2.5 In Dialogue with Nature: An integrated experimental and theoretical approach leading from algorithm design to chemical concepts

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ABSTRACT The department of molecular theory and spectroscopy (DMTS) is involved in three main activities: (1) Theoretical method development with emphasis on efficient algorithms for wavefunctions based calculations on realistic chemical systems (this includes the development of the ORCA program package), (2) Computational chemistry studies in the fields of bioinorganic chemistry, homo- and heterogeneous catalysis as well as molecular magnetism and (3) advanced spectroscopic methods to experimentally study the electronic structure of transition metal complexes with relevance to any of the mentioned fields. The report summarizes the progress that has been made in these areas between March 2017 (date of the previous evaluation at; then at the MPI-CEC) and October 2019.

1. Structure of the department

The DMTS was founded in January 2018 in succession of the theory department of Prof. Thiel. The department had previously existed in similar form at the MPI for Chemical Energy Conversion (MPI-CEC, 2011-2017). In the process of moving, the Joint Workspace (JWS) was established between the institutes, which allows the DMTS to host their experimental facilities at the MPI-CEC.

The work done in the DMTS falls into three main areas. There are currently seven group leaders working in the department who have their main focus within one of the three categories. However, we all work closely together, supervise students jointly and drive projects together thus leading to synergies and frequent exchange between the sub-disciplines covered. The three main areas are:

(1) *Theoretical Method Development* in quantum chemistry. Here we focus on the development of single- as well as multi-reference wavefunction based approaches that are applicable to large systems (molecules, cluster models). The emphasis is not only on total energies, but on molecular properties and theoretical spectroscopy and magnetism. (PIs: Auer, Bistoni, Izsak, Manganas)

(2) *Computational chemistry applications* (mostly) on transition metal containing systems (enzymes, catalysts, solids and surfaces). The emphasis are mechanistic studies in all areas of catalysis as well as the establishment of structure-property relationships (such as in molecular magnetism). (PIs: Atanasov, Auer, Bistoni, Pantazis, Manganas, van Gastel, Ye)

(3) *Spectroscopic studies* aiming at experimentally defining the electronic structure of transition metal species like catalysts or reaction intermediates. A wide variety of techniques is used here including electron paramagnetic resonance (EPR), SQUID magnetometry, Mössbauer spectroscopy (MB), absorption (ABS), circular dichroim (CD), magnetic CD (MCD) and resonance Raman (rR) spectroscopy. (PIs: van Gastel, Manganas in cooperation with Eckhard Bill at the MPI-CEC) A wider variety of X-ray absorption and emission techniques are pursued in collaboration with the department DeBeer at the MPI-CEC.

Two recent perspective articles summarize the philosophy that underlies our approach to science.[1a,b] In essence, we look for a intimate interconnection between theory and experiment using spectroscopy as the main meeting point between the disciplines rather than total energies. In order to develop the full information content of a wide variety of spectroscopic properties, increasingly accurate and versatile tools are being developed for the calculation of spectroscopic properties while on the other hand, methods are also developed to translate the results of elaborate calculations into chemical language ("Interpretation aids").

2. Quantum Chemical method Development

The ORCA program suite is a general-purpose electronic structure package that has been developed in the department since the late 1990s. Being free for academic researchers, it has found a rapidly growing user community of more than 25000 users world-wide.[1c] Commercial users can obtain a license via the company FAccTs. The technical aspects of the ORCA development efforts are described elsewhere in this report (PI: Wennmohs).

2.1. Linear scaling single reference correlation methods.

Our development efforts in this area are based on the concept of domain-based pair natural orbitals (DLPNOs). These efforts have ongoing for more than a decade in the DMTS and are based on resurrecting ideas that have been put forward in the late 1960s. The work in the DMTS has greatly pushed these ideas forward leading to a host of new methods that allow for correlated wavefunction

calculations of unprecedented size and accuracy. The DLPNO methods have been embraced by the computational chemistry community and are now widely used world-wide. It has been our main focus of the past several years to make these methods as versatile as possible in order to allow for computational chemistry applications at correlated levels in a black-box fashion in much the same way that DFT is being used. Noticeable recent developments include the development of an open-shell DLPNO-CCSD(T) method,[2] closed- and open-shell CCSD densities[3] (and hence properties), multireference methods (DLPNO-NEVPT2), explicitly correlated variants[4] of closed- and open-shell approaches (DLPNO-CCSD(T)-F12) and analytic DLPNO-MP2 gradients[5] (closed-shell) (PI: Neese).

Major development efforts were directed towards the formulation and implementation of a DLPNO based excited state methodology (PI: Izsak).[6] This is a vastly difficult problem since electronic rearrangements in electronically excited states lead to completely different local orbital structures compared to the electronic ground states. Hence, PNOs for the ground state are not suitable for excited states. This problem was tackled with the similarity transformed equation of motion (STEOM) approach by Nooijen and Bartlett. In this approach one only need to determine ground state coupled cluster amplitudes and solve an excited state eigenvalue problem of the same size as CI-singles (CIS) in order to arrive at a correlated result. This is achieved, by solving the corresponding non-particle conserving EOM-CCSD equations for ionization potentials (IP) and electron affinities (EA) that are then used together with the ground state CC amplitudes to "dress" the CIS matrix. The advantage of having only to solve a CIS size problem allows for calculations of dozens of states on systems with about 200 atoms.

