

Atomistic Modeling of Materials

Introduction to the Course and Pair Potentials

3.320 Lecture 1 (2/1/05)



Atomistic Computer Modeling of Materials (3.320 Spring 05)

Objective: The class is aimed at beginning graduate students and will introduce a variety of methods used in different fields of materials science.

Instructor: Professor Gerbrand Ceder
Professor Nicola Marzari

Teaching Assistant: none provided this year. Labs will be assisted with graduate students from the Marzari/Ceder groups

When: Tuesday and Thursday, 8.30am-10.00am

Credit: Graduate H-level (3-0-9)

Organization: * two 90 minute lectures with some lectures replaced by a laboratory.
* 5 lab assignments approximately every two or three weeks

Grade: \approx 5 problem assignments -> NO FINAL EXAM

Registration: All students are required to **register for credit**. Postdocs can attend as listeners.

General Literature (specific references will be offered per course topic)

M.P. Allen and Tildesley, "Computer Simulation of Liquids", Oxford Science Publishers .
(mainly MD)

Excellent book on Molecular Dynamics Simulation. Explains well the relevant Statistical Mechanics. A must if you will be doing MD. Not much on solids.

R. Phillips, "Crystals, Defects and Microstructures", Cambridge University Press.
Modeling in Materials Science with emphasis on mechanical behavior. Excellent book

F. 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. Thijsen, "Computational Physics", Cambridge University Press.
Slightly more general book on quantum mechanical methods than Jensen.

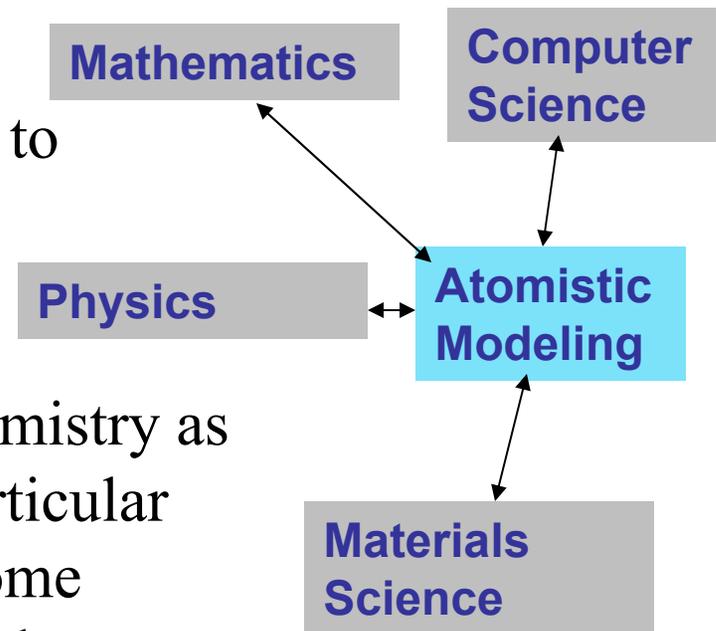
D. Frenkel and B. Smit, "Understanding Molecular Simulation", Academic Press.
Fairly recent book. Very good background and theory on MD, MC and Stat Mech. Applications are mainly on molecular systems

Course Objectives

- Teach the tools of modern computational materials science at the atomistic level
- Evaluate the tools and their applicability to diverse materials problems

Focus

- Teach materials theory, physics and chemistry as is required to understand the basis for a particular method (e.g. some statistical mechanics, some practical Quantum Mechanics to understand Density Functional Theory)
- Less focus on algorithms, unless they are of broad applicability

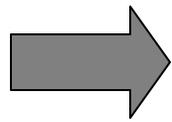


Calendar (subject to change)

Tues, 1 Feb	Introduction & Case Studies		
Thurs, 3 Feb	Potentials, Supercells, Relaxation, Methodology		
Tues, 8 Feb	Potentials 2: Potentials for different materials classes, Embedded atom methods.		
Thurs, 10 Feb	Lab 1: Energetics and structure from empirical potentials.		
Tue, 15 Feb	First principles Energy Methods: Hartree Fock		
Thurs, 17 Feb	First principles Energy Methods: Density Functional Theory		
Tue, 22 Feb	No class – Monday s schedule of lectures		
Thurs, 24 Feb	Technical Aspects of Density Functional Theory		
Tues, 1 Mar	Case studies of DFT. Properties and accuracy.		
Thurs, 3 Mar	Advanced DFT. New developments and alternative algorithms. Car-Parrinello.		
Tues, 8 Mar	Lab 2: Density Functional Theory I.		
Thurs, 10 Mar	Finite temperature: Review of Stat Mech and Thermodynamics. Excitations in materials and how to sample them.		
Tues, 15 Mar	Lab 3: Density Functional Theory II.		
Thurs, 17 Mar	Molecular Dynamics I		
21-25 Mar	No Class: MIT Spring Break		
Tues, 29 Mar	Molecular Dynamics II.		
		Thurs, 31 Mar	Molecular Dynamics III.
		Tues, 5 Apr	Lab 4: Molecular Dynamics. Monte Carlo simulations: Application to lattice models, sampling errors, metastability.
		Thurs, 7 Apr	Coarse graining: Alloy theory. Alloy Theory II, free energy integration. Show different ways of integration (lambda, temperature, field, particle, potentials).
		Tues, 12 Apr	Patriots Day: MIT Vacation
		Thurs, 14 Apr	Lab 5: Monte Carlo (offline) Hyperdynamics
		Tues, 19 Apr	Case Studies I
		Thurs, 21 Apr	Green Kubo
		Tues, 26 Apr	Modeling in industry (Chris Wolverton from Ford Motor Company)
		Thurs, 28 Apr	Case Studies II: Nanotubes
		Tues, 3 May	Case Studies III: High pressure (NM)
		Thurs, 5 May	Conclusions (GC)
		Tues, 10 May	
		Thurs, 12 May	

