PHYSICAL REVIEW A **100**, 020503(R) (2019)

Rapid Communications

Dissociation energy of molecular hydrogen isotopologues

Mariusz Puchalski, Jacek Komasa, and Anna Spyszkiewicz
Faculty of Chemistry, Adam Mickiewicz University, Uniwersytetu Poznańskiego 8, 61-614 Poznań, Poland

Krzysztof Pachucki
Faculty of Physics, University of Warsaw, Pasteura 5, 02-093 Warsaw, Poland

(Received 27 June 2019; published 30 August 2019)

The nonrelativistic energy together with relativistic and quantum electrodynamic corrections for all the molecular hydrogen isotopologues (D_2, T_2, HD, HT, DT) were evaluated without expansion in the electron-nucleus mass ratio. The obtained results significantly improve the uncertainty of theoretical predictions, reaching a value below 1 MHz for the total dissociation energy. We observe good agreement with the experimental value for D_2 and 3σ discrepancy for the HD molecule, while no experimental values for the dissociation energy of molecules involving tritium have yet been obtained.

DOI: 10.1103/PhysRevA.100.020503

Introduction. The dissociation energy of ortho-H_2 has recently been measured with submegahertz uncertainty [1,2], which is smaller than the contribution due to the finite size of the proton. Therefore, for the first time the molecular hydrogen spectroscopy has become sensitive to the nuclear charge radius. Similar progress is expected for HD and D_2 systems, which have been measured so far with 10 MHz uncertainty [3,4]. Moreover, very accurate measurements of several molecular transitions for tritium-containing isotopologues have been obtained [5,6] very recently, which indicates the possibility of measurements of their dissociation energies in the future.

The current theoretical dissociation energy of para-H_2 is $36\,118.069\,632(26)\ \mathrm{cm}^{-1}$ [7], which corresponds to 0.8 MHz of absolute uncertainty. It is in good agreement with the most recent experimental value of $36\,118.069\,45(31)\ \mathrm{cm}^{-1}$ [8], which will soon be improved [9]. In this work we demonstrate that similar accuracy can be reached for all the other molecular hydrogen isotopologues: D_2, T_2, HD, HT, and DT.

The high accuracy of theoretical predictions for molecular levels can only be achieved with the approach based on nonrelativistic quantum electrodynamic (NRQED) theory. According to NRQED, the total energy of an atom or a molecule can be represented by the expansion in powers of the fine-structure constant α,

$$E(\alpha) = \sum_{n=2} m\alpha^n E^{(n)}. \tag{1}$$

In our previous work on H_2 [7], the first three terms—the nonrelativistic energy $E^{(2)}$, the relativistic correction $E^{(4)}$, and the leading QED correction $E^{(5)}$—were calculated to a high numerical precision in direct four-body variational calculations. The higher order QED corrections were evaluated in the framework of the Born-Oppenheimer (BO) approximation, wherein the $E^{(6)}$ correction was evaluated in a complete way, but $E^{(7)}$ was merely estimated from the dominating terms, which are known from the hydrogen atom [10]. Here, the same method is applied to the heavier homonuclear isotopologues D_2 and T_2, as well as extended further to heteronuclear systems HD, HT, and DT. The uncertainties assigned to theoretical predictions are below 1 MHz, which is an improvement by one to two orders of magnitude compared to the most accurate previous results.

Nonrelativistic wave function. The quality of the determination of the nonrelativistic wave function is of critical importance for achieving the high accuracy of theoretical results. In the direct nonadiabatic approach, in which all particles are treated on an equal footing, the wave function Ψ is a solution to the four-body Schrödinger equation $H\Psi = E\Psi$ with $E = E^{(2)}$ and the Hamiltonian

$$H = T + V, \tag{2}$$

$$T = \frac{\vec{p}_0^{\,2}}{2\,m_0} + \frac{\vec{p}_1^{\,2}}{2\,m_1} + \frac{\vec{p}_2^{\,2}}{2\,m} + \frac{\vec{p}_3^{\,2}}{2\,m}, \tag{3}$$

