THEORETICAL METHODS TO TREAT CORRELATED ELECTRON AND NUCLEAR DYNAMICS FOR CLOSED AND OPEN QUANTUM SYSTEMS

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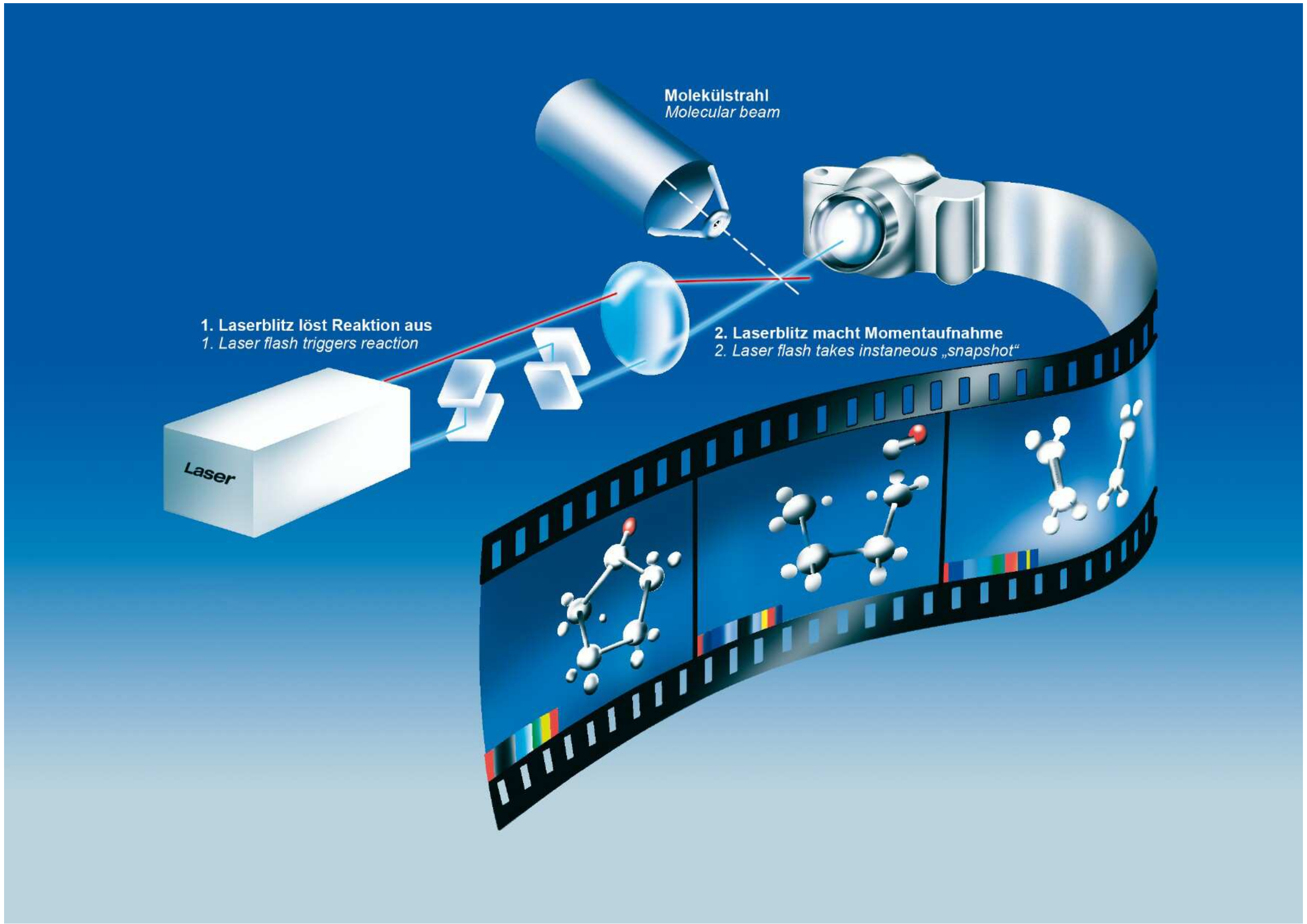
REAL-TIME DYNAMICS: FEMTOCHEMISTRY

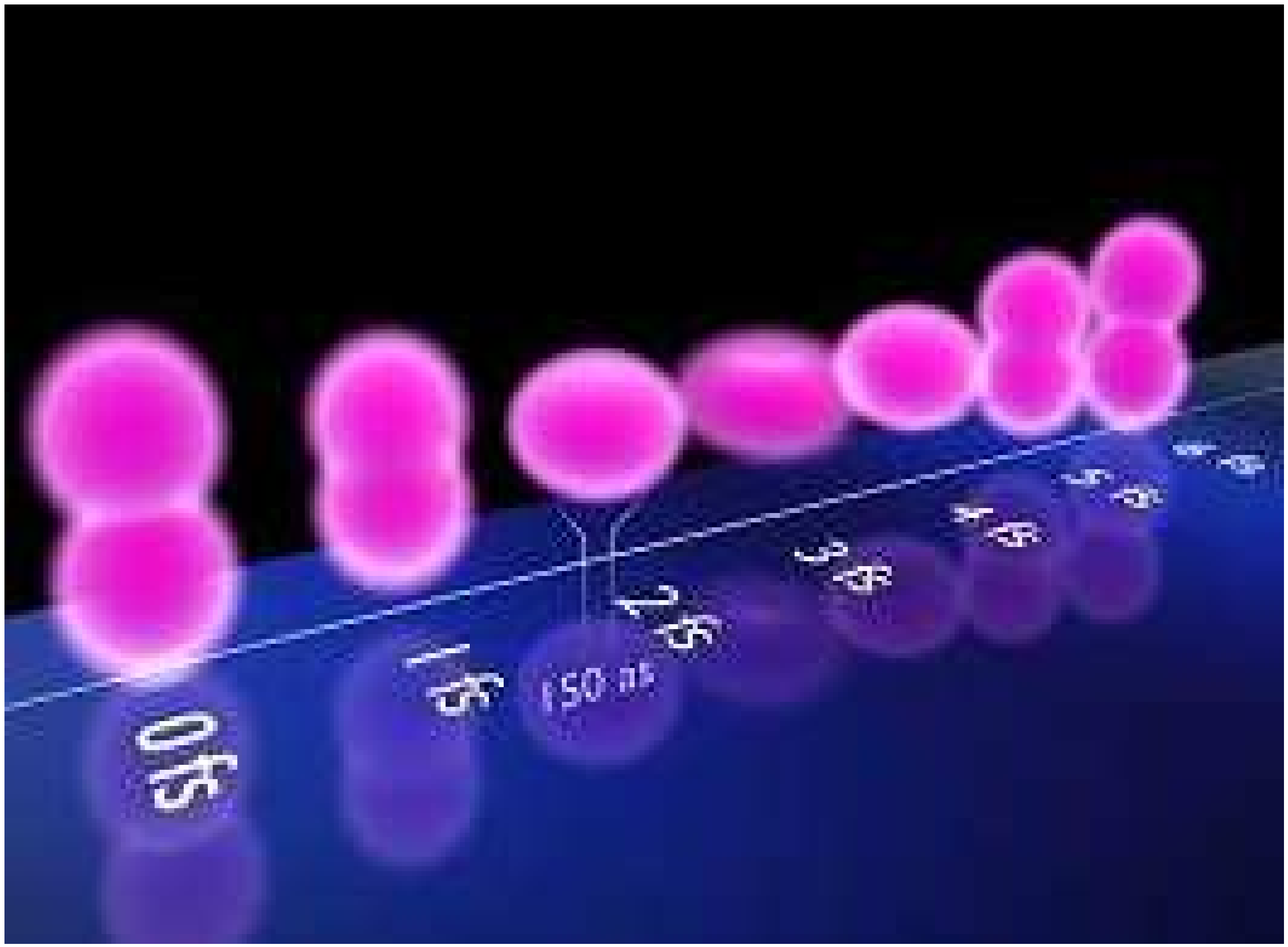


Zewail *et al.*, 1990's

femtosecond chemistry: 1 fs = 10^{-15}s

nuclear (atomic) motions

REAL-TIME DYNAMICS: ATTOPHYSICS



Corkum, Krausz, . . . , > 2000

attosecond physics: 1 as = 10^{-18}s

electronic motions

THIS TALK IS ABOUT . . .

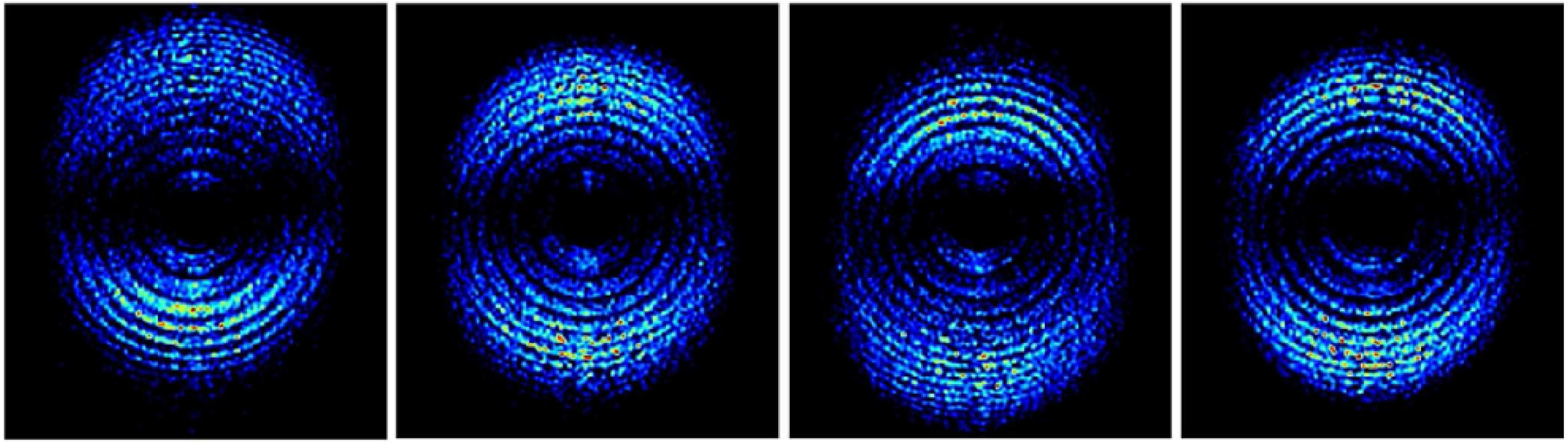
❶ Electron dynamics (mostly light-driven)

- Methods
  - Wavefunction-based: TD-CI, TD-CASSCF (=MCTDHF)
  - Open-system density matrix based: ρ-TDCI
- Some applications
  - Response to laser pulses
  - Correlation and its control

❷ Nuclear dynamics (mostly for system-bath problems)

- Methods
  - Wave-function based: MCTDH
  - Open-system density matrix based: Lindblad approach
- Application
  - Vibrational dynamics and relaxation

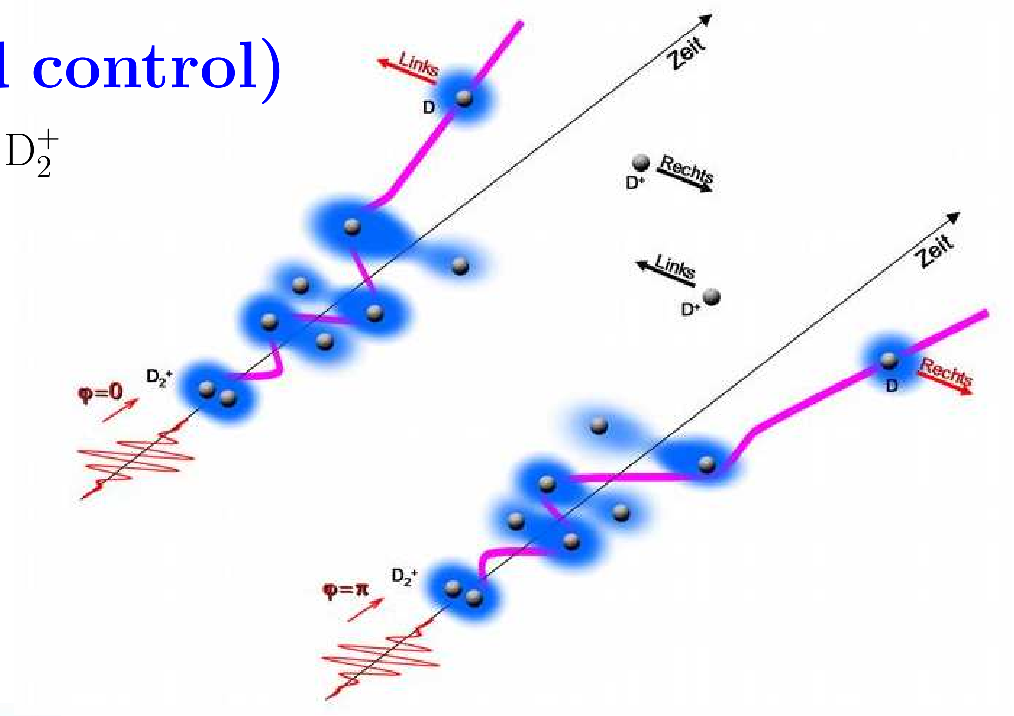
LASER-DRIVEN ELECTRON DYNAMICS



ELECTRON MOTION IN MOLECULES: LASERS

- **Electronic wavepackets (and control)**

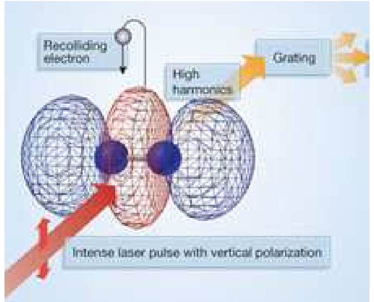
dissociation of D_2^+

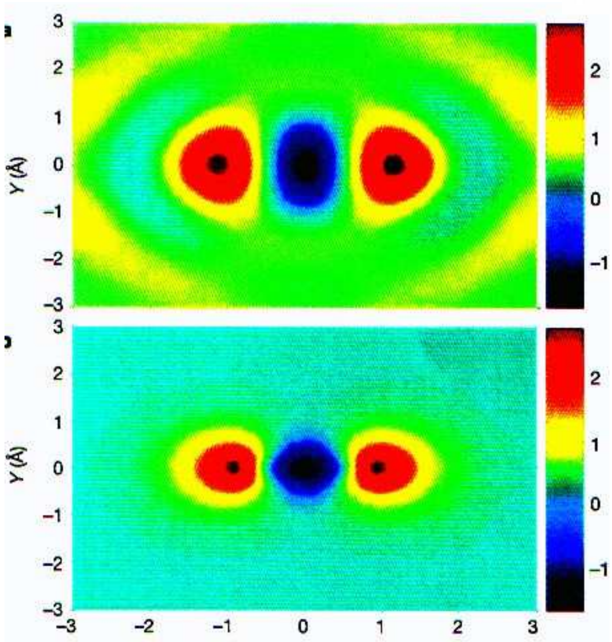


Kling *et al.*, Science **312**, 264 (2006)

- **HHG, orbital tomography**

HOMO of N_2



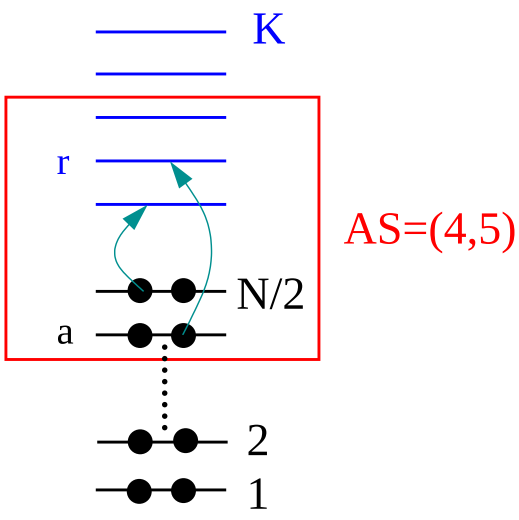


Corkum *et al.*, Nature **432**, 867 (2004)

LASERS AND ELECTRON DYNAMICS: METHODS

- **The N-electron time-dependent Schrödinger equation**

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



- **Solution techniques**
  - One-electron approaches
  - Single-determinant methods
    - TD-HF: $\Psi(t) = \psi_0(t)$
    - TD-DFT: $\Psi(t) = \psi_0^{KS}(t)$
  - 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: $\Psi(t) = C_0(t)\psi_0(t) + \sum_{ar} C_a^r(t)\psi_a^r(t) + \sum_{ab,rs} C_{ab}^{rs}(t)\psi_{ab}^{rs}(t) + \cdots$

TD-CI: TD-CIS, TD-CIS(D), TD-CISD, ... TD-CISD·· N=Full-CI (FCI)

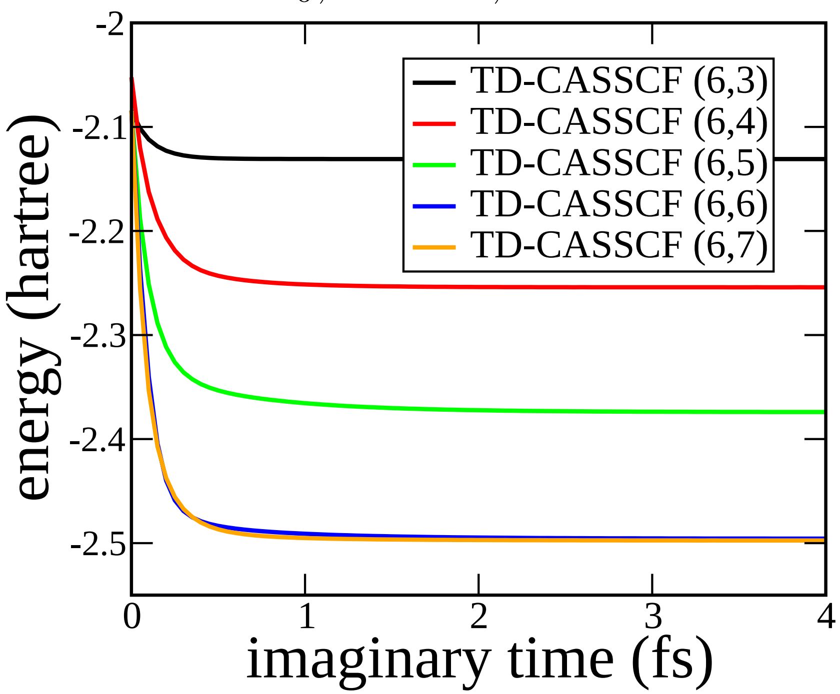
TD-CASSCF(N,M): TD-CASSCF (N,N/2) = TD-HF, ..., TD-CASSCF(N,K) =FCI

EXAMPLE: GROUND STATES FROM TD-CASSCF

- **Dirac-Frenkel variational principle:** $C(t)$, $\phi_n(t)$
- **Imaginary-time propagation: TD-CASSCF(6,K)**

