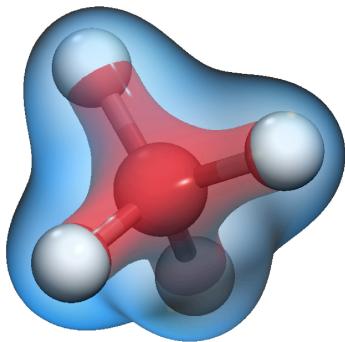


Kinetic Formalism for *ab-initio* Electronic Calculations



Miller Mendoza Jiménez

Collaborations: Hans J. Herrmann, Sauro Succi

Special Thanks to Tobias Kesselring

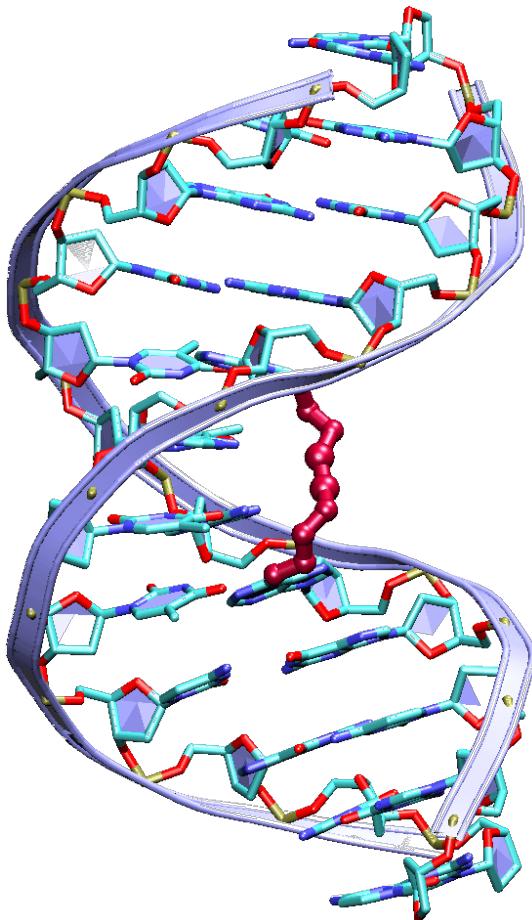


Table of Contents

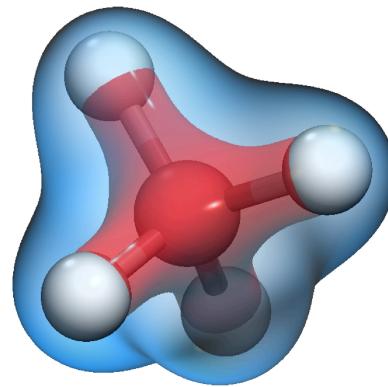
- Motivation
 - Brief Introduction to Kohn-Sham Theory
 - Kinetic Theory and Kohn-Sham Boltzmann Equation
 - Applications
 - Exchange-Correlation of atoms
 - Methane Molecule
 - Hydrogen Oscillations
 - Summary
-
- Model Description
- Some applications

Some atomistic systems

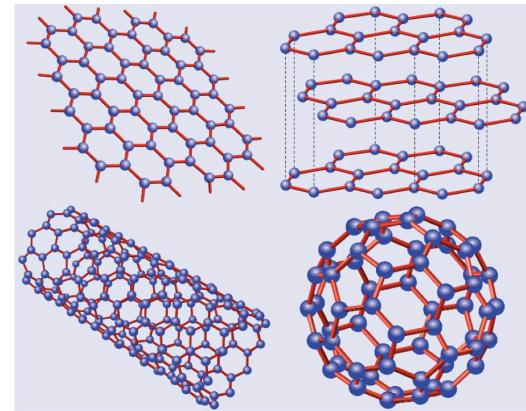
Biology: DNA molecule



Chemistry: Methane molecule



Solid State Physics: Nanotubes and Graphene



Many-Body Electronic System

In a multi-electronic system with N electrons:

$$\Psi = \Psi(\vec{x}_1, \dots, \vec{x}_N, \sigma_1, \dots, \sigma_N)$$

3N + N variables

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi$$

$$\hat{H} = \hat{T} + \hat{V}$$

$$\hat{V} = \hat{V}_{e-e} + \hat{V}_{ext}$$

Due to the Coulomb interactions, the system is not separable!
 becoming extremely difficult to solve

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \sum_{n=0}^{3N_e} \frac{\partial^2 \Psi}{\partial x_n^2} + V(\vec{x}_1, \dots, \vec{x}_{3N_e}) \Psi$$

Many-Body Electronic System

In a multi-electronic system with N electrons:

$$\Psi = \Psi(\vec{x}_1, \dots, \vec{x}_N, \sigma_1, \dots, \sigma_N)$$

3N + N variables

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi$$

$$\hat{H} = \hat{T} + \hat{V}$$

$$\hat{V} = \hat{V}_{e-e} + \hat{V}_{ext}$$

However, in most of the cases, one needs only the total density of the system:

$$\rho(\vec{x}) = \int_{-\infty}^{\infty} |\Psi|^2 d\vec{x}_1 \dots d\vec{x}_{N_e-1}$$

Kohn-Hohenberg Theorems (1964)

1. Total energy is an unique functional of the electron density.
2. The density that minimizes the total energy is the exact ground state of the system.

The ground state of the system can be expressed as:

$$\delta E[\rho] = 0 \quad \rightarrow \quad \rho = \sum_{n=1}^{N_e} \psi_n^* \psi_n$$

$$\epsilon_n \psi_n = -\frac{\hbar^2}{2m} \nabla^2 \psi_n + V \psi_n$$

**Kohn-Sham
(1965)**

Time independent Schrödinger equation

Where the potential is

$$V = V_{e-e} + V_{ext} + V_{xc}$$

Exchange and correlation corrections.

Potential energy of the system:

$$V = V_{e-e} + V_{ext} + V_{xc}$$

$$V_{e-e} = e\Phi, \quad \nabla^2\Phi = e\rho / \epsilon_0$$

Mean field approximation

$$V_{ext} = -\frac{1}{4\pi\epsilon_0} \sum_{l=1}^{N_i} \frac{Z_l e^2}{|\vec{r} - \vec{R}_l|}$$

