

# Schrödinger equation solved for the hydrogen molecule with unprecedented accuracy

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(Dated: 14 April 2016)

The hydrogen molecule can be used for determination of physical constants, including the proton charge radius, and for improved tests of the hypothetical long range force between hadrons, which require a sufficiently accurate knowledge of the molecular levels. In this work we perform the first step toward a significant improvement in theoretical predictions of H<sub>2</sub> and solve the nonrelativistic Schrödinger equation to the unprecedented accuracy of 10<sup>-12</sup>. We hope that it will inspire a parallel progress in the spectroscopy of the molecular hydrogen.

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## I. INTRODUCTION

The spectroscopy of simple atomic systems like hydrogen<sup>1,2</sup>, hydrogenic ions<sup>3</sup>, muonic hydrogen<sup>4</sup>, muonium, and positronium has been used to determine fundamental physical constants and to test the quantum electrodynamic theory. Although experiments for more complicated atomic systems like helium or lithium can be as accurate as for hydrogen, the precision of theoretical predictions, at the moment, is not sufficient to determine physical constants, such as the fine structure constant  $\alpha$ , the Rydberg constant (Ry), or the absolute value of the nuclear charge radius. In contrast, the hydrogen molecule, thanks to its simplicity, has already been used for the most accurate determination of the deuteron magnetic moment from NMR measurements<sup>5</sup>, and for the studies of the unknown hypothetical fifth force at the atomic scale<sup>6</sup>. The precision achieved recently for transition frequencies, of an order of  $10^{-4} \text{ cm}^{-1}$ , has been verified by a series of measurements, which resulted in strong bounds on the fifth force. We will argue in this work that it is possible to achieve  $10^{-6} \text{ cm}^{-1}$  accuracy for energy levels of the hydrogen molecule, which not only will improve tests of quantum electrodynamic theory and will put stronger bounds on the fifth force, but also will allow a resolution of the proton charge radius puzzle which stands as a violation of the Standard Model of fundamental interactions<sup>7</sup>.

The improvement in theoretical predictions for the hydrogen molecule can be achieved by the calculation of the yet unknown higher order  $\alpha^4 \text{ Ry}$  quantum electrodynamic correction and by a more accurate solution of the nonrelativistic Schrödinger equation. This second improvement is performed in this work, while the calculation of QED effects is in progress. The solution of the Schrödinger equation for the hydrogen molecule has been pursued almost since the beginning of the quantum mechanic theory. Over time, there have been many contributions to the development of methods that would ensure increased precision of theoretical predictions. Heitler and London<sup>8</sup>, James and Coolidge<sup>9</sup>, Kołos and Wolniewicz<sup>10</sup>, and many others have made their marks on the history of research on  $\text{H}_2$ . Every breakthrough in the precision of theoretical predictions has been related to the progress in computational techniques. Fig. 1 illustrates the progress made over many decades in the precision of the theoretical determination of the nonrelativistic dissociation energy  $D_0$  for  $\text{H}_2$ .

Not always the results of calculations have been in agreement with the measured values, which has questioned the validity of the theoretical approach. For example, in 1964 Kołos

