

## Complete $\alpha^6 m$ Corrections to the Ground State of $\text{H}_2$

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We perform the calculation of all relativistic and quantum electrodynamic corrections of the order of  $\alpha^6 m$  to the ground electronic state of a hydrogen molecule and present improved results for the dissociation and the fundamental transition energies. These results open the window for the high-precision spectroscopy of  $\text{H}_2$  and related low-energy tests of fundamental interactions.

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The hydrogen atom and various hydrogenic systems like positronium, muonium, muonic hydrogen, and  $\text{He}^+$ , due to highly accurate theoretical predictions [1], are considered for the determination of fundamental physical constants [2] and for the low-energy tests of the Standard Model [3], including possible violation of the lepton universality [4–6]. However, they are frequently limited by uncertainties in the nuclear structure or natural lifetime of the system. The  $1S - 2S$  transition in H is the best example, where the precision of the measurement  $f(1S - 2S) = 2466061413187035(10)$  Hz [7] exceeds by orders of magnitude any theoretical predictions. This is because of the relatively large theoretical uncertainties in the proton structure and resulting inaccuracies in fundamental constants. The lack of another sharp transition in the hydrogen makes the determination of the Rydberg ( $R_\infty$ ) constant, which transforms atomic units to inverse of the transition wavelength, much less accurate than it would be if another such transition was available. Here we point out that the dissociation energy of  $\text{H}_2$  can serve this purpose, as it is stable in the ground electronic state and can be calculated with sufficient precision. So having two accurate and calculable transitions, the two unknowns  $R_\infty$  and  $r_p$  can be determined, which among others, would help resolve the proton charge radius puzzle. Other alternative systems for which high precision calculations are possible include the helium ion  $\text{He}^+$  [8], heavy hydrogenlike ions [9], and the hydrogen molecular ion [10,11].

The calculations for the hydrogen molecule have never been considered to be as accurate as for the hydrogen atom due to the lack of an analytic solution of the Schrödinger equation. However, the numerical solution of this equation, as has been shown recently [12], can be as accurate as  $10^{-12}$ , and, thus, it will not limit the accuracy of theoretical predictions. There are obviously various corrections, such as relativistic and quantum electrodynamic (QED) ones. So far, they have been calculated up to  $\alpha^5 m$  order [13], and only in the adiabatic approximation. Beyond this

approximation, namely, the combined nonadiabatic and relativistic effects, have not yet been obtained and they will limit the accuracy of current predictions. Here we calculate one of the most difficult, the  $\alpha^6 m$  correction, using the so-called nonrelativistic QED approach. Next, we point out that when the higher order  $\alpha^7 m$  correction is determined, energies of the hydrogen molecule can be obtained almost as accurately as those of the hydrogen atom alone, and thus may be used for determination of the  $R_\infty$  constant. Meanwhile, on the basis of the  $\alpha^6 m$  correction obtained herein, we will present improved results for the dissociation and the fundamental transition energies.

*NRQED effective Hamiltonian.*—Since there is no formulation of QED theory based on a multielectron Dirac equation with Coulomb interactions, we use an effective nonrelativistic QED (NRQED) approach that is based on the Schrödinger equation. According to QED theory, the expansion of energy levels in powers of the fine structure constant  $\alpha$  has the following form:

$$E(\alpha) = E^{(2)} + E^{(4)} + E^{(5)} + E^{(6)} + E^{(7)} + O(\alpha^8), \quad (1)$$

where  $E^{(n)}$  is a contribution of order  $\alpha^n m$  and may include powers of  $\ln \alpha$ . Each expansion term  $E^{(n)}$  can be expressed as an expectation value of some effective Hamiltonian with the nonrelativistic wave function  $\Phi$ . The first one,  $E^{(2)} \equiv E_0$ , is the eigenvalue of the nonrelativistic Hamiltonian  $H_0$ . In the infinite nuclear mass approximation (in theoretical units  $\hbar = c = 1$ )

$$H_0 = \frac{\vec{p}_1^2}{2m} + \frac{\vec{p}_2^2}{2m} + V, \quad (2)$$

where

$$V = -\frac{Z_A \alpha}{r_{1A}} - \frac{Z_A \alpha}{r_{2A}} - \frac{Z_B \alpha}{r_{1B}} - \frac{Z_B \alpha}{r_{2B}} + \frac{\alpha}{r} + \frac{Z_A Z_B \alpha}{r_{AB}}, \quad (3)$$

