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NUCLEAR MAGNETIC SHIELDING OF A HYDROGEN
ATOM IN THE FIELD OF AN ELECTRIC DIPOLE*

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The wave function for a hydrogen atom in the field of an electric dipole is found to first order in perturbation theory. The potential function of the dipole is expanded in multipole form about the proton. The proton and dipole are assumed to be held in a fixed configuration. The effect of the dipole, on the electron, is assumed to be effectively given by the potential interior to a sphere of which the surface passes through the point dipole and the center is at the proton. The first order correction to the wave function is in the form of an infinite series. The magnetic shielding factor is calculated. The anisotropic shielding factor contains a part linear in the dipole strength, p ; it may be positive or negative depending on the configuration of the atom-dipole pair. The term linear in p is due to the part of the dipolar potential proportional to $P_2(\mu)$. The isotropic shielding factor, σ , contains a part quadratic in p but not a part linear in p . The diamagnetic and paramagnetic contributions to σ , both of which are negative, are calculated separately. The paramagnetic contribution is calculated with somewhat more accuracy than the diamagnetic contribution. Numerical results are given and discussed.

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I. Introduction

The magnetic shielding tensor for a given nucleus in a molecule may be calculated provided an accurate electronic wave function is known. The ideal situation is one in which the complete molecular electronic wave function is known. Such complete information is, however, rarely available, and, even if it were, such detail would not be necessary. Thus, if the nucleus is part of a localized bond, only the electrons associated with that bond need, to a good approximation, be considered. However, these electrons are subject to perturbations from atoms or groups of atoms at remote positions within the molecule. Of course, the complete molecular electronic wave function would contain the effects of remote groups on the localized bond. It is desirable to simulate the effects of remote groups by various classical potentials. One important effect of many chemical groups is due to an electrical dipole moment associated with the group.

To a first approximation, the electrostatic potential of an electric dipole is that of a uniform electric field. Buckingham and Pople¹ have solved the problem of a hydrogen atom in combined uniform electric (E) and magnetic (H) fields. Their solution resulted in a wave function with additive corrections to the free hydrogen atom wave function, proportional to E, EH and E². Marshall and Pople² used the results of Buckingham and Pople to compute the magnetic shielding tensor, σ , of a hydrogen atom in an electric field. Their analysis showed that the electric field reduces

the magnetic shielding tensor; the reduction is the greatest when the magnetic field is perpendicular to the electric field. Furthermore, the change in σ is quadratic in E . There is no change linear in E since the nucleus is at a center of symmetry.

Buckingham³ observed that a term linear in E would occur in σ if the nucleus is no longer at a center of symmetry such as would be the case for a hydrogen atom involved in a chemical bond. Buckingham and Lawley⁴ have shown that the effect of an electric field gradient on the shielding of a hydrogen atom is linear in the field gradient, but it is ordinarily small compared to the shielding proportional to E^2 . Another instance in which the symmetry is reduced is the case of a hydrogen atom in the field of an electric dipole. It is the purpose of this paper to examine the latter case in detail.

II. The First Order Wave Function

The hydrogen atom and the electric dipole are shown in the accompanying figure. The proton and dipole are assumed to be held fixed at the ends of the vector $\underline{R}$. It will be convenient to speak of the atom and dipole combination as the molecule. A coordinate system is fixed in the molecule with the origin at the proton. The vector (r, θ, ϕ) locates the electron. The dipole moment $\underline{p}$, fixed at $\underline{R}$, and the vector $\underline{R}$ determine the $y z$ plane. If $\underline{p}$ and $\underline{R}$ are collinear, the $y z$ plane may be chosen arbitrarily.

The electrostatic potential, ϕ , is

$$\phi = \underline{p} \cdot \underline{\rho} / \rho^3 \quad (1)$$

where $\underline{\rho} = \underline{R} + \underline{r}$. Within the sphere of radius R with center at the proton, ϕ may be expanded in multipole form.

$$\phi_{<} = - \frac{p_1}{R^2} \sum_{l=0}^{\infty} \frac{(l+1)}{R^l} r^l P_l(\mu) + \frac{p_2}{R^2} \sum_{l=1}^{\infty} \frac{r^l}{R^l} P_l^{(1)}(\mu) \sin \varphi. \quad (2)$$

In (2), $\mu = \cos \theta$, $p_1 = p \cos \eta$ and $p_2 = p \sin \eta$. $P_l(\mu)$ is the Legendre polynomial and $P_l^{(1)}(\mu)$ is the first associated Legendre polynomial. The subscript on ϕ is used to indicate that the expansion (2) has a radius of convergence R . $\phi_{<}$ is an exact expression for ϕ in the region $r < R$, $-1 \leq \mu \leq 1$. For $r > R$, $-1 \leq \mu \leq 1$, ϕ would be given by an expansion in powers of R/r . The latter expansion will not be used for reasons to be discussed later.

