Abstract Submitted
for the MAR12 Meeting of
The American Physical Society

The derivative discontinuity in density functional theory from an electrostatic description of the exchange and correlation potential
XAVIER ANDRADE, ALAN ASPURU-GUZIK, Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138, USA — We present an approach that we have recently proposed [*Phys. Rev. Lett.* **107**, 183002 (2011)] to approximate the exchange and correlation (XC) term in density functional theory. In our approach the XC potential is considered as an electrostatic potential, generated by a fictitious XC density, which is in turn a functional of the electronic density. In this picture, the exact asymptotic limit for low density regions, wrongly predicted by many XC functionals, can be imposed as a local condition. Based on this XC density representation we develop a correction scheme that fixes the asymptotic behavior of any approximated XC potential for finite systems. The procedure is simple, computationally inexpensive, and does not depend on adjusted parameters. Additionally, from the correction procedure it is possible to extract an approximation to the derivative discontinuity of XC energy. This value can be used to directly obtain the gap of the system as a ground-state property. Results are presented for the application of the method to atoms and small molecules. The correction results in a significant improvement in the value of the ionization energy and the gap, with errors that are comparable to the results given by orbital dependent functionals.

Xavier Andrade
Department of Chemistry and Chemical Biology, Harvard University,
12 Oxford Street, Cambridge, Massachusetts 02138, USA

Date submitted: 27 Nov 2011 Electronic form version 1.4