Ab initio molecular dynamics techniques

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CPMD–CP2K tutorial – 08/04/2010
Outline

Lagrangian mechanics

Integrating the equations of motions

The electron fictitious mass in CPMD

Conservation of energy

Summary
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Lagrangian mechanics

- Lagrangian $\mathcal{L}$ for a system consisting of $n$ generalized degrees of freedom $\mathbf{q} = \{q_i\}_{i \in \mathbb{N}}$:

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

where $\mathcal{K}$ is the kinetic energy and $\mathcal{V}$ the potential energy

- Equations of motion generated by Euler-Lagrange equation

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{q}_i} - \frac{\partial \mathcal{L}}{\partial q_i} = 0$$

- Conserved quantity:

$$\mathcal{H}(\mathbf{q}, \dot{\mathbf{q}}) = \mathcal{K}(\mathbf{q}, \dot{\mathbf{q}}) + \mathcal{V}(\mathbf{q})$$
Equations of motion: classical MD

$N$ atoms, $n = 3N$ Cartesian degrees of freedom $\{\mathbf{R}_I\}_{I \in \mathbb{N}}$

$$
\mathcal{L}(\{\mathbf{R}_I\}, \{\dot{\mathbf{R}}_I\}) = \mathcal{K}(\{\dot{\mathbf{R}}_I\}) - \mathcal{V}(\{\mathbf{R}_I\}) = \sum_I \frac{m_I}{2} \dot{\mathbf{R}}_I^2 - \mathcal{V}(\{\mathbf{R}_I\})
$$

Defining momentum $\mathbf{p}_I$ and force $\mathbf{f}_I$ according to

$$
\mathbf{p}_I = \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{R}}_I} = m_I \dot{\mathbf{R}}_I, \quad \mathbf{f}_I = \frac{\partial \mathcal{L}}{\partial \mathbf{R}_I} = - \frac{\partial \mathcal{V}}{\partial \mathbf{R}_I}
$$

we recover Newton’s equations from the Euler-Lagrange equation as

$$
\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{R}}_I} = \frac{\partial \mathcal{L}}{\partial \mathbf{R}_I} \quad \Rightarrow \quad \dot{\mathbf{p}}_I = - \frac{\partial \mathcal{V}}{\partial \mathbf{R}_I} \quad \Rightarrow \quad m_I \ddot{\mathbf{R}}_I = \mathbf{f}_I
$$
\[ \mathcal{L}_{\text{CP}} = \sum_l \frac{m_l}{2} \dot{R}_l^2 + \sum_i \mu \langle \dot{\phi}_i \mid \dot{\phi}_i \rangle - \langle \psi_0 \mid \mathcal{H}_e \mid \psi_0 \rangle + \sum_{i,j} \Lambda_{ij} (\langle \phi_i \mid \phi_j \rangle - \delta_{ij}) \]

where the four terms respectively represent:

- Classical kinetic energy
- Electronic kinetic energy (fictitious)
- Potential energy
- and some Constraints for imposing orbital orthonormality \( \langle \phi_i \mid \phi_j \rangle = \delta_{ij} \) with the use of Lagrange multipliers \( \Lambda_{ij} \)
Equations of motion: Car-Parrinello MD

Propagation of the atomic positions and of the orbitals

\[ m_I \ddot{R}_I = -\frac{\partial}{\partial \mathbf{R}_I} \langle \psi_0 | \mathcal{H}_e | \psi_0 \rangle \]

\[ \mu \ddot{\phi}_i = -\frac{\partial}{\partial \phi_i^*} \langle \psi_0 | \mathcal{H}_e | \psi_0 \rangle + \sum_j \Lambda_{ij} \phi_j \]
The CP Lagrangian – DFT / plane waves framework is given by:

\[ \mathcal{L}_{CP} = \sum_I \frac{m_I}{2} \dot{R}_I^2 + \mu \sum_i \sum_G \mid \dot{c}_i(G) \mid^2 - E^{KS}[\{G\}, \{R_I\}] + \sum_{i,j} \Lambda_{ij} \left( \sum_G c_i^*(G)c_j(G) - \delta_{ij} \right) \]

and the associated Euler-Lagrange equations:

\[ m_I \ddot{R}_I = -\frac{\partial E^{KS}}{\partial R_I} \]

