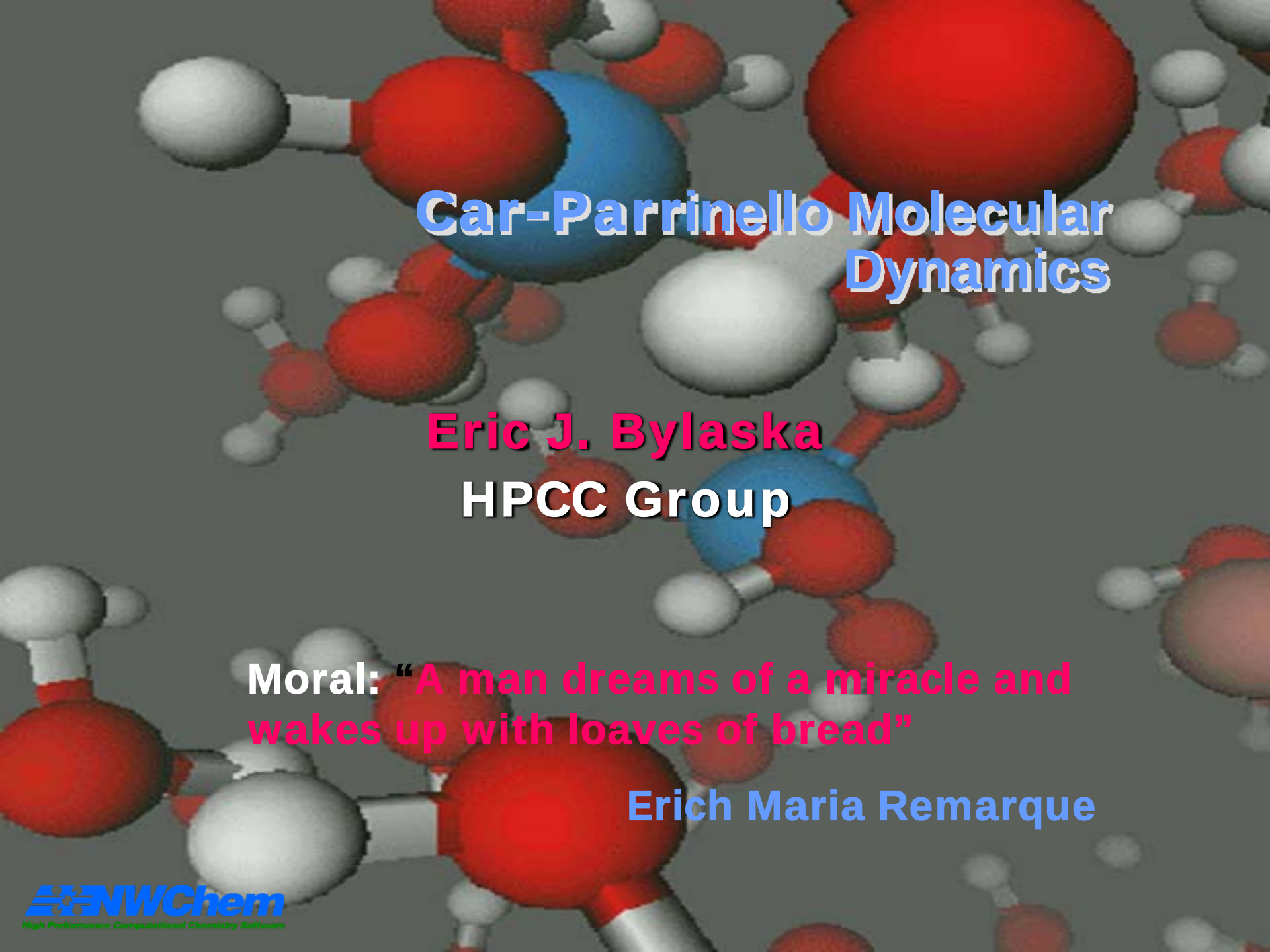


Car-Parrinello Molecular Dynamics

Eric J. Bylaska

HPCC Group

Moral: "A man dreams of a miracle and wakes up with loaves of bread"

Erich Maria Remarque

NWChem
High Performance Computational Chemistry Software

Molecular Dynamics Loop

(1) Compute Forces on atoms, $F_I(t)$ for current atomic configuration, $R_I(t)$

$F_I(t) \leftarrow$

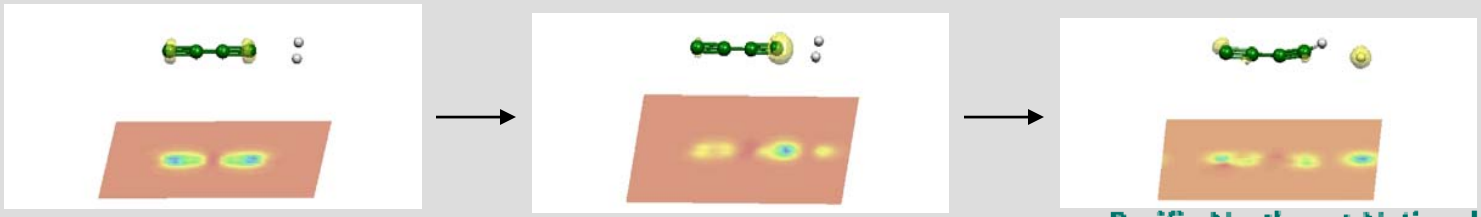
- calculate using classical potentials
(can do large systems and long simulation times)
- calculate directly from first principles by solving many-electron Schrödinger equations
(can treat very complex chemistry, but simulations times are very long)

