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Magnetic Properties of the Hydrogen Molecules

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The diamagnetic susceptibility χ, the rotational magnetic moment μ_r, the magnetic shielding constant σ, and the spin-rotational magnetic interaction constant H_r of the hydrogen molecule are calculated theoretically. The energy of the rotating molecule, under an external magnetic field, is calculated by means of the variational method using 7+2 term wave function. By expanding the energy in powers of the appropriate parameters, χ, μ_r, σ, and H_r are determined and the relations between these quantities are obtained. Comparison with Ramsey's experiments is also made.

1. INTRODUCTION

As a result of the increasing accuracy of microwave and molecular beam measurements, it is found that the apparent magnetic moment of a nucleus has different values when it is contained in different molecules. This phenomenon, called "chemical shift," arises from the fact that the surrounding electric charges create a magnetic field at the position of the nucleus in addition to the external one. Based on Wick's theory,[1] Ramsey has treated this problem in a series of papers.[2]

It seems to be important to study the chemical shift for the hydrogen molecule, since accurate experimental data are available for this molecule, and its nuclear magnetic moment is used as the standard for the measurement of magnetic field strength. The calculations were made by Ramsey[2] and by Hylleraas and Skavlem.[3] In all these calculations, however, the perturbation method was adopted, and the difficulty lies chiefly in the fact that the second-order terms cannot be evaluated accurately.

On the other hand, one of the present authors has succeeded in calculating the polarizability of the hydrogen molecule and in overcoming the difficulty by using the variational method.[4] The aim of the present paper is to show that the same method is also applicable in principle to the calculation of the magnetic properties of this molecule. We have calculated the chemical shift σ (magnetic shielding constant) as well as the other magnetic quantities, i.e., the diamagnetic susceptibility χ, the rotational magnetic moment μ_r, and the spin-rotational magnetic interaction constant H_r, and found that the well-known relations between these quantities can be formulated quite fundamentally.

For the purpose of examining the usefulness of this method, a preliminary calculation has been made and rather good results have been obtained.

2. HAMILTONIAN

The Hamiltonian of a hydrogen molecule placed in the magnetic field $\mathbf{H}$ is given by

$$\mathcal{H}_{\text{tot}}=\frac{1}{2M}\sum_{a,b}\left(\mathbf{P}_k-\frac{e}{c}\mathbf{A}_k\right)^2+\frac{1}{2m}\sum_{j=1}^{2}\left(\mathbf{p}_j+\frac{e}{c}\mathbf{A}_j\right)^2 +V-\mu'\mathbf{H}(\boldsymbol{\sigma}_a+\boldsymbol{\sigma}_b)+f(\mu'\boldsymbol{\sigma}_a,\mu'\boldsymbol{\sigma}_b), \quad (1)$$

where we neglect the electronic spin which has no influence on our final result within the accuracy of our approximations. $\boldsymbol{\sigma}_a$ and $\boldsymbol{\sigma}_b$ denote the Pauli matrices of the two protons a and b, respectively, and μ' is the magnitude of the magnetic moment of the proton. We may adopt the representation in which the total nuclear spin of the molecule can be specified by a set of quantum numbers (I,m_I), and take only the diagonal elements. Then the x and y components of the $\boldsymbol{\sigma}$'s may be omitted. For the states with $m_I=1, 0, -1$, the expectation values of σ_{az} and σ_{bz} are $\langle\sigma_{az}\rangle=\langle\sigma_{bz}\rangle=1, 0, -1$, respectively. Therefore,

$$\mu'\sigma_{az}=\mu'\sigma_{bz}\equiv\mu. \quad (2)$$

The first term of $\mathcal{H}_{\text{tot}}$ represents the kinetic energy of the two-proton system and, neglecting the term for

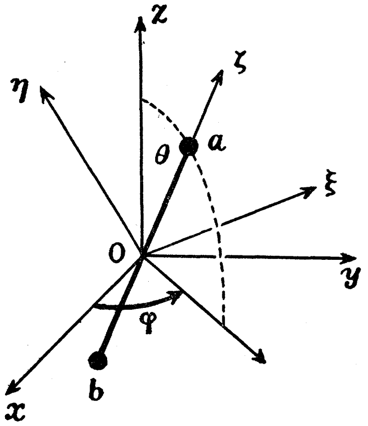

FIG. 1. Relation between the fixed and moving coordinates. a and b denote the nuclei. The ξ axis is taken to lie in the xy plane.

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[1] G. C. Wick, Phys. Rev. 73, 51 (1948); Z. Physik 85, 25 (1933).

[2] N. F. Ramsey, Phys. Rev. 77, 567 (1950); 78, 699 (1950); 83, 540 (1951); 85, 60 (1952); 243 (1952).

[3] E. Hylleraas and S. Skavlem, Phys. Rev. 79, 117 (1950).

[4] Ishiguro, Arai, Mizushima, and Kotani, Proc. Phys. Soc. (London) A65, 178 (1952).

the motion of the center of gravity, we can write in terms of polar coordinates:

$$\mathcal{H}_N=-\frac{\hbar^2}{MR^2}\left\{\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right)+\cot\theta\frac{\partial}{\partial\theta}+\frac{\partial^2}{\partial\theta^2}+\csc^2\theta\frac{\partial^2}{\partial\varphi^2}\right\}$$
$$-\frac{e\hbar}{2MC}H\left(-i\frac{\partial}{\partial\varphi}\right)-\frac{e\hbar}{2MC}\frac{2}{R^3}2\mu\left(-i\frac{\partial}{\partial\varphi}\right),\quad(3)$$

where R denotes the internuclear distance of this molecule. In this derivation, the z direction is chosen to be parallel to the external magnetic field, the vector potentials $\mathbf{A}_a$ and $\mathbf{A}_b$ are assumed to be expressed in terms of the coordinates with their origin at the center of the gravity as

$$A_{aX}=-\tfrac{1}{2}HY_a-\frac{2\mu}{R^3}Y_a,\qquad A_{bX}=-\tfrac{1}{2}HY_b-\frac{2\mu}{R^3}Y_b,$$
$$A_{aY}=\tfrac{1}{2}HX_a+\frac{2\mu}{R^3}X_a,\quad\text{and}\quad A_{bY}=\tfrac{1}{2}HX_b+\frac{2\mu}{R^3}X_b,\quad(4)$$
$$A_{aZ}=0,\qquad A_{bZ}=0,$$

and the small terms proportional to the square of A's are neglected. The last terms of Eqs. (4) are the components of the vector potential due to the presence of the proton magnetic moment.

