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TDDFT in Chemistry and Biochemistry

Lecture 1: Photochemistry and Photobiology
BENASQUE 9th TDDFT: Prospects and Applications

Shane M. Parker
Case Western Reserve University
Department of Chemistry
shane.parker@case.edu
quantumparker.com

Photochemistry

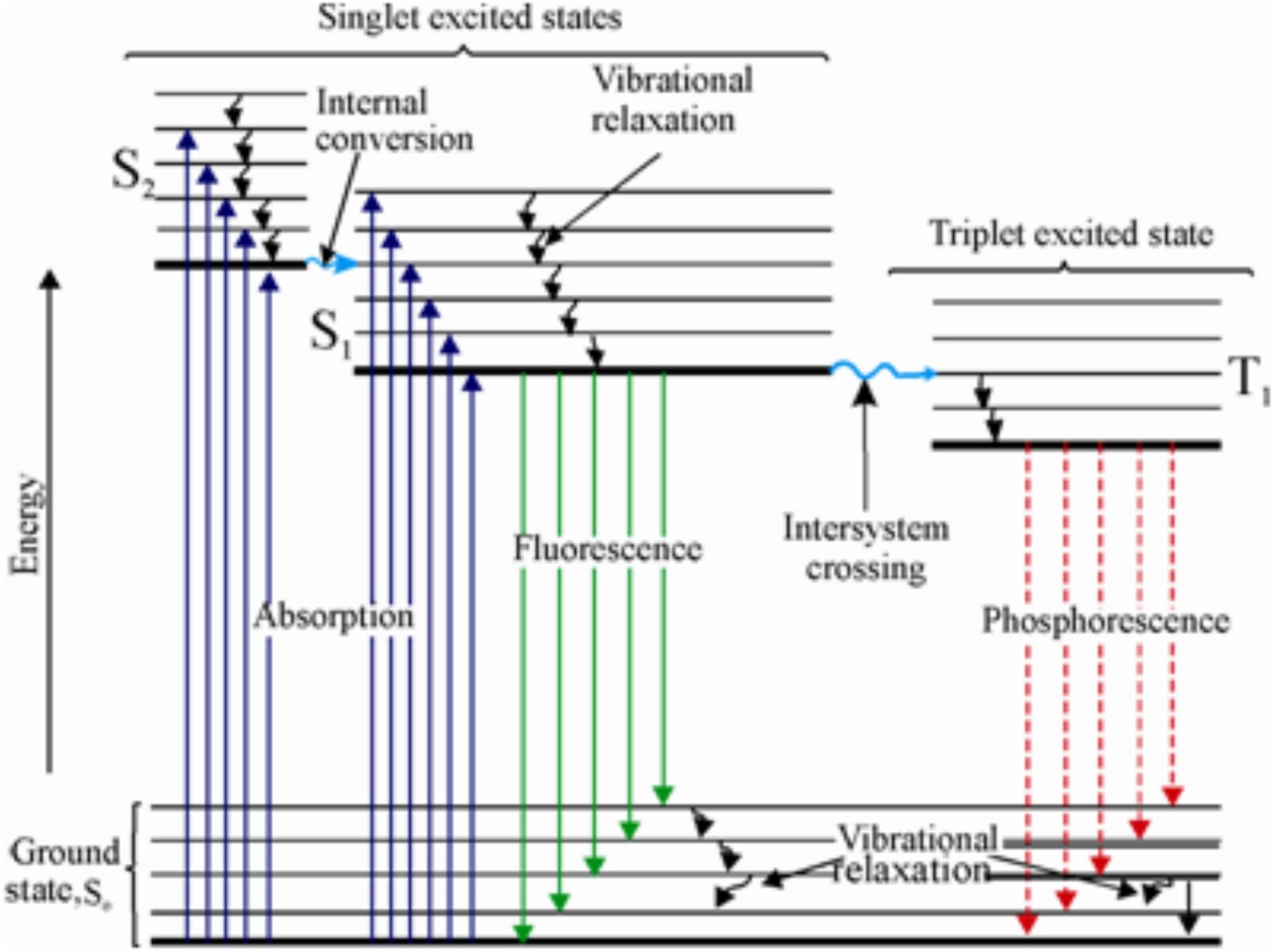
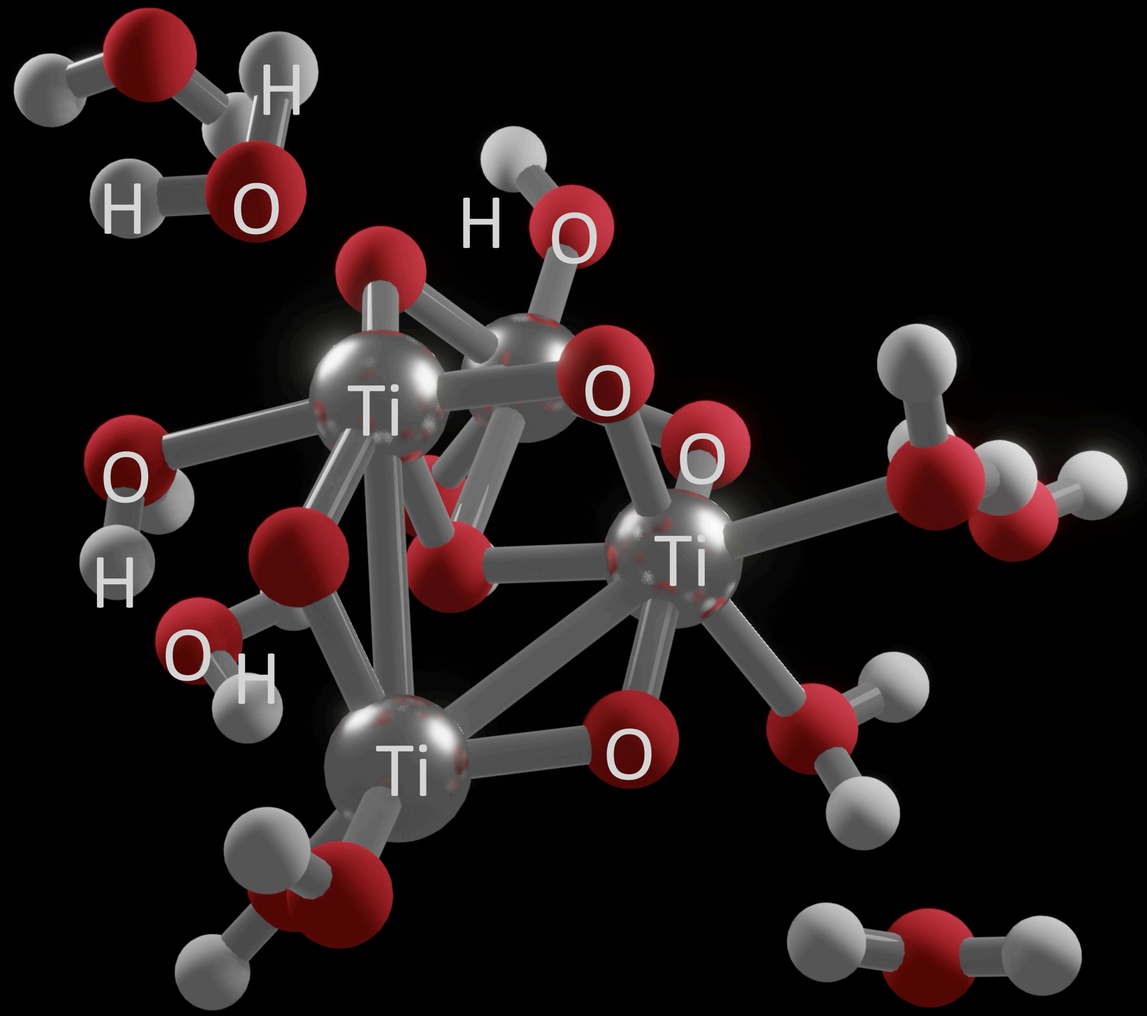


image from quora.com

Use TDDFT to determine

- identities of the states involved? properties?
- **photochemical pathway? timescales?**

