# LECTURE 12 : A survey of ab initio based MD

- Finding approximations
- Density functional theory
- Functionals
- Car Parrinello MD

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## Goals …

- ☐ We want to study glasses or glass-forming liquids without any prerequisite e.g. models coming from the force field (approximation in classical MD).

- ☐ Charge transfer in covalent systems or in metallic glasses.

  q=cst in most classical MD (Coulomb interaction)

- ☐ Description of other (e.g. spectroscopic) properties

  - X-ray, Raman, IR, XPS,…

## How ?

- ☐ Just solve Schrödinger equation $H\Phi=E\Phi$

- ☐ For large systems, there are basically 2 options

  - **Adiabatic approximation**: $e^-$ move faster than nucleus which can be considered as fixed.
  - **Mean field approximation** for the $e^-$ -$e^-$ correlation (DFT)

# A. BASICS

## 1. Finding approximations

- We write the Hamiltonian for molecules or solids

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

- 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 $\mathbf{r}_i$

- Can be also writtent under the simpler form:

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

**Electronic kinetic E**

**Electron-electron potential E**

**Electron-nucleus potential E**

**Nuclear kinetic E**

**Nucleus-nucleus potential E**

# A. BASICS

## 1. Finding approximations

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

- ☐ Adiabatic approximation. Since M=2000-100.000me, there are two different time scales: electrons and nuclei (ions).
  - ➢ Vibrational excitations: hω~10 meV
  - ➢ Electronic excitations: $h_{\omega e}$~1 eV
  - ➢ $\tau_{ion}$>>$\tau_e$…on the time scale of electrons, ions can be considered as frozen.

- ☐ **Consequence.** We can split the wavefunction into an e-part and a ion-part:

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

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

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

# A. BASICS

## 1. Finding approximations

☐ Adiabatic approximation, continued. **1)** We solve for a 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 $\Phi_e(r,R)$ and $E_e(R)$ (**Born-Oppenheimer surface**)

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

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

☐ **Common approximations:**

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

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

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

# A. BASICS

## 2. Solutions for the electronic Hamiltonian

- ❑ Reduction of complexity. We want to compute $\Phi(r_1,r_2,\ldots..r_{Nel})$

- ❑ Discretize space of each variable on a grid of $N_G$ grid points. To define $\Phi$, we need to specify $(N_G)^{Nel}$ values. Ugh ! **Many body problem !**

- ❑ Many properties can be reproduced by an independent electron approach. Description of the system with Nel single particle wavefunctions $\Phi_1$ having $N_G$Nel values. For total energy of the ground state, the best available method is **density functional theory**

- ❑ Many static or quasi-static can be obtained from derivatives of the total energy

  - ➢ Forces $-\dfrac{\partial E_e(\mathbf{R})}{\partial \mathbf{R}}$
  - ➢ Dynamic matrix (vibrations) $-\dfrac{\partial^2 E_e(\mathbf{R})}{\partial \mathbf{R}_i \partial \mathbf{R}_j}$
  - ➢ Polarisation $-\dfrac{\partial E_e(\mathbf{R})}{\partial \mathbf{E}_{elect}}$

# B. DENSITY FUNCTIONAL THEORY

❑ **Idea:** Systems with **interacting** electrons in a potential $V(\mathbf{r}) = -\sum_{i=1}^{N} \frac{Z_i e^2}{|\mathbf{r} - \mathbf{R}_i|}$

can be mapped onto a system with **non-interacting** electrons in a fictitious potential $V'(\mathbf{r}) \neq V(\boldsymbol{r})$ that has the same total energy and the same electronic density.

❑ Definition : *Density is the basic variable*.

❑ N interacting electrons in an external potential $V_{ext}(\mathbf{r})$ in a non degenerate groundstate. (GS) The ground state density is unique (non degenerate):

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

❑ It can be shown (Hohenberg- Kohn th.) that for the non-interacting electronic system, one has :

V’ext(**r**)=Vext(**r**)+const

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# B. DENSITY FUNCTIONAL THEORY

☐ The DFT functional is given by: $F[n] \equiv \langle \Psi_{GS}^{[n]} | T_e + V_{ee} | \Psi_{GS}^{[n]} \rangle$

with: $\int n(\mathbf{r}) d^3\mathbf{r} = N$

Universal functional (does not depend on a specific $V_{ext}(\mathbf{r})$).

