

## Relativistic corrections to the ground state of H<sub>2</sub> calculated without using the Born-Oppenheimer approximation

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(Received 20 April 2018; published 8 June 2018)

The Schrödinger equation for the ground state of the hydrogen molecule H<sub>2</sub> is solved by applying the Rayleigh-Ritz variational method in Hylleraas coordinates without using the Born-Oppenheimer approximation. The nonrelativistic energy eigenvalue is converged to  $-1.164\,025\,030\,880(7)$  atomic units. The leading-order relativistic corrections, including the mass-velocity, Darwin, orbit-orbit, spin-spin, and relativistic recoil terms, are evaluated perturbatively. Together with the higher-order relativistic and quantum electrodynamic corrections obtained by Puchalski *et al.* [*Phys. Rev. Lett.* **117**, 263002 (2016)], we determine the dissociation energy of the hydrogen molecule,  $D_0 = 36\,118.069\,71(33)$  cm<sup>-1</sup>, which agrees with the two recent experimental results of Liu *et al.* [*J. Chem. Phys.* **130**, 174306 (2009)],  $36\,118.069\,62(37)$  cm<sup>-1</sup>, and Altmann *et al.* [*Phys. Rev. Lett.* **120**, 043204 (2018)],  $36\,118.069\,45(31)$  cm<sup>-1</sup>.

DOI: [10.1103/PhysRevA.97.060501](https://doi.org/10.1103/PhysRevA.97.060501)

### I. INTRODUCTION

Recent experimental measurements have been able to determine the dissociation energy of the hydrogen molecule H<sub>2</sub> to an accuracy of  $10^{-4}$  cm<sup>-1</sup> [1,2]. This new level of accuracy has provided an opportunity for theorists to test computational methods and relativistic and quantum electrodynamic (QED) effects in molecular systems. To match this precision theoretically, as demonstrated by Puchalski *et al.* [3], in addition to the nonrelativistic contribution that has to be calculated to sufficiently high accuracy, the leading relativistic and QED corrections of orders  $O(\alpha^2)$  and  $O(\alpha^3)$ , as well as the higher-order corrections of  $O(\alpha^4)$  and  $O(\alpha^5)$ , have to be included in the calculation. For the ground state of H<sub>2</sub>, the nonrelativistic energy has been determined accurately by two groups: Adamowicz's group and Pachucki's group. Adamowicz's group obtained a nonrelativistic dissociation energy  $36\,118.797\,736(13)$  cm<sup>-1</sup> [4] variationally using explicitly correlated Gaussian basis sets without assuming the Born-Oppenheimer approximation. In the Pachucki group's approach, either the nonadiabatic perturbation theory [5] or fully nonadiabatic variational calculation with the James-Coolidge basis functions [6] was applied. Their nonrelativistic dissociation energy is  $36\,118.797\,746\,10(3)$  cm<sup>-1</sup> [7]. These nonrelativistic values have reached or even exceeded present spectroscopic precision. The leading-order relativistic and QED corrections and higher-order corrections have been calculated systematically by Pachucki's group [3,8–10] using an adiabatic approximation. However, the new theoretical dissociation energy determined by Pachucki's group [3] deviates from the experimental values [1,2] by about  $2\sigma$ , which is ascribed to the uncalculated leading relativistic recoil effect of order  $O(\alpha^2 m_e/m_p)$ . The agreement of the two former

theoretical dissociation energies calculated in Refs. [9,10] with the experimental value of Liu *et al.* [1] was considered to be accidental [3]. If we take the leading-order relativistic contribution, including the recoil effect, from Ref. [11] obtained in a fully nonadiabatic way, as well as other contributions from Pachucki group's values, we do not see an agreement with the experimental values [1,2]. It is therefore desirable to perform an independent calculation for the leading-order relativistic corrections and the recoil effect.

