The Valence Multipole Model: Using small molecules to create a new bond energy expression for Molecular Mechanics

M. C. F. Wander
Dept. of Geological Sciences
Brigham Young University

The Group

Co-PIs:

Prof. Barry Bickmore

Dr. Matthew Wander

MS Students:

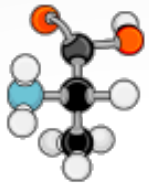
Matthew Davis

Charles Andros

Undergraduate Students:

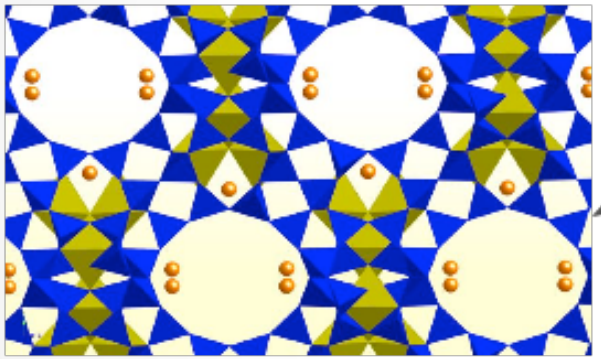
Kendrick Shepherd
Joel Johansen
Larissa Lind
Rose Frank
Kat Robertson
Delyn DeHoyos
Hannah Checketts

John Hunt
Bart Yeates
Chris Shurtleff
Lincoln Gee
Josh Whitmer
Ashley Jarvie
Michael Arnold

