

# Pairwise Spin-Contamination Correction Method and DFT Study of MnH and H<sub>2</sub> Dissociation Curves

Satyender Goel<sup>1</sup> and Artëm E. Masunov<sup>1,2</sup>

<sup>1</sup>Nanoscience Technology Center, Department of Chemistry

<sup>2</sup>Department of Physics, University of Central Florida, 12424 Research Parkway,  
Suite 400, Orlando, FL32826, USA  
amasunov@mail.ucf.edu

**Abstract.** A clear advantage of broken symmetry (BS) unrestricted density functional theory DFT is qualitative correct description of bond dissociation process, but its disadvantage is that spin-polarized Slater determinant is no longer a pure spin state (a.k.a. spin contamination). We propose a new approach to eliminate the spin-contamination, based on canonical Natural Orbitals (NO). We derive an expression to extract the energy of the pure singlet state given in terms of energy of BS DFT solution, the occupation number of the bonding NO, and the energy of the higher state built on these bonding and antibonding NOs (as opposed to self-consistent Kohn-Sham orbitals). Thus, unlike spin-contamination correction schemes by Noodleman and Yamaguchi, spin-correction is introduced for each correlated electron pair individually and thus expected to give more accurate results. We validate this approach on two examples, a simple diatomic H<sub>2</sub> and transition metal hydride MnH.

## 1 Introduction

Difficulties in DFT description of the bond dissociation are rooted in the fact that DFT was derived based on assumption of non-degenerate system [1, 2]. A clear advantage of unrestricted (also known as spin-polarized or broken spin-symmetry) solution is qualitative correct description of bond dissociation process [3, 4]. 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  $\alpha$  and  $\beta$  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) approach.

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  $\langle S^2 \rangle$  is not, generally equal to the correct value of  $S_z(S_z+1)$  [5]. Here  $S_z$  is  $1/2$  of the difference in total numbers of  $\alpha$  and  $\beta$  electrons. This situation is known as spin contamination and  $\langle S^2 \rangle$  is often used as its measure. The common rule [6] is to neglect spin contamination if  $\langle S^2 \rangle$  differs from  $S_z(S_z+1)$  by less than 10%. 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. While some researchers argue that this spin contamination in DFT should be ignored [3] others recognize it as a problem affecting the energy. Possible solutions to spin contamination problem include constrained DFT [7, 8] and spin contamination correction schemes [9, 10], discussed below.

Heisenberg exchange coupling parameter  $J$  is often used to describe the difference in energy between the low and the high spin state. Positive value of  $J$  corresponds to ferromagnetic, and negative value corresponds to anti-ferromagnetic coupling. Since BS-DFT does not produce the energies of the pure spin states, the expression for  $J$  must account for spin contamination. The following expressions had been suggested for this purpose [11-14]:

$$J_1 = \frac{\left( {}^{DFT} E_{BS} - {}^{DFT} E_T \right)}{S_{\max}^2}, J_2 = \frac{\left( {}^{DFT} E_{BS} - {}^{DFT} E_T \right)}{S_{\max} (S_{\max} + 1)}, J_3 = \frac{\left( {}^{DFT} E_{BS} - {}^{DFT} E_T \right)}{\langle S^2 \rangle_T - \langle S^2 \rangle_{BS}} \quad (1)$$

Of these three,  $J_3$  suggested by Yamaguchi can be reduced to  $J_1$  and  $J_2$  in the weak and strong limits, respectively.

A more complicated expressions for variable spin-correction, including dependence of  $J$  on overlap between corresponding spin polarized orbitals  $p$  and  $q$  were also derived recently [15, 16]. This approach was shown to result in more accurate  $J$  values for  $\text{Cu}^{2+}$  binuclear complexes [16, 17]. However, this variable spin-correction approach had not been applied to systems with two or more correlated electron pairs. In this contribution we apply spin correction approach to study two diatomics, a simple dihydride  $\text{H}_2$  and transition metal hydride  $\text{MnH}$ .

