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A Theoretical Study of ^{31}P NMR Chemical Shielding Models for Concentrated Phosphoric Acid Solution

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Calculations on the hydrates, dimer, and trimer of phosphoric acid were carried out in an effort to obtain a viable model of the phosphorus NMR chemical shielding in 85% phosphoric acid solution. The theoretical approaches used the gauge-including-atomic-orbital (GIAO) 6-311+G(nd,p) basis set at both scaled density functional theory (sB3LYP) and estimated infinite order Møller−Plesset (EMPI) approaches and with the aug-cc-pvtz basis in the sB3LYP approach. Shieldings and hydrogen bonding stabilization energies are similar in the three approaches and indicate that the faster sB3LYP/6-311+G(nd,p) approach can be used with larger systems. The changes in shielding compared to the isolated species are small and suggest that the undissociated acid dihydrate could serve as a model entity for modeling the phosphorus shielding in concentrated phosphoric acid solution.

Introduction

The standard reference for phosphorus-31 NMR has been for many years now 85% phosphoric acid. On the basis of the absolute shielding of PH_3 in the gas phase using spin-rotational data, Jameson et al.[1] have established the absolute shielding for 85% phosphoric acid solution at 328.4 ppm at 298 K. In calculations of phosphorus shieldings, some authors[2,3] refuse to perform calculations on H_3PO_4 since the proper species in the concentrated solution are not known experimentally. In some of our own work[4] calculations have been made on the phosphate trianion, PO_4-3, as a model, but this is likely incorrect since phosphoric acid is a weak acid and there is no reason to believe it would ionize to such a degree in very concentrated solutions.

As pointed out by Cotton et al.,[5] phosphoric acid (orthophosphoric acid) is one of the oldest and most important compounds of phosphorus. In the solid it is strongly hydrogen bonded.[6,7] The syrupy nature of concentrated aqueous solutions suggests the persistence of the hydrogen bonds, although this does not differentiate between phosphoric acid dimers or trimers and phosphoric acid monomers connected by strong hydrogen bonds to water. In solutions of concentrations less than 50%, phosphate anions are thought to bond to water rather than each other, which is to be expected on the basis of the strong electrostatic repulsion of the charged species.

The density of 85% phosphoric acid is 1.436 g/mL[8] at 20 °C, which leads to a phosphoric acid molarity of 12.5. The solution's density shows that H_3PO_4 (and all ionized species) are essentially in a 1:1 ratio with water (actually 1.04, favoring the acid species). Since the three hydrogen dissociation constants are 7.5×10^{-3}, 6.2×10^{-8}, and 2.2×10^{-13} [9] (in the 0.1−0.01 N range of concentrations), neglecting any consideration of activities (which almost certainly cannot be done in such a concentrated solution), this molarity indicates that basically only H_3PO_4 and H_2PO_4-1 would be present to any degree, with a ratio of H_2PO_4-1 to H_3PO_4 of 0.025. Although it would appear reasonable to expect only H_3PO_4 and H_2PO_4-1 to be present, it would also be reasonable not to expect them to resemble isolated gas-phase species.

The present paper examines what effects occur when H_3PO_4 and its anions are allowed to hydrogen bond to water and, in the case of the undissociated acid, to each other, or when one attempts to mimic the aqueous solution with a self-consistent reaction field. Our results show that changes upon hydrogen bonding are small and generally smaller than our current theoretical uncertainly in which phosphorus shieldings can be calculated to approximately ±18−20 ppm. This suggests that one can basically perform gas-phase-like calculations on the hydrates to compare to the experimental absolute shielding of 328.4 ppm.

Theoretical Details

Nonrelativistic calculations of absolute chemical shieldings (ppm) were carried out both in a scaled B3LYP[10,11] DFT approach[12] and, in a number of cases, our estimated infinite-order Møller−Plesset[13] (EMPI) method employing Gaussian 03.[14] Gauge-including atomic orbitals[15,16] (GIAO) were used in both a 6-311+G(nd,p) basis and also Dunning's aug-cc-pvtz basis, one of his correlation-consistent basis sets;[17−19] for shielding calculations the 6-311+G(nd,p) basis used six Cartesian d-functions per set and $n = 2$ for phosphorus, $n = 1$ for all other elements, while the Dunning aug-cc-pvtz basis employs three sets of five d-functions and two sets of seven f-functions. Geometries were optimized in the B3LYP approach by using both the 6-311+G(d,p) and aug-cc-pvtz bases and at the MP2 level by using only the 6-311+G(d,p) basis set; frequency calculations confirmed the theoretical geometries as energy minima, and the unscaled zero-point energies were used in the energy difference calculations.

