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Controlling nuclear- and electron-dynamics at a conical intersection

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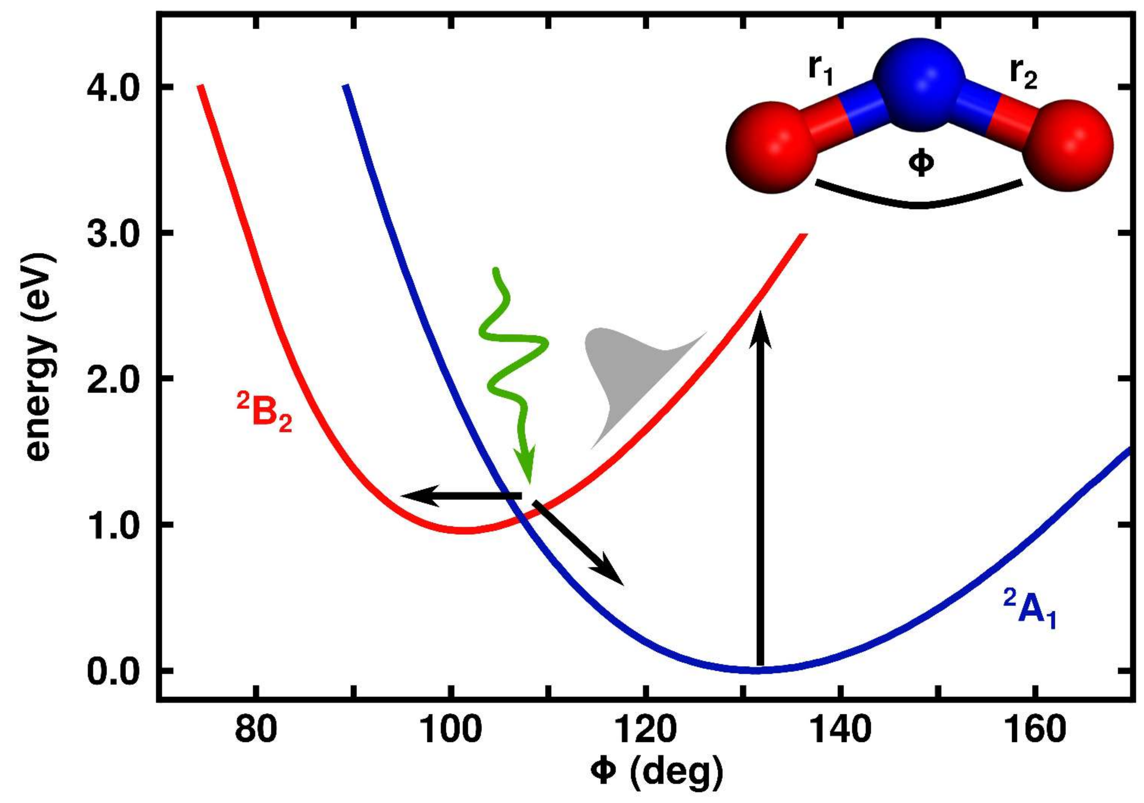
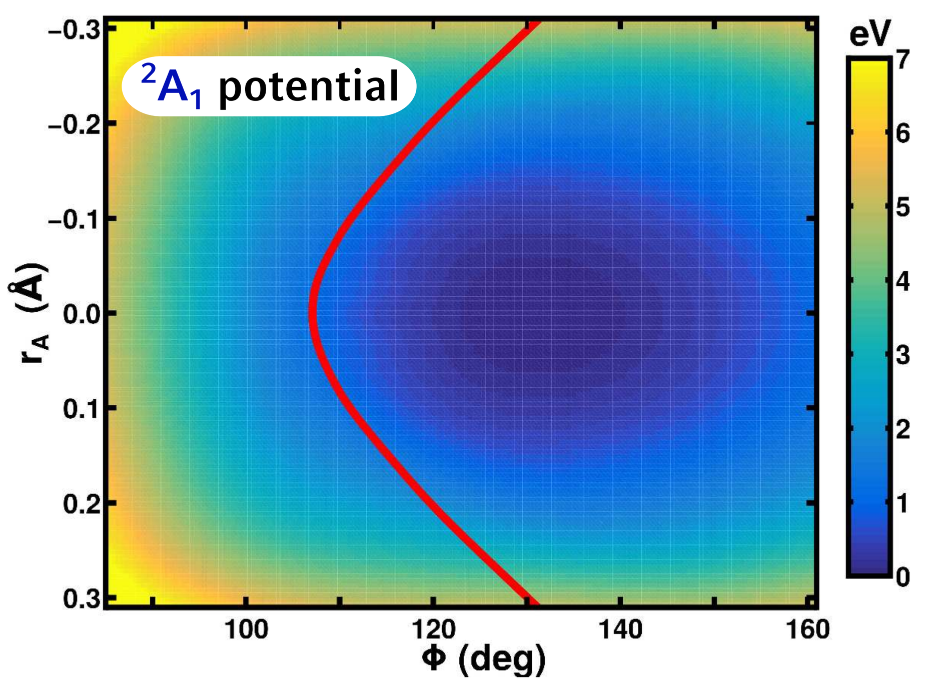
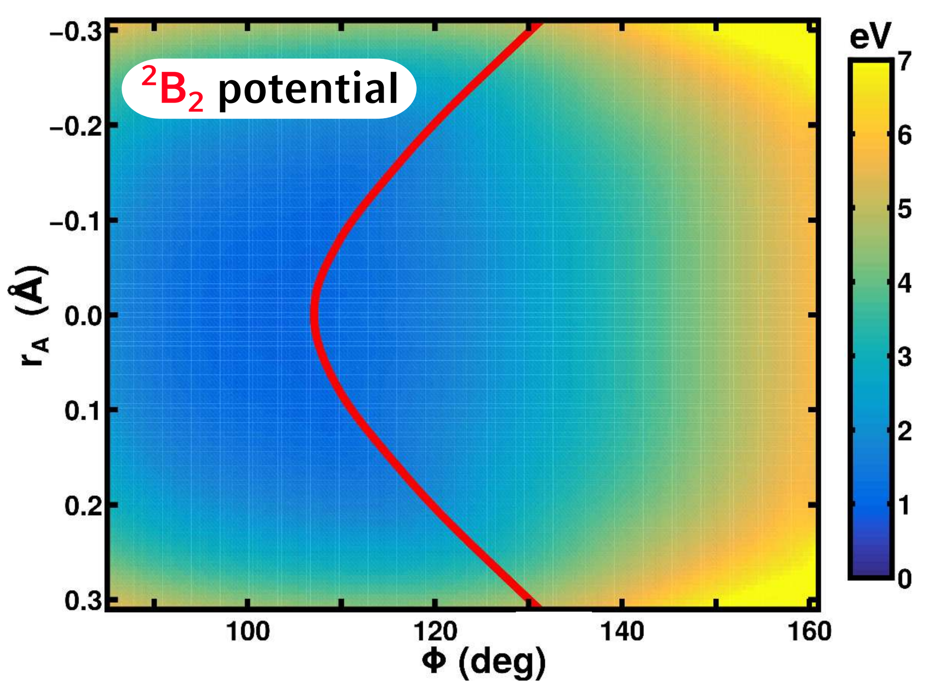
Abstract

