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On the Value of the Electric Quadrupole Moment of the Deuteron*

A. Nordsieck
Columbia University, New York, New York

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The gradient of the electric field at the nucleus in the hydrogen molecule is calculated from a new electronic wave function which gives a simple but accurate formula for the electron density. The wave function is found by a generalization of the procedure first used by S. C. Wang. The calculated field gradient, together with the molecular beam measurements of Kellogg, Rabi, Ramsey and Zacharias, determines the value of the electric quadrupole moment of the deuteron. As stated by the latter authors, the quadrupole moment is 2.73×10^{-27} cm². The writer estimates the limits of error of this value to be ±2 percent.

I. Introduction

In a paper on the radiofrequency spectra of the molecules HD and D_2 in a magnetic field, Kellogg, Rabi, Ramsey and Zacharias[1] have pointed out that the evaluation of the electric quadrupole moment of the deuteron requires the knowledge, in addition to the experimentally measured energy differences, of the quantity

$$q=\sum[(3\cos^2\theta-1)/r^3]_{\text{Av}}. \qquad (1)$$

The sum is taken over all of the molecular charges except that of the nucleus under discussion, electrons contributing with negative sign. In this expression r is the radius vector from the nucleus under discussion to the individual molecular charge; θ is the angle between r and the direction of the constant applied magnetic field. The average is to be taken over the normal electronic state, the normal vibrational state, and the rotational state J, $M_J=J$, that is, the rotational state for which the projection of the rotational angular momentum on the field direction is a maximum. Casimir[2] has developed the theory of the interaction of a nuclear electric quadrupole moment with extranuclear charges for atoms; except for the actual evaluation of q his theory is immediately applicable to molecules as well.

For an atom the quantity q can be related to another quantity which depends on r in the same way and determines the magnitude of the hyperfine-structure separation; in this way q can be found for the atom from the measured hyperfine structure. In the case of a molecule it is not possible, on account of the lack of spherical symmetry, to make use of such a relation, and we must fall back on a direct calculation of q from the theoretical charge distribution in the molecule. The direct calculation of q for HD and D_2 is the subject of the present paper. A preliminary report of this work was made in February, 1940.[3]

In Eq. (1) q is expressed in terms of coordinates relative to axes with a fixed orientation in space. The theoretical electron distribution, on the other hand, is given relative to axes fixed in and rotating with the molecule. The transformation from the former to the latter axes may be made as follows. Let Θ, Φ be the spherical polar coordinates of the internuclear line relative to the field direction. Let θ' be the angle made by the radius vector r with the internuclear line. Then according to the addition theorem for spherical harmonics

$$3\cos^2\theta-1=(3\cos^2\Theta-1)(\tfrac{3}{2}\cos^2\theta'-\tfrac{1}{2})+\text{terms involving } e^{i\Phi}. \qquad (2)$$

The average over the rotational state, i.e., over Θ and Φ, may now be found by multiplying by the absolute square of the rotational wave function $|Y_{JJ}(\Theta,\Phi)|^2$ and integrating over Θ and Φ. The terms involving $e^{i\Phi}$ contribute nothing since $|Y_{JJ}|^2$ does not depend upon Φ, and the result is

$$[3\cos^2\theta-1]_{\text{Av}}=\frac{-2J}{2J+3}(\tfrac{3}{2}\cos^2\theta'-\tfrac{1}{2}). \qquad (3)$$

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[1] J. M. B. Kellogg, I. I. Rabi, N. F. Ramsey and J. R. Zacharias, Phys. Rev. **57**, 677 (1940). See pp. 678, 691, 692.

[2] H. B. G. Casimir, "On the interaction between atomic nuclei and electrons," *Teyler's Tweede Genootschap* (1936).

[3] A. Nordsieck, Phys. Rev. **57**, 556A (1940). (The quantity called q in this abstract is called q' in reference 1 and in the present paper.)