Examples of the growing importance of computational modeling: Modeling to decide on important outcomes

Advanced Simulation and Computing Initiative (ASCI)



Safeguarding the Nuclear Stockpile through Computer Simulation

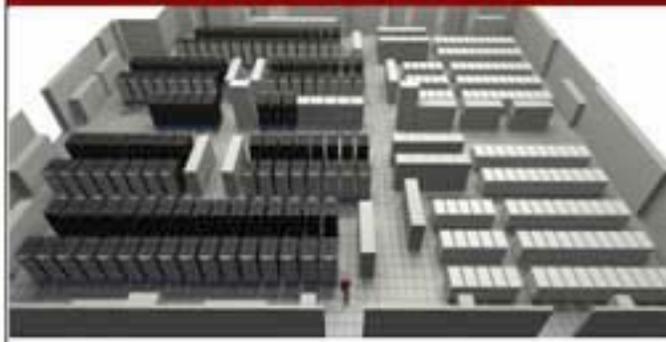
ASCI is an integral and vital element of our nation's Stockpile Stewardship Program. ASCI provides the integrating simulation and modeling capabilities and technologies needed to combine new and old experimental data, past nuclear test data, and past design and engineering experience into a powerful tool for future design assessment and certification of nuclear weapons and their components

With Nuclear Experiments



- Will it work as designed?
- Is the simulation good enough to risk the cost of a nuclear experiment?

Without Nuclear Experiments



- Will it continue to work as it ages?
- Is the simulation adequate for making decisions affecting national security?

Modeling to decide on important outcomes: The Earth Simulator

35.6 Terraflops to simulate atmospheric processes

Photos removed for copyright reasons.

See <http://www.es.jamstec.go.jp/esc/eng/>

Modeling to decide on important outcomes
First Principles Materials Modeling in Industry:

Motorola

Siemens

Phillips

Xerox

Ford

Nippon Steel

Matsushita (Panasonic)

Ricoh

TDK

Hitachi

IBM

Eastman Kodak

Electricité de France

Texas Instruments

Allied Signal

Alcoa

Toyota

General Motors

Lucent

Corning

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Why do you want to learn modeling ?

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

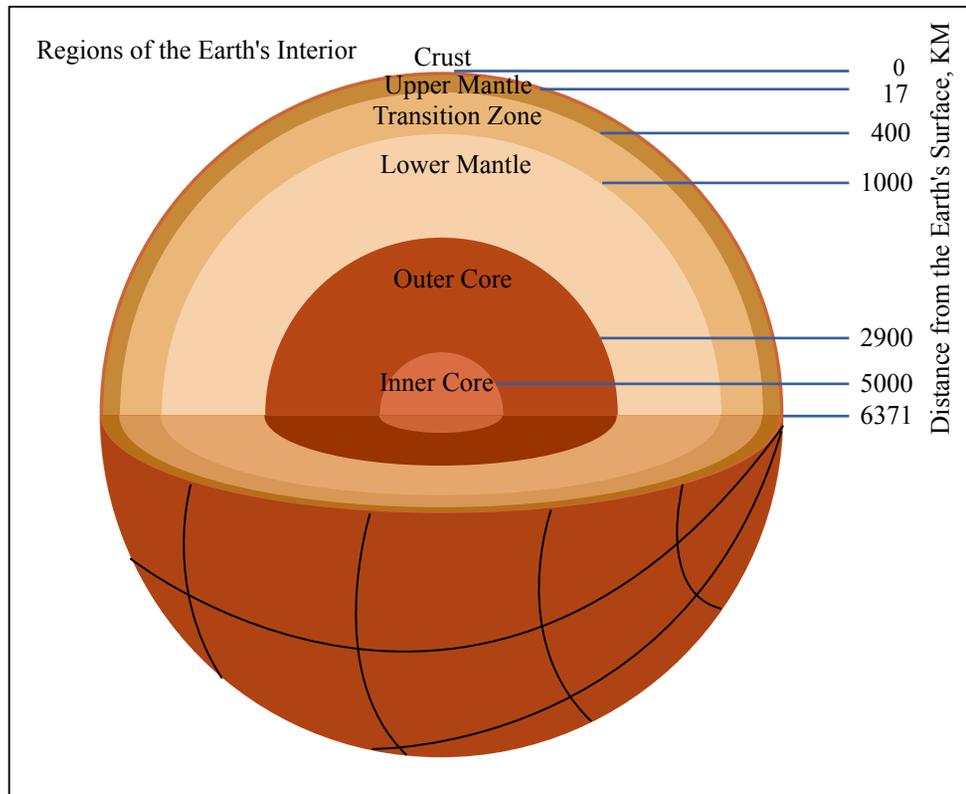
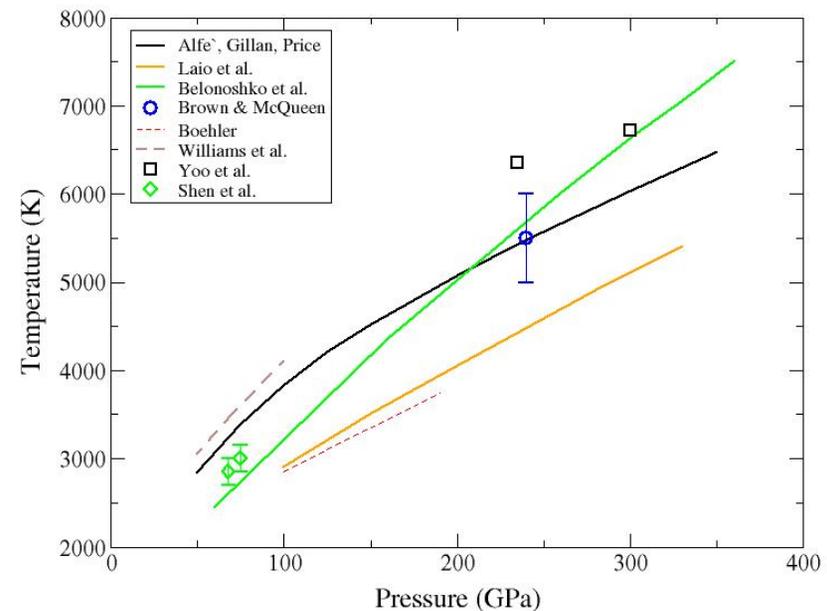