The second term of $\mathcal{H}_{\text{tot}}$ is the kinetic energy of the two electrons and, together with the third term V, the electrostatic potential energy of the four particles, can be expressed most readily in terms of the ξ, η, ζ reference system which has the ζ axis parallel to the axis of molecule and travels with the nuclei (see Fig. 1). We may suppose the ξ axis to lie in the xy plane without loss of generality. Then the moving and fixed systems are connected by

$$\begin{aligned}\xi&=-x\sin\varphi+y\cos\varphi,\\ \eta&=-x\cos\theta\cos\varphi-y\cos\theta\sin\varphi+z\sin\theta,\quad(5)\\ \zeta&=x\sin\theta\cos\varphi+y\sin\theta\sin\varphi+z\cos\theta.\end{aligned}$$

Using these coordinates and adopting as the vector potentials A_1, A_2, the following expressions:

$$\begin{aligned}A_{jx}&=-(1/2)Hy_j-(\mu/r_{aj}^3)y_{aj}-(\mu/r_{bj}^3)y_{bj}\\ A_{jy}&=(1/2)Hx_j+(\mu/r_{aj}^3)x_{aj}+(\mu/r_{bj}^3)x_{bj}\quad(6)\\ A_{jz}&=0,\end{aligned}$$

where

$$x_{aj}=x_j-X_a,\ \text{etc.},\quad(6a)$$

we obtain

$$\mathcal{H}_e=\frac{1}{2m}\sum_i\left(\mathbf{p}_j+\frac{e}{c}\mathbf{A}_j\right)^2+V\quad(7)$$
$$=\mathcal{H}^{(0)}+H\mathcal{H}^{(1)}+\mu\mathcal{H}^{(2)}+H^2\mathcal{H}^{(4)}+H\mu\mathcal{H}^{(5)}+\cdots,$$

where

$$\mathcal{H}^{(0)}=-\frac{\hbar^2}{2m}\sum_i\left(\frac{\partial^2}{\partial\xi_j^2}+\frac{\partial^2}{\partial\eta_j^2}+\frac{\partial^2}{\partial\zeta_j^2}\right)+V,\quad(8a)$$

$$\mathcal{H}^{(1)}=\frac{e\hbar}{2mci}\sum_i\left\{\sin\theta\left(\zeta_j\frac{\partial}{\partial\xi_j}-\xi_j\frac{\partial}{\partial\zeta_j}\right)\right.$$
$$\left.+\cos\theta\left(\xi_j\frac{\partial}{\partial\eta_j}-\eta_j\frac{\partial}{\partial\xi_j}\right)\right\},\quad(8b)$$

$$\mathcal{H}^{(2)}=\frac{e\hbar}{2mci}\sum_i\left[\left\{2\sin\theta\left(\zeta_j\frac{\partial}{\partial\xi_j}-\xi_j\frac{\partial}{\partial\zeta_j}\right)\right.\right.$$
$$\left.+2\cos\theta\left(\xi_j\frac{\partial}{\partial\eta_j}-\eta_j\frac{\partial}{\partial\xi_j}\right)\right\}\left(\frac{1}{r_{aj}^3}+\frac{1}{r_{bj}^3}\right)$$
$$\left.-R\sin\theta\left(\frac{1}{r_{aj}^3}-\frac{1}{r_{bj}^3}\right)\frac{\partial}{\partial\xi_j}\right],\quad(8c)$$

$$\mathcal{H}^{(4)}=\frac{e^2}{8mc^2}\sum_i\{\xi_j^2+(\eta_j\cos\theta-\zeta_j\sin\theta)^2\},\quad(8d)$$

$$\mathcal{H}^{(5)}=\frac{e^2}{2mc^2}\sum_i\left[\{\xi_j^2+(\eta_j\cos\theta-\zeta_j\sin\theta)^2\}\left(\frac{1}{r_{aj}^3}+\frac{1}{r_{bj}^3}\right)\right.$$
$$\left.+\frac{R}{2}\sin\theta(\zeta_j\sin\theta-\eta_j\cos\theta)\left(\frac{1}{r_{aj}^3}-\frac{1}{r_{bj}^3}\right)\right].\quad(8e)$$

In terms of the same coordinate system, we may also take the wave function as the product of two parts:

$$\psi=\Phi(R,\theta,\varphi)\Psi(\xi_1,\eta_1,\zeta_1,\xi_2,\eta_2,\zeta_2;R,\theta).\quad(9)$$

Then, since ξ, η, ζ depend upon θ and φ through the relations (5), the differential operators appearing in the Eq. (3) have to be transformed as

$$\frac{\partial}{\partial\theta}\to\frac{\partial}{\partial\theta}+\sum_i\left(\frac{\partial\xi_j}{\partial\theta}\frac{\partial}{\partial\xi_j}+\frac{\partial\eta_j}{\partial\theta}\frac{\partial}{\partial\eta_j}+\frac{\partial\zeta_j}{\partial\theta}\frac{\partial}{\partial\zeta_j}\right)$$
$$=\frac{\partial}{\partial\theta}-\sum_i\left(\eta_j\frac{\partial}{\partial\zeta_j}-\zeta_j\frac{\partial}{\partial\eta_j}\right),\quad(10a)$$

$$\frac{\partial}{\partial\varphi}\to\frac{\partial}{\partial\varphi}+\sum_i\left(\frac{\partial\xi_j}{\partial\varphi}\frac{\partial}{\partial\xi_j}+\frac{\partial\eta_j}{\partial\varphi}\frac{\partial}{\partial\eta_j}+\frac{\partial\zeta_j}{\partial\varphi}\frac{\partial}{\partial\zeta_j}\right)$$
$$=\frac{\partial}{\partial\varphi}-\sum_i\left\{\sin\theta\left(\zeta_j\frac{\partial}{\partial\xi_j}-\xi_j\frac{\partial}{\partial\zeta_j}\right)\right.$$
$$\left.+\cos\theta\left(\xi_j\frac{\partial}{\partial\eta_j}-\eta_j\frac{\partial}{\partial\xi_j}\right)\right\}.\quad(10b)$$

The physical significance of this transformation is most easily seen if, for instance, we consider the meaning of the operator $\partial/\partial\varphi$. As is well known, $(-i\partial/\partial\varphi)_{R,\theta,x_1,\cdots z_2}$ represents the z component of the angular momentum of the free rotator composed of two protons. On the other hand, since the new $\partial/\partial\varphi$ means differentiation with R, θ, ξ_1, $\cdots$, and ζ_2 kept constant, the new $-i\partial/\partial\varphi$ is the operator which represents the angular momentum of the two-proton system carrying the two electrons with it. Therefore, the difference between the new and the old $-i\partial/\partial\varphi$ should be equal to the z component of the angular momentum of the two electrons relative to the nuclear system. Equations (10b) express this relation. A similar situation is valid for $\partial/\partial\theta$ *mutatis mutandis.*

