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
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 $m$

\[
H = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2M_I} + \sum_{i=1}^{N_e} \frac{\vec{p}_i^2}{2m} + \sum_{i>j} \frac{e^2}{|\vec{r}_i-\vec{r}_j|} + \sum_{I>J} \frac{Z_I Z_J e^2}{|\vec{R}_I-\vec{R}_J|} - \sum_{i,l} \frac{Z_i e^2}{|\vec{R}_I-\vec{r}_i|}
\]

\[
= T_N + T_e + V_{ee}(\vec{r}) + V_{NN}(\vec{R}) + V_{Ne}(\vec{r}, \vec{R})
\]  

(1)

Schrödinger equation

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

(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 $\rightarrow$
quasi-separable ansatz

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

(3)

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

$$[T_e + V_{ee}(\vec{r}) + V_{eN}(\vec{r}, \vec{R})]\Psi_n(x, \vec{R}) = \varepsilon_n(\vec{R})\Psi_n(x, \vec{R})$$

$$[T_N + V_{NN}(\vec{R}) + \varepsilon(\vec{R})]\chi(\vec{R}) = E\chi(\vec{R})$$

(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.

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

(5)

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

\[
\begin{align*}
\frac{\partial^2 \vec{P}_I(t)}{\partial t^2} &= -\nabla I E_0(\vec{R}) \\
E_0(\vec{R}) &= \varepsilon_0(\vec{R}) + V_{NN}(\vec{R})
\end{align*}
\]  

(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.
\begin{equation}
\n\nabla_I \varepsilon_0(\vec{R}) = \frac{\partial}{\partial R_i} \langle \Psi_0 | H_e(\vec{R}) | \Psi_0 \rangle \\
= \langle \nabla_I \Psi_0 | H_e(\vec{R}) | \Psi_0 \rangle \\
+ \langle \Psi_0 | \nabla_I H_e(\vec{R}) | \Psi_0 \rangle \\
+ \langle \Psi_0 | H_e(\vec{R}) | \nabla_I \Psi_0 \rangle \\
= \langle \Psi_0(\vec{R}) | \nabla_I H_e(\vec{R}) | \Psi_0(\vec{R}) \rangle 
\end{equation}

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.
Quantum chemistry: Hartree-Fock and post-HF techniques

- Many-electron wavefunctions = Slater-determinants

\[
\Psi_{\alpha_1 \ldots \alpha_N}^{\alpha}(q_1, \ldots, q_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{\alpha_1}(q_1) & \cdots & \phi_{\alpha_1}(q_N) \\ \vdots & & \vdots \\ \phi_{\alpha_N}(q_1) & \cdots & \phi_{\alpha_N}(q_N) \end{vmatrix} \\
= \frac{1}{\sqrt{N!}} \sum_{P} (-1)^{P} P \phi_{\alpha_1}(q_1) \cdots \phi_{\alpha_N}(q_N)
\]

- Variational condition

\[
\delta \left< \Psi^{\alpha} \middle| H \middle| \Psi^{\alpha} \right> \left/ \left< \Psi^{\alpha} \middle| \Psi^{\alpha} \right> \right. = 0 \tag{9}
\]

Variation with respect to the one-electron orbitals \( \phi_\alpha \)
Hartree-Fock methods II

$\rightarrow$ Hartree-Fock equations

\[
\left( -\frac{\hbar^2}{2m} \Delta - \frac{Ze^2}{r} \right) \phi_i(\vec{r}) + e^2 \sum_{j \neq i} \int \frac{\phi_j(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 r' \phi_i(\vec{r}) = 0
\]

\[
-e^2 \sum_{j \neq i} \Delta s_z i s_z j \int \frac{\phi_j^*(\vec{r}')\phi_i(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 r' \phi_j(\vec{r}) = \varepsilon_i \phi_i(\vec{r})
\]

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 → ”Configuration interactions” - HF-CI

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

J. Hafner, Ab-initio materials simulations
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 $n_0(\vec{r})$,

$$E = E[n_0(\vec{r})] = \min \{E[(\vec{r})]\}$$

$$\frac{\delta E[n(\vec{r})]}{\delta n(\vec{r})} \bigg|_{n(\vec{r})=n_0(\vec{r})} = 0$$
Density-functional theory II

