Investigation of Miller's Recent Quasiclassical Trajectory Model: Analysis of Some Simple Model Systems.

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Content

Computational Chemistry Methods

- *ab initio*
- Density Functional Theory
- Semi-empirical
- Molecular Dynamics

Defining the Problem

- Atomic/molecular trajectories coupled to electronic states.
- The quantum molecular Hamiltonian requires terms for: nuclear K.E., electronic K.E., electron-electron P.E., nucleus-electron P.E., and nucleus-nucleus P.E., as well as a few other smaller terms.
- Quantum methods: accurate, bad scaling
- Classical methods: inaccurate, good scaling.
- Compromises are required.

Meyer-Miller Model

- Classical analogue of a quantum phenomenon.
- Molecular dynamics with electronic transitions.
- Monte-Carlo–Deterministic hybrid.
- Uses potential energy surfaces (PES).
- The specific version of the model, as well as the systems studied are found in [1].

Terms and Variables

Diabatic Hamiltonian in Action-Angle Variables

$$H(\boldsymbol{P},\boldsymbol{R},\boldsymbol{n},\boldsymbol{q}) = \overbrace{\frac{\boldsymbol{P}^2}{2\mu}}^{\text{Kinetic energy.}} + \overbrace{\sum_{k=1}^{F} n_k H_{kk}(\boldsymbol{R})}^{\text{Pure electronic states.}} + \underbrace{2\sum_{k<k'=1}^{F}\sqrt{(n_k+\gamma)(n_{k'}+\gamma)}\times\cos(q_k-q_{k'})H_{kk'}(\boldsymbol{R})}_{\text{Electronic state interactions.}} \quad (1)$$

Terms and Variables

Initial Conditions

$$n_k(0) = N_k + \gamma(2 \cdot RN_k - 1) \tag{2a}$$

$$q_k(0) = 2\pi \cdot RN'_k \tag{2b}$$

Where:

- $N_k = \begin{cases} 0 & \equiv \text{State } k \text{ unoccupied} \\ 1 & \equiv \text{State } k \text{ occupied} \end{cases}$.
- $RN_k, RN'_k \equiv$ uniform random numbers $\in [0, 1]$.
- $n_k \equiv$ electronic state action variable k.
- $q_k \equiv$ electronic state angle variable k.
- $\gamma \equiv$ adjustable zero-point energy contribution parameter.

Terms and Variables

Canonical Transforms

- They save computational time and make deriving the equations of motion less painful.

$$x_k = \sqrt{2(n_k + \gamma)}\cos(q_k) \tag{3a}$$

$$p_k = -\sqrt{2(n_k + \gamma)}\sin(q_k) \tag{3b}$$

$$n_k = \frac{1}{2}p_k^2 + \frac{1}{2}x_k^2 - \gamma \tag{3c}$$

Terms and Variables

Window Functions

- Compile initial and final values into concrete histogram bins corresponding to electronic states.
- Defined in terms of the Heaviside function

$$h(z) = \begin{cases} 1 & \text{if } z \geq 0 \\ 0 & \text{if } z < 0 \end{cases}$$

$$W_{N_k}(n_k) = \frac{1}{\Delta n} h\left(\frac{\Delta n}{2} - |n_k - N_k|\right) \tag{4}$$

- Limits $n_k \in [N_k - \Delta n/2,\ N_k + \Delta n/2]$.
- $\Delta n = 2\gamma$.
- The window function for a state k state is the product of such functions for each electronic degree of freedom.

Terms and Variables

Final Electronic State

- The final electronic states are assigned by:

$$N_k - \gamma \leq n_k \leq N_k + \gamma \tag{5a}$$

$$N_k \leq \frac{1}{2}x_k^2 + \frac{1}{2}p_k^2 \leq N_k + 2\gamma \tag{5b}$$

- They must be simultaneously met for all k states.
- The run is restarted if they don't.

Terms and Variables

Transition Probabilities

- The transition probabilities from initial to final state, $P_{f \leftarrow i}$, are calculated by multiplying the initial and final window functions, and dividing by the sum of the corresponding quantities for all possible final states.

$$P_{f \leftarrow i} = \frac{\left\langle \prod_{k=1}^{F} W_{\delta_{fk}}(n_k(t)) \cdot \prod_{k=1}^{F} W_{\delta_{ik}}(n_k(0)) \right\rangle}{\sum_{f=1}^{F} \left\langle \prod_{k=1}^{F} W_{\delta_{fk}}(n_k(t)) \cdot \prod_{k=1}^{F} W_{\delta_{ik}}(n_k(0)) \right\rangle} \tag{6}$$

Where:

- $\delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases}$.
- $\langle \cdots \rangle$ denotes Monte-Carlo (MC) averaging.

Terms and Variables

Transition Probabilities

- Sometimes problems require us to know whether the atom/molecule was reflected or transmitted, in such cases the transition probabilities are calculated by:

$$P^{a}_{f\leftarrow i} = \frac{\left\langle \prod_{k=1}^{F} W_{\delta_{fk}}(n_k(t)) \cdot \prod_{k=1}^{F} W_{\delta_{ik}}(n_k(0)) \right\rangle_a}{\sum_{a=r,\ t} \left(\sum_{f=1}^{F} \left\langle \prod_{k=1}^{F} W_{\delta_{fk}}(n_k(t)) \cdot \prod_{k=1}^{F} W_{\delta_{ik}}(n_k(0)) \right\rangle \right)_a} \tag{7}$$

Where:

- $r \equiv$ reflection.
- $t \equiv$ transmission.

Diabatic Hamiltonian in Cartesian Variables

$$H(\boldsymbol{P},\boldsymbol{R},\boldsymbol{p},\boldsymbol{x}) = \frac{\boldsymbol{P}^2}{2\mu} + \bar{H}(\boldsymbol{R}) \tag{8a}$$

$$+ \sum_{k<k'=1}^{F} \left\{ \begin{array}{c} \frac{1}{F}(H_{kk}(\boldsymbol{R}) - H_{k'k'}(\boldsymbol{R})) \cdot \left(\frac{1}{2}p_k^2 + \frac{1}{2}x_k^2 - \frac{1}{2}p_{k'}^2 - \frac{1}{2}x_{k'}^2 \right) \\ + H_{kk'}(\boldsymbol{R}) \cdot (p_k p_{k'} + x_k x_{k'}) \end{array} \right\}$$

$$\bar{H}(\boldsymbol{R}) = \frac{1}{F}\sum_{k=1}^{F} H_{kk}(\boldsymbol{R}) \tag{8b}$$

- Where H_{ij} is the ij^{th} element of the Hamiltonian matrix.

Diabatic Hamiltonian in Cartesian Variables

Equations of Motion

$$\dot{\boldsymbol{R}} = \frac{\boldsymbol{P}}{\mu} \tag{9a}$$

$$\dot{\boldsymbol{P}} = -\frac{\partial \bar{H}}{\partial \boldsymbol{R}} - \sum_{k<k'=1}^{F} \left\{ \begin{array}{r} \frac{1}{2F}\left(\frac{\partial H_{kk}}{\partial \boldsymbol{R}} - \frac{\partial H_{k'k'}}{\partial \boldsymbol{R}}\right)(p_k^2 + x_k^2 - p_{k'}^2 - x_{k'}^2) \\ + \frac{\partial H_{kk'}}{\partial \boldsymbol{R}}(p_k p_{k'} + x_k x_{k'}) \end{array} \right\} \tag{9b}$$

$$\dot{x}_i = \sum_{k<k'=1}^{F} \left\{ \frac{1}{2F}(H_{kk} - H_{k'k'})\frac{\partial(p_k^2 - p_{k'}^2)}{\partial p_i} + H_{kk'}\frac{\partial(p_k p_{k'})}{\partial p_i} \right\} \tag{9c}$$

$$\dot{p}_i = -\sum_{k<k'=1}^{F} \left\{ \frac{1}{2F}(H_{kk} - H_{k'k'})\frac{\partial(x_k^2 - x_{k'}^2)}{\partial x_i} + H_{kk'}\frac{\partial(x_k x_{k'})}{\partial x_i} \right\} \tag{9d}$$

Adiabatic Hamiltonian in Cartesian Variables

$$H(\boldsymbol{P},\boldsymbol{R},\boldsymbol{p},\boldsymbol{x}) = \frac{|\boldsymbol{P}+\nabla\boldsymbol{P}|^2}{2\mu} + \bar{E}(\boldsymbol{R}) \tag{10a}$$

$$+ \sum_{k<k'=1}^{F} \frac{1}{F}(E_k(\boldsymbol{R}) - E_{k'}(\boldsymbol{R})) \cdot \left(\frac{1}{2}p_k^2 + \frac{1}{2}x_k^2 - \frac{1}{2}p_{k'}^2 - \frac{1}{2}x_{k'}^2\right)$$

$$\bar{E}(\boldsymbol{R}) = \frac{1}{F}\sum_{k=1}^{F} E_k(\boldsymbol{R}) \tag{10b}$$

- Where E_k is the kk^{th} element of the adiabatic Hamiltonian matrix. This is a diagonal matrix with the eigenvalues of the diabatic one.

Adiabatic Hamiltonian in Cartesian Variables

$$\nabla \boldsymbol{P} \equiv \sum_{k<k'=1}^{F} \omega(\boldsymbol{R}) \cdot (p_k x_{k'} - p_{k'} x_k) \tag{10c}$$

$$\Delta \boldsymbol{P} \equiv \sum_{k<k'=1}^{F} \frac{\partial \omega(\boldsymbol{R})}{\partial \boldsymbol{R}} \cdot (p_k x_{k'} - p_{k'} x_k) \tag{10d}$$

$$\omega(\boldsymbol{R}) \equiv \frac{1}{2} \arctan\left(\frac{2H_{kk'}(\boldsymbol{R})}{H_{kk}(\boldsymbol{R}) - H_{k'k'}(\boldsymbol{R})}\right) \tag{10e}$$

Adiabatic Hamiltonian in Cartesian Variables

Equations of Motion

$$\dot{\boldsymbol{R}} = \frac{\boldsymbol{P} + \nabla \boldsymbol{P}}{\mu} \tag{11a}$$

$$\dot{\boldsymbol{P}} = -\frac{\boldsymbol{P} + \nabla \boldsymbol{P}}{\mu} \cdot \Delta \boldsymbol{P} - \frac{\partial \bar{E}}{\partial \boldsymbol{R}} \tag{11b}$$

$$- \sum_{k<k'=1}^{F} \frac{1}{2F} \left(\frac{\partial E_k}{\partial \boldsymbol{R}} - \frac{\partial E_{k'}}{\partial \boldsymbol{R}} \right) (p_k^2 + x_k^2 - p_{k'}^2 - x_{k'}^2)$$

$$\dot{x}_i = \frac{\boldsymbol{P} + \nabla \boldsymbol{P}}{\mu} \cdot \frac{\partial \nabla \boldsymbol{P}}{\partial p_i} + \sum_{k<k'=1}^{F} \frac{1}{2F} (E_k - E_{k'}) \frac{\partial (p_k^2 - p_{k'}^2)}{\partial p_i} \tag{11c}$$

$$\dot{p}_i = -\frac{\boldsymbol{P} + \nabla \boldsymbol{P}}{\mu} \cdot \frac{\partial \nabla \boldsymbol{P}}{\partial x_i} - \sum_{k<k'=1}^{F} \frac{1}{2F} (E_k - E_{k'}) \frac{\partial (x_k^2 - x_{k'}^2)}{\partial x_i} \tag{11d}$$

Single Avoided Crossing

Diabatic PES

- The diabatic PES were defined by Tully [2] as:

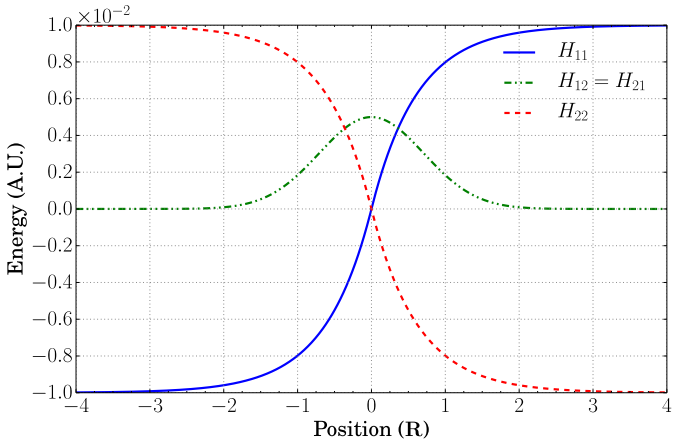
$$H_{11}(R) = \begin{cases} A\left(1 - e^{-BR}\right) & \text{if } R \geq 0 \\ -A\left(1 - e^{BR}\right) & \text{if } R < 0 \end{cases} \tag{12a}$$

$$H_{22}(R) = -H_{11}(R) \tag{12b}$$

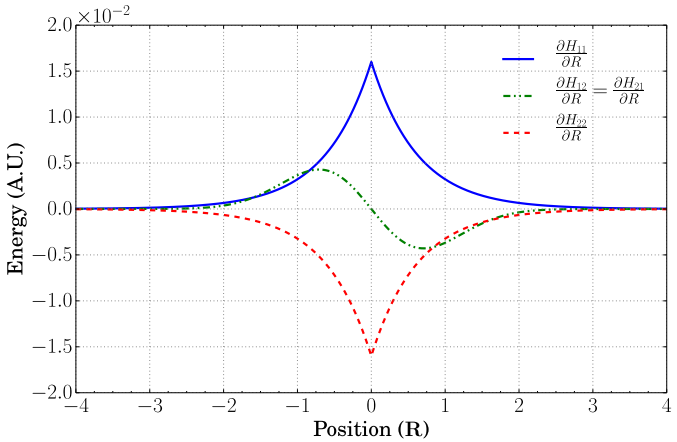
$$H_{12}(R) = H_{21}(R) = Ce^{-DR^2} \tag{12c}$$

