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Relativistic corrections for the ground electronic state of molecular hydrogen

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We recalculate the leading relativistic corrections for the ground electronic state of the hydrogen molecule using the variational method with explicitly correlated functions that satisfy the interelectronic cusp condition. The computational approach allowed for the control of the numerical precision, which reached about eight significant digits. More importantly, the updated theoretical energies became discrepant with the known experimental values and we conclude that the yet unknown relativistic recoil corrections might be larger than previously anticipated.

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I. INTRODUCTION

Theoretical studies of the hydrogen molecule are the cornerstone of molecular quantum mechanics. Due to its simplicity, the achieved precision is the highest among all molecules and still has the potential for significant enhancement. This high precision of theoretical predictions for H_2 leads to improved tests of quantum electrodynamics and improved bounds on hypothetical interactions [1]. Moreover, at the 10^{-7} cm^{-1} precision level, the dissociation energy is sensitive to the proton charge radius, which may help to resolve the so-called proton radius conundrum [2]. This requires high-accuracy calculations of not only nonrelativistic energies, but also leading relativistic $O(\alpha^2)$, QED $O(\alpha^3)$, as well as the higher-order corrections $O(\alpha^4)$ and $O(\alpha^5)$. In fact, the nonrelativistic energies can already be calculated with the precision of 10^{-7} cm^{-1}, as demonstrated in Ref. [3]. The $O(\alpha^4)$ contribution has very recently been calculated [4] using explicitly correlated Gaussian (ECG) functions with $1 + r_{12}/2$ prefactor (rECG) that causes the interelectronic cusp condition to be exactly satisfied. Here, we report the results for the leading $O(\alpha^2)$ relativistic correction using rECG functions and conclude that the compilation of previous results in Ref. [5] has underestimated numerical uncertainties. We improve the numerical precision by 3–4 orders of magnitude and present in detail our computational approach.

II. COMPUTATIONAL METHOD

In the Born-Oppenheimer (BO) approximation, the total wave function is assumed to be a product of the electronic and nuclear functions. The Schrödinger equation for the electronic wave functions in the infinite nuclear mass limit (assuming atomic units) is

$$H\psi(\vec{r}_1,\vec{r}_2) = \mathcal{E}(R)\psi(\vec{r}_1,\vec{r}_2), \tag{1}$$

where

$$H = \tfrac{1}{2}\left(\vec{p}_1^{\,2} + \vec{p}_2^{\,2}\right) + V \tag{2}$$

and

$$V = \frac{1}{R} - \frac{1}{r_{1A}} - \frac{1}{r_{2A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2B}} + \frac{1}{r}, \tag{3}$$

with $R = r_{AB}$ and $r = r_{12}$, and where indices 1 and 2 correspond to electrons, whereas A and B correspond to the nuclei. The leading relativistic correction in the BO approximation is $\mathcal{E}_{\rm rel}(R)$ to the nonrelativistic potential $\mathcal{E}(R)$. This correction can be expressed in terms of the expectation value

$$\mathcal{E}_{\rm rel}(R) = \langle\psi|H_{\rm rel}|\psi\rangle \tag{4}$$

of the Breit-Pauli Hamiltonian [6]

$$H_{\rm rel} = -\frac{1}{8}\left(p_1^4 + p_2^4\right) + \pi\,\delta^3(r) - \frac{1}{2}\,p_1^i\left(\frac{\delta^{ij}}{r} + \frac{r^i\,r^j}{r^3}\right)p_2^j + \frac{\pi}{2}[\delta^3(r_{1A}) + \delta^3(r_{2A}) + \delta^3(r_{1B}) + \delta^3(r_{2B})], \tag{5}$$

where we neglected spin-dependent terms vanishing for the ground electronic state of $^1\Sigma_g^+$ symmetry. The accurate calculation of the above expectation value is the principal goal of this work. We assume that every rECG basis function contains the $1 + r/2$ factor and perform special transformation (regularization) of matrix elements, including those with the Dirac-δ function [7], to improve the numerical convergence. We demonstrate a significant enhancement in numerical precision and indicate that previous numerical results [5] were not as accurate as claimed. In order to be more convincing, we provide results obtained in three approaches: (i) direct (no regularization) with ECG, (ii) standard regularization with ECG, and (iii) modified regularization with rECG functions. To test the convergence of these three different approaches, first we perform calculations for $R = 0$, namely, for the helium atom, for which highly accurate reference results can be obtained using explicitly correlated exponential functions. Next, the ECG calculations are performed for molecular hydrogen. Comparison of individual operators from different approaches is presented for the equilibrium internuclear distance, namely, for $R = 1.4$ a.u. The most accurate predictions were obtained for the regularization with rECG functions at 53 points in the range $R = 0.0$–10 a.u.

Except for our recent paper [4], we are unaware of similar studies of regularization techniques in the literature due to difficulties with two-center integrals involving inverse powers of interparticle distances. In relation to this, we have introduced an algorithm for numerical quadrature of nonstandard ECG two-center integrals [4], which enables very efficient calculation of all complicated matrix elements.

III. REGULARIZATION OF THE RELATIVISTIC CORRECTION

In this section, we provide regularization formulas for matrix elements with Dirac-δ and p^4 operators in $H_{\rm rel}$. The latter operator can be regularized according to two schemes: the standard one, already employed in the past in quantum molecular computations [8], and the modified scheme, valid in the case of the wave function obeying Kato's cusp condition.

