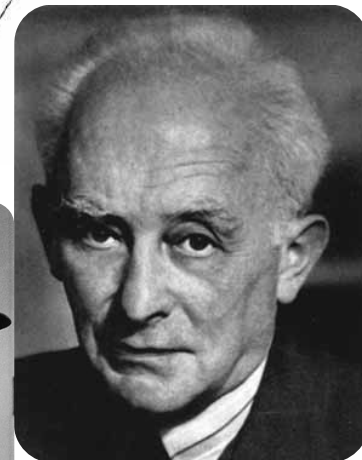


*Electronic Structure Methods for Materials Modelling*

# Ab initio Molecular Dynamics

- Learning Outcomes
  - The idea at the heart of *Car-Parrinello Molecular Dynamics*
  - The old and new generation of *Born-Oppenheimer Molecular Dynamics*

- AIMD: the big deal
- Car-Parrinello MD (CPMD)
  - The idea
  - The Car-Parrinello Lagrangian
  - The price to be paid
  - A critical choice:  $\mu$
- Born-Oppenheimer MD (BOMD)
  - Keep it simple
  - Born-Oppenheimer forces
  - CPMD vs BOMD
- Beyond CPMD & BOMD
  - Quickstep algorithm and CP2K
  - The Kühne method
  - QM/MM



*Next: what if I want to play with temperature or pressure?*

## The big deal

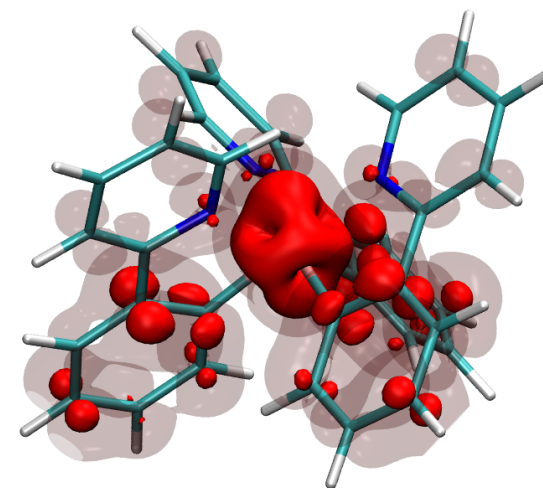
Recall the starting point of every AIMD calculation:  
In principle, we have to solve the Schrödinger equation in order to get the forces...

$$\mathcal{H}|\psi(\mathbf{r}_{el}, \mathbf{R}_{nu}, t)\rangle = i\hbar \frac{\partial}{\partial t} |\psi(\mathbf{r}_{el}, \mathbf{R}_{nu}, t)\rangle$$

*I'm going to assume we are talking KS DFT all the way to the end*

**This is a very complicated thing to do! Why bother?**

- Classical force fields are scarcely available
- Even if they are available, you maybe need something more accurate
- There are no explicit electrons in classical MD. As such:
  - Many properties simply cannot be evaluated
  - It's very difficult to include properly effects like polarization...



**AIMD: (not so) many flavours available:**

- Ehrenfest MD: mainly for the nostalgic...
- **Born-Oppenheimer MD: we calculate the (KS) ground state at each MD step.** Used to be slow, then CP2K came...
- **Car-Parrinello MD: coupled dynamics of nuclei and electrons.** Used to be the fastest tool, then CP2K came...

## The Born-Oppenheimer approximation

The starting point of ab initio MD:  
the (non-relativistic) time dependent Schrödinger equation for a system of nuclei and electrons

$$\mathcal{H}|\psi(\mathbf{r}_{el}, \mathbf{R}_{nu}, t)\rangle = i\hbar \frac{\partial}{\partial t} |\psi(\mathbf{r}_{el}, \mathbf{R}_{nu}, t)\rangle$$

### Born-Oppenheimer approximation

$m_{proton} \sim 2000 m_{electron}$

Due to the large separation of the nuclear and electronic masses,  
the (**fast**) electrons can be expected to be in instantaneous equilibrium with the much heavier (**slower**) nuclei,  
so that the electronic subsystem can be treated independently at constant  $\mathbf{R}_{nu}$

*Electrons in their ground state at every time!*



$$|\psi(\mathbf{r}_{el}, \mathbf{R}_{nu}, t)\rangle = \phi_{el}(\mathbf{r}_{el}, \{\mathbf{R}_{nu}^*\}) \cdot \chi_{nu}(\mathbf{R}_{nu}, t)$$

Is this always a fairly accurate assumption? What if it's not?

