

## 2011-12 UPD Application

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Computational Investigations of Halogen Bonding

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COAS

Chemistry & Biochemistry

Rank: Full Professor

Tenture/TTrack

Lecturer:

Year appointed to TT: 1991

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Name::2:

Rank:

Tenture/TTrack

Lecturer:

Year appointed to T

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Name::3:

Rank:

Tenture/TTrack

3:Year appointed to TT:

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**Total funds requested**

**\$1,918**

Types of funds: Research, Scholarship, and C

Do you have other support for this project: **No**

Amount

Source of support:

Have you submitted or do you plan to submit this proposal to **No**

Amount requested:

Funding source:

Have you received a University Professional Development Grant In the past 3 years: **No**

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### Description-Outcomes-relevance

Computational quantum chemical methods allow theoretical chemists to address a myriad number of outstanding problems in molecular science. These techniques use various models to solve complicated mathematical equations in order to obtain information on the structure and energies of molecular systems. This information can then be used to make predictions about the chemical reactivity and physical properties of these systems. In some cases, this information can complement experimental observations, but in other cases computational techniques provide data and insight that is impossible to obtain through experimental methods. The accuracy of the predictions of computational quantum chemistry depends on the sophistication of the model used to solve the quantum mechanical equations describing the system. There are a number of commercially available computer programs for performing complex computational quantum chemistry, although very few encompass the advanced methods used by researchers specifically trained in quantum chemistry. The purpose of this grant is to purchase one such computational program for use in research. The generality of the methods available in the Gaussian'09 software package allows trained quantum chemists to tackle a variety of problems. This means that this software may be used for many years on different problems of interest. Although there are many areas that can be examined, the first one will be the effect of halogen bonding on the chemical properties of systems of importance in materials chemistry and biochemistry. The effect of halogen bonding on the properties of molecular systems is a fairly new area of research. Although the forces that hold individual molecules together are fairly well understood, theories that describe the intermolecular forces that hold two or more molecules together are still being developed. The interaction between molecules is important since it controls many of the chemical reactions that occur. Complex molecules may approach each other in a variety of orientations and the resultant chemical reaction is often determined by the intermolecular interactions that direct the approach of the reacting systems. For years, scientists have understood the importance of another well known intermolecular interaction called hydrogen bonding (which is not really a chemical bond, but a type of strong intermolecular interaction). This interaction is responsible for holding the two strands of DNA together, and it is also these attractive forces that are overcome when the strands of DNA unwind to replicate. The intermediate strength of this hydrogen bonding interaction, not too strong and not too weak, is what allows DNA to function as it does. The importance of hydrogen bonding also directs the chemical reactions catalyzed by many enzymes, increases the strength of materials such as nylon, and explains the unusual ability of water to dissolve so many compounds. As important as hydrogen bonding is, there are other types of intermolecular interactions that may play a role in determining the structure and properties of molecular systems. One such interaction has been termed halogen bonding. The influence of halogen bonding on molecular systems is just beginning to be explored in depth. Halogen bonding (which is not really a chemical bond, but an intermolecular interaction) occurs when the distribution of electrons in a halogen atom, such as bromine or iodine, is distorted due to the atoms that are chemically bonded to it. This distortion leads to a new interaction of variable strength with an electron-rich portion of a neighboring molecule, i.e. a halogen bond. So far, these interactions have been hypothesized as important in a number of processes. One recent publication has implicated halogen bonding in the activity of iodothyronine deiodinase, an enzyme that activates thyroid hormones. Halogen bonding may therefore be the reason why the element iodine is such an important component in the functioning of a healthy thyroid gland in humans. Another set of reports has indicated that a molecular complex formed through halogen bonding may be important in the action of certain drugs on the human immunodeficiency virus (HIV). A number of research groups are therefore testing HIV drugs that specifically contain one or more iodine atoms. In an different area of scientific research, halogen bonding has been associated with the specific 3D arrangement that certain crystals take and the properties they possess. A specific example is the drastic change in the non-linear optical (NLO) response of certain molecular systems when halogen bonding

