1.021, 3.021, 10.333, 22.00 Introduction to Modeling and Simulation
Spring 2011

Part I – Continuum and particle methods

Reactive potentials and applications

Lecture 8

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Content overview

I. Particle and continuum methods

Lectures 2-13

1. Atoms, molecules, chemistry
2. Continuum modeling approaches and solution approaches
3. Statistical mechanics
4. Molecular dynamics, Monte Carlo
5. Visualization and data analysis
6. Mechanical properties – application: how things fail (and how to prevent it)
7. Multi-scale modeling paradigm
8. Biological systems (simulation in biophysics) – how proteins work and how to model them

II. Quantum mechanical methods

Lectures 14-26

1. It's A Quantum World: The Theory of Quantum Mechanics
2. Quantum Mechanics: Practice Makes Perfect
3. The Many-Body Problem: From Many-Body to Single-Particle
4. Quantum modeling of materials
5. From Atoms to Solids
6. Basic properties of materials
7. Advanced properties of materials
8. What else can we do?

Overview: Material covered so far…

- **Lecture 1: Broad introduction to IM/S**

- **Lecture 2**: **Introduction to atomistic and continuum modeling** (multi-scale modeling paradigm, difference between continuum and atomistic approach, case study: diffusion)

- **Lecture 3**: **Basic statistical mechanics – property calculation I** (property calculation: microscopic states vs. macroscopic properties, ensembles, probability density and partition function)

- **Lecture 4**: **Property calculation II** (Monte Carlo, advanced property calculation, introduction to chemical interactions)

- **Lecture 5: How to model chemical interactions I** (example: movie of copper deformation/dislocations, etc.)

- **Lecture 6: How to model chemical interactions II** (EAM, a bit of ReaxFF—chemical reactions)

- **Lecture 7: Application – MD simulation of materials failure**

- **Lecture 8: Application – Reactive potentials and applications**

Lecture 8: Reactive potentials and applications

Outline:

1. Bond order force fields - how to model chemical reactions
    1.1 EAM potential for metals
    1.2 ReaxFF force field
2. Hybrid multi-paradigm fracture models

Goal of today’s lecture:

- Learn new potential: ReaxFF, to describe complex chemistry (bond breaking and formation)
- Application in hybrid simulation approaches (combine different force fields)

1. Bond order force fields - how to model chemical reactions

Potential energy expressions for more complex materials/chemistry, including bond formation and breaking

Review: atomic interactions – different types of chemical bonds

- **Primary bonds ("strong")**
  - Ionic (ceramics, quartz, feldspar - **rocks**)
  - Covalent (**silicon**)
  - Metallic (copper, nickel, **gold**, silver)
    (high melting point, 1000-5,000K)

- **Secondary bonds ("weak")**
  - Van der Waals (**wax**, low melting point)
  - Hydrogen bonds (proteins, **spider silk**)
    (melting point 100-500K)

- Ionic: Non-directional (point charges interacting)
- Covalent: Directional (bond angles, torsions matter)
- Metallic: Non-directional (electron gas concept)

Difference of material properties originates from different atomic interactions

Interatomic pair potentials: examples

$$\phi(r_{ij}) = D\exp\left(-2\alpha(r_{ij}-r_0)\right) - 2D\exp\left(-\alpha(r_{ij}-r_0)\right)$$

Morse potential

$$\phi(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$

Lennard-Jones 12:6 potential
(excellent model for noble Gases, Ar, Ne, Xe..)

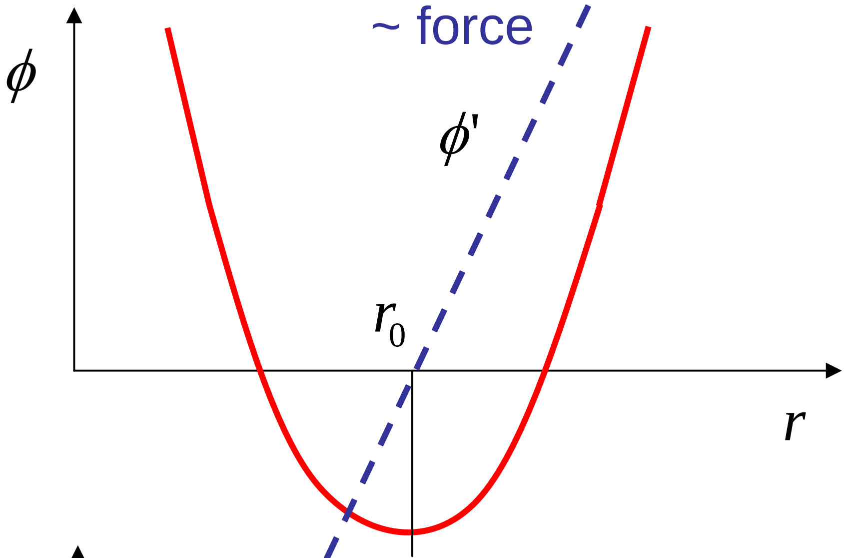
$$\phi(r_{ij}) = A\exp\left(-\frac{r_{ij}}{\sigma}\right) - C\left(\frac{\sigma}{r_{ij}}\right)^{6}$$

Buckingham potential

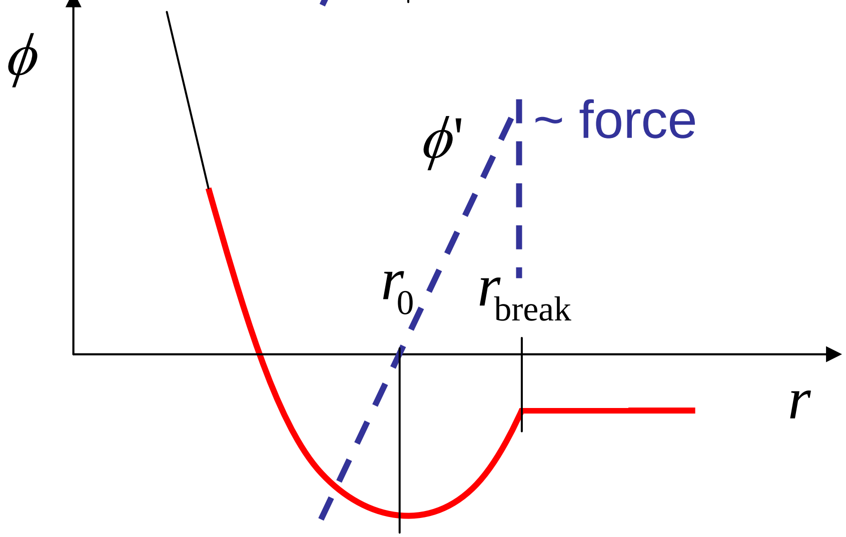
$$\phi(r_{ij}) = a_0 + \frac{1}{2}k(r_{ij}-r_0)^2$$

Harmonic approximation
(no bond breaking)

Another example: harmonic and harmonic bond snapping potential (see lecture 7)

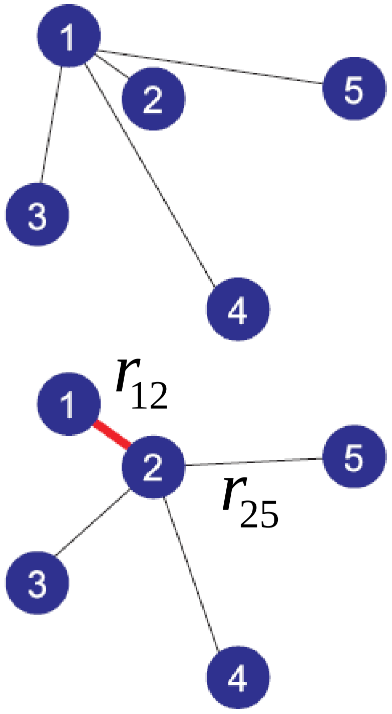


$$\phi = \frac{1}{2}k_0(r - r_0)^2$$



$$\phi = \begin{cases} \frac{1}{2}k_0(r - r_0)^2 & r < r_{\text{break}} \\ \frac{1}{2}k_0(r_{\text{break}} - r_0)^2 & r \geq r_{\text{break}} \end{cases}$$

Example: calculation of total energy "simply" the sum of all energies of pairs of atoms