According to the standard scheme, the relativistic operators are transformed into the regular form by the following relations:

$$4\pi\,\delta^3(r_{1A}) = 4\pi\,[\delta^3(r_{1A})]_r + \left\{\frac{2}{r_{1A}}, H-\mathcal{E}\right\}, \tag{6}$$

$$4\pi\,\delta^3(r) = 4\pi\,[\delta^3(r)]_r + \left\{\frac{1}{r}, H-\mathcal{E}\right\}, \tag{7}$$

$$p_1^4+p_2^4 = \left[p_1^4+p_2^4\right]_r + 4\,\{\mathcal{E}-V, H-\mathcal{E}\} + 4\,(H-\mathcal{E})^2, \tag{8}$$

where

$$4\pi\,[\delta^3(r_{1A})]_r = \frac{4}{r_{1A}}(\mathcal{E}-V) - \vec{p}_1\,\frac{2}{r_{1A}}\,\vec{p}_1 - \vec{p}_2\,\frac{2}{r_{1A}}\,\vec{p}_2, \tag{9}$$

$$4\pi\,[\delta^3(r)]_r = \frac{2}{r}(\mathcal{E}-V) - \vec{p}_1\,\frac{1}{r}\,\vec{p}_1 - \vec{p}_2\,\frac{1}{r}\,\vec{p}_2, \tag{10}$$

$$\left[p_1^4+p_2^4\right]_r = 4\,(\mathcal{E}-V)^2 - 2\,p_1^2\,p_2^2\,. \tag{11}$$

For the exact wave function ψ, which fulfills the electronic Schrödinger equation $(\mathcal{E}-H)\psi = 0$, the expectation-value identity holds, $\langle\psi|\ldots|\psi\rangle = \langle\psi|[\ldots]_r|\psi\rangle$, since for an arbitrary operator Q, $\langle\psi|\{Q,H-\mathcal{E}\}|\psi\rangle = 0$. For an approximate function $\tilde{\psi}$, such expectation values do not vanish, but converge to zero at the limit $\tilde{\psi}\to\psi$. In practice, the numerical convergence of the regularized form is much faster, so the leading relativistic correction shall be evaluated as

$$\mathcal{E}_{\rm rel}(R) = \langle\psi|[H_{\rm rel}]_r|\psi\rangle, \tag{12}$$

with

$$\begin{aligned}[H_{\rm rel}]_r =& -\frac{1}{8}\left[p_1^4+p_2^4\right]_r + \frac{\pi}{2}\{[\delta^3(r_{1A})]_r + [\delta^3(r_{2A})]_r \\ &+ [\delta^3(r_{1B})]_r + [\delta^3(r_{2B})]_r\} + \pi\,[\delta^3(r)]_r \\ &- \frac{1}{2}\,p_1^i\left(\frac{\delta^{ij}}{r}+\frac{r^i\,r^j}{r^3}\right)p_2^j\,.\end{aligned} \tag{13}$$

The modified regularization is applied when the wave function $\tilde{\psi}$ exactly satisfies the interelectronic cusp condition, as, for example, the rECG function does. In this case, the action of $[p_1^4+p_2^4]_r$ on such a function can be represented as

$$\left[p_1^4+p_2^4\right]_r|\tilde{\psi}\rangle = \left\{4\,(\mathcal{E}-V)^2 - 2\,\tilde{p}_1^2\,\tilde{p}_2^2 + 8\pi\,\delta^3(r)\right\}|\tilde{\psi}\rangle. \tag{14}$$

The term $\tilde{p}_1^2\,\tilde{p}_2^2$ (in contrast to $p_1^2\,p_2^2$) is understood as the differentiation $\nabla_1^2\,\nabla_2^2$ of $\tilde{\psi}$ as a function, and what is omitted,

$$-2\,\nabla_1^2\,\nabla_2^2\,(1+r/2) = 8\,\pi\,\delta^3(r), \tag{15}$$

coincides with the last term in Eq. (14). Now, if we are interested in determination of the $\langle\tilde{\psi}|p_1^4+p_2^4|\tilde{\psi}\rangle$ alone, we can additionally replace the Dirac-δ operator by its regularized form and obtain the fully regularized expectation value,

$$\begin{aligned}\langle\psi|p_1^4+p_2^4|\psi\rangle = \langle\psi|&4\,(\mathcal{E}-V)^2 - 2\,\tilde{p}_1^2\,\tilde{p}_2^2 \\ &+ 8\pi\,[\delta^3(r)]_r|\psi\rangle.\end{aligned} \tag{16}$$

We emphasize that here, unlike $p_1^2\,p_2^2$, the $\tilde{p}_1^2\,\tilde{p}_2^2$ term differentiates the right-hand-side wave function only. The specific relationship (14) can also be further employed to simplify the expectation value of the overall Breit-Pauli Hamiltonian (5) by complete elimination of the $\pi\,\delta^3(r)$ term,

$$\mathcal{E}_{\rm rel}(R) = \langle\psi|[H_{\rm rel}]'_r|\psi\rangle, \tag{17}$$

$$\begin{aligned}[H_{\rm rel}]'_r =& -\frac{1}{2}(\mathcal{E}-V)\left(\mathcal{E}-\frac{1}{R}-\frac{1}{r}\right) \\ &+ \frac{1}{4}\left(\tilde{p}_1^2\,\tilde{p}_2^2 + \vec{p}_1\,\tilde{V}\,\vec{p}_1 + \vec{p}_2\,\tilde{V}\,\vec{p}_2\right) \\ &- \frac{1}{2}\,p_1^i\left(\frac{\delta^{ij}}{r}+\frac{r^i\,r^j}{r^3}\right)p_2^j,\end{aligned} \tag{18}$$

with $\tilde{V} = -1/r_{1A} - 1/r_{1B} - 1/r_{2A} - 1/r_{2B}$. Apart from its compactness, this formula has an additional important advantage which is not readily noticeable. Due to the above cancellations, all of the time-consuming integrals with three odd powers of interparticle distances do not appear in the matrix elements with rECG functions. This nontrivial cancellation has a remarkable impact on calculations of the relativistic correction.