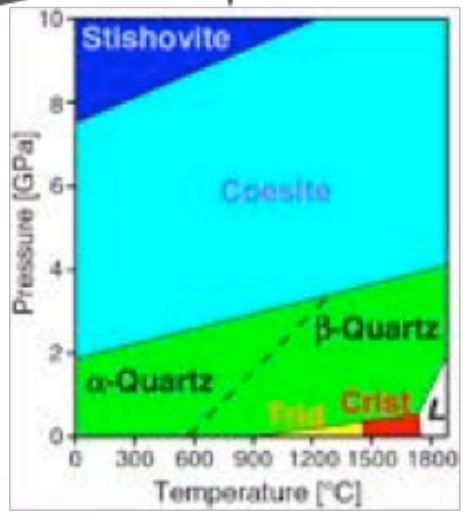


Molecular Modeling

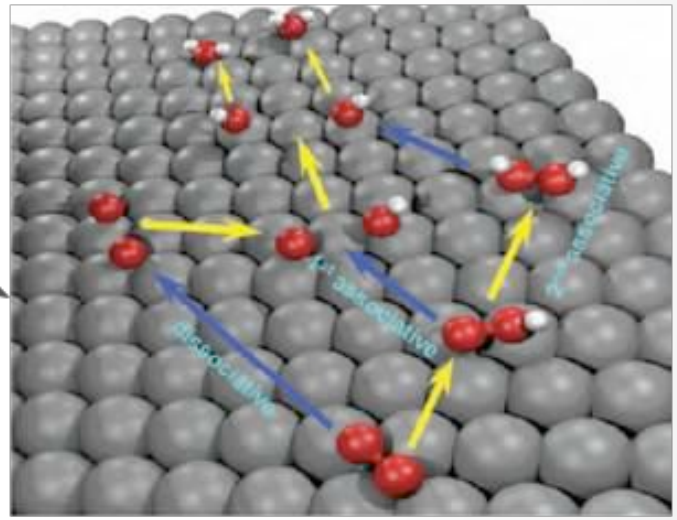
can predict



Structures

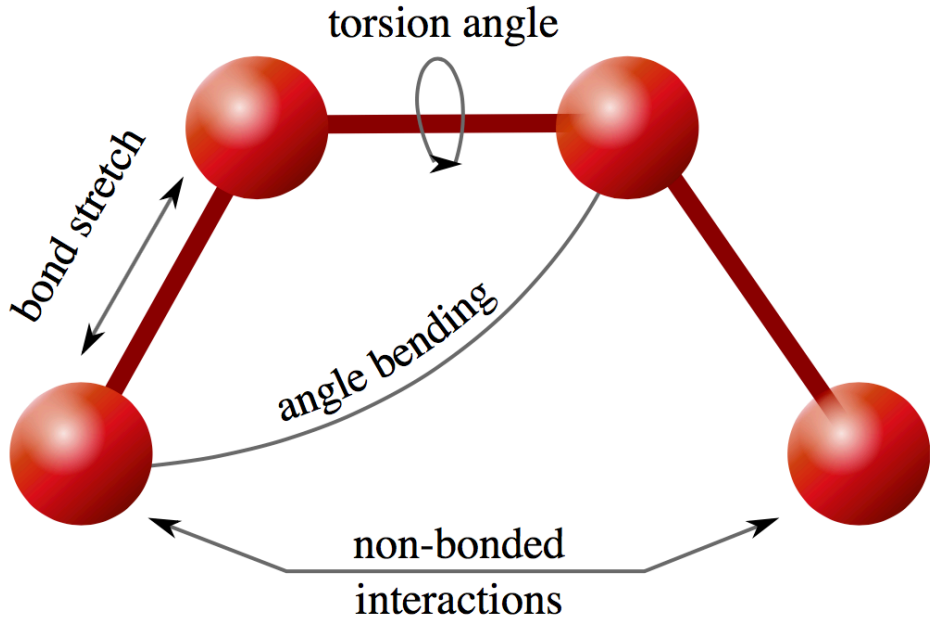


Thermodynamic Properties

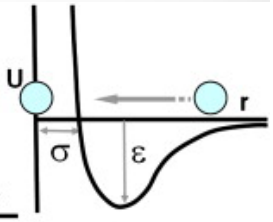


Reaction Mechanisms

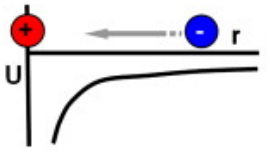
Traditional Molecular Dynamics



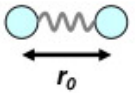
$$U = \sum_{i<j} \sum 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$



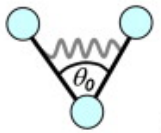
$$+ \sum_{i<j} \sum \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$$



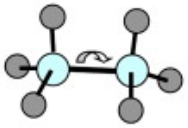
$$+ \sum_{bonds} \frac{1}{2} k_b (r - r_0)^2$$



$$+ \sum_{angles} \frac{1}{2} k_a (\theta - \theta_0)^2$$



$$+ \sum_{torsions} k_\phi [1 + \cos(n\phi - \delta)]$$

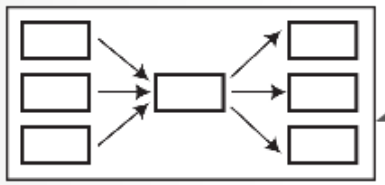


Problems with MM

- There isn't really a single ideal bond length or bond angle value for a given bond type.
  - MM structures tend to be too symmetrical
  - Usually can't do coordination number changes
- The number of "adjustable parameters" in a MM model goes up AT LEAST proportionally to the number of atom types squared (often n^3 or n^4).
  - Especially ridiculous in models that allow chemical reactions
  - Exception: Rule-based models, which can do the entire periodic table, but generally suck.
- Models tuned to reproduce experimental data in a VERY NARROW range of chemical scenarios.