Total-energy functional

\[ E[n] = T[n] + E^H[n] + E^{xc}[n] + \int V(\vec{r})n(\vec{r})d^3r \]  \hspace{1cm} (12)

- \(T[n]\) … kinetic energy,
- \(E^H[n]\) … Hartree energy (electron-electron repulsion),
- \(E^{xc}[n]\) … 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

\[ \rightarrow \] Thomas-Fermi theory
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

\[ n(\vec{r}) = \sum_i |\phi_i(\vec{r})|^2 \]  \hspace{1cm} (13)

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

\[ T[n] = \sum_i \int \phi_i^*(\vec{r}) \left( -\frac{\hbar^2}{2m} \nabla^2 \right) \phi_i(\vec{r}) d^3r \]  \hspace{1cm} (14)

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

\[ \frac{\delta E[n(\vec{r})]}{\delta \phi_i(\vec{r})} = 0 \]  \hspace{1cm} (15)

\[\rightarrow\] Kohn-Sham equations
\[ E[n] = T[n] + E^H[n] + E_{xc}[n] + \int V(\vec{r})n(\vec{r})d^3r \]  \hspace{1cm} (16)

with the exchange-correlation energy

\[ E_{xc}[n(\vec{r})] = \int n(\vec{r})\varepsilon_{xc}[n(\vec{r})]d^3r, \]  \hspace{1cm} (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:

\[
\begin{aligned}
&\left\{ \begin{array}{c}
-\frac{\hbar^2}{2m} \nabla^2 + 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})
\end{array}
\right\} \phi_i(\vec{r}) = \varepsilon_i \phi_i(\vec{r})
\end{aligned}
\hspace{1cm} (18)

with the exchange-correlation potential

\[
\mu_{xc}[n(\vec{r})] = \frac{\delta E_{xc}[n(\vec{r})]}{\delta n(\vec{r})} = \frac{\delta \{n(\vec{r})\varepsilon_{xc}[n(\vec{r})]\}}{\delta n(\vec{r})} \hspace{1cm} (19)
\]
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**
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 $\rightarrow$ Pulay corrections have to be added to the Hellmann-Feynman forces
- Basis-set completeness 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 →
  - 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
- 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 → 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 $\varepsilon$
- 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 $\phi_l$ 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 $2\pi$) if the logarithmic derivatives of $\phi_l$ and $\tilde{\phi}_l$ agree on the surface of the cut-off sphere:

$$\frac{\partial \log \phi_l(r, \varepsilon)}{\partial r} = \frac{\partial \log \tilde{\phi}_l(r, \varepsilon)}{\partial r}, \quad \text{at } r = r_c$$  (20)
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 ($\phi_{lm\varepsilon}, \tilde{\phi}_{lm\varepsilon}$ - partial waves)

$$
| \phi_n \rangle = | \tilde{\phi}_n \rangle - \sum_{\text{atoms}} | \tilde{\phi}_{lm\varepsilon} \rangle c_{lm\varepsilon} + \sum_{\text{atoms}} | \phi_{lm\varepsilon} \rangle c_{lm\varepsilon}
$$

exact WF  pseudo WF  pseudo onsite WF  exact onsite WF
(augmentation)  (compensation)  

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

\[
F_l(\vec{r}) = \left\{ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(\vec{r}, \{\phi_l(\vec{r}')\}) - \varepsilon_l \right\} \phi_l(\vec{r}) \quad (22)
\]

- 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: \( \{ \phi_n \mid n = 1, \ldots, N_{\text{bands}} \} \)

- Improve each wavefunction by adding a fraction of the residual vector \( \mid R(\phi_n) \rangle \),

\[
\mid R(\phi_n) \rangle = (\mathbf{H} - \varepsilon_{n}^{\text{app}}) \mid \phi_n \rangle, \quad \varepsilon_{n}^{\text{app}} = \langle \phi_n \mid \mathbf{H} \mid \phi_n \rangle \tag{23}
\]

- After updating all states, perform subspace diagonalization

- Calculate new charge density \( \rho_{\text{out}} \)

- Determine optimal new input-charge density (mixing old \( \rho_{\text{in}} \) and \( \rho_{\text{out}} \))

- 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 $\langle R_n | R_n \rangle$ 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