IV. INTEGRALS WITH ECG FUNCTIONS

The variational wave function

$$\psi = \sum_i c_i\,\psi_i(\vec{r}_1,\vec{r}_2), \tag{19}$$

$$\psi_i = (1+\hat{\imath})\,(1+P_{1\leftrightarrow 2})\,\phi_i(\vec{r}_1,\vec{r}_2), \tag{20}$$

where $\hat{\imath}$ and $P_{1\leftrightarrow 2}$ are the inversion and the electron exchange operators, can be accurately represented in the basis of ECG functions of the form

$$\phi_{\Sigma^+} = e^{-a_{1A}\,r_{1A}^2 - a_{1B}\,r_{1B}^2 - a_{2A}\,r_{2A}^2 - a_{2B}\,r_{2B}^2 - a_{12}\,r^2} \tag{21}$$

or in the basis of the modified rECG functions,

$$\phi_{\Sigma^+} = \left(1+\frac{r}{2}\right)e^{-a_{1A}\,r_{1A}^2 - a_{1B}\,r_{1B}^2 - a_{2A}\,r_{2A}^2 - a_{2B}\,r_{2B}^2 - a_{12}\,r^2}. \tag{22}$$

Nonlinear a parameters are determined variationally for every ECG or rECG basis function, and linear c parameters come from the solution of the general eigenvalue problem. The primary advantage of the ECG type of functions is that all integrals necessary for the calculations of nonrelativistic and relativistic operators can be evaluated very effectively as described below.

Each matrix element can be expressed as a linear combination of the following ECG integrals:

$$f(n_1,n_2,n_3,n_4,n_5) = \frac{1}{\pi^3}\int d^3r_1 \int d^3r_2\, r_{1A}^{n_1} r_{1B}^{n_2} r_{2A}^{n_3} r_{2B}^{n_4} r_{12}^{n_5} \times e^{-a_{1A}\, r_{1A}^2 - a_{1B}\, r_{1B}^2 - a_{2A}\, r_{2A}^2 - a_{2B}\, r_{2B}^2 - a_{12}\, r_{12}^2}, \tag{23}$$

with integers n_i and real parameters a. Among all the integrals represented by the above formula, we can distinguish two subsets that can be evaluated analytically. The first subset contains the *regular* ECG integrals with the non-negative even integers n_i such that $\sum_i n_i \leqslant \Omega_1$, where the shell parameter $\Omega_1 = 0,2,4,\dots$. These integrals can be generated by differentiation over a parameters of the following master integral:

$$f(0,0,0,0,0) = X^{-3/2} e^{-R^2 \frac{Y}{X}}, \tag{24}$$

where

$$X = (a_{1A} + a_{1B} + a_{12})(a_{2A} + a_{2B} + a_{12}) - a_{12}^2, \tag{25}$$

$$Y = (a_{1B} + a_{1A})\, a_{2A} a_{2B} + a_{1A} a_{1B} (a_{2A} + a_{2B}) + a_{12}(a_{1A} + a_{2A})(a_{1B} + a_{2B}). \tag{26}$$

Each differentiation raises one of the n_i exponents by two. The second subset of integrals permits a single odd index $n_i \geqslant -1$ for which $\sum_i n_i \leqslant \Omega_2$ ($\Omega_2 = -1,1,3,\dots$). These so-called Coulomb ECG integrals can also be obtained analytically by differentiation of another master integral. For instance, when $n_1 = -1$, the master integral reads

$$f(-1,0,0,0,0) = \frac{1}{X\sqrt{X_1}}\, e^{-R^2 \frac{Y}{X}} F\left[R^2\left(\frac{Y_1}{X_1} - \frac{Y}{X}\right)\right], \tag{27}$$

where $X_1 = \partial_{a_{1A}} X$, $Y_1 = \partial_{a_{1A}} Y$, and $F(x) = \operatorname{erf}(x)/x$.

In the standard use of ECG functions, the *regular* integrals with $\Omega_1 = 2$ and *Coulomb* with $\Omega_2 = -1$ are sufficient to evaluate matrix elements of the electronic Schrödinger equation (1) and thus to perform calculations of the nonrelativistic energy of the ground state in molecular hydrogen. If, additionally, analytic gradient minimization is employed, the integrals with $\Omega_1 = 4$ and $\Omega_2 = 1$ are required. Such nonrelativistic calculations have been widely used for many atomic and molecular systems [9].

