TECHNISCHE UNIVERSITÄT MÜNCHEN
Munich-Centre for Advanced Photonics (MAP)

Advances in electron dynamics with real-time time-dependent density-functional theory

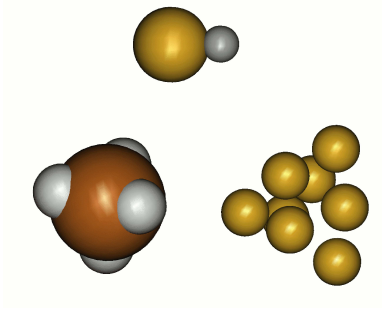
M. Nest

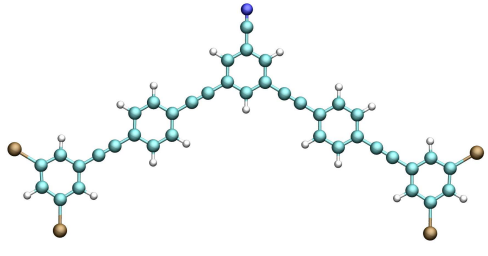
Norderney, Juli 2013

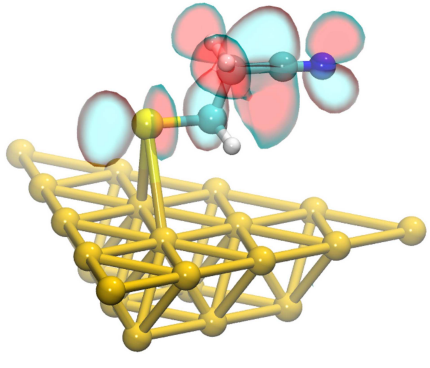
Outline

Electron Dynamics in Atoms, Molecules, and Nanostructures

- Real Time TDDFT
- Laser Driven Systems / Coherent Control
- Static Background TDDFT
- CT Adsorbate $\rightarrow$ Surface







Laser Driven Electron Dynamics with TDDFT?

Not LR-TDDFT

DFT:

$$h_{\mathrm{KS}}[\rho] = \frac{\vec{p}^2}{2m} + v_{\mathrm{eff}}[\rho]$$

Exact effective potential unknown, approximations: LDA, PBE, B3LYP, ...

Dynamics:

$$\varphi_j(0) \overset{h_{\mathrm{KS}}[\rho(0)]}{\longrightarrow} \varphi_j(\Delta t) \qquad \rho(\Delta t) = \sum_j |\varphi_j(\Delta t)|^2$$

$$\varphi_j(\Delta t) \overset{h_{\mathrm{KS}}[\rho(\Delta t)]}{\longrightarrow} \varphi_j(2\Delta t) \qquad \rho(2\Delta t) = \sum_j |\varphi_j(2\Delta t)|^2$$

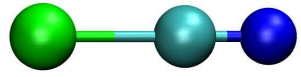
Adiabatic Approximation!

$h_{\mathrm{KS}}[\rho(0), \rho(\Delta t), \rho(2\Delta t), \ldots]$ Full history!

Laser Driven Electron Dynamics and TDDFT

LiCN

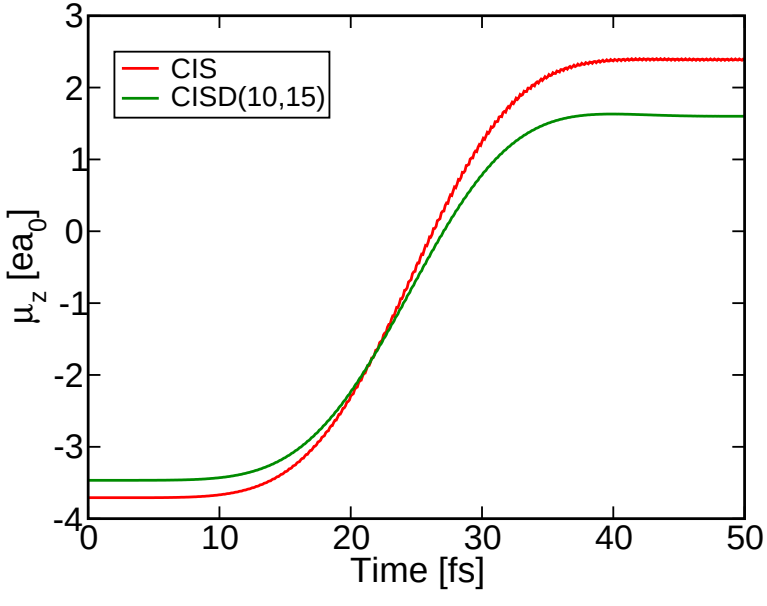
Transition: $|0\rangle \rightarrow |2\rangle$



