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 36118.7978(2), $-0.5319(3)$, $-0.1948(2)$, and $-0.0016(8)$ cm^{-1}, respectively, while

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their sum amounts to 36118.0695(10) cm^{-1}, where the total uncertainty includes the estimated size (±0.0004 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 36118.0696(4) cm^{-1} [J. Liu *et al.*, J. Chem. Phys. **130**, 174306 (2009)]. 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 36748.3633(9) cm^{-1} and the experimental result 36748.343(10) cm^{-1} obtained in a somewhat older and less precise experiment [Y. P. Zhang *et al.*, Phys. Rev. Lett. **92**, 203003 (2004)]. 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 London[1] 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 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 $D_0 = 4.454 \pm 0.013$ eV — a value within error bars of the experimental value 4.46 ± 0.04 eV available at that time[?] (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 Wolniewicz[4] 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 nuclear motion and for the effects of relativity. The theoretical dissociation energy obtained by Kolos and Wolniewicz $D_0 = 36117.4$ cm^{-1}[5,6] could be confronted with the most accurate experimental determination from Herzberg and Monfils amounting to 36113.6±0.3 cm^{-1}.[7] Since by virtue of the variational principle the theoretical result can be viewed as a lower bound, both these values can be correct only if quantum mechanics fails to describe the dissociation of the H-H bond with quantitative accuracy. Fortunately, new experimental determinations from Herzberg[8] (36116.3 cm$^{-1} < D_0 < 36118.3$ cm^{-1}) and Stwalley[9] ($D_0 = 36118.6 \pm 0.5$ 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 foundation for the current faith in the quantitative predictive power of quantum chemistry.

Further theoretical[10–12] and experimental[13–15] work has reduced the discrepancy between theory and experiment to several hundredths of cm^{-1}. Very recently Liu *et al.*[16] described a hybrid, experimental-theoretical determination of D_0 based on several transition frequency measurements[16–19] and theoretical calculations of the energy levels of the H_2^+ ion.[20–23] The dissociation energy $D_0 = 36118.06962\ \mathrm{cm}^{-1}$ determined in this way[16] has been reported with uncertainty of $\pm 0.00037\ \mathrm{cm}^{-1}$ — almost two orders of magnitude smaller than that of the previous most accurate determination $D_0 = 36118.062 \pm 0.010\ \mathrm{cm}^{-1}$ of Zhang *et al.*[15] The best available theoretical predictions of $36118.049\ \mathrm{cm}^{-1}$ from Kolos and Rychlewski[11] and $36118.069\ \mathrm{cm}^{-1}$ from Wolniewicz[12] are significantly less precise and have been reported without any error bar estimates. Both of these predictions involve an incomplete treatment of α^3 QED corrections[24] 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 paper[12] 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,[25,26] and used a simple approximation of the Bethe logarithm[27,28] which was shown to be rather inaccurate when applied to H_2^+.[29]

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.[16]

2 Method

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

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

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 Hamiltonian[24] with the nonrelativistic wave function (assuming the molecular center of mass at rest), $\alpha^3 E^{(3)}$ is the leading QED correction[24–26] and $\alpha^4 E^{(4)}$ collects all relativistic and QED corrections proportional to α^4 [30,31] (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.[32,33] To have a better error control and to generate wave functions and potentials needed in QED calculations we adopted however a step-wise approach and computed D_0 as the sum

$$D_0^{(0)} = D_0^{\mathrm{BO}} + \delta D_0^{\mathrm{ad}} + \delta D_0^{\mathrm{na}}, \tag{2}$$

where D_0^{BO} is the result of standard Born-Oppenheimer calculation, δD_0^{ad} is the adiabatic (diagonal Born-Oppenheimer) correction[34,35] 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}, δD_0^{na}, and of the relativistic/QED corrections was represented in the following form:

