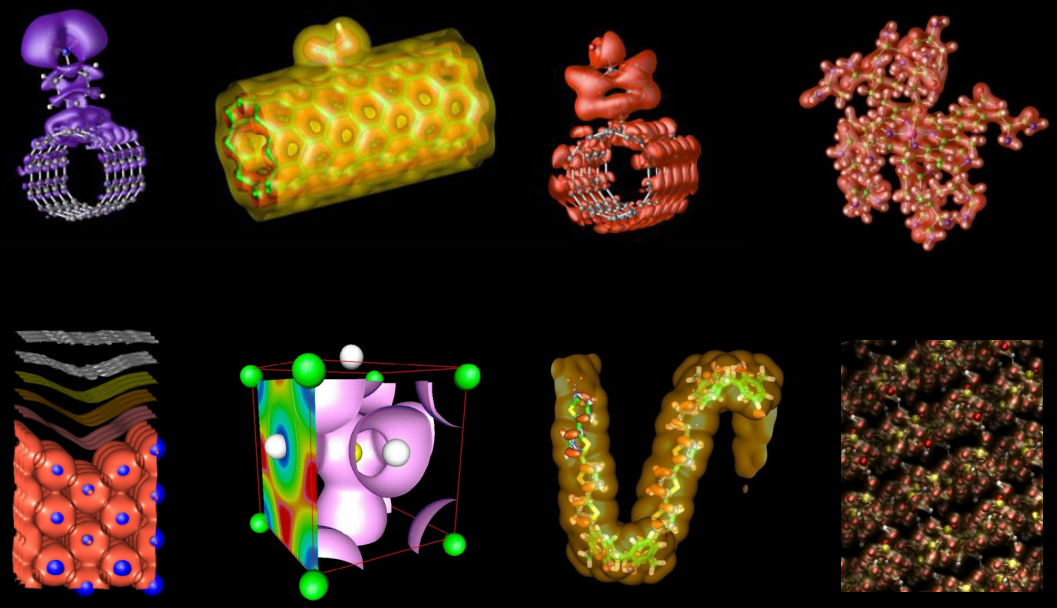
MSE 468 Week 1

Atomistic and Quantum Simulations of Materials

Introduction to the Course and Pair Potentials



Introduction

- **Objective:** The class is aimed at Master students and beginning PhDs with no particular background or experience in modelling, and will introduce a variety of methods used in different fields of materials science

- **Lecturer:** Dr. Giovanni Pizzi, Paul Scherrer Institute PSI
  (you can use my EPFL email to reach me: giovanni.pizzi@epfl.ch)

- **When and where:** Every Friday (10:15-12:00, and 13:15-15:00) **in AAC 1 32**

- **Registration:** All students are required to register on IS-ACADEMIA (isa.epfl.ch) if they need credits. Moodle is not enough! Postdocs can attend as listeners.

- Class is on **Moodle**: https://moodle.epfl.ch/course/view.php?id=18445
  - All information and updates about this course will be linked from there, messages will be sent from there. So *please register.*
  - Master students registered on ISA should be automatically registered.
  - PhD students might need manual registration (please check).

Lecture setup and asking questions

- **<u>The course is held in person and is not recorded/streamed.</u>**

- **In-person participation is strongly recommended.**
  - Nevertheless, to facilitate occasional absences: Google Drive with recordings from past class on Moodle (content relatively similar, even if small updates are to be expected).

- I will try to ask questions now and then.
  - **I encourage you to answer!** Nothing happens even if the answer is not correct! It will help me understand if the topic is clear.

- **If you have a question, raise your hand and ask!**
  - There are no bad or silly questions! You're all here to learn
  - **The more you ask, the more you learn**
  - If you have a question, most probably your colleagues have it as well

Course organization (classes+labs)

- **<u>Course organization</u>:** we have 26 two-hour slots
  - 14 slots for **lectures/classes**
  - 12 slots for **computational labs** (4 assignments, three slots each)
    - Note: online program says 1 hour per week of labs, but we will instead group the labs in 4 groups (see also Moodle)
      - ***Lab 1****: March 7 (full day), 14 (morning)*
      - ***Lab 2****: March 28 (afternoon), Apr 4 (full day)*
      - ***Lab 3****: May 2 (full day), 9 (morning)*
      - ***Lab 4****: May 23 (afternoon), May 30th (full day)*
    - There will be 2 tutors per lab, see Moodle for names/emails
    - Lab slots: work on simulations+report, ask questions to tutors
      - **Prioritize time in classes to ask questions to tutors.** If really needed: OK to write emails to tutors, but *only exceptionally.*
      - Do not expect a quick answer on a weekend!

Lab deadlines and grading

- **Grade:** graded on 4 problem assignments (one per lab)
- **Deadline**: Report PDF due on Moodle on Sunday at 23:59, nine days after last lab slot. *Check deadlines on Moodle and mark them in your calendar!*
  - Exception: one more day for Lab 4 (deadline Mon June 9th, Pentecôte)
  - *Should give you enough time to prepare the report. Normally: 7 days; I added two more days with deadline on Sunday evening, but I do **not** recommend working in the weekend!*
  - **No additional final exam planned** (so: time for report preparation beyond class/lab times replaces time for exam preparation)
  - **Lab assignment will be put on Moodle already 1 week before** (from feedback from students from past years). You are *not* expected to work on this before the first slot, but you can if it helps better distributing your workload

Rules for preparation of lab reports

- **NO PLAGIARISM.** You have to **run the simulations** and **write your report alone (it's your exam)**.
- If there is doubt of plagiarism, people not having run simulations themselves, … I will organise an oral exam (and take measures)
- **Points taken for late submissions**: inform me **in advance** if you have serious reasons for delay (illness, etc.) so we don't take out points.
- **How to write a report**: you don't have to rewrite a textbook, BUT the report must be understandable! Explain what you are doing; Label figures; add caption; explain why you are running certain simulations and with which parameters, … *See some notes on Moodle.*
- **In essence, you have to convince us that 1) you understood the theory and the methods; 2) you run the simulations yourself.**

Running the labs: laptops and VMs

- You will run the labs on **your** laptop/computer, using a virtual machine that we provide. Two versions (in principle identical):
  - via **VirtualBox** for "standard" Intel/AMD64 computers
  - Via **UTM** for recent Apple MacBooks (ARM M1/M2/M3/M4 chips)
- If you want to run on your laptop you can (needs Quantum ESPRESSO and LAMMPS), but only limited support available for compilation issues etc.
- **Inform me as soon as possible if you do not have access to a Windows/Linux/ Mac computer** on which you can install the VM (so we'll look for alternatives)
- Please test already if it works (and if your VM is fast enough), so we have time to help you if issues arise *(otherwise, you will lose time in the first lab slot!)*
  - Please **test + fill Google Forms (see Moodle) by next Thursday 27th February: all instructions on Moodle**, should take max ~30 mins including download

Preliminary knowledge expected

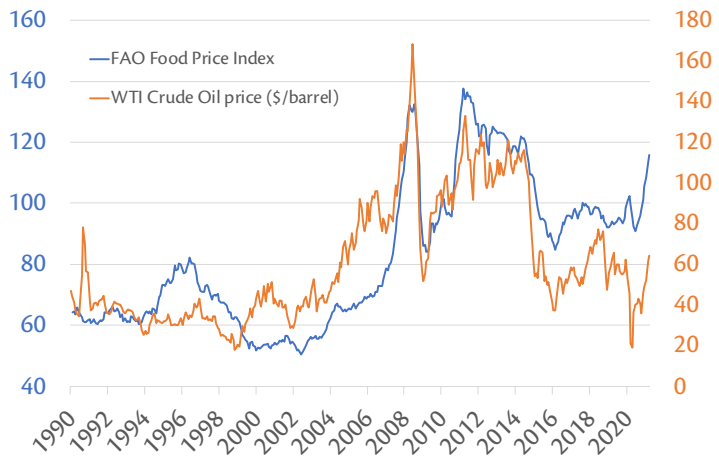
- **You will learn (no preliminary knowledge required):**
  - How to execute an atomistic simulation code (in this course: LAMMPS and Quantum ESPRESSO)
  - How to prepare the input files, understand the meaning of input keywords
  - Understand the output of such codes
  - Learn what inputs means (k-points, cutoffs, …), how to converge input parameters, how to extract physically measurable quantities from the output
- **Expected preliminary knowledge for labs:**
  - **Basic knowledge of Linux terminal (cd, ls, mv, cp, rm, command execution, …)**
    - Text editing can be done with a GUI software if preferred
  - Basic knowledge of how to prepare plots, perform simple fits
  - Not required, but helpful to speed up your work: writing scripts (bash, python, …)
  - You will need to write a clear, concise and understandable report explaining your findings
  - **Who would need a 1-hour introduction to the Linux terminal?**

COURSE MOTIVATION
WHY MATERIALS? WHY SIMULATIONS?

WHAT DO PEOPLE AND SOCIETY NEED MOST?

- Water
- Food
- Wealth
- Health
- Education

} **Energy**

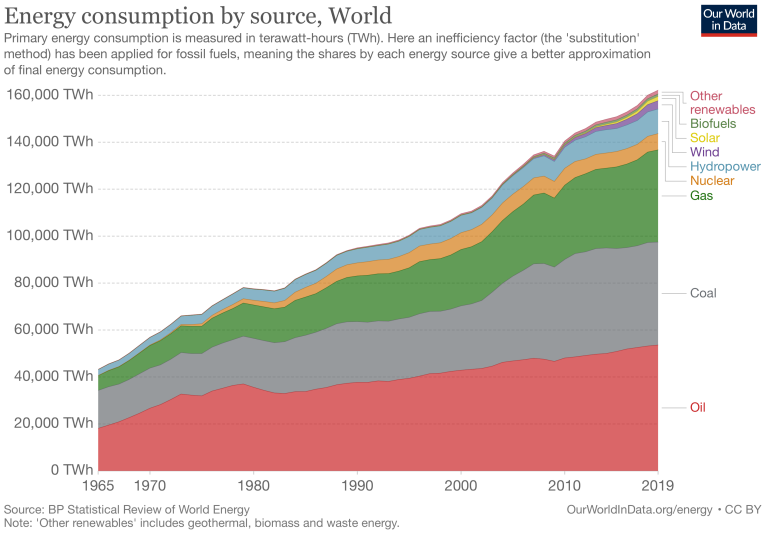


Why?

EVER-INCREASING ENERGY DEMAND

- Water
- Food
- Wealth
- Health
- Education

} **Energy**



HUMAN FOOTPRINT

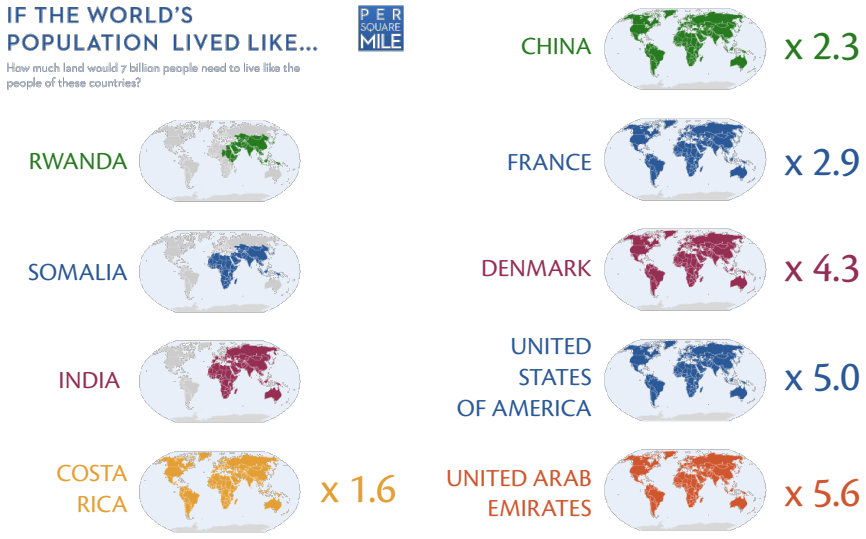


Illustration adapted from Tim De Chant
updated with data from 2020
Data from Global Footprint Network
(http://www.footprintnetwork.org)

Sustainable energy: a materials discovery challenge

Novel materials: key to societal well being

- Energy conversion and harvesting
  (photovoltaics, water splitting,
  fuel cells, thermoelectrics, ...)
- Energy storage
  (batteries, chemical storage/fuels,
  supercapacitors, ...)
- End-use energy efficiency
  (efficient light emitters,
  low-power computing for IoT,
  lightweight alloys for transportation, ...)
- ...

How do we address all these needs?

Experiments

Simulations

Atomistic simulations to predict materials properties

The Nobel Prize in Chemistry 1998

Photo from the Nobel Foundation archive.
Walter Kohn
Prize share: 1/2

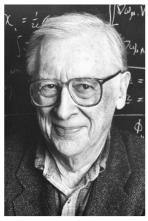
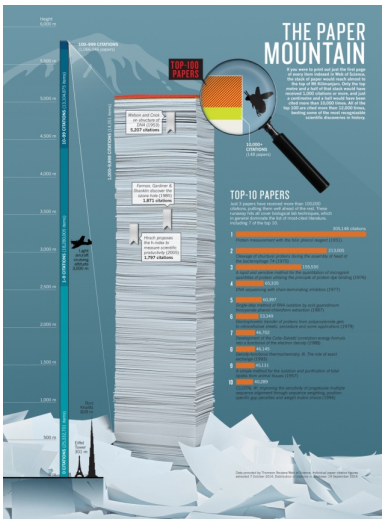


Photo from the Nobel Foundation archive.
John A. Pople
Prize share: 1/2

Development of
Density-Functional Theory (DFT)



R. Van Noorden et al., Nature 514, 550 (2014)

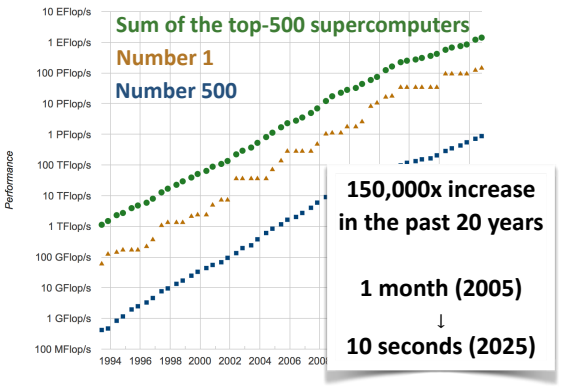
12 out of the top-100 most-cited papers ever are **about DFT** (2 in the top 10)

MOST CITED PAPERS IN THE HISTORY OF APS (FROM 1893)

	Journal	# cites	Title	Author(s)
1	PRL (1996)	78085	Generalized Gradient Approximation Made Simple	Perdew, Burke, Ernzerhof
2	PRB (1988)	67303	Development of the Colle-Salvetti Correlation-Energy ...	Lee, Yang, Parr
3	PRB (1996)	41683	Efficient Iterative Schemes for Ab Initio Total-Energy ...	Kresse and Furthmuller
4	PR (1965)	36841	Self-Consistent Equations Including Exchange and Correlation ...	Kohn and Sham
5	PRA (1988)	36659	Density-Functional Exchange-Energy Approximation ...	Becke
6	PRB (1976)	31865	Special Points for Brillouin-Zone Integrations	Monkhorst and Pack
7	PRB (1999)	30940	From Ultrasoft Pseudopotentials to the Projector Augmented ...	Kresse and Joubert
8	PRB (1994)	30801	Projector Augmented-Wave Method	Blochl
9	PR (1964)	30563	Inhomogeneous Electron Gas	Hohenberg and Kohn
10	PRB (1993)	19903	Ab initio Molecular Dynamics for Liquid Metals	Kresse and Hafner
11	PRB (1992)	17286	Accurate and Simple Analytic Representation of the Electron ...	Perdew and Wang
12	PRB (1990)	15618	Soft Self-Consistent Pseudopotentials in a Generalized ...	Vanderbilt
13	PRB (1992)	15142	Atoms, Molecules, Solids, and Surfaces - Applications of the ...	Perdew, Chevary, ...
14	PRB (1981)	14673	Self-Interaction Correction to Density-Functional Approx. ...	Perdew and Zunger
15	PRB (1986)	13907	Density-Functional Approx. for the Correlation-Energy ...	Perdew
16	RMP (2009)	13513	The Electronic Properties of Graphene	Castro Neto et al.
17	PR (1934)	12353	Note on an Approximation Treatment for Many-Electron Systems	Moller and Plesset
18	PRB (1972)	11840	Optical Constants on Noble Metals	Johnson and Christy
19	PRB (1991)	11580	Efficient Pseudopotentials for Plane-Wave Calculations	Troullier and Martins
20	PRL (1980)	10784	Ground-State of the Electron-Gas by a Stochastic Method	Ceperley and Alder

Transferability and ultimate scalability

- DFT is transferable
  - No fitting parameters ("first principles"): same method for thousands of different materials
- Scalable laboratory: with Moore's law



Atomistic simulations in industry

SANDVIK Coromant, IBM, Ford, SAMSUNG, EDF, BASF, BOSCH, Microsoft, intel, TOYOTA, SONY, GE, JM Johnson Matthey Inspiring science, enhancing life, SOLVAY, saft, MTU Aero Engines, umicore

... and many more!

Why do you want to learn modeling?

Understand, predict, and design materials and devices

- **Understand** microscopic origin of macroscopic properties, probe cause-effect relationships
- **Explore** materials space, to find new materials with optimal properties even before attempting synthesis
- **Discover** new materials or novel materials properties
- **Deploy** materials into devices with application in everyday life, with direct impact on society

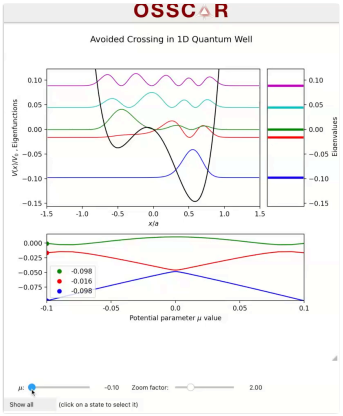
Learning objectives of this course

- **Learn modern methods** of computational materials science (at the atomistic/quantum level)
- **Understand the theory** behind them
- **Assess applicability** for diverse properties
- **Learn (by practice)** how to use simulation tools

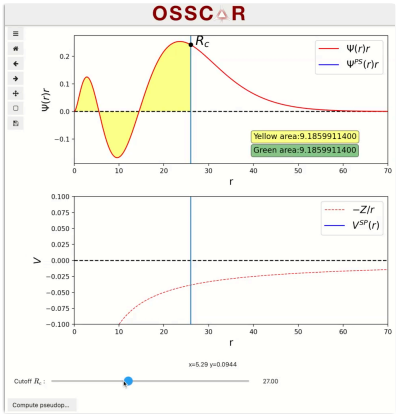
Achieve expertise to address materials discovery challenges
(in academia, industry R&D, ...)

