Computational materials modeling using density functional theory: reactivity of metallic surfaces

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Theoretical treatment

- System of $n$ electrons and $N$ nucleus: Many-body quantum problem
- Born-Oppenheimer approximation
- Basics of DFT

Applications

- Reactivity of gases on surfaces
  - Molecular beam experiments
  - Modelling and simulations
When chemical reactions take place, chemical bonds are broken in the reactants and new chemical bonds are formed in the products.

- From a fundamental perspective: the system is composed by $n$ electrons and $N$ nucleus.
- Interactions between particles are governed by the laws of Quantum Mechanics.
Introduction

**Many-body Quantum problem**

Time-independent Schrödinger Equation for a system of \( n \) electrons and \( N \) nucleus

\[
H_T \Psi (r_1, r_2, \ldots, R_1, R_2, \ldots) = E \Psi (r_1, r_2, \ldots, R_1, R_2, \ldots)
\]

with the **Hamiltonian** operator

\[
H_T = T_{\text{nuc}} + T_{\text{el}} + U_{\text{el-el}} + V_{\text{el-nuc}} + V_{\text{nuc-nuc}}
\]

\[
T_{\text{nuc}} = \sum_{k=1}^{N} -\frac{1}{2M_k} \nabla^2 R_k
\]

\[
T_{\text{el}} = \sum_{i=1}^{n} -\frac{1}{2} \nabla^2 r_i
\]

\[
U_{\text{el-el}} = \frac{1}{2} \sum_{i<j}^{n} \frac{1}{|r_i - r_j|}
\]

\[
V_{\text{el-nuc}} = -\sum_{i=1}^{n} \sum_{k=1}^{N} \frac{Z_k}{|r_i - R_k|}
\]

\[
V_{\text{nuc-nuc}} = \frac{1}{2} \sum_{k=1}^{N} \frac{Z_k Z_{k'}}{|R_k - R_{k'}|}
\]

\( \Psi \) is a many-body **wave function** depending on \( 3n+3N \) coordinates

solutions that are stationary states of the SE for atoms and molecules **Orbitals**

\( E \) is the total energy for the system in state \( \Psi \)

when \( \Psi \) is a stationary state is an **eigenvalue** of the hamiltonian
Introduction

Born-Oppenheimer approximation

Since the nucleus masses are much bigger than the electron, we disregard the $T_{\text{nuc}}$ term and solve the electronic problem for a frozen configuration of the nucleus.

\[
T_{\text{nuc}} = \sum_{k=1}^{N} \frac{1}{2M_k} \nabla_R^2 R_k
\]

\[
T_{\text{el}} = \sum_{i=1}^{n} -\frac{1}{2} \nabla r_i^2
\]

\[
U_{\text{el-el}} = \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} \frac{1}{|r_i - r_j|}
\]

\[
U_{\text{el-nuc}} = -\sum_{i=1}^{n} \sum_{k=1}^{N} \frac{Z_k}{|r_i - R_k|}
\]

\[
V_{\text{nuc-nuc}} = \frac{1}{2} \sum_{k=1}^{N} \sum_{k'=1}^{N} \frac{Z_k Z_{k'}}{|R_k - R_{k'}|}
\]

\[
H_{\text{el}} = T_{\text{el}} + U_{\text{el-el}} + V_{\text{el-nuc}}
\]

\[
H_{\text{el}} \phi (r_1, \ldots, \{R\}) = E_{\text{el}} (\{R\}) \phi (r_1, \ldots, \{R\})
\]

Fundamental Consequence:

- Total electronic energy $E_{\text{el}}$ depends parametrically on $\{R\}$

- Continuous function which can be formally seen as an effective potential acting on the nuclei (potential energy surface)

\[
F_{\text{nuc}} = \nabla_R E_{\text{el}} (\{R\})
\]
% \begin{equation}
H_T = T_{\text{nuc}} + T_{\text{el}} + U_{\text{el-el}} + V_{\text{el-nuc}} + V_{\text{nuc-nuc}}
\end{equation}
% \begin{equation}
H_T \Psi (r_1, \ldots, R_1, \ldots) = E_T \Psi (r_1, \ldots, R_1, \ldots)
\end{equation}
% \begin{equation}
H_{\text{el}} = T_{\text{el}} + U_{\text{el-el}} + V_{\text{el-nuc}}
\end{equation}
% \begin{equation}
H_{\text{el}} \phi (r_1, r_2, \ldots) = E_{\text{el}} \phi (r_1, r_2, \ldots)
\end{equation}
Born-Oppenheimer approximation: summary

\[ H_{el} \phi(r_1, r_2, \ldots) = E_{el} \phi(r_1, r_2, \ldots) \]

We still have a many-body wave function depending on \(3n\) coordinates.

