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Nonadiabatic Dynamics with the Libra code

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"Excited States and Nonadiabatic Dynamics CyberTraining Workshop"
June 15, 2021

What is Nonadiabatic Dynamics?

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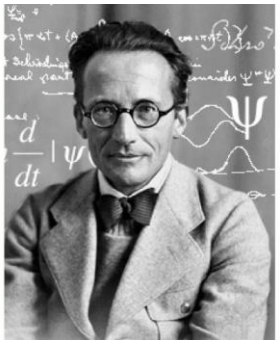
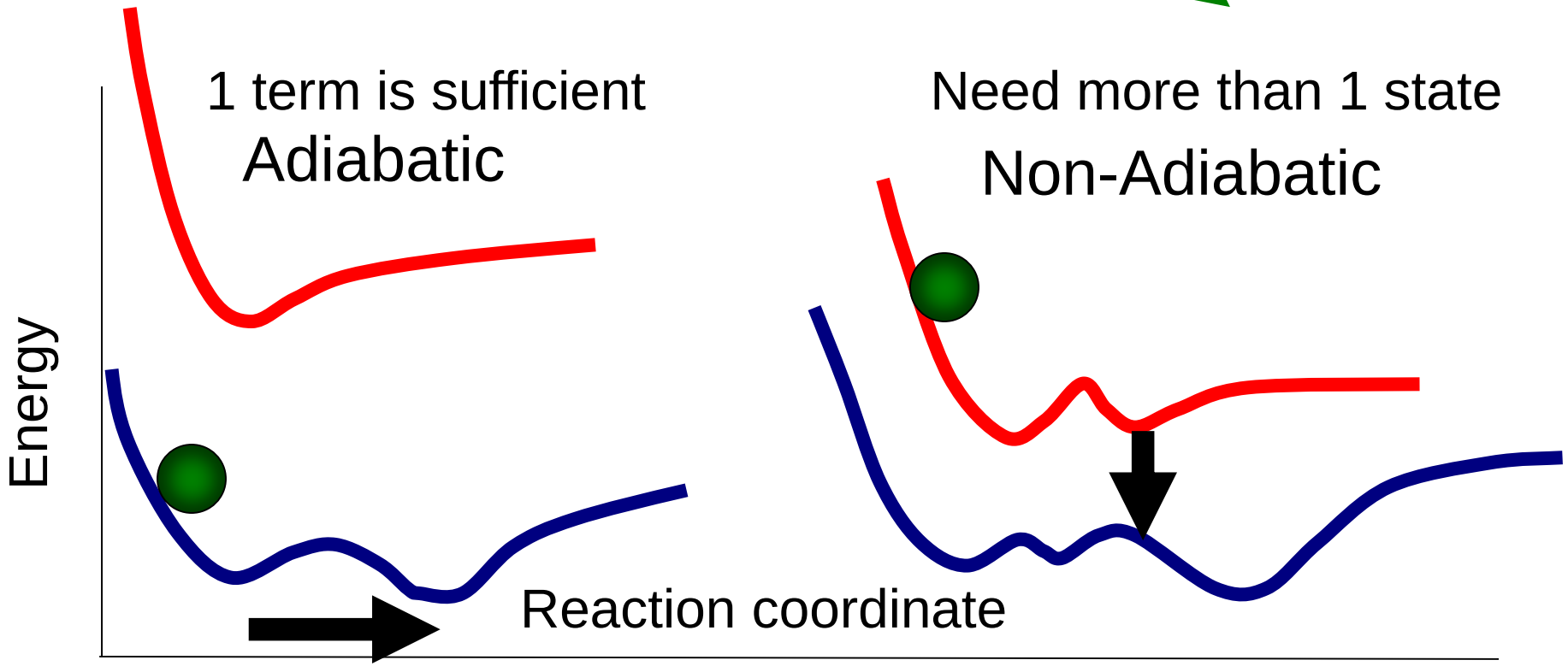
$$i\hbar \frac{\partial \Psi(\mathrm{r},\mathrm{R},\mathrm{t})}{\partial t} = H(\mathrm{r},\mathrm{R},\mathrm{t})\Psi(\mathrm{r},\mathrm{R},\mathrm{t})$$



$$\Psi(\mathrm{r},\mathrm{R},\mathrm{t}) = \sum_i \chi_i\big(t, R(t)\big)\Phi_{\mathrm{i}}(\mathrm{r};\mathrm{R}(\mathrm{t}))$$

1 term is sufficient
Adiabatic

Need more than 1 state
Non-Adiabatic



TSH in the nutshell

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Initialization

Nuclear dynamics

$$\dot{p}_i = -\frac{\partial H}{\partial r_i} \quad \dot{r}_i = \frac{\partial H}{\partial p_i}$$