TD Configuration Interaction: $\omega_L = (E_2 - E_0)/\hbar$, $\vec{F}_0 \vec{\mu}_{02} \sigma = \pi$

(Dipole switching, Klamroth et al. JCP **123**, 074105 (2005))

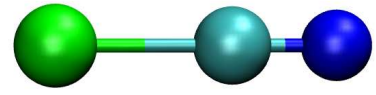
$$\vec{F}(t) = \vec{F}_0 \sin\left(\frac{\pi t}{2\sigma}\right) \sin(\omega_L t)$$

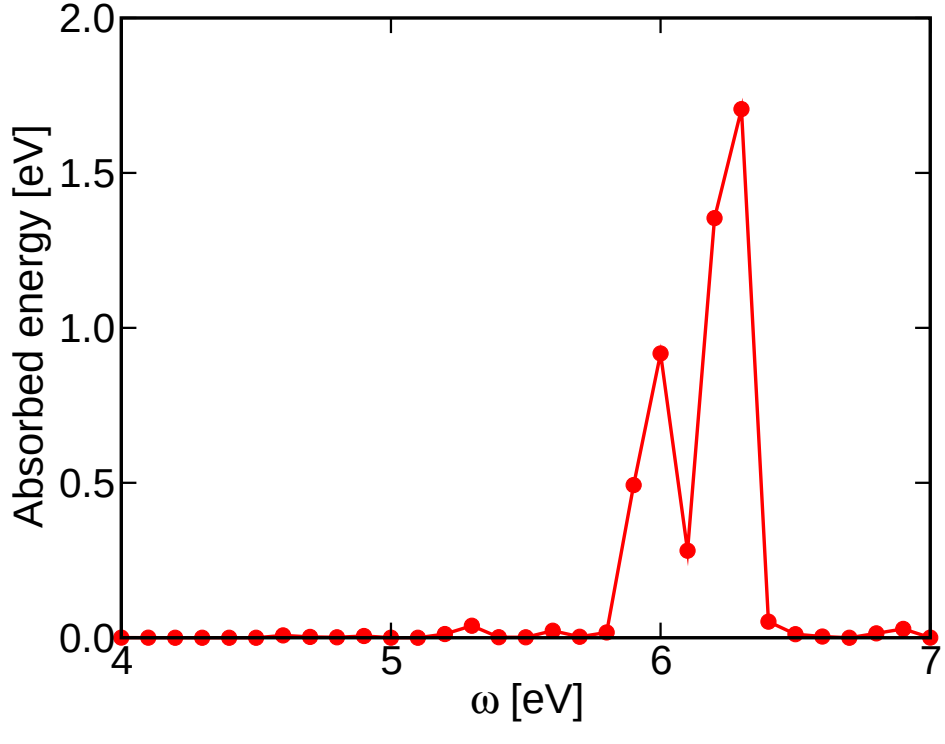


Will TDDFT with a *similar* pulse achieve something *similar*?

Laser Driven Electron Dynamics and TDDFT

TDDFT: Finding the right frequency ω_L: LiCN (weak field, PBE)

