

## Precision spectroscopy of the hydrogen molecular ion $D_2^+$

Pei-Pei Zhang,<sup>1</sup> Zhen-Xiang Zhong,<sup>1,\*</sup> Zong-Chao Yan,<sup>1,2,3</sup> and Ting-Yun Shi<sup>1,2</sup>

<sup>1</sup>*Division of Theoretical and Interdisciplinary Research, State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Wuhan 430071, China*

<sup>2</sup>*Center for Cold Atom Physics, Chinese Academy of Sciences, Wuhan 430071, China*

<sup>3</sup>*Department of Physics, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 5A3*

(Received 10 January 2016; published 15 March 2016)

Expectation values of the Breit operators are calculated for the  $D_2^+$  molecular ion with the vibrational number ( $v = 0-4$ ) and angular momentum ( $L = 0-4$ ). Hyperfine splittings of energy levels of the states ( $v = 0-4$ ,  $L = 3,4$ ) are also determined in the framework of the spin-dependent Breit-Pauli Hamiltonian, which can be considered as an extension of our previous work [Phys. Rev. A **88**, 032519 (2013)]. These theoretical calculations may be used to improve spectroscopic precision of  $D_2^+$  and determine the dissociation or the ionization energy of  $D_2$ .

DOI: 10.1103/PhysRevA.93.032507

### I. INTRODUCTION

The hydrogen molecular ion  $H_2^+$  and its isotopomers are the simplest molecules of fundamental interest for both theoretical [1–3] and experimental [4] research in recent years. The rovibrational transition frequencies of hydrogen molecular ions strongly depend on the nuclear-electron mass ratio, making them promising candidates for improving the nuclear-electron mass ratio directly by combining the precision measurement of rovibrational spectroscopy and QED calculations [5]. Very recently Korobov and coworkers have accomplished the calculation of  $R_\infty\alpha^5$  order radiative corrections for  $H_2^+$  and  $HD^+$  [6,7].  $R_\infty$  and  $\alpha$  are Rydberg constant and fine structure constant respectively. Combining with the previous systematic theoretical results [2,3,8–11], the total relative uncertainty of theoretical spectroscopy has reached the most precise level of about 0.03 ppb. Meanwhile, the most precise measurement of the rovibrational transition of  $HD^+$  was around 1–2 ppb [4], which means that experimental spectroscopy has to be improved at least by one order of magnitude to make this method more competitive with the CODATA 2010 recommended value of the proton-electron mass ratio [12].

Although hydrogen molecular ions  $H_2^+$  and  $HD^+$  have been investigated, the homonuclear molecular  $D_2^+$  has been much less studied so far. Because of the absence of the dipole moment, dipole transitions are forbidden in  $H_2^+$  and  $D_2^+$ . However the doppler-free two-photon transition was proposed a few years ago. For  $H_2^+$  ion, the two-photon spectroscopy is attractive by using  $\Delta v = 1$  transitions around 8–12  $\mu\text{m}$  [13,14], and the corresponding experiments are currently underway in Hilico's group, aiming at 0.1 ppb [15,16]. In 2001, polarizabilities, light shifts, and two-photon transition probabilities between  $J = 0$  states of  $D_2^+$  were calculated by Hilico *et al.* [13], where the wavelength of  $\Delta v = 1$  transition is 12–19  $\mu\text{m}$ . Recently, the quadrupole transition probabilities between states of a same rotational band were calculated by Pilón [17]. These transition probabilities indicate that a two-photon transition experiment on  $D_2^+$  is feasible due to

the coincidences of the transition frequencies with the  $\text{CO}_2$  laser lines. Such an experiment will be a new tool to probe relativistic and radiative corrections in  $D_2^+$ .

The relativistic and radiative corrections of  $D_2^+$  can also be used to determine the dissociation energy or the ionization energy of  $D_2$  [18–22]. The relationship between the ionization energy  $E_i$  and the dissociation energy  $D_0$  of  $D_2$  can be expressed as follows [21]:

$$D_0(D_2) = E_i(D_2) + D_0(D_2^+) - E_i(D), \quad (1)$$

where the dissociation energy of  $D_2^+$  [ $D_0(D_2^+)$ ] is required as an input. In the latest determination of  $D_0(D_2)$  in Ref. [21],  $D_0(D_2^+)$  was estimated based on the calculations of Moss on  $D_2^+$  [23] and of Korobov on  $H_2^+$  and  $HD^+$  [2,8]. The uncertainty of  $D_0(D_2^+)$  was evaluated as  $35 \times 10^{-5} \text{ cm}^{-1}$  which is mainly due to the leading-order relativistic and radiative corrections of  $D_2^+$ . In order to obtain an improved value of  $D_0(D_2^+)$  and subsequently of  $D_0(D_2)$ , higher precision calculation of the leading-order relativistic correction of  $D_2^+$  is essentially needed.

The hyperfine structure of low-lying rovibrational states of  $D_2^+$  with the vibrational quantum number  $v = 0-4$  and the rotational quantum number  $L = 1,2$  have been considered in our previous work [24], wherein the spin-spin tensor interaction between the two nuclei and the contribution of the deuteron quadrupole moment  $Q_d$  to the hyperfine splitting were precisely obtained. We found that the uncertainty in hyperfine splitting of  $D_2^+$  due to the uncertainty of  $Q_d$  is at the level of about 1–3 Hz. It is feasible to obtain an improved value of  $Q_d$  if the precision of experimental spectroscopy reaches a level of sub-Hz or less.

In this paper we present a systematic calculation of rovibrational energy levels of  $D_2^+$ , together with expectation values of the Breit operators for the states of  $v = 0-4$  and  $L = 0-4$ . Moreover, we estimate hyperfine splitting for the states of  $v = 0-4$  and  $L = 3,4$  as an extension to our previous work [24]. We use atomic units ( $\hbar = e = m_e = 1$ ) throughout, unless otherwise stated. The fundamental physical constants involved are taken from the 2010 CODATA (the Committee on Data for Science and Technology) recommended values [12] unless indicated otherwise.

