[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NAGOYA UNIVERSITY]

Variational Calculation of Diamagnetic Susceptibilities, Chemical Shifts and Electronic Polarizabilities

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The variational method has been applied to the calculation of the diamagnetic susceptibility χ and electronic polarizability α of molecules, and of the magnetic shielding of nuclei in molecules σ. The formulas thus derived for χ and σ are identical with those previously proposed. The expression for χ gave satisfactory results when applied to the hydrogen molecule and the π-electron system of benzene. The applicability of the formulas for χ and σ has been discussed.

I. Introduction

As is well known, the general expressions for the diamagnetic susceptibiliy[1] and electronic polarizability[1] of molecules and for the nuclear magnetic shielding[2] of nuclei in molecules are based on the second-order perturbation theory. These expressions, however, are difficult to apply since the wave functions of excited electronic states, which are involved in the expressions, are seldom available. In a previous publication,[3] a simplification of the expression for the nuclear magnetic shielding of nuclei in molecules was presented; this simple formula is easy to apply since it involves only the ground-state wave functions of molecules. It gives quite satisfactory results for the proton magnetic shielding constants of hydrogen and polynuclear aromatic hydrocarbons and for the effect of electrons localized at distant atoms. However, the derivation of the formula involves some ambiguity as mentioned below. The derivation consists in the following procedures: (a) the energy differences $E_n - E_0$ between excited states and the ground state are replaced by an average energy ΔE, (b) the matrix elements obtained with procedure (a) are re-expressed in terms of other kinds of matrix elements and $E_n - E_0$, (c) the energy differences $E_n - E_0$ obtained by (b) are replaced by an average energy $\Delta E'$ and (d) ΔE and $\Delta E'$ are canceled assuming that $\Delta E = \Delta E'$. However, the last postulate is not always valid because ΔE usually varies with the system. Although procedure d seems to be correct for the cases studied as the resultant formula gives satisfactory results, it is desirable to derive the formula on a sounder basis. In the present paper the variational derivation of this formula and corresponding formulas[4] for the diamagnetic susceptibility and electronic polarizability of molecules is studied. The variational method already has been applied to the electronic polarizability of molecules by Guy and Harrand,[5] to the diamagnetic susceptibility of molecules by Tillieu and Guy,[6] and to nuclear magnetic shielding by Das and Bersohn,[7] McGarvey[8] and Stephen.[9] The present study follows essentially that of Tillieu and Guy but it is developed in somewhat different ways. In the following, the polarizability, susceptibility and nuclear magnetic shielding due to each electron in a molecule are studied and the corresponding values of the whole molecule are assumed to be the sum of the one-electron quantities.

II. Diamagnetic Susceptibility and Nuclear Magnetic Shielding

The effective Hamiltonian χ of an electron under an external magnetic field H is given[2] by

$$\chi = \chi^{(0)} + \chi^{(1)} + \chi^{(2)} \tag{1}$$

$$\left.\begin{aligned} \chi^{(0)} &= -(\hbar^2/2m)^2 + V \\ \chi^{(1)} &= -(H + 2\mu/r^3)M_z \\ \chi^{(2)} &= (e^2/8mc^2)(H + 2\mu/r^3)^2(x^2 + y^2) \\ M &= (ie\hbar/2mc)(x\partial/\partial y - y\partial/\partial x) \end{aligned}\right\} \tag{2}$$

where V is the electrostatic potential energy function for the electron; x and y are the x and y coördinates of the electron, respectively, with the z-axis along the external magnetic field and the origin at the nucleus for which the shielding is desired; and r is the distance between the electron and the origin. It is assumed in (2) that all nuclei other than that for which the shielding is desired have zero magnetic moments and that the nucleus concerned has a magnetic moment of magnitude μ in the same direction as the external magnetic field.