Substituting Eqs. (10a) and (10b) into (3) and considering Eq. (1) and $-\mu' H(\sigma_{az}+\sigma_{bz})=-2\mu H$, we finally obtain the total Hamiltonian:

$$\begin{aligned}\mathcal{H}_{\mathrm{tot}}=-\frac{\hbar^2}{MR^2}\bigg\{&\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right)+\cot\theta\left(\frac{\partial}{\partial\theta}-iL_\xi\right)\\&+\left(\frac{\partial}{\partial\theta}-iL_\xi\right)^2+\csc^2\theta\left(\frac{\partial}{\partial\varphi}-iL_z\right)^2\bigg\}\\&+\frac{ie\hbar}{2Mc}H\left(\frac{\partial}{\partial\varphi}-iL_z\right)+\frac{ie\hbar}{2Mc}\frac{4\mu}{R^3}\left(\frac{\partial}{\partial\varphi}-iL_z\right)\\&-2\mu H+\mathcal{H}^{(0)}+H\mathcal{H}^{(1)}+\mu\mathcal{H}^{(2)}\\&+H^2\mathcal{H}^{(4)}+H\mu\mathcal{H}^{(5)},\end{aligned}\tag{11}$$

where use has been made of the following abbreviations:

$$\begin{aligned}L_\xi&=l_\xi^1+l_\xi^2=-i\sum_j\left(\eta_j\frac{\partial}{\partial\zeta_j}-\zeta_j\frac{\partial}{\partial\eta_j}\right),\\L_\eta&=l_\eta^1+l_\eta^2=-i\sum_j\left(\zeta_j\frac{\partial}{\partial\xi_j}-\xi_j\frac{\partial}{\partial\zeta_j}\right),\\L_\zeta&=l_\zeta^1+l_\zeta^2=-i\sum_j\left(\xi_j\frac{\partial}{\partial\eta_j}-\eta_j\frac{\partial}{\partial\xi_j}\right),\\L_z&=L_\eta\sin\theta+L_\zeta\cos\theta.\end{aligned}\tag{12}$$

3. PROCEDURE

The Hamiltonian given by (11) seems to be unmanageable. We will, therefore, treat it in the following manner:

(i) First we determine the internal wave function $\Psi_0(\xi_1,\eta_1,\zeta_1,\xi_2,\eta_2,\zeta_2;R)$ and its lowest eigenvalue E_0 in the case $H=0$ and $\mu=0$, by solving the equation

$$\mathcal{H}^{(0)}\Psi_0=E_0\Psi_0.\tag{13}$$

As is well known, this calculation has been made by many investigators, including one of the present authors.[5] We can, therefore, utilize the results already obtained.

(ii) Using the above Ψ_0, one should be able to determine the vibration-rotation wave function Φ_0 in the case $H=\mu=0$. A rigorous treatment might be difficult, of course. However, it has been shown that to a good approximation Φ_0 can be written as $f(R)\cdot\chi(\theta,\varphi)$, and the rotational eigenfunction $\chi(\theta,\varphi)$ can be expressed by the spherical harmonic $Y_J^{m_J}$ which has the eigenvalue J for the angular momentum and m_J for its z component.

(iii) Finally, introducing H and μ, we calculate the internal wave function $\Psi(\xi_1,\eta_1,\zeta_1,\xi_2,\eta_2,\zeta_2;R,\theta)$ by means of the variation method. In this step, χ is assumed to be not considerably different from the one obtained in (ii). Then we can safely replace the operator $-i\partial/\partial\varphi$ (z component of the angular momentum of nuclear system) with its eigenvalue m_J. From the first term of (11) we pick out the term proportional to m_J and consider it as a perturbation in addition to the terms $H\mathcal{H}^{(1)}$, $\mu\mathcal{H}^{(2)}$, $H^2\mathcal{H}^{(4)}$, and $H\mu\mathcal{H}^{(5)}$. Then,

$$\begin{aligned}m_J\mathcal{H}^{(3)}=-\frac{2\hbar^2m_J}{iMR^2\sin^2\theta}\sum_{j=1}^{2}\bigg\{&\sin\theta\left(\zeta_j\frac{\partial}{\partial\xi_j}-\xi_j\frac{\partial}{\partial\zeta_j}\right)\\&+\cos\theta\left(\xi_j\frac{\partial}{\partial\eta_j}-\eta_j\frac{\partial}{\partial\xi_j}\right)\bigg\}.\end{aligned}\tag{14}$$

The remaining electronic terms are all neglected because they contribute nothing to the quantities in which we are interested. Thus the Hamiltonian in question becomes

$$\begin{aligned}\mathcal{H}=\mathcal{H}^{(0)}+H\mathcal{H}^{(1)}+\mu\mathcal{H}^{(2)}&\\+m_J\mathcal{H}^{(3)}+H^2\mathcal{H}^{(4)}+H\mu\mathcal{H}^{(5)}.&\end{aligned}\tag{15}$$

4. APPLICATION OF THE VARIATION METHOD

The electronic wave function of the ground state of the free hydrogen molecule, which is the solution of Eq. (13), has the symmetry ${}^1\Sigma_g{}^+$. When the perturbations are introduced, the electron distribution is deformed and the wave function loses its symmetry. If the perturbations are sufficiently small, the wave function may be expressed as

$$\begin{aligned}\Psi=\textstyle\sum_i a_i\theta_i+H\sum_k b_k\varphi_k&\\+\mu\textstyle\sum_l c_l\psi_l+m_J\sum_n d_n\chi_n+\cdots,&\end{aligned}\tag{16}$$

where the θ's have the symmetry ${}^1\Sigma_g{}^+$, and φ_k, ψ_l, and χ_n have the other symmetries. Normalization of Ψ gives

$$\begin{aligned}1=\sum_{i,j}a_i{}^*a_jS_{ij}&+H^2\sum_{k,k'}b_k{}^*b_{k'}S_{kk'}\\&+H\mu\sum_{k,l}(b_k{}^*c_lS_{kl}+c_l{}^*b_kS_{lk})\\&+Hm_J\sum_{k,n}(b_k{}^*d_nS_{kn}+d_n{}^*b_kS_{nk})\\&+\mu m_J\sum_{l,n}(c_l{}^*d_nS_{ln}+d_n{}^*c_lS_{nl})+\cdots,\end{aligned}\tag{17}$$

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[5] E. Ishiguro, J. Phys. Soc. Japan 3, 129 (1948).

where $S_{ij}=\int\theta_i^*\theta_j d\tau$, $S_{kl}=\int\varphi_k^*\psi_l d\tau$, etc., and S_{ik}, S_{il}, and S_{in} vanish because of symmetry. The mean value of the Hamiltonian $\mathcal{H}$ with respect to the function Ψ is given by

$$\begin{aligned}E=&\sum a_i^*a_j\mathcal{H}_{ij}{}^{(0)}+H^2\{\sum a_i^*a_j\mathcal{H}_{ij}{}^{(4)}+\sum b_k^*b_{k'}\mathcal{H}_{kk'}{}^{(0)}\\&\quad+\sum(a_i^*b_k\mathcal{H}_{ik}{}^{(1)}+\text{c.c.})\}\\&+H\mu\{\sum(a_i^*c_l\mathcal{H}_{il}{}^{(1)}+\text{c.c.})+\sum(a_i^*b_k\mathcal{H}_{ik}{}^{(2)}+\text{c.c.})\\&\quad+\sum a_i^*a_j\mathcal{H}_{ij}{}^{(5)}+\sum(b_k^*c_l\mathcal{H}_{kl}{}^{(0)}+\text{c.c.})\}\\&+Hm_J\{\sum(a_i^*d_n\mathcal{H}_{in}{}^{(1)}+\text{c.c.})+\sum(a_i^*b_k\mathcal{H}_{ik}{}^{(3)}\\&\quad+\text{c.c.})+\sum(b_k^*d_n\mathcal{H}_{kn}{}^{(0)}+\text{c.c.})\}\\&+\mu m_J\{\sum(a_i^*d_n\mathcal{H}_{in}{}^{(2)}+\text{c.c.})+\sum(a_i^*c_l\mathcal{H}_{il}{}^{(3)}+\text{c.c.})\\&\qquad+\sum(c_l^*d_n\mathcal{H}_{ln}{}^{(0)}+\text{c.c.})\},\end{aligned}\tag{18}$$