- Where $A = 0.01,\ B = 1.6,\ C = 0.005,\ D = 1.$

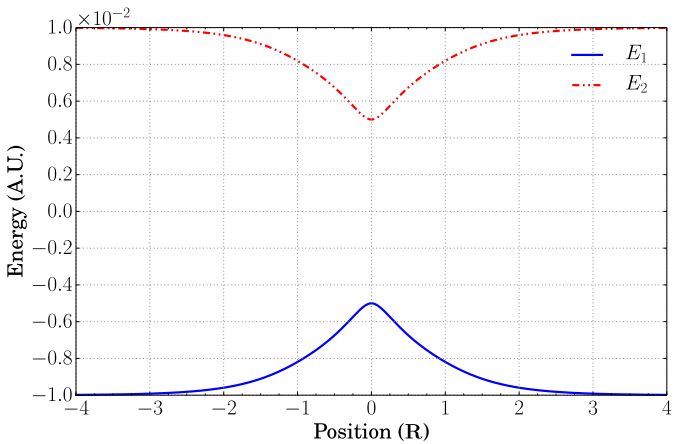
Single Avoided Crossing
PES Plots



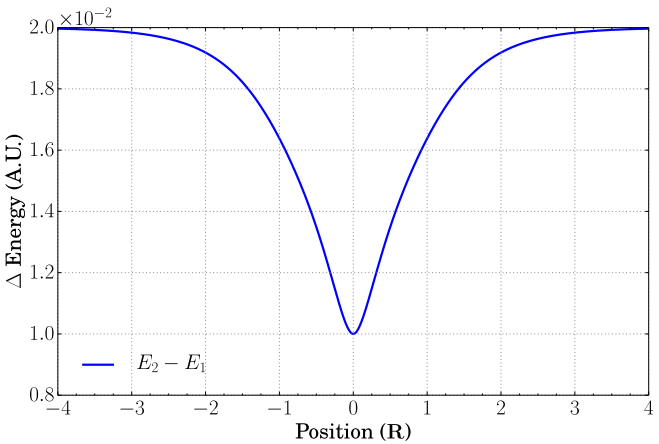
(a) Diabatic PES.



(b) Diabatic PES derivatives (DPES).



(c) Adiabatic PES (APES).



(d) ΔE between APES.

Figure 1 : PES.

Double Avoided Crossing

Diabatic PES

- The diabatic PES were defined by Tully [2] as:

$$H_{11}(R) = 0 \tag{13a}$$

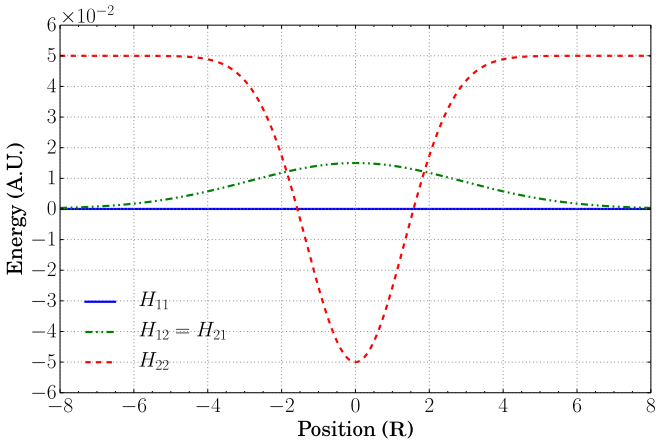
$$H_{22}(R) = -A\,e^{-BR^2} + E_0 \tag{13b}$$

$$H_{12}(R) = H_{21}(R) = Ce^{-DR^2} \tag{13c}$$

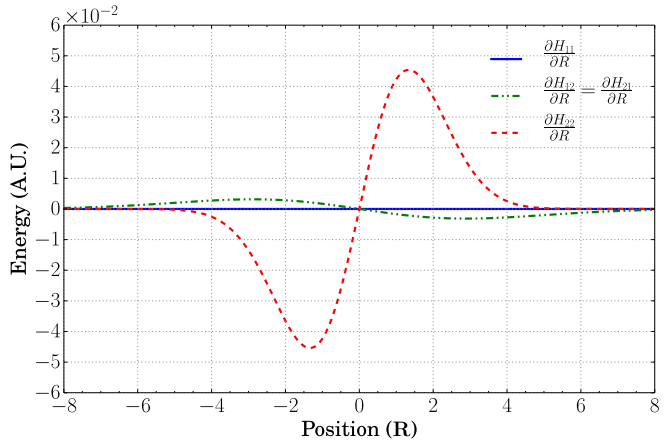
- Where $A = 0.1,\ B = 0.28,\ C = 0.015,\ D = 0.06,\ E_0 = 0.05.$

Double Avoided Crossing

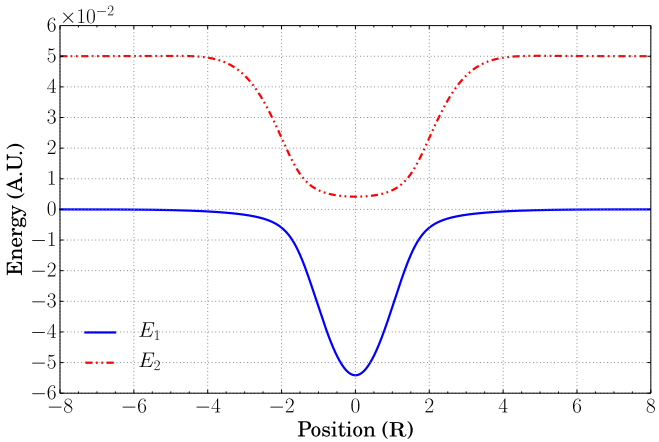
PES Plots



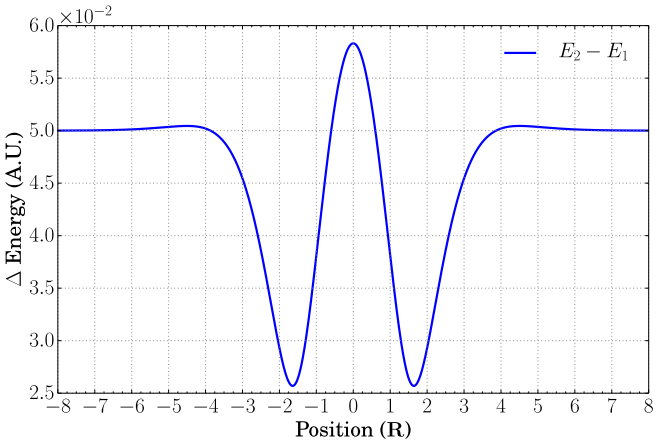
(a) Diabatic PES.



(b) Diabatic PES derivatives (DPES).



(c) Adiabatic PES (APES).



(d) ΔE between APES.

Figure 2 : PES.

Extended Coupling
Diabatic PES

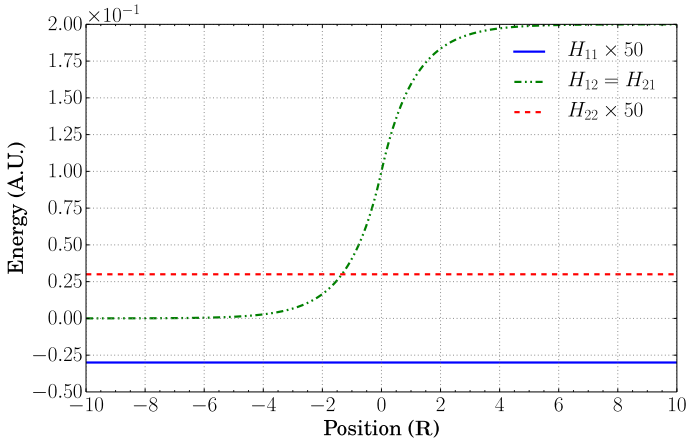
- In order to use the diabatic Hamiltonian the non-diagonal PES must vanish as $R \to \pm\infty$, so we will use the adiabatic version.

- The diabatic PES were defined by Tully [2] as:

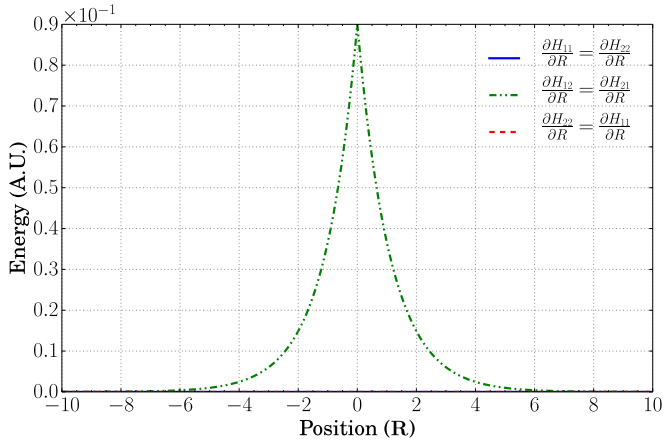
$$H_{11}(R) = -A \tag{14a}$$
$$H_{22}(R) = -H_{11} \tag{14b}$$
$$H_{12}(R) = H_{21}(R) = \begin{cases} B(2 - e^{-CR}) & \text{if } R \geq 0 \\ Be^{CR} & \text{if } R < 0 \end{cases} \tag{14c}$$

- Where $A = 6 \times 10^{-4}$, $B = 0.1$, $C = 0.9$.

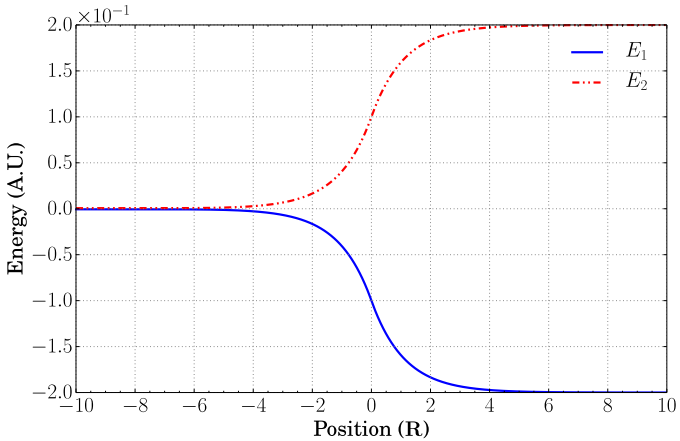
Extended Coupling
PES Plots



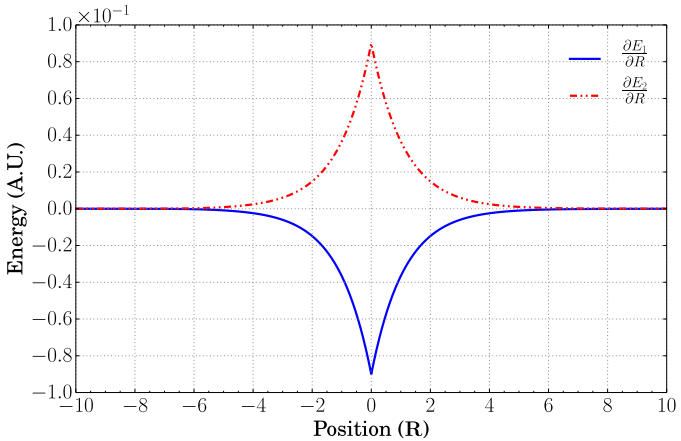
(a) Diabatic PES.



(b) Diabatic PES derivatives (DPES).



(c) Adiabatic PES (APES).



(d) APES derivatives.

Figure 3 : PES.

Spin-Boson
Generalities

- 1D lattice of M coupled oscillators.
- Bulk electronic states.
- The measured quantity is the difference in the probability of both states. When $i = 1$, $D(t) = P_{1\leftarrow 1} - P_{2\leftarrow 1}$; when $i = 2$, $D(t) = P_{1\leftarrow 2} - P_{2\leftarrow 2}$.

Spin-Boson
Diabatic PES

- The diabatic PES are defined as:

$$H_{11}(\boldsymbol{Q}) = V_0(\boldsymbol{Q}) + V_1(\boldsymbol{Q}) + \epsilon \tag{15a}$$
$$H_{22}(\boldsymbol{Q}) = V_0(\boldsymbol{Q}) - V_1(\boldsymbol{Q}) - \epsilon \tag{15b}$$
$$H_{12}(\boldsymbol{Q}) = H_{12}(\boldsymbol{Q}) = \Delta \tag{15c}$$
$$V_0(\boldsymbol{Q}) = \sum_{k=1}^{M} \frac{1}{2} m_k \omega_k^2 Q_k^2 \tag{15d}$$
$$V_1(\boldsymbol{Q}) = \sum_{k=1}^{M} c_k Q_k \tag{15e}$$

- Where $\omega \equiv$ oscillation frequency, $c \equiv$ coupling parameter, $Q \equiv$ position, $m \equiv$ mass.

