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Accurate adiabatic correction in the hydrogen molecule

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Abstract

A new formalism for the accurate treatment of adiabatic effects in the hydrogen molecule is presented, in which the electronic wave function is expanded in the James-Coolidge basis functions. Systematic increase in the size of the basis set permits estimation of the accuracy. Numerical results for the adiabatic correction to the Born-Oppenheimer interaction energy reveal a relative precision of 10^{-12} at an arbitrary internuclear distance. Such calculations have been performed for 88 internuclear distances in the range of $0 < R \leq 12$ bohrs to construct the adiabatic correction potential and to solve the nuclear Schrödinger equation. Finally, the adiabatic correction to the dissociation energies of all rovibrational levels in H_2, HD, HT, D_2, DT, and T_2 has been determined. For the ground state of H_2 the estimated precision is $3 \cdot 10^{-7}$ cm^{-1}, which is almost three orders of magnitude higher than that of the best previous result. The achieved accuracy removes the adiabatic contribution from the overall error budget of the present day theoretical predictions for the rovibrational levels.

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I. INTRODUCTION

Several laboratories have recently measured dissociation energy and certain rovibrational energy intervals of two-electron molecules with precision of one part per 10^{-8} or even better [1–11]. In parallel with these experimental achievements, a theoretical methodology for the determination of rovibrational energy levels of H_2 has recently been pursued [12–15]. The compliance between theory and experiment was obtained by taking rigorously into account various contributions originating from finite nuclear mass, relativistic, and quantum electrodynamic (QED) effects. The agreement made it possible to verify for the first time QED corrections to the rovibrational spectrum of molecular hydrogen [15, 16], and to establish bounds [17] on the hypothetical *fifth force* acting between nuclei.

Theoretically determined energy of a rovibrational level is usually composed of several contributions: the Born-Oppenheimer (BO), adiabatic, nonadiabatic, relativistic, radiative, and others. These contributions can conveniently be interpreted in frames of the nonadiabatic perturbation theory (NAPT) [12, 13] as subsequent terms of the energy expansion into powers of small parameters: α – the fine structure constant and m_e/M – the electron-nucleus mass ratio

$$E = \sum_{i=0} \sum_{j=0} (m_\mathrm{e}/M)^i \, \alpha^j \, E^{(i,j)}, \tag{1}$$

where the coefficients $E^{(i,j)}$ themselves may also depend on the mass ratio. In the particular case of the dissociation energy (D_0) of the ground rovibrational level of H_2, the most significant is the BO term ($i = 0$, $j = 0$), which amounts to $36\,112.5927(1)\,\mathrm{cm}^{-1}$ and constitutes 99.98 % of the total dissociation energy. The next largest contribution ($i = 1$, $j = 0$) owing to the modification of BO potential by the kinetic energy of the nuclei is the adiabatic correction ($\sim 5.7711(1)\,\mathrm{cm}^{-1}$). The remaining corrections altogether bring a contribution to D_0 less than $1\,\mathrm{cm}^{-1}$. In the heavier isotopic species the finite mass effects are smaller than in H_2 but still bring a dominant correction to BO energy. Each contribution adds its own uncertainty to the overall error budget. For H_2, the uncertainties of the best currently available results, shared by all the mentioned contributions, are of the order of 10^{-4} cm^{-1} [14]. Our strategy for a further increase in the precision of theoretical predictions relies on diminishing the estimated errors of subsequent components of Eq. (1). The first step towards this goal has already been made, the BO energy curve has been evaluated with a relative accuracy of 10^{-15} [18], which has practically removed this contribution from the energy error list. Here, we report on the next step in the same direction, that is we propose a new methodology, which enables prediction of the adiabatic correction to the energy levels of H_2 with accuracy of the order of 10^{-7} cm^{-1}, that is three orders of magnitude higher than those available to date. Results concerning subsequent contributions to the total energy are being worked out and will be published later on.

