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 fluctual
  - 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 geometry
- Develop 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

### Universal Force Field (UFF)

- Angle Term Functional Form
  \[ E_{\text{angle}} = K_a \left( \frac{2 \cos^2 \theta + 1}{4 \sin^2 \theta} - \frac{4 \cos \theta \cos \theta}{4 \sin^2 \theta} + \frac{\cos 2\theta}{4 \sin^2 \theta} \right) \]
- 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

### 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

### 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
  - \( \alpha_i \): characterizes bond anharmonicity
  \[ E_{bi} = D_{bi} \left( 1 - \exp \left( -\alpha_i (r - r_i^0) \right) \right)^2 \]

**Displacement from standard value**

<table>
<thead>
<tr>
<th>Bond Energy (cont’d)</th>
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<tbody>
<tr>
<td>Rule-based parameterization</td>
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<tr>
<td>( D_{0i} ) follows Pauling’s definition of electronegativity</td>
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<tr>
<td>Sum of atomic bond parameters for two bonded atoms</td>
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<tr>
<td>( (\text{physically represents bond dissociation energy for two of same atom type in given bond type}) )</td>
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<tr>
<td>( D_{bi} = D_{0i}^0 + G_{bi} )</td>
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<tr>
<td>contribution due to electronegativity difference of bonded atoms</td>
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<tr>
<td>electronegativity difference</td>
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<td>hardness difference</td>
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<tr>
<td>Dative bond correction</td>
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<td>High order correction</td>
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**Displacement from standard value**
ESFF Bond Energy (cont'd)

- Additional rules allow parameterization of
  - electronegativity ($\chi$): first derivative of atomic energy with respect to atomic charge
  - hardness ($\eta$): second derivative of atomic energy with respect to atomic charge
  - anharmonicity ($\alpha$)
  - bond reference value ($r^0$): 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

ESFF Validation

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

Reading