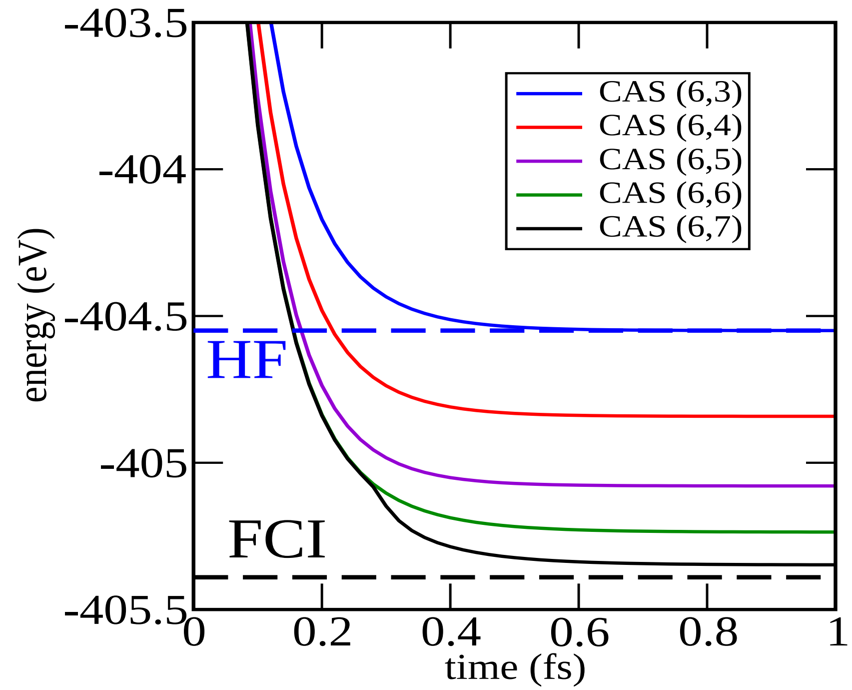
1D jellium model

d=100 a_0, $N = 6$, K orbitals



Molecules: LCAO-MO

Li_2, 6-31G*, $N = 6$



Convergence to Full-CI

M. Nest, T. Klamroth, PS, JCP **122**, 124102 (2005)

M. Nest, JTCC **6**, 653 (2007)

EXCITED STATES FROM TD-CASSCF

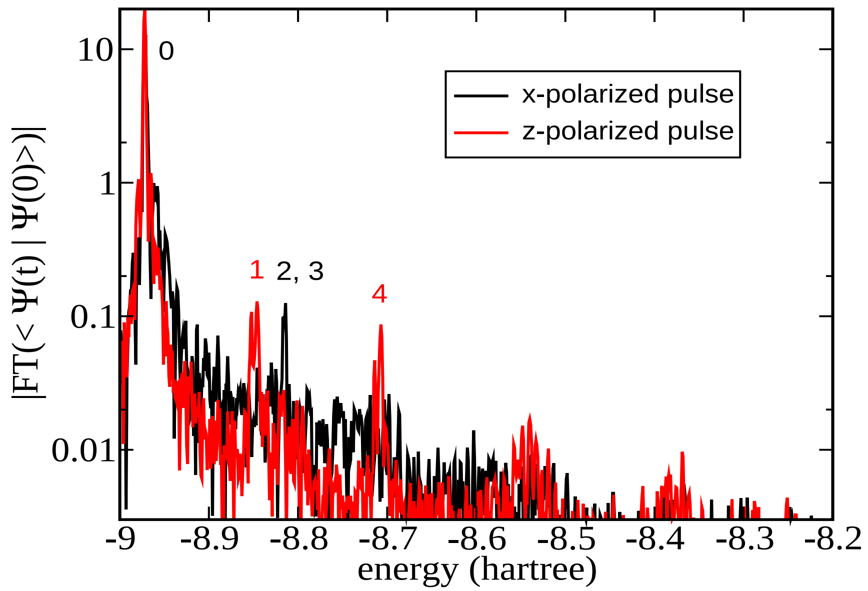
- **Excited states by real-time propagation**

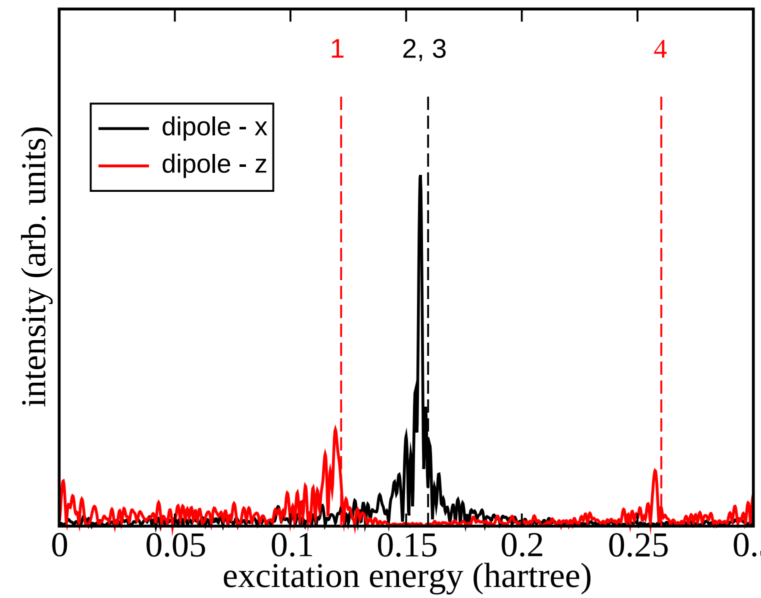
via FT of autocorrelation function

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

via FT of dipole moment

$$\langle \hat{\underline{\mu}} \rangle (t) = \sum_{n,m} C_n^* C_m \; e^{i(E_n - E_m)t/\hbar} \; \langle n | \hat{\underline{\mu}} | m \rangle$$





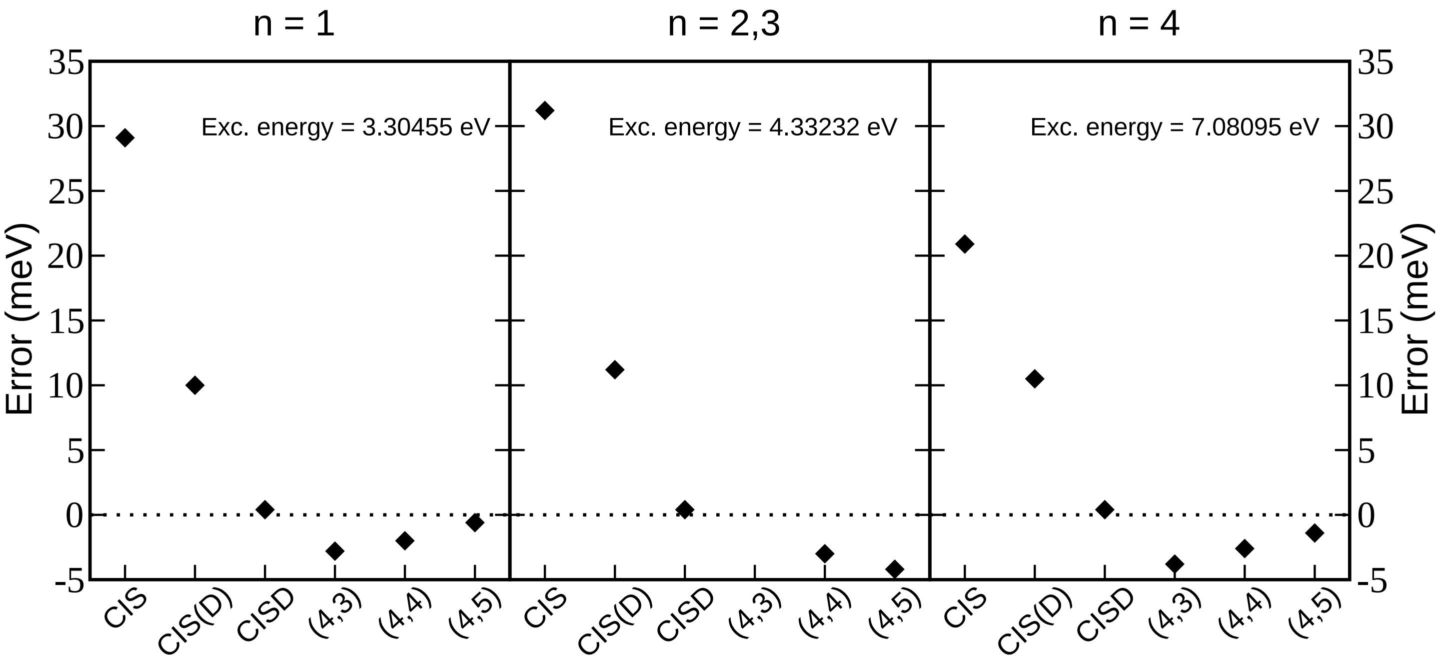
LiH molecule, TD-CASSCF(4,4)/6-31G*

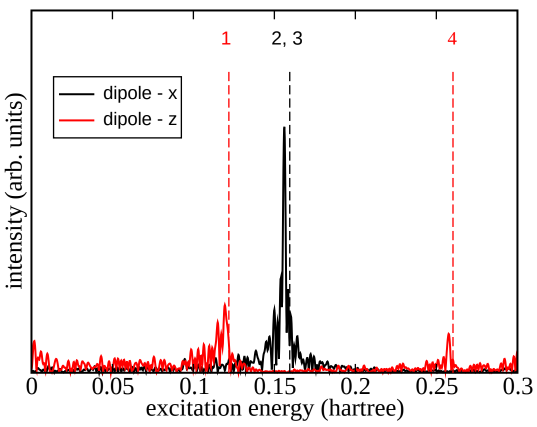
M. Nest, R. Padmanaban, PS, JCP **126**, 214106 (2007)

EXCITED STATES FROM TD-CASSCF

- **Excited states by real-time propagation**

Performance of dipole method (LiH)





M. Nest, R. Padmanaban, PS, JCP **126**, 214106 (2007)

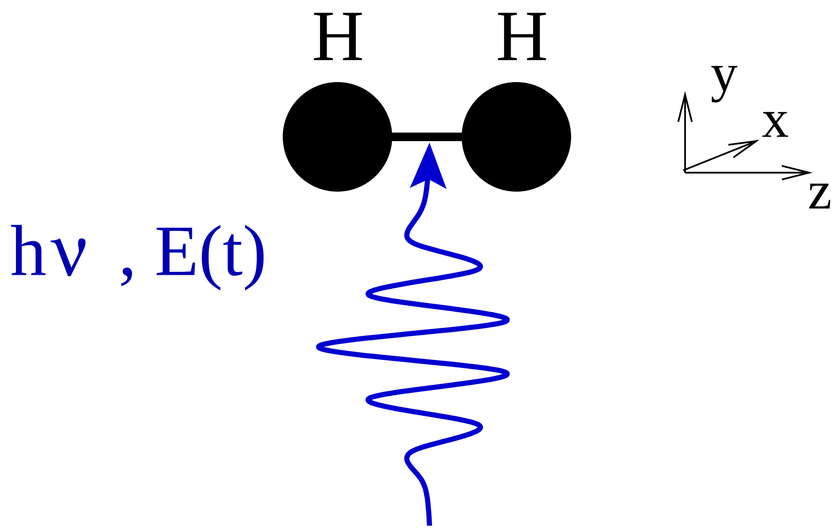
- **Also: Pulsed laser-driven real-time dynamics**

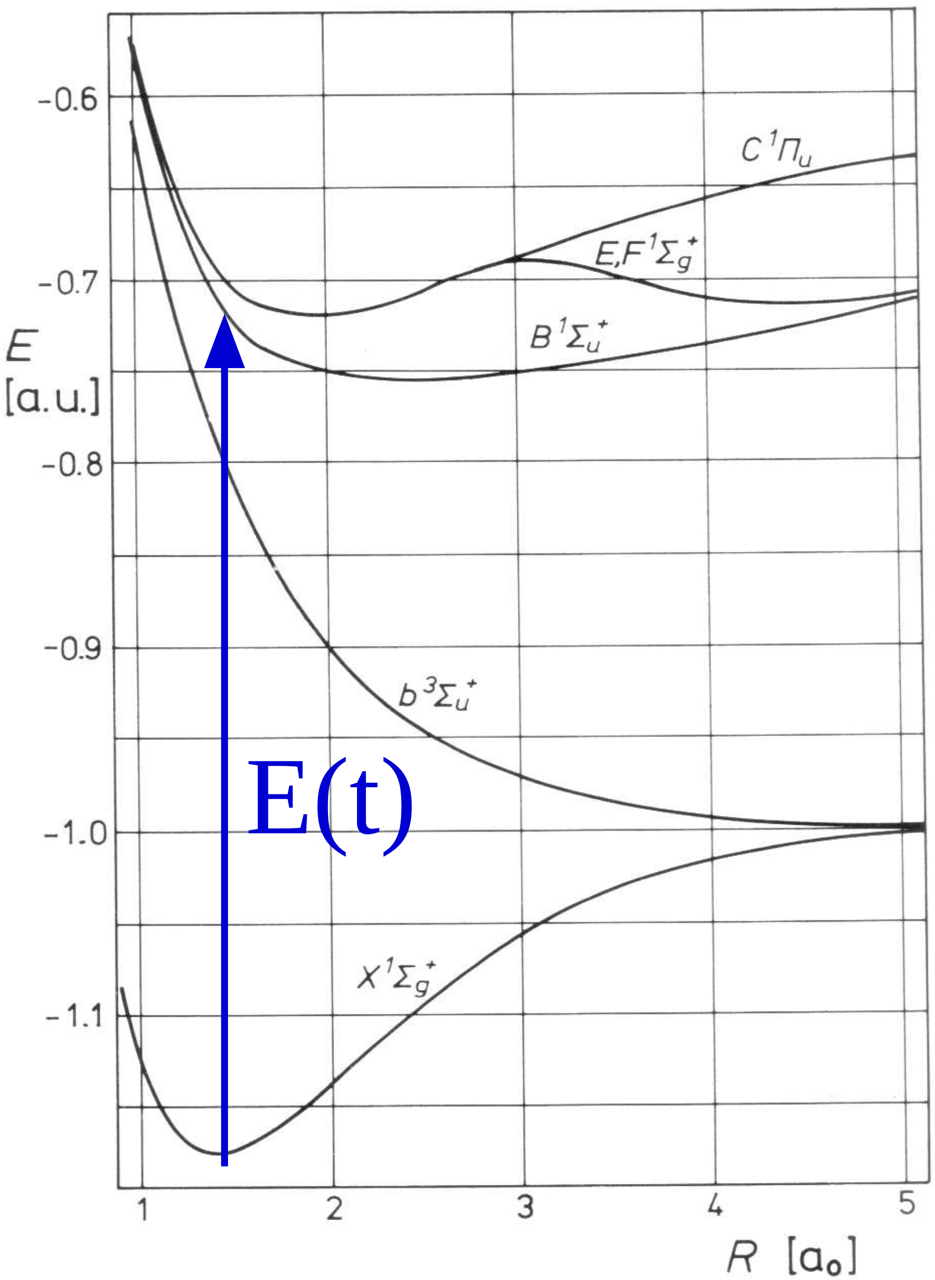
F. Remacle, M. Nest, R.D. Levine, PRL **99**, 183902 (2007)

RESPONSE TO LASER PULSES

A SIMPLE EXAMPLE: THE H_2 MOLECULE

- **The potential curves**



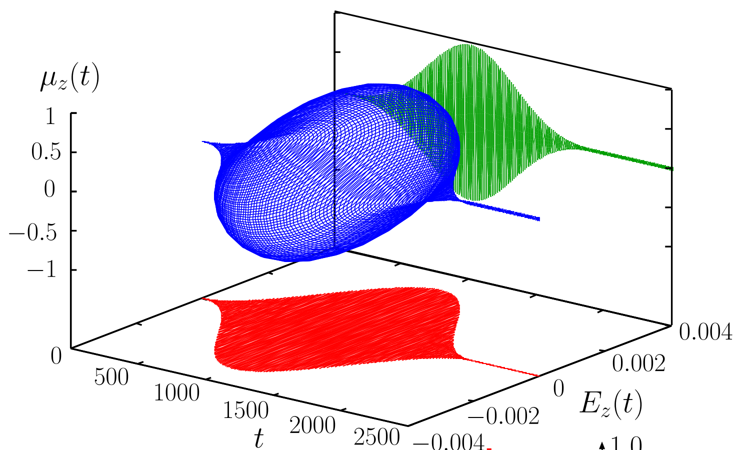


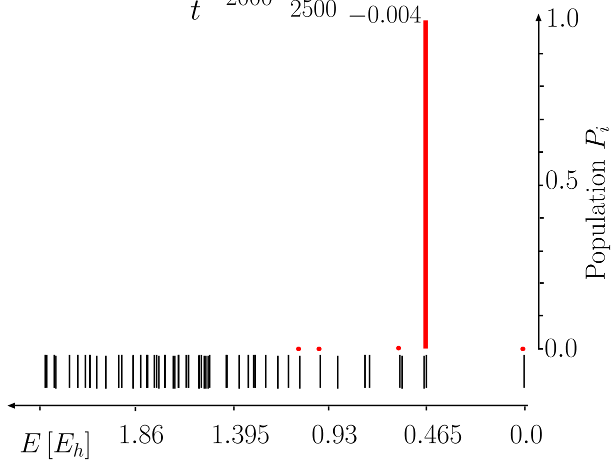
A SIMPLE EXAMPLE: THE H_2 MOLECULE

- **TD-CISD (=FCI) treatment:** aug-cc-pV5Z; $|0\rangle \rightarrow |1\rangle$ laser excitation

  $\sin^2 \pi$ pulses $\boxed{E_z(t) = E_0 \sin^2(\pi t/2\sigma)\ \cos(\omega_{10} t)}$ with FWHM σ

