Development and testing of a python based Trajectory-Surface-Hopping code for simulating Non-adiabatic dynamics

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The Born-Oppenheimer Approximation (BOA)

The electronic degrees of freedom can be seperated from nuclear degrees of freedom due to heavy masss of the nuclei and so we have;

$$\hat{H}_{mol} = \hat{H}_{e^-} + \hat{H}_{Nu} \tag{1}$$
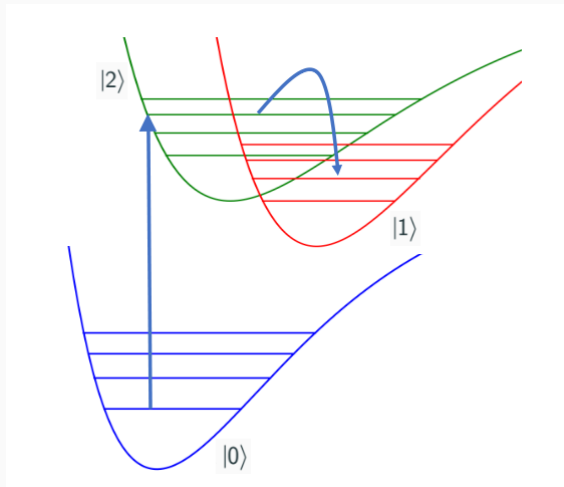
due to which we can seperately solve for;

$$\hat{H}_{e^-}(\mathbf{r}; \mathbf{R})\Psi_{e^-}(\mathbf{r}; \mathbf{R}) = E_{e^-}(\mathbf{R})\Psi_{e^-}(\mathbf{r}; \mathbf{R}) \tag{2}$$

Here $\mathbf{r} \rightarrow e^-$ coordinates and $\mathbf{R} \rightarrow$ Nuclear coordinates and in the above $\mathbf{R}$ is just a parameter.

$\hat{H}_{mol}$ depends on time through $\mathbf{R}(t)$.

$E_{e^-}(\mathbf{R})$ is called an electronic Potential Energy Surface (PES).

Figure 1: Non-adiabaticity in excited states

Origin of non-adiabaticity ....

Lets take our system to be in i^{th} eigenstate, Ψ_i, of hamiltonian $\hat{H}$. The system evolves as;

$$i\hbar\frac{\partial\Psi_i}{\partial t} = \hat{H}\Psi_i \tag{3}$$

Suppose at each instant of time, we have the instantaneous eigenbasis as;

$$\hat{H}(t)\phi_j(t) = E(t)\phi_j(t) \tag{4}$$

Then we can represent out instantaneous wavefunction as;

$$\Psi_i(t) = \sum_i c_j(t)\phi_j(t) \tag{5}$$

The non-adiabatic term...

We can show,

$$\underbrace{i\hbar\dot{c}_k(t) = c_k(t)E_k(t)}_{\text{adiabatic part}} - \underbrace{i\hbar\sum_j c_j\frac{\langle\phi_k|\dot{\hat{H}}|\phi_j\rangle}{E_j - E_k}}_{\text{non-adiabatic part}} \tag{6}$$

So the non-adiabaticity can occur when:

1. Instantaneous eigenvalues are nearly degenerate
2. $|\dot{H}_{kj}| \geqslant |E_j - E_k|$

The non-adiabatic part of eqn(4) is also called the **Non-adiabatic coupling (NAC)** between different instantaneous eigenstates.
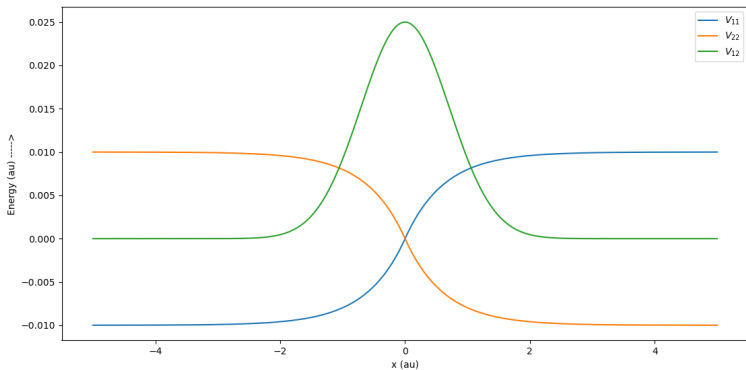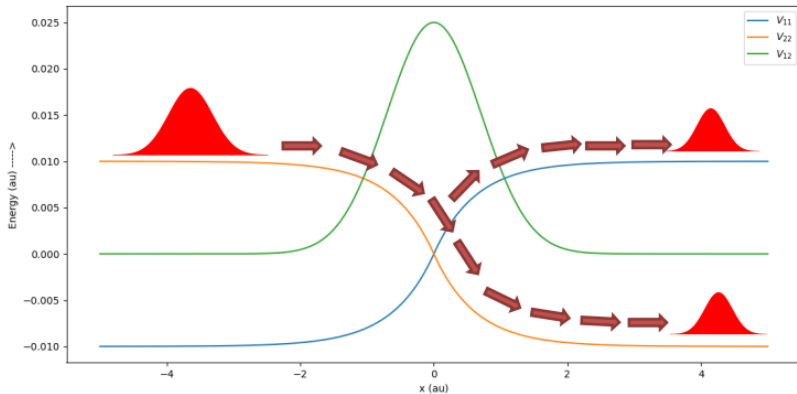
Figure 2: NAC

Figure 3: NAC

Tully's Fewest-Switches-Surface-Hopping (FSSH)

1. We simulate an ensemble of independent-trajectories ($\mathbf{R}(t)$) with different initial conditions.

2. For each trajectory we assume the electronic wavefunction to be of the form:

$$\Psi(\mathbf{r}; \mathbf{R}(t)) = \sum_k c_k(t) \Phi_k(\mathbf{r}; \mathbf{R}(t)) \tag{7}$$

3. The nuclear coordinates evolve according to:

$$M_I \ddot{\mathbf{R}} = -\nabla E_k(\mathbf{R}(t)) \tag{8}$$

4. The electronic coefficients evolve according to eqn(4) which in density matrix notation;

$$i\hbar\dot{\rho}_{kj} = \rho_{kj}(E_k(\mathbf{R}) - E_j(\mathbf{R})) - i\hbar \sum_l \left\{ \rho_{lj}\mathbf{d}_{kl}.\dot{\mathbf{R}} + \rho_{kl}\mathbf{d}_{lj}.\dot{\mathbf{R}} \right\} \tag{9}$$

where,

$$\mathbf{d}_{mn} = \frac{\langle \Phi_m | \nabla_R \hat{H} | \Phi_n \rangle}{E_n - E_m} \tag{10}$$

This is called the Non-Adiabatic coupling vector (NACV) between the different PES. The diagonals terms of the density matrix above are the populations;

$$\dot{\rho}_{kk} = - \sum_{l \neq k} 2 \text{Re}(\rho_{kl}^* \mathbf{d}_{kl}.\dot{\mathbf{R}}) = \sum_{l \neq k} \gamma_{kl} \tag{11}$$

5 At regions of strong coupling, we allow the trajectory to hop from one PES to another based on a stochsic algorithm. The probability of a hop $j \to k$ in between time t and $t + dt$ is calculated by,

$$P_{j \to k}(t) = \frac{\text{change in population of k due to j}}{\text{population of j}}$$
$$= max \left[0, \frac{\gamma_{kj} dt}{\rho_{jj}} \right] \tag{12}$$

6. The switch from an electronic state j to k will occur if,

$$\sum_{m=1}^{k-1} P_{j \to m} < \zeta < \sum_{m=1}^{k} P_{j \to m} \tag{13}$$

where ζ is a random rumber between 0 and 1.

FSSH algorithm

Step1 Generate different initial conditions either by wigner sampling or by Molecular Dynamics.

Step2 Propagate the nuclei starting from an inital PES following eqn(8).

Step3 Calculate the NACs in eqn(4)

Step4 Propagate the electronic coefficients by eqn(4)

Step5 Calculate the hopping probability and decide the hop according to eqn(12) and (13).

Step6 If the hop occurs, change the PES and readjust the momentum along the NACV direction (if available) or distribute momentum uniformly. If no hop occurs, continue along the same PES

Step7 Repeat from **Step2** until a stopping criterion is reached.

