

Application of the fully correlated basis of exponential functions for molecular hydrogen.

Krzysztof Pachucki

Faculty of Physics, University of Warsaw, Hoża 69, 00-681 Warsaw, Poland

Vladimir A. Yerokhin

*St. Petersburg State Polytechnical University,
Polytekhnicheskaya 29, St. Petersburg 195251, Russia*

Abstract

Precision tests with hydrogen molecule are presently limited by unknown higher-order quantum electrodynamic effects. These corrections are represented by matrix elements of some effective operators, most of which are singular. The evaluation of matrix elements of singular operators put high demands on the quality of the representation of the nonrelativistic wave functions. The basis of fully correlated exponential functions is well suited for representing the H_2 wave function, as it has the correct properties both at coalescent points and at asymptotic distances. Moreover, the matrix elements of all operators can be conveniently obtained in this basis via integration or differentiation with respect to nonlinear parameters. In this work we develop an approach that paves the way to practical calculations with this basis.

PACS numbers: 31.15.ac, 03.65.Ge

I. INTRODUCTION

Experimental spectroscopy of hydrogen molecules H_2 , D_2 , and HD has demonstrated an impressive progress during the last decades. The current level of experimental accuracy is at the 10 parts-per-billion (ppb) level [1–3] and is likely to be improved in the future. Very good agreement with theoretical calculations [4] indicates that all physical effects relevant at the 10^{-8} level (10^{-3} cm^{-1} for dissociation energies) are currently well understood. Further progress of theory of the hydrogen molecule is, however, impeded by unknown higher-order QED effects, particularly, the effects of order $m\alpha^6$, where m is the electron mass and α is the fine structure constant.

A calculation of the $m\alpha^6$ QED effects for atoms and molecules is a notoriously problematic task. One of the main difficulties is the evaluation of first-order and second-order matrix elements of singular operators [5]. In undertaking this task, the choice of the type of the basis functions used for solving the Schrödinger equation is of crucial importance. To date, the most advanced calculations of the hydrogen molecule (in particular, those of Ref. [4]) were performed with explicitly correlated Gaussian (ECG) functions. The main advantage of the ECG basis set is its simplicity, which leads to high numerical stability and accessible analytical expressions for integrals with various operators, including the negative powers of r 's, such as r_{12}^{-n} , r_{1A}^{-n} , etc. The main drawback of the ECG functions is that they do not satisfy the cusp condition, which is one of the analytical properties the exact wave function is known to possess. This drawback is usually compensated by a careful global optimization of (thousands of) nonlinear parameters in the basis set. However, the convergence of the ECG basis functions becomes increasingly slower for matrix elements with increasingly singular operators. Because of this, one might expect that a calculation of the second-order $m\alpha^6$ matrix elements of nearly singular operators with the ECG basis set will be very difficult.

Several other basis sets, which satisfy the cusp condition, were successfully applied in the literature to calculations of the hydrogen molecule. In particular, explicitly correlated basis of the form

$$e^{-u(r_{1A}+r_{1B})-w(r_{2A}+r_{2B})-y(r_{1A}-r_{1B})-x(r_{2A}-r_{2B})} r_{12}^{n_1} r_{1A}^{n_2} r_{1B}^{n_3} r_{2A}^{n_4} r_{2B}^{n_5} \quad (1)$$

was introduced by Kołos and Wolniewicz [6] to obtain first accurate results for ground and excited states of the H_2 , D_2 , and HD molecules. Presently the most precise results for the Born-Oppenheimer potential curve of the H_2 molecule [7] are obtained with two particular

subsets of this general basis. At short internuclear distances, the James-Coolidge basis of the form (1) with $x = y = 0$ was shown to be most effective, whereas at large distances, the extended Heitler-London basis of the form (1) with $u = y$ and $w = -x$ yielded the best results. These two sets of basis functions proved to be very effective for calculating the nonrelativistic energy. However, their application for calculations of relativistic and QED corrections is impeded by the absence of tractable analytic expressions for integrals with negative powers of r 's, namely r_{iA}^{-n} and r_{12}^{-n} with $n > 1$.

In the present paper, we aim to solve the problem with integrals with negative powers of r 's in the basis (1) by turning to a more general basis, namely the basis of explicitly correlated exponential functions of the form

$$e^{-w_1 r_{12} - u(r_{1A} + r_{1B}) - w(r_{2A} + r_{2B}) - y(r_{1A} - r_{1B}) - x(r_{2A} - r_{2B})}. \quad (2)$$

This basis is the most general explicitly correlated two-center two-electron basis and thus it is potentially the most flexible and the most powerful. The main advantages are that (i) it satisfies the cusp conditions, which should result in a relatively fast convergence for singular matrix elements, (ii) the integrals with negative powers of r 's can be easily obtained by numerical integrations over the corresponding nonlinear parameters, (iii) it is likely to yield the most compact representation of the electronic wave function. This basis has not, however, been widely used in molecular calculations so far, because of overwhelming technical difficulties in calculating the integrals with such general functions.