Given the solution to

$$\mathcal{H}_0 \psi_0 = E_0 \psi_0,$$

we wish to find the solution to

$$(\mathcal{H}_0 + V) \Psi = E \Psi.$$

Subscripts on wave functions and energy values are used to indicate the order of approximation. The method developed by Dalgarno⁵ and associates and effectively exploited by Schwartz⁶ is particularly appropriate for the problem in this paper. The wave function correct to first order is given by

$$\psi_1 = (1 + F) \psi_0, \quad (3)$$

where F is the solution to the operator equation

$$(E_0 - \mathcal{H}_0) F \psi_0 = (V - \langle V \rangle) \psi_0. \quad (4)$$

In (4), $\langle V \rangle$ is the expectation of V in the unperturbed state. If V is a function of space coordinates only, F is a solution to the inhomogeneous differential equation^{5,6}

$$\psi_0 \nabla^2 F + 2 \nabla F \cdot \nabla \psi_0 = \frac{2m}{\hbar^2} (V - \langle V \rangle) \psi_0. \quad (5)$$

We will be computing quantities which depend in a large part on the behavior of the wave function in the vicinity of the nucleus. The potential energy may be written as

$$V = -e \Phi_{<} , \quad r < R$$

and

$$V = -e \Phi_{>} , \quad r > R .$$

The first order wave function is

$$\psi_1 = (1 + F_{<}) \psi_0 , \quad r < R ;$$

$$\psi_1 = (1 + F_{>}) \psi_0 , \quad r > R .$$

In expressions for physical quantities, $F_{<}$ and $F_{>}$ occur in the various integrals as factors with ψ_0^2 . In the region where $F = F_{<}$, ψ_0^2 is large; but where $F = F_{>}$, ψ_0^2 is small if R is large enough. Thus, to a good approximation the effect of the electric dipole may be neglected outside of the sphere $r = R$. We then write

$$\begin{aligned} \psi_1 &= (1 + F) \psi_0 & r \leq R' < R \\ \psi_1 &= \psi_0 & r > R' \end{aligned} \tag{6}$$

where the $<$ has been dropped as a subscript. In (6), the effective boundary of the perturbation has been labeled R' which is less than R . The reason for this artifice will be made clear later.

It will be convenient to put $V = V_1 + V_2$, where

$$\begin{aligned} V_1 &= \frac{ep_1}{R^2} \sum_{l=1}^{\infty} \frac{(l+1)}{R^l} r^l P_l(\mu) \\ V_2 &= -\frac{ep_2}{R^2} \sum_{l=1}^{\infty} \frac{r^l}{R^l} P_l^{(1)}(\mu) \sin \varphi \end{aligned} \tag{7}$$

Note that the constant $\frac{ep_1}{R^2}$ has been dropped from V since its effect is simply a translation of the energy by that amount leaving the wave function unaffected. The solution of (5) for $V = V_1$ is

$$F_1 = - \frac{p_1}{eR^2} \sum_{l=1}^{\infty} \frac{(l+1)}{R^l} \left[\frac{ar^l}{l} + \frac{r^{l+1}}{l+1} \right] P_l(\mu). \quad (8)$$

The solution for $V = V_2$ is

$$F_2 = \frac{p_2}{eR^2} \sum_{l=1}^{\infty} \frac{1}{R^l} \left[\frac{ar^l}{l} + \frac{r^{l+1}}{l+1} \right] P_l^{(1)}(\mu) \sin \varphi. \quad (9)$$

The total correction F is clearly $F_1 + F_2$.

The series representing V , F , F^2 and VF are absolutely and uniformly convergent in the region $r \leq R' < R$, $-1 \leq \mu \leq 1$. The property of uniform convergence allows termwise integration of the series.

The normalization integral is

$$N = 1 + \langle F_1^2 \rangle + \langle F_2^2 \rangle, \quad (10)$$

where, for example,

$$\langle F_2^2 \rangle = \int_{r \leq R'} \psi_0^2 F_2^2 d\tau.$$

The quantities $\langle F_1 \rangle$, $\langle F_2 \rangle$ and $\langle F_1 F_2 \rangle$ vanish.

In evaluating (10), the radial limit is taken as $R' < R$ to ensure convergence of the resulting series. The results for $\langle F_1^2 \rangle$ and $\langle F_2^2 \rangle$ are

$$\begin{aligned} \langle F_1^2 \rangle = & \frac{a^2 p_1^2}{e^2 R^4} \sum_{l=1}^{\infty} (l+1)^2 \left(\frac{a}{2R} \right)^{2l} (2l)! \left[\frac{l+1}{l^2} K_{2l+2} \right. \\ & \left. + \frac{2l+3}{l} K_{2l+3} + \frac{(l+2)(2l+3)}{2(l+1)} K_{2l+4} \right], \quad (11) \end{aligned}$$

and

$$\begin{aligned} \langle F_2^2 \rangle = & \frac{a^2 p_2^2}{2e^2 R^4} \sum_{l=1}^{\infty} l(l+1) \left(\frac{a}{2R}\right)^{2l} (2l)! \left[\frac{l+1}{l^2} K_{2l+2} \right. \\ & \left. + \frac{2l+3}{l} K_{2l+3} + \frac{(l+2)(2l+3)}{2(l+1)} K_{2l+4} \right] \end{aligned} \quad (12)$$