$r = r_{12}$ , and where indices 1 and 2 correspond to electrons, whereas  $A$  and  $B$  correspond to nuclei. The next term of this expansion  $E^{(4)}$  is the expectation value of the well-known Breit-Pauli (BP) Hamiltonian  $H^{(4)}$  [14].  $E^{(5)}$  is the leading QED contribution, which is well defined and can also be expressed in terms of matrix elements of somewhat more complicated operators [13,15]. The calculation of the next term in  $\alpha$  expansion  $E^{(6)}$  is the subject of the present work. This term can be represented as

$$E^{(6)} = \langle H^{(6)} \rangle + \left\langle H^{(4)} \frac{1}{(E_0 - H_0)} H^{(4)} \right\rangle, \quad (4)$$

where  $H^{(6)}$  is the effective Hamiltonian of order  $\alpha^6 m$ . Its derivation is presented in the following paragraph. Here, the second-order contribution, and, correspondingly,  $H^{(4)}$ , is split into two parts depending on the symmetry of intermediate states.

$$E_A = \left\langle H_A \frac{1}{(E_0 - H_0)} H_A \right\rangle, \quad E_C = \left\langle H_C \frac{1}{E_0 - H_0} H_C \right\rangle, \quad (5)$$

where

$$H_A = -\frac{p_1^4}{8m^3} - \frac{p_2^4}{8m^3} - \frac{\alpha}{2m^2} p_1^i \left( \frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3} \right) p_2^j + \frac{\pi\alpha}{m^2} \delta^3(r) + \frac{\pi Z_A \alpha}{2m^2} \delta^3(r_{1A}) + \frac{\pi Z_A \alpha}{2m^2} \delta^3(r_{2A}) + \frac{\pi Z_B \alpha}{2m^2} \delta^3(r_{1B}) + \frac{\pi Z_B \alpha}{2m^2} \delta^3(r_{2B}), \quad (6)$$

and

$$H_C = \frac{(\vec{\sigma}_1 - \vec{\sigma}_2)}{2} \left[ \frac{Z_A}{4m^2} \left( \frac{\vec{r}_{1A}}{r_{1A}^3} \times \vec{p}_1 - \frac{\vec{r}_{2A}}{r_{2A}^3} \times \vec{p}_2 \right) + \frac{Z_B}{4m^2} \left( \frac{\vec{r}_{1B}}{r_{1B}^3} \times \vec{p}_1 - \frac{\vec{r}_{2B}}{r_{2B}^3} \times \vec{p}_2 \right) + \frac{1}{4m^2 r^3} \times (\vec{p}_1 + \vec{p}_2) \right]. \quad (7)$$

The first term  $E_A$  as well as  $\langle H^{(6)} \rangle$  are separately divergent, but their sum is finite. We follow the approach of Ref. [16] and use the technique of dimensional regularization to eliminate these divergences from the matrix elements.  $H_A$  in the above equation should therefore be written in  $d$  dimensions, but for simplicity we write only the  $d = 3$  form.

