Excited-state dynamics: Tully scheme implementation and models

Edison Salazar
e.x.salazar.quezada@rug.nl

School of Programming for Scientific Research 2
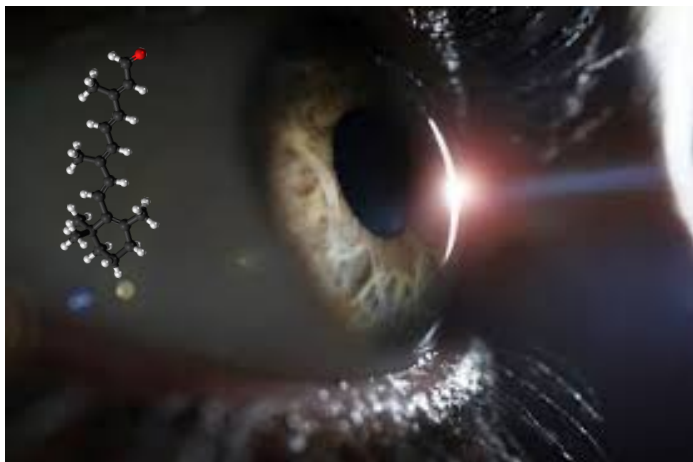(EPIC 2)

October 11-14, 2022
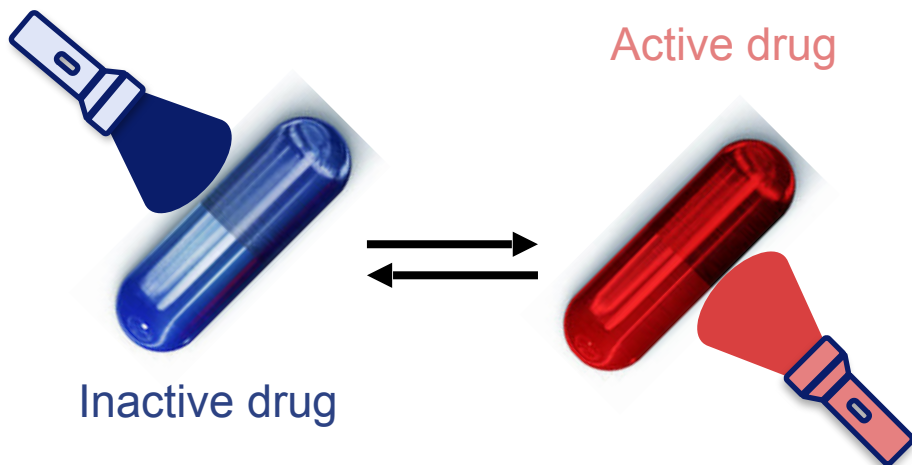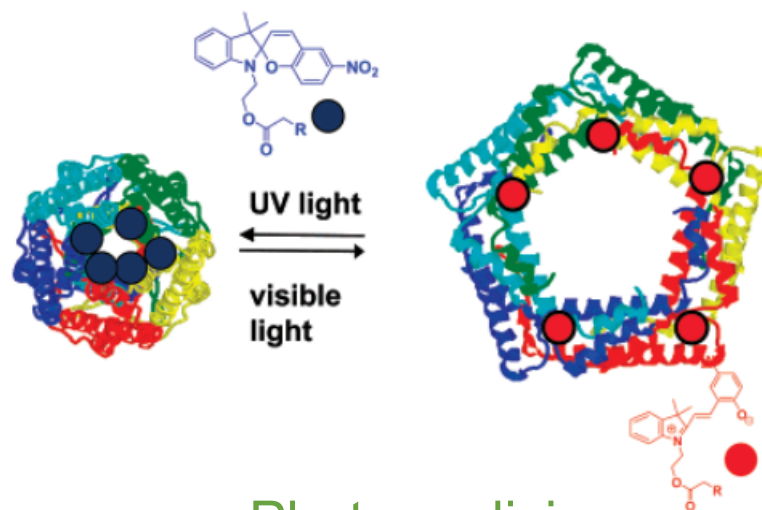
university of
groningen

PYSURF

Photochemistry

Vision

Inactive drug

Active drug

Photopharmacology

Skin

UV light

visible light

Photomedicine

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

Energy

I. Photoexcitation of S_0 to S_1

II. Evolving on S_1

III. Nonadiabatic coupling

IV. Splitting the nuclear wave packet

S_1

S_0

$h\nu$

R.C.

