Computational modeling of inorganic solids

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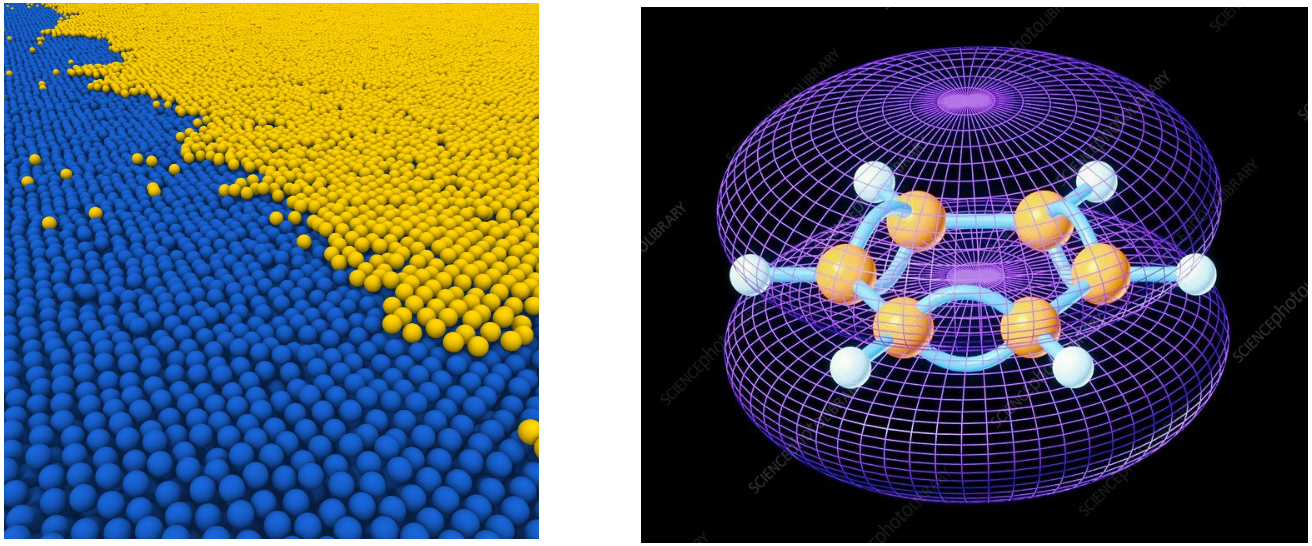
Computational fields

	Computational materials science	*Computational chemistry*
Objects	mostly solids and liquids	mostly molecules and groups of molecules
Methods	mostly Density functional theory and classical molecular dynamics	mostly Hartree-fock and post Hartree fock, and empirical and semi-empirical



Why we need materials modeling?

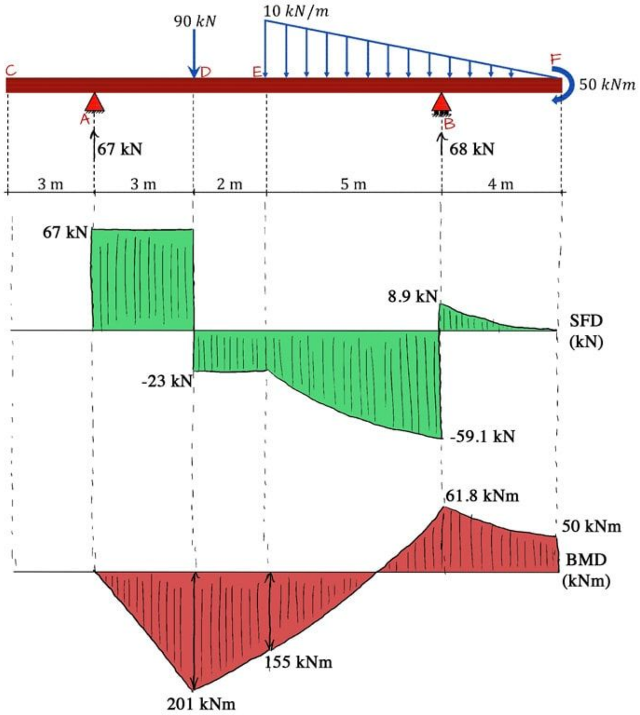
1. Understand and explain the behaviour of matter
    a. Very successful, significantly helped to understand the behaviour of molecules and materials.
    b. The intuition works extremely bad on a quantum-level, modeling helps to improve that.

2. Predict and develop new materials
    a. this is a long-standing goal of materials modeling. Recently, many new materials have been predicted, but almost no of them have become commercially successful that we know of. Several reasons:
    b. Materials modeling only recently have become powerful enough for that task, we need more time
    c. The number of researches doing modeling is still much smaller compared to experiment
    d. Companies do not disclose their results
    e. The modeling is still considered too simple models compared to experiment

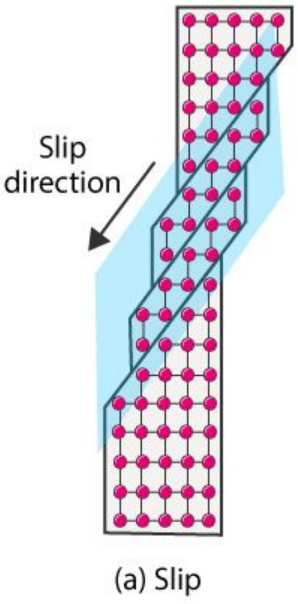
In any case, material modeling is an unparalleled tool which complement experiment

Modeling of solids

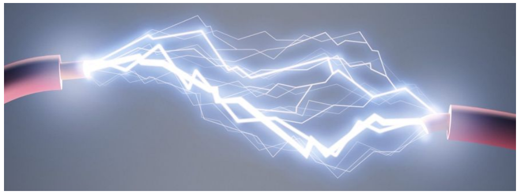
Strength of materials (elastic) - continuum models based on Hooke’s law

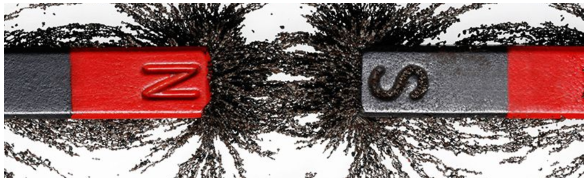


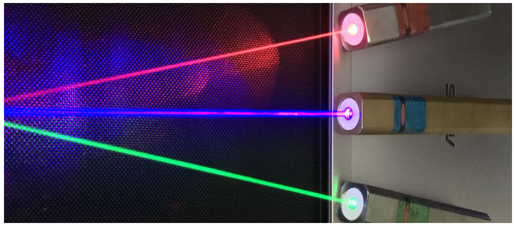
Plastic deformation? - atomic level is required



Functional properties? atomic level is required



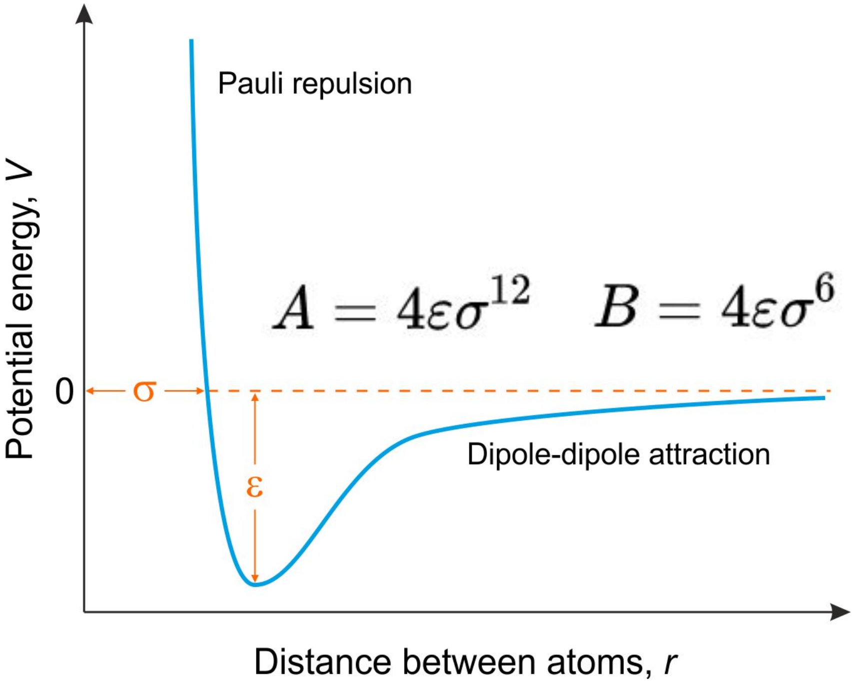




- Atomistic modeling is essentially required for detailed understanding of functional materials
- Only atomistic modeling can help to predict new materials

Interatomic interactions in atomistic modeling

$$V_{\mathrm{LJ}}(r) = \frac{A}{r^{12}} - \frac{B}{r^{6}},$$



$$A = 4\varepsilon\sigma^{12} \quad B = 4\varepsilon\sigma^{6}$$

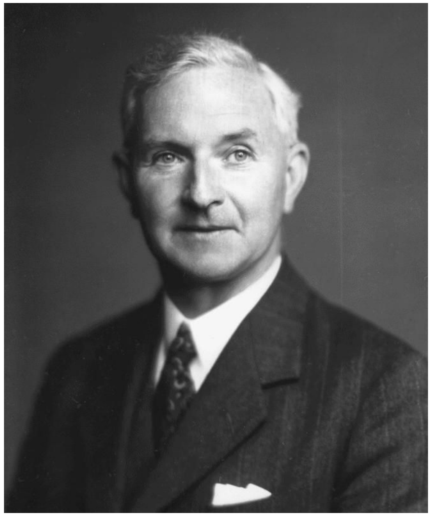
- in 1924 done for Ne and Ar gases
- in 1925 extended to Kr, Xe and like ions

For Kr using only:

1) interatomic distance and compressibility of RbBr
2) Refractivity of Br^-, Kr, Rb^+

Obtained for 32 ionic crystals:

1) Interatomic distance (2% accuracy for mono) predicted for MgSe (5%)
2) Compressibilities
3) Crystal energy



Sir John Edward Lennard-Jones

1. Jones J. E. Proc. R. Soc. Lond. A106 (1924) 441–462; 463-477 (Articles by W.Bragg in the same vol)
2. Lennard-Jones J. E. Proc. R. Soc. Lond. A109 (1925) 584–597 (Articles by P.Dirac in the same vol)

Essential role of electrons in interatomic interaction

- 1897 discovery of electron by E.Wiechert and J. Thomson
- 1913 planetary model of atom by N. Bohr
- 1924 wave properties of electron suggested by Louis de Broglie and proved in 1927 in Davisson–Germer experiment
- 1926 Schrödinger equation - for wave functions and can describe electrons correctly

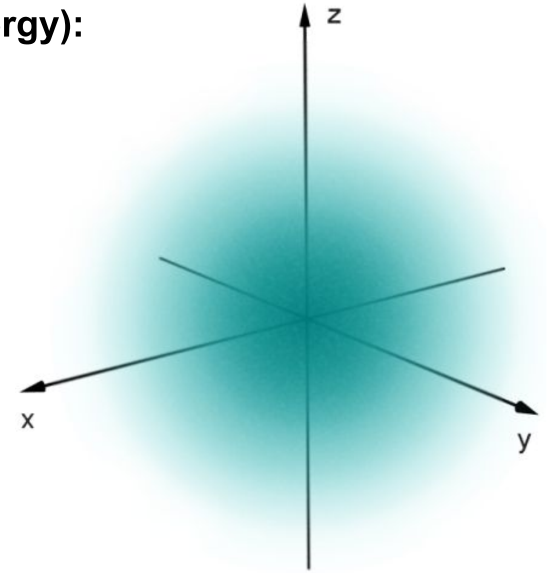
Time dependent SE (*ψ* - wave function, *H* - operator of total energy):

$$\mathbf{i}\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t) = \hat{H}\psi(\mathbf{r},t)$$

$$\hat{H}\Psi(\vec{r}_1,\vec{r}_2,\cdots\vec{r}_N) = E\Psi(\vec{r}_1,\vec{r}_2,\cdots\vec{r}_N)$$

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r},t)$$

kinetic energy + potential energy

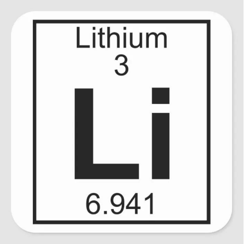


Orbital s ($\ell = 0$, $m_\ell = 0$)

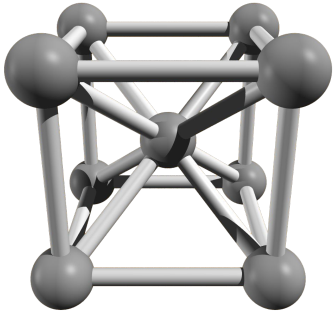
E=-13.6 eV

First principles or *ab initio* approach

Quantum chemistry allowed description of matter from first principles without any information from experiment, except for fundamental constants, such as electron mass, charge and planck constant



$$\longrightarrow \quad \hat{H}\psi = E\psi \quad \longrightarrow$$



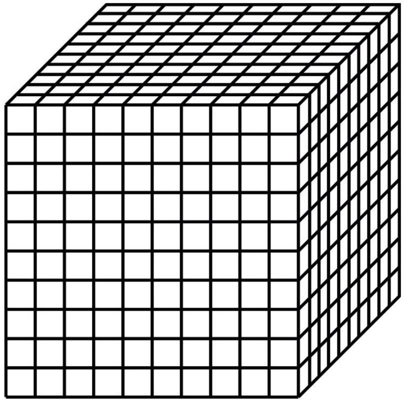
INPUT:
- Atomic number - 3
- Number of atoms in unit cell - 1

OUTPUT:
- Metall, E_{cohesive} = 1.63 eV/atom
- bcc lattice with a = 3.51 A at room T
- Electronic structure and possibility to derive all properties corresponding to ideal crystal

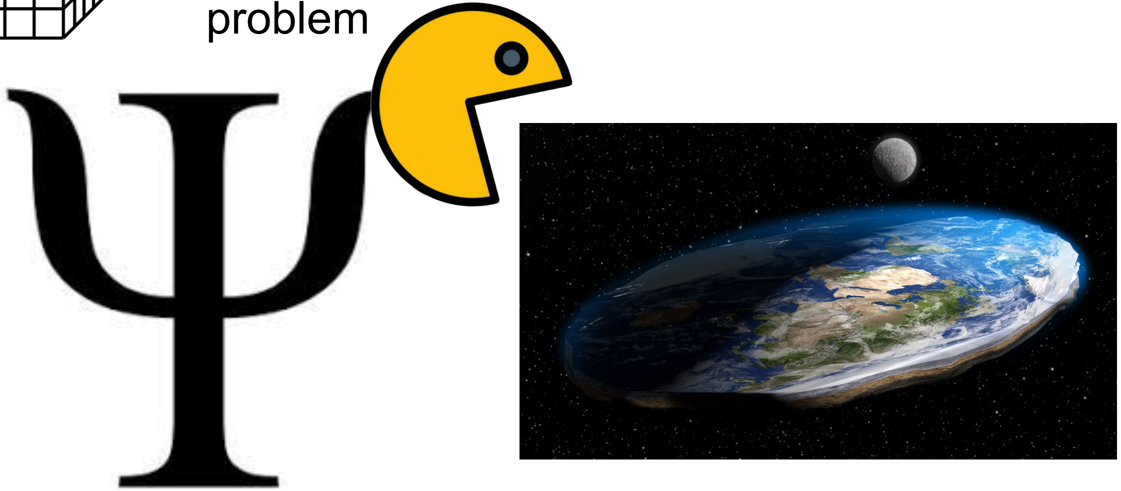
In principle the calculated properties will match experiment almost exactly!
I.e. quantum mechanics completely describes chemical interactions, **but ....**

Quantum description is very complex to treat!

