Excited-state dynamics: Tully scheme implementation and models

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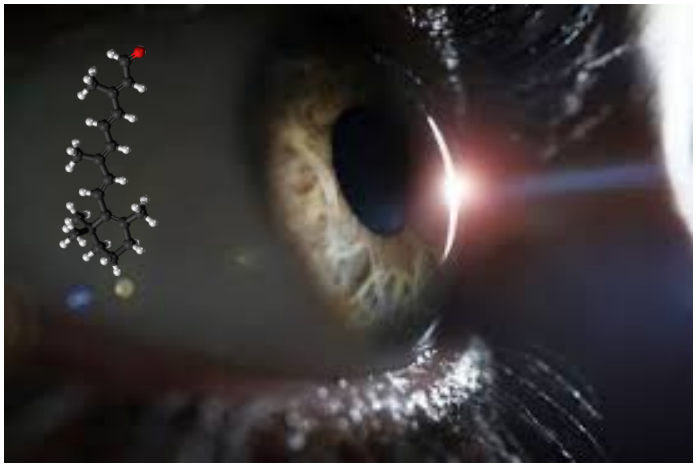
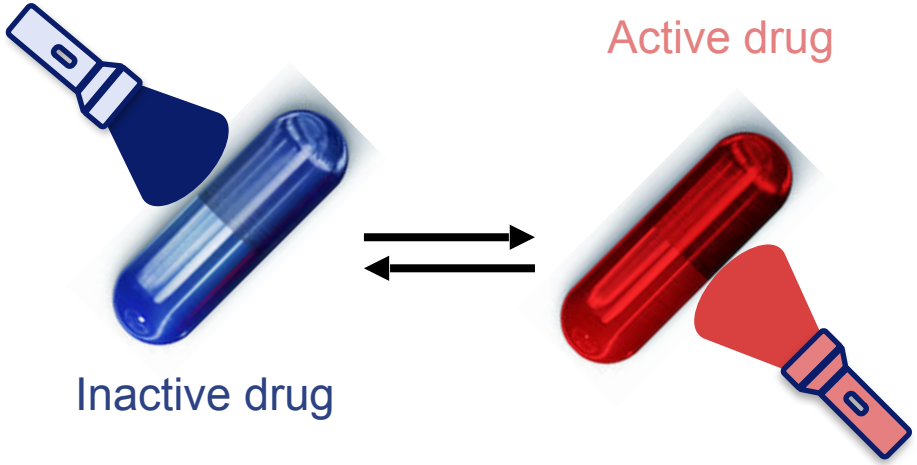
PYSURF

