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Abstract

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CALCULATION OF THE ANISOTROPY OF THE DIAMAGNETIC SUSCEPTIBILITY OF AROMATIC MOLECULES BY THE METHOD OF THE METALLIC MODEL OF THE MOLECULE

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The calculation of the anisotropy of the diamagnetic susceptibility of certain aromatic molecules by the method of the metallic model of the molecule was first carried out by M. V. Vol' kenshtein and L. A. Borovinskii ([1]). In connection with the application of the method of the metallic model of the molecule to the calculation of a broader class of aromatic molecules, it becomes necessary to refine the method for calculating the magnetic properties of molecules within the framework of this model. Below, an error contained in the calculation method used in ([1]) is corrected, and a new method is proposed for calculating the diamagnetic anisotropy of aromatic molecules within the framework of the metallic model, without using perturbation theory.

In ([1]), the diamagnetic anisotropy of aromatic molecules was calculated by perturbation theory. The one-dimensional Hamiltonian describing the behavior of π-electrons in a magnetic field was chosen in the form

$$H = -\frac{1}{2}\frac{d^2}{ds^2} - \frac{i}{c}A_s\frac{d}{ds} + \frac{A_s^2}{2c^2}. \tag{1}$$

(The coordinate s is measured along the bond. Units $e = m = h = 1$ are used.)

As the perturbation operator in ([1]), only the third term in the expression for the Hamiltonian was taken into account. Meanwhile, it is also necessary to take into account the contribution of the second term in expression (1)—in the second approximation of perturbation theory.

However, the problem of the energy spectrum and of the wave functions of π-electrons in the metallic model of the molecule in the case of a homogeneous magnetic field admits an exact solution not based on the application of perturbation theory. It follows from the form of operator (1) that the one-dimensional wave function on the j-th bond has the form

$$\psi(s_j) = a_j \cos(\sqrt{2E}\, s_j + \delta_j) e^{-\frac{i}{c} A_{js} j}. \tag{2}$$

(E is the energy of the π-electron; A_j is the projection of the vector potential on the j-th bond; a_j and δ_j are complex constants.)

At every branching point of the system of conjugated bonds (including every point of inflection of the molecular contour), the following continuity conditions must be satisfied:

$$\psi_1 = \psi_2 = ... = \psi_p; \tag{3}$$

$$\sum_{l=1}^{p} \left(\psi_l' + \frac{i}{c} A_l \psi_l \right) = 0, \tag{4}$$

where ψ_l and ψ_l' are the values of the one-dimensional wave function and its derivative at the beginning of the l-th bond emerging from the branching point. Conditions (4) were first found by us and are a generalization of the continuity conditions that hold in the absence of a magnetic field.

From (2), (3), and (4) there follows the following secular equation for determining the energy spectrum of π-electrons in a magnetic field:

$$\det W(E, \mathcal{H}) = 0, \tag{5}$$

where W is a matrix with elements

$$W_{lm} = -p_l \delta_{lm} \cos \sqrt{2E}\, a + (1 - \delta_{lm}) \eta_{lm} e^{i\mathcal{H} S_{lm}/c}, \tag{6}$$

where δ_{lm} is the Kronecker symbol; p_l is the number of carbon atoms neighboring the l-th carbon atom; a is the length of the aromatic C–C bond; $\eta_{lm} = 1$ or 0, according as atoms l and m are bonded to each other or not; S_{lm} is the algebraic value of the area of the triangle whose vertices are the l-th carbon atom, the m-th carbon atom, and the origin. Equation (5) is close in form to the secular equation determining the energy spectrum of π-electrons in a homogeneous magnetic field in the molecular-orbital method ([2]).

From (5) and (6) there follows the following expression for the diamagnetic anisotropy of cyclic conjugated molecules

$$\Delta\chi = -\frac{S^2}{c^2 a^2 N}, \tag{7}$$

which coincides with Pauling' s semiclassical theory ([3]). (S is the area of the ring, N is the number of carbon atoms.) Formula (7) gives, for the circular and

hexagonal models of the benzene molecule, results that agree exactly with the results obtained in ([1]). This is explained by the high symmetry of the models considered, which leads to the disappearance of the off-diagonal matrix elements from the second term in operator (1). However, in the case of less symmetric molecules the calculation method proposed in ([1]) leads to serious errors.

Using the implicit dependence of the π-electron energy on the magnetic-field strength, given by equations of the type (5), we also calculated the diamagnetic anisotropy of some molecules in which the system

Table 1

Molecule	$\Delta\chi_{\text{theor}}$	$\Delta\chi'_{\text{theor}}$	$\Delta\chi''_{\text{theor}}$	$\Delta\chi_{\text{exp}}$
Naphthalene	2.011	2.185	2.219	2.06–2.11
Azulene	2.141	2.256	2.269	–
Pentalene	−2.840	−2.778	−2.526	–
Heptalene	−9.495	−8.340	−9.926	–
Anthracene	3.077	3.448	3.530	3.08–3.38

of conjugated bonds contains branching points. For simplicity, the lengths of all C–C bonds were assumed equal to the length of the C–C bond in benzene. The results are given in Table 1, where $\Delta\chi_{\text{theor}}$ is the diamagnetic anisotropy calculated by us; $\Delta\chi'_{\text{theor}}$ and $\Delta\chi''_{\text{theor}}$ are the values of the diamagnetic anisotropy calculated by the molecular-orbital method ([4]), respectively without and with allowance for nonorthogonality integrals; $\Delta\chi_{\text{exp}}$ denotes the experimental values of the diamagnetic anisotropy given in ([4]). The unit adopted is the diamagnetic anisotropy of the benzene molecule. In calculating $\Delta\chi_{\text{theor}}$, the theoretical value of the diamagnetic anisotropy of the benzene molecule, calculated for the hexagonal metallic model of this molecule, was used.

Despite the exceptional simplicity of the physical concepts underlying the metallic model of the molecule, the results we have obtained agree with experiment no worse than the results obtained by the molecular-orbital method.

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