Figure by MIT OCW.



Alfe' et al, [Nature, 401, 462-464 \(1999\)](#).

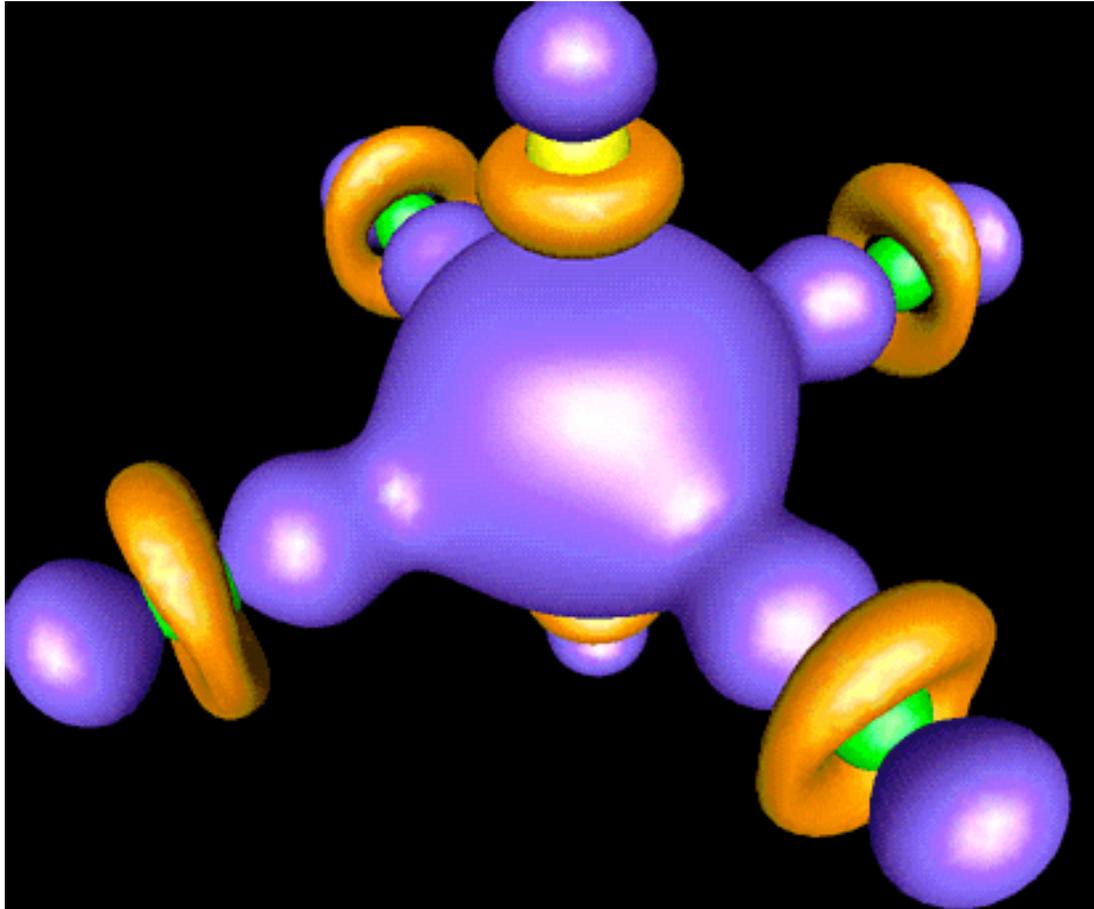
Source: <http://chianti.geol.ucl.ac.uk/~dario/resint.htm>

Some things are easier with calculations

Figure and newspaper clipping removed for copyright reasons.

Browne, Malcom W. "Glue of Molecular Existence Is Finally Unveiled."
New York Times, Sept 2, 1999, p. D1.

Calculated electron densities per orbital in PbTiO_3

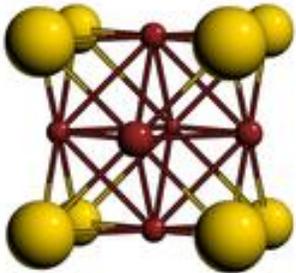


O_{2s} density

Figure courtesy Professor Marzari

Some things can be done FAST: High Throughput Ab-Initio

10,000 first principles structural energies > 120 crystal structures in more than 70 binary alloys in order to determine the stable structures (6 months time frame)