Ψ(r1, r2, .. rN) is a complex function depending on 3N coordinates.
The analytical solution is available only for H_2 therefore numerical methods are used.
To write down Ψ numerically with only 10 values for each coordinate (just the real part without spin):



1 electron - 10^3 ~ 1 KB
2 electrons - 10^6 ~ 1 MB
5 electrons - 10^{15} ~ 1000 TB
8 electrons - 10^{24} ~ **1000 ZB**, Zettabyte
The total storage capacity of all computers on Earth is **60 ZB**
The solution complexity is faster than exponential with respect to number of electrons due to combinatorial nature of the problem



We need approximations! There are 4 of them.

Approximation 1: Born-Oppenheimer

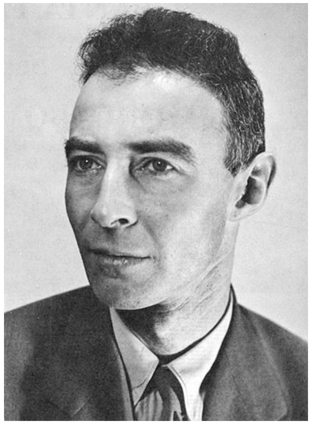
Since nuclei are much heavier than electrons (m_p = 1835 m_e), their dynamics can be decoupled and considered separately:

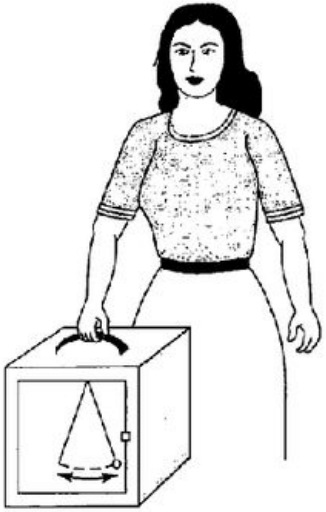
a. Froze cores -> solve electrons -> solve cores classically (error scales as $(M/m_e)^{-1/4}$)

b. Reduces number of variables and simplifies the problem

c. Oftenly used in calculations introducing only small error for ground state

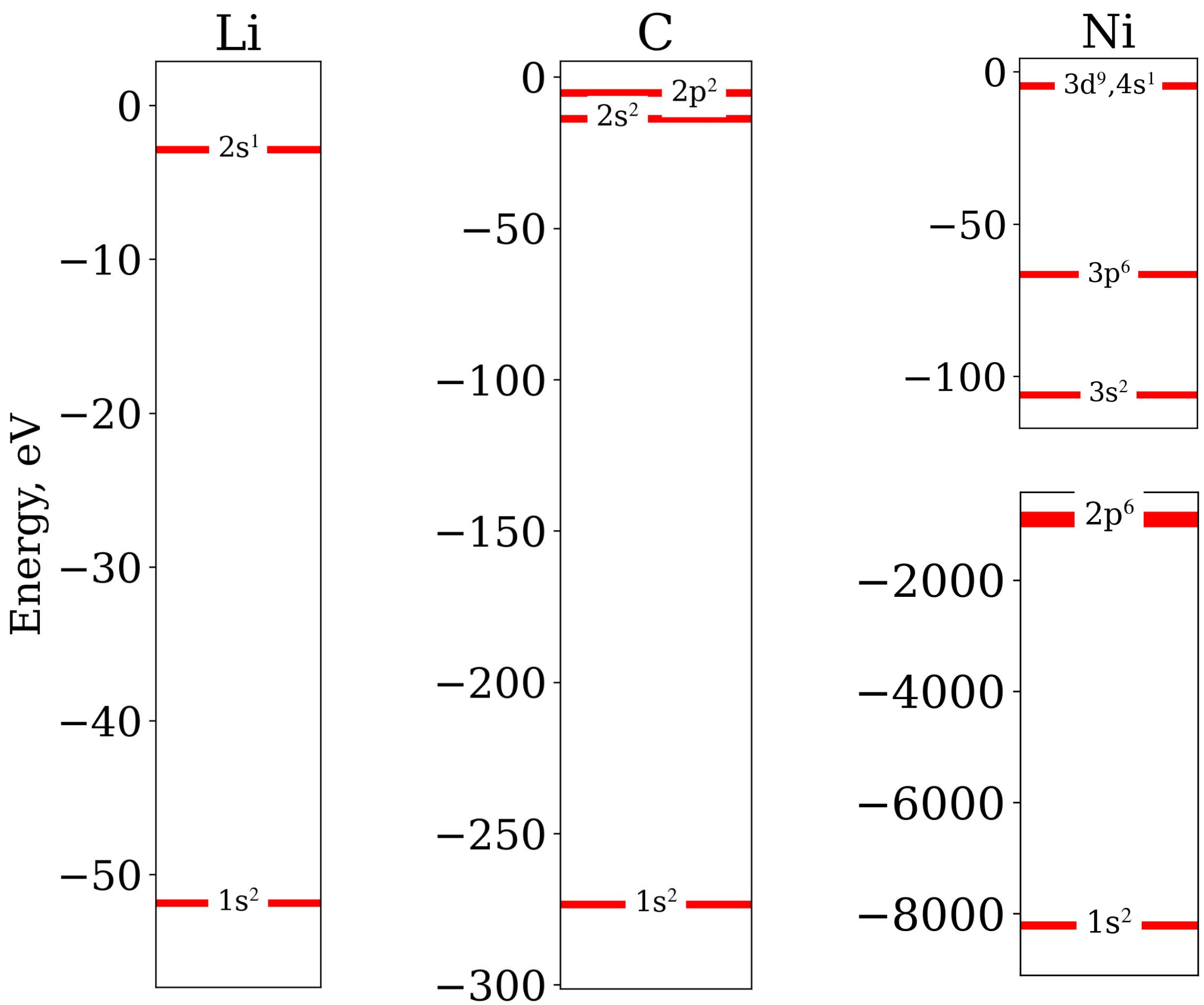

Max Born


Robert Oppenheimer

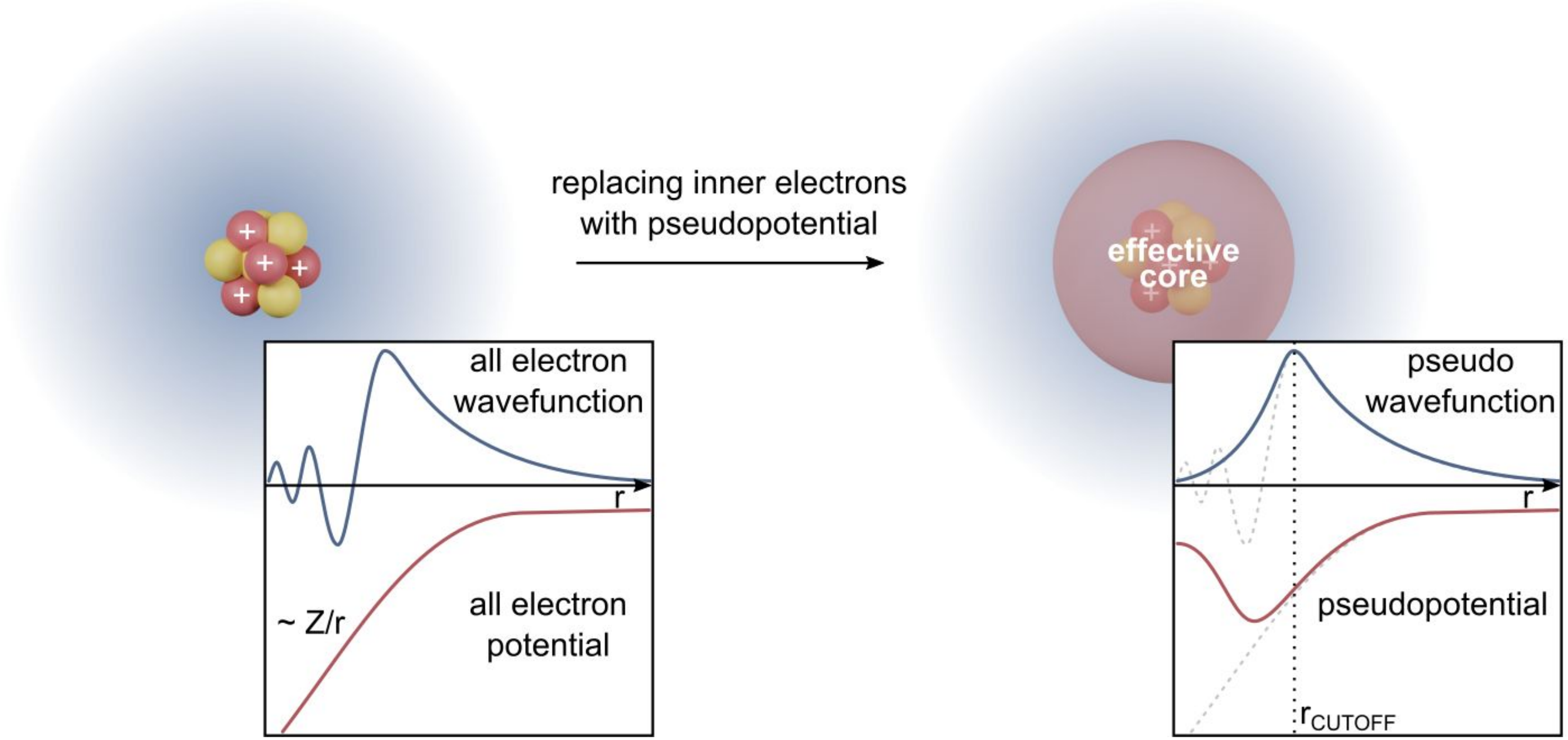


Approximation 2: deals with core electrons

Valence shell: $2s^1$ $2s^2 2p^2$ $3d^9 4s^1$ (only 10 out of 28!)



Approximation 2: Replace core electrons with pseudopotential

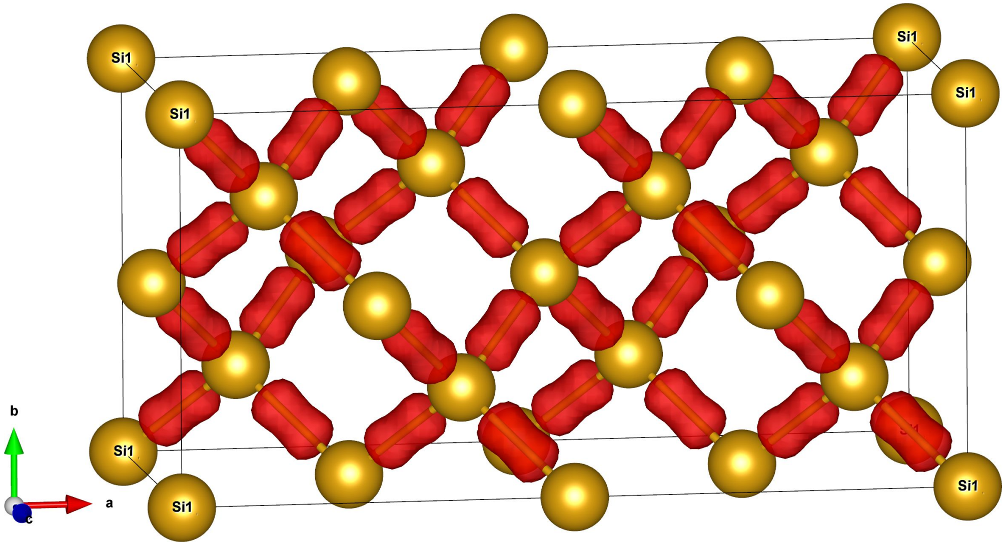


PAW - *projected augmented wave*, introduces only small error compared to full electron description

Approximation 3: electronic density

Use electronic density: $\mathbf{\Psi(r_1, r_2, \ldots, r_N)} \longrightarrow \mathbf{n(x, y, z)}$

$$n(\mathbf{r}) = N \int \mathrm{d}^3\mathbf{r}_2 \cdots \int \mathrm{d}^3\mathbf{r}_N \, \Psi^*(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N)\Psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N)$$



Electronic density is observable

Hohenberg-Kohn proved that 3 is not an approximation

- The idea of using electron density for calculations of solid was first used in semi-classical orbital-free Thomas-Fermi theory (1927); but the accuracy was quite low due to kinetic energy approximation.
- In 1964 Hohenberg and Kohn proved two important theorems according to which the electronic density is equivalent to many body wave functions in the sense that the total energy and all other properties are uniquely determined by density.

