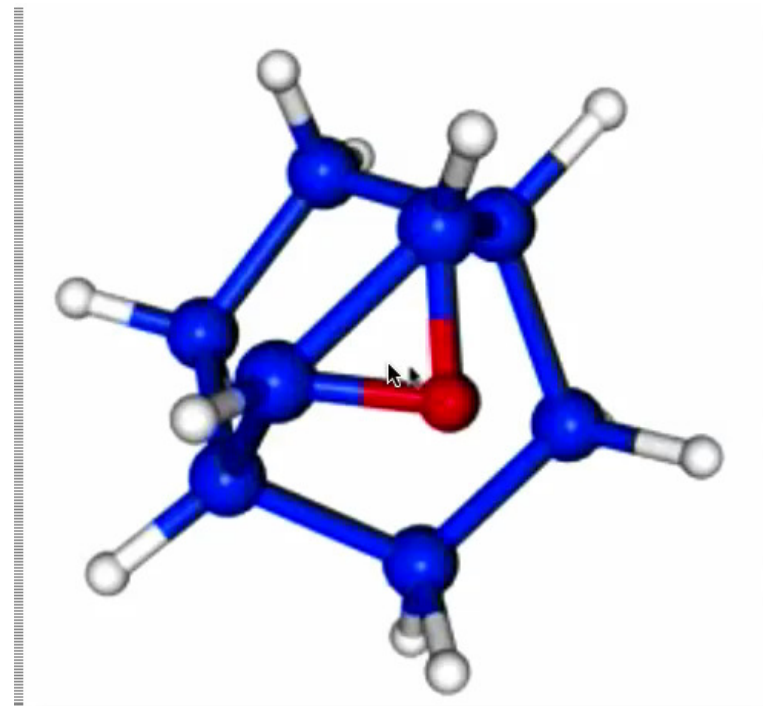# AB INITIO MOLECULAR DYNAMICS

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CHE 883

# What does ab initio molecular dynamics do?

- In ab initio molecular dynamics (AIMD) calculations we calculate a trajectory, the motion of the nuclei and electrons in time
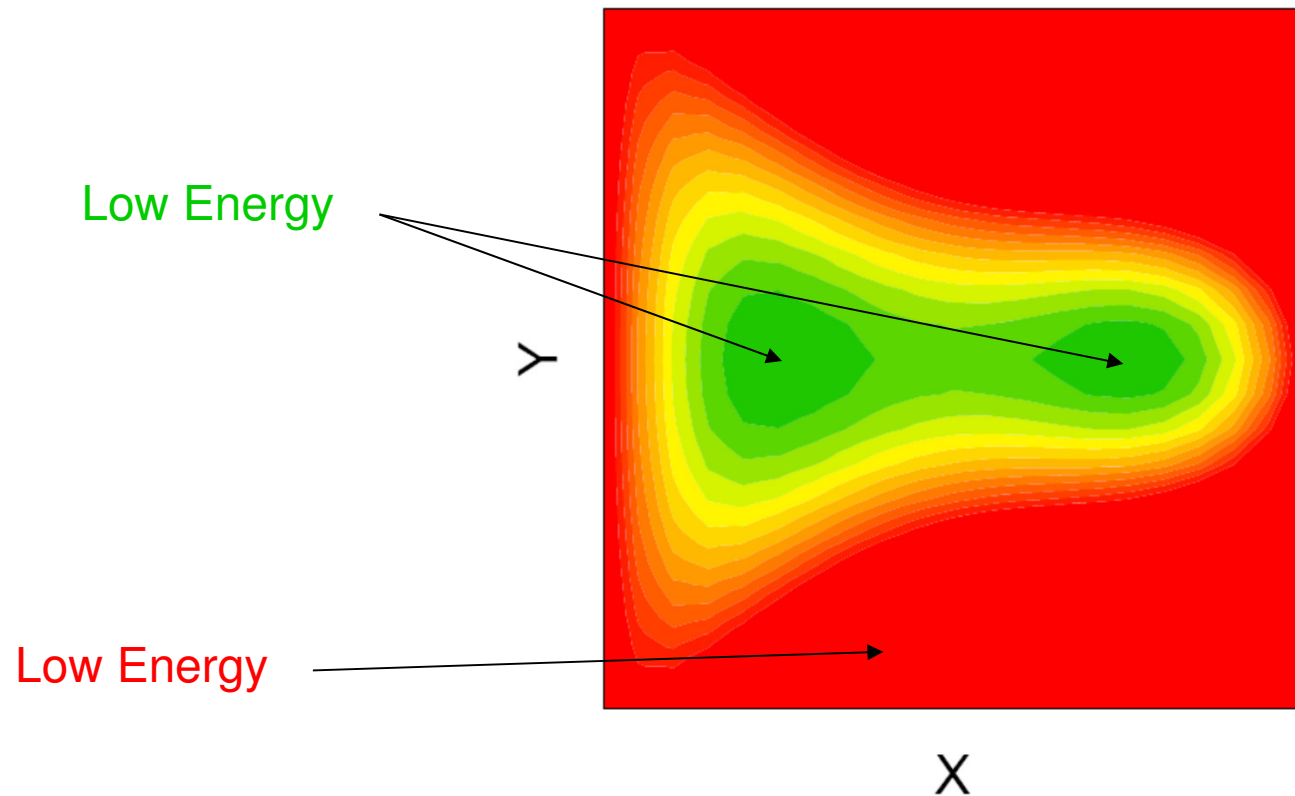
What can AIMD tell us? (Why AIMD and not standard quantum chemistry?)

