

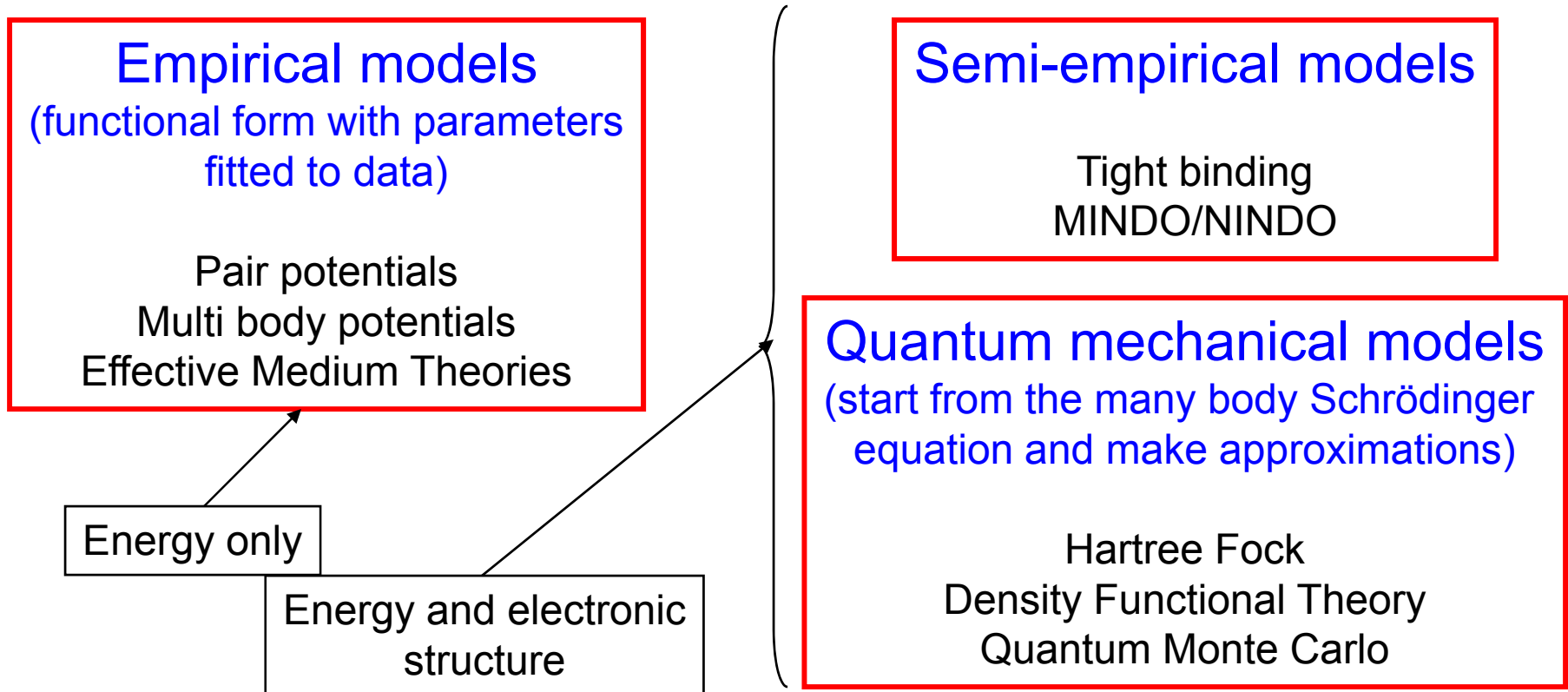
Introduction to Energy Models

Material for these lecture notes was compiled from the references below

- ✓ [MIT's 3.320](#) course notes (Prof. G. Ceder)
- ✓ Physics 460, [Solid State Physics](#) (Prof. R. Martin)
- ✓ C. Kittel, [Introduction to Solid State Physics](#)
- ✓ N.W. Ashcroft and N.D. Mermin, [Solid State Physics](#)
- ✓ A. Leach, [Molecular Modelling: Principles and Applications](#) ([chapter 4](#) and [chapter 6A](#) and [6B](#))
- ✓ [Empirical potentials in Chemistry](#)
- ✓ [Database of published interatomic parameters](#) (exportable to GULP)
- ✓ Daw, M. S., Foiles, S. M. & Baskes, M. I. The EAM: a review of theory and applications [Materials Science Reports](#) **9**, 251 (1993).
- ✓ Collection of papers on [empirical potentials for Silicon](#)
- ✓ Example of the [Clementi and Roetti Tables](#)
- ✓ L. Girifalco and V. Weizer, [Applications of the Morse potential to metals](#), *Phy Rev* 114 (1959) 687.

Energy Models

- We need to have an adequate energetic description of materials for reliable simulations.
- We distinguish these models in (a) **empirical energy**, (b) **semi-empirical** and (c) **ab-initio or quantum mechanical models** (in order of increased transferability and computational cost)



Energy Models

- In **empirical models**, we take some form for the energy and fit it to any data we may have.

