Development of a Python code for Trajectory Surface Hopping on *Ab Initio* Potential Energy Surfaces

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Why should you care?

You should listen to this talk if followings things interest you:

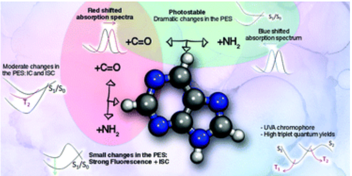

Figure: Photo stability of purine

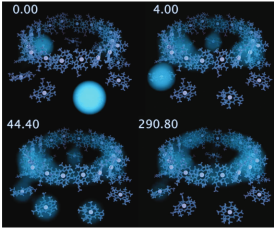

Figure: Population transfer in LH2 complex

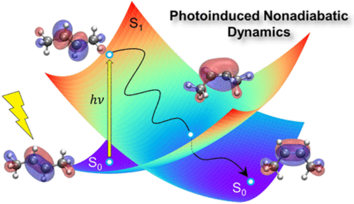

Figure: Non-radiative transitions

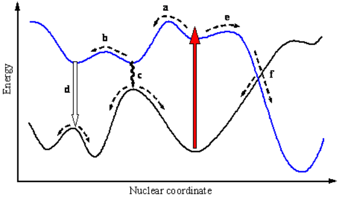

Figure: Photochemical pathways

A good old friend!

- Task at hand: Solve the Schrödinger equation for a molecular system.

$$\hat{\mathcal{H}}_{mol} = \sum_{\alpha}^{N_n} \frac{-\hbar^2}{2M_\alpha}\nabla_\alpha^2 + \hat{\mathcal{H}}_{el}$$

- First line of attack: **The Born-Oppenheimer approximation**
- Physical motivation: Mass of nuclei $\sim (10^3 - 10^5)$ X Mass of electron
- This helps to decouple the electronic and nuclear motion.

$$\hat{\mathcal{H}}_{el}\psi(\mathbf{r};\mathbf{R}) = E_{el}(\mathbf{R})\psi(\mathbf{r};\mathbf{R})$$

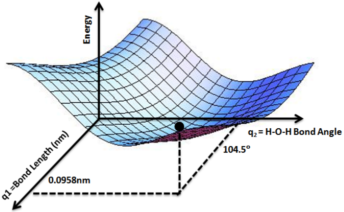

Figure: PES for H_2O[1]

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[1] Image credits: By AimNature - Own work, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=29213158

Failure of Born-Oppenheimer Approximation: Non-Adiabatic Dynamics

Adiabatic Dynamics

The nuclear motion is propagated on a single Potential energy surface(PES).

When does the approximation breakdown? Quick recap of Adiabatic theorem:

Theorem

A physical system remains in its instantaneous eigenstate if a given perturbation is acting on it slowly enough and if there is a gap between the eigenvalue and the rest of the Hamiltonian's spectrum.

$$H(t)\left|\psi_n(t)\right\rangle = E_n(t)\left|\psi_n(t)\right\rangle$$

We attempt to construct the wavefunction through the ansatz $\left|\Psi(t)\right\rangle = \sum_n c_n(t)\left|\psi_n(t)\right\rangle$

$$i\hbar\dot{c}_k = \left(E_k - i\hbar\left\langle \psi_k \middle| \dot{\psi}_k \right\rangle c_k\right) - i\hbar\sum_{n\neq k}\frac{(\dot{H})_{nk}}{E_n - E_k}c_n$$

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Non Adiabatic Dynamics

- We need to consider multiple Potential Energy Surfaces or equivalently, the whole instantaneous eigenbasis for an exact formalism of NAD.
- Indeed, one of the quantum mechanical approaches is the **Bohmian Non-adiabatic Dynamics** which considers the Born-Huang ansatz:

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_k \Omega_k(\mathbf{R}, t)\psi_k(\mathbf{r}; \mathbf{R}) \tag{0.1}$$

- However, we encounter practical issues for large molecules.
- We tackle this problem with **semi-classical** approaches: Nuclei are treated classically and propagated through Molecular Dynamics simulations.
- **Pro:** We can simulate the nuclei with full dimensionality(Control the computational cost).
- **Con:** Accuracy - We loose some quantum mechanical effects.

