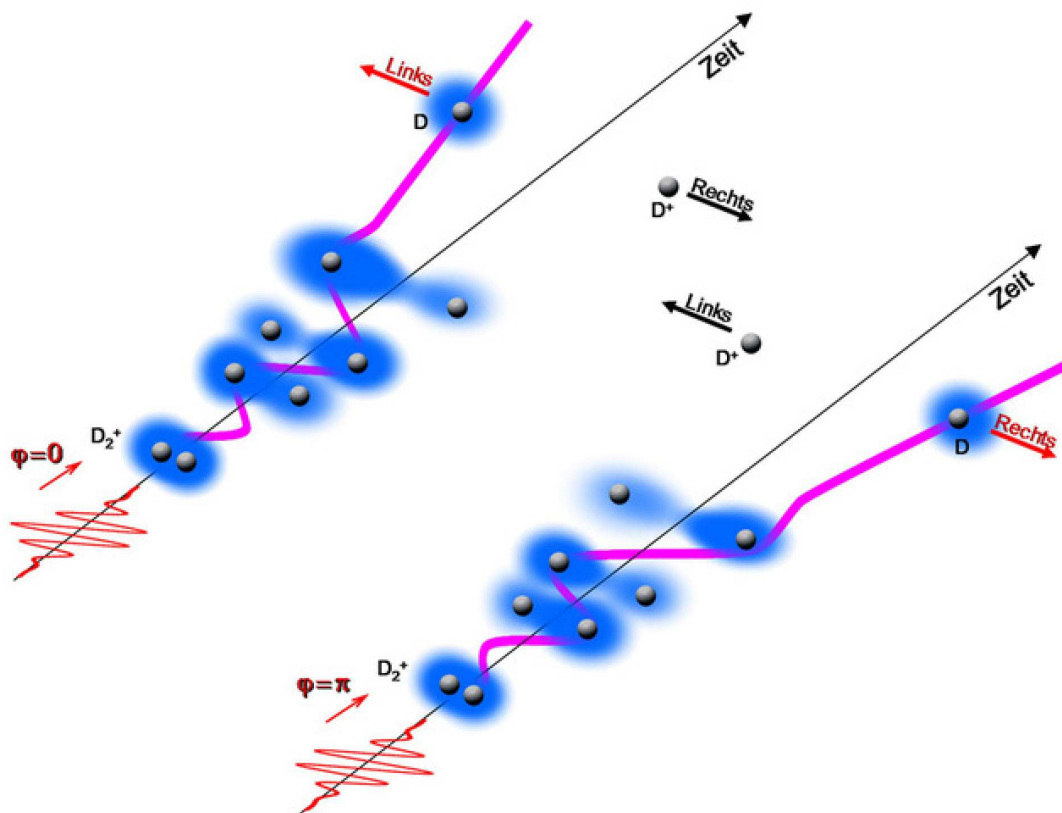
$$\boxed{\text{CEP controls electron localization}}$$

$$A(E_{kin}, \phi) = \frac{P_L - R_R}{P_L + P_R}$$

[1] Kling *et al.*, Science **312**, 246 (2006)

1.2 Ultrafast electron dynamics in molecules (2)

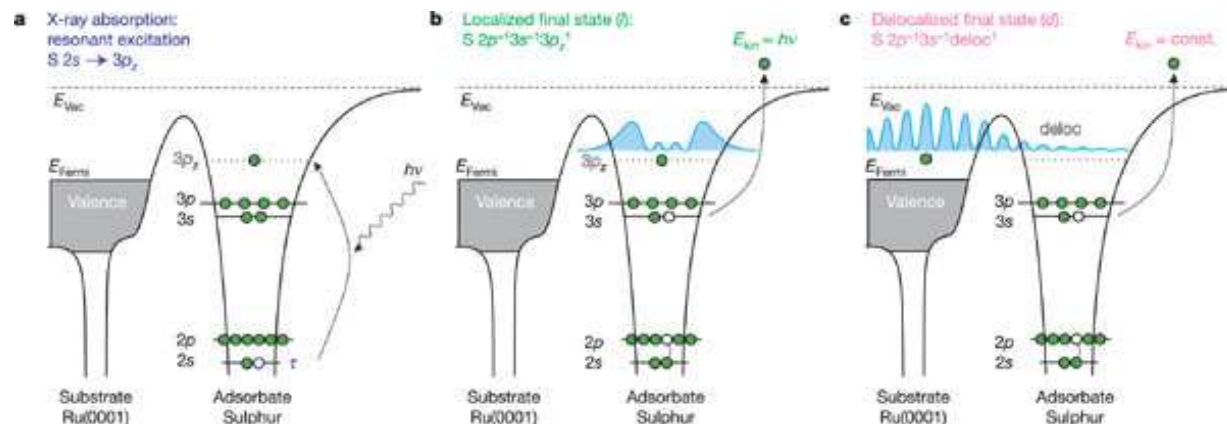- **Theoretical interpretation**

$$\text{creation of a wavepacket: } \Psi(t) = A\, e^{-iE_{1s\sigma_g^+}t/\hbar}\, \psi_{1s\sigma_g^+} + B\, e^{-iE_{2p\sigma_u^+}t/\hbar}\, \psi_{2p\sigma_u^+}$$

$$\langle\Psi|\hat{O}|\Psi\rangle = A^2\,\langle\psi_1|\hat{O}|\psi_1\rangle + B^2\,\langle\psi_2|\hat{O}|\psi_2\rangle + 2\mathrm{Re}\left[e^{i\omega_{12}t}\,AB\,\langle\psi_1|\hat{O}|\psi_2\rangle\right]$$
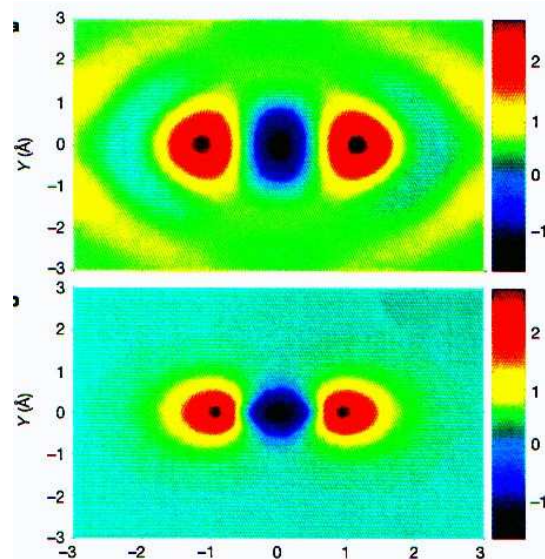
1.2 Ultrafast electron dynamics in molecules (3)

- **Tunnelling**[1]

a. X-ray absorption: resonant excitation S 2s → 3p$_z$

b. Localized final state (l): S 2p^{-1}3s^{-1}3p$_z^{1}$ $E_{kin} = h\nu$

c. Delocalized final state (d): S 2p^{-1}3s^{-1}deloc^{1} E_{kin} = const.

[1] Wurth *et al.*, Nature **436**, 373 (2005)

- **HHG, orbital tomography**[2]

HOMO of N$_2$

[2] Corkum *et al.*, Nature **432**, 867 (2004)

- **Charge migration**[3]

after hole creation in PENNA

t = 0

t = 2 fs

t = 4 fs
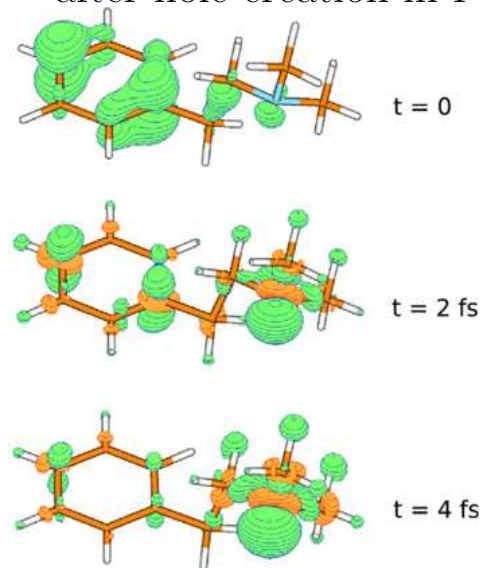
[3] F. Calegari *et al.*, J. Phys. B **49**, 142001 (2016)

2. THE TIME-DEPENDENT ELECTRONIC SCHRÖDINGER EQUATION

2.1 The molecular Schrödinger equation

- **Time-independent molecular Schrödinger equation** (in atomic units)

$$\hat{H}_0 \, \Psi(r, R) = \left(\hat{T}_{el} + V_{el,el} + V_{el,nu} + \hat{T}_{nu} + V_{nu,nu} \right) \Psi(r, R) = E \Psi(r, R)$$

$r := \underline{r} = (\underline{r}_1, \underline{r}_2, \ldots \underline{r}_N)$ electron coordinates, N electrons (mass 1, charge -1)

$R := \underline{R} = (\underline{R}_1, \underline{R}_2, \ldots \underline{R}_{N_A})$ nuclear coordinates, N_A nuclei (masses M_A, charges $+Z_A$)

$\hat{T}_{el} = -\frac{1}{2} \sum_{i=1}^{N} \Delta_i$ kinetic energy operator electrons

$\hat{T}_{nu} = -\frac{1}{2} \sum_{A=1}^{N_A} \frac{1}{M_A} \Delta_A$ kinetic energy operator nuclei

$V_{el,el} = \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}}$ electron-electron repulsion ($r_{ij} = |\underline{r}_i - \underline{r}_j|$)

$V_{el,nu} = -\sum_{A=1}^{N_A} \sum_{i=1}^{N} \frac{Z_A}{R_{iA}}$ electron-nuclear attraction

$V_{nu,nu} = \sum_{A=1}^{N_A} \sum_{B>A}^{N_A} \frac{Z_A Z_B}{R_{AB}}$ nuclear-nuclear repulsion

E total molecular energy

$\Psi(r, R)$ total molecular wavefunction

- **Time-dependent molecular Schrödinger equation** (with explicit $\hbar$)

$$\left(\hat{H}_0 + \hat{V}(t) \right) \Psi(r, R, t) = i\hbar \frac{\partial \Psi(r, R, t)}{\partial t}$$

$\hat{H}_0, \hat{V}(t)$ unperturbed Hamiltonian and time-dependent "perturbation"

2.2 The Born-Oppenheimer approximation

- **The time-independent electronic Schrödinger equation**

$$\underbrace{\left(\hat{T}_{el} + V_{el,el} + V_{el,nu}\right)}_{\hat{H}_{el} \text{ (electronic Hamiltonian)}} \Psi_{el,n}(r; R) = E_{el,n}(R)\, \Psi_{el,n}(r; R)$$

$E_{el,n}(R) =$ electronic energy for state n

$\Psi_{el,n}(r; R) =$ electronic wavefunction for state n (parameter R)

- **The Born-Huang expansion**

$$\Psi(r, R) = \sum_{n}^{M} \Psi_{el,n}(r; R) \cdot \Phi_{nu,n}(R)$$

$\Phi_{nu,n}(R) =$ nuclear wavefunction for state n

                  (translation, vibration, rotation)

- **Coupled nuclear Schrödinger equations**

Putting the BH expansion in the molecular Schrödinger equation gives:

$$\left[\hat{T}_{nu}\underline{\underline{1}} + \underline{\underline{V}} + \underline{\underline{\hat{C}}}\right]\underline{\Phi}_{nu} = E\underline{\Phi}_{nu}$$

$\underline{\Phi}_{nu} = (\Phi_{nu,1}, \Phi_{nu,2}, \cdots, \Phi_{nu,M}) \ =$ nuclear wavefunction vector

2.2 The Born-Oppenheimer approximation (2)

- **The non-BO coupling matrix $\underline{\hat{C}}$**

$$\hat{C}_{mn} = -\sum_{A=1}^{N_A} \frac{\hbar^2}{2M_A} \left[\langle \Psi_{el,m} | \Delta_A \Psi_{el,n} \rangle + 2 \langle \Psi_{el,m} | \underline{\nabla}_A \Psi_{el,n} \rangle \underline{\nabla}_A \right]$$

couples different states, even for diagonal $\underline{\underline{V}}$.

- **The Born-Oppenheimer and adiabatic approximations**
  - ❶ Adiabatic approximation: Neglect all $\hat{C}_{mn}$ for $m \neq n$; if $V_{nm} = V_n \delta_{nm}$, then:

$$\left(\hat{T}_{nu} + V_n(R) + \hat{C}_{nn} \right) \Phi_{nu,n}(R) = E \Phi_{nu,n}(R)$$

  - ❷ Born-Oppenheimer approximation: Neglect all $\hat{C}_{mn}$ (including $\hat{C}_{nn}$)

$$\left(\hat{T}_{nu} + V_n(R) \right) \Phi_{nu,n}(R) = E \Phi_{nu,n}(R)$$

- **Time-dependent nuclear Schrödinger equation**

$$i\hbar \frac{\partial \Phi_{nu,n}(R,t)}{\partial t} = \left(\hat{T}_{nu} + V_n(R) \right) \Phi_{nu,n}(R,t)$$

Describes motion on single potential energy surface. V_n can be t-dependent. (Time-dependent) Potential couplings V_{nm} may still lead to non-adiabatic transitions.

2.2 The Born-Oppenheimer approximation (3)

- **The BO approximation in the time-dependent case**[1]

    Start from time-dependent electronic Schrödinger equation

    $$i\hbar\frac{\partial \Psi_{el}(r,t;R)}{\partial t} = \left(\hat{H}_{el}(+\hat{V}(t))\right)\Psi_{el}(r,t;R)$$

Ansatz for the total wavefunction:

$$\Psi(r,R,t) = e^{i\omega(R,t)/\hbar}\,\Psi_{el}(r,t;R)\,\Phi_{nu}(R,t)$$

gives (with a special choice for the topological phase $\omega(R,t)$), a nuclear Schrödinger equation of the form

$$i\hbar\frac{\partial \Phi_{nu}(R,t)}{\partial t} = \left(\hat{T}_{nu} + W(R,t)\right)\Phi_{nu}(R,t)$$

where

$$W = \frac{\partial\omega}{\partial t} + \text{non-BO terms of type } \hat{C}$$

In case of a stationary electronic state, and neglecting the non-Born-Oppenheimer term, gives $W = \partial\omega/\partial t = V(R)$, *i.e.* the time-dependent Born-Oppenheimer nuclear Schrödinger equation of above.

Extension to "group Born-Oppenheimer" approximation possible.

[1] Cederbaum, *BO approximation and beyond for time-dependent ...*, JCP **128**, 124101 (2008)

2.3 Matter-field interaction

- **TD electronic Schrödinger equation with matter-field interaction**

  Time-dependent electronic Schrödinger equation with external perturbation $\hat{V}(t)$:

  $$i\hbar\frac{\partial\Psi_{el}(r,t;R)}{\partial t} = \left(\hat{H}_{el} + \hat{V}(t)\right)\Psi_{el}(r,t;R)$$

- **Expression for $\hat{V}(t)$ in case of matter-electromagnetic field interaction**

  - Basic quantities:

  $\underline{E}\,(\underline{r},t):$ electrical field strength $(\frac{V}{m}$ in SI or E_h/ea_0 in at.u.$)$

  $\underline{B}\,(\underline{r},t):$ magnetic flux density $(T = \frac{Vs}{m^2}$ in SI or $\hbar/ea_0^2$ in at.u.$)$

  or

  $\phi\,(\underline{r},t):$ electrostatic potential $(V$ in SI$)$

  $\underline{A}\,(\underline{r},t):$ vector potential $(Tm$ in SI$)$

  $$\underline{E} = -\underline{\nabla}\,\phi - \frac{\partial\underline{A}}{\partial t}$$

  $$\underline{B} = \underline{\nabla}\,\times\,\underline{A}$$

  ϕ and $\underline{A}$ are not unique; in Coulomb gauge: $\underline{\nabla}\cdot\underline{A} = 0$

2.3 Matter-field interaction (2)

- **Hamiltonian for single particle** (mass m, charge q, possible static potential V_s):

$$\hat{H} = \frac{1}{2m} \left(\frac{\hbar}{i} \underline{\nabla} - q \underline{A} \right)^2 + V_s \implies$$

$$\boxed{\hat{H} = -\frac{\hbar^2}{2m} \underline{\nabla}^2 + V_s + \frac{i\hbar q}{2m} \left(\underline{\nabla} \, \underline{A} + \underline{A} \, \underline{\nabla} \right) + \frac{q^2}{2m} \underline{A} \, \underline{A} = \hat{H}_0 + \hat{V}}$$

where

$$\hat{H}_0 = -\frac{\hbar^2}{2m} \underline{\nabla}^2 + V_s \qquad \text{unperturbed Hamiltonian}$$

$$\hat{V}(\underline{r}, t) = \frac{i\hbar q}{2m} \left(\underline{\nabla} \, \underline{A} + \underline{A} \, \underline{\nabla} \right) + \frac{q^2}{2m} \underline{A} \, \underline{A} \qquad \text{matter-field coupling}$$

Rewriting:

$$\hat{V} = \frac{q \cdot i\hbar}{m} \underline{A} \cdot \underline{\nabla} + \frac{q^2}{2m} \underline{A} \, \underline{A}$$

For not too strong fields follows the "$A \cdot p$ form" of matter-field interaction:

$$\boxed{\hat{V}(\underline{r}, t) = -\frac{q}{m} \left(\underline{A} \cdot \underline{\hat{p}} \right)}$$

- **For N particles:**

$$\hat{V} = \sum_{i=1}^{N} -\frac{q_i}{m_i} \left(\underline{A}(\underline{r}_i) \cdot \underline{\hat{p}}_i \right)$$

2.3 Matter-field interaction (3)

- **Plane wave electromagnetic fields**

$$\boxed{\underline{A}\,(\underline{r},t) = \underline{A}_0\,\cos(\underline{k}\underline{r} - \omega t)}$$

where $\underline{k}$, ω are wavevector and angular frequency; $\lambda = 2\pi/|\underline{k}|$ (wavelength), $\nu = \omega/2\pi$ (frequency).

$$\implies \quad \hat{V}(\underline{r},t) = -\frac{q}{2m}\,\underline{A}_0\,\left[e^{i\underline{k}\underline{r}}\,e^{-i\omega t} + e^{-i\underline{k}\underline{r}}\,e^{+i\omega t} \right] \hat{\underline{p}}$$

- **Electric dipole approximation**

For not too short wavelengths, $e^{\pm i\underline{k}\underline{r}} = 1 \pm i\underline{k}\underline{r}\cdots \sim 1$ and:

$$\boxed{\hat{V}(t) = -\frac{q}{2m}\,\underline{A}_0\,\left(e^{i\omega t} + e^{-i\omega t} \right) \hat{\underline{p}} =: \hat{V}_0\,\cos(\omega t)}$$

- $V(t)$ is *no longer* coordinate-dependent; for arbitary vector fields, $\hat{V}(t) = -\frac{q}{m}\,\underline{A}(t)\,\hat{\underline{p}}$

- Including $\pm i\underline{k}\underline{r}$ introduces (i) *magnetic dipole* and (ii) *electric quadrupole* interactions

- In terms of matrix elements, it can be shown that

$$\boxed{\hat{V}(t) = -\hat{\underline{\mu}}\,\underline{E}(t)}$$

- $\hat{\underline{\mu}}$ is the *electric dipole operator*, for molecules given as (at.u.):

$$\boxed{\hat{\underline{\mu}} = -\sum_{i}^{N}\underline{r} + \sum_{A}^{N_A} Z_A\underline{R}_A}$$

2.4 Rabi oscillations and π-pulses

- ● **General, coupled two-level system**

E_2^0 , |2>   unperturbed states $|1\rangle$, $|2\rangle$, with energies E_1^0, E_2^0
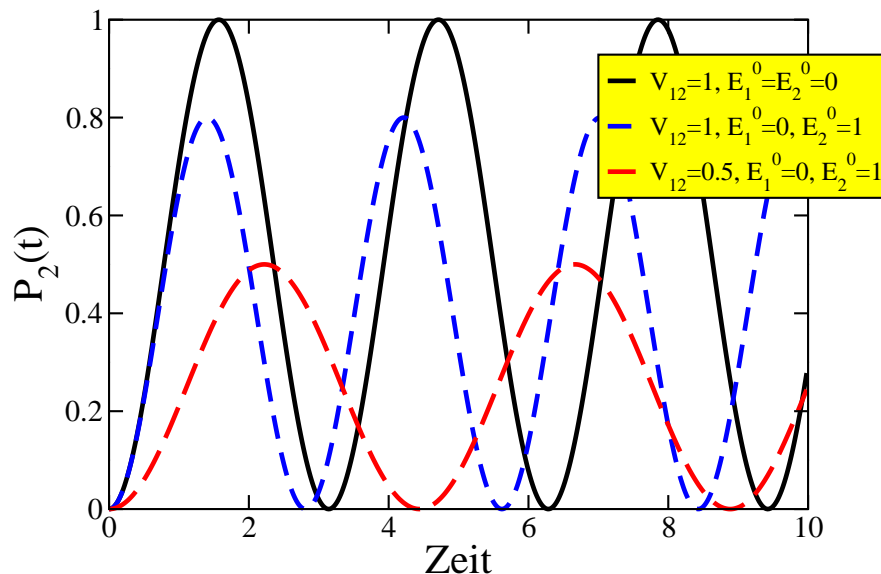
$\hat{V}$
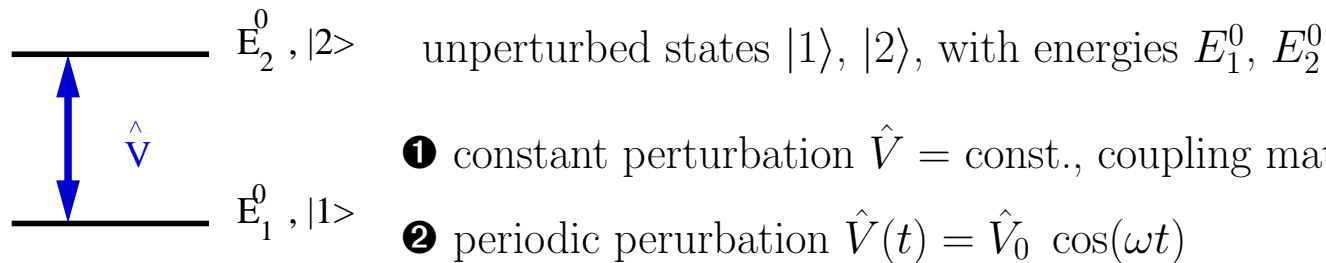
❶ constant perturbation $\hat{V} = \text{const.}$, coupling matrix element $V_{12} = \langle 1|\hat{V}|2\rangle$

E_1^0 , |1>   ❷ periodic perurbation $\hat{V}(t) = \hat{V}_0 \ \cos(\omega t)$

- ● **Case ❶**

Neglecting Stark terms $\langle 1|\hat{V}|1\rangle$, $\langle 2|\hat{V}|2\rangle$ solution of 2-level TDSE gives, for $\Psi(t = 0) = \phi_1^0$, *Rabi oscillations* for the upper state population $P_2(t)$

$$P_2(t) = \frac{4\,|\,V_{12}\,|^2}{4\,|\,V_{12}\,|^2 + (E_1^0 - E_2^0)^2} \cdot \sin^2\left[(4\,|\,V_{12}\,|^2 + (E_1^0 - E_2^0)^2)^{1/2} \cdot \frac{t}{2\hbar}\right]$$

In *degenerate* case $E_1^0 = E_2^0 \Longrightarrow$

$$P_2(t) = \sin^2\left(\frac{|V_{12}| \cdot t}{\hbar}\right)$$

and a *Rabi period*

$$T = \frac{h}{2\,|V_{12}|} = \frac{\pi\hbar}{|V_{12}|}$$

Legend:
- $V_{12}=1$, $E_1^0=E_2^0=0$
- $V_{12}=1$, $E_1^0=0$, $E_2^0=1$
- $V_{12}=0.5$, $E_1^0=0$, $E_2^0=1$

x-axis: Zeit, y-axis: $P_2(t)$

2.4 Rabi oscillations and π-pulses (2)

- **Case ❷**

In the *Rotating Wave Approximation* (RWA), $\hat{V} = \hat{V}_0 \cos(\omega t) = \frac{\hat{V}_0}{2}\left(e^{i\omega t} + e^{-i\omega t}\right) \approx \frac{\hat{V}_0}{2} e^{i\omega t}$, the periodically coupled 2-level TDSE gives

$$P_2(t) = \frac{|V_{12}^0|^2}{|V_{12}^0|^2 + \Delta^2} \cdot \sin^2\left[\left(|V_{12}^0|^2 + \Delta^2\right)^{\frac{1}{2}} \frac{t}{2\hbar}\right]$$

where $V_{12}^0 = \langle 1|\hat{V}_0|2\rangle$ and $\Delta = \hbar\omega - (E_2^0 - E_1^0)$ is the *detuning*.
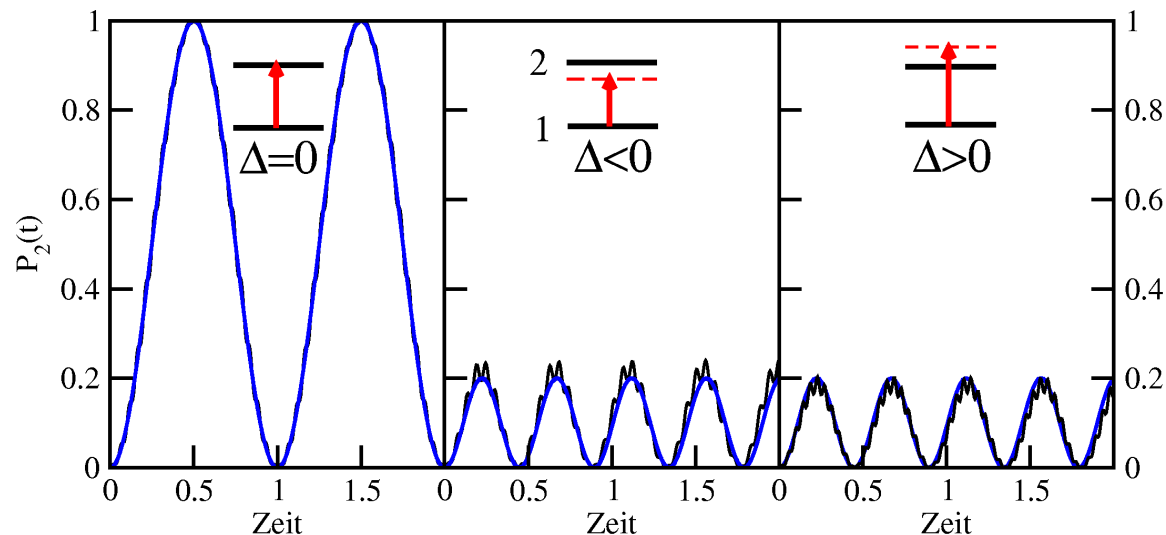
In *resonant* case $\hbar\omega = E_2^0 - E_2^0 \Longrightarrow$

$$P_2(t) = \sin^2\left(\frac{|V_{12}^0| \cdot t}{2\hbar}\right) \qquad\qquad T = \frac{2\pi\hbar}{|V_{12}^0|}$$

A π-*pulse* would be obtained by stopping field after $T/2$, when $P_2 = 1$.

2.4 Rabi oscillations and π-pulses (3)

- ## π-pulse excitation:

Consider perturbations of the form

$$\hat{V}(t) = \hat{V}_0 \; s(t) \; \cos(\omega_{10}t)$$

with *shape function $s(t)$* (=1 in case ❷ above). An example is the electric-dipole excitation by electrical field $E(t)$ (laser pulse)

$$V(t) = -\mu_{12} \; E_0 \; s(t) \; \cos(\omega_{12}t)$$

A π-*pulse* creates a population inversion in a 2-level system. The π-pulse condition is (under the RWA):

$$\mu_{12} E_0 \int s(t)dt = \hbar\pi$$

Example:
$s(t) = $ Gaussian, width $\sigma = 1000 \; \hbar/\mathrm{E}_h$
$V_0 = 0.00017724 \; \mathrm{E}_h$
$\hbar\omega_{12} = E_2^0 - E_1^0 = 0.1 \; \mathrm{E}_h$

- ## $\pi/2$-pulse excitation:

A $\pi/2$-*pulse* creates a $\frac{1}{\sqrt{2}}\left(|1\rangle + |2\rangle\right)$ *wavepacket.*
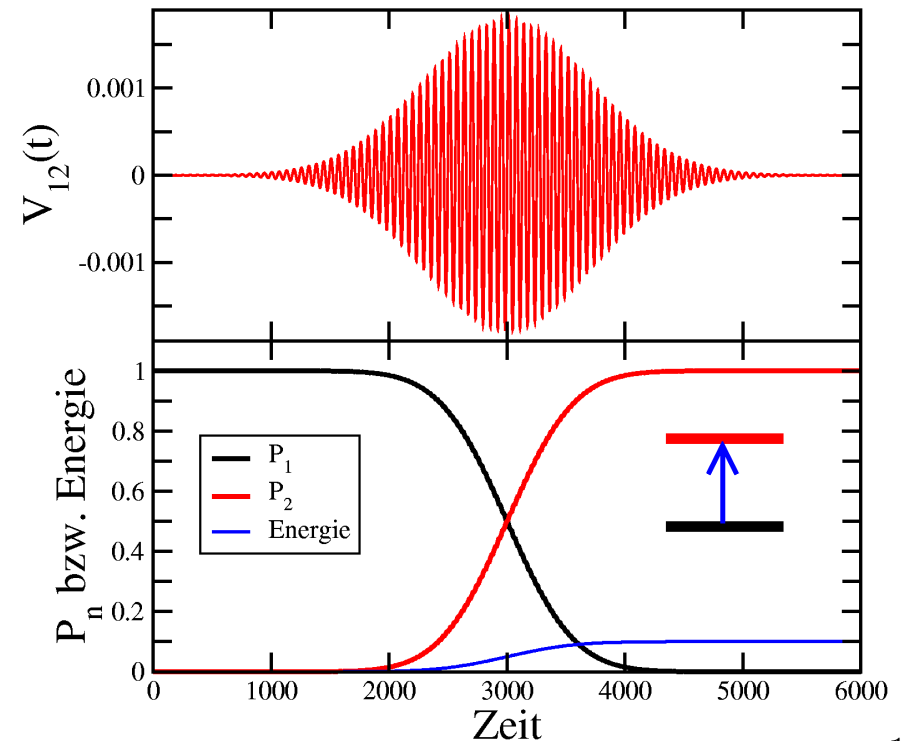
3. METHODS TO SOLVE TIME-DEPENDENT ELECTRONIC SCHRÖDINGER EQUATION

3.1 General overview

- **Fixed-nuclei, N-electron t-dependent Schrödinger equation** ($\Psi = \Psi_{el}$, $\hbar = 1$):

$$i\frac{\partial \Psi(\underline{x}_1, \ldots, \underline{x}_N, t)}{\partial t} = \left[\hat{H}_{el}(\underline{x}_1, \ldots, \underline{x}_N) - \underline{\hat{\mu}} \; \underline{E}(t) \right] \Psi(\underline{x}_1, \ldots, \underline{x}_N, t)$$

with $\underline{x}_i = (\underline{r}_i, \omega_i)$ combined spatial / spin coordinates, and $\underline{\hat{\mu}} = -\sum_i^N \underline{r}_i + \sum_A^{N_A} Z_A \underline{R}_A$.

- **Overview over solution techniques**

  ❶ Numerically exact solutions for N small

  ❷ Single-active electron (SAE) approaches

  ❸ Single-determinant methods

   - TD-HF: $\Psi(t) = \Psi_0(t)$
   - TD-DFT: $\Psi(t) = \Psi_0^{\text{KS}}(t)$

  ❹ Multi-determinant methods

   - TD-CI: $\Psi(t) = C_0(t)\Psi_0 + \sum_{ar} C_a^r(t)\Psi_a^r + \sum_{ab,rs} C_{ab}^{rs}(t)\Psi_{ab}^{rs} + \cdots$
   - TD-CASSCF/MCTDHF: $\Psi(t) = C_0(t)\Psi_0(t) + \sum_{ar} C_a^r(t)\Psi_a^r(t) + \sum_{ab,rs} C_{ab}^{rs}(t)\Psi_{ab}^{rs}(t) + \cdots$
   - TD-CC

  ❺ Others

3.2 Numerically exact methods for few-electron systems

- **Example[1]: Field-driven electron dynamics in H_2**

  - fixed nuclei, dipole approximation

  - cylindrical coordinates ρ_i, z_i, ϕ_i $(i = 1, 2)$

  - nuclei along z at $\pm R/2$

  - dual transformation grid[2]

  - $\underline{E}(t) = (0, 0, E_0)\ s(t)\ \sin \omega t$

  - $\Psi(0) = X^1\Sigma_g^+$ ground state

  - analysis: reduced density

$$P(z_1, z_2) = \int |\Psi(z_1, z_2, \underline{y}, t|^2\ d\underline{y}$$

ionization from ionic state
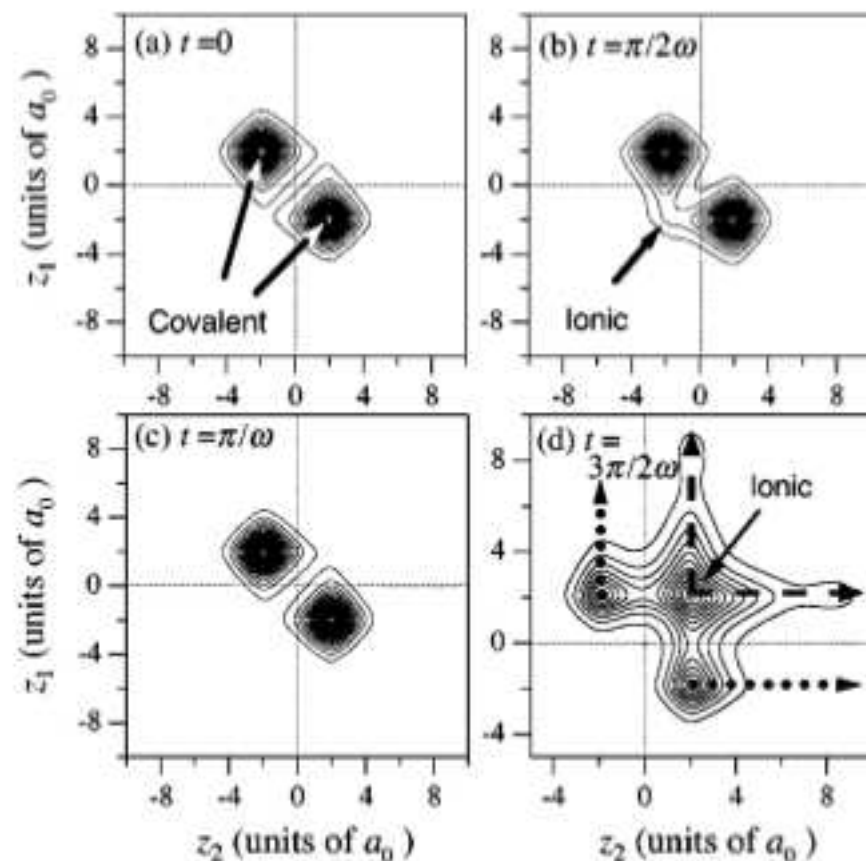
Example: R=4 a$_0$

$\omega = 0.06$ E$_h/\hbar$ (760 nm)

$s(t) =$ linear ramp up to 1 cycle, then constant

$I(\pi/2\omega) = 3.15 \times 10^{13}$ W/cm^2

$I(3\pi/2\omega) = 2.84 \times 10^{14}$ W/cm^2

[1] Kono, Bandrauk and coworkers, Phys. Rev. A **66**, 043403 (2002); [2] Phys. Rev. A **64**, 043411 (2001).