Data can be: experimental, theoretical or computational

- In **quantum mechanical models**, there is no fitting aside -- you just solve the Schrödinger equation.
- **Semi-empirical methods are in between: quantum mechanically informed but empirical in the parameters.**
 - Example of this is **Tight binding** (the chemists often use MINDO and NINDO). Here we have **parameterized Schrödinger equations**, where the 'overall integrals' between wave functions are not computed but are parameterized.

You save a lot of time with these approaches at the expense of accuracy.

Energy Models

- More and more people do ab-initio these days.
- The reason we spent a few lectures on empirical models is because they are useful for making **general predictions about large systems**.
- If you work **with potentials**, you have no information about electrons. **You just have energies as a function of position**.
- If you work with semi-empirical or quantum mechanics methods, you know something about the electronic structure of the material.

The Born-Oppenheimer approximation

- Implicit assumption: Energy is a function of nuclear coordinates only
- To do this, we variationally remove the electronic coordinates (Born-Oppenheimer approximation).

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

- Energy is NOT uniquely determined by the set of nuclear coordinates but also by the electronic states.

In many cases, for a given state of the nuclei, we can have multiple electronic states (ground state, excited states).

The Born-Oppenheimer approximation

- The Born-Oppenheimer approximation, essentially, assumes that for any set of nuclear coordinates, you are always in the electronic ground state. So, $E(\bar{R}_i)$ is derived from $E(\bar{R}_i, \psi)$ by essentially, variationally removing ψ (minimizing over ψ)

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

- If your atoms remain frozen in some position, after 'long time', the electrons will go to their ground states, especially at 0 K.

WHEN BORN-OPPENHEIMER IS NOT APPLICABLE

- In Born-Oppenheimer we assume that if we move the atoms, the electrons follow infinitely fast.

It is when the atoms move really fast or the electrons move really slow that Born-Oppenheimer is not applicable.

- There are long lived excited states in materials (e.g. defects in semiconductors):
 - EL2 in Gallium-Arsenide is a well studied defect that has very long lived excited states where there are, essentially, 2 Born-Oppenheimer surfaces that give you different nuclear coordinates.

Thus you cannot find the lowest energy configuration of the nuclei unless you know what the electrons do. This coupled problem is a non-obvious violation of the Born-Oppenheimer approximation.

WHEN BORN-OPPENHEIMER IS NOT APPLICABLE

- When you have particles like protons (the **lightest nucleus**) that can move fast the electrons will not follow fast enough.
- **Diffusion of charged ions in insulators:**
For example, take battery materials characterized by the diffusion of Li^+ ions. Ions diffuse through the boundary (insulated) , but the negative charges are preferentially retarded (the electrons don't follow fast enough).
- The other obvious violation of Born-Oppenheimer is when you are **at non-zero temperature**.

At non-zero temperature, you have a finite probability to occupy the higher energy electronic states.

This is technically a violation of the Born-Oppenheimer approximation that however is easy to solve.

It is overcome by doing **a statistical weighting of how the levels are populated**. This will be discussed later in the course.

SUMMARY: WHEN BORN-OPPENHEIMER IS NOT APPLICABLE

Born Oppenheimer approximation validity must be understood

Not valid for variety of phenomena

High temperature studies: use statistical mechanics
to overcome limitations

Potential Functions

We will discuss particular forms and the physical limitations that they introduce.

We will start with **pair potentials**: because they are the obvious and simplest ones.

The failures of them will lead us into **many body potentials** and **pair functionals**.

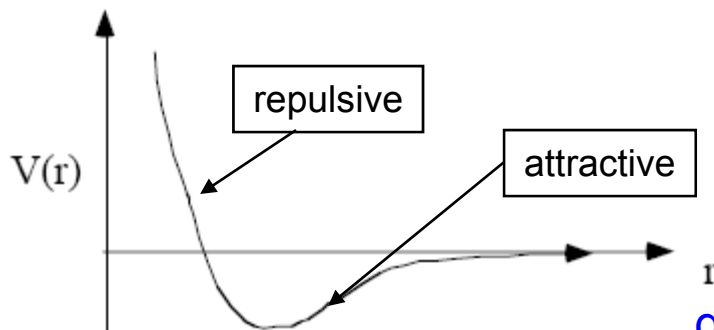
- Pair potentials: Forms and physical limitations
- Classification of empirical models
- Many-body potentials
- Pair functionals
- Environment dependent potentials in chemistry

Pair potentials: Focus on form not parameters

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

Distance between atoms i and j

- Sum their energy from pair-wise interactions.
- Interaction between 2 atoms has nothing to do with whether they are neighbors. The total interaction is just summing the energy.



$$V(R) = -A/R^6 + B/R^{12} \text{ (Lennard - Jones)}$$

$$V(R) = -A/R^6 + B \exp(-R/\rho_0) \text{ (Exponential)}$$

Attractive energy $\sim 1/R^6$ for rare gas solids only (van der Waals interaction)

Pair potentials have always the same form. They are attractive at intermediate to long distance and they are repulsive at short distance.

They have to be repulsive at short distance otherwise the system will collapse into itself.