In the past two decades, the variational method in Hylleraas coordinates has been successfully applied to high-precision calculations of three-electron atomic systems [12–14]. The nonrelativistic variational energy of the ground state of lithium, for example, has been calculated to an accuracy of a few parts in  $10^{15}$  using the Hylleraas basis [13,15]. Though the Hylleraas basis sets have also been extended to the calculations of two-center hydrogen molecular ions with a high accuracy [16–18], the Hylleraas basis sets have not yet been applied to neutral hydrogen molecules. In this Rapid Communication, we present the calculations of the nonrelativistic energy and the leading-order relativistic corrections, including the recoil effect, for the ground state of the hydrogen molecule H<sub>2</sub> fully nonadiabatically using the Hylleraas basis sets. Our calculated values of the nonrelativistic and leading-order relativistic (including the recoil effect) contributions to the ground-state dissociation energy are, respectively,  $36\,118.797\,745\,5(16)$  and  $-0.531\,255(63)$  cm<sup>-1</sup>. Together with the QED and higher-order corrections calculated by Pachucki's group [8], the dissociation energy is thus determined to be  $D_0 = 36\,118.069\,71(33)$  cm<sup>-1</sup>, which is in good accord with the two recent experimental results of  $36\,118.069\,62(37)$  cm<sup>-1</sup> [1] and  $36\,118.069\,45(31)$  cm<sup>-1</sup> [2].

In this Rapid Communication, the following physical constants are used [19]: the fine-structure constant  $\alpha = 1/137.035999139(31)$ , the proton-to-electron mass ratio  $m_p/m_e = 1836.15267389(17)$ , and the Rydberg constant  $R_\infty = 10973731.568508(65) \text{ m}^{-1}$ . Atomic units are used unless otherwise stated.

## II. NONRELATIVISTIC WAVE FUNCTIONS AND ENERGIES

In the laboratory frame, the nonrelativistic Hamiltonian for a general four-body Coulombic system is [20]

$$H = - \sum_{i=0}^3 \frac{1}{2m_i} \nabla_{\mathbf{R}_i}^2 + \sum_{0 \leq i < j}^3 \frac{q_i q_j}{|\mathbf{R}_i - \mathbf{R}_j|}, \quad (1)$$

where  $m_i$ ,  $q_i$ , and  $\mathbf{R}_i$  denote the mass, charge, and coordinates of the  $i$ th particle, respectively. By introducing the center-of-mass coordinates and the relative coordinates

$$\mathbf{X} = \frac{\sum_{i=0}^3 m_i \mathbf{R}_i}{\sum_{i=0}^3 m_i}, \quad (2)$$

$$\mathbf{r}_i = \mathbf{R}_i - \mathbf{R}_0, \quad i = 1, 2, 3, \quad (3)$$

and eliminating the center-of-mass motion, the Hamiltonian describing the internal motion of the system is thus

$$H = - \sum_{i=1}^3 \frac{1}{2\mu_i} \nabla_{\mathbf{r}_i}^2 - \sum_{1 \leq i < j}^3 \frac{1}{m_0} \nabla_{\mathbf{r}_i} \cdot \nabla_{\mathbf{r}_j} + \sum_{i=1}^3 \frac{q_0 q_i}{r_i} + \sum_{1 \leq i < j}^3 \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (4)$$

where  $\mu_i = m_i m_0 / (m_i + m_0)$ . For the  $\text{H}_2$  molecule, we choose one of the two protons to be the reference particle located at  $\mathbf{R}_0$ . The Hamiltonian thus becomes

$$H = - \frac{1 + m_p}{2m_p} (\nabla_{\mathbf{r}_1}^2 + \nabla_{\mathbf{r}_2}^2) - \frac{1}{m_p} \nabla_{\mathbf{r}_3}^2 - \frac{1}{m_p} \sum_{1 \leq i < j}^3 \nabla_{\mathbf{r}_i} \cdot \nabla_{\mathbf{r}_j} - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_3} + \frac{1}{r_{12}} - \frac{1}{r_{23}} - \frac{1}{r_{31}}, \quad (5)$$

where  $\mathbf{r}_1$  and  $\mathbf{r}_2$  are the position vectors of the two electrons relative to the proton at  $\mathbf{R}_0$ , and  $\mathbf{r}_3$  the position vector of the second proton relative to the first.

