Consequences of Spin Contamination in Unrestricted Calculations on Open-Shell Species: Effect of Hartree−Fock and Møller−Plesset Contributions in Hybrid and Double-Hybrid Density Functional Theory Approaches[†]

Ambili S. Menon and Leo Radom*

School of Chemistry and ARC Center of Excellence for Free Radical Chemistry and Biotechnology, University of Sydney, Sydney, NSW 2006, Australia

The extent of spin contamination in unrestricted versions of pure, hybrid and double-hybrid density functional theory (DFT) methods, and its consequences, as manifested in the difference between unrestricted and restricted energies (U − R), has been investigated for 22 homolytic bond dissociation reactions. In accordance with previous studies, increasing the amount of Hartree−Fock (HF) exchange in unrestricted hybrid DFT procedures leads to an increase in the extent of spin contamination. However, in unrestricted *double*-hybrid DFT procedures, which include both a proportion of HF exchange and a perturbative correlation contribution (MP2), the opposing behavior of UHF and UMP2 with respect to spin contamination leads to smaller differences between the energies predicted by unrestricted and restricted variants. For example, for the most spin-contaminated radicals, a 30−100 kJ mol^{-1} |U − R| difference at the HF and MP2 levels is reduced to just 0−5 kJ mol^{-1} with the double-hybrid functionals. The double-hybrid UDFT procedures can thus benefit from the inclusion of UHF and UMP2 contributions without incurring to the same extent the problems associated with spin contamination.

1. Introduction

As a consequence of their highly reactive nature, open-shell systems such as radicals and biradicals are often difficult to study in the laboratory. Theory can therefore potentially play an important role in gaining an understanding of open-shell species. However, quantum chemical calculations on open-shell systems are far from straightforward.[1] One of the major issues in the theoretical description of open-shell species is the selection of an appropriate reference function (restricted or unrestricted) for the calculation.

Molecular orbital calculations[2,3] on molecules with open-shell electronic configurations may be performed by using either restricted (RHF)[4] or unrestricted (UHF)[5] Hartree−Fock procedures. In the RHF procedure, the spatial components of the α and β orbitals are constrained to be the same, which offers the advantage that the resultant wave functions yield pure electronic spin states that are eigenfunctions of the spin-squared operator $\hat{S}^2$. However, restricted wave functions cannot lead to negative spin densities and therefore cannot describe spin polarization.[6] In the UHF procedure, the spatial components of the α and β orbitals are allowed to be different, and the greater flexibility automatically leads to an energy equal to or lower than the RHF energy.[2,3,7] Although UHF yields a more realistic description of the spin distribution in open-shell species, the unrestricted wave functions are not eigenfunctions of $\hat{S}^2$, i.e., they are contaminated by states of higher spin multiplicity. If the spin contamination from higher spin states is large, the potential energy surfaces predicted by unrestricted wave functions can be significantly distorted showing, for example, anomalously high reaction barriers.[8]

A number of approaches have been proposed to reduce the spin-contamination problem in Hartree−Fock wave functions. These include the use of RHF, spin-projected UHF (PUHF)[9−11]

and spin-extended HF (EHF).[9,12] In addition, it has been suggested that the greater the incorporation of dynamic electron correlation by a particular method, the less problematic the spin contamination is likely to be.[13] However, it has been found that in severely spin-contaminated cases, the addition of electron correlation to HF by low orders (2−4) of perturbation theory can sometimes yield poorer results than HF theory itself.[14]

A more effective way of reducing the spin-contamination problem is through the use of coupled-cluster calculations. It has been pointed out that CCSD eliminates the $S + 1$ contaminant,[15] while CCSD(T) eliminates the $S + 1$ contaminant and reduces the $S + 2$ contaminant.[13] Calculations at the CCSD and CCSD(T) levels have indeed been found to be relatively insensitive to the choice of (restricted or unrestricted) orbitals in predicting energies in a number of situations.[16] However, in cases where higher spin contaminants such as $S + 3$ or $S + 4$ become important, the coupled-cluster methods can also fail.[13] In addition, these methods are computationally demanding and therefore difficult to apply to larger systems.

A cost-effective means of including dynamic electron correlation is through the use of density functional theory (DFT) procedures.[17,18] Although the consequences of spin contamination in DFT are not definitively known, there are strong indications that DFT densities and energies are less affected by spin contamination than are the corresponding unrestricted Hartree−Fock quantities.[19,20]

The introduction of a portion of exact Hartree−Fock exchange can lead to significant improvement in the performance of DFT procedures for predicting dissociation energies.[21] However, Cohen et al.[22] have found that the spin contamination associated with B3-LYP (hybrid DFT with 20% HF exchange) is greater than that with B-LYP (pure DFT).[23] It is of interest to examine in more detail the effect of variation in the proportion of HF exchange on spin contamination, and consequently on homolytic

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[†] Part of the "Sason S. Shaik Festschrift".

bond dissociation energies and radical stabilization energies, and that is one of the purposes of the present study.

