Car-Parrinello Molecular Dynamics

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Moral: “A man dreams of a miracle and wakes up with loaves of bread”
Erich Maria Remarque
Molecular Dynamics Loop

(1) Compute Forces on atoms, $F_i(t)$ for current atomic configuration, $R_i(t)$

$$F_i(t) \leftarrow$$

- calculate using classical potentials
  (can do large systems and long simulation times)
- calculate directly from first principles by solving many-electron Schrödinger equations
  (can treat very complex chemistry, but simulations times are very long)

(2) Update atom positions using Newton's laws

- $R_i(t+\Delta t) \leftarrow 2*R_i(t) - R_i(t-\Delta t) + \Delta t^2/(M_i)*F_i(t)$
Ab Initio Molecular Dynamics – For Problems Beyond Classical MD Simulations

- Systems with unusual chemical bonding
  - Clusters, surfaces and defects
  - Metallic and semiconductor liquids
  - Diffusion of impurities and defects

- Phenomena involving changes in electronic structure
  - Band gap of semiconductors in liquid phase
  - Solvation in polar liquids
  - Chemical reactions
Application Goals
- Study complex systems with ab initio dynamics

Al\textsuperscript{3+} Hydrolysis

Enzymatic Active Site

Active Site on iron-oxide

Chemical Reactions
# Comparison of Classical and Ab Initio Molecular Dynamics

<table>
<thead>
<tr>
<th>Classical MD</th>
<th>First Principles MD</th>
</tr>
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<tbody>
<tr>
<td>✅ Phenomenological potential energy surface (typically restricted to two body contributions)</td>
<td>✅ Potential energy surface calculated directly from the Schrödinger equation (many-body terms included automatically)</td>
</tr>
<tr>
<td>✅ Difficult to describe bond breaking/making</td>
<td>✅ Describes bond breaking/making</td>
</tr>
<tr>
<td>✅ Electronic properties are not available</td>
<td>✅ Electronic spectra included in calculation</td>
</tr>
<tr>
<td>✅ Can do millions of particles</td>
<td>✅ Limited to 250 atoms with significant dynamics</td>
</tr>
</tbody>
</table>
Basic Features of Ab Initio Molecular Dynamics

Energy functional

\[ E[n, R_1] = \sum_i \langle \psi_i | -\frac{1}{2} \nabla^2 | \psi_i \rangle + \int V_{\text{ext}} (r; R_1) n(r) dr + \]

\[ \frac{1}{2} \iint \frac{n(r)n(r')}{|r-r'|} dr dr' + \int \varepsilon_{\text{xc}} (n) n(r) dr \]

Ground state energy

\[ -\frac{\delta E}{\delta \psi_i} = \sum_{\beta} \lambda_{ij} \psi_j \]

Ion motion

\[ M_1 \ddot{R}_1 = -\frac{\delta E}{\delta R_1} \]
Pitfalls of Ab Initio Molecular Dynamics

Expensive?

Energy Conservation – Born-Oppenheimer Error

\[
\frac{dE}{dR} = \left( \frac{\partial E}{\partial c} \right) \left( \frac{dc}{dR} \right) + \frac{\partial E}{\partial R}
\]

“Attempts to implement such a dynamical scheme in a straightforward fashion prove to be unstable. Specifically, the atomic dynamics do not conserve energy unless a very high degree of convergence in the electronic structure calculation is demanded. If this is not done the electronic system behaves like a heat sink or source…….”

-- Remler and Madden
$^3\Sigma_g^+$ - $S_2$ Energy Surface from QMD Simulation
Car and Parrinello suggested that ionic dynamics could be run in parallel with a fictitious electronic dynamics via the following Lagrangean

\[ L = \sum_i \frac{1}{2} \mu \langle \dot{\psi}_i | \dot{\psi}_i \rangle + \sum_I \frac{1}{2} M_I \dot{R}_I^2 + E[\{\psi_i\}, \{R_I\}, \text{constraints}] \]

Amazingly these equations of motion result in a conservative ionic dynamics that is extremely close to the Born-Oppenheimer surface.