Sun, Q.; Mosquera-Vazquez, S.; Lawson Daku, L. V. M.; Gu n e, L.; Goodwin, H. A.; Vauthey, E.; Hauser, A. *J. Am. Chem. Soc.* **2013**, *135* (37), 13660–13663.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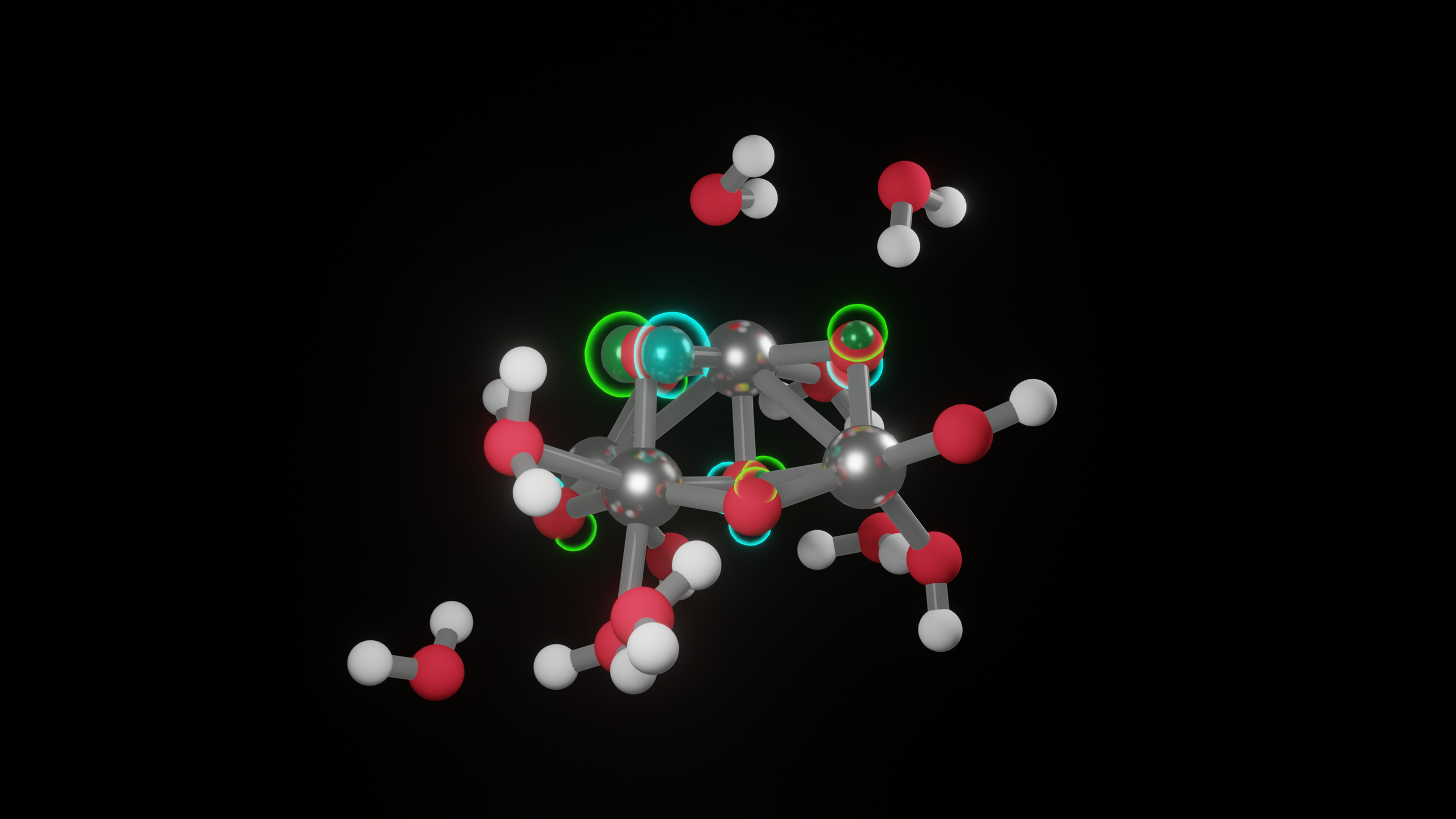
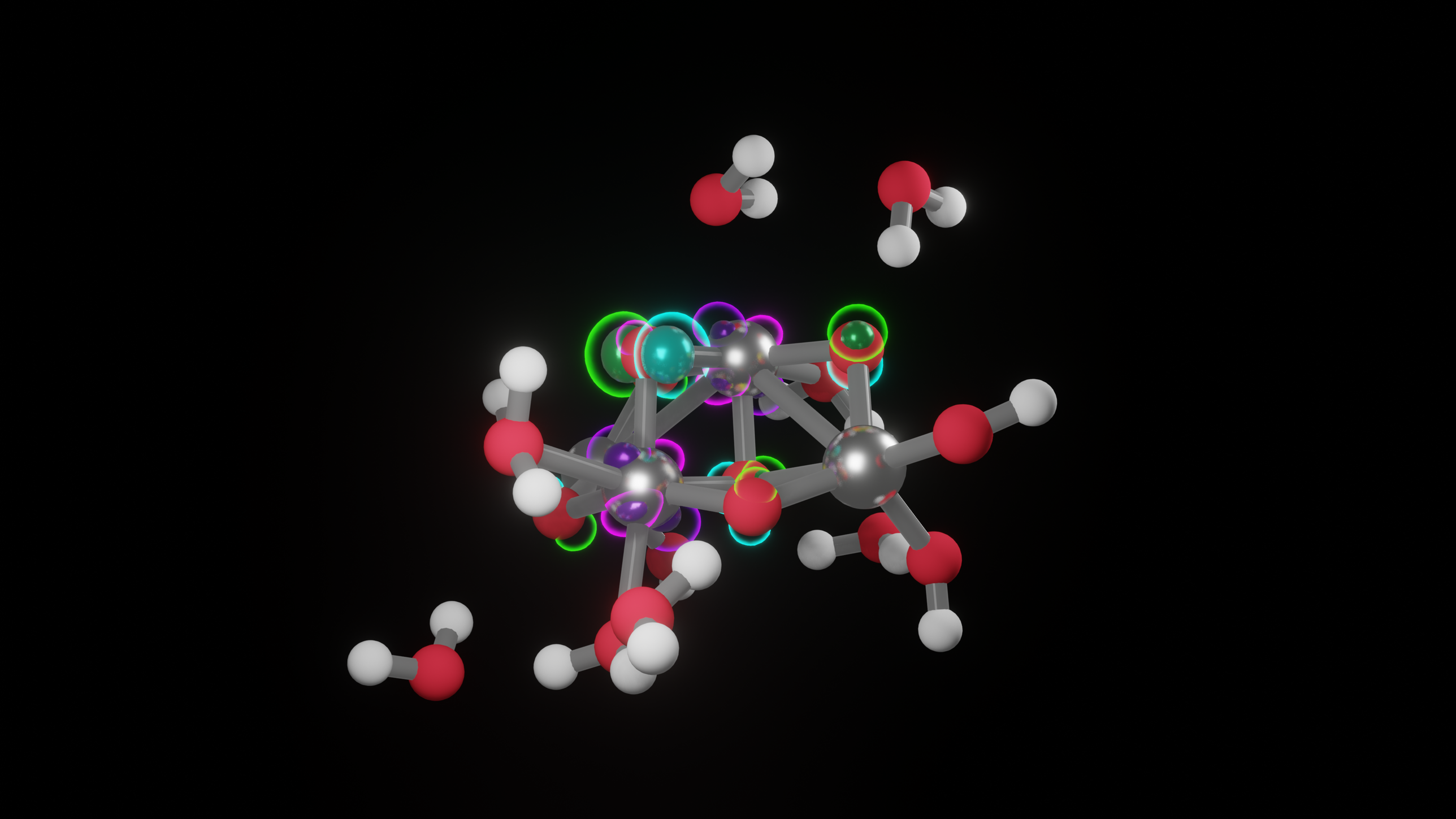
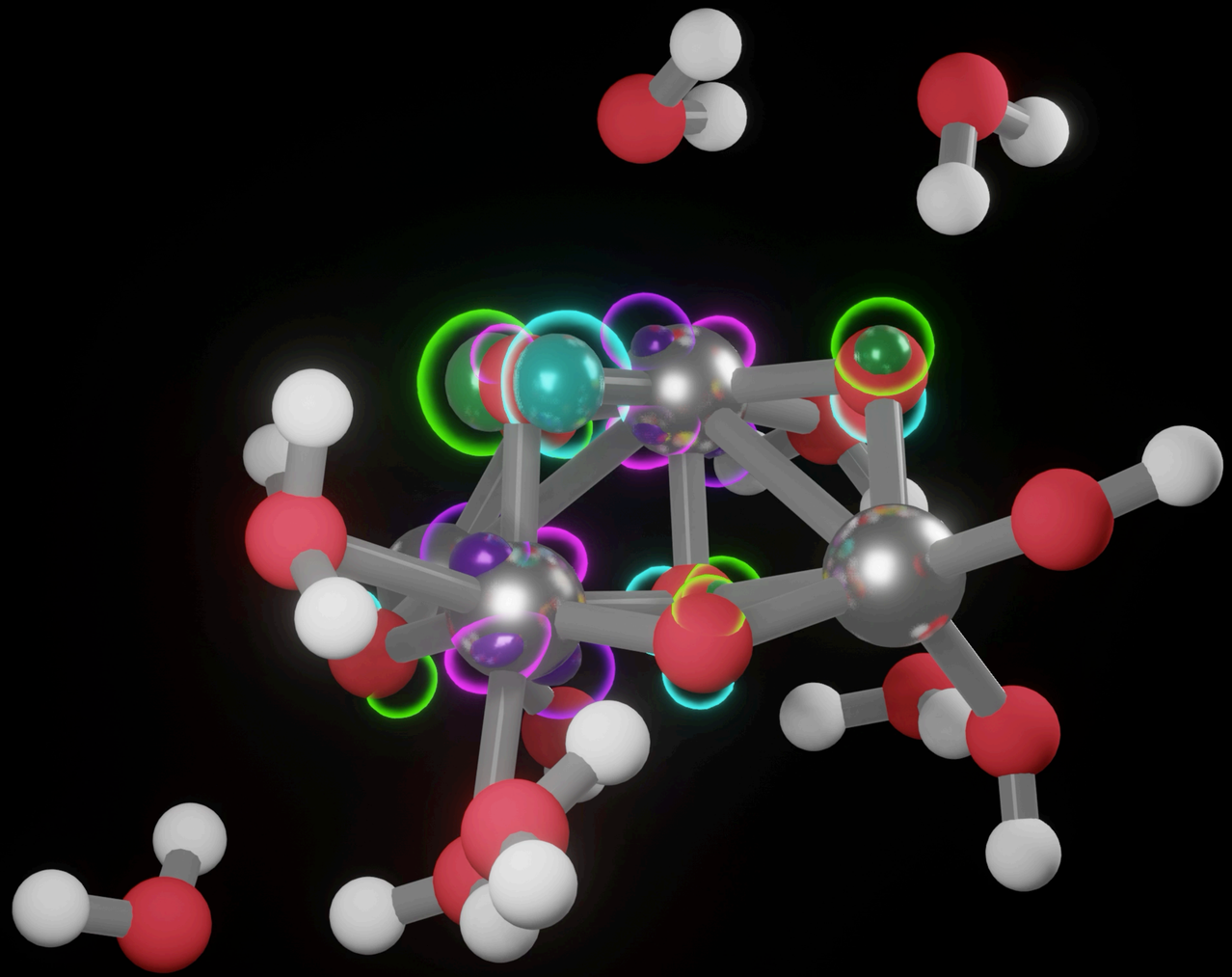




