The Electric Quadrupole Moment of the Deuteron*

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A new electronic wave for the hydrogen molecule is calculated by use of the variation principle. From this the electric field gradient at one of the nuclei is determined and is used in conjunction with the quadrupole interaction energy as given by Kellogg, Rabi, Ramsey, and Zacharias, to find the value of the quadrupole moment of the deuteron. The value obtained is $Q_D=(2.766\pm0.025)\times10^{-27}$ cm². The probable error of 0.9 percent is an improvement over the previous error of 2 percent given for Nordsieck's calculation of $Q_D=2.73\times10^{-27}$ cm² and for Ishiguro's value of $Q_D=2.79\times10^{-27}$ cm².

1. INTRODUCTION

An electric quadrupole interaction in the molecules HD and D_2 was detected by Kellogg, Rabi, Ramsey, and Zacharias[1] and they were able to measure the energy

$$H'''=-5e^2qQ_D/4\mu_D, \tag{1}$$

where Q_D is the quadrupole moment of the deuteron in cm², μ_D the magnetic moment of the deuteron, and q is a quantity closely related to the electric field gradient at the nucleus due to the charge distribution of the molecule. Since no means have been devised for measuring q directly, it is necessary to calculate it from some appropriate charge density of the molecule using the relations given by Nordsieck.[2]

$$\left.\begin{aligned} q&=-2Jq'/(2J+3),\\ q'&=\left[\frac{1}{R^3}-\frac{1}{2}\int d\tau\rho(R,r,\theta')\frac{3\cos^2\theta'-1}{r^3}\right]_{\text{Av}}\equiv q'(R)_{\text{Av}}.\end{aligned}\right\} \tag{2}$$

R is the internuclear distance, $\rho(R,r,\theta')$ the electron charge density, r the radius vector from the nucleus considered to the charge, θ' the angle r makes with the internuclear line, and J the rotational angular momentum of the molecule. The average is to be taken over the lowest vibration state of the molecule corresponding to the angular momentum J.

The integral over all space is not absolutely convergent and must be evaluated outside a small sphere about $r=0$ after which the limit of the integral is taken as the radius of the sphere shrinks to zero. It is necessary to know ρ quite accurately since the value of the integral is quite sensitive to small changes in ρ.

The most accurate electronic wave function for the ground state of the hydrogen molecule is that given by James and Coolidge.[3] This wave function, however, is in the form of a 13 term power series expansion containing the distance between the two electrons as one of the expansion variables. The labor required to integrate this makes it quite inconvenient, whereas other wave functions available are not sufficiently accurate for this calculation.

It was believed that some wave function of a convenient form could be calculated which, though not as accurate as the James-Coolidge function, would give a charge density sufficiently accurate for the purpose stated above. Two previous attempts have been made along this line,[2,4] but both calculations were estimated to give an error in q of as much as ±2 percent as compared with the experimental error of 0.6 percent in the value of H'''.

2. A NEW ELECTRON WAVE FUNCTION

The wave function for the ground state of the hydrogen molecule can be found by minimizing the integral

$$E=\int d\tau_1 d\tau_2\psi^* H\psi \tag{3}$$

over the space $d\tau_1 d\tau_2$ of the two electrons. E is the energy of the state, H the (non-relativistic) Hamiltonian, and ψ, ψ^* some normalized wave function and is complex conjugate, respectively.

A trial wave function is assumed of the form

$$\begin{aligned}\psi=(A^3/R^3N)\exp[-\tfrac{1}{2}A(\xi_1+\xi_2)][\cosh\tfrac{1}{2}B(\eta_1-\eta_2)\\ +a\exp[-\tfrac{1}{2}C(\xi_1+\xi_2)]r_1r_2\cos(\varphi_1-\varphi_2)\\ +b\eta_1\eta_2+c(\xi_1-4/A)(\xi_2-4/A)],\end{aligned} \tag{4}$$

ξ_1, ξ_2, η_1, η_2 are the elliptic coordinates of the electrons 1 and 2 with the two nuclei as foci. $(\varphi_1-\varphi_2)$ is the projection of the angle between the two electrons on a plane perpendicular to the internuclear line, N a normalization factor, and $r_1=(\xi_1^2-1)^{\frac{1}{2}}(1-\eta_1^2)^{\frac{1}{2}}$. The parameters A, B, C, a, b, c are chosen to minimize the energy E (Table I).