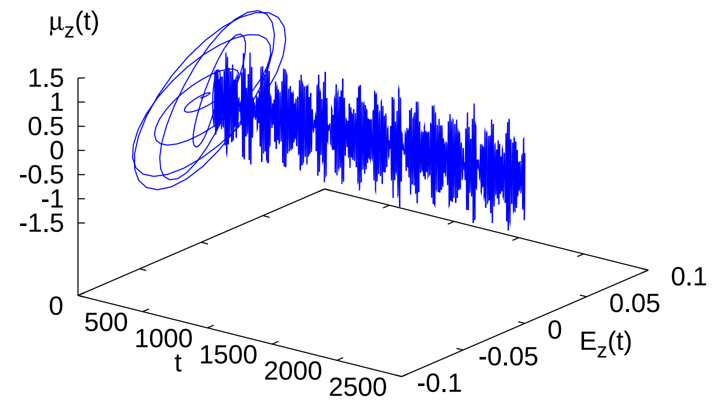
"long pulse": $\sigma = 1000\ \hbar/E_h$

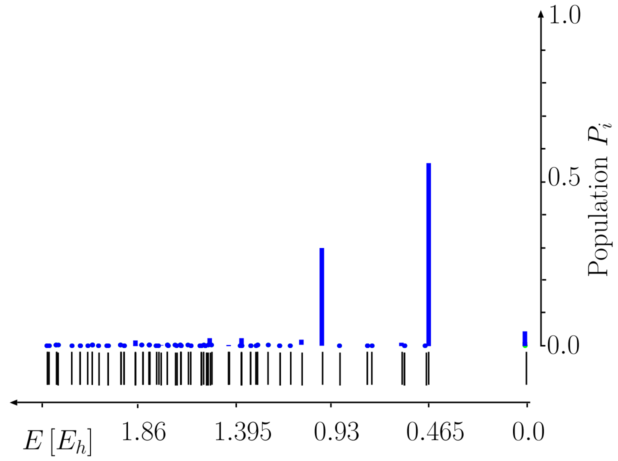




single-photon, state-to-state

"short pulse": $\sigma = 50\ \hbar/E_h$





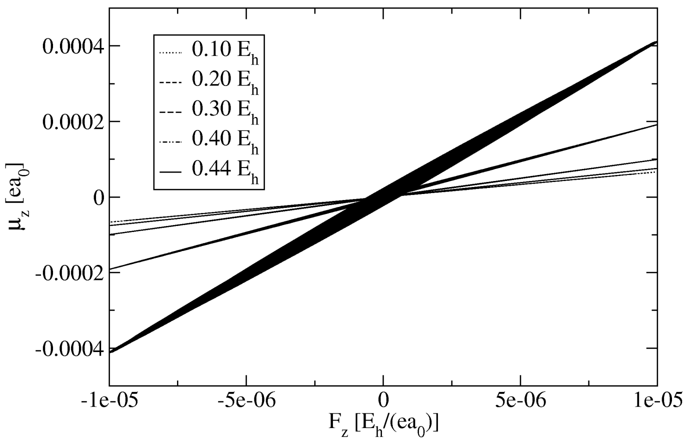
multi-photon, wavepacket

LINEAR RESPONSE: POLARIZABILITY OF H_2

- **Strategy:**

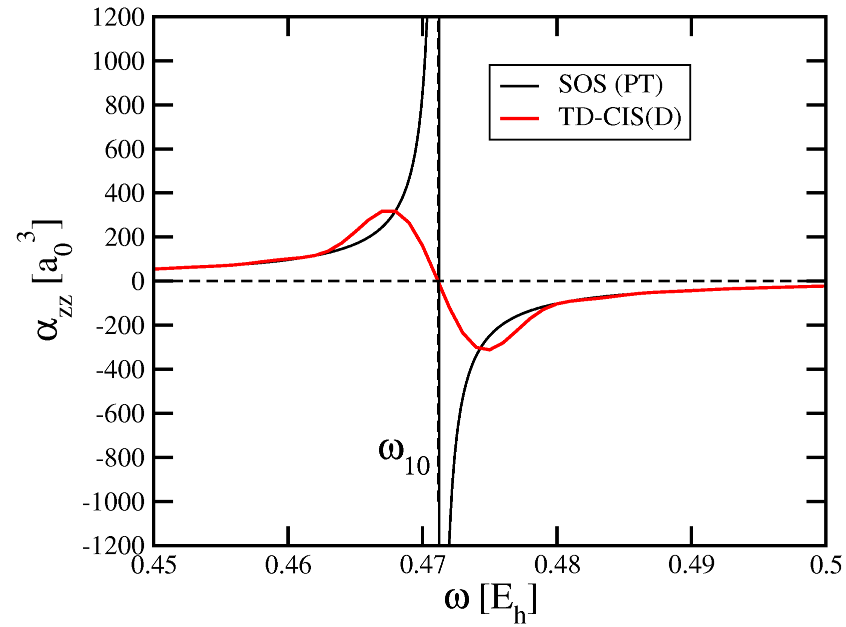
Apply $E_q = E_{0q} \sin^2(\pi t / 2\sigma) \cos(\omega t)$

$$\Longrightarrow \boxed{\mu_q^{ind} = \alpha_{qq'} E_{q'}}$$



Kennlinien for H_2

- **Dynamic:** $\omega \neq 0$



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

- **Static:** $\omega = 0$

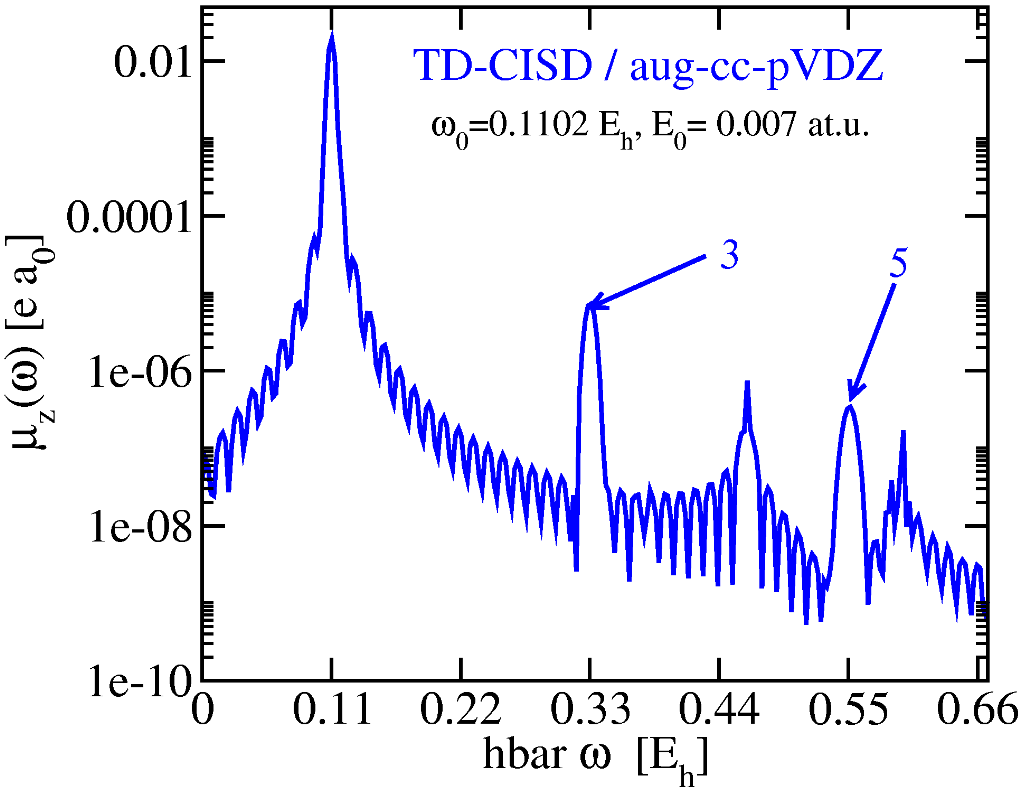
	TD-CISD[a]	Exp.	Stat. QC[b]
$\alpha_{\parallel}$	6.3989	6.303	6.3970
$\alpha_{\perp}$	4.5845	4.913	4.5749

[a] aug-cc-pVQZ; [b] FCI/aug-cc-pVQZ

NONLINEAR RESPONSE: HIGHER HARMONICS

$$E(t), \mu^{ind}(t) \longrightarrow \mathrm{FT} \longrightarrow \mu^{ind}(\omega), E(\omega)$$

- **H_2: Higher harmonics**



only odd

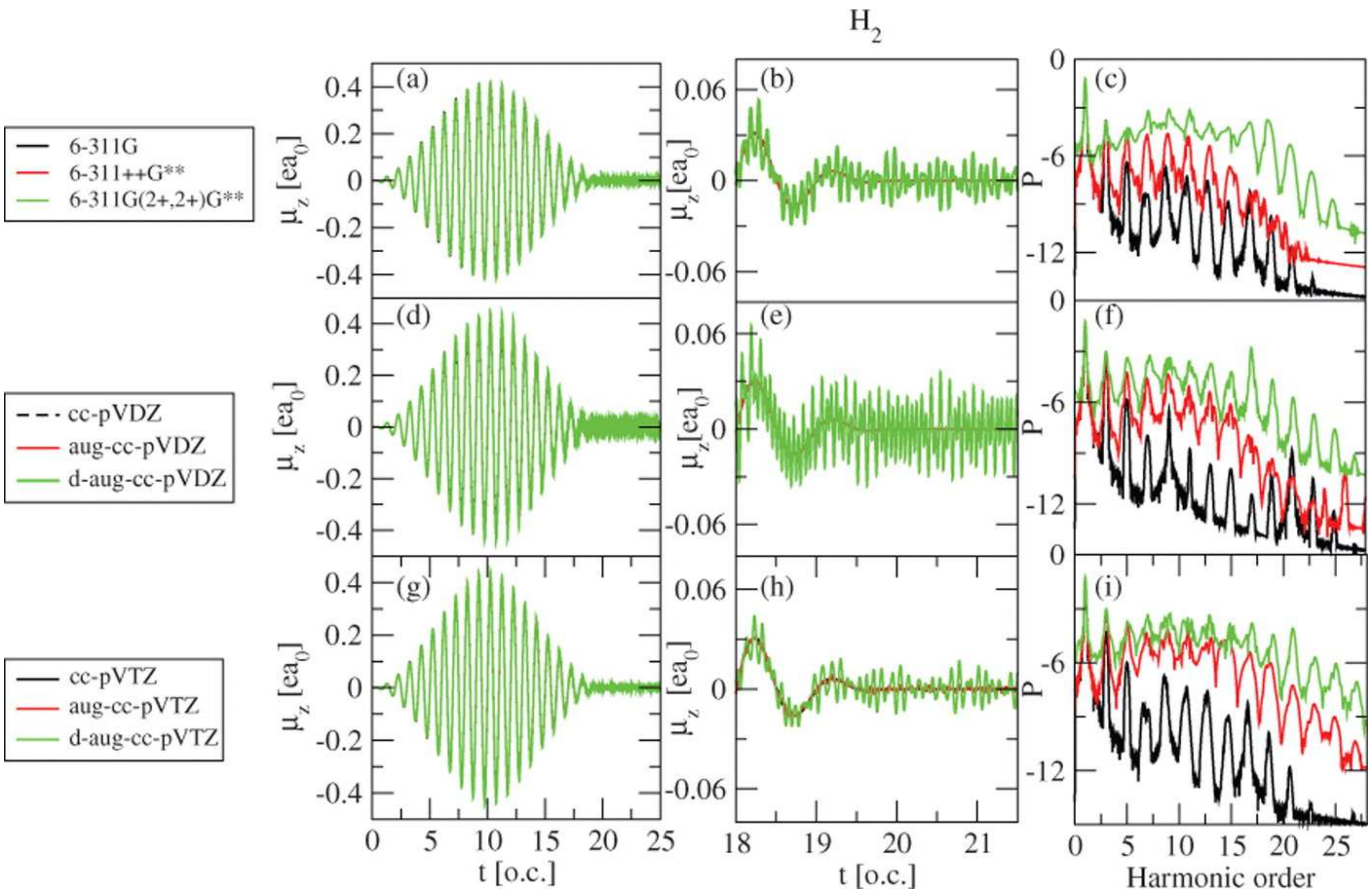
1HG: polarizability $\alpha_{zz}(-\omega, \omega)$
3HG: 2nd hyperpolariz. $\gamma_{zzzz}(-3\omega, \omega, \omega, \omega)$
5HG: 4th hyperpolarizability ...

crossed fields: elements, *e.g.* β_{xyz}

P. Krause, T. Klamroth, PS, JCP **127**, 034107 (2007)

NONLINEAR RESPONSE: HIGHER HARMONICS

- **H_2 HHG: The role of diffuse functions**



HHG cutoff region requires diffuse functions

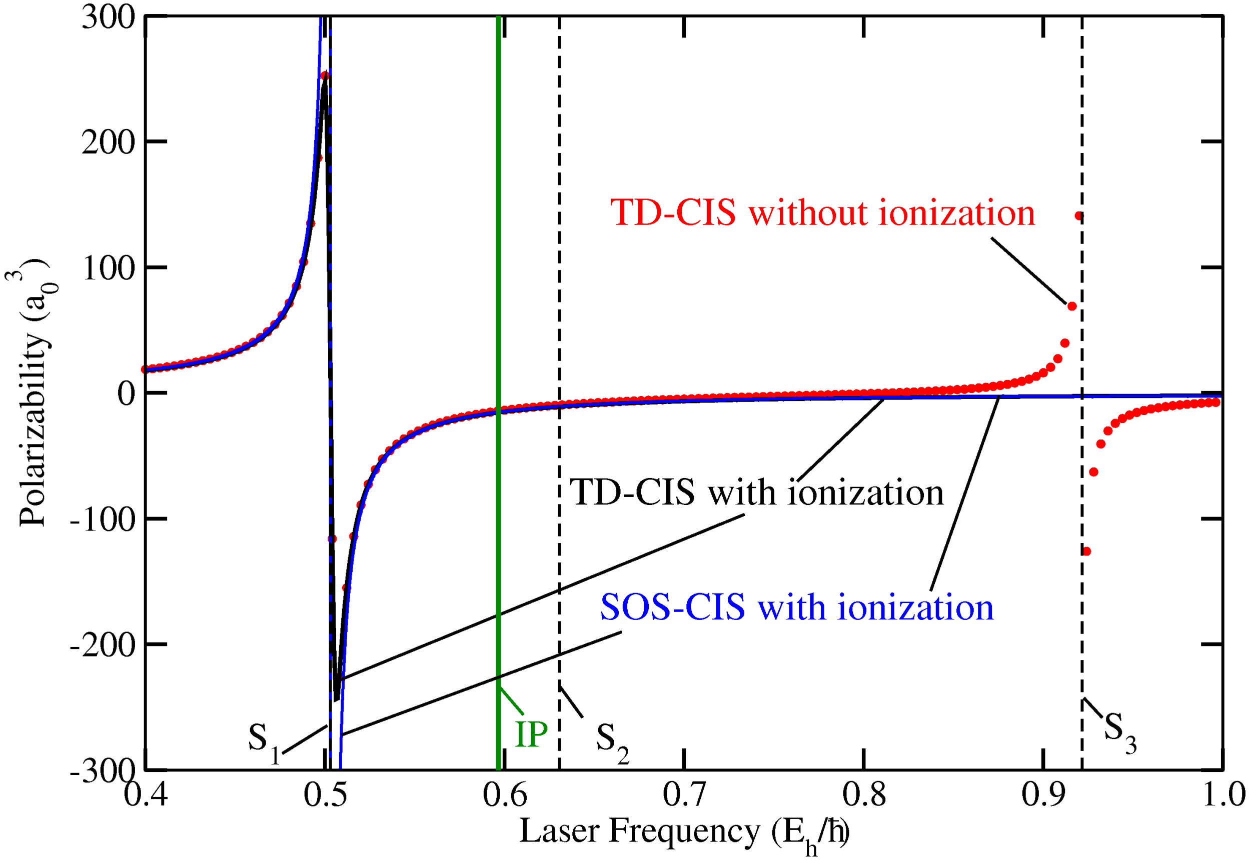
E. Luppi, M. Head-Gordon, Mol. Phys. **110**, 909 (2012)

INCLUSION OF IONIZATION

- **Ionization in TD-CI**

$$E_n \rightarrow E_n - \frac{i}{2}\Gamma_n$$

- **Polarizability H_2, bound → bound/unbound transitions**



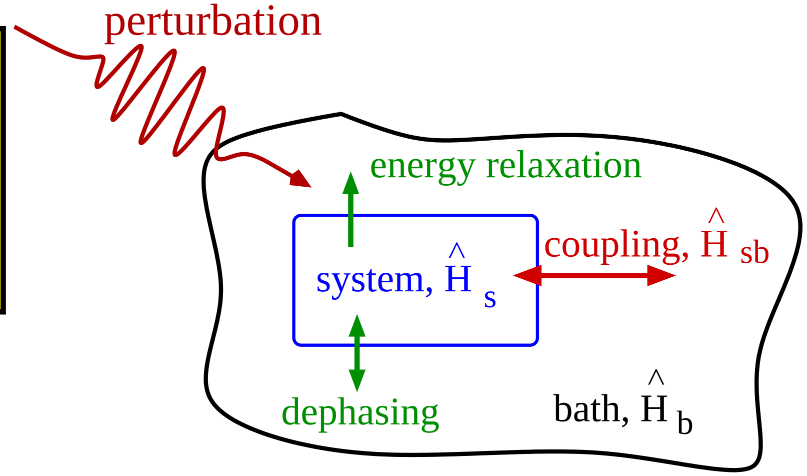
TD-CIS/cc-pVTZ
$\sigma = 2000\ \hbar/E_h$

S. Klinkusch, PS, T. Klamroth, JCP **131**, 114304 (2009)

INCLUSION OF DISSIPATION: ρ-TDCI

- **Liouville-von Neumann equation for laser-driven electrons**

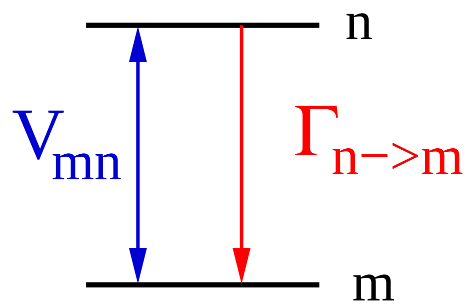
$$\frac{\partial \hat{\rho}}{\partial t} = \underbrace{-\frac{i}{\hbar}[\hat{H}_{el} - \underline{\hat{\mu}}\underline{E}(t), \hat{\rho}]}_{\text{system}} + \underbrace{\left(\frac{\partial \hat{\rho}}{\partial t}\right)_D}_{\text{dissipation}}$$