Recently, Grimme has formulated double-hybrid DFT functionals, which contain both HF exchange and second-order perturbative (MP2) correlation components.[24,25] These show markedly superior performance to conventional hybrid functionals in the calculation of reaction energies.[24-26] It would be interesting to examine the consequences of spin contamination in unrestricted double-hybrid calculations.

The present study investigates the bond dissociation energies (BDEs) and radical stabilization energies (RSEs) predicted by unrestricted and restricted variants of Hartree–Fock, MP2, CCSD and CCSD(T), and pure, hybrid and double-hybrid DFT procedures for 22 homolytic bond dissociation reactions that yield carbon-centered radicals.

2. Theoretical Procedures

Standard ab initio molecular orbital theory[2,3] and density functional theory (DFT)[3,17] calculations were carried out with the Gaussian 03[27] and Molpro 2002.6[28] computer programs. Bond dissociation energies and associated radical stabilization energies at 0 K were calculated for a previously defined set[29] of 22 homolytic bond dissociation reactions that lead to carbon-centered radicals. Geometries of radicals, optimized at the RB3-LYP/6-31G(d) level of theory, and harmonic vibrational frequencies, computed at the same theoretical level and scaled by 0.9806 to give zero-point vibrational energies (ZPVEs),[30] were taken from ref 29. Single-point energy calculations were carried out on the optimized geometries using restricted and unrestricted versions of HF, MP2, CCSD (UCCSD and URCCSD) and CCSD(T) (UCCSD(T) and URCCSD(T)), and a variety of DFT methods, in combination with the 6-311+G(3df,2p) basis set.

The DFT methods that have been examined include the pure DFT method B-LYP,[31] the hybrid DFT procedures B3-LYP[21a,32] (20% HF exchange), BMK[33] (42% variable HF exchange), MPWB1K[34] (44% HF exchange) and M05-2X[35,36] (56% HF exchange), and the double-hybrid methods, B2-PLYP[24] (53% HF exchange and 27% MP2 correlation), MPW2-PLYP[25] (55% HF exchange and 25% MP2 correlation), B2T-PLYP[26] (60% HF exchange and 31% MP2 correlation), B2K-PLYP[26] (72% HF exchange and 42% MP2 correlation), and MPW2K-PLYP[26] (72% HF exchange and 42% MP2 correlation). We were particularly interested in examining the effect on spin contamination of increasing the proportion of HF exchange in hybrid UDFTs, and the inclusion of both HF exchange and MP2 correlation in double-hybrid UDFTs.

The magnitudes of the differences between the bond dissociation energies calculated by the unrestricted and restricted methods under study ($U_{BDE} - R_{BDE}$), and the corresponding differences in the radical stabilization energies ($U_{RSE} - R_{RSE}$), are employed to investigate the consequences of spin contamination in spin-unrestricted methods.

3. Results and Discussion

3.1. Measures of UDFT Spin Contamination. The deviation in the expectation value of the spin-squared expectation value $\langle \hat{S}^2 \rangle$ from the exact values (e.g., 0.75 for a doublet, 2.0 for a triplet) is commonly used as a quantitative measure of spin contamination in an unrestricted wave function. However, it has been argued that, because the KS reference wave function is associated with a fictitious reference system of non-interacting particles, one cannot attribute a direct physical significance to the $\hat{S}^2$ calculated using this KS wave function.[22,37,38] On the
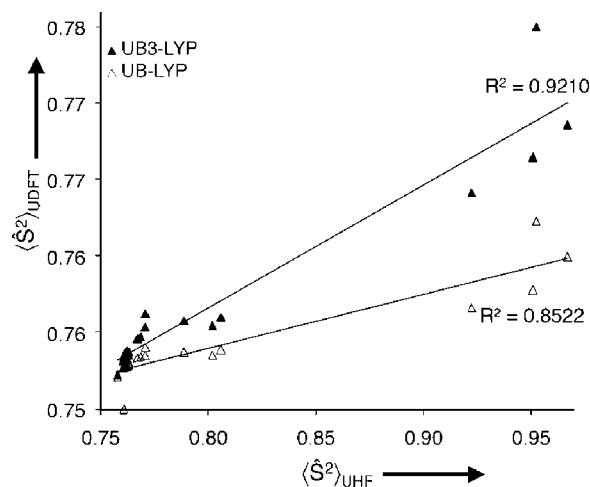
Figure 1. Representative Kohn–Sham $\hat{S}^2$ values for pure ($\langle \hat{S}^2 \rangle_{UB-LYP}$) and hybrid ($\langle \hat{S}^2 \rangle_{UB3-LYP}$) DFT methods plotted against $\langle \hat{S}^2 \rangle_{UHF}$. Benzyl radical is not included because it is off scale (see Table 1).

other hand, there have been studies[19c,22,37b,39] that have shown that the $\hat{S}^2$ values calculated for Kohn–Sham orbitals can be used as qualitative measures of spin contamination, with the correct $\hat{S}^2$ values for the interacting system generally being (quantitatively) larger in magnitude.

