Born-Oppenheimer potential for H_2

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Abstract

The Born-Oppenheimer potential for the ${}^1\Sigma_g^+$ state of H_2 is obtained in the range of 0.1 – 20 au, using analytic formulas and recursion relations for two-center two-electron integrals with exponential functions. For small distances James-Coolidge basis is used, while for large distances the Heitler-London functions with arbitrary polynomial in electron variables. In the whole range of internuclear distance about 10^{-15} precision is achieved, as an example at the equilibrium distance $r = 1.4011$ au the Born-Oppenheimer potential amounts to $-1.174\,475\,931\,400\,216\,7(3)$. Results for the exchange energy verify the formula of Herring and Flicker [Phys. Rev. **134**, A362 (1964)] for the large internuclear distance asymptotics. The presented analytic approach to Slater integrals opens a window for the high precision calculations in an arbitrary diatomic molecule.

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I. INTRODUCTION

In order to accurately obtain vibrational and rotational spectra of molecules not only the non-relativistic Born-Oppenheimer (BO) potential has to be calculated, but also the adiabatic, nonadiabatic, relativistic and quantum electrodynamics effects. An excellent agreement of theoretical results [1] with experimental values achieved for dissociation energies of the hydrogen molecule H_2 [2] and D_2 [3] indicates good understanding of all physical effects up to 10^{-8} precision level. Such a precision has not yet been achieved for molecular systems with more than two electrons. It is because numerical calculations with explicitly correlated functions are very demanding. The commonly used explicitly correlated Gaussian functions require global minimization of thousands of nonlinear parameters, and the accuracy achieved for relativistic effects is difficult to estimate, due to the improper analytic properties of these functions. The largest system considered so far is the helium dimer, where about 10^{-5} precision is achieved for the interaction energy [4].

Herewith, we apply explicitly correlated exponential functions (for a recent review see Ref. [5]), in order to increase numerical accuracy obtained so far for two electrons diatomic systems. The use of exponential functions may allow for a significant improvement not only in rotational and vibrational energies, but also in other important properties like magnetic shielding, spin-rotational or spin-spin coupling constants. It is because evaluation of relativistic effects is very sensitive to correct analytic properties of the basis functions, a good example being the relativistic correction to the magnetic shielding [6].

When 10^{-10} precision is achieved for vibrational transitions, the electron-proton mass ratio can be determined with better accuracy, than it is known presently [7]. Moreover, any non-electromagnetic long-range interactions between nuclei, which cannot in principle be excluded, may be visible not only in vibrational spectra, but also in the spin interaction between nuclei [8], for example in HD molecule. The electromagnetic spin interaction is extremely small, of order $m^3/(m_p\, m_d)\,\alpha^6$, about 43 Hz for the ground molecular state [9], and any deviation between experimental values and theoretical predictions will signal existence of a nonelectromagnetic long-range interactions between nuclei.

In this work we present an effective computational method with the use of exponential functions and numerical results for the Born-Oppenheimer energy of the H_2 molecule. We demonstrate that 10^{-15} numerical precision can be achieved for BO energy with about 22 000 basis functions using the analytic formulae and recursion relations for Slater integrals, which have been obtained in our previous work in [10]. The obtained BO potential is at least two orders of magnitude more accurate, than anything published so far, and at the equilibrium distance our calculations confirm the most accurate so far result of Cencek and Szalewicz in Ref. [11] well within their uncertainties. Our results for large internuclear distances verify the asymptotic formula of Herring and Flicker [12], although we observe significant contributions from the off leading terms. Finally, we analyze possibility of the extension of this method to more than two-electron systems.

II. SHORT RANGE OF INTERNUCLEAR DISTANCES

The Schrödinger equation for H_2 molecule in the Born-Oppenheimer approximation is

$$H\phi(\vec{r}_1\,,\vec{r}_2) = E(r)\phi(\vec{r}_1\,,\vec{r}_2), \tag{1}$$

where

$$H = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{r}. \tag{2}$$

The most efficient basis set to solve this equation is the one introduced by Kołos and Wolniewicz in [13]. However at small nuclear distances $r \equiv r_{AB}$, we can use much simpler James-Coolidge basis [14], namely the functions of the form

$$\begin{aligned}\phi \;=\; & \sum_{\{n\}} c_{\{n\}}(1+P_{AB})\,(1+P_{12})\,e^{-\alpha\,(r_{1A}+r_{1B})}\,e^{-\alpha\,(r_{2A}+r_{2B})}\,r_{12}^{n_1} \\ & (r_{1A}-r_{1B})^{n_2}\,(r_{2A}-r_{2B})^{n_3}\,(r_{1A}+r_{1B})^{n_4}\,(r_{2A}+r_{2B})^{n_5}\end{aligned} \tag{3}$$

such that

$$\sum_{i=1}^{5} n_i \le \Omega \tag{4}$$

with $\Omega = 3,\ldots 20$. This basis have recently been used by Sims and Hagstrom [15] for 10^{-12} precision calculation of BO potential in the range $r = 0.4-6$ au, by a traditional way of numerical evaluation of the corresponding two-center integrals. Here, using Ref. [10] we derive analytic expression for all these integrals up to $\Omega = 20$. They have very simple form and involve only exponential integral (Ei), exponential and logarithmic functions. In this derivation we make use of a differential equation, which is satisfied by the most general two-center two-electron Slater integral, see Ref. [10].

