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# Born-Oppenheimer potential for $H_2$

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The Born-Oppenheimer potential for the ${}^1\Sigma_g^+$ state of $H_2$ is obtained in the range 0.1–20 a.u., using analytic formulas and recursion relations for two-center two-electron integrals with exponential functions. For small distances, the James-Coolidge basis is used, while for large distances, the Heitler-London functions with arbitrary polynomial in electron variables are used. In the whole range of internuclear distance, about $10^{-15}$ precision is achieved; as an example, at the equilibrium distance $r = 1.4011$ a.u., 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. A **134**, 362 (1964)] for the large-internuclear-distance asymptotics. The presented analytic approach to Slater integrals opens a window for 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 nonrelativistic Born-Oppenheimer (BO) potential but also the adiabatic, nonadiabatic, relativistic, and quantum electrodynamics effects need to be calculated. 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 the $10^{-8}$ precision level. Such a precision has not yet been achieved for molecular systems with more than two electrons, 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 the numerical accuracy obtained so far for two-electron 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, and spin-rotational or spin-spin coupling constants. Evaluation of relativistic effects is very sensitive to correct analytic properties of the basis functions, and a good example is 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 is known presently [7]. Moreover, any nonelectromagnetic 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 the HD molecule. The electromagnetic spin interaction is extremely small, of order $m^3/(m_p\,m_d)\,\alpha^6$ and about 43 Hz for the ground molecular state [9], and any deviation between experimental values and theoretical predictions signals the existence of 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 formulas and recursion relations for Slater integrals, which were obtained in our previous work [10]. At the equilibrium distance, our calculations confirm the results of Cencek and Szalewicz [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 the possibility of the extension of this method to systems of more than two electrons.

## II. SHORT RANGE OF INTERNUCLEAR DISTANCES

The Schrödinger equation for an $H_2$ 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 [13]. However, at small nuclear distances $r \equiv r_{AB}$, we can use the much simpler James-Coolidge basis [14], namely the functions of the form

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

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such that

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

with $\Omega = 3,\ldots,20$. This basis was recently used by Sims and Hagstrom [15] for $10^{-12}$ precision calculation of the BO potential in the range $r = 0.4\text{–}6$ a.u., by a traditional way of numerical evaluation of the corresponding two-center integrals. Here, using Ref. [10] we derive an analytic expression for all these integrals up to $\Omega = 20$. They have a 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

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

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

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

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

$$y_0 = e^{-(u+w)}, \tag{7}$$

$$y_1 = \mathrm{Ei}(-2\,w)\,e^{w-u} + \mathrm{Ei}(-2\,u)\,e^{u-w}, \tag{8}$$

$$y_2 = \mathrm{Ei}(-2\,w)\,e^{w-u} - \mathrm{Ei}(-2\,u)\,e^{u-w}, \tag{9}$$

$$y_3 = \mathrm{Ei}[-2\,(u+w)]e^{u+w} + \left[\ln\left(\frac{2\,u\,w}{u+w}\right)+\gamma\right]\,e^{-(u+w)}, \tag{10}$$

$$y_4 = \mathrm{Ei}[-2\,(u+w)]e^{u+w} - \left[\ln\left(\frac{2\,u\,w}{u+w}\right)+\gamma\right]\,e^{-(u+w)}. \tag{11}$$

Then, using Eq. (69) from Ref. [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 $\sum_i n_i \leqslant 4$ are the following:

$$f(0,0,0) = \frac{y_3 - y_1}{4\,u\,w}, \tag{12}$$

$$f(1,0,0) = \frac{y_0}{4\,u\,w}, \tag{13}$$

$$f(2,0,0) = \frac{y_0\,(2\,u\,w + u + w) + y_2\,(u-w) - y_4\,(u+w)}{24\,u^2\,w^2} + \frac{(y_3-y_1)(u^2+w^2)}{24\,u^3\,w^3}, \tag{14}$$

$$f(0,2,0) = \frac{y_3 - y_1}{12\,u\,w}, \tag{15}$$

$$f(0,1,1) = -\frac{y_0}{6\,u\,w} + \frac{y_1\,(u\,w-1) - y_2\,(u-w) + y_3\,(u\,w+1) - y_4\,(u+w)}{12\,u^2\,w^2}, \tag{16}$$

$$f(3,0,0) = \frac{y_0[u^2w^2 + 3uw(u+w) + 3(u^2+w^2)]}{24u^3w^3}, \tag{17}$$

$$f(1,2,0) = \frac{y_0}{12uw}, \tag{18}$$

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

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

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

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 $r = 6.0$. All quantities are in atomic units.