Models

include



Conceptual

$$|s_{ij}| = e^{\left((R_0 - R)/B\right)}$$

Mathematical

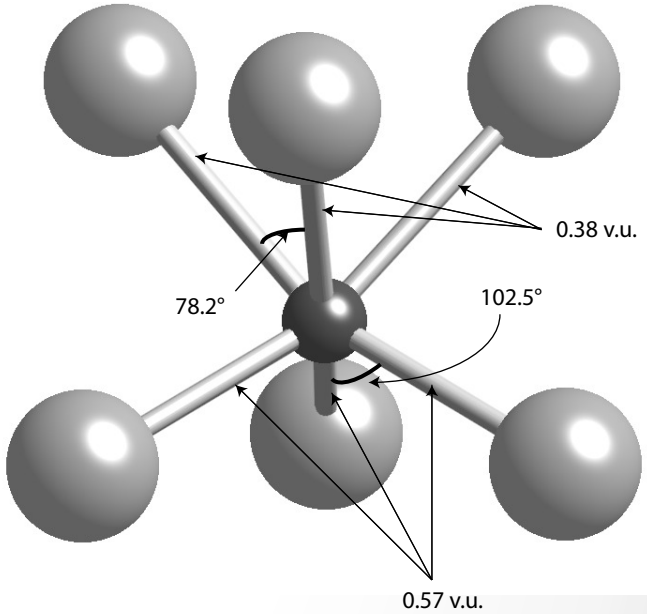
Physical

inform

The Bond-Valence Model

Definitions:

- ***Atomic Valence (V_i):*** a measure of the number of valence electron states available for bonding.
  - Usually taken as the oxidation number



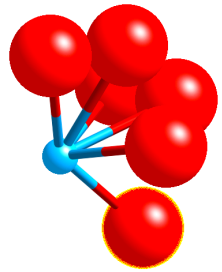
- ***Bond Valence (s_{ij}):*** the number of electron pairs involved in a given bond (by sharing and/or electron transfer).
  - Equivalent to "bond order", related to bond length
  - Does not have to be an integer!

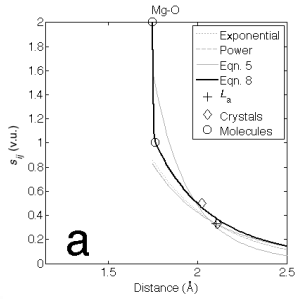
$$\left|S_{ij}\right| = e^{\left((R_0 - R)/B\right)}$$

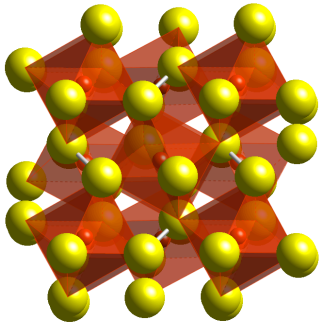
$$\sum_j s_{ij} = |V_i|$$

Problems With the BVM

1. Only addresses bond lengths, not the angular distribution of bonds.
2. Since its calibrated for crystals molecules have had big misfits.
3. Only addresses polar bonds, not 100% covalent bonds.
4. Nobody has a clear idea how bond valence relates to energy.