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

Energy

PES$_2$

PES$_1$

R.C.
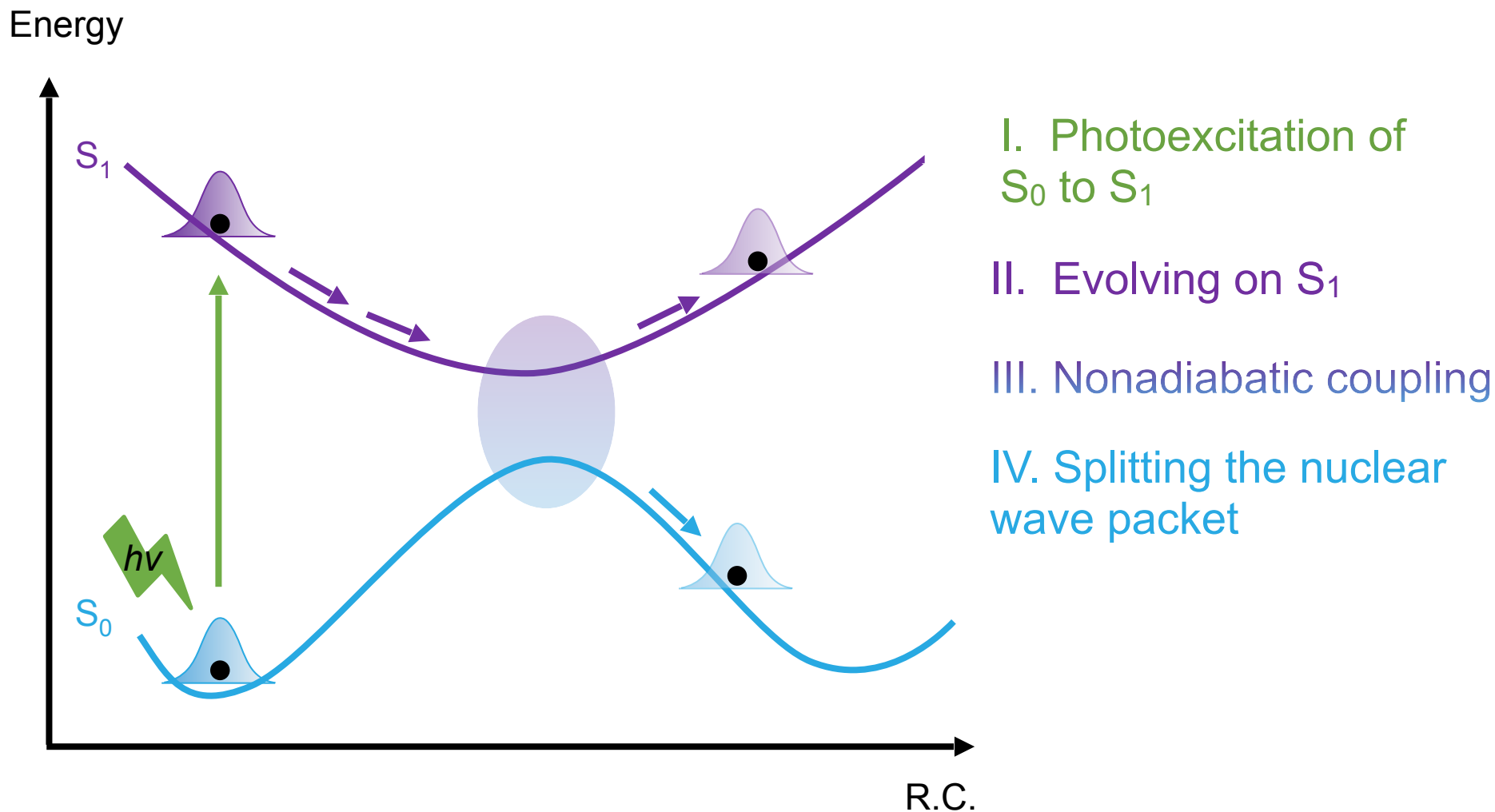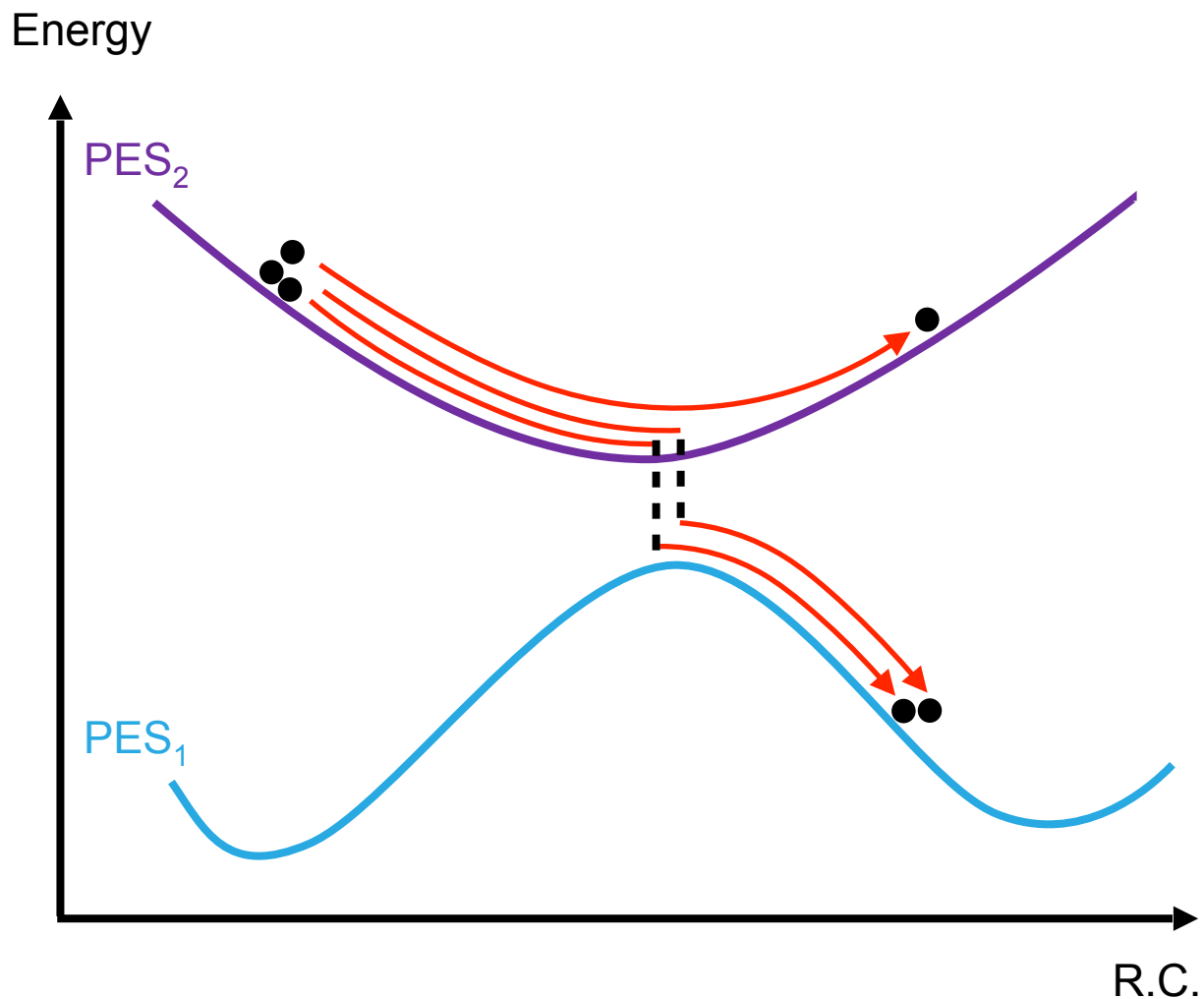
Mixed quantum/
classical method

