Magnetic Aromaticity from NICS to Bond Magnetizability

by

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Nucleus Independent Chemical Shift, NICS, is one of the most employed probes for measuring the so-called "magnetic aromaticity", *whatever it is!*[1] NICS has been used for measuring and comparing the "aromaticity" among different classes of molecules containing main-group and transition-metal atoms. But, to what extent NICS really measures the "electronic ring current", which is assumed to be the source of magnetic aromaticity.

We performed a systematic study to probe the influence of various factors on the magnitude of the NICS values.

Our investigations suggest that NICS values might be contaminated by two main factors; the local electron density [2] and the size of aromatic rings. [3]

Measuring the influence of $\rho(r)$ on the magnetic shielding of arbitrary points in molecular space, i.e. NICS, is not a trivial task. We assumed the following form for the influence of $\rho(r)$ on the non-atom centered shielding, i.e. NICS:

$$NICS_{zz}(r) = g(r) \times F[\rho(r)] \qquad\qquad eq.\ 1$$

Here, the $g(r)$ measures pure contribution of the electronic currents at a point in space and the $F[\rho(r)]$ is an unknown functional of $\rho(r)$ which measures the influence of electronic matter at the same point of space. This equation is a mixed equation; composed of a ground state, $\rho(r)$, and a response property, $g(r)$. The real indicator of aromaticity in this equation is the $g(r)$, which results from the electronic currents. Since the proper form of $F[\rho(r)]$ is unknown, one may remove the ground state contribution by studying the $NICS_{zz}$ in the limit of zero electron density.

$$\lim_{r \to \infty}\left(\frac{NICS_{zz}(r)}{\rho(r)}\right) = g_\infty(r) \qquad\qquad eq.\ 2$$

On the other hand, we proposed a classical ring current model to measure the "ring current intensity", I, which can be related to the magnetic aromaticity. Some models have been proposed for simulating electronic currents in aromatic rings.[4] However, these models are not capable of reproducing the ring currents in π-MOs. Indeed, the π-electron density of a planar aromatic molecule should be zero on the ring plane; a successful model must reflect this simple fact. Accordingly, we employed a double current loop model for measuring the π-ring current intensity as follows:

$$\sigma_\pi = \frac{\mu_0 I_\pi}{2 B_{ext}}\left(\left(\frac{R^2}{(R^2+(z-r)^2)^{\frac{3}{2}}}\right) + \left(\frac{R^2}{(R^2+(z+r)^2)^{\frac{3}{2}}}\right)\right) \qquad eq.\ 3$$

In the equation 3 σ_π, μ_0, I_π, B_{ext}, R, z and r represent the π-magnetic shielding, the permeability of vacuum, π-ring current intensity, the strength of external applied field, the π-current loop radius, the direction perpendicular to the ring plane and the height of the current loop radius above (and below) the ring plane of the molecule, respectively. This model clearly showed that the ring radius is an important factor on the magnitude of non-atom centered magnetic shieldings, e.g. NICS values.

The bond magnetizability, defined within the context of the quantum theory of atoms in molecules, QTAIM, was the latest probe that we employed for evaluating our assumption regarding the NICS. The bond magnetizability, $\chi(\Omega|\Omega')$, measures the extent of the contribution of the induced electronic current flux that passes through the inter-atomic surface between two neighboring atoms, Ω and Ω'.[5] This is in close analogy with the "flux of current density" that is used by Monaco et al. for probing aromaticity among various aromatic systems.[6]

Surprisingly, these three approaches for measuring the magnetic aromaticity converge into the same conclusion; this convergence between three independent methods demonstrates validity of the initial proposal about the nature of NICS.

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