Nonadiabatic Relativistic Correction to the Dissociation Energy of H_2, D_2, and HD

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The relativistic correction to the dissociation energy of H_2, D_2, and HD molecules has been accurately calculated without expansion in the small electron-nucleus mass ratio. The obtained results indicate the significance of nonadiabatic effects and resolve the discrepancy of theoretical predictions with recent experimental values for H_2 and D_2. While the theoretical accuracy is now significantly improved and is higher than the experimental one, we observe about 3σ discrepancy for the dissociation energy of HD, which requires further investigation.

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Introduction.—There is only one very narrow optical transition in the hydrogen atom, $1S-2S$, and all the other transitions have a much broader natural width. This fact limits the precision of the standard model tests as well as the accuracy of the Rydberg constant and of the proton charge radius obtained from hydrogen atom spectroscopy [1]. Moreover, a different value of the proton charge radius obtained from the measurement of the $2S-2P$ transition in muonic hydrogen [2–4] indicates severe problems with the interpretation of high precision spectroscopic results with the ordinary hydrogen atom [5]. Currently, several projects are being pursued to measure the Rydberg constant by other means, for example, from the $1S-2S$ transition in a hydrogenlike helium ion [6,7].

In contrast to the hydrogenlike atoms, there are many transitions between rotational and vibrational levels in hydrogen molecules which can, in principle, be measured very accurately [8–11] because their natural linewidth is much smaller than that of the hydrogenic excited states. This opens up the possibility for improved tests of quantum electrodynamic theory and for the accurate determination of the electron-proton (deuteron) mass ratio, of the Rydberg constant, and of the nuclear charge radius.

On the theoretical side, the rovibrational levels in the hydrogen molecule can, in general, be determined as accurately as those for atomic hydrogen. For this purpose, one employs the nonrelativistic quantum electrodynamic (NRQED) approach based on an expansion in powers of the fine structure constant [12], which was originally developed for hydrogenic systems and applied recently in highly accurate calculations for H_2^+ [13]. However, calculations for molecular hydrogen are much more complex and computationally demanding than those for one-electron systems, due to the importance of electron correlations. Nowadays nevertheless, the variational calculations can reach a precision that does not limit theoretical predictions for the dissociation energy. In fact, the nonrelativistic energy has already been calculated with nonadiabatic James-Coolidge (naJC) functions with numerical precision of about 10^{-13} [14,15].

So far, all the determined corrections, i.e., relativistic $\alpha^4 m$, QED $\alpha^5 m$, and higher order QED $\alpha^6 m$, have been calculated numerically with explicitly correlated Gaussian (ECG) wave functions using the Born-Oppenheimer (BO) approximation, thus omitting the nuclear recoil (nonadiabatic) effect. Moreover, previous attempts to carry out nonadiabatic calculations of the relativistic correction [16] were unreliable.

In our former works, we have estimated the nonadiabatic correction to be of the order of the electron-to-nucleus mass ratio with the coefficient equal to one and observed systematic discrepancies with all the recently reported experimental results for the hydrogen molecule [8]. Because of these discrepancies, we concluded that most probably relativistic nonadiabatic effects are much larger than our previous estimate. Indeed, Wang and Yan have recently calculated a relativistic correction without the BO approximation [17]. They confirmed the reported discrepancy for the dissociation energy of H_2 as coming from relativistic nonadiabatic effects.

In this work, we develop a method based on ECG functions together with certain transformations of relativistic operators suitable for the calculation of nonadiabatic energies to obtain accurate relativistic corrections not only for H_2 but also for D_2 and HD. Our results indicate the importance of the nonadiabatic treatment of the relativistic correction in the interpretation of high precision spectroscopic measurements and, simultaneously, open a route to significantly increased accuracy of theoretical predictions for rovibrational levels of the hydrogen molecule.

Nonrelativistic energy from explicitly correlated Gaussian functions.—The nonrelativistic Hamiltonian for the hydrogen molecule as a bound system of four particles is

$$H = T + V, \tag{1}$$

where (in atomic units)

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

$$V = \frac{1}{r_{01}} - \frac{1}{r_{02}} - \frac{1}{r_{03}} - \frac{1}{r_{12}} - \frac{1}{r_{13}} + \frac{1}{r_{23}}. \tag{3}$$