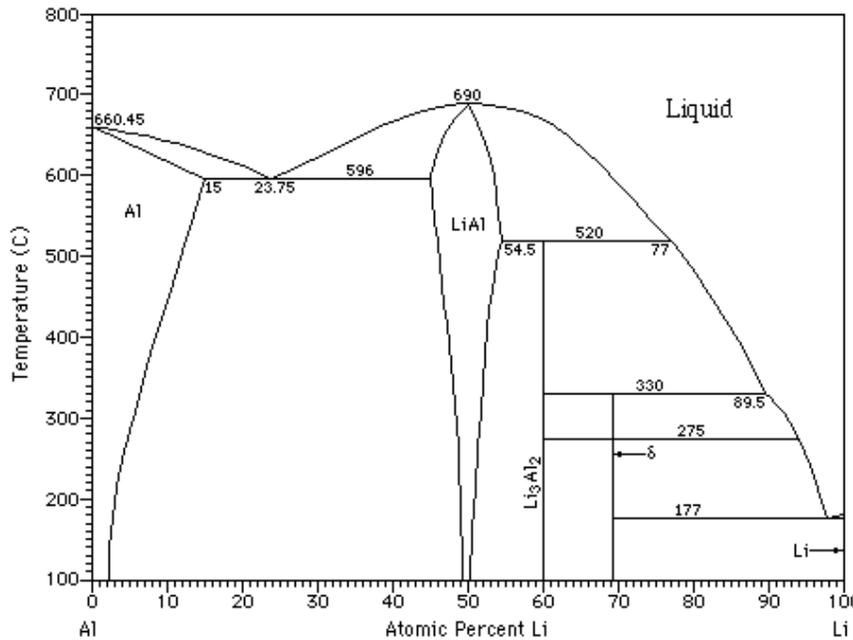
Two graphs ("Independent" and "Correlated") removed for copyright reasons.

Develop into a method to predict crystal structure from scratch

S. Curtarolo et al., Data Mining of Quantum Mechanical Calculations, *Phys. Rev. Lett.*, **91**:135503 1-4 (2003)

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

Experimental



Calculated

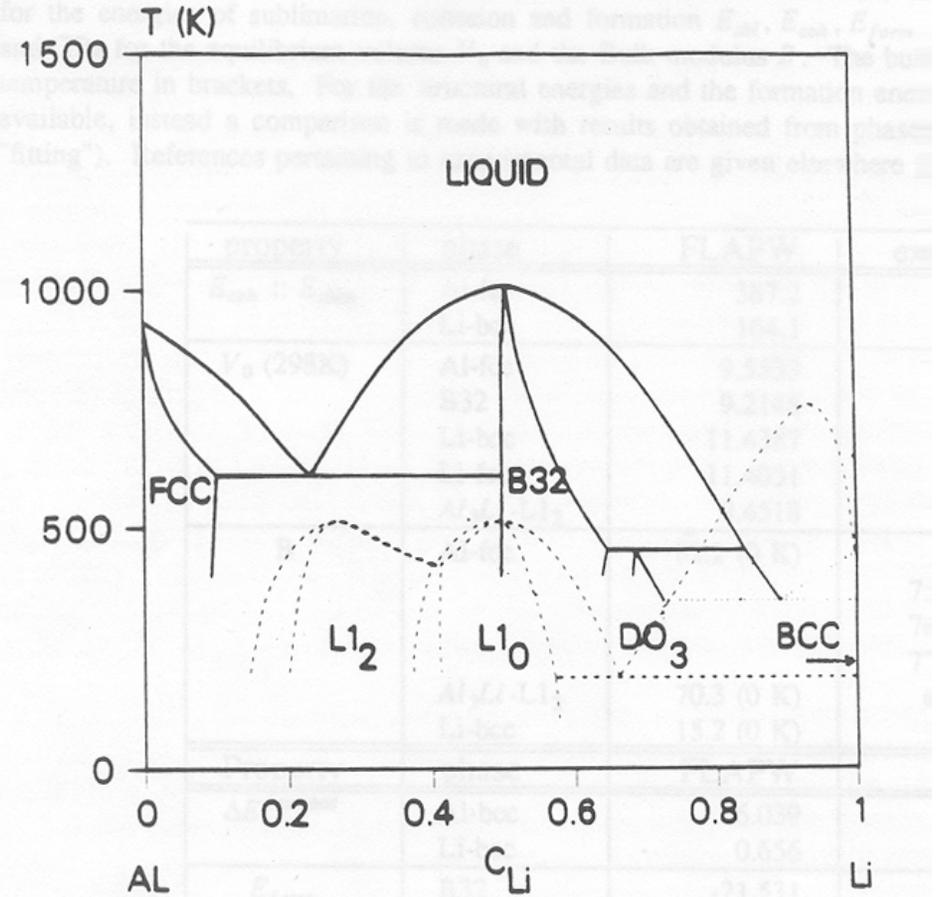


Figure courtesy Dr. M. Sluiter

Computational Design of a High Voltage Li Battery Electrode

- systematic search of effect of crystal structure, cation, and anion chemistry
- search led to Al-doping as light and inexpensive element to raise voltage
- computations used to design synthesis conditions

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Can Systematically Investigate and Prove or Disprove Hypothesis

The Lowest Energy Defect in Silicon ?

Goedecker et al., 2002

FFCD

H interstitial

Vacancy

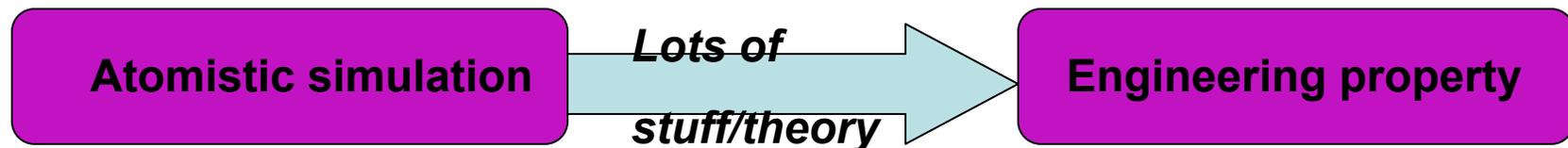
Frenkel

Diagrams and table removed for copyright reasons.