Our sDFT method[12] results from the discovery that a simple constant rescaling of the paramagnetic contribution in the GIAO B3LYP/6-311+G(nd,p) approach can be made such that quantitative predictions are possible. We performed a least-squares fit of the DFT paramagnetic contribution, σ_{para}, against the difference of the observed isotropic shielding and the diamag-

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netic contribution, σ_{dia}, thus deriving a scaling factor, k, for the DFT paramagnetic term. A scaled DFT shielding is then calculated as

$$\sigma_{\mathrm{s,DFT}} = \sigma_{\mathrm{dia}} + k\sigma_{\mathrm{para}} \tag{1}$$

where $\sigma_{\mathrm{s,DFT}}$ is the new estimate of the shielding. The redetermined shieldings are in good agreement with experiment and rival some of the more sophisticated ab initio theoretical approaches.[20] For phosphorus in the sB3LYP/6-311+G(nd,p) approach we find $k = 0.912(\pm 0.010)$ (rmse = 20.3 ppm), the value we use in this study. This differs slightly from that value reported earlier[12] and is based on a larger (16 molecules) and more representative set of molecules that excludes H_3PO_4 itself. A value of 0.952(±0.007) (rsme = 18.1 ppm) was used for the aug-cc-pvtz basis, determined in this study by using the same set of phosphorus-containing molecules.

Our EMPI method[13] uses a particular mixture of RHF and MP2 GIAO approaches. We found that in many cases the Møller−Plesset series of corrections appears to converge in a manner that allows the infinite series to be summed (approximately), so that the EMPI shielding is given by

$$\sigma_{\mathrm{EMPI}} = \sigma_{\mathrm{RHF}} + \frac{2}{3}(\sigma_{\mathrm{MP2}} - \sigma_{\mathrm{RHF}}) \tag{2}$$

Our mixing of Hartree−Fock and MP2 shieldings is similar in spirit to the correlation extrapolation scheme of Rossi and Truhlar,[21] although, as noted above, our method is based on an apparent observed convergence of the various terms in the Møller−Plesset series.

To simulate species in (aqueous) solution we employed the conductor-like solvation model (COSMO) based on the work of Barone and co-workers.[22,23] This procedure was first proposed by Klamt and Schüürmann[24] for classical calculations and then implemented by Andzelm et al.[25] and Truong and Stefanovich[26] for quantum mechanical calculations. COSMO describes the solvent reaction field by means of apparent polarization charges distributed on a cavity surface of molecular shape formed by interlocking spheres centered on the solute atoms or atomic groups. The polarization charges are determined by requiring the total electrostatic potential on the cavity surface to cancel out. Only our density functional theory calculations used this method.

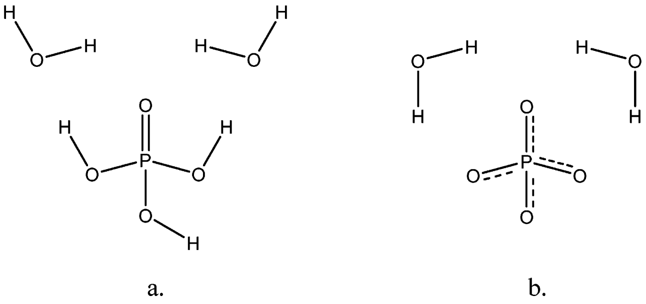
A single optimization was carried out on a counterpoise-corrected potential energy surface using the approach of Simon, Duran, and Dannenberg.[27] No rovibrational corrections were explicitly considered, although the potential effect of these corrections to the shielding is discussed.

Results and Discussion

The purpose of our work is to investigate some—but clearly not all—possible models of the phosphoric acid entities in the very concentrated 85% phosphoric solution in order to see if a sufficiently simple model or models can suffice for theoretical estimates of the NMR shielding. While limited in scope, we do believe that enough of the electronic space has been sampled to reach some useful conclusions.