II. METHOD

In the Schrödinger equation $H\Psi = E\Psi$, the Hamiltonian for the hydrogen molecule, after separation of the center of mass movement, can be split into the electronic and nuclear parts $H = H_{\rm el} + H_{\rm n}$. The electronic part $H_{\rm el}$ includes kinetic energy of electrons and Coulomb interactions between all particles constituting the molecule

$$H_{\rm el} = -\frac{1}{2}\sum_a \nabla_a^2 + V\,, \tag{2}$$

whereas the nuclear one, assuming that the origin is fixed at the geometric center of the nuclei, can be written as

$$H_{\rm n} = -\frac{1}{2\,\mu_{\rm n}}\left(\nabla_R^2 + \nabla_{\rm el}^2\right) \tag{3}$$

where $\vec{\nabla}_{\rm el} = (\vec{\nabla}_1 + \vec{\nabla}_2)/2$, R is the internuclear distance, and $\mu_{\rm n}$ is the nuclear reduced mass.

In the adiabatic approximation the total wave function $\Psi(\vec{r}_1, \vec{r}_2, \vec{R})$ is represented as a product of an electronic wave function $\phi(\vec{r}_1, \vec{r}_2)_R$ being a solution to the electronic eigenproblem

$$[H_{\rm el} - \mathcal{E}_{\rm el}(R)]\,\phi = 0 \tag{4}$$

and the nuclear wave function $\chi(\vec{R})$ which fulfills the nuclear equation

$$\left[-\frac{1}{2\,\mu_{\rm n}}\nabla_R^2 + \mathcal{E}_{\rm el}(R) + \frac{1}{2\,\mu_{\rm n}}\,\mathcal{E}_{\rm a}(R) - E_{\rm a}\right]\chi(\vec{R}) = 0\,. \tag{5}$$

$E_{\rm a}$ is the adiabatic approximation to the total energy, E, and

$$\frac{1}{2\,\mu_{\rm n}}\,\mathcal{E}_{\rm a}(R) = \frac{1}{2\,\mu_{\rm n}}\left(\langle\vec{\nabla}_{\rm el}\phi|\vec{\nabla}_{\rm el}\phi\rangle + \langle\vec{\nabla}_R\phi|\vec{\nabla}_R\phi\rangle\right) \tag{6}$$

is the adiabatic (diagonal) correction to the Born-Oppenheimer potential $\mathcal{E}_{\rm el}(R)$.

III. MATRIX ELEMENTS AND R-DERIVATIVES

The electronic wave function for a two-electron diatomic system is the most efficiently represented in the Kołos-Wolniewicz [19] or the James-Coolidge (JC) [20] basis. In a recent study on the ground state BO potential energy of H_2, the latter basis set has been found very convenient [21], since all the integrals can be obtained analytically. The same basis is used for the evaluation of the adiabatic correction.

The symmetric James-Coolidge basis function is of the form

$$\begin{aligned}\psi = {} & (1+P_{12})\,(1+\hat{\imath}) \\ & (r_{1A}-r_{1B})^{n_2}(r_{2A}-r_{2B})^{n_3}(r_{1A}+r_{1B})^{n_4}(r_{2A}+r_{2B})^{n_5} \\ & e^{-\beta\,(r_{1A}+r_{1B}+r_{2A}+r_{2B})}\, r_{12}^{n_1}\, R^{-n_1-n_2-n_3-n_4-n_5-3}.\end{aligned} \tag{7}$$

The power of the internuclear distance R is introduced to ensure that the overlap integrals are dimensionless. The additional R-dependence of ψ is implicit through electron-nucleus distances $r_{1A}, r_{1B}, r_{2A}, r_{2B}$. The nonlinear parameter β is set for each R separately. Its numerical value has been optimized with respect to the electronic energy $\mathcal{E}_{\rm el}(R)$. Required spin and inversion symmetry (singlet *gerade* for the ground electronic state) of the wave function is ensured by the two projectors containing the electron exchange P_{12} and the electron-coordinate inversion $\hat{\imath}$ operators.

Let ψ_k be the k-th element of the basis set employed to expand the ground state electronic wave function

$$\phi = \sum_k v_k\,\psi_k \tag{8}$$

and let $\vec{v}$ be a vector consisting of real coefficients of this expansion. The subscript k can be treated as a multiindex composed of integer exponents $\{n_1, n_2, n_3, n_4, n_5\}$. We introduce here a shell parameter Ω, employed to arrange the basis functions, related to the exponents n_i by

$$\sum_i n_i \le \Omega\,. \tag{9}$$

Ω is an integer number taken from the range (2,17) and it is pivotal in the basis set convergence study discussed below. In this work we split the expansion (8) into two sectors, one limited by Ω and the other by $\Omega-2$, each with his own nonlinear parameter β and $\{n_i\}$.