- Sample equilibrium distributions under thermodynamic conditions
  - AIMD at finite temperature naturally includes entropy, which is ignored in standard quantum chemistry
  - Can sample various thermodynamic ensembles: NVT, NVE, NPT
- Dynamics of systems out of equilibrium
  - Molecular collisions
  - Electronic excited states
- Explore PES in an unbiased way
  - AIMD at sufficient temperature will cross barriers
  - Find the global minimum of the PES without need for a reasonable initial guess (simulated annealing)

Energy v. Free Energy
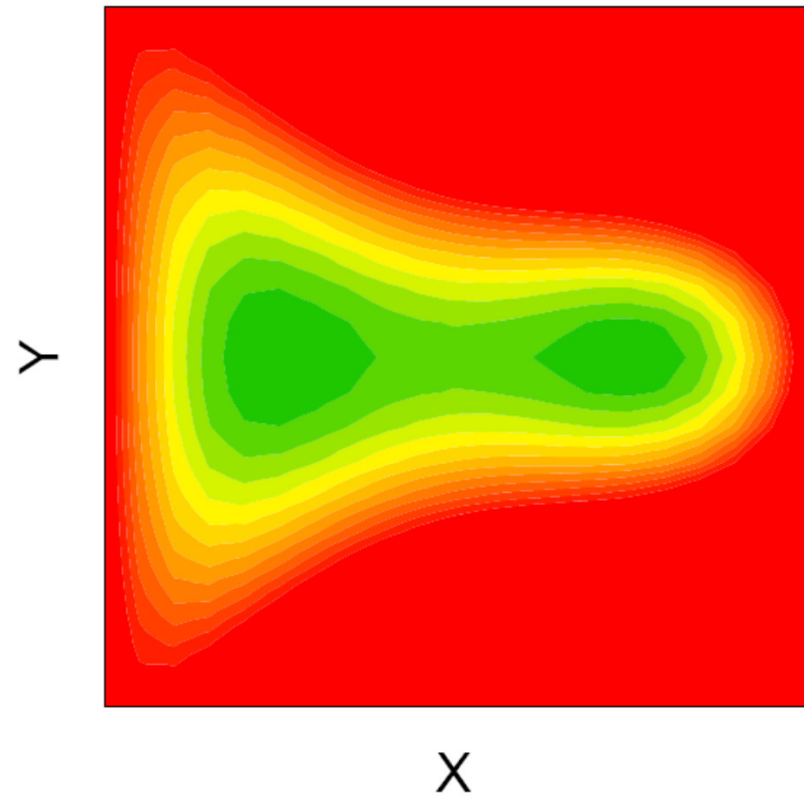
Energy v. Free Energy

