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THE DEVIL'S TRIANGLE IN KS-DFT CALCULATIONS AND HOW TO FIX IT

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Most of the problems with KS-DFT arise from three interconnected failures, self-interaction, the one particle spectrum, and the integer discontinuity. By introducing an eigenvalue ionization potential theorem justified by adiabatic TDDFT, the ground state KS problem has to have all its occupied orbitals tied to eigenvalues that are good approximations to the principal ionization potentials of molecules. When that is achieved then one has the right photo-electron spectrum, which provides meaningful molecular orbitals for a problem. Once that is accomplished, then the KS-DFT method also ameliorates the SI problem. Finally, the integer discontinuity that occurs when adding or removing an electron is mitigated by getting the right IP's and EA's for a problem. The latter turns out to be a by- product of the eigenvalue IP theorem. The above leads to the family of QTP parametrizations of the well-known CAM-B3LYP range separated functional, improving upon it in all respects.

Recent work has addressed the time-dependent coupled-cluster and QTP functional description of core excitation spectra.

Rodney J. Bartlett, Perspective Article, Journal of Chemical Physics, "Adventures in DFT by a Wavefunction Theorist", in press.

Rodney J. Bartlett, Duminda S. Ranasinghe, Frontier Article, "The Power of Exact Conditions in Electronic Structure Theory, " Chemical Physics Letters **669** (2017) 54–70