The recent accomplishment of DLPNO-IP-EOM-CCSD, DLPNO-EA-EOM-CCSD and finally DLPNO-STEOM-CCSD leads to method of unprecedented accuracy and efficiency.[7] The method was subsequently used in a number of application studies with excellent success.[8]

2.2. Multireference methods.

In the field of multi-reference wavefunction methods, we have made significant progress in terms of the performance and convergence of the underlying CASSCF program for large molecules.[9] In addition, we have implemented quasi-degenerate versions of the NEVPT2 correction and have provided a CASPT2 implementation in ORCA (PI: Neese).

The iterative configuration expansion (ICE-CI) is an approximate Full-CI method that has been developed in order to treat large active space. Calculations with up to 40 active electrons and over 100 active orbitals have been done. The achievable accuracy is on the order of 1 mEh relative to FCI. The method is particularly powerful for antiferromagnetically coupled magnetic systems since our implementation can work on individual configuration state functions (CSFs), which allows for the efficient refinement of any branching diagram state. We currently investigate solutions to the size-consistency problem as well as how to incorporate dynamic correlation on top of these enormous active space (PI: Neese).

The new method DCD-CAS(2) is based on the idea to treat static correlation, dynamic correlation and relativity on equal footing.

In this method, the CASCI matrix is "dressed" to second order in perturbation theory with dynamic correlation contributions and the extension to treat spin-orbit coupling and magnetic fields at the same time was also implemented. The method offers well-defined advantages of NEVPT2 and CASPT2, but suffers from the fact that it is state universal and a single 0th order Hamiltonian carries the burden of describing multiple states.[10] Solutions to the problem are under investigation (PI: Neese).

Significant efforts are directed towards finding a practical multireference method that goes beyond second-order in perturbation theory. Since such methods are extremely complex, automatic code generation tools need to be employed. We have developed a powerful framework (ORCA-AGE) that allows for arbitrary single- and multireference wavefunction methods to be implemented. It produces code that is almost as efficient as hand-optimized code. So far, we have implemented full internally contract MRCI (FIC-MRCI), its CEPA-0 variant (FIC-CEPA0) as well a rigorous internally contract multireference coupled cluster method (FIC-MRCC).[11] We are currently investigating their properties, computational efficiency and how to simplify these methods to the point that they can become practical computational tools for large-scale use (PI: Izsak, Neese).

2.3. Chemical Analysis tools.

In order to translate the results of elaborate wavefunction based correlation calculations into chemical language, we have developed two particular powerful tools that have found widespread use in our applied studies.

Given a fragmentation scheme of the supersystem (now automated), the local energy decomposition (LED) is able to decompose the DLPNO-CCSD(T) energy into intra- and inter-molecular components. In particular, it is able to extract intermolecular dispersion- and electrostatic- as well as exchange- interaction energies. This has been found to be extremely fruitful in a number of studies. In the evaluation period, open shell- and multi-level variants of the LED were developed as well as an extremely cost-effective scheme that provides near DLPNO-CCSD(T) accuracy at Hartree-Fock cost (HFLD; PI: Bistoni, see below).[12]

The ab initio ligand field theory (AILFT) is tailored towards d- and f-elements. It allows to uniquely extract ligand field parameters (Racah parameters, one-electron ligand field matrices and the one-electron spin-orbit coupling constant) from the the results of CASSCF, NEVPT2 or DCD-CAS(2) calculations. This has found widespread use in our studies in molecular magnetism (PI: Atanasov, see below).[13]

2.4. Methods for Theoretical Spectroscopy.

In the field of theoretical spectroscopy, a traditional mainstay of the group, three main developments have taken place:

(1) Methods for the prediction of NMR parameters. We have developed accelerated versions of the well-known methods to calculate chemical shifts and spin-spin coupling constants based on DFT. In addition, we have developed and efficient implementation of RI-MP2 and double hybrid DFT chemical shieldings that allow for much more accurate calculations than previously feasible with DFT. We currently extend these methods towards the DLPNO variants (PI's: Auer, Neese).[14]

(2) Methods for the calculation of X-ray spectra. These developments have been ongoing for about a decade and constitute a major collaborative project between the DMTS and the experimental group of Prof. Dr. DeBeer at the MPI-CEC. In the evaluation period, we have developed wavefunction based methods for the calculation of RIXS and XMCD spectra as well as photoelectron spectra on the basis of the ROCIS protocol (PI: Maganas, Neese).[15]

(3) A new module, orca_esd, has been developed that works together with TD-DFT as well as DLPNO-STEOM-CCSD. It allows for the calculation of vibronic band shapes of absorption and emission (fluorescence and phosphorescence) spectra as well as resonance Raman spectra and excited state lifetimes (PI: Izsak).[16]