To obtain the nuclear magnetic shielding constant and the diamagnetic susceptibility of the molecular system in the presence of H and μ, one has to calculate the energy W of each electron. Let φ_0 and W_0 be the wave function and the energy of an unperturbed electron. Then

$$\chi^{(0)}\,\varphi_0 = W_0\varphi_0 \tag{3}$$

In the following, φ_0 is assumed to be real and normalized to unity. The wave function φ of the corresponding perturbed electron is assumed to have the form

$$\begin{aligned} \varphi &= \varphi_0(1 + \lambda f(r)) \\ f(r) &= g(r) + ih(r) \end{aligned} \tag{4}$$

where g and h are both real functions of the coordinates of the electron. The variational parameter λ, which may involve H and μ, is determined for minimum W, where W is given by

$$W = (\varphi|\chi|\varphi)/(\varphi|\varphi) \tag{5}$$

Substituting (4) in (5) and expanding the latter in

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[1] J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, New York, N. Y., 1932.

[2] N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950).

[3] K. Ito, THIS JOURNAL, **80**, 3502 (1958).

[4] These formulas derived by the same method as that used in ref. 3 were given at The Tokyo University Symposium on Molecular Electronic States on 14th October, 1957, and at the Kyushu University Symposium on Molecular Structure and Spectra on 21st November, 1957, both held by The Chemical Society of Japan.

[5] J. Guy and M. Harrand, *Compt. rend.*, **234**, 616 (1952).

[6] J. Tillieu and J. Guy, *J. Chem. Phys.*, **24**, 1117 (1956).

[7] T. P. Das and R. Bersohn, *Phys. Rev.*, **104**, 849 (1956). See also ref. 9.

[8] B. McGarvey, *J. Chem. Phys.*, **26**, 221 (1957).

[9] M. J. Stephen, *Proc. Roy. Soc.* (*London*), **A242**, 264 (1957).

a power series of λ gives

$$W = A + B\lambda + C\lambda^2 + \cdots \qquad (6)$$

Then for minimum W, λ is given by

$$\lambda = -B/2C$$

and consequently

$$W = A - B^2/4C \qquad (7)$$

where

$$\begin{aligned} A &= (\varphi_0|\chi|\varphi_0) \\ B &= 2Re(f\varphi_0|\chi|\varphi_0) - SA \\ C &= (f\varphi_0|\chi|f\varphi_0) - (f\varphi_0|f\varphi_0)A - SB \qquad (8) \\ S &= 2Re(f\varphi_0|\varphi_0) \end{aligned}$$

Substituting (1) and (2) in (8) and integrating gives

$$\begin{aligned} A &= W_0 + (e^2H^2/8mc^2)\,\langle x^2 + y^2\rangle + (e^2\mu H/2mc^2)\,\langle (x^2 + y^2)/r^3\rangle \\ B &= (e\hbar/2mc)[H\,\langle x\partial h/\partial y - y\partial h/\partial x\rangle + 2\mu\langle (x/r^3)\partial h/\partial y - (y/r^3)\partial h/\partial x\rangle] \\ C &= (\hbar^2/2m)\,\langle (\nabla g)^2 + (\nabla h)^2\rangle \qquad (9) \end{aligned}$$

The integrations have been simplified by the use of the Hermitian nature of $\chi^{(0)}$ and $\chi^{(1)}$, and by virtue of the fact that $\chi^{(1)}$ is purely imaginary while φ_0 is real. The integrals involving $\chi^{(0)}$ or M_z have been calculated by integrating by parts. The symbol $\langle x^2 + y^2\rangle$, for instance, indicates the matrix element $(\varphi_0|x^2 + y^2|\varphi_0)$.