The aim of the present paper is to demonstrate how to calculate the nonrelativistic energy of the H_2 molecule and the matrix elements of the negative powers of r 's with the basis set of explicitly correlated exponential functions, having in mind future application of this basis for evaluation of higher-order QED corrections.

II. MASTER INTEGRAL

The key to any practical calculations with the explicitly correlated exponential functions is the master two-electron two-center integral $f(r)$,

$$f(r) \equiv f(r; w_1, y, x, u, w) = r \int \frac{d^3 r_1}{4\pi} \int \frac{d^3 r_2}{4\pi} \frac{e^{-w_1 r_{12} - u(r_{1A} + r_{1B}) - w(r_{2A} + r_{2B}) - y(r_{1A} - r_{1B}) - x(r_{2A} - r_{2B})}}{r_{12} r_{1A} r_{1B} r_{2A} r_{2B}}, \quad (3)$$

where $w_1, u, w, x,$ and y are real nonlinear parameters, the subscripts 1 and 2 numerate the electrons, A and B numerate the nuclei, and $r \equiv r_{AB}$ is the distance between the nuclei. So, r_{12} is the interelectronic distance, whereas r_{1A} is the distance between the first electron and the nuclei A . Since the wave function should be square integrable, one obtains the following restrictions for the nonlinear parameters: $u > 0, w > 0,$ and $w_1 > \max(-2u, -2w)$. It can be easily seen that any additional integer positive powers of r 's can be obtained from the master integral $f(r)$ by differentiation over the corresponding nonlinear parameter, whereas additional negative powers are obtained by integration over the nonlinear parameters.

This master integral $f(r)$ is not known in a closed analytical form. It has several symmetries

$$\begin{aligned}
 f(r; w_1, y, x, u, w) &= f(r; w_1, x, y, u, w) \\
 &= f(r; w_1, y, x, w, u) \\
 &= f(r; w_1, -y, -x, u, w),
 \end{aligned}
 \tag{4}$$

that do not immediately follow from the definition (3). Early studies on the subject used for its evaluation expansions of $e^{-w_1 r_{12}} r_{12}^{-1}$ in spherical oblate coordinates or, alternatively, in terms of spheroidal functions. Usage any of these expansions made practical calculations of $f(r)$ cumbersome, slow and restricted to small internuclear distances. An alternative approach has been pursued in Ref. [9]. In that work, an analytic formula for the general four-body integral g was found, whose inverse Laplace transform is $f(r)$. Due to a very complicated analytic structure of the four-body integral g , the obtained expression in terms of the inverse Laplace transform has never been used in practical calculations so far.

In the recent works [10–12], a tractable way of calculating $f(r)$ was found. The problem of the calculation of the inverse Laplace transform of g has been reformulated into solving a differential equation. The solution of this differential equation was found [11] in terms of one-dimensional integral, which needs to be performed numerically. Moreover, the differential equation allowed one of us to derive analytic recursion relations for integrals with positive integer powers of interparticle distances. In the present paper, we demonstrate how this approach works in practice.

The main result of Ref. [11] was the following compact representation of the master

two-electron two-center integral $f(r)$,

$$f(r) = \int_0^{-\infty} dt e^{tr} \frac{1}{2\sqrt{\sigma}} \left[\theta(t_1 - t) \ln |\beta_{0,0}| + \theta(t_2 - t) \ln |\beta_{3,3}| \right. \\ \left. - \theta(t_3 - t) \ln |\beta_{3,1} \beta_{3,3}| - \theta(t_4 - t) \ln |\beta_{0,1} \beta_{0,0}| \right], \quad (5)$$

where

$$\sigma = \sigma_0 + t^2 \sigma_2 + t^4 w_1^2, \quad (6)$$

$$\sigma_0 = w_1^2 (u + w - x - y) (u - w + x - y) (u - w - x + y) (u + w + x + y) \\ + 16 (w x - u y) (u x - w y) (u w - x y),$$

$$\sigma_2 = w_1^4 - 2 w_1^2 (u^2 + w^2 + x^2 + y^2) + 16 u w x y, \quad (7)$$

$$\beta_{i,j} = \frac{\sqrt{\sigma} - \gamma_{i,j}}{\sqrt{\sigma} + \gamma_{i,j}}, \quad (8)$$

$$\gamma_{0,0} = -t^2 w_1 + w_1^2 (u + w - x - y) + w_1 (u + w - x - y)^2 + 4 (u x y + w x y - u w x - u w y), \\ \gamma_{3,3} = -t^2 w_1 + w_1^2 (u + w + x + y) + w_1 (u + w + x + y)^2 + 4 (u w x + u w y + u x y + w x y), \\ \gamma_{0,1} = 2 t^2 x + t (4 x^2 - w_1^2) - 2 x (u^2 + w^2 - x^2 + y^2) + 4 u w y, \\ \gamma_{3,1} = -2 t^2 x + t (4 x^2 - w_1^2) + 2 x (u^2 + w^2 - x^2 + y^2) - 4 u w y, \quad (9)$$

and

$$-t_1 = u + y + w + x, \\ -t_2 = u - y + w - x, \\ -t_3 = u + y + w - x + w_1, \\ -t_4 = u - y + w + x + w_1. \quad (10)$$

The integrand of Eq. (5) has a damping exponent for large values of t , which greatly facilitates its numerical evaluation. The numerical approach to its evaluation is described in Appendix A.