In this theoretical work we aim to control the nuclear motion coupled to the electron-dynamics in the vicinity of a conical intersection (CoIn) in molecular systems. The control scheme relies on the carrier envelope phase (CEP) of a few-cycle IR pulse [1]. The IR pulse creates an electronic superposition of the involved states before the wavepacket reaches the CoIn and influences the population transfer through the CoIn.
In order to simulate the nuclear motion as well as the electron-dynamics of this process we are using the NEMol (coupled nuclear- and electron-dynamics in molecules) ansatz developed in our group [2]. In this purely quantum mechanical ansatz the quantum-dynamical description of the nuclear motion is combined with the calculation of the electron-dynamics in the eigenfunction basis.
As a first example we focus on the NO_2 molecule. After photoexcitation to the first excited state the molecule can relax back to the ground state via a CoIn on a timescale of a few hundred fs [3,4]. The transition dipole moment is present during the whole process and the nuclear wavepacket stays localized. Therefore we expect a long lived electron-dynamics and an effective CEP control of the system.



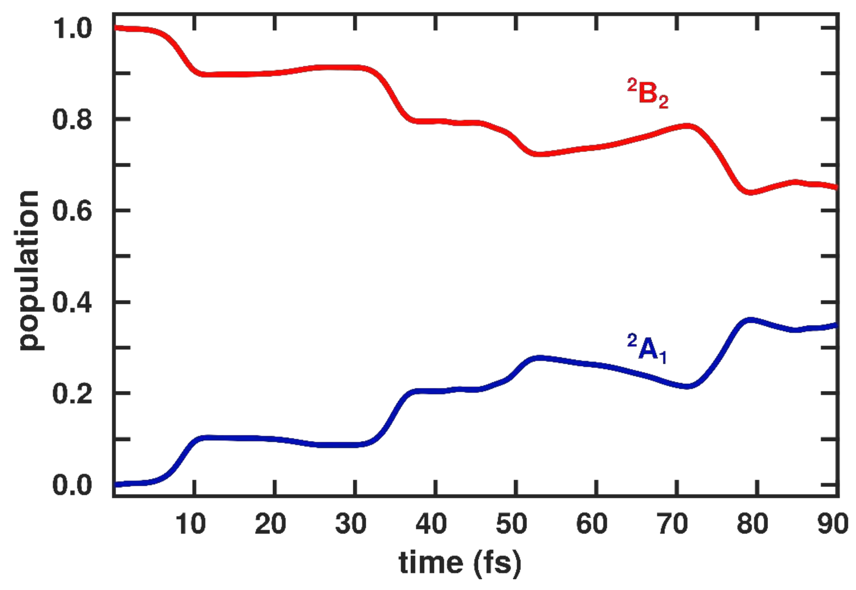
Relaxtion Dynamics and CEP-Control



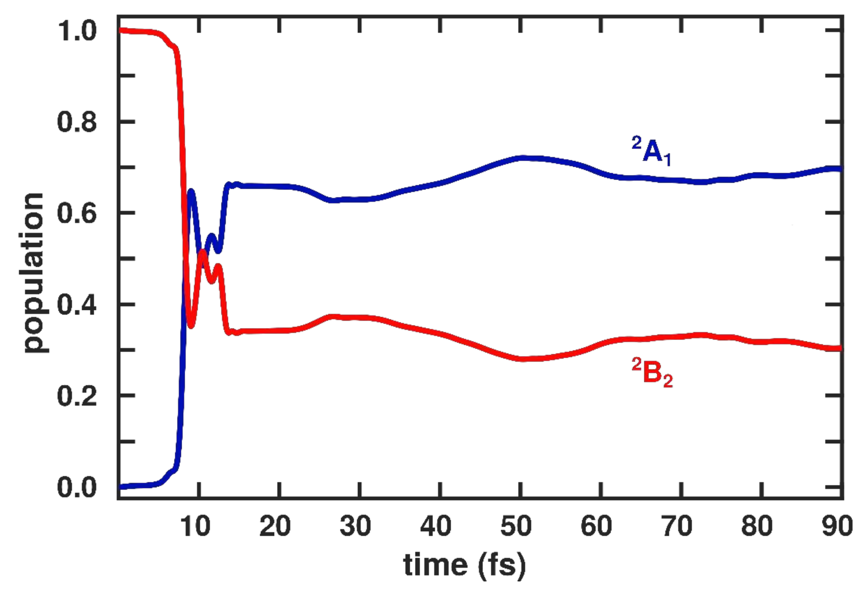


Free Propagation

- nuclear quantum dynamics on coupled diabatic potential surfaces
- fast population transfer between the two states
- good agreement with previous works [3,4]