For the presentation of analytic formulas we consider an integral

$$
\begin{aligned}
f(n_1,n_2,n_3,n_4,n_5;r,u,w) \;=\; & \int\frac{d^3r_1}{4\,\pi}\int\frac{d^3r_2}{4\,\pi}\,\frac{e^{-u\,r_{1A}}}{r_{1A}}\,\frac{e^{-u\,r_{1B}}}{r_{1B}}\,\frac{e^{-w\,r_{2A}}}{r_{2A}}\,\frac{e^{-w\,r_{2B}}}{r_{2B}}\,\frac{r}{r_{12}^{1-n_1}}\\
& (r_{1A}-r_{1B})^{n_2}\,(r_{2A}-r_{2B})^{n_3}\,(r_{1A}+r_{1B})^{n_4}\,(r_{2A}+r_{2B})^{n_5} \quad (5)
\end{aligned}
$$

at the internuclear distance $r=1$, since arbitrary distances can be obtained from the relation

$$
f(n_1,n_2,n_3,n_4,n_5;r,u,w) = f(n_1,n_2,n_3,n_4,n_5,1,r\,u,r\,w)\,r^{2+n_1+n_2+n_3+n_4+n_5} \quad (6)
$$

Positive powers of n_4 and n_5 can be obtained by differentiation with respect to u and w correspondingly, so without loss of generality one can assume $n_4=n_5=0$. Let us introduce auxiliary functions y_i defined by

$$
\begin{aligned}
y_0 &= e^{-(u+w)} && (7)\\
y_1 &= \mathrm{Ei}(-2\,w)\,e^{w-u}+\mathrm{Ei}(-2\,u)\,e^{u-w} && (8)\\
y_2 &= \mathrm{Ei}(-2\,w)\,e^{w-u}-\mathrm{Ei}(-2\,u)\,e^{u-w} && (9)\\
y_3 &= \mathrm{Ei}\big(-2\,(u+w)\big)\,e^{u+w}+\left[\ln\!\Big(\frac{2\,u\,w}{u+w}\Big)+\gamma\right]e^{-(u+w)} && (10)\\
y_4 &= \mathrm{Ei}\big(-2\,(u+w)\big)\,e^{u+w}-\left[\ln\!\Big(\frac{2\,u\,w}{u+w}\Big)+\gamma\right]e^{-(u+w)} && (11)
\end{aligned}
$$

Then, using the equation (69) from [10], all nonvanishing integrals $f(n_1,n_2,n_3)\equiv f(n_1,n_2,n_3,0,0;1,u,w)$ with $\sum_i n_i\le 4$ are the following:

$$
\begin{aligned}
f(0,0,0) &= \frac{y_3-y_1}{4\,u\,w} && (12)\\
f(1,0,0) &= \frac{y_0}{4\,u\,w} && (13)\\
f(2,0,0) &= \frac{y_0\,(2\,u\,w+u+w)+y_2\,(u-w)-y_4\,(u+w)}{24\,u^2\,w^2}+\frac{(y_3-y_1)\,(u^2+w^2)}{24\,u^3\,w^3} && (14)\\
f(0,2,0) &= \frac{y_3-y_1}{12\,u\,w} && (15)\\
f(0,1,1) &= -\frac{y_0}{6\,u\,w}+\frac{y_1\,(u\,w-1)-y_2\,(u-w)+y_3\,(u\,w+1)-y_4\,(u+w)}{12\,u^2\,w^2} && (16)\\
f(3,0,0) &= \frac{y_0\,(u^2\,w^2+3\,u\,w\,(u+w)+3\,(u^2+w^2))}{24\,u^3\,w^3} && (17)\\
f(1,2,0) &= \frac{y_0}{12\,u\,w} && (18)
\end{aligned}
$$

$$
\begin{aligned}
f(4,0,0) \;=\;& \frac{y_0\left(2u^3w^3+6u^3w^2+9u^3w+3u^3+6u^2w^3+4u^2w^2+6u^2w+9uw^3+6uw^2+3w^3\right)}{80u^4w^4} \\
&+\frac{y_2(u-w)\left(3u^2+uw+3w^2\right)}{40u^4w^4}-\frac{y_4(u+w)\left(3u^2-uw+3w^2\right)}{40u^4w^4} \\
&+\frac{(y_3-y_1)\left(u^4w^2+3u^4+u^2w^4+2u^2w^2+3w^4\right)}{40u^5w^5}+\frac{y_3+y_1}{20u^2w^2}
\end{aligned}
\tag{19}
$$