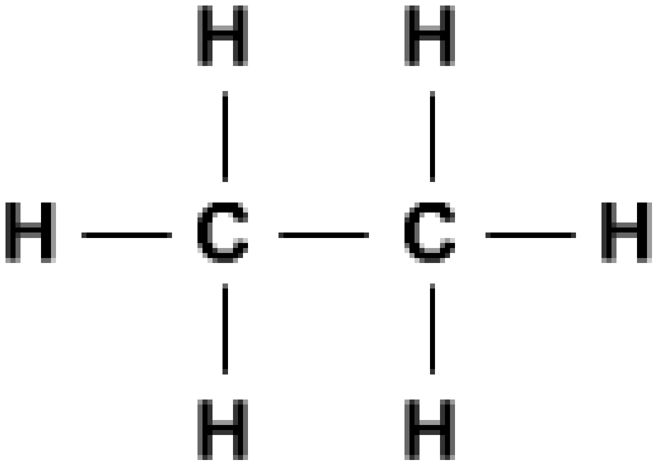
two "loops" over pairs of all particles

$$U_{total} = \tfrac{1}{2} \sum_{i=1, i \neq j}^{N} \sum_{j=1}^{N} \phi(r_{ij})$$

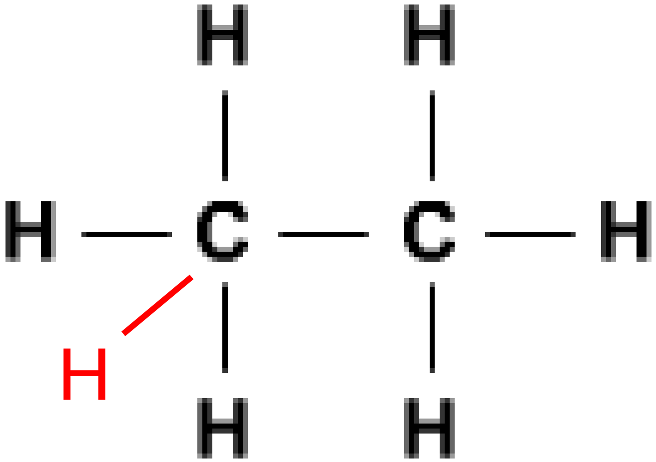
with $\phi_{ij} = \phi(r_{ij})$

$$U_{total} = \frac{1}{2}\left(\phi_{12} + \phi_{13} + \phi_{14} + \phi_{1N} \ldots + \phi_{21} + \phi_{23} + \ldots + \phi_{2N} + \ldots + \phi_{N-1,N}\right)$$

But…are all bonds the same? - valency in hydrocarbons



Ethane C_2H_6
(stable configuration)

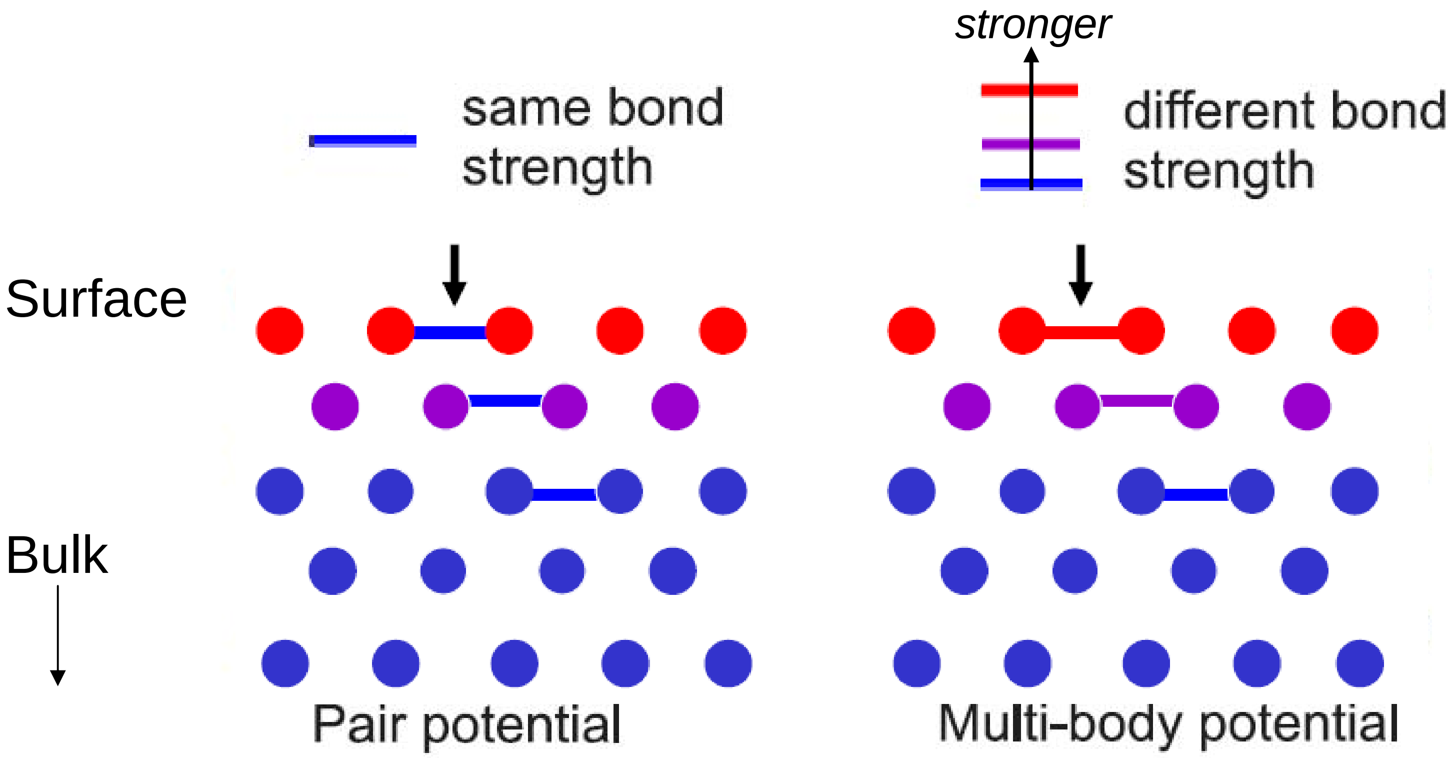


All bonds are not the same!

Adding another H is not favored

Bonds depend on the environment!

Are all bonds the same? – metallic systems



stronger

same bond strength

different bond strength

+ different bond EQ distance

Surface

Bulk

Pair potential

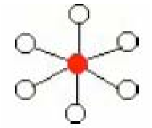
Multi-body potential

Pair potentials: All bonds are equal!

Reality: Have environment effects; it matter that there is a free surface!

Bonds depend on the environment!

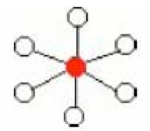
Are all bonds the same?

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

Bonding energy of atom *i*

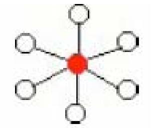
$$U_i = \sum_{j=1}^{N} \phi(r_{ij})$$



$$\boxed{U_i = \sum_{j=1}^{6} \phi(r_{ij}) \quad \longleftrightarrow \quad U_i = \phi(r_{ij})}$$

After: G. Ceder

Are all bonds the same?

