Photoemission spectra from the Extended Koopmans' theorem: capturing weak and strong correlation

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The extended Koopmans' theorem (EKT) [1-2] is a promising method to describe photoemission in solids and, in particular, in strongly correlated systems [3-6]. The EKT can be used with any theory that yields the one- and two-body reduced density matrices, which are the essential ingredients of this approach. In particular within reduced density matrix functional theory, the EKT approach is based on a simple matrix diagonalization. [7,8] However, even with exact density matrices, the EKT tends to overestimate band gaps, with the deviation from experiment increasing with increasing electron correlation. [6] This error is amplified by the use of approximate density matrices. Improvements can be obtained by designing better density matrix approximations, or by going beyond the "quasiparticle ansatz" at the core of the EKT equations, or both. In this talk we show that introducing electron screening either in standard density matrix approximations available for solids or directly in the EKT equations leads to much improved photoemission spectra. [9-10]

[1] M.M. Morrell, R.G. Parr,and M.Levy, J. Chem. Phys. 62, 549 (1975)
[2] O.W. Day, D. W. Smith, and R. C. Morrison, J. Chem. Phys. 62, 115 (1975)
[3] S. Di Sabatino, J. A. Berger, L. Reining, and P. Romaniello, Phys. Rev. B94, 155141 (2016)
[4]S. Di Sabatino, J. A. Berger and P. Romaniello, J. Chem. Theory Comput. 15, 5080 (2019)
[5] S. Di Sabatino, J. Koskelo, J. A. Berger, and P. Romaniello, Phys. Rev. Research,3, 013172 (2021)
[6] S. Di Sabatino, J. Koskelo, J. A. Berger, M. Caffarel, and P. Romaniello, Front. Chem. 9, 819 (2021)
[7] K. Pernal and J. Cioslowski, Chem. Phys. Lett. 412, 71 (2005)
[8] P. Leiva and M. Piris, J. Mol. Struct., Theochem 770, 45 (2006)
[9] S. Di Sabatino, J. A. Berger and P. Romaniello, Phys. Rev. B 105, 235123 (2022)
[10] S. Di Sabatino, J. A. Berger and P. Romaniello arxiv2209.00933 (2022)