From the Kołos-Wolniewicz calculations to the quantum-electrodynamic treatment of the hydrogen molecule: competition between theory and experiment

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Abstract

The hydrogen molecule – two and a half centuries after Cavendish's discovery, a dozen decades after Lyman's first spectroscopic observations and almost a centennial after Heitler and London's quantum-mechanical explanation of its stability – is still the subject of intense research, both theoretical and experimental. Being the simplest neutral molecule, it serves as a benchmark for testing quantum-mechanical theories and methods; being the most ubiquitous molecule in the Universe, plays an essential role in astronomy and the fundamentals of physics. Over decades, advances in increasing experimental precision have stimulated ever more accurate calculations. In this review, we summarize the progress made in the field of the quantum-mechanical description of the electronic structure of the hydrogen molecule, starting from the pioneering calculations of Kołos and Wolniewicz in the early 1960s and ending with the current state of knowledge, including applications of quantum electrodynamics. Bearing in mind the topic of this special issue, we will focus on the achievements of Polish scientists in this matter.

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KEYWORDS

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Contents

1 Introduction

Molecular hydrogen is the simplest molecule that exhibits electron correlations and displays many aspects of chemical binding, to which fundamental studies can be addressed. Therefore it has been the ubiquitous reference system from the very beginning of quantum chemistry and molecular physics. It started in the pioneering work by Heitler and London in 1927 [1] who approximately solved the Schrödinger equation and found that the system is stable against the dissociation into two hydrogen atoms. Consequently, the newly formulated quantum theory could satisfactorily explain the stability of the covalent bond between two neutral atoms. The milestone in the theoretical methods for the hydrogen molecule is the work of James and Coolidge from 1933 [2] who employed the wave function expansion in terms of basis functions ϕ depending explicitly on the interelectron distance r_{12}

$$\phi = e^{-\alpha(\xi_1+\xi_2)}\,\xi_1^k\,\xi_2^m\,\eta_1^l\,\eta_2^n\,r_{12}^\mu\,, \quad \xi_i = \frac{r_{Ai}+r_{Bi}}{R}, \quad \eta_i = \frac{r_{Ai}-r_{Bi}}{R} \tag{1}$$

and achieved the millihartree accuracy ($E = -1.173\,559$ E$_h$) at equilibrium distance $R = 1.4$ bohr using the 13-term expansion only. The calculated dissociation energy $D_0(\mathrm{H}_2) = 4.454(13)$ eV was consistent with the available experimental value of 4.46(4) eV [3]. It turned out that explicit inclusion of the r_{12}-dependent term greatly improves the energy convergence compared to the approaches using the orbital basis sets. The Coulomb singularity in the Hamiltonian imposes a specific behavior on the wave function at the interparticle coalescence point. Indeed, the James-Coolidge wave function can reproduce Kato's cusps. However, introducing the r_{12}^μ factors to exponential functions involves the computation of extremely complicated integrals.

Significant advances were achieved by Kołos and Wolniewicz in 1965 [4], who extended the work of James and Coolidge and proposed a new form of the basis function which was also applicable to long internuclear distances

$$\phi = e^{-\alpha\xi_1-\bar{\alpha}\xi_2}\cosh(\beta\eta_1+\bar{\beta}\eta_2)\,\xi_1^n\,\eta_1^k\,\xi_2^m\,\eta_2^l\,r_{12}^\mu. \tag{2}$$

The developed computational methods, also accounting for the coupling of the electronic and nuclear motions and for relativistic effects, were implemented on electronic computers, which became available at that time. Since then, it has been many times demonstrated that the Schrödinger equation, when solved accurately with the explicitly correlated basis functions and corrected for small relativistic and quantum electrodynamic (QED) effects, can predict the molecular energy levels with very high precision. This, in turn, laid a foundation for the current confidence in the quantitative predictive power of quantum chemistry.

Since 1970, the spectroscopic measurements have undergone significant progress [5–7]. In contrast to atomic systems, the rotational and vibrational degrees of freedom rise to a multitude of states in the ground electronic manifold with long lifetimes. It enabled the contemporary measurements of transition frequencies between rovibrational levels of H_2 and its deuterated and tritiated isotopologues to reach the relative accuracy of 10^{-9}, see, e.g. [8–11]. Advances in both theory and experiment have made molecular hydrogen an essential system in developing quantum chemistry. H_2 has emerged as a benchmark for testing quantum electrodynamics in simple bound systems. Comparison between theory and experiment serves not only as a consistency check between them, but it can also potentially be exploited to determine physical constants such as the proton charge radius, electron-proton mass ratio, or the Rydberg constant R_∞.

In this review, we want to present the most significant achievements of Polish scientists from the perspective of theoretical and computational developments of methods devoted to the hydrogen molecule, starting from the works of Kołos and Wolniewicz published 1960s. During the decades, progress has taken place in many directions of theory. Several research groups have devoted significant resources and participated in this progress. Nowadays, studies on H_2 are also an area of intense research, touching on problems far beyond quantum chemistry. It shows that research on molecular hydrogen occupies a unique place, marking the frontier of research in high-precision applications and allowing a deeper insight into unexplored phenomena occurring in molecules. From today's perspective, the theoretical research on molecular hydrogen can be systematized within the framework of nonrelativistic quantum electrodynamics (NRQED) [12]. Within this theory, all the corrections to the nonrelativistic energy are implemented on top of the nonrelativistic Hamiltonian using the standard perturbation theory with the nonrelativistic wave function. The principal assumption in NRQED, is that the total energy can be expanded in powers of the fine-structure constant $\alpha \simeq 1/137$

$$E(\alpha) = E^{(2)} + E^{(4)} + E^{(5)} + E^{(6)} + E^{(7)} + O(\alpha^8), \tag{3}$$

where $E^{(n)}$ are contribution of order α^n. They are interpreted subsequently as the nonrelativistic energy $E^{(2)}$, the relativistic correction $E^{(4)}$, the leading QED correction $E^{(5)}$, and the higher order QED corrections $E^{(i)}$, $i \geq 6$. All these contributions can be expressed as expectation values, with a Schrödinger's wave function, of certain operators derived within NRQED theory [13]. Based on the NRQED expansion (3), we can attempt to present in an orderly manner the development of theoretical methods for molecular hydrogen.

The most general approach is to treat the hydrogen molecule as a four-body system, where the starting point is the solution of the Schrodinger equation in which electrons and atomic nuclei are treated similarly. Such a direct non-adiabatic (DNA) approach, see Sec. 2.3, accounts strictly for the (nonadiabatic) effects of the finite mass of the nuclei and has been intensively developed in recent years. Such calculations are relatively costly considering a large number of rovibrational states of the diatomic molecule spectrum and the necessity of variational optimization for individual states. An alternative possibility is based on the nonadiabatic perturbation theory (NAPT) of the finite nuclear mass effects, in which the leading order is just the Born-Oppenheimer approximation commonly used in molecules. More details on this method and the numerical results obtained using different types of wave functions are given in Sec. 2.2.3. These two approaches, DNA and NAPT, often complemented in high-precision calculations and allowed for a non-trivial mutual verification. Equally important is the development of computational methods and their implementation on computing machines, the rapid advancement of which undoubtedly was and still is an impulse for further progress.

2 The nonrelativistic energy

The nonrelativistic energy of the hydrogen molecule can be obtained by solving the four-body Schrödinger equation directly or by separating nuclear and electronic variables. The error introduced by the separation can be later compensated by accounting for the finite nuclear mass effects in adiabatic and nonadiabatic corrections.

In this section, we shall review first the results obtained within the BO approximation (Sec. 2.1), for both the ground and the electronically excited states, followed by reports on adiabatic and nonadiabatic corrections (Sec. 2.2) to BO energy. The next part of this section will be devoted to fully nonadiabatic (DNA) calculations. Selected numerical results will accompany a compact description of the methods.

2.1 The Born-Oppenheimer energy curves

The Born-Oppenheimer separation of the electronic and nuclear motions in molecules is probably the most crucial approximation ever introduced in molecular quantum mechanics. It provides rigorous definitions of useful chemical concepts like the geometry of molecules, the molecular dipole moment, or the interaction potential. In this approximation, one assumes that electronic motions are much faster than nuclear ones. Therefore, one can postulate that slow changes in the nuclear positions do not strongly affect the physical description of the electronic motions, leading to an adiabatic separation of the electronic and nuclear problems. In the Born-Oppenheimer approximation, the electronic problem is solved for an (infinite) set of nuclear coordinates. The eigenvalue of the electronic Schrödinger equation, the electronic energy as a function of these coordinates, is nothing else than the potential energy surface. This energy surface is used as the potential operator in the second step of the Born-Oppenheimer approximation, the problem of nuclear motions in a given potential.

2.1.1 James-Coolidge and Kołos-Wolniewicz wave functions

The basis set of James and Coolidge (JC) was the first to be successfully applied in quantitative quantum-chemical calculations on a molecule [2]. and extended by Kołos and Roothaan in 1958 [14, 15]. At that time, this was a veritable tour de force. In these works, a meticulous study of the optimal nonlinear parameter at different interatomic distances was reported, the convergence with the number of terms in the basis was checked, and finally, the accuracy of the result at the equilibrium distance was verified by using the virial theorem. In 1964 the work of Kołos and Roothaan was extended by Kołos and Wolniewicz in [16]. This seminal paper is known for calculating the adiabatic and relativistic corrections to the Born-Oppenheimer energy.

Over time, it became clear that the JC basis set was not flexible enough to extend the calculations of the potential energy curve to the dissociation. Therefore, the JC basis was generalized by Kołos and Wolniewicz in 1965 [4] and made compatible with the Heitler-London function at large distances.

In 1966, the flexibility of the Kołos-Wolniewicz (KW) function was further increased in calculations for the excited $B^1\Sigma_u^+$ state, and in 1974 [17] and 1975 [18] for the ground state. In the 1965 paper [4], the authors reported results for distances between 0.4 and 10 bohr thus covering the full potential from the very repulsive region to the long-range attractive region with the different sizes of the basis sets for different interatomic distances R.