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 $\sim Z$

For metals $\sim \sqrt{Z}$

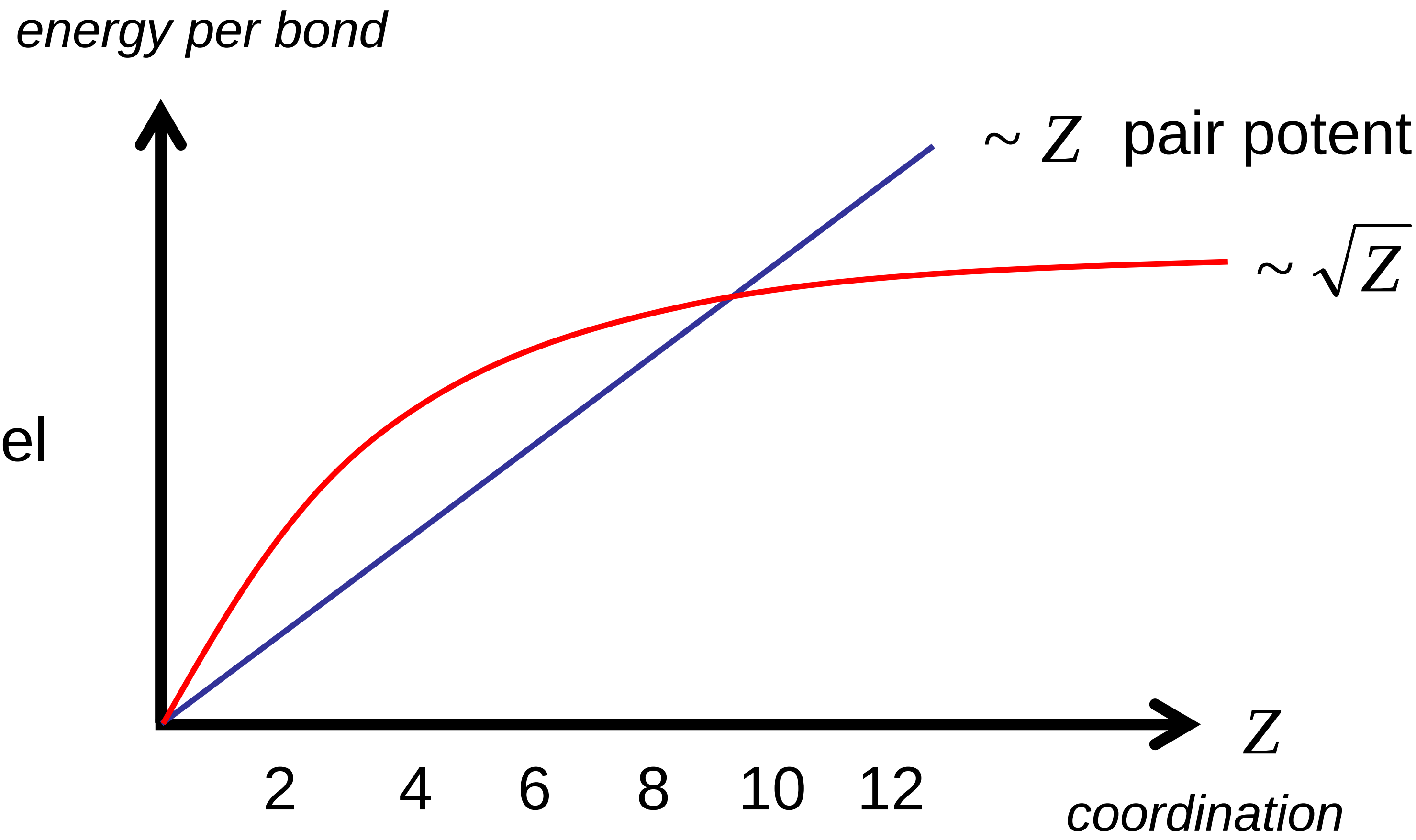
$Z:$ Coordination = how many immediate neighbors an atom has

E.g. in metals, bonds get "weaker" as more atoms are added to central atom

After: G. Ceder

Bond strength depends on coordination

Nickel



Daw, Foiles, Baskes, *Mat. Science Reports*, 1993

Transferability of pair potentials

- Pair potentials have limited **transferability:**

  Parameters determined for molecules can not be used for crystals, parameters for specific types of crystals can not be used to describe range of crystal structures

- E.g. difference between FCC and BCC can not be captured using a pair potential

1.1 EAM potential for metals

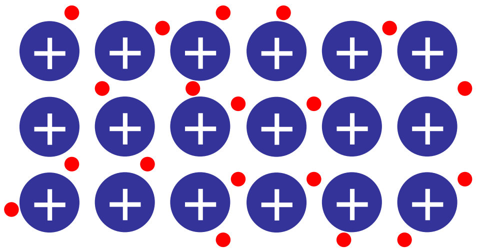
Note: already used in pset #1, nanowire simulation

Metallic bonding: multi-body effects

- Need to consider more details of chemical bonding to understand environmental effects

● Electron (q=-1)

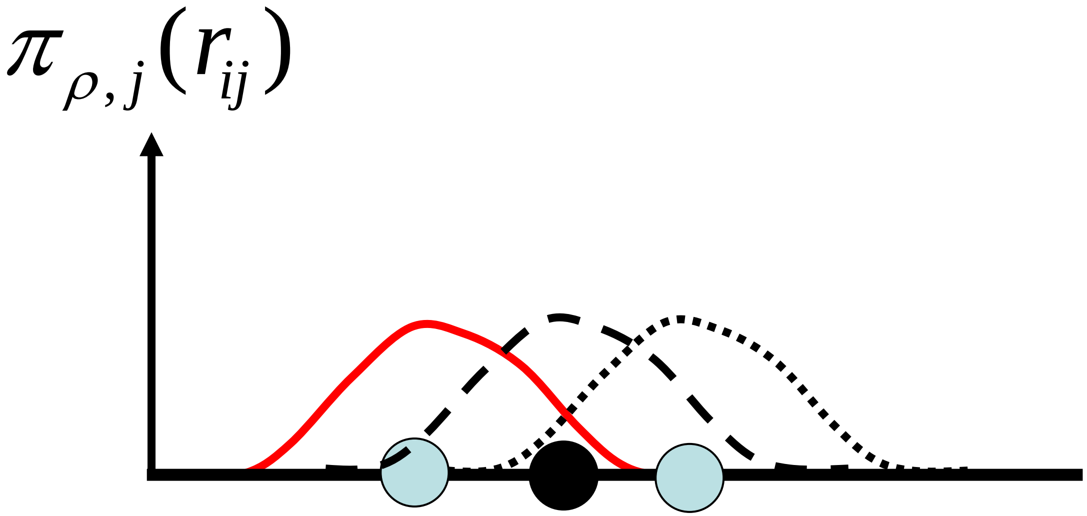
⊕ Ion core (q=+N)



Delocalized valence electrons moving between nuclei generate a binding force to hold the atoms together: **Electron gas model (*positive ions in a sea of electrons*)**

Mostly non-directional bonding, but the bond strength indeed depends on the environment of an atom, precisely the electron density imposed by other atoms

Concept: include electron density effects

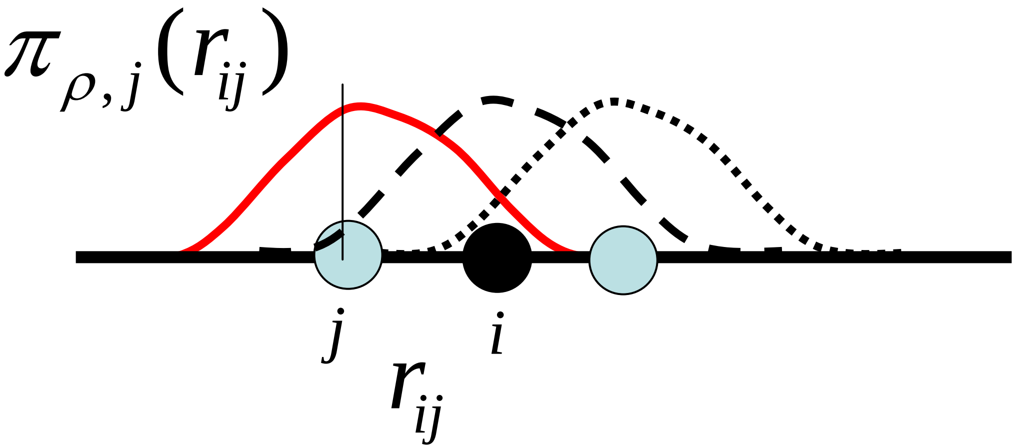


Each atom features a particular distribution of electron density

Concept: include electron density effects

Electron density at atom *i* $\rho_i = \sum_{j=1..N_{neigh}} \pi_{\rho,j}(r_{ij})$

Atomic electron density of atom j



Contribution to electron density at site i due to electron density of atom j evaluated at correct distance (r_{ij})

Concept: include electron density effects

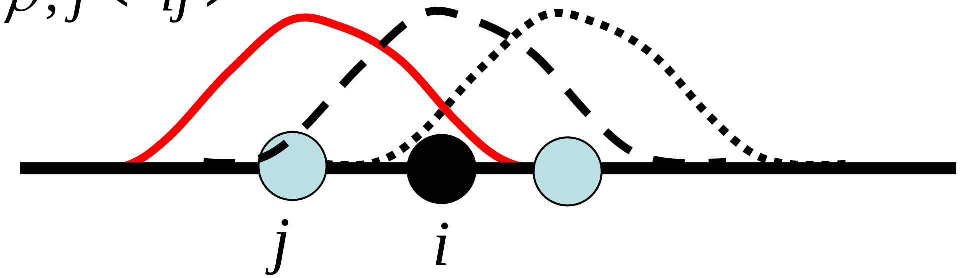
$$\phi_i = \sum_{j=1..N_{neigh}} \frac{1}{2}\phi(r_{ij}) + F(\rho_i)$$

Embedding term F (how local electron density contributes to potential energy)

Electron density at atom i

$$\rho_i = \sum_{j=1..N_{neigh}} \pi_{\rho,j}(r_{ij})$$

$$\pi_{\rho,j}(r_{ij})$$



Atomic electron density of atom j

Embedded-atom method (EAM)