Thus if we call the electron density $\rho(r, \theta')$, we have

$$q = \frac{-2J}{2J+3} q', \tag{4}$$

$$q' \equiv \left[\frac{1}{R^3} - \frac{1}{2} \int d\tau \rho(r, \theta') \frac{3\cos^2\theta' - 1}{r^3} \right]_{\text{Av}}. \tag{5}$$

The relation (4) was stated without derivation in reference 1, page 692. In Eq. (5), R stands for the internuclear distance. The first term is the contribution of the second nucleus; the second comes from the electrons and enters with a negative sign as mentioned above. The average must be taken over the zero-point vibration of the molecule.[4] We shall use the symbol $q'(R)$ for the quantity inside the square bracket.

The integral in (5) is not absolutely convergent, but the theory of a quadrupole moment interaction[2] shows that the integration must be performed in a definite way, which then leads to a unique result in spite of the nonabsolute convergence. One must exclude a small sphere with $r=0$ as center, integrate over the remaining space, and then put the radius of the sphere equal to zero. In practice, therefore, the integration is to be performed in the spherical polar coordinates r and θ', the integration over θ' to be carried out first. This point is mentioned because some proposed electron distributions ρ are not conveniently handled in the coordinates r and θ'.

The physical meaning of q' is the following: $-2eq'$ is the derivative, taken outward along the internuclear line, of the electric field component outward along this line due to all charges outside the small sphere spoken of above.

The chief problem was to find an accurate and convenient approximation for the function ρ. Rather fair accuracy is needed in ρ because of the mutual cancellation of various contributions to q'. The writer has found a simple formula which approximates ρ well for our purposes, by the methods indicated in the following section.

II. CALCULATION OF ELECTRON DENSITY

Two approximate electronic wave functions for the normal state were already available for calculating ρ: one found by Wang,[5] another by James and Coolidge.[6] Both were found unsuitable, the first for reasons of accuracy, the second because of its form. The Wang function was found by inserting an effective nuclear charge Z into the first Heitler-London approximation for the wave function and minimizing the electronic energy as a function of Z. The function is very simple:

$$\Psi_{\text{Wang}} = e^{-Z(r_1+r_2')} + e^{-Z(r_1'+r_2)}, \tag{6}$$

r_1 and r_2 being the distances of electrons 1 and 2 from the one nucleus, r_1' and r_2' the distances from the other nucleus, all in atomic units.[7] The electron density is readily found analytically for any value of R. But the density found from this function is in error by as much as 16 percent, as we shall see below. The function of James and Coolidge is in the form of an exponential times a multiple power series with coefficients determined by the Ritz method. It is accurate, but, for our purposes, very unwieldy. In order to calculate q with this function, the density would have to be tabulated numerically for several values of R (a very laborious procedure) and $q'(R)$ found by numerical integration. The fact that the James-Coolidge function is expressed in elliptic coordinates and is not conveniently handled in the coordinates r and θ' contributes to the difficulty. The writer, therefore, decided to use the James-Coolidge function as a standard of accuracy in finding a simple but reliable analytical expression for ρ rather than to calculate with the James-Coolidge function directly.

The errors in the Wang electron density and in the newly found electron density, relative to the James-Coolidge density taken as standard, were estimated as follows. For $R=1.40$ atomic units (the equilibrium distance) the numerical values of the James-Coolidge wave function and of the

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[4] In the definition of q' in reference 1 (end of p. 691 and beginning of p. 692) a factor $\frac{1}{2}$ was accidentally omitted from before the integral sign, and the average over R is not indicated.

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

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

[7] Atomic units (D. R. Hartree, Proc. Camb. Phil. Soc. **24**, 89 (1928)), were used throughout in the calculation of q. The value of the atomic unit of length (Bohr radius), upon which the final result for the quadrupole moment depends, was taken to be 0.5292×10^{-8} cm.

wave functions to be tested were computed at 42 chosen points in the configuration space of the two electrons. By squaring these values and averaging, with appropriately chosen weights, over the positions of one of the electrons, comparable values of the electron density were found for the three functions at 9 points in the molecule. These values of the density are called estimated values and are given in the second, third and fifth columns of Table I. In the fourth column are given the errors in the Wang density, in the sixth column those in the new density, both relative to the James-Coolidge density. It should be emphasized that the numbers given are reliable not in an absolute sense but only for purposes of comparison, each wave function having been handled in identically the same way to arrive at the numbers given for it. The values of the density given by the exact formula derived from the new function are also given in the last column, and a comparison of the "estimated" and exact values shows that the points chosen in configuration space and the weights assigned in averaging over the positions of one electron were reasonable.