\[ \mu \ddot{c}_i(G) = -\frac{\partial E^{KS}}{\partial c_i^*(G)} + \sum_j \Lambda_{ij} c_j(G) \]
Lagrangian mechanics: Born-Oppenheimer MD

\[ \mathcal{L}_{BO} = \sum_{l} \frac{m_l}{2} \dot{R}_l^2 - \langle \psi_0 | \mathcal{H}_e | \psi_0 \rangle + \sum_{i,j} \Lambda_{ij}(\langle \phi_i | \phi_j \rangle - \delta_{ij}) \]

and the associated Euler-Lagrange equations:

\[
m_l \ddot{R}_l = -\frac{\partial}{\partial \mathbf{R}_l} \min_{\{\phi_i\}} \{ \langle \psi_0 | \mathcal{H}_e | \psi_0 \rangle \}
\]

\[
0 = -\frac{\partial}{\partial \phi_i^*} \langle \psi_0 | \mathcal{H}_e | \psi_0 \rangle + \sum_j \Lambda_{ij} \phi_j
\]
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Integration: velocity Verlet algorithm

\[ \dot{\tilde{R}}_I(t + \delta t) = \dot{R}_I(t) + \frac{\delta t}{2M_I} \mathbf{F}_I(t) \]  

\[ R_I(t + \delta t) = R_I(t) + \delta t \dot{\tilde{R}}_I(t + \delta t) \]  

\[ \dot{\tilde{c}}_i(t + \delta t) = \dot{c}_i(t) + \delta t \frac{2}{2} \mu f_i(t) \]  

\[ c_i(t + \delta t) = c_i'(t + \delta t) + \sum_j X_{ij} c_j(t) \]  

\[ \text{calculate } \mathbf{F}_I(t + \delta t) \]  

\[ \dot{R}_I(t + \delta t) = \dot{\tilde{R}}_I(t + \delta t) + \frac{\delta t}{2M_I} \mathbf{F}_I(t + \delta t) \]
Integration: velocity Verlet algorithm

\[
\begin{align*}
\dot{\tilde{R}}_I(t + \delta t) &= \dot{R}_I(t) + \frac{\delta t}{2M_I} F_I(t) \\
R_I(t + \delta t) &= R_I(t) + \delta t \dot{\tilde{R}}_I(t + \delta t) \\
\dot{c}_i(t + \delta t) &= \dot{c}_i(t) + \frac{\delta t}{2\mu} f_i(t) \\
c_i'(t + \delta t) &= c_i(t) + \delta t \dot{\tilde{c}}_i(t + \delta t) \\
c_i(t + \delta t) &= c_i'(t + \delta t) + \sum_j X_{ij} c_j(t) \\
\dot{R}_I(t + \delta t) = \dot{\tilde{R}}_I(t + \delta t) + \frac{\delta t}{2M_I} F_I(t + \delta t) \\
\dot{c}_i'(t + \delta t) &= \dot{\tilde{c}}_i(t + \delta t) + \frac{\delta t}{2\mu} f_i(t + \delta t) \\
\dot{c}_i(t + \delta t) &= \dot{c}_i'(t + \delta t) + \sum_j Y_{ij} c_j(t + \delta t)
\end{align*}
\]
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Summary
Dynamics of Na$^+$ in a NaCl matrix

Central Na$^+$ displaced at 0.2 Å from its equilibrium position
Dynamics of Na⁺ in a NaCl matrix

Evolution of $\Delta z = z - z_{eq}$ with time for different values of $\mu$. 
First passage time at $\Delta z = 0$
Dynamics with renormalization of time

\[ \Delta z (\text{Å}) \]

\[ \frac{t}{t(\Delta z=0)} \]

- \( \mu = 700 \text{ a.u.} \)
- \( \mu = 1100 \text{ a.u.} \)
- \( \mu = 1800 \text{ a.u.} \)
Interpretation: renormalization of the mass

\[ \omega_{\text{BO}} = \omega_{\text{CP}} \sqrt{\frac{M'_I}{M_I}} \]

where \( M'_I = M_I + \Delta_\mu M_I \), and in a "rigid ion" approximation

\[ \Delta_\mu M_I = \frac{2}{3} \frac{m_e}{\hbar^2} \sum_j \mu \langle \phi^I_j | - \frac{\hbar^2}{2m_e} \nabla^2_j | \phi^I_j \rangle \]
Some conditions on $\mu$