Figure 1 plots KS $\hat{S}^2$ values for the pure ($\langle \hat{S}^2 \rangle_{UB-LYP}$) and hybrid ($\langle \hat{S}^2 \rangle_{UB3-LYP}$) DFT procedures against $\langle \hat{S}^2 \rangle_{UHF}$. The reasonable linear plots, with R^2 values that are quite close to unity, suggests that KS $\hat{S}^2$ values, although smaller in magnitude than the UHF values, give the correct qualitative trend for spin contamination, and that any of these quantities can be used as a qualitative measure against which to measure the consequences of spin contamination.

3.2. Bond Dissociation Energies. Table 1 displays the differences ($U_{BDE} - R_{BDE}$) in bond dissociation energies for CH_3X molecules calculated by unrestricted and restricted versions of the various methods under study. Also included are $\langle \hat{S}^2 \rangle_{UHF}$, $\langle \hat{S}^2 \rangle_{UB-LYP}$ and $\langle \hat{S}^2 \rangle_{UB3-LYP}$ as representative $\hat{S}^2$ values.

Because of the greater flexibility of the UHF wave function, the total energy predicted by UHF is always equal to or lower than that predicted by its restricted counterpart.[3,7] This leads to the negative values of $U_{BDE} - R_{BDE}$ for the HF method. The magnitude of $|U_{BDE} - R_{BDE}|$ increases with increasing $\langle \hat{S}^2 \rangle_{UHF}$, as might have been expected. For the formation of radicals for which $\langle \hat{S}^2 \rangle_{UHF} \leq 0.8060$ (i.e., down to •CH_2COOH in Table 1), the $U_{BDE} - R_{BDE}$ values fall in the range of −9 to −18 kJ mol⁻¹. The five most delocalized radicals, viz., •CH_2CHO, •CH_2CN, •$CH_2CH=CH_2$, •$CH_2C\equiv CH$ and •$CH_2C_6H_5$, show relatively larger $\langle \hat{S}^2 \rangle_{UHF}$ values and larger magnitudes for $U_{BDE} - R_{BDE}$ (−38.4 to −70.4 kJ mol⁻¹). These results are consistent with the proposal by Gill et al.[40] that spin contamination will generally be significant for radicals with low-lying double excitations, i.e., for the most unsaturated radicals.

In contrast to the HF results, the UMP2 energies for radicals are higher than those calculated by RMP2[41] due to the mixing in of higher-energy spin states.[3,7] This leads to the positive values for $U_{BDE} - R_{BDE}$. Consequently, as can be seen in Figure 2, the variations in $U_{BDE} - R_{BDE}$ with $\langle \hat{S}^2 \rangle_{UHF}$ for HF and MP2 are in opposite directions. For radicals down to •CH_2PH_2, UMP2 shows $\langle \hat{S}^2 \rangle_{UMP2}$ values that are relatively close to 0.75,[42] and the $U_{BDE} - R_{BDE}$ values are less than ∼2 kJ mol⁻¹. Larger $U_{BDE} - R_{BDE}$ values, in the range of 7−9 kJ mol⁻¹, are seen for the formation of the radicals •CH_2NO_2, •CH_2COOCH_3 and •CH_2COOH. However, the largest $U_{BDE} - R_{BDE}$ values for MP2,

TABLE 1: $U_{BDE} - R_{BDE}$ Values (0 K, kJ mol^{-1}) for CH$_3$X Molecules for a Variety of Theoretical Procedures