Atomic energy

$$\phi_i = \sum_{j=1..N_{neigh}} \underbrace{\frac{1}{2}\phi(r_{ij})}_{\text{Pair potential energy}} + \underbrace{\overset{\text{new}}{F(\rho_i)}}_{\text{Embedding energy as a function of electron density}}$$

Total energy

$$U_{total} = \sum_{i=1}^{N} \phi_i$$

ρ_i Electron density at atom *i* based on a “pair potential”:

$$\rho_i = \sum_{j=1..N_{neigh}} \pi_{\rho,j}(r_{ij})$$

First proposed by Finnis, Sinclair, Daw, Baskes *et al.* (1980s)

Physical concept: EAM potential

- Describes bonding energy due to electron delocalization

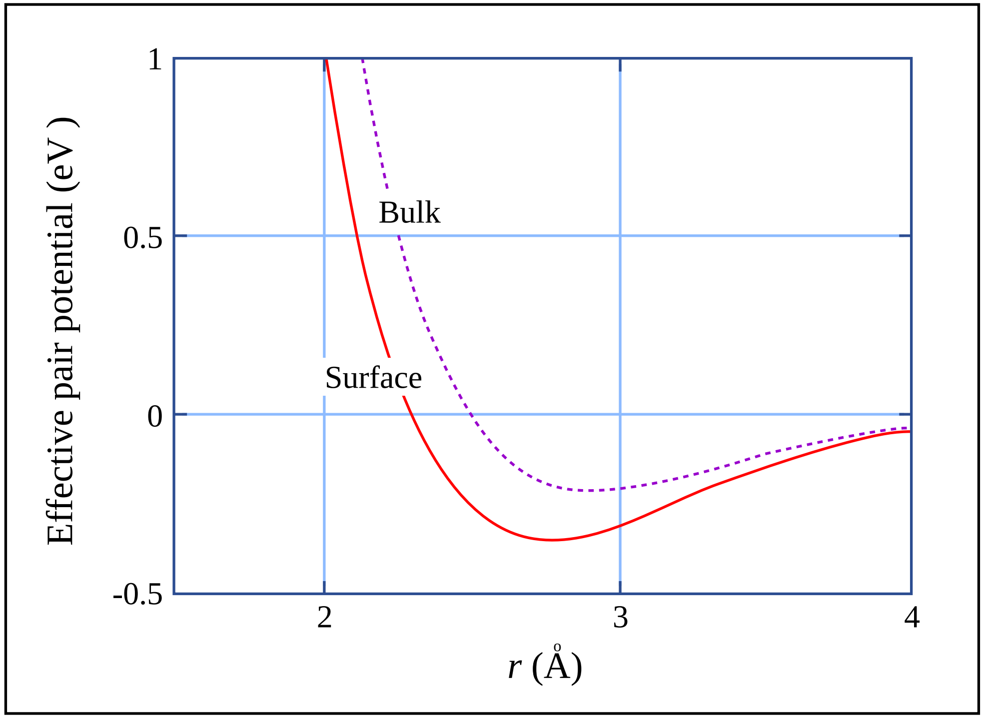
  As electrons get more states to spread out over their kinetic energy decreases

- 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!**

Effective pair interactions



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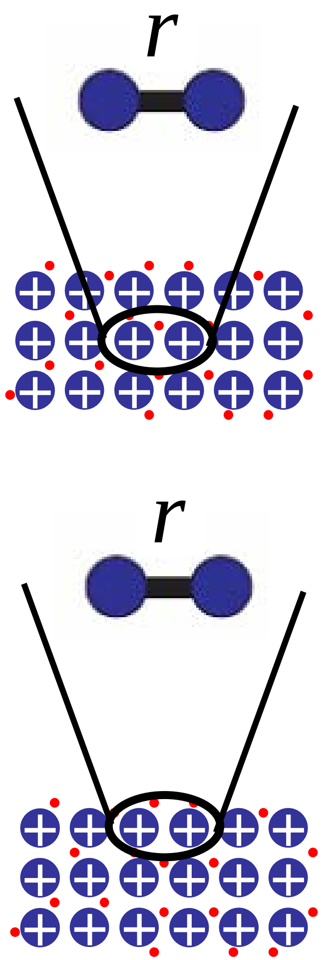


Can describe differences between bulk and surface

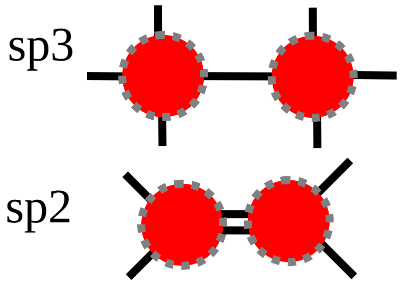
See also: Daw, Foiles, Baskes, *Mat. Science Reports*, 1993

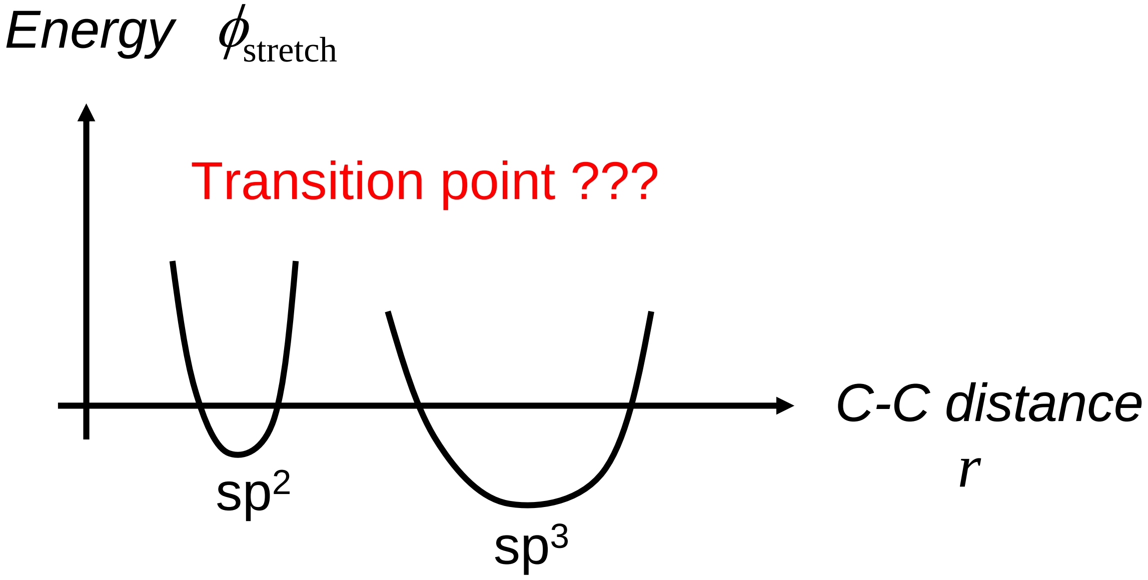
Summary: EAM method

- State of the art approach to model metals
- Very good potentials available for Ni, Cu, Al since late 1990s, 2000s
- Numerically efficient, can treat billions of particles
- Not much more expensive than pair potential (approximately three times), but describes physics much better

- ***Strongly recommended for use!***

Another challenge: chemical reactions





Simple pair potentials can not describe chemical reactions

Why can not model chemical reactions with spring-like potentials?

$$\phi_{\text{stretch}} = \frac{1}{2} k_{\text{stretch}} (r - r_0)^2$$

Set of parameters only valid for particular molecule type / type of chemical bond

$$k_{\text{stretch},sp^2} \neq k_{\text{stretch},sp^3}$$

***Reactive potentials or reactive force fields** overcome these limitations*

1.2 ReaxFF force field

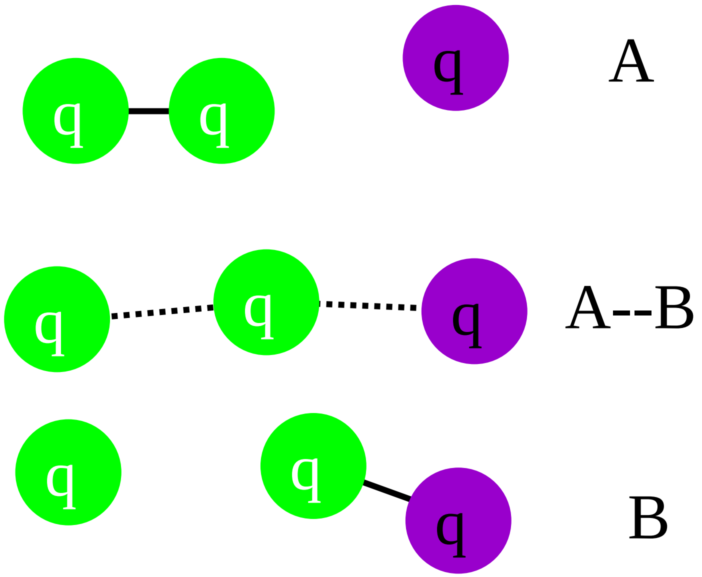
For chemical reactions, catalysis, etc.

