

Reactive Empirical Force Fields

Jason Quenneville

jasonq@lanl.gov

X-1: Solid Mechanics, EOS and Materials Properties

Applied Physics Division

Los Alamos National Laboratory

Timothy C. Germann, Los Alamos

Alejandro Strachan, Purdue

Adri C. T. van Duin, Caltech

William A. Goddard III, Caltech

Alexei A. Stuchebrukhov, UC Davis

2006 Summer School on Computational Materials Science

July 31 - August 11, 2006 · University of Illinois

Motivation

Empirical force fields are used in biology, chemistry, physics and materials science to calculate the potential energy surface and atomic forces.

Most, like CHARMM and AMBER, assume the same atomic connectivity (molecular composition) throughout simulation.

No Chemistry!!!

Straightforward solution: *ab initio* or QM/MM (up to 300 atoms for QM system)

For materials simulation, we may want 10s of 1000s to millions of atoms and as much as a nanosecond of simulation time.

Need a more efficient method!!!

Empirical Force Fields

Empirical force fields contain potential energy functions for each atomic interaction in a molecular system.

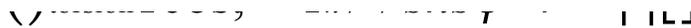
Bond Stretch:



Bond Bending:



Bond Torsion:



Parameters can be taken from experiment (e.g., vibrational spectroscopy) or from *ab initio* quantum chemistry calculations.

Empirical Force Fields

Non-Bonded potentials give the intermolecular interactions:

Coulomb:

$$V(r) = \frac{q_1 q_2}{4\pi\epsilon_0 r}$$

$$V(r) = \frac{q_1 q_2}{r}$$

van der Waals:

$$V(r) = \frac{C_6}{r^6} - \frac{C_{12}}{r^{12}}$$

Parameters obtained through ab initio quantum chemistry and liquid simulations.
e.g. OPLS (optimized potentials for liquid simulations, W. L. Jorgensen and J. Tirado-Rives, *J. Am. Chem. Soc.* **110**, 1657 (1988).)

Empirical Valence Bond (EVB)

EVB attempts to combine empirical potential energy functions with valence bond ideas to describe chemical reactions efficiently and accurately.

EVB Applications

Proton transport in aqueous acid (*CPL*, **284**, 71 ('98); *JPCB*, **102**, 5547 ('98))

Aqueous acid-base reactions (*JPCA*, **105**, 2814 ('01))

Enzyme catalysis (Warshel)

Nucleophilic substitution reactions

Good Introduction:

Computer Modeling of Chemical Reactions in Enzymes and Solutions, A. Warshel
Wiley-Interscience (02/01/1997)

EVB: introduction

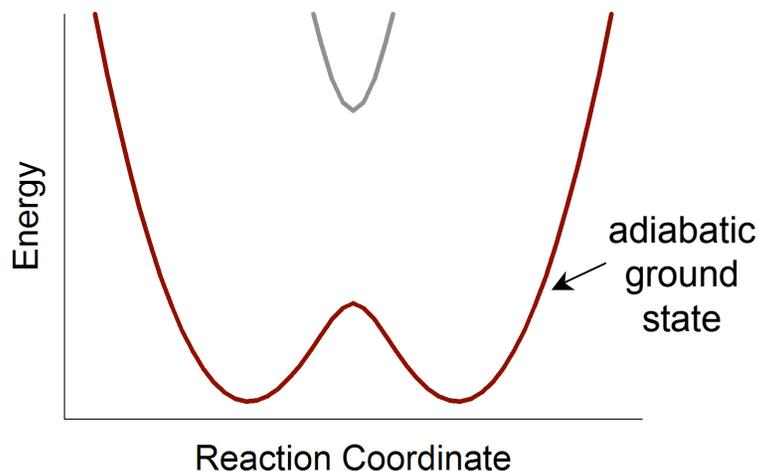
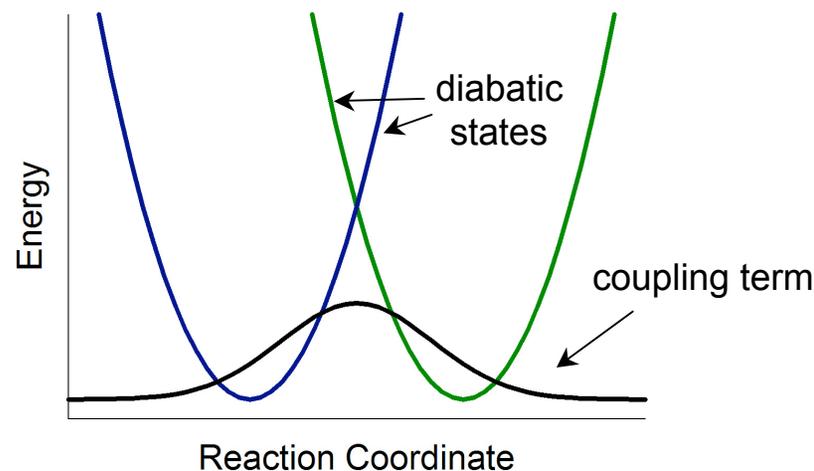
EVB starts with a $N \times N$ potential energy matrix:

N diabatic states (diagonal)
 $\underline{N(N-1)}$ couplings (off-diagonal)

Each diabatic state looks like a configuration in a standard non-reactive force field.

Off-diagonal coupling elements: interaction between each diabatic state and the $N-1$ remaining states.

Diagonalize $V \rightarrow$ adiabatic states. The minimal value is the ground state.