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

The indices $0, 1$ denote nuclei, and $2, 3$ electrons. In the center-of-mass frame, the wave function Ψ depends only on the interparticle distances r_{ij} and is represented as

$$\Psi = \sum_k^N c_k \psi_k(\vec{r}_0, \vec{r}_1, \vec{r}_2, \vec{r}_3), \tag{5}$$

$$\psi_k = (1 + P_{0\leftrightarrow 1})(1 + P_{2\leftrightarrow 3})\phi_{\{k\}}(\vec{r}_0, \vec{r}_1, \vec{r}_2, \vec{r}_3), \tag{6}$$

where the $P_{i\leftrightarrow j}$ operator accounts for the symmetry with respect to the exchange of nuclei (applicable to homonuclear molecules) or electrons. Two types of explicitly correlated basis functions $\phi_{\{k\}}$ are employed to expand the wave function: the nonadiabatic James-Coolidge (naJC) [11] or the explicitly correlated Gaussian (naECG) [12,13] basis.

The spatial function within the naJC approach is

$$\phi_{\{k\}} = e^{-\alpha R - \beta(\zeta_2+\zeta_3)} R^{k_0} r_{23}^{k_1} \eta_2^{k_2} \eta_3^{k_3} \zeta_2^{k_4} \zeta_3^{k_5}, \tag{7}$$

2469-9926/2019/100(2)/020503(6)

TABLE I. Convergence of the nonrelativistic energy $E^{(2)}$ (in a.u.) with the increasing size N of the naECG basis set in comparison with the benchmark values from the naJC wave function. The following CODATA 2018 [28] mass ratios were used in these calculations: $m_\mathrm{p}/m = 1\,836.152\,673\,43(11)$, $m_\mathrm{d}/m = 3\,670.482\,967\,88(13)$, $m_\mathrm{t}/m = 5\,496.921\,535\,73(27)$.

N	D_2	T_2	HD	HT	DT
128	−1.167 167 911 358	−1.168 534 104 823	−1.165 470 991 485	−1.166 000 790 842	−1.167 817 701 507
256	−1.167 168 756 439	−1.168 535 448 080	−1.165 471 628 967	−1.166 001 763 875	−1.167 819 489 839
512	−1.167 168 805 491	−1.168 535 668 007	−1.165 471 916 621	−1.166 002 029 805	−1.167 819 626 122
1024	−1.167 168 808 953	−1.168 535 674 847	−1.165 471 923 256	−1.166 002 036 615	−1.167 819 671 730
2048	−1.167 168 809 201	−1.168 535 675 524	−1.165 471 923 906	−1.166 002 037 196	−1.167 819 673 214
naJC	−1.167 168 809 284 10(5)	−1.168 535 675 732 90(8)	−1.165 471 923 963 66(5)	−1.166 002 037 328 67(6)	−1.167 819 673 436 73(5)

where $\zeta_2 = r_{02} + r_{12},\ \eta_2 = r_{02} - r_{12},\ \zeta_3 = r_{03} + r_{13},\ \eta_3 = r_{03} - r_{13}$, and $R = r_{01}$. The α and β in Eq. (7) denote nonlinear variational parameters, common for the whole set of basis functions called "sector," and k_i are non-negative integers collectively denoted as $\{k\}$. If needed, two or more sectors (with different pairs of $\alpha^{(i)}$ and $\beta^{(i)}$) can be used. In this work, the naJC basis was employed in calculations of the nonrelativistic energy, which converged up to 13 significant figures. This basis has not been used so far for relativistic calculations, as we have not yet worked out all the integrals needed for matrix elements with relativistic operators.