Potential energy due to Ions
and external sources

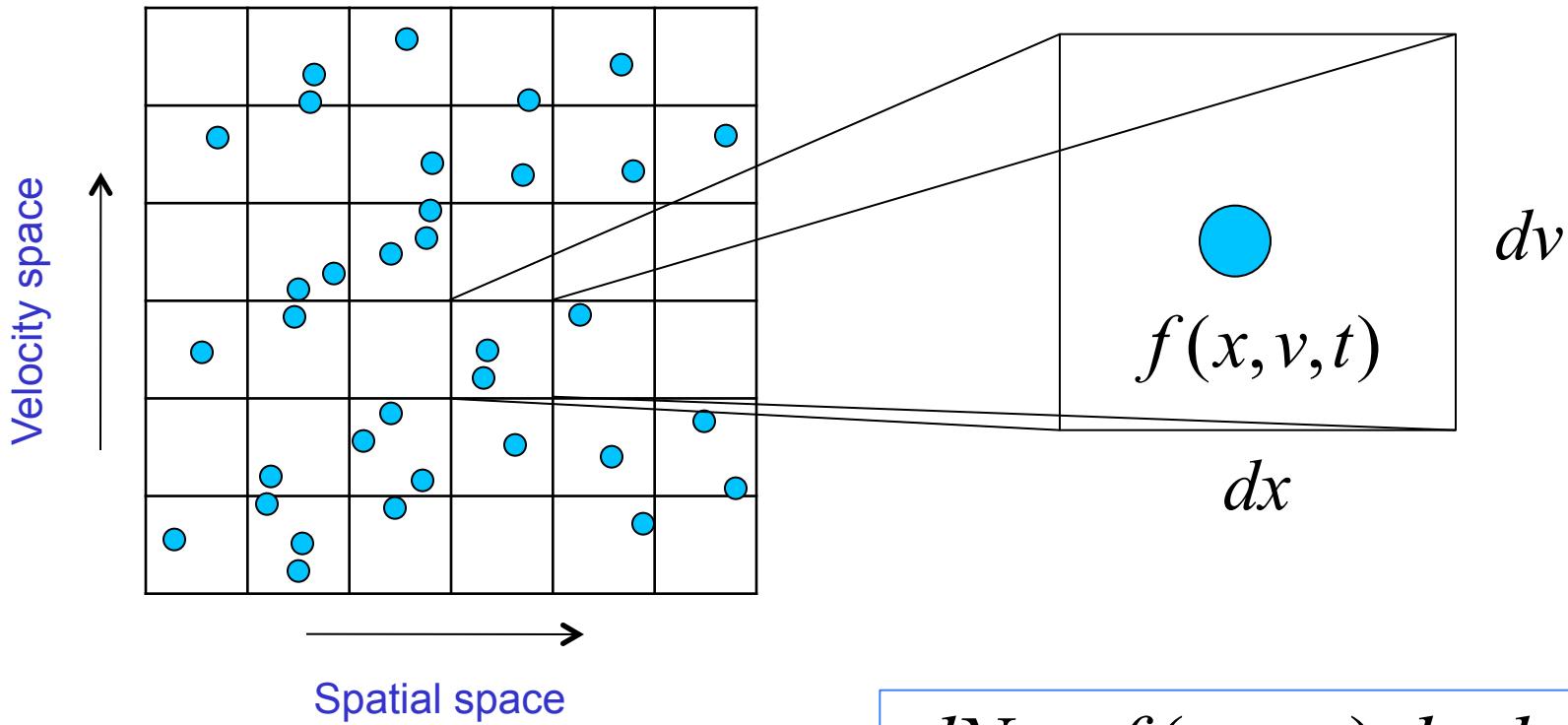
$$V_{xc}$$



A. D. Becke, Phys. Rev. A 38, 3098 (1988).
C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B 37, 785

Kinetic Theory: Classical Gas

Phase space



$$\frac{\partial f}{\partial t} + \vec{v} \cdot \nabla f = \Omega(f) + S$$

Boltzmann Equation

$$dN = f(x, v, t) dx dv$$

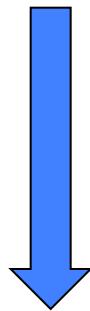
Number of particles

Kohn-Sham and Boltzmann Equations

Boltzmann Equation:

$$\frac{\partial f}{\partial t} + \vec{v} \cdot \nabla f = \Omega(f) + S$$

Leads to:

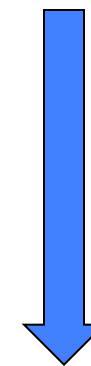


$$\frac{\partial \phi}{\partial t} = D \nabla^2 \phi + \Sigma$$

Kinetic Kohn-Sham Equations



Lead to:

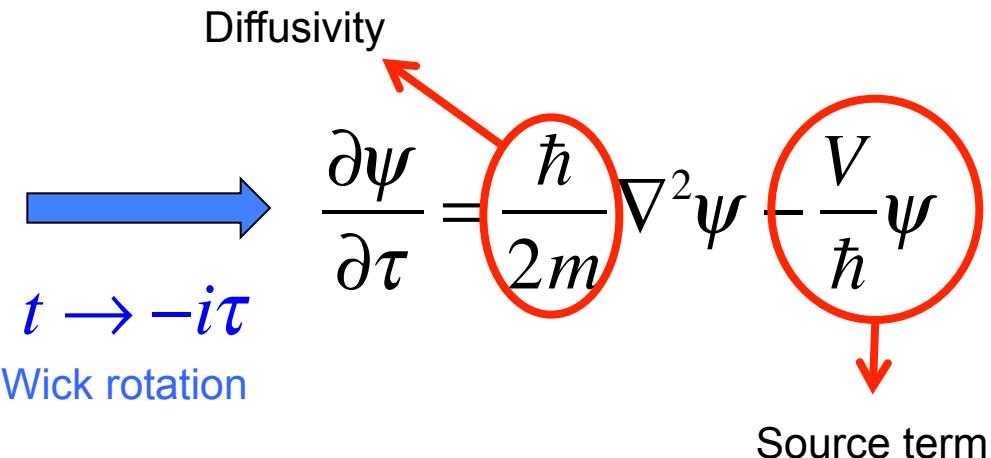


$$\epsilon_n \psi_n = -\frac{\hbar^2}{2m} \nabla^2 \psi_n + V \psi_n$$

Kohn-Sham as Diffusion Equation

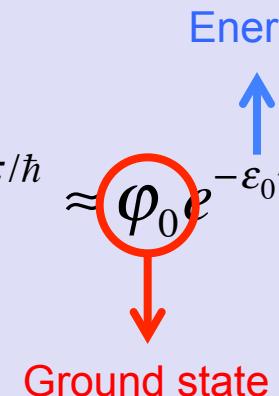
Time-dependent Schrödinger equations:

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + V \psi$$



Wave function and energy value of the ground state:

$$\psi(\vec{x}, \tau) = \sum_{j=0}^{\infty} \varphi_j e^{-\varepsilon_j \tau / \hbar} \approx \varphi_0 e^{-\varepsilon_0 \tau / \hbar}$$



