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The Inclusion of Correlation in the Calculation of Phosphorus NMR Chemical Shieldings

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ABSTRACT

The effects of including correlation in the calculation of phosphorus nuclear magnetic resonance (NMR) chemical shielding has been investigated for a variety of molecules in the Hartree-Fock, second-order Møller-Plesset (MP2), and estimated infinite-order Møller-Plesset theory ab initio approaches in the gauge including atomic orbital (GIAO) scheme. The inclusion of correlation in the shielding calculations often leads to significant changes from the Hartree-Fock theory and provides results that are in improved agreement with experiment.

INTRODUCTION

Great strides have been made in recent years in our ability to calculate accurately nuclear magnetic resonance (NMR) chemical shielding. More efficient algorithms, faster computers, and the implementation of more sophisticated post-Hartree-Fock methods are allowing us to match significantly better experimental values of this important observable. In particular, the theoretical development by Gauss [1,2] for shieldings calculated at second-order Møller-Plesset theory [MP2 or MBPT(2)] and its implementation by Stanton et al. [3] in the ACES II computational chemistry code now permit ready inclusion of the first level of correlation in NMR chemical shielding calculations. There are many instances of shieldings where Hartree-Fock self-consistent field theory (which by definition does not include correlation) fails because it does not take into account the instantaneous interaction between electrons. The inclusion of correlation is especially important in molecules containing multiple bonds and/or lone pairs where a lowering of the HOMO-LUMO gap allows more ready mixing of excited states with the single determinant Hartree-Fock ground state when correlated states are formed.

There have been a number of calculations of phosphorus NMR shieldings at the Hartree-Fock (HF) level [4] but very few that include correlation. Bouman and Hansen [5] carried out a study several years ago on a small set of phosphorus-containing molecules using their LORG method, but agreement with experiment was no better than that obtained at the Hartree-Fock level. More recently, Wolinski et al. [6] studied in detail geometry and basis set effects in PH_3 in the MP2 approach, and Malkin et al. [7] have performed sum-over-states density functional perturbation theory calculations on PN. Effects of correlation in phosphorus-containing molecules can be very large, such as in the PN molecule where the calculated difference between post-Hartree-Fock and Hartree-Fock shieldings is over 300 ppm! In the present article, we discuss phosphorus shielding calculations carried out at both Hartree-Fock and MP2 levels along with a simple method we recently proposed [8] for estimating the infinite-order Møller-Plesset result. We show that correlation effects for this important nucleus can be quite large and that

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Dedicated to Professor Louis D. Quin on the occasion of his retirement from the University of Massachusetts at Amherst.

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their inclusion generally improves agreement with experiment significantly.

THEORETICAL METHODS

Because many of the structures upon which our calculations were carried out are unknown experimentally, structures employed in the present case were all optimized at the MP2 (frozen core) level of theory with the 6-311G(*d*, *p*) basis set [9] as implemented in the Gaussian 94 program [10]. Structure optimizations employed only a single set of *d*-polarization functions for heavy atoms (and a single set of *p* functions for hydrogen), including phosphorus and other elements of the second long row of the periodic table. However, for the chemical shielding calculations, two sets of *d* functions were used for second row elements with the basis sets of Schäfer et al. [11] using the HF and MP2 (full) implementation of Ditchfield's gauge including atomic orbital (GIAO) method [12] found in the ACES II code [3]: tzp for hydrogen (3*s*, *p*) and elements of the first long row of the periodic table (4*s*, 3*p*, *d*), and tz2*p* (7*s*, 5*p*, 2*d*) for phosphorus and other elements of the second long row. All our calculations represent absolute shieldings such that a bare phosphorus nucleus would have a shielding of zero; chemical shifts, or shieldings with respect to a standard, may be determined by taking differences of the appropriate absolute shieldings. All of our calculations were carried out on Cray Y-MP or Cray T-90 platforms located in the North Carolina Supercomputing Center.