Pair potentials: Truncation

TRUNCATION:

- You will need to truncate so the distance does not go to infinity (most potentials slowly decay to zero).
- Have to truncate for computational reasons
- However, truncation leads to discontinuity
- Whenever atoms move in and out of this range they have a strong jump
- Numerical tricks to address this problem: Smoothing, shifted (upwards) potentials, derivative smoothing (the derivative of the potential is the force), etc.

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

- Two terms: r^6 , which is the attractive part. That gives you the attraction, since it has a negative sign in front.
- The r^{12} term gives you the repulsion.

The r^6 term can be physically justified. It comes from the interaction between fluctuating dipoles (rare gas solids, atoms nearly spherical).

Two atoms:

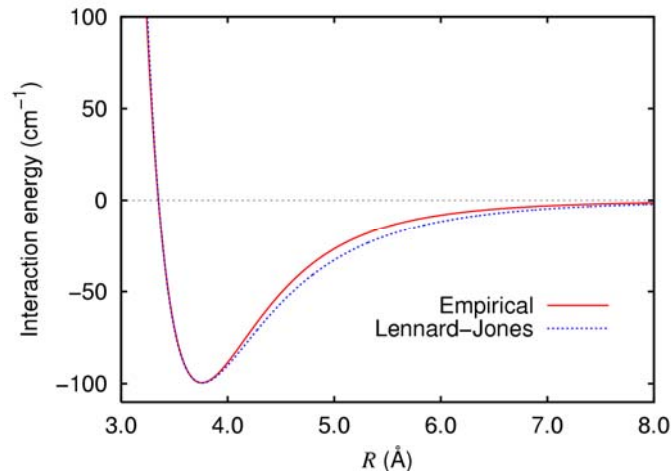
- filled shells, inert atoms
- No bonding, there is no direct covalent interaction
- Only interaction is through formation of dipoles
- Dipoles fluctuate $\sim r^{-6}$ behavior
- Physics is essentially the [van der Waals interaction](#), which is the interaction between inert shells.

LENNARD-JONES: A SIMPLE TWO-PARAMETER FORM

$$V(r) = \epsilon \left[\left(\frac{r_{min}}{r} \right)^{12} - 2 \left(\frac{r_{min}}{r} \right)^6 \right]$$

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

LJ potential
for Argon dimer



$$A = 4\epsilon\sigma^{12}$$

$$B = 4\epsilon\sigma^6$$

ϵ is unit of energy scale
 σ unit of length

- $r_{min} = 2^{1/6}\sigma$ is the distance at the minimum of the potential
- No real justification of the r^{12} term beyond that it's the square of r^6 !
Needs to be steep repulsive part when the ions come very close together.
- Developed for van der Waals interactions ($-r^6$ term, fluctuating dipoles)

Van der Waals Bonding

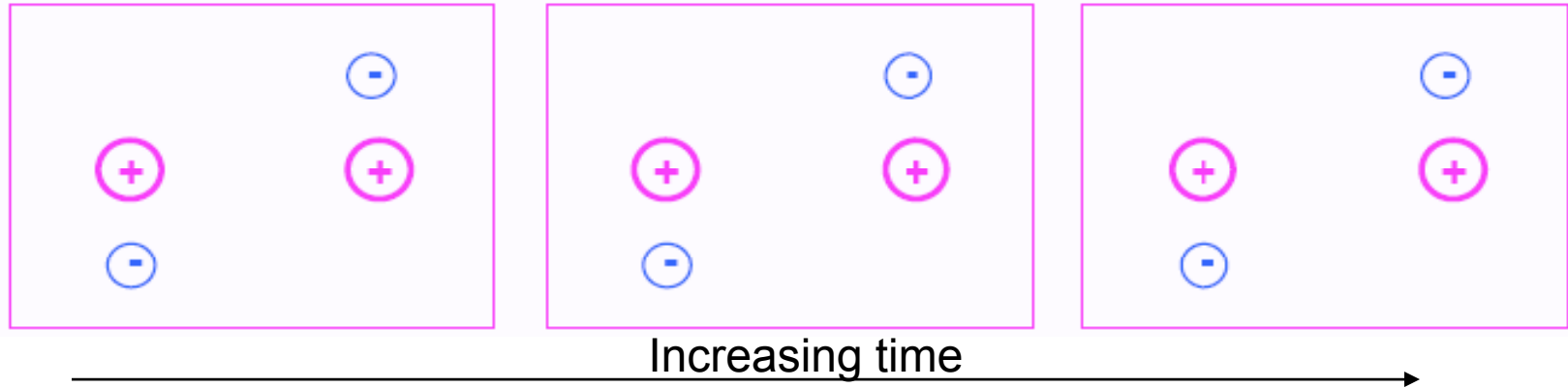
- Attraction because **electrons can interact and be correlated even if they are on well-separated atoms**
- Consider closed shell 'inert' that do not form strong chemical bonds
- **Isolated closed shell atom** - electron distributed symmetrically (spherically) around the atom. **The probability of finding an electron is spherical around the atom.**
- Consider at first one atom alone (no other atoms around).