Semi Classical Approaches

Two such methods exist:

1. Ehrenfest Dynamics: Mean field PES approach
2. Trajectory Surface Hopping: Single PES approach subjected to switch/hop surfaces

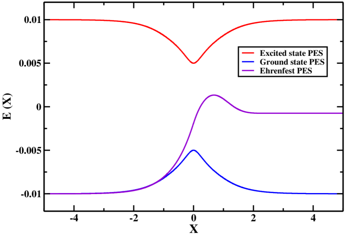

Figure: Ehrenfest Dynamics

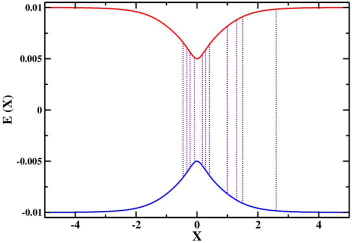

Figure: Trajectory Surface Hopping

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Trajectory Surface Hopping

Hypothesis

The dynamics of nuclear wave-packet through a PES branching region can be approximated by an ensemble of independent classical trajectories distributed stochastically amongst the branching surfaces.

- **Trajectory:** $\mathbf{R} = \mathbf{R}(t) = (\mathbf{R}_1(t), \mathbf{R}_2(t), ..., \mathbf{R}_{N_n}(t))$

Electronic Propagation:

$$\Psi^{\alpha}(\mathbf{r}, \mathbf{R}, t) = \sum_j c_j^{\alpha}(t)\psi_j(\mathbf{r}; \mathbf{R}) \tag{0.1}$$

Time Dependent Schrodinger Equation:

$$i\hbar\frac{\partial}{\partial t}\Psi^{\alpha}(\mathbf{r}, \mathbf{R}, t) = \hat{\mathcal{H}}_{\text{el}}(\mathbf{r}, \mathbf{R})\Psi^{\alpha}(\mathbf{r}, \mathbf{R}, t) \tag{0.2}$$

Time-dependent coefficient propagation

$$i\hbar\dot{c}_k^{\alpha}(t) = c_k^{\alpha}(t)E_k(\mathbf{R}) - i\hbar\sum_j c_j^{\alpha}(t)\dot{\mathbf{R}}^{\alpha} \cdot \mathbf{d}_{kj}^{\alpha} \tag{0.3}$$

TSH(continued)

Non-adiabatic Coupling Vector

$$\mathbf{d}_{kj} = \langle \psi_k(\mathbf{r};\mathbf{R}) | \nabla_{\mathbf{R}} | \psi_j(\mathbf{r};\mathbf{R}) \rangle \tag{0.4}$$

Nuclear Propagation: The nuclei/trajectories are propagated by the gradient of the current PES

Nuclei equation of motion

$$M_I \ddot{\mathbf{R}}_I = -\nabla_I E_k^{el}(\mathbf{R}) \tag{0.5}$$

Stochastic algorithm: Consider a two level system and N trajectories.

- Let ρ'_{11} & ρ'_{22} be the populations of state 1 & 2 respectively at time $t_1 = t$
- after an infinitesimal time Δt, the populations change $\rho'_{11} \rightarrow \rho_{11}$ and $\rho'_{22} \rightarrow \rho_{22}$.(Assume $\rho_{11} < \rho'_{11}$)

Respective trajectories at $t_1 = t$ & $t_2 = t + \Delta t$

$$\begin{aligned} N'_1 &= \rho'_{11} N \qquad & N'_2 &= \rho'_{22} N \\ N_1 &= \rho_{11} N \qquad & N_2 &= \rho_{22} N \end{aligned}$$

TSH(continued)

Probability that one of the initial N_1 trajectories would switch

$$P_{\text{switch}}(1 \rightarrow 2) = \frac{(\rho'_{11} - \rho_{11})N}{\rho'_{11}N} \approx \frac{\dot{\rho}_{22}\Delta t}{\rho'_{11}} \tag{0.6}$$

Probability of switching between two surfaces

$$P_{(j\rightarrow k)}(t) = \max\left[0, \frac{2Re(c_j^*(t)c_k(t)\dot{\mathbf{R}}\cdot\mathbf{d}_{kl})\Delta t}{\rho_{jj}}\right] \tag{0.7}$$

Stochastic algorithm

$$\sum_{m=1}^{k-1} P_{(j\rightarrow m)}(t) < \gamma_t \leq \sum_{m=1}^{k} P_{(j\rightarrow m)}(t) \tag{0.8}$$

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Algorithm

Step 1: Initialize the positions and momenta for nuclear trajectory and also initiate the electronic density matrix elements. Usually, the phase space points are sampled using Wigner distribution for a Harmonic Oscillator or from a molecular dynamic simulation.