*e.g. mixed electronic states*

Most of the times, then, we treat quantum nuclei as classical particles,  
applying all the - classical - machinery we have seen so far! However: how do we deal with the electrons?

Car-Parrinello MD (CPMD) is now maybe not as used as it was...

The very famous CPMD paper (getting closer to 10,000 citations...) dates back to 1985

### Not only an elegant approach

- Elevated DFT from a static method to a tool to perform AIMD
- Often used to build more advanced/complicated AIMD flavours

***The idea:*** CPMD takes the BO approximation very seriously:



Electrons follow adiabatically the nuclei



It is not necessary to optimize the electronic wave function explicitly

***The trick:*** from a quantum/classical system (electrons/nuclei)



(Two!) Purely classical systems with two different energy scales.  
We lose the explicit time dependence of the electrons, but things get much faster!

It's just a matter of remapping the (now classical) problem to a suitable Lagrangian. Recall:

$$\mathcal{L}(\mathbf{r}_1, \dots, \mathbf{r}_N, \dot{\mathbf{r}}_1, \dots, \dot{\mathbf{r}}_N) = K(\dot{\mathbf{r}}_1, \dots, \dot{\mathbf{r}}_N) - U(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

The CP Lagrangian:

$$\mathcal{L}_{CP}(\mathbf{R}_{nu}, \phi_{el}, \dot{\mathbf{R}}_{nu}, \dot{\phi}_{el}) =$$

$$\frac{1}{2} \sum_{i=1}^{N_{nu}} m_{nu,i} \dot{\mathbf{R}}_{nu,i}^2 +$$

Kinetic energy of the nuclei

$$\frac{1}{2} \mu \sum_{j=1}^{N_{el}} \langle \dot{\phi}_{el,j} | \dot{\phi}_{el,j} \rangle -$$

Kinetic energy of the electrons - these are KS orbitals

$$E_{KS}(\phi_{el}, \{\mathbf{R}_{nu}^*\}) +$$

Potential energy - KS energy @ fixed nuclei

$$\sum_{j,k} \Lambda_{j,k} (\langle \phi_{el,j} | \phi_{el,k} \rangle - \delta_{j,k})$$

Constraints - KS states have to be orthonormal (costly!)



\* *The Hidden Math* - on Moodle

This is no different from the classical case! Recall the Eulero-Lagrange equation:

$$\frac{d}{dt} \left( \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{r}}_i} \right) - \frac{\partial \mathcal{L}}{\partial \mathbf{r}_i} = 0$$

Note the partial derivative



Two (sets of...) equations of motion

For the nuclei:

$$\sum_{i=1}^{N_{nu}} m_{nu,i} \ddot{\mathbf{R}}_{nu,i} = - \left. \frac{\partial}{\partial \mathbf{R}_{nu,i}} \right|_{\langle \phi_{el,j} | \phi_{el,k} \rangle = \delta_{j,k}} [E_{KS}(\phi_{el}, \{\mathbf{R}_{nu}^*\})]$$

For the electrons:

$$\mu \sum_{j=1}^{N_{el}} \ddot{\phi}_{el,j} = - \left( \left. \frac{\partial}{\partial \langle \phi_{el,j} |} \right|_{\langle \phi_{el,j} | \phi_{el,k} \rangle = \delta_{j,k}} [E_{KS}(\phi_{el}, \{\mathbf{R}_{nu}^*\})] \right) + \sum_k \Lambda_k |\phi_{el,k}\rangle$$

