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Electric Field Gradient and Magnetic Spin-Spin Interactions in Isotopes of the Hydrogen Molecule*

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Field gradients have been calculated at 12 values of the internuclear distance from 34-, 66-, and 87-term molecular wave functions expanded in prolate-spheroidal coordinates and r_{12}. Convergence of the gradients as the basis enlarges is indicated and the dissociation energy of H_2 is in agreement with experiment. Using vibrationally averaged gradients, experimental values for the quadrupole-interaction constant, and estimating the error in the field gradients arising from truncation of the basis, the electric quadrupole moment of the deuteron is found to be $0.2875 \pm 0.002 \times 10^{-26}$ cm^2, which is 2% larger than the most recent values. This disagreement as well as that among earlier authors is explained. First-order perturbation-theoretic results for the magnetic spin-spin interaction constant for $H_2(J=1)$, $HD(J=1)$, $D_2(J=1)$, and $D_2(J=2)$ are in agreement with experiment and, except for H_2, well inside experimental error.

I. INTRODUCTION

Although it is evidently an easy matter to calculate the electric field gradient q in the hydrogen molecule to an accuracy of 10%,[1] results probably accurate to better than 1% have remained elusive for some time.[2–7] Part of the problem lies in the sensitivity of the field gradient to errors in the molecular wave function, part in actually calculating the field gradient given the wave function, and the remainder in averaging over vibrational motion of the molecule.

On the other hand, while q itself is not presently measurable, Ramsey and co-workers[8–14] have determined the electric-quadrupole-interaction constant eqQ/h, where Q is the magnitude of the electric quadrupole moment of the deuteron, for the $J=1$ state in the HD molecule and the $J=1$ and 2 states of D_2. Using the molecular-beam magnetic-resonance method, with considerable associated experimental refinements, Code and Ramsey[14] improved the accuracy of the quadrupole-interaction constant for the D_2 $J=1$ state to the point where it was possible for them to show that the results of the most recent field-gradient calculation, that of Narumi and Watanabe,[7] were not consistent with their D_2 $J=1$ and the best earlier HD $J=1$[13] interaction constants. Assuming the experimental results to be correct, this implied either that nonadiabatic effects were being observed or that approximations made in the field-gradient calculation were much poorer than believed by Narumi and Watanabe. We return to this point in Sec. IV.

Signell and Parker[15] have noted that quadrupole moments corresponding to previous field-gradient calculations[2–7] are in serious disagreement. As discussed in Sec. IV, we believe that the chief source of the disagreement is the earlier error assignments.

In this paper we report new results for the field gradient and the direct magnetic spin-spin interaction constants. Parts of this work were briefly reported earlier.[16] We use molecular wave functions expanded in a basis some eight times larger than in previous work. The concomitant difficulties in calculating the field gradient introduced by the larger basis were handled by a numerical method incorporating exact, analytic treatment of the singularity occurring in matrix elements of the field-gradient operator. The average over nuclear motion was performed using vibrational wave functions obtained from the adiabatic potential of Kolos and Wolniewicz.[17,18]

Following a brief statement of the formalism in Sec. II we describe the calculations in Sec. III, give results and discuss errors in Sec. IV, and conclude in Sec. V.

II. BACKGROUND THEORY

Working within the framework of the adiabatic approximation[19] we decompose the molecular Hamiltonian H into

$$H = H^0 + H' , \qquad (1)$$

where H^0 is H when the nuclei are fixed. The complete wave function Ψ is approximated by

$$\Psi = \psi(\vec{x}_1, \vec{x}_2, R)\,\chi(\vec{R}) , \qquad (2)$$

where $\vec{x}_1$ and $\vec{x}_2$ are the electronic coordinates and $\vec{R}$ is the relative coordinate for the nuclei. The electronic wave function is then determined by

$$[H^0 - E^0(R)]\,\psi = 0 \qquad (3)$$

and the wave function χ, which describes molecular vibration and rotation, satisfies

$$[(-1/2\mu)\nabla_R^{\,2} + U(R) - E]\,\chi(\vec{R}) = 0 , \qquad (4)$$

where μ is the reduced nuclear mass in a.u. and

$$U(R)=E^0(R)+H'_{00}(R)\ , \tag{5}$$

with

$$H'_{00}(R)=\langle\psi|H'|\psi\rangle\ . \tag{6}$$

By means of H'_{00} the coupling between electronic and nuclear motion is included to first order.

The electric field gradient along the molecular axis evaluated at one of the nuclei is[2,20]

$$q=2e\langle q'(R)\rangle_J\ , \tag{7}$$

with the average being taken over the molecular zero-point vibration in the Jth molecular rotational state using the appropriate χ from Eq. (4) and

$$q'(R)=R^{-3}-\int d^3x_1d^3x_2\psi^2(\vec{x}_1,\vec{x}_2,R)\,V''(\vec{x}_1,\vec{x}_2)\ , \tag{8}$$

where

$$V''(\vec{x}_1,\vec{x}_2)=P_2(\theta_1)x_1^{-3}+P_2(\theta_2)x_2^{-3}\ , \tag{9}$$

x_i is the distance of the ith electron from the nucleus under consideration, and θ_i is the angle between $\vec{x}_i$ and the molecular axis. Using the electron number density $n(x,\theta)$, q' can be written in the transparent classical form

$$q'(R)=R^{-3}-\int d^3x\,n(x,\theta)P_2(\theta)x^{-3}\ . \tag{10}$$

The conditionally convergent integrals appearing in Eqs. (8) and (10) are defined[2,20,21] as the limit $\epsilon\to0$ of the integral evaluated with a sphere, centered upon the nucleus and of radius ϵ, excluded.

