AB-INITIO SIMULATIONS IN MATERIALS SCIENCE

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Overview I

- Levels of computer-simulations in materials science
- Born-Oppenheimer approximation
  - Decoupling ions and electrons
  - Hellmann-Feynman theorem
- Ab-initio electronic structure methods
  - Hartree-Fock (HF) and post-HF approaches
  - Density-functional theory (DFT)
  - Local density approximation

Overview II

- DFT methods - an overview
    - Density-only approaches
        - Thomas-Fermi theory
    - Parametrization of the density in terms of orbitals
        - Kohn-Sham theory
    - Choice of a basis-set
        - Plane waves vs. local orbitals
        - Pseudopotentials vs. all-electron methods
    - Solving the Kohn-Sham equations
        - Total-energy minimization: Car-Parrinello dynamics
        - Iterative diagonalization

Levels of materials modelling

- Ab-initio techniques

  Hartree-Fock and post-HF techniques - Quantum chemistry

  Density functional techniques - Materials science

- Tight-binding techniques

- Force-field simulations

  Molecular dynamics

  Monte Carlo

Born-Oppenheimer approximation I

Hamiltonian of the coupled electron-ion system:

N ions, coordinates $\vec{R}_1,\ldots,\vec{R}_N \equiv \vec{R}$, momenta $\vec{P}_1,\ldots,\vec{P}_N \equiv \vec{P}$, charges $Z_1,\ldots,Z_N$, masses $M_I,\ldots,M_n$

N_e electrons, coordinates $\vec{r}_1,\ldots,\vec{r}_N \equiv \vec{r}$, momenta $\vec{p}_1,\ldots,\vec{p}_N \equiv \vec{p}$, mass m

$$\begin{aligned} H &= \sum_{I=1}^{N} \frac{\vec{P}_I^2}{2M_I} + \sum_{i=1}^{N_e} \frac{\vec{p}_i^2}{2m} + \sum_{i>j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \sum_{I>J} \frac{Z_I Z_J e^2}{|\vec{R}_i - \vec{R}_J|} - \sum_{i,I} \frac{Z_I e^2}{|\vec{R}_I - \vec{r}_i|} \\ &= T_N + T_e + V_{ee}(\vec{r}) + V_{NN}(\vec{R}) + V_{Ne}(\vec{r},\vec{R}) \end{aligned} \tag{1}$$

Schrödinger equation

$$[T_N + T_e + V_{ee}(\vec{r}) + V_{NN}(\vec{R}) + V_{Ne}(\vec{r},\vec{R})]\Phi(x,\vec{R}) = E\Phi(x,\vec{R}) \tag{2}$$

$x \equiv (\vec{r},s)$ full set of electronic positions and spin variables

Born-Oppenheimer approximation II

Difference in the time-scales of nuclear and electronic motions $\longrightarrow$ quasi-separable ansatz

$$\Phi(x,\vec{R}) = \Psi(x,\vec{R})\chi(\vec{R}) \tag{3}$$

$\Psi(x,\vec{R})$ electronic wavefunction, $\chi(\vec{R})$ nuclear wavefunction
$\chi(\vec{R})$ is more localized than $\Psi(x,\vec{R})$ $\longrightarrow \nabla_I\chi(\vec{R}) \gg \nabla_I\Psi(x,\vec{R})$ $\longrightarrow$
decoupled adiabatic Schrödinger equations of electrons and nuclei

$$\begin{aligned} [T_e + V_{ee}(\vec{r}) + V_{eN}(\vec{r},\vec{R})]\Psi_n(x,\vec{R}) &= \varepsilon_n(\vec{R})\Psi_n(x,\vec{R}) \\ [T_N + V_{NN}(\vec{R}) + \varepsilon(\vec{R})]\chi(\vec{R}) &= E\chi(\vec{R}) \end{aligned} \tag{4}$$

Electronic eigenvalue $\varepsilon_n(\vec{R})$ depends parametrically on the ionic positions $\vec{R}$