Energy v. Free Energy

Wide well

Energy v. Free Energy

Wide well

Narrow well

Y

X

Energy v. Free Energy

Wide well

Higher
Entropy

Narrow well

Lower
Entropy

Y

X
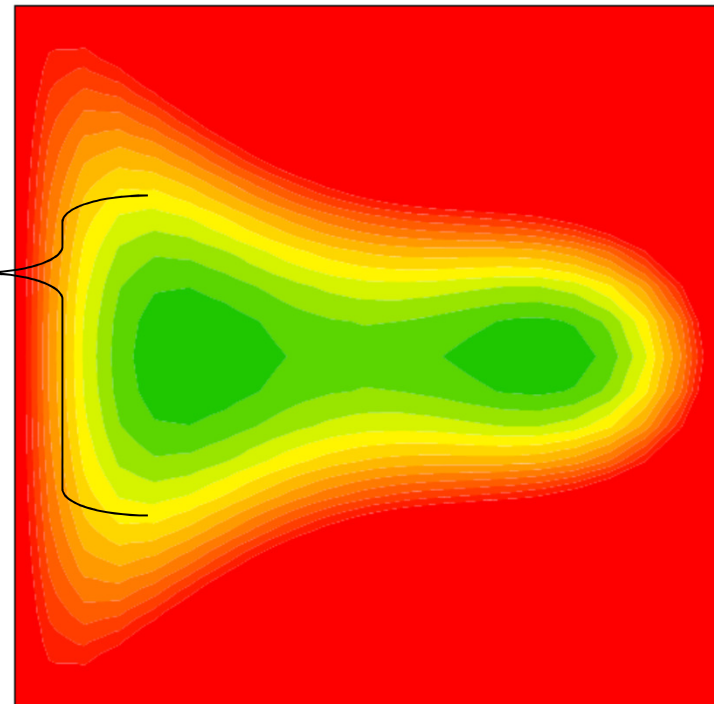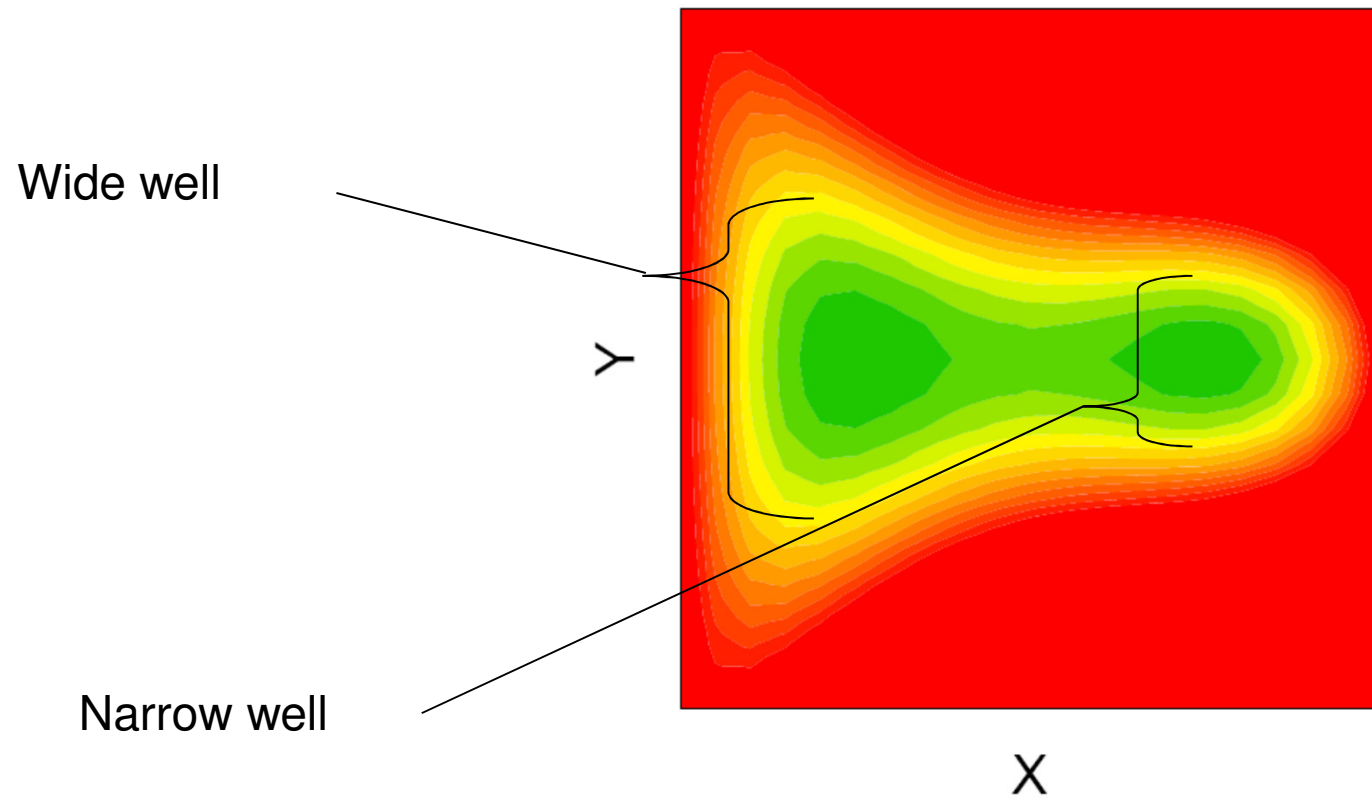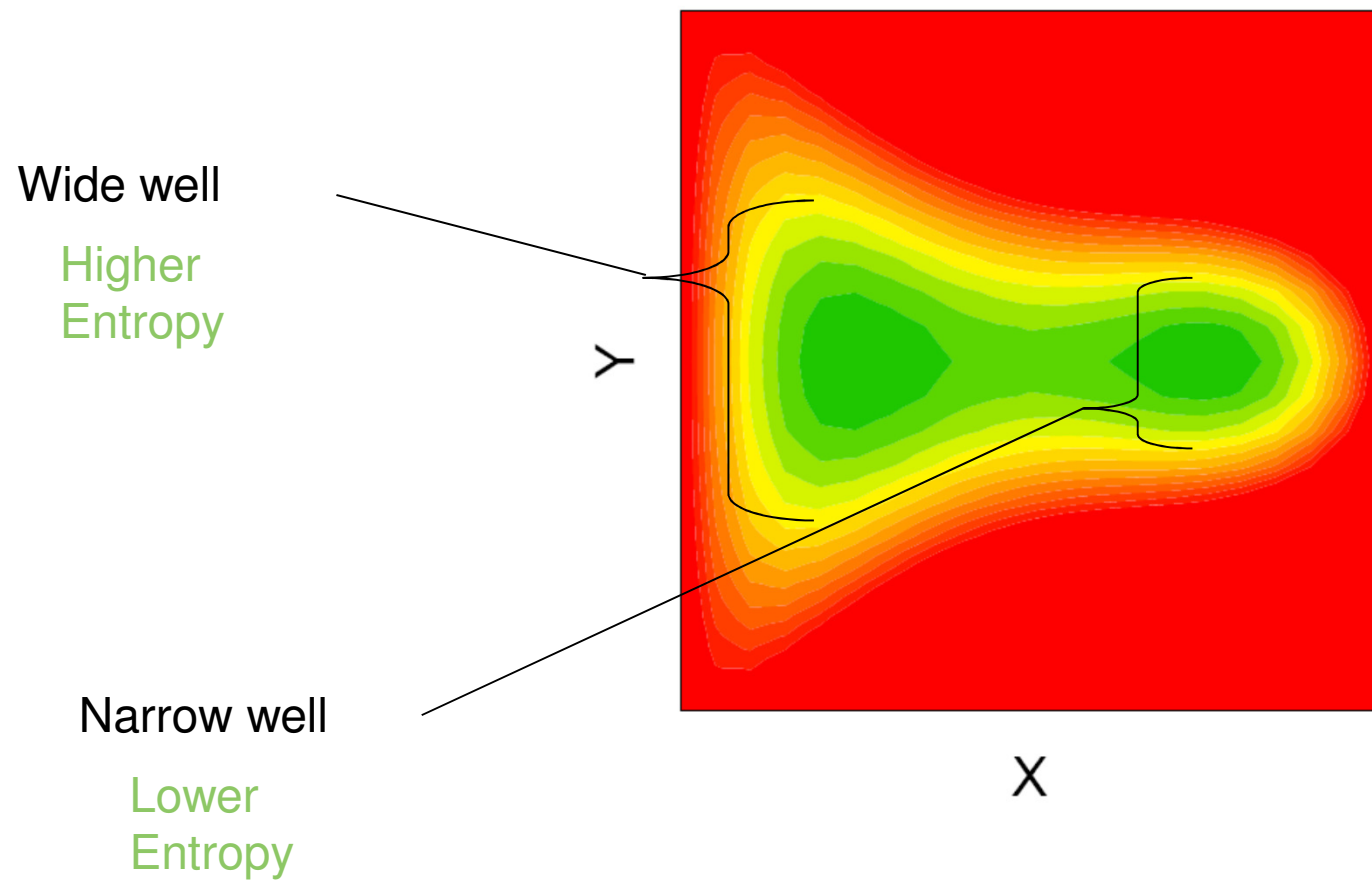
Energy v. Free Energy

