

# Ab initio molecular dynamics: Basic Theory and Advanced Methods

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## Unifying molecular dynamics and electronic structure

Route 1

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# Unifying molecular dynamics and electronic structure

**Starting point:** the non-relativistic Schrödinger equation for electron and nuclei.

$$i\hbar \frac{\partial}{\partial t} \Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_i\}; t) = H\Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_i\}; t) \quad (1)$$

where  $H$  is the standard Hamiltonian:

$$H = -\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 \quad (2)$$

$$+ \frac{1}{4\pi\epsilon_0} \sum_{i < j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \frac{1}{4\pi\epsilon_0} \sum_{I,i} \frac{e^2 Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} + \frac{1}{4\pi\epsilon_0} \sum_{I < J} \frac{e^2 Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \quad (3)$$

$$= -\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + V_{n-e}(\{\mathbf{r}_i\}, \{\mathbf{R}_i\}) \quad (4)$$

$$= -\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + H_e(\{\mathbf{r}_i\}, \{\mathbf{R}_i\}) \quad (5)$$

► **Route 1:**

- 1) The electronic problem is solved in the *time-independent* Schrödinger eq.
- 2) from here the **adiabatic approximation** for the nuclei is derived, and as a special case the **Born-Oppenheimer dynamics**.
- 3) The classical limit leads then to the **classical molecular dynamics** for the nuclei.

Goal: derive the classical molecular dynamics. As intermediate two variant of *ab initio* molecular dynamics are derived.

- Solve the electronic part for fixed nuclei

$$H_e(\{\mathbf{r}_i\}, \{\mathbf{R}_i\})\Psi_k = E_k(\{\mathbf{R}_i\})\Psi_k(\{\mathbf{r}_i\}, \{\mathbf{R}_i\}) \quad (6)$$

where  $\Psi_k(\{\mathbf{r}_i\}, \{\mathbf{R}_i\})$  are a set of orthonormal solutions, satisfying:

$$\int \Psi_k^*(\{\mathbf{r}_i\}, \{\mathbf{R}_i\})\Psi_l(\{\mathbf{r}_i\}, \{\mathbf{R}_i\})d\mathbf{r} = \delta_{kl} \quad (7)$$

Knowing the *adiabatic solutions* to the electronic problem, the total wavefunction can be expanded as:

$$\Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_i\}, t) = \sum_{l=0}^{\infty} \Psi_l(\{\mathbf{r}_i\}, \{\mathbf{R}_i\})\chi_l(\{\mathbf{R}_i\}, t) \quad (8)$$

Eq.8 is the *ansatz* introduced by Born in 1951.

Inserting (8) into Eq.(1) we obtain:

$$\left[ -\sum_l \frac{\hbar^2}{2M_l} \nabla_l^2 + E_k(\{\mathbf{R}_i\}) \right] \chi_k + \sum_l C_{kl} \chi_l = i\hbar \frac{\partial}{\partial t} \chi_k \quad (9)$$

where:

$$C_{kl} = \int \Psi_k^* \left[ -\sum_l \frac{\hbar^2}{2M_l} \nabla_l^2 \right] \Psi_l d\mathbf{r} + \quad (10)$$

$$+ \frac{1}{M_l} \sum_l \left\{ \int \Psi_k^* [-i\hbar \nabla_l] \Psi_l d\mathbf{r} \right\} [-i\hbar \nabla_l] \quad (11)$$

is the exact non-adiabatic coupling operator.

- ▶ The adiabatic approximation to the full problem Eq.9 is obtained considering only the diagonal terms:

$$C_{kk} = -\sum_l \frac{\hbar^2}{2M_l} \int \Psi_k^* \nabla_l^2 \Psi_k d\mathbf{r} \quad (12)$$

$$\left[ -\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + E_k(\{\mathbf{R}_i\}) + C_{kk}(\{\mathbf{R}_i\}) \right] \chi_k = i\hbar \frac{\partial}{\partial t} \chi_k \quad (13)$$

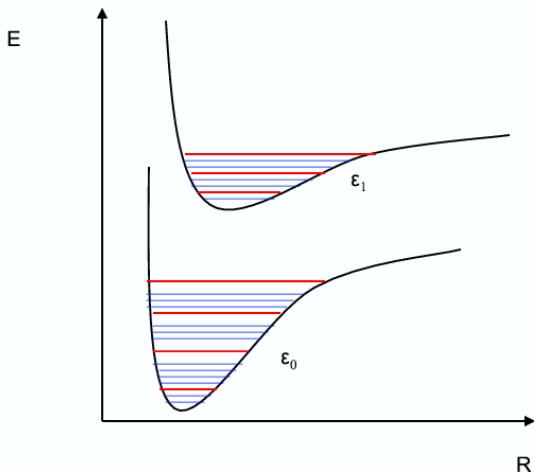
The motion of the nuclei proceed without changing the quantum state,  $k$ , of the electronic subsystem during the evolution. The coupled wavefunction can be simplified as:

$$\Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_i\}, t) \approx \Psi_k(\{\mathbf{r}_i\}, \{\mathbf{R}_i\}) \chi_k(\{\mathbf{R}_i\}, t) \quad (14)$$

the ultimate simplification consist in neglecting also the correction term  $C_{kk}(\{\mathbf{R}_i\})$ , so that

$$\left[ -\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + E_k(\{\mathbf{R}_i\}) \right] \chi_k = i\hbar \frac{\partial}{\partial t} \chi_k \quad (15)$$

This is the **Born-Oppenheimer approximation**.



On each Born-Oppenheimer surface, the nuclear eigenvalue problem can be solved, which yields a set of levels (rotational and vibrational in the nuclear motion) as illustrated in the figure.



