Taking the Strain out of Constraints

A generalised SHAKE and RATTLE algorithm for movable quantum regions

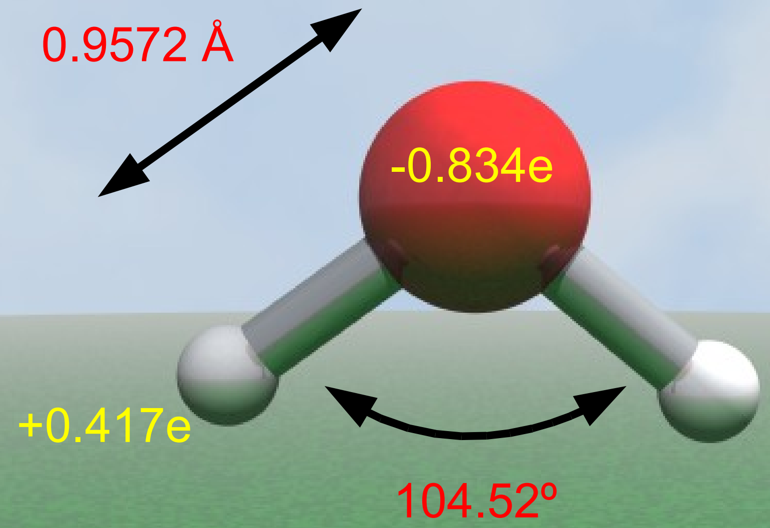
Steven Winfield
ESDG
February 28th 2007

Introduction

- QM/MM – quantum region + classical region.
- Usually fixed → Hamiltonian
- Bio simulations mostly done in condensed phase → solvent is usually water
- Most popular models of water are rigid – TIPnP
- Rigidity is imposed by constraints... quite often all H atoms are constrained as well
- QM/MM Bio sim: select quantum/classical waters at the beginning

TIP3P

$$E_{ab} = \sum_{ij} \frac{q_i q_j}{r_{ij}} + 4\epsilon_0 \left[\left(\frac{\sigma_0}{r_{OO}} \right)^{12} - \left(\frac{\sigma_0}{r_{OO}} \right)^{6} \right]$$



Introduction

- LOTF: Movable quantum region (not Hamiltonian)
- Problem! Quantum waters drifting out of quantum region will generally not have correct structure
- Atoms must be constrained, but they must also move...

Outline

- How to apply constraints (1A revision!)
- Standard algorithms for discrete time-step integrators (SHAKE/RATTLE)
- Extension for movable quantum regions

Applying Constraints

(Not) Applying Constraints

- Lagrangian

$$L = T(\{\dot{r}_i\}) - V(\{r_i\}) = \sum_i \frac{1}{2} m_i \dot{r}_i^2 - V(\{r_i\})$$

- Action

$$S = \int L dt \rightarrow \delta S = 0$$

- E-L equations

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{r}_i}\right) - \frac{\partial L}{\partial r_i} = 0$$

- Newton's 2nd

$$m_i \ddot{r}_i + \nabla_i V = 0 \rightarrow N2$$

$$m_i \ddot{r}_i = F_i$$

$$F_i = -\nabla_i V$$

Applying Constraints

- Constraint

$$\sigma(\{r_i\}) = 0$$

- Modified action

$$\tilde{S} = \int (L - \lambda\sigma)\, dt \rightarrow \delta\tilde{S} = 0$$

- Modified E-L

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{r}_i}\right) - \frac{\partial L}{\partial r_i} - \lambda\left[\frac{d}{dt}\left(\frac{\partial \sigma}{\partial \dot{r}_i}\right) - \frac{\partial \sigma}{\partial r_i}\right] = 0$$