In (11) and (12), the upper limit, R' , occurs in

$$K_n(R') = 1 - e \times p(-2R'/a) \sum_{j=0}^n \frac{(2R'/a)^j}{j!} \quad (13)$$

In terms of V and F the energy, correct to second order⁴, is

$$E_2 = E_0 + \langle V \rangle + \langle VF \rangle - \langle V \rangle \langle F \rangle.$$

Since V and F have zero averages over a sphere, we have

$$E_2 = -e^2/2a + ep_1/R^2 + \langle VF \rangle \quad (29)$$

The evaluation of $\langle VF \rangle$ is straightforward.

$$\begin{aligned} \langle VF \rangle = & -\frac{ap_1^2}{R^4} \sum_{l=1}^{\infty} (l+1)^3 \left(\frac{a}{2R}\right)^{2l} (2l)! \left[\frac{K_{2l+2}}{l} + \frac{2l+3}{2(l+1)} K_{2l+3} \right] \\ & - \frac{ap_2^2}{2R^4} \sum_{l=1}^{\infty} l(l+1)^2 \left(\frac{a}{2R}\right)^{2l} (2l)! \left[\frac{K_{2l+2}}{l} + \frac{2l+3}{2(l+1)} K_{2l+3} \right] \end{aligned} \quad (14)$$

III. Diamagnetic Shielding

The diamagnetic shielding tensor⁷ may be decomposed into a scalar

component and a traceless component which is dependent upon the molecular orientation with respect to the magnetic field. The scalar part is solely responsible for the diamagnetic screening of the nucleus when the molecule is in a liquid state. In the first part of this section, the total diamagnetic shielding will be computed for one particular orientation, to bring out an interesting aspect of the problem.

For a molecule with a well defined orientation, λ , with respect to H , the diamagnetic screening constant is

$$\sigma_d(\lambda) = (e^2/2mc^2) \int r^{-1} \rho \sin^2 \omega d\tau$$

where ω is the polar angle that $\underline{r}$ makes with $\underline{H}$, and ρ is the electron density. We will compute $\sigma_d(\lambda)$ for H parallel to the molecular z axis. This would be one of the principal components of σ if $\eta = 0$ or π . For this particular orientation we denote $\sigma_d(\lambda)$ by $\sigma_{d,z}$.

$$\sigma_{d,z} = (e^2/2mc^2) \int r^{-1} \rho \sin^2 \theta d\tau \quad (15)$$

In terms of the first order correction,

$$\rho \approx N^{-1} (1 + F_1^2 + F_2^2 + 2F_1 + 2F_2 + 2F_1F_2) \rho_0$$

where $\rho_0 = \psi_0^2$. Unfortunately the latter equation for ρ is

not correct through second order in p . This is because the second order wave function is necessary to obtain an accurate second order ρ .

We therefore write, correct to first order,

$$\rho_1 = (1 + 2F_1 + 2F_2) \rho_0 \quad (16)$$

Using (16) in (15) we obtain

$$\sigma_{d,z} = \sigma_0 - \frac{e^2}{mc^2} \int r^{-1} \rho_0 F_1 \cos^2 \theta d\tau, \quad (17)$$

where $\sigma_0 = e^2/3mc^2 a$.

The integral in (17) may be evaluated easily on using the following integral property of Legendre polynomials.

$$\begin{aligned} \int_{-1}^1 \mu^n P_\ell(\mu) d\mu &= 0, \quad n < \ell \quad \text{or} \quad n - \ell = \text{odd integer} \\ &= \frac{n! \Gamma(\frac{n-\ell+1}{2})}{2^\ell (n-\ell)! \Gamma(\frac{n+\ell+3}{2})} \quad \text{for} \\ &\quad n \geq \ell \text{ with } (n-\ell) \text{ even or zero.} \end{aligned}$$

For $n = 2$, we have

$$\int_{-1}^1 \mu^2 P_\ell(\mu) d\mu = \frac{4}{15} \delta_{\ell,2}.$$

The result for $\sigma_{d,z}$ is

$$\sigma_{d,z} = \sigma_0 + \frac{ep_1 a^2}{10mc^2 R^4} \left[3 K_3 + 4 K_4 \right]. \quad (18)$$

As before K_n is given by (13); however, here we may set $R' = R$ since (18) contains a finite number of terms.

We see that the linear contribution to $\sigma_{d,z}$ is due to the second ($\ell = 2$) term in V_1 and no other. In general, $\sigma_d(\lambda)$ will contain contributions only from the second ($\ell = 2$) term of both V_1 and V_2 .

In liquid media the screening constant is

$$\sigma_d = (e^2/3mc^2) \int \rho r^{-1} d\tau. \quad (19)$$

Since $\langle F_1 \rangle = \langle F_2 \rangle = 0$, there is no term linear in ρ .