$$
\begin{aligned}
f(2,2,0) \;=\;& \frac{y_2(u-w)(uw+2)}{120u^3w^3}-\frac{y_4(u+w)(uw-2)}{120u^3w^3}+\frac{y_0(4uw+3u+3w+4)}{120u^2w^2} \\
&-\frac{y_1\left(u^2+2uw+w^2-2\right)}{120u^3w^3}+\frac{y_3\left(u^2-2uw+w^2-2\right)}{120u^3w^3}
\end{aligned}
\tag{20}
$$

$$
\begin{aligned}
f(2,1,1) \;=\;& -\frac{y_0\left(2u^2w^2+3u^2w+6u^2+3uw^2+6w^2\right)}{120u^3w^3} \\
&-\frac{y_2(u-w)\left(u^2w^2+3u^2+3w^2\right)}{120u^4w^4}-\frac{y_4(u+w)\left(u^2w^2+3u^2+3w^2\right)}{120u^4w^4} \\
&+\frac{(y_3+y_1)\left(u^2+w^2\right)}{40u^3w^3}+\frac{(y_3-y_1)\left(2u^2w^2+3u^2+3w^2\right)}{120u^4w^4}
\end{aligned}
\tag{21}
$$

$$
f(0,4,0) \;=\; \frac{y_3-y_1}{20\,u\,w} \tag{22}
$$

$$
f(0,3,1) \;=\; \frac{y_1(uw-1)}{20u^2w^2}-\frac{y_2(u-w)}{20u^2w^2}+\frac{y_3(uw+1)}{20u^2w^2}-\frac{y_4(u+w)}{20u^2w^2}-\frac{y_0}{10uw} \tag{23}
$$

$$
\begin{aligned}
f(0,2,2) \;=\;& \frac{y_2(u-w)(uw-3)}{15u^3w^3}-\frac{y_4(u+w)(uw+3)}{15u^3w^3}-\frac{y_0(uw+2u+2w+6)}{15u^2w^2} \\
&+\frac{y_3+y_1}{2u^2w^2}+\frac{(y_3-y_1)\left(3u^2w^2+4u^2+4w^2+12\right)}{60u^3w^3}
\end{aligned}
\tag{24}
$$

Integrals with higher powers of n_i are similar, with simple polynomial form in $1/u$ and $1/w$. We have tabulated all integrals, such that $\sum_i n_i \leq 45$ what is sufficient for matrix elements involving exponential functions with maximum value of $\Omega = 20$.

III. LONG RANGE OF INTERNUCLEAR DISTANCES

For the large internuclear distance the James-Coolidge basis is not appropriate as it does not include the Heitler-London function. Instead, we employ generalized Heitler-London functions, which are the product of a Heitler London function with an arbitrary polynomial in all electron distances,

$$
\phi \;=\; \sum_{\{n\}} c_{\{n\}}(1+P_{AB})\,(1+P_{12})\,e^{-(r_{1A}+r_{2B})}\,r_{12}^{n_1}\,r_{1A}^{n_2}\,r_{1B}^{n_3}\,r_{2A}^{n_4}\,r_{2B}^{n_5} \tag{25}
$$

such that

$$\sum_{i=1}^{5} n_i \le \Omega, \tag{26}$$

and call them the explicitly correlated asymptotic (ECA) basis. Matrix elements of the nonrelativistic Hamiltonian can be expressed in terms of direct integrals of the form

$$f(n_1,n_2,n_3,n_4,n_5;r,x) = \int \frac{d^3r_1}{4\,\pi} \int \frac{d^3r_2}{4\,\pi}\, \frac{r}{r_{12}^{1-n_1}}\, \frac{e^{-x\,r_{1A}}}{r_{1A}^{1-n_2}}\, \frac{1}{r_{1B}^{1-n_3}}\, \frac{1}{r_{2A}^{1-n_4}}\, \frac{e^{-x\,r_{2B}}}{r_{2B}^{1-n_5}}. \tag{27}$$

with nonnegative integers n_i, and exchange integrals which coincide with that from the previous section. The direct integrals are calculated as follows. When all $n_i = 0$ the so called master integral is given by [10]

$$\begin{aligned} f(r,x) &= \int \frac{d^3r_1}{4\,\pi} \int \frac{d^3r_2}{4\,\pi}\, \frac{e^{-x\,r_{1A}}}{r_{1A}}\, \frac{e^{-x\,r_{2B}}}{r_{2B}}\, \frac{1}{r_{1B}}\, \frac{1}{r_{2A}}\, \frac{r}{r_{12}} \qquad (28)\\ &= \frac{1}{x}\left[I_0(\sqrt{2}\,x\,r)\int_r^\infty dr'\,F(x\,r')\,K_0(\sqrt{2}\,x\,r') + K_0(\sqrt{2}\,x\,r)\int_0^r dr'\,F(x\,r')\,I_0(\sqrt{2}\,x\,r')\right] \end{aligned}$$

