



*For centuries, the battle of morality was fought between those who claimed that your life belongs to God and those who claimed that it belongs to your neighbours – between those who preached that the good is self-sacrifice for the sake of ghosts in heaven and those who preached that the good is self-sacrifice for the sake of incompetents on earth. And no one came to say that your life belongs to you and the good is to live it.*

Ayn Rand

## Lecture 10: *ab initio* molecular dynamics

*Unitary propagation problem, Krylov propagation, symplectic integration methods, BOMD, CPMD, ADMP*

# Unitary propagation problem

The time-dependent Schrödinger equation has a “simple” general solution:

$$\frac{\partial}{\partial t} \psi(t) = -i\hat{H}(t)\psi(t) \quad \Rightarrow \quad \psi(t) = \hat{T} \exp\left(-i \int_0^t \hat{H}(t) dt\right) \psi(0)$$

The time-ordered exponential is notoriously hard to compute and most practical solutions assume piecewise-constant Hamiltonian with a small enough time step:

$$\psi(t + \Delta t) = \exp(-i\hat{H}\Delta t)\psi(t)$$

Because the exponential of an anti-Hermitian matrix is unitary and inherits all the symmetries of the Hamiltonian, all conservation laws are guaranteed to hold. The matrix exponential, however, is often prohibitively expensive:

$$e^{-i\hat{H}_0\Delta\tau} \underset{\text{Padé}}{\approx} \frac{\sum_{j=0}^p \frac{(p+q-j)!p!}{(p+q)!j!(p-j)!} \left(-i\hat{H}_0\Delta\tau\right)^j}{\sum_{j=0}^q \frac{(p+q-j)!p!}{(p+q)!j!(p-j)!} \left(i\hat{H}_0\Delta\tau\right)^j} \quad e^{-i\hat{H}_0\Delta\tau} = \sum_{n=0}^{\infty} \underbrace{(2-\delta_{n0})i^n J_n(1)}_{\text{Chebyshev}} T_n\left(-\hat{H}_0\Delta\tau\right)$$

$$e^{-i\hat{H}_0\Delta\tau} = \sum_{n=0}^{\infty} \frac{(-i\hat{H}_0\Delta\tau)^n}{n!} \quad \text{Taylor}$$

# Unitary propagation problem

The problem can be partially avoided by re-ordering the multiplication operations:

$$\exp(-i\hat{H}\Delta t)\psi = \left[ \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \hat{H}^n \right] \psi = \sum_{n=0}^{\infty} \frac{(-i\Delta t)^n}{n!} \left( \hat{H} \left( \hat{H} \left( \dots \left( \hat{H}\psi \right) \right) \right) \right)$$

(a slight generalization of this is known as *Krylov method*) but this only gets the scaling of one stage down from  $n^3$  to  $n^2$  in matrix dimension. Some simplification can be made using symplectic integrators based on CBH formula:

$$\exp(-i\hat{H}\Delta t) = \exp\left[-i(\hat{T} + \hat{U})\Delta t\right] = \prod_{n=1}^N \exp(-ic_n\hat{T}\Delta t) \exp(-id_n\hat{U}\Delta t) + O(\Delta t^{N+1})$$

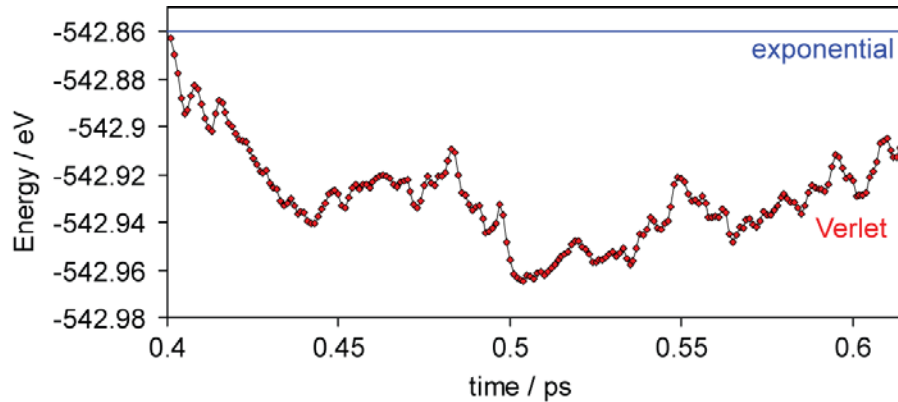
$$\begin{cases} c_1 = 1 \\ d_1 = 1 \end{cases} \longleftarrow \text{symplectic Euler method}$$

$$\begin{cases} c_1 = \frac{1}{2}, c_2 = \frac{1}{2} \\ d_1 = 1, d_2 = 0 \end{cases} \longleftarrow \text{Verlet method}$$

Symplectic integration is cheaper (though less accurate) than exponential propagation, but still approximately obeys all conservation laws. This is not the case with Euler or RK methods.