Photochemistry

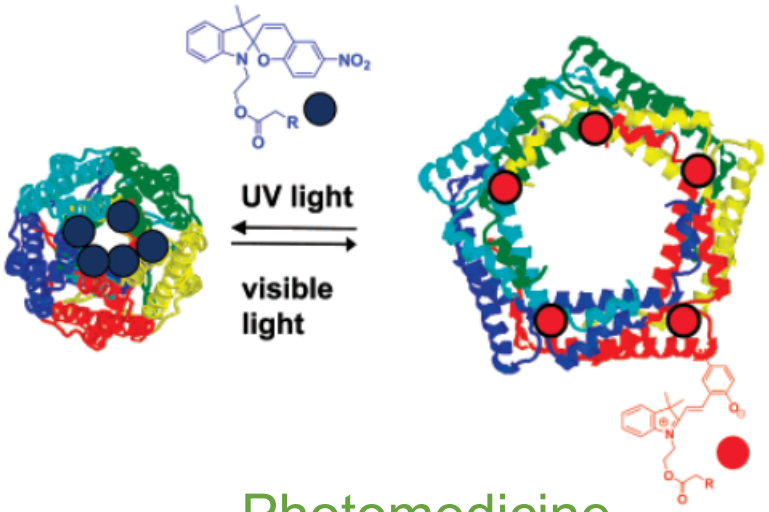


Vision



Photopharmacology

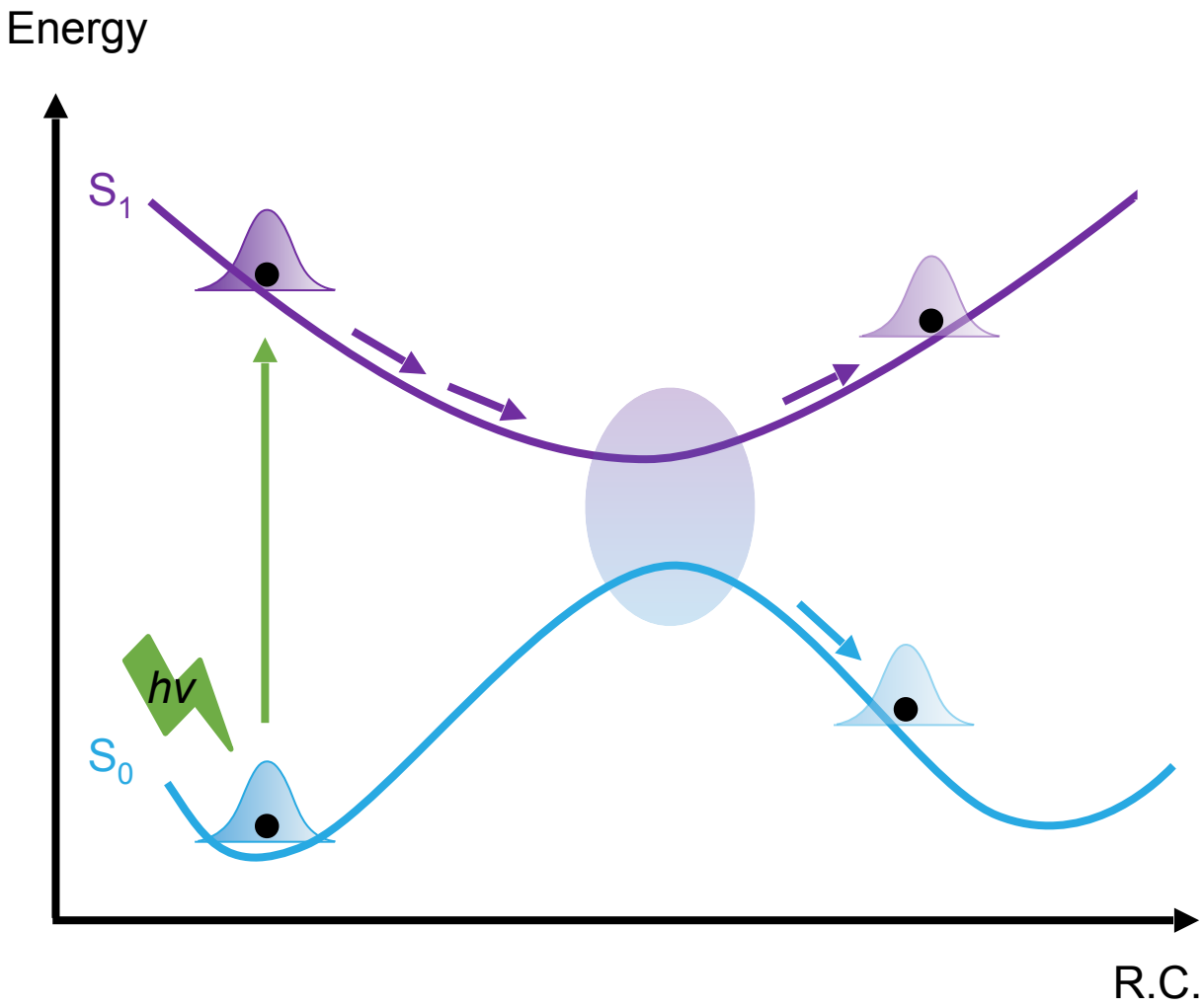
Skin



Photomedicine

B. Feringa. J. Org. Chem., **2007**, 72, 6643

Nonadiabatic molecular dynamics: Photochemistry



I. Photoexcitation of S_0 to S_1

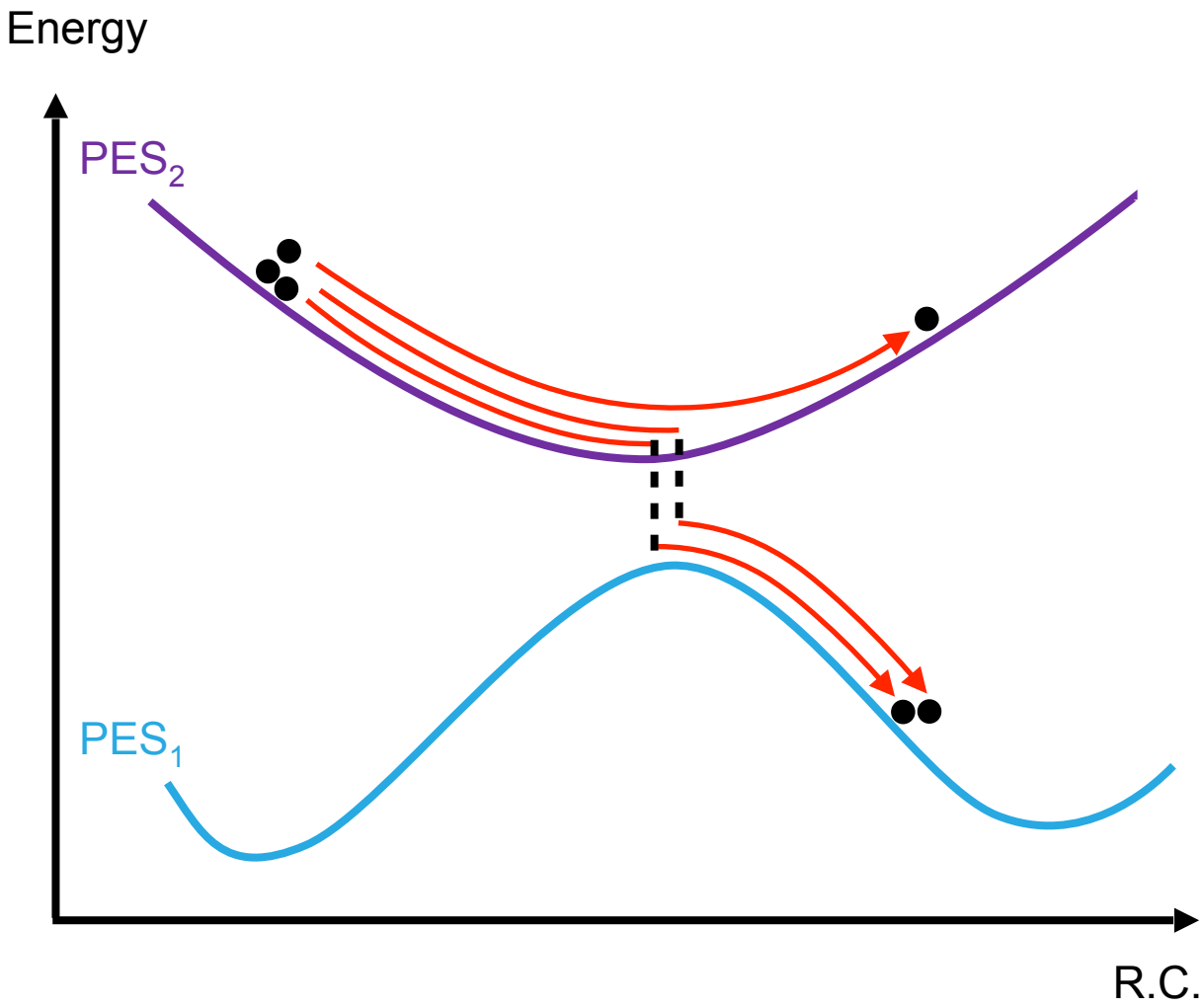
II. Evolving on S_1

III. Nonadiabatic coupling

IV. Splitting the nuclear wave packet

B. F. E. Curchod et al. Chem. Rev., **2018**, 1118, 3305-3336

Trajectory Surface Hopping: Tully scheme



Mixed quantum/ classical method

Nuclei: Classic (MD)

$$m_A \mathbf{a}_A(t) = \mathbf{F}_A$$

Electrons: Quantum Mechanics

$$i\frac{d}{dt}|\Psi\rangle = \hat{H}_{el}|\Psi\rangle$$

Hop controlled by a stochastic switching algorithm

$$\sum_{\alpha}^{\gamma} P_{\beta\to\alpha} < \xi < \sum_{\alpha}^{\gamma+1} P_{\beta\to\alpha}$$

Newton's second law

The nuclear equation of motion (approximated classically)