☐ Energy of the system is : $E[n] = F[n] + \int n(\mathbf{r}) V_{ext}(\mathbf{r}) d^3\mathbf{r}$

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-elec. System that has $n_{GS}(\mathbf{r})$ as the ground state charge density.
- Defines the Kohn-Sham Hamiltonian $\mathcal{H}_{KS} \equiv \frac{p^2}{2m} + V_{KS}(\mathbf{r})$

# B. DENSITY FUNCTIONAL THEORY

☐ Given the KS Hamiltonian $\mathcal{H}_{KS} \equiv \frac{p^2}{2m} + V_{KS}(\mathbf{r})$

we find the eigenvector $|\Psi^i_{KS}\rangle$ with eigenvalue $\varepsilon^i_{KS}$ satisfying

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

☐ The KS exact functional then writes:

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

Ordinary DFT functional

But we define:

$$T_0[n] \;=\; \sum_{i=1}^{N/2} 2\langle \Psi^{i[n]}_{KS}|\frac{p^2}{2m}|\Psi^{i[n]}_{KS}\rangle \longleftarrow$$

**Kinetic energy of the KS system**

Universal functional of n

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

**Hartree Coulomb interaction**

**Classical interaction of the electrons**

# B. DENSITY FUNCTIONAL THEORY

- ☐ By definition, the exchange-correlation (XC) functional is:

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

- ☐ The total energy functional then writes:

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

- ☐ Note that T0 is not the kinetic part of the real interacting system but the fictitious non-interacting one.

- ☐ By construction, one has for the electronic density:

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

- ☐ **Conclusion**: All the difficult part is hidden in $E_{XC}$

# C. EXCHANGE-CORRELATION

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

with $$n_{XC}(\mathbf{r},\mathbf{r}'-\mathbf{r}) \equiv n(\mathbf{r}')\int_0^1 d\lambda[g(\mathbf{r},\mathbf{r}',\lambda)-1]$$

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

- $n_{XC}$ is the **exchange-correlation hole**, a quantum-mechanical zone surrounding every electron in an interacting system that reduces the probability P(**r**,**r'**) of finding other electrons within the immediate vicinity.

- Classically, one would have P(**r**,**r'**)~n(**r**)n(**r'**) (Hartree-Coulomb energy). But this neglects the possibility of (spin) symetry (Pauli **exchange interaction**)

- Exact results when $g(\mathbf{r},\mathbf{r}') \to 1$ (i.e. at infinity) or for other selected cases

# C. EXCHANGE-CORRELATION

- ☐ Otherwise…approximations
  - ➢ Local density approximation (LDA) $E_{XC}[n] \simeq E_{XC}^{LDA}[n]$
  - ➢ Generalized gradient approximation (GGA) $E_{XC}[n] \simeq E_{XC}^{GGA}[n]$

☐ **Local density approximation**: $$E_{XC}^{LDA}[n] \equiv \int d^3\mathbf{r}\, n(\mathbf{r})\, \varepsilon(n(\mathbf{r}))$$

assuming that $\varepsilon(n(\mathbf{r}))$ is just a function of the local electronic density.

- ☐ Advantage: $\varepsilon(n(\mathbf{r}))$ is the exchange and correlation energy per electron of a homogeneous interacting electron gas. Exact for this system.

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

# C. EXCHANGE,-CORRELATION

- ❑ **Generalized gradient approximation:** the functional now also depends on the local gradient of n(r).

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

- ❑ Gradient expansion of the exchange-correlation hole

**Perdew et al. PRL 1999**

- ❑ Provides better geometries for weak bonds which are too short in LDA. Better total energies (e.g. atomisation).

| Solid | $a^{\mathrm{LDA}}$ | $a^{\mathrm{GGA}}$ | $a^{\mathrm{expt}}$ |
|---|---|---|---|
| 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 |
| GaAs | 5.61 | 5.76 | 5.65 |
| Cu | 3.52 | 3.63 | 3.60 |
| W | 3.14 | 3.18 | 3.16 |
| Mean abs. error | 0.078 | 0.051 | ⋯ |