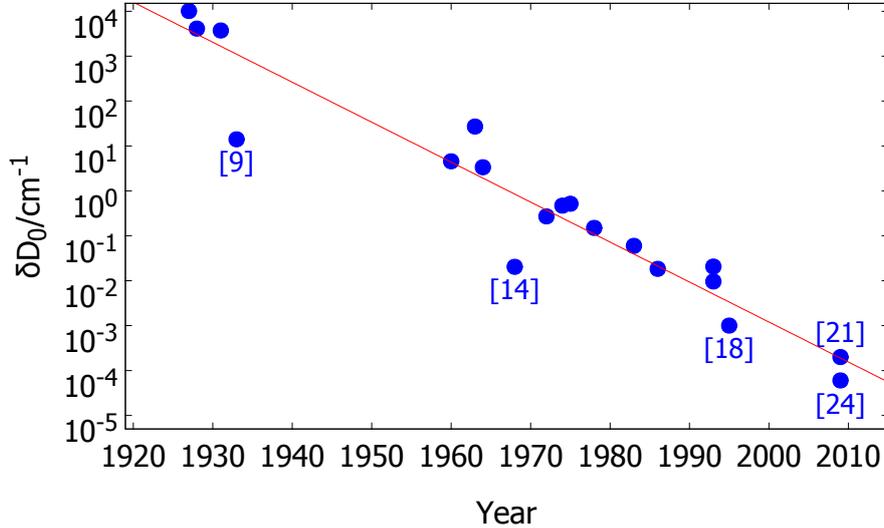


FIG. 1. The accuracy of theoretical predictions of the nonrelativistic dissociation energy  $D_0$  of  $\text{H}_2$  versus time, with the linear fit on the logarithmic scale.

and Wolniewicz<sup>11</sup> solved variationally the nonadiabatic Schrödinger equation for the hydrogen molecule. The calculated dissociation energy appeared to be higher than the measured one<sup>12</sup>, which was in contradiction with the variational principle. Six years later, Stwalley<sup>13</sup> measured  $D_0$  again with the accuracy increased to a few tenths of reciprocal centimeter and obtained a value higher than previously by  $5 \text{ cm}^{-1}$ , in agreement with the Kołos and Wolniewicz result<sup>14</sup>.

Further progress in theoretical predictions was related to the calculations of the leading relativistic corrections and to approximate treatment of QED effects<sup>15–18</sup>. Later on, due to rapid development of computer power, the methods based on exponentially correlated Gaussian (ECG) functions have been developed both in the Born-Oppenheimer approximation<sup>19–22</sup> and in the direct nonadiabatic approach<sup>23,24</sup>. Very recently, we have introduced a nonadiabatic perturbation theory (NAPT), which allowed the accuracy of about  $10^{-3} \text{ cm}^{-1}$  to be achieved for all the rovibrational levels of  $\text{H}_2$  and isotopomers<sup>25</sup>. However, the complexity of NAPT in the higher order of electron-nucleus mass ratio<sup>26</sup> makes further improvements in accuracy quite complicated. For this reason, we propose another

approach to the direct solution of the Schrödinger equation resorting to the special integration technique for explicitly correlated exponential functions and we present its first results in this work. Over fifty years after the pioneering work of Kołos and Wolniewicz<sup>27</sup> employing nonadiabatic exponential wave function, we approach the problem of solving the four-body Schrödinger equation. Our new formulation aims at the precision level of  $10^{-7}$  cm<sup>-1</sup> for  $D_0$ .

## II. THEORY

The main purpose of this work is to solve accurately the stationary Schrödinger equation  $\hat{H}\Psi = E\Psi$  for a diatomic molecule with the nuclei of charge  $Z_A$  and  $Z_B$  and finite masses  $M_A$  and  $M_B$

$$\hat{H} = -\frac{1}{2M_A}\nabla_A^2 - \frac{1}{2M_B}\nabla_B^2 - \frac{1}{2m_e}\nabla_1^2 - \frac{1}{2m_e}\nabla_2^2 + \frac{Z_A Z_B}{r_{AB}} + \frac{1}{r_{12}} - \frac{Z_A}{r_{1A}} - \frac{Z_A}{r_{2A}} - \frac{Z_B}{r_{1B}} - \frac{Z_B}{r_{2B}}, \quad (1)$$

using the variational approach. The trial wave function

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{R}_A, \vec{R}_B) = \sum_{k=1}^K c_k \hat{S} \psi_{\{k\}}(\vec{r}_1, \vec{r}_2, \vec{R}_A, \vec{R}_B) \quad (2)$$

is expanded in properly symmetrized ( $\hat{S}$ ), four-particle basis of exponential functions

