



Theoretical Determination of the Dissociation Energy of Molecular Hydrogen

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Abstract: The dissociation energy of molecular hydrogen is determined theoretically with a careful estimation of error bars by including nonadiabatic, relativistic, and quantum electrodynamics (QED) corrections. The relativistic and QED corrections were obtained at the adiabatic level of theory by including all contributions of the order α^2 and α^3 as well as the major (one-loop) α^4 term, where α is the fine-structure constant. The computed α^0 , α^2 , α^3 , and α^4 components of the dissociation energy of the H_2 isotopomer are 36 118.7978(2), $-0.5319(3)$, $-0.1948(2)$, and $-0.0016(8) \text{ cm}^{-1}$, respectively, while their sum amounts to $36\,118.0695(10) \text{ cm}^{-1}$, where the total uncertainty includes the estimated size ($\pm 0.0004 \text{ cm}^{-1}$) of the neglected relativistic nonadiabatic/recoil corrections. The obtained theoretical value of the dissociation energy is in excellent agreement with the most recent experimental determination $36\,118.0696(4) \text{ cm}^{-1}$ [J. Liu et al. *J. Chem. Phys.* **2009**, *130*, 174 306]. This agreement would have been impossible without inclusion of several subtle QED contributions which have not been considered, thus far, for molecules. A similarly good agreement is observed for the leading vibrational and rotational energy differences. For the D_2 molecule we observe, however, a small disagreement between our value $36\,748.3633(9) \text{ cm}^{-1}$ and the experimental result $36\,748.343(10) \text{ cm}^{-1}$ obtained in a somewhat older and less precise experiment [Y. P. Zhang et al. *Phys. Rev. Lett.* **2004**, *92*, 203003]. The reason of this discrepancy is not known.

1. Introduction

Theoretical determination of the dissociation energy D_0 of the simplest, prototypical chemical bond in the hydrogen molecule has a long history. It started in 1927, very shortly after the discovery of quantum mechanics, by the work of

Heitler and London¹ who approximately solved the Schrödinger equation for two electrons in the Coulomb field of two protons and found that this system is stable against the dissociation to two hydrogen atoms. The approximate dissociation energy they obtained represented only about 60% of the observed value, but it could be argued that by virtue of the variational principle this was only a lower bound and, consequently, that the new quantum theory satisfactorily explained the hitherto puzzling stability of the chemical bond between electrically neutral atoms. A few years later, James and Coolidge^{2,3} computed a much better, 13-term wave function depending explicitly on the interelectron distance and found that $D_0 = 4.454 \pm 0.013 \text{ eV}$ — a value within error bars of the experimental value $4.46 \pm 0.04 \text{ eV}$ available

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at that time⁴ (obtained from the heat of dissociation) and within about 0.5% of the present day value of 4.478 eV. This was an amazing achievement for a computation carried out and checked by, as the authors of ref. 2 put it, “an experienced computer”.

When the electronic computers became available Kolos and Wolniewicz⁵ extended the work of James and Coolidge to much longer wave function expansions (up to about 100 terms) and developed methods and codes to account for the coupling of the electronic and the nuclear motion and for the effects of relativity. The theoretical dissociation energy obtained by Kolos and Wolniewicz $D_0 = 36\,117.4\text{ cm}^{-1}$ ^{6,7} could be confronted with the most accurate experimental determination from Herzberg and Monfils amounting to $36\,113.6 \pm 0.3\text{ cm}^{-1}$.⁸ Since, by virtue of the variational principle, the theoretical result can be viewed as a lower bound, both of these values can be correct only if the quantum mechanics fails to describe the dissociation of the H–H bond with quantitative accuracy. Fortunately, new experimental determinations from Herzberg⁹ ($36\,116.3\text{ cm}^{-1} < D_0 < 36\,118.3\text{ cm}^{-1}$) and Stwalley¹⁰ ($D_0 = 36\,118.6 \pm 0.5\text{ cm}^{-1}$) resolved this difficulty in favor of theory. This development demonstrated that the Schrödinger equation when solved accurately and corrected for small effects of relativity can predict the molecular energy levels with very high precision and, therefore, it laid a foundation for the current faith in the quantitative predictive power of quantum chemistry.

Further theoretical^{11–13} and experimental^{14–16} work has reduced the discrepancy between theory and experiment to several hundredths of a cm^{-1} . Very recently Liu et al.¹⁷ described a hybrid, experimental–theoretical determination of D_0 based on several transition frequency measurements^{17–20} and theoretical calculations of the energy levels of the H_2^+ ion.^{21–24} The dissociation energy $D_0 = 36\,118.06962\text{ cm}^{-1}$ determined in this way¹⁷ has been reported with an uncertainty of $\pm 0.00037\text{ cm}^{-1}$ – almost 2 orders of magnitude smaller than that of the previous most accurate determination $D_0 = 36\,118.062 \pm 0.010\text{ cm}^{-1}$ of Zhang et al.¹⁶ The best available theoretical predictions of $36\,118.049\text{ cm}^{-1}$ from Kolos and Rychlewski¹² and $36\,118.069\text{ cm}^{-1}$ from Wolniewicz¹³ are significantly less precise and have been reported without any error bar estimates. Both of these predictions involve an incomplete treatment of α^3 quantum electrodynamics (QED) corrections,²⁵ so it is not clear if the perfect agreement between the experiment and Wolniewicz’s calculation is not fortuitous. In fact, Wolniewicz has concluded his paper¹³ with the remark that the main uncertainty in his dissociation energy is due to the neglected QED effects. Specifically, he has neglected the α^3 contributions, resulting from two-photon exchanges between electrons—the so-called Araki–Sucher effect^{26,27}—and used a simple approximation of the Bethe logarithm,^{28,29} which was shown to be rather inaccurate when applied to H_2^+ .³⁰

In this communication, we present a complete calculation of the α^3 QED contribution to D_0 and give an approximate value of the next α^4 term in the fine-structure constant expansion of D_0 . We have also recomputed the nonrelativistic and α^2 relativistic parts of D_0 , paying special attention to an

estimation of the error bars for all evaluated contributions. We hope that this estimation will enable a more meaningful comparison of theoretical predictions with the newest experimental result.¹⁷

2. Method

For molecules with light nuclei, the most convenient theoretical framework for the description of molecular properties is the expansion in powers of the fine-structure constant α (in our calculations we assumed that $\alpha = 1/137.0359997$, cf. ref 31). Specifically, the molecular or atomic energy levels needed to compute D_0 can be obtained from the expansion:

$$E = E^{(0)} + \alpha^2 E^{(2)} + \alpha^3 E^{(3)} + \alpha^4 E^{(4)} + \dots \quad (1)$$

where $E^{(0)}$ is the nonrelativistic energy, i.e., an eigenvalue of the Schrödinger equation for the electrons and nuclei (with the center-of-mass motion separated out), $\alpha^2 E^{(2)}$ is the expectation value of the Breit–Pauli Hamiltonian²⁵ with the nonrelativistic wave function (assuming the molecular center of mass at rest), $\alpha^3 E^{(3)}$ is the leading QED correction,^{25–27} and $\alpha^4 E^{(4)}$ collects all relativistic and QED corrections proportional to α^4 .^{32,33} (when expressed in atomic units).