- **Lindblad dissipation, CI eigenstate basis: "ρ-TDCI"**

Populations: Diagonal elements of system density operator $\hat{\rho}$

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



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

energy relaxation rates $\Gamma_{n\to m}$

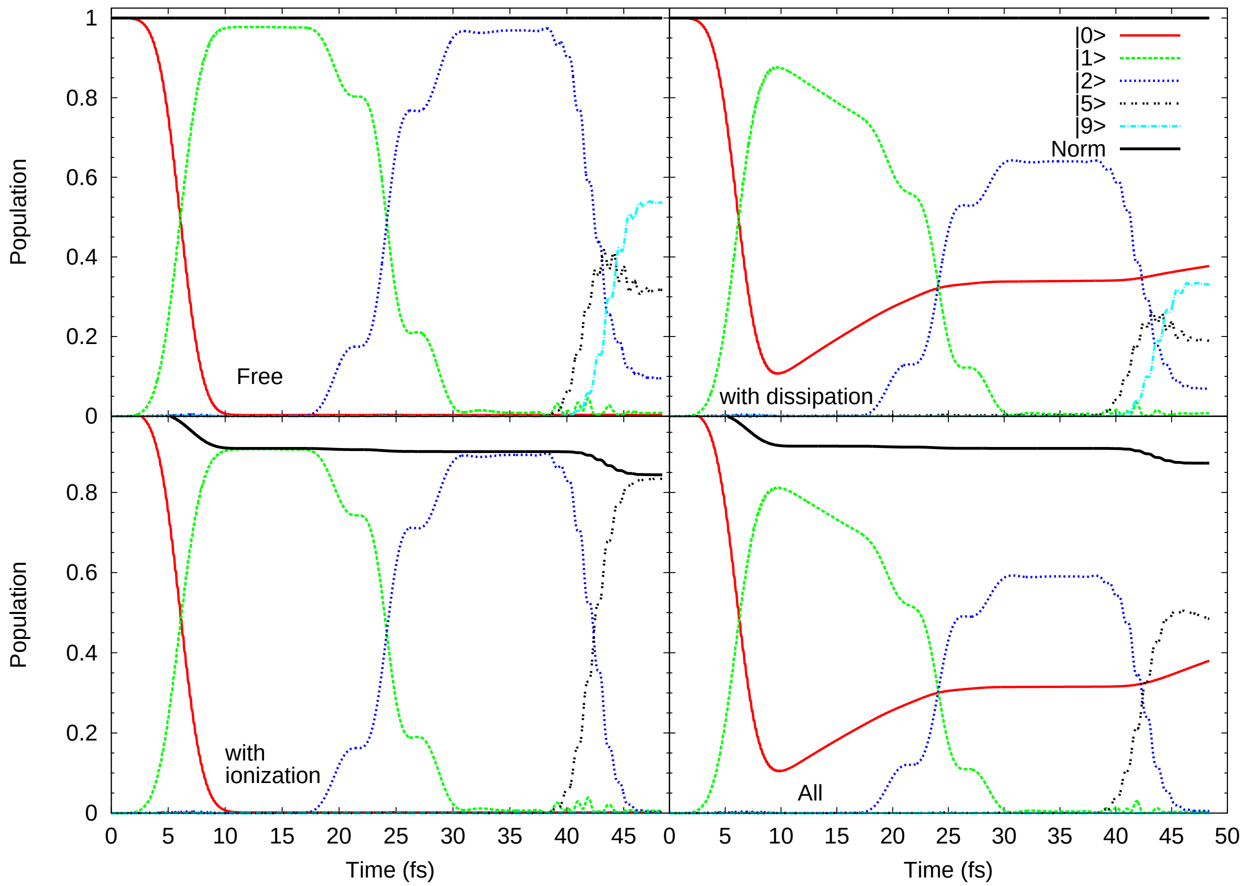
dephasing enters $\dot{\rho}_{mn}$ *via* dephasing rates γ_{mn}

INCLUSION OF IONIZATION AND DISSIPATION

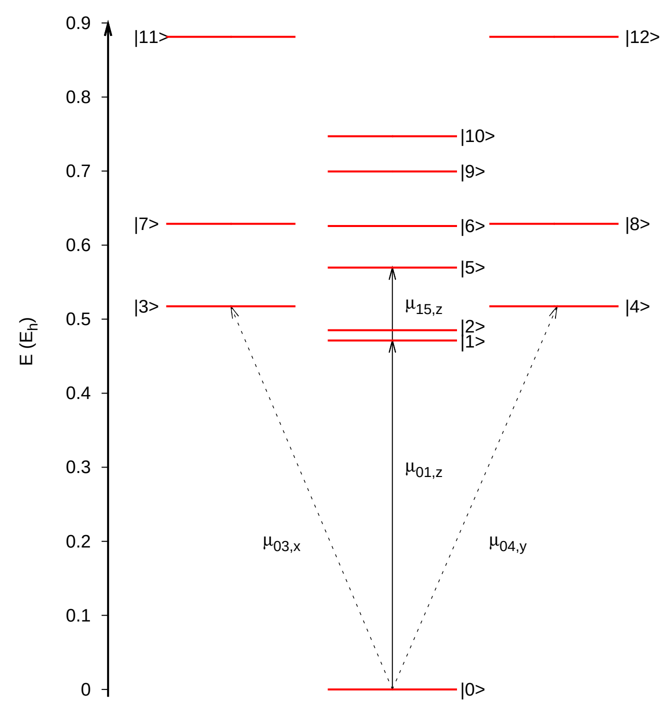
- **The ρ-TD-CI method, and inclusion of ionization**

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

- **Excitation of H_2, bound $\rightarrow$ bound transition**



$|0\rangle \rightarrow |1\rangle \rightarrow |2\rangle \rightarrow |5\rangle$
$\sigma_1, \sigma_2, \sigma_3 = 500\ \hbar/E_h$
TD-CIS(D)/aug-ccpVQZ



J.C. Tremblay, S. Klinkusch, T. Klamroth, PS, JCP **134**, 044311 (2011)

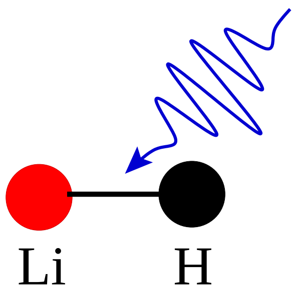
TIME-DEPENDENT ELECTRON CORRELATION

TIME-DEPENDENT CORRELATION

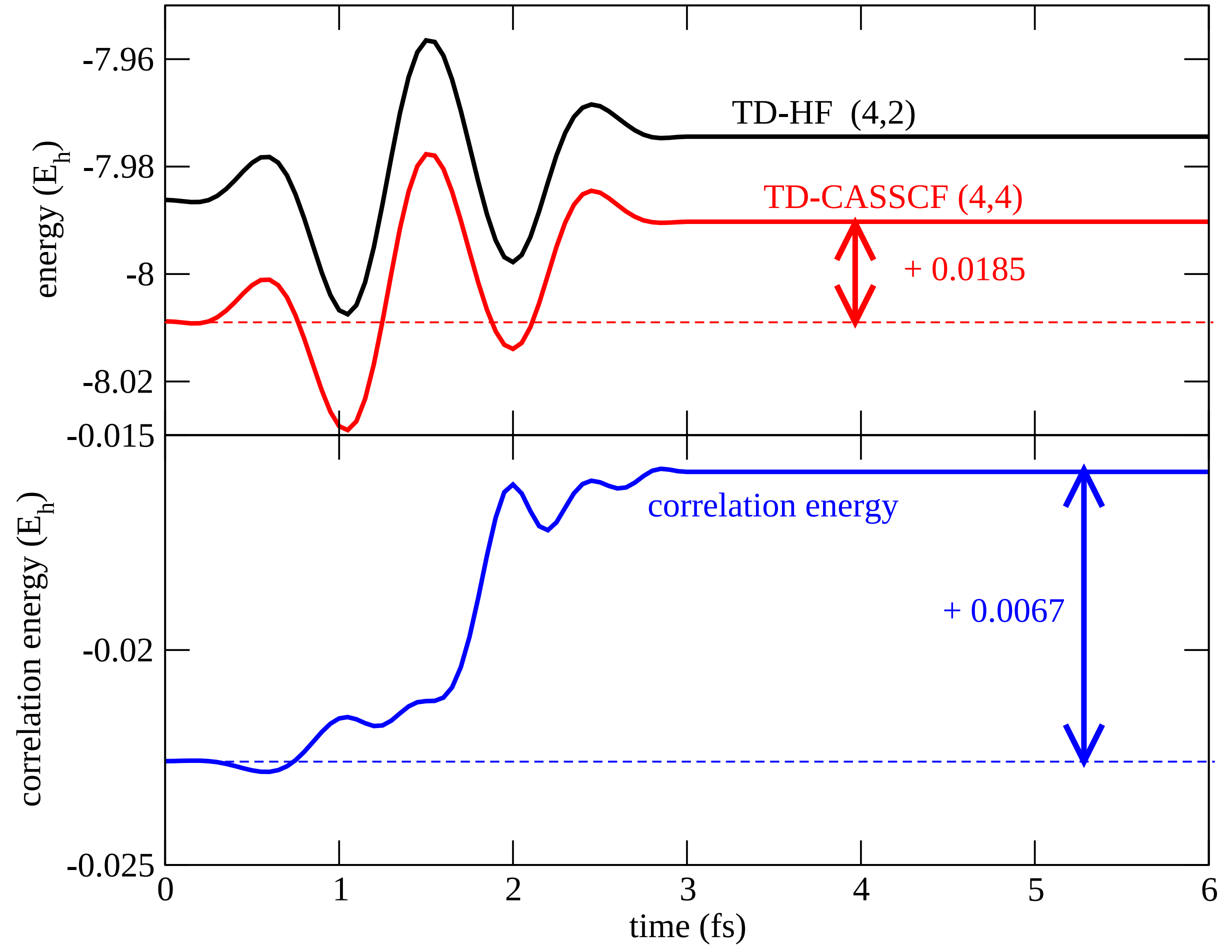
- **Time-dependent correlation energy**

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

$\sin^2$ pulse, 3fs, $E_0 = 0.01$, $\omega = 0.15$



$$E_{\text{corr}}(t) = E(t) - E_{\text{HF}}(t)$$

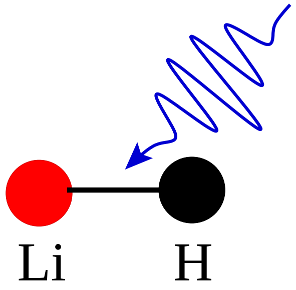


M. Nest, PS, unpublished

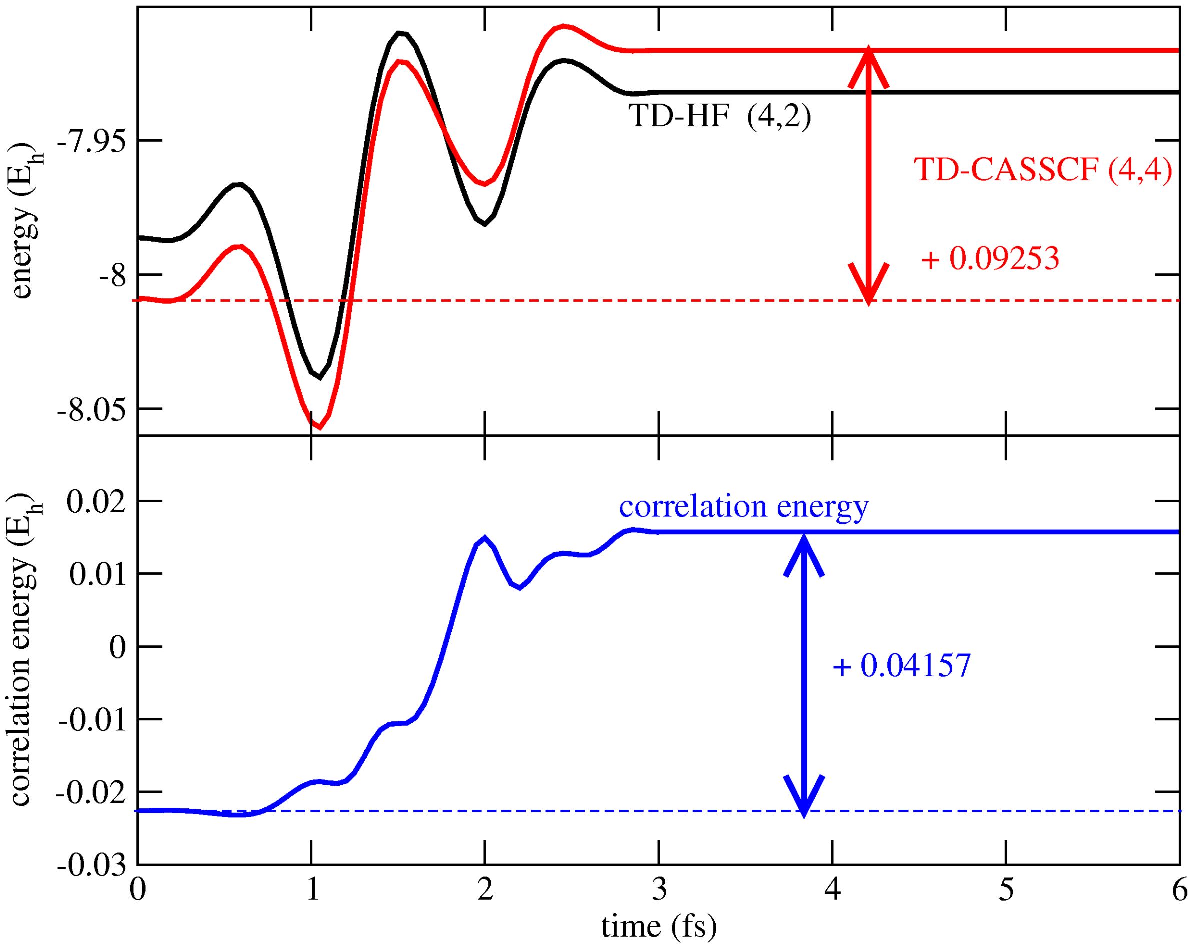
TIME-DEPENDENT CORRELATION

• Time-dependent correlation energy

LiH, TD-CASSCF(4,n)/6-311++G(2df,2p) $\sin^2$ pulse, 3fs, $E_0 = 0.025$, $\omega = 0.15$



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



Nest, PS, unpublished

ELECTRON CORRELATION: OTHER MEASURES

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

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

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

- **H_2 minimal basis, dynamics of a Hartree-Fock state**

  - Full-CI $^1\Sigma_g^+$ states $|0\rangle$, $|1\rangle$ from determinants $\psi_{HF} = |1\bar{1}\rangle$, $|\psi_{1\bar{1}}^{2\bar{2}}\rangle = |2\bar{2}\rangle$

$$|0\rangle = \cos(\beta/2) \, |1\bar{1}\rangle + \sin(\beta/2) \, |2\bar{2}\rangle \quad \text{energy} \quad E_0$$
$$|1\rangle = -\sin(\beta/2) \, |1\bar{1}\rangle + \cos(\beta/2) \, |2\bar{2}\rangle \quad \text{energy} \quad E_1$$

  - Dynamics of an initial Hartree-Fock state

$$\psi(0) = \psi_{HF} = \cos(\beta/2)|0\rangle - \sin(\beta/2)|1\rangle$$

$$\boxed{\psi(t) = e^{-iE_1 t/\hbar}\left(\cos(\beta/2) e^{i\omega_{10} t}|0\rangle - \sin(\beta/2)|1\rangle\right)}$$

$$\omega_{10} = (E_1 - E_0)/\hbar$$

CORRELATION-DRIVEN ELECTRON DYNAMICS

- **H_2, minimal basis: Dynamics of a HF state**

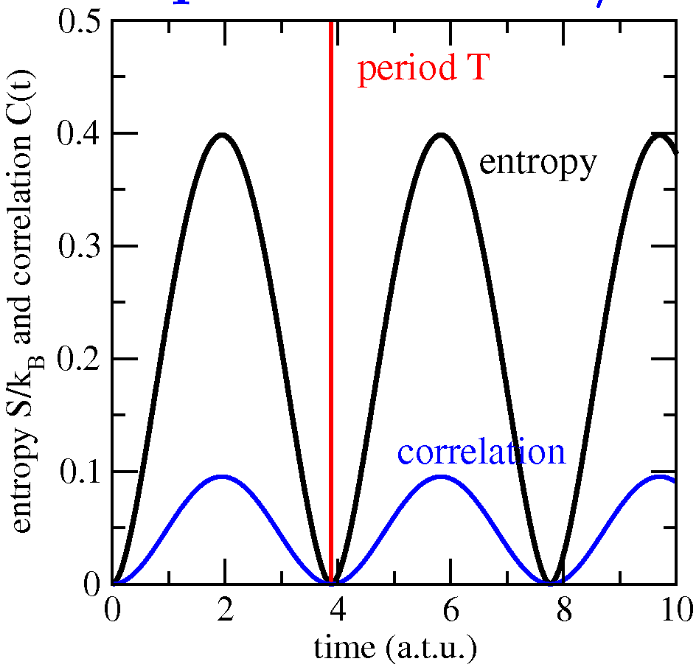
$$S/k_B = -2\left[(k_1 - b(t))\ln(k_1 - b(t)) + (k_2 + b(t))\ln(k_2 + b(t))\right]$$