At the beginning of the 1960's Herzberg and Monfils performed a careful experimental investigation of the dissociation energy of the hydrogen molecule [19]. Interestingly, the Born-Oppenheimer potential obtained by Kołos and Wolniewicz supplemented with the adiabatic and relativistic corrections predicted the dissociation energy $D_0(\mathrm{H}_2) = 36\,117.4\,\mathrm{cm}^{-1}$ which was larger than the experimental value $36\,113.0(3)\,\mathrm{cm}^{-1}$. This, in turn, implied that the total energy was lower than deduced from the experiment, in contradiction with the variational principle. Therefore, Kołos and Wolniewicz repeated the 1964/1965 calculations in the double precision arithmetic [20, 21], confirming the existing discrepancy between theory and experiment. The controversy was resolved in 1970, when Herzberg [22], and independently Stwalley [23], repeated the measurement obtaining a value consistent with the theory.

The Born-Oppenheimer potential for the ground state of H_2 was revisited several times. In 1974 Kołos and Wolniewicz significantly improved the long-range tail of the potential [17] using a much longer expansion (60 terms) for distances ranging from 6 to 10 bohr. Small and intermediate distances were carefully reinvestigated, and the most precise clamped nuclei energy has been computed for the equilibrium distance $R_e = 1.4$ bohr [18]. All the theoretical and computational advances in the calculations on the ground state of the hydrogen molecule were briefly summarized by Kołos in 1978 [24].

Further improvements in the Born-Oppenheimer energies for the ground state of the hydrogen molecule had to wait for a new era of supercomputers. In 1986 Kołos et al. [25] revisited the Born-Oppenheimer potential for H_2 for distances ranging from 0.2 to 12 bohr. For all distances, improvements over the previous results were obtained. The size of the basis set varied depending on the interaction region (repulsive, minimum, or attractive). As many as 249 functions were used to improve the binding energy at the minimum by as little as 0.004 cm^{-1}. At other distances, the improvement was substantially better. After adding terms beyond the non-relativistic Born-Oppenheimer approximation, perfect agreement between theory and experiment [22, 23] was obtained, while for the D_2 isotopologue, a substantial discrepancy remained.

Interestingly, a few years later, in 1993, Kołos and Rychlewski [26] used a smaller basis set than in 1986, and still improved the accuracy of the Born-Oppenheimer potential energy curve, leading to a perfect agreement between theory and experiment for the dissociation energy of all stable isotopologues of the hydrogen molecule, but not for the ionization potentials. In the same year Wolniewicz [27] revisited the 1986 paper by Kołos et al. [25], and constructed a basis of around 249 functions for all distances ranging from 0.2 to 12 bohr by eliminating only those that were responsible for the linear dependencies. With such a constructed basis and newly recomputed adiabatic and relativistic corrections, Wolniewicz reached a perfect agreement for both the dissociation energies and ionization potentials. The last calculation of the Born-Oppenheimer potential by Kołos was published in 1994. After a very careful reoptimization of the nonlinear parameters in the variational wavefunction, the well depth changed only by 0.009 cm^{-1}, still slightly above the best result at that time obtained with explicitly correlated Gaussian (ECG) function, showing that a large number of nonlinear parameters, long basis set expansions, and easy construction of the matrix elements of the Hamiltonian are often more efficient than basis sets carefully crafted to the analytic properties of the Hamiltonian.

2.1.2 Explicitly correlated Gaussian wave functions

In 1960, Boys [28] and Singer [29] presented a set of compact analytic formulas of the integrals necessary to determine the Hamiltonian matrix elements of molecular systems in the basis of explicitly correlated Gaussians (ECG). These works are considered the beginning of ECG computational methods, one of the most important tools for precise quantum chemistry. These formulas can be used in the Born–Oppenheimer approximation calculations for multicenter and multielectron molecules, which is their main advantage over the exponential-function methods. Moreover, the great simplicity of the ECG integrals enables the use of a large number of ECG functions in the expansion of wave functions. On the other hand, ECGs do not have the correct functional form near the coalescence point for Coulomb interactions, and also do not have the correct asymptotics over long distances. For this reason, the potential of these methods for precise computation has not been evident for a long time. In 1979, Jeziorski and Szalewicz [30] showed that this basis enables accurate calculations for the ground electronic state of H_2. Even if the accuracy of the presented energy at the internuclear distance $R = 1.4$ a.u. was lower than the best results at that time obtained with KW functions, they demonstrated that the ECG basis could be used to calculate various properties accurately, which cannot be achieved by other methods [31–33]. Finally, in the 1990s, ECG expansions were successfully employed by Rychlewski, Cencek and Komasa [34, 35] thanks to the development of effective optimization algorithms allowing the use of much larger ECG bases than before. In the next years, the most accurate values of the H_2 binding energy were those from ECG calculations, with estimated uncertainties below one nanohartree [36]. In time, these results were improved by Sims and Hagström [37] and by Nakatsuji and collaborators [38, 39] who employed large exponential basis sets and extended numerical precision packages. Little later, Cencek and Szalewicz [40] increased the accuracy up to $8 \cdot 10^{-14}$ a.u. using 4800 ECG basis function and obtained $E(R = 1.4) = -1.174\,475\,714\,220\,363$ a.u., the most accurate energy obtained from the ECG functions until now. It required the implementation of algorithms going beyond the standard double-precision arithmetic, which drastically increased the costs of computer calculations. The ECG results in Ref. [40] confirm that the analytical deficiencies of ECG functions are not critical for non-relativistic energies and can be compensated by thoroughly optimizing the nonlinear parameters to achieve a fast basis set convergence. It is a consequence of the completeness of the ECG basis set [41, 42].

2.1.3 Exponential wave functions

Significant progress in the development of the methods based on exponential wave functions has been made by Pachucki in 2010 [43, 44]. He constructed analytic formulas and recursion relations for two-center integrals that comprise matrix elements in exponential functions with arbitrary polynomials in all interparticle distances [45]. For short- and middle-range internuclear distances Pachucki employed the James-Coolidge basis and, for long-range, the generalized Heitler-London basis. With the wave function expanded in about 22 thousand basis functions, he achieved the BO energy with the numerical precision of 10^{-15}, thus outweighing the competition between different methods in favor of the exponential functions benchmarking nonrelativistic energy BO calculations. His achievement remains the most accurate energy ever obtained for any neutral molecule. Later, this approach has successfully been applied also in BO calculations on excited states of H_2 (see Sec. 2.1.4). These wave functions were applied to precisely determine adiabatic and nonadiabatic corrections

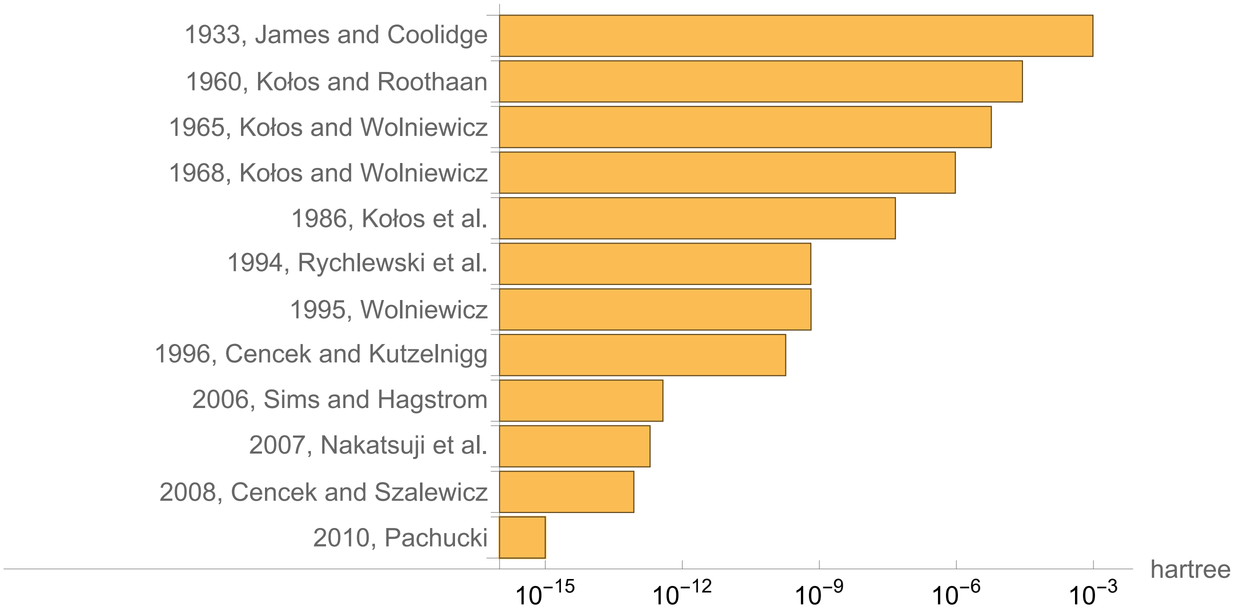


Figure 1: Energy error of the Born-Oppenheimer interaction energy in H_2 at the internuclear distance $R = 1.4$ bohr.

to the BO energy of hydrogen molecule isotopologues (see Sec. 2.2.3). Figure 1 summarizes the progress in reducing the error in the BO interaction energy observed over the years.

The most important implication of the high accuracy offered by both the Gaussian and exponential wave functions was a strong impulse for their applications in competition with the precise spectroscopic measurements of the hydrogen molecule. This direction has dominated the development of theoretical and computational methods for many years and resulted in the accurate determination of adiabatic, non-adiabatic, relativistic and QED corrections to the BO potential; see sections below.

2.1.4 Electronically excited states

Kołos-Wolniewicz wave functions were applied to determine BO potential energy curves for many electronically excited states. An extensive review of such calculations performed by Kołos, Wolniewicz, Rychlewski, and their coworkers before 2003 can be found in [36].