We recently observed that in a number of cases the various orders of Møller-Plesset theory NMR shieldings seem to be converging as a geometric series with a ratio of successive terms of approximately −0.5 [8]. Under the assumption that this is true for all orders, one may sum the infinite perturbation series so that, with the knowledge of HF (σ_{HF}) and MP2 (σ_{MP2}) isotropic shieldings, the estimated Møller-Plesset infinite-order (EMPI) shielding, σ_{EMPI}, is given by

$$\sigma_{EMPI} = \frac{1}{3}\sigma_{HF} + \frac{2}{3}\sigma_{MP2} \tag{1}$$

We found that applying this method to cited literature calculations provided NMR shieldings that were as accurate as available MP4 and coupled cluster calculations and in good agreement with experiment. The EMPI estimates should be viable in those cases where the use of many-body perturbation theory is valid and are included in our tables along with the HF and MP2 results that are directly available from the ACES II code.

RESULTS AND DISCUSSION

In this article, we want to quantify the effects of correlation when calculating phosphorus NMR chemical shieldings. Is the inclusion of correlation at the MP2 or estimated infinite-order perturbation theory level (EMPI) significant? And does the inclusion of correlation lead to better agreement with experiment or not?

Table 1 lists for a variety of phosphorus-containing molecules the experimentally observed isotropic shieldings, our best estimate of the calculated shieldings (the EMPI approach), and the differences between calculated and observed shieldings for the Hartree-Fock, MP2, and EMPI approaches. At the bottom of Table 1 is the average error, the standard deviation of the errors, and the root-mean-square error (rmse) for the theoretical approaches employed here. PH_2^- and PH_4^+ were not included in the statistical analyses because of the unprotected nature of the phosphorus atom in these compounds; whereas our calculations are carried out on isolated species, the shieldings for these two species were measured in solution where solvation likely played an important role. The other ionic species are expected to protect adequately phosphorus from the surroundings and are included in the statistics. The calculated (EMPI) and observed data are also displayed in Figure 1.

It is clear that inclusion of correlation at the MP2 level significantly reduces the rmse by almost a factor of 2 over the Hartree-Fock approach and that our estimate of the infinite-order result (EMPI) is better yet. Hartree-Fock is well known to underestimate chemical shieldings, and MP2 is generally recognized to overcompensate the lack of correlation in the Hartree-Fock approach. The EMPI approach, however, tends to minimize these errors by taking an appropriate mixture of the two results. Taking the rmse value as an appropriate measure of agreement between theory and experiment, we see that Hartree-Fock can calculate shieldings to approximately 8.0% of the phosphorus shielding range, MP2 approximately 4.5%, while the EMPI approach yields a figure of 2.7%. The results are heavily weighted by the calculated results for the PN molecule. Omitting PN from the analysis yields rmse values for the three approaches presented here that are quite comparable. On the other hand, PN (along with molecules such as CO and N_2) long has been a prime example of the failure of Hartree-Fock theory in shielding calculations, and the fact that we can calculate it extremely well in the EMPI approach should not detract from the results here but rather illustrate the importance of properly including correlation in

TABLE 1 Phosphorus Isotropic Shieldings (in ppm on an absolute scale). Our Best Estimate of the Theoretical Shielding, the EMPI Method (Calcd), is Compared to Experiment (Obs.) Along with Differences with Experiment for Hartree-Fock (HF), MP2, and the EMPI Approaches. The Mean Errors ($\bar{x}$), the Standard Deviations (s.d.), and the Root-Mean-Square Errors (rmse) for These Three Methods are Shown at the Bottom of the Columns[a]