Stationary adiabatic states

$$\hat{H}_{el}\psi_i = E_i\psi_i$$

Non-adiabatic Couplings

$$d_{ij} = \frac{\langle \psi_i(t) | \psi_j(t+dt) \rangle - \langle \psi_i(t+dt) | \psi_j(t) \rangle}{2dt}$$

Electronic Dynamics

$$\Psi(\mathrm{r},\mathrm{R},\mathrm{t}) = \sum_i c_i(t)\psi_\mathrm{i}(\mathrm{r};\mathrm{R}(\mathrm{t})) \qquad i\hbar\frac{\partial \mathrm{c_i(t)}}{\partial t} = \sum_j \left(E_i\delta_{ij} - i\hbar d_{ij}\right)c_j$$

NBRA

Decoherence 1

$$c_i \rightarrow c_i \exp\left(-\frac{\Delta t}{\tau_{ij}}\right), \forall i \neq j$$

as in SDM

Proposed Hops Decoherence 2

$$P_{i\rightarrow j} = \Delta t * Re\left(\frac{2\frac{p}{m}d_{ij}c_i^* c_j}{c_i^* c_i}\right)$$

or as in DISH

Accept Hops

based on energy conservation or

$$P_{i\rightarrow f}^A = \min\left(1, exp\left(-\frac{\Delta E}{k_B T}\right)\right)$$

Change state

change active electronic state, rescale velocity

Many ways of doing the dynamics

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Hop proposal probabilities

FSSH

$$P_{i\to f}^{P} = \max\left(0, \frac{\Delta t}{\hbar P_{ii}} Im\left[P_{i,f} H_{f,i}^{vib} - H_{i,f}^{vib} P_{f,i}\right]\right)$$

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

GFSH

$$P_{i\to f}^{P} = \max\left(0, \frac{\Delta P_{ff}}{P_{ff}} \frac{\Delta P_{jj}}{\sum_{k\in A} \Delta P_{kk}}\right). i \in A, j \in B$$

Wang, L.; Trivedi, D.; Prezhdo, O. V. *JCTC* **2014**, 10, 3598

MSSH

$$P_{i\to f}^{P}(t, t+\Delta t) = P_{ff}(t+\Delta t)$$

Akimov, A. V.; Trivedi, D.; Wang, L.; Prezhdo, O. V. *J. Phys. Soc. Jpn.* **2015**, 84, 094002

Hop acceptance probabilities

Boltzmann

$$P_{i\to f}^{A} = \min\left(1, exp\left(-\frac{\Delta E}{k_B T}\right)\right)$$

Prezhdo, O. V.; Duncan, W. R.; Prezhdo, V. V. *Prog. Surf. Sci.* **2009**, *84*, 30

Maxwell-Boltzmann

$$P_{i\to f}^{A} = 1 - \left[\mathrm{erf}\left(\left(\frac{\Delta E}{k_B T}\right)^{\frac{1}{2}}\right) - \sqrt{\frac{4}{\pi}}\left(\frac{\Delta E}{k_B T}\right)^{\frac{1}{2}} \exp\left(-\frac{\Delta E}{k_B T}\right)\right]$$

Smith, B.; Akimov, A. V. *J. Chem.Phys.* **2019**, 151, 124107

Trivial

$$P_{i\to f}^{A} = 1$$

Energy conservation

$$P_{i\to f}^{A} = \Theta\left(E_{kin} + E_f - E_f\right)$$

Can rescale along NACs?

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

Can rescale along other vectors?

(e.g. excited state forces difference)

Many ways of doing the dynamics

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Decoherence schemes

SDM

Granucci, G.; Persico, M. *J. Chem. Phys.* **2007**, *126*, 134114.

gradually change the amplitudes

$$C_i' = C_i \exp\left(-\frac{\Delta t}{\tau_{if}}\right), \forall i \neq f$$

$$C_f' = C_f \sqrt{\frac{1 - \sum_{i \neq f} \left|C_i'\right|^2}{\left|C_f\right|^2}}$$

DISH

Jaeger, H. M.; Fischer, S.; Prezhdo, O. V. *J. Chem. Phys.* **2012**, *137*, 22A545

collapse amplitudes at an event:

at a decoherence event: $t_i \geq t_{decoh}$

Wavefunction reduction

$$C_i' = C_i \sqrt{\frac{1}{1 - \left|C_f\right|^2}}, \forall i \neq f$$

$$C_f' = 0$$

Hops with quantum probabilities

$$P_{i \to f}^{P}(t, t + \Delta t) = \left|C_f(t)\right|^2$$

ID-A

Nelson, T.; Fernandez-Alberti, S.; Roitberg, A. E.; Tretiak, S. *J. Chem. Phys.* **2013**, *138*, 224111.