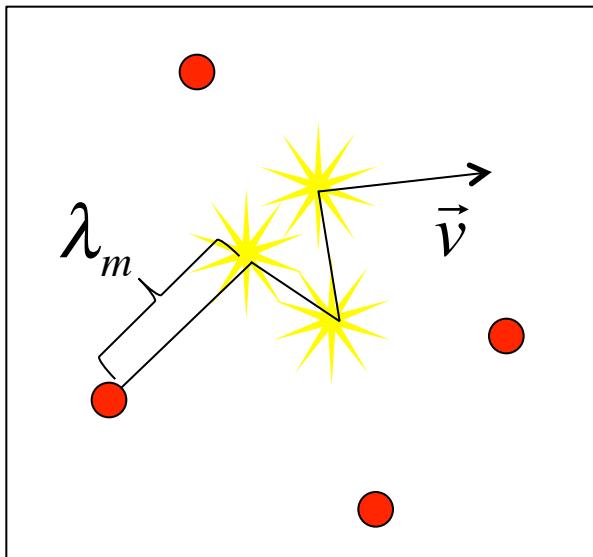
Ground wave function as gas of virtual particles

$$\frac{\partial \varphi_n}{\partial \tau} = \frac{\hbar}{2m} \nabla^2 \varphi_n - \frac{V}{\hbar} \varphi_n$$

$$\int f_n d\vec{v} = \varphi_n$$

$$\frac{\partial f_n}{\partial t} + \vec{v} \cdot \nabla f_n = \Omega(f_n) + S_n$$

Small Knudsen number



Linear approximation BGK

$$\frac{\partial f_n}{\partial t} + \vec{v} \cdot \nabla f_n = -\frac{1}{\tau} (f_n - f_n^{eq}) + S_n$$

Relaxation time

$$?$$

Using Hermite Polynomials. For Simplicity

In general, one can write:

$$f_n^{eq}(\vec{x}, \vec{v}, t) = w(\vec{v}) \sum_{j=0}^{\infty} a_{nj}^{(j)}(\vec{x}, t) H_j^{(j)}(\vec{v})$$

$$S_n(\vec{x}, \vec{v}, t) = w(\vec{v}) \sum_{j=0}^{\infty} b_{nj}^{(j)}(\vec{x}, t) H_j^{(j)}(\vec{v})$$

$$w(\vec{v}) = \frac{e^{-\vec{v}^2/2\theta}}{(2\pi\theta)^{3/2}}$$

Weight function

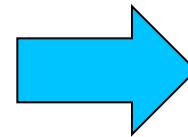
$$a_{nj}^{(j)}(\vec{x}, t) = \int f_n^{eq} H_j^{(j)}(\vec{v}) d^3 v$$
$$b_{nj}^{(j)}(\vec{x}, t) = \int S_n H_j^{(j)}(\vec{v}) d^3 v$$

Projection coefficients

Equilibrium distribution and Source Term

We do not know the expression, but we do not need one. The requirements for the equilibrium distribution and source term:

$$\begin{aligned} \int f_n^{eq} d\vec{v} &= \varphi_n, \\ \int f_n^{eq} \vec{v} d\vec{v} &= 0, \\ \int f_n^{eq} v_\alpha v_\beta d\vec{v} &= \frac{\hbar}{2m\tau} \varphi_n \delta_{\alpha\beta}, \\ \int S_n d\vec{v} &= -V \varphi_n / \hbar. \end{aligned}$$



$$\begin{aligned} f_n^{eq}(\vec{x}, \vec{v}, t) &= w(\vec{v}) \varphi_n \\ S_n(\vec{x}, \vec{v}, t) &= -w(\vec{v}) \frac{V}{\hbar} \varphi_n \\ \frac{\hbar}{2m} &= \theta\tau \end{aligned}$$

Our first guess!

The kinetic formalism:

The Kinetic Kohn-Sham equations:

$$\frac{\partial f_n}{\partial t} + \vec{v} \cdot \nabla f_n = -\frac{1}{\tau_K} (f_n - f_n^{eq}) - \frac{V}{\hbar} w(\vec{v}) \varphi_n - \vartheta_n$$

$$\varphi_n = \int_{-\infty}^{\infty} f_n d\vec{v}$$

$$\epsilon_n = -\frac{\hbar}{2} \frac{\partial \log \langle \varphi_n | \varphi_n \rangle}{\partial t}$$

Kohn-Sham orbitals and energies

$$\vartheta_n = \sum_{j < n} \Lambda_{nj} f_j$$

$$\Lambda_{nj} = \frac{\langle \varphi_n | \varphi_j \rangle}{\langle \varphi_j | \varphi_j \rangle}$$

Orthogonality conditions

Number of dimensions

$$\psi_n$$



$$f_n$$

Kohn-Sham equations: 3D

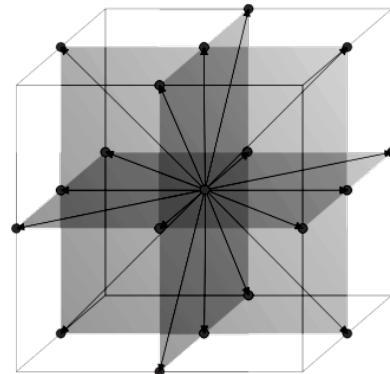
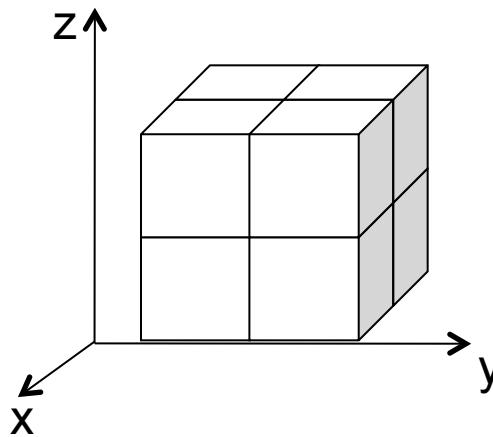
Kinetic Kohn-Sham equations: 6D

Is there any advantage?

YES!

Lattice Boltzmann Method for Fluids

We do not need to discretize the whole velocity, but we can just choose a small number of representative vectors.

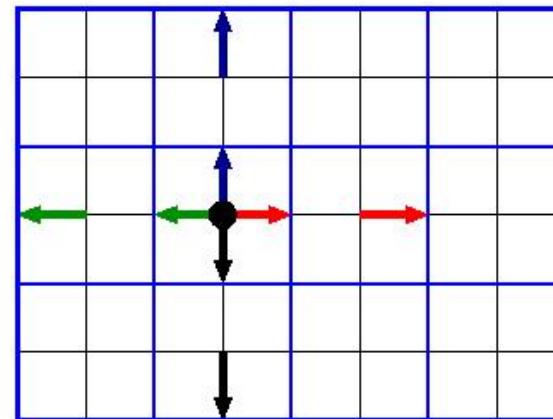


Collision:

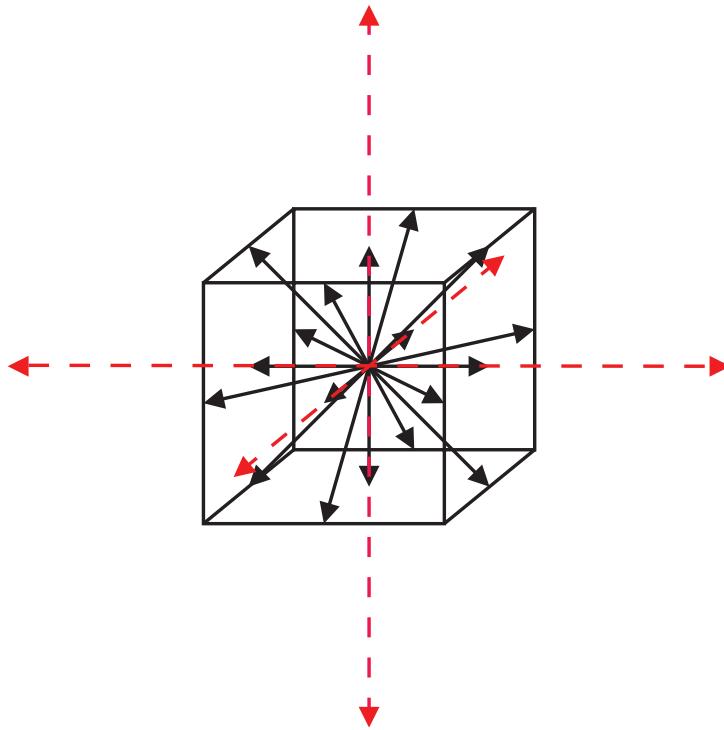
$$f_i^*(x, t) = f_i(x, t) + \frac{1}{\tau} (f_i^{eq}(x, t) - f_i(x, t))$$

Streaming:

$$f_i(x + v_i \delta t, t + \delta t) = f_i^*(x, t) \quad v_i = \frac{\delta x_i}{\delta t}$$



Lattice Kinetic Kohn-Sham Model



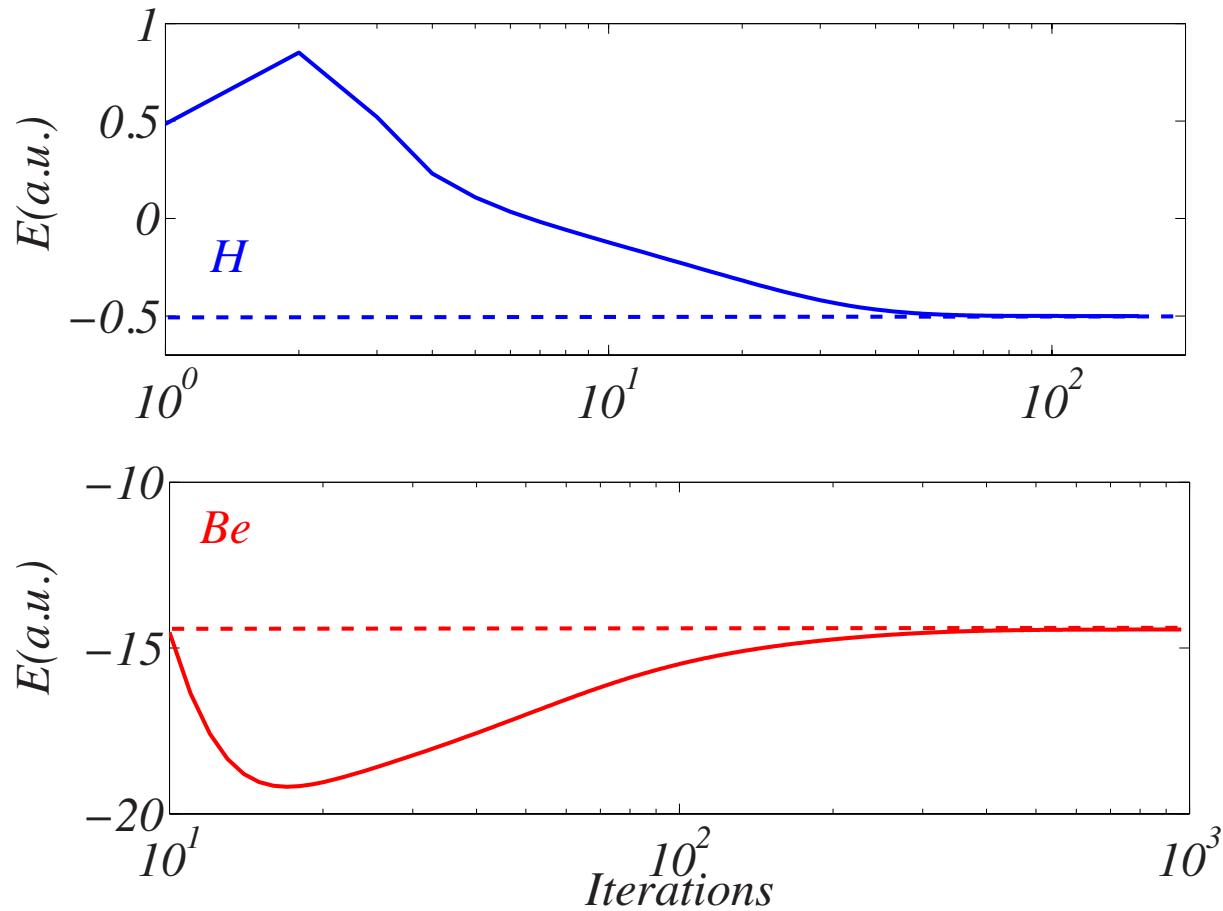
$$\varphi_n = \sum_{j=0}^{24} f_{nj}$$

$$\varepsilon_n = -\frac{\hbar}{2} \frac{\partial \log \langle \varphi_n | \varphi_n \rangle}{\partial t}$$

$$\frac{\hbar}{2m} = \left(1 - \sqrt{\frac{2}{5}}\right) \tau_K$$

$$f_{nj}(\vec{x} + \vec{v}_j, t+1) - f_{nj}(\vec{x}, t) = -\frac{1}{\tau_K} \left(f_{nj} - f_{nj}^{eq} \right) - \frac{V}{\hbar} w_j \varphi_n - \vartheta_{nj}$$

