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Abstract

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CALCULATION OF THE NUCLEAR MAGNETIC SHIELDING CONSTANT FOR CERTAIN MOLECULES

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In paper ([1]) a method was proposed for calculating the nuclear magnetic shielding constant σ, based on the application of the apparatus of the molecular-orbital method. In this approach, the choice of atomic functions φ, from which the molecular orbitals are constructed, is made so that, in calculating σ, one can restrict oneself to a small number of functions φ. However, the application of this method to complex molecules is associated with the computational difficulties usual in quantum chemistry. Below we propose a modification of the method of paper ([1]), which makes it possible in practice to estimate the magnitude of σ.

Let, in the absence of a magnetic field, the wave function of the molecule Ψ_0 be the product of molecular orbitals ψ_0^j: $\Psi_0 = \prod_j \psi_0^j$, and let each molecular orbital be expressible as a linear combination of atomic orbitals:

$$\psi_0^j = \sum_{a,q} c_{aq}^j \varphi_{aq}^0, \tag{1}$$

where the index a denotes the number of the atom, and the index q the number of the atomic orbital. In the presence of a magnetic field $\mathbf{H}$ with vector potential $\mathbf{A} = \frac{1}{2}[\mathbf{Hr}]$, the atomic functions (to within terms of first order in H) have the form:

$$\varphi_{aq} = \varphi_{aq}^0 \exp\left(\frac{ie}{2\hbar c}\,\mathbf{H}\{\mathbf{r}\mathbf{R}_a\}\right), \tag{2}$$

where R_a is the distance from the origin of coordinates to the nucleus of atom a. Let us now consider the function $\Psi = \prod_j \psi^j$, where $\psi^j = \sum_{aq} c_{aq}^j \varphi_{aq}^0 \exp\left(\gamma_a \frac{ie}{2\hbar c}\,\mathbf{H}\{\mathbf{r}\mathbf{R}_a\}\right)$.

If the γ_a are regarded as variational parameters, then with the aid of such a function one can obtain, by the usual variational method, an expression for σ. However, the variational method is associated with the need to know the function Ψ_0 sufficiently accurately (in the variant proposed by Stephen ([2]) it is also necessary to know Ψ_0 to the accuracy of the second derivative, although this is not immediately evident from the final formulae). But we may assume in

advance that the parameters γ_a will be close to unity; indeed, when an electron is near the nucleus of atom a, the influence of the other nuclei is small, and it may be considered that the electron performs the usual Larmor precession; but then the atomic orbital is described precisely by function (2). Thus, we shall assume that, in the presence of a magnetic field, the wave function of the molecule consists of molecular orbitals of the form

$$\psi^j = \sum_{aq} c^j_{aq} \varphi_{aq} \tag{3}$$

or is a function of the valence-bond method, in which instead of the functions $\varphi^0_{aq}(j)$ there stand the functions (2).

Let us note that, since the function Ψ_0 constructed in the indicated way is not an exact solution of the Schrödinger equation in a magnetic field, it is necessary to make sure that the mean values of physical quantities obtained with its aid do not depend on the choice of the vector potential $\mathbf{A}$. Indeed, when $\mathbf{A}$ is replaced by $\mathbf{A} + \operatorname{grad} f$, the molecular orbitals of the form (3) and the functions of the valence-bond method composed of atomic orbitals (2) transform in the same way as the exact solutions, which ensures the invariance of the sought mean values with respect to transformations of the vector potential.

As was indicated in work ([1]), to determine σ one must know the first two terms of the expansion of the wave function in powers of H. Consequently, if molecular orbitals are used, in (3) it is sufficient to restrict oneself to the following terms:

$$\psi^j = \sum_{aq} c^j_{aq} \varphi^0_{aq} + \frac{ie\mathbf{H}}{2\hbar c} \sum_{aq} c^j_{aq} \varphi^0_{aq} [\mathbf{r}\mathbf{R}_a]. \tag{4}$$

We must now find the tensor of nuclear magnetic shielding

$$\sigma_{\alpha\beta} = \left. \frac{\partial^2 \bar{H}}{\partial \mu_\alpha \partial H_\beta} \right|_{\mu_\alpha, H_\beta = 0},$$

where $\vec{\mu}$ is the magnetic moment of the shielded nucleus, and $\bar{H}$ is the mean value of the Hamiltonian

$$H = \frac{1}{2m} \sum_j \left(\mathbf{p}_j + \frac{e}{c} \mathbf{A}_j \right)^2 + \frac{e}{mc} \sum_j \frac{\vec{\mu}[\mathbf{r}_j \mathbf{p}_j]}{r_j^3} + \frac{e^2}{2mc^2} \sum_j \frac{[\mathbf{H}\mathbf{r}_j][\vec{\mu}\mathbf{r}_j]}{r_j^3}. \tag{5}$$