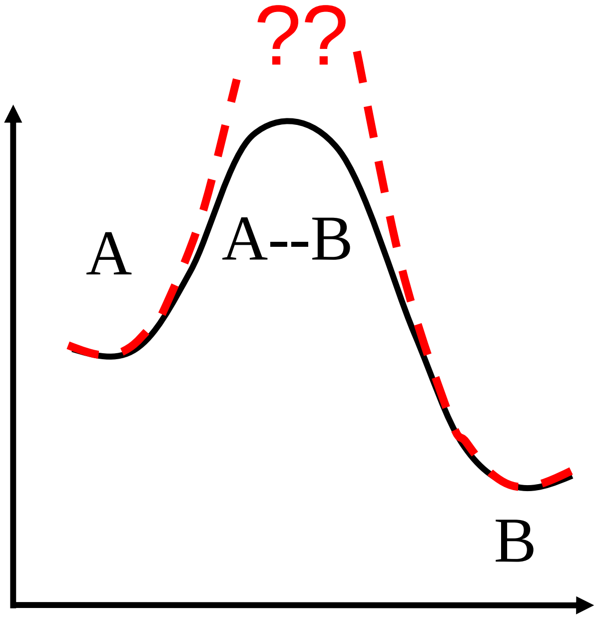
Key features of reactive potentials

- How can one accurately describe the transition energies during chemical reactions?
- Use computationally more efficient descriptions than relying on purely quantum mechanical (QM) methods (see part II, **methods limited to 100 atoms**)

$$H-C\equiv C-H \xrightarrow{+H_2} H_2-C=C-H_2$$

involves processes with electrons





Key features of reactive potentials

- Molecular model that is capable of describing **chemical reactions**
- **Continuous energy landscape during reactions** (key to enable integration of equations)
- No typing necessary, that is, atoms can be sp, sp2, sp3… w/o further “tags” – **only element types**
- **Computationally efficient** (that is, should involve finite range interactions), so that large systems can be treated (> 10,000 atoms)
- **Parameters with physical meaning** (such as for the LJ potential)

Theoretical basis: bond order potential

Concept: Use pair potential that depends on atomic environment (similar to EAM, here applied to covalent bonds)

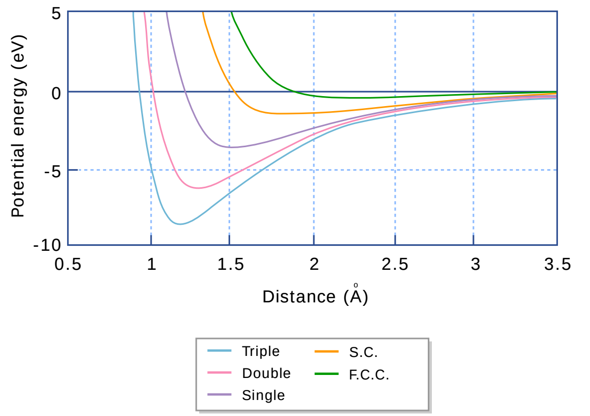
$$\phi(r_{ij}) = \phi_{\mathrm{R}}(r_{ij}) - M_{ij}\phi_A(r_{ij})$$

↓

$$M_{ij} \sim Z^{-\delta}$$

Modulate strength of attractive part
(e.g. by coordination, or “bond order”)

Abell, Tersoff



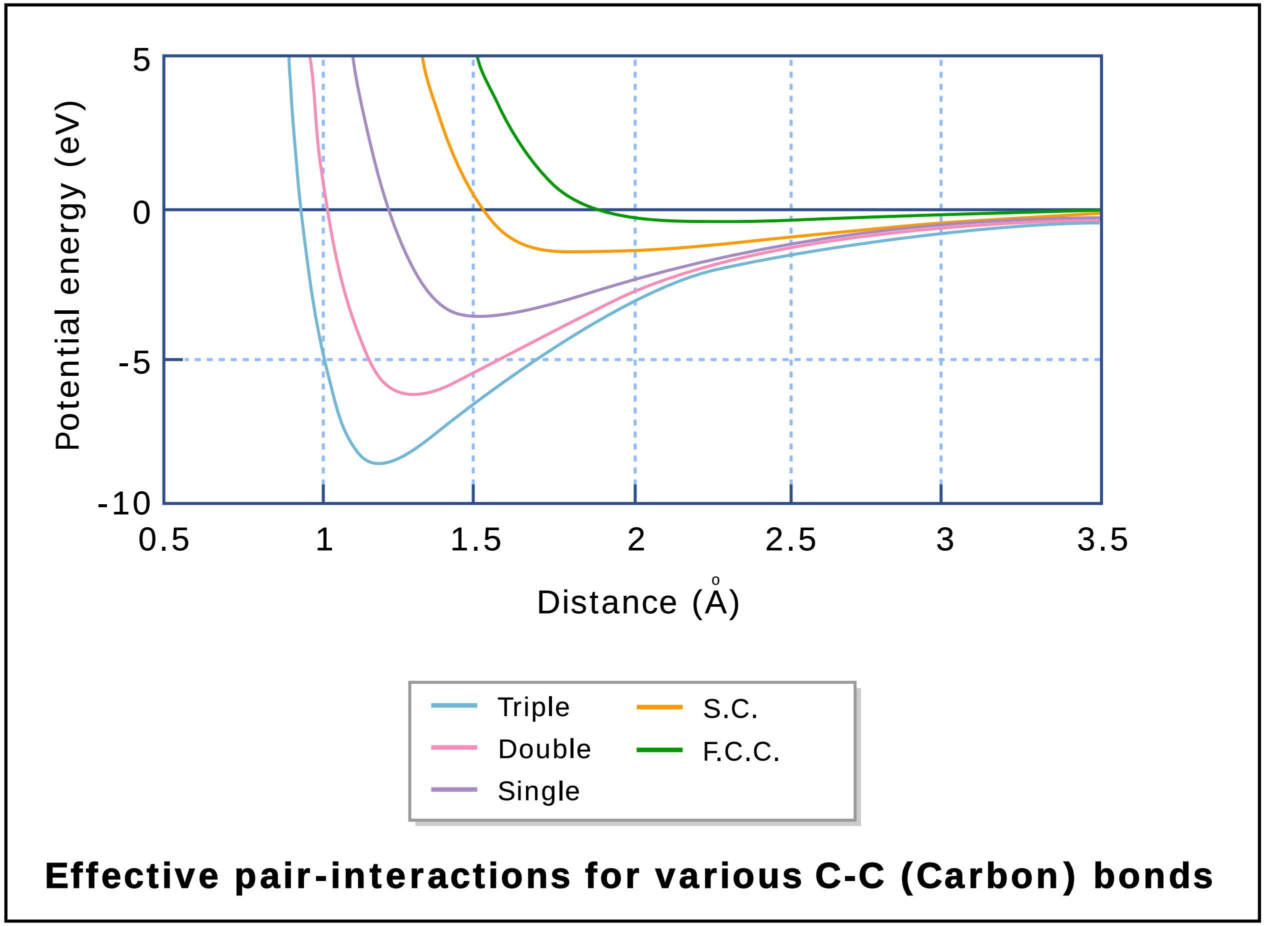
Effective pair-interactions for various C-C (Carbon) bonds

Image by MIT OpenCourseWare.

$$k(r) \sim k_0 M_{ij}(Z, \delta)$$

Changes in spring constant as function of bond order
Continuous change possible
= **continuous energy landscape during chemical reactions**