HK theory is exact (it has no approximations), but it was unsuited for practical problems!
It still relies on many-electron wave function to get density

998

1st theorem:

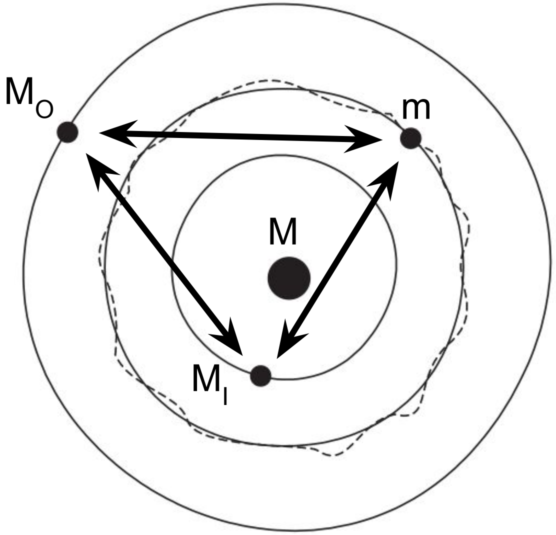
$$E = F[n(\mathbf{r})] + \int V_{ext}(r)n(\mathbf{r})d\mathbf{r} \qquad E_0[n_0] = \min_n(E[n])$$

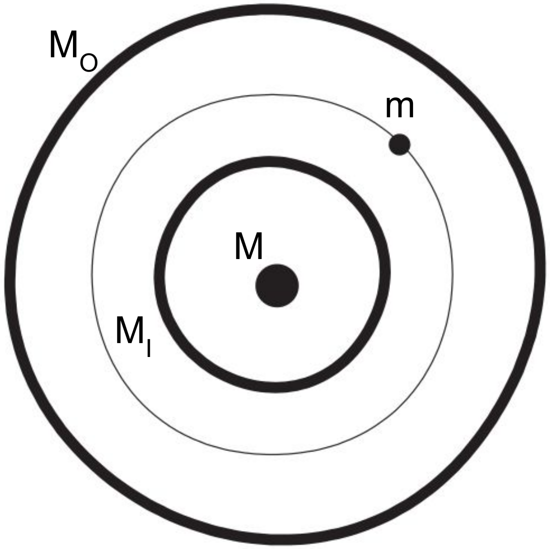
V_{ext} is potential created by nuclei

Approximation 4: replace many-particle system with one particle system in effective potential

Reality:
The real orbit slightly wiggles due to many-particle interaction.

Mean-field approximation:
The orbit is calculated assuming that m rotates around one object with mass $M+M_I$



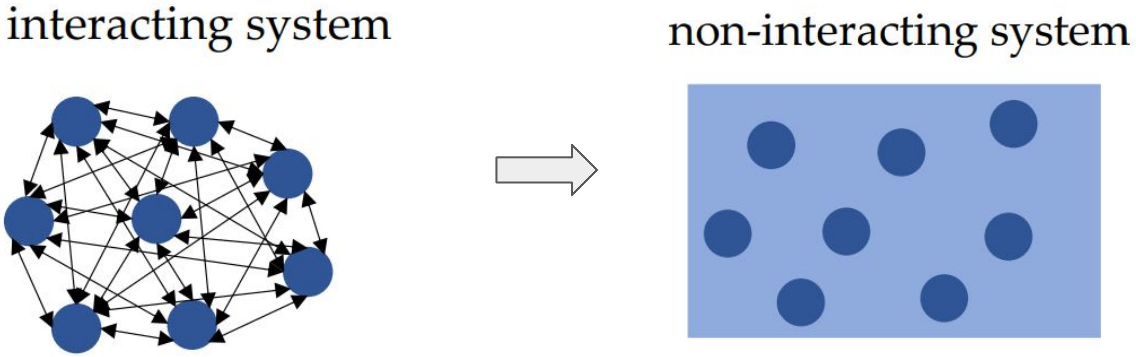


The wiggle due to many-particle interactions is called *correlation*

Approximation 4: Kohn - Sham theory

Replace the original interacting many-body system with an auxiliary one of non-interacting electrons. Take interaction into account with two terms:

1) Interaction of each electron with electron density (V_{Hartree})
2) Interaction of each electron with exchange-correlation potential (V_{XC})



Lu Jeu Sham

n

it is

Hohenberg-Kohn + Kohn-Sham

=

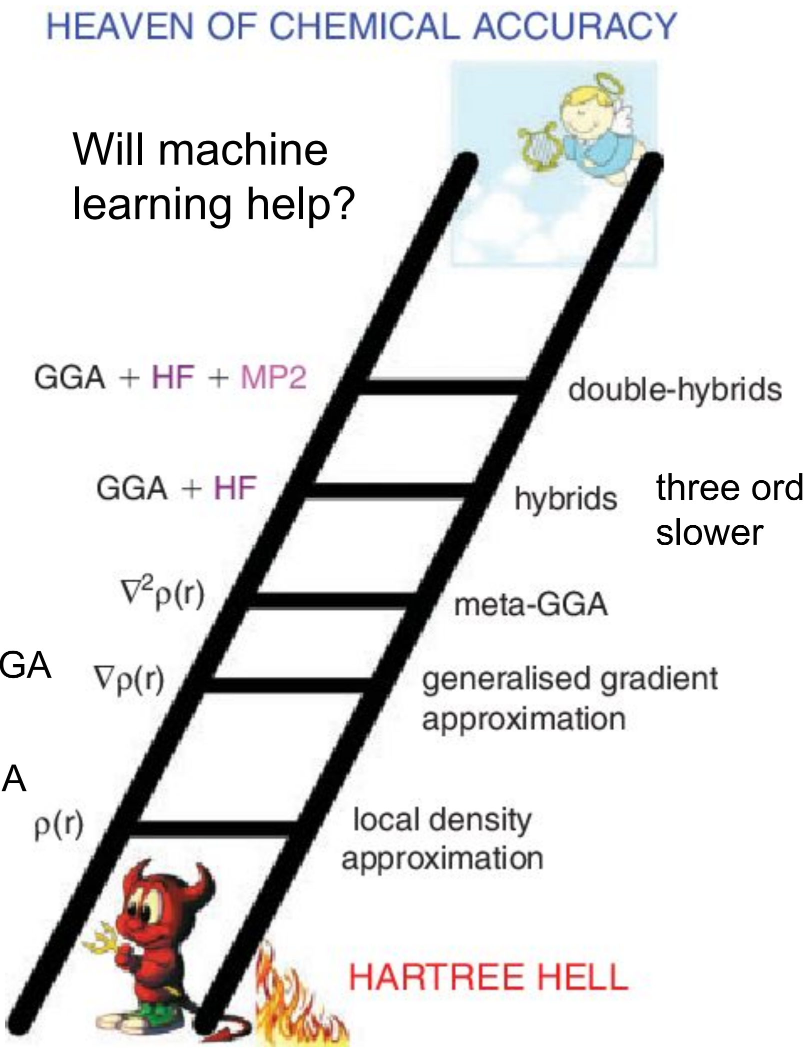
Density functional theory (DFT)

Rush for accurate exchange-correlation potential

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

In principle, if we can know the true form ***V*$_{xc}$[*n*]**, we can have the exact solution of many-particle system

John P. Perdew, one of the developers of exchange correlation functionals made an analogy with **Jacob's Ladder** AIP Conference Proceedings 577, 1 (2001)



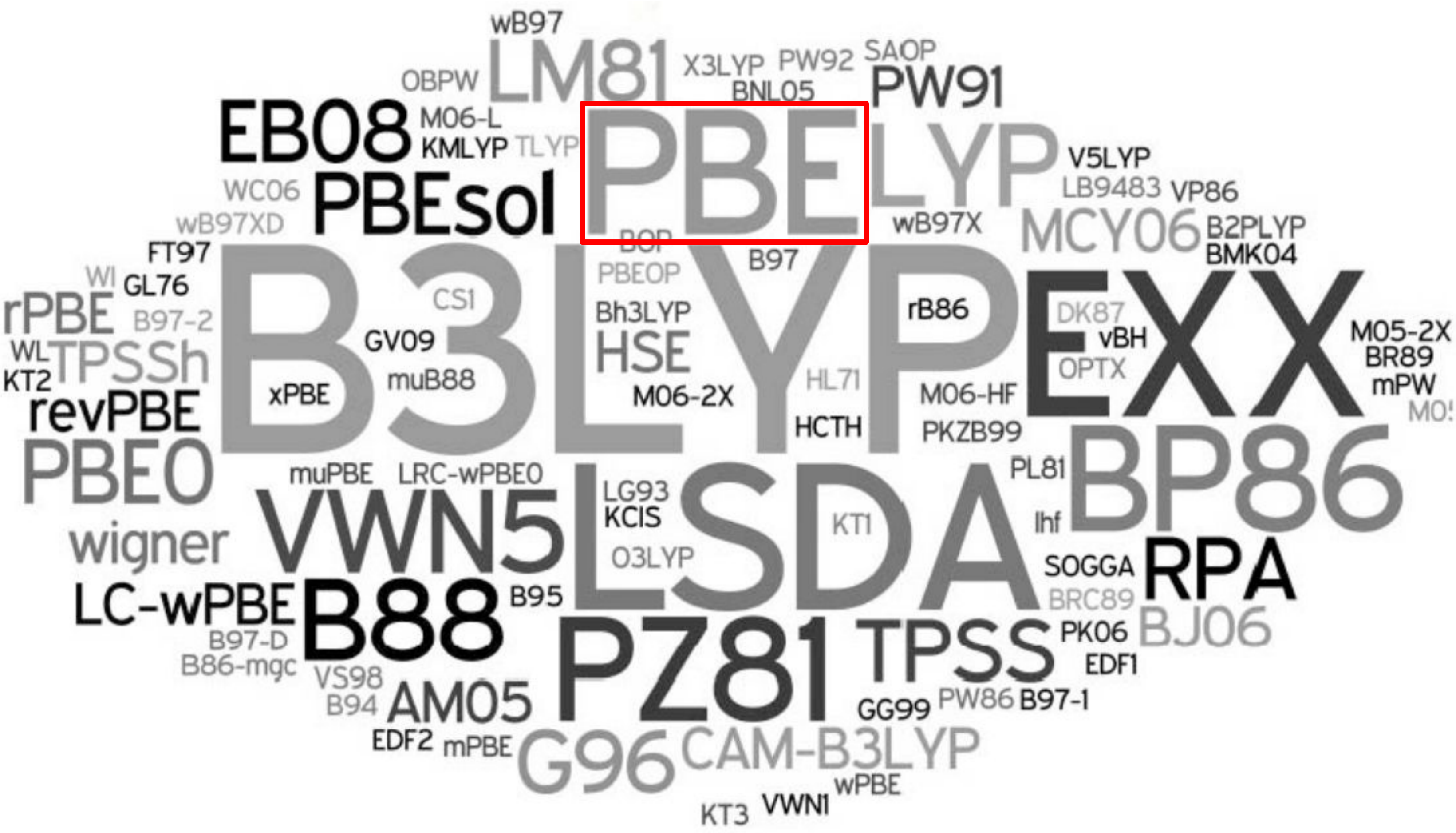
Will machine learning help?

three orders slower

GGA

LDA

Exchange-correlation functional flavours



Perdew, John P., Kieron **Burke**, and Matthias **Ernzerhof** Generalized gradient approximation made simple, *Phys. Rev. Let.* 77 (1996) 3865

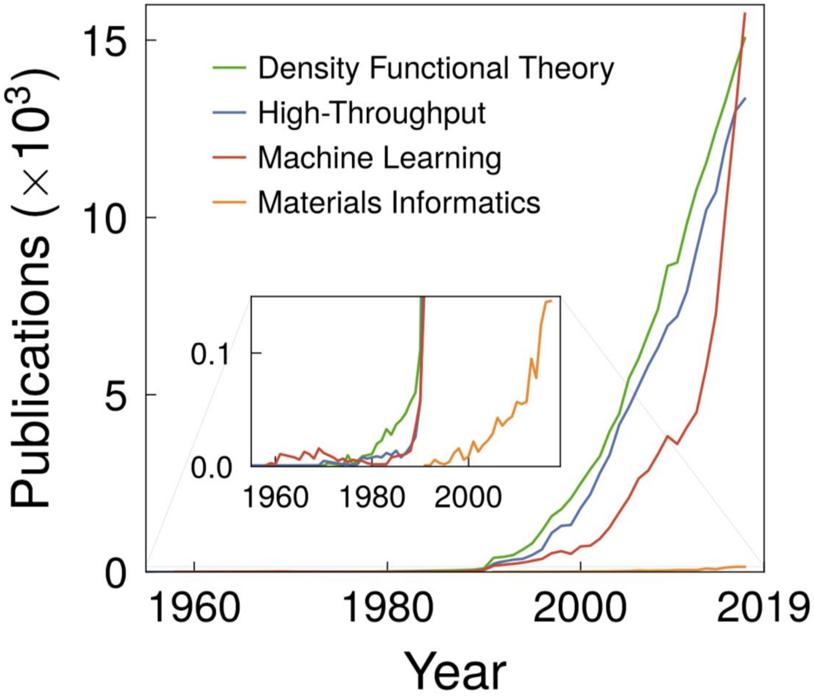
138 000 citations!

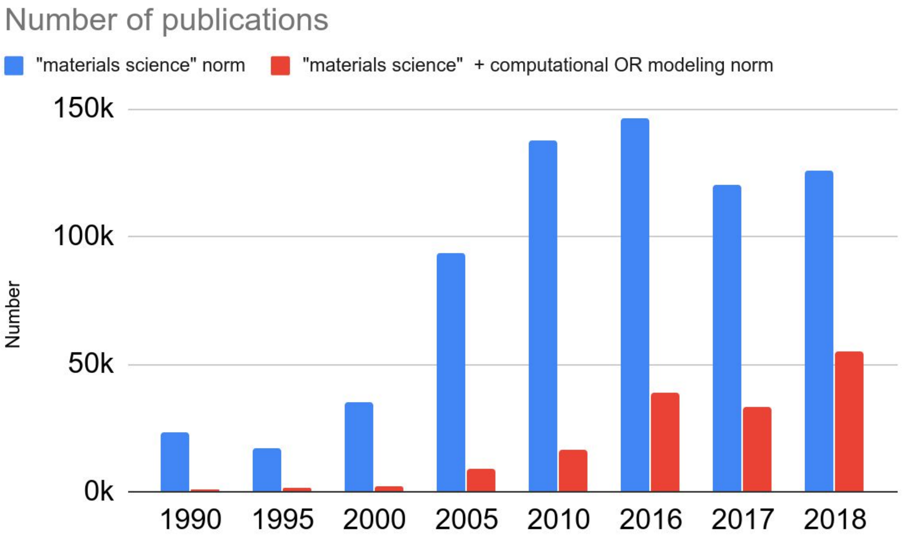
Summary of approximations used in DFT

- 👌Born-Oppenheimer approximation - decouple electron and nuclei dynamics
  - very accurate for ground state properties - lattice constants, energies, elastic, etc.
- 👌Total energy and other properties as a functional of electronic density
  - not an approximation at al, just equivalent description
- 👌Pseudopotential for core electrons
  - very accurate for chemical tasks
- 📛One many-electron system ⇒ many one-electron systems with effective potential;
  - Many-electron effects are inside exchange-correlation potential (V_{XC})
  - In principle can be exact, but exact V_{XC} is unknown,
  - V_{XC} is approximated with several levels of accuracy, but the receipt for systematic improvement is still unknown!
  - The main source of errors in DFT calculations. Binding energies of molecules, band gaps, surfaces and strongly-correlated systems are especially sensitive to V_{XC}

DFT development

1) What can be calculated with DFT for solids?
2) What is the accuracy of calculations?
3) When DFT is useless?