3.3 Time-dependent DFT

- **Time-dependent Kohn-Sham equations**

  - Prerequisites:

    – Electronic density:
    $$\rho(\underline{r}, t) = \int d\omega_1 d\underline{x}_2 \ldots d\underline{x}_N \; |\Psi(\underline{x}, \underline{x}_2, \ldots, \underline{x}_N, t)|^2$$

    – *Runge-Gross* theorem[1] (analogue to Hohenberg-Kohn 1):
    $$\boxed{\rho(\underline{r}, t) \leftrightarrow V(\underline{r}, t) \quad \text{(potential)}}$$

    – *Action integral* and *variational prinicple* (analogue to Hohenberg-Kohn 2):
    $$A = \int \left\langle \Psi(t) \left| i\frac{\partial}{\partial t} - \hat{H}_{el}(t) \right| \Psi(t) \right\rangle \; dt \; \text{ and } \; \frac{\delta A}{\delta \rho(\underline{r}, t)} = 0$$

    – Time-dependent Kohn-Sham-Slater determinant, density:
    $$\Psi = \mathcal{A}\left[\chi_1^{\text{KS}}(\underline{x}_1, t) \; \chi_2^{\text{KS}}(\underline{x}_2, t) \; \chi_N^{\text{KS}}(\underline{x}_N, t) \right]$$
    $$\rho(\underline{r}, t) = \sum_{i=1}^{N} \int |\chi_i^{\text{KS}}(\underline{x}, t)|^2 \; d\omega = \sum_{i=1}^{N} |\psi_i^{\text{KS}}(\underline{r})|^2$$

    $\chi_i^{\text{KS}}(\underline{x}, t) = \psi_i^{\text{KS}}(\underline{r}, t)\gamma_i(\omega)$ are KS spin orbitals, ψ_i^{KS} and $\gamma_i(\omega)$ are spatial orbitals and spin functions

[1] Runge, Gross, PRL **52**, 997 (1984)

3.3 Time-dependent DFT (2)

- **Time-dependent Kohn-Sham equations** (cont'd)

  - Real-time time-dependent Kohn-Sham equations

$$\hat{h}_{\text{KS}}(\underline{r}, t)\, \psi_i^{\text{KS}} = \left[-\frac{1}{2}\Delta + \int \frac{\rho(\underline{r}', t)}{|\underline{r} - \underline{r}'|}\, d\underline{r}' + v(\underline{r}, t) + v_{xc}(\underline{r}, t) \right] \psi_i^{\text{KS}}(\underline{r}, t) = i\frac{\partial}{\partial t}\psi_i^{\text{KS}}(\underline{r}, t)$$

  where $\hat{h}_{\text{KS}}(\underline{r}, t) = KS\ Hamiltonian$ with kinetic energy (1st term), Hartree term (2nd), external potential (3rd), exchange-correlation potential (4th). For molecules in an electric field $\underline{E}(t)$ (dipole approximation)

$$v(\underline{r}, t) = -\sum_{A=1}^{N_A} \frac{Z_A}{|\underline{r} - \underline{R}_A|} - \underline{r}\, \underline{E}(t)$$

  - Adiabatic approximation for exchange-correlation potential

  $v_{xc}(\underline{r}, t)$ depends on density of all (previous) time-points; in *adiabatic* approximation:

$$v_{xc}(\underline{r}, t) \approx \delta E_{xc}[\rho_t(\underline{r})]/\delta \rho_t(\underline{r})$$

  where $\rho_t(\underline{r})$ is the value of $\rho(\underline{r}, t)$ at time t.

- **Linear-response TD-DFT**

  In *linear-response* regime, the *Casida equations*[1] as quasi-stationary eigenvalue equations give excitation energies ω_i (out of the ground state) and oscillator strengths f_i (LR-TDDFT).

[1] Casida *et al.*, JCP **108**, 4439 (1998)

3.3 Time-dependent DFT (3)

- **Advantages of (adiabatic) RT-TDDFT**

  - Applicable to large systems
  - Good for single-electron excitations
  - Reasonable for weak-field excitations
  - Combination with classical MD
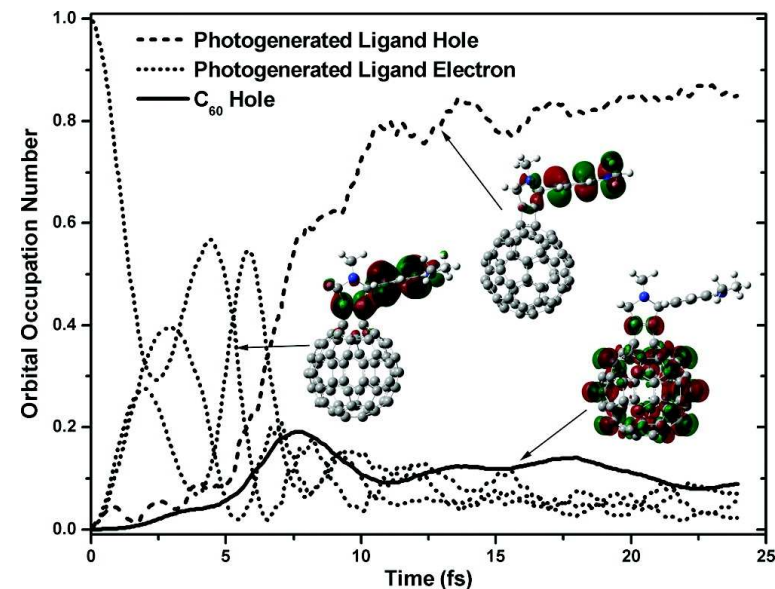
photogenerated holes and electrons in DMA-C_{60}^1

- **Disadvantages of (adiabatic) RT-TDDFT**

  - Multi-electron excitations
  - Strong fields
  - Conical intersections
  - Long-range charge transfer, Rydberg states
  - Resonant & π-pulse excitations, Rabi oscillations
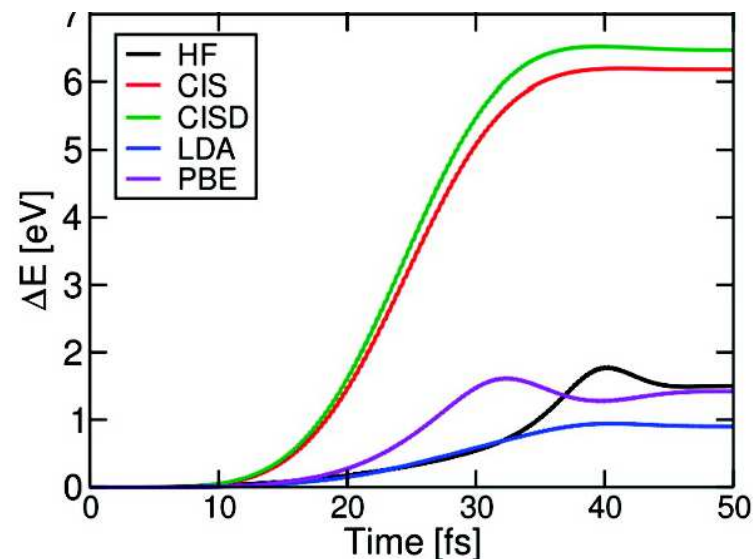
π-pulse excitation of LiCN[2] (with $\hbar\omega \sim 6$ eV)

[1] Chapman *et al.*, JPC Lett. **2**, 1189 (2011);   [2] Raghunathan, Nest, JCTC **7**, 2492 (2011)

3.4 Time-dependent Hartree Fock

- **Time-dependent Hartree-Fock equations**

  - Time-dependent Slater determinant

$$\Psi = \mathcal{A}\left[\chi_1(\underline{x}_1, t)\ \chi_2(\underline{x}_2, t)\ \chi_N(\underline{x}_N, t)\right]$$

  with $\chi_i(\underline{x}) = \psi_i(\underline{r})\gamma_i(\omega)$ the HF spin orbitals (and $\psi_i(\underline{r})$ the HF spatial orbitals).

  - TD-HF equations (for spatial orbitals)

$$\hat{f}(\underline{r}, t)\ \psi_i(\underline{r}, t) = \left[-\frac{1}{2}\Delta + v_H(\underline{r}, t) + \hat{v}_x(t) + v(\underline{r}, t) + \right]\psi_i(\underline{x}, t) = i\frac{\partial}{\partial t}\psi_i(\underline{r}, t)$$

  with $\hat{f}(\underline{r}, t) =$ Fock operator, $v_H(\underline{r}, t) =$ Hartree term, $\hat{v}_x(t) =$ (exact, non-local) exchange term, and $v(\underline{r}, t)$ the external potential as above.

- **Linear-response time-dependent Hartree-Fock equations**

  In *linear-response* regime, the *Random Phase Approximation* (RPA) results which gives excitation energies ω_i (out of the ground state) and oscillator strengths f_i in analogy to LR-TDDFT.

3.4 Time-dependent Hartree Fock (2)

- **Rabi oscillations for H_2^{+1}**[1]

- **Non-resonant excitation of H_2**[1]
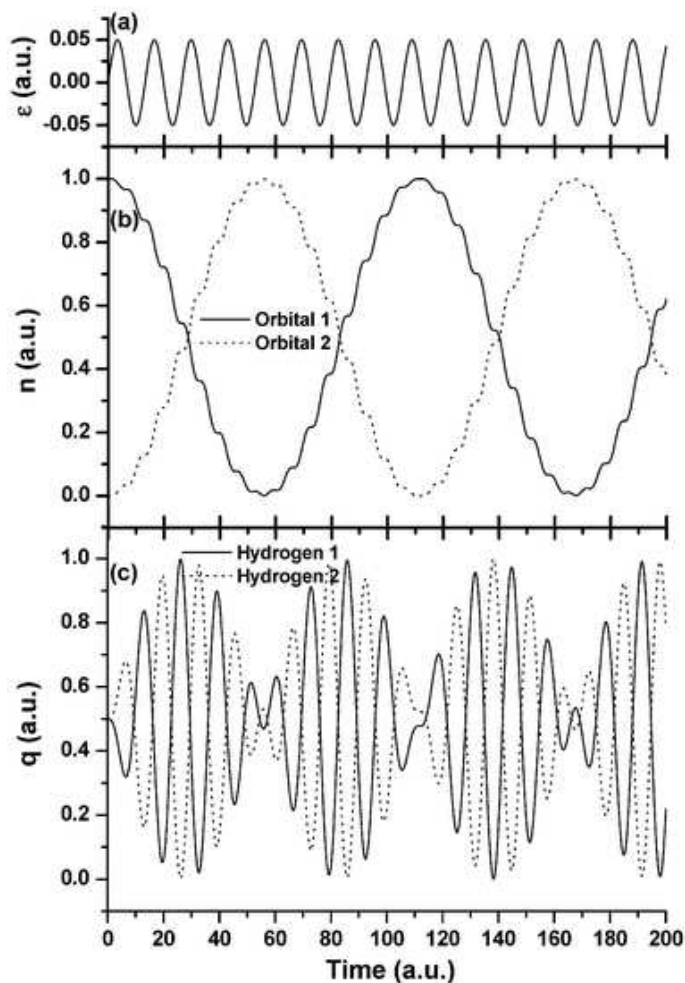
cw field, resonant, $E_0 = 0.05\ \hbar/ea_0$; TD-HF/STO-3G
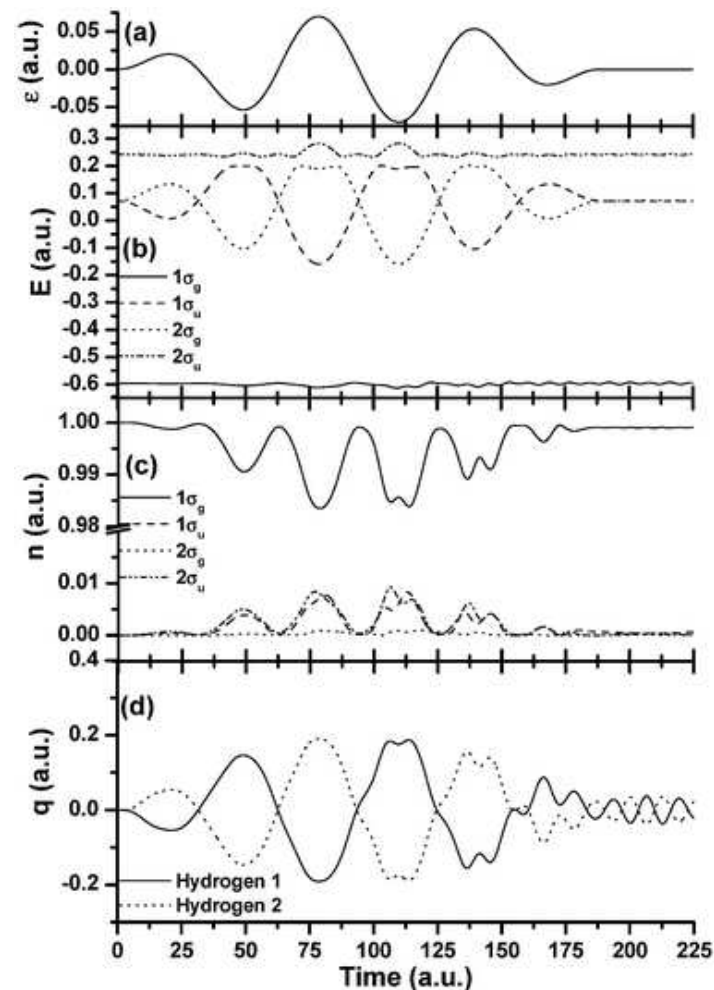
laser pulse, $E_0 = 0.07\ \hbar/ea_0$; TD-HF/6-311++G(d,p)

Rabi accounted for

wavepacket, good agreement with FCI

[1] Schlegel and coworkers, PCCP **7**, 233 (2005)

3.5 Time-dependent Configuration Interaction

- **The CI wavefunction**

$$\Psi^{\text{CI}} = D_0 \ \Psi_0 + \sum_{a=1}^{N} \sum_{r=N+1}^{N_{\text{virt}}} D_a^r \Psi_a^r + \sum_{a<b}^{N} \sum_{r<s}^{N_{\text{virt}}} D_{ab}^{rs} \ \Psi_{ab}^{rs} + \ \text{higher excitations}$$

$$
\begin{aligned}
\Psi_0 \ &= \ \text{HF ground state Slater determinant} \\
\Psi_a^r \ &= \ \text{singly excited determinant } (a \to r) \\
\Psi_{ab}^{rs} \ &= \ \text{doubly excited determinant } (a, b \to r, s) \\
N_{\text{virt}} \ &= \ \text{number of virtual orbitals} \\
D_0, D_a^r, D_{ab}^{rs}, \ldots \ &= \ \text{coefficients}
\end{aligned}
$$

Example: $N = 4$, $N_{\text{virt}} = (2K - N) = 6$ ($2K$ spin orbitals)

-30-
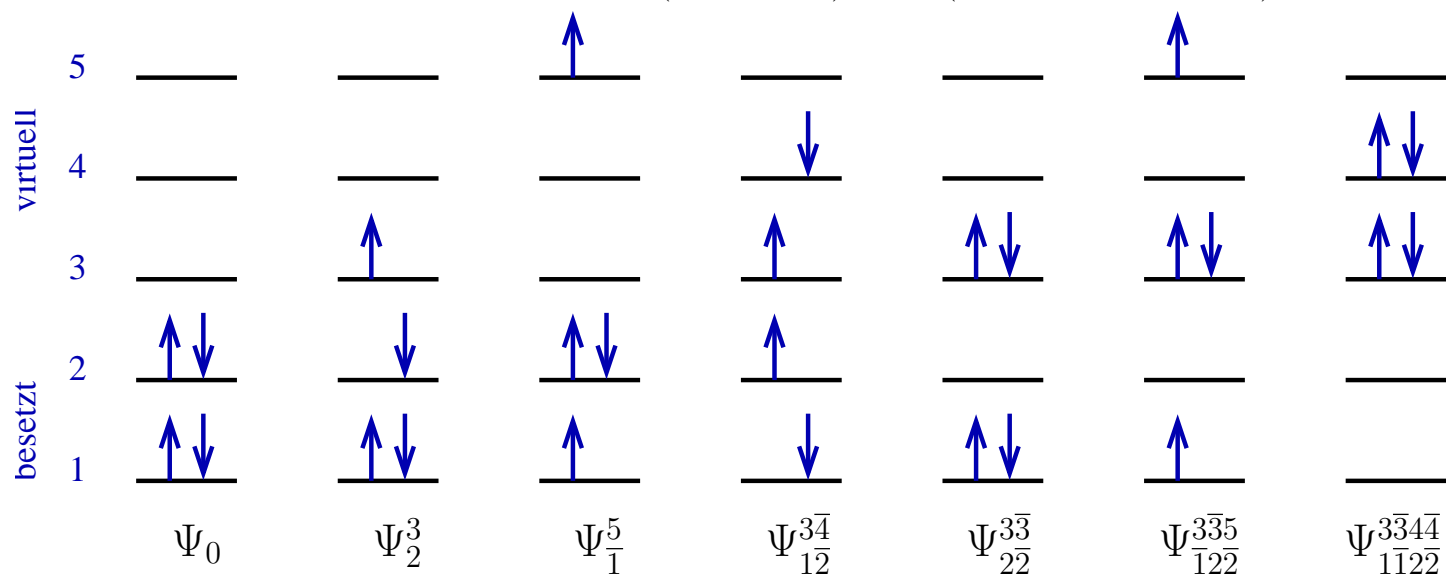
3.5 Time-dependent Configuration Interaction (2)

- **Time-dependent CI: TD-CI[1]**

  ❶ Start from (field-free) ground state HF-Slater determinant Ψ_0

  $$\boxed{\Psi_0 = \mathcal{A}\left[\chi_1(\underline{x}_1)\ \chi_2(\underline{x}_2)\cdots\chi_N(\underline{x}_N)\right]}$$

  ❷ Perform (field-free) CI calculation

  $$\boxed{\underline{\underline{H}}D_i = E_i\ D_i}$$

  $\Longrightarrow$ CI eigenstates $\Psi_i^{\text{CI}} = \sum_J D_{iJ}\Psi_J$ with energy E_i; $H_{IJ} = \langle\Psi_I|\hat{H}_{el}|\Psi_J\rangle$; $\Psi_{I,J}$ = Slater determinants

  ❸ Solve TDSE with field

  $$\boxed{i\partial\Psi(t)/\partial t = \left(\hat{H}_{el} - \underline{\hat{\mu}}\,\underline{E}(t)\right)\Psi(t)} \quad \text{where} \quad \Psi(t) = \sum_i C_i(t)\Psi_i^{\text{CI}}$$

  field-off case: $\Psi(t+\Delta t) = \sum_i C_i(t)\ e^{-iE_i\ \Delta t}\ \Psi_i^{\text{CI}}$

  field-on case: $\underline{C}(t+\Delta t) = \left[\prod_\alpha \underline{\underline{U}}_\alpha^\dagger\ e^{-iE_\alpha(t)\ \underline{\underline{\tilde{\mu}}}_\alpha\ \Delta t}\ \underline{\underline{U}}_\alpha\right]\ e^{-i\underline{\underline{\tilde{H}}}\ \Delta t}\ \underline{C}(t)$

  $\underline{\underline{\mu}}_\alpha\ (\alpha = x, y, z) = $ dipole matrix with elements $\langle\Psi_i^{\text{CI}}|\hat{\mu}_\alpha|\Psi_j^{\text{CI}}\rangle$

  $\underline{\underline{U}}_\alpha$ $\quad\quad\quad$ diagonalizes $\underline{\underline{\mu}}_\alpha$ to $\underline{\underline{\tilde{\mu}}}_\alpha$

  $\underline{\underline{\tilde{H}}}$ $\quad\quad\quad = \text{diag}(E_1, E_2, \dots)$

[1] Klamroth & co.; Rohringer; Santra; Schlegel; Head-Gordon; Luppi; Cederbaum; Bonitz; Saenz; Tremblay $\cdots$

3.5 Time-dependent Configuration Interaction (3)

- ## TD-CIS: Time-Dependent CI Singles

  If only singlet excited states are of interest (optically allowed from singlet ground states), then

  $$\Psi_i^{\text{CIS}} = D_{0,i}\Psi_0 + \sum_a \sum_r D_{a;i}^r \, {}^1\Psi_a^r$$

  with singlet configuration state functions ${}^1\Psi_a^r = \frac{1}{\sqrt{2}}\left(\Psi_a^r + \Psi_{\bar{a}}^{\bar{r}}\right)$

- ## TD-CISD: Time-Dependent CI Singles/Doubles

  $$\Psi_i^{\text{CISD}} = D_{0,i}\Psi_0 + \sum_a \sum_r D_{a,i}^r \, \Psi_a^r + \sum_{a<b} \sum_{r<s} D_{a,b;i}^{r,s} \Psi_{a,b}^{r,s}$$

- ## TD-CIS(D): TD-CIS with perturbative Doubles

  Number of Slater determinants increases rapidly with excitation level; CIS(D)[1] improves CIS *energies* by perturbatively including double excitations but leaving the size of CI matrix as for CIS:

  $$E_i^{\text{CIS(D)}} = E_i^{\text{CIS}} - \frac{1}{4}\sum_{abrs} \frac{\left(u_{ab,i}^{rs}\right)^2}{\left(\Delta_{ab}^{rs} - E_i^{\text{CIS}}\right)} + \sum_{ar} D_{a,i}^r v_{a,i}^r$$

  The u's and v's contain 2-electron integrals and coefficients $D_{a,i}^r$, the Δ's HF-orbital energy differences; the CIS(D) ground state is the MP2 energy.

[1] M. Head-Gordon *et al.*, CPL **219**, 21 (1994)

3.5 Time-dependent Configuration Interaction (4)

- **An example: Laser-driven electrons in a metal film[1]**

  - **The model**

    - N electrons, film of thickness d

    - 1D jellium model with $\rho_+(z)$, regularized Coulomb interaction, e.g. $v(z) = -\int \frac{\rho^+(z')}{\sqrt{(z-z')^2+c}} dz'$

    - coupling to two $\sin^2$ laser pulses, delay $\Delta\tau$

    - Fourier grid representation

    - $\Psi(0) = \Psi_0$

  - **HF calculation**
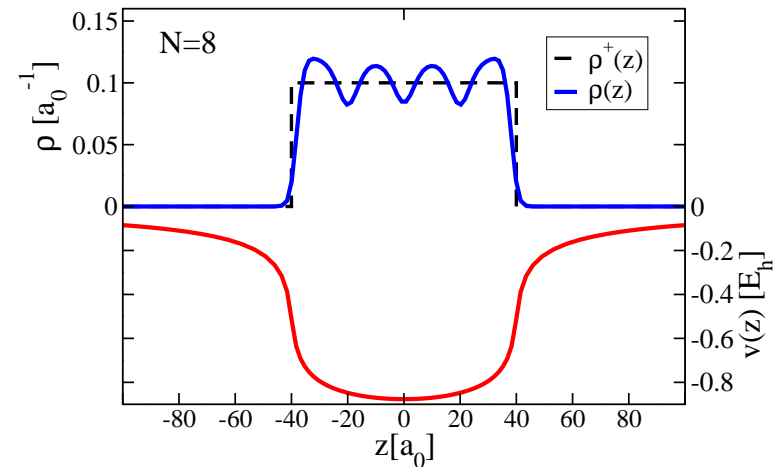
  - **TD-CIS calculation**

    (N=6, $\Delta\tau = 0$, $\hbar\omega_{1,2} = 0.155$ E$_h$, FWHM$_{1,2}$=20 fs)
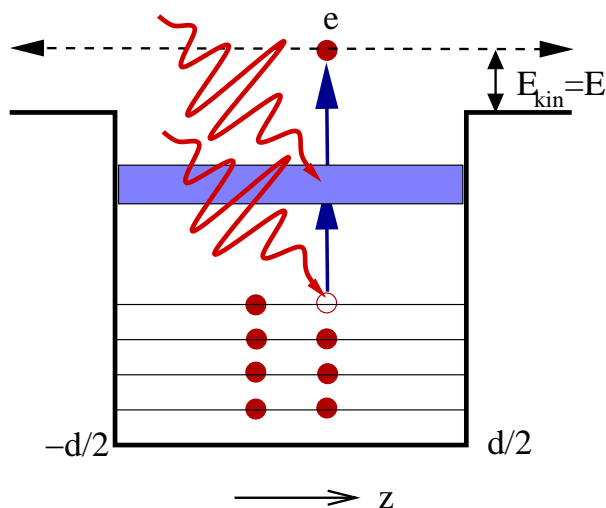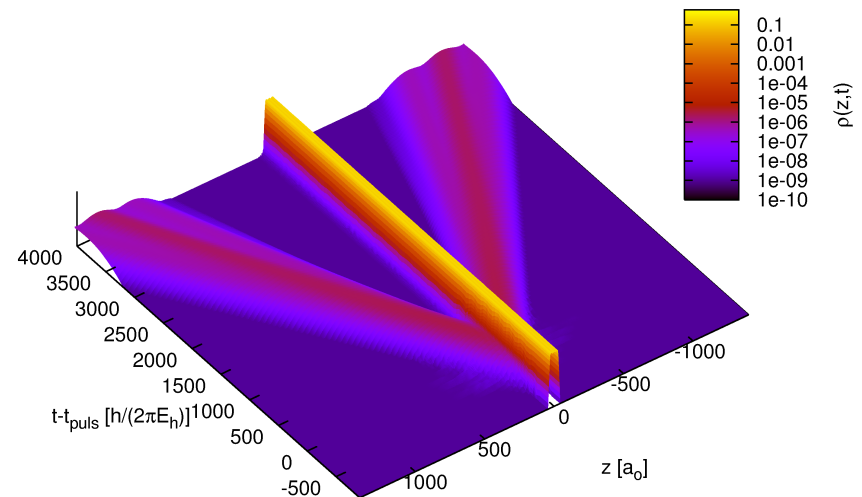
[1] Klamroth *et al*, Appl. Phys. A **78**, 189 (2004); Klamroth, PRB **68**, 245421 (2003)

3.5 Time-dependent Configuration Interaction (5)

- **Variants of TD-CI**
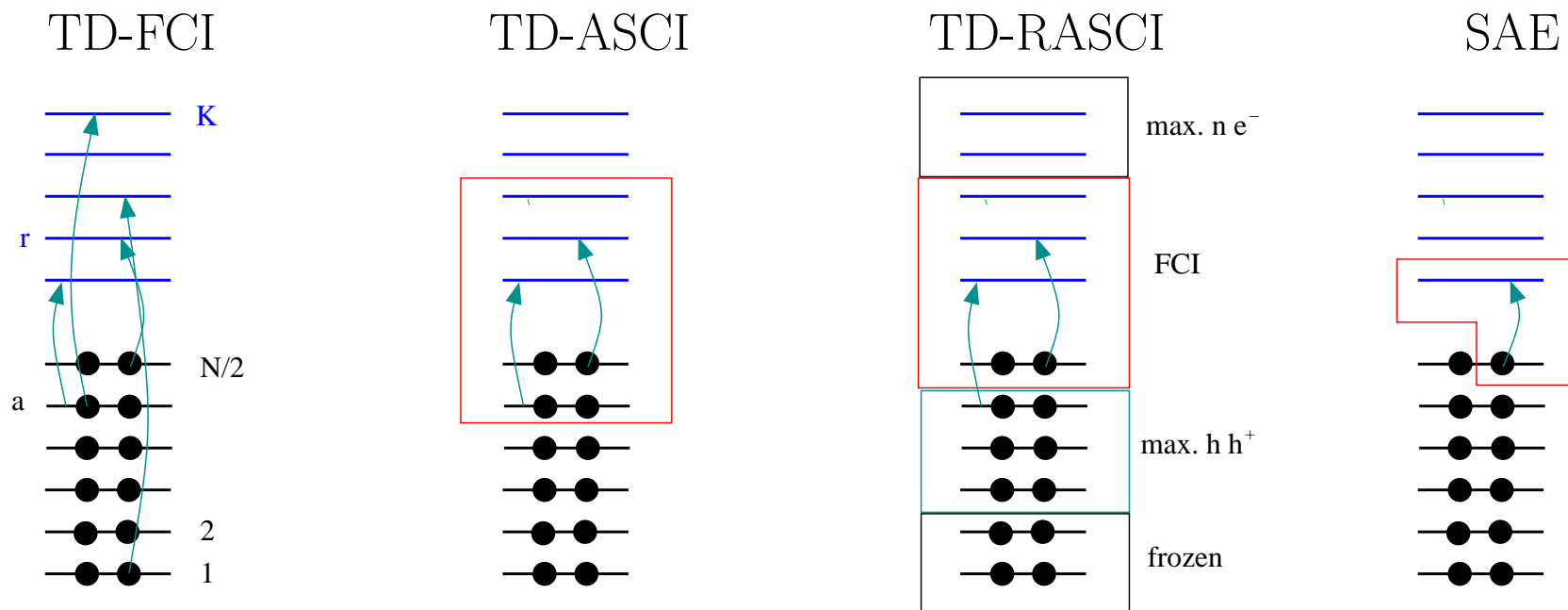
- TDFCI: TD Full CI, all up to N-fold excitations (TD-CISDT$\cdots$N), "exact" solution of the TDSE.

  Problem: for excitation level n, $$N_{det} = \begin{pmatrix} N \\ n \end{pmatrix} \begin{pmatrix} 2K - N \\ n \end{pmatrix} \sim (2K)^n \implies \text{truncation needed}$$

- TD-ASCI: Full or truncated TD-CI in active space

- TD-RASCI[1]: TD Resctricted Active Space CI in various subspaces

- SAE[2]: Single Active Electron approach

[1] Hochstuhl, Hinz, Bonitz, EPJ Spec. Top. **223**, 177 (2014) plus refs.; [2] Kulander *et al.*, IJQC QCS **25**, 415 (1991)

3.6 MCTDHF and TD-CASSCF

- ## Multi-Configurational Time-Dependent Hartree-Fock[1]

  The MCTHF wavefunction is

$$\Psi^{\text{MCTDHF}}(\underline{x}_1, \ldots, \underline{x}_N, t) = \sum_{j_1=1}^{n} \cdots \sum_{j_N=1}^{n} C_{j_1 \cdots j_N}(t) \cdot \mathcal{A}\left[\chi_{j_1}(\underline{x}_1, t) \cdots \chi_{j_N}(\underline{x}_N, t)\right]$$

or
$$\Psi^{\text{MCTDHF}}(\underline{x}_1, \ldots, \underline{x}_N, t) = \sum_{j_1=1}^{n} \cdots \sum_{j_N=1}^{n} A_{j_1 \cdots j_N}(t) \prod_{k=1}^{N} \chi_{j_k}(\underline{x}_k, t)$$

with *antisymmetric* coefficient tensor $A_{j_1 \cdots j_N}(t)$. The χ_i (spin orbitals, single-particle functions) are time-dependent; there are n spin orbitals in the expansion.

- ## TD-CASSCF: TD Complete Active Space Self Consistent Field

  MCTDHF is analogous to CASSCF(M,P):

  - TD-CASSCF(M,P) = M electrons in the active space of P (spatial) orbitals

  - TD-CASSCF(N,N/2) = TD-HF

  - TD-CASSCF(N,2K) = TD-FCI

AS=(4,5)
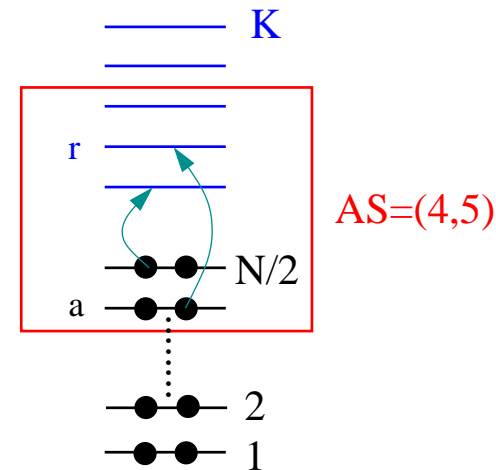
[1] Kono; Scrinzi; Nest; McCurdy; Bonitz; Cederbaum; Bande; Thoss; Tannor; Fisher

3.6 MCTDHF and TD-CASSCF (2)

- **Coefficients A and orbitals χ from Dirac-Frenkel variational principle**

$$\langle \delta\Psi(t)|\hat{H}(t) - i\frac{\partial}{\partial t}|\Psi(t)\rangle = 0$$

- **Equations of motion for coeffcients and orbitals**

  - Coefficients:

$$i\frac{\partial A_J}{\partial t} = \sum_J \langle \Phi_J|\hat{H}_{el}(t)|\Phi_L\rangle$$

  - Orbitals:

$$i\frac{\partial \underline{\chi}}{\partial t} = (1 - \hat{P})\left[\hat{h} + \underline{\underline{\rho}}^{-1}\,\underline{\underline{V}}_{el,el}\right]\underline{\chi}$$

Φ_I	Hartree product, with combined index $I = i_1, \cdots, i_N$
$\Psi_j = \sum_{j_2=1}^{n}\cdots\sum_{j_N=1}^{n} A_{jj_2\cdots j_N}(t)\prod_{k=2}^{N}\chi_{j_k}(\underline{x}_k, t)$	single-hole functions
$\rho_{jl} = \langle\Psi_j|\Psi_l\rangle$	single-particle density matrix
$\langle V_{el,el}\rangle_{jl} = \langle\Psi_j|V_{el,el}|\Psi_l\rangle$	mean fields
$\hat{P} = \sum_{j=1}^{n}|\chi_j\rangle\langle\chi_j|$	projector on space spanned by orbitals
$\hat{h}(\underline{r}, t) = -\frac{1}{2}\Delta + v(\underline{r}, t)$	single-particle Hamiltonian with external potential $v(t)$

- **Note:** EOM are not unique; other choices are possible[1]

[1] Hochstuhl et al., EPJ Sp.Top. **223**, 177 (2014); Kato, Kono, CPL **392**, 533 (2004); Nest *et al.*, JCP **122**, 124102 (2005); Haxton *et al.*, PRA **83**, 063416 (2011)

3.6 MCTDHF and TD-CASSCF (3)

- **Convergence of TD-CASSCF(M,P) to FCI**

Imaginary-time propagation: $\tau = it$

$$\Psi(\tau) = e^{-\hat{H}_{el}\tau} \, \Psi(0) = b_0 e^{-E_0 \tau} \Psi_0 + b_1 e^{-E_1 \tau} \Psi_1 \cdots$$

Two examples with six electrons each:

<div style="text-align:center">

1D jellium model[1]

d=100 a_0, $N = 6$, K orbitals
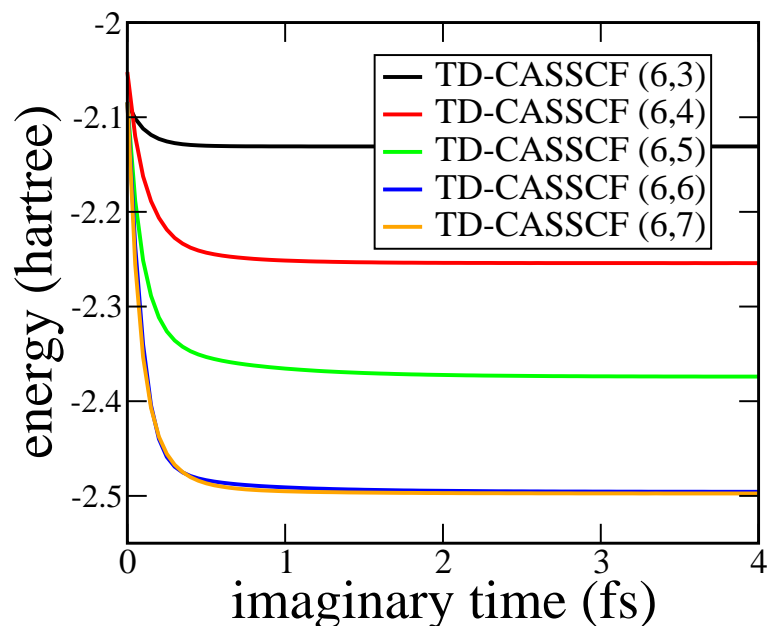
Li$_2$ molecule[2]

LCAO-MO, TD-CASSCF/6-31G*

</div>
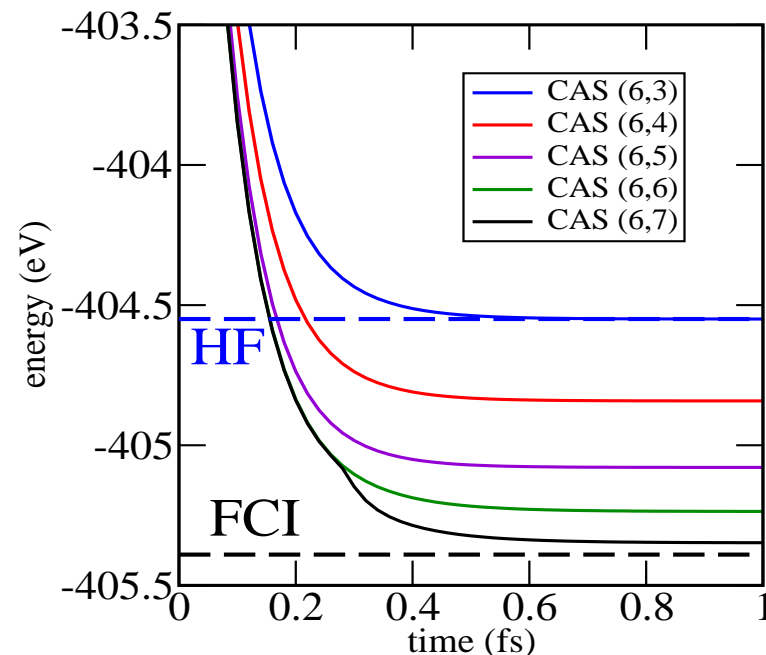
[1] Nest, Klamroth, Saalfrank, JCP **122**, 124102 (2005)

[2] Nest, JTCC **6**, 653 (2007)

3.6 MCTDHF and TD-CASSCF (4)

- **Excited states by real-time propagation**[1]

via FT of autocorrelation function

$$\langle \Psi(0)|\Psi(t)\rangle = \sum_n C_n^* C_n \ e^{-iE_n t}$$

via FT of dipole moment
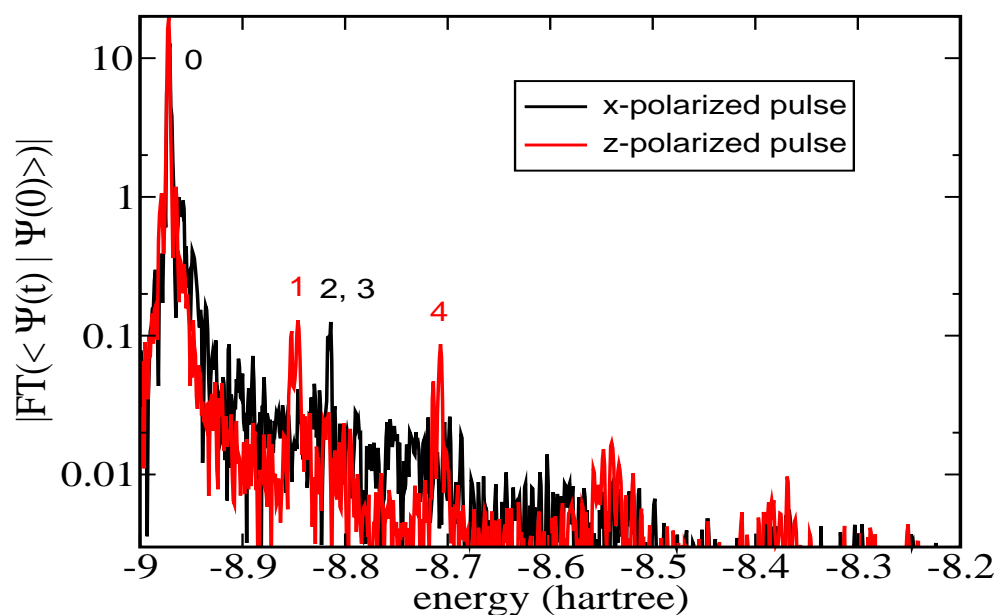
$$\langle \hat{\underline{\mu}}\rangle(t) = \sum_{n,m} C_n^* C_m \ e^{i(E_n - E_m)t} \ \langle n|\hat{\underline{\mu}}|m\rangle$$

gives absolute energies
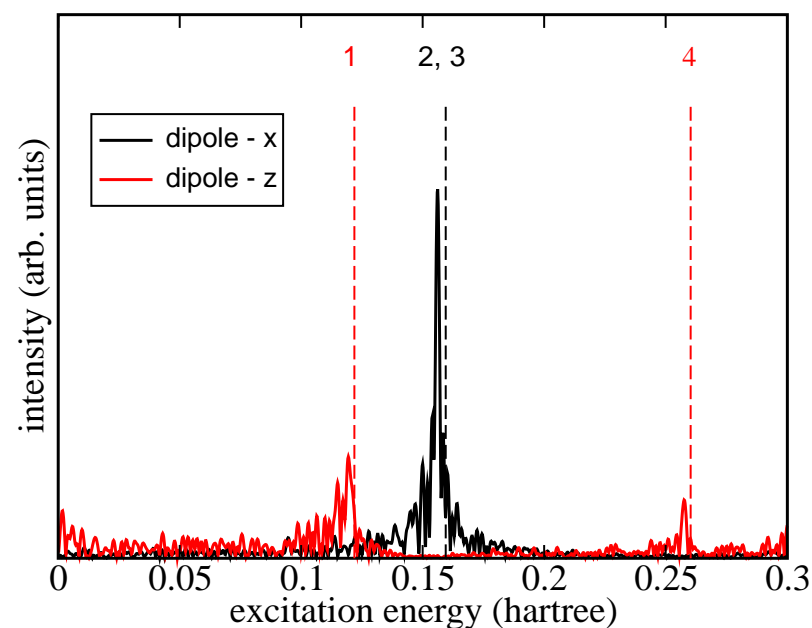
gives energy differences

LiH molecule, TD-CASSCF(4,4)/6-31G*

[1] Nest, Padmanaban, Saalfrank, JCP **126**, 214106 (2007)

- **Excited states by real-time propagation**[1]

Performance of dipole method (LiH)

3.7 TD-CCSD

- **Time-dependent Coupled Cluster theory and wavefunction**

$$i\frac{\partial \Psi^{CC}}{\partial t} = i\frac{\partial}{\partial t}\left(e^{\hat{T}(t)}|\Psi_0\rangle\right) = \hat{H}_{el}(t)\ \left(e^{\hat{T}(t)}|\Psi_0\rangle\right)$$

CC Single Doubles:

$$\hat{T}(t) = \sum_{i=1}^{N}\hat{T}_i(t) \sim \hat{T}_1(t) + \hat{T}_2(t)$$

where $\hat{T}_1\Psi_0 = \sum_{a,r} t_a^r(t)\Psi_a^r$ and $\hat{T}_2\Psi_0 = \sum_{a,b,r,s} t_{ab}^{rs}(t)\Psi_a^r$, and t are cluster amplitudes.