The effective Hamiltonian  $H^{(6)}$  is derived in an analogous way as for the He atom in Ref. [16]. There is no additional complication for the case of  $H_2$ , except obviously for the presence of two Coulomb fields instead of one. It is expressed as a sum of various contributions,  $H^{(6)} = H_Q + H_H + H_{R1} + H_{R2}$ .  $H_Q$  is a sum of all terms that come from one- and two-photon exchange of the

low-energy photons  $k \sim \alpha m$ . We do not write their explicit expression because it is too long. They are divergent at high photon momenta, or equivalently at small distances  $r$  and  $r_{aX}$ . This divergence cancels out with the second-order contribution  $E_A$  and with the hard three-photon exchange, which in  $d = 3 - 2\epsilon$  dimensions is [17]

$$H_H = \left( 4 \ln m - \frac{1}{\epsilon} - \frac{39\zeta(3)}{\pi^2} + \frac{32}{\pi^2} - 6 \ln(2) + \frac{7}{3} \right) \frac{\pi\alpha^3}{4m^2} \delta^d(r). \quad (8)$$

Later, in Eq. (18) and Table I, we present a simplified and regularized form of  $H_Q$ . The remaining contributions are radiative corrections, which at the order  $\alpha^6 m$  are

TABLE I. Expectation values of operators entering  $H^{(6)}$  for the  $1^1\Sigma^+$  state at  $R = 1.4$  a.u. The last digit in  $Q_{9\dots 28}$  is uncertain. The following notation was used in the table:  $\vec{r} = \vec{r}_{12} = \vec{r}_1 - \vec{r}_2$ ,  $V_i = 1/r_{iA} + 1/r_{iB}$ ,  $\vec{V}_i = \vec{r}_{iA}/r_{iA}^3 + \vec{r}_{iB}/r_{iB}^3$ ,  $\vec{P} = \vec{p}_1 + \vec{p}_2$ .

Operator	Expectation value
$Q_1 = 4\pi\delta^3(r_{1A})$	2.888 179 88(1)
$Q_2 = 4\pi\delta^3(r)$	0.210 402 25(1)
$Q_3 = 4\pi\delta^3(r_{1A})/r_{2A}$	2.203 14
$Q_4 = 4\pi\delta^3(r_{1A})/r_{2B}$	2.778 58
$Q_5 = 4\pi\delta^3(r_{1A})p_2^2$	2.952 30
$Q_6 = 4\pi\delta^3(r)V_1$	0.604 74
$Q_7 = 4\pi\delta^3(r)P^2$	0.859 90
$Q_8 = 1/r$	0.587 36
$Q_9 = 1/r^2$	0.517 93
$Q_{10} = 1/r^3$	0.414 34
$Q_{11} = V_1^2$	4.852 07
$Q_{12} = V_1 V_2$	3.265 50
$Q_{13} = V_1/r$	1.193 32
$Q_{14} = V_1 V_2/r$	2.454 64
$Q_{15} = V_1^2 V_2$	8.525 27
$Q_{16} = V_1^2/r$	3.445 33
$Q_{17} = V_1/r^2$	1.195 29
$Q_{18} = \vec{V}_1 \cdot \vec{r}/r^3$	0.406 32
$Q_{19} = \vec{V}_1 \cdot \vec{r}/r^2$	0.488 59
$Q_{20} = V_1 V_2 (r^i r^j - 3\delta^{ij} r^2)/r$	0.547 86
$Q_{21} = p_2^2 V_1^2$	5.186 77
$Q_{22} = \vec{p}_1 V_1^2 \vec{p}_1$	5.145 61
$Q_{23} = \vec{p}_1/r^2 \vec{p}_1$	0.554 62
$Q_{24} = p_1^i V_1 (r^i r^j + \delta^{ij} r^2)/r^3 p_2^j$	0.237 37
$Q_{25} = P^i (3r^i r^j - \delta^{ij} r^2)/r^5 P^j$	-0.190 40
$Q_{26} = p_2^k V_1^i (\delta^{jk} r^i/r - \delta^{ik} r^j/r - \delta^{ij} r^k/r - r^i r^j r^k/r^3) p_1^j$	-0.112 60
$Q_{27} = p_1^2 p_2^2$	1.328 10
$Q_{28} = p_1^2 V_1 p_2^2$	5.208 25
$Q_{29} = \vec{p}_1 \times \vec{p}_2/r \vec{p}_1 \times \vec{p}_2$	0.386 62
$Q_{30} = p_1^k p_2^l (-\delta^{kl} r^i r^j/r^3 - \delta^{ik} r^j r^l/r^3 + 3r^i r^j r^k r^l/r^5) p_1^i p_2^j$	-0.160 82

