COMPUTATION OF FRONTIER ORBITALS IN LINEAR SCALING ELECTRONIC STRUCTURE CALCULATIONS

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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.[1] 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.[2] The proposed algorithms are implemented in the quantum chemistry program Ergo.[3,4] 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

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