In order to calculate integrals with positive powers of interparticle distances, we make use of the differential equation for the master integral $f(r)$

$$\left[w_1^2 \frac{d^2}{dr^2} r \frac{d^2}{dr^2} + \sigma_2 \frac{d}{dr} r \frac{d}{dr} + \sigma_0 r \right] f(r) = F(r), \quad (11)$$

with the inhomogeneous term given by

$$\begin{aligned}
F(r) = & w_1 \left(\frac{1}{r^2} + \frac{2w_1 + u + w + x - y}{r} \right) e^{-r(u+w+w_1+x-y)} \\
& + w_1 \left(\frac{1}{r^2} + \frac{2w_1 + u + w - x + y}{r} \right) e^{-r(u+w+w_1-x+y)} \\
& - w_1 \left(\frac{1}{r^2} + \frac{u + w - x - y}{r} \right) e^{-r(u+w-x-y)} \\
& - w_1 \left(\frac{1}{r^2} + \frac{u + w + x + y}{r} \right) e^{-r(u+w+x+y)} \\
& + \left[\frac{w_1^2}{2} (u - w + x - y) + 2uw(y-x) + 2xy(w-u) \right] F_1 \\
& + \left[\frac{w_1^2}{2} (u - w - x + y) + 2uw(x-y) + 2xy(w-u) \right] F_2 \\
& + \left[\frac{w_1^2}{2} (u + w + x + y) + 2uw(x+y) + 2xy(u+w) \right] F_3 \\
& + \left[\frac{w_1^2}{2} (u + w - x - y) - 2uw(x+y) + 2xy(u+w) \right] F_4 \quad (12)
\end{aligned}$$

where

$$\begin{aligned}
F_1 &= \text{Ei}[-r(w_1 + 2u)] \exp[r(u - w + x - y)] - \text{Ei}[-r(w_1 + 2w)] \exp[-r(u - w + x - y)], \\
F_2 &= \text{Ei}[-r(w_1 + 2u)] \exp[r(u - w - x + y)] - \text{Ei}[-r(w_1 + 2w)] \exp[-r(u - w - x + y)], \\
F_3 &= \text{Ei}[-2r(u + w)] \exp[r(u + w + x + y)] + \left\{ \text{Ei}[2r(x + y)] - \text{Ei}[-r(w_1 - 2x)], \right. \\
&\quad \left. - \text{Ei}[-r(w_1 - 2y)] - \log \left[\frac{(w_1 + 2u)(w_1 + 2w)(x + y)}{(u + w)(w_1 - 2x)(w_1 - 2y)} \right] \right\} \exp[-r(u + w + x + y)], \\
F_4 &= \text{Ei}[-2r(u + w)] \exp[r(u + w - x - y)] + \left\{ \text{Ei}[-2r(x + y)] - \text{Ei}[-r(w_1 + 2x)] \right. \\
&\quad \left. - \text{Ei}[-r(w_1 + 2y)] - \log \left[\frac{(w_1 + 2u)(w_1 + 2w)(x + y)}{(u + w)(w_1 + 2x)(w_1 + 2y)} \right] \right\} \exp[-r(u + w - x - y)], \quad (13)
\end{aligned}$$

and Ei is the exponential integral function. The function (5) is the solution of this differential equation, which vanishes at small and large r .

From the differential equation (11) and similar differential equations for derivatives of f over nonlinear parameters, one can obtain various recurrence relations for the higher order derivatives of $f(r)$. The complete set of differentiation formulas can be found in Ref. [11].

In the present paper, we will need only the following relations,

$$\begin{aligned}
\frac{\partial f'(r)}{\partial w} &= \frac{1}{w_1^2 - 4w^2} \left(-\frac{r f(r)}{2} \frac{\partial \sigma_{02}}{\partial w} - 2rw f''(r) + \frac{-F_1 - F_2 + F_3 + F_4}{2} \right), \\
\frac{\partial f'(r)}{\partial u} &= \frac{1}{w_1^2 - 4u^2} \left(-\frac{r f(r)}{2} \frac{\partial \sigma_{02}}{\partial u} - 2ru f''(r) + \frac{F_1 + F_2 + F_3 + F_4}{2} \right), \\
\frac{\partial f'(r)}{\partial x} &= \frac{1}{w_1^2 - 4x^2} \left(-\frac{r f(r)}{2} \frac{\partial \sigma_{02}}{\partial x} - 2rx f''(r) + \frac{F_1 - F_2 + F_3 - F_4}{2} \right), \\
\frac{\partial f'(r)}{\partial y} &= \frac{1}{w_1^2 - 4y^2} \left(-\frac{r f(r)}{2} \frac{\partial \sigma_{02}}{\partial y} - 2ry f''(r) + \frac{-F_1 + F_2 + F_3 - F_4}{2} \right), \quad (14)
\end{aligned}$$