Born-Oppenheimer approximation III

Adiabatic approximation: Ions move on the potential-energy surface of the electronic ground state only.

$$\begin{aligned}
[T_e + V_{ee}(\vec{r}) + V_{eN}(\vec{r},\vec{R})]\Psi_0(x,\vec{R}) &= \varepsilon_0(\vec{R})\Psi_0(x,\vec{R}) \\
[T_N + V_{NN}(\vec{R}) + \varepsilon(\vec{R})]\chi(\vec{R},t) &= i\hbar\frac{\partial}{\partial t}\chi(\vec{R},t)
\end{aligned} \tag{5}$$

Neglect quantum effects in ionic dynamics ⟶ replace time-dependent ionic Schrödinger equation by classical Newtonian equation of motion

$$\begin{aligned}
\frac{\partial^2 \vec{P}_I(t)}{\partial t^2} &= -\nabla_I E_0(\vec{R}) \\
E_0(\vec{R}) &= \varepsilon_0(\vec{R}) + V_{NN}(\vec{R})
\end{aligned} \tag{6}$$

Force $-\nabla_I E_0(\vec{R})$ contains contributions from the direct ion-ion interaction and a term from the gradient of the electronic total energy

Hellmann-Feynman theorem

$$\begin{aligned}
\nabla_I \varepsilon_0(\vec{R}) &= \frac{\partial}{\partial \vec{R}_I} \langle \Psi_0 \mid H_e(\vec{R}) \mid \Psi_0 \rangle \\
&= \langle \nabla_I \Psi_0 \mid H_e(\vec{R}) \mid \Psi_0 \rangle \\
&\quad + \langle \Psi_0 \mid \nabla_I H_e(\vec{R}) \mid \Psi_0 \rangle \\
&\quad + \langle \Psi_0 \mid H_e(\vec{R}) \mid \nabla_I \Psi_0 \rangle \\
&= \langle \Psi_0(\vec{R}) \mid \nabla_I H_e(\vec{R}) \mid \Psi_0(\vec{R}) \rangle
\end{aligned} \tag{7}$$

First and third terms in the derivative vanish due to variational property of the ground-state → Forces acting on the ions are given by the expectation value of the gradient of the electronic Hamiltonian in the ground-state

The electronic Schrödinger equation and the Newtonian equations of motion of the ions, coupled via the Hellmann-Feynman theorem are the basis of the Car-Parrinello method.

Ab-initio electronic structure - Hartree-Fock methods

Quantum chemistry: Hartree-Fock and post-HF techniques

- Many-electron wavefunctions = Slater-determinants

$$\Psi^{a}_{\alpha_1\ldots\alpha_N}(q_1,\ldots,q_N) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_{\alpha_1}(q_1) & \cdots & \phi_{\alpha_1}(q_N) \\ \vdots & & \vdots \\ \phi_{\alpha_N}(q_1) & \cdots & \phi_{\alpha_N}(q_N) \end{vmatrix} \tag{8}$$

$$= \frac{1}{\sqrt{N!}}\sum_P (-1)^P P\phi_{\alpha_1}(q_1)\cdots\phi_{\alpha_N}(q_N)$$

- Variational condition

$$\delta\frac{\langle\Psi^a\mid H\mid\Psi^a\rangle}{\langle\Psi^a\mid\Psi^a\rangle} = 0 \tag{9}$$

Variation with respect to the one-electron orbitals ϕ_α

Hartree-Fock methods II

$\longrightarrow$ Hartree-Fock equations

$$\begin{aligned}
&\left(-\frac{\hbar^2}{2m}\Delta-\frac{Ze^2}{r}\right)\phi_i(\vec{r})+e^2\sum_{j\neq i}\int\frac{|\phi_j(\vec{r}\,')|^2}{|\vec{r}-\vec{r}\,'|}d^3r'\;\phi_i(\vec{r})\\
&-e^2\sum_{\substack{j\\ j\neq i}}\Delta_{s_{zi}s_{zj}}\int\frac{\phi_j^*(\vec{r}\,')\phi_i(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d^3r'\;\phi_j(\vec{r})=\varepsilon_i\phi_i(\vec{r})
\end{aligned}\tag{10}$$