(2) Update atom positions using Newtons laws

- $R_I(t+\Delta t) \leftarrow 2*R_I(t) - R_I(t-\Delta t) + \Delta t^2/(M_I)*F_I(t)$

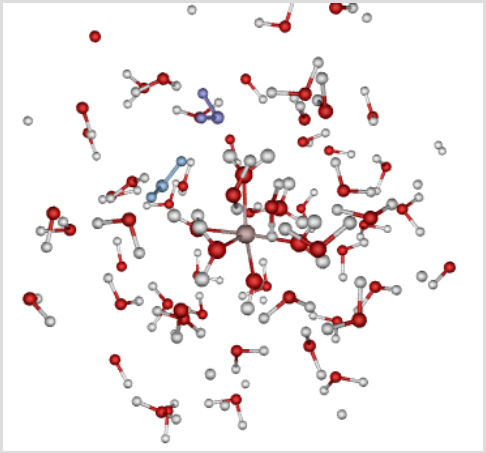
Ab Initio Molecular Dynamics – For Problems Beyond Classical MD Simulations

- 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

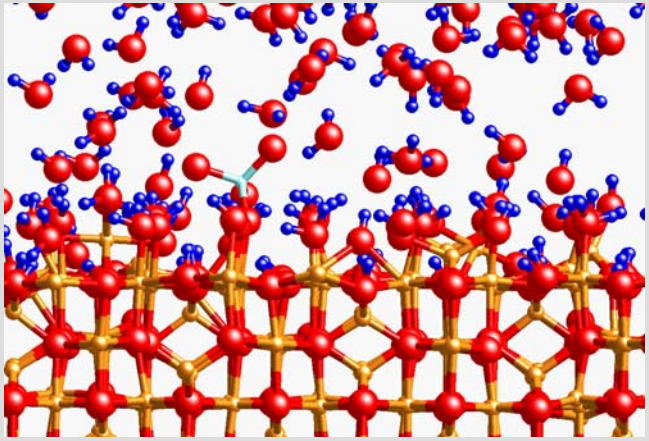


Application Goals
- Study complex systems with ab initio dynamics

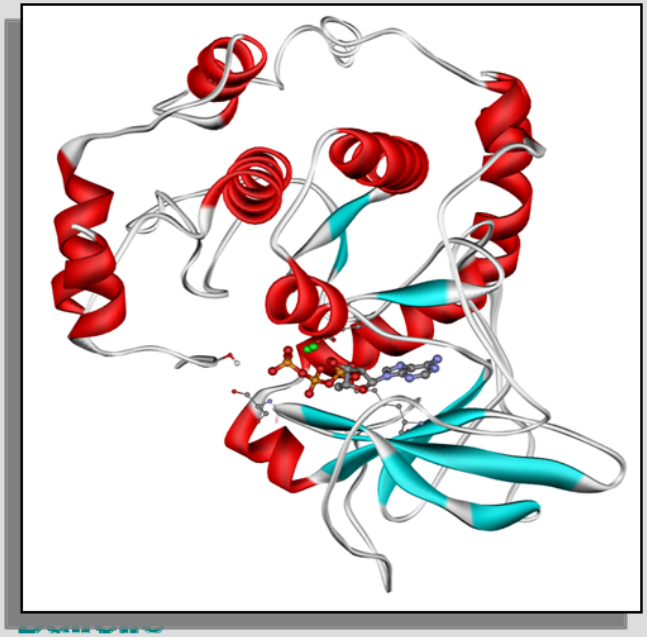
Al^{3+} Hydrolysis

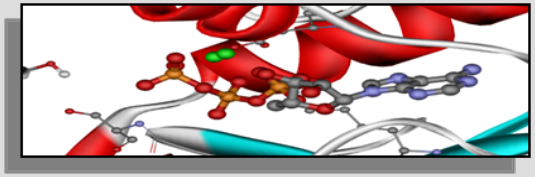


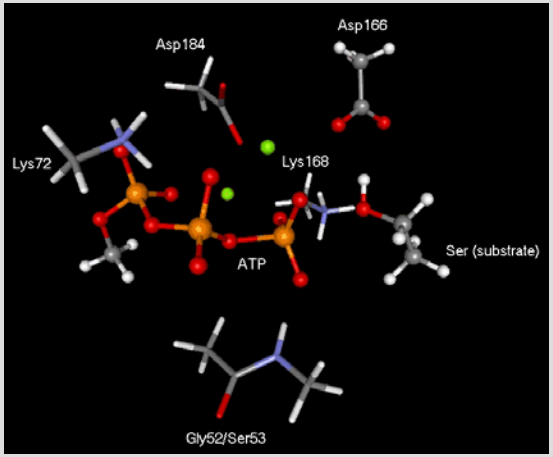
Active Site on iron-oxide



Enzymatic Active Site







Chemical Reactions

Comparison of Classical and Ab Initio Molecular Dynamics

Classical MD	First Principles MD
✓ **Phenomenological potential energy surface** (typically restricted to two body contributions)	✓ **Potential energy surface calculated directly from the Schrodinger equation** (many-body terms included automatically)
✓ **Difficult to describe bond breaking / making**	✓ **Describes bond breaking / making**
✓ **Electronic properties are <u>not</u> available**	✓ **Electronic spectra included in calculation**
✓ **Can do millions of particles**	✓ **Limited to 250 atoms with significant dynamics**