The Gaussian (naECG) basis, used here in the calculations of the the relativistic and QED corrections, is represented by spatial functions of the form

$$\phi_{\{k\}} = r_{01}^n e^{-a_{k1}r_{01}^2 - a_{k2}r_{02}^2 - a_{k3}r_{03}^2 - a_{k4}r_{12}^2 - a_{k5}r_{13}^2 - a_{k6}r_{23}^2}. \tag{8}$$

In the particular case of expectation values of certain relativistic operators, $\phi_{\{k\}}$ is modified to

$$\phi_{\{k\}} = r_{01}^n \left(1 + \frac{r_{23}}{2}\right) \times e^{-a_{k1}r_{01}^2 - a_{k2}r_{02}^2 - a_{k3}r_{03}^2 - a_{k4}r_{12}^2 - a_{k5}r_{13}^2 - a_{k6}r_{23}^2}, \tag{9}$$

which ensures that the nonrelativistic wave function exactly satisfies the electron-electron cusp condition [14]. Namely, due to the electron-electron Coulomb interaction, the exact wave function $\Psi(r_{23})$ must behave for small r_{23} as $\Psi(r_{23}) \approx \Psi(0)(1 + r_{23}/2)$, which is automatically satisfied in the above basis. The internuclear r_{01}^n prefactor enables 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 log-normal distribution. The nonlinear a_{kl} parameters are determined variationally in an extensive optimization process. The naECG wave function Ψ has been optimized for a sequence of growing basis set sizes to observe the convergence of the nonrelativistic energy. This convergence is presented in Table I and compared with the results of naJC calculations used here as a benchmark, because they are by far the most accurate ones in the literature. As can be inferred from this table, the naECG nonrelativistic energy is converged to at least ten significant figures.

The relativistic correction. The relativistic correction can be expressed in terms of the expectation value

$$E^{(4)} = \langle\Psi|H_\mathrm{rel}|\Psi\rangle \tag{10}$$

of the Breit-Pauli Hamiltonian ($m = 1$)

$$\begin{aligned} H_\mathrm{rel} = &-\frac{1}{8}(p_2^4 + p_3^4) + \frac{\pi}{2}\sum_{x,a}\left(1 + \frac{\delta_s^x}{m_x^2}\right)\delta^3(r_{xa}) \\ &+ \pi\,\delta^3(r_{23}) - \frac{1}{2}p_2^i\left(\frac{\delta^{ij}}{r_{23}} + \frac{r_{23}^i r_{23}^j}{r_{23}^3}\right)p_3^j \\ &+ \frac{1}{2}\sum_{x,a}\frac{1}{m_x}p_x^i\left(\frac{\delta^{ij}}{r_{xa}} + \frac{r_{xa}^i r_{xa}^j}{r_{xa}^3}\right)p_a^j \\ &- \frac{1}{2}\frac{1}{m_0 m_1}p_0^i\left(\frac{\delta^{ij}}{r_{01}} + \frac{r_{01}^i r_{01}^j}{r_{01}^3}\right)p_1^j, \end{aligned} \tag{11}$$

where index x goes over nuclei and a over electrons. The coefficient $\delta_s^x = 0$ for the nuclear spin $s = 0$ or 1, and $\delta_s^x = 1$ for $s = 1/2$ [15]. In the above formulas, we have omitted all the electron spin-dependent terms because they vanish for the ground electronic state of ${}^1\Sigma_g^+$ symmetry. Moreover, we have omitted also the $p_x^4/(8\,m_x^3)$ and $\delta^3(r_{01})$ terms because their numerical values are smaller than the uncertainty of the whole relativistic correction.

The result for relativistic correction to the dissociation energy D_0 is shown in Table II. D_0 differs from the expectation values of H_rel by subtraction of the corresponding energy of separated atoms,

$$E_x^{(4)} = -\frac{1}{8} + \frac{1}{4}\left(\frac{1}{m_x}\right)^2 + O\left(\frac{1}{m_x}\right)^3, \tag{12}$$

and the overall sign. It is worth noting that no term proportional to $1/m_x$ is present in the above formula, so the relativistic recoil correction for separated atoms is of higher order in the mass ratio. Thanks to the regularization of the relativistic operators, which we performed in Ref. [7], and the application of the variational wave function (9), the total relativistic contribution has a very good convergence with the size of the basis set, and the extrapolated values are accurate to at least six digits (see Table II).

The leading QED correction. The formula for the leading quantum electrodynamic correction $E^{(5)}$ for H_2 was obtained in Ref. [7]. However, the nonlogarithmic $(m/m_x)^2$ terms are unknown in the case of nuclei with spin $s \neq 1/2$. Because their numerical contribution is negligibly small, such terms

TABLE II. Convergence of relativistic correction to the dissociation energy D_0 (in cm^{-1}) with the increasing size N of the naECG basis set.