Internal consistency of FSSH

Suppose we simulated N^T number of trajectories and at any time step of the FSSH simulation, if we have N^α in the electronic state α, then we should have:

$$\frac{N^\alpha}{N^T} = \frac{1}{N^T} \sum_{j=1}^{N^T} \rho_{\alpha\alpha}^j \tag{14}$$

Eqn(14) is called the internal consistency of FSSH.

Tully's FSSH algorithm is known to be internally inconsistent. Lets understand why?...

How does overcoherence arise???

Consider the Born-Huang ansatz for total wavefunction of the combined nuclei-electron system:

$$|\Psi\rangle = \sum_i f_i |\chi_i\rangle |\phi_i\rangle \tag{15}$$

The density matrix will be;

$$|\Psi\rangle\langle\Psi| = \sum_{i,j} f_i f_j^* |\chi_i\rangle |\phi_i\rangle\langle\phi_j|\langle\chi_j| \tag{16}$$

Now to bring out the electronic density matrix from this;

$$\sigma_{el} = \sum_{i,j} f_i f_j^* \int |\mathbf{R}\rangle\langle\mathbf{R}||\Psi\rangle\langle\Psi| d\mathbf{R} \tag{17}$$

Overcoherence...

This would give;

$$\sigma_{el} = \sum_{i,j} f_i f_j^* \int \langle \chi_j | \mathbf{R} \rangle \langle \mathbf{R} | \chi_i \rangle | \phi_i \rangle \langle \phi_j | d\mathbf{R}$$
$$= \sum_{i,j} f_i f_j^* \langle \chi_j | \chi_i \rangle | \phi_i \rangle \langle \phi_j | \tag{18}$$

The electronic wavefunction in TSH is;

$$|\Psi_{el}\rangle = \sum_i c_i |\phi_i\rangle \tag{19}$$

From this we have the electronic density matrix as;

$$\sigma_{el} = \sum_{i,j} c_i c_j^* |\phi_i\rangle \langle \phi_j| \tag{20}$$

Overcoherence continued...

Comparing equations (18) and (20) we can see that the coherence terms in TSH wave-function represents the nuclear overlap of the total-wavefunction, i.e.,

$$f_i f_j^* \langle \chi_j | \chi_i \rangle = c_i c_j^* \tag{21}$$

1. After branching off of the nuclear wavepackets from strong coupling regions, when these wavepackets are far enough in phase space, then the effective overlap should go to 0 i.e., $\langle \chi_j | \chi_i \rangle \to 0$.
2. BUT, there is no term in equation(eqn(9)) which will make the coherence terms $\to 0$ after the hops.
3. This leads to overcoherence.

Instantaneous Decoherence Correction (IDC)

1. **ID-S:** After each successful hop, the electronic wavefunction is reinitialised as a pure state in the current state

2. **ID-A:** If a hop is accepted, the wavefunction is made to collapse at the current state and if a hop is forbidden, the wavefunction is collapsed back to the current running state.

If a hop $S_2 \rightarrow S_1$ is predicted:

      if successful hop:

            set $c_1 = 1$ and $c_2 = 0$

      else:

            set $c_2 = 1$ and $c_1 = 0$

Energy Based Decoherence Correction (EDC)

Instead of instantaneous collapse, here we allow for decay of the electronic wavefunction to a particular state.

$$c'_\beta(t) = c_\beta(t) e^{\frac{-\Delta t}{\tau_{\beta\alpha}(t)}} \tag{22}$$

and the loss gets accumulated in the current state as:

$$c'_\alpha(t) = c_\alpha(t) \left[\frac{1 - \sum_{\beta \neq \alpha} |c'_\beta(t)|^2}{|c'_\alpha(t)|^2} \right]^{\frac{1}{2}} \tag{23}$$

$\tau_{\beta\alpha}$ is known as the decoherence time and Granucci *et al.* approximated this to be:

$$\tau_{\beta\alpha}(t) = \frac{\hbar}{|E_\beta(t) - E_\alpha(t)|} \left(C + \frac{E_0}{E_{kin}} \right) \tag{24}$$

Thank You