Density functionals of spin-density accuracy for open shells

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Electrons in zero external magnetic field (*B*=0) can be studied either with density functional theory (DFT) or with spin-DFT (SDFT).

In the first part of the talk, I shall present how to correct a qualitative error in the standard KS-DFT treatment of open shell systems. This qualitative error had led to the widespread misconception that SDFT approximations for open shells are inherently superior to those of DFT. As it turns out, correcting this error for open shells allows the approximate DFT exchange and correlation (*xc*) functionals to become as accurate as the corresponding approximate *xc* functionals in SDFT.

In the second part, I shall reveal a link between DFT and SDFT, for *B=0*. Establishing this link fills a fundamental gap in our understanding of the two theories, the younger of which turned 50 last year. When *B=0* there is only one external potential, but two are necessary for SDFT’s formulation. (In the collinear case, two external potentials are conjugate to the density and the magnetization.) Then, it seems that either SDFT would have a singular limit when *B=0* (which it does not), or the KS equations of SDFT should reduce to a set of single-particle equations of DFT. I shall argue that this intuition is correct, and I shall establish the missing link which connects SDFT with DFT. An interesting corollary is that the unrestricted KS equations of SDFT can be re-derived as the generalized KS equations of DFT [1].

[1] TJ Callow, B Pearce and NI Gidopoulos, J. Chem. Phys. 156, 111101 (2022); <https://doi.org/10.1063/5.0071991>