where c.c. means the complex conjugate. We try to find the coefficient of (16) which minimizes E of Eq. (18) under the condition given by (17). Differentiating (18) with respect to a_i^*, b_k^*, c_l^*, and d_n^*, and using the well-known Lagrangian multiplier method, we obtain:

$$\begin{aligned}&\sum_j(\mathcal{H}_{ij}{}^{(0)}-S_{ij}E)a_j+H^2(\sum_j\mathcal{H}_{ij}{}^{(4)}a_j+\sum_k\mathcal{H}_{ik}{}^{(1)}b_k)\\&\quad+H\mu(\sum_l\mathcal{H}_{il}{}^{(1)}c_l+\sum_k\mathcal{H}_{ik}{}^{(2)}b_k+\sum_j\mathcal{H}_{ij}{}^{(5)}a_j)\\&\quad+Hm_J(\sum_n\mathcal{H}_{in}{}^{(1)}d_n+\sum_k\mathcal{H}_{ik}{}^{(3)}b_k)\\&\qquad+\mu m_J(\sum_n\mathcal{H}_{in}{}^{(2)}d_n+\sum_l\mathcal{H}_{il}{}^{(3)}c_l)=0,\end{aligned}\tag{19}$$

$$\begin{aligned}&H^2\{\sum_{k'}(\mathcal{H}_{kk'}{}^{(0)}-S_{kk'}E)b_{k'}+\sum_i\mathcal{H}_{ki}{}^{(1)}a_i\}\\&\qquad+H\mu\{\sum_i\mathcal{H}_{ki}{}^{(2)}a_i+\sum_l(\mathcal{H}_{kl}{}^{(0)}-S_{kl}E)c_l\}\\&\quad+Hm_J\{\sum_n(\mathcal{H}_{kn}{}^{(0)}-S_{kn}E)d_n+\sum_i\mathcal{H}_{ki}{}^{(3)}a_i\}=0,\end{aligned}\tag{20}$$

$$\begin{aligned}&H\mu\{\sum_i\mathcal{H}_{li}{}^{(1)}a_i+\sum_k(\mathcal{H}_{lk}{}^{(0)}-S_{lk}E)b_k\}\\&\quad+\mu m_J\{\sum_i\mathcal{H}_{li}{}^{(3)}a_i+\sum_n(\mathcal{H}_{ln}{}^{(0)}-S_{ln}E)d_n\}=0,\end{aligned}\tag{21}$$

$$\begin{aligned}&\mu m_J\{\sum_i\mathcal{H}_{ni}{}^{(2)}a_i+\sum_l(\mathcal{H}_{nl}{}^{(0)}-S_{nl}E)c_l\\&\quad+Hm_J\{\sum_n\mathcal{H}_{ni}{}^{(1)}a_i+\sum_k(\mathcal{H}_{nk}{}^{(0)}-S_{nk}E)b_k\}=0.\end{aligned}\tag{22}$$

From these we get at once:

$$\sum_{k'}(\mathcal{H}_{kk'}{}^{(0)}-E_0S_{kk'})b_{k'}=-\sum_i\mathcal{H}_{ki}{}^{(1)}a_i^0,\tag{23a}$$

$$\sum_l(\mathcal{H}_{kl}{}^{(0)}-E_0S_{kl})c_l=-\sum_i\mathcal{H}_{ki}{}^{(2)}a_i^0,\tag{23b}$$

$$\sum_n(\mathcal{H}_{kn}{}^{(0)}-E_0S_{kn})d_n=-\sum_i\mathcal{H}_{ki}{}^{(3)}a_i^0,\tag{23c}$$

$$\sum_k(\mathcal{H}_{lk}{}^{(0)}-E_0S_{lk})b_k=-\sum_i\mathcal{H}_{li}{}^{(1)}a_i^0,\tag{23d}$$

$$\sum_n(\mathcal{H}_{ln}{}^{(0)}-E_0S_{ln})d_n=-\sum_i\mathcal{H}_{li}{}^{(3)}a_i^0,\tag{23e}$$

$$\sum_l(\mathcal{H}_{nl}{}^{(0)}-E_0S_{nl})c_l=-\sum_i\mathcal{H}_{ni}{}^{(2)}a_i^0,\tag{23f}$$

$$\sum_k(\mathcal{H}_{nk}{}^{(0)}-E_0S_{nk})b_k=-\sum_i\mathcal{H}_{ni}{}^{(1)}a_i^0.\tag{23g}$$

To satisfy Eqs. (23) consistently, it is necessary that

$$\varphi_k=\psi_l=\chi_n.\tag{24}$$

Thus Eqs. (23) can be reduced to:

$$\sum_{k'}(\mathcal{H}_{kk'}{}^{(0)}-E_0S_{kk'})b_{k'}=-\sum_i\mathcal{H}_{ki}{}^{(1)}a_i^0,\tag{25a}$$

$$\sum_l(\mathcal{H}_{kl}{}^{(0)}-E_0S_{kl})c_l=-\sum_i\mathcal{H}_{ki}{}^{(2)}a_i^0,\tag{25b}$$

$$\sum_n(\mathcal{H}_{kn}{}^{(0)}-E_0S_{kn})d_n=-\sum_i\mathcal{H}_{ki}{}^{(3)}a_i^0.\tag{25c}$$

From Eq. (19) it is seen that a_j can be written as

$$\begin{aligned}a_j=a_j^0+H^2a_j{}^{(1)}+H\mu a_j{}^{(2)}+Hm_Ja_j{}^{(3)}\\+\mu m_Ja_j{}^{(4)}+\cdots.\end{aligned}\tag{26}$$

(The proof of this relation is given in the Appendix.) Substituting (26) into (17), we get

$$\begin{aligned}1=&\sum a_i^0a_j^0S_{ij}+H^2[\sum b_k^*b_kS_{kk'}+\sum(a_i^0a_j{}^{(1)}\\&\quad+a_i{}^{(1)}a_j^0)S_{ij}]+H\mu[\sum(b_k^*c_lS_{kl}+c_l^*b_kS_{lk})\\&\qquad\qquad+\sum(a_i^0a_j{}^{(2)}+a_i{}^{(2)}a_j^0)S_{ij}]\\&+Hm_J[\sum(b_k^*d_nS_{kn}+d_n^*b_kS_{nk})\\&\qquad\qquad+\sum(a_i^0a_j{}^{(3)}+a_i{}^{(3)}a_j^0)S_{ij}]\\&+\mu m_J[\sum(c_l^*d_nS_{ln}+d_n^*c_lS_{nl})\\&\qquad\qquad+\sum(a_i^0a_j{}^{(4)}+a_i{}^{(4)}a_j^0)S_{ij}]\\&+\cdots.\end{aligned}\tag{27}$$