Step 2: Diagonalize the electronic Hamiltonian to obtain potential energy surface and compute its gradients to obtain the forces.

$$\hat{\mathcal{H}}_{el}\Psi(\mathbf{r};\mathbf{R}) = E_{el}(\mathbf{R})\Psi(\mathbf{r};\mathbf{R}) \tag{0.1}$$

Step 3: Propagate the nuclear trajectories using for a small time step Δ using velocity-verlet scheme.

$$M_I\ddot{\mathbf{R}}_I = -\nabla_I E_k^{el}(\mathbf{R}) \tag{0.2}$$

Nuclear time step $\equiv \Delta$ and **electronic time step** $\equiv dt$

Algorithm

Velocity Verlet Scheme

$$\mathbf{R}(t+\Delta) = \mathbf{R}(t) + \mathbf{v}(t)\Delta + \frac{1}{2}\mathbf{a}(t)\Delta^2 \tag{0.3}$$

$$\mathbf{v}(t+\Delta) = \mathbf{v}(t) + \frac{1}{2}[\mathbf{a}(t) + \mathbf{a}(t+\Delta)]\Delta \tag{0.4}$$

Step 4: Obtain Non-Adiabatic Coupling's using auxiliary Many-body wavefunction. Further interpolate and extrapolate to obtain NACs at intermediate steps.

$$\sigma_{kj} \equiv \mathbf{d}_{kj} \cdot \dot{\mathbf{R}} = \langle \psi_k(\mathbf{r};\mathbf{R}) | d/dt | \psi_j(\mathbf{r};\mathbf{R}) \rangle \tag{0.5}$$

Step 5: Integrate electronic coefficients to obtain the time dependent coefficients at a smaller time step *dt* using Runge-Kutta method.

$$i\hbar \dot{c}_k^{\alpha}(t) = c_k^{\alpha}(t) E_k(\mathbf{R}) - i\hbar \sum_j c_j^{\alpha}(t) \dot{\mathbf{R}}^{\alpha} \cdot \mathbf{d}_{kj}^{\alpha} \tag{0.6}$$

Algorithm

Step 6: Evaluate the switching probability and decide the hop according to the stochastic algorithm.

$$P_{(j\to k)}(\Delta) = -2\int_t^{t+\Delta} dt\,\frac{\mathrm{Re}\left\{\rho_{kj}^*(t)\sigma_{kj}(t)\right\}}{\rho_{jj}} \tag{0.7}$$

$$\sum_{m=1}^{k-1} P_{(j\to m)}(t) < \gamma_t \leq \sum_{m=1}^{k} P_{(j\to m)}(t) \tag{0.8}$$

Step 7: If the hop is successful, change the driving surface and re-adjust the momentum to conserve the energy or continue on the same surface otherwise, until the stopping criterion is met in any case.

Step 8: Repeat the entire procedure for a different trajectory.

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Initial Sampling

- The equations of motion(EOM) associated with trajectories are Newton's second law.
- We require a set of initial positions and momenta to integrate these EOM.
- In other words, we need to initialise each trajectory as a pure state in phase space.

The ground state phase space(Temperature T) of a molecule with N_{atoms} can be sampled through a harmonic oscillator **Wigner distribution**:

$$W_{\hat{\rho}}(\mathbf{q}, \mathbf{p}_q) = \frac{1}{(\pi\hbar)^{3N_{\text{atoms}}-6}} \prod_{i=1}^{3N_{\text{atoms}}-6} \alpha_i \text{exp}\left(\frac{-q_i^2}{2\sigma_{q_i}^2}\right) \text{exp}\left(\frac{-p_i^2}{2\sigma_{p_i}^2}\right) \tag{0.1}$$

where

$$\begin{gathered} \sigma_{q_i}^2 = \frac{\hbar}{2\alpha_i\mu_i\omega_i} \qquad \sigma_{p_i}^2 = \frac{\hbar\mu_i\omega_i}{2\alpha_i} \\ \alpha_i = \tanh\left(\frac{\hbar\omega_i}{2k_B T}\right) \end{gathered} \tag{0.2}$$

- The notion of a Wigner distribution arises in the context of Weyl quantization.