- DFT has become a must tool in materials science studies

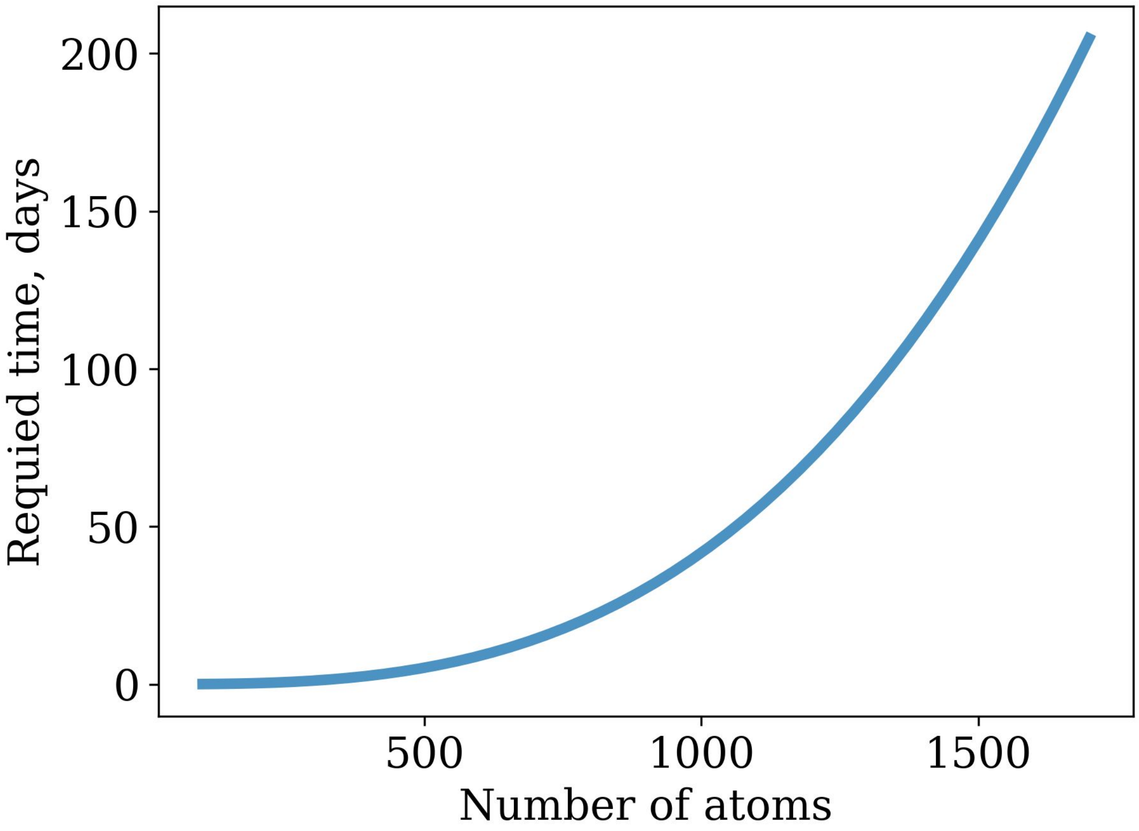
What can be calculated with DFT for solids?

In principle everything!

In practice it is limited by the complexity (size) of a system:

- The computer time required grow as n^3, where n is number of electrons.

- E.g. on a 16-core modern processor, 1000 electrons (100 Ni atoms), one calculation of total energy requires from 20 min to 1 hour

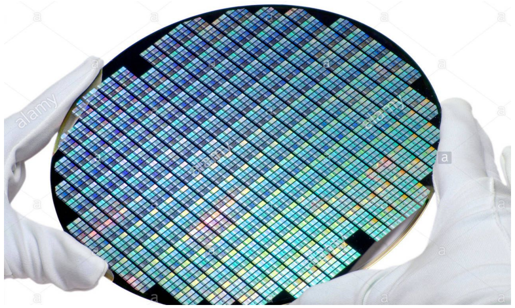


But solids contain in the order of one mole of matter 10^{23} atoms!
How they can be treated computationally?

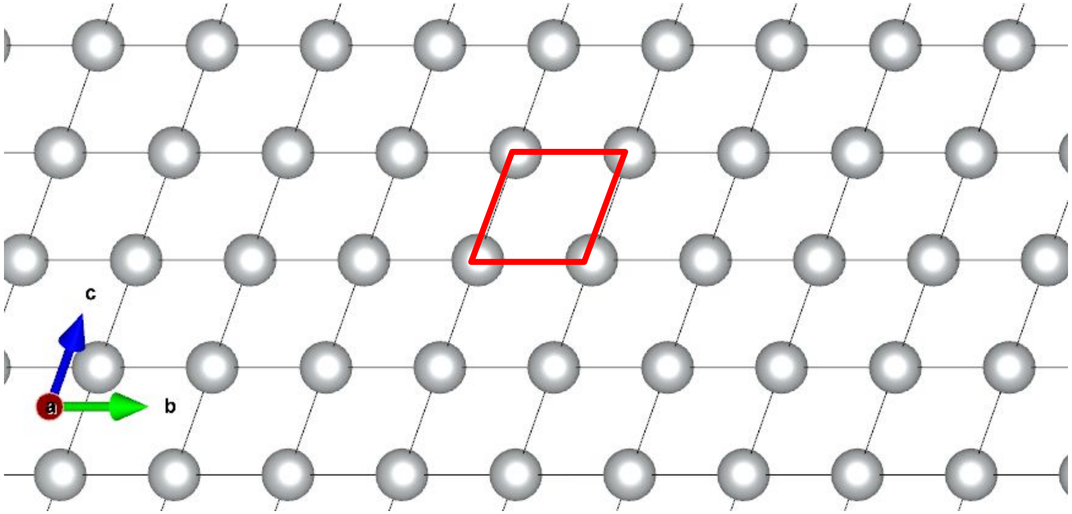
Periodicity of crystals

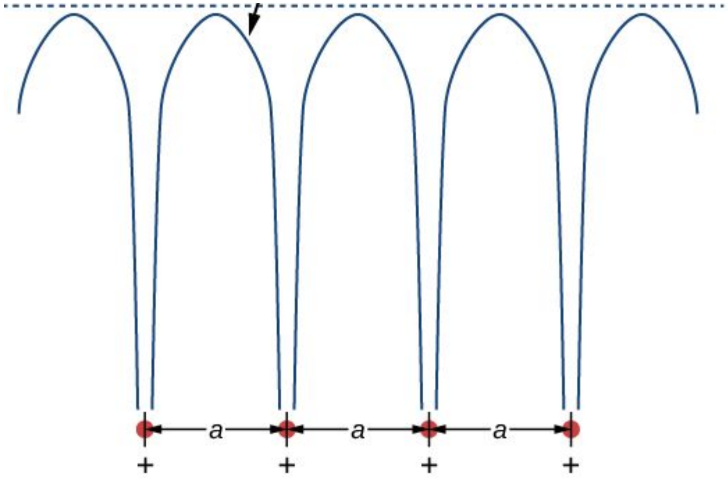
Insulators

Semiconductors



Metals and alloys





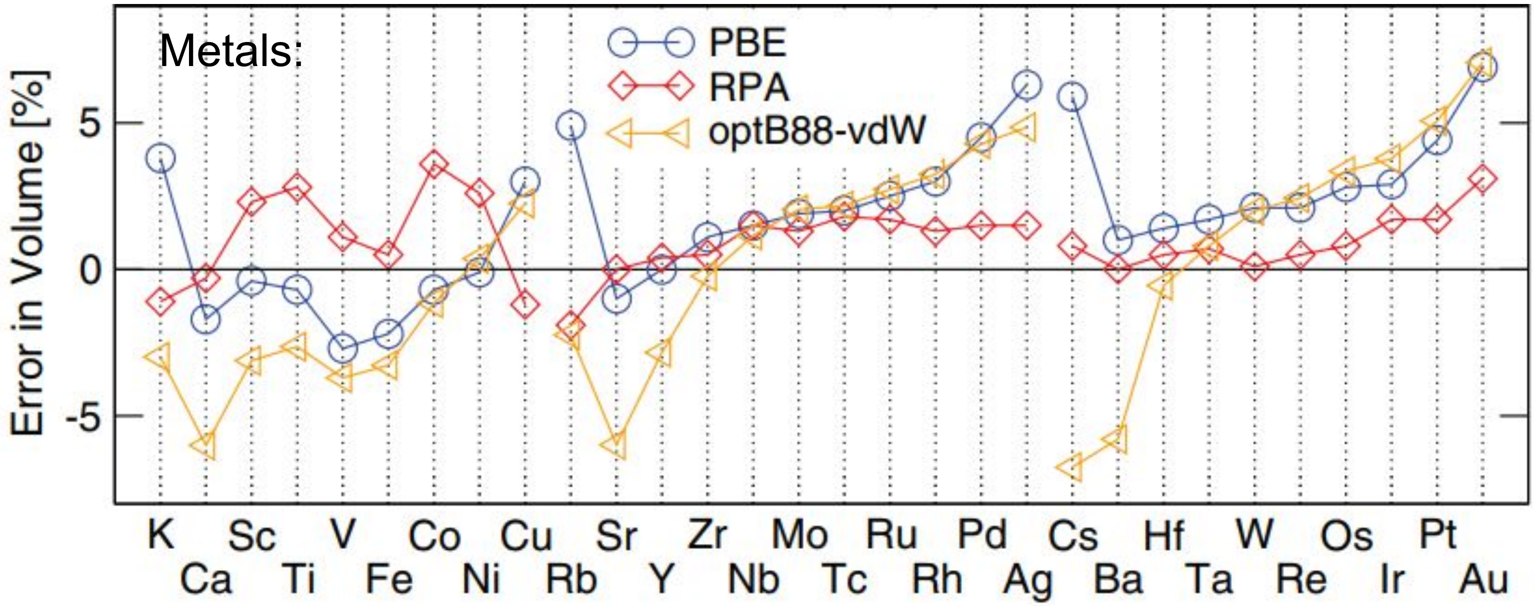
Potential and wave function are periodic therefore only one unit cell can be treated computationally. It is easily realized in DFT

Li - 1 atom, $LiCoO_2$ - 4 atoms, $Li_7La_3Zr_2O_{12}$ - **96 atoms**!

Properties of ideal crystal: crystal structure and lattice constants

It is possible to find lowest energy crystal structure using global minima optimization algorithms

- genetic algorithms (USPEX code), random search (CASTEP code), particle swarm (CALIPSO code)
- Oftenly the structure is known



PBE - Perdew–Burke–Ernzerhof - one of the most popular XC functional for solids
RPA - random phase approximation - one of the most accurate methods
optB88-vdW - hybrid functional with van der Waals correction

Example: Volume shrinkage/expansion of cathode materials

Reaction	DFT volume shrinkage, %	Experimental volume shrinkage,%
$LiCoO_2$ -> $Li_{0.25}CoO_2$	−4 [a]	−3/−4 [c]
$LiFePO_4$ -> $FePO_4$	7 [a]	6.5 [d]
$Li_4Ti_5O_{12}$ -> $Li_7Ti_5O_{12}$	−0.2 [b]	~0 [e]

a Materials project, b Electrochem. Comm. 9 (2007) 1107–1112, c Measurement 94 (2016) 759–770, d J. Electrochem. Soc., 144, (1997) 4, e. J. Electrochem. Soc., 142 (1995) 5

Properties: Total energy. Example: phase stability

Stability of polymorphic phases
$E_{Graphite} < E_{diamond}$ by 30 meV/atom at T_{room} [a]

E($NaFePO_4$, maricite) < E($NaFePO_4$, triphylite) = 2 - 6 meV/atom [b]

E($NaCoO_2$, $P6_3/mmc$) < E($NaCoO_2$, R-3m) = 6 meV/atom (our data)

Stability of new phases
$LiVPO_4 + O_2 \rightarrow 1/3Li_3V_2(PO_4)_3 + 1/6V_2O_5$
DFT show 230 meV/atom!

