A MODIFIED ELECTROSTATIC METHOD FOR CALCULATION OF INDUCTION IN MOLECULES

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ABSTRACT

An electrostatic method has been worked out for calculating the induced dipole moments produced in the non polar parts of a molecule by induction from a primary dipole. This procedure which is an extension of that given by Groves and Sugden is applicable to any type of molecule once the centre of each atom of the molecule in space is specified and allows for the rapid variation of the electric field in the neighbourhood of the dipole.

INTRODUCTION

The first attempt to evaluate the classical inductive effects was made by Smallwood and Herzfeld[1] in an analysis of the electric moments of disubstituted benzenes. The basic assumption of these authors was that the electrostatic laws describing the behaviour of bulk dielectrics can also be applied to molecules. Smyth[2] applied this method to simple derivatives of methane and also to a number of molecules with some success. This method however does not take into account the intramolecular dielectric constant which will tend to reduce the electric intensity and further small errors in r can cause relatively large errors in results owing to the distance entering as the third power. Subsequently Groves and Sugden[3] evaluated group moments in aliphatic compounds with the object of estimating the magnitude of the mesomeric effect in benzene derivatives. The calculations are based on the theory of Frank[4] who has shown by classical electrostatics that the moment induced is proportional to the inverse cube of its distance, from the polarizing dipole so that the inductive effect must be relatively a short range one. Groves and Sugden overcame two defects of the earlier method, by allowing for the field intensity variation over the volume of the atom and the reduction of field strength due to the dielectric behaviour of the molecule. This method has been applied by Thompson[5] in an analysis of the moments of methyl and ethyl carbonates and by Gent[6] in discussing the moments of dimethyl ether and other ethylene oxide homologues. Recently Narasimhan[7] has critically examined certain assumptions involved in the derivations of Groves and Sugden and has modified the equations to achieve greater consistency. Lumbroso[8] has recently discussed the various methods of calculation of the inductive and mesomeric effects in detail.

Though so far no one method has provided an exact treatment, Groves and Sugden's method[3] and its modification[7] are capable of extension to any type of molecule, once the centre of each atom of the molecule in space is specified. It is the purpose of this paper to describe such a procedure, which allows for the rapid variation of the electric field in the neighbourhood of the dipole.

THEORY

Let the primary dipole be placed at the origin O with its axis along OX; if $P(x,y,z)$, is a point in space and $\angle POX = \alpha$, $\angle POY = \beta$, and $\angle POZ = \gamma$, and $OP = r$, then, $x = r\cos\alpha$, $y = r\cos\beta$, $z = r\cos\gamma$. The potential at P is $\frac{\mu x}{\epsilon_0 r^3} = f$ where μ is the primary moment, ϵ_0 the intramolecular dielectric constant[3] and r the distance from O *to* P. (Figure I)