\*zxzhong@wipm.ac.cn

TABLE I. Comparison of the nonrelativistic energy of the ground state (0, 0) of  $D_2^+$ , in atomic units. The deuteron mass<sup>a</sup>  $m_d = 3670.483014m_e$  is taken from recent works listed in this table.

Author (year)	Reference	$E_{nr}$
Rebane and Filinsky (1997)	[32]	-0.598 788 784 33
Taylor <i>et al.</i> (1999)	[33]	-0.598 788 784 330 8(1)
Moss (1999)	[34]	-0.598 788 784 330 7
Hilico <i>et al.</i> (2000)	[35]	-0.598 788 784 330 68(1)
Korobov (2001)	[36]	-0.598 788 784 298 97
Bailey and Frolov (2002)	[37]	-0.598 788 784 330 683 464 54
Yan <i>et al.</i> (2003)	[1]	-0.598 788 784 330 683 464 4(1)
Pilón (2013)	[17]	-0.598 788 784 330 7
This work		-0.598 788 784 330 683 464 542 006 253 0765(4)

<sup>a</sup>This value is adopted in this table only.

## II. THEORY

### A. Nonrelativistic wave function of $D_2^+$

The three-body Hamiltonian for  $D_2^+$  can be expressed in the center-of-mass frame [25],

$$H_0\Psi = E_0\Psi, \quad (2)$$

$$H_0 = \lambda_1\nabla_{r_1}^2 + \lambda_2\nabla_{r_2}^2 + \lambda_{12}\nabla_{r_1} \cdot \nabla_{r_2} + V, \quad (3)$$

where  $\mathbf{r}_1$  and  $\mathbf{r}_2$  represent, respectively, the position vectors of the electron and the deuteron, relative to the other deuteron situated at the origin,  $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$ ,  $\lambda_1 = -(1 + m_d)/(2m_d)$ ,  $\lambda_2 = \lambda_{12} = -1/m_d$  with  $m_d$  being the mass of the deuteron, and  $V = -1/r_1 + 1/r_2 - 1/r_{12}$  is the Coulomb interaction among the three particles. In order to solve the energy eigenvalue problem for  $H_0$  variationally, we seek the common eigenstates of the commuting observables  $\{H_0, \mathbf{L}^2, L_z, \Pi\}$ , where  $\mathbf{L}$  is the total angular momentum operator and  $\Pi$  is the parity operator, using the following basis set in Hylleraas coordinates:

$$r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2} \mathcal{Y}_{l_1 l_2}^{LM}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2). \quad (4)$$

In the above,  $\alpha$  and  $\beta$  are nonlinear parameters, and  $\mathcal{Y}_{l_1 l_2}^{LM}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2)$  is the vector coupled product of spherical harmonics for the electron and the nuclear, forming a common eigenvector of  $\mathbf{L}^2$ ,  $L_z$ , and  $\Pi$  with the corresponding eigenvalues of  $L(L+1)$ ,  $M$ , and  $(-1)^{l_1+l_2}$ , respectively. The construction of the basis set is similar to what we have done for  $H_2^+$  and  $HD^+$ ; see Refs. [25,26] for details.

The matrix elements of the Breit operators can be reduced to some basic integrals, which can be evaluated analytically [27]. Singularities of singular integrals that we need to handle can be canceled out according to the procedure in [28].

### B. Leading-order relativistic and radiative corrections for rovibrational transitions

The leading-order relativistic corrections which are also called the Breit operators are well established and can be found in Refs. [29–31]. The complete spin-independent term of order  $R_\infty\alpha^2$  is

$$E^{(2)} = \alpha^2 \left\{ -\frac{1}{8} \langle \nabla_{r_1}^4 \rangle - \frac{1}{8m_d^3} \langle \nabla_{r_2}^4 \rangle - \frac{1}{8m_d^3} \langle (\nabla_{r_1} + \nabla_{r_2})^4 \rangle \right. \\ \left. + \frac{\pi}{2} [\langle \delta(\mathbf{r}_1) \rangle + \langle \delta(\mathbf{r}_{12}) \rangle] \right.$$

$$\left. + \frac{1}{2m_d} \left[ \frac{1}{m_d} R_{02} - R_{01} - R_{12} \right] \right\}, \quad (5)$$

where

$$R_{01} = -\left\langle \frac{\nabla_{r_1} \cdot (\nabla_{r_1} + \nabla_{r_2})}{r_1} + \frac{\mathbf{r}_1 \mathbf{r}_1 : (\nabla_{r_1} + \nabla_{r_2}) \nabla_{r_1}}{r_1^3} \right\rangle \\ R_{02} = -\left\langle \frac{\nabla_{r_2} \cdot (\nabla_{r_1} + \nabla_{r_2})}{r_2} + \frac{\mathbf{r}_2 \mathbf{r}_2 : (\nabla_{r_1} + \nabla_{r_2}) \nabla_{r_2}}{r_2^3} \right\rangle \\ R_{12} = \left\langle \frac{\nabla_{r_1} \cdot \nabla_{r_2}}{r_{12}} + \frac{\mathbf{r}_{12} \mathbf{r}_{12} : \nabla_{r_1} \nabla_{r_2}}{r_{12}^3} \right\rangle.$$

TABLE II. Nonrelativistic energies for the rovibrational states ( $v = 0-4$ ,  $L = 0-4$ ) of  $D_2^+$ , in atomic units. The deuteron mass<sup>a</sup>  $m_d = 3670.4829652m_e$  is taken from CODATA 2010 [12].

