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## Correlated ab Initio Spin Densities for Larger Molecules: Orbital-Optimized Spin-Component-Scaled MP2 Method

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The performance of the orbital-optimized MP2 method (OO-MP2) and its spin-component-scaled variant is investigated for the prediction of atomic and molecular hyperfine coupling constants (hfccs). The calculated hfccs are compared to experimental as well as to CCSD(T) reference results. The OO-MP2 isotropic hfccs for a series of small radicals are almost of CCSD quality but are obtained with iterative  $\mathcal{O}(N^5)$  effort. The dipolar hfccs are less well predicted by the OO-MP2 methods, whereas spin-component scaling improves the description of the hyperfine structure. The spin contamination in the OO-MP2 wave function is drastically reduced compared to the standard unrestricted Hartree–Fock wave function. The applicability of the OO-MP2 to fairly large systems is demonstrated for the solvated *p*-benzosemiquinone radical anion, where calculations with almost 2000 basis functions have been performed.

### Introduction

The calculation of the hyperfine structure in electron paramagnetic resonance (EPR) spectra and its high resolution variants such as electron–nuclear double resonance (ENDOR) or hyperfine sublevel correlation spectroscopy (HYSCORE) has been recognized to be a difficult field for theoretical chemistry. Unlike the electron density, which is positive everywhere in space, the spin density is a strongly structured function that can be either positive or negative. This has been realized already by the pioneers of EPR spectroscopy that have referred to the phenomenon as “spin polarization”. Classical examples are the aromatic protons of benzylic radicals or the proton hyperfine couplings (hfcs) of CH<sub>3</sub> that are known to be negative. McConnell has given an intuitively appealing valence bond interpretation of the spin polarization phenomenon.<sup>1</sup> However, it is difficult to implement valence bond theory rigorously in terms of ab initio wave functions. In Hartree–Fock (HF) theory, the spin polarization arises in a rather natural way in the unrestricted HF variant (UHF). However, once calculations with large basis sets became feasible it quickly became clear that the UHF prediction of hyperfine couplings is very poor. Typically, spin polarization contributions are too large by about a factor of 3. This has been analyzed in some detail by Hameka<sup>2</sup> and Chipman.<sup>3</sup> Thus, the calculation of accurate first principles spin densities requires the incorporation of a substantial amount of dynamic correlation. The simplest correlation method, second-order Møller–Plesset perturbation theory (MP2), is known to be insufficient and often provides somewhat erratic results when applied to open-shell systems. Provided that basis sets with sufficient flexibility in the core region and adequate polarization functions to cover dynamic correlation are used (e.g., ref 4), the quadratic configuration interaction with single and double excitations (QCISD) or the more rigorous coupled cluster theory

with single- and double excitations (CCSD) are known to provide essentially satisfactory results.<sup>5–11</sup> However, these methods involve iterative steps with  $\mathcal{O}(N^6)$  scaling with respect to system size. Thus, their routine application to larger molecules is presently not possible.

Density functional theory (DFT) often provides much better results than UHF theory,<sup>12,4</sup> and there are many successful applications of DFT to the calculation of hfccs. Among the multitude of functionals that could be used, the “gold standard” B3LYP functional provides good results for organic radicals.<sup>8</sup> For transition metal nuclei all functionals have difficulties since they underestimate the core level spin polarization.<sup>13,14</sup> This can to some extent be compensated by mixing more HF exchange into hybrid density functionals. This is, however, not a satisfactory solution to the problem since the optimum mixing depends strongly on the investigated system. In a previous study it was found that among the standard functionals, the meta-generalized gradient approximation based hybrid functional TPSSH<sup>15</sup> provides the best results for transition metal complexes.<sup>16</sup> Other problem cases for DFT include strongly delocalized radicals where the self-interaction error strongly deteriorates the results.<sup>17,18</sup>

In a recent study, we have investigated the behavior of a new class of double-hybrid density functionals (DHDFs) that have shown in many fields their high potential. In general, excellent results have been obtained for hyperfine couplings with the B2PLYP functional,<sup>16</sup> provided that the calculations are based on the relaxed density approach,<sup>16</sup> which arises naturally in analytic gradient theory of correlated wave function theories.<sup>19–22</sup> However, even B2PLYP was found to suffer to some extent from the unstable MP2 component despite the fact that it was found to be greatly superior to MP2 itself.

Despite all recent progress, we feel that it would be desirable to have an affordable wave function based ab initio method available that reliably provides results of essentially QCISD or CCSD quality. Most recently, it was shown that the results of MP2 for open-shell molecules can be greatly improved in accuracy and stability if the orbitals are optimized alongside with the double excitation amplitudes.<sup>23,24</sup> This orbital optimiza-

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tion is based on the well-known Hylleraas functional<sup>25</sup> that has been shown by Saebø and Pulay to lead to an orbital invariant formulation of MP2 theory.<sup>26</sup> The method has been dubbed OO-MP2 and was further improved by combining it with the concepts of spin-component scaling (SCS-MP2),<sup>27</sup> thus leading to OO-SCS-MP2. The variant with spin-opposite scaling MP2 (SOS-MP2) has been explored by Head-Gordon and co-workers.<sup>28</sup> The computational effort of OO-SCS-MP2 is best characterized as an iterative  $\mathcal{O}(N^5)$  process that is substantially cheaper than QCISD or CCSD but also substantially more expensive than MP2. However, if the OO-SCS-MP2 method is combined with the resolution of the identity (RI) approximation,<sup>29</sup> it is applicable in reasonable computation times to at least medium sized molecules of contemporary chemical interest that are far too large for QCISD and CCSD to be applicable.

In this work, we have investigated the performance of OO-(SCS-)MP2 to calculate hfcs. Following a brief description of the theory, the OO-MP2 and OO-SCS-MP2 methods are benchmarked against the results of CCSD and CCSD(T) calculations. The applicability to larger molecules is demonstrated in the final part of the paper.

## Theory

Throughout this paper, indices  $i, j, k, \dots$  refer to occupied spin orbitals in the reference determinant,  $a, b, c, \dots$  to virtual spin orbitals,  $p, q, r, \dots$  to general spin orbitals from either set and  $P, Q, \dots$  denote auxiliary basis functions.

The second-order Møller–Plesset correlation energy<sup>30</sup> can be regarded as being stationary with respect to the MP2 amplitudes, since the latter can be considered as having been optimized through minimization of the Hylleraas functional.<sup>25,26</sup>

$$\mathcal{E}_{\text{MP2}} = \min_t \{2\langle\Psi_1|\hat{H}|\Psi_0\rangle + \langle\Psi_1|\hat{H}_0 - E_0|\Psi_1\rangle\} \quad (1)$$

$\hat{H}_0$  is the zeroth-order Hamiltonian as proposed by Møller and Plesset,  $\Psi_0$  is the reference determinant,  $\Psi_1$  is the first-order wave function and  $E_0 = E_{\text{HF}} = \langle\Psi_{\text{HF}}|\hat{H}|\Psi_{\text{HF}}\rangle$  corresponds to the HF energy. The MP2 amplitudes are collectively denoted  $t$ .

Since the MP2 energy is not variational with respect to the molecular orbital (MO) coefficients, no orbital relaxation due to the additional dynamic correlation field is taken into account. To allow for orbital relaxation, a new Hylleraas functional can be formulated, which no longer depends on the MP2 amplitudes alone but becomes also a functional of the orbital rotation parameters, which parametrize the changes in the MO coefficients. The total MP2 energy will then become stationary with respect to the MP2 molecular orbital coefficients and with respect to the MP2 double excitation amplitudes. The extended Hylleraas functional to be minimized is

$$\mathcal{J}[\mathbf{t}, \mathbf{R}] = E_0[\mathbf{R}] + 2\langle\Psi_1|\hat{H}|\Psi_0\rangle + \langle\Psi_1|\hat{H}_0 - E_0[\mathbf{R}]|\Psi_1\rangle \quad (2)$$

$\mathbf{R}$  are the orbital rotation coefficients that are used to update the MO coefficients  $\mathbf{c}$  by means of a unitary transformation.<sup>31</sup> If a spin-unrestricted scheme is desired, different orbitals for different spins are used throughout the entire orbital optimization.

$$\mathbf{c}^{\text{new}} = \exp(\mathbf{R})\mathbf{c}^{\text{old}} \quad (3)$$

$\Psi_0$  is the reference determinant, but unlike eq 1, the reference determinant no longer corresponds to the Hartree–Fock determinant. When the total energy is minimized with respect to the MP2 MO coefficients, the reference determinant changes with every variation step. The reference energy  $E_0[\mathbf{R}]$  changes simultaneously, and therefore, it is no longer stationary with respect to the HF MO coefficients. Consequently, Brillouin’s theorem<sup>32</sup> is no longer valid and the off-diagonal blocks of the Fock matrix do not vanish. Hence, the first-order wave function would contain contributions from single excitations. Since orbital optimization introduces all important effects of the singles, we prefer to leave them out of the treatment. Any attempt to the contrary will destroy the convergence properties.

With the first-order wave function excluding single excitations,

$$|\Psi_1\rangle = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} |\Phi_{ij}^{ab}\rangle \quad (4)$$

the explicit form of the orbital-optimized MP2 Hylleraas functional employing the resolution of the identity approximation<sup>29,33,34</sup> (OO-RI-MP2) becomes

$$\mathcal{J}_{\text{OO}}[\mathbf{t}, \mathbf{R}] = \sum_i \langle i|\hat{h}|i\rangle + \frac{1}{2} \sum_{ij} \langle ij||ij\rangle + \sum_{iaP} (ialP)\Gamma_{ia}^P + \sum_{ij} D_{ij}F_{ij} + \sum_{ab} D_{ab}F_{ab} \quad (5)$$

with

$$\Gamma_{ia}^P = \sum_Q V_{PQ}^{-1} \sum_{jb} (Q|jb)t_{ab}^{ij} \quad (6)$$

$$V_{PQ} = (P|Q) = \int Q(\mathbf{r}_1)r_{12}^{-1}P(\mathbf{r}_2) \, d\mathbf{r}_1 \, d\mathbf{r}_2 \quad (7)$$

$F_{pq}$  denotes Fock matrix elements and it is insisted that the orbitals diagonalize its occupied and virtual subspaces, respectively. The MP2-like density blocks are

$$D_{ij} = -\frac{1}{2 \cdot c_{\text{SCS}}} \sum_{kab} t_{ab}^{ik} t_{ab}^{jk} \quad (8)$$

$$D_{ab} = \frac{1}{2 \cdot c_{\text{SCS}}} \sum_{ijc} t_{ac}^{ij} t_{bc}^{ij} \quad (9)$$

with  $c_{\text{SCS}}$  representing the corresponding scaling parameter for the antiparallel- ( $\alpha\beta$ ) and parallel-spin ( $\alpha\alpha$ ,  $\beta\beta$ ) pairs of electrons. If spin-component scaling is employed,  $c_{\text{SCS}}$  takes the specific values  $1/3$  for the parallel-spin compounds and  $6/5$  for the antiparallel-spin pairs; otherwise  $c_{\text{SCS}} = 1$ .<sup>27</sup> The MP2 amplitudes in the case of a block diagonal Fock matrix are obtained through the condition  $(\partial \mathcal{J}_{\text{OO}})/(\partial t_{ab}^{ij}) = 0$ ,

$$t_{ab}^{ij} = -c_{\text{SCS}} \cdot \frac{\sum_{PQ} (ialP)V_{PQ}^{-1}(Q|jb)}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} \quad (10)$$

The orbital changes are parametrized by the anti-Hermitian matrix  $\mathbf{R}$  such that no Lagrangian multipliers are required to ensure orbital orthonormality.

The Fock operator is expanded to first order in the orbital rotations as

$$F_{pq} = \sum_r R_{rp} F_{rq} + R_{rq} F_{pr} + R_{pq}^{(1)} \quad (11)$$

$$R_{pq}^{(1)} = \sum_{kc} R_{ck} \{ \langle pc || qk \rangle + \langle pk || qc \rangle \} \quad (12)$$

Thus, the first-order energy change becomes ( $h_{pq} \equiv \langle p | \hat{h} | q \rangle$ ,  $g_{pqrs} \equiv \langle pq || rs \rangle$ )

$$\begin{aligned} \mathcal{L}_{\text{OO}}[\mathbf{t}, \mathbf{R}] = & \sum_{ic} R_{ci} (h_{ci} + h_{ic}) + \frac{1}{2} \sum_{ijc} R_{ci} (g_{cij} + g_{ijc}) + R_{cj} (g_{icj} + g_{ijc}) + \\ & 2 \sum_{iacP} R_{ci} (ac|P) \Gamma_{ia}^P - 2 \sum_{ikaP} R_{ak} (ik|P) \Gamma_{ia}^P - \sum_{ij} D_{ij} (R_{ij}^{(1)} + \\ & \sum_c \{ R_{ci} F_{cj} + R_{cj} F_{ic} \}) + \sum_{ab} D_{ab} (R_{ab}^{(1)} - \sum_k \{ R_{ak} F_{kb} + R_{bk} F_{ak} \}) \end{aligned} \quad (13)$$

The condition for the energy functional to be stationary with respect to the orbital rotations ( $\partial \mathcal{L}_{\text{OO}}[\mathbf{t}, \mathbf{R}] / \partial R_{ai} = 0$ ), yields the expression for the orbital gradient and hence the expression for the OO-RI-MP2 Lagrangian.

$$\begin{aligned} \frac{\partial \mathcal{L}_{\text{OO}}[\mathbf{t}, \mathbf{R}]}{\partial R_{ai}} \equiv g_{ai} = & 2F_{ai} + 2 \sum_j D_{ij} F_{aj} - 2 \sum_b D_{ab} F_{ib} + \\ & R^{(1)}(\mathbf{D})_{ai} + 2 \sum_{cP} (ac|P) \Gamma_{ia}^P - 2 \sum_{kP} (ik|P) \Gamma_{ia}^P \end{aligned} \quad (14)$$

To implement a practical orbital optimization scheme, we have chosen a simple DIIS method.<sup>35</sup> A matrix  $\mathbf{B}$  that contains the orbital gradient in its off-diagonal blocks and the orbital energies in its diagonal is repeatedly diagonalized and provides the orbital rotation coefficients directly, cf. eq 15.

$$\mathbf{B} = \begin{pmatrix} \varepsilon_0 & \mathbf{g}_{ia} \\ & \varepsilon_1 & \\ \mathbf{g}_{ia} & & \ddots \end{pmatrix} \quad (15)$$

The whole procedure is carried out self-consistently until both  $\|g_{ai}\|$  and  $\Delta E$  fall below predefined thresholds. The orbital energies are obtained by diagonalizing the Fock operator in the occupied/occupied and virtual/virtual spaces of the current orbital set.