- Modified N2

$$m_i \ddot{r}_i + \nabla_i V + \lambda \nabla_i \sigma = 0$$

$$m_i \ddot{r}_i = F_i + G_i$$

$$F_i = -\nabla_i V \quad G_i = -\lambda \nabla_i \sigma$$

Discrete Time-Steps

- Velocity Verlet

$$r_i(t+\Delta t) = r_i(t) + v_i(t)\Delta t + \frac{F_i(t)}{2m_i}(\Delta t)^2$$

$$v_i(t+\Delta t) = v_i(t) + \frac{\Delta t}{2m_i}(F_i(t) + F_i(t+\Delta t))$$

- ...with constraints

$$r_i(t+\Delta t) = r_i(t) + v_i(t)\Delta t + \frac{F_i(t)}{2m_i}(\Delta t)^2 + \frac{G_i^{RR}(t)}{2m_i}(\Delta t)^2$$

$$v_i(t+\Delta t) = v_i(t) + \frac{\Delta t}{2m_i}\left(F_i(t) + F_i(t+\Delta t) + G_i^{RR}(t) + G_i^{RV}(t+\Delta t)\right)$$

$$r_i^C(t+\Delta t) - r_i^U(t+\Delta t) = -\frac{(\Delta t)^2}{2m_i}\sum_k \lambda_k^{RR} \nabla_i \sigma_k(t)$$

$$v_i^C(t+\Delta t) - v_i^U(t+\Delta t) = -\frac{\Delta t}{2m_i}\sum_k \lambda_k^{RV} \nabla_i \sigma_k(t+\Delta t)$$

SHAKE/RATTLE

- Taylor expand constraint function

$$\sigma_j^C(t+\Delta t) = \sigma_j^U(t+\Delta t) + \sum_i \left(\nabla_i \sigma_j^U(t+\Delta t)\right).\left(r_i^C(t+\Delta t) - r_i^U(t+\Delta t)\right) + \cdots = 0$$

$$\sigma_j^U(t+\Delta t) = (\Delta t)^2 \sum_{ik} \left(\nabla_i \sigma_j^U(t+\Delta t)\right).\left(\frac{1}{m_i}\lambda_k \nabla_i \sigma_k(t)\right) \rightarrow \boldsymbol{\sigma}^U(t+\Delta t) = (\Delta t)^2 \boldsymbol{M}\,\boldsymbol{\Lambda}$$

$$r_i^C(t+\Delta t) - r_i^U(t+\Delta t) \approx -\frac{(\Delta t)^2}{2 m_i} \lambda_k^{RR} \nabla_i \sigma_k(t)$$

$$\lambda_k^{RR}(t) \approx \frac{2\sigma_k^U(t+\Delta t)}{(\Delta t)^2 \sum_i \frac{1}{m_i}\left(\nabla_i \sigma_k^U(t+\Delta t)\right)\cdot\left(\nabla_i \sigma_k(t)\right)}$$

$$\dot{\sigma}_j^C(t+\Delta t) = 0$$

$$\vdots$$

$$\lambda_k^{RV}(t+\Delta t) \approx \frac{2\dot{\sigma}_k^U(t+\Delta t)}{\Delta t \sum_i \frac{1}{m_i}\left|\nabla_i \sigma_k^U(t+\Delta t)\right|^2}$$

Examples of constraints

- Bond length

$$\sigma = |r_1 - r_2|^2 - d_{12}^2$$

$$\nabla_1 \sigma = 2(r_1 - r_2)$$

$$\nabla_2 \sigma = -2(r_1 - r_2)$$

- Sphere

$$\sigma = |r|^2 - r_0^2$$

$$\nabla \sigma = 2\mathrm{r}$$

Enough Maths!

Show me a movie...

A solution to the problem?

- Allow time dependent constraints
- Take unconstrained positions/velocities smoothly to constrained values: Fit to cubic polynomial