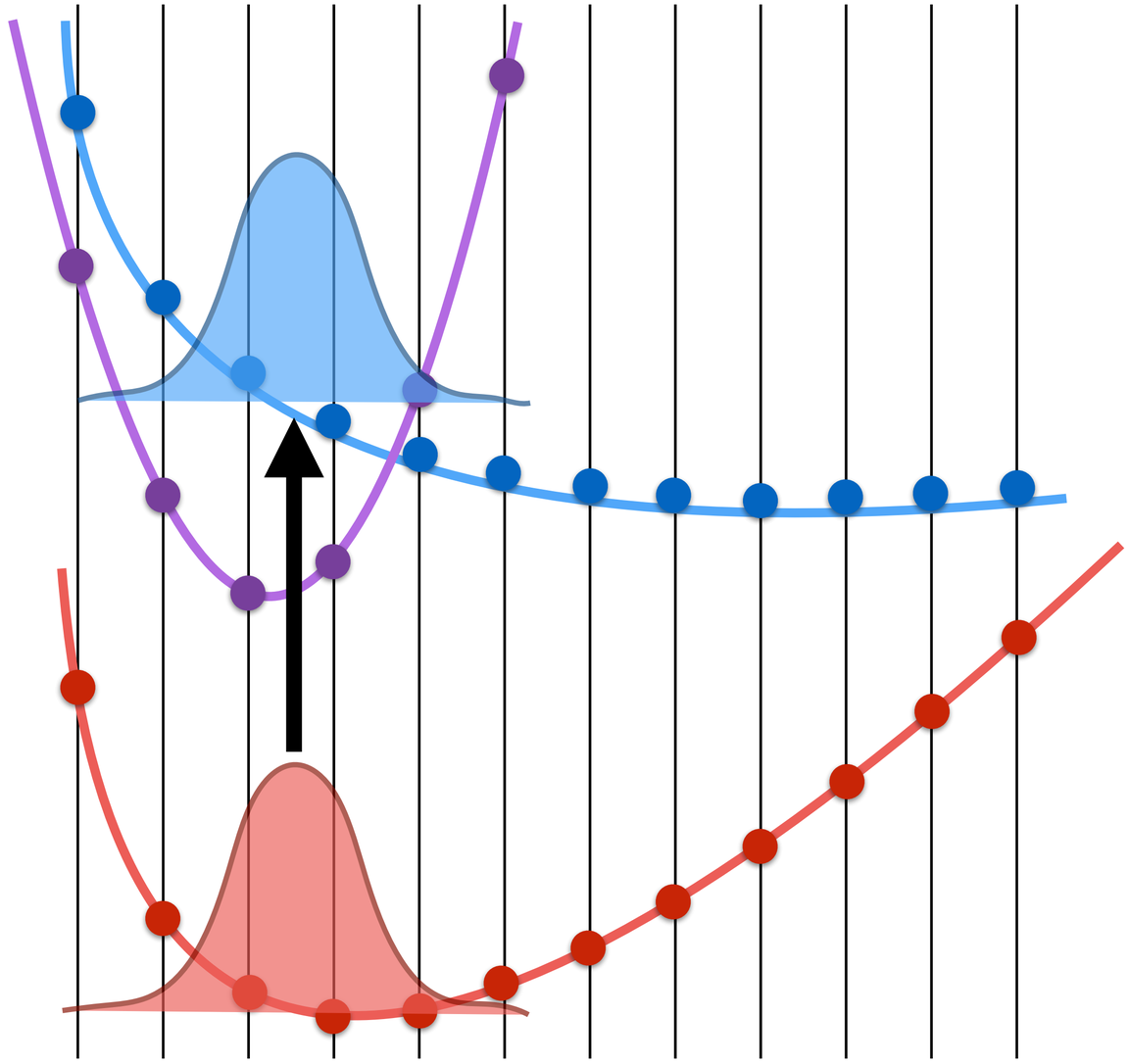


Separated approach

Step through configuration space

Compute potential energy surfaces

Propagate dynamics along potential energy surfaces



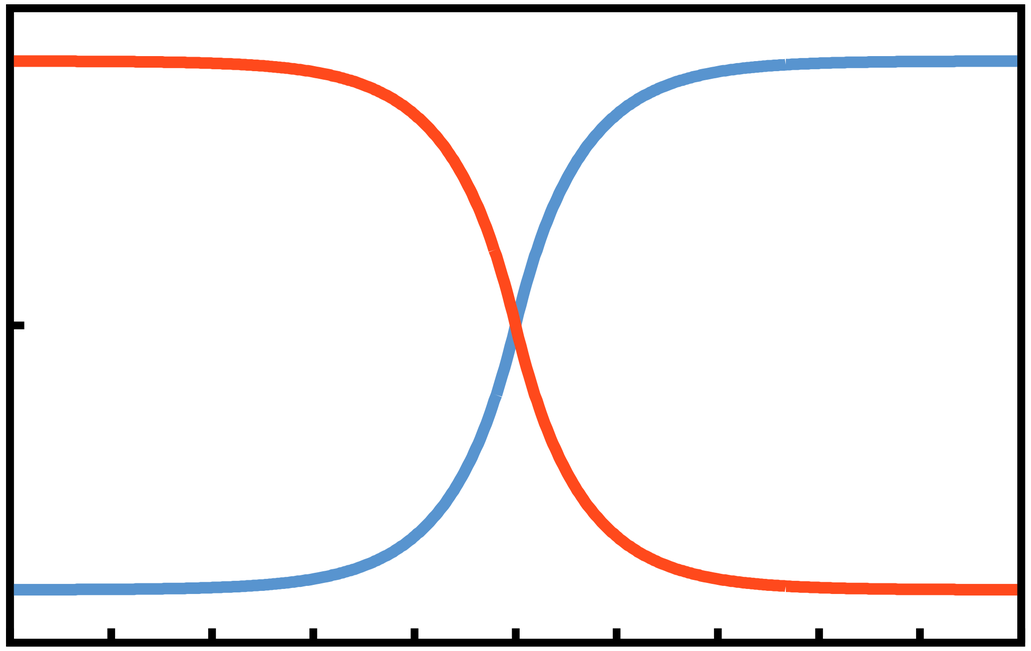
Model quantum dynamics

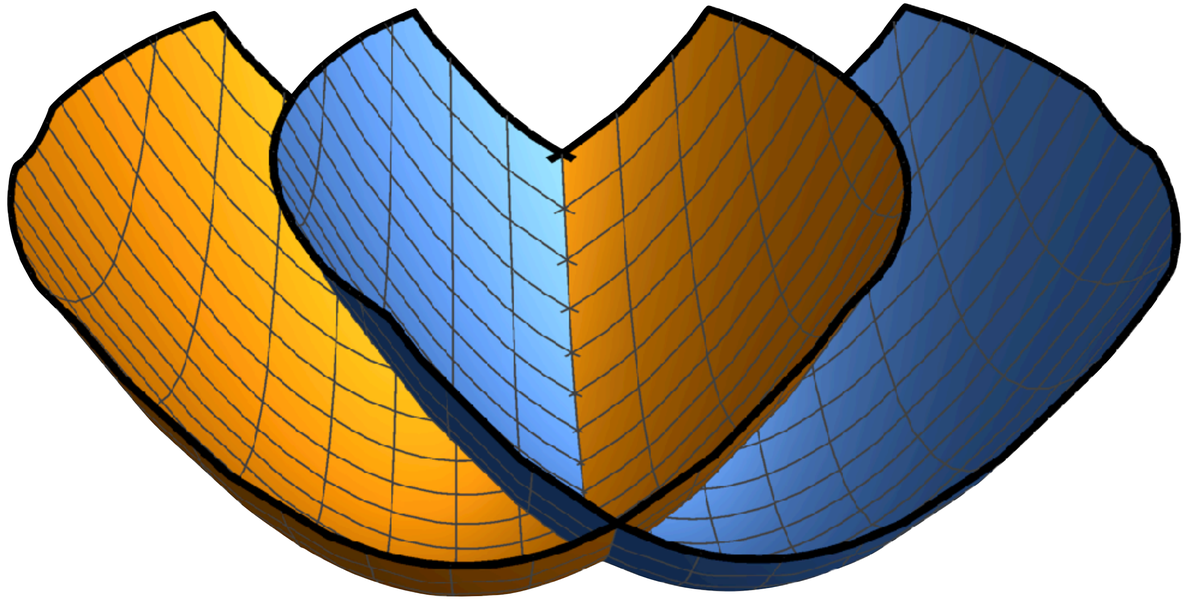
Born-Oppenheimer expansion

Mixed quantum classical

Simplest possible models

Numerical playground: 1D/2D quantum dynamics

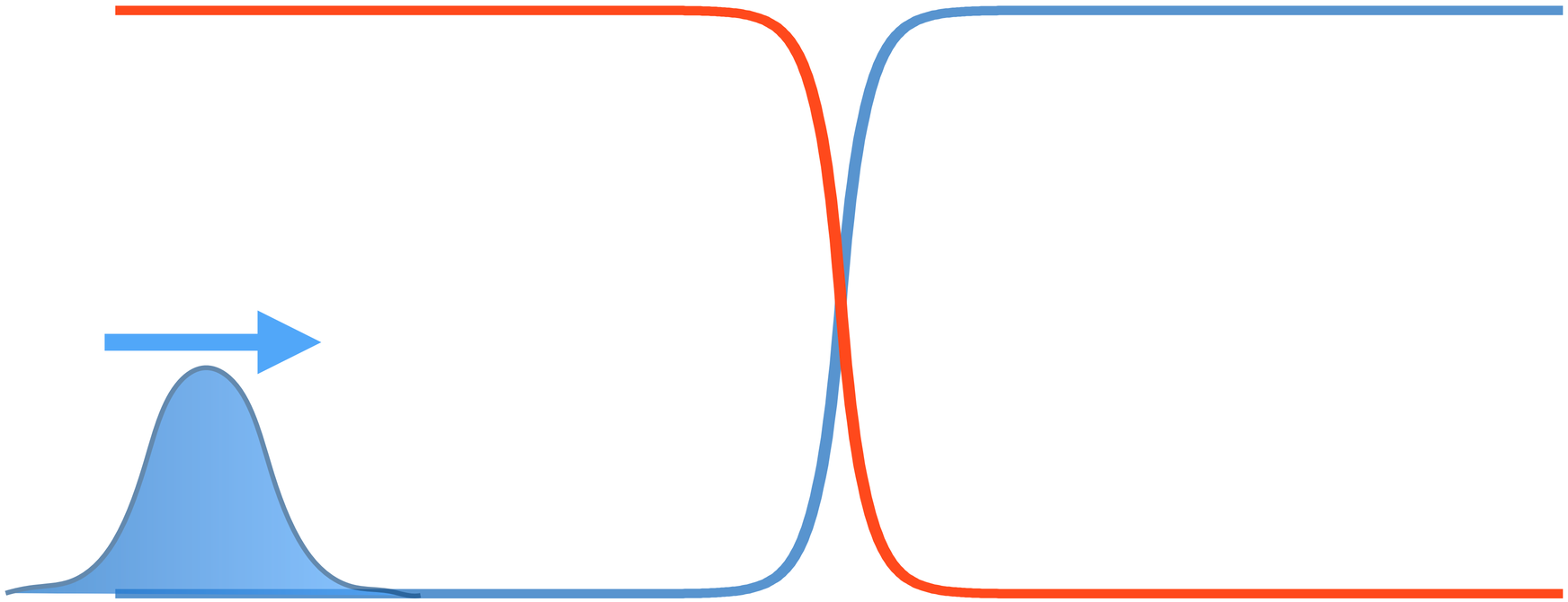




https://www.github.com/smparker/telluride

Wavepacket dynamics

Prepare a wavepacket and propagate



The quantum propagator $|\Psi(t')\rangle = \hat{U}(t,t')|\Psi(t)\rangle$

Grid based propagator

For a time-independent Hamiltonian the propagator is

$$\hat{U}(t, t+\tau) = \mathrm{e}^{-i\hat{H}\tau}$$

Trotter decompose using: $\hat{H} = \hat{T} + \hat{V}$

$$\hat{U}(\tau) = \mathrm{e}^{-i\hat{V}\frac{\tau}{2}}\mathrm{e}^{-i\hat{T}\tau}\mathrm{e}^{-i\hat{V}\frac{\tau}{2}} + \mathcal{O}(\tau^3)$$

Fourier split-operator propagation

$$\hat{U}(\tau) \approx \mathrm{e}^{-i\hat{V}\frac{\tau}{2}}\,\mathrm{e}^{-i\hat{T}\tau}\,\mathrm{e}^{-i\hat{V}\frac{\tau}{2}}$$

$[\mathrm{FFT}]^{-1}$ $[\mathrm{FFT}]$

$[\mathrm{FFT}]$

$\mathcal{O}(n \log n)$

$e^{\alpha \mathbf{T}(k)}|\Psi(k)\rangle$

Local in k-space

$e^{\alpha \mathbf{V}(x)}|\Psi(x)\rangle$

Local in real space

Python split-operator: one-state 1D

For a time-independent Hamiltonian the propagator is

$$e^{\alpha \mathbf{V}(x)}|\Psi(x)\rangle \longrightarrow e^{\alpha V(x)}|\Psi(x)\rangle$$

$V_i = V(x_i)$ →

$T_i = T(p_i)$ →

$\exp(-\mathrm{i}V_i\tau/2)$ →

$\exp(-\mathrm{i}T_i\tau)$ →

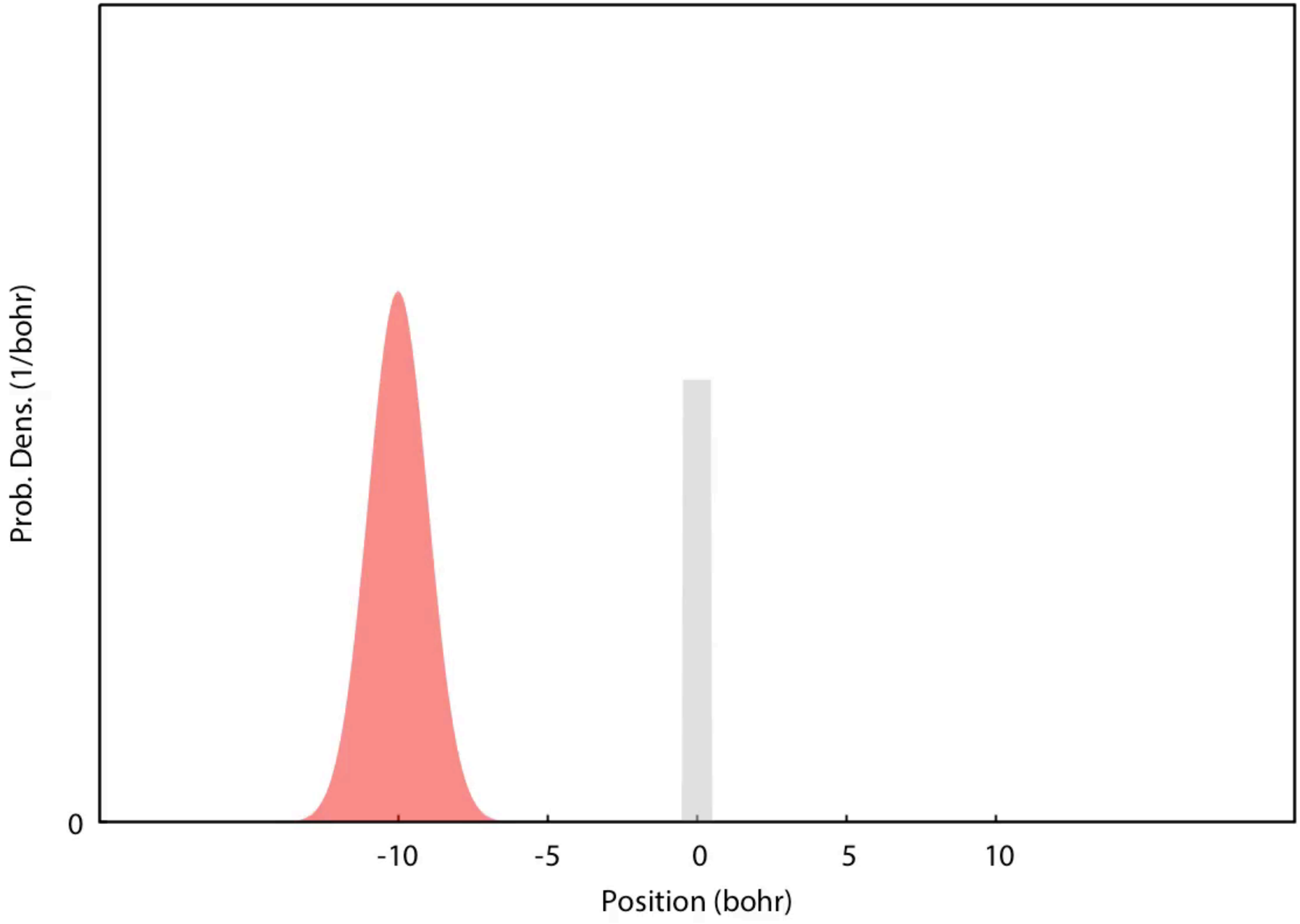
$|\Psi(t=0)\rangle$ →

$\hat{U}(\tau)$ {

```
potential = v(xx)
cpotential = -1j * absorber(xx, absorberleft, absorberright, absorberwidth)
kinetic = 0.5*p*p/mass

prop_v = np.exp(-1j * (potential + cpotential) * dt * 0.5)
prop_t = np.exp(-1j * kinetic * dt)

psi = psi0(xx)

for i in range(nsteps):
    psi *= prop_v
    psi = np.fft.fft(psi)
    psi *= prop_t
    psi = np.fft.ifft(psi)
    psi *= prop_v
```

Ex: /<telluride>/squarewell/squarewell.py

Python split-operator: square-well



Python split-operator: multi-state 1D

$$e^{\alpha \mathbf{V}(x)}|\Psi(x)\rangle \longrightarrow \mathbf{U}(x)|\Psi(x)\rangle$$

