Ab Initio Molecular Dynamics Simulations in Liquids and Glasses
Basics and Applications

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IYOG Graduate Course on the Structures of Glass
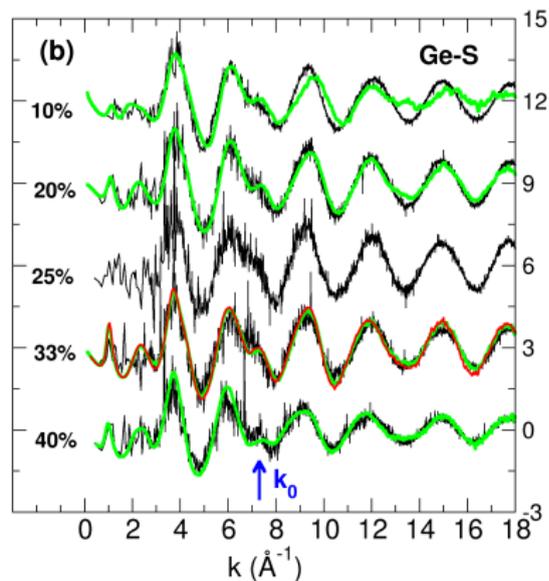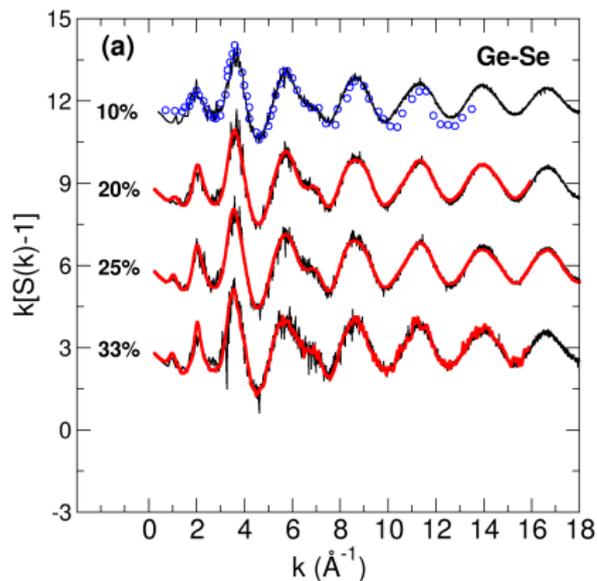November 2, 2022

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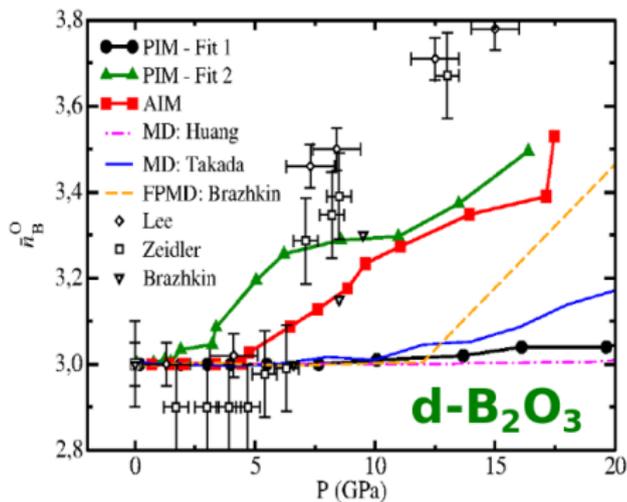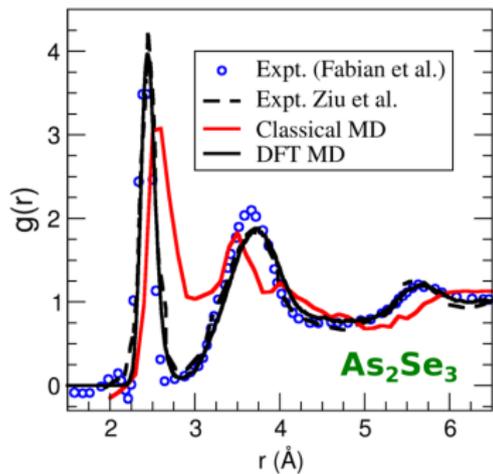
Some personal thoughts and experiences

A. Baroni et al., JCP 151 (2019)

M. Bauchy, M. Micoulaut, JNCS 377 (2013)

Some preliminary remarks...

- Classical force-fields carry their own and intrinsic limitations.

$$V_{ij}(r) = \frac{q_i q_j}{r} + A_{ij} e^{-r/\rho_{ij}} - \frac{C_{ij}}{r}$$

- Force-fields are not always available for a given system (composition) or thermodynamic condition (high pressure).

- No information available on the nature of the chemical bonding

- How to treat explicitly charge transfer in covalent systems (chalcogenides) ?

- Description of spectroscopic/electronic properties in relationship with atomic structure (Raman, IR, XPS,...)
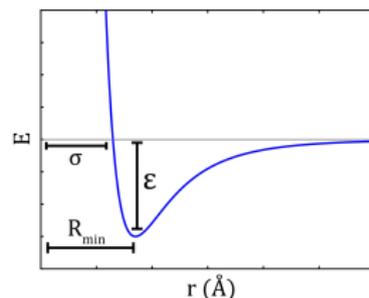
Some preliminary remarks...