Coupled equations of motion



the nuclei and the electrons evolve in time simultaneously

## Why is it faster & the price to be paid

CPMD is - in principle - much faster than calculating the actual KS ground state at each MD step (Born-Oppenheimer MD)

Why? Take a look at the CPMD forces...

$$\mathbf{F}_{CPMD} = \mathbf{F}_{nu} + \mathbf{F}_{el} =$$

$$\frac{\partial}{\partial \mathbf{R}_{nu,i}} \bigg|_{\langle \phi_{el,j} | \phi_{el,k} \rangle = \delta_{j,k}} [E_{KS}(\phi_{el}, \{\mathbf{R}_{nu}^*\})] +$$
$$\frac{\partial}{\partial \langle \phi_{el,j} | \phi_{el,k} \rangle} \bigg|_{\langle \phi_{el,j} | \phi_{el,k} \rangle = \delta_{j,k}} [E_{KS}(\phi_{el}, \{\mathbf{R}_{nu}^*\})]$$



Partial derivatives of  $E_{KS}$  with respect to the independent variables, i.e. the nuclear positions and the KS orbitals.

No SCF cycle is required to ensure that they are consistent with the instantaneous energy, and to force the electrons to adiabatically follow the nuclei.



***This is not the actual dynamics resulting from the Schrödinger equation***

It will be only if  $\phi_{el} = \phi_{el}^{\text{Ground State}}$



The quality of the forces on the ions depends on the extent to which the orbitals are kept close to the instantaneous ground state during the dynamics

Oh, the irony: CPMD forces are formally “exact” (analytical derivatives), but the orbitals are not exactly on the ground state