But it should be remembered that kinetics is also highly important and often determines the stability of phases in experiment. Bulk DFT calculations are useless in this case

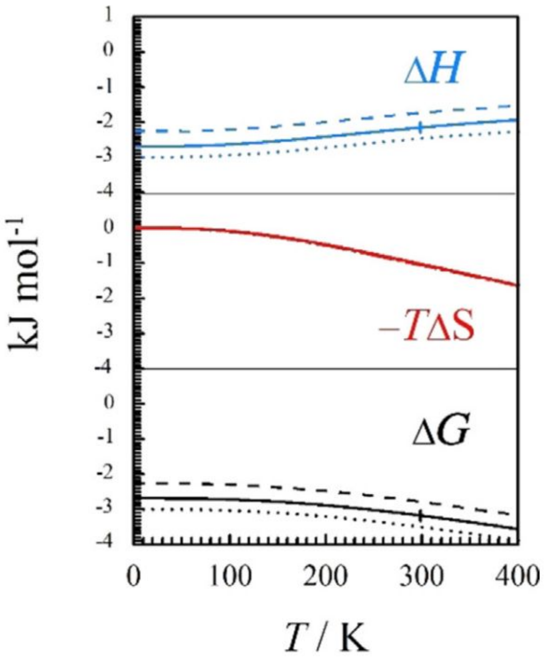
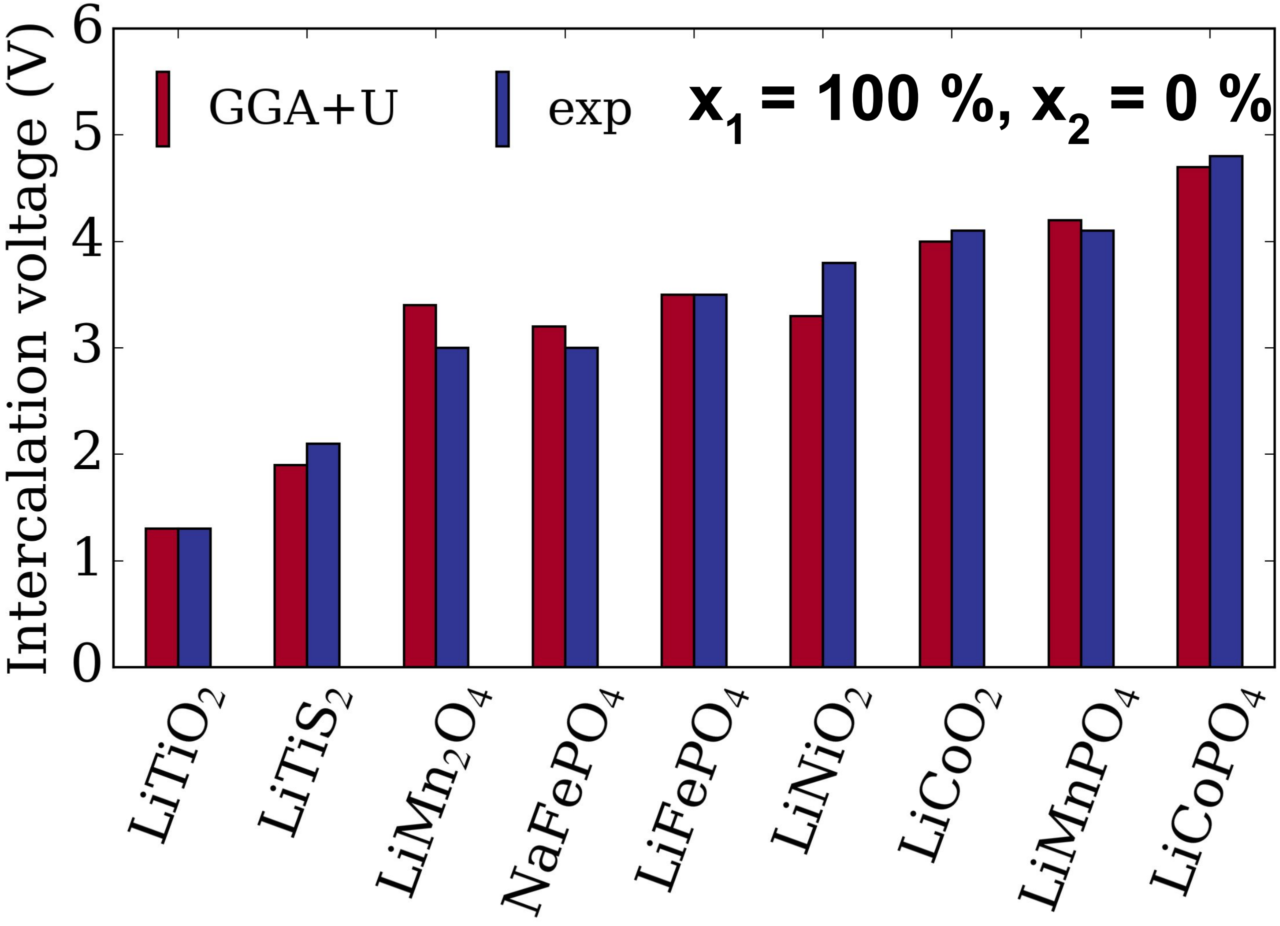


Fig. △G = G(graphite) - G(diamond). Solid line is experiment, dashed and dotted are DFT. [a]

a. Angew. Chem. Int. Ed. 2021, 60, 1546 – 1549, b. Chem. Mater. 2010, 22, 4126–4128, c.

Total energy example: Intercalation potentials

$$\overline{V}(x_1, x_2) \approx -\frac{E(\mathrm{Li}_{x_1}\mathrm{MO}_2) - E(\mathrm{Li}_{x_2}\mathrm{MO}_2) - (x_1 - x_2)\,E(\mathrm{Li})}{(x_1 - x_2)\,F}$$

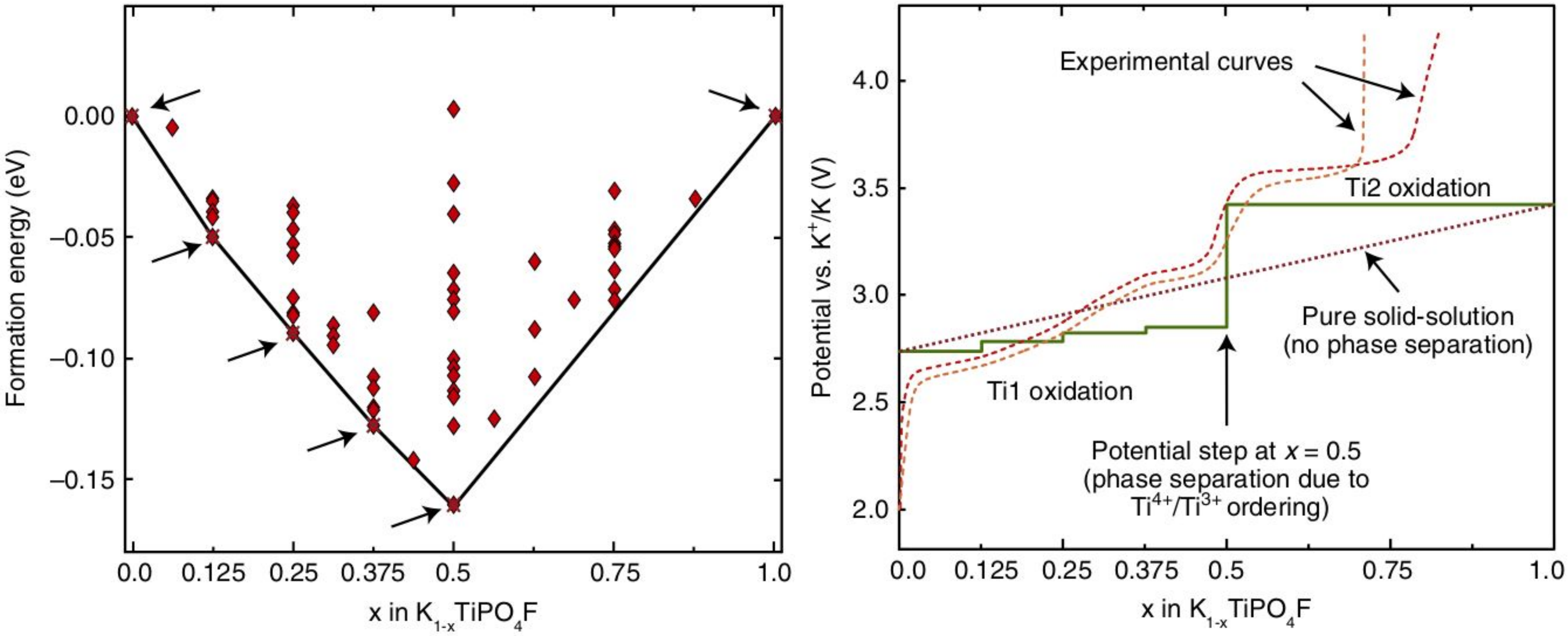


DFT+U is required
The U value can be determined self-consistently from first-principles. However, oftenly it is fitted to experimental data

Another option is to use hybrid functionals, but in this case the calculation time increases by 3 orders of magnitude for plane-wave DFT codes

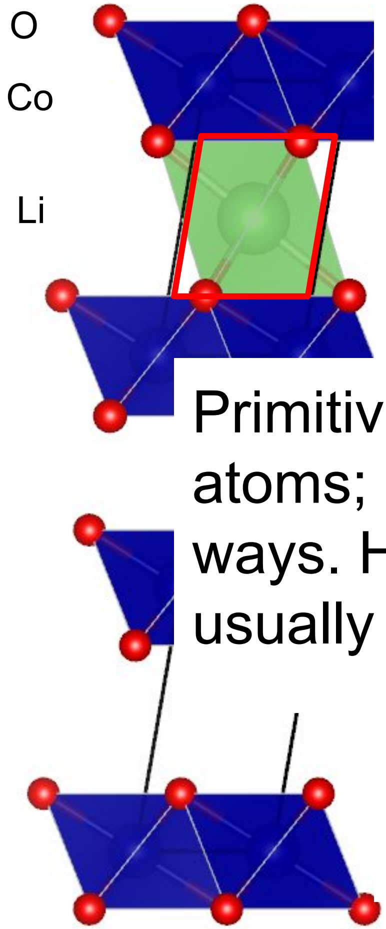
Total energy example: phase diagrams, voltage profile

How to calculate phases with intermediate concentrations?

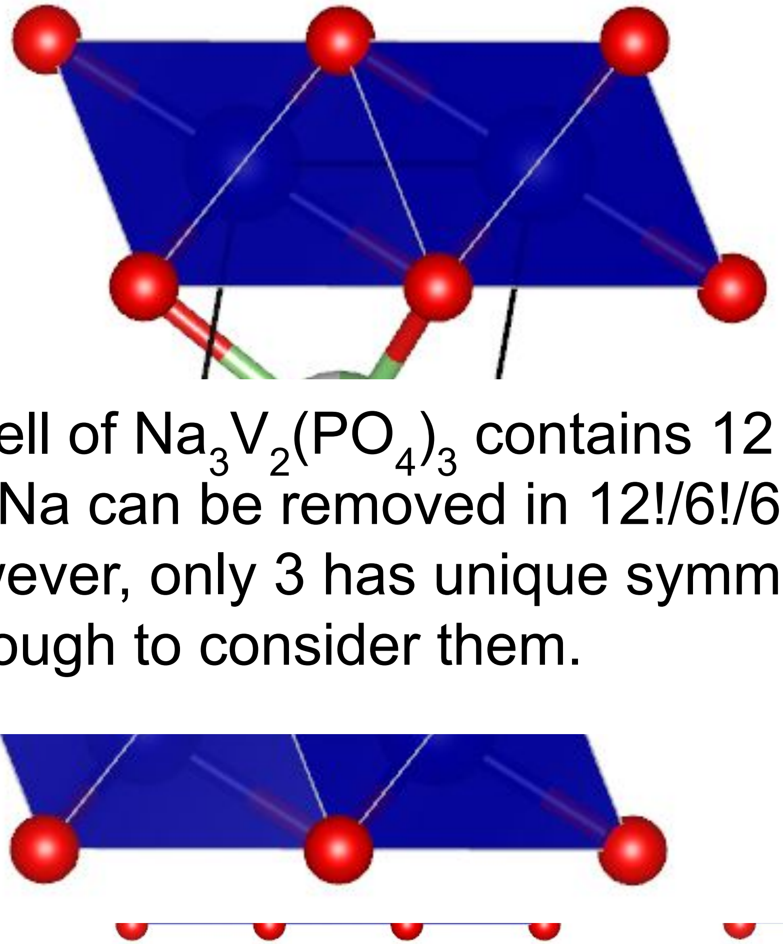


Fedotov et al., *Nat. Comm.* 11 (2020) 1484

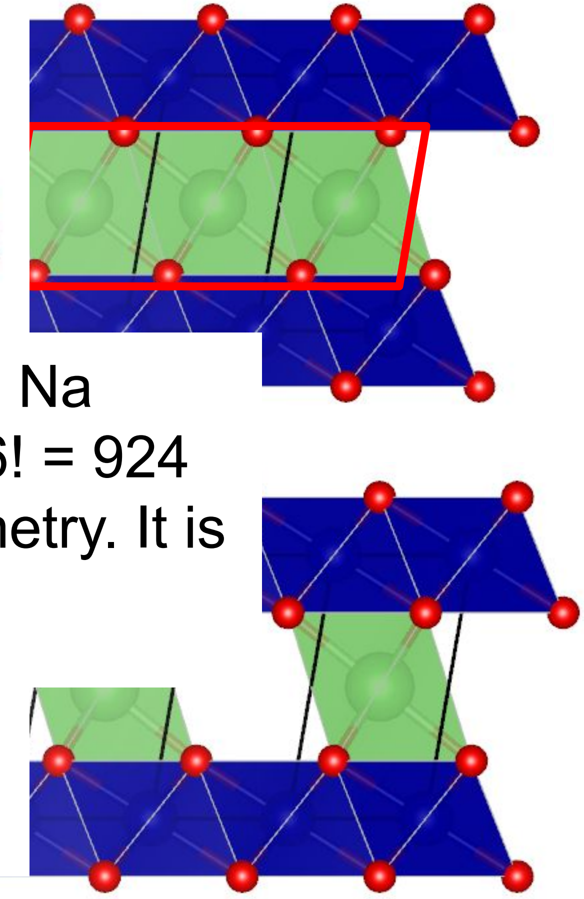
Intermediate concentrations: construct supercells