The molecular ECG integrals, as opposed to the atomic ones, have no known analytic form when two or more n_i are odd. Such *extended* integrals originate from regularization of the relativistic operators, for example from V^2 in Eq. (11), or from matrix elements of the nonrelativistic Hamiltonian with rECG basis. The algorithm for numerical evaluation of this *extended* type of integrals relies on the following relation, which decreases one of the indices by one:

$$f(n_1 - 1,n_2,n_3,n_4,n_5) = \frac{2}{\sqrt{\pi}}\int_0^\infty dy\, f(n_1,n_2,n_3,n_4,n_5)|_{a_{1A}\to a_{1A}+y^2}. \tag{28}$$

The right-hand-side f is understood as the integral $f(n_1,n_2,n_3,n_4,n_5)$ evaluated with the a_{1A} parameter replaced by $a_{1A} + y^2$. The transformation $y = -1 + 1/x$ converts the infinite integration domain to the finite interval $(0,1)$ for which an m-point generalized Gaussian quadrature with logarithmic end-point singularity [10] is applied,

$$\int_0^1 dx [W_1(x) + \ln(x)\, W_2(x)] = \sum_{i=1}^{m} w_i\, [W_1(x_i) + \ln(x_i)\, W_2(x_i)]. \tag{29}$$

The $W_{1,2}$ are arbitrary polynomials of maximal degree $m - 1$, w_i are weights, and x_i are nodes. In terms of this quadrature, the integral (28) can be approximated by the formula

$$f(n_1 - 1,n_2,n_3,n_4,n_5) = \frac{2}{\sqrt{\pi}} \sum_{i=1}^{m} w_i\, (y_i + 1)^2 \times f(n_1,n_2,n_3,n_4,n_5)|_{a_{1A}\to a_{1A}+y_i^2}. \tag{30}$$

This quadrature is very efficient for *extended* integrals with two odd indices, for which typically only $m = 30$ nodes allow about 16 significant digits to be obtained. These extended integrals are sufficient not only for all the relativistic operators with the regularization applied to the ECG wave function, but also for the modified regularization (17) and (18) of H_{rel} with the rECG wave function.

Nevertheless, calculations with the rECG wave function of the expectation values of the individual relativistic operators involve *extended* integrals with three odd indices. They can be obtained by the double numerical integration of *Coulomb* ECG integrals over 30^2 nodes to achieve numerical precision of about 16 significant digits. This two-dimensional integration is numerically stable but time consuming.

V. CALCULATIONS OF RELATIVISTIC CORRECTIONS

Relativistic corrections to the BO potential were calculated according to Eqs. (4), (12), and (17). In order to demonstrate the convergence of these three different approaches with ECG functions, we compared results at $R = 0$, i.e., for the helium atom, to the results obtained with explicitly correlated exponential (ECE) functions. Calculations with ECE functions are well known in the literature (see, e.g., Refs. [11] and [12]) and may serve as an excellent reference point and a rigorous test of the convergence of ECG results. The numerical values presented in Table I were obtained with 128, 256, 512, and 1024 ECG basis functions. Direct and standard regularization methods were used with ECG functions, whereas the modified regularization methods were used with rECG functions. We observe a significant enhancement of numerical convergence of relativistic operators obtained with the rECG basis. The total relativistic correction with $N = 1024$ is accurate to nine digits in the rECG basis, and to five to six digits in the ECG basis. A similar enhancement is observed for H_2 at $R = 1.4$ in Table II, where we compared our results for Dirac-δ functions with those obtained in the ECE basis. The accuracy of the extrapolated value for the total relativistic correction is estimated to have at least eight significant digits after the decimal point. In Table III, we provide results for the nonrelativistic energy $\mathcal{E}$, for the relativistic correction $\mathcal{E}_{\mathrm{rel}}$, and for all four individual components of the relativistic correction evaluated at $R \in (0,10)$ a.u. with the 1024-term basis of rECG functions.

TABLE I. Convergence of matrix elements of relativistic operators at $R = 0$ a.u. (helium atom limit).

Basis	Direct	Standard regularization	rECG (+ modified regularization)
$\mathcal{E}$			
128	–2.903 724 368 357 561		−2.903 724 366 011 805
256	–2.903 724 376 781 020		−2.903 724 376 765 067
512	–2.903 724 377 031 170		−2.903 724 377 030 040
1024	–2.903 724 377 034 103		−2.903 724 377 034 089
∞-Slater[a]			−2.903 724 377 034 119 598(1)
$p_1^4 + p_2^4$			
128	108.103 812 847	108.178 260 879	108.175 893 984
256	108.149 717 136	108.176 705 311	108.176 119 036
512	108.171 069 063	108.176 261 126	108.176 133 296
1024	108.174 593 664	108.176 173 934	108.176 134 411
∞-Slater[a]			108.176 134 45(1)
$\delta^3(r_1) + \delta^3(r_2)$			
128	3.618 072 922 23	3.620 855 927 07	3.620 852 504 90
256	3.619 832 314 29	3.620 858 327 71	3.620 858 263 22
512	3.620 662 493 08	3.620 858 623 04	3.620 858 610 86
1024	3.620 798 945 59	3.620 858 636 28	3.620 858 636 16
∞-Slater[a]			3.620 858 637 00(1)
$\delta^3(r)$			
128	0.106 521 423 626	0.106 345 075 042	0.106 345 517 181
256	0.106 391 759 156	0.106 345 347 318	0.106 345 416 874
512	0.106 355 477 797	0.106 345 369 617	0.106 345 375 554
1024	0.106 348 511 028	0.106 345 370 530	0.106 345 370 708
∞-Slater[a]			0.106 345 370 634(1)
$p_1^i\big(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3}\big)p_2^j$			
128	0.278 191 140 60		0.278 188 211 08
256	0.278 189 536 41		0.278 188 961 40
512	0.278 189 388 13		0.278 189 339 07
1024	0.278 189 381 79		0.278 189 380 36
∞-Slater[a]			0.278 189 381 08(1)
$\mathcal{E}_{\rm rel}$			
128	−1.950 913 941 68	−1.952 030 893 54	−1.951 742 928 89
256	−1.951 531 235 51	−1.951 827 248 21	−1.951 753 660 41
512	−1.951 706 049 93	−1.951 770 653 11	−1.951 754 696 40
1024	−1.951 739 830 39	−1.951 759 709 00	−1.951 754 765 23
∞-Slater[a]			−1.951 754 768(1)

