

Nonadiabatic QED Correction to the Dissociation Energy of the Hydrogen Molecule

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The quantum electrodynamic correction to the energy of the hydrogen molecule has been evaluated without expansion in the electron-proton mass ratio. The obtained results significantly improve the accuracy of theoretical predictions reaching the level of 1 MHz for the dissociation energy, in a very good agreement with the parallel measurement [Hölsch *et al*, Phys. Rev. Lett. LZ15618]. Molecular hydrogen has thus become a cornerstone of ultraprecise quantum chemistry, which opens perspectives for determination of fundamental physical constants from its spectra.

Introduction – The spectra of hydrogenic atoms are being used for determination of physical constants and for precision tests of the fundamental interactions theory. However, the finite lifetime of excited states makes further progress in accuracy very challenging. It would require, among others, determination of the resonance frequency to at least one part in 10,000 of the observed line width [1]. In contrast, the hydrogen molecule (H_2) has many narrow lines, which in principle can be measured very accurately [2–7]. In this work, we demonstrate that they can also be calculated very accurately, namely with 1 MHz uncertainty or better.

Although the hydrogen molecule is one of the simplest molecular systems, the high-precision calculations of its energy levels have been difficult to perform, even in the nonrelativistic limit. The standard Born-Oppenheimer (BO) approximation gives a relative accuracy of the order of $10^{-3} - 10^{-4}$ only as a consequence of the omission of the coupling between electrons and nuclei movements. In principle, the finite nuclear mass corrections to the BO potential can be included systematically within the nonadiabatic perturbation theory (NAPT) [8]. However, evaluation of the higher order terms of the NAPT becomes complicated [9]. For this reason the direct nonadiabatic methods have recently been developed in which two electrons and two protons are treated on the same footing. This allowed the inaccuracy of the nonrelativistic energy $E^{(2)}$ to be reduced to the limit of 4×10^{-12} resulting from the uncertainty in the proton mass [10].

Regarding subsequent terms in the expansion of energy in the fine structure constant α ,

$$E(\alpha) = \alpha^2 E^{(2)} + \alpha^4 E^{(4)} + \alpha^5 E^{(5)} + \alpha^6 E^{(6)} + \alpha^7 E^{(7)} + \dots, \quad (1)$$

the relativistic correction, $E^{(4)}$, has recently been calculated to a high numerical precision both with direct nonadiabatic treatment [11–13] and with the NAPT [14, 15]. Moreover, the quantum electrodynamic (QED) $E^{(5)}$ [16] and the higher order $E^{(6)}$ [17] corrections had been calculated within the BO approximation only, while $E^{(7)}$ is known approximately from the atomic hydrogen theory [18]. Neglected nonadiabatic effects of the order $O(\alpha^5)$ had been the largest source of the uncertainty in theoretical predictions, which for the ground

state dissociation energy equals to $2 \times 10^{-4} \text{ cm}^{-1}$ (6 MHz) [12].

In this work, we report on calculation of the QED correction $E^{(5)}$ in the framework of the direct nonadiabatic approach, improving the accuracy of theoretical prediction for the dissociation energies by an order of magnitude down to $2.6 \times 10^{-5} \text{ cm}^{-1}$ (0.78 MHz), the best ever theoretical prediction for any molecule, which becomes now sensitive to the nuclear charge radii.

Nonrelativistic wave function – The basis of the accurate theoretical predictions is the precise nonrelativistic wave function. In the nonadiabatic approach all particles are treated on an equal footing, and the wave function is an eigenstate of the nonrelativistic H_2 Hamiltonian of the form

$$H = T + V, \quad (2)$$

where

$$T = \frac{\vec{p}_0^2}{2m_p} + \frac{\vec{p}_1^2}{2m_p} + \frac{\vec{p}_2^2}{2m} + \frac{\vec{p}_3^2}{2m}, \quad (3)$$

$$V = \frac{1}{r_{01}} - \frac{1}{r_{02}} - \frac{1}{r_{03}} - \frac{1}{r_{12}} - \frac{1}{r_{13}} + \frac{1}{r_{23}}. \quad (4)$$