Convergence to the Ground State

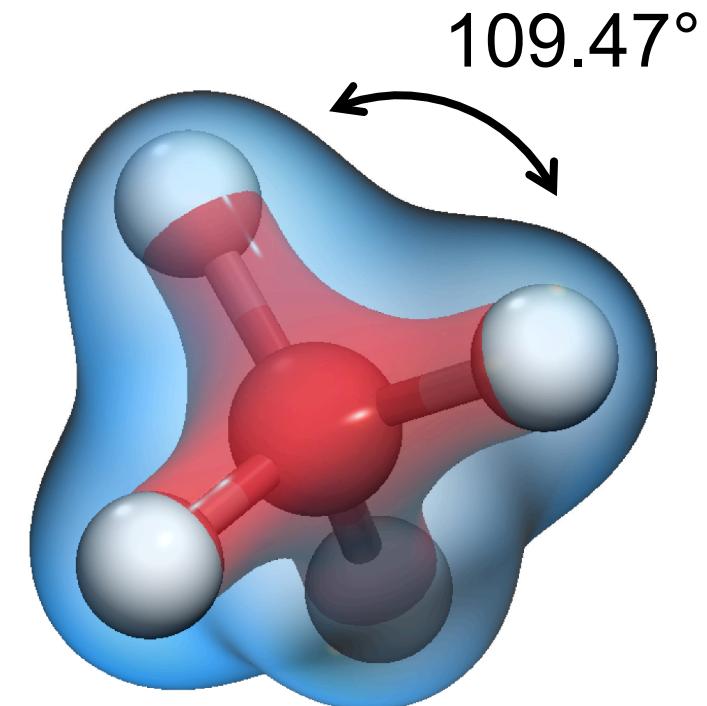
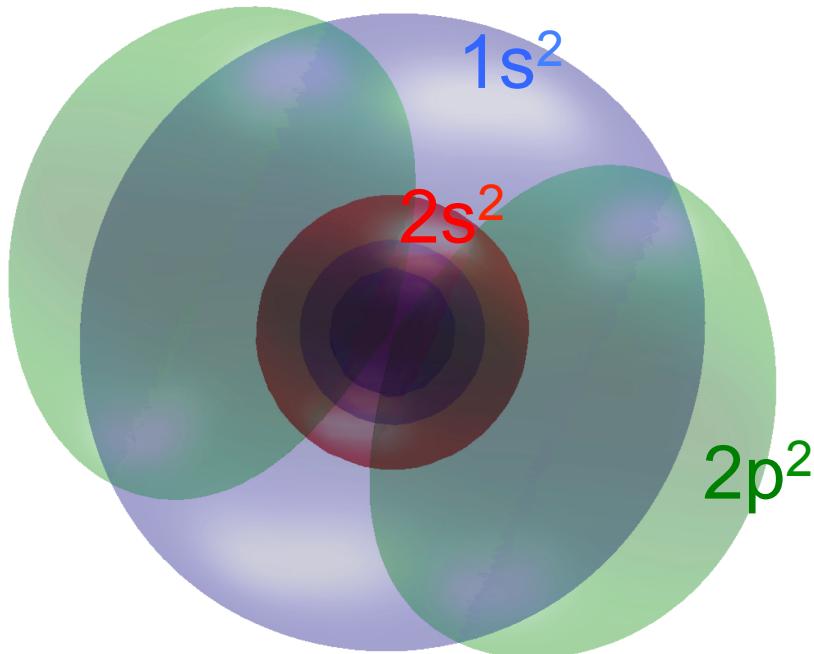


Exchange-Correlation energies

Atom	\mathcal{V}_x	Exp. \mathcal{V}_x	\mathcal{V}_c	Exp. \mathcal{V}_c	Time	Iterations
H	-0.310	-0.310	0	0	3 min	640
Be	-2.651	-2.658	-0.096	-0.095	17 min	3035
B	-3.742	-3.728	-0.127	-0.128	21 min	3009
C	-5.084	-5.032	-0.173	-0.161	18 min	2968

TABLE I. Exchange-Correlation energies for H, Be, B, and C. Computational time and the number of iterations performed by the model to reach the ground state are also shown.

Carbon Orbitals and Methane Molecule



Bond distance: 106 pm
Exp.: \sim 108 pm

Limitation:

To increase the accuracy of the calculations we need to decrease the Knudsen numbers, which implies increasing the system size, and therefore, poor performance compared with traditional methods in DFT.

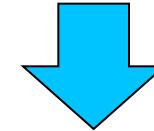
Alternative Solution:

Keep the same Knudsen number, but imposing vanishing higher order moments.

Imposing Vanishing Higher Order Moments

For simplicity and to understand the idea, let us move to the one-dimensional case. One can proof from the stationary Boltzmann equation by consecutive integration:

$$f = f^{eq} + \tau S - \tau \vec{v} \cdot \nabla f$$



$$\Pi^{(j)} = \Pi^{eq(j)} + \tau \Lambda^{(j)} - \tau \nabla \cdot \Pi^{(j+1)}$$

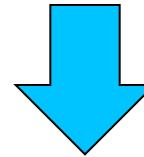
$$\Pi^{(j)} = \int f v_{\alpha_1} \dots v_{\alpha_j} d\vec{v}$$

$$\Lambda^{(j)} = \int S v_{\alpha_1} \dots v_{\alpha_j} d\vec{v}$$

Imposing Vanishing Higher Order Moments

For simplicity and to understand the idea, let us move to the one-dimensional case. One can proof from the stationary Boltzmann equation by consecutive integration:

$$\sum_{j=0}^{\infty} (-1)^j \tau^j \nabla^{j+1} \left[\Pi^{eq(j+1)} + \tau \Lambda^{(j+1)} \right] = \Lambda^{(1)}$$



$$\Pi^{eq(j)} = \int f v_{\alpha_1} \dots v_{\alpha_j} d\vec{v} = 0, \quad j > 2$$

$$\Lambda^{(j)} = \int S v_{\alpha_1} \dots v_{\alpha_j} d\vec{v} = 0, \quad j > 1$$



For the discrete case, we can repeat the same procedure.

Some test for Poisson Equation

Using the lattice Boltzmann expansion and discretization procedure, we obtain, for instance up to 7th order:

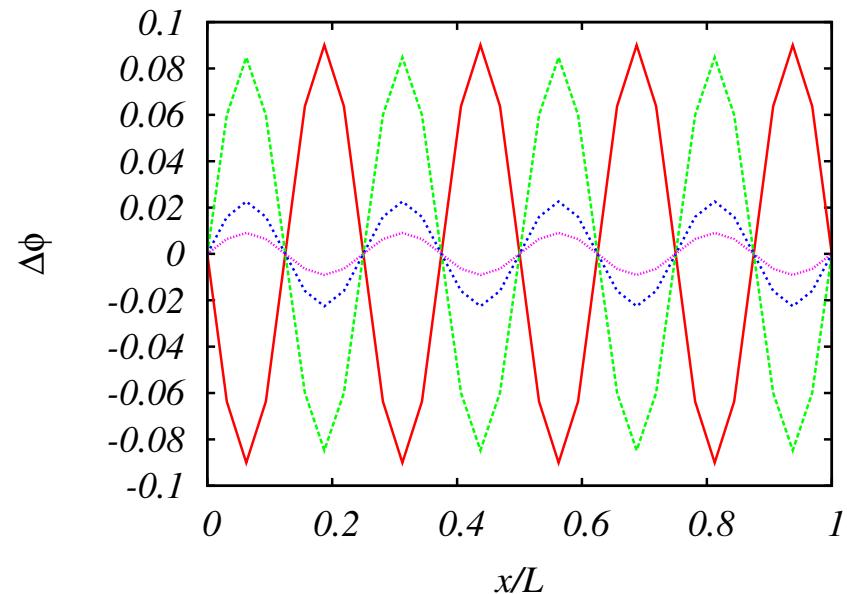
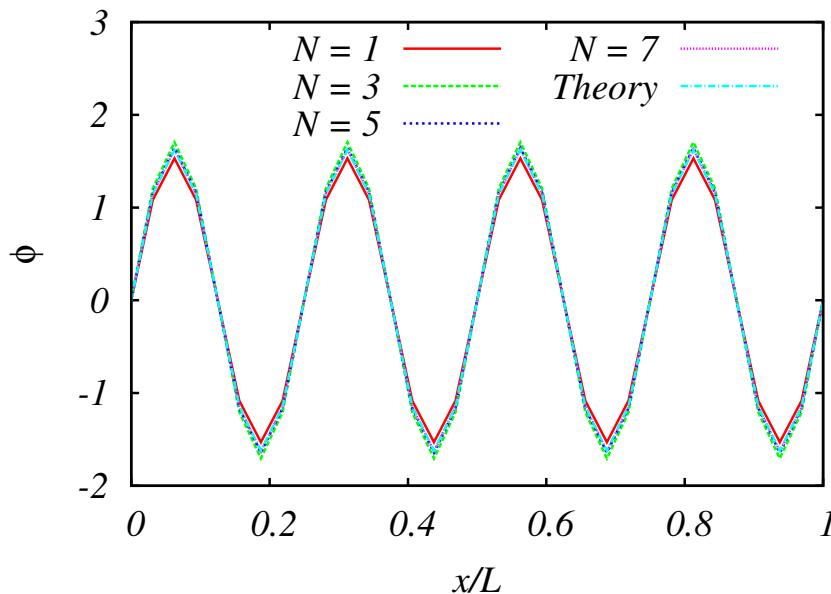
$$f^{eq} = \phi(v) \Pi^{eq(0)}, \quad S = \chi(v) \Lambda^{(0)}$$

$$\phi(v) \simeq w(v) \left(1 - \frac{3c_s^2 - 6c_s^2 v^2 + v^4}{8c_s^4} - \frac{15c_s^6 - 45c_s^4 v^2 + 15c_s^2 v^4 - v^6}{24c_s^6} \right),$$

$$\chi(v) \simeq w(v) \left(1 + \frac{1}{2} \left[1 - \frac{v^2}{c_s^2} \right] + \frac{3c_s^2 - 6c_s^2 v^2 + v^4}{8c_s^4} + \frac{15c_s^6 - 45c_s^4 v^2 + 15c_s^2 v^4 - v^6}{48c_s^6} \right),$$

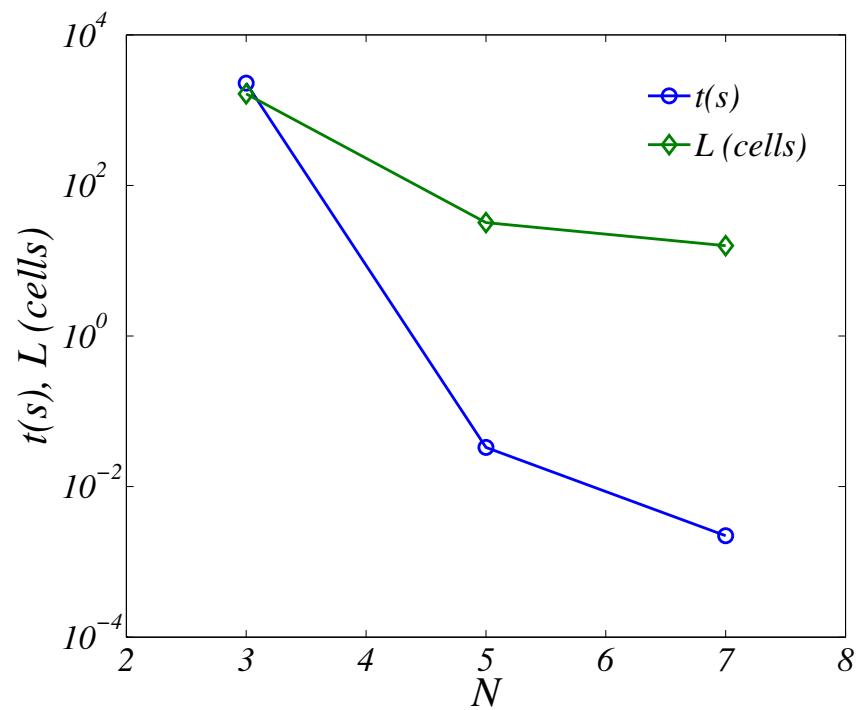
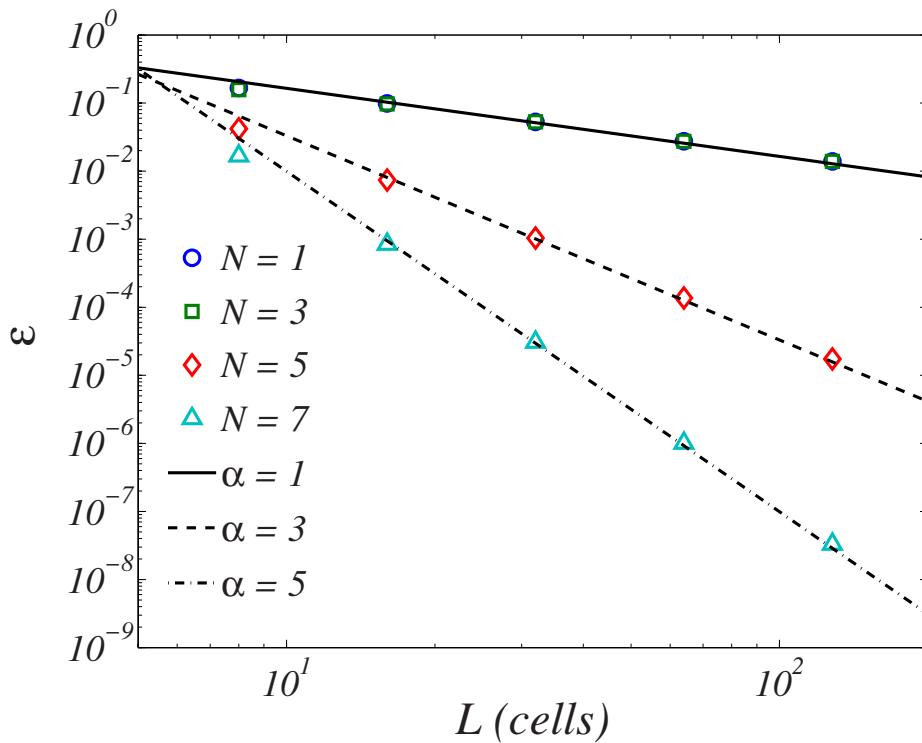
Some test for Poisson Equation