and its first derivative with respect to r

$$f'(r,x) = \sqrt{2}\left[I_1(\sqrt{2}\,x\,r)\int_r^\infty dr'\,F(x\,r')\,K_0(\sqrt{2}\,x\,r') - K_1(\sqrt{2}\,x\,r)\int_0^r dr'\,F(x\,r')\,I_0(\sqrt{2}\,x\,r')\right] \tag{29}$$

where

$$F(x) = -e^{x}\,[\mathrm{Ei}(-2\,x) + \mathrm{Ei}(-x)] + e^{-x}\,[\mathrm{Ei}(x) + 2\,\mathrm{Ei}(-x) - \gamma - \ln(2\,x)]. \tag{30}$$

This one dimensional integration can easily be obtained with the sufficient accuracy and for example at $r = 6,\ x = 2$ the value of f is

$$f(6,2) = 0.001\,790\,194\,708\,681\,916\,168\,871\,495\,878\,339\,876 \tag{31}$$

All integrals with higher powers of electron distances can be obtained from recursion relations, which were derived in Ref. [10]. Since

$$f(n_1,n_2,n_3,n_4,n_5;r,x) = f(n_1,n_2,n_3,n_4,n_5,1,r\,x)\,r^{2+n_1+n_2+n_3+n_4+n_5} \tag{32}$$

we can present formulae at $r = 1$. Let us introduce auxiliary functions

$$y_0 = e^{-x} \tag{33}$$

$$y_1 = [\mathrm{Ei}(x) - \ln(2\,x) - \gamma]\,e^{-x} - [\mathrm{Ei}(-2\,x) - \mathrm{Ei}(-x)]\,e^{x} \tag{34}$$

$$y_2 = [\mathrm{Ei}(x) - \ln(2\,x) - \gamma\,]e^{-x} + [\mathrm{Ei}(-2\,x) - \mathrm{Ei}(-x)]\,e^{x} \tag{35}$$

$$y_3 = [2\,\mathrm{Ei}(-x) + \mathrm{Ei}(x) - \ln(2\,x) - \gamma]\,e^{-x} + [\mathrm{Ei}(-2\,x) + \mathrm{Ei}(-x)]\,e^{x} \tag{36}$$

$$y_4 = [2\,\mathrm{Ei}(-x) + \mathrm{Ei}(x) - \ln(2\,x) - \gamma]\,e^{-x} - [\mathrm{Ei}(-2\,x) + \mathrm{Ei}(-x)]\,e^{x} \tag{37}$$

then all integrals $f(n_1,n_2,n_3,n_4,n_5;x)$ with $\sum_i n_i \le 2$ are the following

$$f(0,0,0,0,0) = f \tag{38}$$

$$f(0,0,1,0,0) = \frac{f}{x} - \frac{f'}{2\,x} \tag{39}$$

$$f(0,1,0,0,0) = \frac{y_2}{2x^3} \tag{40}$$

$$f(1,0,0,0,0) = \frac{(1-y_0)^2}{x^4} \tag{41}$$

$$f(0,0,0,2,0) = \frac{y_0^2-1}{2x^4} + \frac{y_0}{2x^3} + \left(\frac{2}{x^2}+\frac{1}{2}\right) f - \frac{f'}{x^2} \tag{42}$$

$$f(0,0,1,1,0) = -\frac{y_0^2-1}{2x^4} - \frac{y_4}{2x^3} - \frac{y_0}{2x^3} + \left(\frac{1}{x^2}+\frac{1}{2}\right) f - \frac{3f'}{2x^2} \tag{43}$$

$$f(0,0,2,0,0) = \frac{y_0^2-1}{2x^4} + \frac{y_0}{2x^3} + \left(\frac{2}{x^2}+\frac{1}{2}\right) f - \frac{f'}{x^2} \tag{44}$$

$$f(0,2,0,0,0) = \frac{y_0^2}{x^4} + \frac{y_4}{2x^3} + \frac{f}{x^2} + \frac{f'}{2x^2} + \left(\frac{1}{2x^3}-\frac{1}{x^4}\right) y_0 \tag{45}$$

$$f(2,0,0,0,0) = -\frac{y_4}{x^5} - \frac{2y_0}{x^5} - \frac{y_3}{2x^4} + \frac{1}{x^4} + \frac{2f}{x^2} + \left(\frac{2}{x^5}+\frac{1}{x^4}\right) y_0^2 - \left(\frac{1}{x^4}+\frac{1}{2x^2}\right) f' \tag{46}$$

$$f(0,1,0,0,1) = \frac{1}{x^4} - \left(\frac{1}{x^4}+\frac{1}{2x^3}\right) y_0 \tag{47}$$