- **Imaginary time propagation[1]**

TD-CCSD / 6-31G*
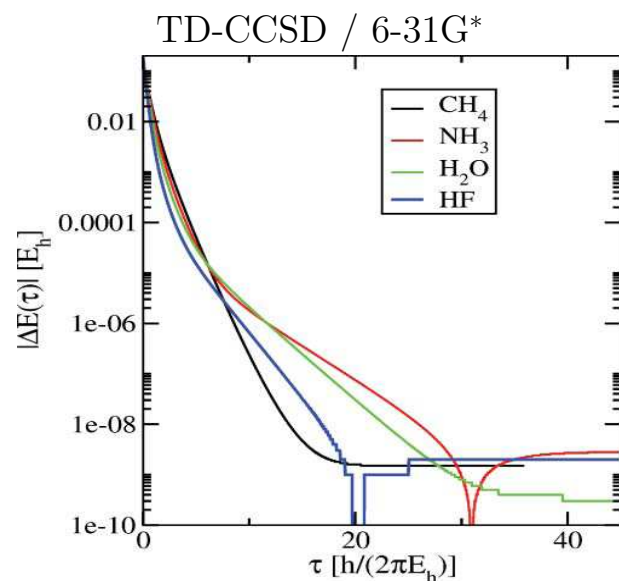
convergence to CCSD ground state

- **Real time propagation[1]**

NH_3, $\omega = 0.389$ $E_h/\hbar$, $\sin^2$ pulse with $\sigma = 100$ $\hbar/E_h$
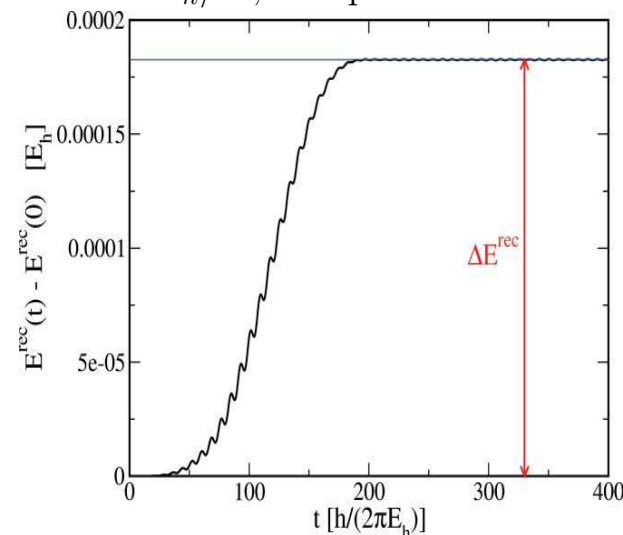
resonant excitation

[1] Klamroth, Huber, JCP **134**, 054113 (2011)

3.8 Other methods

- Semiclassical methods for electron motion[1], Floquet theory[2], ...

- Semiempirical electronic Hamiltonians[3]

- Reduced-dimensional electron dynamics[4]

- TD-CI and TD-CI like approaches with few-state models[5]

- TD-CI like approaches with state energies E_i and dipole matrices $\underline{\underline{\mu}}$ calculated from

  - LR-HF (RPA)[6]
  - LR-DFT[6,7]
  - EOM-CC[6,8]
  - CASSCF[9], ADC[10], ...

$$\Psi(t) = \sum_i C_i(t)\ \Psi_i$$

$$i\ \frac{\partial \underline{C}(t)}{\partial t} = \underline{\underline{H}}(t)\ \underline{C}(t)$$

$$H_{ij} = E_i\ \delta_{ij} - \underline{\mu}_{ij}\ \underline{E}(t)$$

1   E.g., Smirnova, Spanner, Ivanov, PRA **77**, 033407 (2008) (eikonal approach)
2   E.g., Chu *et al.*, Phys. Rep. **390**, 1 (2004)
3   E.g., Mukamel and coworkers, JCP **119**, 4722 (2003)
4   1D and 2D models, e.g., Bandrauk, Lein, Scrinzi, Gross, Potsdam group
5   E.g., Manz (ring currents), and many others
6   E.g., Schlegel and coworkers, JPCA **115**, 4678 (2011)
7   E.g., Tremblay and coworkers, JCP **145**, 174704 (2016)
8   E.g., Head-Gordon and coworkers, Mol. Phys. **110**, 909 (2012)
9   E.g., Smirnova *et al.*
10 Cederbaum, Dreuw and coworkers, e.g. JCP **132**, 144302 (2010)

4. EXTENSIONS / SPECIAL ASPECTS

4.1 Treatment of ionization

- **Ionization in TD-CIS: A heuristic model**[1]
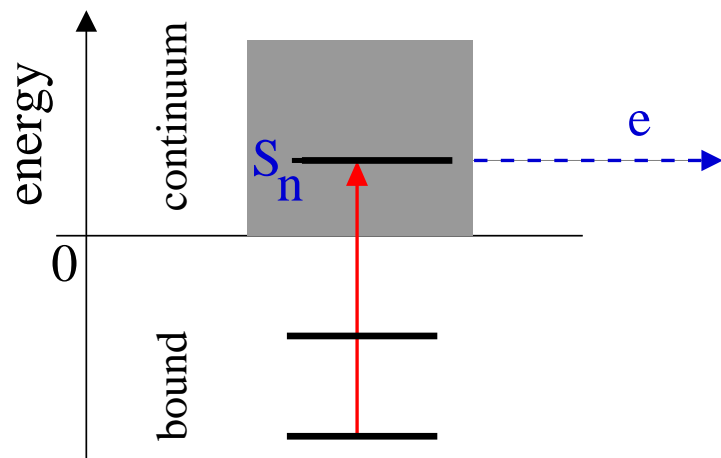
$$E_n^{\text{CIS}} \rightarrow E_n^{\text{CIS}} - \frac{i}{2}\Gamma_n$$

Γ_n = ionization rate of state n, if $E_n^{\text{CIS}} > 0$

$$\Gamma_n = \sum_{a,r} \left| D_{a,n}^r \right|^2 \frac{\sqrt{2\varepsilon_r/m_e}}{d}$$

ballistic model, empirical escape length d
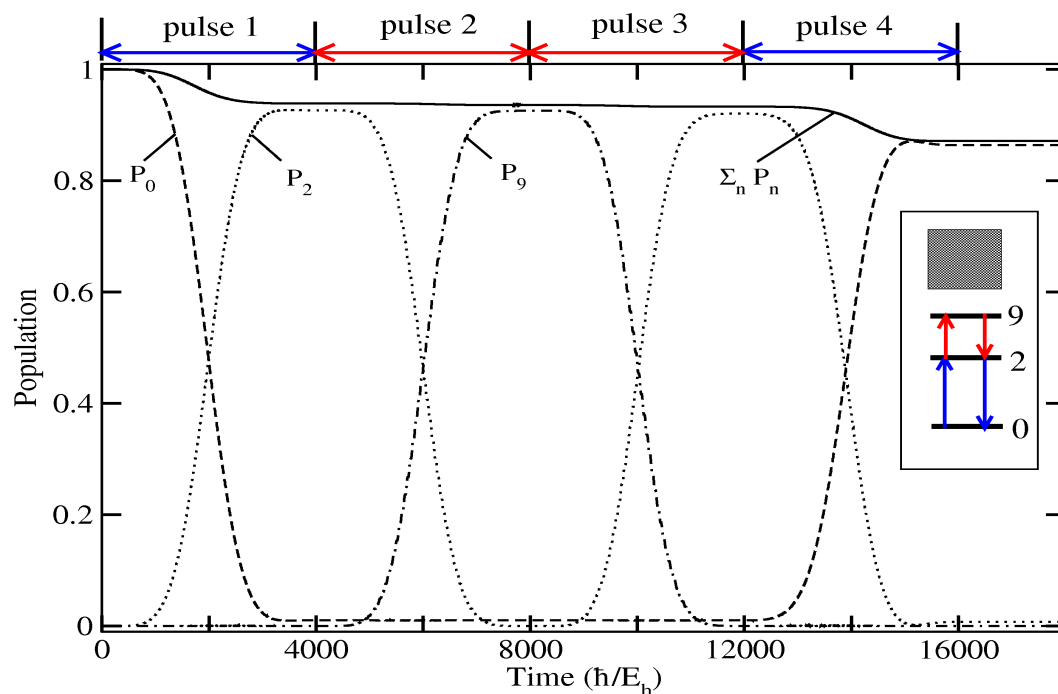
Example: LiCN, 4-pulse excitation

1, 4: $I_{max} \approx 9 \times 10^{13}$ W/cm^2
2, 3: $I_{max} \approx 3.5 \times 10^{11}$ W/cm^2

above threshold ionization

[1] Klinkusch, Saalfrank, Klamroth, JCP **131**, 114304 (2009)

4.1 Treatment of ionization (2)

- **Atom-centered real-space imaginary absorbers**[1] $\boxed{\hat{H}_{el} - \underline{\hat{\mu}}\underline{E}(t) - iV_{abs}(\underline{r})}$

butadiene: absorbers V_{abs}

norm losses depending on field polarization[2]
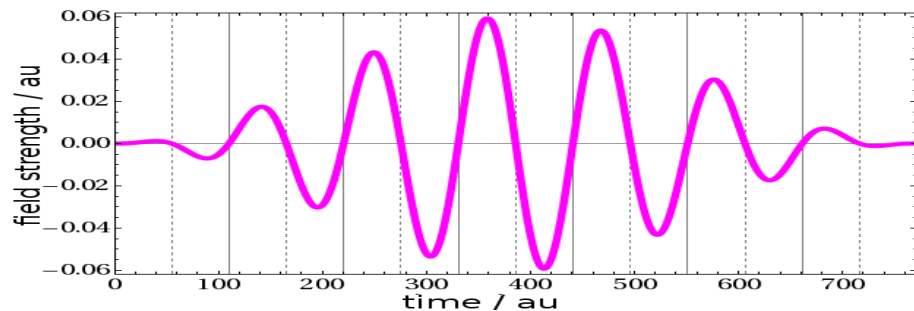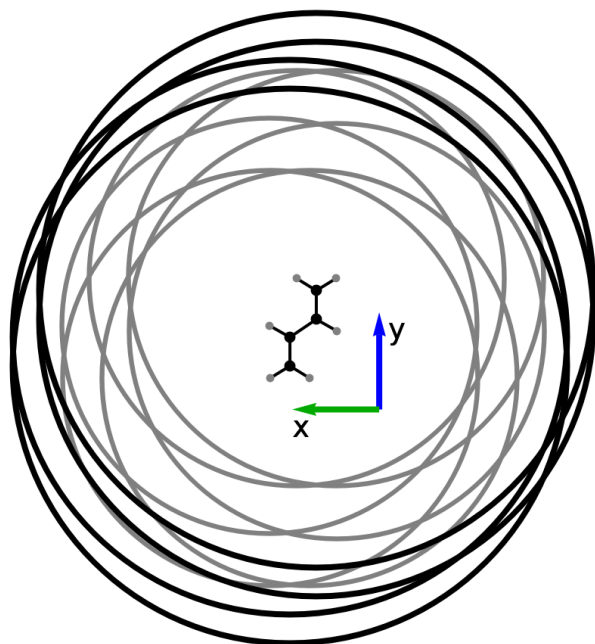
laser field $E(t)$: 800 nm, 7 cycles
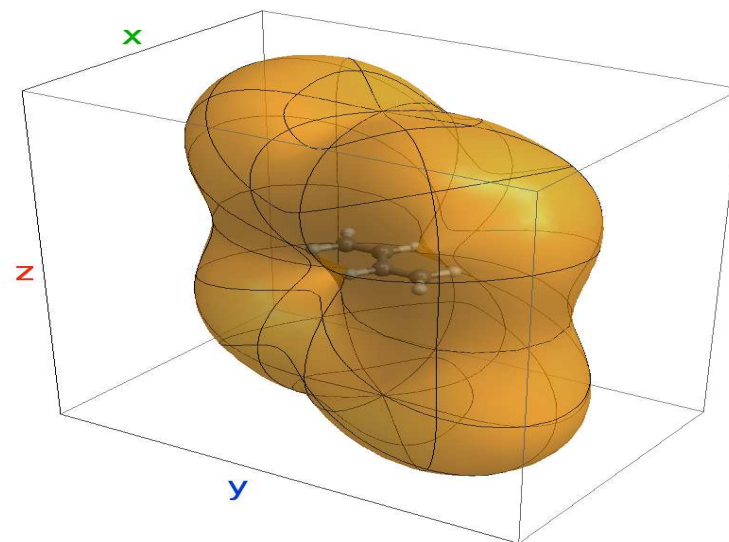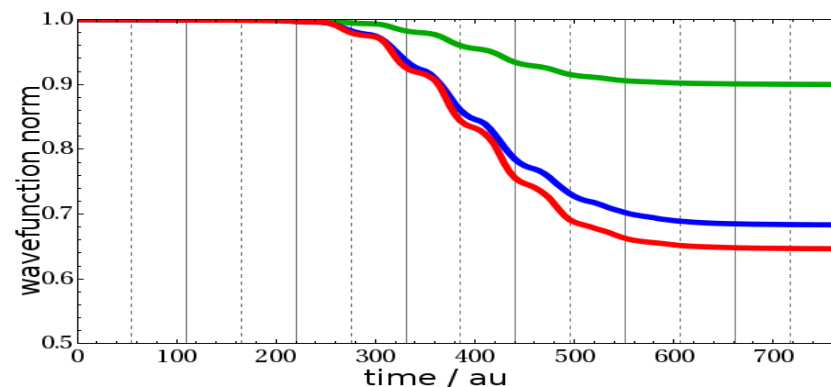
TD-CIS/aug-cc-pVTZ+diffuse fcts.

[1] Schlegel, Krause, JCP **141**, 174104 (2014);   [2] Krause, Saalfrank, unpublished

4.1 Treatment of ionization (3)

- **Atom-centered real-space imaginary absorbers: TD-CIS-CAP[1]** (cont'd)

  - Test: Ionization rates for H_2^+

    - internuclear distance R

    - orientation along z

    - $\sin^2$ pulse, five cycles, 800 nm, $I=10^{14} W/cm^2$

    - various polarizations

    - TD-CIS-CAP[1]/aug-cc-pVTZ *vs.* "exact"[2] calculation
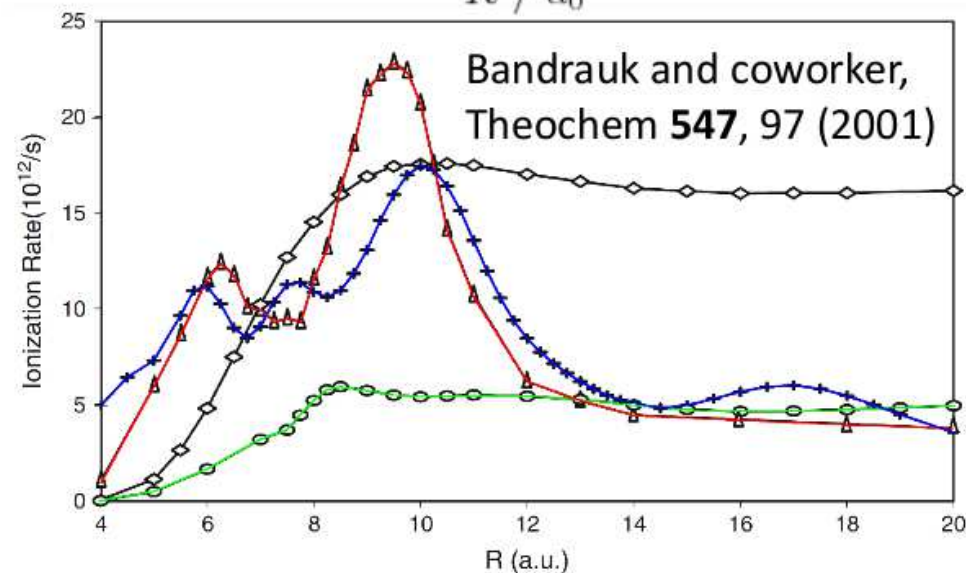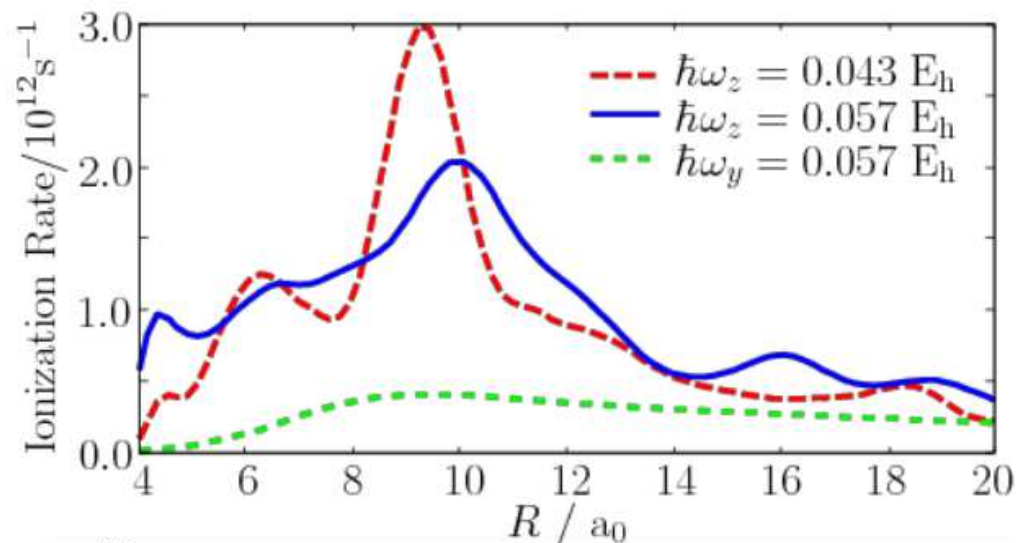
Charge Resonance Enhanced Ionization[2]

[1] Krause, Sonk, Schlegel, JCP **141**, 174104 (2014)   [2] Bandrauk *et al.*, Theochem **547**, 97 (2001)

4.1 Treatment of ionization (4)

- **Further methods / basis sets:**

  - Grid-based methods[1]

  - B-splines/hybrid bases [2]

  - non-AO centered absorbing potentials in real space[3]

  - ADK[4] and other approximate methods

  - R-matrix methods[5]

  - Dyson orbitals[6], . . .

---

[1] Bandrauk; Madsen; Becker; Nest, Klamroth, Saalfrank; McCurdy; many others
[2] Saenz; Martin; Bonitz; Madsen; many others
[3] Scrinzi; Riss, Meyer; Santra; many others
[4] Ammosov, Delone, Krainov, JETP **64**, 1191 (1986)
[5] E.g., Smirnowa and cow., JPB: AMOP **48**, 245101 (2015)
[6] E.g., Oana, Krylov, JCP **127**, 234106 (2007)

4.2 Treatment of nuclear motion

- "Exact" non-Born-Oppenheimer treatment for small systems[1]

- TD-CI and variants: Multi-state models with $\underline{R}$-dependence

$$\left[\hat{T}_{nu}\underline{\underline{1}} + \underline{\underline{V}}(\underline{R},t) + \underline{\underline{\hat{C}}}\right]\underline{\Phi}_{nu}(\underline{R},t) = i\frac{\partial\underline{\Phi}_{nu}(\underline{R},t)}{\partial t}$$

  plus semiclasscial variants ("surface hopping", Landau-Zener)

- (Real-time) TD-DFT: Combination with classical MD[2]

$$\hat{h}_{\text{KS}}(\underline{r},t) = -\frac{1}{2}\Delta + \int \frac{\rho(\underline{r}',t)}{|\underline{r}-\underline{r}'|}\,d\underline{r}' + v(\underline{r},\underline{R}(t),t) + v_{xc}(\underline{r},t)$$

  with, _e.g._, Ehrenfest coupling

- MCEND: Multi Configurational Electron and Nuclear Dynamics[3,4]

$$\Psi(\underline{x},\underline{R},t) = \sum_{J_{el}}\sum_{J_{nu}} A_{J_{el}J_{nu}}(t)\Psi_{el,J_{el}}(\underline{x},t)\,\Phi_{nu,J_{nu}}(\underline{R},t))$$

  with Slater determinants $\Psi_{el,J_{el}}$ and nuclear Hartree products $\Phi_{nu,J_{nu}}$

---

[1] Bandrauk; Manz; Paramonov; Lein; Gross; many others
[2] E.g., Provorse, Isborn, IJQC **116**, 739 (2016), and references therein.
[3] Ulusoy, Nest, JCP **136**, 054112 (2012)
[4] For a similar MCTDH-like approach, see: Haxton, Lawler, McCurdy, PRA **83**, 063416 (2011)

4.3 Treatment of dissipation

- **Open-system density matrix theory in a nutshell**[1]: $\hat{H} = \hat{H}_s + \hat{H}_b + \hat{H}_{sb}$

expectation value $\hat{A}$

$$\boxed{\langle \hat{A} \rangle(t) = \mathrm{tr}\{\hat{\rho}(t)\ \hat{A}\}}$$

$\uparrow$

density operator of system-bath

$$\boxed{\hat{\rho} = \sum_n w_n |\Psi_n\rangle\langle\Psi_n|}$$

Liouville-von Neumann equation

$$\boxed{\frac{\partial\hat{\rho}(t)}{\partial t} = -\frac{i}{\hbar}\left[\hat{H}_s + \hat{H}_b + \hat{H}_{sb}, \hat{\rho}\right]}$$

reduced density matrix: $\hat{\rho}_s = \mathrm{tr}_b\hat{\rho}$

bath approximation

Markov approximation: $\dot{\hat{\rho}}_s(t) = f[\hat{\rho}_s(t)]$

$\downarrow$

LvN equation for *open* system

$$\boxed{\frac{\partial\hat{\rho}_s(t)}{\partial t} = -\frac{i}{\hbar}\left[\hat{H}_s, \hat{\rho}_s\right] + \left(\frac{\partial\hat{\rho}_s}{\partial t}\right)_D}$$

$\downarrow$

Redfield, Lindblad

- **Lindblad disspative part**

$$\boxed{\left(\frac{\partial\hat{\rho}_s}{\partial t}\right)_D = \mathcal{L}_D\hat{\rho} = \sum_k \left(\hat{C}_k\hat{\rho}_s\hat{C}_k^\dagger - 1/2\left[\hat{C}_k^\dagger\hat{C}_k, \hat{\rho}_s\right]_+\right)}$$

with *Lindblad operators* $\hat{C}_k$ accounting for *energy* and *phase relaxation*, for example.

[1] Blum, *Density Matrix Theory and Applications*, Plenum (1996)

4.3 Treatment of dissipation (2)

- ## LvN equation for laser-driven electrons: The ρ-TD-CI method[1]

$$\frac{\partial \hat{\rho}_s}{\partial t} = \underbrace{-\frac{i}{\hbar}[\hat{H}_{el} - \underline{\hat{\mu}}\underline{E}(t), \hat{\rho}_s]}_{\text{system}} + \underbrace{\left(\frac{\partial \hat{\rho}_s}{\partial t}\right)_D}_{\text{dissipation}}$$

perturbation

energy relaxation

coupling, $\hat{H}_{sb}$

system, $\hat{H}_s$

dephasing

bath, $\hat{H}_b$
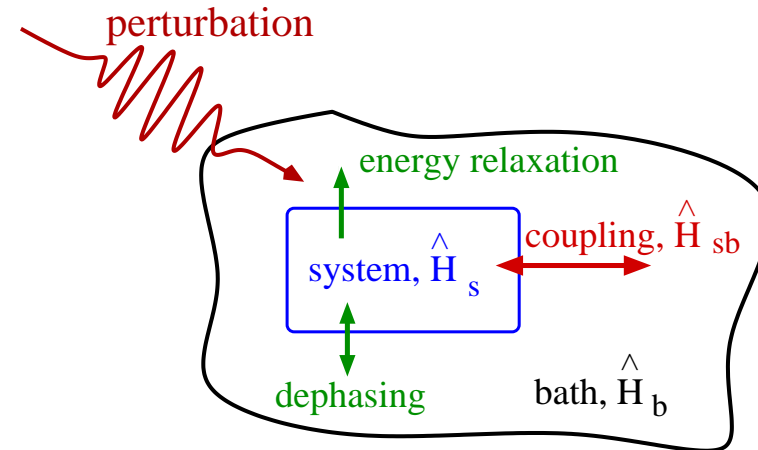
- ## Lindblad dissipation, CI eigenstate basis (N states)

Populations: Diagonal elements of $\hat{\rho}_s$, $\rho_{nn} = \langle n|\hat{\rho}_s|n\rangle$

$$\frac{d\rho_{nn}}{dt} = \sum_{p}^{N}[-\frac{i}{\hbar}[V_{np}(t)\rho_{pn} - \rho_{np}V_{pn}(t)] + (\Gamma_{p\to n}\rho_{pp} - \Gamma_{n\to p}\rho_{nn})]$$

V_{mn} $\Gamma_{n->m}$

n

m
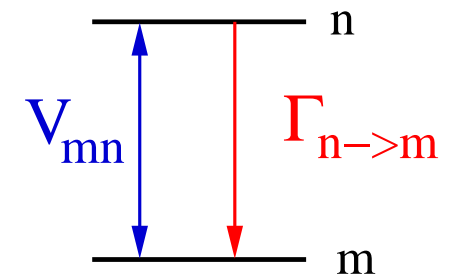
The ρ_{nn} (state populations for state n) change according to:

- dipole coupling: $\boxed{V_{mn}(t) = -\underline{\mu}_{mn}\underline{E}(t)}$

- energy relaxation: $\boxed{\hat{C}_k \to \sqrt{\Gamma_{n\to m}}|m\rangle\langle n|}$, with rates $\Gamma_{n\to m}$

Dephasing enters *via* an e.o.m for off-diagonals $\dot{\rho}_{mn}$ through dephasing rates γ_{mn}.

[1] Tremblay, Klamroth, Saalfrank, JCP **129**, 084320 (2008)

4.3 Treatment of dissipation (3)

- **Spontaneous emission in vacuum**[1]

$$\Gamma_{m \to n} = A_{mn} = \frac{\omega_{mn}^3}{3\pi\hbar\epsilon_0 c^3}\,\mu_{mn}^2$$

LiCN, $|0\rangle \to |2\rangle$ transition, $A_{20}^{-1} = 43$ ns, 50 and 1 ns π pulses, ρ-TD-CIS(D)/6-31G*
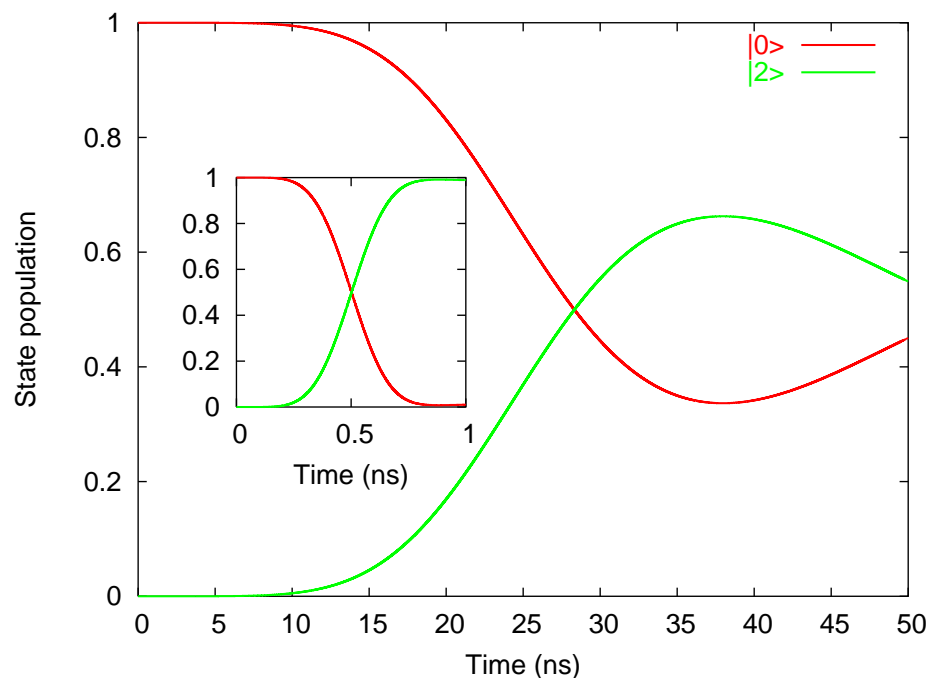
only for long pulses important, selective

- **Relaxation at a "metal surface"**

$$\Gamma_{m \to n} = A_{mn} \cdot 10^5$$

$A_{20}^{-1} = 430$ fs, 5 and 75 fs π pulses
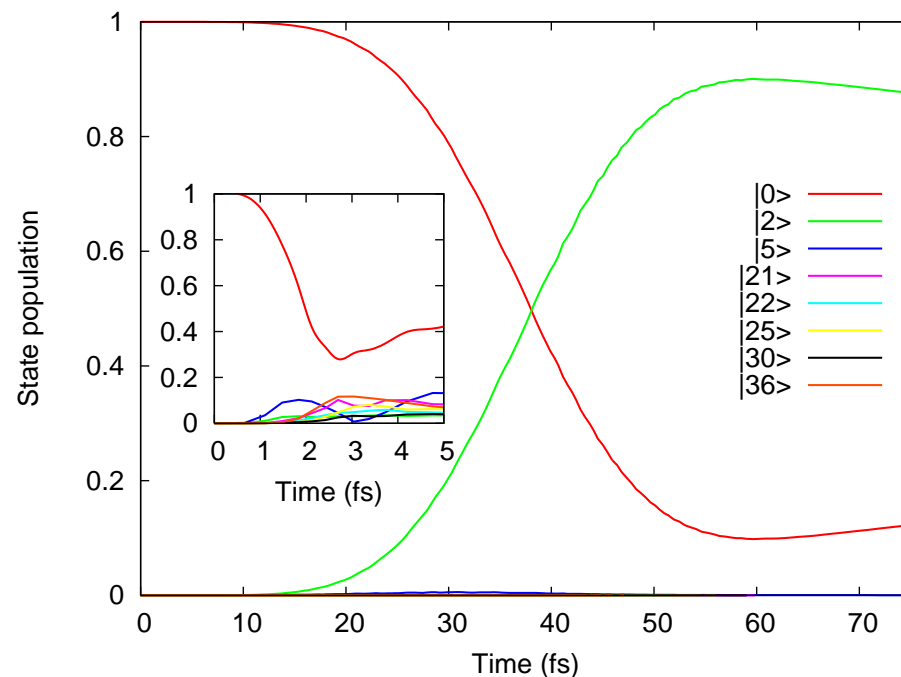
short pulses needed, less selective

[1] Tremblay, Klamroth, Saalfrank, JCP **129**, 084320 (2008)

4.4 Beyond the dipole approximation

- **Inclusion of magnetic dipole term in TD-CI[1]**

  - Chiral distinction by femtosecond laser ionization[2]

    $(R-)A + L/R\text{-circ. pol. } h\nu \rightarrow (R-)A^+ + e^-$

    $(L-)A + L/R\text{-circ. pol. } h\nu \rightarrow (L-)A^+ + e^-$
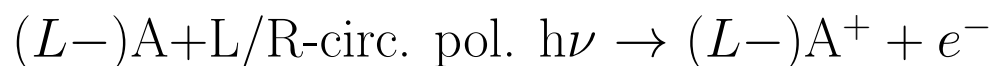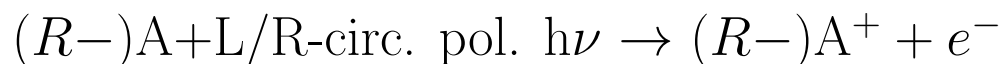
    circular dichroism in ion yield

    $$CD = 2\,\frac{Y_{LCP} - Y_{RCP}}{Y_{LCP} + Y_{RCP}}$$

  - 3-methyl-cyclopentanone

(S)   (R)
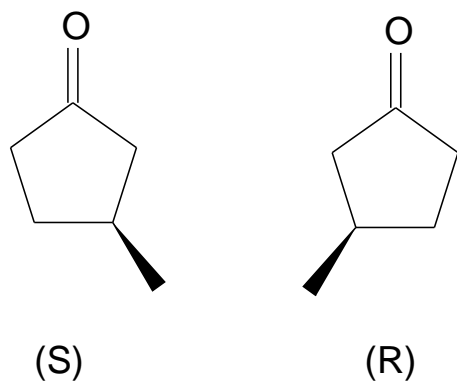
magnetic dipole coupling $n(S_0) \rightarrow \pi^*(S_1)$

$$\hat{V}(t) = -\underline{\mu}\,\underline{E}(t) + \underline{m}\,\underline{B}(t)$$

$n\pi^*$ transition is dipole-forbidden but magnetic-dipole allowed
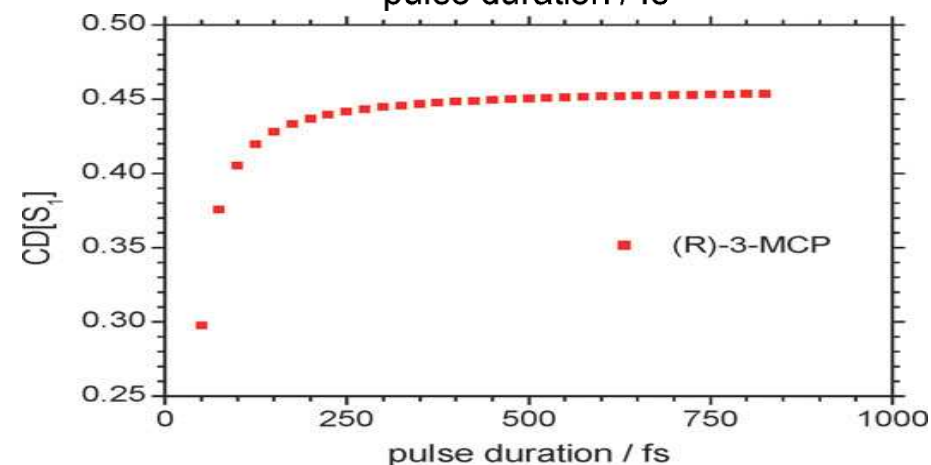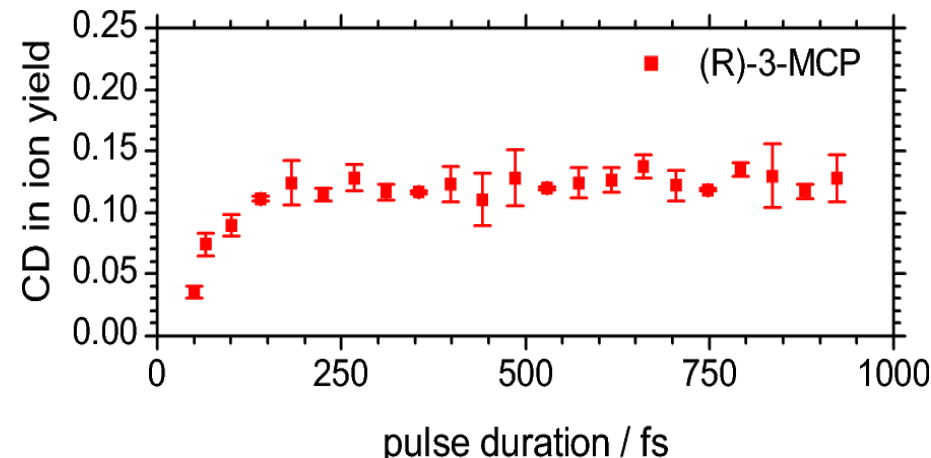
[1] Kröner, PCCP **17**, 19643 (2015) ; Horsch, Urbasch, Weitzel, Kröner, PCCP **13**, 2378 (2011)

4.5 Optimal control of electron dynamics: QOCT

- **Time-dependent Schrödinger equation:**

$$i\hbar \frac{\partial}{\partial t}|\Psi\rangle = \hat{H}_{el}(t)|\Psi\rangle \qquad \text{forward propagation from } t = 0, |\Psi(0)\rangle = |\Psi_0\rangle$$

$\hat{H}_{el}(t) = \hat{H}_{el} - \hat{\mu}\underline{E}(t)$. Optimal field is to be found.

