2.5.8 Research Area "Ab Initio Quantum Chemical Methods for Complex Molecular Systems" (M. Roemelt)

Involved: A. Khedkar

Objective: A physically meaningful theoretical description of many complex molecular systems requires the usage of multireference methods. These methods treat a small part of the molecule, the so-called "active space", exactly while the rest of the molecule is subject to approximations. In the last decade mathematical techniques such as the Density Matrix Renormalization Group (DMRG) have emerged that allow for multireference calculations with active space sizes that are out of reach for comparable standard quantum chemical methods. The objective of this research area is to develop extensions to the DMRG Ansatz that improve its accuracy and to allow the calculation of magnetic properties. Furthermore, application of these methods to transition metal compounds aims at understanding their unique physical and chemical properties.

Results: In the last decade the ab initio density matrix renormalization group (DMRG) has been shown to provide a reasonable and accurate alternative to complete active space (CAS) methods as basis for molecular multireference calculations. It can be regarded as an approximation to the exact diagonalization of the large Hamiltonian matrix in the basis of many-electron wavefunctions within the active orbital space. A great advantage of DMRG is that it approximately solves a problem whose complexity scales exponentially with increasing system size by optimizing only a polynomial number of parameters. Owing to this favorable behavior DMRG is able to treat large active spaces on the order of 20-80 orbitals. However, quantitative accuracy is only reached if dynamic electron correlation effects are considered, too. In the reporting period we have developed a novel approach to the combination of DMRG and strongly contracted second-order N-electron valence perturbation theory (SC-NEVPT2) for quantum chemical multireference calculations [138]. The main objective of this approach is to lower the cost of treating systems with large active spaces and large orbital spaces with a moderate and controllable accuracy. The complexity of the problem and the computational cost are reduced by projecting the perturber functions as well as the unperturbed Hamiltonian onto a reduced Hilbert space. The form of this reduced space is determined by a modified density matrix renormalization procedure. This procedure ensures that both the electronic ground state and the perturber functions are accurately approximated during the calculation. As a result, the total energy (DMRG + SC-NEVPT2) converges rapidly and smoothly towards the exact value with increasing number of states in the renormalized Hilbert space as demonstrated for a dimeric Cu cluster (cf. Figure 22).

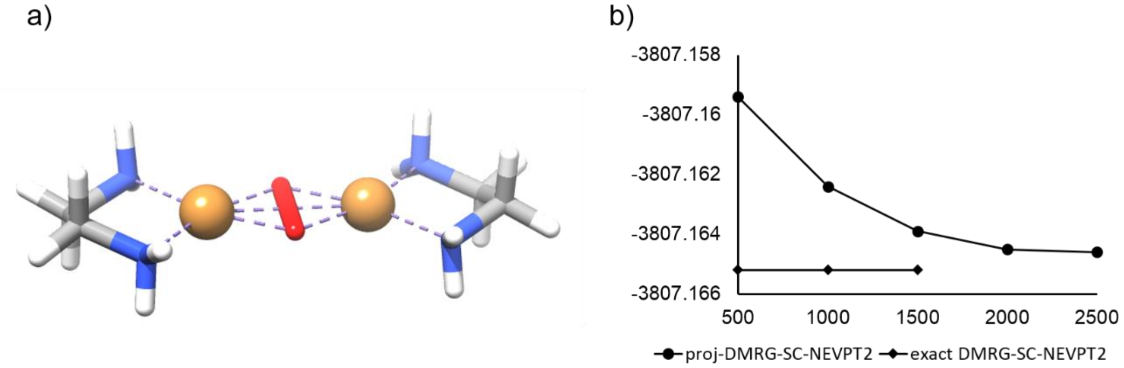

Fig. 22. Ball and stick visualization of $[Cu_2O_2(en)_2]^{2+}$ (a) and total energy calculated with the projected DMRG-NEVPT2 with respect to the bond dimension M (b).

Furthermore we have developed an approach to describe spin-orbit coupling (SOC) on top of a regular Born-Oppenheimer DMRG calculation in the framework of quasi-degenerate perturbation theory (QDPT) [136]. This approach accounts for SOC effects on the many-electron level and can thus be thought of as the molecular equivalent of atomic Russell-Saunders or LS coupling. With the spin-orbit coupled wavefunctions at hand the molecular g-tensors can be calculated in a rigorous and phenomenological way as proposed by Gerloch and McMeeking in 1975. Importantly, since the SOC matrix is fully diagonalized within a finite set of many-electron states, our approach is able to produce qualitatively and quantitatively correct results even for systems with a near-degenerate ground state. For example, the behavior of the molecular g-values of a Mo(III) trisamidoamine catalyst as it is distorted along its Jahn-Teller axis is correctly reproduced (cf. Figure 23). In contrast, regular linear-response type or single reference perturbation theory methods are bound to fail in these cases.

