



THE CYPRUS
INSTITUTE

RESEARCH • TECHNOLOGY • INNOVATION

Computation-based Science and Technology Research Center
CaStoRC

EuroCC National HPC Competence Center

Lecture II, 30 Oct. 2025

Basics of Electronic Structure Theory for Solids

Marios Zacharias

Computation-based Science and Technology Research Center,
The Cyprus Institute, Aglantzia 2121, Nicosia, Cyprus

Presentation Summary

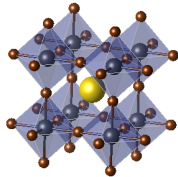
- Introduction
- DFT History
- Many-Body Schrödinger Equation
- Approximations leading to DFT
- DFT and beyond

Computational materials modelling from first principles

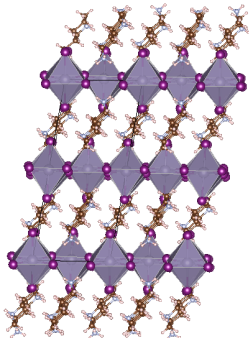
Molecules



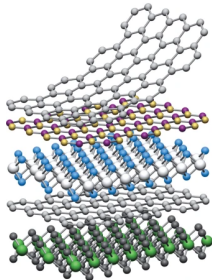
Simple Crystals



Complex Structures

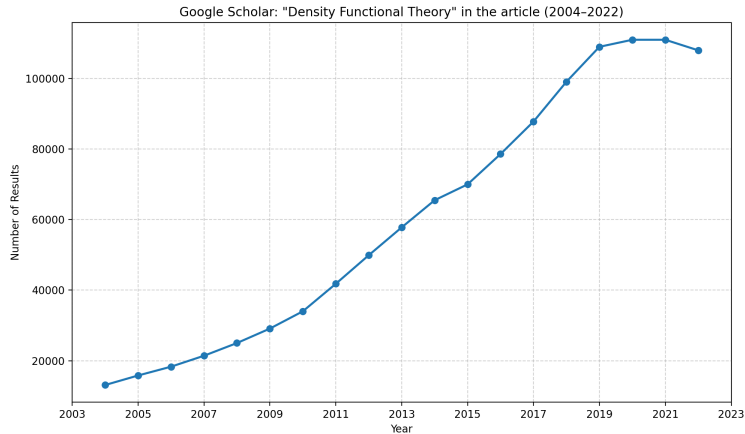
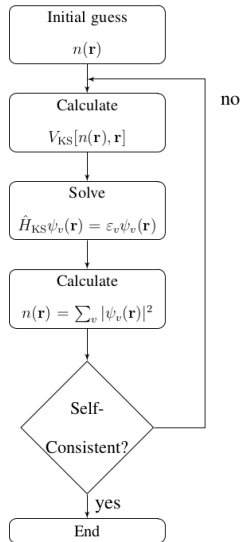


Interfaces
Heterostructures



- **Materials modelling** is the use of mathematical models to describe materials properties.
- **First principles** refers to a bottom up strategy that is empirical free and relies on Quantum Mechanics.
- **Computational** requires high-performance computing (HPC) and highly-parallel codes for solving the Schrödinger equation.

Density functional theory



Codes for DFT calculations

Plane-wave

- **VASP**- commercial
- **Quantum ESPRESSO** - open-source
- **ABINIT** - open-source
- **CASTEP** - commercial
- **GPAW** - open-source
- **CP2K** - open-source



Gaussian-basis quantum chemistry

- **Gaussian** - commercial
- **ORCA** - free for academia
- **Q-Chem** - commercial
- **CRYSTAL** - open-source



Localized numerical orbitals

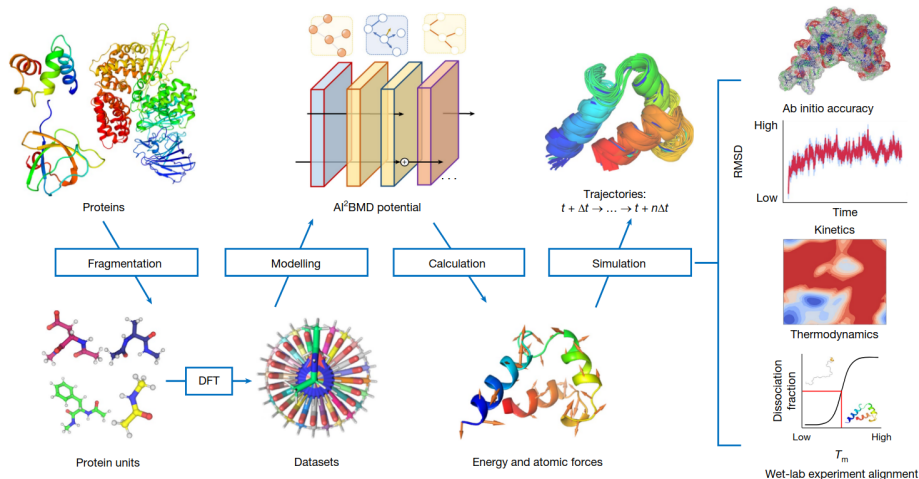
- **FHI-aims** - free for academia
- **SIESTA** - open-source
- **ONETEP** - commercial
- **OpenMX** - open-source