- on a successful hop (ID-S)
- on an attempted hop (ID-A)
- at every timestep (ID-C)

Wavefunction reduction

$$C_f = 1, C_i = 0, \forall i \neq f$$

Decoherence times/rates

SDM/EDC

$$\tau_{ij}^{EDC} = \frac{\hbar}{\left|E_i - E_j\right|}\left(1 + \frac{C}{E_{kin}}\right)$$

Granucci, G.; Persico, M. *J. Chem. Phys.* **2007**, *126*, 134114.

mSDM

$$\tau_{ij}^{-1} = \sqrt{\frac{5\langle \delta E_{ij}^2 \rangle}{12\hbar^2}}$$

Akimov, A. V.; Prezhdo, O. V. *J. Phys. Chem. Lett.* **2013**, *4*, 3857
Smith, B.; Akimov, A. V. *J. Chem.Phys.* **2019**, 151, 124107

DISH

Decoherence interval

$$\tau_i^{-1} = \sum_{j \neq i} P_{jj} \tau_{ij}^{-1}$$

Jaeger, H. M.; Fischer, S.; Prezhdo, O. V. *J. Chem. Phys.* **2012**, *137*, 22A545

Phase-informed Decoherence times

Sifain, A. E.; Wang, L.; Tretiak, S.; Prezhdo, O. V.

$$\tau_{ij}^{-1,PI} = \tau_{ij}^{-1} \frac{\left|E_i - E_j\right|}{\left\langle \left|E_i - E_j\right| \right\rangle}$$

Many ways of doing the dynamics

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Corrections

BBCE

thermal Ehrenfest

$$H_{ij}^{Bastida,adi} = |c_j| f_{ij} V_{ij} + |c_i| f_{ji} V_{ji}$$

$$f_{ij} = \left(\frac{2}{1 + \exp\left(-\frac{E_{ij}}{k_B T}\right)} \right)^{1/2}$$

Bastida, A. et al. *Chem. Phys. Lett.* **2006**, *417*, 53

- State tracking (e.g. mincost)
- Phase corrections (Akimov, A. V *J. Phys. Chem. Lett.* **2018**, *9*, 6096)

Forces & Nuclear Dynamics

- Adiabatic (NBRA, various states)
- TSH
- Ehrenfest
- Quantized nuclei (Bohmian trajectories?)
- Bath: Langevin, Nose-Hoover, etc.

- Frustrated hops:
  - Reverse momenta
  - Keep momenta
- Accepted hops:
  - Don’t rescale momenta
  - Rescale along NACs
  - Rescale along force difference

Libra as a workhorse of our developments

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Akimov *JCC*, **2016**, 37, 1626

Implemented in **Libra:** **https://quantum-dynamics-hub.github.io/libra/index.html**
https://github.com/Quantum-Dynamics-Hub/libra-code

Examples& Tutorials: **https://github.com/compchem-cybertraining**

Some of the implemented methods:

Methods	Paper
Surface hopping schemes	Tully, J. C. *J. Chem. Phys.* **1990**, *93*, 1061 (FSSH); Wang, L., et al. *JCTC* **2014**, 10, 3598 (GFSH); Akimov, A. V. et al. *J. Phys. Soc. Jpn.* **2015**, 84, 094002 (MSSH)
Decoherence schemes	Granucci, G.; Persico, M. *J. Chem. Phys.* **2007**, *126*, 134114 (SDM); Nelson, T. et al. *J. Chem. Phys.* **2013**, *138*, 224111. (ID-A, ID-S); Jaeger, H. M. et al. *J. Chem. Phys.* **2012**, *137*, 22A545 (DISH)
Dephasing times calculations	Smith, B.; Akimov, A. V. *J. Chem.Phys.* **2019**, 151, 124107 Akimov, A. V.; Prezhdo, O. V. *J. Phys. Chem. Lett.* **2013**, *4*, 3857 Sifain, A. E.; Wang, L.; Tretiak, S.; Prezhdo, O. V. Granucci, G.; Persico, M. *J. Chem. Phys.* **2007**, *126*, 134114.
Neglect of back-reaction (NBRA)	Prezhdo, O. V.; Duncan, W. R.; Prezhdo, V. V. *Prog. Surf. Sci.* **2009**, *84*, 30
Boltzmann-corrected Ehrenfest	Bastida, A. et al. *Chem. Phys. Lett.* **2006**, *417*, 53 Smith, B.; Akimov, A. V. *J. Chem.Phys.* **2019**, 151, 124107
Phase corrections	Akimov, A. V *J. Phys. Chem. Lett.* **2018**, *9*, 6096
State tracking	Fernandez-Alberti, S.; et al. *J. Chem. Phys.* **2012**, *137*, 014512 (mincost); Temen, S.; AVA. *JPCL* **2021**, 12, 10587-10597 (stochastic)
Interfaces with ES codes	DFTB+ (Smith, B.; AVA *JPCL*. **2020**, 11, 1456), QE (Pradhan et al. *JPCM,* **2018**, 30, 484002), CP2K (Smith, B. A. et al. JCTC, 2021, 17, 678), Gaussian, GAMESS (Sato et al. *PCCP,* **2018**, 20, 25275)
Exact dynamics	Kosloff, D. and Kosloff, R. J. Chem. Phys. **1983**, *52*, 35-53 (SOFT); Colbert, D. T. and Miller, W. H. **1992**, *96*, 1982-1991 (Colert-Miller DVR)
HEOM	Temen et al. *Int. J. Quant. Chem.,* **2020**, 120, e26373