$LiCoO_2 \rightarrow CoO_2$



$LiCoO_2 \rightarrow Li_{1/2}CoO_2$

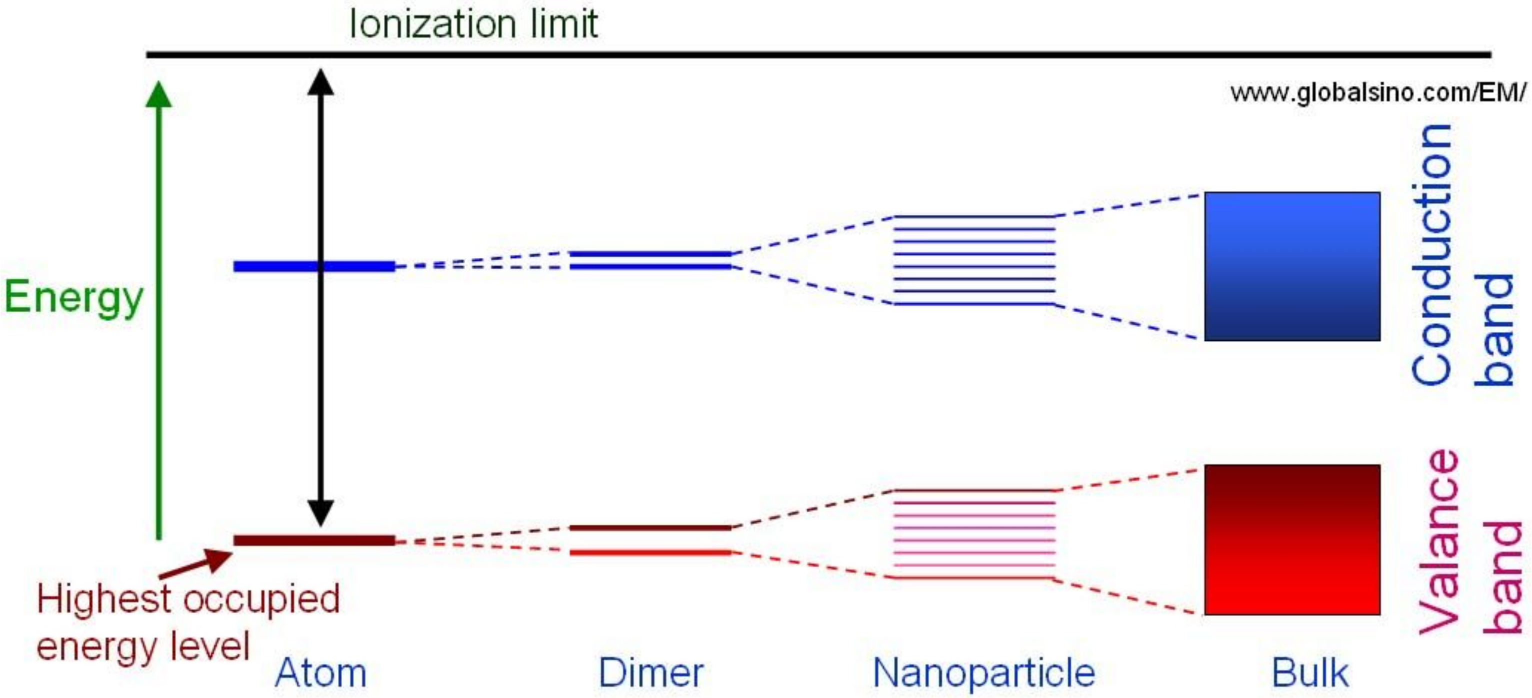


$LiCoO_2 \rightarrow Li_{1/3}CoO_2$

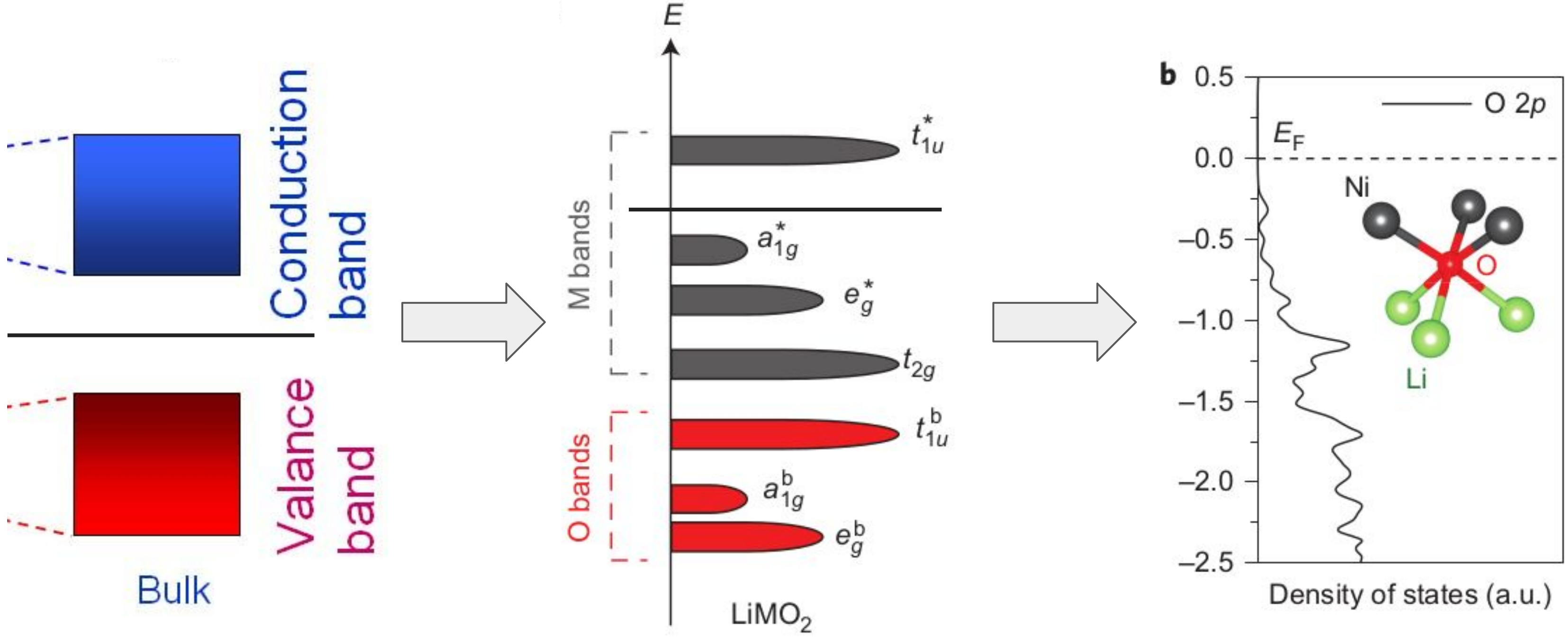
Primitive cell of $Na_3V_2(PO_4)_3$ contains 12 Na atoms; 1/2Na can be removed in 12!/6!/6! = 924 ways. However, only 3 has unique symmetry. It is usually enough to consider them.

Properties: Electronic structure

- Highly important to understand what is going on the level of chemical bonding
- X-ray and TEM does not provide, only spectroscopic methods such as EELS and EXAFS, but it is hard to resolve the fine structure
- DFT readily provides electronic structure with high details
- To understand electronic structure one need to understand band structure of solids:

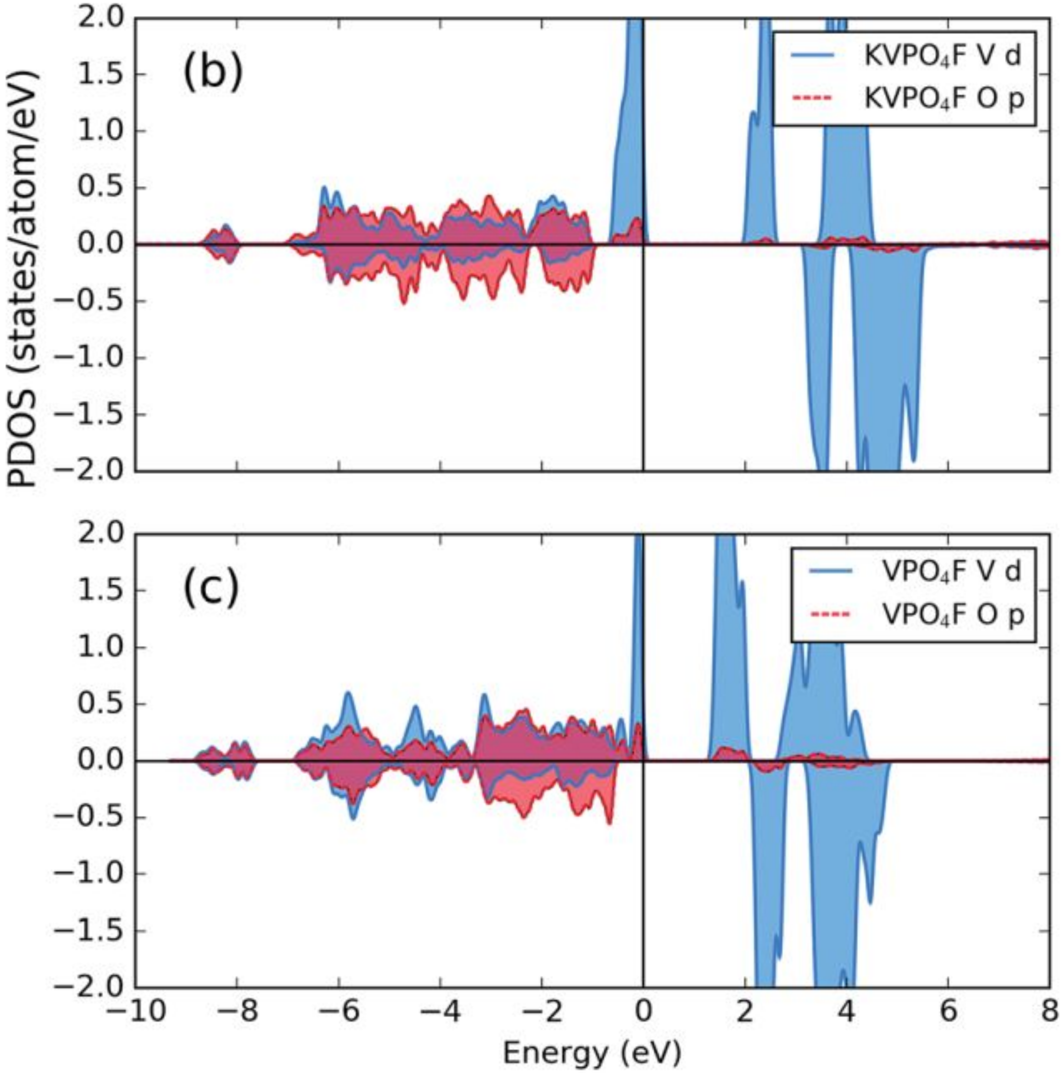


Properties: Density of states



DOI: 10.1038/NCHEM.2524

Properties: Density of states

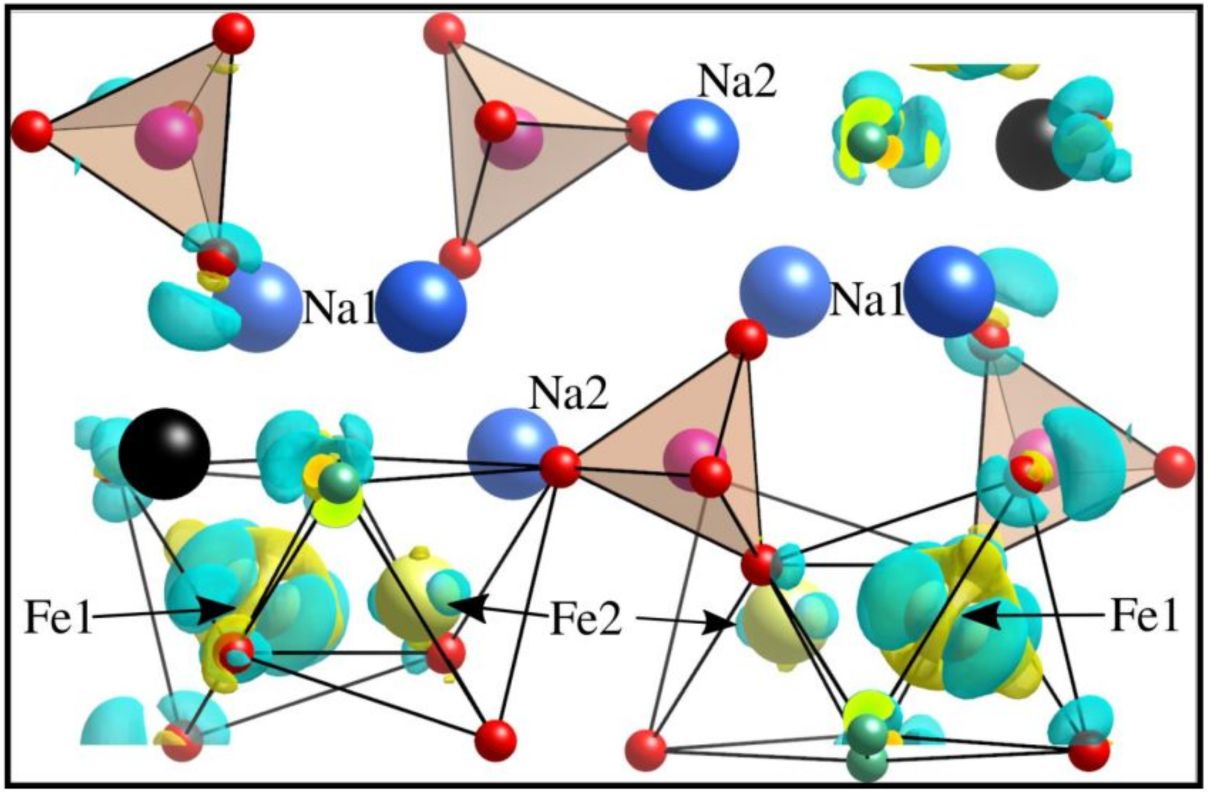


V^{4+}

V^{5+}

Fedotov et al. *J. Mater. Chem. A*, 6 (2018) 14420

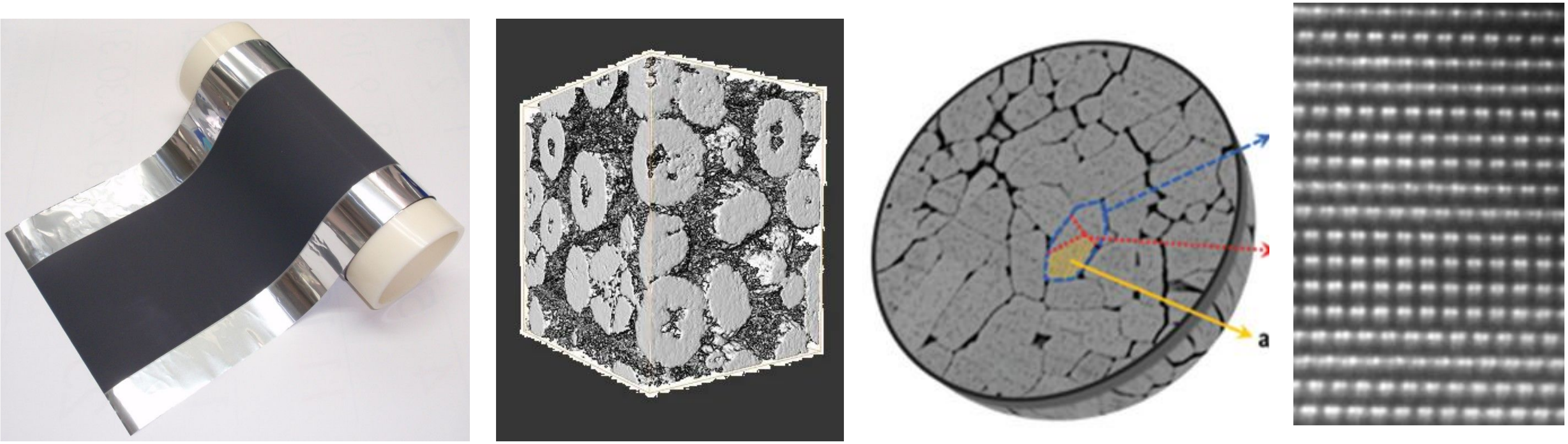
Properties: Charge density difference



dn = n($Na_{1.5}FePO_4F$) - n(Na_2FePO_4F); yellow - positive; green - negative
n is extracted from O and t2g Fe and slightly increases at e^b_g
Only Fe1 is oxidized
Oxidation is accompanied with redistribution of density.
Oxygen participates in redox.