III. CALCULATIONS

A. Electronic Wave Function

Using the interelectronic distance r_{12} in the form $\rho=2r_{12}/R$ and the natural, prolate-spheroidal coordinates of each electron, $\xi=(r_a+r_b)/R$ and $\eta=(r_a-r_b)/R$, where r_a and r_b are distances from nuclei a and b, we write ψ in the form

$$\psi=\sum_{mprs\mu}C_{mprs\mu}\Phi_{mprs\mu}\ , \tag{11}$$

$$\Phi_{mprs\mu}=(\xi_1^m\eta_1^p\xi_2^r\eta_2^s+\xi_1^r\eta_1^s\xi_2^m\eta_2^p)\rho^\mu e^{-\alpha(\xi_1+\xi_2)}\ . \tag{12}$$

For our basis we first chose the six terms $(m,p,r,s,\mu)=(0,0,3,0,0)$, $(0,0,0,4,0)$, $(0,1,1,3,0)$, $(1,0,4,0,0)$, $(1,0,0,4,0)$, and $(3,0,0,2,0)$ which, from the work of Kolos and Wolniewicz,[17] appeared to play a significant role in giving reasonable values of E^0 in the equilibrium region. For the largest basis used we added the 81 terms generated by allowing (m,p,r,s,μ) to assume all combinations of the values 0, 1, 2 subject to the symmetry requirements of the ${}^1\Sigma_g^+$ state, i.e., to $p+s$ being even. This choice was partly motivated by the work of Newell,[4] who found that some terms with small exponents produced considerably greater improvement in the electronic density near the nucleus, and thus in the field gradient, than in the dissociation energy. We kept all 81 terms, regardless of the degree to which they improved the energy, in order to avoid omitting components of the wave function to which the field-gradient operator was more sensitive than the Hamiltonian.

Complete calculations were also carried out with 66- and 34-term bases. The 60 terms added to the original six, for the larger one, were obtained by allowing at most two of the five exponents to be as large as 2. The 28 terms added for the smaller basis were defined by restricting μ to 0, 1 and allowing at most one of the remaining four exponents to be as large as 2.

The expansion coefficients in Eq. (11) and α were, for each R, determined by minimizing the Rayleigh quotient $\langle\psi|H^0|\psi\rangle/\langle\psi|\psi\rangle$. A few remarks regarding the necessary overlap integrals and matrix elements of the Hamiltonian are contained in Appendix A.

B. Field Gradient

Inserting Eq. (11) into Eq. (8) yields

$$q'(R)=R^{-3}-\sum_{i,j}c_ic_j\langle i|V''|j\rangle\ , \tag{13}$$

with

$$\langle i|V''|j\rangle=\int d^3x_1d^3x_2\times\Phi_i(\vec{x}_1,\vec{x}_2,R)\,V''(\vec{x}_1,\vec{x}_2)\,\Phi_j(\vec{x}_1,\vec{x}_2,R); \tag{14}$$

we have condensed the labels on the basis functions defined by Eq. (12). Turning now to prolate-spheroidal coordinates with

$$W(\xi,\eta)=(\xi-\eta)(\xi+\eta)^{-4}[3(\xi\eta+1)^2-(\xi+\eta)^2]\ , \tag{15}$$

which includes the field-gradient operator and part of the volume element, and with the excluded sphere of radius $\frac{1}{2}\epsilon R$, we write

$$\langle i|V''|j\rangle=R^3[\tfrac{1}{3}\pi^2A_{ij}(\alpha)+\tfrac{1}{2}\pi^2B_{ij}(\alpha)]\ , \tag{16}$$

where

$$A_{ij}(\alpha)=\lim\tfrac{3}{2}\int_1^{1+\epsilon}d\xi_1\int_{\epsilon-\xi_1}^1d\eta_1\,W(\xi_1,\eta_1)\times F_{ij}(\xi_1,\eta_1,\alpha)\quad\text{as}\ \epsilon\to0\ , \tag{17}$$

$$B_{ij}(\alpha)=\lim\int_{1+\epsilon}^\infty d\xi_1\int_{-1}^1d\eta_1\,W(\xi_1,\eta_1)\times F_{ij}(\xi_1,\eta_1,\alpha)\quad\text{as}\ \epsilon\to0\ , \tag{18}$$

and

$$F_{ji}(\xi_1,\eta_1,\alpha)=(2\pi)^{-2}\int_1^\infty d\xi_2\int_{-1}^1d\eta_2\,(\xi_2^2-\eta_2^2)\times\int_0^{2\pi}d\phi_1\int_0^{2\pi}d\phi_2\,\Phi_i\Phi_j\ . \tag{19}$$

A_{ij} reduces to[3,22,23]

$$A_{ij}(\alpha)=(-1)^{p_i+p_j}e^{(-2\alpha)}\int_1^\infty d\xi\int_{-1}^1d\eta\,(\xi-\eta)$$

$$\times(\xi+\eta)^{\mu_i+\mu_j+1}e^{-2\alpha\xi}X_{ij}(\xi,\eta)\ , \qquad (20)$$

where, with the notation $[m,p]=\xi^m\eta^p$,

$$X_{ij}(\xi,\eta)=[m_i+m_j,\ p_i+p_j]+[m_i+r_j,\ p_i+s_j]$$
$$+[r_i+m_j,\ s_i+p_j]+[r_i+r_j,\ s_i+s_j]\ . \qquad (21)$$

Consequently A_{ij} can be done analytically.

When $\mu_i+\mu_j$ is even, B_{ij} can also be evaluated in terms of simple integrals.[3,22,24] However, the B_{ij} with $\mu_i+\mu_j$ odd are quite another matter. By themselves, they constitute the major obstacle to using the basis of Eq. (12). The relatively few required by Narumi and Watanabe[7] for the James–Coolidge[25] 11-term wave function involving only one value of the nonlinear parameter were successfully evaluated[22,24] essentially analytically. However, the complexity is sufficient to blur the distinction between an analytical and a numerical approach. We used a combination briefly described in Appendix B.

The A_{ij} and B_{ij} were calculated for the set $\alpha=0.8(0.1)1.4$, which spans the range of α needed. For a given R, the α minimizing the Rayleigh quotient, α_m, was first determined to within $\pm5\times10^{-4}$. If α_m was one of the values in our set, then electronic wave functions were generated and q' calculated using Eqs. (13) and (16). If the deviation of of α_m from one of those in our set did not exceed 0.025, then q' was calculated for the three nearest values in our set and quadratic interpolation, on q' as function of α, was employed. For greater deviations in α it is more accurate to interpolate on q' as a function of R, as described in the next subsection.

C. Vibrational Average

Restricting our attention to the lowest vibrational state, we make the partial-wave decomposition

$$R\chi(\vec{R})=\sum_J f_J(R)P_J(\theta)\ , \qquad (22)$$

after which Eq. (4) becomes

$$\left[\frac{d^2}{dR^2}-2\mu\left(U(R)+\frac{J(J+1)}{2\mu R^2}-E_J\right)\right]f_J(R)=0\ . \qquad (23)$$

We suppress the vibrational quantum number υ; we deal only with ground vibrational states for which $\upsilon=0$.

The adiabatic potential $U(R)$ used was that of Kolos and Wolniewicz.[17,18,26] For $E^0(R)$ their earlier Born–Oppenheimer energies[26] were used outside the range of their 100-term values.[18]

After numerically integrating Eq. (23) and normalizing, we obtain

$$\int_0^\infty dR\,[f_J(R)]^2=1\ , \qquad (24)$$

$$\langle q'(R)\rangle_J=\int_0^\infty dR\,[f_J(R)]^2q'(R)\ . \qquad (25)$$

For the HD molecule, f_1^2 is shown in Fig. 1. This is the case with the greatest spread in $f_J(R)$, relevant to the field gradient.

In order to calculate the integral of Eq. (25), $q'(R)-R^{-3}$ was interpolated by means of a cubic spline fit to the smoother function $R^3q'(R)-1$.

IV. RESULTS

A. Field Gradient

Values of $q'(R)$ calculated with the 87-term basis at 12 points along with a few interpolated values are given in Table I and shown in Fig. 1. Purely numerical errors in our values of $q'(R)$ are primarily systematic. They are believed to be less than 3×10^{-5} and independent of R to less than 1×10^{-5}. Difficulties in calculating the field gradient for a given wave function are exacerbated by the fact that, from Eq. (10), only the $P_2(\theta)$ component of the electronic charge density contributes.

The strong rise in $q'(R)$ as the internuclear distance decreases from its equilibrium value $R_e\cong1.4$ a.u. is largely due to the increasing failure of the electrons to screen the contribution, R^{-3} in Eq. (8), to the field gradient from the other nucleus.

The 34- and 66-term wave functions yield similar field gradients, with the 34-term gradients being always somewhat smaller and the 66-term always slightly larger than the 87-term gradients in Table I. The R dependence of $q'(R)$ with the 34-term basis is nearly the same as, and with the 66-term virtually identical to, that of the 87-term basis.

The differences in Table I among values of $q'(R)$ for given R arise from the different electronic wave functions used by the corresponding authors.

To average over nuclear motion, $q'(R)$ was smoothly extrapolated outside the range of R in

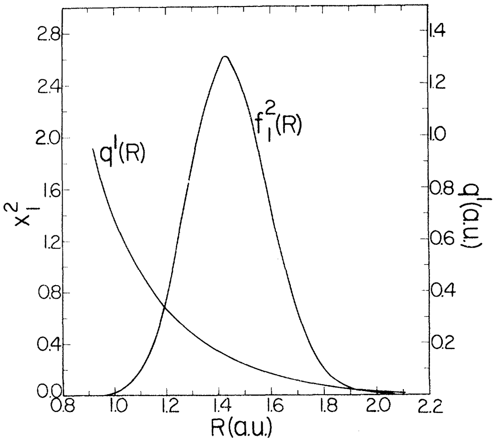

FIG. 1. Squared, zero-point vibrational eigenfunction for HD($J=1$) and the electric field gradient. Note that the scale on the right applies to q'.

TABLE I. Comparison of field gradients calculated at various R.

R (a.u.)	This work[a]	Nordsieck[b]	$q'(R)$ (a.u.) Ishiguro[c]	Newell[d]	Narumi-Watanabe[e]
0.9693	0.78349				
1.00	0.69626[f]				
1.10	0.48010				
1.15	0.40092				
1.20	0.33589[f]			0.34936	0.33842
1.25	0.28203				
1.30	0.23712	0.2462	0.24063	0.24906	0.23995
1.40	0.16815[f]	0.1755	0.16942	0.17816	0.17181
1.45	0.14157				
1.50	0.11902	0.1257	0.11971	0.12769	0.12425
1.60	0.08371[f]				
1.65	0.06982				
1.70	0.05787				
1.80	0.03893				
1.90	0.02475				
2.00	0.01420[f]				
2.055	0.00962				

[a] 87-term electronic wave function.

[b] Reference 2.

[c] Reference 3.

[d] Reference 4.

[e] Reference 7.

[f] Obtained by interpolating on R.

Table I. Since, from Fig. 1, this is the region of the extreme tails of $f_J(R)$, our values of $\langle q'(R)\rangle_J$ given in Table II are independent of any reasonable extrapolation. Our values of $\langle q'(R)\rangle_J$ are also essentially independent of interpolation errors; the maximum change in $\langle q'(R)\rangle_J$ brought about by deleting any one of the 12 calculated values of $q'(R)$ in Table I was 3×10^{-5}.

As can be seen in Fig. 1, $q'(R)$ weights $R<R_e \cong 1.4$ a.u. more heavily than $R>R_e$, and the form of the vibrational wave function, owing to anharmonicity, does the opposite. The anharmonicity is the larger effect and $\langle q'(R)\rangle_J$ is reduced by about 1% from the equilibrium value; compare $q'(1.4)$ in Table I with the $\langle q'(R)\rangle_J$ values in Table II.

The physical constants we used are those of Taylor, Parker, and Langenberg.[30] In particular in Eq. (23) we used $2\mu = 1836.109$, 2447.74, and 3670.4 a.u. for H_2, HD, and D_2, respectively.

If, in the vibrational averaging the nuclear correction $H'_{00}(R)$ is omitted and only the Born–Oppenheimer potential is used, then $\langle q'(R)\rangle_J$ for the 87-term case is 0.16636, 0.16671, and 0.16548 a.u. for HD($J=1$), $D_2(J=1)$, and $D_2(J=2)$, respectively.

B. Quadrupole Moment

Values of the electric quadrupole moment of the deuteron, Q, given in Table III were obtained from Eq. (7) and the corresponding field gradients in Table II using the experimental quadrupole-interaction constants eqQ/h of 224.540(60),[13] 225.044(24),[14] and 223.380(180)[14] kHz for HD ($J=1$), D_2 ($J=1$), and D_2 ($J=2$), respectively.

In Table III one sees at once that as the basis enlarges, Q evidently converges. There is also good agreement among values of Q obtained from different isotopic forms of the hydrogen molecule. Moreover, if the dissociation energies in Table II are used as a rough indication of the accuracy of the corresponding electronic wave functions and the error estimates in Table III are ignored, then the earlier results obtained with less accurate wave functions are not in disagreement with ours. This will be further discussed in Sec. IV D.

Neglecting $H'_{00}(R)$ and using only the Born–Oppenheimer potential for vibrational averaging yields $Q = 0.2873\times10^{-26}$ cm^2, which can be compared with the value of 0.2875×10^{-26} cm^2 in Table III.

C. Magnetic Spin-Spin Interaction

Contained within $\langle q'(R)\rangle_J$ is $\langle R^{-3}\rangle_J$. Our values for the latter quantity in another form are given in Table IV. Code and Ramsey[14] calculated $\langle (R/R_e)^{-3}\rangle$ using Raman spectra as observed by Stoicheff[31] and the Dunham-theory[32] approach of Schlier[33] and Herman and Short.[34] Stoicheff's[31] $R_e = 0.74173(6)$ Å was used to obtain the "experimental" values given

TABLE II. Comparison of field gradients averaged over the ground vibrational state.

Source (Ref.)	Parameters in ψ	D_e (a.u.)	HD($J=1$)	$\langle q'(R)\rangle_J$ (a.u.)[a] $D_2(J=1)$	$D_2(J=2)$
Nordsieck (2)	2	0.149	0.1768	0.1763	···
Ishiguro (3)	7	0.157	0.1729	0.1723	···
Newell (4)	6	0.168	0.1745	0.1749	···
Narumi–Watanabe (7)	11	0.17301	0.17086[b]	0.17116[b]	···[b]
Auffray (6)	10[c]	0.17376	···	0.1698[d]	···
This work	34	0.17432	0.16485	0.16525	0.16402
This work	66	0.1744712	0.16621	0.16662	0.16539
This work	87	0.1744721	0.16620	0.16660	0.16538
Kolos–Wolniewicz (27)	···	0.1744750	···	···	···

[a] For estimated errors see the corresponding quadrupole moments in Table III and the text.

[b] As reported in Ref. 7. See Ref. 28.

[c] Reference 29.

[d] Inferred from the value of the quadrupole moment reported in Ref. 6.

TABLE III. Values of the quadupole moment of the deuteron obtained from field-gradient calculations and experimental interaction constants.

Source (Ref.)		Q (10^{-26} cm^2)[a] HD($J=1$)	 D_2($J=1$)	 D_2($J=2$)	Weighted average
Nordsieck (2)		0.2703	0.2716	...	0.2714 ± 0.005[b]
Ishiguro (3)		0.2764	0.2779	...	0.2777 ± 0.006[b]
Newell (4)		0.2738	0.2738	...	0.2738 ± 0.002[b]
Narumi–Watanabe (7)		0.27967[c]	0.28011[c]	2.8003[c]	0.2800 ± 0.0005[b]
Auffray (6)		...	0.282	...	0.282 ± 0.001[d]
This work:	34 terms	0.28985	0.28979	0.28980	0.2898
	66 terms	0.28748	0.28741	0.28741	0.2874
	87 terms	0.28749	0.28745	0.28743	0.2875 ± 0.002

[a] The quadrupole-interaction constants used are those of Refs. 13 and 14. Values of Q for the first three authors in the table were altered to conform with these constants.

[b] Nominal error estimate by the corresponding author. Accuracy of these error estimates is discussed in the text.

[c] Corrected values. See Ref. 28.

[d] Reference 15.

in Table IV for rough comparison. For the H_2 ($J=1$) case Herman and Short[34] use the data of Foltz *et al.*[35] and apply corrections to the theory to obtain $\langle R^{-3}\rangle^{-1/3} = 0.74695(3)$ Å.

Another observable obtainable from the vibrational wave functions is the nuclear magnetic spin-spin interaction constant[36] d'_m, which in first-order perturbation theory is proportional to $\langle R^{-3}\rangle$. With Ramsey's[37] definition of the proportionality constant it is

$$d'_m = 2\mu_a\mu_b\langle R^{-3}\rangle/5hI_aI_b\,, \tag{26}$$

where μ_a and I_a are the magnetic moment and spin of nucleus a, and similarly for b. Values of d'_m which follow from our $\langle R^{-3}\rangle^{-1/3}$ values of Table IV are given in Table V. For the deuteron we took Wimett's[38] μ_D/μ_p ratio.

The H_2 ($J=1$) case appears anomalous; however, some approximations are made in the experimental analysis[12] and small deviations from the expression for d'_m in Eq. (26) are to be expected. Ramsey[39,40] has examined the effect of electron coupling.

In general, the agreement between our calculated values in Tables IV and V and experiment is satisfactory, and with the slight exception of H_2, the adiabatic results are superior to the Born–Oppenheimer.

TABLE IV. Expectation values of R^{-3} in ground vibrational states.

State	BO[a]	$\langle R^{-3}\rangle^{-1/3}$ (Å) Adiabatic	From experiment[b]
H_2($J=1$)	0.74676	0.74696	0.74683(6)[c]
HD($J=1$)	0.74590	0.74605	0.74601(6)[c]
D_2($J=1$)	0.74494	0.74505	0.74509(6)[c]
D_2($J=2$)	0.74609	0.74619	0.74625(6)[c]

[a] Calculated in the Born–Oppenheimer approximation, in which $H'_{00}(R)$ is neglected.

[b] Calculated from Stoicheff's Raman spectra (Ref. 31) by Code and Ramsey (Ref. 14). See text.

[c] Minimal error, assigned by us, corresponding solely to Stoicheff's stated error (Ref. 31) in R_e for H_2.

In odd rotational states of the D_2 molecule—in particular, for the D_2 ($J=1$) case—matrix elements of eqQ/h and d'_m are proportional; only the combination

$$d = eqQ/10h + d'_m \tag{27}$$

is observable. If one used our value for d'_m from Table V and $d = 25.2414(14)$ kHz, as found by Code and Ramsey,[14] in Eq. (27), then $eqQ/h = 225.037$ kHz, with an error of at least 0.014 kHz. This is directly comparable with the value 225.044(24) kHz given by Code and Ramsey. We ignore this small difference.

D. Errors

Given the error assignments by previous workers, the quadrupole-moment values in Table III are in striking disagreement.[15] For example, our result for Q differs from that of Narumi and Watanabe[7] by 15 times their stated error and from Auffray[6] by 5.5 times his error.

Code and Ramsey[14] have pointed out that a test,

TABLE V. Comparison of calculated and observed magnetic spin-spin interaction constants in ground vibrational states.

State	BO[a]	d'_m (kHz) Adiabatic	Experiment
H_2($J=1$)	115.382	115.289	115.342(48)[b]
HD($J=1$)	17.773	17.762	17.761(12)[c]
D_2($J=1$)	2.7388	2.7377	2.737(1)[d]
D_2($J=2$)	2.7261	2.7250	2.725(14)[d]

[a] Born–Oppenheimer approximation; $H'_{00}(R)$ neglected.

[b] Harrick *et al.* (Ref. 12).

[c] Quinn *et al.* (Ref. 13).

[d] Code and Ramsey (Ref. 14).

TABLE VI. Comparison of "equivalent" quadrupole-interaction constants with experiment.

Source	eqQ/h (kHz) HD($J=1$)	 D_2($J=2$)
Narumi–Watanabe[a]	224.892(80)[b]	223.442(50)[b]
This work; 87 terms	224.504(24)[c]	223.396(24)[c]
Experiment	224.540(60)[d]	223.380(180)[e]

[a] Reference 7.

[b] Code and Ramsey (Ref. 14). Their error assignment includes observational error and the uncertainty in the calculated ratios of the average electric field gradients.

[c] Minimal error corresponding solely to the experimental error in eqQ/h for $D_2(J=1)$.

[d] Quinn *et al.* (Ref. 13).

[e] Reference 14.

primarily of the R dependence of $q'(R)$ but partly also of the averaging procedure, can be made by using the experimental quadrupole-interaction constant for the most accurate case, D_2 ($J=1$), and ratios of vibrationally averaged field gradients to calculate "equivalent" interaction constants for HD ($J=1$) and D_2 ($J=2$). The comparison is made in Table VI.

The failure of the Narumi–Watanabe field gradient seen in Table VI can be traced back to the fact that the James–Coolidge molecular wave function[25] has the same value of the nonlinear parameter, α in the notation of our Eq. (12), at each of the four values of R used by Narumi and Watanabe. We find that the field gradient is more sensitive to improperly optimized α than is E^0, and that holding α fixed introduces spurious oscillations in $q'(R)$.

From Table VI we conclude that the R dependence of our field gradient is in agreement with experiment and that nonadiabatic effects are not, here, being observed. From this and our earlier-mentioned sources of error we believe that, given our form for the molecular wave function, the process of extracting the quadrupole moment produces an error of less than 0.0002×10^{-26} cm^2.

On the other hand, the largest uncertainty in our field gradient may well arise from the fact that our electronic wave function is not exact; we work within a truncated Hilbert space. Our dissociation energy, $D_e = 0.1744721$ a.u. at $R = 1.4$ a.u., differs from that of Kolos and Wolniewicz[18] by 0.1 cm^{-1}, and this difference is approximately constant at points where comparison was possible within the range of R that we have considered. Consequently, our dissociation energy D_0 for the hydrogen molecule, after relativistic corrections[17,41] obtained from the Breit equation and radiative corrections,[42] is[43] 36117.3 cm^{-1}, which is 0.1 cm^{-1} less than that of Kolos and Wolniewicz[18] and in agreement[44] with the experimental bounds of Herzberg[27]: $36116.3 < D_0 < 36118.3$ cm^{-1}. However, since D_e is obtained variationally, it is a lower bound. Using the value 0.1744750 a.u. of Kolos and Wolniewicz,[18] we assume that our D_e is 2.9×10^{-6} a.u. too small.

By varying all parameters in the 87-term electronic wave function of Eq. (11) we find that the maximum possible change in Q consistent with a decrease in D_e if 2.9×10^{-6} a.u. is approximately 0.004×10^{-26} cm^2.[45] We take one-half of this for our estimated error.

In earlier work simpler wave functions were used and more approximate approaches to vibrational averaging. But the main source of disagreement in quadrupole moments is in the earlier error estimates. Assuming that our error scales like $\sqrt{\delta}$, where δ is the dissociation energy error, we obtain the estimates given in Table VII corresponding to earlier values of Q. The authors' errors in the last column are repeated from Table III for comparison here. Clearly they are, without exception, too small.

Briefly, Nordsieck[2] and Newell[4] based their errors on comparisons of their electronic charge density with rough estimates of that of the James–Coolidge[25] wave function, assuming negligible er-

TABLE VII. Values of the quadrupole moment of the deuteron with errors estimated in this work.

Source (Ref.)		Error[a] in D_e (a.u.)	Q (10^{-26} cm^2)	Authors' estimated error in Q (10^{-26} cm^2)
Nordsieck (2)		0.025	0.271 ± 0.19[b]	± 0.005
Ishiguro (3)		0.017	0.278 ± 0.16[b]	± 0.006
Newell (4)		0.0065	0.274 ± 0.095[b]	± 0.002
Narumi–Watanabe (7)		0.0015	0.280 ± 0.045[b]	± 0.0005
Auffray (6)		0.00072	0.282 ± 0.031[b]	± 0.001[c]
This work:	34 terms	0.00016	0.2898 ± 0.015	...
	66 terms	0.0000038	0.2874 ± 0.0023	...
	87 terms	0.0000029	0.2875 ± 0.0020	± 0.002

[a] Difference of D_e from that of Kolos and Wolniewicz (Ref. 18).