The table, together with the accompanying scale diagram (Fig. 1) of the positions of the 9 exploratory points in the molecule, shows that the error in the Wang density varies, roughly speaking, in a long range fashion along the length of the molecule, the density being too low in the plane $r=r'$ and too high at the ends of the molecule. If we introduce the elliptic coordinates $\xi=(r+r')/R$ and $\eta=(r-r')/R$ and write the Wang function in terms of these:

$$\Psi_{\text{Wang}}=e^{-\frac{1}{2}A(\xi_1+\xi_2)}\left[e^{\frac{1}{2}A(\eta_1-\eta_2)}+e^{\frac{1}{2}A(\eta_2-\eta_1)}\right], \qquad (6')$$

where $A=ZR$, it becomes clear how such a long range error arises: The trial function has the same coefficient in the η-exponents as in the ξ-exponent, so that the variation of the function in η (variation lengthwise of the molecule) is constrained by being related to the variation in ξ (variation outward from the internuclear line). It is furthermore evident that considerable improvement could be secured while still keeping the very simple analytical form of this trial function, by introducing independent coefficients A and B in the ξ- and η-exponents, respectively:

$$\Psi=e^{-\frac{1}{2}A(\xi_1+\xi_2)}\left[e^{\frac{1}{2}B(\eta_1-\eta_2)}+e^{\frac{1}{2}B(\eta_2-\eta_1)}\right] \qquad (7)$$

and minimizing the energy as a function of these two parameters. By carrying out this procedure the new function used in the present calculation was found.[8]

TABLE I. *Values of electron density in atomic units (electrons/(Bohr radius)^3) at $R=1.40$ atomic units.*

POINT IN MOLECULE (SEE FIG. 1)	JAMES-COOLIDGE, ESTIMATED	WANG, ESTIMATED	ERROR (%)	NEW FUNCTION, ESTIMATED	ERROR (%)	NEW FUNCTION, EXACT VALUES
a	0.2668	0.2248	−16	0.2694	+1.0	0.2699
b, b'	0.4477	0.4495	+0.4	0.4320	−3.5	0.4304
c, c'	0.06756	0.07734	+14	0.06849	+1.4	0.06825
d	0.1067	0.0942	−12	0.1085	+1.7	0.1087
e, e'	0.04747	0.04686	−1	0.04848	+2.1	0.04849
f	0.00596	0.00606	+2	0.00615	+3.2	0.00616

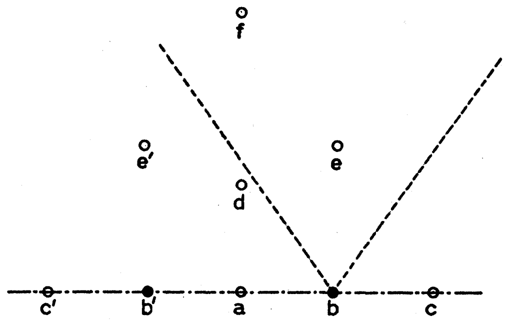

FIG. 1. The circles *a, b, b'* $\cdots$ *f* indicate to scale the points at which the density was estimated. *b, b'* are the positions of the nuclei. The molecule possesses axial symmetry about the internuclear line. The dotted lines separate the two regions in which the electrons contribute to q' with opposite sign.

The formula for the energy in terms of A, B and R is given in the appendix, Section 1. The energy can no longer be calculated in completely closed form as was the case with the original Wang function, for the term $1/r_{12}$ representing the mutual potential energy of the two electrons must be expanded by the method of von Neumann[9] and its contribution calculated term by term. Three terms, namely those involving harmonics of the 0th, 1st and 2nd orders, were

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[8] Returning to the coordinates r and r', one may interpret this improvement in the wave function from the point of view of the Heitler-London approximation. The present function is formed, not from pure atomic functions, but from atomic functions distorted by the proximity of the second atom. The amount of distortion is measured by $(A-B)$, and is determined by the Ritz variation method.