proportional to Dirac  $\delta$  functions, and they are known from the hydrogenic case. The one-loop correction is [1]

$$H_{R1} = \frac{\alpha^3 \pi}{m^2} \left( \frac{427}{96} - 2 \ln(2) \right) [Z_A^2 \delta^3(r_{1A}) + Z_A^2 \delta^3(r_{2A}) + Z_B^2 \delta^3(r_{1B}) + Z_B^2 \delta^3(r_{2B})] + \frac{\alpha^3}{m^2} \left( \frac{6\zeta(3)}{\pi^2} - \frac{697}{27\pi^2} - 8 \ln(2) + \frac{1099}{72} \right) \pi \delta^3(r), \quad (9)$$

and the two-loop correction is [1]

$$H_{R2} = \frac{\alpha^3 \pi}{m^2} \left[ -\frac{9\zeta(3)}{4\pi^2} - \frac{2179}{648\pi^2} + \frac{3 \ln(2)}{2} - \frac{10}{27} \right] \times [Z_A \delta^3(r_{1A}) + Z_A \delta^3(r_{2A}) + Z_B \delta^3(r_{1B}) + Z_B \delta^3(r_{2B})] + \frac{\alpha^3}{m^2} \left[ \frac{15\zeta(3)}{2\pi^2} + \frac{631}{54\pi^2} - 5 \ln(2) + \frac{29}{27} \right] \pi \delta^3(r). \quad (10)$$

At this point we have considered all contributions of the order of  $\alpha^6 m$ . The higher order term is estimated on the basis of the dominant double logarithmic contribution, which for  $Z_A = Z_B = 1$  is

$$H^{(7)} \approx -\frac{\alpha^4}{m^2} \ln^2(\alpha^{-2}) [\delta^3(r_{1A}) + \delta^3(r_{2A}) + \delta^3(r_{1B}) + \delta^3(r_{2B})]. \quad (11)$$

*Elimination of singularities.*—The second-order matrix element  $E_A$  in Eq. (5) requires subtractions of  $1/\epsilon$  singularities. For this we use the transformation (henceforth atomic units will be employed)

$$H_A = H'_A + \{H_0 - E_0, Q\}, \quad (12)$$

where

$$Q = -\frac{1}{4} \left( \frac{Z_A}{r_{1A}} + \frac{Z_B}{r_{1B}} + \frac{Z_A}{r_{2A}} + \frac{Z_B}{r_{2B}} \right) + \frac{1}{2r}, \quad (13)$$

so that  $E_A = E'_A + E''_A$ , where

$$E'_A = \left\langle H'_A \frac{1}{(E_0 - H_0)'} H'_A \right\rangle, \quad (14)$$

$$E''_A = \langle Q(E_0 - H_0)Q \rangle + 2\langle H_A \rangle \langle Q \rangle - \langle \{H_A, Q\} \rangle. \quad (15)$$

$E'_A$  is finite in the limit  $\epsilon \rightarrow 0$ , and

$$H'_A |\Phi\rangle = \left\{ -\frac{1}{2}(E_0 - V)^2 - p_i^i \frac{1}{2r} \left( \delta^{ij} + \frac{r^i r^j}{r^2} \right) p_2^j + \frac{1}{4} \vec{\nabla}_1^2 \vec{\nabla}_2^2 + \frac{1}{2}(E - V)(V_1 + V_2) + \frac{1}{4} \vec{\nabla}_1(V_1 + V_2) \vec{\nabla}_1 + \frac{1}{4} \vec{\nabla}_2(V_1 + V_2) \vec{\nabla}_2 \right\} |\Phi\rangle, \quad (16)$$

where the action of  $\vec{\nabla}_1^2 \vec{\nabla}_2^2$  on  $\Phi$  in the above is understood as a differentiation with omission of  $\delta^3(r)$ , and  $V_i$  is defined in the caption of Table I.