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

where R is the internuclear distance, $C_6,\ldots,C_{26}$ are van der Waals coefficients fixing the large R asymptotics of $V(R)$, and $f_n(x) = 1-e^{-x}(1+x+x^2/2!+\cdots+x^n/n!)$ is the Tang-Toennies damping function.[36] The asymptotic coefficients C_6, C_8, C_{10}, $C_{11},\ldots,C_{26}$ (C_7, C_9 vanish) were taken from the work of Mitroy and Ovsiannikov[37] 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. 37). Accurate values of the asymptotic C_n coefficients are available also for $n > 26$[37?] but we found that their inclusion in the last term of Eq. (3) did not lead to further improvement of the fit [with the fixed form of the short-part of $V(R)$]. It should be noted that the values of C_{24}, C_{25}, and C_{26} reported later by Ovsiannikov and Mitroy[?] 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, $b_0,\ldots,b_{16}$ were obtained by least square fitting the r.h.s. of Eq. (3) to the energies computed by Sims and Hagstrom[38] 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 of the order of 10^{-6} cm^{-1}[38] while for $R = 6.0$, where the basis set used by Sims and Hagstrom is least adequate, the error is smaller than 2×10^{-5} cm^{-1}.[39] For four distances, $R = 0.1, 0.3, 8.0$, and 10.0 bohr, outside the range covered by Sims and Hagstrom, we used values obtained by Cencek[39] using a 1200-term fully optimized Gaussian geminal basis set. These values have an error smaller than 2×10^{-5} cm^{-1}.[39] The linear parameters a_0, a_1 were constrained by the relations:

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

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

$$V(R) = \frac{1}{R} + E_{\mathrm{He}} - 2E_{\mathrm{H}} + \mathscr{O}(R^2)\ , \tag{5}$$

$E_{\mathrm{He}} = -2.903724377034119$ and $E_{\mathrm{H}} = -0.5$ being atomic energies of helium and hydrogen (assuming infinite nuclear mass). The error of our fit is 5×10^{-5} 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 36112.59273 cm^{-1} (using the conversion factor 1 hartree = 219 474.631 37 cm^{-1}[?]). 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 δD_0^{ad}=5.77111 cm^{-1} and the nonadiabatic δD_0^{na}=0.43391 cm^{-1} corrections to D_0^{BO} were recently computed by two of us[40] using a perturbation method formulated in Ref. 41 (the proton mass m_p=1836.15267247 m_e was assumed[?] in obtaining these numbers). The computation of the adiabatic correction reported in Refs. 40,41 was carried out using a novel, very stable numerical procedure[41] 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 four 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. 40 may be of the order of 0.0001-0.0002 cm^{-1}. In fact the value $\delta D_0^{\mathrm{na}} = 0.43391$ 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 $\delta D_0^{\mathrm{na}} = 0.43391$ cm^{-1}.

Adding $D_0^{\rm BO}$, $\delta D_0^{\rm ad}$, and $\delta D_0^{\rm na}$ we find that the nonrelativistic dissociation energy amounts to $D_0^{(0)} = 36118.7978(2)$ 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 36118.79774(1) cm^{-1} obtained very recently[42] using 10000 extensively optimized Gaussians (and more than a year of massively parallel computing). The accuracy achieved in Ref. 42, 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 two orders of magnitude larger than the error of the large-scale variational calculations of Ref. 42.

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[43,44] 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,[45,46] (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