Problems with Hartree-Fock calculations

- Computational effort scales badly with the number of electrons
- Neglect of correlations
  - Too wide band gaps, too small band widths
  - Exchange-operator for metallic systems singular at the Fermi level

Post Hartree-Fock methods

Express wavefunction as linear combination of Slater determinants to include correlation $\longrightarrow$ ”Configuration interactions” - HF-CI

- Even higher computational effort, scaling worse
- Convergence problematic
- Metals ????

Ab-initio electronic structure - Density-functional theory

Hohenberg-Kohn-Sham theorem:

- The ground-state energy of a many-body system is a unique functional of the particle density, $E_0 = E[(\vec{r})]$.

- The functional $E[(\vec{r})]$ has its minimum relative to variations $\delta n(\vec{r})$ of the particle density at the equilibrium density $n_0(\vec{r})$,

$$\begin{aligned} E = E[n_0(\vec{r})] = min\,\{E[(\vec{r})]\} \\ \frac{\delta E[n(\vec{r})]}{\delta n(\vec{r})}\,\Big|_{n(\vec{r})=n_o(\vec{r})} = 0 \end{aligned} \tag{11}$$

Density-functional theory II

Total-energy functional

$$E[n] = T[n] + E^H[n] + E^{xc}[n] + \int V(\vec{r})n(\vec{r})d^3r \qquad (12)$$

$T[n]\dots$ kinetic energy,

$E^H[n]\dots$ Hartree energy (electron-electron repulsion),

$E^{xc}[n]\dots$ exchange and correlation energies,

$V(\vec{r})$ external potential

- the exact form of $T[n]$ and E_{xc} is unknown !

Local density approximation - ”density only”:

- Approximate the functionals $T[n]$ and $E_{xc}[n]$ by the corresponding energies of a homogeneous electron gas of the same local density

$\longrightarrow$ Thomas-Fermi theory

Density-functional theory III

Local density approximation - Kohn-Sham theory:

- Parametrize the particle density in terms of a set of one-electron orbitals representing a non-interacting reference system

$$n(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2 \tag{13}$$

- Calculate non-interacting kinetic energy in terms of the $\phi_i(\vec{r})$'s,

$$T[n] = \sum_i \int \phi_i^*(\vec{r}) \left(-\frac{\hbar^2}{2m}\nabla^2 \right) \phi_i(\vec{r}) d^3r \tag{14}$$

- Determine the optimal one-electron orbitals using the variational condition

$$\frac{\delta E[(n(\vec{r})]}{\delta\phi_i(\vec{r})} = 0 \tag{15}$$

$\longrightarrow$ Kohn-Sham equations

Density-functional theory IV

$$E[n] = T[n] + E^H[n] + E_{xc}[n] + \int V(\vec{r})n(\vec{r})d^3r \tag{16}$$

with the exchange-correlation energy

$$E^{xc}[n(\vec{r})] = \int n(\vec{r})\varepsilon_{xc}[n(\vec{r})]d^3r, \tag{17}$$

where $\varepsilon_{xc}[n(\vec{r})]$ is the exchange-correlation energy of a homogeneous electron gas with the local density $n(\vec{r})$ → Kohn-Sham equations:

$$\left\{ -\frac{\hbar^2}{2m}\nabla^2 + \underbrace{V(\vec{r}) + e^2\int \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|}d^3r + \mu_{xc}[n(\vec{r})]}_{V_{eff}(\vec{r})} \right\}\phi_i(\vec{r}) = \varepsilon_i\phi_i(\vec{r}) \tag{18}$$

with the exchange-correlation potential

$$\mu_{xc}[n(\vec{r})] = \frac{\delta E_{xc}[n(\vec{r})]}{\delta n(\vec{r})} = \frac{\delta\{n(\vec{r})\varepsilon_{xc}[n(\vec{r})]\}}{\delta n(\vec{r})} \tag{19}$$

