Note about the REKS/SSR metodology

Density functional theory (DFT)[1,2] was formulated for the ground electronic states of molecular and solid systems. The major assumption behind the standard Kohn-Sham (KS) methodology[2] is that the exact ground state of any fermionic system can be exactly mapped on the ground state of a system of non-interacting (quasi-)particles moving in an external potential modified in such a way that the density remains invariant.[2] This assumption however was challenged by a number of researchers,[3–8] who demonstrated that not any physical fermionic density can be mapped on a non-interacting pure-state and that the most general representation for the density of any fermionic system is ensemble of densities of non-interacting systems. This conjecture was later supported by a series of numeric experiments[9–11] and put in a general context of DFT in the form of ensemble density functional theory (eDFT).[12,13] The ground state eDFT was subsequently extended to include ensembles of ground and excited states of fermionic systems;[14–17] which paved a way for developing variational time-independent methodology of obtaining excited states and their properties.

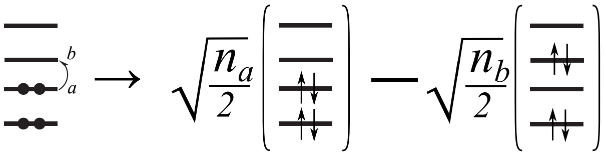
One of the important manifestations of ensemble description in quantum theory occurs during the chemical bond dissociation. For example, when the two hydrogen atoms in the hydrogen molecule are pulled apart, the electron-electron interaction fades away and, after a certain distance, the electrons may be regarded as non-interacting. However, the exact ground state of such a system does not take a form of a pure quantum state (represented by a single Slater determinant), but a form of a classical mixture (ensemble) of quasi-degenerate configurations.[18] In the parlance of KS DFT, where description of quantum system of interacting electrons is projected onto to a system of non-interacting particles, this translates to the necessity of employing an ensemble representation whenever (quasi-)degeneracy between several electronic configurations is present. Hence, eDFT incorporates the multi-configurational (or multi-reference) description of electronic systems, which, at the level of *ab initio* wavefunction theory, is achieved with lengthy expansions of the electronic states in terms of multiple configurations.

The multi-configurational description, usually associated with the strong static (or non-dynamic) electronic correlation, is required not only in molecules with dissociating bonds. The static correlation is ubiquitous and occurs, *inter alia*, in excited states of molecules and solids, in the ground states of transition metal compounds, in ferro- and anti-ferro-magnetic compounds, in biological electron transfer chains, *etc.*. For all these situations eDFT can provide computationally inexpensive and practically exact description. This however requires implementation of eDFT in practically accessible computational methodologies.

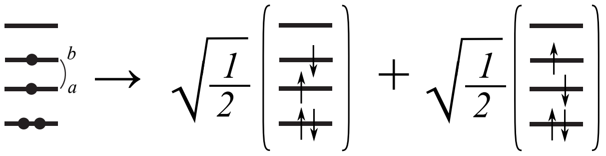
The spin-restricted ensemble-referenced Kohn-Sham (REKS) method and its extensions in the form of the state-averaged (SA) REKS (SA-REKS) and state-interaction state-averaged REKS (SI-SA-REKS, or SSR) employ eDFT for introducing the multi-reference effects into the density functional calculation of the ground and excited electronic states; see Refs. 19 and 20 and references cited therein. The ensemble description is introduced through mixtures of electronic configurations dominant in specific situations, *e.g.*, during the bond dissociation and/or electronic excitation/transition. The use of ensemble mixtures of electronic configurations leads to occurrence of the fractional occupations of several Kohn-Sham orbitals, which are variationally optimized together with the KS orbitals. Currently, the REKS/SSR methods are implemented for systems with two or four fractionally occupied KS orbitals containing in total two or four active electrons, respectively; *i.e.*, the (2,2) and (4,4) active spaces;[21–23] see Figure 1 for detail of electronic configurations. These active spaces are sufficient to describe dissociation of single and double chemical bonds, the excited states occurring in molecules with dissociating bonds, the singly and multiply excited electronic states, *e.g.*, occurring in the singlet exciton fission process.

(2,2) active space:

Perfectly spin-Paired Singlet (PPS) configuration



Open-Shell Singlet (OSS) configuration



(4,4) active space:

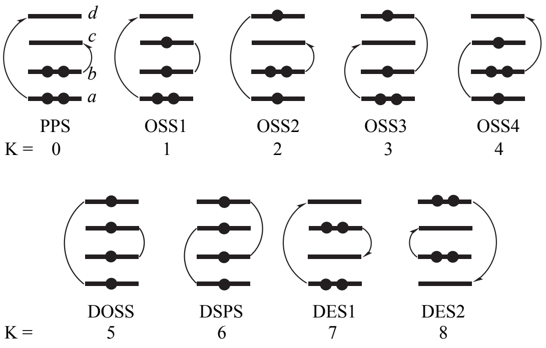


Figure 1: Schematic representation of the electronic configuration included in the REKS(2,2) and REKS(4,4) methods. Round arrows show the double excitations and arrowless brackets show ope-shell singlet spin-coupling between the unpaired electrons.

