theory, particularly since the general idea of using "different orbitals for different spins" is by no means limited to alternant systems.

Note added in proof: A numerical investigation of the direct exchange of $3d$ electrons based on the Heisenberg exchange integral has been reported by R. Stuart and W. Marshall, Phys. Rev. **120**, 353 (1960). A similar investigation based on the more exact definition of the exchange integral presented here has been carried out by A. J. Freeman and R. E. Watson *Theory of Direct Exchange in Ferromagnetism* (available in preprint; to be published).

The two papers on the application of the alternant molecular orbital method to the linear chain by Pauncz, de Heer, and Löwdin has now been accepted for publication in J. Chem. Phys.

REVIEWS OF MODERN PHYSICS VOLUME 34, NUMBER 1 JANUARY, 1962

Theory of Magnetic Properties of Molecules with Particular Emphasis on the Hydrogen Molecule*

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I. INTRODUCTION

DURING the last decade a considerable amount of work has been reported on the calculation of molecular diamagnetic susceptibilities and of proton shielding constants. Although there is not much resemblance between these two quantities from an experimental point of view, their calculations show many points of similarity and it is therefore profitable to consider the theories of both phenomena simultaneously. The theoretical value of a molecular diamagnetic susceptibility χ may be derived from a study of the interaction between the electronic motion in the molecule and a homogeneous magnetic field $\mathbf{H}$, whereas a theoretical determination of a proton shielding constant σ involves a calculation of the interaction between the electronic motion, a homogeneous magnetic field $\mathbf{H}$, and an infinitesimally small magnetic dipole $\boldsymbol{\mu}$ at the position of the proton. Widely different methods for calculating these interaction terms have been suggested. The present paper gives a critical evaluation of the various approaches and investigates whether there are any connections between them. In particular we wish to discuss a few questions that are connected with calculations of χ and σ from gauge invariant atomic orbitals that were either overlooked or not satisfactorily answered in previous work.

A necessary condition that has to be imposed on calculations of molecular magnetic properties is that they lead to correct, or at least reliable, numerical results. Therefore it is necessary to study not only the general theory but also the numerical applications. However, we do not wish to obscure the main points of the argument by many tedious numerical calculations, so that we will take the hydrogen molecule as a basis of our discussion. This follows the customary trend in the calculations where each method is usually tested by applying it to the hydrogen molecule and extended to more complicated systems only after a satisfactory result has been obtained for the simple case. At least a qualitative discussion of the question as to whether each calculation for hydrogen can easily be extended to larger molecules is included in this paper.

We discuss the theory of diamagnetic susceptibilities first. This has the same basic problems as are encountered in calculations of σ but lacks some additional complications.

The various theories on diamagnetic susceptibilities and magnetic shielding constants are often subdivided into three sets, namely (1) those that are derived by means of perturbation theory, (2) those that are based on applications of Ritz' variational principle, and (3) those that make use of additional experimental information connected with the rotational magnetism of the molecule. It is shown that a distinction between the first two sets is artificial because all results may be derived from variational methods.

First we give a general survey of the various variational methods, next we investigate some questions that are connected with calculations from gauge invariant atomic orbitals, and after that we discuss the connection between diamagnetic susceptibilities and rotational magnetism.

II. VARIATIONAL METHODS

We are interested in finding the lowest eigenvalue E_0' of the equation

$$\mathcal{H}_{\mathrm{op}}\Phi=E\Phi, \tag{1}$$

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* Research supported by a grant from the U. S. Army Research Office (Durham) to The Johns Hopkins University.

where

$$\mathcal{H}_{\mathrm{op}}=\frac{1}{2m}\sum_{j=1}^{N}\left(\mathbf{p}_j+\frac{e}{c}\mathbf{A}_j\right)^2+V(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N)\qquad(2)$$

is the Hamilton operator of an N-electron system, V is the potential energy function, and $\mathbf{A}_j$ is the vector potential acting on electron j. Let us now define

$$\mathbf{A}_j'=\tfrac{1}{2}\mathbf{H}\times\mathbf{r}_j\quad\mathbf{A}_j''=r_{aj}^{-3}(\boldsymbol{\mu}\times\mathbf{r}_{aj}),\qquad(3)$$

where $\mathbf{H}$ is a homogeneous magnetic field, $\boldsymbol{\mu}$ is an infinitesimally small dipole at the position of proton a, $\mathbf{r}_j$ denotes the position of electron j, and $\mathbf{r}_{aj}$ denotes the position of electron j with respect to proton a. Substitution of $\mathbf{A}_j=\mathbf{A}_j'$ or of $\mathbf{A}_j=\mathbf{A}_j'+\mathbf{A}_j''$ into Eq. (2) then leads to the calculation of χ or σ, respectively.

In most calculations it is assumed that all eigenvalues E_k and corresponding eigenfunctions Ψ_k of the equation

$$\begin{aligned}\mathcal{H}_{\mathrm{op}}^{(0)}\Psi_k&=E_k\Psi_k\\ \mathcal{H}_{\mathrm{op}}^{(0)}&=(2m)^{-1}\sum_{j=1}^{N}\mathbf{p}_j^2+V\end{aligned}\qquad(4)$$

are known exactly. By means of second-order perturbation theory, it may then be derived that[1]

$$\begin{aligned}\chi=-(2L/H^2)[&(e^2/2mc^2)\langle\Psi_0|\textstyle\sum_j(\mathbf{A}_j')^2|\Psi_0\rangle\\ &-(e^2\hbar^2/m^2c^2)\textstyle\sum_k(E_k-E_0)^{-1}\langle\Psi_0|\sum_j(\mathbf{A}_j'\cdot i\nabla_j)|\Psi_k\rangle\\ &\times\langle\Psi_k|\textstyle\sum_j(\mathbf{A}_j'\cdot i\nabla_j)|\Psi_0\rangle],\end{aligned}\qquad(5)$$

and also that

$$\begin{aligned}\sigma=(\mu H)^{-1}[&(e^2/mc^2)\langle\Psi_0|\textstyle\sum_j(\mathbf{A}_j'\cdot\mathbf{A}_j'')|\Psi_0\rangle\\ &-(e^2\hbar^2/m^2c^2)\textstyle\sum_k(E_k-E_0)^{-1}\{\langle\Psi_0|\sum_j(\mathbf{A}_j'\cdot i\nabla_j)|\Psi_k\rangle\\ &\times\langle\Psi_k|\textstyle\sum_j(\mathbf{A}_j''\cdot i\nabla_j)|\Psi_0\rangle+\langle\Psi_0|\sum_j(\mathbf{A}_j''\cdot i\nabla_j)|\Psi_k\rangle\\ &\times\langle\Psi_k|\textstyle\sum_j(\mathbf{A}_j'\cdot i\nabla_j)|\Psi_0\rangle\}].\end{aligned}\qquad(6)$$

It is instructive to show, before transforming these two expressions, that they may equally well be derived by means of a variational treatment. To this end we expand the function Φ in terms of the complete set of eigenfunctions Ψ_k of Eq. (4),

$$\Phi=\sum A_k\Psi_k.\qquad(7)$$

The expansion coefficients A_k are necessarily functions of H and μ. The summation sign is to be read as a summation over all discrete states and also as an integration over the continuum states, but in order to keep the notation simple we do not denote the latter integration explicitly. Since the functions Ψ_k form a complete set, a variational treatment taking the function Φ of Eq. (7) as a trial function and varying all coefficients A_k simultaneously yields the exact eigenfunctions of $\mathcal{H}_{\mathrm{op}}$ of Eq. (2). This means that the exact value E_0' is obtained as the smallest root of the secular equation

$$\begin{aligned}|H_{kl}-E\delta_{kl}|&=0\\ H_{kl}&=\langle\Psi_k|\mathcal{H}_{\mathrm{op}}|\Psi_l\rangle.\end{aligned}\qquad(8)$$

It is impossible to obtain a solution of Eq. (8) in closed form but fortunately that is not necessary. We can imagine that E_0' is expanded as a power series in H and μ; for a calculation of χ we may then break off the series after the quadratic terms in H and for calculations of σ we may break off after the term containing first powers in both H and μ. Throughout this paper we restrict the calculations to this part of the series. This restriction implies that only an approximate value for E_0' will be obtained, but since the exact values of the coefficients of the series are determined, the calculation yields the exact values of χ and σ. Under these circumstances it may now easily be found that

$$E_0'=H_{00}-\textstyle\sum_k H_{0k}H_{k0}/(E_k-E_0),\qquad(9)$$

which leads directly to Eqs. (5) and (6). These two expressions may be transformed into the well-known Van Vleck and Ramsay formulas[1,2] by substituting Eq. (3) and by averaging over all possible orientations of the molecule with respect to the magnetic field. If we define

$$\begin{aligned}M_x&=i\textstyle\sum_j\left(y_j\dfrac{\partial}{\partial z_j}-z_j\dfrac{\partial}{\partial y_j}\right)\text{ and cycl.,}\\ L_x&=i\textstyle\sum_j\dfrac{1}{r_{aj}^{-3}}\left(y_{aj}\dfrac{\partial}{\partial z_j}-z_{aj}\dfrac{\partial}{\partial y_j}\right)\text{ and cycl.,}\end{aligned}\qquad(10)$$

it is easily found that

$$\begin{aligned}-\chi=(e^2L/6mc^2)&\langle\Psi_0|\textstyle\sum_j r_j^2|\Psi_0\rangle\\ &-(e^2\hbar^2L/6m^2c^2)\textstyle\sum_k(E_k-E_0)^{-1}\\ &\times(\langle\Psi_0|\mathbf{M}|\Psi_k\rangle,\langle\Psi_k|\mathbf{M}|\Psi_0\rangle),\end{aligned}\qquad(11)$$

and also that

$$\begin{aligned}\sigma=(e^2/3mc^2)&\langle\Psi_0|\textstyle\sum_j r_{aj}^{-3}(\mathbf{r}\cdot\mathbf{r}_{aj})|\Psi_0\rangle\\ &-(e^2\hbar^2/6m^2c^2)\textstyle\sum_k(E_k-E_0)^{-1}\\ &\times[(\langle\Psi_0|\mathbf{M}|\Psi_k\rangle,\langle\Psi_k|\mathbf{L}|\Psi_0\rangle)\\ &+(\langle\Psi_0|\mathbf{L}|\Psi_k\rangle,\langle\Psi_k|\mathbf{M}|\Psi_0\rangle)].\end{aligned}\qquad(12)$$

If all lengths and energies are expressed in terms of atomic units these equations become

$$\begin{aligned}\chi&=\chi_0[\langle\Psi_0|\textstyle\sum_j r_j^2|\Psi_0\rangle-\sum_k(E_k-E_0)^{-1}\\ &\qquad\times(\langle\Psi_0|\mathbf{M}|\Psi_k\rangle,\langle\Psi_k|\mathbf{M}|\Psi_0\rangle)],\\ \sigma&=\sigma_0\{\langle\Psi_0|\textstyle\sum_j r_{aj}^{-3}(\mathbf{r}_j\cdot\mathbf{r}_{aj})|\Psi_0\rangle-\frac{1}{2}\sum_k(E_k-E_0)^{-1}\\ &\qquad\times[(\langle\Psi_0|\mathbf{M}|\Psi_k\rangle,\langle\Psi_k|\mathbf{L}|\Psi_0\rangle)\\ &\qquad+(\langle\Psi_0|\mathbf{L}|\Psi_k\rangle,\langle\Psi_k|\mathbf{M}|\Psi_0\rangle)]\},\end{aligned}\qquad(13)$$

where $\chi_0=-(e^2a_0^2L/6mc^2)$ and $\sigma_0=(e^2/3mc^2a_0)$ are the natural units of diamagnetic susceptibility and of magnetic shielding in molecular calculations. They are used throughout the rest of this paper. It may be added that $\chi_0=-0.79242\times10^{-6}$ (cgs units) and $\sigma_0=1.77504\times10^{-5}$.

The variational derivation of Eq. (13) is useful in investigating the gauge invariance of these expressions.

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[1] J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932) p. 275.

[2] N. F. Ramsey, Phys. Rev. **77**, 567 (1950).