The indices 0,1 denote protons of mass m_p and 2,3—electrons of mass m . In the center of mass frame the nonrelativistic wave function depends only on the interparticle distances r_{ij} . The most convenient approach [12] to calculate this function is based on a variational principle with the nonadiabatic explicitly correlated Gaussian (naECG) functions. In this approach, the wave function is represented as

$$\Psi = \sum_i^N c_i \psi_i(\vec{r}_0, \vec{r}_1, \vec{r}_2, \vec{r}_3), \quad (5)$$

$$\psi_i = (1 + P_{0\leftrightarrow 1})(1 + P_{2\leftrightarrow 3})\phi_i(\vec{r}_0, \vec{r}_1, \vec{r}_2, \vec{r}_3), \quad (6)$$

where $P_{i\leftrightarrow j}$ is the particle exchange operator, which accounts for the fact that the ground state H_2 wave function Ψ is symmetric with respect to the exchange of nuclear and electronic variables. The spatial functions ϕ_i in Eq. (6) are naECG functions of the form

$$\phi = r_{01}^n e^{-a_1 r_{01}^2 - a_2 r_{02}^2 - a_3 r_{03}^2 - a_4 r_{12}^2 - a_5 r_{13}^2 - a_6 r_{23}^2}. \quad (7)$$

The nonlinear a parameters are optimized variationally and the internuclear coordinate r_{01}^n prefactor ensures proper representation of the vibrational part of the wave function. The powers n of this coordinate are restricted to even integers within the range 0 – 80 and are generated following the logarithmic distribution. The nonrelativistic wave function Ψ has

$$E^{(5)} = -\frac{2D}{3\pi} \ln k_0 - \frac{7}{6\pi} \left\langle \frac{1}{r_{23}^3} + \frac{m}{m_p} \sum_{a,x} \frac{1}{r_{ax}^3} + \frac{m^2}{m_p^2} \frac{1}{r_{01}^3} \right\rangle_\epsilon + \frac{4}{3} \left\{ \frac{19}{30} + \ln(\alpha^{-2}) + \frac{m}{4m_p} \left[\frac{62}{3} + \ln(\alpha^{-2}) \right] \right. \\ \left. + \frac{m^2}{m_p^2} \left[\ln\left(\frac{m_p}{m}\right) + \ln(\alpha^{-2}) + 4 \right] \right\} \sum_{a,x} \langle \delta^3(r_{ax}) \rangle + \left(\frac{164}{15} + \frac{14}{3} \ln \alpha \right) \langle \delta^3(r_{23}) \rangle - 2E_H^{(5)} \quad (8)$$

$$E_H^{(5)} = -\frac{4}{3\pi} \frac{\mu}{m} \left(\ln k_0^H + \ln \frac{\mu}{m} \right) + \frac{1}{3\pi} \left(\frac{\mu}{m} \right)^3 \left\{ 4 \left(1 + \frac{m}{4m_p} + \frac{m^2}{m_p^2} \right) \ln(\alpha^{-2}) + \frac{38}{15} + \frac{m}{m_p} \left(\frac{62}{3} + 14 \ln 2 \right) \right. \\ \left. + 2 \frac{m^2}{m_p^2} \left(1 + 2 \ln \frac{m_p}{m} \right) \right\}, \quad (9)$$

where $a = 0, 1, x = 2, 3$, the Bethe logarithm is [20]

$$\ln k_0 = \frac{1}{D} \left\langle \vec{J} (H - E) \ln [2(H - E)] \vec{J} \right\rangle \quad (10)$$

$$\ln k_0^H = 2.984\,128\,555\,765\,498 \quad (11)$$

and where

$$\vec{J} = \frac{\vec{p}_0}{m_p} + \frac{\vec{p}_1}{m_p} - \frac{\vec{p}_2}{m} - \frac{\vec{p}_3}{m}, \quad (12)$$

$$D = \left\langle \vec{J} (H - E) \vec{J} \right\rangle = \frac{2\pi}{\mu^2} \sum_{a,x} \langle \delta^3(r_{ax}) \rangle, \quad (13)$$

$$\mu = m_p m / (m_p + m). \quad (14)$$

In all the above formulas the expectation values are taken with the nonrelativistic wave function Ψ . Moreover, the expectation values of singular terms $\langle 1/r^3 \rangle_\epsilon$ are obtained by integration from ϵ to ∞ and subtraction of $\ln \epsilon + \gamma$, where the symbol γ indicates the Euler-Mascheroni constant.