Calculation of Forces

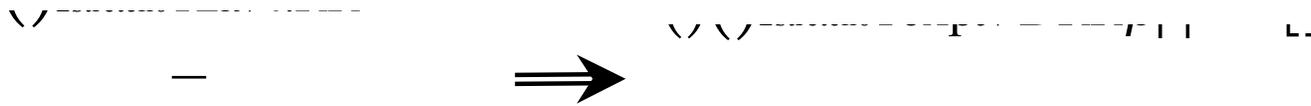
Diagonalizing the $N \times N$ EVB matrix yields the ground state as a linear combination of diabatic states.

If a_n is the set of corresponding coefficients, the forces can be calculated using the Hellman-Feynman theorem:

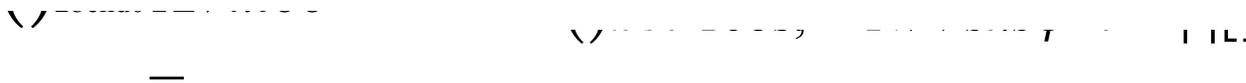
$$\langle \text{---} | \text{---} \rangle$$

EVB: diagonal matrix elements

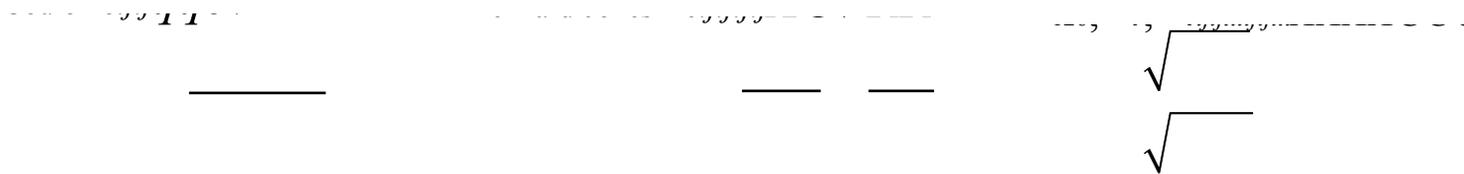
Because we need to treat bond breaking and formation, the Bond Stretch should be anharmonic:



Bending and Torsional potentials can be as before:



System-environment interactions treated with standard non-bonding potentials:



Interaction between EVB States

System-system non-bonding interactions more complicated due to the potential for chemical reaction.

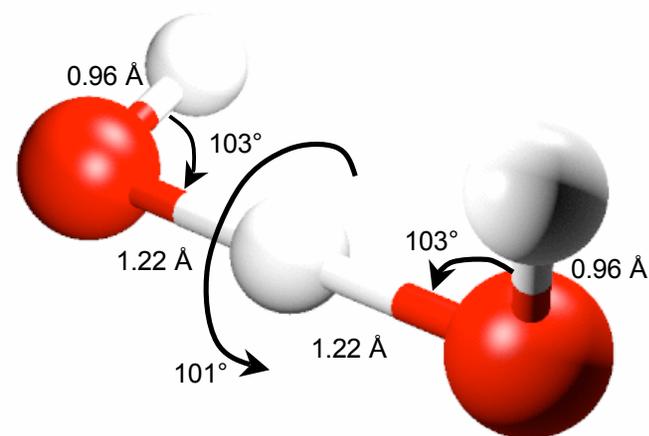
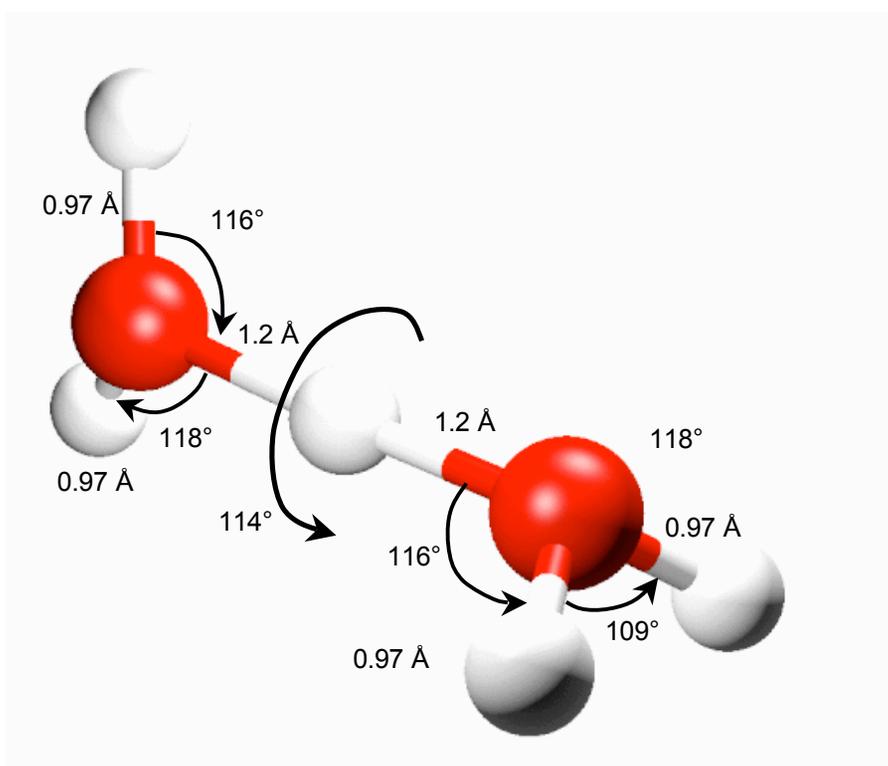
A functional form more flexible than Coulomb + Lennard-Jones is required.

The intermolecular interactions (part of the diagonal element) and the coupling terms (off-diagonal) must be parametrized together in order to describe the reaction correctly.

In the activated complex, the favorable interaction between the two states is controlled by the intermolecular interaction. It is normally written in terms of the distance between the two reactant centers.

The reaction barrier is controlled by coupling term. This term is generally a function of the reaction coordinate.