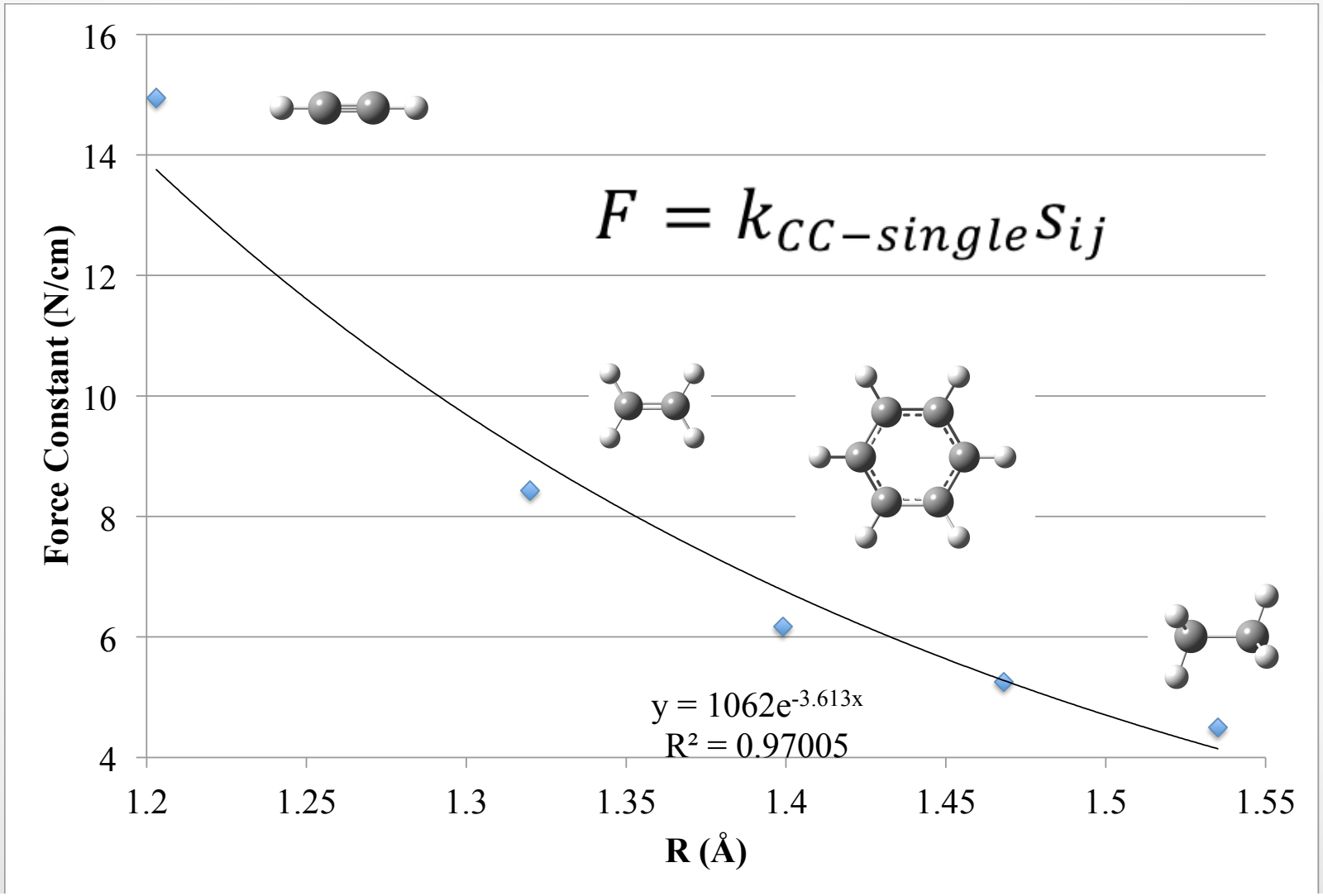




Shepherd et al. The Valence Quadrupole Moment. Am. Min. Submitted 2015.

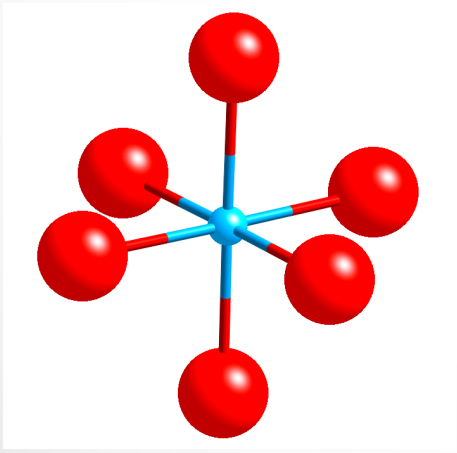
Wander et al., The use of cation-cation and anion-anion bonds to augment the bond-valence model, Am. Min. 2015.

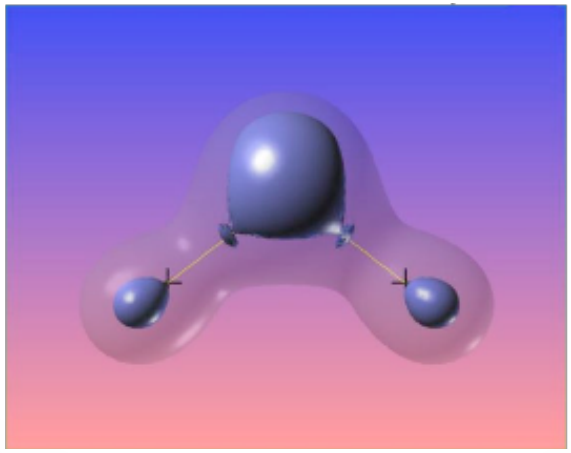
Johnson's Force Constant Model of Bonding

