Brief Synopsis of the REKS/SSR method in GAMESS-US

The spin-restricted ensemble-referenced Kohn-Sham (REKS) method and its extensions in the form of the state-averaged (SA) REKS (SA-REKS) and the 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. 1 and 2 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.

In the current version of GAMESS, the REKS/SSR methods are implemented for systems with two ractionally occupied KS orbitals containing in total two active electrons. This is sufficient to describe the ground and excited states of biradicals and molecules with dissociating chemical bond; *e.g.*, during the π-bond torsion. The S_0 and S_1 states of such a system are represented in REKS/SSR formalism in terms of several electronic configurations. In the REKS(2,2) and the SSR(2,2) method, the perfectly spin-paired singlet (PPS) and the open-shell singlet (OSS) configurations are employed,

$$\Phi_{PPS} = \sqrt{\frac{n_a}{2}} \, |\ldots \phi_a \bar{\phi}_a \rangle - \sqrt{\frac{n_b}{2}} \, |\ldots \phi_b \bar{\phi}_b \rangle \tag{1}$$

$$\Phi_{OSS} = \frac{1}{\sqrt{2}} |\ldots \phi_a \bar{\phi}_b \rangle + \frac{1}{\sqrt{2}} |\ldots \phi_b \bar{\phi}_a \rangle \tag{2}$$

where n_a and n_b are the fractional occupation numbers (FONs) of the active orbitals ϕ_a and ϕ_b in the PPS configuration. The FONs and all the KS orbitals ϕ_p, the active and core orbitals included, are optimized during the REKS SCF cycles.

In the SA-REKS(2,2) method, an ensemble of the two configurations

$$E^{SA-REKS} = w_{PPS} E_0^{PPS} + w_{OSS} E_1^{OSS} \tag{3}$$
$$w_{PPS} + w_{OSS} = 1$$

is self-consistently optimized. The energies of the individual states are then computed using the variationally optimized orbitals and FONs. The E_0^{PPS} energy is assumed to approximate the energy of the ground electronic state and the E_1^{OSS} energy approximates the excited electronic state energy.

The SSR(2,2) method improves the description of the ground and excited states from SA-REKS(2,2) by including (possible) interaction between the PPS and OSS configuration. This is achieved by solving a 2×2 secular problem,

$$\begin{pmatrix} E_0^{PPS} & \Delta_{01}^{SA} \\ \Delta_{01}^{SA} & E_1^{OSS} \end{pmatrix} \begin{pmatrix} a_{00} & a_{01} \\ a_{10} & a_{11} \end{pmatrix} = \begin{pmatrix} E_0 & 0 \\ 0 & E_1 \end{pmatrix} \begin{pmatrix} a_{00} & a_{01} \\ a_{10} & a_{11} \end{pmatrix} \tag{4}$$

where Δ_{01}^{SA} is the coupling element calculated from the off-diagonal Lagrange multiplier ε_{ab}^{SA} between the active orbitals ϕ_a and ϕ_b.

$$\Delta_{01}^{SA} = \left(\sqrt{n_a} - \sqrt{n_b} \right) \varepsilon_{ab}^{SA} \tag{5}$$

The Lagrange multiplier ε_{ab}^{SA} is available from the SA-REKS orbital optimization.

An extension of the SSR(2,2) method, the SSR(3,2) method is available, where the configuration space of

SSR(2,2) is augmented by the doubly excited singlet (DES) configuration.

$$\Phi_{DES} = \sqrt{\frac{n_b}{2}} \, |\ldots \phi_a \bar{\phi}_a\rangle + \sqrt{\frac{n_a}{2}} \, |\ldots \phi_b \bar{\phi}_b\rangle \tag{6}$$

In SSR(3,2), the secular equation becomes,

$$\begin{pmatrix} E_0^{PPS} & \Delta_{01}^{SA} & 0 \\ \Delta_{01}^{SA} & E_1^{OSS} & \Delta_{12}^{SA} \\ 0 & \Delta_{12}^{SA} & E_2^{DES} \end{pmatrix} \begin{pmatrix} a_{00} & a_{01} & a_{02} \\ a_{10} & a_{11} & a_{12} \\ a_{20} & a_{21} & a_{22} \end{pmatrix} = \begin{pmatrix} E_0^{SSR(3,2)} & 0 & 0 \\ 0 & E_1^{SSR(3,2)} & 0 \\ 0 & 0 & E_2^{SSR(3,2)} \end{pmatrix} \begin{pmatrix} a_{00} & a_{01} & a_{02} \\ a_{10} & a_{11} & a_{12} \\ a_{20} & a_{21} & a_{22} \end{pmatrix} \tag{7}$$

where the new coupling element Δ_{12}^{SA} is given by

$$\Delta_{12}^{SA} = \left(\sqrt{n_a} + \sqrt{n_b} \right) \varepsilon_{ab}^{SA} . \tag{8}$$

The SSR(3,2) method offers more accurate description of the situations where the excited open-shell singlet state is strongly polarized by coupling with the doubly excited singlet state; such as, *e.g.*, the sudden polarization.

For the REKS(2,2), SA-REKS(2,2), SSR(2,2), and SSR(3,2) methods, the analytic energy gradient is available. The molecular ionization energies and the electron affinities are available through the use of the extended Koopmans' theorem (EKT).

References

1. 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.

2. 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.