[a] The reference values were evaluated with the atomic ECE basis functions $\phi = \exp(-\alpha\, r_1 - \beta\, r_2 - \gamma\, r)$.

Our results for the overall relativistic correction $\mathcal{E}_{\rm rel}$ for H_2 are estimated to have eight significant decimal digits.

VI. VIBRATIONAL AVERAGING

In order to obtain the final value of the α^2 relativistic component of the dissociation energy, we solved the radial Schrödinger equation for two potentials. The first potential, used as a reference, is the nonrelativistic (BO) potential $\mathcal{E}(R)$ [14], which yielded the nonrelativistic (BO) energy level E. The second was the potential augmented by the relativistic correction $\mathcal{E}_{\rm rel}(R)$, which gave the eigenvalue corresponding to the relativistic energy level $E + E^{(2)}$. The difference between both of the eigenvalues $E^{(2)}$ is the relativistic correction to molecular levels.

To establish reliable uncertainties for the final results, we studied two sources of error: the convergence of single-point calculations and the polynomial interpolation. As mentioned above, the relativistic correction was evaluated using basis sets of increasing size, which permitted a detailed analysis of the convergence at each internuclear distance (see Table II). From this analysis, we estimated that in the vicinity of the equilibrium distance, the $\mathcal{E}_{\rm rel}(R)$ bears an uncertainty of 7×10^{-9} a.u. equivalent to 2×10^{-8} cm^{-1}. The influence of the density of the points, at which $\mathcal{E}_{\rm rel}(R)$ was evaluated, on the accuracy of the final result was assessed by doubling the number of points, which, however, were calculated only with a 512-term basis. As a consequence, $E^{(2)}$ was shifted by 5×10^{-7} cm^{-1}. The related uncertainty due to the selection of the degree of the interpolation polynomial was also investigated. By changing

TABLE II. Convergence of matrix elements of relativistic operators at the equilibrium distance $R = 1.4$ a.u.

Basis	Direct	Standard regularization	rECG (+ modified regularization)
$\mathcal{E}$			
128	–1.174 475 621 659 802		−1.174 475 640 130 736
256	–1.174 475 711 731 700		−1.174 475 711 200 533
512	–1.174 475 714 117 150		−1.174 475 714 015 654
1024	–1.174 475 714 217 171		−1.174 475 714 203 071
∞-JC[a]		.	−1.174 475 714 220 443 4(5)
$p_1^4 + p_2^4$			
128	13.214 563	13.238 771 4	13.237 780 507
256	13.231 849	13.238 308 1	13.237 929 826
512	13.235 568	13.238 045 9	13.237 954 576
1024	13.237 266	13.237 981 4	13.237 956 021
∞	13.238 7(10)	13.237 960(16)	13.237 956 18(7)
$\sum_{a,X} \delta^3(r_{aX})$			
128	0.917 550 7	0.919 331 278 50	0.919 331 321 06
256	0.918 878 9	0.919 335 927 94	0.919 335 741 10
512	0.919 153 5	0.919 336 172 60	0.919 336 127 42
1024	0.919 285 5	0.919 336 210 05	0.919 336 191 74
∞	0.919 37(7)	0.919 336 211 2(18)	0.919 336 206(7)
JC[b]			0.919 336 211(2)
$\delta^3(r)$			
128	0.016 742 915	0.016 742 915 953	0.016 743 529 776
256	0.016 771 639	0.016 743 229 495	0.016 743 316 316
512	0.016 750 461	0.016 743 274 514	0.016 743 287 361
1024	0.016 745 258	0.016 743 277 598	0.016 743 278 963
∞	0.016 743 5(4)	0.016 743 278 1(7)	0.016 743 278 3(5)
JC[b]			0.016 743 278 3(3)
$p_1^i\left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3}\right)p_2^j$			
128	0.095 271 222 30		0.095 266 566 34
256	0.095 269 308 16		0.095 268 588 45
512	0.095 269 010 11		0.095 268 883 81
1024	0.095 268 989 79		0.095 268 976 83
∞	0.095 268 986(6)		0.095 268 987(4)
$\mathcal{E}_{\rm rel}$			
128	−0.205 342 30	−0.205 800 42	−0.205 672 234 22
256	−0.205 554 44	−0.205 733 26	−0.205 685 637 69
512	−0.205 654 50	−0.205 699 82	−0.205 688 363 37
1024	−0.205 675 65	−0.205 691 67	−0.205 688 516 45
∞	−0.205 682(8)	−0.205 689(2)	−0.205 688 526(7)

[a] Evaluated with James-Coolidge wave function; Ref. [14].