Spin-Boson
Frequencies

- It was assumed that ω_k are uniformly distributed $\in [0.01\omega_c,\ 4\omega_c]$ [3], where ω_c is the 'characteristic frequency'.
- Frequencies contribute to the system's energy differently so each has a coupling parameter c_k.

$$c_k = \omega_k \sqrt{\alpha \Delta\omega m_k \exp\left(-\frac{\omega_k}{\omega_c}\right)} \tag{16a}$$

$$\Delta\omega = \frac{\omega_{max} - \omega_{min}}{M-1} \tag{16b}$$

- Where $\alpha \equiv$ Kondo parameter (coupling strength).

Spin-Boson
Initial Conditions

- Electronic initial conditions are set as before.
- Nuclear initial conditions are sampled from the bivariate Gaussian distribution:

$$\rho(\boldsymbol{P}, \boldsymbol{Q}) = \prod_{k=1}^{M} \exp\left(-a_k \frac{P_k^2}{2m_k}\right) \cdot \exp\left(-a_k \frac{1}{2} m_k \omega_k^2 \left[Q_k + \frac{c_k}{m_k \omega_k^2}\right]^2\right) \tag{17a}$$

$$a_k = \frac{2}{\omega_k} \tanh\left(\frac{\beta \omega_k}{2}\right) \tag{17b}$$

Methodology

- Obtaining equations of motion.
- Writing code.
- Testing code.
- Running problems.
- Plotting results.

Notation and Assumptions

- A reflection is denoted as R and a transmission as T.
- The initial state is denoted as i and the final state as f.
- A transition G from an initial state i to a final state f is denoted as $G_{f \leftarrow i}$.
- $h \equiv$ integration interval, $P_i \equiv$ initial momentum and $E_i \equiv$ mean initial energy.
- Unless otherwise mentioned: all calculations were carried out with 15000 Monte-Carlo repetitions (MC reps), $\gamma = 0.366$, all masses $\mu = m_k = 2000$, and all units are in atomic units.
- For the spin-boson model, it was assumed that the number of nuclei $= 100$ $(M = 100)$ and $\omega_c = 1$.

Generalities

- Scaling is linear with MC reps, value of h and number of cores.
- The value of h does not significantly affect the accuracy up to a threshold value, said threshold depends on the problem.

Paralellisation

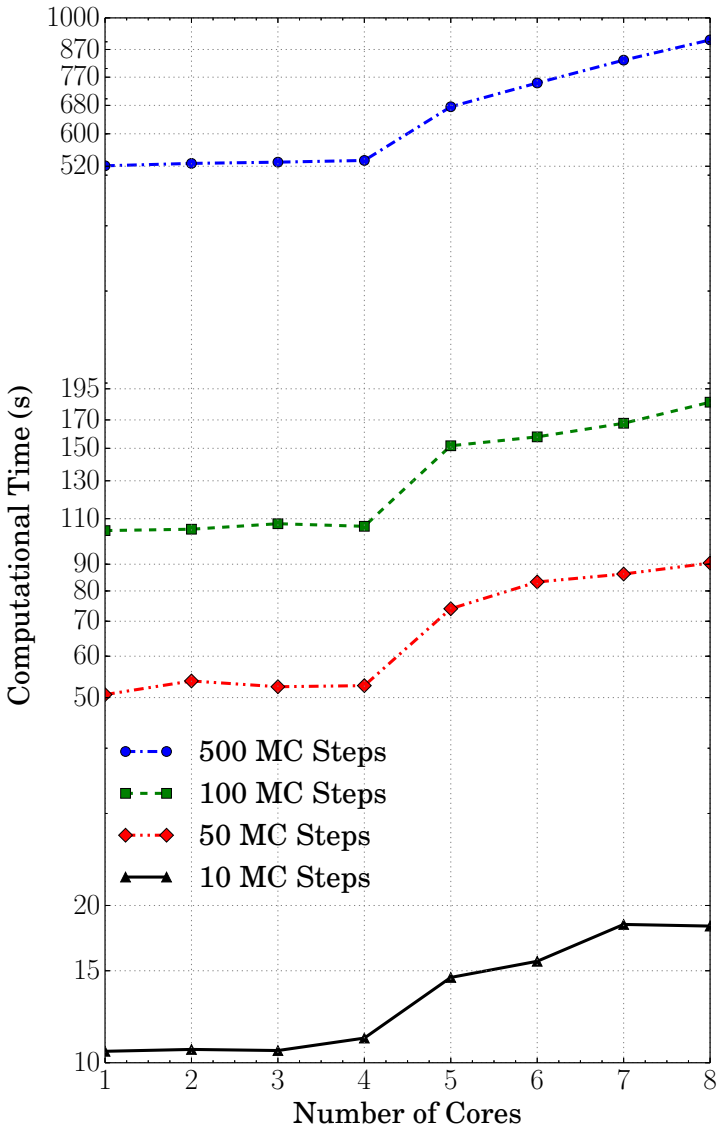
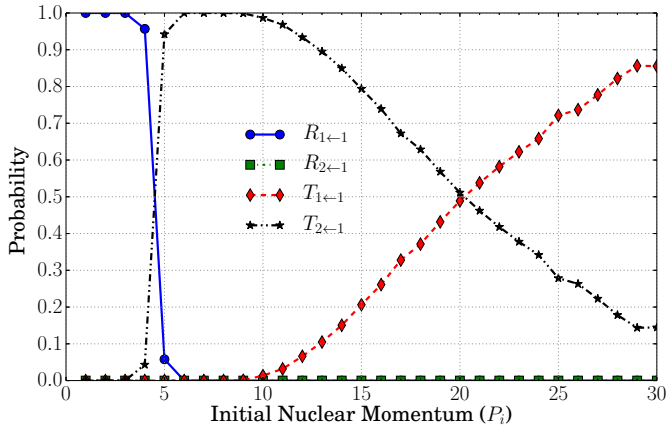
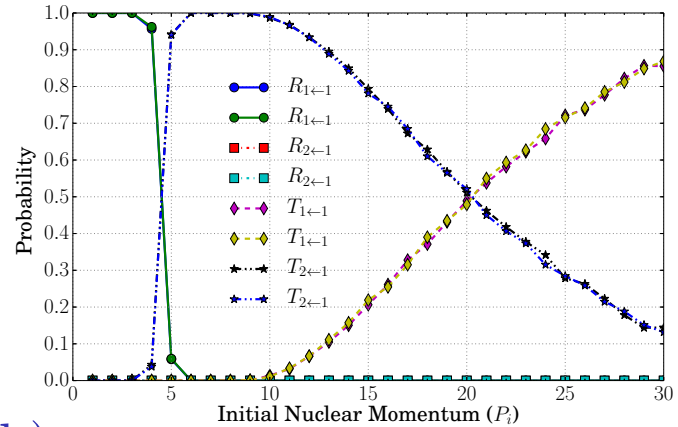


Figure 4 : Temporal scaling as a function of nuclei and MC reps. Scaling is directly proportional to the number of MC reps, and inversely proportional to the number of cores.

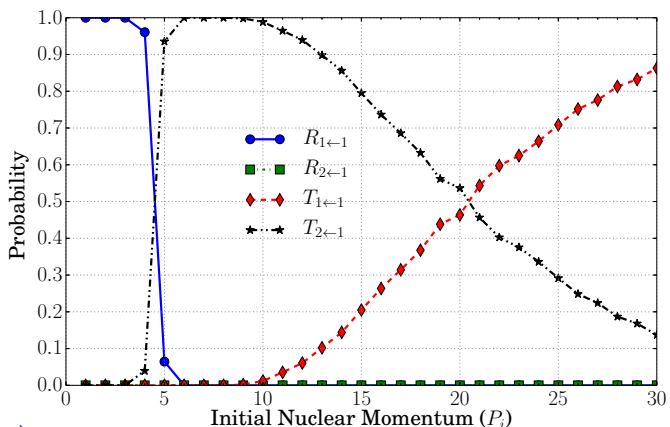
Single Avoided Crossing



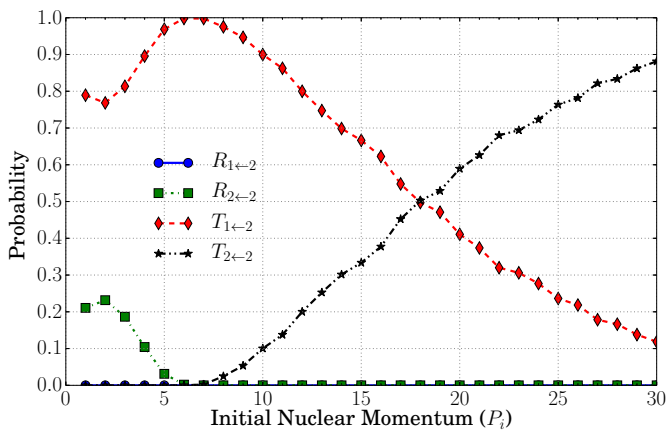
(a) $i = 1$, $h = (5P_i)^{-1}$.



(b) $i = 1$, comparison between $h = (5P_i)^{-1}$ (1^{st} in lengend) and $h = P_i^{-1}$.



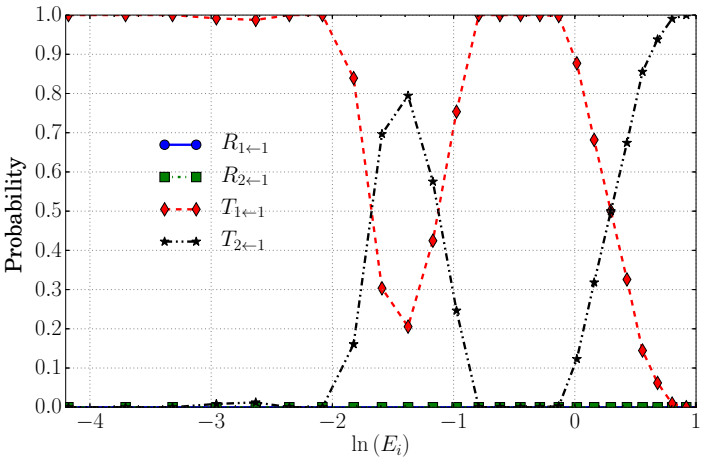
(c) Parallel calculations, 2 nuclei, $i = 1$, $h = (5P_i)^{-1}$.



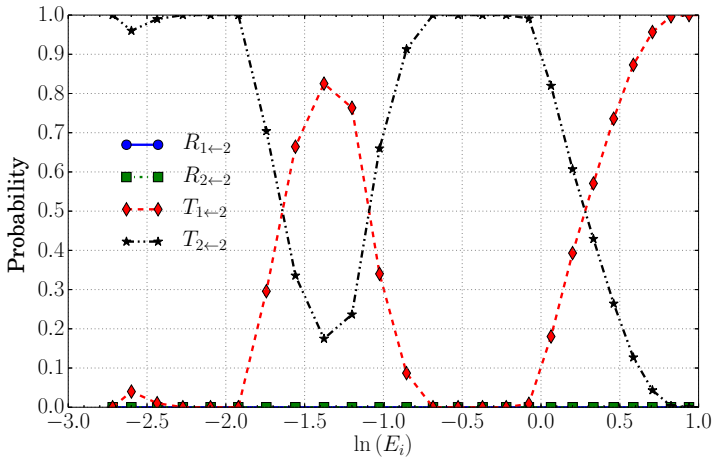
(d) $i = 2$, $h = (0.012P_i)^{-1}$.

Figure 5 : Transition Probabilities.

Double Avoided Crossing



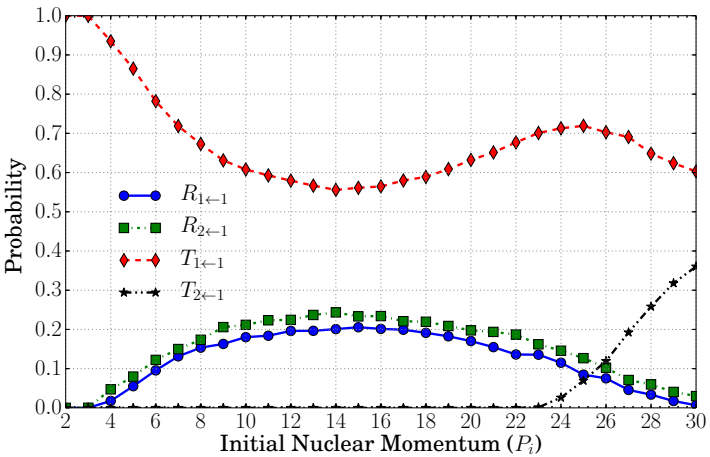
(a) $i = 1$, $h = (0.0125P_i)^{-1}$.



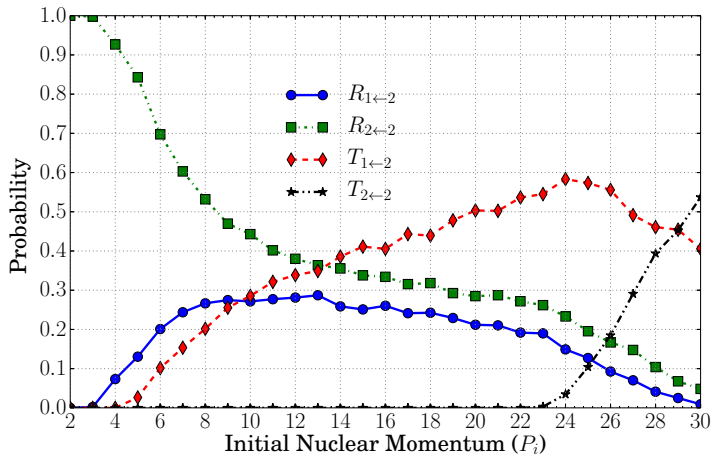
(b) $i = 2$, $h = (0.0125P_i)^{-1}$.