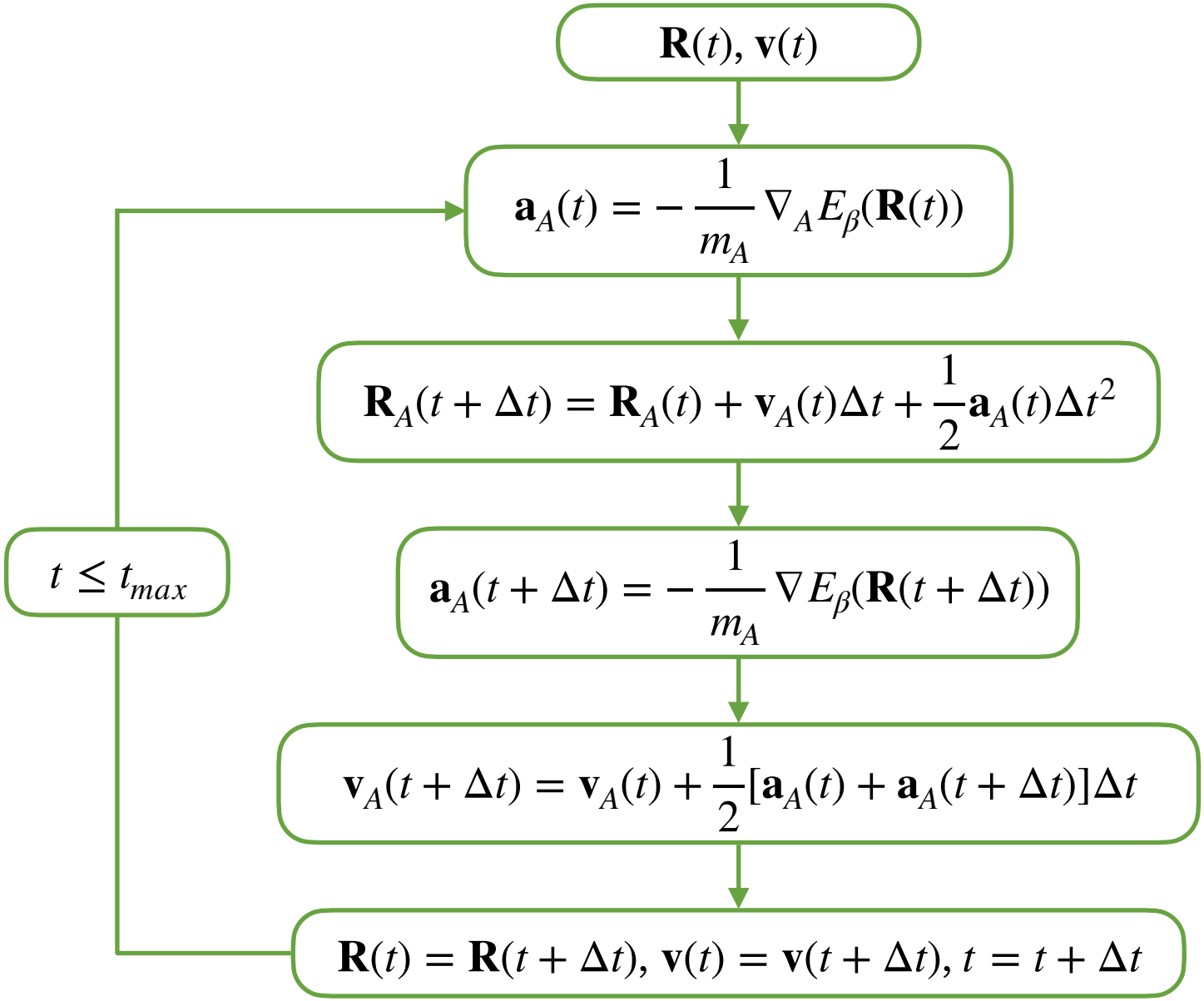
$$m_A \mathbf{a}_A(t) = \mathbf{F}_A$$

$$m_A \frac{d^2}{dt^2} \mathbf{R}_A(t) = -\nabla_A E_\beta(\mathbf{R}(t))$$

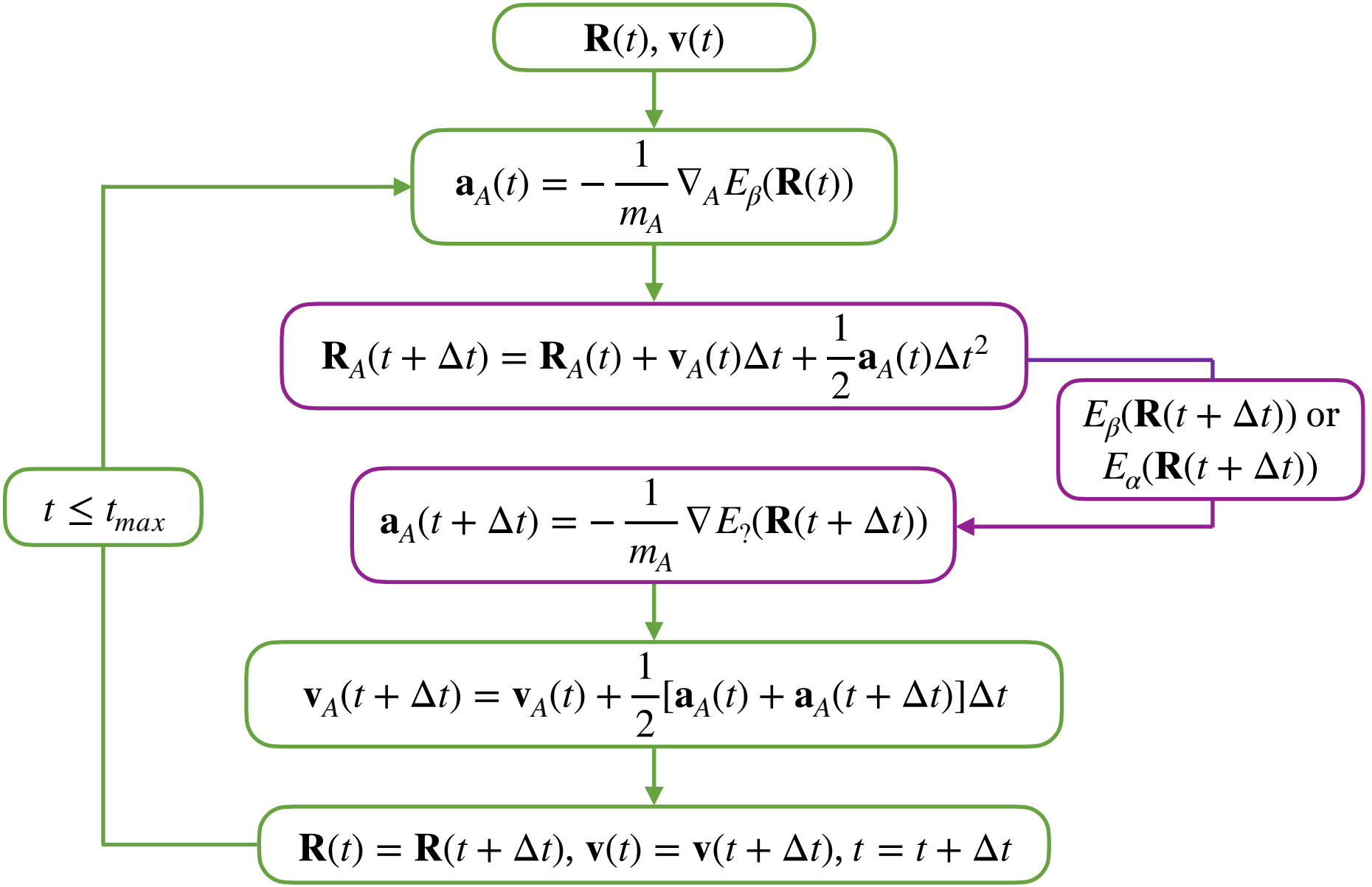
- m_A = Mass of atom A
- $\mathbf{R}_A$ = Position of atom A
- E_β = Energy of the Electronic state β
- $\mathbf{R}$ = Geometry of all atoms

Gradient of the energy: $-\nabla_A E_\beta(\mathbf{R}(t))$ needs to be evaluated at each time step by electronic structure methods.