Wide well

Higher Entropy

Lower Free Energy

Narrow well

Lower Entropy

High Free Energy

Y

X

What can AIMD tell us? (Why AIMD and not standard quantum chemistry?)

- Sample equilibrium distributions under thermodynamic conditions
  - AIMD at finite temperature naturally includes entropy, which is ignored in standard quantum chemistry
  - Can sample various statistical ensembles: canonical, NVE, NPT
- Dynamics of systems out of equilibrium
  - Molecular collisions
  - Electronic excited states
- Explore PES in an unbiased way
  - AIMD at sufficient temperature will cross barriers
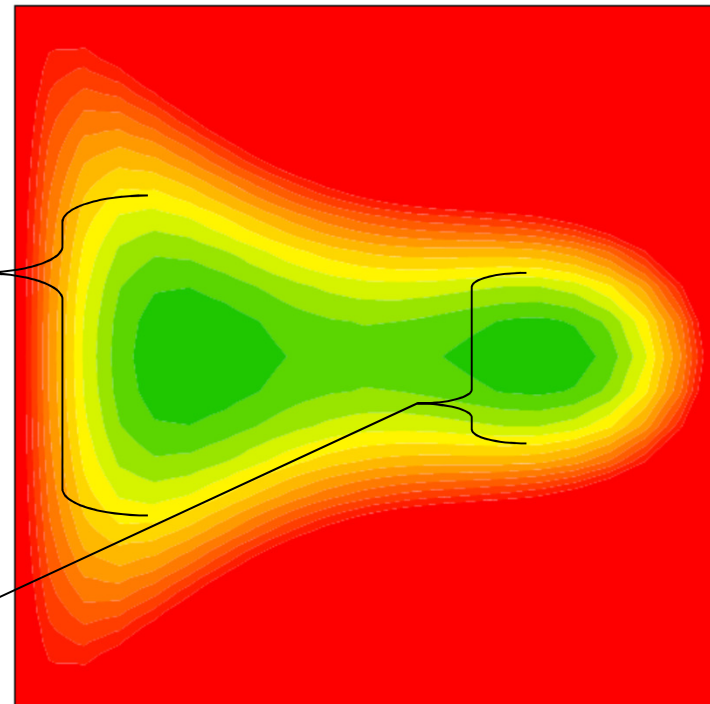 - Find the global minimum of the PES without need for a reasonable initial guess (simulated annealing)

Comparison to classical MD

- Classical MD
  - Approximates molecule to be classical "balls and springs"
  - No explicit treatment of electrons
  - MUCH faster than AIMD
    - Bigger systems (up to billions of atoms, compared to ~1000 atoms)
    - Longer time scales (up to a millisecond, compared to ~100 ps)
- Why can't we go classical for everything?
  - AIMD naturally includes phenomena not (generally) included in classical potential
    - Bond breaking
    - Polarizability
  - Sometimes we want to know what the electrons are doing
  - Classical potentials are parameterized, transferability to other properties is not guaranteed
  - Parameterization to a new system is time consuming

How does AIMD work?

- We assign to each atom a position and momentum vector:

$$\vec{q}(t), \; \vec{p}(t)$$

position   momentum

- The classical equations of motion define the evolutions of these variables in time

time derivative

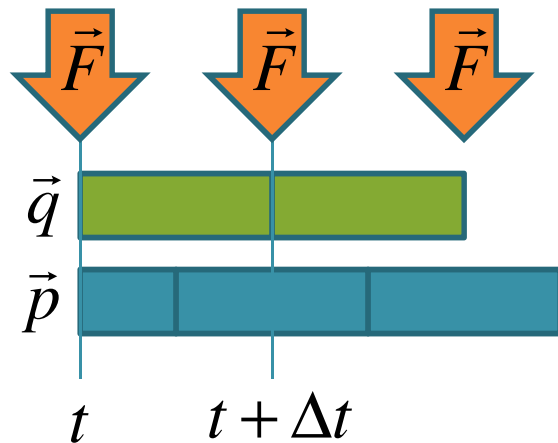$$\dot{\vec{p}} = \boxed{\vec{F}} \qquad \dot{\vec{q}} = \mathbf{m}^{-1}\vec{p}$$