( $v, L$ )	$E_{nr}$
(0,0)	-0.598 788 784 304 455 365 465 257 182 944 4(4)
(1,0)	-0.591 603 121 831 225 680 872 495 313 226 5(3)
(2,0)	-0.584 712 206 896 083 535 935 762 886 30(9)
(3,0)	-0.578 108 591 284 751 379 377 392 371(2)
(4,0)	-0.571 785 598 461 025 575 698 595 42(8)
(0,1)	-0.598 654 873 192 490 599 098 150 279 68(5)
(1,1)	-0.591 474 211 454 953 629 232 356 723(2)
(2,1)	-0.584 588 169 503 356 978 931 666 30(8)
(3,1)	-0.577 989 311 807 813 125 114 745(4)
(4,1)	-0.571 670 974 249 741 561 834 37(6)
(0,2)	-0.598 387 585 778 476 769 639 155 398(3)
(1,2)	-0.591 216 909 547 453 826 820 682 40(4)
(2,2)	-0.584 340 598 262 377 957 381 389 4(6)
(3,2)	-0.577 751 241 739 672 125 004 07(2)
(4,2)	-0.571 442 200 677 765 120 814 4(4)
(0,3)	-0.597 987 984 709 990 826 799 894 9(1)
(1,3)	-0.590 832 246 989 225 819 099 169(6)
(2,3)	-0.583 970 493 614 750 291 861 9(1)
(3,3)	-0.577 395 352 366 394 965 437(2)
(4,3)	-0.571 100 221 122 677 086 96(3)
(0,4)	-0.597 457 646 740 147 377 716 614 51(2)
(1,4)	-0.590 321 753 288 033 535 706 164 4(7)
(2,4)	-0.583 479 339 813 821 488 956 84(2)
(3,4)	-0.576 923 084 610 926 441 594(3)
(4,4)	-0.570 646 435 047 012 938 9(2)

<sup>a</sup>Present results are calculated by using this value except Table I.

TABLE III. Expectation values of the Breit operators for the states  $v = 0-4$  and  $L = 0-4$  of  $D_2^+$ , in atomic units.

$(v, L)$	$\langle \delta(\mathbf{r}_1) \rangle$	$\langle \nabla_{r_1}^4 \rangle$	$\langle \nabla_{r_2}^4 \rangle$	$R_{01}$	$R_{02}$
(0,0)	0.20772754972802160(4)	6.3169270481939487(2)	153.2743420817056(5)	1.1755401956603341(2)	6.616687029136029(5)
(1,0)	0.20379844184745247(5)	6.2000633444096(3)	679.941029935(8)	1.154237940014424(2)	18.9196991814394(8)
(2,0)	0.20008065320941497(1)	6.0898215956396823(1)	1611.961532139(4)	1.13426210505208(5)	29.8564507168134(7)
(3,0)	0.1965643482972(2)	5.985904424561(4)	2857.209177(2)	1.11556115485(6)	39.513256215(5)
(4,0)	0.193240558969(8)	5.888042319(8)	4333.4036(8)	1.09808932(3)	47.9671798(5)
(0,1)	0.20760346337881099(7)	6.3130677517184(4)	160.563740416(8)	1.1748821714776(7)	6.85460762533(4)
(1,1)	0.20368000829240467(8)	6.1963836806472(2)	698.639811535(3)	1.153612629911(5)	19.133415609091(2)
(2,1)	0.19996763995988(4)	6.08631483213831(8)	1640.00530164(1)	1.133668340408(4)	30.0474849762(6)
(3,1)	0.19645656469573(9)	5.9825644608309(1)	2892.7369694(4)	1.114997891449(5)	39.6829708166(4)
(4,1)	0.1931378251448(2)	5.884863661(2)	4374.733879(5)	1.097555657390(5)	48.11679071(1)
(0,2)	0.207356187534222(6)	6.3053778276452(2)	176.54883077(8)	1.1735707583967(2)	7.327540747026(5)
(1,2)	0.20344398372089976(4)	6.18905199911328(8)	737.2903202611(1)	1.152366471131904(2)	19.5580922356988(2)
(2,2)	0.19974244785865(1)	6.079327973483(2)	1697.2065320(4)	1.1324851072962(6)	30.426940325440(3)
(3,2)	0.1962418026749(3)	5.975910266779(2)	2964.779430(4)	1.11387550375(1)	40.019921849(9)
(4,2)	0.192933134843(5)	5.87853111(5)	4458.2636(1)	1.096492271(1)	48.41366040(2)
(0,3)	0.2069874983824573(1)	6.2939140489769(6)	203.984376600(5)	1.171615139648672(1)	8.029742151341430(7)
(1,3)	0.2030921033028088(7)	6.178123041504(3)	798.342872438(2)	1.1505083016415(1)	20.188286601630035(3)
(2,3)	0.1994067290672215(7)	6.0689138205(6)	1785.7391610(4)	1.1307209156452(3)	30.9896585200505(8)
(3,3)	0.1959216564072(3)	5.9659927877(5)	3075.2588(5)	1.1122021897(3)	40.519219193(3)
(4,3)	0.1926280267204(2)	5.8690940171(4)	4585.6852(4)	1.0949070935(6)	48.853152720(5)
(0,4)	0.2065000171137353(1)	6.278760186224(5)	246.8611763991(5)	1.1690288751105(1)	8.952771910985(2)
(1,4)	0.20262688675873407(2)	6.163677567416(5)	885.337213781(3)	1.148051169726641(5)	21.01600669464994(2)
(2,4)	0.19896292093783(1)	6.05515025717(3)	1908.733635794(8)	1.128388327866(6)	31.72806913107(9)
(3,4)	0.19549847735755(8)	5.95288716005(6)	3226.933155(8)	1.1099900514(5)	41.17368979(4)
(4,4)	0.1922247700080(9)	5.8566247178(2)	4759.4179(5)	1.09281175(2)	49.4284692(6)

The Darwin term is the nuclear spin dependent recoil correction for the spin- $\frac{1}{2}$  particle, which exists in  $H_2^+$  and  $HD^+$  but vanishes in  $D_2^+$  (spin 1).

The leading-order radiative corrections for a one electron molecular system may be expressed as follows [38,39]:

$$\begin{aligned}
E^{(3)} = & \alpha^3 \left\{ \frac{4}{3} \left[ -\ln \alpha^2 - \beta(v, L) + \frac{19}{30} \right] \langle \delta(\mathbf{r}_1) + \delta(\mathbf{r}_{12}) \rangle \right. \\
& + \frac{2}{3m_d} \left[ -\ln \alpha - 4\beta(v, L) + \frac{31}{3} \right] \langle \delta(\mathbf{r}_1) + \delta(\mathbf{r}_{12}) \rangle \\
& \left. - \frac{14}{3m_d} [Q(\mathbf{r}_1) + Q(\mathbf{r}_{12})] \right\}, \quad (6)
\end{aligned}$$

where  $\beta(v, L)$  is the Bethe logarithm, and  $Q(\mathbf{r})$  is the  $Q$  term introduced by Araki [40] and Sucher [41]:

$$Q(\mathbf{r}) = \lim_{\rho \rightarrow 0} \left\langle \frac{\Theta(r - \rho)}{4\pi r^3} + (\ln \rho + \gamma_E) \delta(\mathbf{r}) \right\rangle,$$

where  $\gamma_E$  is the Euler-Mascheroni constant.

Higher order corrections are not considered in this work. In addition to the leading-order relativistic and radiative corrections, one needs to consider the finite nuclear size effect. The leading-order correction due to finite nuclear charge distribution is given by

$$E_{\text{nuc-1}} = \frac{2\pi}{3} \left( \frac{R_d}{a_0} \right)^2 \langle \delta(\mathbf{r}_1) + \delta(\mathbf{r}_{12}) \rangle, \quad (7)$$

where  $R_d = 2.1424(21)$  fm [12] is the root-mean-square (rms) radius of the deuteron electric charge distribution and  $a_0$  is the

Bohr radius. The next-order correction is given by [12]

$$E_{\text{nuc-2}} = -\frac{2\pi}{3} C_\eta^{(d)} m_d \left( \frac{R_d}{a_0} \right)^3 \langle \delta(\mathbf{r}_1) + \delta(\mathbf{r}_{12}) \rangle, \quad (8)$$

TABLE IV. Convergence study of  $\langle \delta(\mathbf{r}_1) \rangle$  and  $\langle \nabla_{r_2}^4 \rangle$  for the state (2, 3) of  $D_2^+$ , in atomic units.

$N$	$\langle \delta(\mathbf{r}_1) \rangle$	$\langle \nabla_{r_2}^4 \rangle$
63	0.204 440 537 145 385 139	1907.296 56413
106	0.200 490 008 898 218 335	1870.014 18506
170	0.199 606 191 245 562 456	1824.791 51443
260	0.199 436 483 067 938 665	1795.578 80470
381	0.199 414 016 045 115 230	1786.104 93212
538	0.199 406 561 443 667 001	1785.328 82062
736	0.199 406 902 239 341 991	1785.541 19591
980	0.199 406 721 841 651 119	1785.671 10949
1275	0.199 406 738 050 723 568	1785.724 06284
1626	0.199 406 728 544 853 816	1785.735 86201
2038	0.199 406 729 076 806 081	1785.738 43849
2516	0.199 406 729 172 375 785	1785.739 00525
3065	0.199 406 729 070 177 053	1785.739 12355
3690	0.199 406 729 053 132 042	1785.739 15597
4396	0.199 406 729 071 959 212	1785.739 16019
5188	0.199 406 729 066 167 230	1785.739 16090
6071	0.199 406 729 067 491 765	1785.739 16106
7050	0.199 406 729 067 177 701	1785.739 16105
8130	0.199 406 729 067 221 539	1785.739 16103
9316	0.199 406 729 067 221 595	1785.739 16102
Extrap.	0.199 406 729 067 2215(7)	1785.739 1610(4)

TABLE V. Expectation values of  $Q(\mathbf{r}_1)$  for the states  $v = 0-4$  and  $L = 0-4$  of  $D_2^+$ , in atomic units.

$(v, L)$	$v = 0$	$v = 1$	$v = 2$	$v = 3$	$v = 4$
$L = 0$	-0.135069844234963(1)	-0.132793372948445(2)	-0.130643378591224(1)	-0.1286147286564(3)	-0.12670278697(2)
$L = 1$	-0.13498913816522(1)	-0.132716248483965(2)	-0.13056972074318(1)	-0.1285444336749(3)	-0.1266357619(1)
$L = 2$	-0.134828351302199(7)	-0.1325626048758(8)	-0.13042299112519(3)	-0.12840441123150(3)	-0.12650226135(2)
$L = 3$	-0.1345887214863(3)	-0.13233364031772(5)	-0.130204349713(3)	-0.1281957844557(1)	-0.126303372872(6)
$L = 4$	-0.13427207422339(5)	-0.13203112150409(2)	-0.129915506549(4)	-0.127920208785(2)	-0.1260406993(1)

where  $C_\eta^{(d)} = 2.0(1)$  is a constant that depends on the charge distribution in the deuteron. Therefore, the total correction due to the finite nuclear size is

$$E_{\text{nuc}} = E_{\text{nuc}-1} + E_{\text{nuc}-2}. \quad (9)$$

### C. Hyperfine splitting

The leading-order relativistic correction to the hyperfine structure of  $D_2^+$  is described by spin-dependent terms of the Breit-Pauli Hamiltonian that sums up pairwise interactions of the three particles, including the electron-deuteron and deuteron-deuteron spin-orbit and spin-spin interactions, as well as the contribution of the deuteron quadrupole moment  $Q_d$  to the hyperfine structure. Following [24], the effective Hamiltonian of  $D_2^+$  can be written in the form

$$\begin{aligned}
H_{\text{eff}} = & b_F(\mathbf{I} \cdot \mathbf{s}_e) + c_e(\mathbf{L} \cdot \mathbf{s}_e) + c_I(\mathbf{L} \cdot \mathbf{I}) \\
& + \frac{d_1}{(2L-1)(2L+3)} \left( \frac{2}{3} \mathbf{L}^2(\mathbf{L} \cdot \mathbf{s}_e) - [(\mathbf{L} \cdot \mathbf{I})(\mathbf{L} \cdot \mathbf{s}_e) \right. \\
& \left. + (\mathbf{L} \cdot \mathbf{s}_e)(\mathbf{L} \cdot \mathbf{I}) \right) + \frac{d_2 + 3d_3}{(2L-1)(2L+3)} \left( \frac{1}{3} \mathbf{L}^2 \mathbf{I}^2 \right. \\
& \left. - \frac{1}{2}(\mathbf{L} \cdot \mathbf{I}) - (\mathbf{L} \cdot \mathbf{I})^2 \right), \quad (10)
\end{aligned}$$

where  $\mathbf{s}_e$ ,  $\mathbf{I} = \mathbf{I}_0 + \mathbf{I}_2$  and  $\mathbf{L}$  are the electron spin operator, the total nuclear spin operator and the total orbital angular momentum operator, respectively, and  $b_F$ ,  $c_e$ ,  $c_I$ ,  $d_1$ ,  $d_2$ , and  $d_3$  are the coupling constants of the effective Hamiltonian, which can be derived by averaging the spatial variables of the Breit-Pauli Hamiltonian. The expressions of these coupling constants can be found in [24]. The strongest coupling in the hyperfine structure is the electron-deuteron spin-spin contact interaction, followed by the spin-orbit interaction of the electron. Thus the preferred coupling scheme we adopt

TABLE VI. Summary of contributions to the  $D_2^+$  ( $v, L$ ):  $(0,0) \rightarrow (1,0)$  transition frequency, in MHz.

	$D_2^+$ $(0,0) \rightarrow (1,0)$
$\Delta E_{\text{nr}}$	47 279 387.834 89(24)
$\Delta E_{\alpha^2}$	795.553 630(14)
$\Delta E_{\alpha^3}$	-200.2773(43)
$\Delta E_{\alpha^4}$	-1.435(14)
$\Delta E_{\alpha^5}$	0.087(17)
$\Delta E_{\text{nuc}}$	-0.1247(27)
$\Delta E_{\text{tot}}$	47 279 981.638(25)

here is

$$\mathbf{F} = \mathbf{s}_e + \mathbf{I}, \quad \mathbf{J} = \mathbf{L} + \mathbf{F}. \quad (11)$$

According to this scheme, a hyperfine state may be expressed as  $|v, L, s_e = \frac{1}{2}, I, F, J, M_J\rangle$ . Since  $\mathbf{F}^2$  does not commute with the effective Hamiltonian  $H_{\text{eff}}$ ,  $F$  is an approximate quantum number. Only the eigenstates of  $J = L \pm \frac{3}{2}$  and  $J = L \pm \frac{5}{2}$  are pure states of angular coupling, according to whether  $L$  is odd or even. Other eigenstates are a linear combination of two different  $F$  hyperfine states:

$$\begin{aligned}
|v, L, s_e, I, \tilde{F}, J\rangle = & C_0 |v, L, s_e, I, F_0, J\rangle \\
& + C_{\text{mix}} |v, L, s_e, I, F_{\text{mix}}, J\rangle, \quad (12)
\end{aligned}$$

where  $(F_0, F_{\text{mix}})$  is either  $(I + 1/2, I - 1/2)$  or  $(I - 1/2, I + 1/2)$ .

The matrix elements of the Hamiltonian (10) can be calculated by using the numerical values of the coupling constants. The hyperfine energy levels can then be obtained by a diagonalization of the effective Hamiltonian.

## III. CALCULATIONS AND RESULTS

### A. Nonrelativistic energies and expectation values of the Breit operators

The energy eigenfunctions and the corresponding energy eigenvalues are obtained by solving the Schrödinger equation (2) variationally. The largest basis set contains about 10 000 Hylleraas basis functions (4). Table I shows a comparison of the ground state  $(0, 0)$  energy eigenvalue. It should be pointed out that the present ground state energy is accurate to  $4 \times 10^{-31}$ . The nonrelativistic energies of  $D_2^+$  rovibrational states ( $v = 0-4$ ,  $L = 0-4$ ) are listed in Table II. The precision that we have achieved here for the nonrelativistic eigenvalue problem is sufficient for calculating relativistic and radiative corrections.

For the case of  $D_2^+$ , the permutation symmetry of the two deuterons implies that

$$\langle \delta(\mathbf{r}_1) \rangle = \langle \delta(\mathbf{r}_{12}) \rangle, \quad R_{01} = R_{12}, \quad (13)$$

$$\langle (\nabla_{r_1} + \nabla_{r_2})^4 \rangle = \langle \nabla_{r_2}^4 \rangle, \quad Q(\mathbf{r}_1) = Q(\mathbf{r}_{12}). \quad (14)$$

Therefore, only expectation values of the five operators  $\langle \delta(\mathbf{r}_1) \rangle$ ,  $\langle \nabla_{r_1}^4 \rangle$ ,  $\langle \nabla_{r_2}^4 \rangle$ ,  $R_{01}$ , and  $R_{02}$  need to be considered. Numerical values of these operators for the  $D_2^+$  rovibrational states ( $v = 0-4$ ,  $L = 0-4$ ) are presented in Table III. Table IV shows a convergence study of  $\langle \delta(\mathbf{r}_1) \rangle$  and  $\langle \nabla_{r_2}^4 \rangle$  for the state  $(2, 3)$ . One can see that at least 10 significant digits are achieved for  $\langle \nabla_{r_2}^4 \rangle$ .

TABLE VII. Coupling constants of the effective hyperfine Hamiltonian for the rovibrational states ( $v = 0-4$ ,  $L = 3,4$ ) of  $D_2^+$ , in MHz.  $a[b] = a \times 10^b$ .

$(v,L)$	$b_F$	$c_e$	$c_l$	$d_1$	$d_2$	$d_3$
(0,3)	142.025331(1)	21.2995233(4)	-3.18255262(3)[-3]	19.8318125(2)	1.40023762(2)[-2]	-2.7843(3)[-2]
(1,3)	139.352489(1)	20.3688091(3)	-3.09713305(3)[-3]	18.9359524(2)	1.35832295(2)[-2]	-2.7835(3)[-2]
(2,3)	136.823754(1)	19.4695717(3)	-3.00990935(3)[-3]	18.0720477(2)	1.31616389(2)[-2]	-2.7726(3)[-2]
(3,3)	134.432457(1)	18.5989214(3)	-2.92091025(3)[-3]	17.2373111(1)	1.27373409(2)[-2]	-2.7521(3)[-2]
(4,3)	132.172519(1)	17.7541021(3)	-2.83013741(3)[-3]	16.4290896(1)	1.23099924(2)[-2]	-2.7226(3)[-2]
(0,4)	141.690843(1)	21.1726902(4)	-3.15684706(3)[-3]	19.7404673(2)	4.63043556(8)[-3]	9.1472(9)[-3]
(1,4)	139.033279(1)	20.2466941(3)	-3.07168679(3)[-3]	18.8481653(2)	4.49126353(8)[-3]	9.1447(9)[-3]
(2,4)	136.519233(1)	19.3519222(3)	-2.98475488(3)[-3]	17.9875879(2)	4.35130493(7)[-3]	9.1086(9)[-3]
(3,4)	134.142091(1)	18.4854993(3)	-2.89607703(3)[-3]	17.1559605(1)	4.21046904(7)[-3]	9.0410(9)[-3]
(4,4)	131.895823(1)	17.6446820(3)	-2.80565215(3)[-3]	16.3506409(2)	4.06863870(7)[-3]	8.9436(9)[-3]

### B. Relativistic and radiative corrections for two-photon transition $(v,L): (0,0) \rightarrow (1,0)$

The leading-order relativistic correction  $E^{(2)}$  can be obtained by calculating expectation values of the Breit operators. For example, the value of  $E^{(2)}$  for the reference transition  $(0,0) \rightarrow (1,0)$  is calculated to be

$$E^{(2)} = 795.553630(14) \text{ MHz}, \quad (15)$$

where the uncertainty is due to the uncertainty of fundamental constants.

The next is the calculation of the leading-order radiative corrections (6), where the  $Q$  terms are calculated and presented in Table V. Besides the  $Q$  terms, the Bethe logarithm terms  $\beta(v,L)$  are calculated to be

$$\begin{aligned} \beta(0,0) &= 3.0124349(7), \\ \beta(1,0) &= 3.012697(3). \end{aligned}$$

These values are obtained using the Drake-Goldman method [42] that has been applied to  $H_2^+$  by Zhong *et al.* [43]. Then the correction of order  $R_\infty \alpha^3$  to the reference transition is determined as

$$E^{(3)} = -200.2773(43) \text{ MHz}, \quad (16)$$

where the uncertainty is due to the numerical uncertainty of the Bethe logarithmic terms.

For higher-order corrections, such as orders  $R_\infty \alpha^4$  and  $R_\infty \alpha^5$ , we follow the work of Ref. [8]. The  $R_\infty \alpha^4$  order non-recoil relativistic and radiative corrections can be expressed as [8]

$$\begin{aligned} E^{(4)} &= \alpha^4 \frac{1}{\pi} \left[ -\frac{2179}{648} + \frac{3523}{864} \pi^2 - \frac{1}{2} \pi^2 \ln 2 - \frac{9}{4} \zeta(3) \right] \\ &\times \langle \delta(\mathbf{r}_1) + \delta(\mathbf{r}_{12}) \rangle, \end{aligned} \quad (17)$$

where  $\zeta(3)$  is the Riemann  $\zeta$  function. We shall also consider  $E_{rc}^{(4)}$ , the relativistic correction for the bound electron, which has not been included in Eq. (17). The value of  $E_{rc}^{(4)}$  can be roughly estimated as [8]

$$E_{rc}^{(4)} \approx -\frac{\pi \alpha^4}{16} \langle \delta(\mathbf{r}_1) + \delta(\mathbf{r}_{12}) \rangle. \quad (18)$$

For the reference transition in  $D_2^+$ , this correction is estimated to be 14 kHz. Therefore, the  $R_\infty \alpha^4$  order correction to the transition  $(0,0) \rightarrow (1,0)$  is  $E^{(4)} = -1.435(14) \text{ MHz}$ .

For the  $R_\infty \alpha^5$  order radiative correction, its estimation is done, which is similar to [2,8,26]

$$\begin{aligned} E^{(5)} &= \alpha^5 \left[ -\ln^2 \frac{1}{\alpha^2} + A_{61} \ln \frac{1}{\alpha^2} + A_{60} + \frac{B_{50}}{\pi} \right] \\ &\times \langle \delta(\mathbf{r}_1) + \delta(\mathbf{r}_{12}) \rangle, \end{aligned} \quad (19)$$

where  $A_{61}$ ,  $A_{60}$ , and  $B_{50}$  are taken to be constants for the  $1s$  state of the atomic hydrogen; for example,  $A_{61} = 5.419 \dots$  [44],  $A_{60} = -30.924 \dots$  [45], and  $B_{50} = -21.556 \dots$  [46]. Then the value of  $E^{(5)}$  for the reference transition is estimated as  $E^{(5)} = 0.087(17) \text{ MHz}$ .

For the finite nuclear size effects, its leading-order correction  $E_{nuc-1}$  has been evaluated for  $H_2^+$  [3,8] and  $HD^+$  [8,9]. It was pointed out by Zhong *et al.* [26] that the next-order correction  $E_{nuc-2}$  has a contribution at the 10 kHz level to a transition frequency. For  $D_2^+$ , the present values for  $E_{nuc-1}$  and  $E_{nuc-2}$  are  $-0.17750(35)$  and  $0.0528(26) \text{ MHz}$ , respectively, for the transition  $(0,0) \rightarrow (1,0)$ . The uncertainty in  $E_{nuc-1}$  comes from the uncertainty of the rms radius of the deuteron  $R_d$  and the uncertainty in  $E_{nuc-2}$  comes from  $C_\eta^{(d)}$ . Therefore, the total contribution from the finite nuclear size effect is  $E_{nuc} = -0.1247(27) \text{ MHz}$ .

Summing up all the contributions mentioned above, the transition frequency of  $(0,0) \rightarrow (1,0)$  is determined and presented in Table VI. The relative uncertainty in this frequency is  $5.3 \times 10^{-10}$ , which is mainly due to the theoretical uncertainties of orders  $R_\infty \alpha^4$  and  $R_\infty \alpha^5$ .

### C. Dissociation energies of $D_2^+$ and $D_2$

Based on the above calculations, we determine the ionization energy of  $D_2^+$  to be

$$E_i(D_2^+) = 131\,420.197\,70(4) \text{ cm}^{-1}, \quad (20)$$

where the uncertainty is due to the relativistic and radiative corrections of orders  $R_\infty \alpha^4$  and  $R_\infty \alpha^5$ . This value agrees with the value  $131\,420.197\,90(35) \text{ cm}^{-1}$  obtained by using the data from Table V of Ref. [21]. One can see that the uncertainty of  $E_i(D_2^+)$  is reduced by a factor of about 9. Hence, the dissociation energy of  $D_2^+$  can be evaluated according to

$$D_0(D_2^+) = E_i(D_2^+) - E_i(D) = 21\,711.583\,15(4) \text{ cm}^{-1}, \quad (21)$$

where the ionization energy  $E_i(D)$  is taken from Table V of Ref. [21]. The present value of the dissociation energy

TABLE VIII. Hyperfine splittings of the rovibrational states ( $v = 0-4$ ,  $L = 3,4$ ) of  $D_2^+$ , in MHz.

$(\tilde{F}, J)$	$\Delta E_{\text{hfs}}$	$C_0$	$C_{\text{mix}}$	$F_{\text{mix}}$	$\Delta E_{\text{hfs}}$	$C_0$	$C_{\text{mix}}$	$F_{\text{mix}}$
$(v, L) = (0, 3)$					$(v, L) = (1, 3)$			
(3/2, 9/2)	100.753(5)				98.120(5)			
(3/2, 7/2)	80.657(4)	0.9889477	0.1482643	1/2	78.779(4)	0.9894341	0.1449831	1/2
(3/2, 5/2)	54.117(3)	0.9822703	0.1874700	1/2	53.335(3)	0.9832473	0.1822761	1/2
(3/2, 3/2)	23.147(1)				23.911(1)			
(1/2, 5/2)	-134.444(7)	0.9822703	-0.1874700	3/2	-131.920(7)	0.9832473	-0.1822761	3/2
(1/2, 7/2)	-157.926(8)	0.9889477	-0.1482643	3/2	-154.445(8)	0.9894341	-0.1449831	3/2
$(v, L) = (2, 3)$					$(v, L) = (3, 3)$			
(3/2, 9/2)	95.603(5)				93.194(5)			
(3/2, 7/2)	76.995(4)	0.9899217	0.1416151	1/2	75.301(4)	0.9904108	0.1381534	1/2
(3/2, 5/2)	52.614(3)	0.9842109	0.1769992	1/2	51.952(3)	0.9851609	0.1716330	1/2
(3/2, 3/2)	24.675(1)				25.443(1)			
(1/2, 5/2)	-129.543(7)	0.9842109	-0.1769992	3/2	-127.306(7)	0.9851609	-0.1716330	3/2
(1/2, 7/2)	-151.140(8)	0.9899217	-0.1416151	3/2	-147.999(8)	0.9904108	-0.1381534	3/2
$(v, L) = (4, 3)$								
(3/2, 9/2)	90.887(5)							
(3/2, 7/2)	73.691(4)	0.9909012	0.1345909	1/2				
(3/2, 5/2)	51.348(3)	0.9860969	0.1661710	1/2				
(3/2, 3/2)	26.218(1)							
(1/2, 5/2)	-125.204(7)	0.9860969	-0.1661710	3/2				
(1/2, 7/2)	-145.017(8)	0.9909012	-0.1345909	3/2				
$(v, L) = (0, 4)$					$(v, L) = (1, 4)$			
(5/2, 13/2)	179.214(10)				174.921(9)			
(5/2, 11/2)	164.605(9)	0.9956107	0.0935910	3/2	160.865(9)	0.9958015	0.0915381	3/2
(5/2, 9/2)	145.227(8)	0.9914028	0.1308452	3/2	142.259(8)	0.9918132	0.1276966	3/2
(5/2, 7/2)	123.071(7)	0.9893804	0.1453492	3/2	121.042(6)	0.9899518	0.1414050	3/2
(5/2, 5/2)	100.239(5)	0.9917665	0.1280589	3/2	99.257(5)	0.9922787	0.12402778	3/2
(5/2, 3/2)	79.368(4)				79.449(4)			
(1/2, 9/2)	42.345(2)				40.493(2)			
(1/2, 7/2)	-52.932(3)				-50.617(3)			
(3/2, 5/2)	-182.583(10)	0.9917665	-0.1280589	5/2	-179.768(10)	0.9922787	-0.12402778	5/2
(3/2, 7/2)	-203.606(11)	0.9893804	-0.1453492	5/2	-199.824(11)	0.9899518	-0.1414050	5/2
(3/2, 9/2)	-223.466(12)	0.9914028	-0.1308452	5/2	-218.849(12)	0.9918132	-0.1276966	5/2
(3/2, 11/2)	-240.083(13)	0.9956107	-0.0935910	5/2	-234.821(13)	0.9958015	-0.0915381	5/2
$(v, L) = (2, 4)$					$(v, L) = (3, 4)$			
(5/2, 13/2)	170.827(9)				166.920(9)			
(5/2, 11/2)	157.307(8)	0.9959930	0.0894311	3/2	153.922(8)	0.9961850	0.0872657	3/2
(5/2, 9/2)	139.451(7)	0.9922223	0.1244780	3/2	136.795(7)	0.9926300	0.1211837	3/2
(5/2, 7/2)	119.143(6)	0.9905160	0.1373971	3/2	117.369(6)	0.9910729	0.1333203	3/2
(5/2, 5/2)	98.369(5)	0.9927775	0.1199694	3/2	97.573(5)	0.9932632	0.1158798	3/2
(5/2, 3/2)	79.581(4)				79.765(4)			
(1/2, 9/2)	38.704(2)				36.971(2)			
(1/2, 7/2)	-48.380(3)				-46.214(2)			
(3/2, 5/2)	-177.136(9)	0.9927775	-0.1199694	5/2	-174.679(9)	0.9932632	-0.1158798	5/2
(3/2, 7/2)	-196.259(10)	0.9905160	-0.1373971	5/2	-192.899(10)	0.9910729	-0.1333203	5/2
(3/2, 9/2)	-214.475(11)	0.9922223	-0.1244780	5/2	-210.331(11)	0.9926300	-0.1211837	5/2
(3/2, 11/2)	-229.819(12)	0.9959930	-0.0894311	5/2	-225.063(12)	0.9961850	-0.0872657	5/2
$(v, L) = (4, 4)$								
(5/2, 13/2)	163.188(9)							
(5/2, 11/2)	150.700(8)	0.9963777	0.0850372	3/2				
(5/2, 9/2)	134.284(7)	0.9930364	0.1178079	3/2				
(5/2, 7/2)	115.716(6)	0.9916225	0.1291692	3/2				
(5/2, 5/2)	96.869(5)	0.9937357	0.1117550	3/2				
(5/2, 3/2)	80.004(4)							
(1/2, 9/2)	35.289(2)							
(1/2, 7/2)	-44.112(2)							
(3/2, 5/2)	-172.394(9)	0.9937357	-0.1117550	5/2				
(3/2, 7/2)	-189.739(10)	0.9916225	-0.1291692	5/2				
(3/2, 9/2)	-206.405(11)	0.9930364	-0.1178079	5/2				
(3/2, 11/2)	-220.541(12)	0.9963777	-0.0850372	5/2				

$D_0(D_2^+)$  agrees with the value reported in Refs. [21,23] but with almost a factor of 9 improvement. Finally, using Eq. (1) we can derive a new value of the dissociation energy for  $D_2$  based on the latest experimental value of the ionization energy  $E_i(D_2)$  [21]:

$$D_0(D_2) = 36\,748.362\,67(58)\text{ cm}^{-1}, \quad (22)$$

where the uncertainty of theoretical part is negligible and the remaining uncertainty is entirely from the experimental uncertainty of  $E_i(D_2)$ . Our determination of the  $D_2$  dissociation energy is in good accord with the value  $36\,748.362\,86(68)\text{ cm}^{-1}$  of Ref. [21]. A more precise determination of the dissociation energy of  $D_2$  can be achieved if a furthermore improvement on the ionization energy of  $D_2$  can be made.

#### D. Hyperfine splitting

The numerical results of the coupling constants of the hyperfine effective Hamiltonian for the states ( $v = 3, 4$ ,  $L = 0-4$ ) are calculated and presented in Table VII. It should be pointed out that the uncertainties are mainly from the deuteron magnetic moment  $\mu_d$  and the quadrupole moment  $Q_d$ . Subsequently, the hyperfine splittings of the rovibrational states ( $v = 0-4$ ,  $L = 3, 4$ ) of  $D_2^+$  are obtained and listed in Table VIII. The relative uncertainty of  $\Delta E_{\text{hfs}}$  is caused by an

uncalculated correction of order  $R_\infty\alpha^4$ , which is estimated to be  $5.3 \times 10^{-5}$ .

#### E. Conclusion

In conclusion, we have presented a systematic calculation of the Breit operators for the hydrogen molecular ion  $D_2^+$  in various rovibrational states with the vibrational quantum number  $v = 0-4$  and the rotational quantum number  $L = 0-4$ . Hyperfine splittings for the rovibrational states ( $v = 3, 4$ ,  $L = 0-4$ ) are also taken into account in the frame of the spin-dependent Breit-Pauli Hamiltonian. Our calculations can be used to determine the dissociation energy or the ionization energy of  $D_2$ . Our work may stimulate more experimental activities on  $D_2^+$ , which may lead to an improved determination of the deuteron-electron mass ratio.

#### ACKNOWLEDGMENTS

The work has been supported by the NSFC under Grants No. 11474316 and No. 11274348. Z.C.Y. acknowledges the support by NSERC, SHARCnet, and ACEnet of Canada and by the CAS/SAFEA International Partnership Program for Creative Research Teams.

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