LECTURE 12: A survey of ab initio based MD
- Finding approximations
- Density functional theory
- Functionals
- Car Parrinello MD
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.
  - \( q = \text{cst} \) 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

- 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 written under the simpler form:

$$\mathcal{H} = \sum_{i=1}^{n} \frac{p_i^2}{2m} + \frac{1}{2} \sum_{j,i \neq j}^{n} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i=1}^{n} \sum_{l=1}^{n} \frac{Z_i e^2}{|\mathbf{r}_i - \mathbf{R}_l|} + \sum_{l=1}^{N} \frac{p_l^2}{2M_l} + \frac{1}{2} \sum_{k,l \neq k}^{N} \frac{Z_k Z_l e^2}{|\mathbf{R}_k - \mathbf{R}_l|}$$

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

- 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=2000-100,000 me, there are two different time scales: electrons and nuclei (ions).
  - Vibrational excitations: \( h\omega \approx 10 \text{ meV} \)
  - Electronic excitations: \( h\omega_e \approx 1 \text{ eV} \)
  - \( \tau_{\text{ion}} \gg \tau_e \)...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:
  \[ \Psi_{i,l}(r,R) \equiv \chi_{i,l}(R) \cdot \Phi_e(r,R) \]
  \[ \begin{bmatrix} T_e + V_{ee} + V_{en}(R) + V_{nn}(R) \end{bmatrix} \Phi_e(r,R) = E_e(R) \Phi_e(r,R) \]
  \[ \begin{bmatrix} T_n + E_e(R) \end{bmatrix} \chi_{i,l}(R) = E_{i,e} \chi_{i,l}(R) \]
A. BASICS

1. Finding approximations

- Adiabatic approximation, continued. 1) We solve for a parameter $R$

$$
\begin{bmatrix}
T_e + V_{ee} + V_{eN}(R) + V_{NN}(R)
\end{bmatrix} \Phi_e(r, R) = E_e(R) \Phi_e(r, R)
$$

to obtain $\Phi_e(r, R)$ and $E_e(R)$ (Born-Oppenheimer surface)

2) Knowing $E_e(R)$, we solve

$$
\begin{bmatrix}
T_n + E_e(R)
\end{bmatrix} \chi_{i,l}(R) = E_{i,e} \chi_{i,l}(R)
$$

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

$$
E_e(R) \simeq E_e(R_0) + \frac{1}{2!} (R - R_0)^2 \frac{\partial^2 E_I(R)}{\partial R^2} + ...
$$
  
  - 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 $\Phi(r_1, r_2, \ldots, r_{\text{Nel}})$

- Discretize space of each variable on a grid of $N_G$ grid points. To define $\Phi$, we need to specify $(N_G)^{\text{Nel}}$ 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 $N_G\text{Nel}$ 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 $- \frac{\partial E_e(R)}{\partial R}$
  - Dynamic matrix (vibrations) $- \frac{\partial^2 E_e(R)}{\partial R_i \partial R_j}$
  - Polarisation $- \frac{\partial E_e(R)}{\partial E_{\text{elect}}}$
B. DENSITY FUNCTIONAL THEORY

- **Idea:** Systems with interacting electrons in a potential $V(r) = - \sum_{i=1}^{N} \frac{Z_i e^2}{|r - R_i|}$ can be mapped onto a system with non-interacting electrons in a fictitious potential $V'(r) \neq V(r)$ that has the same total energy and the same electronic density.

- **Definition:** Density is the basic variable.

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

  $$n(r) = N \int \int \Psi^*_\text{GS}(r, r_2, r_3, ..., r_N) \Psi_\text{GS}(r, r_2, r_3, ..., r_N) d^3 r_2 d^3 r_3 ... d^3 r_N$$

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

  $$V'_{\text{ext}}(r) = V_{\text{ext}}(r) + \text{const}$$
B. DENSITY FUNCTIONAL THEORY

- The DFT functional is given by:
  \[ F[n] = \langle \Psi_{GS}^n | T_e + V_{ee} | \Psi_{GS}^n \rangle \]
with:
\[ \int n(r)d^3r = N \]

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

- Energy of the system is:
  \[ E[n] = F[n] + \int n(r)V_{ext}(r)d^3r \]
and minimized by the ground state density
  \[ E[n_{GS}] = E_{GS} \]