[9] F. von Neumann, *Theorie des Potentials* (Leipzig, 1887), p. 341.

kept, terms beyond these contributing in order of magnitude 0.0001 atomic unit (0.003 volt) to the energy. Table II gives the calculated minimal values of A and B and the energy for several values of R. For the Wang function at $R=1.400$, $A=B=1.640$ and the electronic energy is -1.851; the James-Coolidge energy at $R=1.400$ is -1.886. The modification of the Wang function has thus reduced the error in the electronic energy from 1.8 percent to 1.2 percent.[10] The formula for the electron density calculated from the new function appears in the appendix, Section 2. It is hoped that this formula together with the estimated errors in it (see Table I) will prove useful in other problems connected with the hydrogen molecule.

III. Calculation of q'

The integrations involved in finding $q'(R)$ are straightforward and lead to the formula given in the appendix, Section 3. To find the value of the part called M_2 it is best to use its expansion in powers of b/a, which is also given. The values of $q'(R)$ are given in Table III.

The average value q' of $q'(R)$ over the zero-point vibration of the molecule, depends somewhat on the amount and character of the anharmonicity in the molecular potential curve. The average was calculated by fitting a formula $a/R+b/R^2+c/R^3$ to the values in Table III, fitting a Morse potential curve to the vibrational data for the molecule,[11] and averaging over the lowest vibrational state in this potential. This approximate procedure is justified because the amplitude of the zero-point vibration is a small fraction of the equilibrium distance between nuclei (0.035 for HD, 0.028 for D_2). The correction due to centrifugal force in the rotational state $J=1$ is negligible (0.2 percent). For the molecule HD the averaged q' was found to be 0.1768 atomic units $=1.193\times10^{24}$ cm^{-3}.[7] For D_2, which has a slightly smaller amplitude of vibration, $q'=0.1763$ atomic units $=1.190\times10^{24}$ cm^{-3}. It is accidental that the average q' is nearly equal to the value of $q'(R)$ at the equilibrium distance, for the form of $q'(R)$ favors smaller values of R, while the anharmonicity favors larger R.

TABLE II. *Data for new electronic function, all in atomic units. Energy does not include nuclear repulsive term.*

R	A	B	ENERGY
1.300	1.613	1.265	−1.915
1.400	1.706	1.344	−1.863
1.500	1.793	1.420	−1.815

IV. Estimate of Accuracy of q'

The accuracy of the values of $q'(R)$ was estimated as follows: For $R=1.400$ the integrand for $q'(R)$ was integrated separately over the two angular ranges separated by the dotted lines in the figure. The two integrands in r (corresponding to the contributions to $q'(R)$ of opposite sign) were then plotted and estimates made of the errors in these integrands at several points, based on the errors in ρ given in Table I. In this way it was found that the errors in ρ at the points a, c and d caused an error of roughly $+1$ percent in $q'(R)$, while the error at the point b' caused an error of roughly -1 percent in $q'(R)$. The other errors had negligible effect because of their being weighted with $1/r^3$. The contribution of the electrons to $q'(R)$ is very nearly $-\frac{1}{2}$ the contribution $1/R^3$ of the second nucleus, so that the fractional error in $q'(R)$ is equal to the fractional error in the electron contribution. Since these estimates were necessarily rough, limits of error of ±1 percent were assigned to $q'(R)$. The process of averaging over the zero-point vibration may lead to an additional error of at most ±1 percent in the average q'. Hence the writer considers 2 percent a safe estimate of the limits of error of the final value of q'. Roughly the same limits of error then hold for the value[1] 2.73×10^{-27} cm^2 of the quadrupole moment, since the experimentally measured term differences are reliable to about $\frac{1}{2}$ percent.

TABLE III. *Values of $q'(R)$ in atomic units.*

R	$q'(R)$
1.300	0.2462
1.400	0.1755
1.500	0.1257

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[10] The root-mean-square error of any function relative to the James-Coolidge function is easily estimated by the exploratory method described above. For the Wang function we find 17 percent; for the new function 12 percent. These are of the order (relative error in energy)$^{\frac{1}{2}}$, as is to be expected on the basis of general theorems. From the present work it appears, however, that provided long range errors in the trial function are sufficiently reduced, the mean relative error in the *density* is of the same order as that in the energy.

