



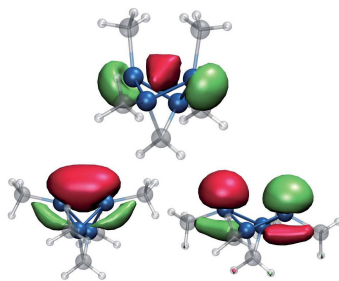
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A quantum chemical study

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1 INTRODUCTION

Complexes, which are of particular interest in this work, are *molecular entities formed by loose association involving two or more component molecular entities*.¹ Coordination compounds of metals and ligands are the most prominent example of complexes. Such species, formed in the reaction of a Lewis acid (metal) and a Lewis base (ligand), are widespread in nature, e.g. in metalloproteins. The local environment of the metal centre influences its electronic structure and also determines the possible interactions with other molecules. The subsequent chemical transformation can then be very selective as only certain molecules can bind to the metal and react mainly in one direction. This idea underlays the premise of homogeneous catalysis with transition metals. In the early 80's it was anticipated that in the next 20 years homogeneous catalysis would be understood well enough to design new catalysts in a rational way.² Nowadays, this task is still a great challenge even though we have an understanding of a large number of reactions. Quantum chemical calculations can with this respect constitute an attractive alternative to expensive experimental trial and error.

In the present work the structures and reactivities of various polynuclear complexes are studied. The project has been carried out in the framework of the Transregio-Sonderforschungsbereich 88 "Cooperative Effects in Homo- and Heteronuclear Complexes (3MET)". In this context, theoretical calculations were undertaken to examine the electronic structure of a number of metal- and metalloid-containing systems in order to explain their properties and reactivities. The applications presented include the analysis of the reaction paths and the design of new paracyclophane-based ligands for the dialkylzinc additions to unsaturated aldehydes, the characterisation of unusual bonding patterns in large metalloid cluster compounds, accurate calculations of the structure of small nickel clusters as isolated molecules and solvated by alcohol molecules as well as studies of molecular oxygen activation by a cobalt complex. Important aspects of this work are careful benchmark studies which allow reliable predictions. It turned out that for some problems only expensive, highly correlated wave-function based methods were able to give qualitatively correct answers whereas for other properties more economical DFT computations provided satisfactory results. Furthermore, strong emphasis is put on the comparison with experimental findings. The topics presented in this work cover a wide range of structural problems (molecular geometry and electronic structure), calculations of spectroscopic data as well as the heart of chemistry – reaction mechanisms. The latter are not only used to explain observed phenomena but also to rationally design new, more selective and more efficient catalysts. In most cases a *less is more* strategy³ is applied to understand qualitatively the investigated systems, i.e. properties which are of particular interest are computed with the smallest possible model



systems. Such reductions allow to carefully check the methods, which are then applied to qualitative analysis of large, metal-containing systems.

The homogeneous metallic catalysts are complicated many-body systems and metallic nanoparticles are already in use as catalysts.⁴ On our way to fully understanding such nano-sized systems or clusters, which are midway between a molecule and the bulk material, like germanium and tin metalloid clusters discussed in chapter 0, we need methods that provide a compromise between accuracy and cost (time of calculations, computer resources needed). On the one hand very accurate methods have been developed over the years and we know how to systematically improve our results but on the other hand the size of the systems of interest limits the applicability of most of these methods. In the last two decades density functional theory (DFT), mainly in the Kohn-Sham formulation,⁵ was without doubts the most successful approach for these systems. However, Jacob's ladder proposed by Perdew,⁶ seems to be rather unstable – higher rungs (better functionals *by design*) do not always give better results for a property of interest.⁷ This was exactly the case in structural studies of small aluminium and tin clusters.⁸ Shortly, we will see that for the case of the nickel dimer, DFT can essentially give any bond distance. Another problem of DFT functionals is the absence of long range, weak interactions.⁹ Unfortunately, accurate geometry optimisation with post-Hartree-Fock methods for systems consisting of more than 50 atoms are extremely time consuming and – at some level of system size and method complexity – simply impossible. Also, calculations become a complicated task when static correlation starts to play an important role, i.e. the investigated system cannot be described by a single-determinant method (like DFT or HF) because of near degeneracies of the electronic states. This is particularly the case when molecules are far from the equilibrium geometries, e.g. if bonds are significantly elongated. Other prominent manifestations of static correlation are *3d* transition metal compounds with partially filled *d* shells. Once the static correlation problem is solved (or is not present) the dynamic correlation due to interaction of the electrons still remains an important contribution to the total energy. While DFT partially covers this type of correlation, the HF wave function must be augmented by excited configurations in order to account for dynamic correlation.

