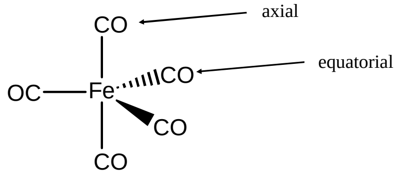
Modeling Metallic Systems

Challenges - I

- Presence of non-equivalent positions around the metal for some geometries



- One solution: different atom types (and parameters for axial vs. equatorial atoms)

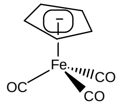
Challenges - II

- Inorganic complexes often have easily deformable geometries (requiring small force constants)

  Thus geometries far from the equilibrium geometry are common (and not well-reproduced by harmonic or quadratic approximations used in most force fields for bond stretching and angle bending)

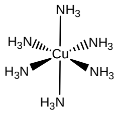
Challenges - III

- Coordination of inorganic compounds is often fluctional
  - A single metal can form complexes with different coordination numbers
  - Coordination numbers are dependent on ligands
  - Coordination numbers when ligands coordinate through a pi system are somewhat ambiguous



Challenges - IV

- Electronic effects can cause large distortions in geometry
  - Electronic nature of ligands 180° apart can strongly influence bond lengths
  - Jahn-Teller distortions can change bond lengths in otherwise apparently equivalent positions

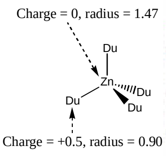


Asymmetric structure, with axial Cu-N bond lengths of 2.62 Å, and equatorial bond lengths of 2.07 Å

Options

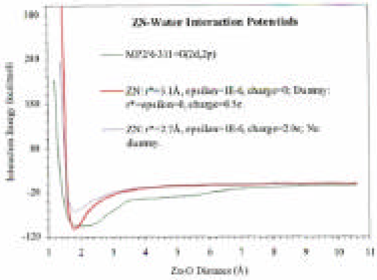
- Standard force field with lots of added parameters and atom types
- Ionic model using dummy atoms to drive coordination geometryDevelop force fields with altered functional form (UFF, SHAPES, ESFF)
- Purely ionic model, VDW drives coordination geometry (Yeti)
- Points-on-a-sphere (VDW-based)

Ionic Model + Dummy Atoms

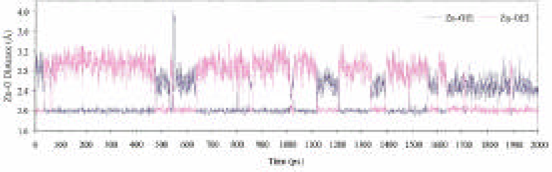


Charge = 0, radius = 1.47

Charge = +0.5, radius = 0.90



Ionic Treatment Allows Ligand Exchange

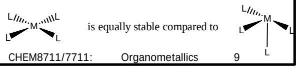


Universal Force Field (UFF)

- Angle Term Functional Form

$$E_{angle} = k_q \left[\frac{2\cos^2 q + 1}{4\sin^2 q} - \frac{4\cos q_0 \cos q}{4\sin^2 q} + \frac{\cos 2q}{4\sin^2 q_0} \right]$$

- Periodicity of cosine function provides for multiple bond angle minima
  - Example: fourfold cosine term gives minima at 90 and 180 °
- Still problematic:
  - trigonal bipyramidal structures
  - square planar structures



is equally stable compared to

ESFF (available in Cerius2)

- Addresses many previously identified problems using:
  - Different functional forms (compared with force fields developed for organics)
  - Rule-based parameterization based on relatively small number of atomic parameters

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ESFF Bond Energy

- Bond types defined based on
  - bond order
  - π one-pair interactions
  - symmetry position (axial/equatorial)
- Functional form: Morse potential
  - D_{bi}: bond dissociation energy
  - α_i: characterizes bond anharmonicity

$$E_{bi} = D_{bi}\left\{1 - \exp\left[-a_i \underbrace{\left(r - r_i^0\right)}_{\text{Displacement from standard value}}\right]\right\}^2$$

ESFF Bond Energy (cont’d)

- Rule-based parameterization
  - D_{bi} follows Pauling’s definition of electronegativity

$$D_{bi} = \overbrace{D_{bi}^0}^{\substack{\text{Sum of atomic bond parameters for two bonded atoms} \\ \text{(physically represents bond dissociation energy for two of same atom type in given bond type)}}} + \underbrace{G_{bi}}_{\text{contribution due to electronegativity difference of bonded atoms}}$$

$$G_{bi} = 23.0609\left[\frac{\overset{\text{electronegativity difference}}{(c_1 - c_2)^2}}{\underset{\text{hardness difference}}{2(h_1 - h_2)}} \underset{\text{dative bond correction}}{d_D d_d} - \underset{\text{high order correction}}{k_i}\right]$$

ESFF Bond Energy (cont'd)

- Additional rules allow parameterization of
  - electronegativity (χ): first derivative of atomic energy with respect to atomic charge
  - hardness (η): second derivative of atomic energy with respect to atomic charge
  - anharmonicity (α)
  - bond reference value (r_i^0): function of covalent radii, hardness, electronegativity, ionization potential and corrections for axial and dative bonds
  - ionization potential: function of atomic energy difference of +1 and 0 charged atoms

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ESFF Validation

- 555 experimental crystal structures minimized with ESFF
- All elements except Na, Rb, Cs, Tc, Bi, Po, At, and rare gases represented

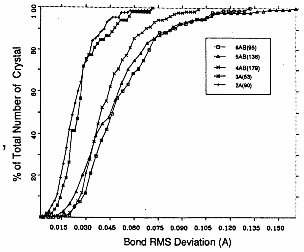

Figure 7. The percentages of total number of crystals as functions of bond RMS deviation in Å are plotted for the crystals involving the elements in the different rows of the periodic table.

Reading

- S. Shi, L. Yan, Y. Yang, J. Fisher-Shaulsky, T. Thacher "An Extensible and Systematic Force Field, ESFF, for Molecular Modeling of Organic, Inorganic and Organometallic Systems", J. Comput. Chem., 2003, 24(9), 1059-1076.
- C. R. Landis, D. M. Root, T. Cleveland "Molecular Mechanics Force Fields for Modeling Inorganic and Organometallic Compounds", Reviews in Computational Chemistry, Volume VI, K. B. Lipkowitz and D. B. Boyd, Eds., VCH Publishers, Inc., New York, 1995.
- Y. –P. Pang "Novel Zinc Protein Molecular Dynamics Simulations: Steps Toward Antiangiogenesis for Cancer Treatment", J. Mol. Mod. 1999, 5, 196-202.