



FRITZ HABER SEMINAR ANNOUNCEMENT

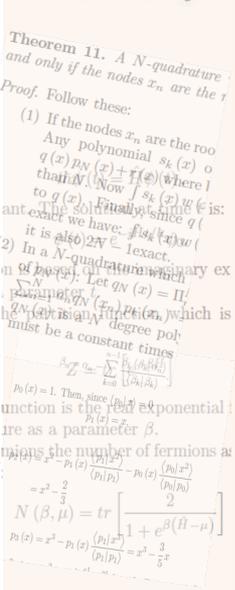
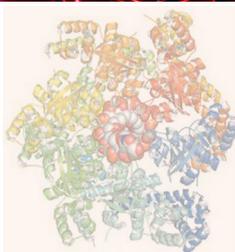
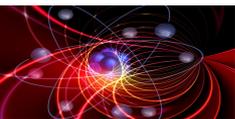
Dept. of Organic Chemistry, Weizmann Institute of Science

Prof. Gershom (Jan) Martin

Atomic Partial Charges in Molecules — Towards A Guide For The Perplexed

Thursday, November 5th 2020 at 13:00
via Zoom:

<https://huji.zoom.us/j/9766578069>



Abstract

Atomic partial charges are among the most commonly used interpretive tools in quantum chemistry. Dozens of different ‘population analyses’ are in use, none of which correspond to a quantum mechanical observable (with one arguable exception, QTAIM). They are best seen as proxies (indirect gauges) rather than measurements of a ‘general ionicity’.

We will give a bird’s eye overview of the different techniques and try to rationalize them using an extension of the Truhlar taxonomy. Then we will explore what actually happens when you consider statistical correlations between them, for a large and chemically diverse dataset that spans a broad swathe of chemical space. For the GMTKN55 benchmark suite of ca. 2,500 main-group molecules, which entail ca. 30,000 unique, non-trivial atomic partial charges, some two dozen different charge distributions were evaluated using the PBE0 density functional near the 1-particle basis set limit.

The correlation matrix between these different charge distributions exhibits a block structure; blocking is, broadly speaking, by charge distribution class. A principal component analysis on the entire dataset suggests that nearly all variation can be accounted for by just two ‘principal components of ionicity’: one has all the distributions going in sync, while the second corresponds mainly to Bader QTAIM vs. all others. A weaker third component corresponds to electrostatic charge models in opposition to the orbital-based ones. The single charge distributions that have the greatest statistical similarity to the first principal component are iterated Hirshfeld (Hirshfeld-I) and a minimal-basis projected modification of Bickelhaupt charges. If three individual variables, rather than three principal components, are to be identified that contain most of the information in the whole dataset, one representative each for three classes of charge distributions is needed: one based on partitioning of the density (such as QTAIM), a second based on orbital partitioning (such as NPA), and a third based on the molecular electrostatic potential (such as HLY or CHELPG).

An Open Access paper summarizing much of this research is available at <http://doi.org/10.1002/cphc.202000040>