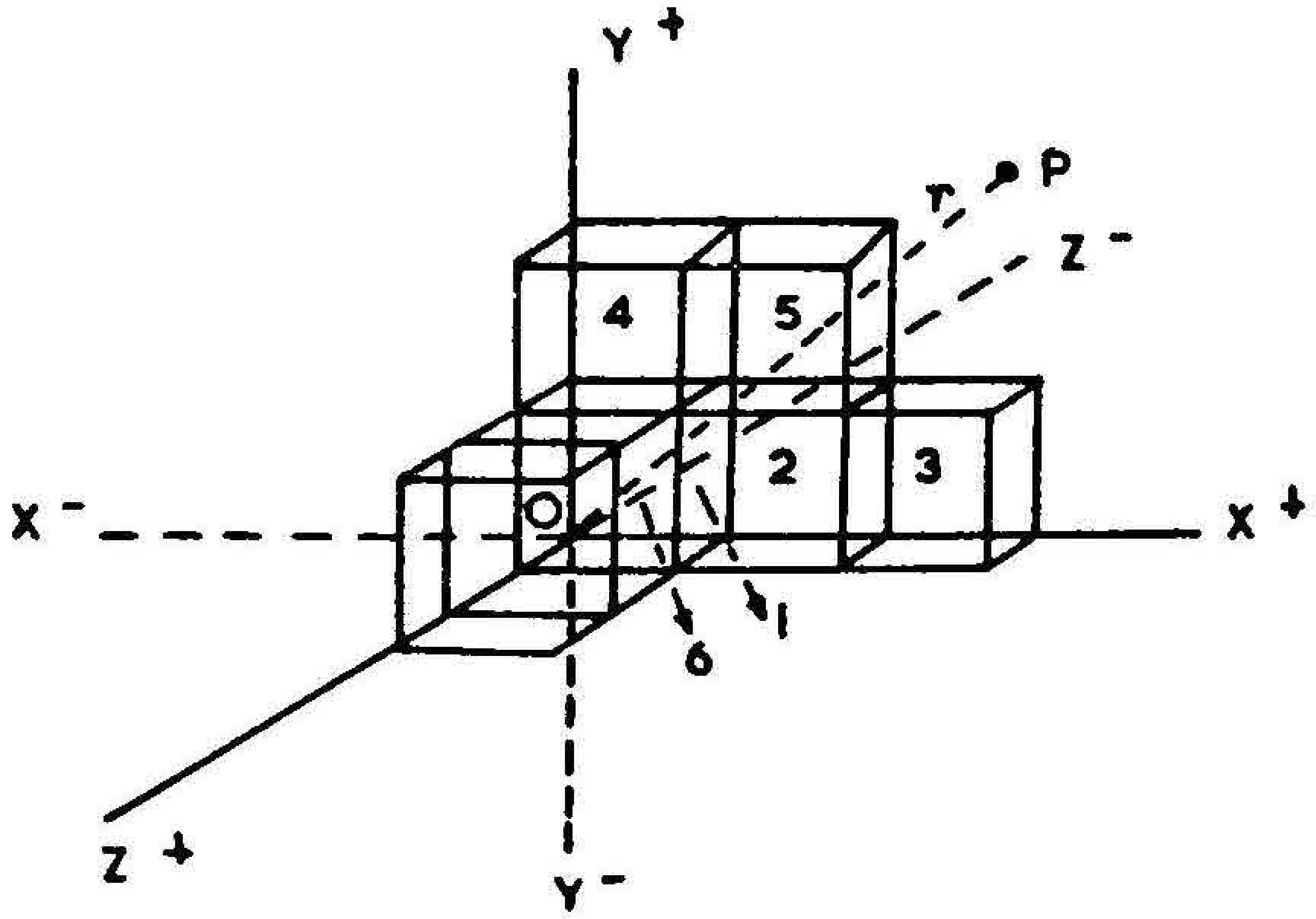

FIG. 1

$$
\begin{aligned}
E_x &= -\frac{\partial f}{\partial x} = -\frac{\mu}{\epsilon_0}\left[\frac{1}{r^3} - \frac{3x}{r^4}\cdot\frac{\partial r}{\partial x}\right] \\
E_y &= -\frac{\partial f}{\partial y} = -\frac{\mu}{\epsilon_0}\left[-\frac{3x}{r^4}\cdot\frac{\partial r}{\partial y}\right] \\
E_z &= -\frac{\partial f}{\partial z} = -\frac{\mu}{\epsilon_0}\left[-\frac{3x}{r^4}\cdot\frac{\partial r}{\partial z}\right] \qquad [1]
\end{aligned}
$$

give the field at P.

$$r\,\partial r/\partial x = x = r\cos\alpha\,; \quad r\,\partial r/\partial y = y = r\cos\beta\,;$$

$$r\,\partial r/\partial z = z = r\cos\gamma$$

$$E_x = \left[\frac{3\cos^2\alpha - 1}{r^3}\right]\frac{\mu}{\epsilon_0}$$

$$E_y = \left[\frac{3\cos\alpha\cos\beta}{r^3}\right]\frac{\mu}{\epsilon_0}$$

$$E_z = \left[\frac{3\cos\alpha\cos\gamma}{r^3}\right]\frac{\mu}{\epsilon_0} \qquad [2]$$