There are certain ambiguities regarding the molecular QED correction of Eq. (8), which need to be explained. The first one is due to the lack of the contact term between protons $\delta^3(r_{01})$. In fact, such a term exists, for example from the strong interaction V_{strong} between protons [21]

$$\delta E_{\text{strong}} = \langle \delta^3(r_{01}) \rangle \int d^3r V_{\text{strong}}(r) \\ = \langle \delta^3(r_{01}) \rangle (-2.389) \text{ fm}^2. \quad (15)$$

It is of the same order as the electron vacuum polarization correction to the Coulomb interaction between protons

$$\delta E_{\text{vp}} = \langle \delta^3(r_{01}) \rangle \left(-\frac{4}{15} \right) \frac{\alpha^2}{m^2}$$

been optimized for several basis sizes to observe the convergence of the nonrelativistic energy and expectation values.

QED correction – The formula for the leading quantum electrodynamic correction $E^{(5)}$, derived here on the basis of QED theory in agreement with the known formulas for H [18] and He [19], is

$$= \langle \delta^3(r_{01}) \rangle (-2.118) \text{ fm}^2. \quad (16)$$

However, both contributions are totally negligible, because $\langle \delta^3(r_{01}) \rangle \sim 10^{-50} (m\alpha)^3$ for the ground state of H_2 .

Another subtle point to be clarified is the proton self-energy correction and the corresponding definition of the proton charge radius. This correction is insignificant for a regular hydrogen atom but non-negligible for muonic hydrogen (μH). So, for consistency with the determination of the proton charge radius r_p in μH [22], we chose to include this effect into the total energy of H_2 . Following [23], we do so in a minimal way, by including only logarithmic terms, and the nonlogarithmic terms are absorbed into the mean square charge radius r_p^2 .

Numerical calculation – QED corrections involve several nontrivial terms: the Bethe logarithm $\ln k_0$, the interparticle Dirac delta $\langle \delta(r_{ab}) \rangle$, and the Araki-Sucher term $\langle 1/r_{ab}^3 \rangle_\epsilon$. Because the naECG basis does not reproduce the electron-electron and electron-nucleus cusps of the wave function, the two latter terms exhibit a slow convergence if calculated directly from their definitions. Therefore, to increase numerical performance, it is crucial to transform singular operators to a more regular form, whose behavior is less sensitive to the local inaccuracies of the wave function. For this purpose, we generalized known relations [14, 24] and obtained the following expectation value identities with $a, b = 0, 1, 2, 3$

$$\langle 4\pi \delta^3(r_{ab}) \rangle = \frac{2m_a m_b}{m_a + m_b} \\ \times \left\langle \frac{2}{r_{ab}} (E - V) - \sum_c \frac{1}{m_c} \vec{p}_c \frac{1}{r_{ab}} \vec{p}_c \right\rangle, \quad (17)$$

$$\left\langle \frac{1}{r_{ab}^3} \right\rangle_\epsilon = (1 + \gamma) \langle 4\pi \delta^3(r_{ab}) \rangle + \frac{2m_a m_b}{m_a + m_b} \quad (18)$$

$$\times \left\langle \frac{2 \ln r_{ab}}{r_{ab}} (E - V) - \sum_c \frac{1}{m_c} \vec{p}_c \frac{\ln r_{ab}}{r_{ab}} \vec{p}_c \right\rangle,$$

$$\left\langle \frac{1}{r_{ab}^4} \right\rangle_\epsilon = \frac{m_a m_b}{m_a + m_b} \left\langle \sum_c \frac{1}{m_c} \vec{p}_c \frac{1}{r_{ab}^2} \vec{p}_c \right. \quad (19)$$

$$\left. - 2(E - V) \frac{1}{r_{ab}^2} \pm 12 \pi \delta^3(r_{ab}) \right\rangle_\epsilon.$$

where + is for particles with the same and – with opposite charges respectively. Results for the expectation values extrapolated to the infinite basis size, along with their estimated uncertainty, are presented in Table I.

TABLE I. Expectation values of the operators present in Eq. (8). Atomic units are used throughout the Table.