- Some glass systems display broken chemical order.

- Classical force-fields do not account for such defects.
  - Ge-Te (phase change), Ge-Se or As-Se
  - HP-SiO_2

- Systems with small band gaps undergo semiconducting to metallic transitions : As_2Te_3, GeTe,...
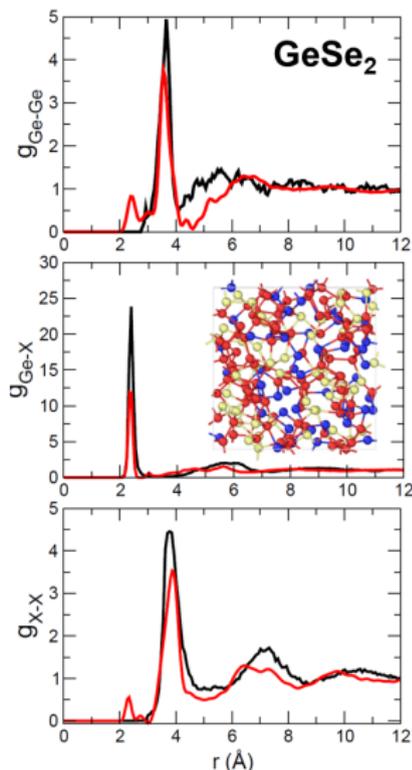
Outline - Basics

Basics

FINDING APPROXIMATIONS

The starting point : the Schrödinger equation

$$H\Psi = E\Psi \qquad (1)$$

for a system with *N* atoms and *n* electrons.

For large systems, there are basically two options :

- **Adiabatic approximation :** e^- move faster than the nuclei which can be considered as fixed.
- **Mean-field approximation** for the e^- – e^- interaction (density functional theory, DFT).

Basics

FINDING APPROXIMATIONS

We write the Hamiltonian for molecules or solids. It contains the interaction and the kinetic energy of N atoms (nuclei of mass M) at positions $\mathbf{R}_I$ and n electrons of mass m at positions $\mathbf{r}_i$.

$$H = \sum_{i=1}^{n} \frac{\mathbf{P}_i^2}{2m} + \frac{1}{2} \sum_{i \neq j}^{n} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i=1}^{n} \sum_{I=1}^{N} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{I=1}^{N} \frac{\mathbf{P}_I^2}{2M_I} + \frac{1}{2} \sum_{k \neq l}^{N} \frac{Z_k Z_l e^2}{|\mathbf{R}_k - \mathbf{R}_l|}$$

A useful form with standard identification

$$H = T_e(\{p\}) + V_{ee}(\{e\}) + V_{eN}\bigg(\{r\}, \{R\}\bigg) + T_N(\{P\}) + V_{NN}(\{R\})$$

Electronic kinetic E   e – e potential   e – nucleus potential   nuclear kinetic E   nucleus-nucleus potential

Basics

FINDING APPROXIMATIONS

We solve the the Schrödinger equation : $H\Psi_{(i,l)}(r, R) = E_{(i,l)}(r, R)$

Adiabatic approximation : Since M= 2000 m_e, there are 2 different timescales involved : electrons and nuclei (ions)

- Vibrational excitations : $\hbar\omega \simeq 10$ meV
- Electronic excitations : $\hbar\omega \simeq 1$ eV

Since $\tau_{ions} \gg \tau_e$, on the timescale of electrons, ions can be considered as frozen.

Consequence : The wavefunction can be split in 2 parts

$$\Psi_{(i,l)}(r, R) = \chi_{(i,l)}(R)\Phi_e(r, R)$$

$$\left[T_e + V_{ee} + V_{eN}(R) + V_{NN}(R) \right]\Phi_e(r, R) = E_e(R)\Phi_e(r, R)$$

$$\left[T_n + E_e(R) \right]\chi_{(i,l)}(R) = E_{i,e}\chi_{(i,l)}(R)$$

Basics

FINDING APPROXIMATIONS

1. $\Phi_e(R)$ is the ground state electronic wavefunction of the electronic Hamiltonian at fixed configuration (parameter) R.

$$\left[T_e + V_{ee} + V_{eN}(R) + V_{NN}(R) \right] \Phi_e(r,R) = E_e(R)\Phi_e(r,R)$$

to obtain $\Phi_e(R)$ and $E_e(R)$ (Born-Oppenheimer energy surface).

2. Knowing $E_e(R)$, one solves

$$\left[T_n + E_e(R) \right] \chi_{(i,l)}(R) = E_{i,e}\chi_{(i,l)}(R)$$

to obtain $\chi_{(i,l)}(R)$ and $E_{i,e}$.

