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# Effect of rotation and vibration on nuclear magnetic resonance chemical shifts: Density functional theory calculations

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The effect of rotation and vibration on the nuclear magnetic resonance (NMR) shielding constants was computed for HF, F<sub>2</sub>, N<sub>2</sub>, CO, and HBr. The shielding constants for H, C, N, O, and F nuclei were calculated using sum-over-states density functional perturbation theory (SOS-DFPT). Diatomic ro-vibrational states were calculated from a discrete variable representation using Morse potentials and potential curves calculated with density functional theory. Our ro-vibrational corrections to shielding constants for HF, CO, F<sub>2</sub>, and N<sub>2</sub> molecules are in good agreement with experimental data and CCSD(T) calculations. These results together with satisfactory first and second derivatives of the shielding constants with respect to interatomic distances confirm that the shielding surfaces produced by the SOS-DFPT method are of good accuracy, providing reassurance of the use of these methods for more complex systems. The unusual temperature dependence of the hydrogen chemical shift in HBr and a first attempt to include both relativistic spin-orbit and ro-vibration effects are discussed. © 1999 American Institute of Physics. [S0021-9606(99)30314-7]

## I. INTRODUCTION

Significant progress has recently been achieved in the development of post-Hartree-Fock<sup>1-4</sup> and density functional theory (DFT)<sup>5-11</sup> methods and programs for calculating nuclear magnetic resonance (NMR) shielding constants and spin-spin coupling constants. Using such programs one is able now to calculate (for example) shielding constants for given molecular geometries. Measured NMR chemical shifts do not, however, correspond to shielding constants computed at fixed molecular geometries, rather they are averaged over the motion of the nuclei (rotations and vibrations). In principle it is possible to measure a shielding constant for a particular ro-vibrational state, but in practice experimental measurements (at a given temperature) are averaged over different states. Fortunately, a chemical shift calculated at the equilibrium geometry is usually close to the observed value (how close depends on the temperature at which the measurement was taken, and the amplitude of the nuclear vibrations).

The difference between a shielding constant calculated at the equilibrium geometry and one averaged over the nuclear motion may be quite significant.<sup>12</sup> Deducing such differences (vibrational and ro-vibrational corrections) from experiment relies on assumptions whose accuracy is difficult to assess. Fortunately, high-level theoretical calculations of

ro-vibrational corrections to NMR shieldings are now accessible for small molecules.<sup>13</sup> The accuracy of such calculations is competitive with the accuracy of the best experiments. Comparison of theoretical and experimental data allows one to judge better the precision and shortcomings of both theory and experiment.

Calculation of a shielding constant for a particular state involves three steps: (i) one calculates the ro-vibrational energy level and the ro-vibrational wave function for the particular state using a Born-Oppenheimer potential; (ii) one calculates the shielding constant as a function of the nuclear coordinates; and (iii) one averages the shielding constant over the ro-vibrational wave function.

A temperature-dependent shielding constant is obtained from a Boltzmann average of the state-dependent shielding constants.<sup>14,15</sup> In principle, if the shielding constant functions, the potential and the ro-vibrational wave functions, are calculated with high accuracy, theoretical and experimental results should be in agreement within experimental error.<sup>14,15</sup> For small molecules the ro-vibrational energy levels and wave functions can be computed very accurately and the quality of the averaged shielding constants depends only on the accuracy of the shielding constant function and potential (energy surface).

At present, some of the most advanced and popular quantum chemical methods are those of DFT.<sup>16,17</sup> Nowadays the calculation of the NMR parameters using DFT has become increasingly popular and many studies devoted to the

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analysis of the accuracy of the DFT-based methods have been published (see, for example, recent reviews: Refs. 18 and 19). However, in chemical applications it is often crucial to know the dependence of the chemical shift (or other NMR parameters) on structural parameters (bond lengths, bond and torsion angles) rather than only at the equilibrium geometry. Therefore, there is a need for benchmark calculations which allow one to assess the quality of such calculated DFT parameter surfaces.

