Theoret. chim. Acta (Berl.) 3, 284—286 (1965)

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The Variation of the Quadrupole Moment of H_2 with Internuclear Distance, as Given by Some One Center Wave Functions

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We have calculated two properties which reflect the dependence of the approximate wave function on the internuclear distance; the quadrupole moment, and A_q, the quotient of the quadrupole moment at the equilibrium distance and the product of equilibrium distance and the derivative of the quadrupole with respect to the internuclear distance [see eq. (1)]. The quadrupole moment has long been of interest to the theoretician and experimentalist [*2*], since being readily calculable it has served as a measure of the shape of a wave function [*5*]. We list in Tab. 1 values of the quadrupole moment computed by other workers and ourselves using various approximate wave functions for the hydrogen molecule. To reproduce the experimental quadrupole moment, one must go considerably beyond the Hartree-Fock type of approximation. Only a fairly lengthy configuration-interaction treatment or explicit inclusion of interparticle distance in the wave function leads to an approximate wave function which gives reasonable values.

Table 1. *Quadrupole Moment* (a) *of the Hydrogen Molecule*

Wave Function	Q^T (Debye-Angstroms)	Reference
HEITLER-LONDON	0.74	b
WANG	0.34	c
r_{12}-five term	1.34	d
SCF-M.O.	0.78	e
r_{12}-28 term	1.25	f
7 term one center	1.10	g
Experimental	1.25	h

(a) Calculated with origin at the molecule midpoint. 1 a. u. = 1.34495 Debye-Angstrom.
(b) HEITLER, W., and F. LONDON: Z. Physik **44**, 455 (1928).
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(g) This work.
(h) Reference 3.

An experimental measure of A_q has recently been obtained [*6*].

$$A_q = Q_{\text{eq}} / \left(\frac{dQ}{dR}\right) R_{\text{eq}} . \tag{1}$$

Using spectroscopic data the experimental value for A_q is 0.815, assuming that Q be a linear function of R, at least over a range of distances of the same order as the vibrational stretching motions.

Using the one center wave functions of BISHOP [1] we have calculated the quadrupole moment and A_q for the hydrogen molecule. We use these wave functions because they are separately minimized at each internuclear distance and fully optimized. The quadrupole moment calculated is derived from a harmonic expansion of the molecular electron charge density [7].

$$p(r, \theta, \varphi) = \sum_{l=0,2,4\cdots}^{\infty} A_l(r)\, Y_{l,0}(\theta, \varphi)\,. \tag{2}$$

The electronic contribution to the quadrupole moment is:

$$Q_e = \frac{1}{\sqrt{5}} \int_0^{\infty} A_2(r)\, r^4\, dr\,. \tag{3}$$

The quadrupole moment was calculated for $R = 1.3, 1.4, 1.5$, and 1.38 (the equilibrium distance) BOHR, truncating the wave function at various points. The nuclear contribution to Q is $eR^2/2$. The results are given in Tab. 2. A factor of $4\sqrt{\pi}$ relates the electronic contribution of the calculated moment, Q_e, to the quadrupole moment defined by BUCKINGHAM [2] (Q^T in Tab. 1).

On plotting $Q(R)$ versus R, one notes the quadrupole moment is very close to being a strict linear function of the internuclear distance. The calculated moments were fitted by a least squares analysis to the equation $Q = a + bR$, and the derivative calculated ($a = -0.680$, $b = 1.084$, sum of squares of residuals $= 4.75 \times 10^{-6}$). The quotient, A_q, was calculated to be 0.545; a 28 term r_{12} function yields 0.678 [3], both to be compared to an experimental value of 0.815.

Table 2. *Electronic Contributions to the Quadrupole Moment**

Wave Function	R = 1.3	R = 1.4	R = 1.5	R = 1.38
(1) $S S^{I}$	0	0	0	0
(2) (1) + $S^{II} S^{III}$	0	0	0	0
(3) (2) + $S^{IV} d_0$	0.05265	0.06612	0.08066	0.06264
(4) (3) + $S^{V} g_0$	0.05462	0.06899	0.08468	0.06530
(5) (4) + $P_0 P_0$	0.11627	0.14057	0.17716	0.13738
(6) (5) + $P_+ P_-$	0.11171	0.13930	0.17197	0.13257
(7) (6) + $P_0 f_0$	0.11492	0.14385	0.17819	0.13678
Total Quadrupole Moment, Q^T, in Debye-Angstroms	0.982	1.125	1.273	1.097

* Atomic units

These results point out two things. First the one center function gives a 12% error in the quadrupole moment, a 23% error in the derivative dependent quantity A_q, while the r_{12} function does not err in the quadrupole moment and predicts A_q to within 17%. Secondly, the quadrupole moment is very close to being a strict linear function of the internuclear distance. The one center functions are fully optimized and are energetically below the Hartree-Fock solution for H_2 [3]. They give the correct value for $\langle r^2 \rangle$ and are correct in their shape [4]. Their *comparative* success in predicting A_q emphasizes the value of fully optimizing the wave function when using a limited basis set. In estimating properties which depend upon derivatives of nuclear coordinates it appears that a crude function carefully minimized does almost as well as the far more complex interparticle coordinate functions.

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(Received July 5, 1965)