Common approximations :

- At LT, harmonic approximation. $\chi_{(i,l)}(R)$ only non-zero around :

$$E_e(R) \simeq E_e(R_0) + \frac{1}{2!}(R - R_0)^2 \frac{\partial^2 E_l(R)}{\partial R^2} + ...$$

- At HT, nuclei behaves as a classical particle : $M\frac{d^2 R}{dt^2} = -\frac{\partial E_e(R)}{\partial R}$

Solutions of the electronic Hamiltonian

Reducing complexity : We want to compute $\Phi_e(r, R) = \Phi_e(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, ... \mathbf{r}_n, R)$

- Discretize space of each variable on a grid of N_G grid points. To define Φ_e, one needs $(N_G)^n$ values ! Many body problem

- Many properties can be reproduced by an independent electron approach (i.e. single particle). In this case, a single particle wavefunction needs only $n \times N_G$ variables (Hartree-Fock).

- How do we construct an ab-initio independent electron approach of the **total energy** of the ground state ?

- Many static and quasistatic properties can be obtained as derivatives of the total energy :

Force: $-\frac{\partial E(R)}{\partial \mathbf{R}}$ Dynamic matrix: $\frac{\partial^2 E(R)}{\partial \mathbf{R}_i \partial \mathbf{R}_j}$ Polarisation: $-\frac{\partial E(R)}{\partial \mathbf{E}_{\text{elec}}}$

Solutions of the electronic Hamiltonian

Reminder from Hartree-Fock : ab initio single particle approach for the total energy. Variational method with exact Hamiltonian and an approximate wavefunction.

$$E_{HF} = min_{\Phi_{HF}} \langle \Phi_{HF}|H|\Phi_{HF} \rangle \geq E_{exact} \tag{2}$$

with

$$\Phi_{HF}(r_1, r_2, ...r_n) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(r_1) & \psi_2(r_1) & ... & \psi_n(r_1) \\ \psi_1(r_2) & \psi_2(r_2) & ... & \psi_n(r_2) \\ ... & ... & ... & ... \\ \psi_1(r_n) & \psi_2(r_n) & ... & \psi_n(r_n) \end{vmatrix}$$

Single Slater determinant. Exact solution for an independent electron Hamiltonian with non-degenerate ground state.

To do better, we change the Hamiltonian

- System with interacting electrons in a potential $V_{ext}(r)$
- **Instead :** System with non-interacting electrons in a fictitious potential $V'_{ext}(r) \neq V_{ext}(r)$ with same total energy and same electronic density.

Density functional theory

Inhomogeneous Electron Gas*

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(Received 18 June 1964)

This paper deals with the ground state of an interacting electron gas in an external potential $v(\mathbf{r})$. It is proved that there exists a universal functional of the density, $F[n(\mathbf{r})]$, independent of $v(\mathbf{r})$, such that the expression $E \equiv \int v(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + F[n(\mathbf{r})]$ has as its minimum value the correct ground-state energy associated with $v(\mathbf{r})$. The functional $F[n(\mathbf{r})]$ is then discussed for two situations: (1) $n(\mathbf{r}) = n_0 + \tilde{n}(\mathbf{r})$, $\tilde{n}/n_0 \ll 1$, and (2) $n(\mathbf{r}) = \varphi(\mathbf{r}/r_0)$ with φ arbitrary and $r_0 \to \infty$. In both cases F can be expressed entirely in terms of the correlation energy and linear and higher order electronic polarizabilities of a uniform electron gas. This approach also sheds some light on generalized Thomas-Fermi methods and their limitations. Some new extensions of these methods are presented.

Density functional theory

STARTING FEATURES

- The electronic density is the basic variable.

- N interacting electrons in an external potential $V_{ext}(\mathbf{r})$ in a unique non degenerate GS:

$$n(\mathbf{r}) = N \int \int \int \Psi^*_{GS}(\mathbf{r}, \mathbf{r}_2, ...\mathbf{r}_N)\Psi_{GS}(\mathbf{r}, \mathbf{r}_2, ...\mathbf{r}_N)d^3\mathbf{r}_2.\mathbf{r}_3...\mathbf{r}_N$$

- Hohenberg-Kohn theorem : It is shown that $V'_{ext}(r) = V_{ext}(r)$+cst where $V'_{ext}(r)$ is the most general potential and $n(\mathbf{r})$ is the GS density.

Density functional theory

- **Definition :** The DFT functional is given by :

$$F[n] = \langle \Psi_{GS} | T_e^{[n]} + V_{ee}^{[n]} | \Psi_{GS} \rangle$$

with : $N = \int n(\mathbf{r}) d^3\mathbf{r}$. The energy of the system is given by :

$$E[n] = F[n] + \int n(\mathbf{r}) V_{ext}(\mathbf{r}) d^3\mathbf{r}$$

and minimized by the ground state density $E[n_{GS}] = E_{GS}$.