Indices 0,1 denote nuclei, and indices 2,3 denote electrons. The wave function Ψ depends on four particle coordinates $\Psi = \Psi(\vec{r}_0, \vec{r}_1, \vec{r}_2, \vec{r}_3)$. In the center of the mass frame, $\vec{p}_0 + \vec{p}_1 + \vec{p}_2 + \vec{p}_3 = 0$, and we may assume that the wave function Ψ is translationally invariant; i.e., it depends only on the differences $\vec{r}_i - \vec{r}_j$. More precisely, we represent the ground electronic state wave function as

$$\Psi = \sum_i^N c_i \psi_i(\vec{r}_0, \vec{r}_1, \vec{r}_2, \vec{r}_3), \tag{4}$$

$$\psi_i = (1 \pm P_{0\leftrightarrow 1})(1 + P_{2\leftrightarrow 3})\phi_i(\vec{r}_0, \vec{r}_1, \vec{r}_2, \vec{r}_3), \tag{5}$$

where $P_{i\leftrightarrow j}$ is the particle exchange operator. In the ground state of H_2 and D_2, the wave function is symmetric with respect to the exchange of nuclear and electronic variables, whereas in the heteronuclear HD molecule both symmetric and antisymmetric basis functions are employed. The functions ϕ_i in Eq. (5) are the nonadiabatic explicitly correlated Gaussians (naECG) of the form

$$\phi = r_{01}^n e^{-a_1 r_{01}^2 - a_2 r_{02}^2 - a_3 r_{03}^2 - a_4 r_{12}^2 - a_5 r_{13}^2 - a_6 r_{23}^2}. \tag{6}$$

In the particular case of an expectation value of a certain operator, ϕ becomes

$$\phi = r_{01}^n \left(1 + \frac{r_{23}}{2}\right) e^{-a_1 r_{01}^2 - a_2 r_{02}^2 - a_3 r_{03}^2 - a_4 r_{12}^2 - a_5 r_{13}^2 - a_6 r_{23}^2}, \tag{7}$$

and exactly satisfies the interelectron cusp condition. This correct analytic behavior significantly improves numerical convergence for this operator and is explained later. The nonlinear a parameters are optimized individually for each basis function, and the powers of the internuclear coordinate r_{01} are needed to represent accurately the vibrational part of the wave function. They are restricted to even integers and are generated randomly for each basis function from the log-normal distribution within the limited 0–80 range.

Matrix elements of the nonrelativistic Hamiltonian are expressed as a linear combination of the following ECG integrals

$$\begin{aligned} f(n_1, n_2, n_3, n_4, n_5, n_6) &= \frac{1}{\pi^3} \int d^3 r_1 \int d^3 r_2 \int d^3 r_3\, r_{01}^{n_1} r_{02}^{n_2} r_{03}^{n_3} r_{12}^{n_4} r_{13}^{n_5} r_{23}^{n_6} \\ &\quad \times e^{-a_1 r_{01}^2 - a_2 r_{02}^2 - a_3 r_{03}^2 - a_4 r_{12}^2 - a_5 r_{13}^2 - a_6 r_{23}^2} \end{aligned} \tag{8}$$

with real a parameters. We can distinguish master integrals that have very simple analytic forms

$$f() = \frac{1}{\sqrt{A^3}}, \qquad f(-1_i) = \frac{2}{\sqrt{\pi}} \frac{1}{A\sqrt{A_i}}, \tag{9}$$

where all zero valued indices have been omitted, -1_i denotes -1 on the ith position, A_1 is the example of a symbol $A_{i\ldots k} = \partial_{a_i} \ldots \partial_{a_k} A$, and

$$\begin{aligned} A &= a_1 a_2 a_3 + a_1 a_3 a_4 + a_2 a_3 a_4 + a_1 a_2 a_5 + a_2 a_3 a_5 \\ &\quad + a_1 a_4 a_5 + a_2 a_4 a_5 + a_3 a_4 a_5 + a_1 a_2 a_6 + a_1 a_3 a_6 \\ &\quad + a_1 a_4 a_6 + a_2 a_4 a_6 + a_3 a_4 a_6 + a_1 a_5 a_6 \\ &\quad + a_2 a_5 a_6 + a_3 a_5 a_6. \end{aligned} \tag{10}$$