force

mass

Force from ab initio calculations

Discretization

- To solve this problem numerically we break the trajectory up into discrete *time steps*
- Leapfrog integrator:

$$\dot{\vec{p}}(t) = \mathbf{m}^{-1}\vec{F}(\vec{q}(t))$$

$$\vec{p}(t + \tfrac{\Delta t}{2}) = \vec{p}(t) + \dot{\vec{p}}(t)\tfrac{\Delta t}{2}$$

$$\dot{\vec{q}}(t + \tfrac{\Delta t}{2}) = \mathbf{m}^{-1}\vec{p}(t + \tfrac{\Delta t}{2})$$

$$\vec{q}(t + \Delta t) = \vec{q}(t) + \dot{\vec{q}}(t + \tfrac{\Delta t}{2})\Delta t$$

$$\dot{\vec{p}}(t + \Delta t) = \vec{F}(\vec{q}(t + \Delta t))$$

$$\vec{p}(t + \tfrac{3\Delta t}{2}) = \vec{p}(t + \tfrac{\Delta t}{2}) + \dot{\vec{p}}(t + \Delta t)\Delta t$$

$$t = t + \Delta t$$

Repeat

$\vec{F}$ $\vec{F}$ $\vec{F}$

$\vec{q}$

$\vec{p}$

t $t + \Delta t$

Discretization

- Choosing a timestep:
  - Too small and the calculation becomes prohibitively expensive
  - Too large and the integration is inaccurate
  - Energy should be conserved
- Symplectic integration
  - Gives an exact solution to a (slightly) approximate problem
  - Conserves energy well over long timescales
  - Examples of symplectic integrators
    - Leapfrog
    - Verlet
    - Velocity Verlet

Born Oppenheimer MD

- Every time step we need forces
  - In Born Oppenheimer MD we calculate these forces by completing a full ab initio calculation at each timestep
- In principle, any electronic structure method can be used
- In practice, the method must be low enough in cost to be repeated many times, and analytic gradients are almost always used
- Wavefunctions from previous timesteps can be used to produce a starting guess for the current calculation

Analytic gradients

- The Hellmann-Feynman Theorem

$$\hat{H}(\vec{q}) \Rightarrow \Psi(r;\vec{q})$$

$$E(\vec{q}) = \left\langle \Psi(r;\vec{q}) \middle| \hat{H}(\vec{q}) \middle| \Psi(r;\vec{q}) \right\rangle$$

$$\frac{dE}{d\vec{q}} = \frac{d}{d\vec{q}} \left\langle \Psi(r;\vec{q}) \middle| \hat{H}(\vec{q}) \middle| \Psi(r;\vec{q}) \right\rangle$$

$$\frac{dE}{d\vec{q}} = \left\langle \tfrac{d}{d\vec{q}} \Psi(r;\vec{q}) \middle| \hat{H}(\vec{q}) \middle| \Psi(r;\vec{q}) \right\rangle +$$

$$\left\langle \Psi(r;\vec{q}) \middle| \tfrac{d}{d\vec{q}} \hat{H}(\vec{q}) \middle| \Psi(r;\vec{q}) \right\rangle + \left\langle \Psi(r;\vec{q}) \middle| \hat{H}(\vec{q}) \middle| \tfrac{d}{d\vec{q}} \Psi(r;\vec{q}) \right\rangle$$