- **Maximize constrained target functional J:**

$$J = \langle\Psi(t_f)|\hat{O}|\Psi(t_f)\rangle - \alpha \int_0^{t_f} |\underline{E}(t)|^2 dt - \int_0^{t_f} dt \langle\Phi(t)|\frac{\partial}{\partial t} + \frac{i}{\hbar}\hat{H}_{el}(t)\Psi(t)\rangle + c.c.$$

$\hat{O} = $ *target operator*; $\alpha = $ penalty to avoid strong fields; $t_f = $ final control time

- **Lagrange function $\Phi(t)$: Backward propagation**

$$i\hbar \frac{\partial}{\partial t}|\Phi(t)\rangle = \left[\hat{H}_{el} - -\hat{\mu}\underline{E}(t)\right]|\Phi(t)\rangle \qquad \text{backward from } t = t_f, |\Phi(t_f)\rangle = \hat{O}|\Psi(t_f)\rangle$$

- **Calculate field iteratively to self-consistency**

$$\underline{E}(t) = -\frac{1}{\hbar\alpha} \text{Im}\langle\Phi(t)|\hat{\mu}|\Psi(t)\rangle$$

[1] Rabitz and cow., JCP **88**, 6870 (1988); Kosloff and cow., CP **139**, 201 (2009); Klamroth, JCP **124**, 144310 (2006)

4.5 Optimal control of electron dynamics (2)

- **A first example: State-selective excitation**[1]

N-methyl-6-quinolone, TD-CIS(D)

hν

e$^-$
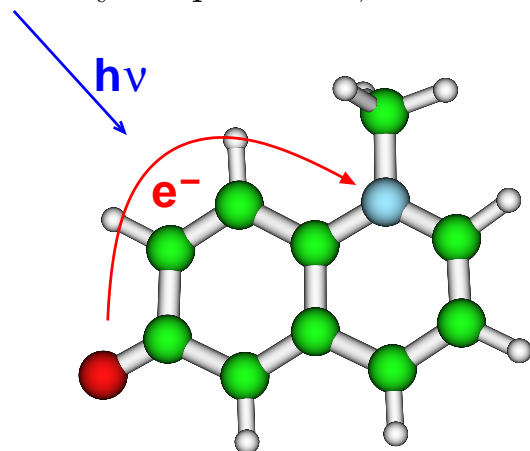
goal: selective $S_0 \to S_1$ transition

an optimal 6fs laser pulse
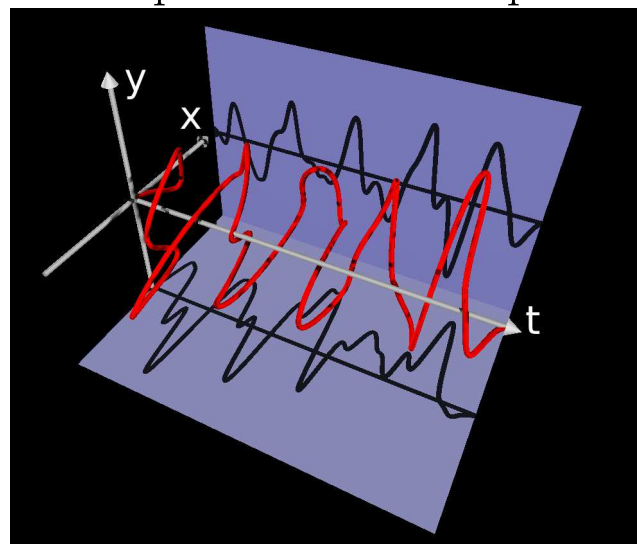
- **Multi-state models and selectivity**

intense pulses require multi-state models
due to multi-photon excitation
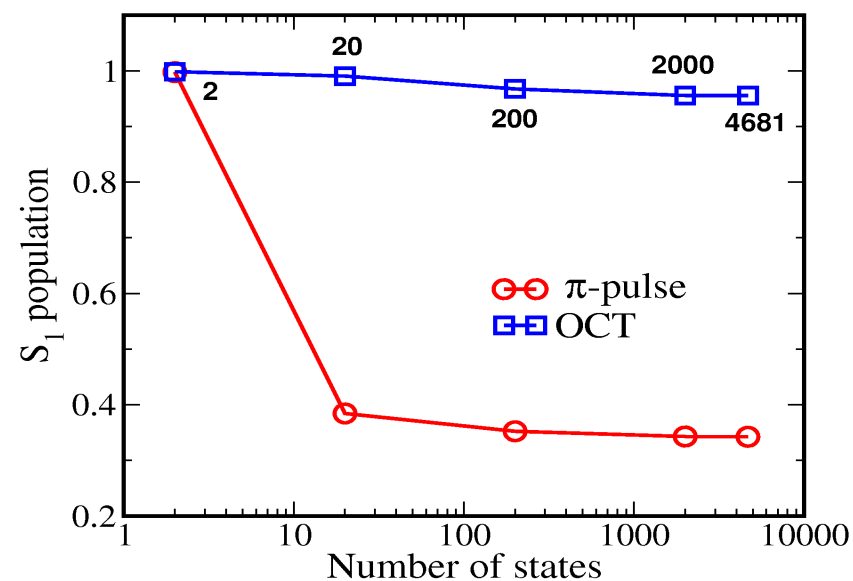
[1] Klamroth, JCP **124**, 144310 (2006)

4.5 Control of electron dynamics (3): Further aspects

- Time-dependent targets[1] and (multiple) "terminal" (t_f) targets

- Further constraints[1]: Frequency range, t-dependent shape $\alpha(t)$, $\int \underline{E}\, dt = 0, \ldots$

- Guided Local Optimal Control[2] (GLOCT)

- Hybrid local / optimal control[3]

- Stochastic Pulse Optimization[4] (SPO)

$$E(t) = s(t) \sum_{l=0}^{l=f-1} \left[a_l \cos\left(2\pi\nu_l t\right) + b_l \sin\left(2\pi\nu_l t\right) \right]$$

define *fitness* to judge on quality of stochastically determined coefficients

- Optimal control in dissipative environments[5,2,3,6]

- Coherent control[7]

- Rational pulse design: Analytic pulses = f$(\omega, s(t), E_0, \phi, \text{polarization})$

[1] E.g., Serban, Werschnik, Gross, PRA **71**, 053810 (2005)
[2] Tremblay, Saalfrank, PRA **78**, 063408 (2008)
[3] Beyvers, Saalfrank, JCP **128**, 074104 (2008)
[4] E.g., Schönborn, Klamroth, P. Saalfrank, JCP **144**, 044301 (2016); Gross *et al.*
[5] E.g., S. Beyvers, Y. Ohtsuki, P. Saalfrank, JCP **124**, 234706 (2006)
[6] RI-sTDCI, where both dissipation and pulse optimization are stochastic: Klinkusch, Tremblay, JCP **144**, 184108 (2016)
[7] E.g., Brumer and Shapiro: Interference strategy

5. APPLICATIONS:
LASER-DRIVEN DYNAMICS

5.1 State-to-state excitation

- **Laser-pulse excitation of H_2**
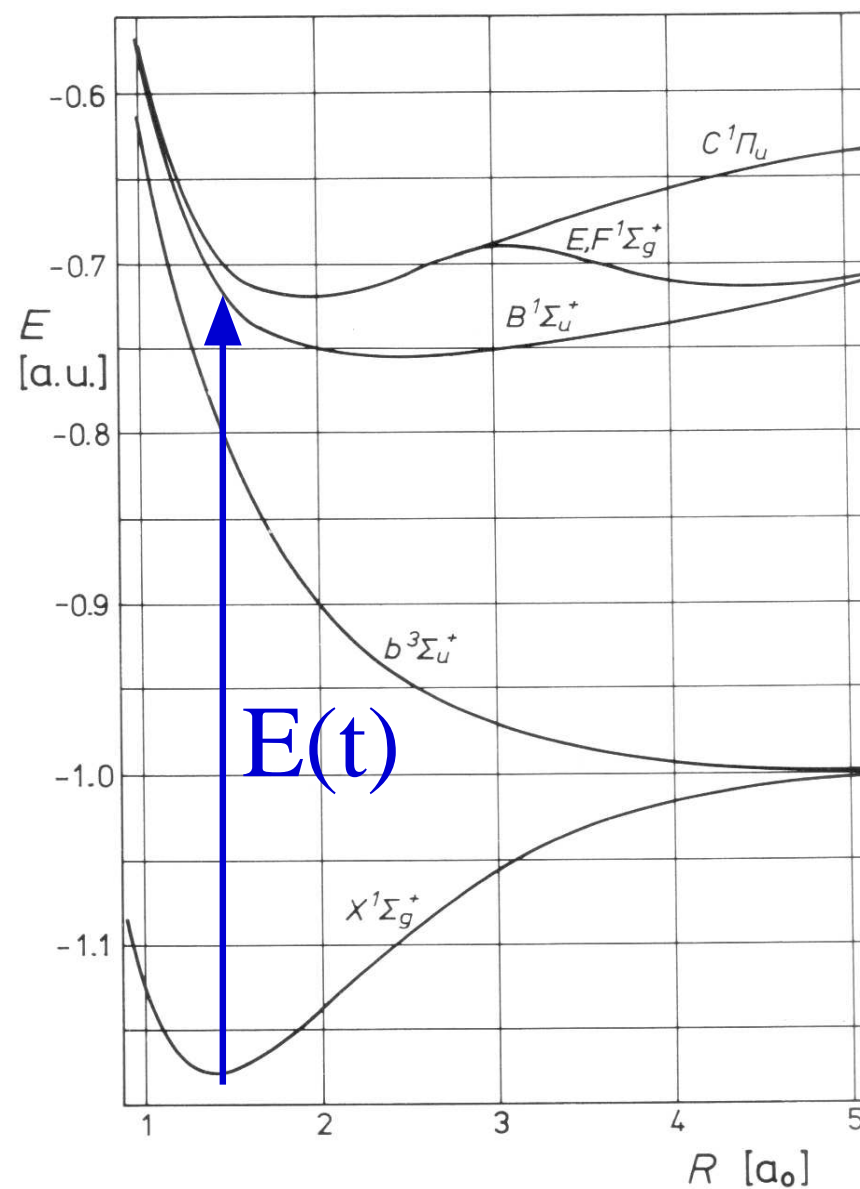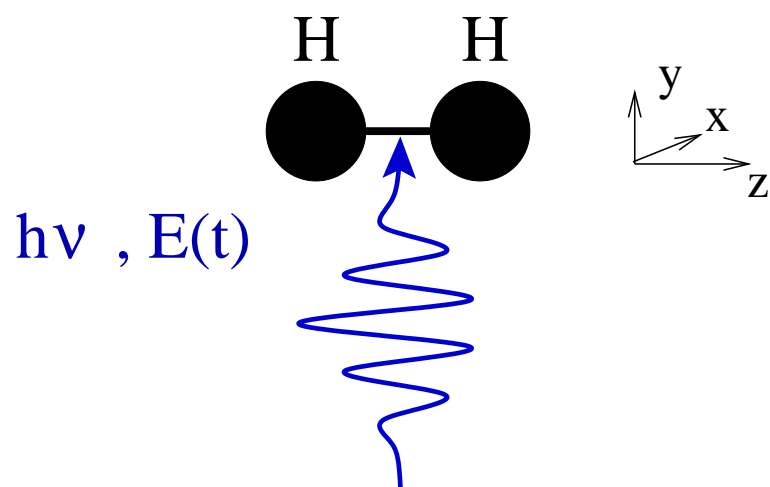
H   H

$h\nu$, E(t)

E(t)

Potential curves: $C\,^1\Pi_u$, $E,F\,^1\Sigma_g^+$, $B\,^1\Sigma_u^+$, $b\,^3\Sigma_u^+$, $X\,^1\Sigma_g^+$

5.1 State-to-state excitation (2)

- **TD-CISD (=FCI): Laser-pulse excitation of H$_2$[1]**

TD-CIS/aug-cc-pV5Z; $|0\rangle \rightarrow |1\rangle$ ($^1\Sigma_u^+$) laser excitation

with sin^2-shaped π-pulses $\boxed{E_z(t) = E_0 \sin^2(\pi t/2\sigma) \cos(\omega_{10}t)}$ with FWHM σ
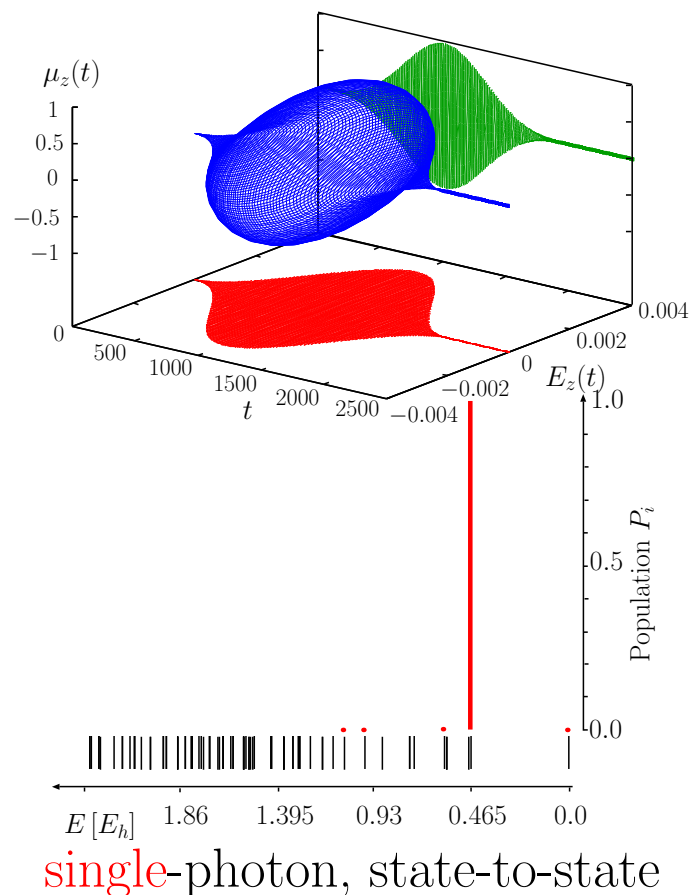
"long pulse": $\sigma = 1000\ \hbar/E_h$ "short pulse": $\sigma = 50\ \hbar/E_h$

single-photon, state-to-state   multi-photon, wavepacket
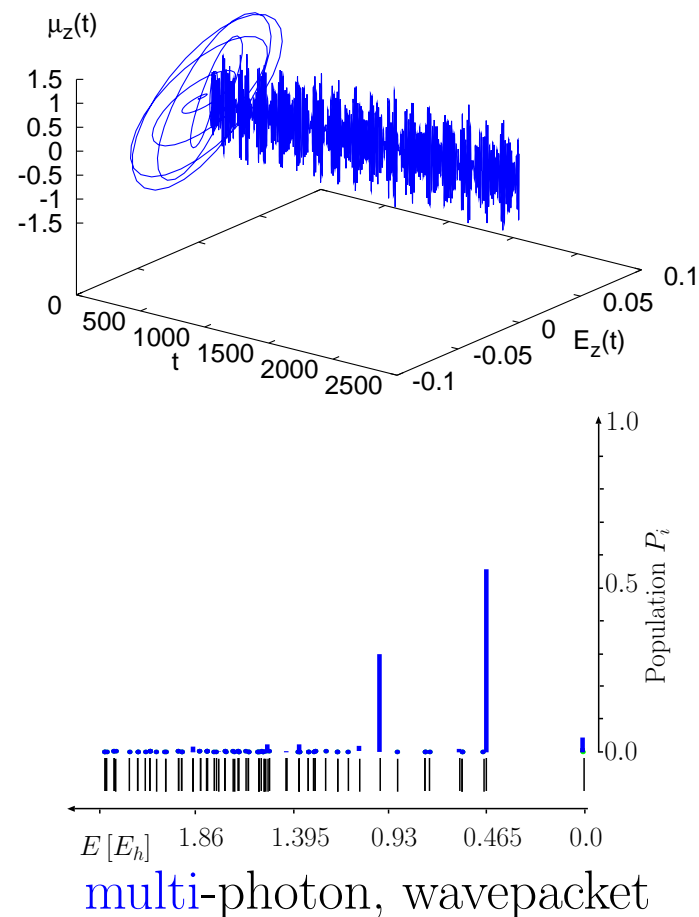
5.1 State-to-state excitation (3)

- **LiCN: A molecular dipole switch?[1]**

CIS(D)/6-31G* state energies of LiCN: $\boxed{E_i^{\text{CIS(D)}} = E_i^{\text{CIS}} + E_i^{(D)}}$
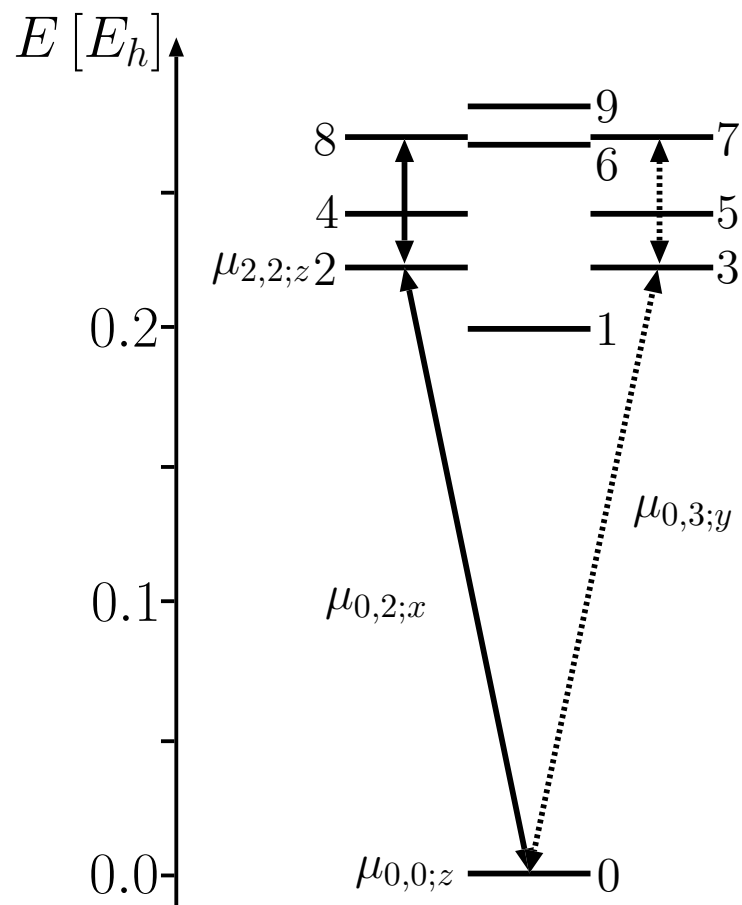
Computed dipole moments:

state	character	dipole μ_z (e a_0)
0	Li^+CN^-	-3.71
2/3	LiCN	+2.80
7/8	$Li^{\delta+}CN^{\delta-}$	-1.18
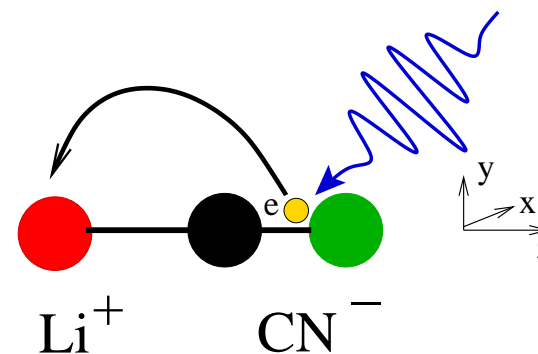
- Goal: Laser-pulse controlled dipole switch

[1] Krause, Klamroth, Saalfrank, JCP **123**, 074105 (2005)

5.1 State-to-state excitation (4)

- **LiCN: TD-CIS(D) calculations**[1]

TD-CIS/6-31G*; $|0\rangle \to |2\rangle$ laser excitation

with $\sin^2$-shaped π-pulses $\boxed{E_x(t) = E_0 \sin^2(\pi t/2\sigma)\ \cos(\omega t)}$ with FWHM σ
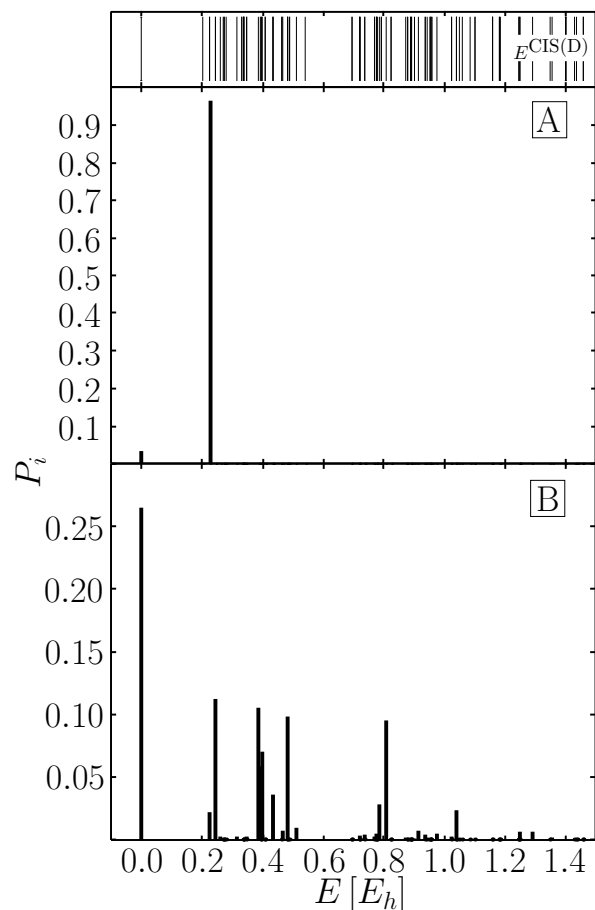
long pulse $[\sigma = 2000\ \hbar/E_h\ (50\ \text{fs})]$

$\Longrightarrow$ eigenstate

short pulse $[\sigma = 100\ \hbar/E_h\ (2\ \text{fs})]$

$\Longrightarrow$ electronic wavepacket

[1] Krause, Klamroth, Saalfrank, JCP **123**, 074105 (2005)

5.1 State-to-state excitation (5)

- **LiCN: TD-CIS(D) calculations[1]**

Dipole moments, obtained with $\sin^2$ laser pulses with different *polarizations*: $E_x(t)$, $E_z(t)$

$\sigma = 100 \; [h/(2\pi E_h)]$

$\sigma = 2000 \; [h/(2\pi E_h)]$

$\mu_z(t) \; [ea_0]$

$t \; [h/(2\pi E_h)]$

$E_x(t)$

$E_z(t)$
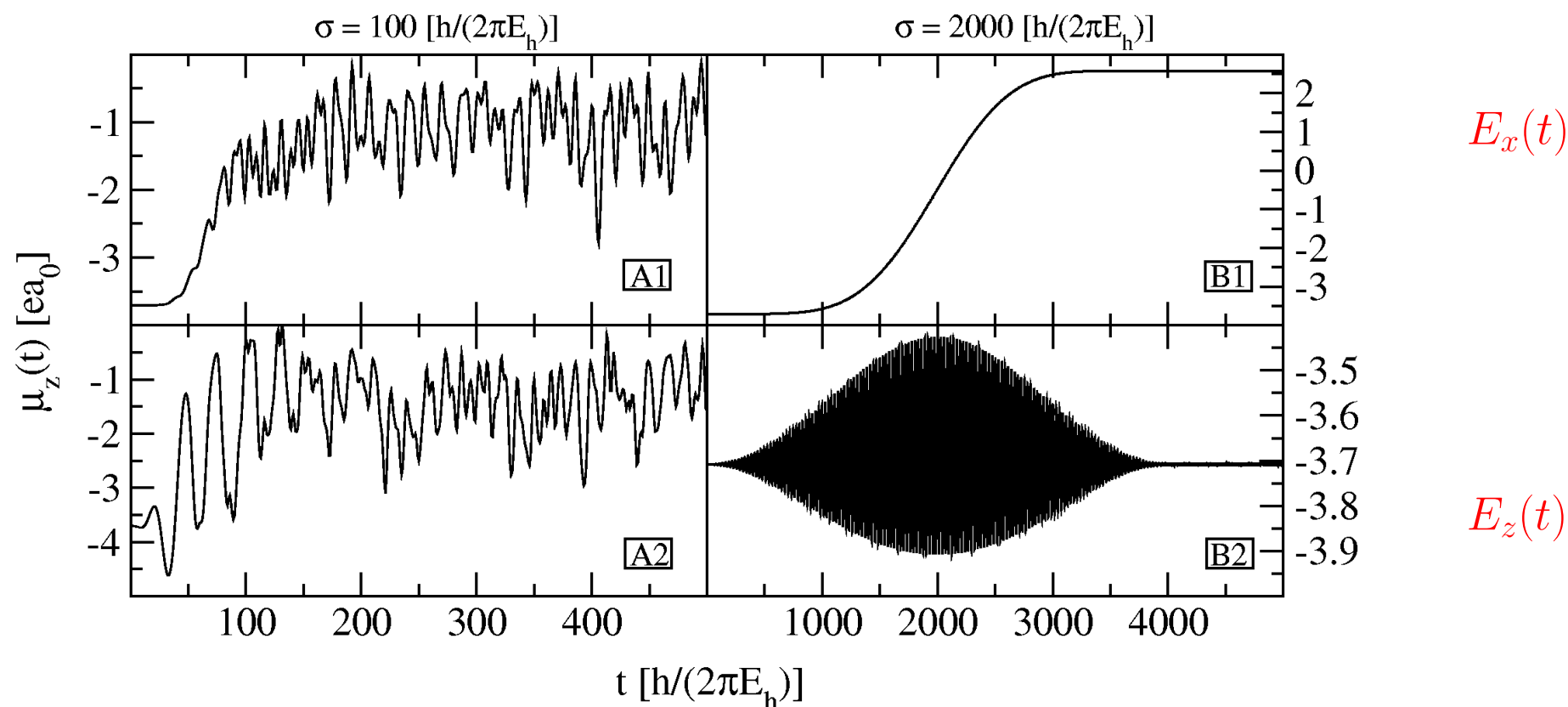
dipole switch with "long", x-polarized pulse

[1] Krause, Klamroth, Saalfrank, JCP **123**, 074105 (2005)

5.1 State-to-state excitation (6)

● **LiCN: TD-CIS(D) calculations**[1]

  Switching sequences of π-pulses
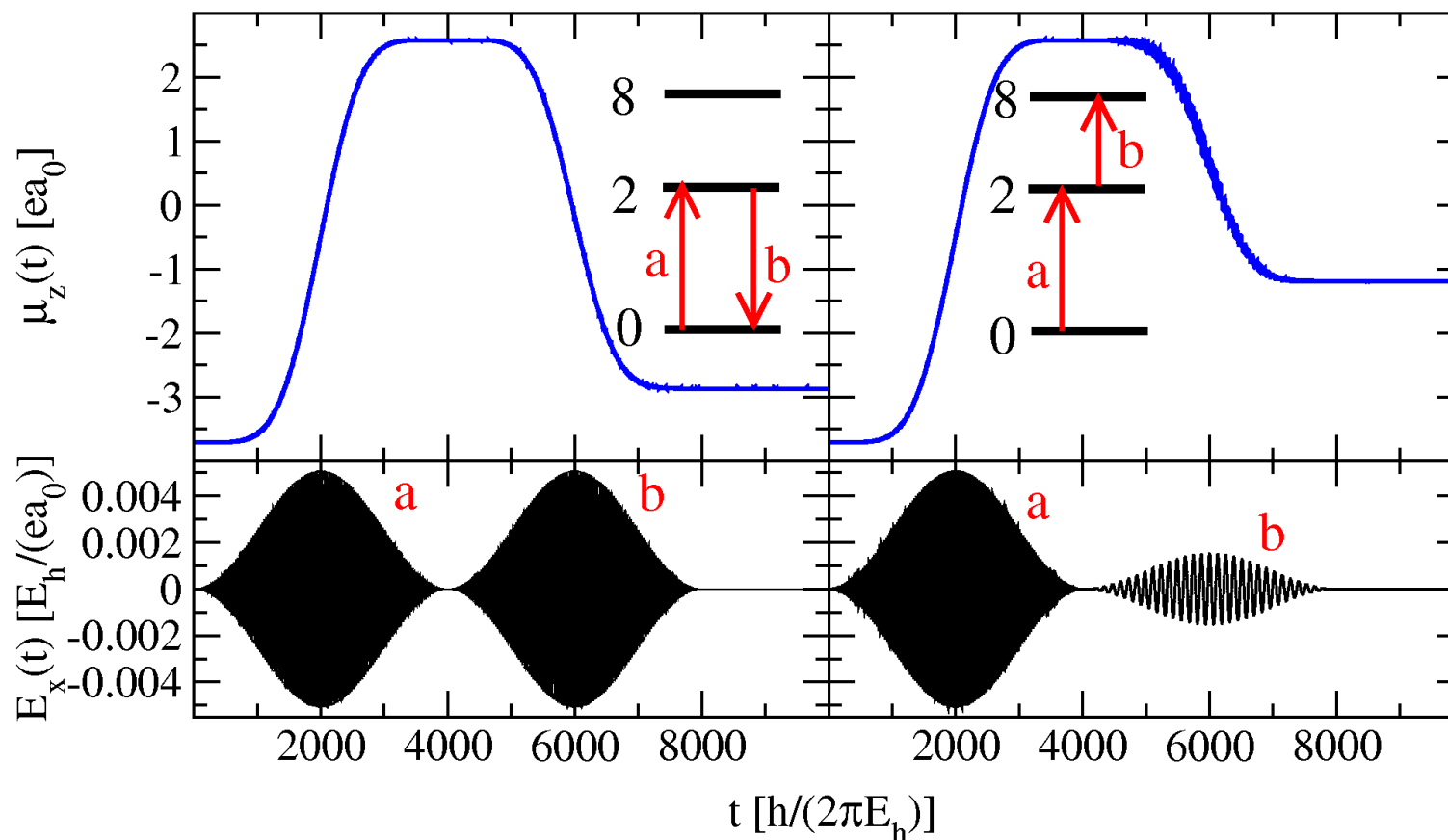
reversible and "branched switching"

[1] Krause, Klamroth, Saalfrank, JCP **123**, 074105 (2005)

5.1 State-to-state excitation (7)

- **Switching in larger molecules[1]**

Molecules NC-(Ph)$_n$-Li with $n = 1, 2, 3$

x = molecular axis
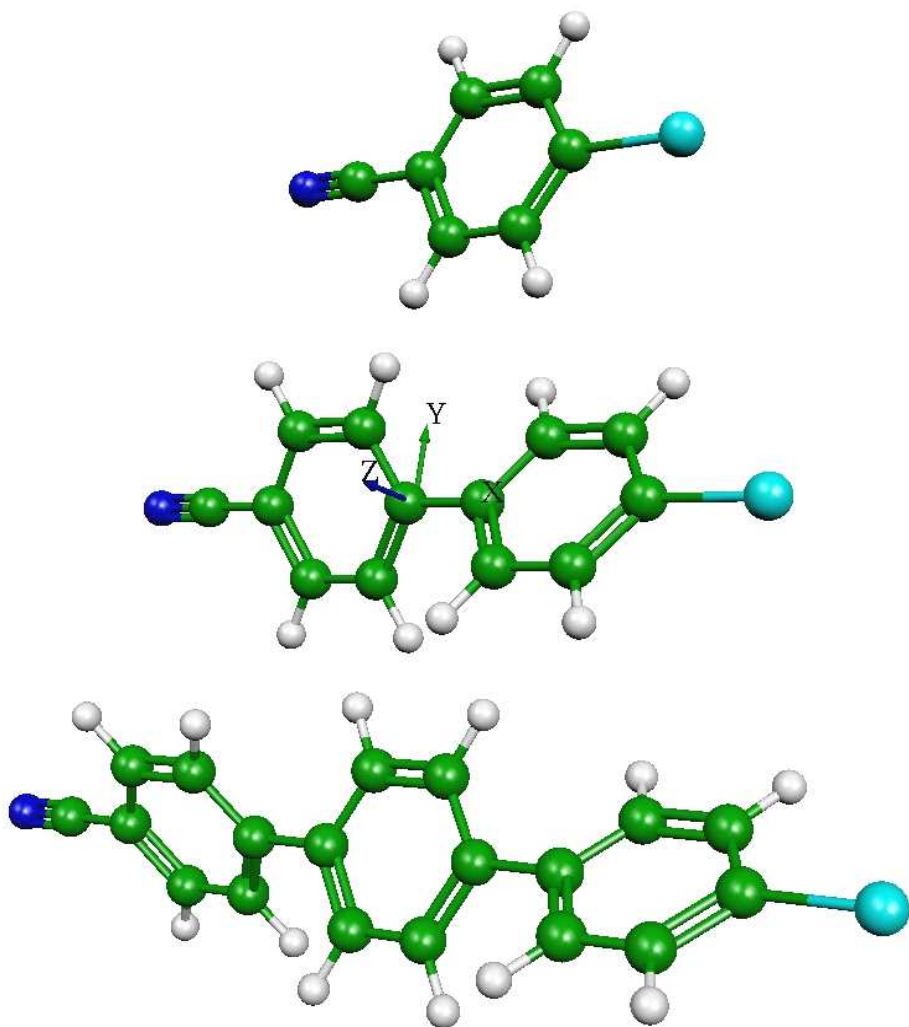
$n = 1$: π pulse $\perp$ to molecular axis
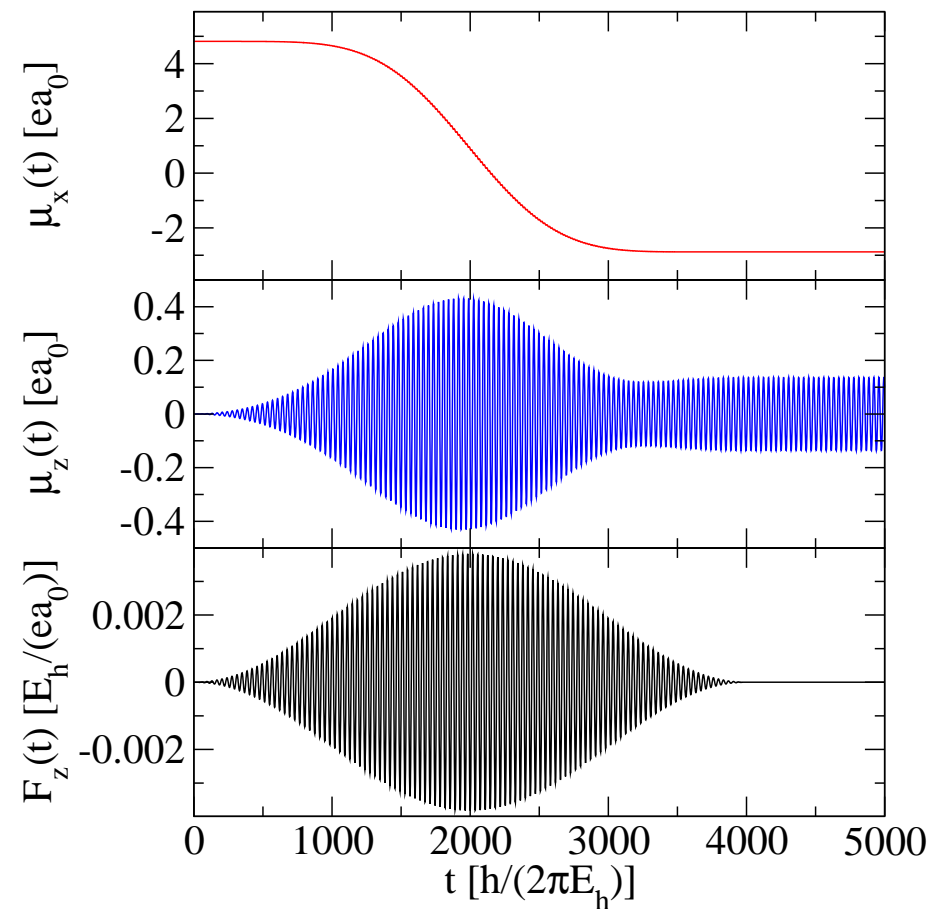
some loss of state-selectivity