Linearized augmented planewave methods

- **Exciting** - open source
- **WIEN2k** - commercial (low-cost for academia)

Examples of DFT calculations I: proteins

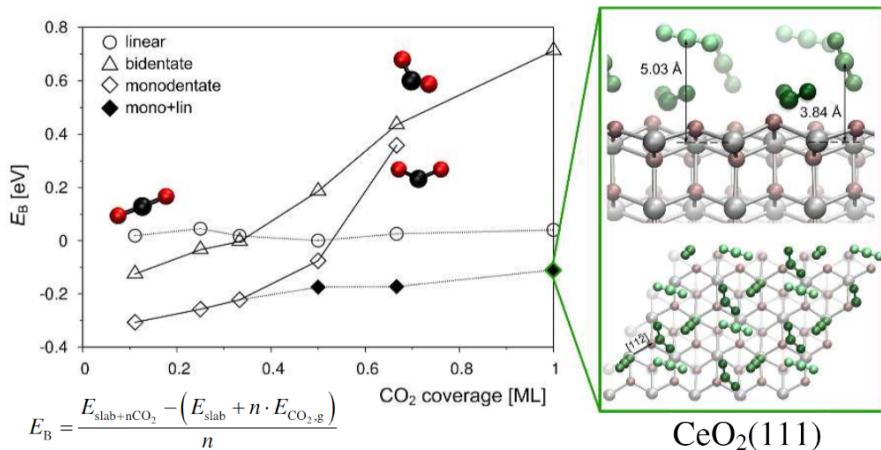
DFT-trained ML force field for large protein folding and properties



T. Wang et al, [Nature 635, 1019-1027 \(2024\)](#)

Examples of DFT calculations II: CO₂ adsorption

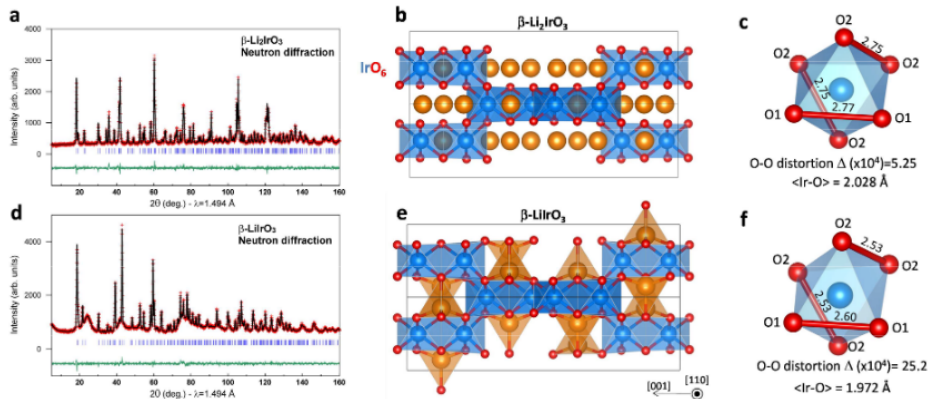
CO₂ adsorption mechanisms on CeO₂(111)



K. R. Hahn et al, *J. Phys. Chem. C* 117, 4, 1701–1711 (2013)

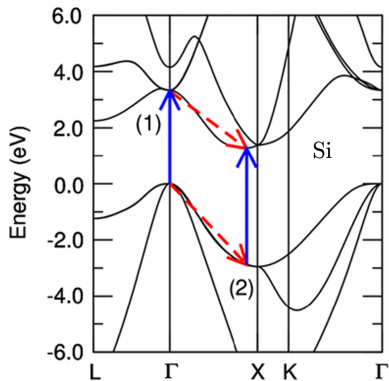
Examples of DFT calculations III: Li-ion batteries

