Abstract Submitted
for the MAR13 Meeting of
The American Physical Society

**The bond-breaking and bond-making puzzle: many-body perturbation versus density-functional theory** FABIO CARUSO, Fritz Haber Institute, Berlin, Germany, DANIEL ROHR, Rice University, Houston, United States, MARIA HELLGREN, Sissa, Trieste, Italy, XINGUO REN, PATRICK RINKE, Fritz Haber Institute, Berlin, Germany, ANGEL RUBIO, Universidad del Pais Vasco, Donostia, Spain, MATTHIAS SCHEFFLER, Fritz Haber Institute, Berlin, Germany — Diatomic molecules at dissociation provide a prototypical situation in which the ground-state cannot be described by a single Slater determinant. For the paradigmatic case of $H_2$-dissociation we compare state-of-the-art many-body perturbation theory in the $GW$ approximation and density-functional theory (DFT) in the exact-exchange plus random-phase approximation for the correlation energy (RPA). Results from the recently developed renormalized second-order perturbation theory (rPT2) are also reported. For an unbiased comparison and to prevent spurious starting point effects both RPA and $GW$ are iterated to *full* self-consistency (i.e. sc-RPA and sc-$GW$). Both include topologically identical diagrams for the exchange and correlation energy but are evaluated with a non-interacting Kohn-Sham and an interacting $GW$ Green function, respectively. This has profound consequences for the kinetic and the correlation energy. $GW$ and rPT2 are both accurate at equilibrium, but fail at dissociation, in contrast to sc-RPA. This failure demonstrates the need of including higher order correlation diagrams in sc-$GW$. Our results indicate that RPA-based DFT is a strong contender for a universally applicable electronic-structure theory. F. Caruso *et al.* arxiv.org/abs/1210.8300.

Fabio Caruso
Fritz Haber Institute, Berlin

Date submitted: 05 Nov 2012

Electronic form version 1.4