[b] Evaluated in this work.

the degree in the range 5–12, we observed changes in the relativistic correction at the level of 10^{-7} cm^{-1}. To summarize, the largest contribution to the uncertainty of the relativistic correction $E^{(2)}$ comes from the limited number of points (and the necessity of interpolation) at which the relativistic potential was evaluated. The final relative uncertainty is assumed to be smaller than 10^{-6} cm^{-1}.

VII. RESULTS AND SUMMARY

Results of our calculations for the dissociation energy and the two selected most accurately measured transitions in H_2 and D_2 are presented in Tables IV and V. The nonrelativistic energy E for H_2 was calculated by solving the full nonadiabatic Schrödinger equation in the exponential basis [3], whereas for D_2, it was calculated using the nonadiabatic perturbation theory (NAPT) [15,16] expansion with the neglect of $O(1/\mu)^3$ terms. All of the corrections were obtained within the adiabatic approximation. The relativistic correction $E^{(2)}$ was evaluated and reported in this work. The leading QED correction $E^{(3)}$ was obtained in Ref. [17], while the higher-order QED, namely $E^{(4)}$, was obtained in Ref. [4]. $E^{(5)}$ was estimated from the correction analogous to that of atomic hydrogen with the assumption that it is proportional to the electron-nucleus Dirac δ, and the related uncertainty was assigned to be 50%.

TABLE III. The electronic energy $\mathcal{E}$, expectation values of individual relativistic operators, and the relativistic correction of Eq. (17) evaluated with the 1024-term rECG basis for H_2 (all entries in a.u.).