**Hartree-Fock**

Approximate the wave function as a Slater determinant

\[ \phi = \begin{vmatrix} \varphi_i & \ldots \\ \ldots & \ldots \end{vmatrix} \]

**Density functional theory**

Use the total electronic density as a main variable

\[ \rho(r) = \int |\phi(r, r_2, r_3, \ldots)|^2 dr_2 dr_3 \ldots \]
Basics of DFT

Kohn-Sham Equations

Kohn and Sham showed [1] that for the groundstate (stationary solution with the lowest eigenvalue) the problem of $n$ interacting e- can be formally mapped to a system of $n$ non interacting e- with the same $\rho(r)$

\[
H_{el}\phi(r_1, r_2, \ldots) = E_{el}^0 \phi(r_1, r_2, \ldots) \quad \leftrightarrow \quad H_{KS}\psi_i(r) = \varepsilon_i\psi_i(r) \quad i = 1, 2, \ldots, n
\]

\[
\rho(r) = \int |\phi(r, r_2, r_3, \ldots)|^2 dr_2 dr_3 \ldots
\]

\[
\rho(r) = \sum_{i=1}^{n} |\psi_i(r)|^2
\]

thus getting a system of $n$ uncoupled single-body SE

$\psi_i(r)$ are the Kohn-Sham orbitals and the $\varepsilon_i$ eigenvalues its associated energies

Hohenberg-Kohn theorem [1] establish:

- All observable quantities of a quantum system are uniquely determined by its density, and all properties can be calculated as an explicit or implicit functional of density.

For instance, by using H-K theorem and Rayleigh-Ritz variational principle

\[
E_{el}^0 = F[\rho(r)]
\]

Basics of DFT

Kohn-Sham Equations

\[ H_{KS} \psi_i(r) = \varepsilon_i \psi_i(r) \quad i = 1, 2, \ldots, n \]

\[ \rho(r) = \sum_{i=1}^{n} |\psi_i(r)|^2 \]

with

\[ H_{KS} = -\frac{1}{2} \nabla^2 + v_{\text{eff}}(r) \]

\[ v_{\text{eff}}(r) = -\sum_{i=1}^{N} \frac{Z_i}{|r - R_i|} + \int \frac{\rho(r')}{|r - r'|} d^3r' + \frac{\delta E_{xc}[\rho]}{\delta \rho} \]

- They provide the basis for a systematic way to solve the problem
- The total energy for the groundstate can be expressed as

\[ E_{el}^0 = F[\rho(r)] = \sum_i \varepsilon_i + E_{xc}[\rho] - \int v_{xc}(r) \rho(r) d^3r - \frac{1}{2} \int d^3r' d^3r \frac{\rho(r') \rho(r)}{|r - r'|} \]

- If we can obtain the exact form of the exchange and correlation functional \( E_{xc}[\rho] \) we would get the exact value for \( E_{el}^0 \) of the original many-body problem

Side note: Walter Kohn was granted the Nobel prize in chemistry in 1999.
Basics of DFT

Kohn-Sham Equations: summary

- Electronic many-body Hamiltonian mapped to a problem of non-interacting particles.
- DFT formalism guarantees that the groundstate density will be the same as the original system if $E_{xc}[^\rho]$ is exact.

$$H_{el} = T_{el} + U_{el-el} + V_{el-nuc}$$

$$H_{el}\phi(r_1, r_2, \ldots) = E_{el}\phi(r_1, r_2, \ldots)$$

$$H_{KS} = -\frac{1}{2}\nabla^2 + v_{eff}(r)$$

$$H_{KS}\psi_i(r) = \varepsilon_i\psi_i(r)$$
**Basics of DFT**

**Kohn-Sham Equations: Basis set**

**Kohn-Sham orbitals** can be represented as a sum of selected **basis functions**

\[ \psi_i(r) = \sum_{\nu}^{N} c_{\nu}^{i} \varphi_{\nu}(r) \]

Basis functions \( \{ \varphi_{\nu} \} \) must be a complete orthonormal set in \( L^2(\mathbb{R}^3) \)

\( N \) will be a convergence parameter.