Since the functions Ψ_k form a complete set, the following expansion is possible:

$$\Phi \exp[(-ie/\hbar c) \textstyle\sum_j \phi_j(\mathbf{r}_j)] = \sum_k B_k \Psi_k, \tag{14}$$

where the ϕ_j are arbitrary functions of the coordinates (x_j, y_j, z_j), and also of H and μ. Consequently Φ may be expanded as

$$\begin{gathered} \Phi = \textstyle\sum_k B_k \Psi_k' \\ \Psi_k' = \Psi_k \exp[(ie/\hbar c) \textstyle\sum_j \phi_j(\mathbf{r}_j)], \end{gathered} \tag{15}$$

where the Ψ_k' form an orthonormal set. It follows again that the exact value E_0' is obtained as the smallest root of the secular equation

$$\begin{gathered} |H_{kl}' - E\delta_{kl}| = 0 \\ H_{kl}' = \langle \Psi_k' | \mathcal{H}_{\mathrm{op}} | \Psi_l' \rangle, \end{gathered} \tag{16}$$

so that

$$E_0' = H_{00}' - \textstyle\sum_k H_{0k}' H_{k0}' / (E_k - E_0). \tag{17}$$

It follows from the properties of the gauge transformation[3] that

$$\langle \Psi_k' | \mathcal{H}_{\mathrm{op}} | \Psi_1' \rangle = \langle \Psi_k | \mathcal{H}_{\mathrm{op}}' | \Psi_1 \rangle, \tag{18}$$

where

$$\mathcal{H}_{\mathrm{op}}' = \frac{1}{2m} \sum_{j=1}^{N} \left(\frac{h}{i} \boldsymbol{\nabla}_j + \frac{e}{c} \{ \mathbf{A}_j' + \mathbf{A}_j'' + \mathrm{grad}_j \phi_j(\mathbf{r}_j) \} \right)^2 + V(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N). \tag{19}$$

This implies that in Eqs. (5) and (6) we may replace $\mathbf{A}_j'$ and $\mathbf{A}_j''$, by $\mathbf{A}_j' + \boldsymbol{\nabla}_j \phi_j$ and $\mathbf{A}_j'' + \boldsymbol{\nabla}_j \phi_j$, respectively, where each function ϕ_j is an arbitrary function of the coordinates x_j, y_j, z_j, and $\mathbf{H}$ and $\boldsymbol{\mu}$. The various functions ϕ_j may all be different. This result was to be expected from purely physical grounds since χ, being a physical observable, should not depend on the gauge of the vector potential, but it is more satisfactory to have proved this point explicitly.

From the gauge invariance of Eq. (5) it is easy to derive a variational method to calculate χ which was first suggested by Rebane[4] who obtained it from a different approach. Equation (5) may be rewritten as

$$\chi = \chi_0 [\langle \Psi_0 | \textstyle\sum_j (\mathbf{A}_j')^2 | \Psi_0 \rangle - \frac{1}{2} \sum_k (E_k - E_0)^{-1} \times | \langle \Psi_k | \sum_j \{ (\mathbf{A}_j' \cdot i\boldsymbol{\nabla}_j) + (\boldsymbol{\nabla}_j \cdot i\mathbf{A}_j') \} | \Psi_0 \rangle |^2], \tag{20}$$

where

$$\mathbf{A}_j' = \tfrac{1}{2} \mathbf{H} \times \mathbf{r}_j + \boldsymbol{\nabla}_j \phi_j(\mathbf{r}_j) \tag{21}$$

since the operators occurring in the infinite series of Eq. (20) are all Hermitian.

Both the first term on the right-hand side of Eq. (20) and the infinite series are functions of the ϕ_j, but their difference is independent of the ϕ_j. Furthermore each term of the infinite series is positive. Consequently

$$(\chi/\chi_0) \leqslant \langle \Psi_0 | \textstyle\sum_j (\mathbf{A}_j')^2 | \Psi_0 \rangle \tag{22}$$

for each possible set of functions ϕ_j. Equation (22) becomes an equality only if for this set of ϕ_j the condition

$$\textstyle\sum_j \{ (\mathbf{A}_j' \cdot \boldsymbol{\nabla}_j) + (\boldsymbol{\nabla}_j \cdot \mathbf{A}_j') \} | \Psi_0 \rangle = 0 \tag{23}$$

is fulfilled.

This enables us to formulate the following variational theorem for a calculation of χ: If we wish to omit the infinite series in Eq. (17) and obtain a value of χ by evaluating the first term only, we will obtain the best possible value of χ by minimizing the right-hand side of Eq. (22) with respect to all ϕ_j. This procedure will yield the correct value for χ only if there exists a set of ϕ_j which form a solution of Eq. (23). Rebane has proved that there exists a solution of Eq. (23) for one-electron systems, but at this moment nothing is known about more complicated situations.

It will be clear that the analogy of this variational theorem for calculations of σ cannot be proved in this way and probably does not exist.

A different approach to the calculation of χ and σ is connected with the use of gauge invariant atomic orbitals.[5,6] Here it is supposed that the eigenfunctions Ψ_k of $\mathcal{H}_{\mathrm{op}}^{(0)}$ [see Eq. (4)] are constructed from atomic orbitals φ_{ka}, where the first subscript denotes the functional form of the orbital and the second subscript denotes the corresponding nucleus. We will now write the vector potential $\mathbf{A}_j$ as

$$\mathbf{A}_j^{(q)} = \tfrac{1}{2} \mathbf{H} \times (\mathbf{r}_j - \mathbf{q}) + r_{aj}^{-3} (\boldsymbol{\mu} \times \mathbf{r}_{aj}), \tag{24}$$

and subsequently define the functions

$$\begin{gathered} \varphi_{ka}^{(q)} = \varphi_{ka} \exp[ie\gamma(\mathbf{q} - \mathbf{a})/\hbar c] \\ \gamma(\mathbf{u}) = \tfrac{1}{2} (\mathbf{H} \times \mathbf{u}) \cdot \mathbf{r}. \end{gathered} \tag{25}$$

The gauge function ϕ_j has been chosen in such a way as to determine the origin of $\mathbf{r}_j$ in the formula for the vector potential and the same gauge is assigned to the atomic orbitals; hence the name gauge invariant atomic orbitals (GIAO). It is now possible to obtain the functions $\Psi_k^{(q)}$ from the functions Ψ_k by replacing all atomic orbitals φ_{ka} by $\varphi_{ka}^{(q)}$:

$$\Psi_k^{(q)} = \Psi_k(\varphi_{ka}^{(q)}, \varphi_{lb}^{(q)}, \varphi_{mc}^{(q)}, \cdots). \tag{26}$$

Although the $\Psi_k^{(q)}$ are not strictly orthonormal, it may be shown that the function Φ may be expanded as

$$\Phi = \textstyle\sum_k C_k \Psi_k^{(q)} \tag{27}$$

by expanding the $\Psi_k^{(q)}$ as power series in H and by considering the coefficients of the various powers of H on the right-hand side of Eq. (27). The energy E_0' is now obtained again as the smallest root of the secular equation

$$|H_{kl} - ES_{kl}| = 0, \tag{28}$$

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[3] H. A. Kramers, *Quantentheorie des Elektrons und der Strahlung* (Akademische Verlagsgesellschaft, Leipzig, Germany, 1938) p. 270.

[4] T. K. Rebane, J. Exptl. Theoret. Phys. (U.S.S.R.) **38**, 963 (1960).

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

[6] H. F. Hameka, Z. Naturforsch. **14a**, 599 (1959).

where

$$H_{kl}=\langle\Psi_k{}^{(q)}|\mathcal{H}_{\mathrm{op}}{}^{(q)}|\Psi_l{}^{(q)}\rangle,$$
$$S_{kl}=\langle\Psi_k{}^{(q)}|\Psi_l{}^{(q)}\rangle=\langle\tilde{\Psi}_k|\tilde{\Psi}_l\rangle;$$
$$\mathcal{H}_{\mathrm{op}}{}^{(q)}=\frac{1}{2m}\sum_{j=1}^{N}\left(\mathbf{p}_j+\frac{e}{c}\mathbf{A}_j{}^{(q)}\right)^2+V(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N). \quad (29)$$

Although the $\Psi_k{}^{(q)}$ are not orthonormal, we have

$$\begin{aligned} S_{kk}&=1+O(H^2),\\ H_{kk}&=E_k+O(H^2),\\ S_{kl}&=O(H)\quad k\neq l,\\ H_{kl}&=O(H)\quad k\neq l, \end{aligned} \quad (30)$$

so that

$$\begin{aligned} E_0'-E_0=&(H_{00}-E_0S_{00})-\textstyle\sum_j (E_j-E_0)^{-1}\\ &\times(S_{00}H_{j0}-S_{j0}H_{00})(S_{00}H_{j0}-S_{j0}H_{00})^*. \end{aligned} \quad (31)$$

Let us first discuss the application of this expression to calculations of χ; in that case μ may be taken equal to zero in Eq. (24). One might say now that the special choice of gauge of $\mathbf{A}_j$ in combination with the introduction of the gauge factors of the atomic orbitals form an approximate solution (or in some cases an exact solution) of Rebane's Eq. (23). The infinite series in Eq. (31) is usually smaller and converges more rapidly than the corresponding series in Eq. (13), so that the former equation is better adapted for numerical applications than the latter.

Each quantity H_{kl} and S_{kl} is independent of $\mathbf{q}$ and may be expressed in a number of integrals involving atomic orbitals multiplied by gauge factors. It follows from the properties of the gauge transformation that in each term the operator and the gauge factor upon which it works may be commuted if simultaneously $\mathbf{q}$ is taken as the position of the nucleus corresponding to the atomic orbital upon which the operator works. After this exchange we expand the operator as a power series in H and write symbolically

$$H_{kl}=\langle\tilde{\Psi}_k|\tilde{\mathcal{H}}_0|\tilde{\Psi}_l\rangle+\langle\tilde{\Psi}_k|i\tilde{\mathcal{H}}_1|\tilde{\Psi}_l\rangle+\langle\tilde{\Psi}_k|\tilde{\mathcal{H}}_2|\tilde{\Psi}_l\rangle. \quad (32)$$

The expansion terms are uniquely determined by this definition although we may have a different expansion in each integral into which H_{kl} may be expressed. Equation (31) may conveniently be rewritten as

$$\begin{aligned} \chi=&\chi_0(Q_0+Q_1+Q_2),\\ -H^2\chi_0Q_0=&\langle\tilde{\Psi}_0|\tilde{\mathcal{H}}_2|\tilde{\Psi}_0\rangle-\textstyle\sum_k (E_k-E_0)^{-1}\langle\tilde{\Psi}_k|i\tilde{\mathcal{H}}_1|\tilde{\Psi}_0\rangle\\ &\times\langle\tilde{\Psi}_k|i\tilde{\mathcal{H}}_1|\tilde{\Psi}_0\rangle^*,\\ -H^2\chi_0Q_1=&\langle\tilde{\Psi}_0|\tilde{\mathcal{H}}_0-E_0|\tilde{\Psi}_0\rangle\\ &-\textstyle\sum_k (E_k-E_0)^{-1}\langle\tilde{\Psi}_k|\tilde{\mathcal{H}}_0-E_0|\tilde{\Psi}_0\rangle\\ &\times\langle\tilde{\Psi}_k|\tilde{\mathcal{H}}_0-E_0|\tilde{\Psi}_0\rangle^*,\\ -H^2\chi_0Q_2=&\langle\tilde{\Psi}_0|i\tilde{\mathcal{H}}_1|\tilde{\Psi}_0\rangle\\ &-\textstyle\sum_k (E_k-E_0)^{-1}[\langle\tilde{\Psi}_k|i\tilde{\mathcal{H}}_1|\tilde{\Psi}_0\rangle\\ &\times\langle\tilde{\Psi}_k|\tilde{\mathcal{H}}_0-E_0|\tilde{\Psi}_0\rangle^*+\langle\tilde{\Psi}_k|i\tilde{\mathcal{H}}_1|\tilde{\Psi}_0\rangle^*\\ &\times\langle\tilde{\Psi}_k|\tilde{\mathcal{H}}_0-E_0|\tilde{\Psi}_0\rangle]. \end{aligned} \quad (33)$$

In former work[6,7] it was erroneously supposed that Q_1 and Q_2 both vanish identically.[8] We investigate this matter in Sec. IV, where it appears that for the H_2 molecule Q_1 and Q_2 give small but non-negligible contributions to the susceptibility.

Also for a calculation of σ it is convenient to commute the Hamiltonian and the gauge factors following it, and subsequently to expand the operator as a power series in H and μ. We write symbolically

$$\begin{aligned} H_{kl}=&\langle\tilde{\Psi}_k|\tilde{\mathcal{H}}_{0,0}|\tilde{\Psi}_l\rangle+\langle\tilde{\Psi}_k|i\tilde{\mathcal{H}}_{1,0}|\tilde{\Psi}_l\rangle+\langle\tilde{\Psi}_k|i\tilde{\mathcal{H}}_{0,1}|\tilde{\Psi}_l\rangle\\ &+\langle\tilde{\Psi}_k|\tilde{\mathcal{H}}_{1,1}|\tilde{\Psi}_l\rangle, \end{aligned} \quad (34)$$

where the first and the second subscripts of $\tilde{\mathcal{H}}$ denote the powers of H and μ, respectively, that are contained in the operators. Then

$$\begin{aligned} \sigma=&\sigma_0(P_0+P_1)\\ \mu H\sigma_0P_0=&\langle\tilde{\Psi}_0|\tilde{\mathcal{H}}_{1,1}|\tilde{\Psi}_0\rangle+\langle\tilde{\Psi}_0|i\tilde{\mathcal{H}}_{0,1}|\tilde{\Psi}_0\rangle\\ &-\textstyle\sum_k (E_k-E_0)^{-1}\{\langle\tilde{\Psi}_k|i\tilde{\mathcal{H}}_{1,0}|\tilde{\Psi}_0\rangle^*\\ &\times\langle\tilde{\Psi}_k|i\tilde{\mathcal{H}}_{0,1}|\tilde{\Psi}_0\rangle+\langle\tilde{\Psi}_k|i\tilde{\mathcal{H}}_{1,0}|\tilde{\Psi}_0\rangle\\ &\times\langle\tilde{\Psi}_k|i\tilde{\mathcal{H}}_{0,1}|\tilde{\Psi}_0\rangle^*\}\\ \mu H\sigma_0P_1=&-\textstyle\sum_k (E_k-E_0)^{-1}\{\langle\tilde{\Psi}_k|i\tilde{\mathcal{H}}_{0,1}|\tilde{\mathcal{H}}_0\rangle^*\\ &\times\langle\tilde{\Psi}_k|\tilde{\mathcal{H}}_{0,0}-E_0|\tilde{\Psi}_0\rangle+\langle\tilde{\Psi}_k|i\tilde{\mathcal{H}}_{0,1}|\tilde{\Psi}_0\rangle\\ &\times\langle\tilde{\Psi}_k|\tilde{\mathcal{H}}_{0,0}-E_0|\tilde{\Psi}_0\rangle^*\}. \end{aligned} \quad (35)$$

Also P_1 was erroneously supposed to vanish identically in previous work[6,8]; we investigate the consequences of this in Sec. V.