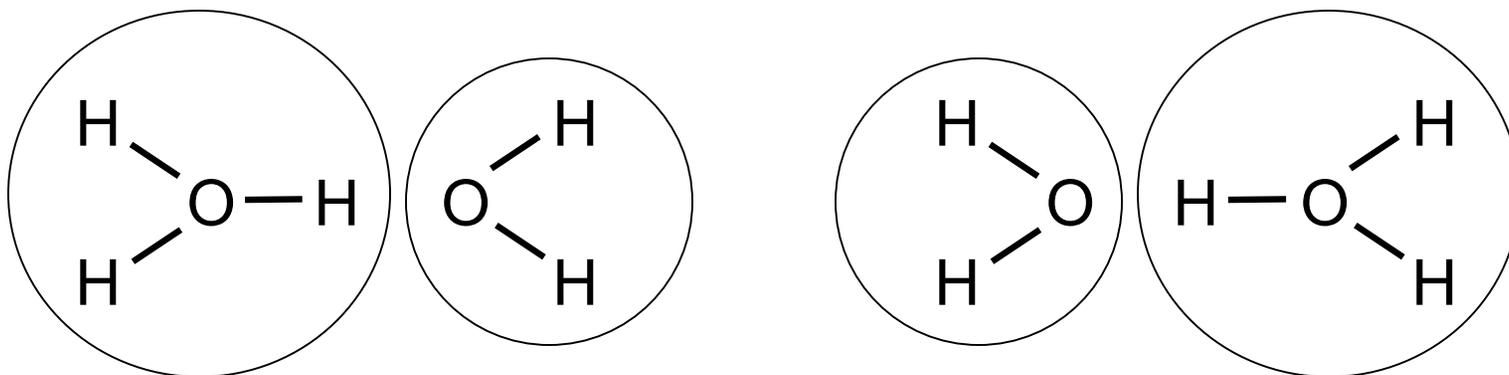
Application: Proton Transfer in Water



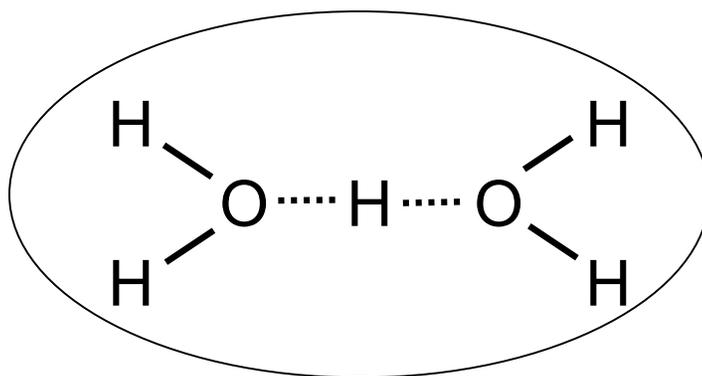
Optimized geometries of the $\{\text{H}_2\text{O}-\text{H}-\text{OH}_2\}^+$ (left) and $\{\text{HO}-\text{H}-\text{OH}\}^-$ (right) complexes, obtained from first principles (MP2/aug-cc-pVTZ).

EVB of $\text{H}_3\text{O}^+ - \text{H}_2\text{O}$ Proton Transfer

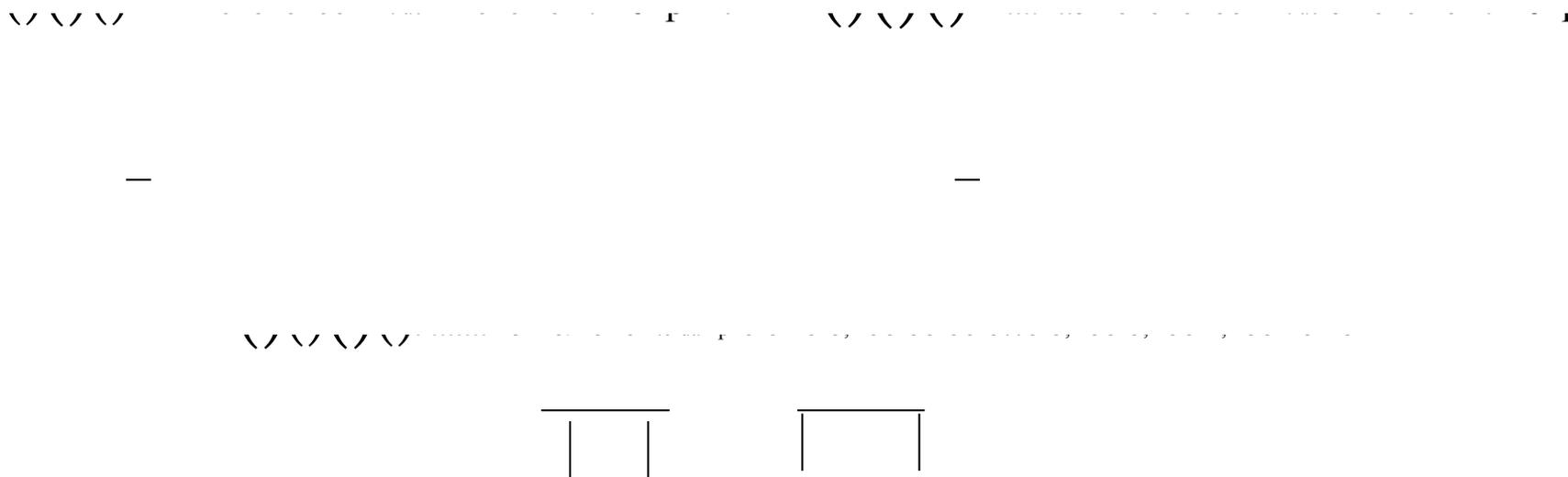
Diabatic States:



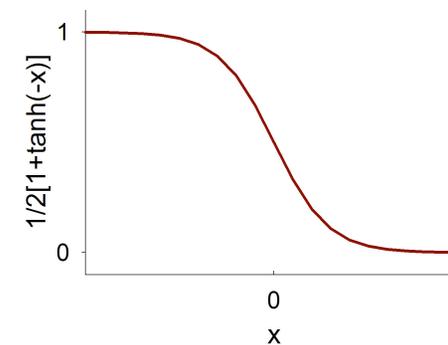
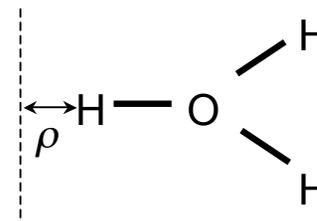
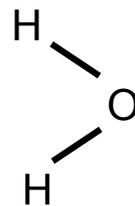
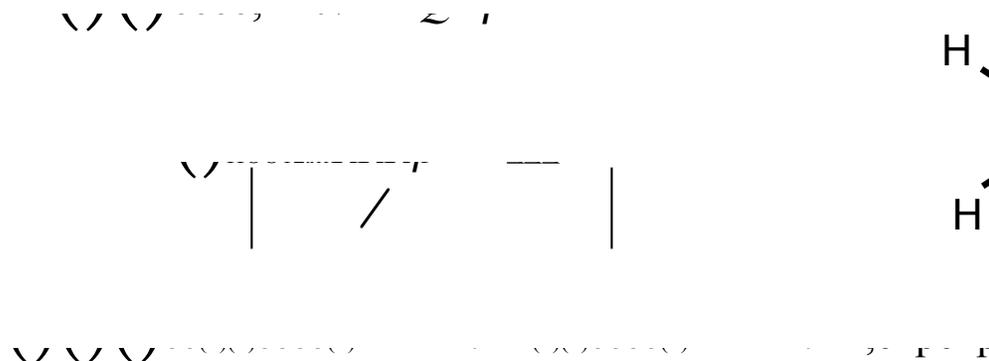
Adiabatic State:



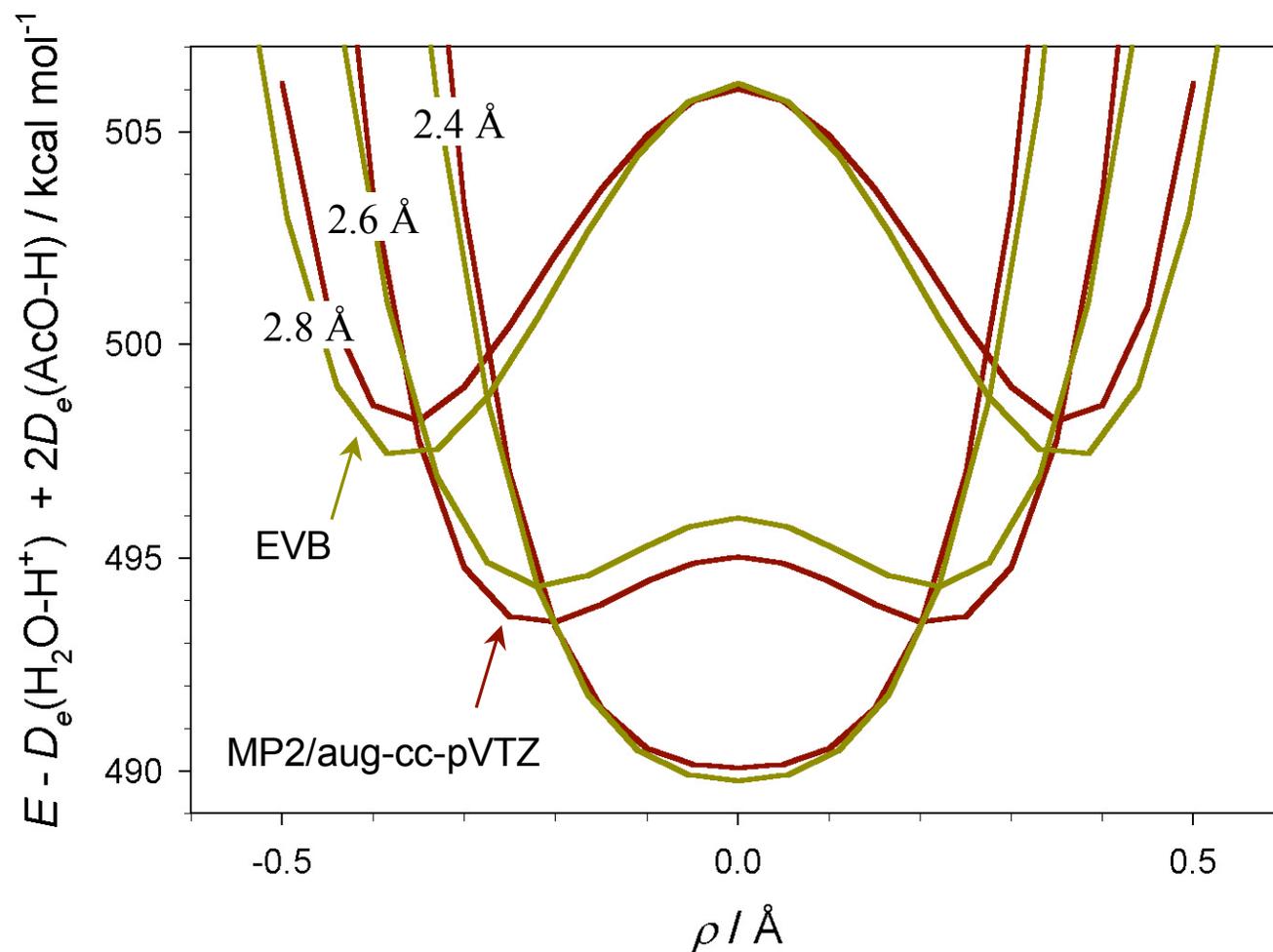
$\text{H}_3\text{O}^+ - \text{H}_2\text{O}$ Proton Transfer: Diagonal Elements