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

referred to successively as the mass-velocity, 1-electron Darwin, 2-electron Darwin, and Breit contributions (the contact spin-spin interaction is included in the 2-electron Darwin term). In Eq. (6) $\mathbf{p}_i$ is the momentum operator for the ith 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 $\psi_{\rm ad} = \chi(R)\psi_{\rm el}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$, where $\psi_{\rm el}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$ 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 $V(R)$.[41] With this approximation for ψ the expectation values in Eq. (6) are obtained by averaging the R dependent electronic expectation values, e.g., $2\pi\langle\psi_{\mathrm{el}}|\delta(\mathbf{r}_{1a})|\psi_{\mathrm{el}}\rangle \equiv D_1(R)$ with the weight function given by the square of $\chi(R)$. This adiabatic procedure is justified since, as discussed in Sec. III, the neglected cross relativistic-nonadiabatic terms can be expected to be of the order of $(m_e/m_p)\,\alpha^2$, and therefore, three 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 Wolniewicz[47] using the basis of Kolos and Wolniewicz.[48] They were tabulated[47] for 55 internuclear distances ranging from R=0.2 to R=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 attention[49] 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. 49 [$D_2(R)$ vanishes exponentially at large R].

For the Breit correction $B(R)$ we considered only the first two terms in the asymptotic expansion $B(R) = W_4 R^{-4} + W_6 R^{-6} + \cdots$. The constants W_4 and W_6 are given by the expressions[50,51]

$$W_4 = -2\langle\phi_0|z_{1a}z_{2b}\mathscr{R}_0\, p_{z1}\, p_{z2}|\phi_0\rangle \tag{7}$$

and

$$\begin{aligned} W_6 = &-9\,\langle\phi_0|\left(Q_2^0\right)_{1a} z_{2b}\mathscr{R}_0(z_{1a}p_{z1} + p_{z1}z_{1a})p_{z2}|\phi_0\rangle \\ &-\frac{12}{5}\,\langle\phi_0|z_{1a}z_{2b}\mathscr{R}_0\left[2r_{1a}^2 p_{z1} - z_{1a}(\mathbf{r}_{1a}\cdot\mathbf{p}_1)\right]p_{z2}|\phi_0\rangle, \end{aligned} \tag{8}$$

where ϕ_0 is the product of atomic wave functions, $\mathscr{R}_0 = (H_a + H_b - E_a - E_b)^{-1}$ 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 $(Q_2^0)_{1a} = \frac{1}{2}(3z_{1a}^2 - r_{1a}^2)$ is the quadrupole moment operator. We computed W_4 and W_6 using *spd* part of the Dunning's one-electron Gaussian basis set of the sextuple-zeta quality with double augmentation, d-aug-cc-pV6Z.[52] The SCF atomic orbitals and all the necessary integrals were taken from the DALTON suite of codes.[53] 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 form the chosen basis set were included in the summation defining $\mathscr{R}_0$. 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 obtained with d-aug-cc-pVXZ bases, X=T, Q, 5, 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.[50,51]

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 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 three of us.[49] 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 1-electron Darwin terms, amounting to 4.4273 cm^{-1} and -4.9082 cm^{-1}, respectively, have the uncertainty of 0.0002 cm^{-1} each.

For the 2-electron Darwin term we found that our values of $D_2(R)$, computed with a basis set of 1200 fully optimized Gaussian geminals, are slightly different than those of Wolniewicz.[47] The observed basis set convergence pattern and independent calculations of Cencek[39] 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 $-\alpha^2 \langle D_2(R) \rangle = -0.5932$ 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 form the correct asymptotics at large R. Therefore for $R > 5.0$ bohr we used the analytic fit

$$B(R) = e^{-bR}(A_0 + A_1 R + A_2 R^2 + A_3 R^3 + A_4 R^4) + \frac{W_4}{R^4} + \frac{W_6}{R^6}, \tag{9}$$

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 $-\alpha^2 \langle B(R) \rangle = 0.5422$ 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:[24–26]

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

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

$$\langle \phi_1 | P(r_{12}^{-3})\, \phi_2 \rangle = \lim_{a \to 0} [\langle \phi_1 | \, \theta(r_{12} - a)\, r_{12}^{-3}\, \phi_2 \rangle + 4\pi\,(\gamma + \ln a)\, \langle \phi_1 | \, \delta(\mathbf{r}_{12})\, \phi_2 \rangle] \tag{11}$$

