

## **Diverting Diradicals -- From Methylene to Metal-Dioxygen Complexes**

Christopher J. Cramer

The diversity of structure and reactivity associated with carbenes, nitrenes, arynes, nitrenium ions, and related reactive intermediates has long been a source of fascination for organic chemists, and of consternation for computational chemists. Accurate predictions of both singlet- and triplet-state electronic structures can be particularly challenging owing to the typically multiconfigurational nature of at least one of the relevant wave functions. The quantitative and qualitative lessons learned from organic systems may be applied to inorganic systems with similar frontier orbital characteristics. This can become an issue when single-determinantal density functional theory, usually well suited to the description of many properties of 1:1 metal:dioxygen complexes, fails to accurately compute state-energy splittings because of limitations associated with diradical character. A key example of this latter situation will be discussed within the context of copper-dioxygen species having relevance to biomimetic C-H bond activation reactions.