

Welcome to the Group of Dr. Michael Römelt

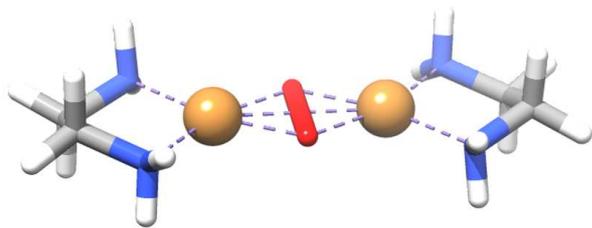
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Complex molecular systems, such as mono- and polynuclear transition metal compounds, play a key role in many areas of chemistry. They serve a multitude of purposes in various applications in homogeneous inorganic and bioinorganic catalysis as well as functional materials. Yet understanding and predicting their properties as well as their reactivity is a great challenge and one of the current frontiers of theoretical chemistry. Our research group focuses on both, the development of novel quantum chemical methods that are especially designed to tackle complex molecules and on the application of existing methods to tackle interesting chemical problems. The former aspect of our work is centered around modern multireference methods such as the density matrix renormalization group. With the help of these methods it is possible to correctly describe complex molecules that are difficult if not impossible to access using conventional methods like the complete active space self-consistent field (CASSCF). In addition to our efforts in theory development we conduct computational studies of different inorganic and organic systems using a variety of quantum chemical methods, ranging from density functional theory to high-level ab initio multireference methods. These studies concern chemical reactivities as well as spectroscopic properties. A short description of some of our recent research projects can be found below.

Our research group is affiliated to the Max-Planck Institute for Coal Research in Mülheim an der Ruhr and is located at the Ruhr-University Bochum. It is funded by the Max Planck society in the framework of the "Otto-Hahn Award" program. If you are interested in our research, please contact us via michael.roemelt@theochem.rub.de.

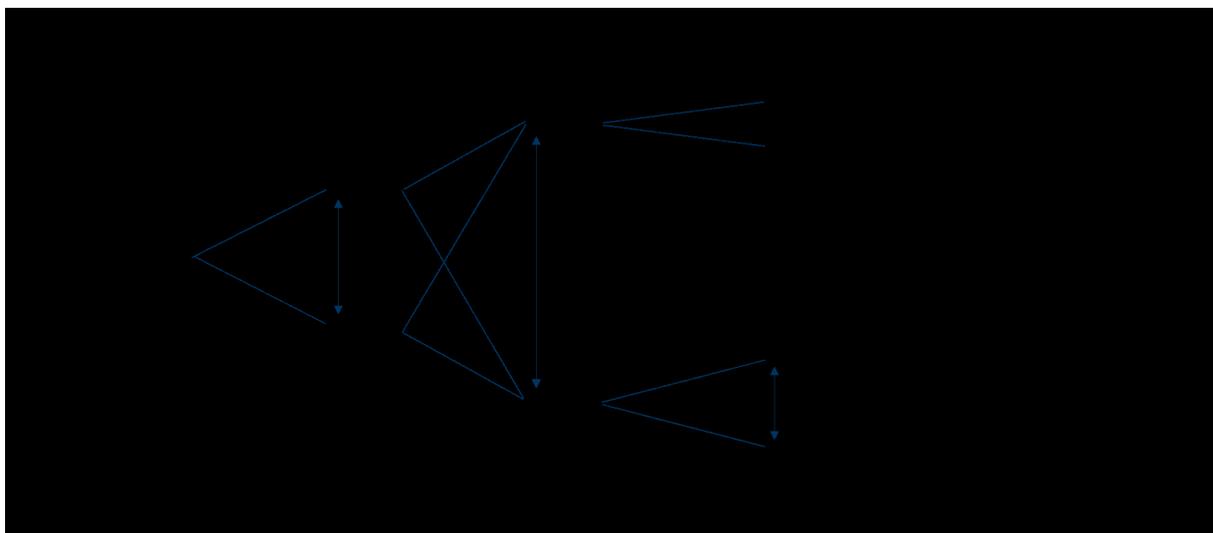
Research Topics

Method Development



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. Therefore 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. The main objective of this approach is to lower the cost to treat systems with large active spaces and large orbital spaces with a moderate and controllable accuracy. As demonstrated for a dimeric Cu cluster the total energy (DMRG + SC-NEVPT2) converges rapidly and smoothly towards the exact value with increasing bond dimension which is a user-defined accuracy parameter. However, the existing method considerably suffers from the comparably high bond dimensions required to achieve chemical accuracy. In this regard, the most promising route forward for the future may be to sacrifice some of the constraints used in the projection approximation associated with the formally low scaling.