The expressions in the square brackets should all vanish, because $\sum a_i^0a_j^0S_{ij}=\int|\Psi_0|^2d\tau=1$. Making use of these relations together with (23) and $\Sigma(\mathcal{H}_{ij}{}^{(0)}-S_{ij}E_0)a_j^0=0$, etc., we can simplify (18) as follows:

$$\begin{aligned}E=&E_0+H^2[\sum a_i^0a_j^0\mathcal{H}_{ij}{}^{(4)}+\sum a_i^0b_k\mathcal{H}_{ik}{}^{(1)}]\\&+H\mu[\sum a_i^0a_j^0\mathcal{H}_{ij}{}^{(5)}+\sum a_i^0c_l\mathcal{H}_{il}{}^{(1)}\\&+\sum a_i^0b_k\mathcal{H}_{ik}{}^{(2)}]+Hm_J[\sum a_i^0b_k\mathcal{H}_{ik}{}^{(3)}\\&+\sum a_i^0d_n\mathcal{H}_{in}{}^{(1)}]+\mu m_J[\sum a_i^0c_l\mathcal{H}_{il}{}^{(3)}\\&\qquad+\sum a_i^0d_n\mathcal{H}_{in}{}^{(2)}]+\cdots.\end{aligned}\tag{28}$$

Since $L_\zeta\theta_i=0$, the second term of $\mathcal{H}^{(1)}$ and $\mathcal{H}^{(3)}$ can be dropped. Then, we can put

$$\mathcal{H}^{(1)\prime}=\mathcal{H}^{(1)}/\sin\theta=-(eMR^2/4mc\hbar)\sin\theta\cdot\mathcal{H}^{(3)},\tag{29}$$

and from (25a) and (25c) we obtain

$$-d_n=(4mc\hbar/eMR^2)\sin\theta b_k',\tag{30}$$

where

$$b_k'=b_k/\sin\theta.\tag{31}$$

Similarly,

$$c_l'=c_l/\sin\theta.\tag{32}$$

Thus (25a) becomes

$$\sum(\mathcal{H}_{kk'}{}^{(0)}-E_0S_{kk'})b_{k'}'=-\sum\mathcal{H}_{ki}{}^{(1)\prime}a_i^0.\tag{33}$$

Furthermore, if we put

$$\mathcal{H}^{(2)}=\sin\theta\cdot\mathcal{H}^{(2)\prime}+\cos\theta\cdot\mathcal{H}^{(2)\prime\prime},\tag{34}$$

it is shown from the symmetry properties that $\mathcal{H}_{ki}{}^{(2)\prime\prime}$ vanishes for those values of k to which the non-vanishing $\mathcal{H}_{ki}{}^{(1)\prime}$ corresponds. On the other hand, if $\mathcal{H}_{ki}{}^{(1)\prime}=0$, then (33) gives $b_k'=0$ which makes $a_i^0b_k\mathcal{H}_{ki}{}^{(2)}$ vanish. Therefore, $\mathcal{H}_{ki}{}^{(2)\prime\prime}$ is of no use for our purposes. Thus (25b) can be written as

$$\sum(\mathcal{H}_{kl}{}^{(0)}-E_0S_{kl})c_l'=-\sum\mathcal{H}_{ki}{}^{(2)\prime}a_i^0.\tag{35}$$

It follows from (33) and (35) that

$$\sum a_i^0b_k'\mathcal{H}_{ik}{}^{(2)\prime}=\sum a_i^0c_l'\mathcal{H}_{il}{}^{(1)\prime}.$$

Taking account of the above relations, we finally get

$$\begin{aligned} E=E_0+H^2[\textstyle\sum a_i{}^0a_j{}^0\mathcal{H}_{ij}{}^{(4)}+\sin^2\theta\sum a_i{}^0b_k{}'\mathcal{H}_{ik}{}^{(1)\prime}] \\ +H\mu[\textstyle\sum a_i{}^0a_j{}^0\mathcal{H}_{ij}{}^{(5)}+\sin^2\theta(2\sum a_i{}^0b_k{}'\mathcal{H}_{ik}{}^{(2)\prime}] \\ -2Hm_J(4mc\hbar/eMR^2)\textstyle\sum a_i{}^0b_k{}'\mathcal{H}_{ik}{}^{(1)\prime} \\ -\mu m_J(4mc\hbar/eMR^2)2\textstyle\sum a_i{}^0b_k{}'\mathcal{H}_{ik}{}^{(2)\prime}+\cdots. \end{aligned} \tag{36}$$

On the other hand, the total energy should be written [see Eq. (11)] as:

$$\begin{aligned} E_{\text{tot}}= &\text{(Rotational energy)}+\text{(vibrational energy)} \\ &-(e\hbar/2\text{Mc})Hm_J-(e\hbar/2\text{Mc})(4/R^3) \\ &\times\mu m_J-2\mu H+E+\cdots \\ =&\text{(Rotational energy)}+\text{(vibrational energy)} \\ &+E_0+(-\chi/2)H^2-2(1-\sigma)H\mu-Hm_J\mu_r \\ &-2\mu m_JH_r+\cdots, \end{aligned} \tag{37}$$

where χ means the magnetic susceptibility of this molecule, σ the magnetic shielding constant, μ_r the rotational magnetic moment, and H_r the rotational magnetic field (spin-rotational magnetic interaction constant). Comparing (36) with (37), we obtain

$$\chi=-2[\textstyle\sum a_i{}^0a_j{}^0\mathcal{H}_{ij}{}^{(4)}+\sin^2\theta\sum a_i{}^0b_k{}'\mathcal{H}_{ik}{}^{(1)\prime}], \tag{38}$$

$$\sigma=(1/2)\textstyle\sum a_i{}^0a_j{}^0\mathcal{H}_{ij}{}^{(5)}+\sin^2\theta\sum a_i{}^0b_k{}'\mathcal{H}_{ik}{}^{(2)\prime}, \tag{39}$$

$$\mu_r=(e\hbar/2Mc)+(8mc\hbar/eMR^2)\textstyle\sum a_i{}^0b_k{}'\mathcal{H}_{ik}{}^{(1)\prime}, \tag{40}$$

$$\begin{aligned} H_r=&(e\hbar/2Mc)(2/R^3) \\ &+(4mc\hbar/eMR^2)\textstyle\sum a_i{}^0b_k{}'\mathcal{H}_{ik}{}^{(2)\prime}. \end{aligned} \tag{41}$$

These results depend upon the molecular orientation θ and the internuclear distance R, and the observed values are considered as averages over θ and R.

5. NUMERICAL CALCULATION

The most accurate wave function Ψ_0 of a hydrogen molecule so far obtained is that of James and Coolidge.[6] It is therefore desirable to use it to calculate the χ's and to take as many additional functions as possible. It is, however, very laborious.

TABLE I. Coefficients and energies of the wave functions.