The next step is to derive the classical molecular dynamics for the nuclei.  
 The route we take is the following:

$$\chi_k(\{\mathbf{R}_i\}, t) = A_k(\{\mathbf{R}_i\}, t) \exp[iS_k(\{\mathbf{R}_i\}, t)/\hbar] \quad (16)$$

the amplitude  $A_k$  and the phase  $S_k$  are both real and  $A_k > 0$ . Next we substitute the expression for  $\chi_k$  into eq. 15.

$$\left[ -\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + E_k(\{\mathbf{R}_i\}) \right] A_k(\{\mathbf{R}_i\}, t) \exp[iS_k(\{\mathbf{R}_i\}, t)/\hbar] = \quad (17)$$

$$i\hbar \frac{\partial}{\partial t} (A_k(\{\mathbf{R}_i\}, t) \exp[iS_k(\{\mathbf{R}_i\}, t)/\hbar]) \quad (18)$$

$$-\sum_I \frac{\hbar^2}{2M_I} \nabla_I (\nabla_I (A_k \exp[iS_k/\hbar])) + E_k A_k \exp[iS_k/\hbar] = \quad (19)$$

$$i\hbar \frac{\partial A_k}{\partial t} \exp[iS_k/\hbar] + i\hbar \frac{i}{\hbar} \frac{\partial S_k}{\partial t} A_k \exp[iS_k/\hbar] \quad (20)$$

$$-\sum_I \frac{\hbar^2}{2M_I} \nabla_I \left( \nabla_I A_k \exp[iS_k/\hbar] + A_k \frac{i}{\hbar} \nabla S_k \exp[iS_k/\hbar] \right) + E_k A_k \exp[iS_k/\hbar] = \quad (21)$$

$$i\hbar \frac{\partial A_k}{\partial t} \exp[iS_k/\hbar] - \frac{\partial S_k}{\partial t} A_k \exp[iS_k/\hbar] \quad (22)$$

$$-\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 A_k - \sum_I \frac{\hbar^2}{2M_I} \nabla_I A_k \frac{i}{\hbar} \nabla_I S_k - \sum_I \frac{\hbar^2}{2M_I} \nabla_I A_k \frac{i}{\hbar} \nabla_I S_k \quad (23)$$

$$-\sum_I \frac{\hbar^2}{2M_I} A_k \left(\frac{i}{\hbar}\right)^2 (\nabla S_k)^2 - \sum_I \frac{\hbar^2}{2M_I} A_k \frac{i}{\hbar} \nabla^2 S_k + E_k A_k = \quad (24)$$

$$i\hbar \frac{\partial A_k}{\partial t} - \frac{\partial S_k}{\partial t} A_k \quad (25)$$

Separating the real and the imaginary parts, we obtain:

$$\frac{\partial S_k}{\partial t} + \sum_I \frac{1}{2M_I} (\nabla S_k)^2 + E_k = - \sum_I \frac{\hbar^2}{2M_I} \frac{\nabla_I^2 A_k}{A_k} \quad (26)$$

$$\frac{\partial A_k}{\partial t} + \sum_I \frac{1}{M_I} \nabla_I A_k \nabla_I S_k + \sum_I \frac{1}{2M_I} A_k \nabla^2 S_k = 0 \quad (27)$$

If we consider the equation for the phase:

$$\frac{\partial S_k}{\partial t} + \sum_I \frac{1}{2M_I} (\nabla S_k)^2 + E_k = - \sum_I \frac{\hbar^2}{2M_I} \frac{\nabla_I^2 A_k}{A_k} \quad (28)$$

it is possible to take the classical limit  $\hbar \rightarrow 0$  which gives the equation:

$$\frac{\partial S_k}{\partial t} + \sum_I \frac{1}{2M_I} (\nabla S_k)^2 + E_k = 0 \quad (29)$$

which is isomorphic to Hamilton-Jacobi of classical mechanics:

$$\frac{\partial S_k}{\partial t} + H_k(\{\mathbf{R}_I\}, \{\nabla_I S_k\}) = 0 \quad (30)$$

with the classical Hamiltonian function

$$H_k(\{\mathbf{R}_I\}, \{\mathbf{P}_I\}) = T(\{\mathbf{P}_I\}) + V_k(\{\mathbf{R}_I\}) \quad (31)$$

With the connecting transformation:  $\mathbf{P}_I = \nabla_I S_k$ .

► **Route 2:**

- 1) Maintain the **quantum-mechanical time evolution for the electrons** introducing the separation for the electronic and nuclear wf function in a time-dependent way
- 2) **Time-dependent self consistent field (TDSCF)** approach is obtained.
- 3) **Ehrenfest dynamics** (and as special case Born-Oppenheimer dynamics)
- 4) The classical limit leads then to the **classical molecular dynamics** for the nuclei.

It is possible to follow an alternative route in order to maintain the dynamics of the electron.

$$\Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t) \approx \Psi(\{\mathbf{r}_i\}, t) \chi(\{\mathbf{R}_I\}, t) \exp\left[\frac{i}{\hbar} \int_{t_0}^t \tilde{E}_e(t') dt'\right] \quad (32)$$

where:

$$\tilde{E}_e = \int \Psi^*(\{\mathbf{r}_i\}, t) \chi^*(\{\mathbf{R}_I\}, t) H_e \Psi(\{\mathbf{r}_i\}, t) \chi(\{\mathbf{R}_I\}, t) d\mathbf{r} d\mathbf{R} \quad (33)$$

Inserting this separation ansatz (single determinant ansatz) into  $i\hbar \frac{\partial}{\partial t} \Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}; t) = H \Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}; t)$  and multiplying from the left by  $\Psi^*$  and by  $\chi^*$  we obtain

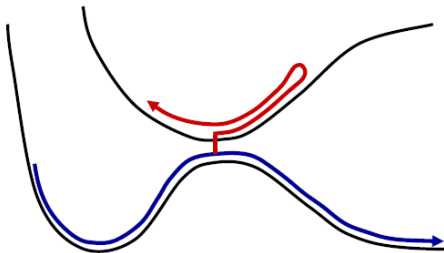
$$i\hbar \frac{\partial \Psi}{\partial t} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 \Psi \quad (34)$$

$$+ \left\{ \int \chi^*(\{\mathbf{R}_I\}, t) V_{ne}(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \chi(\{\mathbf{R}_I\}, t) d\mathbf{R} \right\} \Psi \quad (35)$$

$$i\hbar \frac{\partial \chi}{\partial t} = - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 \chi \quad (36)$$

$$+ \left\{ \int \Psi^*(\{\mathbf{r}_i\}, t) H_e(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \Psi(\{\mathbf{r}_i\}, t) d\mathbf{r} \right\} \chi \quad (37)$$

This set of time-dependent Schrödinger equations define the basis of **time-dependent self-consistent field (TDSCF)** method. Both electrons and nuclei moves quantum-mechanically in time-dependent effective potentials.



