The random phase approximation and beyond: an assessment for molecular binding energies and reaction barrier heights

XIN-GUO REN, PATRICK RINKE, MATTHIAS SCHEFFLER, Fritz Haber Institute (Berlin), JOACHIM PAIER, Humboldt University (Berlin), ANDREAS GRÜENEIS, GEORG KRESSE, University of Vienna (Vienna), GUSTAVO E. SCUSERIA, Rice University (Houston) — The random phase approximation (RPA) for the correlation energy has become a promising approach for describing electronic systems in various bonding situations. Recent efforts have focused mainly on correcting the general tendency of RPA to underestimate bond strengths e.g. by adding corrections from second-order screened exchange (SOSEX) [1,2] or single excitations (SE) [3]. In this work, we systematically assess the influence of SOSEX, SE and their combinations on the atomization energies of the G2-I molecular set, as well as the chemical reaction barrier heights of the HTBH38/04 and NHTBH38/04 benchmark sets [4]. We find that RPA+SOSEX+SE based on PBE gives the most balanced description. However, for reaction barrier heights standard RPA based on PBE turns out to be better and is surprisingly accurate. The underlying mechanism governing the performance of RPA and its variants in different circumstances will be analysed.