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Many-body perturbation theory for excited electrons: from materials to molecules

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The description of excited states is most easily understood in terms of Green's functions. The working approximations to obtain the Green's function have mostly been developed aiming at condensed matter systems. For instance, the *GW* approximation [1] to the electron self-energy has been shown to yield very accurate crystal band structures [2] and the Bethe-Salpeter equation is known to describe very well the excitons in solids [3]. However, until recently, very little was known about the performance of many-body perturbation theory for atoms, molecules, and clusters. Our in-house code named MOLGW [4] addresses the efficient and accurate calculations of electronic excitations for finite systems. This code, based on standard quantum chemistry Gaussian basis sets, is conceptually simple, since it does not require any other convergence parameter besides the initial choice of the basis set. The code works efficiently in parallel and is open-source: it can be freely downloaded on the web [5]. With this unique tool, we have demonstrated the concavity error of the *GW* approximation [6] and we have explored the accuracy of the quasiparticle energy calculations within the *GW* approximation for organic molecules as compared to photoemission spectroscopy or to high level quantum chemistry references [7,8]. We have also measured the quality of the optical excitations obtained from the Bethe-Salpeter equation [9]. Recently, we have evaluated self-energies that go beyond the standard *GW* approximation, the so-called "vertex corrections", giving insight about how to deal with them in practice. [1] L. Hedin, Phys. Rev. 139, A796 (1965). [2] M.S. Hybertsen and S.G. Louie, Phys. Rev. B 34, 5390 (1986). [3] G. Onida, L. Reining, and A. Rubio, Rev. Mod. Phys. 74, 601 (2002). [4] F. Bruneval, T. Rangel, S.M. Hamed, M. Shao, C. Yang, and J.B. Neaton, Computer Phys. Comm. 208, 149 (2016). [5] <http://www.molgw.org> [6] F. Bruneval, J. Chem. Phys. 136, 194107 (2012). [7] F. Bruneval and M.A.L. Marques, J. Chem. Theory Comput. 9, 324 (2013). [8] T. Rangel, S.M. Hamed, F. Bruneval, and J.B. Neaton, J. Chem. Theory Comput. 12, 2834 (2016). [9] F. Bruneval, S.M. Hamed, and J.B. Neaton, J. Chem. Phys. 142, 244101 (2015).