For a pure vibrational state of  $\text{H}_2$ , the angular momentum of the system is zero. The variational wave function can be expanded in terms of the following Hylleraas type basis functions,

$$\phi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = r_1^{j_1} r_2^{j_2} r_3^{j_3} r_{12}^{j_{12}} r_{23}^{j_{23}} r_{31}^{j_{31}} e^{-\alpha r_1 - \beta r_2 - \gamma r_3} \times \chi(1, 2) - (1 \leftrightarrow 2), \quad (6)$$

where the symbol  $(1 \leftrightarrow 2)$  denotes the exchange between the two electrons, and

$$\chi(1, 2) = \alpha(1)\beta(2) - \beta(1)\alpha(2) \quad (7)$$

is the electronic spin function with the total spin  $S = 0$ . Here, the two protons are treated as spinless particles since the hyperfine structure is not considered in the present work. The

TABLE I. Convergence study of the nonrelativistic energy for the ground state of  $\text{H}_2$ , in atomic units.

$\Omega$	No. of terms	$E(\Omega)$	$R(\Omega)$
5	256	-1.163 966 582 926 6	
6	500	-1.164 014 701 977 4	
7	912	-1.164 022 742 555 1	5.98
8	1570	-1.164 024 430 412 5	4.76
9	2570	-1.164 024 883 582 6	3.72
10	4050	-1.164 025 005 934 5	3.70
11	6150	-1.164 025 025 391 4	6.28
12	9070	-1.164 025 029 087 2	5.26
13	13 008	-1.164 025 030 293 0	3.06
14	19 728	-1.164 025 030 779 7	2.47
15	27 456	-1.164 025 030 834 7	8.83
16	37 536	-1.164 025 030 862 5	1.98
17	50 448	-1.164 025 030 873 2	2.60
Extrap.	$\infty$	-1.164 025 030 880(7)	
Ref. [4]	10 000	-1.164 025 030 84(6)	
Ref. [7]	$\infty$	-1.164 025 030 883 1(3)	

basis set is divided into six to ten blocks and the basis functions in the  $i$ th block satisfy the conditions

$$j_1 + j_2 + j_{12} + j_{23} + j_{31} \leq \Omega + 1 - i, \quad (8)$$

$$j_3 = 34 + i, \quad 1 \leq i \leq 10, \quad (9)$$

where  $j_1, j_2, j_3, j_{12}, j_{23}, j_{31}$  are non-negative integers, and  $\Omega$  is an integer that controls the size of the basis set. The terms with  $j_1 > j_2$ , as well as terms with  $j_1 = j_2, j_{23} > j_{31}$ , are omitted to avoid the near linear dependence problem. The integral problems involving Eq. (6) were solved by Drake and Yan two decades ago [21]. For a diatomic molecular system, one essential difference from an atomic system is the high localization of the two nuclei so that the vibrational modes between the two nuclei have to be treated properly. Bhatia and Drachman [22] pointed out that this feature can be simulated satisfactorily by using the function  $\rho^N e^{-b\rho}$ , provided  $N$  is large and  $b \approx N/2$ . In our basis functions, we choose  $j_3 \geq 35$  and  $25 < \gamma < 32$  to describe the vibrational modes between the two protons. The parameters  $\alpha$  and  $\beta$ , which determine the behaviors of the two electrons, are within 1.0 and 2.3. The optimal values of these nonlinear parameters are finally determined by an optimization program.

Table I shows a convergence study of the nonrelativistic energy for the ground state of  $\text{H}_2$  as the size of the basis set increases progressively. The parameter  $R(\Omega)$ , which is a measure of the rate of convergence, is defined by

$$R(\Omega) = \frac{E(\Omega - 1) - E(\Omega - 2)}{E(\Omega) - E(\Omega - 1)}. \quad (10)$$

For  $\Omega \leq 12$ , we divide the basis set into six blocks. For  $\Omega = 13$ , the number of blocks is eight. For  $\Omega \geq 14$ , it is ten blocks. The nonrelativistic energy, calculated to  $-1.164 025 030 873$  a.u. at  $\Omega = 17$ , is extrapolated to  $-1.164 025 030 880(7)$  a.u. Our result is slightly lower than that of Adamowicz's group [4], but is less accurate than that of Pachucki's group [7] by about two orders of magnitude.