In most computations concerning homogeneous catalysis with metal complexes, DFT methods are employed due to the size of investigated systems.^{10,11} However, the unbalanced treatment of static and dynamic correlation make the transition metal chemistry a hard test for any functional because most of the popular exchange-correlation functionals were optimised and benchmarked mainly against compounds consisting of main group elements.¹² Many authors emphasize the need to test a set of DFT functionals before making final conclusions.^{10,12} A typical approach in computations of large, multimetallic systems is to compare various functionals with available experimental data. However, such an approach will certainly fail if experimental numbers have large uncertainties or are not available. This



work aims to go beyond the usual DFT calculations, i.e. for each system reliable wave function based reference data will be obtained and used to gain additional information about the investigated chemical structure or reaction.

This thesis is organised as follows. The presentation of results is preceded by the theoretical background of the methods used. This short outline focuses on the basics of selected quantum chemical concepts and aims to show the scope and limitations of various approaches. The application section is comprised of four topics. It begins with the investigation of the addition reactions of dialkylzinc to π -conjugated systems. The reaction is catalysed by bulky paracyclophane-based ligands and constitutes a challenging theoretical problem. On the one hand the long range interactions have to be handled properly because of the presence of bulky groups in the catalyst whereas on the other hand the correlation effects in the transition states have to be described consistently in order to predict the major product of the reaction quantitatively correct by transition state theory. Next, multireference calculations on large germanium and tin cluster compounds will give insights into the unusual bonding situation in these compounds. Unlike the transition states in the dialkylzinc additions, these molecules possess some significantly elongated bonds, but there is no compensation by formation of another bond. Consequently, multireference calculations have to be employed in order to explain the nature of this interaction. The third topic investigated in this thesis is the structure of small nickel clusters. To describe electron correlation in such systems in a balanced way a number of quantum-chemical methods are benchmarked with the complicated electronic structure of the nickel dimer. Selected methods are then used in studies of the electronic structure of Ni_2^- as well as in the geometry and ground state of the nickel trimer and its anion. The gained knowledge is then used in the calculations of the properties of small nickel clusters interacting with alcohol molecules. The obtained data can be directly compared with upcoming experimental measurements in order to derive the geometry of the clusters. The application section is closed by investigations of the molecular oxygen activation with a cobalt complex where the experience from all previously studied systems is combined in order to explain the reorganisation of spins in the analysed reaction. The energetic effect of the reaction as well as relative energies of states with various spin multiplicities are shown to be highly dependent on the method used. At the same time, the electronic structure of the final adduct with oxygen, e.g. the location and number of unpaired electrons, will directly reflect the reactivity of the system towards unsaturated alcohols. Final conclusive remarks can be found at the end in the summary.



2 THEORETICAL BACKGROUND

The aim of this chapter is to give an outline of the methods applied throughout this work. Theories which are well established and comprehensively described in text books are just briefly introduced. The focus is laid on recently developed methods as well as techniques that made them applicable to large molecular systems. The chapter is divided into four major parts. The first introduces the Schrödinger equation and discusses fundamental approximations which make quantum theory applicable to systems larger than the hydrogen atom. Moreover, through a short discussion of the Dirac equation we introduce approximate methods for the handling of relativistic corrections. The next two parts address two distinct approaches in quantum chemical calculations: single reference – HF-based and DFT – and multi reference (MR) methods. The chapter is closed with a description of the techniques common to all of the reviewed methods like basis sets, potential energy surface exploration or molecular vibrations and thermochemical calculations. For sake of simplification atomic units are used.

2.1 BASICS OF QUANTUM CHEMISTRY

2.1.1 THE SCHRÖDINGER EQUATION

Quantum chemistry was built on the time-independent non-relativistic Schrödinger equation:¹³

$$\hat{H}\Psi(\mathbf{x}, \mathbf{R}) = E\Psi(\mathbf{x}, \mathbf{R}) \quad (1)$$

where Ψ is a wave function of the space and spin coordinates \mathbf{x} of N electrons and spatial coordinates \mathbf{R} of M nuclei, E is the total energy associated with the system described by Ψ and \hat{H} is the Hamilton operator defined as:

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \frac{1}{2} \sum_{A=1}^M \frac{1}{M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \quad (2)$$