2.1. Nonrelativistic Energy. The nonrelativistic approximation $D_0^{(0)}$ to D_0 can be obtained variationally by minimization of the expectation value of the complete four-particle Hamiltonian with an appropriate trial function.^{33,34} To have better error control and to generate wave functions and potentials needed in QED calculations, we adopted, however, a stepwise approach and computed D_0 as the sum:

$$D_0^{(0)} = D_0^{\text{BO}} + \delta D_0^{\text{ad}} + \delta D_0^{\text{na}} \quad (2)$$

where D_0^{BO} is the result of standard Born–Oppenheimer calculation, δD_0^{ad} is the adiabatic (diagonal Born–Oppenheimer) correction,^{36,37} and δD_0^{na} is a (very small) nonadiabatic correction defined essentially as the difference between $D_0^{(0)}$ and the sum of D_0^{BO} and δD_0^{ad} .

The Born–Oppenheimer potential $V(R)$ needed in the computation of D_0^{BO} , δD_0^{ad} , and δD_0^{na} and of the relativistic/QED corrections was represented in the following form:

$$V(R) = e^{-\beta R^2 - \gamma R} \left(R^{-1} + \sum_{n=0}^{16} b_n R^n \right) + \left(\sum_{n=0}^2 a_n R^n + a_3 R^{5/2} \right) e^{-2R} - \sum_{n=6}^{26} f_n(\eta R) \frac{C_n}{R^n} \quad (3)$$

where R is the internuclear distance, C_6, \dots, C_{26} are van der Waals coefficients fixing the large R asymptotics of $V(R)$, and $f_n(x) = 1 - e^{-x}(1 + x + x^2/2! + \dots + x^n/n!)$ is the Tang–Toennies damping function.³⁸ The asymptotic coefficients $C_6, C_8, C_{10}, C_{11}, \dots, C_{26}$ (C_7, C_9 vanish) were taken from the work of Mitroy and Ovsinnikov³⁹ with the full 13 digit accuracy (we recomputed the five leading coefficients C_6, C_8, C_{10}, C_{11} , and C_{12} obtaining the same results as the ones reported in ref 39). Accurate values of the asymptotic C_n coefficients are available also for $n > 26$,^{38,39} but we found that their inclusion in the last term of eq 3 did

Table 1. Parameters Determining the Analytic Form, eq 3, of the Born–Oppenheimer Potential for H₂^a

b_0	−246.146616782077	b_{11}	19.870410304616
b_1	−122.890180187858	b_{12}	−7.564322211157
b_2	−162.863251799668	b_{13}	2.089842241100
b_3	−67.028576007896	b_{14}	−0.400842621727
b_4	−58.308248409124	b_{15}	0.047594467110
b_5	3.483076932756	b_{16}	−0.002719925287
b_6	−52.461380739836	β	0.584358199608
b_7	59.254861689279	γ	3.338428574260
b_8	−70.780756953312	η	2.561607545
b_9	59.254901002422	a_2	5.258436256979
b_{10}	−39.529747868821	a_3	−1.499067595467

^a All parameters are in atomic units.

not lead to further improvement of the fit [with the fixed form of the short-range part of $V(R)$]. It should be noted that the values of C_{24} , C_{25} , and C_{26} reported later by Ovsiannikov and Mitroy⁴⁰ with a smaller number of digits cannot be used in our fit.

The three nonlinear parameters β , γ , η and 19 linear ones a_2 , a_3 , b_0 , ..., b_{16} were obtained by least-squares fitting the right hand side (rhs) of eq 3 to the energies computed by Sims and Hagstrom⁴¹ for 47 internuclear distances R ranging from 0.4 to 6.0 bohr. In the vicinity of the minimum of the potential well, these energies have an error on the order of 10^{-6} cm^{-1} ,⁴¹ while for $R = 6.0$, where the basis set used by Sims and Hagstrom is least adequate, the error is smaller than $2 \times 10^{-5} \text{ cm}^{-1}$.⁴² For 27 distances outside the range covered by Sims and Hagstrom, we used values obtained by Cencek⁴² using a 1200-term fully optimized Gaussian geminal basis set. These values have an error smaller than $2 \times 10^{-5} \text{ cm}^{-1}$.⁴² The linear parameters a_0 , a_1 were constrained by the relations:

$$\begin{aligned} a_0 &= E_{\text{He}} - 2E_{\text{H}} - b_0 + \gamma \\ a_1 &= 2a_0 + \gamma b_0 - b_1 + \beta - \frac{\gamma^2}{2} + \sum_{n=6}^{26} \frac{C_n \eta^{n+1}}{(n+1)!} \end{aligned} \quad (4)$$

required to ensure the right behavior of $V(R)$ at small distances:

$$V(R) = \frac{1}{R} + E_{\text{He}} - 2E_{\text{H}} + \mathcal{O}(R^2) \quad (5)$$

with $E_{\text{He}} = -2.903724377034119$ and $E_{\text{H}} = -0.5$ being atomic energies of helium and hydrogen (assuming infinite nuclear mass). The error of our fit is $5 \times 10^{-5} \text{ cm}^{-1}$ at the bottom of the potential well and is even smaller at larger distances. The fit parameters obtained by us are listed in Table 1. A code generating $V(R)$ is available upon request.

The dissociation energy D_0^{BO} computed using the analytic Born–Oppenheimer potential generated in this way is $36\,112.59273 \text{ cm}^{-1}$ (using the conversion factor 1 hartree = $219\,474.631\,37 \text{ cm}^{-1}$).³¹ We estimate that the error of this value is 0.00010 cm^{-1} . Since the potential points have substantially smaller inaccuracies and since the numerical integration of the radial Schrödinger equation with an analytic potential does not introduce a significant error, most of the uncertainty of D_0^{BO} results from the fitting procedure.

Accurate values of the adiabatic $\delta D_0^{\text{ad}} = 5.77111 \text{ cm}^{-1}$ and the nonadiabatic $\delta D_0^{\text{na}} = 0.43391 \text{ cm}^{-1}$ corrections to D_0^{BO} were recently computed by two of us⁴³ using a perturbation method formulated in ref 44 (the proton mass $m_p = 1\,836.15267247 m_e$ was assumed³¹ in obtaining these numbers). The computation of the adiabatic correction reported in refs 43 and 44 was carried out using a novel, very stable numerical procedure,⁴⁴ avoiding entirely the cumbersome differentiation of the electronic wave function. With basis sets ranging from 600 to 1800 fully optimized Gaussian geminals, the accuracy of at least five significant figures for δD_0^{ad} was achieved. Therefore, we can assume that the error of δD_0^{ad} is smaller than 0.00010 cm^{-1} . Also all five figures of the nonadiabatic correction δD_0^{na} appear to be converged with regard to the extension of the basis set. However, the fourth- and higher-order effects neglected in the perturbation procedure of ref 43 may be of the order of $0.0001\text{--}0.0002 \text{ cm}^{-1}$. In fact, the value $\delta D_0^{\text{na}} = 0.43391 \text{ cm}^{-1}$ differs from the earlier, methodologically very different, calculation of Wolniewicz by 0.0002 cm^{-1} . Therefore, we assign the uncertainty of 0.00020 cm^{-1} to the value $\delta D_0^{\text{na}} = 0.43391 \text{ cm}^{-1}$.