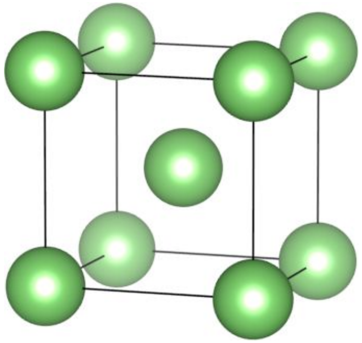
Connection to real materials

- Using one primitive cell an infinite ideal crystal can be modelled allowing to consider numerous properties
    - crystal structure and lattice constants
    - energy phase stability
    - electronic structure and functional properties
- By choosing an appropriate functional very good agreement between theory and experiment can be obtained (within several percents)
- However, one should always keep in mind that real materials are far from ideal

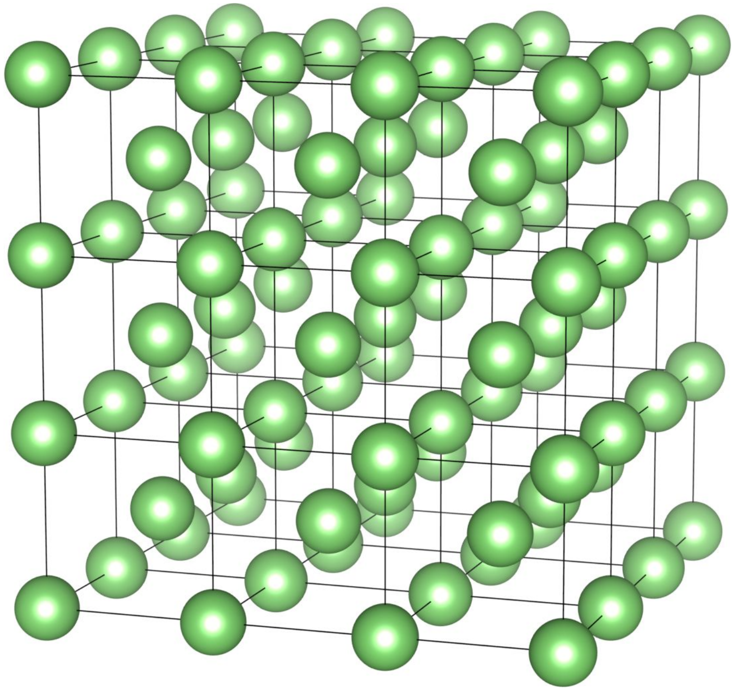


Modeling of defects: vacancies

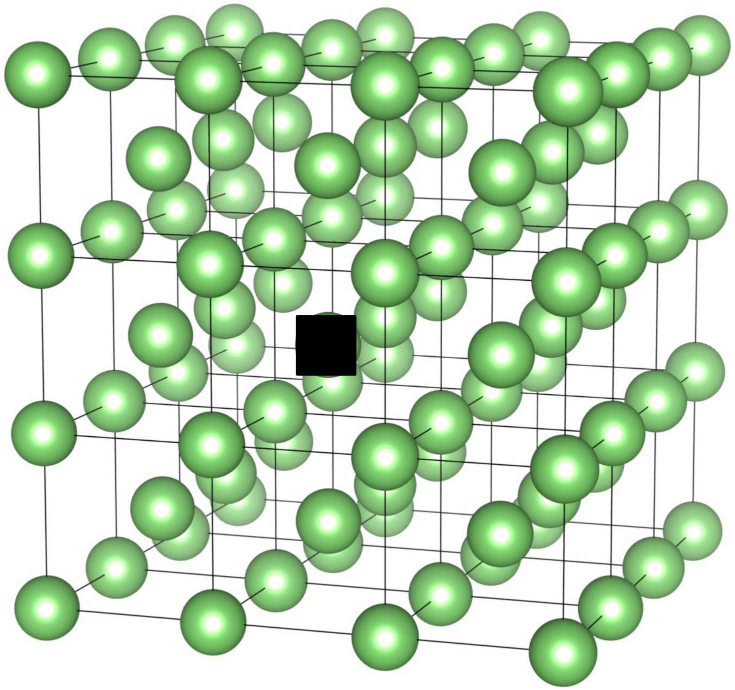
DFT allows modeling of complex defects
Once you can insulate the role of some defect you can study it with DFT modeling



BCC unit cell



3x3 supercell

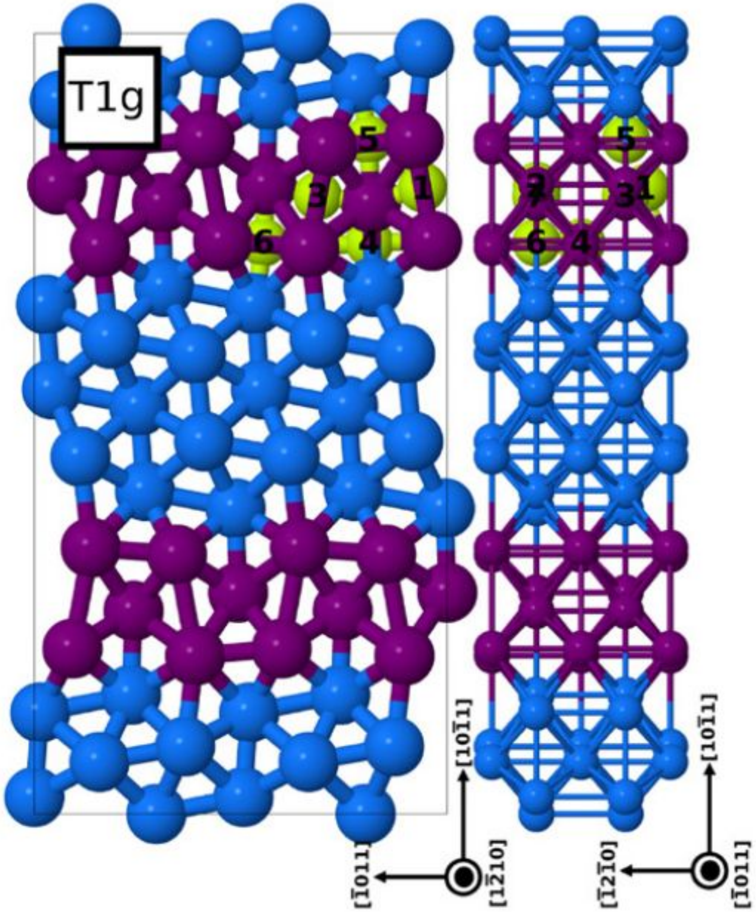


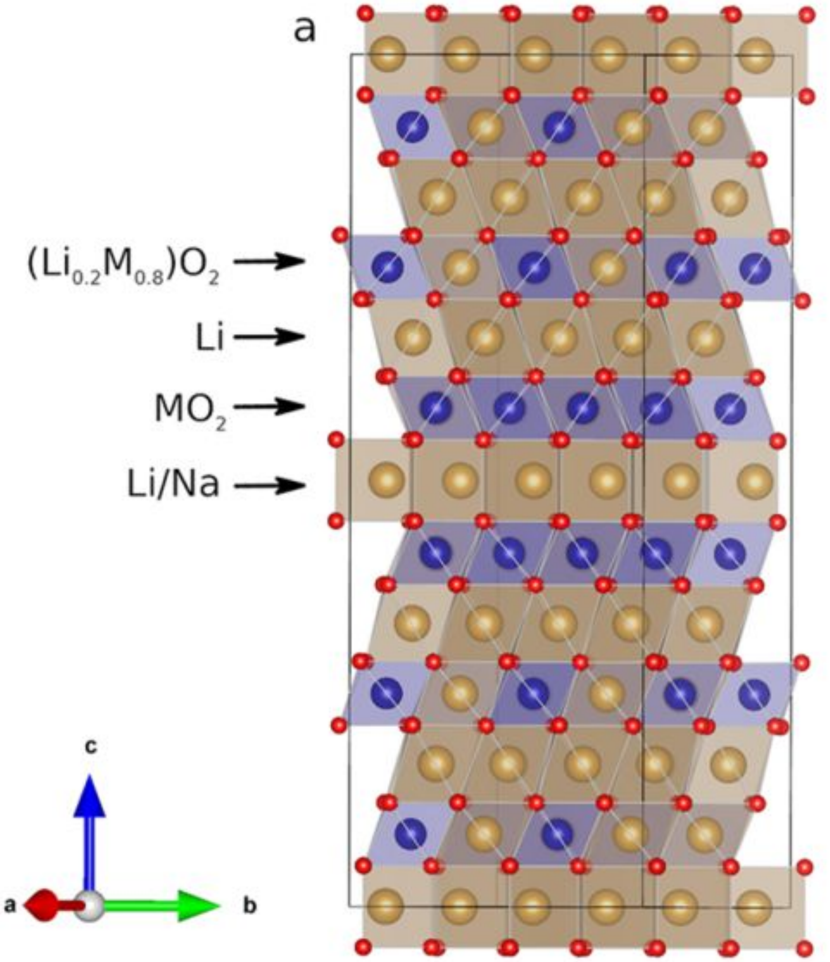
3x3 supercell with vacancy

A vacancy is repeated every third unit cell infinitely -> so we have matrix of vacancies
If the distance is large enough vacancies don’t know about each other and don’t interact
10x10x10 A is usually enough

Modeling of defects: grain boundaries

hcp Titanium:

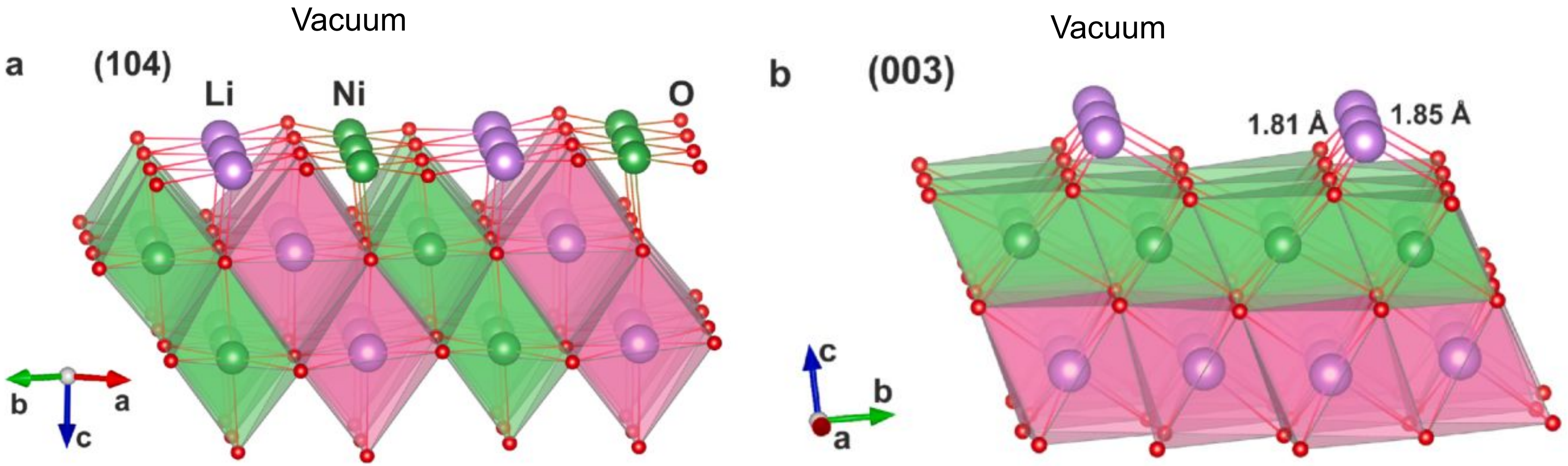


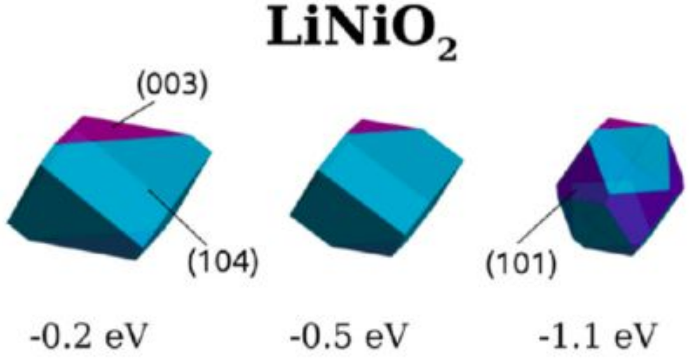


Aksyonov et al. J. Phys.: Condens. Matter 28 (2016) 385001

Abakumov et al. ACS Appl. Energy Mater. 2021, 4, 6777−6786

Modeling of defects: surfaces





Structure (can be difficult) and energetics of defects

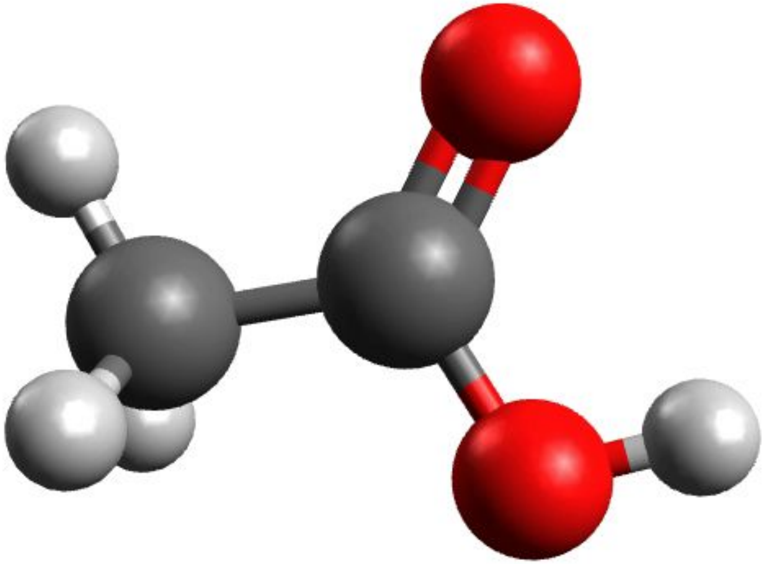
Influence on

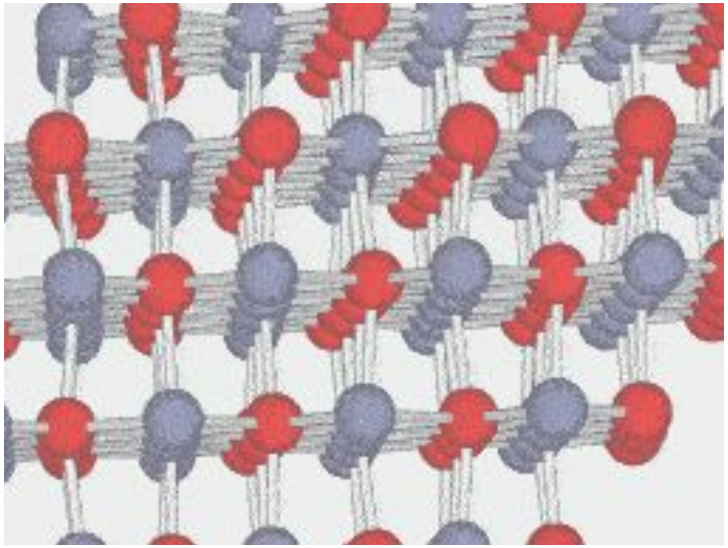
- mechanical strength
- diffusion characteristics
- morphology of particles