At convergence, the relaxed density matrix and the one obtained as an expectation value over the first-order wave function become identical. The entire density is given by the sum over the reference density and the correlation contribution.

$$D_{pq}^{\text{OO}} = P_{pq}^{\text{ref}} + D_{pq} \quad (16)$$

$$P_{\mu\nu}^{\text{ref}} = \sum_i c_{\mu i} c_{\nu i} \quad (17)$$

In an infinite basis set, the Hellmann–Feynman theorem<sup>36,37</sup> becomes valid and the OO-RI-MP2 density matrix can be used for the calculation of expectation values and to calculate the OO-RI-MP2 gradient, respectively.

Consider a one-electron perturbation of the form  $\lambda h_i$ , e.g., an external electric field, and assume the basis functions to be independent of the perturbation. The first derivative of the OO-RI-MP2 energy with respect to the perturbation  $\lambda$  corresponds to the expectation value of  $h_i$ , if the OO-RI-MP2 equations have converged, eq 18.

$$\frac{\partial E_{\text{OO}}}{\partial \lambda} = \sum_{pq} D_{pq} h_{pq}^{\lambda} \quad (18)$$

In a spin-unrestricted scheme, the total electron density and the spin density matrices are obtained as the sum and difference of the spin-up and spin-down densities, respectively. Thus, the isotropic (c) and dipolar (d) parts of the hyperfine coupling tensor are calculated as

$$A_{kl}^{(\text{A};c)} = \delta_{kl} \frac{8\pi}{3} \frac{P_A}{2S} \sum_{\mu\nu} D_{\mu\nu}^{\text{OO}(\alpha-\beta)} \langle \varphi_{\mu} | \delta(\mathbf{R}_A) | \varphi_{\nu} \rangle \quad (19)$$

$$A_{kl}^{(\text{A};d)} = \frac{P_A}{2S} \sum_{\mu\nu} D_{\mu\nu}^{\text{OO}(\alpha-\beta)} \langle \varphi_{\mu} | r_A^{-5} (r_A^2 \delta_{kl} - 3r_{A;k} r_{A;l}) | \varphi_{\nu} \rangle \quad (20)$$

where  $D_{\mu\nu}^{\text{OO}(\alpha-\beta)}$  is the orbital optimized MP2 spin density matrix,  $S$  denotes the total spin, and  $P_A$  is an atom specific constant, defined in eq 24.

### Spin Contamination

The expectation value of the total spin operator  $\hat{S}^2$  is regarded as a diagnostic tool to measure the spin contamination in the UHF reference determinant.<sup>38–40</sup> In post-Hartree–Fock methods  $\langle \hat{S}^2 \rangle$  can be evaluated by means of response theory.<sup>38</sup> The perturbation  $\lambda S^2$  is added to the Hamiltonian, and the derivative of the perturbation dependent energy yields the desired expectation value, eq 21.

$$\langle \hat{S}^2 \rangle = \left. \frac{dE(\lambda)}{d\lambda} \right|_{\lambda=0} \quad (21)$$

Note that the perturbation expansion only corresponds to the exact expectation value of  $S^2$  in the case of variational methods.  $\langle S^2 \rangle$  for the OO-RI-MP2 can be expressed as<sup>39</sup>

$$\langle \hat{S}^2 \rangle_{\text{OO}} = \langle \hat{S}^2 \rangle_{\text{ref}} + 2 \langle \Psi_0 | \hat{S}^2 | \Psi_1 \rangle \quad (22)$$

The correlation correction to the expectation value of the total spin operator over the reference determinant has the explicit form

**TABLE 1:  $g_N$  values and  $P_A$  Factors Employed for the Calculation of hfccs**

atom	$g_N$	$P_A$ (MHz/au <sup>3</sup> )
<sup>1</sup> H	5.5856912	533.5514
<sup>11</sup> B	1.7924240	171.2143
<sup>13</sup> C	1.4048200	134.1900
<sup>14</sup> N	0.4037607	38.5677
<sup>17</sup> O	−0.7575160	−72.3588
<sup>19</sup> F	5.2577320	502.2244
<sup>25</sup> Mg	−0.3421800	−32.6854
<sup>27</sup> Al	1.4566010	139.1361
<sup>29</sup> Si	−1.1106000	−106.0857
<sup>33</sup> S	0.4291100	40.9891
<sup>35</sup> Cl	0.5479157	52.3375

$$2\langle\Psi_0|\hat{S}^2|\Psi_1\rangle = -\frac{1}{2}\sum_{ia}\sum_{jb}^{\beta}S_{ib}^{\alpha\beta}S_{ja}^{\beta\alpha}t_{ab}^{ij} \quad (23)$$

where  $S_{ib}^{\alpha\beta} = \int \Phi_i^{\alpha} s_{+} \Phi_b^{\beta} d\tau$  and  $S_{ja}^{\beta\alpha} = \int \Phi_j^{\beta} s_{-} \Phi_a^{\alpha} d\tau$ .<sup>39</sup>  $\Phi_i^{\alpha}$  and  $\Phi_j^{\beta}$  denote internal and  $\Phi_a^{\alpha}$  and  $\Phi_b^{\beta}$  represent virtual  $\alpha$ -/ $\beta$ -spin orbitals, respectively.

### Computational Details

To benchmark the performance of the OO-SCS-RI-MP2 and OO-RI-MP2 method, hyperfine coupling constants (hfccs) of a series of small radicals and first row main group elements have been calculated. To avoid complicated issues like basis set convergence (that is very slow for singular properties like the isotropic hfccs), vibrational averaging, or matrix effects, we choose to initially calibrate the OO-MP2 methods relative to a higher level method, specifically CCSD(T).

All MP2 and DFT calculations were carried out with a development version of the ORCA program package.<sup>41</sup> The application of the “resolution of the identity” approximation<sup>29</sup> in terms of the Split-RI-J algorithm<sup>42</sup> is indicated with the prefix “RI”. The coupled cluster calculations were performed with the ACES II (now CFour) program suite.<sup>43</sup> All electrons were correlated throughout the study.

The small radicals were optimized on the CCSD(T) level.<sup>44</sup> Dunning’s cc-pVTZ basis set was chosen for these purposes.<sup>45</sup> In the case of the OH, NO, and NH<sub>2</sub> radicals experimental structures were used.

Barone’s triple- $\zeta$  EPR-III<sup>46</sup> basis set was employed for the calculation of the hyperfine coupling constants, except for the elements Al, S, Cl, and Si, for which Kutzelnigg’s IGLO-III<sup>47</sup> basis set was used. For the element Mg a modified TZVPP basis set which has been decontracted in the s-part was employed.<sup>48</sup>

In preliminary studies comparing RI-MP2 to conventional MP2 it was ensured that the auxiliary basis sets used in the

present study lead to an error of  $\leq 1$  MHz in the calculated hfccs. The decontracted def2-TZVPP/JK auxiliary basis set of Weigend et al.<sup>49</sup> was found suitable to reach this level of accuracy.

All energies were converged to  $10^{-9}E_h$ .

The  $P_A$  factor in eqs 19 and 20 is the product of the electronic and nuclear  $g$ -values and Bohr magnetons, respectively, and specific for each atom type.

$$P_A = g_e g_N \beta_e \beta_N \quad (24)$$

The nuclear  $g$ -values employed for the calculation of the hfccs were taken from ref 50 and are listed in Table 1.

### Numerical Results

Throughout the following section  $A_{11}^{(A)}$ ,  $A_{22}^{(A)}$ , and  $A_{33}^{(A)}$  denote the diagonal elements of the total hyperfine coupling tensor,  $A^{(A;c)}$  indicates the isotropic Fermi contact contribution to the hfc tensor, and the anisotropic spin dipolar contributions are assigned by  $A_{11}^{(A;d)}$ ,  $A_{22}^{(A;d)}$ , and  $A_{33}^{(A;d)}$ .

**Atoms.** In Table 2 the isotropic and anisotropic hfccs for the first row main group elements B–F are listed. Denoting the principal values of the anisotropic hfc tensor  $2b$ ,  $-b$ ,  $-b$ , only  $b$  is reported. The CCSD(T) results presented in Table 2 serve as reference. For these systems the effect of the perturbative triples correction is negligible and the CCSD results are very close to CCSD(T). The RI-MP2 method tends to slightly underestimate the isotropic hfc contribution but performs surprisingly good for atomic hfccs.

Both orbital optimized MP2 methods yield excellent results. They tend to slightly overestimate the hfc contributions in absolute value with OO-RI-MP2 performing marginally better than its spin-component scaled variant. As expected, the errors in the anisotropic hfccs tend to be smaller than the error in the isotropic contributions. Orbital optimization yields almost no improvement for the atomic hfccs compared to conventional MP2.

Compared to CCSD(T), the B2PLYP double-hybrid functional performs reasonably well but certainly worse than the OO-MP2 methods for the dipolar contribution to the hfccs. For the Fermi contact interaction, the errors of B2PLYP relative to CCSD(T) are of limited quality. However, relative to the experimental numbers B2PLYP is the most accurate of the tested approaches. This is likely a fortuitous result as basis sets far from the limit are used in this study.

**Radicals.** In Tables 3 and 4 the hyperfine coupling constants for a variety of small radicals are listed.

In general, the deviations from CCSD(T) that are obtained with OO-RI-MP2 and OO-SCS-RI-MP2 methods do not appear

**TABLE 2: Calculated hfccs (MHz) of First Row Main Group Elements**

atom		method						expt
		RI-MP2	OO-RI-MP2	OO-SCS-RI-MP2	B2PLYP	CCSD	CCSD(T)	
<sup>11</sup> B	$A^{(A;d)}$	56.1	56.1	55.9	58.7	55.1	55.1	
	$A^{(A;c)}$	−2.4	2.6	2.7	17.1	3.7	4.2	11.6 <sup>a</sup> /18.7 <sup>b</sup>
<sup>13</sup> C	$A^{(A;d)}$	−47.7	−47.7	−47.5	−49.0	−47.4	−47.3	
	$A^{(A;c)}$	8.4	12.7	13.7	24.3	10.9	11.3	(21.4) <sup>c</sup> /(22.5) <sup>a</sup>
<sup>14</sup> N	$A^{(A;d)}$	0.0	0.0	0.0	0.0	0.0	0.0	
	$A^{(A;c)}$	7.5	8.7	9.5	11.4	7.8	7.9	10.4 <sup>d</sup>
<sup>17</sup> O	$A^{(A;d)}$	72.7	72.6	72.6	74.2	72.4	72.4	
	$A^{(A;c)}$	−23.6	−25.9	−28.5	−31.0	−24.5	−24.5	34.5 <sup>e</sup>
<sup>19</sup> F	$A^{(A;d)}$	1588.9	1588.5	1587.1	1608.8	1581.2	1580.3	
	$A^{(A;c)}$	243.9	259.3	284.6	278.5	247.2	245.8	301.7 <sup>e</sup>

<sup>a</sup> Reference 51. <sup>b</sup> Reference 52. <sup>c</sup> Reference 53. <sup>d</sup> Reference 54. <sup>e</sup> Reference 55.