Integration: Velocity Verlet algorithm



Incorporate nonadiabatic effects



Electronic equation-of-motion

The electronic wavefunction is expanded using $\sum_{\alpha} |\psi_\alpha\rangle\langle\psi_\alpha| = I$:

$$|\Psi\rangle = \sum_{\alpha} |\psi_\alpha\rangle\langle\psi_\alpha|\Psi\rangle \qquad (1)$$

The electronic time-dependent Schrödinger equation:

$$i\frac{d}{dt}|\Psi\rangle = \hat{H}_{el}|\Psi\rangle \qquad (2)$$

Inserting expression 1 in 2 and projecting on $\langle\psi_\beta|$:

$$\frac{d}{dt}\langle\psi_\beta|\Psi\rangle = -\sum_{\alpha}\left[i\langle\psi_\beta|\hat{H}_{el}|\psi_\alpha\rangle + \langle\psi_\beta|\frac{d}{dt}|\psi_\alpha\rangle\right]\langle\psi_\alpha|\Psi\rangle$$

Electronic equation-of-motion

$$\frac{d}{dt}\langle\psi_\beta|\Psi\rangle = -\sum_\alpha \left[i\langle\psi_\beta|\hat{H}_{el}|\psi_\alpha\rangle + \langle\psi_\beta|\frac{d}{dt}|\psi_\alpha\rangle \right] \langle\psi_\alpha|\Psi\rangle$$

Using the chain rule:

$$\frac{d}{dt}\langle\psi_\beta|\Psi\rangle = -\sum_\alpha \left[i\langle\psi_\beta|\hat{H}_{el}|\psi_\alpha\rangle + \langle\psi_\beta|\frac{d}{d\mathbf{R}}\frac{d\mathbf{R}}{dt}|\psi_\alpha\rangle \right] \langle\psi_\alpha|\Psi\rangle$$

Nuclear velocity vector $\mathbf{v}$ and nonadiabatic coupling $\langle\psi_\beta|\nabla|\psi_\alpha\rangle$:

$$\frac{d}{dt}\langle\psi_\beta|\Psi\rangle = -\sum_\alpha \left[i\langle\psi_\beta|\hat{H}_{el}|\psi_\alpha\rangle + \mathbf{v}\langle\psi_\beta|\nabla|\psi_\alpha\rangle \right] \langle\psi_\alpha|\Psi\rangle$$

Electronic equation-of-motion

$$\frac{d}{dt}\langle\psi_\beta|\Psi\rangle = -\sum_\alpha \left[i\langle\psi_\beta|\hat{H}_{el}|\psi_\alpha\rangle + \mathbf{v}\langle\psi_\beta|\nabla|\psi_\alpha\rangle \right] \langle\psi_\alpha|\Psi\rangle$$

Matrix representation (rep):

$$\frac{d}{dt}\mathbf{c}^{rep} = -\left[i\mathbf{H}^{rep} + \mathbf{v}\mathbf{K}^{rep} \right] \mathbf{c}^{rep}$$

Coefficient vector $\mathbf{c}^{rep}$ has the elements $\langle\psi_\beta^{rep}|\Psi\rangle$ and $\langle\psi_\alpha^{rep}|\Psi\rangle$.

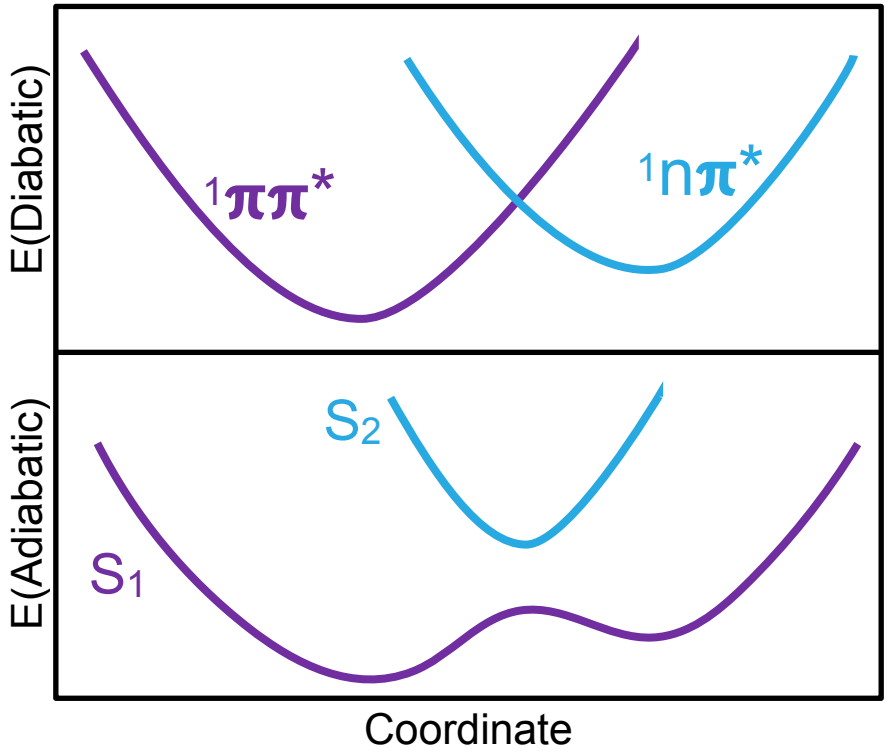
Representation: Diabatic and Adiabatic

In diabatic representation:

$$\langle \psi_\beta^{dia} | \nabla | \psi_\alpha^{dia} \rangle = 0$$

In adiabatic representation:

$$\langle \psi_\beta^{adi} | \hat{H}_{el} | \psi_\alpha^{adi} \rangle = \delta_{\beta\alpha} E_\alpha^{adi}$$



Relationship between diabatic and adiabatic representation:

$$\mathbf{H}^{adi} = \mathbf{U}^\dagger \mathbf{H}^{dia} \mathbf{U}$$

$\mathbf{U}$, the unitary matrix ($\mathbf{U}^\dagger\mathbf{U} = \mathbf{U}\mathbf{U}^\dagger = \mathbf{I}$) that diagonalizes $\mathbf{H}^{dia}$.

Integration and density matrix

Electronic equation of motion:

$$\frac{d}{dt}\mathbf{c}^{adi} = -\left[i\mathbf{H}^{adi} + \mathbf{v}\mathbf{K}^{adi}\right]\mathbf{c}^{adi}$$

Integrating using exponential operator method with small Δt:

$$\mathbf{c}^{adi}(t+\Delta t) = exp\left[-\left(i\mathbf{H}^{adi} + \mathbf{v}\mathbf{K}^{adi}\right)\Delta t\right]\mathbf{c}^{adi}(t)$$

The diagonal of the density matrix is the population of each electronic state:

$$c_\alpha(t) = \langle \psi_\alpha^{adi} | \Psi \rangle;\ \rho_{\alpha\alpha}(t) = c_\alpha c_\alpha^* = |c_\alpha|^2$$

Hopping probabilities: Fewest-switches method

Number of hopping events in Δt is minimized

$$P_{\beta\to\alpha} = \frac{\text{Population increment in } \alpha \text{ due to flux from } \beta \text{ during } \Delta t}{\text{Population of } \beta}$$

We assuming that $N_\beta(t) > N_\beta(t+\Delta t)$. $N_\beta(t)$ is a number of trajectories in state β at time t where $N_\beta(t) = \rho_{\beta\beta}(t)N$.