Sampling from a Multivariate Gaussian Distribution

Suppose we have a two independent Gaussian random variables:

$$f_{(X,Y)}(x,y) = \frac{1}{2\pi}\exp(-\frac{x^2+y^2}{2\sigma^2}) \tag{0.3}$$

Let us introduce two random polar variables R and E on the X,Y plane:

$$x = r\cos\varepsilon \qquad y = r\sin\varepsilon \tag{0.4}$$

By requiring $f_{(X,Y)}(x,y)dxdy = f_{(R,E)}(r,\varepsilon)drd\varepsilon$, we get

$$f_{(R,E)}(r,\epsilon) = \frac{r}{2\pi\sigma^2}\exp(-\frac{r^2}{2\sigma^2}) \tag{0.5}$$

$$= \frac{r}{\sigma^2}\exp(-\frac{r^2}{2\sigma^2})\frac{1}{2\pi} \tag{0.6}$$

$$= f_R(r)f_E(\varepsilon) \tag{0.7}$$

We can draw samples from $f_R(r)$ by finding the CDF, $F(R)$, and then solving $F(R) = \gamma$:

$$R = \sigma\sqrt{-2log\gamma} \qquad E = 2\pi\bar{\gamma} \tag{0.8}$$

Initial conditions(continued)

Once we sample q_i, p_i from the Wigner distribution as described above, we can generate the initial conditions as follows:

$$\mathbf{Q}_{\text{gen}} = \mathbf{Q}_{\text{optimized}} + \sum_{i=1}^{3N_{\text{atoms}}-6} q_i \mathbf{e}_i \tag{0.9}$$

$$\mathbf{P}_{\text{gen}} = \sum_{i=1}^{3N_{\text{atoms}}-6} p_i \mathbf{e}_i \tag{0.10}$$

where $\{\mathbf{e}_i\}$ are the displacement of vibrational modes only.

Non Adiabatic Coupling

The non-adiabatic coupling vector is given by:

$$\mathbf{d}_{kj} = \langle \psi_k(\mathbf{r};\mathbf{R}) |\, \nabla_{\mathbf{R}}\, | \psi_j(\mathbf{r};\mathbf{R}) \rangle \tag{0.11}$$

Evaluating the above equation is computational expensive and we will use the coupling term instead:

$$\sigma_{kj} \equiv \mathbf{d}_{kj} \cdot \dot{\mathbf{R}} = \langle \psi_k(\mathbf{r};\mathbf{R}) | d/dt | \psi_j(\mathbf{r};\mathbf{R}) \rangle \tag{0.12}$$

Using finite difference and linear interpolation, it can be showed that:

$$\begin{split}\sigma_{kj}\left(\mathbf{R}\left(t+\frac{\Delta}{2}\right)\right) \approx \frac{1}{2\Delta}\big(\langle \psi_k(\mathbf{r};\mathbf{R}(t)) | \psi_j(\mathbf{r};\mathbf{R}(t+\Delta)) \rangle \\ - \langle \psi_k(\mathbf{r};\mathbf{R}(t+\Delta)) | \psi_j(\mathbf{r};\mathbf{R}(t)) \rangle\big)\end{split} \tag{0.13}$$

However, we do not have access to Many body wavefunctions. We will use the 'auxiliary' many electron wavefunction to calculate the matrix elements:

$$|\psi_j(\mathbf{r};\mathbf{R}(t))\rangle = \sum_{a,r} C^j_{ar} \left| \Phi^{\text{CSF}}_{a,r}(\mathbf{r};\mathbf{R}(t)) \right\rangle \tag{0.14}$$

NAC(continued)

The spin adapted configurational state functions are given by:

$$\left|\Phi_{a,r}^{\text{CSF}}(\mathbf{r};\mathbf{R}(t))\right\rangle = \frac{1}{\sqrt{2}}\left(\left|\Phi_{a\alpha}^{r\beta}(\mathbf{r};\mathbf{R}(t))\right\rangle + \left|\Phi_{a\beta}^{r\alpha}(\mathbf{r};\mathbf{R}(t))\right\rangle\right) \tag{0.15}$$