**TABLE 3: Hyperfine Coupling Constants (MHz) for a Variety of Small  $S = 1/2$  Systems**

	$\langle S^2 \rangle$			$A_{11}^{(A)}$	$A_{22}^{(A)}$	$A_{33}^{(A)}$	$A^{(A;c)}$	$A_{11}^{(A;d)}$	$A_{22}^{(A;d)}$	$A_{33}^{(A;d)}$
$^2\text{BO}$	0.799945	$^{11}\text{B}$	RI-MP2	973.2	973.2	1067.4	1004.6	-31.4	-31.4	62.8
		$^{11}\text{B}$	SCS-RI-MP2	945.8	945.8	1050.5	980.7	-34.9	-34.9	69.8
		$^{11}\text{B}$	OO-RI-MP2	977.3	977.3	1055.4	1003.3	-26.0	-26.0	52.0
		$^{11}\text{B}$	OO-SCS-RI-MP2	971.7	971.7	1053.2	998.9	-27.2	-27.2	54.3
		$^{11}\text{B}$	B2PLYP	1033.7	1033.7	1116.9	1061.4	-27.7	-27.7	55.5
		$^{11}\text{B}$	CCSD	1016.3	1016.3	1090.9	1041.1	-24.9	-24.9	49.7
		$^{11}\text{B}$	CCSD(T)	978.9	978.9	1057.3	1005.0	-26.1	-26.1	52.3
			expt <sup>57</sup>	998	998	1079	1025	-27	-27	54
		$^{17}\text{O}$	RI-MP2	-93.1	-69.5	-69.5	-77.4	-15.8	7.9	7.9
		$^{17}\text{O}$	SCS-RI-MP2	-95.1	-86.8	-86.8	-89.6	-5.6	2.8	2.8
		$^{17}\text{O}$	OO-RI-MP2	-55.4	9.9	9.9	-11.9	-43.5	21.8	21.8
		$^{17}\text{O}$	OO-SCS-RI-MP2	-50.1	11.3	11.3	-9.2	-40.9	20.5	20.5
		$^{17}\text{O}$	B2PLYP	-55.7	5.5	5.5	-14.9	-40.8	20.4	20.4
		$^{17}\text{O}$	CCSD	-55.3	9.7	9.7	-12.0	-43.9	21.7	21.7
		$^{17}\text{O}$	CCSD(T)	-54.3	5.1	5.1	-14.7	-39.6	19.8	19.8
	0.855236	$^{11}\text{B}$	RI-MP2	730.4	730.4	844.0	768.3	-37.8	-37.8	75.7
		$^{11}\text{B}$	SCS-RI-MP2	675.1	675.1	802.0	717.4	-42.3	-42.3	84.6
		$^{11}\text{B}$	OO-RI-MP2	769.4	769.4	858.5	799.1	-27.9	-27.9	59.4
		$^{11}\text{B}$	OO-SCS-RI-MP2	746.5	746.5	840.2	777.7	-31.2	-31.2	62.5
		$^{11}\text{B}$	B2PLYP	785.7	785.7	883.9	818.4	-32.8	-32.8	65.5
		$^{11}\text{B}$	CCSD	767.0	767.0	852.3	795.5	-28.4	-28.4	56.9
		$^{11}\text{B}$	CCSD(T)	737.2	737.2	826.1	766.8	-29.6	-29.6	59.3
			expt <sup>58</sup>				796			
		$^{33}\text{S}$	RI-MP2	29.0	29.0	60.0	39.3	-10.3	-10.3	20.6
		$^{33}\text{S}$	SCS-RI-MP2	37.2	37.2	55.6	43.3	-6.1	-6.1	12.2
		$^{33}\text{S}$	OO-RI-MP2	-14.2	-14.2	51.2	7.6	-21.8	-21.8	43.6
$^2\text{CN}$	1.159620	$^{33}\text{S}$	OO-SCS-RI-MP2	-17.3	-17.3	45.2	3.5	-20.8	-20.8	41.6
		$^{33}\text{S}$	B2PLYP	-16.0	-16.0	47.6	5.2	-21.2	-21.2	42.4
		$^{33}\text{S}$	CCSD	-19.1	-19.1	47.7	3.2	-22.3	-22.3	44.5
		$^{33}\text{S}$	CCSD(T)	-13.1	-13.1	47.1	7.0	-20.1	-20.1	40.1
		$^{13}\text{C}$	RI-MP2	485.4	485.4	740.7	570.5	-85.1	-85.1	170.2
		$^{13}\text{C}$	SCS-RI-MP2	445.0	445.0	712.6	534.2	-89.2	-89.2	178.4
		$^{13}\text{C}$	OO-RI-MP2	434.7	434.7	601.0	490.2	-55.4	-55.4	110.8
		$^{13}\text{C}$	OO-SCS-RI-MP2	435.2	435.2	603.2	491.2	-56.0	-56.0	112.0
		$^{13}\text{C}$	B2PLYP	343.3	343.3	555.5	414.1	-70.7	-70.7	141.5
		$^{13}\text{C}$	CCSD	602.4	602.4	761.4	655.4	-53.0	-53.0	106.0
		$^{13}\text{C}$	CCSD(T)	499.4	499.4	669.5	556.1	-56.7	-56.7	113.5
			expt <sup>59</sup>	543	543	678	588	-45	-45	90
		$^{14}\text{N}$	RI-MP2	1.7	1.7	30.2	11.2	-9.5	-9.5	18.9
		$^{14}\text{N}$	SCS-RI-MP2	5.6	5.6	31.5	14.2	-8.6	-8.6	17.3
		$^{14}\text{N}$	OO-RI-MP2	-13.8	-13.8	46.8	6.4	-20.2	-20.2	40.4
		$^{14}\text{N}$	OO-SCS-RI-MP2	-20.1	-20.1	39.9	-0.1	-20.0	-20.0	40.0
		$^{14}\text{N}$	B2PLYP	-44.1	-20.1	14.0	-24.7	-19.3	-19.3	38.7
		$^{14}\text{N}$	CCSD	-39.8	-39.8	19.7	-20.0	-19.8	-19.8	39.7
		$^{14}\text{N}$	CCSD(T)	-37.4	-37.4	20.0	-18.3	-19.1	-19.1	38.3
$^2\text{CO}^+$	0.960189		expt <sup>59</sup>	-28	-28	27	-13	-15	-15	30
		$^{13}\text{C}$	RI-MP2	1331.1	1331.1	1583.7	1415.3	-84.2	-84.2	168.4
		$^{13}\text{C}$	SCS-RI-MP2	1275.5	1275.5	1549.5	1366.8	-91.4	-91.4	182.7
		$^{13}\text{C}$	OO-RI-MP2	1413.0	1413.0	1566.3	1464.1	-51.1	-51.1	102.2
		$^{13}\text{C}$	OO-SCS-RI-MP2	1411.0	1411.0	1569.0	1463.6	-52.7	-52.7	105.3
		$^{13}\text{C}$	B2PLYP	1497.5	1497.5	1662.7	1552.6	-55.1	-55.1	110.1
		$^{13}\text{C}$	CCSD	1538.2	1538.2	1675.2	1583.9	-45.7	-45.7	91.3
		$^{13}\text{C}$	CCSD(T)	1460.9	1460.9	1611.6	1511.1	-50.3	-50.3	100.5
			expt <sup>60</sup>	1524	1524	1671	1573	-49	-49	98
		$^{17}\text{O}$	RI-MP2	-103.6	-103.6	-85.1	-97.4	-6.2	-6.2	12.3
		$^{17}\text{O}$	SCS-RI-MP2	-113.3	-113.3	-77.3	-101.3	-12.0	-12.0	24.0
		$^{17}\text{O}$	OO-RI-MP2	-57.8	55.6	55.6	17.8	-75.6	37.8	37.8
		$^{17}\text{O}$	OO-SCS-RI-MP2	-48.6	60.2	60.2	23.9	-72.5	36.3	36.3
		$^{17}\text{O}$	B2PLYP	-45.9	56.3	56.3	22.2	-68.1	34.1	34.1
		$^{17}\text{O}$	CCSD	-55.5	59.2	59.2	21.0	-76.5	38.3	38.3
		$^{17}\text{O}$	CCSD(T)	-49.2	51.8	51.8	18.1	-67.3	33.7	33.7
			expt <sup>60</sup>	-47	52	52	19	-66	33	33
	0.797337	$^{14}\text{N}$	RI-MP2	-205.6	-23.1	60.1	-56.2	-149.4	33.1	116.3
		$^{14}\text{N}$	SCS-RI-MP2	-200.1	-22.2	63.3	-53.0	-147.1	30.8	116.3
		$^{14}\text{N}$	OO-RI-MP2	-18.3	-17.2	88.4	17.6	-36.0	-34.8	70.8
		$^{14}\text{N}$	OO-SCS-RI-MP2	-15.5	-12.6	93.3	21.8	-37.2	-34.3	71.6
		$^{14}\text{N}$	B2PLYP	-16.9	-16.7	96.4	20.9	-37.8	-37.7	75.4
		$^{14}\text{N}$	CCSD	-16.7	-12.9	97.3	22.6	-39.3	-35.5	74.8
		$^{14}\text{N}$	CCSD(T)	-23.1	-18.0	92.3	17.1	-40.2	-35.0	75.2
			expt <sup>60</sup>				22			
		$^{17}\text{O}$	RI-MP2	-630.1	-288.7	19.7	-299.7	-330.4	11.0	319.4
		$^{17}\text{O}$	SCS-RI-MP2	-622.2	-289.4	13.5	-299.4	-322.9	10.0	312.9
		$^{17}\text{O}$	OO-RI-MP2	-155.7	34.7	43.0	-26.0	-129.7	60.7	69.0
$^2\text{OH}$	0.756733	$^{17}\text{O}$	OO-SCS-RI-MP2	-162.9	25.6	36.2	-33.7	-129.2	59.3	69.9
		$^{17}\text{O}$	B2PLYP	-167.6	31.2	35.8	-33.6	-134.0	64.7	69.3
		$^{17}\text{O}$	CCSD	-168.3	23.5	38.8	-35.4	-133.0	58.9	74.1
		$^{17}\text{O}$	CCSD(T)	-169.9	11.5	26.9	-43.7	-125.9	55.2	70.6
		$^{17}\text{O}$	RI-MP2	-321.9	98.5	98.7	-41.6	-280.4	140.1	140.3
		$^{17}\text{O}$	SCS-RI-MP2	-322.1	98.9	100.6	-40.9	-281.2	139.8	141.4
		$^{17}\text{O}$	OO-RI-MP2	-326.5	92.5	93.7	-46.8	-279.7	139.3	140.5
		$^{17}\text{O}$	OO-SCS-RI-MP2	-327.0	93.3	93.5	-46.7	-280.3	140.0	140.2
		$^{17}\text{O}$	B2PLYP	-337.5	89.7	91.0	-52.3	-285.2	142.0	143.2
		$^{17}\text{O}$	CCSD	-324.2	92.9	94.5	-45.6	-278.6	138.5	140.1
		$^{17}\text{O}$	CCSD(T)	-322.8	93.8	95.4	-44.5	-278.2	138.3	139.9

