Kohn-Sham theory with fractional occupations and local reduced density matrix functional theory

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I shall review briefly local reduced density matrix functional theory (local-RDMFT) [1-3], a theoretical electronic structure scheme that although it retains the simplicity of Kohn-Sham (KS) equations, it can incorporate static correlation through the use of fractional occupation numbers.
A fundamental question about local-RDMFT is whether it is intrinsically an approximate scheme, or whether the underlying theory can yield some key quantity exactly. In the initial papers [1,3] it was argued that this quantity cannot be the exact one-body reduced density matrix, since the asymptotic behaviour of any set of KS orbitals originating from a local potential cannot match the expected asymptotic behaviour of the natural orbitals. Still, it is possible that the underlying theory of local-RDMFT yields the exact ground state density of the system (but with fractional occupations).
In the rest of the talk, I shall describe how KS theory can be extended to accommodate fractional occupations by mapping the electronic interacting ground state with density ρ to an ensemble of the ground and the excited of a virtual single-particle system with ensemble density equal to ρ. The formalism leads to an iterative two-step optimisation of the KS total energy and of the fractional weights of the ensemble. The latter are chosen so as to make the KS ensemble kinetic energy equal the interacting kinetic energy. For this optimal choice of the fractional ensemble-weights, the fractional-weight-dependent exchange and correlation energy reduces to the well-known exchange and correlation energy corrected by the kinetic part of the correlation energy. Based on the two-step optimisation of the KS total energy and of the fractional weights, I shall complete the theoretical justification of the local RDMFT method.
The new formulation opens the way to employ popular approximations from density functional theory in the extension of KS equations with fractional occupations to periodic systems.

References

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