Basic Features of Ab Initio Molecular Dynamics

Energy functional

$$E[n,\mathrm{R_I}] = \sum_i \left\langle \psi_i \left| -\frac{1}{2}\nabla^2 \right| \psi_i \right\rangle + \int V_{ext}(\mathrm{r};\mathrm{R_I})\, n(\mathrm{r})\, d\mathrm{r} + \frac{1}{2}\iint \frac{n(\mathrm{r})\, n(\mathrm{r}')}{|\mathrm{r}-\mathrm{r}'|} d\mathrm{r} d\mathrm{r}' + \int \varepsilon_{xc}(n)\, n(\mathrm{r})\, d\mathrm{r}$$

Ground state energy

$$-\frac{\delta E}{\delta \psi_i^*} = \sum_\beta \lambda_{ij} \psi_j$$

Force Calculation

Ion motion

$$M_\mathrm{I} \ddot{\mathrm{R}}_\mathrm{I} = -\frac{\delta E}{\delta \mathrm{R_I}}$$

Pitfalls of Ab Initio Molecular Dynamics

- Expensive?

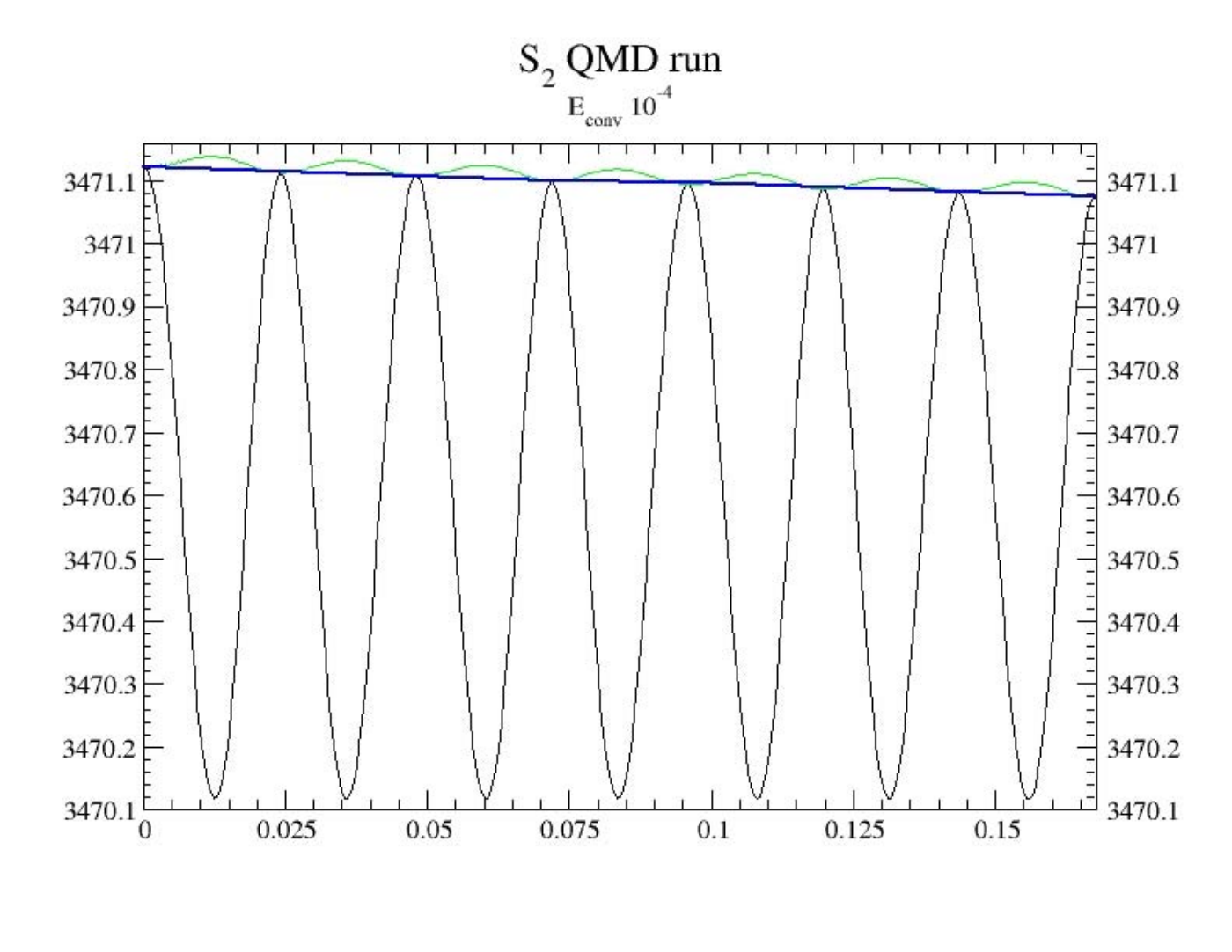
- *Energy Conservation – Born-Oppenheimer Error*

$$dE/dR = (\partial E/\partial c)(dc/dR) + \partial E/\partial R$$

"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-Parrinello Dynamics

- Car and Parrinello suggested that ionic dynamics could be run in parallel with a ficticious electronic dynamics via the following Lagrangean