				Calculated Minus Observed		
	Calcd[a]	*Obs.*	*Ref.*	*HF*	*MP2*	*EMPI*
P_4	922.4	879.8[b]	13	50.6	38.6	42.6
PH_2^-	679.2	(607.8)	14	38.2	88.1	71.4
$(CH)_2PH$	626.9	—	—			
H_3SiPH_2	638.2	602	15	16.0	46.2	36.2
PH_3	602.9	594.4[b]	16	−10.5	18.0	8.5
H_2PPH_2	573.2	532	17	23.8	50.0	41.2
PF_6^-	482.7	472.1	18	41.7	−5.0	10.6
CH_3PH_2	488.7	491.9	19	−16.9	3.6	−3.2
PH_4^+	474.3	433.7	14	32.5	44.6	40.6
$(CH_3)_2PH$	455.1	427	19	21.7	31.2	28.1
PF_5	413.8	408.6	18	31.8	−8.2	5.2
$(CH_3)_3P$	424.6	391.7[b]	16	32.5	33.2	33.0
OPF_3	373.1	363.4[b]	16	18.9	5.1	9.7
HCP	377.0	360	20	−35.6	43.3	17.0
PO_4^{-3}	309.4	328.4[b]	16	−5.7	−25.6	−19.0
$HOPO_2$	239.2	—	—			
PF_3	222.5	222.7	16	21.1	−10.8	−0.2
PCl_3	103.7	111.3[b]	16	17.8	−20.3	−7.6
C_5H_5P	130.3	117	21	−12.4	26.2	13.3
H_2CPH	113.0	—	—			
HOPO	59.6	—	—			
PN	37.2	53[b]	22	−243.1	97.9	−15.8
HPPH	−201.0	—	—			
P_2	−251.7	—	—			
HPO	−313.4	—	—			
$\bar{x}$				−3.0	20.2	12.5
s.d.				66.0	31.1	18.8
rmse				66.0	37.1	22.6

[a] The data for PH_2^- and PH_4^+ were not included in the statistical analyses.
[b] Gas phase data.

shielding calculations on molecules like this. Malkin et al. [7] in their density functional approach also determine a shielding value (46.9) very close to experiment.

The sizable nature of correlation effects in the phosphorus shielding calculations is illustrated in Table 2 where the calculated isotropic shieldings are presented for those molecules having a difference between the MP2 and HF approaches of greater than 50 ppm. The difference between MP2 and Hartree-Fock results is as large as 341.0 ppm in the case of PN, a figure representing approximately 41% of the entire observed shielding range of the molecules in this study!

The molecules in Table 2 are listed according to decreasing shielding. That is, HCP has a shielding that places it upfield of the other molecules, while HPO is at the large deshielding portion of the NMR shielding spectrum. Chemical shieldings are usually decomposed into what are called diamagnetic and paramagnetic contributions. The diamagnetic part is rather insensitive to molecular environment, while the paramagnetic term varies considerably and is essentially the part that is responsible for the range of shieldings for most nuclei. Correlation effects are more important for the paramagnetic part, so it is appropriate in Table 2 that the larger correlation contributions occur for those molecules that are more deshielded (more paramagnetic).

The isotropic chemical shielding is the average of the sum of the principal values of the shielding tensor. As such, often small discrepancies among the principal values can cancel out in obtaining the calculated isotropic shielding. The anisotropy, on the other hand, is less forgiving and is a more sensitive test of theory. The anisotropy of the shielding tensor is generally defined as

$$\Delta\sigma \equiv \sigma_{33} - 0.5(\sigma_{22} + \sigma_{11}), \quad \text{for } \sigma_{33} > \sigma_{22} > \sigma_{11} \tag{2a}$$

$$\Delta\sigma \equiv \sigma_{\text{parallel}} - \sigma_{\text{perpendicular}} \tag{2b}$$

where the expression in Equation 2b is used when axial symmetry is present. Table 3 shows measured anisotropies for six molecules along with the values calculated by the Hartree-Fock, MP2, and EMPI approaches. We note that the rmse values are generally larger here than they were for the isotropic shieldings and that again the EMPI approach is better than simply MP2 by itself, and much better than Hartree-Fock. The PN molecule is again a sensitive molecule to calculate, but it does not dominate the errors in the case of the anisotropies as much as it did for the isotropic shieldings. Omitting the PN data results in rmse values for the MP2 and EMPI approaches that are approximately the same but still much better than Hartree-Fock.