- **Kohn-Sham approach :** Given an interacting GS charge density $n_{GS}(\mathbf{r})$ of a N electron system.
  - There exists just one external potential $V_{KS}(\mathbf{r})$ for a non-interacting N electron system with GS state density $n_{GS}(\mathbf{r})$
  - Defines a Kohn-Sham (single particle) Hamiltonian :

$$H_{KS} = \frac{P^2}{2m} + V_{KS}(\mathbf{r})$$

Density functional theory

The solutions (eigenvectors $|\Psi_{KS}^i\langle$, energies ϵ_{KS}^i) of the KS Hamiltonian satisfy :

$$n(\mathbf{r}) = 2 \sum_{j=1}^{N/2} \langle \Psi_{KS}^j | \mathbf{r} \rangle \langle \mathbf{r} | \Psi_{KS}^j \rangle$$

out of which 2 news quantities can be defined :

- The kinetic energy of the KS system

$$T_0[n] = 2 \sum_{j=1}^{N/2} \left\langle \Psi_{KS}^j \left| \frac{P^2}{2m} \right| \Psi_{KS}^j \right\rangle$$

  It is not the kinetic energy part of the real interacting system but the fictious non-interacting one !

- The Hartree Coulomb interaction ("classical" form)

$$E_H[n] = \frac{1}{2} \int \int d^3\mathbf{r} d^3\mathbf{r}' \frac{e^2 n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Density functional theory

By definition, the exchange-correlation functional is :

$$E_{XC}[n] = F[n] - T_0[n] - E_H[n]$$

with the total energy given by :

$$\begin{aligned}
E[n] &= T_0[n] + E_H[n] + E_{XC}[n] + \int n(\mathbf{r}) V_{ext}(\mathbf{r}) d^3\mathbf{r} \\
&= T_0[n] + E_{KS}[n]
\end{aligned}$$

Conclusion

Most of the difficult (and approximation) part is hidden in E_{XC} !
The choice of E_{XC} dramatically impacts structural properties of the glass.

Density functional theory

EXCHANGE CORRELATION

We want to calculate :

$$E_{XC}[n] = \frac{1}{2} \int n(\mathbf{r}) d^3 r \int d^3 \mathbf{r}' \frac{n_{XC}(\mathbf{r}, \mathbf{r}' - \mathbf{r})}{|\mathbf{r} - \mathbf{r}'|}$$

with :

$$n_{XC}(\mathbf{r}, \mathbf{r}' - \mathbf{r}) = n(\mathbf{r}') \int d\lambda [g(\mathbf{r}, \mathbf{r}', \lambda) - 1]$$

involving the pair correlation function $g(\mathbf{r}, \mathbf{r}', \lambda)$ of a system with density $n(\mathbf{r})$ and electron-electron interaction λ.

- Classically, one would have $P(\mathbf{r}, \mathbf{r}') \simeq n(\mathbf{r})n(\mathbf{r}')$ (Hartree-Coulomb energy). But this neglects the possibility of (spin) symmetry (Pauli exchange interaction).
- n_{XC} is the exchange-correlation hole, a QM zone surrounding every electron in an interacting system that reduces the probability $P(\mathbf{r}, \mathbf{r}')$ of finding other electrons within the immediate vicinity.

Density functional theory

EXCHANGE CORRELATION

Approximations :

- Local density approximation (LDA) :

$$E_{XC}[n] \simeq E_{XC}^{LDA}[n] = \int n(\mathbf{r})\epsilon(n(\mathbf{r}))d^3\mathbf{r}$$

- $\epsilon(n(\mathbf{r}))$ is just a function of the local electronic density. Exchange-correlation energy/electron of a homogeneous interacting electron gas. Exact.

- Allows reproducing shell structure of atoms, bond lengths, vibrational frequencies.

- Generalized gradient approximation (GGA) :

$$E_{XC}^{GGA}[n] = \int d^3\mathbf{r} \, f\left(n(\mathbf{r}), \nabla n(\mathbf{r}) \right)$$

Density functional theory

EXCHANGE CORRELATION

- E_{XC} builds on reasonable electronic models, often broken up into exchange and correlation functionals :

$$E_{XC}[n] \simeq E_X[n] + E_C[n]$$

Several expressions for the correlation energy (fitted to results of accurate QMC calculations, e.g. uniform electron gas).

$$E_X^{GGA}[n] = \frac{4}{3}\left(\frac{3n(\mathbf{r})}{\pi}\right)^{1/3} - \sum_{\sigma} F(s_{\sigma})n_{\sigma}^{4/3}(\mathbf{r})d^3\mathbf{r}$$

with, e.g. :

$$F_{Becke} = \frac{\beta s_{\sigma}}{1 + 6\beta s_{\sigma} sinh^{-1}s_{\sigma}}$$

- Various contributions. Complicated expressions. Usually refereed by their abbreviations : Becke-Perdew-Wang (BPW91), BLYP, PBE, etc. ...
- Hybrid functionals (HF treatment of exchange energy)

Density functional theory

EXCHANGE CORRELATION

Remember : GGA provides better geometries for weak bonds which are too short in LDA.

Solid	a^{LDA} (Å)	a^{GGA} (Å)	a^{expt} (Å)
Na	4.05	4.20	4.23
NaCl	5.47	5.70	5.64
Al	3.98	4.05	4.05
Si	5.40	5.47	5.43
Ge	5.63	5.78	5.66
GeAs	5.61	5.76	5.65
Cu	3.52	3.63	3.60
W	3.14	3.18	3.16

Perdew et al. PRL 82 (1999)

EXCHANGE CORRELATION

- Modelling of such XC functionals beyond the scope of this lecture.

