Ab initio surface-hopping simulations of \( \text{CS}_2 \) photodissociation

Darren Bellshaw
Kirrander group, University of Edinburgh

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Excited state dynamics

- Photochemistry
  - Photosynthesis, bioluminescence
  - DNA damage avoidance

- Photovoltaics/OLEDs
  - Spin-orbit coupling

- Atmospheric chemistry
Nonadiabatic dynamics – challenge for theoreticians...

- Breakdown of BOA
- Must treat:
  - Electronic structure
  - Nuclear dynamics
  - Nonadiabatic effects
- Internal conversion (IC)
- Intersystem crossing (ISC)
Nuclear wavepacket approaches

- Fully quantum
- Pre-calculated potentials
- Limited DoF
- \textit{e.g.} MCTDH


Classical trajectory approaches

- Mixed quantum/classical
- “On-the-fly” potentials
- Fully-dimensional
- \textit{e.g.} \textit{Surface-hopping}

Trajectory surface hopping

- Quantum electrons, classical nuclei
  - “On-the-fly” potentials
  - Newtonian nuclear dynamics

- SHARC - accounts for nonadiabatic (IC) and spin-orbit coupling (ISC)

- Trajectories “hop” probabilistically

CS₂ photodissociation

\[ CS_2 + h\nu \rightarrow CS(X) + \begin{cases} S(1D_1) \\ S(3P) \end{cases} \]
\[
CS_2 + h\nu \rightarrow CS(X) + \begin{cases} 
S\left( ^1D_1 \right) \\
S\left( ^3P \right)
\end{cases}
\]

- Large spin-orbit (SO) coupling
CS₂ photodissociation

\[ CS_2 + h\nu \rightarrow CS(X) + \begin{cases} S(1^D_1) \\ S(3^P) \end{cases} \]

- Large spin-orbit (SO) coupling

- **Simple reaction ≠ simple dynamics!**
  - Competing dissociation channels involving multiple electronic states
**SHARC setup**

<table>
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<th>Simulation details</th>
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<tr>
<td>CASSCF active space</td>
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<td>Basis set</td>
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<td>Coupling approach</td>
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<td>Number of trajectories</td>
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</table>
- Initial rapid redistribution
- Initial rapid redistribution
- Relaxation of bound curves
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- Relaxation of bound curves
- Onset of dissociation
• *Ab initio* dependence...? Drop active space to (8,6).
Conclusions

• IC & ISC considered sequential...
  ... but not the case in some systems.
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  ... but not the case in some systems.

• Simple system, complex dynamics!
Conclusions

• IC & ISC considered sequential...
  ... but not the case in some systems.

• Simple system, complex dynamics!

• Be wary of scrimping on computational expense!
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Thanks!

Duck & Birdie
know what matters in science
"very impressive, professor...,
but does it work in theory?"