Pachucki and coworkers constructed a new method involving the exponential basis functions and again approached the problem of electronically excited BO energy curves. The culmination of these works was presented in recent articles by Pachucki, Siłkowski, *et al.* [46–48]. Relying on efficient evaluation of two-center integrals in Kołos-Wolniewicz basis, they obtained state-of-the-art BO energy curves for the manifold of electronically excited states: 1-7 $^{1,3}\Sigma^+_{g,u}$, 1-4 $^{1,3}\Pi_{g,u}$, 1-3 $^{1,3}\Delta_{g,u}$, 1-3 $^{1,3}\Phi_{g,u}$. The accuracy of new energy curves surpassed all the previous results [49,50] by several orders of magnitude. What is worth emphasizing is the flexibility of the unrestricted Kołos-Wolniewicz basis set used in these calculations, which, combined with thorough optimization, allows the efficient application of this basis for all – very short, medium, and very long – internuclear distances, regardless of the symmetry and spin of the electronic state.

The ECG wave function has also been successfully applied in evaluating the excited states of H_2. To mention a few: calculations of the double-well potential of EF $^1\Sigma^+_g$ state [51] and calculations of doubly-excited states of $^{1,3}\Sigma^-_{g,u}$ symmetry. The latter states are known to play an important role in the dissociative recombination of H_2^+ and have so far eluded experimental observation. Therefore, most information concerning such states' location comes from quantum-mechanical computations.

2.2 Adiabatic and nonadiabatic corrections

2.2.1 James-Coolidge and Kołos-Wolniewicz wave functions

Calculations of the adiabatic correction, also known as diagonal correction for the nuclear motions, in the basis set of James-Coolidge or Kołos-Wolniewicz do not have such a long history as the calculations of the Born-Oppenheimer potential. The first calculation was performed by Kołos and Wolniewicz in 1964 [16] using the same basis set expansion as in the calculations of the Born-Oppenheimer potential in terms of the James-Coolidge functions. At the potential minimum, the adiabatic correction contributed 4.947 cm^{-1} to the well depth. Surprisingly, these calculations' results were considered sufficiently converged for the next twenty years. Only in 1983 Wolniewicz [52] revisited these results. It turned out that around the minimum, they were very well converged but needed improvements for distances smaller than 0.55 bohr and larger than 2.20 bohr. Better converged calculations were reported in 1993 by Kołos and Rychewski with a carefully optimized basis set used in the Born-Oppenheimer calculations [26]. The calculated contribution to the binding energy was 4.938 cm^{-1}, i.e. 0.18% lower than the result from 1964. The same year Wolniewicz [27] confirmed the result of Kołos and Rychlewski.

2.2.2 Born-Handy method

In 1997 ECG geminals were employed by Cencek and Kutzelnigg [53] to evaluate the adiabatic correction at $R = 1.4$ bohr using the approach popularized by Handy [54]. Within this approach, called Born-Handy method, the adiabatic correction is computed as the expectation value of the nuclear kinetic energy operator expressed in laboratory coordinates. The accuracy of such calculations has been analyzed for the ground state of H_2 in Ref. [53]. The optimum choice of $\Delta R_I = 0.0005$ bohr allows obtaining 6–7 correct digits. For H_2, this method was at least as accurate as that using Kołos-Wolniewicz wave functions. The Born-Handy method has also been applied to evaluate the adiabatic corrections of the EF $^1\Sigma_g^+$ state of H_2 [51].

2.2.3 Nonadiabatic Perturbation Theory

The classic calculations of adiabatic and nonadiabatic corrections by Kołos and Wolniewicz were based on the Born-Huang expansion in which the total wave function is represented as a sum of products of eigenfunctions of the electronic Hamiltonian and suitable nuclear functions. $\phi(\mathbf{r},\mathbf{R}) = \sum_k \phi_{\mathrm{el},k}(\mathbf{r};\mathbf{R})\ \chi_k(\mathbf{R})$. In contrast, the nonadiabatic perturbation theory (NAPT), formulated in 2008 by Pachucki and Komasa [55, 56], takes the total wave function as a sum of a single adiabatic product and the nonadiabatic correction obeying specific orthogonality conditions. The adiabatic correction can be considered as the first-order correction in the electron-to-nucleus mass ratio. The higher order corrections can be found by evaluation of the nonadiabatic version of the Schrödinger equation derived in the frameworks of NAPT

$$\left[-\frac{1}{R^2}\frac{\partial}{\partial R}\frac{R^2}{2\,\mu_\parallel(R)}\frac{\partial}{\partial R} + \frac{J\,(J+1)}{2\,\mu_\perp(R)R^2} + \mathcal{Y}(R)\right]\tilde{\chi}_J(R) = E\,\tilde{\chi}_J(R). \tag{4}$$

The finite nuclear mass effects appear in this equation as R-dependent corrections to the nuclear reduced mass, $\mu_\parallel(R)$ and $\mu_\perp(R)$, and to the interaction potential $\mathcal{Y}(R) = \mathcal{E}_{\mathrm{el}}(R) + \mathcal{E}_{\mathrm{a}}(R) + \mathcal{E}_{\mathrm{na}}(R)$. The relativistic and QED potentials can further augment this internuclear potential. In such a case, the eigenvalue of the Schrödinger equation (4) accounts for all the leading corrections resulting from the finite nuclear mass and the finite speed of light, and should be directly comparable to the experimental value. This method, in connection with the ECG wave function, was applied to obtain all the bound energy levels of the hydrogen molecule [56–58].

Several years later, NAPT was reformulated in the language of the matrix elements in the JC basis [59, 60]. Such matrix elements are expressible by combinations of the closed-form integrals derived by Pachucki in 2009 [45]. This method enabled the relative accuracy of 10^{-12} to be reached for the adiabatic correction, which surpassed all the previous results by several orders of magnitude, see Table 1. The contribution of the adiabatic correction numerical uncertainty to the overall error of rovibrational energy levels was estimated as less than $10^{-9}\,\mathrm{cm}^{-1}$ [59].

Table 1: Illustration of the increase in accuracy of the adiabatic correction since the first estimates were published. The adiabatic correction to the interaction BO potential is defined with respect to the separated atoms limit.

Year	Reference	$\mathcal{E}_{\mathrm{a}}(1.4)$/a.u.
1936	Van Vleck [61]	0.954
1964	Kołos and Wolniewicz (JC) [16]	0.958 926
1993	Kołos and Rychlewski (KW) [26]	0.958 691
1993	Wolniewicz (KW) [27]	0.958 683
1997	Cencek and Kutzelnigg (ECG) [53]	0.958 684 72
2009	Pachucki and Komasa (ECG) [56]	0.958 684 14
2014	Pachucki and Komasa (JC) [59]	0.958 684 725 430

The radial nonadiabatic Schrödinger equation derived in the framework of NAPT (4) contains, apart from the clamped nuclei $\mathcal{E}_{\mathrm{el}}(R)$ and adiabatic correction $\mathcal{E}_{\mathrm{a}}(R)$ potentials, other five nonadiabatic, second-order potentials proportional to $1/\mu_{\mathrm{n}}^2$. In 2015 these potentials were reevaluated to a much higher accuracy using JC wave functions [60]. The convergence study performed at fixed internuclear distances revealed a relative accuracy better than 10^{-9} for all these potentials which resulted in 10^{-7} cm^{-1} uncertainty contribution to the energy of rovibrational levels, see Table 2. The third-order nonadiabatic correction has been derived in [60] but has never been evaluated numerically. Its rough numerical estimation can be obtained by a simple scaling of the second-order correction by the mass factor $1/\mu_{\mathrm{n}}$. The missing third- and higher-order corrections remained the primary source of uncertainty in the energy of nonrelativistic rovibrational levels until this energy was evaluated in a direct manner (DNA), i.e. without the expansion in mass factor as described in the next section. The DNA calculations also allowed the estimations mentioned above to be positively verified.

Table 2: The leading-order nonadiabatic corrections to the dissociation energy of the lowest rovibrational levels of the hydrogen molecule.

(v, J)	$\Delta D_{0,0}/\mathrm{cm}^{-1}$
$(0, 0)$	0.433 961 8(1)
$(0, 1)$	0.440 635 4(1)
$(0, 2)$	0.453 975 4(1)
$(0, 3)$	0.473 967 5(1)

2.3 Direct nonadiabatic calculations

This section reviews methods that do not assume the separation of electronic and nuclear degrees of freedom. In such an approach, the notion of the potential energy curve is no longer used, and both the Hamiltonian and the wave function treat all the four particles the hydrogen molecule is built of on equal rights. The four particles are entangled and described by a single state vector, a solution to the four-body Schrödinger equation. The eigenvalue corresponding to this state vector directly gives the nonadiabatic energy of a rovibrational level. We assigned such methods the acronym DNA for direct nonadiabatic.

2.3.1 Kołos and Wolniewicz calculations

To the best of our knowledge, the only full nonadiabatic calculations based on the Born-Huang expansion were carried out in 1963 [62] with the full nonrelativistic four-particle Hamiltonian and in a basis set of products of harmonic oscillator functions for the vibrational motions and James-Coolidge functions for the electronic motions. The electronic part was taken from the work of Kołos and Roothaan [15]. It consisted of 40 terms with an exponent that did not depend on the interatomic distance, and four consecutive harmonic oscillator functions with vibrational quantum numbers ranging from zero to three. The resulting dissociation energy was 27 cm^{-1} above the experimental value. Given the fact that the relativistic effects contribute only ca. 0.6 cm^{-1} to the dissociation energy, this relatively large discrepancy between theory and experiment is probably due to the short expansion of the nonadiabatic wave function and lack of flexibility of the electronic basis.

2.3.2 Nonadiabatic explicitly correlated Gaussian wave functions

The hydrogen molecule is a special case of the four-body problem, where the two atomic nuclei have large masses. It requires the introduction of pre-factors in a variational basis, which enable modeling of the oscillatory motion of the nuclei around the characteristic distance corresponding to the length of the bond. In 1999, Kinghorn and Adamowicz [63] proposed a nonadiabatic basis explicitly correlated Gaussian (naECG) basis for rotationless states of small "diatomic" systems. The basis functions are of the form, $\phi = r_1^m e^{-\vec{r}'\bar{A}\vec{r}}$ with an additional pre-factor multiplying factor r_1^m , the m-th power of the distance between the two heavy particles, hence the approach is restricted to diatomics with any number of electrons. The exponential factor provides a full correlation between all system particles. The challenge here was the need to develop methods for calculating fully correlated integrals that take into account the arbitrary power of the internuclear distance as well as finding the distribution of discrete m-parameters. An indicator of the high accuracy of the 2003 calculations was the upper bound for the H_2 nonrelativistic nonadiabatic ground state energy equal to $-1.164\,025\,030\,0$ hartree using 3000 basis functions and, analogously for excited rotationless states, i.e., states represented by spherically symmetric wave functions [64].