In nonadiabatic molecular calculations, we have an additional complication due to the presence of the factor $r_{01}^{n_1}$ with possible large powers n_1. In order to calculate these integrals, we derive recurrence relations in n_1 for integrals with $n_1 \geq 1$,

$$f(n_1) = \frac{A_1}{2A}(n_1 + 1) f(n_1 - 2), \tag{11}$$

and for Coulomb integrals with even $n_1 \geq 2$,

$$f(n_1, -1_i) = g(n_1, -1_i) + h(n_1, -1_i) \tag{12}$$

$$\begin{aligned} g\Big(n_1, -1_i) &= \frac{A_{1i}}{2A_i}[f(n_1 - 2, -1_i) \\ &\quad + (n_1 - 2) g(n_1 - 2, -1_i)] \end{aligned} \tag{13}$$

$$\begin{aligned} h(n_1, -1_i) &= \frac{A_1}{2A}[2f(n - 2, -1_i) \\ &\quad + (n_1 - 2) h(n_1 - 2, -1_i)] \end{aligned} \tag{14}$$

where the starting point for these recursions are the integrals defined in Eq. (9). In the calculations of the kinetic energy, there are also integrals with even n_1 and $n_i = 2$ on the single positions from $i = 2$ to 6. If gradients with respect to the nonlinear parameters are to be used, one needs additional integrals where arbitrary n_i is again increased by 2. All of the additional recurrence relations with higher n_i powers can be derived explicitly from Eqs. (9), (11), and (12) by differentiation of the above recursions with respect to corresponding a parameters. For calculation of matrix elements with relativistic operators, ECG integrals with two odd n_i are needed. The master ECG integral $f(-1_i, -1_j)$ is known

TABLE I. Convergence of the nonrelativistic energy E (in a.u.) with the size of the naECG basis set. The 'naJC' line contains benchmark values obtained with nonadiabatic James-Coolidge wave functions [14,15]. Nuclear masses used in this work are taken from the 2014 CODATA compilation [1] $m_p/m_e = 1836.152\,673\,89(17)$, $m_d/m_e = 3670.482\,967\,85(13)$.

Basis	$E(H_2)$	$E(HD)$	$E(D_2)$
128	−1.164 023 669 155	−1.165 470 991 485	−1.167 167 911 358
256	−1.164 024 987 878	−1.165 471 628 967	−1.167 168 756 439
512	−1.164 025 027 334	−1.165 471 916 621	−1.167 168 805 491
1024	−1.164 025 030 593	−1.165 471 923 256	−1.167 168 808 953
2048	−1.164 025 030 843	−1.165 471 923 906	−1.167 168 809 193
naJC	−1.164 025 030 883 1(3)	−1.165 471 923 964 38(3)	−1.167 168 809 284 0(1)

analytically [18]; however, it is difficult to obtain compact and numerically stable recurrence relations in n_1 in this case. Instead, it is much more efficient to employ a numerical integration with respect to a corresponding nonlinear parameter a, using the quadrature adapted to the end point logarithmic singularity [19].

The nonrelativistic wave function Ψ has been constructed for several basis lengths $N = 128$, 256, 512, 1024, 2048 to observe the numerical convergence of the nonrelativistic energy and relativistic matrix elements. The obtained nonrelativistic energy is in a very good agreement with the benchmark value calculated with the naJC wave function [14,15], see Table I, and the corresponding naECG wave function Ψ is used for the evaluation of the relativistic correction. In comparison to former works based on a different representation of ECG functions [20], our nonrelativistic results, obtained with approximately five times smaller basis set, are more accurate for all hydrogen molecules H_2, D_2, and HD, which demonstrates the effectiveness of our new methods.

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

$$E_{\rm rel} = \langle\Psi|H_{\rm rel}|\Psi\rangle, \tag{15}$$

of the Breit-Pauli Hamiltonian,

$$\begin{aligned} H_{\rm rel} = &-\frac{1}{8}(p_2^4 + p_3^4) + \frac{\pi}{2}\sum_{x,a}\left(1 + \frac{\delta_s}{m_x^2}\right)\delta^3(r_{xa}) \\ &+ \pi\delta^3(r_{23}) - \frac{1}{2}p_2^i\left(\frac{\delta^{ij}}{r_{23}} + \frac{r_{23}^i r_{23}^j}{r_{23}^3}\right)p_3^j \\ &+ \frac{1}{2}\sum_{x,a}\frac{1}{m_x}p_x^i\left(\frac{\delta^{ij}}{r_{xa}} + \frac{r_{xa}^i r_{xa}^j}{r_{xa}^3}\right)p_a^j \\ &- \frac{1}{2}\frac{1}{m_0 m_1}p_0^i\left(\frac{\delta^{ij}}{r_{01}} + \frac{r_{01}^i r_{01}^j}{r_{01}^3}\right)p_1^j, \end{aligned} \tag{16}$$

where index x goes over 0,1 and a over 2,3. The coefficient $\delta_s = 0$ for the nuclear spin $s = 0$ or 1, and $\delta_s = 1$ for $s = 1/2$. 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. We have omitted also the $p_x^4/(8m_x^3)$ terms because their numerical values are smaller than the uncertainty of the whole relativistic correction. In order to accurately calculate the expectation value of $H_{\rm rel}$, we use the following expectation value identities to transform it to a numerically more regular form,

