Density matrix functional theory for excited states

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In 1988, Gross, Oliveira and Noble laureate Kohn established a density functional theory (DFT) for targeting excited states [1,2]. To overcome its severe practical limitations --- the inability to describe strongly correlated systems --- we generalize this seminal work to a functional theory which involves the full one-particle reduced density matrix (1RDMFT) [3,4,5].

Various obstacles which historically have doomed such an approach to be unfeasible are circumvented. First, we resort to a generalization of the Ritz variational principle to ensemble states with fixed weights w [1]. This in combination with the Levy-Lieb constrained search formalism allows us to establish a universal functional of the one-particle reduced density matrix (1RDM). Then, we employ elegant tools from convex analysis to circumvent the too involved N-representability constraints (see Fig. 1). Remarkably, this identifies Valone's pioneering work on 1RDMFT as a special case of convex relaxation and reveals that crucial information about the excitation structure of molecular systems is contained in the functional's domain [3,6]. Moreover, a generalization of Pauli's famous exclusion principle follows with potentially transformative consequences for the quantum sciences [7].

To initiate the common process of developing more and more accurate and sophisticated functionals, we establish first functional approximations, including a noteworthy generalization of the Hartree-Fock functional to excited states.

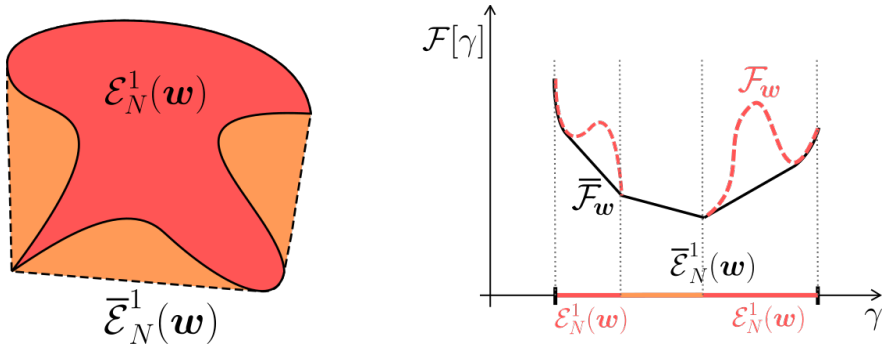

Figure 1. Schematic illustration of an elegant geometric concept underlying our novel functional theory for excites states: An exact convex relaxation simplifies both the functional's domain (left) and the functional (right).

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