

Summary of:

Second edition of QBtopIC, March 31st 16:30-18:00 EST

LIGAND FIELD THEORY

The second QBtopIC took place via Zoom on Wednesday, March 31st. Rob Deeth (RD) was joined by Frank Neese (FN), Paul Walton (PW) and over 100 fellow enthusiasts for 90 minutes of discussion centred on ligand field theory (LFT). RD kicked off with a review of the current text-book view of LFT before delving into the historical development of the subject from Bethe's crystal field theory [1] through to Griffith and Orgel's seminal monograph from 1957 [2], Schäffer and Jorgensen's angular overlap model in 1965 [3] and Gerloch and Woolley's cellular ligand field approach of the early 1980s [4, 5]. FN focussed on the generality of the ligand field model as a basis for interpreting the spectroscopic and magnetic properties of a huge number and variety of transition metal complexes with a particular emphasis on using LFT to guide more sophisticated quantum chemical calculations including the ab initio LFT (AI LFT) approach developed by FN and co-workers based on CASSCF/NEVPT2 wavefunction theory [6, 7]. PW presented an analysis of the ligand field Hamiltonian and his efforts with graduate student, George Nunn, to develop a new program, Kestrel, to carry out parametric LFT calculations 'on-the-fly' which explore the relationships between the parameters and the resulting properties. The Kestrel demonstration used the interesting and unusual electronic structure of linear Co(II) compound $\text{Co}(\text{C}(\text{SiMe}_2\text{ONaph})_3)_2$ [8] to show the program's ability to highlight important features of the structure and bonding which could then guide development of improved complexes with optimal properties. While all three presenters came at LFT from very different directions, we were agreed that LFT is an extremely useful but somewhat misunderstood tool. Although there was some discussion about just how far the model can be pushed and to what extent the LFT parameters are capable of modelling the nature of metal-ligand bonding, the fact that LFT is multiconfigurational was unanimously acknowledged as was the utility of AI LFT which has provided a 'first principles' validation of the ligand field model. Throughout the session, there was a lively question-and-answer session going on in parallel via the chat facility which was expertly moderated by FN. Overall, feedback on the day and since has been very positive. It was an interesting and enjoyable session which will hopefully stimulate the continued and future use of LFT.

Panel members:



invited expert
Frank Neese



invited expert
Paul Walton



discussion leader
Rob Deeth

References:

- [1] H.A. Bethe, Ann. Physik., 395 (1929) 133-208.
- [2] J.S. Griffith, L.E. Orgel, Quart. Rev. Chem. Soc, 11 (1957) 381-393.
- [3] C.E. Schäffer, C.K. Jorgensen, Mol. Phys., 9 (1965) 401.
- [4] M. Gerloch, R.G. Woolley, Prog. Inorg. Chem., 31 (1983) 371-446.
- [5] M. Gerloch, J.H. Harding, R.G. Woolley, Struct. Bond., (1981) 1-46.
- [6] L. Lang, M. Atanasov, F. Neese, J. Phys. Chem. A, 124 (2020) 1025-1037.
- [7] M. Atanasov, D. Ganyushin, K. Sivalingam, F. Neese, A Modern First-Principles View on Ligand Field Theory Through the Eyes of Correlated Multireference Wavefunctions, in: D.M.P. Mingos, P. Day, J.P. Dahl (Eds.) Molecular Electronic Structures of Transition Metal Complexes II, Springer Berlin Heidelberg, Berlin, Heidelberg, 2012, pp. 149-220.
- [8] P.C. Bunting, M. Atanasov, E. Damgaard-Møller, M. Perfetti, I. Crassee, M. Orlita, J. Overgaard, J. van Slageren, F. Neese, J.R. Long, Science, 362 (2018) eaat7319.