The reason for choosing this form is as follows. The first term alone is the trial function used by Inui[5] and Nordsieck.[2] It proved to be quite accurate considering its simplicity and it was believed that it could be easily

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[1] Kellogg, Rabi, Ramsey, and Zacharias, Phys. Rev. **57**, 677 (1940).
[2] A. Nordsieck, Phys. Rev. **58**, 310 (1940).
[3] H. M. James and A. S. Coolidge, J. Chem. Phys. **1**, 825 (1933).
[4] E. Ishiguro, J. Phys. Soc. Japan **3**, 129, 133 (1948).
[5] T. Inui, Proc. Phys. Math. Soc. Japan **20**, 770 (1938).

TABLE I. Values of the parameters for the new wave function. N, R, and E (including nuclear repulsion term R^{-3}) are in atomic units.

R	1.2	1.3	1.4	1.5
E	1.157,48	1.165,35	1.167,81	1.166,48
A	1.545,7	1.636,6	1.727,0	1.814,6
B	1.255,0	1.344,6	1.435,4	1.524,9
C	0.750	0.800	0.817	0.850
a	−0.269	−0.321	−0.354	−0.399
b	0.1081	0.1350	0.1649	0.1952
c	−0.060,90	−0.069,70	−0.079,78	−0.089,88
N	2.894,82	2.795,66	2.701,00	2.613,90

TABLE II. Values of the binding energy of the hydrogen molecule in ev as calculated by various authors. Trials 1 and 2 refer to intermediate results; see Section 2.

Wang[a]	3.76	New values	
Inui[b]—Nordsieck[c]	4.03	Trial 1	4.22
Ishiguro[d]	4.26	Trial 2	4.31
J-C 5 term[e]	4.51	Final result	4.53
13 term[e]	4.70	(Experimental)	(4.73)

[a] S. C. Wang, Phys. Rev. **31**, 579 (1928).
[b] See reference 5.
[c] See reference 2.
[d] See reference 4.
[e] See reference 3.

corrected to give a better wave function by adding some term depending on $(\varphi_1-\varphi_2)$. This would allow the electrons to seek opposite sides of the molecule. An initial attempt was made using only the first two terms of (4) with $C=0$, referred to in Table II as trial 1. From this preliminary calculation it was observed that a significant improvement in E could be made by allowing C to vary independently, referred to in Table II as trial 2. The wave function is then in such a form as to allow for the fact that the interaction between electrons is significant only for small ξ_1 and ξ_2 where the two electrons are on the average close together. One sees from Table II that the energy is appreciably better than the Inui-Nordsieck value, in fact it is better than the Ishiguro[4] value obtained from a six-parameter wave function. A comparison of the charge density $\rho=\int d\tau_1\psi^2$ with an approximate charge density integrated numerically by Nordsieck from the James-Coolidge function showed that the new charge density was worse at the points considered than that obtained using only the first term of (4). Though the error in the wave function itself must be less on the average with each successive correction, this unfortunate coincidence is possible because the change in ψ and in the energy arises mainly from terms linear in a, whereas the charge density contains only terms quadratic in a (ρ does not depend on $\varphi_1-\varphi_2$).

The last two terms of (4) were finally added. The first of these has an appreciable effect on the charge density but little effect on the energy. The last term was added to allow for shielding. If one electron is close to the nuclei, the other is likely to be further away.

It is already apparent from the difficulties encountered here that a substantial improvement in the charge density would require either a tremendous amount of labor or some more fruitful attack than the one attempted here. More convincing evidence is to be found in Section 3. Table I gives the calculated values of the parameters and the energies associated with the wave function (4) for several values of R. In Table II values of the binding energy of the molecule are compared with those of other authors.