The expression for  $E^{(6)}$ , after subtraction and elimination of all singularities, is the main result of this work and has the following form:

$$E^{(6)} = E'_Q + E'_H + E'_A + E_C + E_{R1} + E_{R2} - \ln(\alpha) \pi \langle \delta^3(r) \rangle, \quad (17)$$

where  $E'_H$  is the expectation value of  $H_H$  with dropping the  $1/\epsilon$  and  $\ln m$  terms,  $E'_A$  is defined in Eq. (14),  $E_C$  in Eq. (5),  $E_{R1}$  and  $E_{R2}$  are mean values of the Hamiltonians (9) and (10), correspondingly. The logarithmic term in Eq. (17) agrees with that obtained for helium in Ref. [18]. The sum of the “soft” photon exchange contributions  $E'_Q = \langle H_Q \rangle + E''_A$  for the case of  $H_2$  after (1  $\leftrightarrow$  2) simplification becomes

$$E'_Q = -\frac{E_R^3}{2} + R \frac{dE_R}{dR} \left( \frac{E^{(4)}}{2} - \frac{E_R^2}{4} \right) - \frac{E_R}{4} Q_1 + \frac{1}{8} Q_2 - \frac{1}{4} Q_3 - \frac{1}{2} Q_4 + \frac{3}{8} Q_5 - \frac{1}{4} Q_6 + \frac{1}{24} Q_7 + \frac{2E^{(4)} + E_R^2}{4} Q_8 - \frac{E_R}{2} Q_9 + \frac{1}{4} Q_{10} + \frac{E_R}{2} Q_{11} + E_R Q_{12} - E_R Q_{13} - Q_{14} + Q_{15} - \frac{1}{2} Q_{16} - \frac{1}{2} Q_{17} + \frac{1}{16} Q_{18} + \frac{1}{2} Q_{19} - \frac{1}{8} Q_{20} + \frac{1}{4} Q_{21} + \frac{1}{4} Q_{22} + Q_{23} + \frac{1}{2} Q_{24} - \frac{1}{32} Q_{25} - \frac{1}{4} Q_{26} - \frac{E_R}{8} Q_{27} - \frac{1}{2} Q_{28} + \frac{1}{4} Q_{29} + \frac{1}{8} Q_{30}, \quad (18)$$

where  $R = r_{AB}$ ,  $E_R = E_0 - 1/R$  and  $Q_i$  are defined in Table I. These operators agree with those obtained previously for helium in the  $R \rightarrow 0$  limit, as they should.

*Gaussian integrals.*—Almost all the calculations of matrix elements with  $\alpha^6 m$  operators are performed in this work by using the explicitly correlated Gaussian (ECG) functions

$$\phi_{\Sigma^+} = \left(1 + \frac{r_{12}}{2}\right) e^{-a_{1A}r_{1A}^2 - a_{1B}r_{1B}^2 - a_{2A}r_{2A}^2 - a_{2B}r_{2B}^2 - a_{12}r_{12}^2}. \quad (19)$$

In order to satisfy the electron-electron cusp condition, we include an explicit factor  $(1 + r_{12}/2)$  in the wave function. It not only improves the numerical convergence, but also it is crucial for obtaining a correct numerical value for some of the nearly singular matrix elements, especially  $E'_A$ , otherwise the result would be incorrect. The other second-order matrix element  $E_C$  does not have any singularities, so the  $(1 + r_{12}/2)$  factor can be dropped. It involves intermediate states of  $\Sigma^-$  and  $\Pi$  symmetries, which have the following representations:  $\phi_{\Sigma^-} = \vec{R} \cdot (\vec{r}_{1A} \times \vec{r}_{2A})\phi_{\Sigma^+}$  and  $\vec{\phi}_{\Pi} = (\vec{R} \times \vec{r}_{1A})\phi_{\Sigma^+}$ .

The primary advantage of ECG functions is that all integrals with operators in Table I, as well as in the second-order elements, can be performed either analytically or numerically as follows. All the matrix elements are expressed as a linear combination of the following integrals:

$$f(n_1, n_2, n_3, n_4, n_5) = \frac{1}{\pi^3} \int d^3r_1 \int d^3r_2 r_{1A}^{n_1} r_{1B}^{n_2} r_{2A}^{n_3} r_{2B}^{n_4} r_{12}^{n_5} \times e^{-c_{1A}r_{1A}^2 - c_{1B}r_{1B}^2 - c_{2A}r_{2A}^2 - c_{2B}r_{2B}^2 - c_{12}r_{12}^2}. \quad (20)$$

The ECG integrals with even powers of interparticle distance can be generated by differentiation over nonlinear parameters of the master integral

$$f(0, 0, 0, 0, 0) = X^{-3/2} e^{-R^2/Y}, \quad (21)$$

where

$$X = (c_{1A} + c_{1B} + c_{12})(c_{2A} + c_{2B} + c_{12}) - c_{12}^2, \quad (22)$$

$$Y = (c_{1B} + c_{1A})c_{2A}c_{2B} + c_{1A}c_{1B}(c_{2A} + c_{2B}) + c_{12}(c_{1A} + c_{2A})(c_{1B} + c_{2B}). \quad (23)$$

If one of the  $n_k$  indices is odd, the ECG integrals can also be obtained analytically by differentiation of other master integrals. An exemplary master integral for the case of  $n_1 = -1$  reads

$$f(-1, 0, 0, 0, 0) = \frac{1}{X\sqrt{X_1}} e^{-R^2/Y} F \left[ R^2 \left( \frac{Y_1}{X_1} - \frac{Y}{X} \right) \right], \quad (24)$$

where  $X_1 = \partial_{c_{1A}} X$ ,  $Y_1 = \partial_{c_{1A}} Y$ , and  $F(x) = \text{erf}(x)/x$ . Molecular ECG integrals, as opposed to the atomic case, have no known analytic form when two or more  $n_k$  are odd. In this case, we use numerical integration with the quadrature adapted to the end-point logarithmic singularity [19]. This approach appears to be very efficient for all the integrals with

two and three odd indices, which are required in the evaluation of matrix elements of all the  $\alpha^6 m$  operators.

*Numerical calculations.*—The nonrelativistic wave function  $\Phi$  used for the ground electronic state is the symmetrized ( $1 \leftrightarrow 2$ ,  $A \leftrightarrow B$ ) linear combination of  $N = 128$ , 256, or 512 basis functions  $\phi_{\Sigma^+}$  from Eq. (19). All individual nonlinear parameters are carefully optimized, and the precision achieved for the ground state energy is about  $10^{-11}$  with  $N = 512$  basis. The separate optimization with the same basis size  $N$  was performed to accurately represent the resolvent of  $\Pi$  and  $\Sigma^-$  symmetry in the second-order matrix elements  $E_C$ . Moreover, for  $E'_A$  we use an additional nonoptimized constant sector of  $\phi_{\Sigma^+}$  basis functions, where nonlinear parameters come from the  $\Sigma^+$  wave function of the size  $N/2$ . This is because the electronic ground state has to be subtracted from the resolvent. The global optimization of all nonlinear parameters ensures high accuracy for matrix elements. Nevertheless, in some cases, like for  $Q_{10}$ , we transform matrix elements to a more regular but equivalent form to further improve the numerical accuracy [20]. Moreover, for the  $Q_{27}$ ,  $Q_{28}$ , and  $Q_{30}$  operators it was essential to use the basis functions with  $1 + r/2$  prefactor, so the wave function satisfies exactly the electron-electron cusp condition. Particular attention should be paid to the second-order matrix element  $E'_A$  with the regularized Breit-Pauli Hamiltonian. The use of  $1 + r/2$  prefactor was necessary to subtract the  $\delta^3(r)$  term from the  $\vec{\nabla}_1^2 \vec{\nabla}_2^2$  differentiation of the outer wave function, and it also significantly improves the numerical convergence of  $E'_A$ .