## 2 Theory

Here we propose an alternative approach to variable spin-correction, based on canonical Natural Orbitals (NO) [18]. First, let us consider a diatomic system AB with one correlated electron pair, such as stretched  $\text{H}_2$  molecule. We assume that restricted Kohn-Sham formalism yields higher energy for this system than unrestricted one, as the case of  $\text{H}_2$  molecule far from equilibrium. Unrestricted KS description produces the natural orbitals  $a$ ,  $b$  as eigenvectors of the total density matrix with the orbital occupation numbers  $n_a$ ,  $n_b$  as corresponding eigenvalues. We further assume that  $n_a < n_b$  which means that orbital  $a$  is antibonding, and orbital  $b$  is bonding NO. They are symmetry-adapted ( $a$  is  $\Sigma_u$  and  $b$  is  $\Sigma_g$  in case of  $\text{H}_2$  molecule). Corresponding spin-polarized broken symmetry orbitals  $p$ ,  $q$  can be expressed [19] as a linear combination of  $a$  and  $b$  using polarization parameter  $\lambda$ :

$$p = \frac{1}{\sqrt{1+\lambda^2}}(b + \lambda a); q = \frac{1}{\sqrt{1+\lambda^2}}(b - \lambda a) \quad (2)$$

This parameter is determined by the occupation numbers  $n_a$  and  $n_b$  as shown below. If alpha and beta electrons are localized on different parts of the molecule and do not overlap, the polarization parameter become unity and we arrive to Noodleman's weak interaction limit. In the general case of many-electron system the orbitals of the alpha set, besides being orthogonal to each other, are also orthogonal to the orbitals of

the beta set for a single exception of the corresponding beta orbital. The spin polarized orbitals obtained with the most standard quantum chemistry codes do not possess this property, which is why one has to produce the corresponding spin-polarized orbitals from NOs. BS solution can still be written as the Slater determinant in the basis of these corresponding orbitals as:

$$BS = 1/\sqrt{2} \|p_\alpha q_\beta\| = \frac{1}{\sqrt{2}} \left\| \begin{array}{c} p_1 \alpha_1 p_2 \alpha_2 \\ q_1 \beta_1 q_2 \beta_2 \end{array} \right\| \quad (3)$$

Substitution of the corresponding orbitals from (2) into (3) separates the pure singlet and triplet components:

$$BS = \frac{1}{\sqrt{2}} \left\| \begin{array}{c} p_1 \alpha_1 p_2 \alpha_2 \\ q_1 \beta_1 q_2 \beta_2 \end{array} \right\| = \frac{1}{(1+\lambda^2)} S + \frac{\lambda}{(1+\lambda^2)} T \quad (4)$$

$$BS = \frac{1}{(1+\lambda^2)} (b_1 b_2 - \lambda^2 a_1 a_2) \frac{\alpha_1 \beta_2 - \beta_1 \alpha_2}{\sqrt{2}} + \frac{\lambda}{(1+\lambda^2)} (a_1 b_2 - b_1 a_2) \frac{\alpha_1 \beta_2 + \beta_1 \alpha_2}{\sqrt{2}} \quad (5)$$

where indexes 1 and 2 mark coordinates of the electrons. The first term in this expression contains the linear combination of the two closed-shell singlets, the lower closed shell singlet  $S_1$ :

$$S_1 = b_1 b_2 \frac{\alpha_1 \beta_2 - \beta_1 \alpha_2}{\sqrt{2}} \quad (6)$$

and the higher closed shell singlet  $S_2$ :

$$S_2 = a_1 a_2 \frac{\alpha_1 \beta_2 - \beta_1 \alpha_2}{\sqrt{2}} \quad (7)$$

while the second term is proportional to one of the possible triplet states:  $T = T_0 \sqrt{2}$ ,

$$T_0 = \frac{(a_1 b_2 - b_1 a_2) \alpha_1 \beta_2 + \beta_1 \alpha_2}{\sqrt{2}} \quad (8)$$

This triplet contribution is the reason why UKS solution is spin contaminated. Therefore, we are looking to extract the energy of the singlet term from BS energy  $E_{BS}$  using the energy of the triplet. The expectation value of Kohn-Sham operator  $\hat{H}$  then becomes,

$$E_{BS} = \langle BS | \hat{H} | BS \rangle = \frac{1}{(1+\lambda^2)^2} \langle S | \hat{H} | S \rangle + \frac{\lambda^2}{(1+\lambda^2)^2} \langle T | \hat{H} | T \rangle + \frac{\lambda}{(1+\lambda^2)^2} (\langle S | \hat{H} | T \rangle + \langle T | \hat{H} | S \rangle) \quad (9)$$