$\text{H}_3\text{O}^+ - \text{H}_2\text{O}$ Proton Transfer: Coupling Elements



EVB vs Ab Initio for $\text{H}_3\text{O}^+/\text{H}_2\text{O}$



EVB Summary

Very good for systems with small number of possible reactions

Reaction barriers are treated explicitly

Offers an *empirical* description of chemical reactions

Gives mixing of diabatic states during reaction

Can be difficult to parametrize intermolecular potentials and couplings

Limitation on number of states due to diagonalization (cubic scaling)

ReaxFF

Bond-Order potential, developed at CalTech by Adri van Duin and Bill Goddard

Potential parametrized using *ab initio* calculations (B3LYP/6-31G**) on a “training set” of reactions

Why bond-order based?

non-reactive potentials have *atom-types* that define connectivity



Applications:

High Explosives, Propellants, Catalysis, Fuel Cells, Corrosion, Friction, etc.

Background References

Bond Order/Bond Length relationship

Pauling, *J. Am. Chem. Soc.*, 69, 542 (1947).

Reactive Empirical Bond Order (REBO)

Johnston, *Adv. Chem. Phys.*, 3, 131 (1960).

Johnston, Parr, *J. Am. Chem. Soc.*, 85, 2544 (1963).

Other Bond-Order Potentials

Tersoff, *Phys. Rev. Lett.*, 56, 632 (1986); Tersoff, *Phys. Rev. Lett.*, 61, 2879 (1988).

Brenner, *Phys. Rev. B*, 42, 9458 (1990).

Brenner, et al, *J. Phys.: Condens. Matter*, 14, 783 (2002).

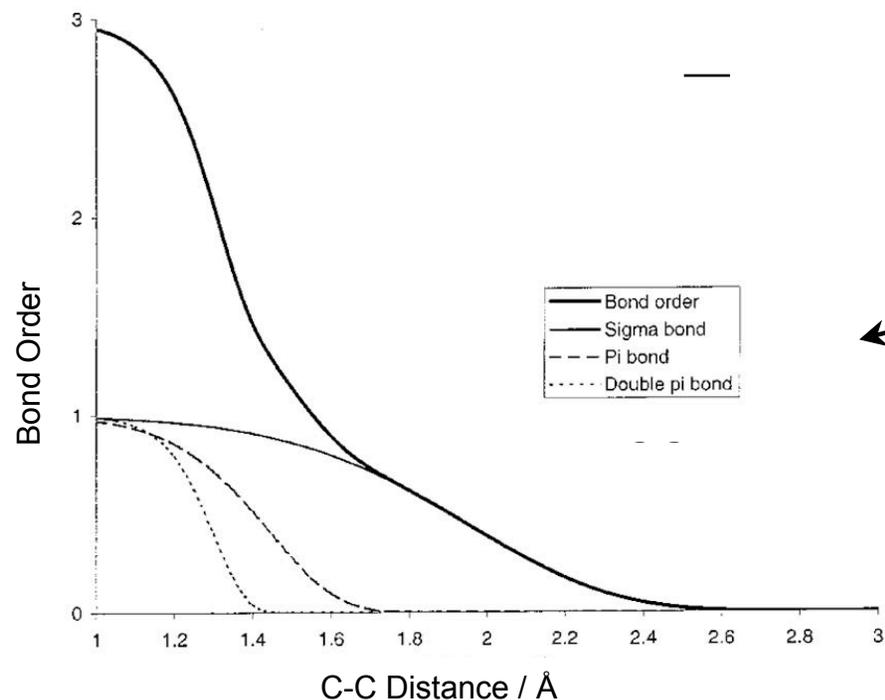
ReaxFF

van Duin, Dasgupta, Lorant, Goddard, *J. Phys. Chem. A*, 105, 9396 (2001).

Strachan, Kober, van Duin, Oxgaard, Goddard, *J. Chem. Phys.*, 122, 054502 (2005).

User Manual: http://www.wag.caltech.edu/home/duin/reax_um.pdf

Bond Order, Bond Energy



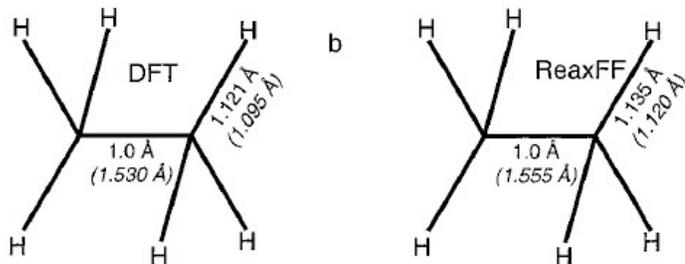
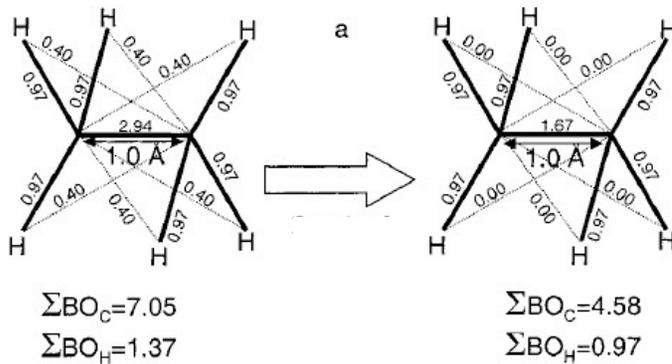
Example: Acetylene

Bond Order goes smoothly from $0 \rightarrow 1 \rightarrow 2 \rightarrow 3$ as C-C Bond Length shortens from large distance to 1.0 Å

...not explicitly a function of bond distance

Bond Order Corrections

Bond orders adjusted to get rid of unphysical bonds.



