AN INTRODUCTION TO QUANTUMCHEMICAL ORGANOMETALLIC CHEMISTRY

1. Introduction

During the last two decades, computational organic chemistry has earned its place as a discipline complementary to experimental chemistry. Starting out as a somewhat esoteric occupation of sometimes doubtful relevance, it is now recognised as a valuable research tool used by many researchers in both industry and academia. The calculations have become accurate enough to be relevant for experimental chemists and they have become quick enough not to be a full-time occupation.

The continuing expansion of computer technology and associated improvement of computer software has made this possible. The improvements are nicely illustrated by a table from the GAUSSIAN brochure, showing the timing for Gaussian92 test job number 178[1]:

<table>
<thead>
<tr>
<th>Program</th>
<th>Computer system</th>
<th>Approx. CPU time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyatom (c. 1967)</td>
<td>CDC 1604</td>
<td>200 years*</td>
</tr>
<tr>
<td>Gaussian 80</td>
<td>VAX 11/780</td>
<td>1 week*</td>
</tr>
<tr>
<td>Gaussian 88</td>
<td>Cray Y-MP</td>
<td>1 hour</td>
</tr>
<tr>
<td>Gaussian 92</td>
<td>IBM RS/6000 Model 550</td>
<td>4.5 hours</td>
</tr>
<tr>
<td></td>
<td>Cray Y-MP</td>
<td>9 minutes</td>
</tr>
<tr>
<td></td>
<td>Cray C90</td>
<td>4.5 minutes</td>
</tr>
<tr>
<td></td>
<td>IBM RS/6000 Model 550</td>
<td>1 hour</td>
</tr>
<tr>
<td></td>
<td>486 DX2/50</td>
<td>20 hours</td>
</tr>
</tbody>
</table>

* Ignoring memory and disk limitations.

In the area of organometallic chemistry, it is taking computational chemistry much longer to achieve similar importance. There are a number of reasons for this, which we will discuss in more detail below. Nevertheless even in this field "computer chemistry" is growing in importance. It has passed the stage of qualitative orbital diagrams and is now making at least semi-quantitative predictions that can help experimental chemists.

The purpose of this book is to highlight some of the insights obtained from theoretical studies and make them available to researchers in organometallic chemistry and homogeneous catalysis. Therefore, attention in this volume is focused on results and interpretation, rather than on methodological aspects. Each of the following chapters focuses on a particular reaction type. Subjects are Oxidative Addition, Alkene Migratory Insertions and C-C Bond Formation, 2+2 reactions, Wacker-type reactions and Epoxidation.

The treatment is not uniform; different authors treat their subjects at different levels of sophistication, which is brought about by a combination of the requirements of the systems studied and hardware and software limitations, as well as by the personal preference of the authors. The chapters contain a significant amount of theoretical background themselves.

In this introductory chapter we summarise the history of computational chemistry in organic and organometallic chemistry. We consider briefly the theoretical methods useful in the study of organometallic compounds and the choices one has to make when using them. Finally, we discuss the kind of results one may obtain from a computational study and list some books, that may be of use to the reader, who is interested in the quantumchemical methods.

2. A history of theoretical organic chemistry

The earliest example of a “theoretical model” used in organic chemistry is probably the development by Le Bel and Van ’t Hoff of the “tetrahedral carbon” model [2, 3]. This model, while purely descriptive, could be used to explain or at least bring some order into a large part of organic chemistry. When quantum mechanics was postulated in the beginning of this century, it was immediately applied to the covalent bonds of organic compounds, leading to qualitative understanding of the nature of the chemical bond [4].

The calculation of π-orbital energies using the Hückel method [5] in the 1930’s is probably the first example of a “computational chemistry” approach. Soon thereafter the treatment was generalised to include σ-bonding, leading to the Extended Hückel method [6–9] in the 1950’s. These qualitative methods provided a framework for discussing the electronic structure and chemical behaviour of organic molecules. They produced concepts like “forbidden” and “allowed” reactions, “frontier orbitals” and the famous Woodward-Hoffmann rules [10].

The advent of electronic computers provided the opportunity for quantitative calculations. Three different classes of methods, each with their own
area of application, made their entry into organic chemistry, approximately simultaneously in the period of 1970–1980:

- *Ab initio* methods attempt to solve the Schrödinger equation in a fairly rigorous way. They are used to study the electronic structure in "small" molecules. Such calculations nearly always employ model systems, i.e. simplified versions of the molecules that are studied experimentally, to investigate some effects in isolation.

- *Semi-empirical* methods use most of the formalisms of *ab initio* methods, but replace the parts of the energy expression, that are difficult or time-consuming to calculate, by approximations fitted to give the best results for a set of reference molecules. These methods can handle larger systems than the *ab initio* approach and are used for "medium sized" molecules. They may fail for molecules with unusual bonding characteristics, which were not present in the "reference set", but they can be at least as accurate as the *ab initio* methods for standard molecules.