- $\mu$ is a "non-physical" parameter controlling the time scale of the "classical" Car Parrinello electronic dynamics.
- It has to be assigned an optimal value such that
  - adiabatic separation between artificial electronic and real ionic motion is ensured
  - time step $\Delta t$ is as large as possible

Upper limit for $\mu$: frequency of the slowest electronic motion determined by HOMO-LUMO energy gap must be higher than fastest nuclear motion:

$$\omega_{\text{min}}^e \approx \left(\frac{E\text{gap}}{\mu}\right)^{1/2} > \omega_{\text{max}}^n$$

Example: system with hydrogen atoms: $\mu \approx 500$ a.u., $\Delta t \approx 5–10$ a.u. = 0.1–0.2 fs.
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CPMD simulation of 32 water molecules

$\delta t = 5$ a.u. (0.12 fs)

$L = 9.865$ Å

TM pseudos

$E_{\text{cut}} = 70$ Ry

BLYP functional

$\mu = 500$ a.u.
Stability of BO and CP compared (PW)

CPMD results for 8 Si atom model system (10 Ry, \( \mu = 300 \) a.u.)
CP and BO molecular dynamics for 1 ps of trajectory

<table>
<thead>
<tr>
<th>Method</th>
<th>Time step (au)</th>
<th>Convergence (au)</th>
<th>Conservation (au/ps)</th>
<th>Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP</td>
<td>5</td>
<td>–</td>
<td>( 6 \times 10^{-8} )</td>
<td>3230</td>
</tr>
<tr>
<td>CP</td>
<td>7</td>
<td>–</td>
<td>( 1 \times 10^{-7} )</td>
<td>2310</td>
</tr>
<tr>
<td>CP</td>
<td>10</td>
<td>–</td>
<td>( 3 \times 10^{-7} )</td>
<td>1610</td>
</tr>
<tr>
<td>BO</td>
<td>10</td>
<td>( 10^{-6} )</td>
<td>( 1 \times 10^{-6} )</td>
<td>16590</td>
</tr>
<tr>
<td>BO</td>
<td>50</td>
<td>( 10^{-6} )</td>
<td>( 1 \times 10^{-6} )</td>
<td>4130</td>
</tr>
<tr>
<td>BO</td>
<td>100</td>
<td>( 10^{-5} )</td>
<td>( 6 \times 10^{-6} )</td>
<td>2250</td>
</tr>
<tr>
<td>BO</td>
<td>100</td>
<td>( 10^{-4} )</td>
<td>( 1 \times 10^{-5} )</td>
<td>1660</td>
</tr>
<tr>
<td>BO</td>
<td>100</td>
<td>( 10^{-4} )</td>
<td>( 1 \times 10^{-3} )</td>
<td>1060</td>
</tr>
</tbody>
</table>
Characteristic parameters for different simulations of 32 water molecules (PW)

\( T = 350 \text{ K}; \ \rho = 0.905 \text{ g.cm}^{-3}; \ \text{TM pseudos}; \ E_{\text{cut}} = 70 \text{ Ry} \)

<table>
<thead>
<tr>
<th>Simulation</th>
<th>Time step (au)</th>
<th>Convergence (au)</th>
<th>( \mu ) (au)</th>
<th>Relative Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP</td>
<td>3</td>
<td>–</td>
<td>300</td>
<td>1.74</td>
</tr>
<tr>
<td>CP</td>
<td>4</td>
<td>–</td>
<td>500</td>
<td>1.29</td>
</tr>
<tr>
<td>CP</td>
<td>5</td>
<td>–</td>
<td>700</td>
<td>1.00</td>
</tr>
<tr>
<td>BO</td>
<td>20</td>
<td>( 10^{-4} )</td>
<td>–</td>
<td>2.08</td>
</tr>
<tr>
<td>BO</td>
<td>20</td>
<td>( 10^{-5} )</td>
<td>–</td>
<td>2.07</td>
</tr>
<tr>
<td>BO</td>
<td>20</td>
<td>( 10^{-7} )</td>
<td>–</td>
<td>3.87</td>
</tr>
</tbody>
</table>
Energy drifts ans standard deviations for different simulations of 32 water molecules (PW)