Next, let us define the following matrices

$$\begin{aligned}
\mathcal{H}_{kl} &= \big\langle\psi_k\big|H_{\rm el}\psi_l\big\rangle\,, &(10)\\
\mathcal{N}_{kl} &= \big\langle\psi_k\big|\psi_l\big\rangle\,, &(11)\\
\mathcal{A}_{kl} &= \big\langle\psi_k\big|\partial_R\psi_l\big\rangle\,, &(12)\\
\mathcal{B}_{kl} &= \big\langle\vec\nabla_R\psi_k\big|\vec\nabla_R\psi_l\big\rangle+\big\langle\vec\nabla_{\rm el}\psi_k\big|\vec\nabla_{\rm el}\psi_l\big\rangle\,. &(13)
\end{aligned}$$

All these matrix elements are expressible by combinations of the f-functions introduced in [22]

$$\begin{aligned}
&f(n_1,n_2,n_3,n_4,n_5;R,\beta) = R^{-n_1-n_2-n_3-n_4-n_5-1} \qquad (14)\\
&\int\frac{d^3r_1}{4\,\pi}\int\frac{d^3r_2}{4\,\pi}\,\frac{e^{-\beta\,r_{1A}}}{r_{1A}}\,\frac{e^{-\beta\,r_{1B}}}{r_{1B}}\,\frac{e^{-\beta\,r_{2A}}}{r_{2A}}\,\frac{e^{-\beta\,r_{2B}}}{r_{2B}}\,\frac{1}{r_{12}^{1-n_1}}\\
&(r_{1A}-r_{1B})^{n_2}(r_{2A}-r_{2B})^{n_3}(r_{1A}+r_{1B})^{n_4}(r_{2A}+r_{2B})^{n_5}.
\end{aligned}$$

With this notation the electronic Schrödinger equation can be written in the matrix form as

$$(\mathcal{H}-\mathcal{E}_{\rm el}\,\mathcal{N})\,\vec v = 0\,. \tag{15}$$

Let us further consider the first order R-derivative of ϕ

$$\partial_R\phi = \sum_k\left(\partial_R v_k\,\psi_k + v_k\,\partial_R\psi_k\right)\,. \tag{16}$$

The term $\partial_R\psi_k$ is assumed to be known, as it is the derivative of a basis function at constant values of nonlinear parameters. The term $\partial_R v_k$ can be obtained by taking the derivative of Eq. (15), namely

$$(\mathcal{H}-\mathcal{E}_{\rm el}\,\mathcal{N})\,\partial_R\vec v + (\partial_R\mathcal{H}-\partial_R\mathcal{E}_{\rm el}\,\mathcal{N}-\mathcal{E}_{\rm el}\,\partial_R\mathcal{N})\,\vec v = 0 \tag{17}$$

so that

$$\partial_R\vec v = \frac{1}{(\mathcal{E}_{\rm el}\,\mathcal{N}-\mathcal{H})'}\,(\partial_R\mathcal{H}-\mathcal{E}_{\rm el}\,\partial_R\mathcal{N})\,\vec v - \frac{1}{2}\,\vec v\,\left(\vec v^T\,\partial_R\mathcal{N}\,\vec v\right) \tag{18}$$

where the last term was obtained by differentiation of the normalization condition

$$\vec v^T\,\mathcal{N}\,\vec v = 1 \tag{19}$$

leading to

$$2\,(\partial_R\vec v)^T\,\mathcal{N}\,\vec v + \vec v^T\,\partial_R\mathcal{N}\,\vec v = 0\,. \tag{20}$$

Now, the mass-independent adiabatic correction of Eq. (6) can be transformed to our working formula

$$\mathcal{E}_{\rm a}(R) = \vec v^T\,\mathcal{B}\,\vec v + (\partial_R\vec v)^T\,\mathcal{N}\,\partial_R\vec v + 2\,(\partial_R\vec v)^T\,\mathcal{A}\,\vec v\,. \tag{21}$$

IV. RESULTS AND DISCUSSION

As we aim at high numerical accuracy of $\mathcal{E}_\mathrm{a}$, we implemented the formula (21) in FORTRAN 90 using the hexuple (∼64 digits) precision with a support from the quad-double arithmetic QD library [23].