$$\psi_{\{k\}} = \exp[-\alpha r_{AB} - \beta(\zeta_1 + \zeta_2)] r_{AB}^{k_0} r_{12}^{k_1} \eta_1^{k_2} \eta_2^{k_3} \zeta_1^{k_4} \zeta_2^{k_5}, \quad (3)$$

where  $\zeta_i = r_{iA} + r_{iB}$  and  $\eta_i = r_{iA} - r_{iB}$  are the coordinates closely related to the prolate spheroidal coordinates of  $i$ -th electron,  $r_{ij}$  are the interparticle distances,  $\alpha$  and  $\beta$  are non-linear variational parameters, and  $k_i$  are non-negative integers collectively denoted as  $\{k\}$ . For its resemblance to the electronic James-Coolidge function, we call this basis function *the nonadiabatic James-Coolidge* (naJC) function.

Application of the naJC function for evaluation of the matrix elements leads to a certain class of integrals. Efficient evaluation of these integrals has become feasible since the discovery of the analytic formulas<sup>28,29</sup> and the differential equation<sup>30,31</sup> which is satisfied by the master integral

$$g = \frac{\int \frac{d^3 \rho_1}{4\pi} \int \frac{d^3 \rho_2}{4\pi} \int \frac{d^3 \rho_3}{4\pi} e^{-w_1 \rho_1 - w_2 \rho_2 - w_3 \rho_3 - u_1 \rho_{23} - u_2 \rho_{31} - u_3 \rho_{12}}}{\rho_{23} \rho_{31} \rho_{12} \rho_1 \rho_2 \rho_3}. \quad (4)$$

This differential equation has the form:

$$\sigma \frac{\partial g}{\partial a} + \frac{1}{2} \frac{\partial \sigma}{\partial a} g + P_a = 0, \quad (5)$$

where  $a$  is  $u_i$  or  $w_i$ , and where

$$\begin{aligned} \sigma = & u_1^2 u_2^2 w_3^2 + u_2^2 u_3^2 w_1^2 + u_1^2 u_3^2 w_2^2 + w_1^2 w_2^2 w_3^2 \\ & + u_1^2 w_1^2 (u_1^2 + w_1^2 - u_2^2 - u_3^2 - w_2^2 - w_3^2) \\ & + u_2^2 w_2^2 (u_2^2 + w_2^2 - u_1^2 - u_3^2 - w_1^2 - w_3^2) \\ & + u_3^2 w_3^2 (u_3^2 + w_3^2 - u_2^2 - u_1^2 - w_1^2 - w_2^2). \end{aligned} \quad (6)$$

The inhomogeneous term  $P_a$  is a combination of several logarithmic functions<sup>31</sup>. Equation (5) enables the analytic evaluation of all necessary integrals. For example, when using the naJC basis, the master integral  $g$  takes the following form

$$\begin{aligned} & \int \frac{d^3 r_{AB} d^3 r_{1B} d^3 r_{2B}}{(4\pi)^3} \frac{e^{-t r_{AB} - u(r_{1A} + r_{1B}) - w(r_{2A} + r_{2B})}}{r_{AB} r_{12} r_{1A} r_{1B} r_{2A} r_{2B}} \\ & = \frac{1}{4uw} \left[ -\frac{\ln\left(\frac{2u}{t+u+w}\right)}{t-u+w} - \frac{\ln\left(\frac{2w}{t+u+w}\right)}{t+u-w} \right. \\ & \quad \left. + \frac{\ln\left(\frac{2uw}{(u+w)(t+u+w)}\right)}{t+u+w} + \frac{\ln\left(\frac{2(u+w)}{t+u+w}\right)}{t-u-w} \right]. \end{aligned} \quad (7)$$

The integrals with additional positive powers of interparticle distances are obtained by differentiation of  $g$  with respect to the corresponding nonlinear parameter, which in turn can be expressed in terms of straightforward algebraic recursion relations. These relations are too long to be written explicitly here, but all of them can be derived using Eq. (5).