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

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

$$b(t) = k_2 \cos(2\pi t/T)$$

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



oscillation with period

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

ultrafast buildup of electron correlation

CORRELATION-DRIVEN ELECTRON DYNAMICS

• H_2 molecule: More than two states

TD-CISD/6-31G*: no field, $\psi(0)$ = Hartree-Fock ground state

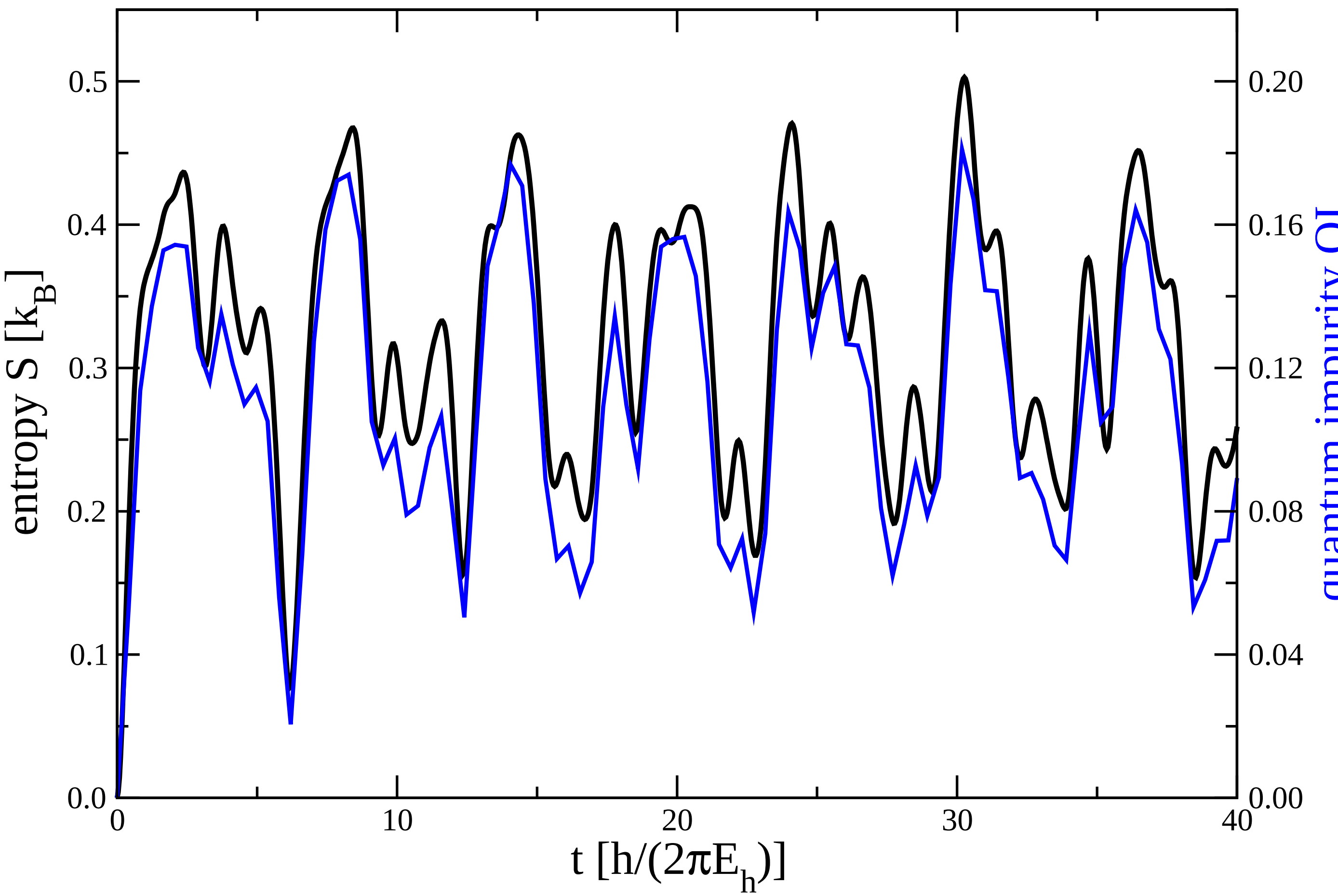
one-electron entropy S

$$S = -k_B \,\mathrm{Tr}\left(\underline{\underline{\gamma}} \ln \underline{\underline{\gamma}}\right)$$

quantum impurity

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

(="correlation")



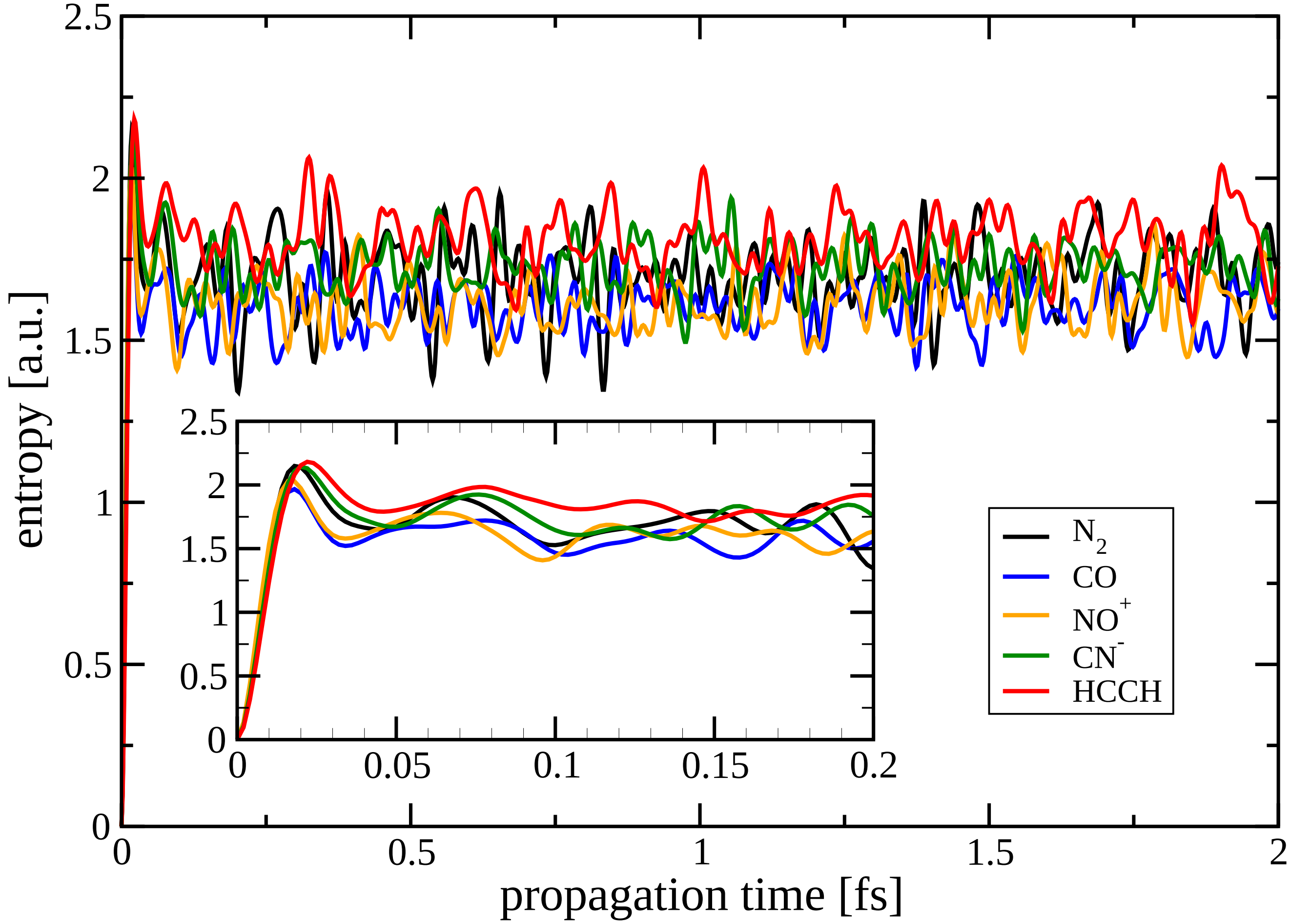
Klinkusch, Klamroth, PS, unpublished

ultrafast buildup of electron correlation

CORRELATION-DRIVEN ELECTRON DYNAMICS

• Correlation-driven electron dynamics: Other molecules

small molecules, TD-CIS/6-31G*: no field, $\psi(0)$ = Hartree-Fock ground state



Beyvers, Nest, Klamroth, Klinkusch, PS, unpublished

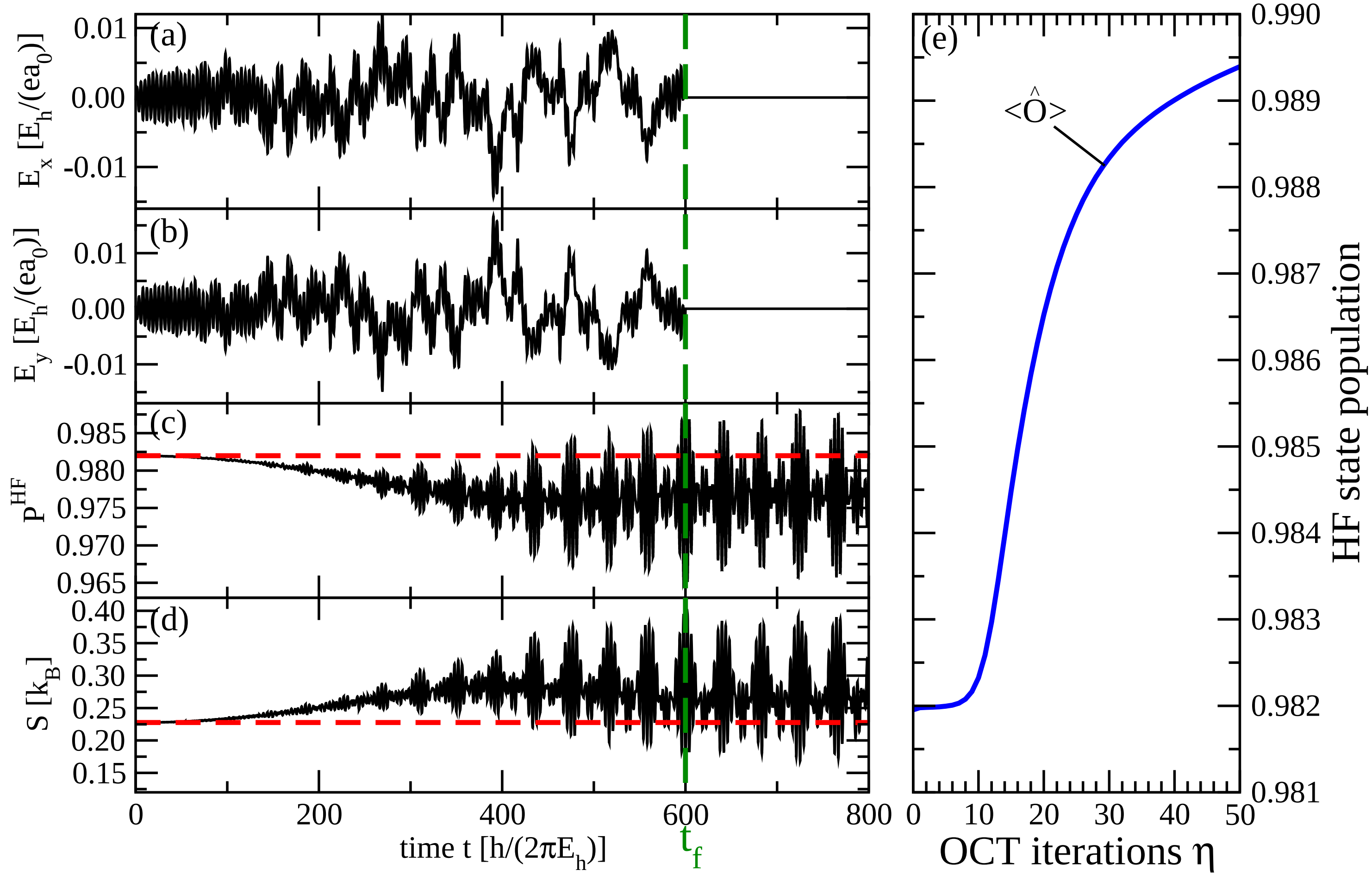
attosecond dynamics

creation of HF state?

ATTEMPTS TO BUILD A HF STATE

• Application of Optimal Control Theory

H_2, TD-CISD/cc-pVQZ with field, $\psi(0)$ = CISD ground state ($P_{HF} = 0.982$, S=0.23 k_B)



Klamroth, Klinkusch, PS, unpublished

partial success

how to stabilize the low-entropy state?

OPTIMAL CONTROL THEORY

- **Time-dependent Schrödinger equation:**

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

$\hat{H}_{el}(t) = \hat{H}_{el} - \hat{\mu}E(t)$

- **Maximize constrained target functional:**

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

$\hat{O}$ = target operator; α = penalty

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

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

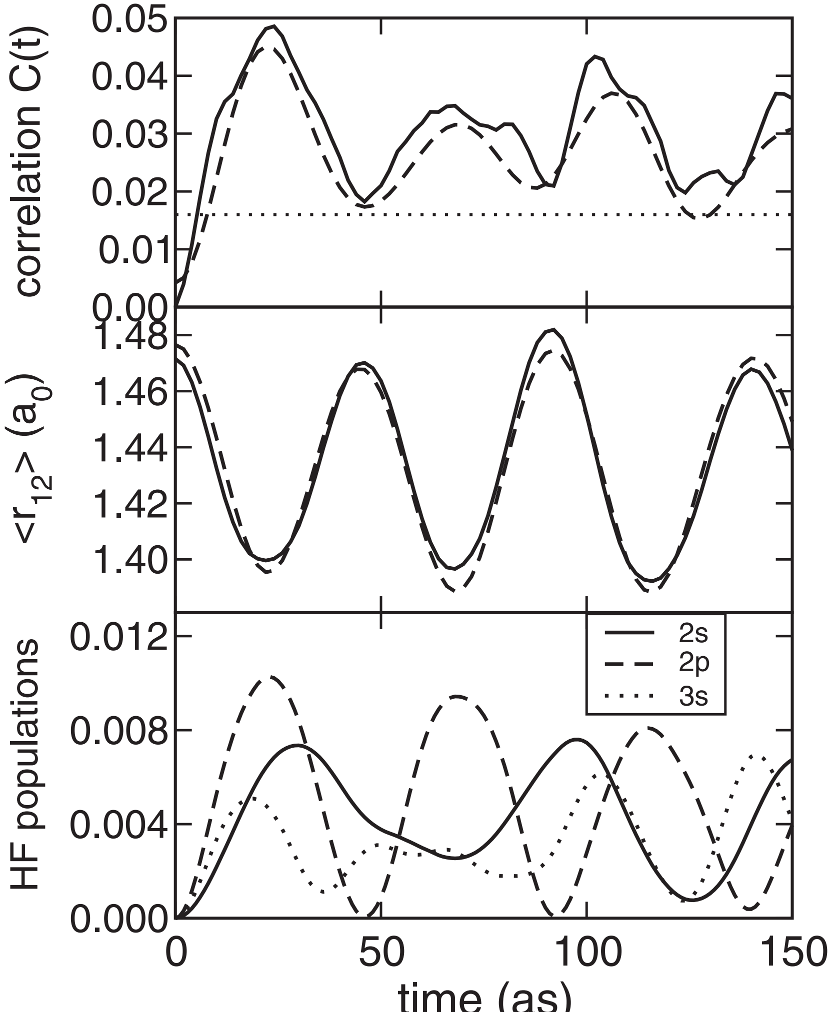
- **Calculate field to self-consistency**