**Most common basis sets**

- Gaussian basis set (different sets of gaussian functions)
- Numerical Basis Sets (numerically defined functions with radial symmetry)
- Linearized augmented plane wave (mixture of radial functions for the central and planewave for valence)
- Plane-wave basis set (fourier expansion)

Proper choice depends on the system to study.

- Periodic systems: Plane-waves or LAPW
- Atomic and molecular systems: Gaussians and Numerical
By introducing the expansion \( \psi_i(r) = \sum_{\nu} c^i_{\nu} \varphi_{\nu}(r) \) the KS equations

\[
H_{\text{KS}} \psi_i(r) = \varepsilon_i \psi_i(r)
\]

become the matrix-eigenvalue equations

\[
\sum_{\nu=1}^{N} (H_{\mu\nu} - \varepsilon_i \delta_{\mu\nu}) c^i_{\nu} = 0
\]

\[
H_{\mu\nu} = \langle \varphi_{\mu} | H_{\text{KS}} | \varphi_{\nu} \rangle = \int \varphi^*_{\mu}(r) H_{\text{KS}} \varphi_{\nu}(r) dr
\]

\[
\varepsilon_i \langle \varphi_{\mu} | \varphi_{\nu} \rangle = \delta_{\mu\nu}
\]

in matrix notation

\[
\begin{bmatrix}
\vdots & H_{\mu\nu} & \vdots \\
H_{\nu\mu} & H_{\mu\mu} - \varepsilon_i & \vdots \\
\vdots & \vdots & \vdots
\end{bmatrix}
\begin{bmatrix}
c^i_1 \\
\vdots \\
c^i_N
\end{bmatrix}
= \begin{bmatrix}
0 \\
\vdots \\
0
\end{bmatrix}
\]

The numerical treatment is reduced to solving an eigenvalue problem.

In usual expansions the size \( N \approx 1000 \) to 10000.
Basics of DFT

Kohn-Sham Equations: Exchange and correlation functional

Local density approximation (LDA)

Kohn and Sham proposed to write $E_{xc}[\rho]$ within a local approximation

$$E_{xc}^{LDA}[\rho] = \int \rho(r)\epsilon_{xc}(\rho)dr$$

$\epsilon_{xc}(\rho)$ is the exchange correlation energy per particle for the homogeneous electron gas (uniformly distributed e-, constant $\rho$).

$\epsilon_{xc}(\rho)$ can be computed with high accuracy.

Generalized gradient approximations (GGA)

Further improvement to the LDA, we add a dependency with the density gradient

$$E_{xc}^{GGA}[\rho] = \int \rho(r)\epsilon_{xc}(\rho, \nabla \rho)dr$$

Dependency with the gradient has no unique way to be defined.

- Parameter-free versions of GGA and others determined by fittings to experimental data.
- Calculations within this approach works really well for metals
- Excellent compromise between precision and computational cost

Kohn-Sham Equations: numerical treatment

Self consistent solution

Initial guess
\[ \rho^0(r) \]

Calculate effective potential
\[ v_{\text{eff}}(r) = - \sum_{i=1}^{N} \frac{Z_i}{|r - R_i|} + \int d^3r' \frac{\rho(r')}{|r - r'|} + \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho} \]

Calculate matrix elements and solve eigenvalue problem
\[ \sum_{\nu} (H_{\mu\nu} - \varepsilon_i \delta_{\mu\nu}) c^i_{\nu} = 0 \]

Calculate new electronic density
\[ \rho^k(r) = \sum_{i=1}^{n} |\psi_i(r)|^2 \]

Converged?