Figure 6 : Transition probabilities.

Extended Coupling



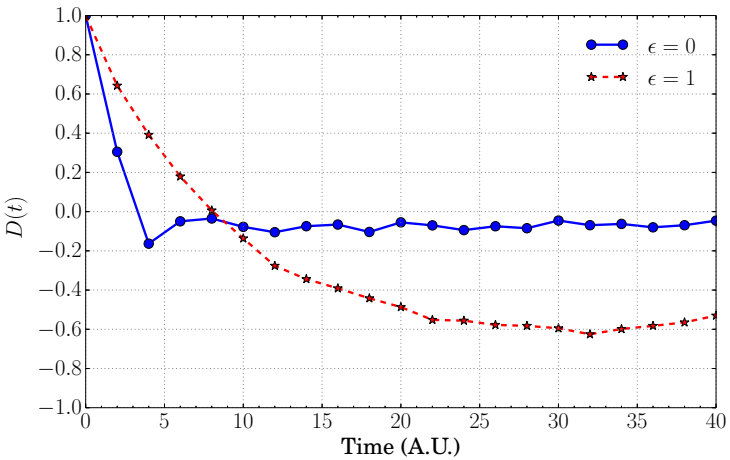
(a) $i = 1$, $h = (0.10125P_i)^{-1}$, 30000 MC reps.



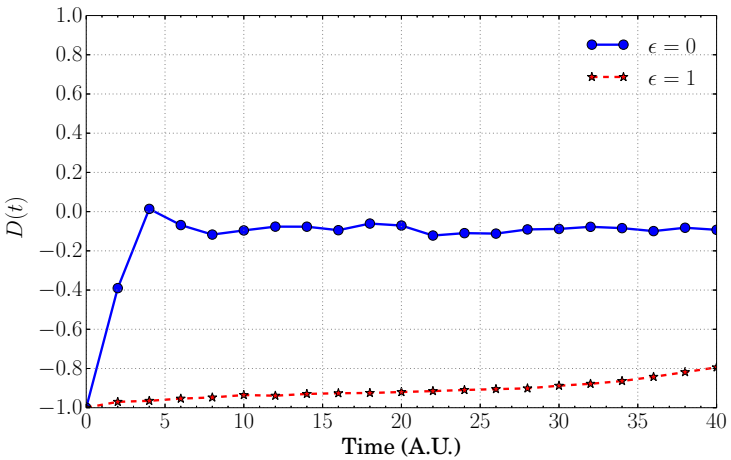
(b) $i = 2$, $h = (0.10125P_i)^{-1}$.

Figure 7 : Transition probabilities.

Condensed-Phase Spin-Boson Model



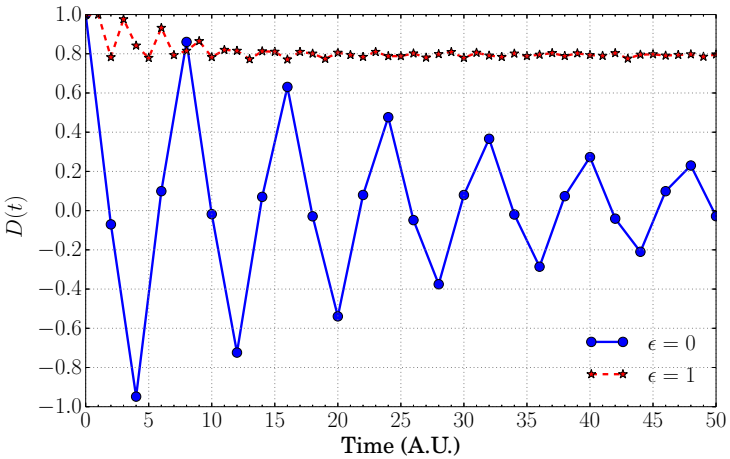
(a) $i = 1$, $h = 0.01$.



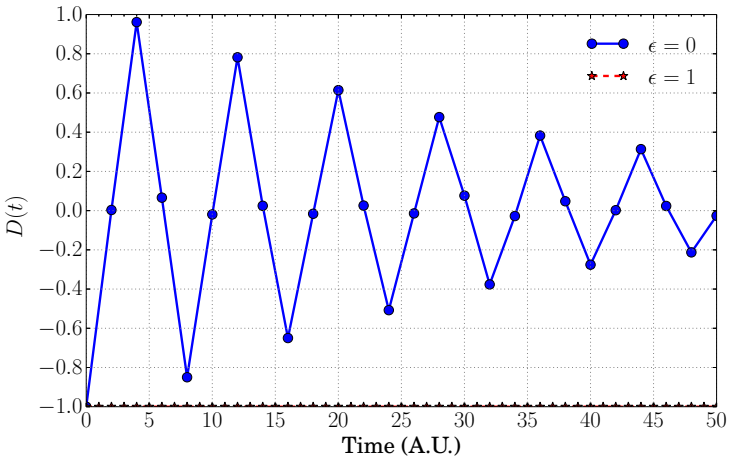
(b) $i = 2$. For the symmetric problem, $h = 0.1$ and MC reps $= 5000$. For the asymmetric one, $h = 0.01$ and MC reps $= 30000$.

Figure 8 : Symmetric ($\epsilon = 0$) and asymmetric ($\epsilon = 1$) problems. $\alpha = 0.09$, $\beta = 0.25$, $\Delta = (2.5)^{-1}$.

Condensed-Phase Spin-Boson Model



(a) $i = 1$. For the symmetric problem, $h = 0.1$ and MC reps $= 5000$. For the asymmetric one, $h = 0.05$ and MC reps $= 30000$.



(b) $i = 2$. For the symmetric problem, $h = 0.1$ and MC reps $= 5000$. For the asymmetric one, $h = 0.05$ and MC reps $= 30000$.

Figure 9 : Symmetric ($\epsilon = 0$) and asymmetric ($\epsilon = 1$) problems. $\alpha = 0.1$, $\beta = 12.5$, $\Delta = (2.5)^{-1}$.

Conclusion

- The model was successfully implemented in FORTRAN 2008.
- The code was validated with four simple model systems.
- New results for all four systems were obtained.
- The model's inner workings can be appreciated through the calculated trajectories found in the Appendix.

Future Work

- Modify the code so it can read input files. Trivial with `read(*,*)` and `module`.
- Make use of an adaptive integration algorithm. Trivial.
- Generalise the code so it can be applied to arbitrary sytems. Trivial with `read(*,*)` and `module`.
- Eliminate the need for analytic PES. Not trivial.
- Apply the model to real systems. Not trivial.

References

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[2] Tully, John C. *The Journal of Chemical Physics*, vol. 93, no. 2, pp. 1061–1071, 1990.

[3] Stock, Gerhard. A semiclassical self-consistent-field approach to dissipative dynamics: The spin–boson problem. *The Journal of Chemical Physics*, vol 103, no. 4, pp. 1561–1573, 1995.

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My friends...

My family...

Cheers!

?

Classical Mechanics
Newtonian Fromalism

$$F = ma = m\frac{\mathrm{d}^2 f(\mathbf{x}, t)}{\mathrm{d}t^2} \tag{18a}$$

$$F = -\nabla V \tag{18b}$$

- Formulated around vectors.
- Rapidly increasing complexity.
- Non-generalised coordinates.

Classical Mechanics
Lagrangian Formalism

$$L = T - V \tag{19a}$$

$$\mathcal{S}[\mathbf{q}(t)] = \int_{t_1}^{t_2} L[\mathbf{q}(t), \dot{\mathbf{q}}(t), t]\mathrm{d}t \tag{19b}$$

$$\frac{\partial L}{\partial q_j} = \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial L}{\partial \dot{q}_j}\right) \tag{19c}$$

- Where $T \equiv$ kinetic energy, $V \equiv$ potential energy, $q_j \equiv$ generalised position, $\dot{q}_j = \frac{\mathrm{d}q_j}{\mathrm{d}t} \equiv$ generalised velocity.
- Partial differential equations.
- Less geometrically-driven than its Newtonian counterpart.
- Non-trivial solutions.

Classical Mechanics
Hamiltonian Formalism

$$H = \sum_j \dot{q}_j \frac{\partial L}{\partial \dot{q}_j} - L = \sum_j \dot{q}_j p_j - L \tag{20a}$$

$$H = T + V \tag{20b}$$

$$\frac{\partial H}{\partial q_j} = -\dot{p}_j \quad , \quad \frac{\partial H}{\partial p_j} = \dot{q}_j \quad , \quad \frac{\partial H}{\partial t} = -\frac{\partial L}{\partial t} \tag{20c}$$

- Where $p_j \equiv$ generalised momentum.
- Ordinary differential equation systems.
- Trivial solutions.

Quantum Mechanics

$$E\Psi = \hat{H}\Psi \tag{21a}$$

$$\hat{H} = -\frac{\hbar}{2\mu}\nabla^2 + V(\boldsymbol{r}) \tag{21b}$$

$$i\hbar\frac{\partial}{\partial t}\Psi = \hat{H}\Psi \tag{22a}$$

$$\hat{H} = -\frac{\hbar}{2\mu}\nabla^2 + V(\boldsymbol{r}, t) \tag{22b}$$

Diabatic Hamiltonian in Cartesian Variables

$F = 2$

$$
\begin{aligned}
H(\boldsymbol{P}, \boldsymbol{R}, \boldsymbol{p}, \boldsymbol{x}) = & \frac{\boldsymbol{P}^2}{2\mu} + \frac{1}{2}(H_{11}(\boldsymbol{R}) + H_{22}\boldsymbol{R}) \\
& + \frac{1}{2}(H_{11}(\boldsymbol{R}) - H_{22}(\boldsymbol{R})) \cdot \left(\frac{1}{2}p_1^2 + \frac{1}{2}x_1^2 - \frac{1}{2}p_2^2 - \frac{1}{2}x_2^2 \right) \\
& + H_{12}(\boldsymbol{R}) \cdot (p_1 p_2 + x_1 x_2)
\end{aligned} \tag{23}
$$

Diabatic Hamiltonian in Cartesian Variables

Equations of Motion ($F = 2$)

$$\dot{\boldsymbol{R}} = \frac{\boldsymbol{P}}{\mu} \tag{24a}$$

$$\dot{\boldsymbol{P}} = -\frac{1}{2}\left(\frac{\partial H_{11}}{\partial \boldsymbol{R}} + \frac{\partial H_{22}}{\partial \boldsymbol{R}}\right) - \frac{1}{4}\left(\frac{\partial H_{11}}{\partial \boldsymbol{R}} - \frac{\partial H_{22}}{\partial \boldsymbol{R}}\right)(p_1^2 + x_1^2 - p_2^2 - x_2^2)$$
$$- \frac{\partial H_{12}}{\partial \boldsymbol{R}}(p_1 p_2 + x_1 x_2) \tag{24b}$$

$$\dot{x}_1 = \frac{1}{2} p_1 (H_{11} - H_{22}) + p_2 H_{12} \tag{24c}$$

$$\dot{p}_1 = -\frac{1}{2} x_1 (H_{11} - H_{22}) - x_2 H_{12} \tag{24d}$$

$$\dot{x}_2 = -\frac{1}{2} p_2 (H_{11} - H_{22}) + p_1 H_{12} \tag{24e}$$

$$\dot{p}_2 = \frac{1}{2} x_2 (H_{11} - H_{22}) - x_1 H_{12} \tag{24f}$$

Adiabatic Hamiltonian in Cartesian Variables

$F = 2$

$$H(\boldsymbol{P}, \boldsymbol{R}, \boldsymbol{p}, \boldsymbol{x}) = \frac{|\boldsymbol{P} + \nabla \boldsymbol{P}|^2}{2\mu} + \frac{1}{2}(E_1 + E_2) \tag{25}$$
$$+ \frac{1}{2}(E_1(\boldsymbol{R}) - E_2(\boldsymbol{R})) \cdot \left(\frac{1}{2}p_1^2 + \frac{1}{2}x_1^2 - \frac{1}{2}p_2^2 - \frac{1}{2}x_2^2 \right)$$

Adiabatic Hamiltonian in Cartesian Variables

Equations of Motion ($F = 2$)

$$\dot{\boldsymbol{R}} = \frac{\boldsymbol{P}}{\mu} + \frac{1}{2\mu} \arctan\left(\frac{2H_{12}}{H_{11} - H_{22}}\right)(p_1 x_2 - p_2 x_1) \tag{26a}$$

$$\dot{\boldsymbol{P}} = -\left[\frac{\boldsymbol{P}}{\mu} + \frac{1}{2\mu} \arctan\left(\frac{2H_{12}}{H_{11} - H_{22}}\right)(p_1 x_2 - p_2 x_1)\right] \tag{26b}$$
$$\times \frac{\left[\frac{\partial H_{12}}{\partial \boldsymbol{R}}(H_{11} - H_{22}) + H_{12}\left(\frac{\partial H_{22}}{\partial \boldsymbol{R}} - \frac{\partial H_{11}}{\partial \boldsymbol{R}}\right)\right](p_1 x_2 - p_2 x_1)}{4H_{12}^2 + (H_{11} - H_{22})^2}$$
$$- \frac{1}{4}\left(\frac{\partial E_1}{\partial \boldsymbol{R}} - \frac{\partial E_2}{\partial \boldsymbol{R}}\right)(p_1^2 + x_1^2 - p_2^2 - x_2^2) - \frac{1}{2}\left(\frac{\partial E_1}{\partial \boldsymbol{R}} + \frac{\partial E_2}{\partial \boldsymbol{R}}\right)$$

$$\dot{x}_1 = \left[\frac{\boldsymbol{P}}{2\mu} + \frac{1}{4\mu} \arctan\left(\frac{2H_{12}}{H_{11} - H_{22}}\right)(p_1 x_2 - p_2 x_1)\right]$$
$$\times x_2 \arctan\left(\frac{2H_{12}}{H_{11} - H_{22}}\right) + \frac{p_1}{2}(E_1 - E_2) \tag{26c}$$