At any time the atom has a dipole moment that averages to zero if one averages a long time

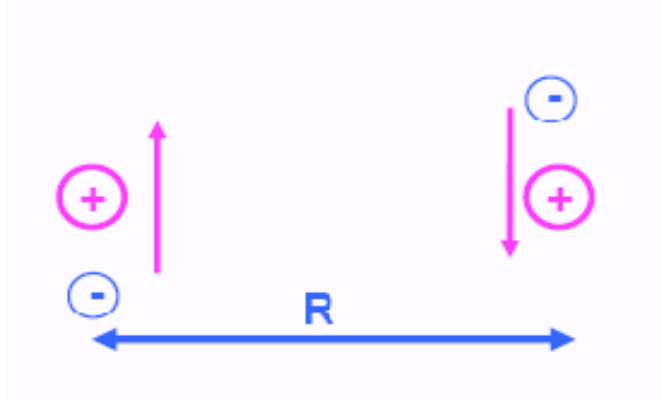
Van der Waals Bonding

- Consider now two closed shell atoms near each other.



- The electrons on the two atoms become correlated
- The electrons interact: the energy is lower if the dipoles on the two atoms are opposite
- At any given time there is increased probability of finding the two atoms in a state with lower energy
- Energy reduced - a net attraction - because the electrons are correlated

Van der Waals Bonding



- Dipole D_1 on atom 1 creates electric field E_{12} on atom 2 proportional to $1/R^3$
- E_{12} generates dipole D_2 on atom 2: $D_2 = \alpha E_{12}$ where α = polarizability
- The attractive interaction between the two dipoles is proportional to $D^2 \sim 1/R^6$

LENNARD-JONES: A SIMPLE TWO-PARAMETER FORM

- Write Lennard-Jones potential using only 2 parameters by normalizing in terms of energy and distance.

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

Units of temperature: ε/k_B

Units of pressure ε/σ^3

Units of density $1/\sigma^3$

NOTICE THE FACTOR OF 2 IN THE EQUATION

WHAT DOES THIS MEAN?

- There is only one Lennard-Jones system !
- There are tabulated Lennard-Jones parameters for a lot of materials
- Energy scale sets temperature and length scale sets volume and pressure
- If you take one Lennard-Jones system at a given temperature and pressure, that will always be the same as a Lennard-Jones system with other parameters but at another temperature and pressure.
- Transformation between all Lennard-Jones systems.

ARE JUST TWO PARAMETERS ENOUGH?

YOU NEED MODELS WITH AT LEAST 3 PARAMETERS

AIM: You want to get at least 3 properties right

- Its length scale, which is its **lattice parameter**.
- Its energy scale, which we think of it as **cohesive energy**, which is the potential debt.
- Its elasticity (e.g. **bulk modulus** $B = V \frac{\partial^2 E}{\partial V^2}$, curvature of the potential at its minimum) because its elasticity gives response to any perturbations.
- Obviously, you cannot fit 3 things with 2 parameters. Thus you need models with at least 3 parameters.

MORSE POTENTIAL

-Include one more parameter to predict elastic response.

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

- The parameter D sets the energy scale.

- r_0 sets the length scale.

- α which sets the elasticity scale. Note that α determines the curvature of the function.

Curve fit the parameters to properties.

Morse potential constants

TABLE I. Morse potential constants for the pairwise atomic interaction in cubic metals, $\varphi = D[e^{-2\alpha(r_j-r_0)} - 2e^{-\alpha(r_j-r_0)}]$.

Metal	αa_0	β	$L(\text{ev}) \times 10^{-22}$	$\alpha = \text{\AA}^{-1}$	$r_0 = \text{\AA}$	$D(\text{ev})$
Pb	2.921	83.02	7.073	1.1836	3.733	0.2348
Ag	2.788	71.17	10.012	1.3690	3.115	0.3323
Ni	2.500	51.78	12.667	1.4199	2.780	0.4205
Cu	2.450	49.11	10.330	1.3588	2.866	0.3429
Al	2.347	44.17	8.144	1.1646	3.253	0.2703
Ca	2.238	39.63	4.888	0.80535	4.569	0.1623
Sr	2.238	39.63	4.557	0.73776	4.988	0.1513
Mo	2.368	88.91	24.197	1.5079	2.976	0.8032
W	2.225	72.19	29.843	1.4116	3.032	0.9906
Cr	2.260	75.92	13.297	1.5721	2.754	0.4414
Fe	1.988	51.97	12.573	1.3885	2.845	0.4174
Ba	1.650	34.12	4.266	0.65698	5.373	0.1416
K	1.293	23.80	1.634	0.49767	6.369	0.05424
Na	1.267	23.28	1.908	0.58993	5.336	0.06334
Cs	1.260	23.14	1.351	0.41569	7.557	0.04485
Rb	1.206	22.15	1.399	0.42981	7.207	0.04644

[Phys Rev 114 \(1959\) 687](#)

BORN-MAYER/BUCKINGHAM POTENTIAL

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

- Used extensively to model oxides.