TABLE 3: Continued

	$\langle S^2 \rangle$		$A_{11}^{(A)}$	$A_{22}^{(A)}$	$A_{33}^{(A)}$	$A^{(A:c)}$	$A_{11}^{(A:d)}$	$A_{22}^{(A:d)}$	$A_{33}^{(A:d)}$
${}^2\text{MgF}$	0.750477	exp <sup>61</sup>				-51			
		${}^1\text{H}$ RI-MP2	-142.1	-87.0	18.9	-70.1	-72.1	-16.9	88.9
		${}^1\text{H}$ SCS-RI-MP2	-133.2	-78.4	26.6	-61.7	-71.5	-16.7	88.3
		${}^1\text{H}$ OO-RI-MP2	-150.2	-95.1	13.2	-77.4	-72.8	-17.7	90.5
		${}^1\text{H}$ OO-SCS-RI-MP2	-144.0	-89.2	18.9	-71.4	-72.6	-17.8	90.3
		${}^1\text{H}$ B2PLYP	-142.0	-87.9	19.2	-70.3	-71.8	-17.7	89.5
	0.751211	${}^1\text{H}$ CCSD	-148.1	-93.5	15.1	-75.5	-72.6	-18.0	90.6
		${}^1\text{H}$ CCSD(T)	-145.6	-91.1	16.8	-73.3	-72.3	-17.8	90.1
		exp <sup>61</sup>				~-69			
		${}^{25}\text{Mg}$ RI-MP2	-308.1	-296.5	-296.5	-300.4	-7.8	3.9	3.9
		${}^{25}\text{Mg}$ SCS-RI-MP2	-303.2	-291.5	-291.5	-295.4	-7.8	3.9	3.9
		${}^{25}\text{Mg}$ OO-RI-MP2	-306.8	-295.2	-295.2	-299.0	-8.0	3.9	3.9
	0.751017	${}^{25}\text{Mg}$ OO-SCS-RI-MP2	-301.7	-290.0	-290.0	-293.9	-7.8	3.9	3.9
		${}^{25}\text{Mg}$ B2PLYP	-324.7	-312.7	-312.7	-316.7	-7.8	4.0	4.0
		${}^{25}\text{Mg}$ CCSD	-306.8	-295.2	-295.2	-299.0	-12	3.9	3.9
		${}^{25}\text{Mg}$ CCSD(T)	-305.3	-293.7	-293.7	-297.6	-7.8	3.9	3.9
		exp <sup>62</sup>	-349	-331	-331	-337	-7.8	6	6
		${}^{19}\text{F}$ RI-MP2	116.2	116.2	302.8	178.4	-62.2	-62.2	124.4
${}^2\text{AlO}$	0.808358	${}^{19}\text{F}$ SCS-RI-MP2	108.9	108.9	291.8	169.9	-61.0	-61.0	121.9
		${}^{19}\text{F}$ OO-RI-MP2	118.1	118.1	313.7	183.3	-65.2	-65.2	130.4
		${}^{19}\text{F}$ OO-SCS-RI-MP2	105.0	105.0	295.7	168.6	-63.6	-63.6	127.1
		${}^{19}\text{F}$ B2PLYP	127.1	127.1	367.6	207.3	-80.2	-80.2	160.3
		${}^{19}\text{F}$ CCSD	123.7	123.7	309.3	185.6	-61.8	-61.8	123.7
		${}^{19}\text{F}$ CCSD(T)	120.6	120.6	315.6	185.6	-65.0	-65.0	130.0
	0.762247	exp <sup>63</sup>	143	143	332	206	-63	-63	126
		${}^{27}\text{Al}$ RI-MP2	-135.8	-135.8	85.4	-62.1	-73.7	-73.7	147.5
		${}^{27}\text{Al}$ SCS-RI-MP2	-155.0	-155.0	52.2	-85.9	-69.1	-69.1	138.1
		${}^{27}\text{Al}$ OO-RI-MP2	1034.1	1034.1	1181.9	1083.4	-49.2	-49.2	98.5
		${}^{27}\text{Al}$ OO-SCS-RI-MP2	970.3	970.3	1118.2	1019.6	-49.3	-49.3	98.6
		${}^{27}\text{Al}$ B2PLYP	922.1	922.1	1094.6	979.6	-57.5	-57.5	115.0
	0.765396	${}^{27}\text{Al}$ CCSD	425.3	425.3	596.7	482.4	-57.2	-57.2	114.3
		${}^{27}\text{Al}$ CCSD(T)	509.1	509.1	677.8	565.3	-56.2	-56.2	112.4
		exp <sup>64</sup>	713	713	872	766	-53	-53	106
		${}^{17}\text{O}$ RI-MP2	0.7	188.7	188.7	126.0	-125.3	62.7	62.7
		${}^{17}\text{O}$ SCS-RI-MP2	-42.5	182.7	182.7	107.6	-150.1	75.1	75.1
		${}^{17}\text{O}$ OO-RI-MP2	-89.3	41.8	41.8	-1.9	-87.4	43.7	43.7
${}^2\text{HCO}$	0.765630	${}^{17}\text{O}$ OO-SCS-RI-MP2	-86.5	53.0	53.0	6.5	-93.0	46.5	46.5
		${}^{17}\text{O}$ B2PLYP	-70.0	62.9	62.9	18.6	-88.6	44.3	44.3
		${}^{17}\text{O}$ CCSD	-109.5	82.0	82.0	18.1	-127.7	63.8	63.8
		${}^{17}\text{O}$ CCSD(T)	-98.5	78.2	78.2	19.3	-117.8	58.9	58.9
		${}^1\text{H}$ RI-MP2	366.1	376.5	401.6	381.4	-15.3	-4.9	20.2
		${}^1\text{H}$ SCS-RI-MP2	363.6	373.7	400.1	379.1	-15.5	-5.5	21.0
	0.752927	${}^1\text{H}$ OO-RI-MP2	352.9	361.0	390.9	368.2	-15.4	-7.3	22.6
		${}^1\text{H}$ OO-SCS-RI-MP2	350.1	358.0	389.0	365.7	-15.6	-7.7	23.3
		${}^1\text{H}$ B2PLYP	366.1	374.2	404.6	381.7	-15.5	-7.4	23.0
		${}^1\text{H}$ CCSD	372.6	391.8	400.8	388.4	-15.8	3.4	12.4
		${}^1\text{H}$ CCSD(T)	374.6	393.8	402.4	390.3	-15.7	3.5	12.1
		exp <sup>65</sup>	~377	~377	~343	354-381	-9	-9	25
	0.753275	${}^{17}\text{O}$ RI-MP2	-152.4	-24.6	5.3	-57.3	-95.2	32.6	62.5
		${}^{17}\text{O}$ SCS-RI-MP2	-153.6	-21.7	3.2	-57.4	-96.3	35.6	60.6
		${}^{17}\text{O}$ OO-RI-MP2	-136.6	7.5	17.0	-37.4	-99.2	44.9	54.3
		${}^{17}\text{O}$ OO-SCS-RI-MP2	-140.3	4.8	15.7	-40.0	-100.4	44.7	55.6
		${}^{17}\text{O}$ B2PLYP	-147.8	9.7	17.4	-40.2	-107.6	50.0	57.6
		${}^{17}\text{O}$ CCSD	-144.6	-1.8	16.1	-43.4	-101.2	41.6	59.5
${}^2\text{H}_2\text{CO}$	0.785332	${}^{17}\text{O}$ CCSD(T)	-141.7	-0.6	13.5	-42.9	-98.7	42.3	56.4
		${}^{13}\text{C}$ RI-MP2	289.4	301.2	429.8	340.1	-50.7	-38.9	89.7
		${}^{13}\text{C}$ SCS-RI-MP2	300.3	308.0	439.1	349.1	-48.9	-41.1	90.0
		${}^{13}\text{C}$ OO-RI-MP2	325.9	332.9	456.4	371.7	-45.9	-38.8	84.7
		${}^{13}\text{C}$ OO-SCS-RI-MP2	332.3	342.2	465.3	379.9	-47.6	-37.7	85.4
		${}^{13}\text{C}$ B2PLYP	338.5	345.2	476.0	386.6	-48.0	-41.4	89.4
	0.755748	${}^{13}\text{C}$ CCSD	284.5	291.2	342.7	306.1	-21.6	-15.0	36.6
		${}^{13}\text{C}$ CCSD(T)	278.3	286.0	336.2	300.2	-21.9	-14.2	36.0
		exp <sup>66</sup>	~337	~353	~437	365-377	-39	-48	50-72
		${}^{17}\text{O}$ RI-MP2	-316.8	89.1	98.9	-42.9	-273.9	132.1	141.8
		${}^{17}\text{O}$ SCS-RI-MP2	-320.4	101.8	108.0	-36.9	-283.5	138.7	144.8
		${}^{17}\text{O}$ OO-RI-MP2	-285.3	56.4	75.4	-51.2	-234.1	107.5	126.6
	0.754596	${}^{17}\text{O}$ OO-SCS-RI-MP2	-305.0	62.6	76.0	-55.5	-249.6	118.1	131.5
		${}^{17}\text{O}$ B2PLYP	-316.4	61.0	84.3	-57.0	-259.4	118.1	141.3
		${}^{17}\text{O}$ CCSD	-318.1	50.0	79.3	-62.9	-255.1	112.9	142.2
		${}^{17}\text{O}$ CCSD(T)	-310.3	56.1	78.6	-58.5	-251.8	114.6	137.2
		${}^1\text{H}$ RI-MP2	272.5	274.9	297.9	281.8	-9.3	-6.9	16.2
		${}^1\text{H}$ SCS-RI-MP2	243.3	245.3	269.9	252.8	-9.5	-7.6	17.1
		${}^1\text{H}$ OO-RI-MP2	355.2	357.3	387.6	366.7	-11.5	-9.4	20.9
		${}^1\text{H}$ OO-SCS-RI-MP2	315.1	317.2	345.6	326.0	-10.8	-8.8	19.6
		${}^1\text{H}$ B2PLYP	313.7	316.3	341.4	323.8	-10.1	-7.5	17.6
		${}^1\text{H}$ CCSD	276.7	292.0	313.7	294.1	-17.4	-2.1	19.5
		${}^1\text{H}$ CCSD(T)	286.5	303.6	326.3	305.5	-19.0	-1.8	20.9

TABLE 3: Continued

	$\langle S^2 \rangle$			$A_{11}^{(A)}$	$A_{22}^{(A)}$	$A_{33}^{(A)}$	$A^{(A:c)}$	$A_{11}^{(A:d)}$	$A_{22}^{(A:d)}$	$A_{33}^{(A:d)}$
$^2\text{H}_2\text{O}^+$	0.761586	$^1\text{H}$	expt <sup>66</sup>	363	376	377	372	-9	4	5
		$^1\text{H}$	RI-MP2	-118.3	-88.4	6.3	-66.8	-51.5	-21.6	73.1
	0.754418	$^1\text{H}$	SCS-RI-MP2	-109.2	-79.5	14.2	-58.2	-51.0	-21.3	72.4
		$^1\text{H}$	OO-RI-MP2	-137.5	-107.6	-9.3	-84.8	-52.7	-22.8	75.5
	0.754004	$^1\text{H}$	OO-SCS-RI-MP2	-132.5	-102.9	-4.7	-80.0	-52.5	-22.9	75.4
		$^1\text{H}$	B2PLYP	-131.7	-102.4	-4.8	-79.6	-52.0	-22.8	74.8
		$^1\text{H}$	CCSD	-174.4	-78.5	5.2	-82.6	-91.8	4.0	87.8
		$^1\text{H}$	CCSD(T)	-170.4	-75.0	8.2	-79.1	-91.3	4.0	87.3
			expt <sup>61</sup>				-73			
		$^{17}\text{O}$	RI-MP2	-366.5	84.4	88.0	-64.7	-301.8	149.1	152.7
		$^{17}\text{O}$	SCS-RI-MP2	-363.8	91.1	93.4	-59.8	-304.0	150.9	153.2
		$^{17}\text{O}$	OO-RI-MP2	-375.7	70.0	75.1	-76.9	-298.8	146.9	152.0
		$^{17}\text{O}$	OO-SCS-RI-MP2	-374.2	74.2	78.3	-73.9	-300.3	148.1	152.2
		$^{17}\text{O}$	B2PLYP	-383.1	72.6	77.5	-77.7	-305.5	150.2	155.2
		$^{17}\text{O}$	CCSD	-375.1	68.8	73.9	-77.5	-297.6	146.2	151.4
		$^{17}\text{O}$	CCSD(T)	-372.6	71.0	75.9	-75.2	-297.4	146.2	151.1
$^2\text{CH}_3$	0.761614	$^{13}\text{C}$	expt <sup>61</sup>				-83			
		$^{13}\text{C}$	RI-MP2	-18.2	-18.2	211.5	58.4	-76.6	-76.6	153.1
	0.754306	$^{13}\text{C}$	SCS-RI-MP2	-33.7	-33.7	197.6	43.4	-77.1	-77.1	154.2
		$^{13}\text{C}$	OO-RI-MP2	-4.8	-4.8	224.4	71.6	-76.4	-76.4	152.8
	0.753550	$^{13}\text{C}$	OO-SCS-RI-MP2	-15.1	-15.1	215.1	61.6	-76.8	-76.8	153.5
		$^{13}\text{C}$	B2PLYP	5.2	5.3	241.4	84.0	-78.8	-78.7	157.5
		$^{13}\text{C}$	CCSD	-3.5	-3.5	225.6	72.8	-76.4	-76.4	152.8
		$^{13}\text{C}$	CCSD(T)	-7.2	-7.2	221.6	69.1	-76.2	-76.2	152.5
			expt <sup>67,68</sup>	13	13	198	75	~-62	~-62	~-123
		$^1\text{H}$	RI-MP2	-111.2	-68.8	-33.9	-71.3	-39.9	2.5	37.4
		$^1\text{H}$	SCS-RI-MP2	-95.5	-53.1	-20.4	-56.3	-39.2	3.3	35.9
		$^1\text{H}$	OO-RI-MP2	-118.1	-75.9	-39.0	-77.7	-40.4	1.8	38.7
		$^1\text{H}$	OO-SCS-RI-MP2	-105.6	-63.5	-28.0	-65.7	-39.9	2.3	37.7
		$^1\text{H}$	B2PLYP	-109.5	-67.9	-31.0	-69.5	-40.0	1.6	38.4
		$^1\text{H}$	CCSD <sup>a</sup>	-124.4	-66.8	-29.5	-73.6	-50.8	6.8	44.0
		$^1\text{H}$	CCSD(T) <sup>a</sup>	-121.4	-64.1	-27.2	-70.9	-50.5	6.8	43.8
			expt <sup>67,68</sup>	-105	-69	-35	-70	-35	1	35
$^2\text{SiH}_3$	0.769857	$^{29}\text{Si}$	RI-MP2	-390.6	-111.9	-111.9	-204.8	-185.8	92.9	92.9
		$^{29}\text{Si}$	SCS-RI-MP2	-351.0	-70.7	-70.7	-164.1	-186.9	93.5	93.5
	0.764049	$^{29}\text{Si}$	OO-RI-MP2	-402.6	-125.0	-125.0	-217.5	-185.0	92.5	92.5
		$^{29}\text{Si}$	OO-SCS-RI-MP2	-373.3	-94.8	-94.8	-187.6	-185.7	92.8	92.8
	0.761726	$^{29}\text{Si}$	B2PLYP	-386.7	-96.0	-96.0	-192.9	-193.8	96.9	96.9
		$^{29}\text{Si}$	CCSD	-401.5	-124.0	-124.0	-216.5	-185.0	92.5	92.5
		$^{29}\text{Si}$	CCSD(T)	-393.1	-116.3	-116.3	-208.6	-184.5	92.3	92.3
		$^1\text{H}$	RI-MP2	-86.7	-67.8	-64.2	-72.9	-13.8	5.1	8.7
		$^1\text{H}$	SCS-RI-MP2	-68.2	-49.3	-46.2	-54.6	-13.6	5.3	8.4
		$^1\text{H}$	OO-RI-MP2	-93.0	-74.0	-70.0	-79.0	-14.0	5.0	9.0
		$^1\text{H}$	OO-SCS-RI-MP2	-78.8	-59.9	-56.1	-65.0	-13.8	5.0	8.8
		$^1\text{H}$	B2PLYP	-77.8	-59.2	-54.9	-64.0	-13.8	4.8	9.0
		$^1\text{H}$	CCSD <sup>a</sup>	-86.8	-66.4	-59.0	-70.7	-16.1	4.3	11.8
		$^1\text{H}$	CCSD(T) <sup>a</sup>	-83.3	-63.0	-55.6	-67.3	-16.0	4.3	11.7
$^2\text{C}_3\text{H}_5^b$	0.833312	$^{13}\text{C}$	RI-MP2	-47.4	-24.7	-14.4	-28.9	-18.6	4.1	14.4
		$^{13}\text{C}$	SCS-RI-MP2	-42.2	-18.2	-8.5	-23.0	-19.2	4.8	14.5
	0.760583	$^{13}\text{C}$	OO-RI-MP2	-64.0	-42.8	-31.3	-46.0	-18.0	3.2	14.7
		$^{13}\text{C}$	OO-SCS-RI-MP2	-60.8	-38.4	-27.1	-42.1	-18.7	3.7	15.0
	0.760700	$^{13}\text{C}$	B2PLYP	-61.8	-36.9	-25.2	-41.3	-20.5	4.4	16.1
			expt <sup>69</sup>				-48			
		$^{13}\text{C}$	RI-MP2	-32.4	-30.9	107.8	14.8	-47.3	-45.8	93.0
		$^{13}\text{C}$	SCS-RI-MP2	-40.7	-39.4	100.8	6.9	-47.6	-46.3	93.9
		$^{13}\text{C}$	OO-RI-MP2	-13.9	-12.3	125.1	32.9	-46.9	-45.3	92.1
		$^{13}\text{C}$	OO-SCS-RI-MP2	-18.3	-16.9	121.6	28.8	-47.1	-45.7	92.9
		$^{13}\text{C}$	B2PLYP	-8.8	-7.2	136.4	40.1	-48.9	-47.3	96.2
			expt <sup>69</sup>				61			
		$^1\text{H}$	RI-MP2	-14.5	-4.0	-3.4	-7.3	-7.2	3.3	3.9
		$^1\text{H}$	SCS-RI-MP2	-20.6	-10.1	-8.7	-13.1	-7.5	3.0	4.5
		$^1\text{H}$	OO-RI-MP2	1.0	9.5	11.6	7.4	-6.4	2.2	4.2
		$^1\text{H}$	OO-SCS-RI-MP2	-1.1	7.8	9.7	5.5	-6.5	2.3	4.2
		$^1\text{H}$	B2PLYP	3.0	11.6	14.2	9.6	-6.6	2.0	4.6
			expt <sup>69</sup>				12			
		$^1\text{H}$	RI-MP2	-60.2	-34.7	-14.3	-36.4	-23.8	1.7	22.1
		$^1\text{H}$	SCS-RI-MP2	-49.9	-24.5	-5.4	-26.6	-23.3	2.1	21.2
$^2\text{O}_2\text{H}$	0.762838	$^{17}\text{O}$	OO-RI-MP2	-71.2	-45.8	-23.1	-46.7	-24.5	0.9	23.6
		$^{17}\text{O}$	OO-SCS-RI-MP2	-64.6	-39.2	-17.1	-40.3	-24.3	1.1	23.2
	0.752418	$^{17}\text{O}$	B2PLYP	-68.7	-43.3	-20.3	-44.1	-24.6	0.8	23.8
			expt <sup>69</sup>				-41			
	0.752900	$^{17}\text{O}$	RI-MP2	-51.5	-31.6	-10.6	-31.2	-20.2	-0.4	20.7
		$^{17}\text{O}$	SCS-RI-MP2	-41.1	-21.3	-1.6	-21.3	-19.8	-0.0	19.8
		$^{17}\text{O}$	OO-RI-MP2	-62.2	-42.3	-19.1	-41.2	-21.0	-1.1	22.1
		$^{17}\text{O}$	OO-SCS-RI-MP2	-55.5	-35.7	-13.1	-34.8	-20.7	-0.9	21.7
		$^{17}\text{O}$	B2PLYP	-60.0	-40.2	-16.7	-39.0	-21.0	-1.2	22.3
			expt <sup>69</sup>				-39			
		$^{17}\text{O}$	RI-MP2	-315.7	60.1	76.0	-59.9	-255.9	120.0	135.9
		$^{17}\text{O}$	SCS-RI-MP2	-325.7	57.1	74.3	-64.8	-261.0	121.9	139.1
		$^{17}\text{O}$	OO-RI-MP2	-276.2	58.0	60.8	-52.5	-223.7	110.5	113.3
		$^{17}\text{O}$	OO-SCS-RI-MP2	-296.8	51.0	52.6	-64.4	-232.4	115.4	117.0
		$^{17}\text{O}$	B2PLYP	-301.5	59.3	63.0	-59.7	-241.7	119.0	122.7
		$^{17}\text{O}$	CCSD	-310.1	58.5	59.0	-64.2	-245.9	122.7	123.2
		$^{17}\text{O}$	CCSD(T)	-299.7	58.9	60.4	-60.1	-239.5	119.0	120.5
		$^{17}\text{O}$	RI-MP2	-146.8	-0.2	7.3	-46.6	-100.2	46.3	53.9