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

CONTROLLING CORRELATION IN ATOMS

- **He: HF state dynamics**

TD-CISD/QZ basis, $\boxed{\psi(0) = \psi_{HF}}$



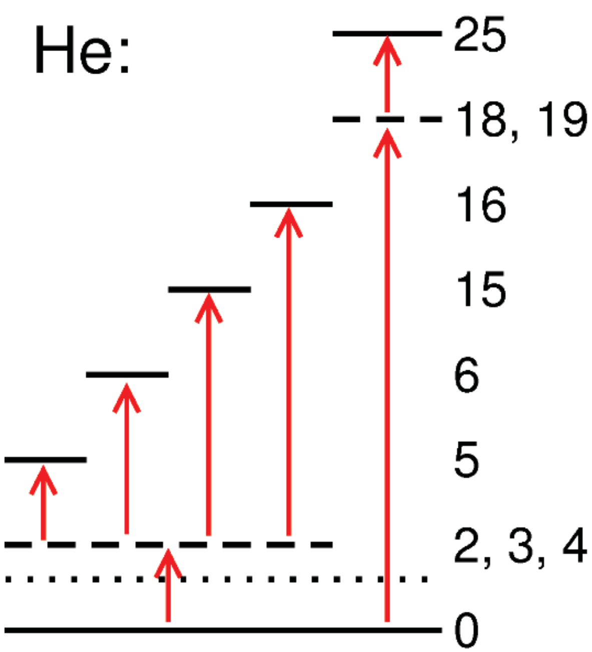
$T = 40$ as, "breathing" electrons

- **Control Strategy**

make approximate HF state

$$\psi_{HF} \sim \sum_{n=0,5,\ldots,25} C_n \psi_n$$

from correlated ground state $\boxed{\psi(0) = \psi_0}$



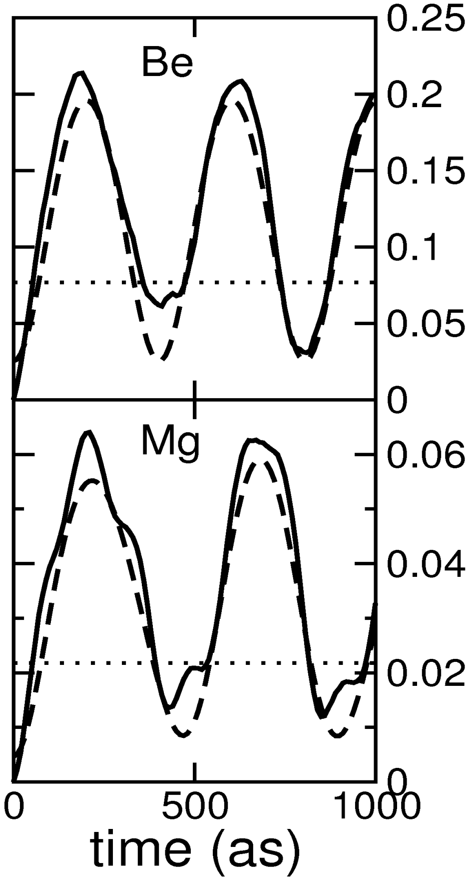
complicated, indirect, ionizing

M. Nest, M. Ludwig, I. Ulusoy, T. Klamroth, PS, JCP **138**, 164108 (2013)

CONTROLLING CORRELATION IN ATOMS

- **Other atoms: Be, Mg**

TD-CISD, $\boxed{\psi(0) = \psi_{HF}}$



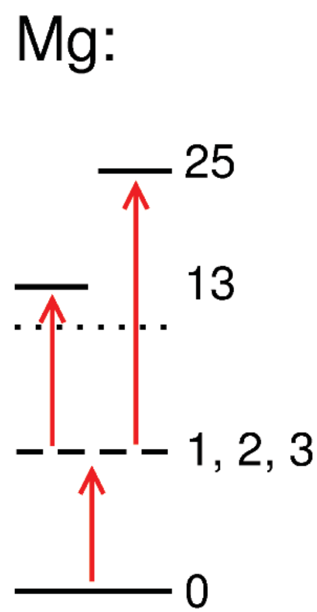
$(ns^2) \rightarrow$ long T

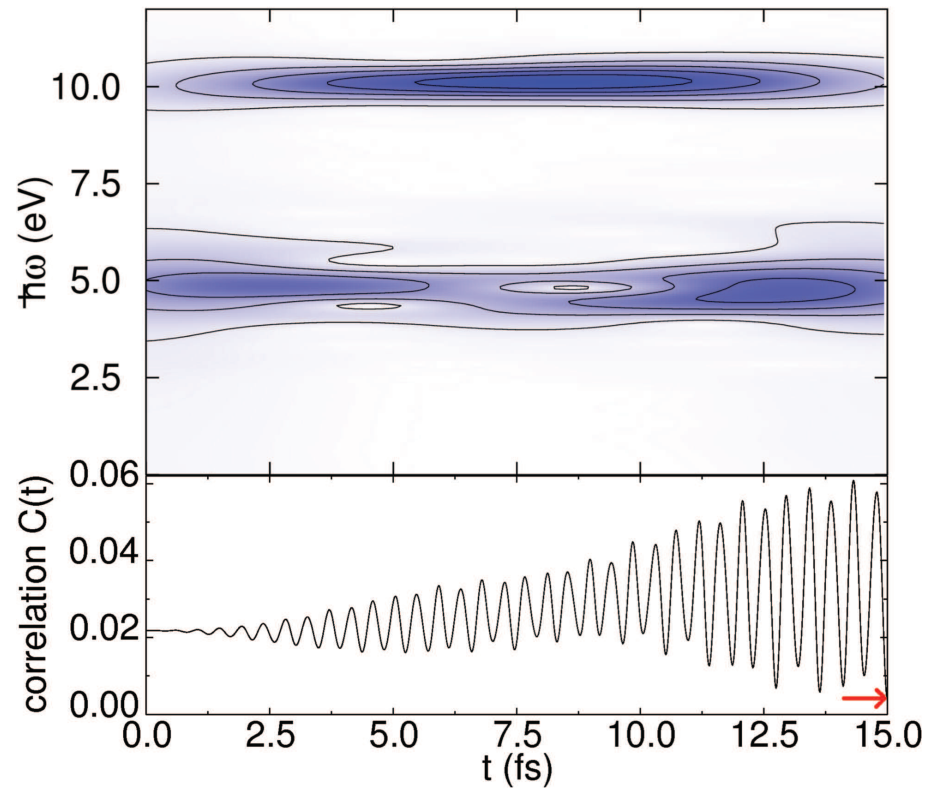
- **Optimal control for Mg atom**

make approximate HF state

$$\psi_{HF} \sim \sum_{n=0,13,25} C_n \psi_n$$

from correlated ground state $\boxed{\psi(0) = \psi_0}$





3-pulse strategy (15 fs) works

M. Nest, M. Ludwig, I. Ulusoy, T. Klamroth, PS, JCP **138**, 164108 (2013)

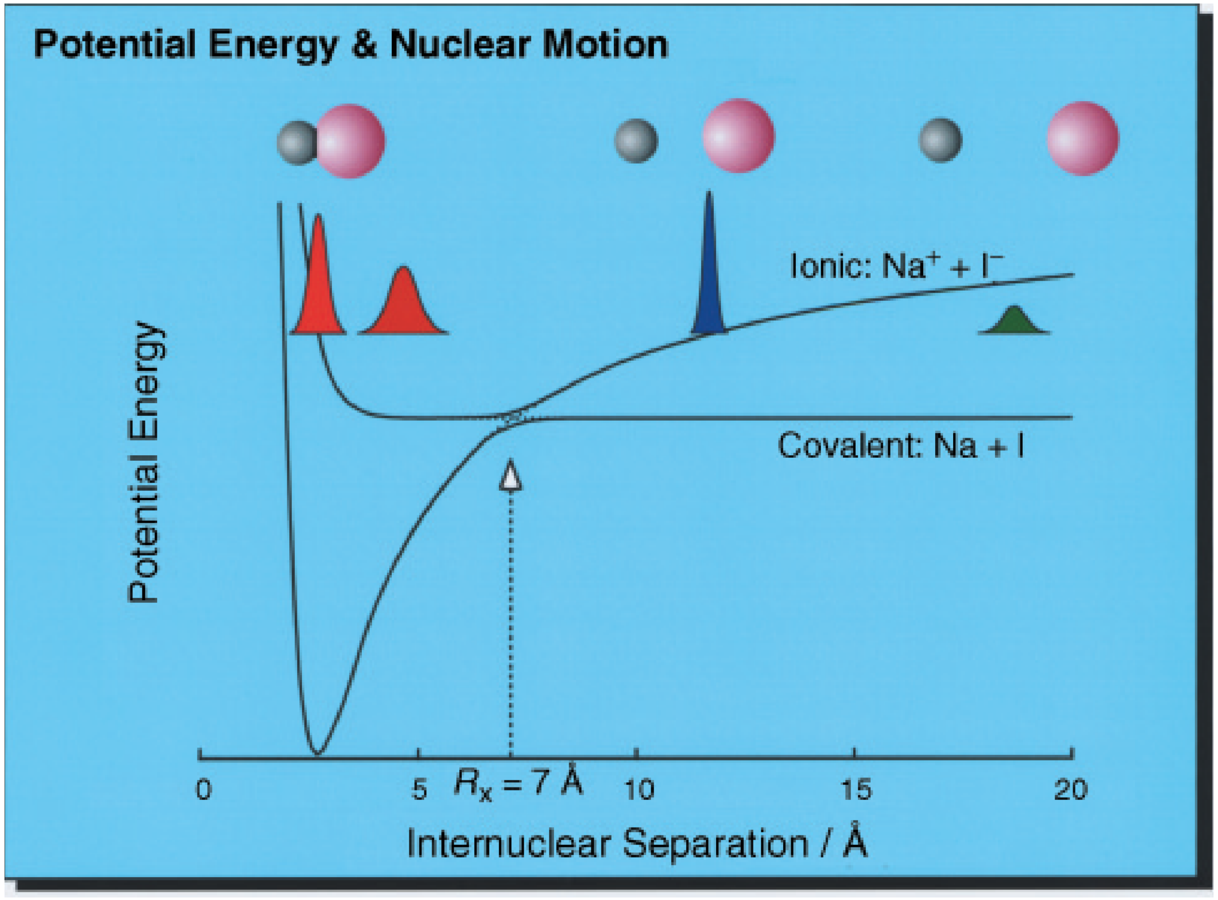
SUMMARY AND OUTLOOK: ELECTRONS

- **Summary**
  - Electron dynamics in real time
  - TD-CI, ρ-TD-CI, TD-CASSCF
  - Response
  - Time-dependent correlation

- **Findings**
  - Ultrafast dynamics (and control)
  - WF-based alternatives to TDDFT
    - systematically improvable
    - correct asymptotics
    - multi-determinant effects

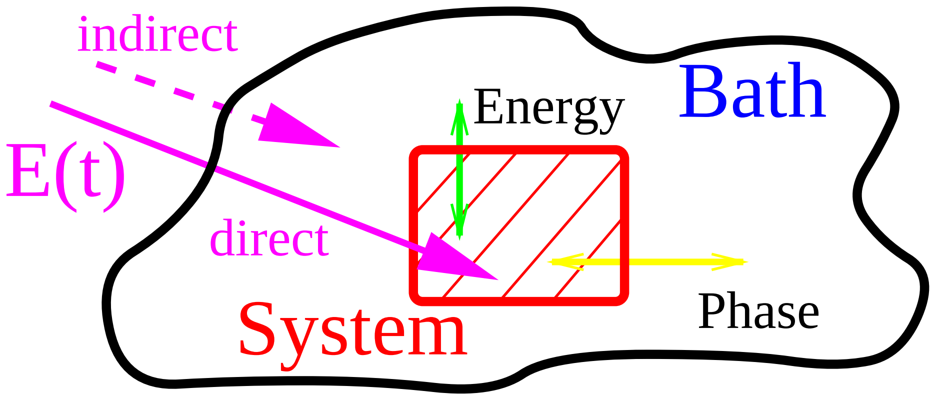
- **Outlook**
  - Test of apprpximate methods, *e.g.* TD-DFT
  - Treatment of ionization, nuclear motion
  - Time-dependent Coupled Cluster

NUCLEAR (ATOM) DYNAMICS



FULL SYSTEM-BATH DYNAMICS

- **The system-bath Hamiltonian**



$$\hat{H} = \underbrace{\left[\hat{H}_s(s) - \underline{\hat{\mu}}\underline{E}(t)\right]}_{\text{system}} + \underbrace{\hat{H}_{sb}(s, q_1, \ldots, q_M)}_{\text{system-bath}} + \underbrace{\hat{H}_b(q_1, \ldots, q_M)}_{\text{bath}}$$

- **The time-dependent Schrödinger equation**

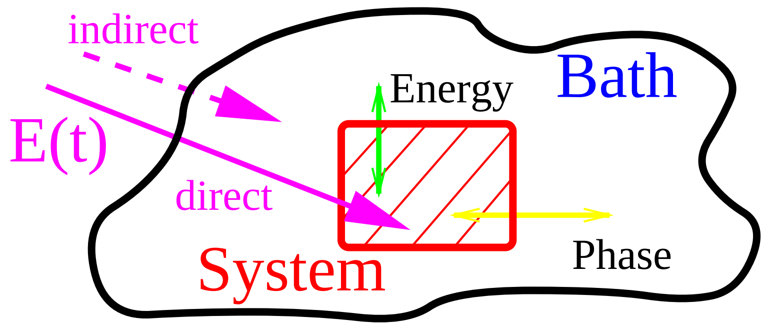
$$\frac{\partial \Psi(s, q_1, \ldots, q_M, t)}{\partial t} = -\frac{i}{\hbar}\hat{H}\Psi(s, q_1, \ldots, q_M, t)$$

- **Methods**

  standard, MCTDH (“exact”), TDSCF (approximation), . . .

REDUCED DYNAMICS

- **Open-system density matrix theory**



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

- **Lindblad in system eigenstate representation:** $\hat{C}_{kl} = \sqrt{\Gamma_{k\to l}}|l\rangle\langle k|$

Populations:

$$\frac{d\rho_{nn}}{dt} = \sum_p^N \underbrace{-\frac{i}{\hbar}\left[V_{np}(t)\rho_{pn} - \rho_{np}V_{pn}(t)\right]}_{\text{system-field}} + \sum_p^N \underbrace{\left[\Gamma_{p\to n}\rho_{pp} - \Gamma_{n\to p}\rho_{nn}\right]}_{\text{dissipation}}$$

Coherences:

$$\frac{d\rho_{mn}}{dt} = -\frac{i}{\hbar}\left[(E_m - E_n) + \sum_p^N \left[V_{mp}(t)\rho_{pn} - \rho_{mp}V_{pn}(t)\right]\right] \underbrace{-\gamma_{mn}\,\rho_{mn}}_{\text{dephasing}}$$

- **Rates Γ, γ: Perturbation theory, non-perturbative**

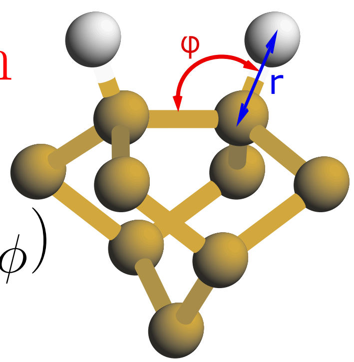
H:Si(100): VIBRATIONAL RELAXATION

- **A "system-bath" model for H on Si(100)**

$$\hat{H} = \underbrace{\hat{T} + V(r,\phi)}_{\hat{H}_s} + \underbrace{\sum_{i=1}^{M} \underbrace{\lambda_i(r,\phi)\; q_i}_{\text{1-phonon}} + \frac{1}{2}\sum_{i,j=1}^{M} \underbrace{\Lambda_{ij}(r,\phi)\; q_i q_j}_{\text{2-phonon}}}_{\hat{H}_{sb}} + \underbrace{\sum_{i=1}^{M}\left(\frac{\hat{p}_i^2}{2m_i} + \frac{m_i\omega_i^2}{2} q_i^2\right)}_{\hat{H}_b}$$

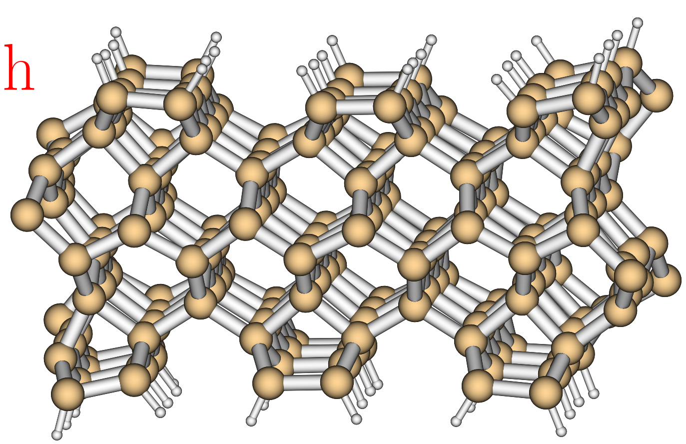
- **The model**

The system



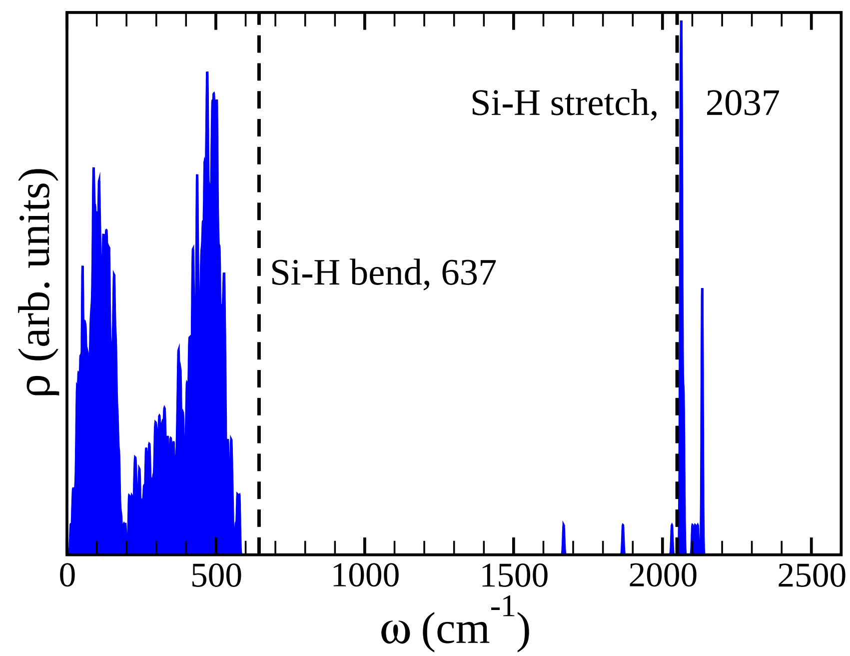
states (n_r, n_ϕ)

The bath



- **Vibrational state density**

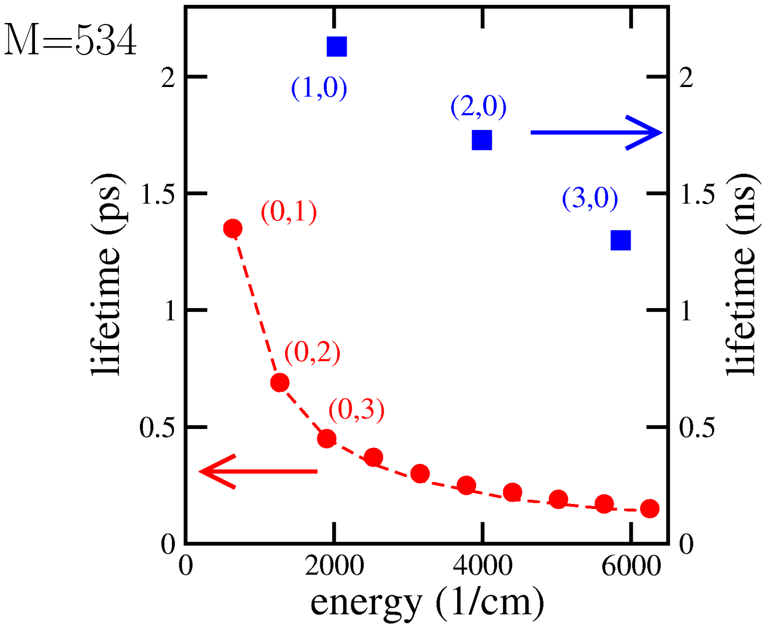
normal mode analysis (N_{at}=180, FF[1])



[1] force field: D. Brenner, PRB **42**, 9458 (1990); NMA: I. Andrianov, PS, JCP **124**, 034710 (2006)