- Classical motion induces electronic transitions
- Quantum state determines classical forces

→ Quantum – Classical Feedback: Self-Consistency

Using the same trick as before of writing

$$\chi_k(\{\mathbf{R}_i\}, t) = A_k(\{\mathbf{R}_i\}, t) \exp[iS_k(\{\mathbf{R}_i\}, t)/\hbar] \quad (38)$$

we obtain

$$\frac{\partial S_k}{\partial t} + \sum_I \frac{1}{2M_I} (\nabla S_k)^2 + \int \Psi^* H_e \Psi d\mathbf{r} = - \sum_I \frac{\hbar^2}{2M_I} \frac{\nabla_I^2 A_k}{A_k} \quad (39)$$

$$\frac{\partial A_k}{\partial t} + \sum_I \frac{1}{M_I} \nabla_I A_k \nabla_I S_k + \sum_I \frac{1}{2M_I} A_k \nabla^2 S_k = 0 \quad (40)$$

And in the classical limit  $\hbar \rightarrow 0$

$$\frac{\partial S_k}{\partial t} + \sum_I \frac{1}{2M_I} (\nabla S_k)^2 + \int \Psi^* H_e \Psi d\mathbf{r} = 0. \quad (41)$$



The Newtonian equation of motion of the classical nuclei are:

$$\frac{dP_I}{dt} = \nabla_I \int \Psi^* H_e \Psi d\mathbf{r} \quad (42)$$

or

$$M_I \ddot{R}_I(t) = -\nabla_I V_e^E(\{R_I(t)\}) \quad (43)$$

here the nuclei move according to classical mechanics in an effective potential  $V_e^E(\{R_I(t)\})$ , often called the Eherenfest potential.

- ▶ The nuclei move according to *classical* mechanics in an effective potential (Ehrenfest potential) given by the quantum dynamics of the electrons obtained by solving the time-dependent Schrödinger equation for the electrons.

$$i\hbar \frac{\partial \Psi}{\partial t} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 \Psi + \left\{ \int \chi^* (\{\mathbf{R}_I\}, t) V_{ne} (\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \chi (\{\mathbf{R}_I\}, t) d\mathbf{R} \right\} \Psi \quad (44)$$

Note: the equation (41) still contains the full quantum-mechanics nuclear wavefunction  $\chi(\{\mathbf{R}_I\}, t)$ . The classical reduction is obtained by:

$$\int \chi^* (\{\mathbf{R}_I\}, t) \mathbf{R}_I \chi (\{\mathbf{R}_I\}, t) d\mathbf{R} \rightarrow \mathbf{R}_I(t) \quad (45)$$

for  $\hbar \rightarrow 0$ .

The classical limits leads to a time-dependent wave equation for the electrons

$$i\hbar \frac{\partial \Psi}{\partial t} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 \Psi + V_{ne}(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \Psi \quad (46)$$

$$i\hbar \frac{\partial \Psi}{\partial t} = H_e(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \quad (47)$$

- ▶ Feedback between the classical and quantum degrees of freedom is incorporated in both direction, even though in a mean field sense.
- ▶ These equations are called Ehrenfest dynamics in honor to Paul Ehrenfest who was the first to address the problem of how Newtonian classical dynamics of point particles can be derived from Schrödinger time-dependent wave equation.

## Difference between Ehrenfest dynamics and Born-Oppenheimer molecular dynamics:

- ▶ In ED the electronic subsystem evolves explicitly in time, according to a time-dependent Schrödinger equation
- ▶ In ED transition between electronic states are possible. This can be showed expressing the electronic wavefunction in a basis of electronic states

$$\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t) = \sum_{I=0}^{\infty} c_I(t) \Psi_I(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t) \quad (48)$$

where

$$\sum_{I=0}^{\infty} |c_I(t)|^2 = 1 \quad (49)$$

and one possible choice for the basis functions  $\{\Psi_k\}$  is obtained solving the time-independent Schrödinger equation:

$$H_e(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \Psi_k(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) = E_k(\{\mathbf{R}_I\}) \Psi_k(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}). \quad (50)$$

The Ehrenfest dynamics reduces to the Born-Oppenheimer molecular dynamics if only one term is considered in the sum:

$$\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t) = \sum_{I=0}^{\infty} c_I(t) \Psi_I(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t)$$

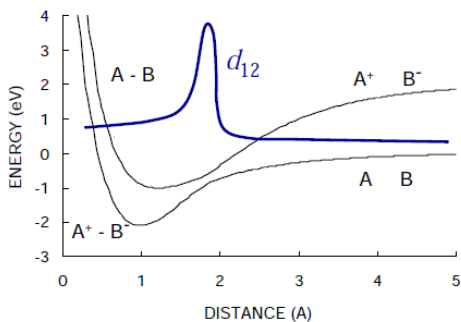
namely:

$$\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t) = \Psi_0 \text{ground state adiabatic wavefunction} \quad (51)$$

This should be a good approximation if the energy difference between  $\Psi_0$  and the first excited state  $\Psi_1$  is large everywhere compared to the thermal energy scale  $K_B T$ .

In this approximation the nuclei move on a single adiabatic potential energy surface,  $E_0(\{\mathbf{R}_I\})$ .

## Ionic Molecule (alkali halide)



Nonadiabatic Coupling: 
$$d_{12} = \langle \varphi_1 | \partial \varphi_2 / \partial X \rangle$$

# Classical trajectory calculations on global potential energy surfaces

In BO one can think to fully decouple the task of generating classical nuclear dynamics from the task of computing the quantum potential energy surface.