The minimum number of transition needed for this change will be $N_\beta(t) - N_\beta(t+\Delta t)$ hops from state β to any other state.

$$P_{\beta\to\alpha}dt = \frac{N_\beta(t) - N_\beta(t+\Delta t)}{N_\beta(t)} \approx -\frac{\dot{\rho}_{\beta\beta}\Delta t}{\rho_{\beta\beta}}$$

J.C. Tully, J. Chem. Phys., **1990**, 93, 1061

Hopping probabilities: Fewest-switches method

$$P_{\beta\to\alpha} = max\left[0, \frac{2\Delta t}{\rho_{\beta\beta}}\Re\left(\rho_{\beta\alpha}\left[\frac{i}{\hbar}H_{\beta\alpha} + vK_{\beta\alpha}\right]\right)\right]$$

Given a random number $0 < \xi < 1$ a switch occurs if:

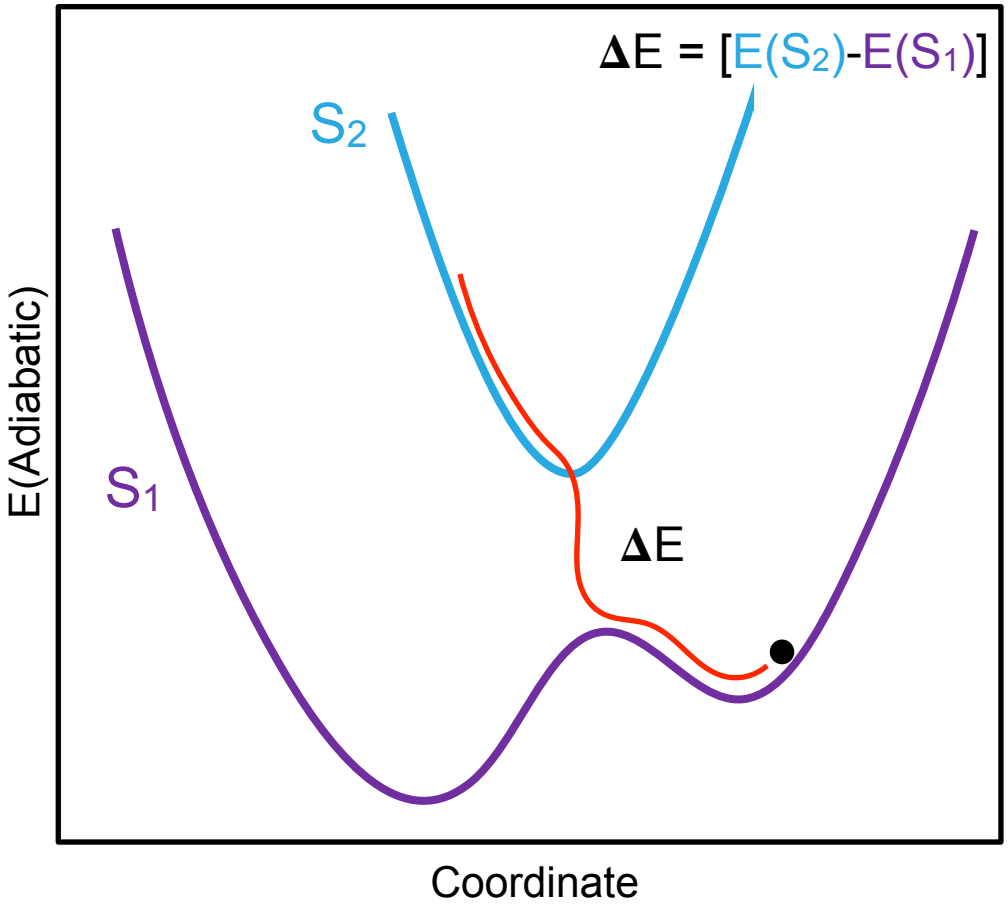
$$\sum_{\alpha}^{\gamma} P_{\beta\to\alpha} < \xi < \sum_{\alpha}^{\gamma+1} P_{\beta\to\alpha}$$

J.C. Tully, J. Chem. Phys., **1990**, 93, 1061

Velocity adjustment

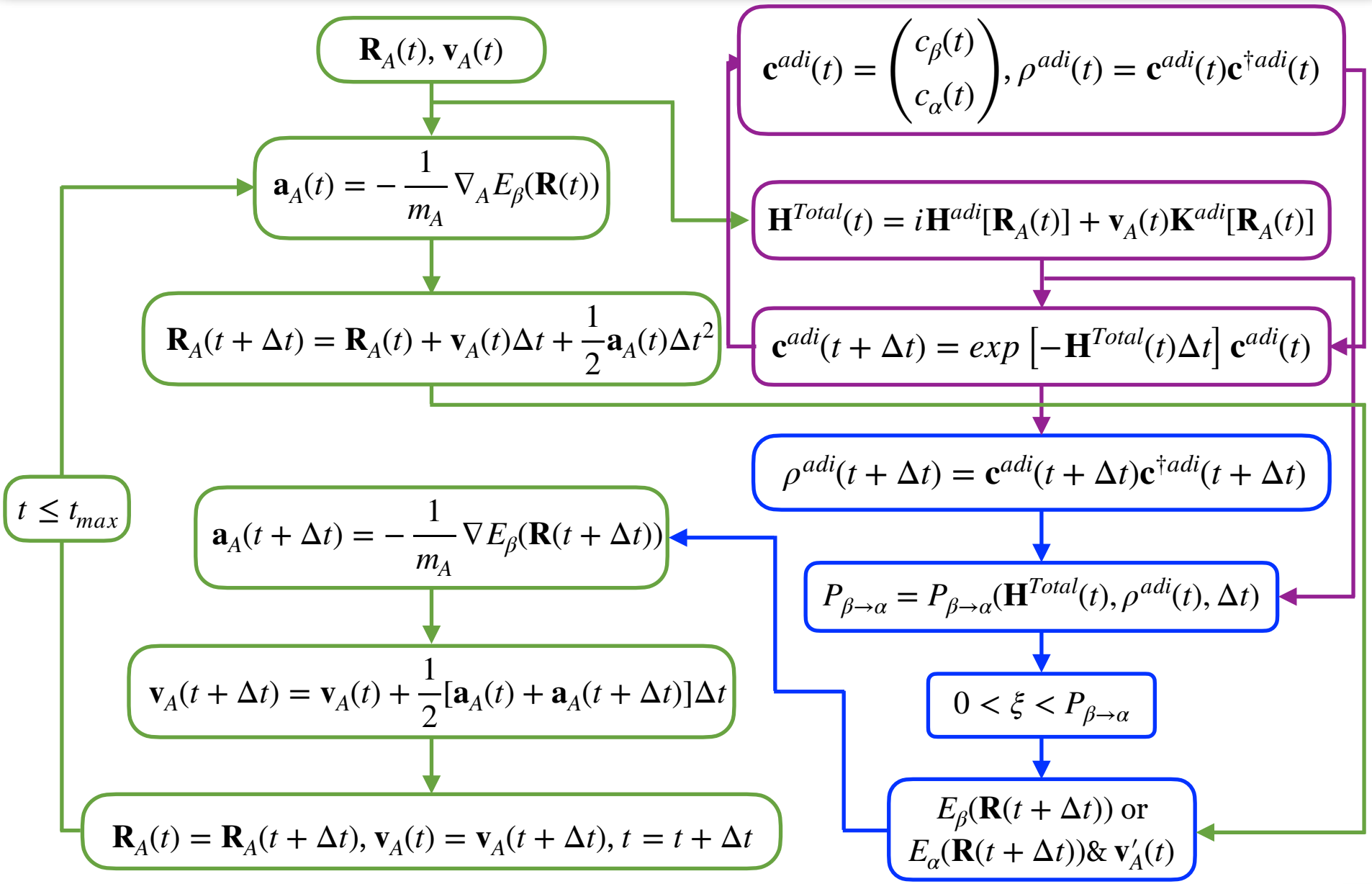
In order to conserve the total energy, the velocity is rescaled to compensate the electronic change when the system jumps from a state β to a state α.