DFT for the next generation electrodes in Li-ion batteries

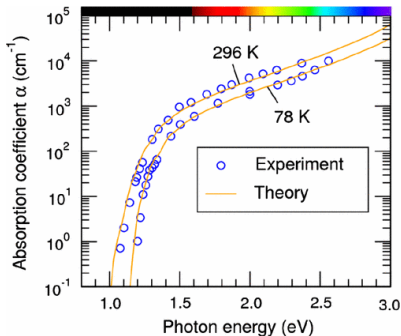


P. E. Pearce et al, [Nature Mater.](#) 16, 580–586 (2017)

Examples of DFT calculations IV: Photovoltaics



J. Noffsinger, E. Kioupakis, C. G. Van de Walle, S. G. Louie, M. L. Cohen, *Phys. Rev. Lett.* **108**, 167402 (2012)



Phonon-assisted transition rate in the [Hall-Bardeen-Blat](#) (HBB) theory:

$$\Gamma_{v \rightarrow c}(\omega) \propto \sum_{\nu} \left| \sum_{n \neq c} \frac{p_{vn} g_{nc, \nu}}{\varepsilon_n - \varepsilon_v - \hbar\omega} + \sum_{n \neq v} \frac{g_{vn, \nu} p_{nc}}{\varepsilon_n - \varepsilon_v \pm \hbar\omega_{\nu}} \right|^2 \delta(\varepsilon_c - \varepsilon_v \pm \hbar\omega_{\nu} - \hbar\omega)$$

DFT history

- **1927–1930s** *Quantum mechanical foundations*, Schrödinger & Dirac
- **1927** Born-Oppenheimer approximation
- **1928** Hartree method, Mean-field approximation
- **1930** Hartree-Fock method (exchange for non-interacting particles)
- **1964** Hohenberg-Kohn Theorems
- **1965** Kohn-Sham Equations (non-interacting particles + correlation)
- **1965** LDA by KS, Ceperley & Alder (1980), Perdew & Zunger (1981)
- **1980-90s** GGA by Perdew (1986), Becke (1988), Lerr-Yang-Parr: LYP (1988), Perdew-Wang: PW (1991), Perdew-Burke-Ernzerhof: PBE (1996)
- **1980-2000s** Beyond DFT: (i) Hedin's GW (1965) → Hybertsen & Louie (1986), (ii) Bohm & Pines' RPA (1953) → F. Furche (2001) and M. Fuchs & X. Gonze (2002), (iii) Runge & Gross' TDDFT (1984) → Reining et al (2002)
- **1990s** DFT+U: Anisimov et al (1991), Dudarev et al. (1998)
- **1990-2000s** Hybrids: Becke's B3LYP (1993), PBE0 (1996), Heyd-Scuseria-Ernzerhof: HSE (2003)
- **2000-2010s** Meta-GGA: TPSS (2003), SCAN (2015)
- **2010-present** High-throughput and automated DFT workflows: ASE, AiiDA, Materials Project, EPWpy
- **2020-present** Machine-learned Functionals / ML-DFT: Kirkpatrick et al.: DM21 (2021)

The Many-Body Schrödinger Equation: N electrons, M nuclei

$$\hat{H} \Phi(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_1, \dots, \mathbf{R}_M) = E_{\text{tot}} \Phi(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{R}_1, \dots, \mathbf{R}_M)$$

$\Phi(\mathbf{r}, \mathbf{R})$: many-body wavefunction (depends on all \mathbf{r}_i and \mathbf{R}_j coordinates and spins),
 E_{tot} : total energy of the system.

$$\begin{aligned} \hat{H} = & - \sum_{i=1}^N \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{I=1}^M \frac{\hbar^2}{2M_I} \nabla_I^2 \\ & - \sum_{i=1}^N \sum_{I=1}^M \frac{e^2}{4\pi\epsilon_0} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_{I=1}^M \sum_{J \neq I}^M \frac{e^2}{4\pi\epsilon_0} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \end{aligned}$$

- m_e electron mass, M_I nuclei mass, ϵ_0 vacuum permittivity, Z_I nucleus charge
- K. E.: electrons & nuclei, +
P. E.: electron-nucleus attraction, electron-electron & nucleus-nucleus repulsion.