NO

Calculate total electronic energy
\[ E_{\text{el}}^0 = \sum_i \varepsilon_i + E_{\text{xc}}[\rho] - \int v_{\text{xc}}(r) \rho(r) d^3r - \frac{1}{2} \int d^3r' d^3r \frac{\rho(r') \rho(r)}{|r - r'|} \]

YES
Basics of DFT

Properties that can be computed

**Electronic structure**
- Energy levels (atoms)
- Band structure, Density of states (solids)
- Bonding properties (covalent, ionic...)
- Charge rearrangements

**Lattice Dynamics**
- Vibrational Frequencies
- Phonon DOS, Vibrational Entropy

**Structural Properties**
- Atomic Forces
- Molecular equilibrium geometry
- Lattice Parameters
- Elastic Constants, stress tensor
- Surface Reconstructions

**Spectroscopy**
- Photoemission
- Electron Energy Loss
- Optical Absorption
- Dielectric Function
- Raman Scattering
- Compton Scattering

Involve electronic excited states, interaction of electrons with time dependent external potentials

**Energetic properties**
- Adsorption of molecules
- Stable surfaces
- Transition state barriers

Some examples were DFT fails with the presented GGA approach
- Van der Waals forces
- Several strongly correlated solids predicted as metallic being oxides
- Band gaps are underestimated in semiconductors
Different structural properties computed for many pure materials in its groundstate crystalline state. Calculations performed with a plane wave basis set and the PBE GGA approximation for $E_{xc}$.

Properties that can be computed: Potential energy surfaces

PES for the simplest molecule $H_2$

\[ H_{el} \phi (r_1, ..., \{ R \}) = E_{el}(\{ R \}) \phi (r_1, ..., \{ R \}) \]

- By solving the SE at different atomic positions is possible to map the PES

- The basis to develop **classical interatomic potentials**, obtain a continuous representation of the nuclei-nuclei interaction:
  - Interpolate
  - Fit to an analytic expression
DFT-based electronic structure calculations is a topic of intensive research, there are multiple codes being developed suited for different systems/problems to tackle.

The fundamental difference between them is the basis set used to represent KS orbitals.

- With the presented DFT approach can be treated systems of \( \sim 100 \) atoms
- With classical interatomic potentials up to \( 10^6 \)
Motivation

In many technologically relevant applications are involved chemical reactions of gases on metallic surfaces:

- Catalytic hydrogen ($H_2$) production from steam methane ($CH_4$) reforming:
  \[
  CH_4 + H_2O \rightarrow CO + 3 H_2
  \]
  This reaction involve many elementary steps.
  **Rate limiting step:** adsorption and cleavage of first C-H bond onto the metallic catalyst
  \[
  CH_4(gas) \rightarrow CH_4(ad) \rightarrow CH_3(ad) + H(ad)
  \]
  \[
  18.7 \text{ kcal/mol}
  \]
  \[
  0.81 \text{ eV}
  \]
- The cleavage of the C-H bond in vacuum requires 4.5 eV for that reason catalysts are used!
A lot of effort is made to elucidate mechanisms to enhance this elementary reaction:

\[
\text{CH}_4(gas) \rightarrow \text{CH}_4(ad) \rightarrow \text{CH}_3(ad) + \text{H}(ad)
\]

**Experiments**

- Molecular beams

**Theory**

- Simulations of reaction dynamics
  
  We need very accurate potentials
  (good description of energetic barriers)

  Challenge: determine all the interaction from first-principles in order to get a parameter-free model which provides predictive power
Reactivity of gases on surfaces

Molecular beam experiments

- Beam of molecules with highly controlled states:
  - Incidence direction
  - Initial kinetic energy $E_i$
  - Initial vibrational state $\nu_k$
  - Well characterized metallic surface

- Goal:
  - Rule out how initial conditions of the molecules affect reactivity
  - Find optimal conditions
  - Selectivity (in bond to break) and control the outcome of the reaction

- These highly controlled state-of-the-art experiments are a perfect suite for comparison with a theoretical treatment
Reactivity of gases on surfaces

Molecular beam experiments: results for CH4 on a Pt(111) surface

- Sticking probability $S_0$ resolved in initial kinetic energy $E_i$ and vibrational state $\nu_k$

- Vibrational excitation of the $1\nu_3$ mode enhances the reaction

Chen et al., Rev. Sci. Instrum. 84, 053902 (2013)
Reactivity of gases on surfaces