N	D_2	T_2	HD	HT	DT
128	−0.528 337 669	−0.527 017 169	−0.529 979 01	−0.529 443 386	−0.527 841 985
256	−0.528 218 423	−0.526 738 994	−0.529 910 95	−0.529 374 084	−0.527 577 232
512	−0.528 201 146	−0.526 756 712	−0.529 883 50	−0.529 372 726	−0.527 532 246
1024	−0.528 205 416	−0.526 750 343	−0.529 886 61	−0.529 378 527	−0.527 524 975
2048	−0.528 205 935	−0.526 750 223	−0.529 887 30	−0.529 378 110	−0.527 523 876
∞	−0.528 206 05(9)	−0.526 750 0(2)	−0.529 887 5(2)	−0.529 377 9(2)	−0.527 523 6(3)

are absent in the formula employed here:

$$E^{(5)} = -\frac{2\mathcal{D}}{3\pi}\ln k_0 - \frac{7}{6\pi}\left\langle\frac{1}{r_{23}^3} + \sum_{a,x}\frac{m}{m_x}\frac{1}{r_{ax}^3}\right\rangle_\epsilon + \frac{4}{3}\sum_{a,x}\left\{\left(1+\frac{m}{4\,m_x}+\frac{m^2}{m_x^2}\right)\ln(\alpha^{-2}) + \frac{19}{30} + \frac{m}{m_x}\frac{31}{6} + \frac{m^2}{m_x^2}\ln\left(\frac{m_x}{m}\right)\right\}\langle\delta^3(r_{ax})\rangle$$
$$+\left(\frac{164}{15}+\frac{14}{3}\ln\alpha\right)\langle\delta^3(r_{23})\rangle - E_0^{(5)} - E_1^{(5)}, \tag{13}$$

$$E_x^{(5)} = -\frac{4}{3\pi}\frac{\mu_x}{m}\left(\ln k_0(\mathrm{H}) + \ln\frac{\mu_x}{m}\right) + \frac{4}{3\pi}\left(\frac{\mu_x}{m}\right)^3\left\{\left(1+\frac{m}{4\,m_x}+\frac{m^2}{m_x^2}\right)\ln(\alpha^{-2}) + \frac{19}{30} + \frac{m}{m_x}\left(\frac{31}{6}+\frac{7}{2}\ln 2\right) + \frac{m^2}{m_x^2}\ln\frac{m_x}{m}\right\}, \tag{14}$$

where $\mu_x = m_x\, m/\,(m_x+m)$. The Bethe logarithm is given by [16]

$$\ln k_0 = \frac{1}{\mathcal{D}}\langle\vec{J}(H-E)\ln[2(H-E)]\vec{J}\rangle, \tag{15}$$

where

$$\vec{J} = \frac{\vec{p}_0}{m_0} + \frac{\vec{p}_1}{m_1} - \frac{\vec{p}_2}{m} - \frac{\vec{p}_3}{m}, \tag{16}$$

$$\mathcal{D} = \langle\vec{J}\,(H-E)\,\vec{J}\rangle = \mathcal{D}_0 + \mathcal{D}_1, \tag{17}$$

$$\mathcal{D}_x = \frac{2\pi}{\mu_x^2}\sum_a\langle\delta^3(r_{ax})\rangle, \tag{18}$$

and the following numerical value of the atomic Bethe logarithm is used in the above:

$$\ln k_0(\mathrm{H}) = 2.984\,128\,555\,765\,498. \tag{19}$$

In the formulas (13)–(18) the expectation values are evaluated with the nonrelativistic wave function Ψ, and the notation in Eq. (13) $\langle\cdots\rangle_\epsilon$ means the following limit:

$$\left\langle\frac{1}{r_{ij}^3}\right\rangle_\epsilon = \lim_{\epsilon\to 0}\left[\left\langle\frac{\theta(r_{ij}-\epsilon)}{r_{ij}^3}\right\rangle + 4\pi(\gamma+\ln\epsilon)\langle\delta^3(r_{ij})\rangle\right], \tag{20}$$

where the symbol γ denotes the Euler-Mascheroni constant, and θ is the Heaviside function.

One subtle point to be clarified is the nuclear self-energy correction and the corresponding definition of the nuclear 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 [17], following Ref. [7], we account for this effect in the total energy of the hydrogen molecule in a minimal way, by including in Eq. (13) only logarithmic terms, and the nonlogarithmic terms are absorbed into the mean-square nuclear charge radius.

Bethe logarithm. Since the calculation of the Bethe logarithm $\ln k_0$ is the most complicated one, we describe below its evaluation in more detail, extending our previous work [7] to two nuclei with different masses. We express $\ln k_0$ in terms of the one-dimensional integral [18]:

$$\ln k_0 = \frac{1}{\mathcal{D}}\int_0^1 dt\,\frac{f(t)-f_0-f_2t^2}{t^3} \tag{21}$$

with the function $f(t)$ defined as

$$f(t) = \left\langle\vec{J}\frac{k}{k+H-E}\vec{J}\right\rangle, \qquad t = \frac{1}{\sqrt{1+2k}} \tag{22}$$

which has the following Taylor expansion:

$$f(t) = f_0 + f_2t^2 + f_3t^3 + (f_{4l}\ln t + f_4)t^4 + O(t^5) \tag{23}$$

with the coefficients ($m = 1$)

$$f_0 = \langle J^2\rangle,$$
$$f_2 = -2\mathcal{D},$$
$$f_3 = \sum_x 8\sqrt{\mu_x}\mathcal{D}_x,$$
$$f_{4l} = \sum_x 16\mu_x\mathcal{D}_x, \tag{24}$$

$$f_4 = 4\left\langle\left[\sum_{a,x}\frac{1}{\mu_x}\frac{\vec{r}_{ax}}{r_{ax}^3} + \left(\frac{1}{m_0}-\frac{1}{m_1}\right)\frac{\vec{r}_{01}}{r_{01}^3}\right]^2\right\rangle_\epsilon$$
$$-2\sum_x\mathcal{D}_x\left(1+4\mu_x\ln\frac{\mu_x}{4}-4\,\mu_x\right), \tag{25}$$

which has been obtained from the known high-k expansion by Korobov [19], with all the terms proportional to $\delta^3(r_{01})$ being neglected. The integrand in Eq. (21), as a smooth function of t, was evaluated at 200 equally spaced points in the range $t \in [0, 1]$, which enabled relative uncertainty higher than 10^{-7}. In the numerical calculation of $f(t)$, the resolvent in Eq. (22) was represented in terms of pseudostates of the form $\vec{\phi}^{\,\Pi} = \vec{r}_{ab}\,\phi$ for all interparticle coordinates. The nonlinear parameters of $\vec{\phi}^{\,\Pi}$ were found by a maximization of f.

TABLE III. Convergence of 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	D_2	T_2	HD	HT	DT
128	3.016 145 65	3.016 557 24	3.018 009 62	3.018 175 20	3.017 480 26
256	3.018 288 11	3.018 323 28	3.018 207 59	3.018 335 11	3.018 259 13
512	3.018 459 13	3.018 487 17	3.018 347 02	3.018 373 25	3.018 439 11
1024	3.018 473 32	3.018 514 61	3.018 385 84	3.018 414 64	3.018 484 83
2048	3.018 475 98	3.018 519 89	3.018 393 11	3.018 418 33	3.018 496 12
∞	3.018 478(2)	3.018 522(3)	3.018 397(4)	3.018 422(4)	3.018 501(5)

The $f(1)$ value can be determined analytically using the generalized Thomas-Reiche-Kuhn sum rule [20]

$$\langle \vec{J}(H-E)^{-1}\vec{J}\rangle = \frac{3}{2}\left(\frac{m}{\mu_0}+\frac{m}{\mu_1}\right), \tag{26}$$

which enables an assessment of the completeness of the pseudostates space and the uncertainty estimation. For the given size N of the wave function Ψ expansion, the size of the pseudostate basis set was chosen as $N' = \frac{3}{2}N$, which appeared to be sufficient for most of the t points. There were also additional factors taken into account for the accurate representation of the resolvent in Eq. (22). The powers of the internuclear coordinate r_{01}, analogously to the wave function, were restricted to even integers and were generated randomly for each basis function from the log-normal distribution within the 0–80 range. However, for small values of t ($\leqslant 0.1$), due to a cancellation in the numerator of Eq. (21), 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 in Eq. (23), and the higher order expansion terms were obtained from the fit to numerical values of $f(t)$. In order to perform the integration in Eq. (21), we used a polynomial interpolation of the integrand for $t > 0.1$, and a 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 III. Six significant figures can be considered stable and the estimated relative uncertainty is a half ppm for all molecules, as previously for H_2.

Higher order QED. The higher order QED corrections are calculated within the Born-Oppenheimer approximation. First let us consider the second iteration of the relativistic correction $\mathcal{E}^{(4)}$ to the BO potential

$$E^{(6)}_{\rm sec} = \langle \chi(R)|\mathcal{E}^{(4)}(R)\frac{1}{(E^{(2)}-H_{\rm n})'}\mathcal{E}^{(4)}(R)|\chi(R)\rangle, \tag{27}$$

where $\chi(R)$ is the radial nuclear wave function obtained from the radial Schrödinger equation with the Hamiltonian consisting of the nuclear kinetic energy and the nonrelativistic BO potential. This term is of α^6 order and is considered separately for consistency with the previous calculations of $E^{(4)}$ using the nonadiabatic perturbation theory. The main α^6 contribution is obtained by averaging the $\mathcal{E}^{(6)}(R)$ potential obtained in the BO framework in Ref. [21] and the unknown $1/\mu$ correction is estimated to be smaller than the numerical uncertainty of $\mathcal{E}^{(6)}(R)$.

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. [21]. Here, following [7], we account for several additional terms, namely,

$$E^{(7)} \approx \pi\left\langle\sum_{a,x}\delta^3(r_{ax})\right\rangle\left\{\frac{1}{\pi}[A_{60}+A_{61}\,\ln\alpha^{-2}+A_{62}\ln^2\alpha^{-2}] + \frac{B_{50}}{\pi^2}+\frac{C_{40}}{\pi^3}\right\} - E^{(7)}_0 - E^{(7)}_1, \tag{28}$$

where A, B, and C coefficients correspond to the well-known one-, two-, and three-loop hydrogenic Lamb shift [10]. Since we calculate the dissociation energy, the atomic values $E^{(7)}_{0,1}$ are subtracted out.

Finally, at the achieved accuracy level, the nuclear finite size effect cannot be neglected and it is accounted for by the following formula:

$$E^{(4)}_{\rm FS} = \alpha^4\,\frac{2\pi}{3}\left\langle\sum_{a,x}\delta^3(r_{ax})\right\rangle\frac{(r^2_{c0}+r^2_{c1})}{2\lambdabar^2} - E^{(4)}_{\rm FS0} - E^{(4)}_{\rm FS1}, \tag{29}$$

where $r^2_{c0/1}$ is the mean-square charge radius of the nucleus 0/1, $\lambdabar$ is the electron Compton wavelength, and atomic values $E^{(4)}_{\rm FS0,1}$ are subtracted out.

Final results and conclusion. Theoretical predictions for the known contributions to the dissociation energies of all molecular hydrogen isotopologues are presented in Table IV. Thanks to the direct nonadiabatic calculation of the nonrelativistic energy [22–24] and also of the relativistic [13,25,26] and leading quantum electrodynamic corrections, the theoretical dissociation energy of all the isotopologues of molecular hydrogen has reached the level of 0.8 MHz (26×10^{-6} cm^{-1} or 8×10^{-10} of relative uncertainty). The higher order $m\alpha^6$ QED contribution has been calculated [21] within the BO approximation, but the corresponding uncertainty is almost negligible. At present the accuracy of theoretical predictions is limited by the poorly known $E^{(7)}$ term of the α expansion (1), which has been estimated using the atomic hydrogen values with 25% uncertainty, as in Ref. [7]. As a result, the significantly improved theoretical predictions for the ground state dissociation energy of the D_2 molecule (as well as for H_2) are in very good agreement with the most recent measurement