The Born-Oppenheimer (clamped nuclei) approximation

- Electrons and nuclei are coupled: Solving SE exactly means dealing with Ψ that depends on $\{\mathbf{r}_i\}$ and $\{\mathbf{R}_I\}$ - impossible.
- $M_I \gg m_e$: electrons adapt adiabatically to nuclear motion:
 $\Phi(\mathbf{r}, \mathbf{R}) = X(\mathbf{R})\Psi(\mathbf{r}, \mathbf{R})$. Allows to:

$$\begin{aligned}\hat{H} = & -\sum_{i=1}^N \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{I=1}^M \frac{\hbar^2}{2M_I} \nabla_I^2 \\ & - \sum_{i=1}^N \sum_{I=1}^M \frac{e^2}{4\pi\epsilon_0} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_{I=1}^M \sum_{J \neq I}^M \frac{e^2}{4\pi\epsilon_0} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}\end{aligned}$$

- $\hat{H}\Psi(\mathbf{r}, \mathbf{R}) = E(\mathbf{R})\Psi(\mathbf{r}, \mathbf{R})$, $E(\mathbf{R})$: total adiabatic electron energy (PES)
- Ψ still depends on $3N$ spatial coords (plus spin): exponentially hard as N grows

Hydrogen: the Exactly Solvable One-Electron Case

We simplify SE and move to Hartree units (as in QE): $\hbar = m_e = 4\pi\epsilon_0 = a_0 = 1$

For H ($N=1$, $Z=1$), no el-el repulsion term:

$$\left[-\frac{1}{2} \nabla^2 - \frac{1}{r} \right] \psi(\mathbf{r}) = E \psi(\mathbf{r})$$

Ground state (1s): $\psi_{1s}(r) = \frac{1}{\sqrt{\pi}} e^{-r}$, $E_{1s} = -\frac{1}{2} = -13.6 \text{ eV}$ ($E_{\text{Hartree}} = 27.2 \text{ eV}$)

Hydrogenic levels:

$$E_n = -\frac{13.6 \text{ eV}}{n^2}, \quad n = 1, 2, \dots$$

and analytic orbitals $\psi_{n\ell m}(r, \theta, \phi)$ built from spherical harmonics.

Helium and Beyond: Why It's Hard

Example: He ($N=2$, $Z=2$ and put nucleus at origin $\mathbf{R} = 0$):

$$\hat{H} = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - 2\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

- The **electron–electron term** couples coordinates \Rightarrow no closed-form solution.
- Cannot be separated into two independent one-electron equations, i.e.:
 $\Psi(\mathbf{r}_1, \mathbf{r}_2) \neq \psi(\mathbf{r}_1)\psi(\mathbf{r}_2)$
The electrons are correlated: motion of one depends on the other's position.
- Approximate methods needed: Hartree(-Fock), post-HF (CI), and DFT.

Independent particle picture / Exclusion principle

- $\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2)\psi_3(\mathbf{r}_3)$
- Electron density at \mathbf{r} = (Probability finding electron \mathbf{r}_1 at \mathbf{r} , \mathbf{r}_2 at \mathbf{r} , and \mathbf{r}_3 at \mathbf{r}):

$$n(\mathbf{r}) = \int |\Psi(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3)| d\mathbf{r}_2 d\mathbf{r}_3 + \int |\Psi(\mathbf{r}_1, \mathbf{r}, \mathbf{r}_3)| d\mathbf{r}_1 d\mathbf{r}_3 + \int |\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r})| d\mathbf{r}_1 d\mathbf{r}_2$$

$$n(\mathbf{r}) = 3 \int |\Psi(\mathbf{r}, \mathbf{r}_2, \mathbf{r}_3)| d\mathbf{r}_2 d\mathbf{r}_3 \text{ electrons are indistinguishable}$$

- Pauli Exclusion Principle (PEP): Ψ antisymmetric under exchange of any two electrons. Including spin: $\mathbf{x} = (\mathbf{r}, s) \rightarrow \Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) = -\Psi(\mathbf{x}_2, \mathbf{x}_1, \mathbf{x}_3)$
We need a Slater Determinant to satisfy PEP: $\Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) = \text{SD}\{\psi(\mathbf{x})\}$

- The 3-electron Slater determinant is

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_2(\mathbf{x}_1) & \psi_3(\mathbf{x}_1) \\ \psi_1(\mathbf{x}_2) & \psi_2(\mathbf{x}_2) & \psi_3(\mathbf{x}_2) \\ \psi_1(\mathbf{x}_3) & \psi_2(\mathbf{x}_3) & \psi_3(\mathbf{x}_3) \end{vmatrix}.$$