| $\Omega$ | $N$ | $r = 1.4011$ | $r = 6.0$ |
|---|---|---|---|
| 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 | 1,182 | −1.174 475 931 266 449 18 | −1.000 835 707 165 465 4 |
| 11 | 1,729 | −1.174 475 931 378 701 09 | −1.000 835 707 596 974 8 |
| 12 | 2,471 | −1.174 475 931 396 395 07 | −1.000 835 707 643 241 4 |
| 13 | 3,444 | −1.174 475 931 399 453 43 | −1.000 835 707 651 449 9 |
| 14 | 4,712 | −1.174 475 931 400 035 47 | −1.000 835 707 653 956 0 |
| 15 | 6,324 | −1.174 475 931 400 162 72 | −1.000 835 707 654 760 4 |
| 16 | 8,361 | −1.174 475 931 400 197 06 | −1.000 835 707 655 025 5 |
| 17 | 10,887 | −1.174 475 931 400 208 48 | −1.000 835 707 655 120 8 |
| 18 | 14,002 | −1.174 475 931 400 213 00 | −1.000 835 707 655 156 0 |
| 19 | 17,787 | −1.174 475 931 400 215 01 | −1.000 835 707 655 168 9 |
| 20 | 22,363 | −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) | |

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

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

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

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 $\sum_i n_i \leqslant 45$, which is sufficient for matrix elements involving exponential functions with a maximum value of $\Omega = 20$.

## III. LONG RANGE OF INTERNUCLEAR DISTANCES

For 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

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

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

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

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]

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

TABLE II. Born-Oppenheimer potential for the $H_2$ molecule with different types of wave functions (w.f.) at $r = 1.4011$ a.u. All quantities are in atomic units.[a]

| Authors | Type of w.f. | $N$ | Energy |
|---|---|---|---|
| 1933 James and Coolidge [14] | JC | 5 | $-1.173\,5$ |
| 1960 Kołos and Roothaan [16] | JC | 50 | $-1.174\,448$ |
| 1968 Kołos and Wolniewicz [17] | KW | 100 | $-1.174\,474\,983$ |
| 1994 Rychlewski *et al.* [18] | ECG | 700 | $-1.174\,475\,931$ |
| 1995 Wolniewicz [19] | KW | 883 | $-1.174\,475\,930\,742$ |
| 2006 Sims and Hagstrom [15] | JC | 7,034 | $-1.174\,475\,931\,399\,84$ |
| 2007 Nakatsuji *et al.* [20] | ICI | 6,776 | $-1.174\,475\,931\,400\,027$ |
| 2008 Cencek and Szalewicz [11] | ECG | 4,800 | $-1.174\,475\,931\,400\,135$ |
| 2010 This work | JC | 22,363 | $-1.174\,475\,931\,400\,215\,99$ |

[a]ECG, explicitly correlated Gaussians; ICI, iterative-complement-interaction; JC, James and Coolidge; KW, Kołos and Wolniewicz.

and its first derivative with respect to $r$,

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

where

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

This one-dimensional integration can easily be obtained with sufficient accuracy; 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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

TABLE III. Numerical values for BO and exchange energies obtained with ECA functions at $r = 12$ a.u. All quantities are in atomic units.

| $\Omega$ | $N$ | $E(^1\Sigma_g^+)$ | $e^{2r}\Delta E$ |
|---|---|---|---|
| 3 | 32 | $-1.000\,002\,515\,756\,981\,4$ | 720.758 075 |
| 4 | 70 | $-1.000\,002\,541\,561\,979\,9$ | 767.006 890 |
| 5 | 136 | $-1.000\,002\,545\,005\,493\,4$ | 791.784 126 |
| 6 | 246 | $-1.000\,002\,545\,635\,613\,0$ | 800.649 925 |
| 7 | 416 | $-1.000\,002\,545\,838\,227\,5$ | 803.989 841 |
| 8 | 671 | $-1.000\,002\,545\,922\,516\,8$ | 805.314 087 |
| 9 | 1036 | $-1.000\,002\,545\,955\,366\,1$ | 805.779 212 |
| 10 | 1547 | $-1.000\,002\,545\,965\,829\,5$ | 805.916 877 |
| 11 | 2240 | $-1.000\,002\,545\,968\,669\,4$ | 805.953 991 |
| 12 | 3164 | $-1.000\,002\,545\,969\,338\,9$ | 805.963 087 |
| 13 | 4368 | $-1.000\,002\,545\,969\,485\,9$ | 805.965 246 |
| 14 | 5916 | $-1.000\,002\,545\,969\,517\,5$ | 805.965 766 |
| 15 | 7872 | $-1.000\,002\,545\,969\,525\,1$ | 805.965 907 |
| 16 | 10 317 | $-1.000\,002\,545\,969\,527\,3$ | 805.965 954 |
| $\infty$ |  | $-1.000\,002\,545\,969\,527\,9(3)$ | 805.965 974(10) |