- Kohn-Sham approach:
  - Given an interacting GS charge density \( n_{GS}(r) \) of a N electron system
  - There exists just one external potential \( V_{KS}(r) \) for a non-interacting N-elec.
    System that has \( n_{GS}(r) \) as the ground state charge density.
  - Defines the Kohn-Sham Hamiltonian
  \[ \mathcal{H}_{KS} = \frac{p^2}{2m} + V_{KS}(r) \]
B. DENSITY FUNCTIONAL THEORY

- Given the KS Hamiltonian
  \[ \mathcal{H}_{KS} \equiv \frac{p^2}{2m} + V_{KS}(r) \]
  we find the eigenvector \( |\Psi_{KS}^i\rangle \) with eigenvalue \( E_{KS}^i \)
  satisfying

\[ n(r) = 2 \sum_{i=1}^{N/2} \langle \Psi_{KS}^i | r \rangle \langle r | \Psi_{KS}^i \rangle \]

- The KS exact functional then writes:
  \[ E[n] = F[n] + \int n(r) V_{ext}(r) d^3r \]
  Ordinary DFT functional

But we define:

\[ T_0[n] = \sum_{i=1}^{N/2} 2 \langle \Psi_{KS}^i | \frac{p^2}{2m} | \Psi_{KS}^i \rangle \]
Kinetic energy of the KS system
Universal functional of \( n \)

\[ E_H[n] = \frac{1}{2} \int \int d^3r d^3r' \frac{e^2 n(r)n(r')}{|r-r'|} \]
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:
  \[ E[n] = T_0[n] + E_H[n] + E_{XC}[n] + \int n(\mathbf{r})V_{\text{ext}}(\mathbf{r})d^3\mathbf{r} \]
  \[ = T_0[n] + E_{KS}[n] \]

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

- **Conclusion:** All the difficult part is hidden in \( E_{XC} \)
C. EXCHANGE-CORRELATION

- We want to calculate:

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

with

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

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

- \( n_{\text{XC}} \) 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 \( P(r, r') \sim n(r)n(r') \) (Hartree-Coulomb energy). But this neglects the possibility of (spin) symmetry (Pauli exchange interaction).

- Exact results when \( g(r, r') \to 1 \) (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:
  \[ E_{XC}^{LDA}[n] \equiv \int d^3 r \ n(r) \ \epsilon(n(r)) \]

assuming that \( \epsilon(n(r)) \) is just a function of the local electronic density.

- Advantage: \( \epsilon(n(r)) \) 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 \( n(r) \).

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

- Gradient expansion of the exchange-correlation hole

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

**Lattice constants a (in A) for some solids**

<table>
<thead>
<tr>
<th>Solid</th>
<th>( a_{\text{LDA}} )</th>
<th>( a_{\text{GGA}} )</th>
<th>( a_{\text{expt}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>4.05</td>
<td>4.20</td>
<td>4.23</td>
</tr>
<tr>
<td>NaCl</td>
<td>5.47</td>
<td>5.70</td>
<td>5.64</td>
</tr>
<tr>
<td>Al</td>
<td>3.98</td>
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<td>4.05</td>
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<tr>
<td>Si</td>
<td>5.40</td>
<td>5.47</td>
<td>5.43</td>
</tr>
<tr>
<td>Ge</td>
<td>5.63</td>
<td>5.78</td>
<td>5.66</td>
</tr>
<tr>
<td>GaAs</td>
<td>5.61</td>
<td>5.76</td>
<td>5.65</td>
</tr>
<tr>
<td>Cu</td>
<td>3.52</td>
<td>3.63</td>
<td>3.60</td>
</tr>
<tr>
<td>W</td>
<td>3.14</td>
<td>3.18</td>
<td>3.16</td>
</tr>
</tbody>
</table>

Mean abs. error: 0.078 for LDA, 0.051 for GGA.
C. EXCHANGE,-CORRELATION

- Generalized gradient approximation:

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

\[ E_{xc}(\rho(\vec{r})) = E_x(\rho(\vec{r})) + E_c(\rho(\vec{r})) \]

\[ E_x^{LDA}(\rho(\vec{r})) = -\frac{3}{4} \left( \frac{3\rho(\vec{r})}{\pi} \right)^{1/3} \]

\[ E_x^{CGA} = E_x^{LDA} - \sum_{\sigma} F(s_\sigma) \rho_\sigma^{4/3}(\vec{r})d\vec{r} \]

\[ s_\sigma = \frac{\nabla \rho_\sigma}{\rho_\sigma^{4/3}} \]

\[ F^B = \frac{\beta s_\sigma}{1 + 6 \beta s_\sigma \sinh^{-1}(s_\sigma)} \]