Slater determinant

- We expand:

$$\Psi = \frac{1}{\sqrt{3!}} \left[\psi_1(\mathbf{x}_1) \begin{vmatrix} \psi_2(\mathbf{x}_2) & \psi_3(\mathbf{x}_2) \\ \psi_2(\mathbf{x}_3) & \psi_3(\mathbf{x}_3) \end{vmatrix} - \psi_2(\mathbf{x}_1) \begin{vmatrix} \psi_1(\mathbf{x}_2) & \psi_3(\mathbf{x}_2) \\ \psi_1(\mathbf{x}_3) & \psi_3(\mathbf{x}_3) \end{vmatrix} + \psi_3(\mathbf{x}_1) \begin{vmatrix} \psi_1(\mathbf{x}_2) & \psi_2(\mathbf{x}_2) \\ \psi_1(\mathbf{x}_3) & \psi_2(\mathbf{x}_3) \end{vmatrix} \right].$$

$$\Psi = \frac{1}{\sqrt{6}} \left[\psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)\psi_3(\mathbf{x}_3) - \psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_3)\psi_3(\mathbf{x}_2) - \psi_2(\mathbf{x}_1)\psi_1(\mathbf{x}_2)\psi_3(\mathbf{x}_3) \right. \\ \left. + \psi_2(\mathbf{x}_1)\psi_1(\mathbf{x}_3)\psi_3(\mathbf{x}_2) + \psi_3(\mathbf{x}_1)\psi_1(\mathbf{x}_2)\psi_2(\mathbf{x}_3) - \psi_3(\mathbf{x}_1)\psi_1(\mathbf{x}_3)\psi_2(\mathbf{x}_2) \right].$$

- $3! = 6$ terms: one for each permutation
- Signs alternate with the parity of the permutation
- Exchanging any two electrons ($1 \rightarrow 2$) flips the sign: antisymmetric
- If two electrons in the same state: $\text{SD}\{\psi(\mathbf{x})\} = 0 \rightarrow \text{PEP satisfied}$

Hartree (Mean-field) Approximation

- Ignoring “Coulomb repulsion” is drastic. Mean-field idea acts on el-el term
- It is replaced by an average classical “mean field” created by all electrons:

$$\frac{1}{2} \sum_{j \neq i}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \rightarrow V_H(\mathbf{r}) = \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

- This allows us to work in the single-particle picture:

$$\left[-\frac{1}{2} \nabla^2 - \sum_{I=1}^M \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + V_H(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$
$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2$$

- SE, $n(\mathbf{r})$, and $V_H(\mathbf{r})$ are solved iteratively \rightarrow *self-consistent field method*

Hartree-Fock

- Adds non-local Fock-exchange (antisymmetry) term, via Slater determinant:

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{x}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$
$$V_{\text{ext}}(\mathbf{r}) = -\sum_{I=1}^M \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|}, \quad V_{\text{x}}(\mathbf{r}) = -\sum_j^N \psi_j(\mathbf{r}) \int d\mathbf{r}' \frac{\psi_j(\mathbf{r}')\psi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

- “Exchange” effect: same spin electrons avoid each other in space
- Still mean-field because it’s an one-body picture.
- Purely quantum correction \rightarrow little correlation but correct spin ordering
- See proof in F. Giustino, *Materials Modelling using Density Functional Theory: Properties and Predictions* (Oxford University Press, Oxford, 2014), p. 32.

Correlation term

- Exact system: All electrons avoid each other dynamically (correlation)
- We need to add another term which we do not know its exact form:

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{x}}(\mathbf{r}) + V_{\text{c}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

- Without correlation \rightarrow Too high energies and poor bond strengths
- Correlated wavefunctions (MP2 or CI) computationally unmanageable
- We need to resort to Density Functional Theory.

Density Functional Theory I

- Hohenberg–Kohn (1964): 1. $V_{\text{ext}}(\mathbf{r})$ is uniquely determined by $n(\mathbf{r})$.
2. The ground state $n(\mathbf{r})$ minimises the ground state E .

$$E[n] = F[n] + \int n(\mathbf{r})V_{\text{ext}}(\mathbf{r})d\mathbf{r} + \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}d\mathbf{r}'$$

$$F[n] = T[n] + \tilde{E}_{xc}[n] \text{ (terms with correlation effects)}$$

- Kohn–Sham (1965): Map the interacting problem to non-interacting electrons in an effective potential so that $n(\mathbf{r})$ is reproduced.
- Replace T of interacting electrons with

$$T_{\text{KS}} = - \sum_i \int d\mathbf{r} \psi_i^*(\mathbf{r}) \frac{\nabla^2}{2} \psi(\mathbf{r})$$

$$E_{\text{KS}} = T_{\text{KS}} + \int n(\mathbf{r})V_{\text{ext}}(\mathbf{r})d\mathbf{r} + \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + E_{xc}[n]$$