Another representation of the naECG basis functions ϕ has been used in DNA calculations since 2018 [65]

$$\phi = r_{01}^n \, e^{-a_1 r_{01}^2 - a_2 r_{02}^2 - a_3 r_{03}^2 - a_4 r_{12}^2 - a_5 r_{13}^2 - a_6 r_{23}^2} \, , \tag{5}$$

where 0 and 1 denote nuclei and 2 and 3 electrons. For the rotational quantum number $J = 1$ the functions ϕ were modified by the factor $\vec{r}$, representing the angular momentum. The nonlinear a_i parameters were optimized individually for each basis function ϕ. Also, the powers n of the internuclear coordinate r_{01} and the shares of different angular momentum factors $\vec{r}_{ab}$ were subject to additional discrete optimization. The nonrelativistic wave function was constructed for several basis lengths to observe the numerical convergence of the energy. The obtained results reached the accuracy of about 10^{-11} (see Table 3) and were in perfect agreement with the benchmark values from the nonadiabatic James-Coolidge (naJC) wave function [66] described below. In comparison to former works based on a different representation of ECG functions [67], the efficient optimization algorithm enabled obtaining more accurate results despite using approximately five times smaller basis set. The naECG wave function was further employed in the evaluation of the relativistic correction, see Sec. (3.3).

Table 3: 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 [68–70].

Basis size	$E(H_2)$	$E(HD)$	$E(D_2)$
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)

2.3.3 Nonadiabatic James-Coolidge wave functions

The direction set forward by Kołos and Wolniewicz in 1963 [62, 71] was based on the use of exponential functions in four-body calculations. Due to apparent technical difficulties, their idea was abandoned for half a century. New perspectives opened after Pachucki's discovery in 2009 [45] of a differential equation satisfied by any integral of the Hamiltonian matrix elements in a four-body exponential basis. With the newly proposed exponential-type basis functions the Hamiltonian matrix elements became expressible in a closed form only in terms of logarithmic, dilogarithmic, and rational functions ensuring high accuracy and efficiency of calculations.

The newly proposed basis function was of the form [66]

$$\phi_{\{k\}} = \exp\left[-\alpha\, R - \beta(\zeta_1 + \zeta_2)\right] R^{k_0}\, r_{12}^{k_1}\, \eta_1^{k_2}\, \eta_2^{k_3}\, \zeta_1^{k_4}\, \zeta_2^{k_5}\,, \tag{6}$$

where the parameters α, and β are positive real numbers, whereas k_i are nonnegative integers, and where the elliptic-type variables are defined as follows $\zeta_1 = r_{1A} + r_{1B}$, $\eta_1 = r_{1A} - r_{1B}$, $\zeta_2 = r_{2A}+r_{2B}$, $\eta_2 = r_{2A}-r_{2B}$, $\vec{R} = \vec{r}_{AB}$. This basis function was named the nonadiabatic James-Coolidge (naJC) function for its resemblance to the original James-Coolidge (JC) basis function used in fixed-nuclei calculations. In contrast to JC function, the four-body nonadiabatic function contains an internuclear correlation factor, and the meaning of the ζ and η variables is different.

Evaluation of matrix elements in the naJC basis presents a serious programming challenge for two reasons. First, this basis, although very efficient from a physical point of view, forms a nearly linearly-dependent set of functions. This fact forces the use of multiple (octuple or higher) precision arithmetic software, which radically increases operating memory requirements and slows down the execution of the computer program. Second, large basis sets (of the order of 10^5) need to be employed to achieve the target precision, which calls for effective code parallelization. Despite the struggles with limitations in available computational resources, high-accuracy solutions to the Schrödinger equation for the hydrogen molecule and its isotopologues were obtained [68–70, 72].

The accuracy achievable using the naJC basis can be assessed by inspecting the energy convergence with the growing size of the wave function expansion, K. The so-called 'shell parameter' Ω, which limits from above the sum $\sum_{i=1}^{5} k_i$ of integer powers in Eq. (6), is a practical guide for such an inspection. As shown in Table 4, the relative numerical accuracy of an eigenvalue can reach the level of 10^{-14} [66, 68]. Further increase in accuracy is still possible but impractical. The nonrelativistic energies quoted in the table were evaluated with the proton-to-electron mass ratio μ_p recommended in CODATA 2018 [73] compilation of physical constants. At the achieved level of accuracy, the significant digits of the eigenvalues are sensitive to changes in physical constants; therefore, it is crucial to accompany the reported energy with the actually used values of nuclear masses. Recomputing the energies every time the recommended nuclear masses change would be impractical. To avoid this, the published energy of each rovibrational level is accompanied by derivatives with respect to nuclear mass parameters. It is demonstrated in Table 5 for HD molecule [69]. Using these

Table 4: Convergence of the $E_{0,0}$ (in a.u.) eigenvalue for H_2 with the growing size of the basis set, K. The CODATA 2018 proton mass was used $\mu_\mathrm{p} = 1836.152\,673\,43(11)$.

Ω	K	$E_{0,0}$
10	42588	$-1.164\,025\,030\,873\,423$
11	61152	$-1.164\,025\,030\,879\,839$
12	85904	$-1.164\,025\,030\,881\,369$
13	117936	$-1.164\,025\,030\,881\,709$
14	159120	$-1.164\,025\,030\,881\,803$
15	210912	$-1.164\,025\,030\,881\,831$
∞	∞	$-1.164\,025\,030\,881\,85(2)$

derivatives one can easily update the energy. The DNA method based on the naJC wave function outperforms the calculations with ECG wave function by several orders of magnitude in accuracy. It can be shown in the example of D_2 molecule in Table 6. As mentioned in Sec. 2.2.3, the accuracy of the nonrelativistic energy offered by the NAPT is limited by the cutoff of the perturbation series. Currently, NAPT is implemented to the second order. The missing higher-order terms are the source of the method's uncertainty. The results obtained using the DNA method correspond to the infinite-order NAPT expansion, which gives the opportunity to determine the contribution from the higher-order NAPT terms. Such calculations were reported in [70] and [72] and revealed

Table 5: Nonadiabatic eigenvalue ($E_{v,J}$) of the selected rovibrational energy levels of HD. The μ_n is the nucleus-to-electron mass ratio, with $n = p, d$.

(v, J)	$E_{v,J}$/hartree	$\frac{\partial E_{v,J}}{\partial \mu_\mathrm{p}} \cdot 10^6$	$\frac{\partial E_{v,J}}{\partial \mu_\mathrm{d}} \cdot 10^6$
$(0, 0)$	−1.165 471 923 964 39(3)	−1.69	−0.424
$(0, 1)$	−1.165 065 376 941 65(3)	−1.84	−0.459
$(0, 2)$	−1.164 255 083 090 94(3)	−2.13	−0.533
$(1, 0)$	−1.148 922 593 494 61(3)	−4.54	−1.14
$(1, 1)$	−1.148 533 615 356 71(3)	−4.68	−1.17
$(1, 2)$	−1.147 758 378 109 83(3)	−4.95	−1.24
$(2, 0)$	−1.133 181 743 156 29(4)	−7.11	−1.78
$(2, 1)$	−1.132 809 980 890 48(6)	−7.23	−1.81
$(2, 2)$	−1.132 069 097 950 27(6)	−7.49	−1.87
$(3, 0)$	−1.118 233 513 220 64(5)	−9.39	−2.35

Table 6: Comparison of the best literature data for the nonrelativistic dissociation energy $D_{0,0}$ of D_2.

Year	Method and reference	$D_{0,0}/\mathrm{cm}^{-1}$	Difference/cm^{-1}
2019	naJC [70]	36 749.090 989 81(1)	
2018	2048-term naECG [65]	36 749.090 970	$2.0 \cdot 10^{-5}$
2015	NAPT [60]	36 749.090 976	$1.3 \cdot 10^{-5}$
2011	10000-term naECG [74]	36 749.090 974	$1.6 \cdot 10^{-5}$

that the missing higher-order remainder is of the order of 10^{-5} cm^{-1} and, within given vibrational state, changes proportionally to $J(J+1)$.

The nonadiabatic effects are the smallest in the heaviest isotopologues, i.e., those containing triton: HT, DT, and T_2. However, even in this favorable case the DNA method in connection with the naJC wave function enabled reducing the error in the nonrelativistic energy by 2-3 orders of magnitude compared with NAPT results. Moreover, the error in the total energy, primarily dominated by the nonrelativistic component, was reduced by order of magnitude [72]. It is well exemplified in Table 7 for the case of transition energies in T_2.

Table 7: Comparison of theoretical data for the fundamental $v = 0 \to 1$ vibrational splitting of selected transition lines in T_2 (in cm^{-1}). The results shown in the second column were obtained entirely from NAPT calculations [75], whereas those in the third column contain analogous results, but the nonrelativistic energy was replaced by that from the DNA calculations.

Line	NAPT	DNA+NAPT
Q(0)	2 464.504 15(6)	2 464.504 142(8)
Q(1)	2 463.348 36(6)	2 463.348 350(8)
Q(2)	2 461.039 17(6)	2 461.039 163(8)
Q(3)	2 457.581 37(6)	2 457.581 366(8)

To summarize the struggles toward accurate determination of the nonrelativistic dissociation energy of the hydrogen molecule we have assembled selected representative results in Table 8.

3 Relativistic corrections

3.1 Kołos and Wolniewicz calculations

The investigations of the relativistic effects in the hydrogen molecule started in 1961. Kołos and Wolniewicz [78,79] derived the expressions for the relativistic integrals in the James-Coolidge basis contributing to the matrix elements of the Breit-Pauli Hamiltonian [80]. These expressions were coded and used in the calculations of the relativistic corrections to the Born-Oppenheimer potential in 1964 [16] obtaining -0.526 cm^{-1} as the contribution to the well depth. In the same year, Kołos and Wolniewicz [71] performed nonadiabatic calculations with the full four-particle nonrelativistic

Table 8: Comparison of the accuracy of the nonadiabatic dissociation energy achieved over the decades of the theoretical studies on H_2.