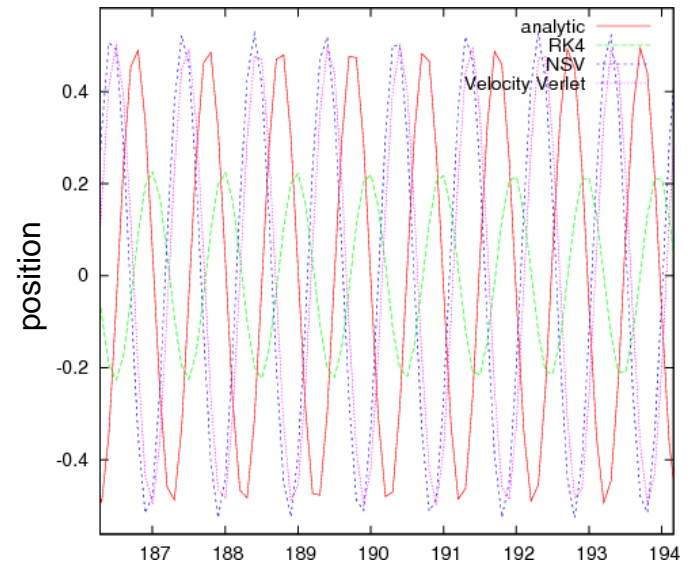
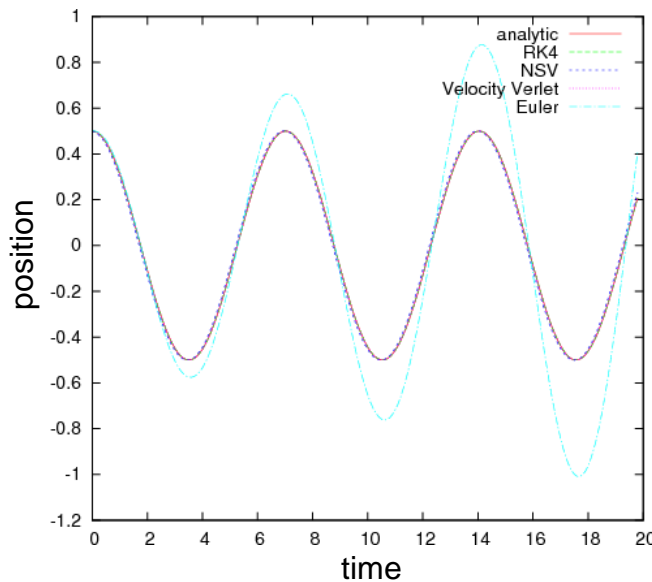
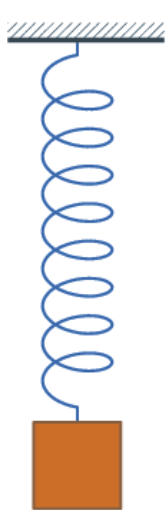
Still, *any integrator other than the Hamiltonian exponential would in practice display energy and momentum drift over long time scales.*

# Unitary propagation problem



It is important to understand that the trajectory is accurate *up to the truncation error of the method*, e.g.:

$$e^{-i\hat{T}\Delta t - i\hat{U}\Delta t} = e^{-i\hat{T}\frac{\Delta t}{2}} e^{-i\hat{U}\Delta t} e^{-i\hat{T}\frac{\Delta t}{2}} + O(\Delta t^3)$$



The parameter that *all* approximate methods quickly lose is phase.