Phase correction

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Akimov, A. V. *J. Phys. Chem. Lett.* **2018** 9, 6096-6102

$$d_{ij} = \frac{\langle \psi_i(t) | \psi_j(t+dt) \rangle - \langle \psi_i(t+dt) | \psi_j(t) \rangle}{2dt}$$

Hammes-Schiffer, S.; Tully, J. C. *J. Chem. Phys.* **1994**, *101*, 4657–4667

But states are defined only up to a complex phase!

Phase correction:

$$f_i = \frac{\langle \psi_i(t) | \psi_i(t') \rangle}{\sqrt{|\langle \psi_i(t) | \psi_i(t') \rangle|}}$$

$$|\tilde{\psi}_i(t')\rangle = f_i^* |\psi_i(t')\rangle$$

$$C_{adi,i} \to \tilde{C}_{adi,i} = f_i C_{adi,i}$$

Indeed:

$$|\psi_i(t)\rangle = e^{i\phi(t)} |\chi_i(t)\rangle$$

$$|\psi_i(t')\rangle = e^{i\phi(t')} |\chi_i(t')\rangle$$

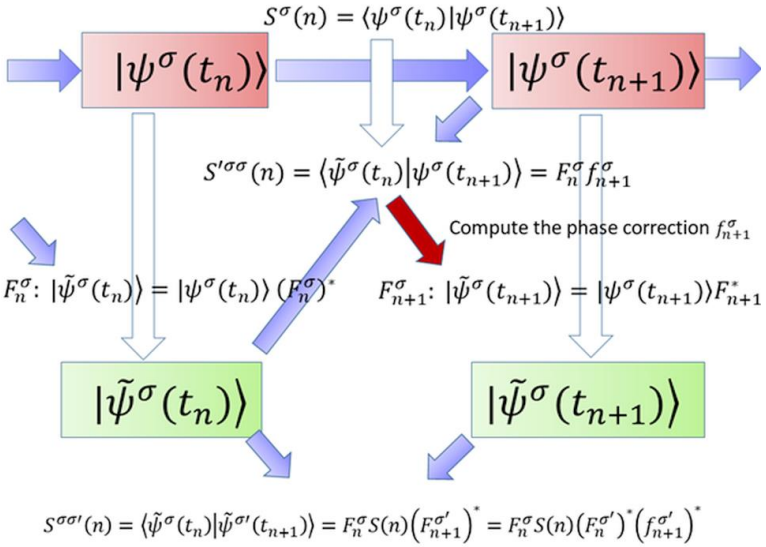
Then:

$$|\tilde{\psi}_i(t')\rangle = f_i^* |\psi_i(t')\rangle = e^{-i[\phi(t')-\phi(t)]} e^{i\phi(t')} |\chi_i(t')\rangle = e^{i\phi(t)} |\chi_i(t')\rangle$$

Phase-correct other properties:

$$d_{ij}^{\alpha} = \langle \psi_i | \nabla_\alpha | \psi_j \rangle \to f_i \langle \psi_i | \nabla_\alpha | \psi_j \rangle f_j^*$$

Implementation in Libra:



Phase correction

Akimov, A. V. *J. Phys. Chem. Lett.* **2018** 9, 6096-6102

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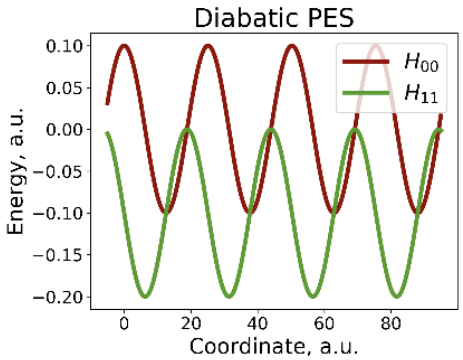
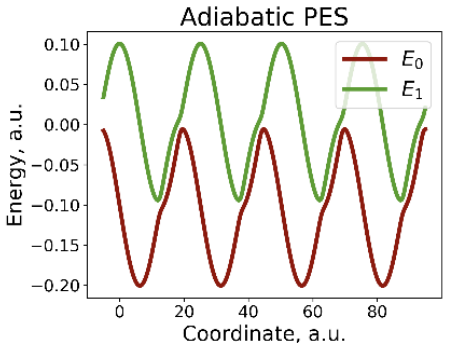
$$H_{ii} = A_i \cos(\omega_i x + \delta_i) + B_i,$$

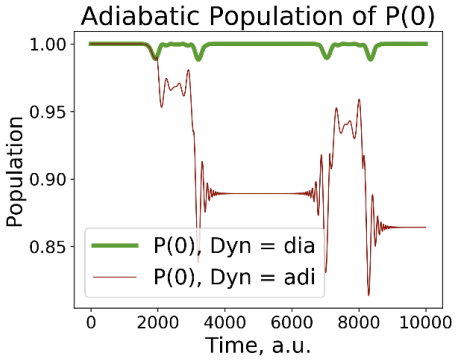
$$H_{ij} = V_{ij} = const.$$

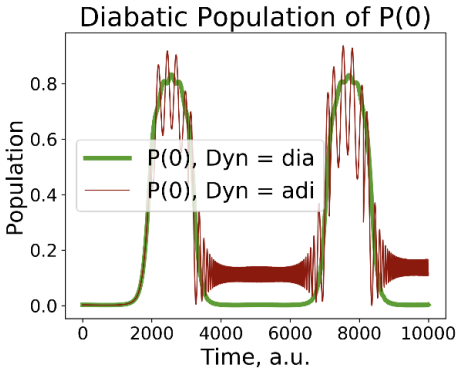
$$\Psi(t=0) = \psi_0$$

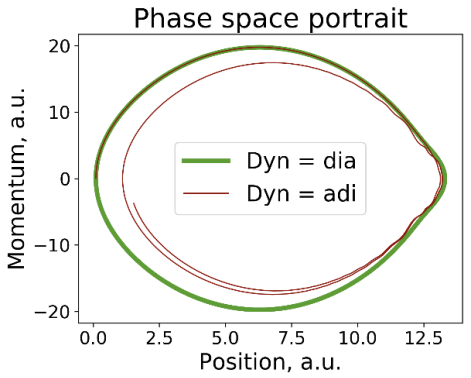




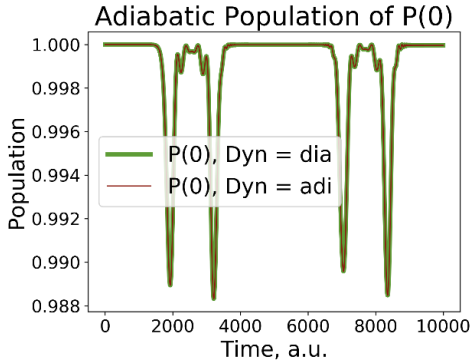
No

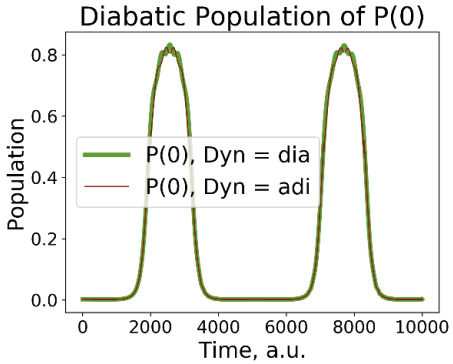


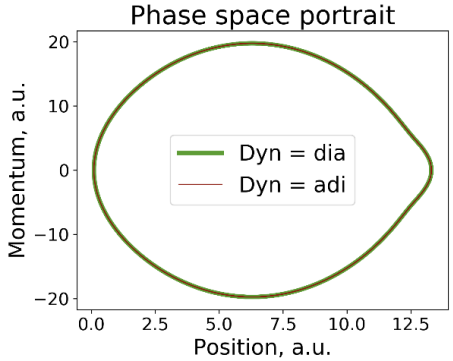




Yes







Comparing methods

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- use various representations
- define properties via external way

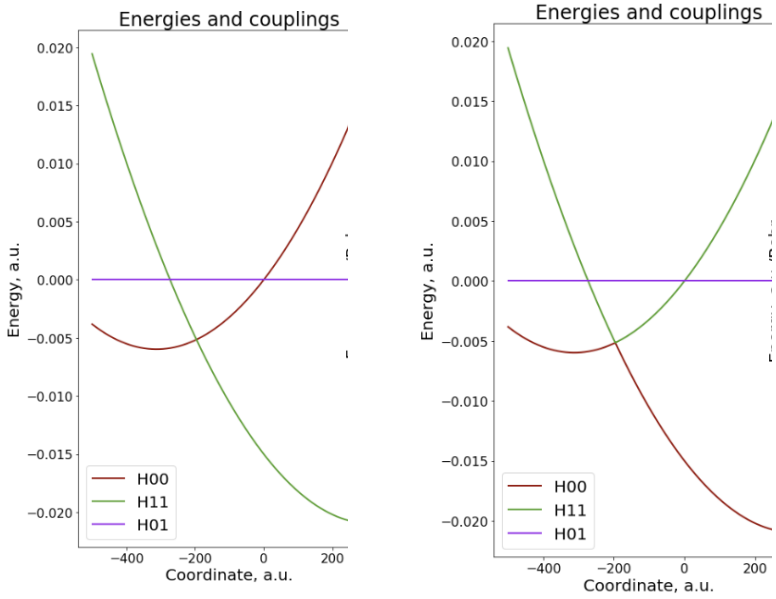
```
def compute_model(q, params, full_id):

    model = params["model"]
    res = None

    if model==1:
        res = my_test_dia_abstract(q, params, full_id)
    elif model==2:
        res = my_test_adi_abstract(q, params, full_id)
    elif model==3:
        res = my_test_adi_files(q, params, full_id)

    return res
```