Reference	$D_{0,0}/\mathrm{cm}^{-1}$
H_2	
Pachucki, Komasa 2018, DNA/naJC [68]	36 118.797 746 10(3)
Pachucki, Komasa, 2015, NAPT/JC [60]	36 118.797 675
Pachucki, Komasa, 2009, NAPT/ECG [56]	36 118.797 8
Kinghorn, Adamowicz, 1999, ECG [63]	36 118.797 74
Wolniewicz, 1995, KW [76]	36 118.795
Kołos, Szalewicz, Monkhorst, 1986, KW [25]	36 118.088
Wolniewicz, 1983 KW [27]	38 118.01
Bishop, Cheung, 1978, JC [77]	36 118.60
Kołos, Wolniewicz, 1964, JC [71]	36 114.7
Kołos, Wolniewicz, 1963, JC [62]	36 091

Hamiltonian and including the electronic part of the relativistic Breit-Pauli Hamiltonian. The basis set used in the calculations consisted of products of the harmonic oscillator functions for the vibrational motions and James-Coolidge functions for the electronic motions leading to dissociation energies larger by 0.6 cm^{-1}, again in contradiction with the variational principle. Surprisingly, the relativistic calculations for H_2 in the James-Coolidge or Kołos-Wolniewicz basis functions were not attempted till 1993, when Wolniewicz [27] derived the relativistic integrals for the KW basis with a completely new algorithm. It turned out that despite very carefully optimized basis functions and much longer basis set expansions, the result did not dramatically change compared to the 1964 paper [16], and the contribution to the binding energy amounts to -0.517 cm^{-1}, i.e., changed by less than 2%.

3.2 Relativistic correction in NAPT

In 2009 there was a new opening in this matter when ECG functions were employed to evaluate the relativistic matrix elements [57, 58]. In the BO approximation, the leading relativistic correction is that to the nonrelativistic potential $\mathcal{E}(R)$. This correction can be expressed in terms of the expectation value $\mathcal{E}_{\rm rel}(R) = \langle\phi_{\rm el}|H_{\rm rel}|\phi_{\rm el}\rangle$ of the Breit-Pauli Hamiltonian [80]

$$\begin{aligned} H_{\rm rel} \;&=\; -\frac{1}{8}\big(p_1^4+p_2^4\big) + \pi\,\delta^3(r_{12}) - \frac{1}{2}\,p_1^i\left(\frac{\delta^{ij}}{r_{12}}+\frac{r_{12}^i\,r_{12}^j}{r_{12}^3}\right)p_2^j \\ &\quad +\frac{\pi}{2}\big(\,\delta^3(r_{1A})+\delta^3(r_{2A})+\delta^3(r_{1B})+\delta^3(r_{2B})\big), \end{aligned} \tag{7}$$

where the spin dependent terms vanish for the electronic states of ${}^1\Sigma$ symmetry.

Highly singular operators, Dirac-δ and p^4, present in the Hamiltonian (7) require special attention if relativistic correction of high accuracy is to be obtained. The expectation value of these operators converges very slowly with the increasing expansion size of a wave function. This effect is especially noticeable when ECG-type functions are used. For that reason, regularization schemes have been developed, which speed up the convergence significantly [81, 82]. Apart from the standard regularization, applied already by Wolniewicz [27], an original regularization, dedicated to wave functions obeying the Kato's cusp condition, has been proposed [83]. Such ECG functions, with the $1+r_{12}/2$ prefactor were introduced in 2016 and nicknamed rECG. A novel algorithm for numerical quadrature of non-standard ECG two-center integrals has been worked out [83]. Apart from the fast convergence, the new regularization scheme has additional advantages. Firstly, it enables complete elimination of the $\pi\,\delta^3(r_{12})$ term from the relativistic Hamiltonian; secondly, a whole class the time-consuming integrals with three odd powers of interparticle distances do not appear in the matrix elements. This non-trivial cancellation has a remarkable impact on the efficiency of the calculations [84].

The leading finite-nuclear-mass relativistic correction has been derived and evaluated numerically using NAPT. The so-called relativistic recoil potential $\mathcal{E}^{(4,1)}(R)$ has been reported in Ref. [85]. The error contributed by the potential is estimated to be $2\cdot 10^{-4}\cdot\langle\chi|\mathcal{E}^{(4,1)}|\chi\rangle$. Thus far, no higher-order finite-nuclear-mass relativistic corrections are known, the effect of their omission is approximated by $E^{(4,1)}\cdot m_{\rm e}/\mu_{\rm n}$ and included in the total $E^{(4)}$ error estimate.

3.3 Relativistic correction in DNA approach

In DNA, the relativistic correction to the energy of a rovibrational level can be expressed in terms of the expectation value of the four-particle Breit-Pauli Hamiltonian

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

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 also omitted the $p_x^4/(8\,m_x^3)$ terms because their numerical values are smaller than the uncertainty of the whole relativistic correction. As in NAPT, regularization techniques and the cusp obeying rECG wave functions are mandatory to achieve high-accuracy results [65, 86]. Table (9) shows how the total relativistic correction $E^{(4)}$ changed over time when evaluated using two different approaches, NAPT and DNA.

Table 9: Representative results showing the accuracy of the relativistic correction to the dissociation energy of H_2 achieved using various wave functions and methods.

Reference	$E_{\mathrm{rel}}/\mathrm{cm}^{-1}$
NAPT	
Kołos and Wolniewicz (1964), JC [71]	−0.5
Wolniewicz (1993), KW [27]	−0.533 0
Piszczatowski *et al.* (2009), ECG [57]	−0.531 9(2)
Komasa *et al.* (2011), ECG [58]	−0.531 8(2)
Czachorowski *et al.*, (2018), ECG [85]	−0.531 213(2)
DNA	
Stanke *et al.* (2013), naECG [87]	−0.569 1
Wang and Yan (2018), naHy [88]	−0.531 255(63)
Puchalski *et al.* (2018), naECG [86]	−0.531 215 6(5)

4 Quantum electrodynamic corrections

4.1 The complete leading QED correction

In 1993, Wolniewicz computed the quantum electrodynamic (QED) correction of H_2 in an approximate way [27]. The first complete, leading QED correction valid in BO approximation was derived and applied with ECG functions by Piszczatowski et al. in 2009 [57]. Subsequent studies aimed at improving the quality of such calculations [58]. The component limiting the accuracy of this correction is the so-called Bethe logarithm – a quantity for which exact values were known for a long time only for the hydrogen atom. The Bethe logarithm and the whole leading QED correction potential have recently been computed to a relative precision of 10^{-8} for an extensive range of internuclear distances by Siłkowski [89]. This potential has been implemented in the publicly available H2Spectre program [75, 90] and can be used in the evaluation of the QED correction for all the rovibrational levels.

Within the fully nonadiabatic approach, the complete formula for the leading QED correction $E^{(5)}$ was presented in [86, 91]. So far, however, numerical calculations have been reported only for the ground rovibrational levels of H_2 and its isotopologues.

4.2 Higher order QED corrections

The derivation of the $E^{(6)}$ term of the α-expansion (3) for H_2 was first reported in 2016 [83]. Calculations were performed only in the framework of the BO approximation. Because this term is represented by a sum of a first-order expectation value and a second-order quantity, both being divergent, a new technique of dimensional regularization to eliminate these divergences from the matrix elements had to be applied. Despite difficulties in its evaluation, the relative numerical accuracy of $3 \cdot 10^{-3}$ for this term has been achieved, and its contribution to $D_{0,0}(H_2)$ amounts to $-0.002\,065(6)\,\mathrm{cm}^{-1}$.

$E^{(7)}$ is the first term of the expansion of energy in powers of α whose explicit form for H_2 is not entirely known yet. Currently, it is approximated using dominating contributions known from the hydrogen atom theory. The first estimation of its magnitude appeared in 2016 [83]. For $D_{0,0}(H_2)$ the $E^{(7)} \approx 0.000\,118(59)\,\mathrm{cm}^{-1}$. Both the higher-order corrections, in the form of a function of internuclear distance, have been implemented in the H2Spectre program [75,90].

5 Theory *versus* experiment

Since the advent of the first theoretical predictions concerning physical observables of the hydrogen molecule – dissociation energy of the ground or excited levels or transitions between them – the reference to experimental data was treated as a mandatory check of the correctness and accuracy of such results. And *vice versa* – accurate theoretical results served as a verification tool for experimentalists. For over a century, a very fruitful competition between theory and experiment has been observed, resulting in continuous progress in both. The beginning of this competition was not very optimistic – in 1913, Niels Bohr theoretically estimated the dissociation energy of H_2 as 21 000 cm^{-1} [92] whereas Irving Langmuir's measurements gave over two times larger value of 46 000 cm^{-1} [93]. Since then, the theory-experiment gap has only narrowed, as exemplified by the famous story of the contradiction Kołos-Wolniewicz vs. Herzberg-Monfils, mentioned in Sec. 2.1, which ended with the reinterpretation of the experiment. Over the last century, the predictive power of theoretical methods and the precision of measurements have increased by several orders of magnitude. Only in the last decade, the advances in spectroscopic techniques enabled the experimental accuracy to be increased by three orders of magnitude. It is shown in Figure 2, which collects a selection of measurements performed for the hydrogen molecule and its isotopologues. It is a great challenge for the theory to keep up with this progress. The theory is expected not only to increase the accuracy of the leading components of the total energy but also to account for the unknown higher-order terms in the α-expansion (3). Although the contribution from such terms is relatively small and could have been neglected for some time, the progress on the experimental side and the consequent expectations placed upon the theory compel the study of these ever-smaller components.

An important physical quantity studied theoretically and experimentally is the dissociation energy of the rovibrational ground level, $D_{0,0}$. A survey of advances in determination of $D_{0,0}$ for H_2 covering period of 1926–2009 can be found in [94]. Here we shall quote a small sample of existing theoretical data contributed by Polish scientists, which illustrates the progress made in this field in juxtaposition with the recent experimental result.