H:Si(100): GOLDEN RULE AND RDM THEORY

- **Lifetimes (T=0)**

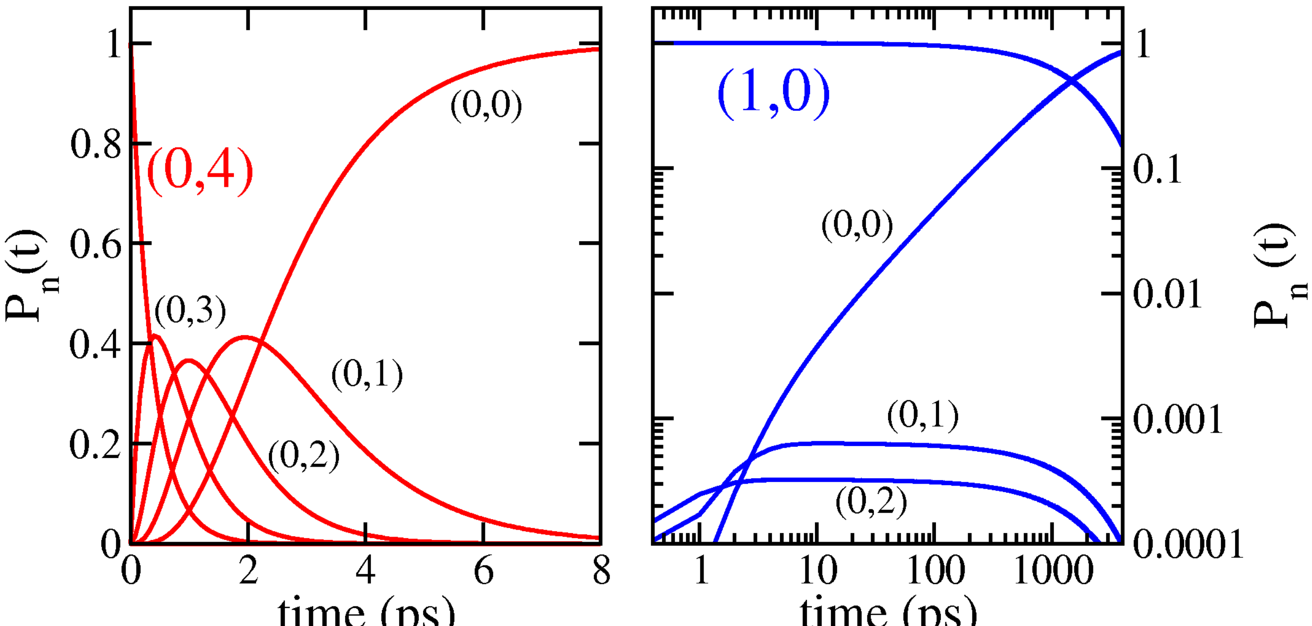


- stretch mode: $\tau_{vib} = \Gamma_{1\to 0}^{-1} =$ ns
- bending mode: ps
- $\Gamma_{n\to m} \approx \tau_{vib}{}^{-1}\, n\, \delta_{m,n-1}$: $\Delta n = -1$

ideal: HO, bilinear coupling

- **Decay mechanism**

Lindblad density matrix theory

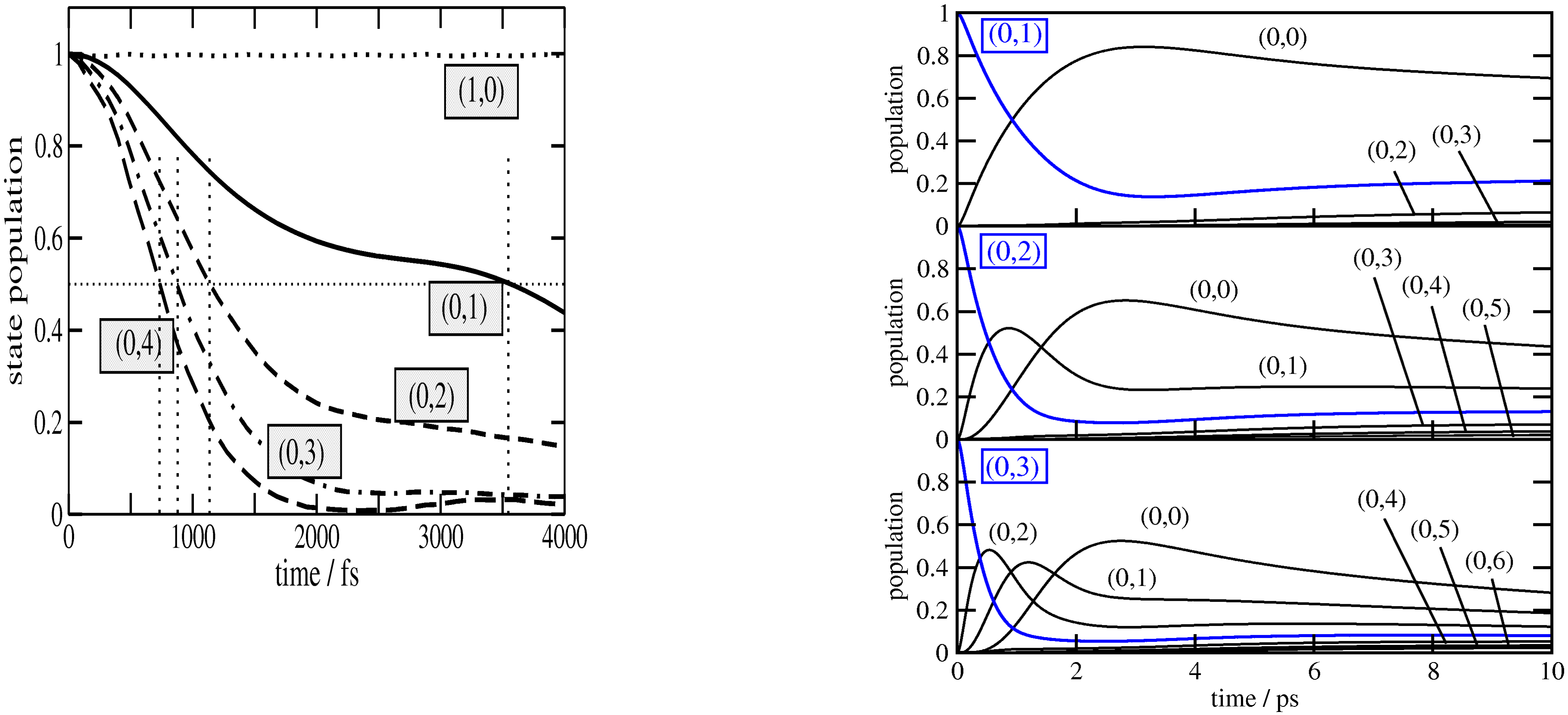


H:Si(100): NON-PERTURBATIVE, FULL DYNAMICS

- Solve $i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi$ by MCTDH or TDSCF for F=M+2 DOF

- **Relaxation of the bending mode: MCTDH and TDSCF**

MCTDH (M=50 oscillators) TDSCF (M=534)



- **Half-life times $T_{1/2}$ of (0,1)**: Golden Rule: 0.94 ps, TDSCF: 0.92 ps

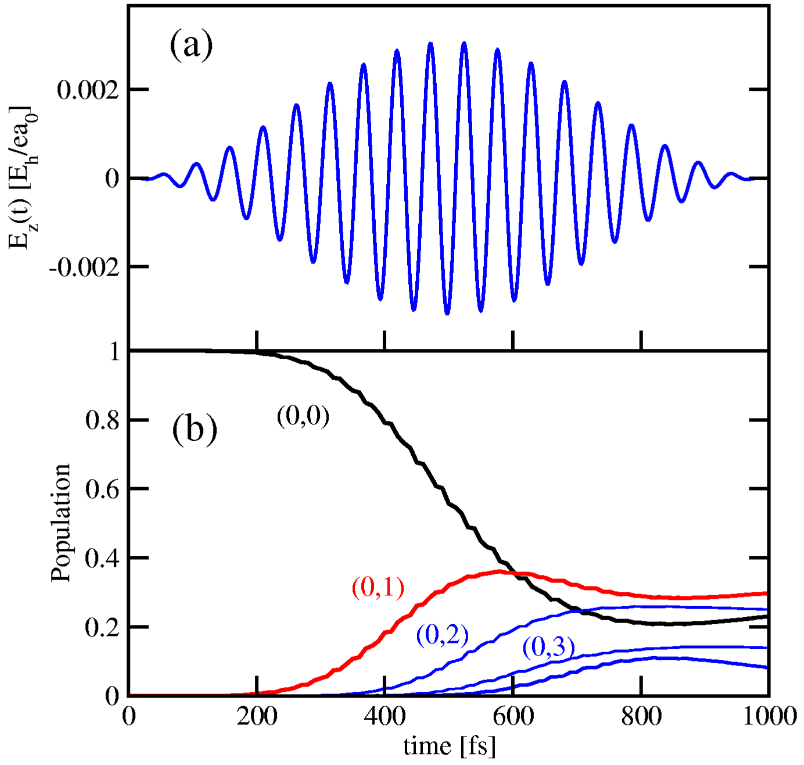
CPL **433**, 91 (2006), JPC C **111**, 5432 (2007)

TEMPERATURE: REDUCED & FULL DYNAMICS

• IR excitation by π-pulses: RDM

Si-H bending mode, $\omega_0 = \omega_\phi$, $t_f = 1$ ps

$$V_{mn}(t) = -\mu_{mn}\ E_0 \sin^2\left(\frac{\pi t}{t_f}\right)\cos(\omega_0 t)$$



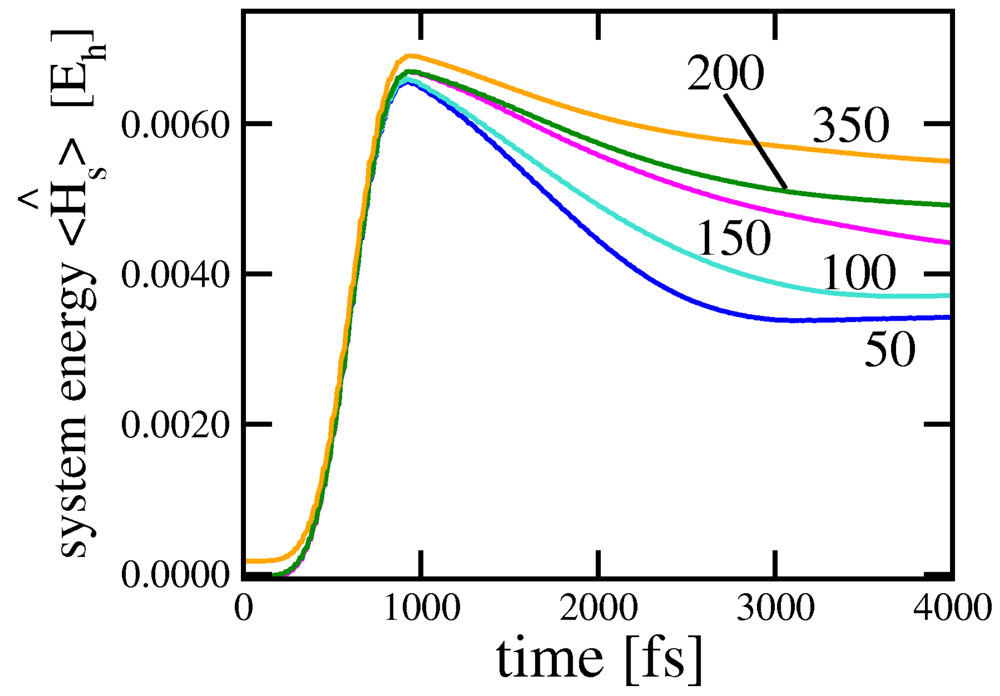
mode-selective, not state selective

G.K. Paramonov, PS *et al.*, PRB **75**, 045405 (2007)

• Full: MCTDH treatment

MCTDH (M=20)

Random Phase Thermal Wavefunction Method



τ_{vib} goes up with T

F. Lüder, M. Nest, PS, TCA **127**, 183 (2010)

THERMAL WAVEFUNCTIONS AND MCTDH

- **"rAvec" method[1]:** $$\Psi(x_1,\ldots,x_F) = \sum_{j_1=1}^{n_1}\cdots\sum_{j_F=1}^{n_F} A_{j_1\cdots j_F} \prod_{k=1}^{F} \phi_{j_k}^{(k)}(x_k)$$

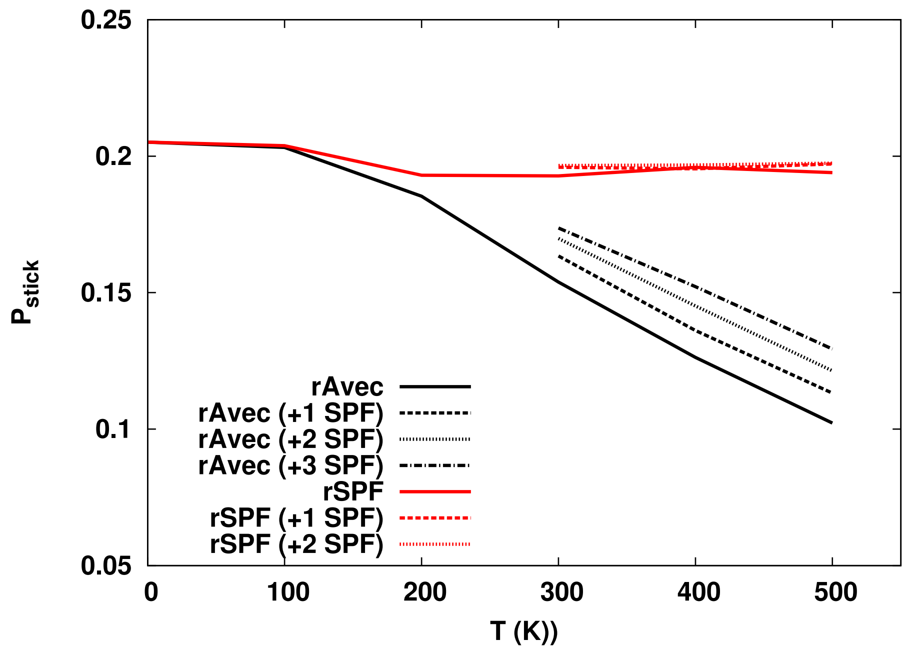
  randomize coefficients $A_{j_1\cdots j_F}$ (replace by random phases $e^{i\theta}$ ($\theta \in [0, 2\pi]$)

- **"rSPF" method[2]:** $$\Psi(x_1,\ldots,x_F) = \psi^{(1)}(x_1)\cdots\psi^{(F)}(x_F)$$

  randomize single-particle functions $\psi^{(i)}(x_i) = \sum_{n_i}(-1)^{\alpha_{n_i}}\,\varphi_{n_i}^{(i)}$ (α= random integer)

- **Example: Atom sticking at surface[3]**

Morse oscillator
and 20 bath oscillators



[1] Nest, Kosloff, JCP **127**, 134711 (2007)

[2] Manthe, Huarte-Larranaga, CPL **127**, 349 (2001)

[3] Lorenz, PS, JCP **140**, 044106 (2014)

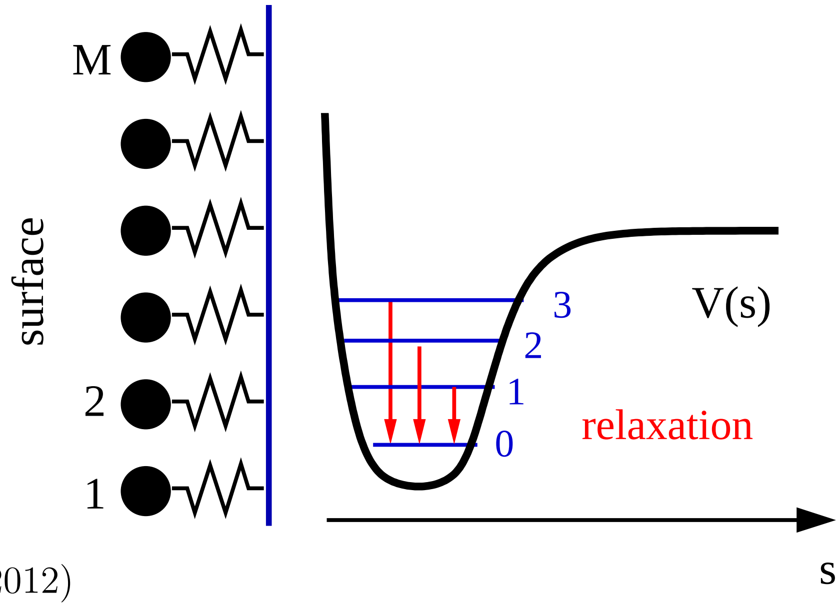
A SIMPLE 1D SYSTEM-BATH MODEL

- **A 1D "system-bath" model vibrational relaxation**

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m_s}\frac{d^2}{ds^2} + D[1-e^{-\alpha s}]^2}_{\hat{H}_s} \underbrace{- f(s)\sum_{i=1}^{M} c_i q_i}_{\hat{H}_{sb}} + \underbrace{\sum_{i=1}^{M}\left(\frac{\hat{p}_i^2}{2m_i} + \frac{m_i\omega_i^2}{2}q_i^2\right)}_{\hat{H}_b}$$

  - Ohmic bath $\omega_i = i\ \Delta\omega = i\omega_f/M$
  - coupling constant $c_i = i\ \left(2m_i m_s \Gamma \Delta\omega^3/\pi\right)^{1/2}$, damping parameter Γ
  - non-linear coupling function $f(s) = (1-e^{-\alpha s})/\alpha \longrightarrow s$ for $s \to 0$

- **Questions**
  - resonant *vs.* non-resonant baths: ω_b, ω_s
  - reduced *vs.* full dynamics
  - scaling of "vibrational lifetimes" with v



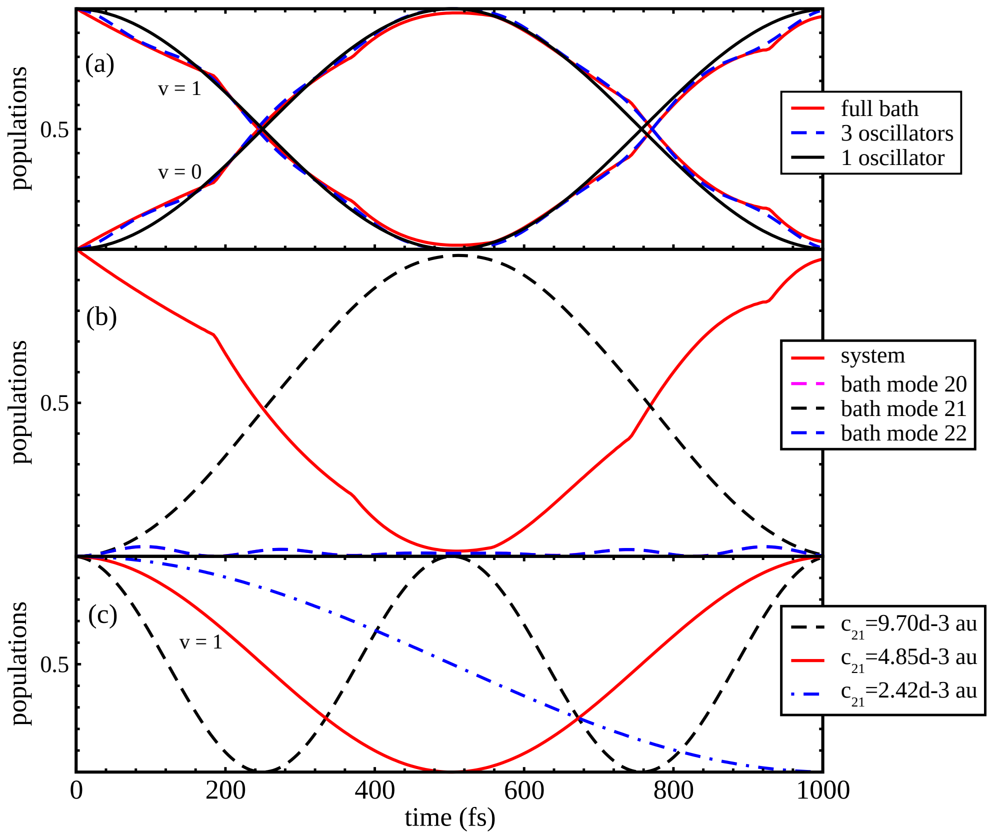
Nest, Meyer, JCP **119**, 24 (2003); Bouakline *et al.*, JPC A **116**, 11118 (2012)

