COMPUTATIONAL CHEMISTRY at NASA – AMES Research Center, Silicon Valley, CA.

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What is Chemistry? Why study it?

- Chemistry involves the study of substances, materials, matter, their properties, structure, and the changes they undergo.
- Matter is the physical material of the universe; it is anything that has mass and occupies space.
- A property is any characteristic that allows us to recognize a particular type of matter and to distinguish it from other types.
- Chemistry is the "central" science because it serves as the interface to practically all of the other sciences as well as to many other areas of human endeavor.

The Main Branches of Chemistry

1. Analytical Chemistry
2. Biochemistry
3. Inorganic Chemistry
4. Organic Chemistry
5. Physical Chemistry
   a. Theoretical / Computational Chemistry
   b. Experimental Chemistry

How do we study Chemistry Effectively?

- Chemistry is an empirical science that can be approached from either the **experimental** viewpoint, and / or the **theoretical** viewpoint. Some folks believe that it is the theoretical "horse" that pulls the experimental "cart" in most cases.
- From the theoretical viewpoint emanates **computational chemistry,** and /or **computational photochemistry,** as major fields of study used to investigate chemical processes at the atomic/molecular level through the absorption of radiant energy, in terms of properties; reactivity; modelling of basic chemical reactions; and the computer-aided development of novel materials for use in fields such as **photodegradation** (paints), **photoprotection** (sunscreens), color regulation (**photochromic devices**) and **fluorescent probes**.
- This field of research also finds relevance in **solar photochemical energy conversion** which is an important option for the generation of electricity and chemical fuels.
- The theoretical information obtained from these investigations will be of interest in such research areas as **organic** and **inorganic photochemistry**, **photocatalysis**, **photoinduced electron** and **energy transfer** in the condensed phase and across interfaces, **photoelectrochemistry,** and artificial assemblies for charge separation and transport that mimic natural photosynthetic systems..

What is Computational Chemistry?

- **Computational chemistry** utilizes **mathematics** and **computers** to solve chemical problems. By utilizing computer software, chemists can simulate experimental results and find properties of substances. The field of computational chemistry helps to explore things that would otherwise be difficult or costly to find because of the tiny nature of molecules, atoms, and nanoparticles. Much of the field is based upon the **Schrodinger equation**, which models atoms and molecules using mathematics. Ab initio, semi-empirical, and molecular mechanics are methods of computational chemistry often used to analyze molecular structures.
- The computational chemistry process begins by looking at a theory, such as the **Electronic Structure Theory.** This helps to determine the motion of the electrons within a molecule. At this point, using mathematical equations, a basis set can be determined based upon the calculations. This information can be inputted into computer software to describe such things as the wave function, which can be used to create models of other physical characteristics of the molecule. Chemists can see a model of the orbitals of the molecule, begin predicting experimental structures, and look at the energy of the molecule.
- Using ***ab initio calculations*** allows chemists to look at physical properties of a substance and use the Schrodinger equation to find out physical characteristics of molecules. This includes such things as the geometry of molecules, the dipole moment, and the energy of a reaction. Vibrational frequencies, the reaction rate, and free energy can also be found using ab initio. Since these physical characteristics are extremely difficult to solve, it is necessary for computational chemists to simplify them enough that the physical characteristics can be found and still be accurate.

Molecular Mechanics

- Molecular mechanics is a method of computational chemistry used in biochemistry experiments and applications. This method can be used for larger structures such as enzymes and relies on traditional physics, but is not able to calculate electronic properties in substances. The field of computational chemistry is constantly changing as technology advances and new theories are developed.
- These techniques allow chemists to examine structures that would be nearly impossible to look at otherwise, due to their extremely small size. Nanoparticles, which are smaller than atoms, can be modeled for use in applications such as electronics, explosives, and medicine. Since much of computational chemistry is based upon modeling of known properties, there is room for error in these experiments. This is why advanced training and knowledge in chemistry and research are necessary to work in computational chemistry.