Lattice constants a (in A) for some solids

# C. EXCHANGE,-CORRELATION

- **Generalized gradient approximation:**

$E_{xc}$ often break up into exchange (e.g. Becke, B) and correlation functionals (e.g. Lee, Yang and Parr, LYP).  Or Perdew-Wang (PW91).

$$\varepsilon_{xc}(\rho(\vec{r})) = \varepsilon_x(\rho(\vec{r})) + \varepsilon_c(\rho(\vec{r}))$$

**LDA** $$\varepsilon_x(\rho(\vec{r})) = -\frac{3}{4}\left(\frac{3\rho(\vec{r})}{\pi}\right)^{1/3}$$

Coulomb correlation
Interpolated by **Ceperley et Alder 1980**

$$E_x^{CGA} = E_x^{LDA} - \sum_{\sigma} F(s_\sigma)\rho_\sigma^{4/3}(\vec{r})d\vec{r} \qquad s_\sigma = \frac{|\nabla \rho|}{\rho_\sigma^{4/3}}$$

**Becke & Perdew/Wang: BPW91**

**Becke & Lee/Parr/Yang: BLYP**

$$F^{B} = \frac{\beta s_\sigma}{1 + 6\beta s_\sigma \mathrm{Sinh}^{-1}(s_\sigma)}$$

**Becke, 1988**

# C. EXCHANGE-CORRELATION

**Perspectives and conclusions**:

- Modelling of such XC functions beyond the scope of the lecture.
- Generation of $E_{XC}$ approximations is still a large and still rapidly expanding field of research.

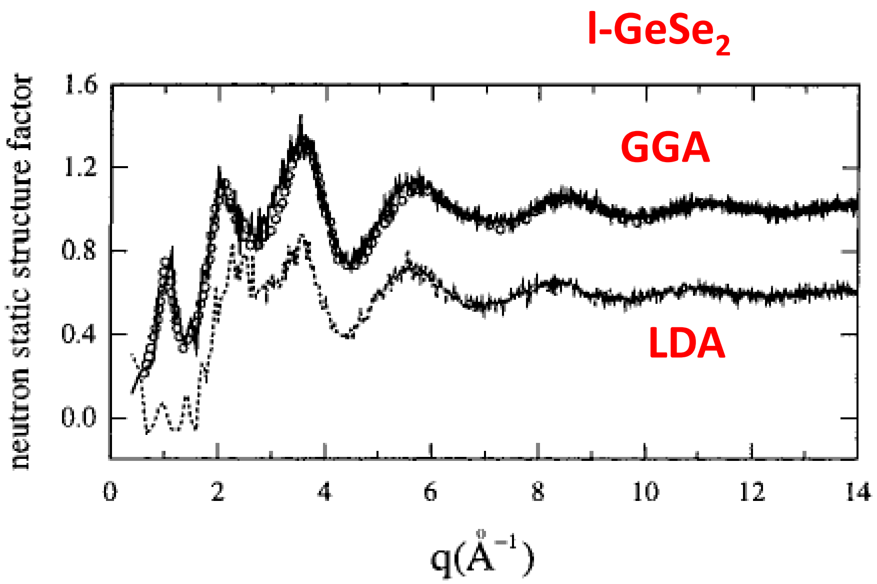

**Figure 1.** Neutron structure factor S(*q*) as a function of magnitude of momentum transfer *q* for liquid GeSe$_2$, obtained within GGA (solid line) and LDA (dots), compared to experiment (circles), ref 8. For clarity, the LDA curve is displaced downward by 0.4. We used scattering lengths of $b^{Ge} = 8.189$ fm and $b^{Se} = 7.97$ fm.

Massobrio et al. JACS 1999

- Many different flavours of functional available which are more or less appropriate for any particular study.
- Ultimately the choice $E_{XC}$ of must be made in terms of results (direct comparison with experimental data).

# D. IMPLEMENTATION

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

$$E_{GGA}^{GS} = min_{\Psi_i^{KS}} \left[ T_0[\{\Psi_i^{KS}\}] + E_{KS}^{GGA}[n(\mathbf{r})] \right]$$

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

- ☐ **In a practical calculation,** one uses a variational approach and expands $\Psi_i^{KS}$ on a finite basis (Hilbert space), e.g. with **atomic orbitals** (most common approach in quantum chemistry):

  I ions, n Q numbers $$|\Psi_i^{KS}\rangle = \sum_I \sum_n C_{In}^i |\Phi_{I,n}\rangle$$

- ☐ Advantages: smart basis and small size. Tight-binding approach. Properties are calculated in terms of atomic orbitals.

