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Short Communication

Calculation of the Diamagnetic Shielding of the Nuclei by the Point-Charge Approximation

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It is shown that the diamagnetic shielding of the nuclei can be calculated to a good accuracy by using point-charge approximation. Very good results were obtained by the semiempirical SCC-MO method employing Clementi–Raimondi AO basis set.

Key words: Magnetic shielding of the nuclei – Semiempirical calculation of NMR chemical shift.

The underlying assumption of the concept of the formal atomic charge in molecules is that the total electron density can be conveniently broken down to atomic contributions only. Although this cannot be achieved in a unique way, the formal atomic charges proved very useful in discussing a number of molecular properties: heats of formation and/or total molecular energies [1–3], inner-shell ionization potentials [4–8], second moments and components of the diamagnetic susceptibility tensor [9] etc. In this contribution we discuss the calculation of the diamagnetic shielding of the nuclei in the framework of the point-charge approximation.

As Ramsey has shown [10] by using perturbation theory, the spherically averaged magnetic shielding is conveniently split into two terms

$$\sigma_{\mathrm{av}}(A) = \sigma^{d}_{\mathrm{av}}(A) + \sigma^{p}_{\mathrm{av}}(A) \tag{1}$$

where the superscripts d and p refer to diamagnetic and paramagnetic contributions, respectively. The diamagnetic term is easily expressed by the ground state

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wavefunction $|0\rangle$

$$\sigma_{\mathrm{av}}^{d}(A) = (e^2/3mc^2)\langle 0|1/r_A|0\rangle \tag{2}$$

which is here represented by the single Slater-determinant. Employing point-charge approximation the formula (2) takes a form

$$\sigma_{\mathrm{av}}^{d}(A) = \sum_{\mu}^{A} (\xi_{A\mu} Q_{\mu}^{A}/n_{A\mu}) + \sum_{B}^{\prime} Q_B/R_{AB} \tag{3}$$

where Q_{μ}^{A} and Q_A are gross orbital and gross atomic electron populations, respectively. The first contribution to $\sigma_{\mathrm{av}}^{d}(A)$ in Eq. (3) is local in character and it is known as the Lamb term. The best way to examine the performance of the formula (3) is to use the *ab initio* orbital populations and the corresponding expectation values (2) obtained within the same basis set. We shall use for this purpose Snyder and Basch [11] *ab initio* results which are of DZ quality. Since the point-charge approach gives in most cases more than 90% of the total expectation value (Table 1) it is justified to make some empirical adjustments in order to increase the predictability of the simple approach. Consequently, we examined also the following formula

$$\sigma_{\mathrm{av}}^{d}(A) = K_{A1} \sum_{\mu}^{A} (\xi_{A\mu} Q_{\mu}^{A}/n_{A\mu}) + K_{A2} \sum_{B}^{\prime} Q_B/R_{AB} + K_{A3} \tag{4}$$

where K_{Ai} $(i = 1, 2, 3)$ are weighting factors which depend only on the nature of the atom A. They are determined by the least squares fitting of the DZ *ab initio* expectation values. The performance of the point-charge approach is increased as evidenced by the decrease of the average absolute error from 1.9 to 0.6 ppm. The concept of formal atomic charge in *ab initio* methods is more useful for interpretative purposes than for the calculation of one-electron properties because if the *ab initio* ground state function is known, then the expectation values of one-electron operators are obtained with relatively little additional effort. In contrast, the rigorous computation of only one property could be much more time consuming than the production of the semiempirical wavefunction itself. Thus the point-charge concept is very important in semiempirical theories of molecular properties. It is well documented by now that the self-consistent charge (SCC-MO) method describes much better charge distribution in molecules than the CNDO/2 approach as evidenced by the calculation of ESCA chemical shifts [8] and molecular quadrupole moments [12]. Here we compare SCC-MO σ_{av}^{d} values calculated by using formulae (3) and (4) and Clementi–Raimondi AOs [13] with *ab initio* DZ results. The semiempirical estimates are in very good accordance with more accurate *ab initio* results, particularly if they are properly scaled (Eq. (4)). Surprisingly, the SCC-MO point-charges yield significantly smaller standard deviations for nitrogen and oxygen than the *ab initio* formal atomic charges themselves. This is encouraging because the SCC-MO method is very efficient and easily applied to very large compounds. Finally, it should be pointed out that *ab initio* diamagnetic shieldings of Snyder and Basch [11] of DZ quality should be quite close to the true values because average

Table 1. Comparison of the diamagnetic shielding of the nuclei calculated in the point-charge approximation by using *ab initio* DZ and semiempirical SCC-MO wave functions (in ppm)