[11] C. R. Jeppeson, Phys. Rev. **45**, 480 (1934); **49**, 797 (1936).

APPENDIX

1. The electronic energy in atomic units, not including the energy of mutual repulsion of the nuclei, as calculated from the approximate function (7), is given by

$$E=\left(1-\frac{k}{S^2+T^2}\right)\left(\frac{A}{R}\right)^2-\frac{l+m_0+m_1+m_2+\cdots}{S^2+T^2}\,\frac{A}{R},$$

where:

$$S_1=\left(\frac{1}{2}A+\frac{1}{2}A^2\right)e^{-A},\qquad S_1'=\left(\frac{1}{2}A-\frac{1}{2}A^2\right)e^{A},$$

$$S=\left(1+A+\frac{1}{3}A^2\right)e^{-A},\qquad S'=\left(1-A+\frac{1}{3}A^2\right)e^{A},$$

$$S_3=\left(\frac{3}{A}+3+\frac{3}{2}A+\frac{1}{2}A^2\right)e^{-A},\qquad S_3'=\left(\frac{3}{A}-3+\frac{3}{2}A-\frac{1}{2}A^2\right)e^{A},$$

$$S_4=\left(\frac{12}{A^2}+\frac{12}{A}+\frac{17}{3}+\frac{5}{3}A+\frac{1}{3}A^2\right)e^{-A},\qquad S_4'=\left(\frac{12}{A^2}-\frac{12}{A}+\frac{17}{3}-\frac{5}{3}A+\frac{1}{3}A^2\right)e^{A},$$

$$y_0=\sinh B/B;\quad y_n=(\partial/\partial B)^n y_0,$$

$$T=y_0\left(1+A+\frac{1}{2}A^2\right)e^{-A}-y_2\left(\frac{1}{2}A^2\right)e^{-A},$$

$$T'=y_0\left(1-A+\frac{1}{2}A^2\right)e^{A}-y_2\left(\frac{1}{2}A^2\right)e^{A},$$

$$k=\left[\frac{1}{3}S(A^2+B^2)+\frac{1}{2}(y_0-y_2)T(A^2-B^2)\right]e^{-A},$$

$$l=4(S+y_0T)(1+A)e^{-A},$$

$$m_0=-(1/A)\Bigg\{(S^2+T^2)\log\gamma A+2(SS'+TT')E(2A)-(S'^2+T'^2)E(4A)$$
$$-\left[\left(-\frac{5}{8}A+\frac{3}{4}A^2+\frac{1}{3}A^3\right)+y_0^2\left(-\frac{5}{8}A+\frac{3}{4}A^2+\frac{1}{2}A^3\right)-y_0y_2\left(\frac{1}{2}A^3\right)\right]e^{-2A}\Bigg\},$$

$$m_1=+\frac{3}{A}\Bigg\{y_1^2\left[S_3^2\log\gamma A+2S_3S_3'E(2A)-S_3'^2E(4A)-\left(18+\frac{95}{8}A+\frac{35}{4}A^2+\frac{5}{2}A^3+\frac{1}{2}A^4\right)e^{-2A}\right]$$
$$-2y_1y_3\left[S_1S_3\log\gamma A+(S_1'S_3+S_1S_3')E(2A)-S_1'S_3'E(4A)-\left(3A^2+\frac{5}{4}A^3+\frac{1}{2}A^4\right)e^{-2A}\right]$$
$$+y_3^2\left[S_1^2\log\gamma A+2S_1S_1'E(2A)-S_1'^2E(4A)-\frac{1}{2}A^4e^{-2A}\right]\Bigg\},$$

$$m_2=-\frac{45}{16A}\Bigg\{(3y_2-y_0)^2\bigg[S_4^2\log\gamma A+2S_4S_4'E(2A)-S_4'^2E(4A)$$

$$-\left(\frac{288}{A^2}+\frac{192}{A}+128+\frac{871}{18}A+\frac{43}{3}A^2+\frac{26}{9}A^3+\frac{1}{3}A^4\right)e^{-2A}\bigg]-2(3y_2-y_0)(3y_4-y_2)$$