In eq. (2) variables A and B run over all M nuclei of charge Z_M while i and j over all N electrons. The first two terms describe the kinetic energy of electrons (\hat{T}_e) and nuclei (\hat{T}_n). The next three terms define the potential energy of electron – nucleus interactions (\hat{V}_{en}), electron – electron interactions (\hat{V}_{ee}) and nucleus – nucleus interactions (\hat{V}_{nn}), respectively. In chemistry, we used to think about the molecules in context of their structure, i.e. spatial distribution of atoms. However, neither electrons nor nuclei are static particles. The conceptual bridge between chemistry and physics, that at the same time greatly reduces the complexity of the Schrödinger equation, is called adiabatic approximation.¹⁴ The idea here relies on the fact that even the smallest nucleus, a proton, is over three orders of magnitude



heavier than an electron. Thus, nuclei move much slower than electrons and it is assumed that the total wave function of the system can be expressed in the following form¹⁵

$$\Psi(\mathbf{x}, \mathbf{R}) \approx \Psi_e(\mathbf{x}, R)f(\mathbf{R}) \quad (3)$$

In the above equation, $\Psi_e(\mathbf{x}, R)$ parametrically depends on the fixed positions R of the nuclei, i.e. for any R there is a certain mathematical form of $\Psi_e(\mathbf{x}, R)$. The function $f(\mathbf{R})$ depends not only on R but also on the direction of the vector \mathbf{R} and therefore can be used in the description of molecular vibrations and rotations. We then group the Hamiltonian into two groups – electronic (\hat{H}_e) and nuclear ($\hat{T}_n + \hat{V}_{nn}$):

$$\hat{H} = (\hat{T}_e + \hat{V}_{en} + \hat{V}_{ee}) + (\hat{T}_n + \hat{V}_{nn}) = \hat{H}_e + (\hat{T}_n + \hat{V}_{nn}) \quad (4)$$

In the adiabatic approximation, $\Psi_e(\mathbf{x}, R)$ is an eigenfunction of the electronic Hamiltonian \hat{H}_e . In calculation of $f(\mathbf{R})$ we assume that the movement of nuclei and electrons is uncoupled, i.e. the nuclei ‘feel’ the average field arising from the fixed configuration of electrons for certain R and therefore the position of electrons determine the potential energy of the nuclei. The last statement is a subject of the Born-Oppenheimer approximation¹⁶ which allows to use such concepts like the shape of a molecule or potential energy surface of a chemical system.

From now on we will focus solely on the electronic problem

$$\hat{H}\Psi(\mathbf{x}) = E\Psi(\mathbf{x}) \quad (5)$$

where $\hat{H} = \hat{H}_e$ as defined in eq. (4), E is electronic energy and $\Psi(\mathbf{x}) = \Psi_e(\mathbf{x}, R)$ for clarity.

2.1.2 THE VARIATIONAL PRINCIPLE

The Schrödinger equation can be solved exactly only for a small number of model problems. If a many-body problem has to be solved then an approximate wave function is needed. It is easy to show that the energy ε , calculated with any trial wave function Φ will be always larger or equal to the energy of the ground state E_0 :

$$\varepsilon[\Phi] = \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} \geq E_0 \quad (6)$$

If we now assume that Φ is a finite, continuously differentiable and normalized function (is a Q -class function) then we have a clear prescription of obtaining approximate wave function which is the variational principle. Such a trial wave function is usually constructed from a linear combination of P known basis functions $\{\Psi_i\}$:

$$\Phi = \sum_{i=1}^P c_i \Psi_i \quad (7)$$

The variational parameters c_i are optimised in order to get the lowest possible energy in the given set of basis functions. This method, firstly formulated by Ritz,¹⁷ paved the way for a



class of quantum-chemical methods called variational where the energy is minimised by a systematic refinement of the trial wave function.

2.1.3 MANY ELECTRON WAVE FUNCTION: THE SLATER DETERMINANT

The variational principle introduced in the previous paragraph is a lighthouse for the search of an optimal wave function. However, it says nothing about the form of this function. Analytical solutions of Schrödinger equation for model systems give some one-electron wave functions but the many electron analogues are not known. From physical considerations we only know that they have to be functions of Q -class that depend on the same variables like the exact solution as well as have to be antisymmetric under permutation of electrons (change the sign upon relabeling of an electron pair). Slater¹⁸ proposed N -electron function of the following determinant-form:

$$\Psi_{\text{Slater}} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \dots & \phi_1(N) \\ \vdots & \ddots & \vdots \\ \phi_N(1) & \dots & \phi_N(N) \end{vmatrix} \quad (8)$$

In this definition ϕ_i are orthonormal one-electron spinorbitals (products of orbitals and spin functions) and the factor before the determinant is a normalization factor. The Slater determinant (8) has desired properties:

- changing the labels of electrons means exchange of columns of the determinant – the function is antisymmetric,
- two electrons cannot occupy the same spinorbital (Pauli principle) – in this case two columns are equal and the determinant vanishes.