Perhaps the optimum approach might be to perform molecular dynamics on the system with the appropriate composition, equilibrate at room temperature, and then sample small clusters of the dynamics cell with periodic boundary conditions. Such was done some time ago in our study of changes in hydrogen and oxygen shielding in water in transitioning from the gaseous to the liquid state,[28] a study repeated in a better way with an improved potential and better results a few years later by Malkin et al.[29] But the clusters of phosphoric acid and water molecules obtained from such a dynamics simulation would likely be unwieldy with our current capabilities, so we have chosen to work with relatively smaller isolated molecular complexes.

CHART 1



Self-consistent reaction fields (COSMO here) tend to mimic forces in the liquid state, but this type of approach is generally thought to be inadequate when hydrogen bonding is present. We briefly investigate this approach but move quickly along to consider finite isolated molecular complexes.

Both the sB3LYP and EMPI methods have been used for some of the species under consideration, with the 6-311+G(d,p) basis used for both of these and the very large aug-cc-pvtz basis used only in the sB3LYP approach. The 6-311+G(d,p) basis with 6 d-functions leads to 141 basis functions for H_3PO_4, while the aug-cc-pvtz basis provides 303 basis functions. We would also point out here that our optimizations did not explicitly force symmetry on the systems. Symmetry will, of course, exhibit itself when present, but several instances showed that the rather flat nature of the potential energy surface can yield slightly different structures when starting from a different initial set of coordinates.

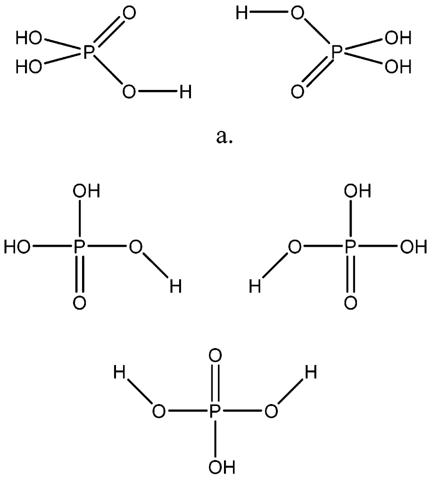
Hydrogen Bonded Structures and Stabilization Energies. We should note at the beginning that there is no indication of proton transfer in any of the complexes studied; hydrogen atoms participating in hydrogen bonds remain attached to their parent molecule. In the case of the phosphoric acid dimer, for example, this rules out any significant autoprotolysis:

$$2H_3PO_4 \rightarrow H_4PO_4^{+} + H_2PO_4^{-} \tag{3}$$

The types of hydrogen-bonded structures we find are illustrated schematically in Charts 1 and 2. Chart 1 shows the dihydrates of H_3PO_4 (a) and PO_4-3 (b), where the charges on the PO_4-3 anion are not shown for ease of presentation. The structure for $H_3PO_4{\cdot}2H_2O$ (a) shows the two kinds of bonds to water where water acts as both a donor (to the phosphoryl oxygen lone pairs) and an acceptor (from the POH hydrogens). When more than one nonprotonated phosphoric acid oxygen is present as in PO_4-3$\cdot 2H_2O$ (b), the waters interact strongly with two sets of P=O lone pairs, giving rise to an especially large stabilization energy; see Table 2.

The dimer and trimer of phosphoric acid are shown in Chart 2. These structures resemble that found in the solid,[6,7] a kind of "head-to-head" arrangement with respect to the phosphoryl groups. While there is but one such interaction in the dimer (a), the phosphoryl oxygen of the "central" acid moiety in the trimer (bottom molecule in Chart 2b) interacts with two POH hydroxyl hydrogens, very much like the situation in the solid. These interactions in the solid hold the phosphoric acid monomers together in sheets parallel to the (001) plane. Blessing[7] in his neutron diffraction study determines

CHART 2



a.

b.

TABLE 1: Stabilization Energies (kcal/mol) of Hydration of H_3PO_4 for the Three Approaches Employed in This Study

	B3LYP 6-311+ G(nd,p)	aug-cc-pvtz	MP2 6-311+ G(nd,p)	$\bar{x} \pm \sigma^a$
$H_3PO_4{\cdot}H_2O$	9.8	8.7	10.2	9.6 ± 0.6
$H_3PO_4{\cdot}2H_2O$	19.2	16.8	20.0	18.7 ± 1.4

[a] $\bar{x} \pm \sigma$ represents an average stabilization energy and standard deviation.