Both Eq. (13) and Eqs. (33) and (35) are exact formulas for χ and σ. For practical applications we have to introduce some approximations. The eigenfunctions Ψ_0 and Ψ_k are not exactly known in general, so that we have to substitute approximate functions Ψ_0 and Ψ_k. Usually the eigenfunctions Ψ_k are known less accurately than Ψ_0. The errors that are introduced in this way are inherent to the approximations in the wave functions and the discussion of this is beyond the scope of this paper. We do believe, however, that the magnitude of these errors has been grossly overestimated in the past.[9,10]

An additional source of error results from the approximations involved in evaluating the infinite series in Eqs. (13), (33), and (35). It would be virtually impossible to calculate every term of this series so that various approximations have been introduced: (i) The energies in the denominators have been replaced by an estimated average energy, so that the sum could be transformed into a single term containing only Ψ_0; (ii) only a finite number of terms have been taken into consideration; and (iii) the series has been omitted altogether. Only the first of these approximations has

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[7] H. F. Hameka, J. Chem. Phys. **34**, 366 (1961).

[8] This error was brought to my attention by J. H. Van Vleck (private communication).

[9] C. A. Coulson, Proc. Phys. Soc. (London) **A54**, 51 (1942).

[10] J. V. Bonet and A. V. Bushkovitch, J. Chem. Phys. **21**, 2199 (1953).

some claim of reliability, but since it is difficult to estimate the average energy it can still lead to a large error.

In various cases the magnitude of the infinite series has been derived from experimental data on rotational magnetism; we discuss this in the next section. Apart from this, only one serious effort to make a detailed study of the behavior of the infinite series is known. Snyder and Parr[11] investigated for the hydrogen atom, for which an exact calculation can be performed, the contribution of the various terms of Eq. (13) to the magnetic susceptibility for a few possible choices of gauge of the vector potential. Although the infinite series is zero if the origin of $\mathbf{r}$ in the vector potential is taken as the nucleus, they deliberately made some unfavorable choices to investigate the behavior of the infinite series. It was found that a large part of χ resulted from contributions of the continuum and that, if the infinite series is calculated by taking an average excitation energy in the denominators, this energy term may vary as much as by a factor 500 for the different choices of gauge that were considered.

This shows that it is very difficult to make reliable theoretical estimates of the infinite series in Eq. (13) for molecules. Therefore it is highly desirable to choose a favorable gauge for the wave function, so that the infinite series becomes as small as possible or at least rapidly converging. This is realized by the procedure that leads to Eqs. (33) and (35). Also Rebane's variational method[4] seems to offer a promising approach into that direction but no practical applications of this procedure have been reported.

Since it seems to be inevitable that use be made of approximations in the calculations, one might just as well introduce them at an earlier stage. The ground state eigenfunction Φ of $\mathcal{H}_{\text{op}}$ may be written as

$$\Phi=\Phi_0+\mathbf{H}\cdot\mathbf{\Phi}_1-\boldsymbol{\mu}\cdot\mathbf{\Phi}_2, \tag{36}$$

where the Φ_i are functions of the electron coordinates only. It is possible to obtain approximate values for E_0', χ, and σ by taking various trial functions for Φ_0, $\mathbf{\Phi}_1$, and $\mathbf{\Phi}_2$, each containing a certain number of parameters, and by minimizing the energy with respect to the parameters. The gauge of the vector potential then becomes irrelevant because the parameters automatically adjust themselves to the most favorable gauge during the minimizing. A very complete calculation of χ and σ of the hydrogen molecule was performed by Ishiguro and Koide[12] along these lines by substituting James-Coolidge type functions[13] for the Φ_i. However, an extension of this method to more complicated molecules than H_2 seems to be practically impossible.

A special type of variational function was proposed by Tillieu and Guy,[14,15] namely

$$\Phi=\Psi_0(1+\mathbf{H}\cdot\mathbf{g}), \tag{37}$$

where for Ψ_0 some known approximate ground-state wave function is substituted, whereas $\mathbf{g}$ is a simple linear or quadratic function of the electron coordinates, the coefficients of which are varied in order to minimize the energy. The accuracy of this procedure is difficult to judge at first sight, but the method has given fairly reliable results in various applications. Das and Bersohn[16] have calculated proton magnetic shielding constants from similar variational functions.

III. ROTATIONAL MAGNETISM

It is expected from general physical considerations that in a rotating molecule there may be a magnetic moment resulting from the ring currents of the electrons around the center of gravity. The theory of this phenomenon was worked out by Wick,[17] who established a connection between the rotational magnetism and some earlier work on the diamagnetic susceptibility by Van Vleck and Frank.[18] A closely related quantity is the value of the magnetic field at the position of a proton in the hydrogen molecule due to the rotational magnetic dipole, which was also calculated by Wick.[19] It was shown that this effect is related to the proton magnetic shielding constant.[20]

These two phenomena have become very important in the theory of diamagnetic susceptibilities and proton magnetic shielding constants, since it was reported that reliable experimental information about them may be obtained from molecular beam experiments.[21–24]

We outline the theory of the rotational magnetism, following the work of Wick.[17,19] The rotational magnetic dipole μ_r may be calculated as the expectation value of the angular momentum operator $\mathbf{M}$ with respect to a fixed coordinate system, and the magnetic field H_r at the position of proton a due to this dipole may be derived from the operator $r_a^{-3}(\mathbf{j}\times\mathbf{r}_a)$, where $\mathbf{j}$ is the electron current density vector. However, there is an additional complication in the calculations, which we investigate for the special case of the hydrogen molecule.

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The Hamiltonian of the hydrogen molecule consists of the sum of the four kinetic energy terms of the two protons and the two electrons, and of the potential energy. Consequently it is a function of 12 variables, namely the four sets of Cartesian coordinates of the protons and of the electrons. It is now profitable to introduce the following new set of coordinates: the coordinates X, Y, and Z of the center of mass; the distance R of the two protons; the angles θ and φ, which denote the orientation of the vector AB connecting the two protons; and the Cartesian coordinates (ξ_1,η_1,ζ_1) and (ξ_2,η_2,ζ_2) of the electrons with the center of mass as origin and AB as z axis. The Hamiltonian may now be rewritten as[25]

$$\begin{aligned}\mathcal{H}=&\mathcal{H}_0(X,Y,Z)+\mathcal{H}_1(\xi_1,\eta_1,\zeta_1;\,\xi_2,\eta_2,\zeta_2;\,R)\\&+\mathcal{H}_2(R)+R^{-2}\mathcal{H}_3(\theta,\varphi)\\&+R^{-2}\mathcal{H}_4(\xi_1,\eta_1,\zeta_1;\,\xi_2,\eta_2,\zeta_2;\,\theta,\varphi),\end{aligned}\tag{38}$$

where $\mathcal{H}_0$ is the kinetic energy of the center of mass, $\mathcal{H}_1$ is the Hamiltonian of the electrons for the case where the nuclei are fixed at distance R, $\mathcal{H}_2$ represents the vibrations of the protons, $\mathcal{H}_3$ stands for the rotation of the molecule, and $\mathcal{H}_4$ is a small correction term that couples the electronic motion with the rotation which is usually neglected but is very important in the theory of rotational magnetism. The term $\mathcal{H}_0$ may be separated and is of no further importance; it will therefore be omitted.

A reliable approximation to the eigenfunctions of Eq. (37) may be obtained as follows: First we find the eigenvalues E_k and eigenfunctions F_k of $\mathcal{H}_1$, they will contain R as a parameter. We substitute this result into Eq. (37) and assume that the derivatives of F_k with respect to R are negligible as compared to the other terms.[26] This enables us to find the eigenfunctions v_n and eigenvalues h_n of $\mathcal{H}_2$; they are to a good approximation the solutions of the harmonic oscillator equation. If we finally neglect $\mathcal{H}_4$ we obtain the eigenvalues ϵ_J and the eigenfunctions $g_{J,M}$ of $\mathcal{H}_3$; the $g_{J,M}$ are the solutions $P_J^{|M|}(\cos\theta)e^{iM\varphi}$ of the rigid rotator equation. The approximate eigenvalues and eigenfunctions of $\mathcal{H}$ are thus

$$\begin{aligned}E(k,n,J)&=E_k+h_n+\epsilon_J,\\ \Phi(k,n,J,M)&=F_k(\xi_1,\eta_1,\zeta_1;\,\xi_2,\eta_2,\zeta_2;\,R)v_n(R)\\&\quad\times P_J^{|M|}(\cos\theta)e^{iM\varphi}.\end{aligned}\tag{38a}$$

If one attempts to evaluate μ_r and H_r from the function $\Phi(k,n,J,M)$ the result is zero. Clearly it is too approximate a wave function for this purpose. From a careful analysis of the various approximations involved in deriving Eq. (38a), Wick concluded that it was inadmissable to omit $\mathcal{H}_4$, whereas the other approximations are allowed for calculations of μ_r and H_r. The detailed form of $\mathcal{H}_4$ is

$$\mathcal{H}_4=\frac{\hbar^2}{M_PR^2}\left[2im_\xi\frac{\partial}{\partial\theta}+m_\xi^2+m_\eta^2+2m_\eta\frac{1}{\sin\theta}\left(i\frac{\partial}{\partial\varphi}+m_\zeta\cos\theta\right)\right],\tag{39}$$

where

$$m_\xi=-i\left(\eta_1\frac{\partial}{\partial\zeta_1}-\zeta_1\frac{\partial}{\partial\eta_1}+\eta_2\frac{\partial}{\partial\zeta_2}-\zeta_2\frac{\partial}{\partial\eta_2}\right)\text{ and cycl.,}\tag{40}$$

and where M_P is the mass of the proton. We may treat $\mathcal{H}_4$ as a small perturbation, so that to a first approximation the wave function for the electronic ground state becomes

$$\begin{aligned}\Psi(0,J,M)=&\Phi(0,J,M)-\textstyle\sum_k\sum_{J'}\sum_{M'}(E_k-E_0)^{-1}\\&\times\langle\Phi(k,J',M')|\Lambda|\Phi(0,J,M)\rangle\\&\times\Phi(k,J',M'),\end{aligned}\tag{41}$$

where

$$\Lambda=\frac{\hbar^2}{M_PR^2}\left[2im_\xi\frac{\partial}{\partial\theta}+\frac{2i}{\sin\theta}m_\eta\frac{\partial}{\partial\varphi}\right].\tag{42}$$

The other terms of Eq. (39) cancel on account of the radial symmetry of the electronic ground state.

The rotational magnetic moment μ_r may be calculated as the expectation value of the angular momentum operator in a fixed coordinate system with respect to the function $\Psi(0,J,M)$. According to Wick[17]

$$\begin{aligned}\mu_r=&(4\hbar^2/M_PR^2)\textstyle\sum_k(E_k-E_0)^{-1}\\&\times(\langle F_0|\mathbf{M}|F_k\rangle,\langle F_k|\mathbf{M}|F_0\rangle)[J(J+1)]^{\frac{1}{2}}.\end{aligned}\tag{43}$$

This infinite series is identical with the sum in the first of the Eqs. (13) if in the latter the gauge is chosen in such a way that the origins of the $\mathbf{r}_j$ occurring in the $\mathbf{A}_j'$ are all taken as the center of mass of the molecule.

By taking the expectation value of $r_a^{-3}(\mathbf{j}\times\mathbf{r}_a)$, where $\mathbf{j}$ is the electron current density, Wick[19] also found

$$\begin{aligned}H_r=&(2\hbar^2/M_PR^2)\textstyle\sum_k(E_k-E_0)^{-1}\\&\times\{(\langle F_0|\mathbf{L}|F_k\rangle,\langle F_k|\mathbf{M}|F_0\rangle)\\&+(\langle F_0|\mathbf{M}|F_k\rangle,\langle F_k|\mathbf{L}|F_0\rangle)\}[J(J+1)]^{\frac{1}{2}}.\end{aligned}\tag{44}$$

The infinite series here is the same as the sum occurring in the second Eq. (13) if in the latter the gauge is chosen in such a way that the origin of the $\mathbf{r}_j$ is taken as the point where the magnetic field H_r is calculated, in this case the proton a.

The connections between Eqs. (43) and (44) and Eqs. (13) have proved to be very useful for calculations of χ and σ, since for a specific choice of gauge we may replace the infinite series by reliable values obtained from measurements of μ_r and H_r. The first one to use this connection was Ramsay[20] in his determination of σ for the hydrogen molecule. There is no experimental value available for this quantity, so in this case it is especially important to obtain a reliable estimate for σ

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[25] R. de L. Kronig, *Band Spectra and Molecular Structure,* (Cambridge University Press, Cambridge, 1930).