$$\mathbf{v}_A(t)' = \mathbf{v}_A(t) - \gamma_{\alpha\beta}\frac{\mathbf{K}^A_{\alpha\beta}(t)}{m_A}$$



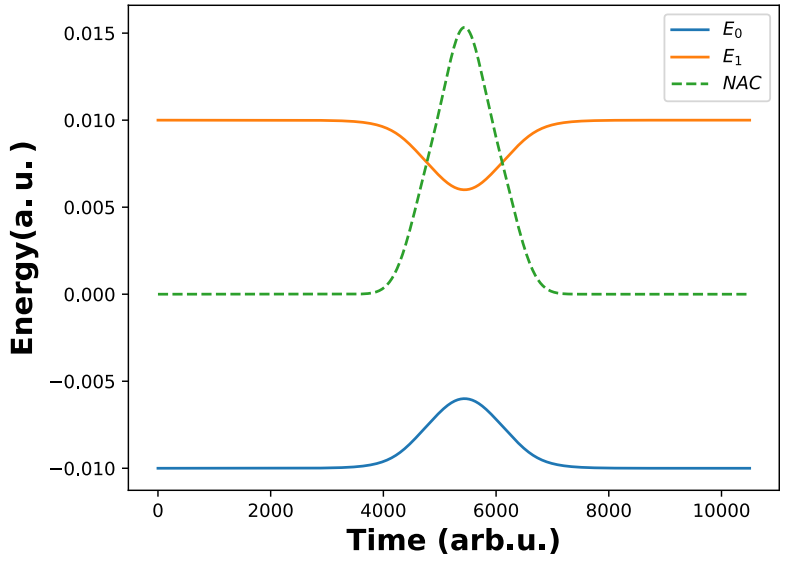
E. Fabiano et al. Chem. Phys., **2008**, 349, 334–347

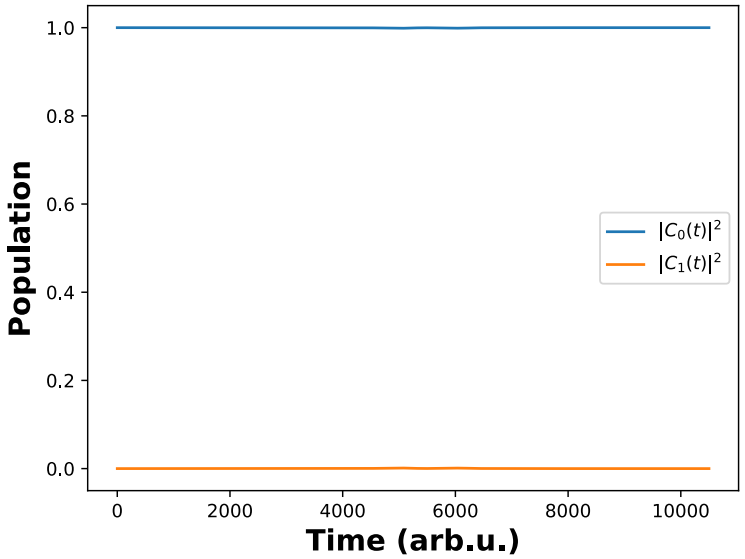
Trajectory Surface Hopping : Tully scheme

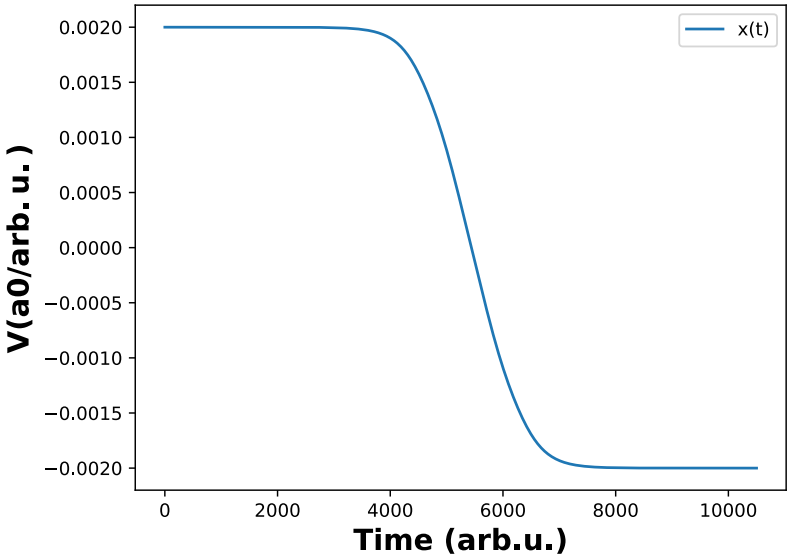


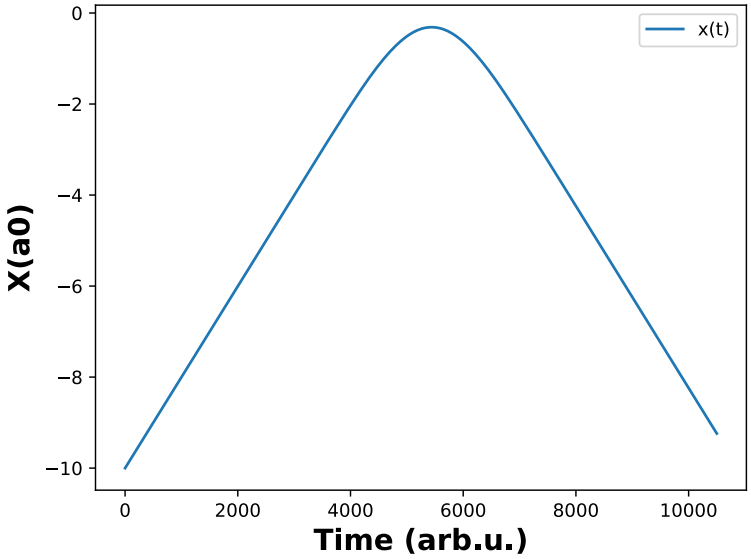
Tully models: Model 1

Simple avoided crossing: p = 4 (a.u.)