3. ERRORS IN THE CHARGE DENSITY

The charge density at $R=1.4$ atomic units obtained by integration from Eq. (4) is compared with the values given in Table I of Nordsieck's paper. He calculated numerically an approximate density from the James-Coolidge function and in the same manner calculated an approximate density from his wave function. The density was also found by exact integration from his wave function. Due to the close agreement between the approximate and exact densities of the Nordsieck wave function, it was believed to be justifiable for further comparisons to assume a value,

$$\rho=\rho'\beta, \tag{5}$$

as the correct charge density at the points considered, where ρ' is the estimated James-Coolidge density, and β the ratio of the exact Nordsieck density to the estimated Nordsieck density. These values are listed in Table III as J-C. The values in the remaining columns are values obtained by exact integration with the corresponding percentage error in parentheses. Figure 1 shows the position of the points $(a, b, \cdots f)$ at which these densities are compared.

If this charge density is to be used in an integral, one must weigh these errors not only according to the magnitude of ρ, but also according to the volume element associated with each point. Since ρ is independent of θ, the charge densities and errors given in Table III are those associated with a volume element of magnitude proportional to the distance from the internuclear line. For most integrals which one might care to evaluate from ρ, including the one of Eq. (2), points such as d and ee' contribute most. The element of volume associated with a, bb', cc' is small, whereas at f the charge density itself is small. For the integral to be considered, the errors must also be weighted according to the value of $(3\cos^2\theta'-1)r^{-3}$.

The error in $q'(R)$ at $R=1.4$ can be estimated in a very crude way by assuming a continuous distribution of errors based on the values of Table III. The errors in the vicinity of a, b' tend to overbalance the errors at other points despite the small volume element assigned to them. One concludes that the new charge density gives a value of $q'(1.4)$ which is almost certain to be larger than the true value. By adjusting the parameters A, B, etc. of Eq. (4), one can obtain a distorted charge density and a second value of $q'(1.4)$ which is even more likely to be too small. The parameters were adjusted to give a charge distribution such that the error at each

of the points a to f was either negligible or contributed to the integral (2) with the same sign. This extreme value of $q'(1.4)$ differs from the first by 1.8 percent. Using either of these charge densities with their assumed error distributions, one can calculate a probable value of $q'(1.4)$. Two such calculations using each of the two charge densities were found to be consistent within ± 0.3 percent, giving a value of $q'(1.4)$ 0.7 percent below the first value and 1.1 percent above the second. That the two calculations were consistent implies only that the continuous distribution of errors assumed in each case gave consistent results. Both error distributions, however, were based on the James-Coolidge values of Table III and were taken to be essentially linear between the given points.

The James-Coolidge wave function should serve as a good standard for comparison of the new function but to evaluate accurately the errors by such a comparison would be a task of comparable difficulty to actually integrating the James-Coolidge function. Though the above procedure is crude, it is felt that it is at least qualitatively correct. A probable error of 0.6 percent is therefore assigned to the new value of $q'(1.4)$ instead of the 0.3 percent mentioned.

4. CALCULATION OF q'

The evaluation of the integral in Eq. (2) presents no serious difficulties and can be done exactly using the wave function (4). The values of $R^3q'(R)$ are given in Table IV for several values of R near the equilibrium position.

Using these values, $R^3q'(R)$ is expanded in a power series about the equilibrium position R_e of the molecule

$$\left.\begin{aligned} R^3q'(R) &= R^3{}_eq'(R_e)(1+\alpha_1\xi+\alpha_2\xi^2+\alpha_3\xi^3), \\ \xi &= (R-R_e)/R_e. \end{aligned}\right\} \quad (6)$$

Since both $\alpha_2\xi^2$ and $\alpha_3\xi^3$ are small for the range of ξ covered by the zero-point vibration of the molecule, no appreciable error need be assumed for the lack of high terms in the expansion. Due to the large change in R^3 over this range, the average of $q'(R)$ over the zero-point of vibration is quite sensitive to errors in the wave function associated with this vibration.