Compound	Point-charge approximation				*Ab initio* DZ expectation value[c]
	ab initio[a]	*ab initio*[b]	SCC-MO[a]	SCC-MO[b]	
H_2O					
H	−105.9	−102.4	−104.7	−102.1	−102.1
O	−413.0	−416.2	−415.9	−416.8	−416.8
NH_3					
H	−98.5	−95.8	−97.3	−95.6	−95.1
N	−352.4	−354.3	−352.4	−354.0	−354.4
N_2H_4					
H_1	−131.8	−129.3	−131.1	−129.1	−129.0
H_2	−133.3	−131.3	−132.3	−130.8	−129.9
N	−396.8	−396.6	−396.2	−396.9	−396.5
H_2O_2					
H	−144.8	−141.5	−143.7	−141.0	−141.4
O	−458.7	−461.4	−461.3	−461.3	−462.0
CH_3OH					
H_1	−122.5	−120.9	−121.6	−120.3	−121.1
H_2	−123.3	−122.0	−122.3	−121.0	−122.0
H_3	−140.3	−137.2	−139.8	−137.8	−136.4
C	−344.6	−344.4	−341.2	−343.5	−344.2
O	−458.0	−459.8	−460.9	−460.4	−460.3
HCN					
H	−101.9	99.1	−102.4	−100.6	−99.6
C	−326.1	−326.3	−324.2	−326.7	−326.6
N	−376.5	−378.8	−377.8	−378.9	−378.6
CHOOH					
H_1	−147.9	−146.5	−148.1	−146.7	−147.4
H_2	−163.3	−159.7	−162.6	−160.3	−159.8
C	−392.2	−391.3	−389.5	−390.9	−390.7
O_1	−482.5	−484.2	−486.0	−485.0	−485.7
O_2	−483.0	−483.9	−484.3	−483.6	−481.5
CH_4					
H	−89.5	−87.7	−88.6	−87.3	−87.2
C	−296.2	−296.7	−293.6	−296.7	−296.7
C_2H_6					
H	−119.9	−118.5	−119.3	−118.3	−118.1
C	−337.5	−337.3	−334.2	−337.1	−337.2
C_2H_4					
H	−111.9	−110.3	−111.6	−110.5	−110.0
C	−329.8	−329.8	−327.5	−330.3	−330.1
C_2H_2					
H	−101.1	−98.6	−101.8	−100.4	−99.1
C	−320.7	−321.0	−319.2	−322.2	−321.5

Table 1 (*Cont.*)

Compound	*ab initio*[a]	Point-charge approximation *ab initio*[b]	SCC-MO[a]	SCC-MO[b]	*Ab initio* DZ expectation value[c]
N_2H_2					
H	−123.5	−121.1	−123.1	−121.2	−120.9
N	−392.3	−392.9	−391.9	−392.8	−392.9
H_2					
H	−33.4	−32.3	−33.9	−32.2	−32.2
H_2CO					
H	−112.2	−110.9	−112.0	−110.4	−112.3
C	−339.3	−339.3	−336.7	−338.8	−338.8
O	−449.9	−453.2	−453.1	−453.0	−452.7
CO_2					
C	−388.4	−387.7	−386.0	−387.2	−386.8
O	−472.9	−475.2	−475.4	−475.1	−476.2
CO					
C	−324.9	−325.4	−324.6	−326.8	−326.1
O	−443.1	−446.9	−444.9	−445.5	−445.1
NNO					
N_1	−412.1	−412.5	−412.9	−413.6	−414.4
N_2	−445.5	−443.9	−442.7	−443.3	−443.1
O	−476.9	−479.2	−479.8	−479.2	−479.6
N_2					
N	−383.0	−384.9	−383.0	−384.4	−384.1

Atoms		weighting factors k_1	k_2	k_3	Standard deviation
H	SCC-MO	−1.486	−1.011	12.279	0.9
	DZ[c]	−1.641	−1.008	14.426	0.7
C	SCC-MO	−1.247	−0.996	11.135	0.6
	DZ[c]	−0.933	−0.980	5.715	0.5
N	SCC-MO	−0.820	−0.977	−17.832	0.4
	DZ[c]	−0.744	−0.941	−28.193	0.9
O	SCC-MO	−0.824	−0.973	−23.807	0.9
	DZ[c]	−0.656	−0.959	−48.864	1.3

[a] Unscaled point-charge values.
[b] Correlated point-charge values.
[c] Double-zeta *ab initio* values of Snyder and Basch, Ref. [11].

of the $1/r_A$ operator is little affected by the increase in basis set (addition of the polarization function) or inclusion of the large CI [14]. In other words, the SCC-MO method offers a quick, inexpensive and quite reliable information about diamagnetic contribution to magnetic screening of the nuclei. This is of importance because there is some controversy regarding the role of local and

nonlocal contributions to σ_{av}^{d} in the theory of NMR chemical shift [15, 16]. In the point-charge approximation (Eqs. (3) and (4)) local and nonlocal contributions are easily determined in a very transparent way. Performance of other semiempirical methods in the calculation of σ_{av}^{d} values by using point-charge approach is under investigation.

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