Ninety years have elapsed since the Old Quantum Theory has emerged, and eighty three over the foundations of Modern Quantum Mechanics. Born in 1901, Ruy Gustavo Couceiro da Costa soon became aware of the importance of Quantum Mechanics in Science, particularly in Chemistry. Such a vision has flourished ever since and its presence in the scientific realm is nowadays unquestionable: Physics, Chemistry, Biology, Astronomy, Engineering and even Philosophy, all such areas of knowledge reflect the importance of judgement in accordance with the quantum laws. This book is a result of a Symposium to honor the memory of Professor Couceiro da Costa for his contribution to the development of Quantum Mechanics in Chemistry and Physics in Portugal.

A tribute to the memory of
Professor Couceiro da Costa
9. Computational Thermochemistry: Accurate Estimation and Prediction of Molecular Thermochemical Parameters

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The problems involved in the Quantum Mechanical calculation of molecular energies are identified, with special emphasis on the problem of correctly describing the effects of the correlated electronic motions. Some of the available Quantum Mechanically based methods for the calculation of molecular energies are then briefly described and their application to some selected systems are detailed. The quality of the results so obtained illustrates the usefulness and the accuracy achieved through the use of conveniently based computational techniques and the fact that contemporary thermochemists have now the real possibility of complementing their experimental measurements with well founded very accurate calculated data or, even, of obtaining original and very accurate thermochemical data entirely from computational techniques.

9.1 Computational Methods

Since the introduction of Quantum Mechanics, in the first quarter of twentieth century, very important advances in chemistry have emerged, particularly in those fields where accurate numerical data is required, such as thermochemistry and chemical kinetics. Indeed, it is now recognized that Quantum Mechanics constitutes the ultimate, most accurate and complete description of the behaviour of matter at the atomic and molecular scale and, as such, much hope has been put in the development of efficient computational methods which can provide accurate estimates of the molecular thermochemical parameters.

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Such achievements would contribute to definitely establish computational thermochemistry as a reliable complement to experimental thermochemistry, thus opening new frontiers to the study of chemical species whose instability or short lifetime has prevented experimental analysis up to now.

This talk is concerned with the difficulties found when the methods of Quantum Mechanics are to be applied to real systems and with the description of some state-of-the-art computational techniques which have been developed to provide accurate molecular thermochemical parameters. We will describe also some applications of those computational methods with particular emphasis to the analysis of the stability of selected molecular species.

The task of accurately describing the properties of molecular systems starting from the concepts of Quantum Mechanics would appear as very straightforward if it is accepted that such theory provides the most accurate and complete description of the behaviour of matter at the atomic and molecular level. According to this point of view it becomes obvious that in order to obtain reliable and accurate estimates of molecular thermochemical parameters it suffices to solve the corresponding Schrödinger equation

$$\hat{H}\Psi = E\Psi$$

which is a differential eigenvalue equation providing, as solutions, the energy, $E$, and the wavefunction, $\Psi$, of the stationary states of the molecular system. In this equation $\hat{H}$ is the Hamiltonian operator, acting on the wavefunction $\Psi$, which depends explicitly on the spatial and spin coordinates of the electrons and the nuclei. Even though Schrödinger equation can be easily solved for hydrogen atom and, in general, for any system with just one electron, in which case it provides accurately the experimentally observed energies, when we proceed to more complex systems, with at least two electrons, such exact solution reveals unattainable, and some kind of approximate solution must be seek instead. The vast majority of the methods used to obtain approximate solutions to the Schrödinger equation is based on a general approximation introduced to the model of the wavefunction used to describe the system under study. This
approximation assumes that each electron in the system moves independently of the other electrons (an independent particle model is thus adopted) and the interactions among the various electrons are accounted for through the introduction of a potential energy function representing just the time average of the instantaneous interactions between each electron and the remaining ones. Thus, each electron will then be described by a particular spatial function, \( \varphi_i \), which depends on its spatial coordinates. According to the Pauli antisymmetry principle each such spatial function, generically called molecular orbital, can really accommodate two electrons, as long as they have different spin coordinates, \( \alpha \) or \( \beta \). The wavefunction describing the overall electronic system can then be represented by a function with the following general form:

\[
\Psi = \frac{1}{\sqrt{n!}} \det |(\varphi_1\alpha)(\varphi_1\beta)(\varphi_2\alpha)\cdots| \tag{9.2}
\]

where the determinant, called Slater determinant, ensures the proper antisymmetry of the wavefunction, as is required for systems constituted by fermions. The energy of the system can then be obtained through variation of the molecular orbitals in order to minimize the expectation value of the Hamiltonian operator:

\[
E = \langle \Psi | \hat{H} | \Psi \rangle \tag{9.3}
\]

Such variational procedure leads to a system of coupled differential equations, called Fock equations, whose solutions are the molecular orbitals, \( \varphi_i \). Thus, in the Hartree-Fock model each electron feels a potential which is the average of the instantaneous potential created by the other electrons. Such replacement of the true (instantaneous) potential by the average potential ensures that the Hartree-Fock method can easily lead to approximate solutions of the Schrödinger equation. However, those solutions will certainly reflect the nature of the adopted approximations, in the sense that they should incorporate the errors associated with the assumptions assumed for the wavefunction model. We must stress that the solutions of the Fock equations (the molecular orbitals, \( \varphi_i \)) are obtained in numerical form, as tables of numerical values, instead of some kind of analytical form, which would be preferable for those aiming to