The electronic system behaves quasi-adiabatically. That is the electronic system follows the ionic system and there is very little additional motion wandering away from the Born-Oppenheimer surface.
In order to solve the AIMD equations we need to expand the wavefunctions $\Psi$ in a basis set.

$$\psi_i = \sum_{\alpha} c_\alpha \varphi_\alpha$$

<table>
<thead>
<tr>
<th>Atomic centered basis set (e.g. gaussians, ...)</th>
<th>Plane wave basis set</th>
</tr>
</thead>
<tbody>
<tr>
<td>• All-electron (both core and valence electrons included in calculation)</td>
<td>• Typically requires pseudopotentials (defined on following slide) but can be made all electron with PAW</td>
</tr>
<tr>
<td>• Forces are expensive to calculate</td>
<td>• Forces can be calculated efficiently</td>
</tr>
<tr>
<td>• First principles MD expensive</td>
<td>• Efficient first principles MD</td>
</tr>
</tbody>
</table>
Elements of Ab Initio Molecular Dynamics

Local Density Functional Theory

\[ E = \sum \int \psi_i^*(r)[-1/2\Delta] \psi_i(r)dr + \int V_{\text{ext}}(r) n(r)dr \]

\[ + (1/2) \int \int n(r) n(r') dr dr' + E_{xc}[n,|\nabla n|] \]

\[ n(r) = \sum \psi_i^*(r) \psi_i(r) \]

\[ \int \psi_i^*(r) \psi_j(r)dr = \delta_{i,j} \]
Elements of Ab Initio Molecular Dynamics

Car-Parrinello Equation - Local Density Functional Theory

if \( \mu = 0 \) then Kohn-Sham

\[
\frac{\ddot{\mu}}{\psi_i} = \frac{\delta E}{\delta \psi_i^*} - \sum_j \Lambda_{i,j} \psi_j
\]

\[
\frac{\delta E}{\delta \psi_i^*} = ((-1/2)\Delta + V_{\text{ext}} + V_c + V_{xc})\psi_i
\]

\[
M_I \ddot{R}_I = F_I
\]

\[
F_I = \sum_i \langle \psi_i | \frac{\partial H}{\partial R_I} | \psi_i \rangle
\]

We use plane-waves and pseudopotentials

\[
\psi_i(r) = \sum_k c_{k,i} \exp(ik \cdot r)
\]

\( V_{\text{ext}} \rightarrow \) pseudopotentials
Scaling for calculating $H\Psi + \Lambda\Psi$

- $N_e N_g$ - diagonal in k-space
- $(N_a N_g + N_g \log N_g + N_e N_g) + (N_a N_e N_g)$ - diagonal in r-space and k-space
- $N_e N_g \log N_g + N_e N_g + 2 N_g \log N_g + N_g + N_e N_g$ - diagonal in r-space
- $N_e N_g \log N_g + N_e N_g + N_e N_g$ - diagonal in r-space
- Orthonormalization: $N_e^2 N_g + N_e^3$
Example 1b: $S_2$ molecule LDA Car-Parrinello Simulation.

title "S2 MD LDA/25Ry"
start s2.md
g geometry
S 0.0 0.0 0.0
S 0.0 0.0 1.95
end
pspw
car-parrinello
time_step 5.0  #Typically between 1 and 20
fake_mass 600.0  #Typically between 300 and 1500
loop 10 100
end
mult 3
end
set nwpw:minimizer 2
task pspw energy
task pspw car-parrinello
$^3\Sigma_g^{-} \text{ S}_2$ Energy Surface from Car-Parrinello Simulation
Energy Conservation

Total Energy Conservation of triplet S2 simulation
Born-Oppenheimer Error

Born-Oppenheimer surface error in Car-Parrinello triplet S2 dimer simulation

Error (a.u.)

time (a.u.)
Ionic and Fictitious Electronic Kinetic Energies
Adiabicity is not built into the Car-Parrinello equations of motion. As pointed out by Remler and Madden:

“equipartion principle tells us that the average kinetic energies of all degrees of freedom in the classical system will be equal at equilibrium. The adiabatic state, in which the ficticious system is at a very low temperature and the ionic system is hot is therefore metastable.”

The metastable motion is the result of a good start-up procedure and the overlap of the ficticious electronic motion with the ionic motion must be small (i.e. Start simulation on BO surface! Also, standard CP works best for large band gap systems)

Total ionic momentum is NOT rigorously conserved
Electronic heating can be controlled with thermostats. However, this can result in a serious fluctuation of the total ionic momentum, especially in isolated systems.
Ab Initio Molecular Dynamics References