- ▶  $E_0$  is computed for many different  $\{\mathbf{R}_I\}$
- ▶ data points fitted to analytical function
- ▶ Newton equation of motion solved on the computed surfaces for different initial conditions

Problem: **dimensionality bottleneck**. It has been used for scattering and chemical reactions of small systems in vacuum, but is not doable when nuclear degrees of freedom increase.

## Force Field - based molecular dynamics

One possible solution to the dimensionality bottleneck is the force field based MD.

$$V_e^E \approx V_e^{FF} = \sum_{I=1}^N v_1(\mathbf{R}_I) + \sum_{I<J}^N v_2(\mathbf{R}_I, \mathbf{R}_J) + \quad (52)$$

$$\sum_{I<J<K}^N v_3(\mathbf{R}_I, \mathbf{R}_J, \mathbf{R}_K) + \dots \quad (53)$$

The equation of motion for the nuclei are:

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I V_e^{FF}(\{\mathbf{R}_I(t)\}). \quad (54)$$

The electrons follow adiabatically the classical nuclear motion and can be integrated out. The nuclei evolve on a single BO potential energy surface, approximated by a few body interactions.



# Ehrenfest molecular dynamics

To avoid the dimensionality bottleneck the coupled equations:

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \langle H_e \rangle \quad (55)$$

$$i\hbar \frac{\partial \Psi}{\partial t} = \left[ -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + V_{ne}(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \chi(\{\mathbf{R}_I\}, t) \right] \Psi \quad (56)$$

can be solved simultaneously.

The time-dependent Schrödinger equation is solved *on the fly* as the nuclei are propagated using classical mechanics.

Using

$$\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t) = \sum_{I=0}^{\infty} c_I(t) \Psi_I(\{\mathbf{r}_i\}, \{\mathbf{R}_I\})$$

the Ehrenfest equations reads:

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \sum_k |c_k(t)|^2 E_k \quad (57)$$

$$= -\sum_k |c_k(t)|^2 \nabla_I E_k + \sum_{k,l} c_k^* c_l (E_k - E_l) \mathbf{d}_I^{kl} \quad (58)$$

$$i\hbar \dot{c}_k(t) = c_k(t) E_k - i\hbar \sum_l c_l(t) D^{kl} \quad (59)$$

where the non-adiabatic coupling elements are given by

$$D^{kl} = \int \Psi_k^* \frac{\partial}{\partial t} \Psi_l d\mathbf{r} = \sum_I \dot{\mathbf{R}}_I \int \Psi_k^* \nabla_I \Psi_l = \sum_I \dot{\mathbf{R}}_I \mathbf{d}^{kl}. \quad (60)$$

# Car-Parrinello molecular dynamics



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## Description

Roberto Car with Michele Parrinello, during the Stig Lundqvist Research Conference on the Advancing Frontiers in Condensed Matter Physics, Adriatico Guest House, July 2001

- ▶ Combine the advantages of Ehrenfest and BO dynamics
- ▶ Integrate the equation of motion on a longer time-step than in Ehrenfest, but at the same time
- ▶ take advantage of the smooth time evolution of the dynamically evolving electronic subsystem

## Unified Approach for Molecular Dynamics and Density-Functional Theory

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(Received 5 August 1985)

We present a unified scheme that, by combining molecular dynamics and density-functional theory, profoundly extends the range of both concepts. Our approach extends molecular dynamics beyond the usual pair-potential approximation, thereby making possible the simulation of both covalently bonded and metallic systems. In addition it permits the application of density-functional theory to much larger systems than previously feasible. The new technique is demonstrated by the calculation of some static and dynamic properties of crystalline silicon within a self-consistent pseudopotential framework.

Car-Parrinello method just turned 25!

## Car-Parrinello Lagrangian and equations of motion

CP dynamics is based on the adiabatic separation between fast electronic (quantum) and slow (classical) nuclear motion. They introduced the following Lagrangian

$$\mathcal{L}_{CP} = \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \sum_i \mu \langle \dot{\phi}_i | \dot{\phi}_i \rangle - \langle \Psi_0 | H_e | \Psi_0 \rangle + \text{constraints} \quad (61)$$

where  $\Psi_0 = 1/\sqrt{N!} \det\{\phi_i\}$   
and  $\mu$  is the fictitious mass of the electrons.

the associated Euler-Lagrange equations are:

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{R}}_I} = \frac{\partial \mathcal{L}}{\partial \mathbf{R}_I} \quad (62)$$

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{\phi}_i^*} = \frac{\partial \mathcal{L}}{\partial \phi_i^*} \quad (63)$$

from which the Car-Parrinello equations of motion:

$$M_I \ddot{\mathbf{R}}_I(t) = -\frac{\partial}{\partial \mathbf{R}_I} \langle \Psi_0 | H_e | \Psi_0 \rangle + \frac{\partial}{\partial \mathbf{R}_I} \{constraints\} \quad (64)$$

$$\mu \ddot{\phi}_i(t) = -\frac{\delta}{\delta \phi_i^*} \langle \Psi_0 | H_e | \Psi_0 \rangle + \frac{\delta}{\delta \phi_i^*} \{constraints\} \quad (65)$$

For the specific case of the Kohn-Sham Theory the CP Lagrangian is:

$$\mathcal{L}_{CP} = \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \sum_i \mu \langle \dot{\phi}_i | \dot{\phi}_i \rangle - \langle \Psi_0 | H_e^{KS} | \Psi_0 \rangle + \sum_{i,j} \Lambda_{ij} (\langle \phi_i | \phi_j \rangle - \delta_{ij}) \quad (66)$$

and the Car-Parrinello equations of motion:

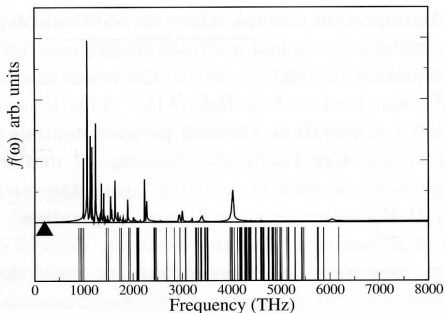
$$M_I \ddot{\mathbf{R}}_I(t) = - \frac{\partial}{\partial \mathbf{R}_I} \langle \Psi_0 | H_e^{KS} | \Psi_0 \rangle \quad (67)$$

$$\mu \ddot{\phi}_i(t) = - H_e^{KS} \phi_i + \sum_j \Lambda_{ij} \phi_j \quad (68)$$

The nuclei evolve in time with temperature  $\propto \sum_I M_I \dot{\mathbf{R}}_I^2$ ;  
 the electrons have a fictitious temperature  $\propto \sum_i \mu \langle \dot{\phi}_i | \dot{\phi}_i \rangle$ .