[1] Krause, Klamroth, JCP **128**, 23407 (2008)

5.1 State-to-state excitation (8)

- **Intermolecular, long-range charge transfer in a Donor-Acceptor system[1]**

  - Model system: $C_2H_4 \cdots C_2(CN)_4$

HOMO (D)

LUMO (A)
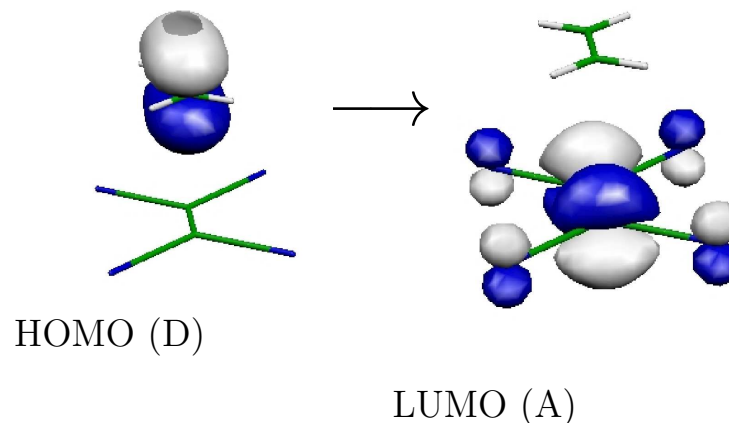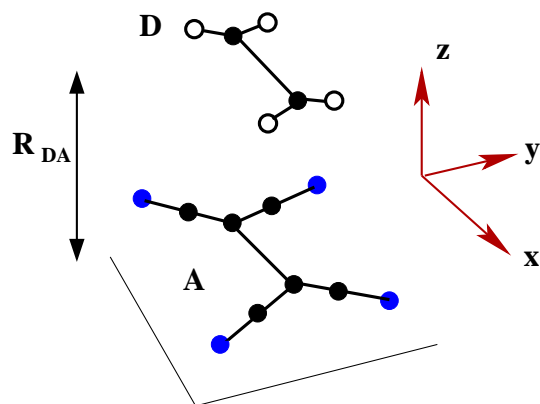
  - Potential energy curves: CIS vs. LR-TD-DFT

CIS/6-31G*

TD-BP86/6-31G*
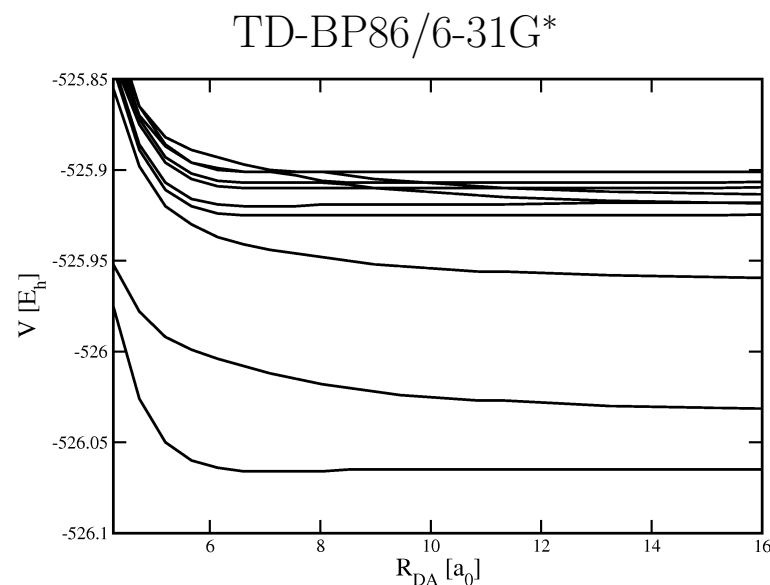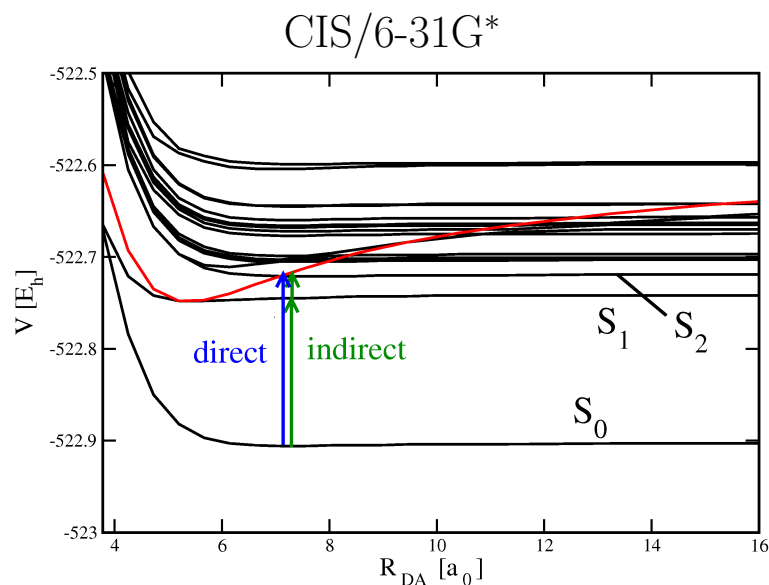
correct 1/R behaviour (ideal: $\Delta = IP(D)+EA(A)-1/R$)

no correct 1/R behaviour

[1] Klinkusch, Klamroth, Saalfrank, PCCP **11**, 3875 (2009)

5.1 State-to-state excitation (9)

- **Intermolecular, long-range charge transfer** (cont'd)

  - Single ($\sin^2$) π pulses $S_0 \rightarrow S_2$

    $\mu_{02,x} = 0.86$ ea$_0$, $\hbar\omega_{02,x} = 0.2207$ E$_h$, $R_{DA} = 7.21$ a$_0$

    ethylene   TCNE

    dipole moment μ_z:

    σ = 125
    σ = 250
    σ = 2000

    Long pulses selective

  - Back-switching with π: √

  - π pulse *vs.* OCT pulse

    σ = 125 ℏ/E$_h$, dipole moment μ_z
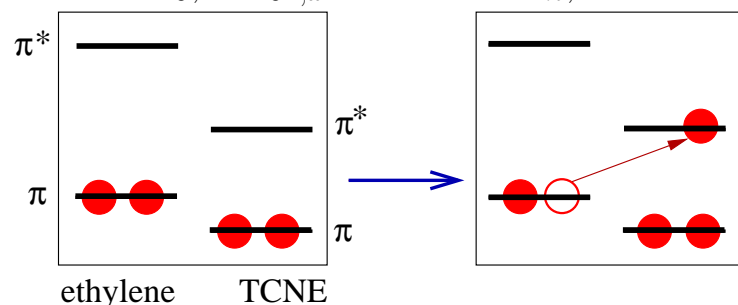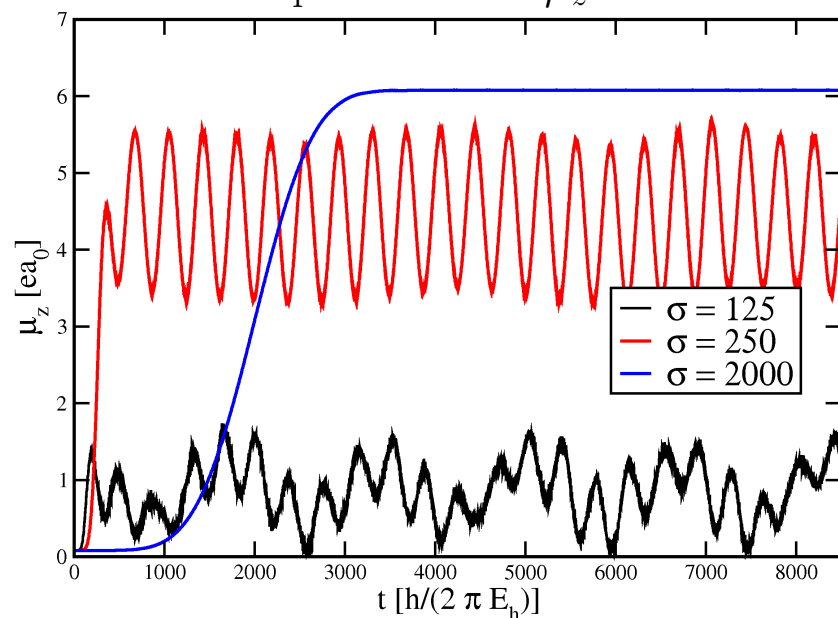
    π pulse
    OCT pulse
    target (S$_2$)
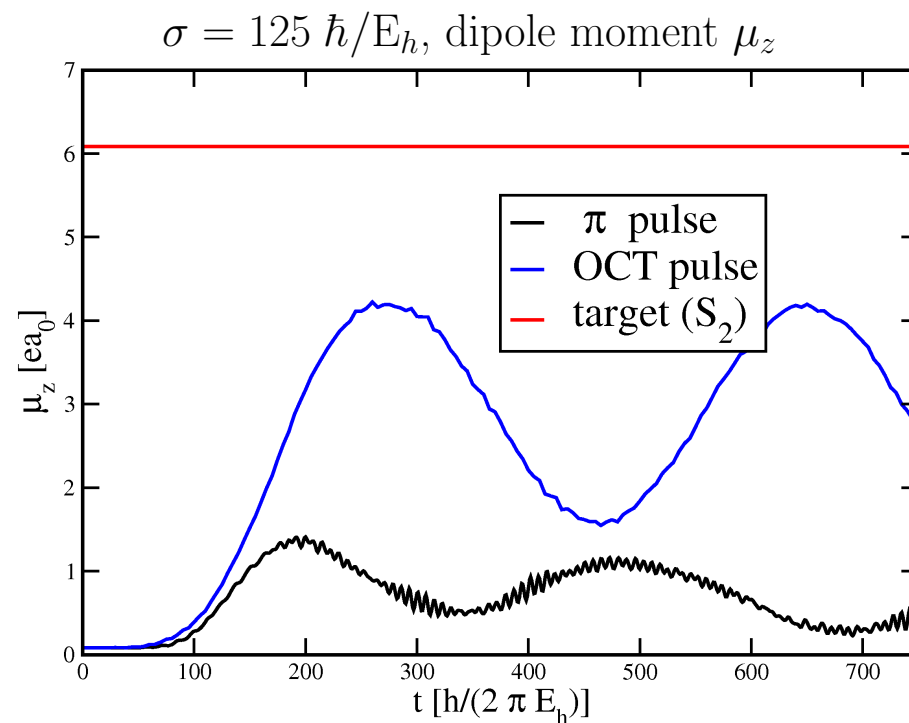
    Better selectivity for short pulses

[1] Klinkusch, Klamroth, Saalfrank, PCCP **11**, 3875 (2009)

5.1 State-to-state excitation (10)

- **Intermolecular, long-range charge transfer** (cont'd)

- **π pulse sequence $S_0 \to S_1 \to S_2$**

  - **Trimer: DDA**

2 pulses, $\sigma_{1,x} = \sigma_{2,z} = 2000\ \hbar/E_h$, can overlap
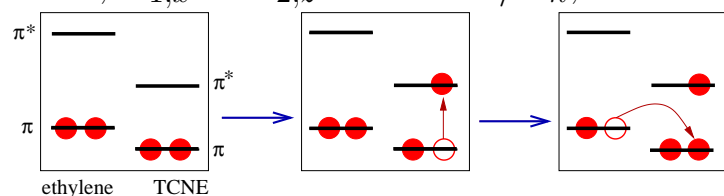
2 pulses, $\sigma_{1,x} = \sigma_{2,z} = 1000\ \hbar/E_h$, non-overlapping
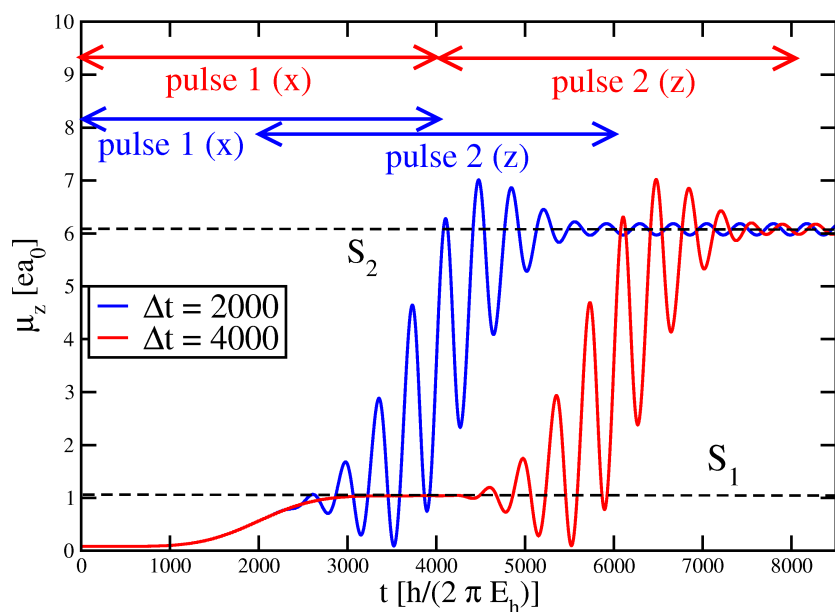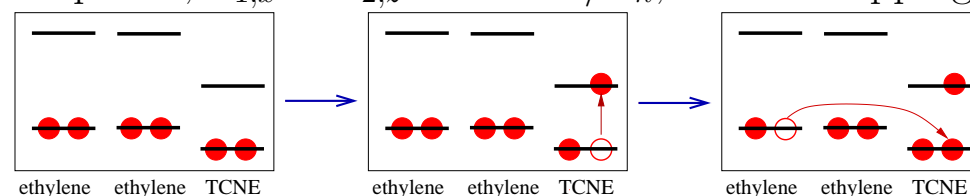
| still highly selective, F small | | Long-distance transfer |
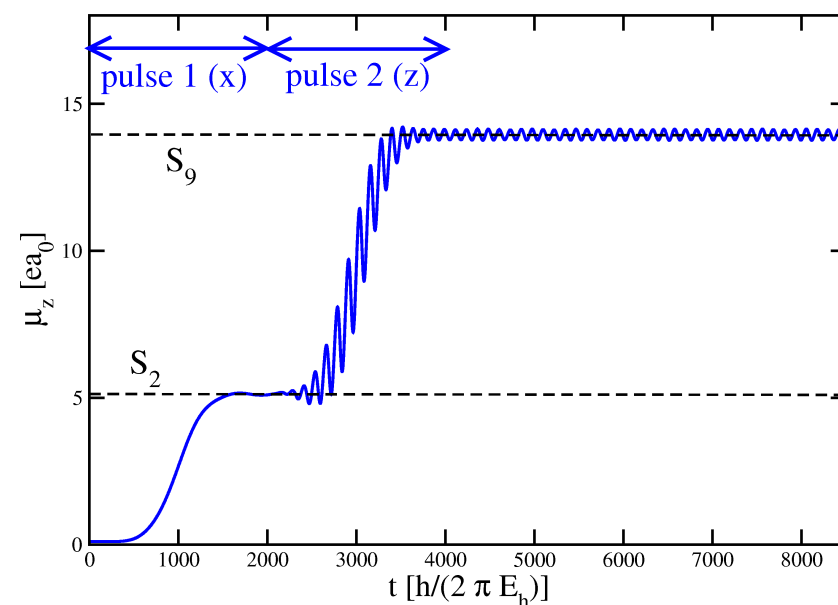
Also: DDDA, 3 pulses

[1] Klinkusch, Klamroth, Saalfrank, PCCP **11**, 3875 (2009)

5.1 State-to-state excitation (11)

- **Effects of ionization and dissipation**[1]

  - ρ-TDCI extended by complex absorbers in state-space[1]

    Liouville-von Neumann equation with loss terms

    $$\frac{\partial \hat{\rho}}{\partial t} = -\frac{i}{\hbar}\left[\left(\hat{H}_{el} - \frac{i}{2}\hat{W}\right) - \underline{\hat{\mu}}\underline{E}(t), \hat{\rho}\right] + \mathcal{L}_{\mathcal{D}}\hat{\rho}$$

  - Absorbing boundaries for states above IP: Ionization

    $$\hat{W} = \sum_n \Gamma_n |n\rangle\langle n|$$

    with heuristic ionization rate model for states above IP

  - Lindblad dissipation

    $$\mathcal{L}_{\mathcal{D}}\hat{\rho} = \sum_n \left(\hat{C}_n\hat{\rho}\hat{C}_n^\dagger - 1/2\left[\hat{C}_n^\dagger\hat{C}_n, \hat{\rho}\right]_+\right)$$

    with Lindblad operators and transition rates calculated as before:

    $$\hat{C}_n \to \sqrt{\Gamma_{k\to l}}|l\rangle\langle k| \qquad \Gamma_{k\to l} = A\,\mu_{kl}^2\,\omega_{kl}^3$$

[1] Tremblay, Klinkusch, Klamroth, Saalfrank, JCP **134**, 044311 (2011)

- **Effects of ionization and dissipation**[1] (cont'd)
  - H$_2$, bound $\rightarrow$ bound excitation $|0\rangle \rightarrow |1\rangle \rightarrow |2\rangle \rightarrow |5\rangle$

    3-pulse π-pulse excitation with $\sigma_1 = 0.5\sigma_2 = \sigma_3 = 500\ \hbar/E_h$, TD-CIS(D)/aug-cc-pVQZ
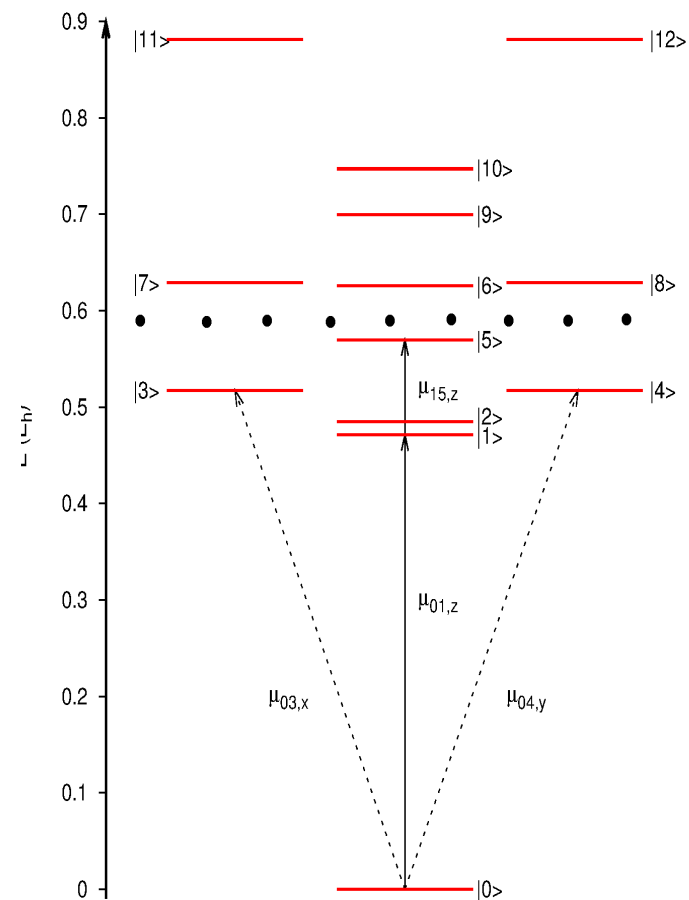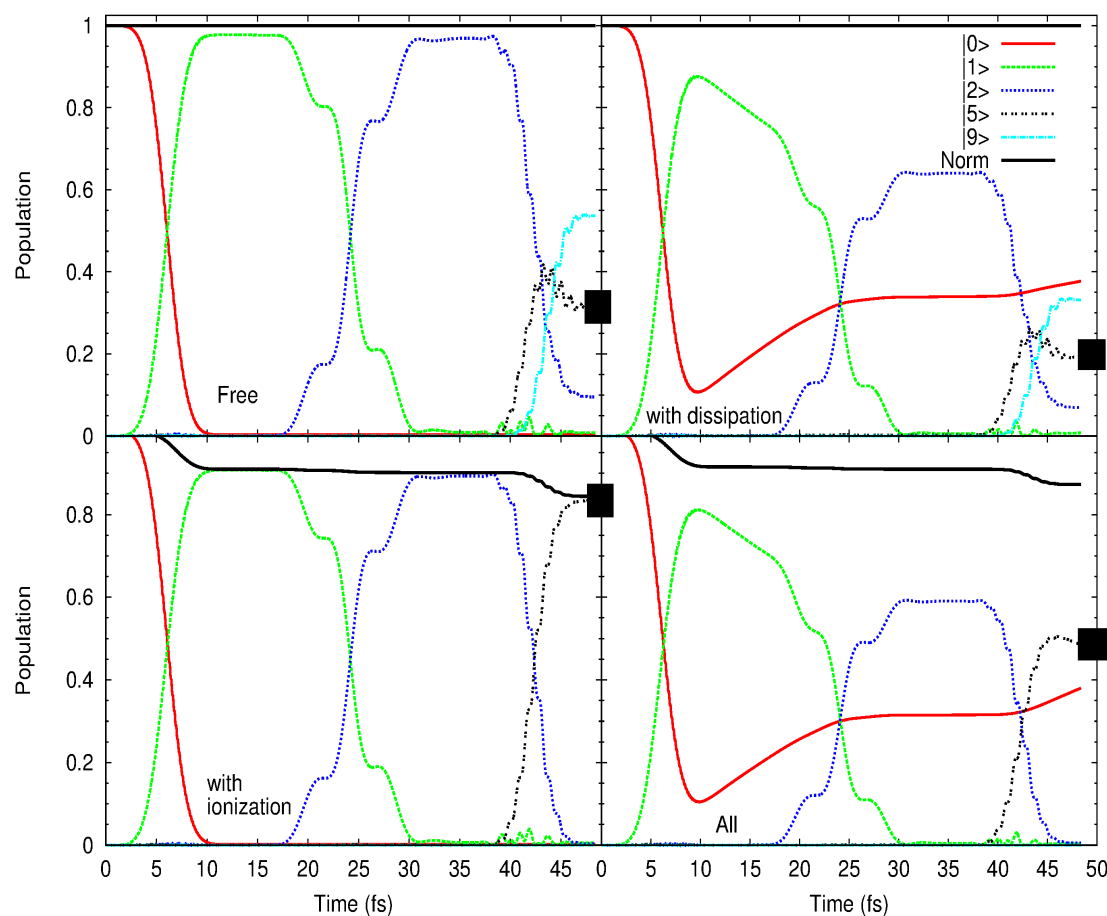
Note: Ionization can enhance target yield

[1] Tremblay, Klinkusch, Klamroth, Saalfrank, JCP **134**, 044311 (2011)

5.2 Electronic wavepackets

- **Electronic wavepackets in LiH obtained with MCTDHF**[1]

  - Excited states

state n	ΔE_{0n} (E_h)	μ_n^z (ea$_0$)	$\mu_{0n}^{x,y}$ (ea$_0$)	μ_{0n}^z (ea$_0$)
$^1\Sigma^+$	0.1139	-2.301	–	1.157
$^1\Pi$	0.1502	-0.193	1.521	–
$^1\Sigma^+$	0.1962	3.259	–	-0.421

  CASSCF(4,5)/6-311++G(2df,2p), $R = R_0 = 2.472$ Å

  - Few-cycle laser pulses

  $$\underline{E}(t) = \underline{E}_0 \, e^{-\frac{t-t_0}{2\sigma^2}} \, \cos\left(\omega_0 t + \phi\right)$$

  Li   H
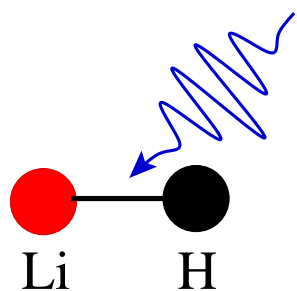
  $z =$ molecular axis

  also: large role of CEP phase ϕ

  - Dipole moments after pulse excitation

  $\sigma = 40 \, \hbar/E_h$, $|\underline{E}_0| = 0.025$ E$_h$/(ea$_0$)

  $\phi = -\pi/3$, $\hbar\omega_0 = 0.133$ E$_h$ $(T = 47 \, \hbar/E_h)$

  (a) z-polarized   (b) (xz)-polarized

  $|0\rangle, |1\rangle$ WP $|0\rangle, |1\rangle, |2\rangle$ WP
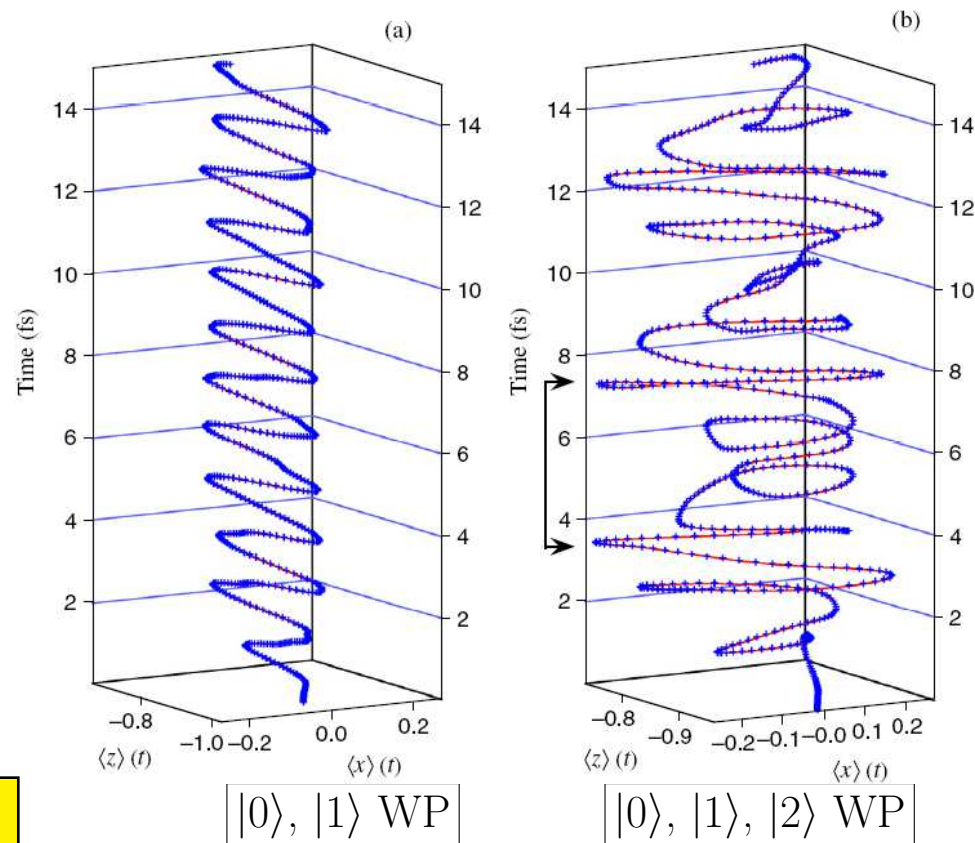
[1] Nest, Remacle, Levine, New J. Phys. **10**, 025019 (2008)

5.2 Electronic wavepackets (2)

- **Validity of fixed-nuclei approximation in quantum electron dynamics[1]**

  - MCEND wavefunction:
  $$\Psi(\underline{x}, \underline{R}, t) = \sum_{J_{el}} \sum_{J_{nu}} A_{J_{el}J_{nu}}(t)\Psi_{el,J_{el}}(\underline{x}, t)\ \Phi_{nu,J_{nu}}(\underline{R}, t))$$

    N-tuple $J_{el} = (j_1^{el}, \ldots, j_N^{el})$, Slater determinants $\Psi_{el,J_{el}}$; $(3N_A - 6(5))$-tuple $J_{el} = (j_1^{nu}, \ldots)$, Hartree products $\Phi_{nu,J_{nu}}$; coefficients $A_{J_{el}J_{nu}}$. Expansion length $(n_e/2, n_k)$ if n_e spin orbitals (electrons), n_k SPFs for k-th nuclear DOF.

  - Laser-driven electron-nuclear dynamics for LiH

    $\sin^2$-shape envelope, $2\sigma = 4$ fs, frequency ω, amplitude E_0, $\phi = 0$; MCEND(x,y)/6-31G**+ add. basis functions

(3,2), initial vibrational ground state ($\hbar\omega = 0.120$ E$_h$, $E_0^z = 0.02$ E$_h$/(ea$_0$))

no large effect

(4,1), two initial vibrational wavepackets ($\hbar\omega = 0.125$ E$_h$, $E_0^z = 0.025$ E$_h$/(ea$_0$))

some effect at later times
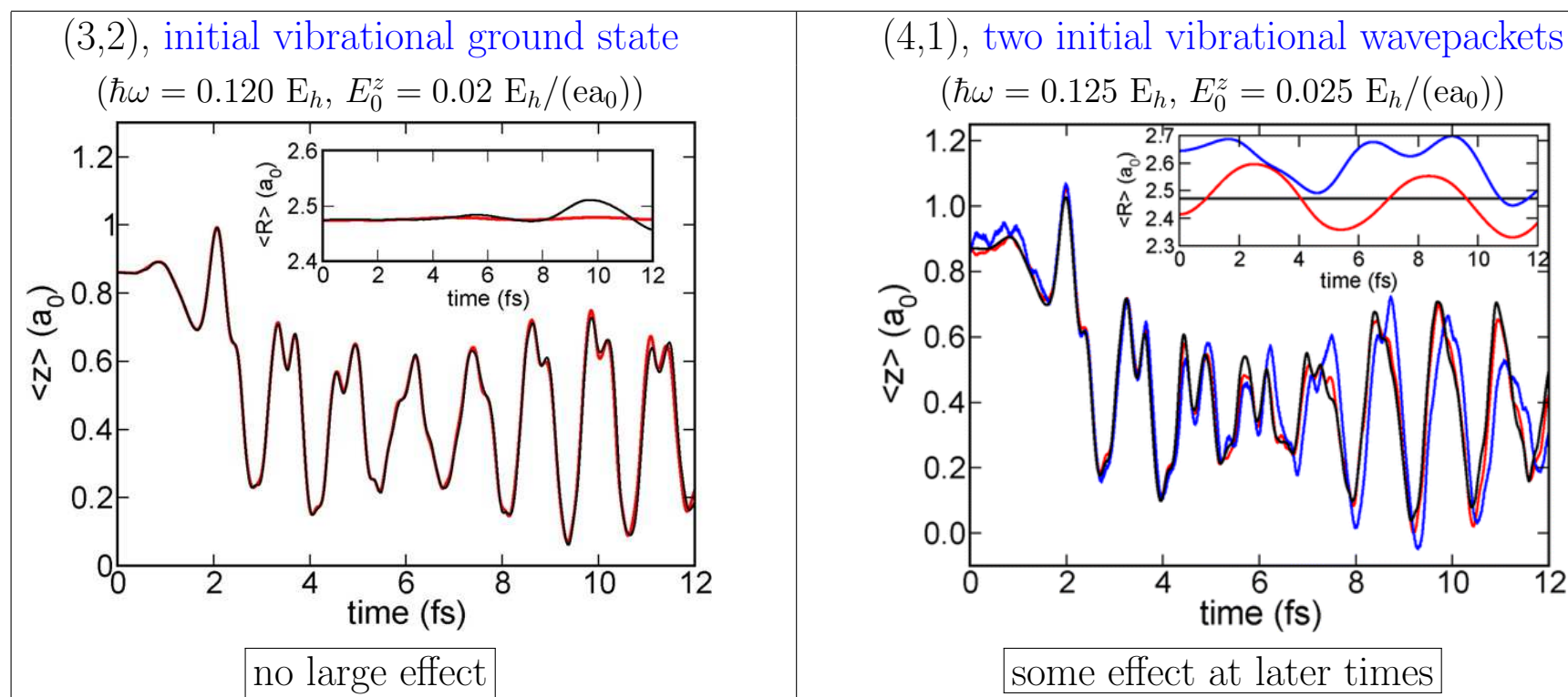
[1] Ulusoy, Nest, J. Phys. Chem. A **116**, 11107 (2012)

5.2 Electronic wavepackets (3)

- ## Charge migration after hole creation[1]

  - Initial state

  $$\boxed{|\Psi(0)\rangle = \hat{a}_i|\Psi_0\rangle}$$

  $\hat{a}_i$ creates hole in MO i, Ψ_0 = HF ground state

  - CI-like expansion of $|\Psi(t)\rangle$, ADC(3) states

  - Three donor-acceptor molecules

  - Sudden hole creation in donor site

a)   b)   c)
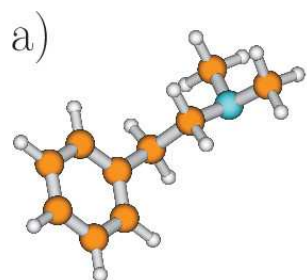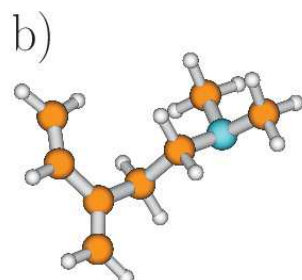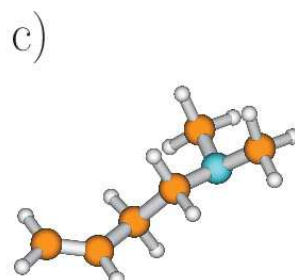
PENNA   MePeNNA   BUNNA

Hole migration along molecular axis

a)
hole density $Q(z,t)$

b)
hole density $Q(z,t)$

c)
hole density $Q(z,t)$
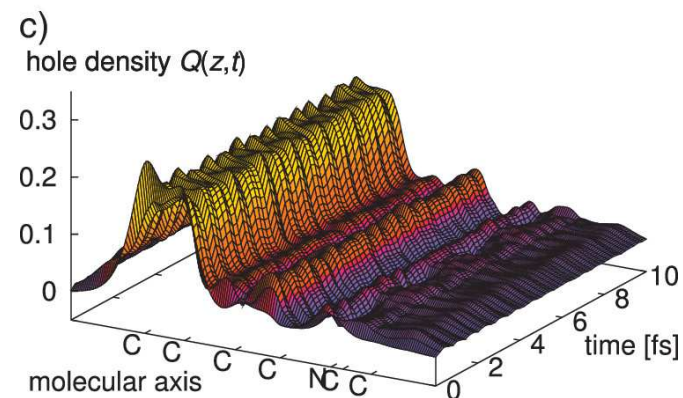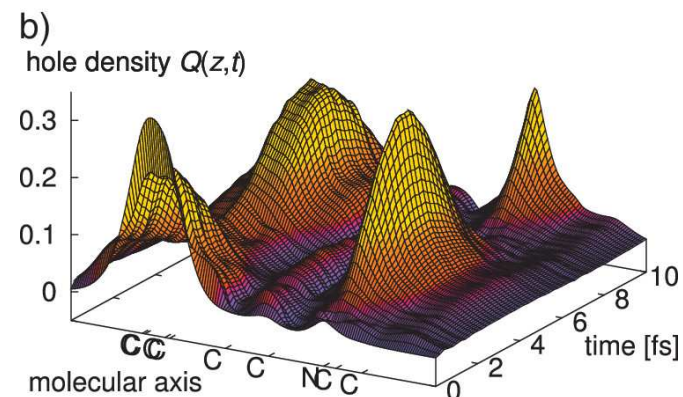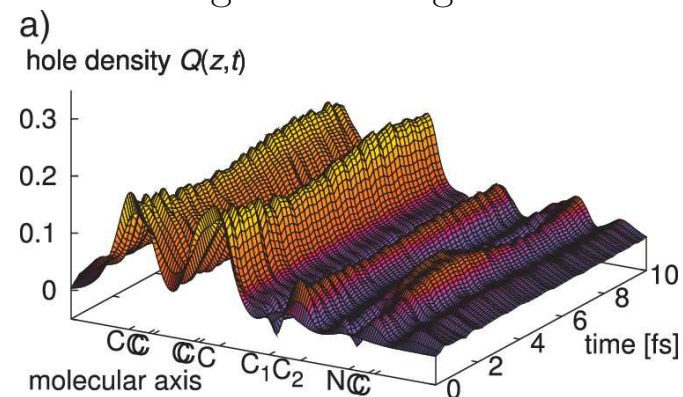
[1] Lünnermann, Kuleff, Cederbaum JCP **129**, 104305 (2012)

5.3 Response

- **Linear response: Static polarizability of H_2**[1]
  - General strategy:

    Apply $E_q = E_{0q} \sin^2(\pi t/2\sigma) \cos(\omega t)$ and compute induced dipole moment,

$$\mu_q^{ind} = \sum_{q'} \alpha_{qq'} E_{q'}(t) + \frac{1}{2} \sum_{q'} \sum_{q''} \beta_{qq'q''} \, E_{q'}(t) \, E_{q''}(t) + \cdots$$

    with $q, q', \cdots = x, y, z$, α = polarizability, β = 1st hyperpolarizability.

