CONCEPTUAL DENSITY FUNCTIONAL THEORY : THE LINEAR RESPONSE FUNCTION AND THIRD ORDER DERIVATIVES

Paul Geerlings[1], Nick Sablon[1], Tim Fievez[1], Paul Ayers[2], Pablo Jaque[1], Frank De Proft[1]

[1]Vrije Universiteit Brussel, Chemistry, Pleinlaan 2, 1050 Brussels, Belgium
[2]McMaster University, Hamilton, Canada
email: pgeerlin@vub.ac.be

Within the context of Density Functional Theory, chemical reactivity is described in terms of response functions representing the sensitivity of the system to perturbations in the number of electrons N and/or the external potential v. Until recently the focus has been on first and second order derivatives (1), the latter with the exception of the linear response function $\chi(r,r')$ essentially due to the computational burden involved in the calculation of this second order functional derivative of the energy with respect to the external potential. In the first part of this contribution it will be shown how starting from a MO based expression a direct, generally applicable, and easily interpretable methodology can be developped. The results for a series of linear substituted alkanes and polyenes are used to quantify inductive and mesomeric effects (2). An alternative scheme, based on the extension of explicit numerical evaluation of the first order functional derivative with respect to the external potential is presented (3)(4)(5). In the second part of the contribution some recent examples are presented on the relevance of third order derivatives, involving among others studies on the computation and use of the dual descriptor (the N-derivative of the Fukui function) (5) for example in regaining the Woodward Hofmann rules in chelotropic and sigmatropic reactions (6).

1. Geerlings, P.; De Proft F., PCCP, 10, 3028 (2008).
2. Sablon, N.; De Proft, F.; Geerlings, P.; J. Phys. Chem. Lett., 1, 1228 (2010).
3. Ayers, P.W.; De Proft, F.; Borgoo, A.; Geerlings, P., J. Chem. Phys., 126, 224107 (2007).
4. Sablon, N.; De Proft, F.; Ayers, P.W.; Geerlings, P.; J. Chem. Phys., 126, 224108 (2007).
5. Fievez, T.; Sablon, N.; De Proft, F., J. Chem. Theory. Comp., 4, 1065 (2008).
6. Jaque, P.; Correa, J.V.; Toro-Labbé, A.; De Proft, F.; Geerlings, P., Can. J. Chem., 88, xxx (2010) and references therein.