Solving the Kohn-Sham equations I

Choice of a basis set

- Plane waves and related basis functions

  Plane waves

  (Linearized) augmented plane waves - (L)APW's

  (Linearized) muffin-tin orbitals - (L)MTO's

  Projector augmented waves -PAW's

- Localized orbitals

  Atomic orbitals - LCAO's

  Gaussian orbitals

- Mixed basis sets

- Discrete variable representations

Basis sets I

Localized orbitals

- Well localized orbitals allow, at least in principle, linear scaling of DFT calculations with the system size.
- Loss of accuracy for strong localization
- Basis depends on ionic positions $\longrightarrow$ Pulay corrections have to be added to the Hellmann-Feynman forces
- Basis-set completness and superposition errors are difficult to control
- For Gaussians: many integrals appearing in the DFT functional can be done analytically

Basis sets II

Plane waves (PW's)

- Natural choice for system with periodic boundary conditions
- It is easy to pass from real- to reciprocal space representation (and vice versa) by FFT
- No Pulay correction to forces on atoms
- Basis set convergence easy to control
- Convergence slow $\longrightarrow$
  - Electron-ion interaction must be represented by pseudopotentials or projector-augmented wave (PAW) potentials
  - Use LAPW's or mixed basis sets

Pseudopotentials I

- Slow convergence of PW expansion caused by the necessity to reproduce nodal character of valence orbitals
- Nodes are the consequence of the orthogonality to the tightly-bound core-orbitals $\longrightarrow$
- Eliminate the tightly-bound core states and the strong potential binding these states:
  - Use ”frozen-core” approximation
  - Project Kohn-Sham equations onto sub-space orthogonal to core-states $\longrightarrow$ orthogonalized plane waves ...., or
  - Replace strong electron-ion potential by a weak pseudopotential which has the same scattering properties as the all-electron potential beyond a given cut-off radius

Pseudopotentials II

Scattering approach to pseudopotentials

- Perform all-electron calculation for atom or ion at a reference energy ε
- Define a cut-off radius r_c well outside the node of the highest core-state
- Construct a pseudo valence-orbital $\tilde{\phi}_l$ that is identical to the all-electron orbital ϕ_l for $r \geq r_c$, but nodeless for $r \leq r_c$ and continuous and continuously differentiable at r_c
- The scattering phase-shifts for electrons agree (modulo 2π) if the logarithmic derivatives of ϕ_l and $\tilde{\phi}_l$ agree on the surface of the cut-off sphere:

$$\frac{\partial \, log \phi_l(r,\varepsilon)}{\partial r} = \frac{\partial \, log \tilde{\phi}_l(r,\varepsilon)}{\partial r}, \quad \text{at } r = r_c \tag{20}$$

Pseudopotentials III

Modern pseudopotentials

- Norm-conserving pseudopotentials (NC-PP)

  Norm-conservation: charge within cut-off sphere fixed

  High cut-off energies for first-row and transition elements

- Ultrasoft pseudopotentials - (US-PP)
  - Norm-conservation relaxed - more freedom for pseudizing $2p$ and $3d$ states
  - Add augmentation charges inside the cut-off sphere to correct charge
  - Multiple reference energies - improved transferability
  - Lower cut-off energies

Pseudopotentials IV

Projector-augmented waves - PAW's

- Pseudization as for ultrasoft potentials
- Reconstruction of exact wavefunction in the core region →

Decomposition of wavefunctions ($\varphi_{lm\varepsilon}, \tilde{\varphi}_{lm\varepsilon}$ - partial waves)

$$
\begin{array}{ccccc}
|\,\phi_n\rangle = & |\,\tilde{\phi}_n\rangle & -\sum\limits_{atoms} |\,\tilde{\varphi}_{lm\varepsilon}\rangle c_{lm\varepsilon} & +\sum\limits_{atoms} |\,\varphi_{lm\varepsilon}\rangle c_{lm\varepsilon} & \\
exact\ WF & pseudo\ WF & pseudo\ onsite\ WF & exact\ onsite\ WF & (21) \\
 & & (augmentation) & (compensation) &
\end{array}
$$