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

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

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 $\mathrm{Ry}_\infty = \alpha^2 m_e c^2/2 = 1/2$ 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 r.h.s. 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

$$\ln K^{\mathrm{ad}} = \frac{\langle\,\ln K^{\mathrm{el}}(R)\,D_1(R)\,\rangle}{\langle\,D_1(R)\,\rangle}, \tag{13}$$

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, $\ln K^{\mathrm{el}}(R)$, appearing in Eq. (13), is defined exactly by Eq. (12) but with ψ replaced by the electronic wave function $\psi_{\mathrm{el}}(\mathbf{r}_1,\mathbf{r}_2;\mathbf{R})$, H by the electronic Hamiltonian H^{el}, $E^{(0)}$ by the Born-Oppenheimer energy $-2\,\mathrm{Ry}_\infty + V(R)$ 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 $\ln K^{\mathrm{ad}}$ for the H_2^+ ion using the values of $\ln K^{\mathrm{el}}(R)$ reported in Ref. 29 (note that the definition of $\ln K$ adopted in this reference differs from ours by $\ln 2$). The obtained adiabatic value $\ln K^{\mathrm{ad}} = 3.01276$ agrees very well with the result $\ln K = 3.01225$ of the complete nonadiabatic calculation of Korobov.[20] 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. 24, p. 101). With this correction the adiabatic value, equal now 3.01222, differs only in 1 part per 10^5 from the result of Korobov's calculation. Similarly excellent agreement is observed for 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 $\ln K^{\mathrm{el}}(R)$ we followed closely the technique described in Refs. 55–57. The present work is the first molecular application of this technique and probably the first calculation of the Bethe logarithm for a molecule other then H_2^+ and HD^+. The method employed by us is based on the integral representation of $\ln K$ introduced by Schwartz[58] 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. 59,60. By inspecting the basis convergence pattern we found that the values of $\ln K^{\mathrm{el}}(R)$, 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 $\ln K^{\mathrm{el}}(R)$ agree rather well with the values one can obtain using approximate models proposed by Garcia[27] and Bishop and Cheung[28] and used by Wolniewicz.[12] In fact the Garcia model works somewhat better underestimating $\ln K^{\mathrm{el}}(R)$ by 2% at R=1 bohr and even less for larger distances. The model of Bishop and Cheung overestimates $\ln K^{\mathrm{el}}(R)$ 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^+.[29]

We obtained a very accurate analytic fit of $\ln K^{\mathrm{el}}(R)$ interpolating between the atomic hydrogen, $\ln K_{\mathrm{H}}$, and helium, $\ln K_{\mathrm{He}}$, 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 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 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 1-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 2-electron Lamb-shift, gives only 0.0166 cm^{-1}, with 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 $A(R) = -(7/6\pi)\langle\psi_{\text{el}}|P\left(r_{12}^{-3}\right)\psi_{\text{el}}\rangle$ and subsequently averaging $A(R)$ with 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 **P** and **T** in the bra and **R** and **Q** in the ket

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

were obtained from the formula

$$\begin{aligned} I = W_1 W_2 \frac{2\pi^{5/2}}{(a+b)^{3/2}} \exp\left[-\frac{ab}{a+b}(\mathbf{FH})^2\right] \\ \times\left[\gamma - \log\left(\frac{\xi}{a+b}\right) + g\left(\frac{a^2b^2(\mathbf{FH})^2}{\xi(a+b)}\right)\right] \end{aligned} \tag{16}$$

where:

$$a = a_1 + a_2 \qquad b = b_1 + b_2 \qquad c = c_1 + c_2 \qquad \xi = ab + bc + ca \tag{17}$$

and:

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

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

The function $g(x)$ appearing in Eq. (16) is defined as an integral involving the usual Boys function $F_0(x) = \sqrt{\pi/x}\,\mathrm{erf}(\sqrt{\mathrm{x}})/2$:

$$g(x) = \int_0^x \frac{1}{t}\,[e^t\,\mathrm{F}_0(t) - 1]dt. \tag{20}$$

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

$$g(x) = \sum_{k=1}^{n} \frac{2^k}{(2k+1)!!\,k} x^k + \mathscr{O}(x^{n+1})\;, \tag{21}$$

