The linear response function as an interpretational tool : retrieving atomic shell structure, inductive and mesometric effects, aromaticity and anti-aromaticity

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Within the context of our ongoing interest in Conceptual Density Functional Theory [1] [2] as an interpretational tool for discussing chemical reactivity we focused in recent years on the linear response function $(\partial^2 E/\delta v(\underline{r})\delta v(\underline{r}'))_N$ or $(\delta\rho(\underline{r})/\delta v(r'))_N$ representing the response of the system's electron density ρ at position $\underline{r}$ to a perturbation at position $(\underline{r}')$.

Recent results are reported on a judiciously chosen set of closed shell atoms, throughout the periodic table [3] reporting the most intensive study of this property hitherto. Different graphical representations of the kernel are presented and discussed, the atomic shell structure is retrieved and the polarizability values obtained started from the kernel are compared with high level calculations showing that the simple KS type ansatz for the evaluation of the kernel [4] [5] captures the trend governing α throughout the Periodic Table.

In a second part of the presentation the focus is on the use of the condensed form of the linear response function as a descriptor of aromaticity and anti-aromaticity with a series of examples varying from cyclic hydrocarbon type molecules via inorganic rings (borazine, boroxine, s-triphosphatriborin) to planar metallic systems E_4^{2-} and E_4^{2-} (E = Al, Ga) [5,6] [7].

The evolution of the linear response function along the reaction coordinate for the aromatic TS reaction between ethane and butadiene is also investigated.   Combined with the earlier work on the retrieval of inductive and mesomeric effects from the condensed linear response function [8-10] this overview illustrates that this hitherto relatively unexplored second derivative in the E = E[N,v] functional Taylor expansion turns out to be of high chemical relevance.

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