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

- 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 electonic 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 Ψ in a basis set

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

Atomic centered basis set (e.g. gaussians, …)	Plane wave basis set
• All-electron (both core and valence electrons included in calculation)	• Typically requires pseudopotentials (defined on following slide) but can be made all electron with PAW
•Forces are expensive to calculate	• Forces can be calculated efficiently
•First principles MD expensive	•Efficient first principles MD

Elements of Ab Initio Molecular Dynamics

Local Density Functional Theory

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

$$+ (1/2)\int\int \frac{n(\mathbf{r})\, n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}' + E_{xc}[n,|\nabla n|]$$

$$n(\mathbf{r}) = \sum \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}) \qquad \int \psi_i^*(\mathbf{r})\psi_j(\mathbf{r})d\mathbf{r} = \delta_{i,j}$$

Elements of Ab Initio Molecular Dynamics

Car-Parrinello Equation - Local Density Functional Theory

if $\mu=0$ then Kohn-Sham

$$\mu\ddot{\psi}_i = \frac{\delta E}{\delta \psi_i^*} - \sum_j \Lambda_{i,j}\psi_j \qquad \frac{\delta E}{\delta \psi_i^*} = ((-1/2)\Delta + V_{ext} + V_c + V_{xc})\psi_i$$

need to be efficient

$$M_I \ddot{\mathbf{R}} = \mathbf{F}_I \qquad \mathbf{F}_I = \sum_i \langle \psi_i | \frac{\partial H}{\partial \mathbf{R}_I} | \psi_i \rangle$$

We use plane-waves and pseudopotentials

$$\psi_i(\mathbf{r}) = \sum_{\mathbf{k}} c_{\mathbf{k}}^{\,i} \exp(\iota \mathbf{k} \cdot \mathbf{r}) \qquad V_{ext} \text{ --> pseudopotentials}$$

$$(-1/2)\,\Delta\Psi + V_{ext}\Psi + V_c\Psi + V_{xc}\Psi = E\Psi$$

$$\langle\Psi_i \mid \Psi_j\rangle = \delta_{i,j}$$

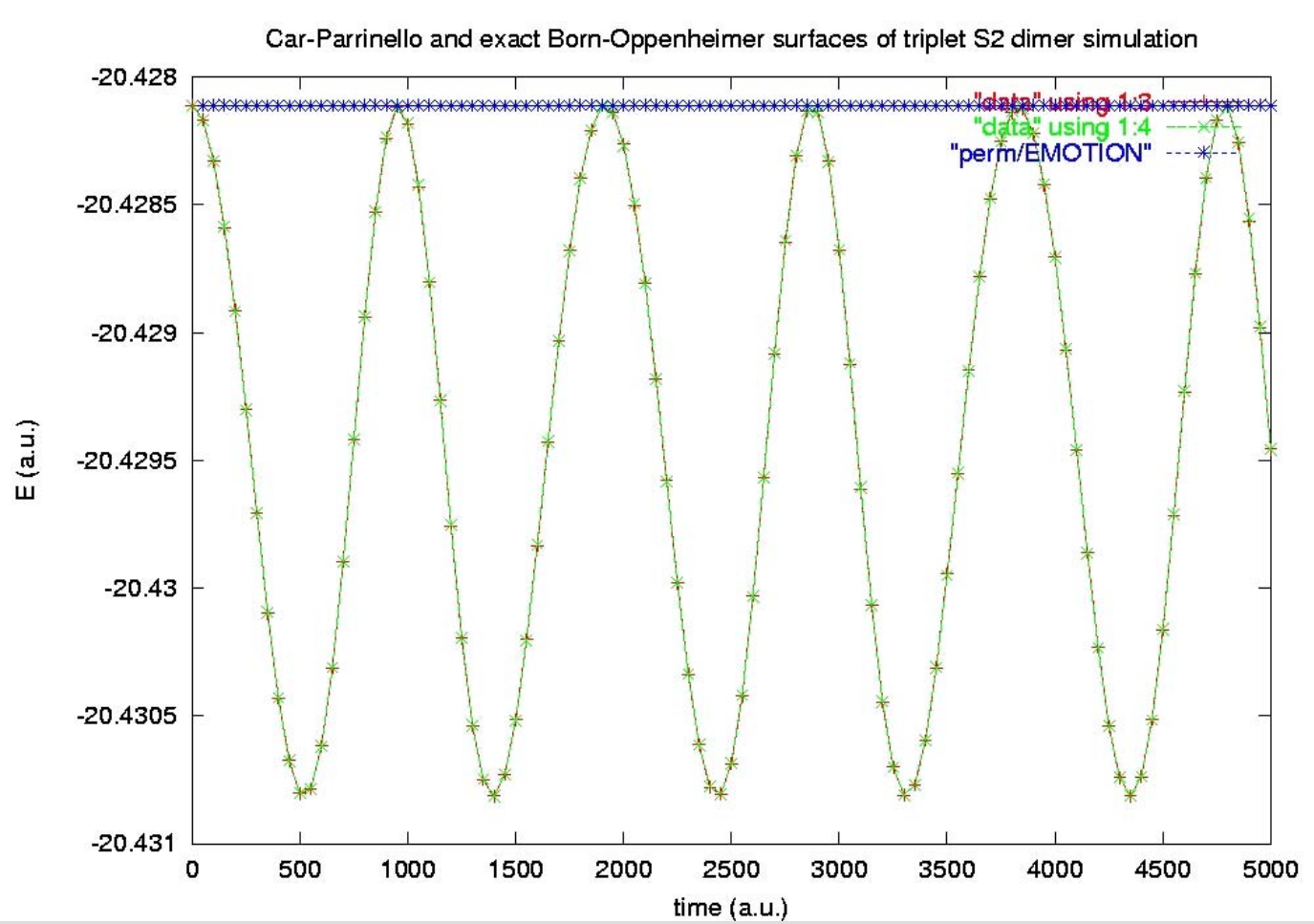
Scaling for calculating $H\Psi + \Lambda\Psi$