Adiabatic Hamiltonian in Cartesian Variables

Equations of Motion ($F = 2$)

$$\dot{p}_1 = \left[\frac{\boldsymbol{P}}{2\mu} + \frac{1}{4\mu}\arctan\left(\frac{2H_{12}}{H_{11}-H_{22}}\right)(p_1x_2 - p_2x_1)\right] \times p_2 \arctan\left(\frac{2H_{12}}{H_{11}-H_{22}}\right) - \frac{x_1}{2}(E_1 - E_2) \tag{26d}$$

$$\dot{x}_2 = -\left[\frac{\boldsymbol{P}}{2\mu} + \frac{1}{4\mu}\arctan\left(\frac{2H_{12}}{H_{11}-H_{22}}\right)(p_1x_2 - p_2x_1)\right] \times x_1 \arctan\left(\frac{2H_{12}}{H_{11}-H_{22}}\right) - \frac{p_2}{2}(E_1 - E_2) \tag{26e}$$

$$\dot{p}_2 = -\left[\frac{\boldsymbol{P}}{2\mu} + \frac{1}{4\mu}\arctan\left(\frac{2H_{12}}{H_{11}-H_{22}}\right)(p_1x_2 - p_2x_1)\right] \times p_2 \arctan\left(\frac{2H_{12}}{H_{11}-H_{22}}\right) + \frac{x_2}{2}(E_1 - E_2) \tag{26f}$$

Single Avoided Crossing
Diabatic PES Derivatives (DPES)

$$\frac{\partial H_{11}}{\partial R} = \begin{cases} ABe^{-BR} & \text{if } R \geq 0 \\ ABe^{BR} & \text{if } R < 0 \end{cases} \tag{27a}$$

$$\frac{\partial H_{22}}{\partial R} = -\frac{\partial H_{11}}{\partial R} \tag{27b}$$

$$\frac{\partial H_{12}}{\partial R} = \frac{\partial H_{21}}{\partial R} = -2CDe^{-DR^2}R \tag{27c}$$

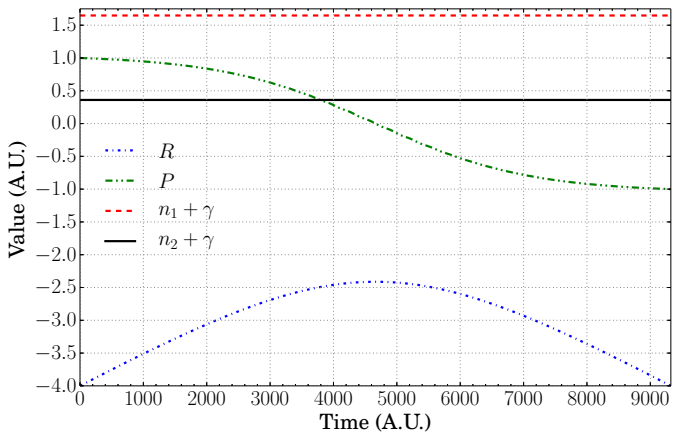
Single Avoided Crossing
Adiabatic PES (APES)

$$E_1 = -e^{-DR^2}\sqrt{C^2 + e^{2DR^2}\begin{cases} A^2(1-e^{-BR})^2 & \text{if } R \geq 0 \\ A^2(1-e^{BR})^2 & \text{if } R < 0 \end{cases}} \tag{28a}$$

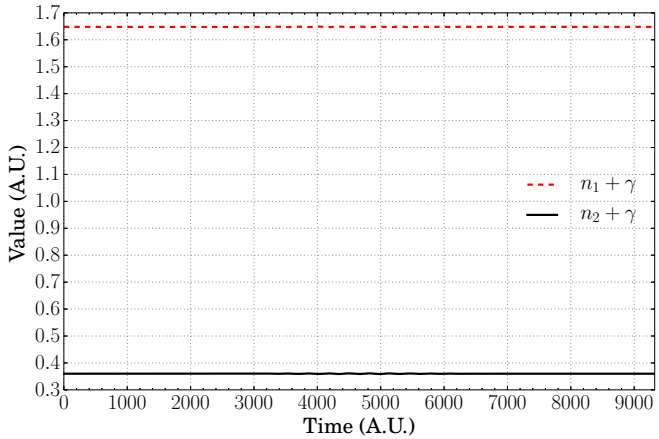
$$E_2 = -E_1 \tag{28b}$$

Single Avoided Crossing

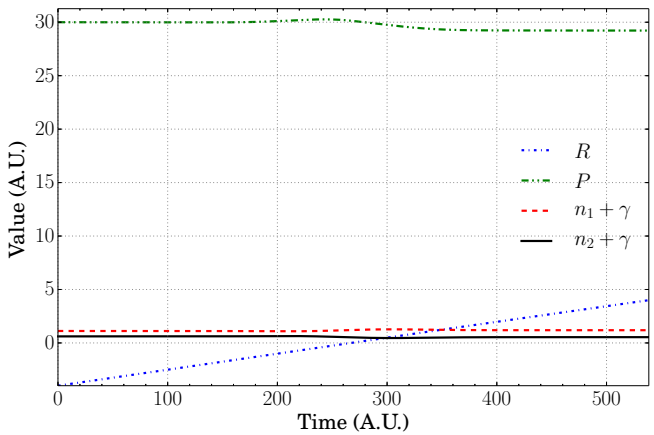
Sample Trajectories ($i = 1$).



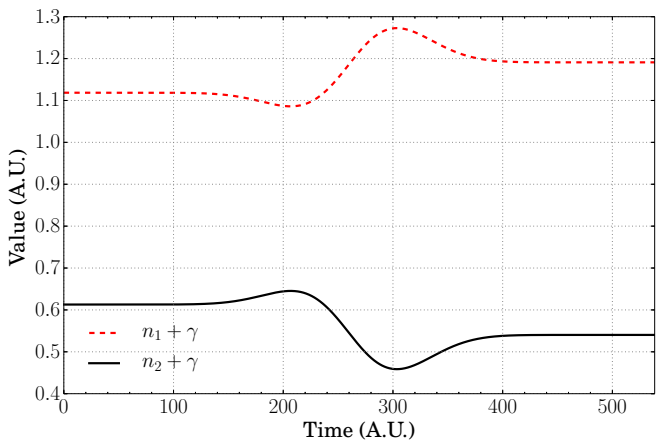
(a) $R_{1\leftarrow 1}$.



(b) $R_{1\leftarrow 1}$, zoom into n_1, n_2.



(c) $T_{1\leftarrow 1}$.

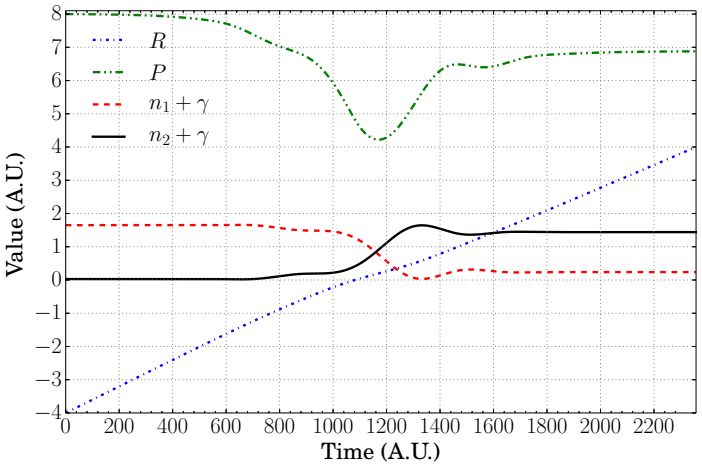


(d) $T_{1\leftarrow 1}$, zoom into n_1, n_2.

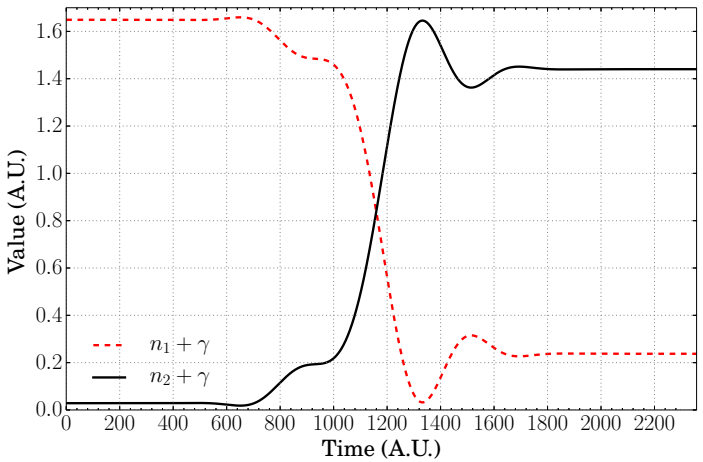
Figure 10 : $i = 1$, sample trajectories.

Single Avoided Crossing

Sample Trajectories ($i = 1$).



(a) $T_{2\leftarrow 1}$.

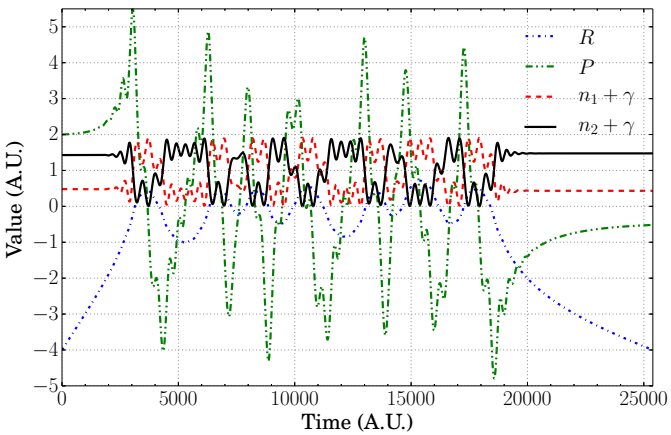


(b) $T_{2\leftarrow 1}$, zoom into n_1, n_2.

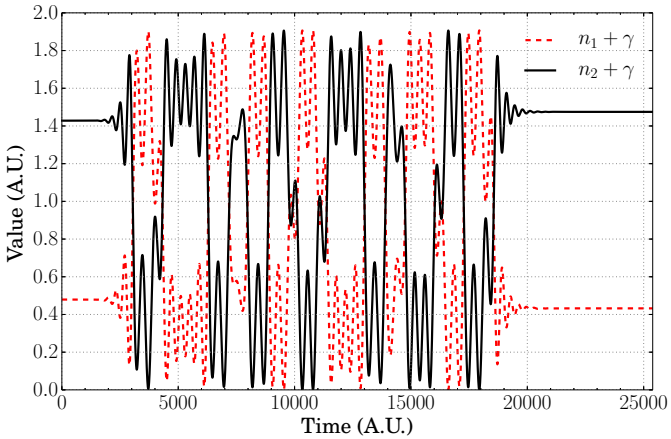
Figure 11 : $i = 1$, sample trajectories.

Single Avoided Crossing

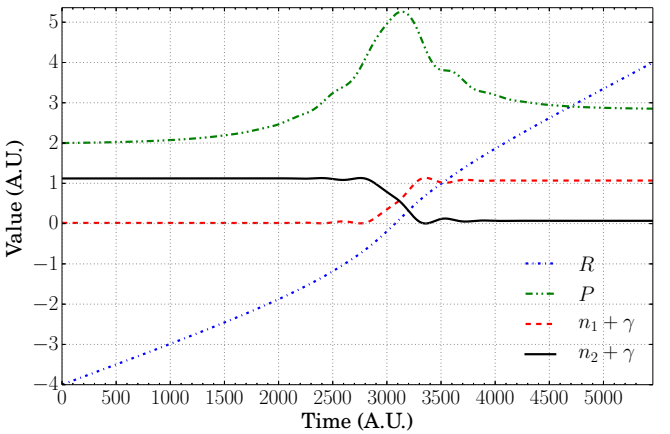
Sample Trajectories ($i = 2$).



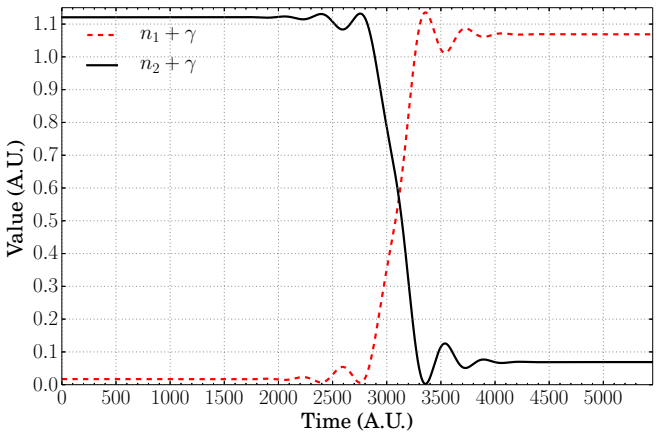
(a) $R_{2\leftarrow 2}$.