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

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

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

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

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

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

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 $\sum_i n_i \leqslant 37$, 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

TABLE IV. Numerical values for BO potential at different internuclear distance $r$. Results are obtained by extrapolation to complete set of basis functions. All quantities are in atomic units.

| $r$/a.u. | $E(r)$ | $r$/a.u. | $E(r)$ |
|---|---|---|---|
| 0.10 | 7.127 216 731 132 0(55) | 3.00 | −1.057 326 268 872 661 7(70) |
| 0.20 | 2.197 803 295 226 18(33) | 3.10 | −1.051 333 772 268 017 8(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 | −1.036 075 395 190 759 9(41) |
| 0.60 | −0.769 635 429 485 909 2(80) | 3.50 | −1.031 858 084 855 093 4(29) |
| 0.70 | −0.922 027 461 527 463 6(26) | 3.60 | −1.028 046 308 379 734 8(90) |
| 0.80 | −1.020 056 666 360 515 1(4) | 3.70 | −1.024 618 188 410 962(10) |
| 0.90 | −1.083 643 239 958 834 3(8) | 3.80 | −1.021 549 795 533 649(12) |
| 1.00 | −1.124 539 719 546 870 8(7) | 3.90 | −1.018 815 827 696 496(12) |
| 1.10 | −1.150 057 367 738 565 0(3) | 4.00 | −1.016 390 252 950 668 1(55) |
| 1.20 | −1.164 935 243 440 309 9(7) | 4.20 | −1.012 359 959 683 166(11) |
| 1.25 | −1.169 419 627 390 902 2(7) | 4.40 | −1.009 256 516 261 586 2(34) |
| 1.30 | −1.172 347 149 038 090 4(8) | 4.60 | −1.006 895 223 822 740 6(46) |
| 1.32 | −1.173 138 736 333 479 3(8) | 4.80 | −1.005 116 006 100 383 8(50) |
| 1.34 | −1.173 734 874 958 345 1(3) | 5.00 | −1.003 785 658 583 970 6(38) |
| 1.36 | −1.174 148 498 570 419 3(9) | 5.20 | −1.002 796 816 311 254 7(33) |
| 1.38 | −1.174 391 683 632 253 2(6) | 5.40 | −1.002 065 057 209 705 9(27) |
| 1.39 | −1.174 452 917 278 457 4(4) | 5.60 | −1.001 525 251 886 613 7(16) |
| 1.40 | −1.174 475 714 220 443 4(5) | 5.80 | −1.001 127 880 852 417 3(36) |
| 1.41 | −1.174 461 370 870 680 0(11) | 6.00 | −1.000 835 707 655 180 4(23) |
| 1.42 | −1.174 411 141 239 231 7(11) | 6.50 | −1.000 400 548 534 537 6(60) |
| 1.44 | −1.174 207 836 585 095 0(11) | 7.00 | −1.000 197 914 480 038 1(38) |
| 1.46 | −1.173 875 042 749 203 4(8) | 7.50 | −1.000 102 106 147 808 9(22) |
| 1.48 | −1.173 421 418 292 081 7(12) | 8.00 | −1.000 055 604 973 073 0(4) |
| 1.50 | −1.172 855 079 578 583 8(12) | 8.50 | −1.000 032 171 832 828 8(55) |
| 1.55 | −1.170 994 919 897 018 0(6) | 9.00 | −1.000 019 781 832 491 1(2) |
| 1.60 | −1.168 583 373 371 459 3(8) | 9.50 | −1.000 012 856 876 826 8(1) |
| 1.70 | −1.162 458 726 898 458 8(5) | 10.00 | −1.000 008 755 746 051 5(1) |
| 1.80 | −1.155 068 737 611 609 4(11) | 10.50 | −1.000 006 189 995 106 9(1) |
| 1.90 | −1.146 850 697 029 688 7(28) | 11.00 | −1.000 004 505 989 436 2(1) |
| 2.00 | −1.138 132 957 132 648 0(34) | 11.50 | −1.000 003 356 174 575 4(1) |
| 2.10 | −1.129 163 836 101 319 3(40) | 12.00 | −1.000 002 545 969 528 5(1) |
| 2.20 | −1.120 132 116 849 221 8(48) | 13.00 | −1.000 001 529 286 669 8(1) |
| 2.30 | −1.111 181 765 204 439 1(17) | 14.00 | −1.000 000 960 680 791 1 |
| 2.40 | −1.102 422 606 011 326 3(65) | 15.00 | −1.000 000 625 453 631 9 |
| 2.50 | −1.093 938 129 955 879 0(75) | 16.00 | −1.000 000 419 586 312 2 |
| 2.60 | −1.085 791 237 396 132 1(12) | 17.00 | −1.000 000 288 826 239 2 |
| 2.70 | −1.078 028 484 183 828 7(46) | 18.00 | −1.000 000 203 340 505 9 |
| 2.80 | −1.070 683 233 481 424 9(55) | 19.00 | −1.000 000 146 028 236 8 |
| 2.90 | −1.063 778 008 806 021 1(65) | 20.00 | −1.000 000 106 740 128 3 |