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

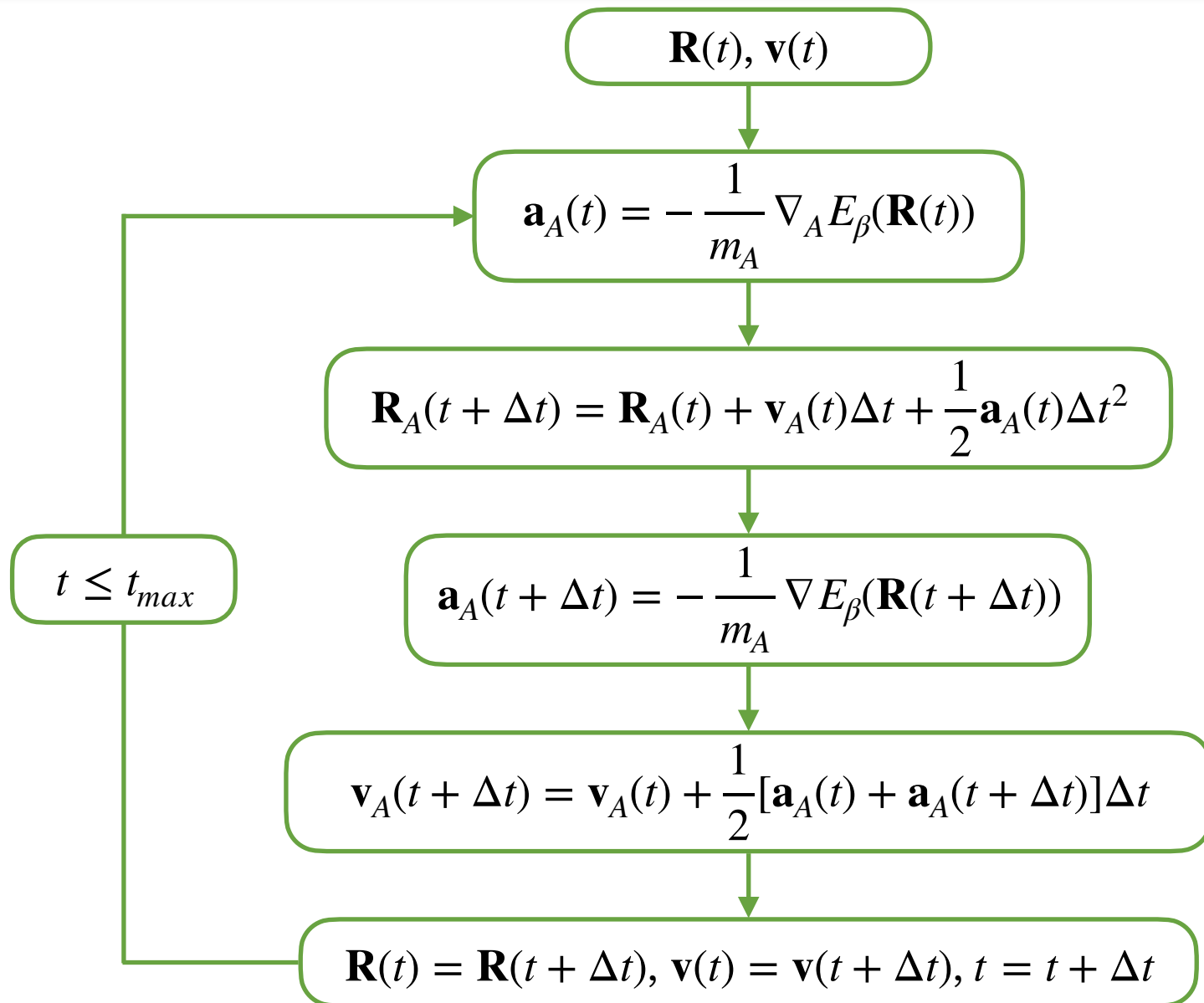The nuclear equation of motion (approximated classically)

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

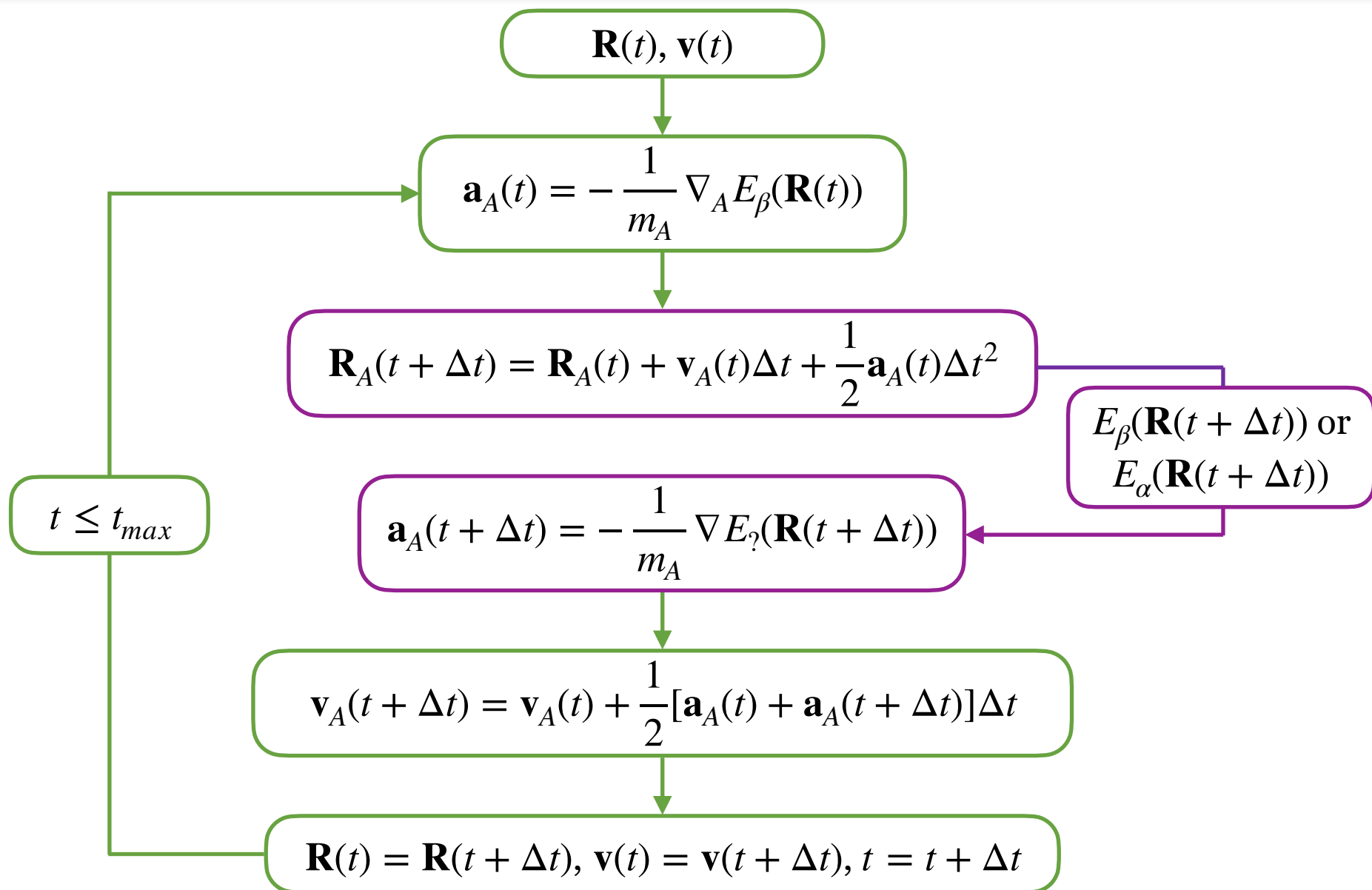$$m_A \frac{d^2}{dt^2} \mathbf{R}_A(t) = - \nabla_A E_\beta(\mathbf{R}(t))$$

- 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.

