Summary of:
Third edition of QBtopIC, June 10th, 16:30-18:00 EST via Zoom

Electronic Structure of Polynuclear Transition Metal Clusters via Multiconfigurational Wave Functions

Giovanni Li Manni (GLM) started the section with an introduction to polynuclear transition-metal systems and explained the advantages of multiconfigurational over single-reference methods in particular for non-collinear spin states. He introduced the wavefunction representations in terms of Slater determinans (SD) and configuration state functions (CSF) showing fundamental advantage of the latter [1, 2, 3]. Namely, he showed that simple orbital localization and site reordering can greatly reduce the complexity of the WF. Moreover, it also leads to quasi-block-diagonal Hamiltonian structure and makes possible to directly optimize excited states with different leading components even within the same spin sector. As an example GM showed a detailed study of Fe_4S_4 cubane considering using *d*-orbitals-only complete active space CAS(20,20) and results of more involved CAS(44,32) calculations that explicitly taking into account charge-transfer excitations. Impressive fully resolved manifold of singlet states within 100 meV window was presented [2]. GLM also introduced the stochastic generalized active space approach he developed together with Oskar Weser and presented how it can be used to selective target different correlation paths and understand complex electronic structures.

In his talk Werner Dobrautz (WD) introduced the full configuration interaction quantum Monte Carlo (FCIQMC) in its spin-pure formulation, a method with stochastic sampling of multiconfigurational WF that gets around the exponential scaling of the full configuration interaction [4, 5]. WD presented benefits of spin-symmetry adapted basis and introduced the Graphical Unitary Group Approach (GUGA) that can be used for efficient treatment of spin symmetry. Namely, he introduced the Gel'fand-Tsetlin basis [6], showed graphical representation of CSF and presented an efficient algorithm for on-the-fly evaluation of Hamiltonian matrix elements [7, 8]. WD showed the results of spin-adapted FCIQMC-based CASSCF calculations manifested the importance of orbital optimization to dig up the fine details of multiconfigurational WF that show as the higher-order terms upon mapping to spin models.

The topic continued by Nikolay Bogdanov (NB), who presented in detail the concept of model spin Hamiltonian. On top of well-known isotropic spin Hamiltonian, the higher-order biquadratic, ring and anisotropic exchange terms were discussed. NB presented the spin model and its solution for the fully oxidized Fe_4S_4 cubanes [4]. It turns out that each state is characterized not only by the total spin value, but also by two well-defined 'pair spins' quantum numbers [9]. NB discussed the underlying general local spin coupling scheme that was be used to solve the model and showed its connection to GUGA CSF construction. At the end of his talk NB presented the mapping of the *ab initio* energies and corresponding WF's onto the extended Heisenberg model and emphasized the importance of choosing the right model for the correct interpretation of computational data.

The the concluding discussion incorporated the details of compressed local-site-reordered wavefunctions beyond the dominant spin part and proposal for the extension of the presented methodologies to mixed-valence systems.

Panel members:

invited expert
Werner Dobrautz

invited expert
Nikolay Bogdanov

discussion leader
Giovanni Li Manni

References:

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[3] G. Li Manni, ChemRxiv (https://doi.org/10.26434/chemrxiv.14498361.v1)

[4] G. Booth, Thom, and A. Alavi, JCP, **131**, 054106 (2009)

[5] K. Guther et al., JCP, **153**, 034107 (2020)

[6] I. Gel'fand and M. Tsetlin, Doklady Akad. Nauk SSSR, **71**, 1017 (1950)

[7] J. Paldus, J. Chem. Phys. **61**, 5321 (1974)

[8] I. Shavitt, Int. J. Quantum Chem., **12**, 131 (1977)

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