Chemical Concepts from Density Functional Theory: Chemistry from the Linear Response Function

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Within Density Functional Theory[1], the so called Conceptual Density Functional Theory[2] has proved to be a valuable tool for interpreting and predicting chemical reactivity. As opposed to the more traditional reactivity descriptors such as electronegativity, hardness,… the linear response function $\chi(\underline{r},\underline{r}')$ representing the response of the density $\rho(\underline{r})$ at position $\underline{r}$ to an external potential perturbation v ($\underline{r}'$) at position $\underline{r}'$, $(\delta\rho(\underline{r})/\delta v(\underline{r}'))_N$ remained nearly unexploited. Although well known, in its time dependent form, in the solid state physics and time-dependent DFT communities the study of the "chemistry" present in the kernel was, until recently, relatively unexplored.

After a brief introduction to the basics of conceptual DFT, the evaluation of the linear response function as such and its study in the time independent form are highlighted in the present talk[3]. On the fundamental side, the focus is on the approaches of increasing complexity to compute and represent $\chi(\underline{r},\underline{r}')$, its visualization going from plots of the unintegrated χ ($\underline{r},\underline{r}'$) to an atom condensed matrix. The study on atoms reveals its physical significance, retrieving atomic shell structure, while the results on molecules illustrate that a variety of chemical concepts are retrieved: inductive and mesomeric effects, electron delocalization, aromaticity and anti-aromaticity, σ and π aromaticity,… The applications show that the chemistry of aliphatic (saturated and unsaturated) chains, saturated and aromatic/ anti-aromatic rings, organic, inorganic or metallic in nature, can be retrieved via the linear response function, including the variation of the electronic structure of the reagents along a reaction path. The connection of the linear response function with the alchemical derivatives[4] is also highlighted and applied in the case of transmutation energies[5] of diatomics and carbocyclic systems. If time permits some applications in the field of inverse molecular design will be commented, pushing the boundaries of intrinsically stable radicals[6].

References:

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