Learn with interactive tools and visualisations

Jupyter-based interactive visualisations: help understand the theory



States anticrossing in an asymmetric double quantum well



Building a norm-conserving pseudopotential

- All code open-source
  - Go into the code and modify/improve them!
- Computational thinking: interactive coding exercises
- Developed in our project

OSSCAR

Open Software Services for Classrooms and Research

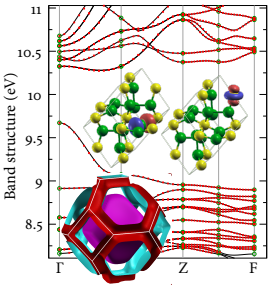
https://www.osscar.org

Interested in developing more as a project? Contact me!

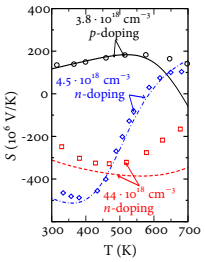
Goal 1: learn to use DFT to predict materials properties

Content we will learn

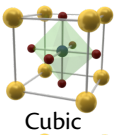
- **Energetics and phases**
- **Electronic structure, magnetic materials, ...**
- **Electronic transport**
- **Vibrational spectroscopy, thermal transport**
- **Ionic transport**

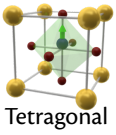


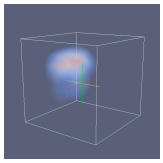
Electronic structure



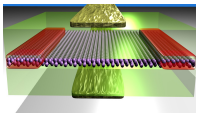
Thermoelectric figures of merit

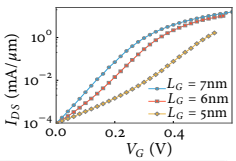

Cubic


Tetragonal



Ferroelectric & piezoelectric materials and phase transitions

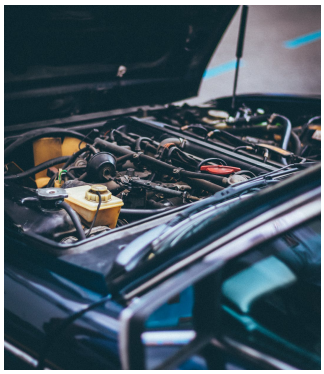




Low-dimensional (2D) transistor devices

Goal 2: From understanding to automation

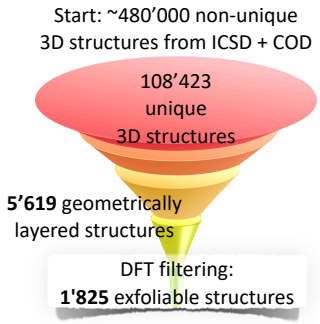
We can now automate typical scientific workflows as "turn-key" solutions

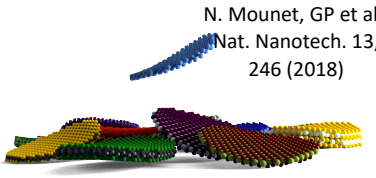


- Like in a car: many end-users, drive without need to know how the engine works
  - Engines are "robust"
  - Just turn the key and drive
- I still need a driving license and cannot drive trucks; but many needs addressed by driving my own car

Robust "turn-key" workflows for high-throughput simulations

- Outcome of recent research:
  - **Robust "turn-key" workflows** with parameter choice/failure correction
  - "Democratisation" of simulations
- **Course focus**:
  - Use the quantum codes for accurate predictions
- If you want to become an expert, you can also learn to "drive the trucks"
  (phonon scattering for thermal transport, many-body effects for optical excitations, ...)

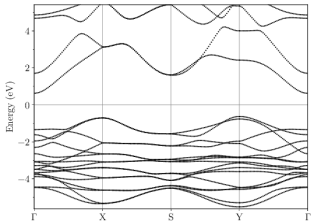




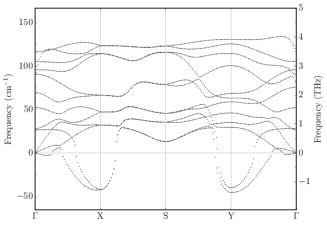
N. Mounet, GP et al., Nat. Nanotech. 13, 246 (2018)

Portfolio of > 1'800 2D exfoliable materials
Applications: catalysis, nanoelectronics, ferroelectrics, superconductors, ...

Electronic band structures

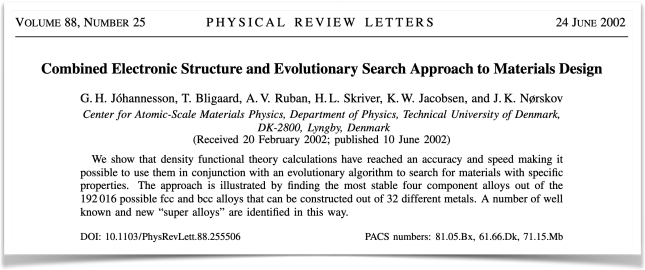


Phonon band structures



What's the next challenge?

- **High-throughput discovery**
  - Emerged as powerful approach in the past 10-20 years



VOLUME 88, NUMBER 25 PHYSICAL REVIEW LETTERS 24 JUNE 2002

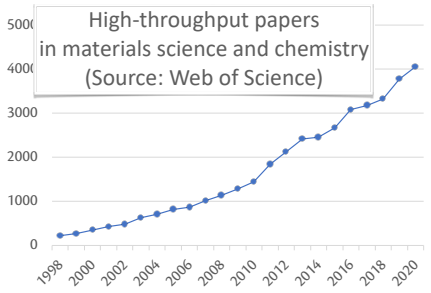
Combined Electronic Structure and Evolutionary Search Approach to Materials Design

G. H. Jóhannesson, T. Bligaard, A. V. Ruban, H. L. Skriver, K. W. Jacobsen, and J. K. Nørskov
Center for Atomic-Scale Materials Physics, Department of Physics, Technical University of Denmark, DK-2800, Lyngby, Denmark
(Received 20 February 2002; published 10 June 2002)

We show that density functional theory calculations have reached an accuracy and speed making it possible to use them in conjunction with an evolutionary algorithm to search for materials with specific properties. The approach is illustrated by finding the most stable four component alloys out of the 192 016 possible fcc and bcc alloys that can be constructed out of 32 different metals. A number of well known and new "super alloys" are identified in this way.

DOI: 10.1103/PhysRevLett.88.255506 PACS numbers: 81.05.Bx, 61.66.Dk, 71.15.Mb

- **Next challenge**: autonomous coupling:
  - atomistic and multiscale simulations
  - robotic experiments
  - combined with Artificial Intelligence (AI)



Automatic vs. autonomous

Automatic

Search strategy defined at the start

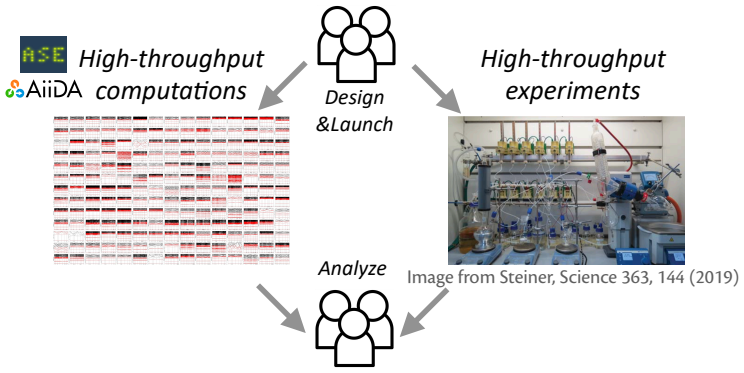
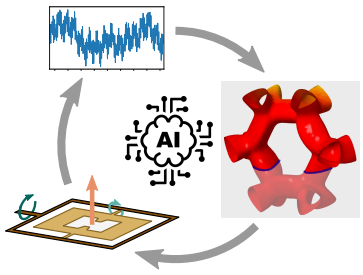


Image from Steiner, Science 363, 144 (2019)

Autonomous

Closed-loop, decisions taken based on real-time results



Robust simulation/ experimental workflows → Accelerated discovery

Want to learn more?

- Learn how to use atomistic and quantum simulations in this course
- Want to learn more? **Apply for a master project**
    - Help shape the future of materials discovery
    - Push the frontiers of integration of Artificial Intelligence (AI) and robotics

Syllabus

- Theory and application of atomistic computer simulations to model, understand, and predict the properties of real materials
- Energy models: from classical potentials to first-principles approaches
- Density-functional theory and the total-energy pseudopotential method
- Errors and accuracy of quantitative predictions
- Thermodynamic ensembles: molecular dynamics simulations and Monte Carlo sampling
- Free energies and phase transitions
- Laboratories: classical force fields, density-functional theory (I and II), molecular dynamics

General literature

General

- Ellad Tadmor and Ronald Miller, “Modelling Materials” Cambridge University Press
- Rob Phillips, "Crystals, Defects and Microstructures", Cambridge University Press; Modeling in materials science with emphasis on mechanical behavior.

Computational physics/chemistry

- Frank Jensen, “Introduction to Computational Chemistry”, Wiley; Focus on methods in computational chemistry. Good introductory book if you want to focus on chemistry applications
- J.M. Thijssen, “Computational Physics”, Cambridge University Press; slightly more general book on quantum mechanical methods than Jensen.

Electronic-structure and DFT

- **Feliciano Giustino, “Materials Modelling using Density Functional Theory”, Oxford University Press**
- Richard Martin, “Electronic Structure”, Cambridge University Press
- Efthimios Kaxiras, “Atomic and Electronic Structure of Solids”, Cambridge University Press
- Jorge Kohanoff, “Electronic Structure Calculations for Solids and Molecules”, Cambridge University Press
- Weitao Yang and Robert Parr, “Density-Functional Theory of Atoms and Molecules”, Oxford University Press
- Wolfram Koch and Max Holthause, “A Chemist’s Guide to Density-Functional Theory”, Wiley
- Kieron Burke, “The ABC of DFT”, free at https://dft.uci.edu/learnDFT.php

General literature

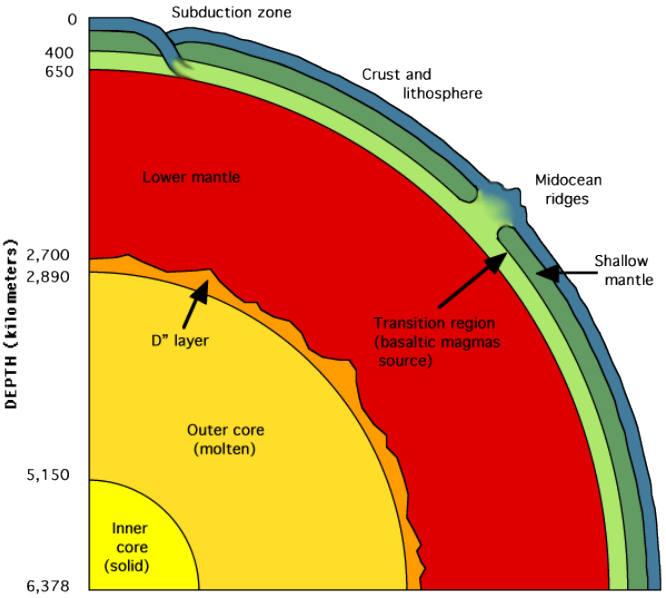
Molecular Dynamics

- M.P. Allen and D. Tildesley, “Computer Simulation of Liquids”, Oxford Science Publishers. Excellent book on molecular dynamics simulations. Explains well the relevant statistical mechanics. A must if you will be doing MD. Not much on solids.
- **D. Frenkel and B. Smit, "Understanding Molecular Simulation", Academic Press. Very good background and theory on MD, MC and Stat Mech. Applications are mainly on molecular systems. Excellent book.**
- Dominic Marx and Juerg Hutter, “Ab-initio Molecular Dynamics”, Cambridge University Press

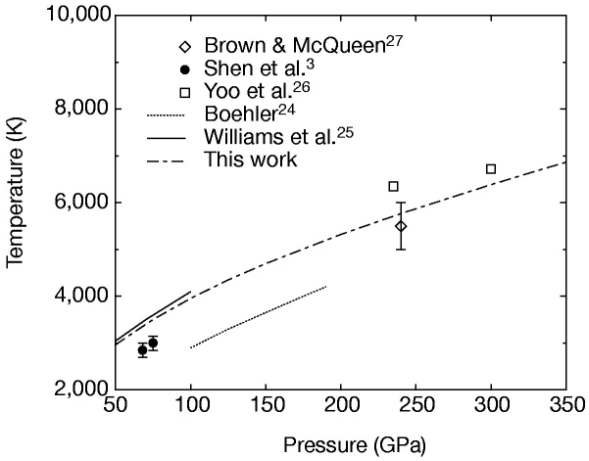
Monte Carlo

- David Landau and Kurt Binder, “A Guide to Monte Carlo Simulations in Statistical Physics”, Cambridge University Press
- David Chandler, “Introduction to Modern Statistical Mechanics”, Oxford University Press

Calculating things that are difficult to do experimentally: Inside the Earth



Taken from http://chianti.geol.ucl.ac.uk/~dario/resint.htm



Alfè et al, Nature, 401, 462-464 (1999)

Some things are easier with calculations

NY Times, Sept. 7, 1999 p.D1

Glue of Molecular Existence Is Finally Unveiled

By MALCOLM W. BROWNE

Of the roughly 20 million chemical substances scientists have catalogued, ranging from simple ones like water to gigantic compounds like DNA, nearly all are assemblages of atoms linked together by electronic bonds. The quest to understand these tiny bonds — the very glue of material existence — is the heart of chemical science.

An important step in this quest was reported last week with the publication by the journal Nature of the sharpest direct images ever made of electronic bonds (known as orbitals). The shapes revealed by these images — doughnutlike rings, dumbbell-shaped lobes and arrays suggestive of butterfly wings — confirmed theoretical predictions of what these bonds should look like in the molecule under study.

The remarkable pictures also contained fresh evidence bearing on a debate over what kind of bonds may be present in a molecule made of copper and oxygen atoms. Future applications of the new imaging technique, chemists said, may eventually shed light on one of the most intractable mysteries of solid-state physics: why it is that certain compounds of copper and oxygen can conduct electricity without resistance at relatively high temperatures.

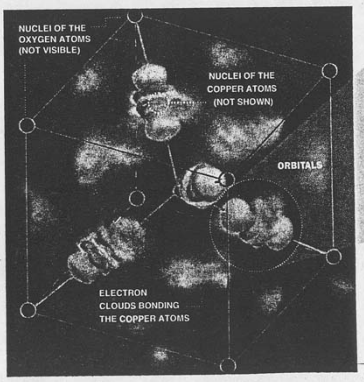
Some scientists predict that these "high-temperature superconductors" will underlie much of the technology of the 21st century.

The imaging of bonds was achieved by a team of chemists and physicists at Arizona State University, Tempe, headed by Dr. John C. H. Spence and Dr. Jian-Min Zuo, and financed by the National Science Foundation. Their technique, using beams of both X-rays and electrons to probe molecules, was the first system capable of imaging both the atoms in a crystal lattice and the electron bonds holding them together.

It was once thought that an atom was like a miniature solar system, with planetary electrons orbiting a spherical sunlike nucleus. But since the development of quantum mechanics in the 1920's, scientists have known that a more realistic way of thinking about atomic electrons is to plot the regions in space where each of an atom's electrons is most likely to be found. The shapes and sizes of these regions, called orbitals, are determined by the electrons' energies and three other quantum properties.

The all-important orbitals of an atom define how the atom can bond with other atoms. There are three main types of electronic bonds. The simplest, the metal-to metal bond, is thought of as a sea of loos

Continued on Page 2



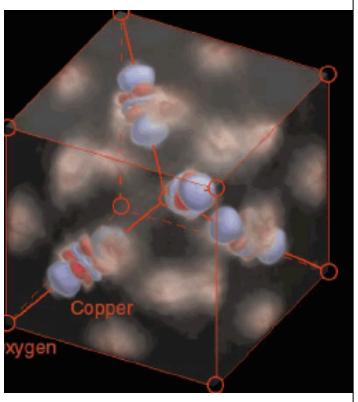
ORBITALS are the clouds of electrons shared between atoms in a molecule.

The Ties That Bind

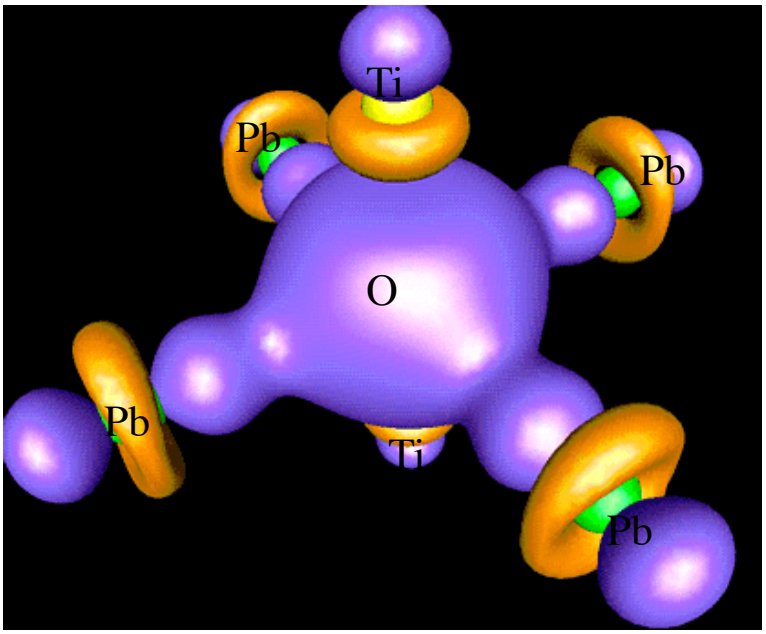
A group of scientists at Arizona State University has used X-rays and electron diffraction techniques to capture direct images of the electronic bonds that keep together the atoms of oxygen and copper in a compound called cuprite.