octuple precision arithmetic 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 Roothaan [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 the inverse iteration method for various lengths of the basis set. Following Sims and Hagstrom [15], we use a 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 $\Omega$. Numerical calculations with James-Coolidge functions are performed in general using quadruple-precision arithmetic, and for checking the numerical accuracy, the one point at $r = 1.4011$ a.u. is calculated using octuple precision. We observe a significant loss of digits for large values of $\Omega$. The quadruple-precision arithmetic 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 $r = 6$ a.u. for various sizes of basis length are presented in Table I. The most accurate result obtained at the equilibrium distance $r = 1.4011$ a.u. is compared in Table II to all the previous results obtained so far in the literature.

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

TABLE V. Exchange energy $\Delta E = E_u - E_g$ at different internuclear distances. All quantities are in atomic units.

| $r$ | $e^{2r} r^{-5/2} \Delta E$ |
|---|---|
| 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) |

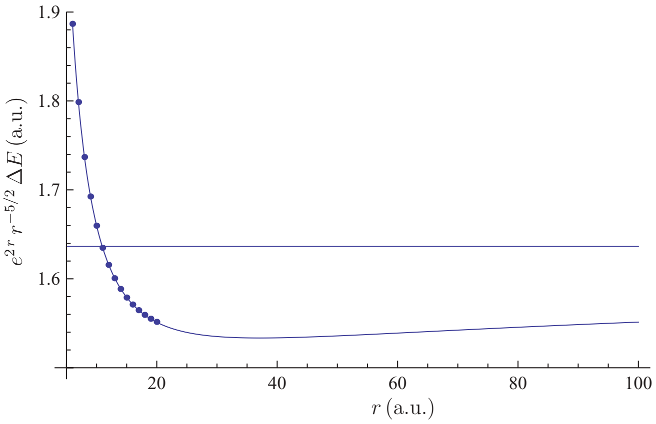

FIG. 1. (Color online) Rescaled exchange energy $e^{2r} r^{-5/2} \Delta E$ fitted to numerical points in Table V in the range $r = 6$–20 a.u., assuming Herring and Flicker [12] asymptotics, straight line.

The calculations for the internuclear distances $r = 6$–20 a.u. are performed in the ECA basis set using octuple-precision arithmetic 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, which makes the extrapolation to infinity quite simple (see Table III, which has detailed results for various lengths of the basis set). For $r \leqslant 12$, results obtained with the James-Coolidge basis are more accurate, while for $r > 12$ the ECA basis functions give more accurate energy. Extrapolated results for the whole BO potential curve in the range 0.1–20 a.u. 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 $\Delta E$, which is the difference between singlet and triplet electronic energies. Table V presents our numerical results for the exchange energy at internuclear distances $r = 6$–20 a.u. It was found by Herring and Flicker [12] that the asymptotic limit is $e^{-2r} r^{5/2}[\gamma + O(r^{-1/2})]$ with $\gamma = 1.636\,571\,460\,2\ldots$. The fit to our numerical data (see Fig. 1) gives $\gamma = 1.6(1)$ which can be regarded as a first numerical confirmation of the Herring-Flicker result. When assuming their constant, the fit of the first three terms in the $1/\sqrt{r}$ expansion gives $-1.117\,32/\sqrt{r} + 2.131\,87/r + 5.169/r^{3/2}$, which indicates very slow convergence of this expansion at typical interatomic distances $r \sim 10$.

## 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 a.u. The extended Heitler-London basis with about 10,000 functions gives a similarly accurate description at internuclear distances $r \sim 10$ a.u. 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, which is not a simple problem, at least 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 the recursion relations of Ref. [10], which also includes the exchange integrals involving Coulomb interaction between electrons. More challenging would be an 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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