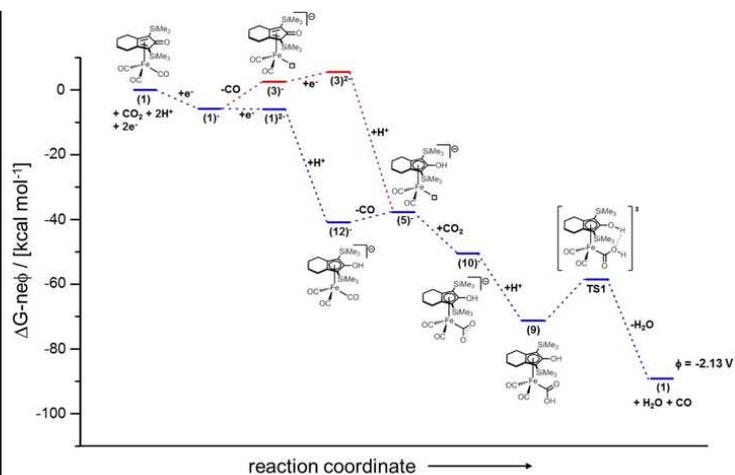
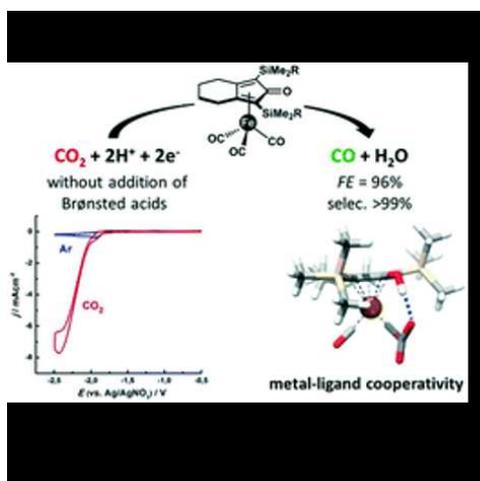
M. Roemelt, S. Guo, G. K.-L. Chan *J. Chem. Phys.* **2016**, 144, 204113



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). 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. In contrast, regular linear-response type or single reference perturbation theory methods are bound to fail in these cases. Our method will serve to investigate the magnetic properties of complex molecular systems that cannot be properly treated by conventional DFT or CASSCF based approaches. Moreover, future developments might concern the inclusion of SOC to excited states outside the active space regime and the combination with schemes to incorporate dynamic electron correlation.

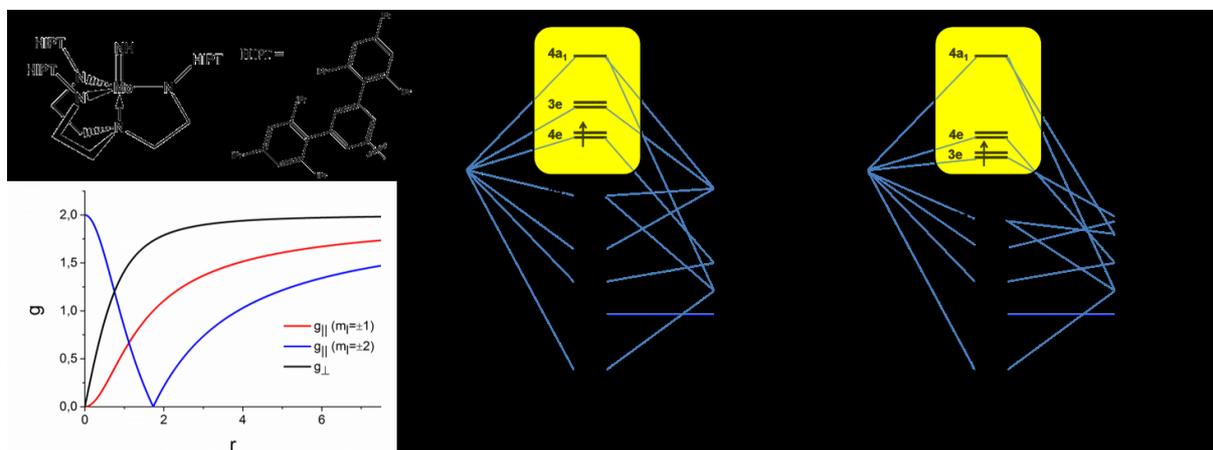
M. Roemelt *J. Chem. Phys.* **2015**, 143, 044112