Analytic gradients

$$\frac{dE}{d\vec{q}} = \left\langle \tfrac{d}{d\vec{q}} \Psi(r;\vec{q}) \middle| \hat{H}(\vec{q}) \middle| \Psi(r;\vec{q}) \right\rangle +$$

$$\left\langle \Psi(r;\vec{q}) \middle| \tfrac{d}{d\vec{q}} \hat{H}(\vec{q}) \middle| \Psi(r;\vec{q}) \right\rangle + \left\langle \Psi(r;\vec{q}) \middle| \hat{H}(\vec{q}) \middle| \tfrac{d}{d\vec{q}} \Psi(r;\vec{q}) \right\rangle$$

$$\frac{dE}{d\vec{q}} = E(\vec{q}) \left\langle \tfrac{d}{d\vec{q}} \Psi(r;\vec{q}) \middle| \Psi(r;\vec{q}) \right\rangle +$$

$$\left\langle \Psi(r;\vec{q}) \middle| \tfrac{d}{d\vec{q}} \hat{H}(\vec{q}) \middle| \Psi(r;\vec{q}) \right\rangle + E(\vec{q}) \left\langle \Psi(r;\vec{q}) \middle| \tfrac{d}{d\vec{q}} \Psi(r;\vec{q}) \right\rangle$$

$$\frac{dE}{d\vec{q}} = E(\vec{q}) \frac{d}{d\vec{q}} \left\langle \Psi(r;\vec{q}) \middle| \Psi(r;\vec{q}) \right\rangle + \left\langle \Psi(r;\vec{q}) \middle| \tfrac{d}{d\vec{q}} \hat{H}(\vec{q}) \middle| \Psi(r;\vec{q}) \right\rangle$$

Analytic gradients

$$\frac{dE}{d\vec{q}} = E(\vec{q})\frac{d}{d\vec{q}}\left\langle \Psi(r;\vec{q}) \middle| \Psi(r;\vec{q}) \right\rangle + \left\langle \Psi(r;\vec{q}) \middle| \tfrac{d}{d\vec{q}}\hat{H}(\vec{q}) \middle| \Psi(r;\vec{q}) \right\rangle$$

$$\frac{dE}{d\vec{q}} = \left\langle \Psi(r;\vec{q}) \middle| \tfrac{d}{d\vec{q}}\hat{H}(\vec{q}) \middle| \Psi(r;\vec{q}) \right\rangle$$

- In practice, this means that there is no need to calculate
  - The derivative of the orbital coefficients in HF or DFT
  - The derivative of the CI vectors in CI or MCSCF (though derivatives of orbital coefficients are necessary in these cases)

What *was* wrong with the Born Oppenheimer approach?

- Converging the wavefunction at every time step is expensive.

- Simply using the wavefunction from the previous timestep as the starting guess for the current calculation biases the result. Unless the wavefunction is converged extremely tightly, a drag force is observed in the dynamics simulation.

- These problems have been overcome by modern extrapolation techniques, e.g.:
    - "Curvy steps"
    - Always stable predictor corrector (ASPC)

The Car-Parrinello approach

- Based on DFT
- Uses an extended Lagrangian approach
  - Equations of motion are defined for the molecular orbital coefficients analogous to the classical equations of motion

fictitious mass

constraint on orthonormality

$$\mu\ddot{\psi}_i = -\frac{\partial E}{\partial \psi_i} + \sum_j \Lambda_{ij}\psi_j$$

KS orbitals

The Car-Parrinello approach

- Based on DFT
- Uses an extended Lagrangian approach
  - Equations of motion are defined for the molecular orbital coefficients analogous to the classical equations of motion

$$\mu \ddot{\psi}_i = -\frac{\partial E}{\partial \psi_i} + \sum_j \Lambda_{ij} \psi_j$$

$$m\ddot{q} = -\frac{\partial E}{\partial q}$$

The Car-Parrinello approach

- Based on DFT
- Uses an extended Lagrangian approach
  - Equations of motion are defined for the molecular orbital coefficients analogous to the classical equations of motion
- Eliminates the need to converge the wavefunction at every step
- In the limit that fictitious mass approaches zero, Car-Parrinello (CP) dynamics approach true Born-Openheimer dynamics
- In practice, fictitious mass must be greater than zero, and results can depend on its choice

Summary

- AIMD allows you to
  - Investigate equilibrium chemical systems under thermodynamics conditions
  - Consider the dynamics of nonequilibrium systems
  - Explore the PES of complex systems in an unbiased way
- The classical equation of motion are integrated using
  - A numerical integrator which discretizes the trajectory according to a user defined time step
  - Forces determined from the wavefunction (or density)
- BOMD solves the electronic structure problem at each timestep
- CPMD defines fictional equations of motion for the electronic degrees of freedom which approximate BOMD