In this study we use a sum over states density functional perturbation theory (SOS-DFPT) method<sup>5,7</sup> to calculate the shielding constant function. This DFT based SOS-DFPT method is fast and accurate: for molecules for which correlation is relatively unimportant it is almost as good as MP2 and for molecules with strong correlation effects it is significantly more reliable<sup>7,20</sup> and much faster than MP2. As a result, this method is now used for studies of large transition metal complexes,<sup>21–23</sup> biological systems,<sup>24–26</sup> and solvation effects.<sup>27</sup> For many of these systems the effects of nuclear motion on shielding constants (and, in general, the dependence of shielding constants on structural parameters) are important.

Experimentally known isotope shifts and the temperature dependence of NMR chemical shifts provide a very good probe of the quality of the calculated NMR shielding constants as a function of structural parameters. In addition, for a few diatomic molecules, high-level CCSD(T) calculations of ro-vibration and isotope effects recently became available.<sup>13</sup> Therefore, in this paper we study the effect of vibration and rotation on the NMR shielding constants of HF, F<sub>2</sub>, CO, and N<sub>2</sub> for which ro-vibrational effects have been studied experimentally<sup>12,28,29</sup> and theoretically.<sup>13</sup> In ad-

dition, we have calculated the temperature dependence of the <sup>1</sup>H shielding constant in HBr, taking into account spin-orbit (SO) corrections to the shielding constant. It has previously been demonstrated that such corrections are important for an accurate calculation of the <sup>1</sup>H shielding constant of HBr at its equilibrium geometry,<sup>30–32</sup> but in this paper we calculate temperature-dependent shielding constants and (for the first time) the geometry dependence of the SO correction.

## II. METHOD

The temperature dependence of the shielding constant may be obtained by calculating the averaged shielding constant for many ro-vibrational states and evaluating a Boltzmann average. We calculate an independent molecule value for the shielding constant, i.e., we neglect interactions between molecules, but we assume nonetheless that the molecule's ro-vibrational states are thermally populated. To calculate the averaged shielding constants one requires ro-vibrational wave functions and the shielding constant  $\sigma$  as a function of the internuclear separation  $r$ . For a given diatomic molecule we calculate ro-vibrational wave functions from either the potential obtained using the deMon-KS code<sup>33</sup> or a Morse potential, determined from experimental parameters. In all cases the spectroscopic constants required to define the Morse potential were taken from Ref. 34.

For a heteronuclear diatomic molecule we calculate  $\sigma(T)$  using

$$\sigma(T) = \frac{\sum_n \sum_J (2J+1) \sigma_{nJ} e^{-E_{nJ}/KT}}{\sum_n \sum_J (2J+1) e^{-E_{nJ}/KT}}. \quad (1)$$

For a homonuclear diatomic molecule we calculate  $\sigma(T)$  using

$$\sigma(T) = \frac{\sum_n \sum_J \sum_{I'} \sum_{M_I'=-I'+1}^{I'} [I(I+1) - M_I'(M_I'-1)] (2J+1) \sigma_{nJ} e^{-E_{nJ}/KT}}{\sum_n \sum_J \sum_{I'} \sum_{M_I'=-I'+1}^{I'} [I(I+1) - M_I'(M_I'-1)] (2J+1) e^{-E_{nJ}/KT}}, \quad (2)$$

where

$$\sigma_{nJ} = \langle nJ | \sigma(r) | nJ \rangle \quad (3)$$

and

$$H | nJ \rangle = E_{nJ} | nJ \rangle \quad (4)$$

with

$$H = -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + U + \frac{\hat{J}^2}{2\mu r^2}. \quad (5)$$

$\mu$  is the reduced mass, and  $U$  is the potential.  $\hat{J}$  is the total angular momentum operator,  $J$  is the corresponding quantum number,  $n$  is the vibrational quantum number, and  $I$  is the total nuclear spin. The primed summations denote restricted sums over the allowed spin states. For a homonuclear molecule with two nuclei of integral spin, if  $J$  is even, one sums over only the symmetric spin states and, if  $J$  is odd, one sums over only the antisymmetric spin states. For nuclei of

half-integral spin, if  $J$  is even, one sums over only the antisymmetric spin states and, if  $J$  is odd, one sums over only the symmetric spin states.

