Ultrafast fragmentation of N_2^{2+}.

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SFB 925: Light induced dynamics and control of strongly correlated quantum systems
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Motivation

- Traditional molecular dynamics assumes Born-Oppenheimer approximation.
- Fails in cases, such as photoexcited dynamics, electron transfer, and surface chemistry.
- To develop a machinery which is computationally efficient to study non-adiabatic dynamics.
- Time-resolved X-ray/IR pump-probe experiments on N_2 at SLAC using Linac Coherent Light Source (LCLS)[1].

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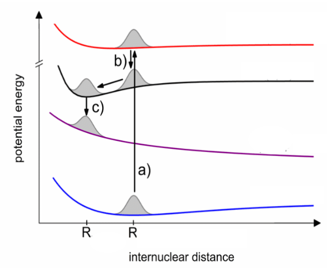
- 1s core e^- X-ray photoionization of N_2 followed by Auger decay onto valence N_2^{2+} states in the presence of IR probe.

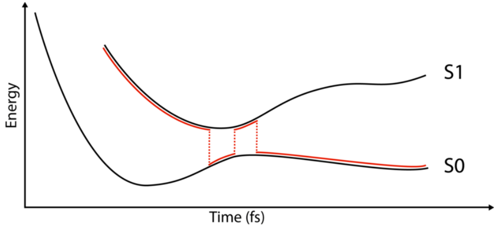


- Perform mixed quantum-classical molecular dynamics and compare with Quantum Dynamics (QD)[1].

[1] A. M. Hanna, O. Vendrell, A. Ourmazd and R. Santra, Phys. Rev. A, 95, 043419, (2017).

Tully's Fewest Switches Surface Hopping (FSSH)

- Electrons → quantum mechanically and nuclei → ensemble of classical trajectories $R(t)$, evolves on potential energy surface (PES).



- A trajectory hops from $S_0 = j$ to $S_1 = k$ with probability $P_{j\rightarrow k}$

$$P_{j\rightarrow k} = \frac{-\left[\sum_{k\neq j} -2\Re[\rho_{jk}\dot{\vec{R}}\cdot\vec{d}_{kj}] - 2\Re[i\rho_{jk}\vec{E}(t)\cdot\vec{\mu}]\right]\Delta t}{\rho_{jj}}$$

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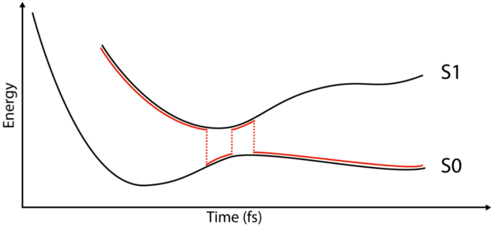

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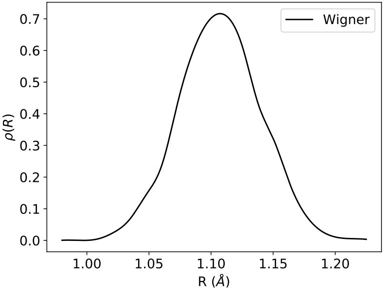
Initial Condition Sampling



- Wigner sampling of the ground state normal mode coordinate of N_2.
- Wigner sampling reproduces initial quantum wavepacket.
- $\Delta E = 0.14$ eV (Wigner) & $\Delta E = 0.12$ eV (Quantum wavepacket).

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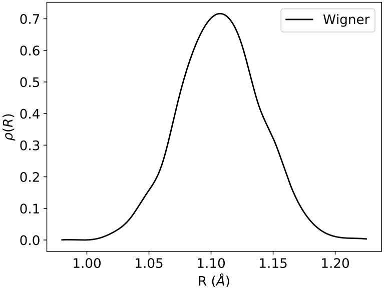

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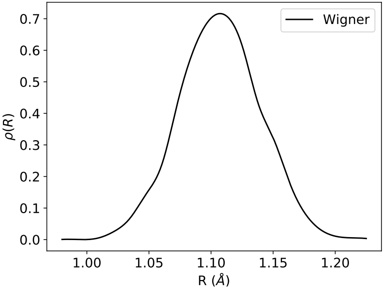