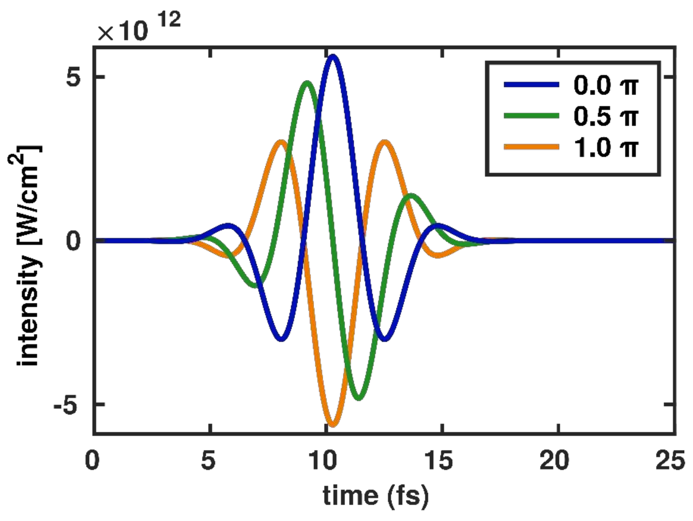


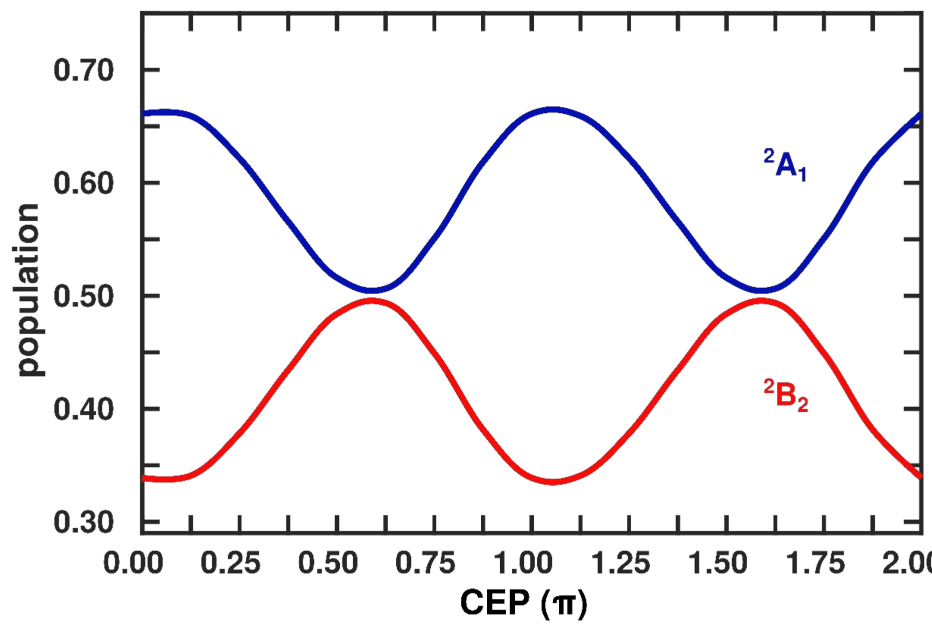
Propagation with Laser



Laser paramters:
- Intensity 5.6 10^{12} Wcm^{-2}
- Frequency 1518 nm
- FWHM 5 fs

- coupling with a IR-laser accelerates population dynamics
- Population dynamics is sensetive to CEP