Becke, 1988

Becke & Perdew/Wang: BPW91
Becke & Lee/Parr/Yang: BLYP

Coulomb correlation
Interpolated by Ceperley et Alder 1980
C. EXCHANGE-CORRELATION

Perspectives and conclusions:

- Modelling of such XC functions beyond the scope of the lecture.
- Generation of $E_{\text{XC}}$ approximations is still a large and still rapidly expanding field of research.
- Many different flavours of functional available which are more or less appropriate for any particular study.
- Ultimately the choice $E_{\text{XC}}$ of must be made in terms of results (direct comparison with experimental data).

**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 $\delta_{\text{Ge}} = 8.189$ fm and $\delta_{\text{Se}} = 7.97$ fm.

Massobrio et al. JACS 1999
D. IMPLEMENTATION

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

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

\[
n(r) = 2 \sum_{i=1}^{N/2} \langle \Psi_{i}^{KS} | r \rangle \langle r | \Psi_{i}^{KS} \rangle
\]

- **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):

  1 ions, n Q numbers

  \[
  | \Psi_{i}^{KS} \rangle = \sum_{l} \sum_{n} C_{ln}^{i} | \Phi_{l,n} \rangle
  \]

- **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 an empty region are hard to describe (e- in a crystal vacancy).
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.

\[
|\Psi_{i,q}^{KS}\rangle = e^{i\mathbf{q}\cdot\mathbf{r}} \sum_{\mathbf{G}} C_{G}^{i,q} |\mathbf{G}\rangle
\]

Exact if the basis set is infinite, otherwise fixed by an energy cutoff \( E_{\text{cutoff}} \).

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

- **Disadvantages:** To have a converged result with reasonable small \( E_{\text{cutoff}} \), 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.

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.
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 applications, 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.”

- 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:
  \[ M_I \frac{d^2 R_I}{dt^2} = F_I \]
  the forces being calculated from the electronic density, via:

  \[ F_I = - \frac{\partial}{\partial R_I} V \left( \{ R_I \} \right) \]

  \[ V \left( \{ R_I \} \right) = \min_{\Psi_{KS}} E_{GGA}^{GGA} \left[ \{ \Psi_{KS} \}, \{ R \} \right] = E_{GGA}^{GGA} \left[ \Psi_{GS}^{KS}, \{ R \} \right] \]

  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:

\[
\begin{align*}
\mu \frac{d^2 |\Psi_i^{KS}\rangle}{dt^2} &= -\frac{\partial}{\partial \langle \Psi_i \rangle} E^{GGA}[\Psi_{KS}, \mathbf{r}] \\
M_I \frac{d^2 \mathbf{R}_I}{dt^2} &= -\frac{\partial}{\partial \mathbf{R}_I} E^{GGA}[\{|\Psi_{KS}\rangle, \{R\}|] = \sum_{i=1}^{N/2} 2 \langle \Psi_i^{KS} | \frac{\partial V_{ext}}{\partial \mathbf{R}} | \Psi_i^{KS} \rangle
\end{align*}
\]

- Conserved energy is:

\[
\frac{1}{2} M_I \left| \frac{d \mathbf{R}_I}{dt} \right|^2 + \mu \sum_i \left( \frac{d |\Psi_i^{KS}\rangle}{dt} \right) \left( \frac{d |\Psi_i^{KS}\rangle}{dt} \right)^* + E^{GGA}[\Psi_{KS}, \mathbf{R}]
\]
E. MOLECULAR DYNAMICS

Meaning of the fictitious electronic mass $\mu$:

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

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

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

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

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

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

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

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

CPMD simulation of 200 atomic $\text{As}_2\text{Se}_3$

- $t=10$ a.u. (0.24 fs)
- $L=17.98$ Å
- Trouillier-Martins pseudos
- $E_{\text{cut}}=20$ Ry
- BLYP functional
- $m=2000$ a.u.

- Kinetic energy of the electrons $K_e$ remains small.
- Total energy $E_H$ 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](http://www.cpmd.org)
  - ABINIT [www.abinit.org](http://www.abinit.org)
  - VASP [https://www.vasp.at](https://www.vasp.at)
  - Fireball [http://fireball-dft.org](http://fireball-dft.org)

- Lectures. Need of a detailed course on quantum chemistry, DFT, and ab initio methods.
  - CECAM tutorials [www.cecam.org/](http://www.cecam.org/)
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:**