TABLE I: A sample of the convergence of the mass-independent adiabatic correction $\mathcal{E}_\mathrm{a}(R)$ (in a.u.) with the growing size of JC basis at selected internuclear distances R. Ω is the shell parameter of Eq. (9) and N is the number of basis functions.

Ω	N	$\mathcal{E}_\mathrm{a}(0.8)$	$\mathcal{E}_\mathrm{a}(1.4)$	$\mathcal{E}_\mathrm{a}(6.0)$
13	3444	1.199 493 971 179 86	0.958 684 725 421 67	0.998 341 126 273 17
14	4712	1.199 493 971 177 61	0.958 684 725 428 33	0.998 341 126 278 71
15	6324	1.199 493 971 176 92	0.958 684 725 429 49	0.998 341 126 279 85
16	8361	1.199 493 971 175 62	0.958 684 725 429 72	0.998 341 126 280 17
17	10887	1.199 493 971 175 28	0.958 684 725 429 79	0.998 341 126 280 26

A. Numerical convergence of $\mathcal{E}_\mathrm{a}(R)$

In order to asses an accuracy of our calculations we have checked the numerical convergence of the adiabatic correction with the growing length of the wave function expansion at several short-, medium-, and long internuclear distances. Table I shows sample data at selected internuclear distances. A general conclusion from the data analysis is that at least twelve significant digits remain stable while approaching the highest value of $\Omega = 17$. Hence, we conclude that for the whole range of the internuclear distances at least twelve significant digits are exact and an uncertainty would appear only on the thirteenth or further digit. The accuracy could be increased by another order of magnitude using an extrapolation to the infinite basis size. However, since the present accuracy of twelve significant digits is by far sufficient, we omitted this step. In comparison with the most accurate previous calculations, performed using ECG functions [14], the accuracy of the present results has been increased by at least five orders of magnitude. Presently, the estimated contribution of the uncertainty in evaluation of a single $\mathcal{E}_\mathrm{a}(R)$ value to the error of the dissociation energy is

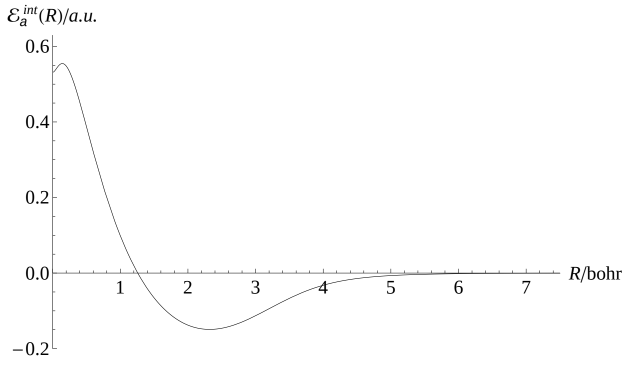

FIG. 1: Mass-independent adiabatic correction to the BO interaction energy.

less than $10^{-9}\,\mathrm{cm}^{-1}$, and is much smaller than the errors from the other sources described below. Table II shows how the accuracy of the adiabatic correction, evaluated near the equilibrium internuclear distance, has been changing over the years. The final values of the mass-independent $\mathcal{E}_\mathrm{a}(R)$ are presented in Table III where all the listed digits are supposed to be exact.

TABLE II: Comparison of the accuracy of the present results at $R = 1.4$ bohr with literature data.

Reference	$\mathcal{E}_\mathrm{a}(1.4)$/a.u.
Van Vleck, 1936 [24]	0.954
Kołos and Wolniewicz, 1964 [25]	0.958 926
Kołos and Rychlewski, 1993 [26]	0.958 691
Wolniewicz, 1993 [27]	0.958 683
Cencek and Kutzelnigg, 1997 [28]	0.958 684 72
Pachucki and Komasa, 2009 [13]	0.958 684 14
This work, 2014	0.958 684 725 430

B. Adiabatic correction to the interaction energy

The adiabatic correction to the interaction BO potential is defined with respect to the separated atoms limit

$$\mathcal{E}_\mathrm{a}^\mathrm{int}(R) = \mathcal{E}_\mathrm{a}(R) - \mathcal{E}_\mathrm{a}(\infty), \tag{22}$$

TABLE III: $\mathcal{E}_{\mathrm{a}}(R)$ – values of the mass-independent adiabatic correction to the BO interaction potential. All figures are supposed to be exact.