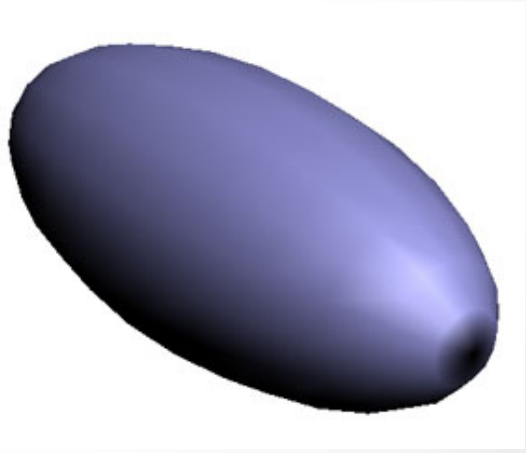


Valence Multipole Model

- Breaks energy into total bonding (S_{Total}): monopolar, no directionality, Vector (VVS): dipolar, non-centrosymmetric, quadrupole(QVS): centrosymmetric….







- Bickmore et al., Electronic structure effects in the vectorial bond-valence model, Am. Min. 2013

A More Flexible Equation

- One of a family of forms (exp-exp, pow-pow, geometric).

$$|s_{ij}| = (1-w)(R/R_0)^{-1/B_{pow}} + we^{(R_0-R)/B_{exp}}$$

- Can flexibly and accurately fit anything from triple bonds to bonds as small as a few hundredths of a bond order.
- Suggests ionic-covalent character change around 1v.u.

Wander et al., AIM analysis and the form of the bond-valence equation, Am. Min. 2015

Energy Expression

- Many body energy (atom centered) composed of only two body terms (Bond Valence Vectors).

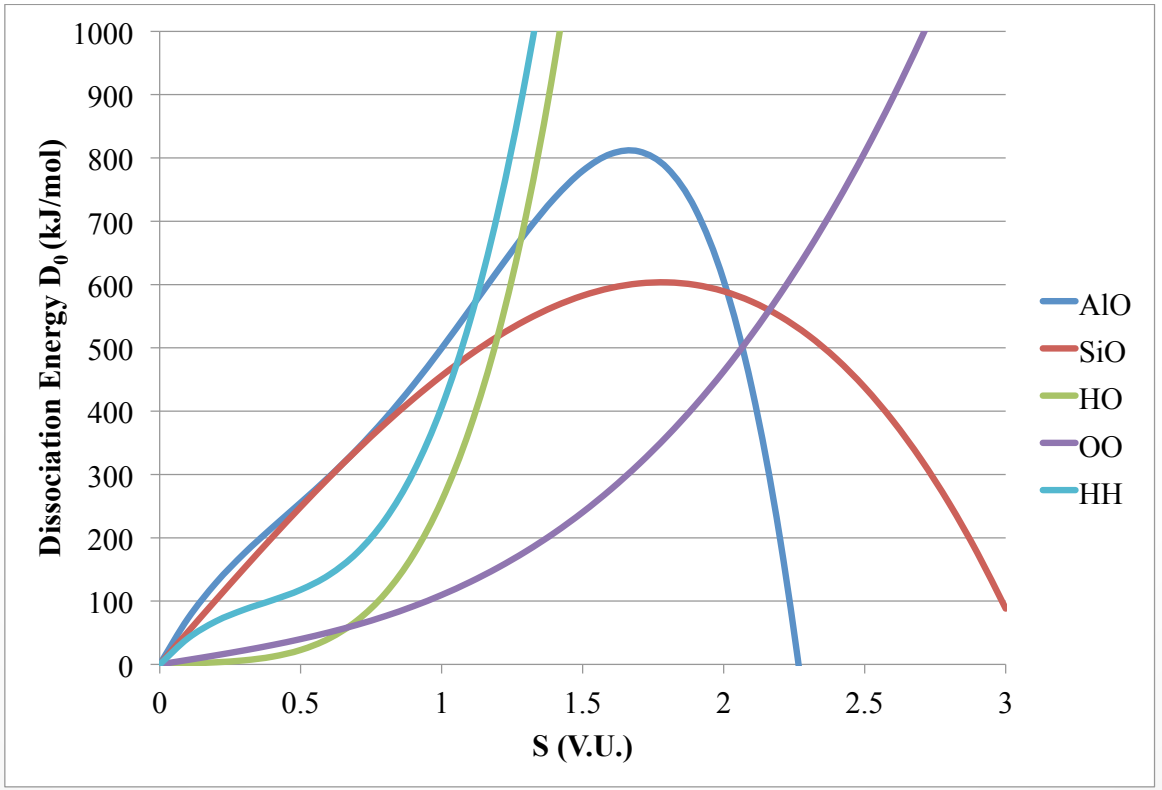
$$E_{Total} = \frac{1}{2} V_I D_{E1} \left(\left(\frac{S_{Tot}}{V_I} \right)^{B \sqrt{\frac{F_1}{2D_{E1}}}} - 1 \right)^2 + k_{VVS} (VVS - VVS_{Ideal})^2 + E_{QV} + E_{Charge}$$