- ☐ Disadvantages: Basis depends on atomic position. No systematic way to increase the basis, delocalized states in en empty region are hard to describe (e- in a crystal vacancy).

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# D. IMPLEMENTATION

- ☐ **Plane-wave basis set.** Alternative for periodic systems (Bloch's theorem): $\Psi_i^{KS}$ can be written as the product of the lattice periodic part (e.g. reciprocal lattice vectors **G**) and a wavelike part.

$$|\Psi_{i,\mathbf{q}}^{KS}\rangle = e^{i\mathbf{q}.\mathbf{r}} \sum_{\mathbf{G}} C_{\mathbf{G}}^{i,\mathbf{q}} |\mathbf{G}\rangle$$

Exact if the basis set is infinite, otherwise fixed by an energy cutoff $E_{cutoff.}$

- ☐ Advantage: Basis covers all space uniformaly, does not depend on position (good for weak bonds), simple and fast evaluation, fixed by a single parameter $E_{cutoff}$.

- ☐ Disadvantages: To have a converged result with reasonable small $E_{cutoff}$, one describes only valence electrons. Need of pseudopotentials.

**Pseudopotentials.** Concept related to replacing the effects of the core electrons with an effective potential.

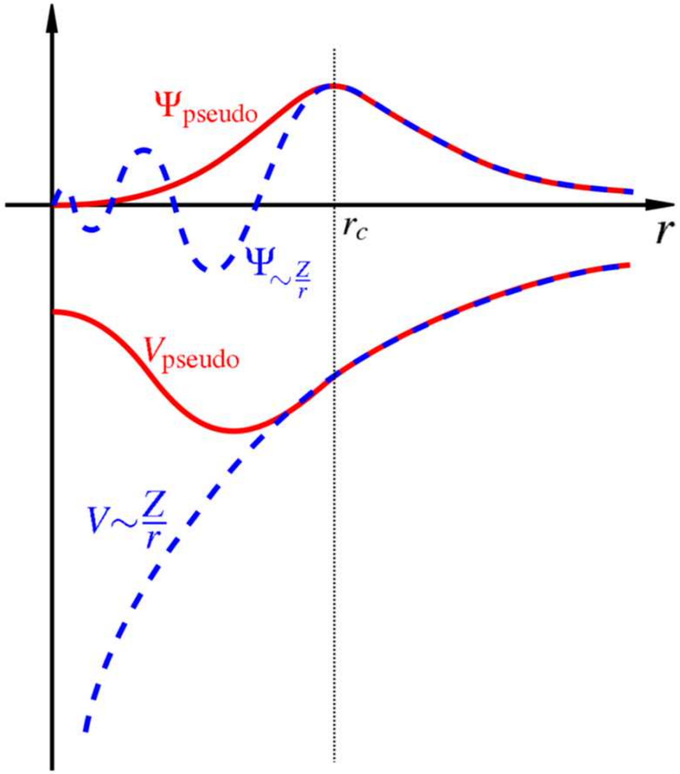
# D. IMPLEMENTATION

**Pseudopotentials.** Concept related to replacing the effects of the core electrons with an effective 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.

**Refs. Blöchl, PRB 50, 17953 (1994).**

# D. IMPLEMENTATION



☐ General conditions for pseudo-potential generation (Hamann, et al. PRL 43, 1494 (1979).

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

☐ **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.

