PHYSICS

I. V. ALEKSANDROV

1958

SovietRxiv

Abstract

Full Text

PHYSICS

I. V. ALEKSANDROV

CALCULATION OF THE NUCLEAR MAGNETIC SHIELDING CONSTANT

(Presented by Academician V. N. Kondrat' ev, 7 XII 1957)

For the interpretation of nuclear magnetic resonance spectra it is important to know the magnetic shielding constant σ, which determines the magnitude of the chemical shift of a line. There are two principal methods for calculating σ. The first ([1]) is based on perturbation theory and requires knowledge of the wave functions of all excited electronic states of the molecule. The second method ([2]) uses the variational principle, and for its application it is necessary to know sufficiently accurately the wave function of the ground state, since in order to calculate σ one has to take the second derivative of the wave function. But the wave functions of the excited states are usually unknown; it is also not possible to determine the wave function of the ground state with a high degree of accuracy, so that neither method can be considered reliable. The method proposed in the present work for calculating σ is based on the method of molecular orbitals.

Let us consider a molecule placed in a homogeneous external magnetic field $\mathcal{H}$; let μ be the magnetic moment of the nucleus for which the shielding is being calculated. Then the Hamiltonian of the molecule (for fixed nuclei) has the form

$$\hat{H} = \frac{1}{2m} \sum_i \left(\mathbf{p}_i + \frac{e}{c} \mathbf{A}_i^{\mathcal{H}} + \frac{e}{c} \mathbf{A}_i^{\mu} \right)^2 + V', \tag{1}$$

where V' is the potential energy of the electrons and nuclei; $\mathbf{A}_i^{\mathcal{H}}$, $\mathbf{A}_i^{\mu}$ are the values of the vector potentials (at the point where the electron with number i is located) of the external magnetic field $\mathcal{H}$ and of the field produced by the magnetic moment of the nucleus μ, respectively.

We write (1) in the form

$$\hat{H} = \hat{H}_0' + \frac{e}{mc} \sum_i \left(\mathbf{p}_i + \frac{e}{c} \mathbf{A}_i^{\mathcal{H}} \right) \mathbf{A}_i^{\mu} + \frac{e^2}{2mc^2} \sum_i \left(\mathbf{A}_i^{\mu} \right)^2, \tag{2}$$

where

$$\hat{H}_0' = \frac{1}{2m}\sum_i \left(\mathbf{p}_i + \frac{e}{c}\mathbf{A}_i^{\mathcal{H}}\right)^2 + V'. \tag{3}$$

In expression (2), the terms containing $\mathbf{A}_i^{\mu}$ and $\left(\mathbf{A}_i^{\mu}\right)^2$ will be regarded as a perturbation. The formulation of the problem differs from Ramsey' s work ([1]) in that the interaction of the electrons with the external magnetic field is included in the unperturbed Hamiltonian $\hat{H}_0'$. Therefore the eigenfunctions ψ_n of the unperturbed Hamiltonian depend on $\mathcal{H}$. We expand ψ_n in a series in powers of $\mathcal{H}$:

$$\psi_n = \sum_{q=0}^{\infty} \mathcal{H}^q \psi_n^{(q)}. \tag{4}$$

Writing now, in first approximation, the perturbation energy and retaining in the resulting expression only the terms proportional to $\mu\mathcal{H}$, we find for the shielding constant

$$\sigma_\lambda = \frac{1}{\mu\mathcal{H}}\left\{\frac{e^2}{mc^2}\left(\psi_n^{(0)*}\left|\sum_i A_i^H A_i^{\mu}\right|\psi_n^{(0)}\right)_\lambda + \right.$$

$$\left. + \frac{e\mathcal{H}}{mc}\left(\psi_n^{(0)*}\left|\sum_i \mathbf{p}_i A_i^{\mu}\right|\psi_n^{(1)}\right)_\lambda + \frac{e\mathcal{H}}{mc}\left(\psi_n^{(1)*}\left|\sum_i \mathbf{p}_i A_i^{\mu}\right|\psi_n^{(0)}\right)_\lambda\right\}, \tag{5}$$

where λ is the parameter determining the orientation of the molecule relative to the external field (for example, the Euler angles). In a coordinate system rigidly fixed to the skeleton of the molecule, not only the form of the operators A_i^H, A_i^{μ}, but also the function $\psi_n^{(1)}$, depends on λ. Therefore it is not possible, in general form, to average expression (5) over all orientations until the dependence of $\psi_n^{(1)}$ on λ has been established explicitly. We note that in expression (5) the first term is exactly equal to the diamagnetic term of Ramsey' s formula ([1]), and the last two correspond to the paramagnetic part of this formula.

