

# Density Cumulant Functional Theory with Improved Description of the One-Particle Density Matrix

A.Yu. Sokolov<sup>†</sup>, A.C. Simmonett, H.F. Schaefer III

Center for Computational Quantum Chemistry

University of Georgia, Athens, GA, 30602

<sup>†</sup>E-mail: alex@ccqc.uga.edu

Density *cumulant* functional theory (DCFT) has recently emerged as an attractive *ab initio* method for the treatment of electron correlation. Among the appealing properties of DCFT are size-consistency and size-extensivity, Hermitian and stationary energy functional. In DCFT the exact energy is expressed as a known functional of the one-particle density matrix (OPDM) and the two-particle density cumulant. The energy is obtained by constraining the cumulant to be at least approximately  $n$ -representable, *i.e.* corresponding to a  $n$ -electron wavefunction. In the simplest DCFT method (denoted here as DC-06) the perturbatively-derived  $n$ -representability conditions were employed, and the correlation part of OPDM was approximately derived from the density cumulant in a low-order power series expansion. Here, we propose a new formulation of DCFT (DC-12) with improved description of OPDM, where the correlation contribution is obtained exactly from the  $n$ -representability conditions. By a simple transformation to the natural spin-orbital basis, we arrive at an efficient formulation of the DC-12 method, which has the same  $\mathcal{O}(N^6)$  asymptotic scaling as the old DC-06 method. Our results demonstrate that higher-order non-linear cumulant-dependent terms in the OPDM expansion are important due to the large magnitude of one-electron terms in the energy and cumulant residual equations. Preliminary benchmark results indicate that the new DC-12 method exhibits improved stability with respect to increasing electron correlation effects, compared to DC-06. In addition, our experience shows that DC-12 exhibits better convergence and numerical stability than the old DC-06 formulation.