| radical (•CH$_2$X)	$\langle\hat{S}^2\rangle_{UHF}$	HF	MP2	CCSD	CCSD (T)	$\langle\hat{S}^2\rangle_{UB\text{-}LYP}$	B-LYP	$\langle\hat{S}^2\rangle_{UB3\text{-}LYP}$	B3-LYP	BMK	MPW-B1K	M05-2X	B2-PLYP	MPW2 PLYP	B2T-PLYP	B2K-PLYP	MPW2K-PLYP
•CH$_2$BH$_2$	0.7579	−9.0	1.6	−0.8	−0.6	0.7521	−2.8	0.7523	−3.1	−3.1	−2.6	−2.5	−2.7	−2.8	−2.7	−3.4	−2.3
•CH$_2$F	0.7605	−10.9	0.8	−0.2	0.0	0.7526	−3.3	0.7531	−4.0	−3.6	−3.8	−4.0	−3.6	−3.8	−3.6	−3.3	−3.3
•CH$_2$OCH$_3$	0.7610	−11.2	1.0	−0.2	0.0	0.7500	−3.0	0.7535	−3.9	−3.7	−2.5	−4.2	−3.4	−3.8	−3.5	−3.3	−3.2
•CH$_2$OH	0.7612	−11.3	1.0	0.5	0.6	0.7527	−3.1	0.7536	−4.0	−3.8	−4.2	−4.3	−3.5	−3.9	−3.6	−3.2	−3.3
•CH$_2$OCOCH$_3$	0.7617	−11.8	1.7	−0.3	0.1	0.7528	−3.2	0.7537	−4.0	−3.7	−3.6	−4.0	−3.5	−3.8	−3.5	−3.2	−3.2
•CH$_2$CF$_3$	0.7617	−12.1	1.4	0.4	0.3	0.7528	−3.7	0.7532	−4.3	−4.3	−3.0	−3.7	−3.8	−4.0	−3.8	−3.5	−3.4
•CH$_3$	0.7618	−11.8	1.1	−0.1	0.0	0.7530	−3.8	0.7535	−4.2	−4.1	−3.9	−3.3	−3.8	−4.0	−3.8	−3.4	−3.4
•CH$_2$CF$_2$CF$_3$	0.7621	−12.4	1.7			0.7529	−3.7	0.7532	−4.3	−4.3	−2.4	−3.6	−3.8	−4.0	−3.8	−3.4	−3.3
•CH$_2$NH$_2$	0.7623	−11.9	1.2	−0.4	0.0	0.7528	−3.0	0.7538	−4.0	−3.8	−4.2	−4.4	−3.6	−3.9	−3.6	−3.4	−3.3
•CH$_2$CH$_2$CH$_3$	0.7632	−12.5	1.7	0.0	0.1	0.7529	−3.6	0.7536	−4.3	−4.4	−3.8	−3.8	−3.8	−4.1	−3.8	−4.2	−3.4
•CH$_2$CH$_3$	0.7634	−12.7	1.6	−0.3	0.0	0.7530	−3.7	0.7537	−4.4	−4.4	−4.2	−3.8	−3.9	−4.2	−3.9	−3.8	−3.5
•CH$_2$Cl	0.7673	−14.4	2.2	0.3	0.6	0.7534	−3.6	0.7546	−4.7	−4.6	−4.7	−4.9	−4.1	−4.4	−4.1	−3.7	−3.7
•CH$_2$Br	0.7688	−14.0	2.1	−0.3	0.1	0.7534	−3.5	0.7547	−4.6	−4.7	−4.8	−4.5	−4.0	−4.3	−4.0	−3.6	−3.6
•CH$_2$SH	0.7707	−15.4	2.2	0.6	1.0	0.7535	−3.4	0.7554	−4.7	−4.7	−5.2	−5.3	−4.1	−4.6	−4.2	−2.3	−3.8
•CH$_2$PH$_2$	0.7710	−14.4	1.1	0.0	0.3	0.7540	−3.6	0.7562	−4.8	−4.8	−5.2	−5.2	−4.4	−4.8	−4.5	−2.0	−4.2
•CH$_2$NO$_2$	0.7888	−17.6	7.8	0.8	0.5	0.7537	−3.9	0.7558	−5.0	−5.2	−5.6	−5.1	−3.4	−3.9	−3.3	−2.4	−2.3
•CH$_2$COOCH$_3$	0.8020	−16.9	8.8	−0.7	0.4	0.7535	−3.6	0.7555	−4.9	−5.3	−4.9	−4.9	−3.4	−3.9	−3.3	0.0	−2.4
•CH$_2$COOH	0.8060	−17.3	9.2	−0.7	0.4	0.7539	−3.7	0.7560	−5.0	−5.5	−5.2	−5.1	−3.4	−4.0	−3.4	1.3	−2.4
•CH$_2$CHO	0.9224	−38.4	35.6	−2.1	1.2	0.7566	−4.8	0.7641	−7.6	−8.9	−10.1	−9.0	−2.5	−3.9	−2.0	−2.4	1.3
•CH$_2$CN	0.9507	−41.3	46.7	−2.0	1.3	0.7578	−5.0	0.7665	−8.3	−9.4	−10.9	−9.7	−2.2	−3.8	−1.5	−2.4	2.4
•CH$_2$CH=CH$_2$	0.9523	−62.6	34.4	−2.8	1.6	0.7623	−5.6	0.7750	−10.2	−12.1	−13.8	−14.9	−5.1	−7.2	−5.1	−3.2	−2.0
•CH$_2$C≡CH	0.9668	−45.2	39.0	−2.0	1.3	0.7600	−5.1	0.7686	−8.7	−10.3	−11.4	−11.4	−3.2	−4.9	−2.9	2.4	0.2
•CH$_2$C$_6$H$_5$	1.3453	−70.4	95.8	0.1	7.2	0.7606	−4.3	0.7729	−8.1	−9.5	−10.5	−11.1	0.0	−2.0	0.0	−2.4	0.0
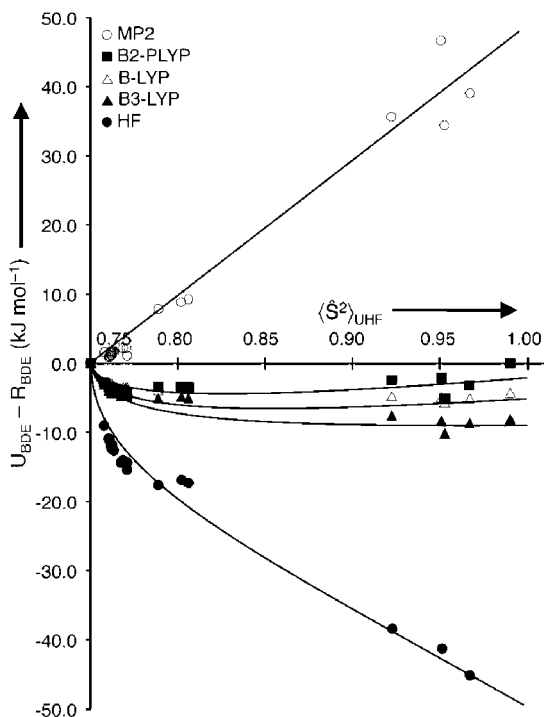
Figure 2. Differences between the magnitudes of BDEs calculated by the unrestricted and restricted variants of HF, MP2, B-LYP, B3-LYP and B2-PLYP, plotted against $\langle\hat{S}^2\rangle_{UHF}$. Benzyl radical is not included because it is off scale (see Table 1).

