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Influence of the Nuclear Charge Distribution and Electron Correlation Effects on Magnetic Shieldings and Spin-Rotation Tensors of Linear Molecules

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Table 1 Nuclear spin-rotation constants ($M_\perp$) and isotropic shieldings (σ^{iso}) of the H and Br nuclei in HBr, employing the two analyzed nuclear models: a point-type one and a Gaussian-type one. The experimental internuclear distance was used: d = 1.4145 Å. Values between brackets correspond to calculations including (SS|SS) type integrals, whereas those between parenthesis include (SS|SS) and Gaunt integrals.

Y		PZOA ($30c_0$)	RPA ($30c_0$)	PZOA	RPA	LDA	KT2	KT3	PBE	PBE0	BP86
					Nuclear spin-rotation constant, $M_{\perp,Y}$ [kHz]						
Br	PNM	-108.6606	-284.5379	-111.1213 [-111.1209] (-111.0160)	-281.1629 [-281.1691] (-281.1502)	-302.5772 [-302.5758]	-305.3965 [-305.3957]	-316.7480 [-316.7474]	-314.6035 [-314.6030]	-300.2340 [-300.2351] (-300.0609)	-320.4714 [-320.4709]
	GNM	-108.6597	-284.5349	-111.1394 [-111.1389] (-111.0337)	-281.2376 [-281.2436] (-281.2234)	-302.6449 [-302.6434]	-305.4669 [-305.4660]	-316.8214 [-316.8208]	-314.6770 [-314.6764]	-300.3065 [-300.3076] (-300.1321)	-320.5455 [-320.5449]
	NChDE	0.0009	0.0030	-0.0181 [-0.0181] (-0.0177)	-0.0747 [-0.0745] (-0.0732)	-0.0677 [-0.0676]	-0.0704 [-0.0703]	-0.0734 [-0.0734]	-0.0734 [-0.0734]	-0.0726 [-0.0725] (-0.0711)	-0.0740 [-0.0740]
H	PNM	21.7669	32.0639	24.4273 [24.4258] (24.4072)	45.4058 [45.3968] (45.1899)	43.1662 [43.1577]	46.0621 [46.0513]	46.7120 [46.7008]	45.4836 [45.4737]	44.4968 [44.4875] (44.3096)	45.6609 [45.6509]
	GNM	21.7669	32.0638	24.4271 [24.4256] (24.4070)	45.4053 [45.3962] (45.1894)	43.1658 [43.1573]	46.0616 [46.0509]	46.7116 [46.7003]	45.4832 [45.4733]	44.4964 [44.4871] (44.3092)	45.6605 [45.6505]
	NChDE	0.0000	-0.0001	-0.0002 [-0.0001] (-0.0002)	-0.0005 [-0.0006] (-0.0005)	-0.0004 [-0.0004]	-0.0004 [-0.0004]	-0.0004 [-0.0004]	-0.0004 [-0.0004]	-0.0004 [-0.0004] (-0.0004)	-0.0004 [-0.0004]
					Isotropic shielding, σ_Y^{iso} [ppm]						
Br	PNM	2934.7759	2632.7988	3226.0599 [3225.9587] (3222.1472)	2950.6485 [2950.6349] (2947.4196)	2910.8943 [2910.7192]	2919.0271 [2918.8493]	2898.9895 [2898.8116]	2893.5890 [2893.4118]	2918.3226 [2918.1864] (2915.2386)	2883.9257 [2883.7485]
	GNM	2934.7550	2632.7819	3224.3662 [3224.2652] (3220.4664)	2948.7959 [2948.7822] (2945.5751)	2909.0611 [2908.8867]	2917.1402 [2916.9631]	2897.1082 [2896.9311]	2891.7377 [2891.5613]	2916.4730 [2916.3373] (2913.3978)	2882.0706 [2881.8942]
	NChDE	-0.0209	-0.0169	-1.6937 [-1.6935] (-1.6808)	-1.8526 [-1.8527] (-1.8445)	-1.8332 [-1.8325]	-1.8869 [-1.8862]	-1.8813 [-1.8805]	-1.8513 [-1.8505]	-1.8496 [-1.8491] (-1.8408)	-1.8551 [-1.8543]
H	PNM	26.0275	30.4725	27.1497 [27.1492] (27.1467)	35.9329 [35.9296] (35.8549)	34.8382 [34.8350]	36.5981 [36.5940]	37.0650 [37.0607]	36.2181 [36.2143]	35.7171 [35.7136] (35.6493)	36.3191 [36.3153]
	GNM	26.0275	30.4724	27.1496 [27.1491] (27.1466)	35.9327 [35.9293] (35.8547)	34.8380 [34.8348]	36.5979 [36.5938]	37.0648 [37.0605]	36.2179 [36.2141]	35.7169 [35.7134] (35.6491)	36.3189 [36.3151]
	NChDE	0.0000	-0.0001	-0.0001 [-0.0001] (-0.0001)	-0.0002 [-0.0003] (-0.0002)	-0.0002 [-0.0002]	-0.0002 [-0.0002]	-0.0002 [-0.0002]	-0.0002 [-0.0002]	-0.0002 [-0.0002] (-0.0002)	-0.0002 [-0.0002]