Computational Chemistry at NASA-Ames Research Center

- NASA-Ames RC has been designated as NASA's lead center for information technology.
- Computational Chemistry began at **NASA Ames Research Center in 1971** with the help of **Dr. A.C. Wahl**, and several other eminent quantum chemists.
- This effort has flourished for more than three decades because of their ability to predict observable physical properties of molecules from first principles (*ab initio*).
- This heritage is briefly recounted and a summary of the group's recent activities is presented

Computational Chemistry, Aerothermodynamics Branch NASA Ames Research Center: Summary of Topics

1. ab initio calculations involving diatomic molecules: The results obtained from the ***ab initio*** calculations, and the properties derived from them have been obtained for several diatomic molecules that are important in **entry / re-entry physics studies** for a new class of NASA's space vehicles (to fly in the 1988 to 2000 time frame) and for photodiagnostics of gases in cold aerodynamic flows and combustion environments.
2. Combustion Studies: Recent results on hydrocarbon species of interest for studies of combustion.
3. Ab initio studies of large clusters of transition metal atoms in the presence of H, O and CO relating to the nature of chemisorption and understanding mechanisms involved in catalysis and hydrogen embrittlement.
4. Computational Molecular Nanotechnology: using computation to understand, design and control programmable molecular machines, their products, and related manufacturing processes. Such machines could revolutionize launch vehicles, spacecraft, aircraft, and computer systems.

Computational Molecular Nanotechnology at NASA Ames Research Center

- Specifically, computation will allow Ames and partners to:

1. Compute what the law of physics and chemistry allow but is beyond the state-of-the-art in fabrication.
2. Work with experimentalists to gain deeper understanding of results leading to faster progress.
3. Design molecular systems with billions of interconnect parts executing complex software instructions. Note: a flawed molecular manufacturing system may convert to carbon dust on failure making debug difficult. Test and validation via simulation are essential.
4. Control complex molecular manufacturing systems and products.

NASA-Ames Strengths

- A robust program in **computational molecular nanotechnology** requires massive **computational capabilities**, excellent **computational chemistry expertise**, and **expertise in the most capable existing "nanotechnology" -- molecular biology**. Ames has all three.
- **Supercomputers**. The NAS supercomputer center at Ames, originally developed for computational fluid dynamics, is an excellent computational resource. In addition to large scale operational vector supercomputers, NAS has experimented for many years with massively parallel supercomputing. The Ames nanotechnology initiative has focused on these resources.
- In addition to acquiring, configuring and maintaining the supercomputers, a nationwide network, and a large local network of workstations, NAS has developed tremendous expertise and capabilities in supercomputing related software such as:
  - Parallel algorithms and tools
  - Visualization
  - Virtual reality
  - Supercomputer benchmarks
  - Mass storage
- **Computational chemistry**. The NASA Ames computational chemistry branch has long exercised their world class expertise to understand **atmospheric** and **space chemistry** (such as the effects of low Earth orbit atomic oxygen bombardment) affecting aircraft and spacecraft. Turning to nanotechnology, they have used their molecular structure and classical dynamics expertise to design nano-size tools and components, determined reaction mechanisms and rates to address questions of mechano-syntheses, and are addressing questions of entropy and finite temperature on the stability of nano-devices.
- **Computational molecular biology**. Collaboration between the nanotechnology group and computational molecular biologists at Ames has just begun. The biologists have been studying hypothetical molecular mechanisms that may have existed in early proto-cells. This is part of investigations into the origin of life. Similar mechanisms are of considerable interest in nanotechnology

Current Activities at Ames

- Fullerene nanotechnology. The NanoDesign project is developing a hypothetical functionalized fullerene based nanotechnology. This project is presently focused on development of gears made of carbon nanotubes with o-benzyne teeth [Han 96], design software [Globus 96], parallelized molecular dynamics based on Brenner's potential [Brenner 90], and quantum calculations characterizing the teeth [Jaffe 96a]. This work points to a nanotechnology that is relatively synthetically accessible.
- Diamonoid mechanosynthesis. This work investigates reaction pathways for diamond creation.
- Properties of clusters. This work investigates the properties of matter for clusters up to sizes exhibiting bulk properties.
- Nanotube strength. The tensile strength of various carbon nanotubes is determined using Brenner's potential [Brenner 90].
- Entropy and temperature effects. Methods are under development to address questions of entropy and finite temperature on stability of nanodevices.
- High density atomically precise memory. See above [Bauschlicher 96].
- Laplacian of the Electronic Charge Density. This project uses FAST to visualize and understand molecular electronic structure and reactivity.
- A grant program in computational nanotechnology (see the synopsis). Proposals were due on 15 October 1996. We expect another call for proposals next year.
- The NAS parallel supercomputers are supporting six 1997 operational year proposals in computational molecular nanotechnology; up from one in 1996. Computational scientists from CalTech, Harvard University, North Carolina State University and the University of Kentucky, among others, will use the NAS computers to study nanotechnology. Parties interested in access to the NAS parallel supercomputers for preliminary investigations to prepare for 1998 operational year proposals should contact the author.
- A workshop on computational molecular nanotechnology sponsored by NAS was held on March 4-5, 1996 at NASA Ames Research Center