- Many functionals available which are more or less appropriate for a particular glass/liquid system.

- Importance of GGA for the reproduction of intermediate range ordering in glass-forming liquids.
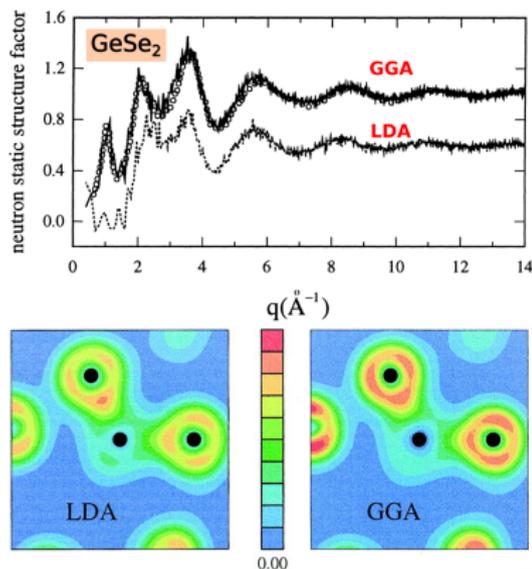
Density functional theory

EXCHANGE CORRELATION

Micoulaut, Vuillemier and Massobrio. PRB 79 (2009)

Micoulaut and Massobrio, JOAM 11 (2009) (2009)

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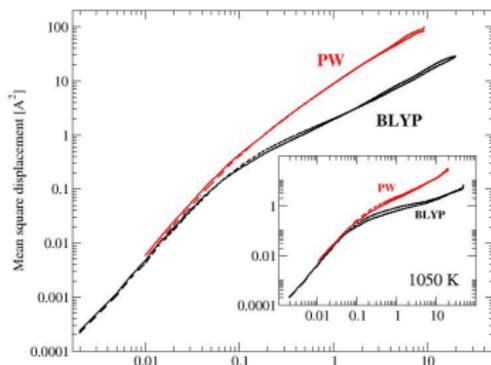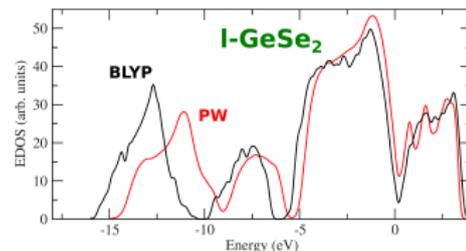
Density functional theory

EXCHANGE CORRELATION

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- Additional correction (dispersion forces)

$$E_{disp} = -s_6 \sum_i \sum_j \frac{C_{ij}}{R_{ij}^6} f_{damp}(R_{ij})$$
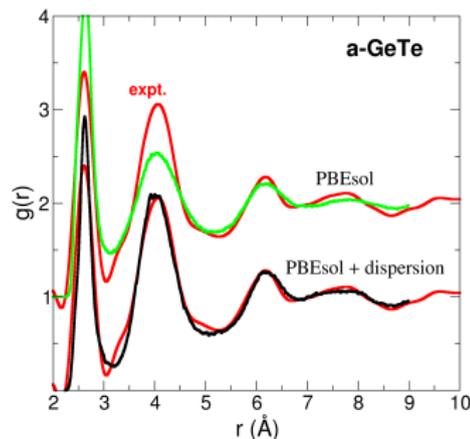
Micoulaut et al. PRB 96 (2017)

Density functional theory

EXCHANGE CORRELATION... IN SUMMARY

- Libraries of functionals routinely available.

- Aspects of accuracy problems encountered with classical force fields are also present in DFT calculations.

- Electronic treatment of the chemical bonding should not be overlooked.

- Check/compare your "candidate" functional with respect to experiments and results from other published functionals.

Implementation

PLANE WAVES

We are now trying to obtain the ground state (GS) energy and the electronic density

$$E_{GGA}^{GS} = min_{\Psi_i^{KS}} H_{KS}(\Psi_i^{KS}, n(\mathbf{r}))$$

- In quantum chemistry, one often expands Ψ_i^{KS} on a finite basis (Hilbert space, tight-binding), e.g. with atomic orbitals:

$$\left| \Psi_i^{KS} \right\rangle = \sum_I \sum_n C_{I,n}^i |\Phi_{I,n}\rangle$$

- **Advantages:** smart basis and small size. Properties are calculated in terms of atomic orbitals.
- **Disadvantages :** Basis depends on atomic positions. No systematic way to increase the basis size (precision). Delocalized states in an empty region are hard to describe (e.g. crystal vacancy).
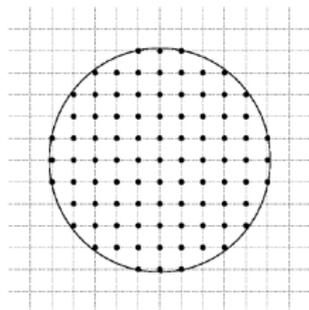
Implementation

PLANE WAVES

Plane wave basis set : Alternative for periodic systems : the basis functions of Ψ_i^{KS} can be expanded as plane waves.

$$\Psi_i^{KS} \propto \sum_{\mathbf{G}} c_i(\mathbf{G}) e^{i\mathbf{G}.\mathbf{r}}$$

with $\mathbf{G}$ a vector of the reciprocal lattice.

$$\mathbf{G} = \mathbf{i}.\frac{2\pi}{L_x} + \mathbf{j}.\frac{2\pi}{L_y} + \mathbf{k}.\frac{2\pi}{L_z}$$

- Infinite sum is the FT of the wavefunction.
- **Advantages:** Basis covers all space uniformly. Does not depend on positions (weak bonds), fast evaluation (FFT). Improvement related to a cutoff value E_{cutoff}.
- **Disadvantages:** Large number of basis needed. Wavefunction in the chemical bond region varies too rapidly (pseudopotentials).

