

# Computational Chemistry for Inorganic Chemists

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## Computational Chemistry for Inorganic Chemists

This course will explore the foundations and use of computational chemistry methods as applied to inorganic systems.

- Introduce generally used computational chemistry methods with enough mathematical detail to understand the method, accuracy, and common usage.
- Provide a broad sense of understanding so that the theoretical component of a combined synthetic/theoretical paper can be understood, and the quality of the work assessed.
- Develop an understanding of potential energy surfaces, how they are explored and represented, and what relationship they have to reaction paths.
- Describe the physical properties that can be calculated, and how such calculations can help in interpreting spectra or in analyzing mechanisms.
- Develop an understand how electronic structure and molecular dynamics calculations can be used as an aid for interpreting chemical bonding and reactivity.

The course will be taught in both lecture and tutorial format with discussion of the materials and case studies given out before each meeting.

**Important:** preparation for each meeting is essential.

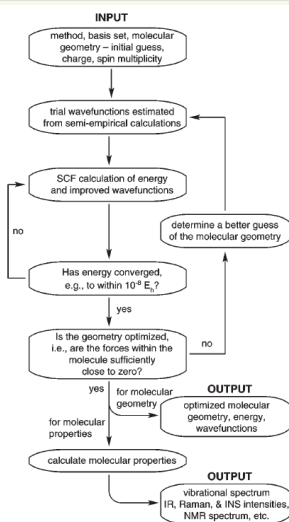
January 17, 2012

Computational Chemistry for Inorganic Chemistry

2

## Electronic Structure Calculations

Flowchart illustrating the steps involved in quantum chemical calculations of molecular structures and properties.



January 17, 2012

Computational Chemistry for Inorganic Chemistry

3

## Computational Chemistry in Inorganic Research Papers

### Electronic Structure Calculations: Salient Points

**The Method:** The Density Functional Theory (DFT) will generally be used for transition metal compounds.

However, it may also be possible to use Hartree-Fock methods including electron correlation.

**The Basis Set:** Generally the 6-31G\* basis is used for ligand atoms composed of H, C, N, O.

The LANL2DZ, SBKJ, SDD, basis plus polarization functions is used for heavy atoms (P, Cl, S, ...) and transition metal atoms.

These basis sets use an effective core (ECP) because of a sharp increase in computation time is required to treat atoms of large atomic number  $Z$ . The ECP method circumvents this problem by replacing the core electrons with an approximate pseudopotential.

This is useful in most cases since it is the valence electrons that determine many chemical properties such as bond strengths, polarizabilities, electron affinities, and ionization potentials, as well as molecular geometries.

**Energies** Results based on small energy differences ( $\leq \sim 5$  kcal/mol) between calculated structures may be suspect.

**Geometries** Structures may be accurate to  $\sim \pm 0.01$  Å except when comparing similar systems qualitatively.

**Models** Model compounds are frequently used in calculations to reduce computational time.

For example, to model isomers of  $\text{Mo}(\text{CO})_4\text{L}_2$  where  $\text{L} = \text{PPh}_3$ , it is possible to replace the phenyl rings with less computational demanding Cl atoms which have a similar electronic contribution to bonding as phenyl groups and are sterically quite large.

Check to make sure the substitution makes sense from a chemical, electronic, and steric point of view.

**Programs** There are many programs capable of performing electronic structure calculations including Gaussian, GAMESS, ORCA, NWChem, Molpro, Molcas, ...

They all are capable of giving similar results for certain properties, but also have specific capabilities.

January 17, 2012

Computational Chemistry for Inorganic Chemistry

4

## Electronic Structure Calculations: Many Choices

### Which Method?

Density Functional Theory (DFT) as it gives the most accurate results for transition metal and organometallic compounds using a smaller amount of computational resources.

### Which Basis Set?

Basis sets are approximations to atomic orbitals.

The LANL2DZ or SDD basis sets are usually used for transition metals, and all-electron basis sets (6-31G\*) are used for ligand atoms.

### Which Property to Calculate?

Geometry Optimization, Vibrational or Electronic Spectra, Reaction Coordinate

## Quantum Chemistry Calculations In a Research Paper

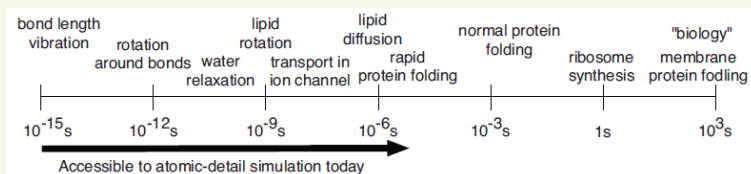
### A Computational Chemistry Section in a Research Paper Might Look Like ...

All calculations were performed with the Gaussian 09 (G09) electronic structure package with the B3LYP functional with unrestricted wave functions used for all triplet state calculations.

The LANL2DZ basis which included an ECP + double zeta valence was used for Rh, P, and CL, while the 6-31G\* basis was used for C, N, and all H atoms.

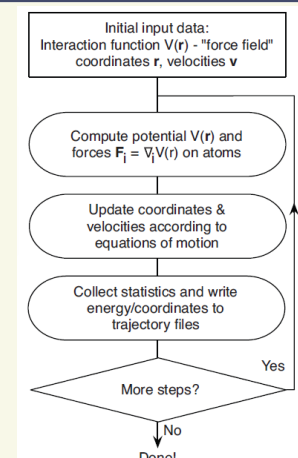
All optimizations were performed with C1 symmetry, and all minima were confirmed by analytical calculation of frequencies. Zero point energy corrections were calculated without scaling.

## Molecular Dynamics Simulations



## Molecular Dynamics Simulations

### Simplified flowchart of a standard molecular dynamics simulation



## Molecular Dynamics Simulations in a Research Paper

All molecular dynamics simulations were carried out using the CHARMM program. The minimizations were done using 1500 steps of Newton-Raphson minimization. The calculations included explicit water molecules. The stochastic boundary method was used to increase computational efficiency. The reactive region had a radius of 16 Å around the [3Fe-4S] cluster, and the buffer region was 5 Å in thickness.

The systems consisted of 1637 protein atoms and 469 water molecules for 7FDR, and 1639 protein atoms and 462 water molecules for the D15N mutant, respectively. Simulations were carried out using Langevin dynamics (LD) with friction coefficients of  $62 \text{ kcal mol}^{-1}$  for water molecules and mass-scaled friction coefficients (up to  $250 \text{ kcal mol}^{-1}$ ) for heavy atoms in the buffer region.

Non-bonded interactions were damped using a switch function for the van der Waals terms and a shifted function for electrostatics at 12 Å. SHAKE was used to constrain the hydrogen bond lengths and the time step was 1 fs.