$$f(0,1,0,1,0) = \frac{y_2}{2x^4} + \frac{y_1}{2x^3} + \frac{y_0}{2x^3} \tag{48}$$

$$f(0,1,1,0,0) = \frac{y_2}{x^4} - \frac{y_0}{2x^3} \tag{49}$$

$$f(1,0,1,0,0) = \frac{2}{x^5} - \left(\frac{4}{x^5}+\frac{1}{x^4}\right) y_0 + \left(\frac{2}{x^5}+\frac{1}{x^4}\right) y_0^2 \tag{50}$$

$$f(1,1,0,0,0) = \frac{1-y_0}{x^4} \tag{51}$$

Integrals with higher powers n_i are of analogous form, they are all linear combinations of f, f', y_0^2 and y_i with coefficients being polynomials of $1/x$. We have generated a table of integrals with $\sum_i n_i \le 37$, which corresponds to a maximum value of $\Omega = 16$. It is less than $\Omega = 20$ in the case of James-Coolidge functions, but anyway, requires the use of octuple precision arithmetics due to near linear dependence of these basis functions.

IV. NUMERICAL RESULTS

The matrix elements of the nonrelativistic Hamiltonian between exponential functions are obtained as described by Kołos and Roothan in [16]. The resulting expression is a linear combination of various Slater integrals which are calculated using analytic formulas as presented in the previous sections. This evaluation is fast and accurate, thus allowing the use of a large number of basis functions.

Eigenvalues of the Hamiltonian matrix are obtained by inverse iteration method for various length of the basis set. Following Sims and Hagstrom [15] we use double basis set $(\Omega, \Omega - 2)$ with two different nonlinear parameters, which were obtained by minimization of energy at $\Omega = 12$. For the calculations with basis functions up to $\Omega = 20$, the second nonlinear parameter is additionally multiplied by 1.5 in order to improve the numerical stability for the large values of Ω. Numerical calculations with James-Coolidge functions are performed in general using quadruple precision arithmetics, and for checking the numerical accuracy, the one point at $r = 1.4011$ au is calculated using the octuple precision. We observe a significant loss of digits for large values of Ω. The quadruple precision arithmetics was not always sufficient for the whole range of internuclear distances. In many cases values with $\Omega = 20$, and sometimes even $\Omega = 19$ had to be disregarded due to numerical instabilities in the inverse iteration procedure. Numerical results at $r = 1.4011$ and $r = 6$ au for various sizes of basis length are presented in Table I. The most accurate result obtained at the equilibrium distance $r = 1.4011$ au is compared in Table II to all the previous results obtained so far in the literature.

In performing extrapolation, we observe the exponential $e^{-\beta\,\Omega}$ convergence. In other words the $\log$ of differences in energies for subsequent values of Ω fits well to the linear function. This allows for a simple and reliable extrapolation to infinity. For example at the equilibrium distance the parameter β is about 0.9, and convergence in the James-Coolidge basis preserve its exponential behavior for all the distances.

The calculations for the internuclear distances $r = 6 - 20$ au. are performed in ECA basis set using octuple precision arithmetics up to $\Omega = 16$. This basis is probably the most effective one at large distances. We also observe exponential convergence for BO and even exchange energies, what makes quite simple the extrapolation to infinity, see Table III with detailed results for various length of the basis set. For $r \leq 12.0$ results obtained with James-Coolidge basis are more accurate, while for $r > 12.0$ the ECA basis functions give more accurate energy. Extrapolated results for the whole BO potential curve in the range $0.1 - 20$ au are presented in Table IV. The ECA functions have the right large r behavior and thus can be used to study the long range tails in the interatomic interactions. Particularly interesting is the long range asymptotics of the exchange energy ΔE, which is the difference between singlet and triplet electronic energies. Table V presents our numerical results for the exchange energy at internu-

TABLE I: Numerical values for BO energy obtained with James-Coolidge functions, double basis set $(\Omega, \Omega-2)$ with nonlinear parameters: $\alpha_1 = 0.9650,\ \alpha_2 = 4.6716$ for $r = 1.4011$ and $\alpha_1 = 0.57050,\ \alpha_2 = 2.36925$ for $r = 6.0$