[26] This is inherent with the Born-Oppenheimer approximation: M. Born and J. R. Oppenheimer, Ann. Physik **84**, 457 (1927).

and it is very useful if one is able to reduce the possible errors in the theory by making use of experimental results. For more complicated molecules the experimental data of H_r seem to be less reliable than for hydrogen, so that semi-empirical calculations in which values of H_r are incorporated are less accurate than for H_2.

In the theory of magnetic susceptibilities Weltner[27] made use of experimental values of μ_r to derive the χ values for a series of molecules, including hydrogen.

Now that connections have been established between χ and μ_r, and also between σ and H_r it is obvious that there are various possibilities in doing theoretical work. Apart from performing *ab initio* calculations of either χ or μ_r it is possible to perform calculations of χ in which experimental data on μ_r are incorporated and vice versa. In general the theoretical values of μ_r are much less reliable than the results for χ. This was already observed in the original paper by Wick,[17] which confirmed the results of earlier work by Van Vleck and Frank,[18] where it was found that it is difficult to make accurate estimates of the infinite series. Only in a recent paper by Espe,[28] who based his calculations on a model assuming irrotational flow of the electronic motion, satisfactory values were obtained for μ_r and H_r in the hydrogen molecule.

IV. CALCULATIONS OF χ WITH GIAO

In Sec. II we discussed the calculation of χ and σ from molecular wave functions that are constructed from gauge invariant atomic orbitals (GIAO). In particular we derived Eq. (33) for χ and Eq. (35) for σ. The magnetic susceptibility χ was found to be a sum of three terms: Q_0, Q_1, and Q_2; and similarly the proton magnetic shielding constant σ is the difference of P_0 and P_1. It was mentioned that in earlier work[6,7] the contributions of Q_1, Q_2, and P_1 were erroneously supposed to be all zero.[8] In the present section we investigate what are the consequences of this error for calculations of χ, the next section is dedicated to similar considerations for calculations of σ. In this paper we consider only the hydrogen molecule; this does not mean that there is no need to consider more complicated molecules, but solely that the consequences of this omission may be better understood for a simple system. We will consider more complicated molecules only after the theory has been put on a satisfactory basis for hydrogen.

The values obtained for Q_0, Q_1, and Q_2 depend on the particular approximate function Ψ_0 that is substituted into Eq. (33). In the following three subsections we first consider the case where Ψ_0 is a molecular orbital function suggested by Coulson,[29] next we substitute a function that was derived by Wang[30] and finally a function proposed by Rosen.[31] For both Coulson's and Wang's functions Q_2 is equal to zero.

Table I. Integrals for Coulson's function.

S	$\langle h_a \| h_b\rangle$	0.675 998
I_1'	$\langle h_a \| r_a^{-1} \| h_a\rangle$	1.197 000
I_2'	$\langle h_b \| r_a^{-1}-Rz_ar_a^{-3} \| h_b\rangle$	0.182 458
I_3'	$\langle h_b \| r_a^{-1} \| h_a\rangle$	0.599 456
I_4'	$\langle h_a \| r_a^2 \| h_a\rangle$	2.093 789
I_5'	$\langle h_b \| r_a^2 \| h_a\rangle$	2.009 196
I_6'	$\langle h_a \| x^2 \| h_a\rangle$	0.697 930
I_7'	$\langle h_b \| x^2 \| h_a\rangle$	0.537 237
I_8'	$2\langle h_a \| \partial^2/\partial x^2 \| h_a\rangle$	−0.955 206
I_9'	$2\langle h_b \| \partial^2/\partial x^2 \| h_a\rangle$	−0.478 366
I_{10}'	$\langle h_b \| r_a^{-1} \| h_b\rangle$	0.647 337
M_1'	$\langle h_a \| x^2r_a^{-3}r_b^{-1} \| h_b\rangle$	0.121 437
M_3'	$\langle h_b \| x^2r_a^{-3}r_b^{-1} \| h_b\rangle$	0.099 074
M_5'	$\langle h_a \| x^2r_a^{-4}r_b^{-1} \| h_b\rangle$	0.203 129
M_6'	$\langle h_b \| x^2r_a^{-3}r_b^{-2} \| h_b\rangle$	0.083 853

1. Calculations with Coulson's Function

Coulson[29] proposed the following simple molecular orbital function for the ground state of the hydrogen molecule:

$$\Psi_0=\phi_0(1)\phi_0(2), \tag{45}$$

where

$$\begin{aligned} \phi_0(i)&=(2+2S)^{-\frac{1}{2}}\{h_a(i)+h_b(i)\} \\ S&=\langle h_a|h_b\rangle \\ h_a&=(q^3/\pi)^{\frac{1}{2}}\exp(-qr_a)\quad q=1.197. \end{aligned} \tag{46}$$

This approximation, where Ψ_0 is written as a simple product of one-electron functions, implies the assumption that there exists an effective Hamiltonian $\mathcal{H}_0'$, such that

$$\mathcal{H}_0'\phi_0=\epsilon_0\phi_0, \tag{47}$$

where ϵ_0 is the smallest eigenvalue of the operator. There exist also the higher eigenvalues ϵ_k and corresponding eigenfunctions ϕ_k:

$$\mathcal{H}_0'\phi_k=\epsilon_k\phi_k \tag{48}$$

which together with ϕ_0 form a complete set.

For this particular function Ψ_0 we have

$$\tilde{\mathcal{H}}_1|\tilde{\Psi}_0\rangle=0 \tag{49}$$

where the notation of Eq. (32) is used. Consequently

$$\begin{aligned} Q_2&=0, \\ Q_0&=\langle\tilde{\Psi}_0|\tilde{\mathcal{H}}_2|\tilde{\Psi}_0\rangle, \end{aligned} \tag{50}$$

which simplifies the calculation of χ considerably.

The contribution of Q_0 to the susceptibility may now easily be expressed in terms of the integrals that are defined and tabulated in Table I:

$$Q_0=(3/H^2)(1+S)^{-1}[(I_4'-I_6'+I_5'-I_7')(H_x^2+H_y^2)+2(I_6'+I_7')H_z^2]. \tag{51}$$

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[27] W. Weltner Jr., J. Chem. Phys. **28**, 477 (1958).

[28] I. Espe, Phys. Rev. **103**, 1254 (1956).

[29] C. A. Coulson, Trans. Faraday Soc. **33**, 1479 (1937).

[30] S. Wang, Phys. Rev. **31**, 579 (1928).

[31] N. Rosen, Phys. Rev. **38**, 2099 (1931).

The quantity Q_1 may be expressed in terms of the operator $\mathcal{H}_0'$ and its solutions ϵ_k and ϕ_k:

$$\begin{aligned}\chi_0 Q_1 = (2/H^2)[\langle\tilde{\phi}_0|\tilde{\mathcal{H}}_0'-\epsilon_0|\tilde{\phi}_0\rangle \\ -\textstyle\sum_k (\epsilon_k-\epsilon_0)^{-1}\langle\tilde{\phi}_k|\tilde{\mathcal{H}}_0'-\epsilon_0|\tilde{\phi}_0\rangle \\ \times\langle\tilde{\phi}_k|\tilde{\mathcal{H}}_0'-\epsilon_0|\phi_0\rangle^*],\end{aligned} \tag{52}$$

where the following notation is used:

(a) The functions $\tilde{\phi}_k$ are derived from the functions ϕ_k by replacing the atomic orbitals by GIAO;

$$\begin{aligned}\phi_k &= \varphi_{ka}+\varphi_{kb} \\ \tilde{\phi}_k &= f_a\varphi_{ka}+f_b\varphi_{kb},\end{aligned} \tag{53}$$

where

$$\begin{aligned}f_a &= \exp[ie\gamma(\mathbf{q}-\mathbf{a})/\hbar c] \\ f_b &= \exp[ie\gamma(\mathbf{q}-\mathbf{b})/\hbar c].\end{aligned} \tag{54}$$

(b) The operator $\tilde{\mathcal{H}}_0'$ is obtained from $\mathcal{H}_0'$ by commuting the latter with each gauge factor f_a and f_b following it.

We may now write

$$\begin{aligned}\tilde{\phi}_0 &= \tfrac{1}{2}(f_a+f_b)\phi_0+\tfrac{1}{2}(f_a-f_b)g_0 \\ g_0 &= (2+2S)^{-\frac{1}{2}}(h_a-h_b)\end{aligned} \tag{55}$$

and consequently,

$$\mathcal{H}_0'-\epsilon_0|\tilde{\phi}_0\rangle = \tfrac{1}{2}(f_a-f_b)(\mathcal{H}_0'-\epsilon_0)|g_0\rangle. \tag{56}$$

If this result is substituted into Eq. (52) we obtain

$$\begin{aligned}\chi_0 Q_1 = (4L/H^2)[\langle g_0|\tfrac{1}{2}(f_a-f_b)^*\tfrac{1}{2}(f_a-f_b)(\mathcal{H}_0'-\epsilon_0)|g_0\rangle \\ -\textstyle\sum_k (\epsilon_k-\epsilon_0)^{-1}\langle\phi_k|\tfrac{1}{2}(f_a-f_b)(\mathcal{H}_0'-\epsilon_0)|g_0\rangle \\ \times\langle\phi_k\tfrac{3}{2}(f_a-f_b)(\mathcal{H}_0'-\epsilon_0)|g_0\rangle^*].\end{aligned} \tag{57}$$

If we define

$$\alpha_i = eR(H_y x_i - H_x y_i)/4\hbar c, \tag{58}$$

where R is the distance between the two protons, this expression may be simplified to

$$\begin{aligned}\chi_0 Q_1 = (4L/H^2)[\langle g_0|\alpha^2(\mathcal{H}_0'-\epsilon_0)|g_0\rangle \\ -\textstyle\sum_k (\epsilon_k-\epsilon_0)^{-1}\langle\phi_k|\alpha(\mathcal{H}_0'-\epsilon_0)|g_0\rangle \\ \times\langle\phi_k^*|\alpha(\mathcal{H}_0'-\epsilon_0)|g_0^*\rangle].\end{aligned} \tag{59}$$

By making use of the following two relations:

$$\begin{aligned}\langle\phi_k^*|\alpha(\mathcal{H}_0'-\epsilon_0)|g_0^*\rangle &= \langle g_0|(\mathcal{H}_0'-\epsilon_0)\alpha|\phi_k\rangle \\ &= (\epsilon_k-\epsilon_0)\langle g_0|\alpha|\phi_k\rangle-\langle g_0|\Lambda|\phi_k\rangle,\end{aligned}$$

$$\Lambda_i = \frac{eR\hbar}{4mc}\left(H_y\frac{\partial}{\partial x_i}-H_x\frac{\partial}{\partial y_i}\right) \tag{60}$$

and

$$\begin{aligned}\langle g_0|\alpha^2(\mathcal{H}_0'-\epsilon_0)|g_0\rangle \\ = \textstyle\sum_k \langle g_0|\alpha|\phi_k\rangle\langle\phi_k|\alpha(\mathcal{H}_0'-\epsilon_0)|g_0\rangle,\end{aligned} \tag{61}$$

we may transform Eq. (59) into

$$\chi_0 Q_1 = \frac{4L}{H^2}\sum_k \frac{\langle\phi_k|\alpha(\mathcal{H}_0'-\epsilon_0)|g_0\rangle\langle g_0|\Lambda|\phi_k\rangle}{\epsilon_k-\epsilon_0}. \tag{62}$$

Again, since

$$\begin{aligned}\langle\phi_k|\alpha(\mathcal{H}_0'-\epsilon_0)|g_0\rangle = (\epsilon_k-\epsilon_0)\langle\phi_k|\alpha|g_0\rangle \\ +\langle\phi_k|\Lambda|g_0\rangle, \\ \langle g_0|\Lambda\alpha|g_0\rangle = \textstyle\sum_k \langle g_0|\Lambda|\phi_k\rangle\langle\phi_k|\alpha|g_0\rangle,\end{aligned} \tag{63}$$

we obtain

$$\begin{aligned}(H^2\chi_0 Q_1/4L) = \langle g_0|\Lambda\alpha|g_0\rangle+\textstyle\sum_k (\epsilon_k-\epsilon_0)^{-1} \\ \times\langle g_0|\Lambda|\phi_k\rangle\langle\phi_k|\Lambda|g_\theta\rangle.\end{aligned} \tag{64}$$

We may define an average excitation energy $\bar{\epsilon}-\epsilon_0$ by means of

$$\begin{aligned}(\bar{\epsilon}-\epsilon_0)^{-1}\textstyle\sum_k \langle g_0|\Lambda|\phi_k\rangle\langle\phi_k|\Lambda|g_0\rangle \\ = \textstyle\sum_k (\epsilon_k-\epsilon_0)^{-1}\langle g_0|\Lambda|\phi_k\rangle\langle\phi_k|\Lambda|g_0\rangle.\end{aligned} \tag{65}$$

This definition allows us to rewrite Eq. (64) as

$$\frac{H^2\chi_0 Q_1}{4L} = \langle g_0|\Lambda\alpha|g_0\rangle+\frac{1}{\bar{\epsilon}-\epsilon_0}\langle g_0|\Lambda^2|g_0\rangle, \tag{66}$$

or

$$Q_1 = \frac{3R^2(H_x^2+H_y^2)}{4H^2(1+S)}\left[(1-S)+\frac{I_8'-I_9'}{\bar{\epsilon}-\epsilon_0}\right], \tag{67}$$

where I_8', I_9', and S are reported in Table I.