Milestones

- The ultimate goal at NARC is to use **programmable molecular machines to build aerospace systems**; and our piece of the problem is the computational aspect.
- Develop a software environment conducive to research: Two software environments are in place:
  1. the **NanoDesign [Globus 96] software** for development and
  2. **the Cerius2 and Insight/Discover commercial computational chemistry software** for standard operations and small, special purpose development efforts.
- Develop **a numerically validated atomically precise replicator point design** within five to seven years. The system should be able to reproduce and build something of aerospace interest. The chosen product is any long thin structure with tensile strength comparable to diamond. Such structures are necessary for orbital towers in the very long term. However, any increase in fiber length should be of great near term value in aerospace composites production. The replicator design may use either terrestrial or orbital conditions and does not necessarily need to be efficient or synthetically accessible although these properties are desirable.
- Develop **a molecular manufacturing CAD system in ten to fifteen years**. Searching the space of all possible molecular manufacturing systems for efficient and synthetically accessible systems is extremely difficult. The CAD system is to support such an engineering development. The system must support environmental conditions consistent with terrestrial laboratories and orbital conditions where micro-gravity and hard vacuum are readily accessible.
- Develop **a numerically validated, synthetically accessible, efficient molecular manufacturing system design** within fifteen to twenty-five years.

Computational Photochemistry at ECSU

- The main thrust of the work we would like to do at ECSU in this regard **is to train undergraduate students** majoring in biology, chemistry, computer science, physics, who are in their junior, and senior years, in computational photochemistry in order to stimulate their interests into pursuing this field at the graduate level, thereby enhancing the professional STEM gainful employment pipeline.
- In the first part of their training, ECSU students will be introduced to the field of computational photochemistry through a course entitled**: "An Introduction to Computational Photochemistry".**
- The next phase in their training will involve **the use of the following research software**:
- ***MOLCAS*** – is a software program used in quantum chemistry, and it was conceived at Lund University in Sweden. The software allows one to conduct *ab initio* calculations involving electronic structure problems for molecular systems in both the ground state and in excited states.
- ***MOLCAS/Tinker***: The second software to be mastered by ECSU students allows MOLCAS to work in tandem with Tinker to perform quantum-mechanical and molecular modeling calculations.
- ***FIREFLY***: The third software to be used is called Firefly which is a quantum mechanics software program used for *ab ignition* and ***DFT*** calculations.

- The major emphasis in the research activity ECSU students will pursue will **focus on the development and application of the state-of-the-art computational protocols used for the simulation of the photophysical and photochemical processes in both isolated chromophores and in the condensed phase with the ultimate goal of using these methodologies to provide an atomic-level description of the mechanism of light energy transduction from the single-molecule level to more complex systems.**
- In collaboration with an NSF Gateway Center in Computational Photochemistry such as the **Computational Chemistry Grid** (https://www.gridchem.org/about/index.shtml), and a specialized laboratory, such as the **Laboratory for Computational Photochemistry and Photobiology at Bowling Green State University in Ohio** (?), ECSU student participants will be able to broaden their horizons in their training in this field, with the symbiotic benefit to the host laboratory and host university of them applying for admission into their Graduate Program for a master's or a terminal degree in this field. It is also possible for a new NSF-Gateway Center to be created through the powerful supercomputer clusters now existing at the Ohio Supercomputer Center (OSC), if it is not already a Gateway recognized by the NSF.

Computational Chemistry through Science Gateways

Summer Workshop for MSIs at ECSU – Summer 2015

This is a collaborative workshop where science gateways developers, application scientist and teachers from MSI institutions would work together to develop plans and venues to use the cyber infrastructure for computational chemistry, physical chemistry and photochemistry. This workshop will introduce Computational Chemistry Grid cyber infrastructure to the participants and present how it is being used by research and teaching communities presently. During this workshop we will develop plans for using XSEDE resources for integrating computations with curriculum with specific examples from current exemplars. We will develop specific computational components, experiments for specific courses in physical chemistry and photochemistry by identifying aspects of the curriculum for which computational chemistry is a critical adjunct. We will demonstrate research projects at MSIs where computations are used successfully and identify potential new research projects for the faculty and obtain requirements for future projects that can be supported by the cyber infrastructure.