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Reduced Density Matrices in Full Configuration Interaction Quantum Monte Carlo CATHERINE OVERY, DEIDRE CLELAND, The University Chemical Laboratory, University of Cambridge, UK, GEORGE H. BOOTH, Department of Chemistry, Frick Laboratory, Princeton University, USA, JAMES J. SHEPHERD, ALI ALAVI, The University Chemical Laboratory, University of Cambridge, UK — Reduced density matrices are a powerful construct in quantum chemistry, providing a compact representation of highly multi-determinantal wavefunctions, from which the expectation values of important physical properties can be extracted, including multipole moments, polarizabilities and nuclear forces[1,2]. Full configuration interaction quantum Monte Carlo (FCIQMC)[3] and its initiator extension (i-FCIQMC)[4] perform a stochastic propagation of signed walkers within a space of Slater determinants to achieve FCI-quality energies *without* the need to store the complete wavefunction. We present here a method for a stochastic calculation of the 1- and 2-body reduced density matrices within the framework of (i)-FCIQMC, and apply this formulation to a range of archetypal molecular systems. Consideration is also given to the source and nature of systematic and stochastic error, and regimes to effectively alleviate these errors are discussed[5]. [1] P.-O. Löwdin, Phys. Rev. 97, 1474 (1955). [2] C. A. Coulson, Rev. Mod. Phys. 32, 170 (1960). [3] G. H. Booth, A. Thom, and A. Alavi, J. Chem. Phys. 131, 054106 (2009). [4] D. Cleland, G. H. Booth, and A. Alavi, J. Chem. Phys. 132, 041103 (2010). [5] D. Cleland, PhD thesis, University of Cambridge, 2012.

Catherine Overy
The University Chemical Laboratory, University of Cambridge, UK

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