Thus, it is necessary to find the functions $\psi_n^{(0)}$ and $\psi_n^{(1)}$, i.e., to find the eigenfunction of the operator $\hat{H}_0'$ accurate to terms of first order in $\mathcal{H}$. We shall seek this function by a method similar to that proposed in the papers of London and Pople ([3]). Let us replace $\hat{H}_0'$ by the one-electron operator:

$$\hat{H}_0 = \frac{1}{2m}\left(\mathbf{p} + \frac{e}{c}\mathbf{A}\mathcal{H}\right)^2 + V_{\text{eff}}, \tag{6}$$

where V_{eff} is the potential of the effective field in which the electron moves. Since we shall seek the solution of the equation

$$\hat{H}_0\psi_n = E_n\psi_n \tag{7}$$

in the form of a linear combination of atomic orbitals, it is convenient to write V_{eff} in the following form:

$$V_{\text{eff}} = \sum_B U_B(r_B) + V, \tag{8}$$

where $U_B(r_B)$ is the spherically symmetric part of the effective potential of atom B, while for V equation (8) serves as the definition.

We now seek ψ_n in the form:

$$\psi_n = \sum_B \sum_k c^n_{Bk}\Phi_{Bk}, \tag{9}$$

where Φ_{Bk} satisfies the equation

$$\left[\frac{1}{2m}\left(\mathbf{p} + \frac{e}{c}\mathbf{A}\mathcal{H}\right)^2 + U_B(r_B)\right]\Phi_{Bk} = E_{Bk}\Phi_{Bk}. \tag{10}$$

The coefficients c^n_{Bk} are determined in the usual way (see, for example, ([5])) by solving the secular equation, provided the functions Φ_{Bk} are known. We note that it follows from expression (9) that it is sufficient to calculate Φ_{Bk} accurate to terms of first order in $\mathcal{H}$ (to this accuracy one must know ψ_n). But this means that in equation (10) one may omit the term $\frac{e^2}{2mc^2}(\mathbf{A}\mathcal{H})^2$, since it is proportional to $\mathcal{H}^2$. Equation (10) then becomes the equation

$$\left[\frac{1}{2m}\mathbf{p}^2 + \frac{e}{mc}\mathbf{A}\mathcal{H}\mathbf{p} + U_B\right]\Phi_{Bk} = E_{Bk}\Phi_{Bk}. \tag{11}$$

Using the circumstance that, upon replacing $\mathbf{A}^H$ by $\mathbf{A}^H + \operatorname{grad} f$, the functions Φ_{Bk} go over into $\Phi_{Bk}\exp\left(-\frac{ie}{\hbar c}f\right)$, it is easy to see that the solution of equation (11) is

$$\Phi_{Bk} = \Phi^0_{Bk}\exp\left\{-\frac{ie\mathcal{H}}{2\hbar c}(yX_B - xY_B)\right\}; \qquad E_{Bk} = E^0_{Bk} - \frac{e\hbar\mathcal{H}}{mc}M_{Bk}. \tag{12}$$

In expression (12) the following notation has been introduced: X_B, Y_B are the coordinates of nucleus B in the coordinate system xyz, whose z-axis coincides

with the direction of the external field $\mathcal{H}$; Φ^0_{Bk} is the eigenfunction of the operators

$$\hat{H}_B = -\frac{\hbar^2}{2m}\nabla^2_B + U_B$$

and

$$\hat{m}_{zB} = -i\hbar\left(x_B\frac{\partial}{\partial y_B} - y_B\frac{\partial}{\partial x_B}\right),$$

where the origin of the coordinate system $x_{By_{Bz}}B$ is at the same point as nucleus B, and the axes of this system are parallel to the axes xyz; E^0_{Bk} and M_{Bk} are the eigenvalues of the operators $\hat{H}_B$ and $\hat{m}_{zB}$, respectively. In addition, we put

$$\mathbf{A}^H = \frac{\mathcal{H}}{2}(-y, x, 0).$$

The secular equation by means of which the c^n_{Bk} are determined contains the matrix elements $(\hat{H}_0)^{Bk}_{B'k'}$ and

$$S^{Bk}_{B'k'} = \int \Phi^*_{Bk}\Phi_{B'k'}\,d\tau.$$

To terms of order $\mathcal{H}$, we have:

$$(\hat{H}_0)^{Bk}_{B'k'} = \int\left(E^0_{B'k'} + \sum_{B''\neq B'} U_{B''} + V\right)\Phi^{0*}_{Bk}\Phi^0_{B'k'}\,d\tau -$$

$$-\mathcal{H}\int\left\{\frac{ie}{2\hbar c}(yX_{BB'} - xY_{BB'})\left(E^0_{B'k'} + \sum_{B''\neq B'} U_{B''} + V\right) - \frac{e\hbar}{2mc}M_{B'k'}\right\}\Phi^{0*}_{Bk}\Phi^0_{B'k'}\,d\tau; \tag{13}$$

$$S^{Bk}_{B'k'} = \int\left\{1 - \frac{ie\mathcal{H}}{2\hbar c}(yX_{BB'} - xY_{BB'})\right\}\Phi^{0*}_{Bk}\Phi^0_{B'k'}\,d\tau,$$

where $X_{BB'} = X_B - X_{B'}$, $Y_{BB'} = Y_B - Y_{B'}$.