Density Functional Theory II

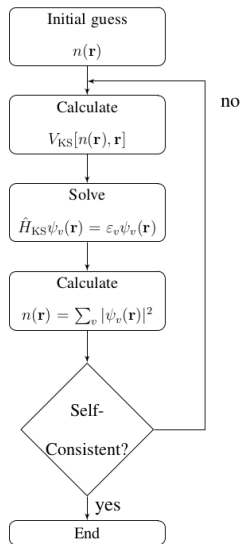
- Effective potential that accounts for interactions with other electrons

$$\boxed{H_{\text{KS}} \psi_i(\mathbf{r}) = \left[-\frac{1}{2} \nabla^2 + V_{\text{eff}}[n(\mathbf{r})] \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})}, \quad n(\mathbf{r}) = \sum_i^{\text{occ}} |\psi_i(\mathbf{r})|^2$$

$$V_{\text{eff}}[n] = V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}[n] + V_{\text{xc}}[n]$$

- Find the ground state by looking for stationary points of $E[n]$
- Complexity reduces from wavefunction in $3ND$ to density in $3D$.
- Accuracy controlled by the exchange-correlation functional $E_{\text{xc}}[n]$.

Density Functional Theory III



Treatments to E_{xc}

- **Local Density Approximation (local):** $E_{xc}^{LDA} = \int d\mathbf{r} n(\mathbf{r}) E_{xc}^{HEG}[n(\mathbf{r})]$
Splits $E_{xc}^{LDA} = E_x^{LDA} + E_c^{LDA}$,
 $E_x^{LDA} = -3/4(3/\pi)^{1/3} n^{4/3}$ from Hartree-Fock exchange energy of a uniform gas
 E_c^{LDA} non-analytic from Quantum Monte Carlo sim. of HEG [Ceperley & Alder, 1980](#)
- **Generalized Gradient Approximation (semi-local):** $E_{xc}^{GGA} = \int d\mathbf{r} n(\mathbf{r}) E_{xc}[n(\mathbf{r}), \nabla n(\mathbf{r})]$
Different flavors (i.e. PBE, B88) treat differently the exchange factor F_x .
- **Hybrid functional (semi-nonlocal):** $E_{xc}^{hybrid} = aE_x^{HF} + (1 - a)E_x^{GGA} + E_c^{GGA}$
PBE0: $a = 0.25$ derived from theoretical test on a large set of molecules
- **GW (fully nonlocal)** $\left[-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + \Sigma(E_i^{QP}) \right] \psi_i(\mathbf{r})^{QP} = E_i^{QP} \psi_i(\mathbf{r})^{QP}$
 $E_i^{QP} = \varepsilon_i^{DFT} + Z_i \langle \psi_i^{DFT} | \Sigma(E_i^{QP}) - V_{xc}^{DFT} | \psi_i^{DFT} \rangle$
Start from ψ_i^{DFT} and correct their energies, captures xc effects beyond DFT

Why Reciprocal Space in DFT?

- **Periodic systems:** In crystals, the external potential satisfies

$$V(\mathbf{r} + \mathbf{R}) = V(\mathbf{r})$$

where \mathbf{R} is a Bravais lattice vector.

- **Bloch's theorem:** The electronic wavefunctions can be written as

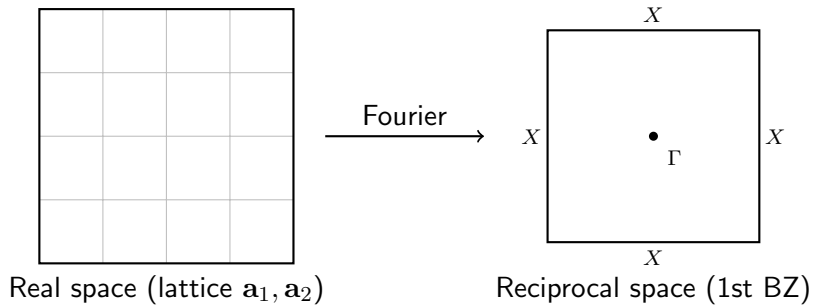
$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}), \quad u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$$

Only \mathbf{k} values in the **first Brillouin zone** are unique.

- **Why work in reciprocal space?**
 - ▶ Periodic potentials and densities become **simple Fourier series**.
 - ▶ The Laplacian (∇^2) turns into multiplication by $|\mathbf{k} + \mathbf{G}|^2$.
 - ▶ Enables efficient use of **plane waves** as basis functions:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{n\mathbf{k}}(\mathbf{G}) e^{i(\mathbf{k} + \mathbf{G})\cdot\mathbf{r}}$$

Real-to-Reciprocal space schematic



Reciprocal Lattice and k -points in Practice

Reciprocal Lattice

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}, \quad \mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$$

Any periodic quantity (potential, density) can be expanded as

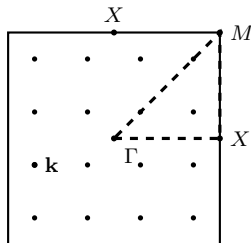
$$f(\mathbf{r}) = \sum_{\mathbf{G}} f_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}}.$$