### III. NUMERICAL RESULTS

Results of our calculations for  $\text{H}_2$  are presented in Tab. I in the form a sequence of energies resulting from increasing length ( $K$ ) of expansion (2). The selection of  $K$  was made on the basis of the saturation of consecutive 'shells' limited by  $\sum_{k=1}^5 k_i \leq \Omega$  with  $k_0$  fixed at 30. The observed regular convergence, obeying the inverse power law ( $\sim K^{-4}$ ), permits a firm extrapolation to the complete basis set as well as an estimation of uncertainty. The final value agrees well with the previous estimation of  $-1.16402503084(6)$  a.u. obtained by Bubin et al.<sup>24</sup> but has a significantly smaller uncertainty.

TABLE I. Convergence of the Schrödinger equation eigenvalue  $E$  (in a.u.) and of the corresponding dissociation energy  $D_0$  (in  $\text{cm}^{-1}$ ) for  $\text{H}_2$  with the size of the basis set.

$\Omega$	$K$	$E$	$D_0$
10	36642	-1.164 025 030 821 4	36 118.797 732 57
11	53599	-1.164 025 030 870 9	36 118.797 743 43
12	76601	-1.164 025 030 880 4	36 118.797 745 52
13	106764	-1.164 025 030 882 5	36 118.797 745 97
$\infty$	$\infty$	-1.164 025 030 884(1)	36 118.797 746 3(2)

Further increase in the accuracy of eigenvalue of the four-body Schrödinger equation is feasible, but the problem we face is the lack of the efficient parallel code in multiprecision arithmetics for the  $LDL^T$  matrix decomposition with pivoting, which results in a long computation time. However, current uncertainties in the electron-proton (proton-deuteron) mass ratio and in the Rydberg constant are much more significant than those due to numerical uncertainties. For example, the CODATA 2014<sup>32</sup> electron-proton mass ratio has a relative uncertainty of  $9.5 \cdot 10^{-11}$ , which affects the eigenvalue of  $\text{H}_2$  at the level of  $4.3 \cdot 10^{-12}$  a.u. and the corresponding dissociation energy at  $8.5 \cdot 10^{-7} \text{cm}^{-1}$ . Similarly, the current uncertainty in the Rydberg constant affects the conversion of  $D_0$  value from a.u. to reciprocal centimeters at the level of  $2.1 \cdot 10^{-7} \text{cm}^{-1}$ . This situation indicates that one cannot exclude the possibility to determine the electron-proton mass ratio from future high precision studies of  $\text{H}_2$ .

#### IV. CONCLUSIONS

The approach based on explicitly correlated exponential functions and the obtained results pave the way to a significant progress in the theory of the hydrogen molecule. Not only the ground but also all the rovibrational levels can be obtained with a similar approach. From the experience with James-Coolidge functions in the Born-Oppenheimer approximation<sup>33</sup>, we know that they work very well up to the distances as large as 12 a.u., therefore they can be used also for all excited states. Nevertheless, we see the possibility of using exponential

functions with arbitrary nonlinear parameters, for a more efficient representation of the total wave function. In fact, the main problem we face for excited states, is the increased size of the basis which can be solved by tuning values of all nonlinear parameters in exponential functions and using a double or triple basis with different parameters.

Considering the leading relativistic corrections, they can be expressed in terms of an expectation value with the nonrelativistic wave function, so their evaluation does not pose a significant problem, and they have already been calculated in the BO approximation. The leading quantum electrodynamic effects are more complicated due to Bethe logarithm contribution which involves the logarithm of the nonrelativistic Hamiltonian. Its calculation beyond the BO approximation might be problematic. However, much more challenging is the calculation of the higher order  $\alpha^4$  Ry contribution, which apart from hydrogen, was calculated only for He atom. The dominant component of the  $\alpha^4$  Ry—the radiative correction—was calculated in Ref. 21 to be  $16 \cdot 10^{-4} \text{ cm}^{-1}$ , whereas its remaining part was estimated as  $8 \cdot 10^{-4} \text{ cm}^{-1}$ . Another estimate of the non-radiative contribution, made on the basis of an assumption that it is equal to  $2\alpha^2$  multiplied by the known leading relativistic correction to  $D_0$  ( $\approx 0.5 \text{ cm}^{-1}$ ), leads to a much smaller value of  $5 \cdot 10^{-5} \text{ cm}^{-1}$ . Because of this discrepancy, a more accurate estimation of the  $\alpha^4$  Ry correction and its uncertainty can be obtained only by explicit calculations. In order to achieve the  $10^{-6}$  accuracy, it would probably be necessary to approximately evaluate also the  $\alpha^5$  Ry correction as it is enhanced by the presence of  $\ln \alpha^{-2}$  factors.

