pySpawn User Manual

Version 0.0

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# Introduction

## What Is PySpawn?

PySpawn is an implementation of ab initio multiple spawning (AIMS) in Python 2.7.

## What Are The Primary Goals of the PySpawn Project?

PySpawn is designed with the following goals in mind:

* The core of pySpawn is designed to be small and thus easy to maintain.
* PySpawn is designed to be extensible. At present, the following functionality can, in principle, be implemented without modification of existing code:
  + Interfaces to additional electronic structure codes/methods
  + Quantum mechanical Hamiltonians (e.g. adiabatic representation vs. diabatics vs. diabatized Gaussians on adiabatic surfaces, interpolated vs. analytical derivative couplings, spin orbit Hamiltonian, explicit light field)
  + Quantum mechanical integrators
  + Classical mechanical integrators
* PySpawn is designed with large, shared computer resources in mind. Specifically, pySpawn is designed to facilitate
  + Subdivision of large jobs into small chunks
  + Restart
  + Parallelization

## Features

* Runs FMS/AIMS jobs in the adiabatic representation
* Derivative couplings computed by norm preserving interpolation (NPI)
* PySpawn interfaces to a development version of TeraChem via a protobuf interface

## Citing pySpawn

If you use pySpawn please cite the following:

“pySpawn is a nonadiabatic molecular dynamics software package written by Benjamin G. Levine”

This citation will eventually be replaced by a true publication.

## License

PySpawn is distributed under the MIT License:

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## Acknowledgements

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# Obtaining and Installing PySpawn

## Obtaining PySpawn

PySpawn can be obtained from GitHub: <https://github.com/blevine37/pySpawn17>.

## Requirements and Dependencies

PySpawn is written in Python 2.7 and is not currently compatible with Python 3.

PySpawn requires the following dependencies:

* numpy
* h5py
* tcpb (TeraChem protobuf interface; required to run with TeraChem only)
* google (required by tcpb for TeraChem interface only)
* protobuf (required by tcpb for TeraChem interface only)

These can easily be installed using pip:

pip install numpy h5py google protobuf

## Installing PySpawn

Having obtained pySpawn and installed the necessary dependencies, cd to the top directory and install it by running

python setup.py install

# Abbreviations Used in this Manual

Various abbreviations will be used in this manual:

AIMS ab initio multiple spawning

a.u. atomic units

CAS complete active space

CASCI complete active space configuration interaction

CASSCF complete active space self-consistent field

CISNO configuration interaction singles natural orbital

FMS full multiple spawning

FOMO floating occupation molecular orbital

NPI norm-preserving interpolation

PES potential energy surface

SA state averaged

TBF trajectory basis function

# Guided Tour of Your First PySpawn Simulation

This chapter will trace the example calculation in examples/ethylene\_sacasscf. This job simulates the dynamics of ethene on the SA2-CAS(2/2)/6-31G potential energy surface. A single initial nuclear basis function is initiated, with its initial position and momentum sampled from the ground state vibrational Wigner distribution computed in the harmonic approximation. This section will not detail all the inner workings of the code, but instead will highlight

* the series of steps needed to run a simulation with pySpawn
* the input scripts
* the output structure

**Most of what you need to know to start using pySpawn to run simulations is in this chapter, so it will be in your best interest to read it carefully!** A more detailed description of input parameters, the analysis module, and simulation workflow will be presented in subsequent chapters.

## Building Hessian File for Initial Condition Sampling

The first step in any AIMS simulation is choosing the initial conditions. One popular choice, used here, is to sample the average position and momentum of the initial TBF from the vibrational Wigner distribution, computed in the harmonic approximation. This requires three pieces of information:

* the ground state minimum structure
* the Hessian (2nd derivative) matrix of PES at the ground state minimum
* the masses of the atoms

Before beginning, one must compute the minimum and Hessian and store them in pySpawn’s preferred format: hessian.hdf5. We will assume that the reader can optimize the ground state minimum energy geometry of their chosen molecule. The script build\_hessian.py takes this structure, drives TeraChem to compute the Hessian matrix, and then stores both the geometry and Hessian in hessian.hdf5.