## Why does the CP method work?

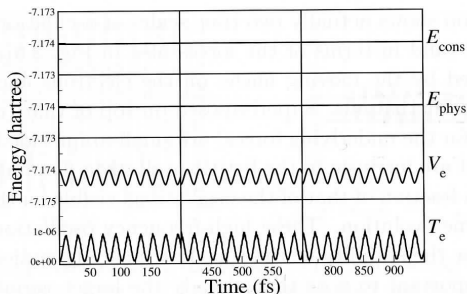
- ▶ Separate in practice nuclear and ionic motion so that
- ▶ electrons keep cold, remaining close to  $\min_{\{\phi_i\}} \langle \Psi_0 | H_e | \Psi_0 \rangle$ , namely close to the Born-Oppenheimer surface



$$f(\omega) = \int_0^\infty \cos(\omega t) \sum_i \langle \dot{\phi}_i; t | \dot{\phi}_i; 0 \rangle dt \quad (69)$$



# Energy Conservation



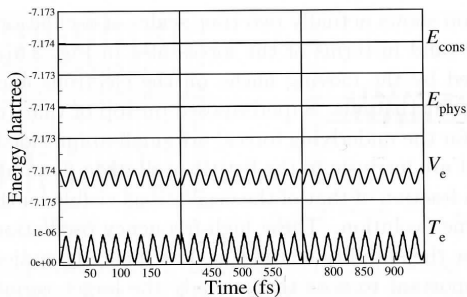
$$E_{cons} = \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \sum_i \mu \langle \dot{\phi}_i | \dot{\phi}_i \rangle + \langle \Psi_0 | H_e^{KS} | \Psi_0 \rangle \quad (70)$$

$$E_{phys} = \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \langle \Psi_0 | H_e^{KS} | \Psi_0 \rangle = E_{cons} - T_e \quad (71)$$

$$V_e = \langle \Psi_0 | H_e^{KS} | \Psi_0 \rangle \quad (72)$$

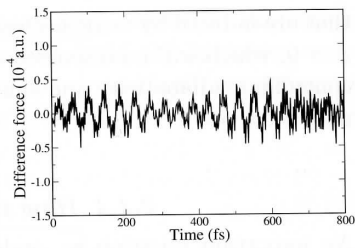
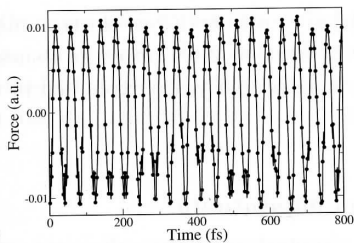
$$T_e = \sum \mu \langle \dot{\phi}_i | \dot{\phi}_i \rangle \quad (73)$$

# Energy Conservation



- ▶ Electrons do not heat-up, but fluctuate with same frequency as  $V_e$
- ▶ Nuclei drag the electrons
- ▶  $E_{\text{phys}}$  is essentially constant

## Deviation from Born-Oppenheimer surface



Deviation of forces in CP dynamics from the true BO forces small and/but oscillating.

# How to control of adiabaticity?

In a simple harmonic analysis of the frequency spectrum yields

$$\omega_{ij} = \sqrt{\frac{2(\epsilon_i - \epsilon_j)}{\mu}} \quad (74)$$

where  $\epsilon_i$  and  $\epsilon_j$  are the eigenvalues of the occupied/unoccupied orbitals of the Kohn-Sham Hamiltonian. The lowest possible electronic frequency is:

$$\omega_e^{min} \propto \sqrt{\frac{E_{gap}}{\mu}}. \quad (75)$$

The highest frequency

$$\omega_e^{max} \propto \sqrt{\frac{E_{cut}}{\mu}}. \quad (76)$$

Thus maximum possible time step

$$\Delta t^{max} \propto \sqrt{\frac{\mu}{E_{cut}}}. \quad (77)$$

In order to guarantee adiabatic separation between electrons and nuclei we should have

- ▶ large  $\omega_e^{min} - \omega_n^{max}$ .

$\omega_n^{max}$  and  $E_{gap}$  depend on the physical system, so **the parameter to control adiabaticity is the mass  $\mu$** .

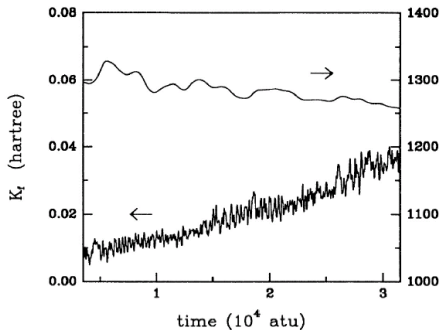
However the mass cannot be reduced arbitrarily otherwise the timestep becomes too small.

Alternatively if  $\Delta t$  is fixed and  $\mu$  is chosen

- ▶  $\mu$  too small: Electrons too light and adiabaticity will be lost
- ▶  $\mu$  too large: Time step eventually large and electronic degrees of freedom evolve too fast for the Verlet algorithm

# Loss of adiabaticity: the bad cases

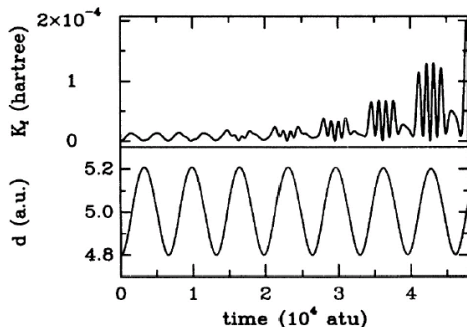
- Vacancy in hot 64-atom Si cell



Due to the presence of the vacancy there is a small gap in the system.

