

Chemical reactivity in density functional theory: Beyond the zero temperature limit

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Chemical reactivity in the framework of density functional theory (DFT) is, basically, centered in the response coefficients that arise from the changes in the energy and the electron density, with respect to changes in the number of electrons or the external potential. This analysis has led to the identification of the chemical potential with the first derivative of the energy with respect to the number of electrons (minus the electronegativity), and the chemical hardness with the second derivative of the energy with respect to the number of electrons. Electronegativity and hardness are intuitive concepts that have been very useful to describe chemical interactions through the electronegativity equalization, the maximum hardness, and the hard and soft acids and basis principles.

However, this development has been based in the zero temperature expressions. Thus, it seems to be important to take into account the temperature effects in all these reactivity criteria. In this work we will present an analysis of the chemical potential, the hardness and the softness, and the derivatives of the electron density with respect to the number of electrons (first – Fukui function and second – dual descriptor) in the Hohenberg-Kohn-Mermin formalism, within the grand canonical ensemble [1-3]. Additionally, we will apply this temperature dependent development to the study of charge transfer processes [4].

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[3] M. Franco-Pérez, P. W. Ayers, J. L. Gázquez, and A. Vela, *J. Chem. Phys.*, 143, 244117 (2015).

[4] M. Franco-Pérez, J. L. Gázquez, P. W. Ayers, and A. Vela, to be published.