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

used, respectively, for small and medium, and for large values of the argument x. To independently verify our calculations we computed $\langle\psi_{\mathrm{el}}|P\left(r_{12}^{-3}\right)\psi_{\mathrm{el}}\rangle$ using also the integral transform method of Ref. 61 obtaining the same results at basis set convergence. The values of $\langle\psi_{\mathrm{el}}|P\left(r_{12}^{-3}\right)\psi_{\mathrm{el}}\rangle$ 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 $\langle \psi_{\rm el}|P\left(r_{12}^{-3}\right)\psi_{\rm el}\rangle$ 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

$$\langle \psi_{\rm el}|P\left(r_{12}^{-3}\right)\psi_{\rm el}\rangle = \frac{1}{R^3}+\frac{6}{R^5}+\frac{75}{R^7}+\mathscr{O}(R^{-8})\,. \tag{23}$$

Using the values given in Table 2 and the asymptotic formula (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 Wolniewicz[47] neglected also the first part $(164/15)\big\langle\delta(\mathbf{r}_{12})\big\rangle$ of the 2-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[30,31] and could not be carried out for the purpose of this investigation. It is well known,[31] however, that this α^4 contribution is dominated by the one-loop term given by

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

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 $\alpha^4E^{(4)}$ 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 formula[?] are smaller than 0.0001 cm^{-1}, i.e., are well within the error bars assumed for the complete $\alpha^4E^{(4)}$ contribution.

3 Results and discussion

Dissociation energies for the H_2 and D_2 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 H_2 we must not add 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 Sec. II. Here we still have to estimate the relativistic nonadiabatic/recoil corrections that have not been computed. Within the perturbation formalism of Ref. 41 the leading nonadiabatic contribution to each of the four terms in Eq. (6) is given by the expression

$$2\langle\psi_{\rm el}\chi|W\frac{1}{(E_{\rm el}-H_{\rm el})'}H_{\rm n}|\psi_{\rm el}\chi\rangle\,, \tag{25}$$

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,

$$H_{\rm n}=-\frac{1}{m_p}\nabla^2_{\mathbf{R}}+\frac{1}{4m_p}(\mathbf{p}_1+\mathbf{p}_2)^2\,, \tag{26}$$

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

$$\frac{1}{2m_p}\langle\psi_{\rm el}|W\frac{1}{(E_{\rm el}-H_{\rm el})'}(\mathbf{p}_1+\mathbf{p}_2)^2|\psi_{\rm el}\rangle_{\rm el}\,, \tag{27}$$

with $4\pi R^2\chi^2(R)$. The bracket $\langle\cdots\rangle_{\rm el}$ 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 $\nabla^2_{\mathbf{R}}$ 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

$$\begin{aligned}&-\frac{2}{m_p}\int\chi^2(R)\langle\psi_{\rm el}|W\frac{1}{(E_{\rm el}-H_{\rm el})'}|\nabla^2_{\mathbf{R}}\psi_{\rm el}\rangle_{\rm el}\mathrm{d}^3R\\&-\frac{4}{m_p}\langle\psi_{\rm el}\chi|W\frac{1}{(E_{\rm el}-H_{\rm el})'}|\nabla_{\mathbf{R}}\psi_{\rm el}\nabla_{\mathbf{R}}\chi\rangle\,.\end{aligned} \tag{28}$$

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

$$\frac{2}{m_p}\langle\nabla_{\mathbf{R}}\psi_{\rm el}|W\frac{1}{(E_{\rm el}-H_{\rm el})'}|\nabla_{\mathbf{R}}\psi_{\rm el}\rangle_{\rm el}+\frac{2}{m_p}\langle\psi_{\rm el}|\nabla_{\mathbf{R}}W\frac{1}{(E_{\rm el}-H_{\rm el})'}|\nabla_{\mathbf{R}}\psi_{\rm el}\rangle_{\rm el} \tag{29}$$