At the level of accuracy of  $10^{-6} \text{ cm}^{-1}$ , the proton charge radius, which contributes about  $1.2 \cdot 10^{-4} \text{ cm}^{-1}$  to the dissociation energy of  $\text{H}_2$ , can be determined with 0.5% precision, provided that equally accurate measurement is performed. This certainly will resolve the proton charge radius discrepancy, which is at the level of 4%, and will open a new era in precision quantum chemistry. Regarding the tests of hypothetical forces, which are beyond those in the Standard Model, the atomic scale is the natural region for the long range hadronic interactions. Moreover, it has recently been shown that vibrational levels of the hydrogen molecule<sup>34</sup> are particularly sensitive to the interactions beyond the Coulomb repulsion between nuclei. So any deviation between hopefully improved theoretical predictions and the experiment may signal a new physics.

## ACKNOWLEDGMENT

We thank Prof. Bogumil Jeziorski for valuable comments to the manuscript. This research was supported by the National Science Center (Poland) Grants No. 2012/04/A/ST2/00105 (K.P.) and 2014/13/B/ST4/04598 (J.K.), as well as by a computing grant from the Poznan Supercomputing and Networking Center, and by PL-Grid Infrastructure.

## REFERENCES

- <sup>1</sup>C. G. Parthey, A. Matveev, J. Alnis, B. Bernhardt, A. Beyer, R. Holzwarth, A. Maistrou, R. Pohl, K. Predehl, T. Udem, T. Wilken, N. Kolachevsky, M. Abgrall, D. Rovera, C. Salomon, P. Laurent, and T. W. Hänsch, *Phys. Rev. Lett.* **107**, 203001 (2011).
- <sup>2</sup>C. Schwob, L. Jozefowski, B. de Beauvoir, L. Hilico, F. Nez, L. Julien, F. Biraben, O. Acef, J.-J. Zondy, and A. Clairon, *Phys. Rev. Lett.* **82**, 4960 (1999).
- <sup>3</sup>S. Sturm, F. Kohler, J. Zatorski, A. Wagner, Z. Harman, G. Werth, W. Quint, C. H. Keitel, and K. Blaum, *Nature* **506**, 467 (2014).
- <sup>4</sup>R. Pohl, A. Antognini, F. Nez, F. D. Amaro, F. Biraben, J. M. R. Cardoso, D. S. Covita, A. Dax, S. Dhawan, L. M. P. Fernandes, A. Giesen, T. Graf, T. W. Hänsch, P. Indelicato, L. Julien, C.-Y. Kao, P. Knowles, E.-O. Le Bigot, Y.-W. Liu, J. A. M. Lopes, L. Ludhova, C. M. B. Monteiro, F. Mulhauser, T. Nebel, P. Rabinowitz, J. M. F. dos Santos, L. A. Schaller, K. Schuhmann, C. Schwob, D. Taqqu, J. a. F. C. A. Veloso, and F. Kottmann, *Nature* **466**, 213 (2010).
- <sup>5</sup>M. Puchalski, J. Komasa, and K. Pachucki, *Phys. Rev. A* **92**, 020501 (2015).
- <sup>6</sup>W. Ubachs, W. Vassen, E. J. Salumbides, and K. S. E. Eikema, *Annalen der Physik* **525**, A113 (2013).
- <sup>7</sup>R. Pohl, R. Gilman, G. A. Miller, and K. Pachucki, *Annu. Rev. Nucl. Part. Sci.* **63**, 175 (2013).
- <sup>8</sup>W. Heitler and F. London, *Z. Phys.* **44**, 455 (1927).
- <sup>9</sup>H. M. James and A. S. Coolidge, *J. Chem. Phys.* **1**, 825 (1933).
- <sup>10</sup>W. Kołos and L. Wolniewicz, *J. Chem. Phys.* **41**, 3663 (1964).
- <sup>11</sup>W. Kołos and L. Wolniewicz, *J. Chem. Phys.* **41**, 3674 (1964).
- <sup>12</sup>G. Herzberg and A. Monfils, *J. Mol. Spectrosc.* **5**, 482 (1960).