## Loss of adiabaticity: the bad cases

- $\text{Sn}_2$ : Degeneracy of HOMO and LUMO at short distances



In this system the gap is periodically opened (up to 0.3 eV) and nearly closed at short distances. The electrons gain kinetic energy in phase with the ionic oscillations.

## Zero or small electronic gaps: thermostatted electrons

- ▶ One way to (try to) overcome the problem in coupling of electronic and ionic dynamics is to thermostat also the electrons (Blöchl & Parrinello, PRB 1992)
- ▶ Thus electrons cannot heat up; if they try to, thermostat will adsorb the excess heat
- ▶ Target fictitious kinetic energy  $E_{kin,0}$  instead of temperature
- ▶ Mass of thermostat to be selected appropriately:
  - Too light: Adiabacity violated (electrons may heat up)
  - Too heavy: Ions dragged excessively
- ▶ Note: Introducing the thermostat the conserved quantity changes



$$M_I \ddot{\mathbf{R}}_I(t) = -\frac{\partial}{\partial \mathbf{R}_I} \langle \Psi_0 | H_e^{KS} | \Psi_0 \rangle - M_I \dot{\mathbf{R}}_I \dot{\mathbf{X}}_R \quad (78)$$

$$\mu \ddot{\phi}_i(t) = -H_e^{KS} \phi_i + \sum_j \Lambda_{ij} \phi_j - \mu \dot{\phi}_i \dot{\mathbf{X}}_e \quad (79)$$

in blue are the frictionous terms governed by the following equations:

$$Q_e \ddot{\mathbf{X}}_e = 2 \left[ \sum_i \mu \dot{\phi}_i^2 - E_{kin,0} \right] \quad (80)$$

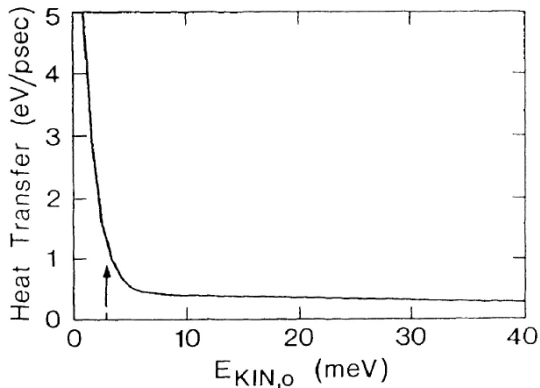
$$Q_R \ddot{\mathbf{X}}_R = 2 \left[ \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}^2 - \frac{1}{2} g K_B T \right] \quad (81)$$

The masses  $Q_e$  and  $Q_R$  determines the time scale for the thermal fluctuations. The conserved quantity is now:

$$E_{tot} = \sum_I \frac{1}{2} M_I \dot{\mathbf{R}}_I^2 + \sum_i \mu \langle \dot{\phi}_i | \dot{\phi}_i \rangle + \langle \Psi_0 | H_e^{KS} | \Psi_0 \rangle + \frac{1}{2} Q_e \dot{\mathbf{X}}_e^2 + 2E_{kin,0} \mathbf{X}_e + \frac{1}{2} Q_R \dot{\mathbf{X}}_R^2 + g K_B T \mathbf{X}_R \quad (82)$$

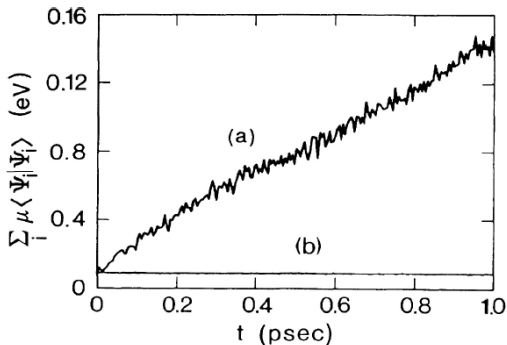
## Thermostat on the electrons: examples

- Example: Aluminium
- Dependence of the heat transfer on the choice of  $E_{\text{kin},0}$  in solid Al



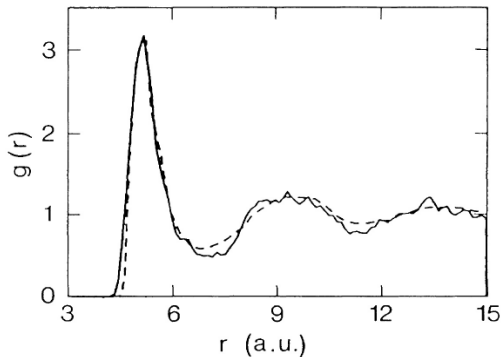
# Thermostat on the electrons: examples

- 64 atoms of molten aluminium
- (a): Without thermostat
- (b): With thermostat



## Thermostat on the electrons: examples

- Check: Radial pair correlation function
  - Solid line: CP-MD with thermostat
  - Dashed line: Calculations by Jacucci *et al*



## Analytic and numerical error estimates

- ▶ The CP forces necessarily deviate from the BO
- ▶ The primary effect of  $\mu$  makes the ions "heavier"
- ▶ No effect on the thermodynamical and structural properties, but affect the dynamical quantities in a *systematic* way (vibrational spectra)

$$\phi_i(t) = \phi_i^0(t) + \delta\phi_i(t) \quad (83)$$

Inserting this expression into the CP equations of motions:

$$\mathbf{F}_{I,\alpha}^{CP}(t) = \mathbf{F}_{I,\alpha}^{BO}(t) + \sum_i \mu \left\{ \langle \ddot{\phi}_i | \frac{\partial |\phi_i^0\rangle}{\partial \mathbf{R}_{I,\alpha}} \frac{\partial \langle \phi_i^0|}{\partial \mathbf{R}_{I,\alpha}} | \ddot{\phi}_i \rangle \right\} + \mathcal{O}(\delta\phi_i^2) \quad (84)$$

the additional force is linear in the mass  $\mu$  so that it vanishes properly as  $\mu \rightarrow 0$ .