- Bond energy only definable in context of other bonds reaching an atom.
- VVS_{Ideal} depends on number and row number (electronegativities) of atoms surrounding it.

Wander et al., The Valence Multipole Model. In Prep. 2015.

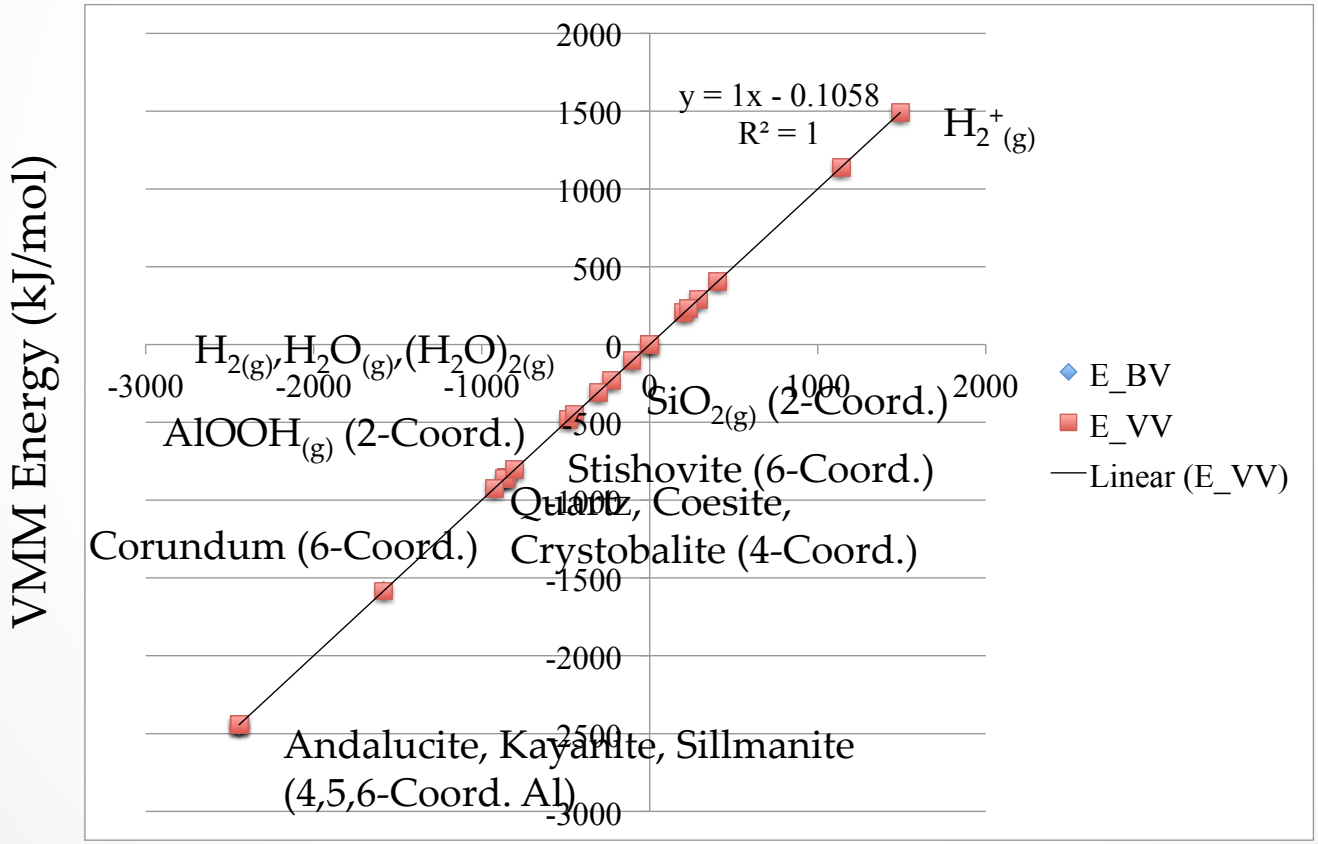
New challenges

- Quality bond energy per unit valence curves essential to getting high accuracy predictions.