POH···O=P distances of 1.59 ± 0.03 Å with an OH···O angle of 175.2 ± 2.3° compared to our calculated values (B3LYP/6-311+G(d,p)) in the dimer of 1.588 Å and 171.7°, and 1.616 ± 0.024 Å and 171.9 ± 2.0° in the trimer, in reasonably good agreement. The slightly longer hydrogen bond distance in the trimer is commensurate with the slightly lower energy per hydrogen bond found there (vide infra). Attempts to form a dimer starting with a head-to-tail structure fail, resulting in the head-to-head complex shown in Chart 1a.

While the best way to calculated hydrogen bonding energies would be to optimize geometries and obtain energies by using a counterpoise-corrected potential energy surface, the energy results we present below have resulted from geometry optimizations without such counterpoise considerations. To obtain an estimate of the counterpoise correction we carried out one determination involving the $H_3PO_4{\cdot}H_2O$ complex in the B3LYP/6-311+G(d,p) approach. Without the counterpoise correction the lowering in energy is 9.80 kcal/mol, while using the counterpoise-correcting optimization method due to Dannenberg[27] the energy lowering is reduced to 8.82 kcal/mol. Accordingly, one may obtain a somewhat rough but better estimate of the hydrogen bond stabilization energies in the various cases by subtracting about 1.0 kcal/mol per hydrogen bond from the energies determined without counterpoise correction.

Table 1 shows that the three theoretical approaches used here give rise to basically similar stabilization energies, supporting our use of the smaller and faster sB3LYP/6-311+G(d,p) approach for the other hydrogen bonded systems studied. Table 2 contains all the stabilization energy data for this latter approach for all the phosphoric acid hydrates and for the phosphoric acid dimer and trimer. Again, the fact that several complexes are found for the H_2PO_4-1 and HPO_4-2 species illustrates the rather flat nature of the potential energy surface of these complexes.

Although the types of hydrogen bonds differ somewhat among the various complexes, the stabilization energy per hydrogen bond, a useful quantity, clearly shows that the bond energy increases noticeable as the charge on the phosphoric acid species, mainly on the phosphoryl oxygen, increases. This is to be expected since hydrogen bonding is thought to be essentially an electrostatic interaction, but the effect is likely a subtle one. Some of the hydrogen bond stabilization energies are rather impressive. The hydrogen bond stabilization energies found in the dimer and trimer are intermediate in character. The energy

TABLE 2: Hydrogen Bond Stabilizing Energies (Δ*E*, kcal/mol) and Stabilization Energies per Hydrogen Bond (Δ*E*/*n*, kcal/mol) for Hydrated H_3PO_4, Its Ionized Species, and the Dimer and Trimer of Phosphoric Acid at the B3LYP/6-311+G(d,p) Level[a]

	Δ*E*	HOH···O=P	POH···OH_2	POH···O=P	Δ*E*/*n*
			A. H_3PO_4		
$H_3PO_4{\cdot}H_2O$	9.8	1	1		4.9
$H_3PO_4{\cdot}2H_2O$	19.2	2	2		4.8
					4.8 ± 0.1
			B. H_2PO_4-1		
H_2PO_4-1·H_2O	13.7	2			6.8
	13.0	1	1		6.5
	14.2	1	1		7.1
H_2PO_4-1·$2H_2O$	27.0	3	1		6.8
	25.3	2	2		6.3
					6.7 ± 0.3
			C. HPO_4-2		
HPO_4-2·H_2O	29.2	2			14.6
HPO_4-2·$2H_2O$	54.9	4			13.7
	53.1	3	1		13.3
					13.9 ± 0.6
			D. PO_4-3		
PO_4-3·H_2O	47.0	2			23.5
PO_4-3·$2H_2O$	88.9	4			22.2
					22.9 ± 0.6
			E. phosphoric acid dimer and trimer		
$(H_3PO_4)_2$	22.2			2	11.1
$(H_3PO_4)_3$	35.9			4	9.0

[a] The numbers and types of hydrogen bonds are indicated in the table. Δ*E*/*n* averages for the parent compound are given as the final entry for each species.