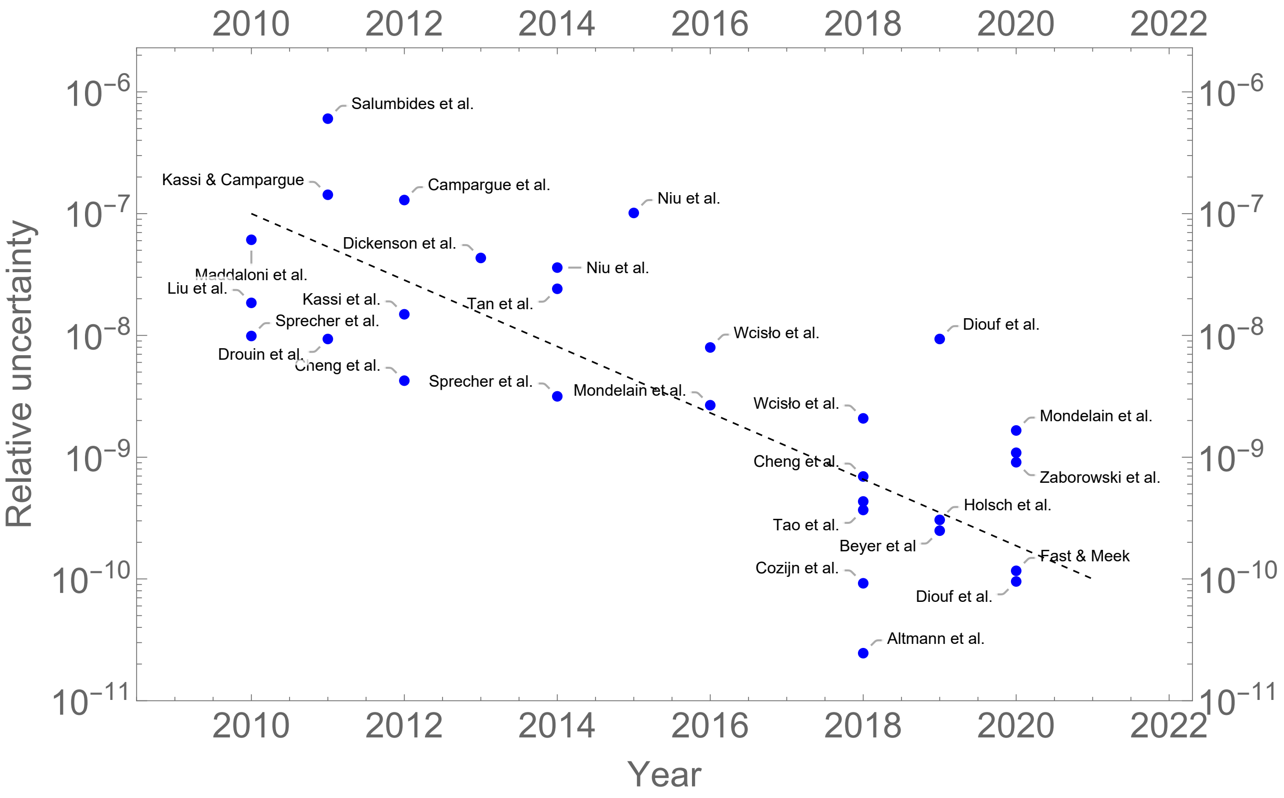


Figure 2: The relative uncertainty of spectroscopic experiments performed recently. The measurements concern a variety of observables – dissociation energy of rovibrational levels, transition energies, ionization potential – of all isotopologues of molecular hydrogen.

Table 10: Total dissociation energy $D_{0,0}$ of H_2 including nonrelativistic (NR), relativistic (REL), quantum-electrodynamic (QED), and higher-order QED (HQED) components. The meaning of the wave function symbols is as follows: JC – James-Coolidge, KW – Kołos-Wolniewicz, ECG – explicitly correlated Gaussian, naECG – nonadiabatic ECG, naJC – nonadiabatic JC. For comparison, the most accurate experimental $D_{0,0}$ is shown at the bottom of the table.

Year	Reference, components, wave function	$D_{0,0}/\text{cm}^{-1}$
1964	Kołos and Wolniewicz [71], NR+REL, JC	36 114.2
1983	Wolniewicz [52], NR+REL+QED, KW	36 118.01(1)
1986	Kołos, Szalewicz, Monkhorst [25], NR+REL, KW	36 118.088
1993	Wolniewicz [27], NR+REL, KW	36 118.060
1995	Wolniewicz [76], NR+REL, KW	36 118.069
2009	Piszczatowski *et al.* [57], NR+REL+QED, ECG	36 118.069 5(10)
2011	Komasa *et al.* [58], NR+REL+QED+HQED, JC+ECG	36 118.069 6(1)
2019	Puchalski *et al.* [86], NR+REL+QED+HQED, naJC+naECG+ECG	36 118.069 632(26)
2018	Altmann *et al.* [95], EXPERIMENT	36 118.069 45(31)

The agreement achieved between calculations and experimental results is not given once and for all. An excellent example is the dissociation energy of the lightest isotopologues of the hydrogen molecule, for which full compliance was achieved in 2010. However, after a dozen years, tightening the uncertainties on both sides of the competition has caused discrepancies to reappear, see Figure 3.

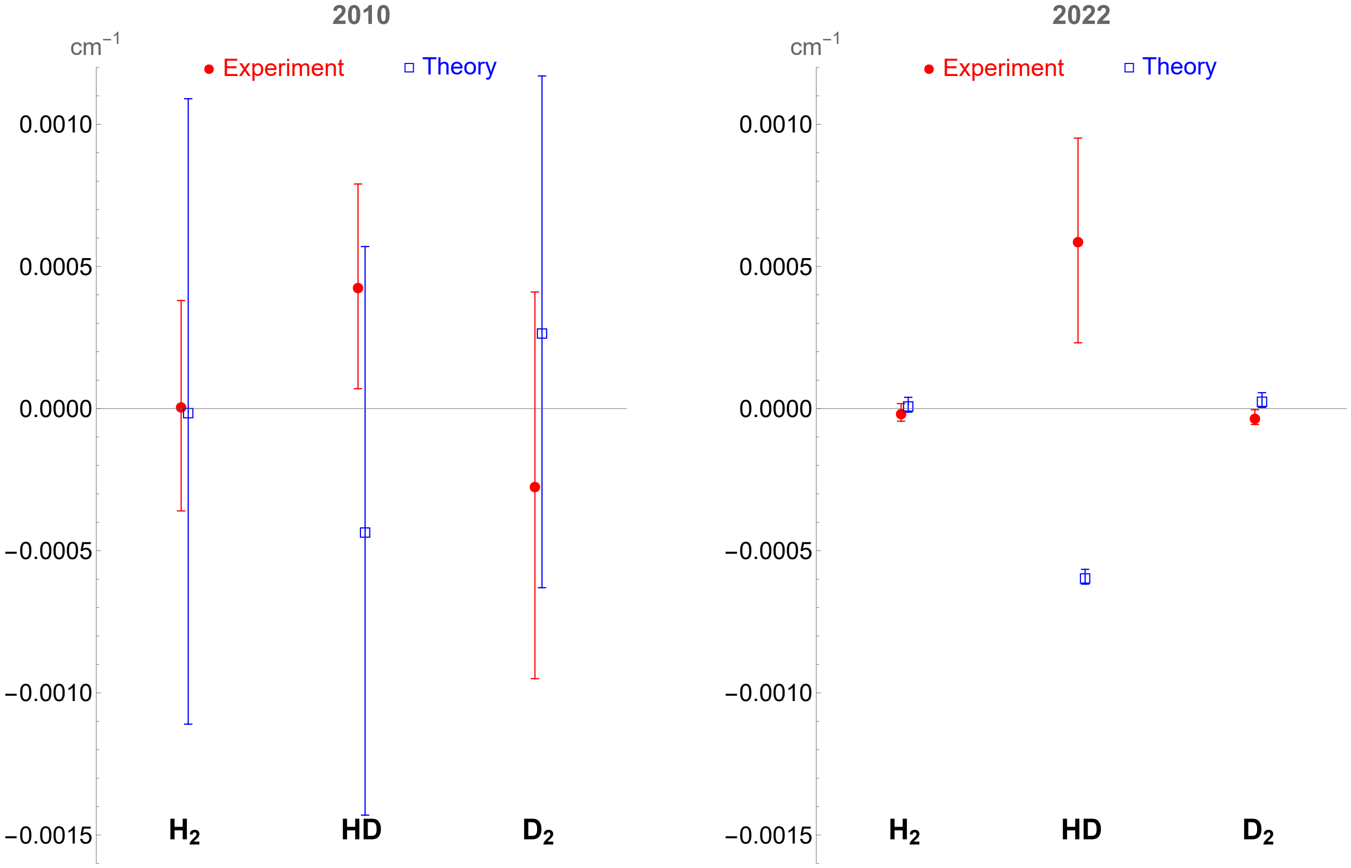


Figure 3: Changes in accuracy and agreement between theory [86,91,96] and experiment [10,97–99] of the dissociation energy $D_{0,0}$ of H_2, HD, and D_2 observed over the last decade. The zero level corresponds to the mean of the theoretical and experimental values.

In the further part of this section, we will present, in a tabular or graphical form, a comparison of theoretical and experimental results for the energy of rovibrational excitations in H_2, starting from the energetically lowest and ending with excitations to states close to the dissociation threshold. We will also show similar comparisons for other isotopic variations of the hydrogen molecule.

Table 11 shows the transition energy between the ground and the first rotationally excited level for three isotopologues H_2, HD, and D_2. Theoretical results were obtained using state-of-the-art methods and wave functions [86]. The experiments come from three different experimental research groups [10,97,100]. As inferred from the table, the differences fit in the combined uncertainties.

Figure 4, in turn, displays just the differences between theoretical [90] and experimental [101] results for the growing rotational quantum number, J, in the ground vibrational level of H_2. As can be seen, the theoretical uncertainty band fits within the experimental error bars. The only exception is the $J = 4$ dot, which lies outside the expected region for unknown reasons.