$$\begin{aligned} \langle\Psi|4\pi\delta^3(r_{xa})|\Psi\rangle = &\frac{2m_x}{1+m_x}\langle\Psi|\frac{2}{r_{xa}}(E - V) \\ &- \sum_y \frac{1}{m_y}\vec{p}_y\frac{1}{r_{xa}}\vec{p}_y - \sum_b \vec{p}_b\frac{1}{r_{xa}}\vec{p}_b|\Psi\rangle, \end{aligned} \tag{17}$$

$$\begin{aligned} \langle\Psi|p_2^4 + p_3^4|\Psi\rangle = &\langle\Psi|4(E - V)^2 - 2p_2^2 p_3^2 \\ &- 4(E - V)\left(\frac{p_0^2}{m_0} + \frac{p_1^2}{m_1}\right) \\ &+ \left(\frac{p_0^2}{m_0} + \frac{p_1^2}{m_1}\right)^2|\Psi\rangle, \end{aligned} \tag{18}$$

which hold for the exact wave function Ψ. For an approximate function $\tilde\Psi$, such expectation values are not equivalent, but the rhs quickly converges in the limit $\tilde\Psi \to \Psi$ as long as $\tilde\Psi$ satisfy proper analytic properties. This feature is especially important for the $p_2^2 p_3^2$ operator in Eq. (18). In this case, the function ϕ is that given by Eq. (7), and then,

$$p_2^2 p_3^2|\tilde\Psi\rangle = [\tilde p_2^2 \tilde p_3^2 - 4\pi\delta^3(r_{23})]|\tilde\Psi\rangle. \tag{19}$$

The new term $\tilde p_2^2 \tilde p_3^2$ (in contrast to $p_2^2 p_3^2$) is understood as the differentiation $\nabla_2^2\nabla_3^2$ of $\tilde\Psi$ as a function, thus omitting $\delta^3(r_{23})$. This $\delta^3(r_{23})$ term cancels exactly with the same term in $H_{\rm rel}$, so it is not necessary to calculate it [21]. We nevertheless do so for the comparison with previous results.

Results and discussion.—The relativistic correction to the dissociation energy D_0 is shown in Table II, while results for individual operators are presented in the Supplemental Material [22]. Here, D_0 differs from the

TABLE II. Convergence of relativistic correction to the dissociation energy D_0 (in cm^{-1}) with the size of the naECG basis set. For comparison, the relativistic correction evaluated with the BO approximation is also given. The difference corresponds to the nonadiabatic correction, see also Fig. 1.

Basis	H_2	HD	D_2
128	−0.531 427 54	−0.529 979 01	−0.528 337 669
256	−0.531 194 19	−0.529 910 95	−0.528 218 423
512	−0.531 206 99	−0.529 883 50	−0.528 201 146
1024	−0.531 212 77	−0.529 886 61	−0.528 205 416
2048	−0.531 214 84	−0.529 887 30	−0.528 205 935
∞	−0.531 215 6(5)	−0.529 887 5(2)	−0.528 206 05(9)
BO, [21]	−0.533 129(1)	−0.531 337(1)	−0.529 178(1)
difference	0.001 914	0.001 449	0.000 972

expectation values of H_{rel} by subtraction of the corresponding energy of separated hydrogen atoms,

$$E_{\mathrm{rel}}(H) = -\frac{1}{8} + \frac{1}{4}\left(\frac{1}{m_p}\right)^2 + O\left(\frac{1}{m_p}\right)^3, \qquad (20)$$

and the overall sign. It is worth noting that the term proportional to $1/m_p$ is not present in the above formula, so the relativistic recoil correction for separated hydrogen atoms is very small.

Because of the regularization of relativistic operators with the use of a variational wave function which exactly satisfies the electron-electron cusp condition, the total relativistic contribution has a very good convergence with the size of the basis set. The extrapolated value is accurate to about six digits. For comparison, the lower part of Table II contains the expectation values of the Breit-Pauli Hamiltonian calculated within the BO approximation. The "difference" line gives directly the nonadiabatic correction to the relativistic contribution, and we find that it is several times larger than the previous estimate [23]. These nonadiabatic corrections scale approximately with the inverse

