Towards Efficient Direct Semiclassical Molecular Dynamics for Complex Molecular Systems

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XSEDE 2014 Atlanta, Georgia
Introduction

• Chemical processes are intrinsically quantum mechanical.

• Classical dynamics using fitted force fields are routinely applied to complex molecular systems, but force fields have some limitations:
  — tuned to experimental/electronic structure data, compensation for quantum effects are artificial and *ad hoc*;
  — often biased by the functional forms chosen --- may not be transferable, i.e. it cannot be applied *a priori* to other molecular systems;
  — do not account for bond dissociation or excited vibrational processes, due to the harmonic approximation.
  — Fitting atomic forces is a trade-off between the desired accuracy and the human and computational effort required to construct them, could be fairly human effort demanding for “large” complex molecular systems.
The Direct Semiclassical Dynamics

• Direct semiclassical (SC) molecular dynamics is an attractive alternative, and has undergone a “rebirth of interest” since recently [J. Phys. Chem. A, 104, 10321-10327, 2000]:

— With direct dynamics, nuclear classical dynamics is coupled with atomic forces calculated from quantum mechanical electronic structure theory.

— Semiclassical dynamics employs thousands of direct dynamics trajectories to calculate the Feynman Path Integral propagator, and reproduces fairly accurate quantitative quantum effects.
High Computation Cost of Direct SC Dynamics

- Direct semiclassical dynamics incurs much lower computation cost than purely quantum dynamics, but is much more expensive than classical dynamics.

- Thus, even on large HPC machines, substantial reduction of computation cost is needed for many interesting molecular systems.

- The high computation cost of direct semiclassical dynamics comes from two sources:
  - the large number of trajectories needed, and
  - the enormous computation cost to calculate a single trajectory.
Solution to Large Number of Trajectories

- A simulation for molecular systems with around 10 atoms could require hundreds of thousands of trajectories for a usual semiclassical method. To reduce this requirement, we developed a semiclassical algorithm that needs only hundreds to thousands of trajectories, with
  - longer trajectories and
  - carefully chosen initial states of the trajectories.

- The computations of different trajectories are embarrassingly parallel. Hence large HPC systems like those at XSEDE can help — calculate different trajectories in parallel.
The Computation Cost of Single Trajectory

- The semiclassical propagator needs the Hessian of the potential energy in every time step, important quantities that
  - take into account the quantum “jiggling” of the atoms [Feynman, R. P.; Hibbs, A. R. *Quantum Mechanics and Path Integrals* (McGraw-Hill, 1965)] by calculating second order fluctuations around the classical paths; and
  - are by far the dominant source of computation cost, leading to days or weeks for a single trajectory calculation on a powerful multi-core processor.

- For instance, our on-going study of 10-atom glycine with the very modest B3LYP/6-31G** electronic structure theory takes about 11.5 days on two quad-core Intel Xeon 2.26GHz processors (8 cores total) for a trajectory of 5000 time steps.

Not practical if our simulation needs hundreds of trajectories with more accurate electronic structure theory, unless a huge allocation.
Reducing the Computation Cost of Single Trajectory

- **Target**: the Hessian, the dominant computation cost, is our target of computation reduction.

- **How**: the future (of the Hessian) exists in its past, at least partially.
  
  - The Hessian $H(t_{k+1})$ at time $t_{k+1}$ may differ from the Hessian $H(t_k)$ at time $t_k$ mainly in some subspace, but differ not much in other subspace.
  
  - How to identify the difference: $H(t_{k+1}) - H(t_k) = ?$
Directional Approximation of the Hessian

- The Hessian is a function of the positions of atoms, that is, \( H(t) = H(X(t)) \), where \( X(t) \) is the coordinates of atoms.

- Directional approximation via compact finite difference (CFD)

\[
\frac{1}{2} (H_{k+1} + H_k)(X_{k+1} - X_k) = G_{k+1} - G_k,
\]  

--- one order of accuracy higher than first-order Taylor expansion but with the same stencil (i.e. the set of sampling points);

--- compact refers to the compactness of the set of sampling points --- higher accuracy without incurring more data.

