Abstract: MATH/CHEM/COMP 2007, Dubrovnik, June 11-16, 2007

THE HIRSHFELD ATOM IN THE MOLECULE CRITICALLY EXAMINED

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The concept of an atom in a molecule is a very important one in chemistry because molecules are usually considered as a set of atoms held together by chemical bonds. Unfortunately, such an approach barely has a good theoretical basis. Moreover, the lack of a good definition has opened the door to the existence of many different approaches to identifying the atom in the molecule (AIM).
Among the AIM definitions currently in use, one of the preferred ones is based on the Hirshfeld method.[1] There, an AIM density function is constructed using a weight function as follows:

$$\rho_A(\mathbf{r}) = w_A(\mathbf{r})\rho(\mathbf{r})$$

Where the weight function is a positive definite one:

$$w_A^H(\mathbf{r}) = \frac{\rho^0_{A,Z_A}(\mathbf{r})}{\sum_{A=1}^{M}\rho^0_{A,Z_A}(\mathbf{r})}$$

A so-called promolecular density function $\rho^0(\mathbf{r}) = \sum_{A=1}^{M}\rho^0_{A,Z_A}(\mathbf{r})$ is constructed by the simple superposition of atomic densities for the atoms arranged in the same way as in the molecule.
All applications of the Hirshfeld-technique up to now rely on the use of neutral atom densities $\rho^0_{A,Z_A}(\mathbf{r})$, that is: atomic densities that integrate to for every atom to the atomic number Z_A. This, however, has long been recognized as a flaw.[2] Moreover, the information entropy background of the Hirshfeld recipe entails that for the proper definition of the AIM, the isolated atom density should have the same population as that for the AIM.[3]
In the present lecture, a new algorithm[4] is introduced where several problems with the Hirshfeld scheme are solved. The so-called iterative or self consistent Hirshfeld-I scheme removes arbitrary decisions, is more in line with information entropy and allows the use of the Hirshfeld scheme for charged systems.

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