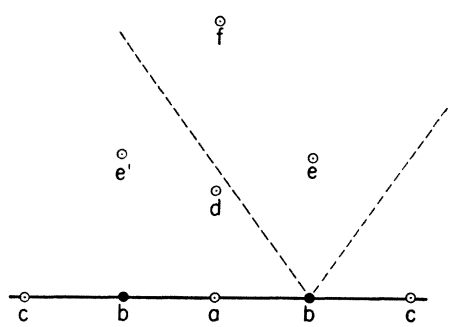

FIG. 1. The circles indicate the positions of the points $(a, b\cdots f)$ relative to the two nuclei bb'. The dashed line separates regions for which $3\cos^2\theta'-1$ has opposite sign.

TABLE III. Values of the charge densities in atomic units with percent error in parentheses for $R=1.4$ atomic units. The positions of the points are shown in Fig. 1.

Point	J-C	Nordsieck[a]		Ishiguro[b]		New values	
a	0.267,3	0.269,9	(+1.0)	0.271,39	(+1.5)	0.264,65	(−1.0)
bb'	0.446,1	0.430,4	(−3.5)	0.434,45	(−2.6)	0.439,76	(−1.4)
cc'	0.067,32	0.068,25	(+1.4)	0.069,34	(+3.0)	0.069,42	(+3.1)
d	0.106,9	0.108,7	(+1.7)	0.106,23	(−0.6)	0.107,22	(+0.3)
ee'	0.047,47	0.048,49	(+2.1)	0.047,28	(−0.4)	0.047,78	(+0.1)
F	0.005,97	0.006,16	(+3.2)	0.005,85	(−2.0)	0.006,16	(+3.2)

[a] See reference 2.
[b] See reference 4.

The shape of the potential well for the molecular vibration can be obtained more accurately from spectroscopic data than from the calculations of Section 2. Using the formulas of Dunham[6] and the experimental data of Jeppeson,[7] the potential can be evaluated in the form

$$V=a_0\xi^2(1+a_1\xi+a_2\xi^2+a_3\xi^3+a_4\xi^4). \quad (7)$$

The values obtained for the Dunham coefficients are given in Table V. The merits of such an expansion are discussed by Coolidge, James, and Vernon.[8] While it may be in serious error for large values of ξ, it should represent the potential quite accurately for the small values of ξ corresponding to the zero-point vibration.

To test the sensitivity of q' to the shape of the potential well, calculations were performed using Morse[9] functions. The two parameters of the Morse potential were assigned in one case to give the correct binding energy and the correct vibration frequency, and in another case to give the correct vibration frequency and the value a_1 of (7) when the Morse potential is expanded in a similar series. The differences between the corresponding values of q' were 1 percent for D_2 and 1.3 percent for HD. The second of these two Morse functions was corrected by means of perturbation theory to conform to the potential of Eq. (7). This last correction gave an additional 0.2 percent change.

It is assumed that no significant error arises from averaging $q'(R)$ over the zero-point vibration. The results for $J=1$ are

$$q'=0.1761 \text{ for } D_2, \quad q'=0.1757 \text{ for HD}. \quad (8)$$

In Section 3, it was argued that the value of $q'(1.4)$ given in Table IV is too large by 0.7 percent. The vibrational wave function has a maximum at about $R=1.4$ and a half-width $\Delta R\sim 0.15$. If one assumes that the error in $q'(R)$ does not change appreciably over the short range of R about 1.4, then the error in q' may also be taken as $+0.7$ percent. The corrected values of q' are

$$q'=0.1749 \text{ for } D_2, \quad q'=0.1745 \text{ for HD}. \quad (9)$$

5. CONCLUSION

The value of H''' as given by Kellogg *et al.*[1] is 87.2 ± 0.5 gauss. Within experimental error no difference is

[6] J. L. Dunham, Phys. Rev. **41**, 713, 721 (1932).
[7] C. R. Jeppeson, Phys. Rev. **45**, 480 (1934); **49**, 797 (1936).
[8] Coolidge, James, and Vernon, Phys. Rev. **54**, 726 (1938).
[9] P. M. Morse, Phys. Rev. **34**, 57 (1929).