TABLE 3: (A) Phosphorus Absolute Shieldings for H_3PO_4 and (B) Shieldings Relative to H_3PO_4 ($\delta_i = \sigma_{ref} - \sigma_i$) (All in ppm)[a]

	sB3LYP 6-311+ G(nd,p)	aug-cc-pvtz	EMPI 6-311+ G(nd,p)	$\bar{x} \pm \sigma$
	A. absolute shieldings			
H_3PO_4	345.1	337.5	332.2	338.3 ± 5.3
	B. shieldings relative to H_3PO_4.			
H_2PO_4-1	2.2	1.0	1.9	1.7 ± 0.5
HPO_4-2	25.2	17.8	25.2	22.7 ± 3.5
PO_4-3	43.4	32.2	43.1	39.6 ± 5.2
$H_4PO_4^+$	-4.5	-7.6	-1.3	-4.5 ± 2.5
$H_3PO_4{\cdot}H_2O$	8.1	2.4	4.0	4.8 ± 2.4
$H_3PO_4{\cdot}2H_2O$	7.6	-2.0	10.9	5.5 ± 5.5
$(H_3PO_4)_2$	−3.3			
$(H_3PO_4)_3$	3.4[b]			
	−3.5[c]			

[a] Positive δ values represent shifts to lower fields. $\bar{x} \pm \sigma$ represents an average shielding and standard deviation. The absolute experimental shielding for 85% phosphoric acid is 328.4. [b] The "outside" monomers in Chart 2b. [c] The central monomer in Chart 2b.

per hydrogen bond is lower in the trimer than in the dimer and is thought to be due to the slightly longer hydrogen bond distances found in the trimer.

SCRF Shielding Methods. One way to determine the effect of solvent is to use a self-consistent reaction field (SCRF) approach. To examine this approach we employed the COSMO method[22−26] to study the H_3PO_4 molecule using both the frozen gas-phase geometry and the geometry optimized with COSMO. Since one does not know here what is "solvent" and what "solute", we examined a range of dielectric constants ranging from 5.0 to 80.0 employing the sB3LYP/6-311+G(nd,p) approach. The *range* of shieldings was found to be 0.5 ppm in the former case and 1.2 ppm in the latter, completely negligible. The average shielding was 342.6 in the frozen geometry case and 343.5 in the COSMO-optimized case, these to be compared to the calculated gas-phase value of 345.1 ppm. But we know that SCRF approaches cannot properly treat systems in which hydrogen bonding occurs, so one must explicitly consider those cases.

Hydrogen Bonding Shielding Effects. We have considered phosphoric acid and its ions hydrogen bonded to one or two water molecules as well as the phosphoric acid dimer, $(H_3PO_4)_2$, and trimer, $(H_3PO_4)_3$. We have not performed a complete examination of all the complexes. While the water monomer, dimer, and trimer of H_3PO_4 would seem to be unique, we do not claim uniqueness for the water *n*-mers of the ionic species. What was done was to start with $H_3PO_4{\cdot}H_2O$ and $H_3PO_4{\cdot}2H_2O$ and remove one, two, and then three hydrogens from the acid in all possible combinations and optimize the resulting species. While likely not exhaustive, we do think our results provide a reasonable picture of the effects of bonding to water, both in terms of the hydrogen-bond stabilizing energy and the phosphorus chemical shielding. The structures of the hydrogen-bonded species were discussed earlier.

Table 3 shows the calculated shieldings for phosphoric acid, its anions, its protonated cation, and the mono- and dihydrates for the three theoretical approaches used here. Data for the dimer and trimer species are also given in Table 3, although because of time and space limitations they were only calculated in the sB3LYP/6-311+G(nd,p) approach. As was noted earlier for the hydrogen bond stabilization energies, results for the three approaches are all very similar, indicating again that the smaller and more rapid sB3LYP/6-311+G(nd,p) approach may be considered satisfactory for other studies. The last column in Table 3 provides means and standard deviations to illustrate this point; the mean values could be taken as an overall best estimate of the indicated shieldings. Table 3 shows that the EMPI results are consistently some 12.8 ppm to lower field than the sB3LYP/6-311+G(nd,p) approach, while the sB3LYP/aug-cc-pvtz are intermediate in character. We note a distinct break in the behavior of H_3PO_4 and H_2PO_4-1 compared to the other anionic species. Because the three approaches are so similar, further calculations involved only the sB3LYP/6-311+G(nd,p) approach.