- Kennlinien for H_2:

  $\sigma = 1000 \, E_h/\hbar$, $E_{0q} = 10^{-5} \, E_h/ea_0$, variable ω
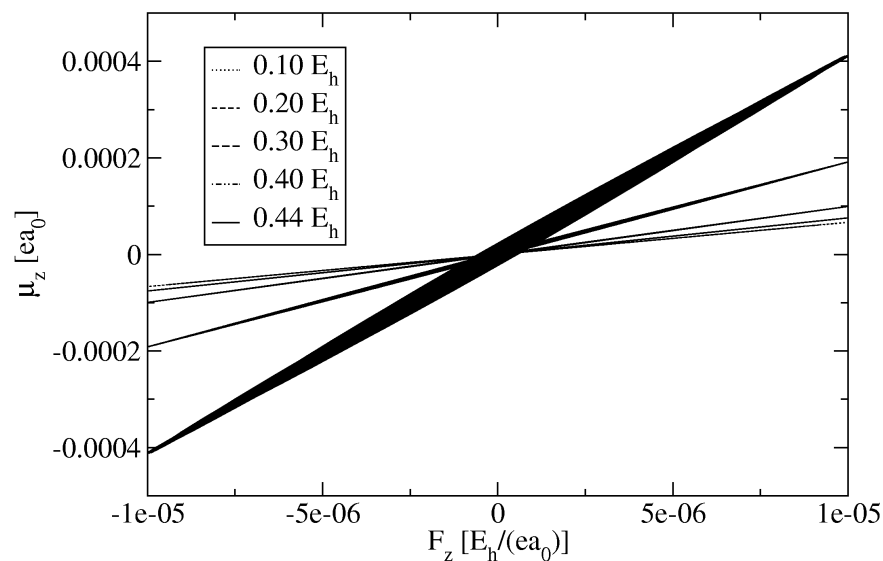
- Static polarizability: $\omega = 0$

	TD-CISD[a]	Exp.	Stat. QC[b]
$\alpha_\parallel$	6.3989	6.303	6.3970
$\alpha_\perp$	4.5845	4.913	4.5749
α_{av}	5.1893	5.554	5.1822

  all in a_0^3; [a] aug-cc-pVQZ; [b] FCI/aug-cc-pVQZ

[1] Krause, Klamroth, Saalfrank, JCP **127**, 034107 (2007)

5.3 Response (2)

- **Linear and non-linear static response at fixed $\omega \neq 0$: H_2O[1]**

  - Kennlinien for H_2O: y-polarization

$\sigma = 1000$ $E_h/\hbar$, $E_{0y} = 0.05$ E_h/ea_0, $\hbar\omega = 0.03675$ E_h
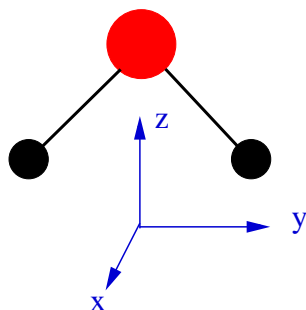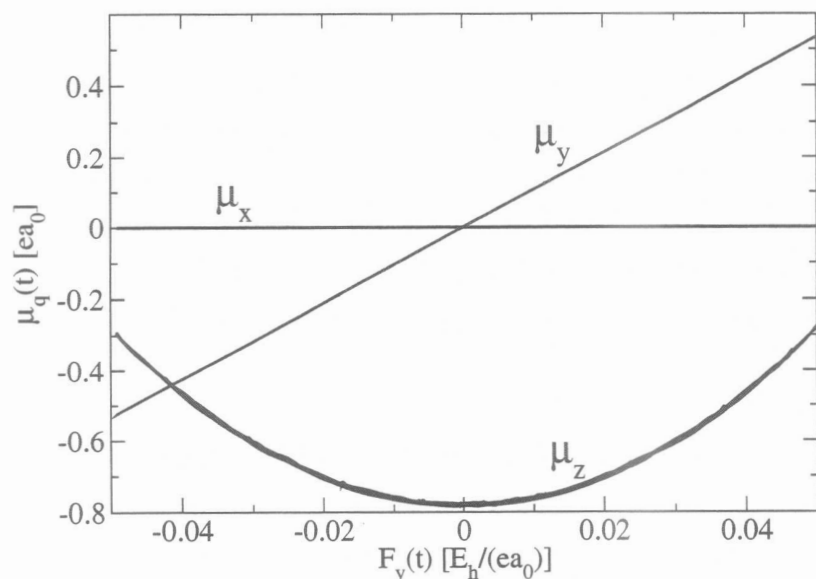
  - Polarizability: $\hbar\omega = 0.08856$ E_h

	TD-CIS[a]	TD-CISD[b]	exp.
α_{xx}	8.3166	2.64	9.549
α_{yy}	10.5923	5.83	10.311
α_{zz}	9.39	4.3	9.907
α_{av}	9.4363	4.26	9.223

all in a_0^3; [a] aug-cc-pVDZ; [b] cc-pVDZ

  - Hyperpolarizability:

$$\mu_z(t) \sim \mu_{0;z} + \alpha_{zy}(-\omega;\omega)E_y(t;\omega) + \frac{1}{2}\beta_{zyy}(-2\omega;\omega,\omega)E_y^2(t;\omega)$$

$\beta_{zyy}(-2\omega;\omega,\omega)$ for different methods, $\hbar\omega = 0.08856$ E_h:

TD-CIS/aug-cc-pVDZ $= 18.8$ a_0^5

TD-CIS(D)/aug-cc-pVDZ $= 25.2$ a_0^5

[1] Krause, Klamroth, Saalfrank, JCP **127**, 034107 (2007)

5.3 Response (3)

- ## **Dynamic polarizability of H_2** [1]

  - ### General strategy (for cw field $\underline{E} = \underline{E}_0 \cos(\omega t)$):

$$\mu_q^{ind}(t) = \sum_{q'} \alpha_{qq'}(-\omega;\omega)\, E_{0,q'} \cos(\omega t) + \frac{1}{4} \sum_{q',q''} \beta_{qq'q''}(-2\omega;\omega,\omega)\, E_{0,q'}\; E_{0,q''} \cos^2(\omega t) + \cdots$$

where … give $\gamma(-3\omega;\omega,\omega,\omega)$ etc. With variable field components, *e.g.*, $E_{0q}\cos(\omega_1 t)$, $E_{0q}\cos(\omega_2 t)$ etc., one can obtain $\beta(-(\omega_1+\omega_2);\omega_1,\omega_2)$, $\gamma(-(\omega_1+\omega_2+\omega_3);\omega_1,\omega_2,\omega_3)$ etc.

- ### α_{zz} for H_2: TD-CI/aug-cc-pVQZ

$\sin^2$, $\sigma = 1000\ E_h/\hbar$, $E_{0q} = 10^{-5}\ E_h/ea_0$
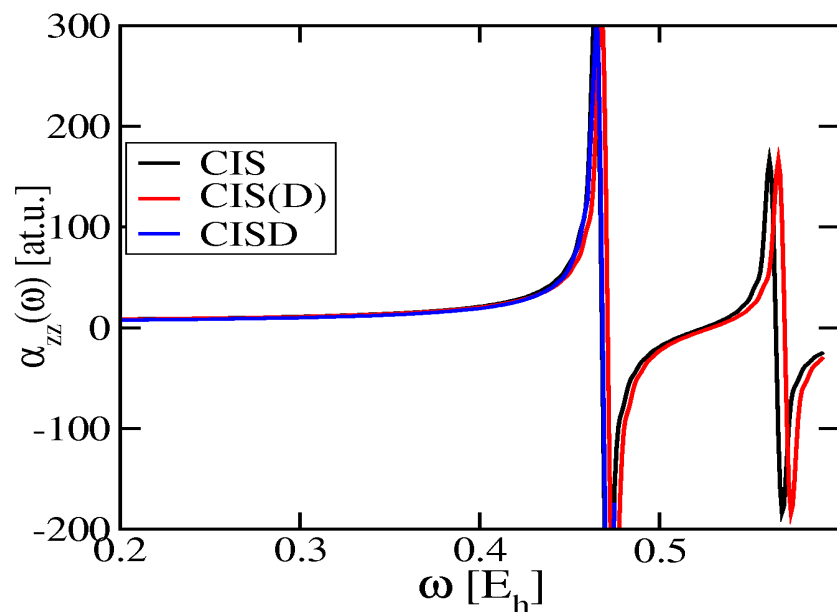
- ### Static Sum-Over-States *vs.* TD approach

$$\text{SOS / PT: } \alpha_{zz} = 2 \sum_{n \neq 0} \frac{\mu_{0n,z}^2\ \omega_{n0}}{\omega_{n0}^2 - \omega^2}$$

with transition dipole moments $\mu_{0n,q} = \langle \Psi_0 | \hat{\mu}_q | \Psi_n \rangle$.
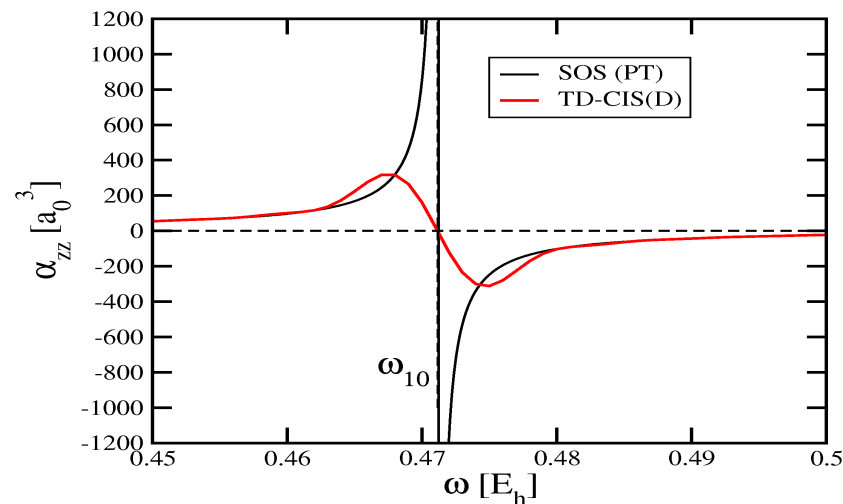
[1] Krause, Klamroth, Saalfrank, JCP **127**, 034107 (2007)

5.3 Response (4)

- **Dynamic polarizability of H_2: Effects of ionization and dissipation[1,2]**

  - SOS expression for polarizability of systems with finite lifetimes[1]

$$\alpha_{qq'}^R(-\omega, \omega) = \sum_{n \neq 0} \left(\frac{\mu_{0n,q} \; \mu_{n0,q'} \; (\omega_{n0} - \omega)}{(\omega_{n0} - \omega)^2 + (\frac{1}{2}\Gamma_n)^2} + \frac{\mu_{0n,q} \; \mu_{n0,q'} \; (\omega_{n0} + \omega)}{(\omega_{n0} + \omega)^2 + (\frac{1}{2}\Gamma_n)^2} \right)$$

  with decay rate Γ_n for state n.

  - TDCI ionization and SOS calculations for H_2[2]: TD-CIS/cc-pVTZ

$\sin^2$ pulse with $\sigma = 2000 \; \hbar/E_h$; α_{zz} values
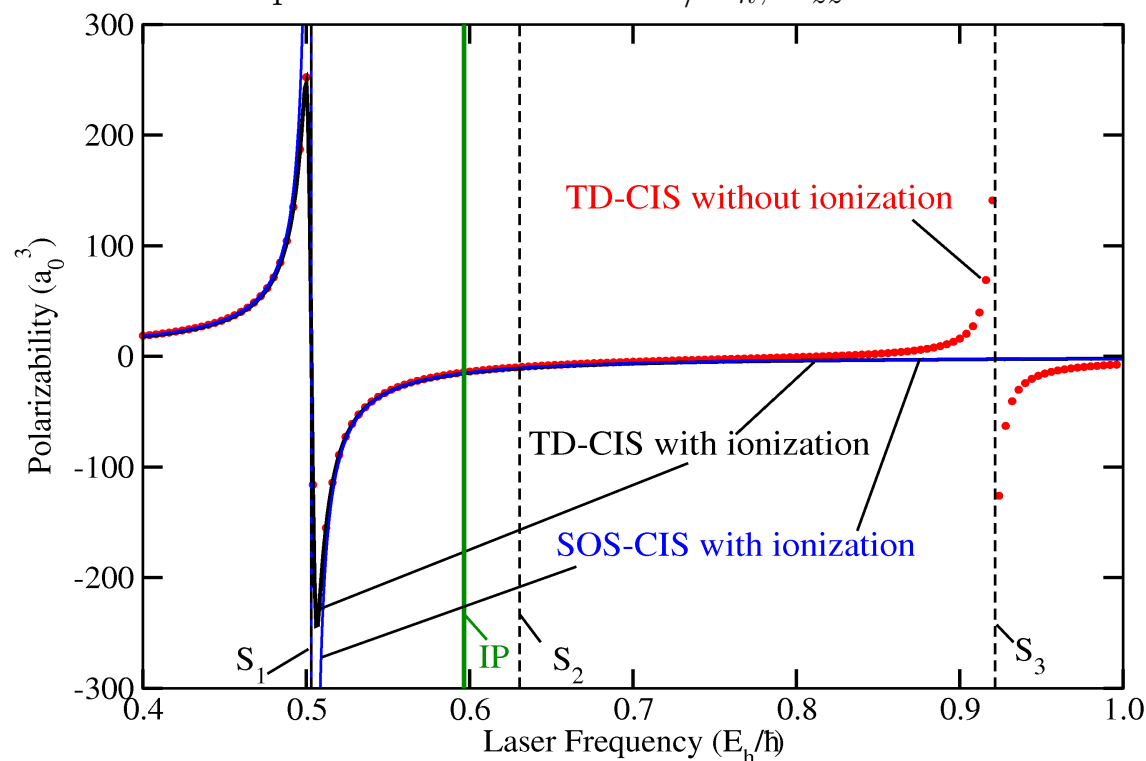
[1] Jensen *etal.*,, JCP **122**, 224115 (2005)   [2] Klinkusch, Saalfrank, Klamroth, JCP **131**, 114304 (2009)

5.3 Response (5)

- ## High Harmonic Generation (HHG)

  - 3-step model for High Harmonic Generation (HHG) of Corkum[1]
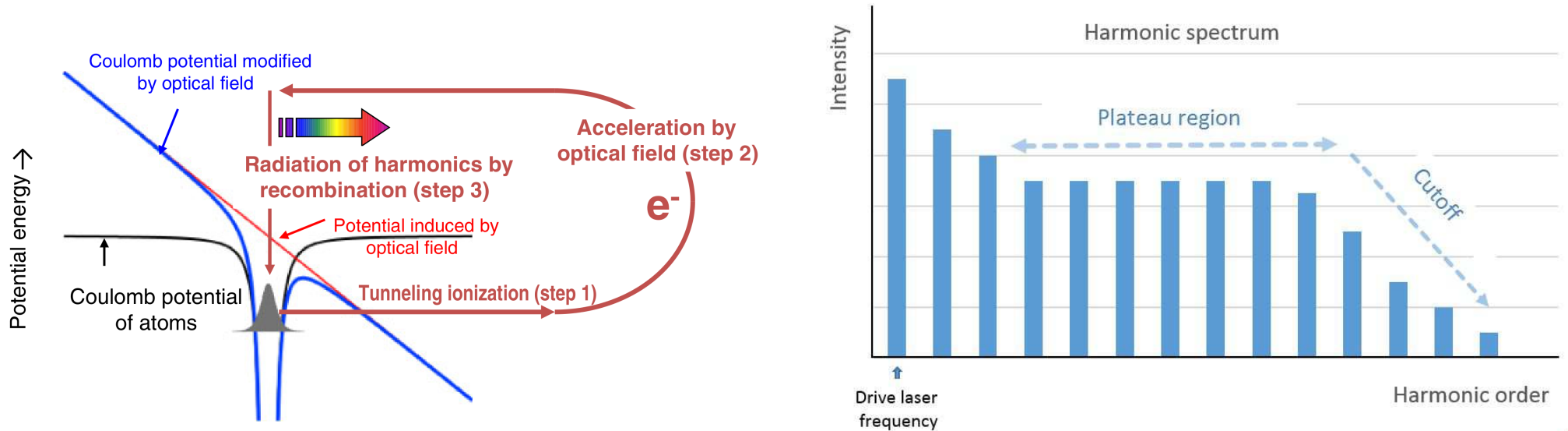
  - ## The (classical) cutoff formula

    The cutoff region is determined by $\boxed{N_{max} = (\mathrm{IP} + 3.17\,U_p)/\omega_0}$

with driving frequency ω_0, ionization potential IP, and *ponderomotive energy*

$$\boxed{U_p = I^2/(4\omega_0^2)}$$

and laser intensity $I = \varepsilon_0\,c\,E_0^2$. Also useful: The *Keldysh parameter* $\boxed{\gamma = (\mathrm{IP}/(2U_p))^{1/2}}$. For $\gamma > 1$, multi-photon ionization dominates and for $\gamma < 1$, over-barrier or tunneling ionization.

[1] Figure from Midorikawa, Jpn. J. Appl. Phys. **50**, 090001 (2011)

5.3 Response (6)

- **Three ways to compute HHG spectra from power spectra[1,2]**

$$P_\zeta(\omega) = \left| \frac{1}{t_f - t_i} \int_{t_i}^{t_f} \langle \Psi(t)|\zeta|\Psi(t)\rangle \, e^{-i\omega t} \, dt \right|^2$$

with the choices:

$P_z(\omega)$: $\zeta = z$ dipole form (or $\underline{r}$, $\underline{\mu}$)

$P_v(\omega)$: $\zeta = \frac{dz}{dt}$ dipole-velocity form (or $\frac{d\mu}{dt}$)

$P_a(\omega)$: $\zeta = \frac{d^2z}{dt^2}$ dipole-accelaration form (or $\frac{d^2\mu}{dt^2}$)

and relation $\omega^2 P_z(\omega) \sim P_v(\omega) \sim \frac{1}{\omega^2} P_a(\omega)$.

- **An example: H atom[2]**
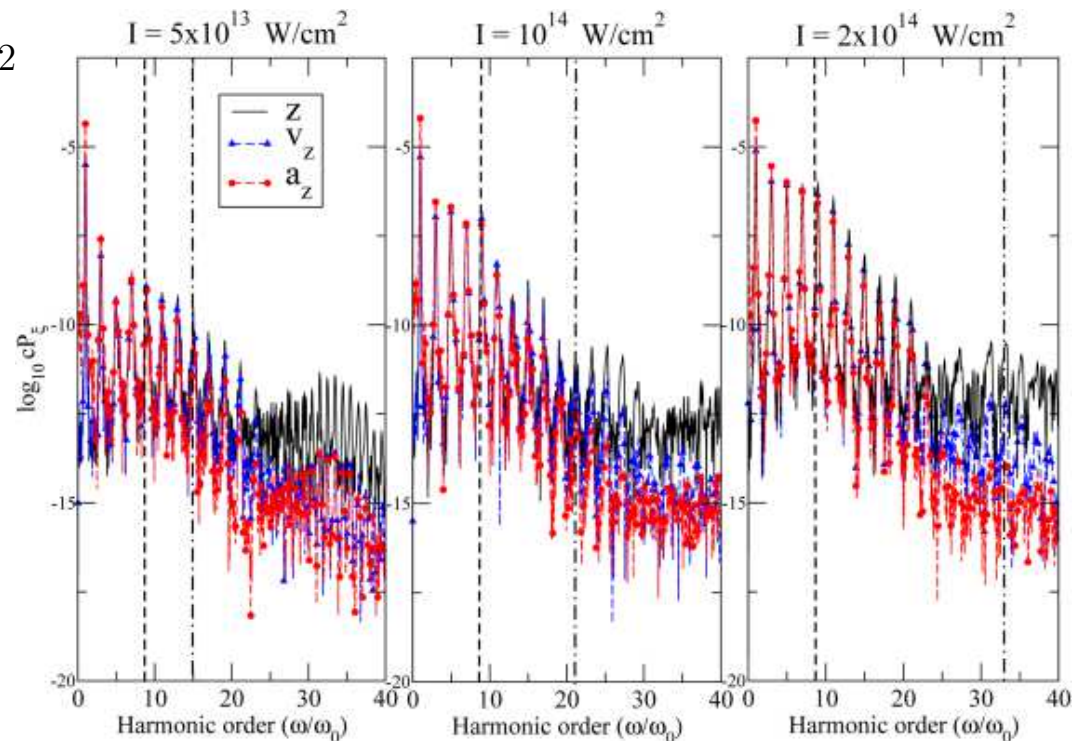
[1] Bandrauk *et al.*, PRA **79**, 023403 (2009)   [2] Coccia *et al.*, IJQC **116**, 1120 (2016)

- **Calculating "HHG spectra" from TD-CI[1]**

H$_2$: Inversion symmetry

TD-CISD / aug-cc-pVDZ

ω_0=0.1102 E$_h$, E$_0$= 0.007 at.u.

$\mu_z(\omega)$ [e a$_0$]

hbar ω [E$_h$]

only odd signals

H$_2$O: No inversion symmetry

TD-CISD / cc-pVDZ

ω_0=0.037 E$_{0h}$

	E$_0$ = 0.05
	E$_0$ = 0.07
	E$_0$ = 0.09

$\mu_z(\omega)$ [ea$_0$]

ω [E$_h$]
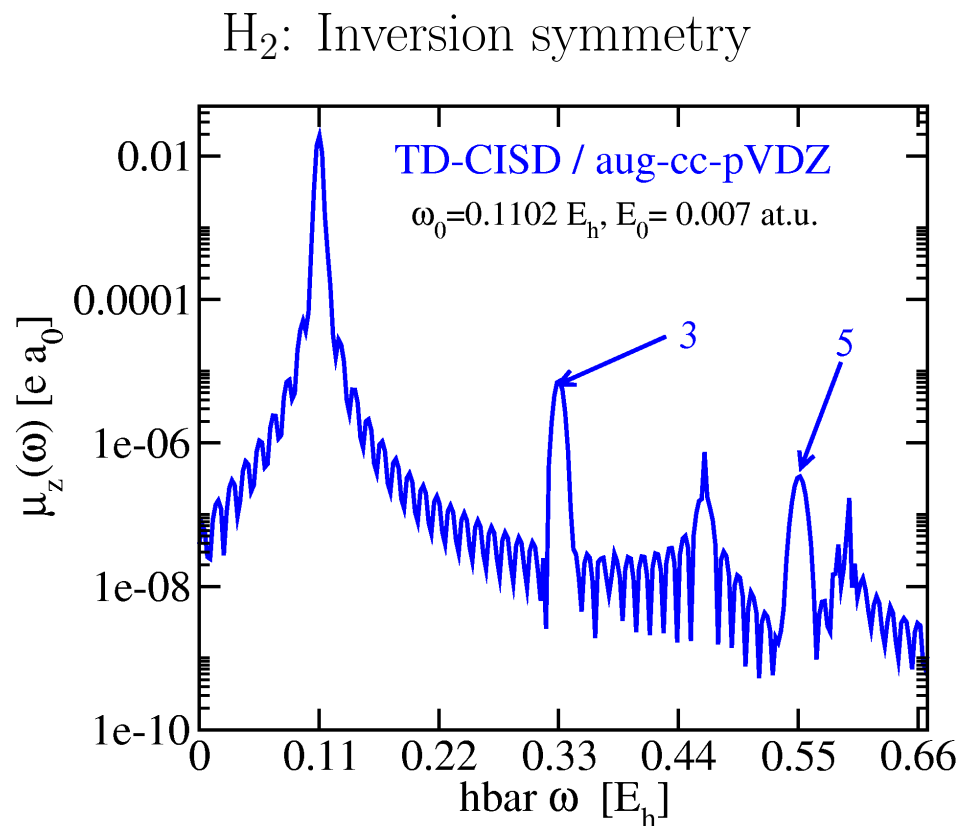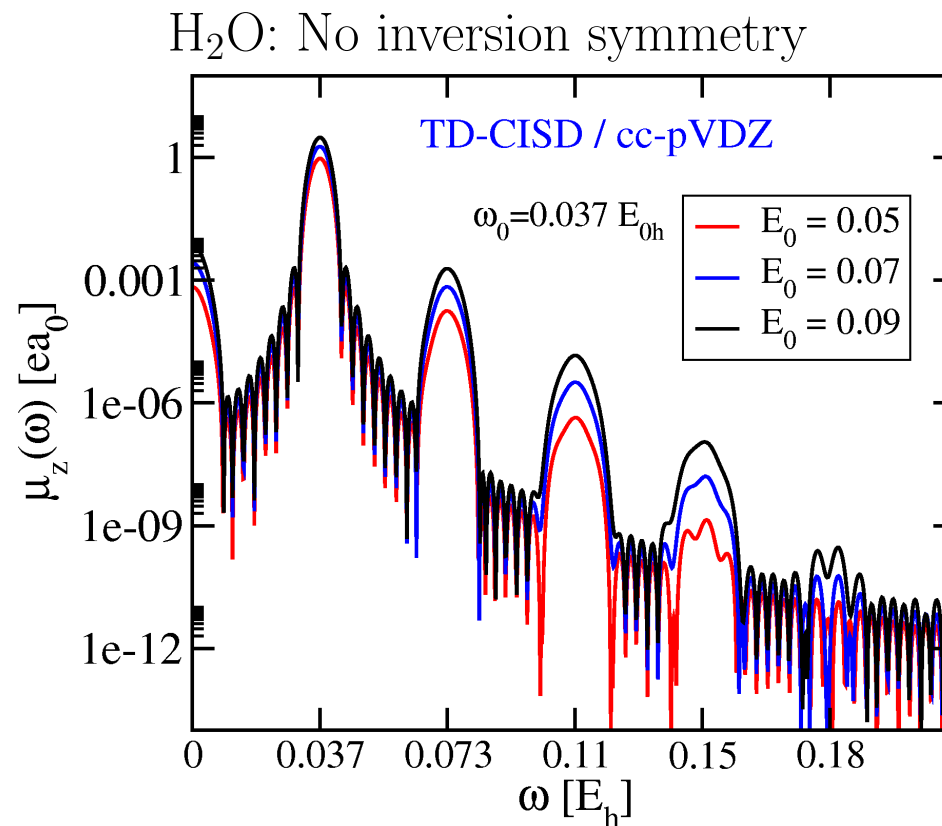
even and odd signals

[1] Krause, Klamroth, Saalfrank, JCP **127**, 034107 (2007)

- **H_2 HHG: Accessible by Gaussian basis sets?[1]**

$\hbar\omega_0 = 0.057$ E$_h$, $\sigma = 1102$ $\hbar/E_h$, $I = 10^{14}$ W/cm^2, TD-CIS
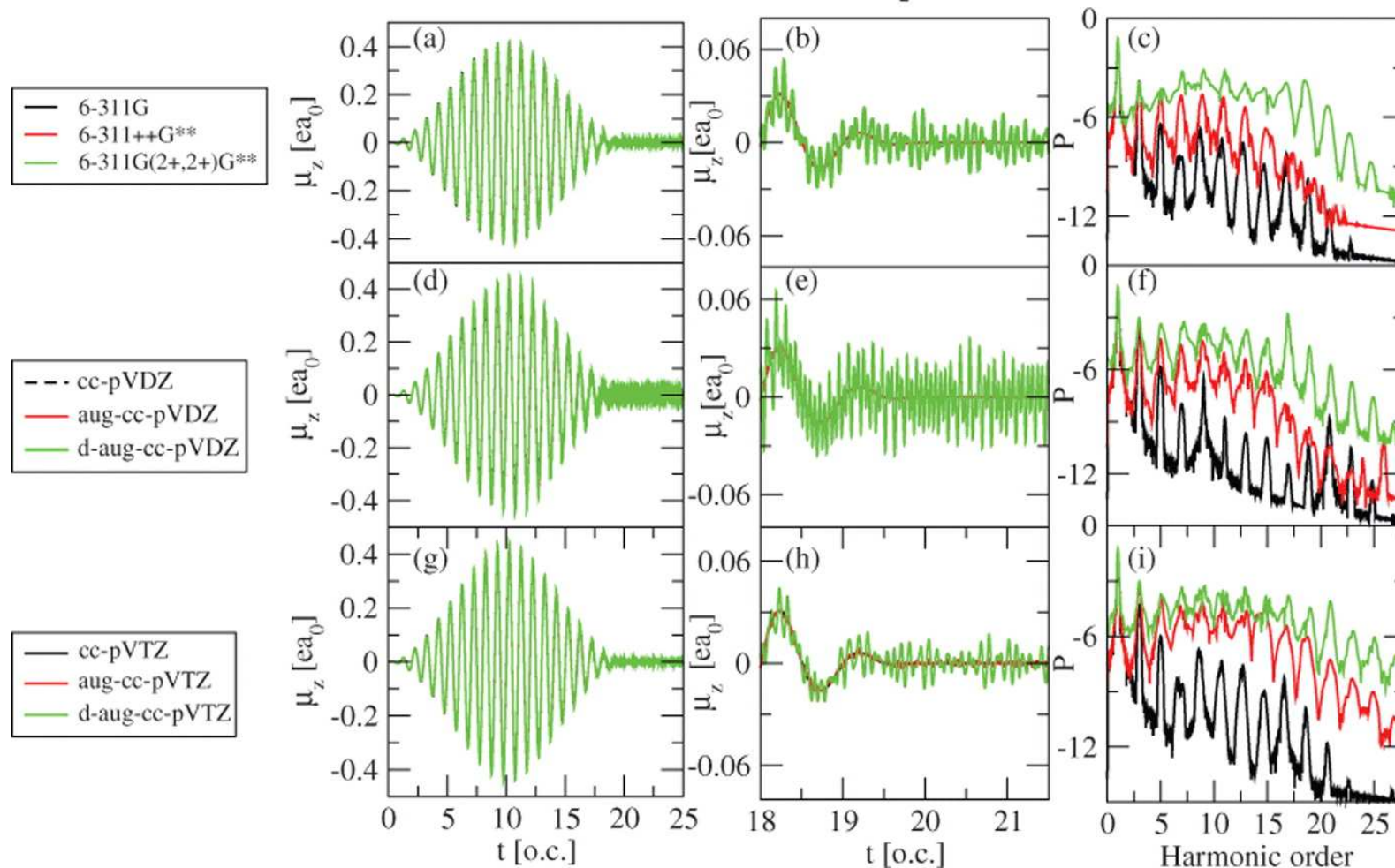
HHG cutoff requires diffuse functions (+Rydberg, continuum ...), hard to converge

[1] Luppi, Head-Gordon, Mol. Phys. **110**, 909 (2012), JCP **139**, 164121 (2013)

5.3 Response (9)

- **H$_2$ HHG: The role of ionization losses**[1]

HHG spectrum of H$_2$, TD-CISD

dipole moment
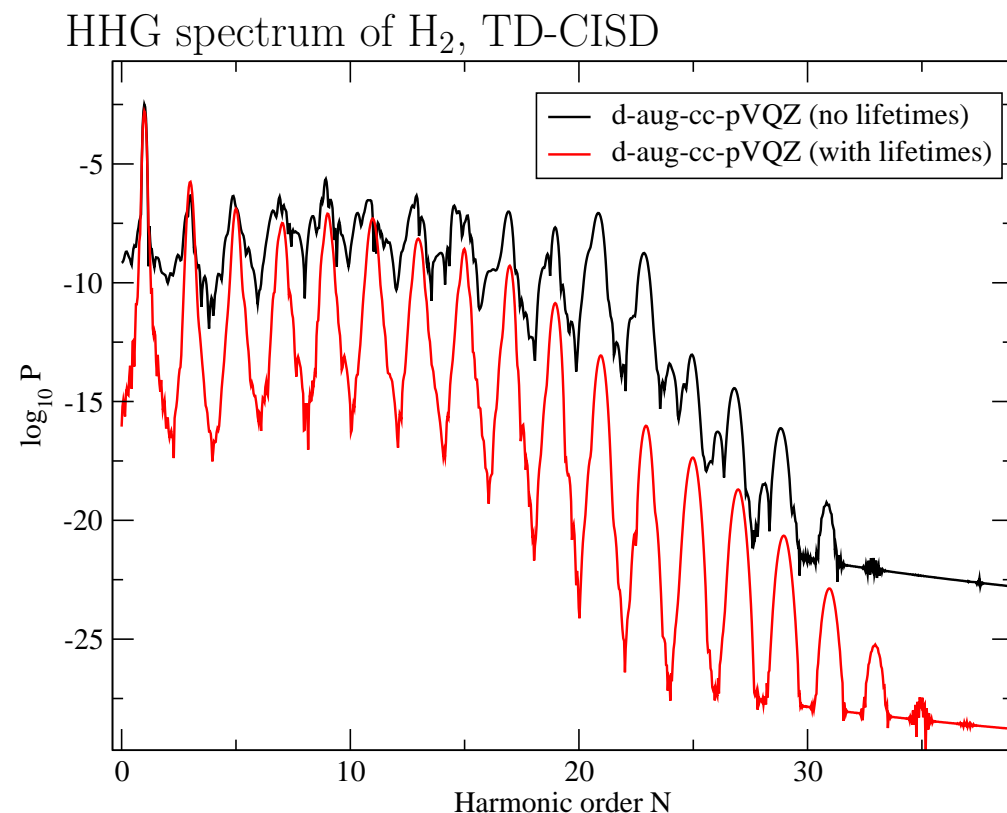
$\omega_0 = 0.057 \; E_h, \; \sigma = 1102 \; \hbar/E_h, \; I = 10^{14} \; W/cm^2$
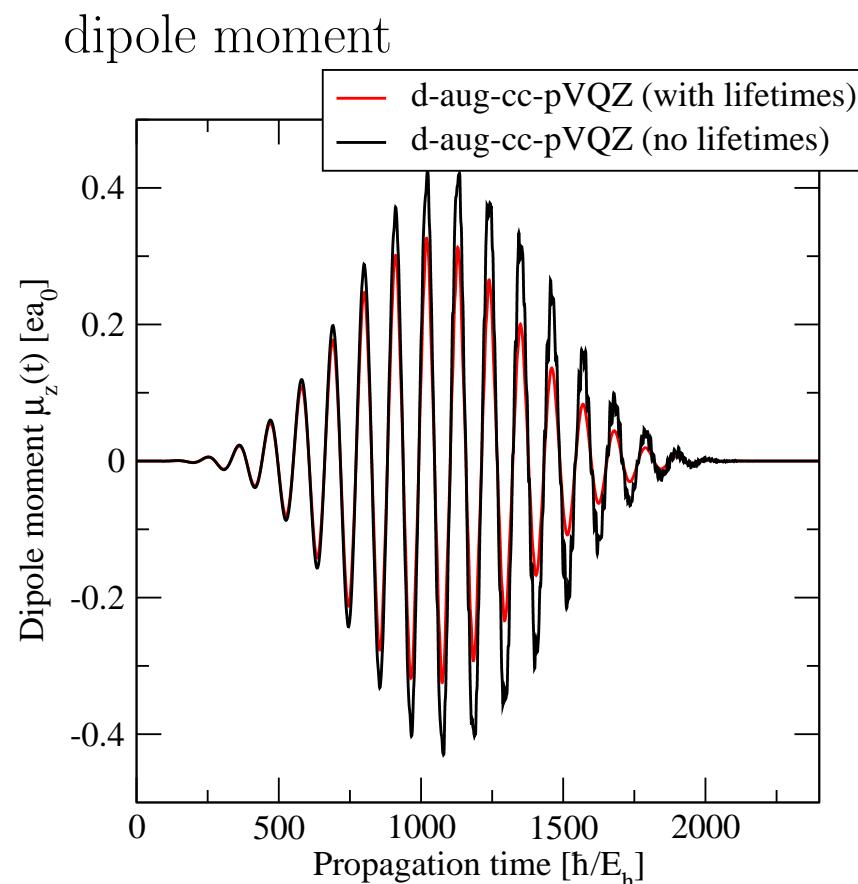
Further improved HHG spectra (?), but what are the benchmarks?