### III. LEADING-ORDER RELATIVISTIC CORRECTIONS

The leading relativistic corrections of order  $\alpha^2 R_y$ , including the relativistic recoil corrections of order  $(m_e/m_p)\alpha^2 R_y$  and  $(m_e/m_p)^2\alpha^2 R_y$ , are calculated using the first-order perturbation theory,

$$\Delta E_{\text{rel}} = \langle \Psi_0 | H_{\text{rel}} | \Psi_0 \rangle, \quad (11)$$

where  $\Psi_0$  is the nonrelativistic wave function for the state of interest and  $H_{\text{rel}}$  is the total leading-order relativistic correction operator that includes several terms. These relativistic correction operators have been studied for a general Coulombic system by Stone [23]. In the center-of-mass frame, these relativistic terms, specific to the ground state of  $H_2$ , are

$$H_{MV} = -\frac{1}{8}\alpha^2(p_1^4 + p_2^4), \quad (12)$$

$$H_{SS} = 2\pi\alpha^2\delta^3(\mathbf{r}_{12}), \quad (13)$$

$$H_D = \frac{\pi}{2}\alpha^2[\delta^3(\mathbf{r}_1) + \delta^3(\mathbf{r}_2) + \delta^3(\mathbf{r}_{23}) + \delta^3(\mathbf{r}_{31}) - 2\delta^3(\mathbf{r}_{12})] \\ + \frac{\pi}{2}\frac{1}{m_p^2}\alpha^2[\delta^3(\mathbf{r}_1) + \delta^3(\mathbf{r}_2) + \delta^3(\mathbf{r}_{23}) + \delta^3(\mathbf{r}_{31})], \quad (14)$$

where  $\delta^3(\mathbf{r}_{23}) + \delta^3(\mathbf{r}_{31}) = \delta^3(\mathbf{r}_1) + \delta^3(\mathbf{r}_2)$  due to the symmetry of the system, and

$$H_{OO} = \frac{1}{2}\alpha^2 \left[ \frac{1}{r_{21}} \nabla_2 \cdot \nabla_1 + \frac{1}{r_{21}^3} \mathbf{r}_{21}(\mathbf{r}_{21} \cdot \nabla_2) \nabla_1 \right] \\ - \frac{1}{2}\alpha^2 \frac{1}{m_p} \sum_{i=1}^2 \left[ \frac{1}{r_{3i}} \nabla_3 \cdot \nabla_i + \frac{1}{r_{3i}^3} \mathbf{r}_{3i}(\mathbf{r}_{3i} \cdot \nabla_3) \nabla_i \right] \\ + \frac{1}{2}\alpha^2 \frac{1}{m_p} \sum_{i=1}^2 \left[ \frac{1}{r_i} \nabla_i \cdot \sum_{j=1}^3 \nabla_j + \frac{1}{r_i^3} \mathbf{r}_i(\mathbf{r}_i \cdot \nabla_i) \sum_{j=1}^3 \nabla_j \right] \\ - \frac{1}{2}\alpha^2 \frac{1}{m_p^2} \left[ \frac{1}{r_3} \nabla_3 \cdot \sum_{j=1}^3 \nabla_j + \frac{1}{r_3^3} \mathbf{r}_3(\mathbf{r}_3 \cdot \nabla_3) \sum_{j=1}^3 \nabla_j \right], \quad (15)$$

where  $H_{MV}$  is the correction due to the variation of mass with velocity,  $H_{SS}$  a spin-spin type of interaction between the two electrons,  $H_D$  is the contact interaction which is also called the Darwin term, and  $H_{OO}$  is the correction due to retardation effects. The terms proportional to  $(m_e/m_p)^3$  in Eq. (12) have been omitted at the present level of precision. For the sake of convenience we rewrite  $H_{OO}$  in the form

$$H_{OO} = \frac{\alpha^2}{2} \left( O_1 - \frac{1}{m_p} O_2 + \frac{1}{m_p} O_3 - \frac{1}{m_p^2} O_4 \right), \quad (16)$$

where

$$O_1 = \frac{1}{r_{21}} \nabla_2 \cdot \nabla_1 + \frac{1}{r_{21}^3} \mathbf{r}_{21}(\mathbf{r}_{21} \cdot \nabla_2) \nabla_1, \quad (17)$$

$$O_2 = \sum_{i=1}^2 \left[ \frac{1}{r_{3i}} \nabla_3 \cdot \nabla_i + \frac{1}{r_{3i}^3} \mathbf{r}_{3i}(\mathbf{r}_{3i} \cdot \nabla_3) \nabla_i \right], \quad (18)$$

$$O_3 = \sum_{i=1}^2 \left[ \frac{1}{r_i} \nabla_i \cdot \sum_{j=1}^3 \nabla_j + \frac{1}{r_i^3} \mathbf{r}_i(\mathbf{r}_i \cdot \nabla_i) \sum_{j=1}^3 \nabla_j \right], \quad (19)$$

$$O_4 = \frac{1}{r_3} \nabla_3 \cdot \sum_{j=1}^3 \nabla_j + \frac{1}{r_3^3} \mathbf{r}_3(\mathbf{r}_3 \cdot \nabla_3) \sum_{j=1}^3 \nabla_j. \quad (20)$$

In order to improve the rate of convergence for the expectation value of  $H_{MV}$ , we use the following general transformation,

$$\langle \psi | H_{MV} | \psi \rangle = \frac{\alpha^2}{4} \langle \psi | p_1^2 p_2^2 + \frac{2}{1+m_p} p_1^2 p_3^2 \\ + \frac{2}{1+m_p} p_2^2 p_3^2 | \psi \rangle \\ - \frac{\alpha^2}{2} \frac{m_p^2}{(1+m_p)^2} \langle \psi | (E - V)^2 | \psi \rangle \\ - \frac{\alpha^2}{2} \frac{m_p}{(1+m_p)^2} \langle \psi | (E - V) \sum_{i<j}^3 \nabla_i \cdot \nabla_j \\ + \sum_{i<j}^3 \nabla_i \cdot \nabla_j (E - V) | \psi \rangle \\ + \frac{\alpha^2}{2} \frac{1}{(1+m_p)^2} \langle \psi | p_3^4 | \psi \rangle \\ - \frac{\alpha^2}{2} \frac{1}{(1+m_p)^2} \langle \psi | \left( \sum_{i<j}^3 \nabla_i \cdot \nabla_j \right)^2 | \psi \rangle, \quad (21)$$

where  $E$  and  $\psi$  are, respectively, the energy eigenvalue and the corresponding eigenfunction of the state of interest. For  $\delta^3(\mathbf{r}_i)$  and  $\delta^3(\mathbf{r}_{ij})$ , the Drachman's globalization method [24] can be generalized to the  $H_2$  system,

$$\langle \psi | \delta^3(\mathbf{r}_i) | \psi \rangle = \frac{1}{2\pi\lambda_i} \langle \psi | \frac{1}{r_i} (V_d - E) | \psi \rangle \\ - \frac{1}{2\pi\lambda_i} \sum_{s=1}^3 \lambda_s \langle \nabla_s \psi | \frac{1}{r_i} | \nabla_s \psi \rangle, \quad (22)$$

TABLE II. Expectation values of the relativistic correction operators, in atomic units.

$\Omega$	$p_1^4 + p_2^4$	$\delta^3(\mathbf{r}_1) + \delta^3(\mathbf{r}_2)$	$\delta^3(\mathbf{r}_{12}) \times 10^2$
5	13.005 250	0.451 544 206 5	1.611 685 62
6	13.009 415	0.451 477 426 1	1.613 290 10
7	13.009 026	0.451 463 095 9	1.613 712 54
8	13.008 319	0.451 462 580 9	1.613 904 82
9	13.007 529	0.451 465 150 0	1.614 080 95
10	13.007 380	0.451 462 356 4	1.614 069 00
11	13.007 343	0.451 461 981 1	1.614 066 58
12	13.007 326	0.451 461 942 7	1.614 065 28
13	13.007 315	0.451 461 945 2	1.614 066 56
14	13.007 306	0.451 461 952 3	1.614 068 15
15		0.451 461 953 0	
Extrap.	13.007 27(4)	0.451 461 95(2)	1.614 068(4)

TABLE III. Expectation values of  $O_1$ ,  $O_2$ ,  $O_3$ , and  $O_4$ , in atomic units.

$\Omega$	$O_1 \times 10^2$	$O_2$	$O_3$	$O_4$
5	-9.338 293	2.489 114	-2.495 529 126	-12.385 413
6	-9.284 777	2.493 504	-2.494 464 842	-12.358 607
7	-9.269 364	2.494 225	-2.494 373 948	-12.357 297
8	-9.263 620	2.494 329	-2.494 356 207	-12.357 169
9	-9.259 710	2.494 345	-2.494 356 512	-12.357 125
10	-9.259 437	2.494 352	-2.494 356 044	-12.357 130
11	-9.259 354	2.494 354	-2.494 356 097	-12.357 123
12	-9.259 313	2.494 357	-2.494 356 054	-12.357 115
13	-9.259 292		-2.494 356 069	-12.357 114
14	-9.259 268		-2.494 356 060	-12.357 115
15	-9.259 248			
Extrap.	-9.259 24(4)	2.494 356(2)	-2.494 356 06(3)	-12.357 115(5)

$$\begin{aligned} \langle \psi | \delta^3(\mathbf{r}_{ij}) | \psi \rangle &= \frac{1}{2\pi(\lambda_i + \lambda_j)} \langle \psi | \frac{1}{r_{ij}} (V_d - E) | \psi \rangle \\ &\quad - \frac{1}{2\pi(\lambda_i + \lambda_j)} \sum_{s=1}^3 \lambda_s \langle \nabla_s \psi | \frac{1}{r_{ij}} | \nabla_s \psi \rangle, \end{aligned} \quad (23)$$

with

$$V_d = -\frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_3} + \frac{1}{r_{12}} - \frac{1}{r_{23}} - \frac{1}{r_{31}} - \frac{1}{m_p} \sum_{i<j} \nabla_i \cdot \nabla_j, \quad (24)$$

and

$$\begin{aligned} \lambda_1 = \lambda_2 &= -\frac{1+m_p}{2m_p}, \quad \lambda_3 = -\frac{1}{m_p}, \\ \lambda_{12} = \lambda_{23} = \lambda_{31} &= -\frac{1}{m_p}. \end{aligned} \quad (25)$$

In the calculations of the matrix elements of these operators, some singular integrals such as  $\langle r_{ij}^{-2} \rangle$  and  $\langle r_{ij}^{-3} \rangle$  will emerge. The methods to deal with these singular integrals have been developed by Yan and Drake [25].

The expectation values of the relativistic operators and their convergence behaviors are listed in Tables II and III. It can be seen that all the expectation values of these operators converge to an accuracy of  $10^{-6}$  or better, yielding the total leading-order relativistic correction (including the recoil effect) to the ground state of  $\text{H}_2$  to be  $\Delta E_{\text{mol}}^{(2)} = -2.390\,574(63) \text{ cm}^{-1}$ . As for the leading-order relativistic correction to the ground state of the atomic hydrogen, we use the following formula [19,26],

$$\Delta E_{\text{ato}}^{(2)} = -m_r \alpha^2 \left[ \frac{1}{8} + \frac{m_r}{8(1+m_p)} \right], \quad (26)$$

where  $m_r = m_e m_p / (m_e + m_p)$  is the reduced mass of the electron. Then we obtain the leading-order relativistic contribution to the dissociation energy of the hydrogen molecule  $\Delta E_{\text{diss}}^{(2)} = -0.531\,255(63) \text{ cm}^{-1}$ , which is in better agreement

TABLE IV. Contributions to the dissociation energy  $D_0$  of  $\text{H}_2$  and comparison with other calculations and experiments, in  $\text{cm}^{-1}$ . In the table, "BO" stands for the Born-Oppenheimer approximation.

