Application of new pairwise Spin-Contamination Correction approach

Satyender Goel[†‡] **and Artëm E. Masunov**[†‡*]

† Nanoscience Technology Center, ‡ Department of Chemistry, * Department of Physics,
University of Central Florida, Orlando, FL – 32826, Email: amasunov@mail.ucf.edu

ABSTRACT

Chemical bond between transition metal atom and hydrogen is important in surface chemistry and nanoparticle cluster catalysis, as the energetics of this bond breaking plays a critical role in hydrogen transfer process. The studies of Transition Metal (TM) systems present a challenge for theoretical description due to the presence of several electronic states close in energy which results in strong electron correlation. For this reason molecules containing TMs serve as an important testing ground for various methods in theoretical chemistry and molecular physics. Density functional theory (DFT) is the method of choice to study large systems, due to relatively low computational cost.

A clear advantage of unrestricted (also known as spin-polarized or broken spin-symmetry) solution is qualitatively correct description of bond dissociation process. Since exact exchange-correlation functional is not known, unrestricted Kohn-Sham (UKS) treatment improves approximate functionals by taking part of the static electron correlation into account. The situation can be seen as localization of α and β electrons on the left and right atoms of the dissociating bonds, respectively (left-right electron correlation). Broken symmetry (BS) UKS thus describes the transition from closed shell system to biradical smoothly, which is not possible with restricted open shell KS (ROKS).

A disadvantage of UKS approach is that spin-polarized Slater determinant is no longer an eigenfunction of the spin operator. Hence, the average value of $<\hat{S}^2>$ is not, generally equal to the correct value of $S_z(S_z+1)$ (Here S_z is ½ of the difference in total numbers of α and β electrons). This situation is known as spin contamination and $<\hat{S}^2>$ is often used as its measure. As a result of spin contamination, molecular geometry may be distorted toward the high-spin state one, spin density often becomes incorrect, and electron energy differs from the pure spin state ones.

Here we propose an alternative approach to variable spin-correction, based on canonical Natural Orbitals (NO). Unlike conventional spin-contamination correction schemes spin-correction is introduced for each correlated electron pair individually and therefore is expected to give more accurate results. Spin-correction in our new approach is implemented as a combination of unix shell script and FORTRAN code. We apply it to study potential energy curves for *3d*-TM hydrides. The equilibrium bond lengths and dissociation energies were found in good agreement with published *ab initio* results. Fermi smearing combined with wavefunction stability analysis was found necessary to obtain correct description.