[1] White, Heide, Luppi, Head-Gordon, Saalfrank, Mol. Phys. **114**, 947 (2016)

- **HHG for larger molecules: Useful for analytics?**

experiment[1]
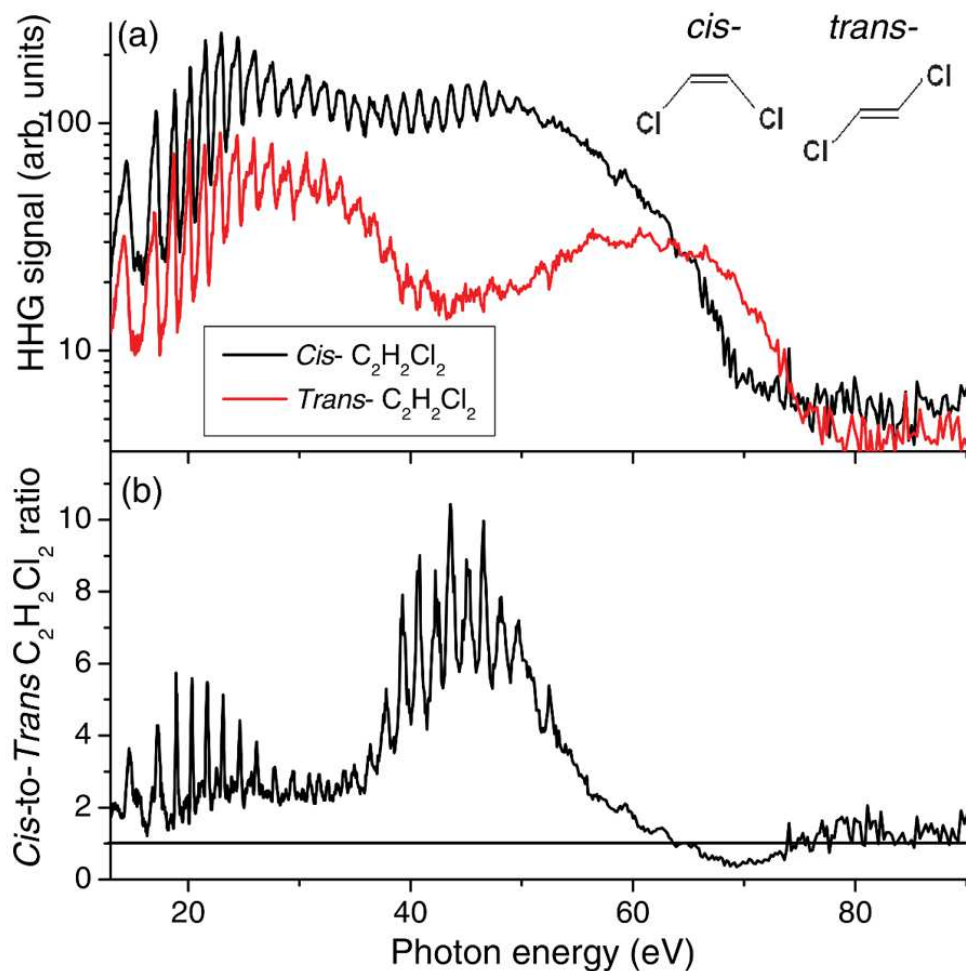
theory[2] (TD-CIS-CAP)

1800 nm, 1.1×10^{14} W/cm^2
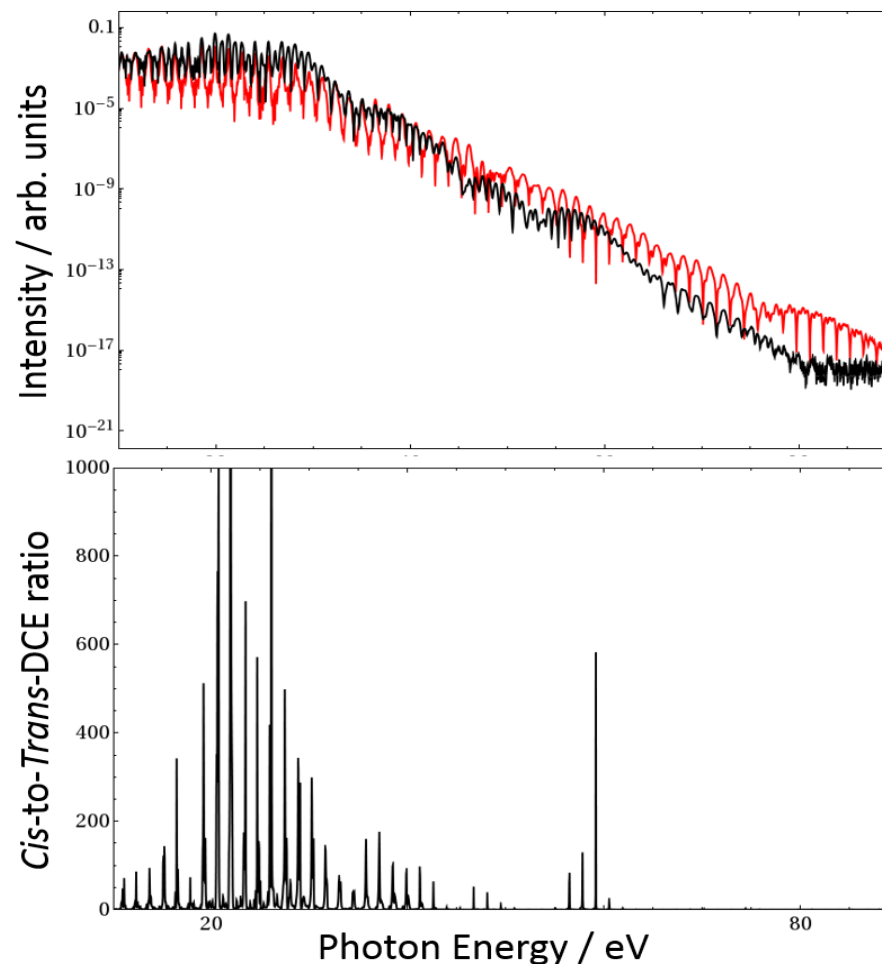
[1] Wong *et al.*, PRA **84**, 051403(R) (2011)

[2] Krause, Saalfrank, unpublished

- **HHG of molecules: Active control of H$_2$ HHG spectrum[1]**
  - Stochastic pulse optimization, Fourier form, with *fitness* function

$$F = \frac{\sum_k W_k |\mu_z(\omega_k)|^2}{\sum_k U_k |\mu_z(\omega_k)|^2}$$

with weights for wanted (W) and unwanted (U) frequency regions

suppressed and enhanced areas   pure and optimized fields
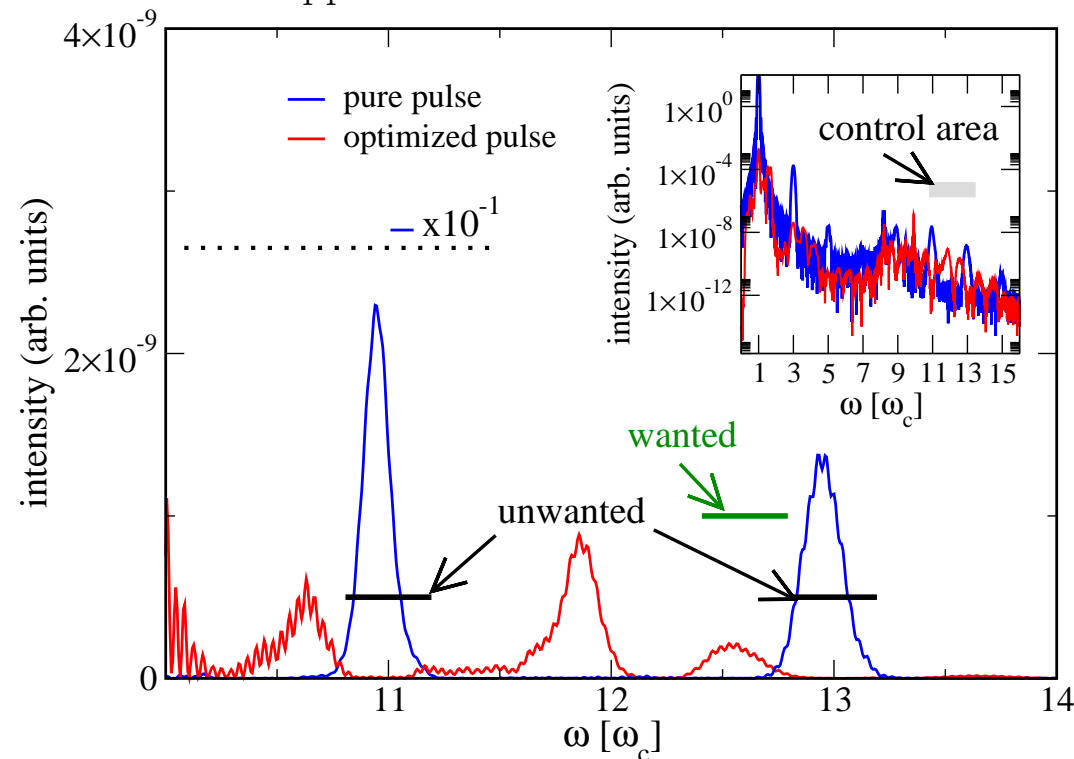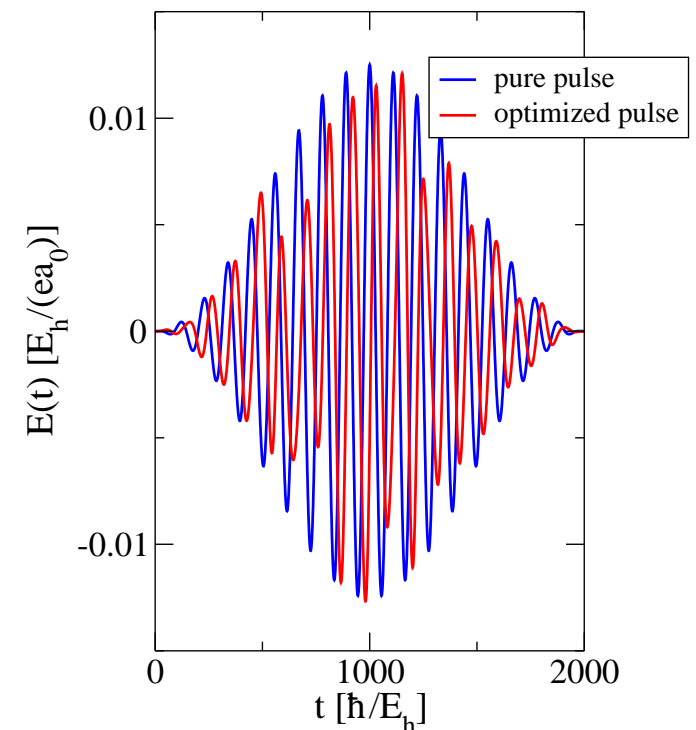
$\hbar\omega_0 = 0.057$ E$_h$, $\sigma = 1000$ $\hbar/E_h$

[1] Schönborn, Saalfrank, Klamroth, JCP **144**, 044301 (2016)
see also: Räsänen, Madsen, PRA **86**, 033426 (2012); Hong *et al.*, PRA **80**, 053407 (2009)

5.4 Controlled electron dynamics

- **"Controlling" electron transport through MIM junctions**[1]

  - Metal-Insulator-Metal junctions
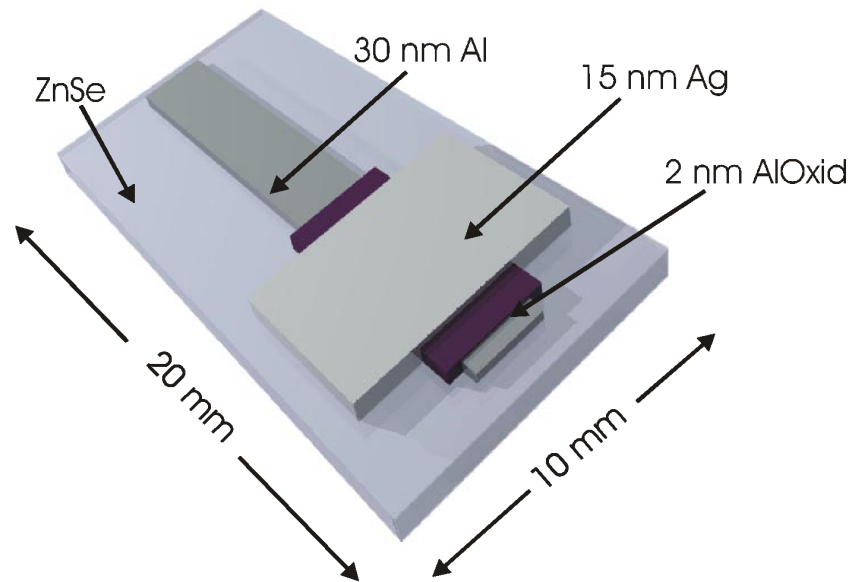
  - Possible processes $(\hbar\omega = 1.5 \text{ eV})$
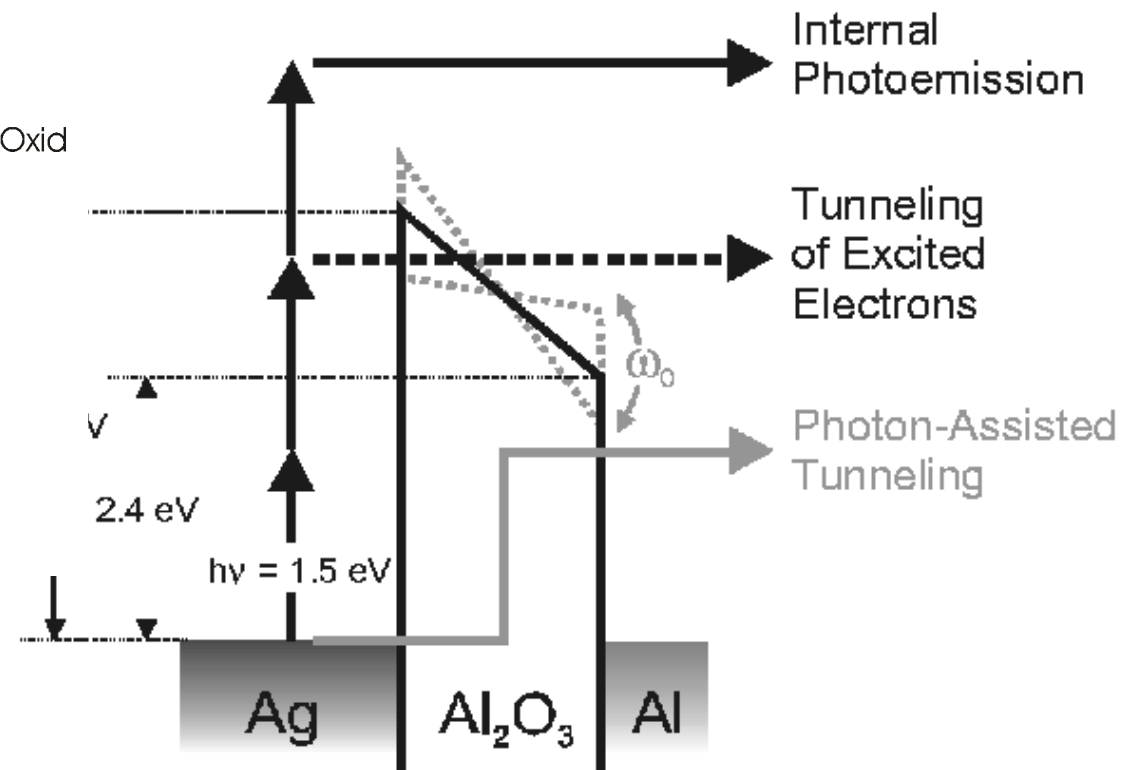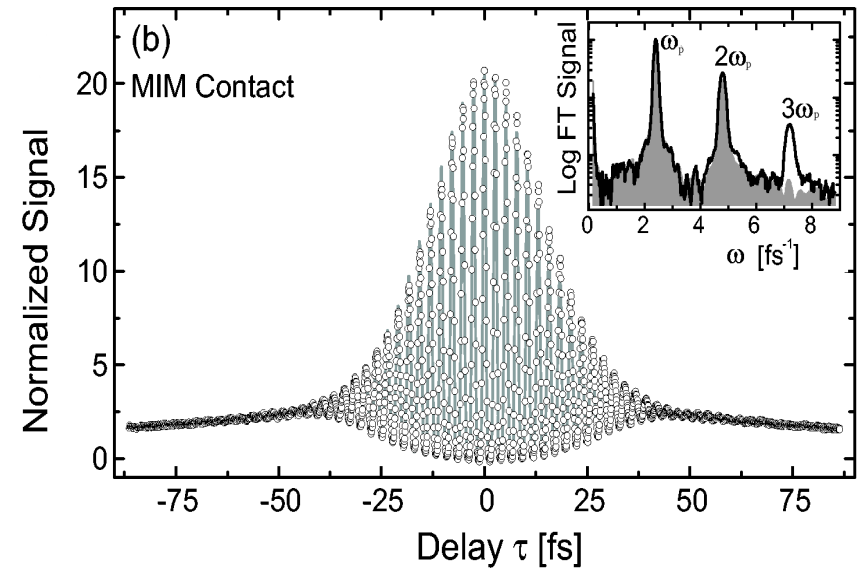

  - "Control parameters"

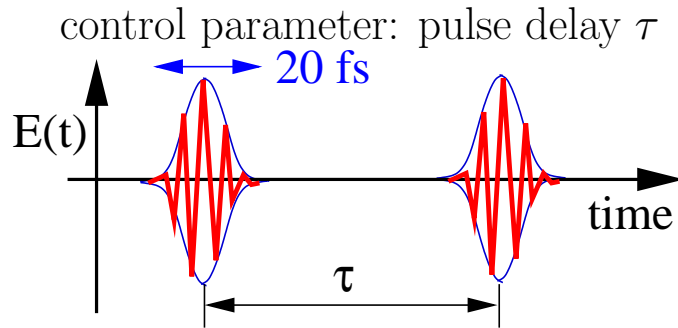   1. bias V
    2. laser pulses $E_z(t)$
    3. film thickness

[1] Thon, Merschdorf, Pfeiffer, Klamroth, Saalfrank, Diesing, Appl. Phys. A **78**, 189 (2004)
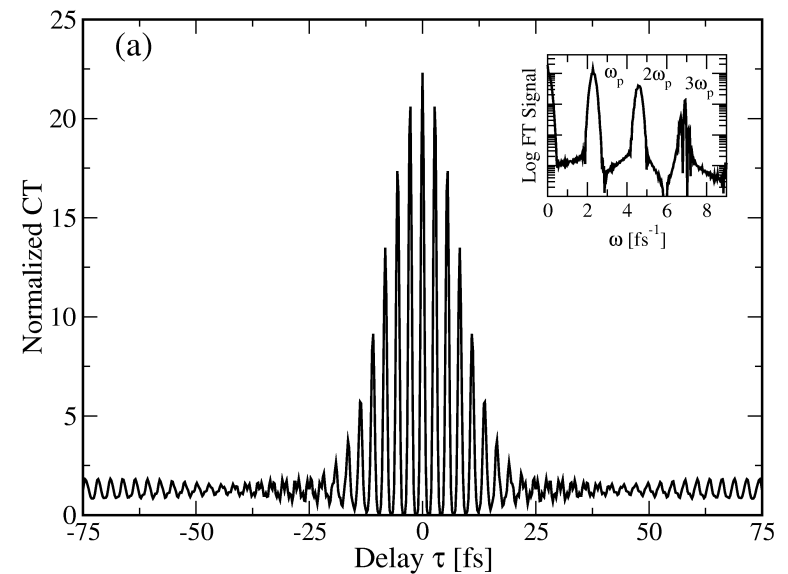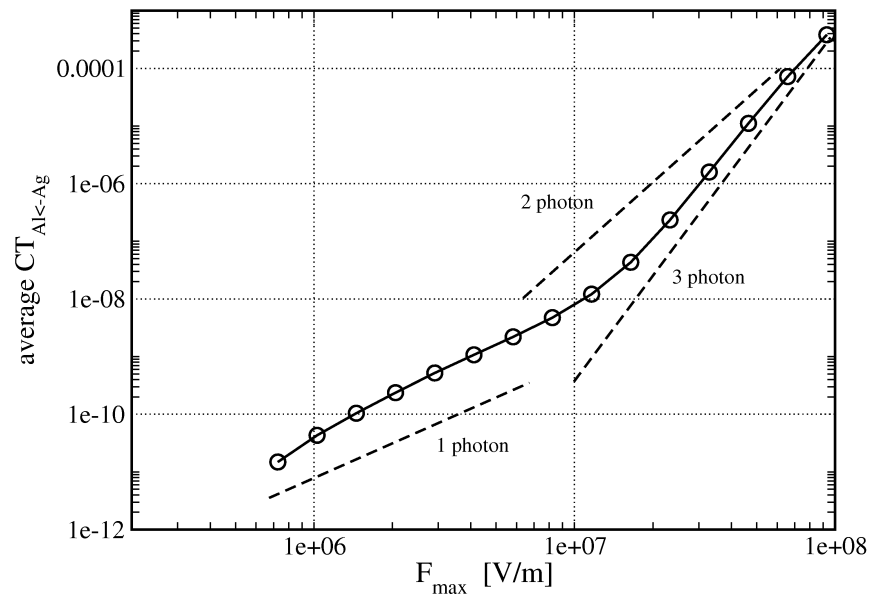
5.4 Controlled electron dynamics (2)

- **"Controlling" electron transport through MIM junctions**[1] (cont'd)

  - Experiment: 2-pulse-correlation

control parameter: pulse delay τ

20 fs

E(t)

time

τ

  - Theory: TD-CIS, 1D jellium model

[1] Thon, Merschdorf, Pfeiffer, Klamroth, Saalfrank, Diesing, Appl. Phys. A **78**, 189 (2004)

5.4 Controlled electron dynamics (3)

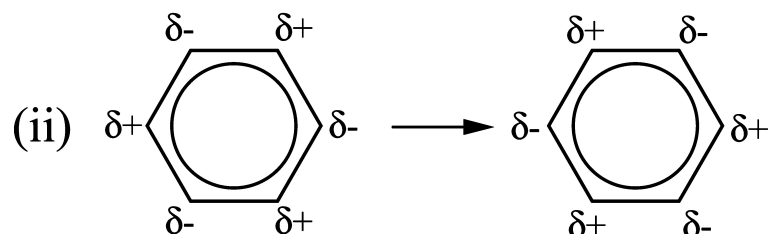- **Optimal control of aromaticity: Creating wavepackets[1]**

  - Bond orders B and Mulliken charges Q in benzene

state	$B_{i,i+1}$	$B_{i+1,i+2}$	Q_i	Q_{i+1}	ΔE	character
S_0	1.41	1.41	-0.19	-0.19	0.0000	aromatic
S_1	1.21	1.21	-0.21	-0.21	0.2138	
S_2	1.24	1.24	-0.21	-0.21	0.2932	
WP (i): $S_0 + S_1$	1.04	1.75	-0.20	-0.20		non-aromatic
WP (ii): $S_0 + S_2$	1.32	1.32	0.05	-0.45		non-aromatic

CISD(18,18)/6-31G*; all in atomic units

(i)
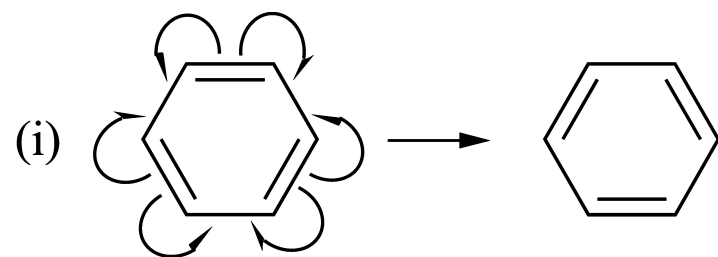
target $\boxed{\hat{O} = |S_0 + S_1\rangle\langle S_0 + S_1|}$
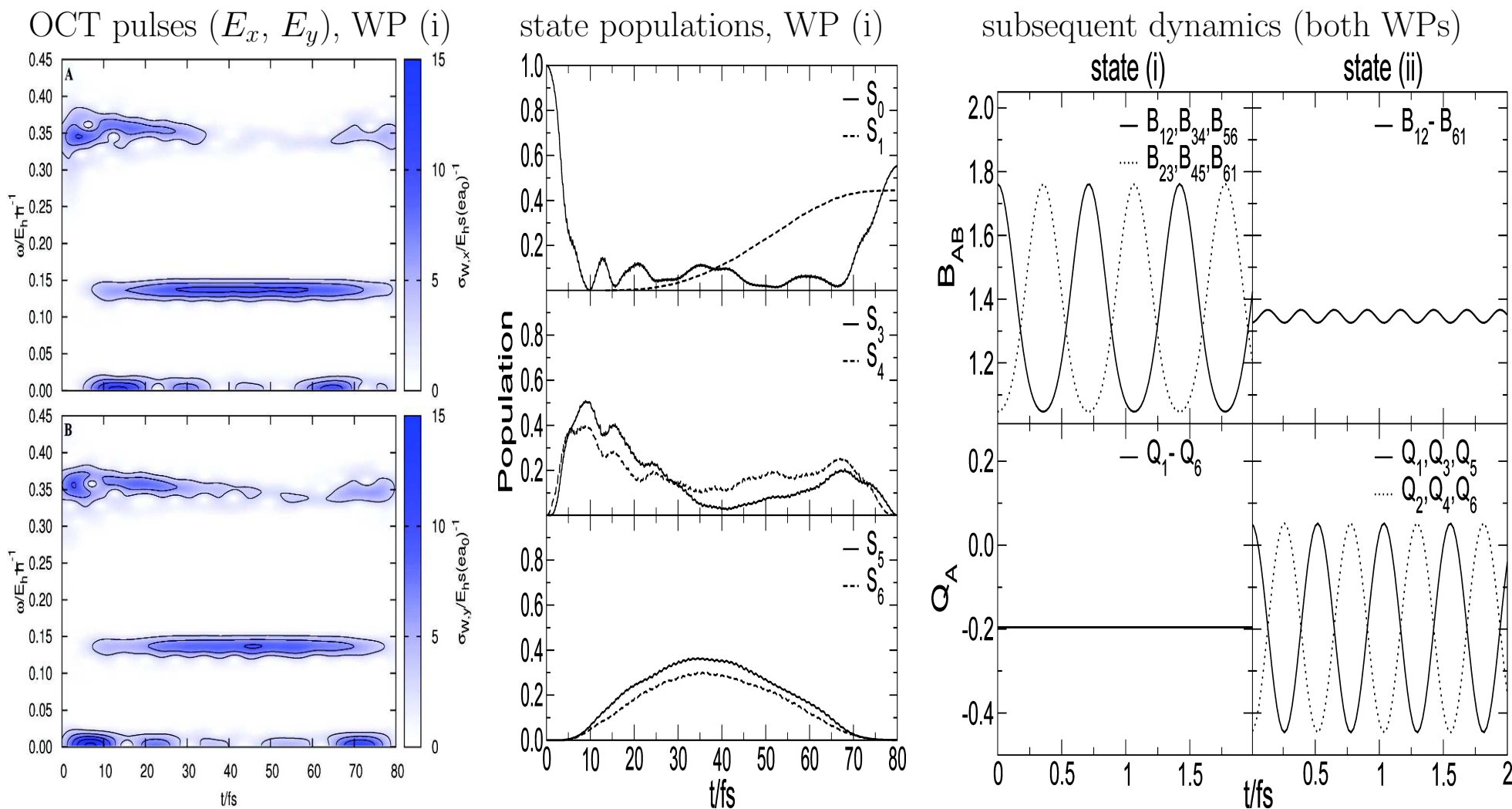path $S_0 \rightarrow S_0 + S_3 \rightarrow S_0 + S_5 \rightarrow S_0 + S_1$

(ii)

target $\boxed{\hat{O} = |S_0 + S_2\rangle\langle S_0 + S_2|}$
path $S_0 \rightarrow S_0 + S_4 \rightarrow S_0 + S_5 \rightarrow S_0 + S_2$

[1] Ulusoy, Nest, JACS **133**, 20230 (2011)

5.4 Controlled electron dynamics (4)

- **Optimal control of aromaticity: Creating wavepackets[1]** (cont'd)
  - Controlled destruction of aromaticity and subsequent dynamics:

    TD-CISD/6-31G* (20 states)

OCT pulses (E_x, E_y), WP (i)   state populations, WP (i)   subsequent dynamics (both WPs)

[1] Ulusoy, Nest, JACS **133**, 20230 (2011)

5.4 Controlled electron dynamics (5)

- **Control of electron correlation**[1]
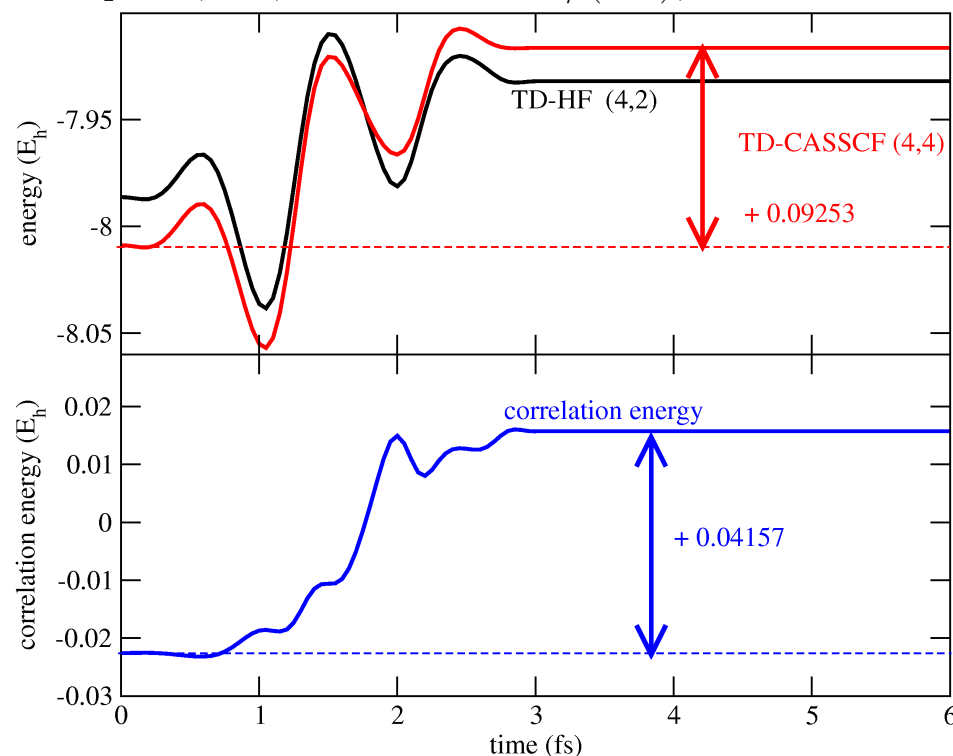 - Time-dependent "correlation energy"

    LiH, TD-CASSCF(4,n)/6-311++G(2df,2p), excitation with laser pulse

$\sin^2$ pulse, 3fs, $E_0 = 0.01$ $E_h/(ea_0)$, $\hbar\omega = 0.15$ E_h
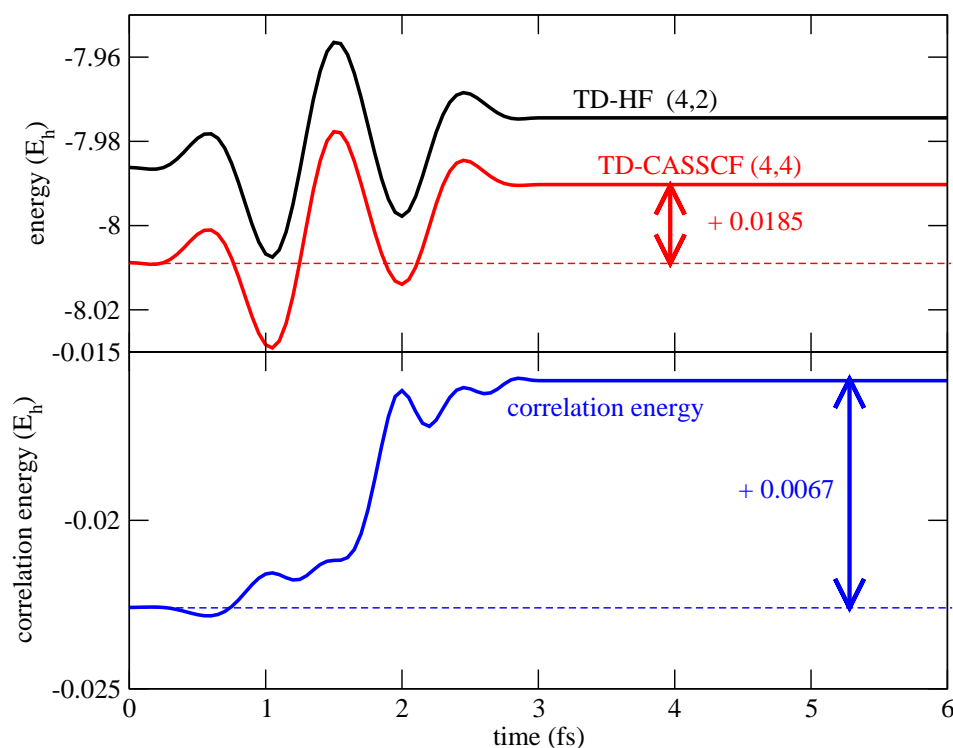
$\sin^2$ pulse, 3fs, $E_0 = 0.025$ $E_h/(ea_0)$, $\hbar\omega = 0.15$ E_h

$E_{\text{corr}}(t) < 0$

$E_{\text{corr}}(t) > 0!$

"Correlation energy": $\boxed{E_{\text{corr}}(t) = E_{\text{TD-CASSCF}}(t) - E_{\text{HF}}(t)}$

[1] Nest, Saalfrank, unpublished

5.4 Controlled electron dynamics (6)

- **Other (statistical) measures of correlation**

  - One-electron density operator $\hat{\gamma}$ and matrix $\underline{\underline{\gamma}}$

    $$\hat{\gamma}(1, 1') = N \int \Psi(1, 2, \ldots, N)\, \Psi^*(1', 2, \ldots, N)\, d2 \ldots dN$$ 1-density operator

    $$\gamma_{ij} = \int d1\, d1'\, \chi_i^*(1)\, \gamma(1, 1')\, \chi_j(1')$$ 1-density matrix in HF orbital basis

    If Ψ is the HF ground state, then $\underline{\underline{\gamma}} = \underline{\underline{1}}_N$.

  - One-electron entropy S and and "quantum impurity" C

    $$S = -k_B \, \mathrm{Tr}\left(\underline{\underline{\gamma}} \ln \underline{\underline{\gamma}}\right)$$ $$C = 1 - \frac{1}{N} \, \mathrm{Tr}\left(\underline{\underline{\gamma}}^2\right)$$

    "entanglement of formation[1]"   "correlation", "linearized entropy"

    If Ψ is a single-determinant state (such as the HF ground state), then $\boxed{S = C = 0}$.
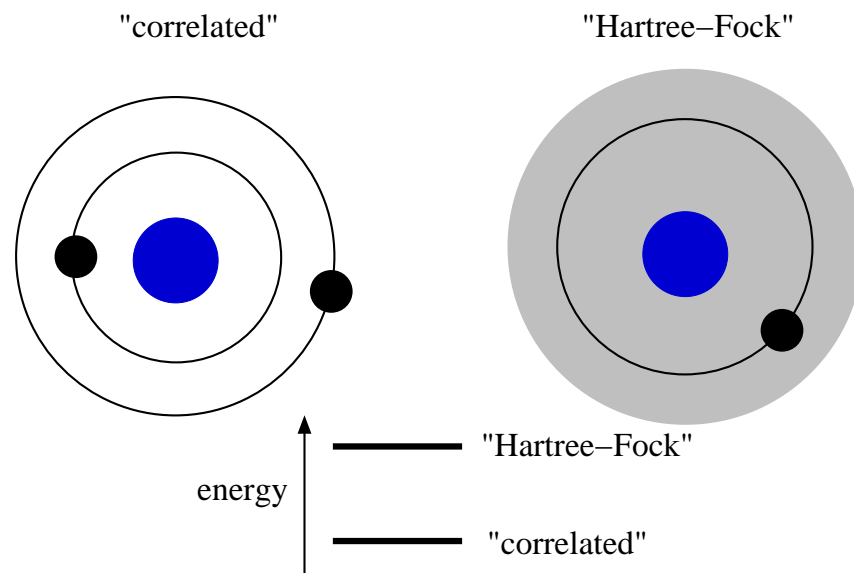
  - Two questions:

    ❶ What is the dynamics of a HF state under the influence of $\hat{H}_{el}$?