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)

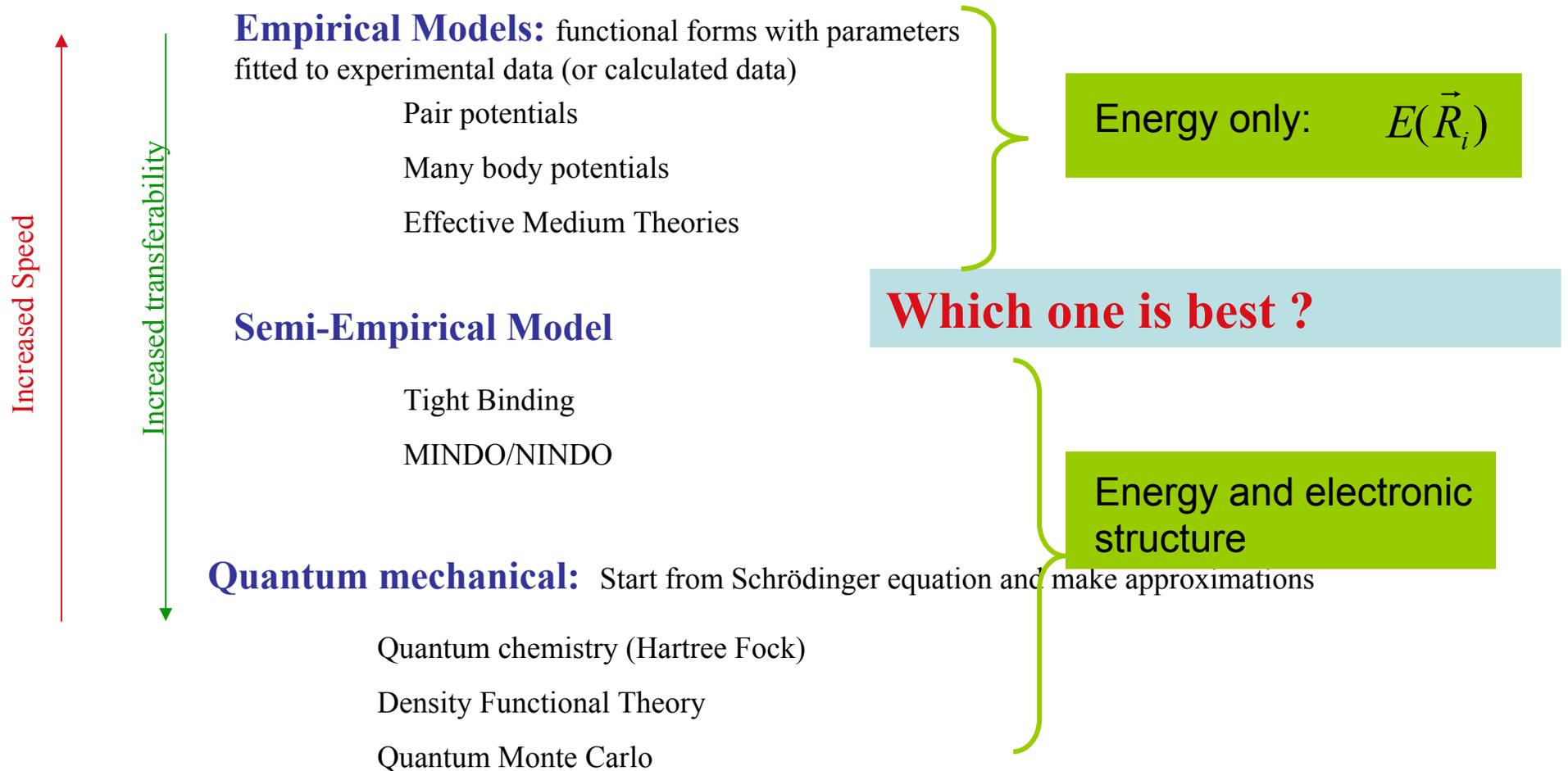
Is Computing Theory ?

Image of scanned article removed for
copyright reasons.

Langer, James. "Computing in Physics: Are We Taking It Too Seriously? Or Not Seriously Enough?" *Physics Today*, July 1999, p. 11.

Energy Models

Important because it is representation of the chemistry/material



Born Oppenheimer Approximation

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

System characterized by wavefunction ψ

Born Oppenheimer

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

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

Discussion of applicability of BO

Temperature

Long lived excitations

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

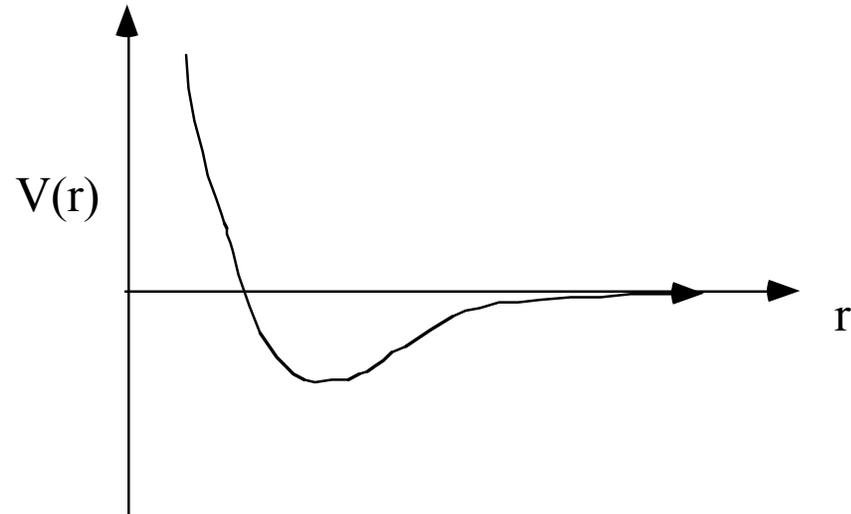
Objective: Become familiar with typical forms and understand limitations of various choices. Focus is on forms, not on parameters

