‘Tis not folly to dream: Using Molecular Dynamics to Solve Problems in Chemistry

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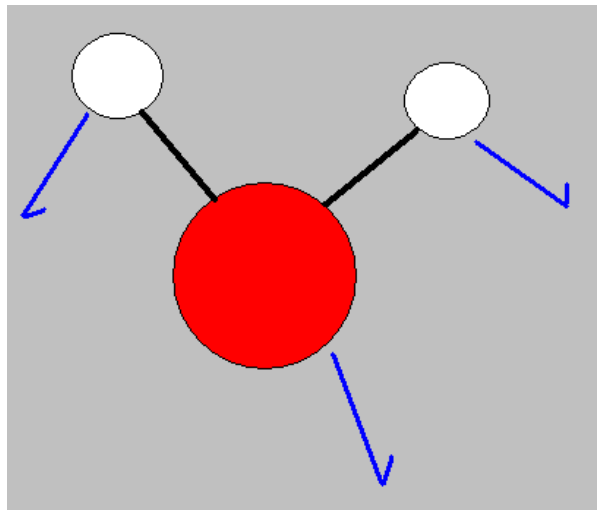
Classical Problems in Computational Chemistry

- Geometry Optimization
  - Finding the “best” shape of a molecule
  - Requires finding the minimum on an energy surface
- Free Energy Calculations
  - Can be used to determine the “spontaneity” of a process
  - Current methods require averaging a large amount of data

Molecular Dynamics (MD) is a powerful tool

$r(t) = r(0) + t\,v(t) + t^2\,a(t)$

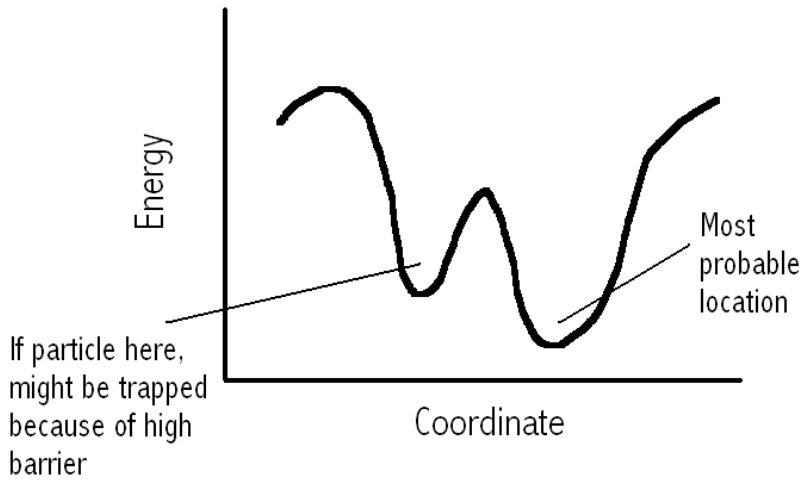


- For perfect MD, we need to know velocities and accelerations for all time.
- Must settle for approximation, using discrete algorithm.

Calculate accelerations at a given position and then move system.

Applying MD to geometry optimizations

- If constant temperature MD is used, Boltzmann distribution applies, $P \sim \exp(-\beta E)$, β is an expression of the temperature as an energy
- Low energy states more probable!



Applying MD to calculate free energy differences (Free Energy Perturbation Method)

- Free energy perturbation (FEP) can use averages from MD to approximate statistical mechanical integrals.

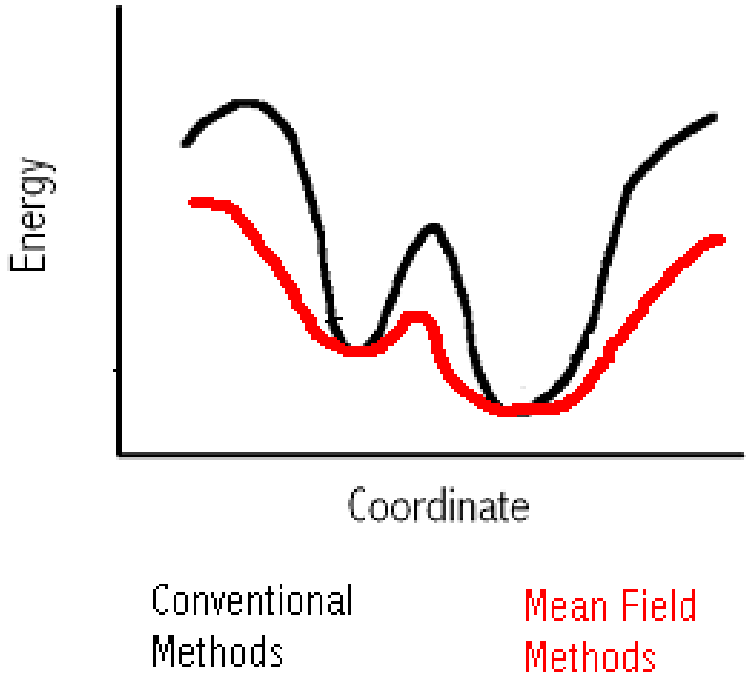
$$\Delta F = -\frac{1}{\beta} \ln < \exp(-\beta[H_j(\Gamma) - H_i(\Gamma)]) >_{H_i}$$