where $\sigma_{02} = (u + w - x - y)(u - w + x - y)(u - w - x + y)(u + w + x + y)$, and the inhomogeneous terms F_i terms are given by Eq. (13) and $f'(r)$ means derivative with respect to r . The derivative with respect to w_1 can be easily obtained from the fact that function $r^{-2} f(r)$ is dimensionless, which entails that

$$w_1 \frac{\partial f(r)}{\partial w_1} = -w \frac{\partial f(r)}{\partial w} - u \frac{\partial f(r)}{\partial u} - x \frac{\partial f(r)}{\partial x} - y \frac{\partial f(r)}{\partial y} + r f'(r) - 2f(r). \quad (15)$$

Using the recurrence relations (14)-(15), we can express all derivatives of $f(r)$ over the nonlinear parameters in terms of the master integral $f(r)$, its n th derivatives with respect to r , $f^{(n)}(r)$, and its n th-fold integrals with respect to r , $f^{(-n)}(r)$. All $f^{(\pm n)}(r)$ can be evaluated exactly in the same way as the master integral itself, by differentiation or integration of the main formula (5).

III. ASYMPTOTIC EXPANSION

Calculation of the master integral and its derivatives can be greatly simplified in the case when one of the nonlinear parameters is much larger than the others, by using the asymptotic expansion over the large parameter. Such situation may occur when matrix elements of singular operators are evaluated. In particular, the matrix element of the operator $1/r_{1A}^2$ is calculated in the present work by numerical integration over the corresponding nonlinear parameter,

$$\left\langle \frac{1}{r_{1A}^2} \right\rangle = \int_0^\infty dq \left\langle \frac{e^{-qr_{1A}}}{r_{1A}} \right\rangle. \quad (16)$$

In order to calculate the matrix element of $e^{-qr_{1A}}/r_{1A}$ for large q , we need master integral $f(r; w_1, y + q/2, x, u + q/2, w)$. If q is much larger than w_1, y, x, u , and w , the dominating

part of σ is σ_0 . So, the solution of the differential equation (11) can be represented as

$$\begin{aligned} f(r) &= \left[w_1^2 \frac{d^2}{dr^2} r \frac{d^2}{dr^2} + \sigma_2 \frac{d}{dr} r \frac{d}{dr} + \sigma_0 r \right]^{-1} F(r) \\ &= \frac{F(r)}{\sigma_0 r} - \frac{1}{\sigma_0 r} \left[w_1^2 \frac{d^2}{dr^2} r \frac{d^2}{dr^2} + \sigma_2 \frac{d}{dr} r \frac{d}{dr} \right] \frac{F(r)}{\sigma_0 r} + \dots \end{aligned} \quad (17)$$

The leading term of this expansion is $\sim q^{-2}$, whereas each next term contains additional factor of q^{-2} . Terms of this expansion and their derivatives over the nonlinear parameters can be obtained analytically,

$$\begin{aligned} f(r) &= \frac{1}{2r q^2 (w-x)} \left[\text{Ei}(-r(w_1 + 2x)) e^{-r(u+w-x-y)} - \text{Ei}(-r(w_1 + 2w)) e^{-r(u-w+x-y)} \right. \\ &\quad \left. + \ln \left(\frac{w_1 + 2w}{w_1 + 2x} \right) e^{-r(u+w-x-y)} \right] + O(q^{-3}), \end{aligned} \quad (18)$$

where terms with e^{-qr} were neglected.

IV. NONRELATIVISTIC HAMILTONIAN

The nonrelativistic Hamiltonian for the diatomic molecule in the Born-Oppenheimer approximation is given by

$$H = -\frac{\Delta_1^2}{2} - \frac{\Delta_2^2}{2} - \frac{Z_A}{r_{1A}} - \frac{Z_B}{r_{1B}} - \frac{Z_A}{r_{2A}} - \frac{Z_B}{r_{2B}} + \frac{1}{r_{12}} + \frac{Z_A Z_B}{r}, \quad (19)$$

where Z_A and Z_B are the charge numbers of the nuclei A and B , respectively. The Hamiltonian is conveniently divided into the kinetic T and the potential V parts, $H = T + V$, where T is given by the first two terms in the right-hand-side of Eq. (19) whereas V is given by the rest.