The calculation of Q_1 is straightforward if we can make a reliable estimate of $\bar{\epsilon}-\epsilon_0$. Unfortunately this is not easy; in order to solve it for this and other cases let us reconsider Eq. (65). It is always permissible to define $\bar{\epsilon}-\epsilon_0$ by means of Eq. (65), but this definition is meaningful only if certain conditions are fulfilled, the most important of which is in our case that the terms of the infinite series are either all positive or all negative. This requirement is satisfied for the series in Eq. (65). Fortified by these considerations one might be tempted to state that the value of $\bar{\epsilon}-\epsilon_0$ should be taken between the energies of the lowest antibonding π orbital and the highest bound state of the molecule, that is $0.504<\bar{\epsilon}-\epsilon_0<0.567$ a.u. (compare[32]). However, it may easily be shown that this type of approach leads to incorrect results.

Let us imagine that everywhere in Eq. (59) the function g_0 is replaced by the function ϕ_0, obviously the right-hand side then becomes identically zero. By means of the procedure that led to Eq. (67) we then find

$$\langle\phi_0|\Lambda\alpha|\phi_0\rangle+\sum_k \frac{\langle\phi_0|\Lambda|\phi_k\rangle\langle\phi_k|\Lambda|\phi_0\rangle}{\epsilon_k-\epsilon_0} = 0. \tag{68}$$

Replacing the energies in the denominators by an effective average energy $\epsilon'-\epsilon_0$ [see Eq. (65)], we obtain

$$(1+S)+(\epsilon'-\epsilon_0)^{-1}(I_8'+I_9') = 0, \tag{69}$$

which yields $\epsilon'-\epsilon_0=0.855$ a.u. There is not much doubt that this value is outside the range of values between

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[32] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950) p. 340.

the lowest bonding π state and the highest bound state of the molecule; the value of ϵ' lies somewhere in the continuum.

The preceding argument has only a negative value; it has shown that an obvious way of estimating $\bar{\epsilon}$ is wrong, but it does not offer an alternative method of obtaining a more reliable value of $\bar{\epsilon}$.

However, there is a different procedure by means of which we may obtain a reliable estimate for $\bar{\epsilon}$. Let us again consider Eq. (59) and let ϕ_1 and ϵ_1 be the eigenfunction and eigenvalue of the lowest antibonding σ state. Then

$$\langle\phi_1|\alpha^2(\mathcal{H}_0'-\epsilon_1)|\phi_1\rangle-\sum_k(\epsilon_k-\epsilon_1)^{-1}\langle\phi_k|\alpha(\mathcal{H}_0'-\epsilon_1)|\phi_1\rangle \times\langle\phi_k|\alpha(\mathcal{H}_0'-\epsilon_1)|\phi_1\rangle^*=0. \quad (70)$$

Although the function ϕ_1 is not exactly equal to g_0, it bears a close resemblance to it, so that for an estimate of an average excitation energy we may assume that

$$\langle g_0|\alpha^2(\mathcal{H}_0'-\epsilon_1)|g_0\rangle-\sum_k(\epsilon_k-\epsilon_1)^{-1}\langle\phi_k|\alpha(\mathcal{H}_0'-\epsilon_1)|g_0\rangle \times\langle\phi_k|\alpha(\mathcal{H}_0'-\epsilon_1)|g_0\rangle^*\approx 0 \quad (71)$$

and consequently

$$\langle g_0|\Lambda\alpha|g_0\rangle+\sum_k(\epsilon_k-\epsilon_1)^{-1}\langle g_0|\Lambda|\phi_k\rangle \times\langle\phi_k|\Lambda|g_0\rangle\approx 0. \quad (72)$$

If we now define

$$(\bar{\epsilon}_1-\epsilon_1)^{-1}\sum_k\langle g_0|\Lambda|\phi_k\rangle\langle\phi_k|\Lambda|g_0\rangle =(\epsilon_k-\epsilon_1)^{-1}\langle g_0|\Lambda|\phi_k\rangle\langle\phi\cdot|\Lambda|g_0\rangle, \quad (73)$$

then

$$(1-S)+(\bar{\epsilon}_1-\epsilon_1)^{-1}(I_8'-I_9')\approx 0, \quad (74)$$

which makes $\bar{\epsilon}_1-\epsilon_1=1.472$ a.u. To within a good approximation we may now take $\bar{\epsilon}-\epsilon_0=(\bar{\epsilon}_1-\epsilon_1)+(\epsilon_1-\epsilon_0)$ and since $\epsilon_1-\epsilon_0=0.410$ a.u. (see reference 32), we obtain $\bar{\epsilon}-\epsilon_0=1.882$. Substitution of this value into Eq. (67) yields

$$H^2Q_1=0.06195(H_x^2+H_y^2). \quad (75)$$

From Eq. (51) it follows that

$$H^2Q_0=5.13333(H_x^2+H_y^2)+4.42184H_z^2. \quad (76)$$

Consequently, by combining Eq. (75) and (76):

$$\chi_x=\chi_y=5.19528\chi_0;\quad \chi_z=4.42184\chi_0;\quad \chi=4.93747\chi_0. \quad (77)$$

The contribution of Q_1 to the susceptibility is $0.0413\chi_0$, which is 0.8% of the total effect.

We can take this result as a basis for calculating μ_r. Let us calculate the first term of Eq. (13):

$$\chi'=\chi_0\langle\Psi_0|r_1^2+r_2^2|\Psi_0\rangle, \quad (78)$$

taking the origins for both $\mathbf{r}_1$ and $\mathbf{r}_2$ as the center of gravity of the molecule. Then

$$\chi'=2\chi_0(1+S)^{-1}[I_4'+I_5'+\tfrac{1}{4}(1-S)R^2] \quad (79)$$

or $\chi'=5.08562\chi_0$. Consequently $\mu_r'=\chi'-\chi=0.14815\chi_0$.

2. Calculations with Wang's Function

In this subsection we take Ψ_0 as the following function:

$$\Psi_0=(2+2\Delta^2)^{-1}\{s_a(1)s_b(2)+s_b(1)s_a(2)\},$$
$$\Delta=\langle s_a|s_b\rangle;$$
$$s_a=(\beta^3/\pi)\exp(-\beta r_a)\quad \beta=1.17. \quad (80)$$

Also in this case Eq. (50) is valid so that we are concerned only with the first term of Q_0 and with Q_1. It is profitable to make use of integrals that were defined and evaluated in previous work.[6] We have recalculated all required integrals and corrected some of them together with some additional integrals that were not calculated previously; they are all defined and reported in Table II.

From Eqs. (33) and (80) we find that now

$$Q_0=(3\chi_0/H^2)(1+\Delta^2)^{-1}[(I_4+\Delta I_5-\Delta_{aa}'-\Delta\Delta_{ab}')(H_x^2+H_y^2)+2(\Delta_{aa}'+\Delta\Delta_{ab}')H_z^2], \quad (81)$$

TABLE II. Integrals for Wang's and Rosen's functions.

Δ	$\langle s_a\vert s_b\rangle$	0.686 577
Δ_{aa}	$\langle u_a\vert u_a\rangle$	1.007 305
Δ_{ab}	$\langle u_a\vert u_b\rangle$	0.779 704
Δ_{aa}'	$\langle p_{xa}\vert p_{xa}\rangle$	0.730 514
Δ_{ab}'	$\langle p_{xa}\vert p_{xb}\rangle$	0.568 552
I_1	$\langle s_a\vert r_a^{-1}\vert s_a\rangle$	1.170 000
I_2	$\langle s_b\vert r_a^{-1}-Rz_ar_a^{-3}\vert s_b\rangle$	0.189 006
I_3	$\langle s_b\vert r_a^{-1}\vert s_a\rangle$	0.599 910
I_4	$\langle s_a\vert r_a^2\vert s_a\rangle$	2.191 541
I_5	$\langle s_b\vert r_a^2\vert s_a\rangle$	2.109 364
I_8	$2\langle s_a\vert\partial^2/\partial x^2\vert s_a\rangle$	−0.912 600
I_9	$2\langle s_a\vert\partial^2/\partial x^2\vert s_b\rangle$	−0.467 930
I_{10}	$\langle s_b\vert r_a^{-1}\vert s_b\rangle$	0.643 099
J_1	$\langle u_a\vert r_a^2\vert u_a\rangle$	2.231 564
J_2	$\langle u_a\vert r_a^2\vert u_b\rangle$	2.369 811
J_4	$\langle u_a\vert x^2\vert u_a\rangle$	0.738 519
J_5	$\langle u_a\vert x^2\vert u_b\rangle$	0.643 886
J_6	$2\langle u_a\vert\partial^2/\partial x^2\vert u_a\rangle$	−0.916 600
J_7	$2\langle u_a\vert\partial^2/\partial x^2\vert u_b\rangle$	−0.532 528
J_8	$\langle u_a\vert r^2\vert u_a\rangle$	2.536 685
J_9	$\langle u_a\vert r^2\vert u_b\rangle$	1.993 258
K_1	$\langle u_a\vert r_a^{-1}\vert u_a\rangle$	1.174 273
K_2	$\langle u_b\vert r_a^{-1}-Rz_ar_a^{-3}\vert u_b\rangle$	0.210 323
K_3	$\langle u_b\vert r_a^{-1}\vert u_a\rangle$	0.682 923
K_4	$\langle u_b\vert x^2r_a^{-3}\vert s_a\rangle$	0.195 216
K_5	$\langle u_b\vert r_a^{-1}\vert u_b\rangle$	0.682 620
L_1	$\langle s_a\vert x^2r_a^{-3}\vert s_a\rangle$	0.390 000
L_2	$\langle s_a\vert x^2r_a^{-3}\vert s_b\rangle$	0.175 338
L_3	$\langle s_b\vert x^2r_a^{-3}\vert s_b\rangle$	0.125 044
L_4	$\langle u_a\vert x^2r_a^{-1}\vert s_a\rangle$	0.427 350
L_5	$\langle u_a\vert x^2r_a^{-1}\vert s_b\rangle$	0.316 412
M_1	$\langle s_a\vert x^2r_a^{-3}r_b^{-1}\vert s_b\rangle$	0.121 309
M_3	$\langle s_b\vert x^2r_a^{-3}r_b^{-1}\vert s_b\rangle$	0.099 009
M_5	$\langle s_a\vert x^2r_a^{-4}r_b^{-1}\vert s_b\rangle$	0.207 365
M_6	$\langle s_b\vert x^2r_a^{-3}r_b^{-2}\vert s_b\rangle$	0.082 145
M_7	$\langle u_a\vert x^2r_a^{-3}r_b^{-1}\vert u_b\rangle$	0.162 327
M_8	$\langle u_b\vert x^2r_a^{-3}r_b^{-1}\vert u_b\rangle$	0.113 016
M_9	$\langle u_a\vert x^2r_a^{-4}r_b^{-1}\vert u_b\rangle$	0.236 518
M_{10}	$\langle u_b\vert x^2r_a^{-3}r_b^{-2}\vert u_b\rangle$	0.090 000
N_1	$\langle u_a\vert x^2r_a^{-3}\vert s_a\rangle$	0.390 000
N_2	$\langle u_b\vert x^2r_a^{-3}\vert s_b\rangle$	0.133 259
N_3	$\langle u_a\vert x^2r_a^{-3}\vert s_b\rangle$	0.180 008
N_4	$\langle u_b\vert x^2r_a^{-3}\vert s_a\rangle$	0.195 216
N_5	$\langle u_a\vert x^2r_a^{-4}\vert s_a\rangle$	0.912 600
N_6	$\langle u_b\vert x^2r_a^{-3}r_b^{-1}\vert s_b\rangle$	0.104 690
N_7	$\langle u_a\vert x^2r_a^{-4}\vert s_b\rangle$	0.112 071
N_8	$\langle u_b\vert x^2r_a^{-3}r_b^{-1}\vert s_a\rangle$	0.133 465

or

$$H^2Q_0=5.13579(H_x^2+H_y^2)+4.57066H_z^2. \tag{82}$$

For a calculation of Q_1 it is profitable to write

$$\begin{aligned}\tilde{\Psi}_0&=\tfrac{1}{2}\{f_a(1)f_b(2)+f_b(1)f_a(2)\}\Psi_0\\&\quad+\tfrac{1}{2}\{f_a(1)f_b(2)-f_b(1)f_a(2)\}G_0,\\G_0&=(2+2\Delta^2)^{-1}\{s_a(1)s_b(2)-s_b(1)s_a(2)\},\end{aligned} \tag{83}$$

and to observe that

$$\tilde{\mathcal{H}}_0-E_0|\tilde{\Psi}_0\rangle=\tfrac{1}{2}\{f_a(1)f_b(2)-f_b(1)f_a(2)\}\times(\mathcal{H}_0-E_0)|G_0\rangle. \tag{84}$$