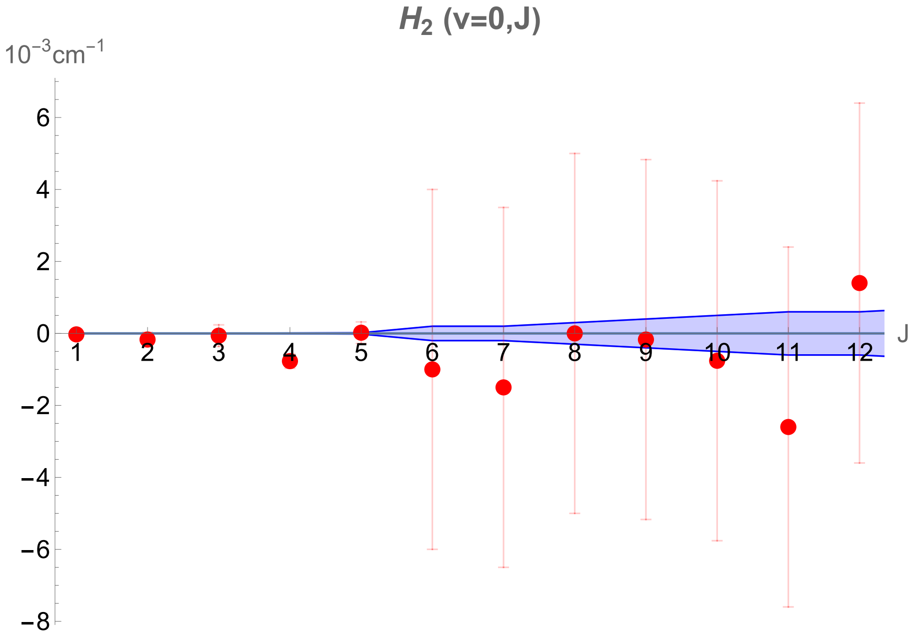


Figure 4: Difference between theory and experiment for the lowest rotational energy levels of H_2 (in units of $10^{-3}\,\mathrm{cm}^{-1}$). The blue band shows the range of theoretical uncertainties obtained in calculations using the H2Spectre program [90]. The red dots with error bars come from the experiment [101].

There is an agreement between theory and experiment at the level of $10^{-3}\,\mathrm{cm}^{-1}$ also for higher energy regions. It is demonstrated in Figure 5 and Table 12 referring to higher vibrational bands.

There is a growing number of experimental data on transition energies in heavier isotopologues of the hydrogen molecule, which enables simultaneous verification of calculations and measurements.

Table 11: Fundamental rotational splitting $(0,1) \rightarrow (0,0)$ in cm^{-1}. A comparison of calculated [86] and experimental [10, 97, 100] data.

	H_2	HD	D_2
Theory	118.486 812 7(11)	89.227 930 9(8)	59.780 615(3)
Experiment	118.486 770(50)	89.227 931 6(8)	59.781 30(95)
Difference	0.000 042(50)	−0.000 000 7(11)	−0.000 68(95)

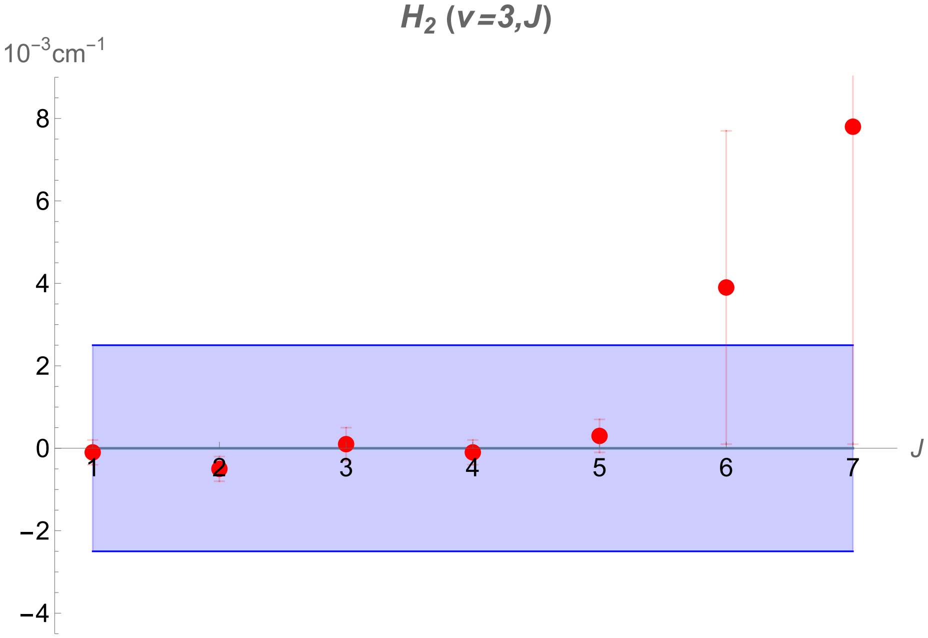


Figure 5: Difference between theory and experiment for the rotational energy levels ($J = 1 - 7$) of $v = 3 - 0$ vibrational band of H_2 (in units of $10^{-3}\,\mathrm{cm}^{-1}$). The blue band shows the range of theoretical uncertainties [102]. The red dots with error bars come from the experiment [103].

Table 12: Highly-excited vibrationally ($v = 11, 12$) rotational energy levels (in cm^{-1}, relative to the ground level) of H_2.

Level (v, J)	$(11, 1)$	$(11, 3)$	$(11, 4)$	$(11, 5)$
Theory [58]	32 937.7494(53)	33 186.4802(52)	33 380.1019(52)	33 615.5293(51)
Experiment [104]	32 937.7554(16)	33 186.4791(16)	33 380.1025(33)	33 615.5371(18)
Difference	0.0060(55)	−0.0011(54)	0.0006(62)	0.0078(54)
Level (v, J)	$(12, 0)$	$(12, 1)$	$(12, 2)$	$(12, 3)$
Theory [58]	34 302.1741(47)	34 343.8483(46)	34 426.2179(46)	34 547.3332(45)
Experiment [105]	34 302.1823(35)	34 343.8531(35)	34 426.2216(35)	34 547.3362(35)
Difference	0.008(6)	0.005(6)	0.004(6)	0.003(6)

Generally, the heavier the nuclei, the smaller the finite nuclear mass effect present in all the terms of α-expansion (3). Hence, the corresponding theoretical predictions usually have tighter uncertainties related to this effect. Table 13 exemplifies the level of agreement for in selected rovibrational transitions in D_2 molecule.

Advances in handling radioactive samples enabled accurate spectroscopic measurements of tritiated isotopologues of hydrogen molecule [108]. The current state of agreement between theory and experiment can be illustrated by Figure 6, which presents a comparison of the accuracy obtained

Table 13: Comparison of selected rovibrational transitions $(v', J') \to (v'', J'')$ in D_2. Theoretical line positions were obtained using H2Spectre program [90] whereas the experimental data come from [106, 107].

	$(1,0) \to (0,0)$	$(2,2) \to (0,2)$	$(2,2) \to (0,0)$	$(2,4) \to (0,2)$
Theory	2 993.617 048(9)	5 855.583 348(22)	6 034.650 446(24)	6 241.127 614(25)
Experiment	2 993.617 06(15)	5 855.583 358(14)	6 034.650 463(10)	6 241.127 637(17)
Difference	−0.000 01(15)	0.000 010(26)	0.000 017(26)	0.000 023(30)

in recent measurements [11, 109, 110] for the line positions in Q branch of the $v = 1 - 0$ band with the corresponding theoretical predictions [72].

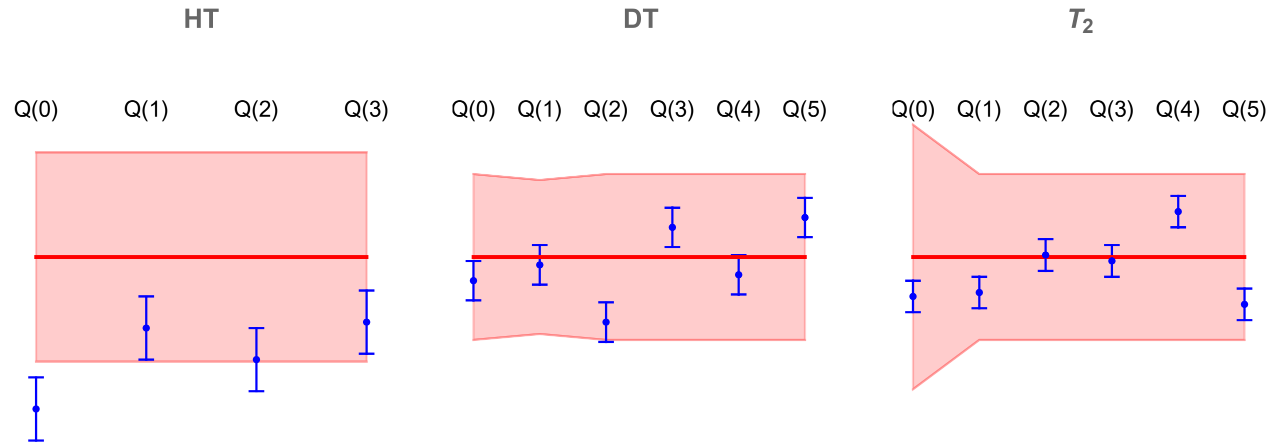


Figure 6: Differences between theory and experiment in the Q branch of the $v = 1 - 0$ band in HT, DT, and T_2. Theoretical results (blue dots with error bars) [72] superimposed on the experimental uncertainty band (in red) [110].

The increasing accuracy of both calculations and measurements can reveal discrepancies at a higher level. For instance, there is a systematic difference of ca. $6 \cdot 10^{-5}\,\mathrm{cm}^{-1}$($\approx 1.9$ MHz) between several observed and calculated line positions in HD molecule. A sample of such a discrepancy is depicted in Figure 7 for the $R_2(1)$ line, for which independent measurements agree with each other but differ with the theoretical value. Currently, the source of this discrepancy is unknown. The presumed cause may lie in the as-yet-unknown finite mass effects in the QED correction.