Most of the quantum chemical methods use the Slater approach either in one-determinant form (single reference methods) or in multi-determinant formulation (multireference methods). Nevertheless, one should have in mind that the wave function in form of eq. (8) does not depend on the interelectronic distance r_{12} . Therefore, in order to at least approximately describe the electronic cusp one has to use large orbital basis sets. A different approach is to explicitly correlate the motion of electrons which can be achieved for example by means of f_{12} methods.¹⁹ However, due to its mathematical complexity this approach is still limited to medium-sized molecules containing main-group elements.

2.1.4 SOME REMARKS ABOUT RELATIVITY

Ground state energies and properties of molecular systems obtained with eq. (5) suffer from the non-relativistic treatment of motion. While this effect is negligible for light elements, it contributes significantly to the chemical behaviour of heavy elements mainly through contraction of orbitals.²⁰ Recently, an extreme example of the importance of relativistic correction has been shown for the calculation of the standard voltage of the lead-acid battery.²¹ It appeared, that only 20% of the voltage can be recovered in non-relativistic calculations.



The treatment of a finite speed of light with all its consequences requires the usage of the electron-positron Dirac equation:²²

$$[\boldsymbol{\beta}c^2 + c(\boldsymbol{\alpha} \cdot \mathbf{p}) + V]\psi = i\hbar \frac{\partial}{\partial t} \psi; \quad \psi = \begin{bmatrix} \psi^L \\ \psi^S \end{bmatrix} \quad (9)$$

where c is the speed of light, V an external potential, \mathbf{p} the momentum operator, and $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$ are the 4×4 Dirac matrices.²³ The spinor ψ which appears in eq. (9) in place of Schrödinger's wave function consists of a so-called small (ψ^S) and large (ψ^L) component. In Dirac theory we are mainly interested in the stationary electronic solution. The Dirac equation for an electron in a molecular field has the following form:

$$\begin{aligned} h_D \psi &= E^+ \psi \\ h_D &= \boldsymbol{\beta}' c^2 + c(\boldsymbol{\sigma} \cdot \mathbf{p}) + V = \begin{bmatrix} V & c(\boldsymbol{\sigma} \cdot \mathbf{p}) \\ c(\boldsymbol{\sigma} \cdot \mathbf{p}) & V - 2c^2 \end{bmatrix} = \begin{bmatrix} h_{LL} & h_{LS} \\ h_{SL} & h_{SS} \end{bmatrix} \\ \boldsymbol{\beta}' &= \boldsymbol{\beta} - \mathbf{I}_4 \end{aligned} \quad (10)$$

where $\boldsymbol{\sigma}$ is a vector that collects the Pauli spin matrices and \mathbf{I}_4 denotes a 4×4 identity matrix. The one-electron Dirac operator h_D can be used in place of the nonrelativistic one-electron operator in the electronic structure calculations. To take into account the relativistic effects in the two electron repulsion terms, $g(1,2)$, the Breit terms²⁴⁻²⁶ have to be considered in addition to the classical $1/r_{12}$ term:²⁷

$$g(1,2) = \frac{1}{r_{12}} - \frac{\boldsymbol{\alpha}(1) \cdot \boldsymbol{\alpha}(2)}{r_{12}} + \frac{1}{2} \left[\frac{\boldsymbol{\alpha}(1) \cdot \boldsymbol{\alpha}(2)}{r_{12}} - \frac{(\boldsymbol{\alpha}(1) \cdot \mathbf{r}_{12})(\boldsymbol{\alpha}(2) \cdot \mathbf{r}_{12})}{r_{12}^3} \right] \quad (11)$$

In conjunction with h_D for the one electron part, the resulting Hamiltonian is the Dirac-Coulomb-Breit (DCB) Hamiltonian.

