# Electronic structure of excited states (a mathematical treasure trove from ensemble density functional theory)

Tim Gould

*Qld Micro- and Nanotechnology Centre, Griffith University, Nathan, Qld 4111, Australia*

Density functional theory (DFT) can yield excited state properties as functionals of the density, by working from ensemble instead of pure states. Facilitating excited states requires exact functionals to be carefully generalized to weight-dependent forms, to avoid spurious interactions from misapplied ansatze. This talk will discuss recent advances on rigorous definitions for the kinetic, Hartree and exchange [PRL 119, 243001 (2017); 125, 233001 (2020)] and correlation [PRL 123, 016401 (2019); 130, 106401 (2023)] ensemble energy functionals, which together yield a complete generalisation of pure state DFT and inspire new ways of looking at approximations [https://arxiv.org/abs/2306.04023]. These works reveal unusual (yet tractable) properties of density functionals -- notably the need for multi-configurational Kohn-Sham states, and strong absence of weight-dependence in the low density limit. Ensemble generalized Kohn-Sham theory based on these functionals, and its successful applications to excited state chemical problems [JPCL 13, 2452-2458 (2022)], will finally be discussed.