[b] Obtained from the 87-term error estimate by assuming that it scales as the square root of the error in D_e.

[c] Reference 15.

ror in that wave function. Ishiguro[3] used Nordsieck's error. Narumi and Watanabe,[7] who used the James–Coolidge wave function, considered *only* the error involved in interpolating and extrapolating their four values of $q'(R)$. In contrast, James and Collidge estimated errors in their ψ^2 or expectation values using their ψ to be about 8–10%.

From Table VII one observes that not only is our result for Q consistent with earlier work but also the consistency would remain even if our error were reduced by a factor of, say 5. We let it stand; the error remains only an estimate.

V. CONCLUSIONS

Our field gradients appear to converge as the size of the basis increases and the dissociation energy approaches experiment. Values of the deuteron's quadrupole moment obtained from different isotopes of the hydrogen molecule and different rotational states are in good agreement.

The theoretical results sketched in Sec. II involve approximations. In that connection, on a cruder level, we note that problems which can arise in the transformation of atomic orbitals from one center to another, where the field gradient is evaluated,[46] are absent in our approach, and that Sternheimer corrections[47] do not apply, since we have included effects due to all electrons.

Although no particular attempt was made to optimize the dissociation energy, our value is less than the best value known by 0.1 cm^{-1}, which, for perspective, is half the radiative corrections in H_2. Nevertheless, we estimate an error of about 0.7% in Q due to the possible omission of unknown components in the molecular electronic wave function relatively much more important for Q than for the Hamiltonian.

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APPENDIX A: MATRIX ELEMENTS OF H^0

Minimization of the Rayleigh quotient leads immediately to the eigenvalue problem

$$(H^0 - E^0 S)\psi = 0, \tag{A1}$$

where $S_{ij} = \langle \Phi_i | \Phi_j \rangle$ and $H^0_{ij} = \langle \Phi_i | H^0 | \Phi_j \rangle$ define the overlap and Hamiltonian matrices in Eq. (A1) and we abbreviate the indices on the basis functions of Eq. (12). Following Ruedenberg[48] and Kolos and Roothaan,[49] S_{ij} and H^0_{ij} were expressed in terms of the primitive integrals

$$K^{\mu}_{mprs} = \int dV_1 dV_2 (\xi_1^2 - \eta_1^2)^{-1} \times \xi_1^m \eta_1^p \xi_2^r \eta_2^s r_{12}^{\mu} e^{-2\alpha(\xi_1+\xi_2)}. \tag{A2}$$

Except for the misprint we have noted in connection with Ref. 49, our expressions can be cast in the form of those of Kolos and Roothaan.[49]

The primitive integrals of Eq. (A2) can be done analytically for even μ, and for μ odd are reducible to integrals of the form

$$\Phi^L_{rs}(z) = \int_1^\infty d\xi\, (\xi^2 - 1)^{-1} f_r^L(\xi, z) f_s^L(\xi, z), \tag{A3}$$

where

$$P_L(\xi) f_r^L(\xi, z) = \int_1^\xi dt\, t^r P_L(t)\, e^{-zt}. \tag{A4}$$

Except for another misprint we have noted in connection with Ref. 50 we agree with Kolos and Roothaan.[50]

$\Phi^L_{rs}(z)$ was evaluated by 64-point Gaussian quadrature[51] after expressing the integral of Eq. (A4) as a linear combination of terms of the form

$$\begin{aligned} g_n(\xi, z) &= \int_1^\xi dt\, t^n e^{-zt} \\ &= [n g_{n-1}(\xi, z) + e^{-z} - \xi^n e^{(-z\xi)}]\, z^{-1} \\ &= \sum_{m=0}^{\infty} \frac{(-z)^m (\xi^{n+m+1} - 1)}{(n+m+1)\, m!}\, . \end{aligned} \tag{A5}$$

We used the recursion relation for $z(\xi - 1) \geq 5$ and the power series otherwise.

APPENDIX B: FIELD-GRADIENT MATRIX ELEMENTS

As described in Sec. III B, the chief problems in evaluating the $\langle i | V'' | j \rangle$ reside in the $B_{ij}(\alpha)$ with $\mu_i + \mu_j$ odd. Our approach to these is outlined here.