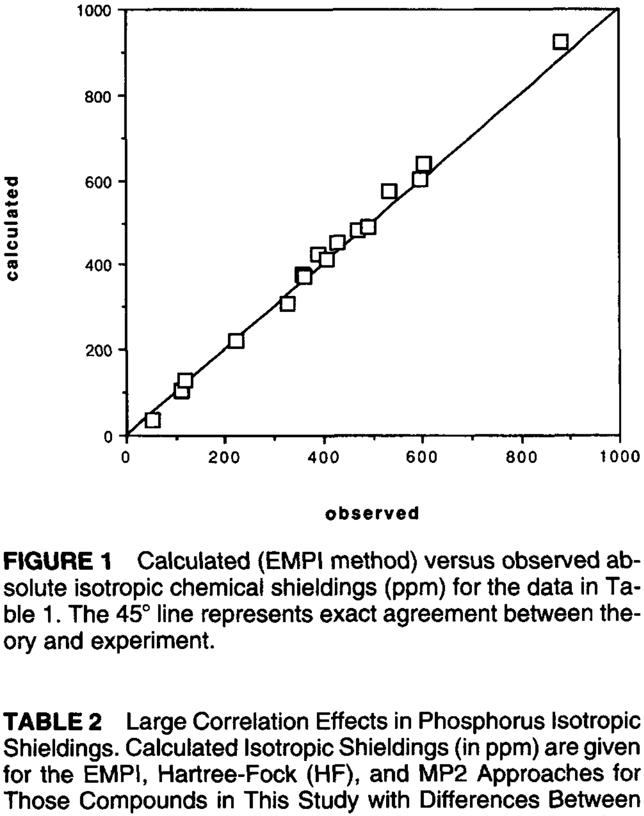

FIGURE 1 Calculated (EMPI method) versus observed absolute isotropic chemical shieldings (ppm) for the data in Table 1. The 45° line represents exact agreement between theory and experiment.

TABLE 2 Large Correlation Effects in Phosphorus Isotropic Shieldings. Calculated Isotropic Shieldings (in ppm) are given for the EMPI, Hartree-Fock (HF), and MP2 Approaches for Those Compounds in This Study with Differences Between MP2 and Hartree-Fock Shieldings [Δ(MP2-HF)] greater than 50 ppm

	EMPI	*HF*	*MP2*	*Δ(MP2-HF)*
HCP	377.0	324.4	403.3	78.9
$HOPO_2$	239.2	200.4	258.6	58.2
H_2CPH	113.0	72.9	133.1	60.2
HOPO	59.6	4.6	87.2	82.6
PN	37.2	−190.1	150.9	341.0
HPPH	−201.0	−356.9	−123.0	233.9
P_2	−251.7	−464.9	−145.1	319.8
HPO	−313.4	−424.2	−258.0	166.2

The anisotropy of the shielding provides a measure of the spread of resonances one may observe in a single-crystal measurement, or the width of the resonance pattern in powder studies [24]. A more appropriate measure of the powder spread would be what is called the *range*, or $\sigma_{33} - \sigma_{11}$, the difference between the largest and smallest principal values of the shielding tensor. Because it may be more likely to observe some phosphorus resonances from powder spectra, our best estimates (the EMPI approach) of the principal values are given in Table 4 along with the isotropic shielding (repeated from Table 1) and the anisotropy as defined in Equations 2a and 2b. While the spread of calculated isotropic shieldings is over 1200 ppm, some of the shielding ranges for individual molecules are larger. The extreme examples are HPPH and P_2, where the shielding ranges are over 1800 ppm!