The equation for  $\sigma(T)$  for a homonuclear diatomic is justified as follows. In principle, with enough resolution, an experimentalist could measure  $\sigma_{nJ}$  for each ro-vibrational state  $|nJ\rangle$ . In practice, one observes a superposition of the individual  $\sigma_{nJ}$ . We propose that to compare with experimental results an intensity-weighted average is appropriate. If the transition associated with  $\sigma_{nJ}$  is intense, it makes a more important contribution to the average. To compute the average we therefore weight the  $\sigma_{nJ}$  with the intensities of the corresponding transitions. To compute the intensities one needs the population of the ro-vibrational level within which the spin transition occurs and also the intensities of the spin transitions within a ro-vibrational level. The sums over  $M_I$  account for the spin transitions which contribute to  $\sigma_{nJ}$  for a particular value of  $I$ . The factor of  $[I(I+1) - M_I(M_I-1)]$

is proportional to the intensity of a single transition (from  $IM_I$  to  $IM_I - 1$ ). For a molecule with two spin 1/2 nuclei (for example,  $F_2$ ) there are two possible values of  $I$ : 1 and 0. The  $I=1$  states are symmetric under exchange and associated with odd values of  $J$ ; there are two possible transitions. There are no transitions between antisymmetric spin states because there is only one of them (the  $I=0$  state). Hence, for a molecule with two spin 1/2 nuclei the sums over the nuclear spin labels and the sums over the ro-vibrational labels are independent so the sums over the nuclear labels in the numerator and denominator cancel. For a molecule with two spin 1 nuclei (such as  $^{14}N_2$ ) there are three possible values of  $I$ : 2, 1, and 0. The  $I=2$  and  $I=0$  states are symmetric under exchange, there are four possible transitions for  $I=2$  and no possible transitions for  $I=0$  (because there is only one  $I=0$  state). These transitions occur for even values of  $J$ . The  $I=1$  states are antisymmetric under exchange; there are two possible transitions for  $I=1$  ( $J$  is odd). In this case the sums are not independent and the intensity factors do not cancel.

Several authors have calculated  $\sigma(T)$  using Eq. (1) with  $\sigma_{vJ}$  being computed perturbatively or semiclassically<sup>12,35,36</sup> or from numerically exact ro-vibrational wave functions (e.g., Ref. 13). For a diatomic molecule it is easy to calculate  $\sigma_{nJ}$  exactly (numerically). We have calculated diatomic ro-vibrational wave functions by diagonalizing a matrix representation of the Hamiltonian. In this work we use the discrete variable representation (DVR)<sup>37</sup> which corresponds to the Morse-like basis functions defined as in Ref. 38. The Morse-like basis functions are chosen so that (if matrix elements are evaluated exactly)  $N$  basis functions span exactly the space spanned by  $N$  eigenfunctions of  $H$  if  $J=0$ . We calculate enough ro-vibrational wave functions to converge the sums in Eq. (1): for each value of  $J$  we compute solutions of Eq. (3) until the contribution of  $|nJ\rangle$  with the largest value of  $n$  to the sum in the denominator of Eq. (1) is less than 0.001.

To calculate  $\sigma_{vJ}$  we use the matrix of eigenvectors ( $\mathbf{L}$ ) of the DVR of  $H$ :

$$\sigma_{vJ} = \sum_{\alpha} (L_{\alpha,vJ})^t \sigma(r_{\alpha}) L_{\alpha,vJ}, \quad (6)$$

where the  $r_{\alpha}$  are the DVR points. If one uses the DVR, it is not necessary to fit a functional form to shielding constants computed at specific bond lengths nor to employ some kind of interpolation; if shielding constants are computed at the DVR points, they can be used directly. We first determine which DVR points are required to converge the sum of Eq. (1) and then computed  $\sigma(r)$  at these (and only at these) points.