$$\mathbf{R}(t), \mathbf{v}(t)$$

$$\mathbf{a}_A(t) = -\frac{1}{m_A} \nabla_A E_\beta(\mathbf{R}(t))$$

$$\mathbf{R}_A(t + \Delta t) = \mathbf{R}_A(t) + \mathbf{v}_A(t)\Delta t + \frac{1}{2}\mathbf{a}_A(t)\Delta t^2$$

$$\mathbf{a}_A(t + \Delta t) = -\frac{1}{m_A} \nabla E_\beta(\mathbf{R}(t + \Delta t))$$

$$\mathbf{v}_A(t + \Delta t) = \mathbf{v}_A(t) + \frac{1}{2}[\mathbf{a}_A(t) + \mathbf{a}_A(t + \Delta t)]\Delta t$$

$$t \leq t_{max}$$

$$\mathbf{R}(t) = \mathbf{R}(t + \Delta t), \mathbf{v}(t) = \mathbf{v}(t + \Delta t), t = t + \Delta t$$

$$\mathbf{R}(t), \mathbf{v}(t)$$

$$\mathbf{a}_A(t) = -\frac{1}{m_A} \nabla_A E_\beta(\mathbf{R}(t))$$

$$\mathbf{R}_A(t + \Delta t) = \mathbf{R}_A(t) + \mathbf{v}_A(t)\Delta t + \frac{1}{2}\mathbf{a}_A(t)\Delta t^2$$

$$E_\beta(\mathbf{R}(t + \Delta t)) \text{ or } E_\alpha(\mathbf{R}(t + \Delta t))$$

$$\mathbf{a}_A(t + \Delta t) = -\frac{1}{m_A} \nabla E_?(\mathbf{R}(t + \Delta t))$$

$$t \leq t_{max}$$

$$\mathbf{v}_A(t + \Delta t) = \mathbf{v}_A(t) + \frac{1}{2}[\mathbf{a}_A(t) + \mathbf{a}_A(t + \Delta t)]\Delta t$$

$$\mathbf{R}(t) = \mathbf{R}(t + \Delta t), \mathbf{v}(t) = \mathbf{v}(t + \Delta t), t = t + \Delta t$$

Electronic equation-of-motion

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

$$|\Psi\rangle = \sum_{\alpha} |\psi_\alpha\rangle\langle\psi_\alpha|\Psi\rangle$$

①

The electronic time-dependent Schrödinger equation:

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

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:

$$\langle \psi_\beta^{adi} | \hat{H}_{el} | \psi_\alpha^{adi} \rangle = \delta_{\beta\alpha} E_\alpha^{adi}$$
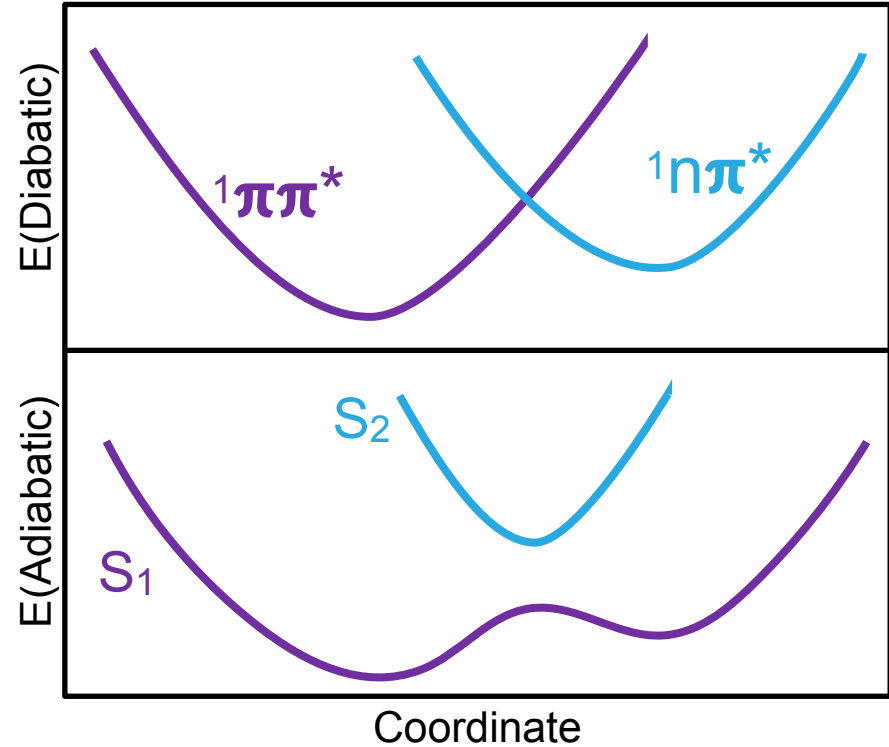
Relationship between diabatic and adiabatic representation:

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

$\mathbf{U}$, 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:

$$c_{\alpha}(t) = \langle\psi_{\alpha}^{adi}\,|\,\Psi\rangle; \ \rho_{\alpha\alpha}(t) = c_{\alpha}c_{\alpha}^{*} = |c_{\alpha}|^{2}$$
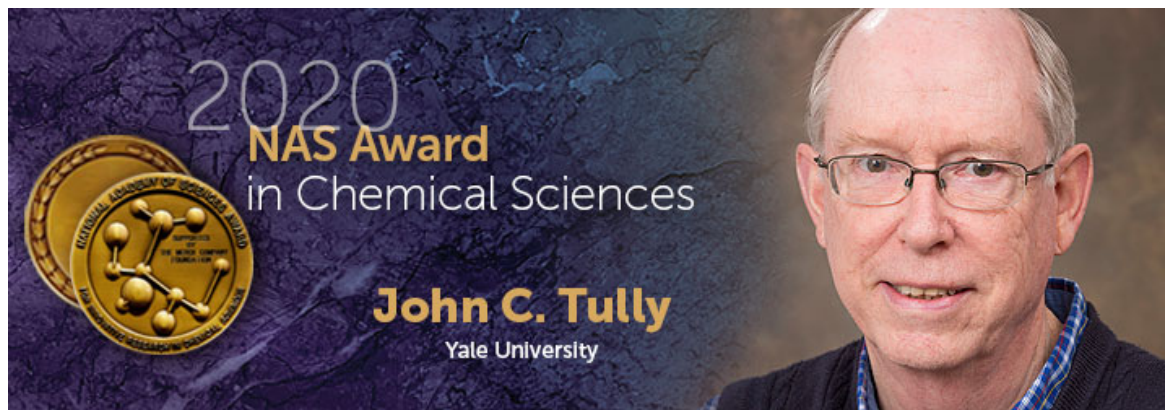
Molecular dynamics with electronic transitions

John C. Tully
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

A method is proposed for carrying out molecular dynamics simulations of processes that involve electronic transitions. The time dependent electronic Schrödinger equation is solved self-consistently with the classical mechanical equations of motion of the atoms. At each integration time step a decision is made whether to switch electronic states, according to probabilistic "fewest switches" algorithm. If a switch occurs, the component of velocity in the direction of the nonadiabatic coupling vector is adjusted to conserve energy. The procedure allows electronic transitions to occur anywhere among any number of coupled states, governed by the quantum mechanical probabilities. The method is tested against accurate quantal calculations for three one-dimensional, two-state models, two of which have been specifically designed to challenge any such mixed classical–quantal dynamical theory. Although there are some discrepancies, initial indications are encouraging. The model should be applicable to a wide variety of gas-phase and condensed-phase phenomena occurring even down to thermal energies.