Integration over the Brillouin Zone

$$E_{\text{band}} = \frac{1}{\Omega_{\text{BZ}}} \sum_n \int_{\text{BZ}} f_{n\mathbf{k}} \epsilon_{n\mathbf{k}} d\mathbf{k} \quad \longrightarrow \quad \frac{1}{N_k} \sum_{\mathbf{k}} f_{n\mathbf{k}} \epsilon_{n\mathbf{k}}$$

k -points (Monkhorst–Pack grids) sample this integral. ($f_{n\mathbf{k}}$: Fermi occup. factor)

Reciprocal Lattice and k -points in Practice



Square: 1st BZ with Monkhorst-Pack k -mesh and a band path $\Gamma \rightarrow X \rightarrow M \rightarrow \Gamma$

- Finer k -meshes \Rightarrow better convergence of:
 - ▶ Total energies and forces (see next slide)
 - ▶ Band structures, Density of states
 - ▶ Optical spectra
- For large simulations cells (supercells) \Rightarrow only the Γ -point may be sufficient.

Hellmann-Feynman Theorem, Hellmann-Feynman Forces

- $\mathbf{F}_I = -\frac{dE}{d\mathbf{R}} = -\frac{d[\langle\Psi|H|\Psi\rangle]}{d\mathbf{R}} = -\langle\frac{d\Psi}{d\mathbf{R}}|H|\Psi\rangle - \langle\Psi|\frac{dH}{d\mathbf{R}}|\Psi\rangle - \langle\Psi|H|\frac{d\Psi}{d\mathbf{R}}\rangle$

$$\mathbf{F}_I = -\langle\Psi|\frac{dH}{d\mathbf{R}}|\Psi\rangle - \cancel{E\frac{d}{d\mathbf{R}}\langle\Psi|\Psi\rangle}$$

cancels since wavefunctions obey $\langle\psi_i|\psi_j\rangle = \delta_{ij}$, Note: $\langle\Psi|O|\Psi\rangle = \int d\mathbf{r} n(\mathbf{r}) O$ for local operators like V_{ext}

- $H_{\text{KS}}[n] = T_{\text{KS}}[n] + \underline{V_{\text{ext}}[n]} + V_{\text{H}}[n] + V_{\text{xc}}[n] + \underline{V_{\text{II}}[n]}$, add ion-ion class. Coulomb repulsion
- Only $V_{\text{ext}}[n]$ (term from slide 18) and $V_{\text{II}}[n]$ (term from slide 12) survive the derivative

$$\mathbf{F}_I = Z_I \int d\mathbf{r} n(\mathbf{r}) \frac{\mathbf{r}_i - \mathbf{R}_I}{|\mathbf{r}_i - \mathbf{R}_I|^3} + \sum_{J \neq I}^M Z_I Z_J \frac{\mathbf{R}_I - \mathbf{R}_J}{|\mathbf{R}_I - \mathbf{R}_J|^3}$$

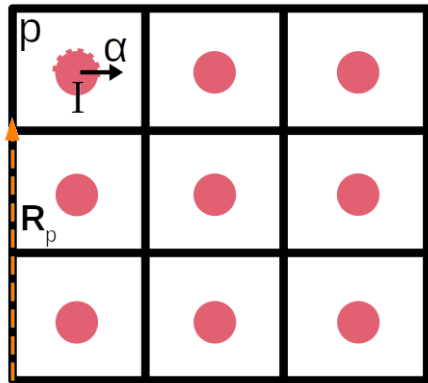
If basis functions of Ψ move with atoms (i.e. LCAO and not plane waves) \rightarrow add Pulay correction

- E_{xc} does not enter \mathbf{F}_I , but forces depend on xc functional (i.e. PBE or hybrids) via $n(\mathbf{r})$

Nuclei displacements and potential energy surface (PES)

Expansion of the PES (E_{KS}) with respect to nuclei displacements

$$E_{\text{KS}}^{\{\mathbf{R}\}} = E_{\text{KS}}^0 + \frac{1}{2} \sum_{\substack{pI\alpha \\ p'I'\alpha'}} \frac{\partial^2 E_{\text{KS}}}{\partial \mathbf{R}_{pI\alpha} \partial \mathbf{R}_{p'I'\alpha'}} \Delta \mathbf{R}_{pI\alpha} \Delta \mathbf{R}_{p'I'\alpha'} + \dots$$