Theoretical basis: bond order potential

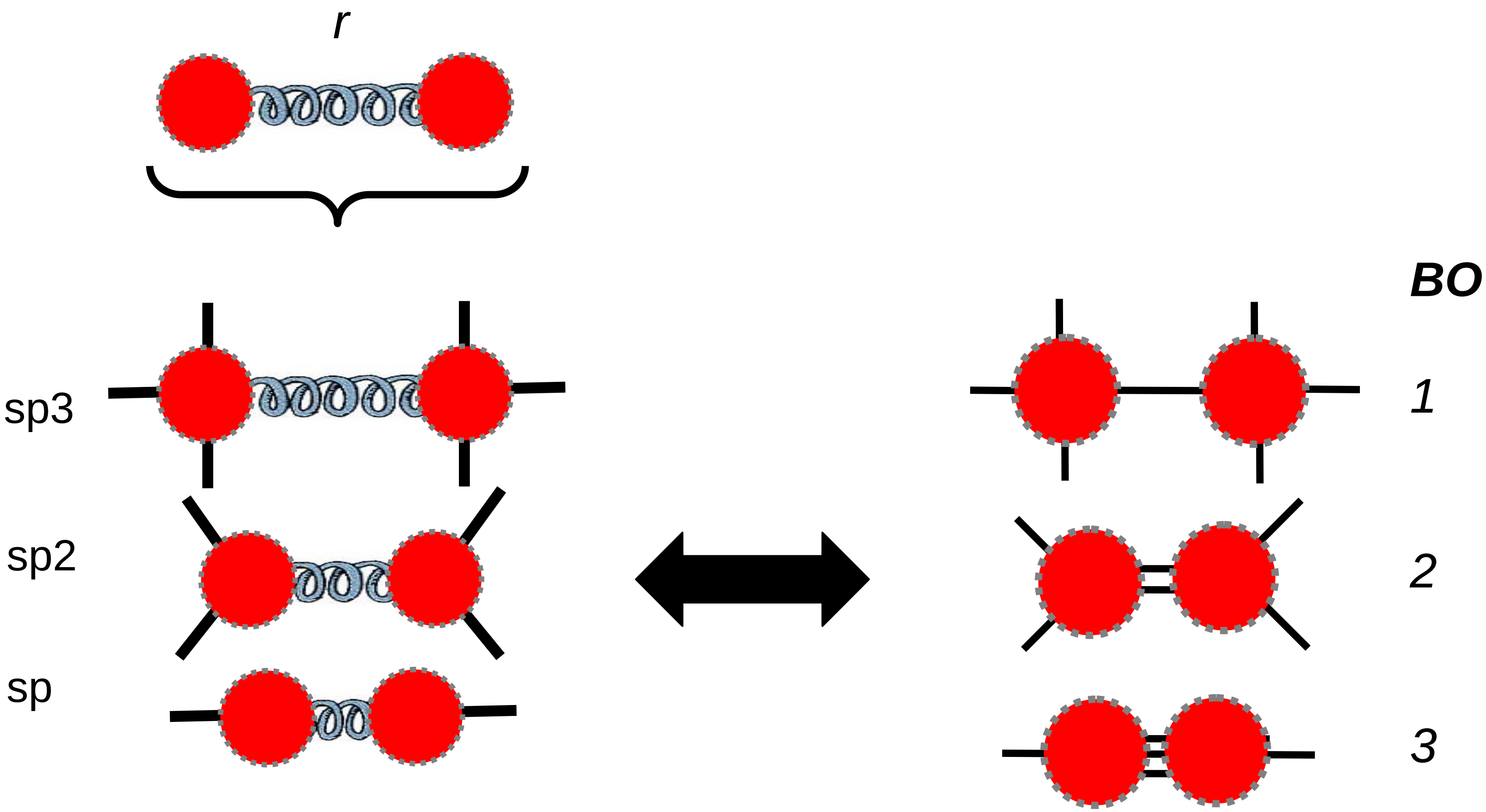


Effective pair-interactions for various C-C (Carbon) bonds

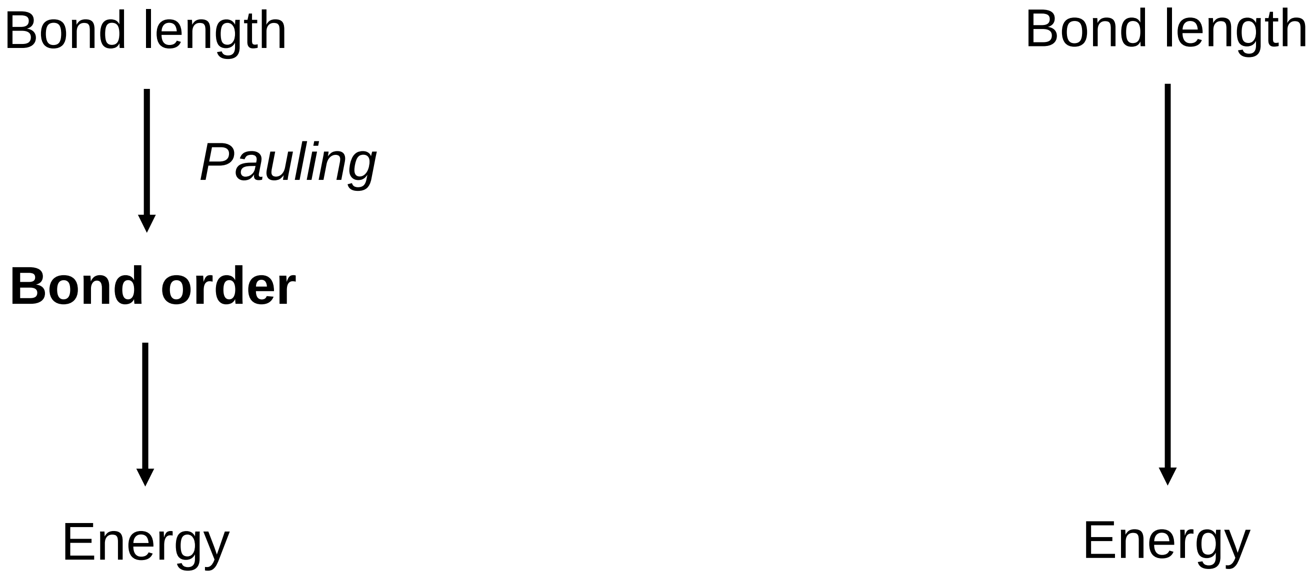
Image by MIT OpenCourseWare.

D. Brenner, 2000

Concept of bond order (BO)



Bond order based energy landscape



Bond length

Pauling

Bond order

Energy

Bond order potential
Allows for a more general description of chemistry
All energy terms dependent on bond order

Bond length

Energy

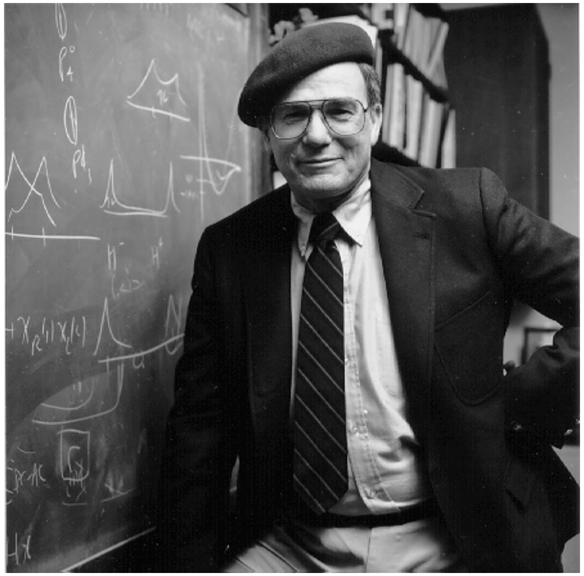
Conventional potential (e.g. LJ, Morse)

Historical perspective of reactive bond order potentials

- 1985: Abell: General expression for binding energy as a sum of near nieghbor pair interactions moderated by local atomic environment
- 1990s: Tersoff, Brenner: Use Abell formalism applied to silicon (successful for various solid state structures)
- 2000: Stuart et al.: Reactive potential for hydrocarbons
- 2001: Duin, Godddard et al.: Reactive potential for hydrocarbons “ReaxFF”
- 2002: Brenner et al.: Second generation “REBO” potential for hydrocarbons
- 2003-2005: Extension of ReaxFF to various materials including metals, ceramics, silicon, polymers and more in Goddard‘s group

Example: ReaxFF reactive force field

William A. Goddard III
California Institute of Technology



Courtesy of Bill Goddard. Used with permission.