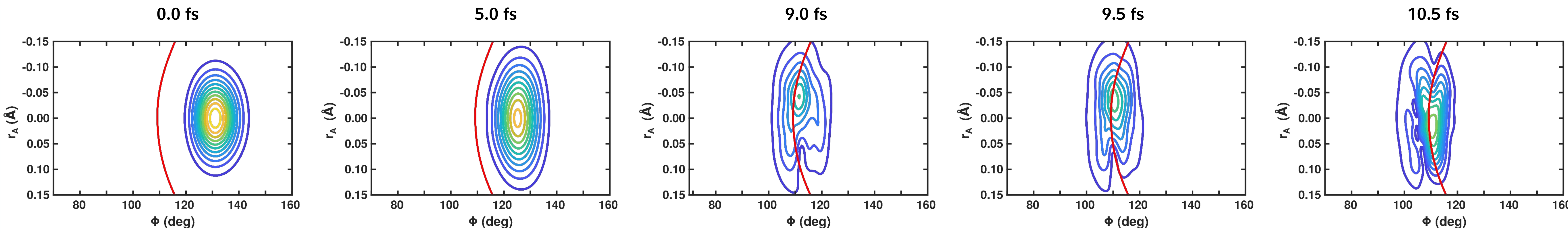
Coupeled Nuclear and Electron Dynamics

- quantumdynamical description of nuclear motion in the $^2A_1$ and $^2B_2$ states
- calculating the electron dynamics in the eigenfunction basis of $^2A_1$ and $^2B_2$

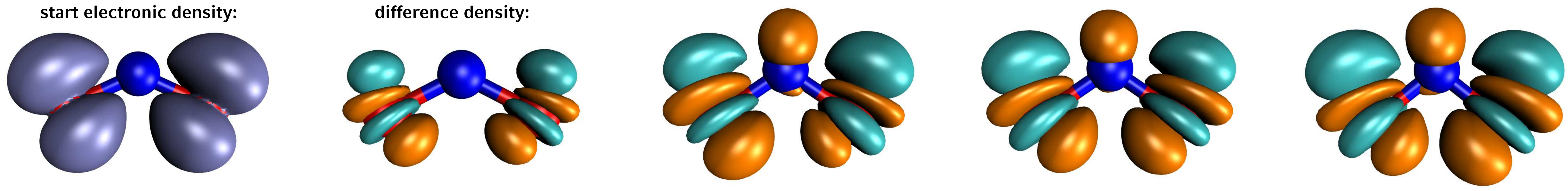
⟶ timedependent electron density $\rho(r,t;R)$

- discretization of the potential surfaces into 16 sections along the bending mode
- overlaps $\langle\chi_i^a(R,t)|\chi_i^b(R,t)\rangle$ and populations a_i^2 and b_i^2 evaluated for all sections
- electron dynamics between two orbitals $\varphi_i^a(r;R)$ and $\varphi_i^b(r;R)$ included

$$\rho(r,t;R) = \sum_{i=1}^{N} a_i^2(t)|\varphi_a^i(r;R)|^2 + b_i^2(t)|\varphi_b^i(r;R)|^2 + 2Re\{\langle\chi_i^a(R,t)|\chi_i^b(R,t)\rangle\, \varphi_b^i(r;R)\varphi_a^i(r;R)e^{-i\Delta E_i t}\}$$



start electronic density: difference density:



Dynamics shown for relaxtion with laser coupling; wave packet shown in the $^2B_2$ state

Outlook

- Optimizing the laser paramters with optimal control theory (OCT) [1]
- Including the second dimension in the coupled electron dynamics
- Comparison of our electron dynamics with diffrent methods (real time TD-DFT)
- Connection to experiment to observe the CEP-control and the electron dynamics

References

[1] P. von den Hoff et al., Phys. Chem. Chem. Phys. 14, 14460 (2012).
[2] D. Geppert et al., J. Phys. B: At. Mol. Opt. Phys. 41, 074006 (2008).
[3] P. M. Kraus et al., Phys. Rev. A 85, 043409 (2012).
[4] M. Richter et al., Phys. Chem. Chem. Phys. 21, 10038-10051 (2019).