TABLE 3: Continued

	$\langle S^2 \rangle$		$A_{11}^{(A)}$	$A_{22}^{(A)}$	$A_{33}^{(A)}$	$A^{(A:c)}$	$A_{11}^{(A:d)}$	$A_{22}^{(A:d)}$	$A_{33}^{(A:d)}$
${}^2\text{CO}_2^-$	0.763529	${}^{17}\text{O}$ SCS-RI-MP2	-141.3	-7.9	3.2	-48.7	-92.7	40.8	51.8
		${}^{17}\text{O}$ OO-RI-MP2	-139.7	22.0	27.9	-29.9	-109.7	52.0	57.8
		${}^{17}\text{O}$ OO-SCS-RI-MP2	-145.4	7.0	13.0	-41.8	-103.6	48.8	54.8
		${}^{17}\text{O}$ B2PLYP	-147.7	15.7	20.7	-37.1	-110.6	52.8	57.8
		${}^{17}\text{O}$ CCSD	-133.4	9.2	15.3	-36.3	-97.1	45.5	51.6
		${}^{17}\text{O}$ CCSD(T)	-136.6	12.6	16.9	-35.7	-100.9	48.3	52.6
		${}^1\text{H}$ RI-MP2	-56.8	-49.8	1.9	-34.9	-21.9	-14.9	36.8
		${}^1\text{H}$ SCS-RI-MP2	-53.1	-47.3	2.4	-32.6	-20.4	-14.6	35.0
		${}^1\text{H}$ OO-RI-MP2	-53.5	-41.7	5.2	-30.0	-23.5	-11.7	35.2
		${}^1\text{H}$ OO-SCS-RI-MP2	-50.0	-39.6	5.2	-28.1	-21.8	-11.5	33.3
	0.753048 0.753120	${}^1\text{H}$ B2PLYP	-51.3	-42.0	6.6	-28.9	-22.4	-13.1	35.5
		${}^1\text{H}$ CCSD	-39.8	-34.4	-8.8	-27.7	-12.2	-6.8	18.9
		${}^1\text{H}$ CCSD(T)	-40.5	-36.3	-7.8	-28.2	-12.3	-8.1	20.4
		expt <sup>50</sup>					-11	-8	20
		${}^{17}\text{O}$ RI-MP2	-148.3	-65.0	-55.6	-89.6	-58.6	24.7	34.0
		${}^{17}\text{O}$ SCS-RI-MP2	-147.1	-61.4	-53.2	-87.3	-59.9	25.9	34.0
		${}^{17}\text{O}$ OO-RI-MP2	-158.2	-81.7	-74.4	-104.7	-53.4	23.0	30.4
		${}^{17}\text{O}$ OO-SCS-RI-MP2	-155.0	-74.4	-67.3	-98.9	-56.1	24.5	31.6
		${}^{17}\text{O}$ B2PLYP	-157.3	-67.2	-60.6	-95.0	-62.3	27.9	34.4
		${}^{17}\text{O}$ CCSD	-156.3	-64.3	-52.1	-90.9	-65.4	26.6	38.8
		${}^{17}\text{O}$ CCSD(T)	-157.9	-68.8	-57.0	-94.6	-63.4	25.8	37.6
${}^2\text{NH}_2$	0.759428	${}^{13}\text{C}$ RI-MP2	303.2	311.3	407.5	340.6	-37.5	-29.4	66.8
		${}^{13}\text{C}$ SCS-RI-MP2	298.2	306.6	407.2	337.3	-39.1	-30.7	69.8
		${}^{13}\text{C}$ OO-RI-MP2	274.7	278.7	360.9	304.8	-30.1	-26.1	56.1
		${}^{13}\text{C}$ OO-SCS-RI-MP2	278.2	284.0	372.3	311.5	-33.3	-27.5	60.8
		${}^{13}\text{C}$ B2PLYP	297.2	303.3	403.4	334.6	-37.5	-31.3	68.8
		${}^{13}\text{C}$ CCSD	290.1	298.5	406.4	331.7	-41.6	-33.1	74.8
		${}^{13}\text{C}$ CCSD(T)	275.4	282.5	380.6	312.9	-37.4	-30.4	67.8
		${}^{14}\text{N}$ RI-MP2	-18.8	-18.3	109.2	24.0	-42.8	-42.3	85.1
		${}^{14}\text{N}$ SCS-RI-MP2	-21.3	-21.0	107.6	21.8	-43.0	-42.8	85.8
		${}^{14}\text{N}$ OO-RI-MP2	-15.2	-14.5	112.5	27.6	-42.8	-42.1	84.9
	0.753988 0.753602	${}^{14}\text{N}$ OO-SCS-RI-MP2	-16.8	-16.3	111.5	26.1	-42.9	-42.5	85.4
		${}^{14}\text{N}$ B2PLYP	-12.7	-11.8	118.6	31.4	-44.0	-43.2	87.2
		${}^{14}\text{N}$ CCSD	-15.8	-15.0	111.6	26.9	-42.7	-42.0	84.7
		${}^{14}\text{N}$ CCSD(T)	-16.7	-16.0	110.4	25.9	-42.6	-41.9	84.5
		expt <sup>70,69</sup>	-17	-15	116	28	-45	-43	88
		${}^1\text{H}$ RI-MP2	-120.3	-70.3	-3.4	-64.7	-55.7	-5.6	61.3
		${}^1\text{H}$ SCS-RI-MP2	-107.0	-57.1	7.6	-52.2	-54.8	-5.0	59.8
		${}^1\text{H}$ OO-RI-MP2	-128.5	-78.7	-9.1	-72.1	-56.4	-6.6	63.0
		${}^1\text{H}$ OO-SCS-RI-MP2	-118.6	-69.1	-0.6	-62.8	-55.9	-6.3	62.1
		${}^1\text{H}$ B2PLYP	-120.3	-71.3	-2.3	-64.6	-55.7	-6.7	62.3
		${}^1\text{H}$ CCSD	-155.3	-63.4	9.8	-69.6	-85.6	6.2	79.4
${}^2\text{NO}_2$	0.770946	${}^1\text{H}$ CCSD(T)	-152.7	-61.3	11.5	-67.5	-85.2	6.2	79.0
		expt <sup>70,69</sup>	-123	-72	-1	-67	-56	-5	66
		${}^{14}\text{N}$ RI-MP2	129.5	131.9	182.0	147.8	-18.3	-15.8	34.2
		${}^{14}\text{N}$ SCS-RI-MP2	132.4	139.2	189.1	153.6	-21.2	-14.4	35.5
		${}^{14}\text{N}$ OO-RI-MP2	130.6	131.3	177.8	146.6	-16.0	-15.3	31.2
		${}^{14}\text{N}$ OO-SCS-RI-MP2	134.4	139.4	186.9	153.5	-19.2	-14.2	33.3
		${}^{14}\text{N}$ B2PLYP	127.9	130.7	187.2	148.6	-20.7	-17.9	38.6
		${}^{14}\text{N}$ CCSD	121.6	126.2	187.3	145.0	-23.5	-18.8	42.3
		${}^{14}\text{N}$ CCSD(T)	122.9	126.7	183.3	144.3	-21.4	-17.6	39.0
		expt <sup>65</sup>	131	138	190	153	-22	-15	37
	0.751284 0.752347	${}^{17}\text{O}$ RI-MP2	-166.0	-17.3	-10.9	-64.7	-101.3	47.4	53.8
		${}^{17}\text{O}$ SCS-RI-MP2	-164.5	-14.5	-4.6	-61.2	-103.3	46.7	56.6
		${}^{17}\text{O}$ OO-RI-MP2	-177.6	-33.6	-27.7	-79.7	-98.0	46.0	52.0
		${}^{17}\text{O}$ OO-SCS-RI-MP2	-176.0	-28.7	-21.8	-75.5	-100.5	46.8	53.7
		${}^{17}\text{O}$ B2PLYP	-171.5	-11.1	-7.4	-63.3	-108.1	52.2	56.0
		${}^{17}\text{O}$ CCSD	-169.1	-6.4	1.5	-58.0	-111.1	51.6	59.5
		${}^{17}\text{O}$ CCSD(T)	-171.6	-13.6	-5.1	-63.4	-108.2	49.9	58.3
		expt <sup>65</sup>	~160	~-7	~5	-47-61	-106	47	59
		${}^{14}\text{N}$ RI-MP2	-7.2	-3.8	144.8	44.6	-51.8	-48.4	100.2
		${}^{14}\text{N}$ SCS-RI-MP2	-7.2	-3.5	147.1	45.5	-52.7	-49.0	101.6
		${}^{14}\text{N}$ OO-RI-MP2	-3.8	-1.3	136.6	43.8	-47.7	-45.1	92.8
${}^2\text{NF}_2$	0.764471	${}^{14}\text{N}$ OO-SCS-RI-MP2	-1.0	1.9	143.1	48.0	-49.0	-46.1	95.1
		${}^{14}\text{N}$ B2PLYP	-1.4	1.7	147.5	49.3	-50.7	-47.5	98.2
		${}^{14}\text{N}$ CCSD	-1.0	1.8	147.1	49.3	-50.3	-47.5	97.8
		${}^{14}\text{N}$ CCSD(T)	-4.3	-1.7	140.5	44.8	-49.1	-46.6	95.7
		${}^{19}\text{F}$ RI-MP2	-61.5	-4.0	616.1	183.5	-245.1	-187.5	432.6
		${}^{19}\text{F}$ SCS-RI-MP2	-58.7	40.1	595.7	192.4	-251.1	-152.3	403.4
		${}^{19}\text{F}$ OO-RI-MP2	-128.1	-90.5	626.1	135.8	-263.9	-226.3	490.2
		${}^{19}\text{F}$ OO-SCS-RI-MP2	-71.6	-50.1	631.5	169.9	-241.5	-220.1	461.6
		${}^{19}\text{F}$ B2PLYP	-90.6	-65.2	653.6	165.9	-256.5	-231.2	487.7
		${}^{19}\text{F}$ CCSD	-91.9	-22.1	612.2	166.1	-258.0	-188.2	446.2
	0.784752	${}^{19}\text{F}$ CCSD(T)	-97.8	-48.1	617.7	157.3	-255.1	-205.4	460.4
		${}^{14}\text{N}$ RI-MP2	-34.3	-34.3	121.3	17.5	-51.9	-51.9	103.7
		${}^{14}\text{N}$ SCS-RI-MP2	-40.2	-40.2	117.7	12.4	-52.6	-52.6	105.3
		${}^{14}\text{N}$ OO-RI-MP2	33.1	33.1	170.6	78.9	-45.8	-45.8	91.7
		${}^{14}\text{N}$ OO-SCS-RI-MP2	40.5	40.5	182.2	87.8	-47.2	-47.2	94.4
		${}^{14}\text{N}$ B2PLYP	31.5	31.5	176.6	79.8	-48.4	-48.4	96.7
		${}^{14}\text{N}$ CCSD	53.6	53.6	201.5	102.9	-49.3	-49.3	98.6
		${}^{14}\text{N}$ CCSD(T)	42.7	42.7	186.5	90.6	-47.9	-47.9	95.9
		expt <sup>50</sup>				276			
		${}^{19}\text{F}$ RI-MP2	-134.6	-75.3	659.4	149.8	-284.4	-225.2	509.5
		${}^{19}\text{F}$ SCS-RI-MP2	-145.3	-53.0	629.4	143.7	-289.0	-196.7	485.7
		${}^{19}\text{F}$ OO-RI-MP2	-77.8	25.5	814.9	254.2	-332.0	-228.7	560.7

