Ab initio Molecular Dynamics

Jürg Hutter
MPI für Festkörperforschung
Stuttgart

May 16, 1995

Classical Mechanics

The state of a classical system of particles can be described by their positions $\mathbf{q}$ and velocities $\dot{\mathbf{q}}$. The Lagrangian function of such a system is

$$L(\mathbf{q}, \dot{\mathbf{q}}) = T(\dot{\mathbf{q}}) - V(\mathbf{q})$$

where T is the kinetic energy and V the potential energy. The Lagrange equation

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

define the equations of motion for the system.

Constraints

If we can write the constraints on the system as a system of equations of the form

$$\sigma(\mathbf{q}, t) = 0$$

then the constraints are called holonomic. Systems with holonomic constraints are conservative. They can be described by a Lagrangian and the total energy is a constant of motion.

Molecular Dynamics

For a system with M particles and mass m_i the kinetic energy is

$$T = \sum_{i=1}^{M} \frac{1}{2} m_i \dot{r}_i^2$$

and the potential energy

$$V = V(\mathbf{r}).$$

Forces on the particles are defined by

$$f_i = \nabla_{r_i} L = -\nabla_{r_i} V(\mathbf{r})$$

and the equations of motion become

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

Integration of the equations of motion

Given $\mathbf{r}$(t) and $\dot{\mathbf{r}}$(t) we need a recipe to calculate $\mathbf{r}$(t+δt) and $\dot{\mathbf{r}}$(t+δt).
The most popular algorithm in molecular dynamics is the Verlet algorithm.

$$r_i(t+\delta t) = 2r_i(t) - r_i(t-\delta t) + \frac{\delta t^2}{m_i} f(r(t))$$

The velocity at time t is calculated from

$$\dot{r}_i(t) = \left(r_i(t+\delta t) - r_i(t-\delta t)\right)/2\delta t.$$

There are some problems associated with the Verlet algorithm. We only know the velocity at time t after propagating the trajectory to t + δt. This makes the implementation of thermostats and multiple time scale methods difficult. It is also not easy to change the time step δt during a run.
An equivalent integrator, that solves these problems is the velocity Verlet algorithm.

$$\begin{aligned} r_i(t+\delta t) &= r_i(t) + \frac{\delta t}{m_i}\dot{r}_i(t) + \frac{\delta t^2}{2m_i} f(r(t)) \\ \dot{r}_i(t+\delta t) &= \dot{r}_i(t) + \frac{\delta t}{2m_i}\left[f(r(t)) + f(r(t+\delta t))\right] \end{aligned}$$

Constraints with velocity Verlet

The equations of motion for a system with constraints are

$$m_i\ddot{r}_i(t) = f(r(t)) + g(r(t))$$

derived from the Lagrangian

$$L = T(\dot{\mathbf{r}}(t)) - V(\mathbf{r}) + \lambda\sigma(\mathbf{r})$$

The equations for velocity Verlet are

$$\begin{aligned} r_i(t+\delta t) &= r_i(t) + \frac{\delta t}{m_i}\dot{r}_i(t) + \frac{\delta t^2}{2m_i}\left[f(r(t)) + g(r(t))\right] \\ \dot{r}_i(t+\delta t) &= \dot{r}_i(t) + \frac{\delta t}{2m_i}\left[f(r(t)) + g(r(t)) + f(r(t+\delta t)) + g(r(t+\delta t))\right] \end{aligned}$$

If we now would choose g(t) to fulfill σ(t+δt) = 0 then we could not find a solution to the second equation.
Solution: (Rattle algorithm) use different approximations to g(t) for the update of positions and velocities.

$$\begin{aligned} r_i(t+\delta t) &= r_i(t) + \frac{\delta t}{m_i}\dot{r}_i(t) + \frac{\delta t^2}{2m_i}\left[f(r(t)) + g_p(r(t))\right] \\ \dot{r}_i(t+\delta t) &= \dot{r}_i(t) + \frac{\delta t}{2m_i}\left[f(r(t)) + g_p(r(t)) + f(r(t+\delta t)) + g_v(r(t+\delta t))\right] \end{aligned}$$

There are now two independent approximations to the constraint forces. This makes it possible not only to fulfill the constraint for the positions but also for the velocities.

Implementation

- given r(t) and $\dot{r}$(t); calculate f(t)
- Loop over number of time steps
  - $\dot{r}' = \dot{r}(t) + \frac{\delta t}{2m_i} f(t)$
  - $r' = r(t) + \delta t \dot{r}'$
  - calculate $g_p(t) = -\lambda \nabla \sigma(t)$ such that $\sigma(t+\delta t) = 0$
  - $r(t+\delta t) = r' + \frac{\delta t^2}{2m_i} g_p(t)$
  - calculate $f(t+\delta t)$
  - $\dot{r}" = \dot{r}' + \frac{\delta t}{2m_i}\left(g_p(t) + f(t+\delta t)\right)$
  - calculate $g_v(t) = -\lambda \nabla \sigma(t+\delta t)$ such that $\dot{\sigma}(t+\delta t) = 0$
  - $\dot{r}(t+\delta t) = \dot{r}" + \frac{\delta t}{2m_i} g_v(t)$
- end loop

Homework Derive the Rattle algorithm for a distance constraint of the form $|r_i - r_j|^2 - r_{ij}^0 = 0$

The Car-Parrinello Lagrangian

Treat the wavefunction as classical variables and choose a convenient form for the kinetic energy of the wavefunction variables.

$$\begin{aligned}\mathcal{L} &= \mu \sum_i \int d\mathbf{r} |\dot{\psi}(\mathbf{r})|^2 + \frac{1}{2} \sum_I M_I \dot{\mathbf{R}}_I^2 - E[\{\psi_i\}, \{\mathbf{R}_I\}] \\ &+ \sum_{i,j} \Lambda_{ij} \left(\langle \psi_i | \psi_j \rangle - \delta_{ij} \right)\end{aligned}$$

where μ is the fictitious electron mass, and $\{M_I\}$ are the ionic masses.
The equations of motion for the wavefunctions are

$$\mu |\ddot{\psi}_i\rangle = |\varphi_i\rangle + \sum_j \Lambda_{ij} |\psi_j\rangle$$

with the constraints

$$\begin{aligned}\langle \psi_i | \psi_j \rangle &= \delta_{ij} \\ \langle \dot{\psi}_i | \psi_j \rangle + \langle \psi_i | \dot{\psi}_j \rangle &= 0\end{aligned}$$

and the forces $|\varphi_i\rangle$.
A prediction of the orbital positions and velocities is then made according to

$$\begin{aligned}|\dot{\bar{\psi}}_i\rangle &= |\dot{\psi}_i(t)\rangle + \frac{\delta t}{2\mu} |\varphi_i(t)\rangle \\ |\bar{\psi}_i\rangle &= |\psi_i(t)\rangle + \delta t |\dot{\bar{\psi}}_i\rangle\end{aligned}$$

The new orbital positions are then obtained from

$$|\psi_i(t+\delta t)\rangle = |\bar{\psi}_i\rangle + \frac{\delta t^2}{2\mu} \sum_j \Lambda_{ij} |\psi_j(t)\rangle$$

The Lagrange multipliers are calculated from

$$\mathbf{X}\mathbf{X}^\dagger + \mathbf{X}\mathbf{B} + \mathbf{B}^\dagger \mathbf{X}^\dagger = 1 - \mathbf{A}$$

where

$$\begin{aligned}\mathbf{X} &= \frac{\delta t^2}{2\mu} \Lambda \\ A_{ij} &= \langle \bar{\psi}_i | \bar{\psi}_j \rangle \\ B_{ij} &= \langle \psi_i(t) | \bar{\psi}_j \rangle\end{aligned}$$

The equation is solved iteratively by

$$\mathbf{X}^{(n)} = \frac{1}{2}\left[1 - \mathbf{A} + \mathbf{X}^{(n-1)}(1-\mathbf{B}) + (1-\mathbf{B}^\dagger)\mathbf{X}^{(n-1)} - (\mathbf{X}^{(n-1)})^2\right]$$

and $\mathbf{X}^{(0)} = \frac{1}{2}(1-\mathbf{A})$.

$$|\dot{\tilde{\psi}}_i\rangle = |\dot{\bar{\psi}}_i\rangle + \frac{\delta t}{2\mu}\sum_j \Lambda_{ij}|\psi_j\rangle + \frac{\delta t}{2\mu}|\varphi_i(t)\rangle$$

Imposing the constraints on the velocities

$$\begin{aligned} |\dot{\psi}_i(t+\delta t)\rangle &= |\dot{\tilde{\psi}}_i\rangle + \sum_j Y_{ij}|\psi_j(t+\delta t)\rangle \\ \mathbf{Y} &= -\frac{1}{2}(\mathbf{C}+\mathbf{C}^\dagger) \\ C_{ij} &= \langle\psi_i(t\delta t)|\dot{\bar{\psi}}_j\rangle \end{aligned}$$