



Cooperative approach to the research process on a new conceptual couple stiffness-stability, with regard to chemical bonding, by means of quantum chemical calculations

Arturo Espinosa Ferao (artuesp@um.es)

Depto. de Química Orgánica, Universidad de Murcia (ESPAÑA)

UNIVERSIDAD DE MURCIA



Introduction

On the course of the teaching activity in *Advanced Organic Chemistry* (and other subjects), it becomes evident that the undergraduate students have a deep gap between general (or organic) chemical concepts and the theoretical background relying on the Quantum Chemistry (QC) body of knowledge. In between there exist a number of computational tools that the students could be provided with (nowadays they are not) and be trained to handle in order to get deeper insight into the concepts or to solve doubts or problems related to them.

Once detected these specific needs, the aim of the current work is providing the students with the required intermediate knowledge and skills in QC computational tools (filling the gap) by means of a combined collaborative and individual working experience.

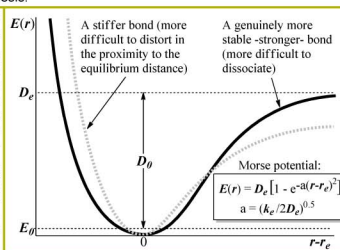
Scientific approach

The concepts of **bond strength** and **bond order** are at the very heart of molecular sciences and especially computational chemistry, from both the academic and practical points of view. Even nowadays the study of specific *bond strengths* for inter- and intramolecular interactions is still a non-trivial task. Although several parameters have been proposed for the quantification of this phenomenon, a clear distinction regarding to what of its two possible dimensions are they related to, is still missing. Moreover the recognition of the bidimensional character of bond strength (stiffness/stability) has never been brought to discussion and commonly used terminology such as "stability" or "strength" are not properly distinguished or are even misused among the scientific community.

On the other hand, quantum chemistry (QC) calculations can provide a valuable tool for obtaining a deep insight into a wide variety of chemical concepts. Nevertheless students of the degree in Chemistry (or related areas) receive a large amount of theoretical information about Quantum Chemistry but –excepting specialists– are not trained in its use to solve "normal chemical problems".

Although it is easy to assume that a "strong" or stable bond (difficult to cleave) is usually also stiff (difficult to distort, normally by elongation), it becomes interesting, under both a conceptual and practical point of view, to explore the boundaries of these classifications in which limiting situations could be found: on the one hand those bonds that are strong (stable) but flexible and, on the other hand, the opposite limiting situation of bonds that are intrinsically stiff while being moderately strong (or even weak). Within this context we are intending to study computationally a wide range of model systems containing different types of bonds. In a first stage we are aimed to study simple typical bonds such as C-C, C-H, C-N, C-O, C-S, C-Si, Si-Si, Si-O, etc. under several representative environments. They will constitute the *reference set of bonds* for checking the working research hypothesis.

In a nutshell, the methodology starts from the evaluation of the dependence of the system energy $E(r)$ as a function of the internuclear distance r between the involved atoms in a bond, around the equilibrium distance r_e , in discrete steps (0.1 or 0.2 Å). A typical curve corresponding to a dissociative process is obtained (see Figure, eg black bold curve). By means of a purely mathematical procedure of root mean squares this curve can be fitted to a *Morse potential* function, thus allowing the obtaining of the *dissociation energy* D_0 and the "a" parameter from which the *anharmonic bond force constant* k_a is extracted. The directly obtained *dissociation energy* D_0 does not correspond to the measurable and tabulated^[5] quantities D_e that differ in the energy corresponding to the first vibrational level E_0 , that also can be easily obtained (not shown) from the parameters in the *Morse potential* function.



The next step requires the calculation of several commonly used bond-strength related parameters,^[6] by means of single-point (SP) calculations performed onto frozen equilibrium geometries. The most representative of them are the so-called *bond orders* (Wiberg, Mayer, Löwdin, etc.), the electron density at bond critical points (within the atoms-in-molecules framework) and the relaxed force constants (obtained as reciprocals of the compliance constants). Almost all of them (excluding the last one that requires an expensive frequency calculation) are extremely easy to compute and should therefore constitute a convenient entry for the quantification of the stiffness or stability of chemical bonds, except for the fact that they have not been properly identified as pertaining to one or other category.

Thus, the last step consists on the graphical representation of the above mentioned bond strength related parameters *versus* D_0 on the one hand and k_a on the other. This will allow ascertaining which of them preferentially correspond to a genuine (thermodynamic) bond stability (showing higher Pearson regression coefficient, R^2 , vs D_0) and which others are mainly related to the other bond stiffness dimension (higher R^2 vs k_a).

Scheduled procedure

FIRST STAGE: Getting the concepts and tools

1.1) The students in *Advanced Organic Chemistry* (3rd year undergraduates in Chemistry) were proposed to join a workshop in Molecular Modelling. Their agreed own benefit was:

- Specific training in handling real QC calculations software (suitable for high level research proposes), and
- An increase in their record for the subject, by means of a coefficient (ranging from 1.00 to 1.05, depending on their engagement degree) multiplying the previous overall (exams and others) mark.