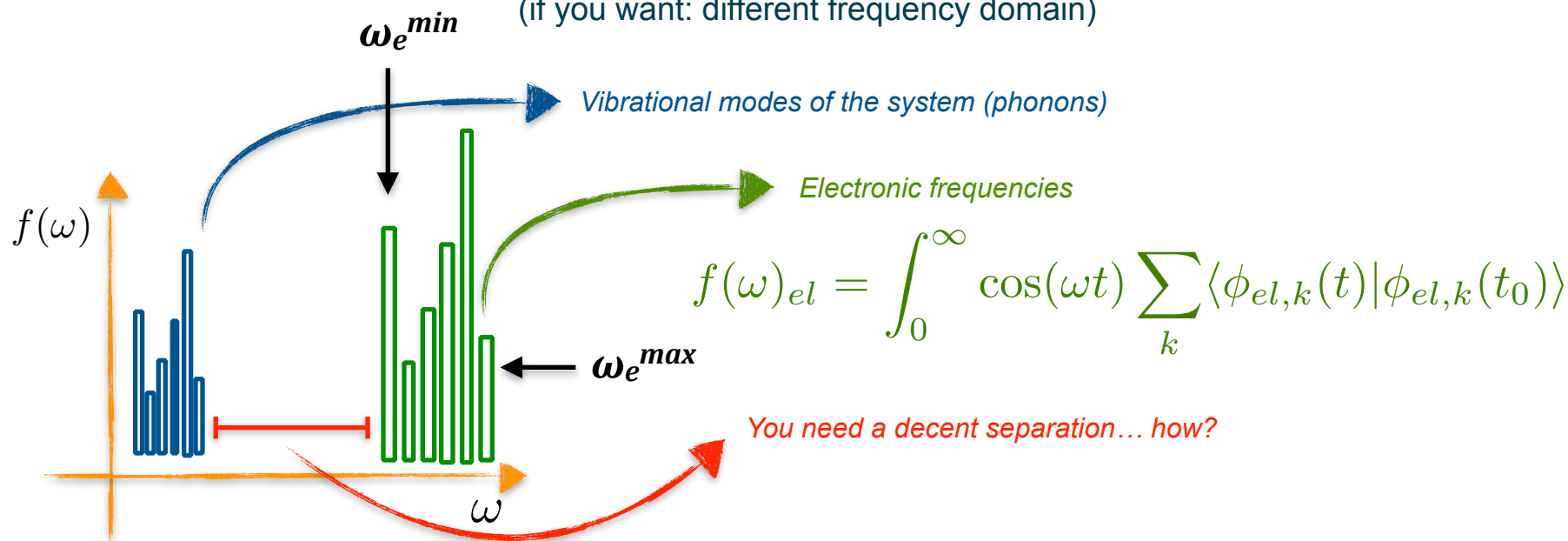
## A critical choice: $\mu$

So, how do we keep the CPMD orbitals close enough to the actual ground state?  
We have to ensure a truly (well, decently) adiabatic separation between nuclei and electrons.  
The two systems must not exchange energy.

CPMD people talk about this in terms of temperature:  
you want “cold” electrons & “hot” nuclei

A ground-state electronic wavefunction optimized for the initial configuration of the nuclei will stay close to its ground state also during time evolution if it is kept at a sufficiently low temperature.

How? Avoid any overlap between the power spectra of electrons and nuclei  
(if you want: different frequency domain)



The critical choice: tuning the electronic fictitious mass  $\mu$

$$\omega_e^{min} \propto \left( \frac{E_{gap}}{\mu} \right)^{\frac{1}{2}}$$

- It has to be lighter than the lightest atomic species in the system
- If the system is metallic, things gets complicated (additional thermostat for the electron, extended functional...)

There is another subtlety related to the choice of  $\mu$

In principle, the smaller  $\mu$  the better (the constant of motion is conserved, the dynamics is truly adiabatic, and the error on the forces are small) *lim  $\mu \rightarrow 0$ , CPMD  $\rightarrow$  BOMD!*

However, decreasing  $\mu$  shifts and stretches the electronic spectrum, so that the maximum frequency is

$$\omega_e^{max} \propto \left( \frac{E_{cut}}{\mu} \right)^{\frac{1}{2}}$$

Where  $E_{cut}$  is the kinetic energy cutoff in the expansion of the wave function in terms of a plane wave basis set - the cutoff parameter you tune all the times...

But then, this sets an hard limit to the time step for the integration of the equations of motion, as  $\Delta t$  is inversely proportional to the highest frequency in the system. Thus:

$$\Delta t^{max} \propto \left( \frac{\mu}{E_{cut}} \right)^{\frac{1}{2}}$$

# Born-Oppenheimer MD

Keep it “simple”

Born-Oppenheimer MD is possibly the most intuitive way of doing AIMD:  
At each step, we get the actual ground state by minimising the KS orbitals

Here is the Lagrangian:

$$\mathcal{L}_{BO}(\mathbf{R}_{nu}, \dot{\mathbf{R}}_{nu}) =$$

$$\frac{1}{2} \sum_{i=1}^{N_{nu}} m_{nu,i} \dot{\mathbf{R}}_{nu,i}^2 - \quad \Rightarrow \quad \text{Kinetic energy of the nuclei}$$

$$\min_{\{\phi_{el,j}\}} E_{KS}(\phi_{el}, \{\mathbf{R}_{nu}^*\}) + \quad \Rightarrow \quad \begin{array}{l} \text{Minimum of the KS energy} \\ \text{(Total ground-state energy of the interacting system} \\ \text{of electrons with classical nuclei fixed)} \end{array}$$

$$\sum_{j,k} \Lambda_{j,k} (\langle \phi_{el,j} | \phi_{el,k} \rangle - \delta_{j,k}) \quad \Rightarrow \quad \text{Constraints - KS states have to be orthonormal}$$

Once more, let's apply Eulero-Lagrange to find the equations of motion

$$\sum_{i=1}^{N_{nu}} m_{nu,i} \ddot{\mathbf{R}}_{nu,i} = - \frac{\partial}{\partial \mathbf{R}_{nu,i}} \left[ \min_{\{\phi_{el,j}\}} E_{KS}(\phi_{el}, \{\mathbf{R}_{nu}^*\}) \right]$$