Implementation

PLANE WAVES **A crucial parameter :** E_{cutoff}

- Kinetic energy associated with plane waves (PW, $T_0 \propto 1/2\partial_x^2$):
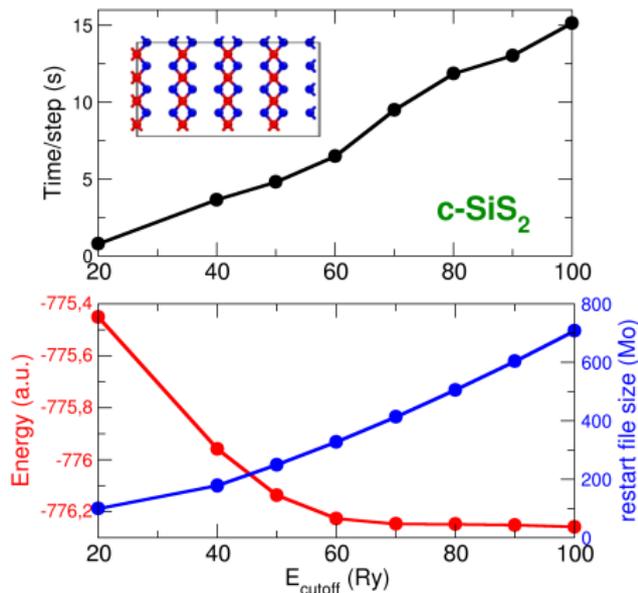
$$E_{cutoff} = \frac{1}{2} G_{max}^2$$

- Volume of the sphere containing all PW, volume occupied by a single PW :

$$V = \frac{4\pi}{3} G_{max}^3 \qquad V_{PW} = \frac{2\pi}{\Omega}$$

- Number of PWs :

$$N_G \propto \Omega E_{cutoff}^{3/2}$$

Properties converge with increasing cutoff value !

Implementation

PSEUDOPOTENTIALS

- Concept related to replacing the effects of the core electrons with an effective (pseudo) potential. Just the outer shell electrons participate in the chemical bonding.

- The pseudopotential generation procedure starts with the solution of the atomic problem (all electrons) using the Kohn-Sham approach.

- Once the KS orbitals are obtained, one makes an arbitrary distinction between valence and core states.

- The core states are assumed to change very little due to changes in the environment so their effect is replaced by a model potential derived in the atomic configuration and it is assumed to be transferable.

- Outside the core region, the pseudo-wavefunction coincides with the all electron calculation.

Implementation

PSEUDOPOTENTIALS

- General conditions for pseudo-potential generation

    1. All-electron and pseudo eigenvalues agree for the reference configuration.
    2. AE and PS wavefunctions agree beyond a certain cutoff value, r_c.

Hamann, et al. PRL 43, 1494 (

- Two opposing considerations :

    1. Good transferability small rc.
    2. Large rc smoother pseudopotentials.
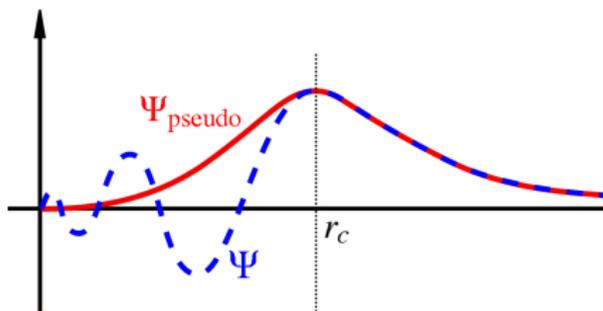
A good pseudopotential is one that strikes a balance between these two contraints.

Ab initio molecular dynamics

AB INITIO MOLECULAR DYNAMICS

We would now like to follow the positions **R** of the ions with time, in order to obtain the dynamics of liquids and glasses or to obtain vibrational dynamics (VDOS, IR,...). Two possible approaches :

- **Minimization technique:** Integration of the ion motion with Δt fixed by the largest ion frequency. After each ion move, re-minimization of Ψ. Born-Oppenheimer MD

$$m_i \ddot{\mathbf{R}}_i = -\frac{\partial}{\partial \mathbf{R}_i} min_{\Psi} \langle \Psi | H | \Psi \rangle$$

- **Fictitious ion dynamics:** Separation of the dynamics into ion (classical) and electronic (fictitious) dynamics. Newton's equation of motion for the ions is solved. Car-Parrinello MD

Ab initio molecular dynamics

Unified Approach for Molecular Dynamics and Density-Functional Theory

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and

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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 approach is demonstrated by the calculation of some static and dynamic properties of crystalline silicon within a self-consistent pseudopotential framework.

