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

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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 those specific needs, the aim of the current work is providing the students with the required information, tools and skills in QC computational tools (telling 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 strength for infrared and Raman intermolecular interactions is still a non-trivial task, although several parameters have been proposed for the quantification of this phenomenon, a clear definition regarding to what if two. In other words, they are of utmost importance. Moreover, the direct measurement of bond strength (1) by simple means has never been transferred to common and commodity used terminology such as “stability” or “strength” are not properly distributed. In other words, there is no real equivalent of this property.

On the other hand, quantum chemical (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 specialities—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 distort) is usually also still (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 modeled 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, S-Si, Si-O, etc. under several representative environments. They will constitute the reference set of bonds for checking the working hypothesis.

In a more advanced approach the distance for the relaxation of the size of dependence of the system energy (as a function of the internuclear distance) between the minimum energy state in the absence of the influence around the equilibrium distance D_e, in discrete steps (0.1 or 0.2 Å). A typical curve corresponding to a dissociative process (as observed in Figure see block black curve) by means of a purely mathematical procedure of root mean squares this curve can be divided into a Morse potential bond strength regime and an exponentially decreasing regime. The energy corresponding to the mode of path of the system is connected to the so-called bond strength (related with the atomic strength of the bond) energy.

The next step requires the calculation of several common used bond-strength related parameters, by means of single-point (SP) calculations performed onto frozen in equilibrium geometries. The most representative of them are the so-called overlap integrals (Helminger, Moller, Laidlaw, etc.), the electron density at bond critical points (within the atoms-in-molecules framework) and the related 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 an easy 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 another category.

The last step consists on the graphical representation of the above mentioned bond-strength related parameters versus D_e on the one hand and k_e on the other. This will allow assessing which of them predominantly refer to a genuine (thermodynamics) bond stability (showing higher Pearson regression coefficient, R², vs D_e) and which others are mainly related to the other bond stiffness dimension (higher R² vs k_e).

Suggested 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 projects), and
- An increase in their record for the subject, by means of a coefficient (ranging from 1.0 to 1.5, depending on their engagement degree) multiplying the previous overall (exams and others) mark.

A group of 23 third-year students and a group of at least 30 that followed roughly 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 recent trend of desktop software and web-based applications is that it is available for either Windows, Mac or Linux operating systems and can be run even in laptops or personal computers. For visualization, the ArgusLab(1) and VDI(7) are two widely used applications with a more easily used interface which contains an initial cooperate stage within a 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

References and footnotes


(7) We wish to thank the Supercomputing Center at “Fundación Parque Científico de Murcia” for their technical support and the use of computational resources at the Supercomputer Ben-Idriss.

Additional notes:

1.3) In six hours (three two-hour sessions) they were instructed about:

- An overview and different aspects of software 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 calculations
- How to run a simple ORCA job under MS-DOS and how to visualize the results.

SECOND STAGE: Running a set of simple calculations

2.1) All the initially involved students were informed about the scientific relevance of the bond stiffness/character of chemical bonding (the "chemical problem") and were introduced to the hands-on computational chemistry (using a simple empirical 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

2.2) All the students who 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).

2.3) All the six members of the group were provided with full access to a supercomputer(5) instructed on how to access it by means of a secure shell client, how to submit jobs and how to send and retrieve files (by protocol).

2.4) An internal ranking 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 the 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.

2.5) Every student was faced with a similar research situation

2.5.1) 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/soft. Once horde 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’). 2.5.2) Then the student is asked to compute, for a limited number of representative simple chemical bonds (one sum of the total reference set of bonds, their association curves (from which they obtain D_e and k_e data) and the appropriate SP calculations for obtaining the other bond-strength descriptors (Windberg’s indices (WBI), MAYER’s (RBC) and Laidle’s (USBC bond orders), electron density at bond critical points (xc) and related force constants (f)).

2.5.3) By themselves these data are not enough for being statistically relevant, but together with the data of the other students, can be used in the calculation of the statistical significance and significant size of bond situations for which overweighting correlations versus stability (D_e) or stiffness (k_e) can be established. The classification of the bond-strength related parameters to one of the two categories will confirm the initial working hypothesis.

2.5.4) In order to check the validity and generality of the conclusions drawn so far, some new specific (even fancy) bonding situations (apart 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.

2.5.5) 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 for being submitted to an appropriate—high level—international journal.

2.5.6) 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.