The new equations of motion:

$$(M_I + \Delta_\mu M_I) \ddot{R}_I = F_I \quad (85)$$

where, in the isolated atom approximation,

$$\Delta_\mu M_I = \frac{2}{3} \mu E_{kin}^I = \frac{2}{3} \frac{m_e}{\hbar^2} \sum_j \langle \phi_j^I | -\frac{\hbar^2}{2m_e} \nabla_j^2 | \phi_j^I \rangle > > 0 \quad (86)$$

is an unphysical mass, or drag, due to the fictitious kinetics of the electrons

- ▶ for a system where electrons are strongly localized close to the nuclei there more pronounced renormalization effect

## Example: Vibrations in water molecule

mode	harmonic	BOMD	50	100	200	400	dM/M [%]
bend	1548	1543	1539	1535	1529	1514	$0.95 \times 10^{-3} \mu$
sym.	3515	3508	3494	3478	3449	3388	$1.81 \times 10^{-3} \mu$
asym.	3621	3616	3600	3585	3556	3498	$1.71 \times 10^{-3} \mu$

To correct for finite- $\mu$  effects:

- ▶ Perform simulation for different  $\mu$ -values and extrapolate for  $\mu \rightarrow 0$ .
- ▶ use mass renormalization according to:

$$\omega_{BO} = \omega_{CP} \sqrt{1 + \frac{\Delta_{\mu} M}{M}} \quad (87)$$

## Car-Parrinello vs Born-Oppenheimer dynamics

### Born-Oppenheimer MD

Exactly on BO surface

$\Delta t \approx$  ionic time scales,  
maximum time step possible

Expensive minimisation  
at each MD step

Not stable against deviations  
from BO surface  
 $\Rightarrow$  Energy/temperature drift,  
thermostatting of ions necessary

Same machinery in zero-gap systems

Most applications in solids

### Car-Parrinello MD

Always slightly off BO surface

$\Delta t \ll$  ionic time scales,  
(much) shorter time step necessary

Orthogonalisation only,  
less expensive per MD step

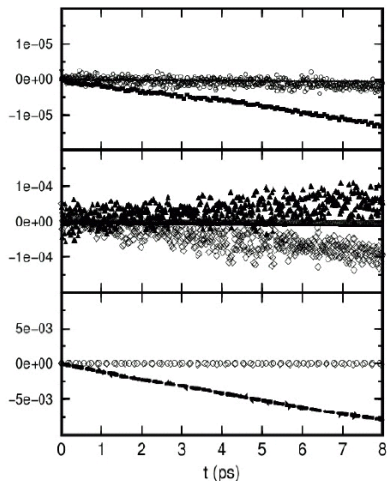
Stable against deviations  
from BO surface

Thermostatting of electrons  
to prevent energy exchange

Superior for liquids



## CP vs BO: energy conservation

 $\Delta t$ , convergence*Top:*

solid line : CP, 5 a.u.;  
 open circ. : CP, 10 a.u.;  
 filled squar. : BO, 10 a.u.,  $10^{-6}$ .

*Middle:*

open circ. : CP, 10 a.u.;  
 filled squar. : BO, 10 a.u.,  $10^{-6}$ ;  
 filled trian. : BO, 100 a.u.,  $10^{-6}$ ;  
 open diam. : BO, 100 a.u.,  $10^{-5}$ .

*Bottom:*

open circ. : CP, 10 a.u.;  
 open diam. : BO, 100 a.u.,  $10^{-5}$ ;  
 dashed line : BO, 100 a.u.,  $10^{-4}$

## CP vs BO: timing

### STABILITY OF BO AND CP MD COMPARED

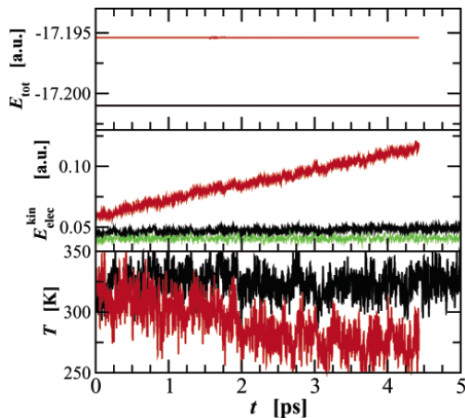
CPMD results for the **8 Si atom model system**

Timings in cpu seconds and energy conservation in a.u. / ps for CP and BO Molecular dynamics simulations for 1 ps of trajectory on an IBM RS6000 / model 390 (Power2) workstation

Method	Time step	Convergence	Conservation (au/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

Timing in CPU seconds and energy conservation in a.u./ps for

## CP of liquid water: Energy conservation



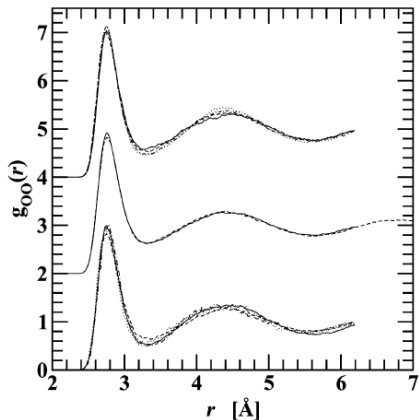
CPMD-800-NVE-64

CPMD-400-NVE-128

CPMD-800-NVT-64

J. Phys. Chem. B 2004, 108, 12990.

## CP of liquid water: structure



### Oxygen-oxygen radial distribution

BOMD-NVE (solid line)

CPMD-NVE

CPMD-NVE-400-64

CPMD-NVE-400-128

CPMD-NVT-400

CPMD-NVT-800

CP2K-MC-NVT

The radial distribution functions are correct and independent of the method used.