Ab initio molecular dynamics

CAR PARRINELLO MOLECULAR DYNAMICS

Reminder : Equations of motions from classical MD for *N* atoms with position $\mathbf{R_i}$

$$L\left(\mathbf{R}_i, \dot{\mathbf{R}}_i\right) = T_0\left(\dot{\mathbf{R}}_i\right) - V\left(\mathbf{R}_i\right)$$

From the momentum $\mathbf{p}_i = \partial L / \partial \dot{\mathbf{R}}_i$ and force $\mathbf{F}_I = \partial L / \partial \mathbf{R}_i$, one recovers Newton's equations from the Euler-Lagrange equation as :

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{\mathbf{R}}_i} = \frac{\partial L}{\mathbf{R}_i} \qquad \Longrightarrow \qquad \mathbf{p}_i = -\frac{\partial V}{\partial \mathbf{R}_i} \qquad \Longrightarrow \qquad m_i \ddot{\mathbf{R}}_i = \mathbf{F}_i$$

Ab initio molecular dynamics

CAR PARRINELLO MOLECULAR DYNAMICS

Postulated Lagrangian by Car and Parrinello (1985):

$$L = \sum_I \frac{1}{2} M_I v_I^2 + \sum_i \frac{1}{2} \mu_i \langle \dot{\Psi}_i | \dot{\Psi}_i \rangle - E\Big[\{\Psi\}, \{\mathbf{R}\} \Big] + \sum_{ij} \Lambda_{ij} \Big(\langle \Psi_i | \Psi_j \rangle - \delta_{ij} \Big)$$

nuclear   electron   potential   orbital
kinetic energy   "kinetic energy"   energy   orthogonality (L.M)

From Lagrangian mechanics, one obtains the equations of motion :

$$\frac{d}{dt} \frac{\partial L}{\partial \mathbf{v}} = \frac{\partial L}{\partial \mathbf{R}} \qquad \Longrightarrow \qquad M_I \ddot{\mathbf{R}} = -\frac{\partial V}{\partial \mathbf{R}}$$

$$\frac{d}{dt} \frac{\partial L}{\partial \langle \dot{\Psi}_i |} = \frac{\partial L}{\partial \langle \Psi_i |} \qquad \Longrightarrow \qquad \mu_i |\ddot{\Psi}_i\rangle = -\frac{\partial V}{\partial \langle \Psi_i |} + \sum_j \Lambda_{ij} |\Psi_j\rangle$$

Decoupling between a "real" ion dynamics (mass M_I) and the fictitious electronic dynamics (mass μ_i).

Ab initio molecular dynamics

THE CAR PARRINELLO MOLECULAR DYNAMICS RECIPE

1 For a given set of $\{\mathbf{R}_I\}$, within DFT minimize $V[\Psi_{KS}]$ to obtain Ψ_{KS}^{GS}.

$$V\left(\{\mathbf{R}_I\}\right) = min_\Psi \ V\left[\{\Psi_{KS}\}, \{\mathbf{R}_I\}\right]$$

**2** Compute the forces on the ions from :

$$\mathbf{F}_I = -\frac{\partial}{\partial \mathbf{R}_I} V\left(\{\mathbf{R}_I\}\right)$$

3 Move the ions with Newton's equation

4 Integration with Verlet algorithm to get a trajectory

$$\mathbf{R}_I(t + \Delta t) + \mathbf{R}_I(t - \Delta t) = 2\mathbf{R}_I(t) + \frac{\mathbf{F}_I}{M_I}(\Delta t)^2$$

Ab initio molecular dynamics

THE CAR PARRINELLO MOLECULAR DYNAMICS RECIPE

- **CPMD simulations of 249 atom $Ge_{10}As_{10}Se_{80}$**

- Δt=5 a.u. (0.24 fs), L=17.98 Å.

- $E_{cutoff} = 20\ Ry$, $BLYP$, μ=2000 a.u.

- Kinetic energy T_e of the electrons (electronic sub-system) remains small.

- Kohn-Sham energy E_{KS} equivalent to $V(r)$ in classical MD.

- $E_{classic} = E_{KS}$+ionic kinetic energy

- $E_H = E_{classic} + T_e$, the conserved parameter in CPMD

- Total energy E_H conserved.
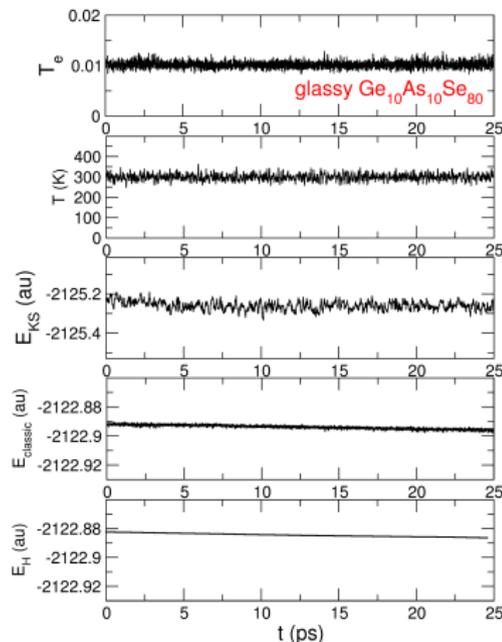
Ab initio molecular dynamics