Adding D_0^{BO} , δD_0^{ad} , and δD_0^{na} , we find that the nonrelativistic dissociation energy amounts to $D_0^{(0)} = 36\,118.7978(2) \text{ cm}^{-1}$, where the uncertainty (given in the parentheses as the error in the last digit) is calculated by quadratically adding the errors of summed contributions. Our result for $D_0^{(0)}$ is consistent with the value $36\,118.79774(1) \text{ cm}^{-1}$ obtained very recently⁴⁵ using 10 000 extensively optimized Gaussians (and more than a year of massively parallel computing). The accuracy achieved in ref 45, however impressive, is not relevant for our purposes since the experimental uncertainty of D_0 and, even more so, the uncertainty of the relativistic and QED contributions to D_0 are 2 orders of magnitude larger than the error of the large-scale variational calculations of ref 45.

2.2. Lowest-Order Relativistic Contribution. The lowest-order, α^2 relativistic correction to the nonrelativistic energy is expressed by the expectation value of the Breit–Pauli Hamiltonian^{46,47} over the nonrelativistic wave function ψ . When the electrons and nuclei are in their singlet states and when the terms containing the proton charge radius and the so-called recoil terms,^{48,49} (of the order of $(m_e/m_p)^n \alpha^2$, $n = 1, 2, 3$) are neglected, this correction is given by the sum of four terms:

$$E^{(2)} = -\frac{1}{4} \langle \mathbf{p}_1^4 \rangle + 2\pi \langle \delta(\mathbf{r}_{1a}) \rangle + \pi \langle \delta(\mathbf{r}_{12}) \rangle - \frac{1}{2} \left\langle \mathbf{p}_1 \frac{1}{r_{12}} \mathbf{p}_2 + \mathbf{p}_1 \cdot \mathbf{r}_{12} \frac{1}{r_{12}^3} \mathbf{r}_{12} \cdot \mathbf{p}_2 \right\rangle \quad (6)$$

referred to successively as the mass–velocity, the one- and two-electron Darwin, and the Breit contributions (the contact spin–spin interaction is included in the two-electron Darwin term). In eq 6, \mathbf{p}_i is the momentum operator for the i th electron, \mathbf{r}_{1a} is the vector pointing from nucleus a to electron 1, \mathbf{r}_{12} is the vector pointing from electron 2 to electron 1, and $\delta(\mathbf{r})$ is the three-dimensional Dirac distribution. We made use of the fact that the wave function ψ employed to compute the expectation values is symmetric in the spatial electronic

and nuclear coordinates. When computing the expectation values in eq 6, we used the adiabatic function $\psi_{\text{ad}} = \chi(R)\psi_{\text{el}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$, where $\psi_{\text{el}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$ is the electronic wave function depending parametrically on the vector \mathbf{R} joining the nuclei, and $\chi(R)$ is the solution of the radial Schrödinger equation with the potential $V(R)$ plus the adiabatic correction to $V(R)$.⁴⁴ With this approximation for ψ , the expectation values in eq 6 are obtained by averaging the R dependent electronic expectation values, e.g., $2\pi\langle\psi_{\text{el}}|\delta(\mathbf{r}_{1a})|\psi_{\text{el}}\rangle \equiv D_1(R)$ with the weight function given by the square of $\chi(R)$. This adiabatic procedure is justified since, as discussed in Section 3, the neglected cross relativistic–nonadiabatic terms can be expected to be of the order of $(m_e/m_p)\alpha^2$, and therefore, 3 orders of magnitude smaller than the relativistic correction of eq 6. The R dependent electronic expectation values corresponding to the four successive terms in eq 6 will be denoted by us as $P(R)$, $D_1(R)$, $D_2(R)$, and $B(R)$. These radial functions were computed by Wolniewicz⁵⁰ using the basis of Kolos and Wolniewicz.⁵¹ They were tabulated⁵⁰ for 55 internuclear distances ranging from $R = 0.2$ to 12.0 bohr in the form of functions $\varepsilon_k(R)$ related to ours by $\varepsilon_1(R) = P(R)$, $\varepsilon_2 = B(R)$, $\varepsilon_4(R) = D_1(R) - D_2(R)$, $\varepsilon_5(R) = 2D_2(R)$.

We recomputed these radial functions using extensively optimized sets of Gaussian geminals and paying special attention⁵² to larger internuclear separations. We also computed the constants determining the asymptotic behavior of $P(R)$, $D_1(R)$, and $B(R)$ at large R . The first three constants (at $1/R^6$, $1/R^8$, and $1/R^{10}$), fixing $P(R)$ and $D_1(R)$ at large R were already reported in ref 52 [$D_2(R)$ vanishes exponentially at large R].

For the Breit correction $B(R)$, we considered only the first two terms in the asymptotic expansion $B(R) = W_4R^{-4} + W_6R^{-6} + \dots$. The constants W_4 and W_6 are given by the expressions:^{53,54}

$$W_4 = -2\langle\phi_0|z_{1a}z_{2b}\mathbf{R}_0p_{z1}p_{z2}|\phi_0\rangle \quad (7)$$

and

$$W_6 = -9\langle\phi_0|(Q_{22}^0)_{1a2b}\mathbf{R}_0(z_{1a}p_{z1} + p_{z1}z_{1a})p_{z2}|\phi_0\rangle - \frac{12}{5}\langle\phi_0|z_{1a}z_{2b}\mathbf{R}_0[2r_{1a}^2p_{z1} - z_{1a}(\mathbf{r}_{1a} \cdot \mathbf{p}_1)]p_{z2}|\phi_0\rangle \quad (8)$$

where ϕ_0 is the product of atomic wave functions, $\mathbf{R}_0 = (H_a + H_b - E_a - E_b)^{-1}$ is the reduced resolvent for two noninteracting hydrogen atoms, z_{1a} , z_{2b} , p_{z1} , and p_{z2} are the z components of the vectors \mathbf{r}_{1a} , \mathbf{r}_{2b} , \mathbf{p}_1 , and \mathbf{p}_2 , and finally, $(Q_{22}^0)_{1a} = 1/2(3z_{1a}^2 - r_{1a}^2)$ is the quadrupole moment operator. We computed W_4 and W_6 using the spd part of the Dunning's one-electron Gaussian basis set of the sextuple- ζ quality with double augmentation, d-aug-cc-pV6Z.⁵⁵ The atomic orbitals and all the necessary integrals were obtained using the DALTON suite of codes.⁵⁶ The values of both coefficients were calculated using the sum-over-states technique with a code written especially for this purpose. All excited states resulting from the chosen basis set were included in the summation defining \mathbf{R}_0 . We found that $W_4 = 0.4627(7)$ and $W_6 = 3.995(7)$ atomic units. The proposed error bars were determined by observing changes of the W_4 and W_6 values