Shielding constants have been calculated using a modified version of the deMon-KS program<sup>33</sup> augmented by the deMon-NMR code using sum-over-states density functional perturbation theory (within the Loc.1 approximation<sup>5</sup>) combined with the "individual gauge for localized orbitals" (IGLO) method.<sup>39,5,7</sup> All shielding constants have been calculated with the Perdew and Wang exchange-correlation potential<sup>40</sup> (PW91), a FINE grid with 64 radial shells<sup>41</sup> (F64), and the basis set BIII (also called IGLO-III in some previous publications) of Kutzelnigg *et al.*<sup>39</sup> Since the basis

TABLE I. Experimental and calculated equilibrium bond lengths (in Å).

Molecule	$r_{\text{exp}}$	$r_{\text{calc}}$
$F_2$	1.412	1.418
$N_2$	1.098	1.101
HF	0.917	0.931
CO	1.128	1.135
HBr	1.414	1.432

set BIII is not available for Br, in calculations for HBr we used the basis set BII<sup>39</sup> (also known as IGLO-II).

A new method for the calculation of the SO correction to shielding constants was recently described in detail.<sup>30</sup> For the calculation of the SO correction to the  $^1H$  shielding constant in HBr, the Perdew and Wang exchange<sup>42</sup> with Perdew correlation functional<sup>43</sup> (PP) was employed.

Shielding constants were calculated for a set of interatomic distances for HF,  $F_2$ , CO,  $N_2$ , and HBr. These points are the DVR quadrature points generated for each molecule. For numerical calculation of the first and second derivatives of  $\sigma$  with respect to  $\xi = (r - r_e)/r_e$  a two-point finite difference formula and the points  $r = r_e \pm 0.05$  Å have been used (where  $r_e$  is the equilibrium bond length).

For the calculation of ro-vibrational states we use two different approximations for the potentials: a Morse potential and the total energies calculated by the DFT method with the deMon-KS code using the same options as for the NMR calculation. In both cases the potential was calculated at the DVR quadrature points. In calculations with the Morse po-

TABLE II. First [ $\sigma'(r_e)$ ] and second [ $\sigma''(r_e)$ ] derivatives of  $\sigma$  (in ppm) with respect to  $\xi = (r - r_e)/r_e$ .

Molecule	Nucleus	Method	$\sigma'(r_e)$	$1/2 \cdot \sigma''(r_e)$
$F_2$	$^{19}F$	Exp. (Ref. 35)	-6587	
		DFT	-3750	-7764
		CCSD(T) (Ref. 13) <sup>a</sup>	-3913	-9576
$N_2$	$^{14}N$	Exp. (Ref. 46)	-850 ± 100	
		DFT	-779	-912
		CCSD(T) (Ref. 13) <sup>a</sup>	-801	-919
HF	$^1H$	Exp. (Ref. 29)	-37	57
		DFT	-35.5	60.5
		CCSD(T) (Ref. 13) <sup>a</sup>	-36.2	58.5
	$^{19}F$	Exp. (Ref. 29)	-378	-568
		DFT	-429	-724
		CCSD(T) (Ref. 13) <sup>a</sup>	-370	-610
CO	C	Exp. (Ref. 29)	-404 ± 13	
		(Ref. 46)	-255 ± 50	
		DFT	-399	-276
		CCSD(T) (Ref. 13) <sup>a</sup>	-442	-320
		RPA (Ref. 14)	-648	-1048
		SOPPA (Ref. 14)	-583	-760
	O	MECI (Ref. 14)	-423	-632
		Exp. (Ref. 29)	-1019 ± 115	
		DFT	-890	-1259
		CCSD(T) (Ref. 13) <sup>a</sup>	-991	-1420
		RPA (Ref. 14)	-1298	-2915
		SOPPA (Ref. 14)	-1110	-1763
		MECI (Ref. 14)	-717	-1382

<sup>a</sup>Values obtained from the fitting procedure (see Ref. 13).

tential the experimental equilibrium distances were taken from Ref. 34 whereas the equilibrium distances employed with deMon-KS potentials were determined by optimizing with the deMon-KS code (see Table I).