The last two terms in (9) vanish out due to orthogonality of S and T states, introduced in (4).

$$\langle S | S \rangle = \langle b_1 b_2 - \lambda^2 a_1 a_2 | b_1 b_2 - \lambda^2 a_1 a_2 \rangle = 1 + \lambda^4 \quad (10)$$

Using normalization condition and Substituting (10) into (4) one can obtain:

$$BS = \frac{\sqrt{1+\lambda^4}}{1+\lambda^2} \cdot S_0 + \frac{\lambda\sqrt{2}}{1+\lambda^2} \cdot T_0 \quad (11)$$

Where,

$$S_0 = \frac{S}{\sqrt{1+\lambda^4}} = \frac{1}{\sqrt{1+\lambda^4}} (S_1 + \lambda^2 S_2) \quad (12)$$

Hence the BS UKS energy can be written in terms of renormalized singlet and triplet  $S_0, T_0$  as:

$$E_{BS} = \frac{1+\lambda^4}{(1+\lambda^2)^2} \langle S_0 | \hat{H} | S_0 \rangle + \frac{2\lambda^2}{(1+\lambda^2)^2} \langle T_0 | \hat{H} | T_0 \rangle \quad (13)$$

In non-relativistic case, the energy of the triplet  $T_0$  is the same as the energy  $E_T$  for the single determinant triplet  $T_1 = a_1 \alpha_1 b_2 \alpha_2$ ;

$$E_T = \langle T_1 | \hat{H} | T_1 \rangle = \langle T_0 | \hat{H} | T_0 \rangle \quad (14)$$

Then the energy  $E_{S_0}$  of the pure singlet  $S_0$  can be found from (14) as

$$E_{S_0} = \frac{(1+\lambda^2)^2}{1+\lambda^4} E_{BS} - \frac{2\lambda^2}{1+\lambda^4} E_T \quad (15)$$

This energy includes the non-dynamic electron correlation effects arising from the mixing of  $S_1$  and  $S_2$  states. In order to relate the polarization parameter  $\lambda$  to the occupation numbers  $n_a, n_b$ , we can expand the electron density matrix in the basis of  $a$  and  $b$  orbitals.

$$\rho(BS) = \begin{bmatrix} n_a & 0 \\ 0 & n_b \end{bmatrix}, \rho(S_1) = \begin{bmatrix} 0 & 0 \\ 0 & 2 \end{bmatrix}, \rho(S_2) = \begin{bmatrix} 2 & 0 \\ 0 & 0 \end{bmatrix}, \rho(T_0) = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad (16)$$

From (11-12)

$$\rho(BS) = \frac{1}{1+\lambda^2} \rho(S_1) + \frac{\lambda^4}{(1+\lambda^2)^2} \rho(S_2) + \frac{2\lambda^2}{(1+\lambda^2)^2} \rho(T_0) \quad (17)$$

then

$$n_a = \frac{2\lambda^4}{(1+\lambda^2)^2} + \frac{2\lambda^2}{(1+\lambda^2)^2} = \frac{2\lambda^2}{1+\lambda^2} \quad (18)$$

$$n_b = \frac{2}{(1+\lambda^2)^2} + \frac{2\lambda^2}{(1+\lambda^2)^2} = \frac{2}{1+\lambda^2} \quad (19)$$

And finally

$$\lambda = \sqrt{2/n_b - 1} \quad (20)$$

$$E_{S_0} = \frac{4}{2n_b^2 + 4n_b + 4} E_{BS} - \frac{4n_b - 2n_b^2}{2n_b^2 + 4n_b + 4} E_T \quad (21)$$

Thus, for a system with one correlated electron pair one can obtain the pure singlet energy expressed in terms of energy of BS UKS solution, the occupation number of the bonding NO, and the energy of the triplet built on these bonding and antibonding NOs (as opposed to self-consistent KS orbitals). This expression is applicable to two-electron systems as well as to the systems which have in addition the unpolarized electron core or ferromagnetically coupled unpaired electrons. Extension to this technique to the case of several correlated electron pairs will be presented elsewhere. All systems, considered in this study were found to have only pair of fractionally occupied NOs, in addition to singly occupied and unpolarized MOs.

Most importantly our approach does not use spin operator for the correction; it considers natural occupancies. At present our approach is good to study spin contaminated systems with one correlated pair.

