# Ti Finishing (off) the Klopman–Salem modeltle

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Using information pertaining to excited states to predict or rationalize the reactivity of a molecule is deeply rooted in the Perturbation Theory of Quantum Mechanics. Indeed, the perturbation theory starts by projecting the perturbed wave function upon the excited states wave function of the unperturbed system. The pioneers that used this approach to describe the reactivity of the ground state were Pearson[1] and Bader[2] . They even proposed a set of rules based symmetry to unveil which excited states are triggered and among them, which drive the reaction. We have tried for several years to follow their footsteps by looking at the electron density polarization through transition densities [3,4].

$$\Delta\rho(\vec{r}) \approx 2\sum_{k\neq 0} \frac{\Delta_0^k\rho(\vec{r})}{E_0^{(0)} - E_k^{(0)}} \int \Delta_0^k\rho(\vec{r}\,')\hat{P}(\vec{r}\,')d\vec{r}\,'$$

This approach has resulted in a proposal to define two new concepts; namely the polarization entropy and the polarization temperature [5].It is believed that both polarization entropy and temperature open a new avenue to define temperature dependent DFT descriptors. More recently, we have also looked at the information provided by the diagonal element of the linear response function[13] again through the transition densities. The aim of this talk is to present these new concepts and several supporting examples.

$$\chi(\vec{r},\vec{r}) = \left(\frac{\partial^2 E}{\delta v(\vec{r})\delta v(\vec{r})}\right)_N = \left(\frac{\delta\rho(\vec{r})}{\delta v(\vec{r})\delta v(\vec{r})}\right)_N = 2\sum \frac{\rho_0^k(\vec{r})\,\rho_0^k(\vec{r})}{\left(E_0^{(0)} - E_k^{(0)}\right)} = 2\sum \frac{\left(\rho_0^k(\vec{r})\right)^2}{\left(E_0^{(0)} - E_k^{(0)}\right)}$$

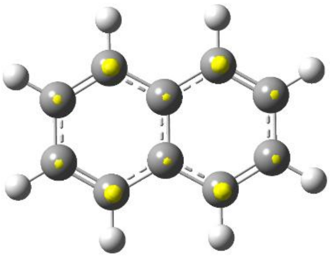

Figure 1. Map of the diagonal element of the linear response function for naphthalene

**Keywords:** Conceptual DFT, Klopman-Salem Model, Polarisation density, Temperature, Entropy

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