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Nonadiabatic rotational states of the hydrogen molecule

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We present a new computational method for the determination of energy levels in four-particle systems like H_2, HD, and HeH^+ using explicitly correlated exponential basis functions and analytic integration formulas. In solving the Schrödinger equation, no adiabatic separation of the nuclear and electronic degrees of freedom is introduced. We provide formulas for the coupling between the rotational and electronic angular momenta, which enable calculations of arbitrary rotationally excited energy levels. To illustrate the high numerical efficiency of the method, we present results for various states of the hydrogen molecule. The relative accuracy to which we determined the nonrelativistic energy reached the level of 10^{-12}–10^{-13}, which corresponds to an uncertainty of 10^{-7}–$10^{-8}\,cm^{-1}$.

Introduction

The hydrogen molecule gives an opportunity to test the foundations of quantum chemistry, which are based on quantum electrodynamic theory. In principle, there are no limits to the theoretical precision of the determination of molecular levels, apart from the limited accuracy of fundamental constants, such as the electron-proton mass ratio, the Rydberg constant, or the nuclear mean square charge radii. This opens up the possibility to determine these fundamental constants from molecular spectroscopic data, or alternatively to look for any discrepancies between theoretical predictions and experimental results to search for as yet unknown interactions.[1] In fact, in recent years we have observed significant progress in the accuracy of molecular spectroscopy.[2–10] In the particular case of the hydrogen molecule, contemporary measurements have reached the accuracy of $10^{-5}\,cm^{-1}$ (relative 10^{-9}) for selected transitions.[11–13] On the theoretical side, various relativistic and quantum electrodynamic corrections have recently been calculated,[14,15] but the principal problem up to now has been the insufficient accuracy of nonrelativistic energy levels. In a general multiparticle case, the complexity of the Schrödinger equation prevents its accurate solution and enforces approximations to be made. The most common one is the adiabatic approximation, which assumes the separation of the electronic and nuclear dynamics. Only a few attempts to solve directly, *i.e.* without the adiabatic approximation, the four-body Schrödinger equation for H_2 have been published. The first successful method was developed by Kołos and Wolniewicz over 50 years ago.[16,17] They employed a nonadiabatic expansion of a trial wave function in products of electronic James-Coolidge basis functions[18] and the vibrational functions of the form $h_n(R) = R^{-3} e^{-x^2/2} \mathscr{H}_n(x)$ with $x = \beta |R - R_e|$, where β and R_e are variational parameters, and $\mathscr{H}_n$ denotes the n-th Hermite polynomial. The expansion was composed of 54 electronic terms and six h_n functions yielding 147-terms in total. Because of this relatively short expansion, the obtained nonrelativistic dissociation energy $D_0 = 36\,114.7\,cm^{-1}$ differed by ca. $3\,cm^{-1}$ from the exact value. Nevertheless, the pioneering work by Kołos and Wolniewicz has set the foundations of the theoretical techniques for accurate calculations and, regarding the then available computing capabilities, should be considered as a great success of theory. Fifteen years later, using the same type of wave functions with significantly larger (1070-term) and carefully optimized expansion, a refined integration method, and much more powerful computers, Bishop and Cheung[19] reduced the error to $0.2\,cm^{-1}$. Quite a different approach, based on the quantum Monte Carlo method, was presented by Traynor et al.[20] in 1991 and improved later by Chen and Anderson[21]. Their trial wave function was a product of four terms ψ_i. The first two terms were a combination of one-electron functions centered on nuclei A and B, $\psi_i = e^{-a\,r_{iA}} + e^{-a\,r_{iB}}$. The third term was the Jastrow factor responsible for interparticle correlation and cusps $\psi_3 = \exp\left(\sum_{ij} \frac{a_{ij}r_{ij}}{1 + b_{ij}r_{ij}}\right)$ and the last term accounted for nuclear vibration and was of the Gaussian form $\psi_4 = e^{-d(R-c)^2}$. The quantum Monte Carlo method allowed the finite basis set error to be eliminated but introduced instead a statistical (sampling) error, which in the latter calculations was of about $\pm 0.2\,cm^{-1}$. A breakthrough result has been published by Kinghorn and Adamowicz.[22,23] Using a 512-term basis of explicitly correlated Gaussian

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functions, they have diminished the error in the nonrelativistic D_0 to $1.7 \cdot 10^{-3}\,\text{cm}^{-1}$. Later on, successively improving the optimization technique and expanding the basis set size to 10 000 terms, Bubin and Adamowicz[24–26] arrived at an extremely accurate solution of the four-particle Schrödinger equation to obtain $D_0 = 36\,118.797\,74(1)\,\text{cm}^{-1}$.

All these calculations have been limited to the nonrotational state of the molecule ($J = 0$). In this work, we show how to incorporate the coupling between the rotational and electronic angular momentum in the straightforward manner and increase the accuracy of the nonrelativistic dissociation energy up to the level of 10^{-7}–$10^{-8}\,\text{cm}^{-1}$ for the ground as well as for the rotationally and vibrationally excited energy levels of the electronic $X^1\Sigma_g^+$ state. This project comprises one of the stages heading toward the prediction of the total energies of the hydrogen molecule with the accuracy of $10^{-6}\,\text{cm}^{-1}$. The other contributions are relativistic $O(\alpha^2)$, leading quantum electrodynamics $O(\alpha^3)$, and higher order $O(\alpha^4)$ which are known only within the adiabatic approximation.[15] The knowledge of nonadiabatic wave functions obtained here, is essential for the calculation of these contributions.