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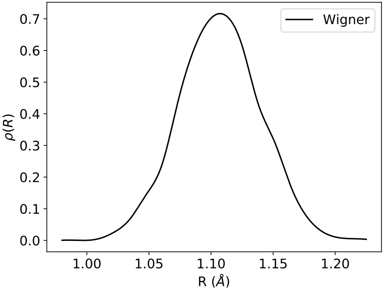

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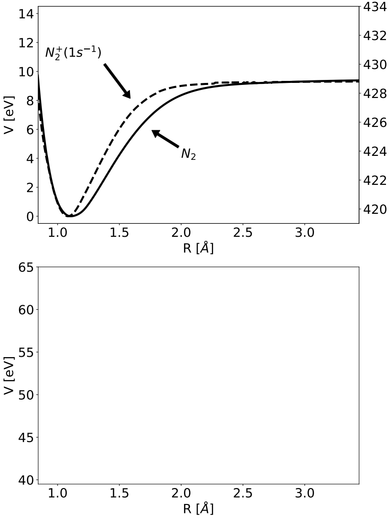

- Ground and core hole state of N_2 (relative to -2971.64 eV).
- Assume: trajectories are lifted vertically upwards to N_2^+.
- 8 N_2^{2+} states.
- $X^1\Sigma_g^+$ and $1^1\Sigma_u^+$ - local minimum in the Franck-Condon region.
- $1^1\Delta_g$, $2^1\Sigma_g^+$ and $1^1\Pi_u$ - outside the Franck-Condon region.

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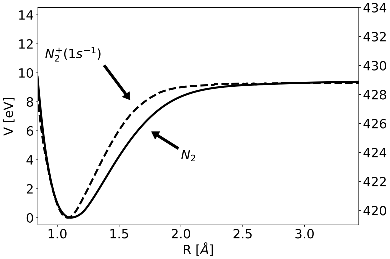

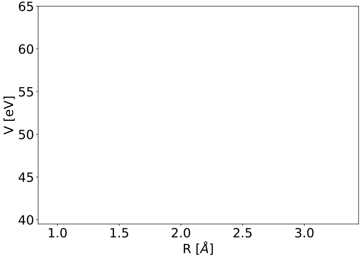

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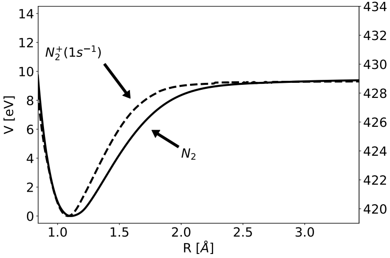

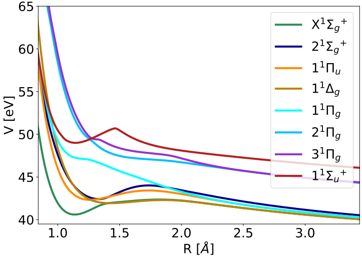

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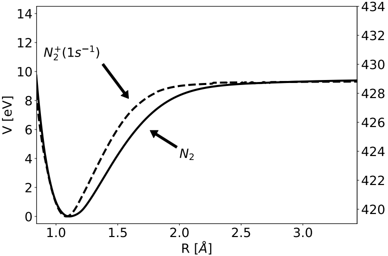

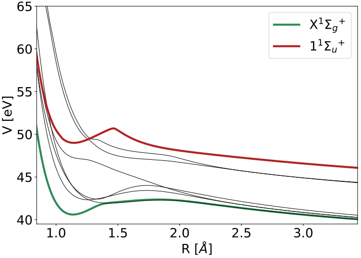

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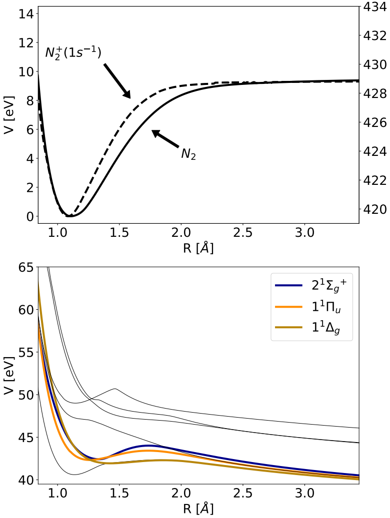

