THE CHEMICAL SHIFT DUE TO THE EFFECT OF THE UNSHARED PAIR OF ELECTRONS ON OXYGEN

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In the interpretation of high-resolution NMR spectra of molecules of organic compounds one must consider the effect of separate molecular fragments on chemical shifts of magnetic nuclei. Normally this effect is evaluated semiempirically in the dipole approximation using effective values of the anisotropy of magnetic susceptibility of localized groups in the molecule (for example, see [1]). We carried out the non-empirical calculation of the change in constants of magnetic shielding of nuclei by the unshared pair of electrons on the oxygen atom.

We propose that the perturbed wave function $\Psi$ of the molecular system containing a nucleus having magnetic moment $\mu$ and found in magnetic field $H$ can be separated into powers of $\mu$ and $H$:

$$\Psi = \Psi_0 + \Psi_{1H} H_a + \Psi_{1\mu} \mu_a + \ldots$$

Substituting (1) into the expression for the current vector of density probability

$$\mathbf{j}_k = \frac{i\hbar}{2mc} (\mathbf{\psi}_0^{\dagger} \mathbf{\psi} - \mathbf{\psi}^{\dagger} \mathbf{\psi}) + \frac{e}{mc} \mathbf{A}_k \mathbf{\psi}^{\dagger} \mathbf{\psi},$$

(e and m are the charge and mass of an electron, $\mathbf{A}_k$ is magnetic vector-potential of the k-th electron), we find the magnetic field $H'$ created on the nucleus by a shift of electrons in the applied field $H$, ignoring in this case the terms higher than the first power in $H$:

$$H'_{k} = - \mathbf{r}_k \cdot \mathbf{j}_k.$$

Here $\mathbf{r}_k$ is the radius-vector of the k-th electron directed from the studied nucleus. Considering that $\Psi_{1H}^{\dagger} H \Psi_{1H}$ is a purely imaginary function [2], we obtain from the determination of $H_{1H}^{\dagger} = - \sigma_{\alpha\beta} \mathbf{H}_\beta$ the expression for the tensor component of magnetic shielding of the nucleus in the form

$$\sigma_{\alpha\beta} = \sigma_{\alpha\beta}^{\text{pre}} + \sigma_{\alpha\beta}^{\text{pol}},$$

where

$$\sigma_{\alpha\beta}^{\text{pre}} = \frac{e^2}{2mc^2} \int \mathbf{\psi}_0^{\dagger} \mathbf{r}_k^2 \mathbf{j}_k - \mathbf{r}_0^2 \mathbf{j}_0^\dagger \mathbf{\psi}_0 \mathbf{d}x,$$

$$\sigma_{\alpha\beta}^{\text{pol}} = - 2 \int \mathbf{\psi}_0^{\dagger} \sum_k \frac{2M_k}{r_k^3} \mathbf{\psi}_0 \mathbf{d}x.$$
obtained in [2] from the examination of energies of systems in the second order of perturbation theory. Assuming that \( \Psi_{s\sigma} = \Psi_{s\sigma_0} \) (\( \sigma_0 \) is a certain function of the electron coordinate) it is not difficult to obtain for the polarization contribution to shielding

\[
\sigma_{\text{pol}}^{\text{pol}} = -2 \sum_k \psi_0^k M_{k\sigma_0} \xi_0^k \xi_0^0 dt.
\]  

(4)

We used Eqs. (2) and (4) in the calculation of changes in constants of nuclear magnetic shielding by the unshared pair of electrons. It was assumed that the unshared pair of electrons on the oxygen atom is described by a 2p\(_2\) Slater wave function having an orbital exponent equal to 2.226 [3]. The variation method was used in the calculation of the magnetic effect of the 2p\(_2\) electrons on shielding of remote nuclei. In this case the correction wave functions were chosen in the form

\[
g_x = ia_1 \left( x_0 y_0 \cos \theta_2 + \frac{y_0}{z_0} \sin \theta_2 \right),
\]

\[
g_y = i a_2 \left( y_0 x_0 \cos \theta_2 + \frac{x_0}{z_0} \sin \theta_2 \right),
\]

(5)

where \( a_1 \) and \( a_2 \) are the varied parameters, \( \theta_2 \) is the angle between the symmetry axis of the unshared pair and the direction to the studied nucleus found at point \( 0' \); \( x_0, y_0, z_0 \) are coordinates of the \( k \)-th electron in the \( x, y, z \) system with the center on the nucleus of the oxygen atom (see Fig. 1).

The choice of correction functions was made on the basis of the following reasons. Magnetic shielding was calculated in various regions of space. If the points of interest to use are distributed along the \( z \) axis (axis of symmetry of the unshared pair, \( \theta_2 = 0 \)) then, as was shown in [4], the symmetry of the problem permits the choice of correction functions in the form

\[
g_x = ia_0 y_0', \quad g_y = ib_0 x_0'.
\]

(6)

Results of calculation of magnetic susceptibility of a molecule carried out in [4] with these functions are similar to experimental values. Calculation of the subsequent term in the correction function \( g_{\alpha} \) led to an even better agreement. If the wave function has a nodal surface at \( z = 0 \), then according to [5], the use of a correction function of type (6) leads to rupture of continuity of one of the derivatives of the wave function at \( z = 0 \). Therefore, upon calculating the magnetic shift of a nucleus found at a nodal surface the correction functions must be proportional to \( y_0/z_0 \) (or \( x_0/z_0 \)). Functions \( \psi_0 (1 + g_{\alpha} H_{\alpha}) \), where \( g_{\alpha} \) is chosen according to [5], are continuous together with their derivatives at \( z = 0 \). As results of [6] on the calculation of nuclear magnetic shielding in diatomic molecules showed functions of similar type give good agreement with experimental data for shielding of lighter nuclei, in particular, of protons. Therefore, it should be assumed that the functions used by us are reasonable in the calculation of shielding of protons by the unshared pair in complex molecules.

Since in expressions for the total energy of a system in a magnetic field the term characterizing shielding is \( 10^4 \) times smaller than the term characterizing susceptibility of the system, parameters \( a_1 \) and \( a_2 \) should be looked for in experimental values of the functional for magnetic susceptibility of the system [4]. As a result the final expression for the average value of the magnetic shielding on start of the nucleus found at point \( 0' \) (see Fig. 1) due to the effect of both electrons of the unshared pair on the oxygen atom has the form

\[
\sigma = \frac{\alpha}{3mc^2} \int \psi_0^2 \frac{2\pi^2 \delta}{r_0^2} dt \frac{\psi_0^2 \left[ \left( x_0^2 - z_0^2 \right) \cos \theta_2 - \left( x_0^2 + z_0^2 \right) \sin \theta_2 \right]}{\left( \frac{x_0}{z_0} + \frac{z_0}{x_0} \right) \sin \theta_2 + 2 \left( \frac{x_0^2 - z_0^2}{z_0^2} \right) \sin \theta_2 \cos \theta_2} dt
\]

\[
\times \frac{\psi_0^2}{r_0^2} \left[ \left( x_0 y_0 + y_0 x_0 - 2z_0 x_0 \right) \cos \theta_2 - \left( x_0 y_0 + y_0 x_0 + 2z_0 x_0 \right) \sin \theta_2 \right] dt,
\]

(7)