Method

From a general exponential to the nonadiabatic James-Coolidge basis function

The method described here is relevant to a molecule consisting of two electrons, labeled 1 and 2, and two nuclei, labeled A and B, with masses M_A and M_B and charges Z_A and Z_B. The nonrelativistic Hamiltonian for this system is

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

We start the description of the method with a general exponential basis function of the following form

$$\Phi_{\{k\}} = e^{-u_1 R - w_1 r_{12} - y\eta_1 - x\eta_2 - u\zeta_1 - w\zeta_2}\, R^{k_0}\, r_{12}^{k_1}\, \eta_1^{k_2}\, \eta_2^{k_3}\, \zeta_1^{k_4}\, \zeta_2^{k_5}, \quad (2)$$

where u_1, w_1, y, x, u, and w are real numbers, whereas k_i are nonnegative integers, and where

$$\zeta_1 = r_{1A} + r_{1B}, \qquad \eta_1 = r_{1A} - r_{1B},$$
$$\zeta_2 = r_{2A} + r_{2B}, \qquad \eta_2 = r_{2A} - r_{2B}, \qquad \vec{R} = \vec{r}_{AB}. \quad (3)$$

By setting $u_1 \equiv \alpha$, $w_1 = 0$, $y = 0$, $x = 0$, and $u = w = \beta$ we arrive at simplified basis functions

$$\Phi_{\{k\}} = e^{-\alpha R - \beta(\zeta_1 + \zeta_2)}\, R^{k_0}\, r_{12}^{k_1}\, \eta_1^{k_2}\, \eta_2^{k_3}\, \zeta_1^{k_4}\, \zeta_2^{k_5}, \quad (4)$$

which still form a complete basis set. We call this function the nonadiabatic James-Coolidge (naJC) function for its resemblance to the original James-Coolidge (JC) basis function used in fixed-nuclei calculations. The difference between our nonadiabatic function and the JC function is in the internuclear correlation factor as well as in the meaning of the ζ and η variables.

The variational nonadiabatic wave function for an arbitrary rotational angular momentum

The rotational angular momentum of nuclei couples to the electronic angular momentum, $\vec{L}$, and gives the total angular momentum $\vec{J}$ of a molecule. For this reason, the wave function $\Psi^{J,M}$ of a rotational level J (formally depending also on the projection of $\vec{J}$ on the Z axis in the laboratory frame) must contain components that describe the electronic Σ, Π, Δ, $\ldots$ states. In the following set of formulas we construct such a wave function and we introduce a necessary notation. The total wave function is a sum of the components with growing Λ—the eigenvalue of the $\vec{n} \cdot \vec{L}$ operator

$$\Psi^{J,M} = \Psi_\Sigma^{J,M} + \Psi_\Pi^{J,M} + \Psi_\Delta^{J,M} + \ldots \quad (5)$$

where

$$\Psi_\Sigma^{J,M} = Y_M^J \Phi_\Sigma^J, \qquad \text{for } J \geq 0 \quad (6)$$

$$\Psi_\Pi^{J,M} = \sqrt{\frac{2}{J(J+1)}} R\rho^i \left(\nabla_R^i Y_M^J\right) \Phi_\Pi^J, \qquad \text{for } J \geq 1 \quad (7)$$

$$\Psi_\Delta^{J,M} = \sqrt{\frac{4}{(J-1)J(J+1)(J+2)}} R^2 (\rho^i \rho'^j)^{(2)} \left(\nabla_R^i \nabla_R^j Y_M^J\right) \Phi_\Delta^J,$$
$$\text{for } J \geq 2. \quad (8)$$

The particular form of functions in Eqs. (6)–(8) is convenient for the calculation of matrix elements as for example, the overlap matrix is block diagonal. In the above equations we use the following notation

$$(\rho^i \rho'^j)^{(2)} \equiv \frac{1}{2}\left(\rho^i \rho'^j + \rho^j \rho'^i - \left(\delta^{ij} - n^i n^j\right)\vec{\rho} \cdot \vec{\rho}'\right) \quad (9)$$

$$\vec{\rho}, \vec{\rho}' \equiv \vec{\rho}_1 \text{ or } \vec{\rho}_2 \quad (10)$$

$$\rho_a^i = \left(\delta^{ij} - n^i n^j\right) r_{aB}^j = \left(\delta^{ij} - n^i n^j\right) r_{aA}^j, \quad \text{with} \quad n^i = \frac{R^i}{R} \quad (11)$$

and we assume the Einstein summation convention, i.e. an implicit sum over all values of a repeated Cartesian index. The symbol $Y_M^J = Y_M^J(\vec{n})$ denotes the spherical harmonic. The functions Φ_Λ^J represent linear expansions in the above-defined naJC basis functions (4)

$$\Phi_\Lambda^J = R^J \sum_{\{k\}} c_{\{k\}} \left(1 + \mathscr{P}_{12}\right) \Phi_{\Lambda\{k\}}^J \quad (12)$$

for $\Lambda = \Sigma, \Pi, \Delta, \ldots\ldots$. For each pair J and Λ, the function Φ_Λ^J has its own set of nonlinear parameters, therefore we distinguish $\Phi_{\{k\}}$ of Eq. (4) by indices J and Λ.

A note concerning a linear dependence and a completeness of the basis set is in place here. To ensure the completeness, the function $\Psi_\Delta^{J,M}$ appears in two variants. The one in which both ρ and ρ' point at the same electron, and the other, in which they point at different electrons. Certain combinations of these two

variants exhibit linear dependence, which originates from the following identity

$$2\vec{\rho}_1\vec{\rho}_2\,(\rho_1^i\rho_2^j)^{(2)} = \vec{\rho}_2^{\,2}\,(\rho_1^i\rho_1^j)^{(2)} + \vec{\rho}_1^{\,2}\,(\rho_2^i\rho_2^j)^{(2)}. \tag{13}$$

This linear dependence can be avoided by, for example, an elimination of the second variant basis functions with at least one $k_i = 0$, for $i = 2,\ldots,5$.

Symmetry of the wave function

The nonrelativistic Hamiltonian (1) is invariant under translation, rotation, and spatial inversion $\hat{P}$. The inversion $\hat{P}$ reverses the sign of spatial coordinates of all particles leaving their spin unchanged, and the wave function is an eigenstate of $\hat{P}$ with eigenvalues ± 1. The wave function has also a definite symmetry with respect to the exchange of electrons —it is either symmetric or antisymmetric for the total electronic spin $S = 0$ or 1, respectively. In practice, this symmetry is enforced by acting on the spatial wave function with the $\frac{1}{2}(1 \pm \hat{P}_{12})$ operator, where $\hat{P}_{12}$ exchanges the electron labels.