R	$\mathcal{E}$	$p_1^4 + p_2^4$	$\sum_{a,X} \delta^3(r_{aX})$	$\delta^3(r)$	$p_1^i\left(\frac{\delta^{ij}}{r} + \frac{r^i r^j}{r^3}\right)p_2^j$	$\mathcal{E}_{\rm rel}$
0.0	∞	108.176 134 41	7.241 717 273 9	0.106 345 370 636	0.278 189 381 06	−1.951 754 765
0.05	17.104 840 595 733 8	97.883 437 11	6.489 043 177 5	0.105 003 823 908	0.276 266 361 42	−1.850 717 847
0.1	7.127 216 731 179 9	87.359 441 20	5.770 597 148 6	0.101 570 564 053	0.271 273 759 54	−1.672 040 901
0.2	2.197 803 295 242 6	69.106 095 40	4.568 931 840 2	0.091 368 192 666	0.255 825 956 08	−1.302 271 866
0.4	−0.120 230 341 173 2	44.926 748 48	3.007 974 262 0	0.068 873 279 242	0.218 115 094 21	−0.783 614 393
0.6	−0.769 635 429 474 0	31.455 544 41	2.135 554 220 2	0.050 763 240 175	0.183 036 489 08	−0.509 463 149
0.8	−1.020 056 666 340 7	23.551 412 69	1.616 559 002 3	0.037 667 878 063	0.153 865 267 48	−0.363 237 148
1.0	−1.124 539 719 525 6	18.631 892 59	1.288 195 811 0	0.028 345 276 112	0.130 210 595 68	−0.281 549 312
1.1	−1.150 057 367 720 2	16.862 669 10	1.168 538 437 1	0.024 725 634 292	0.120 121 309 61	−0.254 680 537
1.2	−1.164 935 243 421 7	15.417 026 26	1.069 918 912 8	0.021 643 994 354	0.111 012 509 31	−0.234 013 225
1.3	−1.172 347 149 015 1	14.225 963 31	0.987 949 432 3	0.019 008 309 934	0.102 764 094 19	−0.218 043 755
1.4	−1.174 475 714 202 3	13.237 956 02	0.919 336 191 7	0.016 743 278 963	0.095 268 976 86	−0.205 688 516
1.4011	−1.174 475 931 376 0	13.228 062 27	0.918 645 775 7	0.016 720 183 220	0.095 190 366 90	−0.205 569 553
1.45	−1.174 057 071 449 9	12.807 526 10	0.889 230 483 6	0.015 730 076 395	0.091 773 957 00	−0.200 610 272
1.5	−1.172 855 079 551 8	12.414 016 28	0.861 572 931 7	0.014 787 413 515	0.088 432 824 23	−0.196 156 821
1.6	−1.168 583 373 346 2	11.724 276 68	0.812 728 747 6	0.013 090 471 717	0.082 173 146 96	−0.188 864 898
1.7	−1.162 458 726 874 9	11.145 591 08	0.771 298 695 7	0.011 611 319 478	0.076 418 016 59	−0.183 376 700
1.8	−1.155 068 737 586 8	10.659 827 14	0.736 097 157 4	0.010 316 180 045	0.071 104 900 35	−0.179 362 896
1.9	−1.146 850 697 001 6	10.252 633 62	0.706 180 601 1	0.009 177 235 715	0.066 179 438 68	−0.176 571 891
2.0	−1.138 132 957 102 2	9.912 536 44	0.680 790 743 4	0.008 171 495 990	0.061 594 536 96	−0.174 809 213
2.1	−1.129 163 836 066 7	9.630 266 86	0.659 312 181 5	0.007 279 910 924	0.057 309 396 71	−0.173 922 389
2.2	−1.120 132 116 815 1	9.398 255 83	0.641 240 366 5	0.006 486 644 310	0.053 288 924 14	−0.173 790 035
2.3	−1.111 181 765 169 5	9.210 246 40	0.626 157 014 6	0.005 778 509 183	0.049 503 041 98	−0.174 313 461
2.4	−1.102 422 605 975 9	9.060 993 78	0.613 710 992 0	0.005 144 501 580	0.045 926 280 03	−0.175 410 463
2.5	−1.093 938 129 920 1	8.946 029 98	0.603 603 282 8	0.004 575 430 210	0.042 537 333 71	−0.177 010 457
2.6	−1.085 791 237 362 5	8.861 476 93	0.595 575 000 5	0.004 063 603 931	0.039 318 826 34	−0.179 050 818
2.7	−1.078 028 484 147 9	8.803 898 42	0.589 397 852 6	0.003 602 589 090	0.036 256 887 42	−0.181 473 897
2.8	−1.070 683 233 449 8	8.770 183 99	0.584 866 570 4	0.003 186 984 950	0.033 341 021 16	−0.184 225 040
2.9	−1.063 778 008 771 7	8.757 458 14	0.581 792 947 1	0.002 812 250 937	0.030 563 703 83	−0.187 250 948
3.0	−1.057 326 268 838 3	8.763 015 72	0.580 001 450 5	0.002 474 548 852	0.027 920 059 06	−0.190 498 823
3.2	−1.045 799 661 390 2	8.818 766 65	0.579 608 528 2	0.001 897 578 330	0.023 025 370 71	−0.197 450 152
3.4	−1.036 075 395 153 1	8.918 013 44	0.582 448 331 7	0.001 434 600 771	0.018 655 309 93	−0.204 664 704
3.6	−1.028 046 308 339 0	9.043 109 19	0.587 399 895 4	0.001 068 345 909	0.014 820 897 94	−0.211 757 192
3.8	−1.021 549 795 379 5	9.178 853 16	0.593 491 357 9	0.000 783 739 899	0.011 529 591 76	−0.218 405 205
4.0	−1.016 390 252 917 8	9.313 279 23	0.599 942 199 5	0.000 566 901 578	0.008 773 121 69	−0.224 378 488
4.2	−1.012 359 959 653 3	9.438 064 55	0.606 187 454 4	0.000 404 933 730	0.006 522 438 89	−0.229 550 124
4.4	−1.009 256 516 218 8	9.548 395 99	0.611 872 426 5	0.000 286 163 107	0.004 729 595 59	−0.233 888 328
4.6	−1.006 895 223 788 3	9.642 347 77	0.616 819 321 1	0.000 200 467 812	0.003 334 249 31	−0.237 433 284
4.8	−1.005 116 006 012 2	9.720 046 26	0.620 980 427 9	0.000 139 467 088	0.002 271 426 58	−0.240 269 571
5.0	−1.003 785 658 541 8	9.782 862 62	0.624 391 465 4	0.000 096 514 570	0.001 478 031 56	−0.242 501 813
5.2	−1.002 796 816 280 7	9.832 762 96	0.627 132 969 7	0.000 066 524 898	0.000 897 184 78	−0.244 236 803
5.4	−1.002 065 057 189 4	9.871 870 41	0.629 303 290 7	0.000 045 719 642	0.000 480 298 37	−0.245 573 020
5.6	−1.001 525 251 817 8	9.902 201 97	0.631 001 580 7	0.000 031 354 765	0.000 187 505 16	−0.246 595 529
5.8	−1.001 127 880 827 6	9.925 541 76	0.632 318 772 1	0.000 021 470 798	−0.000 012 912 40	−0.247 374 807
6.0	−1.000 835 707 602 8	9.943 392 93	0.633 333 420 5	0.000 014 686 948	−0.000 145 606 65	−0.247 967 362
6.5	−1.000 400 547 946 1	9.971 478 81	0.634 946 087 8	0.000 005 668 125	−0.000 293 186 06	−0.248 899 471
7.0	−1.000 197 914 426 6	9.985 482 43	0.635 760 762 7	0.000 002 183 134	−0.000 307 901 17	−0.249 373 815
7.5	−1.000 102 106 038 0	9.992 439 90	0.636 169 798 9	0.000 000 839 980	−0.000 274 910 15	−0.249 621 706
8.0	−1.000 055 604 611 0	9.995 922 78	0.636 376 259 1	0.000 000 323 028	−0.000 230 376 86	−0.249 756 677
8.5	−1.000 032 171 701 7	9.997 700 01	0.636 482 218 0	0.000 000 124 123	−0.000 188 104 44	−0.249 834 155
9.0	−1.000 019 781 690 9	9.998 632 62	0.636 537 991 1	0.000 000 047 661	−0.000 152 289 86	−0.249 881 211
9.5	−1.000 012 855 993 3	9.999 142 48	0.636 568 497 4	0.000 000 018 282	−0.000 123 345 87	−0.249 911 507
10.0	−1.000 008 755 693 5	9.999 434 61	0.636 586 008 8	0.000 000 007 007	−0.000 100 390 54	−0.249 932 046
∞	−1.0	10.0	0.636 619 772 3	0.0	0.0	−0.25

TABLE IV. Contributions to the dissociation energy D_0 and two selected most accurate experimental transitions in H_2 (in cm^{-1}). There are additional 10^{-3} relative uncertainties on the $E^{(2)}$, $E^{(3)}$, and $E^{(4)}$ terms due to the BO approximation, which are included in the final result only. E_{FS} is the finite nuclear size correction.