Thus, for a system with one correlated electron pair one can obtain the pure singlet energy expressed in terms of energy of BS UKS solution, the occupation number of the bonding NO, and the energy of the triplet built on these bonding and antibonding NOs (as opposed to self-consistent KS orbitals). This expression is applicable to two-electron systems as well as to the systems which have in addition the unpolarized electron core or ferromagnetically coupled unpaired electrons.

We will turn next to the systems with two correlated electron pairs, In that case (9) can be written as:

$$E_{BS} = \langle BS_1 \cdot BS_2 | \hat{H} | BS_1 \cdot BS_2 \rangle \quad (22)$$

Using (4),

$$BS_1 \cdot BS_2 = \left( \frac{\sqrt{1+\lambda_1^4}}{(1+\lambda_1^2)} S_{01} + \frac{\sqrt{2}\lambda_1}{(1+\lambda_1^2)} T_{01} \right) \left( \frac{\sqrt{1+\lambda_2^4}}{(1+\lambda_2^2)} S_{02} + \frac{\sqrt{2}\lambda_2}{(1+\lambda_2^2)} T_{02} \right) \quad (23)$$

$$= \frac{1}{(1+\lambda_1^2)(1+\lambda_2^2)} \left( \sqrt{1+\lambda_1^4} \sqrt{1+\lambda_2^4} S_{01} S_{02} + \sqrt{2}\lambda_2 \sqrt{1+\lambda_1^4} T_{02} S_{01} + \sqrt{2}\lambda_1 \sqrt{1+\lambda_2^4} T_{01} S_{02} + 2\lambda_1 \lambda_2 T_{01} T_{02} \right) \quad (24)$$

Simplifying above eq. by replacing  $S_{01}$  and  $S_{02}$ :

$$S_{01} = \left( BS_1 - \frac{\sqrt{2}\lambda_1}{(1+\lambda_1^2)} T_{01} \right) \frac{(1+\lambda_1^2)}{\sqrt{1+\lambda_1^4}} \quad (25)$$

$$S_{02} = \left( BS_2 - \frac{\sqrt{2}\lambda_2}{(1+\lambda_2^2)} T_{02} \right) \frac{(1+\lambda_2^2)}{\sqrt{1+\lambda_2^4}} \quad (26)$$

We have

$$BS_1 \cdot BS_2 = \frac{1}{(1 + \lambda_1^2)(1 + \lambda_2^2)} \left( \sqrt{1 + \lambda_1^4} \sqrt{1 + \lambda_2^4} S_{01} S_{02} + \sqrt{2} \lambda_2 (1 + \lambda_1^2) T_{02} BS_1 + \sqrt{2} \lambda_1 (1 + \lambda_2^2) T_{01} BS_2 + 2 \lambda_1 \lambda_2 T_{01} T_{02} \right) \quad (27)$$

Hence the BS UKS energy can be written in terms of renormalized singlet, triplet and mixture of triplet and BS state,  $S_{01}S_{02}$ ,  $T_{01}T_{02}$ ,  $T_{02}BS_1$ ,  $T_{01}BS_2$  as:

$$E_{BS} = \frac{(1 + \lambda_1^4)(1 + \lambda_2^4)}{(1 + \lambda_1^2)^2(1 + \lambda_2^2)^2} \langle S_{01} S_{02} | \hat{H} | S_{01} S_{02} \rangle + \frac{2\lambda_2^2(1 + \lambda_1^2)^2}{(1 + \lambda_1^2)^2(1 + \lambda_2^2)^2} \langle T_{02} BS_1 | \hat{H} | T_{02} BS_1 \rangle + \frac{2\lambda_1^2(1 + \lambda_2^2)^2}{(1 + \lambda_1^2)^2(1 + \lambda_2^2)^2} \langle T_{01} BS_2 | \hat{H} | T_{01} BS_2 \rangle - \frac{4\lambda_1^2\lambda_2^2}{(1 + \lambda_1^2)^2(1 + \lambda_2^2)^2} \langle T_{01} T_{02} | \hat{H} | T_{01} T_{02} \rangle \quad (28)$$