As previously mentioned, the first order wave function is not adequate to produce the correct p^2 correction to the screening constant. We need to know the second order wave function. The differential equations which give us ψ_2 are quite complicated for the present problem. For ψ_2 write

$$\psi_2 = (1 + F + \bar{F}) \psi_0.$$

The second order correction, $\bar{F}$, is given by⁸

$$[H_0, \bar{F}] \psi_0 = [\langle VF \rangle - VF] \psi_0 \quad (20)$$

We have tried to solve (20) but without complete success.

Marshall and Pople² found $\bar{F}$ for the case of a hydrogen atom in a uniform electric field. In the uniform field case a simple calculation shows that, for the purpose of computing σ_d , $\bar{F}$ may to a good approximation be replaced by F^2 in ψ_2 . Now in (20), if we set $\eta = 0$ and neglect all terms for which $\ell > 1$ we obtain a solution of the same spatial dependence as Marshall and Pople found in their parallel field case. If in (20) we set $\eta = \pi/2$ and neglect all terms for which $\ell > 1$ we obtain a solution of the same spatial dependence as Marshall and Pople found for their perpendicular field case. Thus in analogy to the above noted approximation valid in the uniform electric field problem we write

$$\rho \approx [1 + 2F + 3F^2 - 3 \langle F^2 \rangle] \psi_0^2. \quad (21)$$

No theoretical justification of (21) has been given. As will be discussed later, its only justification is its reasonable numerical success in the uniform field problem.

Substitution of (21) into (19) leads to

$$\sigma_d \approx \sigma_o [1 - 3 \langle F^2 \rangle + 3a \langle r^{-1} F^2 \rangle] , \quad (22)$$

$\langle F_1^2 \rangle$ and $\langle F_2^2 \rangle$ are given in (11) and (12). The computation of $\langle r^{-1} F_1^2 \rangle$ and $\langle r^{-1} F_2^2 \rangle$ is straightforward. The results are

$$\begin{aligned} \langle r^{-1} F_1^2 \rangle = & \frac{ap_1^2}{e^2 R^4} \sum_{l=1}^{\infty} (l+1)^2 \left(\frac{a}{2R}\right)^{2l} (2l)! \left[\frac{K_{2l+1}}{l^2} + \frac{2K_{2l+2}}{l} \right. \\ & \left. + \frac{(2l+3) K_{2l+3}}{2(l+1)} \right] , \end{aligned} \quad (23)$$

$$\begin{aligned} \langle r^{-1} F_2^2 \rangle = & \frac{ap_2^2}{2e^2 R^4} \sum_{l=1}^{\infty} l(l+1) \left(\frac{a}{2R}\right)^{2l} (2l)! \left[\frac{K_{2l+1}}{l^2} + \frac{2K_{2l+2}}{l} \right. \\ & \left. + \frac{(2l+3) K_{2l+3}}{2(l+1)} \right] . \end{aligned} \quad (24)$$

IV. Paramagnetic Shielding

The paramagnetic shielding factor may also be decomposed into an anisotropic component with zero trace and a scalar component independent of molecular orientation. For a molecule in the liquid state, only the scalar component, σ_p , survives. We have⁷

$$\sigma_p = \frac{4\beta^2}{3} \text{Re} \sum_i \sum_n' \frac{(\psi_o, L_i \psi_n) (\psi_n, r^{-3} L_i \psi_o)}{\mathcal{E}_o - \mathcal{E}_n} , \quad (25)$$

where now, departing from the subscript convention of the previous sections, the subscripts on Ψ and $\mathcal{E}$ denote the state of the molecule in the absence of a magnetic field. Thus, we have

$$K \Psi_n = (K_0 + V) \Psi_n = \mathcal{E}_n \Psi_n,$$

and

$$K_0 \Psi_0 = E_0 \Psi_0.$$

In (25), L_1 is the 1'th component of the angular momentum $\underline{L}$.

$$\underline{L} = -i \underline{r} \times \underline{\nabla}$$

The sums (25) could be effected if there could be found functions

$\mathcal{G}_\lambda$ such that

$$(\mathcal{E}_0 - K) \mathcal{G}_\lambda \Psi_0 = L_1 \Psi_0 - (\Psi_0, L_1 \Psi_0) \Psi_0. \quad (26)$$

The ground state, Ψ_0 , is real so that $(\Psi_0, L_1 \Psi_0)$ is zero. From (26)

it follows that

$$\frac{(\Psi_0, L_1 \Psi_n)}{\mathcal{E}_0 - \mathcal{E}_n} = (\mathcal{G}_\lambda \Psi_0, \Psi_n).$$

Equation (25) becomes

$$\sigma_p = \frac{4\beta^2}{3} \operatorname{Re} \sum_1 \sum_n (\mathcal{G}_\lambda \Psi_0, \Psi_n) (\Psi_n, r^{-3} L_1 \Psi_0)$$

or, by virtue of the closure relation,

$$\sigma_p = \frac{4\beta^2}{3} \operatorname{Re} \sum_1 (\mathcal{G}_\lambda \Psi_0, r^{-3} L_1 \Psi_0). \quad (27)$$