### III. RESULTS

We start our discussion with calculated first and second derivatives of  $\sigma(r)$  with respect to  $\xi$ . Although we do not use these derivatives directly to calculate ro-vibrational corrections to chemical shifts it is nonetheless useful to examine derivatives of  $\sigma(r)$  at the equilibrium geometry. In Table II we present our results for the first and second derivatives of  $\sigma$  calculated by the deMon-NMR code (DFT) in comparison with available theoretical [CCSD(T),<sup>13</sup> RPA, SOPPA, MECI<sup>14</sup>] and experimental data. The DFT results are in good agreement with CCSD(T) results (with a somewhat bigger deviation for F in F<sub>2</sub> and for O in CO) whereas other theoretical methods give a bigger scatter. Also, the DFT and CCSD(T) results agree significantly better with experimental data than the results of other methods. For the F<sub>2</sub> molecule the DFT and CCSD(T) values for  $\sigma'(r_e)$  are in good mutual agreement, but in obvious disagreement with the experimental value. We believe the latter should be reexamined.

Since CCSD(T) is likely the most accurate method now available for calculating NMR shielding constants (competitive in accuracy with experiment), it gives us an opportunity to evaluate the quality of the DFT results. According to the results presented in Table II the SOS-DFPT method yields quite accurate shielding derivatives at the level of theory used in this study (BIII basis set, PW91 exchange-correlation potential, and F64 grid for the numerical integration). These computational choices are typical of the numerous applications of the method in a variety of contexts. We have not attempted to get to the basis set limit, nor explore other computational options exhaustively. We do not see the DFT methods as competition for the very high accuracy correlated ab initio techniques but, rather, view the level of agreement shown in Table II as being highly reassuring for the practical applications of DFT for NMR. Being computationally very fast, SOS-DFPT can be applied at the same level of theory to large systems of real chemical interest. We expect the same accuracy of the SOS-DFPT method in other applications.

The shielding constants calculated at the equilibrium geometries and the temperature dependence of  $\sigma$  are reported in Table III. The accuracy of our computed  $\sigma(T)$  values depends not only on the quality of the  $\sigma(r)$  calculations, but also on the quality of the potential used to compute the ro-vibrational states. The deMon and Morse potentials give somewhat different results for  $\sigma(0\text{ K})$  and  $\sigma(300\text{ K})$  but the differences,  $\sigma(300\text{ K}) - \sigma(0\text{ K})$ , are closer to each other. This suggests that the difference between the Morse and deMon results is mainly due to the difference in the equilibrium bond lengths but the shape of the potential curves is similar. The difference in the temperature shift [ $\sigma(300\text{ K}) - \sigma(0\text{ K})$ ] calculated with Morse and deMon potentials is larger for F in F<sub>2</sub> and HF which indicates a larger deviation between the shape of these potentials.

The vibrational and ro-vibrational corrections for  $\sigma$  calculated with the deMon and Morse potentials are compared

TABLE III.  $\sigma(0\text{ K})$ ,  $\sigma(300\text{ K})$ , and  $\sigma(r_e)$  (in ppm) calculated using Morse and deMon potentials.