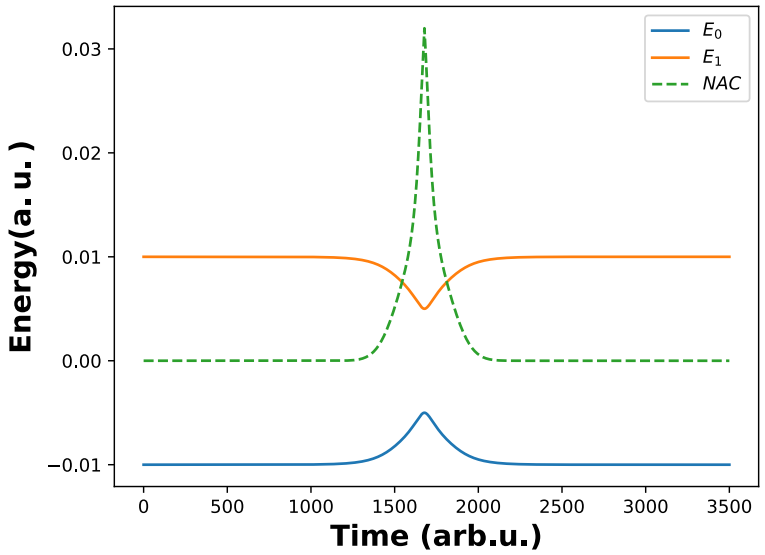


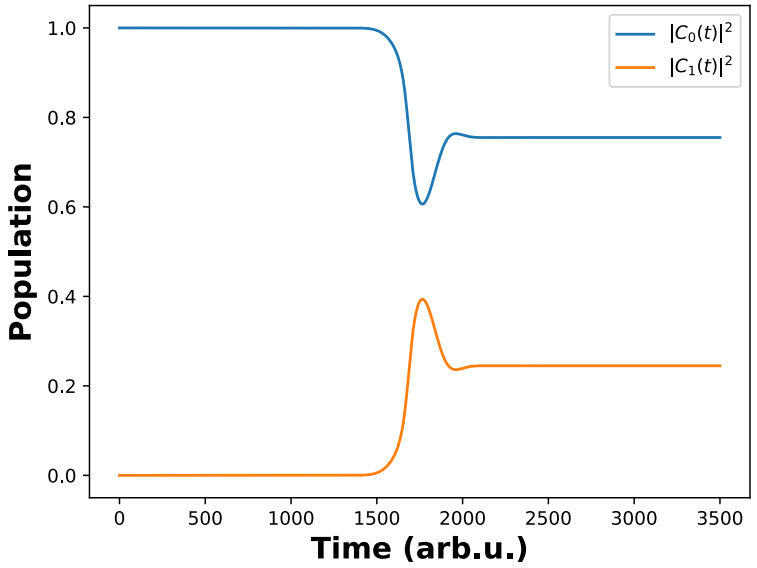


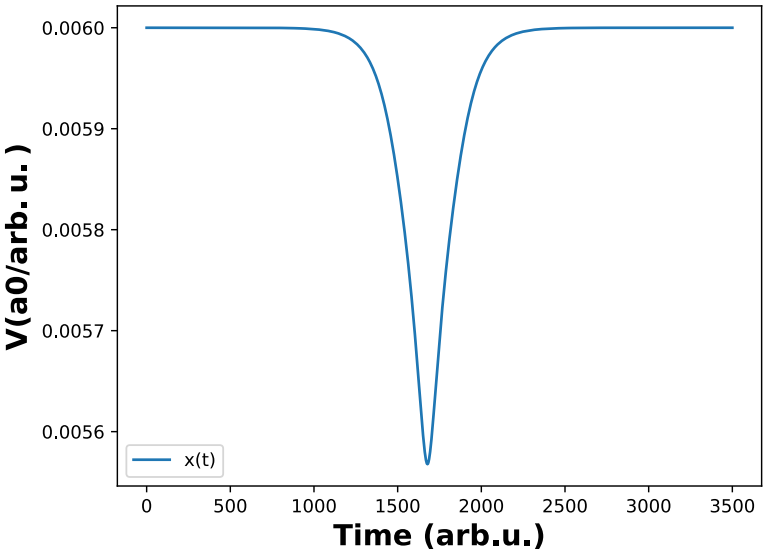


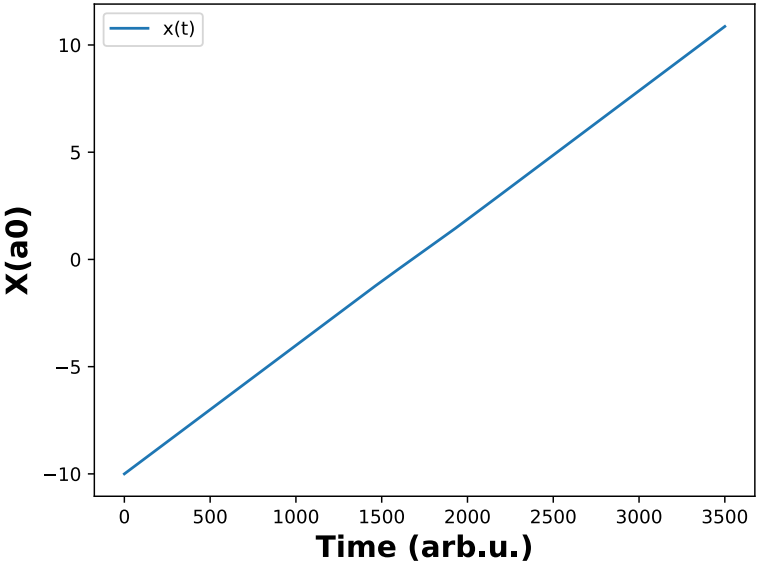
Tully models: Model 1

Simple avoided crossing: p = 6 (a.u.)