Denoting further $Q^j_{a\alpha} = [\mathbf{r}_j \mathbf{R}_a]_\alpha$, $\hbar \mathbf{M}_j = [\mathbf{r}_j \mathbf{p}_j]$, and taking Ψ in the form $\Psi = \prod_j \psi^j$, we find

$$\sigma_{\alpha\beta} = \frac{e^2}{2mc^2}\sum_j \left(\psi_0^j \left| \frac{r_j^2\delta_{\alpha\beta} - r_{j\alpha}r_{j\beta}}{r_j^3} \right| \psi_0^j\right) - \frac{ie^2}{mc^2}\sum_j \left(\sum_{aq} c_{aq}^j \varphi_{aq}^0 Q_{a\alpha} \left| \frac{M_{j\beta}}{r_j^3} \right| \psi_0^j\right). \tag{6}$$

In obtaining this formula we used the Hermiticity of the operator M_j/r_j^3 and assumed that ψ_0^j are real functions. With the aid of (6) the shielding constant is easily determined: $\sigma = \frac{1}{3}\sigma_{\alpha\alpha}$ (summation is implied over repeated Greek indices).

We shall always assume that the origin of coordinates is at the shielded nucleus and that $\mathbf{A} = \frac{1}{2}[\mathbf{Hr}]$. Then both terms in formula (6) are determined uniquely. The value of the first term, $\sigma_{\alpha\beta}^d$, which coincides with Ramsey' s diamagnetic term ([3]), is determined by the function Ψ_0, and its calculation presents no fundamental difficulties. The method proposed in the present work is intended for estimating the second term in (6), $\sigma_{\alpha\beta}^p$, corresponding to the paramagnetic term of Ramsey' s formula. As is known, for linear molecules the value of σ^p can be obtained from experimental data ([3]).

Expression (6) is considerably simplified for the case when the molecular orbital consists of atomic (hybridized) orbitals of only two atoms. In this case $Q_{a\alpha} = 0$, $Q_{bx} = yR$, $Q_{by} = -xR$, $Q_{bz} = 0$ (nucleus a is shielded; R is the internuclear distance). Choosing the axis in the direction from a to b, we find for the sigma bond:

$$\sigma_{xx}^p = \sigma_{yy}^p = \frac{-ie^2R}{mc^2}\left(c_b\varphi_e^0 \left| \frac{yM_x}{r_a^3} \right| \psi_0\right), \qquad \sigma_{zz}^p = 0. \tag{7}$$

If we are dealing with a function of the valence-bond method, then a general formula for $\sigma_{\alpha\beta}^p$ cannot be obtained; for the function of a two-electron covalent sigma bond of atoms a and

$$\Psi^0 = (2+2S^2)^{-1/2}\left[\varphi_a(1)\varphi_b(2) + \varphi_b(1)\varphi_a(2)\right]$$

(where $S = (\varphi_a^0|\varphi_b^0)$), one can obtain an expression analogous to (7). Then, using the reality of the functions φ^0 and the properties of the operator M, we obtain for a sigma bond

$$\sigma = \frac{e^2}{3mc^2}\,\frac{1}{N}\left[\int \frac{1}{r_a}\left(\varphi_a^{0\,2} + 2\varkappa\varphi_a^0\varphi_b^0 + \varphi_b^{0\,2}\right)d\tau + R\frac{d}{dR}\int \frac{\psi_b^{1\,0?}}{r_a}\,d\tau + k\frac{iR}{2}\int \varphi_b^0 \frac{xM_y - yM_x}{r_a^3}\varphi_a^0\,d\tau\right],$$

where $N = 1 + S$, $k = \varkappa = 1$ for molecular orbitals and $k = 2S$, $\varkappa = S$, $N = 1 + S^2$ for a covalent bond. The first term in square brackets corresponds to σ^d, the last two to σ^p.

Using formula (8), we calculated σ^p for the H_2 molecule with different functions Ψ^0 at $R = 1.4$ at. units. The atomic functions were taken in the form $\varphi_a^0 = \xi(1 + cz_a)e^{-\alpha r_a}$; ξ is the normalization constant. As the calculation showed, inclusion in φ^0 of terms of the form $cze^{-\alpha r}$ has practically no effect on the result (if $c \sim 0.1$). Therefore we give the results of calculations for $c = 0$.

	$\alpha = 1.00$	$\alpha = 1.17$	$\alpha = 1.19$
Molecular orbitals, $-10^5\sigma^p$	0.38	0.48	0.49
Covalent bond, $-10^5\sigma^p$	0.43	0.55	0.56
Semiempirical value ([3]), $-10^5\sigma^p$		0.56	

For the molecular orbital with $\alpha = 1.17$, a variation of the parameter γ_b was carried out. The value obtained for γ_b is indeed close to unity: $\gamma_b = 1.1$. In this case $\sigma^p = -0.53 \cdot 10^{-5}$.