For our purpose we may replace Eqs. (83) and (84) by

$$\begin{aligned}\tilde{\Psi}_0&=\Psi_0+i(\alpha_1-\alpha_2)G_0,\\\tilde{\mathcal{H}}_0-E_0|\tilde{\Psi}_0\rangle&=i(\alpha_1-\alpha_2)(\mathcal{H}_0-E_0)G_0,\end{aligned} \tag{85}$$

[compare with Eq. (58)], so that

$$\begin{aligned}H^2\chi_0Q_1=\langle G_0|(\alpha_1-\alpha_2)^2(\mathcal{H}_0-E_0)|G_0\rangle\\-\textstyle\sum_k(E_k-E_0)^{-1}\langle\Psi_k|(\alpha_1-\alpha_2)(\mathcal{H}_0-E_0)|G_0\rangle\\\times\langle\Psi_k^*|(\alpha_1-\alpha_2)(\mathcal{H}_0-E_0)|G_0^*\rangle.\end{aligned} \tag{86}$$

By means of a procedure analogous with Subsection IV.1, one finds

$$\begin{aligned}H^2\chi_0Q_1=\langle G_0|(\Lambda_1-\Lambda_2)(\alpha_1-\alpha_2)|G_0\rangle\\+\textstyle\sum_k(E_k-E_0)^{-1}\langle G_0|\Lambda_1-\Lambda_2|\Psi_k\rangle\\\times\langle\Psi_k|\Lambda_1-\Lambda_2|G_0\rangle\end{aligned} \tag{87}$$

[compare with Eq. (60)]. Again we define an average excitation energy $\bar{E}-E_0$ by means of

$$\begin{aligned}(\bar{E}-E_0)^{-1}\textstyle\sum_k\langle G_0|\Lambda_1-\Lambda_2|\Psi_k\rangle\langle\Psi_k|\Lambda_1-\Lambda_2|G_0\rangle\\=\textstyle\sum_k(E_k-E_0)^{-1}\langle G_0|\Lambda_1-\Lambda_2|\Psi_k\rangle\\\times\langle\Psi_k|\Lambda_1-\Lambda_2|G_0\rangle.\end{aligned} \tag{88}$$

This definition is meaningful as all terms of the series have the same sign. As a consequence

$$\begin{aligned}H^2\chi_0Q_1=\langle G_0|(\Lambda_1-\Lambda_2)(\alpha_1-\alpha_2)|G_0\rangle\\+(\bar{E}-E_0)^{-1}\langle G_0|(\Lambda_1-\Lambda_2)^2|G_0\rangle\end{aligned} \tag{89}$$

or

$$Q_1=\frac{3R^2(H_x^2+H_y^2)}{4H^2(1+\Delta^2)}\left[(1-\Delta^2)+\frac{I_8-\Delta I_9}{\bar{E}-E_0}\right]. \tag{90}$$

The critical point of the calculation is again finding a reliable estimate for $\bar{E}$. Following the procedure of Subsection IV.1, we will again define an energy $\bar{E}_1$ from

$$\begin{aligned}(\bar{E}_1-E_1)^{-1}\textstyle\sum_k\langle G_0|\Lambda_1-\Lambda_2|\Psi_k\rangle\langle\Psi_k|\Lambda_1-\Lambda_2|G_0\rangle\\=\textstyle\sum_k(E_k-E_1)^{-1}\langle G_0|\Lambda_1-\Lambda_2|\Psi_k\rangle\\\times\langle\Psi_k|\Lambda_1-\Lambda_2|G_0\rangle,\end{aligned} \tag{91}$$

and make use of the approximate equality

$$(1-\Delta^2)+(\bar{E}_1-E_1)^{-1}(I_8-\Delta I_9)\approx0, \tag{92}$$

where E_1 is the energy of the lowest antibonding σ state. It follows from Eq. (92) that $\bar{E}_1-E_1=1.119$ and if we take again $\bar{E}-E_0=(\bar{E}_1-E_1)+(E_1-E_0)$ we find that $\bar{E}-E_0=1.529$ a.u. and also that

$$H^2Q_1=0.14174(H_x^2+H_y^2). \tag{93}$$

Combination of Eq. (82) and (93) gives

$$\chi_x=\chi_y=5.27753\chi_0;\ \chi_z=4.57066\chi_0;\ \chi=5.04191\chi_0. \tag{94}$$

The contribution of Q_1 to the susceptibility is 1.9% of the total effect.

Also in this case we calculate χ', namely the first term of Eq. (13) with the origin of $\mathbf{r}_j$ as the center of gravity of the molecule:

$$\chi'=2\chi_0(1-\Delta^2)^{-1}[I_4+\Delta I_5+\tfrac{1}{4}(1-\Delta^2)R^2]. \tag{95}$$

It follows that $\chi'=5.29949\chi_0$ and that μ_r', which is the difference of χ' and χ, is $\mu_r'=0.25758\chi_0$.

3. Calculations with Rosen's Function

In this section we substitute for Ψ_0 a function that was first proposed by Rosen[31]:

$$\begin{aligned}\Psi_0&=(2\Delta_{aa}^2+2\Delta_{ab}^2)^{-\frac{1}{2}}\{u_a(1)u_b(2)+u_b(1)u_a(2)\},\\u_a&=s_a+bp_{za},\\u_b&=s_b-bp_{zb},\\s_a&=(\beta^3/\pi)^{\frac{1}{2}}\exp(-\beta r_a),\\p_{za}&=z_as_a\quad p_{zb}=z_bs_b\quad\text{and cycl.},\\\beta&=1.17\quad b=0.10,\end{aligned} \tag{96}$$

where the positive z axis points from nucleus a to nucleus b.

Now we have an additional complication since $\mathcal{H}_1|\tilde{\Psi}_0\rangle$ is not equal to zero. Instead we have

$$\begin{aligned}\tilde{\mathcal{H}}_1|\tilde{\Psi}_0\rangle=-(e\hbar/2a_0mc)b[H_y\{p_{xa}(1)u_b(2)\\-p_{xb}(1)u_a(2)+p_{xa}(2)u_b(1)-p_{xb}(2)u_a(1)\}\\-H_x\{p_{ya}(1)u_b(2)-p_{yb}(1)u_a(2)+p_{ya}(2)u_b(1)\\-p_{yb}(2)u_a(1)\}],\end{aligned} \tag{97}$$

so that now we have to calculate Q_2 and the second term of Q_0. Fortunately it appears that the function of Eq. (97) may be taken as a linear combination of the eigenfunctions of the lowest antibonding π state in our model, so that only one term of the infinite series in Q_0 is different from zero. It thus follows easily that

$$\begin{aligned}Q_0&=Q_0'+Q_0''.\\H^2Q_0'&=3(\Delta_{aa}^2+\Delta_{ab}^2)^{-1}[(\Delta_{aa}J_1+\Delta_{ab}J_2-\Delta_{aa}J_4\\&\quad-\Delta_{ab}J_5)(H_x^2+H_y^2)+2(\Delta_{aa}J_4+\Delta_{ab}J_5)H_z^2],\\H^2Q_0''&=-(\Delta_{aa}^2+\Delta_{ab}^2)^{-1}(\Delta E)^{-1}b^2(\Delta_{aa}\Delta_{aa}'\\&\quad-\Delta_{ab}\Delta_{ab}')(H_x^2+H_y^2),\end{aligned} \tag{98}$$

where ΔE is the energy difference between the lowest antibonding π state and the ground state. We will follow Herzberg[32] in taking $\Delta E=0.504$ a.u.; then

$$\begin{aligned}H^2Q_0'&=5.26869(H_x^2+H_y^2)+4.60725H_z^2,\\H^2Q_0''&=-0.01073(H_x^2+H_y^2).\end{aligned} \tag{99}$$

The contribution Q_1 may be computed according to the method outlined in Subsections 1 and 2. The result is

$$Q_1=\frac{3R^2(H_x^2+H_y^2)}{4H^2(\Delta_{aa}^2+\Delta_{ab}^2)}\times\left[(\Delta_{aa}^2-\Delta_{ab}^2)+\frac{\Delta_{aa}J_6-\Delta_{ab}J_7}{\bar{E}-E_0}\right]. \qquad (100)$$

In order to estimate $\bar{E}-E_0$ we first calculate $\bar{E}_1-E_1$ from

$$(\Delta_{aa}^2-\Delta_{ab}^2)+(\bar{E}_1-E_1)^{-1}(\Delta_{aa}J_6-\Delta_{ab}J_7)\approx 0, \qquad (101)$$

which yields $\bar{E}_1-E_1=1.249$ a.u. Consequently we take $\bar{E}-E_0=1.659$ a.u. (see Subsection 1), so that

$$H^2Q_1=0.09102(H_x^2+H_y^2) \qquad (102)$$

In order to calculate Q_2 we make use of the following expression:

$$\begin{aligned}\chi_0H^2Q_2=&\langle i(\alpha_1-\alpha_2)G_0|-i\tilde{\mathcal{H}}_1|\Psi_0\rangle\\&+\langle\Psi_0|i(\alpha_1-\alpha_2)(-i\tilde{\mathcal{H}}_1)|G_0\rangle\\&-\textstyle\sum_k(E_k-E_0)^{-1}[\langle\Psi_k|-i\tilde{\mathcal{H}}_1|\Psi_0\rangle^*\\&\times\langle\Psi_k|i(\alpha_1-\alpha_2)(\mathcal{H}_0-E_0)|G_0\rangle+\langle\Psi_k|-i\tilde{\mathcal{H}}_1|\Psi_0\rangle\\&\qquad\times\langle\Psi_k|i(\alpha_1-\alpha_2)(\mathcal{H}_0-E_0)|G_0\rangle^*],\end{aligned} \qquad (103)$$

where

$$\begin{aligned}&G_0=(2\Delta_{aa}^2+2\Delta_{ab}^2)^{-\frac{1}{2}}[u_a(1)u_b(2)-u_b(1)u_a(2)],\\&\mathcal{H}_1=(e\hbar/2a_0mc)\mathbf{H}\cdot\mathbf{M},\\&M_x=\textstyle\sum_j\{y_{qj}(\partial/\partial z_j)-z_{qj}(\partial/\partial y_j)\}\text{ and cycl.,}\end{aligned} \qquad (104)$$

and where q denotes the nucleus belonging to the atomic orbital upon which the operator works. These expressions were also used in obtaining Eq. (97).

We may transform Eq. (103) into

$$\begin{aligned}\chi_0H^2Q_2=&-\langle G_0|(\alpha_1-\alpha_2)\tilde{\mathcal{H}}_1|\Psi_0\rangle+\langle\Psi_0|(\alpha_1-\alpha_2)\tilde{\mathcal{H}}_1|G_0\rangle\\&+\textstyle\sum_k[\langle G_0|\alpha_1-\alpha_2|\Psi_k\rangle\langle\Psi_k|\mathcal{H}_1|\Psi_0\rangle\\&+\langle G_0|\alpha_1-\alpha_2|\Psi_k\rangle^*\langle\Psi_k|\tilde{\mathcal{H}}_1|\Psi_0\rangle^*]\\&-\textstyle\sum_k(E_k-E_0)^{-1}[\langle G_0|\Lambda_1-\Lambda_2|\Psi_k\rangle\langle\Psi_k|\tilde{\mathcal{H}}_1|\Psi_0\rangle\\&\qquad+\langle G_0|\Lambda_1-\Lambda_2|\Psi_k\rangle^*\langle\Psi_k|\tilde{\mathcal{H}}_1|\Psi_0\rangle^*],\end{aligned} \qquad (105)$$

or

$$\begin{aligned}H^2\chi_0Q_2=&\langle G_0^*|(\alpha_1-\alpha_2)\tilde{\mathcal{H}}_1|\Psi_0^*\rangle+\langle\Psi_0|(\alpha_1-\alpha_2)\tilde{\mathcal{H}}_1|\Psi_0\rangle\\&-\textstyle\sum_k(E_k-E_0)^{-1}[\langle G_0|\Lambda_1-\Lambda_2|\Psi_k\rangle\langle\Psi_k|\tilde{\mathcal{H}}_1|\Psi_0\rangle\\&\qquad+\langle G_0^*|\Lambda_1-\Lambda_2|\Psi_k^*\rangle\langle\Psi_k^*|\tilde{\mathcal{H}}_1|\Psi_0^*\rangle].\end{aligned} \qquad (106)$$

This may be reduced to

$$Q_2=-\frac{6Rb(H_x^2+H_y^2)}{H^2(\Delta_{aa}^2+\Delta_{ab}^2)}\times\left[\Delta_{aa}\Delta_{aa}'-\frac{\beta}{\Delta E}(L_4\Delta_{aa}-L_5\Delta_{ab})\right], \qquad (107)$$

since the only Ψ_k that need to be considered in Eq. (106) are those that belong to the lowest antibonding π orbital. The numerical value is

$$H^2Q_2=-0.16010(H_x^2+H_y^2). \qquad (108)$$

The final result is obtained by taking Eqs. (99), (102), and (108) together:

$$\chi_x=\chi_y=5.18888\chi_0;\quad \chi_z=4.60725\chi_0;\quad \chi=4.99500\chi_0. \qquad (109)$$

In order to determine μ_r' we calculate χ', the first term of the right-hand side of Eq. (13) with the center of mass of the molecule as the origin of $\mathbf{r}_j$:

$$\chi'=2\chi_0(\Delta_{aa}^2+\Delta_{ab}^2)^{-1}(\Delta_{aa}J_8+\Delta_{ab}J_9), \qquad (110)$$

or $\chi'=5.06516\chi_0$. The rotational dipole is found as the difference of χ' and χ: $\mu_r'=0.07016\chi_0$.