- It contains a decaying exponential, a van der Waals term and a 2nd order term in van der Waals perturbation theory (r^8).
- Note that $V(r)$ diverges for small r . This can be a problem in MD where you can find two atoms in small r during numerical simulations. For example, you may start with a configuration far from equilibrium. Atoms move with tremendous force and can overshoot or shoot into each other. Then you obtain a state with two atoms on the top of each other – and this is a highly-bonded state in this potential that you cannot escape from.

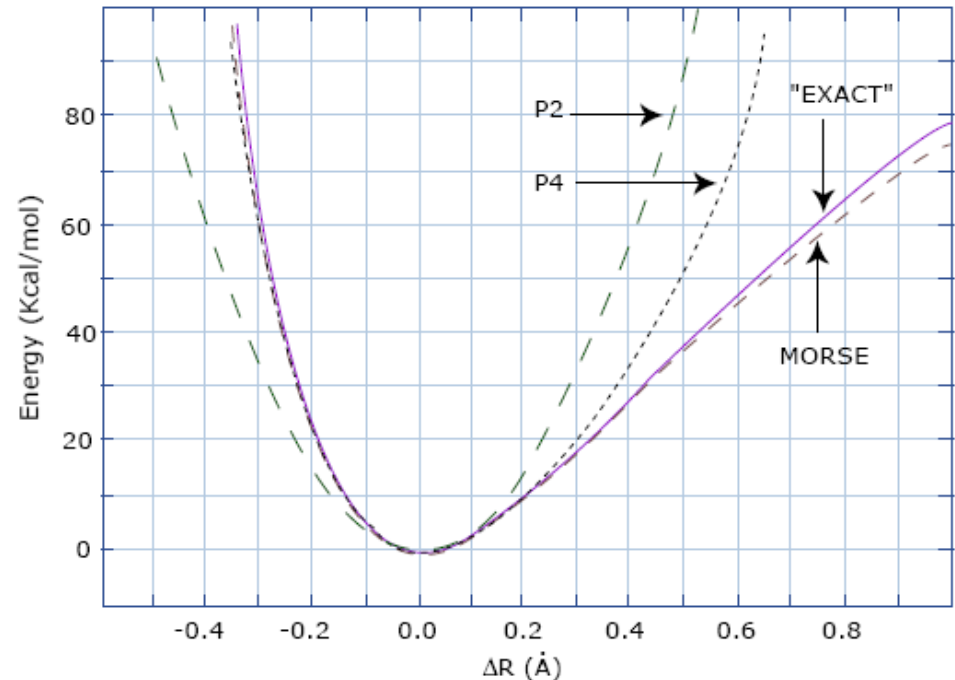
Potentials can be fitted, but underlying physics of particular form is lost

We should use the simplest representation while accounting for as many facts as reproducibly as possible

WHAT POTENTIAL SHOULD YOU CHOOSE? C-H Bond in Methane

- All models shown here are fitted to have the same bonding energy and elastic modulus and the same bond distance.
- The Morse potential is very accurate
- P2 is a harmonic potential, like $\sim k (\Delta r)^2$ where Δr is the distance away from the equilibrium bond geometry.
- P4 is a 4th order polynomial in Δr
- Equivalent near the minimum
- Same curvature and minima
- What potential to use depends on application demands (are you interested close or further away from the equilibrium point?)

Morse Potential for Stretching of C-H in CH₄



How to fit and what can we fit to?

HOW TO FIT?

- No systematic way to curve fit potentials
- Depends on issues to be addressed
- Potentials only have a limited region of applicability
- Fit as close as possible to the things you are going to calculate or to the environments you are going to calculate
- At least try to get correctly the length scale, the energy scale and stiffness
- Low symmetry environment (e.g. reproduction of surface energies, etc.)

WHAT CAN WE FIT TO?

- Lattice constants
- Cohesive energy
- Bulk modulus, other elastic constants
- Equation of state
- Phonon frequencies
- Forces
- Stable crystal structures and energy differences
- Surface energy and relaxation
- Liquid pair correlation functions

DYNAMICS OF RADIATION DAMAGE

- The first example of energy models (1960): Radiation damage in Cu.
- Shooting atoms with ions and monitoring the orbit that the radiation damage will follow.

PHYSICAL REVIEW

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Dynamics of Radiation Damage*

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(Received July 14, 1960)

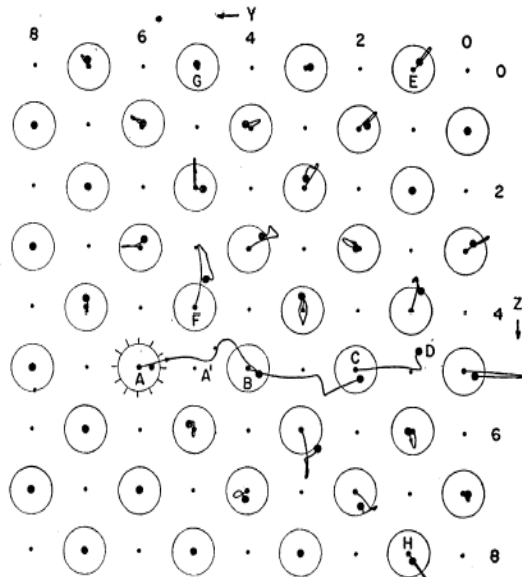


FIG. 6. Atomic orbits produced by shot in (100) plane at 40 ev. Knock-on was at A and was directed 15° above -y axis. Large circles give initial positions of atoms in plane; small dots are initial positions in plane below. Vacancy is created at A, split interstitial at D. Run to time 99. (Run No. 12).