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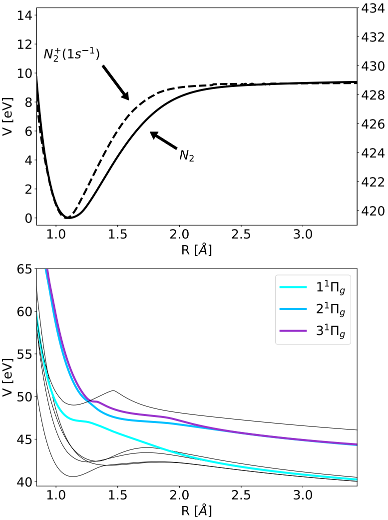

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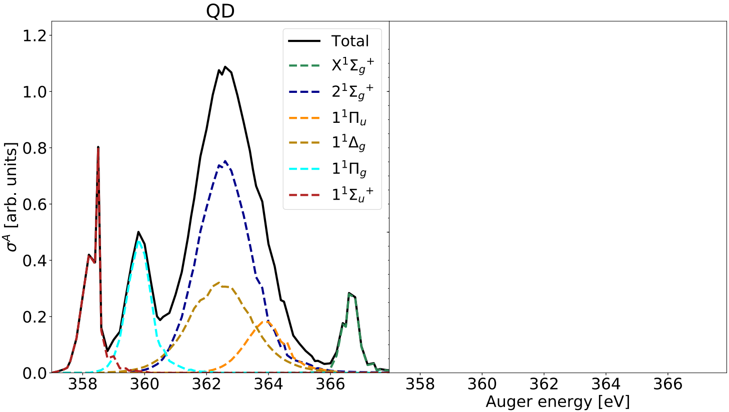
FSSH vs QD

Auger spectrum



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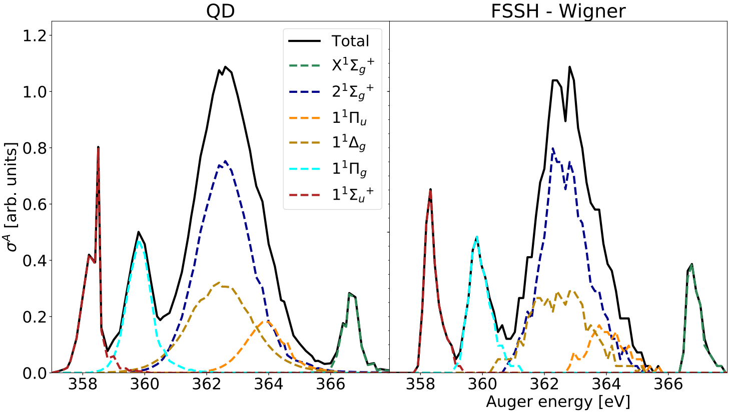

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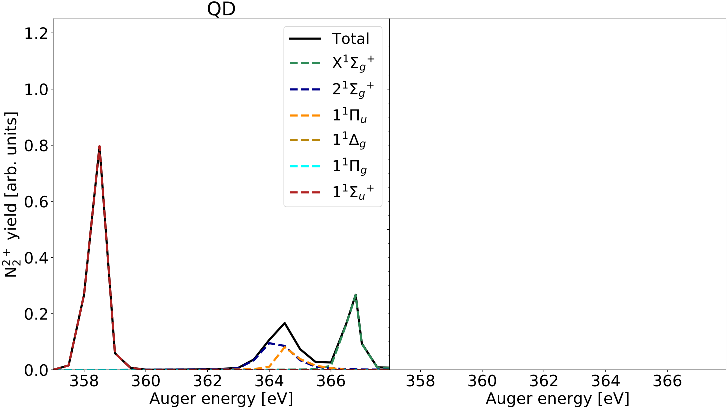
N_2^{2+} yield as a function of Auger energy



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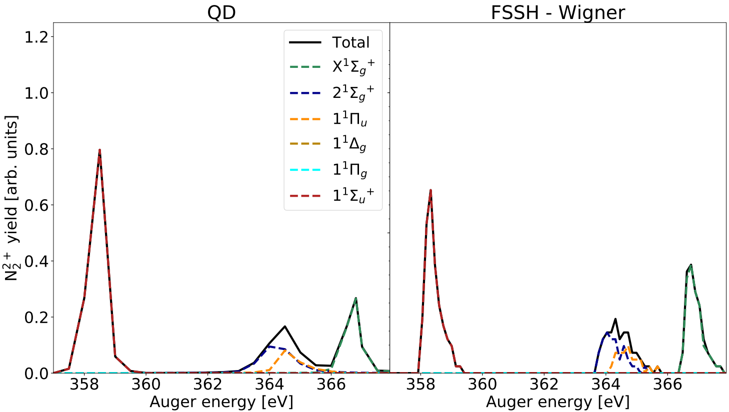

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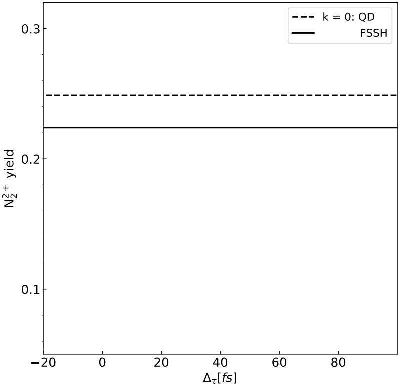

- Gaussian shaped IR-pulse.

IR pulse	I_0 [10^{14} W cm^{-2}]	Δ_{IR} (FWHM) [fs]
k = 0	-	-

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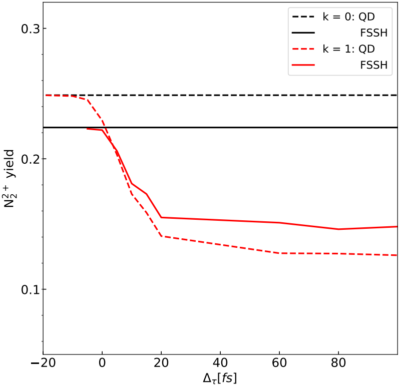

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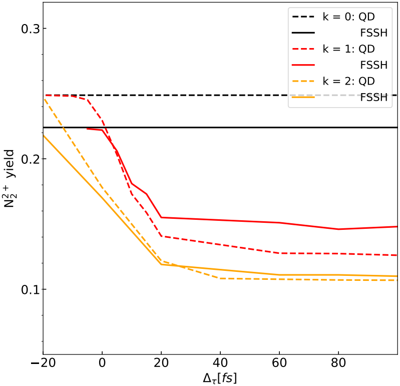

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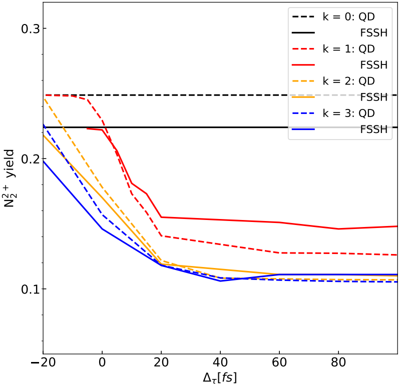

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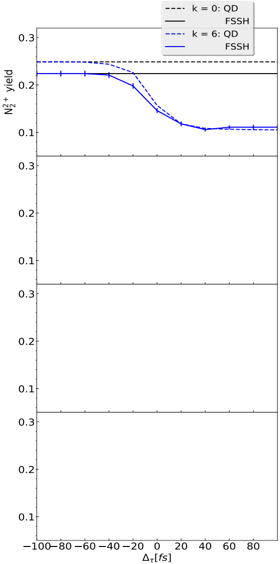

- Total N_2^{2+} yield.
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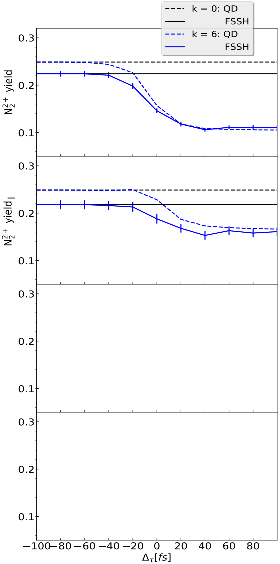

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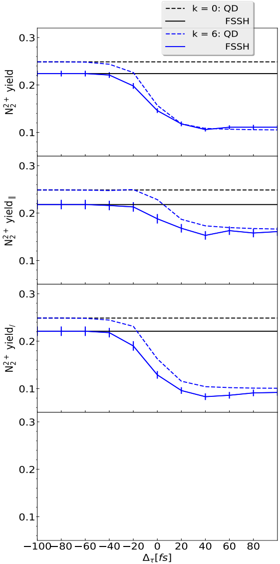