Unfortunately we know only the first order approximation to Ψ_0 . In order to estimate σ_p we proceed in the following way. If we write

$$\mathcal{E}_0 = E_0 + W(p) ,$$

(26) may be written

$$[(E_0 + W) - (K_0 + V)] \mathcal{G}_\lambda \psi_0 = L_1 \psi_0 . \quad (28)$$

In (28), we replace ψ_0 by its first order approximation, ψ_1 , and neglect all terms which involve powers of p greater than one. This is accomplished after noting that V , F , W and $\mathcal{G}_\lambda$ all vanish when $p = 0$. The result is

$$(E_0 - K_0) G_1 \psi_0 = L_1 F \psi_0 \quad (29)$$

where G_1 is a first order approximation to $\mathcal{G}_\lambda$. The next step is to replace, in (27), $\mathcal{G}_\lambda$ with G_1 and ψ_0 with $(1 + F)\psi_0$ and retain only those terms proportional to p or p^2 . The result is

$$\sigma_p \approx \frac{4\beta^2}{3} \sum_1 \int \psi_0^2 G_1^* r^{-3} L_1 F d\tau \quad (30)$$

As in the case of the isotropic diamagnetic shielding σ_p does not contain any linear dependence on p .

The function G_1 has a broader meaning than that indicated by its use in the above treatment. To see this, consider the Hamiltonian

$$\mathcal{K} = K_0 + V + \mathcal{K}'$$

with

$$\mathcal{K}' = (eh/2mc) \underline{H} \cdot \underline{L}$$

Since $\mathcal{K}'$ does not contribute to a first order correction to the wave function, eq. (4) still holds in that order. For the second order correction we proceed to (20) and replace $\bar{F}$ with Ξ and V with $V + \mathcal{K}'$.

Then

$$[E_0 - K_0] \Xi \psi_0 = \mathcal{K}' F \psi_0 + \text{terms of higher order in } p.$$

Let ξ be the solution to the latter equation upon neglecting the higher order terms. It is evident that $\xi \psi_0$ is the correction to the wave function proportional to $p H$. ξ may be decomposed into a sum of components, ξ_i , along the three coordinate directions. On comparing with (29), we see that ξ_i differs from G_i by only a factor $(eh/2mc)H_i$.

The functions G_i are given by

$$\left. \begin{aligned} G_x &= -i \frac{ma}{eh^2 R^2} \sum_{l=1}^{\infty} R^{-l} R_l(r) \left\{ p_1(l+1) P_l^{(1)}(\mu) \sin \varphi + \frac{1}{2} p_2 \left[P_l^{(2)}(\mu) \cos 2\varphi + l(l+1) P_l(\mu) \right] \right\} \\ G_y &= i \frac{ma}{eh^2 R^2} \sum_{l=1}^{\infty} R^{-l} R_l(r) \left\{ p_1(l+1) P_l^{(1)}(\mu) \cos \varphi - \frac{1}{2} p_2 P_l^{(2)}(\mu) \sin 2\varphi \right\} \\ G_z &= i \frac{ma p_2}{eh^2 R^2} \sum_{l=1}^{\infty} R^{-l} R_l(r) P_l^{(1)}(\mu) \cos \varphi \end{aligned} \right\} \quad (31)$$

where

$$R_l(r) = -\frac{2}{a} \chi_l(r)$$

From (30) and (31), we obtain

$$\left. \begin{aligned} \sigma_{px} &= -\frac{2ap_1^2}{mc^2 R^4} \sum_{l=1}^{\infty} \frac{(l+1)^2}{(l+2)(2l+1)} \left(\frac{a}{2R} \right)^{2l} (2l)! M_l \\ &\quad - \frac{ap_2^2}{2mc^2 R^4} \sum_{l=1}^{\infty} \frac{3l^3 + 6l^2 + l - 2}{(l+1)(l+2)(2l+1)} \left(\frac{a}{2R} \right)^{2l} (2l)! M_l \\ \sigma_{py} &= -\frac{2ap_1^2}{mc^2 R^4} \sum_{l=1}^{\infty} \frac{(l+1)^2}{(l+2)(2l+1)} \left(\frac{a}{2R} \right)^{2l} (2l)! M_l \\ &\quad - \frac{ap_2^2}{2mc^2 R^4} \sum_{l=1}^{\infty} \frac{(l-1)}{2l+1} \left(\frac{a}{2R} \right)^{2l} (2l)! M_l \\ \sigma_{pz} &= -\frac{2ap_2^2}{mc^2 R^4} \sum_{l=1}^{\infty} \frac{1}{(l+1)(2l+1)} \left(\frac{a}{2R} \right)^{2l} (2l)! M_l \end{aligned} \right\} \quad (32)$$

where

$$M_l = \left\{ \frac{3l^2+6l+2}{2l^3} K_{2l-1} + \frac{3l^2+6l+2}{l(l+1)} K_{2l} \right. \\ \left. + \frac{1}{4} \left[1 + \frac{3l^2+6l+2}{(l+1)^2} \right] (2l+1) K_{2l+1} + \frac{1}{4} l(2l+1) K_{2l+2} \right\},$$

and

$$\sigma_p = 1/3 (\sigma_{px} + \sigma_{py} + \sigma_{pz}).$$

The paramagnetic part of the shielding tensor must be negative.