Operator	Expectation value
E	-1.164 025 030 86(3)
$\langle J^2 \rangle$	2.518 270 507 19(12)
$4\pi \sum_{a,x} \langle \delta^3(r_{ax}) \rangle$	11.346 476 34(9)
$4\pi \langle \delta^3(r_{23}) \rangle$	0.202 830 306(6)
$\sum_{a,x} \langle r_{ax}^{-3} \rangle_\epsilon$	-7.191 104 3(10)
$\langle r_{23}^{-3} \rangle_\epsilon$	0.401 943 51(6)
$\langle r_{01}^{-3} \rangle_\epsilon$	0.357 215 411 7(3)
$\sum_{a,x} \langle r_{ax}^{-4} \rangle_\epsilon$	-5.712 727(17)
$\sum_{(a,x) < (b,y)} \left\langle \frac{\vec{r}_{ax}}{r_{ax}^3} \cdot \frac{\vec{r}_{by}}{r_{by}^3} \right\rangle$	-0.254 515 18(18)

Bethe logarithm – Among all the terms in Eq. (8), the calculation of the Bethe logarithm $\ln k_0$ is the most complicated one. We express $\ln k_0$ in terms of the one-dimensional integral

$$\ln k_0 = \frac{1}{\mathcal{D}} \int_0^1 dt \frac{f(t) - f_0 - f_2 t^2}{t^3} \quad (20)$$

with the function $f(t)$ defined as

$$f(t) = \left\langle \vec{J} \frac{k}{k + H - E} \vec{J} \right\rangle, \quad t = \frac{1}{\sqrt{1 + 2k}} \quad (21)$$

which has the following Taylor expansion

$$f(t) = f_0 + f_2 t^2 + f_3 t^3 + (f_{4l} \ln t + f_4) t^4 + O(t^5). \quad (22)$$

with the first two coefficients

$$f_0 = \langle J^2 \rangle, \quad f_2 = -2\mathcal{D}. \quad (23)$$

The integrand in Eq. (20), as a smooth function of t was evaluated at 200 equally spaced points in the range $t \in [0, 1]$, which enabled relative accuracy higher than 10^{-7} . In the numerical calculation of $f(t)$, the resolvent in Eq. (21) was represented in terms of pseudostates of the form $\phi^\Pi = \vec{r}_{ab} \phi$ for all interparticle coordinates. The nonlinear parameters of ϕ^Π are found by a maximization of f . In the particular case of $t = 1$ ($k = 0$), f can be evaluated analytically using the generalized Thomas-Reiche-Kuhn sum rule

[25] $\langle \vec{J} (H - E)^{-1} \vec{J} \rangle = 3(1 + m/m_p)$. We used this opportunity to assess the completeness of the pseudostates space and to estimate uncertainties.

For the given size N of the wave function Ψ expansion, the size of pseudostate basis set was chosen as $N' = \frac{3}{2}N$, which appeared to be sufficient for most of the t points. There are also additional factors taken into account for the accurate representation of the resolvent in Eq. (21). The powers of internuclear coordinate r_{01} , analogously to the wave function, are restricted to even integers and are generated randomly for each basis function from the log-normal distribution within the 0 – 80 range. However, for small values of t (≤ 0.1), due to a cancellation in the numerator of Eq. (20), an additional tuning of the distribution was made and $N' = 2N$ was set to achieve high accuracy. Moreover, in this critical region of small t , the function $f(t)$ was expanded in a power series with f_3 , f_4 , and f_{4l} coefficients deduced from the known high- k expansion by Korobov [26] ($\mu' = \mu/m$)

$$f_3 = 8 \sqrt{\mu'} \mathcal{D},$$

$$f_{4l} = 16 \mu' \mathcal{D}, \quad (24)$$

$$f_4 = \frac{4}{\mu'^2} \sum_{(a,x),(b,y)} \left\langle \frac{\vec{r}_{ax}}{r_{ax}^3} \frac{\vec{r}_{by}}{r_{by}^3} \right\rangle_\epsilon - 2\mathcal{D} \left(1 + 4 \mu' \ln \frac{\mu'}{4} - 4 \mu' \right).$$

The higher order expansion terms are obtained from the fit to numerical values of $f(t)$. As a test, $f_4 = 72.114 86(7)$ calculated using the above formula, agrees well with 72.0(3) obtained from the numerical fit. In order to perform integration in Eq. (20), we use a polynomial interpolation of the integrand for $t > 0.1$, and power expansion for the critical region $t \in [0, 0.1]$.