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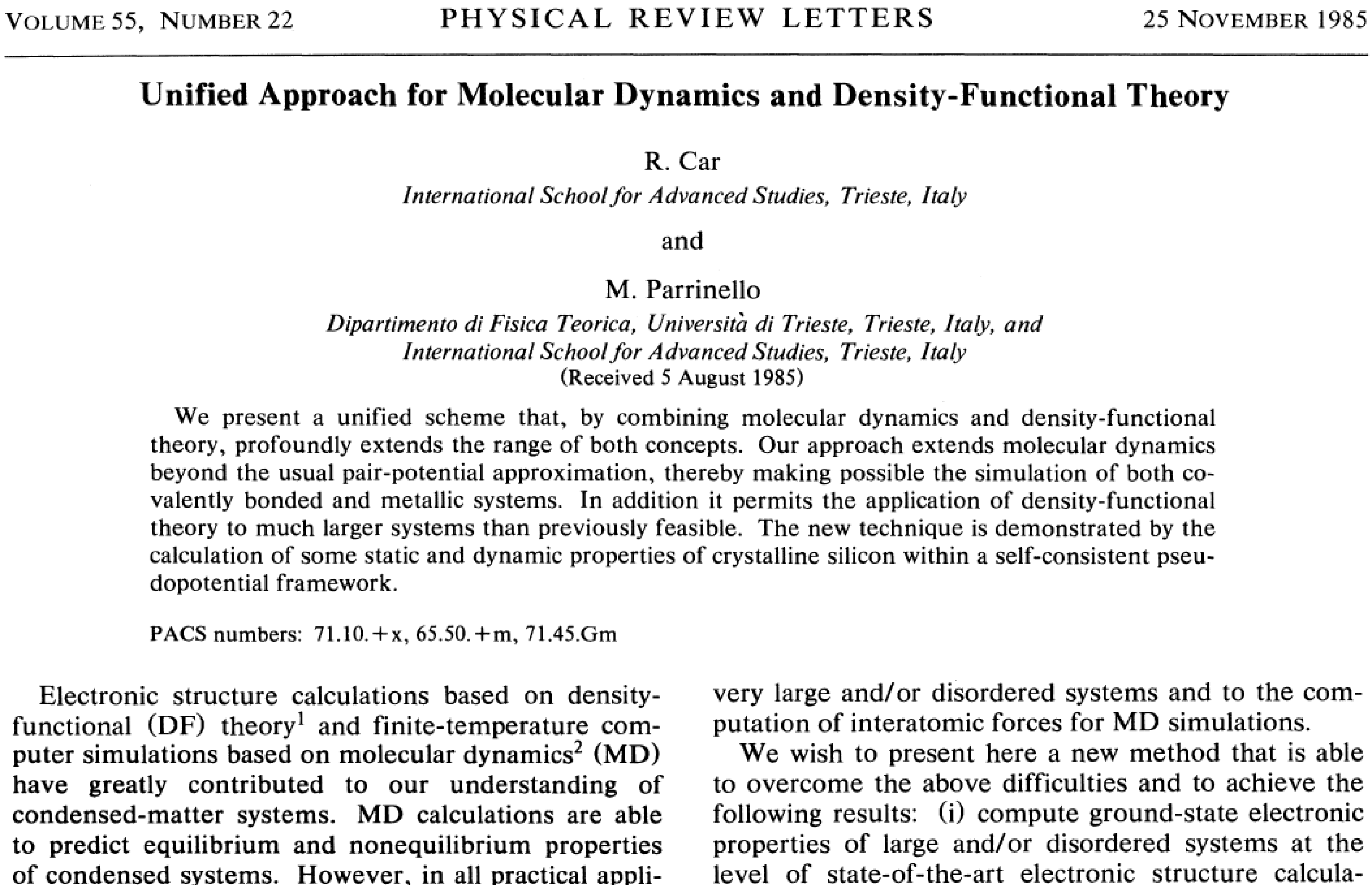
# E. MOLECULAR DYNAMICS



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

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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.

PACS numbers: 71.10.+x, 65.50.+m, 71.45.Gm

Electronic structure calculations based on density-functional (DF) theory[1] and finite-temperature computer simulations based on molecular dynamics[2] (MD) have greatly contributed to our understanding of condensed-matter systems. MD calculations are able to predict equilibrium and nonequilibrium properties of condensed systems. However, in all practical appli-

very large and/or disordered systems and to the computation of interatomic forces for MD simulations.