We have to take the derivative of the ground state with respect to the positions of the nuclei:

$$F_{BO} = - \frac{\partial}{\partial \mathbf{R}_{nu,i}} \left[ \min_{\{\phi_{el,j}\}} E_{KS}(\phi_{el}, \{\mathbf{R}_{nu}^*\}) \right]$$

$$= - \frac{\partial E_{KS}(\phi_{el}, \{\mathbf{R}_{nu}^*\})}{\partial \mathbf{R}_{nu,i}} + \quad \text{Hellman-Feynman force}$$

$$\sum_{j,k} \Lambda_{j,k} \frac{\partial}{\partial \mathbf{R}_{nu,i}} \langle \phi_{el,j} | \phi_{el,k} \rangle -$$

$$2 \sum_j \frac{\partial \langle \phi_{el,j} |}{\partial \mathbf{R}_{nu,i}} \left[ \frac{\delta E_{KS}(\phi_{el}, \{\mathbf{R}_{nu}^*\})}{\delta \langle \phi_{el,j} |} - \sum_k \lambda_{j,k} | \phi_{el,k} \rangle \right]$$

Pulay or wavefunction force: due to the usual holonomic orthonormality constraints.  
It's actually zero if the orbitals don't depend explicitly on the ionic positions

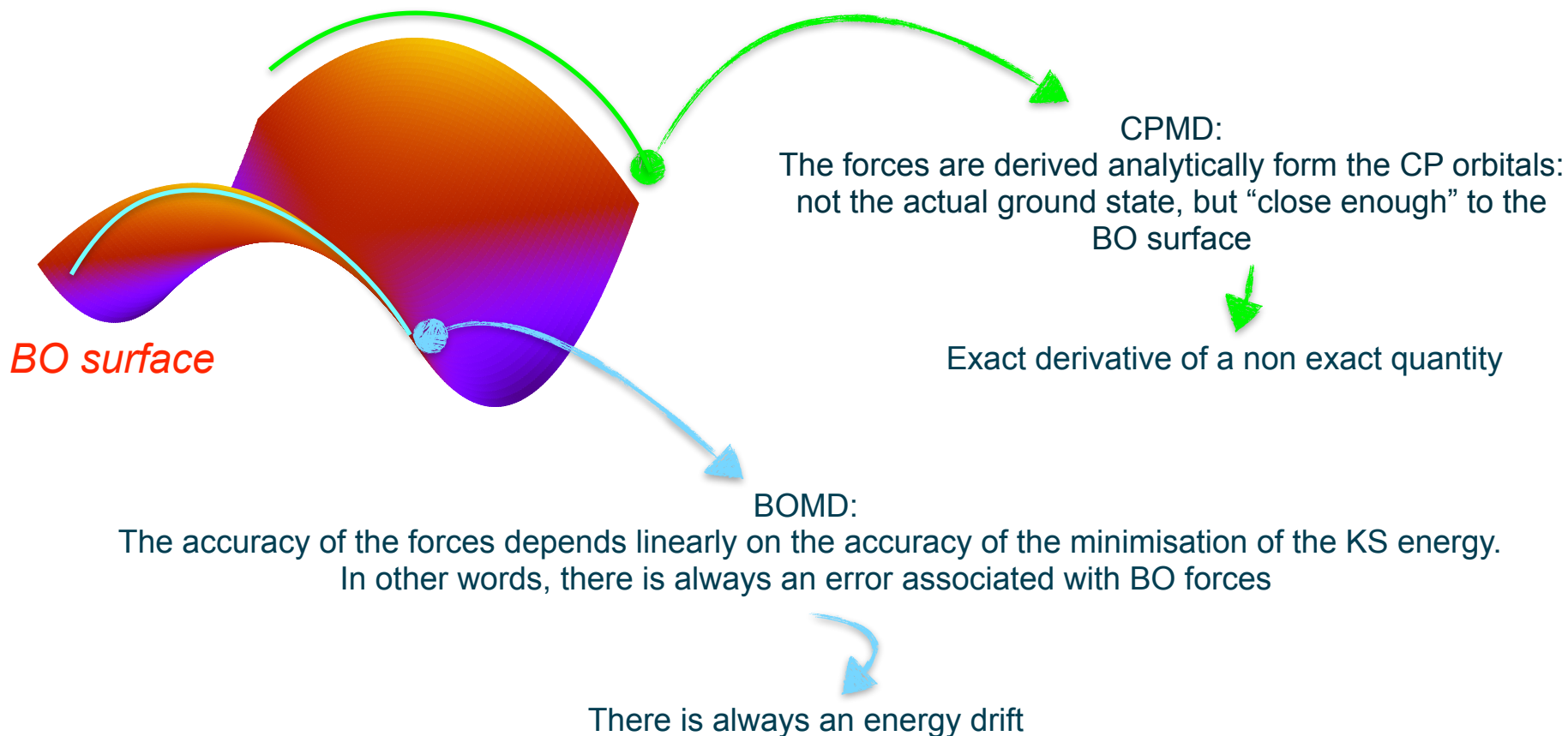
This one is tricky. No matter which basis set you are using, there is always a dependence of the wavefunctions on  $\mathbf{R}$  through the expansion coefficients