Eigendecompose

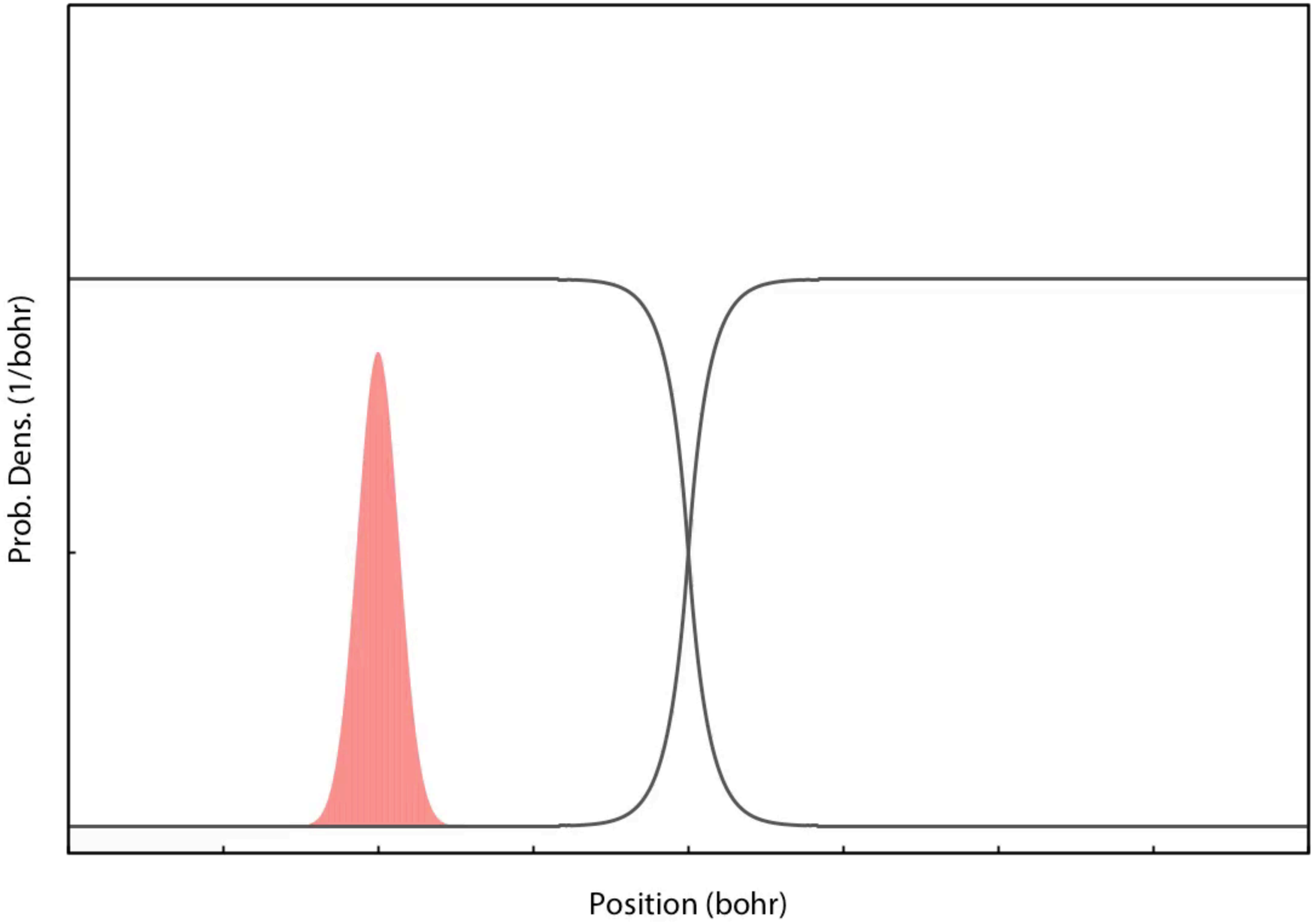
$$\mathbf{C}^\dagger \mathbf{V}(x)\mathbf{C} = \begin{pmatrix} v_0(x) & & \\ & \ddots & \end{pmatrix} \longrightarrow \mathbf{V}(x) = \mathbf{C}\begin{pmatrix} v_0(x) & & \\ & \ddots & \end{pmatrix}\mathbf{C}^\dagger$$

$$\mathbf{V}^2(x) = \mathbf{C}\begin{pmatrix} v_0(x) & & \\ & \ddots & \end{pmatrix}\mathbf{C}^\dagger\mathbf{C}\begin{pmatrix} v_0(x) & & \\ & \ddots & \end{pmatrix}\mathbf{C}^\dagger = \mathbf{C}\begin{pmatrix} v_0^2(x) & & \\ & \ddots & \end{pmatrix}\mathbf{C}^\dagger$$

$$e^{\alpha \mathbf{V}(x)} = \mathbf{C}\begin{pmatrix} e^{\alpha v_0(x)} & & \\ & \ddots & \end{pmatrix}\mathbf{C}^\dagger$$

Ex: /<telluride>/avoidedcrossing/avoidedcrossing.py

Python split-operator: avoided crossing



Model quantum dynamics

Born-Oppenheimer expansion

Mixed quantum classical

Born-Huang expansion: two is better than one

The full quantum molecular Hamiltonian

$$\hat{H} = \hat{T}_N + \hat{V}_{NN} + \hat{V}_{eN} + \hat{T}_e + \hat{V}_{ee}$$

pure nuclear **electron-nuclear attraction** **pure electronic**

is usually avoided by separating energy scales

$$\hat{H}^R = V^R_{NN} + \hat{h}^R + \hat{V}_{ee}$$

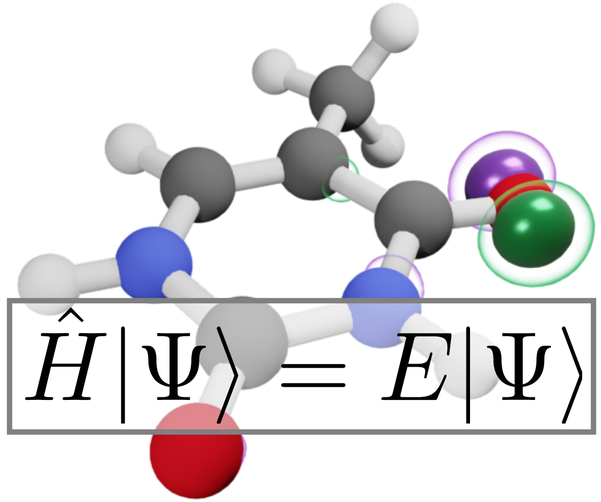
Electronic problem

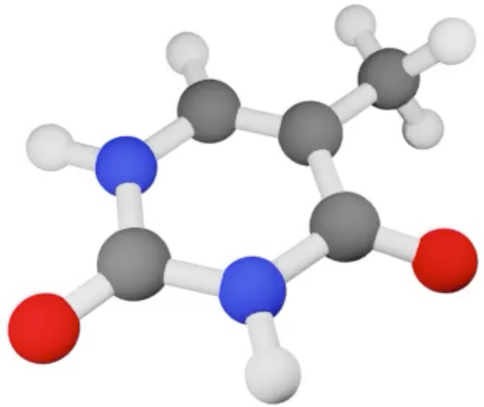
+

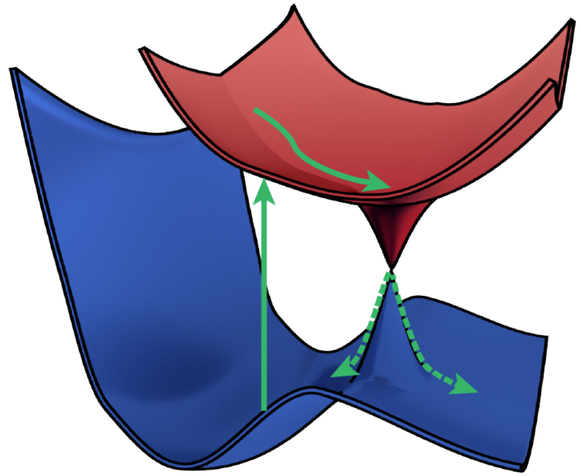
$$\hat{H} = \hat{T}_N + \hat{V}$$

Nuclear problem

Born-Oppenheimer approximation for rivers







Different problems with different solutions

Electronic problem defines a many-electron basis

$$\hat{H}^R|\Phi_n(R)\rangle = E_n(R)|\Phi_n(R)\rangle$$

$$\hat{H}^R = V_{NN}^R + \hat{h}^R + \hat{V}_{ee}$$

Electronic problem

+

Nuclear problem is then solved within this basis

$$|\Psi\rangle = \sum_n \int \mathrm{d}R\; C_n(R)|\Phi_n(R)\rangle$$

$$\hat{H} = \hat{T}_N + \hat{V}$$

Quantum dynamics

Separation anxiety

BO expansion amounts to a unitary transformation

$$\hat{U}^\dagger \hat{H} \hat{U} = \hat{U}^\dagger \hat{T}_N \hat{U} + \hat{U}^\dagger \hat{V} \hat{U} = \hat{T}_{\mathrm{ad}} + \hat{V}_{\mathrm{ad}}$$

Potential energy becomes diagonal

$$\hat{V}_{\mathrm{ad}} = \sum_n |\Phi_n(R)\rangle E_n(R) \langle \Phi_n(R)| \Rightarrow \begin{pmatrix} E_0(R) & & \\ & E_1(R) & \\ & & \ddots \end{pmatrix}$$

but nuclear kinetic becomes dense

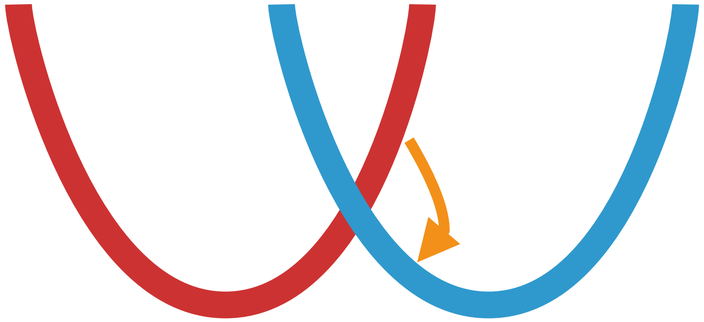
$$\hat{T}_{\mathrm{ad}} = -\sum_A \frac{1}{2m_A} \left[\hat{U}^\dagger (\nabla^2_{R_A} \hat{U}) + 2\hat{U}^\dagger \nabla_{R_A} \hat{U} \nabla_{R_A} + \hat{U}^\dagger \hat{U} \nabla^2_{R_A} \right]$$

$$\hat{T}_{(0)} + \sum_A \hat{D}_{R_A} \nabla_{R_A} + \hat{T}_{N,ad}$$

Contrasting representations

Diabatic picture

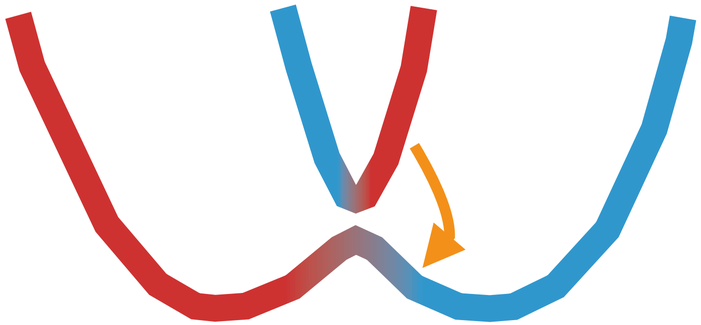
- consistent state characteristics
- coupling due to electronic Hamiltonian
- may not exist for finite number of states
- nonunique



$$\mathbf{H} = \begin{pmatrix} T_1^{\mathrm{d}} & 0 \\ 0 & T_2^{\mathrm{d}} \end{pmatrix} + \begin{pmatrix} E_1^{\mathrm{d}}(R) & V(R) \\ V(R) & E_2^{\mathrm{d}}(R) \end{pmatrix}$$