The convergence of the Bethe logarithm with the increasing size of the naECG basis is shown in Table II. Six significant figures can be considered stable and the estimated relative accuracy is a half ppm. Our recommended value $\ln k_0 = 3.018 304 9(15)$ is consistent with 3.0188 obtained in the framework of adiabatic approximation [16], and the difference between them divided by $\ln k_0$ is smaller than the electron-proton mass ratio. An analogous difference of 0.0005 between adiabatic and nonadiabatic $\ln k_0$ has been noted for H_2^+ [16, 27].

TABLE II. Convergence of the nonrelativistic energy E and the Bethe logarithm $\ln k_0$ with the increasing size N of the naECG basis set. The final uncertainty for $\ln k_0$ is due to numerical inaccuracy of $f(t)$ at small t .

N	E	$\ln k_0$
128	-1.164 023 669 155	3.016 586 1
256	-1.164 024 987 878	3.018 137 0
512	-1.164 025 027 334	3.018 258 91
1024	-1.164 025 030 593	3.018 301 73
2048	-1.164 025 030 843	3.018 303 90
∞	-1.164 025 030 86(3)	3.018 304 9(15)

Higher order QED – Because of the significant increase in

the accuracy of the QED correction achieved in this work, the dominating contribution to the uncertainty comes from the higher order $E^{(7)}$ correction. Currently, an explicit form of this correction is unknown, which prevents its accurate evaluation. Its first estimation, made within the BO approximation framework, was reported in Ref. [17]. Here, we account for several additional terms, namely

$$E^{(7)} \approx \pi \left\langle \sum_{a,x} \delta^3(r_{ax}) \right\rangle \left\{ \frac{1}{\pi} [A_{60} + A_{61} \ln \alpha^{-2} + A_{62} \ln^2 \alpha^{-2}] + \frac{1}{\pi^2} B_{50} + \frac{1}{\pi^3} C_{40} \right\} - 2 E^{(7)}(\text{H}), \quad (25)$$

and assume a conservative 25% uncertainty. All the coefficients A , B , and C can be found in Ref. [18], and we use the values for the $1S$ state of H. The dominating term is the one containing $A_{62} = -1$ and inclusion of all the other terms decreases $E^{(7)}$ by about 14%.

Summary – Theoretical predictions for all the known contributions to $D_{0,0}$ and $D_{0,1}$ are assembled in Table III. By $D_{v,J}$ we denote there the dissociation energy of the hydrogen molecule in the state with the vibrational number v and rotational J . The nonrelativistic contribution was calculated directly for $D_{0,0}$ and $D_{0,1}$. All the corrections were calculated for $D_{0,0}$ and separately for the rotational excitation energy using NAPT. However, the QED correction for this excitation energy was calculated within the BO approximation only, but the related uncertainty is small. Finally, the dissociation energy $D_{0,1}$ was obtained as the difference between $D_{0,0}$ and the rotational excitation.

The improved theoretical result for the ground state dissociation energy $D_{0,0}$ of the hydrogen molecule is in very good agreement with the most recent measurements [2, 7], but their uncertainties are an order of magnitude larger. The situation is more intriguing for the dissociation energy $D_{0,1}$ of the first rotationally excited state. Although, our theoretical prediction differs by 2σ from the equally accurate recent measurement [6], it is in very good agreement with the twice as accurate measurement reported in parallel to this work [32], see Table III.

Conclusions – This work concludes efforts to increase the accuracy of theoretical predictions for the dissociation energy of H_2 , feasible within the framework of the existing theory. Further progress is likely, provided an explicit formula for the $E^{(7)}$ term in the expansion Eq. (1) is found. Currently, the main uncertainty of $25 \times 10^{-6} \text{ cm}^{-1}$ (0.75 MHz) comes from this correction, which for the time being, is estimated using the known atomic hydrogen formula, see Eq. (25). Despite this approximation, the new results for dissociation energies of the hydrogen molecule become the most accurate ever obtained for any molecule.