Molecule	Nucleus	Potential	$\sigma(0\text{ K})$	$\sigma(300\text{ K})$	$\sigma(r_e)$	$\sigma(300\text{ K}) - \sigma(0\text{ K})$
F <sub>2</sub>	<sup>19</sup> F	Morse	-231.64	-236.01	-204.02	-4.37
F <sub>2</sub>	<sup>19</sup> F	deMon	-243.23	-246.79	-219.57	-3.56
N <sub>2</sub>	<sup>14</sup> N	Morse	-58.95	-59.08	-55.50	-0.13
N <sub>2</sub>	<sup>14</sup> N	deMon	-61.54	-61.66	-58.19	-0.12
N <sub>2</sub>	<sup>15</sup> N	Morse	-58.84	-59.07	-55.50	-0.23
N <sub>2</sub>	<sup>15</sup> N	deMon	-61.43	-61.67	-58.19	-0.24
HF	<sup>1</sup> H	Morse	29.27	29.24	29.52	-0.035
HF	<sup>1</sup> H	deMon	28.70	28.67	28.99	-0.035
HF	<sup>19</sup> F	Morse	399.36	398.87	410.25	-0.48
HF	<sup>19</sup> F	deMon	391.08	390.53	403.49	-0.54
DF	<sup>2</sup> D	Morse	29.25	29.21	29.52	-0.035
DF	<sup>2</sup> D	deMon	28.69	28.66	28.99	-0.036
DF	<sup>19</sup> F	Morse	402.81	402.34	410.19	-0.47
DF	<sup>19</sup> F	deMon	394.91	394.38	403.49	-0.54
<sup>13</sup> C <sup>16</sup> O	<sup>13</sup> C	Morse	8.01	7.87	9.63	-0.139
<sup>13</sup> C <sup>16</sup> O	<sup>13</sup> C	deMon	5.69	5.54	7.35	-0.144
<sup>12</sup> C <sup>17</sup> O	<sup>17</sup> O	Morse	-45.65	-45.96	-41.42	-0.313
<sup>12</sup> C <sup>17</sup> O	<sup>17</sup> O	deMon	-50.89	-51.21	-46.53	-0.328
<sup>13</sup> C <sup>17</sup> O	<sup>13</sup> C	Morse	8.03	7.90	9.63	-0.139
<sup>13</sup> C <sup>17</sup> O	<sup>13</sup> C	deMon	5.72	5.57	7.35	-0.145
<sup>13</sup> C <sup>17</sup> O	<sup>17</sup> O	Morse	-45.55	-45.86	-41.42	-0.313
<sup>13</sup> C <sup>17</sup> O	<sup>17</sup> O	deMon	-50.78	-51.11	-46.53	-0.328

with CCSD(T) results and experimental data in Tables IV and V. Since the experimental estimates involve some assumptions and approximations, we will compare our results mostly with available CCSD(T) data, considering them as more reliable.

For H in HF the results with the deMon potential are very close to the experimental and CCSD(T) values whereas the Morse potential results slightly underestimate the vibrational and ro-vibrational corrections. However, the opposite trend is found for <sup>19</sup>F corrections in HF: the results with the Morse potential are in good accord with experiment and CCSD(T) values and the results are slightly worse for the deMon potential. For CO the deMon and Morse potentials

TABLE IV. Vibrational corrections for shielding constants;  $\sigma(0\text{ K}) - \sigma(r_e)$  (in ppm).

Molecule	Nucleus	Morse	deMon	Others
<sup>19</sup> F <sub>2</sub>	F	-27.62	-23.66	-30.87 (Ref.13)
<sup>14</sup> N <sub>2</sub>	N	-3.45	-3.35	-3.39 (Ref.12)
<sup>15</sup> N <sub>2</sub>	N	-3.34	-3.24	-4.03 (Ref.13)
<sup>1</sup> H <sup>19</sup> F	H	-0.25	-0.29	-0.34 (Ref.12)
				-0.323 (Ref.13)
	F	-10.89	-12.41	-9.3 (Ref.12)
				-10.00 (Ref.13)
<sup>13</sup> C <sup>16</sup> O	C	-1.62	-1.66	-2.13 (Ref.12)
				-2.24 (Ref.13)
<sup>12</sup> C <sup>17</sup> O	O	-4.23	-4.36	-2.48 (Ref.12)
				-5.73 (Ref.13)

TABLE V. Ro-vibrational corrections for shielding constants;  $\sigma(300\text{ K}) - \sigma(r_e)$  (in ppm).

Molecule	Nucleus	Morse	deMon	Others	
$^{19}\text{F}_2$	F	-31.99	-27.22	-40	(Ref.12)
				-35.56	(Ref.13)
$^{14}\text{N}_2$	N	-3.58	-3.47		
$^{15}\text{N}_2$	N	-3.57	-3.48	-4.27	(Ref.13)
$^1\text{H}^{19}\text{F}$	H	-0.28	-0.32	-0.38	(Ref.47)
				-0.358	(Ref.13)
	F	-11.38	-12.96	$-9.75 \pm 3$	(Ref.47)
				-11.2	(Ref.48)
				-10.42	(Ref.13)
$^{13}\text{C}^{16}\text{O}$	C	-1.76	-1.80	-2.0	(Ref.49)
				-2.74	(Ref.48)
				-2.39	(Ref.13)
$^{12}\text{C}^{17}\text{O}$	O	-4.54	-4.69	-5.56	(Ref.48)
				-6.07	(Ref.13)

produce very similar results for both nuclei. These results are also in reasonable agreement with CCSD(T) and experimental values.