The matrix elements of the Hamiltonian with the wave functions

$$\phi_i = e^{-w_{1i} r_{12} - u_i (r_{1A} + r_{1B}) - w_i (r_{2A} + r_{2B}) - y_i (r_{1A} - r_{1B}) - x_i (r_{2A} - r_{2B})} \quad (20)$$

and the corresponding overlap integrals can be easily expressed in terms of the derivatives

of the master integral over the nonlinear parameters. The result is

$$\begin{aligned}
\langle \phi_l | T | \phi_k \rangle &= \frac{1}{16 w_1} \left\{ 2 (u_l^2 w_{1k} - y_l^2 w_{1k} + u_k^2 w_{1l} - y_k^2 w_{1l}) r^2 [f(1, 0, 0, 0, 2) - f(1, 0, 2, 0, 0)] \right. \\
&\quad + 2 (w_l^2 w_{1k} - x_l^2 w_{1k} + w_k^2 w_{1l} - x_k^2 w_{1l}) r^2 [f(1, 0, 0, 2, 0) - f(1, 2, 0, 0, 0)] \\
&\quad + (2 w_l^2 w_{1k} + 2 y_l^2 w_{1k} + 2 w_k^2 w_{1l} + 2 y_k^2 w_{1l} - w_1 w_{1k} w_{1l}) f(1, 2, 0, 0, 2) \\
&\quad + (2 u_l^2 w_{1k} + 2 x_l^2 w_{1k} + 2 u_k^2 w_{1l} + 2 x_k^2 w_{1l} - w_1 w_{1k} w_{1l}) f(1, 0, 2, 2, 0) \\
&\quad - (2 u_l^2 w_{1k} + 2 w_l^2 w_{1k} + 2 u_k^2 w_{1l} + 2 w_k^2 w_{1l} - w_1 w_{1k} w_{1l}) f(1, 0, 0, 2, 2) \\
&\quad - (2 y_l^2 w_{1k} + 2 x_l^2 w_{1k} + 2 y_k^2 w_{1l} + 2 x_k^2 w_{1l} - w_1 w_{1k} w_{1l}) f(1, 2, 2, 0, 0) \\
&\quad + 4 (u_l w_{1k} + u_k w_{1l}) [f(1, 0, 0, 1, 2) - f(1, 0, 2, 1, 0)] \\
&\quad + 4 (w_l w_{1k} + w_k w_{1l}) [f(1, 0, 0, 2, 1) - f(1, 2, 0, 0, 1)] \\
&\quad + 4 (y_l w_{1k} + y_k w_{1l}) [f(1, 1, 2, 0, 0) - f(1, 1, 0, 0, 2)] \\
&\quad \left. + 4 (x_l w_{1k} + x_k w_{1l}) [f(1, 2, 1, 0, 0) - f(1, 0, 1, 2, 0)] \right\}, \\
\langle \phi_l | V | \phi_k \rangle &= \frac{1}{16} \left\{ f(0, 0, 0, 2, 2) - f(0, 0, 2, 2, 0) - f(0, 2, 0, 0, 2) + f(0, 2, 2, 0, 0) \right. \\
&\quad + 2 (Z_A + Z_B) [f(1, 0, 2, 1, 0) + f(1, 2, 0, 0, 1) - f(1, 0, 0, 1, 2) - f(1, 0, 0, 2, 1)] \\
&\quad + 2 (Z_A - Z_B) [f(1, 0, 1, 2, 0) + f(1, 1, 0, 0, 2) - f(1, 1, 2, 0, 0) - f(1, 2, 1, 0, 0)] \\
&\quad \left. + \frac{Z_A Z_B}{r} [f(1, 0, 0, 2, 2) - f(1, 0, 2, 2, 0) - f(1, 2, 0, 0, 2) + f(1, 2, 2, 0, 0)] \right\}, \\
\langle \phi_l | \phi_k \rangle &= \frac{1}{16} [f(1, 0, 0, 2, 2) - f(1, 0, 2, 2, 0) - f(1, 2, 0, 0, 2) + f(1, 2, 2, 0, 0)], \quad (21)
\end{aligned}$$

where $w_1 \equiv w_{1k} + w_{1l}$, and

$$f(n_1, n_2, n_3, n_4, n_5) = \left(-\frac{\partial}{\partial w_1} \right)^{n_1} \left(-\frac{\partial}{\partial y} \right)^{n_2} \left(-\frac{\partial}{\partial x} \right)^{n_3} \left(-\frac{\partial}{\partial u} \right)^{n_4} \left(-\frac{\partial}{\partial w} \right)^{n_5} f(r). \quad (22)$$

The wave function of the ground electronic Σ_g^+ state of the H_2 molecule is expressed in terms of the basis wave functions ϕ_i (20) as follows

$$\psi = \sum_i c_i (1 + P_{AB}) (1 + P_{12}) \phi_i, \quad (23)$$

where P_{AB} permutes the nuclei A and B , P_{12} interchanges the two electrons, and c_i are linear coefficients, obtained as components of the eigenvector of the Hamiltonian matrix. Our numerical approach to the evaluation of the Hamiltonian matrix is described in Appendix B.

TABLE I: Nonrelativistic energy of the ground electronic Σ_g^+ state of the H_2 molecule for two internuclear distances r , in a.u.