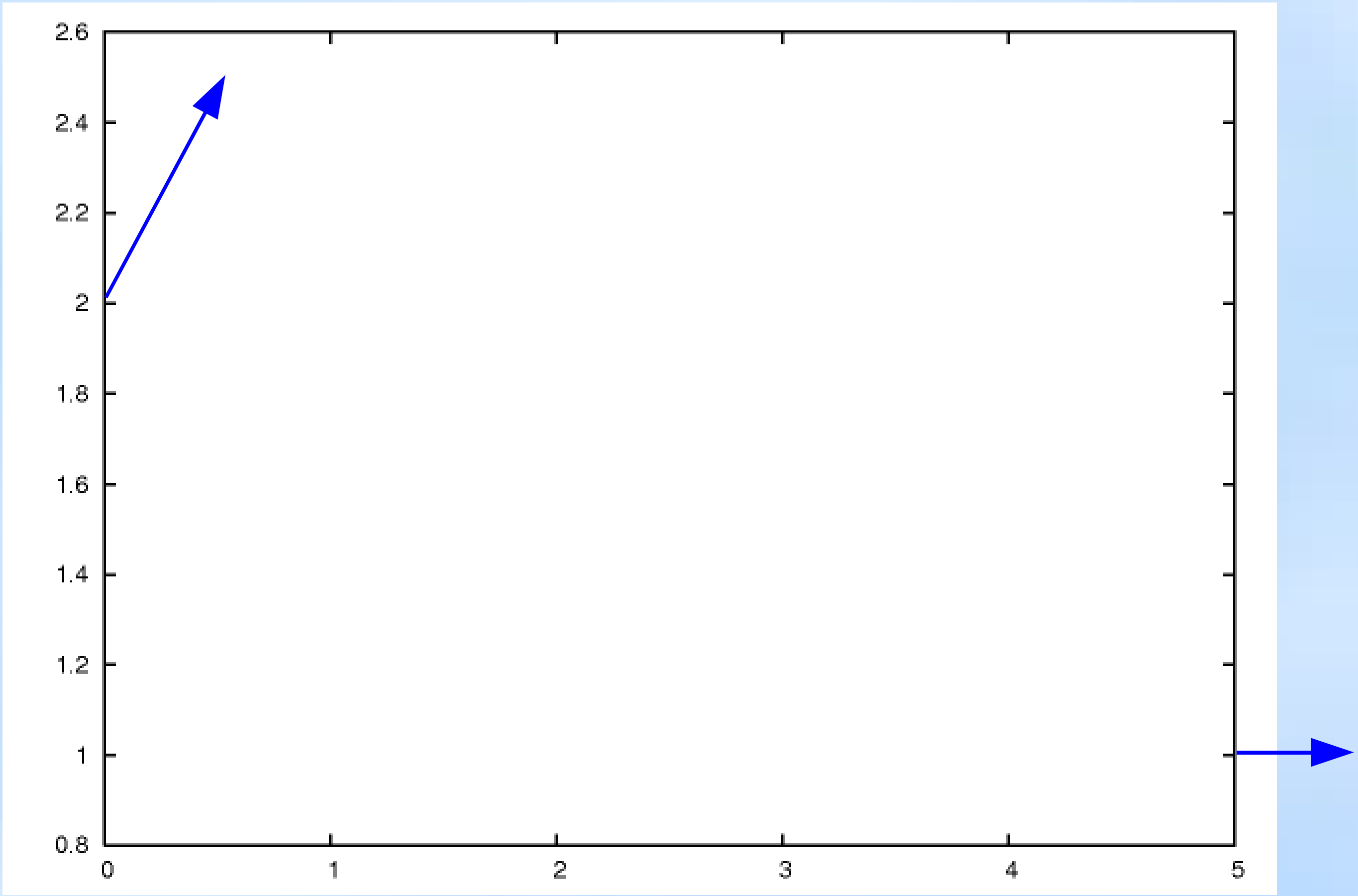
$$\sigma \equiv \sigma(\{r_i\}, t) = 0$$

$$\dot{\sigma} = \sum_i \left(\frac{\partial \sigma}{\partial r_i} \right) . \dot{r}_i + \frac{\partial \sigma}{\partial t} \rightarrow \frac{\partial \dot{\sigma}}{\partial \dot{r}_i} = \frac{\partial \sigma}{\partial r_i}$$