References

1. P. Hohenberg and W. Kohn. Inhomogeneous electron gas. *Phys. Rev.*, 136:B864–B871, 1964.
2. W. Kohn and L. J. Sham. Self-consistent equations including exchange and correlation effects. *Phys. Rev.*, 140:A1133–A1138, 1965.
3. S. M. Valone. A one-to-one mapping between one-particle densities and some n-particle ensembles. *J. Chem. Phys.*, 73:4653–4655, 1980.
4. E. H. Lieb. Density functionals for coulomb systems. *Int. J. Quantum Chem.*, 24:243–277, 1983.
5. J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz Jr. Density-functional theory for fractional particle number: Derivative discontinuities of the energy. *Phys. Rev. Lett.*, 49:1691–1694, 1982.
6. H. Englisch and R. Englisch. Hohenberg-kohn theorem and non-v-representable densities. *Physica*, A121: 253–268, 1983.
7. H. Englisch and R. Englisch. Exact density functionals for ground-state energies. i. general results. *Phys. Stat. Sol. (b)*, 123:711–721, 1984.
8. H. Englisch and R. Englisch. Exact density functionals for ground-state energies ii. details and remarks. *Phys. Stat. Sol. (b)*, 124:373–379, 1984.
9. P. R. T. Schipper, O. V. Gritsenko, and E.-J. Baerends. One-determinantal pure state versus ensemble kohn-sham solutions in the case of strong electron correlation: Ch2 and c2. *Theor. Chem. Acc.*, 99:329–343, 1998.
10. P. R. T. Schipper, O. V. Gritsenko, and E.-J. Baerends. Benchmark calculations of chemical reactions in density functional theory: Comparison of the accurate kohn–sham solution with generalized gradient approximations for the h2+h and h2+h2 reactions. *J. Chem. Phys.*, 111:4056–4067, 1999.
11. R. C. Morrison. Electron correlation and noninteracting v-representability in density functional theory: The be isoelectronic series. *J. Chem. Phys.*, 117:10506–10511, 2002.
12. C. A. Ullrich and W. Kohn. Kohn-sham theory for ground-state ensembles. *Phys. Rev. Lett.*, 87:093001, 2001.
13. Robert van Leeuwen. Density functional approach to the many-body problem: Key concepts and exact functionals. In *Advances in Quantum Chemistry*, volume 43, pages 25–94. Academic Press, 2003. doi: https://doi.org/10.1016/S0065-3276(03)43002-5.
14. E. K. U. Gross, L. N. Oliveira, and W. Kohn. Rayleigh-ritz variational principle for ensembles of fractionally occupied states. *Phys. Rev. A*, 37:2805–2808, 1988.
15. E. K. U. Gross, L. N. Oliveira, and W. Kohn. Density-functional theory for ensembles of fractionally occupied states. i. basic formalism. *Phys. Rev. A*, 37:2809–2820, 1988.
16. L. N. Oliveira, E. K. U. Gross, and W. Kohn. Density-functional theory for ensembles of fractionally occupied states. ii. application to the he atom. *Phys. Rev. A*, 37:2821–2833, 1988.
17. L. N. Oliveira, E. K. U. Gross, and W. Kohn. Ensemble-density functional theory. *Int. J. Quantum Chem.: Quantum Chem. Symp.*, 24:707–716, 1990.
18. L. Ding and C. Schilling. Correlation paradox of the dissociation limit: A quantum information perspective. *J. Chem. Theory Comput.*, 16:4159–4175, 2020. URL `https://doi.org/10.1021/acs.jctc.0c00054`.
19. M. Filatov. Spin-restricted ensemble-referenced kohn-sham method: basic principles and application to strongly correlated ground and excited states of molecules. *WIREs Comput. Mol. Sci.*, 5:146–167, 2015.

20. M. Filatov. Ensemble dft approach to excited states of strongly correlated molecular systems. In N. Ferré, M. Filatov, and M. Huix-Rotllant, editors, *Density-functional methods for excited states*, volume 368 of *Top. Curr. Chem.*, pages 97–124. Springer, Heidelberg, 2016.

21. M. Filatov, T. J. Martínez, and K. S. Kim. Using the gvb ansatz to develop ensemble dft method for describing multiple strongly correlated electron pairs. *Phys. Chem. Chem. Phys.*, 18:21040–21050, 2016.

22. M. Filatov, F. Liu, K. S. Kim, and T. J. Martínez. Self-consistent implementation of ensemble density functional theory method for multiple strongly correlated electron pairs. *J. Chem. Phys.*, 145:244104, 2016.

23. M. Filatov, T. J. Martínez, and K. S. Kim. Description of ground and excited electronic states by ensemble density functional method with extended active space. *J. Chem. Phys.*, 147:064104, 2017.