Excited states in organic systems from many-body-perturbation theory: the FIESTA initiative

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We present recent studies exploring the merits of specific many-body-perturbation theories, the so-called GW and Bethe-Salpeter (BSE) formalisms, in predicting the quasiparticle and optical excitation energies in organic systems. We will focus on three important examples, namely: (a) charge-transfer excitations [1] in donor-acceptor complexes – including "hot" charge-transfer excitations [2] relevant for understanding organic or hybrid photovoltaic cells, (b) recent developments in calculating electron-phonon coupling matrix elements within the GW formalisms, [3] and (c) a comparison between GW/BSE and high-level coupled-cluster (exCC3) calculations in predicting the excitation energies of an important family of fluorescent dyes. [4] In the later case, the importance of nonlocal correlations is emphasized, with much consequences on the future design of range-separated nonlocal exchange-correlation functionals. Our calculations are performed with the FIESTA package, implementing the GW and Bethe-Salpeter formalisms with an accurate contour deformation, resolution-of-the-identity (Coulomb metric) and Gaussian bases formulation. Scalability tests beyond 60,000 cores and for systems comprising several hundred atoms will be presented.

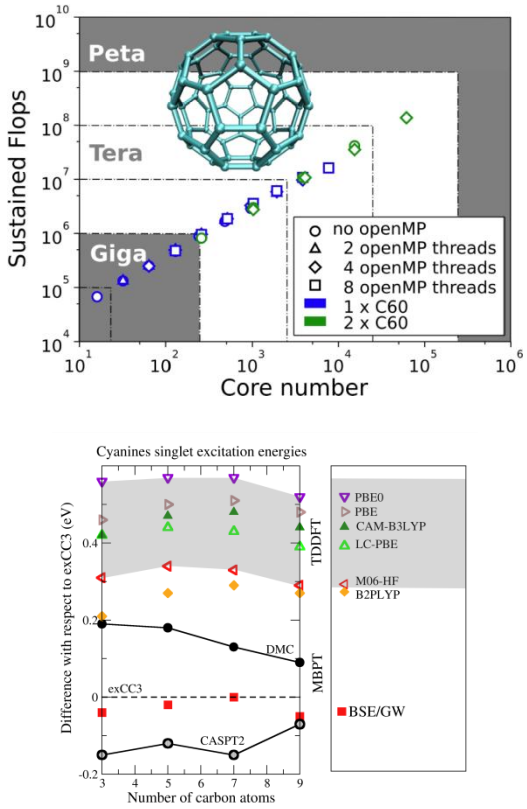

Figure 1. (Top) Scalability of the Fiesta code up to 61440 cores and 128 TFlops (GENCI Curie thin nodes). Performances for one GW iteration performed on a C60 molecule and a C60 dimer at the TZP basis level (courtesy Ivan Duchemin and European PRACE project SolarFiesta). (Bottom) Lowest singlet excitation energies in cyanine chains as a function of the number of carbon atoms. The shaded area represents TDDFT calculation with semilocal, global and range separated hybrids. The red squares are the GW/BSE results. Energies are reported as differences with respect to the coupled-cluster exCC3 reference.

References

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