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 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

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

$$\frac{V(r)}{\varepsilon} = \left[\left(\frac{\sigma}{r} \right)^{12} - 2 \left(\frac{\sigma}{r} \right)^6 \right]$$

ε is unit of energy scale

σ is unit of length

When expressing Temperature,
Pressure and Density in renormalized
units all LJ systems are identical

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

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

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

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There is only one Lennard-Jones Material

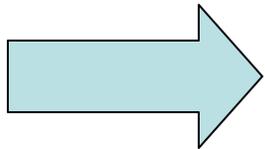
e.g.: If fit lattice parameter and cohesive energy, then bulk modulus will be determined

σ

ϵ

$$B = V \frac{\partial^2 E}{\partial V^2}$$

curvature in minimum



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

$$V(r) = D \exp[-2\alpha(r - r_o)] - 2D \exp[-\alpha(r - r_o)]$$

Born-Mayer/Buckingham

$$V(r) = A \exp\left[-\frac{r}{\rho}\right] - \frac{C}{r^6} - \frac{D}{r^8}$$


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

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Morse Potential for Stretching of C-H in CH₄

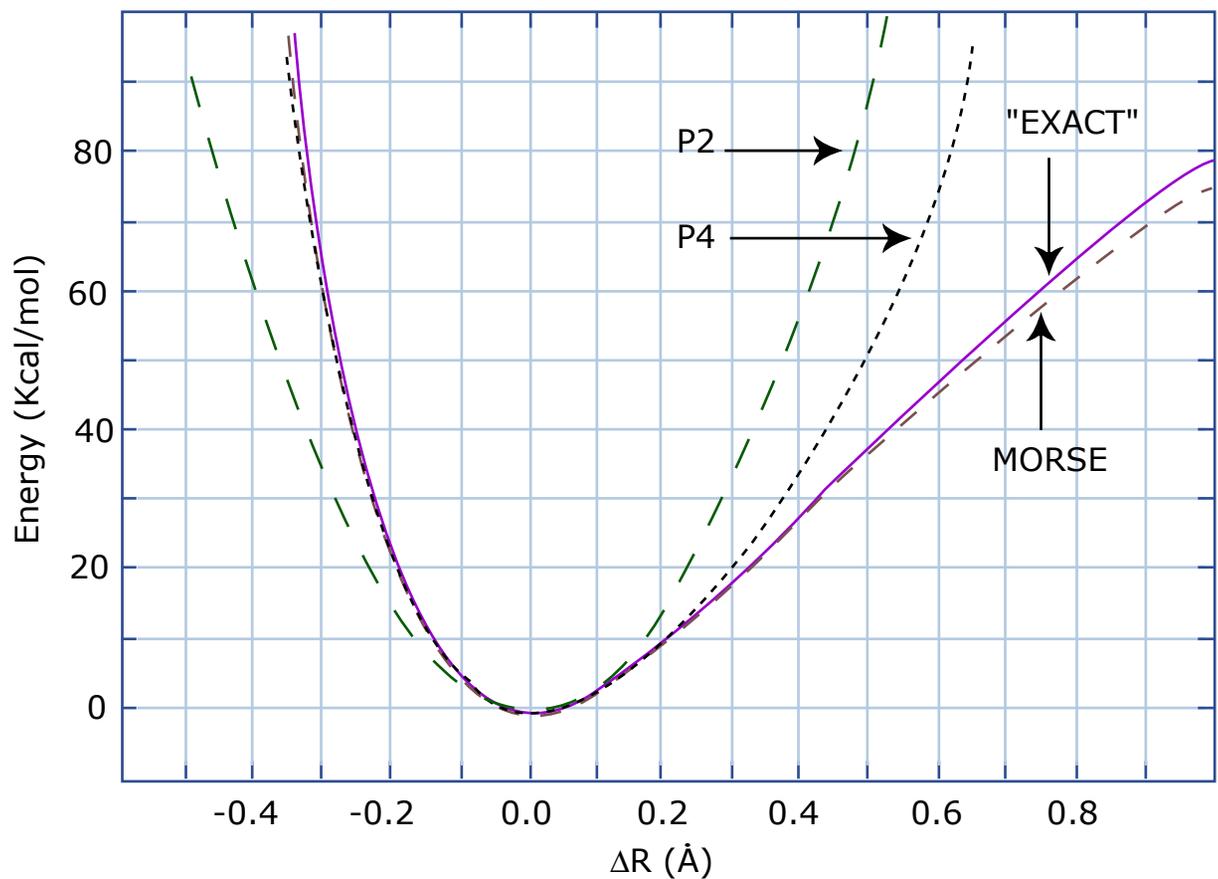


Figure by MIT OCW.

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 !

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

Two diagrams removed for copyright reasons.

Source: Figure 6 in Gibson, J. B., A. N. Goland, M. Miligram, and G. H. Vineyard. "Dynamics of Radiation Damage." *Physical Review* 120, no. 4 (November 15, 1960).

