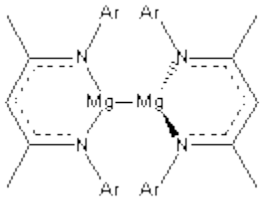
NON-NUCLEAR ATTRACTOR IN THE ELECTRON DENSITY

This one is a bit afield from organic chemistry, but the result is important for computational chemists who are interested in electron density analysis.

The topological electron density analysis of Bader (also called Atoms-In-Molecules – AIM) carves up a molecular electron density into regions associated with an attractor. The attractor is a critical point in the electron density that is a maximum in all directions. Gradient paths, paths that trace increasing electron density, terminate at such an attractor. The union of all such paths defines a basin. Bader found that for typical molecules, the attractor is coincident with the position of the atomic nucleus. He has then assumed a 1:1 correspondence between these two – all nuclei are attractors and all attractors correspond with nuclei.

This correspondence has been questioned in computations on some metals. For example, Li_n and Na_n (n=2,4,6) have a non-nuclear attractor. However, no clear-cut unambiguous experimental observation of non-nuclear attractors has been made, until now. Platts and Stasch[1] have obtained the x-ray diffraction electron density of **1** and they find a non-nuclear attractor near the midpoint of the Mg-Mg bond.

This is corroborated by DFT computations of **1** and some related systems. It should be said that the electron density along the Mg-Mg path is quite flat in the middle, but the attractor is present, and the integrated number of electrons within the basin associated with this non-nuclear attractor is a non-trivial 0.81 e (experiment) or 0.79 e (DFT).



1

Ar=2,6-di-*i*-propylphenyl

It now appears incontrovertible that non-nuclear attractors of the molecular electron density can exist. It would be especially interesting if these types of points could be located in organic species.

Source: http://comporgchem.com/blog/?p=1370