- $N_e * N_g$ - diagonal in k-space
- $(N_a * N_g + N_g \mathrm{Log}\, N_g + N_e * N_g) + (N_a * N_e * N_g)$ - diagonal in r-space and k-space
- $N_e * N_g \mathrm{Log}\, N_g + N_e * N_g + 2\, N_g \mathrm{Log}\, N_g + N_g + N_e * N_g$ - diagonal in r-space
- $N_e * N_g \mathrm{Log}\, N_g + N_e * N_g + N_e * N_g$ - diagonal in r-space
- Orthonormalization: $N_e^2 * N_g + N_e^3$

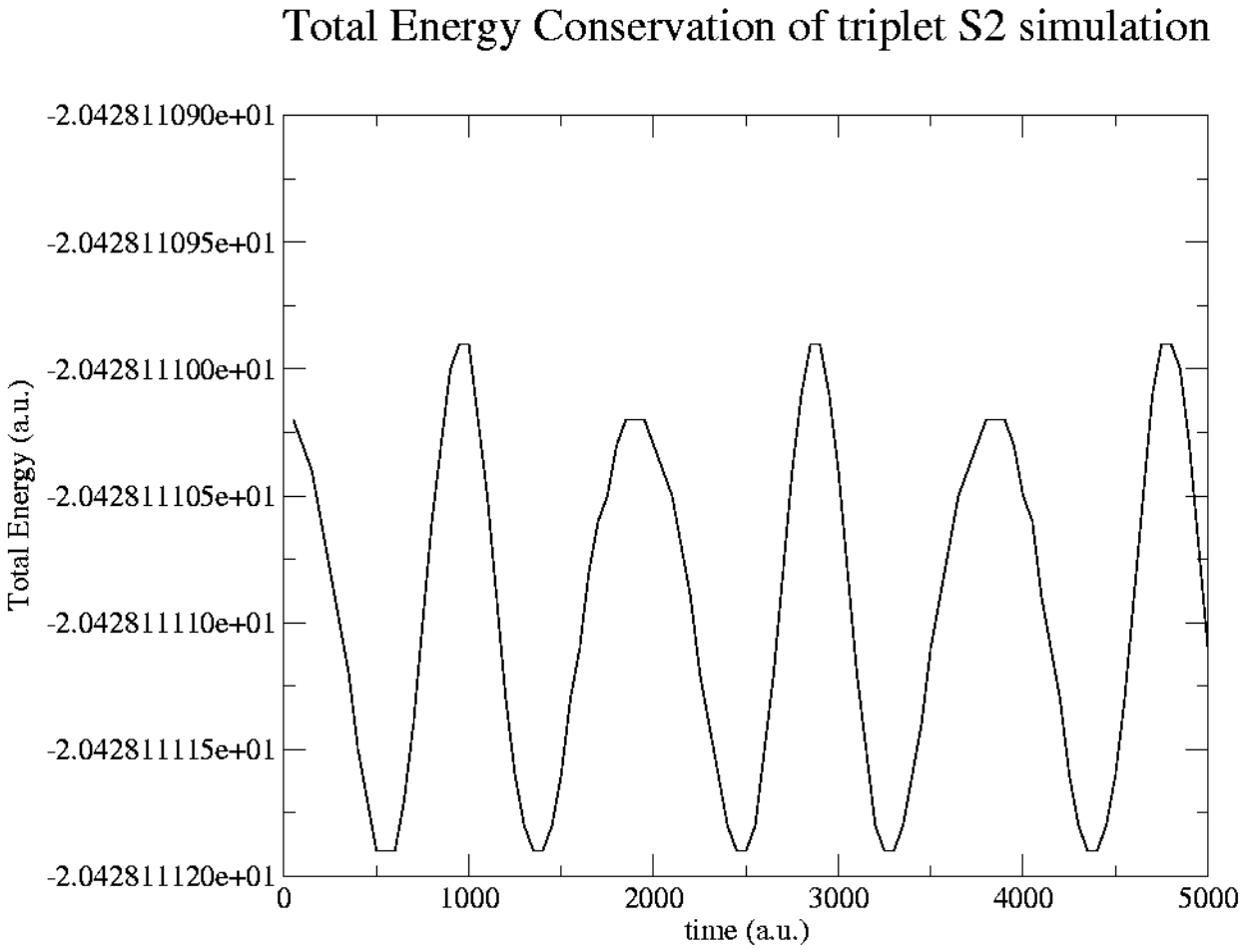
Example 1b: S_2 molecule LDA Car-Parrinello Simulation.

```
title "S2 MD LDA/25Ry"
start s2.md
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 and 1500
     loop 10  100
   end
   mult 3
end
set nwpw:minimizer 2
task pspw energy
task pspw car-parrinello
```