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 36118.0695(10) cm^{-1}, is not only within the rather wide error bars of the experimental determinations form Eyler group,[14,15] but agrees impresively well with the very precise hybrid, experimental-theoretical value 36118.0696(4) cm^{-1} determined recently by Liu *et al.*[16] 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. 16 can be viewed as very reliable (it contains data from extremely high accuracy calculations for the H_2^+ ion[20–22]) 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 $m_d = 3670.4829654\, m_e$**?**). 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 value[15] 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 experimental results. Both 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 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 theoretical and experimental determinations. This excellent agreement is very gratifying since the ortho-para energy difference was employed in Ref. 16 to obtain the most precise to date experimental value of the dissociation energy.

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. 62 leads indeed to much more accurate result than the older value measured by Dabrowski,[63] amounting to 4161.14 cm^{-1} and lying about 30σ (theoretical) off our result.

Acknowledgment

The authors thank W. Cencek and L. Wolniewicz for making available their unpublished results.

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 literature[62] and we made an effort to use the results of Ref. 62 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. 62 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 III and the other which could be calculated as the difference between the 5th and 2nd column in their Table II.

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, 1-electron Darwin, 2-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 almost 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 $9\,\sigma$. However, the total relativistic energy from their Table II, after eliminating the α^3 terms (using results from their Table III), 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 experimental result. For the reasons discussed above we did not use the results of Ref. 62 in our theoretical determination of the dissociation energy of H_2.

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Table 1: Parameters determining the analytic form, Eq. (3), of the Born-Oppneheimer potential for H_2. All parameters are in atomic units.

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

Table 2: Electronic Bethe logarithm $\ln K^{\mathrm{el}}(R)$ and the electronic expectation values of $\delta\left(\mathbf{r}_{ia}\right)$, $\delta\left(\mathbf{r}_{12}\right)$, and of $P\left(r_{12}^{-3}\right)$ for H_2 as functions of internuclear separation R. All values in atomic units.

R	$\ln K^{\mathrm{el}}$	$\delta\left(\mathbf{r}_{ia}\right)$	$\delta\left(\mathbf{r}_{12}\right)$	$P\left(r_{12}^{-3}\right)$
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

Table 3: Parameters determining the analytic form, Eq. (14), of the Bethe logarithm $\ln K^{\mathrm{el}}(R)$. All parameters are in atomic units.

$\ln K_{\mathrm{He}}$	4.370160222
$\ln K_{\mathrm{H}}$	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

Table 4: Dissociation energies for H_2 and D_2 (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)
	1-el. Darwin	$-4.9082(2)$	$-4.9873(2)$
	2-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	1-el. Lamb shift	$-0.2241(1)$	$-0.2278(1)$
	2-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		36118.0695(10)	36748.3633(9)[a]
Expt.	Ref. 14	36118.06(4)	36748.32(7)
Expt.	Ref. 15	36118.062(10)	36748.343(10)
Expt.	Ref. 16	36118.0696(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 H_2 molecule is smaller than 0.0001 cm^{-1} and can be neglected for our purposes.

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)	4163.4035(1)
	Adiabatic	−0.06365(4)	−1.4029(1)
	Nonadiabatic	−0.00667(8)	−0.8365(2)
	Total α^0	118.48526(9)	4161.1641(2)
α^2	Mass-velocity	0.02713(4)	0.5341(2)
	1-el. Darwin	−0.02383(4)	−0.4994(2)
	2-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	1-el. Lamb shift	−0.00109(2)	−0.0231(1)
	2-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)	4161.1661(5)
Experiment		118.48684(10)[a]	4161.1660(3)[b]

[a] Ref. 17

[b] Ref. 62