ranging between 35.6 and 95.8 kJ mol^{-1}, can be seen for the five most delocalized radicals noted above. The highest $U_{BDE} - R_{BDE}$ of 95.8 kJ mol^{-1} occurs for the formation of the benzyl radical.

In coupled-cluster methods, although $U_{BDE} - R_{BDE}$ values increase slightly with increasing $\langle\hat{S}^2\rangle_{UHF}$, both CCSD and CCSD(T) energies are relatively insensitive to the choice of orbitals. This is consistent with earlier studies of Stanton.[16] With the exception of the benzyl radical, which has an exceptionally low $U_{BDE} - R_{BDE}$ of −0.1 kJ mol^{-1} for CCSD and a relatively

large $U_{BDE} - R_{BDE}$ of 7.2 kJ mol^{-1} for CCSD(T), there is a minor yet consistent improvement in going from CCSD to CCSD(T).

In a similar manner to the situation with UHF, the use of broken-symmetry wave functions in UDFT procedures allows static correlation effects to be described.[39b] This leads to the negative $U_{BDE} - R_{BDE}$ values for all the DFT methods. BDEs predicted by the pure DFT method B-LYP are much less affected by spin contamination than are the HF or MP2 BDEs. Although a slight increase in $|U_{BDE} - R_{BDE}|$ with increasing $\langle\hat{S}^2\rangle$ can be seen (Figure 2), the $|U_{BDE} - R_{BDE}|$ values are generally low, even for the radicals for which UHF and UMP2 show very large spin contamination. The largest magnitude for $U_{BDE} - R_{BDE}$ of −5.6 kJ mol^{-1} occurs for the formation of allyl radical.

$U_{BDE} - R_{BDE}$ values predicted by hybrid DFTs (in the range of −2.4 to −14.9 kJ mol^{-1}) indicate that they are more affected by spin contamination than pure DFTs (in the range of −2.8 to −5.6 kJ mol^{-1}). This is consistent with the earlier findings of Cohen et al.[22] For radicals with $\langle\hat{S}^2\rangle_{UB3\text{-}LYP} \leq 0.7560$, the $U_{BDE} - R_{BDE}$ values calculated for the hybrid DFT methods lie in the range of −3 to −5 kJ mol^{-1}. However, in a similar manner to the behavior shown by HF and MP2, the hybrid DFTs predict larger $U_{BDE} - R_{BDE}$ values (in the range of −7.6 to −14.9 kJ mol^{-1}) for the five most delocalized radicals, •CH$_2$CHO, •CH$_2$CN, •CH$_2$CH=CH$_2$, •CH$_2$C≡CH and •CH$_2$C$_6$H$_5$. In these cases, the $U_{BDE} - R_{BDE}$ values show a clear increase in magnitude as we go from B3-LYP (20% HF exchange) to BMK (42% HF exchange) to MPWB1K (44% HF exchange) to UM05-2X (56% HF exchange). It is not surprising that the greater the percentage mixing of HF exchange in hybrid DFTs, the more spin-contaminated will be the KS determinant, and consequently the greater will be the differences in the energies predicted by their restricted and unrestricted variants.