Source: Arizona State University

The New York Times



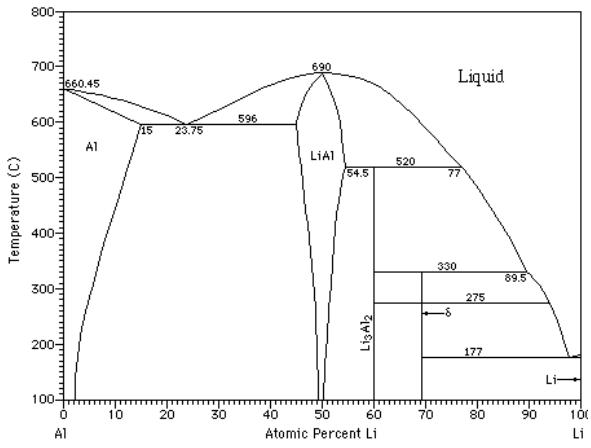
Calculated electron densities in $PbTiO_3$



O_{2s} density

Can control phenomena that take place: Investigating metastability in Al-Li

Experimental



Calculated

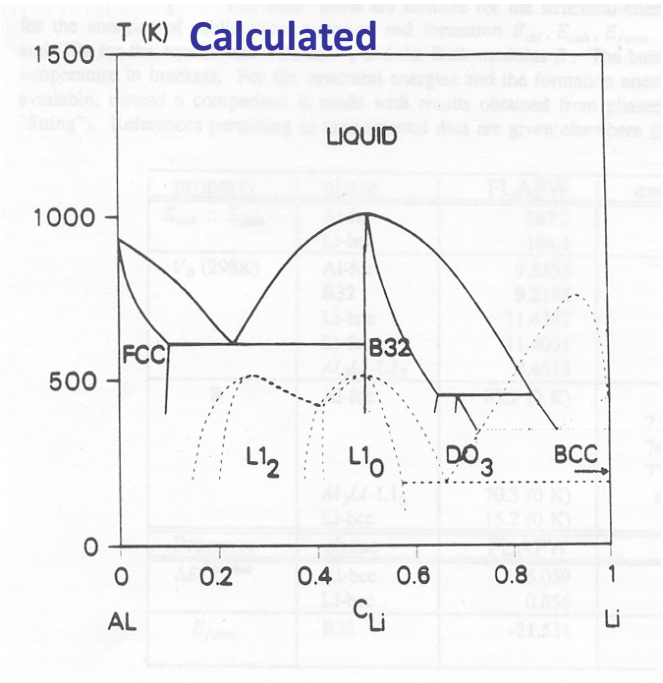


Figure courtesy Dr. M. Sluiter

Can systematically investigate and prove or disprove hypothesis

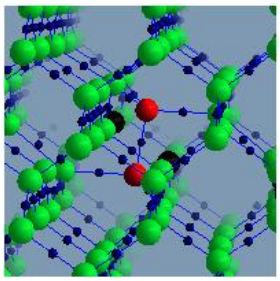
The Lowest Energy Defect in Silicon

Goedecker et al.,PRL 88, 235501 (2002)

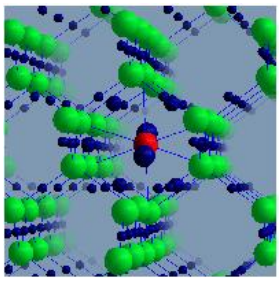
A new stable point defect in silicon that has fourfold coordination and is lower in energy than the traditional defects?

New hypothesized 4-fold coordinated defect

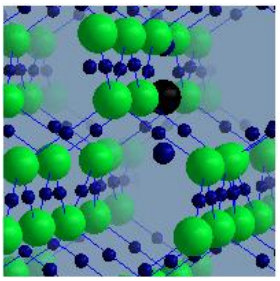
FFCD



H interstitial



Vacancy



Frenkel pair
(vacancy+interstitial)

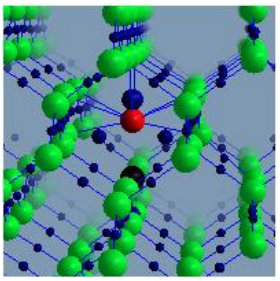


TABLE I. The GGA formation energy in eV of the point defects described in the text and depicted in Figs. 1 and 2. For comparison, the LDA values are given in parentheses for intrinsic silicon.

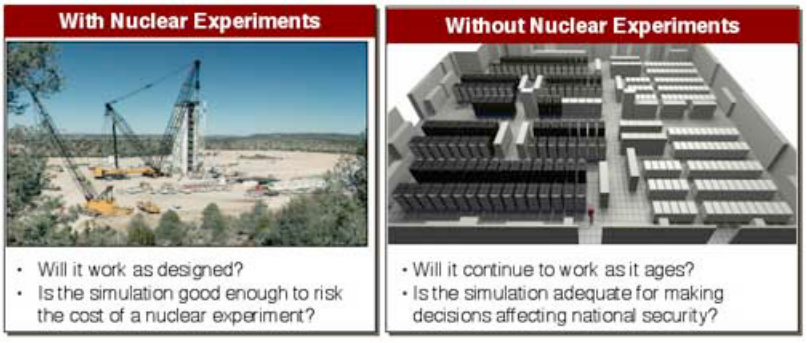
	p-type	Intrinsic	*n*-type
FFCD	2.45	2.42 (2.34)	2.39
Frenkel	5.65	4.32 (4.26)	5.77
X interstitial	3.33	3.31 (2.88)	2.98
H interstitial	2.80	3.31 (2.87)	3.12
Vacancy	3.01	3.17 (3.56)	3.14

Modeling to decide on important outcomes

Advanced Simulation and Computing Program (ASC), 1995

https://en.wikipedia.org/wiki/Advanced_Simulation_and_Computing_Program

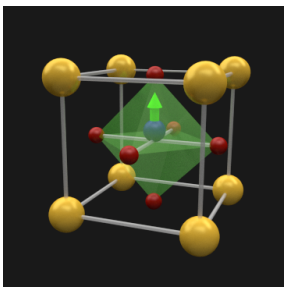
Use simulations on supercomputers instead of (banned) live nuclear testing

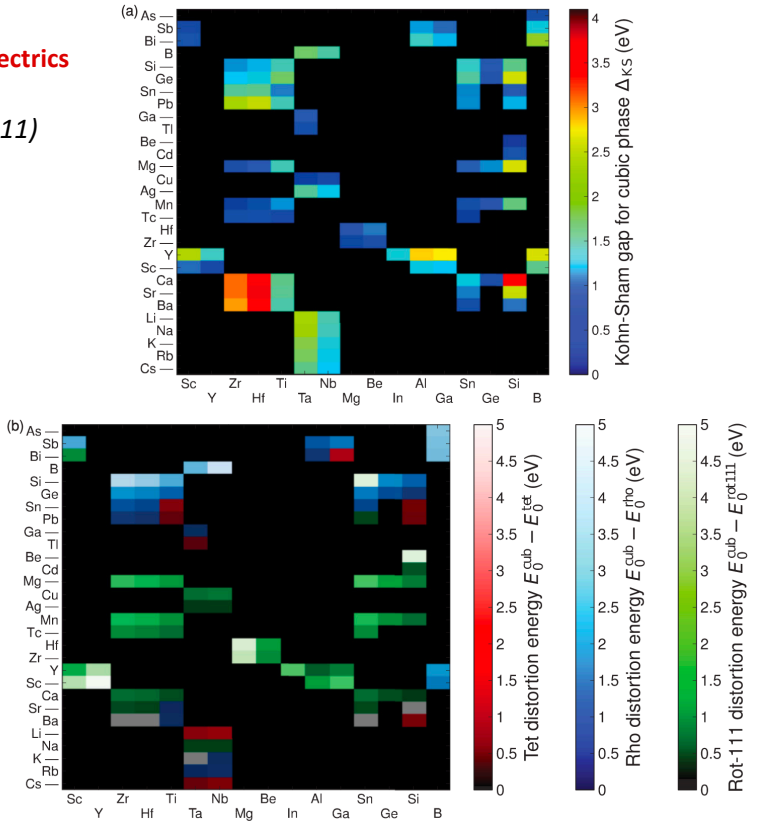


Computation is the ultimate scalable research method

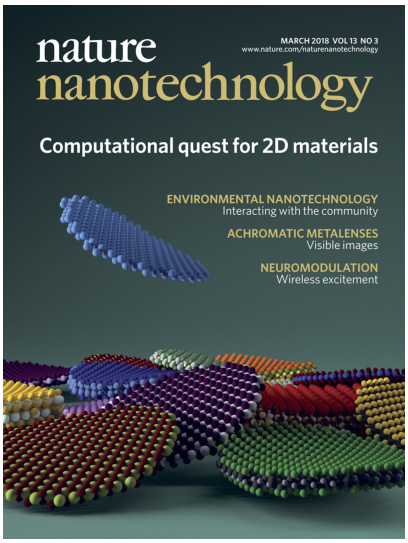
Screening for high-performance piezoelectrics in ABO_3 perovskites

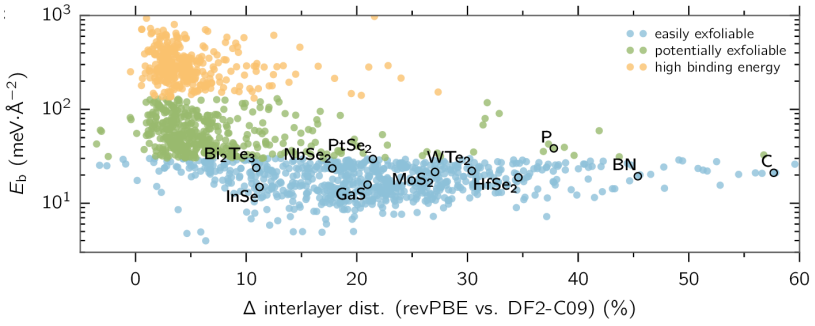
Armiento et al., PRB 84, 014103 (2011)





High-throughput ab-initio discovery of 2D materials



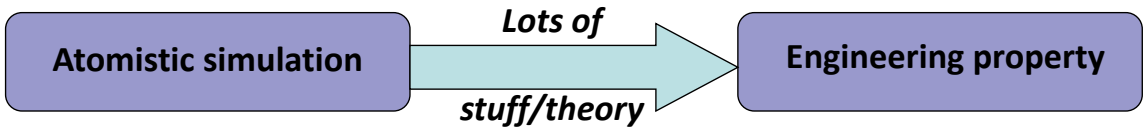


N. Mounet et al., Nature Nanotechnology 13, 246 (2018)

There are still many things experiments can do better (e.g faster and more accurately) than computations

Understanding when to use what resource is key to efficient materials research

Modeling rarely is "Simulation of reality".
Rather it is the accurate computation of quantities that are essential to prove/ disprove a theory, or guarantee a property



Computers don't solve problems, people do
(Frank Jensen)

Energy Models

Empirical Models: functional forms with parameters fitted to experimental data (or calculated data)

- *Pair potentials*
- *Many body potentials*
- *Effective medium theories*
- *Aggregates (ReaxFF etc.)*
- *Neural networks*

Energy only: $E(\vec{R}_i)$

Semi-Empirical Model: physical model for Hamiltonian, fit parameters to reproduce relevant electronic properties

- *Tight-binding*
- *MINDO/MNDO/...*

Quantum mechanical: Start from Schrödinger equation and make approximations

- *Quantum chemistry (Hartree-Fock and beyond)*
- *Density-functional theory*
- *Quantum Monte Carlo*

Energy and electronic structure

Increased Speed

Increased transferability

Energy Models

Empirical Models: functional forms with parameters fitted to experimental data (or calculated data)

Pair potentials

Many body potentials

Effective medium theories

Aggregates (ReaxFF etc.)

Neural networks

Energy only: $E(\vec{R}_i)$

Increased Speed

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Semi-Empirical Model: physical model for Hamiltonian, fit parameters to reproduce relevant electronic properties

Tight-binding

MINDO/MNDO/...

Quantum mechanical: Start from Schrödinger equation and make approximations

Quantum chemistry (Hartree-Fock and beyond)

Quantum Monte Carlo

Energy and electronic structure

Which one is best?

Born-Oppenheimer Approximation

All **atoms** *i* characterized by coordinate vector $\vec{R}_i$

System characterized by wavefunctions

Born Oppenheimer

$$E(\vec{R}_i) \quad = \quad \min_{\psi} E(\vec{R}_i, \psi)$$

For every set of coordinates R_i electrons are in their ground state

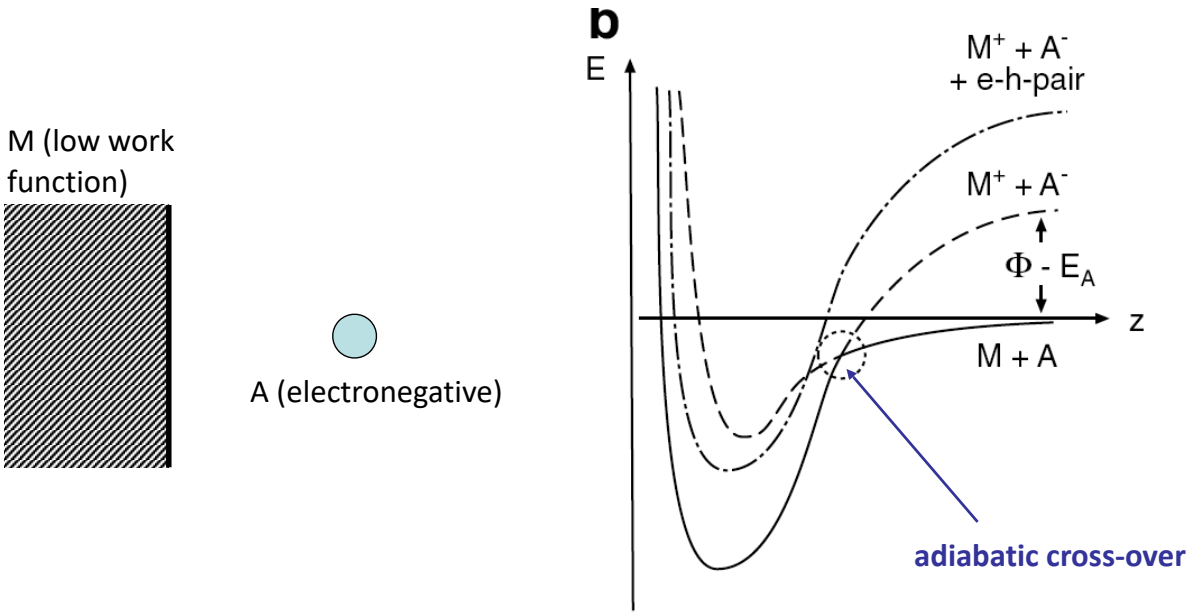
Discussion of applicability of BO

Temperature (OK if excitations are fast on nuclear motion time scale)

Long lived excitations/slow electron dynamics

Coupling of nuclear and electron degrees of freedom

Example of delayed charge transfer as atom approaches a surface



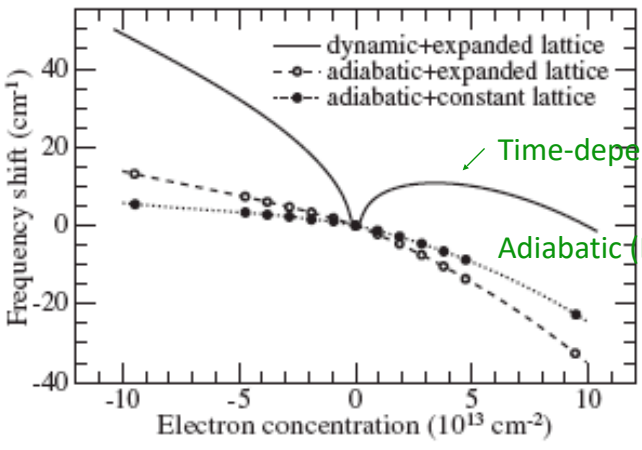
From E. Hasselbrink, Current Opinion in Solid State and Materials Science, 10 (2006) 192-204

Example of BO violations

PRL 97, 266407 (2006) PHYSICAL REVIEW LETTERS week ending 31 DECEMBER 2006

Nonadiabatic Kohn Anomaly in a Doped Graphene Monolayer

Michele Lazzeri and Francesco Mauri
IMPMC, Universités Paris 6 et 7, CNRS, IPGP, 140 rue de Lourmel, 75015 Paris, France
(Received 23 October 2006; published 29 December 2006)



Shift of phonon frequency with doping of a single graphene layer

Time-dependent DFT

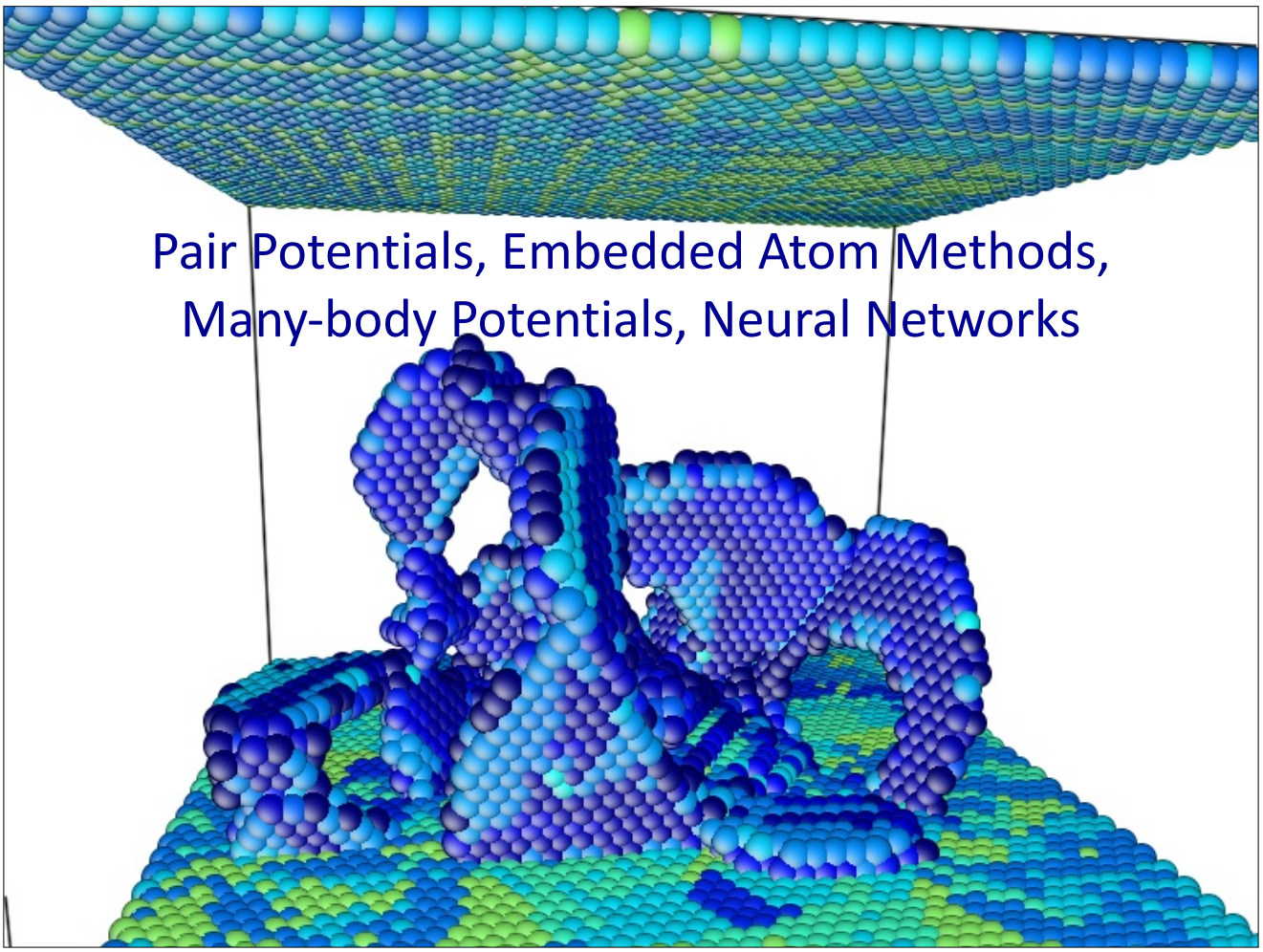
Adiabatic (BO) DFT

Strong coupling between electron and nuclear coordinates for phonons with $\boldsymbol{q} = 2\,\boldsymbol{k}_F$ *(Kohn anomaly)*

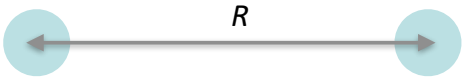
Outline for discussion of empirical energy models

- Discussion of pair potentials: forms and physical limitations
- Classification of empirical models
- Many-body potentials
- Pair functionals
- Environment dependent potentials in chemistry

Objective: Become familiar with typical forms and understand limitations of various choices. Focus is on **forms**, not on **parameters**



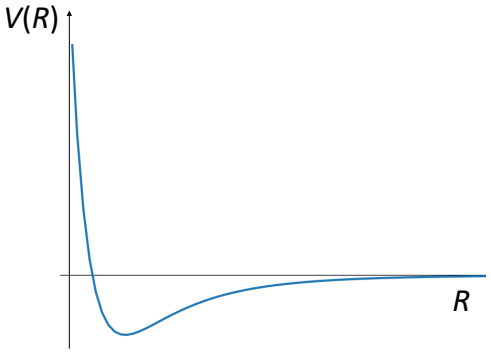
Interaction energy between 2 atoms



What shape do you expect?

