Hyperfine structure of the first rotational level in H\textsubscript{2}, D\textsubscript{2} and HD molecules and the deuteron quadrupole moment

Mariusz Puchalski and Jacek Komasa
Faculty of Chemistry, Adam Mickiewicz University, Uniwersytetu Poznańskiego 8, 61-614 Poznań, Poland

Krzysztof Pachucki
Faculty of Physics, University of Warsaw, Pasteura 5, 02-093 Warsaw, Poland
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We perform the four-body calculation of the hyperfine structure in the first rotational state \( J = 1 \) of the H\textsubscript{2}, D\textsubscript{2}, and HD molecules and determine the accurate value for the deuteron electric quadrupole moment \( Q_d = 0.285\,699(15)\) fm\textsuperscript{2} in significant disagreement with former spectroscopic determinations. Our results for the hyperfine parameters agree very well with the currently most accurate molecular-beam magnetic resonance measurement performed several decades ago by N.F. Ramsey and coworkers, and indicate the significance of previously neglected nonadiabatic effects. Moreover, a very good agreement with the recent calculation of \( Q_d \) based on the chiral effective field theory, although being much less accurate, indicates the importance of spin dependence of nucleon interactions in accurate description of nuclei.

Precise atomic and molecular spectroscopy provides information on the nuclear electromagnetic moments important for testing theories of nuclear interactions \([1-5]\) or even for searching for new physics \([6]\). This, however, requires a thorough understanding of the variety of interparticle interactions in atoms and molecules. For instance, the proton mean square charge radius has been extracted with unprecedented accuracy from the muonic hydrogen Lamb shift \([7]\) only after careful analysis of all the important quantum electrodynamical effects. A similar determination has recently been performed for the alpha particle from the corresponding measurement in muonic helium \([8]\). Regarding nuclear magnetic moments, the direct measurement in a Penning trap was performed only for the proton \([9]\), while magnetic moments of heavier stable nuclei have been determined by the nuclear magnetic resonance (NMR) or the atomic hyperfine splitting measurements. Accordingly, the currently most accurate magnetic moments of deuteron and triton were determined by combining the NMR measurements with precise calculations of the molecular shielding factor \([10]\). Concerning determination of nuclear magnetic moments from the hyperfine splitting, its accurate calculation is particularly difficult due to a large contribution from the not well known spin-dependent nuclear structure.

The widely accepted Bohr-Weiskopf correction only partially accounts for the nuclear effects \([11]\). A clear indication of this problem is a strong and still unexplained discrepancy for the Zemach radius of \(^6\)Li between the nuclear model value \([12]\) and the result based on the spectroscopic data of the lithium atom \([13]\), which has recently been confirmed by independent measurements and calculations in the Li\textsuperscript{+} ion \([14, 15]\).

In this work we investigate the electric quadrupole moment \( Q_d \) of the deuteron on the basis of the hyperfine splitting in HD and D\textsubscript{2} molecules. The total electron spin of such a two-electron system is zero, and the strengths of all couplings among nuclear spins and the rotational angular momentum are of the same order of magnitude. Therefore, \( Q_d \) can be extracted from the molecular hyperfine splitting with an accuracy that is limited only by the measurement uncertainty provided that sufficiently accurate theoretical calculations with all significant contributions are available.

The recent determinations of \( Q_d = 0.285\,98(3) \) fm\textsuperscript{2} \([16]\) and \( Q_d = 0.285\,783(30) \) fm\textsuperscript{2} \([17]\) considered to be the most accurate value to date \([18]\), neglect or underestimate nonadiabatic effects, i.e. the effects beyond the commonly employed Born-Oppenheimer (BO) approximation. Indeed, these results disagree with the recommended value reported in this work (see Eq. \([24]\)) obtained in the nonadiabatic approach, i.e. without separation of nuclear and electronic motions.

In the following we describe shortly the theory of the molecular hyperfine splitting, its accurate calculations with nonadiabatic wave functions, and the determination of \( Q_d \) from Ramsey and coworkers measurements. Henceforth, we use the original notation by Ramsey \([19, 20]\).

Hyperfine Hamiltonian.— There are three angular momenta in the ground electronic state of the heteronuclear HD molecule, which all couple to each other—the proton spin \( \vec{I}_p \), that of the deuteron \( \vec{I}_d \), and the rotational angular momentum \( \vec{J} \). The effective Hamiltonian describing these interactions reads

\[
H_{\text{hfs}} = -c_p \vec{I}_p \cdot \vec{J} - c_d \vec{I}_d \cdot \vec{J} + \frac{5 d_1}{(2 J + 1)(2 J + 3)} \left[ \frac{3}{2} (\vec{I}_p \cdot \vec{J}) (\vec{I}_d \cdot \vec{J}) + 3 \vec{I}_d \cdot \vec{J} (\vec{I}_p \cdot \vec{J}) - (\vec{I}_p \cdot \vec{I}_d) \vec{J}^2 \right]
+ \frac{5 d_2}{(2 J + 1)(2 J + 3)} \left[ 3 (\vec{I}_d \cdot \vec{J})^2 + \frac{3}{2} (\vec{I}_d \cdot \vec{J}) - \vec{I}_d^2 \vec{J}^2 \right].
\]

The above coefficients \( c_p, c_d, d_1, \) and \( d_2 \) are related, respectively, to the interactions between the following: the proton spin and molecular rotation, the deuteron spin and rotation, the proton and deuteron spins, and the electric quadrupole moment of the deuteron with the electric field gradient \([21]\). For homonuclear molecules with odd \( J \) the effective Hamiltonian
and the spin-rotation coefficient is
\[ d_1 = - \frac{1}{5} \langle \phi^i | Q_{ij}^{AB} | \phi^j \rangle \] (11)

The omitted part of the spin-spin interaction, proportional to \( \delta^3 r_{AB} \), is negligibly small.

The interaction of a particle with the charge \( e \), possessing the electric quadrupole moment \( Q^{ij} \) with the gradient of the electric field, is given by
\[ \delta H = - \frac{e}{6} Q^{ij} \partial_j E^i. \] (12)

For a particle with a definite spin \( I \geq 1 \), the \( Q^{ij} \), as a traceless and symmetric tensor, can be expressed in terms of a single scalar electric quadrupole moment \( Q \) defined by
\[ Q^{ij} = \frac{Q}{I(I-1)} \left( \frac{3}{2} I^i I^j + \frac{3}{2} I^j I^i - \delta^{ij} I^2 \right). \] (13)

Referring to Eq. (1), the Ramsey’s constant \( d_2 \) becomes (in atomic units)
\[ d_2 = -\alpha^2 \frac{Q q}{5 \hbar^2}, \] (14)
where
\[ q = \left( \phi^i \frac{\partial^2 V}{\partial r_A^i \partial r_A^j} - \frac{\delta^{ij}}{3} \frac{\partial^2 V}{\partial r_A^i \partial r_A^j} \right) \phi^j \] (15)
is the electric field gradient at the nucleus \( A \), \( V \) is the Coulomb potential of Eq. (18), and \( \hbar \) is the reduced Compton wavelength of the electron.

Numerical calculations.—The nonadiabatic wave function \( \Psi \) is obtained from the variational principle with the following nonrelativistic Hamiltonian for the hydrogen molecule
\[ H = T + V, \] (16)
where (in atomic units)
\[ T = \frac{\mu_A r_A^2}{2 m_A} + \frac{\mu_B r_B^2}{2 m_B} + \frac{\mu_e r_e^2}{2}, \] (17)
and
\[ V = \frac{1}{r_{AB}} - \frac{1}{r_{A1}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}} - \frac{1}{r_{B2}} + \frac{1}{r_{12}}. \] (18)

Here, indices \( A, B \) and 1, 2 denote nuclei and electrons, respectively. The nuclear masses are those currently recommended by CODATA [22]. The wave function \( \Psi \) depends on four particle coordinates \( \Psi = \Psi (r_A, r_B, r_1, r_2) \).

In the center of mass frame the total momentum vanishes \( \vec{p}_A + \vec{p}_B + \vec{p}_1 + \vec{p}_2 = 0 \), and thus we may assume that the wave function \( \Psi \) depends only on the coordinate differences.

In the variational approach the wave function is represented as a linear combination
\[ \Psi = \sum_k c_k \psi_k (r_A, r_B, r_1, r_2), \] (19)
of properly symmetrized basis functions

\[ \psi_k = (1 \pm P_{A \leftrightarrow B}) (1 + P_{1 \leftrightarrow 2}) \phi_k(\vec{r}_A, \vec{r}_B, \vec{r}_1, \vec{r}_2), \]  

(20)

where \( P_{A \leftrightarrow B} \) is the particle exchange operator. In the \( J = 1 \) state of \( \text{H}_2 \) and \( \text{D}_2 \) the wave function is antisymmetric with respect to the exchange of nuclear spatial variables and symmetric in electronic spatial variables, whereas in the heteronuclear \( \text{HD} \) molecule, only electronic symmetry is imposed, and both (nuclear) symmetric and antisymmetric basis functions are employed. For \( J = 1 \) the functions \( \phi_k \) in Eq. (20) are the nonadiabatic explicitly correlated Gaussians (naECG) of the form

\[ \phi_k = r^j r^n_{AB} \times e^{-a_{k,1} r^2_{AB} - a_{k,2} r^2_{A1} - a_{k,3} r^2_{A2} - a_{k,4} r^2_{B1} - a_{k,5} r^2_{B2} - a_{k,6} r^2_{12}}, \]  

(21)

where \( r^j \) (or \( r^i \)) is the factor representing the angular momentum \( J = 1 \), and is either \( r^j_{AB}, r^j_{A1}, r^j_{A2}, r^j_{B1}, r^j_{B2} \) or \( r^j_{12} \). The nonlinear \( a_k, j \) parameters are optimized individually for each basis function \( \phi_k \). The powers \( n \) of the internuclear coordinate \( r_{AB} \), needed to represent accurately the vibrational part of the wave function, are restricted to even integers and are generated randomly for each basis function from the log-normal distribution within the limited \( 0 \rightarrow 80 \) range. Moreover, the number of basis functions with particular prefactor \( r^n_{AB} \) is subject to additional discrete optimization. As a result, the nonrelativistic energy reaches an accuracy of about \( 10^{-11} \) (see Table I).

Hyperfine parameters.—The hyperfine parameters for the hydrogen molecule isotopologues obtained with the above wave function are presented in Table I. The numerical convergence for the spin-orbit couplings \( c_p \) and \( c_d \) is relatively slow, and the resulting numerical uncertainties are not negligible. Most importantly, their difference from BO values fits within the uncertainties, which indicates that the estimation of the magnitude of nonadiabatic effects by the ratio of the electron mass to the nuclear reduced mass is correct. Moreover, the nonadiabatic and BO values are, within uncertainties, in perfect agreement with the Ramsey measurements.

In contrast, the numerical convergence of \( d_1 \) and \( q \) parameters is very fast, and the corresponding inaccuracy is negligible compared to the uncertainty due to unknown higher order relativistic and QED effects. Again, the difference with BO values is consistent with the estimate of nonadiabatic effects, represented as an inaccuracy of the BO values. We also note that the nonadiabatic \( d_1 \) for HD agrees with Ramsey’s measurements up to its uncertainty, while for \( \text{H}_2 \) it fits within \( 1.2 \sigma \). Regarding the \( q \) parameter, fast numerical convergence of the gradient of the electric field enables six significant digits to be quoted. Our recommended nonadiabatic value of

\[ q = 0.335 \pm 0.002 \text{ a.u.} \]  

(22)

obtained for \( \text{D}_2 \) will be used in the next paragraph for the determination of the deuteron quadrupole moment \( Q_d \). We note that this value differs by \( 0.0006 \text{ a.u.} \) from \( q = 0.33466 \) a.u. obtained in the pioneering nonadiabatic calculations by Bishop and Cheung [30]. This difference is relatively large and shows that the former results in [30] are not accurate enough to draw definite conclusions about the magnitude of the nonadiabatic effects.

The quadrupole moment of deuteron.—\( Q_d \) can be determined most accurately from the coupling constant \( d \) measured by the molecular-beam magnetic resonance method by Code and Ramsey [26] for \( \text{D}_2 \) in the first rotational level. We obtain \( d_2 \) from the difference \( d_2 = d_1 - d \) of calculated \( d_1 \) and measured \( d_\) . Finally, we evaluate the quadrupole moment from

\[ Q_d = -\frac{d_2}{2Ryc} \frac{10\alpha^2}{\alpha^2 q} \]  

(23)

obtaining the recommended value of

\[ Q_d = 0.285699(15)(18) \text{ fm}^2. \]  

(24)

Results of such calculations are summarized in Table II. A comparison with literature data reported within the last fifty years is presented in Table II and Fig I. The first uncertainty assigned to our \( Q_d \) is due to unknown higher order relativistic and QED corrections to \( q \), which are estimated by a relative factor \( \alpha^2 \), the second uncertainty comes from the measurement of \( d \), while numerical uncertainties are negligible. This nonadiabatic \( Q_d \) is in agreement with our BO value [23], relative uncertainty of which was estimated by the ratio of the electron mass to the nuclear reduced mass, but is in significant disagreement with the recent most accurate determination by Pavanello et al. [17] and Jóźwiak et al. [16] (see Tab. II and Fig I). However, it is in agreement with the revised result by Bishop, quoted in 1983 by Ericson et al. [3], which served for a long time as a reference value for \( Q_d \). Comparison of our result with recent literature data indicates the significance of nonadiabatic effects and also draws attention to the need for correct use of BO potential, as the above mentioned results [16, 17, 23] differ with each other due to different potentials used to average the \( q \) parameter. In order to verify our result, we used the obtained value of \( Q_d \) to evaluate the \( d_2 \) parameter for the HD molecule in \( J = 1 \) state, and we achieved a perfect agreement with \( d_2 \) as measured by Ramsey et al. [25] (see Table II).

![FIG. 1. Comparison of literature data for \( Q_d \).](image)
et al. only very recently Filin et al. [3] reported potential model (see e.g. [3] and references therein), but deuterium hyperfine splitting, where significant discrepancies clear structure effects in atomic spectra, particularly in muonic good agreement with our result. This agreement opens the deed, for a long time, can serve as a benchmark for the nuclear structure theory. In- precise atomic and molecular structure calculations but also periodic table [18]. This accurate result can be used not only in mined with the highest accuracy among all nuclei in the peri-

\[ E_c \approx 2.5 \times 10^{-5} \]

\[ \alpha = \text{the fine structure constant.} \]

Summary.— The deuteron quadrupole moment \( Q_d \) is determined with the highest accuracy among all nuclei in the periodic table [18]. This accurate result can be used not only in precise atomic and molecular structure calculations but also can serve as a benchmark for the nuclear structure theory. Indeed, for a long time, \( Q_d \) could not be reproduced by any modern potential model (see e.g. [3] and references therein), but only very recently Filin et al. [31] reported \( Q_d = 0.285 \pm 0.018 \) \( \text{fm}^2 \) obtained from chiral effective field theory (\( \chi \text{EFT} \)), in very good agreement with our result. This agreement opens the possibility of better understanding of the spin dependent nuclear structure effects in atomic spectra, particularly in muonic deuterium hyperfine splitting, where significant discrepancies with the measurement [34] have been reported [35].

Apart from the deuteron quadrupole moment, by accounting for nonadiabatic effects, we obtained all the other hyperfine constants in very good agreement with Ramsey’s molecular beam magnetic resonance measurements, see Table I. However, current theory includes only the leading relativistic effects. Because the inclusion of higher order relativistic and QED corrections is certainly within reach, more accurate measurements are desirable. This may open new windows for high-precision tests of fundamental interactions on the molecular scale.