- 1. Choose a path $H(\lambda) = H_i(1-\lambda) + H_f\lambda$.
- 2. Equilibrate at $\lambda = 0$
- 3. Collect data at $\lambda = 0$
- 4. Repeat 2 & 3 at other values of λ until the path is mapped from $\lambda = 0$ to $\lambda = 1$.

Method only useful if adequate sampling achieved. Barriers that interfere in geometry optimizations interfere here as well

Mean Field Methods Reduce Energy Barriers

- Mean field methods break equations of motion, but reduce energy barriers.
- Done by "copying" a small part of system, and force felt by rest is average of copied parts.



The EXACT approximation

- EXACT (Ensembles Extracted from A Coordinate Transformation) is a way devised by our group (Hixson, Wheeler, *in preparation*) to interpolate between conventional and mean field MD.
- Works by a coordinate transformation, so that the average coordinate (used in mean field methods) becomes main coordinate used in dynamics, other coordinates only used when important.
- Method intended to provide an alternate technique to solve the geometry optimization problem.

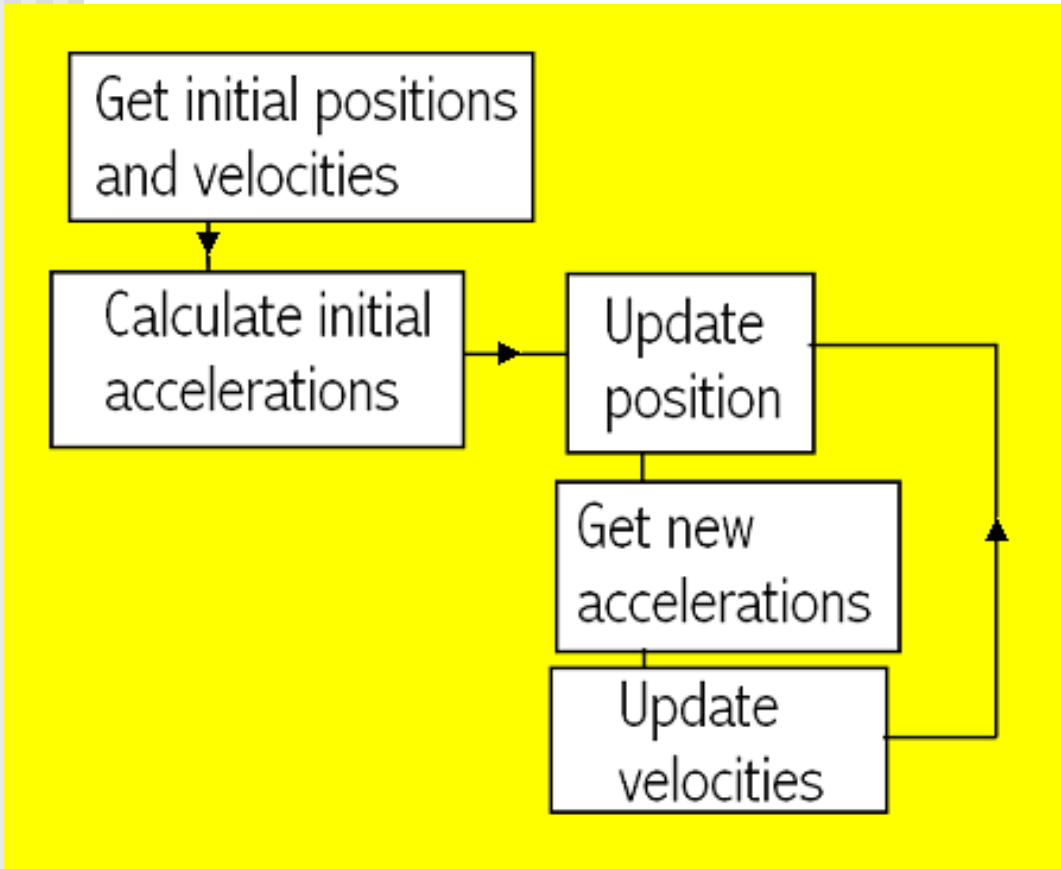
Ensemble Free Energy Perturbation Method (EFEP)

- Uses same coordinate transformation in EXACT to solve an alternate FEP-like equation.
- Uses either constraint or restraint to keep uncopied parts of system together – cons-(re)straint energy used to calculate correction factor.
- Possible benefits of this method:
  - Reduces barriers as in mean field methods, so sampling better.
  - Faster than conventional method – instead of iterating over "windows," is done in a single step.