Having determined c^n_{Bk} and representing (in accordance with expansion (4)) ψ_n in the form

$$\psi_n = \psi^{(0)}_n + \mathcal{H}\psi^{(1)}_n,$$

one can, by formula (5), calculate σ_λ and, averaging over all orientations λ, obtain the magnetic shielding constant σ^*.

Thus, the problem of calculating σ is reduced to a calculation of approximately the same degree of difficulty as the determination of the wave function by the molecular-orbital method.

As an example of the application of the method described, we calculated the proton magnetic shielding constant in the hydrogen molecule, using the simplest form of the effective potential. Namely, we took

$$V_{\text{eff}} = -\frac{e^2}{r_a} - \frac{e^2}{r_b},$$

where r_a, r_b are the distances from the electron to the protons a and b.

As atomic orbitals we took the functions

$$\Phi_a^0 = e^{-r_a}/\sqrt{\pi}$$

and

$$\Phi_b^0 = e^{-r_b}/\sqrt{\pi}.$$

The calculation gives $\sigma = \sigma_d - \sigma_p$, where for the paramagnetic part σ_p one obtains the expression

$$\sigma_p = \frac{e^2}{3mc^2(2+2S)} \frac{1}{R} \left[1 - e^{-2(R/a_0)} \left(2 \left(\frac{R}{a_0} \right)^2 + 2 \left(\frac{R}{a_0} \right) + 1 \right) \right], \qquad (14)$$

---

* If the linear combinations

$$\psi_n^{(0)} = \sum_{Bk} c_{Bk}^{n(0)} \Phi_{Bk}^0,$$

which represent molecular orbitals at $\mathcal{H} = 0$, are known, then one can explicitly find the dependence of $\psi_n^{(1)}$ on λ and average formula (5) over all orientations. The resulting expression for σ is in general too cumbersome, and we do not give it.

where $S = \int \Phi_a^0 \Phi_b^0 \, d\tau$; R is the equilibrium distance between the protons; a_0 is the Bohr radius. The diamagnetic part σ_d has the same form as in Ramsey' s formula ([1]).

The molecular-orbital method (in our approximation) gives for R the value $R = 1.6a_0$ ([4]). Then $\sigma_d = 2.77 \cdot 10^{-5}$, $\sigma_p = 0.40 \cdot 10^{-5}$, and $\sigma = 2.37 \cdot 10^{-5}$. Taking the experimental value $R = 1.4a_0$, we obtain: $\sigma_d = 2.83 \cdot 10^{-5}$, $\sigma_p = 0.38 \cdot 10^{-5}$, $\sigma = 2.45 \cdot 10^{-5}$. If one uses as the ground-state function $\psi = (\Phi_a^0 + \Phi_b^0)/(2 + 2S)$, then the variational method gives, for $R = 1.4a_0$: $\sigma_d = 2.83 \cdot 10^{-5}$, $\sigma_p = 0.13 \cdot 10^{-5}$, and $\sigma = 2.70 \cdot 10^{-5}$ ([2]). Ramsey' s calculation, in which the value of σ_p was determined indirectly from experimental data, leads to the result: $\sigma_d = 3.24 \cdot 10^{-5}$, $\sigma_p = 0.56 \cdot 10^{-5}$, and $\sigma = 2.68 \cdot 10^{-5}$ ([1]). Thus, for the quantity σ_p, our method gives somewhat better agreement with Ramsey' s semi-phenomenological result than does the variational method. As for the diamagnetic part σ_d, its value in any method of calculation is determined by

the wave function of the molecule in the absence of an external magnetic field. It should be noted that σ_d and σ_p separately depend on the choice of the vector potential A_i^H (whereas $\sigma = \sigma_d - \sigma_p$, of course, does not depend on the form of A^H). In all the calculations whose results have been presented, it is assumed that

$$A_i^H = \frac{\mathcal{H}}{2}(-y_i, x_i, 0),$$

with the origin of coordinates located at the same point as the nucleus being shielded.

The author thanks Prof. N. D. Sokolov for numerous discussions of this work.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
29 XI 1957

CITED LITERATURE

1. N. E. Ramsey, Phys. Rev., **77**, 567 (1950); **78**, 699 (1950); **83**, 540 (1951); **86**, 243 (1952).

2. J. F. Honig, J. O. Hirschfelder, J. Chem. Phys., **23**, 474 (1955); B. R. McGarvey, J. Chem. Phys., **26**, 221 (1957); **27**, 68 (1957).

3. F. London, Phys. Radium, **8**, 397 (1937); J. A. Pople, Proc. Roy. Soc., A, **239**, 541 (1957).

4. G. Hellmann, *Quantum Chemistry*, 1937.

5. G. Eyring, J. Walter, J. Kimball, *Quantum Chemistry*, Ch. XI, 1948.

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