Table 2 Nuclear spin-rotation constants ($M_\perp$) and isotropic shieldings (σ^{iso}) of the H and I nuclei in HI, employing the two analyzed nuclear models: a point-type one and a Gaussian-type one. The experimental internuclear distance was used: d = 1.6090 Å. Values between brackets correspond to calculations including (SS|SS) type integrals, whereas those between parenthesis include (SS|SS) and Gaunt integrals.

Y		PZOA ($30c_0$)	RPA ($30c_0$)	PZOA	RPA	LDA	KT2	KT3	PBE	PBE0	BP86
					Nuclear spin-rotation constant, $M_{\perp,Y}$ [kHz]						
I	PNM	-134.2340	-346.5791	-141.7894 [-141.7871] (-141.5623)	-323.2582 [-323.2981] (-323.3529)	-366.9842 [-366.9835]	-367.2402 [-367.2453]	-383.0108 [-383.0188]	-378.4064 [-378.4109]	-358.0007 [-358.0154] (-357.7010)	-386.3860 [-386.3901]
	GNM	-134.2312	-346.5700	-141.8726 [-141.8700] (-141.6437)	-323.8411 [-323.8800] (-323.9274)	-367.3687 [-367.3671]	-367.6544 [-367.6585]	-383.4683 [-383.4752]	-378.8431 [-378.8465]	-358.4662 [-358.4798] (-358.1596)	-386.8215 [-386.8245]
	NChDE	0.0027	0.0091	-0.0832 [-0.0829] (-0.08136)	-0.5829 [-0.5819] (-0.5745)	-0.3845 [-0.3835]	-0.4143 [-0.4132]	-0.4576 [-0.4564]	-0.4367 [-0.4356]	-0.4654 [-0.4640] (-0.4575)	-0.4355 [-0.4344]
H	PNM	17.0918	25.4931	22.7365 [22.7314] (22.6966)	59.8888 [59.8514] (59.4958)	49.6970 [49.6657]	56.4414 [56.4007]	58.3918 [58.3486]	53.9112 [53.8748]	53.3935 [53.3587] (53.0795)	54.1477 [54.1112]
	GNM	17.0917	25.4929	22.7358 [22.7307] (22.6959)	59.8843 [59.8468] (59.4914)	49.6946 [49.6633]	56.4385 [56.3978]	58.3888 [58.3455]	53.9086 [53.8722]	53.3907 [53.3559] (53.0767)	54.1451 [54.1087]
	NChDE	-0.0001	-0.0002	-0.0007 [-0.0007] (-0.0007)	-0.0046 [-0.0045] (-0.0044)	-0.0024 [-0.0023]	-0.0029 [-0.0029]	-0.0030 [-0.0030]	-0.0026 [-0.0025]	-0.0029 [-0.0028] (-0.0028)	-0.0026 [-0.0025]
					Isotropic shielding, σ_Y^{iso} [ppm]						
I	PNM	5128.7423	4537.2284	6355.1037 [6354.2965] (6343.7810)	5885.4731 [5885.2471] (5877.0775)	5759.6292 [5758.3801]	5782.3643 [5781.0879]	5736.4805 [5735.1992]	5734.4430 [5733.1762]	5791.1468 [5790.1362] (5783.0043)	5712.0920 [5710.8278]
	GNM	5128.6466	4537.1502	6337.7902 [6336.9903] (6326.5699)	5866.4338 [5866.2074] (5858.0949)	5741.1681 [5739.9342]	5763.3332 [5762.0726]	5717.4484 [5716.1832]	5715.7642 [5714.5130]	5772.3940 [5771.3947] (5764.3185)	5693.3976 [5692.1491]
	NChDE	-0.0957	-0.0782	-17.3135 [-17.3062] (-17.2111)	-19.0381 [-19.0397] (-18.9826)	-18.4611 [-18.4459]	-19.0311 [-19.0153]	-19.0321 [-19.0160]	-18.6788 [-18.6632]	-18.7528 [-18.7415] (-18.6858)	-18.6944 [-18.6787]
H	PNM	26.5857	31.3008	29.4971 [29.4950] (29.4880)	48.0670 [48.0519] (47.9163)	42.9733 [42.9603]	46.9451 [46.9281]	48.1207 [48.1026]	45.5363 [45.5211]	45.1497 [45.1353] (45.0277)	45.6874 [45.6723]
	GNM	26.5856	31.3007	29.4965 [29.4944] (29.4875)	48.0648 [48.0496] (47.9140)	42.9720 [42.959]	46.9436 [46.9265]	48.1191 [48.1010]	45.5349 [45.5197]	45.1482 [45.1338] (45.0262)	45.6860 [45.6709]
	NChDE	-0.0001	-0.0001	-0.0006 [-0.0006] (-0.0005)	-0.0023 [-0.0023] (-0.0023)	-0.0013 [-0.0013]	-0.0015 [-0.0016]	-0.0016 [-0.0016]	-0.0014 [-0.0014]	-0.0015 [-0.0015] (-0.0015)	-0.0014 [-0.0014]