Ah, sweet folly.

- We have two new methods to test, EFEP and EXACT.
- Tests have been performed to date using simple, custom programs.
- More ambitious tests are planned with our nearly ready self-written MD code, “folly”.
- “folly” is the name we’ve given to our suite of MD programs constructed with the consultation of Henry Neeman (Director, OSCER).

folly explained



- Uses periodic boundary conditions, Ewald sums, Nose-Hoover chains temperature control, and velocity Verlet integration method, and the Amber force field.

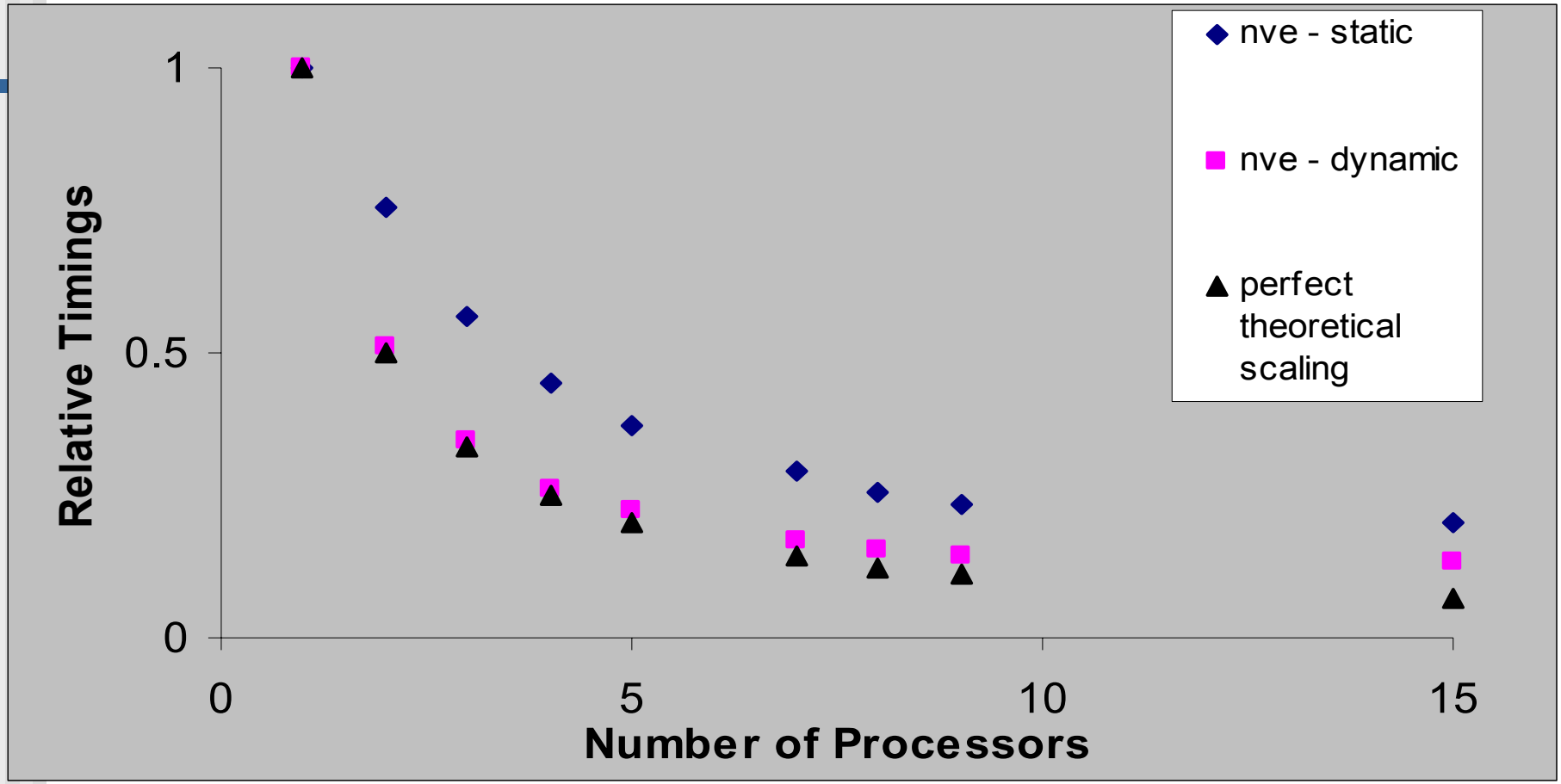
OpenMP parallelization scheme

- OpenMP is a standard used to parallelize programs on SMP machines (such as OSCER's new IBM Regatta machine)
- OpenMP is used in folly only to speed the calculation of the forces – only a single function is modified.
- Nearly perfect scaling up to 8 processors