Marcus-type (spin-Boson Hamiltonian)



Options

4.1. non-NBRA

- 4.1.1. adiabatic dynamics on the ground adiabatic state
- 4.1.2. adiabatic dynamics on the excited adiabatic state
- 4.1.3. non-adiabatic dynamics on the both states via FSSH
- 4.1.4. non-adiabatic dynamics on the both states via FSSH + SDM (user-defined decoherenc
- 4.1.5. non-adiabatic dynamics on the both states via FSSH + SDM (EDC decoherence rates,
- 4.1.6. non-adiabatic dynamics on the both states via FSSH + ID
  - 4.1.6.1. non-adiabatic dynamics on the both states via FSSH + ID-S
  - 4.1.6.2. non-adiabatic dynamics on the both states via FSSH + ID-A
  - 4.1.6.3. non-adiabatic dynamics on the both states via FSSH + ID-C

4.2. NBRA-FSSH

- 4.2.1. FSSH along the adiabatic dynamics on the ground state
- 4.2.2. FSSH along the adiabatic dynamics on the excited state
- 4.2.3. FSSH along the non-adiabatic dynamics trajectories obtained with FSSH
- 4.2.4. FSSH along the non-adiabatic dynamics trajectories obtained with FSSH + mSDM

4.3. NBRA-mSDM

- 4.3.1. mSDM along the adiabatic dynamics on the ground state
- 4.3.2. mSDM along the adiabatic dynamics on the excited state
- 4.3.3. mSDM along the non-adiabatic dynamics trajectories obtained with FSSH
- 4.3.4. mSDM along the non-adiabatic dynamics trajectories obtained with FSSH + mSDM

How to define your model

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```
class tmp:
    pass

def my_test_dia_abstract(q, params, full_id):
    """

    2-state spin
         | 0.5*m
    H =  |
         |

    M = sqrt(E_r

    Args:
        q ( MATR
        params (

            * **
            * **
            * **
            * **
            * **

    Returns:
        PyObject

            * ob
            * ob
            * ob

            * ob
zero ]
    """
                    critical_params = []
                    default_params = { "omega":3.5e-4, "E_r":2.39e-2, "mass":1.0, "V":1.49e-5, "epsilon":1.5e-2  }
                    comn.check_input(params, default_params, critical_params)

                    omega = params["omega"]
                    E_r = params["E_r"]
                    mass = params["mass"]
                    V = params["V"]
                    epsilon = params["epsilon"]

                    n = 2

                    Hdia = CMATRIX(n,n)
                    Sdia = CMATRIX(n,n)
                    d1ham_dia = CMATRIXList();  d1ham_dia.append(
                    dc1_dia = CMATRIXList();  dc1_dia.append( CMAT

                    Id = Cpp2Py(full_id)
                    indx = Id[-1]

                    x = q.col(indx).get(0)

                    Sdia.identity()

                    M = omega * math.sqrt(0.5*E_r * mass)

                    Hdia.set(0,0,  (0.5*mass*omega*omega*x*x + M *
                    Hdia.set(1,1,  (0.5*mass*omega*omega*x*x - M *
                    Hdia.set(0,1,  V  * (1.0+0.0j) )
                    Hdia.set(1,0,  V  * (1.0+0.0j) )

                    d1ham_dia[0].set(0, 0, (omega*omega*x + M)*(1.
                    d1ham_dia[0].set(1, 1, (omega*omega*x - M)*(1.
                    d1ham_dia[0].set(0, 1, (0.0+0.0j) )
                    d1ham_dia[0].set(1, 0, (0.0+0.0j) )


                    obj = tmp()
                    obj.ham_dia = Hdia
                    obj.ovlp_dia = Sdia
                    obj.d1ham_dia = d1ham_dia
                    obj.dc1_dia = dc1_dia

                    return obj
```

```
import numpy as np
import psi4
import os
import sys


def run(grad_method, charge, spin_multiplicity, coords, options):

    psi4.core.set_output_file('tmp.dat',False)

    mol = psi4.geometry(F"""
    {charge} {spin_multiplicity}
    Li 0.0 0.0 0.0
    H  0.0 0.0 1.0

    units bohr
    """)

    mol.set_geometry(psi4.core.Matrix.from_array(coords))
    #mol.set_options( {'reference': 'rhf', 'basis':'6-31Gss', 'guess':'core'} )
    psi4.set_options(options)

