Abstract Submitted
for the MAR14 Meeting of
The American Physical Society

Behavior of the *GW* approximation of Many-Body Pertubation Theory upon electron addition or removal FABIEN BRUNEVAL, CEA, DEN, Service de Recherches de Metallurgie Physique, F-91191 Gif-sur-Yvette, France, MIGUEL MARQUES, ILM Université Lyon 1 et CNRS, 43 blv du 11 novembre 1918, F-69622 Villeurbanne Cedex, France — Within Many-Body Perturbation Theory (MBPT), the position of highest occupied molecular orbital (HOMO) is a quasiparticle energy. It should be hence stable upon an electron removal. The situation is slightly more complicated within Density-Functional Theory, for which the exchange-correlation potential may experience discontinuities. However, once this technicality has been considered, the HOMO energy should also be stable [1]. In other words, within an exact theory, the LUMO of a positive ion should be equal to the HOMO of the neutral molecule. It is remarkable that most approximations within DFT and MBPT fail with this sanity check. Here we demonstrate for isolated atoms and molecules that the *GW* approximation, though not perfect, presents the weakest deviation from the ideal behavior among all the approximation studied [2]. The results have been obtained with a newly developed *GW* code based on the Gaussian basis, which does not employ any further technical approximation besides the basis set [3]. We show that the convergence is unexpectedly slow, in constrast with earlier reports.

[1] A.J. Cohen, P. Mori-Sanchez, and W.T. Yang, Science 321, 792 (2008).
[2] F. Bruneval, JCP 136, 194107 (2012).
[3] F. Bruneval and M.A.L. Marques, JCTC 9, 324 (2013).

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Date submitted: 12 Nov 2013 Electronic form version 1.4