Pairwise energy summation: pair potentials

$$E = E_0 + \frac{1}{2}\sum_{i,j\neq i}^{N} V(\vec{R}_i - \vec{R}_j)$$



Common features

- *repulsive at short distances*
- *attractive at intermediate and long distance*
- *usually applied with a distance cutoff!*

Analytical forms of potentials are usually based on some basic physics. Physical relevance tends to disappear when the potential constants are fitted

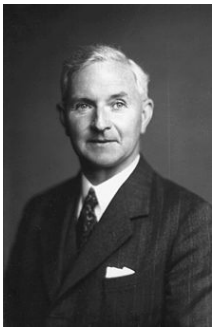
Minimal set of parameters: energy scale and length scale

Lennard-Jones: A simple two-parameter form

$$V(r) = \frac{A}{r^{12}} - \frac{B}{r^6}$$

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

ε is unit of energy scale
σ is unit of length

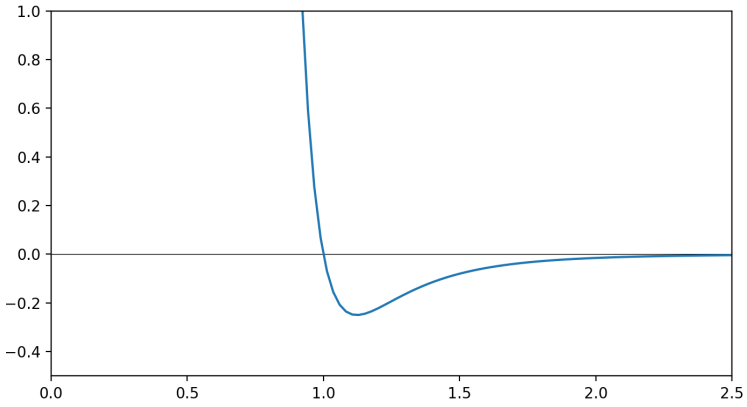


John Lennard-Jones
(source: Wikipedia)

***1/r⁶**: coupling of fluctuating dipoles*

***1/r¹²**: mimics atomic repulsion! Just computationally convenient*

Works well for e.g. noble gases, poorly for the rest, BUT good test model potential



Lennard-Jones: A simple two-parameter form

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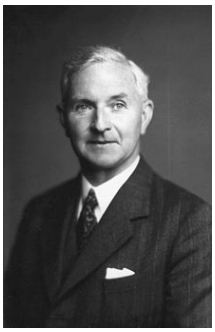


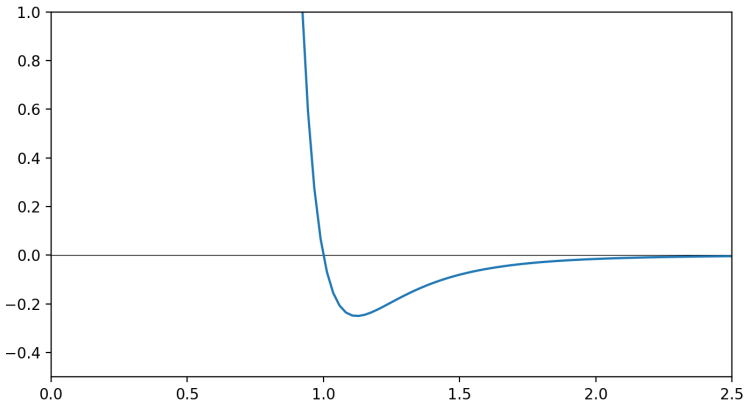
John Lennard-Jones
(source: Wikipedia)

When expressing temperature, pressure and density in renormalized units: all LJ systems are identical

$$\text{Temperature: } \frac{\varepsilon}{k_b}$$

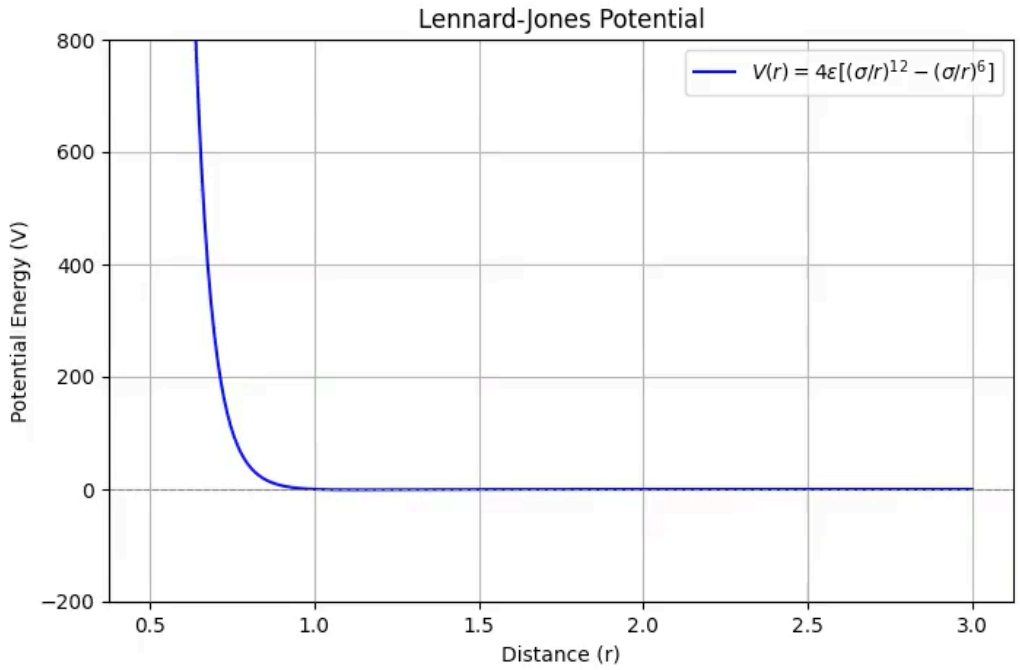
$$\text{Pressure: } \frac{\varepsilon}{\sigma^3}$$

$$\text{Density: } \frac{1}{\sigma^3}$$



MSE 468 Atomistic and Quantum Simulations of Materials, Giovanni Pizzi, Spring 2025, EPFL

Don't forget to zoom!



There is only one Lennard-Jones material

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

e.g.: If fit lattice parameter and cohesive energy, then bulk modulus will be determined

a

E_c

$$B_0 = -V_0 \left.\frac{\partial P}{\partial V}\right|_{V_0} = V_0 \left.\frac{\partial^2 E}{\partial V^2}\right|_{V_0}$$

curvature at minimum
(as a function of volume!)

Bulk modulus of a FCC Lennard-Jones

$$B_0 \approx 75.2\frac{\varepsilon}{\sigma^3}$$

The Lennard-Jones model for a given material is always equal to the Lennard-Jones model for another material at different conditions of temperature and pressure.

To represent lattice parameter, energy and elastic properties more parameters are needed

Morse Potential

$$V(r) = D(e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)})$$

Born-Mayer/Buckingham

$$V(r) = Ae^{-\frac{r}{\rho}} - \frac{C}{r^6} - \frac{D}{r^8}$$

Unphysical behavior for short distances

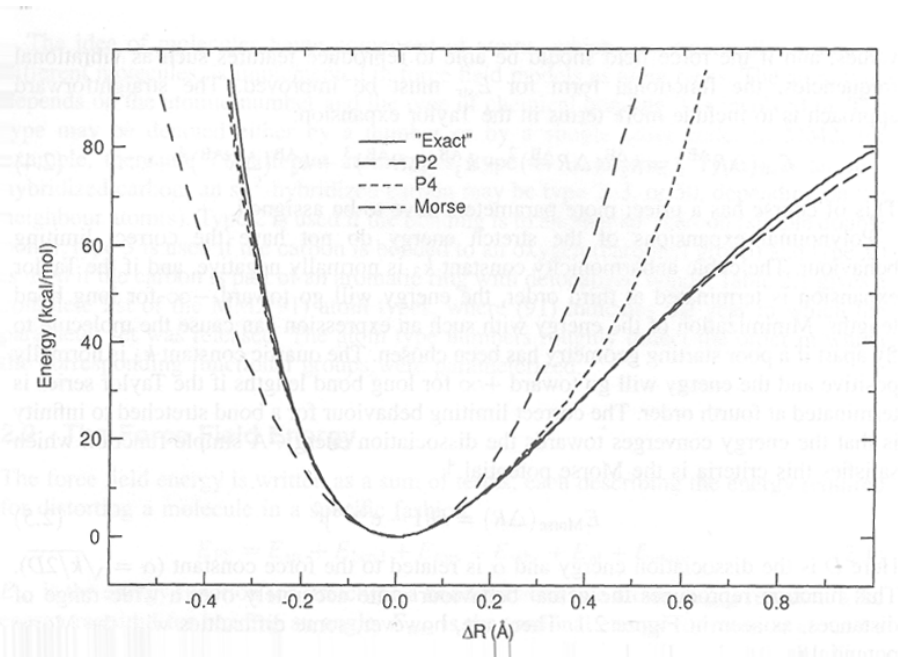
Many more forms can be used. Fitting usually removes the particular physics of analytical form

MORSE POTENTIAL PARAMETERS FOR 16 METALS

Metal	αa_0	β	$L \times 10^{-22}$ (eV)	$\alpha(A^{-1})$	$r_0(A)$	D (eV)
Pb	2.921	83.02	7.073	1.183 6	3.733	0.234 8
Ag	2.788	71.17	10.012	1.369 0	3.115	0.332 3
Ni	2.500	51.78	12.667	1.419 9	2.780	0.420 5
Cu	2.450	49.11	10.330	1.358 8	2.866	0.342 9
Al	2.347	44.17	8.144	1.164 6	3.253	0.270 3
Ca	2.238	39.63	4.888	0.805 35	4.569	0.162 3
Sr	2.238	39.63	4.557	0.737 76	4.988	0.151 3
Mo	2.368	88.91	24.197	1.507 9	2.976	0.803 2
W	2.225	72.19	29.843	1.411 6	3.032	0.990 6
Cr	2.260	75.92	13.297	1.572 1	2.754	0.441 4
Fe	1.988	51.97	12.573	1.388 5	2.845	0.417 4
Ba	1.650	34.12	4.266	0.656 98	5.373	0.141 6
K	1.293	23.80	1.634	0.497 67	6.369	0.054 24
[illegible]	1.267	23.28	1.908	0.589 93	5.336	0.063 34
Cs	1.260	23.14	1.351	0.415 69	7.557	0.044 85
Rb	1.206	22.15	1.399	0.429 81	7.207	0.046 44

[a] After Girifalco and Weizer [9].

Morse Potential for Stretching of C-H in CH_4



Think about how far from equilibrium you need the potential

What can potentials be fit to?

- lattice constants
- cohesive energy
- bulk modulus
- equation of state
- other elastic constants
- phonon frequencies
- forces
- stable crystal structures and energy differences
- surface energy and relaxation
- liquid pair correlation functions
- ...

Important to include some lower-symmetry information if the potential will be used for non-perfect crystals

Be careful !

In mixed (e.g. A-B) systems: more difficult to fit separate interactions (A-A, B-B, A-B)

PHYSICAL REVIEW VOLUME 120, NUMBER 4 NOVEMBER 15, 1960

Dynamics of Radiation Damage*

J. B. Gibson, A. N. Goland,† M. Milgram, and G. H. Vineyard
Brookhaven National Laboratory, Upton, New York
(Received July 14, 1960)

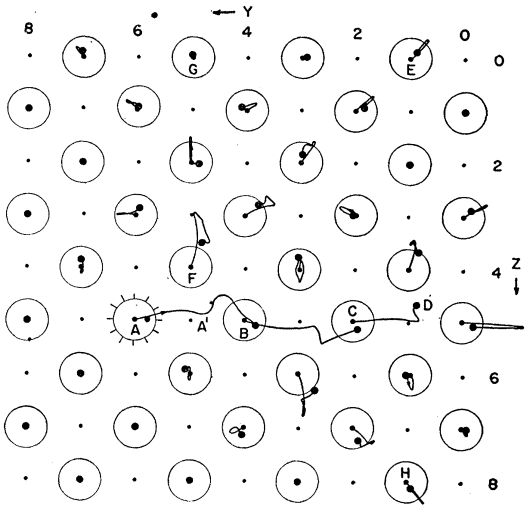
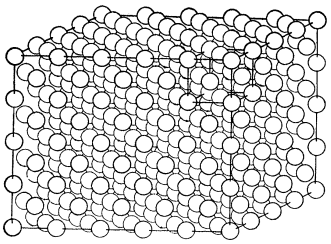


FIG. 6. Atomic orbits produced by shot in (100) plane at 40 ev. Knock-on was at A and was directed 15° above $-y$ axis. Large circles give initial positions of atoms in plane; small dots are initial positions in plane below. Vacancy is created at A, split interstitial at D. Run to time 99. (Run No. 12).

Example: Radiation Damage in Cu (first example of atomistic modeling on materials)



Periodic boundary conditions, convergence and practical issues

System sizes and Periodicity

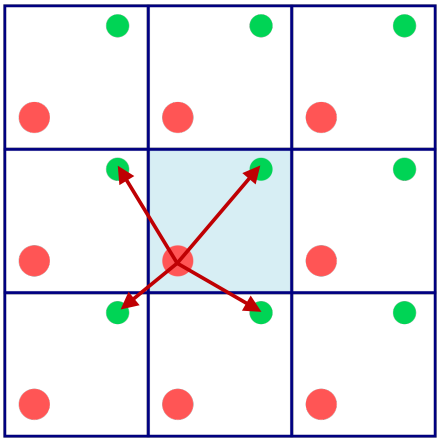
Finite System (e.g. molecule or cluster)

No problem -> simply use all the atoms

Infinite System (e.g. solids/liquids)

Do not approximate as finite -> use Periodic Boundary Conditions

Interactions also across boundaries

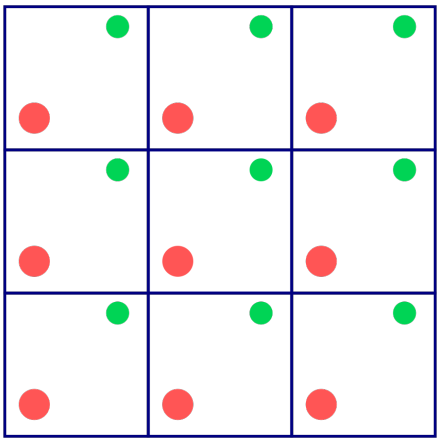


Interaction A-B: interaction of (all periodic replicas of) A with *all* periodic replicas of B!

In principle with all other atoms!

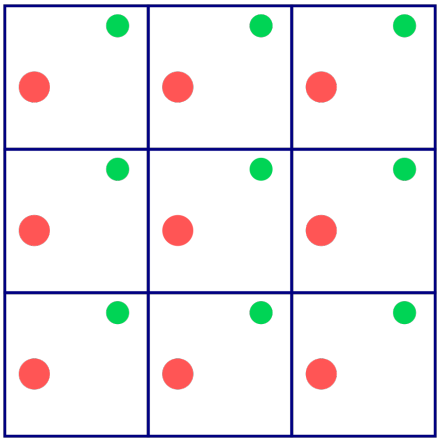
System sizes and Periodicity

Moving an atom moves all periodic replicas!



System sizes and Periodicity

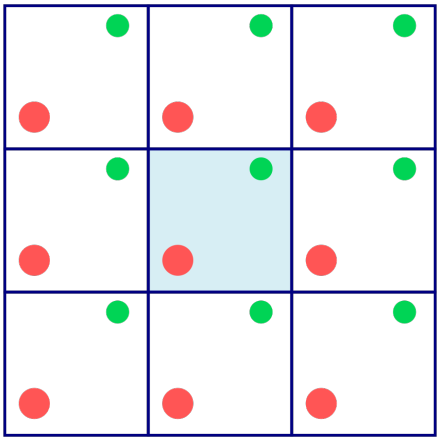
Moving an atom moves all periodic replicas!



System sizes and Periodicity

Translational invariance

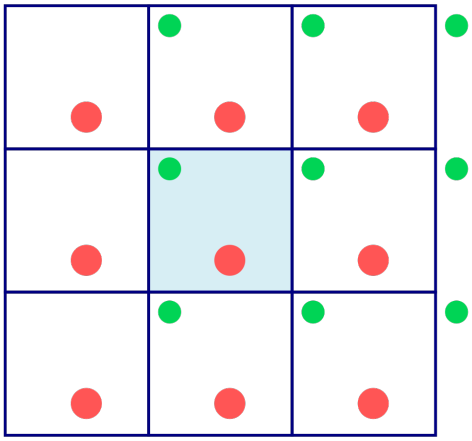
Independent of origin choice for unit cell!



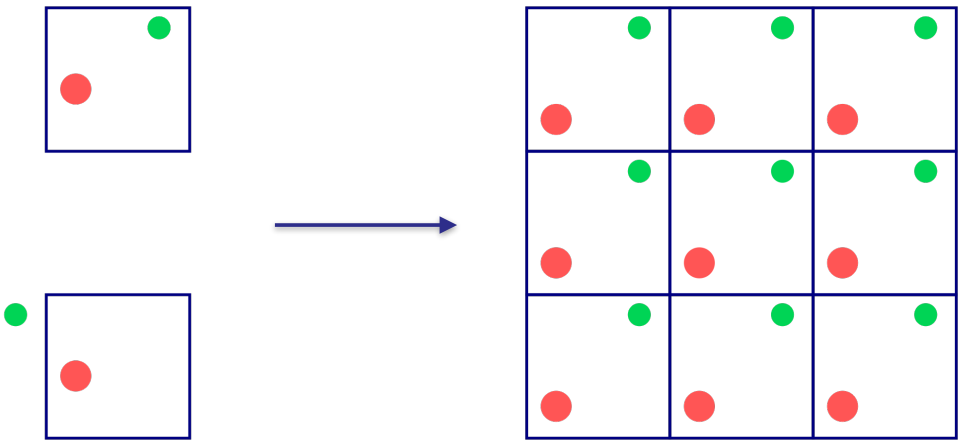
System sizes and Periodicity

Translational invariance

Independent of origin choice for unit cell!