Phonons from first-principles

1. Harmonic approximation for the PES

$$E_{\text{KS}}^{\{\mathbf{R}\}} = E_{\text{KS}}^0 + \frac{\partial^2 E_{\text{KS}}}{\partial \mathbf{R}_{pI\alpha} \partial \mathbf{R}_{p'I'\alpha'}} \frac{\Delta \mathbf{R}_{pI\alpha} \Delta \mathbf{R}_{p'I'\alpha'}}{2}$$

2. Evaluate the IFCs from finite differences or DFPT:

$$C_{pI\alpha,p'I'\alpha'} = \frac{\partial^2 U}{\partial \mathbf{R}_{pI\alpha} \partial \mathbf{R}_{p'I'\alpha'}} = \frac{\partial F_{pI\alpha}}{\partial \mathbf{R}_{p'I'\alpha'}}$$

3. Evaluate the dynamical matrix as:

$$D_{I\alpha,I'\alpha'}(\mathbf{q}) = \sum_{p'} \frac{C_{0I\alpha,p'I'\alpha'}}{\sqrt{M_I M_{I'}}} e^{i\mathbf{q} \cdot (\mathbf{R}_{p'} + \mathbf{R}_{I'} - \mathbf{R}_I)}$$

4. Diagonalize the dynamical matrix:

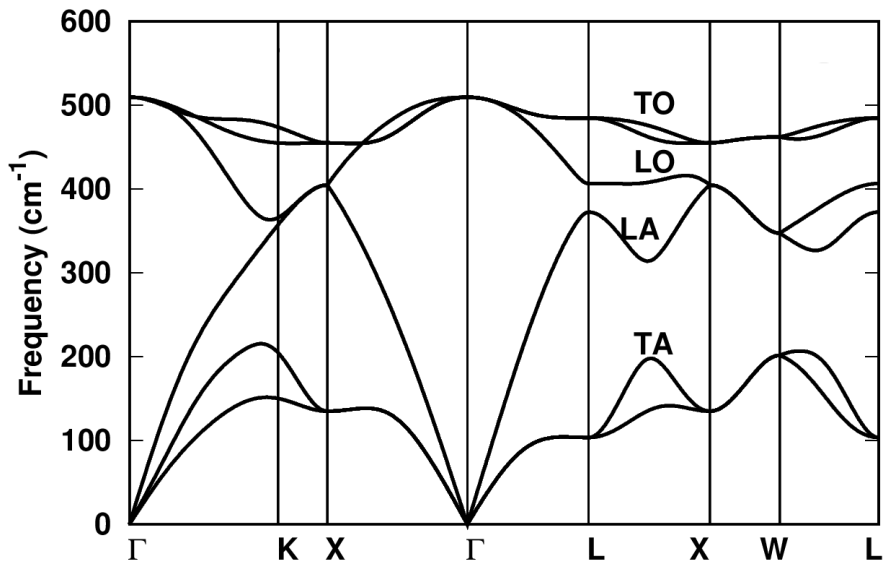
$$\sum_{I'\alpha'} D_{I\alpha,I'\alpha'}(\mathbf{q}) e_{I'\alpha',\nu}(\mathbf{q}) = \omega_{\mathbf{q}\nu}^2 e_{I\alpha,\nu}(\mathbf{q})$$

$\{\omega_{\mathbf{q}\nu}, e_{I\alpha,\nu}(\mathbf{q})\}$ define the phonons.

5. For polar materials include the dipole-dipole interaction term:

$$D_{I\alpha,I'\alpha'}^{\text{dd}}(\mathbf{q} \rightarrow 0) = \frac{4\pi e^2}{\sqrt{M_I M_{I'}} \Omega} \frac{\sum_{\beta} q_{\beta} Z_{I,\beta\alpha}^* \sum_{\beta'} q_{\beta'} Z_{I',\beta'\alpha'}^*}{\sum_{\beta\beta'} q_{\beta} \epsilon_{\beta\beta'}^{\infty} q_{\beta'}}$$

Phonon dispersion of silicon



Useful References

- F. Giustino, *Materials Modelling using Density Functional Theory: Properties and Predictions* (Oxford University Press, Oxford, 2014)
- R. M. Martin, *Electronic Structure: Basic Theory and Practical Methods* (Cambridge University Press, 2004)
- F. Bassani and G. P. Parravicini, *Electronic States and Optical Transition in Solids* (Pergamon, Oxford, 1975)
- F. Nogueira, A. Castro, and M. A. L. Marques, *A tutorial on density functional theory* in *A Primer in Density Functional Theory* (Springer Berlin Heidelberg, Berlin, Heidelberg, 2003).
- S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, *Phonons and related crystal properties from DFPT*, Rev. Mod. Phys. 73, 515 (2001).