Adiabatic picture

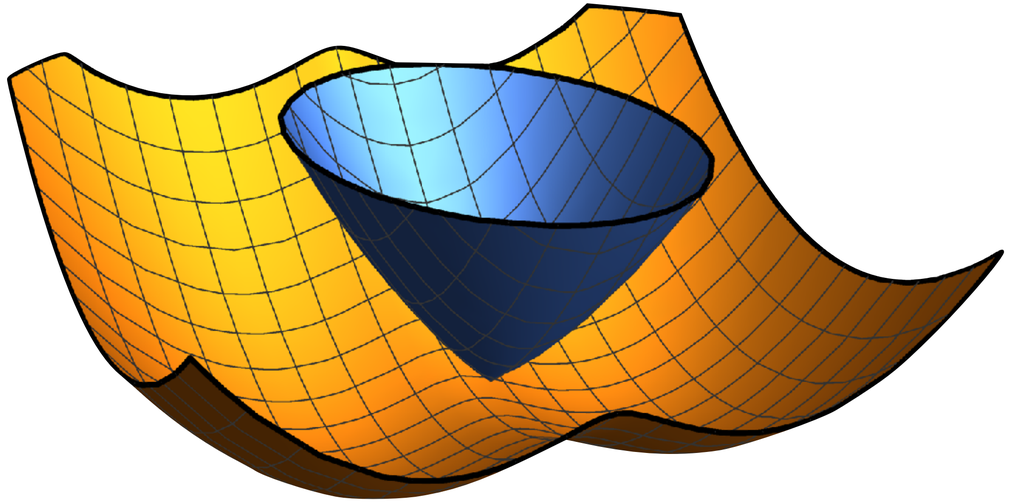
- rapid changes in state character
- coupling due to nuclear momentum
- Berry phase
- can be unique



$$\mathbf{H} = \begin{pmatrix} T_1^{\mathrm{ad}}(R) & T_{12}^{\mathrm{ad}}(R) \\ T_{21}^{\mathrm{ad}}(R) & T_2^{\mathrm{ad}}(R) \end{pmatrix} + \begin{pmatrix} E_1^{\mathrm{ad}}(R) & 0 \\ 0 & E_2^{\mathrm{ad}}(R) \end{pmatrix}$$

Dynamics largely determined by state crossings

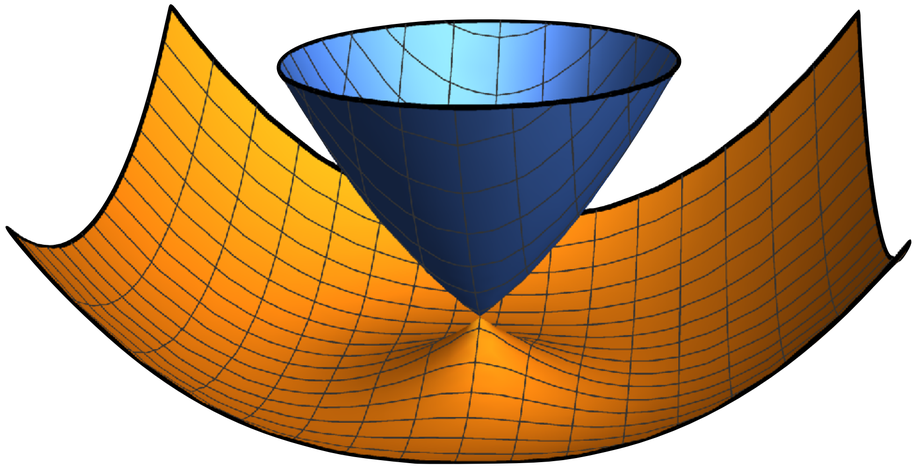
Primary features on potential energy surfaces



glancing intersection

or

avoided crossing



conical intersection

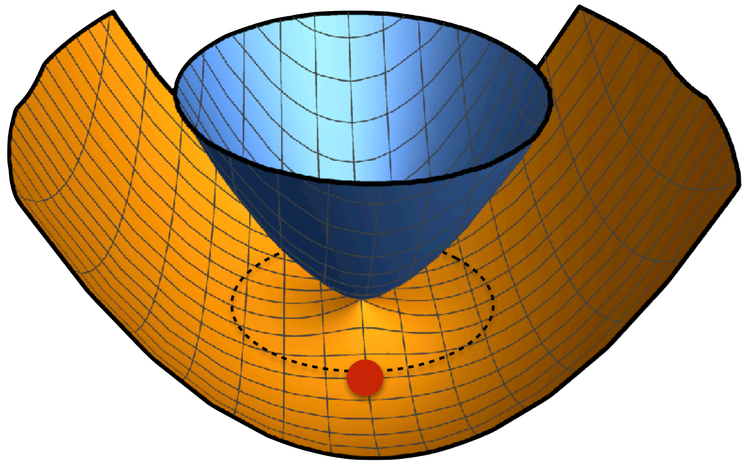
N-2 dimensional seam

Berry phase and geometric phase

Peculiar feature of conical intersections

$$\oint_C \langle \Phi_0 | \vec{\nabla} \Phi_1 \rangle \cdot d\vec{S} = \pi$$

$|\Phi_0\rangle$  $-|\Phi_0\rangle$



Electronic and nuclear wavefunctions must have a cut

or

A gauge-transformation can restore single-valued-ness

$$|\Psi(R)\rangle \rightarrow e^{if(R)}|\Psi(R)\rangle$$

Herzberg, G.; Longuet-Higgins, H. C. *Discuss. Faraday Soc.* **1963**, *35*, 77–82.

Mead, C. A.; Truhlar, D. G. *J. Chem. Phys.* **1979**, *70* (5), 2284–2296.

Berry, M. V. *Proc. Roy. Soc. A* **1984**, *392* (1802), 45–57.

X

Model quantum dynamics

Born-Oppenheimer expansion

Mixed quantum classical

Many dimensional quantum dynamics are unaffordable

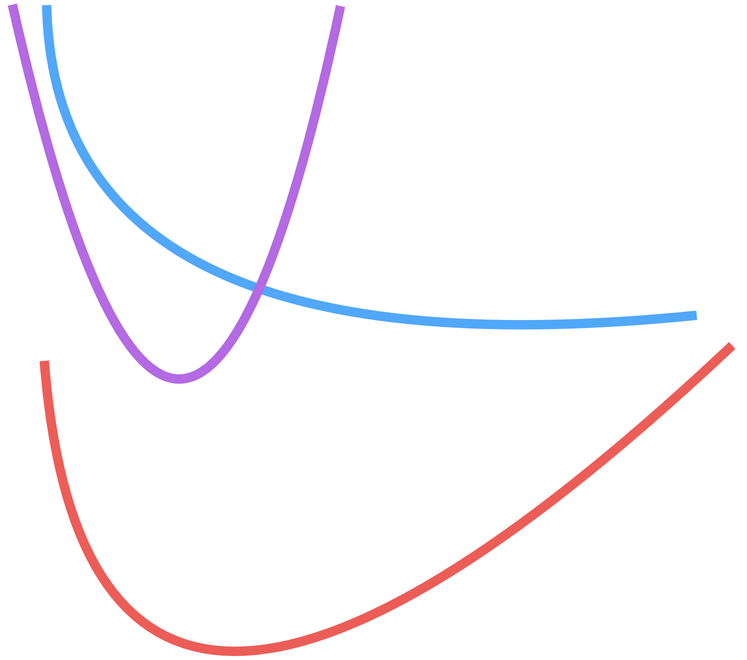
Consider methane: 5 atoms, 9D, 32 points per dimension

	Wfn	Hamiltonian	Storage	CPU
Naïve	Real space grid	Pre-computed	N^f (9D: ~ 1PB)	$N^f \log(N^f)$ (9D: 4 mo/step)
MCTDH	LC of Hartree products	Pre-computed sum of products	n^f (9D: 7 GB)	$n^f \log(n^f)$ (9D: 1 wk/step)
Semiclassical	Quantum-classical	Any	N (9D: negligible)	N (9D: gradient)

Mixed Quantum-Classical: Quantum electrons, classical nuclei

Classical nuclei + electronic wavefunction

$$|\Psi(t)\rangle \longrightarrow (R, P) \otimes |\Phi(t; R(t))\rangle$$



Electronic basis depends parametrically on the nuclei

$$|\Phi(t; R(t))\rangle = \sum_n C_n(t) |\Phi_n^{R(t)}\rangle$$

Goal: Propagate such that information flows

$$(R, P) \longleftrightarrow |\Phi(t)\rangle$$

https://www.github.com/smparker/mudslide

Propagate TDSE

$$\mathrm{i}|\dot{\Phi}(t;R(t))\rangle = \mathbf{H}(R)|\Phi(t;R(t))\rangle$$

Expand

$$\mathrm{i}\sum_k \dot{C}_k(t)|\Phi_k^{R(t)}\rangle + \mathrm{i}\sum_k C_k(t)|\dot{\Phi}_k^{R(t)}\rangle = \mathbf{H}(R)|\Phi(t;R(t))\rangle$$

Inner product with $\langle\Phi_n^{R(t)}|$

$$\mathrm{i}\dot{C}_n(t) + \mathrm{i}\sum_k C_k(t)\langle\Phi_n^{R(t)}|\dot{\Phi}_k^{R(t)}\rangle = \langle\Phi_n^{R(t)}|\mathbf{H}(R)|\Phi(t;R(t))\rangle$$

Chain rule

$$W_{nm} = \langle\Phi_n^{R(t)}|\dot{\Phi}_m^{R(t)}\rangle = \langle\Phi_n^{R(t)}|\frac{\mathrm{d}}{\mathrm{d}R}\Phi_m^{R(t)}\rangle\cdot\dot{R}$$

Finally

$$\dot{\mathbf{C}}(t) = -\mathrm{i}\left(\mathbf{H} - \mathrm{i}\mathbf{W}\right)\mathbf{C}(t)$$

Nonadiabatic coupling

$$\dot{\mathbf{C}}(t) = -\mathrm{i}\,(\mathbf{H} - \mathrm{i}\mathbf{W})\,\mathbf{C}(t)$$

Need $d_R^{nm} = \langle \Phi_n | \nabla_R \Phi_m \rangle$

Eigenvalue equation

$$\mathbf{H}|\Phi_m\rangle = E_m|\Phi_m\rangle$$

Differentiate

$$(\nabla\mathbf{H})|\Phi_m\rangle + \mathbf{H}|\nabla\Phi_m\rangle = E_m|\nabla\Phi_m\rangle$$

Inner product $\langle \Phi_n |$

$$\langle\Phi_n|(\nabla\mathbf{H})|\Phi_m\rangle + E_n\langle\Phi_n|\nabla\Phi_m\rangle = E_m\langle\Phi_n|\nabla\Phi_m\rangle$$

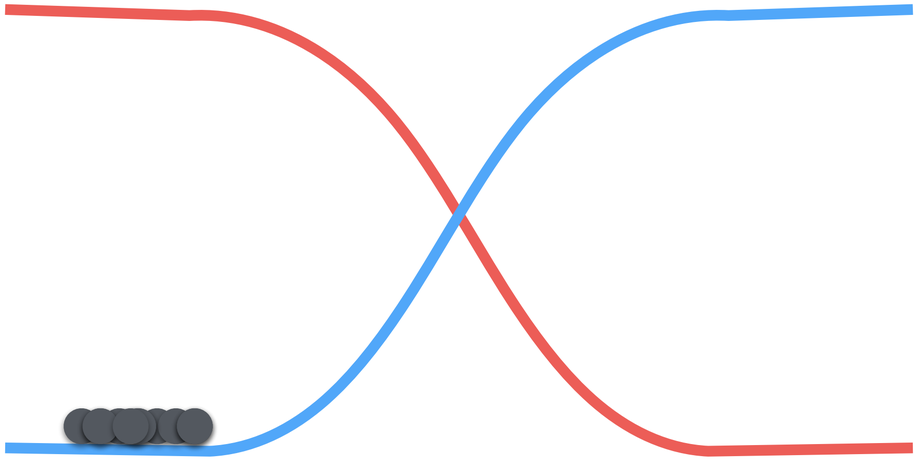
Gives

$$d^{nm} = \langle\Phi_n|\nabla\Phi_m\rangle = \frac{\langle\Phi_n|(\nabla\mathbf{H})|\Phi_m\rangle}{E_m - E_n}$$

Swarms

Classical descriptions of quantum processes are inescapably probabilistic

?