One should always be aware of those facets of an exact calculation that are being omitted in any approximate calculation (even at correlated levels), such as those done here. Our calculations are carried out on rigid molecules that are not rotating or vibrating, and they are carried out at geometries optimized by theoretical methods as opposed to experimental ones. Effects of rovibration can be significant [25,26] and generally tend to cause shieldings to be somewhat reduced, that is, moved to more paramagnetic (low field) values. The fact that the mean shielding errors for the (preferred) MP2 and EMPI approaches in Table 1 are positive is a good sign in that inclusion of rovibration effects

TABLE 3 Anisotropies (in ppm) Observed (With Uncertainties Given in Parentheses) and Calculated in the Hartree-Rock (HF), MP2, and Estimated Infinite-Order Perturbation Theory (EMPI) Approaches. The Mean Errors ($\bar{x}$) Between Calculated and Observed Anisotropies are Given Along with the Standard Deviations (s.d.) and the (rmse). With the exception of PN[a], the Experimental Data are due to Jameson et al. [16]

	Observed		*HF*	*MP2*	*EMPI*
P_4	−405	(15)	−481.4	−460.4	−467.4
PH_3	−56.0		−39.4	−59.9	−53.1
$(CH_3)_3P$	7.6	(0.05)	−8.1	−29.0	−22.0
OPF_3	284	(15)	306.5	308.1	307.6
PF_3	181	(15)	324.2	275.2	291.4
PN	1376		1733.2	1222.9	1393.0
$\bar{x}$			74.6	−21.8	10.4
s.d.			142.4	75.8	53.6
rmse			160.7	78.9	54.6

[a] The data for PN were estimated by Appleman and Dailey [23].

TABLE 4 EMPI Principal Values ($\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}$) of the Phosphorus Shielding Tensors, the Isotropic Shieldings, σ_{iso}, and the Shielding Anisotropies, $\Delta\sigma$, All in ppm. The Anisotropy is Defined as $\Delta\sigma = \sigma_{33} - 0.5(\sigma_{22} + \sigma_{11})$ When All the Principal Values Differ, or as $\Delta\sigma = \sigma_{\text{parallel}} - \sigma_{\text{perpendicular}}$ When Axial Symmetry is Present

	σ_{11}	σ_{22}	σ_{33}	σ_{iso}	$\Delta\sigma$
P_4	610.8	1078.2	1078.2	922.4	−467.4
PH_2^-	523.6	641.3	872.9	679.2	290.4
$(CH)_2PH$	378.2	397.9	1104.7	626.9	716.6
H_3SiPH_2	582.8	605.9	725.8	638.2	131.4
PH_3	567.5	620.6	620.6	602.9	−53.1
H_2PPH_2	512.7	589.5	617.6	573.2	66.5
PF_6^-	482.7	482.7	482.7	482.7	0.0
CH_3PH_2	440.3	460.2	565.5	488.7	115.2
PH_4^+	474.3	474.3	474.3	474.3	0.0
$(CH_3)_2PH$	422.2	439.1	503.9	455.1	73.2
PF_5	327.9	456.7	456.7	413.8	−128.8
$(CH_3)_3P$	410.0	432.0	432.0	424.6	−22.0
OPF_3	270.6	270.6	578.1	373.1	307.6
HCP	81.6	81.6	967.7	377.0	886.0
PO_4^{-3}	309.4	309.4	309.4	309.4	0.0
$HOPO_2$	4.8	180.6	532.3	239.2	439.6
PF_3	125.3	125.3	416.7	222.5	291.4
PCl_3	48.4	48.4	214.2	103.7	165.8
C_5H_5P	−119.1	−18.2	528.2	130.3	596.9
H_2CPH	−363.6	194.8	507.9	113.0	592.3
HOPO	−343.9	153.1	369.8	59.7	465.2
PN	−427.1	−427.1	965.9	37.2	1393.0
HPPH	−1271.0	95.4	572.7	−201.0	1160.5
P_2	−862.0	−862.0	969.0	−251.7	1831.0
HPO	−1134.1	27.7	166.2	−313.4	719.4

would likely make this average error less positive and therefore smaller.