TABLE 3: Continued

$\langle S^2 \rangle$			$A_{11}^{(A)}$	$A_{22}^{(A)}$	$A_{33}^{(A)}$	$A^{(A;c)}$	$A_{11}^{(A;d)}$	$A_{22}^{(A;d)}$	$A_{33}^{(A;d)}$
$^2\text{O}_3^-$	0.788861	$^{19}\text{F}$ OO-SCS-RI-MP2	-24.8	59.4	831.0	288.6	-313.3	-229.1	542.5
		$^{19}\text{F}$ B2PLYP	-82.0	20.7	836.4	258.4	-340.4	-237.7	578.0
		$^{19}\text{F}$ CCSD <sup>a</sup>	-24.3	129.2	853.7	319.6	-343.8	-190.4	534.2
		$^{19}\text{F}$ CCSD(T) <sup>a</sup>	-41.4	76.2	825.9	286.9	-328.3	-210.6	539.0
	0.751039	$^{17}\text{O}$ RI-MP2	-39.9	174.2	180.8	105.0	-144.9	69.1	75.8
		$^{17}\text{O}$ SCS-RI-MP2	-87.5	160.3	163.1	78.6	-166.1	81.7	84.5
		$^{17}\text{O}$ OO-RI-MP2	-184.7	10.8	14.9	-53.0	-131.7	63.8	67.9
		$^{17}\text{O}$ OO-SCS-RI-MP2	-238.9	-29.4	-21.3	-96.6	-142.4	67.1	75.3
	0.753723	$^{17}\text{O}$ B2PLYP	-205.0	20.5	24.1	-53.4	-151.5	74.0	77.6
		$^{17}\text{O}$ CCSD	-251.8	1.1	5.3	-81.8	-170.0	82.9	87.0
		$^{17}\text{O}$ CCSD(T)	-229.4	7.0	10.9	-70.5	-158.9	77.5	81.4
		$^{17}\text{O}$ RI-MP2	-109.9	60.1	115.5	21.9	-131.8	38.2	93.6
		$^{17}\text{O}$ SCS-RI-MP2	-100.4	48.0	114.1	20.6	-121.0	27.4	93.5
		$^{17}\text{O}$ OO-RI-MP2	-105.9	30.0	33.7	-14.1	-91.8	44.1	47.8
		$^{17}\text{O}$ OO-SCS-RI-MP2	-128.7	4.2	19.3	-35.0	-93.7	39.3	54.4
		$^{17}\text{O}$ B2PLYP	-131.5	27.3	29.6	-24.9	-106.7	52.2	54.5
		$^{17}\text{O}$ CCSD	-136.3	12.6	17.8	-35.3	-101.0	48.0	53.1
		$^{17}\text{O}$ CCSD(T)	-129.7	19.6	21.5	-29.5	-100.2	49.1	51.0
	0.788737	$^{17}\text{O}$ RI-MP2	-111.4	44.9	49.3	-5.7	-105.7	50.6	55.1
		$^{17}\text{O}$ SCS-RI-MP2	-121.0	36.4	44.1	-13.5	-107.5	49.9	57.6
		$^{17}\text{O}$ OO-RI-MP2	-120.4	35.6	37.4	-15.8	-104.6	51.4	53.2
		$^{17}\text{O}$ OO-SCS-RI-MP2	-141.7	13.3	26.7	-33.9	-107.8	47.2	60.6
	0.751049	$^{17}\text{O}$ B2PLYP	-143.8	33.0	33.3	-25.8	-118.0	58.8	59.1
		$^{25}\text{Cl}$ RI-MP2	-45.6	-44.0	169.0	26.5	-72.1	-70.4	142.5
		$^{25}\text{Cl}$ SCS-RI-MP2	-10.2	-6.6	213.3	65.5	-75.7	-72.1	147.8
		$^{25}\text{Cl}$ OO-RI-MP2	-38.7	-36.0	155.0	26.8	-65.4	-62.8	128.2
	0.757835	$^{25}\text{Cl}$ OO-SCS-RI-MP2	2.6	7.7	205.7	72.0	-69.4	-64.3	133.7
		$^{35}\text{Cl}$ B2PLYP	-43.8	-39.6	176.1	30.9	-74.7	-70.5	145.2
		$^{35}\text{Cl}$ expt <sup>50</sup>					-83	-77	46

<sup>a</sup> Dipolar contributions are averaged over the three corresponding atoms. <sup>b</sup> CCSD and CCSD(T) calculations were not feasible.

to be systematic. In fact, the orbital optimized MP2 (OO-MP2) methods do not generally tend to either underestimate or overestimate the hfccs either in magnitude or in absolute value. This behavior is well reflected in the mean error statistics presented in Table 5. The mean error of the OO-MP2 methods is close to zero and is very similar to the mean error of the CCSD method.

Regarding the mean absolute errors, CCSD is the closest to the CCSD(T) reference data. Anyway, not by a large margin. However, the OO-MP2 methods are only worse by about  $\sim 10$ – $15$  MHz in the total and isotropic hfccs. The deviations in the dipolar hfccs are small for both the CCSD and OO-MP2 methods. Interestingly, it can be seen from Table 5 that the spin component scaled variant of the OO-RI-MP2 method (OO-SCS-RI-MP2) improves upon the results of the initial OO-RI-MP2 method. However, comparison of individual entries shows that this improvement is not systematic.

In Table 7 the individual deviations with respect to the CCSD(T) results are scaled with the corresponding  $P_A$  factor for each element A. Due to the possibly large magnitude of the  $P_A$  factor (e.g., for the hydrogen atom  $P_H = 533.5514$  MHz/au<sup>3</sup>, cf. Table 1), the scaling by  $P_A$  offers an element independent insight into the error statistics.

Table 7 shows a slight tendency for overestimation of the total and isotropic hfccs by the OO-MP2 methods, which is indicated by the overall positive mean error. The mean absolute error confirms the slightly superior performance of CCSD, when compared to the CCSD(T) reference. Importantly, the OO-MP2 methods reduce the errors of the MP2 method itself by a factor of 2–3 and hence they represent a definite improvement.

To gain more insight into the individual description of different nuclei, the scaled error statistics are broken down into the contributions of H, C, N, O, and F atoms and compared to CCSD(T) results. From the results in Table 9 it is seen that the  $^1\text{H}$  hfccs are well described by all employed MP2 methods. However, for  $^{13}\text{C}$ ,  $^{14}\text{N}$ ,  $^{17}\text{O}$ , and  $^{19}\text{F}$  hfccs the orbital optimization leads to large improvements in the results. This is

most clearly seen in the  $^{14}\text{N}$  hfccs. In the case of the  $^{13}\text{C}$  and  $^{19}\text{F}$  hfccs, the OO-SCS-RI-MP2 method even performs almost as well as CCSD.

In Table 6 we compare the results of our calculations to experiment. The scaled error statistics in Table 8 display the same overall trends. Obviously, the performance of the OO-MP2 methods is extremely good—in fact, as good as what is obtained for CCSD and even CCSD(T). This excellent behavior should certainly be taken with a grain of salt as one is not close to the basis set limit and vibrational effects have not been included in the calculations.

The OO-MP2 results are now compared to previously published hfccs, calculated with the double-hybrid functional B2PLYP.<sup>56</sup> The B2PLYP functional combines the advantages of hybrid density functional theory with a scaled MP2 correction to account for semilocal dynamic correlation effects, and has shown to provide excellent results for the prediction of hyperfine structure.<sup>16</sup> All DFT functionals failed to predict the hfccs of the molecules CN, AlO, and  $\text{NF}_3^+$  properly, and therefore, these molecules were excluded from the error statistics in ref 16. However, in this paper we decided to include all molecules in our error analysis, shown in Table 5. The B2PLYP mean absolute error compared to the CCSD(T) reference in the total hfccs is  $\sim 27$  MHz, which is similar to the deviations of the OO-MP2 methods from CCSD(T). The same is valid for the isotropic (24 MHz) and anisotropic ( $\sim 7$  MHz) contributions to the hfccs. Thus, the OO-MP2 methods are at least not inferior to B2PLYP and it might be speculated that they could be more reliable in situations where the self-interaction error of DFT becomes important. In comparison to the experimental results, the OO-MP2 methods even outperform the B2PLYP functional concerning the isotropic hfcc, with a mean absolute error of 58 MHz, whereas the errors in the total and anisotropic hfccs remain unchanged.

The expectation value of the total spin operator is listed in the second column of Tables 3 and 4. The spin contamination, i.e., the deviation of  $\langle S^2 \rangle$  from the ideal value, is in

TABLE 4: Hyperfine Coupling Constants (MHz) for a Variety of Small  $S > 1/2$  Systems