Using the lattice Boltzmann expansion and discretization procedure, we obtain, for instance up to $N = 7$ order, and lattice size of $L = 32$ cells:



Some test for Poisson Equation

Using the lattice Boltzmann expansion and discretization procedure, we obtain, for instance up to 7th order:

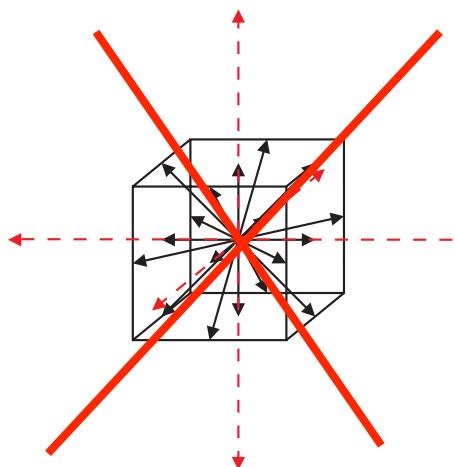


Repeating the same for lattice kinetic KS, in 3D

$$\int f_n^{eq} d\vec{v} = \varphi_n, \quad \int f_n^{eq} \vec{v} d\vec{v} = 0, \quad \int f_n^{eq} v_\alpha v_\beta d\vec{v} = \frac{\hbar}{2m\tau} \varphi_n \delta_{\alpha\beta},$$

$$\int f_n^{eq} v_{\alpha_1} \dots v_{\alpha_m} d\vec{v} = 0, \quad m > 2$$

$$\int S_n d\vec{v} = -V \varphi_n / \hbar, \quad \int S_n v_{\alpha_1} \dots v_{\alpha_m} d\vec{v} = 0, \quad m > 1$$



For $N = 5$, we need 111 vectors

For $N = 7$, we need 385 vectors

Do we gain computational speed?
 YES!

Comparison with the Previous Approach

Atom	\mathcal{V}_x	Exp. \mathcal{V}_x	\mathcal{V}_c	Exp. \mathcal{V}_c	Time	Iterations
H	-0.310	-0.310	0	0	3 min	640
Be	-2.651	-2.658	-0.096	-0.095	17 min	3035
B	-3.742	-3.728	-0.127	-0.128	21 min	3009
C	-5.084	-5.032	-0.173	-0.161	18 min	2968

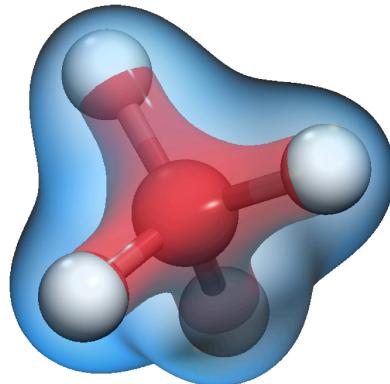
BEFORE

Atom	\mathcal{V}_x	Exp. \mathcal{V}_x	\mathcal{V}_c	Exp. \mathcal{V}_c	Time	Iterations
H	-0.310	-0.310	0	0	9 sec	158
Be	-2.658	-2.658	-0.095	-0.095	3 min	965
B	-3.728	-3.728	-0.128	-0.128	29 min	2704
C	-5.032	-5.032	-0.161	-0.161	33 min	2305

NOW

Comparison with Standard Methods

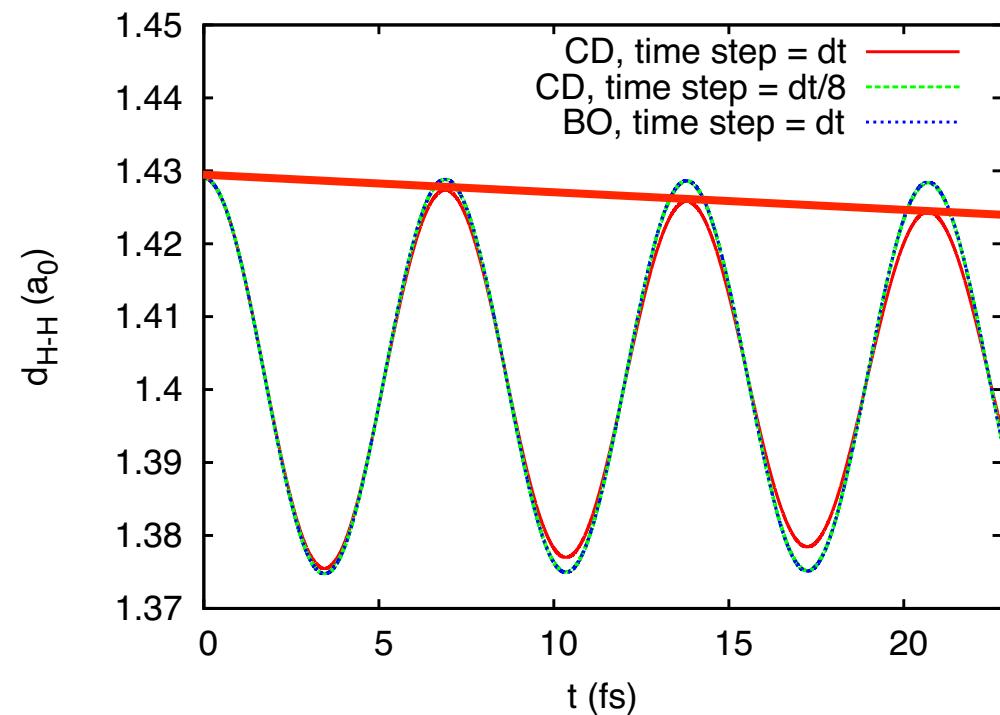
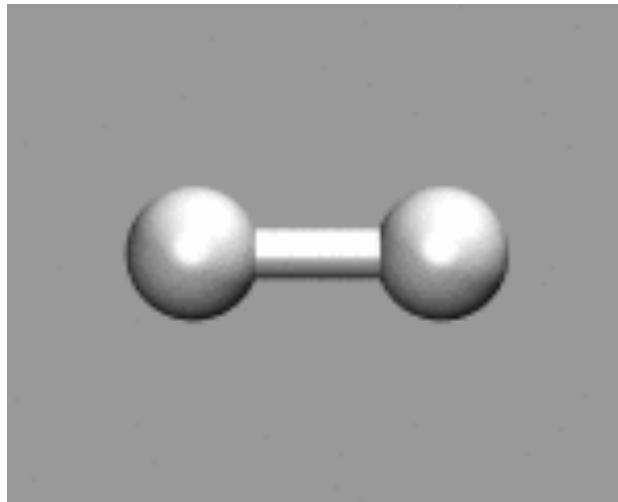
Model	LKKS (58^3)	LKKS (60^3)	LKKS (62^3)	CPMD (70)	CPMD (140)	CPMD (280)	CPMD (560)
Time	3 h	3.8 h	6 h	1.2 h	6 h	14 h	15 h
C-H ₁ (pm)	108.9	108.7	108.6	108.5	108.6	108.4	108.6
C-H ₂ (pm)	108.9	108.7	108.6	107.6	108.6	107.6	108.6
C-H ₃ (pm)	108.9	108.7	108.6	108.4	108.6	108.4	108.6
C-H ₄ (pm)	108.9	108.7	108.6	107.6	108.6	107.6	108.6
Angle 1 (°)	109.73	109.48	109.47	109.26	109.46	109.31	109.47
Angle 2 (°)	109.80	109.50	109.47	109.23	109.47	109.20	109.47
Angle 3 (°)	109.12	109.55	109.47	109.26	109.47	109.31	109.47
Angle 4 (°)	109.81	109.35	109.47	109.36	109.48	109.31	109.47
Angle 5 (°)	109.84	109.58	109.47	110.36	109.48	110.37	109.47
Angle 6 (°)	109.52	109.37	109.47	109.35	109.46	109.31	109.47
Error Bonds (%)	0.74	0.37	0.18	1.18	0.18	1.18	0.18
Error Angles (%)	0.68	0.19	$< 10^{-3}$	0.9	0.02	0.9	$< 10^{-3}$



