We propose methods to compute the frontier (homo and lumo) orbitals during recursive polynomial expansions for construction of the density matrix in linear scaling self-consistent field calculations. The recursive polynomial expansion facilitates the computation of the frontier orbitals giving accelerated convergence of iterative methods. We take advantage of eigenvalue estimates that can be extracted from the recursive expansion by a simple and robust procedure at a negligible computational cost. The proposed algorithms are implemented in the quantum chemistry program Ergo. The orbitals are calculated “on the fly” adding only a small overhead to the polynomial expansion. We show that linear scaling is achieved for systems where the homo-lumo gap and the distance between the frontier orbitals and the rest of the eigenvalue spectrum is preserved with increasing system size.

References