- *Force-field* calculations treat molecules as "ball and spring" classical systems, ignoring electronic structure and quantum mechanics altogether. Again parameters (bond strengths, steric repulsion, etc.) are fitted to reproduce experimental data. Since organic chemistry is dominated by localised, covalent bonds, force field methods can be very accurate in this area (better than either *ab initio* or *semi-empirical* methods), provided that the molecule studied is very similar to the ones used in the reference set from which the parameters were determined. Because of the very simple nature of the energy expressions *force-field* calculations can handle very large systems (up to 10⁶ atoms). A serious disadvantage is that the user has to assign atom and bond types *a priori*, based on chemical knowledge or intuition, which degrades the predictive value of the theory.

All three approaches owe much of their success and acceptance to the development by dedicated research groups of widely distributed general purpose computer codes. For *ab initio* programs the premier example is the GAUSSIAN series of programs by Pople et al. [11, 12] and many others are now available like GAMESS, CADPAC, MOLPRO, TURBOMOL, SPARTAN, etc. For *Semi-empirical* programs the scene was set by the MINDO [13–15]-MND0 [16]-AM [17] series of programs by Dewar and others, and for *Force-field* calculations we may mention Allinger’s MM [18–20] programs. Although there is a wealth of programs to choose from, considerable standardisation has been obtained in the field of computational organic chemistry.
3. A history of theoretical organometallic chemistry

Coordination and organometallic chemistry are much younger subjects than organic chemistry. The first organometallic compound was prepared around 1850 [21] and the first structurally characterised organo-transition metal compound was ferrocene, prepared in 1951 [22, 23]. Soon after its discovery, the Dewar-Chatt-Duncanson model was put forward [24, 25] to explain the nature of the interaction between the metal and its ‘ligands’ in ferrocene and related compounds. From early in the seventies Hoffmann and others used the extended Hückel method to understand bonding and reactivity in organometallic compounds. As in organic chemistry, these calculations provided a framework for the classification of the interactions, as is exemplified by the famous “isolobal analogy” [26].

Following these early applications of computational methods to organometallic chemistry, one could have expected, in analogy to organic chemistry, a fairly rapid development of standardised ab initio, semi-empirical and force-field calculations. The primary reason this did not happen is probably the wide range of structures and bonding types observed in organometallic and coordination chemistry. A single metal atom can have a bewildering variety of oxidation states, coordination geometries and can participate in a choice of bond types, as is exemplified by the series of iron compounds Fe(CO)₅, Fe(CO)₅, [CpFe(CO)]₂, (Fe-Fe), [CpFe(CO)]₄ (4 Fe-Fe), Cp₂Fe, Fe(H₂O)₅²⁺, (C₅H₅)Fe(CO)J, Fe₃Cl, FeCl₂. It appears to be very difficult to devise a parametrization scheme for a semi-empirical or force-field method, that gives reliable results for each of these environments. Also, if possible at all, such a parametrization requires a large set of reference compounds and a corresponding large amount of thermochemical data, which are scarce for organometallic compounds. There are now a few “reasonable” semi-empirical methods for transition metals (e.g. ZINDO [27] and SINDO [28]), but their reliability can not bear a comparison with that of typical “organic” methods like MNDO. For force-field methods one might have to use a different “iron type” for each of examples mentioned above, leading to an inordinate number of force-field parameters to be determined. In practice, one either develops a dedicated set of parameters for a small group of very similar compounds, or alternatively one lets a program guess parameters “on the fly” without too much worry about accuracy. Clearly neither approach will result in a good general purpose computational method.

Ab initio methods do not suffer from the problems mentioned above and should thus be ideally suited for calculations on organometallic complexes.
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While this may be true in principle, there do exist a number of problems that have contributed towards delaying the widespread use of \textit{ab initio} methods in this area.

A first problem is that even the simplest model of an organometallic complex is often large compared to a model organic compound, if only because of the large number of electrons and valence shells of the metal atom. For example, ferrocene (96 electrons) cannot be simplified much, if we aim to understand its electronic structure; compare this to typical organic model molecules like ethene (16 electrons) or benzene (42 electrons) bearing in mind that \textit{ab initio} calculations scale at least with $N^3$, the third power of the system size.

A second problem is that electron correlation may be quite important in organometallic chemistry. In view of the often small energy differences involved in homogeneous catalysis and the probably subtle differences in reaction mechanisms, sophisticated and hence expensive calculation methods are called for. Also, in particular for third-row transition metals relativistic effects can be significant. These can be handled at various levels of accuracy at the expense of even more computer time.