    # Compute the Counterpoise-Corrected interaction energy
    # bsse_type='cp'
    E, wfc = psi4.energy(grad_method, molecule=mol, return_wfn=True)

    # Compute force at the converged density
    force = -np.asarray(psi4.gradient(grad_method,ref_wfn=wfc))

    print(E, force)


    return E,force
```

Simplicity

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```
# Random numbers generator object
rnd = Random()

ntraj = 25

# Initialize nucle
init_nucl = {"init
q, p, iM = dynamic
```

```
DR = MATRIX(2,2)
AG = MATRIX(2,2)

dyn_params = { "rep_tdse":1, "rep_ham":0, "rep_sh":1, "rep_lz":0, "tsh_method":-1,
               "force_method":1, "nac_update_method":1, "rep_force":1,
               "hop_acceptance_algo":20, "momenta_rescaling_algo":201,
               "use_boltz_factor":0, "Temperature":300.0, "do_reverse":1, "vel_rescale_opt":-1,
               "do_phase_correction":1, "tol":1e-3,
               "state_tracking_algo":2, "MK_alpha":0.0, "MK_verbosity":0,
               "entanglement_opt":0, "ETHD3_alpha":0.0, "ETHD3_beta":0.0,
               "decoherence_algo":-1, "decoherence_rates":DR,
               "decoherence_times_type":0, "decoherence_C_param":1.0,
               "decoherence_eps_param":0.1, "dephasing_informed":0,
               "ave_gaps":AG, "instantaneous_decoherence_variant":1, "collapse_option":0,
               "ensemble":0, "thermostat_params":{},
```

Case 1.1.1. Ehrenfest, adiabatic tdse, diabatic Ham

```
# Dynamics (Simulation) parameters
dyn_params.update({ "force_method":2, "rep_tdse":1, "rep_ham":0, "prefix":"T1-1-1-1", "tsh_method":-1, "re
p_sh":1 })
dyn_params.update({"state_tracking_algo":2, "do_phase_correction":1, "tol":1e-3, "nsteps":500 })

print(dyn_params)
res = dynamics.run_dynamics(q, p, iM, Cdia, Cadi, projectors, states, dyn_params, compute_model, {"model":
1}, rnd)

plot_dyn(res)
```

Variety of options

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Initialization, sampling

```
# Random numbers generator object
rnd = Random()

ntraj = 25

# Initialize nuclear variables
init_nucl = {"init_type":3, "force_constant":[0.001], "ntraj":ntraj}
q, p, iM = dynamics.init_nuclear_dyn_var([-300.0], [20.0], [10.0], init_nucl, rnd)
```

Model, methods, common options

```
DR = MATRIX(2,2)
AG = MATRIX(2,2)

dyn_params = { "rep_tdse":1, "rep_ham":0, "rep_sh":1, "rep_lz":0, "tsh_method":-1,
               "force_method":1, "nac_update_method":1, "rep_force":1,
               "hop_acceptance_algo":20, "momenta_rescaling_algo":201,
               "use_boltz_factor":0, "Temperature":300.0, "do_reverse":1, "vel_rescale_opt":-1,
               "do_phase_correction":1, "tol":1e-3,
               "state_tracking_algo":2, "MK_alpha":0.0, "MK_verbosity":0,
               "entanglement_opt":0, "ETHD3_alpha":0.0, "ETHD3_beta":0.0,
               "decoherence_algo":-1, "decoherence_rates":DR,
               "decoherence_times_type":0, "decoherence_C_param":1.0,
               "decoherence_eps_param":0.1, "dephasing_informed":0,
               "ave_gaps":AG, "instantaneous_decoherence_variant":1, "collapse_option":0,
               "ensemble":0, "thermostat_params":{},

               "dt":0.1*units.fs2au, "nsteps":500,
               "output_level":2, "file_output_level":0
             }
```