Envision a swarm sampled from Wigner distribution

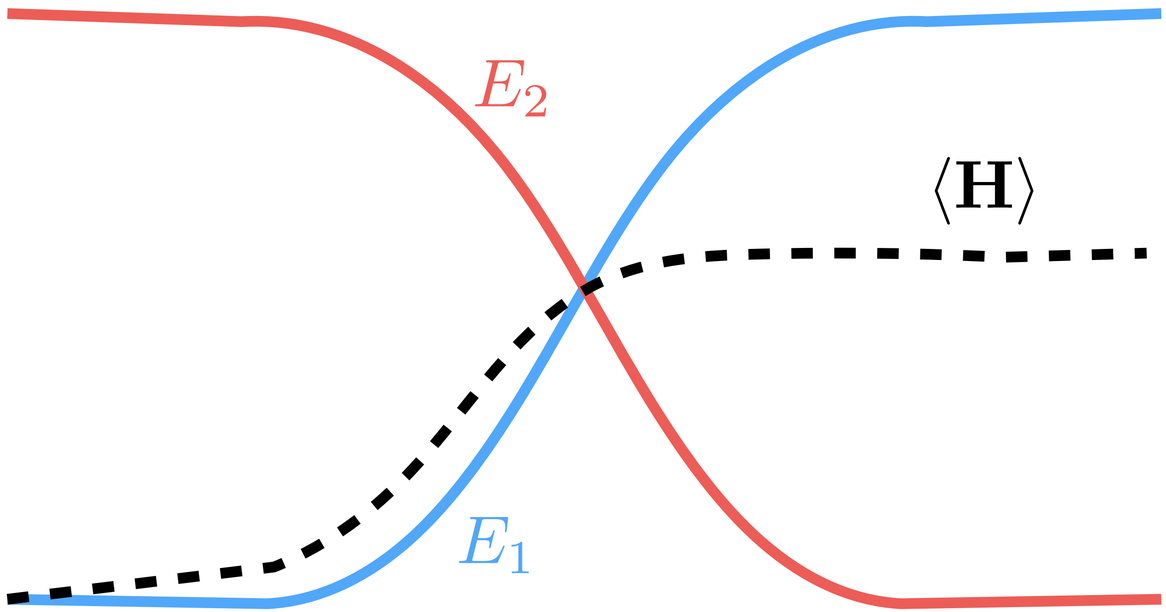
$$P(x,p) = \frac{1}{\pi\hbar}\int_{-\infty}^{\infty} \mathrm{d}y \psi^*(x+y)\psi(x-y)\mathrm{e}^{\mathrm{i}2py/\hbar}$$

Tully, J. C. *JCP.* **1990**, *93* (2), 1061.

Ehrenfest dynamics

Nuclear forces given by weighted average

$$\vec{F}(t) = -\nabla(\mathbf{C}^\dagger \mathbf{H} \mathbf{C}) = -\nabla\langle \mathbf{H} \rangle$$



Ehrenfest analysis

The good:

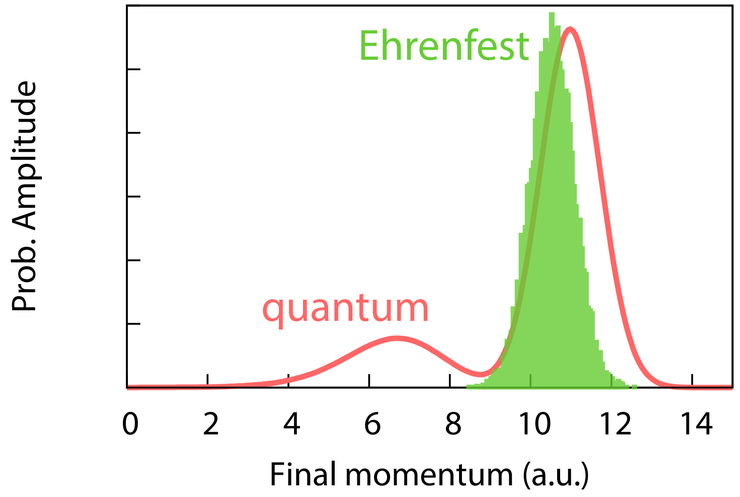
Representation independent

Accurate at short times

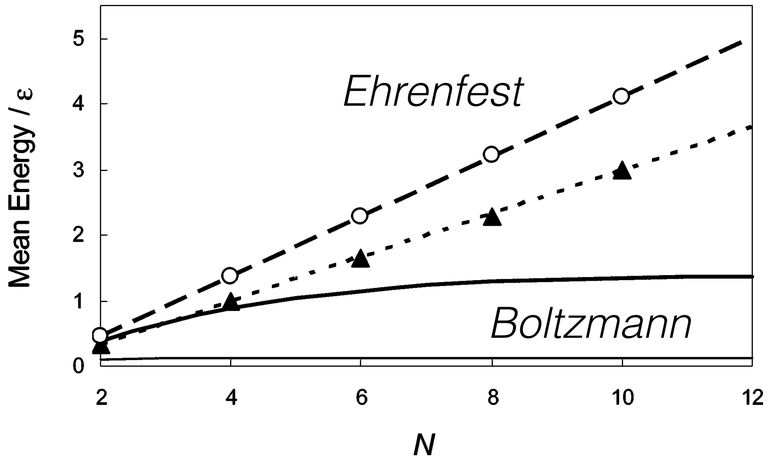
Inexpensive

The bad:

No bifurcation



Violates detailed balance

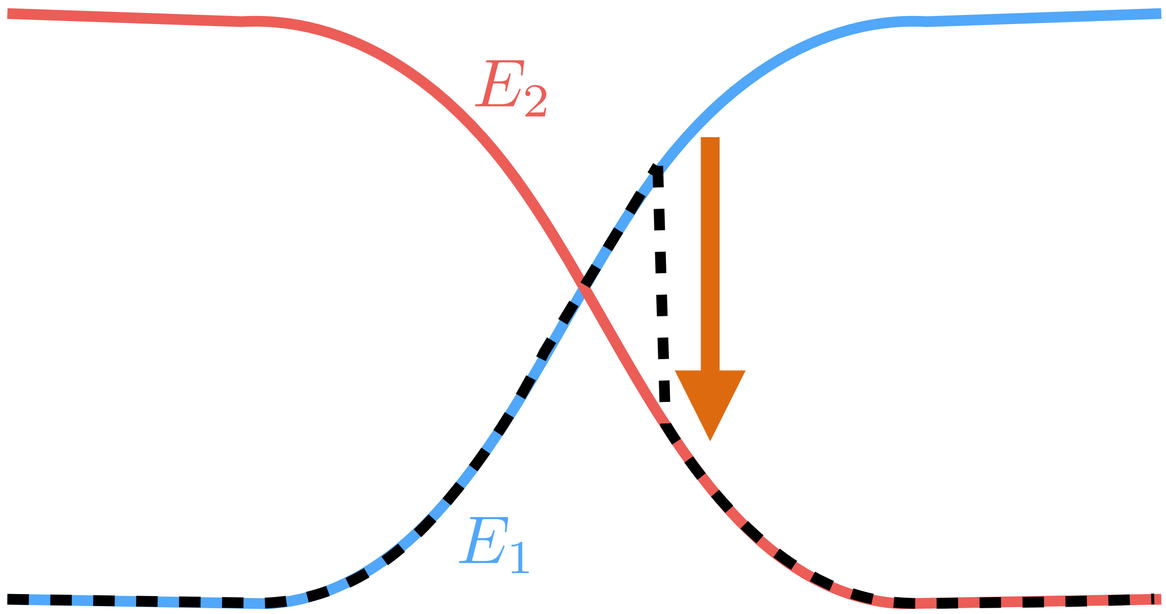


Parandekar, P. V.; Tully, J. C. *JCTC.* **2006**, *2* (2), 229–235.

Fewest Switches Surface Hopping (FSSH)

Nuclear forces always come from a *single* PES

$$\vec{F}(t) = -\nabla H_{i(t)i(t)}$$



Tully, J. C. *JCP.* **1990**, *93* (2), 1061.

Hopping

"Active" wavefunction

$$C_n^{\text{active}}(t) = \delta_{nk(t)}$$

Auxiliary wavefunction

$$\mathbf{C}(t) \longrightarrow k(t)$$

Tully: *Stochastically hop the minimum number so that*

$$|C_n(t)|^2 \longleftrightarrow \langle |C_n^{\text{active}}(t)|^2 \rangle_{\text{swarm}}$$

Instantaneous hopping probability (this should actually be scaled to make it a Poisson prob.)

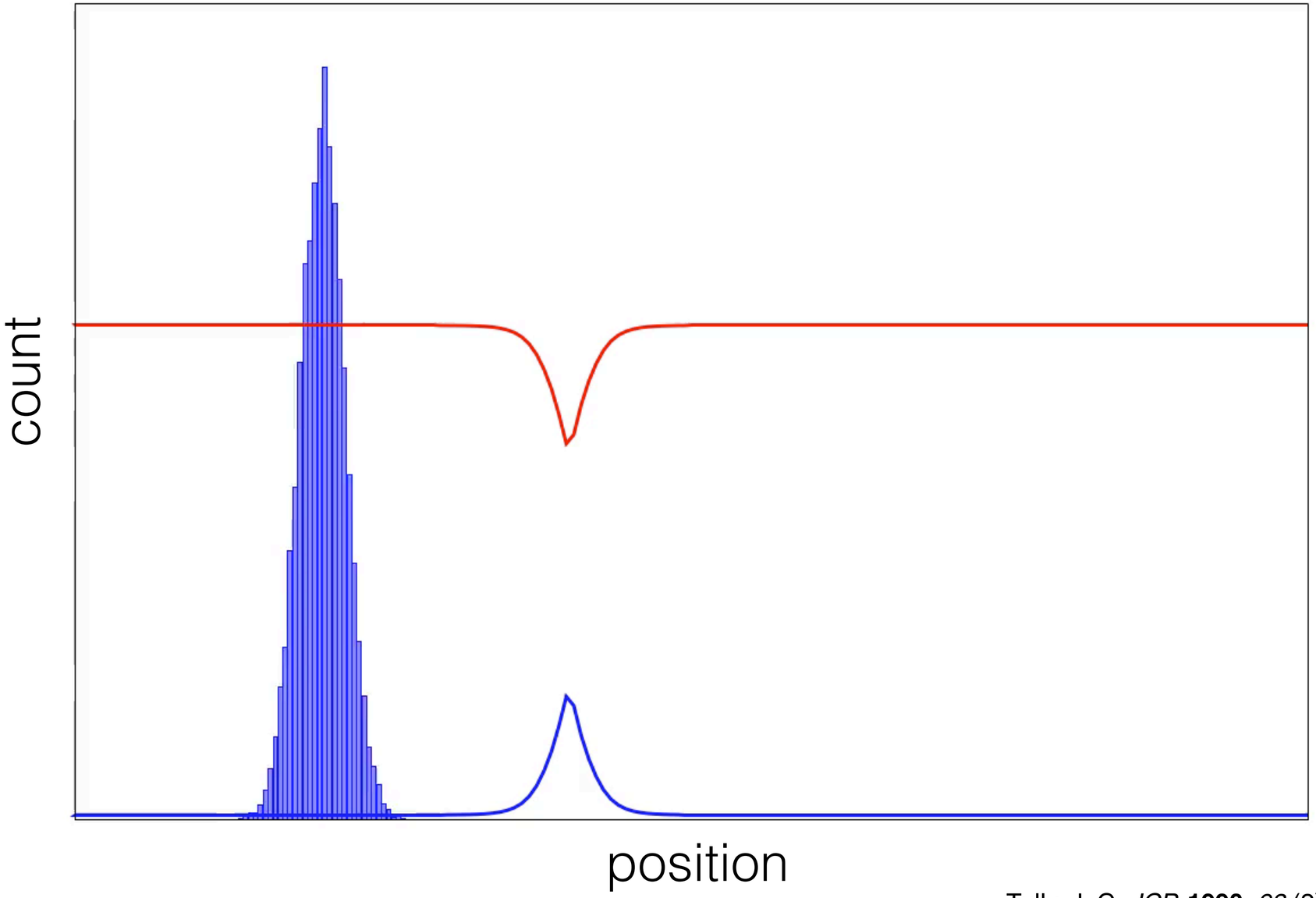
$$g_{kl}(t) = 2\text{Im}\left[\frac{C_k^*(t)(H - \text{i}W)_{lk}C_l(t)}{|C_k(t)|^2}\right]$$

Rescale momenta upon hops to conserve energy

Tully, J. C. *JCP.* **1990**, *93* (2), 1061.

Parker, S. M.; Schiltz, C. J. *JCP.* **2020**, *153* (17), 174109. https://doi.org/10.1063/5.0024372.

Swarm in action

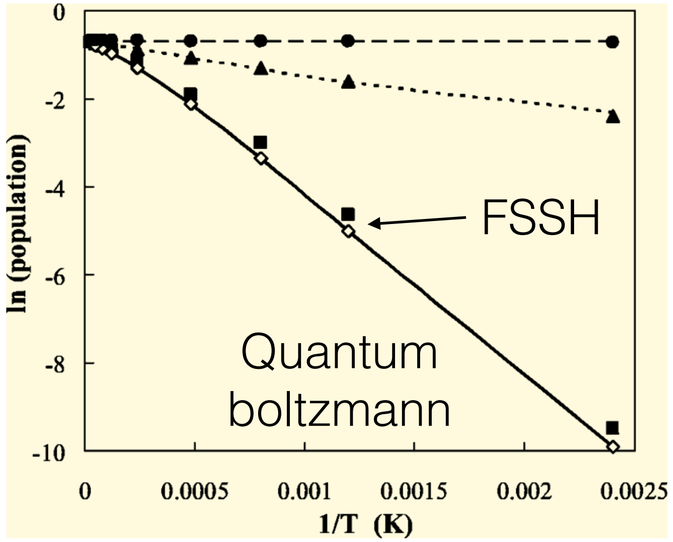


Tully, J. C. *JCP.* **1990**, *93* (2), 1061.