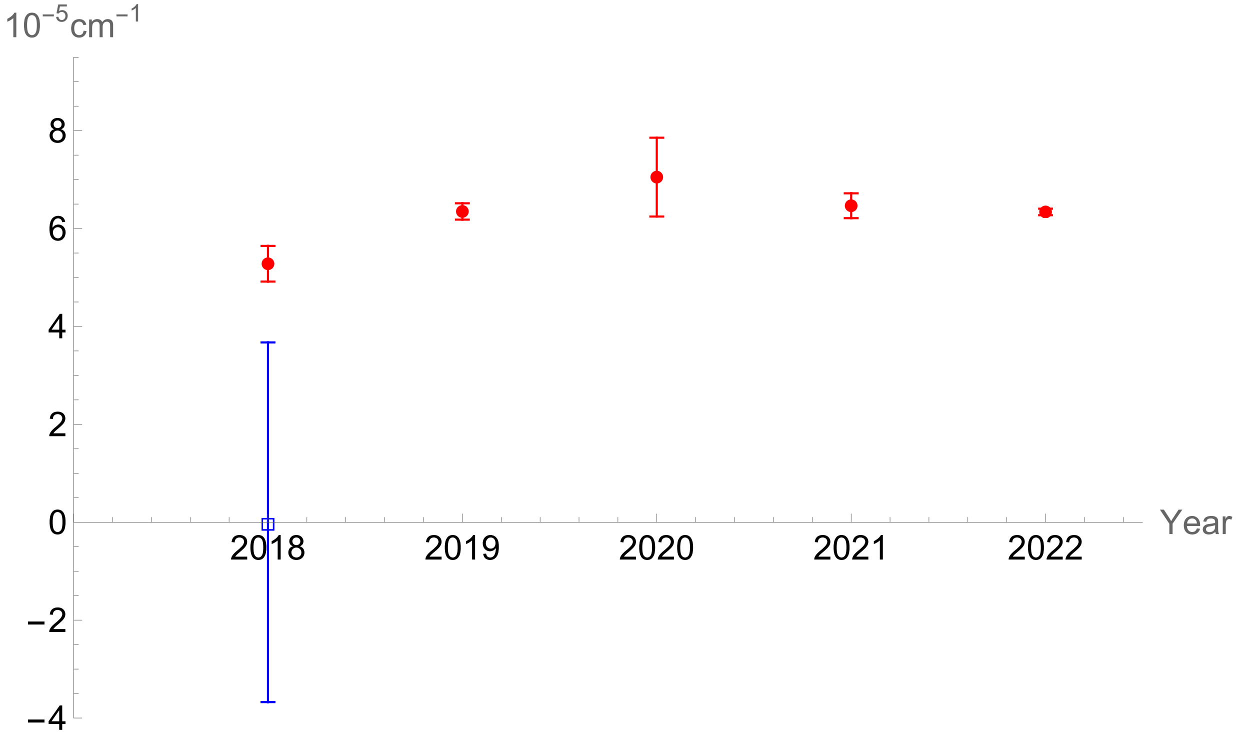
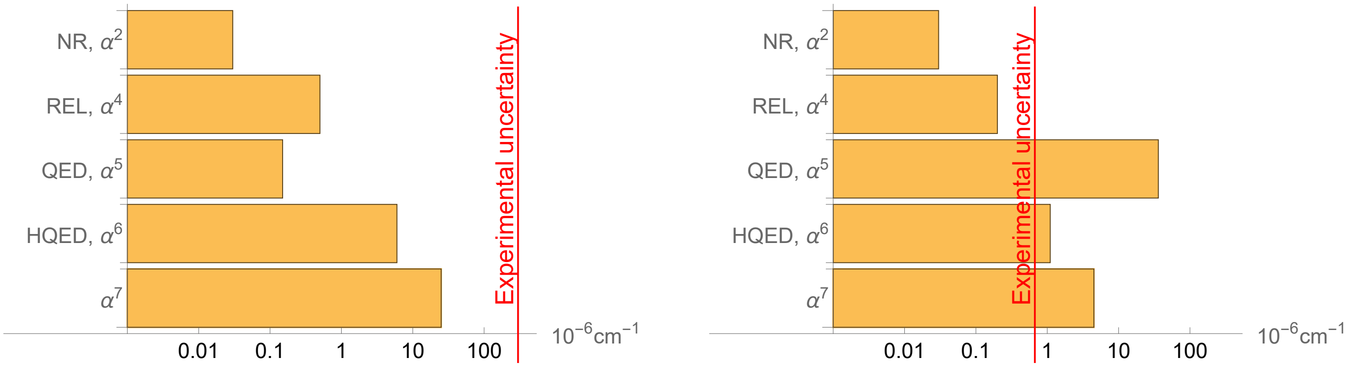


Figure 7: The discrepancy between theory and experiment in the $R_2(1)$ line position of HD. Theoretical result [85] (open blue square) is compared to the spectroscopic data (filled red circles) of several independent measurements [111–115].

6 Summary

The total theoretical energy of a bound rovibrational level of the hydrogen molecule is composed of terms defined in the α-power series, Eq. (3). The least accurate or cutoff terms of this series determine the accuracy of the total energy. Therefore, increasing the accuracy of the dominating terms has to be accompanied by accounting for subsequent smaller and smaller components of this series. For example, the accuracy of the theoretical dissociation energy of H_2 [86] is currently limited by the estimated uncertainty of the unknown correction of the order α^7; see Figure 8a. Another instance concerns the most accurately measured energy of the $R(1)$ transition of (2-0) vibrational band in HD. The line position is calculated as a difference between two rovibrational energy levels, and its uncertainty accounts for the cancellation of errors of individual contributions. In this case, the total uncertainty is dominated by the uncertainty of the QED term; see Figure 8b. These two examples show where the current studies should concentrate on to make further progress.

In this article, we have presented an overview of research conducted by Polish scientists aimed



(a) Uncertainties of the components of the dissociation energy $D_{0,0}$ of H_2.

(b) Uncertainties of the components of the $R(1)$ transition energy of (2-0) vibrational band in HD.

Figure 8: Examples of state-of-the-art uncertainties of the components of selected observables.

at constructing methods for a more and more accurate description of the electronic structure of the hydrogen molecule. Studies initiated by Włodzimierz Kołos over 60 years ago were continued by the next generations of researchers at the Universities of Warsaw, Toruń, and Poznań. The timeline of the most significant events related to the development of such methods is summarized in Figure 9.

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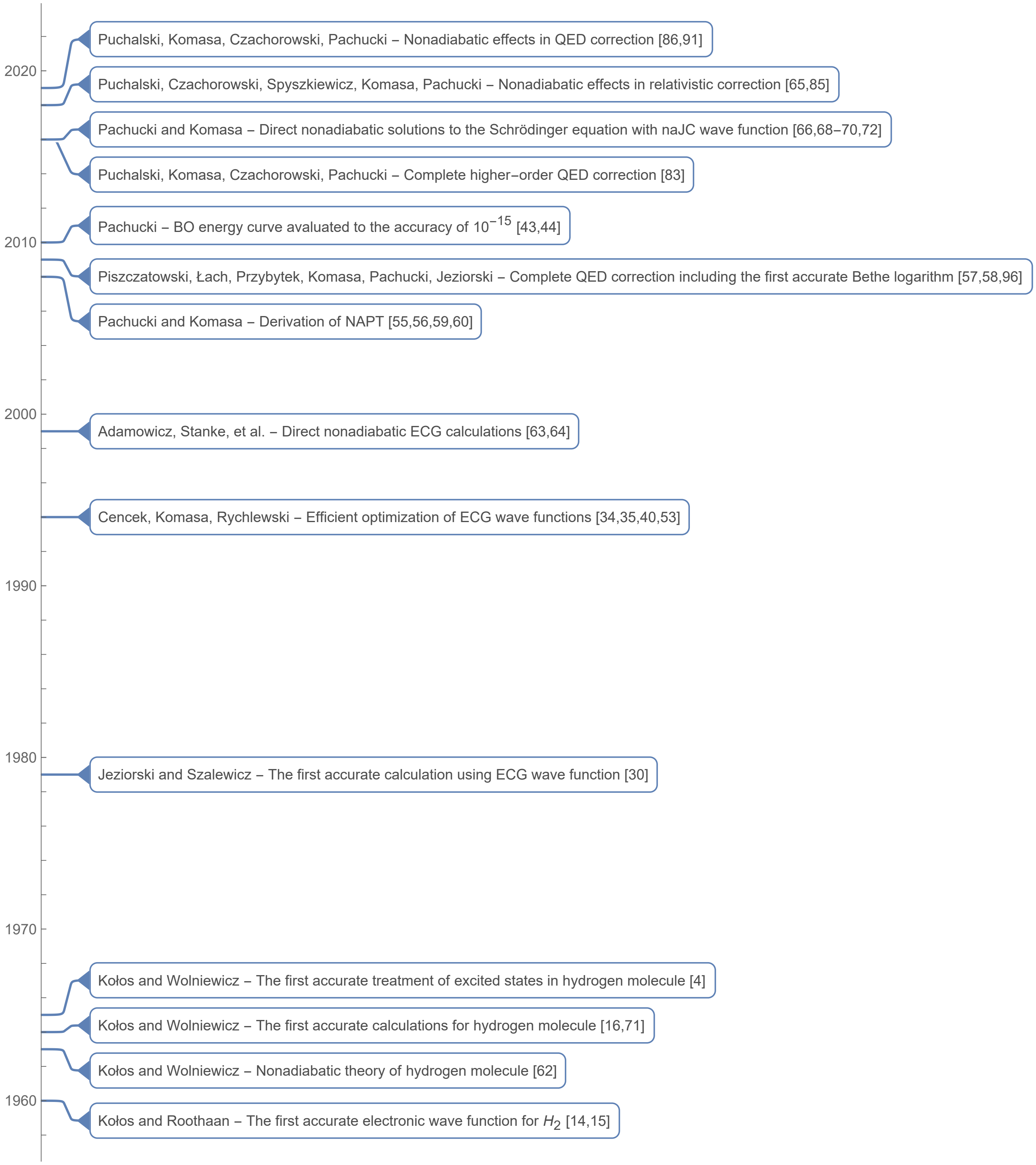

Figure 9: The chronological overview of key events in the development of theory and methods of description of the hydrogen molecule involving Polish researchers.

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