TABLE 4: Relative Chemical Shieldings ($\delta_i = \sigma_{ref} - \sigma_i$) for the Water Monomers and Dimers for H_3PO_4 and Its Ionized Species in the SB3LYP/6-311+G(nd,p) Approach[a]

	water monomer	water dimer
H_3PO_4	8.1	7.6
H_2PO_4-1	−0.3 ± 1.6	0.9 ± 1.6
HPO_4-2	−5.9	−8.2
PO_4-3	−8.8	−15.0

[a] Relative values for each species are with regard to the corresponding gas-phase phosphoric acid species given in the left-most column. Where several complexes were found, only the average δ is reported. Positive δ values represent shifts to lower fields.

The situation for experimental results for solutions of phosphoric acid is unclear. Tebby and Glonek[30] indicate that "It is impractical to attempt to relate the chemical shifts of most naturally occurring phosphates to a specific acidic or anionic form; between pH 4 and 10 they often occur in an equilibrium mixture of undissociated, partially dissociated, and completely dissociated species"; the tabulated chemical shifts for these species[30] span the extremely small range of δ 0.1−2.6 ppm, in sharp contrast to the ranges we calculate of some 40 ppm (in the sB3LYP/6-311+G(nd,p) approach) for the isolated species. Although, as we point out later, this span is cut almost in half (21 ppm) when hydrated species are calculated, it is still an order of magnitude larger than that reported by Tebby and Glonek.

The second and more important point illustrated by the data in Table 3 is that hydration and di- and trimerization effects are small, less than 11 ppm, this to be compared to the current general error in calculating phosphorus chemical shieldings of about 18−20 ppm. We show in Table 4 the relative shieldings of the mono- and dihydrates in the sB3LYP/6-311+G(nd,p) approach. Only in the case of the phosphate trianion is the calculated effect significant at 15.0 ppm upfield. Note that while the hydrates of the undisocciated acid are shifted to lower field, those of the anions are either very small (H_2PO_4-1) or shifted upfield (HPO_4-2 and PO_4-3). Taking the dihydrate case this results in a decrease in the shielding range from H_3PO_4 to PO_4-3 from 43.4 to 20.8 ppm.

Dimer and trimers may well be present in concentrated solution, but the shielding effects of such aggregation are almost negligible, δ −3.5 to +3.4. These results and the expectation that the phosphoric acid anions (or cation) are likely not present in any significant amount suggest that the dihydrates might well be used as models for calculating the phosphorus shielding in 85% phosphoric acid. For the three approaches used here, the shieldings would be 337.5, 339.5, and 321.3 ppm for the sB3LYP/6-311+G(nd,p), sB3lYP/aug-cc-pvtz, and EMPI methods, respectively, yielding errors with respect to the observed shielding (328.4) of 9.1, 11.1, and −7.1, all quite "acceptable" in terms of our current ability to calculate phosphorus shieldings. We suggest, then, that the dihydrate would constitute a viable model for further, more sophisticated determinations of phosphorus shielding in 85% phosphoric acid.

A more complete determination, however, should involve rovibrational effects. Such effects can be sizable as shown most recently by Dransfeld[31] with rovibrational corrections for PH_3, CH_3PH_2, HCP, and CH_3CP of −9.2, −44.7, −50.7, and −24.0 ppm, respectively. But since our scaled DFT method is based on scaling the paramagnetic term of the shielding against experiment, in effect such rovibrational corrections as well as others not explicitly considered are to some extent already included. In a less empirical calculation, rovibrational corrections could be most important. Since our EMPI method is based on theoretical calculations which do not involve such corrections, this particular approach by itself should be used with some caution.

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(20) A referee has pointed out that the GIAO diamagnetic and paramagnetic contributions separately are not gauge invariant, but only their sum. In the GIAO approach, however, the diamagnetic contributions are quite uniform while the shielding range is determined almost exclusively by the paramagnetic term. It is the paramagnetic term that we scale in an empirical manner, much like DFT theory itself.

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