Adri C.T. v. Duin
California Institute of Technology

ReaxFF: A reactive force field

$$E_{system} = \underbrace{E_{bond} + E_{vdWaals} + E_{Coulomb}}_{\text{2-body}} + \underset{\text{3-body}}{E_{val,angle}} + \underset{\text{4-body}}{E_{tors}}$$

$$+ \underbrace{E_{over} + E_{under}}_{\text{multi-body}}$$

Total energy is expressed as the sum of various terms describing individual chemical bonds

All expressions in terms of bond order

All interactions calculated between ALL atoms in system…

No more atom typing: Atom type = chemical element

Example: Calculation of bond energy

$$E_{system} = \boxed{E_{bond}} + E_{vdWaals} + E_{Coulomb} + E_{val,angle} + E_{tors} + E_{over} + E_{under}$$

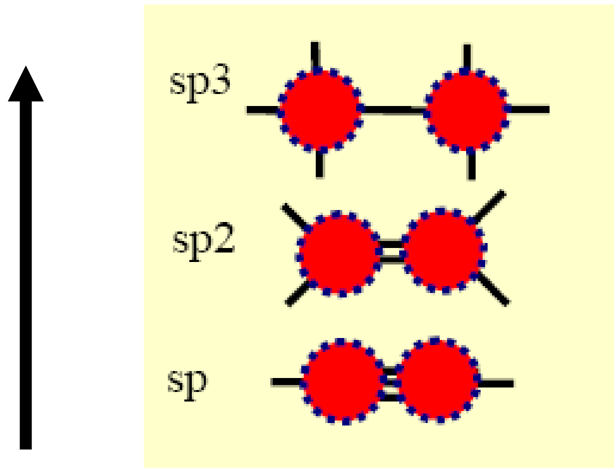
$$E_{\mathrm{bond}} = -D_{\mathrm{e}} \cdot \mathrm{BO}_{ij} \cdot \exp\left[p_{\mathrm{be},1} \left(1 - \mathrm{BO}_{ij}^{p_{\mathrm{be},1}} \right) \right]$$

Bond energy between atoms *i* and *j* does not depend on bond distance

Instead, it depends on bond order

Bond order functions

BO goes smoothly from 3-2-1-0



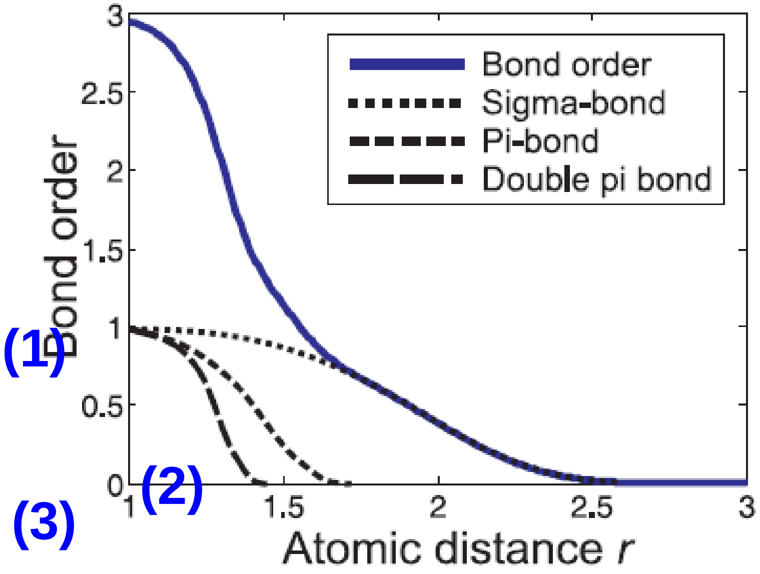


Fig. 2.21c in Buehler, Markus J. *Atomistic Modeling of Materials Failure*. Springer, 2008. © Springer. All rights reserved. This content is excluded from our Creative Commons license. For more information, see http://ocw.mit.edu/fairuse.

$$\mathrm{BO}_{ij} = \exp\left[\alpha_\sigma \cdot \overset{(1)}{\left(\frac{r_{ij}}{r_0}\right)^{\beta_\sigma}}\right] + \exp\left[\alpha_\pi \cdot \overset{(2)}{\left(\frac{r_{ij}^{\pi}}{r_0}\right)^{\beta_\pi}}\right] + \exp\left[\alpha_{\pi\pi} \cdot \overset{(3)}{\left(\frac{r_{ij}^{\pi\pi}}{r_0}\right)^{\beta_{\pi\pi}}}\right]$$

Characteristic bond distance

All energy terms are expressed as a function of bond orders

Illustration: Bond energy

$$E_{bond} = -D_e^{\sigma} \cdot BO_{ij}^{\sigma} \cdot f(BO_{ij}^{\sigma}) - D_e^{\pi} \cdot BO_{ij}^{\pi} - D_e^{\pi\pi} \cdot BO_{ij}^{\pi\pi}$$

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Please see slide 10 in van Duin, Adri. "Dishing Out the Dirt on ReaxFF."
http://www.wag.caltech.edu/home/duin/FFgroup/Dirt.ppt.

vdW interactions

$$E_{system} = E_{bond} + E_{vdWaals} + E_{Coulomb} + E_{val,angle} + E_{tors} + E_{over} + E_{under}$$

- Accounts for short distance repulsion (Pauli principle orthogonalization) and attraction energies at large distances (dispersion)
- Included for all atoms with shielding at small distances

$$E_{\mathrm{vdWaals}} = D_{ij} \cdot \left\{ \exp\left[\alpha_{ij} \cdot \left(1 - \frac{f_{13}(r_{ij})}{r_{\mathrm{vdW}}} \right) \right] - 2 \cdot \exp\left[\frac{1}{2} \cdot \alpha_{ij} \cdot \left(1 - \frac{f_{13}(r_{ij})}{r_{\mathrm{vdW}}} \right) \right] \right\}$$

$$f_{13}(r_{ij}) = \left[r_{ij}^{\lambda_{29}} + \left(\frac{1}{\lambda_w} \right)^{\lambda_{28}} \right]^{1/\lambda_{28}}$$

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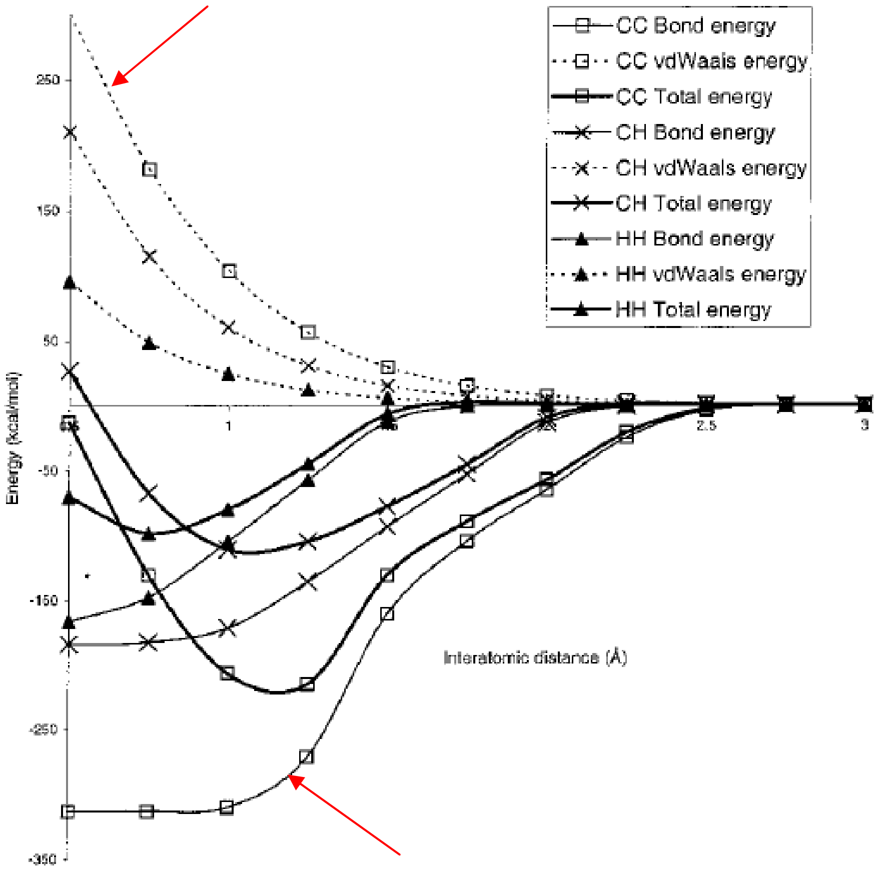
Please see slide 11 in van Duin, Adri. "Dishing Out the Dirt on ReaxFF." http://www.wag.caltech.edu/home/duin/FFgroup/Dirt.ppt.