Ω	N	$r = 1.4011$	$r = 6.0$
3	23	$-1.173\,189\,743\,241\,832\,33$	$-0.969\,640\,616\,224\,699\,7$
4	51	$-1.174\,345\,859\,790\,847\,31$	$-0.995\,618\,908\,838\,543\,1$
5	98	$-1.174\,463\,692\,797\,208\,81$	$-1.000\,157\,746\,708\,230\,0$
6	180	$-1.174\,474\,907\,247\,221\,29$	$-1.000\,781\,343\,551\,690\,1$
7	306	$-1.174\,475\,841\,117\,269\,47$	$-1.000\,831\,730\,125\,255\,5$
8	501	$-1.174\,475\,923\,062\,032\,59$	$-1.000\,835\,509\,296\,673\,5$
9	781	$-1.174\,475\,930\,460\,077\,70$	$-1.000\,835\,696\,691\,923\,9$
10	1182	$-1.174\,475\,931\,266\,449\,18$	$-1.000\,835\,707\,165\,465\,4$
11	1729	$-1.174\,475\,931\,378\,701\,09$	$-1.000\,835\,707\,596\,974\,8$
12	2471	$-1.174\,475\,931\,396\,395\,07$	$-1.000\,835\,707\,643\,241\,4$
13	3444	$-1.174\,475\,931\,399\,453\,43$	$-1.000\,835\,707\,651\,449\,9$
14	4712	$-1.174\,475\,931\,400\,035\,47$	$-1.000\,835\,707\,653\,956\,0$
15	6324	$-1.174\,475\,931\,400\,162\,72$	$-1.000\,835\,707\,654\,760\,4$
16	8361	$-1.174\,475\,931\,400\,197\,06$	$-1.000\,835\,707\,655\,025\,5$
17	10887	$-1.174\,475\,931\,400\,208\,48$	$-1.000\,835\,707\,655\,120\,8$
18	14002	$-1.174\,475\,931\,400\,213\,00$	$-1.000\,835\,707\,655\,156\,0$
19	17787	$-1.174\,475\,931\,400\,215\,01$	$-1.000\,835\,707\,655\,168\,9$
20	22363	$-1.174\,475\,931\,400\,215\,99$	$-1.000\,835\,707\,655\,175\,9$
∞		$-1.174\,475\,931\,400\,216\,7(3)$	$-1.000\,835\,707\,655\,180\,4(22)$
∞	Cencek [11]	$-1.174\,475\,931\,400\,21(6)$	

clear distances $r = 6 - 20$ au. It was found by Herring and Flicker in [12] that the asymptotic limit is $e^{-2\,r}\, r^{5/2}\left(\gamma + O(r^{-1/2})\right)$ with $\gamma = 1.636\,571\,460\,2....$ The fit to our numerical data, see Fig. 1, gives $\gamma = 1.6(1)$ what can be regarded as a first numerical confirmation of the Herring and Flicker result. When assuming their constant, the fit of first three terms in $1/\sqrt{r}$ expansion gives: $-1.11732/\sqrt{r} + 2.13187/r + 5.169/r^{3/2}$, what indicates very slow convergence of this expansion at typical interatomic distances $r \sim 10$.

TABLE II: Born-Oppenheimer potential for the H_2 molecule with different types of wave functions at $r = 1.4011$ au

Authors	type of w.f.	N	energy
1933 James and Coolidge [14]	JC	5	$-1.173\,5$
1960 Kołos and Roothan [16]	JC	50	$-1.174\,448$
1968 Kołos and Wolniewicz [17]	KW	100	$-1.174\,474\,983$
1994 Rychlewski, Cencek, Komasa [18]	ECG	700	$-1.174\,475\,931$
1995 Wolniewicz [19]	KW	883	$-1.174\,475\,930\,742$
2006 Sims and Hagstrom [15]	JC	7034	$-1.174\,475\,931\,399\,84$
2007 Nakatsuji *et al.*[20]	ICI	6776	$-1.174\,475\,931\,400\,027$
2008 Cencek, Szalewicz [11]	ECG	4800	$-1.174\,475\,931\,400\,135$
2010 this work	JC	22363	$-1.174\,475\,931\,400\,215\,99$

