Chemical Verification of Variationally Optimized Second Order Density Matrices

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Size-consistency is a highly desirable property for any quantum chemical method. Variational second order density matrix theory aims to replace the role of the wavefunction in quantum chemical calculations by a variationally optimized second order density matrix [1,2]. Practical implementations of this method are not size-consistent, because they apply a necessary but not sufficient subset of N-representability constraints.
We identify several problems of this method in describing dissociating molecular systems under the approximate 2-positivity conditions [1,3] for N-representability. First of all, it tends to dissociate molecules incorrectly into fractionally charged dissociation products with too low energies, thereby violating size-consistency [4]. Secondly, the second order density matrix of a non-interacting system is not separable into density matrices for each of the non-interacting units. The first shortcoming, dissociation into fractionally charged products, is a consequence of the method's faulty relationship between energy and the number of electrons. We propose simple 2-index constraints to solve this problem [5]. Nonetheless, these constraints do not solve the second problem, non-separability of the second-order density matrix for a system of non-interacting units.

References:

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