Applications



Among the numerous methods for the activation of carbon dioxide and its use as C1-building block, its electrocatalytic reduction constitutes a promising approach. In particular, the electrogeneration of carbon monoxide is attractive, since CO is used as a key feedstock in industry for a wide range of organic transformations. Due to the high overpotential and a variety of possible reaction pathways, a selective electroreduction of CO₂ to CO is not trivial. A general possibility to overcome the issue of kinetic inhibition of an electrochemical reaction is the use of homogeneous redox-active catalysts in an indirect electrolysis. Under given conditions (substrate concentration, electrode material, electrolyte, etc.), the employment of such redox catalysts can lower kinetic barriers and often leads to an increased and/or entirely different selectivity. Recently, the groups of Dr. Robert Francke and Prof. Dr. Matthias Beller identified a cyclopentadienone iron(0) complexes as molecular catalysts for the electroreduction of CO₂. It effectively converts CO₂ into CO with two electrons and two protons to yield H₂O. Interestingly, the reaction occurs without the addition of any acid. With the help of our quantum chemical computations it was possible to propose a reasonable reaction mechanism that it is in good agreement with the experimental results. According to our results, binding of CO₂ to the catalyst in the desired 1:1 fashion via its C-atom can only be observed after the catalyst has been twofold reduced. Furthermore, protonation of the catalyst prior to CO₂ binding facilitates the binding process through formation of a hydrogen bond. Although the highest calculated barrier is associated to the breaking of the CO bond and the simultaneous formation of an OH bond, recent experimental findings indicate that the effectiveness of the reaction is controlled by a dimerization equilibrium of a crucial intermediate. Further experimental and computational studies on this system are currently conducted in the labs of Dr. Francke, Prof. Dr. Beller and Prof. Dr. Ludwig at the University of Rostock and the Leibniz Institute for Catalysis as well as our group.

A. Rosas-Hernández, H. Junge, M. Beller, M. Roemelt, R. Francke *Cat. Sci. Technol.* **2017**, *7*, 459-467



Another recent computational study of our group involves the magnetic properties of two derivatives of the molybdenum trisamidoamine (TAA) complex $[\text{Mo}]$ ($= (3,5\text{-}(2,4,6\text{-}i\text{-Pr}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3\text{NCH}_2\text{CH}_2\text{N})\text{Mo}$). In particular, we investigated $[\text{Mo}]\text{NH}$ and $\{[\text{Mo}]\text{N}\}^-$ by means of EPR spectroscopy as well as multireference quantum chemistry. Because of the degeneracy of the electronic ground states of both $\{[\text{Mo}]\text{N}\}^-$ and $[\text{Mo}]\text{NH}$, only multireference-based methods such as the complete active-space self-consistent field (CASSCF) and related methods provide a qualitatively correct description of the electronic ground state and vibronic coupling. The molecular g values of $\{[\text{Mo}]\text{N}\}^-$ and $[\text{Mo}]\text{NH}$ exhibit large deviations from the free-electron value g_e . Their actual values reflect the nature of the ground state as well the relative strengths of vibronic and spin-orbit coupling. In the course of the computational treatment, the utility and limitations of a formal two-state model that describes this competition between couplings are illustrated, and the implications of our results for the chemical reactivity of these states are discussed.

A. Sharma, M. Roemelt, M. Reithofer, R. R. Schrock, B. M. Hoffman, F. Neese *Inorg. Chem.* **2017**, DOI: 10.1021/acs.inorgchem.7b00364

- Curriculum Vitae
- Publication List