Table 2. Electronic Bethe Logarithm, $\ln K^{\text{el}}(R)$, and the Electronic Expectation Values of $\delta(\mathbf{r}_{1a})$, $\delta(\mathbf{r}_{12})$, and $P(r_{12}^3)$ for H_2 as Functions of Internuclear Separation, R^a

R	$\ln K^{\text{el}}$	$\delta(\mathbf{r}_{1a})$	$\delta(\mathbf{r}_{12})$	$P(r_{12}^3)$
0.0	4.37016	3.62086	0.10635	0.98927
0.1	3.765	2.88530	0.10157	0.98082
0.2	3.526	2.28447	0.09137	0.96236
0.4	3.279	1.50399	0.06887	0.88474
0.6	3.1596	1.06778	0.05076	0.77747
0.8	3.09331	0.80828	0.03767	0.66964
1.0	3.05490	0.64410	0.02835	0.57115
1.1	3.04206	0.58427	0.02473	0.52685
1.2	3.03215	0.53496	0.02164	0.48593
1.3	3.02448	0.49397	0.01901	0.44828
1.4	3.01855	0.45967	0.01674	0.41430
1.5	3.01396	0.43079	0.01479	0.38169
1.6	3.01040	0.40636	0.01309	0.35199
1.7	3.00763	0.38565	0.01161	0.32500
1.8	3.00547	0.36805	0.01032	0.30005
1.9	3.00377	0.35309	0.00918	0.27685
2.0	3.00240	0.34040	0.00817	0.25544
2.2	3.00034	0.32062	0.00649	0.21731
2.4	2.99878	0.30686	0.00514	0.18412
2.6	2.99742	0.29779	0.00406	0.15552
2.8	2.99610	0.29243	0.00319	0.13036
3.0	2.99476	0.29000	0.00247	0.10847
3.5	2.99137	0.29236	0.00124	0.06613
4.0	2.98848	0.29997	0.00057	0.03881
4.5	2.98650	0.30722	0.00024	0.02277
5.0	2.98534	0.31220	0.00010	0.01390
5.5	2.98473	0.31510	0.00004	0.00903
6.0	2.98442	0.31667	0.00001	0.00625
7.0	2.98420	0.31788	0.00000	0.00347
8.0	2.98415	0.31819	0.00000	0.00219
10.0	2.98413	0.31829	0.00000	0.00107
12.0	2.98413	0.31831	0.00000	0.00061

^a All values in atomic units.

obtained with d-aug-cc-pVXZ bases, $X = \text{T, Q, 5, and 6}$, and by making a comparison with the results computed using the alternative form of eqs 7 and 8 in which the linear momentum operators are replaced by operators corresponding to the Cartesian coordinates.^{53,54}

Except for large distances, $R > 10$ bohr, our values of $P(R)$ and $D_1(R)$ agree very well with those of Wolniewicz, so we used Wolniewicz's values (available for a larger number of distances) in computing the averages $\langle P(R) \rangle$ and $\langle D_1(R) \rangle$. For $R > 10.0$ bohr, we used our values, which appear to agree somewhat better with the exact asymptotics. For $R > 12.0$, we applied the three-term (undamped) asymptotic expansion with the constants (at $1/R^6$, $1/R^8$, and $1/R^{10}$) published earlier by the three of us.⁵² By observing the basis set convergence patterns and by comparing our values of $P(R)$ and $D_1(R)$ with those published by Wolniewicz, we estimate that the computed dissociation energy contributions due to the mass–velocity and one-electron Darwin terms, amounting to 4.4273 and -4.9082 cm^{-1} , respectively, have the uncertainty of 0.0002 cm^{-1} each.

For the two-electron Darwin term, we found that our values of $D_2(R)$, computed with a basis set of 1 200 fully optimized Gaussian geminals, are slightly different than those of Wolniewicz.⁵⁰ The observed basis set convergence pattern and the independent calculations of Cencek⁴² suggest that our values, listed in Table 2, are more accurate (especially at smaller values of R), and we used them to calculate

$\langle D_2(R) \rangle$. We estimate that the dissociation energy contribution $-\alpha^2 \langle D_2(R) \rangle = -0.5932 \text{ cm}^{-1}$ computed using these values has an uncertainty of 0.0001 cm^{-1} .

For $R \leq 5.0$ bohr, our values of $B(R)$ agree very well with those of Wolniewicz, and we used the latter in calculating $B(R)$. For $R > 5.0$ bohr, however, the Wolniewicz's values appear to be less accurate, deviating significantly from the correct asymptotics at large R . Therefore, for $R > 5.0$ bohr we used the analytic fit:

$$B(R) = e^{-bR}(A_0 + A_1R + A_2R^2 + A_3R^3 + A_4R^4) + \frac{W_4}{R^4} + \frac{W_6}{R^6} \quad (9)$$

with parameters $b = 1.351860240$, $A_0 = 2.077615180$, $A_1 = -2.519175275$, $A_2 = 0.577315005$, $A_3 = -0.051870326$, and $A_4 = 0.001715821$, all in atomic units, adjusted to values computed by us for $R > 5.0$ bohr. We estimate that the resulting contribution to the dissociation energy $-\alpha^2 \langle B(R) \rangle = 0.5422 \text{ cm}^{-1}$ has an uncertainty of 0.0001 cm^{-1} .