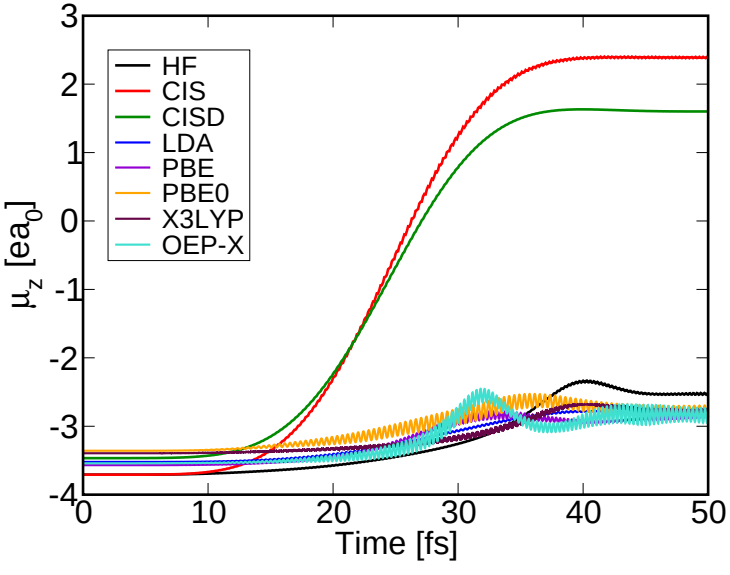




Frequency Scan

Laser Driven Electron Dynamics and TDDFT

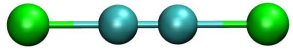
Fixing Field Strength 'by Hand'

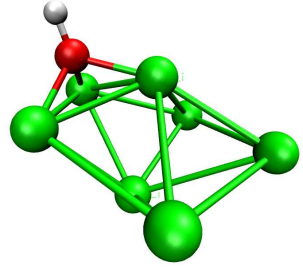


- No State-to-State transition possible with simple laser pulse
- TDHF behaves like TDDFT
- TDHF and TDDFT propagate reduced density matrix
- Adiabatic Approximation (no memory)
- Ground State Functionals
- Linear Chirp does not improve results

Laser Driven Electron Dynamics and TDDFT

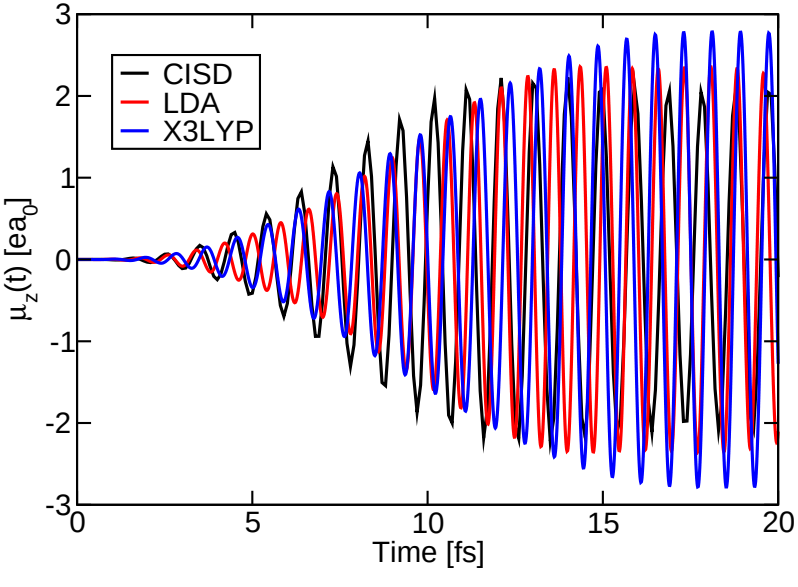
Wave Packet : $|0\rangle \rightsquigarrow (|0\rangle + |n\rangle)/\sqrt{2}$



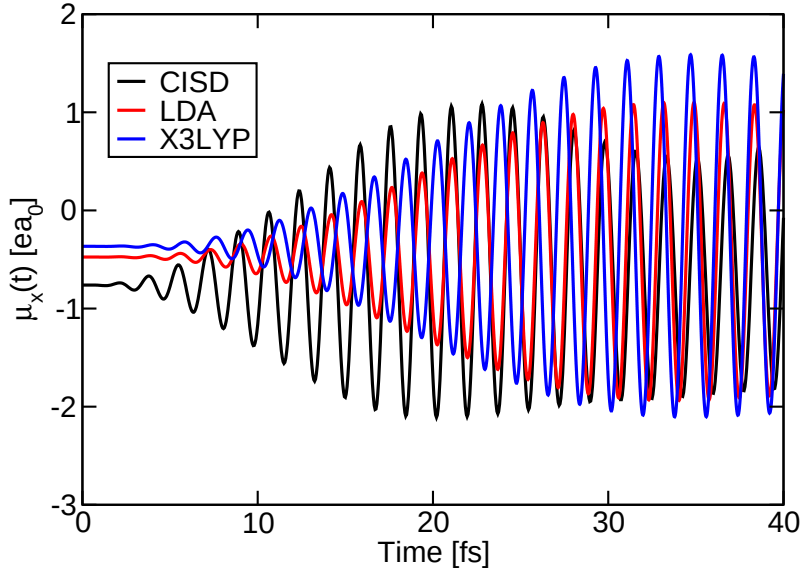


Similarity:

- Frequency
- Amplitude
- Average



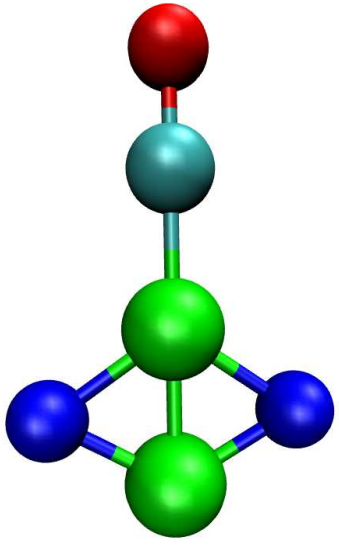
Li_2C_2



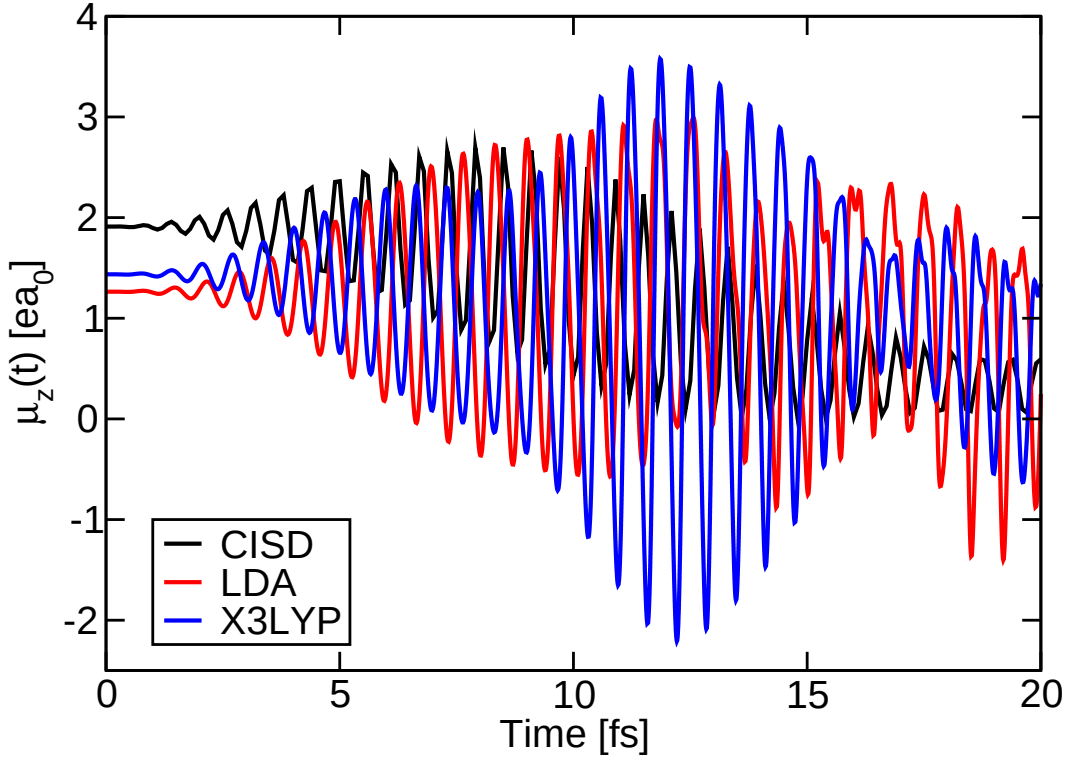
Li_7OH

Laser Driven Electron Dynamics and TDDFT

Wave Packet : $|0\rangle \rightsquigarrow (|0\rangle + |n\rangle)/\sqrt{2}$



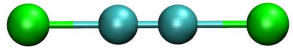
B_2N_2CO



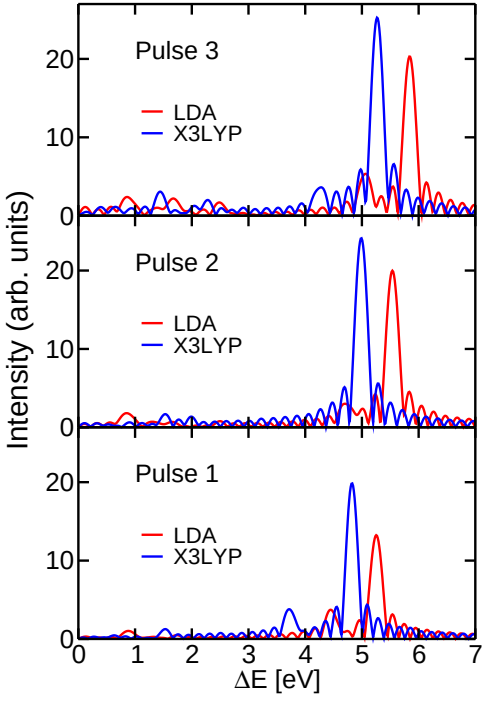
If $\mu_{00} \neq \mu_{nn} \Rightarrow$ 'Quality' of Wave Packet deteriorates

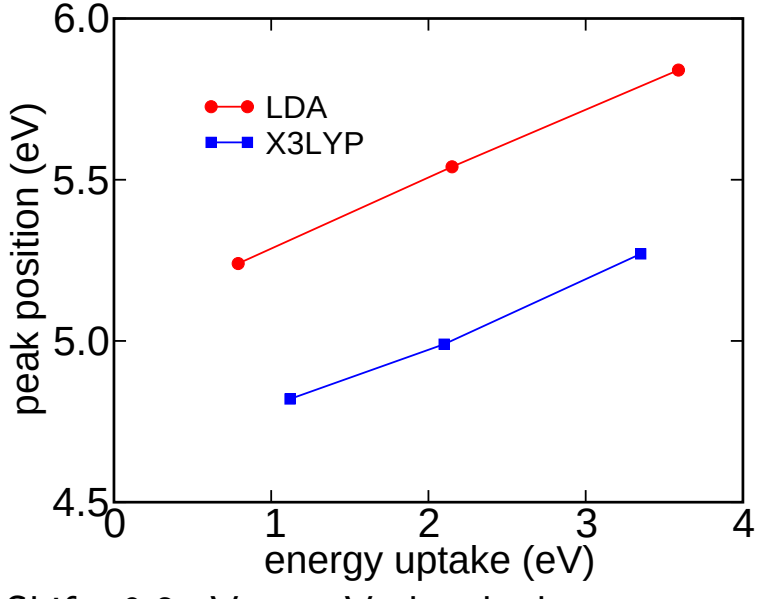
Laser Driven Electron Dynamics and TDDFT

Sequence of ultrashort, soft laser pulses,
followed by field free 20 fs intervals



$$\langle \mu \rangle(t) = \sum_{n,m} c_n^* c_m \mu_{nm} e^{i(E_n - E_m)t}$$





Shift: 0.2 eV per eV absorbed energy
(not universal)

Lack of Resonance $\Rightarrow$ TDDFT + Laser Control?

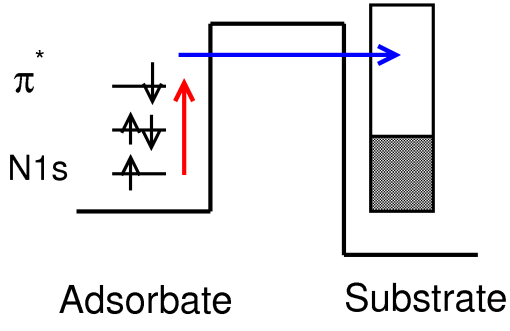
Charge Transfer at Surfaces

Ultrafast Charge Transfer: NC-$(CH_2)_n$-S@Au

Excitation by synchrotron radiation: N1s $\rightarrow$ CNπ^*

Subsequent tunneling of excited electron to conduction band of Au

Experiment: Core Hole Clock (P. Feulner, TUM)