3. Computational Chemistry applications

3.1. Enzyme modelling.

The DMTS traditionally has a major focus on theoretical studies in bio-inorganic chemistry. Among many other enzymes, the studies on the oxygen evolving complex (OEC) (PI: Pantazis) particularly fruitful has been. In the evaluation period, we have contributed to clarifying the geometric and electronic structure of the oxygen-evolving complex of photosystem II in the last observable step of its catalytic cycle (the S3 state) by critically analyzing conflicting experimental and theoretical data to eventually propose alternative rationalizations for the structural models presented in recent XFEL crystallographic studies and to elaborate the concept of structural heterogeneity that we proposed a few years ago. A central tenet of this concept is that water binding at the active site can be decoupled from the oxidation of the inorganic cofactor. In a 2019 publication we showed that this idea can lead to a novel formulation for the active oxygen-evolving intermediate of the catalytic cycle, specifically a species that contains a genuine Mn(V)-oxo unit where Mn(V) adopts a five-coordinate trigonal-bipyramidal geometry.[17]

In a number of QM/MM studies, the DLPNO-CCSD(T) method allowed us to compute extremely accurate energies for very large systems. As an example, we have recently performed quantum mechanical/molecular mechanical (QM/MM) calculations using a QM region of more than 300 atoms and nearly 7000 basis functions to quantify a series of enzymatic reaction barriers accurately.[18]

3.2. Weak intermolecular interactions.

The LED has been proven instrumental in obtaining insight into a wide variety of intermolecular interactions (PI: Bistoni). These include transition metal (TM)-ligand interactions in organometallic chemistry and catalyst-substrate interactions in organocatalytic transformations. For instance, agostic and alkane-σ complexes of TMs are key intermediates in CH activation reactions. An in-depth study of the CH…TM interaction in these systems allowed us to propose a series of design principles for new complexes, highlighting for the first time the importance of London dispersion for their structural stability.[19a]

The DLPNO-CCSD(T)/LED methodology has also been fruitfully used in collaboration with the department of Prof. List for the case of enantioselective Diels-Alder reactions involving a,b-unsaturated methyl esters.[19c]

Many of our studies are performed in the framework of the SPP 1807 ("Control of London dispersion in Molecular chemistry") in which Alexander Auer[19d,e] and Giovanni Bistoni[19a-c] are involved as PIs.

3.3. Heterogeneous systems.

The DMTS has been involved in modelling surfaces and solids together with their spectroscopic and reactive properties for a number of years (PI: Manganas). Our approach consists of studying ECP capped and electrostatically embedded cluster models of increasing size. The clusters are considered converged once the results of DFT calculations agree with truly periodic DFT calculations on the same system using the same functional. However, we are then able to apply powerful single- and multireference wavefunction based correlation methods to the problem for which no periodic counterparts exist. In a recent example it has been demonstrated that for both organic and inorganic semiconductors the back-transformed Pair Natural Orbital Similarity Transformed Equation of Motion Coupled-Cluster (bt-PNO-STEOM-CCSD) method provides the best agreement with the available experimental values resulting in errors that are on average lower than 0.2 eV.[8b]

3.4. Molecular Magnetism.

Molecular magnetism is another mainstay of the DMTS (PI: Atanasov). These studies have been particularly successful in the evaluation period resulting in a number of high-profile publications.[20] Particularly noteworthy is a study that, for the first time, experimentally as well as theoretically analyzed and rationalized the all-important spin-phonon coupling that is instrumental for the relaxation mechanisms that spoil the hysteresis that underlies the desired construction of molecular switches.[20a]

Another important study has found a mononuclear Co(II) transition metal complex with a record unquenched orbital angular momentum of L=3. This molecule was theoretical predicted by us in 2015 and finally synthesized. It showed the spectacular world record magnetic moment anticipated together with the extremely unusual situation of featuring an electronic ground state that does not obey the Aufbau principle.[20b] In all these studies a crucial element was to be able to perform large-scale CASSCF/NEVPT2 calculations with inclusion of spin-orbit coupling and coupled to AILFT.

4. Spectroscopic Studies

Our spectroscopic studies are typically done in collaboration with synthetic groups. A noteworthy collaboration with the department of Alois Fürstner has investigated di-rhodium paddlewheel complexes and bismuth-rhodium analogs that are indispensable tools in modern organometallic catalysis for the controlled decomposition of diazo-compounds. (PI: van Gastel) Here, we have used absorption and rR spectroscopy coupled to calculations in order to establish the underlying electronic structure reasons for

the enhanced reactivity of BiRh(esp)2C(p-MeOPh)2 over Rh2(esp)$_2$C(p-MeOPh)$_2$.[21]

High-valent iron centers and their reactivity has been a long-standing research interest of the DMTS. In the evaluation period, we investigated the electronic structure and reactivity of low spin tetragonal FeV-nitrido and oxo-complexes using a wide variety of spectroscopic techniques (MCD, EPR, MB, UV/vis). (PI:Ye)[22a] On the basis of that, we proposed a EPR signal for such species.[22b] Very recently, we investigated oxygenation of a fleeting FeV-nitrido intermediate to furnish the corresponding Fe-nitrosyl complex using in situ EPR and MB spectroscopy.[22c]

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