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

14

$$P_{\beta \to \alpha} = max \left[0, \frac{2\Delta t}{\rho_{\beta\beta}} \Re \left(\rho_{\beta\alpha} \left[\frac{i}{\hbar} H_{\beta\alpha} + v K_{\beta\alpha} \right] \right) \right]$$
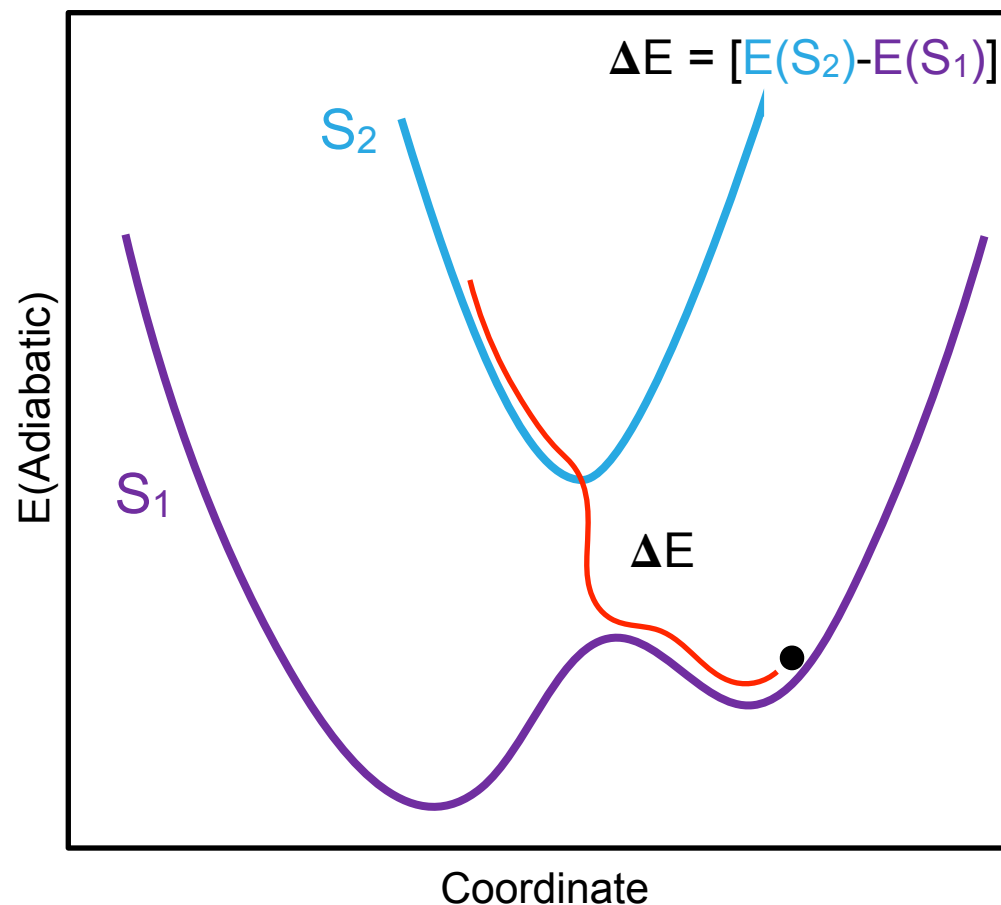
Given a random number $0 < \xi < 1$ a switch occurs if:

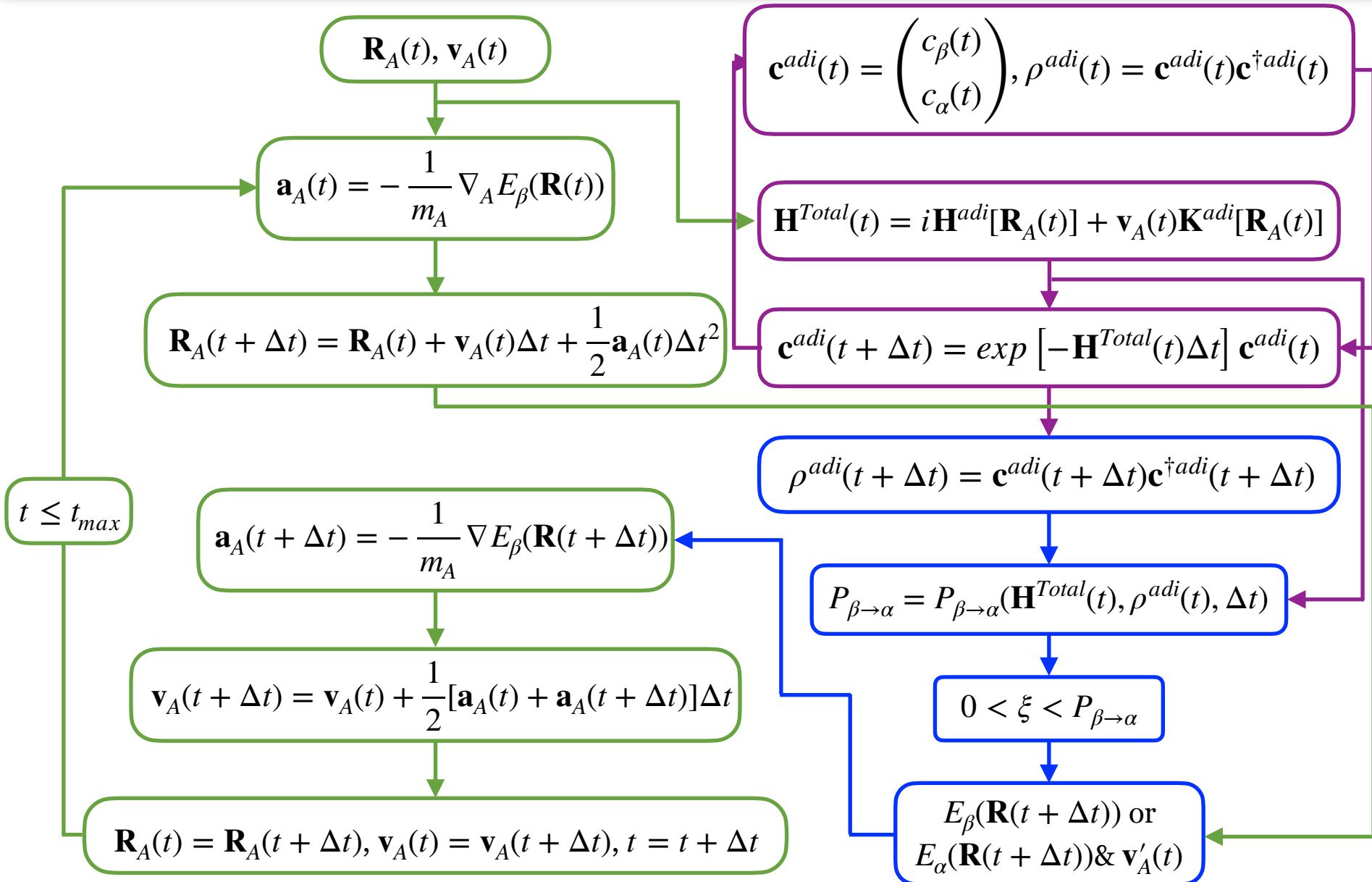$$\sum_{\alpha}^{\gamma} P_{\beta \to \alpha} < \xi < \sum_{\alpha}^{\gamma+1} P_{\beta \to \alpha}$$

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.

