

Atomic and Molecular Structure

Chemistry 421/521

Introduction

This is a course in quantum chemistry, in particular quantum chemistry applied to atomic and molecular structure. Quantum chemistry is often thought of as the application of the fundamental laws of physics, especially the laws of quantum mechanics, to chemical systems. We will be looking at both formalistic aspects of quantum chemistry and applications of quantum chemistry (quantum mechanics) ideas to some real chemical systems.

The course will begin with some formal lectures on "basic material" --- the idea being to bring everyone to approximately the same level in a relatively short period of time. I trust you all have had a decent undergraduate course in physical chemistry (using McQuarrie, Atkins, Levine, Engel or whatever...) that contained some quantum chemistry and spectroscopy. There will be several (or many) of these initial mini-topics that you have seen before [I hope ;-)]. Then we will move on to descriptions of the electronic structures of atoms and molecules, both theoretically and computationally. The overall focus will be on molecules, but the road to molecules goes through atoms. We will try to provide some answers to the question "What are electrons doing in molecules?" [a question attributed to Professor R. S. Mulliken (Chicago), "Mr. Molecule" and Nobel Laureate 1966; <http://www.nobel.se/chemistry/laureates/1966/>]. The mathematical and physical basis of a number of theoretical/computational methods will be discussed. We will also talk about applicability and reliability of these methods and provide examples, as appropriate. Several "models" based on molecular orbital theory will be described, since the Professor teaching the course is a big fan of "models".

A major revolution has taken place in the area of applied quantum chemistry in the last 10-20 years with the arrival and widespread use of computers as major new instruments on which we can perform experiments of chemical relevance. Computational quantum chemistry may be used as an interpretative as well as a predictive tool. It may stand on its own; complement experimental work; or even guide and suggest experimental work. We can perform chemical experiments on a computer, which can or can not be reproduced in a laboratory setting - sometimes you may not want to reproduce them in the lab at all...(simulations of nuclear waste treatment, for example). The use of computers in this course (Chem 421/521) dates further back than some of us want to remember (or be reminded of), well beyond the year of birth for all of you (!). Professor W. H. Adams (retired ~ 2000), who taught this material many times, introduced computer exercises back in the 1970's. Your current Professor in the course carried out his first quantum chemistry computer experiments more than 35 years ago (38 to be exact...boy, he must be old!).

Computer modeling of chemically relevant (and irrelevant) systems and their properties is made possible not only by the continuing developments in computer hardware, but also by software developments. The software people do probably not get the credit they really deserve. The 1998 Nobel Prize in chemistry was awarded jointly to Professors W. Kohn (UCSB) and J. A. Pople (Northwestern) for their "pioneering contributions in developing methods that can be used for theoretical studies of the properties of molecules and the chemical processes in which they are involved" <http://www.nobel.se/chemistry/laureates/1998/>

I am assuming, that you have some interest in molecular properties such as structure and energetics from your prior (or current) experimental or computational lives and may even be asking inquisitive questions such as: What is the structure of this molecule? Why does it behave the way it does? Can I modify its structure and properties in a controlled, rational fashion (molecular design)? What is an ab initio electronic structure calculation and what can it do for me - does it do me any good? One goal of this course is to make you feel semi-comfortable in thinking about applying modern electronic structure theory and methods in your future research. At the end of this course, you should be able to decipher some of the acronyms in a literature statement such as "The relative energies of the isomers were obtained from calculations at the B3LYP/6-311+G(d,p)level with ZPE corrections included at the HF/6-31G(d,p) level", and even be able to judge whether this calculation is a good one or not!

Perhaps no-one said it better than Gay-Lussac:
"We are perhaps not far removed from the time, when we shall be able to submit the bulk of chemical phenomena to calculation" Joseph Louis Gay-Lussac, Memoire de la Societe D'Arcueil, 2, 207 (1808).

But then, about 100 years later, Dirac had to put a damper on all the excitement:

"The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble" (P. A. M. Dirac, 1929).

Just "a large part of physics" but "the whole of chemistry" ???

There is, however, a second, often ignored, follow-up sentence to Dirac's Statement above, in which he expresses a sentiment very pertinent to what we do in this course:

"...too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation".