Quadrupole moment of the deuteron from a precise calculation of the electric field gradient in D_2

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The electric field gradient along the molecular axis at the nucleus in D_2 has been calculated at $R = 1.4$ a.u. by means of the Kołos-Wolniewicz 54-term Born-Oppenheimer wave function. The result is a confirmation of the Reid-Vaida value. A nonadiabatic calculation using a 540-term wave function (explicitly containing the vibronic component) also confirms the earlier value of the electric field gradient and necessarily, therefore, the predicted quadrupole moment of the deuteron (i.e., $Q = 0.2860 \pm 0.0015$ fm^2).

I. INTRODUCTION

An accurate value of the quadrupole moment of the deuteron Q is of pivotal importance in the nuclear-structure theory of the deuteron, and any nucleon model must satisfactorily account for its value. Though there is no purely experimental value, a semi-empirical value can be determined, if the electric field gradient q is known, from the electric-quadrupole-interaction constant eqQ/h. The latter has been accurately measured by Ramsey and co-workers[1] for the $J=1$ state in the HD molecule and the $J=1$ and $J=2$ states in the D_2 molecule using the molecular-beam magnetic-resonance method. Consequently a precise value of Q revolves around an accurate calculation of q in HD or D_2. This has been done by Reid and Vaida[2] and the result for Q is 0.2860 ± 0.0015 fm^2. This is a few percent larger than older semi-empirical values and too large to be fitted, in the single-nucleon approximation, by energy-independent nucleon-nucleon interactions that yield the experimental values of the triplet scattering length and deuteron binding energy with sufficient precision.[3] To obtain agreement between the nuclear-model and semiempirical values of Q it is necessary to introduce one of two related and nontrivial modifications to the theory: the inclusion of energy dependence in the nucleon-nucleon interaction or the consideration of contributions to Q from meson-exchange currents involving the exchange of a single pion.[4]

Because of the seriousness of the proposed modifications to the nuclear model, taken in the light of Reid and Vaida's value of Q, it is important that there be an independent accurate calculation of q (it is assumed that the experimental value of eqQ/h is precise). We report here such an undertaking which includes an analysis of the sensitivity of q to basis set, variational parameters, and nonadiabatic effects. Our primary conclusion is that the semiempirical value of $Q = 0.2860 \pm 0.0015$ fm^2 is correct.

The calculations were performed on an IBM 360/65 computer in double precision; the mass ratio of electron to deuteron (m_e/m_d) was taken[5] as 0.000 272 444.

II. CALCULATIONS

The basis of the calculations was the evaluation of an expectation value (q) using both adiabatic and nonadiabatic variational wave functions and the terminology and notation for these wave functions is that of Ref. 6. The electric field gradient along the molecular axis at one of the nuclei is then

$$q = 2e\langle q' \rangle, \tag{1}$$

where, in the non adiabatic formalism,

$$\langle q' \rangle = \langle \Psi V \Psi \rangle, \tag{2}$$

Ψ is the nonadiabatic wave function involving explicitly both nuclear and electronic coordinates, and

$$V = R^{-3} - \tfrac{1}{2}[(3z_1^2 - r_1^2)/r_1^5 + (3z_2^2 - r_2^2)/r_2^5]. \tag{3}$$

R is the internuclear separation, r_i is the distance of electron i from the nucleus under consideration, and z_i is the corresponding component along the internuclear axis. In the adiabatic formalism, q' is the expectation value of V over the Born-Oppenheimer electronic wave function Ψ_B and $\langle q' \rangle$ is the expectation value of q' over the adiabatic vibrational-rotational wave function for the appropriate vibrational-rotational state. The conditionally convergent integrals which appear in these expectation values are defined as the limit $\epsilon \to 0$ of the integral evaluated with a sphere, centered on the nucleus of radius ϵ, excluded.

The Born-Oppenheimer electronic wave functions were of the James-Coolidge type, i.e., Eqs. (9) and (10) of Ref. 6 with $\alpha_1 = \alpha_2 = \alpha$ and $\beta_1 = \beta_2 = 0$, and the integrals required for q' were

evaluated as by Reid and Vaida.[2] The treatment we used for the most difficult integral, B_{ij} with $\mu_i + \mu_j$ odd, was numerical and is described in the Appendix.

In order to be certain that we were free of programming and algebraic errors, we recomputed q' with the 11-term James-Coolidge wave function used by Narumi and Watanabe.[7] These workers had essentially evaluated all the integrals analytically. Our results agreed with theirs to at least four significant figures for four different values of R. We also recomputed q' with the 34-term wave function of Reid and Vaida[2] at $R = 1.5$ a.u. and obtained $q' = 0.119\,96$ a.u., where they obtained (unpublished data) 0.119 97 a.u. We are therefore confident that our techniques and programming are error free.

Next we used the 54-term wave function of Kołos and Wolniewicz[8] for $R = 1.4$ a.u. (with $\alpha = 1.027$) and found q' to be 0.168 96 a.u., which compares favorably with Reid and Vaida's[2] interpolated value of 0.168 88 a.u. derived from an 87-term wave function of the same type. It is clear from this agreement that both wave functions contain the basis functions which contribute most importantly to the evaluation of q'. In Table I the change in q' is shown as the basis-function expansion length is expanded from 38 to 54. It would appear that additional basis functions are not going to change the fourth significant figure in q'.

If at $R = 1.4$ a.u. only the basis functions in the 54-term wave function having $\mu = 0$ (μ is the power of the interelectronic coordinate r_{12}) are included then $q' = 0.165\,95$ a.u.; if only terms with $\mu = 0, 1$ are included then $q' = 0.168\,99$ a.u. (c.f. 0.168 96 a.u. when r_{12}^2 terms are also included). This seems to imply that higher powers than two in the interelectronic coordinate will not change the fourth significant figure in q'.

TABLE I. Change in q' (in atomic units) as the number of terms (N) in the wave function is increased from 38 to 54.

N	q'
38	0.168 965
39	0.168 967
40	0.168 997
41	0.168 977
42	0.168 996
43	0.168 983
44	0.168 983
45	0.168 975
46	0.168 978
47	0.168 970
48	0.168 977
49	0.168 977
50	0.168 969
51	0.168 975
52	0.168 968
53	0.168 967
54	0.168 962

TABLE II. Values of $\langle q' \rangle$ (in atomic units) for the ground vibrational state and various rotational states for D_2.

J	This work	Ref. 2
0	0.167 95	...
1	0.167 33	0.167 44
2	0.166 13	0.166 22

We also investigated the sensitivity of q' to changes in the nonlinear parameter α. We found that with the 54-term wave function that at $R = 1.3$ a.u., and taking $\alpha = 1.027$ rather than the optimum value[8] of 0.9723, q' was 0.237 93 a.u. which can be compared with Reid and Vaida's value of 0.237 78 a.u. At $R = 1.5$ a.u. and using the 54-term wave function with $\alpha = 1.027$ (the optimum value[8] is 1.078) we found q' to be 0.119 93, where Reid and Vaida's value is 0.119 96 a.u. Clearly with appropriate basis sets q' is not particularly sensitive to the value of α, the slack, so to speak, being taken up by the linear coefficients in the wave function.

We have also checked Reid and Vaida's averaging of q' over the ground-vibrational state and different rotational states. We have used the Numerov-Cooley method[9] and the adiabatic-relativistic potential curve of Ref. 10 to obtain the vibrational-rotational wave functions for D_2. The results are shown in Table II and the differences are well within Reid and Vaida's error estimate.

Finally, we have carried out the first nonadiabatic calculation of $\langle q' \rangle$. We have used for Ψ for D_2 all combinations of the previous 54 electronic basis functions with 10 radial basis functions, see Eqs. (17) and (18) of Ref. 6. For the lowest nonrotational state with $\gamma = 5.1$ and $\delta = 1.4$ (the radial nonlinear parameters) we obtain $\langle q' \rangle = 0.168\,12$ a.u.; the adiabatic result for this state is 0.167 95 a.u. Again, the difference is trivially small. From this we deduce two facts: (a) nonadiabatic effects are negligible and (b) the interpolation of q' made by Reid and Vaida for many R values and the averaging carried out in obtaining the adiabatic result are satisfactory. A check was made that $\langle q' \rangle$ is not sensitive to the choice of γ; with $\gamma = 5.0$, $\langle q' \rangle = 0.168\,12$ a.u. and, so clearly, it is not.