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

$\Delta E = [E(S_2) - E(S_1)]$

S_2

S_1

ΔE

E(Adiabatic)

Coordinate

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

$$\mathbf{R}_A(t), \mathbf{v}_A(t)$$

$$\mathbf{c}^{adi}(t) = \begin{pmatrix} c_\beta(t) \\ c_\alpha(t) \end{pmatrix}, \rho^{adi}(t) = \mathbf{c}^{adi}(t)\mathbf{c}^{\dagger adi}(t)$$

$$\mathbf{a}_A(t) = -\frac{1}{m_A}\nabla_A E_\beta(\mathbf{R}(t))$$

$$\mathbf{H}^{Total}(t) = i\mathbf{H}^{adi}[\mathbf{R}_A(t)] + \mathbf{v}_A(t)\mathbf{K}^{adi}[\mathbf{R}_A(t)]$$

$$\mathbf{R}_A(t + \Delta t) = \mathbf{R}_A(t) + \mathbf{v}_A(t)\Delta t + \frac{1}{2}\mathbf{a}_A(t)\Delta t^2$$

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

$$\rho^{adi}(t + \Delta t) = \mathbf{c}^{adi}(t + \Delta t)\mathbf{c}^{\dagger adi}(t + \Delta t)$$

$$t \le t_{max}$$

$$\mathbf{a}_A(t + \Delta t) = -\frac{1}{m_A}\nabla E_\beta(\mathbf{R}(t + \Delta t))$$

$$P_{\beta \to \alpha} = P_{\beta \to \alpha}(\mathbf{H}^{Total}(t), \rho^{adi}(t), \Delta t)$$

$$\mathbf{v}_A(t + \Delta t) = \mathbf{v}_A(t) + \frac{1}{2}[\mathbf{a}_A(t) + \mathbf{a}_A(t + \Delta t)]\Delta t$$

$$0 < \xi < P_{\beta \to \alpha}$$

$$\mathbf{R}_A(t) = \mathbf{R}_A(t + \Delta t), \mathbf{v}_A(t) = \mathbf{v}_A(t + \Delta t), t = t + \Delta t$$

$$E_\beta(\mathbf{R}(t + \Delta t)) \text{ or } E_\alpha(\mathbf{R}(t + \Delta t))\& \mathbf{v}'_A(t)$$

Code: Classes

Tully model → [Velocity Verlet Propagator, Rescale Velocity, Surface Hopping, Print Results, State] → Plot
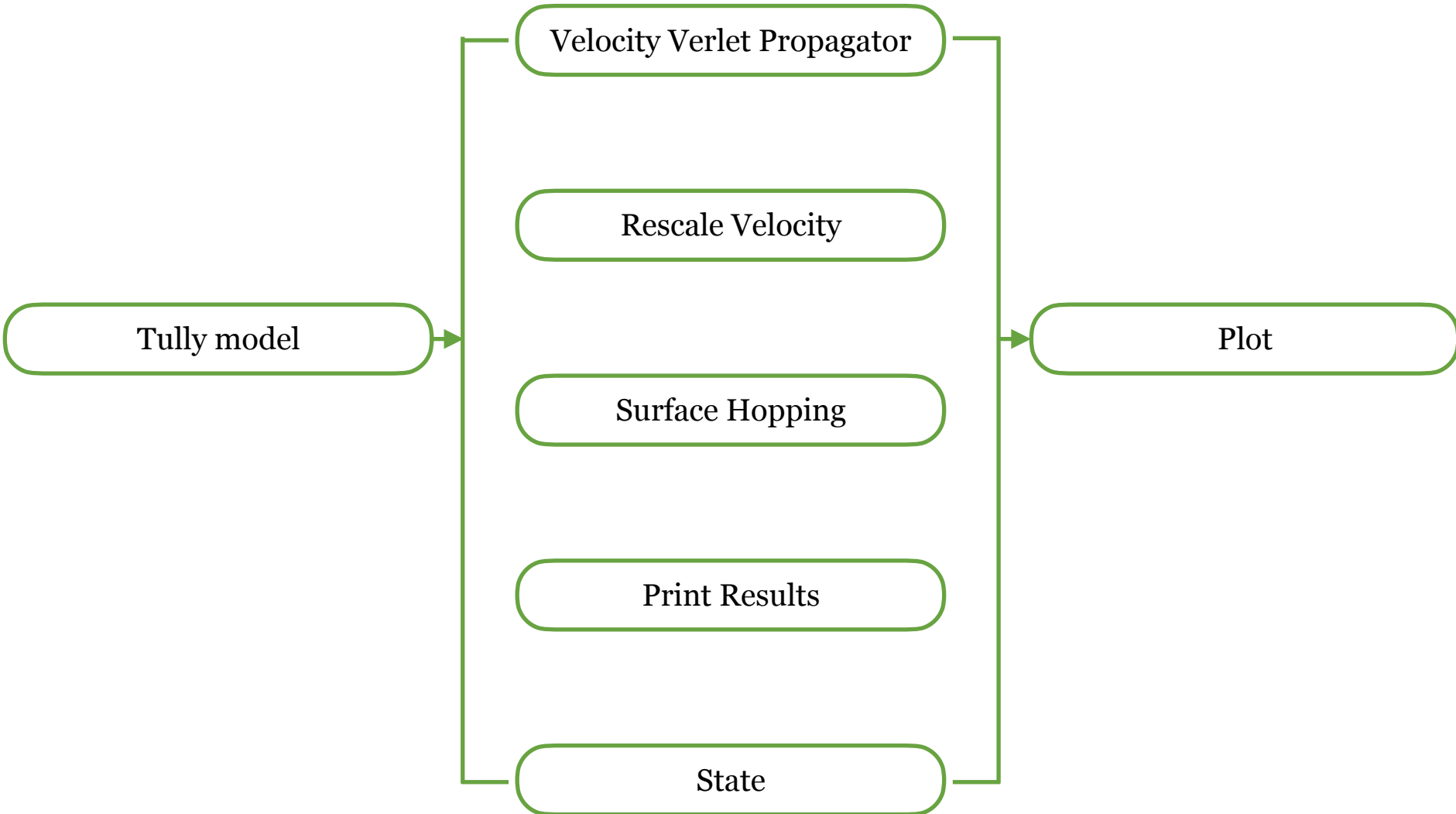
Tully models:

Potential Energies Surfaces

ENERGY (a.u.)

x (a₀)
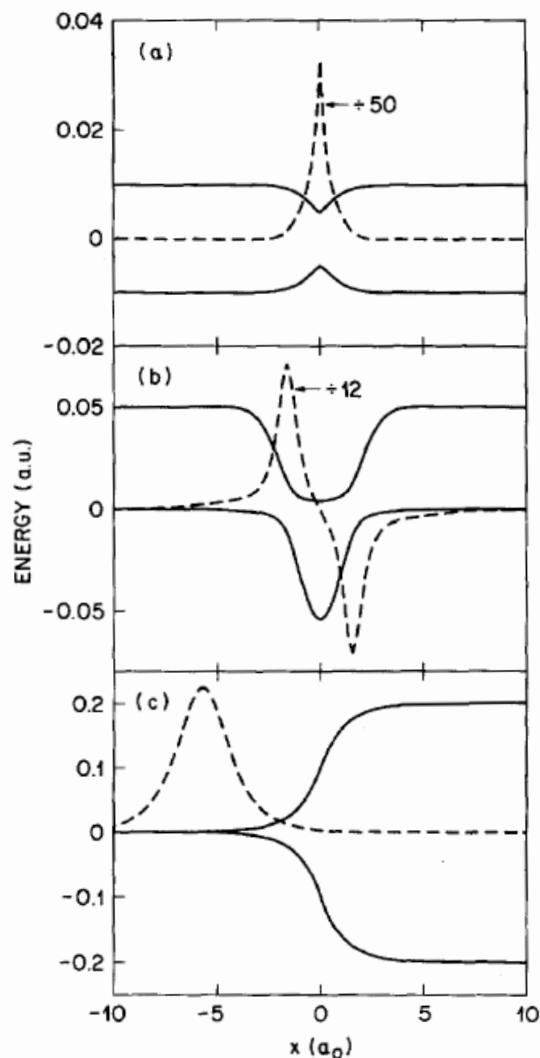
a) Simple avoided crossing:

$$V_{11}(x) = A[1 - exp(-Bx)], \qquad x > 0,$$
$$V_{11}(x) = -A[1 - exp(Bx)], \qquad x < 0,$$
$$V_{22}(x) = -V_{11}(x)$$
$$V_{12}(x) = V_{21}(x) = C\ exp(-Dx^2).$$

$A = 0.01,\ B = 1.6,\ C = 0.005,\ and\ D = 1.0$

b) Dual avoided crossing:

$$V_{11}(x) = 0,$$
$$V_{22}(x) = -A\ exp(-Bx^2) + E_0$$
$$V_{12}(x) = V_{21}(x) = C\ exp(-Dx^2)$$