2.3. QED Contribution. The lowest-order QED correction, $\alpha^3 E^{(3)}$, to the energy of an atomic or molecular bound state is given by^{25–27}

$$E^{(3)} = \frac{16}{3} \left(\frac{19}{30} - 2 \ln \alpha - \ln K \right) \langle \delta(\mathbf{r}_{1a}) \rangle + \left(\frac{164}{15} + \frac{14}{3} \ln \alpha \right) \langle \delta(\mathbf{r}_{12}) \rangle - \frac{7}{6\pi} \langle P(r_{12}^{-3}) \rangle \quad (10)$$

where the expectation values are computed with the eigenfunction ψ of the nonrelativistic Hamiltonian H . $P(r_{12}^{-3})$ is the distribution defined in atomic units by

$$\langle \varphi_1 | P(r_{12}^{-3}) | \varphi_2 \rangle = \lim_{a \rightarrow 0} [\langle \varphi_1 | \theta(r_{12} - a) r_{12}^{-3} | \varphi_2 \rangle + 4\pi(\gamma + \ln a) \langle \varphi_1 | \delta(\mathbf{r}_{12}) | \varphi_2 \rangle] \quad (11)$$

where $\theta(x)$ is the Heaviside step function, and γ is the Euler–Mascheroni constant. The so-called Bethe logarithm, $\ln K$, in eq 10 is defined as

$$\ln K = \frac{\langle \psi | \mathbf{j} (H - E^{(0)}) \ln [(H - E^{(0)}) / \text{Ry}_\infty] | \mathbf{j} \psi \rangle}{\langle \psi | \mathbf{j} (H - E^{(0)}) | \mathbf{j} \psi \rangle} \quad (12)$$

where $\mathbf{j} = -\mathbf{p}_1/m_e - \mathbf{p}_2/m_e + \mathbf{p}_a/m_p + \mathbf{p}_b/m_p$ is the electric current operator for the system (\mathbf{p}_a and \mathbf{p}_b are proton momenta), and $\text{Ry}_\infty = \alpha^2 m_e c^2 / 2 = 1/2$ hartree is the Rydberg constant. The expectation values $\langle \delta(\mathbf{r}_{1a}) \rangle$ and $\langle \delta(\mathbf{r}_{12}) \rangle$ are already known from the calculation of the α^2 contribution, so the only new quantities to be calculated are the Bethe logarithm $\ln K$ and the so-called Araki–Sucher term – the last on the rhs of eq 10.

The evaluation of eq 12 for the four-body system using an accurate nonadiabatic wave function ψ appears to be very demanding computationally and was not attempted. Instead we used an adiabatic approximation to $\ln K$ defined as

$$\ln K^{\text{ad}} = \frac{\langle \ln K^{\text{el}}(R) D_1(R) \rangle}{\langle D_1(R) \rangle} \quad (13)$$

where $D_1(R)$ is the already computed electronic expectation value of $2\pi\delta(\mathbf{r}_{1a})$, and the averaging over R is carried out with the adiabatic nuclear wave function $\chi(R)$. The R dependent electronic Bethe logarithm, $\ln K^{\text{el}}(R)$, appearing in eq 13, is defined exactly by eq 12 but with ψ replaced by the electronic wave function $\psi_{\text{el}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$, H by the electronic Hamiltonian H^{el} , $E^{(0)}$ by the Born–Oppenheimer energy $-2\text{Ry}_\infty + V(R)$, and \mathbf{j} by the total electronic momentum operator $\mathbf{p}_1 + \mathbf{p}_2$. Note that after these substitutions, the denominator in eq 12 becomes equal to $4D_1(R)$.

One can ask how well does this simple adiabatic approximation for $\ln K$ work? To answer this question we used eq 13 to compute $\ln K^{\text{ad}}$ for the H_2^+ ion using the values of $\ln K^{\text{el}}(R)$ reported in ref 30 (note that the definition of $\ln K$ adopted in this reference differs from ours by $\ln 2$). The obtained adiabatic value $\ln K^{\text{ad}} = 3.01276$ agrees very well with the result $\ln K = 3.01225$ of the complete nonadiabatic calculation of Korobov.²¹ In fact, the adiabatic value (obtained with the real electron mass m_e) should be corrected by $\ln(\mu/m_e)$, where $\mu = m_e(1 + m_e/m_p)^{-1}$ is the reduced electron mass (see ref 25, p. 101). With this correction, the adiabatic value, equal now to 3.01222, differs only in 1 part per 10^5 from the result of Korobov's calculation. Similarly excellent agreement is observed for the excited vibrational levels. Since using this reduced electron mass correction gives an energy effect of the order of $(m_e/m_p)\alpha^3$, much smaller than the neglected relativistic recoil effects, we did not include this correction in our H_2 calculations.

To compute $\ln K^{\text{el}}(R)$, we followed closely the technique described in refs 57–59. The present work is the first molecular application of this technique and probably the first calculation of the Bethe logarithm for a molecule other than H_2^+ and HD^+ . The method employed by us is based on the integral representation of $\ln K$ introduced by Schwartz⁶⁰ and involves essentially an integration over the photon momenta k . Using large Gaussian geminal bases fully optimized at each value of R and k (by minimizing the relevant Hylleraas-type functionals) allows for a very efficient modeling of perturbed wave functions at different k and R dependent length scales. The mathematical completeness of Gaussian geminal bases for functions of Σ and Π symmetries, appearing in our calculations, is guaranteed by theorems proved in refs 61, 62. By inspecting the basis convergence pattern, we found that the values of $\ln K^{\text{el}}(R)$, obtained with 3000-term geminal bases, and listed in Table 2, may be inaccurate only at the last figure given in this table. It may be of some interest to note that our values of $\ln K^{\text{el}}(R)$ agree rather well with the values one can obtain using approximate models proposed by Garcia²⁸ and Bishop and Cheung²⁹ and used by Wolniewicz.¹³ In fact, the Garcia model works somewhat better underestimating $\ln K^{\text{el}}(R)$ by 2% at $R = 1$ bohr and even less for larger distances. The model of Bishop and Cheung overestimates $\ln K^{\text{el}}(R)$ by 4% at $R = 1$ bohr, by 2% at the minimum of the potential well, and by less than that at larger internuclear separations. Note, however, that the good performance of these models does not hold generally, since they do not work so well for H_2^+ .³⁰

We obtained a very accurate analytic fit of $\ln K^{\text{el}}(R)$ interpolating between the atomic hydrogen, $\ln K_{\text{H}}$, and

Table 3. Parameters Determining the Analytic Form, eq 14, of the Bethe Logarithm, $\ln K^{\text{el}}(R)^a$

$\ln K_{\text{He}}$	4.370160222
$\ln K_{\text{H}}$	2.984128555
L_6	2.082773197
A_1	-2.296997851
A_2	2.791145918
A_3	-1.589533050
A_4	0.408542881
b	2.292743496

^a All parameters are in atomic units.

helium, $\ln K_{\text{He}}$, values and exhibiting the correct L_6/R^6 fall off at large R . The asymptotic constant L_6 was calculated independently from appropriate perturbation theory expressions using the Slater basis set. The specific form of the fit function is

$$\ln K^{\text{el}}(R) = \ln K_{\text{H}} + e^{-bR}(\ln K_{\text{He}} - \ln K_{\text{H}} + A_1 R + A_2 R^2 + A_3 R^3 + A_4 R^4) + \frac{f_6(R)L_6}{R^6} \quad (14)$$

The parameters of the fit are given in Table 3. For $R > 1$ bohr, the error of this fit is of the order of 10^{-4} (at few points in the vicinity of $R = 3$ bohr it reaches 4×10^{-4}), but using the fit function in evaluating the formula (13) leads to errors much smaller than 0.0001.