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interactions are present. The NLO response is an important property in the design of new materials for carrying optical (i.e. light) signals through materials. Therefore an understanding of these effects can be used to design better fiber optic materials for carrying digital signals used in telecommunications. Given the potential importance of halogen bonding to a variety of areas in modern science, it would be useful to have more information as to the actual strength of these intermolecular interactions. So far, there appears to be some disagreement in the scientific literature as to exact importance of halogen bonding. A number of computational studies have indicated that halogen bonding is as strong as hydrogen bonding. However, the quantum mechanical methods used to obtain these results may be inadequate to give an accurate measure of the true strength of the interaction. The purpose of this proposed work is to use computational quantum chemistry to investigate the strength of halogen bonding with iodine in a number of medium-sized molecular systems. The methods used will be of high quality and therefore computationally time consuming, but should be able to clear up some inconsistencies in the scientific literature. Furthermore, this work will attempt to elucidate how and why halogen bonding interactions affect the properties of molecular systems. As part of this work, a comparison will be made between the importance of hydrogen bonding vs. halogen bonding interactions in influencing chemical and physical properties. Due to the subtleties involved in halogen bonding, high-quality computational data can only be obtained using quite sophisticated quantum mechanical methodologies. These methodologies are available in the Gaussian '09 program suite and provide the expert quantum chemist essentially all the software tools s/he needs to investigate intricate problems in chemical bonding and intermolecular interactions.

### Components-Activities

Since the purchase of the Gaussian '09 software is the only request in this proposal, the activity associated with the direct funding is rather well defined. The purchased software will be loaded onto one of the computers in the PIs laboratory and computations will begin immediately on selected halogen bonded systems. The initial studies will focus on the energies and structures of the systems under study. When this aspect of the project is well underway, then more extensive studies of the effect of halogen bonding on molecular properties will be started. (The specific molecular systems to be studied and properties investigated can be provided if more specific information is needed). I currently have an undergraduate student working on a similar project that uses less sophisticated quantum chemistry software and I am hoping that I can get another student to join the effort. However, progress on this project will occur whether or not more undergraduate students participate. With or without undergraduate research students, I will be involved intimately with the day-to-day work in this project.

### Timeline:

July 2011 Purchase Gaussian '09 software  
August 2011 – June 2012 Install software and perform calculations on halogen bonded systems

### Enhance Professional Growth

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The principal investigator (PI) in this proposed work has had many years of specific training in the area of computational quantum chemistry. However, during the past few years the demands of other aspects of his position at CSUSM have forced him put aside research work in his area of expertise. As will all skills, specific expertise in the area of quantum chemistry will slowly degrade from lack of use. This affects not only the ability of the PI to publish and effectively mentor undergraduate research students in this area, but also affects the quality of course instruction. Specifically, the PI teaches a core upper-division course for all Chemistry majors that is entitled Quantum Chemistry and Spectroscopy. Recently, the PI has had the pleasure of having an undergraduate student take up a project in computational quantum chemistry that looks at some aspects of halogen bonding using currently available software. It became obvious during this work that the computational tools needed to perform high-quality research and involve other undergraduate students are not currently available. Obtaining this copy of the Gaussian '09 suite of programs will supplement the less sophisticated quantum chemistry software currently used and allow higher quality calculations to be performed, thus increasing the chances of publishable results. Having additional software will also allow other students into the PI's lab to participate in undergraduate research. These students will be able to use the currently available low-level computational tools for preliminary work and make use of the advanced capabilities in the Gaussian '09 software when necessary. Being able to involve more students in this work is particularly important in the Department of Chemistry and Biochemistry where each undergraduate is required to perform two semesters of independent research under faculty guidance. While expanding the PI's knowledge of the rapidly changing area of computational quantum chemistry, it also will provide the PI with more applications to share with students in the upper-division core course in quantum chemistry.

### Supplies

Gaussian 09W	\$1000
GaussView5	\$750
CA Sales Tax	\$153
Shipping & Handling	\$15
TOTAL	\$1918

### Travel

Registration:	Mileage:Travel::
Lodging:	Auto Rental:
Air:	Parking:
Per diem:	Other:

### Consultants:

### Student Assistants:

### Other:

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### Faculty Assigned Time

Budget justification:

The Gaussian 09W for Windows and GaussView5 for Windows are both required in order to carry out the proposed work. Gaussian 09W is the computational software and GaussView5 is the graphical user interface used to set up the calculations and allow visualization of many of the calculated properties. The input for the calculations is so complex, it is virtually impossible to set it up without the GaussView5 interface.