

## Computational Transition Metal Chemistry

The title of this thematic issue reflects the shift in emphasis and possibilities that has taken place in theoretical modeling of transition metal chemistry in the last few years. Chemists are mostly concerned with synthesis and characterization of materials. Computational modeling of chemistry needs to account for reaction mechanisms, structure, and spectra. Since we are still far from the time when artificial intelligence methods can be used to conceive of new materials with predesignated properties and then plan their synthesis, the results of computational modeling must be transmitted to people with real intelligence who will use the insights gained to plan new experiments. The review articles in this issue are written with that in mind—the emphasis is on results from calculations without undue discussion of methods.

Even a decade ago, theoretical inorganic chemistry was heavily dependent on empirical models. Ligand field theory provided insight into the assignment of d–d transitions. Extended Huckel theory, INDO, and other approximate molecular methods provided some insight into bonding at known (or assumed) equilibrium geometries.  $X\alpha$  and other density functional theory (DFT) based methods were in use but were not generally available in convenient programs. By today's standards, computers were still either very slow or very expensive (or both). *Ab initio* Hartree–Fock calculations with simplified ligands gave more-or-less useless results—bond lengths were wrong by tenths of angstroms, the relative energies of isomers were often wrong, the relative energies of possible spin multiplicities were wrong, etc. This was quite unlike the situation for organic chemistry where Hartree–Fock methods generally provided at least a reasonable starting point to gain insight into reaction mechanisms, structure, and spectra for small molecules (up to about six carbon atoms) in the gas phase. More advanced methods, such as Møller–Plesset perturbation theory, configuration interaction, or coupled cluster theory, were then routinely used to provide semiquantitative agreement with experiment and proof of the basic reasonableness of the results. For transition metals, the error in the *ab initio* Hartree–Fock energy—usually called the 'correlation energy'—was just too large. More precisely, the change in the error with bond length and

with electronic state exceeded the change in the actual energy. This swamped other errors such as use of simplified models for the ligands, neglect of the solvent, and neglect of relativistic corrections. The change in correlation energy along a reaction path could not be neglected even for qualitative purposes.

What has happened in the last decade to change the situation? Computers have gotten much faster and cheaper. UNIX workstations and even PCs are now faster, have more memory, and have more disk space available to a single user than the supercomputers initially funded by the NSF at the supercomputer centers. Commercial programs incorporating the latest methods have become widely available and require little knowledge beyond the chemical formula to produce some result for a variety of properties. The overwhelming change, however, was the widespread acceptance of density functional methods. Because DFT included corrections to HF energies for correlation energy, the structures and relative energies became much more reliable while the computations with Kohn–Sham orbitals became simpler (compare the review of Cundari on multiple metal–metal bonds described by conventional methods). Computational transition metal chemistry today is almost synonymous with DFT for medium-sized molecules. When the core electrons are replaced by an effective potential, the largest relativistic effects can be automatically included (see reviews by Rohmer, Bénard, Poblet on metallocarbenes, Dedieu on Pt and Pd compounds, Masaras et al. on polyhydrides).

Niu and Hall show that DFT is the only viable approach to understanding reactions with realistic ligands. They review work on a large number of reaction mechanisms. Loew and Harris discuss the use of DFT for iron–heme enzymatic reactions. As Siegbahn and Blomberg point out, progress in the last five years on modeling such difficult problems as metal-mediated enzyme kinetics has been faster than we imagined because DFT for large ligand-saturated systems is more reliable than could have been expected from the poor results on small unsaturated metal centers. While our best understanding of electronic structure has always been integrated mentally into experimental work, Torrent et al. emphasize the present possibilities where computational modeling is used as a complement to experi-

ment in studying catalytic reactions of industrial importance.

This is not to say that DFT solves all the problems! The magnetism and spin states of multimetal clusters and solids are not well described by DFT. These are still most easily described by an empirical Heisenberg Hamiltonian and tight-binding models (see the reviews by Alonzo and Ceulemans et al.). Detailed potential curves and states of very small molecules to spectroscopic accuracy require configuration interaction methods (see review by Harrison). No review here really addresses the traditional problem of assigning and correlating the trends in the vibronic spectra of transition metal complexes. Loew and Harris do discuss the spectroscopic problem for iron-heme complexes and notes that INDO/SCF/CI is still the method of choice. Solvent effects on spectra remain a difficult problem. Hush and Reimers compare their approach to other treatments of the solvent but emphasize that one must first understand the gas-phase spectrum.

Frenking and Fröhlich discuss the difficult problem of understanding the energetic contributions to the chemical bonds in terms of what the electrons are doing. While present-day approximations to DFT such as B3LYP usually give good estimates of the ground-state energy, they do not lend themselves to an easy interpretation of the results. The Kohn-Sham determinant is not a wave function. Interpret-

ing the Kohn-Sham orbitals as though they gave a good density matrix rather than just an accurate density leads to the same logical difficulties as interpreting orbitals from a semiempirical method that gives the correct energy but a very poor approximation to the wave function. The improved energies derived from DFT do not indicate that the Kohn-Sham orbitals are an improvement over Hartree-Fock orbitals. The improved geometries, vibrational frequencies, and bond energies, however, do allow improved understanding of bonding using the traditional methods for extracting bonding pictures from experimental data.

I wish to thank John Gladysz, Josef Michl, and their staff for all their help in putting this special issue together. They have made the task almost effortless. I also thank all the authors of the reviews. Writing a review requires enormous effort as witnessed by the fact that over 3000 papers are cited in this special issue. In accordance with the truly international nature of theoretical research, two-thirds of the authors are from outside the United States.

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