The value of $\ln K^{\text{ad}}$, found using eq 14 and our values of $D_1(R)$, amounts to 3.0188 and has an uncertainty smaller than 0.0001. Using this value, we can compute the dissociation energy contribution from the first term in eq 10, referred to as the one-electron Lamb shift. This term, dominating the total α^3 contribution, is equal to -0.2241 cm^{-1} , and we estimate its uncertainty as 0.0001 cm^{-1} . It is worthwhile to note that using the atomic hydrogen value of $\ln K$, which is a natural and inexpensive approximation, one obtains -0.2277 cm^{-1} instead of -0.2241 cm^{-1} , i.e., a value which is not sufficiently accurate for our purpose. Thus, including the correct R dependence of the electronic Bethe logarithm is essential for a meaningful comparison with high-precision experimental data. The second term in eq 10, which we refer to as the two-electron Lamb shift, gives only 0.0166 cm^{-1} with an uncertainty smaller than 0.0001 cm^{-1} .

The Araki–Sucher term, the last in eq 10, was also obtained in the adiabatic approximation by computing the R -dependent electronic expectation value $A(R) = -(7/6\pi)\langle\psi_{\text{el}}|P(r_{12}^{-3})|\psi_{\text{el}}\rangle$ and subsequently averaging $A(R)$ with the square of the adiabatic nuclear wave function $\chi(R)$. The numerical calculation was performed using Gaussian geminal basis. The needed matrix elements of the distribution $P(r_{12}^{-3})$ between Gaussian geminal functions located at points \mathbf{P} and \mathbf{T} in the bra and \mathbf{R} and \mathbf{Q} in the ket:

$$I = \lim_{\lambda \rightarrow 0} \int \exp(-a_1 r_{1P}^2 - b_1 r_{2T}^2 - c_1 r_{12}^2) [\theta(r_{12} - \lambda) r_{12}^{-3} + 4\pi(\gamma + \ln \lambda) \delta(\mathbf{r}_{12})] \exp(-a_2 r_{1R}^2 - b_2 r_{2Q}^2 - c_2 r_{12}^2) d\mathbf{r}_1 d\mathbf{r}_2 \quad (15)$$

were obtained from the formula:

$$I = W_1 W_2 \frac{2\pi^{5/2}}{(a+b)^{3/2}} \exp\left[-\frac{ab}{a+b}(\mathbf{F}-\mathbf{H})^2\right] \times \left[\gamma - \ln\left(\frac{\xi}{a+b}\right) + g\left(\frac{a^2 b^2 (\mathbf{F}-\mathbf{H})^2}{\xi(a+b)}\right)\right] \quad (16)$$

where

$$a = a_1 + a_2 \quad b = b_1 + b_2 \quad c = c_1 + c_2 \\ \xi = ab + bc + ca \quad (17)$$

and

$$\mathbf{F} = \frac{a_1 \mathbf{P} + a_2 \mathbf{R}}{a_1 + a_2} \quad W_1 = \exp\left[-\frac{a_1 a_2}{a_1 + a_2}(\mathbf{P}-\mathbf{R})^2\right] \quad (18)$$

$$\mathbf{H} = \frac{b_1 \mathbf{T} + b_2 \mathbf{Q}}{b_1 + b_2} \quad W_2 = \exp\left[-\frac{b_1 b_2}{b_1 + b_2}(\mathbf{T}-\mathbf{Q})^2\right] \quad (19)$$

The function $g(x)$ appearing in eq 16 is defined as an integral involving the usual Boys function $F_0(x) = (\pi/x)^{1/2} \text{erf}(\sqrt{x})/2$:

$$g(x) = \int_0^x \frac{1}{t} [e'F_0(t) - 1] dt \quad (20)$$

To compute $g(x)$ we used the following expansions:

$$g(x) = \sum_{k=1}^n \frac{2^k}{(2k+1)!!k} x^k + \mathcal{O}(x^{n+1}) \quad (21)$$

$$g(x) = \frac{\sqrt{\pi}e^x}{2x^{3/2}} \sum_{k=0}^n \frac{(2k+1)!!}{2^k} x^{-k} + \mathcal{O}(x^{-(n+1)}) \quad (22)$$

used, respectively, for small and medium and for large values of the argument x . To independently verify our calculations we computed $\langle\psi_{\text{el}}|P(r_{12}^{-3})|\psi_{\text{el}}\rangle$ using also the integral transform method of reference 63 obtaining the same results at basis set convergence. The values of $\langle\psi_{\text{el}}|P(r_{12}^{-3})|\psi_{\text{el}}\rangle$ computed with an extensively optimized 1200-term explicitly correlated Gaussian basis set are given in Table 2. We estimate that their accuracy is better than one unit in the last digit shown in the table.

The integral $\langle\psi_{\text{el}}|P(r_{12}^{-3})|\psi_{\text{el}}\rangle$ exhibits a slow R^{-3} decay at large R . To compute it for values of R larger than 12.0 bohr, we used its asymptotic expansion:

$$\langle\psi_{\text{el}}|P(r_{12}^{-3})|\psi_{\text{el}}\rangle = \frac{1}{R^3} + \frac{6}{R^5} + \frac{75}{R^7} + \mathcal{O}(R^{-8}) \quad (23)$$

Using the values given in Table 2 and the asymptotic formula (eq 23), we found that the Araki–Sucher contribution to the dissociation energy $-\alpha^3\langle A(R) \rangle$ amounts to 0.0127 cm^{-1} with an uncertainty of one unit at the last digit. This contribution has not been computed before for H_2 . It should be noted that in his calculations Wolniewicz⁵⁰ neglected also the contribution from the first part (164/15) $\langle\delta(\mathbf{r}_{12})\rangle$ of the two-electron Lamb shift, amounting to -0.01457 cm^{-1} .

Calculation of the complete α^4 contribution to the dissociation energy is a very complex task^{32,33} and could not be carried out for the purpose of this investigation. It is well-

Table 4. Dissociation Energies for H₂ and D₂ (in cm⁻¹) Compared with Experimental Data

		H ₂	D ₂
α^0	Born–Oppenheimer	36112.5927(1)	36746.1623(1)
	adiabatic	5.7711(1)	2.7725(1)
	nonadiabatic	0.4339(2)	0.1563(2)
	total α^0	36118.7978(2)	36749.0910(2)
α^2	mass–velocity	4.4273(2)	4.5125(2)
	one-el. Darwin	−4.9082(2)	−4.9873(2)
	two-el. Darwin	−0.5932(1)	−0.5993(1)
	Breit	0.5422(1)	0.5465(1)
	total α^2	−0.5319(3)	−0.5276(3)
$\alpha^2 m_e/m_p$	estimate	0.0000(4)	0.0000(2)
α^3	one-el. Lamb shift	−0.2241(1)	−0.2278(1)
	two-el. Lamb shift	0.0166(1)	0.0167(1)
	Araki–Sucher	0.0127(1)	0.0128(1)
	total α^3	−0.1948(2)	−0.1983(2)
$\alpha^3 m_e/m_p$	estimate	0.0000(2)	0.0000(1)
α^4	one-loop term	−0.0016(8)	−0.0016(8)
total theory		36 118.0695(10)	36 748.3633(9) ^a
expt.	ref 15	36 118.06(4)	36 748.32(7)
expt.	ref 16	36 118.062(10) ^b	36 748.343(10)
expt.	ref 17	36 118.0696(4)	