	$R=1.3$	$R=1.4$	$R=1.5$	(atomic units)
$a_1{}^0$	2.61810	2.46595	2.29591	
$a_2{}^0$	0.98603	0.90325	0.82526	
$a_3{}^0$	−0.70138	−0.67659	−0.64411	
$a_4{}^0$	−0.49117	−0.59722	−0.66111	
$a_5{}^0$	0.05030	0.05031	0.05333	
$a_6{}^0$	0.00090	0.01191	0.01891	
$a_7{}^0$	−0.04938	−0.03731	−0.02839	
E_0 (atomic units)	−1.1553615	−1.1575046	−1.1556648	
$b_1{}'$	$-0.003335i$	$-0.003257i$	$-0.003144i$	
$b_2{}'$	$0.001910i$	$0.001819i$	$0.001720i$	
$c_1{}'$	$0.004416i$	$0.003194i$	$0.002320i$	
$c_2{}'$	$0.000668i$	$0.000636i$	$0.0005815i$	

TABLE II. The calculated values of χ_{mol}, σ, μ_r, and H_r for $R=1.3$, 1.4, and 1.5 atomic units and for arbitrary θ.[a]

	R (atomic units)		Unit
χ_{mol}	1.3	$-3.4674-0.5974\sin^2\theta+0.1469\sin^2\theta$	10^{-6} erg G^{-2} mol^{-1}
	1.4	$-3.5814-0.7339\sin^2\theta+0.1947\sin^2\theta$	10^{-6} erg G^{-2} mol^{-1}
	1.5	$-3.7206-0.8838\sin^2\theta+0.2485\sin^2\theta$	10^{-6} erg G^{-2} mol^{-1}
σ	1.3	$2.897-0.1515\sin^2\theta+0.0706\sin^2\theta$	10^{-5}
	1.4	$2.774-0.0573\sin^2\theta+0.0683\sin^2\theta$	10^{-5}
	1.5	$2.657+0.0292\sin^2\theta+0.0643\sin^2\theta$	10^{-5}
μ_r	1.3	$1-0.1466$	$e\hbar/2Mc$
	1.4	$1-0.1675$	$e\hbar/2Mc$
	1.5	$1-0.1862$	$e\hbar/2Mc$
H_r	1.3	$31.004+2.138$	Gauss
	1.4	$24.823+1.783$	Gauss
	1.5	$20.182+1.463$	Gauss

[a] The first and the second terms of χ_{mol} come from the first term of (38), and the third terms (high-frequency terms) from the second term of (38). The first two terms of each σ come from the first term of (39), and the last from the second term of (39). The dominant part of H_r (the first terms) is obtained from the first term of (41).

In the present paper, for $\sum a_i{}^0\theta_i$, we tentatively adopt the seven-term wave function obtained by one of the present authors:[5]

$$\begin{aligned} \Psi_0=&(1/2\pi)\exp\{-\delta(\lambda_1+\lambda_2)\}[2a_1{}^0+a_2{}^0(\mu_1{}^2+\mu_2{}^2) \\ &+2a_3{}^0\mu_1\mu_2+a_4{}^0(\lambda_1+\lambda_2)+a_5{}^0(\lambda_1{}^2+\lambda_2{}^2) \\ &+2a_6{}^0\lambda_1\lambda_2\mu_1\mu_2+2a_7{}^0\rho\cos(\phi_1-\phi_2)], \end{aligned} \tag{42}$$

where

$$\lambda_j=(r_{aj}+r_{bj})/R,\quad \mu_j=(r_{aj}-r_{bj})/R, \tag{43}$$

and

$$\rho=\{(\lambda_1{}^2-1)(\lambda_2{}^2-1)(1-\mu_1{}^2)(1-\mu_2{}^2)\}^{\frac{1}{2}}. \tag{44}$$

ϕ_1 and ϕ_2 denote the azimuthal angles of the two electrons, and δ is fixed as 0.75 throughout this calculation. The values of $a_i{}^0$ and E_0 are tabulated in Table I for $R=1.3$, 1.4, and 1.5 (atomic units). For the additional function, we have used two functions:

$$\begin{aligned} \varphi_1=\psi_1=\chi_1=&(1/2\pi)\exp\{-\delta(\lambda_1+\lambda_2)\} \\ &\times[\mu_1(\lambda_1{}^2-1)^{\frac{1}{2}}(1-\mu_1{}^2)^{\frac{1}{2}}\cos\phi_1 \\ &+\mu_2(\lambda_2{}^2-1)^{\frac{1}{2}}(1-\mu_2{}^2)^{\frac{1}{2}}\cos\phi_2], \\ \varphi_2=\psi_2=\chi_2=&(1/2\pi)\exp\{-\delta(\lambda_1+\lambda_2)\} \\ &\times[\mu_2(\lambda_1{}^2-1)^{\frac{1}{2}}(1-\mu_1{}^2)^{\frac{1}{2}}\cos\phi_1 \\ &+\mu_1(\lambda_2{}^2-1)^{\frac{1}{2}}(1-\mu_2{}^2)^{\frac{1}{2}}\cos\phi_2]. \end{aligned} \tag{44}$$

The details of the calculation are quite analogous to those of the polarizability calculation[4] and we shall omit them here. The numerical values of the integrals required for our problem have been taken in part from the tables published by Kotani *et al.*[7] The tables made for the calculation of the polarizability have also been utilized. The results obtained are shown in Table II.

6. RESULTS AND DISCUSSION

In the preceding section, we obtained expressions for χ, σ, μ_r, and H_r, for fixed R and θ. We will now average these quantities over R for the lowest vibrational state. The method is the same as that used for calculat-

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[6] H. M. James and A. S. Coolidge, J. Chem. Phys. **1**, 825 (1933).

[7] Kotani, Amemiya, and Simose, Proc. Phys. Math. Soc. Japan **20**, extra number (1938); M. Kotani and A. Amemiya, Proc. Phys. Math. Soc. Japan **22**, extra number (1940).

TABLE III. The values a, b, c. Each figure in this table corresponds to that of Table II in the same arrangement. The units used are also the same as in Table II.

χ_{mol}	a	-3.5827	-0.7353	$+0.1952$	
	b	-1.2685	-1.4333	$+0.5086$	
	c	-1.26	-0.67	$+0.300$	
	$\langle\chi_{\text{mol}}\rangle_R=-3.6750-0.8168\sin^2\theta+0.2260\sin^2\theta$				(H_2)
	$\langle\chi_{\text{mol}}\rangle_R=-3.6469-0.7923\sin^2\theta+0.2167\sin^2\theta$				(D_2)
σ	a	$+2.773$	-0.0564	$+0.0683$	
	b	-1.199	$+0.9027$	-0.0317	
	c	$+0.300$	-0.385	-0.085	
	$\langle\sigma\rangle_R=2.731-0.0294\sin^2\theta+0.0667\sin^2\theta$				(H_2)
	$\langle\sigma\rangle_R=2.743-0.0372\sin^2\theta+0.0672\sin^2\theta$				(D_2)
$\Delta\mu_r$	a		-0.1677		
	b		-0.1978		
	c		$+0.110$		
	$\langle\Delta\mu_r\rangle_R=-0.1728$				(H_2)
	$\langle\Delta\mu_r\rangle_R=-0.1714M_p/M_d=-0.0857$				(D_2)
H_r	a	$+24.7689$		$+1.780$	
	b	-53.956		-3.372	
	c	$+77.000$		$+1.750$	
	$\langle H_r\rangle_R=24.783+1.689$				(H_2)
	$\langle H_r\rangle_R=(24.738+1.715)M_p/M_d$				(D_2)

ing the polarizability: we may express the R dependence of any quantity as

$$f(R)=a+b(R-R_e)+c(R-R_e)^2, \tag{45}$$

and average it by using the eigenfunction of the Morse-potential. (See Table III.)