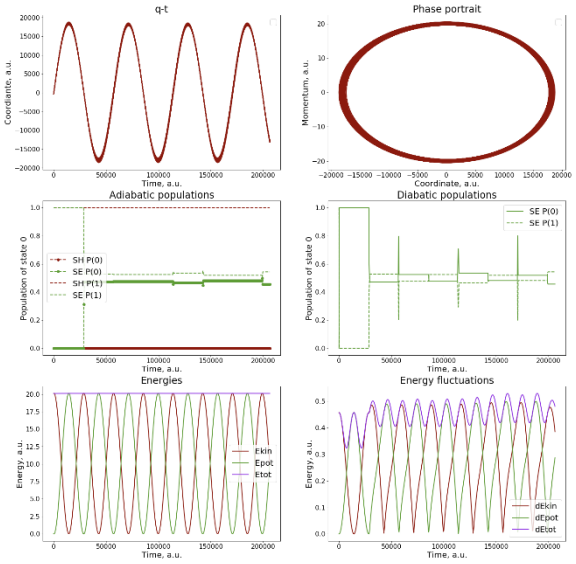
Ehrenfest

Case 1.1.1. Ehrenfest, adiabatic tdse, diabatic Ham

```
# Dynamics (Simulation) parameters
dyn_params.update({ "force_method":2, "rep_tdse":1, "rep_ham":0, "prefix":"T1-1-1-1", "tsh_method":-1, "rep_sh":1 })
dyn_params.update({"state_tracking_algo":2, "do_phase_correction":1, "tol":1e-3, "nsteps":500 })

print(dyn_params)
res = dynamics.run_dynamics(q, p, iM, Cdia, Cadi, projectors, states, dyn_params, compute_model, {"model":1}, rnd)

plot_dyn(res)
```



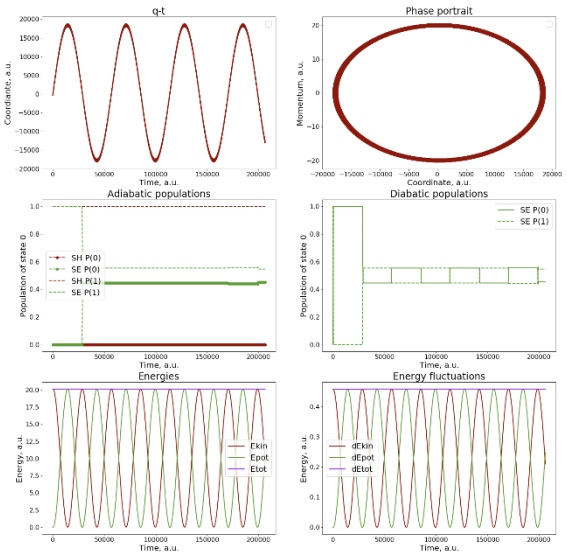
Adiabatic MD

Case 2.1.1.1. Adiabatic dynamics (no hops), TDSE is in adiabatic rep, Ham in diabatic

In this case, the SH populations won't change, but the TD-SE popultations may change - but regard this simply as the TD-SE evolution along a classical (adiabatic) trajectories. The evolved amplitudes do not affect the nuclear dynamics.

```
# Dynamics (Simulation) parameters
dyn_params.update({ "force_method":1, "rep_tdse":1, "rep_ham":0, "prefix":"T1-2-1-1-1", "tsh_method":-1, "rep_sh":1 })
dyn_params.update({"state_tracking_algo":2, "do_phase_correction":1 })

print(dyn_params)
res = dynamics.run_dynamics(q, p, iM, Cdia, Cadi, projectors, states, dyn_params, compute_model, {"model":1}, rnd)
plot_dyn(res)
```

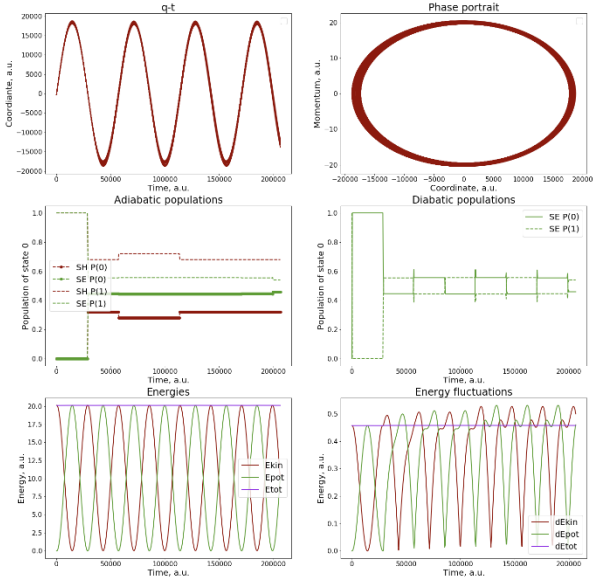


FSSH dynamics

Case 2.1.1.2.1. FSSH, TDSE is in adiabatic rep, Ham in diabatic

```
# Dynamics (Simulation) parameters
dyn_params.update({ "force_method":1, "rep_tdse":1, "rep_ham":0, "prefix":"T1-2-1-1-2-1", "tsh_method":0, "rep_sh":1 })
dyn_params.update({"hop_acceptance_algo":20, "momenta_rescaling_algo":201 })

print(dyn_params)
res = dynamics.run_dynamics(q, p, iM, Cdia, Cadi, projectors, states, dyn_params, compute_model, {"model":1}, rnd)
plot_dyn(res)
```



Acknowledgements

Funds:

UB startup

Computing resources:

OAC-NSF

Thank you! Questions?