^a This value includes the -0.0002 cm⁻¹ correction for the finite size of the deuteron (the charge radius of 2.14 fm was assumed). The corresponding correction for the H₂ molecule is smaller than 0.0001 cm⁻¹ and can be neglected for our purposes. ^b In the footnote to Table III the authors of ref 16 report also the value $36\,118.073(4)$ cm⁻¹ contingent on the assumption that a particular resonance is a bound state and not a quasi-bound, above threshold state.

known,³³ however, that this α^4 contribution is dominated by the one-loop term given by

$$E_{1\text{-loop}}^{(4)} = 4\pi \left(\frac{427}{96} - 2 \ln 2 \right) \langle \delta(\mathbf{r}_{1a}) \rangle \quad (24)$$

The corresponding correction to the dissociation energy is -0.0016 cm⁻¹, and we estimate that it differs from the exact value of the complete $\alpha^4 E^{(4)}$ contribution by less than 50%. We also verified that the α^4 , α^5 , and higher-order QED corrections due to retardation and taken into account by the Casimir–Polder formula⁶⁴ are smaller than 0.0001 cm⁻¹, i.e., are well within the error bars assumed for the complete $\alpha^4 E^{(4)}$ contribution.

3. Results and Discussion

Dissociation energies for the H₂ and D₂ molecules are presented in Table 4 together with all components computed by us. The experimental dissociation energies shown for comparison are already corrected for the effects of hyperfine interactions, i.e., the true energies of atoms into which the molecule dissociate are replaced by the center of gravity of the hyperfine structure of the $1^2S_{1/2}$ atomic states. This means that in the case of H₂ we must not subtract the 2×0.0355 cm⁻¹ correction corresponding to the difference between this center of gravity and the $F = 0$ hyperfine level of hydrogen atom.

The error bars of all computed components were discussed in Section 2. Here we still have to estimate the relativistic

nonadiabatic/recoil corrections that have not been computed. Within the perturbation formalism of ref 44, the leading nonadiabatic contribution to each of the four terms in eq 6 is given by the expression:

$$2 \langle \psi_{\text{el}} | \chi | W \frac{1}{(E_{\text{el}} - H_{\text{el}})} H_n | \psi_{\text{el}} \rangle \quad (25)$$

where W stands for $\mathbf{p}_1^4/4$, $2\pi\delta(\mathbf{r}_{1a})$, $\pi\delta(\mathbf{r}_{12})$ or for the Breit operator,

$$H_n = -\frac{1}{m_p} \nabla_{\mathbf{R}}^2 + \frac{1}{4m_p} (\mathbf{p}_1 + \mathbf{p}_2)^2 \quad (26)$$

H_{el} is the electronic Hamiltonian, E_{el} is the eigenvalue of H_{el} corresponding to the wave function ψ_{el} , \mathbf{R} is the vector joining the nuclei, and the prime indicates the orthogonalization to ψ_{el} . The term involving $(\mathbf{p}_1 + \mathbf{p}_2)^2$ can be obtained by averaging the R dependent function:

$$\frac{1}{2m_p} \left\langle \psi_{\text{el}} \left| W \frac{1}{(E_{\text{el}} - H_{\text{el}})} (\mathbf{p}_1 + \mathbf{p}_2)^2 \right| \psi_{\text{el}} \right\rangle_{\text{el}} \quad (27)$$

with $4\pi R^2 \chi^2(R)$. The bracket $\langle \dots \rangle_{\text{el}}$ denotes the integration over electronic coordinates only. Since the integral in eq 27 is mass independent the corresponding contribution to the energy is clearly of the order of $\alpha^2 m_e/m_p$. The term involving $\nabla_{\mathbf{R}}^2$ can also be written in terms of mass independent radial functions. To see that we note that this term can be expressed as the sum of two terms:

$$\begin{aligned} & -\frac{2}{m_p} \int \chi^2(R) \left\langle \psi_{\text{el}} \left| W \frac{1}{(E_{\text{el}} - H_{\text{el}})} \left| \nabla_{\mathbf{R}}^2 \psi_{\text{el}} \right| \right\rangle_{\text{el}} d^3R \\ & -\frac{4}{m_p} \left\langle \psi_{\text{el}} | \chi \left| W \frac{1}{(E_{\text{el}} - H_{\text{el}})} \left| \nabla_{\mathbf{R}} \psi_{\text{el}} \nabla_{\mathbf{R}} \chi \right| \right\rangle_{\text{el}} \end{aligned} \quad (28)$$

The first one is explicitly in the form of an average of a mass independent radial function and is clearly of the order of $\alpha^2 m_e/m_p$. Performing integration by parts the mass dependent gradient of χ in the second term can be eliminated, and this term can be written as an average of the radial function:

$$\begin{aligned} & \frac{2}{m_p} \langle \nabla_{\mathbf{R}} \psi_{\text{el}} | W \frac{1}{(E_{\text{el}} - H_{\text{el}})} | \nabla_{\mathbf{R}} \psi_{\text{el}} \rangle_{\text{el}} + \\ & \frac{2}{m_p} \langle \psi_{\text{el}} | \nabla_{\mathbf{R}} W \frac{1}{(E_{\text{el}} - H_{\text{el}})} | \nabla_{\mathbf{R}} \psi_{\text{el}} \rangle_{\text{el}} \end{aligned} \quad (29)$$

proportional to $1/m_p$. This term is, thus, also of the order of $\alpha^2 m_e/m_p$.

Since all relativistic nonadiabatic/recoil terms are of the order of $\alpha^2 m_e/m_p$, we decided to estimate their magnitude by scaling the total α^2 correction by the factor m_e/m_p . We view this estimate as a conservative one since for separated hydrogen atoms the $\alpha^2 m_e/m_p$ contributions to the mass–velocity, Darwin, and Breit terms (equal to $5\alpha^2 m_e/m_p$, $-3\alpha^2 m_e/m_p$, and $-2\alpha^2 m_e/m_p$) add up exactly to zero, and this cancellation must persist to a significant degree when the atoms are bound. The resulting estimate of the total relativistic nonadiabatic/recoil correction is $\pm 0.0000(4)$ and gives the second largest (after the α^4 term) contribution to the error budget

of our calculation. We applied the same scaling procedure to the QED contribution of the order $\alpha^3 m_e/m_p$.