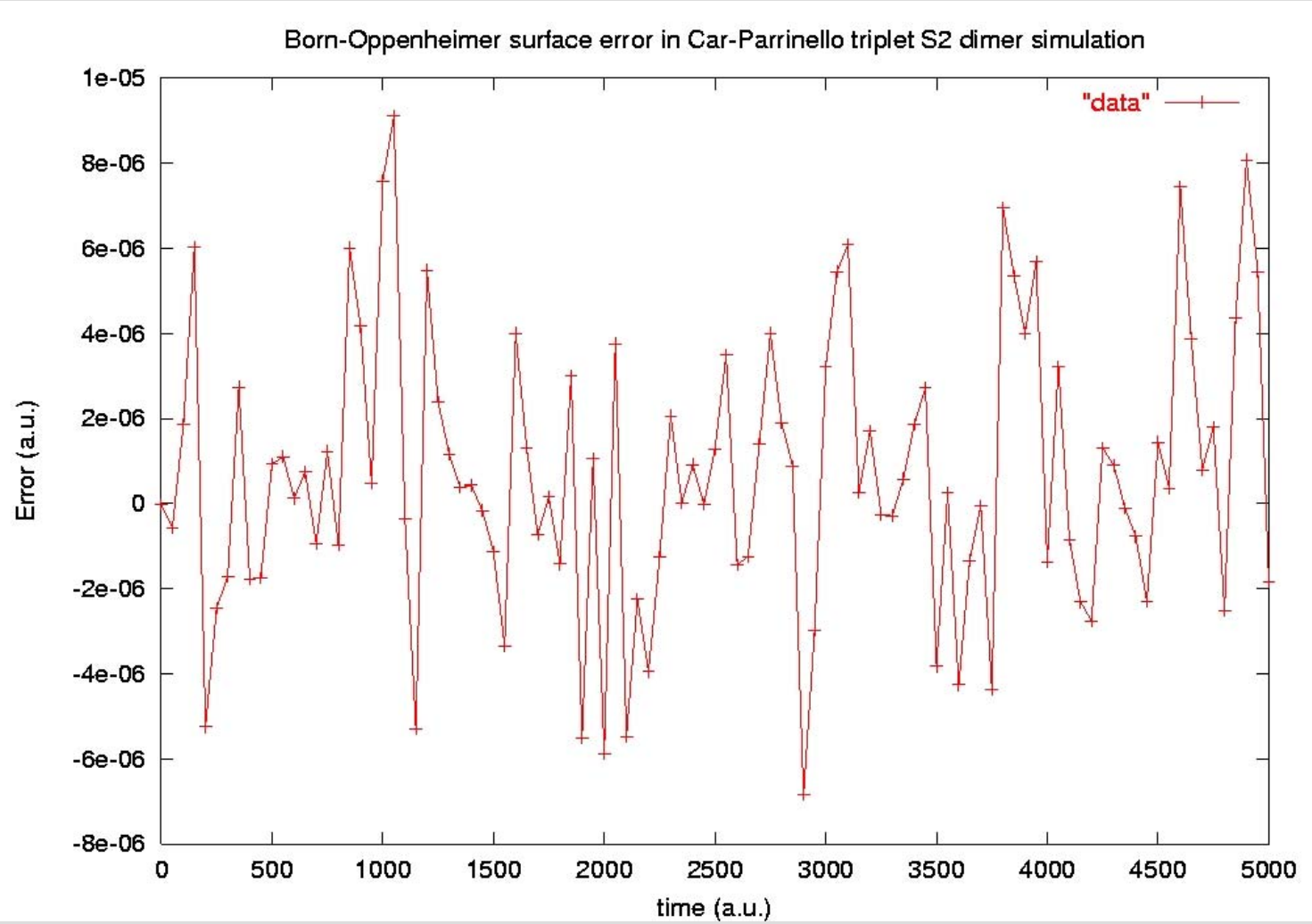
$^3\Sigma_g^-$ S_2 Energy Surface from Car-Parrinello Simulation