The difference between the DFT (calculated with the DFT potential) and CCSD(T) vibrational corrections presented in Table IV varies from about 20% to 26%. At the same time  $\sigma'(r_e)$  and  $\sigma''(r_e)$  calculated by DFT have smaller (some times much smaller) deviations from their CCSD(T) counterparts (see Table II). In particular, the derivatives differ from their CCSD(T) counterparts by about 2.7% and 0% for  $\text{N}_2$ , 2% and 3% for  $^1\text{H}$  in HF, and from 4% to 19% for  $\text{F}_2$ , CO, and  $^{19}\text{F}$  in HF. Two factors determine the accuracy of our calculated ro-vibrational corrections: the quality of the dependence of NMR shielding constants on the bond length and the quality of the potential curves. To some extent the quality of the dependence of the NMR shielding constant on the bond length can be judged by  $\sigma'(r_e)$  and  $\sigma''(r_e)$ . As the DFT and CCSD(T) first and second derivatives are close it might be that the differences between DFT and CCSD(T) vibrational corrections are due mostly to differences in the potential functions.

Comparison of experimental isotopic shifts with their calculated counterparts provides another sensitive test of the quality of the theoretical shielding and energy surfaces. The results for different isotopes calculated with deMon and Morse potentials are shown in Table VI together with experimental and other calculated data.

TABLE VI. Isotope shifts (in ppm).

Molecule	Isotope shift	MECI (Ref. 14)	RPA (Ref. 14)	SOPPA (Ref. 14)	CCSD(T) (Ref. 50)	DFT Morse	DFT deMon	Exp.
CO	$\sigma_c(^{13}\text{C}^{16}\text{O})$ $-\sigma_c(^{13}\text{C}^{17}\text{O})$	-0.029	-0.044	-0.035	-0.0267	-0.022	-0.023	$-0.0247 \pm 0.0045$ (Ref. 29)
CO	$\sigma_o(^{12}\text{C}^{17}\text{O})$ $-\sigma_o(^{13}\text{C}^{17}\text{O})$	-0.09	-0.172	-0.128	-0.117	-0.098	-0.103	$-0.110 \pm 0.011$ (Ref. 29)
HF	$\sigma_F(\text{DF})$ $-\sigma_F(\text{HF})$				2.88	3.46	3.84	$2.5 \pm 0.5$ (Ref. 47)

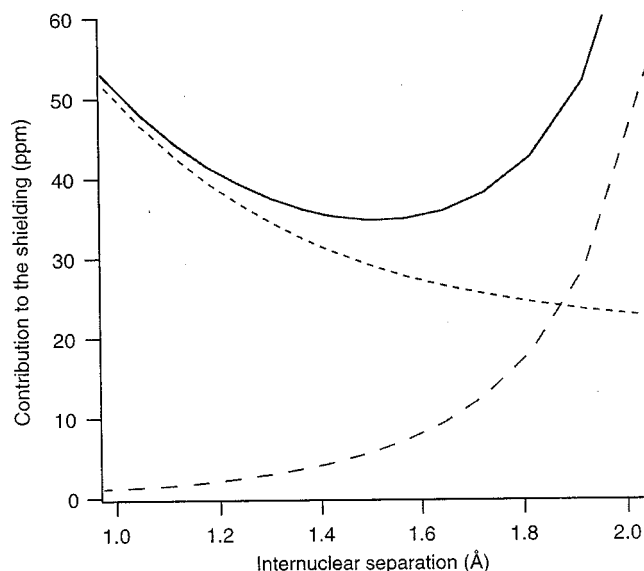


FIG. 1. The shielding constant we employ (the solid curve) is a sum of the spin-orbit term (the long dashed curve) and the standard term (the short dashed curve).