Contrib.	D_0	$S_3(3)$	$Q_1(0)$
E	36 118.797 746 12(5)	12 559.749 918 95(8)	4 161.163 977 09(6)
$E^{(2)}$	−0.533 121(1)[a]	0.065 366	0.023 397
$E^{(3)}$	−0.194 8(2)	−0.065 73(6)	−0.021 29(2)
$E^{(4)}$	−0.002 067(6)	−0.000 599	−0.000 192
$E^{(5)}$	0.000 12(6)	0.000 037(19)	0.000 012(6)
E_{FS}	−0.000 031	−0.000 010	−0.000 003
Total	36 118.067 8(6)	12 559.748 98(8)	4 161.165 90(3)
Expt.	36 118.069 62(37)[b]	12 559.749 52(5)[c]	4 161.166 36(15)[d]
Diff.	0.001 8(6)(4)	0.000 54(8)(5)	0.000 46(3)(15)

[a] For comparison, Wolniewicz [8] obtained −0.5330, Piszczatowski *et al.* [5] −0.5319, and Stanke *et al.* [19] −0.5691 cm^{-1} (the latter value comes from nonadiabatic calculations).

[b] Reference [18].

[c] Reference [20].

[d] Reference [21].

Our results for the leading relativistic corrections significantly differ from those by Piszczatowski *et al.* [5], whose compilation partially relies on the former calculations by Wolniewicz [8]. For example, our relativistic correction to D_0 of H_2 is −0.533 121(1) cm^{-1}, whereas Piszczatowski *et al.* reported −0.531 9(3) cm^{-1}. Interestingly, our result is closer to that obtained by Wolniewicz, −0.533 0 cm^{-1}, despite the differences at the level of individual operators. In our opinion, these differences come from the much more accurate calculation of relativistic matrix elements performed here.

Most importantly, our final theoretical predictions for D_0 are now in disagreement with experimental values, in contrast to the previous theoretical results [5]. This disagreement probably comes from the underestimation of the relativistic nuclear recoil correction. We have previously assumed that these corrections are of the order of the ratio of the electron mass to the reduced mass of the nuclei, which for H_2 is $\sim 10^{-3}$. This might be incorrect because the nonrecoil relativistic correction is anomalously small. This assertion is supported by the example of the helium atom. The nonrecoil relativistic correction to the ^{4}He ionization energy is 16 904.024 MHz, while the nuclear recoil is −103.724 MHz, so the ratio is 6×10^{-3}, which is an order of magnitude higher than the estimate based on the helium mass ratio of 10^{-4}. On the other hand, in the separated atoms limit, the relativistic recoil correction exactly vanishes. Therefore, at present, this correction cannot be reliably estimated.

If the relativistic nuclear recoil correction in H_2 is underestimated, the difference between our predictions and the experimental values for D_2 should be smaller than that for H_2, and this is actually the case (see Tables IV and V). We emphasize that our theoretical predictions should be treated as preliminary until the relativistic nuclear recoil corrections are reliably calculated. In fact, such corrections have already been obtained by Stanke and Adamowicz [19] for purely vibrational states. However, their result for the total relativistic dissociation energy of H_2 (with $E^{(2)} = -0.5691$ cm^{-1}), when augmented by missing higher-order corrections, yields

TABLE V. Contributions to the dissociation energy D_0 and two selected most accurate experimental transitions in D_2 (in cm^{-1}). There are additional 5×10^{-4} relative uncertainties on the $E^{(2)}$, $E^{(3)}$, and $E^{(4)}$ terms due to the BO approximation, which are included in the final result only. E_{FS} is the finite nuclear size correction.

Contrib.	D_0	$S_2(2)$	$Q_1(0)$
E	36 749.090 98(8)	6 241.120 96(30)	2 993.614 88(15)
$E^{(2)}$	−0.529 170(1)	0.040 057	0.017 677
$E^{(3)}$	−0.198 2(2)	−0.033 15(3)	−0.015 39(2)
$E^{(4)}$	−0.002 096(6)	−0.000 299	−0.000 139
$E^{(5)}$	0.000 12(6)	0.000 019(10)	0.000 009(5)
E_{FS}	−0.000 204	−0.000 032	−0.000 015
Total	36 748.361 4(4)	6 241.127 55(30)	2 993.617 02(15)
Expt.	36 748.362 86(68)[a]	6 241.127 64(2)[b]	2 993.617 06(15)[c]
Diff.	0.001 5(4)(7)	0.000 09(30)(2)	0.000 04(15)(15)

[a] Reference [22].

[b] Reference [23].

[c] Reference [21].

$D_0 = 36\,118.0318\ \mathrm{cm}^{-1}$, which differs from the experimental value by as much as $0.038\ \mathrm{cm}^{-1}$, so its numerical uncertainty is out of control. We plan to calculate these nonadiabatic corrections using the fully nonadiabatic wave function in an exponential basis as in Ref. [3] or by using nonadiabatic perturbation theory (NAPT) [13]. Certainly, this calculation has to be performed to resolve discrepancies with H_2 experiments.

In conclusion, the former excellent agreement of theoretical predictions with experimental D_0 values was accidental and the improved calculations of the leading relativistic corrections result in a few σ disagreements with experimental values for dissociation energies and transition energies, which is probably caused by the unknown relativistic nuclear recoil (nonadiabatic) effects in the relativistic corrections.

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