Then the energy  $E_{SO}$  of the pure singlet  $S_{01}S_{02}$  can be found from (28) as

$$E_{BS} \cdot (1 + \lambda_1^2)^2 (1 + \lambda_2^2)^2 = (1 + \lambda_1^4)(1 + \lambda_2^4) E_{S_0} + 2\lambda_2^2 (1 + \lambda_1^2)^2 E_{T_{02}BS_1} + 2\lambda_1^2 (1 + \lambda_2^2)^2 E_{T_{01}BS_2} - 4\lambda_1^2\lambda_2^2 E_{T_{01}T_{02}} \quad (29)$$

$$E_{S_0} = \frac{1}{(1 + \lambda_1^4)(1 + \lambda_2^4)} \left( E_{BS} \cdot (1 + \lambda_1^2)^2 (1 + \lambda_2^2)^2 - 2\lambda_2^2 (1 + \lambda_1^2)^2 E_{T_{02}BS_1} - 2\lambda_1^2 (1 + \lambda_2^2)^2 E_{T_{01}BS_2} + 4\lambda_1^2\lambda_2^2 E_{T_{01}T_{02}} \right) \quad (30)$$

Here we derive an expression to extract the energy of the pure singlet state from the energy of the broken symmetry DFT description of the low-spin state and energies of the high-spin states: pentuplet and two spin-contaminated triplets. Thus, unlike spin-contamination correction schemes by Noodleman [20] and Yamaguchi [13], spin-correction is introduced for each correlated electron pair individually and there fore is expected to give more accurate results.

### 3 Computational Details

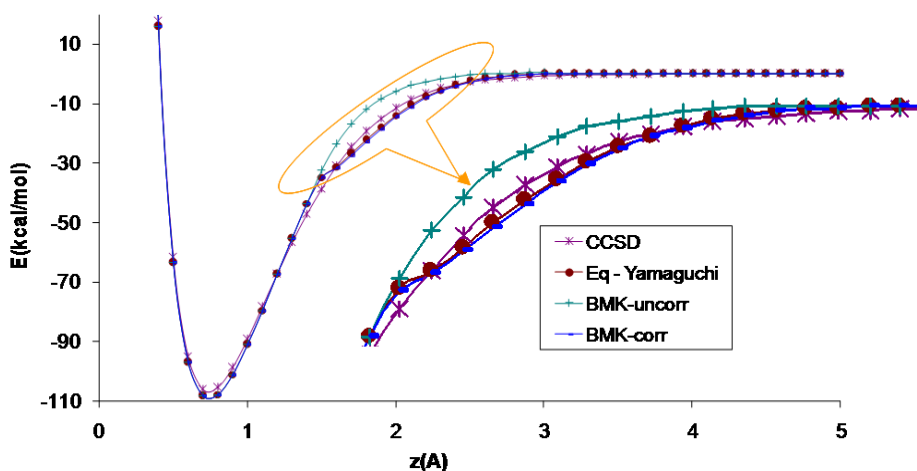
We studied Potential Energy Curves (PEC) for hydrogen dimer  $H_2$  and transition metal hydride  $MnH$  to validate the spin-contamination correction approach described above in section 2.  $MnH$  calculations were done with Gaussian03 [21] program using all-electron Wachters+f [22, 23] basis set. For  $H_2$  we have used aug-cc-pVQZ basis set with CCSD and spin-polarized (unrestricted) DFT calculations.

Spin-correction described above in theory section is implemented as a combination of unix shell script and FORTRAN code. It reads Natural Orbitals (NO) printout from Gaussian03 job (keyword used was Punch=NO) and converts them into spin-polarized molecular orbitals. Script uses a threshold parameter to identify the correlated pair. The spin polarization of the electron core was neglected by adjusting the

threshold value to consider natural occupations integer. The provision is made for the spin-up orbital  $p$  to be the one largely localized on metal atom and, so that spin-down orbital  $q$  is predominantly localized on H atom. The new alpha orbital set is made of doubly occupied NOs, orbital  $p$ , singly occupied NOs, and weakly occupied NOs. The new beta orbital set was identical, except that  $p$  was replaced with  $q$ . These orbitals were further used to evaluate the energy with single SCF step and verify that it is close to BS energy obtained at self-consistence. The energy of the triplet is calculated with another single SCF step using the original NOs only. It was used by the script to extract the energy of the pure singlet. The keywords used for single SCF step with the modified orbital set were SCF (MaxCycle=1) and Guess=Cards.