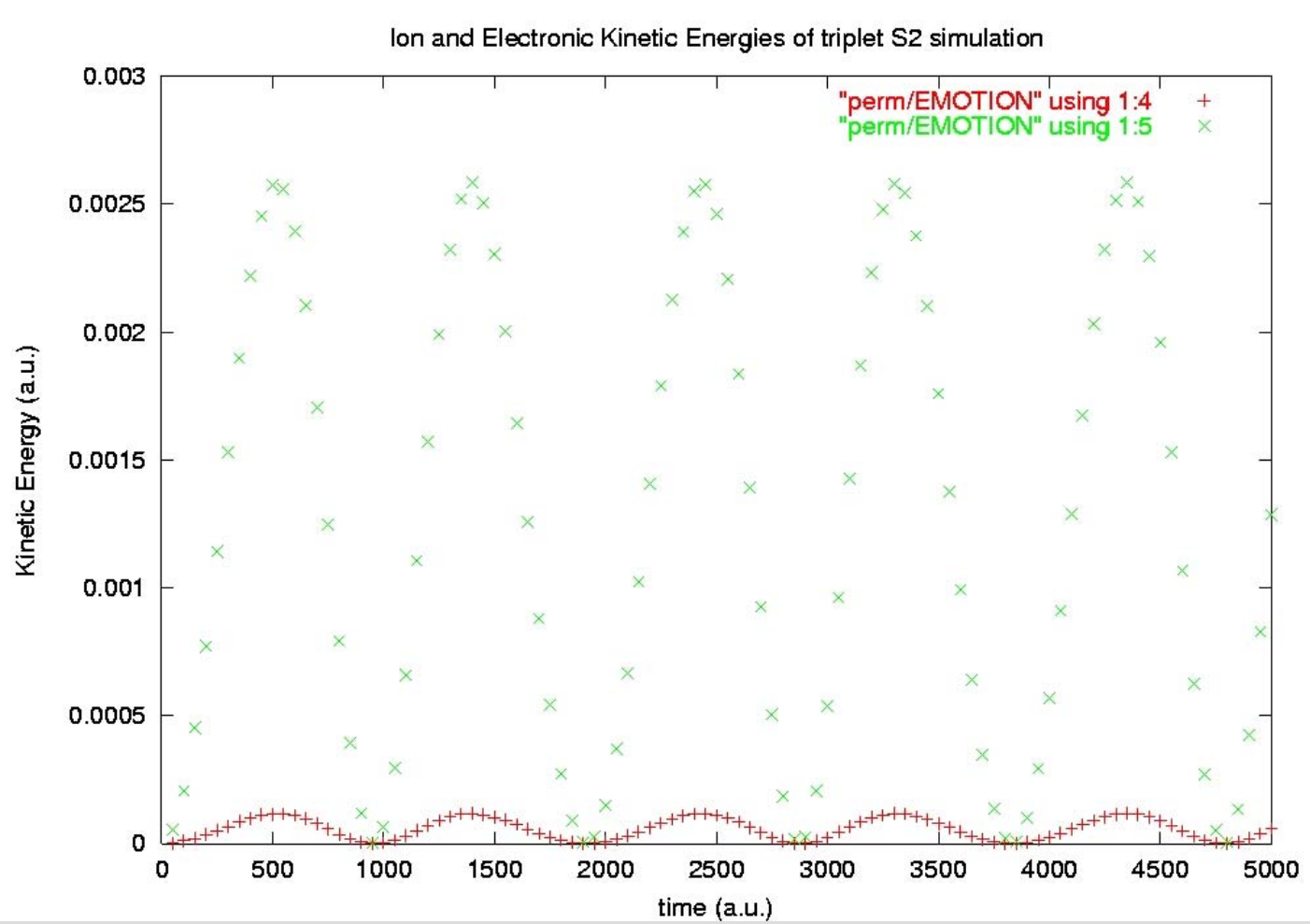
Energy Conservation



Born-Oppenheimer Error



Ionic and Ficticious Electronic Kinetic Energies



A Closer look at Born-Oppenheimer and Car-Parrinello

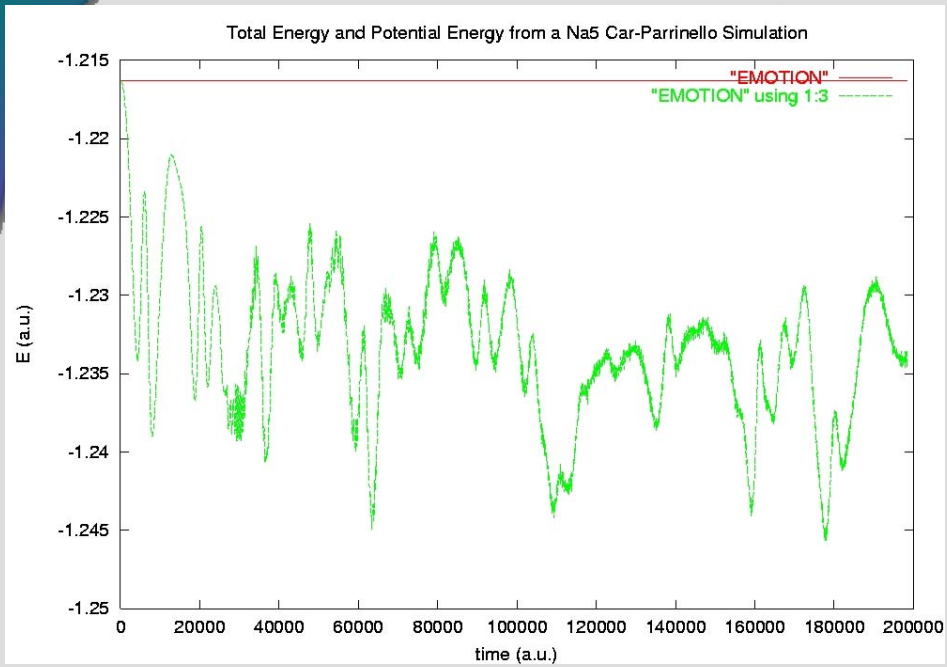
- Adiabicity is not built into the Car-Parrinello equations of motion. As pointed out by Remler and Madden

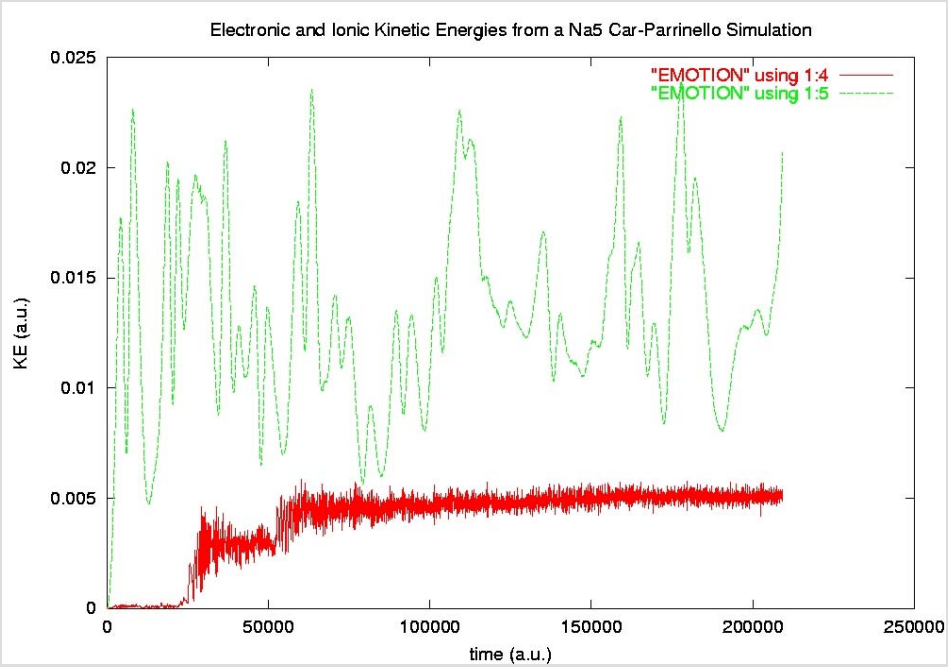
  "equipartion principle tells us that the average kinetic energies of all degrees of freedom in the classical system will be equal at equilibrium. The adiabatic state, in which the ficticious system is at a very low temperature and the ionic system is hot is therefore metastable."

- 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

Na_5 Car-Parrinello Simulation – Electronic heating in Car-Parrinello





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

- R. Car and M. Parrinello (1985), "Unified Approach for Molecular Dynamics and Density Functional Theory", Phys. Rev. Lett, **55**(22), pages 2471-2474.