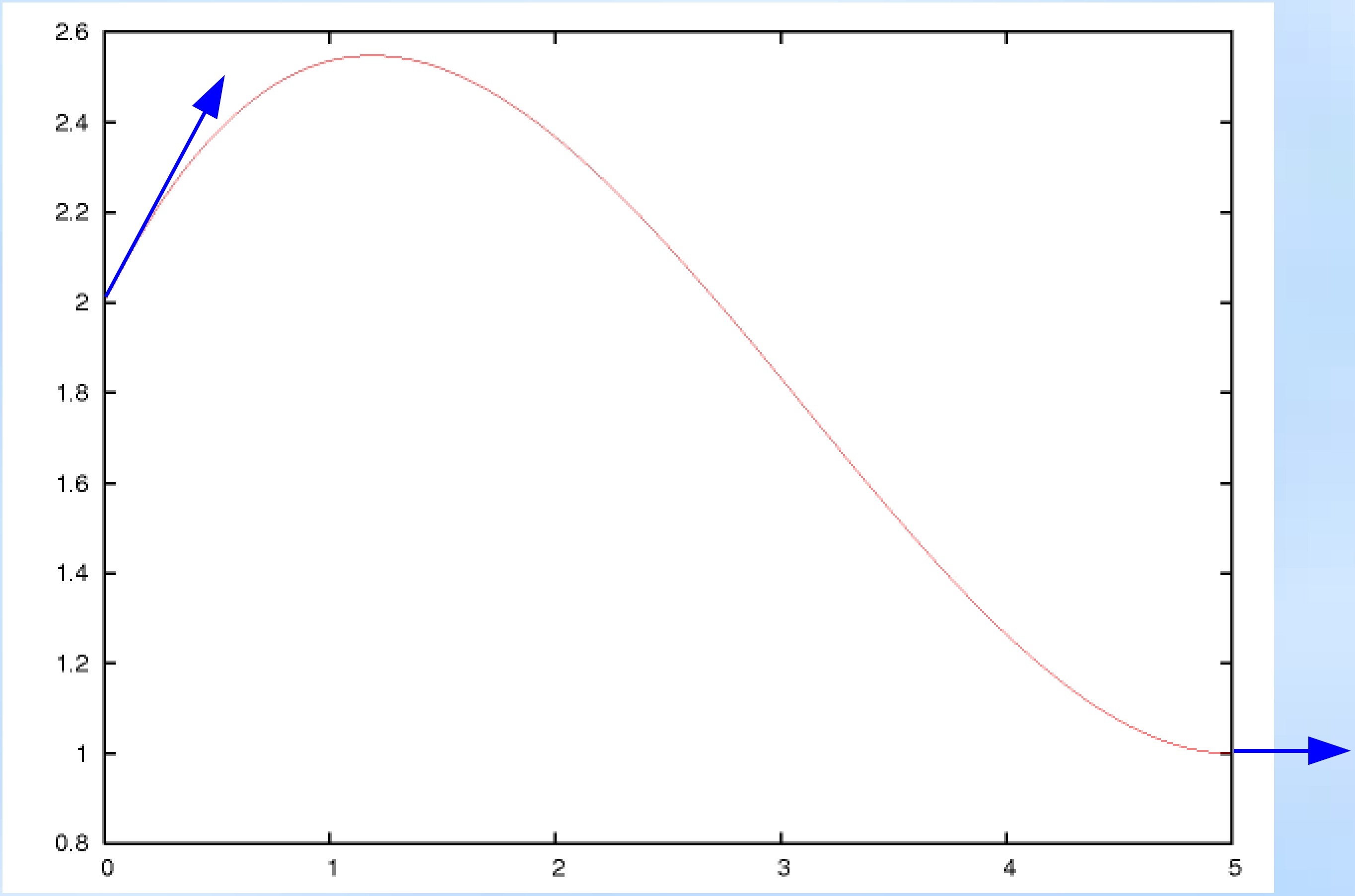
$$\sigma(r_1, r_2, t) = |r_1 - r_2|^2 - d(t)^2$$

$$d(t) = at^3 + bt^2 + ct + d_0$$

Cubic Polynomial



Cubic Polynomial



Does it work?

Further tests...

- ... are needed!
- Hybrid QM/MM molecular dynamics run with semi-empirical PM3 Hamiltonian in quantum region

Thank-you for listening

References:

M.W. Mahoney, W.L. Jorgensen, *"A five-site model for liquid water and the reproduction of the density anomaly by rigid, nonpolararizable potential functions"*, J. Chem. Phys **112**(20) 8910 (2000)

J.-P. Ryckaert, G. Ciccotti, H. J. C. Berendsen, *"Numerical Integration of the Cartesian Equations of Motion of a System with Constraints: Molecular Dynamics of n-Alkanes"*, J. Comp. Phys. **23** 327 (1977)

H. C. Andersen, *"Rattle: A "Velocity" Version of the Shake Algorithm for Molecular Dynamics Calculations"*, J. Comp. Phys. **52** 24 (1983)