The induced moment per unit volume I is equal to $E\,[(\epsilon - 1)/(4\pi)]$ where ϵ is the dielectric constant of the atom at P. Hence if V is the volume of the atom and R the refraction of the atom

$$\frac{R}{N} = \frac{\epsilon - 1}{\epsilon + 2}\cdot\frac{M}{d} = \frac{\epsilon - 1}{\epsilon + 2}\,V = \frac{4\pi\alpha_0}{3} \text{ whence } V = \left[\frac{4\pi\alpha_0}{3}\cdot\frac{\epsilon + 2}{\epsilon - 1}\right]$$

The induced moment in the

$$OX \text{ direction} = \mu_{ix} = \mu\,\alpha_0\,[(\epsilon + 2)/(3\epsilon_0)]\ (3\cos^2\alpha - 1)/r^3$$

$$OY \text{ direction} = \mu_{iy} = \mu\alpha_0\ [(\epsilon + 2)/(3\,\epsilon_0)]\ (3\cos\alpha\cos\beta)/r^3$$

$$OZ \text{ direction} = \mu_{iz} = \mu\,\alpha_0\,[(\epsilon + 2)/(3\,\epsilon_0)\,]\ (3\cos\alpha\cos\gamma)/r^3 \qquad [3]$$

Now the quantities

$$A_x = \frac{3\cos^2\alpha - 1}{r^3}, \quad A_y = \frac{3\cos\alpha\cos\beta}{r^3} \quad\text{and}\quad A_z = \frac{3\cos\alpha\cos\gamma}{r^3}$$

are computed for each of a number of small cubes in the $OXYZ$ octant and the actual value of A entered into each element of volume, each edge of which has a magnitude "h". For example let the centre of cube 1 be represented by:

$$\left(\frac{h}{2}, \frac{h}{2}, \frac{h}{2}\right);$$

Then, $\cos\alpha_1 = 1/\sqrt{3}$, $\cos\beta_1 = 1/\sqrt{3}$ and $\cos\gamma_1 = 1/\sqrt{3}$

Similarly for Cube 2,

$$\mathrm{cas}\,\alpha_2 = 3/\sqrt{11}, \quad \cos\beta_2 = 1/\sqrt{11} \quad\text{and}\quad \cos\gamma_2 = 1/\sqrt{11}$$

The values of E_x, E_y and E_z for cube 1 will be

$$(E_x)_1 = \frac{\mu}{\epsilon_0}(0) = 0\,; \quad (E_y)_1 = \frac{\mu}{\epsilon_0}\left[\frac{4}{3h^2}\right]^{3/2} \quad \text{and} \quad (E_z)_1 = \frac{\mu}{\epsilon_0}\left[\frac{4}{3h^2}\right]^{3/2} \qquad [4]$$

This calculation can be done for say 1000 cubes in the $OXYZ$ octant and entered into ten centimetre graph sheets each containing 100 sq. cms., each of which represents a cube. The first graph sheet contains values for 100 cubes for which the centers range from $z = h/2$, $x = h/2$, $y = h/2$ to $z = h/2$, $x = 19\,h/2$, $y = 19\,h/2$. The ten graph sheets are for values of z from $h/2$ to $19\ h/2$. Once these values are known, the values for the corresponding cubes in the other seven octants are known according to the sign of the axes X, Y and Z. The values will be according as, $l = \cos\alpha$, $m = \cos\beta$ and $n = \cos\gamma$ are positive or negative.