Choice of representative atom

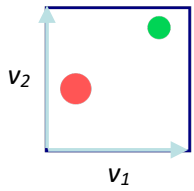


These two cell choices are equivalent

(You can pick any of the equivalent replicas as the representative atom)

Example of how to represent coordinates

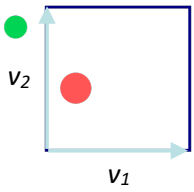
Cell:
v_1 = (4Å, 0Å)
v_2 = (0Å, 4Å)



Cell area
$|(\vec{v}_1 \times \vec{v}_2)|$

Scaled (relative) coordinates
(as a multiple of the lattice vectors, adimensional)
RED -> (0.2, 0.3) → *= 0.2 v_1 + 0.3 v_2*
GREEN -> (0.85, 0.9)

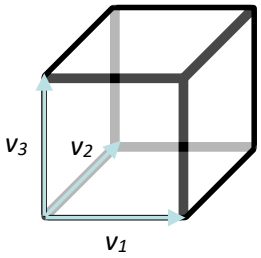
Absolute (Cartesian) coordinates
RED -> (0.8Å, 1.2Å)
GREEN -> (3.4Å, 3.6Å)



Scaled (relative) coordinates
(as a multiple of the lattice vectors, adimensional)
RED -> (0.2, 0.3)
GREEN -> (-0.15, 0.9)

Absolute (Cartesian) coordinates
RED -> (0.8Å, 1.2Å)
GREEN -> (-0.6Å, 3.6Å)

Coordinates and cell in 3D



Abs. coords *Scaled coords*

$$\vec{r} = \tilde{r}_1\vec{v}_1 + \tilde{r}_2\vec{v}_2 + \tilde{r}_3\vec{v}_3$$

$$\downarrow$$

$$r_x = \tilde{r}_1 v_{1x} + \tilde{r}_2 v_{2x} + \tilde{r}_3 v_{3x}$$

$$\dots$$

$$C = \begin{pmatrix} v_{1x} & v_{1y} & v_{1z} \\ v_{2x} & v_{2y} & v_{2z} \\ v_{3x} & v_{3y} & v_{3z} \end{pmatrix} \qquad C^T = \begin{pmatrix} v_{1x} & v_{2x} & v_{3x} \\ v_{1y} & v_{2y} & v_{3y} \\ v_{1z} & v_{2z} & v_{3z} \end{pmatrix}$$

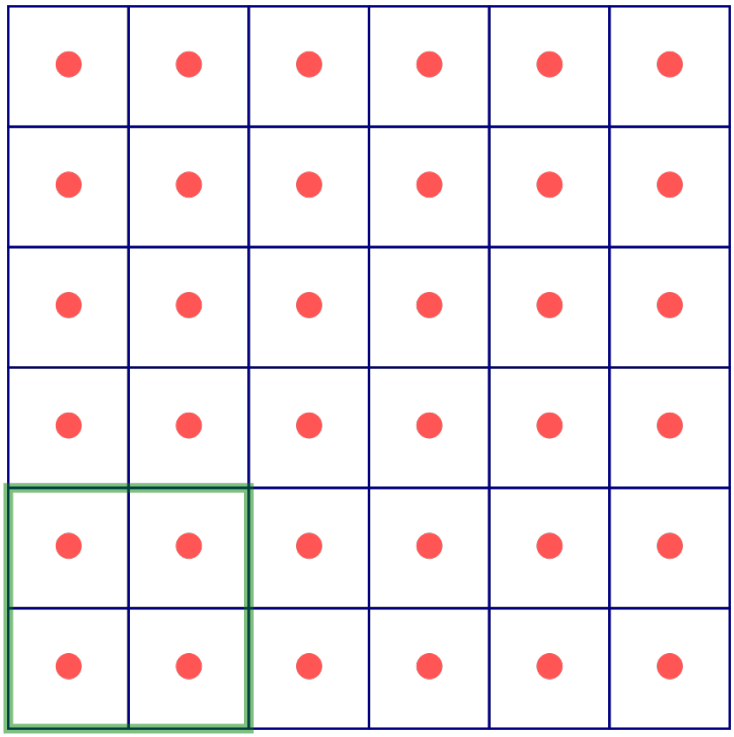
Cell volume

$$\left|(\vec{v}_1 \times \vec{v}_2) \cdot \vec{v}_3\right|$$

$$\begin{pmatrix} r_x \\ r_y \\ r_z \end{pmatrix} = C^T \cdot \begin{pmatrix} \tilde{r}_1 \\ \tilde{r}_2 \\ \tilde{r}_3 \end{pmatrix}$$

Abs. coords *Scaled coords*

Supercells



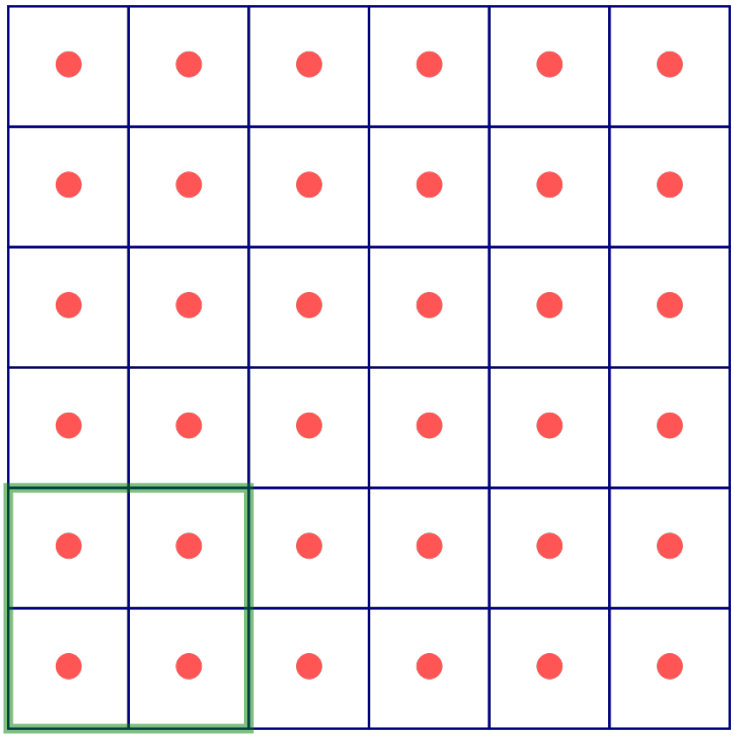
All physical properties remain the same if you use a "supercell" (e.g. use 2x2 primitive cells in the simulation)

You want the smallest to make the simulation faster

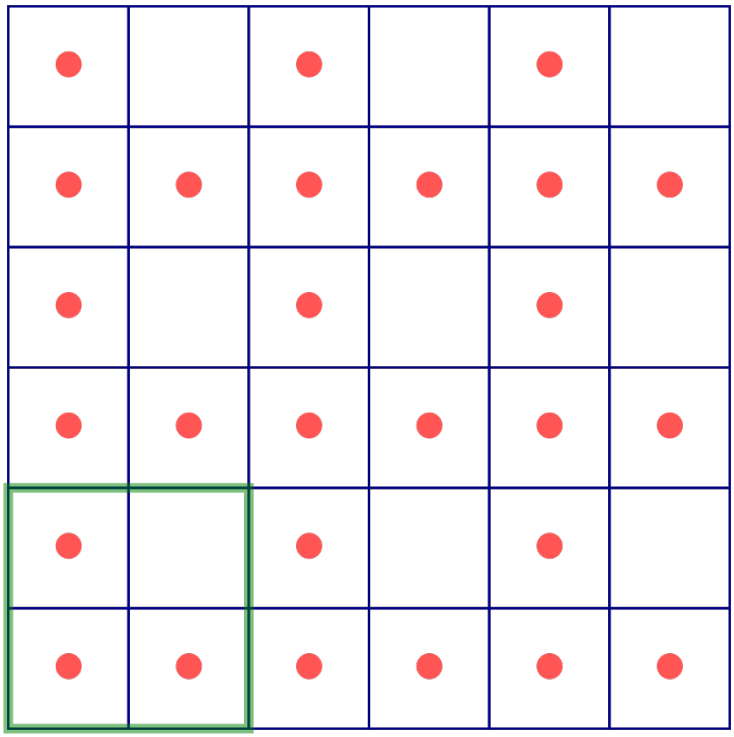
Remember to scale extrinsic properties

(e.g.: total energy of a 2x2 cell is 4 times larger than the primitive cell)

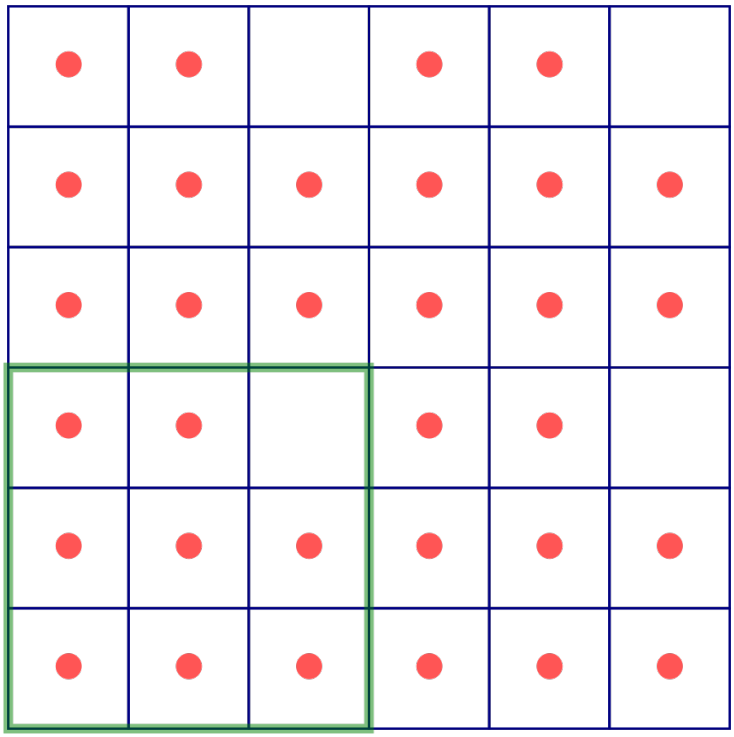
Defects and supercells



Defects and supercells



Defects and supercells



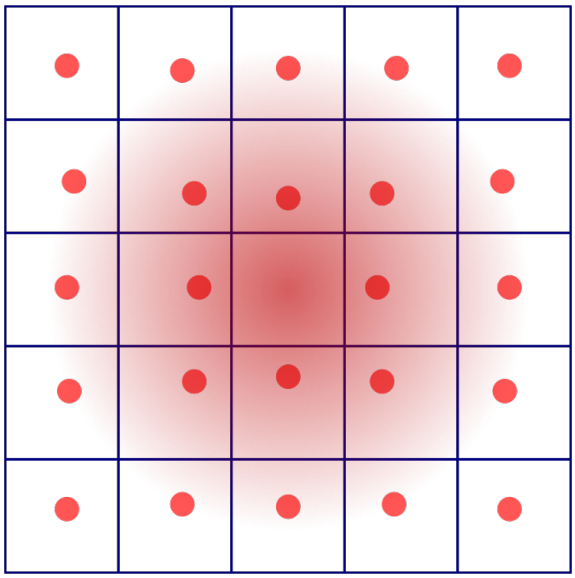
*You must **converge with supercell size** to eliminate interaction between periodic replicas of the vacancy!*

Relaxation

When removing an atom, the nearby ones "relax"

Important to take this effect into account by allowing atoms to move

The relaxation effects are typically longer-ranged than electronic interactions



Vacancy formation energy

Energy to remove an atom from a site

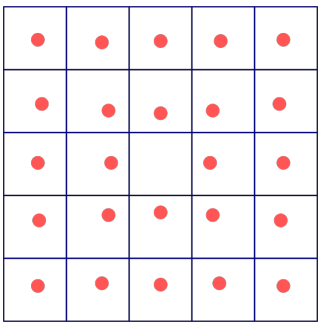
For these simple potentials, we can assume that the energy of an isolated atom is zero

Supercell size

$$E_{\text{vacancy}} = E_{(n-1)\ \text{atoms}}(n\ \text{sites}) - \frac{n-1}{n} E_{n\ \text{atoms}}(n\ \text{sites})$$

Scaling to conserve the number of atoms

Perfect crystal



25 sites, 24 atoms

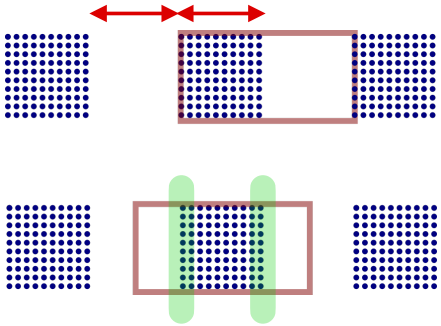
Surface energy

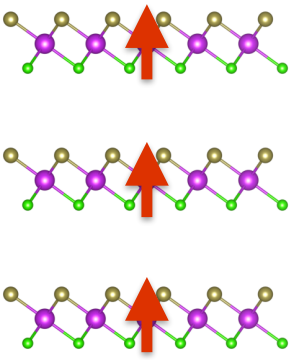
How do we create a surface in Periodic Boundary Conditions (PBC)?

Surface energy

Energy to create a surface (per unit surface)

Note: in a periodic cell there are 2 surfaces (per unit cell)!

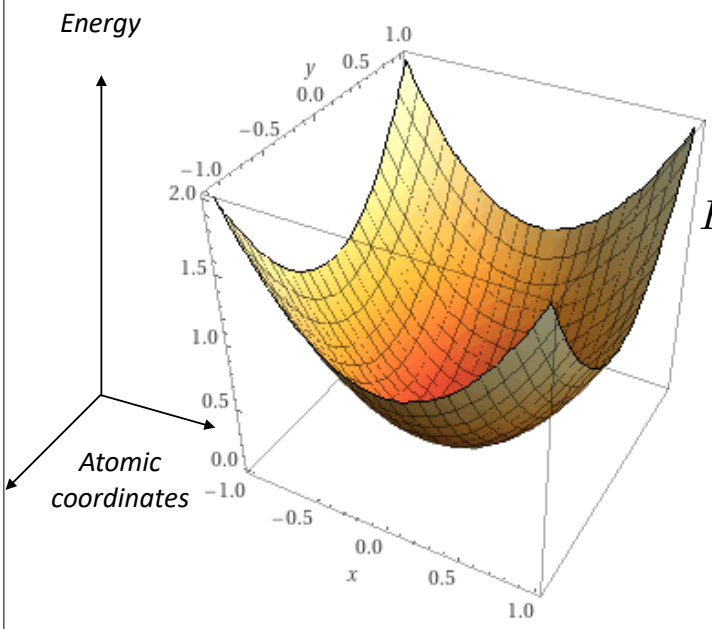




Converge: both the **slab thickness** (we want to simulate a surface over *the bulk*) and the **vacuum thickness** (so far away that surfaces don't "feel" each other)

(NOTE: if the slab is polar, there is the need of special corrections to screen the long-range electrostatic interactions between periodic replicas!)
(see e.g. Makov, Payne, PRB 51, 4014 (1995))

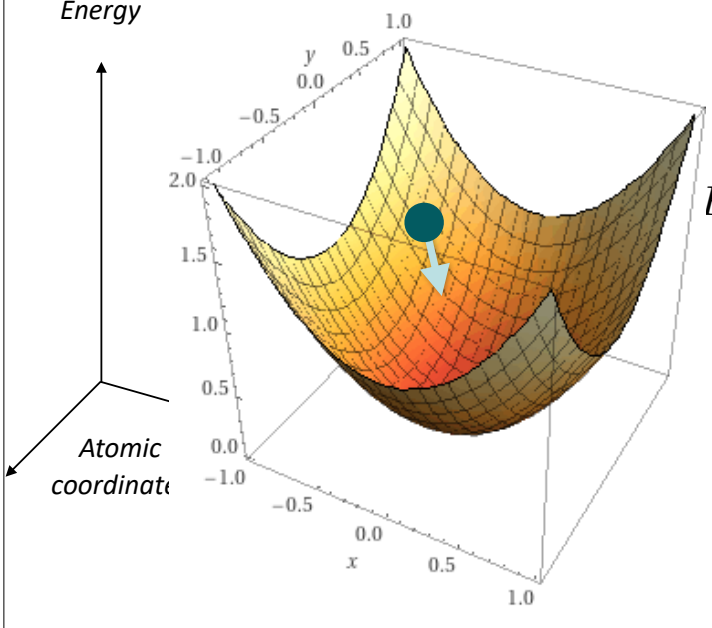
Optimizing atom coordinates



$$E = \frac{1}{2}\sum_{i,j\neq i}^{N} V(\vec{R}_i - \vec{R}_j)$$

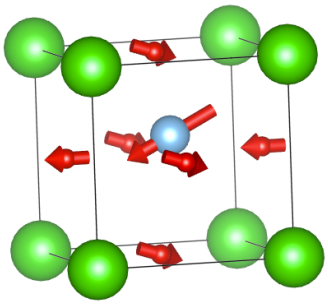
$$F = -\vec{\nabla}_i E = -\sum_{j\neq i}^{N} \frac{\partial V(\vec{R}_i - \vec{R}_j)}{\partial \vec{R}_i}$$

Optimizing atom coordinates

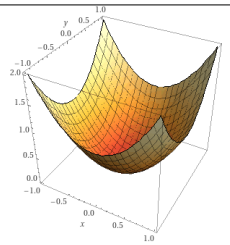


$$E = \frac{1}{2}\sum_{i,j\neq i}^{N} V(\vec{R}_i - \vec{R}_j)$$

$$F = -\vec{\nabla}_i E = -\sum_{j\neq i}^{N} \frac{\partial V(\vec{R}_i - \vec{R}_j)}{\partial \vec{R}_i}$$



Minimisation methods



Gradient (or steepest) descent
Simple, but slows down near minimum, slow for "narrow" valleys
Conjugate gradient
Faster for simple parabolic potentials, quite robust
Newton's method, BFGS, ...
Much faster, but might not work

OK to mix methods!