$$| \phi_{el,l} \rangle = \sum_m c_{l,m}(\mathbf{R}_{nu,i}) \psi_m$$

However, if the KS orbitals are truly optimised, this is basically zero

# Born-Oppenheimer MD

## *BO forces vs CP forces*



On the plus side, the time step in BOMD is dictated by the timescale of the atomic (classical ions!) motion...

# CPMD or BOMD?

*A matter of personal taste...*

	<i>CPMD</i>	<i>BOMD</i>
<i>The idea</i>	Coupled dynamics of ions and electrons	Ionic dynamics minimizing the ground state at every MD step
<i>Forces</i>	Analytic -exact- derivatives of orbitals that are not ground state orbitals. Can be made arbitrarily accurate - but you have to pay for it!	Actual forces from the actual ground state, but linearly dependent on the accuracy of the minimisation of the latter
<i>Time step</i>	Limited by the choice of the electronic fictitious mass	Limited by the motion of the ions
<i>Energy conservation</i>	Usually very good	It depends on the accuracy of the minimization of the ground state
<i>Computational Efficiency</i>	No need for any SCF procedure at any step	The wave functions have to be optimised at each time step
<i>Metallic systems</i>	Things get ugly	The way to go

In 1985, CPMD was usually much more efficient than BOMD  
Nowadays, clever ways to optimise the wave functions exist



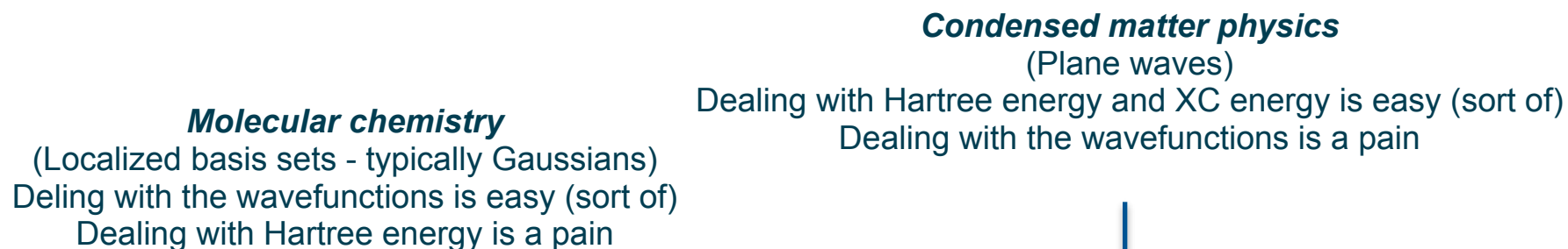
BOMD is now the tool of the trade

# Quickstep BOMD

*At the heart of CP2K...*

CP2K can do an awful lot of things - too bad 90% of them are not explained anywhere...

At the heart of the - fast!- BOMD as implemented in CP2K stands the Quickstep algorithm



## **Gaussian & Plane Waves (GPW) method**

The wave functions are written in terms of a Gaussian basis set,  
but the electronic density is mapped onto an auxiliary set of plane waves

$$\phi_j(\mathbf{r}_{el}) = \sum_l d_{lj} g_l(\mathbf{r})$$

$$n(\mathbf{r}_{el}) = \sum_{jk} \rho^{jk} \phi_j(\mathbf{r}_{el}) \phi_k(\mathbf{r}_{el})$$

$$n(\mathbf{r}_{el}) = n^*(\mathbf{r}_{el}) = \frac{1}{\Omega} \sum_{\mathbf{G}} n^*(\mathbf{G}) \exp(i\mathbf{G} \cdot \mathbf{r})$$

You need pseudopotentials expressed as a  
linear combination of Gaussians  
(e.g. GTH pseudopotentials)

# Quickstep BOMD

*At the heart of CP2K...*

Plane waves representation



Dealing with the Hartree energy is now much easier  
(you can use FFTW to solve the Poisson equation)

Gaussian representation



Dealing with wave functions is now much easier  
(you have -not so many- Gaussians to deal with)

Finding the ground state: global minimisation of the KS energy

In Quickstep, the KS energy is a high dimensional function of the basis set coefficients

- Clever algorithms exist to deal with the minimization of functions in multidimensional spaces (Direct Inversion of the Iterative Subspace, DIIS)
- And, clever algorithms exist to ease the cost of the orthonormalisation of the orbitals, such as the Orbital Transformation (OT) method

This way, finding the ground state at each MD step (the real bottleneck of BOMD) is not that costly anymore!



# Kühne method

*Best of both BO and CP - handle with care, though...*

*The Kühne method :*

A CPMD approach to BOMD

BOMD (with BOMD timesteps!) without SCF cycles at every MD step (CPMD-like)

The ground state is properly minimized only at the very first MD steps

Then, the density matrix is propagated along the dynamics using e.g. the Always Stable Predictor Corrector (ASPC) algorithm

$$\mathbf{C}^p(t_n) \cong \sum_{m=1}^K (-1)^{m+1} m \frac{\binom{2K}{K-m}}{\binom{2K-2}{K-1}} \underbrace{\mathbf{C}(t_{n-m}) \mathbf{C}^T(t_{n-m}) \mathbf{S}(t_{n-m}) \mathbf{C}(t_{n-1})}_{=\mathbf{P}(t_{n-m})}$$

This is of course an approximation. In doing so, an error emerge in the ground state electronic density  
Luckily, the consequent error in the forces is basically white noise

As a result, the dynamics is dissipative, i.e. the forces within the predictor corrector ( $\mathbf{F}_{PC}$ ) are:

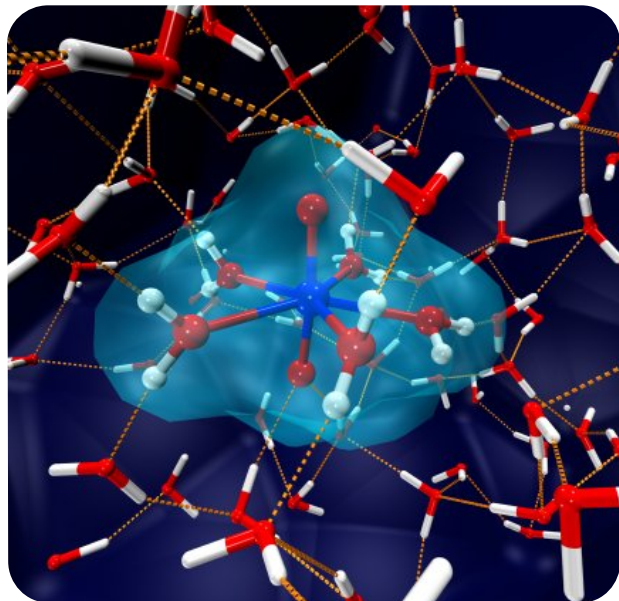
$$\mathbf{F}_{PC} = \mathbf{F}_{BO} - \gamma_D \dot{\mathbf{R}}_{nu}$$

