

## Quadrupole Moment of the Electron Distribution in Hydrogen Molecules\*

NORMAN F. RAMSEY

*Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts*

(Received January 16, 1950)

In molecular beam experiments on hydrogen molecules, measurements have been made in the past both of the rotational magnetic moment and of the dependence of the diamagnetic susceptibility on the orientation of the molecules' rotational angular momentum. It is shown in this paper that these two experimental results can be combined to give an experimental determination of the quadrupole moment of the electron distribution in hydrogen molecules. The results of this analysis are that the mean value of  $\sum_j(3z_j^2-r_j^2)$  with  $z$  taken along the internuclear axis of the molecule is  $(0.38 \pm 0.15) \times 10^{-16}$  cm<sup>2</sup>. Alternatively, if the  $z$  axis is the axis of quantization, the mean value of  $\sum_j(3z_j^2-r_j^2)$  in the rotational state  $M_J=J=1$  is  $(0.076 \pm 0.030) \times 10^{-16}$  cm<sup>2</sup>. The first figure can be compared to the value  $0.31 \times 10^{-16}$  cm<sup>2</sup> calculated from the hydrogen molecular wave function by James and Coolidge. Although the precision of the past measurements is small, a gain of a factor of about a hundred in the precision of this measurement should be possible with some experiments now in progress.

### 1. INTRODUCTION

IN studying the rotational magnetic moments of hydrogen molecules by the molecular beam magnetic resonance method, Ramsey<sup>1</sup> also measured the dependence of the diamagnetic susceptibility of the hydrogen molecule on the orientation of its rotational angular momentum. Thus if  $\xi_M$  represents the diamagnetic susceptibility of a molecule with rotational quantum number  $J=1$  and with the rotational magnetic quantum number equal to  $M$ , a result of his experiment was that

$$\xi_{\pm 1} - \xi_0 = -(4.5 \pm 2.0) \times 10^{-31}. \quad (1)$$

At the time of the experiments no special interpretation was given to this result. However, this quantity is directly related to the quadrupole moment of the electron distribution in the hydrogen molecule.

The detailed derivation of the relationship is somewhat complicated by the occurrence of high frequency matrix elements in the theory of the diamagnetic susceptibility of molecules as discussed by Van Vleck.<sup>2</sup> As is shown in the next section, the contribution of the high frequency elements can be directly evaluated from the experimentally measured molecular rotational magnetic moment. It is also shown in this way that the contribution of the high frequency matrix elements is only about 10 percent. Once the contribution of the high frequency terms has been evaluated, it can be seen that (1) provides a measure of the departure of the molecular electron distribution from spherical symmetry since, for a magnetic field along the  $z$  axis, the ordinary diamagnetic susceptibility is proportional to the mean value of  $\sum_j(x_j^2+y_j^2)$ . That (1) directly yields the quadrupole moment of the electron distribution in the hydrogen molecule is shown in the next section.

### 2. DERIVATION

Ordinarily the quadrupole moment of the electron distribution of a molecule is referred to the internuclear axis of the molecule so a transformation will be made to such axes. Let  $\xi_a$  be the diamagnetic susceptibility of the molecule for a field applied perpendicular to the nuclear axis and  $\xi_c$  be the susceptibility for a field along the internuclear axis. Then if  $\theta$  is the angle between the axis of quantization and the internuclear axis and if the brackets indicate that the enclosed quantity is averaged over the state concerned.

$$\xi_M = \xi_a \langle \sin^2 \theta \rangle_M + \xi_c \langle \cos^2 \theta \rangle_M \quad (2)$$

$\langle \sin^2 \theta \rangle_M$  and  $\langle \cos^2 \theta \rangle_M$  may be evaluated from

$$\begin{aligned} \psi_{\pm 1} &= \mp \frac{1}{2} (3/[2\pi])^{1/2} \sin \theta \exp(\pm i\phi) \\ \psi_0 &= \frac{1}{2} (3/\pi)^{1/2} \cos \theta \end{aligned} \quad (3)$$

with the result that

$$\begin{aligned} \langle \sin^2 \theta \rangle_{\pm 1} &= \frac{4}{5} & \langle \sin^2 \theta \rangle_0 &= \frac{2}{5} \\ \langle \cos^2 \theta \rangle_{\pm 1} &= \frac{1}{5} & \langle \cos^2 \theta \rangle_0 &= \frac{3}{5}. \end{aligned} \quad (4)$$

Therefore

$$\begin{aligned} \xi_{\pm 1} &= \frac{4}{5} \xi_a + \frac{1}{5} \xi_c \\ \xi_0 &= \frac{2}{5} \xi_a + \frac{3}{5} \xi_c \end{aligned} \quad (5)$$

and

$$\xi_{\pm 1} - \xi_0 = \frac{2}{5} (\xi_a - \xi_c). \quad (6)$$

As is shown by Van Vleck<sup>2</sup> if  $\alpha_j, \beta_j, \gamma_j$  are coordinates of the  $j$ th electron relative to axes fixed in the molecule with the  $\gamma_j$ -axis being parallel to the internuclear axis,

$$\xi_a = \xi_{a,D} + \xi_{a,HF}, \quad (7)$$

where

$$\xi_{a,D} = [e^2/(4mc^2)] \sum_j (\beta_j^2 + \gamma_j^2) \quad (8)$$

and

$$\xi_{a,HF} = 2 \sum_n' |(0| m_a^0 | n)|^2 / (E_n - E_0) \quad (9)$$

with

$$m_a^0 = -\frac{e\hbar}{2mci} \sum_j \left( \beta_j \frac{\partial}{\partial \gamma_j} - \gamma_j \frac{\partial}{\partial \beta_j} \right). \quad (10)$$

\* This work was partially supported by the joint program of the ONR and the AEC.