A.O. Boev, et al. Applied Surface Science 537 (2021) 147750

Dynamics

Even at zero T atoms have zero-point T vibrations. At higher temperatures the vibrations increases. Collective modes are known as phonons





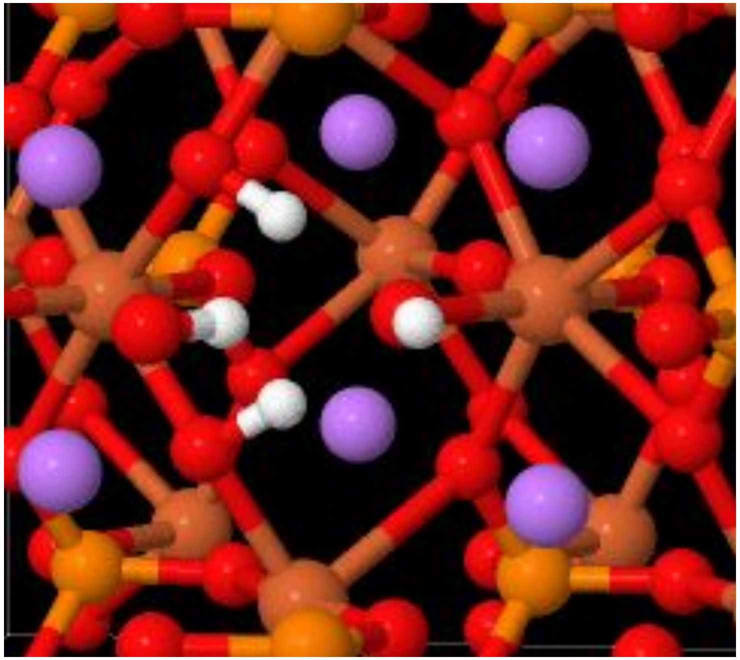
- Vibrations makes possible chemical reaction providing energy for barrier overcoming
- Vibrations and dynamics are also actively studied

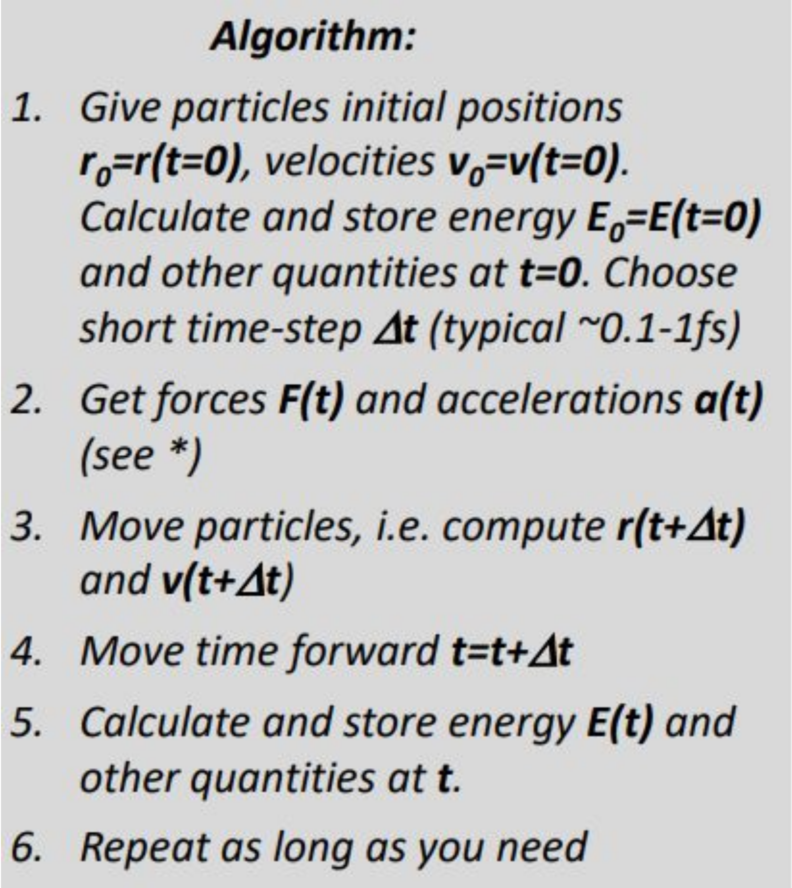
Molecular dynamics

- Solve Newtonian equation of motion for N classical particles (3N coupled equations)
- The force between atoms is determined either from DFT or using classical force field

$$\mathbf{F} = m\mathbf{a}$$

$$E_{\text{tot}} = \sum_{i=1}^{N} \tfrac{1}{2} m_i \mathbf{v}_i^2 + V(\mathbf{r}) \qquad -\frac{dV}{d\mathbf{r}} = m\frac{d^2\mathbf{r}}{dt^2}$$



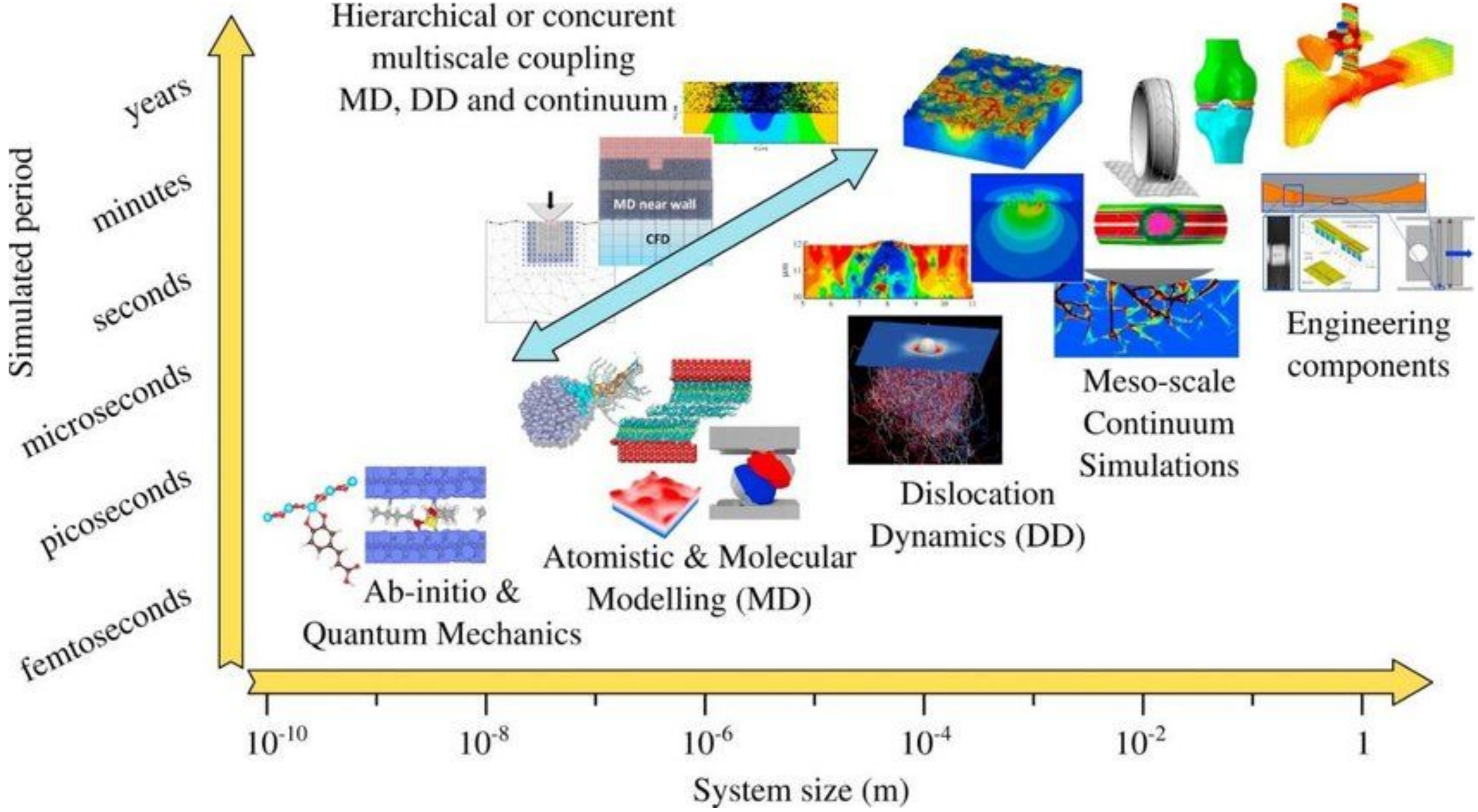


Algorithm:

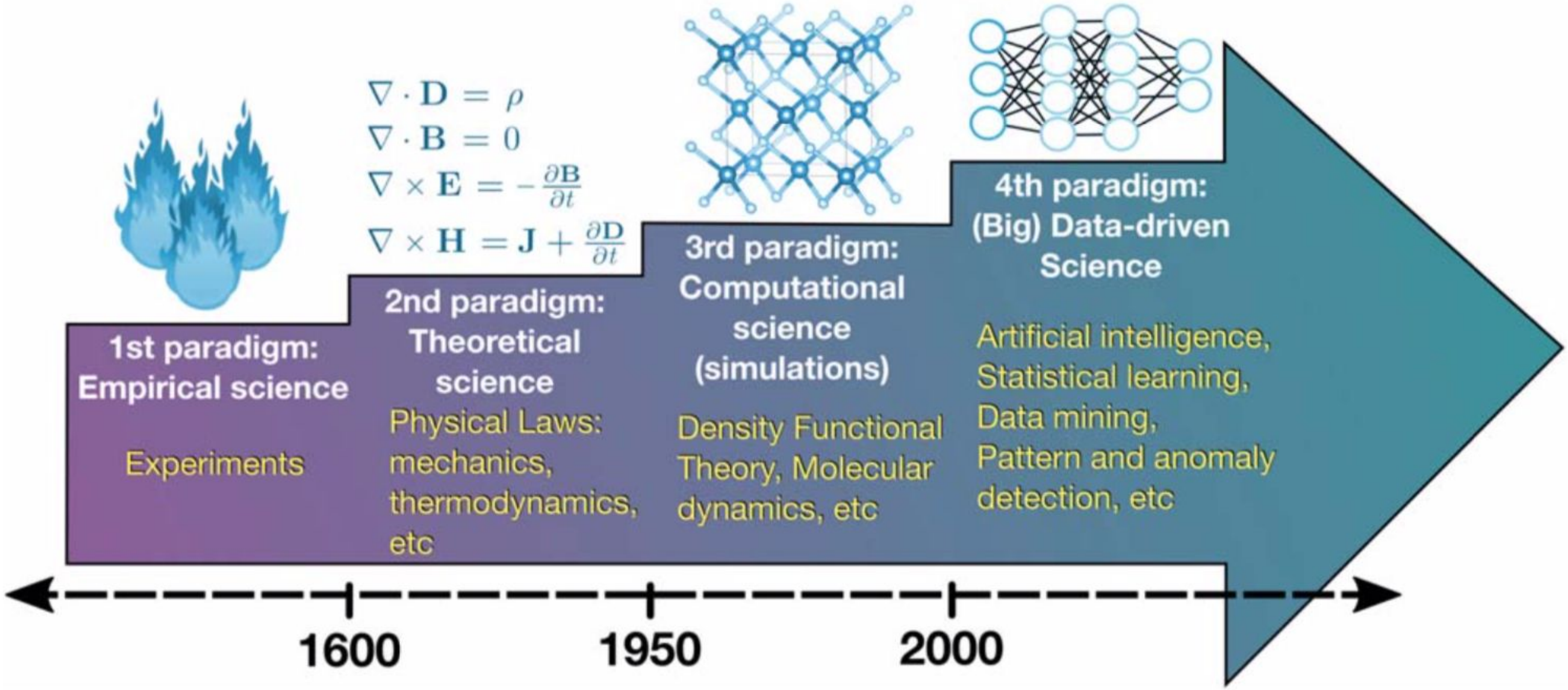
1. *Give particles initial positions* ***r_0=r(t=0)****, velocities* ***v_0=v(t=0)****. Calculate and store energy* ***E_0=E(t=0)*** *and other quantities at* ***t=0****. Choose short time-step* ***Δt*** *(typical ~0.1-1fs)*
2. *Get forces* ***F(t)*** *and accelerations* ***a(t)*** *(see *)*
3. *Move particles, i.e. compute* ***r(t+Δt)*** *and* ***v(t+Δt)***
4. *Move time forward* ***t=t+Δt***
5. *Calculate and store energy* ***E(t)*** *and other quantities at* ***t****.*
6. *Repeat as long as you need*

Aksyonov et al. Inorg. Chem. 2021, 60, 5497−5506

Hierarchy of modeling levels



Perspective



Schleder et al, *J. Phys.: Mater. 2* (2019) 032001

Thank you for your attention!