Thus it is understandable that the use of \textit{ab initio} methods in organometallic chemistry has lagged behind their application in organic chemistry. Developments in computer algorithms and hardware open up new possibilities every year, so routine application of these methods is coming within reach now.

4. Methods and choices in computational organometallic chemistry

In this book mostly \textit{ab initio} methods are used. We define this concept here pragmatically as methods, that do not require experimental information, as opposed to semi-empirical and force-field approaches, which require parameters that are fitted to reproduce experimental data. The value of the result of a calculation critically depends on the appropriateness of the quantumchemical approach chosen and there is still a large amount of research going on. There is no such thing as a generally applicable quantumchemical technique.

The customary way to view \textit{ab initio} methods is as attempts to find approximate solutions to the time-independent Schrödinger equation [29]:

$$\hat{H}\Psi = E\Psi$$  \hspace{1cm} (1)

Where $\hat{H}$ is the Hamiltonian, defining all relevant details of the chemical system (position and kind of the nuclei, number of electrons, etc.) and $\Psi$ and $E$ are the wavefunction and energy of the system, respectively. The nuclear
motion is generally left out of the equation. This is the Born-Oppenheimer [30] or "clamped nuclei" approximation. It is such a common approximation that it is often not even mentioned.

The Hartree-Fock [31–35] or SCF method is the simplest such ab initio technique. A single set of occupied orbitals is combined into a determinant to define the wave function. An effective one-electron operator, the Fock operator, is employed to obtain unique optimal molecular orbitals. An attractive feature of the method is that it offers a readily interpretable orbital picture of the electronic structure of a molecule. Unfortunately, this simple approach cannot describe some bond breaking and forming processes, occurring in chemical reactions, correctly. Neither can it yield highly accurate results. The former specific shortcomings can be rectified by using Multi Configuration SCF methods like Generalized Valence Bond (GVB [36]) or more general MCSCF [37] approaches. Also at a cost of forfeiting the fact that the wave function adheres to the proper spin, one could use the Unrestricted Hartree-Fock method [38]. These methods still support a useful orbital picture of chemical bonding and reactivity, though the interpretation is somewhat more difficult than in the simple Hartree-Fock model. These orbital methods may be collectively referred to as HF models.

For quantitative results, it is usually necessary to go beyond the Hartree-Fock approximation and include correlation using treatments that may be collectively labelled as HF+. The more sophisticated methods are not only more expensive, in terms of computer resources, they also lack the simple orbital picture of the HF methods. Therefore the understanding may come from a HF calculation whereas the higher accuracy is achieved using some correlation treatment without trying to interpret the improvement too closely. There is an abundance of HF+ methods, ranging from simple perturbation theory (e.g. MP2 [39]) to sophisticated correlation treatments. This is still very much an area of active research, making it difficult to give general rules as to which methods perform best for which systems.

An approach that falls a bit outside this classification is Density Functional Theory (DFT) [40, 41]. In contrast to the ab initio methods discussed above, no attempt is made to solve the Schrödinger equation, but the energy is sought as a (formally unknown but existing) functional of the one-electron density. It does include some correlation and employs no fitted parameters, though there is an extending range of functionals to choose from. A problem is that formally, there is no way to describe proper spin states or excited electronic states, which may make application to open-shell transition metal complexes difficult.
A problem, which falls in a different category, is whether relativity is taken into account [42], either at great cost by explicit inclusion in the Hamiltonian or by applying relativistic corrections. Relativistic corrections tend to make atoms more compact, increase bond strengths and reaction barriers. For third-row transition metals relativistic corrections are nearly always required. For second-row metals they are needed if more subtle effects are considered as in comparing different spin states or if accurate inner-shell ionisation energies are sought, but they are not required for a description of most chemical reactions.

Apart from the formalism to be used for the calculation, there are a number of choices to make in performing a proper calculation. The most important one is the choice of basis set, which determines the flexibility electron density has to adapt to changing molecular situations. In contrast to the situation in organic chemistry no general agreement exists on which basis set is needed in a given situation. The basis sets, that are used in practice are in order of increasing flexibility, accuracy and cost:

- Minimal (e.g. STO3G): use only for qualitative calculations.
- Split-Valence (SV) or Double Zeta (DZ), e.g. 3-21G, 6-31G: gives reasonable results at the HF level. In order to obtain reliable estimates of bond angles, polarisation functions are required.
- Many special-purpose extended basis sets have been developed: these are needed to accurately calculate energies or sensitive properties like polarisabilities, NMR parameters, etc.

The number of basis functions that are included may be reduced by treating only the “valence” electrons explicitly and replacing the inner shells of transition metals by effective core potentials (ECP’s), assuming that these are not important for the chemistry. This is particularly attractive for third-row transition metals, since the ECP’s may be adapted to include some relativistic corrections. ECP’s like any approximations must be handled with care.