All numerical matrix elements have been checked against the  $R \rightarrow 0$  and  $R \rightarrow \infty$  limits. Every operator  $Q_i$  in Table I as well as  $E'_A$ ,  $E_C$ , and  $E_{R2}$  have a well-defined limit  $R \rightarrow 0$  to the corresponding helium ground state mean value [16]. However, in the particular case of  $\Pi$  contribution to  $E_C$  the helium limit is achieved at extremely low values of  $R$ , indicating the significant change in the character of the electronic wave function at distances  $R = 0-0.2$  where the  $E_C(\Pi)$  curve has a local sharp minimum. The exceptional case is  $E_{R1}$ , which does not go to the helium limit at  $R = 0$ . The reason for this is that  $Z\alpha$  expansion of the electron self-energy assumes that all interparticle distances are of the order of the Bohr radius. When the internuclear distances are of the order of the electron Compton wavelength the  $Z\alpha$  expansion takes a different form and the proper helium limit is then achieved.

All the numerical matrix elements have also been verified against the long-distance asymptotics  $R \rightarrow \infty$ , which coincide with hydrogenic values as they should. It was essential to perform all possible tests, in order to avoid mistakes in derivation and coding of matrix elements. Moreover, matrix elements of  $Q_1 \dots Q_7$  have also been calculated with the double James-Coolidge basis [21] because the achieved numerical accuracy with exponential functions is much higher than with Gaussians. So far, we

TABLE II. Contributions to  $E^{(6)}$  for the ground electronic state of  $\text{H}_2$  at  $R = 1.4$  a.u.  $E_{LG}$  is the logarithmic correction, the last term in Eq. (17).  $E_D$  is the  $\alpha^6 m$  contribution from the Dirac equation.

$\alpha^6 m$	$\text{H}_2(\Sigma^+)$
$E'_Q$	0.688 40(16)
$E'_H$	-0.043 832
$E'_A$	-0.641 4(5)
$E_C$	-0.059 54(4)
Subtotal	-0.056 4(6)
$E_{R1}$	9.254 583
$E_{R2}$	0.142 233
$E_{LG}$	0.258 811
Total	9.599 3(6)
$-2E_D(\text{H})$	0.125 000
$-2E_{R1}(\text{H})$	-6.123 245
$-2E_{R2}(\text{H})$	-0.109 212
$E^{(6)}(\text{H}_2) - 2E^{(6)}(\text{H})$	3.491 8(6) $\alpha^6 m$

have not been able to calculate all the matrix elements with explicitly correlated exponential functions because they involve integrals that are too complicated, but we plan to do this in the near future.

*Results.*—The exemplary expectation value at  $R = 1.4$  a.u. of all  $Q_i$  operators is presented in Table I. The numerical accuracy is about five significant digits, and we observe a significant cancellation, so the sum, as expressed by  $E_Q$ , is smaller than most of the individual terms; see Table II. The overall dependence of the nonlogarithmic photon exchange contribution  $E_Q + E_A + E_C + E_H = E'_Q + E'_A + E_C + E'_H$  on the internuclear distance is presented in Fig. 1. We observe the extremum around 1.5 a.u., which is not far from the mean internuclear distance where the radial wave function is localized, so the photon exchange contribution to the dissociation energy is relatively small.