When it comes to the double-hybrid DFT methods, it can be seen from Table 1 that the $U_{BDE} - R_{BDE}$ values do not smoothly increase with increasing spin contamination. For example, the $U_{BDE} - R_{BDE}$ values are not large even for the formation of the benzyl or propargyl radicals, in contrast to the results for

the UHF, UMP2 and standard hybrid DFT methods. We suggest that this arises because the double-hybrid functionals include portions of both HF exchange and MP2 correlation, and they benefit from the opposing effects with respect to $U_{BDE} - R_{BDE}$ of these components. For benzyl radical, these opposing effects are such that $U_{BDE} - R_{BDE}$ is 0.0 kJ mol^{-1} for B2-PLYP and −2.0 kJ mol^{-1} for MPW2-PYLP, despite HF and MP2 values for benzyl radical of −70.4 and +95.8 kJ mol^{-1}, respectively. Figure 2 shows this trend clearly. It is worth noting that allyl radical has larger negative $U_{BDE} - R_{BDE}$ values of −5.1 kJ mol^{-1} for B2-PLYP and −7.2 kJ mol^{-1} for MPW2-PLYP. Presumably, there is less complete cancelation of effects in these cases, with HF showing an abnormally large negative $U_{BDE} - R_{BDE}$ value of −62.6 kJ mol^{-1}, while MP2 shows a relatively smaller value of +34.4 kJ mol^{-1}. The double-hybrid B2T-PLYP for thermochemistry shows similar trends to its parent functional B2-PLYP, which is not surprising considering the similar percentages of HF exchange and MP2 correlation contributions, namely (60,31) compared with (53,27).

It is interesting that the kinetics double-hybrid functionals UB2K-PLYP and UMPW2K-PLYP, which include larger proportions of HF exchange and MP2 correlation (72,42), perform better than their parent functionals UB2-PLYP and UMPW2-PLYP. This presumably arises through improved cancelation of effects associated with the HF and MP2 components. The $U_{BDE} - R_{BDE}$ values for these functionals are generally negative and less than 4 kJ mol^{-1}.

In closing this section, we note that, although the $|U_{BDE} - R_{BDE}|$ values for double-hybrid functionals are never very large (generally less than 5 kJ mol^{-1}), they are not as small as the $|U_{BDE} - R_{BDE}|$ values for CCSD and CCSD(T), which are less than ∼2 kJ mol^{-1} (except for benzyl radical).

3.3. Radical Stabilization Energies. The radical stabilization energy (RSE) for a monosubstituted methyl radical (•CH$_2$X) is commonly defined as the energy change in the isodesmic reaction:

$$CH_2X + CH_4 \rightarrow CH_3X + \bullet CH_3 \qquad (1)$$
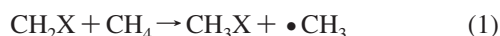
Equivalently, the RSE can be written as a difference in BDEs:

$$RSE(\bullet CH_2X) = BDE(CH_4) - BDE(CH_3X) \qquad (2)$$

The $(U_{RSE} - R_{RSE})$ values (Table 2) thus reflect the differences between the $U_{BDE} - R_{BDE}$ values associated with the formation of •CH$_2$X and •CH$_3$. We therefore comment only briefly on our results.

For HF and MP2, if we exclude the eight most contaminated radicals (i.e., from •CH$_2$NO$_2$ down in Table 2), $|U_{RSE} - R_{RSE}|$ is ≤3.6 kJ mol^{-1} for HF or ≤1.1 kJ mol^{-1} for MP2. For all the other methods listed in Table 2, we need only to exclude the five most contaminated radicals (i.e., from •CH$_2$CHO down). For those radicals above •CH$_2$CHO, $|U_{RSE} - R_{RSE}|$ is less than or equal to 1.0 kJ mol^{-1} (for CCSD and CCSD(T)), 0.9 kJ mol^{-1} (for B-LYP), 2.0 kJ mol^{-1} (for hybrid functionals) and 0.8 kJ mol^{-1} (for double-hybrid functionals).

For the more spin-contaminated radicals, there is a useful partial cancelation for HF, B-LYP, the hybrid DFTs and the "non-K" double-hybrid DFTs, leading to an improvement in $|U_{RSE} - R_{RSE}|$ in most cases. Since MP2 shows only a small $U_{BDE} - R_{BDE}$ of 1.1 kJ mol^{-1} for methyl radical, the canceling effects are less relevant. B2-KPLYP and MPW2-KPLYP methods do not benefit from canceling effects for the more contaminated radicals because of the more negative $U_{RSE} - R_{RSE}$ values for methyl radical compared with those for the set of five more contaminated radicals (Table 1).

These trends in RSEs once again confirm the generally favorable canceling effects of HF and MP2 energy components in unrestricted double-hybrid DFT calculations.