III. CONCLUSIONS

Our principal conclusion is that Reid and Vaida's calculation of the electric field gradient

in H_2 is correct, as is their value (0.2860 ± 0.0015 fm^2) derived therefrom for the quadrupole moment of the deuteron. If anything, their error limits on Q are on the conservative side. We have not only confirmed their value of q' but also its average value in the $v=0$ and $J=1,2$ states of D_2. We have also carried out a nonadiabatic calculation of the field gradient for the $v=0$, $J=0$ state of D_2 and find that it is insignificantly different from the adiabatic results for that state. We therefore discount nonadiabatic effects as contributing to the value of the electric field gradient for other states. This conclusion is in conformity with the effects of nonadiabatic contributions to other expectation values.[13] It is also a verification that the method of averaging q' over vibrations and rotations in the adiabatic calculation and the interpolation used to find q' at other than the R values at which it was calculated, was sufficiently precise.

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APPENDIX

From both the mathematical and computational point of view, the greatest difficulty in calculating the electric field gradient is the evaluation of integrals of the form

$$B_{ij}(\alpha) = \lim \int_{1+\epsilon}^{\infty} d\xi_1 \int_{-1}^{+1} d\eta_1 \, W(\xi_1, \eta_1) \times F_{ij}(\xi_1, \eta_1, \alpha) \quad \text{as} \quad \epsilon \to 0 ,$$

where

$$W(\xi_1, \eta_1) = (\xi_1 - \eta_1)(\xi_1 + \eta_1)^{-4}[3(\xi_1\eta_1 + 1)^2 - (\xi_1 + \eta_1)^2]$$

and

$$F_{ij}(\xi_1, \eta_1, \alpha) = (2\pi)^{-2} \int_1^{\infty} d\xi_2 \int_{-1}^{+1} d\eta_2 \, (\xi_2^2 - \eta_2^2) \times \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 \, \Phi_i \Phi_j$$

for the case where the sum of the powers of r_{12} appearing in the basis functions Φ_i and Φ_j is odd. At first we took the approach of Narumi and Watanabe[7] and attempted to use analytic integration using the equations of Refs. 11 and 12. However, it became evident that multiple precision would be required (a not unusual situation where singularities are involved) and this scheme was abandoned.

Instead we approached the problem numerically and in a similar fashion to Reid and Vaida.[2] For F_{ij} we used a 16-point Gauss-Laguerre quadrature for integration over ξ_2, a 16-point Gauss-Legendre for integration over η_2, and analytical integration over ϕ_1 and ϕ_2. The integral B_{ij} was divided into three regions: (a) $1.4 \leq \xi_1 \leq \infty$, $-1 \leq \eta_1 \leq 1$, where a 48×16 crossed Gauss-Laguerre-Gauss-Legendre quadrature was used; (b) $1 \leq \xi_1 \leq 1.4$, $-0.8 \leq \eta_1 \leq 1$, where a 16×16 crossed Gauss-Legendre quadrature was used; (c) $1 \leq \xi_1 \leq 1.4$, $-1 \leq \eta_1 \leq -0.8$. The last region, containing the singularity was divided into 800 rectangles in the (ξ_1, η_1) plane by dividing the ξ_1 and η_1 range as follows:

$1 \leq \xi_1 \leq 1.05$ (16 divisions),

$1.05 \leq \xi_1 \leq 1.1$ (8 divisions),

$1.1 \leq \xi_1 \leq 1.2$ (8 divisions),

$1.2 \leq \xi_1 \leq 1.4$ (8 divisions),

$-1 \leq \eta_1 \leq -0.975$ (8 divisions),

$-0.975 \leq \eta_1 \leq -0.95$ (4 divisions),

$-0.95 \leq \eta_1 \leq -0.9$ (4 divisions),

$-0.9 \leq \eta_1 \leq -0.8$ (4 divisions).

For each rectangle, F_{ij} was evaluated at six points (the center, mid-edges, and one corner) and the results expressed as

$$F_{ij} = c_1 + c_2\xi_1 + c_3\eta_1 + c_4\xi_1\eta_1 + c_5\xi_1^2 + c_6\eta_1^2 ,$$

the integral of $W(\xi_1, \eta_1)F_{ij}$ was then evaluated analytically for each rectangle and the results summed.

The above scheme was chosen after other ranges of integration had been investigated using the integral B_{ij}, but with F_{ij} replaced by $\exp(-\alpha\xi_1)\xi_1^m\eta_1^n$ and with various values of m and n (up to and including $m=9$, $n=8$). The results with this scheme agreed to seven significant figures with an analytical evaluation based on the analysis in Refs. 11 and 12. Further, it was verified by calculating the B_{ij} integrals which occur when the 11-term James-Coolidge wave function is used and agreement found to at least five significant figures with those deduced from the analytical calculations of Narumi *et al.*[11,12]

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