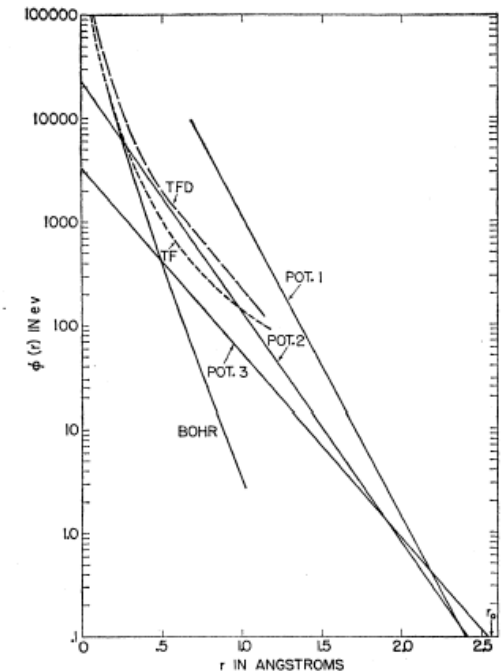


FIG. 2. Various forms of repulsive potential energy for a pair of copper atoms. Potentials 1, 2, and 3 were used in the calculations. r_0 is the equilibrium separation in the crystal.

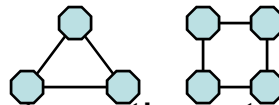
Failures of the pair potential

- Understand the physical limitations of pair potentials
- Nothing to do with the parameters, only with the form (which up to now is pair-wise interactions)

Can never compute certain properties.

- pair potentials count bonds and do not care about the organization of atoms.
- The cohesive energy on an atom is largely determined by how many things are around the atom because in a sense you sum bonds around an atom. Pair potentials do not care about the organization of atoms.

Triangle versus chain of four

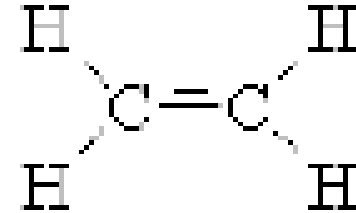


Every atom has 2 nearest neighbors

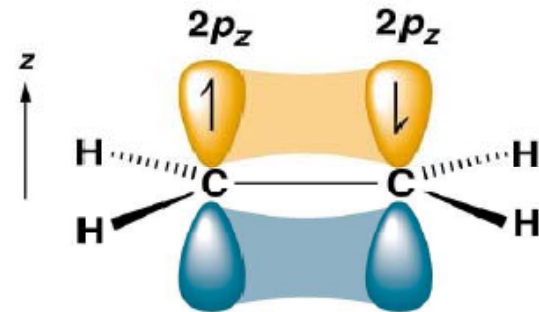
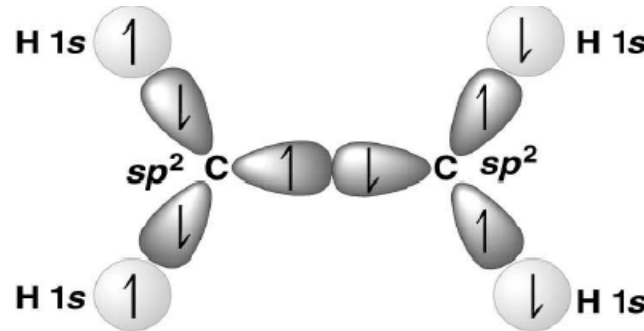
- Need to include longer range interactions to see a difference (but usually that's not where the differences come from)
- The missing physics could be **angular bonding** or **multiple body interactions**
- We will address this in the following lecture

Ethylene C_2H_4

- Model ethylene with pair potentials.
- If we kind of bend open the Hydrogens, this flipping of the H atoms will not cost any energy. If you have a pair potential, distances between the atoms is only what counts.
- If you made a potential between the Hydrogens, you'd be putting the wrong physics in because the reason that energy changes as I change that bond has nothing to do with the interaction between the Hydrogens.