3.4. Choice of Unrestricted vs Restricted Procedures in Calculating Bond Dissociation Energies and Radical Stabilization Energies. We have previously discussed the performance of unrestricted and restricted procedures in calculating bond dissociation energies and radical stabilization energies,[29a] and make only brief comments here. The key point is that for methods for which the $U - R$ difference is small, the choice between U and R is less crucial. Nevertheless, for virtually all the DFT procedures, the restricted procedure shows overall better performance (i.e., lower MAD values, Table S3, Supporting Information) for BDEs and RSEs. The same is true for CCSD(T) determinations of RSEs.

TABLE 2: $U_{RSE} - R_{RSE}$ Values (0 K, kJ mol^{-1}) for •CH$_2$X Radicals for a Variety of Theoretical Procedures

radical (•CH$_2$X)	$\langle \hat{S}^2 \rangle_{UHF}$	HF	MP2	CCSD	CCSD (T)	$\langle \hat{S}^2 \rangle_{UB\text{-}LYP}$	B-LYP	$\langle \hat{S}^2 \rangle_{UB3\text{-}LYP}$	B3-LYP	BMK	MPW-B1K	M05-2X	B2-PLYP	MPW2-PLYP	B2T-PLYP	B2K-PLYP	MPW2K-PLYP
•CH$_2$BH$_2$	0.7579	−2.8	−0.5	0.7	0.6	0.7521	−0.9	0.7523	−1.1	−1.0	−1.4	−0.8	−1.1	−1.1	−1.1	−1.1	−1.1
•CH$_2$F	0.7605	−0.9	0.3	0.1	0.0	0.7526	−0.4	0.7531	−0.2	−0.5	−0.2	0.7	−0.2	−0.2	−0.2	−0.1	−0.1
•CH$_2$OCH$_3$	0.7610	−0.6	0.1	0.1	0.0	0.7500	−0.8	0.7535	−0.3	−0.4	−1.4	1.0	−0.3	−0.2	−0.3	−0.2	−0.2
•CH$_2$OH	0.7613	−0.5	0.1	−0.6	−0.6	0.7527	−0.6	0.7536	−0.2	−0.3	0.2	1.0	−0.3	−0.1	−0.2	−0.1	−0.1
•CH$_2$OCOCH$_3$	0.7617	0.0	−0.6	0.1	−0.1	0.7528	−0.6	0.7537	−0.2	−0.4	−0.3	0.7	−0.3	−0.2	−0.2	−0.2	−0.2
•CH$_2$CF$_3$	0.7617	0.3	−0.3	−0.5	−0.3	0.7528	0.0	0.7532	0.1	0.2	−1.0	0.4	0.0	0.0	0.0	0.0	0.0
•CH$_2$CF$_2$CF$_3$	0.7621	0.6	−0.6			0.7529	0.0	0.7532	0.1	0.2	−1.6	0.3	0.0	0.0	0.0	−0.1	−0.1
•CH$_2$NH$_2$	0.7623	0.1	−0.1	0.2	0.0	0.7528	−0.8	0.7538	−0.2	−0.2	0.3	1.1	−0.2	−0.1	−0.2	−0.1	−0.1
•CH$_2$CH$_2$CH$_3$	0.7632	0.7	−0.6	−0.2	−0.1	0.7529	−0.1	0.7536	0.1	0.3	−0.1	0.5	0.0	0.1	0.0	0.0	0.0
•CH$_2$CH$_3$	0.7634	0.9	−0.5	0.1	0.0	0.7530	0.0	0.7537	0.2	0.3	0.2	0.6	0.1	0.2	0.1	0.1	0.1
•CH$_2$Cl	0.7673	2.6	−1.1	−0.4	−0.6	0.7534	−0.1	0.7546	0.5	0.5	0.8	1.6	0.3	0.5	0.3	0.3	0.3
•CH$_2$Br	0.7688	2.2	−1.0	−0.2	−0.1	0.7534	−0.2	0.7547	0.4	0.6	0.9	1.2	0.2	0.3	0.2	0.2	0.2
•CH$_2$SH	0.7707	3.6	−1.1	−0.7	−1.0	0.7535	−0.4	0.7554	0.5	0.6	1.2	2.0	0.3	0.6	0.4	0.4	0.4
•CH$_2$PH$_2$	0.7710	2.6	0.0	−0.1	−0.3	0.7540	−0.2	0.7562	0.6	0.7	1.2	1.9	0.6	0.8	0.7	0.8	0.8
•CH$_2$NO$_2$	0.7888	5.8	−6.7	−0.9	−0.5	0.7537	0.2	0.7558	0.8	1.1	1.6	1.8	−0.4	−0.1	−0.5	−1.1	−1.0
•CH$_2$COOCH$_3$	0.8020	5.1	−7.7	0.6	−0.4	0.7535	−0.1	0.7555	0.7	1.2	0.9	1.7	−0.4	−0.1	−0.5	−1.0	−1.0
•CH$_2$COOH	0.8060	5.5	−8.1	0.6	−0.4	0.7539	−0.1	0.7560	0.8	1.4	1.3	1.8	−0.4	0.0	−0.4	−1.0	−1.0
•CH$_2$CHO	0.9224	26.6	−34.5	2.0	−1.2	0.7566	1.1	0.7641	3.4	4.8	6.2	5.7	−1.3	0.0	−1.8	−4.7	−4.7
•CH$_2$CN	0.9507	29.5	−45.6	1.9	−1.3	0.7578	1.2	0.7665	4.1	5.3	7.0	6.4	−1.6	−0.2	−2.2	−5.8	−5.7
•CH$_2$CH=CH$_2$	0.9527	50.8	−33.3	2.7	−1.6	0.7623	1.9	0.7750	6.0	8.0	9.8	11.6	1.3	3.2	1.3	−1.4	−1.4
•CH$_2$C≡CH	0.9669	33.4	−37.9	1.9	−1.3	0.7600	1.4	0.7686	4.5	6.2	7.5	8.1	−0.6	0.9	−0.9	−3.6	−3.6
•CH$_2$C$_6$H$_5$	1.3453	58.6	−94.7	−0.2	−7.2	0.7606	0.6	0.7729	3.9	5.4	6.6	7.8	−3.8	−2.0	−3.8	−3.4	−3.4