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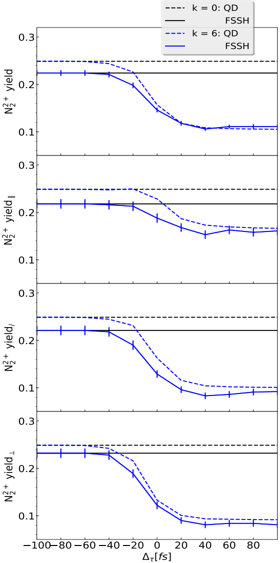

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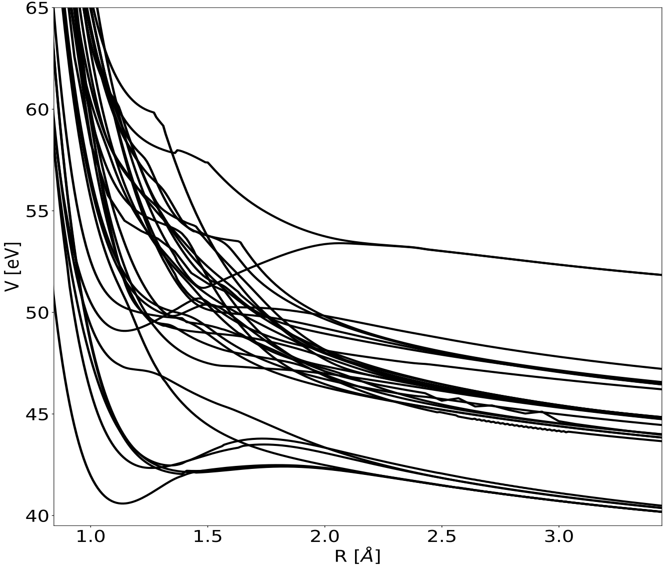

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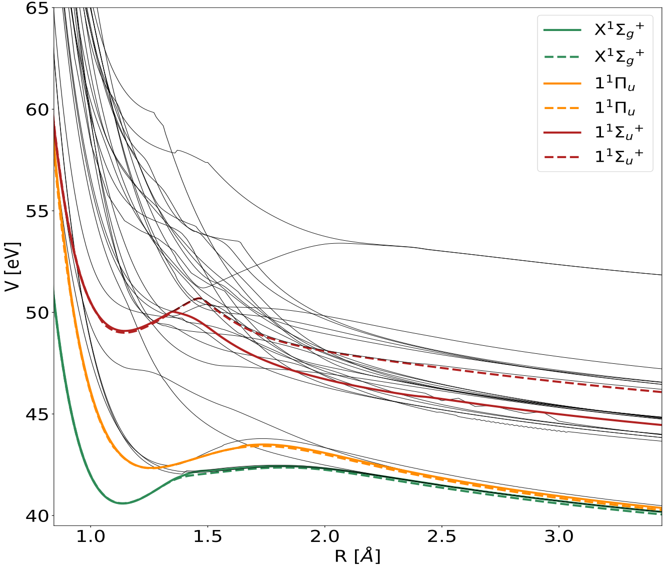

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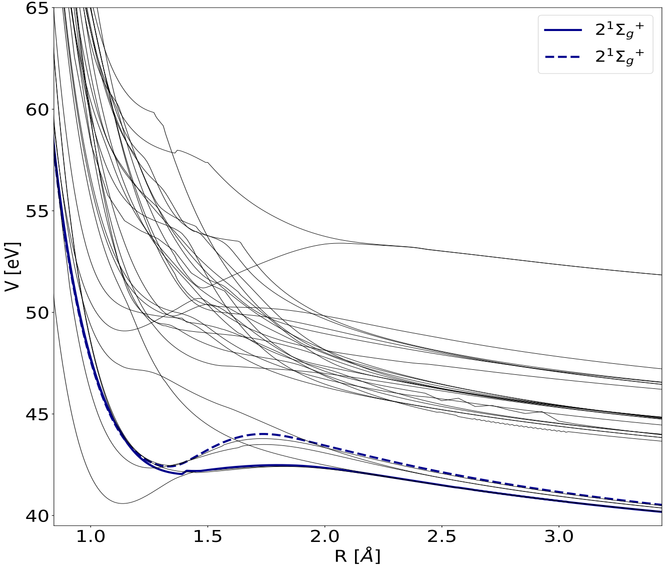