R	$\mathcal{E}_{\mathrm{a}}(R)$	R	$\mathcal{E}_{\mathrm{a}}(R)$
0.1	1.550 958 100 21	2.0	0.862 170 945 858
0.2	1.548 102 462 02	2.1	0.856 115 986 498
0.3	1.510 616 374 14	2.2	0.852 432 649 972
0.35	1.483 439 368 64	2.3	0.850 957 550 559
0.4	1.453 009 380 55	2.35	0.850 996 542 639
0.45	1.420 676 967 07	2.4	0.851 524 934 042
0.5	1.387 464 880 06	2.5	0.853 961 054 324
0.55	1.354 124 732 60	2.6	0.858 079 416 594
0.6	1.321 195 464 19	2.7	0.863 677 387 075
0.65	1.289 054 076 78	2.8	0.870 534 706 921
0.7	1.257 956 514 79	2.9	0.878 414 396 024
0.75	1.228 069 372 96	3.0	0.887 066 358 688
0.8	1.199 493 971 18	3.1	0.896 233 697 879
0.85	1.172 284 405 12	3.2	0.905 661 337 333
0.9	1.146 460 975 38	3.3	0.915 106 115 057
0.95	1.122 020 127 13	3.4	0.924 347 155 575
1.0	1.098 941 778 57	3.5	0.933 195 163 296
1.05	1.077 194 705 46	3.6	0.941 499 379 332
1.1	1.056 740 482 07	3.7	0.949 151 309 990
1.15	1.037 536 351 40	3.8	0.956 084 885 196
1.2	1.019 537 301 62	3.9	0.962 273 299 755
1.25	1.002 697 553 89	4.0	0.967 723 281 613
1.3	0.986 971 613 714	4.2	0.976 558 381 612
1.32	0.980 983 093 331	4.4	0.983 033 195 995
1.34	0.975 162 863 317	4.6	0.987 680 270 678
1.36	0.969 508 181 666	4.8	0.990 988 213 951
1.38	0.964 016 351 899	5.0	0.993 346 349 776
1.39	0.961 330 676 863	5.2	0.995 040 257 943
1.4	0.958 684 725 430	5.4	0.996 269 883 897
1.4011	0.958 396 081 986	5.6	0.997 172 293 732
1.405	0.957 376 544 913	5.8	0.997 841 172 093
1.41	0.956 078 174 316	6.0	0.998 341 126 280
1.42	0.953 510 703 442	6.5	0.999 117 827 776
1.44	0.948 491 738 318	7.0	0.999 511 361 323
1.449	0.946 283 124 517	7.5	0.999 716 677 766
1.46	0.943 625 334 674	8.0	0.999 827 480 672
1.48	0.938 909 050 051	8.5	0.999 889 772 815
1.5	0.934 340 495 289	9.0	0.999 926 440 000
1.55	0.923 550 229 153	9.5	0.999 949 061 160
1.6	0.913 633 773 608	10.0	0.999 963 643 443
1.65	0.904 558 107 268	10.5	0.999 973 410 827
1.7	0.896 292 149 182	11.0	0.999 980 165 450
1.8	0.882 074 017 855	11.5	0.999 984 959 857
1.9	0.870 764 620 658	12.0	0.999 988 435 895

where $\mathcal{E}_{\rm a}(\infty) = +1$. For the hydrogen molecule the united atom limit is also well known from accurate helium atom calculation $\mathcal{E}_{\rm a}(0) = 1.531\,396\,926\,06$ [29]. Consequently, the analytic form of the $\mathcal{E}_{\rm a}^{\rm int}(R)$ function was obtained by fitting the following multiparameter formula

$$\mathcal{E}_{\rm a}^{\rm int}(R) = e^{-a\,R} \sum_{i=0}^{14} P_i\, R^i + e^{-b\,R - c\,R^2} \left(\mathcal{E}_{\rm a}^{\rm int}(0) - P_0 + \sum_{i=1}^{32} Q_i\, R^i \right) \tag{23}$$