    ❷ Can we make a HF state, at a given time, from a correlated ground state?

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[1] Wootters, PRL **80**, 2245 (1998)

5.4 Controlled electron dynamics (7)

- ● **The Hartree Fock state**

"correlated"   "Hartree–Fock"

D.R. Hartree (1897-1958)   V.A. Fock (1898-1974)

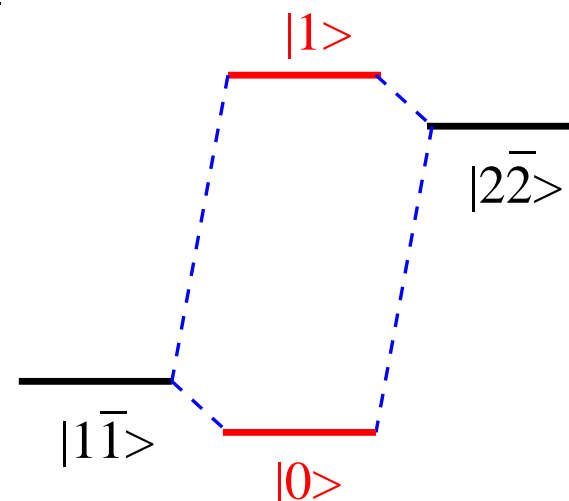- ● **The Hartree Fock state as an excited state: H_2 minimal basis**

The Full-CI $^1\Sigma_g^+$ correlated states $|0\rangle$, $|1\rangle$ derive from determinants $\Psi_{\text{HF}} = |1\bar{1}\rangle$, $|\psi_{1\bar{1}}^{2\bar{2}}\rangle = |2\bar{2}\rangle$ as

$$\Psi_0^{\text{CISD}} = |0\rangle = \cos(\beta/2)\,|1\bar{1}\rangle + \sin(\beta/2)\,|2\bar{2}\rangle \quad \text{energy} \quad E_0$$

$$\Psi_1^{\text{CISD}} = |1\rangle = -\sin(\beta/2)\,|1\bar{1}\rangle + \cos(\beta/2)\,|2\bar{2}\rangle \quad \text{energy} \quad E_1$$

with mixing angle

$$\beta = \tan^{-1}\left(2|\langle 1\bar{1}|\hat{H}_{el}|2\bar{2}\rangle|/\left(E_{1\bar{1}} - E_{2\bar{2}}\right)\right)$$

$|1\rangle$

$|2\bar{2}\rangle$

$|1\bar{1}\rangle$

$|0\rangle$

5.4 Controlled electron dynamics (8)

- ## Dynamics of an initial Hartree Fock state

  - Initial state: $\boxed{\Psi(0) = \Psi_{\text{HF}} = \Psi_0 = \cos(\beta/2)\,|0\rangle - \sin(\beta/2)\,|1\rangle}$

  - Propagated state: $\boxed{\Psi(t) = e^{-i\hat{H}_{el}t/\hbar}\,\Psi(0) = e^{-iE_1 t/\hbar}\left(\cos(\beta/2)e^{i\omega_{10}t}|0\rangle - \sin(\beta/2)|1\rangle\right)}$

    with the Bohr frequency $\omega_{10} = (E_1 - E_0)/\hbar$.

  - Entropy and correlation:

    $$\boxed{S/k_B = -2\left[(k_1 - b(t))\ln(k_1 - b(t)) + (k_2 + b(t))\ln(k_2 + b(t))\right]}$$

    $$\boxed{C(t) = 1 - \left((k_1 - b(t))^2 + (k_2 + b(t))^2\right)}$$

    with $k_1 = \cos^4(\beta/2) + \sin^4(\beta/2)$ and $k_2 = 2\sin^2(\beta/2)\cos^2(\beta/2)$ and

    $$\boxed{b(t) = k_2\,\cos(\omega_{10}t) = k_2\,\cos(2\pi t/T)}$$

  - Example: TD-CID/STO-3G, R=1.4 a_0

    $\implies$ oscillation with period

    $$\boxed{T = \frac{2\pi\hbar}{E_1 - E_2}}$$

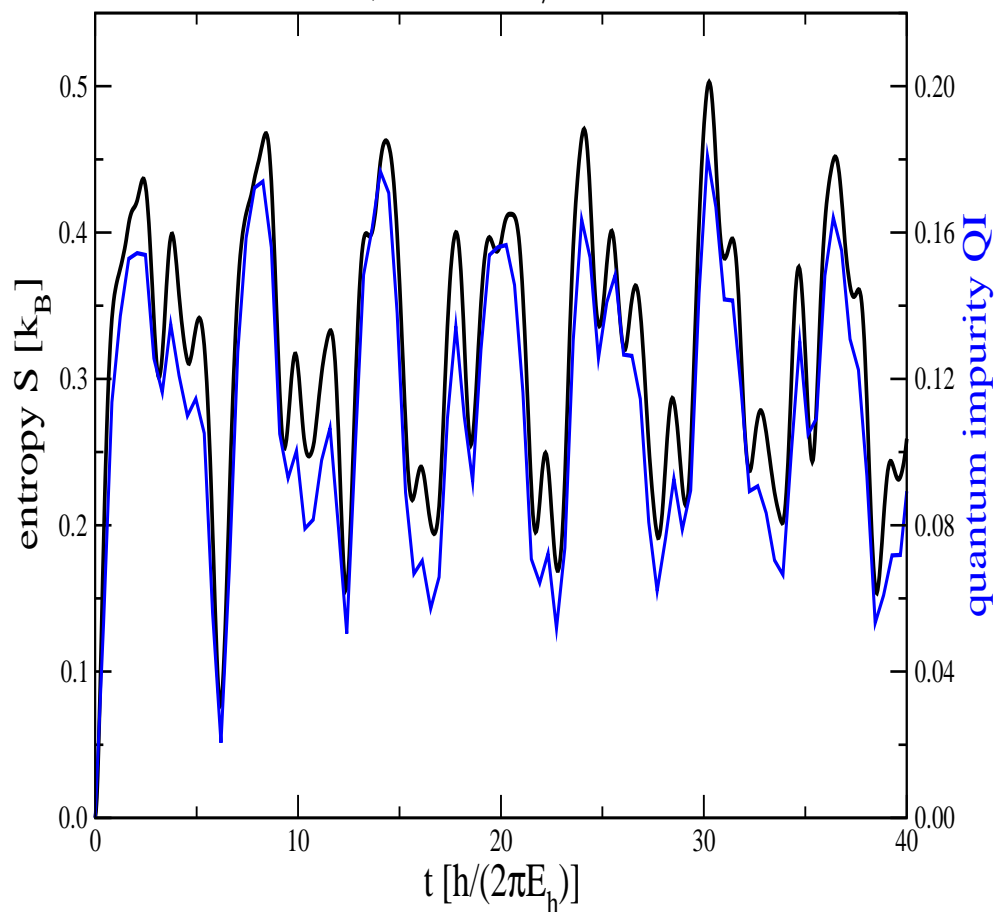   ultrafast buildup of electron correlation

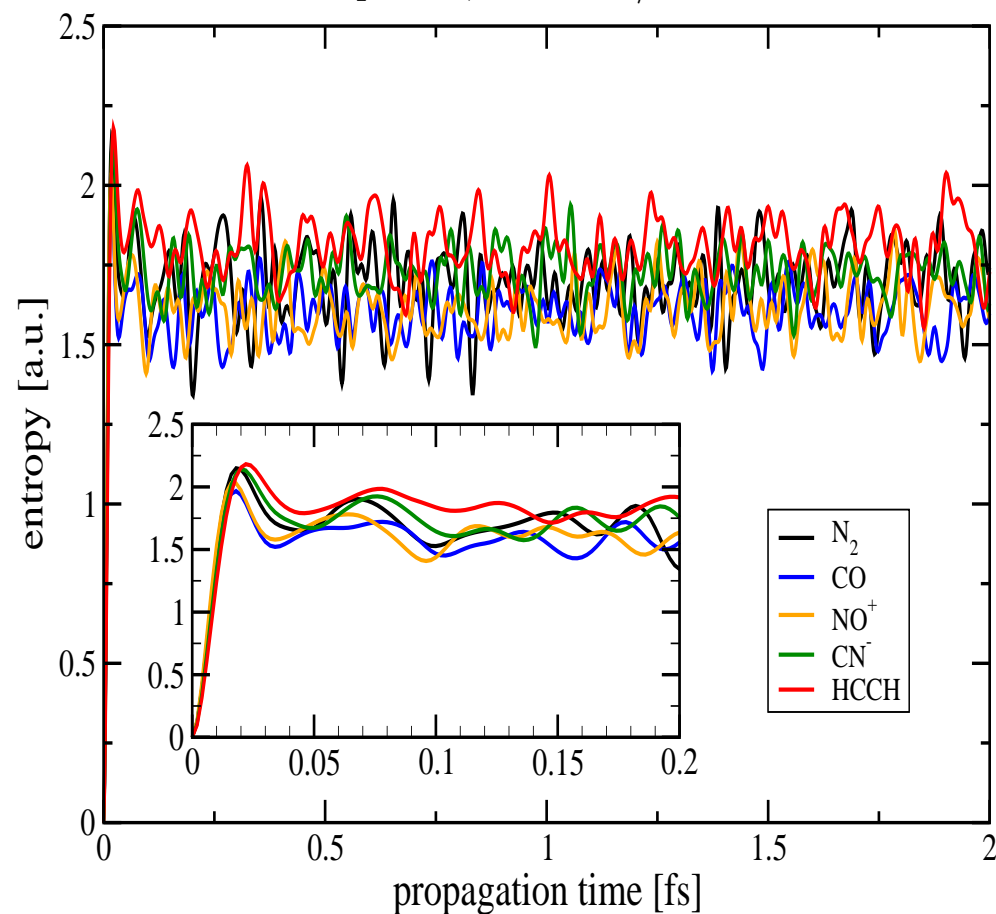[1] Nest, Ludwig, Ulusoy, Klamroth, Saalfrank, JCP **138**, 164108 (2013)

- ## Dynamics of an initial Hartree Fock state (cont'd)

H$_2$, TD-CIS/6-31G*

other species, TD-CIS/6-31G*

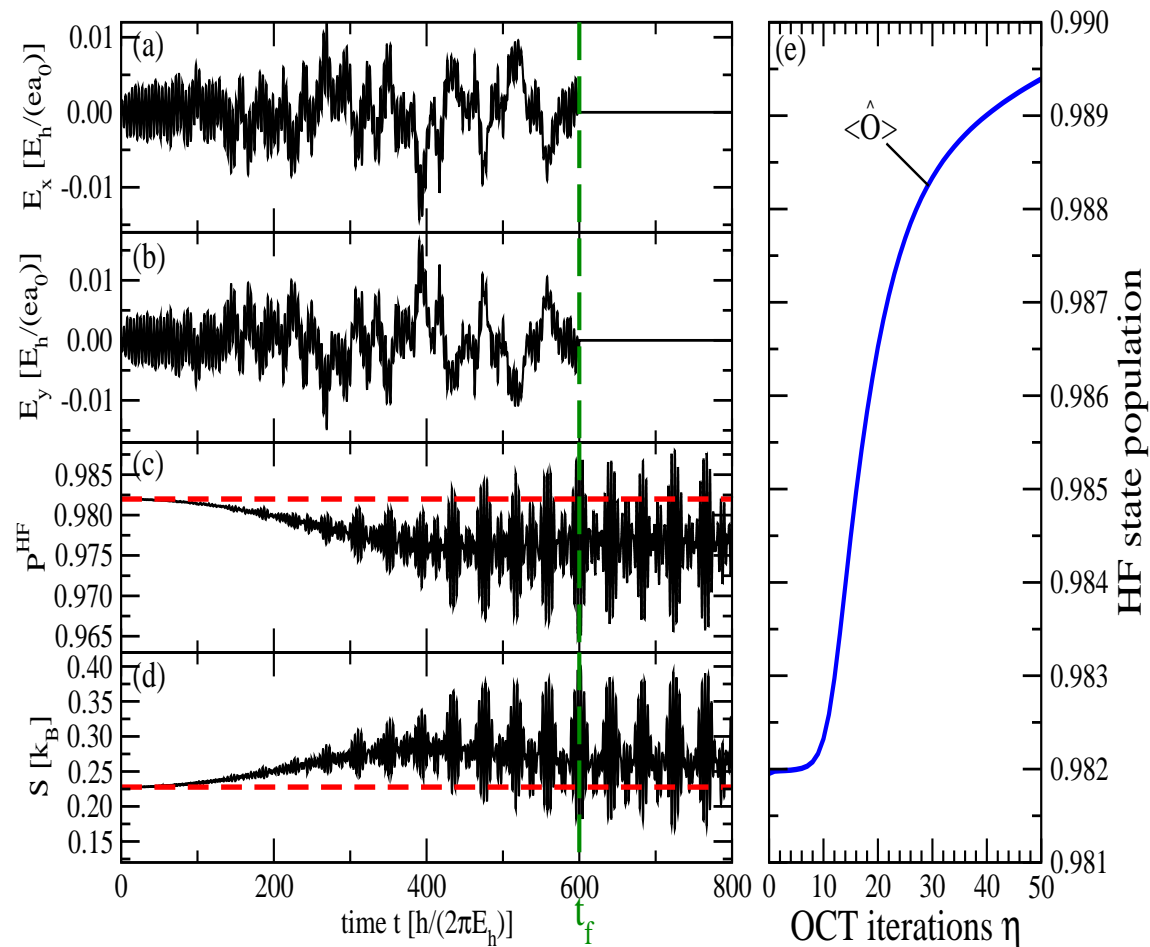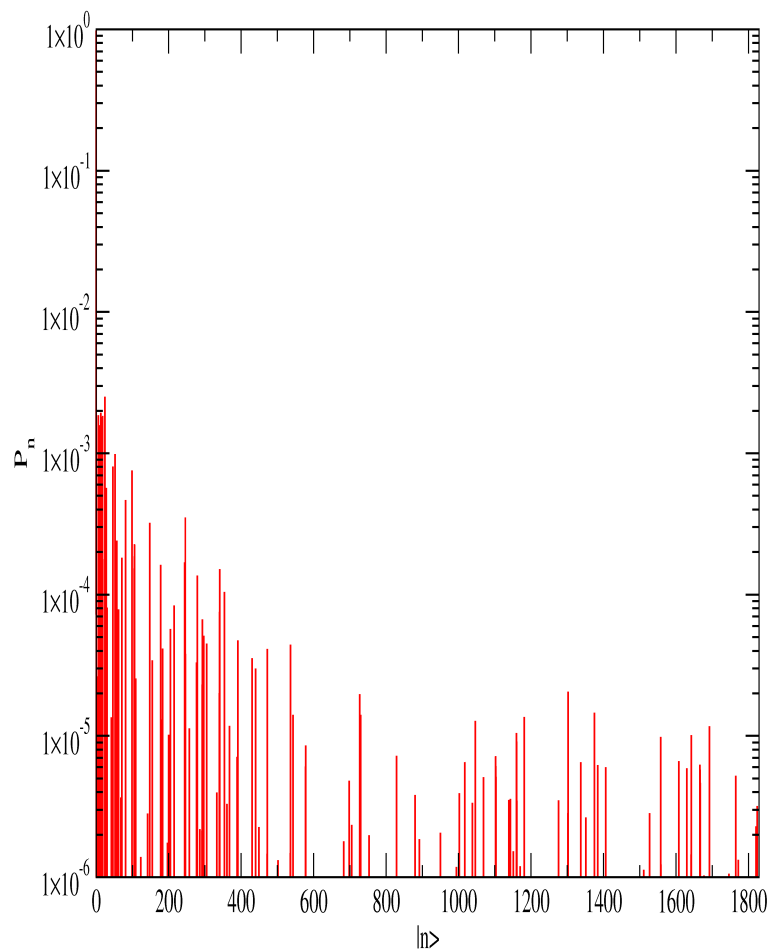attosecond dynamics and ultrafast buildup of correlation

● **Building a Hartree Fock state from a correlated ground state**

H_2, TD-CISD/cc-pVQZ with field optimized field, $\Psi(0) =$ TD-CISD ground state Ψ_0^{CISD}

$\Psi_0 = \Psi_{HF} = \sum_n C_n |n\rangle$, $\boxed{P_n = |C_n|^2}$

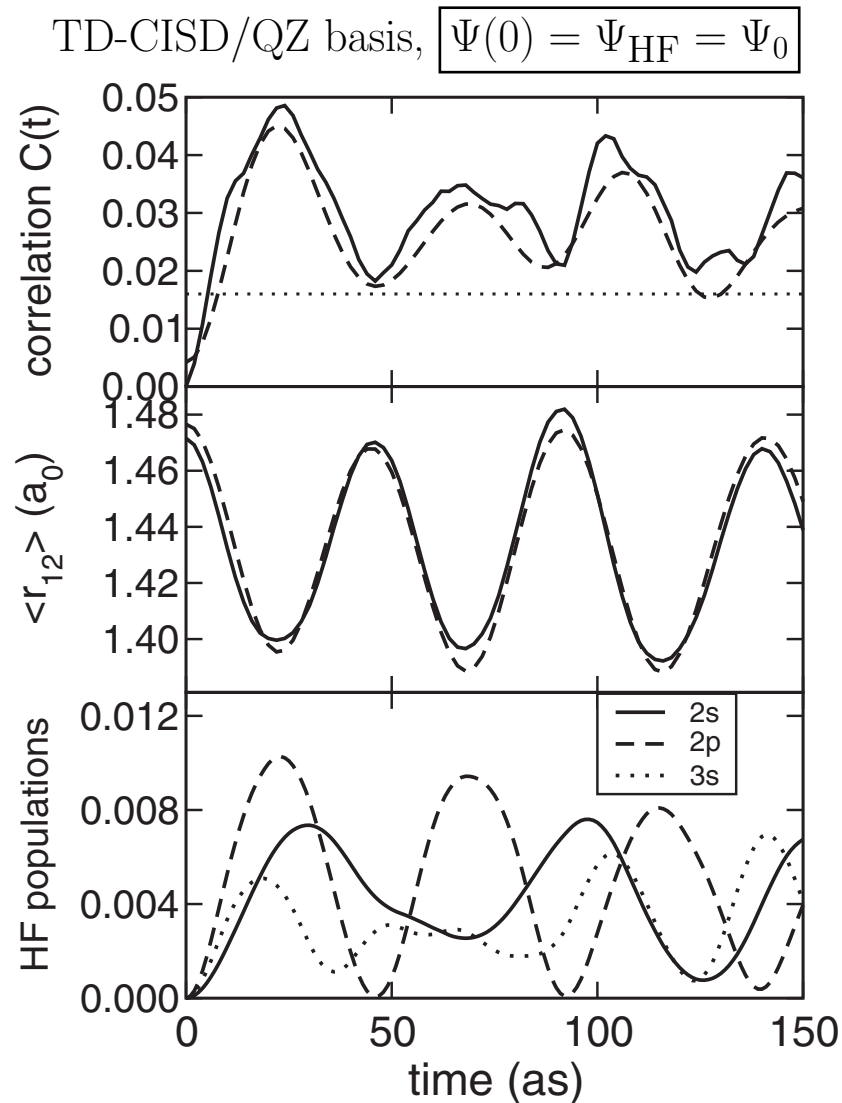Optimal Control Theory: $\boxed{\hat{O} = |\Psi_0\rangle\langle\Psi_0|}$

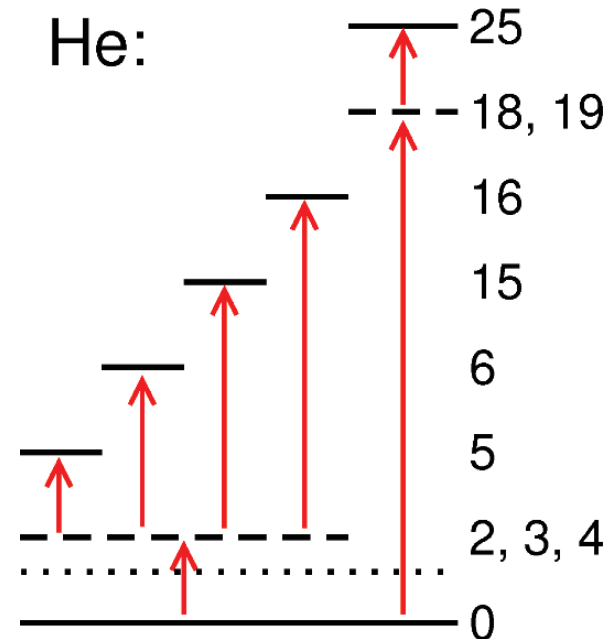complicated pulse, partial success

[1] Klinkusch, Saalfrank, Klamroth, unpublished

5.4 Controlled electron dynamics (10)

- **Building a Hartree Fock state from a correlated ground state: He[1]**

  - Dynamics of HF state
  - Control Strategy

TD-CISD/QZ basis, $\boxed{\Psi(0) = \Psi_{\text{HF}} = \Psi_0}$

Make *approximate HF state* $|\Psi_{\text{HF}}\rangle \sim \sum_{n=0,5,\ldots,25} C_n |n\rangle$ from correlated ground state
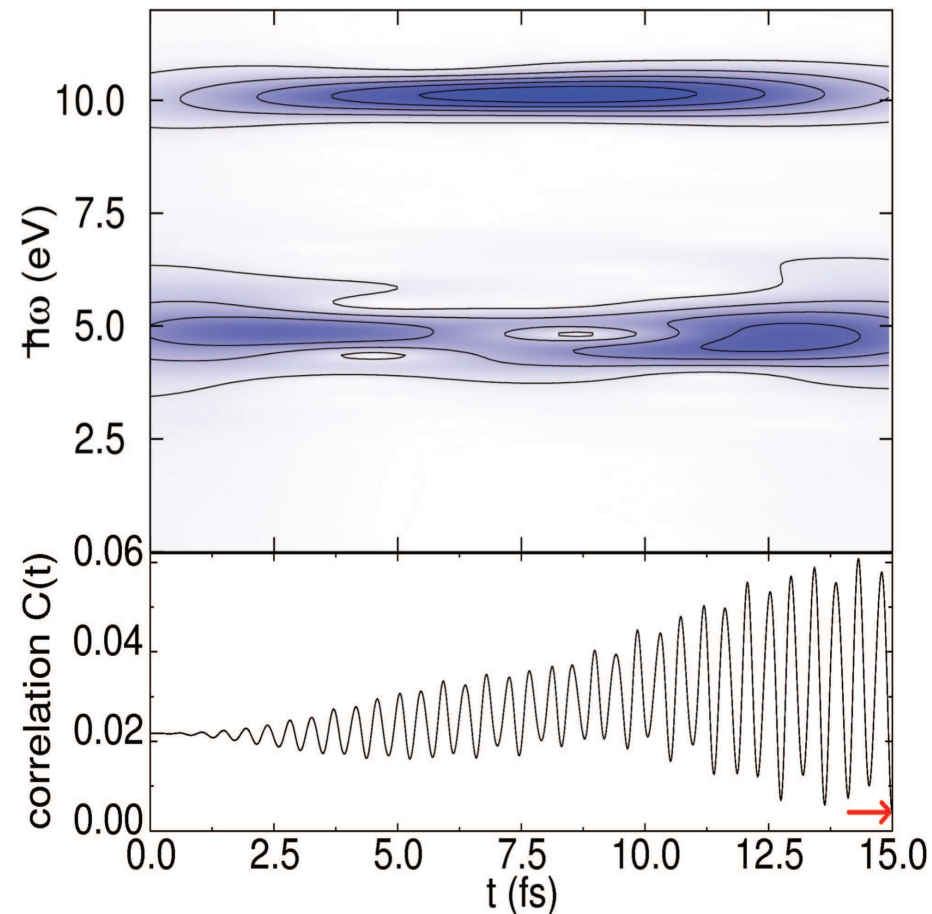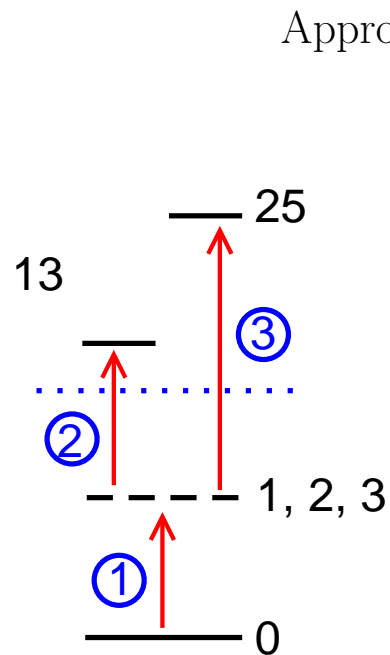

$T = 40$ as, "breathing" electrons
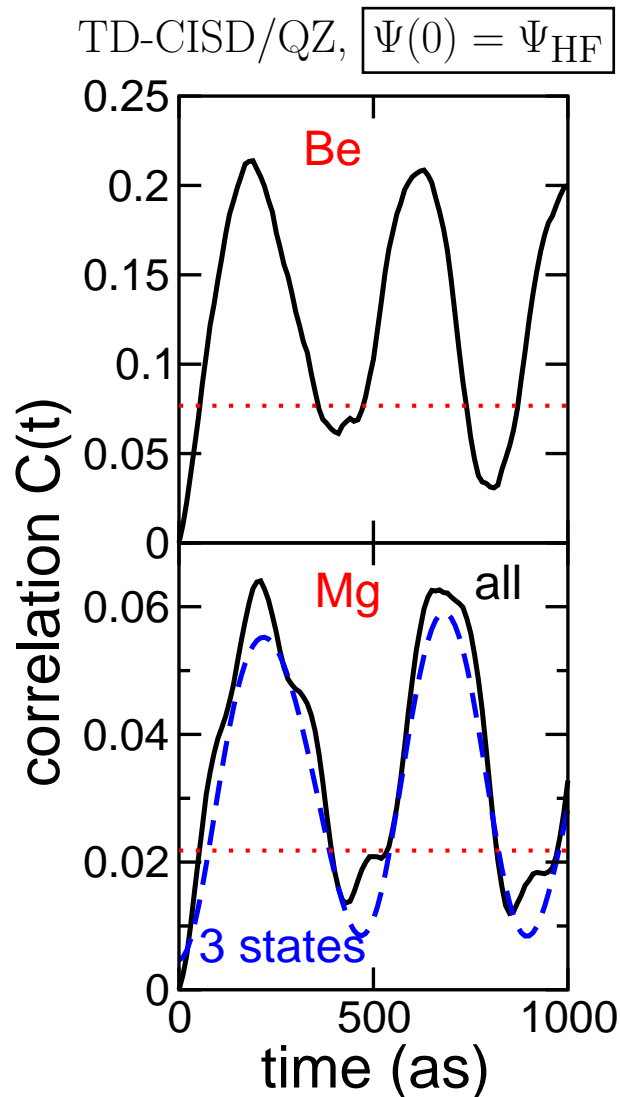

He:

complicated, indirect, ionizing

[1] Nest, Ludwig, Ulusoy, Klamroth, PS, JCP **138**, 164108 (2013)

5.4 Controlled electron dynamics (11)

- **Building a Hartree Fock state from a correlated ground state: Be, Mg[1]**

  - Dynamics of HF state

  - Optimal control for Mg atom

TD-CISD/QZ, $\boxed{\Psi(0) = \Psi_{HF}}$

Approximate HF state $\Psi_{HF} \sim \sum_{n=0,13,25} C_n |n\rangle$

3-pulse strategy ($t_f = 15$ fs) works

[1] Nest, Ludwig, Ulusoy, Klamroth, Saalfrank, JCP **138**, 164108 (2013)

5.4 Controlled electron dynamics (12)

- **Optimal Control Theory and TD-DFT**[1]

  - Target functional to be maximized (closed-shell, $N/2$ spatial orbitals):

$$J = J_1[\rho(\underline{r}, t_f)] - \alpha \int_0^{t_f} |E(t)|^2 dt - 2 \sum_{j=1}^{N/2} \int_0^{t_f} dt \langle \phi_i^{\text{KS}} | \frac{\partial}{\partial t} + \frac{i}{\hbar} \hat{h}_{\text{KS}}(t) | \psi_i^{\text{KS}} \rangle + c.c.$$
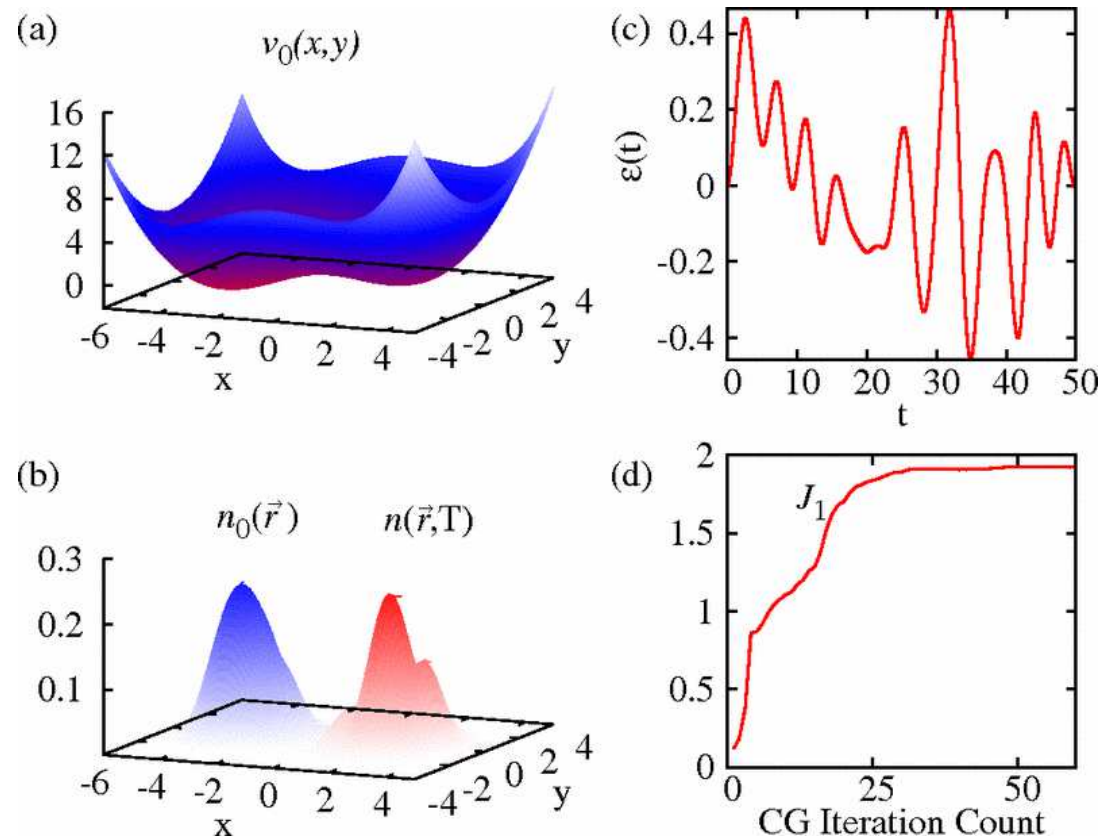
with $\hat{h}_{\text{KS}}(t)$ and ψ_i^{KS} as before. ϕ_i^{KS} are Lagrange-KS orbitals, obtained in more complicated manner than in normal OCT due to *non-linearity* of $\hat{h}_{\text{KS}}(t)$.

- Charge transfer in a quantum dot

  - 2D double well $V(x, y)$
  - two electrons, initially "left"
  - $J_1 = \int_{x>0} \rho(\underline{r}, t_f) \, d\underline{r}$
  - field x-polarized
  - several field constraints

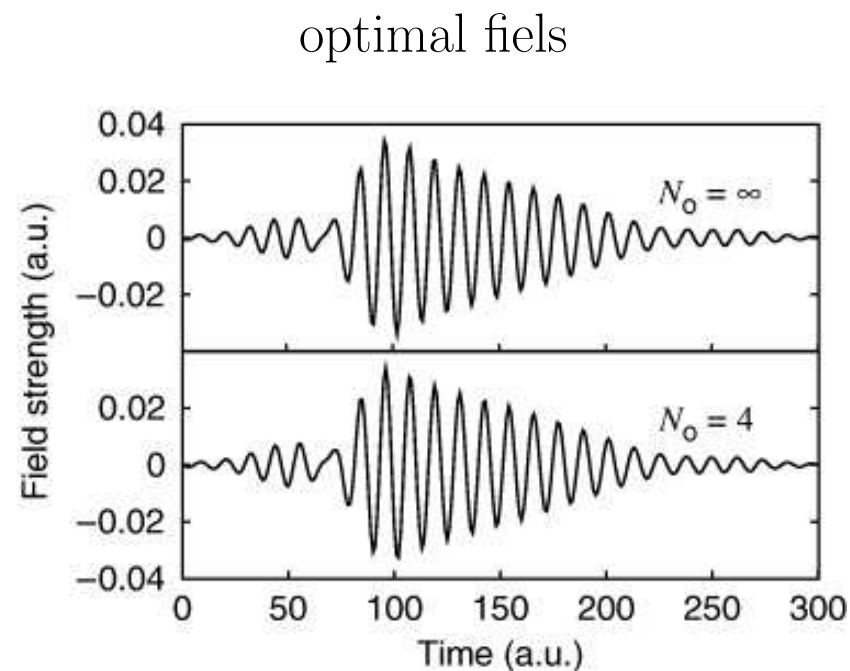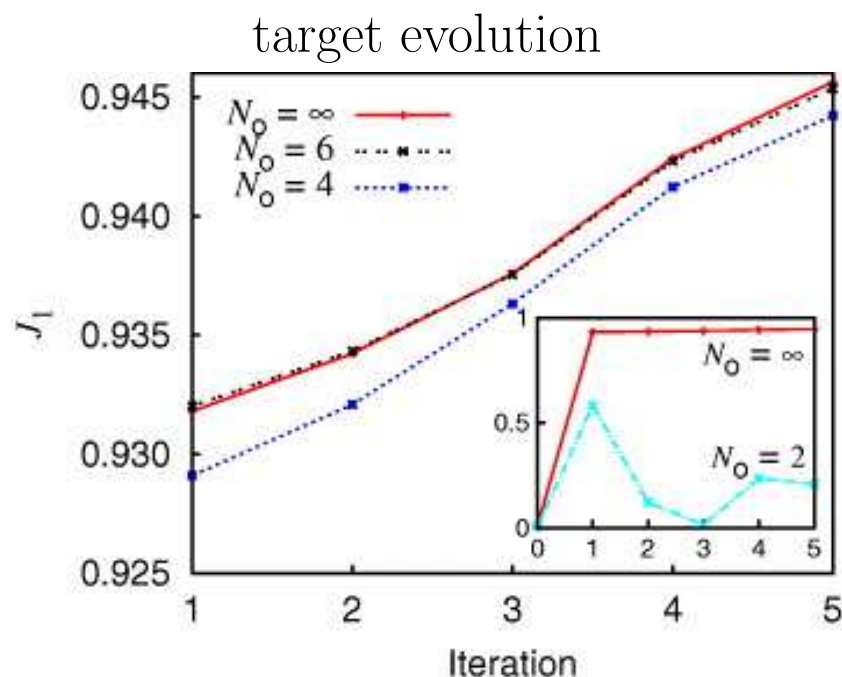[1] Castro, Werschnik, Gross, PRL **109**, 153603 (2012)

- **Optimal Control Theory and MCTDHF**[1]

  - Problem:

    Due to form of Ψ^{MCTDHF} : non-linear optimal control problem. Way out: Solve as linear control problem and use MCTDHF to solve for Ψ^{MCTDHF} and Lagrange-WF Φ^{MCTDHF} for backward propagation.

  - Example: State-to-state transition in 1D He

target evolution   optimal fiels

N_o controls the accuracy of MCTDHF: $N_o = N_{grid} = \infty = $ "exact", $N_o = 2 = $ TDHF

[1] Mundt, Tannor, NJP **11**, 105038 (2009)

6. Summary and Outlook

- **Summary**

- Methods for electron dynamics

  – Density- and WFT-based

  – Linear and non-linear methods

  – TD-CI, MCTDHF systematic

- Extensions

  – ionization

  – beyond dipole approximation

  – nuclear motion

  – dissipative systems

  – optimal control

- Applications

  – state-to-state transitions

  – wavepacket creation

  – response

  – controlled electron dynamics

- **Outlook**

- Methods

  – ionization

  – *multidimensional* nuclear motion

  – beyond dipole approximation

  – quantized fields

  – very strong fields

  – bosons (*e.g.*, MCTDHB[1])

- Applications

  – real environments

  – solids and surfaces

  – open systems (dissipation, transport)

[1] Streltsov, PRA **88**, 041602(R) (2013)