	$\langle S^2 \rangle$			$A_{11}^{(A)}$	$A_{22}^{(A)}$	$A_{33}^{(A)}$	$A^{(A;c)}$	$A_{11}^{(A;d)}$	$A_{22}^{(A;d)}$	$A_{33}^{(A;d)}$
$^3\text{NH}$	2.016491	$^{14}\text{N}$	RI-MP2	-28.0	37.8	37.8	15.9	-43.8	21.9	21.9
		$^{14}\text{N}$	SCS-RI-MP2	-29.6	37.1	37.1	14.9	-44.5	22.2	22.2
		$^{14}\text{N}$	OO-RI-MP2	-25.6	40.0	40.0	18.1	-43.7	21.9	21.9
	2.007690	$^{14}\text{N}$	OO-SCS-RI-MP2	-26.5	39.7	39.7	17.7	-44.2	22.1	22.1
	2.006912	$^{14}\text{N}$	B2PLYP	-23.4	44.3	44.3	21.7	-45.1	22.6	22.6
		$^{13}\text{N}$	CCSD	-26.6	38.9	38.9	17.1	-43.6	21.8	21.8
		$^{14}\text{N}$	CCSD(T)	-27.0	38.4	38.4	16.6	-43.6	21.8	21.8
			expt <sup>50</sup>	-26	43	43	20	-46	23	23
		$^1\text{H}$	RI-MP2	-98.8	-98.8	-5.5	-67.7	-31.1	-31.1	62.2
		$^1\text{H}$	SCS-RI-MP2	-87.0	-87.0	4.7	-56.4	-30.6	-30.6	61.2
		$^1\text{H}$	OO-RI-MP2	-103.1	-103.1	-8.6	-71.6	-31.5	-31.5	63.0
		$^1\text{H}$	OO-SCS-RI-MP2	-94.2	-94.2	-0.5	-62.9	-31.2	-31.2	62.4
		$^1\text{H}$	B2PLYP	-91.8	-91.8	1.1	-60.8	-31.0	-31.0	62.0
		$^1\text{H}$	CCSD	-98.9	-98.9	-4.9	-67.6	-31.4	-31.4	62.7
		$^1\text{H}$	CCSD(T)	-97.3	-97.3	-3.6	-66.1	-31.2	-31.2	62.4
			expt <sup>50</sup>	-100	-100	-10	-70	-30	-30	60
	2.014161	$^{17}\text{O}$	RI-MP2	-120.5	-120.5	115.0	-42.0	-78.5	-78.5	157.0
		$^{17}\text{O}$	SCS-RI-MP2	-120.5	-120.5	116.9	-41.4	-79.1	-79.1	158.3
		$^{17}\text{O}$	OO-RI-MP2	-123.9	-123.9	110.5	-45.8	-78.1	-78.1	156.2
$^3\text{OH}^+$	2.006706	$^{17}\text{O}$	OO-SCS-RI-MP2	-124.5	-124.5	111.3	-45.9	-78.6	-78.6	157.2
	2.006180	$^{17}\text{O}$	B2PLYP	-127.5	-127.5	112.8	-47.4	-80.1	-80.1	160.2
		$^{17}\text{O}$	CCSD	-123.6	-123.6	110.3	-45.6	-78.0	-78.0	155.9
		$^{17}\text{O}$	CCSD(T)	-122.9	-122.9	110.9	-45.0	-77.9	-77.9	155.9
		$^1\text{H}$	RI-MP2	-120.4	-120.4	9.8	-77.0	-43.4	-43.4	86.8
		$^1\text{H}$	SCS-RI-MP2	-115.0	-115.0	15.0	-71.1	-43.3	-43.3	86.7
		$^1\text{H}$	OO-RI-MP2	-126.1	-126.1	5.2	-82.3	-43.8	-43.8	87.5
		$^1\text{H}$	OO-SCS-RI-MP2	-122.4	-122.4	8.9	-78.6	-43.8	-43.8	87.6
		$^1\text{H}$	B2PLYP	-116.0	-116.0	13.7	-72.8	-43.2	-43.2	86.4
		$^1\text{H}$	CCSD	-121.4	-121.4	9.6	-77.7	-43.7	-43.7	87.3
		$^1\text{H}$	CCSD(T)	-119.5	-119.5	11.1	-76.0	-43.6	-43.6	87.1
$^3\text{SH}^+$	2.020489	$^{33}\text{S}$	RI-MP2	-58.2	82.6	82.6	35.6	-93.8	46.9	46.9
		$^{33}\text{S}$	SCS-RI-MP2	-58.9	83.0	83.0	35.7	-94.6	47.3	47.3
		$^{33}\text{S}$	OO-RI-MP2	-53.5	88.7	88.7	41.3	-94.8	47.4	47.4
	2.007451	$^{33}\text{S}$	OO-SCS-RI-MP2	-52.8	90.3	90.3	42.6	-95.3	47.7	47.7
	2.006436	$^{33}\text{S}$	B2PLYP	-63.8	84.1	84.1	34.8	-98.6	49.3	49.3
		$^{33}\text{S}$	CCSD	-44.9	96.4	96.4	49.3	-94.2	47.1	47.1
		$^{33}\text{S}$	CCSD(T)	-43.4	97.5	97.5	50.5	-93.9	46.9	46.9
		$^1\text{H}$	RI-MP2	-89.5	-89.5	-52.3	-77.1	-12.4	-12.4	24.8
		$^1\text{H}$	SCS-RI-MP2	-78.5	-78.5	-41.5	-66.2	-12.3	-12.3	24.7
		$^1\text{H}$	OO-RI-MP2	-83.4	-83.4	-46.5	-71.1	-12.3	-12.3	24.6
		$^1\text{H}$	OO-SCS-RI-MP2	-74.9	-74.9	-38.0	-62.6	-12.3	-12.3	24.6
		$^1\text{H}$	B2PLYP	-67.4	-67.4	-30.8	-55.2	-12.2	-12.2	24.4
		$^1\text{H}$	CCSD	-77.6	-77.6	-40.9	-65.4	-12.2	-12.2	24.5
		$^1\text{H}$	CCSD(T)	-76.4	-76.4	-39.8	-64.2	-12.2	-12.2	24.4
$^3\text{O}_2$	2.048075	$^{17}\text{O}$	RI-MP2	-75.8	-75.8	55.4	-32.1	-43.7	-43.7	87.5
		$^{17}\text{O}$	SCS-RI-MP2	-91.2	-91.2	42.0	-46.8	-44.4	-44.4	88.8
		$^{17}\text{O}$	OO-RI-MP2	-84.9	-84.9	46.1	-41.2	-43.7	-43.7	87.3
	2.004177	$^{17}\text{O}$	OO-SCS-RI-MP2	-101.3	-101.3	31.8	-56.9	-44.4	-44.4	88.7
	2.006328	$^{17}\text{O}$	B2PLYP	-93.3	-93.3	45.0	-47.2	-46.1	-46.1	92.2
		$^{17}\text{O}$	CCSD	-102.0	-102.0	36.7	-55.7	-46.2	-46.2	92.5
		$^{17}\text{O}$	CCSD(T)	-97.0	-97.0	39.3	-51.6	-45.4	-45.4	90.9
			expt <sup>71</sup>	-102	-102	39	-55	-47	-47	94
	2.049667	$^{33}\text{S}$	RI-MP2	-39.9	34.7	34.7	9.8	-49.7	24.9	24.9
		$^{33}\text{S}$	SCS-RI-MP2	-34.4	40.5	40.5	15.5	-49.9	25.0	25.0
$^3\text{S}_2$	2.015132	$^{33}\text{S}$	OO-RI-MP2	-33.4	41.1	41.1	16.2	-49.6	24.8	24.8
	2.018289	$^{33}\text{S}$	OO-SCS-RI-MP2	-27.8	47.1	47.1	22.1	-49.9	25.0	25.0
		$^{33}\text{S}$	B2PLYP	-36.2	40.9	40.9	15.2	-51.4	25.7	25.7
		$^{33}\text{S}$	CCSD	-26.7	49.8	49.8	24.3	-51.0	25.5	25.5
		$^{33}\text{S}$	CCSD(T)	-26.5	48.6	48.6	23.6	-50.1	25.1	25.1
$^3\text{SO}$	2.054070	$^{33}\text{S}$	RI-MP2	-52.0	39.2	39.2	8.8	-60.8	30.4	30.4
		$^{33}\text{S}$	SCS-RI-MP2	-44.0	48.6	48.6	17.7	-61.7	30.9	30.9
		$^{33}\text{S}$	OO-RI-MP2	-49.2	42.1	42.1	11.7	-60.9	30.4	30.4
	2.012992	$^{33}\text{S}$	OO-SCS-RI-MP2	-41.5	51.2	51.2	20.3	-61.8	30.9	30.9
	2.015130	$^{33}\text{S}$	B2PLYP	-50.3	43.8	43.8	12.4	-62.8	31.4	31.4
		$^{33}\text{S}$	CCSD	-42.3	52.0	52.0	20.5	-62.8	31.4	31.4
		$^{33}\text{S}$	CCSD(T)	-40.8	51.5	51.5	20.7	-61.5	30.8	30.8
		$^{17}\text{O}$	RI-MP2	-38.2	-38.2	48.8	-9.2	-29.0	-29.0	58.0
		$^{17}\text{O}$	SCS-RI-MP2	-43.3	-43.3	42.8	-14.6	-28.7	-28.7	57.4
		$^{17}\text{O}$	OO-RI-MP2	-57.3	-57.3	30.9	-27.9	-29.4	-29.4	58.8
		$^{17}\text{O}$	OO-SCS-RI-MP2	-63.6	-63.6	23.9	-34.4	-29.2	-29.2	58.4
		$^{17}\text{O}$	B2PLYP	-65.8	-65.8	30.8	-33.6	-32.2	-32.2	64.4
		$^{17}\text{O}$	CCSD	-72.3	-72.3	21.2	-41.1	-31.2	-31.2	62.3
		$^{17}\text{O}$	CCSD(T)	-67.9	-67.9	23.9	-37.3	-30.6	-30.6	61.2

most cases drastically reduced by the OO-MP2 methods compared to the conventional RI-MP2 methods that are based on UHF reference determinants. The only exception represents the MgF molecule, for which the spin contamination in the OO-MP2 methods is slightly increased compared to the standard MP2 methods.

The spin contamination often serves as an indicator for the quality of the underlying wave function. In the present context,

this would imply an improved wave function, due to orbital relaxation within the dynamic correlation field. However, there is no obvious correlation between the reduced spin contamination and improved hyperfine coupling constants. Regarding the CN molecule, where the spin contamination is drastically reduced (RI-MP2, 0.409724; OO-RI-MP2, 0.010045), the  $^{13}\text{C}$  hfccs are even worse for the OO-MP2 methods than for the conventional MP2 methods. Thus, no direct conclusion should

**TABLE 5: Error Statistics (MHz) for a Variety of Small  $S \geq 1/2$  Systems in Comparison to CCSD(T) Results**

	$A_{11}^{(A)}$	$A_{22}^{(A)}$	$A_{33}^{(A)}$	$A^{(A;c)}$	$A_{11}^{(A;d)}$	$A_{22}^{(A;d)}$	$A_{33}^{(A;d)}$
mean error RI-MP2	-24	-27	-19	-24	-1	-4	5
mean absolute error RI-MP2	49	49	44	45	16	9	16
mean error SCS-RI-MP2	-26	-26	-21	-24	-2	-2	4
mean absolute error SCS-RI-MP2	55	53	47	50	16	11	18
mean error OO-RI-MP2	3	-5	-1	-1	4	-4	0
mean absolute error OO-RI-MP2	30	30	28	27	7	6	7
mean error OO-SCS-RI-MP2	5	-3	-0	0	5	-4	-1
mean absolute error OO-SCS-RI-MP2	24	23	23	21	7	5	5
mean error B2PLYP	2	-2	6	2	0	-4	4
mean absolute error B2PLYP	28	26	26	24	7	6	8
mean error CCSD	-4	-1	-3	-3	-2	2	0
mean absolute error CCSD	15	17	15	16	3	3	2

**TABLE 6: Error Statistics (MHz) for a Variety of Small  $S \geq 1/2$  Systems in Comparison to Experimental Results**

	$A_{11}^{(A)}$	$A_{22}^{(A)}$	$A_{33}^{(A)}$	$A^{(A;c)}$	$A_{11}^{(A;d)}$	$A_{22}^{(A;d)}$	$A_{33}^{(A;d)}$
mean error RI-MP2	-51	-55	-39	-57	-2	-7	8
mean absolute error RI-MP2	61	65	56	67	9	8	14
mean error SCS-RI-MP2	-56	-60	-42	-60	-3	-7	9
mean absolute error SCS-RI-MP2	72	77	61	77	9	9	14
mean error OO-RI-MP2	-11	-17	-8	-23	1	-5	3
mean absolute error OO-RI-MP2	40	41	36	45	7	6	9
mean error OO-SCS-RI-MP2	-5	-6	2	-19	-2	-3	4
mean absolute error OO-SCS-RI-MP2	30	32	31	36	4	4	7
mean error B2PLYP	-4	-3	10	-18	-4	-4	8
mean absolute error B2PLYP	27	27	28	36	5	6	9
mean error CCSD	-23	-16	-11	-27	-5	1	4
mean absolute error CCSD	35	31	33	37	8	5	8
mean error CCSD(T)	-25	-19	-13	-33	-5	-1	4
mean absolute error CCSD(T)	30	28	27	39	8	5	8

**TABLE 7: Error Statistics ( $\text{au}^3$ ) for a Variety of Small  $S \geq 1/2$  Systems in Comparison to CCSD(T) Results<sup>a</sup>**

	$A_{11}^{(A)}$	$A_{22}^{(A)}$	$A_{33}^{(A)}$	$A^{(A;c)}$	$A_{11}^{(A;d)}$	$A_{22}^{(A;d)}$	$A_{33}^{(A;d)}$
mean error RI-MP2	-0.1440	-0.1502	-0.2197	-0.1713	0.0273	0.0211	-0.0484
mean absolute error RI-MP2	0.5025	0.4262	0.3541	0.4108	0.1832	0.0974	0.1771
mean error SCS-RI-MP2	-0.1316	-0.1391	-0.2166	-0.1624	0.0313	0.0237	-0.0550
mean absolute error SCS-RI-MP2	0.5236	0.4538	0.3619	0.4329	0.1957	0.1184	0.1951
mean error OO-RI-MP2	0.0293	0.0375	0.0609	0.0426	-0.0134	-0.0051	0.0186
mean absolute error OO-RI-MP2	0.1792	0.1742	0.1795	0.1684	0.0557	0.0344	0.0472
mean error OO-SCS-RI-MP2	0.0739	0.0722	0.0891	0.0784	-0.0046	-0.0064	0.0110
mean absolute error OO-SCS-RI-MP2	0.1365	0.1508	0.1463	0.1363	0.0429	0.0325	0.0373
mean error B2PLYP	0.0627	0.0287	0.0783	0.0566	0.0062	-0.0283	0.0220
mean absolute error B2PLYP	0.1800	0.1605	0.1743	0.1539	0.0559	0.0433	0.0540
mean error CCSD	0.0453	0.0352	0.0315	0.0373	0.0083	-0.0023	-0.0060
mean absolute error CCSD	0.0818	0.0840	0.0762	0.0765	0.0230	0.0163	0.0208

<sup>a</sup> Error scaled by the corresponding element-specific factor  $P_A$  (MHz/ $\text{au}^3$ ).

be drawn from the decreased spin contamination in the OO-MP2 methods.

In summary, the results assembled here show that the OO-MP2 methods can rival the already excellent B2PLYP results for the prediction of hfccs. Importantly, the results of OO-MP2 predictions are of quality similar to the already excellent CCSD numbers. In general, the OO-SCS-RI-MP2 method represents, at most, a modest improvement of the parent OO-RI-MP2 method.

**Naphthalene Anion.** To demonstrate the applicability of the OO-MP2 methods to larger molecules, we have calculated the naphthalene anion and collected the results in Table 10. For these calculations an augmented EPR-III<sup>46</sup> basis set was employed, which contains additional core polarization functions (2s2p1d) for all carbon atoms. The hydrogen and carbon atoms are numbered according to Figure 1. The RI-MP2 method can reproduce neither the carbon nor the hydrogen hfccs correctly. Both OO-MP2 methods underestimate the isotropic hfccs for  $C_2$  and  $C_5$  by about 5 MHz and overestimate the hfccs for  $C_3$

and  $C_4$  by  $\sim 2.5$  MHz in magnitude. However, the hydrogen hfccs are in excellent agreement with experiment, considering that no vibrational corrections are taken into account.

The carbon hfccs are best described by the B2PLYP functional and the error in the hydrogen hfccs is also small.

In Table 11 the calculated Mulliken spin populations are shown. The spin populations for the carbon atoms differ by  $\sim 2$ –4% for the OO-MP2 methods compared to the B2PLYP functional. This difference is reflected in the corresponding isotropic hfccs. The deviations for the  $H_7$  and  $H_{10}$  atoms are considerably smaller, but for  $H_8$  and  $H_9$  the spin populations vary by 4–5%. Interestingly, contrary to many qualitative discussions, the hydrogen spin populations do not correlate well with the corresponding isotropic hfccs.

In conclusion, the B2PLYP functional performs best for the hfccs of the naphthalene anion radical, followed by the OO-SCS-RI-MP2 method. The RI-MP2 method fails completely for the prediction of naphthalene anion hfccs.