RESULTS

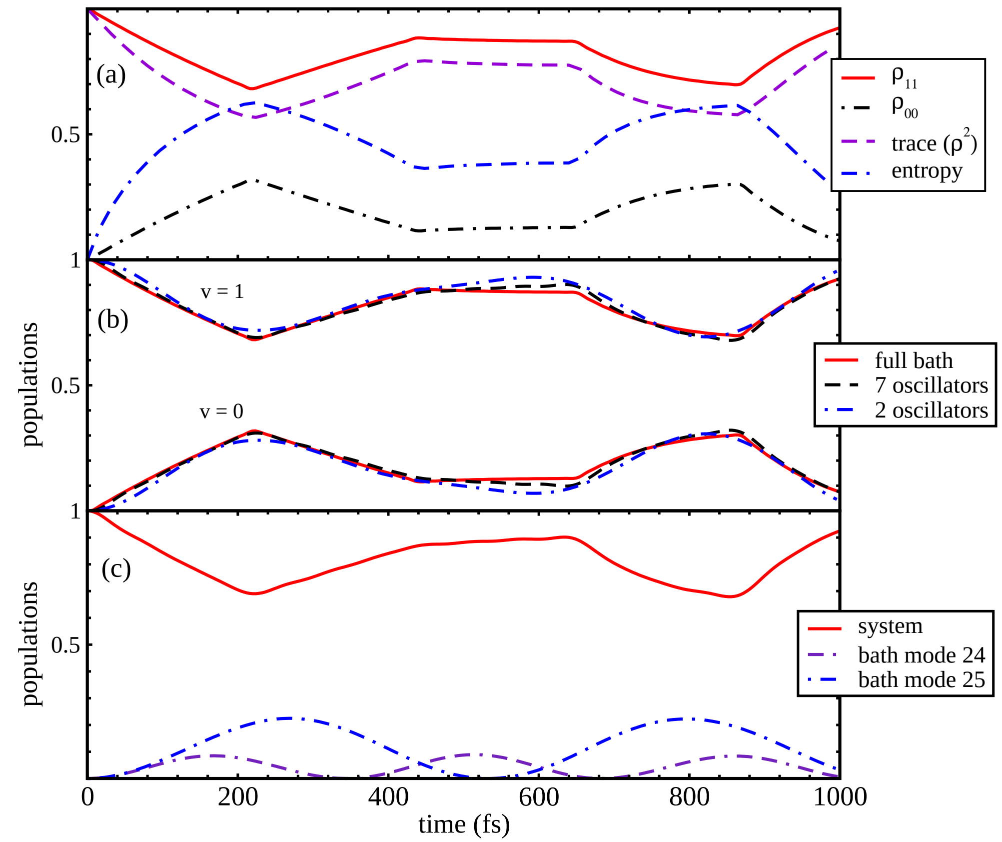
• Resonant *vs.* non-resonant bath

MCTDH (full) calculation, M=40, $\Gamma = (500\ \mathrm{fs})^{-1}$

resonant bath



non-resonant bath



complete *vs.* incomplete Rabi oscillations

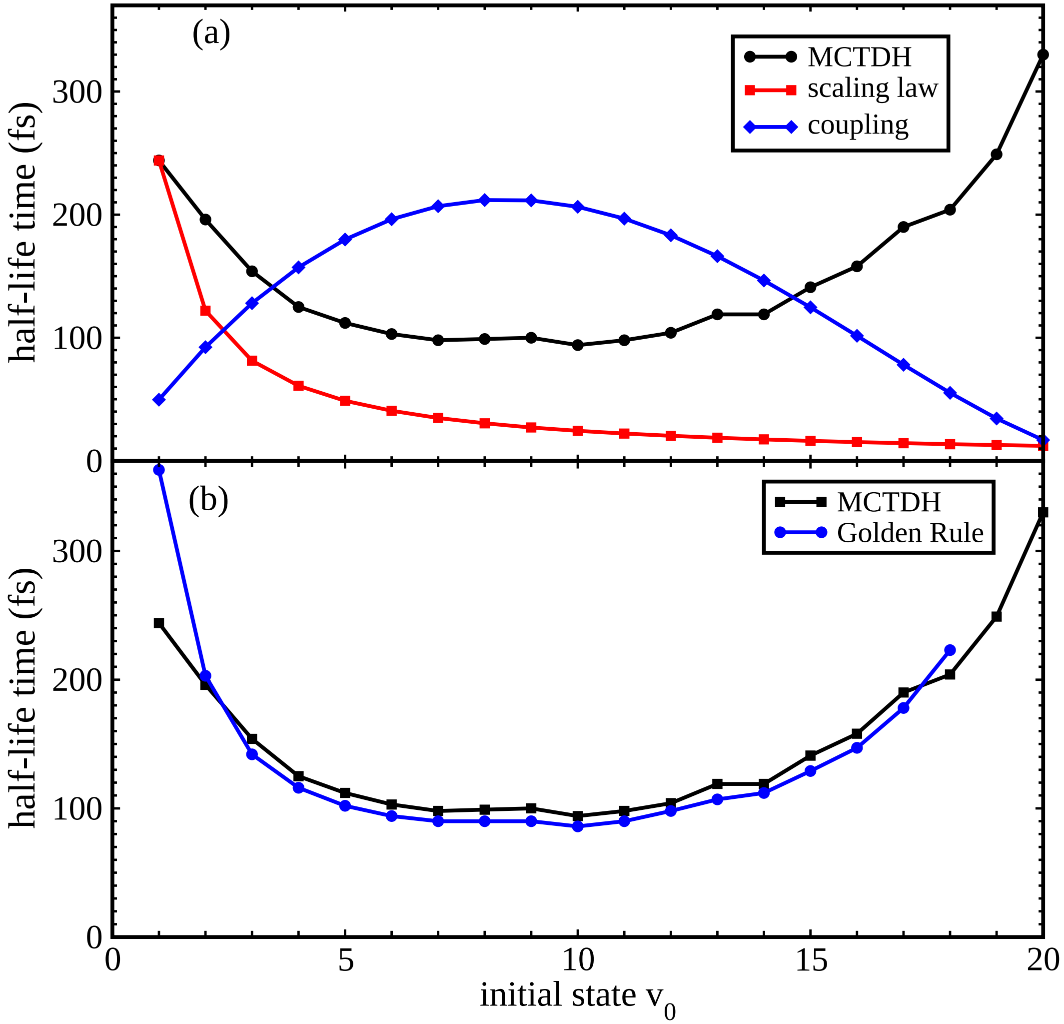
resonant: single bath oscillators dominate dynamics

Bouakline, Lüder, Martinazzo, PS, J. Phys. Chem. A **116**, 11118 (2012)

RESULTS

- **“Half-lifetime” scaling, “full” *vs.* “reduced” dynamics**

MCTDH *vs.* Golden Rule; M=40, $\Gamma = (500\text{ fs})^{-1}$; HO system *vs.* Morse oscillator



HO scaling, bilinear:

$$\tau(v \to v-1) = \tau(1 \to 0)/v$$

non-monotonic scaling in real system

Golden Rule:

$$\Gamma_{i\to f} = \frac{2\Delta\omega}{\hbar} \; |\langle i|f(s)|f\rangle|^2 \; m_s\Gamma \sum_{b=1}^{M} \omega_b \, \delta(\omega_b - \omega_{i,f})$$

agreement full and reduced

Bouakline, Lüder, Martinazzo, PS, J. Phys. Chem. A **116**, 11118 (2012)

LARGE BATHS WITH WAVEFUNCTIONS

- **MCTDH[1] and variants thereof**

$$\Psi(x_1,\ldots,x_F) = \sum_{j_1=1}^{n_1} \cdots \sum_{j_F=1}^{n_F} A_{j_1\cdots j_F} \prod_{k=1}^{F} \phi_{j_k}^{(k)}(x_k)$$

Variants: Mode combination, ML-MCTDH (Thoss, Wang), ...

- **TDSCF**

$$\Psi(x_1,\ldots,x_F,t) = \prod_{k=1}^{F} \varphi_\kappa(x_k,t)$$

single-configuration approximation

- **LCSA[2]**

$$|\Psi\rangle = \sum_\alpha C_\alpha \underbrace{|\xi_\alpha\rangle}_{\text{DVR states subsystem}} \underbrace{|\Phi_\alpha\rangle}_{\text{bath}}$$

Local Coherent State Approximation
"diagonal approximation to MCTDH"

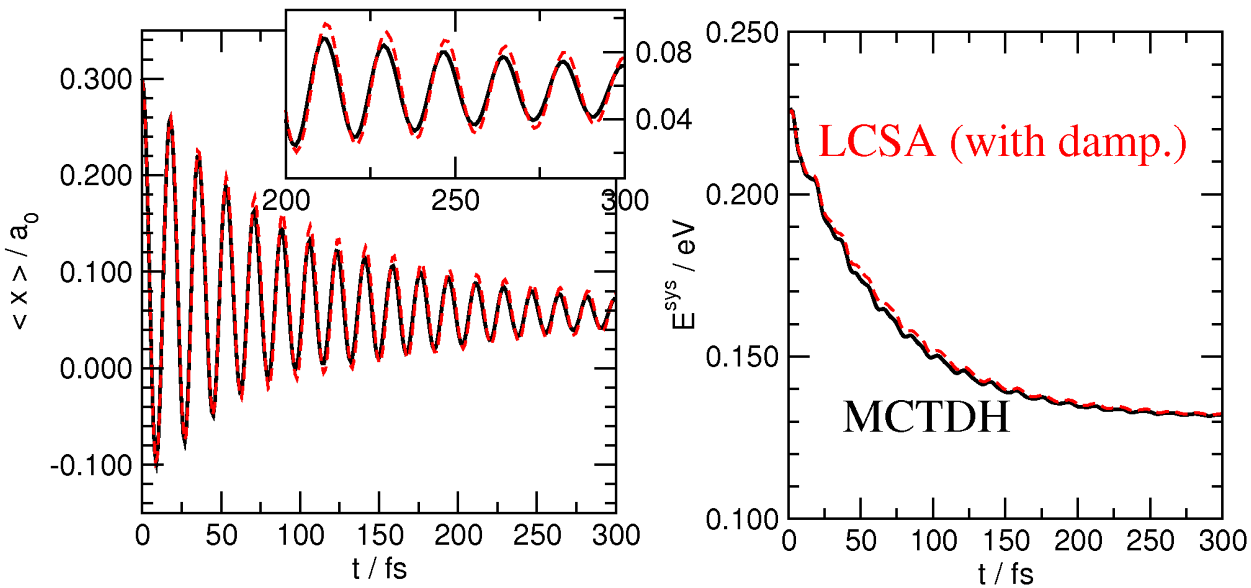
- **G-MCTDH[3], CC-TDSCF[4], ...**

[1] Meyer, Manthe, Cederbaum: CPL **165**, 73 (1990)
[2] Martinazzo *et al.*, JCP **125**, 194102 (2006)
[3] Burghardt *et al.*, JCP **111**, 1927 (1999)
[4] Zhang *et al.*, JCP **122**, 091101 (2005)

LARGE BATHS, LONG-TIME DYNAMICS

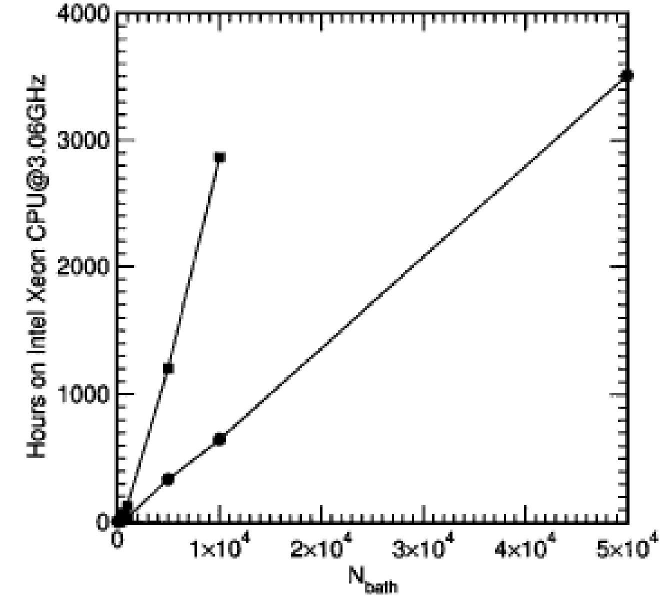
• LCSA

MCTDH and LCSA, 1D+M=50, $\Gamma = (50\ \text{fs})^{-1}$



Martinazzo et al., JCP 125, 194102 (2006)

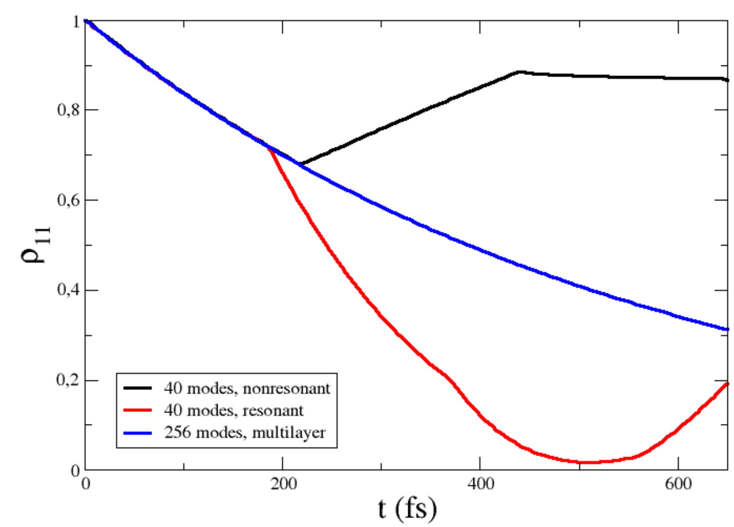
Scaling behaviour



• ML-MCTDH

Decay of $v = 1$, $\Gamma = (500\ \text{fs})^{-1}$, $\Delta\omega = \omega_c/M$

recurrence time $\tau = 2\pi/\Delta\omega$



SUMMARY AND OUTLOOK: NUCLEI

- **Summary**
  - System-bath models
  - MCTDH and variants
  - Lindblad open-system density matrix

  - Vibrational relaxation

- **Findings**
  - “Easy” and “real” Hamiltonians
  - Anharmonicity matters

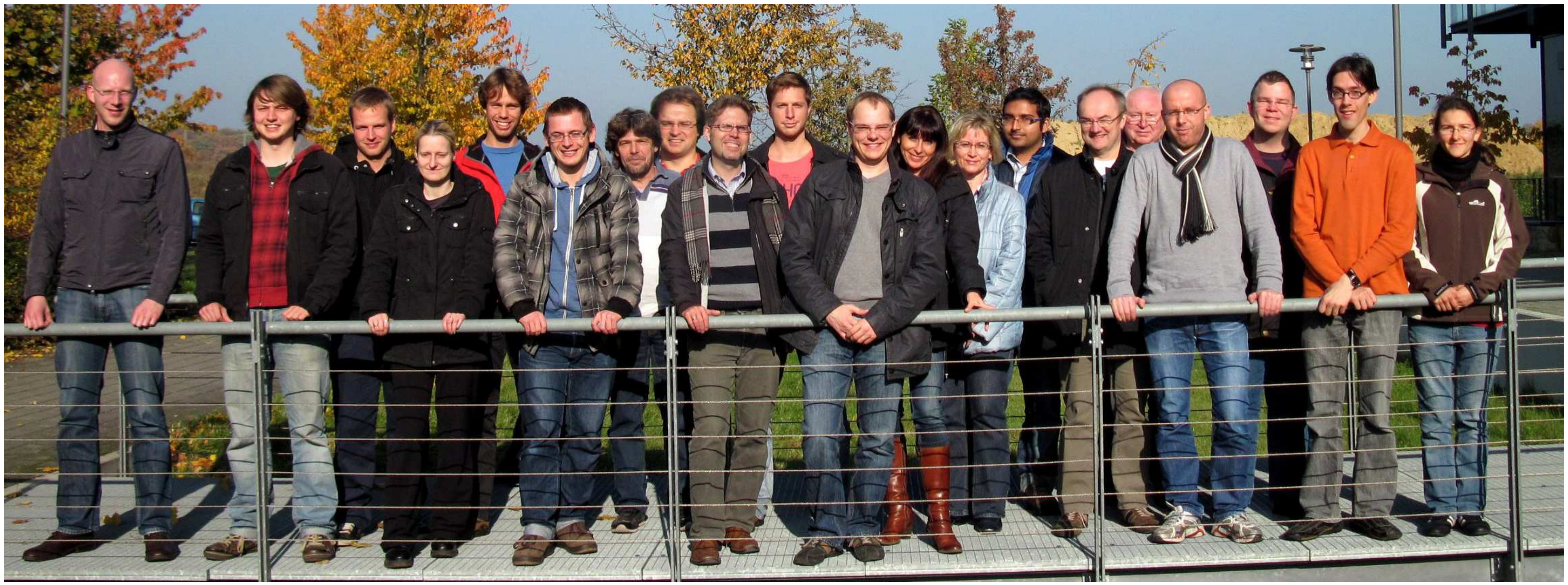
- **Outlook**
  - Redfield and non-Markovian theories
  - Non-Markovian measures
  - Light-induced processes

SUMMARY AND OUTLOOK

CORRELATION MATTERS

THANKS TO ...

- ... **the group:**



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