$T=350$ K; $\rho=0.905$ g.cm$^{-3}$; TM pseudos; $E_{cut}=70$ Ry

<table>
<thead>
<tr>
<th>Simulation</th>
<th>Physical energy drift (K.ps$^{-1}$)</th>
<th>Conserved energy drift (K.ps$^{-1}$)</th>
<th>Physical energy std (K)</th>
<th>Conserved energy std (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP300</td>
<td>0.276</td>
<td>0.007</td>
<td>1.02</td>
<td>0.004</td>
</tr>
<tr>
<td>CP500</td>
<td>0.736</td>
<td>0.012</td>
<td>1.61</td>
<td>0.006</td>
</tr>
<tr>
<td>CP700</td>
<td>3.070</td>
<td>0.019</td>
<td>2.37</td>
<td>0.008</td>
</tr>
<tr>
<td>BO4</td>
<td>2.980</td>
<td>1.584</td>
<td>0.16</td>
<td>2.980</td>
</tr>
<tr>
<td>BO5</td>
<td>1.584</td>
<td>1.584</td>
<td>0.13</td>
<td>0.129</td>
</tr>
<tr>
<td>BO6</td>
<td>0.092</td>
<td>0.092</td>
<td>0.12</td>
<td>0.119</td>
</tr>
<tr>
<td>BO7</td>
<td>0.033</td>
<td>0.033</td>
<td>0.11</td>
<td>0.113</td>
</tr>
</tbody>
</table>
BO in CPMD vs. QUICKSTEP: forces for 32 water molecules

basis set gives already an excellent overall agreement and for the QZV3P most distances coincide within the expected errors. Note, that a full agreement with the NUMOL values is not possible, since NUMOL uses a slightly different LDA implementation and it employs a frozen core approximation for the elements beyond Beryllium that differs from the GTH pseudopotentials used by QUICKSTEP. These differences may cause a change of the bond distances of about 0.001 Å. This small error also shows that the effect of the pseudopotential is often negligible compared to typical basis set effects concerning structural properties. Thus a basis set can be chosen according to the accuracy requirements of the actual application. However, the ultimate accuracy of QUICKSTEP is determined by the error of the available exchange and correlation functionals.

8.2. Condensed phase systems

Standard benchmarks to judge the quality of an electronic structure method for the liquid phase do not yet exist. Therefore, in order to assess the accuracy of QUICKSTEP for calculations in the condensed phase, comparisons with the program CPMD [66] have been made. CPMD employs a plane wave basis set to represent the wave functions which is a natural basis set for periodic condensed phase systems. Furthermore, plane waves provide an orthogonal basis that allows to reach conveniently the basis set limit for a given pseudopotential only by increasing a single parameter, i.e. the plane wave cutoff. In principle, identical total energies can be obtained by QUICKSTEP and CPMD, if the same system is described by the same pseudopotentials. Nevertheless, this is a non-trivial and very stringent test for the accuracy of both methods, since the two methodologies and basis sets are very different. We have already mentioned that the GTH pseudopotentials are rather hard (see Section 2.2) and that they require a higher plane wave cutoff than the pseudopotentials of Troullier and Martins [76] that are commonly used in CPMD calculations.

Fig. 10 shows a correlation plot between forces...
BO in CPMD vs. QUICKSTEP: energies for 64 water molecules

<table>
<thead>
<tr>
<th>Method</th>
<th>CPMD</th>
<th>QUICKSTEP (TZV2P)</th>
<th>QUICKSTEP (340 Ry)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>70 Ry</td>
<td>85 Ry</td>
<td>100 Ry</td>
</tr>
<tr>
<td>MAD</td>
<td>15.5</td>
<td>10.8</td>
<td>3.6</td>
</tr>
<tr>
<td>RMSD</td>
<td>7.7</td>
<td>4.2</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MAD</td>
<td>11.1</td>
<td>9.3</td>
<td>5.3</td>
</tr>
<tr>
<td>RMSD</td>
<td>5.1</td>
<td>4.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Ref: CPMD – 200 Ry
RMSD: Root mean square deviation
MAD: Maximum absolute deviation (in $10^{-3}$ a.u.)
Comparison of BO and CP dynamics

BO MD
Exactly on BO surface, more accurate in principle
\[ \delta t \approx \text{ionic time scales} \]
Diagonalization or minimization expensive at every time step
Not stable against deviation from BO surface

CP MD
Always slightly off BO surface, less accurate
\[ \delta t < \text{ionic time scales} \]
Only orthogonalization, far less expensive time steps
Stable
Need to choose \( \mu \)
References