Regarding the possibility of determination of the Rydberg constant or the proton charge radius, let us point out that in the atomic hydrogen, apart from $1S$ - $2S$ transition, there is no other narrow transition, and the present charge radius determination relies on an average of many transitions with much

larger natural linewidth than the accuracy of individual measurements. The alternative route suggested by Merkt [31] is to use the ionization energy of the hydrogen molecule, as a second transition, because its natural width is exactly zero. The determination of the dissociation energy in Refs. [2, 6, 7, 32] is in fact the measurement of the ionization energy $E(\text{H}_2, \text{IP})$,

$$E(\text{H}_2, \text{IP}) = D_0(\text{H}_2) + E(\text{H}, \text{IP}) - D_0(\text{H}_2^+) \quad (26)$$

which for ortho- H_2 amounts to about $124\,357 \text{ cm}^{-1}$ [6]. The ratio with the precisely known $2S$ - $1S$ transition $82\,259 \text{ cm}^{-1}$ [33] is independent of the Rydberg constant, but depends on the proton charge radius through

$$\frac{E(\text{H}_2, \text{IP})}{E(\text{H}, 2S-1S)} = 1.512 \dots - 1.4 \cdot 10^{-10} r_p^2 / \text{fm}^2. \quad (27)$$

Consequently, one needs to achieve

$$\begin{aligned} \delta E(\text{H}_2, \text{IP}) &= E(\text{H}, 2S-1S) 2 \cdot 0.01 \cdot 1.4 \cdot 10^{-10} r_p^2 / \text{fm}^2 \\ &= 1.6 \cdot 10^{-7} \text{ cm}^{-1} \quad (5 \text{ kHz}) \end{aligned} \quad (28)$$

accuracy for the ionization energy of H_2 to obtain the proton radius with 1% precision. Among the contributions to $E(\text{H}_2, \text{IP})$ in Eq. (26), the last two are known with much higher precision [34] than required. Therefore, it is only $D_0(\text{H}_2)$ which needs to be improved. This can be achieved by the evaluation of the nonadiabatic $E^{(6)}$, $E^{(7)}$ in the BO approximation, and the $E^{(8)}$ contribution using the atomic hydrogen theory. Among them, the calculation of $E^{(7)}$ is the most demanding task, since it has not yet been accomplished for helium or for any other system except the hydrogen atom and H_2^+ ion [18, 35], but it is feasible using present-day technologies.

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TABLE III. Theoretical predictions for the dissociation energy budget for the ground level of H₂. $E_{\text{sec}}^{(6)}$ is a second order correction due to relativistic BO potential; E_{FS} is the finite nuclear size correction with $r_p = 0.84087(39)$ fm [28]. All the energy entries are given in cm⁻¹.

Contribution	$D_{0,0}$	$D_{0,1}$	$(0, 1) \rightarrow (0, 0)$	Remarks and references
$E^{(2)}$	36 118.797 746 10(3)	36 000.312 485 66(2)	118.485 260 44(4)	naJC; [29]
$E^{(4)}$	-0.531 215 6(5)	-0.533 799 2(5)	0.002 583 56(1)	naECG; [12], this work
$E^{(5)}$	-0.194 910 43(15)	-0.193 887 7(11)	-0.001 022 7(11)	naECG; [14], this work
$E^{(6)}$	-0.002 067(6)	-0.002 058(6)	-0.000 008 9	BO; [17]
$E_{\text{sec}}^{(6)}$	0.000 009 2	0.000 009 1	0.000 000 1	BO; this work
$E^{(7)}$	0.000 101(25)	0.000 101(25)	0.000 000 5(1)	BO; [14, 17]
$E_{\text{FS}}^{(4)}$	-0.000 031	-0.000 031	-0.000 000 2	BO; [14, 17]
Total	36 118.069 632(26)	35 999.582 820(26)	118.486 812 7(11)	
Exp.	36 118.069 62(37)	35 999.582 894(25)	118.486 8(1)	[2], [6], [30]
Diff.	-0.000 01(37)	0.000 074(36)	0.000 0(1)	
Exp.	36 118.069 45(31)	35 999.582 834(11)		[7], [32]
Diff.	-0.000 18(31)	0.000 014(28)		

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