Theoretical treatment

Bottom-up approach

- DFT calculations: Determine interatomic interactions characterize the critical regions of the PES (transition states)
- Build a continuous representation of the PES Develop force field that describe bond breaking
- Run the reaction dynamics simulations Treatment of vibrations
Reactivity of gases on surfaces

DFT modelling: CH4 on Pt(111)

- Calculations with the VASP code, uses plane waves and requires the system to have 3D periodicity
- The system is treated under the supercell approach by periodically repeating a big unit cell in 3D
- The Pt(111) surface is assumed to be with the ideal arrangement and five layers of atoms are used
Reactivity of gases on surfaces

Model for the PES

Challenge: we need a force field able to describe the bonded interactions but also allowing these bonds to be cleaved

**Reactive force field** based on the Tersoff proposal [1]

- The bonding between two species is affected by its chemical environment
  - The more coordinated the less strong
  - Proper model for covalent and metallic bonding

\[
V^\text{RFF} = \sum_{i,j} \left[ V^R(r_{ij}) - b_{ij} V^A(r_{ij}) \right]
\]

- ReaxFF reactive force field is based on this proposal [2]. But the proposed development scheme gave a not accurate enough potential for another gas-surface system


Reactivity of gases on surfaces

Model for the PES: potential development

The analytic form of the RFF for the CH4/Pt(111) system presents 77 free parameters

Least squares fitting

\[ \chi^2(a, b, \ldots) = \sum_{i}^{N_{\text{conf}}} \omega_j (V_j^{\text{DFT}} - V_j^{\text{RFF}})^2 \]

It is not only controlled the least square deviation, but also to have a proper description of critical points of the PES (transition states, normal modes)

When the database grow is converged RFF vs. DFT differ in \( \approx 0.1 \text{ eV} = 2 \text{ kcal/mol} \)

DFT calculations

GGA-PBE

Parameters fit

RFF-N

Initial database

Transition states, arbitrary distortions

Configuration space

Select explored configurations

Dynamics

Converged

End
Reactivity of gases on surfaces

Simulations of reaction dynamics

Quasiclassical approach [1]

- Nuclei assumed to behave as classical particles, integration of the Newton equations
- The quantum Zero Point Energy and vibrational excited states energies are included.
- All the non controlled initial conditions are randomly tossed (impact site, orientation)
- $N$ trajectories are integrated for a given $E_i$ and $\nu_k$ and then $S_0 = \frac{N_{\text{react}}}{N_{\text{tot}}}$

All the molecular dynamics simulations were carried out with an in-house developed code

Simulations of reaction dynamics: comparison to experiments

- Correct qualitative description of the sticking curves
- Description of the reactivity enhancement with $1\nu_3$
- Overestimation of the sticking for the vibrational groundstate

¿Problem with the potential or the treatment of the vibrations?

Quantum dynamics of the nuclei are required to rule out quasiclassical approach shortcomings

In the experiments are able to control the bond to break by vibrational preexcitation.

Initial total energy maintained constant \( \approx 0.55 \text{ eV} \)

Theoretical results describes all the tendencies properly and they account for the observed selectivity.

Reactivity of gases on surfaces

Simulations of reaction dynamics: comparison to experiments

Bond cleavage selectivity in methane isotopologues CHxDx

When increasing the initial kinetic energy with an extra 0.5 eV it is observed a selectivity loss for the initially excited modes.
Reactivity of gases on surfaces

Simulations of reaction dynamics

Selectivity as a function of impact energy: explanation

2D cut of the PES spanning heights of the carbon atom over the surface $Z_C$ and C-H internuclear distances $r_{C-H}$

At every point of the 2D cut all the rest of the coordinates are optimized
Reactivity of gases on surfaces

Simulations of reaction dynamics

Examples of the approach for other systems
DFT calculations are a valuable tool to investigate the properties of materials. Under the presented approach they are reliable mainly for structural and energetic parameters for systems composed of metals and closed shells molecules. The approach of developing potentials with Reactive Force Fields proposals fitted to DFT data, seems quite promising if the fitting is performed for the specific system to be studied.
Thanks for your attention