Hybridization of the Carbon is what causes differences.
The C is sp^2 hybridized and wants certain bond angles

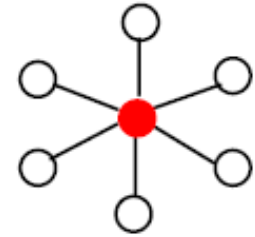


Problems with pair potentials

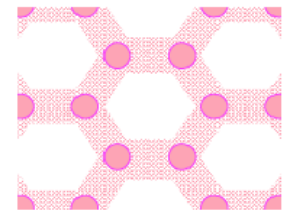
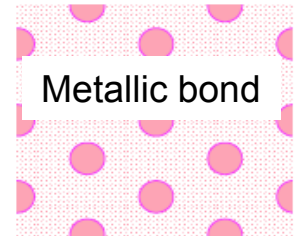
- Lets discuss for material classes like metals or organic solids, what the failure is of pair potentials.

$$E_{\text{cohesion per atom}} = 1/2 E_{\text{pair}}(R) \times Z$$

- Lets consider metals and look at the red atom.
If you do a pair potential model and you look at the bonding energy of this red atom, it's essentially 6 times the single bond energy between 



- That's why, for pair potentials, we say that **the cohesive energy scales with Z, which is the coordination number.**
- If you do experiments, quantum mechanics simulations or even more approximate theories that have the essentials of hybridization in them, you find that, for metals (covalent delocalized bonding, which we call metallic bonding), **the cohesive energy of an atom goes like the square root of Z, not linear in Z.** So, **with more bonds (increasing Z), you start gaining less and less incrementally.**

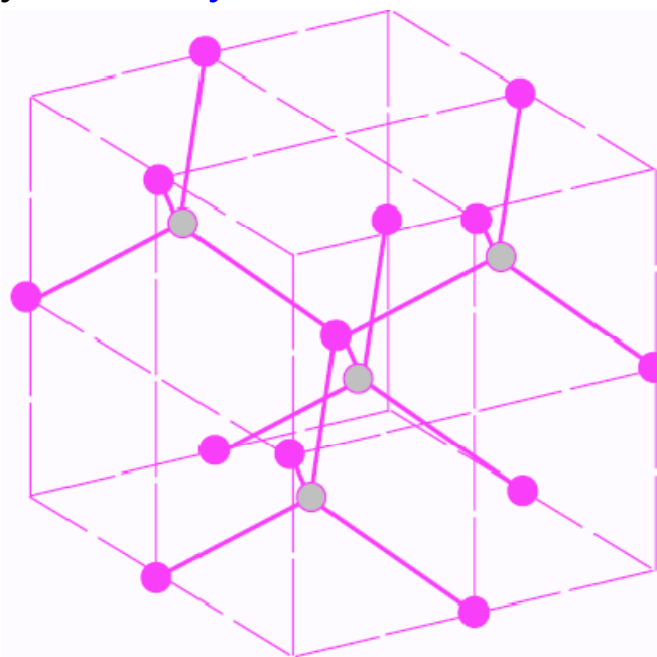


Covalent bond

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

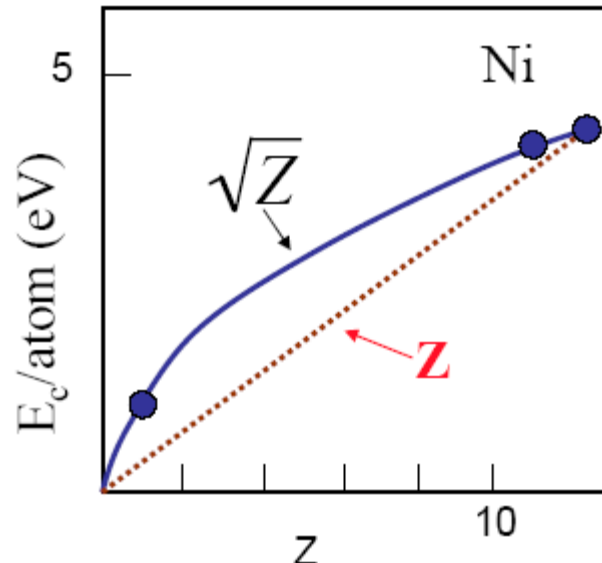
Coordination issues

- ✚ If you use pair potentials when looking for low energy crystal structures, you will almost always end up in close packed systems.
- ✚ The reason is that in pair potential models, atoms try to maximize their coordination. You sum the energy pair-wise coming from atoms around you, so and having negative bonding energy with atoms around you, you try to get as many atoms as you can around you – i.e. you maximize coordination.
- ✚ The ground states of most potential models for elements are HCP and FCC. So, it is extremely hard to stabilize things like a Diamond cubic structure which is an open structure.



An example of Ni

Cohesive energy per atom



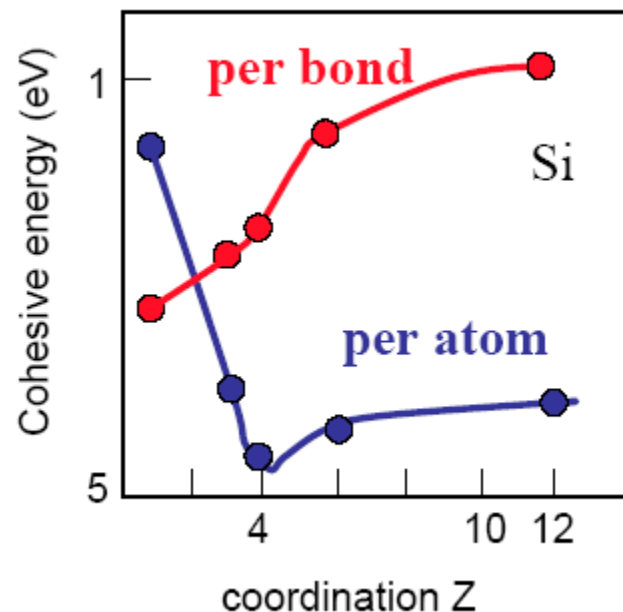
From: Daw, M. S., Foiles, S. M. & Baskes, M. I. The embedded-atom method: a review of theory and applications. [Materials Science Reports](#) **9**, 251 (1993).