Thus, since there is no zero order contribution to σ_p , there can be no terms here linear in p . This is true not only for the scalar factor calculated here but for the paramagnetic shielding for any fixed orientation.

V. Convergence

The several infinite series derived in the previous sections must be examined for convergence. These series were obtained by the termwise integration of series which are uniformly convergent in the interval $r \leq R' < R$, $-1 \leq \mu \leq 1$. The upper limit, R' , of the r integration was left unspecified, since the termwise integration may lead to erroneous results if the terminal points of the integration are not in the region of convergence of the integrated series. Indeed if R' is chosen infinitely large, all of the series diverge.

Each of the series $\langle F^2 \rangle$, $\langle r^{-1} F^2 \rangle$, $\langle VF \rangle$, σ_{px} , σ_{py} and σ_{pz} depend on R' through the function $K_n(R')$ given by (13). One may easily prove the inequality

$$K_n(R') < \frac{t^{n+1} e^{-t}}{(n+1-t)n!}, \quad n > t - 1 \quad (33)$$

where $t = 2R'/a$.

The inequality (33), in conjunction with the comparison test, may be used to show that $\langle F^2 \rangle$, $\langle r^{-1} F^2 \rangle$ and σ_{pz} converge for $R' \leq R$ while the other series, $\langle VF \rangle$, σ_{px} and σ_{py} converge for $R' < R$. The behaviors of the latter three series on the circle $R' = R$ are not obtained by this analysis. Numerical analysis indicates that $\langle VF \rangle$, σ_{px} and σ_{py} do not converge for $R' = R$.

The problem of divergent series, which results in the use of multipole expansions of potential energy functions, has been treated from two different standpoints. Brooks⁹ has pointed out that the whole concept of multipole representation is only meaningful within the region of convergence. Brooks, in an application of Unsöld's¹⁰ approximation, neglects contributions to the interaction energy arising from that part of space outside the sphere of convergence of the multipole expansion. Brooks points out that utilizing the multipole expansion in regions of space where it is not convergent leads to divergent series for second order interaction energies. This is indeed true for the series developed in this paper, as can easily be seen by replacing K_n by unity. However, this is not the complete explanation of the origin of the divergent series which can occur on using multipole expansions. Dalgarno and Lewis¹¹ have shown that Unsöld's approximation, in the case of a ρ^{-1} potential, leads to a divergent series for the second order energy even if the multipole expansion is not used. Because of arguments based on the mathematics of asymptotic expansions, the latter authors assign numerical magnitudes to their divergent series by stopping the summation at the index at which the terms begin to increase.

Each of the two methods discussed above for obtaining numerical results in the face of divergent series has its own advantages. Still, if one is going to use a multipole expansion of the perturbing potential, one should follow the conditions for which the theorem on termwise integration of uniformly convergent series is valid. This theorem is not valid if the termini of the integral are out of the region of convergence. Therefore, the artifice described by (6) has been chosen for use in this paper.

VI. Discussion

A first order wave function of a hydrogen atom in the field of an electric dipole has been obtained via the differential equation approach of Dalgarno⁵ and associates. Aside from the assumptions inherent in perturbation theory, the validity of the solution rests on the assumption that the total effect of the dipole is described by the multipole expansion of eq. (7). Since the solution for $r > R$ has not been obtained, only qualitative remarks may be made concerning the error in neglecting that part of the solution. For convenience, suppose the proton-dipole distance, R , is $1.4 \text{ \AA}$. The probability that the unperturbed electron may be found within the sphere of radius R , with center at the proton, is $K_2(R)$, or 0.9, for the assumed distance of $1.4 \text{ \AA}$. In the region exterior to this sphere we have $F = F_{>}$. For very large r , Ψ approaches ψ_0 ; hence $F_{>}$ must approach zero. From these considerations, it is evident that eq. (6) is an adequate first order wave function for reasonably small values of R .

In order to discuss the numerical behavior of the series $\langle VF \rangle$, σ_d and σ_p we have chosen R' such that for each R

$$R' = R - 0.2 \text{ \AA}.$$

This choice for R' is arbitrary and was chosen for convenience. However, for $R-R'$ as small as .01 the numerical results are not significantly different from the results reported here for $R-R' = .2$.

The second order term, $\langle VF \rangle$, is summarized in Table I for each of the two cases $\eta = 0$ and $\pi/2$. The dipole moment is taken as 1×10^{-18} e.s.u. The energy of any configuration at a given R may be found by using the data given in Table I.

As was shown in section III, the second terms in V_1 and V_2 , i.e., those proportional to $P_2(\mu)$ and $P_2^{(1)}(\mu)$, contribute a term, linear in p , to the diamagnetic shielding tensor of a molecule which has a well defined orientation. The orientation with the magnetic field parallel to the molecular z axis was examined. Equation (18) gives the result. If the magnetic field were oriented along the molecular x axis, the contribution to $\sigma_{d,x}$, linear in p , would be of opposite sign and half the magnitude as that in $\sigma_{d,z}$. The second term of V_2 contributes a linear shielding whenever the azimuth of H in the molecular coordinate system is different from 0 or π .