For a homonuclear molecule, additional symmetries arise. The *gerade/ungerade* inversion symmetry is the inversion of all electronic coordinates with respect to the geometric center of a molecule. Recalling how the inversion operator $\hat{i}$ acts on the electronic variables $\hat{i}\zeta_i = \zeta_i$, $\hat{i}\eta_i = -\eta_i$, and $\hat{i}r_{12} = r_{12}$, one finds that $\hat{i}\Phi_{\{k\}} = (-1)^{k_2+k_3}\Phi_{\{k\}}$ and hence

$$\hat{i}\Phi_{\{k\}} = \begin{cases} +\Phi_{\{k\}}, & \text{for } k_2+k_3 \text{ even } (gerade) \\ -\Phi_{\{k\}}, & \text{for } k_2+k_3 \text{ odd } (ungerade). \end{cases} \tag{14}$$

A wave function of a homonuclear molecule also has a symmetry due to the exchange of the nuclei. For a specified *gerade/ungerade* inversion symmetry and the total nuclear spin, only even or odd J levels are allowed depending on the statistics (boson or fermion) of the nuclei. For example, if we restrict our considerations to the electronic ground state ($^1\Sigma_g^+$) of H_2, we observe that the subsequent rotational levels assume alternate nuclear spins. As a result, the even J levels correspond to the nuclear singlet (*para*-hydrogen) and the odd J levels to the triplet state (*ortho*-hydrogen).

Reduction of the angular factor

An important step in the analytic evaluation of the matrix elements with functions $\Psi_\Lambda^{J,M}$ is the integration over the nuclear angular variables. In this section, we supply formulas for the reduction of the general matrix elements by performing the integration $\int d\Omega_R$. Let us first note, that for an arbitrary scalar operator Q we have $\left\langle \Psi_\Lambda^{J,M}\middle|Q\middle|\Psi_\Lambda^{J,M'}\right\rangle \sim \delta_{M,M'}$. In the simplest case of matrix elements with a scalar electronic (*i.e.* containing no differentiation

over R) operator Q_{el} we have

$$\left\langle \Psi_\Sigma^{J,M}\middle|Q_{el}\middle|\Psi_\Sigma^{J,M}\right\rangle = \left\langle \Phi_\Sigma^J\middle|Q_{el}\middle|\Phi_\Sigma^J\right\rangle \tag{15}$$

$$\left\langle \Psi_\Pi^{J,M}\middle|Q_{el}\middle|\Psi_\Pi^{J,M}\right\rangle = \left\langle \rho^i\Phi_\Pi^J\middle|Q_{el}\middle|\rho^i\Phi_\Pi^J\right\rangle \tag{16}$$

$$\left\langle \Psi_\Delta^{J,M}\middle|Q_{el}\middle|\Psi_\Delta^{J,M}\right\rangle = \left\langle (\rho^i\rho'^j)^{(2)}\Phi_\Delta^J\middle|Q_{el}\middle|(\rho^i\rho'^j)^{(2)}\Phi_\Delta^J\right\rangle \tag{17}$$

and all the off-diagonal matrix elements vanish. The next set of formulas applies to the diagonal matrix elements with the nuclear kinetic energy operator

$$\hat{T} = -\frac{1}{2M_A}\nabla_A^2 - \frac{1}{2M_B}\nabla_B^2, \tag{18}$$

namely

$$\left\langle \Psi_\Sigma^{J,M}\middle|\nabla_X^2\middle|\Psi_\Sigma^{J,M}\right\rangle = \left\langle \Phi_\Sigma^J\middle|\nabla_X^2 - J(J+1)R^{-2}\middle|\Phi_\Sigma^J\right\rangle \tag{19}$$

$$\left\langle \Psi_\Pi^{J,M}\middle|\nabla_X^2\middle|\Psi_\Pi^{J,M}\right\rangle = \left\langle \rho^i\Phi_\Pi^J\middle|\nabla_X^2 - [J(J+1)-2]R^{-2}\middle|\rho^i\Phi_\Pi^J\right\rangle \tag{20}$$

$$\left\langle \Psi_\Delta^{J,M}\middle|\nabla_X^2\middle|\Psi_\Delta^{J,M}\right\rangle =$$
$$= \left\langle (\rho^i\rho'^j)^{(2)}\Phi_\Delta^J\middle|\nabla_X^2 - [J(J+1)-6]R^{-2}\middle|(\rho^i\rho'^j)^{(2)}\Phi_\Delta^J\right\rangle \tag{21}$$

with $X = A$ or B. Finally, the nondiagonal matrix elements read

$$\left\langle \Psi_\Pi^{J,M}\middle|\nabla_X^2\middle|\Psi_\Sigma^{J,M}\right\rangle = \pm\sqrt{2J(J+1)}\left\langle \rho^i\Phi_\Pi^J\middle|R^{-1}\middle|\nabla_X^i\Phi_\Sigma^J\right\rangle \tag{22}$$

$$\left\langle \Psi_\Delta^{J,M}\middle|\nabla_X^2\middle|\Psi_\Pi^{J,M}\right\rangle =$$
$$\pm\sqrt{2(J-1)(J+2)}\left\langle (\rho^i\rho'^j)^{(2)}\Phi_\Delta^J\middle|R^{-1}\middle|\rho^j\nabla_X^i\Phi_\Pi^J\right\rangle. \tag{23}$$

where $+$ and $-$ is for $X = A$ and B, correspondingly, with $\vec{R} = \vec{R}_A - \vec{R}_B$. All the remaining matrix elements vanish, so that the overlap $\mathbb{N}$ and Hamiltonian $\mathbb{H}$ matrices have the following block-band structure

$$\mathbb{N} = \begin{pmatrix} \mathbb{N}_{\Sigma\Sigma} & 0 & 0 & \cdots \\ 0 & \mathbb{N}_{\Pi\Pi} & 0 & \cdots \\ 0 & 0 & \mathbb{N}_{\Delta\Delta} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \quad \mathbb{H} = \begin{pmatrix} \mathbb{H}_{\Sigma\Sigma} & \mathbb{H}_{\Sigma\Pi} & 0 & \cdots \\ \mathbb{H}_{\Pi\Sigma} & \mathbb{H}_{\Pi\Pi} & \mathbb{H}_{\Pi\Delta} & \cdots \\ 0 & \mathbb{H}_{\Delta\Pi} & \mathbb{H}_{\Delta\Delta} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}. \tag{24}$$