The observed values are considered to be the averages of the above-obtained values over θ for the rotational states. As is well known, the rotational eigenfunctions can be expressed by spherical harmonics. It follows from the properties of the spherical harmonics that

$$\begin{aligned}\langle\cos^2\theta\rangle_{J,m_J}&=\frac{2J^2+2J-1-2m_J{}^2}{(2J-1)(2J+3)},\\ \langle\sin^2\theta\rangle_{J,m_J}&=\frac{2J^2+2J-2+2m_J{}^2}{(2J-1)(2J+3)}.\end{aligned} \tag{46}$$

Taking into account the relation

$$\sum_{m_J=-J}^{+J} m_J{}^2=(1/3)(2J+1)(J+1)J, \tag{47}$$

we get

$$\langle\cos^2\theta\rangle_J=\tfrac{1}{3},\quad \langle\sin^2\theta\rangle_J=\tfrac{2}{3}. \tag{48}$$

The final results thus obtained are shown in Table IV, and indicate that our method is useful and gives good results even in the rough approximation. It should be noted that we have been able to avoid the difficulty in the perturbation treatment that the high-frequency terms become too large. Compared with the observed values, the calculated values of χ_{HF} and $\Delta\mu_r$ are large, and the high-frequency term of H_r is small. However, the errors arose to the same extent in the calculation of the polarizability when only three terms were added to the unperturbed wave function. Therefore, we may expect the situation to be improved by taking more terms. In our results, H_r of D_2 is smaller than $H_r/2$ of H_2. Experimentally the reverse is the case. This disagreement seems to come from the approximation in (45), which is not good for the first term of H_r.

To get more accurate results by our method, it is necessary (i) to adopt the more accurate wave function for Ψ_0, (ii) to increase the number of the added functions, and (iii) to carry out the calculations for a larger number of different values of R. Considerable improvement, however, may be expected by increasing the added functions to five or more.

It follows from (38), (39), (40), and (41) that

$$\chi=-2\sum a_i{}^0a_j{}^0\mathcal{H}_{ij}{}^{(4)}-(\alpha^2a_0R^2/8\mu_N)\sin^2\theta(\mu_r-\mu_N), \tag{49}$$

$$\sigma=(1/2)\sum a_i{}^0a_j{}^0\mathcal{H}_{ij}{}^{(5)}-(\alpha^2a_0R^2/4\mu_N)\sin^2\theta(\mu_N/R-H_r/2), \tag{50}$$

where

$$a_0=\hbar^2/me^2,\quad \alpha=e^2/\hbar c,\quad\text{and}\quad \mu_N=e\hbar/2Mc. \tag{51}$$

TABLE IV. Results of the calculations and comparison with experiment.

	H_2		D_2		
	Calculated	Observed	Calculated	Observed	Unit
χ_{mol}	-4.0689	-3.94, -3.99[a]	-4.0306		10^{-6} erg G^{-2} mole^{-1}
σ	2.756		2.763		10^{-5}
$\Delta\mu_r$	-0.1727	-0.11709 ± 0.00007[b]	-0.0857	-0.0594 ± 0.0030[c]	$e\hbar/2Mc$
H_r	26.472	27.32[d], 26.74 ± 0.05[e]	13.227	14.0 ± 0.6[d] 13.43 ± 0.06[f]	Gauss
χ_{HF}	0.1507	0.0990 ± 0.001[b] 0.093 ± 0.007[c]	0.1445		10^{-6} erg G^{-2} mole^{-1}
$\xi_\pm-\xi_0$	-3.922	-3.66 ± 0.20[b] -3.9 ± 2.5[c]	-3.820	-5.1 ± 2.5[c]	10^{-31}/mole

[a] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, Oxford, 1932), p. 279.
[b] N. J. Harrick and N. F. Ramsey, Phys. Rev. **88**, 228 (1951).
[c] N. F. Ramsey, Phys. Rev. **58**, 226 (1940).
[d] Kolsky, Rabi, and Ramsey, Phys. Rev. **57**, 677 (1940).
[e] Kolsky, Phipps, Ramsey, and Silsbee, Phys. Rev. **79**, 883 (1950).
[f] Kolsky, Phipps, Ramsey, and Silsbee, Phys. Rev. **80**, 483 (1950).

TABLE V. Comparison of our values χ_{mol} with those of other investigators.

	Hylleraas-Skavlem	Ramsey	Present calculation	Semi-empirical
Lamb's formula	3.1648	3.24		3.24
First-order correction	−0.5034	−0.63		−0.50
Sum	2.6614	2.61	2.711	2.74
Second-order correction	0.2864	0.07 (0.05[a])	0.045	0.05
Total	2.9478	2.68 (2.66)	2.756	2.79

[a] The value obtained by the use of $H_r=26.74$ gauss.

On the other hand, Ramsey gives the formulas:[8]

$$\chi_{\mathrm{Ramsey}}=\chi_0+\chi_{HF},\quad \chi_0=-\frac{\alpha^2a_0}{6}\langle\textstyle\sum r_j^2\rangle,$$

$$\chi_{HF}=\frac{\alpha^2a_0R^2}{12}\left(1-\frac{\mu_r}{\mu_N}\right), \tag{52}$$

and

$$\sigma_{\mathrm{Ramsey}}=\tfrac{2}{3}\alpha^2a_0\left\langle\frac{1}{r_{a1}}-\frac{1}{4R}\right\rangle-\frac{\alpha^2a_0R^2}{6\mu_N}\left(\frac{\mu_N}{R^3}-\frac{H_r}{2}\right). \tag{53}$$

Putting $\sin^2\theta=\frac{2}{3}$, Eq. (49) agrees with (52) and the first term of (50) corresponds to the Hylleraas-Skavlem expression [Eq. (17) of reference 3]:

$$\tfrac{2}{3}\alpha^2a_0\langle 1/r_{a1}-RZ_{a1}/2r_{a1}^3\rangle_{\mathrm{Av}}. \tag{54}$$

This, however, seems to be different from the corresponding term of (53). The explanation lies in Ramsey's assumption that "*the nuclei are at positions where the electric field is approximately zero.*" Under this assumption we obtain $\langle 1/4R\rangle=\langle Rz_{a1}/2r_{a1}^3\rangle$. The results of these calculations are shown in Table V. The difference between −0.63 (Ramsey) and −0.50 (Hylleraas-Skavlem) seems to be caused by Ramsey's assumption, and we list in column 4 the most appropriate values for the semiempirical σ value. The agreement with our values is quite excellent.

As to HD, the calculations become somewhat complicated because of the lower symmetry of this molecule. We will therefore publish it in a separate paper.

From the above calculation we see that if the Born-Oppenheimer (B-O) approximation holds, then $\mu_r=1$ and $\Delta\mu_r=0$; namely, electrons are completely separate from the nuclear system. This rather curious situation is most easily visualized if we consider the one-dimensional model. When a proton and an electron move in the x direction, then the correct wave function of the system may be described as

$$\exp\{ik(mx+MX)/(m+M)\}\cdot\chi(x-X),$$

where m,M, and x,X are the masses and coordinates of the electron and the proton, respectively. Then by the usual procedure we obtain the current due to both electron and proton.