Static Background TDDFT:

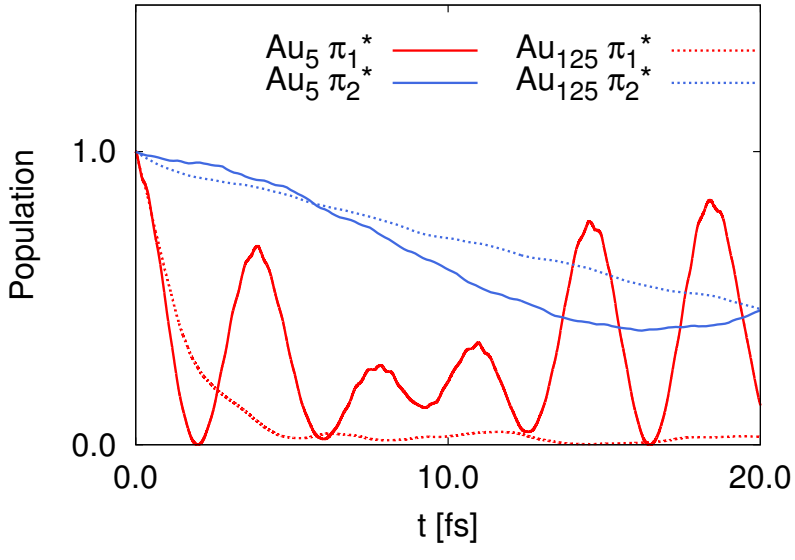
- Propagate only φ_{π^*}

$$\dot{\varphi}(t) = -ih_{\mathrm{KS}}\varphi(t)$$

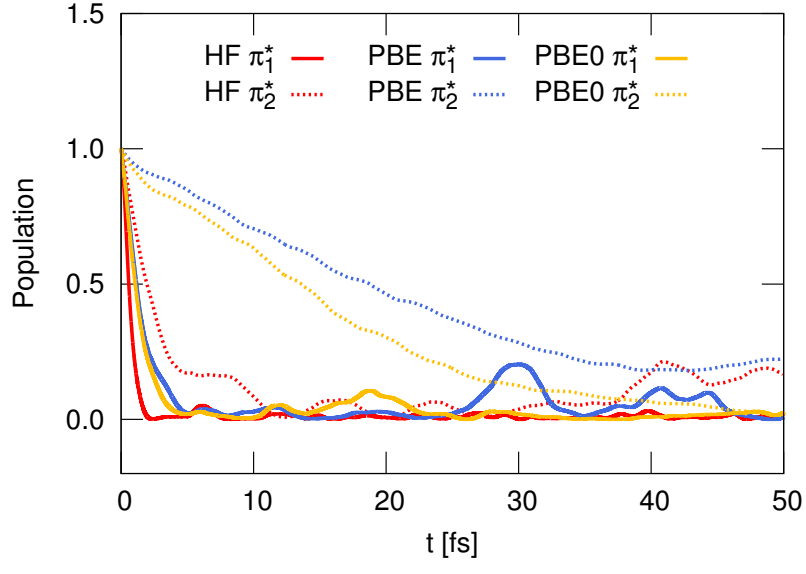
- Keep ρ fixed: static background
- 100 e^- $\rightarrow$ 10000 e^-
- Process 3 fs $\rightarrow$ 1.4 eV energy resolution
- unoccupied bands ($\approx$ 3 ev above E_F)