The nuclear magnetic shielding constant σ and the diamagnetic susceptibility χ are defined by the coefficients in a power series

$$W = W_0 - (\chi_z/2)H^2 + \sigma_z\mu H + \cdots \qquad (10)$$

Then by referring to (10), one obtains these equations from (7) and (9)

$$\chi_z = -(e^2/4mc^2)\,\langle x^2 + y^2\rangle + (e^2/4mc^2)[\langle x\partial h/\partial y - y\partial h/\partial x\rangle^2/\langle (\nabla g)^2 + (\nabla h)^2\rangle] \qquad (11a)$$

$$\sigma_z = (e^2/2mc^2)\langle (x^2 + y^2)/r^3\rangle - (e^2/2mc^2)[\langle x\partial h/\partial y - y\partial h/\partial x]\rangle\cdot\langle (x/r^3)\partial h/\partial y - (y/r^3)\partial h/\partial x\rangle/\langle (\nabla g)^2 + (\nabla h)^2\rangle] \qquad (11b)$$

where the suffix z denotes the direction of the external magnetic field. The second terms of (11a) and (11b) are the so-called paramagnetic terms. The larger the absolute values of these terms, the lower is the energy W, and the best function in the form of (4) may therefore be obtained by putting $g = 0$.

The function h for (11a) should be so chosen that the resulting formula for χ is independent of the choice of the origin.[1] As shown later, the simplest expression for h which satisfies such a condition is

$$h = ax + by + cz \qquad (12)$$

Substituting (12) in (11a) gives

$$\chi_z = -(e^2/4mc^2)[\langle x^2 + y^2\rangle - (b\langle x\rangle - a\langle y\rangle)^2/(a^2 + b^2 + c^2)]$$

The ratio $a:b:c$ for minimum W is

$$a:b:c = -\langle y\rangle:\langle x\rangle:0$$

and consequently

$$h = -\langle y\rangle x + \langle x\rangle y \qquad (13)$$

By substituting (13) in (11a), and taking the sum of the values for all the electrons, one obtains the molecular diamagnetic susceptibility.

$$\chi_z = -(e^2/4mc^2)\sum_i[\langle x_i^2 + y_i^2\rangle - \langle x_i\rangle^2 - \langle y_i\rangle^2] \qquad (14a)$$

The average susceptibility is the average of the values for all orientations of the molecule.

$$\begin{aligned} \chi_{av} &= (\chi_x + \chi_y + \chi_z)/3 \\ &= -(e^2/6mc^2)\sum_i[\langle r_i^2\rangle - \langle x_i\rangle^2 - \langle y_i\rangle^2 - \langle z_i\rangle^2] \qquad (15a) \end{aligned}$$

Equations 14a and 15a are independent of the origin. These equations are identical with those previously proposed.[4] If one assumes that $h = xy$, eq. 11a agrees with the formula presented by Tillieu and Guy.[6]

In the case of atoms, the function h of form (13) may be interpreted as follows. Let φ_0 be the eigenfunction of an electron of an unperturbed atom. If the function is represented by a hydrogen-like wave function with a proper effective nuclear charge φ_0 is approximately the eigenfunction of an electron of the atom in an external magnetic field provided that the center of the coördinates is taken at the center of the atom. If the atom is not located at the center of the coördinates, the eigenfunction may be written as[10]

$$\begin{aligned} &\varphi_0\exp[i(He/2\hbar c)(-\langle y\rangle x + \langle x\rangle y)] \\ &\quad = \varphi_0[1 + i(He/2\hbar c)(-\langle y\rangle x + \langle x\rangle y) + \cdots] \qquad (16) \end{aligned}$$

A comparison of (16) with (4) gives the form of h shown in (13).

These arguments concerning h suggest that (14a) or (15a) may be applicable especially to (a) highly symmetric molecules such as benzene, (b) molecules in which the electron clouds of constituent atoms overlap to a considerable extent and (c) molecules in which the overlap of these electron clouds is very small. Equation 14a applied to the π-electron system of benzene gives Pauling's "induced-current" model.[11] Equation 14a also has been applied to hydrogen using the molecular orbital wave function with the effective nuclear charge[12] of 1.197 at the equilibrium position. The results obtained which are shown in Table I seem quite satisfactory in comparison with the experimental values,[13–15] $\chi_{av} = -3.94$, -3.99 and -4.01×10^{-6}, the last of which is probably the most accurate.