N	$r = 1.4$		$r = 14.0$	
	E	δE	E	δE
2	-1.173 468 555		-0.999 999 778 930	
4	-1.174 125 505	-0.000 783 527	-1.000 000 480 057	-0.000 764 402 260
8	-1.174 373 774	-0.000 248 268	-1.000 000 942 482	-0.000 000 462 425
16	-1.174 469 553	-0.000 095 779	-1.000 000 955 376	-0.000 000 012 893
32	-1.174 474 880	-0.000 005 327	-1.000 000 958 807	-0.000 000 003 430
64	-1.174 475 260	-0.000 000 379	-1.000 000 959 559	-0.000 000 000 934
	-1.174 475 714 220 ^a		-1.000 000 960 680 791 ^b	

^a James-Coolidge basis with $N \approx 20000$ [7];

^b Explicitly correlated asymptotic basis with $N \approx 20000$ [7].

TABLE II: Expectation value of the operators r_{12}^{-2} and r_{1A}^{-2} for the ground electronic Σ_g^+ state of the H_2 molecule for two internuclear distances r , in a.u.

N	$r = 1.4$		$r = 14.0$	
	$\langle r_{12}^{-2} \rangle$	$\langle r_{1A}^{-2} \rangle$	$\langle r_{12}^{-2} \rangle$	$\langle r_{1A}^{-2} \rangle$
8	0.518 482	1.604 12	0.005 155 876	1.002 558 4
16	0.517 917	1.601 65	0.005 155 881	1.002 555 5
32	0.517 948	1.601 73	0.005 155 882	1.002 562 3
64	0.517 934	1.601 70	0.005 155 882	1.002 563 1
	0.517 913 ^a	1.597 56 ^a		

^a Gaussian basis with $N \approx 1200$ [8].

V. NUMERICAL RESULTS AND DISCUSSION

Table I presents numerical results for the nonrelativistic energy of the ground electronic Σ_g^+ state of the H_2 molecule obtained with the exponential correlated basis. Comparison with previous results obtained with the James-Coolidge and asymptotic functions shows that the exponential basis set yields reasonably accurate results with very small number of

basis functions. Because it has the correct analytical properties of the true wave function both at the coalescent points and in the asymptotic region, it works equally well at small and at large internuclear distances. This is in contrast to the James-Coolidge and the explicitly correlated asymptotic basis, which are effective, respectively, only at the small or large internuclear distances.

The main drawback of the exponential correlated basis is that the calculations are generally more expensive than those with other basis functions, because of the numerical integration in the master integral and also because of numerical instabilities inherent in recurrence relations, which call for extended-precision arithmetics. In our calculations, we used the octuple-precision arithmetics and performed optimization of the nonlinear parameters with an explicit check of numerical stability (i.e., only the numerically stable results were taken into account during the optimization procedure).

Because of slowness of the numerical procedure, our calculations of the nonrelativistic energy with the exponential correlated basis are much less accurate than the best calculations with the James-Coolidge or ECG basis functions. However, our main purpose in developing this basis set is their applicability for calculations of higher-order QED effects. The QED effects of order $m\alpha^6$ for molecules are presently unknown, even the complete formulas for them have not been derived so far. However, from the calculations for helium [13] we know that these effects are described by highly singular operators. The basis of the explicitly correlated exponential functions turned out to be the best choice for for helium atom, so we think that it is an appropriate choice for solving this problem for molecules as well.

Calculation of matrix elements of singular operators (in particular, operators with inverse powers of interparticle distance) with the exponential correlated basis are nontrivial because no closed-form analytical formula were found for them. In the present work, we propose to evaluate these operators by integration with respect to the corresponding nonlinear parameter, see Eq. (16). A numerical proof of principle of this method is given in Table II, which presents the results of our test calculations of matrix elements of the operators $1/r_{12}^2$ and $1/r_{1A}^2$. Certainly, the same method can be applied to all operators involved in calculation of the $m\alpha^6$ QED contribution, but the open issue is its numerical accuracy.

VI. SUMMARY

In this paper we have developed a numerical procedure for calculating the nonrelativistic energy of the H_2 (or, in fact, any other diatomic) molecule with the fully correlated basis of exponential functions. This basis is the most general two-electron two-center basis. Having the correct analytical properties both at coalescent points of $r_i = r_j$ and at asymptotic distances $r_i \rightarrow \infty$, this basis yields accurate and very compact representations of the nonrelativistic wave function. We presented numerical results for the nonrelativistic energy obtained with this basis and demonstrated that the matrix elements of the negative powers of the interparticle distances can be calculated by numerical integration over the corresponding nonlinear parameter.

The correlated exponential basis looks a promising tool for the evaluation of higher-order QED effects in H_2 and the other diatomic molecules. We hope that speed and stability of our present numerical procedure can be improved further by calculating the master integral and its derivatives with help of the Taylor expansion in r .

Acknowledgments

This work was supported by NCN grant 2012/04/A/ST2/00105.