The script is self-explanatory. There are a few important points to keep in mind:

* **Most importantly, if you wish to recompute the Hessian you must remove any existing** hessian.hdf5 **files!**
* It is your responsibility to make sure that the structure that is inputted is the desired ground state minimum structure.
* The final hessian.hdf5 file contains both the geometry and Hessian matrix. When sampling the initial conditions, both the geometry and Hessian will be drawn from this file.
* If the job should die before the hessian is completed, it can be restarted trivially by running this same script. The restarted job will read the existing hessian.hdf5 file and pick up where it left off.

## AIMS Simulation Script

With hessian.hdf5 in hand, we are ready to run an AIMS simulation of ethene. The Python script that does this is start\_c2h4.py. This first section of this script defines several important parameters of the simulation:

* seed is the random number seed (for Wigner initial conditions).
* clas\_prop defines the classical propagator. vv opts for velocity Verlet integration.
* qm\_prop defines the propagator of the quantum amplitudes (the expansion coefficients in the AIMS wave functions). rk2 opts for adaptive second-order Runge-Kutta.
* qm\_ham defines the Hamiltonian used to propagate these amplitudes. adiabatic opts for AIMS in the adiabatic basis with NPI time-derivative couplings.
* potential defines the means by which the electronic structure and PES will be computed. terachem\_cas opts for on-the-fly calculation at a CAS level of theory using TeraChem. This option will work for SA-CASSCF, FOMO-CASCI, or CISNO-CASCI.
* t0 is the initial time of the simulation (in a.u.).
* ts is the time step of the simulation (in a.u.).
* tfinal is the final time of the simulation (in a.u.).
* numdims is dimensionality of the system (3 \* number of atoms).
* numstates is the number of electronic states in the calculation.

The definition of these scalar and string variables is followed by the creation of three dictionary objects:

* tc\_options contains options to be passed to TeraChem. Most of these options are documented in the TeraChem documentation, and thus are not discussed here. Exceptions:
  + atoms is a list of the abbreviations for the atoms in the molecule, in order.
  + cas\_energy\_labels is a list of tuples defining the states whose energies will be passed from TeraChem to pySpawn. The first element of each tuple is the state index (ground state is 0, first excited state is 1…) while the second element is the spin multiplicity (singlet is 1…)
* traj\_params contains parameters of the individual TBFs:
  + time is the initial time of the simulation.
  + timestep defines the time step for classical propagation.
  + maxtime defines the maximum time to which each TBF will be propagated.
  + spawnthresh defines the coupling above which spawning will be triggered.
  + istate is the index of the electronic state to which this TBF belongs (0 is the ground states…)
  + widths is a numpy array containing the widths, α, associated with each degree of freedom (in units of bohr-2).
  + atoms contains the list of atom labels (and should be identical to atoms in tc\_options in all normal cases).
  + masses is a numpy array containing the masses associated with each degree of freedom (in a.u., i.e. electron masses).
  + tc\_options is the dictionary structure defined above which contains options to be passed to TeraChem.
* sim\_params contains parameters of the entire simulation, including the quantum propagation:
  + quantum\_time is the initial time of the simulation (and should be identical to time in the traj\_params object in all normal cases).
  + timestep is the time step for quantum propagation (and should be identical to timestep in the traj\_params object in all normal cases).
  + max\_quantum\_time is the simulation time at which quantum propagation should stop (and should be identical to maxtime in the traj\_params object in all normal cases).
  + qm\_amplitudes is the initial quantum amplitudes.
  + qm\_energy\_shift is an energy shift applied to the diagonal of the Hamiltonian. For numerical convenience, these diagonals should be roughly zero.

Other options for traj\_params and sim\_params are documented in a subsequent chapter.

To this point the script is a simple Python script, defining various variables and data structures that will be passed to pySpawn. Now, we begin by importing methods into the simulation and traj classes that will enable propagation. An instance of the simulation class will contain information pertaining to the entire simulation, including the quantum propagation. An instance of the traj class will describe each TBF. (For those familiar with FMS90, the simulation class is similar in spirit to the “bundle.”)