Integrals with the exponential function

The previous section dealt with matrix elements without any reference to a specific shape of the spatial part of the basis function. Therefore, the above formulas can be utilized also with types of basis functions other than that presented in this article, e.g. with explicitly correlated Gaussian functions.[26] The present section, in turn, is devoted to the exponential basis functions, in particular to the naJC functions of Eq. (4). We start, however, with the most

general integral for a four-body system

$$G = \int \frac{d^3R}{4\pi} \int \frac{d^3 r_{1A}}{4\pi} \int \frac{d^3 r_{2A}}{4\pi} e^{-u_1 R - w_1 r_{12} - y\eta_1 - x\eta_2 - u\zeta_1 - w\zeta_2}$$

$$\times R^{n_0} r_{12}^{n_1} \eta_1^{n_2} \eta_2^{n_3} \zeta_1^{n_4} \zeta_2^{n_5} / \mathcal{D} \qquad (25)$$

where

$$\mathcal{D} = R r_{12} r_{1A} r_{1B} r_{2A} r_{2B} = \frac{1}{16} R r_{12} (\zeta_1 + \eta_1)(\zeta_1 - \eta_1)(\zeta_2 + \eta_2)(\zeta_2 - \eta_2).$$
$$(26)$$

The matrix elements of the Hamiltonian evaluated in the exponential basis (2) can be expressed by a combination of integrals belonging to the class defined in Eq. (25). All of these integrals can be obtained through a recurrence relation starting from the so called master integral

$$g = \int \frac{d^3R}{4\pi} \int \frac{d^3 r_{1A}}{4\pi} \int \frac{d^3 r_{2A}}{4\pi} \frac{e^{-u_1 R - w_1 r_{12} - y\eta_1 - x\eta_2 - u\zeta_1 - w\zeta_2}}{\mathcal{D}}. \qquad (27)$$

The analytical form of the integral (27) was obtained by Fromm and Hill[27] in 1987. Their result, although terribly troublesome for a numerical evaluation, was a milestone in the evaluation of the four-body exponential integrals. A special case of this integral was evaluated analytically by Remiddi[28], who expressed his result in terms of the logarithmic and the Euler dilogarithmic functions. In 1997 a significant simplification of the result obtained by Fromm and Hill was achieved by Harris[29], who managed to eliminate the original singularities and arrive to a much more computationally friendly formulation. Another significant step in this field was made in 2009 when the effective recurrence relations were discovered[30] enabling evaluation of an arbitrary integral out of the whole class given by Eq. (25).

The master integral g and its derivatives satisfy the following differential equations[30]

$$\sigma \frac{\partial g}{\partial a} + \frac{1}{2} \frac{\partial \sigma}{\partial a} g + P_a = 0, \qquad (28)$$

where a is one of the parameters $u_1 \equiv t$, w_1, y, x, u, or w, and where

$$\sigma = \sigma_0 + t^2 \sigma_2 + t^4 \sigma_4, \qquad (29)$$

$$\sigma_0 = w_1^2 (u+w-x-y)(u-w+x-y)(u-w-x+y)(u+w+x+y)$$

$$+ 16(wx - uy)(ux - wy)(uw - xy),$$

$$\sigma_2 = w_1^4 - 2w_1^2(u^2 + w^2 + x^2 + y^2) + 16uwxy,$$

$$\sigma_4 = w_1^2.$$

The inhomogeneous term P_a is a combination of several logarithmic functions and is presented explicitly in Appendix A of Ref. 31.

The most general integral of Eq. (25) can be obtained by suc-

cessive, multiple differentiation of the master integral g

$$G(n_0, n_1, n_2, n_3, n_4, n_5)$$

$$= \left(-\frac{\partial}{\partial t}\right)^{n_0} \left(-\frac{\partial}{\partial w_1}\right)^{n_1} \left(-\frac{\partial}{\partial y}\right)^{n_2} \left(-\frac{\partial}{\partial x}\right)^{n_3} \left(-\frac{\partial}{\partial u}\right)^{n_4} \left(-\frac{\partial}{\partial w}\right)^{n_5}$$

$$g(t, w_1, y, x, u, w). \qquad (30)$$

Each differentiation raises by one the power of the associated variable in the pre-exponential factor of the integrand in Eq. (27). However, from the practical point of view, it is much more convenient to use recursion relations for raising the powers n_i. Let us briefly overview the steps leading to these recurrence relations. First, in Eq. (28) we set $a = y$ and generate the pertinent inhomogeneous term P_y. Next, we differentiate Eq. (28) n_2 times with respect to y and then set $y = 0$. We proceed analogously with the variables x and w_1, and obtain the relation connecting different integrals of the G-class. From this equation we extract $G(n_0, n_1, n_2, n_3, n_4, n_5)$ and obtain the recurrence relation which, starting from $G(0,0,0,0,0,0)$, enables the integrals G to be obtained for an arbitrary combination of non-negative integers n_i, expressed in terms of derivatives of P_y. The multiple derivatives of P_y are combinations of rational and logarithmic functions, and are numerically stable for $t - 2u$ sufficiently far from zero. This condition can be easily satisfied and does not introduce limitations in practical calculations. Setting w_1, y, and x to zero simplifies significantly the analytic expressions for integrals in the naJC basis, in particular the σ from Eq. (29) vanishes.

A small sample of explicit expressions for G and P_y is given below (for $w = u$). Note that the master integral (27) for the naJC basis is represented explicitly by $G(0,0,0,0,0,0)$.

$$G(0,0,0,0,0,0) = P_y(0,0,1,0,0,0)/(16u^4) \qquad (31)$$

$$G(0,0,0,0,0,1) = P_y(0,0,1,0,0,0)/(8u^5) + P_y(0,0,1,0,0,1)/(16u^4) \qquad (32)$$

$$G(0,0,0,0,1,0) = G(0,0,0,0,0,1) \qquad (33)$$

$$G(0,0,0,1,0,0) = 0 \qquad (34)$$

$$G(0,0,1,0,0,0) = 0 \qquad (35)$$

$$G(0,1,0,0,0,0) = P_y(0,1,1,0,0,0)/(16u^4) \qquad (36)$$

where

$$P_y(0,0,1,0,0,0) = \frac{-16u^3 \ln(2u)}{t(t+2u)} + \frac{16u^3 \ln(4u)}{(t-2u)(t+2u)} - \frac{32u^4 \ln(t+2u)}{t(t-2u)(t+2u)} \qquad (37)$$

$$(38)$$

$$P_y(0,0,1,0,0,1) = -\frac{16u^3}{(t-2u)(t+2u)^2} + \frac{16u^2(t+u)^2\ln(2u)}{t^2(t+2u)^2}$$

$$+ \frac{8u^2(t^2-2u^2)\ln(2u)}{t^2(t+2u)^2} - \frac{8u(3t^2u-4u^3)\ln(4u)}{(t-2u)^2(t+2u)^2}$$

$$+ \frac{64u^3(t^2-2u^2)\ln(t+2u)}{t(t-2u)^2(t+2u)^2} \tag{39}$$

$$P_y(0,1,1,0,0,0) = \frac{4u^2}{(t+2u)^2} \tag{40}$$

We note that, by symmetry, the integrals G with n_2+n_3 odd vanish, as do P_y with n_2+n_3 even. The procedure sketched above allows the whole G-class of integrals to be evaluated analytically in a simple form.

Numerical approach

A perturbative solution of the eigenvalue problem

The solution of the Schrödinger equation in terms of the basis functions (4) is now reformulated into the generalized eigenvalue problem with the Hamiltonian $\mathbb{H}$ and overlap $\mathbb{N}$ matrices

$$(\mathbb{H} - E\,\mathbb{N})\,\mathbb{C} = 0, \tag{41}$$

where $\mathbb{C}$ is a vector of linear coefficients from Eq. (12). For all states this equation can be solved directly, e.g. by the inverse iteration method. However, due to the large size of the matrices $\mathbb{H}$ and $\mathbb{N}$ for rotational states, it is more economical to apply the inverse iteration method only for the Σ component, and obtain the Π and Δ components from the standard perturbation theory. In other words, when $J > 0$, the wavefunction $\Psi^{J,M}$, as defined in Sec. 2.2, is composed of mutually orthogonal Λ-segments. The orthogonality is manifested in the block-diagonal structure of the overlap matrix, Eq. (24). The smallness of the block-off-diagonal terms of $\mathbb{H}$ enables rapidly converging perturbative expansion. In this section, we supply explicit formulas for the subsequent perturbational corrections.

Let us first consider the approximated energy level $E^{(0)} = E_\Sigma$ obtained from the unperturbed wavefunction $\Psi^{J,M} = \Psi_\Sigma^{J,M}$. The Rayleigh-Schrödinger perturbation theory yields the second order (with respect to the power of the off-diagonal parts of the Hamiltonian) energy shift $E_\Pi^{(2)}$

$$E_\Pi^{(2)} = \left\langle \Psi_\Sigma^{J,M} \left| H_{\Sigma\Pi} \frac{1}{E_\Sigma - H_{\Pi\Pi}} H_{\Pi\Sigma} \right| \Psi_\Sigma^{J,M} \right\rangle = \left\langle \Psi_\Sigma^{J,M} \left| V_\Pi(E_\Sigma) \right| \Psi_\Sigma^{J,M} \right\rangle \tag{42}$$

where

$$V_\Pi(E) = H_{\Sigma\Pi} \frac{1}{E - H_{\Pi\Pi}} H_{\Pi\Sigma}. \tag{43}$$

The fourth order correction $E_\Pi^{(4)} + E_\Delta^{(4)}$ can be evaluated from

$$E_\Pi^{(4)} = \left\langle \Psi_\Sigma^{J,M} \left| V_\Pi(E_\Sigma) \frac{1}{(E_\Sigma - H_{\Sigma\Sigma})'} V_\Pi(E_\Sigma) \right| \Psi_\Sigma^{J,M} \right\rangle$$

$$+ \left\langle \Psi_\Sigma^{J,M} \left| \frac{\partial V_\Pi}{\partial E} \right|_{E_\Sigma} \right| \Psi_\Sigma^{J,M} \right\rangle E_\Pi^{(2)}, \tag{44}$$

$$E_\Delta^{(4)} = \left\langle \Psi_\Sigma^{J,M} \left| H_{\Sigma\Pi} \frac{1}{E_\Sigma - H_{\Pi\Pi}} H_{\Pi\Delta} \frac{1}{E_\Sigma - H_{\Delta\Delta}} H_{\Delta\Pi} \frac{1}{E_\Sigma - H_{\Pi\Pi}} H_{\Pi\Sigma} \right| \Psi_\Sigma^{J,M} \right\rangle. \tag{45}$$

Each $H_{\Lambda'\Lambda}$ Hamiltonian contains the m/μ factor of the order of 10^{-3}, which makes the perturbation series converge very rapidly. In particular, the $E_\Delta^{(6)}$ correction would be approximately 5-6 orders of magnitude smaller than $E_\Delta^{(4)}$. Therefore, taking into account just the first four terms of the perturbative expansion is sufficient for our purposes

$$E \approx E_\Sigma + E_\Pi^{(2)} + E_\Pi^{(4)} + E_\Delta^{(4)}. \tag{46}$$

A similar perturbation expansion holds for the wave function, namely

$$\Phi = \begin{bmatrix} \Phi_\Sigma^{(0)} + \Phi_\Sigma^{(2)} + \Phi_\Sigma^{(4)} + \dots \\ \Phi_\Pi^{(1)} + \Phi_\Pi^{(3)} + \dots \\ \Phi_\Delta^{(2)} + \dots \end{bmatrix} \tag{47}$$

where

$$\Phi_\Sigma^{(0)} \text{ is the unperturbed function} \tag{48}$$

$$\Phi_\Pi^{(1)} = \frac{1}{E_\Sigma - H_{\Pi\Pi}} H_{\Pi\Sigma} \Phi_\Sigma^{(0)}, \tag{49}$$

$$\Phi_\Sigma^{(2)} = \frac{1}{(E_\Sigma - H_{\Sigma\Sigma})'} H_{\Sigma\Pi} \Phi_\Pi^{(1)} - \frac{1}{2} \left\langle \Phi_\Pi^{(1)} | \Phi_\Pi^{(1)} \right\rangle \Phi_\Sigma^{(0)} \tag{50}$$

$$\Phi_\Delta^{(2)} = \frac{1}{E_\Sigma - H_{\Delta\Delta}} H_{\Delta\Pi} \Phi_\Pi^{(1)}. \tag{51}$$