Some features and problems with Pair Potentials

Pair Potentials “Count” bonds but do not take into account their organization

e.g. triangle of three atoms versus chain of four

e.g. ethylene molecule

Tendency to form **close-packed structures** (as they have high coordination number; many bonds)

e.g. Very difficult to stabilize diamond-cubic structure for Si with pair potential

No stability against **shear**. Lack of Cauchy Pressure

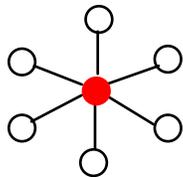
No angular dependence



In particular a problem for localized covalently bonded materials

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

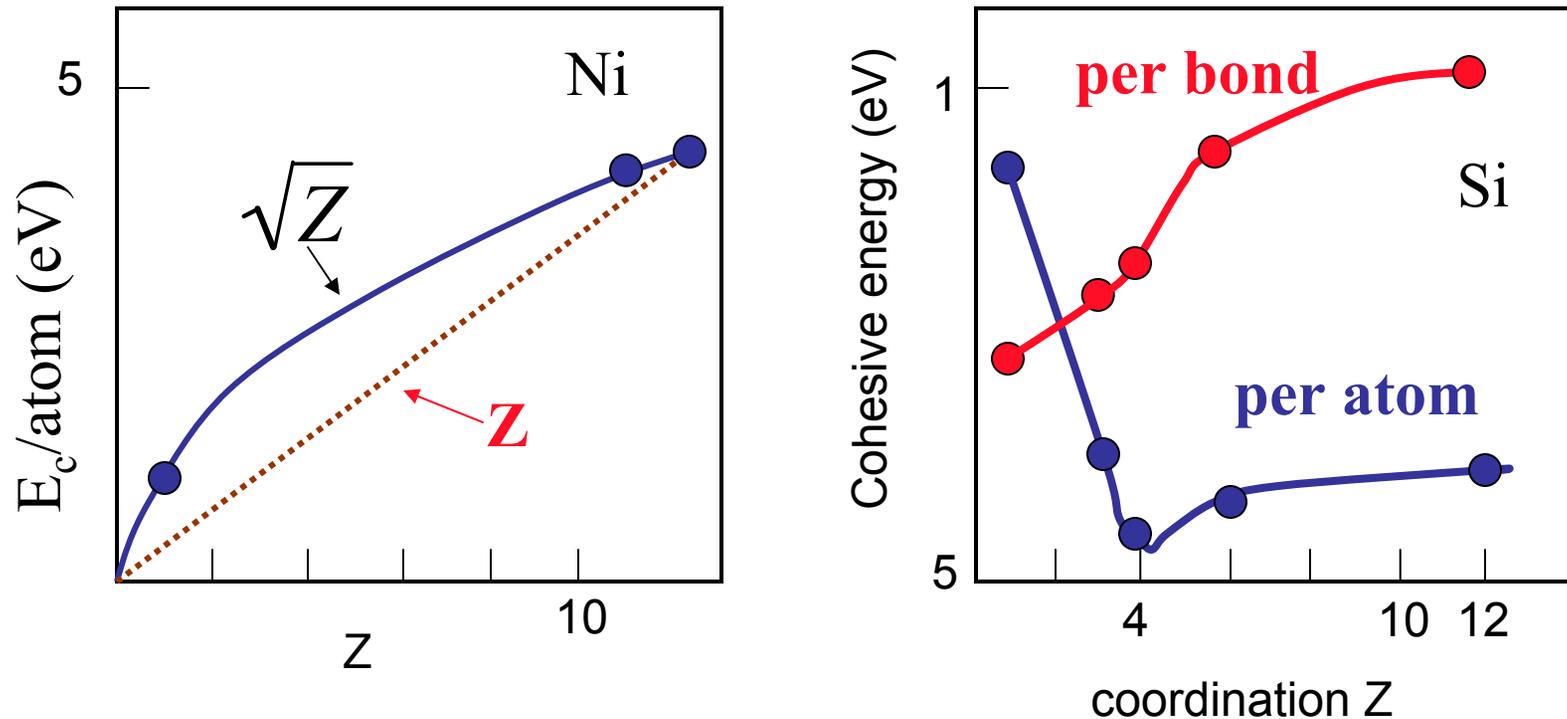


Figure by MIT OCW.

Source: 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).