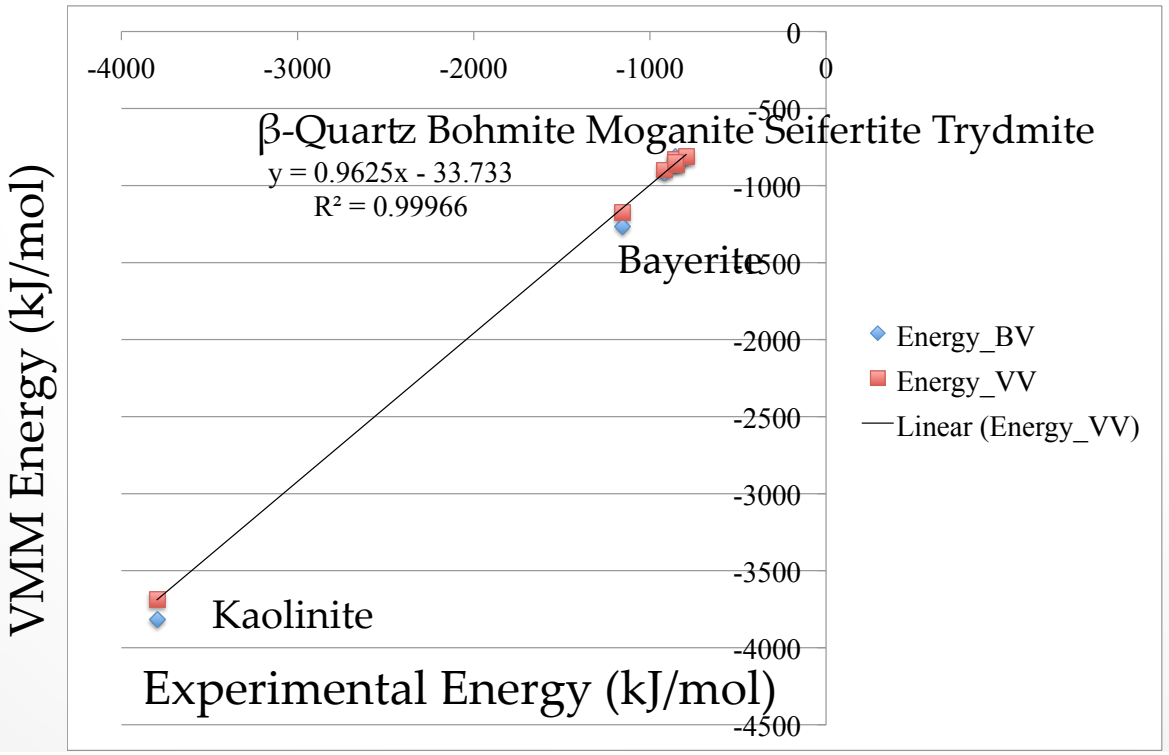
AlSiHO Fitting Set Results

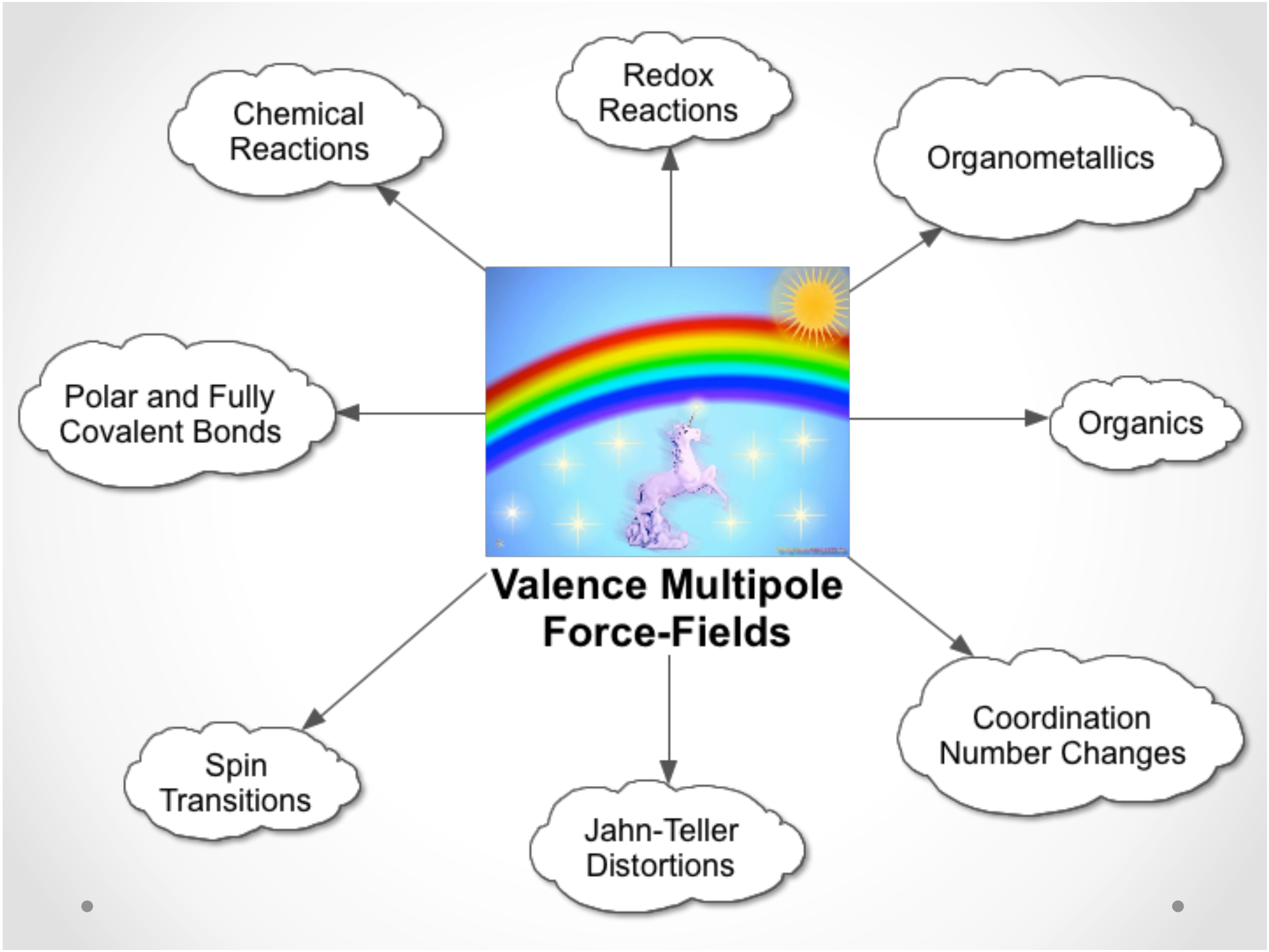
- Fitting Set Contains Both Molecules and Crystals



AlHSiO Check Set

- Some outliers: Unsatisfied Valences (Radicals), Bad Vector Sums (Poor H Positions).
- Otherwise errors less than 5kJ/mol/atom.
- Results oxidation state dependent. Reduced Ai Si different force field.




Chemical Reactions
Redox Reactions
Organometallics
Polar and Fully Covalent Bonds
Organics
Valence Multipole Force-Fields
Spin Transitions
Jahn-Teller Distortions
Coordination Number Changes

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