In addition to HF,  $\text{F}_2$ ,  $\text{N}_2$ , and CO, HBr was chosen as an example because of its very unusual  $^1\text{H}$  shielding constant (35.63 ppm at 0 K) and because ro-vibrational corrections have been reported.<sup>12,28</sup> [We note that in the review of Jameson<sup>12</sup>  $\sigma(300\text{ K}) - \sigma(r_e)$  was given as 7.11 ppm despite the fact that in the original experimental paper<sup>28</sup> only a combination of  $\sigma(r_e)$  and  $\sigma''(r_e)$  was given.] As demonstrated earlier<sup>30-32</sup> the unusual  $^1\text{H}$  chemical shift is due to relativistic spin-orbital effects. Since we have shown that our DFT approach gives a good description of such effects for the  $^1\text{H}$  chemical shift of HF, HCl, HBr, and HI<sup>30,31</sup> and for  $^{13}\text{C}$  shifts<sup>30,31,44</sup> at equilibrium we use it in this study to estimate the influence of spin-orbit effects on ro-vibrational corrections to  $^1\text{H}$  shielding constants in HBr. To do this, we calculated the SO correction to the shielding as a function of the interatomic distance in HBr. After adding the SO correction to the uncorrected  $\sigma$  at every grid point we calculated temperature-dependent shielding constants as described above. To the best of our knowledge this is the first time a geometry-dependent SO correction has been calculated and used to compute  $\sigma(T)$ . The dependence of the  $^1\text{H}$  shielding constant without and with the spin-orbit correction and of the SO correction itself (in HBr) on the H-Br bond length are presented in Fig. 1.  $\sigma$  without the SO correction has a typical

form (shielding constants usually decrease as the interatomic distance is increased), whereas the SO correction behaves differently. As a result, the total shielding constant (with the SO correction) as a function of the internuclear distance has a non-monotonic U-shape and the corresponding ro-vibrational correction is small (0.34 ppm) with an unusual positive sign (in contrast to the experimental value of  $-7.11 \text{ ppm}^{28}$ ). This discrepancy might plausibly be due to the fact that we used only the one-electron SO term in our calculations. The influence of the omitted two-electron SO terms is quite small at the equilibrium bond lengths for hydrogen halides<sup>31</sup> but the two-electron terms could conceivably have a strong dependence on the interatomic distance and therefore might contribute noticeably to the temperature dependence and ro-vibration corrections for the  $^1\text{H}$  chemical shift. To verify these speculations both one- and two-electron terms for the SO corrections to chemical shifts should be calculated. This work is in progress. However, we expect that the two-electron contributions will not change our results dramatically. It seems more likely that the experimental result is in error. The author of the experimental study<sup>28,45</sup> has also indicated that an additional experimental study of HBr would be desirable to clarify the reliability of the present experimental data. We have established that the one-electron contribution to the SO correction to  $\sigma$  for HBr depends strongly on the interatomic distance and that this affects ro-vibrational corrections. To determine the shielding it would not be sufficient to simply add on the SO correction at equilibrium.

#### IV. CONCLUSION

We have demonstrated that it is possible to calculate temperature-dependent shielding constants of good accuracy by combining the density functional based SOS-DFPT approach<sup>5,7</sup> for chemical shift calculations and ro-vibrational wave functions calculated in the DVR. The first and second derivatives of the shielding constants of HF, F<sub>2</sub>, N<sub>2</sub>, and CO are in good agreement with available experimental and CCSD(T) data. This validates the quality of the shielding surfaces calculated with the SOS-DFPT method. This is important because the method is potentially useful for NMR structure determination where the ability of a method to provide reliable dependences of the NMR chemical shifts and indirect spin-spin coupling constants on geometrical parameters is crucial.

In addition, for the first time, the spin-orbit contribution to ro-vibrational corrections to the  $^1\text{H}$  chemical shift in HBr was calculated. We demonstrate that the SO correction not only changes the value of the shielding constant but also, due to the strong dependence of the SO correction on the interatomic distance, rather dramatically affects the temperature dependence of the shielding constant. Although including the SO correction at equilibrium appears to improve the agreement with experiment, the calculated ro-vibrational correction is in dramatic disagreement with experimental data. More theoretical and experimental work is needed to explain the published<sup>28</sup> unusual behavior of the  $^1\text{H}$  chemical shift in HBr.

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