V. CALCULATIONS OF σ WITH GIAO

In this section we discuss the calculation of the magnetic proton shielding constant σ of the hydrogen molecule. In particular we consider the evaluation of the quantity P_1 of Eq. (35), which was omitted in previous work.[6,8] Again we consider the three cases where Ψ_0 is approximated by Coulson's function,[29] by Wang's function,[30] and by Rosen's function.[31]

1. Calculations with Coulson's Function

If we substitute in Eq. (35) Coulson's function for Ψ_0, as defined in Eqs. (45) and (46), both quantities P_0 and P_1 may be expressed in terms of one-electron integrals. The calculation of P_0 yields

$$P_0=(1+S)^{-1}(I_1'+I_2'+2I_3')=1.53841. \qquad (111)$$

For a calculation of P_1 it is convenient to define the one-electron operator

$$\begin{aligned}\mathcal{H}_{0,1}'(j)=-\frac{e\hbar}{mc}\frac{1}{r_{aj}^3}\Bigg[&\mu_x\left(y_{aj}\frac{\partial}{\partial z_j}-z_{aj}\frac{\partial}{\partial y_j}\right)\\&+\mu_y\left(z_{aj}\frac{\partial}{\partial x_j}-x_{aj}\frac{\partial}{\partial z_j}\right)\\&+\mu_z\left(x_{aj}\frac{\partial}{\partial y_j}-y_{aj}\frac{\partial}{\partial x_j}\right)\Bigg].\end{aligned} \qquad (112)$$

We may then write

$$\begin{aligned}\mu H\sigma_0P_1=&-2\textstyle\sum_k(\epsilon_k-\epsilon_0)^{-1}[\langle\tilde{\phi}_k|i\mathcal{H}_{0,1}'|\tilde{\phi}_0\rangle^*\\&\times\langle\tilde{\phi}_k|\tilde{\mathcal{H}}_0'-\epsilon_0|\tilde{\phi}_0\rangle+\langle\tilde{\phi}_k|i\mathcal{H}_{0,1}'|\tilde{\phi}_0\rangle\\&\qquad\times\tilde{\phi}_k|\mathcal{H}_0'-\epsilon_0|\tilde{\phi}_0\rangle^*].\end{aligned} \qquad (113)$$

It is useful to note that

$$\begin{aligned}&\mathcal{H}_{0,1}'(j)\phi_0(j)=(2+2S)^{-\frac{1}{2}}\Omega_jh_b(j),\\&\Omega_j=(qRe\hbar/mc)r_{aj}^{-3}r_{bj}^{-1}(\mu_yx_j-\mu_xy_j),\end{aligned} \qquad (114)$$

which permits us to write Eq. (113) as

$$\mu H\sigma_0 P_1 = -\sqrt{2}(1+S)^{-\frac{1}{2}} \sum_k (\epsilon_k-\epsilon_0)^{-1}[\langle\phi_k|\Omega|h_b\rangle \times\langle\phi_k|\alpha(\mathcal{H}_0'-\epsilon_0)|g_0\rangle + \langle\phi_k|\Omega|h_b\rangle \times\langle\phi_k|\alpha(\mathcal{H}_0'-\epsilon_0)|g_0\rangle], \quad (115)$$

or

$$\mu H\sigma_0 P_1 = -\sqrt{2}(1+S)^{-\frac{1}{2}}\{2\langle g_0|\alpha\Omega|h_b\rangle - \sum_k (\epsilon_k-\epsilon_0)^{-1}[\langle g_0|\Lambda|\phi_k\rangle\langle\phi_k|\Omega|h_b\rangle + \langle g_0|\Lambda|\phi_k^*\rangle\langle\phi_k^*|\Omega|h_b\rangle]\}. \quad (116)$$

If we define an energy $\bar{\epsilon}-\epsilon_0$ by

$$(\bar{\epsilon}-\epsilon_0)^{-1}\sum_k [\langle g_0|\Lambda|\phi_k\rangle\langle\phi_k|\Omega|h_b\rangle + \langle g_0|\Lambda|\phi_k^*\rangle\langle\phi_k^*|\Omega|h_b\rangle] = \sum_k (\epsilon_k-\epsilon_0)^{-1}[\langle g_0|\Lambda|\phi_k\rangle\langle\phi_k|\Omega|h_b\rangle + \langle g_0|\Lambda|\phi_k^*\rangle\langle\phi_k^*|\Omega|h_b\rangle], \quad (117)$$

then we can transform Eq. (116) into

$$\mu H\sigma_0 P_1 = -2\sqrt{2}(1+S)^{-\frac{1}{2}}[\langle g_0|\alpha\Omega|h_b\rangle - (\bar{\epsilon}-\epsilon_0)^{-1}\langle g_0|\Lambda\Omega|h_b\rangle], \quad (118)$$

or

$$P_1 = -qR^2(1+S)^{-1} \times[(M_1'-M_3')-q(\bar{\epsilon}-\epsilon_0)^{-1}(M_5'-M_6')]. \quad (119)$$

At this point we are faced with a similar problem to that involved in evaluating Eq. (67), namely how to make a reliable estimate for $\bar{\epsilon}-\epsilon_0$. Now the situation is even worse because the terms of the infinite series of Eq. (65) all had the same sign, whereas this is not necessarily true for Eq. (117). Consequently we may argue that from a mathematical viewpoint, Eq. (117) determines a value $\bar{\epsilon}$, but that from a physical viewpoint this is not a meaningful quantity. The only available procedure to estimate $\bar{\epsilon}-\epsilon_0$ is to use a method similar to Eqs. (70)–(72), that is to make use of

$$(M_1'-M_3')-q(\bar{\epsilon}_1-\epsilon_1)^{-1}(M_5'-M_6')\approx 0, \quad \bar{\epsilon}-\epsilon_0 \approx (\bar{\epsilon}_1-\epsilon_1)+(\epsilon_1-\epsilon_0), \quad (120)$$

where $\epsilon_1-\epsilon_0$ is the excitation energy from the ground state to the lowest anti-bonding σ state and where $\bar{\epsilon}_1$ is defined by

$$(\bar{\epsilon}_1-\epsilon_1)^{-1}\sum_k [\langle g_0|\Lambda|\phi_k\rangle\langle\phi_k|\Omega|h_b\rangle + \langle g_0|\Lambda|\phi_k^*\rangle\langle\phi_k^*|\Omega|h_b\rangle] = \sum_k (\epsilon_k-\epsilon_1)^{-1}[\langle g_0|\Lambda|\phi_k\rangle\langle\phi_k|\Omega|h_b\rangle + \langle g_0|\Lambda|\phi_k^*\rangle\langle\phi_k^*|\Omega|h_b\rangle]. \quad (121)$$

We find then that $\bar{\epsilon}_1-\epsilon_1=6.366$ a.u., $\bar{\epsilon}-\epsilon_0=6.776$ a.u., and $P_1=-0.00190$.

The total value is $\sigma=1.53651\sigma_0$.

This result may be taken as a basis for a calculation of H_r', the rotational magnetic field at the position of proton a. We calculate σ', that is the first term of the second equation (13) taking the origin of each $\mathbf{r}_j$ as proton a:

$$\sigma'=(1+S)^{-1}(I_1'+2I_3'+I_{10}')\sigma_0 \quad (122)$$

or $\sigma'=1.81578\sigma_0$. H_r' is then found as the difference of σ' and σ: $H_r'=0.27927\sigma_0$.

2. Calculations with Wang's Function

If we substitute Wang's function as defined by Eq. (80) into Eq. (35), the calculation of σ is very similar to that of the preceding subsection. We obtain

$$P_0=(1+\Delta^2)^{-1}(I_1+I_2+2\Delta I_3) \quad (123)$$

or $P_0=1.48348$.

The contribution P_1 is given by

$$\mu H\sigma_0 P_1 = -(2+2\Delta^2)^{-\frac{1}{2}}\sum_k (E_k-E_0)^{-1}[\langle\Psi_k^*|(\alpha_1-\alpha_2)(\mathcal{H}_0-E_0)|G_0\rangle\langle\Psi_k|\Omega_2'|s_a(1)s_b(2)\rangle + \langle\Psi_k^*|(\alpha_1-\alpha_2)(\mathcal{H}_0-E_0)|G_0\rangle\langle\Psi_k|\Omega_1'|s_b(1)s_a(2)\rangle + \langle\Psi_k|(\alpha_1-\alpha_2)(\mathcal{H}_0-E_0)|G_0\rangle\langle\Psi_k^*|\Omega_2'|s_a(1)s_b(2)\rangle + \langle\Psi_k|(\alpha_1-\alpha_2)(\mathcal{H}_0-E_0)|G_0\rangle\langle\Psi_k^*|\Omega_1'|s_b(1)s_a(2)\rangle], \quad (124)$$

where

$$\Omega_j'=(\beta Re\hbar/mc)r_{aj}^{-3}r_{bj}^{-1}(\mu_y x_j-\mu_x y_j). \quad (125)$$

Equation (124) may be transformed into

$$\mu H\sigma_0 P_1 = -\sqrt{2}(1+\Delta^2)^{-\frac{1}{2}}[\langle G_0|\alpha_1-\alpha_2|\Omega_2's_a(1)s_b(2) + \Omega_1's_b(1)s_a(2)\rangle - \sum_k (E_k-E_0)^{-1} \times\langle G_0|\Lambda_1-\Lambda_2|\Psi_k\rangle\langle\Psi_k|\Omega_2's_a(1)s_b(2) + \Omega_1's_b(1)s_a(2)\rangle], \quad (126)$$

which may be reduced to

$$P_1=\frac{\beta R^2}{1+\Delta^2}\left[(M_3-\Delta M_1)-\frac{\beta(M_6-\Delta M_5)}{\bar{E}-E_0}\right] \quad (127)$$

if $\bar{E}-E_0$ is defined by

$$(\bar{E}-E_0)^{-1}\sum_k \langle G_0|\Lambda_1-\Lambda_2|\Psi_k\rangle \times\langle\Psi_k|\Omega_2's_a(1)s_b(2)+\Omega_1's_b(1)s_a(2)\rangle = \sum_k (E_k-E_0)^{-1}\langle G_0|\Lambda_1-\Lambda_2|\Psi_k\rangle \times\langle\Psi_k|\Omega_2's_a(1)s_b(2)+\Omega_1's_b(1)s_a(2)\rangle. \quad (128)$$

If we make use of the relation

$$(M_3-\Delta M_1)-\beta(\bar{E}_1-E_1)^{-1}(M_6-\Delta M_5)\approx 0, \quad (129)$$

where $\bar{E}_1$ is defined by

$$(\bar{E}_1-E_1)^{-1}\sum_k \langle G_0|\Lambda_1-\Lambda_2|\Psi_k\rangle \times\langle\Psi_k|\Omega_2's_a(1)s_b(2)+\Omega_1's_b(1)s_a(2) = \sum_k (E_k-E_1)^{-1}\langle G_0|\Lambda_1-\Lambda_2|\Psi_k\rangle \times\langle\Psi_k|\Omega_2's_a(1)s_b(2)+\Omega_1's_b(1)s_a(2)\rangle, \quad (130)$$

for a calculation of $\bar{E}_1 - E_1$, the result is $\bar{E}_1 - E_1 = -4.482$ a.u. This is a peculiar value from a physical point of view, but we argued already that no actual physical meaning may be attributed to energy values that are defined by a series as in Eq. (130) unless the terms of the series all have the same sign, which is clearly not the case here. Apparently the series on the left-hand side of Eq. (130) contains terms that have the same sign as the sum of the series and also terms that have opposite sign. If every term is divided by the corresponding energy, as in the right-hand side of Eq. (130), it is possible that the values of the former terms are decreased with respect to the latter and if this effect is large enough $\bar{E}_1 - E_1$ may become negative. From this reasoning it should follow that this effect diminishes if E_1 is replaced by E_0. We therefore suggest taking $\bar{E} - E_0 = (\bar{E}_1 - E_1) - (E_1 - E_0) = -4.892$ a.u. This supplies a very crude estimate for $\bar{E} - E_0$, but since both $M_3 - \Delta M_1$ and $M_6 - \Delta M_5$ are very small we need not worry about the approximations in deriving the value of $\bar{E} - E_0$. Substitution into Eq. (129) gives $P_1 = 0.00132$ and $\sigma = 1.48480\sigma_0$.

In order to determine H_r' we first evaluate σ':

$$\sigma' = (1+\Delta^2)^{-1}(I_1 + 2\Delta I_3 + I_{10}), \tag{131}$$

which yields $\sigma' = 1.79151\sigma_0$. Consequently H_r' is found as the difference of σ' and σ: $H_r' = 0.30671$.

3. Calculations with Rosen's Function

In calculating σ from Eq. (35) by substituting Rosen's function, as defined by Eq. (96), we encounter more difficulties than in Subsections 1 and 2 because various terms that could be omitted there are now different from zero.

In calculating P_0, the first two terms may be taken together. If we call their sum P_0', then

$$P_0' = (\Delta_{aa}^2 + \Delta_{ab}^2)^{-1} \times \{\Delta_{aa}(K_1 + K_2) + 2\Delta_{ab}K_3 - 2bRK_4\} \tag{132}$$

or $P_0' = 1.48371$.