In (18), let us place $R = 1.6 \text{ \AA}$, $R' = 1.4 \text{ \AA}$ and $p_1 = p_0 \times 10^{-18}$. The result for $\sigma_{d,z} - \sigma_0$ is $1.0 \times 10^{-7} p_0$. If R' is taken equal to R the result is $1.4 \times 10^{-7} p_0$. We will see later that the quadratic contri-

bution to the isotropic shielding factor is at least the same order of magnitude or larger than the linear term in $\sigma_d(\lambda)$. Thus we expect that the quadratic terms in $\sigma_d(\lambda)$ would be of importance. The reason for this is that the quadratic part of $\sigma_d(\lambda)$ contains the effect of all portions of V , including the $\ell = 1$ term. We will not write down equations relating to the quadratic part of $\sigma_d(\lambda)$ mainly for the reason that the calculation, although straightforward, is tedious and the resulting series are rather lengthy. We have performed the calculation by replacing $\bar{F}$ with F^2 in the second order density. The results show that the quadratic part of $\sigma_d(\lambda)$ may be as large or larger than the linear part.

The approximate second order density given in equation (21) appears to be quite good as far as calculating magnetic screening constants. As explained previously we truncated all series after the $\ell = 1$ term and solved (20) for the separate cases $\eta = 0$ and $\eta = \pi/2$.¹² For $R' \geq 1.0$ the value of σ_d found with $\bar{F}$ replaced by F^2 is in error by 20% or less. The approximation tends to overestimate $|\sigma_d|$. It is probably safe to assume that the accuracy of the approximation remains about the same when the series for F and V are not truncated in (20).

In the absence of a dipole field there is no paramagnetic shielding factor; as a consequence, σ_p has no part linear in p . As we have seen, however, the presence of the magnetic field creates an additional correction to the wave function, linear in p . Since σ_p is a second order quantity, it is necessary only to know the wave function to first order in p , in the presence of a magnetic field, to compute σ_p correct to second order in p .

The quantities $\langle F^2 \rangle \sigma_0$, $\langle r^{-1} F^2 \rangle \sigma_0 a$, $\frac{1}{3} \sigma_{px}$, $\frac{1}{3} \sigma_{py}$, $\frac{1}{3} \sigma_{pz}$ and $\sigma_d + \sigma_p - \sigma_0$ are tabulated for various values of R , in Tables II and III, for the special cases $\eta = 0$ and $\eta = \pi/2$, respectively. Equation (22) was used to calculate σ_d . From Table II, we see that at $R = 1.6$ the quadratic part of σ is almost the same magnitude as the linear part of $\sigma_d(\lambda)$.

Several interesting facts are to be noted from Tables II and III. With $\eta = 0$ (or π), σ_{pz} is zero since the wave function is invariant to a rotation about the polar axis. For the configuration $\eta = \pi/2$, we note that σ_{py} is much smaller than σ_{px} or σ_{pz} . This is because the first term in V_2 (the $\ell = 1$ or uniform electric field term) does not contribute to σ_{py} . For the latter configuration, we also note that σ_{px} and σ_{pz} are approximately equal.

Table IV illustrates the significance of successive terms in the series for σ_{px} and σ_{pz} with $R = 1.5 \text{ \AA}$ and $\eta = \pi/2$. Although in the beginning σ_{px} is somewhat smaller than σ_{pz} , it eventually converges to a value very nearly equal to that of σ_{pz} . We have extended each summation in Table IV until a change of one in the fourth significant figure was obtained. Such accuracy is out of experimental attainment. However, the calculations are for a unit dipole. For a dipole of p_0 units, the reported values in Table IV should be increased by a factor of p_0^2 . Thus, for very polar groups, the summations should be extended to constancy in the third significant figure.

It is interesting to apply the results obtained by Marshall and Pople², for a hydrogen atom in a uniform electric field, to the problem posed in this paper. If we set $\eta = 0$, the electric field of the dipole has a uniform field component E which is related to p by

$$E = 2p/R^3.$$

The paramagnetic shielding perpendicular to the uniform field is, in the notation of reference 2,

$$\sigma_{\perp}^p = - \frac{233}{144} \frac{a^3 E^2}{mc^2} = - \frac{233}{36} \frac{a^3 p^2}{mc^2 R^6},$$

The comparison between $\sigma_{\perp}^p$ and σ_{px} is summarized in Table V for several values of R . The good agreement is actually due to two opposite but almost equal effects. In the calculations presented in this paper, the effect of the dipole was cut off at a finite distance from the proton. In the calculation leading to $\sigma_{\perp}^p$ no cut-off was necessary. Thus, from this consideration, σ_{px} should be less than $\sigma_{\perp}^p$. However, σ_{px} is influenced by the complete potential, V_1 , whereas $\sigma_{\perp}^p$ contains only the contribution from the first term of V_1 . As is seen from Table V, these two effects are opposite but practically equal in magnitude. The approximate cancellation of these two effects should be considered as accidental.