Working from the right, F_{ij} of Eq. (19) is first expressed as

$$\begin{aligned} F_{ij}(\xi_1, \eta_1, \alpha) = \int_1^\infty d\xi_2 \int_{-1}^1 d\eta_2 (\xi_2^2 - \eta_2^2) \\ \times e^{(-2\alpha\xi_2)} \Lambda_{ij}(\xi_1, \eta_1, \xi_2, \eta_2) \\ \times \lambda(\xi_1, \eta_1, \xi_2, \eta_2, \mu_i + \mu_j), \end{aligned} \tag{B1}$$

where, suppressing the coordinates,

$$\lambda(\mu_i + \mu_j) = (2\pi)^{-2} \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2\, \rho^{\mu_i + \mu_j} \tag{B2}$$

and, using the notation

$$[m, p, r, s] = \xi_1^m \eta_1^p \xi_2^r \eta_2^s + \xi_1^r \eta_1^s \xi_2^m \eta_2^p, \tag{B3}$$

$$\begin{aligned} \Lambda_{ij} = [m_i + m_j, p_i + p_j, r_i + r_j, s_i + s_j] \\ + [m_i + r_j, p_i + s_j, r_i + m_j, s_i + p_j]. \end{aligned} \tag{B4}$$

In Eq. (B2) one can use

$$\rho = [T - S\cos(\phi_1 - \phi_2)]^{1/2}, \tag{B5a}$$

$$T = \xi_1^2 + \eta_1^2 + \xi_2^2 + \eta_2^2 - 2 - 2\xi_1\eta_1\xi_2\eta_2, \tag{B5b}$$

$$S = 2[(\xi_1^2 - 1)(1 - \eta_1^2)(\xi_2^2 - 1)(1 - \eta_2^2)]^{1/2} \tag{B5c}$$

to obtain[52]

$$\lambda(1) = (2/\pi)(T + S)^{1/2} E(k), \tag{B6a}$$

$$\lambda(3) = (2/3\pi)(T + S)^{1/2}[4TE(k) + (S - T)K(k)], \tag{B6b}$$

where $K(k)$ and $E(k)$ are complete elliptic integrals of the first and second kind and

$$k^2 = 2S/(S+T). \tag{B7}$$

F_{ij} was then evaluated by means of crossed 12-point Gauss and Gauss-Laguerre quadratures after using approximations for $E(k)$ and $K(k)$ due to Cody,[53] with an absolute error of less than 10^{-11}, to achieve an explicit realization of the coordinate dependence of λ.

The remaining integration, that of Eq. (18), was broken down into ones over three regions. The area $1 \leq \xi_1 \leq 1.4$ and $-1 \leq \eta_1 \leq -0.8$, which contains the singular point, was treated by constructing a two-dimensional quadrature[54] using W from Eq. (15) as weight function, a locally quadratic approximation to F_{ij}, and the indefinite integrals

$$\int d\xi \int d\eta W(\xi, \eta) \xi^i \eta^j \quad \text{for} \quad i, j = 0, 1, 2.$$

Seventeen points were used on ξ and nine on η. Integration over $1 \leq \xi_1 \leq 1.4$ and $-0.8 \leq \eta$ was done with crossed 8×12 Gauss quadratures and that over $1.4 \leq \xi_1$ with crossed 14×12 Gauss and Gauss-Laguerre quadratures.

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Two-Photon Emission of X Rays

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Two-photon emission from heavy elements with a single K-shell vacancy (e.g., Cu^+) is considered. Simple closed-form expressions are given for the spontaneous, singly stimulated, and doubly stimulated two-photon emission rates. The material parameters relevant to these two-photon processes are shown to be the one-photon absorption cross sections and oscillator strengths.

I. INTRODUCTION

We describe here a simple theory of the decay of a K-shell vacancy in heavy elements such as Cu by the process of two-photon emission.[1] Spontaneous, singly stimulated, and doubly stimulated processes are considered. We show that with suitable approximations the matrix elements describing the material parameters important to the two-photon emission process can be obtained from those describing one-photon emission and absorption. This permits us to obtain simple closed-form expressions which contain only known material parameters. The close relationship between corresponding linear (one-photon) and nonlinear (two-photon) processes is similar to that found previously,[2–4] and appears to be characteristic of the x-ray region. Since the two-photon emission rate is found to be comparatively intense, $\sim 10^{-6}$ the one-photon rate, there exists the possibility of experimentation.

Two-photon absorption and emission by atomic hydrogen[5] and by heavy hydrogenic ions[6] have received very considerable attention. Although inner-shell electrons are often considered to be hydrogenic in nature, this important body of work—which provides the necessary background to our present treatment—cannot simply be applied to many-electron ions. The reason is that the sets of intermediate states available to an L-shell electron in atomic hydrogen, for example, are very different from those which are available in Cu. These distinctions are made more apparent later when the similarities and differences between the two kinds of systems are discussed.

The model we use here is that of a single electron moving in some effective spherical potential. It is supposed that this potential reproduces the set of energy levels which are available to the electron. Such a description considers only the existence of single-particle excitations and is thus equivalent to a representation of the wave function in terms of a single Slater determinant. We explicitly neglect electron spin, since we assume that two-photon emission accompanied by a spin flip is a weaker process than one in which no spin flip is required.[7]

In order to be specific, we treat the case of a Cu^+ ion with a single K-shell vacancy, and consider the process of two-photon emission by an L-shell electron dropping down to fill this vacancy. The initial state of the system is thus an electron in the L shell and a hole in the K shell, while in the final state the position of the electron and hole are reversed. The energy levels available to the electron are shown in Fig. 1. While we treat an isolated ion, we consider our results to be applicable to solid copper. The reason for this is that the deep K- and L-shell electrons are not much affected by the presence of other atoms, while the