to the 88 discrete values of Table III, shifted beforehand by $\mathcal{E}_{\rm a}(\infty)$. The fit parameters are listed in the supplemental material [30], where a FORTRAN procedure evaluating this formula is also supplied. The largest residuum value of this fit was $2.1 \cdot 10^{-9}\,{\rm cm}^{-1}$ and the square root of the single-deletion variances was less than $8 \cdot 10^{-12}\,{\rm cm}^{-1}$. As an additional check of the fit accuracy, 18 values for points located in between the nodes were compared with direct numerical evaluation, and the differences were found smaller than $10^{-9}\,{\rm cm}^{-1}$. The long distance part of the $\mathcal{E}_{\rm a}^{\rm int}(R)$ was modeled using the asymptotic function

$$\frac{1}{2\,\mu_{\rm n}}\, \mathcal{E}_{\rm a}^{\rm as}(R) = -\left(\frac{A_6}{R^6} + \frac{A_8}{R^8} + \frac{A_{10}}{R^{10}} \right) \tag{24}$$

with the A_i parameters determined for H_2 by Przybytek and Jeziorski [31]: $A_6 = 0.017\,699(2)$, $A_8 = 0.144(2)$, and $A_{10} = 2.28(2)$ a.u. The asymptotic and the fit functions were joined together at $R = 11.5$ bohr and employed to generate the adiabatic interaction potential of Eq. (5) on pertinent integration grid. A graphical representation of the $\mathcal{E}_{\rm a}^{\rm int}(R)$ function is given in Fig. 1.

C. Adiabatic correction to the rovibrational levels

The newest and also the most accurate value of the proton-electron mass ratio $m_{\rm p}/m_{\rm e} = 1\,836.152\,673\,77(17)$ [32] was used in the numerical computations. The remaining fundamental physical constants (CODATA 2010) were obtained from [33] (see also the NIST web page [34]): the deuteron-electron mass ratio $m_{\rm d}/m_{\rm e} = 3\,670.482\,9652(15)$ and the triton-electron mass ratio $m_{\rm t}/m_{\rm e} = 5\,496.921\,5267(50)$. The conversion factor from atomic units to inverse centimeters was $2\,{\rm Ry} = 219\,474.631\,37078(110)\,{\rm cm}^{-1}$.

The radial Schrödinger equation (5) with the adiabatic potential was solved numerically using two independent methods. The first one relies on the integration method described in

[35]. We checked the influence of the integration grid parameters, step h and range $(0-R_{\max})$, on the values of D_0 (in cm^{-1}) for all 301 bound adiabatic states of H_2. The final calculations were performed with $h \approx 0.000\,537$ bohr and $R_{\max} = 40$ bohr, which ensured nine stable decimal digits of D_0 for the lower half of the rovibrational levels ladder ($D_0 > 20\,000\,\mathrm{cm}^{-1}$). In the worst case observed, the eighth decimal digit of D_0 changed for some levels located near the dissociation threshold. The second method of solving Eq. (5) is based on a discrete variable representation (DVR). We performed the integration on a grid of 9600 nodes evenly distributed with a step of 0.0025 bohr. The DVR calculations confirmed those of the direct integration approach for all H_2 levels with the largest deviation of $\pm 4\cdot 10^{-8}\,\mathrm{cm}^{-1}$. In general, we claim that the uncertainties of the energy levels and their adiabatic corrections resulting from the numerical integration are distinctly smaller than $10^{-7}\,\mathrm{cm}^{-1}$.

Another source of the error in D_0 are the uncertainties of the physical constants: the nuclear masses and the Rydberg constant. While changing the proton mass by its one standard deviation we observed changes in dissociation energy ranging from $1\cdot 10^{-7}\,\mathrm{cm}^{-1}$ for the lowest rotational quantum numbers to $2\cdot 10^{-6}\,\mathrm{cm}^{-1}$ for the highest J levels. The uncertainty of the Rydberg constant affects only the conversion of D_0 from a.u. to cm^{-1}. It influences D_0 proportionally to its value and for the ground level the variation in D_0 amounts to $2\cdot 10^{-7}\,\mathrm{cm}^{-1}$.

In summary, the dominant factor limiting the accuracy of the current theoretical predictions for adiabatic energies is the uncertainty of the nucleus-electron mass ratio and it changes from one level to another in the range $1\cdot 10^{-7} - 2\cdot 10^{-6}\,\mathrm{cm}^{-1}$. The final uncertainties assigned to the adiabatic corrections were estimated by quadratically adding error bars of various sources and amount to $3\cdot 10^{-7}\,\mathrm{cm}^{-1}$ for the lowest levels and grow to $20\cdot 10^{-7}\,\mathrm{cm}^{-1}$ for the highest states. All the considered uncertainty sources are collected in Table IV.