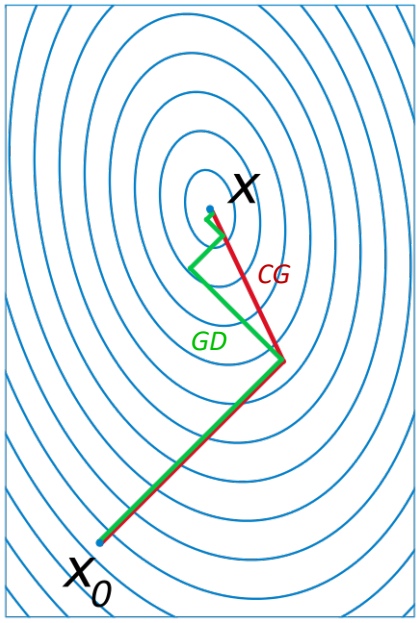
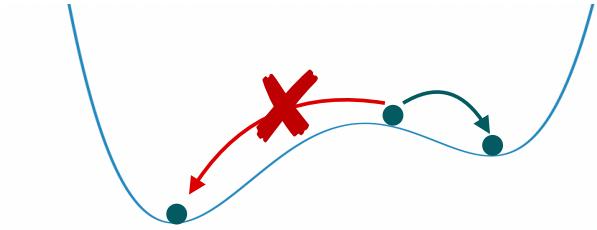


Image from Wikipedia

NOTE: One always finds a LOCAL minimum!



Scaling

Energy $E = \frac{1}{2} \sum_{i,j \neq i}^{N} V(\vec{R}_i - \vec{R}_j)$

What is the scaling (or "computational complexity") of computing the energy of a system With *N* atoms?

Scaling

Energy $E = \frac{1}{2}\sum_{i,j\neq i}^{N} V(\vec{R}_i - \vec{R}_j)$ ⟹

Double summation

Number of operations proportional to N^2

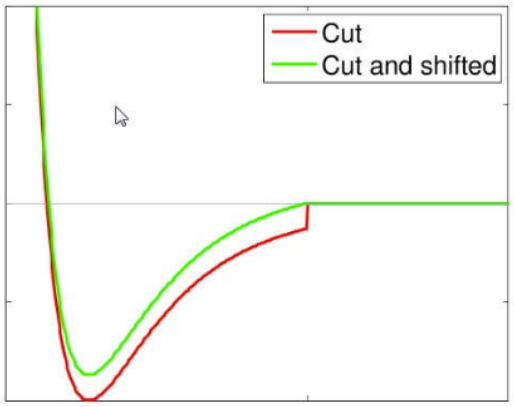
Force $F = -\vec{\nabla}_i E = -\sum_{j\neq i}^{N} \frac{\partial V(\vec{R}_i - \vec{R}_j)}{\partial \vec{R}_i}$

- Computational speed 10^4-10^6 faster than DFT
- **Still, essential to have linear scaling if you want to simulate millions or billions of atoms!**

Linear scaling

- Short-range potentials can be cut off at a certain distance
- This introduces a jump in energy at the cutoff distance, that is, *large unphysical forces!*

$$F = -\vec{\nabla}_i E = -\sum_{j\neq i}^{N} \frac{\partial V(\vec{R}_i - \vec{R}_j)}{\partial \vec{R}_i}$$



- Use cut and shifted potential to alleviate problem
- We need then only to sum over atoms within the cutoff distance
- Their number is ~constant even for huge cells: **reduce computation cost scaling from N^2 to N (linear scaling)**
- In a minimisation or a dynamics: Use (fixed or updated) neighbour lists to avoid to have to check who are the neighbours at every step

Limitations of pair potentials

Limitations of Pair Potentials: Application to Physical Quantities

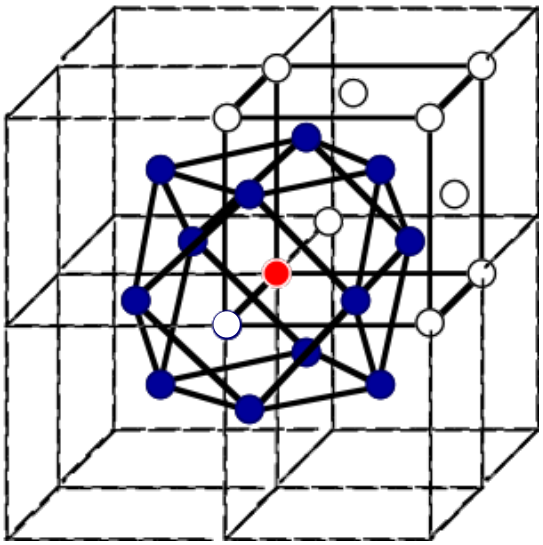
Vacancy Formation Energy

$$\frac{E_{\mathrm{vac}}}{E_{\mathrm{coh}}}$$

Ratio of vacancy formation energy over cohesive energy

Exactly 1 (in abs value) in pairwise potentials (*if no relaxation is allowed*)

BUT: Lower than 1 in metals!



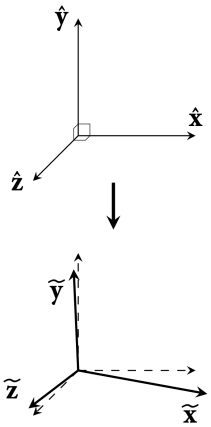
(Reminder on **cohesive energy** E_{coh}: energy required to separate a solid into neutral independent atoms)

Some data for real systems

Solid	$\frac{E_v^f}{E_{coh}}$
pair potential	
LJ	1.00
rare gases	
Ar	0.95
Kr	0.66
fcc metals	
Ni	0.31
Cu	0.37
Pd	0.36
Ag	0.39
Pt	0.26
Au	0.23

From Daw, M. S., Foiles, S. M. & Baskes, M. I. The embedded-atom method: a review of theory and applications. Materials Science Reports 9, 251 (1993).

Cauchy relation



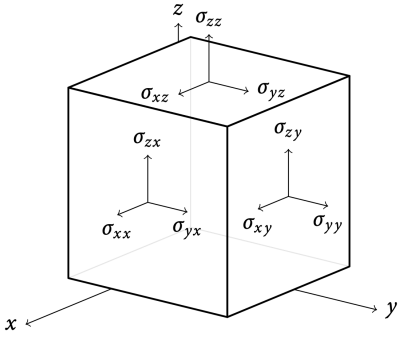
Strain

$$\tilde{\mathbf{x}} = (1+\varepsilon_{xx})\hat{\mathbf{x}} + \varepsilon_{xy}\hat{\mathbf{y}} + \varepsilon_{xz}\hat{\mathbf{z}}$$
$$\tilde{\mathbf{y}} = \varepsilon_{yx}\hat{\mathbf{x}} + (1+\varepsilon_{yy})\hat{\mathbf{y}} + \varepsilon_{yz}\hat{\mathbf{z}}$$
$$\tilde{\mathbf{z}} = \varepsilon_{zx}\hat{\mathbf{x}} + \varepsilon_{zy}\hat{\mathbf{y}} + (1+\varepsilon_{zz})\hat{\mathbf{z}},$$

"Engineering strains" $\gamma_{ii} = \varepsilon_{ii}, \qquad \gamma_{ij} = \varepsilon_{ij} + \varepsilon_{ji} = 2\varepsilon_{ij} \ (i \neq j).$

Stress

$$\sigma_{ij} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix}$$



Cauchy relation

Elastic tensor

$$\begin{pmatrix}\sigma_{xx}\\ \sigma_{yy}\\ \sigma_{zz}\\ \sigma_{yz}\\ \sigma_{zx}\\ \sigma_{xy}\end{pmatrix} = \begin{pmatrix}C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16}\\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26}\\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36}\\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46}\\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56}\\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66}\end{pmatrix}\begin{pmatrix}\gamma_{xx}\\ \gamma_{yy}\\ \gamma_{zz}\\ \gamma_{yz}\\ \gamma_{zx}\\ \gamma_{xy}\end{pmatrix}$$

For cubic systems (because of symmetry):

$$C_{ij} = \begin{pmatrix}C_{11} & C_{12} & C_{12} & 0 & 0 & 0\\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0\\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0\\ 0 & 0 & 0 & C_{44} & 0 & 0\\ 0 & 0 & 0 & 0 & C_{44} & 0\\ 0 & 0 & 0 & 0 & 0 & C_{44}\end{pmatrix}$$

For Pair Potentials in cubic systems: $C_{12} = C_{44}$

Some data for real systems

Solid	$\frac{C_{12}}{C_{44}}$	$\frac{E_v^f}{E_{coh}}$	$\frac{E_{coh}}{kT_m}$
pair potential			
LJ	1.0	1.00	13
rare gases			
Ar	1.1	0.95	11
Kr	1.0	0.66	12
fcc metals			
Ni	1.2	0.31	30
Cu	1.6	0.37	30
Pd	2.5	0.36	25
Ag	2.0	0.39	27
Pt	3.3	0.26	33
Au	3.7	0.23	34

From Daw, M. S., Foiles, S. M. & Baskes, M. I. The embedded-atom method: a review of theory and applications. Materials Science Reports 9, 251 (1993).

Crystal Structures

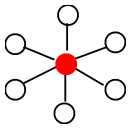
Pair potentials can fundamentally not predict crystal structures in metals or covalent solids

E.g.: FCC-BCC energy difference can be shown to be a "fourth moment" effect
(i.e. it needs *four-body interactions*)

Beyond simple pair potentials

Lack of environment-dependence in pair potentials

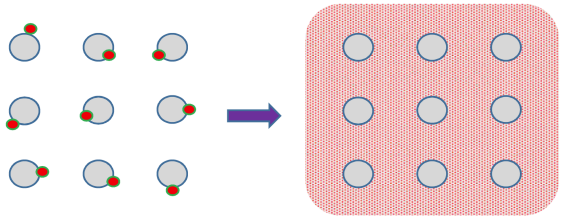
One bond does not "know" about the other

Bonding energy of red atom in  is six times bonding energy in 

This is in contradiction with both experiments and more accurate quantum mechanical calculations on many materials

For pair potentials: $\propto Z$

For metals: $\propto \sqrt{Z}$



Bonds get "weaker" as more atoms are added to central atom

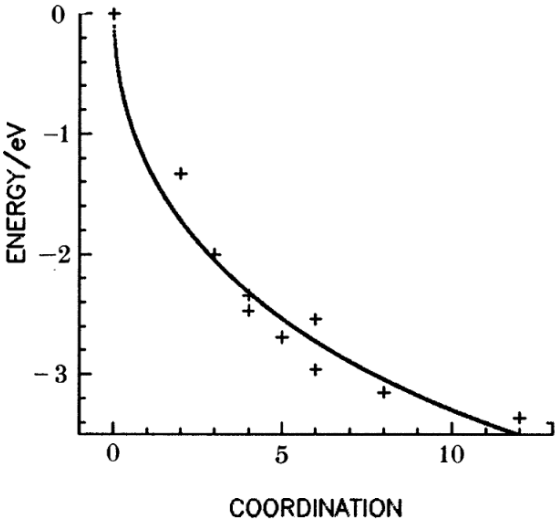
Energy as function of coordination: quantum mechanical results for Al

Many-atom interactions in solids

By Volker Heine, I. J. Robertson and M. C. Payne
Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, U.K.

Table 2. *Calculated formation energy U of various structures spanning a range of coordinated numbers*

structure	coordination	energy (atom eV)	U eV
atom	0	−54.95	0
line	2	−56.28	−1.33
graphite mesh	3	−56.95	−2.00
diamond	4	−57.42	−2.47
square mesh	4	−57.29	−2.34
square bilayer	5	−57.64	−2.69
simple cubic	6	−57.91	−2.96
triangular mesh	6	−57.49	−2.54
vacancy lattice	8	−58.10	−3.15
face centred cubic	12	−58.31	−3.36

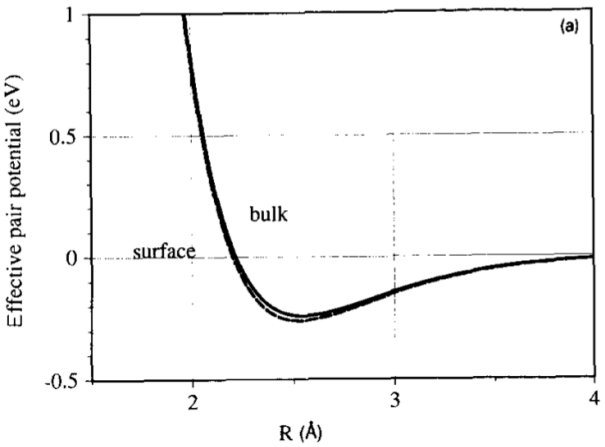


Bond strength depends on coordination

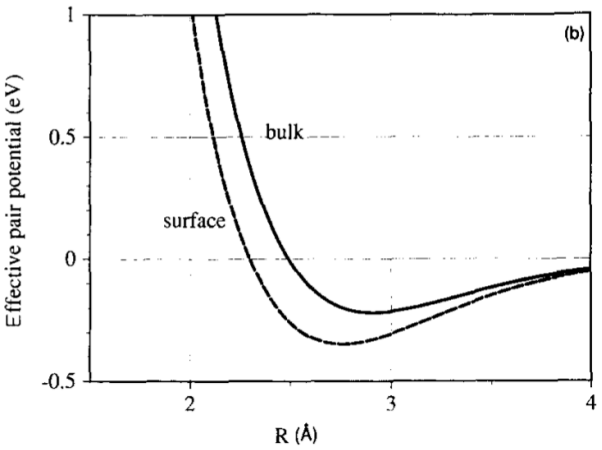
Effective potentials in different conditions

Difference in effective pair potential depending on environment (i.e., coordination number)

Ni



Pt



From Daw, M. S., Foiles, S. M. & Baskes, M. I. The embedded-atom method: a review of theory and applications. Materials Science Reports 9, 251 (1993).

Effective Medium Theories: The Embedded Atom Method

Problem with potentials

Cohesive energy depends on number of bonds, but non-linearly

Solution

Write energy per atom as $E = f$(number of bonds) where f is non-linear function

→ Energy Functionals

How to measure "number of bonds"

In Embedded Atom Method (EAM) proximity of other atoms is measured by the electron density they project on the central atom

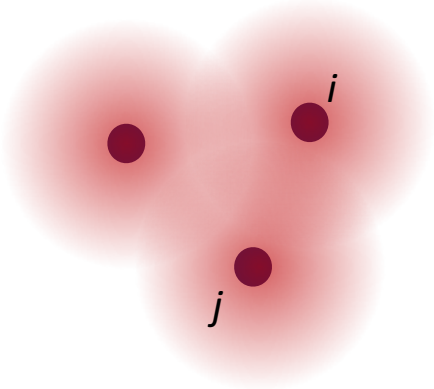
How to quantify the coordination number: Atomic Electron Densities

Electron Density on Site *i*

Proxy for the coordination number

$$n_i = \sum_{\substack{j=1 \\ (j \neq i)}}^{N} \rho(r_{ij})$$

Mimicking atomic electron density of atom *j*



EAM: The Physical Concept

Bonding energy (embedding energy) due to Electron Delocalization

As electrons get more states to spread out over,
their kinetic energy decreases.
When an impurity is put into a metal, **its energy is lowered**
because the electrons from the impurity can delocalize
into the solid

The embedding density (electron density at the embedding site)
is a measure of the number of states available to delocalize onto

Inherently MANY BODY effect

EAM functionals

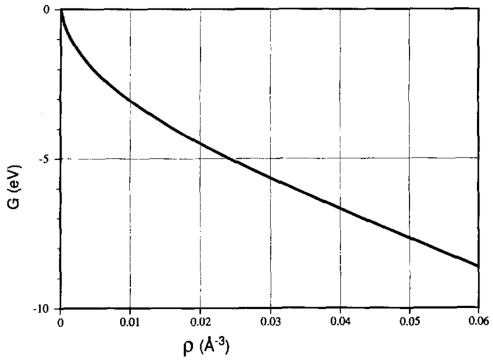
Electron Density on Site i $n_i = \sum_{\substack{j=1 \\ (j \neq i)}}^{N} \rho(r_{ij})$

$$E_{\mathrm{coh}} = \sum_i G_i(n_i) + \frac{1}{2} \sum_{i,j \neq i} V(R_{ij})$$

Embedding energy G for nickel

Energy of an atom as a function of a "generalised coordination" n

Negative, attractive term



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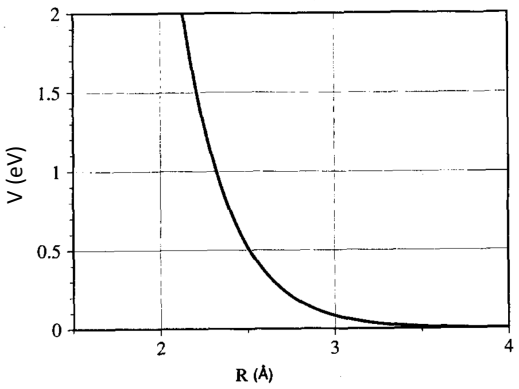
Two-body interaction for nickel

E.g. only repulsion term



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EAM functionals

Electron Density on Site i $n_i = \sum_{\substack{j=1 \\ (j \neq i)}}^{N} \rho(r_{ij})$

$$E_{\mathrm{coh}} = \sum_i G_i\left(n_i\right) + \frac{1}{2} \sum_{i,j \neq i} V(R_{ij})$$

NOTE! Non-unique separation of G and V

Clementi and Roetti Tables

Atomic densities are, for instance, tabulated in
E. Clementi and C. Roetti, Atomic Data and Nuclear Data Tables, Vol 14, p177 (1974)

BORON 1S(2)2S(2)2P(1), 2P
T.E. = −0.24527920D + 02 P.E. = −0.49056561D + 02
K.E. = 0.24528640D + 02 V.T. = −0.19999706D + 01

Configuration and state Energies (see above) in hartrees D + 02 means × 10^2

S		1S	2S	P		2P
BASIS/ORB E		−7.69443*	−0.49408*	BASIS/ORB E		−0.30989*
1S	6.56657	0.19030	0.00754	2P	2.21734	0.21526
1S	4.24927	0.82091	−0.25055	2P	1.00551	0.84052
2S	1.41314	−0.00364	0.87099			
2S	0.87564	0.00251	0.18515			
n,λ	Orbital exponents ζ	$\phi(1s)$ expansion coefficients	$\phi(2s)$ expansion coefficients	n,λ	Orbital exponents ζ	$\phi(2p)$ expansion coefficient
Description of orbitals of s symmetry				. . . of orbitals of p symmetry		

*Orbital energy

Clementi and Roetti, At. Data Nucl. Data Tables 14, 177 (1974)

Or, other forms for a **short-ranged, decreasing function of distance**

EAM is similar to many other effective medium theories

Various theories differ in the "non-linearity" used or the measure of "embedding density", or even tabulated so as to give an exact fit to the equation of state (energy vs. volume)

Examples:

$$G(\rho) = -G_0 \left[1 - \ln\left(\frac{\rho}{\rho_e}\right)^n\right]\left(\frac{\rho}{\rho_e}\right)^n$$ *Banerjea, Smith, PRB 37, 6632 (1988)*

$$G(\rho) = -G_0 \left[1 - \ln\left(\frac{\rho}{\rho_e}\right)^n\right]\left(\frac{\rho}{\rho_e}\right)^n + G_1\left(\frac{\rho}{\rho_e}\right)$$ *Cai, Ye, PRB 54, 8398 (1996)*

- Effective Medium Theory (Puska, Nieminen, Manninen)
- Glue model (Ercolessi, Tosatti and Parrinello)
- Finnis Sinclair Potentials
- Equivalent Crystal Models (Smith and Banerjea)

The complete energy expression: Embedding energy + pair potential

$$E_{\text{coh}} = \sum_i G_i\left(n_i\right) + \underbrace{\frac{1}{2}\sum_{i,j\neq i} V(R_{ij})}_{\text{Pair Potential}}$$

Pair potential can have any form, often screened electrostatic used

$$\phi_{AB}(r) = \frac{q_A(r)q_B(r)}{r}$$

$$\text{with } q(r) = q_0(1+\beta r^\nu)e^{-\alpha r}$$

Some results: Activation Energy for Self Diffusion (in eV)

Significant improvement of certain materials properties in EAM vs LJ

Metal	EAM	"Exp."
Cu	2.02	2.07
Ag	1.74	1.78
Au	1.69	1.74
Ni	2.81	2.88
Pd	2.41	< 2.76
Pt	2.63	2.66

data from Elsevier from Daw, M. S., Foiles, S. M. & Baskes, M. I. The embedded-atom method: a review of theory and applications. Materials Science Reports 9, 251 (1993).