Technical details

Each naJC basis function $\Phi_{\{k\}}$, apart from the set of integers k_i, depends on two real positive parameters α_k and β_k. The set of the basis functions with a common pair α_k and β_k will be called the sector. Such a sector contains all basis functions with integer powers of R ranging from $k_0^{\min}$ to $k_0^{\max}$. The total wave function can be composed of a number of such sectors. The optimal value $k_0^{\max}$ was determined through numerical experiments for each state separately. The $k_0^{\min}$ in turn was set to Λ. The 'electronic' integer parameters $k_1 \dots, k_5$ are used to organize the basis functions in 'shells'. The given basis function $\Phi_{\{k\}}$ belongs to the shell number $\Omega_k = \sum_{i=1}^5 k_i$. To describe a sector of basis functions for given J and Λ values, we use a four parameter symbol $(k_0^{\max}, \Omega, \alpha, \beta)$. Such a sector involves basis functions with the nonlinear parameters α and β, and with the integer powers k_i fulfilling $k_0^{\min} \le k_0 \le k_0^{\max}$ and $0 \le \Omega_k \le \Omega$. By increasing Ω we can systematically add new

basis functions to the expansion and observe the convergence of energy with increasing total size of the basis set K.

To solve the eigenproblem (41) we employed the inverse iteration method, which consists of the $\mathbb{M}\mathbb{D}\mathbb{M}^T$ decomposition of the $\mathbb{H} - E\mathbb{N}$ matrix followed by a solution of the linear equations set performed several times up to the assumed convergence. The matrix $\mathbb{D}$ is block diagonal with blocks of the order 1 or 2, and $\mathbb{M}$ is unit lower triangular. The workload of the decomposition step grows with the basis size like K^3 whereas that of the remainder steps like K^2; therefore, for large matrices the decomposition step determines the timing of all of the computations. The linear algebra calculations, as well as the evaluation of matrix elements, were performed using extended precision arithmetics implemented with the help of the QD library.[32] It enables nearly octuple precision (212 bit, 62 digits), which is sufficient to obtain the required accuracy of the energy levels considered in this work.

We consider H_2 in its electronic ground state $X^1\Sigma_g^+$ and, due to limited space for tables, we restrict the presentation of numerical results to the ground vibrational level $v = 0$. This restriction, however, is not related to limitations of the method.

$J = 0$ level

We consider here the ground rotational level $J = 0$, which requires no coupling to the electronic states with higher angular momentum to be involved, that is $\Psi^{J,M} = \Psi_\Sigma^{J,M}$. We used a two-sector basis of Σ-functions: $(30,\Omega,\alpha,\beta^{(1)})$ and $(30,\Omega\text{-}2,\alpha,\beta^{(2)})$. The parameters α, $\beta^{(1)}$, and $\beta^{(2)}$ were optimized variationally with respect to the energy of the level separately for each Ω. The optimal parameters, the total size of the basis, and the resulting energy are listed in Table 1. Extrapolation of the energy to an infinite basis set size enables determination of the recommended energy value and its estimated numerical uncertainty. For this particular level, we assess the accuracy of the energy as $3 \cdot 10^{-13}$ hartree. By subtracting the energy $E_{0,0}$ from the exactly known sum of the energy of two hydrogen atoms, $2E(H) = \frac{m_p}{m_p + m_e}$ hartree, we calculated the dissociation energy $D_{0,0}$ listed in the last column of the table. The numerical accuracy of $D_{0,0}$ is estimated as $3 \cdot 10^{-8}$ cm^{-1}. This estimation, however, does not account for the uncertainty originating from determination of the fundamental physical constants. All calculations reported in this work were performed with the best currently available values of the proton-to-electron mass ratio $m_p/m_e = 1\,836.152\,673\,89(17)$ and of the Rydberg constant $R_\infty = 109\,737.315\,685\,08(65)$ cm^{-1} obtained from the 2014 CODATA compilation.[33] The uncertainties of both physical constants limit the accuracy of our final results. On the other hand, the problem can be reversed and future high-accuracy relativistic calculations, in connection with high-accuracy measurements, can be applied to refine these physical constants. At present, however, the accuracy of the final value for the dissociation energy of the ground level of H_2 is restricted by the lack of the relativistic nuclear recoil contribution and the limited accuracy of the leading QED correction.

$J > 0$ levels

We consider here rotationally excited states of the ground vibrational level ($v = 0$, $J = 1$–9). In this case the admixture of states with non-zero electronic angular momentum has to be taken into account in forming the wave function (see Sec. 2.2 and 3.1). However, still a vast contribution of energy comes from the Σ wave function and the main effort in the calculations has to be focused in the convergence of the energy within the space formed by the Σ basis functions. For this purpose, in analogy with the $J = 0$ case described above, we composed the Σ wave function of two sectors of basis functions with a common α parameter: $(30,\Omega,\alpha,\beta^{(1)})$ and $(20,\Omega,\alpha,\beta^{(2)})$. By increasing the shell parameter Ω we determined the extrapolated energy value and its uncertainty. Sample data illustrating the energy convergence for a selection of states are given in Table 2. A general observation made from this table is that the convergence does not deteriorate significantly with the increasing angular momentum J, so that for the highest state considered ($J = 9$), the uncertainty is about the same as that for $J = 1$, amounting to 10^{-13} hartree. In each case, the attained accuracy in dissociation energy is better than $5 \cdot 10^{-8}$ cm^{-1}.

To evaluate the perturbational corrections $E_\Pi^{(2)}$, $E_\Pi^{(4)}$, and $E_\Delta^{(4)}$ we employed one-sector wave functions of proper symmetry. This time, the sector formally depends on a single α and three β (β^Σ, β^Π, β^Δ) parameters. However, numerical experiments have shown that the optimal β^Δ is very close to the optimal β^Σ, and for convenience it was fixed at the value of the latter, $\beta^\Delta = \beta^\Sigma$. Table 3 contains sample results of our convergence study of the three energy corrections computed according to the formulas presented in Sec. 3.1. An inspection of the last three columns of the table gives a view on the rate of convergence and the estimated uncertainties of particular corrections. It also informs how fast the particular corrections grow with increasing J.

We would like to emphasize that the perturbational approach described in Sec. 3.1 is numerically, within the assumed goal of accuracy, totally equivalent to the variational one. The perturbational approach requires three decompositions of pertinent chunks ($\mathbb{H}_{\Sigma\Sigma}$, $\mathbb{H}_{\Pi\Pi}$, and $\mathbb{H}_{\Delta\Delta}$) of the Hamiltonian matrix, whereas in the variational approach the matrix must be decomposed as a whole. Because the decomposition effort is proportional to cubic size of the matrix ($\sim K^3$), the perturbational approach is, for large matrices, significantly more effective than the variational one. We have confronted the results obtained for $D_{0,J}$ in both ways and obtained agreement better than 10^{-10} cm^{-1}. This numerical agreement shows also that consideration of only those three corrections ($E_\Pi^{(2)}, E_\Pi^{(4)}, E_\Delta^{(4)}$) is totally sufficient for our purposes.

The final dissociation energies obtained for the lowest nine rotational levels $J = 1, \ldots, 9$ of the ground vibrational state are presented in Table 4. The total energy was composed of the E_Σ energy evaluated using a two-sector wave function and the subsequent perturbational corrections $E_\Pi^{(2)}, E_\Pi^{(4)}, E_\Delta^{(4)}$ obtained from a one-sector wave function. It can be seen that the final accuracy is determined mainly by the accuracy achieved for the E_Σ term. For higher J though, the uncertainty originating from $E_\Pi^{(2)}$ be-

Table 1 Convergence of the lowest eigenvalue $E_{0,0}$ (in a.u.) and of the corresponding dissociation energy $D_{0,0}$ (in cm^{-1}) for H_2 with the basis set size K. Two-sector wave function was employed: $(30,\Omega,19.19,\beta^{(1)})$ and $(30,\Omega\text{-}2,19.19,\beta^{(2)})$.

Ω	$\beta^{(1)}$	$\beta^{(2)}$	K	$E_{0,0}$	$D_{0,0}$
10	0.9304	2.664	36 642	−1.164 025 030 822 08	36 118.797 732 723
11	0.953	3.041	53 599	−1.164 025 030 870 90	36 118.797 743 437
12	0.978	3.45	76 601	−1.164 025 030 880 47	36 118.797 745 538
13	1.011	3.20	106 764	−1.164 025 030 882 36	36 118.797 745 953
14	1.039	2.80	146 072	−1.164 025 030 882 87	36 118.797 746 064
∞			∞	−1.164 025 030 883 1(3)	36 118.797 746 10(3)

Table 2 Convergence of the Σ-component of selected eigenvalues $E_{v,J}$ (in a.u.) with the increasing size of the basis set. Two-sector wave functions have been employed: $(30,\Omega,\alpha,\beta^{(1)})$ and $(20,\Omega,\alpha,\beta^{(2)})$. K is the total size of the basis set and $D_{v,J}$ — the dissociation energy in cm^{-1}.

				$J=1$		
Ω	α	$\beta^{(1)}$	$\beta^{(2)}$	K	$E_{0,1}$	$D_{0,1}$
9	16.92	0.866	2.183	27650	−1.163 485 139 5410	36 000.305 292 83
10	16.93	0.912	2.487	40950	−1.163 485 139 5785	36 000.305 301 06
11	16.99	0.929	3.064	61152	−1.163 485 139 5847	36 000.305 302 43
12	16.93	0.968	3.265	82600	−1.163 485 139 5863	36 000.305 302 77
13	16.93	1.05	3.4776	117936	−1.163 485 139 5866	36 000.305 302 83
∞				∞	−1.163 485 139 5867(1)	36 000.305 302 85(2)
				$J=5$		
Ω	α	$\beta^{(1)}$	$\beta^{(2)}$	K	$E_{0,5}$	$D_{0,5}$
9	16.69	0.8599	2.282	28756	−1.156 095 754 6635	34 378.522 770 78
10	15.62	0.8998	2.659	42588	−1.156 095 754 7011	34 378.522 779 04
11	15.62	0.9225	3.026	61152	−1.156 095 754 7073	34 378.522 780 40
12	15.62	0.974	3.300	85904	−1.156 095 754 7088	34 378.522 780 73
13	15.62	1.013	3.350	117936	−1.156 095 754 7091	34 378.522 780 79
∞				∞	−1.156 095 754 7092(1)	34 378.522 780 82(3)
				$J=9$		
Ω	α	$\beta^{(1)}$	$\beta^{(2)}$	K	$E_{0,9}$	$D_{0,9}$
9	16.45	0.847	2.265	28756	−1.141 233 218 3826	31 116.573 099 32
10	16.29	0.888	2.641	42588	−1.141 233 218 4218	31 116.573 107 91
11	15.39	0.913	3.041	61152	−1.141 233 218 4285	31 116.573 109 38
12	15.39	0.955	2.750	85904	−1.141 233 218 4298	31 116.573 109 66
13	15.39	0.988	3.425	117936	−1.141 233 218 4301	31 116.573 109 74
∞				∞	−1.141 233 218 4302(1)	31 116.573 109 76(3)

comes significant. The second-order correction resulting from the coupling of the nuclear rotational angular momentum with the electronic Π-state is indispensable for accurate calculation, even for the $J=1$ level. This correction increases with growing J proportionally to $J(J+1)$ and for $J=9$ contributes to the dissociation energy as much as $0.3\,cm^{-1}$. The fourth-order Π-states correction and the Δ-states correction are much smaller but grow even more rapidly ($\sim [J(J+1)]^2$) and become important when higher-J states or still higher accuracy is of interest.