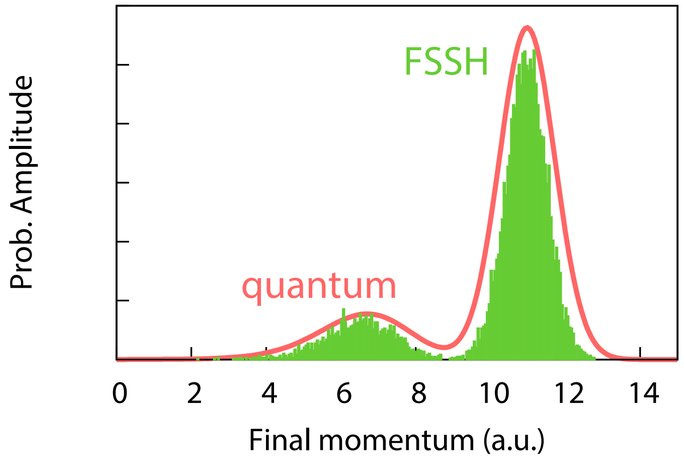
FSSH analysis

Improvements:

~ satisfies detailed balance

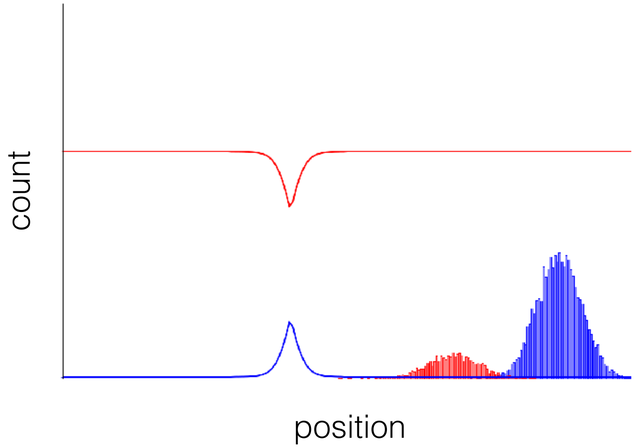


Allows bifurcation



The bad:

Inconsistent ‘coherence’



No first-principles derivation

Representation dependent
(and a lot of analysis only uses adiabatic or vice-versa)

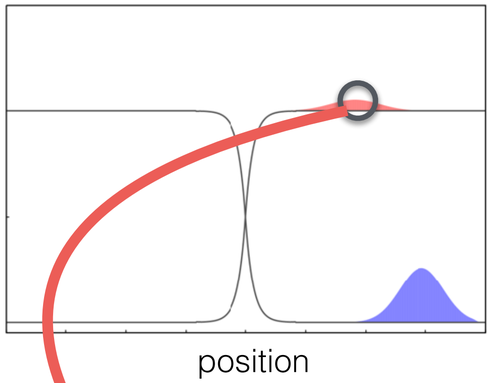
Parandekar, P. V.; Tully, J. C. JCTC. 2006, 2, 229–235.

Coherence in surface hopping

Electronic reduced density matrix

$$\hat{\rho}^e = \mathrm{tr}_{\mathrm{nuc}}\left(|\Psi\rangle\langle\Psi|\right) \quad \longleftrightarrow \quad \rho^e_{nm} = \int \mathrm{d}R \Psi^*_n(R)\Psi_m(R)$$

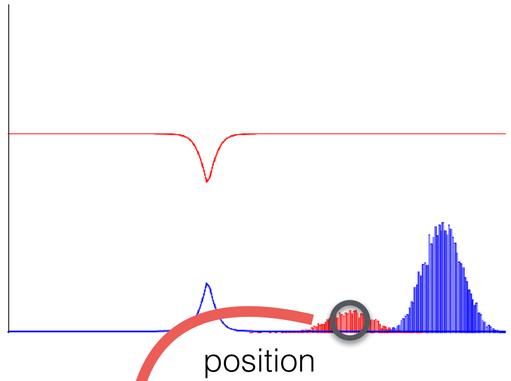
quantum



$$|\Psi(R)\rangle = \begin{pmatrix} 0 \\ \alpha \end{pmatrix}$$

$$\boldsymbol{\rho}^e = \begin{pmatrix} \rho^e_{11} & 0 \\ 0 & \rho^e_{22} \end{pmatrix}$$

FSSH

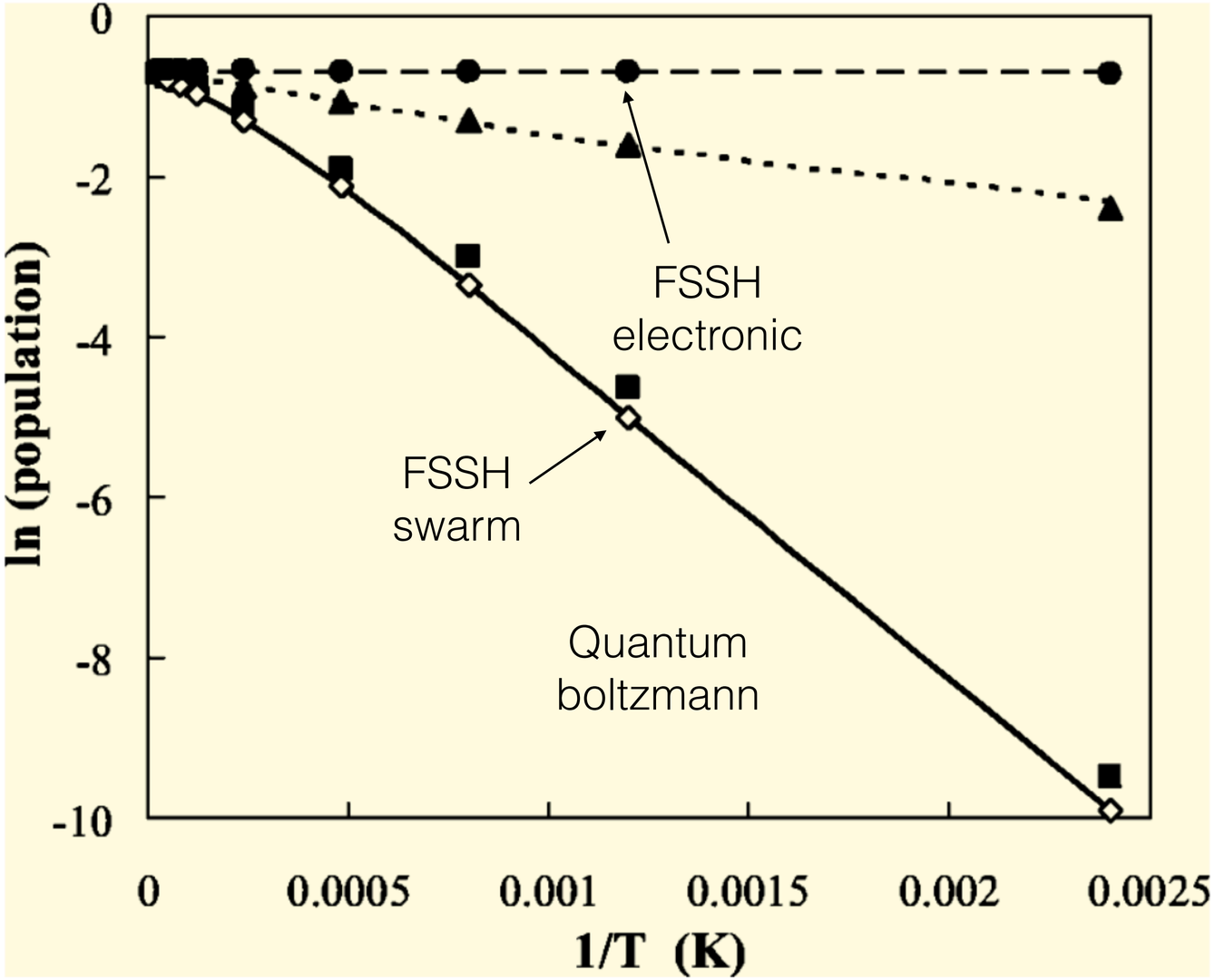


$$\mathbf{C}^{\mathrm{active}} = \begin{pmatrix} 0 \\ \alpha \end{pmatrix}$$

$$\mathbf{C} = \begin{pmatrix} \beta \\ \alpha \end{pmatrix}$$

Different interpretations for different “wavefunctions"

Populations are contradictory



Remember, FSSH hops chosen so that

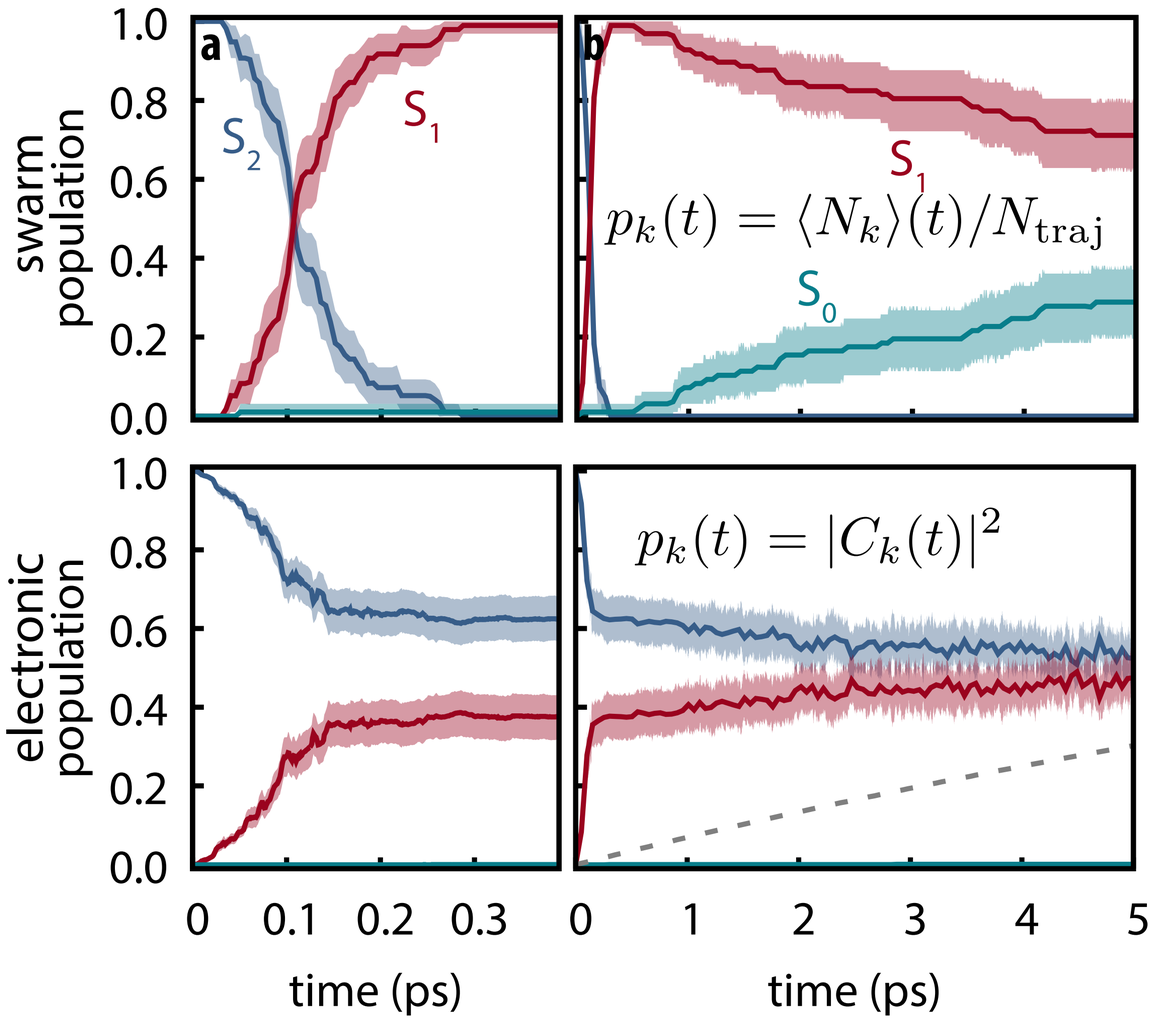
$$\langle \frac{N_k}{N_{\text{total}}} \rangle_{\text{swarm}} \approx |C_k|^2$$