Some results: Linear Thermal Expansion (10^{-6}/K)

Element	α(EAM)	α(exp)
Cu	16.4	16.7
Ag	21.1	19.2
Au	12.9	14.1
Ni	14.1	12.7
Pd	10.9	11.5
Pt	7.8	8.95

data from Elsevier from Daw, M. S., Foiles, S. M. & Baskes, M. I. The embedded-atom method: a review of theory and applications. Materials Science Reports 9, 251 (1993).

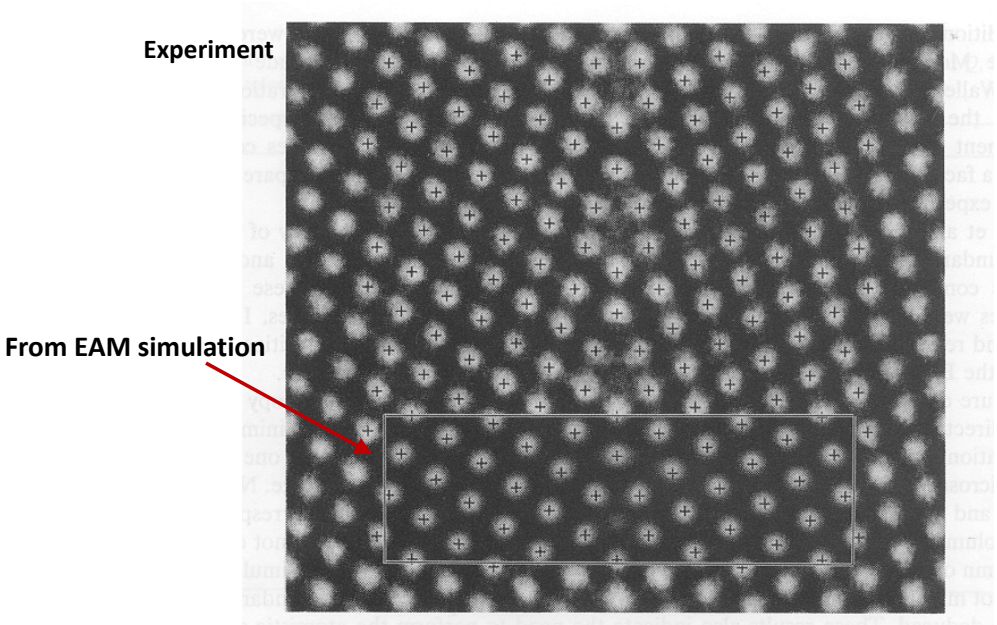
MSE 468 Atomistic and Quantum Simulations of Materials, Giovanni Pizzi, Spring 2025, EPFL

Some results: Melting Points

Element	EAM	Exp.
Cu	1340	1358
Ag	1170	1234
Au	1090	1338
Ni	1740	1726
Pd	1390	1825
Pt	1480	2045

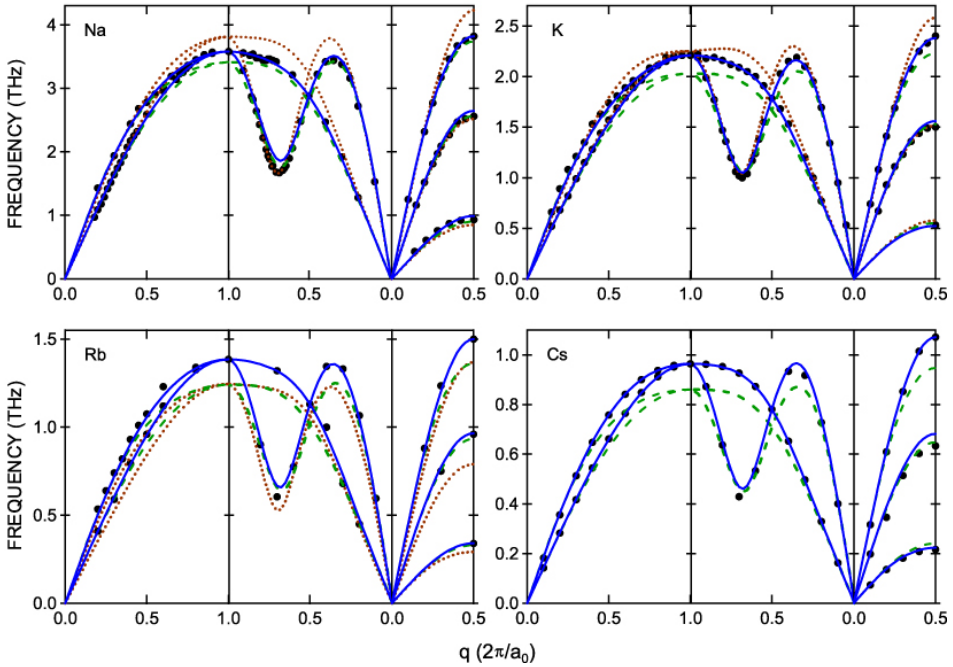
data from Elsevier from Daw, M. S., Foiles, S. M. & Baskes, M. I. The embedded-atom method: a review of theory and applications. Materials Science Reports 9, 251 (1993).

Some results: Grain Boundary in Al



From Daw, M. S., Foiles, S. M. & Baskes, M. I. The embedded-atom method: a review of theory and applications. Materials Science Reports 9, 251 (1993).

Some results: Phonon dispersions for alkali



R B Wilson and D M Riffe 2012 J. Phys.: Condens. Matter 24 335401

Computational cost

EAM is similar to Pair Potentials in computational intensity!

$$E_{\mathrm{coh}} = \sum_i G_i\left(n_i\right) + \frac{1}{2}\sum_{i,j\neq i} V(R_{ij}) \qquad n_i = \sum_{\substack{j=1 \\ (j\neq i)}}^{N} \rho(r_{ij})$$

Take-home message: Effective Medium Theories: significant improvement over pair potentials for metals, at almost no computational cost.

Hence: no reason NOT to use them.

BUT: be aware of problems trying to do too much subtle chemistry with them!

Issues and Problems with EAM

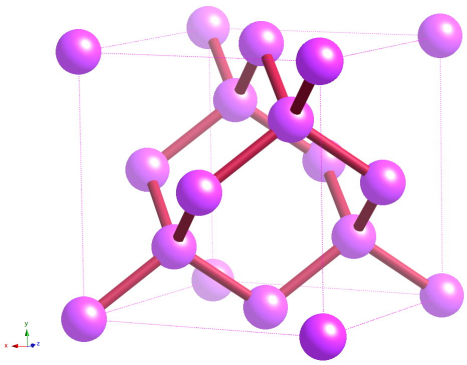
Bonding is Spherical: Limitation in early transition metals and covalent systems -> MEAM (modified EAM)

Potential is not unique: Some part of the energy can be divided arbitrarily between pair potential and embedding function.
Note: the linear part of the embedding function is equivalent to a pair potential

Limitations in Alloys:

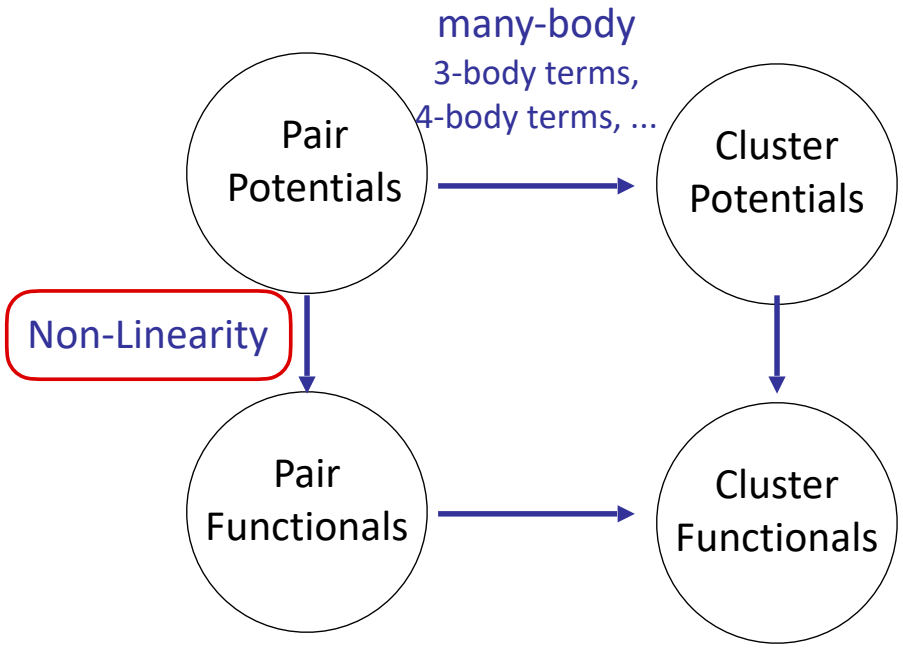
In elements, any error arising form using the atomic electron density is absorbed when the Embedding function F is fitted. In A-B alloys F has to work for electron density from both A and B

Directional bonding in Silicon



- 4 electrons centered on each atom
- Repulsion between sp^3 orbitals lead to angular dependence
- Very hard to stabilize diamond cubic structure with pair potentials
- Need 3-body interactions
- An atom needs to know more about it neighbors distances and directions

How to Fix the Pair-Potential Problem ?



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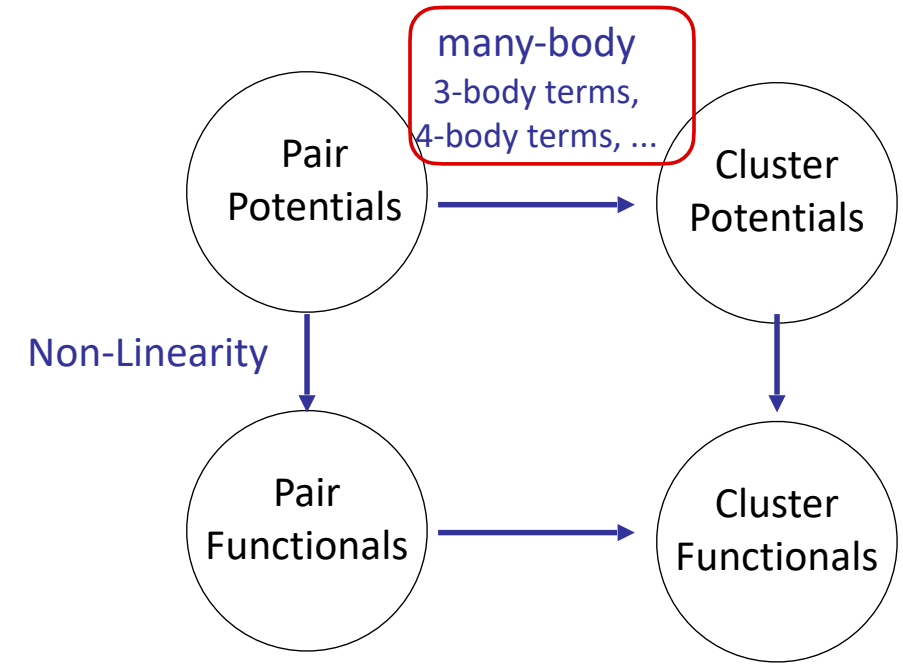

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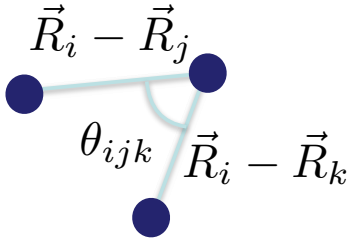
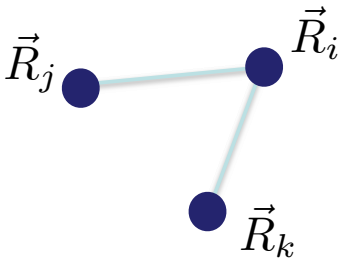
Three-body potentials

$$E = E_0 + \frac{1}{2}\sum_{i\neq j} V_2(\vec{R}_i, \vec{R}_j) + \frac{1}{3!}\sum_{i\neq j\neq k} V_3(\vec{R}_i, \vec{R}_j, \vec{R}_k)$$

Equivalently, parametrize as a function of distances and angles:

$$V_3 \rightarrow V_3'(|\vec{R}_i - \vec{R}_j|, |\vec{R}_i - \vec{R}_k|, \theta_{ijk})$$





Three-body potentials

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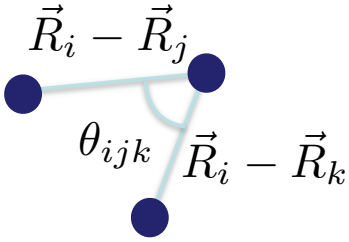


Angular dependency often factored out explicitly:

$$V_3' = V_3''(|\vec{R}_i - \vec{R}_j|, |\vec{R}_i - \vec{R}_k|) \cdot K(\theta_{ijk})$$

For instance (encoding expected angles in the bulk structure):

$$K(\theta) = K_0(\theta - \theta_0)^2 \quad \text{or} \quad K(\theta) = K_0\left(\cos\theta - \cos\theta_0\right)^2$$

What is the scaling w.r.t. *N* now?

Now need N^3 operations for evaluating potential!

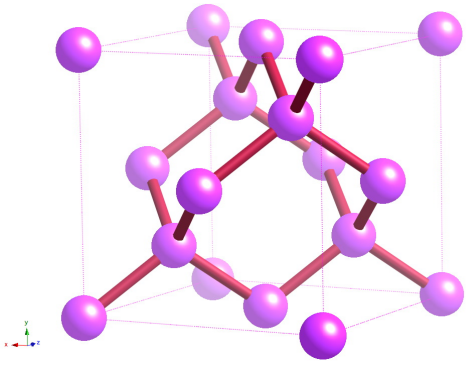
Example: Stillinger-Weber potential for silicon

One "classical" choice (out of many possible) for a Si potential

$$E = \sum_i \sum_{j>i} \phi_2(r_{ij}) + \sum_i \sum_{j\neq i} \sum_{k>j} \phi_3(r_{ij}, r_{ik}, \theta_{ijk})$$

2-body $$\phi_2(r_{ij}) = A_{ij}\epsilon_{ij}\left[B_{ij}(\frac{\sigma_{ij}}{r_{ij}})^{p_{ij}} - (\frac{\sigma_{ij}}{r_{ij}})^{q_{ij}}\right] \exp\left(\frac{\sigma_{ij}}{r_{ij} - a_{ij}\sigma_{ij}}\right)$$

3-body $$\phi_3(r_{ij}, r_{ik}, \theta_{ijk}) = \lambda_{ijk}\epsilon_{ijk}\left[\cos\theta_{ijk} - \cos\theta_{0ijk}\right]^2 \exp\left(\frac{\gamma_{ij}\sigma_{ij}}{r_{ij} - a_{ij}\sigma_{ij}}\right) \exp\left(\frac{\gamma_{ik}\sigma_{ik}}{r_{ik} - a_{ik}\sigma_{ik}}\right)$$



$$\left(\cos\theta + \frac{1}{3}\right)^2$$

Encodes the sp^3 bonding: fourfold-coordinated bulk, $\cos\theta_0 = -1/3$

Tersoff potential

Combining **bond-order** (potential depends on number of bonds) and **bond angle** information (3-body term)

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Empirical interatomic potential for silicon with improved elastic properties

J. Tersoff

$$E = \sum_i E_i = \tfrac{1}{2} \sum_{i \neq j} V_{ij} \ ,$$

$$V_{ij} = f_C(r_{ij})[a_{ij} f_R(r_{ij}) + b_{ij} f_A(r_{ij})] \ ,$$

$$f_R(r) = A \exp(-\lambda_1 r) \ ,$$

$$f_A(r) = -B \exp(-\lambda_2 r) \ ,$$

Similar to glue model in metals (coordination as a parameter)

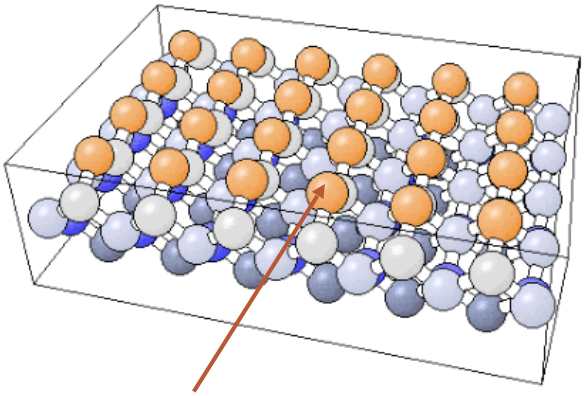
Bond order: don't focus on atom positions, but on bonds

b_{ij} *depends on a bond-length term and on an angular term*

Surface Reconstruction for Si

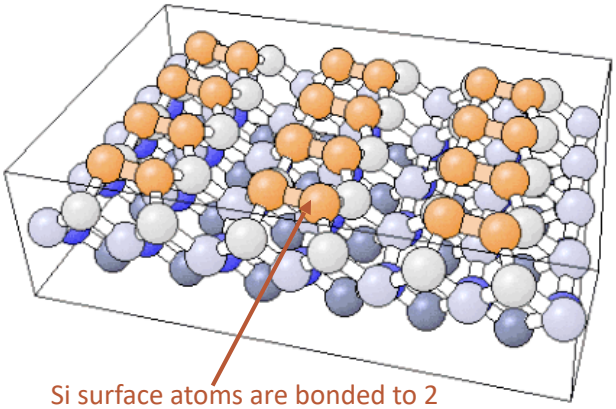
Now possible to predict 2x1 surface reconstruction for Si

unreconstructed Si(100)



Si surface atoms are bonded to 2 atoms below

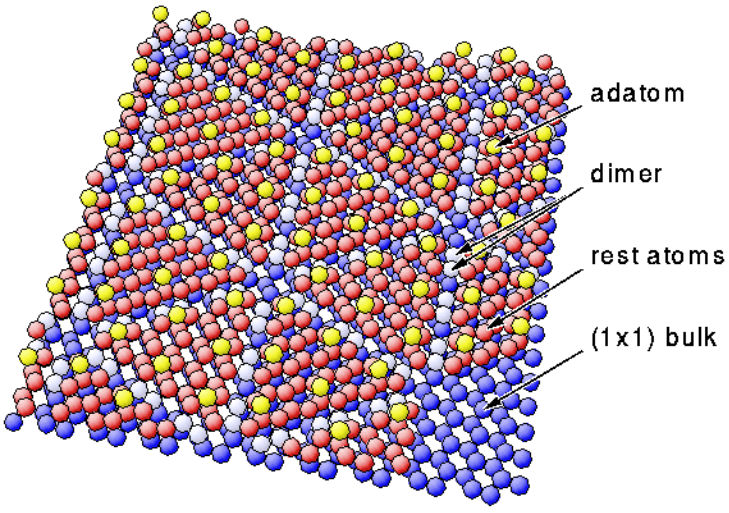
2x1 reconstruction for Si(100)



Si surface atoms are bonded to 2 atoms below and one on surface -> dimer formation on surface

See e.g. Khor, Das Sarma, Phys. Rev. B 36, 7733(R) (1987)

Surface Reconstruction for Si



Si(111)-(7x7) DAS model (Takayanagi/Tong) BALSAC plot

7x7 reconstruction for Si(111) is however **not** reproduced! (Requires DFT)

Some conclusions so far

Bond strength depends on environment:

- either through angular dependence with other bonds
- or through dependence on number of other bonds (density)

This limits the transferability of pair potentials

Fitted for one particular coordination environment, they cannot be used without significant error for other coordination (e.g., fit to bulk but use on surface).