# Born-Oppenheimer molecular dynamics

Within the Born-Oppenheimer approximation, the system Lagrangian is:

$$L = \sum_N \frac{m_N v_N^2}{2} - \min_{\Psi} \langle \Psi | \hat{H}(\{\vec{r}_N\}) | \Psi \rangle \longleftarrow \text{ab initio calculation}$$

$$L = \sum_N \frac{m_N v_N^2}{2} - \min_{\{\phi_i\}} E[\{\phi_i\}, \{\vec{r}_N\}] \longleftarrow \text{density functional theory}$$

This produces the following equation of motion for the nuclei:

$$m_k \frac{\partial^2 \vec{r}_k}{\partial t^2} = -\nabla_k \left[ \min_{\Psi} \langle \Psi | \hat{H}(\{\vec{r}_N\}) | \Psi \rangle \right] \longleftarrow \text{ab initio calculation}$$

$$m_k \frac{\partial^2 \vec{r}_k}{\partial t^2} = -\nabla_k \left[ \min_{\{\phi_i\}} E[\{\phi_i\}, \{\vec{r}_N\}] \right] \longleftarrow \text{density functional theory}$$

This may be solved forward in time using any of the methods mentioned above. BOMD method tends to be expensive because analytical derivatives of the total molecular energy with respect to nuclear coordinates are required at each step.

# Car-Parrinello molecular dynamics

The following Lagrangian was postulated by Car and Parrinello:

$$L = \underbrace{\sum_N \frac{m_N v_N^2}{2}}_{\text{nuclear kinetic energy}} + \underbrace{\sum_i \frac{\mu_i \langle \dot{\phi}_i | \dot{\phi}_i \rangle}{2}}_{\text{electron "kinetic energy"}}$$

$$- \underbrace{E[\{\phi_i\}, \{\vec{r}_N\}]}_{\text{potential energy}} + \underbrace{\sum_{ij} \Lambda_{ij} (\langle \phi_i | \phi_j \rangle - \delta_{ij})}_{\text{orbital orthogonality}}$$

From Lagrangian mechanics we get the following equations of motion:

$$\frac{d}{dt} \frac{\partial L}{\partial \vec{v}_N} = \frac{\partial L}{\partial \vec{r}_N} \quad \Rightarrow \quad m_N \ddot{\vec{r}}_N = -\frac{\partial E}{\partial \vec{r}_N} + \sum_{ij} \Lambda_{ij} \frac{\partial}{\partial \vec{r}_N} \langle \phi_i | \phi_j \rangle$$

$$\frac{d}{dt} \frac{\delta L}{\delta \langle \dot{\phi}_i |} = \frac{\delta L}{\delta \langle \phi_i |} \quad \Rightarrow \quad \mu_i |\ddot{\phi}_i\rangle = -\frac{\delta E}{\delta \langle \phi_i |} + \sum_j \Lambda_{ij} |\phi_j\rangle$$

The downside of the CP approach is that the dynamics would deviate from the Born-Oppenheimer surface. The advantage over BOMD is that expensive energy minimization is no longer required at each step.

# Car-Parrinello molecular dynamics

The requirement to maintain adiabaticity (*i.e.* to stay near the Born-Oppenheimer surface) means that the electron subsystem must be kept “cold” and there should be no exchange of energy between the nuclear and the orbital degrees of freedom:

$$E = \sum_N \frac{m_N v_N^2}{2} + \sum_i \frac{\mu_i \langle \dot{\phi}_i | \dot{\phi}_i \rangle}{2} - E[\{\phi_i\}, \{\vec{r}_N\}] \approx \sum_N \frac{m_N v_N^2}{2} + \min_{\{\phi_i\}} E[\{\phi_i\}, \{\vec{r}_N\}]$$

To avoid energy exchange, the power spectra of the two subsystems should not overlap – the lowest orbital frequency must be far from the highest nuclear one:

$$\omega_{ij} = \left( \frac{2(\epsilon_i - \epsilon_j)}{\mu} \right)^{1/2} \Rightarrow \omega_e^{\min} \sim \left( \frac{E_{LUMO} - E_{HOMO}}{\mu} \right)^{1/2} \gg \omega_n^{\max}$$

The simplest way to achieve this is to reduce the fictitious mass. This, however, requires smaller time steps, because the highest electron frequency also goes up:

$$\Delta t \sim \frac{\pi}{\omega_e^{\max}} \quad \omega_e^{\max} \sim \left( \frac{\epsilon_{\text{virt}}^{\max} - \epsilon_{\text{occ}}^{\min}}{\mu} \right)^{1/2}$$

# Car-Parrinello molecular dynamics

What time step should one choose?