Our recommended eigenvalue E_a of the ground $(v, J){=}(0,0)$ rovibrational energy level of H_2 amounts to $-0.164\,567\,373\,835$ hartree, which corresponds to the adiabatic dissociation energy of

$$D_0 = 36\,118.363\,713\,2(3)\,\mathrm{cm}^{-1}.$$

As the corresponding BO dissociation energy equals to $36\,112.592\,731\,58\,\mathrm{cm}^{-1}$, the adiabatic correction to this energy is

$$\Delta D_0 = 5.770\,981\,7(3)\,\mathrm{cm}^{-1}.$$

TABLE IV: Various sources of the error in the computed adiabatic dissociation energy of H_2 in units of $10^{-7}\,\mathrm{cm}^{-1}$. The total uncertainty was estimated by quadratically adding all these contributions.

Single point evaluation of $\mathcal{E}_\mathrm{a}(R)$	< 0.01
Fitting of $\mathcal{E}_\mathrm{a}(R)$	< 0.1
Numerical integration	< 1
Uncertainty of the Rydberg constant	< 2
Uncertainty of the proton-electron mass ratio	1–20
Total state-dependent uncertainty	3–20

This value differs from the previous estimation of $5.77111(10)\,\mathrm{cm}^{-1}$ [14] by $13 \cdot 10^{-5}\,\mathrm{cm}^{-1}$.

For the non-symmetric isotopologues of H_2, the nuclear Hamiltonian (3) contains an additional term of mixed derivatives $(1/M_A - 1/M_B)\vec{\nabla}_R \cdot \vec{\nabla}_\mathrm{el}$. Because the origin of the coordinate system was chosen at the geometric center of the nuclei, the electronic wave function has a definite symmetry with respect to the inversion of electronic variables (*gerade* for the electronic ground state) irrespective of whether we consider homo- or hetero-isotopic molecule. Hence, because $\vec{\nabla}_R \cdot \vec{\nabla}_\mathrm{el}$ is odd with respect to inversion in the electronic coordinates, its expectation value with the adiabatic wave function vanishes. As a result, the $\mathcal{E}_\mathrm{a}(R)$ function is valid for all the isotopic variants of the hydrogen molecule. To obtain the adiabatic correction potential for a given combination of hydrogen isotopes, it is sufficient to multiply the mass-independent $\mathcal{E}_\mathrm{a}(R)$ function by $\frac{1}{2\,\mu_\mathrm{n}}$ with the pertinent nuclear reduced mass μ_n.

The adiabatic corrections to the dissociation energy the ground level of these species are shown in Table V. One can notice, that the uncertainty in ΔD_0 increases with the reduced mass of the nuclei in accordance with growing uncertainty in the mass of the heavier isotopes. A full set of the bound adiabatic energy levels and their adiabatic corrections was evaluated for H_2 (301 states), HD (400 states), HT (449 states), D_2 (601 states), DT (720 states), and T_2 (897 states). Extensive tables with the results for all the levels are supplied as a supplemental material [30].

TABLE V: Adiabatic corrections to the dissociation energy of the ground level of all the six isotopic species of hydrogen molecule.

Molecule	$\Delta D_0[\mathrm{cm}^{-1}]$
H_2	5.770 981 7(3)
HD	4.250 777 7(3)
HT	3.754 041 2(4)
D_2	2.772 394 4(4)
DT	2.291 553 1(6)
T_2	1.816 999 8(7)

V. CONCLUSION

The novelty of the results presented above is twofold. Firstly, a new method of dealing with derivatives of the electronic wave function over nuclear variable was presented. Secondly, this methodology was combined with the James-Coolidge basis functions ensuring very high accuracy of the calculations. As a result, an increase in the accuracy of determination of the adiabatic correction for the hydrogen molecule reached three orders of magnitude in comparison with the best previous results. Compared to the other components of the total energy error (i.e. nonadiabatic, relativistic, radiative, etc.), the achieved level of accuracy is by far sufficient to eliminate the contribution of the adiabatic correction from the error budget of the total energy.

In the next step of our project, the nonadiabatic corrections will be evaluated using the JC basis functions, the ultimate goal being an increase in the accuracy of the total energy levels in molecular hydrogen matching the recently reported progress in spectroscopy.

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