$A = 0.10,\ B = 0.28,\ E_0 = 0.05,\ C = 0.015,\ and\ D = 0.06$
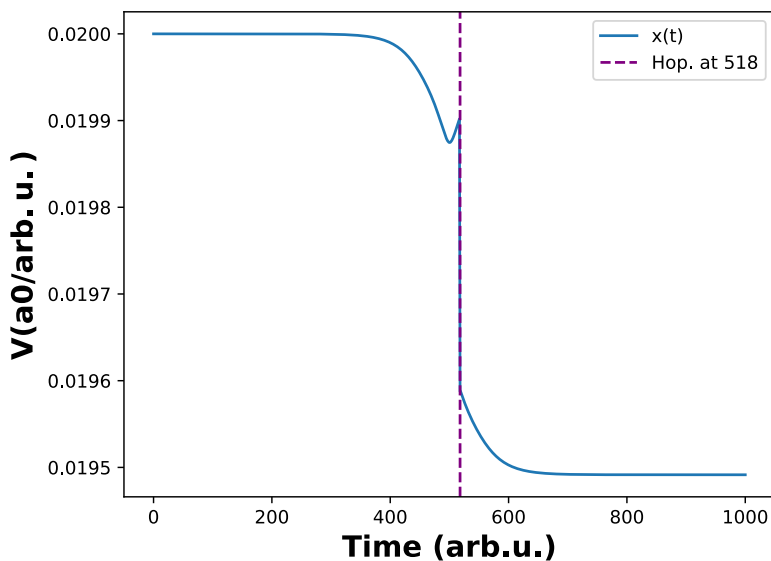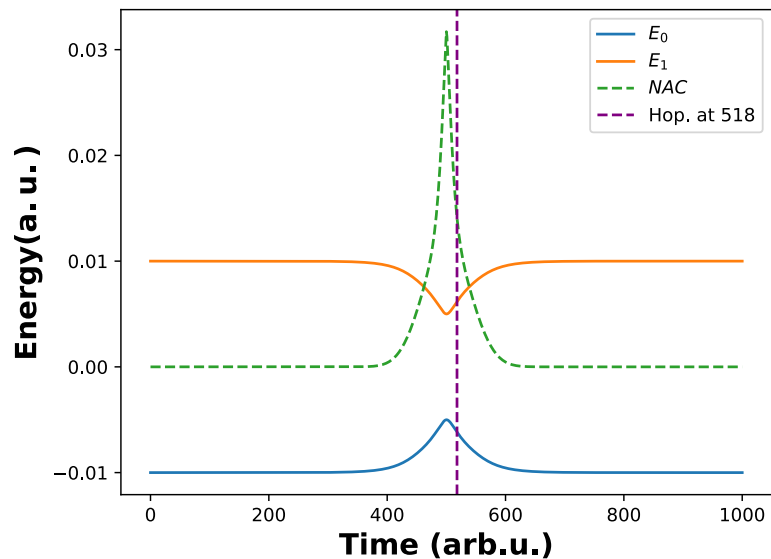
Simple avoided crossing: p = 4 (a.u.)
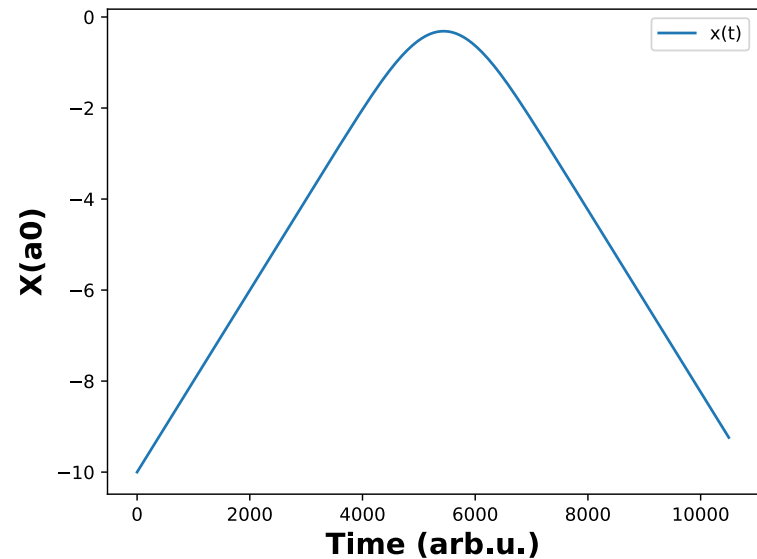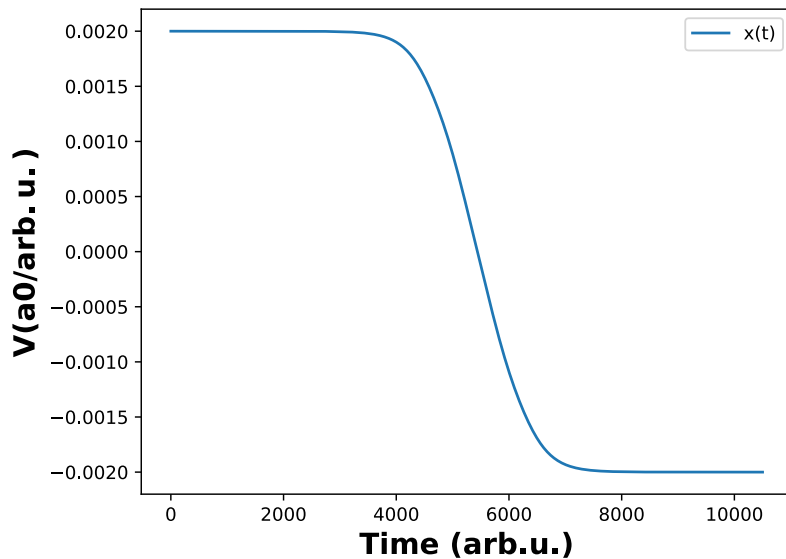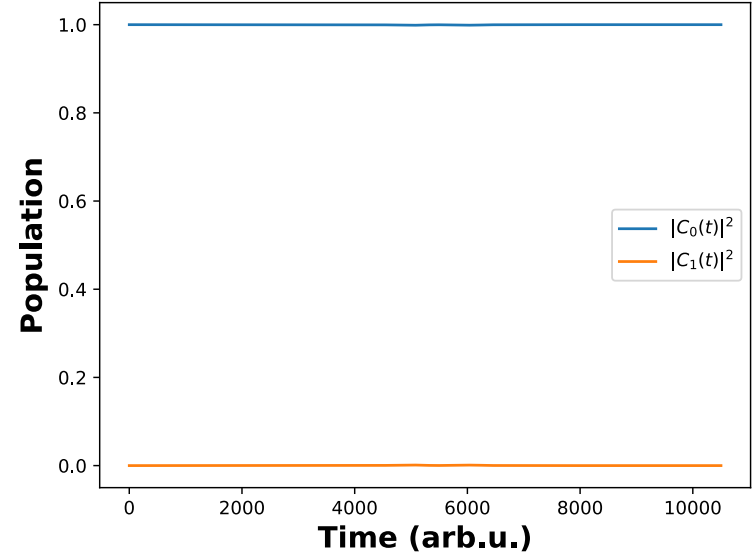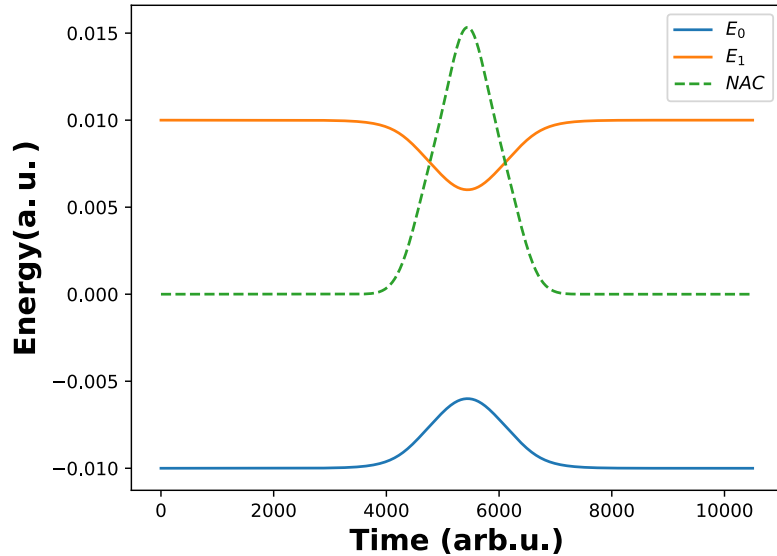
Tully models: Model 1

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

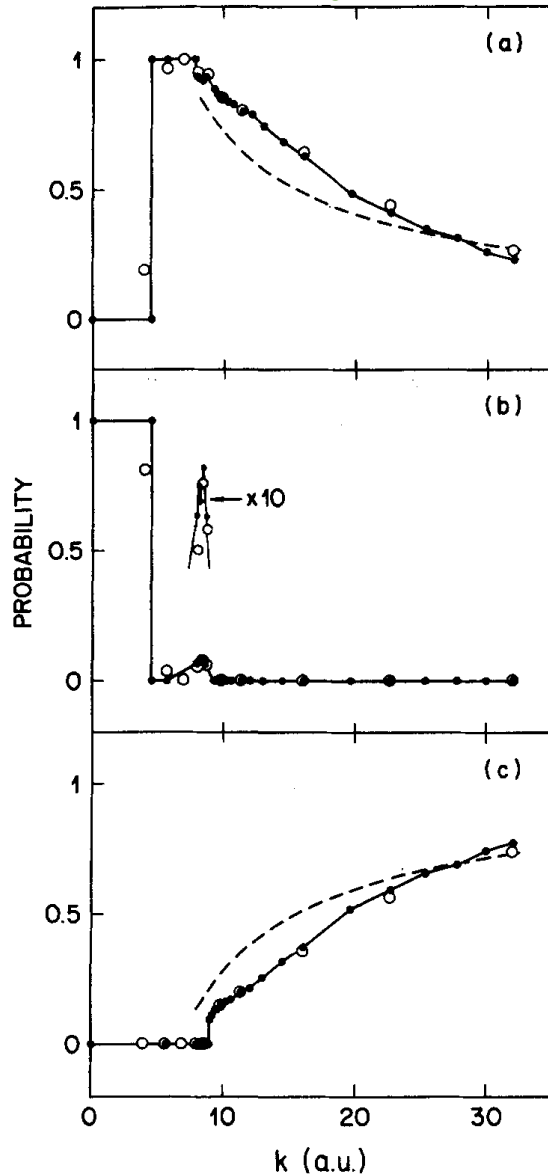# Tully models: Model 1

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

Tully

Our work