J. Phys. Chem. B 2004, 108, 12990.

## Car-Parrinello method: Summary

- ▶ Molecular dynamics can be used to perform real-time dynamics in atomistic systems
- ▶ Verlet algorithm yields stable dynamics (in CPMD implemented algorithm velocity Verlet)
- ▶ Born-Oppenheimer dynamics: Max time step 1 fs (highest ionic frequency  $2000-3000 \text{ cm}^{-1}$ )  
Car-Parrinello dynamics: Max time step 0.1 fs
- ▶ Car-Parrinello method can yield very stable dynamical trajectories, provided the electrons and ions are adiabatically decoupled
- ▶ The method is best suited for e. g. liquids and large molecules with a wide electronic gap
- ▶ The speed of the method is comparable or faster than using Born-Oppenheimer dynamics and still more accurate (i. e. stable)
- ▶ One has to be careful with the choice of  $\mu!$

# Forces calculation

Efficient calculation of the forces

One possibility is the numerical evaluation of :

$$\mathbf{F}_I = -\nabla \langle \Psi_0 | H_e | \Psi_0 \rangle \quad (88)$$

which can be costly and not so accurate. So analytical derivative is desirable:

$$\nabla_I \langle \Psi_0 | H_e | \Psi_0 \rangle = \quad (89)$$

$$\langle \Psi_0 | \nabla_I | H_e | \Psi_0 \rangle + \langle \nabla_I \Psi_0 | H_e | \Psi_0 \rangle + \langle \Psi_0 | H_e | \nabla_I \Psi_0 \rangle \quad (90)$$

For the Hellmann Feymann Theorem:

$$\mathbf{F}_I^{HFT} = \langle \Psi_0 | \nabla_I H_e | \Psi_0 \rangle \quad (91)$$

if  $\Psi_0$  is an exact eigenfunction of  $H_e$ .

in numerical calculation that is not the case and contribution to the forces also arise from variation of the wf with respect to atomic positions.

We need to calculate the additional forces coming from the wf contribution.

Let's start with

$$\Psi_0 = 1/N! \det \phi_i \quad (92)$$

where the orbitals  $\phi_i$  can be expanded as:

$$\phi_i = \sum_{\nu} c_{i\nu} f_{\nu}(r, \{R_I\}) \quad (93)$$

Two contributions to the forces emerge from the variation of the wf:

$$\nabla_I \phi_i = \sum_{\nu} (\nabla_I c_{i\nu}) f_{\nu}(r, \{R_I\}) + \sum_{\nu} c_{i\nu} (\nabla_I f_{\nu}(r, \{R_I\})) \quad (94)$$

We calculate now the contribution due to the incomplete-basis-set correction. Using:

$$\nabla_I \phi_i = \sum_{\nu} (\nabla_I c_{i\nu}) f_{\nu}(r, \{R_I\}) + \sum_{\nu} c_{i\nu} (\nabla_I f_{\nu}(r, \{R_I\})) \quad (95)$$

into

$$\langle \nabla_I \Psi_0 | H_e | \Psi_0 \rangle + \langle \Psi_0 | H_e | \nabla_I \Psi_0 \rangle \quad (96)$$

we obtain:

$$\sum_{i\mu\nu} c_{i\mu}^* c_{i\nu} (\langle \nabla_I f_{\mu} | H_e | f_{\nu} \rangle + \langle f_{\mu} | H_e | \nabla_I f_{\nu} \rangle) + \quad (97)$$

$$\sum_{i\mu\nu} (\nabla_I c_{i\mu}^* H_{\mu\nu} c_{i\nu} + c_{i\mu}^* H_{\mu\nu} \nabla_I c_{i\nu}) \quad (98)$$

Making use of

$$\sum_{\nu} H_{\mu\nu} c_{i\nu} = \epsilon_i \sum_{\nu} S_{\mu\nu} c_{i\nu} \quad (99)$$



We obtain:

$$\sum_{i\mu\nu} c_{i\mu}^* c_{i\nu} (\langle \nabla_I f_\mu | H_e | f_\nu \rangle + \langle f_\mu | H_e | \nabla_I f_\nu \rangle) + \sum_{i\mu\nu} \epsilon_i (\nabla_I c_{i\mu}^* S_{\mu\nu} c_{i\nu} + c_{i\mu}^* S_{\mu\nu} \nabla_I c_{i\nu}) \quad (100)$$

which can be rewritten as:

$$\sum_{i\mu\nu} c_{i\mu}^* c_{i\nu} (\langle \nabla_I f_\mu | H_e | f_\nu \rangle + \langle f_\mu | H_e | \nabla_I f_\nu \rangle) + \sum_{i\mu\nu} \epsilon_i S_{\mu\nu} \nabla_I (c_{i\mu}^* c_{i\nu}) \quad (101)$$

and

$$\sum_{i\mu\nu} c_{i\mu}^* c_{i\nu} (\langle \nabla_I f_\mu | H_e | f_\nu \rangle + \langle f_\mu | H_e | \nabla_I f_\nu \rangle) + \quad (102)$$

$$\sum_i \epsilon_i [\nabla_I \sum_{\mu\nu} S_{\mu\nu} c_{i\mu}^* c_{i\nu} - \sum_{i\mu\nu} \nabla_I S_{\mu\nu} c_{i\mu}^* c_{i\nu}] \quad (103)$$

And finally:

$$\sum_{i\mu\nu} c_{i\mu}^* c_{i\nu} (\langle \nabla_I f_\mu | H_e - \epsilon_i | f_\nu \rangle + \langle f_\mu | H_e - \epsilon_i | \nabla_I f_\nu \rangle) \quad (104)$$

In the case of plane waves Pulay forces vanish

- this is due to the fact that plane wave do not depend on the atomic coordinates

- it is only true if number of plane waves is kept fixed.

An additional contribution to the forces comes from the non-self-consistency

$$\mathbf{F}^{\text{NSC}}_I = - \int dr (\nabla_I n) (V^{\text{SCF}} - V^{\text{NSC}}) \quad (105)$$

Such a force vanishes when the self consistency is reached, meaning  $\Psi_0$  is the exact wavefunction within the subspace spanned by the finite basis set.

In Car-Parrinello, as well as in Ehrenfest MD there is no minimization full self-consistency is not required, so this force is irrelevant.