Charge Transfer at Surfaces

Effect of Cluster Size



Effect of Functional



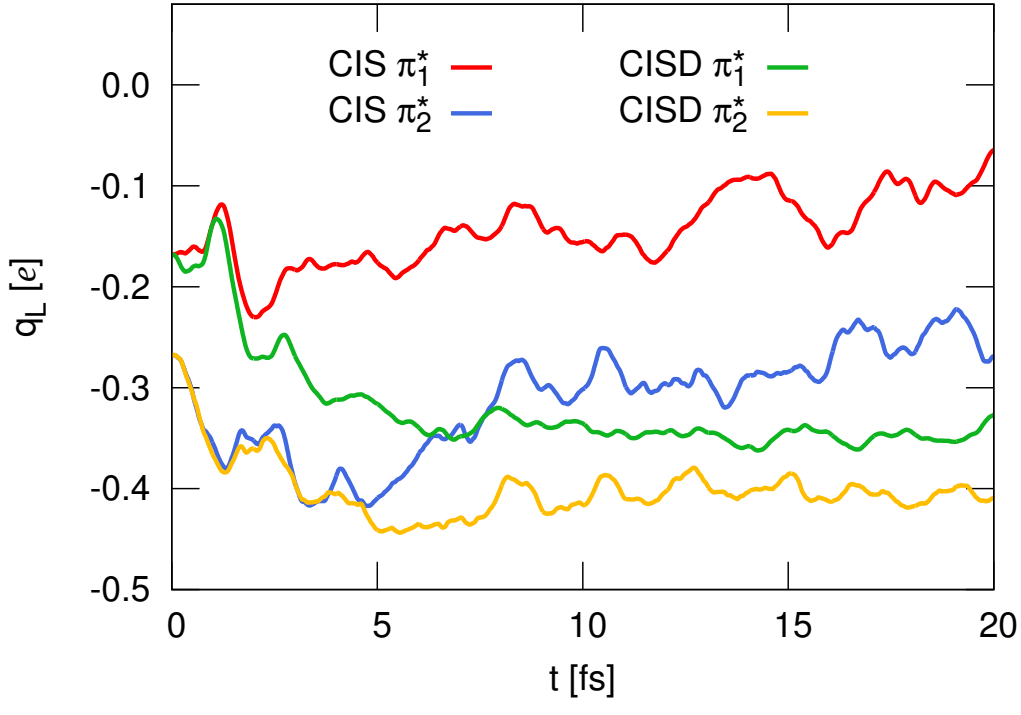
- Population $P_{\pi^*}(t) = |\langle\varphi_{\pi^*}|\varphi(t)\rangle|$
- Au_{125} : 2420 electrons
- Initial decay characteristics similar $Au_5 \leftrightarrow Au_{125}$
- Different functionals $\rightarrow$ different time-scales
- TDHF closes to experiment, predictability?

Charge Transfer at Surfaces

TD Configuration Interaction?

NC-$(CH_2)_n$-S@Au_5

Quantity: Lowdin charge of Au-cluster



Charge Transfer at Surfaces

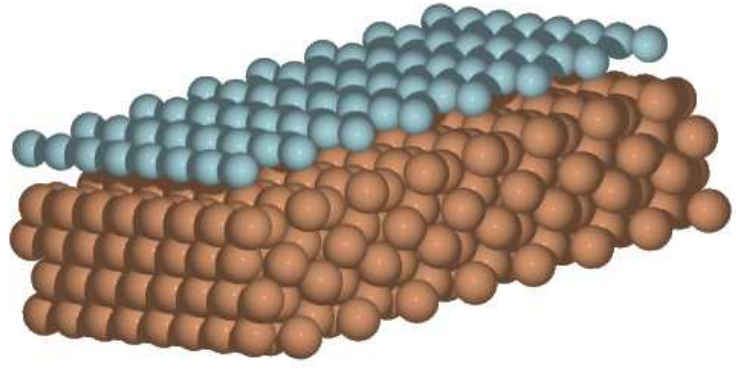
Planned: Spin resolved Charge Transfer to Magnetic Substrates

Experiment: Ar 2p $\rightarrow$ 4s

CT times:

Fe, Co: minority spins 0.3 fs faster

Ni: no difference



THANKS

Group

R. Ramakrishnan
S. Raghunathan
B. J. Rao
D. Strobusch

Former Members

I. Ulusoy
S. Raghunathan
S. Lopez-Lopez
B. Schäfer-Bung
P. Ramanathan
F. Lüder

€ : Deutsche Forschungsgemeinschaft
Munich-Centre for Advanced Photonics
German-Israeli Foundation

Collaborators

E. Pollak
T. Klamroth
P. Saalfrank
F. Remacle
R. Levine
A. Scrinzi
M. Thoss
M. Kling
V. Yakovlev
E. Suraud
H.-D. Meyer
I. Burghardt
R. Kosloff
R. Martinazzo
R. Folman
D. Tannor