(b) $R_{2\leftarrow 2}$, zoom into n_1, n_2.



(c) $T_{1\leftarrow 2}$.

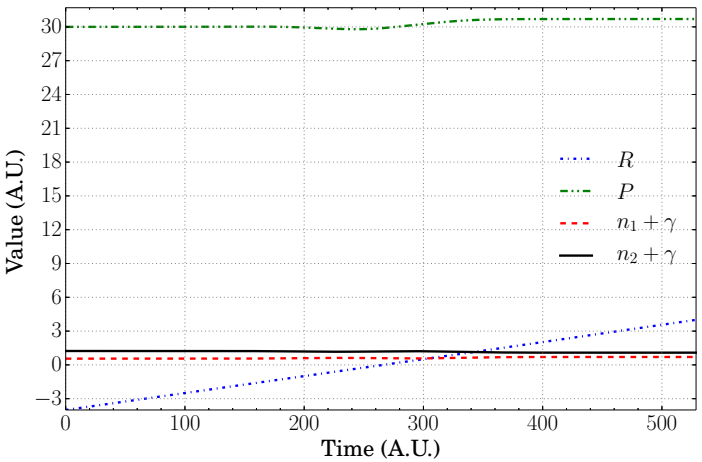


(d) $T_{1\leftarrow 2}$, zoom into n_1, n_2.

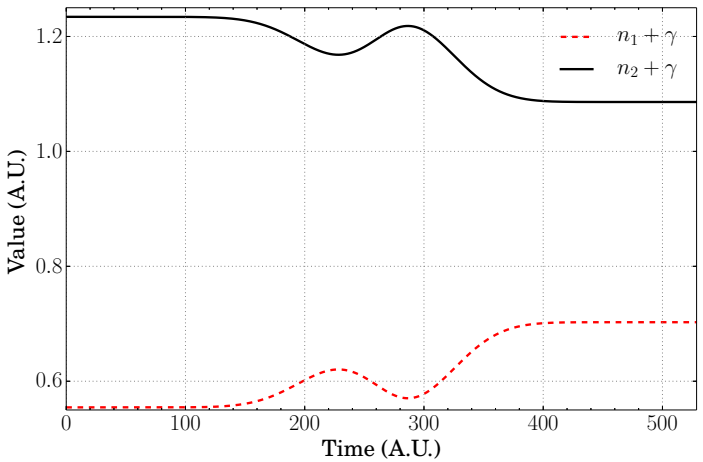
Figure 12 : $i = 2$, sample trajectories.

Single Avoided Crossing

Sample Trajectories ($i = 2$).



(a) $T_{2\leftarrow 2}$.



(b) $T_{2\leftarrow 2}$, zoom a n_1, n_2.

Figure 13 : $i = 2$, sample trajectories.

Double Avoided Crossing

Diabatic PES Derivatives (DPES)

$$\frac{\partial H_{11}}{\partial R} = 0 \tag{29a}$$

$$\frac{\partial H_{22}}{\partial R} = 2ABe^{-BR^2}R \tag{29b}$$

$$\frac{\partial H_{12}}{\partial R} = \frac{\partial H_{21}}{\partial R} = -2CDe^{-DR^2}R \tag{29c}$$

Double Avoided Crossing

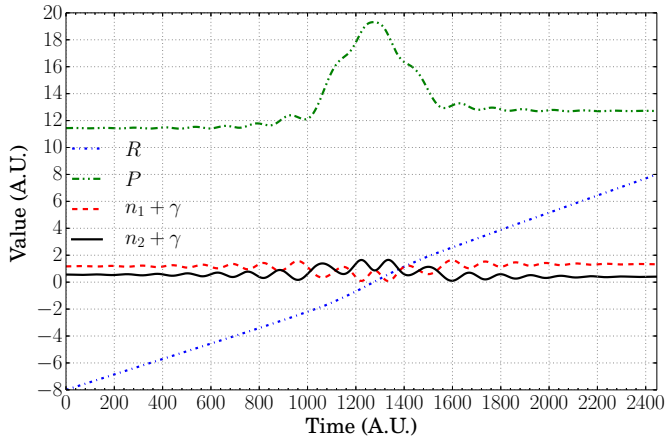
Adiabatic PES (APES)

$$E_1 = \frac{1}{2} e^{-(B+D)R^2} \left(- A e^{DR^2} + e^{(B+D)R^2} E_0 - \sqrt{4C^2 e^{2BR^2} + e^{2DR^2} \left(A - e^{BR^2} E_0 \right)^2} \right) \tag{30a}$$

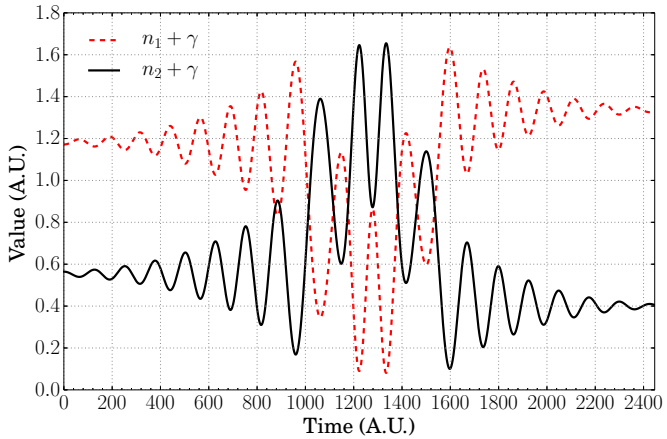
$$E_2 = \frac{1}{2} e^{-(B+D)R^2} \left(- A e^{DR^2} + e^{(B+D)R^2} E_0 + \sqrt{4C^2 e^{2BR^2} + e^{2DR^2} \left(A - e^{BR^2} E_0 \right)^2} \right) \tag{30b}$$

Double Avoided Crossing

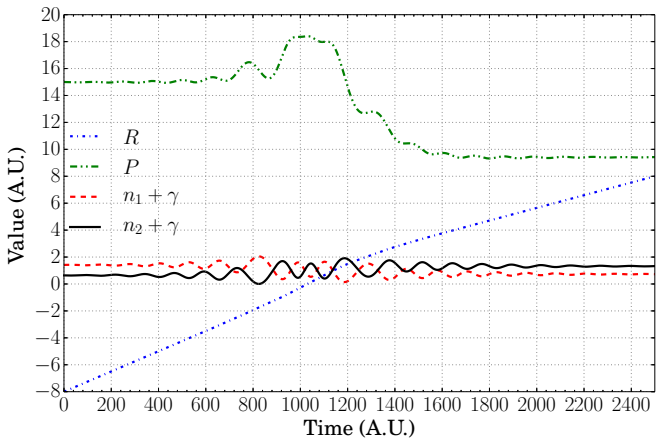
Sample Trajectories ($i = 1$).



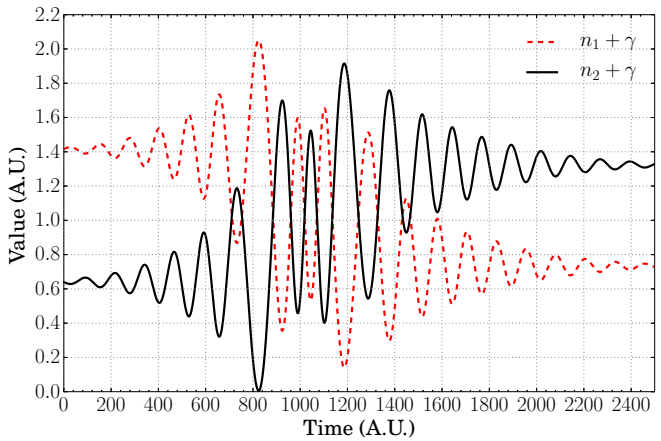
(a) $T_{1\leftarrow 1}$.



(b) $T_{1\leftarrow 1}$, zoom into n_1, n_2.



(c) $T_{2\leftarrow 1}$.

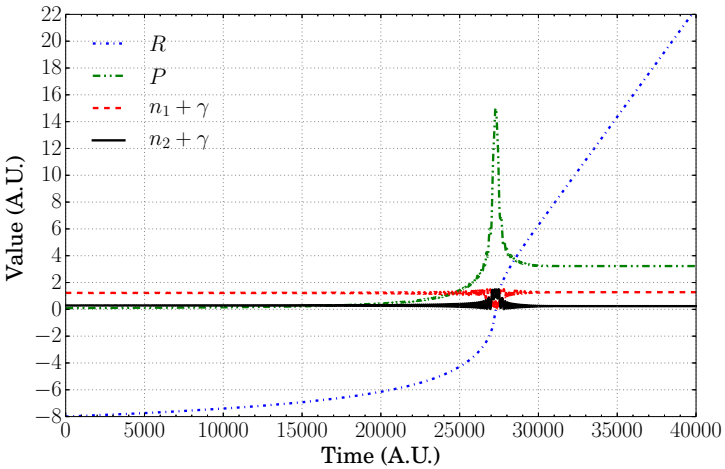


(d) $T_{2\leftarrow 1}$, zoom into n_1, n_2.

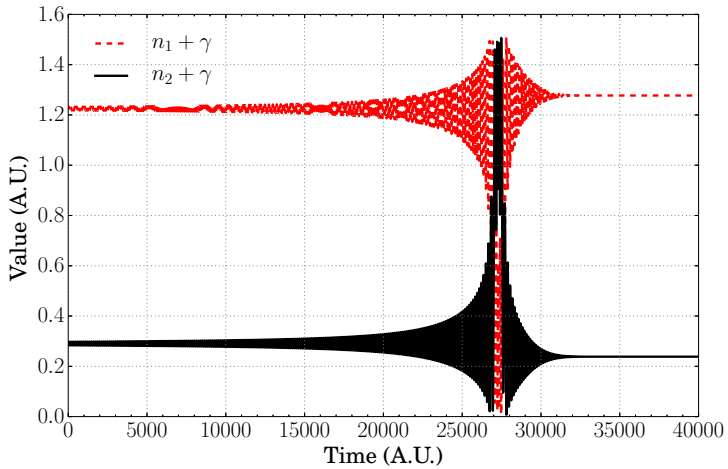
Figure 14 : $i = 1$, sample trajectories.

Double Avoided Crossing

Sample Trajectories ($i = 1$).



(a) Low nuclear momentum.

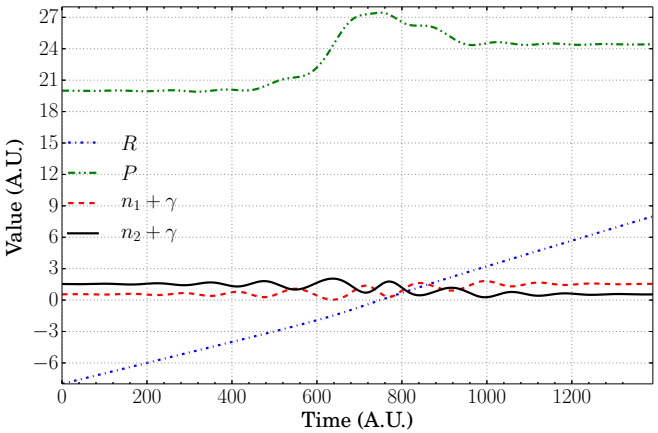


(b) Low nuclear momentum, zoom into n_1, n_2.

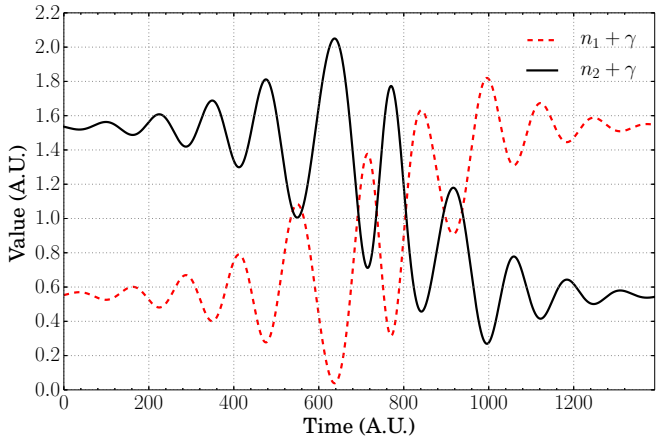
Figure 15 : $i = 1$, trajectory examples.

Double Avoided Crossing

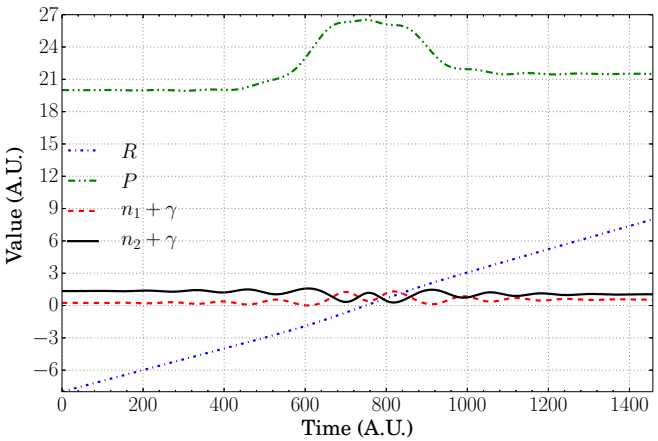
Sample Trajectories ($i = 2$).