We wish to present here a new method that is able to overcome the above difficulties and to achieve the following results: (i) compute ground-state electronic properties of large and/or disordered systems at the level of state-of-the-art electronic structure calcula-

# E. MOLECULAR DYNAMICS

- ☐ *"We present a unified scheme that, by combining molecular dynamics and density-functional theory, profoundly extends the range of both concepts."*

  R. Car and M. Parrinello, Phys. Rev. Lett. 55, 2471-2474 (1985).

- ☐ **Car-Parrinello Molecular Dynamics (CPMD)**. Idea: Split the dynamics (as expected from Lagrangian) into ion (classical) and electronic (fictitious) dynamics. Newton's equation of motion **for the ions** is solved:

$$\boxed{M_I \frac{d^2\mathbf{R_I}}{dt^2} = \mathbf{F}_I}$$

the forces being calculated from the electronic density, via:

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

$$V\Big(\{\mathbf{R}_I\}\Big) = min_{\Psi_{KS}}\, E^{GGA}\Big[\{\Psi_{KS}\},\{\mathbf{R}\}\Big] = E^{GGA}\Big[\{\Psi_{KS}^{GS}\},\{\mathbf{R}\}\Big]$$

plus some usual (classical) MD ingredients (Verlet algorithm, time step,…)

# E. MOLECULAR DYNAMICS

☐ Minimization technique in CPMD

1. For a given set of {R}, minimize E[$\Psi_{KS}$] to obtain $\Psi_{KS}^{GS}$
2. Compute the forces on the ions from $\Psi_{KS}^{GS}$
3. Move the ions with the Newton equation

☐ Car Parrinello fictitious dynamics:

**μ Fictitious electronic mass**

$$\boxed{\mu\frac{d^2|\Psi^i_{KS}}{dt^2} = -\frac{\partial}{\partial\langle\Psi^i|}E^{GGA}[\Psi_{KS},\mathbf{r}]}$$

plus

$$M_I\frac{d^2\mathbf{R_I}}{dt^2} = -\frac{\partial}{\partial\mathbf{R_I}}E^{GGA}\Big[\{\Psi_{KS}\},\{\mathbf{R}\}\Big] = -2\sum_{i=1}^{N/2}2\langle\Psi^i_{KS}|\frac{\partial V_{ext}}{\partial\mathbf{R}}|\Psi^i_{KS}\rangle$$

☐ Conserved energy is:

$$\frac{1}{2}M_I|\frac{d\mathbf{R_I}}{dt}|^2+\mu\sum_i\langle\frac{d\Psi^i_{KS}\rangle}{dt}|\frac{d\Psi^i_{KS}}{dt}\rangle+E^{GGA}[\Psi_{KS},\mathbf{R}]$$

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# E. MOLECULAR DYNAMICS

**Meaning of the fictitious electronic mass μ:**

- “Non-physical" parameter controlling the time scale of the "classical" Car Parrinello electronic dynamics.

- Close to the minimum $\Psi^i_{KS}$ , $\Psi_{KS}$ oscillates at frequencies

$$\omega_{electron} = \sqrt{\frac{2(E_e^{KS} - E_o^{KS})}{\mu}}$$

with $E_e^{KS}$ and $E_o^{KS}$ the eigenvalues of empty/occupied states, so that a minimum frequency is