$$\times\left[SS_4\log\gamma A+(SS_4'+S'S_4)E(2A)-S'S_4'E(4A)-\left(24+16A+\frac{22}{3}A^2+\frac{19}{9}A^3+\frac{1}{3}A^4\right)e^{-2A}\right]$$

$$+\left[\left(\frac{4}{15}\right)^2+(3y_4-y_2)^2\right]\left[S^2\log\gamma A+2SS'E(2A)-S'^2E(4A)-\left(2A^2+\frac{4}{3}A^3+\frac{1}{3}A^4\right)e^{-2A}\right]\Bigg\},$$

$\gamma=$ Euler–Mascheroni constant $=0.5772$,

$$E(x)\equiv\int_x^\infty e^{-y}\frac{dy}{y}.$$

2. The electron density in atomic units derived from the approximate function (7) is

$$\rho(\xi,\eta)=\frac{2}{\pi}\left(\frac{A}{R}\right)^3\frac{1}{S^2+T^2}e^{-A\xi}[S+T\cosh B\eta]$$

or

$$\rho(r,r')=\frac{2}{\pi}\left(\frac{A}{R}\right)^3\frac{1}{S^2+T^2}e^{-A(r+r')/R}\left[S+T\cosh\frac{B}{R}(r-r')\right].$$

A and B for various R are given in Table II. S and T are defined in Appendix 1.

3. $q'(R)$, as calculated from the above formula for the electron density, is given by

$$q'(R)=\frac{1}{R^3}\left[1-\frac{LS+MT}{S^2+T^2}\right],$$

where

$L=(24A+12A^2+4A^3/3)e^{-A}-12S\log 2\gamma A-12S'E(2A)$,

$M=M_1+M_2$,

$$M_1=2A^3\Bigg\{\left[\frac{4}{a^3}-\frac{5b}{a^3}-\frac{15b^2}{a^5}-\frac{b^2}{a^3}\right]e^{-b}-\left[\left(\frac{4}{a^3}+\frac{4}{a^2}+\frac{2}{a}+\frac{2}{3}\right)-\left(\frac{15}{a^5}+\frac{15}{a^4}+\frac{6}{a^3}+\frac{1}{a^2}\right)b^2\right]e^{-a}$$

$$+\left[\left(\frac{9}{2a^4}+\frac{9}{2a^3}+\frac{2}{a^2}+\frac{1}{2a}\right)b-\left(\frac{15}{2a^6}+\frac{15}{2a^5}+\frac{3}{a^4}+\frac{1}{2a^3}\right)b^3\right][\log(a+b)-\log|a-b|+\overline{\mathrm{Ei}}(a-b)]e^{-a}$$

$$+\left[\left(\frac{9}{2a^4}-\frac{9}{2a^3}+\frac{2}{a^2}-\frac{1}{2a}\right)b-\left(\frac{15}{2a^6}-\frac{15}{2a^5}+\frac{3}{a^4}-\frac{1}{2a^3}\right)b^3\right]E(a+b)e^{a}\Bigg\}.$$

$M_2=$ same as M_1 with a and b interchanged and $\overline{\mathrm{Ei}}(a-b)$ replaced by $-E(a-b)$.

$$M_2=A^3b\Bigg\{\frac{4}{15}\left[\frac{1}{a^2}-\left(\frac{1}{a^2}+\frac{1}{a}\right)e^{-a}+e^{-a}-aE(a)\right]$$

$$-\frac{4}{35}\left[\frac{6}{a^4}-\left(\frac{6}{a^4}+\frac{6}{a^3}+\frac{3}{a^2}+\frac{1}{a}\right)e^{-a}+\left(\frac{1}{3}-\frac{a}{6}+\frac{a^2}{6}\right)e^{-a}-\frac{a^3}{6}E(a)\right]\Bigg\}+0(b^3),$$

$$a\equiv A+B;\quad b\equiv A-B.$$

$\overline{\mathrm{Ei}}(x)$ is defined in Jahnke-Emde, *Funktionentafeln* (Leipzig, 1933), p. 79.