TABLE IV. Theoretical predictions for the dissociation energy budget for the ground level of the molecular hydrogen isotopologues. E_{FS} is the finite nuclear size correction with $r_p = 0.8414(19)$ fm [28], $r_d = 2.12799(74)$ fm [28], and $r_t = 1.7591(363)$ fm [29]. All the energy entries are given in cm^{-1}.

Contribution	D_2	T_2	HD	HT	DT
$E^{(2)}$	36 749.090 990 00(1)	37 029.224 867 00(1)	36 406.510 890 07(1)	36 512.928 009 11(1)	36 882.009 843 48(1)
$E^{(4)}$	−0.528 206 05(9)	−0.526 750 0(2)	−0.529 887 5(2)	−0.529 377 9(2)	−0.527 523 6(3)
$E^{(5)}$	−0.198 256(3)	−0.199 735(4)	−0.196 441(4)	−0.197 005(5)	−0.198 958(5)
$E^{(6)}$	−0.002 096(6)	−0.002 110(6)	−0.002 080(6)	−0.002 085(6)	−0.002 103(6)
$E^{(6)}_{\mathrm{sec}}$	0.000 009 4	0.000 009 4	0.000 009 3	0.000 009 3	0.000 009 4
$E^{(7)}$	0.000 103(25)	0.000 103(25)	0.000 102(25)	0.000 102(25)	0.000 103(25)
$E^{(4)}_{\mathrm{FS}}$	−0.000 202	−0.000 139(6)	−0.000 116	−0.000 084(3)	−0.000 171(3)
Total	36 748.362 342(26)	37 028.496 245(27)	36 405.782 477(26)	36 512.199 569(26)	36 881.281 200(26)
Expt.	36 748.362 86(68)		36 405.783 66(36)		
Diff.	0.000 52(68)		0.001 18(36)		

[27], but the experimental uncertainty is more than 20 times larger than the theoretical one. The situation is more intriguing for the dissociation energy of the HD molecule. Our theoretical prediction differs by 3σ from the most recent measurement in Ref. [4]. If this experimental value is confirmed, this could indicate the existance of yet unknown physical effects, which are specific to heteronuclear molecules only.

Acknowledgments. We thank the referees for their pertinent suggestions which helped to improve the paper. This research was supported by National Science Center (Poland) Grants No. 2014/15/B/ST4/05022 (M.P.) and No. 2017/25/B/ST4/01024 (J.K.) as well as by a computing grant from Poznań Supercomputing and Networking Center and by PL-Grid Infrastructure.

APPENDIX: EXPECTATION VALUES OF INDIVIDUAL OPERATORS

In Table V we present nonrelativistic energies and expectation values (in a.u.) of individual operators with the nonrelativistic four-body naECG wave function for a possible comparison with any future calculations.

TABLE V. Mean values of various operators with naECG wave function for the ground molecular state.