Substituting (0.14) and (0.15) in (0.13), we get:

$$\begin{aligned}\left\langle\Phi_{a,r}^{\text{CSF}}(\mathbf{r};\mathbf{R}(t))\middle|\Phi_{a',r'}^{\text{CSF}}(\mathbf{r};\mathbf{R}(t+\Delta))\right\rangle &= \sum_{a,r}\sum_{a',r'} C_{ar}^{k*}\,C_{a'r'}^{j} \\ \text{X}\quad \frac{1}{2}\Big[&\left\langle\Phi_{a\alpha}^{r\beta}(\mathbf{r};\mathbf{R}(t))\middle|\Phi_{a'\alpha}^{r'\beta}(\mathbf{r};\mathbf{R}(t+\Delta))\right\rangle \\ &+\left\langle\Phi_{a\alpha}^{r\beta}(\mathbf{r};\mathbf{R}(t))\middle|\Phi_{a'\beta}^{r'\alpha}(\mathbf{r};\mathbf{R}(t+\Delta))\right\rangle \\ &+\left\langle\Phi_{a\beta}^{r\alpha}(\mathbf{r};\mathbf{R}(t))\middle|\Phi_{a'\alpha}^{r'\beta}(\mathbf{r};\mathbf{R}(t+\Delta))\right\rangle \\ &+\left\langle\Phi_{a\beta}^{r\alpha}(\mathbf{r};\mathbf{R}(t))\middle|\Phi_{a'\beta}^{r'\alpha}(\mathbf{r};\mathbf{R}(t+\Delta))\right\rangle\Big]\end{aligned} \tag{0.16}$$

NAC(continued)

Although, the above equation looks complex, they can be broken down into determinant of overlap matrices between KS orbitals:

$$\left\langle \Phi_{a\alpha}^{r\beta}(\mathbf{r};\mathbf{R}(t)) \middle| \Phi_{a'\alpha}^{r'\beta}(\mathbf{r};\mathbf{R}(t+\Delta)) \right\rangle = \det \begin{pmatrix} \langle\phi_1|\phi'_1\rangle & \cdots & \langle\phi_1|\phi'_{a'}\rangle & \cdots & \langle\phi_1|\phi'_{n'}\rangle \\ \vdots & & \vdots & & \vdots \\ \langle\phi_a|\phi'_1\rangle & \cdots & \langle\phi_a|\phi'_{a'}\rangle & \cdots & \langle\phi_a|\phi'_{n'}\rangle \\ \vdots & & \vdots & & \vdots \\ \langle\phi_n|\phi'_1\rangle & \cdots & \langle\phi_n|\phi'_{a'}\rangle & \cdots & \langle\phi_n|\phi'_{n'}\rangle \end{pmatrix} \begin{pmatrix} \langle\phi_1|\phi'_1\rangle & \cdots & \langle\phi_1|\phi'_{r'}\rangle & \cdots & \langle\phi_1|\phi'_{n'}\rangle \\ \vdots & & \vdots & & \vdots \\ \langle\phi_r|\phi'_1\rangle & \cdots & \langle\phi_r|\phi'_{r'}\rangle & \cdots & \langle\phi_r|\phi'_{n'}\rangle \\ \vdots & & \vdots & & \vdots \\ \langle\phi_n|\phi'_1\rangle & \cdots & \langle\phi_n|\phi'_{r'}\rangle & \cdots & \langle\phi_n|\phi'_{n'}\rangle \end{pmatrix} \tag{0.17}$$

where ϕ and ϕ' represents KS orbitals at time t and $t+\Delta$ respectively. Furthermore, these overlaps can be expressed in terms of overlaps between atomic basis functions $|\tilde{g}_i(\mathbf{R})\rangle$ at the corresponding time steps

$$\left\langle \phi_a(\mathbf{R}(t)) \middle| \phi'_{a'}(\mathbf{R}(t+\Delta)) \right\rangle = \sum_{l,m} D^*_{al} D_{a'm} \langle \tilde{g}_l(\mathbf{R}(t)) | \tilde{g}_m(\mathbf{R}(t+\Delta)) \rangle \tag{0.18}$$