Over- and under-coordination of atoms must be avoided.

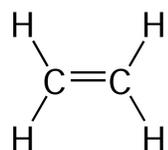
Energy penalty added to the potential energy function for the case where an atom has more bonds than its valence allows.

e.g., Carbon can't have more than 4 bonds; Hydrogen no more than 1

If an atom is under-coordinated, the stabilization of π bonding should be used if possible.

Bond Angles, Bond Torsion

Bond Angles and Torsions are intimately tied to the bond types.

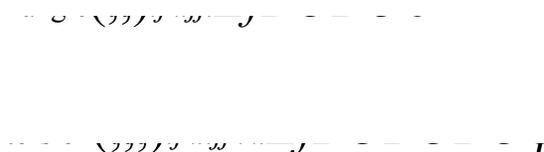


$$\angle \text{CCH} \approx 120^\circ$$



$$\angle \text{CCH} = 180^\circ$$

With a bond order potential, angles and torsions must be written in terms of the bond order.



Angle and torsion energy terms must $\rightarrow 0$ as B.O. $\rightarrow 0$.

See *J. Phys. Chem. A*, 105, 9396 (2001) for full potential form.

Lone Pair Electrons, Conjugation

implicit in AMBER/CHARMM-like potentials
through atom type

The creation or reaction of lone-pair electrons should be assigned an energy term.

$E_{\text{lone pair}}$ → corresponds to an energy penalty for having too many lone pairs on an atom
(i.e., overcoordination)

Conjugated systems should have added stabilization.

E_{conj} → has maximum contribution when successive bonds have bond-order values of 1.5.

Hydrogen Bonding

Hydrogen bonding extremely important in biological systems but also in many organic solids.



Hydrogen bonds are calculated between group X-H and Y, where X and Y are atoms known to form H-bonds (e.g., N, O)

The H-bond energy term is written in terms of the bond-order of X-H, the distance between H and Y, as well as the X-H-Y angle.



Can be an expensive part of the calculation because many acceptor (Y) atoms could be available for any given X-H group. All interactions must be calculated out to a cutoff distance ($\sim 10 \text{ \AA}$) in order to remain consistent from timestep to timestep.

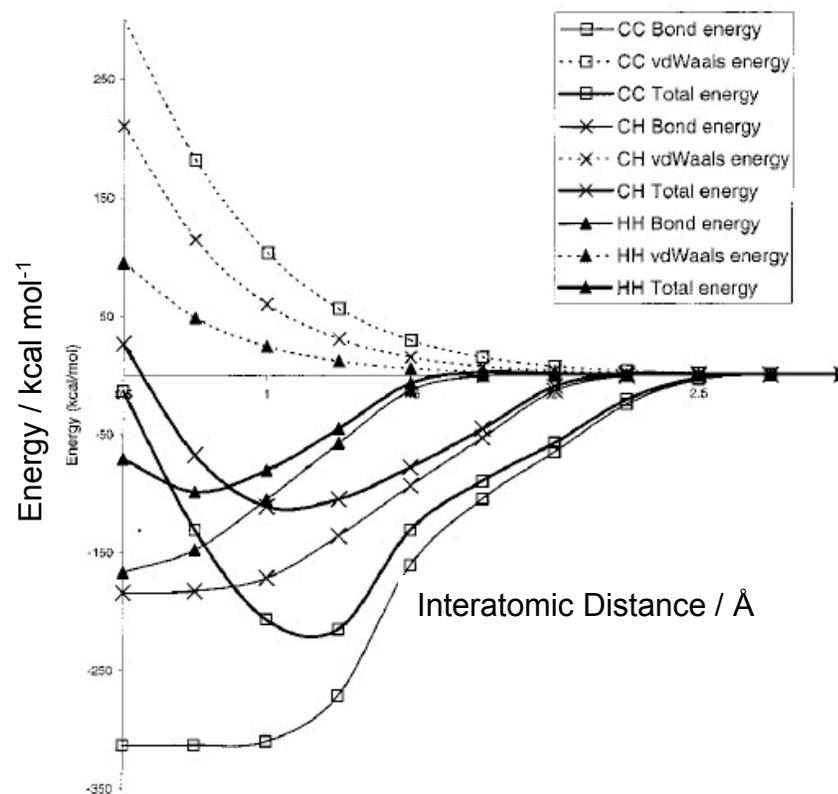
Non-Bonded Interactions

- Short-range Pauli Repulsion
- Long-range attraction (dispersion)
- Coulomb forces

van der Waals and Coulomb terms are included for **all atom pairs** (whether bonded or non-bonded)!

This avoids changing the potential when chemistry occurs. Such alterations, which are natural in the EVB formalism, would be awkward in ReaxFF.

Shielding included for both Coulomb and van der Waals in order to avoid excessive interaction between atoms sharing bond and/or bond angle.



Charge Equilibration

The charge on an atom depends on the molecular species:



Atomic charges are adjusted with respect to connectivity and geometry.

Many QEq methods available. ReaxFF uses Electronegativity Equalization Method (EEM: Mortier, et al, JACS, 108, 4315, ('86).)