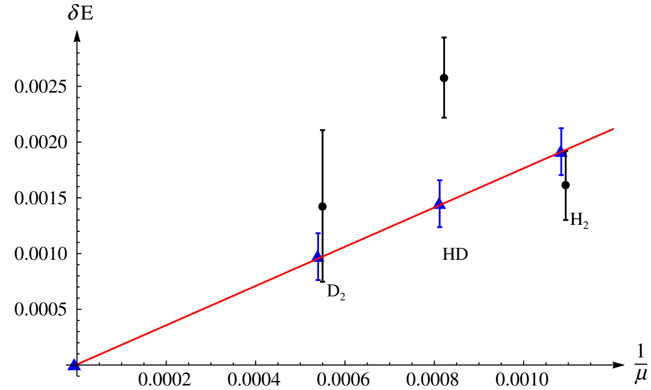

FIG. 1. Nonadiabatic relativistic correction to energy, namely, the difference δE (in cm^{-1}) between the total relativistic energy and the relativistic energy calculated in the BO approximation as a function of $1/\mu$. Analogously, experimental results include subtraction of all theoretical contributions with a relativistic correction in the BO approximation. The theoretical values are represented by blue triangles and the experimental by black circles.

of the reduced nuclear mass $1/\mu$, which is demonstrated by the straight line in Fig. 1.

Our result for the nonadiabatic relativistic correction in H_2 is in significant disagreement with the earlier result of $-0.5691\ \mathrm{cm}^{-1}$ obtained by Stanke and Adamowicz [16], which indicates the importance of regularization of relativistic operators and the use of the $1 + r_{23}/2$ prefactor in the naECG functions.

Table III presents the individual contributions to the ground state dissociation energy D_0. The comparison with experimental dissociation energies reveals agreement for H_2 and D_2 and surprisingly 3σ disagreement for the HD molecule. To investigate this inconsistency further, we present in Fig. 1 experimental and theoretical values of the recoil correction versus $1/\mu$. The experimental value for the relativistic nonadiabatic correction is obtained by subtraction, from the total dissociation energy, of the exact

TABLE III. Current state of the theoretically predicted dissociation energy budget for the ground level of H_2, HD, and D_2 (in cm^{-1}). Here, $\mathcal{E}^{(2)}_{\mathrm{rel}}$ is a second order correction due to relativistic BO potential, which in former works was automatically included in $\alpha^4 m$; FS is the finite nuclear size correction with $r_p = 0.84087(39)$ [3] and $r_d = 2.12771(22)$ fm [24].

Contribution	$D_0(H_2)$	$D_0(\mathrm{HD})$	$D_0(D_2)$	Remarks & Refs.
$\alpha^2 m$	36 118.797 746 10(3)	36 406.510 891 37(1)	36 749.090 990 99(2)	naJC, [14,15]
$\alpha^4 m$	−0.531 215 6(5)	−0.529 887 5(2)	−0.528 206 05(9)	naECG, this work
$\alpha^5 m$	−0.194 8(2)	−0.196 4(2)	−0.198 2(2)	BO, [23,25,26]
$\alpha^6 m$	−0.002 067(6)	−0.002 080(6)	−0.002 096(6)	BO, [12,21]
$\mathcal{E}^{(2)}_{\mathrm{rel}} \sim \alpha^6 m$	0.000 008 5	0.000 008 6	0.000 008 6	BO
$\alpha^7 m$	0.000 12(6)	0.000 12(6)	0.000 12(6)	BO, [12,21]
FS	−0.000 031	−0.000 117	−0.000 204	BO, [12,21]
Total	36 118.069 76(21)	36 405.782 54(21)	36 748.362 41(21)	
Exp.	36 118.069 62(37)	36 405.783 66(36)	36 748.362 86(68)	[27–29]
Exp.	36 118.069 45(31)			[30]

nonrelativistic value and all the other theoretical contributions evaluated within the BO approximation. Because of an agreement for H_2 and D_2, it seems that the experimental value for the dissociation energy of HD has underestimated uncertainty.

The theoretical uncertainty of the total dissociation energy is at present smaller than the experimental one and is dominated by the contribution from nonadiabatic QED effects of order $\alpha^5 m$, which has been estimated by the ratio of the electron-to-reduced-nuclear mass with the coefficient equal to one [23]. Once this correction is calculated, the uncertainty for the dissociation energy will be reduced to $6 \times 10^{-5}\ \mathrm{cm}^{-1}$ and even better for vibrational and rotational transitions. Further improvements would require the calculation of an $\alpha^7 m$ contribution, which will open the window for determination of the proton mass from measurement of a vibrational transition in H_2 and even determination of nuclear charge radii. However, such calculations are very challenging, and they have not yet been performed even for atomic two-electron systems.

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