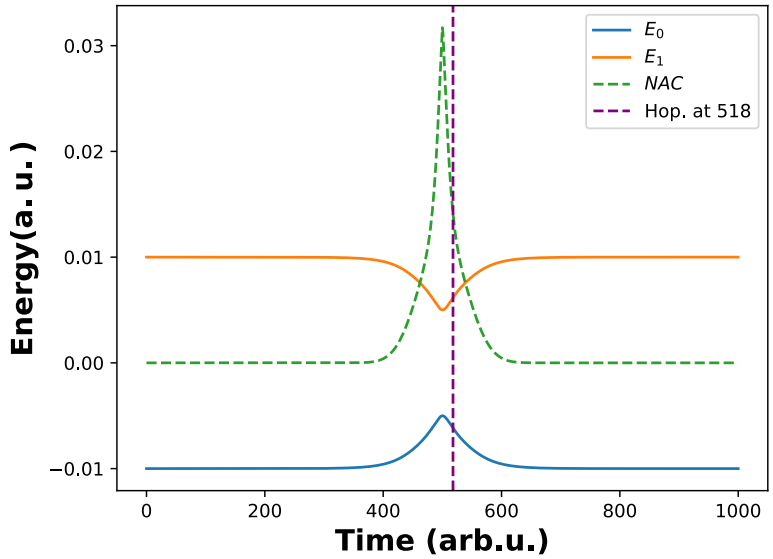


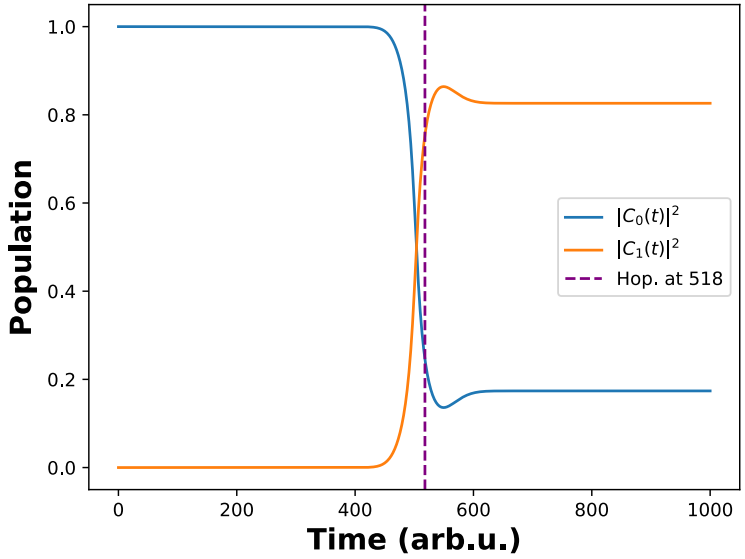


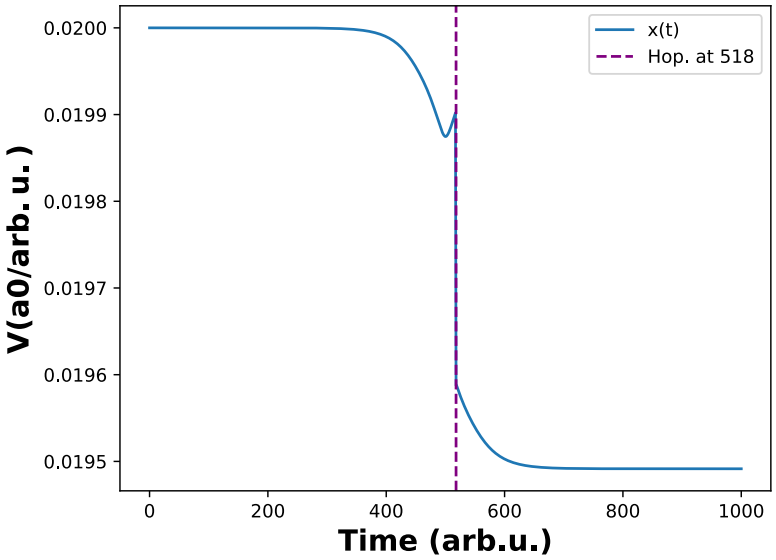


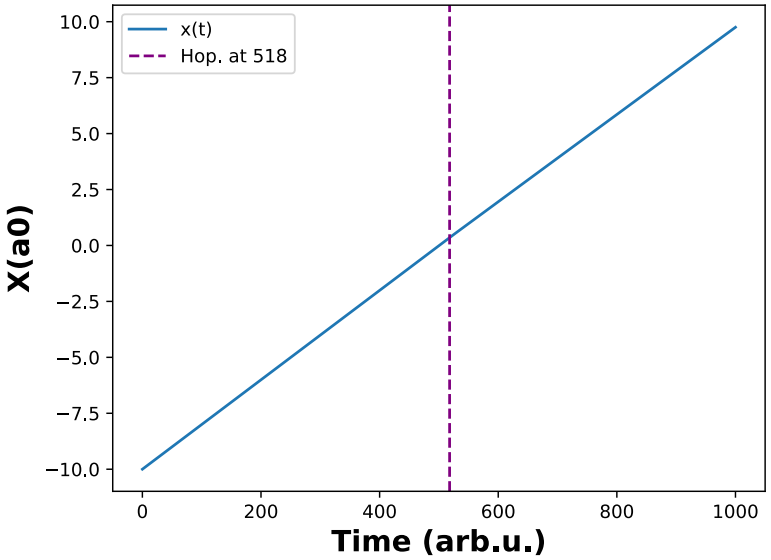
Tully models: Model 1

Simple avoided crossing: p = 20 (a.u.)



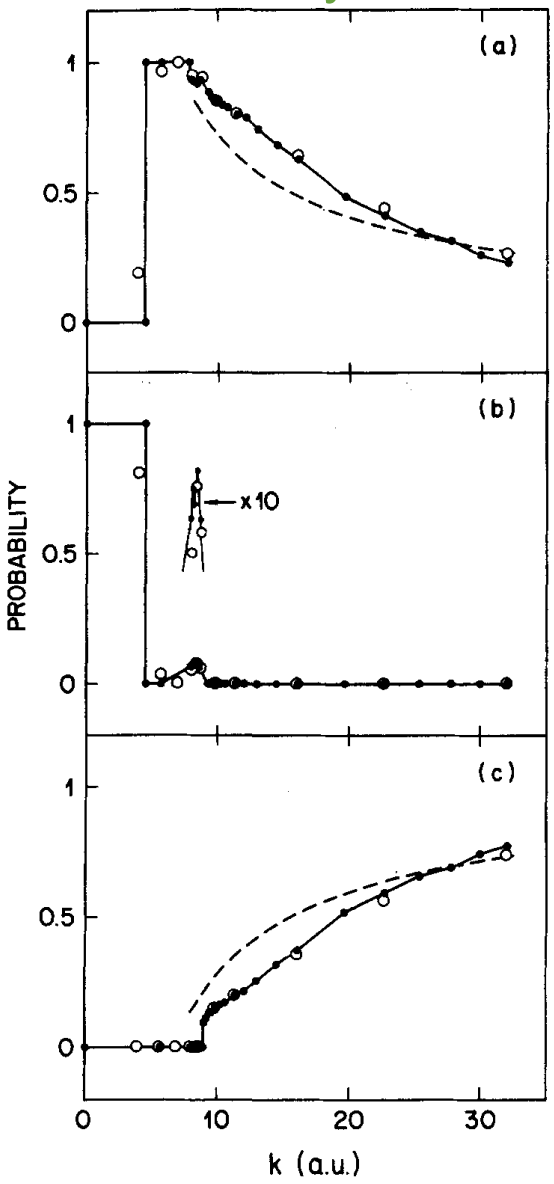






Validation: 2000 trajectories

Tully



Our work