Abstract Submitted
for the MAR15 Meeting of
The American Physical Society

Elimination of the fractional dissociation problem in Kohn-Sham DFT using the ensemble-generalization approach ELI KRAISLER, LEEOR KRONIK, Department of Materials and Interfaces, Weizmann Institute of Science, Israel — Many approximations within density-functional theory (DFT) spuriously predict that a many-electron system can dissociate into fractionally charged fragments. Here, we revisit the case of infinitely separated diatomic molecules, known to exhibit this problem when studied within standard approximations, including the local spin-density approximation (LSDA). We apply the recently suggested ensemble-generalization to LSDA (eLSDA) [1,2] and find that fractional dissociation is eliminated in all systems examined. The eLSDA Kohn-Sham potential develops a spatial step, associated with the emergence of the derivative discontinuity in the exchange-correlation energy functional. This step, predicted in the past for the exact Kohn-Sham potential and observed in some of its more advanced approximate forms, is a desired feature that prevents any fractional charge transfer between the system's fragments. Our findings show that, if appropriately generalized for fractional electron densities, even the most simple approximate functionals correctly predict integer dissociation [3]. [1] E. Kraisler, L. Kronik, Phys. Rev. Lett. 110, 126403 (2013) [2] E. Kraisler, L. Kronik, J. Chem. Phys. 140, 18A540 (2014) [3] E. Kraisler, L. Kronik, submitted.

Eli Kraisler
Department of Materials and Interfaces, Weizmann Institute of Science, Israel

Date submitted: 12 Nov 2014 Electronic form version 1.4