Pseudo-WF represented on FFT-grid, on-site terms on atom-centred radial grids

Same decomposition holds for charge densities, kinetic, Hartree, and exchange-correlation energies and potentials

Pseudopotentials vs. all-electron methods

FLAPW

- Plane-wave expansion in interstitial region
- Expansion in terms of spherical waves inside muffin-tin spheres (up to $l = 12$)

US-PP, PAW

- Plane-wave expansion throughout entire cell
- Onsite terms represented on radial grids (up to $l = 2(3)$)

PAW's combine the accuracy of all-electron methods such as FLAPW with the efficiency of pseudopotentials

Solving the Kohn-Sham equations I

Direct minimization of the Kohn-Sham total-energy functional

- Preconditioned conjugate-gradient minimization

$$\text{Gradient}: \; F_l(\vec{r}) = \left\{ -\frac{\hbar^2}{2m}\nabla^2 + V_{eff}(\vec{r}, \{\phi_l(\vec{r}\,')\}) - \varepsilon_l \right\} \phi_l(\vec{r}) \qquad (22)$$

- Car-Parrinello (CP) method: Use dynamical-simulated annealing approach for minimization → pseudo-Newtonian equations of motion for coupled electron-ion system

Difficulties with direct minimization approaches:

- Difficult to keep wavefunctions orthogonal
- Bad scaling for metallic systems (”charge sloshing”)
- In CP calculations: no adiabatic decoupling for metals, the system ”drifts away from the Born-Oppenheimer surface”

Solving the Kohn-Sham equations II

Iterative matrix diagonalization and mixing

General strategy:

- Start with a set of trial vectors (wavefunctions) representing all occupied and a few empty eigenstates: $\{\phi_n \mid n = 1, \ldots, N_{bands}\}$
- Improve each wavefunction by adding a fraction of the residual vector $\mid R(\phi_n)\rangle$,

$$\mid R(\phi_n)\rangle = (\mathbf{H} - \varepsilon_n^{app}) \mid \phi_n\rangle, \quad \varepsilon_n^{app} = \langle \phi_n \mid \mathbf{H} \mid \phi_n\rangle \tag{23}$$

- After updating all states, perform subspace diagonalization
- Calculate new charge density ρ_{out}
- Determine optimal new input-charge density (mixing old ρ_{in} and ρ_{out})
- Iterate to selfconsistency

Solving the Kohn-Sham equations III

Algorithms implemented in VASP

- Updating the wavefunctions
  - Blocked Davidson algorithm
  - RMM-DIIS: Residuum minimization method - direct inversion in the iterative subspace: minimize norm $\langle R_n \mid R_n \rangle$ of residual vector to each eigenstate (no orthogonality constraint)
- Mixing:
  - DIIS

Ionic structure and dynamics I

Static optimization of crystal structure

Atomic coordinates at fixed cell-shape:Hellmann-Feynman forces
Geometry of the unit cell: Hellmann-Feynman stresses

Algorithms implemented in VASP:

- Conjugate gradient technique
- Quasi-Newton scheme
- Damped molecular dynamics

Ionic structure and dynamics II

Ab-initio molecular dynamics (AIMD)

- Car-Parrinello MD (not implemented in VASP):
  - Works well for insulators and semiconductors
  - Time-step controlled by evolution of eigenstates
  - For metals, the systems tends to drift away from the Born-Oppenheimer surface due to the coupling of electrons and ions
  - Must use ”Two-thermostat” approach for metals
- MD on the Born-Oppenheimer surface: Hellmann-Feynman MD
  - Stable also for metals, canonical ensemble realized using Nosé thermostat
  - Time-step controlled by ionic dynamics