Suppose a suitable scale say 0.2 Å = 1 cm. is chosen and the molecule is represented in space, with the primary dipole placed along OX axis of the $OXYZ$ octant. The primary dipole is assumed to be situated at the point of contact of the two atoms concerned. Let ΣA_x be the sum of the values of A for the elementary cubes in the volume occupied by the atom, *e.g.*, the hydrogen of the methyl group attached to the carbon of the cyano group in acetonitrile. Then the induction in the sphere, in the OX axis direction is given as

$$\frac{\mu_{ix}}{\mu} = \left[\frac{\epsilon + 2}{3\,\epsilon_0}\right]\beta_0\,\Sigma A_x. \text{ Substituting for } \beta_0 = \frac{\alpha_0}{(4\pi/3)\,(r_1^3)}$$

we get

$$\frac{\mu_{ix}}{\mu} = \alpha_0 \left[\frac{\epsilon + 2}{\epsilon_0}\right]\frac{\Sigma A_x}{4\,\pi\,r_1^3}$$

Simlarly in the OY axis direction

$$\frac{\mu_{iy}}{\mu} = \alpha_0 \left[\frac{\epsilon + 2}{\epsilon_0}\right]\frac{\Sigma\,Ay}{4\,\pi r_1^3}$$

in the OX axis direction

$$\frac{\mu_{iz}}{\mu} = \alpha_0 \left[\frac{\epsilon + 2}{\epsilon_0}\right]\frac{\Sigma A_z}{4\,\pi\,r_1^3} \qquad [5]$$

where r_1 is the radius of the atom.

Values of the constant α_0 for aliphatic compounds are readily obtained from the refractions and those for aromatic compounds from the work of Stuart and Volkman[9]. The values of ϵ and ϵ_0 are 2.0 for aliphatic compounds and 2.4 for aromatic compounds[3]. We can adopt the convention of neglecting the induction in the atoms which form the dipole.

In the conception of a molecule oriented in space with its primary dipole lying on the OX axis, one can know which of the cubes are inside the sphere. Suppose M is the centre of a particular cube, the direction cosines of which are $\cos\alpha$, $\cos\beta$ and $\cos\gamma$, and $OM = r$ and $C_0 =$ the centre of the atom S of radius ρ. If $(P-a^2)+(Q-b^2)+(R-c^2) < \rho_0^2$, where $a = r\cos\alpha$, $b = r\cos\beta$, $c = r\cos\gamma$, then M lies within S, where $P = \rho_0\cos\theta_0$, $Q = \rho_0\cos\phi_0$ and $R = \rho_0\cos\psi_0$; $OC_0 = \rho_0$ when θ_0, ϕ_0 and ψ_0 are the angles made by OC_0 with OX, OY and OZ.

If the distance of the atom from the origin O, i e, OC_0 and the values of the angles θ_0, ϕ_0 and ψ_0 made by OC_0 with OX, OY and OZ are known, it is possible to calculate the moments induced in an atom S, by the primary dipole, in the OX, OY and OZ directions. The induced moments thus calculated can then be vectorially added along with the primary moment and other bond moments to give the resultant moment of the molecule.

DISCUSSION

The primary dipole has been treated as a point dipole and is assumed to be placed at the point of contact of the two atoms forming the dipole. The field at any point is first taken as that due to the primary dipole in vacuum and allowance is made later for the effect of the intervening medium by dividig the field by the dielectric constant. The above assumptions are the same as those of Groves and Sugden[3]. But the effect of the field on the polarizable matter has been treated differently, bearing in mind the error in Groves and Sugden's derivation, wherein the volume of the atom is taken equal to $(4\pi\alpha/3)\cdot(\epsilon+2)/(\epsilon-1)$ since $R/N = (\epsilon-1)/(\epsilon+2)(M/d) = (4\pi\alpha/3)$ which does not represent the volume of the atom or group but includes " the free space" as well[7]. In the application of the method since it is essential to assume that the atom concerned is a sphere of uniform polarizability, the volume of the atom is taken as equal to $(4\pi/3)\,r_1^3$ where r_1 is the radius of the atom or group. Consequently this procedure is expected to yield values for the induced moments which will be much less than those obtained by the method of Groves and Sugden. This treatment can be used to allow for induction effects in quantitative sterochemical applications and in attempts to calculate individual bond moments or to detect abnormalities in moments of a whole molecule.

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