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| Basis  | State | \( E \) (in a.u.) | Parameters | \( d = d_1/2 \) (in kHz) |
|--------|-------|-----------------|------------|--------------------------|
| 512    |       | 112.39316       |            | 57.643938 90475          |
| 1024   |       | 113.88980       |            | 57.643937 92923          |
| 1536   |       | 113.90433       |            | 57.643937 89930          |
| 2048   |       | 113.91255       |            | 57.643937 88609          |
| NA     |       | 113.920(8)      |            | 57.643937 873(13)        |
|        | BO    | 114.00(12)      |            | 57.69(6)                 |
|        | NA-BO | -0.08(12)       |            | -0.05(6)                 |
|        | Measured | 113.904(30)   |            | 57.671(24)              |

| Basis  | State | \( E \) (in a.u.) | Parameters | \( d_1 \) (in kHz) | \( q \) |
|--------|-------|-----------------|------------|----------------|--------|
| 512    |       | 83.74019        | 13.28198   | 17.761872 17998 | 0.334510 892 |
| 1024   |       | 85.4467         | 13.11642   | 17.761872 28917 | 0.334493 539 |
| 1536   |       | 85.5501         | 13.13552   | 17.761872 43313 | 0.334493 100 |
| 2048   |       | 85.5923         | 13.12704   | 17.761872 44031 | 0.334924 601 |
| NA     |       | 85.634(4)       | 13.11189   | 17.761872 447(7) | 0.334492 1(5) |
|        | BO    | 85.675(60)      | 13.1329(9) | 17.77312(12)  | 0.3347(3) |
|        | NA-BO | -0.04(7)        | -0.014(14) | -0.012(12)   | -0.0002(3) |
|        | Measured | 85.600(18)     | 13.122(11) | 17.761(12)   |         |

| Basis  | State | \( E \) (in a.u.) | Parameters | \( d_1 \) (in kHz) | \( q \) |
|--------|-------|-----------------|------------|----------------|--------|
| 512    |       | 8.72372         | 2.737626 13122 | 0.335240 662 |
| 1024   |       | 8.76377         | 2.737626 04301 | 0.335233 684 |
| 1536   |       | 8.76541         | 2.737626 03804 | 0.335232 171 |
| 2048   |       | 8.76638         | 2.737626 03689 | 0.335231 363 |
| NA     |       | 8.7674(10)      | 2.737626 035(2) | 0.335230 7(7) |
|        | BO    | 8.770(5)        | 2.730(2)    | 0.33535(18)|        |
|        | NA-BO | -0.003(5)       | -0.002(2)   | -0.00012(18)|        |
|        | Measured | 8.768(3)       |            |            |        |

\( ^a \) This is a reference energy obtained from explicitly correlated exponential functions [27][29].
### TABLE II. Determination of the deuteron quadrupole moment (in fm$^2$) from $D_2$ hyperfine parameters and its verification for HD.

| Quantity | $D_2$ | Source |
|----------|-------|--------|
| $d$      | 25.241 4(14) kHz | Code & Ramsey, 1971 |
| $d_1$    | 2.737 626 035(2) kHz | This work, Eq. 11 |
| $d_2$    | $-22.503 8(14)$ kHz | $d_2 = d_1 - d$ |
| $q$      | 0.335 230 7(7) a.u. | This work, Eq. 15 |
| $Q_d$    | 0.285 699(15)(18)$^a$ | This work, Eq. 23 |
|          | 0.285 4$^b$ | Filin et al., 2020 |
|          | 0.285 99(3) | Jóźwiak et al., 2020 |
|          | 0.285 6(2) | Komasa et al., 2020 |
|          | 0.285 78(30) | Pavanello et al., 2010 |
|          | 0.285 90(30) | Bishop revisited, 1983, cited in 15 |
|          | 0.286 0(15) | Bishop & Cheung, 1979 |
|          | 0.286 0(15) | Reid & Vaida, 1972/5 |

**HD**

| $q$      | 0.334 492(1) a.u. | This work, Eq. 15 |
| $d_2$    | $-22.454 2(14)^a$ kHz | This work, Eq. 14 |
| $d_2$    | $-22.454(6)$ kHz | Ramsey et al., 1978 |
| Diff.    | $-0.000(6)$ kHz | |

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$^a$ The first uncertainty accounts for missing relativistic correction, the second one is due to the experimental uncertainty of $d$.

$^b$ Calculated in the framework of $\chi$EFT.

$^c$ This uncertainty comes from the experimental uncertainty in $Q_d$.
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