CAR PARRINELLO VERSUS BORN-OPPENHEIMER
Simulations performed on liquid (1000 K) 93 B_2O_3 - 7 Li_2O (N=146 atoms)

Method	Time step (a.u.)	Convergence (a.u.)	Conservation (a.u./ps)	Time (s)
CP	5	-	6×10^{-8}	30 270
CP	7	-	1×10^{-7}	21 648
CP	10	-	3×10^{-7}	15 088
BO	10	10^{-6}	1×10^{-6}	155 492
BO	50	10^{-6}	1×10^{-6}	38 709
BO	100	10^{-6}	6×10^{-6}	21 088
BO	100	10^{-5}	1×10^{-5}	15 558
BO	100	10^{-4}	1×10^{-3}	9 934

Table: Timing in CPU seconds and energy minimization for 1 ps trajectory

Ab initio molecular dynamics

FICTITIOUS MASS OF THE ELECTRON (ADIABATICITY PARAMETER)

- **Meaning:** μ is non-physical parameter controlling the time-scale of the "classical" CP electronic dynamics.

- An optimal value permits to stay near the Born-Oppenheimer surface: an diabaticity separation between electronic and ionic motion.

- The electron "subsystem" must be kept "cold" (thermostats). In this case, the e-system remains close to GS and T_e is small.

- To avoid energy exchange between the nuclear and orbital degrees of freedom, power spectra should not overlap.

$$\omega_{ij} = \sqrt{\frac{2(E_i^{KS} - E_j^{KS})}{\mu}} \implies \omega_e^{min} \simeq \sqrt{\frac{2(E_{lumo} - E_{homo})}{\mu}} = \sqrt{\frac{2E_{gap}}{/\mu}} \gg \omega_{ions}^{Max}$$

FICTITIOUS MASS OF THE ELECTRON (ADIABATICITY PARAMETER)

- E_{cutoff}, E_{gap}, μ and timestep Δt_{max} are related.

- The highest frequency for the subsystem also depends on μ and constrains the maximum allowed MD timestep:

$$\Delta t_{max} \propto \frac{1}{\omega_e^{Max}} \propto \sqrt{\frac{\mu}{E_{cutoff}}}$$

- Commonly used values : μ=300-2000 a.u. Δt=0.1-0.2 fs.

Practical
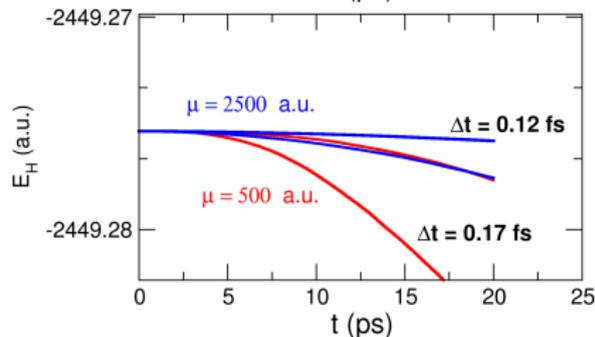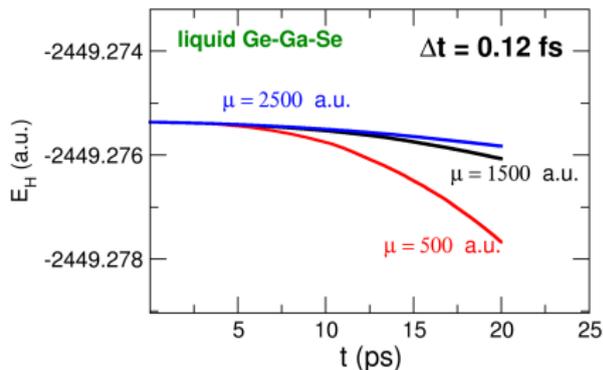
HOW TO GET STARTED

1. What you need to specify to run a DFT computation.
   - Coordinates
   - Exchange-correlation functionals: BLYP, PW, HS06, PBE...
   - Corresponding pseudopotentials
2. Packages
   - CPMD or Quantum Espresso (CP2K)
   - ABINIT
   - VASP
   - Wikipedia : List of quantum chemistry and solid-state physics software
3. Lectures
   - Detailed course on quantum chemistry, DFT, and ab initio methods.
   - CECAM tutorials   www.cecam.org
4. Analysis tools (similar to classical MD).

Practical

CONCLUSION

- Ab initio methods allow to investigate glass properties using atomic number as only input.

- Theoretical background provided by density functional theory (DFT).

- Additional approximations are needed to make DFT useful and applicable.

- Combination of DFT with dynamics through different techniques (minimisation, fictitious dynamics).

- **Next:** Application of ab initio methods to liquids and glasses