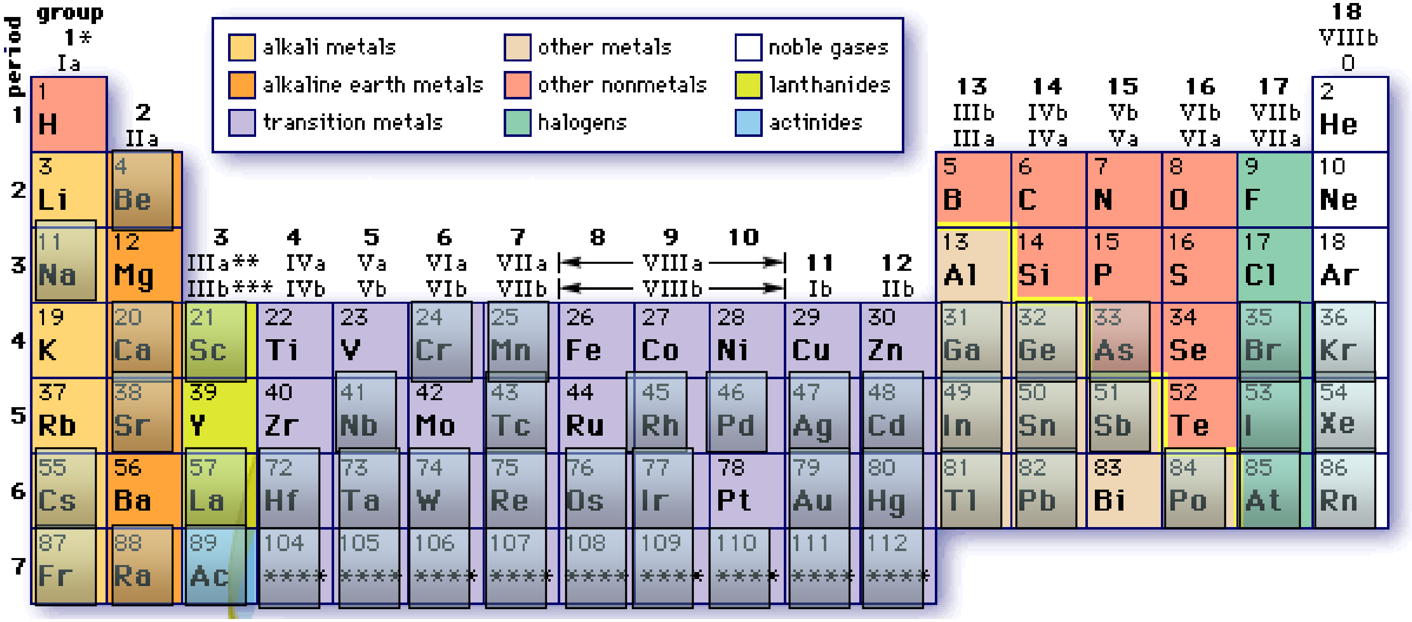
Resulting energy landscape



Contribution of E_{bond} and vdW energy

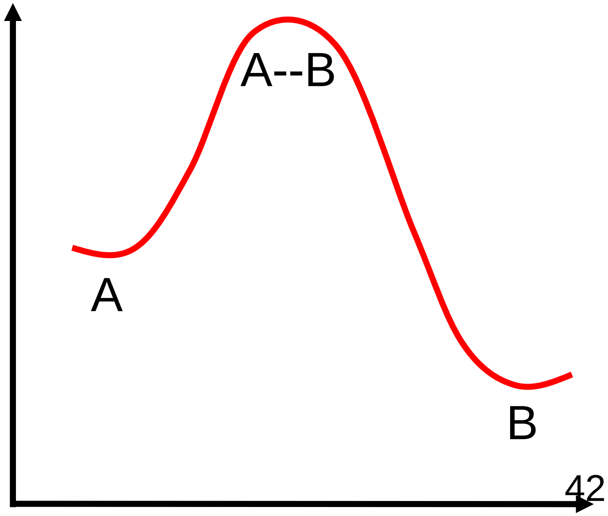
Source: van Duin, C. T. Adri, et al. "ReaxFF: A Reactive Force Field for Hydrocarbons." *Journal of Physical Chemistry A* 105 (2001). © American Chemical Society. All rights reserved. This content is excluded from our Creative Commons license. For more information, see http://ocw.mit.edu/fairuse.

Current development status of ReaxFF



period	1* Ia	2 IIa	3 IIIa** IIIb***	4 IVa IVb	5 Va Vb	6 VIa VIb	7 VIIa VIIb	8	9 VIIIa VIIIb	10	11 Ib	12 IIb	13 IIIb IIIa	14 IVb IVa	15 Vb Va	16 VIb VIa	17 VIIb VIIa	18 VIIIb 0
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 ****	105 ****	106 ****	107 ****	108 ****	109 ****	110 ****	111 ****	112 ****						

▨ : not currently described by ReaxFF



Allows to interface metals, ceramics with organic chemistry: Key for complex materials, specifically biological materials

Periodic table courtesy of Wikimedia Commons.

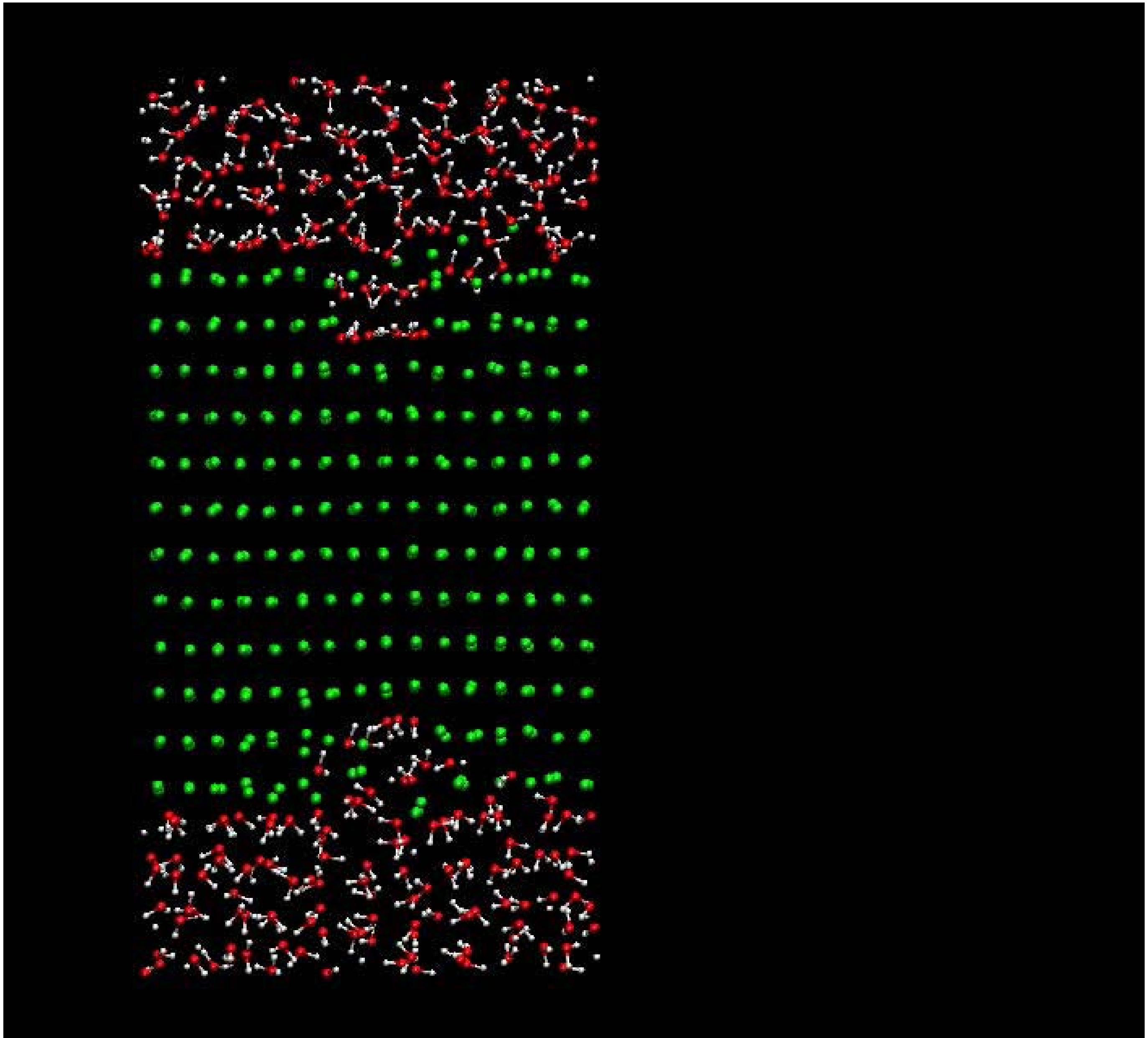
Mg-water interaction: How to make fire with water

Images removed due to copyright restrictions.
Images from video showing explosive reaction of magnesium, silver nitrate, and water, which can be accessed here: http://www.youtube.com/watch?v=QTKivMVUcqE.

Mg

http://video.google.com/videoplay?docid=4697996292949045921&q=magnesium+water&total=46&start=0&num=50&so=0&type=search&plindex=0

Mg – water interaction – ReaxFF MD simulation



3.021J / 1.021J / 10.333J / 18.361J / 22.00J Introduction to Modeling and Simulation
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