In order to calculate the infinite series occurring in P_0, let us observe that

$$\begin{aligned}\mathfrak{H}_{1,0}|\tilde{\Psi}_0\rangle = {} & (2\Delta_{aa}^2 + 2\Delta_{ab}^2)^{-\frac{1}{2}}(e\hbar/2mc)b[(H_y x_1 - H_x y_1) \\ & \times\{s_a(1)u_b(2) - s_b(1)u_a(2)\} - (H_y x_2 - H_x y_2) \\ & \times\{u_a(1)s_b(2) - u_b(1)s_a(2)\}],\end{aligned} \tag{133}$$

and also that

$$\begin{aligned}\mathfrak{H}_{0,1}|\Psi_0\rangle = {} & (2\Delta_{aa}^2 + 2\Delta_{ab}^2)^{-\frac{1}{2}}(e\hbar/mc)[br_{a1}^{-3}(\mu_y x_1 - \mu_x y_1)\{s_a(1)u_b(2) - s_b(1)u_a(2)\} - br_{a2}^{-3}(\mu_y x_2 - \mu_x y_2) \\ & \times\{u_a(1)s_b(2) - u_b(1)s_a(2)\} + \beta R r_{a2}^{-3} r_{b2}^{-1}(\mu_y x_2 - \mu_x y_2)u_a(1)u_b(2) \\ & + \beta R r_{a1}^{-3} r_{b1}^{-1}(\mu_y x_1 - \mu_x y_1)u_b(1)u_a(2)].\end{aligned} \tag{134}$$

Consequently the contribution P_0'' of the infinite series to P_0 becomes

$$\begin{aligned}P_0'' = {} & -(\Delta_{aa}^2 + \Delta_{ab}^2)^{-1}(\Delta E)^{-1} \\ & \times[b^2\{\Delta_{aa}(L_1 + L_3) - 2\Delta_{ab}L_2\} \\ & - b\beta R\{\Delta_{aa}N_6 - \Delta_{ab}N_8\}],\end{aligned} \tag{135}$$

where the value 0.504 may be substituted for ΔE (compare Sec. IV. 3). It follows that $P_0'' = -0.00272$ and that $P_0 = 1.48099$.

In order to calculate P_1 we observe that

$$\begin{aligned}\mu H\sigma_0 P_1 = {} & -\textstyle\sum_k (E_k - E_0)^{-1}\{\langle\Psi_k|i\mathfrak{H}_{0,1}|\Psi_0\rangle^* \\ & \times\langle\Psi_k|i(\alpha_1 - \alpha_2)(\mathfrak{H}_0 - E_0)|G_0\rangle + \langle\Psi_k|i\mathfrak{H}_{0,1}|\Psi_0\rangle \\ & \times\langle\Psi_k|i(\alpha_1 - \alpha_2)(\mathfrak{H}_0 - E_0)|G_0\rangle^*]\end{aligned} \tag{136}$$

where G_0 is given by Eq. (83). If we substitute Eq. (134), it seems profitable to write P_1 as a sum of two terms, P_1' and P_1'':

$$\begin{aligned}P_1' = {} & -bR(\Delta_{aa}^2 + \Delta_{ab}^2)^{-1} \\ & \times[\{\Delta_{aa}(N_1 + N_2) - \Delta_{ab}(N_3 + N_4)\} \\ & -\{\Delta_{aa}(N_5 + N_6) - \Delta_{ab}(N_7 + N_8)\}(E' - E_0)^{-1}], \\ P_1'' = {} & \beta R^2(\Delta_{aa}^2 + \Delta_{ab}^2)^{-1}[(\Delta_{aa}M_8 - \Delta_{ab}M_7) \\ & -(\Delta_{aa}M_{10} - \Delta_{ab}M_9)(E'' - E_0)^{-1}],\end{aligned} \tag{137}$$

where E' and E'' are average excitation energies pertaining to P_1' and P_1'', respectively. In order to estimate the values of E' and E'' we make use of the method proposed in Sec. IV.1: First we notice that

$$\begin{aligned}& \{\Delta_{aa}(N_1 + N_2) - \Delta_{ab}(N_3 + N_4)\} \\ & \quad -\{\Delta_{aa}(N_5 + N_6) - \Delta_{ab}(N_7 + N_8)\}(E_1' - E_1)^{-1} \approx 0, \\ & (\Delta_{aa}M_8 - \Delta_{ab}M_7) - (\Delta_{aa}M_{10} - \Delta_{ab}M_9) \\ & \quad \times(E_1'' - E_1)^{-1} \approx 0,\end{aligned} \tag{138}$$

which yields $E_1' - E_1 = 3.5532$ a.u. and $E_1'' - E_1 = 7.3679$ a.u. It is assumed then that E' and E'' may be obtained from

$$\begin{aligned}E' - E_0 &\approx (E_1' - E_1) + (E_1 - E_0), \\ E'' - E_0 &\approx (E_1'' - E_1) + (E_1 - E_0),\end{aligned} \tag{139}$$

so that $E' - E_0 = 3.963$ a.u. and $E'' - E_0 = 7.778$ a.u. It follows that $P_1' = -0.00209$, $P_1'' = -0.00093$ and $\sigma = 1.47797\sigma_0$.

For a calculation of H_r' we first determine σ':

$$\sigma' = (\Delta_{aa}^2 + \Delta_{ab}^2)^{-1} \times(\Delta_{aa}K_1 + \Delta_{aa}K_5 + 2\Delta_{ab}K_3). \tag{140}$$

It follows that $\sigma' = 1.80908\sigma_0$ and also that $H_r' = \sigma' - \sigma = 0.33111$.

VI. DISCUSSION

In Tables III and IV are collected various theoretical results for χ, μ_r', σ, and H_r' together with the experi-

TABLE III. Theoretical values of magnetic susceptibilities and rotational magnetic moments.

χ_x	χ_z	χ	μ_r'	Wave function
5.1953	4.4218	4.9375	0.1481	Coulson[a]
5.2775	4.5707	5.0419	0.2576	Wang[a]
5.1889	4.6072	4.9950	0.0702	Rosen[a]
5.21	4.42	4.95	0.18	Coulson[b]
5.48	4.61	5.19	0.21	Wang[b]
...	...	5.1348	0.1902	James-Coolidge[c]
...	...	5.30	0.64	Wang[d]
...	...	...	0.085	Coulson[e]
...	...	...	0.096	Nordsieck[f]
...	...	5.00	0.1068	Experimental

[a] This paper, GIAO method.

[b] Obtained by means of a variational procedure where the trial function contains terms proportional to the magnetic field. See Tillieu and Guy, references 14 and 15.

[c] A very complete variational calculation with a James-Coolidge type wave function, expanded in elliptical coordinates and containing the magnetic field. See Ishiguro and Koide, reference 12.

[d] The original calculation of Van Vleck and Miss Frank, reference 18, where the center of the molecule is taken as the origin of the vector potential.

[e] See reference 27.

[f] See reference 28.

mental values as far as they are known (all expressed in terms of χ_0 or σ_0).

If an attempt is made to classify the merits of the various methods by comparing their results with the experimental data, one is hampered by the lack of accuracy in the experimental values, for example the reported χ values vary between $4.97\chi_0$ and $5.05\chi_0$. The experimental value of μ_r' seems to be known with similar accuracy. An experimental result of σ is not available, but H_r' is known to within a few percent.

Considering Table III first, we are tempted to believe that the most reliable value of χ is supplied by the calculation of Ishiguro and Koide[12] because a very accurate wave function was used, but the numerical results do not seem to justify this idea. This calculation has also a more essential disadvantage, namely that the method cannot easily be extended to molecules larger than hydrogen. A convenient method of calculating χ is the one proposed by Tillieu and Guy.[14,15] The only objection one might have against their calculation is that it is hard to estimate which errors are introduced by employing the variational trial function proportional to **H**. The accuracy of the theoretical results seem to be satisfactory. It seems that the best agreement with the experimental value is obtained by our present calculation from Wang's and Rosen's functions, but this is probably fortuitous; considering the approximations in the wave functions we would not expect the theoretical results to be more accurate than 1% or 2%. Also, the result for μ_r' obtained from Wang's function differs considerably from the experimental value.

The results for σ and H_r' may be discussed in a similar fashion. The most reliable value of σ is probably the one derived by Ramsay from a semi-empirical argument. Our results agree satisfactorily with this value, also the difference between the value of Ishiguro and Koide and ours is not large.

If we compare the GIAO method for calculating σ with Eq. (13) and also with Rebane's variational principle, it is easy to see what the advantages of the GIAO method are; it constitutes a convenient simple approximation to Rebane's Eq. (23). For spherically symmetric atomic orbitals we have an exact solution of Eq. (23), and if the atomic orbitals contain angular terms, we have at least an approximate solution of Eq. (13). In the latter case it might be possible also to obtain an exact solution of Eq. (23) but the resulting gauge factors would be much more complicated and it would be more difficult to apply the method. The present GIAO method thus forms a compromise between simple gauge factors and as accurate as possible a solution of Eq. (23). A disadvantage is that now we have to consider the terms Q_1 and Q_2, but it seems that these terms are smaller than the infinite series in Eq. (13) and that it is also easier to evaluate them.

From an analogous physical argument, in the case of angular dependence of the atomic orbitals, the GIAO method supplies us with a satisfactory but not the best possible choice of gauge.[33] Instead of an electron in a 1s orbital, we consider a harmonic oscillator. Clearly the best possible choice of origin of the vector potential is the center of the 1s orbital in the first case and the equilibrium position of the harmonic oscillator in the second case. If we add a homogeneous electric field to the potential function we obtain a new harmonic oscillator with a displaced equilibrium position; clearly this new equilibrium position is to be taken as the origin of the vector potential now. In a similar fashion one may argue that for an electron occupying an asymmetric atomic orbital the origin of the vector potential should not be taken as the nucleus belonging to the atomic orbital but slightly toward the center of mass of the electronic charge cloud. However, our gauge factors still are a good approximation to the best possible gauge factors and as long as we calculate all infinite series in Eq. (33) we should still get the correct result.

The GIAO method is less satisfactory for calculations of σ than for calculations of χ, because in general the

TABLE IV. Theoretical values of σ and H_r'.

σ	H_r'	Wave function
1.5365	0.2793	Coulson[a]
1.4848	0.3067	Wang[a]
1.4780	0.3311	Rosen[a]
1.510	0.315	Nordsieck[b]
...	0.299	Coulson[c]
...	0.276	Wang[c]
...	0.293	Nordsieck[c]
1.5526	0.328	James-Coolidge[d]
...	0.315	Experimental

[a] This paper, GIAO method.

[b] Ramsay's semi-empirical determination of σ, see references 2 and 20.

[c] Das and Bersohn's calculation, analogous with Tillieu and Guy's method of computing χ, see reference 16.

[d] See reference 12.

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[33] The following argument was supplied by D. Polder (private communication).

term that we called $\mathcal{H}_{0,1}|\Psi_0\rangle$ in Eq. (34) is not zero. One might attempt to improve the theory by adding gauge factors containing μ to the atomic orbitals, but we have been unable to find a simple gauge factor that would make $\tilde{\mathcal{H}}_{0,1}|\tilde{\Psi}_0\rangle$ at least approximately zero. Again, this should not affect the results as long as we calculate all infinite series in Eq. (35).

The present method would be relatively simple if it would be permissible to neglect Q_1, Q_2, and P_1; a procedure that has been followed in previous work.[6,7,34] The results obtained in this fashion for the molecules H_2, N_2, and CH_4 seem to be satisfactory and also from the present calculations it seems that the contributions of Q_1, Q_2, and P_1 to χ and σ are small for the hydrogen molecule, but it still remains to be investigated for some different molecules how large these contributions are before one may make any predictions as to whether they may be neglected. It is suspected that in a previous calculation on the proton magnetic resonance shift due to hydrogen bonding in ammonia,[35] the omission of P_1 may have had serious consequences and may be responsible for some unrealistic results that followed from the theory.

The most unsatisfactory part of the present calculation is connected with the estimates of the various average excitation energies in Secs. IV and V. The least we can say in favor of the procedure that was followed in obtaining these estimates is that it seems to give reasonable results, that it has some logical foundation, and that it seems more reliable than any alternative procedure we could think of.

Let us finally set out to answer the essential question one may ask: Given an exact ground-state wave function of a molecule, is it possible to obtain the exact values of χ and σ with the GIAO method? The answer would be yes if we knew the exact values of the average excitation energies to be substituted, but since this is not the case we cannot answer in the affirmative. However, it seems that the deviations that are introduced by this uncertainty are of the same order of magnitude or smaller than the approximations in the molecular wave functions that are known at present.

ACKNOWLEDGMENTS

This paper would not have been written but for some very essential suggestions by Professor J. H. Van Vleck who I also wish to thank for his encouragement and constructive criticism throughout the calculations. Helpful discussions with Dr. T. Arai, Professor T. H. Berlin, Professor R. G. Parr, and Professor D. Polder are gratefully acknowledged; in particular I thank Professor Parr for bringing Rebane's work to my attention.

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[34] H. F. Hameka, Physica **25**, 626 (1959).

[35] H. F. Hameka, Nuovo cimento **11**, 382 (1959).