

## **Derivative discontinuity and Kohn-Sham frontier orbital energies in the generalized gradient approximation: The case of negative electron affinities**

José L. Gázquez<sup>a</sup>, Javier Carmona-Espindola<sup>b</sup>, Alberto Vela<sup>c</sup> and S. B. Trickey<sup>d</sup>

<sup>a</sup>*Universidad Autónoma Metropolitana-Iztapalapa, Departamento de Química, Av. San Rafael Atlixco 186, Cd. de México, 09340, México.*

<sup>b</sup>*Conacyt-Universidad Autónoma Metropolitana-Iztapalapa, Departamento de Química, Av. San Rafael Atlixco 186, Cd. de México, 09340, México.*

<sup>c</sup>*Centro de Investigación y de Estudios Avanzados, Departamento de Química, Av. Instituto Politécnico Nacional 2508, Cd. de México, 07360 México.*

<sup>d</sup>*University of Florida, Quantum Theory Project, Dept. of Physics and Dept. of Chemistry, P.O. Box 118435, Gainesville, Florida 32611-8435, USA.*

The electronic energy as a function of the number of electrons  $N$ , according to the zero-temperature grand canonical ensemble composed of systems with  $N_0 - 1$ ,  $N_0$ , and  $N_0 + 1$  electrons in their ground state, is given by a pair of lines connecting the integer values of  $N$  (with  $N = N_0$  for the reference system). In the Kohn-Sham approach to density functional theory, this behavior leads to a discontinuity in the exchange-correlation potential that has important consequences for the frontier orbital eigenvalues. In this work, we present an analysis of the exact theory that allows one to infer the effects of current approximations on the highest occupied and lowest unoccupied molecular orbital eigenvalues. Then, we show the importance of the asymptotic behavior of the exchange-correlation potential in the generalized gradient approximation to determine the shift of the frontier orbital eigenvalues towards the exact values. Finally, we make use of this approach in combination with the NCAP (nearly correct asymptotic potential) exchange-correlation energy functional [J. Chem. Theory Comput. 15, 303-310 (2019)] or with second-order perturbation theory [J. Chem. Phys. 126, 214105 (2007)], to determine ionization potentials and electron affinities through a single calculation of the ground state of the reference system. In particular, we show that this procedure leads to a rather accurate description of negative electron affinities.

JLG was supported by Conacyt grant 237045; AV was supported by Conacyt grant Fronteras-867; SBT was supported by U.S. Dept. of Energy grants DE-SC0002139 and DE-SC0019330.