TABLE I

THE MAGNETIC SUSCEPTIBILITIES[a] OF THE HYDROGEN MOLECULE CALCULATED FROM EQ. 14a AND 15a

	Diamag. term	Paramag. term	Sum
$\chi_{av} \times 10^6$	−4.81	0.78	−4.03
$\chi_{\parallel} \times 10^6$	−3.50	0	−3.50
$\chi_{\perp} \times 10^6$	−5.46	1.17	−4.29

[a] χ_{av}, mean susceptibility; $\chi_{\parallel}$, principal susceptibility parallel to the molecular axis; $\chi_{\perp}$, principal susceptibility perpendicular to the molecular axis.

Since χ, σ, μ and H in (10) usually have the order of magnitude of about 10^{-30} (per molecule), 10^{-6} to 10^{-4}, 10^{-24}, and 10^4 (Gauss), respectively, the second term of (10) is about 10^4 to 10^2 times larger than the third term. Therefore, function (13), which is derived from the second term of (10) for minimum W, may also be a fairly good variational

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(10) F. London, *J. phys. radium*, **8**, 397 (1937).

(11) L. Pauling, *J. Chem. Phys.*, **4**, 673 (1936).

(12) C. A. Coulson, *Trans. Faraday Soc.*, **33**, 1479 (1937).

(13) A. P. Wills and L. G. Hector, *Phys. Rev.*, **23**, 209 (1924); L. G. Hector, *ibid.*, **24**, 418 (1924).

(14) T. Sone, *Phil. Mag.*, **39**, 105 (1920).

(15) G. G. Havens, *Phys. Rev.*, **43** 992 (1933).

function for (11b). By substituting (13) in (11b) and taking the sum of the values for all the electrons, one obtains σ_z of the molecule

$$\sigma_z = (e^2/2mc^2)\sum_i[\langle(x_i^2 + y_i^2)/r_i^3\rangle - \langle x_i\rangle\langle x_i/r_i^3\rangle - \langle y_i\rangle\langle y_i/r_i^3\rangle] \quad [14b)$$

Averaging the molecular values for all orientation of a molecule gives

$$\begin{aligned}\sigma_{av} &= (\sigma_x + \sigma_y + \sigma_z)/3 \\ &= (e^2/3mc^2)\sum_i[\langle 1/r_i\rangle - \langle x_i\rangle\langle x_i/r_i^3\rangle - \langle y_i\rangle\langle y_i/r_i^3\rangle - \langle z_i\rangle\langle z_i/r_i^3\rangle] \quad (15b)\end{aligned}$$

Equations 14b and 15b are identical with those proposed by Ito.[3] If one assumes that $h = xy$, eq. 11b gives the formula proposed by Das and Bersohn.[7]

The comments on the form of h which were given under the discussion of diamagnetic susceptibility hold also for the nuclear magnetic shielding constant.[16] Therefore eq. 14b and 15b should give satisfactory results for (a) the types of molecules to which (14a) and (15a) are applicable, and (b) for the effects of electrons localized at atoms relatively distant from the nucleus under study; (14b) and (15b) have been applied in a few cases.[3]

III. Electronic Polarizability

The effective Hamiltonian of an electron under an external electric field E may be expressed in the form of (1) with

$$\begin{aligned}\chi^{(1)} &= ezE \\ \chi^{(2)} &= 0\end{aligned} \quad (2')$$

where the field is along the z-axis. By the use of the variational function (4), the energy W of the perturbed electron may be expressed in the form of (7) with

$$\begin{aligned}A &= W_0 + eE\langle z\rangle \\ B &= 2eE(\langle zg\rangle - \langle z\rangle\langle g\rangle) \\ C &= (\hbar^2/2m)\langle(\nabla g)^2 + (\nabla h)^2\rangle\end{aligned} \quad (9')$$