- R. Car and M. Parrinello (1989), "The Unified Approach for Molecular Dynamics and Density Functional Theory", in Simple Molecular Systems at Very High Density, vol. 186 of NATO ASI Series, series B, Physics, P.P. Loubeyre and N. Boccara (Eds.) (Plenum Press, NY) pages 455-476.

- D.K. Remler, and P.A. Madden (1990), "Molecular dynamics without effective potentials via the Car-Parrinello approach", Mol. Phys., 70(6), page 921-966.

- T. Morishita, S. Nose (1999), "Momentum conservation law in the Car-Parrinello method," Phys Rev. B., 59 (23) pages 15126-15132

- D. Marx and J. Hutter (2000), "Ab Initio Molecular Dynamics: Theory and Implementation", Modern Methods and Algorithms fo Quantum Chemistry, Proceedings, Second Edition, J. Grotendorst(Ed.), John von Neumann Institute for Computing, Julich, NIC Series, Vol. 3. (http://www.fz-juelich.de/nic-series/Volume3/marx.pdf)

- M. Valiev, E.J. Bylaska, A. Gramada, and J.H. Weare (2002), *First Principle Molecular Dynamics Simulations using Density-Functional Theory*, chapter 56, in Reviews In Modern Quantum Chemistry: A Celebration Of The Contributions Of R. G. Parr, Ed. K.D. Sen (World Scientific, Singapore).