TABLE 8: Error Statistics (au<sup>3</sup>) for a Variety of Small  $S \geq 1/2$  Systems in Comparison to Experimental Results<sup>a</sup>

	$A_{11}^{(A)}$	$A_{22}^{(A)}$	$A_{33}^{(A)}$	$A^{(A;c)}$	$A_{11}^{(A;d)}$	$A_{22}^{(A;d)}$	$A_{33}^{(A;d)}$
mean error RI-MP2	-0.3488	-0.2950	-0.2067	-0.4179	-0.0641	-0.0146	0.0781
mean absolute error RI-MP2	0.4852	0.5436	0.4465	0.5444	0.0893	0.0718	0.1132
mean error SCS-RI-MP2	-0.3622	-0.3085	-0.2276	-0.4365	-0.0616	-0.0123	0.0732
mean absolute error SCS-RI-MP2	0.5410	0.5943	0.4488	0.5860	0.0838	0.0770	0.1083
mean error OO-RI-MP2	-0.0259	-0.0283	0.0261	-0.1578	-0.0172	-0.0216	0.0382
Mean absolute error OO-RI-MP2	0.2755	0.2821	0.2790	0.3121	0.0484	0.0327	0.0672
mean error OO-SCS-RI-MP2	-0.0411	-0.0402	0.0121	-0.1568	-0.0186	-0.0198	0.0377
mean absolute error OO-SCS-RI-MP2	0.2429	0.2508	0.2572	0.2914	0.0394	0.0303	0.0594
mean error B2PLYP	-0.0449	-0.0535	0.0332	-0.1570	-0.0235	-0.0340	0.0570
mean absolute error B2PLYP	0.2144	0.2079	0.2044	0.2753	0.0357	0.0412	0.0615
mean error CCSD	-0.1463	-0.1514	-0.1217	-0.2378	-0.0067	-0.0142	0.0203
mean absolute error CCSD	0.2272	0.2148	0.2220	0.2861	0.0505	0.0356	0.0554
mean error CCSD(T)	-0.1859	-0.1809	-0.1480	-0.2815	-0.0143	-0.0121	0.0258
mean absolute error CCSD(T)	0.2180	0.2117	0.2056	0.3031	0.0422	0.0302	0.0509

<sup>a</sup> Error scaled by the corresponding element-specific factor  $P_A$  (MHz/au<sup>3</sup>).TABLE 9: Mean Absolute Error (au<sup>3</sup>) for H, C, N, O, and F Atoms in a Variety of Small  $S \geq 1/2$  Systems in Comparison to CCSD(T) Results<sup>a</sup>

	$A_{11}^{(A)}$	$A_{22}^{(A)}$	$A_{33}^{(A)}$	$A^{(A;c)}$	$A_{11}^{(A;d)}$	$A_{22}^{(A;d)}$	$A_{33}^{(A;d)}$
<b><sup>1</sup>H</b>							
RI-MP2	0.0294	0.0189	0.0171	0.0135	0.0216	0.0123	0.0133
SCS-RI-MP2	0.0496	0.0280	0.0226	0.0315	0.0220	0.0123	0.0142
OO-RI-MP2	0.0379	0.0351	0.0336	0.0255	0.0208	0.0132	0.0111
OO-SCS-RI-MP2	0.0318	0.0173	0.0148	0.0113	0.0222	0.0137	0.0124
B2PLYP	0.0302	0.0179	0.0145	0.0091	0.0226	0.0138	0.0129
CCSD	0.0064	0.0066	0.0062	0.0064	0.0007	0.0003	0.0009
<b><sup>13</sup>C</b>							
RI-MP2	0.2474	0.2490	0.2892	0.2386	0.1163	0.1120	0.2238
SCS-RI-MP2	0.4293	0.4155	0.3528	0.3634	0.1371	0.1328	0.2570
OO-RI-MP2	0.2312	0.2376	0.3368	0.2684	0.0440	0.0444	0.0887
OO-SCS-RI-MP2	0.2247	0.2278	0.3144	0.2500	0.0448	0.0414	0.0800
B2PLYP	0.3605	0.3556	0.4326	0.3827	0.0609	0.0621	0.1214
CCSD	0.2603	0.2560	0.2427	0.2531	0.0181	0.0177	0.0311
<b><sup>14</sup>N</b>							
RI-MP2	1.1529	0.4874	0.4263	0.6750	0.4779	0.3177	0.2902
SCS-RI-MP2	1.1944	0.5582	0.4660	0.7283	0.4711	0.3258	0.3061
OO-RI-MP2	0.1817	0.1561	0.2209	0.1608	0.0540	0.0276	0.0811
OO-SCS-RI-MP2	0.1570	0.1589	0.1252	0.1460	0.0286	0.0262	0.0526
B2PLYP	0.1465	0.1358	0.1666	0.1494	0.0311	0.0245	0.0292
CCSD	0.0833	0.0777	0.1066	0.0852	0.0239	0.0175	0.0380
<b><sup>17</sup>O</b>							
RI-MP2	0.6826	0.7025	0.5474	0.6294	0.2976	0.1167	0.2851
SCS-RI-MP2	0.6256	0.6857	0.5297	0.6023	0.3047	0.1517	0.2823
OO-RI-MP2	0.1559	0.1417	0.1388	0.1343	0.1194	0.0606	0.0700
OO-SCS-RI-MP2	0.0581	0.1356	0.1157	0.0911	0.0772	0.0504	0.0478
B2PLYP	0.0851	0.0760	0.0740	0.0484	0.0729	0.0474	0.0454
CCSD	0.0704	0.0660	0.0538	0.0540	0.0470	0.0258	0.0303
<b><sup>19</sup>F</b>							
RI-MP2	0.1182	0.1816	0.1711	0.1562	0.0513	0.0273	0.0497
SCS-RI-MP2	0.1333	0.1911	0.2181	0.1711	0.0431	0.0505	0.0936
OO-RI-MP2	0.0572	0.0794	0.0172	0.0476	0.0096	0.0319	0.0415
OO-SCS-RI-MP2	0.0391	0.0232	0.0208	0.0156	0.0244	0.0286	0.0052
B2PLYP	0.0473	0.0688	0.0514	0.0413	0.0179	0.0490	0.0669
CCSD	0.0221	0.0710	0.0334	0.0460	0.0184	0.0327	0.0164

<sup>a</sup> Error scaled by the corresponding element-specific factor  $P_A$  (MHz/au<sup>3</sup>).

**Quinone Radical Anion.** An even larger example, solvated quinones, is studied in this section. These systems were studied experimentally and theoretically (with the B3LYP functional) in ref 74. Specifically, we recalculated the hfccs of the *p*-benzosemiquinone radical anion (BQ<sup>•-</sup>) coordinated with 1, 2, 4, and 20 deuterated water molecules employing the double-hybrid functional B2PLYP as well as the OO-RI-MP2 method and its SCS variant. The structures of BQ<sup>•-</sup> coordinated with one and two water molecules were optimized with the TPSS

meta-GGA functional<sup>75</sup> and a basis set of triple-  $\zeta$  quality (TZVP<sup>76,77</sup>). The reference structures of ref 74 were used for the 4 and 20 water coordinated BQ<sup>•-</sup>.

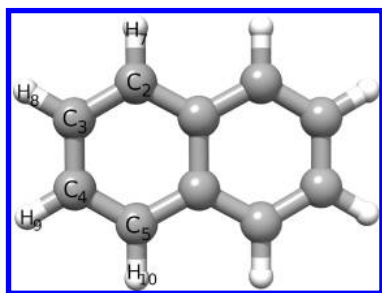
For the calculation of the hfccs, Barone's EPR-III basis set<sup>46</sup> in combination with the def2-TZVPP-JK<sup>49</sup> auxiliary basis set was employed. Furthermore, core polarization functions (2s2p1d) for first row elements were added to the one-electron basis and the auxiliary basis set was decontracted. For the BQ<sup>•-</sup> coordinated with 20 water molecules, the EPR-III basis set was only



**TABLE 10: Isotropic Hyperfine Coupling Constants of the Naphthalene Anion (MHz)<sup>a</sup>**

atom	$A^{(A;c)}$				expt
	RI-MP2	OO-RI-MP2	OO-SCS-RI-MP2	RI-B2PLYP	
C <sub>2</sub>	-5.33	13.68	13.87	18.21	(-)19.9 <sup>72</sup>
C <sub>5</sub>	-9.62	13.76	13.96	18.26	
C <sub>3</sub>	-5.06	-5.69	-5.71	-3.55	-3.4 <sup>72</sup>
C <sub>4</sub>	2.41	-5.94	-6.01	-3.79	
H <sub>7</sub>	-5.43	-14.76	-12.91	-15.27	-13.9 <sup>73</sup>
H <sub>10</sub>	-3.29	-14.77	-12.94	-15.28	
H <sub>8</sub>	-7.61	-6.93	-5.91	-6.01	-5.1 <sup>73</sup>
H <sub>9</sub>	-11.55	-6.75	-5.72	-5.85	

<sup>a</sup>  $\langle S^2 \rangle$  values for the different methods are 0.785493, 0.865290, 0.750170, 0.750087.

**Figure 1.** Numbering of the atoms in the naphthalene anion radical.**TABLE 11: Mulliken Spin Populations (%)**

atom	$\rho^{(A)}$		
	OO-RI-MP2	OO-SCS-RI-MP2	RI-B2PLYP
C <sub>2</sub>	21.1	21.3	21.8
C <sub>5</sub>	21.2	21.4	21.8
C <sub>3</sub>	9.0	8.6	8.0
C <sub>4</sub>	8.7	8.3	7.8
H <sub>7</sub>	-1.8	-1.7	-1.6
H <sub>10</sub>	-1.8	-1.7	-1.6
H <sub>8</sub>	-0.9	-0.9	-0.7
H <sub>9</sub>	-0.9	-0.8	-0.6

employed for all carbon atoms and for the bridging hydrogens. A split-valence basis plus polarization functions (SVP<sup>78,77</sup>) was used otherwise.

The RIJCOSX<sup>79</sup> approximation was applied in both OO-MP2 methods, whereas the RI approximation was employed for the B2PLYP calculations.

The single point calculation of the BQ<sup>•-</sup> solvated with 20 D<sub>2</sub>O molecules and an orbital basis of 1890 basis functions as well as an auxiliary basis of dimension 3596 was computed on 16 processors and took roughly 4 days to complete.

In Table 12 the calculated hfccs for the bridging <sup>2</sup>H atoms are listed. The dipolar hfccs are generally slightly underestimated in magnitude by the OO-MP2 methods and decrease with increasing number of D<sub>2</sub>O molecules. The B2PLYP functional slightly overestimates the magnitude of the anisotropic hfccs, but the trend with increasing solvent molecules is the same as for the OO-MP2 methods. The isotropic hfccs are excellently predicted by the OO-RI-MP2 method as well as by the B2PLYP functional. The SCS variant of the OO-RI-MP2 method slightly overestimates the isotropic contribution but still yields predictions of excellent quality. The BQ<sup>•-</sup> solvated with 20 D<sub>2</sub>O molecules represents the most realistic model, and the calculated hfccs are in good agreement with experiment. All tested methods perform very well in this respect with B2PLYP being perhaps the most successful method tested here.

**TABLE 12: Calculated <sup>2</sup>H hfccs (MHz) of BQ<sup>•-</sup> in Coordination with 1, 2, 4, and 20 Water (D<sub>2</sub>O) Molecules ( $P_D = 81.8989$  MHz/au<sup>3</sup>) (Comparison with Experimental Results)**

method		number of water molecules				expt
		one	two	four	20	
OO-RI-MP2	$A_{11}^{(A;d)}$	-0.46	-0.46	-0.44	-0.47	-0.49
	$A_{22}^{(A;d)}$	-0.43	-0.43	-0.40	-0.41	-0.47
	$A_{33}^{(A;d)}$	0.89	0.87	0.84	0.88	0.95
	$A^{(A;c)}$	0.02	0.03	0.04	0.01	0.03
OO-SCS-RI-MP2	$A_{11}^{(A;d)}$	-0.44	-0.44	-0.42	-0.46	-0.49
	$A_{22}^{(A;d)}$	-0.42	-0.41	-0.39	-0.40	-0.47
	$A_{33}^{(A;d)}$	0.86	0.85	0.82	0.86	0.95
	$A^{(A;c)}$	0.08	0.08	0.08	0.07	0.03
RI-B2PLYP	$A_{11}^{(A;d)}$	-0.50	-0.50	-0.48	-0.51	-0.49
	$A_{22}^{(A;d)}$	-0.48	-0.46	-0.44	-0.44	-0.47
	$A_{33}^{(A;d)}$	0.98	0.96	0.92	0.95	0.95
	$A^{(A;c)}$	0.01	0.02	0.03	0.00	0.03

## Discussion

In this work, the orbital-optimized MP2 method was evaluated for the calculation of hyperfine coupling constants. The method was benchmarked for a series of small radicals and compared to CCSD(T) reference results. The resulting isotropic hfccs are almost of CCSD quality but are obtained with iterative  $\mathcal{O}(N^5)$  effort. The dipolar contribution to the hfccs are, however, less well predicted by the OO-MP2 methods. On average, spin-component scaling improves the description of the hfccs for small radicals. Overall, it seems to be the best choice among the wave function based methods.

Of the tested methods OO-MP2 is perhaps slightly inferior to the double hybrid functional B2PLYP that is also computationally more attractive. We do, however, believe that it is highly useful to have a pure wave function based methodology available that is not plagued by self-interaction problems that occasionally can complicate calculations on radicals with extended  $\pi$ -systems. It is of course possible to also optimize the orbitals in the double hybrid DFT approach. It remains an open question whether this would improve the results in a similar way as OO-MP2 improves upon MP2. Work in this direction is in progress.

The spin contamination in the OO-MP2 wave function is drastically reduced compared to the standard UHF wave function. In combination with the RIJCOSX approximation the OO-RI-MP2 method becomes applicable to fairly large systems, as demonstrated for the solvated *p*-benzosemiquinone radical anion where calculations with almost 2000 basis functions have been performed.

## Conclusions

From the extensive set of hyperfine coupling constant calculations on small radicals it emerges that the OO-MP2 method represents a viable alternative to double hybrid functionals, although the computational effort for OO-MP2 is considerably higher. Nevertheless, using various approximations discussed in the manuscript, the method is still applicable to fairly large molecules.

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