

PROLOGUE

On the Significance of Theoretical Models of Chemical Bonding

»Imagination and shrewd guesswork are powerful instruments for acquiring scientific knowledge quickly and inexpensively«

J. H. van't Hoff

The last decades brought a tremendous increase in a number of very accurate *ab initio* calculations of the electronic structure of molecules yielding admirable numerical results. The accuracy of the modern theoretical methods, involving the first principles only, is competitive with many experimental techniques. Thus, they provide results which serve as severe tests of the very basis of quantum mechanics. The rigorous *ab initio* procedures are an invaluable tool for studying systems not easily amenable to measurements, *viz.*, molecules in space, short lived transient species *etc.* Hence, the computer can nowadays play the role of a very specific and sophisticated experimental device. It can supplement the experimental information gained by traditional techniques in a complementary way, thus improving the quality of our scientific knowledge. There are, however, two less favourable features of the contemporary *ab initio* branch of quantum chemistry. Firstly, technical obstacles and/or economical reasons confine high quality calculations to quite small molecules. Consequently, in tackling large systems one has to resort to approximate treatments. Since the *ab initio* methods will remain prohibitively laborious in view of the enormous increase of computational complexities in sizeable molecules, the situation is not likely to be changed significantly for a long time to come, despite the forthcoming new generations of computers. Secondly, the role of theory is not limited only to disclosure of the basic principle underlying the laws of Nature or to the production of new sets of data. Theory should additionally provide a systematization and rationalization of the myriads of established facts. The importance of the latter can not be overestimated. Unfortunately, the heuristic side of quantum chemistry has been somewhat neglected owing to the ever-increasing computability and number production.

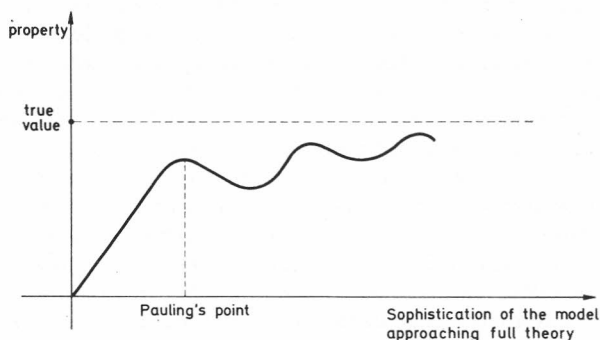
Both of these aspects call for the modelling of the behaviour of nuclei and electrons in molecules. Theoretical models in general, sacrifice accuracy in order to gain in simplicity and feasibility. By reducing the studied phenomenon to the most essential features, models enlarge the domain of applicability of theoretical concepts in chemistry. At the same time, they have a high cognitive value, because complex situations are appropriately simplified and made manageable to human mind. We can comprehend and interpret molecular properties only in terms of conceptual models. It goes without saying that one is often interested in seeing the wood instead of each tree, branch or even each leaf. In chemistry, one would usually like to understand and explain

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the trend of changes of a particular property within a family of related molecules. This is rarely accomplished by numbers with six or more decimal places. Models are better endowed for this purpose.

Finally, it should be strongly emphasized that *models do not only add agnoseological dimension to quantum chemistry but also contribute to its authenticity as a specific scientific field*, a fact which is amusingly enough sometimes overlooked. Without versatile models, quantum chemistry would be a mere numerical application of the quantum theory (which, incidentally, »solved in principle all problems of chemistry« already in the early 1930s) and/or a part of computational mathematics.

There is a wide variety of models designed for the description of molecular properties. They differ in their nature, their aims and degrees of sophistication. The Hartree-Fock method is based on the one-electron picture, which is obviously a model. On the opposite side of the scale one can find hybridization, point-charge approximation, qualitative MO *etc.* models, which are intuitively appealing and easy to visualize. These concepts are customarily considered as models in a narrower sense of the word. The approximate (semi-empirical) procedures employing model hamiltonians are placed somewhere in between these extremes. The performance of the models does not necessarily follow the hierarchy given above. Simple models can yield more accurate estimates of some molecular properties than the HF method, particularly if minimum basis sets are utilized in the latter. The reason behind it is that suitable model can stress the *subtle but critical* details, which are extremely important for the investigated feature but difficult to reproduce by the full calculation. This is rather nicely illustrated by the Figure, where the complexity of the models is plotted schematically against their performance. The



first maximum corresponds to the so called L. Pauling's point, named after the great pioneer of the modern 20th century chemistry. It can be defined as the simplest possible description of the studied property which gives reasonably close estimates of the true values. In other words, the underlying model is *the best in the sense of the Occam razor principle*. It is, therefore, not surprising that after Pauling's point, the first (local) minimum appears and that the curve approaches the accurate value asymptotically in a characteristic oscillatory way.

The simple and transparent Pauling-type models deserve some more comments not only because of their high explanatory power. It is important to

stress that they are closest to chemical intuition. Consequently, they are best suited for fulfilling one of the principal goals of the theory of chemical bonding not mentioned so far — *reconciliation of the empirical concepts emerging from the rich chemical experience with the fundamental principles of quantum mechanics*. A lot has to be done here and future work along this line is highly desirable. The simplicity of the model should not be considered necessarily as its weakness. On the contrary, omission of many details usually gives more insight and clarity, *i. e.*, it is the main strength of the model. Bohr's model of the hydrogen atom offers an illuminating example. One can suspect with good reasons that N. Bohr would not have been able to unravel so easily the periodic properties of elements, if he had a more complicated model at hand. This type of enlightening simple models has appreciable potentialities in directing careful experimental examinations and rigorous *ab initio* calculations which should be better exploited.

It is perhaps not self-evident that construction of good models is a difficult task. Apart from mathematical modelling, quantum models of chemical bonding should have a sound physical basis. They should be designed in a most economical way (Occam razor principle) implying that dominant effects are clearly and explicitly identified. Models must be internally consistent and capable of being extended if necessary. Parametrization of the model is a delicate problem requiring special attention. There is always a danger of getting the right answers for the wrong reasons. Parametrization should be guided by theoretical arguments and performed on the characteristic set of gauge molecules. Unjustified, *i. e.* fudge, factors are to be strictly avoided. They seemingly improve the agreement with the experiment, but in fact obscure the picture. Special care has to be exercised in determining the range of applicability of models. This can be accomplished only by their wide use and permanent testing against the experimental data and *rigorous theories*. The geocentric system of Ptolemy is a warning which conclusively shows that a wrong model could be in perfect accordance with experimental observations. The nature and the scope of the models should be well understood in order to avoid confusion. It appears that quantum modelling of the electronic structure of molecules involves more subtleties and requires more skill than the brute force *ab initio* methods. A lot of work still remains to be done in this area, particularly in establishing strong links with theories originating from the first principles and with the phenomenological concepts on the other side.

It is regrettable that rigorous quantum chemistry, conceptual modelling of the molecular structure and phenomenological approach have so far developed almost independently, with little mutual interaction. A rich harvest could be expected by increasing the overlap between these areas. Hence, efforts for surpassing this schism by bridging the gap would be highly beneficial for chemistry. It is my firm belief that the papers presented in this special theoretical issue are an important step toward this goal.