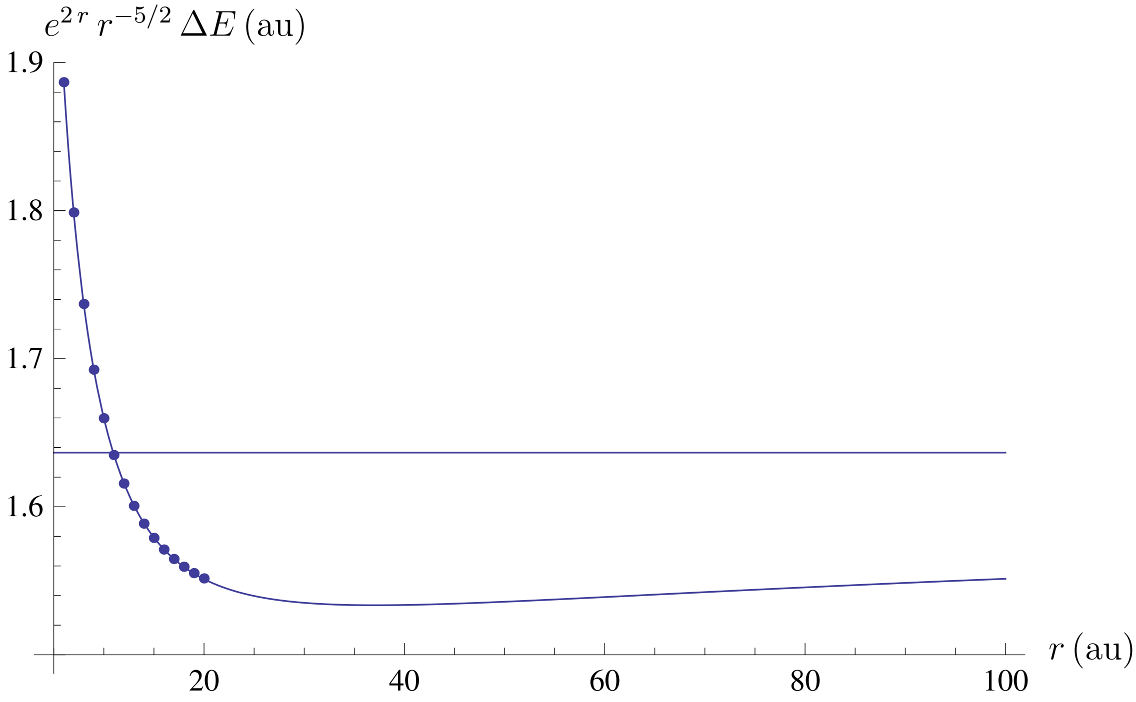

FIG. 1: Rescaled exchange energy $e^{2r}\,r^{-5/2}\,\Delta E$ fitted to numerical points in Table V in the range $r = 6 - 20$ au, assuming Herring and Flicker [12] asymptotics, straight line.

TABLE III: Numerical values for BO and exchange energies obtained with ECA functions at $r = 12$ au

Ω	N	$E(^1\Sigma_g^+)$	$e^{2r}\,\Delta E$
3	32	$-1.000\,002\,515\,756\,9814$	$720.758\,075$
4	70	$-1.000\,002\,541\,561\,9799$	$767.006\,890$
5	136	$-1.000\,002\,545\,005\,4934$	$791.784\,126$
6	246	$-1.000\,002\,545\,635\,6130$	$800.649\,925$
7	416	$-1.000\,002\,545\,838\,2275$	$803.989\,841$
8	671	$-1.000\,002\,545\,922\,5168$	$805.314\,087$
9	1036	$-1.000\,002\,545\,955\,3661$	$805.779\,212$
10	1547	$-1.000\,002\,545\,965\,8295$	$805.916\,877$
11	2240	$-1.000\,002\,545\,968\,6694$	$805.953\,991$
12	3164	$-1.000\,002\,545\,969\,3389$	$805.963\,087$
13	4368	$-1.000\,002\,545\,969\,4859$	$805.965\,246$
14	5916	$-1.000\,002\,545\,969\,5175$	$805.965\,766$
15	7872	$-1.000\,002\,545\,969\,5251$	$805.965\,907$
16	10317	$-1.000\,002\,545\,969\,5273$	$805.965\,954$
∞		$-1.000\,002\,545\,969\,5279(3)$	$805.965\,974(10)$

V. SUMMARY

We have demonstrated the applicability of analytic formulas for two-center two-electron integrals in high precision calculations of Born-Oppenheimer potential for the ground electronic state of the hydrogen molecule. The symmetric James-Coolidge basis with as much as 22 000 functions provided energies with relative precision of about 10^{-15} for internuclear distances up to 10 au. The extended Heitler-London basis with about 10 000 functions give similarly accurate description at internuclear distances $r \sim 10$ au and greater. The extension of the analytic approach to excited states of H_2 and other diatomic molecules, such as HeH^+ requires the evaluation of Slater integrals with arbitrary nonlinear parameters (Kołos-Wolniewicz basis [13]). These integrals are solved analytically, see Ref. [10], but the explicit expression for higher powers of electron distances is very lengthy. This may need further work to find a more compact analytical form.

Further improvement in energy requires more accurate calculations of relativistic effects, possibly including nonadiabatic corrections. For this, integrals with quadratic inverse powers of interparticle distances have to be worked out analytically, and this is not a simple problem, at least

TABLE IV: Numerical values for BO potential at different internuclear distance r. Results are obtained by extrapolation to complete set of basis functions