It is interesting to note that the function describing two noninteracting atoms, $\Psi_0 = \varphi_a^0(1)\varphi_b^0(2)$, gives a result rather close to the experimental value: $\sigma^p = -0.67 \cdot 10^{-5}$. The diamagnetic term calculated with this function is $\sigma^d = 2.8 \cdot 10^{-5}$, which almost coincides with the result obtained with molecular orbitals ($2.83 \cdot 10^{-5}$) or with the Heitler–London function ($2.78 \cdot 10^{-5}$). This is an indirect confirmation of the assumption of local Larmor precession of the electrons.

The shielding constant for the proton in C–H bonds was calculated for different types of hybridization of the atomic orbitals of the C atom; moreover, we considered the shielding due only to the two electrons forming the bond; the results of the calculation are given below.

Type of hybridization	sp^3		sp^2		sp	
	$10^5\sigma$	$-10^5\sigma^p$	$10^5\sigma$	$-10^5\sigma^p$	$10^5\sigma$	$-10^5\sigma^p$
Molecular orbitals	2.32	0.71	2.37	0.70	2.35	0.74
Covalent bond	2.22	0.82	2.27	0.80	2.24	0.84
Experiment	2.92 (CH_4)		2.57 (C_2H_4)		2.86 (C_2H_2)	

In all cases Slater atomic functions were used; the equilibrium distance was $R = 1.08$ Å.

Thus, the difference in types of hybridization cannot explain the chemical shifts in the series CH_4, C_2H_4, C_2H_2.

Remaining within the framework of valence-bond theory, one can try to take into account the influence of electrons not participating in the given bond. In work ([2]) this is done with the aid of the formula $\delta\sigma_i = -2\gamma_i/R_i^3$, where $\delta\sigma_i$ is the contribution made to

screening by the i-th bond of the molecule; χ_i is the diamagnetic susceptibility of this bond; R_i is the distance from the screened nucleus to the center of gravity of the electron density of the bond. When this formula is applied, the sequence of change of σ in the series CH_4, C_2H_4, C_2H_2 agrees with experiment. Nevertheless, because of the incorrectness of the derivation, this formula is wrong. This is easily verified by calculating, for example, the screening of a nucleus by the electron of a hydrogen atom in the $1s$ state, removed from it (it is assumed that the electron does not interact with the charge of the screened nucleus). The calculation gives

$$\delta\sigma = \frac{e^2}{3mc^2a_0}e^{-2R/a_0}\left(1+2\frac{R}{a_0}\right)$$

(a_0 is the Bohr radius), and not $\delta\sigma = \dfrac{e^2}{mc^2}\dfrac{a_0^2}{R^3}$, as Stephen' s formula requires (for large R).

The influence of distant bonds could be taken into account in the following way. Let the tensor of the diamagnetic susceptibility of a bond be $\chi_{\alpha\beta}$ ($\chi = \frac{1}{3}\chi_{\alpha\alpha}$). Then, when a field $\mathbf{H}$ is applied, the bond acquires a magnetic moment $m_\alpha = \chi_{\alpha\beta}H_\beta$, producing, at the point where the screened nucleus is located, a magnetic field

$$\delta H'_\alpha = \frac{1}{R^5}\left[3R_\alpha R_\beta m_\beta - m_\alpha R^2\right].$$

Since, by definition, $H'_\alpha = -\sigma_{\alpha\beta}H_\beta$, it follows that

$$\delta\sigma_{\alpha\beta} = -\frac{1}{R^5}\left[3R_\alpha R_\gamma\chi_{\gamma\beta} - \chi_{\alpha\beta}R^2\right]$$

and

$$\delta\sigma = -\frac{1}{R^5}\left[R_\alpha R_\beta\chi_{\alpha\beta} - \chi R^2\right].$$

The formula obtained can be used if all three principal values of the tensor $\chi_{\alpha\beta}$ are known. For the molecules under consideration these quantities were calculated in work ([4]), but with insufficient accuracy: for different wave functions of one and the same molecule, substantially different values of $\chi_{xx}, \chi_{yy}, \chi_{zz}$ are obtained. This has little effect on the value of χ, but has a very strong effect (even as to the sign) on $\delta\sigma$.

A qualitative explanation of the spectrum of the indicated molecules was given in Pople' s work ([5]) on the basis of the idea of circulation of atomic currents. However, in that work the overlap of the wave functions is neglected, and allowance for this circumstance makes a contribution to the screening of the same order of magnitude as the current circulation considered by Pople. In our calculations the effects due to overlap give more than half of the entire value of σ, i.e., a quantity of order 10^{-5}. Estimates of the effects of paramagnetic current circulation, however, give a quantity of order 10^{-6}–10^{-5} ([5]).

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Note: Figure translations are in progress. See original paper for figures.