

Calculation of Ab Initio Forces for Optically Excited States

Sohrab Ismail-Beigi and Steven G. Louie

Department of Physics, University of California at Berkeley, and
Lawrence Berkeley National Laboratory (USA)

The recent development of first principles Green's functions methods has allowed for the reliable calculation of optically excited electronic states properties. These methods employ the GW approximation for the one-particle Green's function and solve the Bethe-Salpeter Equation for the two-particle Green's function (GW-BSE method). Up to now, however, the method provided energetic information for a fixed ionic configuration, and, except for inefficient finite-difference schemes, there was no way to calculate the direction in the space of ionic configurations in which the excited state geometry was best optimized. We present a new formalism for calculating such excited-state forces within the GW-BSE methodology. This advance enables the efficient optimization of the photo-excited geometry for the study of phenomena such as photoluminescence or excitonic self-trapping and allows for the possibility of excited-state molecular dynamics. We have implemented the formalism and performed tests on small molecules and show that the GW-BSE method is as accurate as leading quantum chemical methods while offering superior computational scaling. We are now studying photoinduced defects in the solid state, particularly the self-trapping of excitons in silicon dioxide (α -quartz).