The desired charge distribution is that which minimizes,

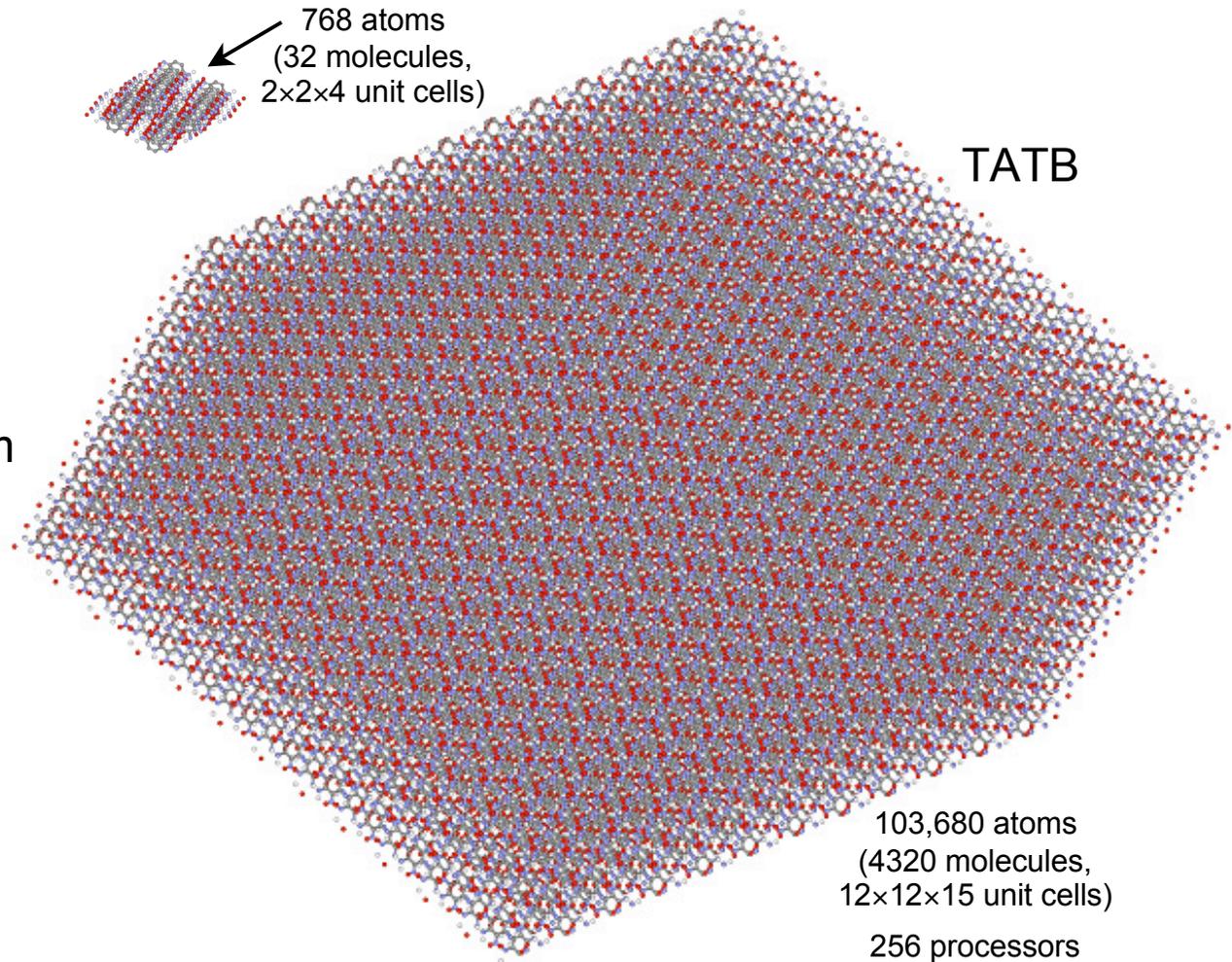
$$\sum_i \frac{1}{2} q_i^2 + \sum_{i < j} \frac{q_i q_j}{r_{ij}}$$

Final Coulomb energy from screened potential – all atom-pairs calculated

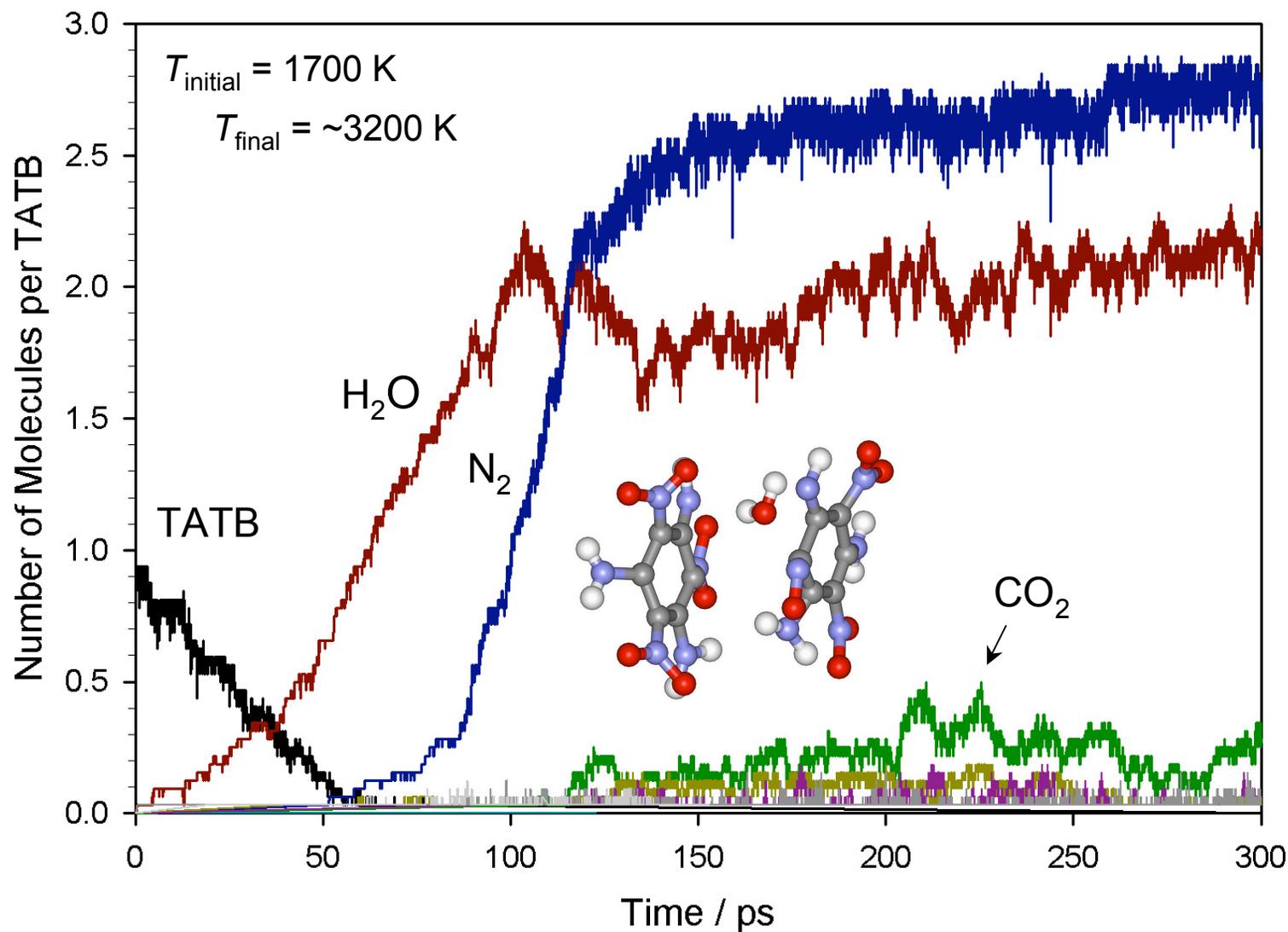
$$\sum_{i < j} \frac{q_i q_j}{r_{ij} + \lambda}$$