Table I. Second order energy correction, $\langle VF \rangle$, for
 $\eta = 0, \pi/2$ and for various values of R .

$\eta = 0$ $\langle VF_1 \rangle \times 10^{14} (\text{erg})$	$R (\text{\AA})$	$\eta = \pi/2$ $\langle VF_2 \rangle \times 10^{14} (\text{erg})$
2.503	2	0.7436
3.215	1.9	0.9571
4.133	1.8	1.232
5.314	1.7	1.585
6.826	1.6	2.035
8.749	1.5	2.604
11.18	1.4	3.317
14.19	1.3	4.197

Table II. Values of $\langle F_1^2 \rangle \sigma_o$, $\langle r^{-1} F_1^2 \rangle \sigma_o a$, $-\frac{1}{3} \sigma_{px}$, $\frac{1}{3} \sigma_{py}$, $-\frac{1}{3} \sigma_{pz}$ and $(\sigma_d + \sigma_p - \sigma_o)$. $p = 10^{-18}$,

$$\eta = 0, R' = R - .2 \times 10^{-18}$$

$R (\text{\AA})$	$\langle F_1^2 \rangle \sigma_o \times 10^8$	$\langle r^{-1} F_1^2 \rangle \sigma_o a \times 10^8$	$-\frac{1}{3} \sigma_{px} \times 10^8$	$-\frac{1}{3} \sigma_{py} \times 10^8$	$-\frac{1}{3} \sigma_{pz}$	$-(\sigma_d + \sigma_p - \sigma_o) \times 10^8$
2.0	1.731	0.7936	0.7407	0.7407	0	4.293
1.9	2.169	1.030	1.007	1.007	0	5.431
1.8	2.718	1.343	1.385	1.385	0	6.895
1.7	3.403	1.760	1.931	1.931	0	8.791
1.6	4.255	2.315	2.728	2.728	0	11.276
1.5	5.306	3.056	3.911	3.911	0	14.572
1.4	6.589	4.046	5.694	5.694	0	19.017
1.3	8.133	5.369	8.430	8.430	0	25.152

Table III. Values of $\langle F_2^2 \rangle \sigma_c$, $\langle r^{-1} F_2^2 \rangle \sigma_o a$, $-\frac{1}{3} \sigma_{px}$, $-\frac{1}{3} \sigma_{py}$, $-\frac{1}{3} \sigma_{pz}$ and $-(\sigma_d + \sigma_p - \sigma_o)$.

$$p = 10^{-18}, \eta = \pi/2, R' = R - .2 \times 10^{-8}.$$

$R \text{ (Å)}$	$\langle F_2^2 \rangle \sigma_o \times 10^8$	$\langle r^{-1} F_2^2 \rangle \sigma_o a \times 10^8$	$-\frac{1}{3} \sigma_{px} \times 10^8$	$-\frac{1}{3} \sigma_{py} \times 10^8$	$-\frac{1}{3} \sigma_{pz} \times 10^8$	$-(\sigma_d + \sigma_p - \sigma_o) \times 10^8$
2.0	0.4786	0.2153	0.2257	0.02247	0.2350	1.275
1.9	0.6002	0.2799	0.3094	0.03196	0.3168	1.618
1.8	0.7524	0.3655	0.4288	0.04571	0.4326	2.069
1.7	0.9420	0.4792	0.6013	0.06574	0.5991	2.655
1.6	1.177	0.6305	0.8535	0.09510	0.8420	3.432
1.5	1.466	0.8321	1.2241	0.1384	1.203	4.469
1.4	1.816	1.101	1.788	0.2026	1.748	5.886
1.3	2.236	1.458	2.644	0.2984	2.590	7.866

Table IV. Values of σ_{px} and σ_{pz} after ℓ terms in their respective series in which $\eta = \pi/2$, $p = 1 \times 10^{-18}$ and $R = 1.5 \text{ \AA}$.

ℓ	$-\frac{1}{3} \sigma_{px} \times 10^8$	$-\frac{1}{3} \sigma_{pz} \times 10^8$
1	0.7342	1.101
2	0.9671	1.179
3	1.074	1.195
4	1.132	1.199
5	1.166	1.201
6	1.187	1.202
7	1.200	
8	1.209	
9	1.215	
10	1.219	
11	1.221	
12	1.223	
13	1.224	

Table V. Comparison of $\sigma_{\perp}$, eq. (57), and σ_{px} , eq. (53).

$$p = 1 \times 10^{-18} \text{ and } \eta = 0.$$

$-\frac{1}{3} \sigma_{\perp} \times 10^8$	$R \text{ (Å)}$	$-\frac{1}{3} \sigma_{px} \times 10^8$
0.611	2.0	0.741
1.150	1.8	1.385
2.330	1.6	2.728
5.193	1.4	5.694

COORDINATE SYSTEM FOR A HYDROGEN ATOM

PERTURBED BY AN ELECTRIC DIPOLE

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