On the other hand, if we use the B-O wave function instead of the correct one, namely

$$\exp\{ikX\}\cdot\chi(x-X),$$

we cannot obtain the electronic current moving with the proton. This consideration shows that the B-O approximation is not justified for the calculation of the electronic current moving within the nuclear framework.

For the H_2 molecule, however, the B-O approximation is adequate, as we know from experiment that electrons are almost completely separate from the nuclear system. The correction for the B-O approximation due to the incompleteness of the separability of variables introduces $\Delta\mu_r$, which is calculated by our formalism. We will consider the treatment of the other extreme case in a later paper.

In conclusion, the authors wish to express their sincere thanks to Professor M. Kotani for his guidance and to the members of his laboratory for their aid. They are also much indebted to Professor G. Araki for his discussions, and to Professor N. F. Ramsey for his kind interest. They are grateful to Mr. T. Kawai, Mr. S. Kawasaki, and Mr. S. Kuroda for their assistance in carrying out the numerical work. Part of this work was made possible by research grants from the Educational Ministry.

APPENDIX

Differentiating Eq. (19) with respect to H and taking the limit of vanishing H, μ and m_J, one obtains

$$\Sigma_j(\mathcal{H}_{ij}^{(0)}-S_{ij}E_0)(\partial a_j/\partial H)_0 -(\partial E/\partial H)_0\Sigma_jS_{ij}a_j^0=0. \tag{A-1}$$

Multiplying by $\Sigma_ia_i^0$ and using the relations

$$\Sigma_i(\mathcal{H}_{ij}^{(0)}-S_{ij}E_0)a_i^0=0, \tag{A-2}$$

$$\Sigma_{ij}S_{ij}a_i^0a_j^0=1,$$

we get

$$(\partial E/\partial H)_0=0$$

and therefore,

$$\Sigma_j(\mathcal{H}_{ij}^{(0)}-S_{ij}E_0)(\partial a_j/\partial H)_0=0. \tag{A-3}$$

Comparing (A-3) with (A-2), one can see that

$$(\partial a_j/\partial H)_0=pa_j^0. \tag{A-4}$$

Similarly, the derivatives of (19) with respect to μ and m_J give

$$(\partial a_j/\partial \mu)_0=qa_j^0 \tag{A-5}$$

and

$$(\partial a_j/\partial m_J)_0=ra_j^0, \tag{A-6}$$

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[8] Ramsey's original form of this expression [Phys. Rev. **78**, 703 (1950), Eq. (24)] is as follows:

$$\sigma=(e^2/3\,\mathrm{mc}^2)(0|\Sigma_k1/r_k|0)-(\alpha^2a_0a^2/6\mu_N)(2Z\mu_N/a^3-\mu'H_r/MJ).$$

This is equivalent to Eq. (53) where some of the notation is altered for uniformity. The second and the third terms of Eq. (53) correspond to the second term of Ramsey's expression. This recombination is due to the different choice of gauge.

respectively. Thus we get:

$$\begin{aligned} a_j &= a_j^0 + (\partial a_j/\partial H)H + (\partial a_j/\partial \mu)_0 \mu \\ &\qquad + (\partial a_j/\partial m_J)_0 m_J + \cdots \\ &= a_j^0(1 + pH + q\mu + rm_J + \cdots). \end{aligned} \tag{A-7}$$

The normalization condition (17) gives

$$\begin{aligned} 1 = S = \Sigma a_i^{0*} a_j^0 |1 + pH + q\mu + rm_J|^2 S_{ij} + H^2(\cdots) \\ + H\mu(\cdots) + \mu m_J(\cdots) + \cdots. \end{aligned} \tag{A-8}$$

From this we obtain

$$0 = (\partial S/\partial H)_0 = \Sigma a_i^{0*} a_j^0 S_{ij}(p^* + p);$$

i.e.,

$$p^* + p = 0,$$

which shows that p is purely imaginary. Similarly q and r are also shown to be purely imaginary. We can therefore write

$$\begin{aligned} a_j &= a_j^0\{1 + i(\alpha H + \beta\mu + \gamma m_J) + \cdots\} \\ &= a_j^0 \exp\{i(\alpha H + \beta\mu + \gamma m_J)\} \\ &\qquad + (\text{second order terms}). \end{aligned} \tag{A-9}$$

This shows that, if we multiply the wave function by an appropriate phase factor, the a's can be reduced to the form

$$\begin{aligned} a_j = a_j^0 + H^2 a_j^{(1)} + H\mu a_j^{(2)} \\ + Hm_J a_J^{(3)} + \mu m_J a_j^{(4)} + \cdots. \end{aligned} \tag{A-10}$$

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Electron-Electron and Positron-Electron Scattering Measurements

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A counter experiment is described which measures the absolute differential electron-electron scattering cross section in the energy interval 0.6 to 1.2 Mev and the absolute differential positron-electron scattering cross section in the energy interval 0.6 to 1.0 Mev. The ratio of these cross sections is also measured with somewhat increased accuracy. The technique of measurement combines good resolution with large energy transfers between the particles to permit a sensitive test of the relativistic features of the Møller and Bhabha formulas. The results verify the Møller formula within the 7 percent experimental error. The Bhabha formula is verified within the 10 percent experimental error. The ratio of the Møller to the Bhabha formula is verified within about 8 percent experimental error.

INTRODUCTION

THE purpose of this report is to collect and summarize the results obtained at this laboratory on electron-electron and positron-electron scattering experiments.[1] The object of these experiments was to check the Møller and Bhabha formulas which are the predictions for *e-e* and *p-e* scattering, respectively, based on the Dirac theory. When these experiments were begun the only previous work in this field had been done with cloud chamber techniques.[2] Such experiments were not adequate to check properly either formula, since the relativistic features of the scattering begin to be appreciable only at large energy transfers between the incident and scattered particles, and these are rarely seen in the cloud chamber.

It is customary to discuss scattering cross sections in terms of angular distribution, since this is usually the experimentally measured quantity. However, our apparatus measures directly the energy transferred in the collision and this is probably a more meaningful concept in this particular problem. In any event the conservation laws provide a ready means of going from one to the other. We prefer to talk about the fraction v of the incident kinetic energy transferred in the collision.

The present experiments were designed to study the scattering at large energy transfers using a counter technique. A method has been devised which gives simultaneously a high resolution and good solid angle.

Apparatus was first designed for *e-e* scattering work, and extensive measurements were made in the energy range 0.6–1.7 Mev with $v=0.5$. Due to the inability to distinguish incident from scattered particles in *e-e* scattering, the Møller formula is symmetrical about $v=0.5$, the largest distinguishable energy transfer. Thus $v=0.5$ represents the most favorable situation for checking the Møller formula. In the energy range 0.6–1.7 Mev the electrons are sufficiently relativistic to check the essential features of the Møller formula, which include, besides the Coulomb scattering, additional contributions arising from spin interactions. Since the first reports of this work showing agreement

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