Chemical reactivity concepts in density functional theory

José L. Gázquez [a], Marco Franco-Pérez[a], Paul W. Ayers[b] and Alberto Vela [c]

a) Departamento de Química, Universidad Autónoma Metropolitana-Iztapalapa, Ciudad de México, México.
b) Department of Chemistry, McMaster University, Ontario, Canada.
c) Departamento de Química, Centro de Investigación y de Estudios Avanzados, México, Ciudad de México, México.

The pioneer work of Robert Parr in the identification of intuitive concepts with great chemical significance, such as electronegativity and hardness, with fundamental variables of density functional theory, set the basis for a deeper understanding of these quantities, their usefulness and their limitations in studies of a wide variety of chemical interactions. Additionally, through this theoretical framework, he was able to introduce new important concepts at the global, local and non-local levels, and to establish relationships among all these quantities. This approach provides a chemically meaningful language that has become an important support in many studies of electronic structure, and represents nowadays a line of thought within theoretical chemistry. An important aspect is that this development has been based, basically, although not entirely, in the zero temperature condition, a situation that has had two important consequences. On one hand, the restriction of zero temperature leads in some cases to quantities that are mathematically "ill defined", or to relationships among them that are only valid in this limit. On the other hand, the effects of temperature on these quantities had not been quantified.

Thus, in this talk we will present an analysis of these chemical reactivity concepts in the Hohenberg-Kohn-Mermin formalism, within the grand canonical ensemble, to obtain the corresponding temperature dependent expressions, to establish the general relationships among them, and to show how to obtain well behaved quantities, in the cases where they are "ill defined" at zero temperature.

[1] M. Franco-Pérez, J. L. Gázquez, P. W. Ayers, and A. Vela, J. Chem. Phys., 143, 154103 (2015).
[2] M. Franco-Pérez, P. W. Ayers, J. L. Gázquez, and A. Vela, J. Chem. Phys., 143, 244117 (2015).
[3] M. Franco-Pérez, F. Heidar-Zadeh, P. W. Ayers, J. L. Gázquez, and A. Vela, Phys. Chem. Chem. Phys. 19, 11588 (2017).
[4] M. Franco-Pérez, J. L. Gázquez, P. W. Ayers, and A. Vela, J. Chem. Phys. 147, 074113 (2017).
[5] M. Franco-Pérez, J. L. Gázquez, P. Ayers, and A. Vela, Acta Phys.-Chim. Sin, Accepted for publication (2017).
[6] M. Franco-Pérez, J. L. Gázquez, P. Ayers, and A. Vela, J. Chem. Theory Comput., Accepted for publication (2017).