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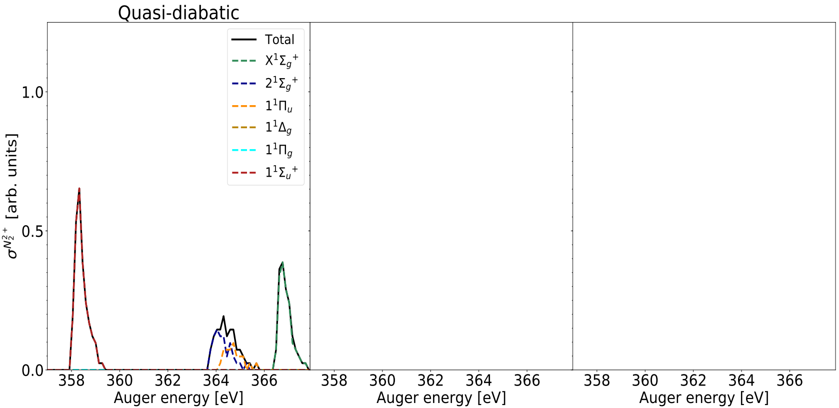

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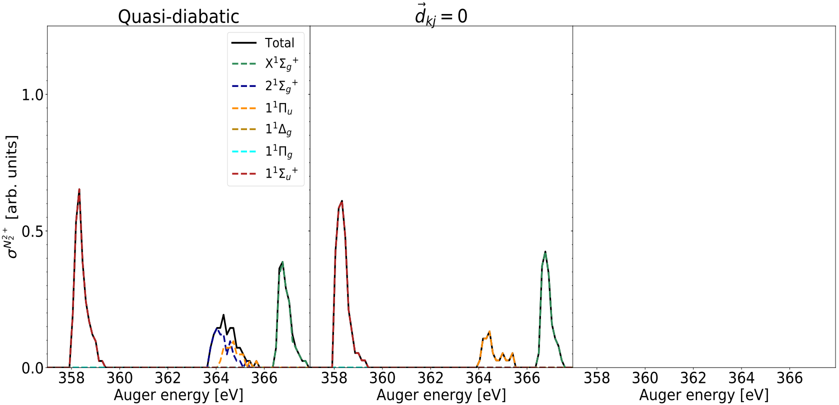

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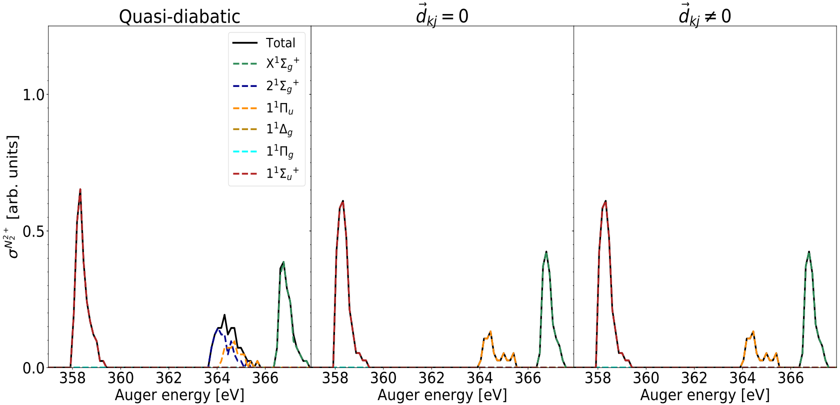

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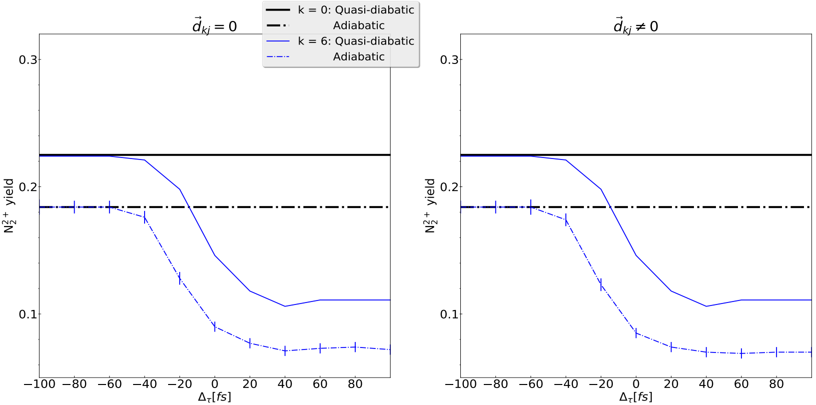

