Hardness of Molecules and Band Gap of Solids from a Generalized Gradient Approximation Exchange Energy Functional

José L. Gázquez[a], Javier Carmona-Espíndola[b], Anaid Flores[a], Alberto Vela[c] and S. B. Trickey[d]

[a]*Universidad Autónoma Metropolitana-Iztapalapa, Departamento de Química, Av. San Rafael Atlixco 186, Cd. de México, 09340, México.*
[b]*Conacyt-Universidad Autónoma Metropolitana-Iztapalapa, Departamento de Química, Av. San Rafael Atlixco 186, Cd. de México, 09340, México.*
[c]*Centro de Investigación y de Estudios Avanzados, Departamento de Química, Av. Instituto Politécnico Nacional 2508, Cd. de México, 07360 México.*
[d]*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 those integer N values. In the Kohn-Sham realization of density functional theory, that linear behavior leads to a discontinuity in the exchange-correlation potential that has important consequences for the calculation of hardnesses in molecules and band gaps in solids. 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 (GGA) to determine the shift of the frontier orbital eigenvalues towards the exact values. Finally, we make use of this approach in combination with a reparametrized version of NCAP (nearly correct asymptotic potential) GGA exchange-correlation energy functional [J. Chem. Theory Comput. 15, 303-310 (2019)] to determine molecular hardnesses and solid band gaps through a single calculation of the ground state of the reference system. We show that this procedure leads to a description of this property that is as accurate as the one obtained from hybrid exchange-correlation energy functionals.