Application: HE at High T , P

- Interested in chemical reaction dynamics of high explosives (HE) under shock conditions
- Want as big a system (10^5 to 10^6 atoms) as possible in order to study the spread of reactions, temperature distribution, carbon-clustering, etc.

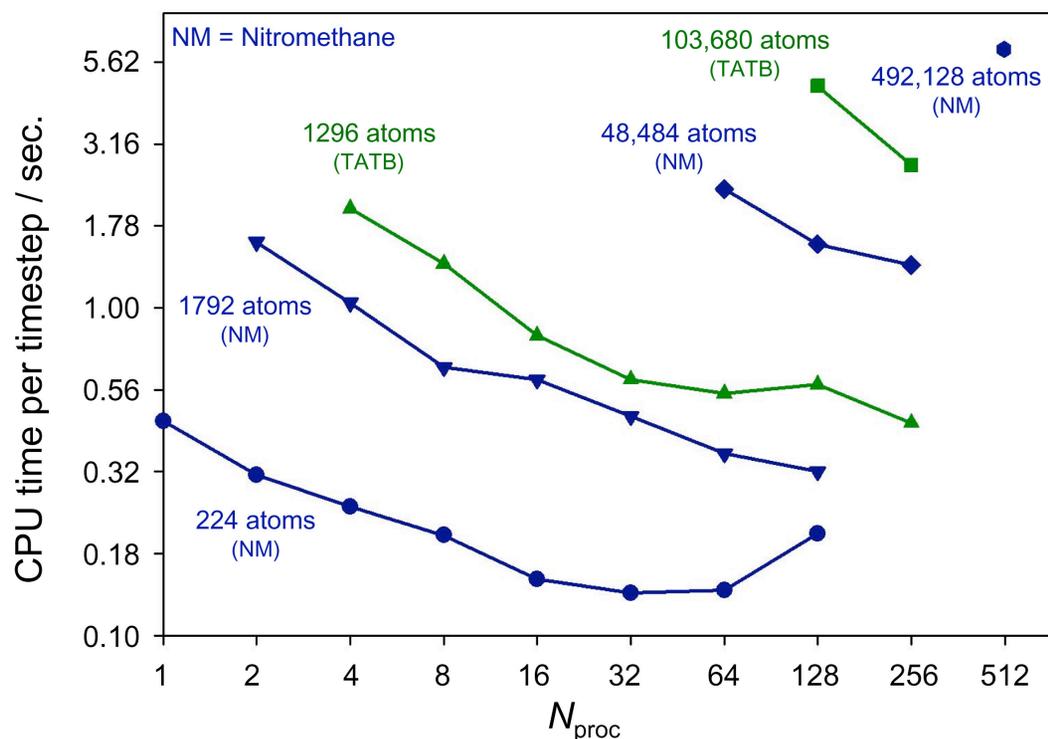


Decomposition of TATB at High T



ReaxFF in Parallel

- GRASP (General Reactive Atomistic Simulation Program) developed at Sandia National Lab by Aidan P. Thompson.
- Objective: Parallel scalable MD code (C++) which enables implementation of a wide range of force field types, *particularly reactive force fields*, including ReaxFF.



CPU Time per timestep:
serial code: 2.8 seconds
parallel code: 0.6 seconds
(32 CPUs)

System size limits:
serial code: 5000 atoms
parallel code: 500,000 atoms
(510 CPUs)

ASC Flash:
2.0-GHz procs
8 GB memory per node

ReaxFF Summary

Can simulate chemistry for a wide range of materials significantly faster than ab initio and semi-empirical methods

Accuracy similar to semi-empirical methods

Hydrocarbons, CHNO explosives, silicon oxides, etc.

Main limitation is governed by the size of reaction training set

Used extensively for explosives under extreme conditions - many possible reactions

Simulation sizes up to a half million atoms