Operator	D_2	T_2	HD	HT	DT
H	−1.167 168 809 26(4)	−1.168 535 675 59(17)	−1.165 471 923 93(6)	−1.166 002 037 24(12)	−1.167 819 673 31(16)
$\vec{J}^2$	2.527 565 218 16(15)	2.531 714 163 5(6)	2.522 506 446 2(3)	2.524 076 110 3(5)	2.529 532 438 3(8)
$\sum_a 4\pi\,\delta(r_{0a})$	5.703 646 95(5)	5.716 698 5(2)	5.685 102 31(6)	5.689 493 73(8)	5.709 140 6(3)
$\sum_a 4\pi\,\delta(r_{1a})$	5.703 646 95(5)	5.716 698 5(2)	5.689 495 06(7)	5.695 351 91(11)	5.710 607 5(4)
$4\pi\,\delta(r_{23})$	0.205 013 236(5)	0.205 964 94(3)	0.203 833 913(15)	0.204 202 05(2)	0.205 466 14(3)
$\sum_a p_a^4$	−13.076 757 2(3)	−13.106 197 7(9)	13.039 562 0(3)	−13.051 261 4(5)	−13.090 834 4(7)
$p_2^i\Big(\frac{\delta^{ij}}{r_{23}}+\frac{r_{23}^i r_{23}^j}{r_{23}^3}\Big)p_3^j$	0.093 386 335(4)	0.093 728 50(2)	0.092 959 18(4)	0.093 093 113(14)	0.093 549 582(9)
$\sum_a p_0^i\left(\frac{\delta^{ij}}{r_{0a}}+\frac{r_{0a}^i r_{0a}^j}{r_{0a}^3}\right)p_a^j$	−2.507 167 22(8)	−2.512 657 3(3)	−2.495 702 4(3)	−2.496 033 9(4)	−2.507 855 6(5)
$\sum_a p_1^i\left(\frac{\delta^{ij}}{r_{1a}}+\frac{r_{1a}^i r_{1a}^j}{r_{1a}^3}\right)p_a^j$	−2.507 167 22(8)	−2.512 657 3(3)	−2.504 864 8(3)	−2.508 852 1(4)	−2.511 717 0(5)
$p_0^i\left(\frac{\delta^{ij}}{r_{01}}+\frac{r_{01}^i r_{01}^j}{r_{01}^3}\right)p_1^j$	−17.802 138 7(4)	−21.964 332 6(11)	−14.388 033 5(7)	−15.304 814 1(15)	−19.550 968 3(15)
$\sum_a\langle r_{0a}^{-3}\rangle_\epsilon$	−3.614 687 9(8)	−3.622 724(3)	−3.602 242 6(8)	−3.604 722 9(11)	−3.617 784(2)
$\sum_a\langle r_{1a}^{-3}\rangle_\epsilon$	−3.614 687 9(8)	−3.622 724(3)	−3.606 688 1(7)	−3.610 649 1(8)	−3.619 274(3)
$\langle r_{23}^{-3}\rangle_\epsilon$	0.405 522 77(4)	0.407 090 24(16)	0.403 586 4(5)	0.404 190 4(11)	0.406 268 9(9)
$\sum_a\langle r_{0a}^{-4}\rangle_\epsilon$	−2.865 27(2)	−2.869 32(5)	−2.871 97(3)	−2.877 83(4)	−2.895 29(4)
$\sum_a\langle r_{1a}^{-4}\rangle_\epsilon$	−2.865 27(2)	−2.869 32(5)	−2.875 51(3)	−2.882 62(4)	−2.896 50(4)
$\sum_{a<b}\frac{\vec{r}_{0a}}{r_{0a}^3}\cdot\frac{\vec{r}_{0b}}{r_{0b}^3}$	−0.011 661 1(7)	−0.011 686(3)	−0.011 580 5(16)	−0.011 571 3(5)	−0.011 653 9(4)
$\sum_{a<b}\frac{\vec{r}_{0a}}{r_{0a}^3}\cdot\frac{\vec{r}_{1b}}{r_{1b}^3}$	−0.234 951 712(6)	−0.236 540 76(3)	−0.232 986 687(5)	−0.233 599 584(7)	−0.235 707 73(3)
$\sum_{a<b}\frac{\vec{r}_{1a}}{r_{1a}^3}\cdot\frac{\vec{r}_{1b}}{r_{1b}^3}$	−0.011 661 1(6)	−0.011 686(3)	−0.011 677 8(2)	−0.011 704 7(5)	−0.011 687 7(4)
$\sum_a\frac{\vec{r}_{01}}{r_{01}^3}\cdot\frac{\vec{r}_{0a}}{r_{0a}^3}$	−1.173 53(6)	−1.177 4(2)	−1.167 84(9)	−1.168 92(12)	−1.174 56(10)
$\sum_a\frac{\vec{r}_{01}}{r_{01}^3}\cdot\frac{\vec{r}_{1a}}{r_{1a}^3}$	1.173 53(6)	1.177 4(2)	1.169 50(8)	1.171 16(11)	1.175 13(11)

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