<sup>1</sup> N. F. Ramsey, Phys. Rev. **58**, 226 (1940).

<sup>2</sup> J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932), pp. 145 and 275 ff.

On the other hand

$$\xi_c = \xi_{c,D} = [e^2/(4 mc^2)] \sum_j \langle \alpha_j^2 + \beta_j^2 \rangle, \quad (11)$$

since  $\xi_{c, HF}$  is zero because of the symmetry of the Hamiltonian of the electrons about the internuclear axis of the molecule as a result of which there are no non-diagonal matrix elements of the angular momentum about this axis between electronic states of different energy.

From the above

$$\begin{aligned} \xi_{\pm 1} - \xi_0 &= \frac{2}{5}(\xi_{a,D} - \xi_{c,D}) + \frac{2}{5}\xi_{a, HF} \\ &= [e^2/(10 mc^2)] \sum_j \langle \gamma_j^2 - \alpha_j^2 \rangle + \frac{2}{5}\xi_{a, HF} \\ &= [e^2/(20 mc^2)] \sum_j \langle 3\gamma_j^2 - r_j^2 \rangle + \frac{2}{5}\xi_{a, HF}, \end{aligned} \quad (12)$$

since  $\langle \alpha_j^2 \rangle$  equals  $\frac{1}{2}\langle r_j^2 - \gamma_j^2 \rangle$  as a result of  $\langle \alpha_j^2 \rangle$  and  $\langle \beta_j^2 \rangle$  being equal by symmetry. If  $\xi_{HF}$  is the average contribution of the high frequency matrix elements averaged over all molecular orientations

$$\xi_{HF} = \frac{1}{3}(\xi_{a, HF} + \xi_{b, HF} + \xi_{c, HF}) = \frac{2}{3}\xi_{a, HF}. \quad (13)$$

Therefore,  $Q_e$ , the quadrupole moment of the electron distribution is

$$Q_e = \sum_j \langle 3\gamma_j^2 - r_j^2 \rangle = (20 mc^2/e^2) [(\xi_{\pm 1} - \xi_0) - \frac{2}{3}\xi_{HF}]. \quad (14)$$

This is the quadrupole moment relative to the internuclear axis of the molecule, which is the form in which electronic quadrupole moments of molecules are usually expressed. However, one can also express this in the form which is characteristic of the definition of nuclear quadrupole moments, i.e., in terms of

$$Q_e' = \int \rho_{M=J} (3z^2 - r^2) d\tau, \quad (15)$$

where  $\rho_{M=J}$  is the probability density of the electrons in the state with magnetic quantum number  $M$  equal to  $J$ . In this case, as shown by Nordsieck,<sup>3</sup>

$$Q_e' = -[J/(2J+3)]Q_e \quad (16)$$

and if  $J$  is 1

$$Q_e' = \frac{1}{5}Q_e. \quad (17)$$

### 3. NUMERICAL RESULTS

From the experimental measurements of the rotational magnetic moment, Ramsey<sup>1</sup> has determined the value of the contribution of the high frequency terms

<sup>3</sup> A. Nordsieck, Phys. Rev. 58, 310 (1940).

to the molar susceptibility of  $H_2$  to be  $(0.093 \pm 0.007) \times 10^{-6}$  per mole. Therefore, per molecule

$$\xi_{HF} = 1.54 \times 10^{-31}. \quad (18)$$

From (1), (14), and (18)

$$Q_e = (0.38 \pm 0.15) \times 10^{-16} \text{ cm}^2. \quad (19)$$

Hence from (17)

$$Q_e' = (0.076 \pm 0.030) \times 10^{-16} \text{ cm}^2. \quad (20)$$

The above result may be compared with the quadrupole moment of the ground state of  $H_2$  calculated by James and Coolidge<sup>4</sup> where, with  $a$  being the internuclear distance, they define the quadrupole moment of the molecule as

$$\begin{aligned} N &= 2e \langle \frac{1}{4}a^2 + \alpha_1^2 - \gamma_1^2 \rangle = e \langle \frac{1}{2}a^2 - (3\gamma_1^2 - r_1^2) \rangle \\ &= \frac{1}{2}e(a^2 - Q_e). \end{aligned} \quad (21)$$

With the James-Coolidge computed value of  $N$  and with 0.74 Å for  $a$ , the theoretical value of  $Q_e$  is

$$Q_e = 0.31 \times 10^{-16} \text{ cm}^2, \quad (22)$$

which agrees with the above experimental results within the experimental error.

### 4. DISCUSSION

Although the experimental results for the quadrupole moment of the electron distribution by the above method at present are of relatively low precision, the precision can be markedly improved in future experiments. The chief source of error is in the experimental value of  $\xi_{\pm 1} - \xi_0$ . Since the diamagnetic interaction energy is proportional to  $H^2$  the precision of the experimental results can be increased by about a factor of ten by making the measurements at 10,000 gauss instead of at the 3000 gauss used in the past experiments. A further increase in precision should be obtainable by lengthening the time the molecules are in the homogeneous magnetic field and by using the new molecular beam resonance technique recently suggested by Ramsey.<sup>5</sup> Experiments incorporating all of these improvements are now being prepared at Harvard as a result of which the precision in the above experimental determination of the quadrupole moment of the electron distribution in an  $H_2$  molecule should be increased by a factor of about one hundred.

<sup>4</sup> H. M. James and J. S. Coolidge, Astrophys. J. 87, 447 (1938).

<sup>5</sup> N. F. Ramsey, Phys. Rev. 76, 996 (1940).