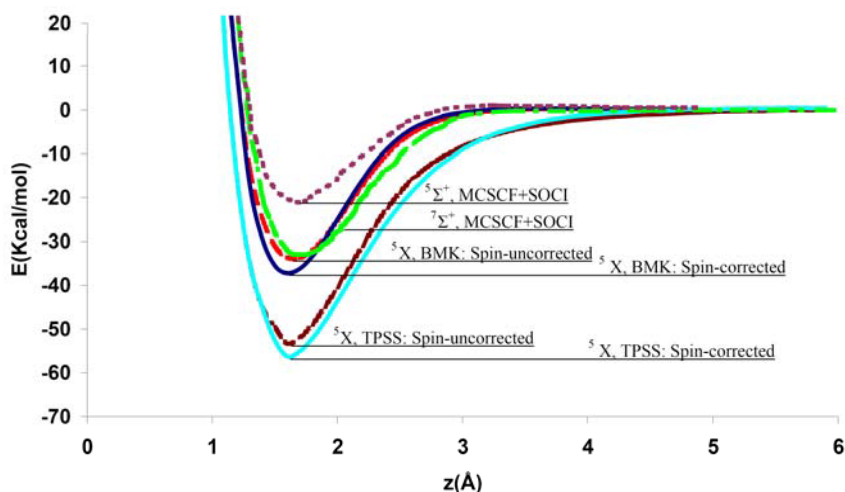
## 4 Results and Discussion

Fig. 1 illustrates potential energy curves for  $H_2$  with CCSD, BMK (uncorrected and corrected) and conventional Yamaguchi spin contamination correction based on  $S^2$  value. One can see from the figure the difference appear at the shoulder of the potential energy surface, where uncorrected BMK curve significantly overestimate the energies. The corrected curve with our new spin-contamination correction code efficiently finds the point of difference and corrects the energy to give potential energy curve similar to that of wavefunction method CCSD. We have also plotted the conventional correction based spin operator by Yamaguchi et. al. for comparison purpose. Though both the corrections are equally good in predicting energies at the accuracy of wavefunction theory level CCSD, our approach is based on actual occupation nos., which would perform better when number of electron correlated pair will increase in the study. The further validation of the system with more than two electron correlation pairs will be discussed in future.



**Fig. 1.** Potential Energy Curves for hydrogen dimer with and without spin-contamination correction from our new approach, along with CCSD and Yamaguchi correction

In another attempt to check our new approach we considered more complex system MnH. Fig. 2 illustrates potential energy curve of two spin states of transition metal hydride, MnH with pure and hybrid DFT functionals TPSS and BMK. Our results are compared with PEC of only available WFT method MCSCF+SOC1 in Fig 2 to equilibrium bond length for M=5. Table 1 shows the correction, introduced in Section 2, stabilizes this spin state by 3.1 kcal/mol below M=7, in agreement with experimental value reported in Borane et. al. [24] Thus, spin-corrected BMK predicts the ground state for MnH to have the multiplicity of 5 and accurately reproduces experimental  $D_e$ .



**Fig. 2.** Spin-corrected Potential Energy Curves of MnH with multiplicity 5 and 7, calculated by TPSS, BMK, and WFT (19) methods

**Table 1.** Spin corrected and uncorrected dissociation energies of MnH in Kcal/mol calculated with BMK and compared with *ab-initio* and experiment

	MnH
<b>Multiplicity</b>	<b>5</b>
<b>BMK - Spin Uncorrected</b>	<b>34.1</b>
<b>BMK - Spin Corrected</b>	<b>37.2</b>
<b>MCSCF+SOC1<sup>a</sup></b>	<b>21.8</b>
<b>Experiment<sup>b</sup></b>	<b>39.0</b>

<sup>a</sup>[19], <sup>b</sup>[24]



## 5 Conclusion

Here we derive an expression to extract the energy of the pure singlet state expressed in terms of energy of BS UKS solution, the occupation number of the bonding NO, and the energy of the triplet built on these bonding and antibonding NOs (as opposed to self-consistent KS orbitals). Thus, unlike spin-contamination correction schemes by Noodleman and Yamaguchi, spin-correction is introduced for each correlated electron pair individually and thus expected to give more accurate results. Diatomics considered for this study were found to have only pair of fractionally occupied NOs, in addition to singly occupied and unpolarized MOs. Our approach successfully predicts the correct spin state as validated by dihydrogen and manganese hydride in this study. This opens the venue to study more complicated enzymatic systems involving transition metals, more accurately with the help of DFT.

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