Modeling self interaction in the spin-decomposed correlation holes of second-row atoms

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The Perdew-Zunger model for removing self interaction error (PZ-SIC) has seen a resurgence in attention recent years, with the development of robust ways to implement it, particularly the FLO-SIC methodology. The basic model, however, has significant problems, usually only working well when applied to the local density approximation and often worsening structural predictions when applied to more sophisticated density functionals. These issues may be caused by more fundamental problems – the PZ SIC breaks important constraints in scaling to the homogeneous electron gas limit, and the limit of large-Z neutral atoms.

I analyze self-interaction effects in system-averaged correlation holes for a pseudopotential model of second row atoms. These are calculated by accurate Slater-Jastro wavefunctions and variational Monte Carlo using a correlated estimates technique that nearly eliminates the effects of statistical noise. They show a surprising failure for the Perdew-Zunger SIC for correlation, which strongly over corrects systems with very few electrons. Analysis of the correlation hole suggests simple modifications to this model, including a variant of "Koopman's compliant" SIC that greatly improves upon the PZ results, and is nearly exact for the systems studied. This work also suggests that GGA's such as PBE would benefit from splitting correlation into explicit spin-decomposed pieces, at least as an aid in removing self-interaction effects.