On the one hand: Nyquist-Shannon sampling theorem

*“correct sampling of a time domain signal requires two points per period of the fastest oscillation present in the signal”*

On the other hand: CPU time

*“the current charging rate at the Oxford Supercomputing Centre is £0.06 per core hour on both clusters and the shared-memory system”*

Commonly used values:  $\mu=300-1500$  a.u.,  $\Delta t=0.1-0.2$  fs (5-10 a.u.).

1. Longer trajectories require smaller fictitious mass.
2. It is sometimes reasonable to increase nuclear mass.
3. A thermostat may be used to drain the energy from the electrons.
4. BOMD allows much greater time steps due to absence of orbital dynamics.

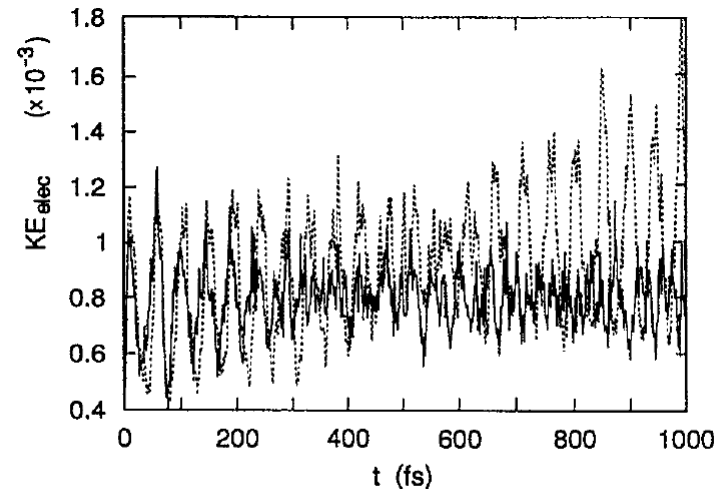


FIG. 7. (a) The fictitious electronic kinetic energy corresponding to the cases  $\mu=2400$ ,  $\delta t = 5$  a.u. with (solid line) and without (dashed line) thermostats.

# Car-Parrinello molecular dynamics

The primary advantage of CPMD over BOMD is cheaper forces:

$$\begin{aligned}
 F_O(\varphi_i) &= -\hat{H}|\varphi_i\rangle & F_N(\vec{r}_N) &= -\frac{\partial E[\{\varphi_i\}, \{\vec{r}_N\}]}{\partial \vec{r}_N} \\
 F_C(\varphi_i) &= \sum_j \Lambda_{ij}|\varphi_j\rangle & F_C(\vec{r}_N) &= \sum_{ij} \Lambda_{ij} \frac{\partial}{\partial \vec{r}_N} \langle \varphi_i | \varphi_j \rangle \\
 F_N(\vec{r}_N) &= -\nabla_k \left[ \min_{\Psi} \langle \Psi | \hat{H}(\{\vec{r}_N\}) | \Psi \rangle \right]
 \end{aligned}$$

} CPMD forces  
← BOMD force

The following conditions should always be checked when running CPMD:

1. Electron temperature should be much smaller than the nuclear temperature.
2. Electron temperature should not increase.
3. The total energy should remain stationary.

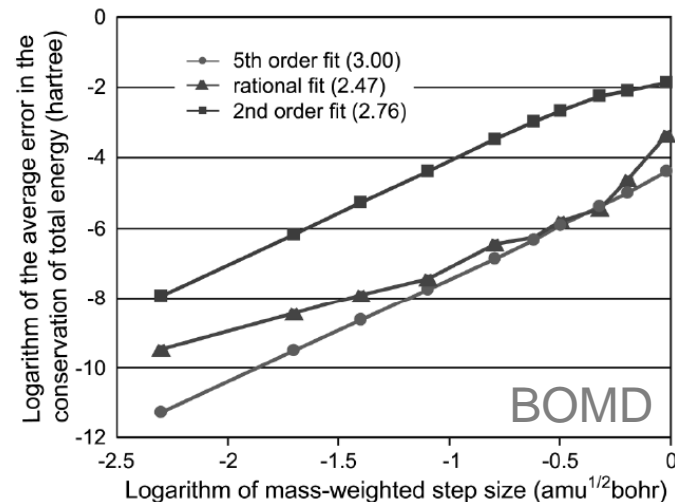


Figure 3. Comparison of the error in the conservation of energy versus step size for trajectories integrated with the second order Hessian-based method (squares) and the Hessian-based predictor-corrector method with a fifth order polynomial (circles) or a rational function (triangles) for the corrector step (slopes of the least squares fits in parenthesis).