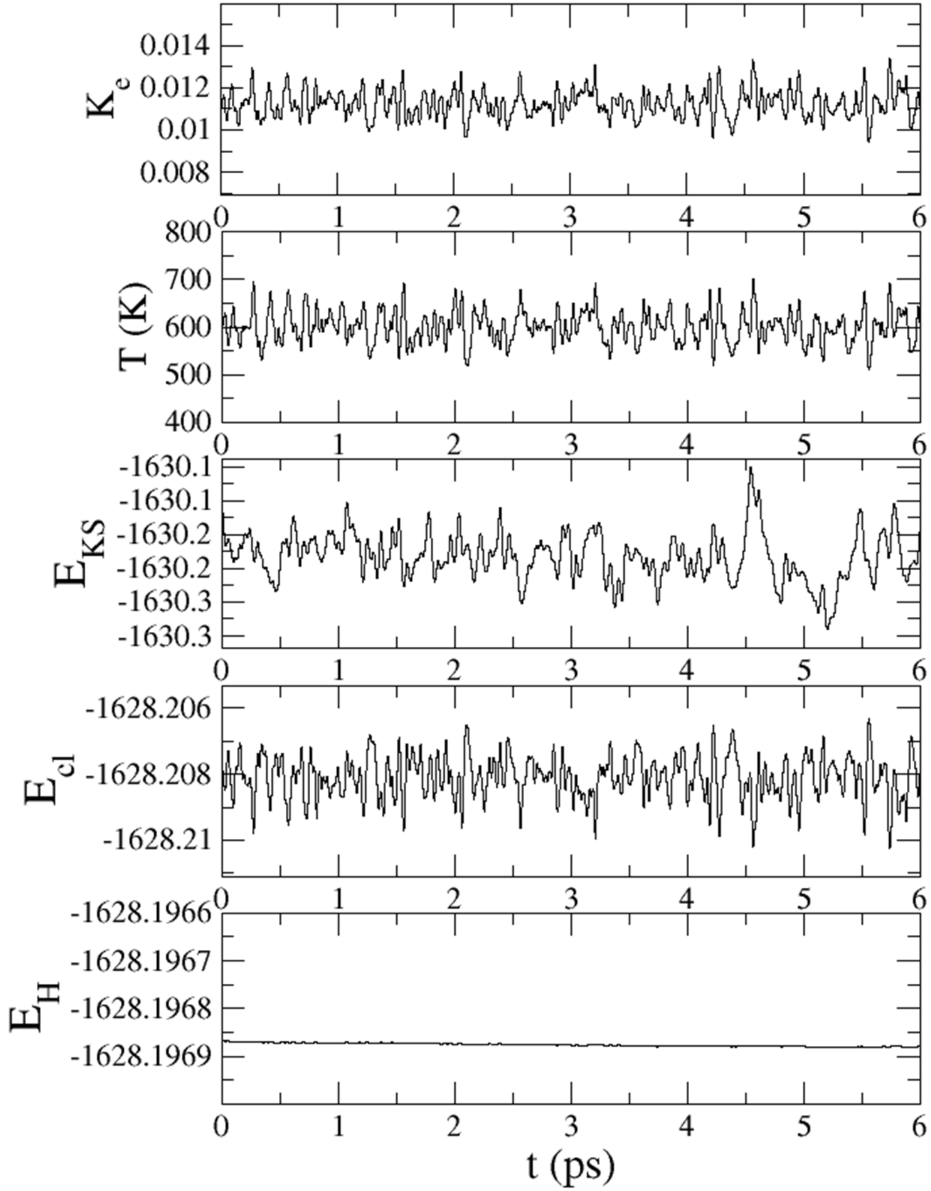
$$\omega_{min}^{electron} \simeq \sqrt{\frac{2E_{gap}}{\mu}}$$

- To be sure of adiabatic separation between artificial electronic and real ionic motion, one must have :

$$\omega^{ions} \ll \omega_{min}^{electron} \simeq \sqrt{\frac{2E_{gap}}{\mu}}$$

In this case, the electronic system remains near the ground state and $K_e$ is small.

# E. MOLECULAR DYNAMICS



**CPMD simulation of 200 atomic $As_2Se_3$**
t=10 a.u. (0.24 fs)
L=17.98 A
Trouillier-Martins pseudos
Ecut=20 Ry
BLYP functional
m=2000 a.u.

- Kinetic energy of the electrons Ke remains small.
- Total energy EH conserved

# F. GETTING STARTED

- ☐ **What you need to specify to run a DFT computation**
  - Basis set
  - Coordinates
  - Exchange functional: B, B3, etc.
  - Correlation functional: LYP, PW91, etc.

- ☐ **Packages**

| | |
|---|---|
| **CPMD** | *www.**cpmd.org*** |
| ***ABINIT*** | *www.**abinit**.org* |
| ***VASP*** | *https://www.**vasp**.at* |
| ***Fireball*** | ***http://fireball-dft**.org* |

- ☐ **Lectures.** Need of a detailed course on quantum chemistry, DFT, and ab initio methods.
  - CECAM tutorials *www.**cecam.org/***
  - Salanne-Vuilleumier lectures on CPMD- CP2K http://www.pecsa.upmc.fr/spip.php?rubrique155

# Conclusion

- ☐ Ab initio methods allow to investigate materials 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

- ☐ The combination of DFT with MD is provided through the Car-Parrinello approach involving the fictitious dynamics of the electron.

**Next (last) lecture:** Application of ab initio methods to glasses
**Home reading: The impact of DFT on Materials research**

**Useful references:**

- D. Marx and J. Hutter, *Ab Initio Molecular Dynamics : Basic Theory and Advanced Methods*. Cambridge University Press, 2009.

- R. Vuilleumier, *Density functional theory based ab initio molecular dynamics using the Car-parrinello approach*, Lect. Notes Phys., 703(1) :223–285, 2006.