--- Challenge: When the variable \( X \) is a vector with \( n \) entries, that is, \( X = (x_1, x_2, \ldots, x_n) \), Equation (1) has a \( \frac{1}{2} n(n-1) \)-dimensional solution space.

--- The approach is to identify the difference \( H(t_{k+1}) - H(t_k) \) with something known.
Directional Hessian Approximation --- continued

- Eq. (1), i.e. \( \frac{1}{2}(H_{k+1} + H_k)(X_{k+1} - X_k) = G_{k+1} - G_k \), is equivalent to
  \[
  (H_{k+1} - H_k)(X_{k+1} - X_k) = 2(G_{k+1} - G_k) - 2H_k(X_{k+1} - X_k). \tag{2}
  \]
  Thus, if have the gradient \( G_{k+1} \) at time \( t_{k+1} \), one may find a “good” solution \( (H_{k+1} - H_k) \) of Eq. (2), which can be added to \( H_k \).

- Re-writing, Equation (2) into
  \[
  (H_{k+1} - H_k)\Delta X = R, \tag{3}
  \]
  where \( \Delta X = X_{k+1} - X_k \) and \( R = 2(G_{k+1} - G_k - H_k\Delta X) \), a solution of Eq. (3) that is symmetric and “minimizes” the component of \( H_{k+1} - H_k \) in subspace orthogonal to \( \Delta X \) is the Powell Symmetric Broyden (PSB) scheme
  \[
  H_{k+1} - H_k = \frac{\Delta X R^T + R \Delta X^T}{\|\Delta X\|^2} - \frac{R^T \Delta X}{\|\Delta X\|^4} \Delta X \Delta X^T. \tag{4}
  \]
A generalization, due to Bofill, of Scheme (4) is

\[ H_{k+1} = H_k + (1 - \lambda) \frac{R R^T}{R^T \Delta X} + \lambda \left( \frac{\Delta X R^T + R \Delta X^T}{\| \Delta X \|^2} - \frac{R^T \Delta X}{\| \Delta X \|^4} \Delta X \Delta X^T \right). \]  

where \( \lambda \) is a parameter allowed to vary. Scheme (5) is called the CFD-Bofill family of Hessian update schemes, where the CFD contribution is effected through the formula of \( R \).

A good choice for \( \lambda \) in (5) is \( \lambda = 1 - \frac{(R^T \Delta X)^2}{\| R \|^2 \| \Delta X \|^2} \), and scheme (5) with this \( \lambda \) is called the CFD-Bofill scheme. Scheme (5) reduces to the CFD-Powell Symmetric Broyden (CFD-PSB) scheme when \( \lambda = 1 \).
Numerical Experiments

• We tested CFD-Bofill and CFD-PSB in dynamics simulations for CO₂. The ab initio calculations for CO₂ use B3LYP/cc-pVDZ theory. The code the two of the CFD-based Hessian update schemes was integrated with a development version of VESNUS/NWChem package.

• In the simulation, for every K time steps (K varies) one ab initio Hessian is calculated followed by (K−1) approximated Hessians. We varied the values of K in the tests, and used monodromy matrix calculated using ab initio or updated Hessian as a metric to measure the accuracy of Hessian approximation. Since accurate Hessian would keep the determinant of the monodromy matrix at the constant 1, we calculated the deviation of the determinant of M(t)^T M(t) away from 1, and plotted the deviations on Figures 1-3 for CO₂.
Figure 1: Plot of $|1-\text{det}[M(t)^TM(t)]|$ for CO$_2$
Figure 2: Plot of $|1-\text{det}[M(t)^TM(t)]|$ for CO$_2$
Figure 3: Plot of $|1-\text{det}[M(t)^{T}M(t)]|$ for CO$_2$
Acknowledgement

This work was supported in part by the National Science Foundation under Grant Nos. CHE-0957521, and OISE-0730114.

The authors thank the High Performance Computing Center at Texas Tech University for their support.