Table II supplies all contributions to  $E^{(6)}$  as given in Eq. (17) at  $R = 1.4$  a.u. It is worth noting that the by far

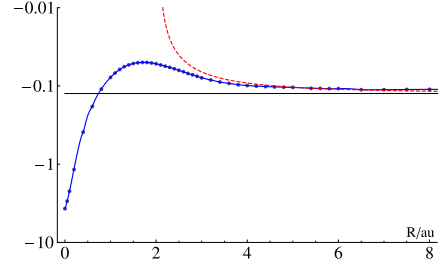


FIG. 1. Nonlogarithmic photon exchange contribution  $E'_Q + E'_A + E_C + E'_H$  as a function of the internuclear distance  $R$ . The horizontal line is located at  $-1/8$ , which is twice the atomic hydrogen value, and the dashed curve shows the  $0.529947904/R^2 - 1/8$  asymptotics, which is obtained from the small  $R$  expansion of the Casimir-Polder potential [22].

largest contribution comes from the one-loop radiative correction  $E_{R1}$ , which legitimizes the previous estimations for  $\alpha^6 m$  contribution [13]. Table III presents a summary of all contributions to the dissociation, fundamental vibrational, and rotational transitions. In particular, this table contains significantly more accurate results for the  $\alpha^2 m$  nonrelativistic energies obtained using explicitly correlated exponential functions [12].

*Summary.*—We have calculated the complete  $\alpha^6 m$  contribution to the molecular hydrogen energy levels. This is the first calculation of the higher order relativistic effects ever performed for molecules, except for the one-electron molecular ion  $\text{H}_2^+$  [10]. Besides significant improvements in the  $\text{H}_2$  levels, it shows how to properly incorporate electron correlations with relativistic and QED effects.

The improvement of the  $\text{H}_2$  levels down to the  $10^{-7} \text{ cm}^{-1}$  level will lead to a more accurate determination of the  $R_\infty$  constant and may shed light on the proton charge radius puzzle. The ratio of the nuclear finite size effects to the transition energy for  $1S - 2S$  in H is  $3.9 \times 10^{-10}$ , while for the  $\text{H}_2$  dissociation energy it is  $8.6 \times 10^{-10}$ . Since the ratios are sufficiently different, one can use these transitions

TABLE III. Contributions to dissociation, vibrational, and rotational transitions in  $\text{H}_2$  in  $\text{cm}^{-1}$ . Physical constants are from Ref. [2] and  $r_p = 0.8409(4)$  fm. There are additional  $10^{-3}$  uncertainties of  $\alpha^4$ ,  $\alpha^5$ , and  $\alpha^6 m$  terms due to the BO approximation, which are included in the final result only. The  $\alpha^7 m$  term is estimated from the known leading double logarithmic contribution in Eq. (11) and the related 50% uncertainty is assumed.  $E_{r_p^2}$  is the finite proton size correction.

	$D_0$	$v = 0 \rightarrow 1$	$J = 0 \rightarrow 1$
$\alpha^2 m$	36 118.797 746 12(5)	4 161.164 070 3(1)	118.485 260 46(3)
$\alpha^4 m$	-0.531 8(3) <sup>a</sup>	0.023 41(1) <sup>c</sup>	0.002 580(1)
$\alpha^5 m$	-0.194 8(2) <sup>b</sup>	-0.021 29(2) <sup>c</sup>	-0.001 022(1)
$\alpha^6 m$	-0.002 065(6)	-0.000 192 3(6)	-0.000 008 9(1)
$\alpha^7 m$	0.000 118(59)	0.000 012 0(60)	0.000 000 6(3)
$E_{r_p^2}$	-0.000 031	-0.000 003 2	-0.000 000 2
Theory	36 118.069 1(6)	4 161.166 01(4)	118.486 810(4)
[23–25]	36 118.069 62(37)	4 161.166 32(18)	118.486 84(10)

<sup>a</sup>[26]; <sup>b</sup>[13]; <sup>c</sup>[24]

to determine  $R_\infty$  and  $r_p$  without referring to the other, less well-known transitions in hydrogen. To achieve this, however, further improvement in the  $H_2$  levels is required, in particular the calculation of the  $\alpha^7 m$  contribution.

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*Note added in proof.*—Our preliminary calculations of the leading relativistic correction indicate that the related uncertainty from Refs. [13,26] is underestimated.

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