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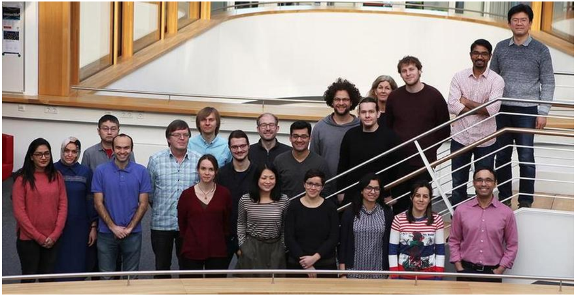
Thank you for your kind attention!



SFB

SFB 925: Light induced dynamics and control of strongly correlated quantum systems

Tully's Fewest Switches Surface Hopping (FSSH)

- Electrons $\rightarrow$ quantum mechanically and nuclei $\rightarrow$ ensemble of classical trajectories $R(t)$, evolves on potential energy surface (PES).
- In the presence of an external field $\vec{E}(t)$.
- Solve Time-dependent Schrödinger Equation along $R(t)$.

$$i\hbar\dot{c}_k(t) = \sum_j c_j(t)\left[V_{kj} - i\hbar\dot{\vec{R}}\cdot\vec{d}_{kj} - \vec{E}(t)\cdot\vec{\mu}\right]$$

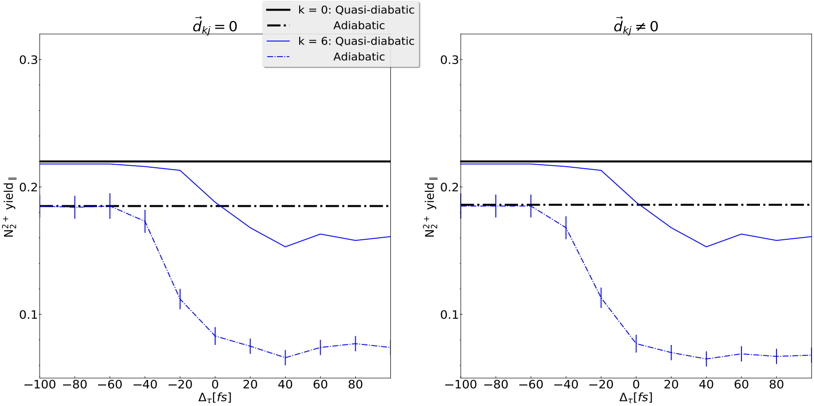
- Probability of hopping $P_{j\rightarrow k}$

$$P_{j\rightarrow k} = \frac{-b_{kj}\Delta t}{\rho_{jj}}, \tag{1}$$

- where $b_{kj} = \sum_{k\neq j} -2\Re[\rho_{jk}\dot{\vec{R}}\cdot\vec{d}_{kj}] - 2\Re[i\rho_{jk}\vec{E}(t)\cdot\vec{\mu}]$ (adiabatic representation).

Additional results

N_2^{2+} yield$_{||}$ - $(0^\circ < \theta < 30^\circ$ & $150^\circ < \theta < 180^\circ)$.



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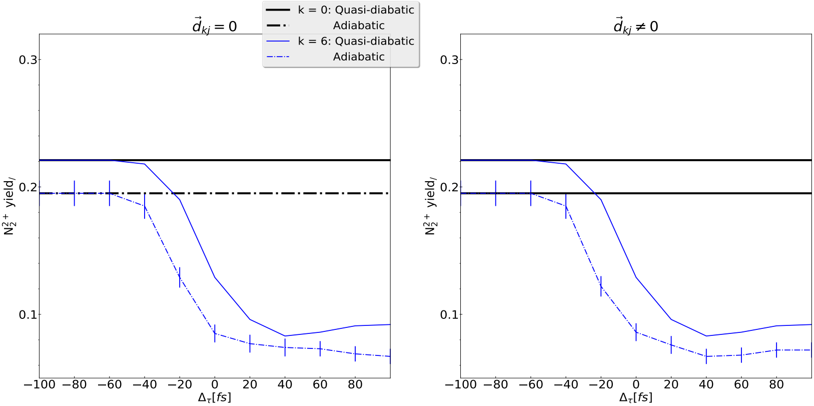

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