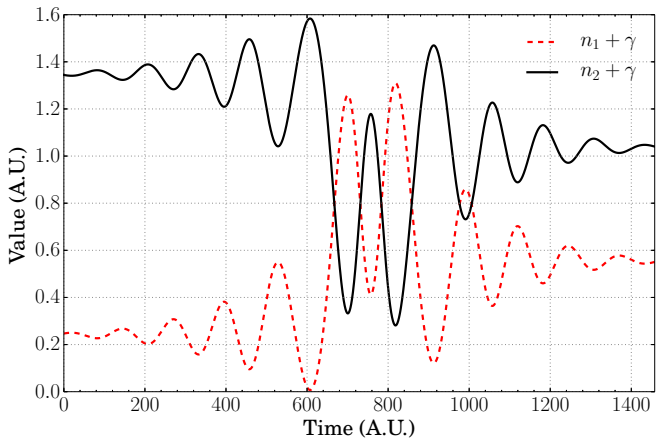
(a) $T_{1\leftarrow 2}$.



(b) $T_{1\leftarrow 2}$, zoom into n_1, n_2.



(c) $T_{2\leftarrow 2}$.

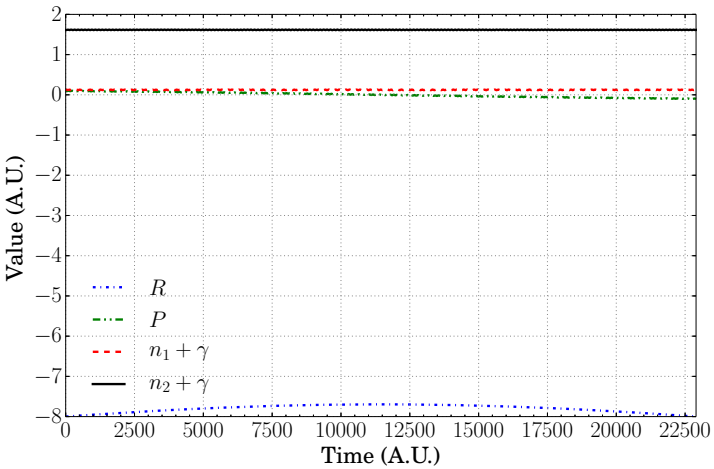


(d) $T_{2\leftarrow 2}$, zoom into n_1, n_2.

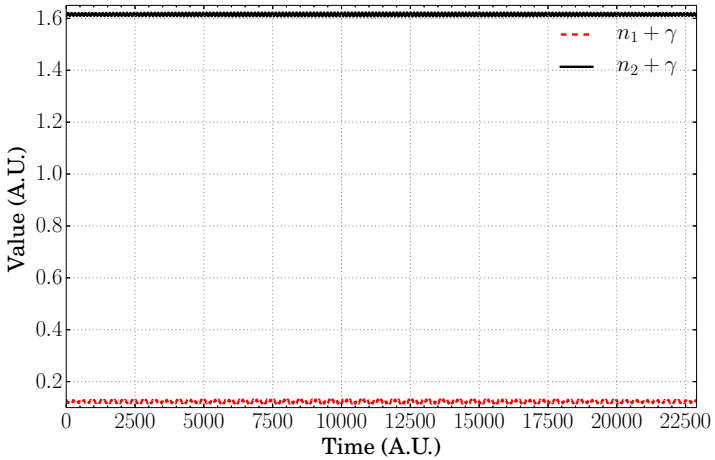
Figure 16 : $i = 2$, trajectory examples.

Double Avoided Crossing

Sample Trajectories ($i = 2$).



(a) Low nuclear momentum.



(b) Low nuclear momentum, zoom into n_1, n_2.

Figure 17 : $i = 2$, trajectory examples.

Extended Coupling
Diabatic PES Derivatives (DPES)

$$\frac{\partial H_{11}}{\partial R} = \frac{\partial H_{22}}{\partial R} = 0 \tag{31a}$$

$$\frac{\partial H_{12}}{\partial R} = \frac{\partial H_{21}}{\partial R} = \begin{cases} BCe^{-CR} & \text{if } R \geq 0 \\ BCe^{CR} & \text{if } R < 0 \end{cases} \tag{31b}$$

Extended Coupling
Adiabatic PES (APES)

$$E_1 = -\sqrt{A^2 + \begin{cases} B^2(2 - e^{-CR})^2 & \text{if } R \geq 0 \\ B^2 e^{2CR} & \text{if } R < 0 \end{cases}} \tag{32a}$$

$$E_2 = -E_1 \tag{32b}$$

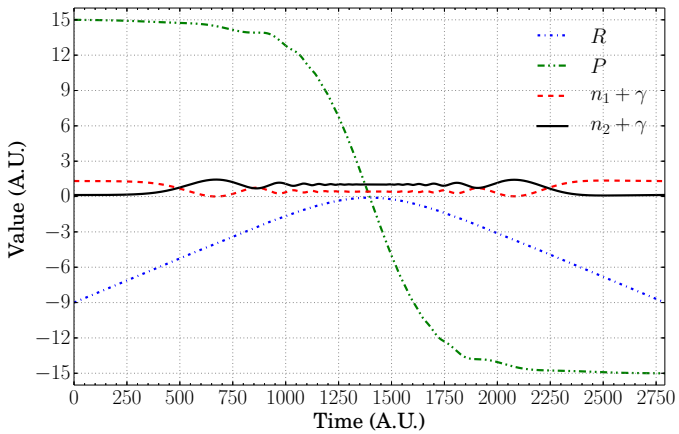
Extended Coupling
Derivatives of the APES (DAPES)

$$\frac{\partial E_1}{\partial R} = \begin{cases} -\dfrac{B^2 C e^{-2CR}\left(2e^{CR}-1\right)}{\sqrt{A^2+B^2\left(e^{-CR}-2\right)^2}} & \text{if } R \geq 0 \\ -\dfrac{B^2 C e^{2CR}}{\sqrt{A^2+B^2 e^{2CR}}} & \text{if } R < 0 \end{cases} \tag{33a}$$

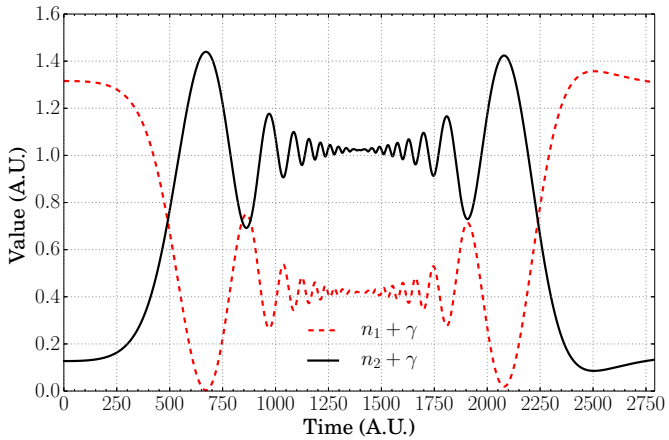
$$\frac{\partial E_2}{\partial R} = -\frac{\partial E_1}{\partial R} \tag{33b}$$

Extended Coupling

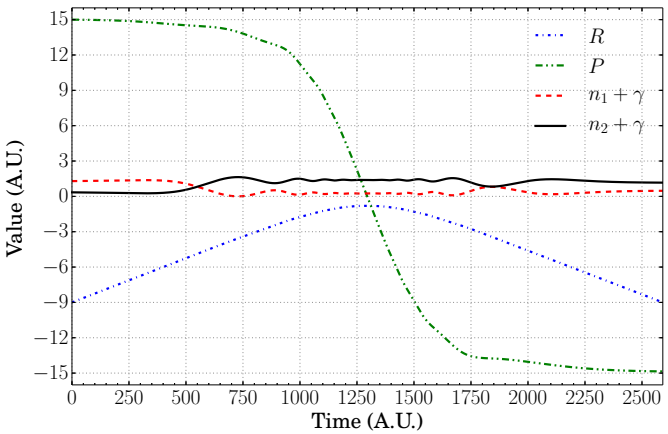
Sample Trajectories ($i = 1$).



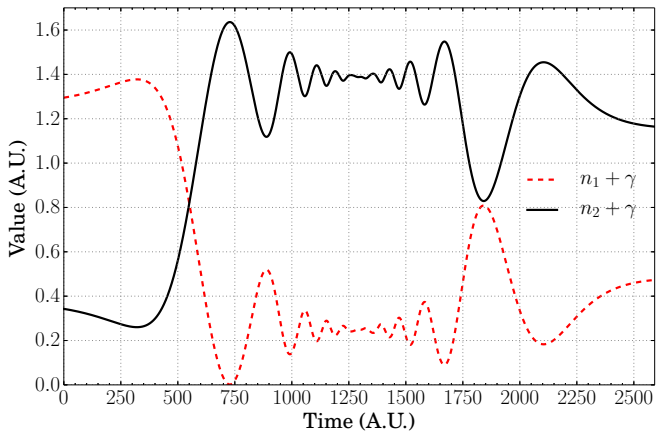
(a) $R_{1\leftarrow 1}$.



(b) $R_{1\leftarrow 1}$, zoom into n_1, n_2.



(c) $R_{2\leftarrow 1}$.

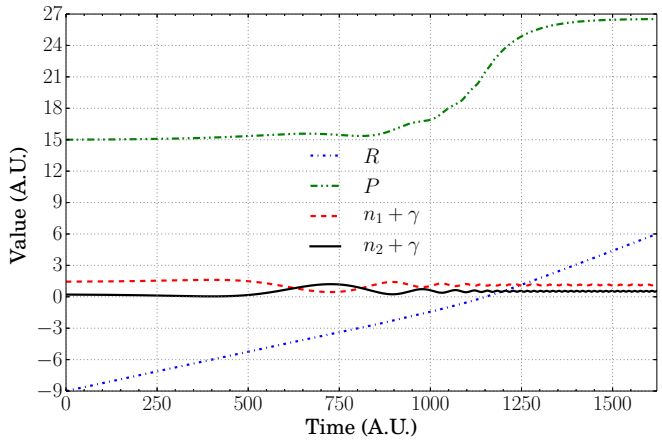


(d) $R_{2\leftarrow 1}$, zoom into n_1, n_2.

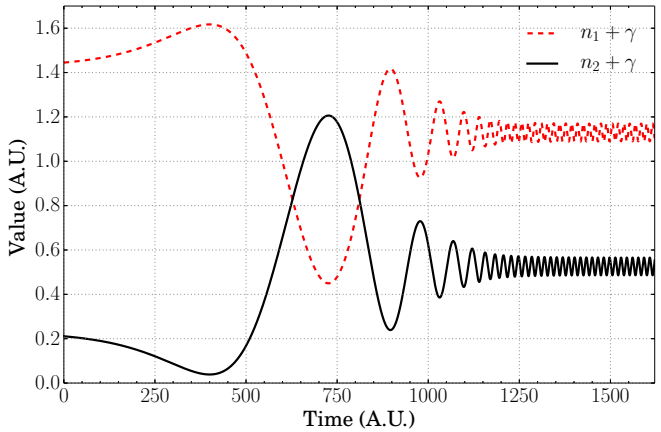
Figure 18 : $i = 1$, sample trajectories.

Extended Coupling

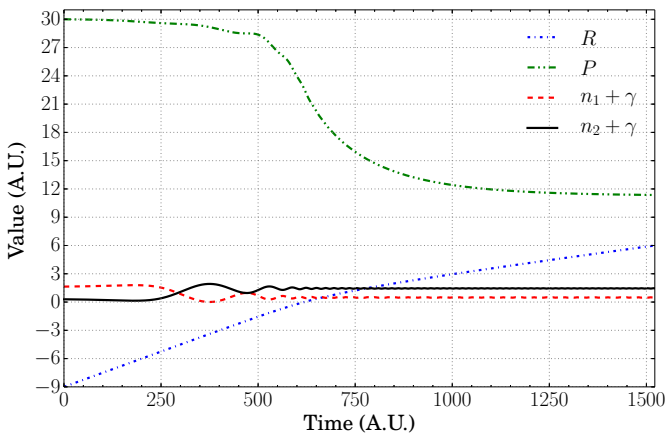
Sample Trajectories ($i = 1$).



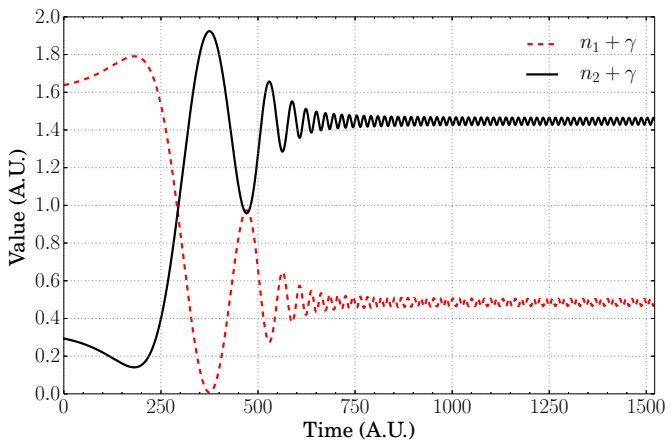
(a) $T_{1\leftarrow 1}$.



(b) $T_{1\leftarrow 1}$, zoom into n_1, n_2.



(c) $T_{2\leftarrow 1}$.