The electronic polarizability α is defined by the coefficient in a power series

$$W = W_0 - (\alpha_z/2)E^2 + \cdots \quad (10')$$

Then substitution of (9′) in (7) gives

$$\alpha_z = (4/a_0)(\langle zg\rangle - \langle z\rangle\langle g\rangle)^2/\langle(\nabla g)^2 + (\nabla h)^2\rangle \quad (11c)$$

where a_0 is the Bohr radius. For minimum W (10′), function h is made equal to zero. Function g is assumed to have a form analogous to (12)

$$g = ax + by + cz \quad (12')$$

Substitution of (12′) in (11c) and determination of the ratio $a{:}b{:}c$ for the minimum energy (10′) gives

$$a{:}b{:}c = (\langle xz\rangle - \langle x\rangle\langle z\rangle){:}(\langle yz\rangle - \langle y\rangle\langle z\rangle){:}(\langle z^2\rangle - \langle z\rangle^2) \quad (13')$$

By substituting (12′) and (13′) in (11c) and taking the sum of the values for all the electrons, one obtains the molecular electronic polarizability

$$\alpha_z = (4/a_0)\sum_i[(\langle x_iz_i\rangle - \langle x_i\rangle\langle z_i\rangle)^2 + (\langle y_iz\rangle - \langle y_i\rangle\langle z_i\rangle)^2 + (\langle z_i^2\rangle - \langle z_i\rangle^2)^2] \quad \langle 14c)$$

The mean value of α is given by

$$\begin{aligned}\alpha_{av} &= (\alpha_x + \alpha_y + \alpha_z)/3 \\ &= (4/3a_0)\sum_i[(\langle x_i^2\rangle - \langle x_i\rangle^2)^2 + (\langle y_i^2\rangle - \langle y_i\rangle^2)^2 + (\langle z_i^2\rangle - \langle z_i\rangle^2)^2 + 2(\langle x_iy_i\rangle - \langle x_i\rangle\langle y_i\rangle)^2 + 2(\langle y_iz_i\rangle - \langle y_i\rangle\langle z_i\rangle)^2 + 2\langle\langle z_ix_i\rangle - \langle z_i\rangle\langle x_i\rangle)^2] \quad (15c)\end{aligned}$$

Equations 14c and 15c are independent of the choice of the origin. For atoms, eq. 15c gives the well known formula

$$\alpha_{av} = (4/9a_0)\sum_i\langle r_i^2\rangle^2$$

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[16] H. F. Hameka, *Mol. Phys.*, **1**, 203 (1958).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Dipole Moments and Optical Dispersion of Perchloro-fluorobutanes, Butadienes, Butenes and Propylenes[1]

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Dipole moments and refractive indices between 4358 and 6565 Å. were measured for a series of perchloro-fluorobutanes, butadienes, butenes and propylenes. The optical dispersion was found to obey the relation $(n_\lambda^2 + 2)/(n_\lambda^2 - 1) = a + c_i\cdot[1/\lambda^2 - 1/\lambda_i^2]$, where λ_i is a "characteristic frequency," and a and c_i are constants characteristic of the substance. From the increments in refractivities for the substitution of F for Cl for a series of fluorocarbons, a consistent set of bond refractivities was deduced for the CF bond (1.75 cc.) and for the CCl bond (6.48 cc.) in a perhalogenated environment. Similarly, by using the increment of dipole moment for the substitution of F for Cl (0.5 D) in a perhalogenated environment and a value of μ (1.05 D) for the CCl bond moment, the minimum, maximum and free rotation dipole moments for the series of perhalocarbons studied were calculated and related to the measured dipole moments. The barrier height hindering free rotation in $CF_2{=}CCl{-}CCl{=}CF_2$ was estimated from the measured dipole moment (0.35 D).

Data on the optical dispersions and dipole moments of perhalogenated butanes, butenes and butadienes have not as yet been reported. A study of these molecular properties of perchloro-fluorobutanes, butenes, butadienes and propylenes was undertaken with the expectation of relating the evident trends in these properties to the corresponding changes in molecular structures.

Experimental

Materials.—The synthesis and purification of some of the compounds used will be described elsewhere[2]; herein we have

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[1] Part of the Ph.D. Thesis, submitted by E. Rutner, to the Faculty of the Graduate School, Cornell University, June, 1951.

[2] W. T. Miller and E. Rutner (to be published).