And the equations of motion read

$$m_{nu} \ddot{\mathbf{R}}_{nu} = \mathbf{F}_{BO} - (\gamma_D + \gamma_L) \dot{\mathbf{R}}_{nu} + \Xi_{nu}(t)$$

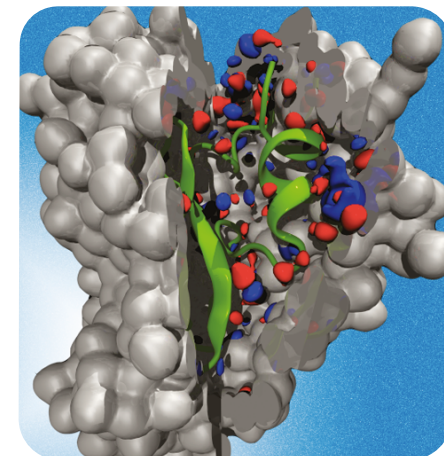
# What can I do with AIMD?

## *Lengthscales and Timescales*



AIMD is possibly the most accurate tool we have to look into dynamical processes at the atomic/molecular level

- Chemical reactions
- Adsorption processes
- Charge transfer and polarisation



### ***Two main limitations***

- AIMD still relies on - approximate - electronic structure methods (e.g. within DFT, which XC functional?)
- AIMD is still extremely computationally expensive ( $10^2$  atoms,  $10^2$  ps) - albeit exceptions exist



Remember: if you are interested in something happening on a given time and length scale, you have to simulate a sufficiently large system for a sufficiently long simulation time

An awful lot of stuff is out of the table...

Not to mention rare events! - More on those in the next lectures...

## Tricky but it won the Nobel...

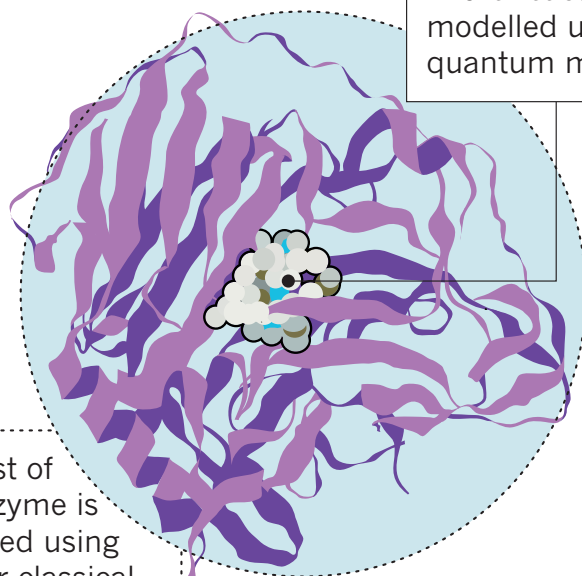
### QM/MM

Not really straightforward but hey, it won a Nobel Prize!

Nobel Prize in Chemistry 2013: Karplus, Warshel and Levitt, for “the development of multi scale models for complex chemical systems”

#### An enzymatic reaction

Only the atoms directly involved in the reaction are modelled using quantum methods.



The rest of the enzyme is modelled using simpler classical methods.

Something tricky (electron transfer between to species, the adsorption of a molecule on a substrate, the binding of a metallic ion within a big protein) is happening in a **tiny region** of...

*AIMD can deal with that!*



*Classical MD can deal with that*



... a much larger system (an amorphous glass, a catalytic surface, a globular protein)

**QM/MM: A unified framework**

- Learning Outcomes

- The idea at the heart of ***Car-Parrinello Molecular Dynamics***
- The old and new generation of ***Born-Oppenheimer Molecular Dynamics***