r/au	$E(r)$	r/au	$E(r)$
0.10	7.127 216 731 132 0(55)	3.00	−1.057 326 268 872 6617(70)
0.20	2.197 803 295 226 18(33)	3.10	−1.051 333 772 268 0178(65)
0.30	0.619 241 659 796 226(60)	3.20	−1.045 799 661 432 432(17)
0.40	−0.120 230 341 178 823(15)	3.30	−1.040 717 365 351 395(11)
0.50	−0.526 638 758 743 001(11)	3.40	−1.036 075 395 190 7599(41)
0.60	−0.769 635 429 485 9092(80)	3.50	−1.031 858 084 855 0934(29)
0.70	−0.922 027 461 527 4636(26)	3.60	−1.028 046 308 379 7348(90)
0.80	−1.020 056 666 360 5151(4)	3.70	−1.024 618 188 410 962(10)
0.90	−1.083 643 239 958 8343(8)	3.80	−1.021 549 795 533 649(12)
1.00	−1.124 539 719 546 8709(7)	3.90	−1.018 815 827 696 496(12)
1.10	−1.150 057 367 738 5650(3)	4.00	−1.016 390 252 950 6681(55)
1.20	−1.164 935 243 440 3099(7)	4.20	−1.012 359 959 683 166(11)
1.25	−1.169 419 627 390 9022(7)	4.40	−1.009 256 516 261 5862(34)
1.30	−1.172 347 149 038 0904(8)	4.60	−1.006 895 223 822 7406(46)
1.32	−1.173 138 736 333 4793(8)	4.80	−1.005 116 006 100 3838(50)
1.34	−1.173 734 874 958 3451(3)	5.00	−1.003 785 658 583 9706(38)
1.36	−1.174 148 498 570 4193(9)	5.20	−1.002 796 816 311 2547(33)
1.38	−1.174 391 683 632 2532(6)	5.40	−1.002 065 057 209 7059(27)
1.39	−1.174 452 917 278 4574(4)	5.60	−1.001 525 251 886 6137(16)
1.40	−1.174 475 714 220 4434(5)	5.80	−1.001 127 880 852 4173(36)
1.41	−1.174 461 370 870 6800(11)	6.00	−1.000 835 707 655 1804(23)
1.42	−1.174 411 141 239 2317(11)	6.50	−1.000 400 548 534 5376(60)
1.44	−1.174 207 836 585 0950(11)	7.00	−1.000 197 914 480 0381(38)
1.46	−1.173 875 042 749 2034(8)	7.50	−1.000 102 106 147 8089(22)
1.48	−1.173 421 418 292 0817(12)	8.00	−1.000 055 604 973 0730(4)
1.50	−1.172 855 079 578 5838(12)	8.50	−1.000 032 171 832 8288(55)
1.55	−1.170 994 919 897 0180(6)	9.00	−1.000 019 781 832 4911(2)
1.60	−1.168 583 373 371 4593(8)	9.50	−1.000 012 856 876 8268(2)
1.70	−1.162 458 726 898 4588(5)	10.00	−1.000 008 755 746 0515(1)
1.80	−1.155 068 737 611 6094(11)	10.50	−1.000 006 189 995 1069(1)
1.90	−1.146 850 697 029 6887(28)	11.00	−1.000 004 505 989 4362(1)
2.00	−1.138 132 957 132 6480(34)	11.50	−1.000 003 356 174 5754(1)
2.10	−1.129 163 836 101 3193(40)	12.00	−1.000 002 545 969 5285(1)
2.20	−1.120 132 116 849 2218(48)	13.00	−1.000 001 529 286 6698(1)
2.30	−1.111 181 765 204 4391(17)	14.00	−1.000 000 960 680 7911
2.40	−1.102 422 606 011 326(65)	15.00	−1.000 000 625 453 6319
2.50	−1.093 938 129 955 879(75)	16.00	−1.000 000 419 586 3122
2.60	−1.085 791 237 396 1321(12)	17.00	−1.000 000 288 826 2392
2.70	−1.078 028 484 183 8287(46)	18.00	−1.000 000 203 340 5059
2.80	−1.070 683 233 481 4249(55)	19.00	−1.000 000 146 028 2368
2.90	−1.063 778 008 806 0211(65)	20.00	−1.000 000 106 740 1283

for arbitrary nonlinear parameters.

Even more important is the extension of this approach to few and many electron diatomic systems. Integrals with (uncorrelated) Slater functions with arbitrary nonlinear parameters can be evaluated using recursion relations of Ref. [10], this includes also the exchange integrals in-

TABLE V: Exchange energy $\Delta E = E_u - E_g$ at different internuclear distances

r	$e^{2\,r}\,r^{-5/2}\,\Delta E$
6	$1.886\,757\,524(7)$
7	$1.798\,767\,166(8)$
8	$1.736\,967\,949(9)$
9	$1.692\,575\,090(10)$
10	$1.659\,770\,272(12)$
11	$1.634\,919\,801(15)$
12	$1.615\,710\,667(20)$
13	$1.600\,619\,338(31)$
14	$1.588\,607\,797(56)$
15	$1.578\,947\,36(11)$
16	$1.571\,113\,18(24)$
17	$1.564\,718\,78(50)$
18	$1.559\,474\,1(11)$
19	$1.555\,157\,8(22)$
20	$1.551\,599\,0(44)$

volving Coulomb interaction between electrons. More challenging would be implementation of coupled-clusters with the explicit r_{12} factor. The analytic form for the corresponding three-electron integrals is however not yet known.

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