In Table 4 we compared the total nonadiabatic dissociation energy with the energy obtained from the second order nonadiabatic perturbation theory (NAPT)[34]. The difference between these two numbers comes from the higher order $\mathscr{O}(m_e/M)^3$ terms not included in the perturbational calculations of Ref. 34.

Summary and outlook

The numerical results presented in this work concern only the hydrogen molecule, but the method described is applicable to any four-particle Coulomb system. The achieved accuracy surpasses that available to date for such systems. Until now, such an accuracy was available only for systems with three or fewer particles. Apart from the high accuracy, the main advantage of this method is in the formalism that enables straightforward calculations for non-zero rotational angular momentum. This feature opens up a window for accurate prediction of nonrelativistic energy for all bound levels in such systems.

The numerical results presented here constitute an introductory but indispensable part of a larger project aimed at predicting the energy levels of H_2 with an accuracy of $10^{-6}\,cm^{-1}$. This part must be followed by accurate (at least 1 ppm) calculations of the leading relativistic ($\sim \alpha^2$) and QED ($\sim \alpha^3$) corrections as

Table 3 Convergence of the Σ-, Π-, and Δ-components of selected rotational energy levels (in a.u.) with the increasing size of the basis set. One-sector wave functions have been employed: $(30, \Omega, \alpha, \beta^\Sigma, \beta^\Pi, \beta^\Delta)$. K is the total size of the basis set.

Ω	α	$\beta^\Sigma = \beta^\Delta$	β^Π	K	E_Σ	$E_\Pi^{(2)} \cdot 10^8$	$E_\Pi^{(4)} \cdot 10^{13}$	$E_\Delta^{(4)} \cdot 10^{13}$
					$J = 1$			
9	19.84	0.930	0.875	37429	−1.163485134761	−3.27271900	−0.492866	0.0
10	19.82	0.973	0.904	55965	−1.163485138021	−3.27272362	−0.492887	0.0
11	19.83	1.008	0.940	81144	−1.163485138961	−3.27272388	−0.492892	0.0
12	19.84	1.049	0.968	114716	−1.163485139347	−3.27272431	−0.492894	0.0
∞				∞	−1.1634851403(3)	−3.272725(1)	−0.492896(2)	0.0
					$J = 5$			
9	22.19	0.923	0.873	58669	−1.156095749888	−48.9145866	−104.5339	−31.0603
10	22.19	0.964	0.893	87342	−1.156095753145	−48.9146524	−104.5382	−31.0614
11	22.20	0.999	0.936	126120	−1.156095754085	−48.9146553	−104.5390	−31.0616
12	22.20	1.044	0.964	177644	−1.156095754471	−48.9146609	−104.5395	−31.0618
∞				∞	−1.1560957548(4)	−48.91467(1)	−104.541(2)	−31.0622(4)
					$J = 9$			
9	23.90	0.915	0.860	58669	−1.141233213617	−145.750039	−836.830	−259.851
10	23.91	0.958	0.889	87342	−1.141233216875	−145.750228	−836.864	−259.857
11	23.91	0.994	0.926	126120	−1.141233217812	−145.750240	−836.871	−259.857
12	23.92	1.034	0.953	177644	−1.141233218194	−145.750258	−836.875	−259.858
∞				∞	−1.1412332186(4)	−145.75028(2)	−836.880(5)	−259.859(1)

Table 4 Nonadiabatic dissociation energy ($D_{0,J}$) of the lowest rotational energy levels of the ground vibrational state. The total as well as the Σ-, Π-, and Δ-components are given (in cm^{-1}). For comparison, results from the second order nonadiabatic perturbation theory (NAPT) [34] are also given. The difference Total-NAPT reflects the value of the higher order terms missing in the NAPT calculations.

Component	$J = 1$	$J = 2$	$J = 3$
E_Σ	36000.30530285(2)	35764.40769523(2)	35413.24498004(2)
$E_\Pi^{(2)}$	0.00718280	0.02153694	0.04304002
$E_\Pi^{(4)}$	0.00000001	0.00000010	0.00000038
$E_\Delta^{(4)}$	0.00000000	0.00000002	0.00000010
Total	36000.31248566(2)	35764.42923228(2)	35413.28802054(2)
NAPT	36000.312413	35764.429157	35413.287941

Component	$J = 4$	$J = 5$	$J = 6$
E_Σ	34949.94357900(2)	34378.52278082(3)	33703.78059609(3)
$E_\Pi^{(2)}$	0.07165975(1)	0.10735529(1)	0.15007908(2)
$E_\Pi^{(4)}$	0.00000104	0.00000229	0.00000439
$E_\Delta^{(4)}$	0.00000030	0.00000068	0.00000133
Total	34950.01524009(2)	34378.63013908(3)	33703.93068089(4)
NAPT	34950.015154	34378.630045	33703.930576

Component	$J = 7$	$J = 8$	$J = 9$
E_Σ	32931.16623829(3)	32066.64655399(3)	31116.57310976(3)
$E_\Pi^{(2)}$	0.19977878(3)	0.25639928(3)	0.31988489(4)
$E_\Pi^{(4)}$	0.00000759	0.00001216	0.00001837
$E_\Delta^{(4)}$	0.00000233	0.00000376	0.00000570
Total	32931.36602699(4)	32066.90296919(4)	31116.89301872(5)
NAPT	32931.365910	32066.902838	31116.892871

well as corrections resulting from higher-order ($\sim \alpha^4$ and α^5) contributions and other tiny effects like the finite size of the nucleus or *gerade-ungerade* mixing [35]. We have recently evaluated the relativistic correction and the higher-order QED corrections in the Born-Oppenheimer regime. [14,15] The new nonadiabatic wave functions will enable us to take into account also the finite nuclear mass effects in the corrections mentioned above.

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Conflict of interest

"There are no conflicts to declare"

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