In order to propagate, two sets of methods must be imported into the simulation class to enable propagation: one for quantum integration and one for the quantum Hamiltonian. We have already specified the flavor of integrator (qm\_prop = “rk2”) and Hamiltonian (qm\_ham = “adiabatic”) that we wish to use above. These two lines simply import the necessary methods:

exec("pyspawn.import\_methods.into\_simulation(pyspawn.qm\_integrator." + qm\_prop + ")")

exec("pyspawn.import\_methods.into\_simulation(pyspawn.qm\_hamiltonian." + qm\_ham + ")")

Similarly, two sets of methods must be imported into the traj class to enable propagation: one to choose the potential and one to choose the classical integrator. Again, we have already specified the flavors we wish above (potential = “terachem\_cas”; clas\_prop = “vv”). These two lines simply import the necessary methods into the traj class:

exec("pyspawn.import\_methods.into\_traj(pyspawn.potential." + potential + ")")

exec("pyspawn.import\_methods.into\_traj(pyspawn.classical\_integrator." + clas\_prop + ")")

Before preceding further, pyspawn.general.check\_files() checks to make sure that there is not any pySpawn hdf5 output in the current directory. The job will fail here if there is. **By default, pySpawn will append to an existing hdf5 output file, not overwrite it, so it is important to delete unrelated output before running a new job. Similarly, every pySpawn job must run in its own directory.**

Now, the following lines instantiate a single traj object and set its various attributes:

traj1 = pyspawn.traj()

traj1.set\_numstates(numstates)

traj1.set\_numdims(numdims)

traj1.set\_parameters(traj\_params)

It’s important that numstates and numdims be set **before** setting the remaining parameters, because the size of various attributes of the traj object depend on these attributes.

Next we set the initial positions and momenta by sampling from the Wigner distributions:

traj1.initial\_wigner(seed)

This routine will read the geometry and Hessian matrix from hessian.hdf5 (created above). The masses were included in traj\_params, and thus have been set. The masses are required in order to construct the Wigner distribution, so it is important that they be set the masses before calling initial\_wigner.

Now we instantiate the simulation object, add the traj object that we just created to it, and set the various simulation parameters:

sim = pyspawn.simulation()

sim.add\_traj(traj1)

sim.set\_parameters(sim\_params)

Finally, it is time to propagate the AIMS wave function:

sim.propagate()

To run the script at the linux command prompt, use something like:

python start\_c2h4.py >pyspawn.log 2>&1 &

And we are off to the races!

## Output

PySpawn creates three types of output during a dynamics run: text output (standard output), HDF5 output, and json output, as described in this section.

The text output is produced in the standard output. (If you run the command in the previous section, it will be recorded in pyspawn.log.) The purpose of the text output is to track the progress of the simulation. Each significant step in the calculation results in a line being printed to this output. It is useful for tracking the progress of a job and for debugging. The text output does not contain the quantitative output of the simulation.

The quantitative output of the simulation is recorded in the HDF5 output. Several HDF5 output files are produced. working.hdf5 is the working copy which is being modified on the fly by the simulation. sim.hdf5 is a copy that is synchronized with the most recent json output (described below) for restart purposes. sim.hdf5 should be viewed as the quantitative output of the simulation. It contains all of the time-dependent information needed to reconstruct the time-dependent AIMS wave function, e.g. classical positions and momenta of each TBF at each time step, quantum amplitudes as a function of time, electronic structure information (e.g. CI vectors and orbitals) as a function of time, derivative couplings as a function of time, etc.

HDF5 is a binary format and thus is not directly human readable. One can easily glimpse the contents using h5dump or any HDF5 viewer. However, the pySpawn analysis module (described below) is designed to process sim.hdf5 into human readable format, so that direct viewing of the HDF5 files should not be necessary in most cases. If desired functionality is missing, it should be relatively easy to implement (and contribute) it within the framework of the analysis module.

The final output file is sim.json, which contains a complete snap shot of the current simulation object. It primarily exists for restart purposes, but can be useful to troubleshooting/debugging as well. Unlike sim.hdf5, sim.json does not contain any data prior to the current state of the system, and thus cannot be used for analysis of time-dependent AIMS wave function.

sim.json and sim.hdf5 are synchronized, and are both required for restart. Each time a new pair of files is stored, the previous pair is renamed (e.g. sim.1.json and sim.1.hdf5, etc.) so that at any given time several synchronized pairs are available for restart, in the event that a file should be corrupted or accidently deleted. working.hdf5 is not synchronized with a json file, and thus cannot be used for restart.