-
- [1] J. Liu et al., J. Chem. Phys. **130**, 174306 (2009).
 - [2] J. Liu et al., J. Chem. Phys. **132**, 154301 (2010).
 - [3] G.D. Dickenson *et al.*, Phys. Rev. Lett. **110**, 193601 (2013).
 - [4] J. Komasa, K. Piszczatowski, G. Łach, M. Przybytek, B. Jeziorski, and K. Pachucki, JCTC **7**, 3105 (2011).
 - [5] V. A. Yerokhin and K. Pachucki, Phys. Rev. A **81**, 022507 (2010).
 - [6] W. Kołos and L. Wolniewicz, J. Chem. Phys. **49**, 404 (1968).
 - [7] K. Pachucki, Phys. Rev. A **82**, 032509 (2010).
 - [8] J. Komasa, priv. comm. (2013).
 - [9] D. M. Fromm and R. N. Hill, Phys. Rev. A **36**, 1013 (1987).
 - [10] K. Pachucki, Phys. Rev. A **80**, 032520 (2009).

- [11] K. Pachucki, Phys. Rev. A **86**, 052514 (2012).
 [12] M. Lesiuk and R. Moszyński, Phys. Rev. A **86**, 052513 (2012).
 [13] K. Pachucki, Phys. Rev. A. **74**, 022512 (2006).
 [14] F.E. Harris, Phys. Rev. A **55**, 1820 (1997).
 [15] M. Puchalski and K. Pachucki, Phys. Rev. A **73**, 022503 (2006).

Appendix A: Numerical evaluation of the master integral

For the numerical evaluation of the master integral by numerical integration, one needs to eliminate all singularities on the integration path [9] in Eq. (5). For this one has to consider all possible orderings of t_i . Because of the symmetry $1 \leftrightarrow 2$ and $A \leftrightarrow B$ of the wave function, one can assume, without losing the generality, that $y \leq |x|$, so that $t_1 \geq t_2$ and $t_3 \geq t_4$. This leaves us with six possible orderings of t_i . The six corresponding representations of the master integral f are:

$$\begin{aligned}
 f(r) &= \left(\int_{t_1}^{t_2} \ln |\beta_{0,0}| + \int_{t_2}^{t_3} \ln |\beta_{0,0} \beta_{3,3}| + \int_{t_3}^{t_4} \ln |\beta_{0,0}/\beta_{3,1}| - \int_{t_4}^{-\infty} \ln |\beta_{0,1} \beta_{3,1}| \right) \frac{e^{tr}}{2\sqrt{\sigma}} dt \\
 &= \left(\int_{t_1}^{t_3} \ln |\beta_{0,0}| - \int_{t_3}^{t_2} \ln |\beta_{0,2}| + \int_{t_2}^{t_4} \ln |\beta_{0,0}/\beta_{3,1}| - \int_{t_4}^{-\infty} \ln |\beta_{0,1} \beta_{3,1}| \right) \frac{e^{tr}}{2\sqrt{\sigma}} dt \\
 &= \left(\int_{t_1}^{t_3} \ln |\beta_{0,0}| - \int_{t_3}^{t_4} \ln |\beta_{0,2}| - \int_{t_4}^{t_2} \ln |\beta_{0,0} \beta_{0,1} \beta_{0,2}| - \int_{t_2}^{-\infty} \ln |\beta_{0,1} \beta_{3,1}| \right) \frac{e^{tr}}{2\sqrt{\sigma}} dt \\
 &= \left(- \int_{t_3}^{t_1} \ln |\beta_{0,0} \beta_{0,2}| - \int_{t_1}^{t_2} \ln |\beta_{0,2}| + \int_{t_2}^{t_4} \ln |\beta_{0,0}/\beta_{3,1}| - \int_{t_4}^{-\infty} \ln |\beta_{0,1} \beta_{3,1}| \right) \frac{e^{tr}}{2\sqrt{\sigma}} dt \\
 &= \left(- \int_{t_3}^{t_1} \ln |\beta_{0,0} \beta_{0,2}| - \int_{t_1}^{t_4} \ln |\beta_{0,2}| - \int_{t_4}^{t_2} \ln |\beta_{0,0} \beta_{0,1} \beta_{0,2}| - \int_{t_2}^{-\infty} \ln |\beta_{0,1} \beta_{3,1}| \right) \frac{e^{tr}}{2\sqrt{\sigma}} dt \\
 &= \left(- \int_{t_3}^{t_4} \ln |\beta_{0,0} \beta_{0,2}| - \int_{t_4}^{t_1} \ln |\beta_{0,0}^2 \beta_{0,1} \beta_{0,2}| - \int_{t_1}^{t_2} \ln |\beta_{0,0} \beta_{0,1} \beta_{0,2}| - \int_{t_2}^{-\infty} \ln |\beta_{0,1} \beta_{3,1}| \right) \frac{e^{tr}}{2\sqrt{\sigma}} dt.
 \end{aligned} \tag{A1}$$