The results of Table 4 show that the dissociation energy of H_2 computed by us, amounting to 36 118.0695(10) cm^{-1} , is not only within the rather wide error bars of the experimental determinations from the Eyler group^{15,16} but agrees impressively well with the very precise hybrid, experimental–theoretical value of 36 118.0696(4) cm^{-1} determined recently by Liu et al.¹⁷ The difference between the experiment and our theoretical prediction is only 1 unit at the ninth decimal place. It should be emphasized that the theoretical input used in ref 17 can be viewed as very reliable (it contains data from extremely high-accuracy calculations for the H_2^+ ion)^{21–23} and is totally independent of the results of present calculations. The fact that the experimental value lies rather close to the center of the energy range determined by our error bars may not be accidental. We believe that as a result of the cancellation of terms (complete at the separated atoms limit), the actual value of the $\alpha^2 m_e/m_p$ contribution is smaller than our estimate, and that our estimate of the uncertainty of the α^4 contribution is very conservative. Before the α^4 contribution and the relativistic nonadiabatic/recoil terms are accurately calculated it will be very difficult to further reduce the uncertainty of the theoretical value of the dissociation energy. It may be interesting to observe that the achieved agreement with experiment would have been impossible without the inclusion of the Araki–Sucher term, the radial dependence of the electronic Bethe logarithm, and the one-loop α^4 contribution.

The dissociation energy for D_2 was computed using the same method as for H_2 and the same approach to estimate the $\alpha^2 m_e/m_d$ and $\alpha^3 m_e/m_d$ terms (we assumed that $m_d = 3\,670.4829654\,m_e$).⁴² These terms are smaller for D_2 , so in this case, 90% of the error budget comes from the uncertainty in the value of the α^4 contributions other than the one-loop term included in our calculations. For D_2 , the agreement with the most recent experimental value¹⁶ is not satisfactory despite the large experimental uncertainty (25 times larger than for H_2). The observed discrepancy is, however, only 2σ (experimental). A more precise experiment should be possible now and could shed some light on the reason of this small discrepancy.

To demonstrate better the level of accuracy of our calculations, we also computed the energy differences between the ground-state energy of H_2 and energies of the first rotationally and vibrationally excited states. These energies are shown in Table 5 and compared with the experimental results. Both the theoretical and experimental energies of the $J = 1$ state refer to the center of gravity of the hyperfine structure, so we did not have to consider nuclear spin interactions in computing the rotational (ortho–para) energy difference.

In computing small energy differences, there is a significant cancellation of errors, so the error bars for some contributions are smaller than for the dissociation energy. These error bars were estimated by performing computations with several reasonable approximations to the radial functions [like $V(R)$, $D_1(R)$, or $D_2(R)$] and observing the resulting

Table 5. The Energy Differences (in cm^{-1}) between the Ground-State Energy of H_2 and Energies of the First Rotationally and Vibrationally Excited States

		$J = 0 \rightarrow 1$	$v = 0 \rightarrow 1$
α^0	Born–Oppenheimer	118.55558(2)	4 163.4035(1)
	adiabatic	−0.06365(4)	−1.4029(1)
	nonadiabatic	−0.00667(8)	−0.8365(2)
	total α^0	118.48526(9)	4 161.1641(2)
α^2	mass–velocity	0.02713(4)	0.5341(2)
	one-el. Darwin	−0.02383(4)	−0.4994(2)
	two-el. Darwin	−0.00160(2)	−0.0391(1)
	Breit	0.00088(2)	0.0279(1)
	total α^2	0.00258(6)	0.0235(3)
α^3	one-el. Lamb shift	−0.00109(2)	−0.0231(1)
	two-el. Lamb shift	0.00004(1)	0.0011(1)
	Araki–Sucher	0.00002(1)	0.0007(1)
	total α^3	−0.00103(2)	−0.0213(2)
α^4	one-loop term	−0.00001(1)	−0.0002(2)
total theory		118.48680(11)	4 161.1661(5)
experiment		118.48684(10) ^a	4 161.1660(3) ^b

^a Ref 18. ^b Ref 65.

scatter of energy differences. We assumed that the error of the nonadiabatic contribution is twice as large as the error of the adiabatic contribution, as suggested by the observed ratio of uncertainties for the individual energy levels.

The inspection of the last two rows of Table 5 shows that the theoretical and experimental values of the ortho–para energy gap differ only by 0.00004 cm^{-1} , which is much less than the error of either the theoretical and experimental determinations. This excellent agreement is very gratifying since the ortho–para energy difference was employed in ref 17 to obtain the most precise experimental value of the dissociation energy to date.

The results presented in Table 5 show also an excellent agreement (up to seventh significant digit) between the theoretical and experimental vibrational energy difference. The experimental value, which has a very small uncertainty of 0.0003 cm^{-1} , differs only by 0.0001 cm^{-1} from the theoretical result and lies well within the error bars of the latter. It appears that the new evaluation of experimental data reported in ref 65 leads indeed to a much more accurate result than the older value measured by Dabrowski,⁶⁶ amounting to 4 161.14 cm^{-1} and lying about 30σ (theoretical) off our result.

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Note Added after ASAP Publication. This paper was published ASAP on September 30, 2009. A correction was made in the Method section to clarify calculation procedures, and a portion of eq 16 was corrected as well. The revised paper was reposted on October 1, 2009. Additional corrections were made referring to equation 3 instead of equation 6 and the journal title for reference 57 corrected. The updated version was reposted on October 7, 2009.

Appendix

A calculation of the complete α^2 contribution to the ground-state energy of H_2 without the adiabatic approximation, i.e., including the relativistic nonadiabatic/recoil effects, has already been presented in the literature⁶⁵ and we made an effort to use the results of ref 65 to extract the magnitude of the $\alpha^2 m_e/m_p$ contribution to the dissociation energy. This was not an easy task since the authors of ref 65 included partly the α^3 QED contribution (by using the anomalous magnetic moment of electron in their α^2 Hamiltonian) and because they provided two values of their relativistic energy differing by 0.0083 cm^{-1} : one obtained as the sum of the mass–velocity, Darwin, Breit and spin–spin contributions from their table 3 and the other which could be calculated as the difference between the 5th and 2nd column in their table 2.

We were able to eliminate the α^3 contributions from their Darwin energies, and after subtracting the correct atomic values, we found that their mass–velocity, one-electron Darwin, two-electron Darwin, and Breit contributions to the dissociation energy differ from ours by -0.0030 , -0.0032 , -0.0043 , and 0.0020 cm^{-1} . The sum of these four contributions amounts to -0.0085 cm^{-1} . This value is by an order of magnitude larger than our estimate of the $\alpha^2 m_e/m_p$ contribution. If we added this additional -0.0085 cm^{-1} to our dissociation energy, the disagreement with experiment would increase to 9σ . However, the total relativistic energy from their table 2, after eliminating the α^3 terms (using results from their table 3), differs from our α^2 contribution by only -0.0002 cm^{-1} . This magnitude of the $\alpha^2 m_e/m_p$ effect is within our error bars and including it would not affect the comparison with the experimental results. For the reasons discussed above, we did not use the results of ref 65 in our theoretical determination of the dissociation energy of H_2 .

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