✦ We see for Nickel the cohesive energy per atom as a function of the coordination. Three points are shown (and a square root function is fitted):

- $Z=12$, which is the FCC solid
- $Z=2$ is the dimer (2 atoms in the gas phase) and
- $Z=11$ is from the vacancy formation energy (if you make a vacancy in a crystal, the atoms around there are 11-fold coordinated instead of 12).

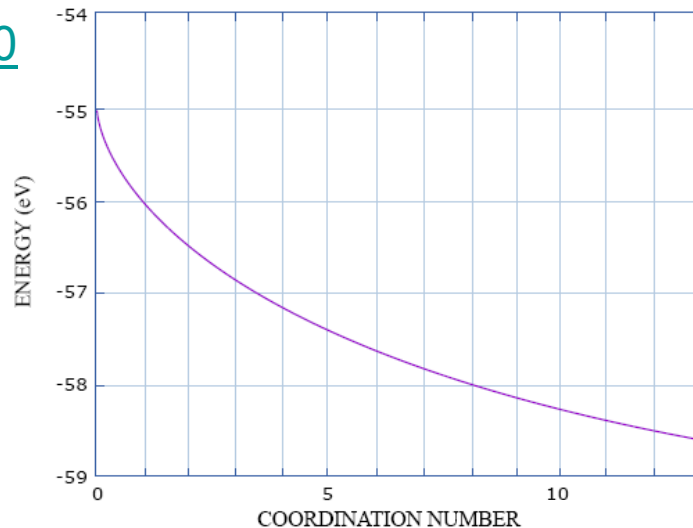
An example in Si

- ✦ You can see the same thing in Silicon. The red curve is the energy per bond for Si in different coordinations.
- ✦ The energy per bond goes down as you make more bonds. So, even though you coordinate an atom with more atoms around it, the total cohesive energy may go down. If you divide that energy by the number of bonds, that number becomes smaller and smaller.
- ✦ If an atom only bonds to one atom, it gives all its bonding power to that one atom. If it has to bond to a lots of atoms, it has to kind of divide that between all those. This is an important concept: **in covalent materials, cohesive energy is not linear in coordination.**
- ✦ Bonding strength gets weaker as you add more bonds.
- ✦ This is important when you make potentials in one coordination environment and start using them in another one.



In example in Aluminum

MIT's 3.320



Aluminum
Cohesive energy
as a function
of the
coordination
number

➤ Here's a quantum mechanical result for Aluminum.

-The cohesive energy with coordination is a convex function. You get less cohesive energy as you increase Z (e.g. going from 10 to 11 vs going from 1 to 2).

-You cannot get this result with pair potentials. With pair potentials, this essentially looks linear.

And what's the slope of it in pair potentials? Its proportional to Z , but the constant of proportionality depends on where you fit it.

Transferability of pair potentials

- Bond strength depends on environment for covalent materials
 - ✓ through angular dependence with other bonds
 - ✓ through dependence on number of other bonds (density)

TRANSFERABILITY OF PAIR POTENTIALS

- If you fit for one particular coordination environment, you cannot use them without significant error for other coordination (e.g. if you fit in the bulk cannot use for surface calculations)
- Fitting to all environments simultaneously only averages the error.

Pair potentials cannot handle shear

- ✚ Pair potentials are not stable against shear.
- ✚ If you take a square of atoms (simple cubic lattice) and you shear it, all the distances will remain the same.
- ✚ In a nearest neighbor pair potential model, all the energy has not changed. This means that the elastic constant in shear is zero.
- ✚ One can argue this is why real materials don't form simple cubic lattices (and this is true). But a real material has some amount of resistance against shear even in this configuration. However, when using pair potentials, by construction, it does not have any shear resistance.

Pair functionals and cluster potentials

- The problem is that the bonding energy is linear in coordination with a pair potential. So, all we need to do to fix this problem is to make it non-linear.
- That leads you into what we call **pair functionals** rather than pair potentials (embedded atom method, glue models, effective medium theory, etc.). **These are still methods that count the coordination around you, in some form or another. It's just that they make the energy evolve non-linearly with coordination.**
- They are still empirical but very elegant methods that solve the essential problem of pair potentials without a lot of extra work.
- We will finally discuss at the last few lectures of the course on cluster potentials that are effectively account for interactions between clusters of atoms (2,3,4..).

How to fix the pair potential problems?