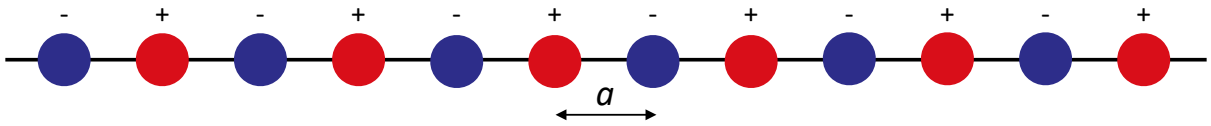
Fitting to all environments simultaneously only "averages" the error

Long-range interactions

- In ionic compounds:
  long-range Coulomb interactions dominate
  - E.g.: NaCl, CaO, MgO, ...
  - Dependence: **1/r**
- Neutral but polarised particles (dipoles): **$1/r^3$** interaction
- Van-der-Waals interactions (induced fluctuating dipole moments): **$1/r^6$** (see Lennard-Jones)
- **No exponential decay: cannot cut-off after a certain distance, all atoms need to be included!**

Long-range interactions and Ewald sums

1D example



$$\sum_{n=1}^{\infty} \frac{(-1)^n}{n \cdot a}$$

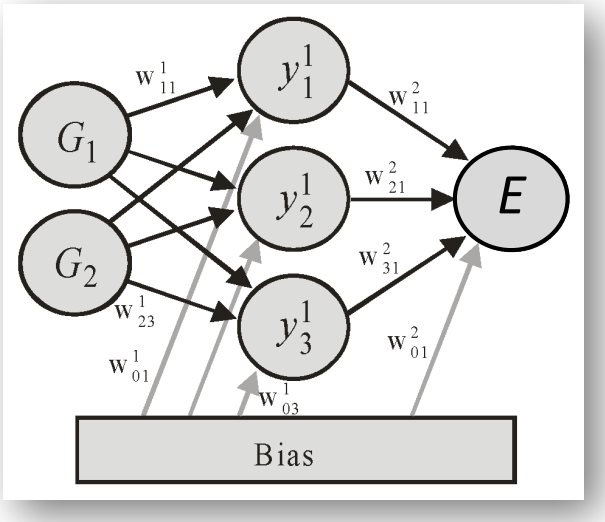
This sum is finite, but the sum of only the positive and negative terms diverges!

- Requires "tricks" in periodic boundary conditions: "**Ewald sums**". In a nutshell:
  - *add localised neutralising charges* around each ion: interaction screened, can use short-range techniques
  - *subtract it again to obtain original system*: if the neutralising charges have a simple analytical shape (e.g. Gaussians), this can be computed effectively in reciprocal space (Fourier transforms)

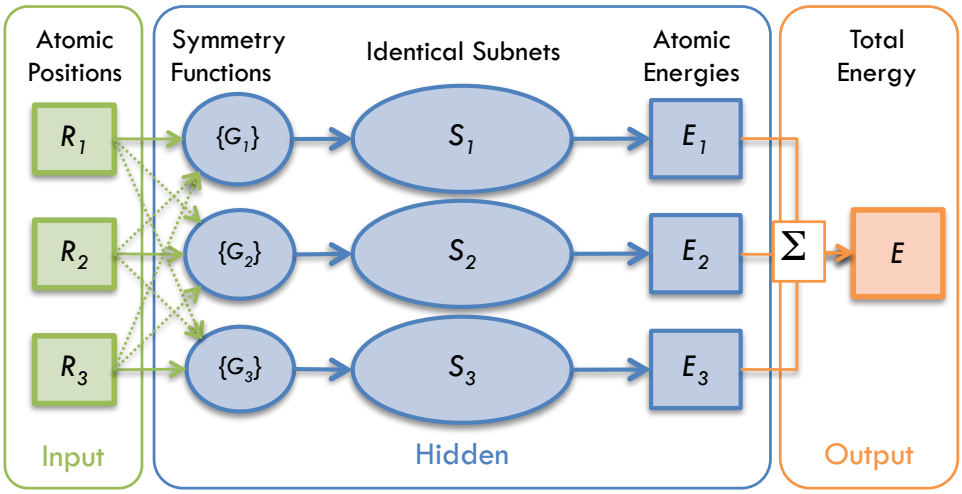
Neural Network for DFT-based potential-energy surfaces

- Fix the network topology
- Optimize the parameters to reproduce input data (training)
- Use it to get *E* from {*R*}

$$E = f_a^2\left(w_{01}^2 + \sum_{j=1}^{3} w_{j1}^2 \cdot f_a^1\left(w_{0j}^1 + \sum_{i=1}^{2} w_{ij}^1 G_i \right) \right)$$



Neural Network for DFT-based PES

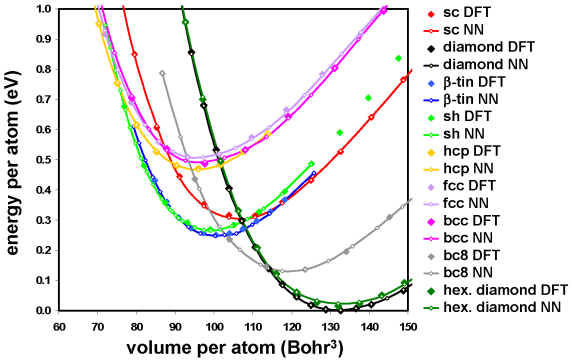


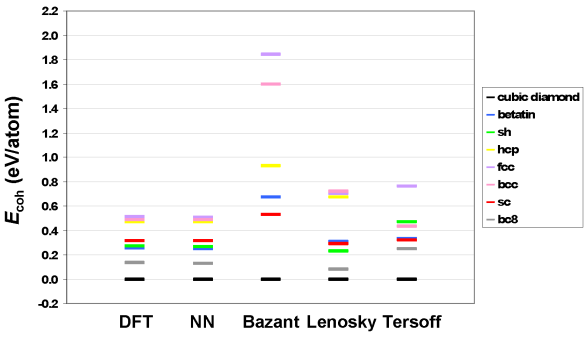
- System size independent
- Independent of the coordination number

Neural Network for Silicon

DFT results reproduced at a fraction of the cost

- **20000** DFT energies used in fitting
  (PWSCF http://www.quantum-espresso.org)
  - LDA 64 atoms
  - 20 Ry cutoff
  - 3x3x3 *k* points
- Few thousand parameters for NN
  - 2 hidden layers of 40 nodes
  - 48 symmetry functions
  - Cutoff 6 Å
- RMSE (training set) 4 meV/atom
- RMSE (test set) 5 meV/atom
- 10^5 times faster than DFT
- Scales linearly with system size





Thermodynamic Properties

- Perfect agreement with DFT results
- **IMPORTANT: if you fit against DFT, your target is DFT, NOT experiments!**

	Neural Network	DFT-LDA [1]	Experiments
T_m(K)	1350(5)	1350(10)	1685(2)
S_s	7.001(2)k_b	6.9(1)k_b	7.4k_b
S_l	9.98(2)k_b	9.9(2)k_b	11.0k_b , 10.7k_b
H_s (eV/atom)	H_s(0 K)+0.355(5)	H_s(0 K)+0.33(2)	H_s(0 K)+0.41
ΔH (eV/atom)	0.38 (1)	0.35(2)	0.52 , 0.47
C_s (eV/K atom)	2.66x10^{-2}	3.0(4)x10^{-2}	3.03x10^{-2}
C_l (eV/K atom)	2.54x10^{-2}	2.7(4)x10^{-2}	3.03x10^{-2}
V_s [(a.u.)³/atom]	136.8	135.0(5)	138.0
$\Delta V/V_s$	13.3%	10(1)%	11.9% , 9.5%
dT_m/dP (K/GPa)	-58.6	-50(5)	-38

[1] O. Sugino and R. Car, Phys. Rev. Lett. 74, 1823 (1995)

Building a dataset for the GAP potentials

Relevant configurations: cover the target volume/temperature phase diagram

~ 10^5 local environments (much more for sampling)

~ 10^6 CPU hours

~ 2 years

GAP_6 model

DB_1.c *Elastic constants* → MC sampling in the lattice space
4000 environments
MC temperature=300 K
Lattice1: +0.36/0.17% wrt a_0^{el} / a_0^{zpe}
Lattice2: +1.17/0.98% wrt a_0^{el} / a_0^{zpe}
• slice sampling algorithm
• primitive unit cell
• training from energies(low_cutoff) and stresses(high_cutoff)

DB_2.c *Phonon spectrum* → MD, no defects
20538 environments
• 54 at. 333 simulation box
MD temperature=400/600/1000/1400 K
Lattice a_0^{el}, ±0.7% a_0^{el} (-0.88%,+0.51% a_0^{zpe})
Lattice +1.17% a_0^{el} (+0.98% a_0^{zpe}) [no MD run]
• 128 at. 444 simulation box
MD temperature=800 K
Lattice a_0^{el}, ±0.7 a_0^{el}, +1.17% a_0^{el} (±0.51%,+0.98% a_0^{zpe})
• training from energies and forces

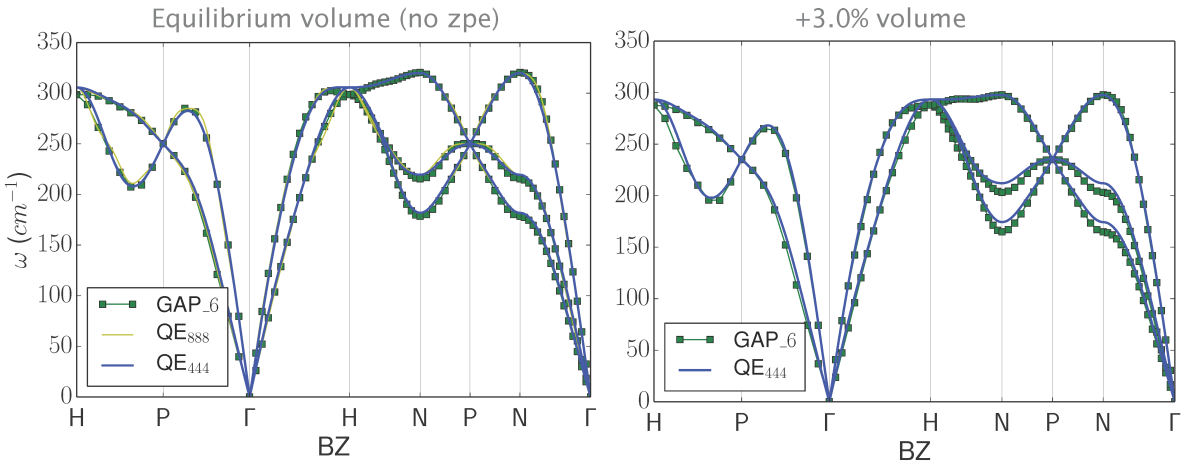
DB_3.a *Vacancies* → MD, mono-vacancy + di-vacancy
32346 environments
MD temperature=400/600/1000 K
• 53 at. 333 simulation box
Lattice a_0^{el}, ±0.7% a_0^{el} (-0.88%,+0.51% a_0^{zpe})
• 127 at. 444 simulation box
Lattice a_0^{el}
• 126 at. 3*nn*, 444 simulation box
Lattice a_0^{el}
• training from energies and forces

DB_4.a *Surfaces* → MD, (100) (110) (111) (211)
2412 environments
MD temperature=300 K
• 12 at. simulation box
In-plane Lattice a_0^{el}
• training from energies and forces

Ready to be included

DB_5.a *γ Surfaces* → MD, (110) (211)
75000 environments
MD temperature=300 K
Lattice a_0^{el}, ±1.0% a_0^{el}
• 12 at. simulation box
• training from energies and forces

Phonons



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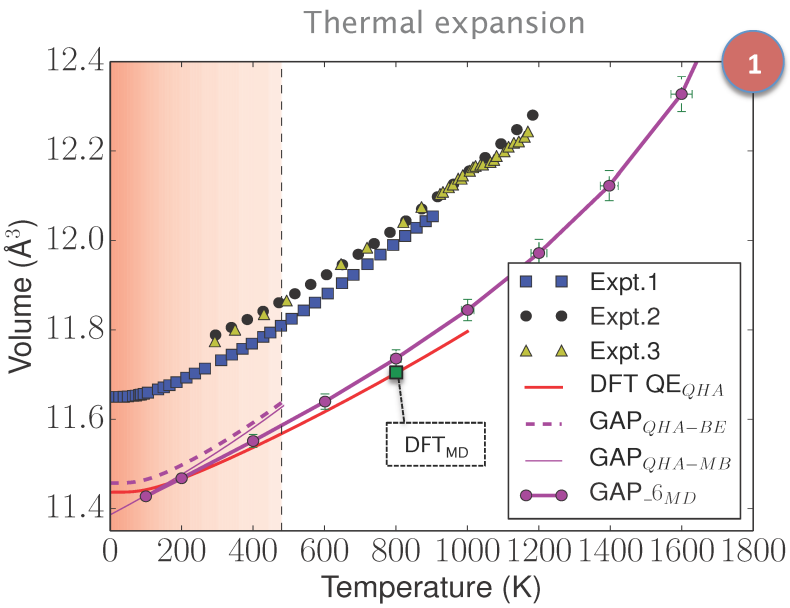
Thermal expansion



Daniele Dragoni et al., Phys. Rev. Materials (2018)

Past few years: foundation ML potentials

- Foundation models developed and now available
  - *"machine learning or deep learning model that is trained on vast datasets so it can be applied across a wide range of use cases"*
  - Different underlying architectures
  - They all require ability to run a lot of DFT simulations to create a training set
    - Should not only contain relaxed structures, but also distorted ones, to capture energetics
    - They are not specific to a given chemistry, but in general should work for any material. Can then be reused to train other models

Past few years: foundation ML potentials

- Very active field. Some very recent examples, with various architectures:
  - MACE-MP-0 (https://github.com/ACEsuit/mace-mp)
    I. Batatia et al., arXiv:2401.00096 (2023)
  - MatterSim (https://microsoft.github.io/mattersim/)
    H. Yang et al., arXiv:2405.04967 (2024)
  - OMat24 (https://huggingface.co/datasets/fairchem/OMAT24)
    Barroso-Luque et al., arxiv:2410.12771 (2024)
  - And many many more (also before: M3GNET, CHGNET, ALIGNN, …)
    - See also comparison on MatBench (https://matbench.materialsproject.org/) or various recent papers (also benchmarking phonons, thermal transport, …)
      H. Yu et al., arXiv:2403.05729 (2024); A. Loew et al., arXiv:2412.16551 (2024), Póta et al., arXiv:2408.00755 (2024), …
- Also generative models are being developed, see e.g. MatterGen (https://github.com/microsoft/mattergen)
  C. Zeni et al., arXiv:2312.03687 (2023), Nature (2025)

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1) Keating:
P.N.Keating,Phys.Rev. 145,637(1966)
Valid only for small deviations from the ideal diamond lattice sites. Used for elastic constants and phonon properties.

2) Stillinger-Weber:
F.H.Stillinger and T.A. Weber, Phys. Rev. B 31, 5262 (1985) 2 and 3 body terms. Fitted to stable crystal structure, reasonable melting temperature and g(r) in the liquid.

3) Tersoff:
J. Tersoff, Physical Review B, vol.38, (no.14):9902-5 (1988) pair functional. gets good elastic properties, stable crystal structures, liquid properties.

4) Biswas-Hamann
R. Biswas and D.R. Hamann, Phys.Rev.Lett. 55,2001(1985)
R. Biswas and D.R. Hamann, Phys.Rev.B 36, 6434 (1987)
Rather complicated to evaluate. Two versions. The first is longer ranged than the second. The old one is better at bulk metallic Si phases and high pressure transitions of Si. The new one does better for layered and interstitial structures.

5) Embedded Atom
M.I.Baskes, Phys.Rev.Lett. 59,2666(1987)
Modification of the EAM of metals to deal with covalent bonding, including
and angle-dependent electron density to model the effects of bond bending.
Fitted to Si lattice constant, sublimation energy and elastic constants. Reproduces well the LDA structural geometries and energies.

6) Kaxiras-Pandey
Kaxiras, E.; Pandey, K.C., Physical Review B vol.38, 12736 (1988)
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M. Z. Bazant and E. Kaxiras, Phys. Rev. Lett. 77, 4370 (1996).
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Others:
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- Chelikowsky, J.R.; Phillips, J.C.; Kamal, M.; Stauss, M., Phys Rev Lett 62, 292(1989)

A comparison between 6 of these potentials can be found in Balamane, H.; Halicioglu, T.; Tiller, W.A. Comparative study of silicon empirical interatomic potentials. Physical Review B 46,2250 (1992)

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Philosophical Magazine A 58,93 (1988)

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An excellent review paper on the need to go beyond pair potentials is: A.E. Carlsson, “Beyond Pair Potentials in Elemental Transition Metals and Semiconductors”, Solid State Physics, ed Ehrenreich and Turnbull, 43, 1-91 (1990).

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