Spin Contamination in Unrestricted DFT Calculations

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4. Conclusions

Among the various steps toward the development of more accurate density functional theory procedures, an important milestone was the introduction by Becke[21a] of hybrid functionals through the inclusion of a proportion of exact exchange. Grimme[24] took a further step forward by adding a proportion of correlation, calculated using second-order perturbation theory, in double-hybrid DFT procedures. In the present study, we have examined the consequences on spin contamination and energies of mixing HF and MP2 components in hybrid and double-hybrid density functionals for a test set of 22 homolytic bond dissociation reactions that lead to the formation of monosubstituted carbon-centered radicals. Some important conclusions emerge from our calculations.

(1) We confirm that, in comparison with the wave function-based methods UHF and UMP2, the bond dissociation energies and radical stabilization energies predicted by unrestricted DFT procedures are generally much less affected by the spin-contamination problem. However, compared with CCSD and CCSD(T), the consequences of spin contamination, as reflected in the energy differences predicted by the unrestricted and restricted methods, are more pronounced for the DFT procedures.

(2) The pure DFT B-LYP method shows little sensitivity to whether the underlying procedure is U or R, although a very slight increase in the $|U - R|$ values for both BDEs and RSEs is found for more delocalized radicals.

(3) The unrestricted hybrid DFT functionals UB3-LYP, UBMK, UMPWB1K and UM05-2X are more adversely affected by spin contamination than UB-LYP, due to the incorporation of Hartree−Fock exchange. We find that increasing the exact-exchange admixture generally increases the spin-contamination problem in unrestricted hybrid DFT procedures. This is reflected in the increase in $|U - R|$ values (both for BDEs and RSEs) in going from B3-LYP (20% HF exchange) to BMK (42% HF exchange) to MPWB1K (44% HF exchange) to M05-2X (56% HF exchange).

(4) Since the energy predicted by UHF is always less than that for its restricted counterpart due to the greater variational flexibility, and since the energy predicted by unrestricted MP2 is always greater than that predicted by restricted MP2 due to the mixing in of higher-energy spin states, the double-hybrid UDFT functionals, with a proportion of both HF exchange and MP2 correlation, are found to benefit from the canceling effects of the UHF and UMP2 components of spin contamination. Thus we find that the effect of spin contamination is significantly reduced in the unrestricted double-hybrid functionals B2-PLYP, MPW2-PLYP and B2T-PLYP for the calculation of both BDEs and RSEs.

(5) The BDEs predicted by the recently proposed kinetics double-hybrid functionals B2K-PLYP and MPW2K-PLYP, which have larger proportions of HF and MP2 contributions, show even smaller $|U - R|$ values than those predicted by their parent functionals, B2-PLYP and MPW2-PLYP.

(6) The double-hybrid UDFT procedures can thus benefit from the inclusion of UHF and UMP2 contributions without incurring to the same extent the problems associated with spin contamination.

Supporting Information Available: The $\langle \hat{S}^2 \rangle$ values for UMP2 and for the pure and hybrid UDFT procedures are provided in Table S1. Table S2 contains the total energies that lead to the BDEs and RSEs of Tables 1 and 2, respectively. The BDEs and RSEs calculated at various levels of theory are compared with the high-level composite method W1 and with experiment in Table S3. This material is available free of charge via the Internet at http://pubs.acs.org.

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JP803064K