In order to eliminate singularities algebraically, the products and ratios of β can be combined together by using the identity [14]

$$\frac{\sqrt{\sigma} - \gamma}{\sqrt{\sigma} + \gamma} \frac{\gamma' - \sqrt{\sigma}}{\gamma' + \sqrt{\sigma}} = \frac{\sqrt{\sigma} - \Gamma}{\sqrt{\sigma} + \Gamma}, \tag{A2}$$

where

$$\Gamma = \frac{\sigma + \gamma \gamma'}{\gamma + \gamma'}. \tag{A3}$$

The evaluation of the logarithms in Eq. (A1) proceeds as follows

$$\operatorname{Re} \left[\frac{1}{2\sqrt{\sigma}} \ln \left(\frac{\sqrt{\sigma} - \gamma}{\sqrt{\sigma} + \gamma} \right) \right] = \begin{cases} -\frac{1}{\gamma}, & \text{for } \sigma = 0, \\ -\frac{1}{\sqrt{\sigma}} \operatorname{arctanh} \left(\frac{\gamma}{\sqrt{\sigma}} \right), & \text{for } \sigma > 0, |\gamma| < \sqrt{\sigma}, \\ -\frac{1}{\sqrt{\sigma}} \operatorname{arctanh} \left(\frac{\sqrt{\sigma}}{\gamma} \right), & \text{for } \sigma > 0, |\gamma| > \sqrt{\sigma}, \\ -\frac{1}{\sqrt{-\sigma}} \left[\operatorname{arctan} \left(\frac{\sqrt{-\sigma}}{\gamma} \right) + k\pi \right], & \text{for } \sigma < 0. \end{cases} \quad (\text{A4})$$

In the last line, the phase prefactor $k = 0, \pm 1$ is introduced, which is determined as follows. On a part \mathcal{C} of the integration path where σ is negative, the parameter γ may change a sign. At this point, a phase factor $\pm\pi$ is introduced so as to make the integrand continuous. Since γ changes sign twice on \mathcal{C} , the correction term vanishes at the beginning and at the end of \mathcal{C} .

Numerical integration over t in the master integral is facilitated by the presence of an exponent e^{tr} , which provides strong damping for large negative t . The integrand is generally a smooth function everywhere except for vicinities of points t_i , around which it may possess one or maximum two logarithmic singularities, which need to be taken care of. We perform numerical integrations by subdividing the integration interval in several parts and applying the extended Gauss-Legendre quadratures with logarithmic end-point singularity (see Appendix of Ref. [15] for details), the standard Gauss-Legendre quadratures, and the Gauss-Laguerre quadratures, depending on the properties of the integrand on the particular sub-divided interval. Using an extended-precision arithmetics, we were able to perform the integration in the master integral up to typically 30 (in worst cases, 20) digits of precision.

Appendix B: Numerical evaluation of the Hamiltonian matrix

For calculation of the Hamiltonian matrix, we need integrals $f(n_1, n_2, n_3, n_4, n_5)$ with $n_1 = 0$ and 1 and $n_2 \dots n_5 = 0 \dots 2$. Taking into account Eq. (15), we can reduce the set of integrals to the case of $n_1 = 0$ and $n_2 \dots n_5 = 0 \dots 3$. In order to calculate them, we first evaluate the master integral $f(r)$, its derivatives $f^{(n)}(r)$ with $n = 1 \dots 5$, and integrals $f^{(-n)}$ with $n = 1 \dots 10$,

$$f^{(-n)}(r) = - \int_r^\infty f^{(-n+1)}(r) dr. \quad (\text{B1})$$

All $f^{(n)}$ with $n = -10 \dots 5$ are obtained directly from the integral representation for the master integral (5) and calculated by performing the integration over t numerically. Alter-

natively, one can also use the master differential equation (11) for $f^{(-n)}(r)$, but this will not be stable for exchange integrals $\vec{r}_1 \leftrightarrow \vec{r}_2$ where $\sigma \approx 0$, so we did not use this method.

Next, we apply the relations (14) to generate the set of derivatives over nonlinear parameters $f^{(n)}(0, n_2, n_3, n_4, n_5)$ with $n_2 + n_3 + n_4 + n_5 = \Omega$ and $n = (-10 + 2\Omega) \dots (5 - \Omega)$, with Ω being increased from 1 to 5. Finally, the integrals with $n_1 = 1$ are calculated by using Eq. (15).

Applying relations (14) for calculation of $f^{(n)}(0, n_2, n_3, n_4, n_5)$, we need multiple derivatives (and integrals over r) of the inhomogeneous terms F_i . The functions F_i are given by relatively simple combinations of elementary functions and the exponential integrals [see Eqs. (13)]. We find it convenient just to generate a table of explicit expressions for these terms, by using following identities,

$$\begin{aligned} \frac{d}{dr} \text{Ei}(ar) &= \frac{1}{r} \exp(ar), \\ - \int_r^\infty \exp(ar) \text{Ei}(br) &= \frac{1}{a} [\exp(ar) \text{Ei}(br) - \text{Ei}((a+b)r)]. \end{aligned} \quad (\text{B2})$$

Note that in the second identity, an integration over r produce an spurious singularity at $a = 0$, which may lead to numerical instabilities for small a 's. Because of this, a series expansion in a was used for the evaluation of inhomogeneous terms in the vicinity of the instability points.