A group of 23 third-year undergraduate students (out of a group of a bit more than 30 that followed roughly all the classes), together with 3 PhD students, joined this first stage.

1.2) They were provided with appropriate software (by e-mailing the corresponding links for downloading). The recently developed ORCA^[1] software package was chosen for calculations because it is available for either Windows, Linux or Macintosh operating systems and can be run even in laptops or personal computers. For visualization, the ArgusLab^[2] VMD^[3] and ChemSketch^[4] freely distributed programs were recommended. All this software was also installed in Virtual Machines available through any PC at the "ALAs" (Free access classrooms) in the Faculty.

- 1.3) In six hours (three two-hours sessions) they were instructed about:
- An overview on different levels of theory that are often used in QC calculations.
 - How to install all required software (the students were asked to bring their own laptops).
 - The syntax in ORCA input files for common jobs.
 - How to run a simple ORCA job under MS-DOS and how to visualize the results.

SECOND STAGE: Running a simple set of calculations

2.1) All the initially involved students were informed about the scientific relevance of the binomial stiffness/stability of chemical bonding (the "chemical problem"), proposed a research hypothesis on how tackling the underlying study (see scientific approach) and invited to conduct the full study of two representative simple chemical bonds in two simple molecules. A total of seven undergraduates accepted and completed the task.

THIRD STAGE: Going one step further – jumping into the research pool

3.1) The students that completed the second stage were invited to undertake a real –high level– research task using the computational tools and skills recently acquired. Six of them (out of seven) accepted the proposal (the other one had applied, and got the position, for starting a PhD program abroad within the following two months).

3.2) All the six members of the group were provided with full access to a supercomputer,^[7] instructed on how to access it by means of a secure shell client, how to submit jobs and how to send and retrieve files (*ftp* protocol).

3.3) An internal mailing list was created for fast communication between the professor and the members of the group, and mainly aimed for solving problems related with either the computational work or the interpretation of results. One important rule was initially proposed and systematically maintained: in this e-mailing communication activities, the professor always writes (and answers) in English as a way to improve the fluency of the students in using (at least) written English. They were encouraged (though not forced) to do the same.

3.4) Every student was faced with a similar research situation:

3.4.1- First of all the student is asked to investigate in the literature if some bonding situations could be classified as strong/weak, stable/unstable or stiff/flexible. Once he/she concludes that the terminology is not properly defined in the literature, an initial hypothesis is formulated on the basis of the given conceptual approach ("scientific approach").

3.4.2- Then the student is asked to compute, for a limited number of representative simple chemical bonds (one sixth of the total *reference set of bonds*), their dissociation curves (from which they obtain D_0 and k_a data) and the appropriate SP calculations for obtaining the other bond-strength descriptors: Wiberg's bond indices (WBI), Mayer's (MBO) and Löwdin's (LBO) bond orders, electron density at bond critical points ($\rho(r_c)$) and relaxed force constants (k^r).

3.4.3- By themselves these data are not enough for being statistically relevant, but together with the data of the other group members, constitute a wide, general and significant set of bonding situations for which meaningful correlations *versus* stability (D_0) or stiffness (k_a) can be established. The classification of the bond-strength related parameters to one of the two categories will confirm the initial working hypothesis.

3.4.4- In order to check the validity and generality of the conclusions drawn so far, some new specific (even fancy) bonding situations (eg some metal-ligand bonds, hydrogen bonding, etc.) are proposed to every student. A critical discussion on the new results is of high relevance under both the academic and scientific points of view.

3.5) The last step is writing, in a proper technical/scientific style, both the state of the art, the hypothesis formulation, the description of the employed methodology and computational details, as well as the obtained results and conclusions. With the appropriate help from the supervisor, the results of the whole group can be conveniently transformed into a scientific paper suitable for being submitted to an appropriate –high level– international journal.

3.6) Some feed-back from the students has been retrieved by e-mailed surveys. Worth is to mention that they reveal, for instance, that 1) the main difficulties they face are related to their initial lack of computational skills, and 2) they understand this experience as highly interesting and useful for them.

Conclusions

Any "chemical problem" can provide the required excuse for attracting undergraduate students to analyse it using computational tools which they are lacking beforehand. In such a situation they become interested in learning the use of QC calculations –and visualization– software.

Under the appropriate formulation of a conceptual hypothesis to be checked, the student can even feel the attraction by a research proposal, which is more easily undertaken if it contains an initial cooperative stage within an small group.

Despite growing up in a technological-digital era, the undergraduates surprisingly show important deficiencies related to handling PCs and software.

References and footnotes

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- [6] For instance see: A. Espinosa, R. Streubel, *Chem. Eur. J.*, **2011**, *17*, 3166-3178 and references cited therein.
- [7] We wish to thank the Supercomputer Center at "Fundación Parque Científico de Murcia" for their technical support and the use of computational resources at the Supercomputer Ben-Arabi.