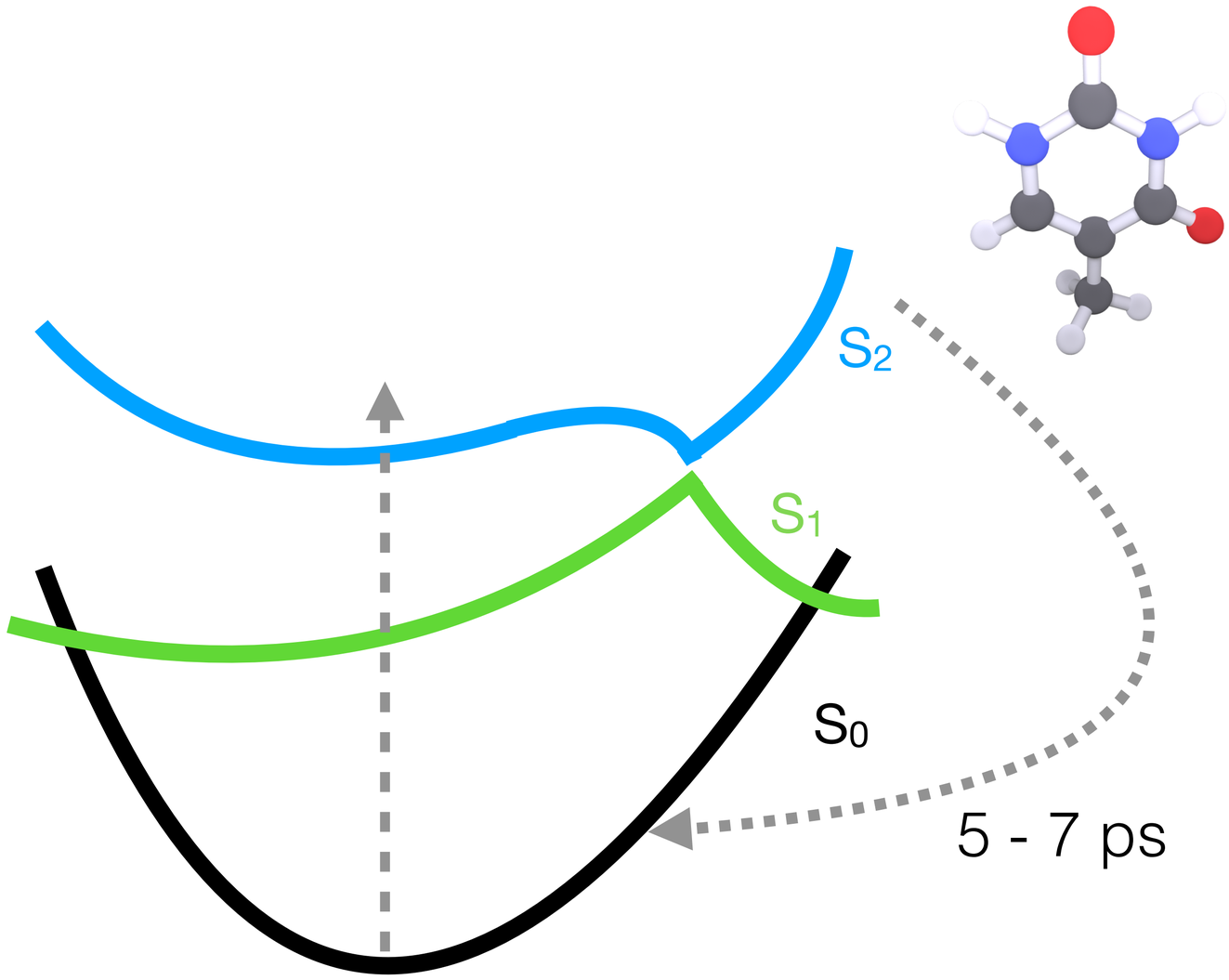
But this is not satisfied in equilibrium

Schmidt, J. R.; Parandekar, P. V.; Tully, J. C. *JCP.* **2008**, *129* (4), 044104. https://doi.org/10.1063/1.2955564.

Populations are contradictory: thymine

Thymine photodeactivation

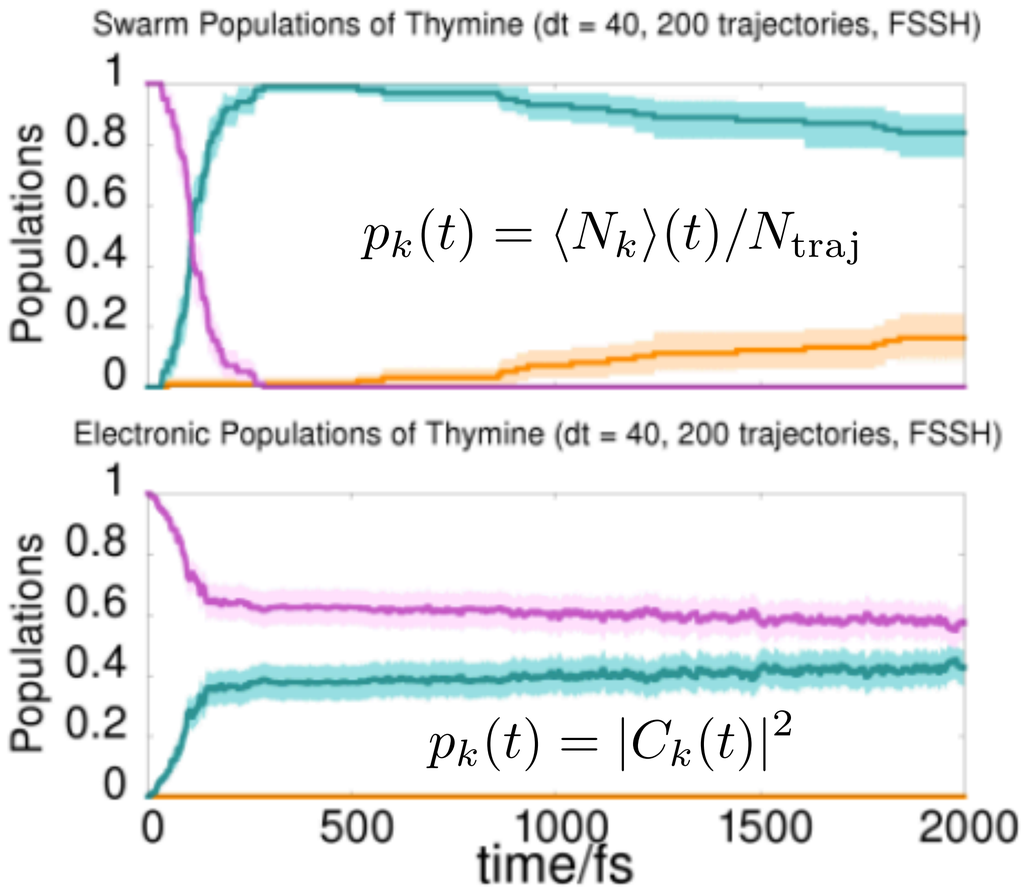




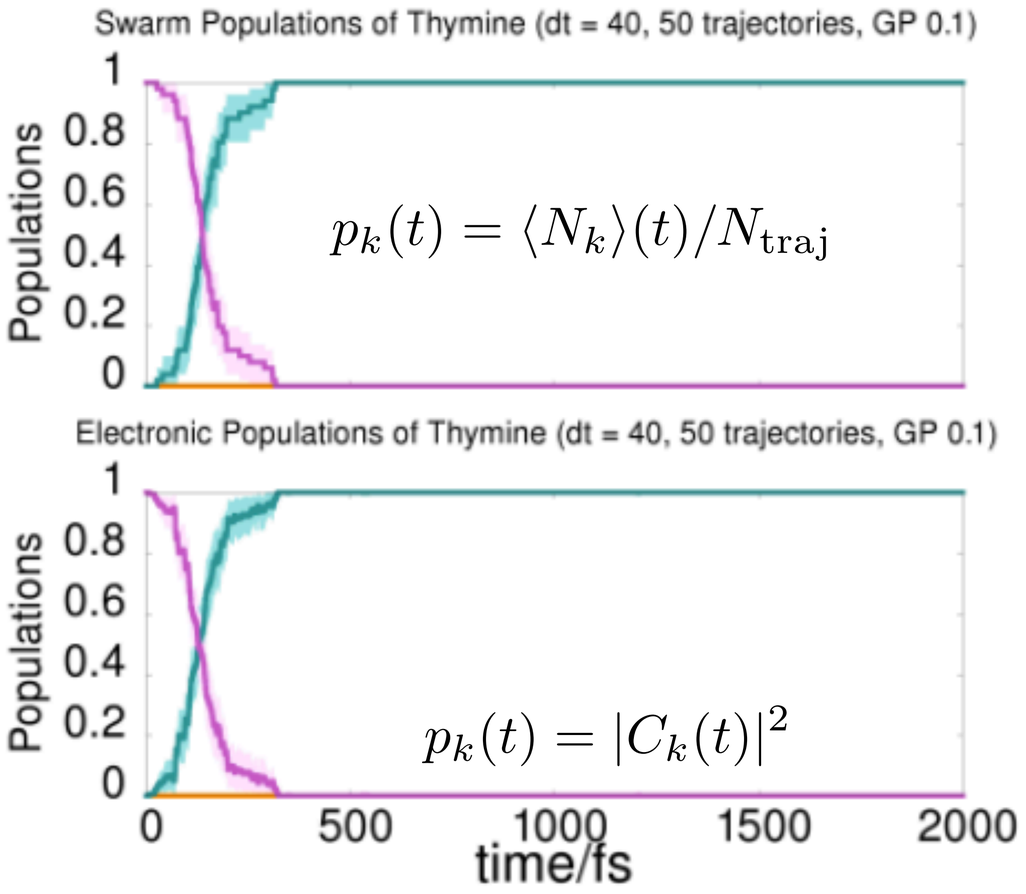
Parker, S. M.; Roy, S.; Furche, F. *PCCP.* **2019**, *21* (35), 18999–19010. https://doi.org/10.1039/C9CP03127H.

Populations are contradictory and maybe have to be?

FSSH



FSSH + decoherence corrections



Parker, S. M.; Roy, S.; Furche, F. *PCCP.* **2019**, *21* (35), 18999–19010. https://doi.org/10.1039/C9CP03127H.

(Some) related methods

Decoherence corrections

Augmented-FSSH	Subotnik, J. E.; Shenvi, N. *JCP* **2011**, *134* (2), 024105.
Continuous Surface Switching	Volobuev; Hack; Topaler; Truhlar JCP **2000**, *112* (22), 9716–9726.

“Frustrated” hops

Momentum reversal	Sifain, A. E.; Wang, L.; Prezhdo, O. V. *JCP* **2016**, *144* (21), 211102.
Time uncertainty	Jasper, A. W.; Stechmann, S. N.; Truhlar, D. G. *JCP* **2002**, *116* (13), 5424–5431.

Coupled trajectories

CT-MQC	Min, S. K.; Agostini, F.; Tavernelli, I.; Gross, E. K. U. *JPC Lett.* **2017**, 3048–3055.
Consensus surface hopping	Martens, C. C. *J. Phys. Chem. Lett.* **2016**, 2610–2615.

Alternate pictures

Global flux	Wang, L.; Trivedi, D.; Prezhdo, O. V. *JCTC* **2014**, *10* (9), 3598–3605.
Liouville space	Wang, L.; Sifain, A. E.; Prezhdo, O. V. *JPC Lett* **2015**, 3827–3833.

Intermediate Quantum/semiclassical

Multiple spawning	Martínez, T. J.; Ben-Nun, M.; Levine, R. D. *JPC* **1996**, *100* (19), 7884–7895.
Trajectory guided basis functions	Saller, M. A. C.; Habershon, S. *JCTC* **2015**, *11* (1), 8–16.

Key takeaways

- **Electrons and nuclei are strongly correlated** even within the Born-Oppenheimer approximation, but **move on different time scales**
- Photochemistry is all the things that happen when **both move rapidly**
- To get accurate rates and pathways, need to run dynamics
- **Quantum wavepackets split** when they encounter avoided crossings
- Mixed quantum-classical simulations are state-of-the-art for photochemistry
- FSSH is perhaps the most widely applied mixed quantum-classical method
- Seems to be an interplay between electron-nuclear coherence and quality of results
  - reminiscent of self-interaction errors in DFT?