Proposed MPI parallelization scheme

- MPI is a standard library used to parallelize programs on distributed architecture machines (such a a Linux cluster)
- folly is not as well suited to MPI as OpenMP
- Will parallelize forces as in OpenMP, doing load balancing using previous step's information

Benchmarks on OSCER's IBM Regatta



A typical system was tested. Good scaling was achieved using OpenMP's dynamic method for large numbers of processors

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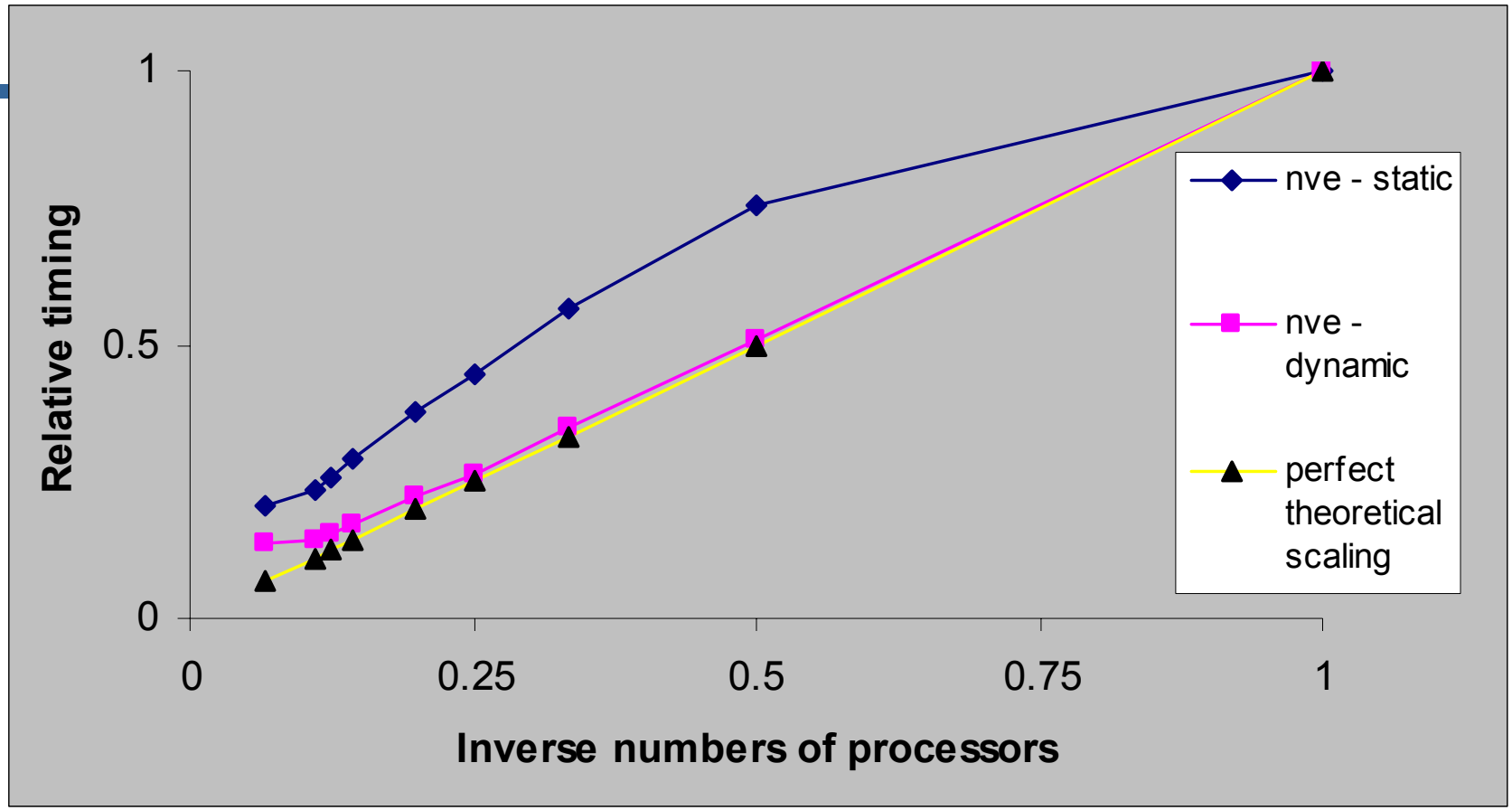

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Conclusions

- We are currently writing MD code to be used on parallel machines.
- Will use this code to test two new methods we've developed, EXACT for difficult geometry optimizations and EFEP to calculate free energy differences faster.
- Tests of currently written code shows that **near theoretical maximum speedup with increasing numbers of processors** can be achieved on OSCER resources.

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