- <sup>13</sup>W. C. Stwalley, *Chem. Phys. Lett.* **6**, 241 (1970).
- <sup>14</sup>W. Kołos and L. Wolniewicz, *J. Chem. Phys.* **49**, 404 (1968).
- <sup>15</sup>W. Kołos and L. Wolniewicz, *J. Mol. Spectrosc.* **54**, 303 (1975).
- <sup>16</sup>L. Wolniewicz, *J. Chem. Phys.* **78**, 6173 (1983).
- <sup>17</sup>L. Wolniewicz, *J. Chem. Phys.* **99**, 1851 (1993).
- <sup>18</sup>L. Wolniewicz, *J. Chem. Phys.* **103**, 1792 (1995).
- <sup>19</sup>B. Jeziorski and K. Szalewicz, *Phys. Rev. A* **19**, 2360 (1979).
- <sup>20</sup>J. Rychlewski, W. Cencek, and J. Komasa, *Chem. Phys. Lett.* **229**, 657 (1994).
- <sup>21</sup>K. Piszczatowski, G. Lach, M. Przybytek, J. Komasa, K. Pachucki, and B. Jeziorski, *J. Chem. Theory Comput.* **5**, 3039 (2009).
- <sup>22</sup>J. Mitroy, S. Bubin, W. Horiuchi, Y. Suzuki, L. Adamowicz, W. Cencek, K. Szalewicz, J. Komasa, D. Blume, and K. Varga, *Rev. Mod. Phys.* **85**, 693 (2013).
- <sup>23</sup>S. Bubin and L. Adamowicz, *J. Chem. Phys.* **118**, 3079 (2003).
- <sup>24</sup>S. Bubin, F. Leonarski, M. Stanke, and L. Adamowicz, *Chem. Phys. Lett.* **477**, 12 (2009).
- <sup>25</sup>K. Pachucki and J. Komasa, *J. Chem. Phys.* **130**, 164113 (2009).
- <sup>26</sup>K. Pachucki and J. Komasa, *J. Chem. Phys.* **143**, 034111 (2015).
- <sup>27</sup>W. Kołos and L. Wolniewicz, *Rev. Mod. Phys.* **35**, 473 (1963).
- <sup>28</sup>D. M. Fromm and R. N. Hill, *Phys. Rev. A* **36**, 1013 (1987).
- <sup>29</sup>F. E. Harris, *Phys. Rev. A* **55**, 1820 (1997).
- <sup>30</sup>K. Pachucki, *Phys. Rev. A* **80**, 032520 (2009).
- <sup>31</sup>K. Pachucki, *Phys. Rev. A* **86**, 052514 (2012).
- <sup>32</sup>P. J. Mohr, D. B. Newell, and B. N. Taylor, *ArXiv e-prints* (2015), arXiv:1507.07956 [physics.atom-ph].
- <sup>33</sup>K. Pachucki, *Phys. Rev. A* **82**, 032509 (2010).
- <sup>34</sup>E. J. Salumbides, J. C. J. Koelemeij, J. Komasa, K. Pachucki, K. S. E. Eikema, and W. Ubachs, *Phys. Rev. D* **87**, 112008 (2013).