Calculating Simple Force Constants with Computational Quantum Chemistry

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Experiment Overview

This experiment allows the student to calculate the force constant by quantum mechanical calculations for the three diatomic molecules, F_2, O_2 and N_2. It uses the Gaussian and Mopac quantum chemistry codes running on a server and accessed by forms through a web browser. A selection of Hartree-Fock and Density Functional Theory methods are available, along with the semi-empirical AM1 and PM3 methods. Rather than using the "black box" calculation of the force constants from a calculation of the frequencies, here the student calculates the energy at the optimum bond length and with the bond length increased and decreased by 0.01 A. They then fit a parabola through these points to calculate the second derivative and hence the force constant. For some more advanced calculations the appropriate energies are provided rather then calculated.

This experiment is a suitable introduction to quantum mechanical calculations. It provides insight into the principles of vibrational spectroscopy and particularly a deeper appreciation of the concept of force constants.

- It reinforces students understanding of bond strengths in single, double and triple bonds.
- It shows that bond-stretching energy curve is not harmonic, so they can appreciate that anharmonic terms may sometimes be needed.
- It allows the student to learn how to do simple quantum chemistry calculations and recognise that that this is no longer a complex and hard to learn activity.
- It can support the teaching of Molecular Mechanics methods in Computational Chemistry courses.

Feedback supports the view that this experiment is relevant to students who are studying molecular modelling and/or spectroscopy and that it helps to appreciate the link between bond length and bond strength.

Level of Experiment

2nd year undergraduate or 3rd year undergraduate in either Physical Chemistry Laboratory in B Sc or Computational Chemistry Laboratory in B Med Chem. The experiment does not need to be modified for the different groups, but the demonstrator can limit the number of calculations to be performed or spread the calculations over a small group. In this way the least experienced classes can still complete the experiment in the 3 hours normally set aside for it.

Keyword Descriptions of the Experiment

Domain
physical chemistry, theoretical chemistry

Specific Descriptors
computational chemistry

Course Context

This experiment has been used in two contexts:

 Chemistry students with a generally limited mathematics background doing a physical chemistry unit who need to learn the basics of physical chemistry. For these students the experiment relates to the spectroscopy component of the course and assists their ability to process numerical data with spreadsheets.

 Medicinal Chemistry students who need to know about force constants to understand molecular mechanics force fields.

Prerequisite Knowledge and Skills

Students should have a basic understanding of molecular structure and bonding, experience using a computer to access the internet and use of simple spreadsheets.

Time Required to Complete

Prior to Lab: 30 min
In Laboratory: 3 h
After Laboratory: 30 min (if simple report and discussion with demonstrator);
2 h (if complete report prepared outside lab class)

Experiment History

This experiment owes its origins to section 5.13, pages 280 – 287 of Mathews (1985). Here the Extended Huckel method is used to calculate the bending force constant of carbon dioxide by calculating the energy of the linear molecule and the molecule bent by 5°. A parabola is fitted through the three points (linear and bent in opposite directions) and the force constant determined. The computing is done via punched cards submitted to a batch queue.

This experiment was modified to use web submission of data to an Extended Huckel program, and also programs for semi-empirical and ab initio methods, by Dr Brian Salter-Duke, at the Northern Territory University (now Charles Darwin University) around 1995. The experiment was used in a 3rd year undergraduate laboratory as support for the spectroscopy part of an Advanced Physical Chemistry unit.

The experiment in this form was submitted to the APCELL project. Although the experiment was seen as reasonably successful, the feedback suggested to Dr Salter-Duke that he modify the experiment into essentially its present form by dropping the Extended Huckel method and applying the theory to the stretching force constant of diatomic molecules. Due to the fact that the 2rd year unit was not run in the next few years, it was impossible to obtain student feedback for the new experiment and so it was never resubmitted for peer review by the APCELL Project. The experiment has also been run in the Chemistry Department at the University of Tasmania.

In 2005, the situation changed. At Charles Darwin University, Dr Vinutha Ramakrishna was able to contribute to the development of the experiment and run it in a new 2nd year undergraduate unit on Biophysical Chemistry. At the Department of Medicinal Chemistry, at the Monash University Parkville campus, Dr David Chalmers saw value in this experiment for 2nd year students in the B. Medicinal Chemistry in a unit called Computational Chemistry. He also contributed to the development of the experiment and ran it in the second semester.

Submission Details

This experiment has been developed by the authors of the authors of the educational analysis, and this submission is made by them in their own right.

References

Mathews, G. P. (1985). *Experimental Physical Chemistry.* Oxford: Clarendon Press.