TABLE IV. Calculated values of $R^3q'(R)$ in atomic units.

R	$R^3q'(R)$
1.2	0.603,69
1.3	0.547,18
1.4	0.488,86
1.5	0.430,96

found in the value for HD and D_2. The values of q' given above are consistent with this observation. Taking the average of the two values of q' for HD and D_2, Q_D is found to be 2.766×10^{-27} cm². On the basis of the errors discussed in Section 3, a probable error of 0.6 percent is assigned to q'. Combining this with the error of 0.6 percent in H''' gives $\sqrt{2}(0.6)=0.9$ percent as the probable error in Q_D:

$$Q_D=(2.766\pm0.025)\times10^{-27}\ \text{cm}^2. \tag{10}$$

This differs from the value 2.73×10^{-27} cm² ±2 percent obtained by Nordsieck[2] chiefly because the latter performed the average over the zero-point vibration using a Morse function fitted to give the correct binding energy. Though the new value does not differ much from the value 2.79×10^{-27} cm² obtained by Ishiguro, the values of $q'(1.4)$ differ by as much as five percent. On the basis of the James-Coolidge density values of Table III, the errors in Ishiguro's density are very badly distributed in the vicinity of the nucleus. The errors are negative for points e and b, presumably also for points in between, whereas the errors at a and c are both definitely positive. The percentage error in $q(R)$ can be considerably larger than the percentage error in ρ due to the cancellation in the integral of the spherically symmetric part of the distribution. Thus one can account for the five percent difference in the values of $q'(1.4)$. That the two values of Q_D are so close is partly due to the 0.7 percent correction of the new value made in Section 4 and partly because Ishiguro used a Morse function for his average over the zero-point vibration, probably the same one used by Nordsieck.

TABLE V. Values of the Dunham[a] coefficients as calculated from spectroscopic data.[b] a_0 is in cm⁻¹.

	HD	D_2
a_0	79,795	79,873
a_1	−1.608,2	−1.589,2
a_2	+1.846,4	+1.750,7
a_3	−1.840	−1.708
a_4	+1.664	+2.07

[a] See reference 6.
[b] See reference 7.

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A Hodoscope Study of Penetrating Cosmic-Ray Showers. I. Local Showers*

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Showers produced locally in a lead absorber were studied with a hodoscope arrangement. It is shown that, in order to record "local penetrating showers," a rigid selection demanding high penetrating power of the secondaries as well as of the primary must be used. If this is done, some of the discrepancies of recent investigations are removed. For showers capable of penetrating at least 200 g/cm² Pb one finds a collision mean free path of (162±10) g/cm², and for showers of at least 100 g/cm² penetration a mean free path of (196±13) g/cm². Besides, "local soft showers" due to electronic or photonic secondaries of ordinary μ-mesons were studied. Their frequency at 3260-m elevation is about 1 in 10^5 traversals of the lead absorber.

I. THE EXPERIMENTAL TECHNIQUE

IN its present stage, work on penetrating showers is particularly strongly affected by the limitations of current experimental methods. Counter arrangements, though suitable for detection and for selection of showers, cannot usually provide a unique answer to questions concerning the nature of the particles involved, or concerning details of their interactions. Cloud chambers, on the other hand, could adequately answer this purpose, but it is troublesome and difficult to stack in them a sufficiently large amount of absorber, and they tend to become slow in operation because of the inevitably long interval between successive expansions of a large chamber, and its equally inevitable unfavorable solid angle of detection. It appeared, therefore, that in this field the use of what one might consider a compromise technique, namely a hodoscope arrangement, is well justified. It offers speedier work than a cloud chamber, as better solid angles and recovery times can be obtained, and it offers more extended evidence than a simple counter arrangement would reveal, though, of course, it is inferior in this respect to the cloud chamber.

* The expense of constructing the equipment and of running the experiment were partly provided by an AEC contract.