Molecular geometry also can have a significant effect on the theoretically determined shielding. This is very evident in the case of PN, where the theoretical PN bond length varies from 1.4515 Å in an HF/6-311G(*d*) optimization to 1.5278 Å in an MP2/6-311G(*d*) calculation. The experimental value is 1.491 Å [27], intermediate between these extremes. Figure 2 shows the isotropic shielding for PN as a function of bond distance for Hartree-Fock, MP2, and EMPI approaches; the horizontal line represents the observed shielding for phosphorus in PN of 53 ppm [22]. Both the Hartree-Fock and MP2 results show significant errors at all these geometries, while the estimated infinite-order perturbation theory result (EMPI) is much closer to experiment. In particular, the EMPI calculated shielding of 56.7 at the experimentally observed bond distance is almost in perfect agreement with experiment. In this particular molecule, another test of our EMPI method is provided by the shielding of the nitrogen nucleus. Again, at the experimentally observed geometry of 1.491 Å, the Hartree-Fock shielding is −486.6, the MP2 value is −243.1, while our EMPI approach provides a result of −324.3; the experimentally observed result is −349 ppm [5]. Malkin et al. [7] with their density functional approach determined a value of −347.8 ppm.

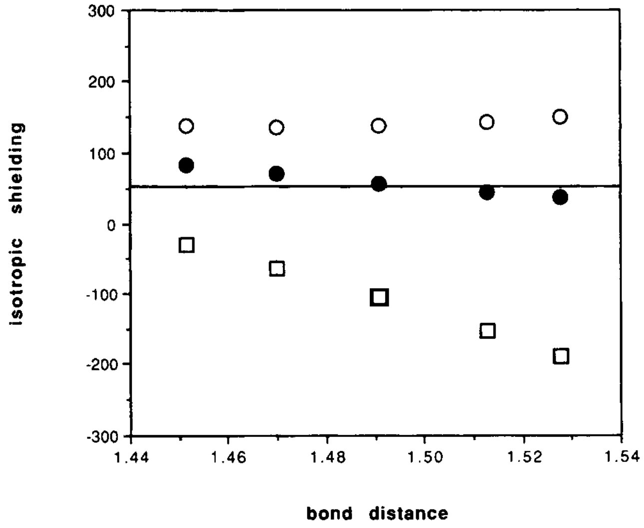

FIGURE 2 Phosphorus isotropic shielding (in ppm) in PN as a function of bond length. Calculated Hartree-Fock (open squares), MP2 (open circles), and EMPI (closed circles) data are shown. The horizontal line represents the observed shielding.

In conclusion, correlation plays an important role in the calculation of phosphorus NMR shieldings as it does with other elements. The effects of correlation can be quite large, especially so for a nucleus like phosphorus with a large chemical shielding range, and in many cases, its inclusion is mandatory if one is to approach reasonable agreement with experiment. Our estimated infinite-order perturbation theory approach (EMPI) provides a more accurate estimate of both isotropic shieldings and anisotropies than MP2 or, of course, the Hartree-Fock approach, which often fails badly.

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It is a pleasure for me (DBC) to acknowledge the personal friendship and professional relationship over the years with Louis Quin. My own work on the

theoretical determination of NMR chemical shieldings was stimulated by conversations with Louis Quin in the late 1970s, and it has been most gratifying that subsequent efforts developed sufficiently well since then to allow the two of us to finally collaborate in the 1990s on several articles [28,29] that explained phosphorus shielding phenomena which had been mysterious for many years. It has been my privilege to know him as a friend and colleague, and I am most pleased to be able to contribute an article to this special issue celebrating his contributions to chemistry in general and phosphorus chemistry in particular.

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