The small and large components of the spinor ψ are coupled through eq. (9) by the coupling operator \mathbf{R} :

$$\psi^S = \mathbf{R}\psi^L; \quad \mathbf{R} = (2c^2 - V + E^+)^{-1} c(\boldsymbol{\sigma} \cdot \mathbf{p}) \quad (12)$$

Thus, the one-electron operator h_D can be block-diagonalised by some unitary transformation:

$$U^\dagger h_D U = U^\dagger \begin{bmatrix} h_{LL} & h_{LS} \\ h_{SL} & h_{SS} \end{bmatrix} U = \begin{bmatrix} \tilde{h}_{++} & 0 \\ 0 & \tilde{h}_{--} \end{bmatrix} \quad (13)$$

The operator \tilde{h}_{++} will then only act on the large, electronic component. The exact unitary transformation is given as:

$$U = \begin{bmatrix} \Omega_+ & -\mathbf{R}^\dagger \Omega_- \\ \mathbf{R} \Omega_+ & \Omega_- \end{bmatrix}; \quad \Omega_+ = \frac{1}{\sqrt{1 + \mathbf{R}^\dagger \mathbf{R}}}; \quad \Omega_- = \frac{1}{\sqrt{1 + \mathbf{R} \mathbf{R}^\dagger}} \quad (14)$$

However, the unitary transformation (14) is usually done in an approximate way because the coupling \mathbf{R} depends explicitly on the electronic energy (see eq. (12)). For example by taking

$$\mathbf{R} = (2c^2 - V + E^+)^{-1} c(\boldsymbol{\sigma} \cdot \mathbf{p}) \approx \frac{1}{2c} (\boldsymbol{\sigma} \cdot \mathbf{p}) \quad (15)$$



and applying the unitary transformation to the Dirac Hamiltonian one obtains the Pauli one-electron Hamiltonian:²⁸

$$\hat{h}^{Pauli}(i) = V + T_i - \frac{p_i^4}{8c^2} + \frac{1}{4c^2} \boldsymbol{\sigma} [(\nabla V) \times \mathbf{p}_i] + \frac{1}{8c^2} (\nabla^2 V) \quad (16)$$

where only terms to $O(c^{-2})$ were retained. In the Hamiltonian (16), the non-relativistic terms are extended by three relativistic corrections: mass-velocity, spin-orbit and Darwin term, respectively.²³ The Hamiltonian which combines the Pauli approach to the one-electron part and the Breit correction to the two-electron interactions is called the Breit-Pauli Hamiltonian.²⁹ However, the computations with the resulting operator are rather demanding, especially for the spin-orbit terms. Thus, in many cases the effective nuclear charge approximation is used.³⁰ Alternatively, the mean-field approach of Hess *et. al.*³¹ can be employed. Other possibilities to carry out the unitary transformation (14) include the zeroth-order regular approximation (ZORA)^{32–34} or the Douglas-Kroll-Hess (DKH) method.^{35–37} In the latter, the spin-dependent terms are usually neglected (scalar DKH).²⁹ Therefore, the spin-orbit effects can be included in the next step, e.g. from the spin-orbit operator based on the Pauli Hamiltonian (16):

$$h^{SO}(i) = \sum_{A=1}^N \frac{Z_A e^2}{4c^2 r_{iA}^3} \boldsymbol{\sigma} \cdot \mathbf{l}_{Ai} \quad (17)$$

where the orbital angular momentum operators \mathbf{l}_{Ai} are defined with respect to each nucleus A . Even more routinely, scalar relativistic effects are introduced into non-relativistic calculations using relativistic effective core potentials (ECP).³⁸ This approach is based on the observation that relativistic effects have the largest influence on the low lying, core electrons, which in chemical reactions do not play as important a role as the valence electrons. Therefore, core electrons can be substituted by a special effective potential which then is used in the Hamiltonian from eq. (5) while valence shells are described in the usual way with accordingly optimised exponents of the basis sets.

2.2 SINGLE REFERENCE METHODS

2.2.1 THE HARTREE-FOCK METHOD

The Hartree-Fock method belongs to the class of variational methods with a trial function consisting of a Slater determinant. By minimising the energy with respect to spinorbitals one can derive the canonical Hartree-Fock equations:

$$\hat{F} \phi_i = \epsilon_i \phi_i \quad (18)$$

where ϕ_i are canonical Hartree-Fock orbitals (molecular orbitals, MOs) and ϵ_i are respective orbital energies. The Fock operator, \hat{F} , is an effective one-electron operator defined as a sum of three operators:

$$\hat{F} = \hat{h} + \hat{J} - \hat{K} \quad (19)$$