Energy as Function of Coordination: Quantum mechanical results for Al

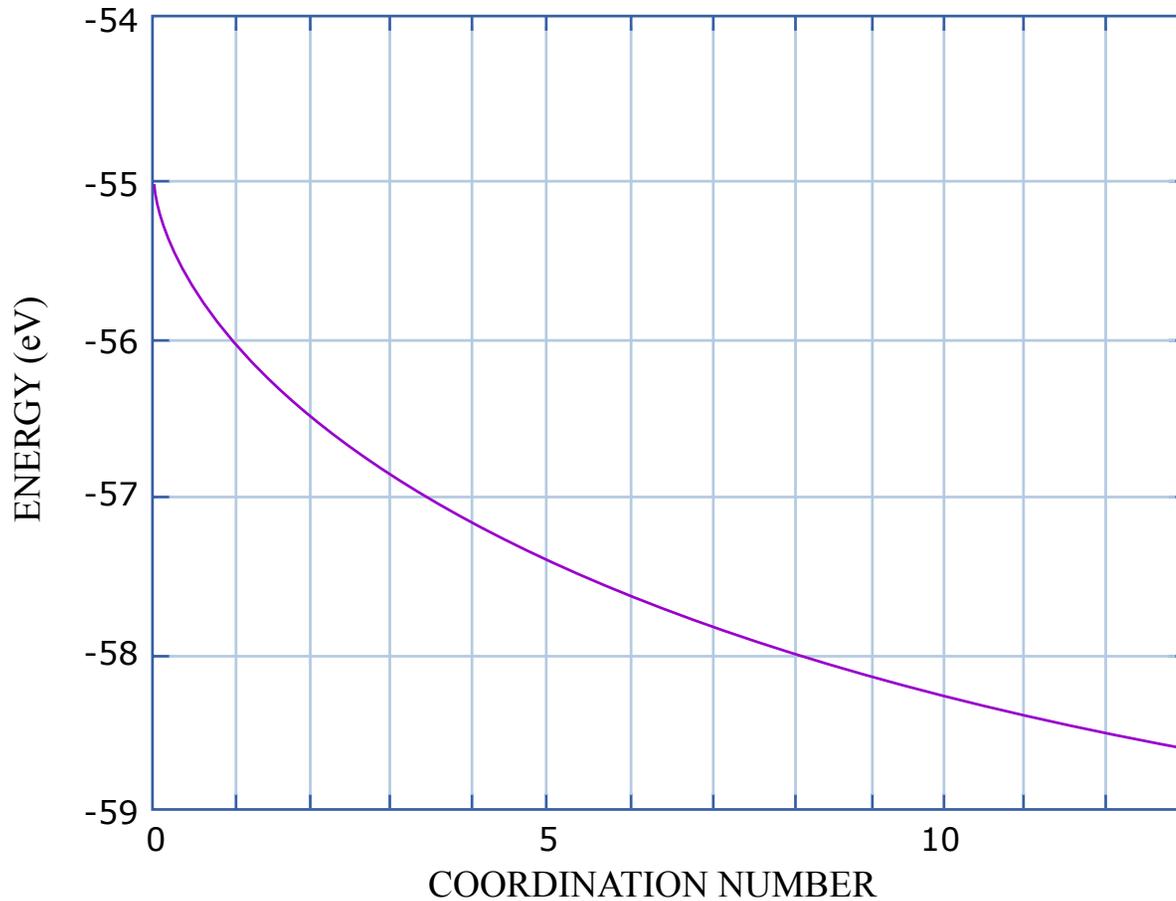


Figure by MIT OCW.



Bond Strength depends on coordination

Potentials fitted to various properties of Cu

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Some conclusions so far

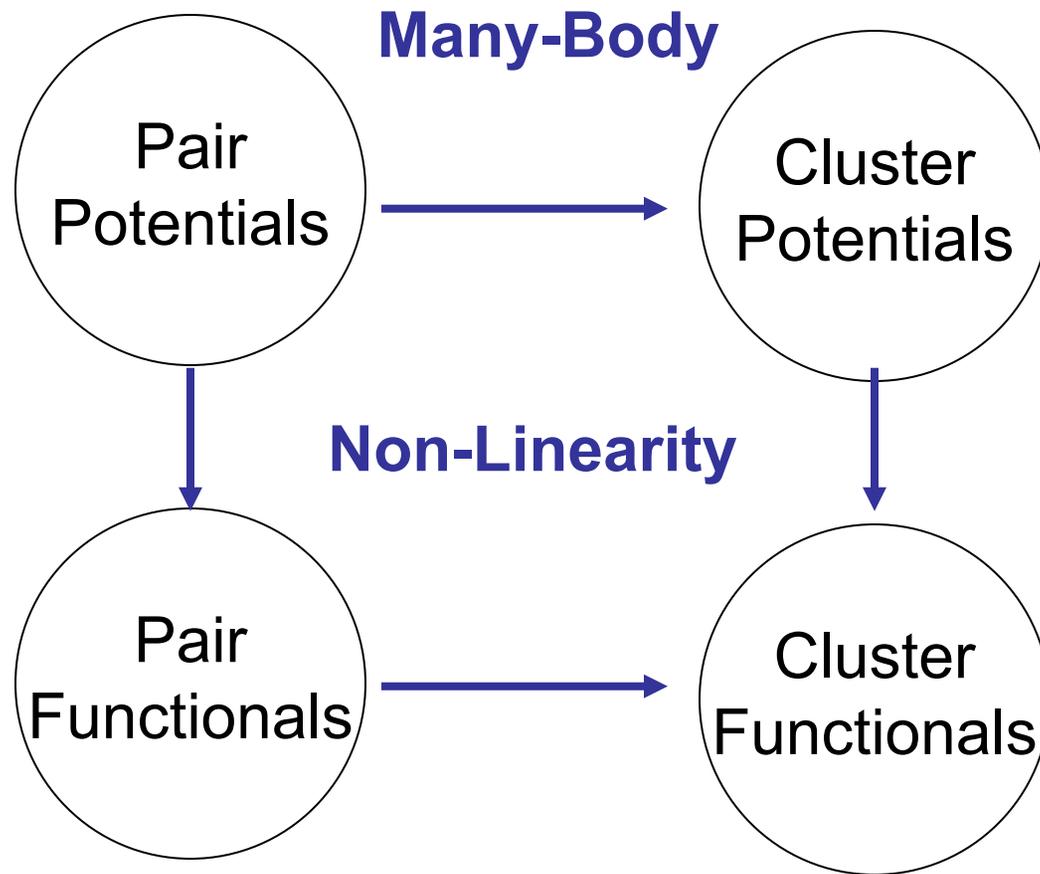
Bond strength depends on environment for covalent materials:

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 can not 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.

How to Fix Pair Potential Problem ?



after : A.E. Carlsson, "Beyond Pair Potentials in Elemental Transition Metals and Semiconductors", Solid State Physics, ed Ehrenreich and Turnbull, **43**, 1-91 (1990).