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Free Electron Model and Magnetic Susceptibility of Aromatic Hydrocarbons

By

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Using a free electron model for the π-electron system in aromatic hydrocarbons the π-electron susceptibility due to Langevin diamagnetism and Van Vleck High frequency paramagnetism (H. F.) have been calculated. The H. F. term has been found to increase rapidly with the ring size.

Mit Hilfe eines Modells freier Elektronen für das π-Elektronensystem in aromatischen Kohlenwasserstoffen wird der Langevinsche diamagnetische Anteil und der Van Vlecksche paramagnetische Beitrag zur π-Elektronensuszeptibilität berechnet. Dabei findet man, daß letzterer mit der Ringgröße schnell wächst.

Au cadre du modèle de l'electron libre, la susceptibilité π-électronique des hydrocarbures benzéniques due au diamagnétisme de Langevin et au paramagnétisme de Van Vleck (H. F.) a été calculée. Le terme H. F. s'agrandit rapidement avec les dimensions de la molécule.

For a polyatomic molecule with effective spin quantum number zero the magnetic susceptibility is given by [5]

$$\chi_{\text{mol}} = -\frac{\text{Ne}^{2'}}{6\,mc^2}\Sigma\overline{r^2} + \frac{\text{Ne}^2}{6\,m^2\,c^2}\sum_{n'\neq n}\frac{|P(n',n)|^2}{h\,\nu\,(n',n)}\,. \tag{1}$$

The first term is the Langevin contribution which is responsible for the diamagnetism of all molecules while the second term is the Van Vleck High Frequency (H. F.) contribution and is responsible for the temperature independent paramagnetism of molecules. For most organic molecules the H. F. term is very small but is notoriously difficult to calculate theoretically. Recently the Free Electron model of RUEDENBERG and PARR [3] has been used by BASU [1] to calculate the doublet splitting in hydrocarbon ions. This model is very well suited for the calculation of both the Langevin term and the H. F. term in the π-electron susceptibility of aromatic hydrocarbons.

The unsaturation electrons in aromatic molecules are assumed to move in a circular orbit of radius R (A) in an axial potential field given by

$$\begin{aligned} V_z &= \tfrac{1}{2}kz^2 \\ V_r &= \frac{h^2}{8\,\pi^2\,m}\,\frac{1}{4\,R^2\,\alpha^2}\left[(R/r)^2 + (r/R)^2 - 2\right] \qquad (2) \\ \text{and} \qquad V_\varphi &= 0 \end{aligned}$$

where k and α are two parameters to be determined from experimental data. The allowed energy levels of an electron in such a potential field may be given as

$$E = E_z + E_r + E_\varphi \tag{3}$$

where

$$E_z = (n_z + \tfrac{1}{2}) \frac{h}{2\pi} (k/m)^{\frac{1}{2}} , \qquad n_z = 1, 3, 5, \text{etc.} \tag{4}$$

(since π-electron wave function must have a node in the molecular plane)

$$E_r = (n_r + 1) \frac{h^2}{8 \pi^2 m R^2 \alpha^2} , \qquad n_r = 0, 2, 4, \text{etc.} \tag{5}$$

and

$$E_\varphi = \frac{h^2}{8 \pi^2 m R^2} l^2 f (\alpha^2 l^2) , \qquad l \pm 0, \ \pm 1, \ \pm 2, \text{etc.} \tag{6}$$

where

$$1 + 2 \alpha^2 l^2 f (\alpha^2 l^2) = (1 + 4 \alpha^2 l^2)^{\frac{1}{2}} . \tag{7}$$

The wave function of an electron in such a system is given as

$$\psi_{n_z n_r l} (z, r, \varphi) = \mathrm{N} e^{\frac{-K:^2}{2}} H_{n_z} (\sqrt{K} z) e^{\frac{-Cr^2}{2}} F_{n_r |l|} (\sqrt{C} r) e^{im\varphi} \tag{8}$$

$H (\sqrt{k} z)$ being a Hermit polynomial and $F (\sqrt{C} r)$ is also a polynomial given by

$$F (\sqrt{C} r) = (\sqrt{C} r)^\eta \sum_{\nu=0}^{n_r} a_\nu (\sqrt{C} r)^\nu \tag{9}$$

where

$$\eta^2 = \frac{1}{4 \alpha^2} + l^2, K = \frac{4 \pi^2 m k}{h^2} \text{ and } C = \frac{1}{2 R^2 \alpha} . \tag{10}$$

Assuming that the long wave length absorption spectra in aromatic hydrocarbons arise from the electronic excitation in the E_φ levels [*3*], α was estimated to be about 0.0925. Similarly associating the absorption band near 1000 Å with the excitation in the E_z levels k was estimated to be about 10^{-16} gm/cm^2 expressing the frequency in cm^{-1}.

Since α is small it can be shown that $r^2 \approx R^2$, which enables us to estimate the Langevin term in (1) very easily from the radius of the ring. For the H. F. term in (1) it can be shown that

$$P^2 (n, n) = \Sigma P (n, n') P (n', n) = \Sigma | P (n', n) |^2$$

where $n = n_z + n_r + l$. The separation between the E_z and the E_r levels are much larger than those between E_φ levels [*1*]. So in most cases of interest to us, the lowest E_z and E_r level will be occupied and the E_φ levels will be filled by electrons progressively two per level, from $l = 0$ onwards, in the ground state of the molecule.

The variable denominator $\nu (n', n)$ in H. F. term was replaced by a constant ν_1, where ν_1 is a sort of mean absorption frequency [*5*] which was estimated from the π-electron polarisability using the relation $\alpha_\pi = e^2/4\pi^2 m \nu_1^2$. In the evaluation of the expectation value of $P^2 =$

$$\left\{ \frac{h^2}{4 \pi^2} \left[r^2 \frac{\partial^2}{\partial z^2} + \left(\frac{z^2}{r^2} + 1 \right) \frac{\partial^2}{\partial \varphi^2} - r \frac{\partial}{\partial r} + \frac{1}{r} \frac{\partial}{\partial r} \left(z^2 r \frac{\partial}{\partial r} \right) - 2 z \frac{\partial}{\partial r} \left(r \frac{\partial}{\partial z} \right) \right] \right\}$$

the integration over the z and φ were performed analytically but that over r was carried out numerically (approximately). The radius of the ring was determined by usual area approximation [*1*].

In the table are summarised the calculated values of the various terms in the equation (1) for rings of various sizes.

Table. *Magnetic susceptibility of aromatic hydrocarbons*

number of rings	α_π [4]	ν_1 (Rydberg unit)	R (A)	Langevin term	H. F. term	Exp. χ_{mol}
one	41×10^{-25}	0.36	1.32	-39×10^{-6}	2.2×10^{-6}	54×10^{-6}
two	77	0.27	1.78	−143	26.1	146
three	125	0.21	2.18	−300	69.4	223
four	153	0.19	2.58	−457	160.2	218

Although we may not attach much importance to the absolute magnitude of the susceptibility values calculated the present analysis shows that the H. F. term increases rather rapidly as the ring size is increased thereby reducing considerably the diamagnetism of the molecule calculated by the Langevin term alone.

Literature

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