Ab-initio Molecular Dynamics

- Born-Oppenheimer (BO) Molecular Dynamics (Adiabatic Approximation)
 - Ions move, electrons find the ground state, ions move ...
- Concurrency Dynamics (CD):
 - Ions and electrons move at the same time. No relaxation to the ground state needed.

Hydrogen Molecule: First vibrational mode



LOSS OF TOTAL ENERGY IN THE SYSTEM !!

The problem: Non-reversibility of the BE

$$\frac{\partial f_n}{\partial t} + \vec{v} \cdot \nabla f_n = -\frac{1}{\tau_K} (f_n - f_n^{eq}) - \Lambda_n - \vartheta_n$$

Presence of non-equilibrium terms in the distribution function.

Alternative solution, however, it needs more discussion:

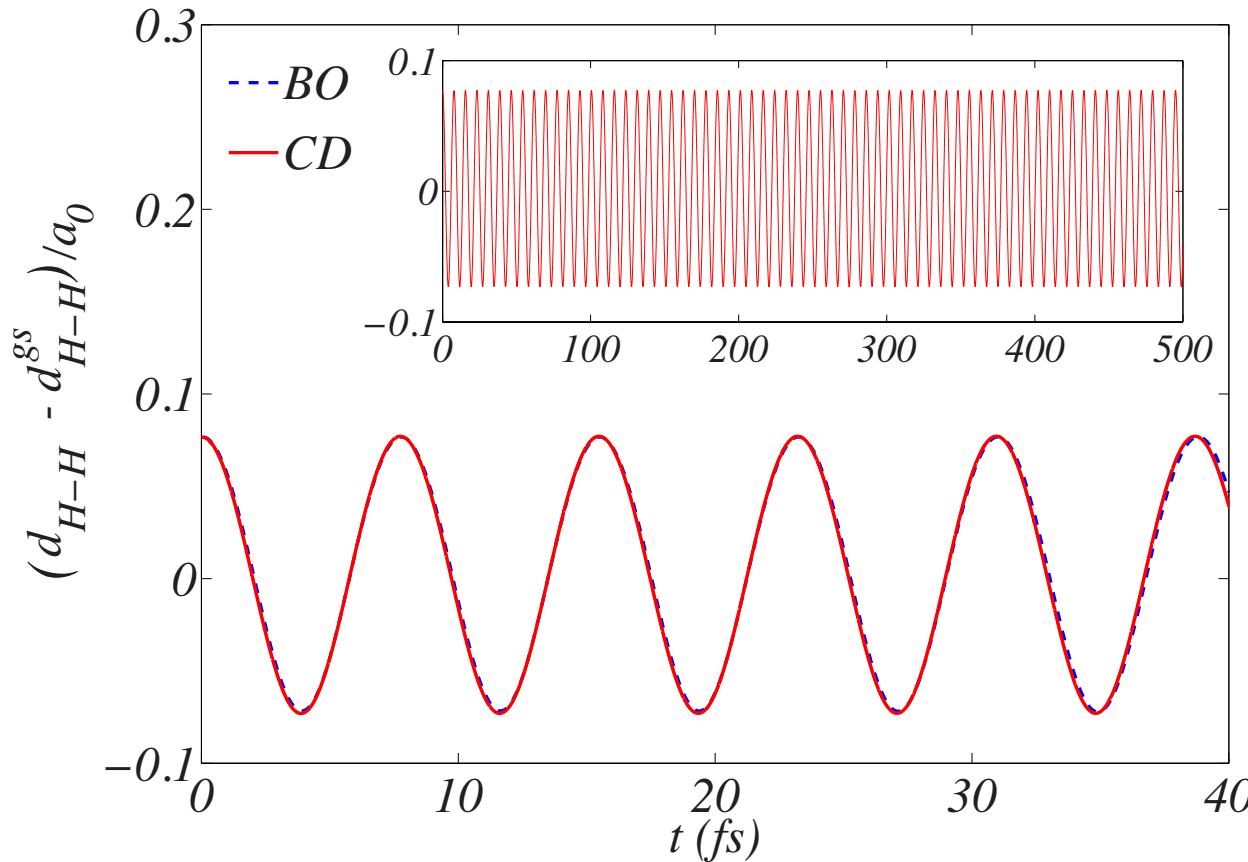
$$\frac{\partial f_n}{\partial t} + \vec{v} \cdot \nabla f_n = U_n - i\Lambda_n - i\vartheta_n$$

$$\int U_n d^3v = 0$$

$$\int U_n \vec{v} d^3v = 0$$

$$\int U_n v_\alpha v_\beta d^3v = \varepsilon_n \kappa \varphi_n \delta_{\alpha\beta}$$

Ab-initio Molecular Dynamics



CD is 17 times
faster than BO

$$\frac{\partial f_n}{\partial t} + \vec{v} \cdot \nabla f_n = U_n - i\Lambda_n - i\vartheta_n$$

Summary and Outlook

1. We have developed a new kinetic formalism for the Kohn-Sham equations. It can be more suitable to develop an equation for the total density, instead of solving the electronic orbitals.
2. A discretization of the velocity space in a small number of vectors makes the model competitive for solving many-body quantum systems.
3. Numerical results show very good performance and efficiency compared with other numerical methods.
4. Ab-initio molecular dynamics can be performed one order of magnitude faster using CD than BO.
5. Is it possible to derive the kinetic Kohn-Sham from the Kohn-Hohenberg theorem?