Obviously one has to balance the choices of method and basis sets. It does not make sense to employ a very sophisticated correlation treatment combined with a minimal basis set. Also the cost of a calculation must be taken into account. The amount of computer resources (time, memory, disk) that is required, rises as the third power of the number of basis functions ($N^3$) for the simpler $\text{ab initio}$ approaches. For the more sophisticated methods the dependence of the computational expenditure on the system size may be like $N^4$ to $N^7$.

There is no agreement in the literature to what is the required combination in a given situation as may become clear from reading the other chapters in this book. There are few standards as yet and computational organometallic chemistry is still a developing and fascinating discipline.
5. Interpreting the results of \textit{ab initio} calculations

A straightforward HF (or DFT) calculation produces an energy and a wave function, which may be used to interpret the bonding and to calculate a wealth of molecular properties. Often only the energy is actually used. This energy as a function of all or some of the atomic positions is a Potential Energy Surface (PES). Due to the generally large number of nuclear coordinates (degrees of freedom) it is expensive to sample a large part. Also interpretation of a PES is difficult, particularly if the number of degrees of freedom is large. One may derive molecular structure or a reaction path from it.

The \textit{molecular structure} can be compared directly with experiment, for instance with a X-ray diffraction structure. In organic compounds one should expect agreements within a few hundredths of an Ångström for bond lengths or within a few degrees for angles at the HF/split-valence level. For organometallic compounds, where bonding is often much “softer” and correlation corrections are more important larger deviations (up to $\sim 0.2$ Å and 10° for “soft bonds”) are common.

Calculating a \textit{reaction path} and especially the \textit{transition state} (TS) gives the activation energy of a chemical reaction. Usually the system size precludes the calculation of absolute reaction rates, which ideally should be done quantum mechanically. Activation energies calculated at the HF level are usually too high, typically by some 10 kcal/mole for “allowed” reactions. In organic chemistry, reactions that are “forbidden” by spin or space symmetry usually do not take place at all. In organometallic chemistry ground and excited states are often so close, that formally forbidden reactions are actually quite easy, even though it is often not possible to describe them at the HF level. Therefore one should always try to follow the orbitals in going from reactants to products and be alert to possible orbital crossings that might require a GVB or MCSCF treatment. Also one should be aware of spin-orbit interactions, which, especially in transition metal compounds, may make “spin-forbidden” reactions quite possible.

Calculating a reaction path or part of a Potential Energy surface can provide the basic information for quantitative data on reaction rates, but it does not explain by itself why a particular reaction is easy or difficult. To understand energy differences or reaction rates attempts are made to analyze and compare the wave functions of reactants, products and transition states. HF wavefunctions can be analyzed in the same way as the Extended Hückel MO (EHMO) wavefunctions that Hoffmann and others used for their interpretation of organometallic chemistry [26]. In particular, frontier orbital arguments
(HOMO-LUMO interactions) are valuable for understanding attractive and repulsive interactions [43]. Interpretation of wavefunctions that are beyond the HF approximation, is more difficult.

The molecular properties, like charge distributions, dipole moments, equipotential surfaces or polarisabilities, which may be obtained from a HF or HF+ calculation can be very helpful in understanding the course of a reaction. Most interpretations in organometallic chemistry have centered on MO arguments, but there is little doubt that charge control can be at least as important as orbital control, particularly in the early stages of a reaction. Interpretations and predictions based on molecular properties, e.g. Molecular Electrostatic Potential Surfaces (MEPS) [44], have become quite important in pharmacochemistry [45] and there is no reason to believe, that they could not rise to the same status in organometallic chemistry.

6. Background reading

The following list gives a short description of some books discussing quantumchemical methods.

W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople: *ab initio* Molecular Orbital Theory [46].

This standard guide gives a simple account of molecular orbital theory and describes various techniques used in practical calculations. It also give some insight in the way a computation and a quantumchemistry program is set up. Most of the information is pertinent to the GAUSSIAN series of programs, one of the most popular program packages.


This book provides a qualitative pictorial picture of concepts in quantum theory. Each subject is treated in generally less than a page as separate entry.

A. Hinchcliffe: Computational Quantum Chemistry [48].

A little booklet (only 110 pages) discussing in a practical way many of the subjects hinted at in this introduction.

A. Szabo and N. S. Ostlund: Modern Quantum Chemistry, Introduction to Advanced Electronic Structure Theory [49].

A graduate textbook focusing on the more formal and mathematical background of Hartree-Fock and sophisticated methods. Various methods are illustrated by calculations on very simple molecules.

R. McWeeny: Methods of Molecular Quantum Mechanics (second edition) [50].

A standard textbook at graduate to advanced graduate level for someone who really wants to get into Quantum Chemistry.
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