Contribution	$D_0$	BO or Non BO	Reference
$E^{(0)}$	36 118.797 736(13)	Non BO	Bubin <i>et al.</i> [4]
	36 118.797 746 10(3)	Non BO	Pachucki and Komasa [7]
	36 118.797 745 5(16)	Non BO	This work
$E^{(2)}$	-0.531 9(3)	BO	Piszczatowski <i>et al.</i> [9]
	-0.531 8(3)	BO	Puchalski <i>et al.</i> [8]
	-0.533 121(1)	BO	Puchalski <i>et al.</i> [3]
	-0.569 1	Non BO	Stanke and Adamowicz [11]
	-0.531 255(63)	Non BO	This work
$E^{(3)}$	-0.194 8(2)	BO	Komasa <i>et al.</i> [10]
$E^{(4)}$	-0.002 067(6)	BO	Puchalski <i>et al.</i> [8]
$E^{(5)}$	0.000 12(6)	BO	Puchalski <i>et al.</i> [8]
$E_{\text{FS}}$	-0.000 031	BO	Puchalski <i>et al.</i> [8]
Theory	36 118.069 5(10)		Piszczatowski <i>et al.</i> [9]
	36 118.069 1(6)		Puchalski <i>et al.</i> [8]
	36 118.067 8(6)		Puchalski <i>et al.</i> [3]
	36 118.069 71(33)		This work
Experiment	36 118.069 62(37)		Liu <i>et al.</i> [1]
	36 118.069 45(31)		Altmann <i>et al.</i> [2]

with Pachucki group's earlier values [8,9] than their most recent one [3]. There is a large discrepancy between our value and the one in Ref. [11].

Together with the higher-order relativistic and QED corrections calculated by Pachucki's group [8,10], we finally determine the dissociation energy of  $H_2$  to be  $D_0 = 36\,118.069\,71(33)\text{ cm}^{-1}$ , which agrees with the two recent experimental results of  $36\,118.069\,62(37)\text{ cm}^{-1}$  [1] and  $36\,118.069\,45(31)\text{ cm}^{-1}$  [2]. The various contributions to the dissociation energy of  $H_2$  are listed in Table IV, where  $E^{(n)}$  is the contribution of order  $\alpha^n$  Ry, and  $E_{FS}$  is the one from the proton charge distribution.

#### IV. SUMMARY

The Schrödinger equation for the ground state of the hydrogen molecule  $H_2$  has been solved in Hylleraas coordinates without assuming the Born-Oppenheimer approximation. The nonrelativistic energy calculated by us is slightly better than that of Adamowicz's group [4]; however, it is less accurate than that of Pachucki's group [7], by about two

orders of magnitude. The leading-order relativistic corrections, including the relativistic recoil effect, have then been calculated perturbatively. We have found that the leading-order relativistic effect contributes to the dissociation energy of  $H_2$  by an amount of  $-0.531\,255(63)\text{ cm}^{-1}$ . Together with the higher-order relativistic and QED corrections obtained by Pachucki's group [8,10], we have determined the dissociation energy to be  $D_0 = 36\,118.069\,71(33)\text{ cm}^{-1}$ , which is in perfect agreement with the most recent experimental results of  $36\,118.069\,62(37)\text{ cm}^{-1}$  [1] and  $36\,118.069\,45(31)\text{ cm}^{-1}$  [2].

#### ACKNOWLEDGMENTS

This work was supported by the Chinese National Natural Science Foundation Grant No. 11404101 and by NSERC of Canada. The computing facilities at SHARCnet and ACEnet of Canada and at the School of Physics, Wuhan University of China are gratefully acknowledged. Z.C.Y. was also supported by the CAS/SAFEA International Partnership Program for Creative Research Teams.

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