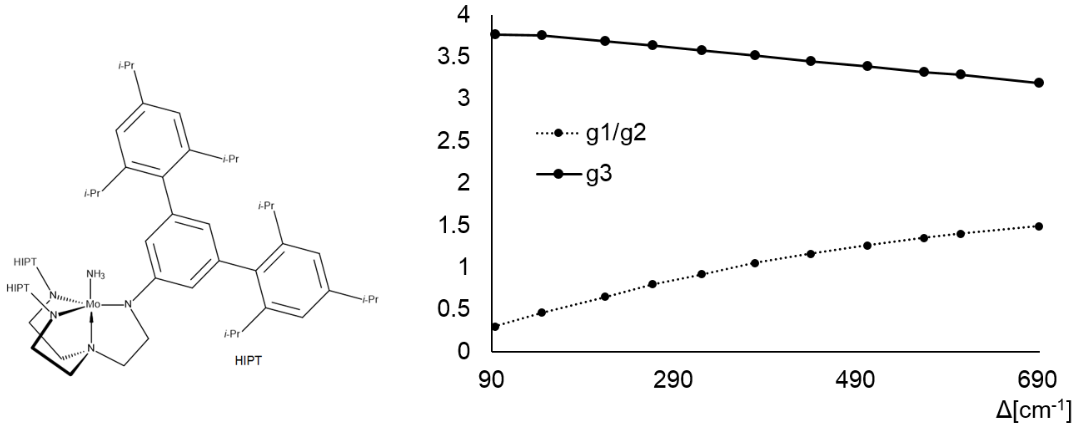

Fig. 23. Left: The chemically active Mo(III) trisamidoamine ammonia complex that is a crucial intermediate in the Yandulov/Schrock cycle. HIPT = hexaisopropylterphenyl. Right: The evolution of its molecular g-values with increasing Jahn-Teller splitting of the near-degenerate electronic ground state doublet.

During the reporting period our group has written our own standalone SCF and DMRG-SCF program from scratch. It has a variety of features including

- SCF for closed and open-shells
- DMRG-SCF (DIIS and full Newton Raphson)
- Density fitting
- Nuclear gradients
- Conventional and projected (vide supra) DMRG SC-NEVPT2
- Automated formula generation based on second quantization operator algebra
- Interfaces to the ORCA and PySCF program packages

The code is fully parallelized and utilizes the LibInt integral generation library by E. Valeev as well as the BLOCK code by G.K.-L. Chan. In the future it will be used in computational studies and moreover serve as basis for further developments in this field such as automated active orbital selection schemes and nonadiabatic coupling coefficients.

A study of the magnetic coupling constants of dimeric Mn compounds (cf. Figure 24), including a mixed-valence species, with DMRG-based methods elucidated the importance of different orbital subspaces for the description of magnetic coupling with *ab initio* techniques (manuscript in preparation). As anticipated, it could be shown that in addition to the Mn *3d* orbitals, the occupied *2p* orbitals of bridging oxo groups play an important qualitative role in magnetic coupling. In contrast, unoccupied oxo-orbitals or any orbitals that are located on bridging carboxylate groups contribute only in a minor way to the observed antiferromagnetic behavior. Moreover, the obtained results demonstrate that quantitative correct results can only be expected when dynamic electron correlation is explicitly taken into account.

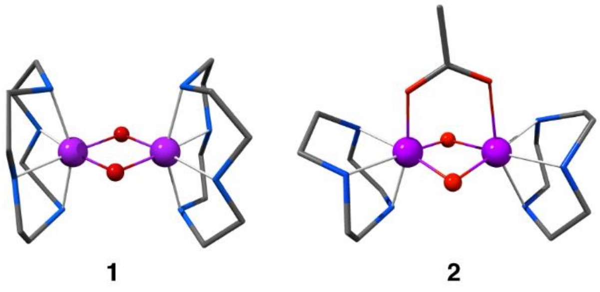

Fig. 24. Structures of the investigated Mn complexes. Color scheme: Mn purple, O red, N blue, C grey. Hydrogen atoms are omitted for clarity.

Future directions: Applications of the aforementioned theoretical methods will yield insight into the physical and chemical properties of complex molecular systems. A second scheme for the inclusion of SOC in molecular DMRG calculations will be implemented and applied. In addition, our code will be supplemented by a novel automated selection scheme for large-scale active spaces as well as the ability to calculate nonadiabatic coupling coefficients to study chemical reactions on multiple adiabatic surfaces.

Publications resulting from this research area: 136, 138

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