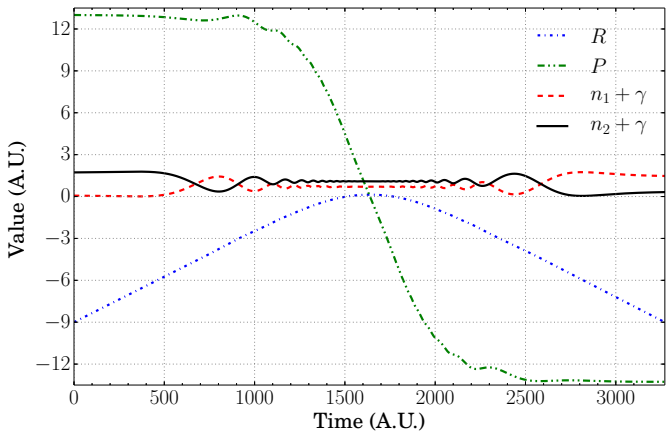


(d) $T_{2\leftarrow 1}$, zoom into n_1, n_2.

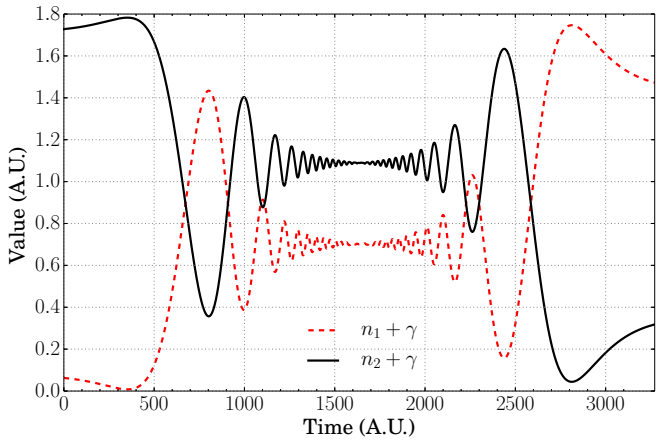
Figure 19 : $i = 1$, sample trajectories.

Extended Coupling

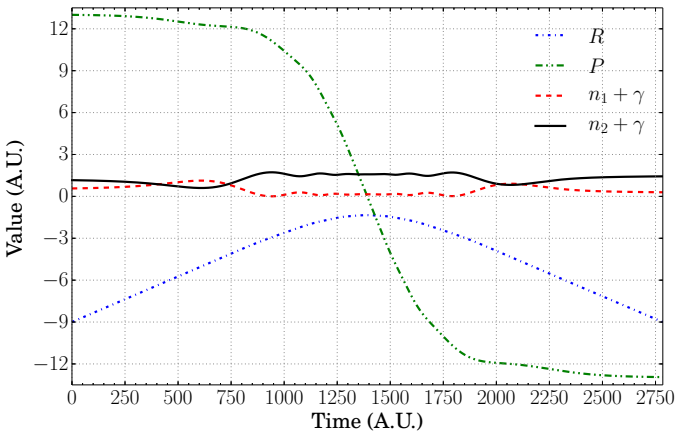
Sample Trajectories ($i = 2$).



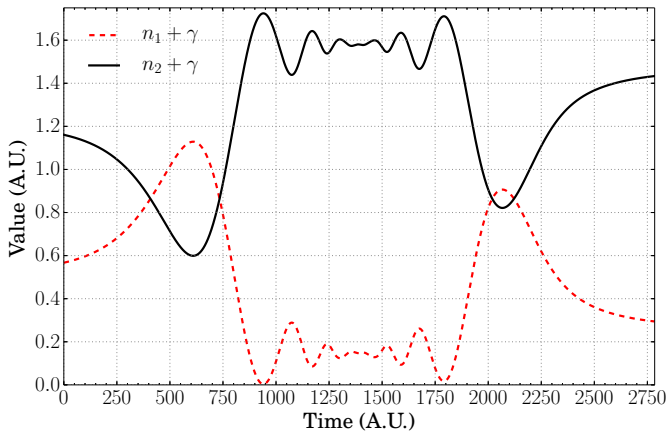
(a) $R_{1 \leftarrow 2}$.



(b) $R_{1 \leftarrow 2}$, zoom into n_1, n_2.



(c) $R_{2 \leftarrow 2}$.

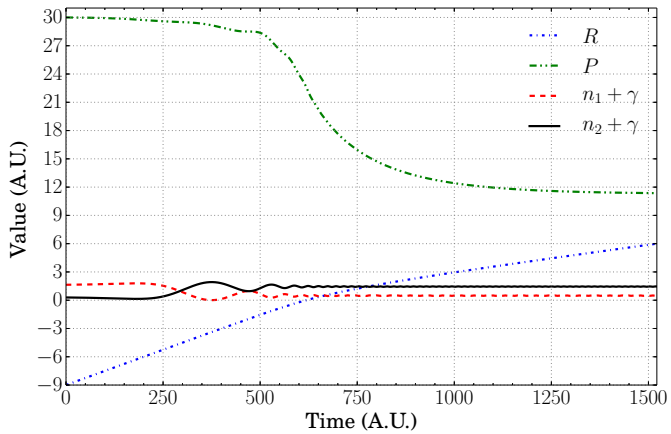


(d) $R_{2 \leftarrow 2}$, zoom into n_1, n_2.

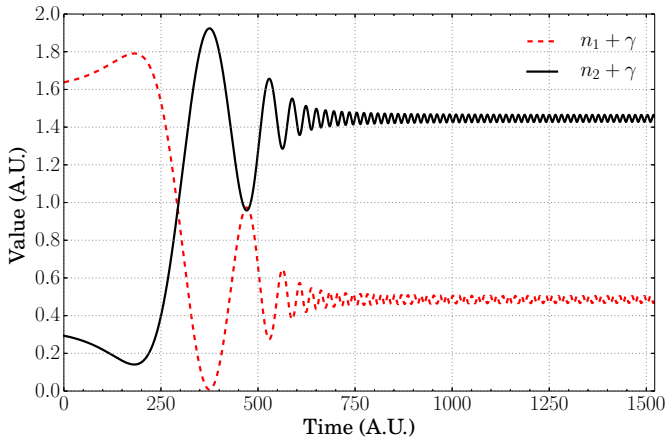
Figure 20 : $i = 2$, sample trajectories.

Extended Coupling

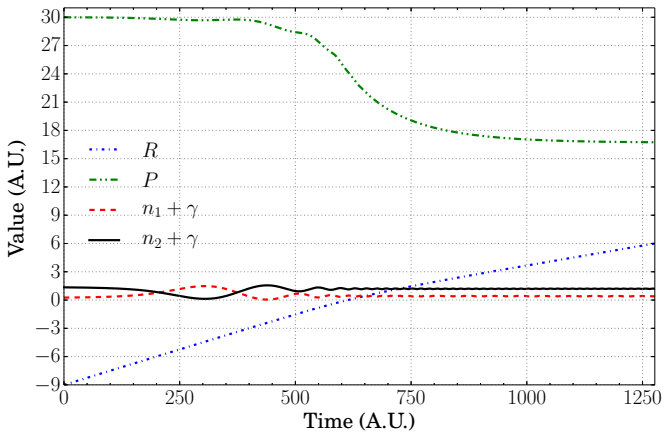
Sample Trajectories ($i = 2$).



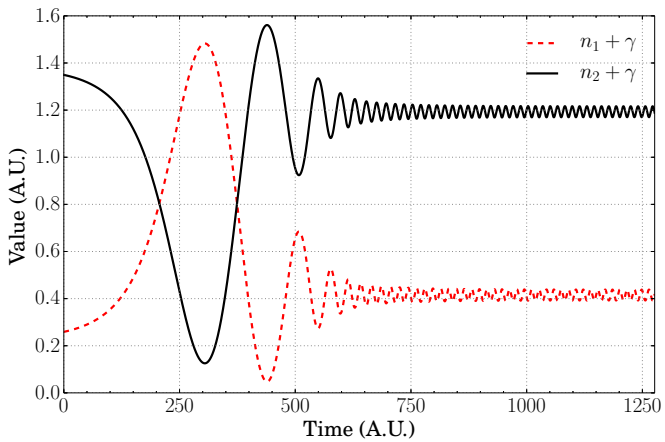
(a) $T_{2\leftarrow 1}$.



(b) $T_{2\leftarrow 1}$, zoom into n_1, n_2.



(c) $T_{2\leftarrow 2}$.



(d) $T_{2\leftarrow 2}$, zoom into n_1, n_2.

Figure 21 : $i = 2$, sample trajectories.

Condensed-Phase Spin-Boson Model

Diabatic PES Derivatives (DPES)

$$\frac{\partial H_{11}}{\partial \boldsymbol{Q}} = \sum_{k=1}^{M} m_k \omega_k^2 Q_k + \sum_{k=1}^{M} c_k \tag{34a}$$

$$\frac{\partial H_{22}}{\partial \boldsymbol{Q}} = \sum_{k=1}^{M} m_k \omega_k^2 Q_k - \sum_{k=1}^{M} c_k \tag{34b}$$

$$\frac{\partial H_{12}}{\partial \boldsymbol{Q}} = \frac{\partial H_{21}}{\partial \boldsymbol{Q}} = 0 \tag{34c}$$

Condensed-Phase Spin-Boson Model

Nuclear Equations of Motion

- There are M nuclear degrees of freedom (DOFs) and F electronic degrees of freedom $\therefore$ there are $2M + 2F$ equations of motion.
- In our case, $F = 2$ so the nuclear equations of motion are:

$$\dot{Q}_j = \frac{P_j}{m_j} \tag{35a}$$

$$\dot{P}_j = -m_j \omega_j^2 Q_j - \frac{1}{2} c_j (p_1^2 + x_1^2 - p_2^2 - x_2^2) \tag{35b}$$

- They were implemented with a loop.

Condensed-Phase Spin-Boson Model

Frequencies

- It was assumed that ω_k are uniformly distributed $\in [0.01\omega_c,\ 4\omega_c]$ [3], where ω_c is the 'characteristic frequency'.
- Frequencies contribute to the system's energy differently so each has a coupling parameter c_k.

$$J(\omega) = \frac{\pi}{2} \sum_{k=1}^{M} \frac{c_k^2}{m_k \omega_k} \delta(\omega - \omega_k) \tag{36a}$$

$$J(\omega) = \frac{\pi}{2} \alpha \omega \exp\left(-\frac{\omega}{\omega_c}\right) \tag{36b}$$

- Where $\alpha \equiv$ Kondo parameter (coupling strength).

Condensed-Phase Spin-Boson Model

Frequencies

- Upon integrating with respect to ω, the coupling parameters can be calculated as:

$$c_k = \omega_k \sqrt{\alpha \Delta\omega m_k \exp\left(-\frac{\omega_k}{\omega_c}\right)} \tag{37a}$$

$$\Delta\omega = \frac{\omega_{max} - \omega_{min}}{M - 1} \tag{37b}$$

Condensed-Phase Spin-Boson Model

Initial Conditions

- There is no covariant element ∴ nuclear momenta and positions can be independently sampled from gaussian distributions.
- The standard deviation (σ) and mean values (μ) for each of them are:

$$\sigma_{P_k} = \sqrt{\frac{m_k \omega_k}{2 \tanh\left(\frac{\beta \omega_k}{2}\right)}} \quad , \quad \mu_{P_k} = 0 \tag{38a}$$

$$\sigma_{Q_k} = \sqrt{\frac{1}{2 m_k \omega_k \tanh\left(\frac{\beta \omega_k}{2}\right)}} \quad , \quad \mu_{Q_k} = -\frac{c_k}{m_k \omega_k^2} \tag{38b}$$

Main Code

- Main program.
  1) Call data collection subroutine.
  2) Call print PES and DPES subroutine.
- Data collection subroutine.
  1) Declare and initialise variables.
  2) Open output file.
  3) Write heading on file.
  4) Define value of initial momentum.
  5) Call Monte-Carlo averaging routine.
  6) Write final results.
     - Repeat 4) to 6) for other initial momentum values.

Main Code

- Monte-Carlo averaging subroutine.
  1) Declare and intialise variables.
  2) Define Monte-Carlo steps loop.
     a) Call solution subroutine.
     b) Add results.
  3) Average results with the number of Monte-Carlo steps.
  4) Calculate transition probabilities for reflection and transmission.

Main Code

- Solution subroutine.
  1) Declare and initialise variables.
  2) Define and calculate initial conditions and window functions.
  3) Define integration loop.
     a) Call RK4G subroutine using the appropriate equations of motion as argument.
     b) Check for reflection, exit loop if the particle was reflected.
     c) Update the initial conditions for next integration step.
  4) Calculate final values for the acceptance criteria.
  5) Calculate final window functions.
  6) Calculate results for the Monte-Carlo averaging subroutine.

Main Code

- Equations of motion subroutine.
  1) Define and initialise variables.
  2) Define equations of motion.
     - PES or DPES subroutines.
       1) Define and initialise variables.
       2) Check which PES or DPES are required.
       3) Define PES or DPES.

Main Code

- Runge-Kutta 4 Gill numerical integration routine (RK4G).
  1) Define and initialise variables.
  2) Call equations of motion subroutine.
     - Calculate the intermediate step for all independent variables.
  3) Repeat 2. for every intermediate step.
  4) Calculate the final value of every independent variable, to be used in the next integration step.

Main Code

- PES and DPES printing subroutine.
  1) Define and initialise variables.
  2) Define loop to print all functions.
     a) Open relevant output file.
     b) Call PES and DPES subroutines.
     c) Write numerical values of each PES and DPES function, evaluated at any given distance.
        - Repeat b) and c) for all desired distances.