Table 3 Isotropic values of the shielding and SR constants for the At and H nuclei in HAt, at the PZOA, RPA and DFT levels of approach. Optimized internuclear distances were employed, each of them calculated at the corresponding level of approach. All values are in ppm.

Method	d(H-At) [Å]	Y		$\sigma_Y^{(e-e)}$	$\sigma_Y^{(p-p)}$	$\frac{2}{3}\frac{m_p I}{g_Y} M_{\perp,Y}^{(e-e)}$		$\frac{2}{3}\frac{m_p I}{g_Y} M_{\perp,Y}^{(p-p)}$	NChDE	
						L	S		$\Delta\sigma_Y$	$\frac{2}{3}\frac{m_p I}{g_Y}\Delta M_{\perp,Y}^{elec}$
PZOA	1.7117	At	PNM	9766.1854	8600.8555	-3456.5794	2703.6242	-0.0001	-530.1694	-9.8033
			GNM	9195.2640	8641.6075	-3308.4956	2545.7372	-0.0003		
		H	PNM	14.5067	19.5864	18.2506	-1.3001	0.0009	-0.0101	-0.0077
			GNM	14.5024	19.5807	18.2412	-1.2984	0.0009		
RPA	1.7117	At	PNM	10222.0816	8596.8899	-2963.7890	2922.1959	0.7173	-644.9436	-142.9047
			GNM	9536.3418	8637.6861	-2947.2362	2762.7068	0.7490		
		H	PNM	55.3711	19.5859	98.2302	-14.6863	0.0012	-0.0588	-0.1057
			GNM	55.3180	19.5802	98.0975	-14.6594	0.0012		
LDA	1.7393	At	PNM	8573.3659	8600.7257	-4807.2178	2931.5438	0.1444	-564.5014	-45.5992
			GNM	7968.2173	8641.3729	-4688.5166	2767.2392	0.1486		
		H	PNM	40.0231	19.3136	63.0940	-7.7996	0.0014	-0.0216	-0.0328
			GNM	40.0056	19.3094	63.0538	-7.7921	0.0014		
KT2	1.7237	At	PNM	8878.1482	8607.3095	-4649.2714	2980.8326	0.1931	-591.9374	-58.3475
			GNM	8244.2472	8649.2731	-4538.3134	2811.4936	0.2267		
		H	PNM	48.4726	19.9375	78.0488	-10.0254	0.0035	-0.0277	-0.0451
			GNM	48.4493	19.9331	77.9929	-10.0146	0.0035		
KT3	1.7209	At	PNM	8855.9620	8609.1720	-4676.2287	3000.9844	0.2517	-596.9808	-66.5315
			GNM	8217.5630	8650.5903	-4573.5550	2831.7713	0.2596		
		H	PNM	50.0759	20.2299	81.9615	-10.8523	0.0034	-0.0268	-0.0455
			GNM	50.0537	20.2253	81.9044	-10.8406	0.0034		
PBE	1.7473	At	PNM	8591.9758	8601.3385	-4845.8139	2977.7127	0.2591	-578.8844	-58.7929
			GNM	7972.4900	8641.9399	-4738.6794	2811.7929	0.2514		
		H	PNM	44.6748	19.8044	73.1366	-9.6721	0.0003	-0.0215	-0.0357
			GNM	44.6577	19.8000	73.0916	-9.6628	0.0003		
PBE0	1.7272	At	PNM	9070.4648	8600.5054	-4353.1376	2968.1610	0.4092	-592.5615	-74.1924
			GNM	8437.2560	8641.1526	-4262.1751	2803.0073	0.4080		
		H	PNM	44.5778	19.7198	72.4860	-9.5030	0.0005	-0.0273	-0.0445
			GNM	44.5553	19.7150	72.4305	-9.4920	0.0005		
BP86	1.7486	At	PNM	8501.0411	8601.6205	-4912.4320	2967.7778	0.2517	-576.8559	-56.8047
			GNM	7883.5229	8642.2827	-4803.5779	2802.1270	0.2436		
		H	PNM	44.6874	19.8374	73.1401	-9.6606	0.0005	-0.0208	-0.0350
			GNM	44.6710	19.8330	73.0958	-9.6513	0.0005		