# Car-Parrinello molecular dynamics

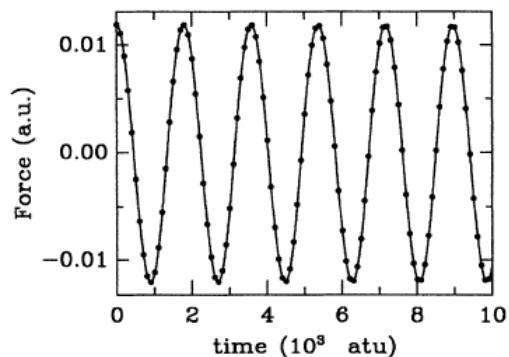


FIG. 7. Component  $z$  of the force on one silicon atom of the system of Fig. 1 as a function of time. Solid line: force from CP dynamics ( $F_{CP}$ ). Dots: force from a well-converged electronic minimization performed at each ionic step ( $F_{BO}$ ). Not all the data for  $F_{BO}$  were plotted.

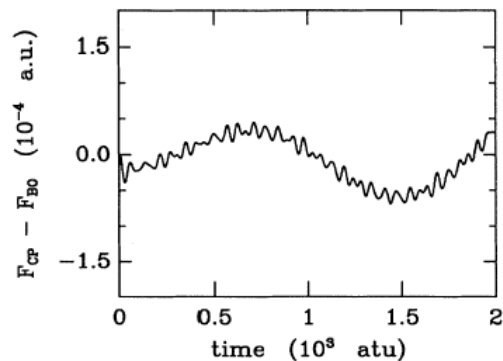


FIG. 8. Difference between  $F_{CP}$  and  $F_{BO}$  from Fig. 7 on an enlarged scale.

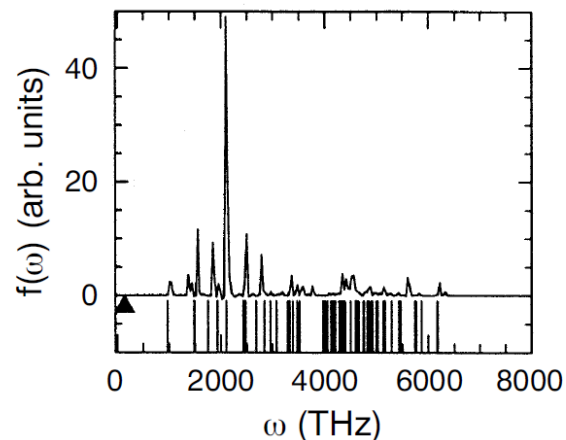


Figure 2. Vibrational density of states Eq. (47) (continuous spectrum in upper part) and harmonic approximation thereof Eq. (52) (stick spectrum in lower part) of the electronic degrees of freedom compared to the highest-frequency phonon mode  $\omega_n^{\max}$  (triangle) for a model system; for further details see text. Adapted from Ref. 467.

Table 1. Timings in CPU seconds and energy conservation in a.u. / ps for Car-Parrinello (CP) and Born-Oppenheimer (BO) molecular dynamics simulations of a model system for 1 ps of trajectory

Method	Time step (a.u.)	Convergence (a.u.)	Conservation (a.u./ps)	Time (s)
CP	5	—	$6 \times 10^{-8}$	3230
CP	7	—	$1 \times 10^{-7}$	2310
CP	10	—	$3 \times 10^{-7}$	1610
BO	10	$10^{-6}$	$1 \times 10^{-6}$	16590
BO	50	$10^{-6}$	$1 \times 10^{-6}$	4130
BO	100	$10^{-6}$	$6 \times 10^{-6}$	2250
BO	100	$10^{-5}$	$1 \times 10^{-5}$	1660
BO	100	$10^{-4}$	$1 \times 10^{-3}$	1060

CPMD has the advantage of accurate gradients.